Honoring the Late Prof. Keiji Morokuma

PL001

Dr. Kazuo Kitaura

R-CCS, Riken, Kobe, Japan

I will talk about Prof. Keiji Morokuma's great achievements in theoretical/quantum chemistry.

How Could Life Have Emerged?

PL002

Prof Addy Pross

Ben Gurion University of the Negev, Be'er Sheva, Israel

The origin of life question is one of science's greatest mysteries and normally posed as *how did life emerge?* But given the principles governing chemical processes, and in particular the Second Law of thermodynamics, the deeper question would be: *how* ***could*** *life have emerged*? How was it at all possible for dynamic, far-from-equilibrium, functional chemical systems to have emerged from inanimate matter in the first place? Through a newly emergent area of chemistry, *systems chemistry*, an answer to that question is beginning to materialize. Its essence: the stability concept in nature has two distinct facets, *time-stability* and *energy-stability*, with the former facet being the more general one. Life can be understood as the evolutionary process associated with energy-fueled, replicative chemical networks, driven toward increasing time-stability. The path toward the chemical synthesis of rudimentary proto-life systems appears to be opening up.

Pross, A. *What is life?* Oxford University Press, Oxford (2016).
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Materials Intelligence

PL003

Dr Amanda S Barnard

CSIRO Data61, Docklands, Australia

A fundamental aim of materials research is to identify features of materials that can be tuned to control how the material performs under specific application conditions. The combination of computational materials science with machine learning provides a powerful way of relating structural features with functional properties, but combining these fundamentally different scientific approaches is not as straightforward as it seems. Machine learning methods were developed for large data sets with small numbers of consistent features. Typically materials data sets are small, with high dimensionality and high variance in feature space, and suffer from numerous destructive biases. None of the established data science or machine learning methods in widespread use today were devised with materials data sets in mind, but there are ways to overcome these issues and use them reliably. In this presentation we will discuss the impact of domain-specific constraints on data-driven materials design, and explore the differences between materials simulation and materials informatics that can be leveraged for greater impact.

A Phase Separation Perspective for Chromatin Structure Change in Development, Differentiation, Senescence and Certain Diseases

PL004

Dr. Yi Qin Gao

Peking University, Beijing, China

The high-order chromatin structure plays an important role in gene regulation. The mechanism, especially the sequence dependence for the formation of varied chromatin structures in different cell states remain to be elucidated. In this talk, we try to touch on three questions: (1) What is the sequence dependence and chemical structure basis in the formation of high order chromatin structure, such as compartments? (2) How does the chromatin structure reflect the biological function of different cellular states and tissue-specificity? (3) How does this sequence-dependent chromatin structure formation manifest in different species? We identified CGI (CpG island) forest and prairie genomic domains based on CGI densities, and divided the genome into two sequentially, epigenetically, and transcriptionally distinct regions. Forests and prairies show enhanced segregation from each other in development, differentiation, and senescence, meanwhile the multi-scale forest-prairie spatial intermingling is cell-type specific and increases in differentiation, helping to define cell identity.

Time-Domain Quantum Chemistry Beyond the Born-Oppenheimer Paradigm

PL005

Dr. Kazuo Takatsuka

Kyoto University, Kyoto, Japan

There is no doubt that molecular properties and reactivity are overwhelmingly dominated by their electronic states, and hence the role of quantum chemistry based on the Born-Oppenheimer (BO) approximation cannot be overemphasized. Some of the main directions of current quantum chemistry include the very accurate methods of the stationary-state Schrödinger equation, efficient treatments of large molecules, relativistic theory, and so on. These are followed by tremendous number of chemical applications.

All these progresses are about energetics. Yet, another direction for us to proceed to is to retrieve time-coordinate in the electronic wavefunctions, by taking account of quantum entanglement between electrons and nuclei through their kinematic (or the so-called nonadiabatic) interactions. Development of such field is demanded also by the recent advent of atto-second level ultrashort lases, which are short enough to track electron dynamics directly. This field may be referred to as time-domain quantum chemistry, in analogy to time-domain spectroscopy, which is now used as a tool for dynamical studies beyond the realm of the so-called frequency-domain spectroscopy.

There should exist a vast area of electron-dynamics yet to be studied in chemistry, which stays out of the realm of the BO approximation. We have been developing such a chemical theory to explore the beyond-BO chemistry. The real-time electronic wavepackets are tracked along the kinematically coupled nuclear dynamics, which are often represented in terms of branching paths (in laser fields). The theory has been extended so as to treat electron dynamics in direct photoionization and auto ionization, up to a QED treatment of relativistic electrons driven by intense laser fields.

In this talk, among others, I discuss the characteristic symmetry properties of the electronic-nuclear dynamical wavefunctions in chemical reactions, some chemical principles behind water splitting, and electron dynamics in densely quasi-degenerate electronic states in highly excited states of boron clusters.

Metal Ions & Brain Signaling

PL006

Prof. Carmay Lim

Academia Sinica, Institute of Biomedical Sciences, Taipei, Taiwan

Our research interests are to

(i)unravel the principles governing biological processes and use them to identify novel drug targets, guide drug design, and elucidate drug mechanisms, and

(ii)develop new methods for studying macromolecular interactions.

I will first give an overview of research work [1]. Then I will describe how our studies help to elucidate the competition between native and non-native cations for metal-binding sites in proteins involved in brain signaling and thus the mechanism of lithium's therapeutic actions [2-5].

1.Competition Among Metal ions for Protein Binding Sites: Determinants of Metal Ion Selectivity in Proteins. Todor Dudev & Carmay Lim, Chem. Rev. 2014114: 538.
2.Competition Between Li+and Mg2+in Metalloproteins. Implications for Lithium Therapy. Todor Dudev & Carmay Lim, J. Am. Chem. Soc.(2011) 133: 9506–9515. DOI: 10.1021/ja201985s
3.How native and alien metal cations bind ATP. Implications for lithium as a therapeutic agent. Todor Dudev, Cédric Grauffel, & Carmay Lim, Sci. Rep.20177, 42377. DOI: 10.1038/srep42377
4.How native & non-native cations bind and modulate the properties of GTP/ATP. Todor Dudev, Cédric Grauffel, Shang-Te Danny Hsu,& Carmay Lim, J. Chem.Theory & Comput. 201812, 3311–3320. DOI:10.1021/acs.jctc.8b00259
5.Competition between Li+and Na+in sodium transporters and receptors: Which Na+-binding sites are "therapeutic" Li+targets? Todor Dudev, Karine Mazmanian, & Carmay Lim, Chem. Sci. 20189, 4093–4103. DOI:10.1039/C7SC05284G

A Unified Thermostat Scheme for Efficient Configurational Sampling for Classical/Quantum Canonical Ensembles via Molecular Dynamics: From the Single-Electronic-State System to the Non-Adiabatic System

PL007

Professor Jian Liu

Peking University, Beijing, China

We show a unified second-order scheme for rationally designing simple, robust, and accurate algorithms for most typical thermostats for configurational sampling for the canonical ensemble, regardless of whether the thermostat is deterministic or stochastic. Accuracy may be increased by an order of magnitude for estimating coordinate-dependent properties in molecular dynamics (when the same time interval is used), irrespective of which type of thermostat is applied. The scheme is especially useful for path integral molecular dynamics (PIMD) because it consistently improves the efficiency for evaluating all thermodynamic properties for any type of thermostat. We further extend the methodology to offer a numerically exact as well as practical tool in either of the diabatic and adiabatic representations for studying exact quantum statistics of complex/large coupled multi-electronic-state systems when the Born-Oppenheimer approximation, Condon approximation, and harmonic bath approximation are broken.

Progress and Problems in the Design of Density Functionals

PL008

Prof. Martin Head-Gordon

UC Berkeley, Berkeley, USA

Density functional theory (DFT) is the most widely used electronic structure theory. Crucial to its future is the problem of designing functionals with improved predictive power. In the first part of my talk, I shall describe a new approach to functional design, “survival of the most transferable”, which my group has developed over the past five years, and show how the resulting functionals offer greatly improved accuracy for chemical energy differences relative to existing functionals of a given class. In the second part of the talk, I will discuss the performance of present-day DFT on additional types of data, such as electrical properties, and bond-stretching that represent challenges to present-day density functionals, including those designed in my group.

Rebuilding the Foundations of Density Functional Theory

IL001

Professor Peter M. W. Gill

University of Sydney, Sydney, Australia

Density Functional Theory (DFT) has become the most popular approach to modelling electronic structure within the physics, chemistry and materials science communities. Nonetheless, it is not perfect, and it suffers from a well-documented and increasingly well-understood list of deficiencies. Recognising those shortcomings, we are undertaking a radical reconstruction of the cornerstone of DFT, the uniform electron gas (UEG). Having discovered that infinite and finite UEGs of the same electron density can have different energetic properties, we have initiated a comprehensive study of the correlation energies of finite UEGs in one, two and three dimensions. To achieve this, we perform highly accurate calculations of the energies of electrons on one-, two- and three-dimensional spheres.

In my lecture, I will outline the guiding philosophy behind our investigations and the new "Jacob's Ladder" that we are constructing. In particular, I will highlight the ways in which the extremely high symmetry of spheres enables us to perform MP2, MP3 and CI calculations with astonishingly large basis sets. My talk will also set the stage for the lecture by Dr Stephen Dale who will present results for two-dimensional UEGs and the lecture by Prof Henryk Witek who will discuss problems and solutions for three-dimensional UEGs.

Uniform Electron Gas on a 3-Sphere

IL002

Prof Henryk A Witek[1,2], Dr Stephen G Dale[2], Prof Peter MW Gill[2]

[1]National Chiao Tung University, Canberra, Taiwan. [2]Australian National University, Canberra, Australia

A 3-sphere (i.e., the surface of a 4D ball) is a very convenient and the most natural three-dimensional geometrical object suitable for studying uniform electron gases formed by finite assemblies of electrons. Continuous variation of the 3-sphere radius allows for systematic exploration of assemblies with low and high electron densities. Numerically exact solutions to the Schrödinger equation for N electrons on a 3-sphere can prove useful for constructing new accurate density functionals [1,2] describing atoms and molecules, in addition and—more importantly—in opposition to the usual jellium data. Further discussion of the implications of the current talk on the development of DFT is presented in a talk given by Peter Gill.

The current talk addresses various methodological aspects of performing efficient configuration interaction (CI) calculations for a system of N electrons on a 3-sphere, including symmetry classification of CI basis functions, robust treatment of angular momentum on a 3-sphere, and determination of symmetry terms. Numerical data obtained with the resulting CI code will be presented in a talk given by Stephen Dale.

The talk reports the outcome of the six months research visit (sabbatical leave) of the present author in the group of Prof. Peter Gill at Research School of Chemistry of Australian National University.

[1] PMW Gill, PF Loos, "Uniform electron gases", Theor. Chem. Acta 131, 1069 (2012)
[2] PF Loos, CJ Ball, PMW Gill, "Uniform electron gases. II. The generalized local density approximation in one dimension", J. Chem. Phys. 140, 18A524 (2014)

Benefits of Inconsistent Density Functional Calculations

IL003

Professor Eunji Sim

Yonsei University, Seoul, Korea, Republic of

The energy error of any variational density functional calculation can be decomposed into errors contributed from the approximate functional and that from the self-consistent Kohn-Sham density. In most DFT calculations, the energy error stems from inaccurate functional approximation. However, for some calculations known as the limits of standard DFT, the error actually occurs due to a large density-driven error that can only be cured by improving the density. Density-corrected density functional theory (DC-DFT) uses a more accurate density rather than its self-consistent approximate density to reduce the density-driven error. We show that HF-DFT, one of the simplest methods to perform DC-DFT, can dramatically improve the accuracy and precision of standard density functional approximations for interesting chemical systems including torsional barriers, halogen bonds, spin gaps of transition metal complexes, radical geometries, molecular dissociation curves, anion electron affinities, and more.

Mechanistic Understanding of Catalysis by Combining Computation and Mass Spectrometry

IL004

Prof. Yun-Dong Wu[1,2], Dr. Xinhao Zhang[1,2], Dr. Guijuan Cheng[1,3]

[1]Lab of Computational Chemistry and Drug Design, Peking University Shenzhen Graduate School, Shenzhen, China. [2]Shenzhen Bay Laboratory, Shenzhen, China. [3]Warshel Institute for Computational Biology, School of Life and Health Science, The Chinese University of Hong Kong, Shenzhen, China

Mechanistic studies are of great importance for the understanding, optimization, and design of chemical reactions, especially catalysis. Computational chemistry and mass spectrometry have been utilized for investigating reaction mechanism. However, validation of computational results relies very much on comparison with experimental data. On the other hand, lacks of detailed structural information limit understanding of chemistry in mass spectrometry. Combining computational chemistry and mass spectrometry provide a solution for both. Computational chemistry gives detailed structural information of reaction intermediates and explores reaction energy profiles, MS provides information of possible reaction intermediates, which are difficult to obtain by other experimental methods. Here we present several examples to demonstrate the synergy of ion-mobility mass spectrometry and computational chemistry in studying reaction mechanism. [1-8]

[1] Cheng, G.-J.; Yang, Y.-F.; Liu, P.; Chen, P.; Sun, T.-Y.; Li, G.; Zhang, X.; Houk, K. N.; Yu, J.-Q.; Wu, Y.-D., J. Am. Chem. Soc. 2014, 136 (3), 894-897;
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[3] Zhong, X.-M.; Cheng, G.-J.; Chen, P.; Zhang, X.; Wu, Y.-D., Org. Lett. 2016, 18 (20), 5240-5243;
[4] Sun, H.; Zhang, Y.; Chen, P.; Wu, Y.-D.; Zhang, X.; Huang, Y., Adv. Synth. Catal. 2016, 358 (12), 1946-1957
[5] Cheng, G.-J.; Zhang, X.; Chung, L. W.; Xu, L.; Wu, Y.-D. J. Am. Chem. Soc. 2015, 137 (5), 1706-1725
[6] Zhang, X.; Chung, L. W.; Wu, Y.-D. Acc. Chem. Res. 2016, 49 (6), 1302-1310
[7] Song, L.-J.; Wang, T.; Zhang, X.; Chung, L. W.; Wu, Y.-D. ACS Catalysis 2017, 1361-1368
[8] Zhang, Q.; Liu, Y.; Wang, T.; Zhang, X.; Long, C.; Wu, Y.-D.; Wang, M.-X., J. Am. Chem. Soc. 2018, 140, 5579

Orbital Concept for Methane Activation

IL005

Professor Kazunari Yoshizawa

Kyushu University, Fukuoka, Japan

Although there exists a commercial gas-to-liquid method involving a two-step process via syngas production, a novel route of methane conversion should be developed. Among all the conceptually possible methods for converting methane to methanol, the direct methane hydroxylation ($CH_4 + ½O_2 \rightarrow CH_3OH$) at low temperature seems to be the most viable because it provides a direct route of conversion and allows a much lower operational cost. The major causes why the activation of methane is so intricate are: the sp^3 C-H bond is too strong as exemplified by its large bond dissociation energy (104 kcal/mol), its non-polar nature makes it difficult to be trapped in solvents or on surfaces which may catalyze the C-H bond cleavage, and we need to take care of a problem of overoxidation because the products of the methane functionalization often include a C-H bond which is more reactive than that of methane. We have studied the reaction mechanism for the C-H activation of methane and the direct conversion of methane to methanol by methane monooxygenase, bare transition-metal oxides (1), metal-exchanged zeolites (2,3), and metal-oxide surfaces (4). This talk presents an overview of the recent progress in the computational elucidation of the catalytic mechanism of methane hydroxylation by catalysts and enzymes in terms of orbital interactions between methane and metal-oxide active centers. A second-order perturbation theory approach is applied to the analysis of the electronic structure of methane, which is found to be significantly distorted at the active centers.

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Quantum Interference Effects in ICN dissociation Reaction

IL006

Prof. Satoshi Yabushita, Dr. Tatsuhiko Kashimura

Keio Uiversity, Yokohama, Japan

Molecular photodissociation has provided us with a wealth of information of molecular dynamics. If two excited states are simultaneously prepared by a photon and are led to an identical quantum state of the photoproducts, quantum interference can be observed in their fragment properties [1,2]. Such interference effects have been discussed in the ICN photodissociation for many years, but their details are still unclear. In this study, such quantum interference effects are investigated using the spin-orbit CI method and semiclassical methods.

One of the most spectacular yet unsolved problems was the spin-rotation F_1 (J=N+1/2) and F_2 (J=N-1/2) populations for each rotation level N of CN fragments.

$$\mathrm{ICN} + h\nu \rightarrow \mathrm{I}\,(^2P_{3/2}) + \mathrm{CN}(X^2S^+, N, F_1 \text{ or } F_2)$$

$$\rightarrow \mathrm{I}^*(^2P_{1/2}) + \mathrm{CN}(X^2S^+, N, F_1 \text{ or } F_2)$$

Zare *et al.* found that the degree of the non-statistical population, $f(N)=[P(F_1) - P(F_2)]/ [P(F_1) + P(F_2)]$, exhibited an oscillatory behavior with N [3]. Here, $P(F_i)$ is the respective F_i population. We have derived the semiclassical expression for $f(N)$ and found that its oscillatory behavior is caused by quantum interference between the two dissociative wave packets on the 3A' and 4A' surfaces, and eventually correlated to the F_1 or F_2 levels through Rosen-Zener-Demkov type nonadiabatic transitions at the asymptotic regions [4].

Significant non-Condon effects were found in the z (parallel) component of the transition dipole moment (TDM) to $^1\Pi_1$ (5A') at slightly bent geometries. Our semiclassical formula for the orientation parameter $C(N)$ using the new TDM functions gave a satisfactory agreement with the experimental results [5].

[1] A.G. Suits and O.S. Vasyutinskii, Chem Rev **108**, 3706 (2008). [2] T. Matsuoka *et al*, *JPCA* **119**, 9609 (2015). [3] H. Joswig, *et al.*, *Farad Discuss Chem Soc*, **82**, 79 (1986). [4] T. Kashimura *et al.*, *JCC*, **40**, 482 (2019). [5] T. Kashimura *et al*, *JPCA* **123**, 4000 (2019).

Exploring the Stable Pre-Nucleation Species for Calcium Phosphate Materials

IL007

Ms Natalya A Garcia, Dr Raffaella Demichelis, A/Prof Paolo Raiteri, Prof Julian D Gale

Curtin University, Perth, Australia

Calcium phosphate materials, such as the mineral apatite, are important both in nature, as bones and teeth, and potentially in battery applications. It is therefore valuable to understand how such minerals precipitate from aqueous solution in order to control their properties. Following the proposal of the existence of stable pre-nucleation clusters for calcium carbonate, it has also been demonstrated that calcium phosphate phases can also follow complex nucleation pathways that involve precursors. Experimentally, it has been suggested by Habraken *et al.* [1] that the dominant initial species close to neutral pH is $Ca(HPO_4)_3^{4-}$, which subsequently forms a dimer, and ultimately higher aggregates, via hydrogen bond bridging.

In this study, the plausibility of the proposed experimental mechanism is examined using free energy methods based on classical molecular dynamics using a force field that is derived and carefully benchmarked against experimental thermodynamics [2]. Specifically, well-tempered multiple walker metadynamics is used to map the free energy landscape as a function of up to three collective variables, including distances and the Ca-water coordination number, where the latter is necessary due to the slow exchange of ligands on the simulation timescale.

Based on extensive sampling of the thermodynamics, it is found that the current literature pathway for association appears to be unlikely, as expected from the significant net negative charge of the resulting species. Alternative speciation mechanisms will be proposed, as well as other factors that might alter the state of pre-nucleation clusters.

[1] W.J.E.M. Habraken *et al*, *Nature Comm.*, **4**, 1507 (2013)
[2] R. Demichelis *et al*, *J. Phys. Chem. B*, **122**, 1471 (2018)

Understanding the Self-Assembly Process: A Global and Local Approach

IL008

Professor Hirofumi Sato

Kyoto University, Kyoto, Japan

Self-assembly is a process in which a large number of molecules assemble to form a highly ordered structure spontaneously. Over the past few years, a number of metal complexes consisting of coordination bonds, have been synthesized. However, until now the geometry of the final product has been noted, and its formation process has not been understood at all. Recently developed by Hiraoka et al., QASAP is a very powerful experimental method to observe the details of this process. For the octahedral capsule complex M6L8, we investigated the self-assembly process using various theoretical approaches. More specifically, our results are summarized as follows:

(1) A reaction network consisting of transient species of all sizes up to the final product was considered, and the transition between them was analyzed based on a master equation. As a result, it was found that transient species of gradually larger size were generated and then formed an intramolecular bond. At the final stage, it was suggested that there were two transient species leading to the final product.

(2) M6L8 contains many transition metals. In addition, in the process of self-assembly, there are innumerable intermediates and transition states, meaning that it is not possible to understand the phenomenon only by conventional quantum chemical calculations. Here, by constructing a quantum-chemical effective Hamiltonian model developed by Iuchi et al., we realized a global search on the potential energy surface. It was found that the chiral isomer of the ligand plays an important role in determining the reaction-limited final step.

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2. Y. Matsumura, S. Iuchi and H. Sato, *Phys. Chem. Chem. Phys.* **20**, 1164, (2018).
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Ionic Liquids for PEDOT:PSS Conductivity Enhancement: Multiscale Molecular Modeling

IL009

Mr. Ambroise de Izarra[1,2], Mr. Changwon Choi[1], Prof. Yves Lansac[2,1], Prof. Yun Hee Jang[1]

[1]DGIST, Daegu, Korea, Republic of. [2]University of Tours, Tours, France

Flexible and transparent conductive materials are essential for the implementation of foldable displays, rollable TVs, wearable solar cells, and skin adhesion sensors. The most promising candidate is PEDOT:PSS, a transparent conducting polymer, which is also thermally stable and environmentally friendly owing to its water-processability. However, the excess hydrophilic insulator PSS(-) encapsulates the hydrophobic conductor PEDOT(+) by electrostatic attraction and interferes with the formation of the PEDOT conduction network, resulting in too low conductivity. The conductivity of PEDOT: PSS has recently increased to 5,000 times after treatment with ionic liquid. Our multiscale molecular modeling demonstrates the conductivity enhancement mechanism that ion exchange between PEDOT:PSS and the ion pairs in the ionic liquids helps PEDOT to decouple from PSS and to grow into a conductive PEDOT network. We propose that the most efficient ionic liquids triggering the most favorable ion exchange with PEDOT:PSS should be a combination of hydrophilic small hard cations which can bind tightly to hydrophilic PSS(-) and hydrophobic bulky soft anions which can bind tightly to hydrophobic PEDOT(+).

Allosteric Regulation of Biological Function from Multistate Density Functional Theory

IL010

Professor Jiali Gao

Shenzhen Bay Laboratory, Shenzhen, China. University of Minnesota, Minneapolis, USA

Kohn-Sham density functional theory is widely used in chemistry and physics. Yet, there are some well known shortcomings, especially for treating systems with strong correlation. Furthermore, for applications to processes involving charge transfer and energy transfer, which are ubiquitous in chemistry and biological systems, it is often necessary to define charge or spin localized states. To model these reactions through atomistic (molecular dynamics) simulations, I will discuss a block-localization scheme for defining diabatic states by construction (DAC). In particular, a multistate density functional theory (MSDFT) is described to model charge transfer reactions induced by photoexcitation of receptor proteins to initiate allosteric conformation changes.

Modeling Human DNA Repair Processes

IL011

Dr. Stacey D Wetmore

University of Lethbridge, Lethbridge, Canada

Despite its relatively simplistic structure, DNA contains all information vital to life. However, the genetic information contained within the sequence of nucleobases in DNA can become damaged by both external (e.g., pollutants) and internal (e.g., estrogen) agents. Common nucleobase modifications arise from agents that lead to nonbulky alkylation (e.g., formaldehyde) or oxidation products (e.g., hydroxyl radicals), and agents that result in the addition of bulky carcinogenic moieties (e.g., aromatic amines). Such modifications can distort the structure of the canonical DNA duplex and disrupt the function of polymerases that replicate DNA, including the mechanism and the mutagenic outcomes. However, the magnitude of these effects will depend on the chemical composition of the nucleobase lesion. Nevertheless, efficient defense mechanisms exist to combat the effects of DNA damage, including base excision, nucleotide excision and direct repair processes. Multiscale computational techniques can provide detailed molecular level information about the structure of modified DNA and its interactions with enzymes that repair damaged DNA. This talk will highlight recent work from my group that employs a multipronged computational approach, including quantum chemical calculations, molecular dynamics simulations, and combined QM/MM techniques, to understand the biochemical impact of DNA damage. In addition to unveiling key information about the structure and processing of damaged DNA that has potential applications in the development of adjuvant chemotherapeutic approaches, the findings from this work expand our understanding of the chemistry of modified nucleic acids purposely designed for applications such as bioprobes or nanomaterials.

Bonder: Convenient Analysis of Non-Covalent Interactions

IL012

Assoc. Prof. Joseph R Lane

University of Waikato, Hamilton, New Zealand

Non-covalent interactions are important in a diverse range of applications in the fields of chemistry and biology including solvation, crystal packing, DNA base pairing, enzyme-drug binding, and protein folding. The so-called Non-Covalent Interactions (NCI) theory, which is based on an analysis of the reduced density gradient, is a popular approach for identifying and analysing non-covalent interactions.[1] While NCI theory has largely been used for qualitatively interpreting non-covalent interactions, we have recently shown that the integrated kinetic energy density within a reduced density gradient isovolume [$G(s_r)$] is a good predictor of hydrogen bond strength.[2]

There are several existing software packages that incorporate NCI analysis, however, these programmes exhibit scaling challenges when they are used on larger molecules. To accurately determine integrated properties, such as [$G(s_r)$], a fine grid-size must be used for NCI analysis, which with cubic scaling, makes the computational and storage costs significant, even for modest-sized systems. To alleviate these challenges, we have developed a local software programme, Bonder, which automatically generates a series of small 3D grids only in the regions where non-covalent interactions are present. This approach greatly reduces the computational and storage costs of NCI analysis, allowing it to be applied to systems as large as proteins.

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Full Coupled-Cluster Reduction for Strongly Correlated Electrons

IL013

Prof. Seiichiro L. Ten-no

Kobe University, Kobe, Japan

A full coupled-cluster (FCC) expansion for arbitrary electronic systems is developed by explicitly expanding the commutators of the Baker-Campbell-Hausdorff series for cluster operators in binary representations. A full coupled-cluster reduction (FCCR) [1], that is capable of providing very accurate solutions of the many-body Schrödinger equation exploiting the sparsity of the exponential ansatz of FCC,is then introduced employing screenings to the projection manifold and commutator operations. The projection manifold is iteratively updated using the interaction space connected to the primary clusters with large amplitudes. The operation of the commutators is further reduced by introducing a correction, taking into account the so-called exclusion-principle-violating (EPV) terms that provides a fast and near-variational convergence in many cases. Numerical results will be presented for systems including polyacenes and the chromium dimer. We shall further discuss a partially linearized adaptation of FCCR(l) [2], which allows a massively parallel implementation for a large excitation manifold.

[1] E. Xu, M. Uejima, and S. L. Ten-no, Phys. Rev. Lett., **121**113001 (2018).
[2] E. Xu, M. Uejima, and S. L. Ten-no, in preparation.

Interlacing and Avoided Crossings of a Manifold of Potential Energy Surfaces Studied by a Spin-Free State Specific Many-Body Approach

IL014

Professor Debashis Mukherjee[1], Ms Riya Kayal[2], Mr Dibyajyoti Chakravarti[2], Mr Koustav Hazra[2]

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Any effective Hamiltonian based many-body formalism describing a manifold of states dominated by a set of 'model functions' spanning a CAS is numerically unstable due to the notorious problem of intruder states. This is why generating PES of a group of states can rarely be studied in a size-consistent manner via an $\mathbf{H}_{\mathbf{eff}}$. CAS based state-specific theories which target just one root of interest at a time has the potentiality of bypassing intruders, yet providing accurate PES. The state-specific multi-reference coupled cluster and perturbation theory (SS-MRCC/PT) of Mukherjee et al realized this goal and it has been very successful in describing multiple bond-breaking in a size-consistent manner. For studying states of different spin-multiplicities, we require a spin free theory to avoid spin contamination and the attendant spuriosities. We have used our Unitary Group Adapted SSMRPT (UGA-SSMRPT), which possesses all the desirable features of UGASSMRCC but computationally much cheaper, for generating a manifold of PES of same or different spatial symmetries. One expects in such situations interlacing for the PES of different symmetry and strong/weak avoided crossings for states of same symmetry. It is not immediately clear how a state-specific theory, generating successively higher-lying PES one at a time, would retain sufficiently accurate information of the lower lying wavefunctions to demonstrate the above features. We present here the results for a variety of electronic states of a set of diatomics in their various spin multiplicities which display striking accuracy by the rather low order UGA-SSMRPT for all the states studied by us. To get the best results dynamic state averaging at the CASSCF level appears to be very important. Accuracy of our results has been benchmarked against IC-MRCISD+Q. We will discuss the implications of such an accomplishment in some detail.

Effects of Triples in Fock Space Coupled Cluster: Fourth Order Perturbation Corrections to Electron Affinity and Excitation Energy

IL015

Ms Suhita Basumallick[1], Prof Sourav Pal[2]

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Fock space coupled-cluster is a well-established method to study ionization, electron affinity and excited states in a direct manner using 1-hole, 1-particle and 1 hole-particle model space respectively at singles and doubles level (FSCCSD) [1]. The method is based on diagonalization of an effective Hamiltonian constructed within the sectors of holes and particles to which model space belongs. The normal ordering of wave operator used in Fock space leads to partial decoupling and the higher Fock space solutions require progressive solutions at lower sectors. Thus, for excited states using 1 hole-particle model space, solutions to 1 hole and 1 particle are also obtained, leading to direct ionization and electron attachment energies. It was realized that the inclusion of triples is necessary to improve the quality of FSCC description of direct calculation of all these quantities. However, the full description of triples (FSCCSDT) is unfeasible in terms of computer time and storage capacities. Therefore non-iterative perturbation approximation is designed as a compromise between the cost and performance of full model in improvement of wave function and energy due to the inclusion of triples. An improvement to ionization was done by inclusion of triples at third and upto fourth order on top of full FSCCD calculation [2]. In this presentation, inclusion of all triples, up to fourth order for 1-particle Fock space sector as well as 1hole-1 particle Fock space, is presented. This will lead to improved calculateion of electron affinity and excitation energy.

Iterative Configuration Interaction with Selection

IL016

Mr. Ning Zhang[1], Professor Wenjian Liu[2], Professor Mark R. Hoffmann[3]

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According to when the static and dynamic components of electron correlation are treated, the available wave function-based correlation methods can be classified into three families, viz., "static-then-dynamic", "dynamic-then-static", and "static-dynamic-static (SDS)" [1]. Herewith we report a *restricted* SDS framework [2], which employs *the same number* (Np; the number of target states) of primary, secondary and external states for describing the static, dynamic, and again static components of correlation. That is, the secular equation to be diagonalized is of dimension 3Np, irrespective of the numbers of correlated electrons and orbitals. Even the lowest-order realizations of this seemingly *restricted* SDS framework, i.e., SDSPT2 and SDSCI, are already very accurate for classic test problems of variable degeneracies [2,3], whereas a high-order realization, i.e., iCI (iterative Configuration Interaction), can converge monotonically and quickly to full CI from above, even when a rather poor reference is taken as the start [1]. Interestingly, the micro-iteration of iCI can be reformulated as an iterative Vector Interaction (iVI) method for exterior or interior roots of general large matrices[4,5]. In this lecture, we will introduce a tabulated orbital-configuration based unitary group approach (TOC-UGA) for the selection of important configurations in iCI, so as to make the latter as efficient as possible.

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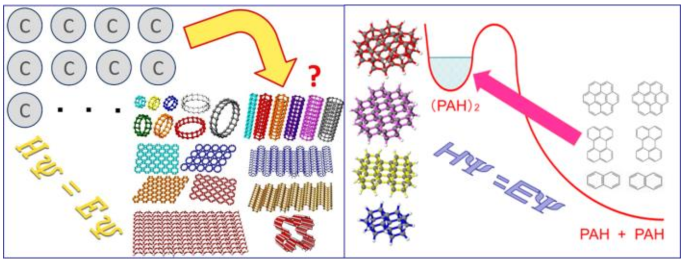
Quantum Chemical Exploration of Novel Chemistry on Potential Energy Surfaces

IL017

Professor Emeritus Koichi Ohno

Tohoku University, Sendai, Japan. Institute for Quantum Chemical Exploration, Minato-ku, Tokyo, Japan

Study of potential energy surfaces (PESs) by quantum chemical calculations can answer the fundamental questions of chemistry to elucidate chemical structures and chemical reactions for a given set of atomic compositions specified by a chemical formula. A basic approach to this goal is Global Reaction Route Mapping (GRRM) of PES, which shows all equilibrium structures (EQs), transition structures (TSs), and reaction pathways (intrinsic reaction coordinates, IRC) connecting them on the PES. Although locating all TSs on PES by quantum chemical calculations seemed to be impossible for chemical systems with more than three or four variables [1], an automated technique to perform GRRM was proposed based on scaled-hypersphere-search (SHS)/anharmonic-downward-distortion-following (ADDF) method [2] and later also on the artificial force induced reaction method [3].   In this talk, the study of PES towards GRRM is briefly summarized [4]. GRRM for simple hydrocarbons, C4H4 and C6H4, lead to unexpected discoveries of novel carbon allotropes on PES [5], which is illustrated in Fig.-Left. Further quest of novel chemistry has yielded a series of high-energy caged dimers of polycyclic aromatic hydrocarbons [6,7] as shown in Fig.-Right.



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Understanding Reaction Mechanisms Using Reaction Path Networks Generated by the Artificial Force Induced Reaction Method

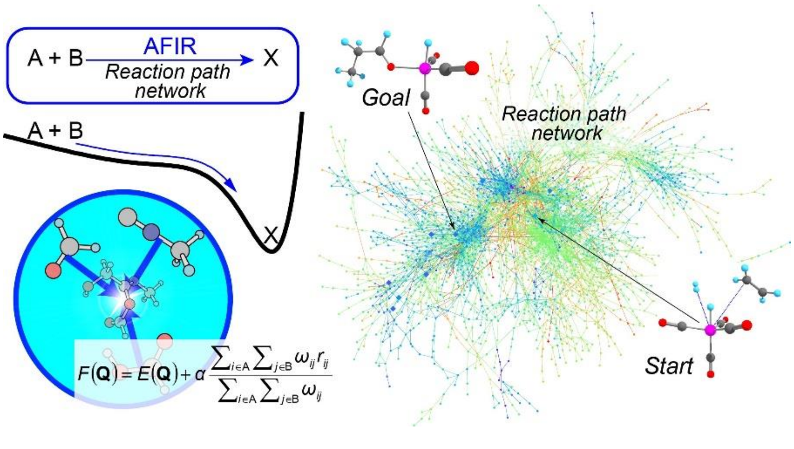
IL018

Prof. Satoshi Maeda

WPI-ICReDD, Hokkaido University, Sapporo, Japan

The mechanisms of chemical reactions have been elucidated by obtaining transition states through quantum chemical calculations. On the other hand, in actual chemical reactions, a huge number of intermediate and/or resting state structures should be involved. These stable and metastable structures form so called the reaction path network. By analyzing such a reaction path network through a kinetic method, an entire picture of the underlying reaction mechanism can be elucidated.

Here, it is the key how to generate a reaction path network which includes all relevant intermediate and resting state structures. We have developed so called the artificial force induced reaction (AFIR) method [*J. Chem. Phys.*, **2010**, *132*, 241102; *Chem. Rec.*, **2016**, *16*, 2232]. The AFIR method searches for these structures automatically by inducing structural deformations in a given system systematically by adding artificial force between fragments in the system. The AFIR method is available in the GRRM17 program [*J. Comput. Chem.*, **2018**, *39*, 233].
The AFIR method provides a complex reaction path network including thousands or more of intermediate and resting state structures. It is thus hard to extract reaction mechanisms from such a complex network. We therefore developed a kinetic method so called the rate constant matrix contraction (RCMC) method [*J. Phys. Chem. A*, **2015**, *119*, 11641]. The RCMC method systematically reduces the size of rate equations and allows one to extract the reaction mechanism automatically from the reaction path network.
In my talk, automated generation of the complex reaction path network by the AFIR method and its systematic analysis by the RCMC method will be discussed with some representative examples.



Reaction Path Concept: Intrinsic Reaction Coordinate, Anharmonic Downward Distortion Following, and Ab Initio MD

IL019

Professor Tetsuya Taketsugu, Mr Takuro Tsutsumi, Mr Shuichi Ebisawa, Dr Yuriko Ono

Hokkaido University, Sapporo, Japan

In quantum chemistry, the intrinsic reaction coordinate (IRC) has been utilized as a uniquely defined reaction path for a given elementary reaction. The IRC is defined as a steepest descent pathway starting from a transition state (TS) geometry to reactant and product minima on a multi-dimensional potential energy surface. Ohno and Maeda proposed an anharmonic downward distortion following (ADDF) approach which can find, in principle, all the TS geometries starting from the minimum. A combination of the ADDF and IRC computations can generate a global reaction route map for a given molecular system. In this talk, I will introduce our recently developed theoretical methods (1) to analyze ab initio molecular dynamics (AIMD) trajectories on the basis of the global reaction route map, (2) to visualize the IRC and the global reaction route map by a classical multidimensional scaling method, and (3) to determine the ADDF pathways by the non-iterative algebraic method. In these approaches, one can discuss the dynamics effect beyond the static global reaction route map (the molecule can hop from the IRC to another IRC), and also elucidate the mechanism of generation of the ADDF pathway around the equilibrium structure.

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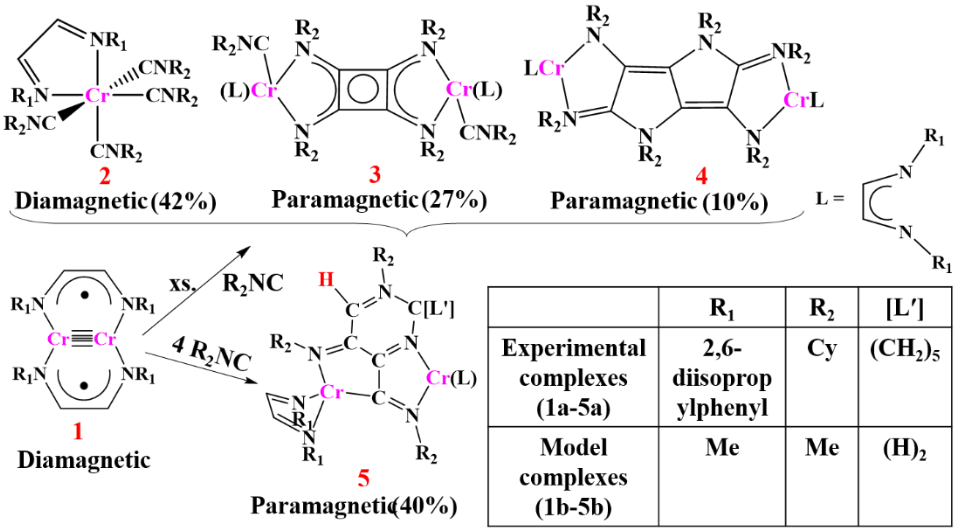
MECP (Minimum Energy Crossing Point) Barrier Controls Reductive Coupling of Isocyanides Mediated by Cr-Cr Quintuple Bond: A DFT Study Involving 50 Intermediates, 23 Transition States and a Range of Spin Multiplicities

IL020

Mr. Sagar Ghorai, Prof. Eluvathingal D Jemmis

Indian Institute of Science, Bangalore, India

Most of the reactions of small molecules mediated by Cr-Cr quintuple bonds take place in the singlet potential energy surface. In 2014 Theopold et al reported a unique isocyanide coupling reaction mediated by Cr-Cr quintuple bonded complex, $[LCr]_2$ (L = N,N′-bis(2,6-diisopropylphenyl-1,4-diazadiene) (1a) with a variety of products, $[LCr(CyNC)_4]$ (2a, diamagnetic), $[L_2Cr_2[C_4(NCy)_4](CyNC)_2]$ (3a, paramagnetic) and $[L_2Cr_2[C_6(NCy)_6]]$ (4a, paramagnetic), with an excess of CyNC (Scheme 1). Treatment of four equivalents of CyNC with 1a resulted in 5a (paramagnetic) with 40% yield where one of the cyclohexyl substituents shows a C-H activation (Scheme 1). We present computational studies of the electronic structure of the products with different spin states, mechanistic pathways for their formation, and MECPs, to understand details of the reactions.



	R_1	R_2	[L′]
Experimental complexes (1a-5a)	2,6-diisopropylphenyl	Cy	$(CH_2)_5$
Model complexes (1b-5b)	Me	Me	$(H)_2$

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Proposal of Periodic-QM/MM Method and Its Application to a Molecular Crystal Consisting of a Transition Metal Complex

IL021

Professor Shigeyoshi Sakaki

Kyoto University, Kyoto city, Japan

Molecular crystals consisting of transition metal complex exhibit adsorption and emission spectra different from those of their isolated molecule, in general. Also, some of them exhibit adsorption and/or emission spectral change(s) by gas adsorption. Vapochromism by volatile organic toxic molecule is one good example, which is a prototype of a gas sensor. To understand such phenomena, we need to know electronic structure of target molecule in crystal.

Though infinite system can be investigated using periodic DFT method, the use of hybrid DFT functional is still limited and post Hartree-Fock method cannot be employed for realistic unit cells. To investigate emission spectra, we need to optimize excited states of target molecules surrounded by molecules in their ground states because population of excited state is marginal in general. For such geometry optimization, usual periodic DFT calculation is not useful because very large unit cell consisting of one target molecule in an excited state and many molecules in their ground state must be employed as model but such calculation is very time-consuming.

To investigate absorption and emission spectra of molecular crystal, we proposed a periodic QM/MM method.[1] In this method, the target molecule is calculated at QM level, where the remaining moiety is constructed as mirror image of QM molecule (the same geometry) and represented at MM level using point charges distribution and Lennard-Jones potentials.

Using this periodic-QM/MM method, we successfully elucidated change of spin state of Ni(II) quinonoide complex by MeOH adsorption into crystal and emission spectrum change of Au(I) complexes by mechanical stimulation.[2] Both are new findings in molecular crystals, though such changes cannot be observed in solution.

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Computational Fullerene Thermochemistry

IL022

Dr Bun Chan

Nagasaki University, Nagasaki, Japan

Fullerenes continue to attract a great deal of attention from nano-technologists. Whereas much of this attention has been directed at their practical applications, we are interested to fill the knowledge gap in their basic properties, which could assist the design of functional fullerene species from a more fundamental perspective. Recent advances in computational quantum chemistry have enabled calculation of such quantities with accuracies that may rival experimental determinations. We have in recent years used large-scale quantum chemistry computations to obtain thermochemical stabilities of a variety of fullerenes, which we have used to gain a deeper understanding of their unique chemistry.

Calculation of Local Diffusion Coefficients for Inhomogeneous Systems

IL023

Ms Michelle A. Hunter[1], Professor Debra J. Searles[1,2]

[1]The Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Australia.
[2]School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, Australia

Equilibrium simulations are widely used to determine linear transport coefficients, but the Einstein and Green-Kubo expressions provide a measurement of the average over the whole of a closed system. For inhomogeneous systems where there is exchange of matter between regions there are several approaches that have been applied to determine local properties such as diffusion coefficients and viscosity. We will show how an expression for local transport coefficients in equilibrium and nonequilibrium systems can be rigorously obtained. It has been used to study homogeneous systems, and to determine the shear-dependent viscosity in evolving inhomogeneous, nonequilibrium systems. Here we will also present results for the local diffusion coefficients in equilibrium inhomogeneous systems and compare the results with other approaches.

Transferability of Carbon Interatomic Potentials: Lessons from Amorphous Carbon & Graphitization

IL024

Dr Carla de Tomas, Mr Alireza Aghajamali, A/Prof Nigel Marks, Dr Irene Suarez-Martinez

Curtin University, Perth, Australia

Assessing the transferability of a potential is a challenging and sometimes thankless task. Over the last couple of years we have used LAMMPS to perform an ongoing systematic comparison of 14 common potentials for carbon, ranging from the original Tersoff and REBO methods to modern approaches employing screening and machine learning. Amorphous carbons generated by liquid quenching and graphitization induced by annealing provide a vigorous test of bond-making and bond-breaking processes, and reveal disturbingly large differences between potentials. In many cases the variability can be traced to the level of sophistication of the potential, providing an impetus for future developments.

To address this lack of transferability, we have developed a web application tool, www.carbonpotentials.org which collates all carbon potentials and enables real-time and equivalent comparison. Unlike a traditional publication that is frozen in time, the tool is expandable and can accommodate new potentials and data.

The newly developed machine learning potential, known as GAP shows promising results but at much computational cost. While not perfect, the Environment Dependent Interaction Potential (EDIP) provides surprisingly good performance in many contexts.

The Year of the Periodic Table - Going Superheavy

IL025

Prof. Peter Schwerdtfeger[1], Dr. Jan S[1], Mrs. Odile Smits[1], Dr. Paul Jerabek[2]

[1]Massey University, Auckland, New Zealand. [2]Max-Planck-Institut, Mülheim, Germany

In the last decade we have seen the production of new elements for the Periodic Table up to nuclear charge 118. How far can we go? Where does the Periodic Table end and can we place the elements correctly into the Periodic Table as for example suggested by Pekka Pyykkö? What chemistry can we do with such exotic elements? What is the chemical and physical behavior of these exotic elements, and do we have to go beyond standard relativistic quantum mechanics to understand them? Recent developments in relativistic quantum theory have made it possible to obtain accurate electronic properties for the trans-actinide elements with the aim to predict their chemical and physical behavior. We are now able, albeit with some computational effort and sophisticated algorithms, to correctly predict the aggregate state of these elements. First-principles relativistic quantum simulations show that Cn is a liquid at standard conditions with a narrow temperature range to the gas phase, behaving more like a rare gas, whilst Og shows a rather unusual Fermi-gas like behavior being more reactive than the lighter rare gas elements and a semi-conducting solid at ambient conditions.

Coordination Asymmetry: Frenkel-Exciton Decomposition Analysis of Circular Dichroism and Circularly Polarized Luminescence for Multichromophoric Systems

IL026

Professor Masahiro Ehara[1,2,3], Mr. Takafumi Shiraogawa[2]

[1]Institute for Molecular Science, Research Center for Computational Science, Okazaki, Japan. [2]SOKENDAI,The Graduate University for Advanced Studies, Okazaki, Japan. [3]ESICB (Element Strategy Initiative for Catalysts and Batteries), Kyoto, Japan

In chiroptical spectroscopy, a photophysical property of chiral molecules such as circular dichroism (CD) has been successfully used to probe their configuration or conformation in the wide field of chemistry and biology. Recently, circularly polarized luminescence (CPL) has attracted much attention because of its potential utility for technological applications. Among various kinds of CPL molecules, multichromophoric systems composed of organic chromophore units have been recognized as one of the most promising candidates because of its high absorption coefficient and quantum yield. In the design or development of the CPL molecules, the control of electronic interactions between the units is important to achieve a high dissymmetry factor, which is a key parameter for the optical chirality.

Recently, we worked on the method of decomposing the CD and CPL spectra of a multichromophoric system into chromophore contributions and applied it to recently developed through-space conjugated oligomers. It enables us to evaluate the contribution from each chromophoric unit and locally excited state to the CD and CPL spectra of the total system. We demonstrate that the interactions between electric transition dipole moments of adjacent chromophoric units are crucial in the CD and CPL spectra of the multichromophoric systems. We also proposed post-modification strategy of emission and CPL of multichromophoric systems based on excitonic analysis.

We will also introduce our recent study on characteristic photoreaction in a porous crystal, Pd(II)-mediated metal-macrocycle framework (MMF). We report 1,6-diene, which normally forms an intramolecular [2+2] cycloadduct under photo-irradiation, preferentially undergoes a photo-induced olefin migration in MMF, and alternatively [2+2] cycloaddition is completely inhibited in the confined space. A plausible reaction mechanism for olefin migration triggered by the photo-induced dissociation of the Pd-Cl bond was proposed by MS-CASPT2 and DFT calculations.

Ab Initio Models for Lanthanide Complexes in Molecular Magnetism

IL027

A/Prof Alessandro Soncini, Dr Simone Calvello, Dr Matteo Piccardo, Mr Shashank V Rao

School of Chemistry, University of Melbourne, Melbourne, Australia

The most efficient Single-Molecule Magnets (SMMs) known to date are lanthanide (Ln) complexes, where molecule-based magnetic memory behaviour has been observed above liquid nitrogen temperature. [1,2] SMM behaviour arises from the crystal field splitting of the electronic ground J level of the Ln ion perturbed by the ligands, determining a large energy barrier to spin reorientation.

While in some cases ligand-metal interactions can be described via electrostatics models [3], more in general, ab initio calculations are crucial to unravel meaningful magneto-structural correlations in SMMs. However, the complexity of the electronic structure problem, featuring strong electron correlation and strong spin orbit coupling, introduces challenges, which will be discussed here together with a proposal for an efficient ab initio strategy we have implemented in a new quantum chemistry code (CERES) developed in our group. [4-6]

The performance of our computational strategy will be discussed, together with applications to challenging problems in molecular magnetism, including the identification of toroidal moments [7-10] i.e. vortex magnetic quantum states that are promising for molecular applications to spintronics and quantum computation.

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Ab Initio Crystal Field for Lanthanides

IL028

Dr. Liviu Ungur[1], Dr. Liviu F. Chibotaru[2]

[1]National University of Singapore, Singapore, Singapore. [2]KU Leuven, Leuven, Belgium

The talk will describe the derivation methodology of the parameters of the crystal field (CF) for the ground and excited *J* multiplets of lanthanides [1] from rigorous *ab initio* calculations, as implemented in the SINGLE_ANISO program. The methodology is applied to the analysis of CF parameters in $[Tb(Pc)_2]^-$anion and Dy_4K_2complex and compared with several approximate and model descriptions. It is found that the application of geometry symmetrization, the use of electrostatic point-charge and phenomenological CF models, lead to unacceptably large deviations from predictions based on *ab initio* calculations for experimental geometry. It is shown how the predictions of standard CASSCF (Complete Active Space Self-Consistent Field) calculations (with 4*f* orbitals in the active space) can be systematically improved by including effects of dynamical electronic correlation (CASPT2 step) and by admixing electronic configurations of the 5*d* shell. This is exemplified for the well-studied Er-trensal complex. The electrostatic contributions to CF parameters in this complex, calculated with true charge distributions in the ligands, yield less than half of the total CF splitting, thus pointing to the dominant role of covalent effects. This analysis allows the conclusion that *ab initio* crystal field is an essential tool for the decent description of lanthanides.

The accuracy of the CASSCF / CASPT2 / RASSI / SINGLE_ANISO ab initio methodology for the description of the crystal field of the excited multiplets and requirements for the future development of the *ab initio* methods for this purpose will be discussed.

Combining Ab Initio Valence Bond Method with Density Functional Theory

IL029

Professor Wei Wu

College of Chemistry and Chemical Engineering, Xiamen Univwesity, Xiamen, China

A hybrid method that combines ab initio valence bond (VB) method with density functional theory, named DFVB, would be presented in this talk. DFVB is a multi-reference DFT, where ab initio valence bond method is used for providing a multi-reference wave function, and covers the static correlation energy, while the dynamic correlation energy is taken into account by using density functional scheme. Owing to the incorporation of DFT into VB methods, on one hand, DFVB provides an economic route for improving the accuracy of ab initio VB method. On the other hand, DFVB overcomes some disadvantages of Kohn-Sham DFT that arise from the use of single determinant.

Extended Koopmans' Theorem at the Second Order Perturbation Theory: From Wave Function Theory to Density Functional Theory

IL030

Professor Xin Xu

Collaborative Innovation Center of Chemistry for Energy Materials, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, MOE Laboratory for Computational Physical Science, Department of Chemistry, Fudan University, Shanghai, China

Ionization potential (IP) is a fundamental property of atoms, molecules and solids, which is often associated with the orbital energy via Koopmans' theorem in wave function theory (WFT) or Janak theorem in density functional theory (DFT). However, relaxation and correlation effects are often important in the electron detachment process, calling for the respective extensions.

The extended Koopmans' theorem (EKT[1]) at the level of second order perturbation theory (MP2) provides a straightforward way to calculate IPs as one electron quantities. Such an EKT-MP2 method[2], by employing the relaxed density matrices, often suffers from the negative occupation problem, failing to provide the complete IP spectrum. Here a small positive number approximation is proposed[3] to cure this problem and the associated unphysical results. As an extension of the EKT formalism to DFT, a combination of EKT and the doubly hybrid functionals (EKT-DH)[4] is presented using a partial interaction system based on the adiabatic connection path of DFT, while a rigorous connection of EKT with the Perdew-Parr-Levy-Balduz condition is established. When EKT-MP2 and EKT-XYG3 are applied to a set of atoms and molecules, new insights are gained on the roles played by the relaxation and correlation effects in the IP calculations. In particular, the EKT-XYG3 method[5] is shown to be capable of describing the breakdowns of the quasi-particle approximations for the inner valence IPs with high efficiency.

We appreciate the support from National Natural Science Foundation of China (Grant 21688102).

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A New Minimal-Determinant Electronic Structure Model that Interpolates Between Molecular Orbital and Valence Bond Theories

IL031

Mr Chris J Stinson, Dr Deborah L Crittenden

University of Canterbury, Christchurch, New Zealand

The static correlation problem is a well is a well-known problem in computational quantum chemistry. It fundamentally stems from the single-reference approximation used within molecular orbital theory, which effectively assumes that there is only a single way of "filling up" molecular orbitals with electrons.

However, this assumption breaks down at dissociation, where neither a doubly-occupied bonding molecular orbital nor doubly-occupied anti-bonding orbital is an appropriate representation of the system. It also breaks down in cases where multiple, different bonding patterns are plausible. A well-known example is the electronic ground state of ozone, which admits multiple "Lewis dot diagram" structures.

Our solution is a new electronic structure model based upon a series of spin-flip optimised molecular orbitals. These provide a basis for constructing wavefunctions that smoothly interpolate between the molecular orbital model at equilibrium and a valence bond like wavefunctions at dissociation. Our model is black-box, computationally efficient, size-consistent and numerically stable.

It will be illustrated using lithium hydride as a prototype system, which has non-trivial electronic structure due to avoided crossings between the ground state and first excited singlet state upon dissociation. It has also been well-characterised experimentally and computationally.

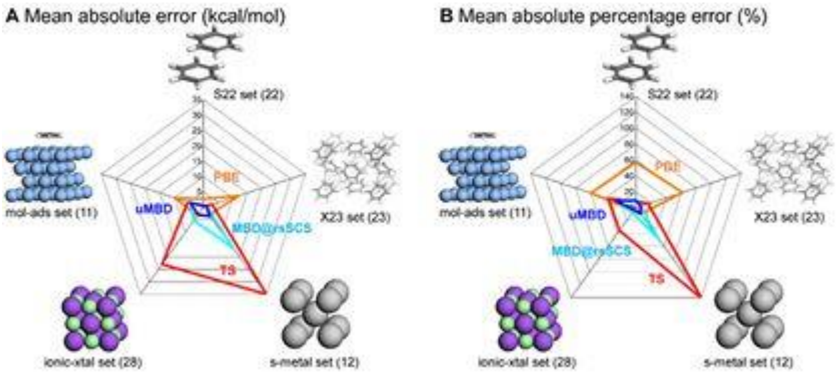
uMBD: A Materials-Ready Dispersion Correction that Uniformly Treats Metallic, Ionic, Covalent, and van der Waals Bonding

IL032

Prof. Hyungjun Kim

KAIST, Daejeon, Korea, Republic of

Materials design increasingly relies on first-principles calculations for screening important candidates and for understanding quantum mechanisms. Density functional theory (DFT) is by far the most popular first-principles approach due to its efficiency and accuracy. However, to accurately predict structures and thermodynamics, DFT must be paired with a van der Waals (vdW) dispersion correction. Therefore, such corrections have been the subject of intense scrutiny in recent years. Nevertheless, no existing model can adequately cover the full range of common materials, from metals to ionic solids, hampering the applications of DFT for modern problems such as battery design. Here, we introduce a universally optimized vdW-correction that demonstrates an unbiased reliability for predicting molecular, layered, ionic, metallic, and hybrid materials without incurring a large computational overhead. We use our method to accurately predict the intercalation potentials of layered electrode materials of a Li-ion battery system – a problem for which the existing state-of-the-art methods fail. Thus, we envisage broad use of our method in the design of chemo-physical processes of new materials.



Dispersion Interactions Between "Zero Dimensional Metals"

IL033

Prof. John F. Dobson

Griffith University, Nathan, Australia

Dispersion (van der Waals, vdW) interactions arise, in one view, from the Coulomb coupling (correlation) between charge density fluctuations on each of the interacting bodies. For two atoms or molecules in their groundstate, second-order Coulomb perturbation theory predicts the vdW energy to fall off as D^{-6} where D is the inter-species separation.

For large systems a similar analysis gives other power laws - for example two thick parallel macroscopic plates interact as D^{-2} where D is their separation, and nano-thin plates interact as D^{-4} in the simplest theories. The perturbation theory behind these results fails when the HOMO-LUMO gap is zero, leading to a vanishing energy denominator. Correspondingly [1,2], nano-thin metals interact via $D^{-5/2}$ rather than D^{-4}, two graphenes interact via D^{-3}, and one-dimensional metals interact via D^{-2} to leading order, instead of the conventional D^{-5}.

These zero-gap anomalies are absent in thick (3D) systems and are more pronounced in lower dimensions, leading to the hypothesis that a "zero-dimensional metal" would show a dramatic effect. Such a "0D metal" could be realised in a molecule with an electronically degenerate groundstate. Non-perturbative (limited CI) calculations [3] show that, under certain conditions, a pair of such molecules will have a giant vdW interaction with a D^{-3} falloff instead of the usual D^{-6}.

The static Jahn-Teller effect could, however, break the degeneracy and remove this effect. It appears likely, however, that the DYNAMIC Jahn-Teller effect can restore the symmetry, but analysis will require a sophisticated nuclear-electronic wavefunction. Candidate molecules will be discussed.

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The van der Waals Force: How it Can Outcompete Covalent and Ionic Bonding, and How it Can Be Switched Off

IL034

Prof Jeffrey R Reimers

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The van der Waals force is normally thought to be a weak force that gains importance through its universitality: all atoms in two interacting molecules or materials contribute in an additive way, much like gravity, so when the system size becomes large then so does the total van der Waals force. We provide an example in which this view is strongly supported, showing how it competes with entropy to control polymorphism in porphyrin-graphite self-assembled monolayers. Alternatively, we show that the force is susceptible to the same effects that cause Faraday caging, allowing the van der Waals force between two objects to be switched off by adding graphene in between. Finally, we show that it does not always require large systems for the force to be large. Pure atom-atom van der Waals interactions are able to overpower covalent and ionic forces to control chemical binding, demonstrated by applications in gold-sulphur chemistry and in the control of coordination and ferroelectricity in laminar materials. The formation of sulfur-stabilized gold nanoparticles is shown to be controlled by the disappearance of covalent Au(I)-thiolate bonding character and the production of van-der-Walls Au(0)-thiyl bonding. How popular computational methods perceive the van der Waals force at intermolecular distances and at covalent-bonding distances is shown to be uncorrelated, indicating that most methods embody inconsistent treatments of long-range and short-range electron correlation.

Theoretical Spectroscopy of Semiconductor Defects with Application to 2D hBN Nanophotonics

IL035

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The discovery of single-photon emission from hBN [1] has generated considerable interest and efforts are underway to characterise its spectroscopy [2. However computational approaches for the determination of excited-state energies for large periodic systems remains a significant challenge [3].

A widely-used approach to this problem are Density Functional Theory (DFT) based methods offering a good balance between computational expediency and reliability. The HSE06 functional reproduces bandgaps in semiconductors well and, combined with methods to constrain orbital occupation, is perhaps the most favoured approach.

Electronic states of defects are often inherently multi-reference open-shell and closed-shell states that involve broken chemical bonds and charge-transfer. Here, we assess the performance of DFT by comparing with ab initio wavefunction based methods such as coupled cluster and multi-reference configuration interaction, along with time-dependent DFT. We also present an extension of the empirical methods for estimating energies of low-spin multiplicity to states containing more than 2 open shell electrons, and a symmetry based methodology for ensuring that constrained DFT calculations converge to the expected excited state. Our aim is to understand the reliability of excited state energies calculated using the common approach of constrained HSE06 DFT. This is an important problem that impacts our understanding of the nanophotonics of semiconductor in general.

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Computational Design of Boron Clusters and Materials

IL089

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While carbon-based fullerene, graphene, graphdiyne, and nanotube materials were widely studied in the past three decades, similar boron-materials and clusters have received much less attention. Boron clusters and materials exhibit unique properties in a variety of areas, including catalysis, superhard solids, and magnetic materials. In this talk we will present our research in this area and provide an overview of the recent developments of computational design of boron clusters and materials, including metallo-borophenes, -borospherenes, and –boronanotubes. [1-6]

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How Stable is 2D gallium, aka Gallenene? Electronic and Thermodynamic Aspects

IL037

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Atomically thin gallium layers have been experimentally produced via solid-melt exfoliation, and have been shown to have promise as robustly metallic 2D materials for electronic applications [1]. However the extent to which the experimental technique can be extended to other metals relies on understanding how the 2D structures relate to the bulk form of gallium, which is itself unique as an elemental 'molecular metal' (Fig. 1). We relate the experimentally formed 2D materials to the theoretically predicted 'bilayer gallium' which has previously been shown to be stable in vacuum at the nanoscale, via density functional theory calculations [2,3]. We also study the variation of electronic structure with temperature, to assess the stability of this novel, metallic 2D material under a range of experimentally relevant conditions.

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Identification of Absolute Configuration of Diptoindonesin D by Quantum Chemical Calculations and interaction with Penicillin-Binding Protein 2a, based on Molecular Docking

IL038

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Diptoindonesin D was isolated from the stem bark of *Shorea roxburghii* G. Don in Khon Kaen province, Thailand and exhibits potent antibacterial activity against *Staphylococcus epidermis* and *Staphylococcus aureus*. The possible conformation of R- and S-configuration of diptoindonesin D were built and optimized at M062X/6-31g(d) level of theory. The ECD spectra were calculated to the selected conformation using TD-CAM-B3LYP/6-311++G(d,p) method including PCM model with methanol. The Boltzmann weight was applied to generate the calculated ECD spectra and the similarity factor between experimental and calculated ECD spectra were determined to select the configuration of diptoindonesin D. The ECD results indicated that the possible configuration of diptoindonesin D is R-configuration. Furthermore, reverse docking was performed to identify the protein target of diptoindonesin D based on four scoring functions using GOLD program. This study is the first investigation between diptoindonesin D and its binding interaction with cell wall synthesis protein targets. The results confirmed that, penicillin-binding protein 2a (PBP2a), an antibacterial cell wall, might be the potential target for the binding of diptoindonesin D. The obtained results can be useful as a guideline for the development of effective diptoindonesin D as a PBP2a inhibitor.

Anticancer Drug Screening and Development

IL039

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Epidermal growth factor receptor (EGFR) are the key molecular targets for cancer treatment due to their major contributions to complex signaling cascades modulating the survival of cancer cells. In the present study, the derivatives of mansonone G (MG, a naphthoquinone-containing compound), and chalcone (a flavonoid analog) were subjected to theoretically and experimentally investigate the anticancer effects on EGFR signaling pathways in cancer cell lines expressing wild-type EGFR (A549 and A431) and mutant EGFR (H1975 and H1650). *In vitro* cytotoxicity screening results demonstrated that butoxy MG (MG3) was more susceptible to H1975 mutant cells (IC_{50} of 4.21 µM) than A549 wild-type cells (IC_{50} of 8.54 µM). All 47 chalcones seemed to be more active against the A431 than the A549 cell line. Moreover, these five chalcones **1c**, **2a**, **3e**, **4e** and **4t** showed more potent on H1975 than H1650 cell lines. Importantly, MG3 and chalcones was low toxic against normal fibroblast cells. Western blotting and flow cytometric analyses revealed that MG3 induced caspase-dependent apoptosis mechanism through: (*i*) inhibition of p-STAT3 and p-Akt without affecting upstream p-EGFR, as supported by MM/GBSA binding free energy calculations and (*ii*) activation of p-Erk. The binding of MG3 toward STAT3 and Akt dramatically induced protein conformational changes, especially the residues in the binding pocket. In contrast, chalcones **1c**, **2a**, and **3e** exhibited an EGFR-TK inhibitory activity with IC_{50} in range 10.3 - 15.4 µM. Molecular dynamics studies on their complexes with EGFR-TK domain in aqueous solution affirmed that chalcones were well occupied within the ATP binding site and strongly interacted with seven hydrophobic residues, including the important hinge region residue M793.

Ligand Design for Intrinsically Disordered Proteins

IL040

Prof. Luhua Lai

Peking University, Beijing, China

Intrinsically disordered proteins (IDPs) play central roles in many cellular processes, which can serve as potential therapeutic targets because of their prevalence in various diseases. However, IDPs are generally considered as undruggable due to the dynamic nature of their structures and the complexity of their binding with other molecules. Most currently known small molecules targeting IDPs were discovered by experimental screening. Conventional structure based drug design methods cannot be directly applied in IDPs ligand design. The author's group has been working on IDP drug design using computational and experimental approaches. In this talk, I will discuss about the binding features of IDP and ligands and our approaches for IDP ligand design. Examples in the c-Myc and p53 systems will be given. Characteristics of compounds that bind to IDPs will be compared. Challenges and opportunities for IDP drug design will be discussed.

How Can Artificial Intelligence Help Quantum Chemists?

IL041

Professor Hiromi Nakai

Waseda University, Tokyo, Japan

In my previous talk entitled "Quantum Chemistry Meets Artificial Intelligence (AI)" at APATCC8 in Mumbai, India, I mainly explained machine-learned (ML) kinetic energy functional for the orbital-free (OF) density functional theory (DFT) [1]. Due to the success of the previous study, we have been greatly encouraged to utilize AI techniques in quantum chemical studies. In this presentation, I will talk about three topics. (I) ML correlation model [2], which is based on our extrapolation/composite model for the complete-basis-set (CBS) correlation energies [3] and the grid-based EDA of correlation energies [4]. (II) Informatics-based bond energy density analysis (EDA) [5], which is an extension of our previous models [6,7] with the help of the least absolute shrinkage and selection operator (LASSO). (III) ML virtual reaction condition optimization [8].

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Simulating Non-Adiabatic Chemical Dynamics on Quantum Computers

IL042

Dr Ivan Kassal

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Chemistry and materials science are among the most promising applications of quantum computation, especially using near-term quantum devices. Indeed, quantum computing offers a promising new paradigm to address some of the most important—but persistently intractable—problems in this field. In the past, most work on applying quantum computing to chemistry has focused on the static problem of finding energies of stationary states. The dynamic problem—e.g., simulating chemical reactions—is also important, but has widely been thought to require too many qubits. We describe a completely new approach to the quantum simulation of chemical dynamics that exploits particular properties of trapped-ion quantum computers. Our scheme makes a fully non-adiabatic simulation of a simple chemical reaction possible with existing technology.

Atom-Centred Potentials: A Tool for Fast and Accurate Modelling of Molecular Systems.

IL043

Professor Gino DiLabio

The University of British Columbia, Kelowna, Canada

We have been actively developing a low-cost approach to improve the accuracy of results obtained from Hartree-Fock and density-functional theory calculations. The approach makes use of atom-centred potentials (ACPs), which are similar in structure and used in the same way as effective core potentials. Instead replacing core electrons, ACPs are designed to produce corrections to calculated energies that result in a remarkable improvement in a wide-range of calculated properties, either by mitigating the effects of basis set incompleteness error or the errors arising from incomplete correlation treatment, or both. The motivation for the use of ACPs for improved electronic structure calculations will be presented, along with examples demonstrating their performance for a variety of chemical systems.

Theoretical Study of Uranium Isotope Fractionation by Bacteria

IL044

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Tokyo Metropolitan University, Tokyo, Japan

Some bacteria can reduce water-soluble uranium (VI) to water-insoluble uranium (IV). This function is used to prevent the spreading of toxic uranium known as bioremediation. During that reduction, heavy uranium (^{238}U) more reduces to U(IV) than light uranium (^{235}U) with bacteria, whereas the isotopic trend is not significant or opposite in general abiotic cases [1]. To elucidate the mechanism of uranium reduction and isotope fractionation by bacteria, we calculated the *equilibrium* isotope fractionation coefficient for each elementary reaction, proposed in [2]. The leading cause of isotope fractionation in heavy elements is called a nuclear volume effect. It arises from the electronic energy difference of different size of nuclear charge radii of two isotopes [3]. It is affected by relativistic effect because it is the property close to the nucleus [4]. To calculate nuclear volume effects, we performed highly accurate relativistic calculations based on X2C Hamiltonian using the Gaussian finite nucleus model in DIRAC16 program. Obtained theoretical results support the experimental trend that the heavier isotope enriched in U(IV). However, the magnitude of the isotope fractionation coefficient (2.71 per mil) is three times larger than the experiment one (0.85~0.88 per mil), and it suggests that non-equilibrium processes are essential in some elementary reaction.

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Rule Breaking Main Group Compounds Stabilized by Donor-Acceptor Interactions

IL045

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The coordination chemistry at the main group elements has attracted growing research interest over the last two decades.[1] The stabilization of rather unusual geometries, which in turn leads to the unusual reactivities, is one of the major factors contributing to this growing interest. Consequently, traditional bonding concepts have been expanded to account for the unusual coordination chemistry of the main group elements. The bonding and reactivity of ligand-stabilized beryllium, aluminum, and group-14 elements will be presented.[2-3] The variation of the bonding pattern as a function of the oxidation state of the central main group element will be illustrated. The rationalization of differential reactivities of β-diketiminate aluminum compounds and the detailed reaction mechanism will be presented.[2] The β-diketiminate aluminum compound (**1Al**) with an exocyclic double bond undergoes stoichiometric reactions with two equivalents of benzophenone and 2-benzoylpyridine to generate macrocyclic complexes of aluminum. On the other hand, the β-diketiminate aluminum compounds without an exocyclic double bond (**2Al** and **3Al**) function like transition metal complexes in catalysis.

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QMTSDock - Automatic Conformational Search of Transition States for Catalytic Reactions Using Genetic Algorithm

IL046

Prof. Richard M. W. Wong

Department of Chemistry, National University of Singapore, Singapore

Halogen bond (XB), a noncovalent interaction involving a halogen atom as an acceptor of electron density, has emerged in recent years as an important element of molecular recognition and has numerous applications such as molecular self-assembly of functional materials, crystal engineering, catalysis, and protein-ligand recognition and drug design. A positive σ-hole is widely accepted as the origin of electrophilicity of halogen atom. In the case of fluorine atom, positive σ-hole is very difficult to achieve because of its high electronegativity and low polarizability. As a result, the fluorine atom is the poorest XB donor. There is hardly any example of XB involving fluorine as XB donor in the literature. In the course of our theoretical studies, we found that fluorine atom is capable of forming significant halogen bonding with XB acceptors. In this presentation, we report our computational studies on these interesting fluorine-containing XB dimers. We analyze the nature of the XB interaction and geometrical features of these intriguing systems by means of molecular orbital theory, energy decomposition analysis, based on SAPT and 2nd generation ALMO schemes, and charge density analysis based on theory of atoms in molecules

Effect of Defects on the Gas Sensing Reaction of CH_2O and H_2S with ZnO Nanostructures

IL047

Associate Professor Michelle JS Spencer

RMIT University, Melbourne, Australia

Detection of pollutant gases, such as formaldehyde (CH_2O) and hydrogen sulphide (H_2S) in our homes and surrounding environment is of high importance for our health and safety. Nanostructured forms of zinc oxide (ZnO) have shown great promise in detecting gaseous pollutants, where the sensor incorporating the ZnO operates by measuring a change in conductivity due to the interaction between the gas and the surface of the sensor material [1]. ZnO nanostructures are highly crystalline, however, their surfaces contain defects which play an important role in the sensing mechanism. While the reaction of CH_2O and H_2S on stoichiometric nanostructured surfaces have been examined [2,3], it is not known how the presence of defects, such as surface-adsorbed oxygen, affect the gas sensing reaction. In this work, we use density functional theory and *ab initio* molecular dynamics simulations to determine the gas-sensor reaction of CH_2O and H_2S with a ZnO facetted-nanotube and nanowire containing pre-adsorbed surface oxygen (Figure 1). We calculate the adsorption geometry, binding energies, vibrational frequencies, charge transfer and density of states.

We show that both gases are able to adsorb molecularly and dissociatively in multiple sites and orientations on both nanostructures. The direction of charge transfer was calculated to be dependent on the adsorbed structure, illustrating the importance of nanostructure morphology on the surface reaction. Furthermore, the reactions involved some interesting reactions where the gas dissociated on the surface or in some cases resulted in formation and subsequent desorption of H_2O and CO that led to restoration of the stoichiometric surface of the nanostructure. This work provides useful insights into the gas-surface reaction mechanism of ZnO-nanostructures for applications in chemical sensors.

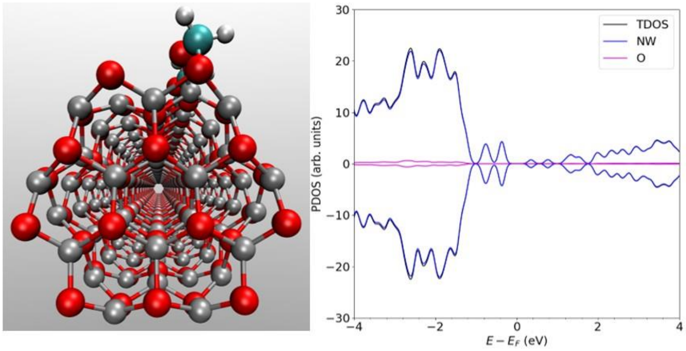

Figure 1: (left) CH_2O adsorbed on ZnO nanowire with pre-adsorbed oxygen; (right) calculated atom resolved density of states.

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Formaldehyde Oxidation over Metal-Supported Titanium Dioxide

IL048

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Formaldehyde (HCHO) is a major toxic indoor pollutant, which may cause severe health problems to human. Several methods have been used to remove it from indoor air. Complete catalytic oxidation of HCHO to CO_2 and H_2O is considered a promising technique for HCHO abatement due to its low cost and eco-friendly reaction condition [1,2]. In this work, pure metals (Ag and Pt) and core-shell metals (Pt@Ag and Ag@Pt) doped on titanium dioxide (TiO_2) have been synthesized as the catalysts for HCHO decomposition. Density functional theory calculations have been carried out to explain the catalytic behaviour of four catalytic systems, Pt/TiO_2, Ag/TiO_2 and Pt@Ag/TiO_2 and Ag@Pt/TiO_2, for HCHO adsorption and oxidation. The calculation results show that all pure and core-shell metals are strongly adsorbed on the TiO_2 surface with binding energy ranging from 6-11 eV, indicating the high stability of the catalysts. For the core-shell systems, Ag donates electrons to Pt once it is acting as either core or shell. Ag@Pt/TiO_2, in which Ag is a core and Pt is a shell, is the predominantly stable system since electrons are transferred from Ag and gained on the Pt surface. HCHO prefers to adsorb at the perimeter site between the metal and the TiO_2 surface, and the Ag@Pt/TiO_2 catalyst is the most reactive to HCHO adsorption. We found that such performance of Ag@Pt/TiO_2 originates from the electron rich Pt, which is not only stabilized the catalyst but also activated the C-H bond in HCHO oxidation.

Coordination of Ligands to Gallium Nanoclusters: Structure, Stability and Reactivity

IL049

Assoc. Prof. David J Henry, Miss Lorraine Rosson

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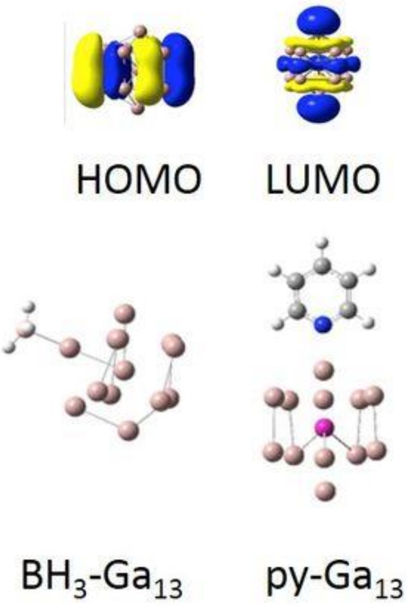
Gas-phase gallium nanoclusters can be thermodynamically stabilised through doping with p-block elements.[1] However, without surface stabilisation these clusters will aggregate in the condensed phase. Ligands provide a mechanism to achieve both stabilisation and modulation of nanocluster reactivity.[2,3] Here results of a preliminary study into the interaction of a range of different ligands with a gallium nanocluster ($Ga_{12}X$) are presented. Traditional Lewis based ligands interact well with the surface of these clusters. However, the amphoteric nature of $Ga_{12}X$ clusters means that Lewis acids also strongly adsorb to the surface of the particles. Furthermore, ligand coordination modifies the electronic structure of the cluster and can be used to modulate the reactivity of the different species.



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Chemical Dynamics in Living Cells

IL050

Professor Jaeyoung Sung

Creative Research Initiative Center for Chemical Dynamics in Living Cells, Seoul, Korea, Republic of. Chung-Ang University, Seoul, Korea, Republic of

We introduce a new type of kinetic network model and theory for biological networks, enabling an accurate quantitative description of chemical dynamics in living cells. An advantage of our approach is its applicability to biological networks producing biomolecules with arbitrary lifetime distributions to which the conventional approaches, such as the classical chemical kinetics, chemical master equation, and chemical Langevin equation are not applicable. Our approach also enables quantitative investigation into biological networks composed of multi-step or multi-channel reactions whose rates may fluctuate due to their coupling to cell environments. We demonstrate these advantages by providing an unprecedented quantitative explanation of non-classical chemical dynamics observed in various biological systems including single enzymes, *in vivo* motor-protein multiplexes, and cell systems with various synthetic gene networks. Time-permitting, we will also discuss how the frequency-spectrum of biological noise is related to the structure and dynamics of biological networks and the lifetime distribution of the biomolecules.

Does the Choice of Molecular Dynamics Forcefield or Starting Crystal Structure Influence Membrane Protein Dynamics?

IL051

A/Prof Megan L O'Mara[1], Ms Lily Wang[1], Dr Karmen Condic-Jurkic[1,2], Dr Nandhitha Subramanian[2,1], Prof Alan E Mark[2]

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In 2009, the structure of the multidrug transporter P-glycoprotein (PDB ID 3G5U) was solved at 3.8 Å resolution [1]; however questions arose as to whether or not this structure does indeed represent a physiological conformation. Recently, two further structures of P-glycoprotein were solved at 3.8 Å resolution [2, 3]. These three structures each have a different assignment in the amino acid register of four of the twelve helices, giving three conflicting medium resolution structures. Here molecular dynamics simulation techniques were used to investigate the conformation and stability of the three structures, in order to identify which structure best represents that of P-glycoprotein under physiological conditions. Conformational divergence between three systems revealed that while certain observations could be attributed to the intrinsic flexibility of the protein, others appear to reflect problems with each of the starting crystallographic models. A range of commonly used MD forcefields were also investigated to determine which best characterized biochemical data, such as residue distance maps. This work highlights the importance of the choice of simulation conditions and starting structure when simulating flexible membrane proteins.

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Unraveling How Enzyme Channel Drives Stepwise Translocation and Optimal Binding of Prostaglandin H2 for Cyclization

IL052

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Enzymes are dynamical systems that perform homeostatic abilities, in precise control of their local environment through inter-conversions of chemical and mechanical energy and self-regulating feedback connections organized hierarchically across many scales of states. Enzymes can carry out effective rate accelerations by virtue of their ability to utilize substrate-channeling forces to act as a mechanochemical valve. Such a channeling process is treated quantitatively using the key aspects of the free energy landscape; the balance between substrate positioning and conformational changes reflects the severe geometric and electronic requirements for the relatively tight transition state. The observed k_{cat}/K_M of about 10^6 M^{-1} s^{-1} for PGH_2 cyclization has been revealed to be brought about by bringing together two properly oriented reactants of substrate and enzyme regarding the magnitude significance of the contribution from outer- and inner-binding stereopopulation along the free-energy channeling pathway and thus shapes the cascade cyclization route, enforcing precise spatial and temporal control. The apparent constant k_{cat} of many P450 reactions involving the heme catalytic cycle, which is often on the order of 10^1–10^2 s^{-1} and is usually attributed to compound 0 to compound I formation, may be in large part a consequence of channeling conformation changes toward the rate-limiting state that is made possible by preorganizing the proximal hydrogen-bonding pattern of the amide groups to the cysteine sulfur, and to the push−pull modulation of the relevant heme axial ligation and activation.

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Systematic Molecular Fragmentation by Annihilation

IL053

Prof. Michael A Collins

Research School of Chemistry, Australian National University, Canberra, Australia

Systematic Molecular Fragmentation by Annihilation (SMFA) is a general method for approximating the electronic energy and other properties of large molecules. The approximation involves decomposing a molecule into relatively small molecular fragments. The method provides a systematic series of approximations in which the size of the fragments increases and the accuracy of the approximation increases accordingly; allowing the ab initio energy of large organic/biological molecules to be estimated to within a few kJ mol^{-1}.

The method is now freely available as a general program package. The program can calculate electronic energies, energy gradients and second derivatives; perform geometry optimization; find first order saddle points (transition states); perform energy optimized scans along a user-defined path; and evaluate various molecular properties. The program can use any of the following quantum chemistry packages: GAMESS(US), GAUSSIAN, NWChem and Q-Chem. In addition, SMFA provides a number of utility programs that, *inter alia*, calculate vibrational frequencies and infrared spectra with isotopic substitutions, the electrostatic potential on the solvent-accessible-surface, and isodesmic and higher order near-iso-energetic reaction schemes. Calculations of the electronic energy and related properties can be carried out using a scheme that provides a computation time that is linearly dependent on the size of the molecule or, if the user has enough processing units available, in a wall time that is independent of the size of the molecule. Some examples will be presented in this talk.

R. Kobayashi, M. A. Addicoat, A. T. B. Gilbert, R. Amos, and M. A. Collins, WIREs Comput Mol Sci. 2019, DOI: 10.1002/wcms.1413

“Cluster-in-Molecule” Local Correlation Approach for Large Molecules and Periodic Systems

IL054

Prof Shuhua Li

School of Chemistry and Chemical Engineering, Institute of Theoretical and Computational Chemistry, Nanjing University, Nanjing, China

In this talk, I will present recent progresses in developing “cluster-in-molecule” (CIM) local correlation approaches for large systems and periodic systems. In the CIM method, the correlation energy of a system can be approximately obtained from electron correlation calculations of clusters, each of which contains a subset of localized molecular orbitals.[1-6] We have recently proposed a new procedure for building virtual molecular orbitals of various clusters.[7] Numerical results show that the updated CIM approach is reliable for electron correlation calculations of large systems. Analytical CIM-MP2 energy gradients have been implemented. The present CIM-MP2 gradient program reproduces the conventional MP2 gradients reasonably well, and is reliable for geometry optimization of large systems.[8] Very recently, we have extended the CIM approach to periodic crystals.[9] The correlation energy per unit cell can be evaluated as the summation of the correlation contributions from a series of finite-sized clusters. Each cluster is defined to contain a subset of localized Wannier functions (for the occupied space) and projected atomic orbitals (for the virtual space). Illustrative calculations show that CIM is a powerful framework for accurate electron correlation calculations of crystals.

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Studying Large-Scale Systems with Wavefunction-based Methods: Improving Accuracy

IL055

A/Prof. Ekaterina Pas, Ms Anh Nguyen

Monash University, Clayton/Melbourne, Australia

The definition of large-scale applied to chemistry covers a wide range of molecular systems from long polymer chains and DNA strands to liquids and molecular crystals. The latter have been of particular interest to theoretical chemists for the last two decades as the race to develop a wavefunction-based method that can accurately predict their lattice energy. Majority of organic molecular crystals are known to exhibit polymorphism, a phenomenon that results in the compound crystallising in more than one crystal structure. Although these structures can be vastly different in terms of leading intermolecular interactions their lattice energies range very slightly. 90% of the studied polymorphs have as little as 4 kJ mol^{-1} separating their lattice energies. It is not surprising that the prediction of this property of molecular crystals strongly depends on the accuracy of a WFN method at hand. There are two requirements for such a method: 1) treatment of any type of intermolecular interaction (from hydrogen bonding to pure van der Waals forces) with high accuracy and 2) linear scalability with increasing size of the simulation box.

Recently our group have developed a method based on MØller-Plesset perturbation theory, SRS-MP2, that predicts intermolecular interaction within 2 kJ mol^{-1}. In combination with the Fragment Molecular Orbital (FMO) Approach the linear scaling can be achieved for any size of the simulation box, provided massively parallel computers are used. In this talk, I will present a new strategy developed in our group for the prediction of lattice energies of molecular crystals based on the combination of SRS-MP2 and the FMO approach. The application of this strategy to two well-studied polymorphs of benzene and aspirin will be presented.

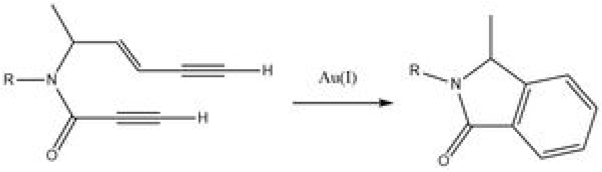
The Dual Role of Gold in Catalysis of Cycloaromatisation

IL056

Prof Brian F Yates[1], Mr Rasool Babaahmadi[1], Dr Alireza Ariafard[1], Dr Chris JT Hyland[2]

[1]University of Tasmania, Hobart, Australia. [2]University of Wollongong, Wollongong, Australia

Cycloaromatisation of compounds containing an alkene and two alkyne groups has been shown to be a facile process in the presence of a gold catalyst. Intriguingly, DFT calculations show that the gold catalyst acts in two different ways in this process. One gold compound forms a sigma bond with the alkyne group while the other gold compound acts in a more conventional pi coordination role to the second alkyne. The differentiation between the two alkyne groups is a key feature of the reaction. This leads to the formation of nucleophilic and electrophilic gold moieties in close proximity and ring closure follows rapidly. Our calculations help to validate the mechanism and explain the deuterium experiments.

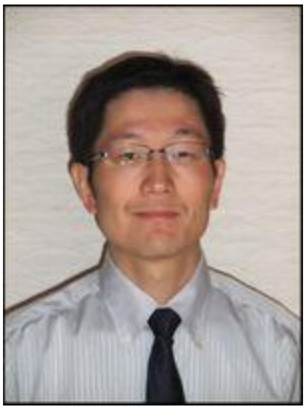


Computational Studies of Chemical Reactions in Various Catalytic Environments

IL057

Dr. Hajime Hirao

City University of Hong Kong, Hong Kong, China



In recent decades, chemistry has become increasingly diverse, and its interdisciplinary nature has been strengthened. Amid such a tide, computational chemistry has grown tremendously into an indispensable partner of experimentalists. We believe that, because of its ability to provide atomic-level insights into elusive aspects of molecular events, computational chemistry must have the potential to influence other fields in many positive ways, and cross-disciplinary interactions will offer great opportunities to make new discoveries and find exciting scientific directions. Based on this belief, we have been computationally studying molecular interactions and chemical reactions that occur in relatively small homogeneous catalytic systems, porous materials and other heterogeneous systems, and biological enzymatic systems, with the ultimate goal of contributing to resolving critical sustainability-related issues such as CO_2 separation/utilization and biomass valorization. For such studies, we apply advanced computational chemistry techniques to molecules and materials of different sizes.

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Transition State Models for Asymmetric Catalysis and Rational Predictions

IL058

Professor Raghavan B. Sunoj

IIT Bombay, Bombay, India

Asymmetric catalysis is an important area of research that help create chiral products with high enantio-purity. The control of which one of the stereoisomers would be preferred in a catalytic transformation depends on the corresponding transition state for the stereoselective bond formation step. Computational quantum chemistry has been increasingly employed toward rationalizing the stereochemical outcome in catalytic reactions.[1] In our laboratory, ab initio as well as DFT methods are employed to gain insights into carbon-carbon and carbon-heteroatom bond-forming reactions of immediate practical significance.[2] The key objective of our research is to gain molecular insights on the factors responsible for stereoselectivity and to exploit such insights toward *in silico* design of novel asymmetric catalysts.[3]

Through this talk, we intend to propose the need for a timely rethink on a number of working hypotheses on asymmetric induction that places an over-emphasis on steric interaction.[4] Interesting interpretations/rationalizations of experimental observations besides meaningful guidelines for rational improvements in the design of asymmetric catalysts would remain the key focus of the presentation.

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Materials Discovery using Computational and Data-Driven Approaches

IL059

Prof Yousung Jung

KAIST, Daejeon, Korea, Republic of

Novel materials discovery is a key to addressing many challenges in energy, climate change, and future sustainability. The usual procedure of finding innovative materials is based mainly on experiments, however, can take far too long due to a vast and discrete search space, and thus accelerating this process by orders of magnitude using scalable computations would significantly reduce the time and cost of new discovery. In achieving this grand goal, density functional first principles simulation offers a sweet spot between prediction accuracy and feasibility. I will demonstrate some of the examples to discover new materials in energy storage and conversion applications using them. I will also talk about some of our recent efforts to use machine learning for chemical science that can contribute greatly to creating potential solutions to some of these materials problems.

Database and Machine-Learning Enabled New Insights into the Lanthanide Luminescence Materials

IL060

Dr. Miho Hatanaka

Nara Institute of Science and Technology, Nara, Japan

Lanthanide compounds have been widely applied for optical materials because they show visible emissions originating from 4f-4f transitions. To better understand the mechanism and rationally design materials, computational studies are indispensable. However, *ab initio* calculations for lanthanide compounds are highly demanding because the relativistic effect and electron correlation need to be considered explicitly. To overcome the problem, we have proposed the energy shift method, a reasonable approximation to describe the potential energy surfaces (PESs), which enables us to find the local minima and minimum energy crossing points related to the emission and quenching. By using this approximation, we succeeded in explaining the thermosensitivity as well as luminescence quantum yield of Tb complexes qualitatively.

Even though the computational cost was decreased dramatically by the energy shift approximation, there were two remaining problems. One was the difficulty of proofing strong luminescence because it required the information of all the energy crossing points related to the quenching. To avoid the thorough search of crossing points, we constructed the database of quenching pathways of model complexes and found the rules about the most stable crossing points, which enabled us to find the most stable crossing point without the exhaustive search.

Another remaining problem was that the experimental quantum yield of Eu compounds could not be predicted and understood by the PESs obtained by the energy shift approximation. To understand the reason for inconsistency, we gathered the experimental data of quantum yield from literatures and built the correlation model by machine learning techniques. Based on the analyses of important descriptors, we got the new insights about the role of ligand-to-metal charge transfer and auxiliary ligands.

Computational Chemistry at the NCI supercomputer facility

IL061

Dr Rika Kobayashi

Australian National University, Canberra, Australia

NCI Australia is a highly integrated high-performance research computing and data infrastructure for delivering world-class computational services to Australian researchers. It has a history stretching over decades of supporting the computational chemistry community of Australia and looks to keep doing so into the future. This talk will give a brief overview of NCI, especially focusing on the capabilities, both hardware and software, NCI can offer chemistry researchers. I will also take this opportunity to introduce NCI's new supercomputer which is due to be operational later this year.

Insights into the Mechanisms of Cytochrome P450-Catalyzed Hydroxylations from Studies on an Ultrafast Probe Substrate

IL062

Associate Professor Elizabeth Krenske

The University of Queensland, Brisbane, Australia

Many cytochrome P450-catalyzed hydroxylation reactions are thought to follow a rebound mechanism; first, a reactive enzyme ironoxo species abstracts a hydrogen atom from the substrate C–H bond, and then, the resulting radical and Fe(OH) intermediates combine to form a new C–O bond. Specially designed probe substrates, derived from radicals that rearrange with known rate constants, have enabled quantification of the rate constants for rebound. The rate constants for rebound versus rearrangement have previously been explained by Shaik in terms of the two-state reactivity paradigm of cytochrome P450 reactivity. This presentation will report on a study conducted with a probe substrate that appears to engage in unexpectedly fast rebound. Ideas on how the observed reactivity may be accounted for by concepts beyond the two-state paradigm will be presented.

Singly-bonded Dimanganese Coordination Complexes and Manganese-binding Proteins

IL063

Mr. Ming-Hsiu Hsieh[1,2], Dr. Gou-Tao Huang[2], Mr. Pei-Chuan Chu[1], Prof. Jen-Shiang K. Yu[1,2,3]

[1]Institute of Bioinformatics and Systems Biology, National Chiao Tung University, Hsinchu City, Taiwan. [2]Department of Biological Science and Technology, National Chiao Tung University, Hsinchu City, Taiwan. [3]Center for Intelligent Drug Systems and Smart Bio-devices (IDS2B), Hsinchu City, Taiwan

The electronic structure and potential energy surface of the singly-bonded Mn–Mn and Cd–Cd complexes[1] of which geometrical motifs exactly match the theoretically predicted intermediates,[2] are reported. Reduction mechanisms and magnetic properties in the Mn–Mn bonding system are investigated and rationalized by broken-symmetry density functional theories (BS-DFT). Multireference calculations demonstrate that in the dinuclear manganese systems with even numbers of 10*e* and 12*e*, corresponding to the reactant and the product, are antiferromagnetic while the intermediate with odd number of 11*e* prefers a ferromagnetic behavior. Calculations also reveal that the rearrangement of the ligands from bridging motif to chelating coordination occurs after reduction.

Metallothioneins (MTs) without their crystal structures experimentally determined, are simulated by quantum mechanics combined with molecular mechanics (QM/MM) to predict possible geometries starting from the structural templates in the analogous system[3] as the initial guess, and to investigate their ferromagnetic and/or antiferromagnetic natures while binding with different numbers of metal ions of groups 7 and 12. It is observed that conventional DFTs at QM level perform similarly accurate in the geometry optimization to suggest possible structures of MTs, which is consistent with the model studies reported in the literature.[4] However, to predict the (anti-)ferromagnetism for further design of MTs, it is advised to reconfirm the ground state using wavefunction theories with multireference characters in the QM region.

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Atomistically Deciphering Functional Processes of -receptor and Redox Proteins with Molecular Simulations

IL064

Prof. Shigehiko Hayashi

Kyoto University, Kyoto, Japan

Functional processes of photoreceptor and redox proteins are often fulfilled by dynamic and global molecular conformational changes of complex protein systems which correlate with local chemical events at reaction centers. Hence the multi-scale functional coupling of chemical local events with protein global molecular dynamics need to be revealed for understanding of molecular nature of protein functions. In this talk, I will present our recent studies on photo-activation processes of a channelrhodopsin (ChR) photo-sensitive ion transporter and redox processes of cytochrome c (cyt c) and photosystem II (PSII) by a hybrid QM/MM free energy geometry optimization technique, which allows one to optimize electronic wave function and molecular geometry of a reaction center at the ab initio quantum chemistry level of theory on a free energy surface constructed with statistically extensive conformational ensemble of the protein environment obtained by long-time MD simulations.

I will first present an atomic structural model of a chimeric ChR, in a precursor state of the channel opening. The photo-activated structure features extensive tilt of the chromophore accompanied by redistribution of water molecules in its binding pocket which is absent in previously known photo-activated structures of analogous proteins, and widely agrees with experimental evidences of ChRs. The atomistic model manifests a photo-activated ion conduction pathway which is markedly different from a previously proposed one and successfully explains experimentally observed mutagenic effects on key channel properties. I will also present theoretical investigations of redox processes of cyt c and PSII which include transition metal complexes as reaction centers. Through ab initio QM/MM free energy geometry optimizations for many combinations of redox and protonation states of the reaction centers free from difficult force field determination for the electronically complex reaction centers, we successfully revealed significant structural differences of the redox centers with the different redox and protonation states.

Excitation Energies can be Expressed in Terms of Orbital Energies Obtained from KS-DFT with LC Functionals

IL065

Dr Kimihiko Hirao[1,2], Dr Bun Chan[3], Dr Jong-Won Song[4], Dr Subrata Tewary[1]

[1]RIKEN, Kobe, Japan. [2]Kyoto University, Kyoto, Japan. [3]Nagasaki University, Nagasaki, Japan. [4]Taegu University, Taegu, Korea, Republic of

The solution of the exact Kohn-Sham (KS) equation satisfies the Koopmans' theorem. Therefore, one electron excitation energy can be expressed using the solutions of the KS equation. KS-DFT with long-range corrected (LC) functionals satisfies the Koopmans' theorem with high accuracy. Thus, one electron excitation energies can be expressed accurately by the difference between occupied orbital energies for the neutral molecule and unoccupied orbital energies of its cation. There are two alternative expressions for the excitation energies. One is to express the excitation energies in terms of orbital energies for neutral and cationic systems. The other is a method using only orbital energies of the cation. In general, when approximate functionals are used, two representations give different excitation energies. The electron affinity of a molecule is the ionization energy of its anion. Using this relationship two expressions coincide and give the same excitation energies. Furthermore, when a wavefunction is approximated by determinants using KS orbitals, excitation energies with different spin states can also be calculated. The present scheme was successfully applied to valence, inner-valence and core excitations.

Exploring Time-Dependent Double Hybrids with Range-Separation

IL066

Dr Lars Goerigk, Mr Marcos Casanova-Páez

Melbourne Centre for Theoretical and Computational Chemistry, School of Chemistry, The University of Melbourne, Melbourne, Australia

We have seen tremendous improvements in the development of quantum-chemical procedures and we now have access to methods that allow the accurate treatment of systems with even hundreds of atoms. However, the large number of available methods also makes it hard for the computational-chemistry user to understand their benefits or potential risks. As a consequence, one can therefore observe the trend to stick to a few familiar — albeit sometimes older — levels of theory, such as the B3LYP or M06-2X density functional theory (DFT) approximations. Meanwhile, there is ample evidence that double-hybrid density functionals (DHDFs) are the most reliable and robust DFT approximations, for instance for thermochemistry, kinetics, and noncovalent interactions. This has been shown recently by our group in a series of papers that together constitute one of the largest DFT benchmark studies ever published on which I will briefly elaborate.[1]

Most researchers in the DFT community are probably unfamiliar with earlier work that has shown DHDFs to be accurate candidates for the calculation of excitation energies.[2] However, the older generation of DHDFs still fails to describe long-range excitations, such as Rydberg and the more important charge transfer excitations. This presentation discusses our new range-separated DHDFs,[3] which are not only the first excited-state optimised DHDFs without the aforementioned long-range problem, but belong to some of the most balanced, robust and accurate DFT methods for excitation-energy calculations.

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Excitation Energies from Time-Dependent Thermally-Assisted-Occupation Density Functional Theory

IL067

Dr. Chao-Ping Hsu[1], Mr. Shu-Hao Yeh[1,2], Dr. Aaditya Manjanath[1], Dr. Jeng-Da Chai[2]

[1]Academia Sinica, Taipei, Taiwan. [2]National Taiwan University, Taipei, Taiwan

The linear response time-dependent density functional theory (LR-TDDFT) has been broadly used to investigate excited-state properties of various molecular systems. However, current LR-TDDFT methods heavily rely upon outcomes from ground-state DFT calculations which may be prone to errors due to lack of treatment in the non-dynamical correlation effects with commonly used functionals. Recently, the thermally-assisted-occupation (TAO) DFT scheme [J.-D. Chai, J. Chem. Phys. 136, 154104 (2012), and J.-D. Chai, J. Chem. Phys. 140, 18A521 (2014)] was proposed, which explicitly incorporates the non-dynamical correlation effect in the ground-state simulation, but retains the low computational complexity of conventional DFT. In this work, we develop the linear-response theory for TAO-DFT (TDTAO-DFT) to study excited states of H_2. The correct feature of the first triplet excited state including the non-imaginary excitation energies, as well as zero singlet-triplet gap in the dissociation limit, are correctly reproduced by TDTAO-DFT. In addition, the overall excited-state potential energy surfaces (PESs) obtained from TDTAO-DFT also have excellent agreement with results from the state-of-the-art equation-of-motion coupled cluster singles doubles (EOM-CCSD) calculations.

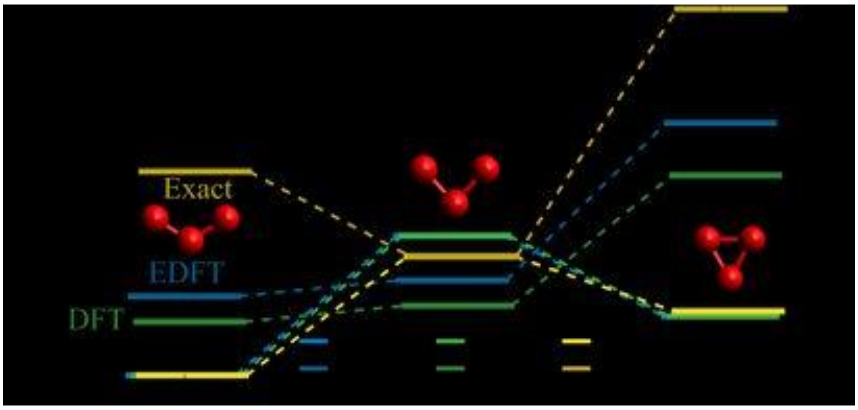
Ensemble Density Functional Theory: Stories from the Quest for a Low-Cost Quantum Chemical Approach for Excitations

IL068

Dr Tim Gould[1], Dr Stefano Pittalis[2]

[1]Queensland Micro- and Nano-technology Centre, Griffith University, Gold Coast, Australia. [2]CNR-Istituto Nanoscienze, Via Campi 213A, I-41125, Modena, Italy

Chemistry and physics increasingly use engineered quantum systems, often by going beyond well-studied ground-state properties and utilising low-lying excited states. Ensemble density functional theory (EDFT) offers the promise of routine, low-cost access to reasonably accurate excited states. Accessing these states with present methods is typically costly (e.g., time-dependent DFT, EOM-CCSD) or depends on expert users (e.g., constrained DFT). This talk reports on recent innovations in EDFT that have shown it is amenable to division into Hartree-exchange and correlation physics [1], like regular DFT; but that, unlike DFT, it naturally inherits appropriate symmetries, including singlet-triplet splitting, via superposition physics even at the Hartree-exchange level. Considering EDFT within this maths-driven formalism also reveals a new type of "density-driven" correlation energy [2] that is unique to ensemble systems, and which must be dealt with in low-cost approximations. Results are presented for several test cases, which show that EDFT within the introduced formalism is competitive with existing state-of-art.



[1] Phys. Rev. Lett. **119**, 243001(2017)
[2] https://doi.org/10.26434/chemrxiv.6964874 (accepted in *Phys. Rev. Lett.*)

The Computational Evidence for Homonuclear Dative Bonds

IL069

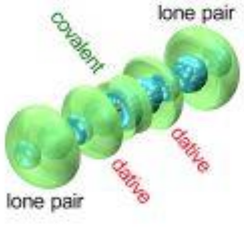
Prof. Chin-Hui Yu, Dr. Timm Lankau

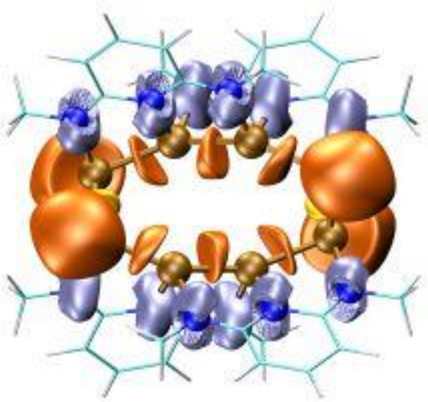
National Tsing Hua University, Hsinchu, Taiwan

Dative bonds are commonly observed between atoms with different electronegativities. However, the AIM and ELF analysis of the electron density in germanium polycations at the B3LYP/6-31G(d,p) level shows conclusively that geometric and electronic constraints can enforce homonuclear dative bonds.

The dative bonds can be formally described as the interaction of a lone pair of a Ge ion in the center of the cluster with the overall positive charge of another Ge ion. At first glance, the dative bonds resemble weak covalent bonds, but can be readily distinguished from covalent bonds by the properties of the associated bond critical points in the AIM analysis and the shape of their ELF basins. The receiving Ge ion effectively draws electron density from central ions and the associated distribution of positive charge is stabilized by bracketing ligand anions.

The concept of homonuclear dative bonds can be used to rationalize counterintuitive charge pattern in polycations and offers a facile way to predict the disproportion of the germanium backbone of the cluster.





Calculating Lewis-Structures and Curly Arrows from Ab-Initio Wavefunctions

IL070

Dr Timothy W Schmidt[1], Dr Philip Kilby[2], A/Prof. Terry J Frankcombe[3], Prof. Timothy W Schmidt[4]

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Lewis structures and chemical mechanisms based on the "curly arrow" notation are at the heart of chemical thought. However, both are regarded with some suspicion – the connection with rigorous molecular quantum mechanics being unclear. The connection requires a view of the electronic wavefunction that goes beyond the molecular orbital approximation and rests on the most fundamental property of electrons. The (anti-)symmetry properties of electronic wavefunctions require that an *N*-electron wavefunction repeat itself in 3*N* dimensional space, thus exhibiting a "tiling". Inspection of wavefunction tiles permits insight into chemical structure and mechanism.

We demonstrate that analysis of the wavefunction tile reveals motifs such as: core electrons; lone-pairs; single-bonds; and banana-bonds. The structures determined for N_2, O_2, F_2, and other molecules correspond to the double-quartet theory of Linnett.

Incorporation of multiple configurations into molecular orbital theory wavefunctions allows us to visualize static electron correlation. When the procedure is applied to C_2, we arrive at an interpretation of its bonding in terms of a near triple bond with singlet-coupled outer electrons, closely resembling the quadruple bond posited by Shaik. Benzene reveals α and β electrons to occupy alternate Kekulé structures, as does ozone.

Analysis of the wavefunction tile along a reaction coordinate reveals the electron movements depicted by the canonical curly-arrow notation for several reactions: The Diels-Alder reaction is revealed to involve the separation and counter-propagation of electron spins.

The Enigmatic Quadruple Bonding in C_2: What do the Excited States Tell?

IL071

Ms Ishita Bhattacharjee, Dr. Debashree Ghosh, Professor Ankan Paul

School of Chemical Sciences, Indian Association for the Cultivation of Science, Kolkata, India

Multiple bond order has attracted a lot of interest from the moment metal-metal bonding has been observed in transition metals and lanthanides/actinides where practically the maximum bond order can reach up to six bonds.[1] However, when it comes to the main group elements, the maximum bond order has remained three with one σ-bond and two π-bonds.The presence of a fourth bond in C_2 was first suggested several decades back.[2] The interest on the presence of a fourth bond was reignited by Shaik and co-workers when they studied the bonding in the ground electronic state of C_2 with Valence Bond Techniques.[3] They had even estimated the strength of the fourth bond in C_2. However, other researchers have challenged this claim,[4] while there are others who have supported the presence of a fourth bond.[5] The debate surrounding the presence of the fourth bond is yet to be settled. We have tried to understand the bonding in C_2 by conducting Multi-reference Configuration Interaction Studies on excited states of C_2, diatomic systems isoelectronic to C_2 and also on analogous diatomic systems belonging to the 2nd period. Insights from the excited state studies tend to tilt the balance towards a certain side of the dispute and can possibly seal the debate. In this talk the findings and the implications from these electronic structure studies would be discussed.

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Theoretical Analysis of Donor-Acceptor Bonding

IL072

Associate Professor David J Wilson

La Trobe University, Melbourne, Australia

Both the use of carbenes and utilisation of donor-acceptor bonding have had a significant impact on main-group and s-block chemistry over the last decade. Here, we present results from recent investigations into the use of carbene ligands to stabilise s-block and main group elements, which have also resulted in experimental observations of unusual reactivity. Theoretical calculations have been critical to understanding the electronic structure and reactivity of these systems. In particular, energy decomposition analysis (EDA) has proven a powerful technique to probe the nature of bonding interactions.

A particular focus of this talk is the chemistry and electronic structure of beryllium and boron-containing heterocyclic systems. Beryllium, despite its toxicity, exhibits the greatest covalent tendency of the group 2 elements. Results will be presented utilising novel ligands to stabilise Be-containing compounds with donor-acceptor bonding. For boron heterocycles, theoretical results will be presented of a comparison of N-heterocyclic carbene (NHC) and boryl anions (boron analogues of NHC) and their propensity for pi-backbonding with metals.

Efficient Methods for Simulation of Stimuli-Responsive Materials in Condensed Phases

IL073

Prof. Jing Ma

School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, China

Stimuli-responsive materials have aroused intensive interest in recent years. Many efforts have been made towards developing functional surfaces exhibiting specific property changes triggered by variations in electrical potential, temperature, pH and chemical concentration, irradiation with light or exposure to a magnetic field. Molecular dynamics (MD) simulations with quantum chemical calculation based polarizable force fields and reactive force fields, which could give proper description of the charge polarization and reversible isomerization process caused by electrical or light stimulus, have helped not only back many of the experimental observations but also to rationalize the mechanism of switching behavior.

1. E. Cantini, X. Wang, P. Koelsch, J. Preece, J. Ma, P. M. Mendes, *Acc. Chem. Res.*, **2016**, *49*, 1223-1231.
2. D. Zheng, Y. Gu, X. Li, L. Zhang, W. Zhao, J. Ma, J. Chem. Inf. Model. **2019**, DOI:10.1021/acs.jcim.8b00985.

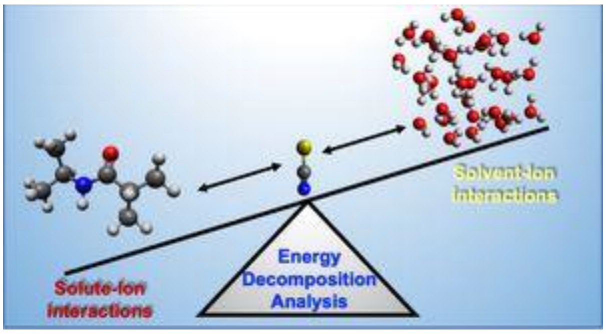
Specific-Ion Effects in Aqueous, Non-Aqueous and Nanostructured Solvents: Multiscale Quantum Chemistry Approaches

IL074

Mr Kasimir Gregory, Dr Ryan Stefanovic, Mr Tom Bourke, Mr Gareth Elliott, A/Prof Grant Webber, Prof. Erica Wanless, A/Prof. Alister Page

University of Newcastle, Newcastle, Australia

Specific-ion effects and the Hofmeister series have been known since the 1880s. Despite intense research, our understanding of their origins remains poor. We present multiscale quantum chemical investigations showing how inorganic salts influence the structure and solvation of polymers in aqueous and non-aqueous molecular solvents. Complex nanostructured solvents, such as ionic liquids (ILs) and deep eutectic solvents (DES) are also explored. These simulations provide new and fundamental insights into the origins of specific ion effects, for both aqueous and non-aqueous solvents. On the basis of GKS-EDA (energy decomposition analysis), we propose a new mechanism for explaining reversals to the Hofmeister series based on the competing magnitudes of ion-solvent and ion-solute interactions and their relative Lewis Strengths. We also report a new *ab initio* descriptor of ions that both predicts and explains post-hoc observed specific-ion effects and Hofmeister series in a range of contexts, from polymer cosolvency, enzyme activity and the Gibbs Free Energy of transfer of ions between various aqueous and non-aqueous solvents.

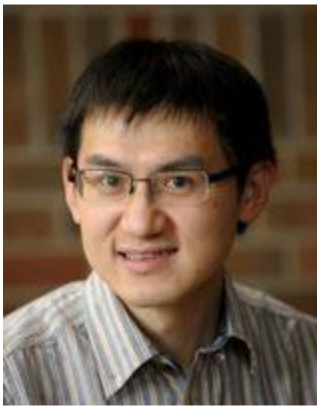


Multiscale Simulations of Peptide Assembly into Nanostructures

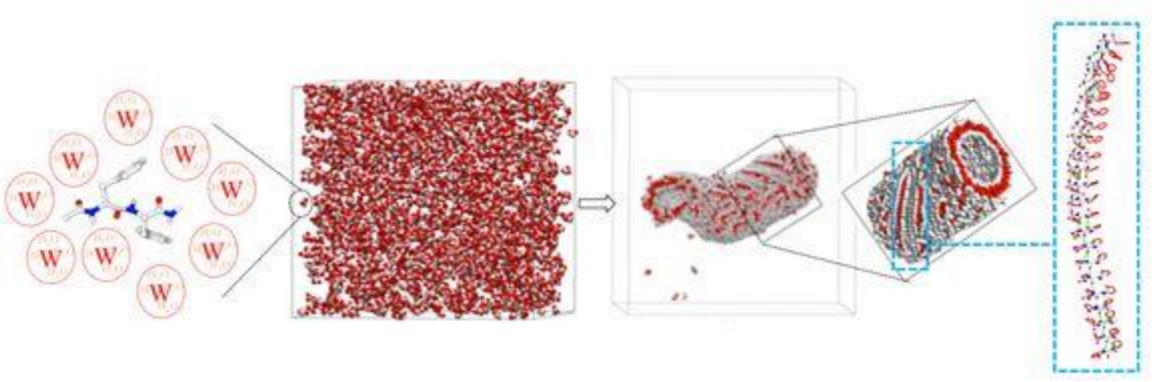
IL075

Dr Wei Han

Peking University Shenzhen Graduate School , Shenzhen, China



The molecular design of peptide-assembled nanostructures relies on extensive knowledge pertaining to the relationship between structural features of peptide constituents and their behavior regarding self-assembly, and characterizing the conformational details of peptides during their self-assembly is experimentally challenging. Here, I will present our recent efforts in deciphering this relationship with a multiscale computational approach. In particular, I will demonstrate that a hybrid-resolution modeling method can be employed to elucidate conformations and molecular packing of peptides in assembled nanostructures. These simulation results are consistent with various experimental observations. Moreover, the atomic details provided by our method allowed us to uncover conformation dependence of assembly structures and dynamics. Finally, a common flaw of current atomistic models for modelling self-assembly of very short peptides will be discussed and our solution to this problem will be presented. Collectively, the structural details provided from our works advance the understanding of the peptide-assembly mechanism, and our multiscale method shows promise for studying peptide-assembled nanostructures and their rational design.



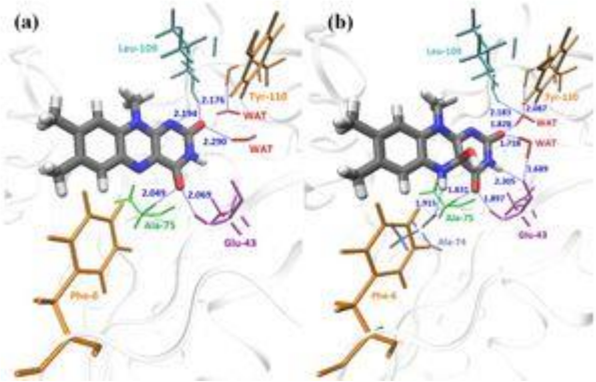
Computational Bioluminescence - Assignment of Bacterial Bioluminophore

IL076

Prof. Ya-Jun Liu

College of Chemistry, Beijing, China

Bioluminescence (BL) is an amazing phenomenon produced by a living organism. It has received extensive attention as a subject of life science and a powerful analytical tool in medical applications, such as noninvasive real-time imaging for target molecules in vivo. Bioluminescence arises from a series of complicated chemical reactions. However, the details and mechanisms of these chemical reactions are largely unknown. Theoretical study plays an irreplaceable role in this field. Our group have worked in this field for 10 years. In this talk, I will introduce the theoretical study in our group by: bioluminescent systems we are working on; what we concern; theoretical approaches we employ. As specific examples, the fluorescence quenching of excited flavin in the luciferase and the assignment of the light emitter of bacterial BL will be narrated in details.



Ab-Initio Anharmonic Algorithms and their Applications to Understand Vibrational Coupling

IL077

Prof. Dr. Jer-Lai Kuo

IAMS, Academia Sinica, Taipei, Taiwan

Vibrational motions of molecules are intrinsically “anharmonic”, for example vibrational spectra of protonated species often consist of complex vibrational features that cannot be accounted for by normal modes of the target molecule due to the vibrational coupling between proton modes and other dark states. Since proton stretch modes in protonated molecules often carry large oscillator strength which in term gives rise to a great chance to understand the vibrational coupling in these molecular systems via their vibrational spectra. We have recently developed two *ab initio* anharmonic algorithms. These algorithms have been applied to a range of protonated species to reveal simple pictures behind their complex vibrational feature. Some of the selected systems are solvated hydronium and a few proton-bound dimers. Complex vibrational feature of functional group containing N-H and C-H due to Fermi Resonance has also been resolved with the assistance of our ab initio anharmonic schemes.

Quantum Trajectory Mean-Field Approach and its Implementation for Exploring the Dynamics of the induced Ring-Opening of 2-Thiophenone

IL078

Professor Wei-Hai Fang

Beijing normal University, Beijing, China

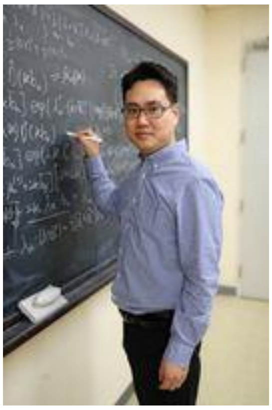
Recently, we proposed a quantum trajectory mean-field (QTMF) approach for simulation of non-adiabatic processes[1,2], which was numerically implemented for direct *ab initio* dynamical simulation of photodissociation of diazirinone[2] and acetylacetone[3]. The combined QTMF/MM simulation has been performed for exploring the dynamics of the photoinduced ring-opening of 2-thiophenone in acetonitrile. The ring-opening reaction is predicted to be an ultrafast process with a time constant of ~230 fs and proceeds mainly along the diabatic $S_2(^1\pi\pi^*)$ pathway, while the $^1\pi\pi^{*}$®$^1\pi s^*$ transition takes place with little probability via the $^1\pi s^*/^1\pi\pi^*$ conical intersection and the $^1\pi s^*$ excited state plays a minor role in the ring-opening reaction, which is quite different from those reported for many heterocyclic molecules. All of these will be discussed in this presentation.

Quantum Simulation Methods for Molecular Vibronic Spectra

IL079

Prof. Joonsuk Huh

Sungkyunkwan University, Suwon, Korea, Republic of



Quantum computer is expected to attempt the quantum supremacy in near-term with potentially useful applications. Among the various quantum simulation problems, a quantum sampling problem with noninteracting bosonic particles, i.e. boson sampling, is very likely to demonstrate the quantum supremacy with relatively limited physical resources. In my talk, I will present a molecular problem (molecular vibronic spectra), which can be interpreted as a Gaussian boson sampling problem. Additionally, a quantum circuit based algorithm for the same molecular problem will be presented.

Beyond Scalar Measures: Directional Chemical Perspective with Next Generation QTAIM

IL080

Miss Tian Tian[1], Mr Tianlv Xu[1], Professor Steven R. Kirk[1], Mr Ian TayRongde[2], Mr Tan YongBoon[2], Dr Sergei Manzhos[2], Professor Yasuteru Shigeta[3], Professor Samantha Jenkins[1]

[1]Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research and Key Laboratory of Resource National and Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, China. [2]Department of Mechanical Engineering, National University of Singapore, Singapore, Singapore. [3]3Center for Computational Sciences, University of Tsukuba, Tsukuba, Japan

The theoretical chemical physics/bio-chemistry that the BEACON research group undertakes seeks to develop new theory and explanations for chemical observations whilst also posing questions to be answered by future experiments. Our (next generation) QTAIM based research pioneers new theoretical tools that provide a new 3-D vector based perspective to solve what was only until recently considered unsolvable. An example of this was our explanation of chirality using only chemical measures [1]. By providing new tools based on ignoring previous assumptions in theoretical chemistry/chemical physics we can currently address new areas such as isotope separation, excited state dynamics [2], prediction of competitive and non-competitive ring-opening reactions [3], excited state phenomena [4], physical properties including the application of E-fields [5] and spectroscopic response.

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http://www.beaconresearch.org

[1] Chirality-Helicity Equivalence in the S and R Stereoisomers: A Theoretical Insight, *Journal of the American Chemical Society*, **141**(13), 5497–5503 (2019). DOI: 10.1021/jacs.9b00823.
[2] QTAIM and Stress Tensor Characterization of Intramolecular Interactions Along Dynamics Trajectories of a Light-Driven Rotary Molecular Motor, *J. Phys. Chem. A* **121**(25), 4778–4792, (2017). DOI: 10.1021/acs.jpca.7b02347.
[3] A vector-based representation of the chemical bond for predicting competitive and noncompetitive torquoselectivity of thermal ring-opening reactions, *International Journal of Quantum Chemistry* **118**(20), e25707 (2018). DOI:10.1002/qua.25707
[4] A 3-D Bonding Perspective of the Factors Influencing the Relative Stability of the S_1/S_0 Conical Intersections of the Penta-2,4-dieniminium Cation (PSB_3), *International Journal of Quantum Chemistry*, **119**(11), e25903 (2019). DOI: 10.1002/qua.25903
[5] The Destabilization of Hydrogen-bonds in an External E-Field for Improved Switch Performance, *Journal of Computational Chemistry*, Early View (2019). DOI: 10.1002/jcc.25843

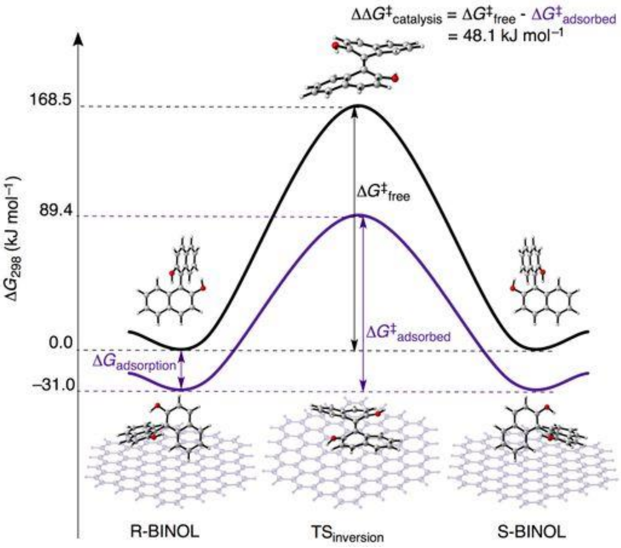
Graphene Catalysis via Dispersion Interactions and Shape Complementarity

IL081

A/Prof. Amir Karton, Ms Asja A Kroeger

The University of Western Australia, Perth, Australia

Whilst potential chemical applications of graphene have been extensively explored in recent years, applications of pure unfunctionalized graphene in catalysis are in their infancy. Using accurate quantum chemical calculations, we show that large graphene nanoflakes can efficiently catalyze a range of chemical reactions via dispersion interactions and shape complementarity. These reactions include binaphthyl racemization and bowl-to-bowl inversion of curved polycyclic aromatic hydrocarbons. We find that large graphene nanoflakes can achieve significant catalytic enhancements of up to 70% relative to the uncatalyzed reaction barrier heights.



Solvation Modelling – Are Explicit Solvent Models more Accurate than Continuum Models?

IL082

Dr Junming Ho

UNSW, Sydney, Australia

Many chemical and biochemical reactions occur in the solution phase and the solvent can often exert a strong influence on the outcome of a reaction. As such, our ability to accurately predict the rate and equilibrium constants of reactions depends on how well solute-solvent interactions are described by our computational models.

Currently, quantum mechanical (QM) implicit solvent models (*e.g.* PCM and SMD) are the most popular methods for modelling solvation because of their computational cost, moderate accuracy and ease of use. On the other hand, explicit solvent models are in principle more robust but they have not been demonstrated to the extent to which the extra computational cost translates to better accuracy.

In this talk, I will present several case studies comparing the performance of implicit and explicit solvent models, and highlight a strategy to systematically improve the accuracy of some of these models.

Mechanism of Carbon Dioxide Adsorption by Primary and Secondary Amines

IL083

Dr Maneeporn Puripat[1,2], Professor Waraporn Parasuk[3], Prof Suttichai Assabumrungrat[4], Professor Vudhichai Parasuk[1]

[1]Center of Excellence in Computational Chemistry, Department of Chemistry, Chulalongkorn University, Bangkok, Thailand. [2]Institute for Research Initiatives, Division for Research Strategy, Nara Institute of Science and Technology, Nara, Japan. [3]Department of Chemistry, Kasetsart University, Bangkok, Thailand. [4]Center of Excellence in Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand

Carbon dioxide (CO_2) adsorption by monoethanolamine (MEA) was studied at the M06-2X/6-31+g(d,p) level of theory. There are three main reactions for the capture reactions, i.e. carbamate formation, bicarbonate formation, and carbamate reversion. Among the three reactions, the carbamate formation has the lowest reaction barrier and is considered as the main reaction for this process. The reaction barrier for the carbamate formation is 11.46 kcal/mol compared with 19.66 kcal/mol for the bicarbonate formation and 31.78 for the carbamate reversion. The carbamate formation takes place via zwitterion and consists of two steps, zwitterion formation and base abstraction. The zwitterion formation is the rate-determining step (RDS). Compared the RDS of MEA with other primary and secondary amines, diethylenetriamine (DETA) which has primary and secondary amine groups possesses the lowest activation free energy (7.81 and 8.90 kcal/mol at primary and secondary positions). Ethylenediamine (EDA) and diethanolamine (DEA) have activation energies of 9.67 and 10.68 kcal/mol, respectively. The CO_2 capture activity is linked to the basicity of the compounds. The compound with weaker basicity tends to have higher activity.

Prediction of Chemical Reaction Paths through Graph-Theoretic Approach

IL084

Prof Woo Youn Kim

KAIST, Daejeon, Korea, Republic of

Despite remarkable advances in computational chemistry, prediction of chemical reactions is still challenging, because investigating possible reaction pathways is computationally prohibitive due to the high complexity of chemical space. For instance, their brute-force sampling is too demanding because of their large degrees of freedom. A stochastic sampling method inherently requires many trials no matter how effective it is, because it cannot guarantee 100% probability of finding a designated target structure within a finite number of samplings. A feasible strategy for efficient prediction is to utilize chemical heuristics and machine learning techniques. We proposed a novel approach to search reaction paths in a fully automated fashion by combining chemical theory and heuristics. A key idea of our method is to extract a minimal reaction network composed of only favorable reaction pathways from the complex chemical space through molecular graph and reaction network analysis. This can be done very efficiently by exploring the routes connecting reactants and products with minimum dissociation and formation of bonds. Finally, the resulting minimal network is subjected to quantum chemical calculations to determine kinetically the most favorable reaction path at the predictable accuracy. To further accelerate the graph-based method, we introduce state-of-the art machine learning techniques. They can replace chemical heuristics and expensive calculations with more systematic, unbiased computational rules. In this talk, we show the recent progress in this project with several examples.

Materials Design of Hole-Transporting Materials for Perovskite Solar Cells

IL085

Dr. Takahito Nakajima, Dr. Takahide Matsuoka

RIKEN, Kobe, Japan

In this study, the efficient search of optimum hole-transport materials (HTMs) was achieved by applying machine learning techniques. We employed deep neural networks to predict the power conversion efficiency of perovskite solar cells with HTMs by utilizing molecular descriptors as input features. We also employed Gaussian process regression to evaluate the acquisition function in Bayesian optimization and implement uncertainty and reliability to the prediction model. Discrete particle swarm optimization was applied to tackle the optimization problem in the vast chemical space.

Molecular Design using Traditional Computations and Machine Learning

IL086

Dr. U. Deva Priyakumar

International Institute of Information Technology, Hyderabad, India

One of the principal outcomes of computations and experiments alike in chemistry is the ability to design and realize hitherto unknown molecules with desirable properties. Conventionally, computational methods such as quantum mechanical and density functional theory are systematically employed to understand the underlying factors responsible for a given phenomenon, which is then utilized to conceive new molecules to improve predictions. Alternatively, last few years have witnessed a surge in the use of modern machine learning methods for problems in chemistry and biology, which to some extent is changing the nature of computations that we are used to. The first part of the talk will discuss the results of a systematic exploration of the chemical space for identifying molecules with tetracoordinate-tetrahedral centers that can undergo racemization via a planar transition or intermediate state without having to break a covalent bond. The thermodynamic, kinetic and dynamic properties derived from state of the art computational methods that include high level *ab initio* calculations, Born-Oppenheimer molecular dynamics simulations and direct chemical dynamics simulations will be presented. In the second part of the talk, we will discuss the use of modern machine learning generative methods such as reinforcement learning and variational encoders for *de novo* molecular design. The ability of these methods to predict molecular structures starting from molecular properties instead of the conventional molecule to property prediction will be discussed. Case studies involving generation of small organic and inorganic molecular structures with desired properties such as molecular volume, logP and formation enthalpy will be presented.

A Computational Molecular Technology for Complex Chemical Reaction Systems: Red Moon Methodology

IL087

Dr. Masataka Nagaoka1-3

1) Graduate School of Informatics, Nagoya University, Nagoya, Japan. ; 2) CREST, JST, Kawaguchi, Japan. ; 3) ESICB, Kyoto University, Kyoto, Japan

When we try to apply computational chemistry (CC) to diffusion and chemical reactions in "molecular aggregation states" where many atoms and molecules are gathered in condensation, such fact that these phenomena occur only very rarely has made it restrictive or sometime impossible to deal with them by first principles CC methods. Even with traditional classical molecular simulations, it is difficult to determine long-term properties and stereochemical characteristics. Under the circumstances, we have recently developed Red Moon Method, a new efficient and practical 'atomistic' simulation method combining Monte Carlo (MC) and molecular dynamics (MD) method with a Rare Event-Driving Mechanism, for large-scale chemical reaction systems [1] and applied successfully to analyse several materials important and valuable in next-generation industrial development [2]. In this talk, several applications of Red Moon Method will be shown from the practical viewpoint of molecular controlling of complex chemical reactions, stereochemistry and aggregate structures. In particular, we would like to take a novel olefin polymerization catalyst (pyridylamido)Hf(IV) complex (I), which is activated by a cocatalyst $B(C_6F_5)_3$ to form a cationic active species [2,3] and explain the role of the counteranion in the reaction mechanism of ethylene polymerization, i.e., ionpair dynamics [2]. Finally, I would like to discuss the microscopic mechanism of catalytic polymerization (CP) by I and $B(C_6F_5)_3$ in solvent heptane, which is clarified by applying Red Moon simulation to the present system [3].

[1] M.Nagaoka, Y.Suzuki, T.Okamoto, N.Takenaka, *Chem. Phys. Lett*. **583**, 80 (2013).
[2] M.Nagaoka, M.Takayanagi, N.Takenaka, Y.Suzuki, K.Matsumoto, N.Koga, S.K. Sankaran, P.Uppula, Y.Kitamura. (2019). In H.Yamamoto, T.Kato (Eds.), *Molecular Technology*, *Vol. 3: Materials Innovation*, 201, Weinheim:Wiley-VCH.
[3] K.Matsumoto, Y.Suzuki, M.Takayanagi, N.Koga, M.Nagaoka. *J. Comp. Chem.*, **40**, 421 (2019).

Simulations of Materials for Catalysis and Energy Based on Biomolecule-Nano Interfaces

IL088

Prof Tiffany R. Walsh

Institute for Frontier Materials, Deakin University, Geelong, Australia

An in-depth appreciation of how to control the interaction of peptides with materials interfaces, including nanoparticles, at the molecular level will advance application areas such as self-organised metamaterials for photonics and plasmonics, biosensing, catalysis, energy generation and harvesting, and nano-medicine. However, to fully exploit applications of such biomolecule-surface interactions, a molecular-level understanding of these processes at the interface is needed. Structural characterisation of the surface-adsorbed biomolecules is essential for establishing the required structure/property relationships in these systems but is challenging to accomplish via experimental approaches alone. In partnership with experimental characterisation, molecular simulations can suggest routes to manipulating these phenomena for realising new types of hybrid materials. I will outline our developments and applications of advanced molecular simulation approaches for investigating these challenging interfacial systems, and our findings for manipulating the adsorption of biomolecules at the aqueous interface for bio/nano applications in catalysis and energy applications.

Eighteen Functional Monolayer Metal Oxides: Wide-Bandgap 2D Semiconductors with Superior Oxidation Resistance and Ultrahigh Carrier Mobility

IL036

Prof. Jijun Zhao

Dalian University of Technology, Dalian, China

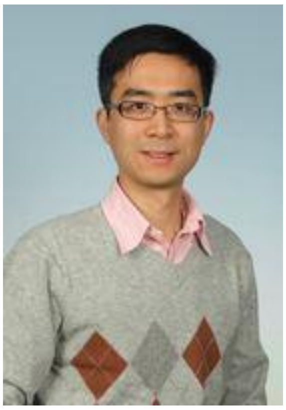
Layered metal oxides have emerged as an up-and-comer in the family of two-dimensional materials due to their natural abundance, intrinsic bandgaps, and chemical inertness. Based on first-principles calculations, we systematically investigated the atomic structures, energetic stability, and electronic properties of 18 monolayer metal oxides. All these monolayer metal oxides are predicted to be energetically favorable with negative formation energies in the range of −4.27 ~ −0.47 eV/atom, suggesting good experimental feasibility for synthesis. Monolayer metal oxides exhibit superior oxidation resistance, possess modest to wide bandgaps (1.22 ~ 6.48 eV) and high carrier mobility (especially up to 8540 $cm^2V^{-1}s^{-1}$ for the InO monolayer), thereby rendering these low-dimensional materials promising candidates for carrier transport. Also, the pronounced in-plane anisotropy for the carrier mobility with a longitudinal/horizontal ratio as large as 115 is revealed for the monolayer metal oxides. By comparing the band edges with the redox potentials of water, we identified that monolayer TiO2, GeO, SnO, SnO, ZrO_2 and HfO_2 can be potential functional photocatalysts for water splitting in acidic or neutral environments. These 2D metal oxides exhibit notable absorption in the ultraviolet range with the absorption coefficient > 10^5 cm^{-1}. The combined novel properties of these monolayer metal oxides offer wide range of opportunities for advanced electronic and optoelectronic applications.

Constructing Markov State Models to Elucidate the Functional Conformational Changes of Complex Biomolecules

IL090

Prof. Xuhui Huang

Department of Chemistry, The Hong Kong University of Science and Technology, Kowloon, Hong Kong



Simulating biologically relevant timescales at atomic resolution is a challenging task since typical atomistic simulations are at least two orders of magnitude shorter. Markov State Models (MSMs), a kinetic network model, built from molecular dynamics (MD) simulations provide one means of overcoming this gap without sacrificing atomic resolution by extracting long time dynamics from short MD simulations through the coarse graining on the phase space and time. In this talk, I will demonstrate the power of kinetic network models by applying it to simulate the complex conformational changes, that occurs at tens to hundreds of microsecond timescales for a large RNA Polymerase II complex containing nearly half million atoms. Furthermore, I will introduce a new efficient dynamic clustering algorithm for the automatic construction of MSMs for multi-body systems. We have successfully applied this new algorithm to model the protein-ligand recognition and self-assembly of co-polymers. Finally, I will introduce a new algorithm using the projection operator approach to identify optimal kinetic lumping and recover slowest conformational dynamics of complex systems.

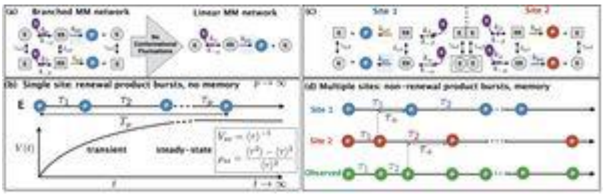
Transients Generate Memory and Break Hyperbolicity in Single-Enzyme Kinetics

IL091

Dr. Arti Dua

Indian Institute of Technology Madras, Chennai, India

The celebrated Michaelis-Menten (MM) expression provides a fundamental hyperbolic relation between the rate of enzyme catalysis and substrate concentration. The ubiquity of this classical equation in chemical and biological processes has now been rationalized by a graph-theoretic analysis of deterministic enzymatic networks. Recent experiments have measured fluctuations in the catalytic rate to reveal that the MM equation, though valid in the classical limit, is not obeyed at the molecular level. This, combined with the observation of temporal correlations between enzymatic turnovers, in an effect termed as molecular memory, has shown that fluctuations govern enzyme kinetics at the molecular level. An understanding of these results, of a generality comparable to the deterministic case, is currently lacking. Here we study stochastic networks of multiple enzymes, using a chemical master equation, to show that an initial, and observably long, transient is the source of both molecular memory and non-hyperbolicity. The transient yields, asymptotically, to a steady-state in which memory vanishes and hyperbolicity is recovered. We find that transients are always absent in networks corresponding to a single enzyme with a single binding site. We propose new statistical measures, defined in terms of waiting times between product turnovers, to distinguish between the transient and steady states. Our study demonstrates that catalysis at the molecular level with more than one participating enzyme always contains a non-classical regime where turnovers are correlated and the MM equation is violated.



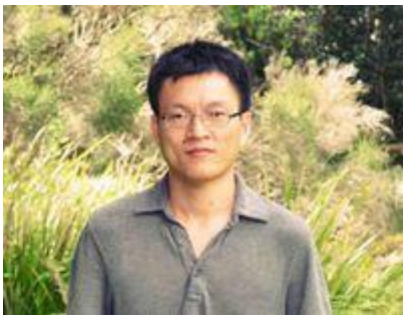
Minimal model showing the emergence of transients and molecular memory in an enzyme with single and multiple site(s)

Coelenterazine and Oxygen Binding in Obelin: A Computational Study into the Formation of Active proteins

IL092

Dr Thomas M Griffiths[1], A/Prof Aaron J Oakley[1,2], A/Prof Haibo Yu[1,2]

[1]University of Wollongong, Wollongong, Australia. [2]Illawarra Health and Medical Research Institute, Wollongong, Australia



Bioluminescence in marine systems is dominated by the use of coelenterazine for light production. The bioluminescent reaction of coelenterazine is an enzyme catalysed oxidative decarboxylation: coelenterazine reacts with molecular oxygen to form carbon dioxide, coelenteramide and light. One such class is the Ca^{2+}-regulated photoproteins. These proteins bind coelenterazine and oxygen, and trap 2-hydroperoxycoelenterazine, an intermediate along the reaction pathway. The reaction is halted until Ca^{2+} binding triggers the completion of the reaction. There are currently no reported experimental, atomistic descriptions of this ternary Michaelis complex. This study utilised computational techniques to develop an atomistic model of the Michaelis complex. Extensive molecular dynamics simulations were carried out to study the interactions between four tautomeric/protonation states of coelenterazine and wide-type and mutant obelin. Only minor differences in binding modes were observed across all systems. Interestingly, no basic residues were identified in the vicinity of the N_7-nitrogen of coelenterazine. This observation was surprising considering that deprotonation at this position is a key mechanistic step in the proposed bioluminescent reaction. This work suggests that coelenterazine binds either as the $O_{10}H$ tautomer, or in the deprotonated form. Implicit ligand sampling simulations were used to identify potential O2 binding and migration pathways within obelin. A key oxygen binding site was identified close to the coelenterazine imidazopyrazinone core. The O_2 binding free energy was observed to be dependent on the protonation state of coelenterazine. Taken together, the description of the obelin-coelenterazine-O_2 complexes established in this study provides the basis for future computational studies of the bioluminescent mechanism.

PCCP Emerging Investigator Lecture: Density Matrix Renormalization Group Studies on Polyaromatic Hydrocarbons – Effect of Spin Frustration and Topology

IL093

Dr. Debashree Ghosh

Indian Association for the Cultivation of Science, Kolkata, India

Polyaromatic hydrocarbons (PAHs) such as acenes have long been studied due to its interesting optical properties and low singlet triplet gaps. Earlier studies[1,2] have already noticed that use of complete valence active space is imperative to the understanding of its quanlitative and quantitative properties. Since complete active space based methods cannot be applied to such large active spaces, we have used density matrix renormalization group (DMRG)[3] based approaches. Further small modification to the PAH topology shows interesting new phases of behavior in its optical gaps. We have understood the effect of these effects based on spin frustration due to the presence of odd membered rings. In this talk, I will discuss these observations from molecular and model Hamiltonian perspectives.

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2. Singlet triplet gaps in polyacenes: a delicate balance between static and dynamic correlations investigated by spin flip methods, C.U. Ibeji, D. Ghosh, Phys. Chem. Chem. Phys., 17(15), 9849 (2016).
3. Orbital Optimization in the density matrix renormalization group, with applications to polyenes and beta carotene, D. Ghosh, J. Hachmann, T. Yanai, G. K.-L. Chan, J. Chem. Phys., 128(14), 144117 (2008).

Hybrid TD-DMRG/TD-Hartree Algorithm for Spectroscopy at Finite Temperature

IL094

Prof. Zhigang Shuai

Tsinghua University, Beijing, China

DMRG has been successfully extended to quantum chemistry, for example for studying the low-lying excited state orderings and nonlinear optical response for conjugated polymers [1]. We present here some of our recent progresses on developing the finite temperature time-dependent DMRG formalism coupled with thermofield dynamics for molecular aggregates [2]. The time domain algorithm is compared with frequency domain algorithms such as the Correction Vector method and Chebyshev Expansion methods [3]. Finally, we proposed a combined TD-DMRG with TD-Hartree algorithm which can handle large system [4].

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Dynamic Electron Correlation and Real-Time Simulation for Density Matrix Renormalization Group Quantum Chemistry

IL095

Prof. Dr. Haibo Ma

Nanjing University, Nanjing, China

The recent development of the density matrix renormalization group (DMRG) method in multireference quantum chemistry makes it practical to evaluate static correlation in a large active space. In order to further account for the remaining dynamic electron correlations, I introduce our new effective implementation of DMRG-MRCI, in which we use reconstructed CASCI-type configurations from DMRG wave function via the entropy-driving genetic algorithm (EDGA) and integrate it with MRCI by an external contraction (ec) scheme. This bypasses the bottleneck of computing high-order RDMs in traditional DMRG dynamic correlation methods with ic approximation, and the number of MRCI configurations is not dependent on the number of virtual orbitals. Therefore, the DMRG-ec-MRCI method is promising for dealing with a larger active space than 30 orbitals and large basis sets. In this talk, I will also introduce our new implementation for real-time quantum dynamics simulations of realistic electron-phonon systems using the adaptive time-dependent DMRG (t-DMRG) method.

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Excited-State Quantum Dynamics with Time-Dependent Matrix-Product States

IL096

Prof Yuki Kurashige

Kyoto Univ., Kyoto, Japan

A matrix product state formulation of the multiconfiguration time-dependent Hartree (MPS-MCTDH) theory will be presented. The Hilbert space that is spanned by the direct products of the phonon degree of freedoms, which is linearly parameterized in the MCTDH ansatz and thus results in an exponential increase of the computational cost, is parametrized by the MPS form. Equations of motion based on the Dirac-Frenkel time-dependent variational principle is derived by using the tangent space projection and the projector-splitting technique for the MPS, which have been recently developed. The mean-field operators, which appear in the equation of motion of the MCTDH single particle functions (SPF), are written in terms of the MPS form and efficiently evaluated by a sweep algorithm that is similar to the DMRG sweep. The efficiency and convergence of the MPS approximation to the MCTDH are demonstrated by quantum dynamics simulations of extended excitonic molecular systems.

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MRSF-TDDFT: An Improved TDDFT for Excited State Properties

IL097

Dr. Seunghoon Lee[1], Dr. Hiroya Nakata[2], Dr. Michael Filatov[1], Prof Cheol Ho Choi[1]

[1]Kyungpook National University, Daegu, Korea, Republic of. [2]R&D Center Kagoshima, Kyocera, Kagoshima, Japan

The use of mixed reference (MR) reduced density matrix (RDM), which combines the RDMs of M_S= +1 and −1 triplet-ground states, is proposed in the context of the collinear SF(Spin-Flip)-TDDFT methodology. This leads to a new MRSF-TDDFT, which doubles the response space such that the notorious spin-contamination of SF-TDDFT is eliminated. In test calculations, the MRSF-TDDFT yields quite different optimized structures and energies as compared to SF-TDDFT. These differences turned out to mainly come from the spin-contamination of SF-TDDFT, which are largely cured by MRSF-TDDFT. In addition, it was demonstrated that the separation of singlet states from triplets dramatically simplifies the location of minimum energy conical intersection (MECI). As a result, it is clear that the MRSF-TDDFT has advantages over SF-TDDFT in terms of both accuracy and practicality. Therefore, it can be a preferred method for the “black-box” type applications, such as the automatic geometry optimization, reaction path following, or non-adiabatic molecular dynamics simulations.

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Theoretical Characterization of Excess Electrons in Various Loosely-Bound Electron Systems: Structures, Localization Dynamics and the Medium Effects

IL098

Prof. Dr. Yuxiang Bu

Shandong University, Jinan, China

In this series of works, we mainly investigate the structures and evolution dynamics behaviors of the loosely bound excess electrons in several representative biological aqueous media e.g. glucose aqueous solution and amide aqueous solutions with different bioactive ions (H^+, Ca^{2+}), and nucleobase aqueous solutions. Our main conclusions include that i) in supercritical CO_2 the excess electron can exist in three types of states: CO_2-core localized, dual-core localized, and diffuse states. All these states undergo continuous state conversions via a combination of long lasting breathing oscillations and core switching which are closely related with the electron-interacted bending vibration of the core CO_2 and liquid thermal fluctuation; ii) in ionic liquid a dielectron prefers to be distributed over more cations, with long-lived diffuse and short-lived localized distributions, and with a triplet ground state and a low-lying, open-shell singlet excited state. The two electrons evolve nonsynchronously in both states via a diffuse-versus-localized interconversion mechanism that features a dynamic bipolaron with a modest mobility; iii) in glucose aqueous solution an excess electron can formed solvated electron with a glucose molecule in the cavity, and different densities of glucose could noticeably affect the structures and localization dynamics of an excess electron; iv) the excess electron in amide aqueous solution could localize at the anion ($-COO^-$) group and electron localization could also trigger the dissociation of amide acid molecule; v) the acidity of solution can modulate the electron localization modes and thus the structures of solvated electrons (hydrated versus anion-centered) and the existing other bioactive ions (e.g. Ca^{2+}) could also change the localization modes of excess electron through bifurcate mechanism; vi) excess electrons may localize towards nucleobases but with different localization mechanisms and rates.

Computational Design of chemistry of Light Driven Molecular Rotary Motors

IL099

Dr Michael Filatov

Kyungpook National University, Daegu, Korea, Republic of

Synthetic light driven molecular rotary motors are a novel class of functional compounds capable of converting the light energy into mechanical motion. The design and synthesis of molecular motors still remains a formidable challenge for chemistry, which, so far, was driven by modification of their ground state properties; e.g., barriers of the ratcheting thermal helix inversion step. This led to only a limited improvement of their performance; the efficiency of converting the light energy into mechanical work still remains very low, 10-20%. Further progress in this field can only be achieved through detailed understanding of the light-induced excited state dynamics of the motors, which should aim at improvement of their quantum efficiency through chemical modulation.

Photoisomerisation about the double bond is the crucial step in the operation of molecular motors. Sterical strain present in the ground electronic state is released due to photoinduced breaking of the π-bond, which leads to rotation of the rotor blade through ca.180°. This step is often followed by the thermally activated helix inversion, which resets the double bond into a conformation suitable for further photoisomerisation. New concept for rational design of molecular motors is based on understanding the ways of modulating the conical intersections involved in the photoisomerisation. Reshaping the design of the rotor and the stator blades of the motor, a remarkable increase in the quantum efficiency is achieved; as evidenced by the non-adiabatic molecular dynamics simulations. Furthermore, the ratcheting helix inversion step can be eliminated from the working cycle of the motor; thus leading to photon only molecular machines. The design concept and the results of the recent non-adiabatic molecular dynamics simulations will be presented in this lecture.

The Atmospheric chemistry of Acetaldehyde

IL100

Associate Professor Meredith J. T. Jordan[1], Ms Maggie E. Corrigan[1], Dr Miranda F. Shaw[1], Ms Isabella C. Russell[1], Mr Keiran N. Rowell[2], Professor Scott H. Kable[2]

[1]The University of Sydney, Sydney, Australia. [2]The University of NSW, Sydney, Australia

Carbonyls are the most important non-methane volatile organic species in the atmosphere. The C=O chromophore absorbs actinic ultraviolet radiation (290-340 nm) and subsequent photolysis can yield radicals, which influence the production of atmospheric HO_xspecies. The atmospheric photochemistry of acetaldehyde involves three electronic states, S_0, T_1 and S_1. Although T_1 reactions dominate photolysis, the importance of S_0 ground state reactions of vibrationally hot acetaldehyde has been increasingly recognised over recent years, with new mechanisms being discovered. As we close in on a comprehensive understanding of the atmospheric chemistry of acetaldehyde we need to consider all its possible fates. These include both ground and excited state reactions as well as intersystem crossing and collisional stabilisation. This presentation summarises our calculations on acetaldehyde and presents our current best understanding of acetaldehyde photochemistry and its atmospheric implications.

Development and Applications of the WMS Model Chemistry Method

IL101

Professor Yan Zhao

Wuhan University of Technology , Wuhan, China

We have developed a new composite model chemistry method called WMS (Wuhan-Minnesota scaling method) with threee characteristics: (1) a composite scheme to approximate the complete configuration interaction valence energy with the affordability condition of requiring no calculation more expensive than CCSD(T)/jul-cc-pV(T+d)Z, (2) low-cost methods for the inner-shell correlation contribution and scalar relativistic correction, (3) accuracy comparable to methods with post-CCSD(T) components. The new method is shown to be accurate for the W4-17 database of 200 atomization energies with an average mean unsigned error (averaged with equal weight over strongly correlated and weakly correlated subsets of the data) of 0.45 kcal/mol, and the performance/cost ratio of these results compares very favorably to previously available methods. We also assess the WMS method against the DBH24-W4 database of diverse barrier heights and the energetics of the reactions of three strongly correlated Criegee intermediates with water. These results demonstrate that higher-order correlation contributions necessary to obtain high accuracy for molecular thermochemistry may be successfully extrapolated from the lower-order components of CCSD(T) calculations, and chemical accuracy can now be obtained for larger and more complex molecules and reactions.

Applications of the WMS method for Li-Sulphur battery materials and for CO2 reduction mechanism on Si-nanosheet hydride will be presented.

A Pragmatic Many-Body Approach for Economic Correlation Energy Estimation of Molecular Clusters

IL102

Professor Shridhar R. Gadre, Mr. Subodh S. Khire

Savitribai Phule Pune University, Pune, India

We propose a procedure, within many body analysis (MBA) framework, for economic yet accurate estimation of the correlated method-based energies of large molecular clusters employing Dunning's augmented basis sets. The basis of the procedure is to segregate the Hartree-Fock (E_{HF}) and correlation energy (E_C) estimation. E_{HF} is found to differ by 10's of millihartrees (mH) from its full calculation (FC) counterpart on truncating the MBA expansion at 2-body (MBA-2) level. To the contrary, E_C is estimated with a smaller error on a modest hardware within limited computation time at (MBA-2) level. In view of this, we adopt a pragmatic method wherein the E_{HF} (accurate to 5 decimal digits) is taken from the FC, while E_C is estimated at MBA-2 level. This method is applied to a variety of medium- to large-sized molecular clusters at MP2 level. Preliminary results at CCSD(T) level for $(H_2O)_{16}$ and $(H_2O)_{17}$ are also reported reflecting tremendous saving in wall clock time and computational resources. The typical errors in MP2 and CCSD(T) energies per monomer are 0.1mH and 0.2mH respectively.

In summary, due to all these strategies, the accurate energy estimation of large molecular clusters with correlated methods employing large basis sets, using off-the-shelf hardware is indeed made feasible.

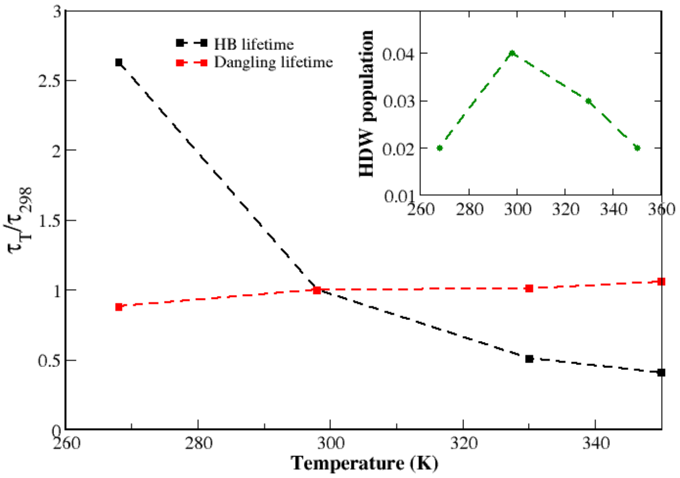
Water and its Anomalous Property: Interplay Between Low Density and High Density Water

IL103

Dr. Debashree Chakraborty[1], Dr. Bhabani S Mallik[2]

[1]National Institute of Technology Karnataka, Mangalore, India. [2]Indian Institute of Technology Hyderabad, Hyderabad, India

Water is the most studied liquid to date for its anomalous properties, which made life possible on earth. The uniqueness in water is due to the presence of hydrogen bonds which can readjust between themselves according to thermodynamic parameters. This results in a mixture of non-uniform density regions commonly known as low density water (LDW) and high density water (HDW). LDW and HDW are characterized by their difference in structural and dynamical properties. The population of LDW-HDW varies with temperature, pressure and also with model potentials. We performed a series of first-principle molecular dynamics simulations for liquid water at five different temperatures to observe the effect of temperature on the structure, density, isothermal compressibilility, cohesive energy, LDW-HDW population, void space, orientational dynamics and vibrational spectral diffusion. The presence of interstitial water molecules between the first and second solvation shell creates HDW. Around 298K, a density maxima is observed and a distinctive region for interstitial water molecules was found apart from the first and second solvation shell, which mixes up with these solvation shells at higher temperature. This results in a smaller void space at 298K. The orientational relaxation time for the water molecules present at first solvation shell and in the interstitial regions are found to be different at lower and ambient temperature which becomes indistinguishable at higher temperature. HDW population also effects the hydrogen bond dynamics of the system. The lifetime of LDW is found to be much greater than the hydrogen bond lifetime of water which decreases with increase in temperature, whereas the lifetime of HDW is found to be smaller, < 1 ps and is maximum at 298K. The existence of the anomalous properties of water can be related to the presence of interstitial molecules.



Distribution of Hydrogen Bond lifetime, dangling lifetime and HDW population(inset) with temperature.

A Challenge for Quantum Chemistry: Spectroscopic Accuracy for TiO Rovibronic Spectroscopy

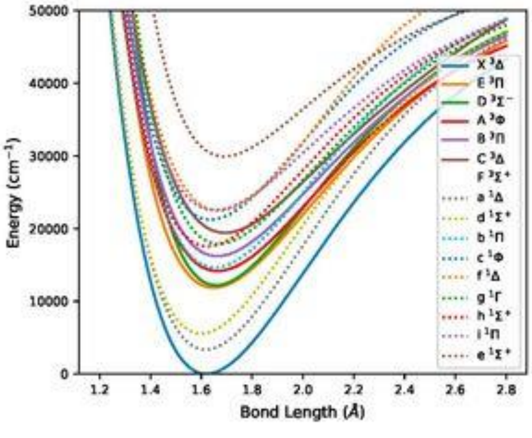
IL104

Dr Laura K McKemmish

University of New South Wales, Sydney, Australia

TiO is an unusual diatomic molecule whose rovibronic spectroscopy is of vital importance to astronomy due to the dominance of this molecule's absorption in the spectra of cool stars and hot Jupiter exoplanets. New ultrahigh resolution ground-based astronomy of exoplanets has led to the desire for sub cm^{-1} accuracy in the available molecular data for this molecule and similar diatomic species like VO, C_2, FeH.

I present the latest, keenly awaited model for the rovibronic spectroscopy of TiO, the Toto line list[1]. This list contains over 300,000 energy levels and almost 59 million transitions, and is already being used to model stellar and planetary atmospheres with temperatures up to 5000 K by astronomers. The new Toto line list represents an important milestone in line list creation for the astrochemistry community, taking advantage of high quality experimental data[2] and a new nuclear motion program that treats coupled electronic states for diatomics[3]. However, there are significant issues[4,5] with the theoretical electronic structure treatment of TiO and related transition metal diatomics, with errors in electronic term energies often exceeding 100 cm^{-1} and off-diagonal transition moment and spin-orbit couplings being qualitatively inaccurate, especially for higher lying electronic states.



The importance of TiO for astronomical applications, combined with the availability of a large amount of benchmark data make this system an important target for future theoretical studies using modern electronic structure methodologies. Off-diagonal dipole moment and spin-orbit coupling curves are particularly important for quantitative intensities.

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Exploring Protein–Ligand Interactions using Multilayer Molecules-in-Molecules (MIM) Fragmentation-Based Approach

IL105

Dr. Bishnu Thapa, Professor Krishnan Raghavachari

Indiana University, Bloomington, IN, USA

Accurate estimation of the binding affinities of protein–ligand complexes is an extremely challenging task. Typically, the protein–ligand binding affinities are estimated based on scores obtained from knowledge-based or empirical scoring functions, or from energy functions based on molecular mechanics (MM) force-fields. Although such methods are extensively used in predicting protein–ligand binding affinities, they inherently lack a rigorous description of the underlying intermolecular interactions (e.g., charge-transfer, π-π interactions, many-body effects, etc.), and do not provide a reliable quantification of such interactions critical to design a potent drug. In such cases, a high-level quantum mechanical (QM) treatment can be very useful to correct for the deficiencies in the classical description of such interactions. Unfortunately, the steep computational scaling of traditional quantum mechanical methods limits their applicability for large molecules. We have developed the Molecules-in-Molecules (MIM) fragment-based approach to overcome these bottlenecks and to enable accurate calculations on such systems.

In this presentation, we present the application of our MIM method for the computation of interaction energies associated with the protein–ligand binding. The performance of our approach has been assessed using a diverse sets of ligands bound to different proteins where experimental binding affinities are available, and compared with other theoretical methods. We also present a difference energy analysis protocol within our MIM framework (MIM-DEA) to break down the total interaction energies into the contributions from individual ligand-residue pairs, solvation energy and entropy. MIM-DEA provides a quantitative description of the residue-specific interactions responsible for the observed difference in binding potencies of seemingly identical ligands. Using a representative set of protein-ligand complexes, we discuss the performance of our protocol for the accurate estimation of relative binding potencies as well as the interaction energy partitioning method.

A Linear Scaling Approach for Efficient Geometry Optimization in Perturbed DNAs

IL106

Prof. Yuriko Aoki, Dr. Yuuichi Orimoto, Dr. Anna Pomogaeva

Kyushu University, Kasuga, Japan

For efficient calculations by high-level quantum chemical approach, we developed a linear-scaling method, Elongation (ELG) method, as a tool for the large-scale complex systems. ELG method that we have been developing since early 1990’s shows several advantages when we treat large-scale complex systems for which conventional method cannot handle because of the difficulties in SCF convergence or geometry optimization. It has been developed for efficiently determining the electronic structure of polymers without considering any periodic boundary conditions. A target polymer is built up by adding a monomer unit to the active side of a starting cluster step by step. As there is no periodicity presumed, that is, in a general sense the adding monomers during the elongation steps can be random, any random polymer can be theoretically synthesized. Contrast to some other approximation methods for large systems, the elongation is fully variational. This original method has been initiated for one-dimensional systems targeting biopolymers as DNAs and now it was generalized to be applicable to three-dimensional (3D) systems like complicated proteins (named as 3D-ELG method). This method has been applied to various biopolymers like collagen, insulin, DNA, and so on and confirmed that the total energy errors by the ELG method are within 10^{-8} Hartree/atom in comparison with those by conventional direct calculations for entire systems. Therefore, we are now applying it to the efficient geometry optimization in locally perturbed DNA by the interaction with ligands toward constructing a tool for drug discovery.

CherryPicker: Automated Parameterisation of Large Biomolecules for Molecular Simulation

IL107

Dr Ivan Welsh, Dr Jane Allison

School of Biological Sciences, University of Auckland, Auckland, New Zealand

Molecular simulations allow investigation of the structure, dynamics and thermodynamics of molecules at an atomic level of detail, and as such, are becoming increasingly important across many areas of science. As the range of applications increases, so does the variety of molecules. Simulation of a new type of molecule requires generation of parameters that result in accurate representation of the behaviour of that molecule, and, in most cases, are compatible with existing parameter sets. While many automated parameterisation methods exist, they are in general not well suited to large and conformationally dynamic molecules. I will describe the CherryPicker method for automated assignment of parameters for large, novel biomolecules, and demonstrate its usage for peptides of varying degrees of complexity. CherryPicker uses a graph theoretic representation to facilitate matching of the target molecule to molecular fragments for which reliable parameters are available. It requires minimal user input and creates parameter files compatible with the widely-used GROMACS simulation software.

Global Simulations of Enzymatic Degradation of Organophosphates and Phosphorylation of Sugars

IL108

Prof. Zexing Cao

Department of Chemistry, Xiamen University, Xiamen, China

Enzymatic catalysis generally comprises multiple chemical and nonchemical steps, such as breaking and making of chemical bonds, substrate delivery, and product release. Due to the complex protein environment, any nonchemical or chemical step may dominate the enzymatic efficiency. In order to comprehensively understand the catalytic activity and specificity of enzymes, extensive QM/MM MD and MD simulations on phosphorylation of sugars by NahK and degradation of oganophosphates by PTE have been performed. Plausible reaction mechanisms and the importance of noncovalent interactions for the whole catalytic process have been discussed, which enrich the knowledge of reactivity in proteins.

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Are Fullerenes Strongly Correlated Molecules?

IL109

Professor Gustavo E Scuseria

Rice University, Houston, USA

Quantum Chemistry is a successful field because for weakly correlated problems, we can get accurate answers at reasonably low polynomial computational cost instead of the combinatorial expense of brute force approaches. Despite many advances, however, the so-called strong correlation problem, where the chemist's molecular orbital picture breaks down, remains quite open, particularly for large molecules and solids. This lecture will address challenges and progress on the treatment of strong correlation, and its connection with quantum symmetries and degeneracy. Methods recently developed in our research group for strong correlation will be discussed. In particular, I will address the question of strong correlation in fullerenes.

Some Small Calcium Hydrides

IL110

Professor Henry F Schaefer, Mr Michael C Bowman

University of Georgia, Athens, USA

Small calcium hydrides have to speculated upon, and there are a few experiments claiming to observe them. In this talk we will discuss our investigations of these claims.

Electrostatic Catalysis of Chemical Reactions

IL111

Professor Michelle L Coote

Australian National University, Canberra, Australia

Chemists appreciate that the rate of redox reactions can be manipulated by means of an electrical potential gradient. However, it was only recently that it was shown that an external electric field can also be used to catalyse non-redox reactions, thereby opening up a new dimension to chemical catalysis. So-called electrostatic catalysis arises because most chemical species have some degree of polarity and so can be stabilized by an appropriately aligned electric field; when this occurs to a greater extent in transition states compared with reactants, reactions are catalysed. However, by their nature such effects are highly directional and so implementing them in practical chemical systems is problematic. We have been using a combination of theory and experiment to explore various solutions to this problem. The first is using surface chemistry techniques, in conjunction with the break-junction technique in scanning tunnelling microscopy. This allows us to detect chemical reaction events at the single molecule level, whilst delivering an oriented electrical field-stimulus across the approaching reactants. The second is making use of the electric fields within the double layers of electrochemical cells to manipulate both redox and non-redox unimolecular reactions. Here we find that molecules actually self-align and interact with electrolyte ions to facilitate catalysis. Finally, in an approach that is truly scalable, we have instead addressed problem of orientation of the electric field by making use of appropriately placed charged functional groups to provide the electrostatic stabilization for solution-phase reactions. In this way, the direction of the local field experienced by the reaction centre is fixed, and by associating the stabilization or destabilization with the protonation state of an acid or base group, it has the advantage of providing a convenient pH switch. In this talk our latest results will be presented and the prospects for electrostatic catalysis discussed.

Understanding the High Activity of Mildly Reduced Graphene Oxide Electrocatalysts in Oxygen Reduction to Hydrogen Peroxide

IL113

Professor Sean C. Smith

Integrated Materials Design Laboratory, Department of Applied Mathematics, Research School of Physics and Engineering, The Australian National University, Canberra, Australia

The direct electrochemical synthesis of hydrogen peroxide (H_2O_2) would provide an attractive alternative to the traditional anthraquinone oxidation process for continuous on-site applications. Its industrial viability depends greatly on developing cost-effective catalysts with high activity and selectivity. Recent experiments have demonstrated that mildly reduced graphene oxide (mrGO) electrocatalysts exhibit highly selective and stable H_2O_2 formation activity [e.g., H. W. Kim, M. B. Ross, N. Kornienko, L. Zhang, J. Guo, P. Yang and B. D. McCloskey, *Nat. Catal.*, **2018**, 1, 282–290]. However, the identification of active site structures for this catalytic process on mrGO is doubtful. Herein, by means of first-principles calculations, we examine the H_2O_2 formation activities of active site structures proposed in the experiments and find that their activities are actually very low. Then, we systematically investigate the H_2O_2 formation activities of different oxygen functional group structures on mrGO based on experimental observations, and discover two types of oxygen functional group structures (2EP and 1ET+1EP) that have comparable or even lower overpotentials (<0.10 V) for H_2O_2 formation compared with the state-of-the-art $PtHg_4$ electrocatalyst. Our theoretical results reveal that the graphene edge and the synergetic effects between different oxygen functional groups are essential for the superior performance of mrGO for H_2O_2 production. This work not only provides a feasible explanation of the cause of high H_2O_2 formation activity of mrGO, but also offers a guide for the design, synthesis, and mechanistic investigation of advanced carbon-based electrocatalysts for effective H_2O_2 production.

Influence of Oxygen Vacancy Location on Charge Carrier Dynamics in Reduced TiO_2 Nanoparticles

IL114

Prof Jin Yong Lee, Mr Yeonsig Nam

Sungkyunkwan University, Suwon, Korea, Republic of

In our previous study, we reported the influence of size and shapes on the electronic structure of reduced TiO_2 nanoparticles[1,2] as well as functional dependence on band gaps of metal oxides.[3,4] We provided a predictive map of anatase-rutile level alignment from the size of nanoparticles[6] and the enhanced catalytic activity of TiO_2 nanoparticles with oxygen vacancies.[5] In this talk, we focus on charge carrier dynamics in the presence of oxygen vacancies in TiO_2 nanoparticles (NPs).[7] Quantum dynamics simulations show that electrons and holes are trapped within several picoseconds, while recombination of the trapped charges varies broadly in time, ranging from tens of picoseconds to nanoseconds.[8] The diverse charge recombination scenarios revealed by the nonadiabatic molecular dynamics simulations rationalize the contradictory experimental results on TiO_2 NP photocatalytic activity and provide guidelines for rational design of nanoscale metal oxides for solar energy harvesting and utilization.

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Understanding Biological Micro-machines: From Cytokine Receptors to Viral Fusion

IL115

Prof Alan E Mark, Dr David Poger, Ms Shelley Barfoot

The University of Queensland, St Lucia, Australia

At their most basic level many proteins and peptides can be thought of as mechanical components (switches, pumps, pipes, rods and motors) which come together to form functional complexes, in essence self-organized micromachines. Whether these are transmembrane pores formed by antimicrobial peptides or large multi-component viral complexes which facilitate infection the challenge in understanding these systems is that key processes in their mode of action are transitory. Thus, while the mechanisms of action can be speculated upon they cannot be observed directly. The talk will focus on how atomistic molecular dynamics simulations have been used to examine the mechanism of action of increasingly complex systems spaning anti-microbial peptides, type I cytokine receptors, efflux pumps and viral fusion proteins. For example, simulations of the conformational changes within the extracellular domains of the growth hormone receptor, the prolactin receptor, erythropoietin receptor and the epidermal growth factor receptor associated with the binding (or removal) of ligand. Although multiple mechanisms of action have been proposed for these systems, simulations suggest that the removal of the cytokine from the ligand-bound homodimeric receptor complexes results in a rotation of the two subunits relative to each other of between 30° and 45° in all cases. The similarity of the motion in repeated simulations suggests that relative rotation of the extra cellular domains represents a general mechanism of type I cytokine activation. The talk will cover how simulations can have been used to both support and challenge proposed mechanisms providing unique insights and facilitating the interpretation of experimental data.

Hydration Pattern of Intrinsically Disordered Proteins

IL116

Professor Parbati Biswas

Department of Chemistry, University of Delhi, Delhi, India

Intrinsically disordered proteins lack a unique three-dimensional tertiary structure either entirely or partially and exist as dynamic ensemble of inter-convertible conformations under standard physiological conditions. These proteins are characterized by a preponderance of charged residues and low content of hydrophobic residues Based on a combination of polymer theory and computer simulations we explore the hydration pattern of different classes of disordered proteins, i.e., intrinsically disordered protein regions (IDPR) which represent partially disordered proteins and the completely disordered proteins (IDP). Analysis of the hydration capacity reveals that the disordered proteins have a larger binding capacity for hydration water as compared to the globular proteins. The surface and radial distributions of the water molecules also confirm this trend. The local structure of the hydration water evaluated in terms of the tetrahedral order parameter depicts a higher order among water molecules surrounding the disordered proteins/regions. The orientation of the water molecules is distinctly different for the ordered and disordered proteins/regions. Enhanced hydration water mobility in the vicinity of the disordered proteins/regions is related to their high hydration capacity, low hydrophobicity and increased internal motions. Three-dimensional RISM theory is employed to investigate and interpret the 3D hydration profile, specifically in the vicinity of the charged and hydrophobic residues.

Complete Basis Set Limit Convergence for Finite Uniform Electron Gases

IC001

Dr. Stephen G. Dale[1], Prof. Henryk A. Witek[2], Prof. Peter M. W. Gill[1]

[1]Australian National University, Canberra, Australia. [2]National Chiao Tung University, Hsinchu, Taiwan

The infinite uniform electron gas (UEG) is the foundation for almost all current density-functionals. Current density-functionals suffer from a number of well known shortcomings, some of which are inseparable from the infinite nature of jellium. Finite UEGs have been proposed by the Gill group to be more representative of finite molecular nature. New UEGs have subsequently been constructed on the n-sphere (a sphere in (n+1)-D space with electrons constrained to the surface of the sphere in n-D space). Before these finite UEGs can be used to construct new density functionals exact energy behaviour of these gases must be well characterised. To date only the 1-sphere has been sufficiently characterised to be the foundation of a new class of density functionals (GLDA1[1]). Discussion regarding the benefits of finite UEGes as a foundation for development of density-functional approximations and strategies for efficient computation of exact correlation energies on an n-sphere will be provided by Peter Gill. Mathematical details pertaining the analysis of the 3-sphere will be provided by Henryk Witek.

In this talk exact correlation energies for the 2-sphere and 3-sphere will be presented. Particular attention will be paid to convergence to the complete basis set limit and unique challenges inherent to the n-sphere models.

[1] Pierre-François Loos, Caleb J. Ball, Peter M. W. Gill. J. Chem. Phys. 140, 18A524 (2014).

Implementation of Slater-Type One-Center Atomic Integrals for Accurate Variational Calculations of Small Atoms by Free Complement Theory

IC002

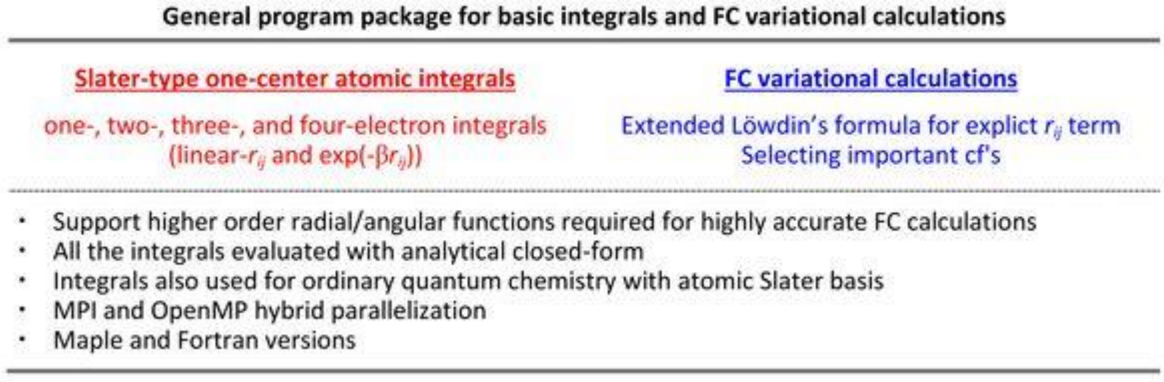
Dr. Hiroyuki Nakashima, Dr. Yusaku I. Kurokawa, Prof. Hiroshi Nakatsuji

Quantum Chemistry Research Institute, Kyoto, Japan

We implemented one-, two-, three-, and four-electron atomic integrals of Slater functions for exact atomic calculations by the free complement (FC) theory. All the integrals are evaluated with analytical closed-form and adapted to higher order radial and angular momentum functions, which are required for highly accurate FC calculations. The general integral code that satisfies above requirements seems not exist except for the present program. In addition, we developed an efficient method to evaluate matrix elements by extending Löwdin's formula for the complement functions (cf's) of the FC theory, including explicit correlated r_{ij} terms. We also proposed the cf selection method: small compact set of cf's can be selected without loss of accuracy based on the local nature of cf's.

This code has been applied to the FC calculations of small atoms. For He, Li, and Be atoms, the energy differences from the exact ones: $\Delta E = E_{FC} - E_{exact}$ were 0.00010 kcal/mol (n(order)=11, M(dimension)=203), 0.029 kcal/mol (n=6, M=502), and 0.081 kcal/mol (n=4, M=457), respectively. Thus, all results satisfy the chemical accuracy: less than 1 kcal/mol as absolute solutions of the Schrödinger equations. Moreover, by applying the cf selection method, the chemical accuracy was achieved with only M=6, 10, and 21 cf's for He, Li, and Be atoms, respectively. We also performed the FC calculations for $^5S^o$: sp^3 state of C atom, which is the excited state but most important for chemistry. The chemical accuracy was almost achieved: ΔE=0.832 kcal/mol in case E_{exact} estimated by the experiment and only M=113 cf's was selected within 1 kcal/mol by the cf selection method.

Thus, by the present work, accurate variational FC calculations for atoms with compact wave functions have now been realized and will be extended to molecular calculations.



General program package for basic integrals and FC variational calculations

Slater-type one-center atomic integrals	FC variational calculations
one-, two-, three-, and four-electron integrals (linear-r_{ij} and $\exp(-\beta r_{ij})$)	Extended Löwdin's formula for explict r_{ij} term Selecting important cf's

- Support higher order radial/angular functions required for highly accurate FC calculations
- All the integrals evaluated with analytical closed-form
- Integrals also used for ordinary quantum chemistry with atomic Slater basis
- MPI and OpenMP hybrid parallelization
- Maple and Fortran versions

Competing Molecular and Radical Pathways in the Dissociation of Halons via Direct Chemical Dynamics Simulations

IC003

Ms. Sumitra Godara, Dr. Manikandan Paranjothy

Indian Institute of Technology Jodhpur, Jodhpur, India

Decomposition chemistry of Halons has received much attention due to their role in ozone depletion. An important aspect of dissociation of halons is the competition between radical and molecular pathways. Recently, role of isomerization in the molecular pathways were studied using electronic structure theory. In the present work, we investigated the dissociation chemistry of CF_2Cl_2, CF_2Br_2, $CHBr_3$, and CH_2BrCl using chemical dynamics simulations. Classical trajectories were generated *on-the-fly* at the density functional PBE0/6-31G* level of electronic structure theory at a fixed total energy. Simulations showed that molecular products, in general, were dominant for all the four molecules at the chosen energy. A variety of reaction mechanisms including isomerizations and *roaming* pathways contributed to the formation of molecular products.

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2. Paranjothy, M.; Sun, R.; Zhuang, Y.; Hase, W. L. *WIREs Comput. Mol. Sci.* **2013,** *3,* 296 - 316.

Theoretical Simulation of Carrier Quantum Dynamics in Organic Materials

IC004

Dr Yi Zhao

Xiamen University, Xiamen, China

The carriers in organic materials commonly follow hopping-type motions because of strong carrier-phonon interactions. However, they can also present a band-like behaviour in well-performed organic crystals or mixed inorganic-organic materials. Therefore, their dynamics should be described by a unified way covering from band-like to hopping-type motions. Development of such a method for large systems is interesting in theoretical chemistry and still meets a great challenge. Focusing on this problem, we have proposed a time-dependent wavepacket diffusion method[1]. In the method, the effects of carrier-phonon interaction and inter- or intra-molecular electronic couplings are considered as the fluctuations on carrier dynamics. Based on this concept, we have also proposed a rigorous hierarchy of stochastic Schrödinger equation, and the relationship between two methods are built[2]. We further present how to combine electronic structure calculations with these quantum dynamics methods to reveal the carrier dynamics in realistic organic semiconductors, such as exciton energy relaxation and singlet fission[3].

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[3] Ke YL, Liu YX and Zhao Y, J. Phys. Chem. Lett., 2015, 6, 1741. Zang H, Zhao Y and Liang WZ, J. Phys. Chem. Lett., 2017, 8, 5105. Ke YL and Zhao Y, J. Chem. Phys., 2018, 149, 014104.

Thermodynamic Phases and Structural Organization of Ionic Liquids within Nanoscale Solvophobic Confinement

IC005

Mr. Harender S. Dhattarwal[1], Dr. Richard C. Remsing[2], Dr. Hemant K. Kashyap[1]

[1]Indian Institute of Technology Delhi , New Delhi , India. [2] Temple University, Philadelphia, USA

Due to the wide variety of unique properties, ionic liquids (ILs) have gained enormous attention in basic research and industrial application. More recently, ILs have garnered attention for controlling the mechanism of nanoscale assembly [1]. Nanoscale solutes, such as graphene sheets, form stable dispersions in ILs, and these dispersions have been used to improve the characteristics of electrical double-layer capacitors (EDLCs) [2]. Understanding wetting and de-weting behavior of ILs sheds light on the finding out the ideal pore sizes in nanoporous carbon electrodes. In particular, one can envision combining capillary evaporation in nanopores with electrowetting to enhance capacitance. Here, we have utilized molecular dynamics simulations to characterize the dewetting thermodynamics of [EMIM][BF_4] in nanoscale confinement between model rigid and flexible solvophobic surfaces [3,4]. We find that enhanced density fluctuations at the surface of solvophobic sufaces can reduce free energy barriers to capillary evaporation, similar to previous investigations involving water. Our findings additionally suggest that flexibility of the confining material can significantly impact the free energy barrier to capillary evaporation [4].

(1) T. L. Greaves and C. J. Drummond, Chem. Soc. Rev. **42**, 1096 (2013).
(2) S. Kondrat, P. Wu, R. Qiao, and A. A. Kornyshev, Nat. Mater. **13**, 387 (2014).
(3) G. Shrivastav, R. C. Remsing and H. K. Kashyap, J. Chem. Phys. **148**, 193810 (2018).
(4) Harender S. Dhattarwal, R. C. Remsing and H. K. Kashyap (Submitted).

A Chemical Mechanism of Unidirectional Proton Transfers Driven by Coupled Proton and Electron-Wavepacket Transfers

IC006

Dr Kentaro Yamamoto, Prof Kazuo Takatsuka

Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, Japan

Unidirectional proton transfers frequently identified in biological systems are among the most exciting challenges not only in biology but also in chemistry because there can exist unknown “chemical mechanisms” hidden behind. By chemical mechanism we mean one-way dynamics not based on the physical mechanism such as diffusion and irreversibility due to ratchet machinery and so on but making use of a series of chemical reactions. In this presentation, we theoretically propose a chemical reaction mechanism of unidirectional proton transfers (Fig. 1), which may possibly work as an elementary process in chemical and biological systems. The present mechanism includes two nonadiabatic processes, namely, coupled proton electron-wavepacket transfer (CPEWT) and inverse CPEWT, which are responsible for the unidirectional proton transfers. To show that the proposed mechanism can be materialized in a molecular level, we perform the ab initio calculations of nonadiabatic electron-wavepacket dynamics for a model system consisting of biochemically familiar molecules.

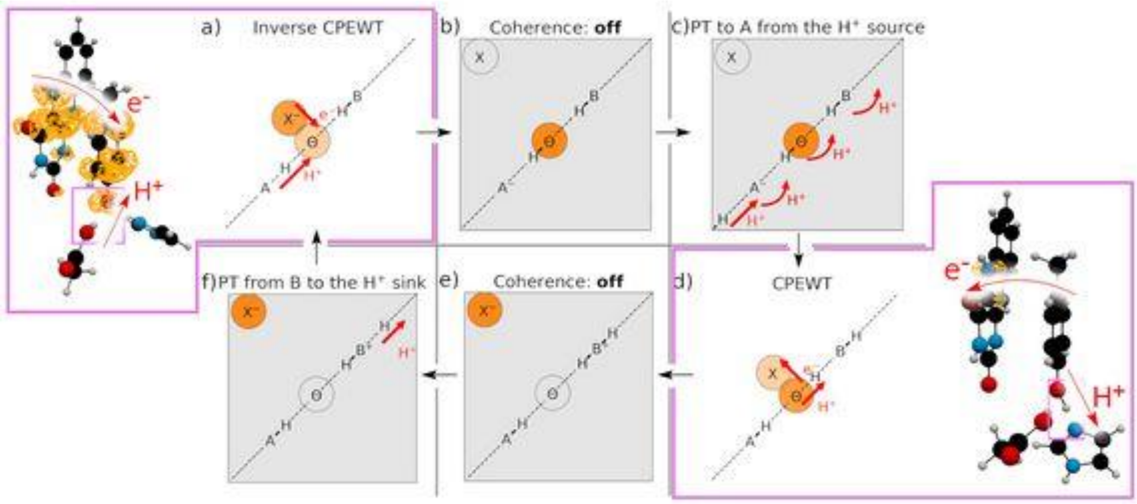


Fig. 1. Schematic representation of the present mechanism to induce unidirectional proton transfer by reciprocal motions of electron. The core subsystem consists of AH = acid, BH = base, H = (reaction center) and X = (electron buffer), along with snapshots of the results of dynamics calculations for (a) and (d) using mutually corresponding model systems.

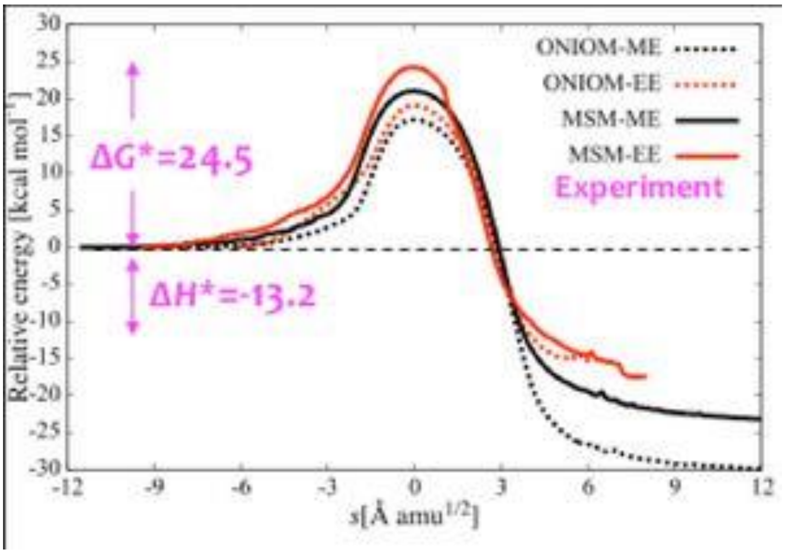
Multistructural Microiteration Technique Adopting the Electrostatic Embedding Scheme

IC007

Dr. Kimichi Suzuki[1,2], Dr. Satoshi Maeda[1,2]

[1]WPI-ICReDD, Sapporo, Japan. [2]Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan

We have extended the multistructural microiteration (MSM) technique so that the electrostatic embedding (EE) scheme in the ONIOM method can be adopted. MSM is a method to take multiple surrounding structural contributions into account in reaction path calculations. In the original MSM formulation, the electrostatic interaction between QM and MM layers can only be evaluated through the so-called mechanical embedding (ME) scheme. In this study, we show an MSM-EE formulation as an extension of the previous MSM-ME scheme. As a numerical result, the IRC path of the chemical transformation of chorismate into prephenate in the aqueous solution by ONIOM and MSM methods are presented in Figure. Here, the initial surrounding structures were prepared by MD simulation with fixing QM atomic coordinates of an optimized reactant structure. Among MD trajectories, configurations of five lowest energies were used as initial surrounding structures in MSM calculations, while that of the lowest one was used for ONIOM calculations. In the IRC paths by ONIOM and MSM based on the ME schemes, barrier heights are underestimate compared to experimental data, while reaction energies are overestimated. On the other hand, those by the MSM-EE scheme are shown that both barrier height and relative energy are close to experimental values. It is concluded that the improvement is because electrostatic interactions and surrounding structural changes are taken into account properly during the path calculation. We will present details of proposed method and results in the poster.



TCR Recognition in Chronic Beryllium Disease – Molecular level Understanding of Be^{2+} Binding to HLADP2-Peptide Complex

IC008

Dr. Susmita De[1], Ms. Gopika Sabu[1], Prof. Martin Zacharias[2]

[1]Cochin University of Science and Technology, Kochi, India. [2]Technical University Munich, Garching, Germany

The chemistry of beryllium is rather unusual, however, less explored as compared to other main group elements.[1] This is mainly attributed to the high toxicity of the beryllium compounds. The exposure of beryllium compounds results in respiratory failure by a chronic granulomatous pneumonitis, called chronic beryllium disease (CBD).[2] Even though genetic susceptibility of CBD is reported, the detailed molecular-level understanding of the disease is still elusive.[3] Our molecular dynamics (MD) simulations combined with quantum mechanical/molecular mechanical (QM/MM) studies indicated that Be^{2+} binds to four negatively charged amino acid residues, viz. GLU (β26E) and GLU (β69E) from HLADP2 protein and GLU (p7E) and ASP (p4D) from M2 peptide. The resultant HLADP2-M2 complex gives rise to one static and one dynamic binding site for Na^+ ions near the genetic marker GLU (β69E). The binding of Be^{2+}, as well as two Na^+ ions, induces major conformational changes of the amino acid residues at the surface of HLADP2-M2 complex creating negatively charged binding pockets for binding of positively charged residues of T-cell receptor (TCR) protein. The binding of TCR initiates immune-mediated toxicity leading to CBD. The selectivity may be ascribed to the smaller size and high charge density of Be^{2+} ion, which have been further explored by replacing Be^{2+} by other ions such as Na^+, Ca^{2+}, and Mg^{2+}. Our studies indicate that these replacements could not generate suitable binding pockets at the surface of HLADP2-M2 complex for TCR binding.

Reference:

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3. Richeldi, L., Sorrentino, R., Saltini, C., *Science.,***1993**, *262*, 242.

Predicting the Emission Efficiency of Phosphorescent Emitters in OLEDs

IC009

Dr Xiuwen Zhou, Prof Benjamin J Powell

University of Queensland, Brisbane, Australia

Organic light-emitting diodes (OLEDs) are widely viewed as the basis for next generation displays and lighting. However, to apply this technology widely and for it to reach its full potential, improvements in the emission efficiency and device lifetime are vital. So far, the development of blue, and especially deep blue, emitters in OLEDs has progressed rather slowly. Therefore being able to predict the emission efficiency prior to the synthesis and measurement of properties is of crucial importance for the discovery of new highly efficient blue emitters. Our recent work[1,2] has shown that it is possible to predict the emission efficiency through the calculation of the radiative rate[3] and non-radiative rate[1,2] using state-of-the-art computational strategies. Specifically, we find that the main non-radiative process of a series of iridium(III) complexes is the elongation or even breaking of a metal-ligand bond, and the non-radiative rate can be predicted from the energy barrier to this non-emissive state. In this talk, I will present our recent advances in predicting the emission efficiency of a series of deep blue light-emitting complexes that allows us further proposing new highly efficient deep blue emitters for OLEDs.[4]

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Computational Strategies to Achieve Highly Efficient and Stable OLEDs: An Industrial Perspective

IC010

Dr Hyeonho Choi

Samsung Advanced Institute of Technology (SAIT), Samsung Electronics, Suwon, Korea, Republic of

Organic light emitting diodes (OLEDs) represent a disruptive technology that has changed the display industry. A key component of significantly increasing the efficiency of OLED devices is employing transition metal-based triplet emitters that theoretically are capable of showing quantitative phosphorescence efficiencies. We report a new formulation for Golden Rule-based predictions of photoluminescence quantum yields (PLQY) of phosphorescent emitters containing a heavy element, and its implementation compatible with first-principles computation frameworks. We applied this new approach to the photophysical properties of 34 Pt(II) complexes designed for the organic light-emitting diode (OLED) applications and observed a good agreement between predictions and experiments over diverse scaffolds.

Although we have figured out that intrinsic degradation of the materials composing emitting layers is responsible for the short operation lifetime, the mechanism underlying the degradation processes have yet to be fully understood. We examined how to enhance the lifetime of organic light-emitting diodes (OLEDs) based on bipolar host molecules ET-HT, where ET and HT refer to electron- and hole-transporting units, respectively, by analyzing their thermodynamic and kinetic stabilities. Our DFT calculations reveal that the thermodynamic stability of ET-HT is determined by that of its anion, which is difficult to improve by chemical modifications of ET and HT. The kinetic stability of ET-HT can be enhanced by the spiroconjugation between ET and We examined how to enhance the lifetime of organic light-emitting diodes (OLEDs) based on bipolar host molecules Green OLED devices were fabricated by using ET-HTs with and without spiroconjugation, to find that the device with spiroconjugation has a lifetime that is approximately 6 times longer than the one without spiroconjugation.

Insight into the Chemical Reactions from the Molecular Dynamics Simulation

IC011

Prof. Toshiaki Matsubara

Kanagawa University, Hiratsuka, Japan

Since the recent development of the computation has made the molecular dynamics (MD) simulation of the chemical reaction possible, we have been increasingly interested in the dynamical event that happens during the reaction. For example, we want to know how does the reaction start, how does the reaction go over the energy barrier and so on. Although the various examinations concerning the dynamics of the chemical reaction have recently provided the new findings, the problem how does the rare event of the chemical reaction take place remains unsolved. It is a still challenging subject to understand the chemical reaction from the dynamical point of view.

In this talk, we will present our latest results of the QM- and the ONIOM-MD simulations for one of the typical organic reactions, the S_N2 reaction, in the gas phase and the water solvent.[1] Our analyses showed that the migration of the kinetic energy inside the substrate caused by the fluctuation of the kinetic energy of the atoms triggers the reaction and the requirements of the velocity vectors of the specific atoms must be satisfied in turn to reach the transition state and go down to the product. Dynamical effects of the surrounding solvent molecules were also revealed to be crucial factors that significantly affect the time required to pass the transition state and the requirements of the velocity vectors to complete the reaction. Our recent reports of another nucleophilic substitution[2] and the reaction of germanone,[3] where we suggested that the distribution of the kinetic energy in the substrate and the dynamical effects of the solvent are important factors to cause the reaction, would also be included.

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[2] T. Matsubara, T. Ito, *J. Phys. Chem. A,* 120, 2636–2646 (2016).
[3] T. Matsubara, T. Ito, *J. Phys. Chem. A,* 121, 1768–1778 (2017).

Decomposition of PFOS and PFOA: A Density Functional Theory and Transition State Theory Study

IC012

Mr Yasir Khan, Dr Sui So, Dr Gabriel da Silva

The University of Melbourne, Melbourne, Australia

Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are a widespread and persistent pollutants of concern to human health and the environment. Although incineration is often used to treat material contaminated with per- and polyfluoroalkyl substances (PFAS), little is known about the precise chemical mechanism for the thermal decomposition of these substances of concern. Here, we present the first study of the thermal decomposition kinetics of PFOS and PFOA, using a suite of DFT methods coupled with reaction rate theory methods. We discovered low-energy decomposition channels for both PFOS and PFOA, and predict rate coefficients as a function of temperature. Both substances have half-lives that are predicted to be short at the modest incineration temperature of 1000 K.

Density-Functional Tight-Binding Metadynamics Study of Oxy-Carbon Diffusion on (100)-γ-Al_2O_3 Surface

IC013

Dr. Aditya Wibawa Sakti[1], Dr. Chien-Pin Chou[2], Prof. Hiromi Nakai[1,2,3]

[1]Element Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto, Japan. [2]Waseda Research Institute for Science and Engineering (WISE), Waseda University, Tokyo, Japan. [3]Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, Tokyo, Japan

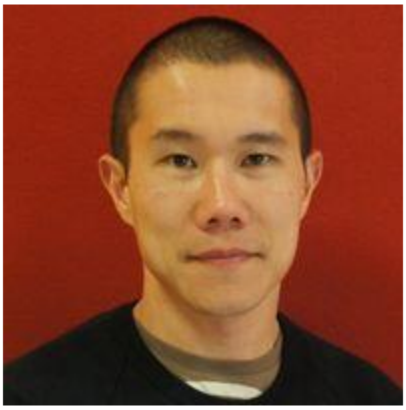
Exhaust gases produced by the automobile, typically, contain harmful chemicals, namely, CO, unburned hydrocarbon, and NO_x. To prevent air pollution caused by those gases, the three-way catalyst (TWC) technologies were developed. Oxide supported metal cluster, e.g. M_n/Al_2O_3 (M=Pt, Rh, Pd) catalysts are widely used in the automobile catalytic converter. During the catalytic combustion of the unburned hydrocarbon, chemical compounds containing C, H, and O, namely, oxy-carbon species are formed as intermediates. The oxy-carbon species spill and grow on the metal oxide surface. Their growth may affect the catalytic activity and selectivity. Experimentally, it was observed that the diffusion of oxy-carbon species is the rate-determining step of the growth process. In the present study, plausible mechanisms of the diffusion process are studied via metadynamics (MTD) simulations at the density-functional tight-binding (DFTB) level. The free energy barriers of acetate, formate, and methoxy diffusions are estimated in the present study and are in the range of the experimental values of 5.74-26.05 kcal/mol. More details on the molecular insight as well as the surface coverage dependence of free energy barriers will be discussed in the presentation.

Entrance Effects in Concentration Gradient-Driven Flow Through an Ultrathin Porous Membrane

IC014

A/Prof. David M. Huang

The University of Adelaide, Adelaide, Australia



Flow of liquid mixtures through pores and porous membranes plays a key role in many processes of fundamental and practical interest, including cellular homeostasis in biological systems, chemical separations, desalination, and energy harvesting. Most theoretical models and simulations of fluid flow in porous media have considered flow only within pores assumed to be of infinite length and have neglected the effect of transport between the membrane pores and the fluid outside the membrane. But these so-called entrance or access effects can dominate fluid flow when the membrane thickness approaches the characteristic pore size. The most extreme examples of this situation are membranes of atomic thickness made from novel 2D nanomaterials, such as graphene or molybenum disulfide, which have attracted great interest recently, as they have shown exceptional properties compared with conventional membranes in a number of applications. I will present the first general theory of fluid flow through an ultrathin membrane driven by a solute concentration gradient, which predicts how solute and solvent fluxes are controlled by important microscopic parameters such as pore size and the strength and range of fluid-membrane interactions. The theory is quantitatively accurate, as shown by comparisons with continuum and molecular dynamics simulations, and predicts markedly different flow behaviour compared with that through a thick membrane. These results have broad implications for fluid-flow processes through membranes of molecular thickness.

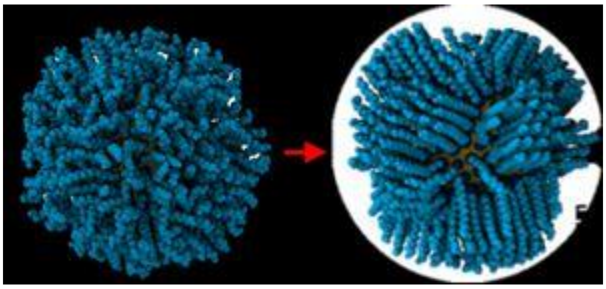
Colloidal Stability of Apolar Nanoparticles: Insights from Simulations and Theory

IC015

Dr Asaph Widmer-Cooper, Ms Debora Monego

ARC Centre of Excellence in Exciton Science, School of Chemistry, The University of Sydney, Sydney, Australia

Being able to predict and tune the colloidal stability of nanoparticles is of vital importance for technological applications, yet our ability to do so is poor due to a lack of understanding of how nanoparticles interact with one another [1]. One area that has seen increased attention is the organic ligand shell that coats most inorganic nanoparticles dispersed in apolar solvents. This ligand shell is essential for keeping the particles from randomly aggregating in solution, but can affect the particle stability in subtle and surprising ways. In particular, the ligands can undergo a temperature-dependent order-disorder transition (figure) that switches the particle-particle interaction in solution from repulsive to attractive [2-4]. The temperature of this transition is sensitive to a range of factors, including the particle dimensions, density of ligand coverage, and ligand length, often leading to non-linear trends that cannot be explained using conventional colloid theory [3-5].



In this talk, I will explain how the ability of the ligand shell to order (or not) can make sense of a diverse range of surprising phenomena, including an inversion of the effect of ligand length on particle stability, solvent effects that run opposite to the rule of like-dissolves-like, and stabilities that increase by orders of magnitude upon the addition of a single methyl group to the tail of the ligands [6]. Our results for Au and CdSe nanoparticles provide a microscopic description of the forces that determine the colloidal stability of apolar nanoparticles and explain why classical colloid theory fails.

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4) Kister, T. et al. *ACS Nano* **2018**, *12*, 5969.
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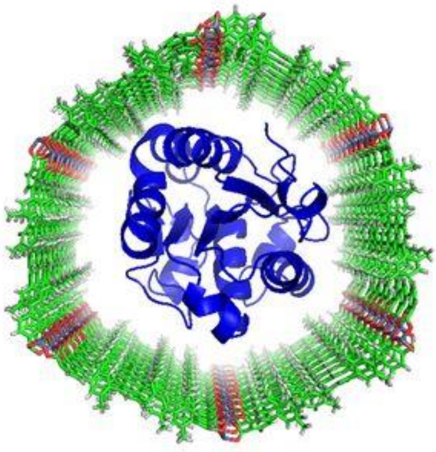
The Structural and Dynamics Properties of Enzyme Encapsulated in Metal-Organic Framework

IC016

Ms. Tuan Nurul Azura Tuan Kob@Yaakub[1], Dr. Mohd Farid Ismail[1], Prof. Dr. Mohd Basyaruddin Abdul Rahman[1], Dr. Muhammad Alif Mohammad Latif[1,2]

[1]Integrated Chemical BioPhysics Research, Faculty of Science, Universiti Putra Malaysia, Selangor, Malaysia. [2]Center of Foundation Studies for Agricultural Science, Universiti Putra Malaysia, Selangor, Malaysia

Metal-organic frameworks (MOFs) are porous materials made by coordination bonding between metal ions and organic linkers to form one-, two-, or three-dimensional structures. Isoreticular synthesis has provided a way to increase the pore apertures of MOFs, which allows for biomolecules such as enzymes to enter the pore. There has been evidence reported, showing that enzyme stability under extreme conditions can be increased via encapsulation or biomineralization with MOFs. Here, we present an atomic level investigation on the effect of encapsulation towards the structure and dynamics properties of a model enzyme. Cutinase, a cutin hydrolase, was encapsulated inside an isoreticular MOF named IRMOF-74-VI. Single point *ab initio* calculations were performed on a single crystal structure of IRMOF-74-VI to determine the partial charge distribution among each atom in the MOF structure. We carried out 50 ns molecular dynamics (MD) simulations at five different temperatures on free-cutinase and cutinase-IRMOF-74-VI complex in aqueous solution in order to determine the effect of encapsulation towards the stability and flexibility of the protein structure.



MD simulation results showed that the structural stability of cutinase at 450 and 500 K was markedly improved when encapsulated with IRMOF-74-VI. This was further confirmed by atomic fluctuations analysis. At high temperatures, the flexibility of several regions of the protein structure was found greatly reduced in the presence of IRMOF-74-VI. Intermolecular interactions between cutinase and IRMOF-74-VI were predominated by hydrophobic interactions with arginine residues forming the highest number of interactions. IRMOF-74-VI has shown that it can improve enzyme stability to prevent denaturation at extreme temperatures. This is a positive indication that MOFs can be an alternative towards improving the stability and efficiency of biocatalysts.

Natural Orbital Functional for Multiplets

IC017

Prof. Mario Piris

University of the Basque Country, San Sebastian, Spain. Donostia International Physics Center, San Sebastian, Spain. IKERBASQUE, Bilbao, Spain

The energy of an electron system can be determined exactly from the knowledge of the one- and two-particle reduced density matrices (1- and 2-RDMs). In practical applications, we employ this exact energy functional but using an approximate 2-RDM that is built from the 1-RDM. Approximating the energy functional has important consequences: the theorems obtained for the exact functional of the 1-RDM [1] are no longer valid. As a consequence, the functional N-representability problem arises, that is, we have to comply the requirement that reconstructed 2-RDM must satisfy N-representability conditions to ensure a physical value of the approximate ground-state energy. In this presentation, the role of the N-representability in approximate one-particle functional theories [2] will be analyzed.

The 1-RDM functional is called Natural Orbital Functional (NOF) [3] when it is based upon the spectral expansion of the 1-RDM. Appropriate forms of the two-particle cumulant have led to different implementations, being the most recent an interacting-pair model called PNOF7 [4]. The latter is able to treat properly the static (non-dynamic) correlation and recover an important part of dynamic correlation. In the second part of the presentation, a new NOF [5] that allows to properly describe an electronic system with any value of the spin, that is, a new reconstruction of the 2RDM for spin-multiplets will be presented. The values obtained are in outstanding agreement with the experimental data.

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Benchmarking Real-Space Quantum Monte Carlo for Quantum Chemistry

IC018

Dr Manolo C Per, Dr Deidre M Cleland

CSIRO Data61, Melbourne, Australia

The real-space diffusion quantum Monte Carlo method (DMC) is a stochastic approach to the quantum many-body problem. It has the potential to be a reference method for medium-sized electronic systems, due to its low power-law scaling of cost with system size, and its immense parallelisability. Despite its promise, there have been relatively few studies of the accuracy that can be obtained with the method for quantum chemistry applications.

We have developed a state-of-the-art implementation of electronic-structure DMC in our software package CMQMC (CSIRO Molecular Quantum Monte Carlo), with the specific aim of making the method as simple as possible to use. In this talk, I will outline some of the developments that enable an almost black-box application of DMC to arbitrary molecular systems. This ease of use allows us to perform high-throughput calculations, which we are using to assess the accuracy of DMC for important classes of chemical problems. As part of this benchmarking effort, we have developed the notion of Chemical Reliability, a simple scalar measure which simultaneously reflects how likely a method is to provide errors smaller than 1 kcal/mol, as well as the impact of outliers far from the mean error. I will present recent results for calculations of carbon-centred radical stabilisation energies and reaction barrier heights.

Origin of Intermolecular Interactions in Open Shell Singlet State

IC019

Dr. Peifeng Su

Xiamen University, Xiamen, China

The energy decomposition analysis (EDA) schemes bridge the gap between electronic structure theory and conceptual interpretations of intermolecular interactions. The recently developed generalized Kohn-Sham energy decomposition analysis scheme (GKS-EDA) [1] can perform interaction analysis for open and closed systems in gas phase and solvated environments by various DFT functionals. In this talk, based on broken symmetry unrestricted density functional theory (BS-UDFT) with a spin projection approximation, GKS-EDA is extended to molecular interactions with open-shell singlet states, which is a challenge for the single reference based EDA methods due to the multi-reference character. Using the extension of GKS-EDA, the physical origins of several typical intermolecular interactions in open shell singlet state are revealed and compared.

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Second-Order Perturbation Theory with Spin-Projected Hartree-Fock

IC020

Dr. Takashi Tsuchimochi

Kobe University, Kobe, Japan

Spin-projected spin-unrestricted Hartree-Fock (SUHF) has been recently revisited to capture static correlation efficiently. A variety of post-SUHF methods that simultaneously add the dynamical correlation effect have been also developed subsequently, including configuration-interaction and coupled-cluster. While these methods are much more accurate than those of post-HF, their applications have been hindered due to high costs. From this perspective, second-order perturbation theory (PT2) is expected to be a good compromise between cost and accuracy, and therefore is desired for practical applications for large systems.

In this presentation, I will propose two different PT2 formulations with SUHF. The first one is the generalization of spin-extended second-order Møller-Plesset (EMP2). In our previous study of EMP2, the first-order wave function was approximated by spin-projecting an unrestricted MP1 wave function, and hence, in this EMP2(0), the amplitudes may not be suitable. The new version of EMP2 exploits the one-particle Fock-like operator in the normal-ordered Hamiltonian that can be defined within the spin-projection integration space. Formulated this way, the EMP2 amplitudes can be optimized by minimizing a well-defined Hylleraas functional.

The second approach is based on the generalized Fock operator as in CASPT2. In what we call SUPT2, the spin-free nature of the zeroth-order Hamiltonian permits us to rigorously define Rayleigh-Schrödinger perturbation theory with SUHF as a zeroth-order wave function. However, in practice, SUPT2 suffers from intruder states, a issue common in CASPT2. We have adopted real and imaginary level shift techniques to alleviate the intruder state problem.

Our preliminary numerical tests on the dissociation curves of HF, H2O, and N2 show EMP2 provides slightly better results than EMP2(0). SUPT2 turns out to be by far the best, and provides accuracy akin to CASPT2. It is also found that imaginary level shifts are much more appropriate than real ones, reducing a large amount of errors.

High-Stability and Fast-ion Transport in Mg-based Compounds for Mg batteries from First-Principles Calculations

IC021

Prof. Pieremanuele Canepa

The National University of Singapore, Singapore, Singapore

Mg batteries utilizing a Mg metal anode with a high-voltage intercalation cathode define a potential pathway toward energy storage with high energy density. However, the realisation of Mg batteries is plagued by the instability of existing electrolytes against the Mg-metal anode and high-voltage cathode materials [1-5]. One viable solution to this problem is the identification of protective coating materials that could effectively separate the distinct chemistries of the metal-anode and the cathode materials from the electrolyte. Using first-principles density functional theory calculations we map the ion transport and the electrochemical stability windows for non-redox-active Mg binary and ternary compounds in order to identify potential coating materials for Mg batteries. Our results identify Mg-halides and $Mg(BH_4)_2$ and sulphide or selenides compounds, e.g. MgX_2Z_4 (X=In, Sc and Y; and Z=S or Se) as promising anode coating materials based on their significant reductive stability [4,5]. On the cathode side, we identify MgF_2, $Mg(PO_3)_2$ and MgP_4O_{11} as effective passivating agents [5].

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Metal-Organic Frameworks for Energy and Environmental Applications: From Molecular Modeling to Mass Production

IC022

Dr Ravichandar Babarao

RMIT University, Melbourne, Australia. CSIRO, Melbourne, Australia

Metal-organic frameworks (MOFs) have emerged as a special class of hybrid nanoporous materials. The variation of metal oxides and the vast choice of controllable organic linkers allow the pore size, volume and functionality of MOFs to be tailored in a rational manner for designable architectures. MOFs thus provide a wealth of opportunities for engineering new functional materials and are considered as versatile candidates for storage, separation, sensing, catalysis, drug delivery and other important applications. With ever-growing computational resources and advance in mathematical techniques, molecular simulations have become an indispensable tool for materials characterization, screening and design. At a molecular level, simulations can provide microscopic insights from the bottom-up and establish structure-function relationships. An overview is presented here on how molecular modelling can a powerful tool in intelligent design of new smart porous materials for greenhouse capture and hydrocarbon separations.

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The Michaelis Complex for Nitroaromatic Substrates in Bacterial Nitroreductases Determined by Molecular Dynamics Simulations

IC023

Dr Andrew J Christofferson

RMIT University, Melbourne, Australia

Nitroreductase enzymes are of interest as antibiotic targets and as activators in enzyme prodrug therapy, but the precise substrate binding orientation and reaction mechanism are poorly understood. In order to design more effective antibiotics and improve enzyme prodrug therapy, an atomistic description of nitroaromatic substrate binding in the active Michaelis complex is highly desirable. Using an iterative molecular dynamics (MD) simulation protocol, the binding of nitroaromatic substrates such as p-nitrobenzoic acid (p-NBA) in oxidized and reduced bacterial nitroreductases was investigated. For the oxidized enzyme, the MD simulations distinguished between the two possible binding orientations of p-NBA from X-ray crystal structure data. For the reduced enzyme, a distinct active binding orientation of p-NBA was found (Figure 1) when the second active site of the homodimer was occupied by a NADH analogue. This model of the active Michaelis complex of p-NBA provides a rationale for the reduction of p-NBA via a hydride transfer reaction mechanism suggested by experimental results, and brings the proposed reaction mechanism from experiment and computational models into agreement.

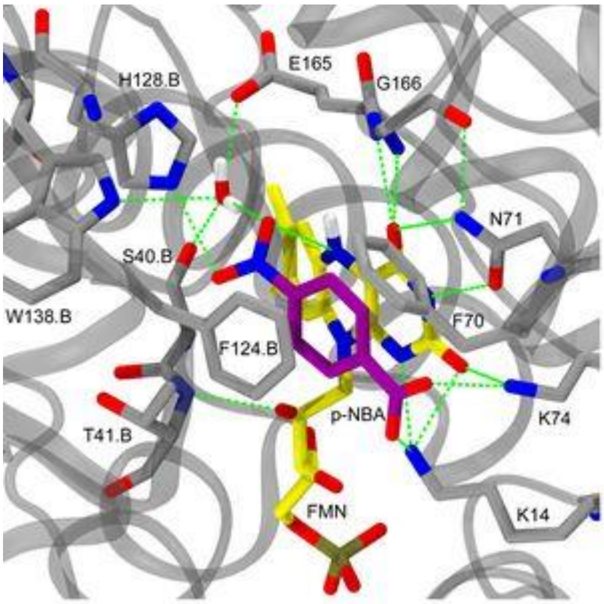


Figure 1. Binding of the active Michaelis complex of p-NBA in a bacterial nitroreductase active site. Hydrogen bonds are shown as green dashed lines. The FMN cofactor carbons are colored yellow, while p-NBA carbons are colored purple and protein carbons grey. Oxygen, nitrogen, phosphorous, and hydrogen are colored red, blue, tan, and white, respectively. Only the hydrogens of reduced FMN N5 and the persistent water molecule are shown.

Gene Silencing Mechanisms Revealed by Dynamics of Guide, Target and Duplex Binding to Argonaute

IC024

Dr Hui-Chung Tai, Dr Carmay Lim

[1]Institute of Biomedical Sciences, Academia Sinica, Taipei 115, Taiwan [2]Department of Chemistry, National Tsing Hua University, Hsinchu 300 Taiwan

Argonaute (Ago) protein plays a central role in silencing gene expression by binding a “guide” strand to base-pair with a complementary mRNA and degrading the mRNA. Current understanding of how Ago-guide and Ago-guide- mRNA complexes assemble is based mainly on static crystal structures; the associated kinetic pathways remain unknown/unclear. By simulating the successive binding of guide/target strand to Thermus thermophilus Ago (TtAgo) and computing the respective free energy landscapes, we directly visualize how TtAgo silencing complexes form and function. We show that the guide binding rate depends on its initial loading position onto TtAgo. Subsequent target recognition beyond the scissile 10-11 nucleotides must overcome a substantial energy barrier for TtAgo’s nucleotide-binding groove to expand widely. This work reveals novel roles for the core TtAgo domains and show how the kinetic barriers that must be overcome for critical structural changes to occur lead to target repression/cleavage.

Gaussian Basis Function Methods for Propagating Molecular Wave Functions: BEL MCG

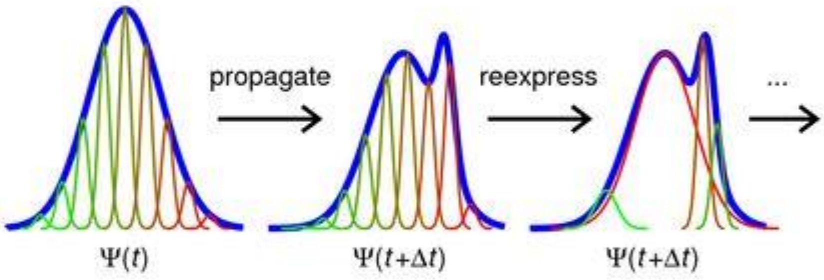
IC025

Dr Terry J Frankcombe

UNSW, Canberra, Australia

The use of Gaussian basis functions (GBFs) within quantum dynamics simulations offers several benefits, and several methods have been developed to take advantage of these. Usually the benefits come coupled with several drawbacks, one of the most notable being the question of how the basis set should be adapted to the changing wave function. Indeed, most GBF methods (e.g. vMCG, AIMS, G-MCTDH, CCS, aTG, MP-SOFT, etc.) differ primarily in how they allow basis functions to move as the simulation proceeds. In most cases the movement of the basis functions depends on some equations of motion, which vary from fully quantum mechanically variational through to purely classical.

Over the past few years we have developed a method specifically designed to avoid the problems associated with selecting and implementing GBF equations of motion, the Basis Expansion Leaping multiconfiguration Gaussian (BEL MCG) method. In this method we use the variational flexibility afforded by the non-orthogonal nature of GBFs to propagate for short periods in a set of *stationary* GBFs. Critically, we then use a novel algorithm to *reexpress* the wave packet in a set of new GBFs, appropriate for the time-evolved state. This process is repeated as the wave packet evolves in time. In this talk I will briefly describe the BEL MCG method and illustrate some of its features with recent applications.

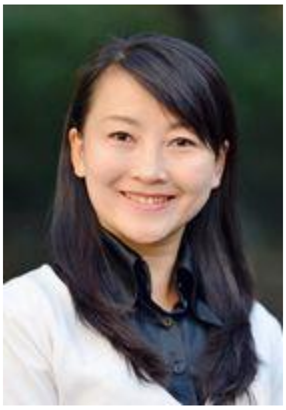


Macroscopic Combustion Mechanism Representation Method Based on Complex Network Theory and Feedback Analysis

IC026

Prof Lin Ji, Mr Jie Wang, Miss Yue Li

Capital Normal University, Beijing, China



Chemical mechanism research aims to provide explanation for certain function or phenomenon in molecular or electronical level. But some targets are not of significance in the microscopic level. Large scale of microscopic chemical reaction mechanism heavily burdened, or even prevents their application in other areas. This requires the investigation of coarse grained mechanism representation. Mechanism reduction in combustion chemistry is among the investigations of such motivation. This talk introduces our recent progress in expressing the detailed microscopic combustion mechanism on the macroscopic level by the two typical macroscopic feather of mechanism: the community structure and feedback loops. This method was applied into the highly nonlinear combustion system of H2. The reduced mechanism with 7 reactions out of 19 in the original detailed one shows good prediction capability of nonlinear behavior like ignition over a wide range of temperature and pressure scope.

Large-scale Quantum Mechanical Molecular Dynamics Simulations for the Long-distance Proton Transfer in Bacteriorhodopsin

IC027

Dr. Junichi Ono[1], Ms. Chika Okada[2], Dr. Yoshifumi Nishimura[1], Dr. Prof. Hiromi Nakai[1,2,3]

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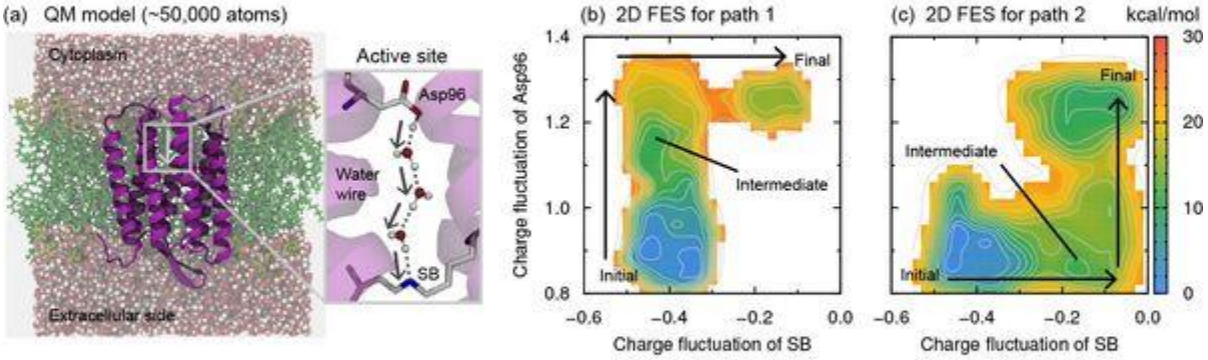
Bacteriorhodopsin (BR) is a model protein for light-driven proton pumps, in which five consecutive proton transfers achieve the unidirectional active proton translocation. Since the resulting proton concentration gradient is utilized for synthesis of adenosine triphosphate (ATP), elucidating the individual proton transfer mechanism in BR is indispensable for understanding the energy conversion mechanism in biological systems. The third proton transfer of BR occurs from Asp96 to the Schiff base (SB) of the chromophore on the photocycle from M to N intermediates. From previous experiments, this reaction is expected to occur by the long-distance proton transfer of ~12 Å via the Grotthuss mechanism through three internal water molecules connecting Asp96 and SB with hydrogen bonds (water wire). However, the actual proton transfer has not been directly observed due to the limitation of the spatio-temporal resolution in experiments. Therefore, the microscopic mechanism of this proton transfer has still been unclear.

In the present study, the large-scale quantum-mechanical (QM) molecular dynamics (MD) and metadynamics simulations based on the divide-and-conquer density-functional tight-binding (DC-DFTB) method were performed to clarify the detailed molecular mechanism of the third proton transfer in the N state of BR. Here, all the atoms including BR, lipid membranes, and solvents (In total ~50,000 atoms) were treated quantum-mechanically (Figure 1a). From several 10-ps DC-DFTB-metadynamics simulations after 50-ps DC-DFTB-MD equilibration, two pathways along the water wire were actually observed for the first time. One is the predicted pathway via the Grotthuss mechanism with H_3O^+ intermediates (path 1), and the other is an unprecedented pathway via the Grotthuss-like mechanism with different intermediates (path 2). In this presentation, analyses of free energy surfaces (FESs) for these two pathways obtained from the projection to the charge fluctuations of SB and Asp96 using the reweighting method will be discussed in detail (Figures 1b and 1c).



Path Integral Simulation for Accurate Calculation of Hyperfine Coupling Constants of Muoniated Molecules

IC028

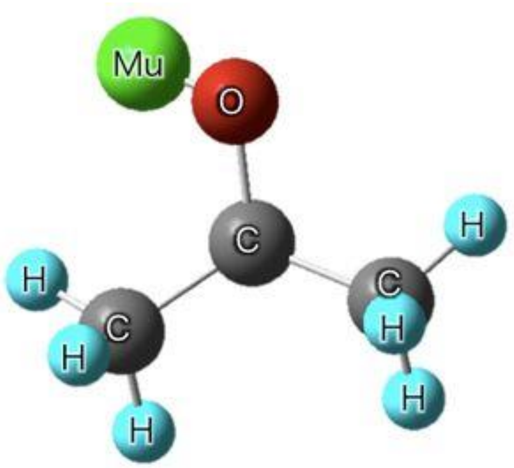
Mr. Yuki Oba[1], Ms. Sakura Okano[1], Dr. Tsutomu Kawatsu[2], Prof. Masanori Tachikawa[1]

[1]Yokohama City University, Yokohama, Japan. [2]RIKEN, Wako, Japan

A considerable amount of knowledge for muonium (Mu; complex of positive muon and electron) chemistry has been accumulated for over 30 years. Compared with a proton, positive muon (µ+) has a smaller mass and larger magnetic moment. Because of these unique features, Mu is used as the muon spin resonance/rotation/relaxation (µSR), where hyperfine coupling constant (HFCC) is a good index for the magnetic interaction between electron and muon spins.

For instance, the HFCC value of muoniated acetone radical (Mu-ACE) is measured by Percival et al [2] as 10.27 MHz at 300 K (reduced using the proton magnetic moment). However, the reduced HFCC value for Mu-ACE is calculated as -5.8 MHz with the conventional DFT calculation [3], where the quantum effect of nuclei and thermal effect are excluded.

In this study, thus, we performed on-the-fly ab initio path integral molecular dynamics (PIMD) simulation, which can include these effects, to Mu-ACE and hydrogenated acetone radical (H-ACE). Our HFCC values for Mu-ACE and H-ACE are calculated as 32.1 and 3.97 MHz, respectively, which are in reasonable agreement with the corresponding experimental values of 10.3 and 1.51 MHz. Such mass-dependence on HFCC values is due to the large quantum effect of muon.



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Electrochemical Alkoxyamine Cleavage; a ‘On-Demand’ Source of Radicals and Cations for Synthesis

IC029

Dr Benjamin B Noble[1], Miss Chelsey L Hammill[1], Dr Philip L Norcott[1], Dr Simone Ciampi[2], Prof Michelle L Coote[1]

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Alkoxyamines have been widely used as initiators and mediators for Nitroxide Mediated Polymerization (NMP). Unfortunately, relatively high temperatures (ca. 80-120 °C) are needed to maintain sufficient levels of alkoxyamine homolysis, and at those temperatures unwanted side reactions limit the scope and utility of the process. We recently demonstrated that alkoxyamines can be cleaved electrochemically (via a 1-electron oxidation) under much more mild conditions. This cleavage occurs via a radical-cation intermediate that fragments at room temperature to release a nitroxide and alkyl cation. In the present work, we use a combination of high-level quantum chemistry and experimental techniques to explore the electrochemical cleavage of a wide array of different alkoxyamines. The influence of different alkyl and nitroxide functionality on this oxidative cleavage and the use of the resulting species as initiators/ mediators for polymer synthesis is also investigated. Finally, the scope and utility of alkoxyamines as energy storage materials and for electrochemical organic synthesis is explored.

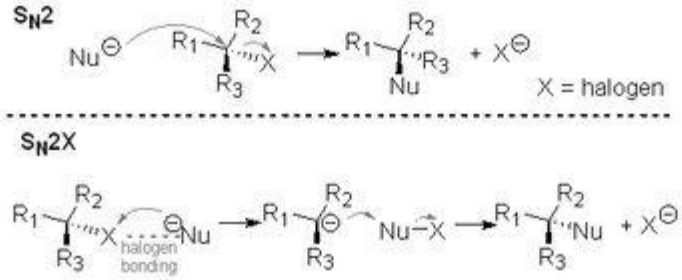
Halogenophilic Nucleophilic Substitution Reaction from a Theoretical Perspective

IC030

Dr Richmond Lee

SUTD, Singapore, Singapore

The classical dogma of the "backside" nucleophilic substitution, S_N2, is being challenged head-on by our recently published work which illuminated an alternative and uncommon substitution mechanism to be operative,[1] termed halogenophilic nucleophilic substitution (S_N2X). In the S_N2X mechanism, the nucleophile executes a "frontal" attack on the halide.



Such halogenophilic substitution reaction is not unprecedented,[2] but the rediscovery of this mechanism forces us to reinterpret the very well known S_N2 and see substitution reactions generally in a very different light. I will thus attempt to interpret this unusual but interesting S_N2X mechanism from theoretical perspectives.

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chemistry of Criegee Intermediate Revealed by Multireference Ab Initio Calculation and Nonadiabatic Molecular Dynamics

IC031

Prof. Fengyi Liu, Prof. Wenliang Wang

Key Laboratory for Macromolecular Science of Shaanxi Province, Key Laboratory of Syngas Conversion of Shaanxi Province, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an, China

The photochemistry of Criegee intermediates (CIs) plays a significant role in atmospheric chemistry but is relatively less known compared with their thermal reactions. Using multireference CASPT2 electronic structure calculations and CASSCF trajectory surface-hopping (TSH) molecular dynamics, we have revealed the unimolecular photochemical reactions of simplest CI (CH_2OO, sCI) and substituted CI (CRHCOO, R=-CH_3, -CH=CH_2), etc. In addition to the known photodissociation channel, a dark-state-involved $A^1A \rightarrow X^1A$ photoisomerization channel to a cyclic dioxirane has been found. The molecule on A^1A state is driven by the out-of-plane motion to reach a perpendicular A/X^1A minimal-energy crossing point (MECI), then nonradiatively decays to the ground state. The dynamics of these processes, including the excited-state lifetime, hopping probabilities and product quantum yields have been revealed by the TSH simulations. The findings are expected to broaden the reactivity profile and deepen the understanding of the photochemistry of Criegee intermediates.

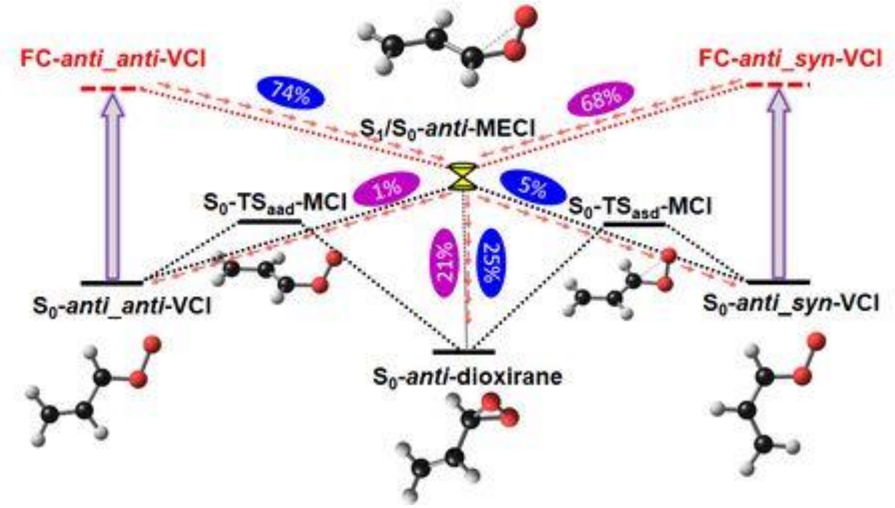

Figure 1. A scheme PES of Vinyl substituted Criegee Intermediate (CH2=CHCHOO).

Isolated Iron(II)Phthalocyanine Exhibits Quintet Ground-State: A Nexus Between Theory and Experiment

IC032

Dr. Dana Nachtigallová[1,2,3], Dr. Rabindranath Lo[1,3,2], Dr. Debashree Manna[1,3,2], Prof. Radek Zbořil[2,3], Prof. Pavel Hobza[1,2,3]

[1]Institute of organic chemistry and bio-chemistry, Prague, Czech Republic. [2]RCPTM, Olomouc, Czech Republic. [3]Palacký University, Olomouc, Czech Republic

Iron(II) phthalocyanine (FePc), an important member of the phthalocyanine family has potential applications in various fields, such as electrocatalysis, magnetic switching, electrochemical sensing etc. In spite of the importance of electronic properties of FePc in such wide applications, a reliable determination of its ground electronic state is still challenging. Here we present combined state-of-the-art computational methods and experimental approaches i.e. Mössbauer spectroscopy and SQUID magnetic measurements to identify the ground-state of FePc. Depending on the functional, DFT calculations assign an either quintet or, more frequently triplet, ground-state. However, at the CASSCF level the quintet is by 22.2 kcal/mol more stable with respect to the triplet, which is reduced to 8.6 kcal/mol by a subsequent perturbation treatment. The same ordering was also found using the DMRG approach. This has been confirmed by the hyperfine parameters obtained from ^{57}Fe Mössbauer spectroscopy performed in frozen monochlorobenzene. The use of monochlorobenzene guarantees the isolated nature of the FePc as indicated by a zero Weiss temperature. The results open doors for exploring the ground-state of other metal porphyrin molecules and their controlled spin transitions via external stimuli.

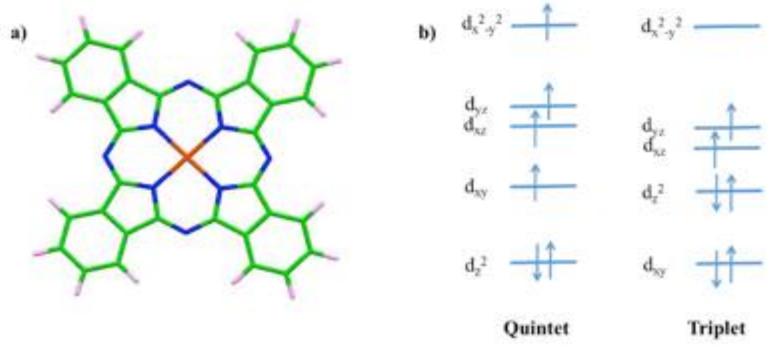

Figure 1. a) FePc (C-green, N-blue, Fe-red, H- pink), Fe-N distance is 2.008 Å (quintet) and 1.941 Å (triplet), and 1.926 Å (X-Ray experiment); b) the occupation of Fe(II) d-orbitals in quintet and triplet states.

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Enhanced Catalytic Performance of Ni(111) surface doped with Cu for the decomposition of CH_4

IC033

Miss Qinghong Yuan[1,2], Miss Nan Yao[3], Miss Michelle Hunter[2], Prof. Debra Bernhardt[2], Dr. Qinghong Yuan[2,1]

[1]East China Normal University, St Lucia, China. [2]The University of Queensland, Brisbane, Australia. [3]East China Normal University, Shanghai, China

Bimetallic nanocrystals (NCs) have emerged as an important class of catalysts due to their applications in numerous catalytic reactions, including catalytic reforming reactions, pollution control, and hydrogen generation etc. It is widely observed that bimetallic alloy NCs have higher catalytic efficiencies than their monometallic counterparts, owing to strong synergy between the metals. Experimentally, the catalytic performances of the bimetallic alloy strongly depend on the electronic and geometric structures that are determined by their composition. However, little is known about how the composition and surface structure affect the activity of the alloy.

In this work, by calculating C adsorption and CH_4 decomposition on CuNi alloy surfaces, we found that the reactivity of Ni(111) surface can be greatly improved by alloying Cu atoms with a percentage of less than 50 at%. CuNi(111) surface with a Cu doping concentration of 25 at% has the optimum reactivity. In contrast to (111) surface, the (100) and (110) surfaces has no improved catalytic ability by alloying with Cu. The increased reactivity of CuNi(111) surface is attributed to the modified d-band center of Ni. Compared with (100) and (110) surfaces, Cu doped on Ni(111) surface has the strongest binding with Ni atom and thus more charge transfer occurred between the Cu and Ni, which leads to the shift of d-band center of Ni to the Fermi level and increased reactivity.

Density Functional Theory Calculations on Surface Oxygen Vacancy Formation in Metal Oxides

IC034

Dr Yoyo Hinuma[1,2], Dr Takashi Toyao[3,4], Dr Takashi Kamachi[5,4], Dr Zen Maeno[3], Dr Satoru Takakusagi[3], Dr Shinya Furukawa[3,4], Dr Ichigaku Takigawa[6,3], Dr Ken-ichi Shimizu[3,4]

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Properties of materials may be significantly changed from those that are intrinsic by making small physical and chemical changes in the form of defects. As a result, various point and extended defects are intentionally introduced to govern their chemical reactivity, and their catalytic, electrical, optical, and mechanical properties. One mechanism important in catalysis is the Mars-Van Krevelen mechanism, an example of which is where O vacancy sites on a metal oxide catalyst surface act as the reaction site.

Accurate calculation of the surface vacancy formation energy based on first principles calculations requires calculation of a surface model and is much more computationally expensive than a bulk calculation. Catalysts typically require a certain physical quantity to be within a certain range, hence rapid judgement of whether a candidate material is viable or not based on quantities (descriptors) that are easy to calculate can significantly accelerate the screening process. Moreover, obtaining a rough estimation of the molecule adsorption energy at an O vacancy site without actually calculating a model with adsorbed molecules would be very helpful because finding how molecules adsorb to the surface necessitates exploration of various adsorption geometries that are often not trivial.

We report on correlations between the O vacancy formation energy of various insulating binary oxide materials and descriptors such as the band gap and formation energy, together with correlations between small molecule adsorption (for instance, CO, O_2, and CO_2) adsorption energy and the O vacancy formation energy.

Carbon Nitride Materials as Anodes in Lithium Ion Batteries

IC035

Dr Marlies Hankel

The University of Queensland, Brisbane, Australia

Carbon structures have been extensively studied over recent decades as energy storage materials. One of the industry applications is as the anode of lithium (Li) ion batteries (LIBs). Graphite, a layered material consisting of sp^2 bonded carbon sheets is currently the predominant anode material offering a theoretical capacity of LiC_6 with Li inserted between the layers.

Doping carbon materials with nitrogen has been shown to increase the storage capacity if used as an anode material. Graphitic C_3N_4 is a well used material with a high nitrogen content. However, it is not suitable as an anode material, as its interaction with lithium is too strong so that the lithium can not be discharged again.

We have performed comprehensive studies of a range of carbon nitride materials to understand the mechanism of the interaction of the lithium with the carbon nitride material. We have modified graphitic C_3N_4, by breaking it into ribbon like structures and combining it with a carbon backbone, to increase its reversible storage capacity and to provide a path to harness carbon nitrides as lithium ion anode materials.

Density functional theory (DFT) calculations are employed to obtain the maximum lithium storage capacity. We also calculate diffusion barriers for the lithium movement from one site to another to determine their mobility. In addition to this we also show how the lithium binds to the material by consideration of the charge density distribution and the charge transfer from the lithium to and from the material. The volume change of the material on the insertion of lithium is determined by employing a bilayer or bulk configuration of the material.

Theoretical Investigation for the Mechanism of Copolymerization of CO_2 and Cyclohexene Oxide Catalyzed by Novel Bifunctional Al(III) Porphyrin Catalyst

IC036

Dr. Manussada Ratanasak[1], Mr. Jingyuan Deng[2], Mr. Hideki Tokuda[3], Mr. Chihiro Maeda [3], Prof. Tadashi Ema[3], Prof Kyoko Nozaki [2], Prof. Jun-ya Hasegawa[1]

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Copolymerization of CO_2 and cyclohexene oxide (CHO) catalyzed by novel bifunctional Al^{III} porphyrin complexes with four quaternary ammonium (QA) halide groups which revealed that excellent catalytic activity (TOF = 18,000 h^{-1}) and high selectivity (>99%). To the best of our knowledge, this is the highest TOF among monometallic catalysts reported so far for the CHO/CO_2 copolymerization. In this work, origin of the excellent catalytic activity and selectivity were elucidated in detail by means of DFT calculations. Moreover, comparative DFT calculations on two catalysts models (Al^{III} and Mg^{II} complexes) were examined. Our calculation results clearly indicated that the high polymerization activity and carbonate-linkage selectivity of bifunctional Al^{III} complex originate from the cooperative actions of the metal center and the QA cation, both of which facilitate the epoxide-ring opening by the carbonate anion in the key transition state to form the carbonate linkages. In addition, we found that the stronger Lewis acid of Al^{III} metal center reduces the nucleophilicity of the carbonate anion which make the Al^{III} porphyrin catalyst is higher catalytic performance than the Mg^{II} porphyrin catalyst. The calculated activation energy for the formation of poly(cyclohexene carbonate) (PCHC) obtained by DFT calculations showed a good agreement to the kinetic studies from experiments.

CGMD Approach: Mutation Studies on the Thermostability and Activity Improvement of a Plant Fructosyltransferase from *Pachysandra terminalis*

IC037

Mr. Christopher Llynard D Ortiz[1], Dr. Hosea D Matel[1,2], Dr. Ricky B Nellas[3]

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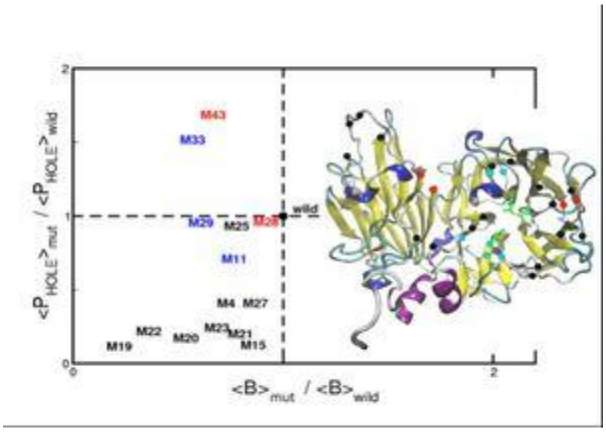

Fructosyltransferases (FTs) are agriculturally and industrially important enzyme. FTs are inserted to crops to increase their prebiotic content. Nowadays, fungal FTs are used for the production of fructooligosaccharides useful in the food and pharmaceutical industries. In the absence of FTs in most crops and due to the limitations of industrially-used FTs, a search for a more efficient enzyme from other sources is in need. As shown in previous studies, plant FTs are more thermostable and active compared to fungal FTs being used today [1]. Recently, the first crystal structure of a plant fructosyltransferase from *Pachysandra terminalis* was resolved [2]. With this, we performed initial *in silico* mutation studies via introduction of disulfide bridge using Martini Coarse-grained molecular dynamic (CGMD) simulations [3]. Preliminary results have shown that mutants, M33 and M43, was observed to be thermostable and active relative to the wild type. In contrast, other mutants (Figure 1) were thermostable but inactive relative to the wild type. Is distance-specific or domain-specific mutation triggers high thermostability and high activity? Towards the end of this project, we expect to be able to come up with a deeper understanding of this enzyme's structure-activity relationship.

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A New, Flexible Enhanced Sampling Method to Predict Binding Free Energy of Small Molecules – Membrane Systems

IC038

Mr Carlo Martinotti [1], Dr Evelyne Deplazes[1,2], Dr Ricardo L Mancera[1]

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Understanding the interactions of drug-like molecules with biological membranes is important to fields such as pharmacology, toxicology and rational drug design. Molecular dynamics (MD) simulations can complement experimental techniques to study small molecule-membrane interactions with atomic level resolution, providing information on both structural and dynamical properties as well as the ability to predict the binding free energy (ΔG_b). However, the accurate prediction of ΔG_b remains a very challenging task. The most commonly used approach to calculate ΔG_b is umbrella sampling (US). US though is known to suffer from insufficient roto-translational sampling of the molecule, resulting in a 'kinetically trapped' molecule that remains in the same local energy minima for long times. This leads to inaccurate ΔG_bestimations and/or prohibitively long simulations to reach convergence.

To address this, we have developed a version of replica exchange with solute tempering (REST) that allows the selective scaling of non-bonded interactions between any pairs of components in the system as well as separate modulation of electrostatic and vdW interactions. For example, to calculate ΔG_b for a small molecule-membrane system the non-bonded interactions for solute-membrane and solute-water are scaled while leaving the solute-solute and membrane-membrane interactions unscaled to ensure the integrity of the membrane. The method was tested by simulating the interactions of 3 terpene molecules (DPAC, LIM and PALC) with POPC and DMPC phospholipid bilayers. These scaled replica-exchange simulations combined with US were used to estimate the molecule-membrane ΔG_b. A comparison between classical and enhanced sampling US ability to predict $\Delta G_b$was conducted and compared with previously reported simulation and experimental data for the same systems. The method can be used for other types of small molecules and is currently being tested on larger molecules such as peptides.

The Pharmacophore Network: A Computational Method for Exploring Structure−Activity Relationships from a Large Chemical Data Set

IC039

Pr Ronan Bureau[1], Dr Jean-Philippe Metivier[1], Dr Nhat Vinh Vo[2], Dr Bertrand Cuissart[2], Dr Alban Lepailleur[1]

[1]CERMN, University of Caen Normandie, Caen, France. [2]GREYC, University of Caen Normandie, Caen, France

Historically, structure−activity relationship (SAR) analysis has focused on small sets of molecules, but in recent years, there has been increasing efforts to analyze the growing amount of data stored in public databases like ChEMBL. Pharmacophores represent steric and electronic properties (IUPAC definition) associated to specific chemicals named ligands (specificity related to a pharmacological profile) The pharmacophore network introduced herein is dedicated to the organization of a set of pharmacophores automatically discovered from a large data set of molecules. The network navigation allows to derive essential tasks of a drug discovery process, including the study of the relations between different chemical series, the analysis of the influence of additional chemical features on the compounds' activity, and the identification of diverse binding modes. We propose to describe the method used to construct the pharmacophore network, and to show the application on biological case studies[1].

Protamine-Triggered DNA Self-Assembly Unveiled at the Molecular Level by Molecular Dynamics Simulations

IC040

Prof. Yves Lansac[1,2], Prof. Yun Hee Jang[2]

[1]University of Tours, Tours, France. [2]DGIST, Daegu, Korea, Republic of

Protamines are highly charged proteins compacting efficiently DNA during the spermatogenesis process. They are also used as non-toxic gene carriers for therapy purposes. Using salmon proteins (+21e) and short DNA fragments (146 bps), we have explored the physico-chemical conditions required for protamines to condense DNA. At low salt concentration, a set of experiments combining electrophoresis, light scattering and cryoelectron microscopy reveals the existence of small charged DNA–protamine complexes coexisting either with DNA or protamines in solution. Atomistic molecular dynamics simulations have been used to probe the adsorption of protamines on a single DNA fragment as well as the interactions between a pair of DNA fragments. A coarse-grained model capturing the main molecular characteristics of DNAs and proteins and integrating out the atomistic degrees of freedom in order to probe larger timescale and length scale has been used to demonstrate that aggregation can be driven solely by electrostatic interactions.

Q-MP2-OS: an Inherently Parallel MP2 by Quadrature

IC041

Dr Giuseppe M J Barca, Mr Simon C McKenzie, Mr Nathaniel Bloomfield, Dr Andrew T B Gilbert, Prof. Peter M W Gill

Australian National University, Canberra, Australia

As computational hardware morphs into massively parallel architectures, quantum chemical methods and their underpinning implementations must evolve accordingly. In this lecture, we present a novel algorithm for the computation of the opposite-spin (OS) MP2 correlation energy that is well suited to large-scale parallelization. Our method employs a combination of deterministic quadratures and screening techniques, bypassing entirely the computation of two-electron integrals. Speedup, scaling and accuracy results for a variety of molecules and reactions reveal that the new algorithm achieves a 1 kcal/mol accuracy with nearly-ideal parallelizability on over 800 CPU cores, and a computational scaling reduced from $O(N^4)$ to $O(N^2)$.

Fragmentation Approach to Electronic Excitations

IC042

Dr. Xinsheng Jin[1], Prof. Xiao He[1,2,3], Prof. William J Glover[2,3,4]

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Electronic excitations correspond to a rearrangement of the electrons in a molecule in response to absorption of electromagnetic radiation and are important in a wide range of systems of technological and biological interest, such as fluorescent proteins, photoswitches, and solvated dye molecules. Unfortunately, the large size and complexity of these systems precludes the application of standard ab initio electronic structure methods such as time-dependent density functional theory to the full system. Building on the ground-state Electrostatically Embedded Generalized Molecular Fractionation with Conjugate Caps (EE-GMFCC) method, we have developed a fragmentation approach for electronic excited states that is able to treat localized excitations and excited-state properties in systems of thousands of atoms in essentially quantitative agreement with full-system calculations. We show the method is linear scaling and trivially parallelizable. Applying the method to the Green Fluorescent Protein (GFP) allows us to understand how each residue of the protein contributes to the chromophore's excitation energy. This information will be valuable in the rational design of GFP mutants with tailored colors.

Theoretical View on Gas Phase Water Catalysis at Room Temperature

IC043

Dr. Kaito Takahashi

IAMS, Academia Sinica, Taipei, Taiwan

Water has been termed as the “matrix of life” and some have claimed that life may not exist without it. When considering chemical reaction in the aqueous phase, water molecules can act as an environment to modulate the energies of the transition state (TS) of the reacting solutes, or can actively participate in modifying the reaction coordinate as well as the TS energies. When one looks at gas phase experiments, there have been only a few reports where a single water molecule is reported to catalyze reactions. Recently, we have disproved a previous notion that room temperature hydrogen abstraction from CH_3OH by OH radical is enhanced by water.[1] On the other hand, we have observed an enhancement in selected reaction rates for Criegee intermediates, i.e., carbonyl oxides, by the participation of a single water molecule.[2,3] In these reactions, the water molecule acts as a bridge to connect the two active sites of the reactants at the TS; thus, is an active participant of the reaction. In the present talk, we will theoretically evaluate why we can see catalysis for certain substituted Criegee intermediates but not for others. Furthermore, we will clarify why this water catalysis is likely to occur of hydration reaction of carbonyl bonds, but not for radical abstraction by OH radical.

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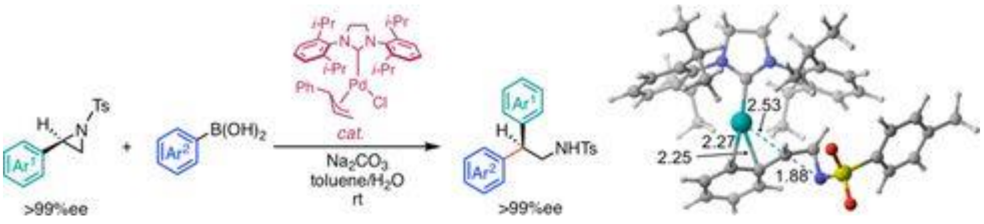
Exploring Mechanistic Puzzles in Pd-Catalyzed Aziridine Ring-Opening Reactions

IC044

Prof. W. M. C. Sameera

Hokkaido University, Sapporo, Japan

Homogeneous catalysis is one of the efficient ways to synthesise chemically or biologically relevant compounds. Quantitative details of the reaction mechanism and origin of the selectivity of a catalytic reaction are very important for the development of efficient catalysts. These properties are difficult to characterise from experimental data alone. In this direction, computational chemistry has been made significant contributions.[1]



We have developed novel quantum mechanics/molecular mechanics (QM/MM) methods[2],[3],[4] and reaction path search approaches[5] to explore complex reaction mechanisms. In my presentation, I will focus on mechanistic puzzles in Pd-catalyzed enantiospecific and regioselective ring-opening reactions of aziridines.[6][7]

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[7] A. K. Sharma, W. M. C. Sameera, Y. Takeda, S. Minakata, *ACS Catal.*2019, 9, 4582-4592.

Surface Model Calculation Database for Predicting Catalytic Activity: An Application to Methane Steam Reforming

IC045

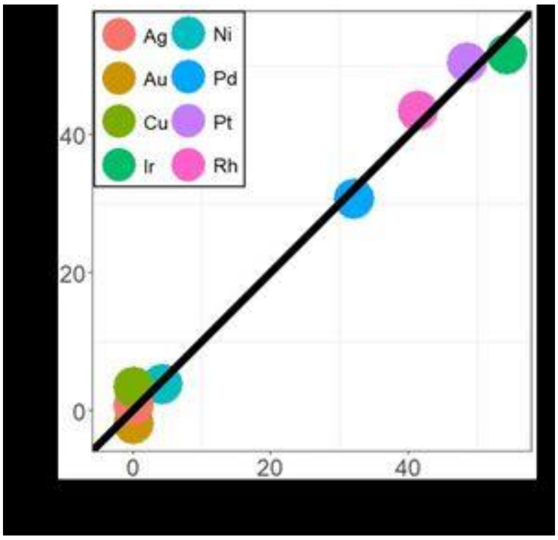
Dr. Masato Kobayashi[1,2], Mr. Haruka Onoda[3], Prof. Tetsuya Taketsugu[1,2]

[1]Faculty of Science and WPI-ICReDD, Hokkaido University, Sapporo, Japan. [2]ESICB, Kyoto University, Kyoto, Japan.
[3]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Japan

Recent advances in data-science methods have drawn attention to high-throughput quantum chemical calculations. In this presentation, we will report a surface model calculation database for heterogeneous catalytic reaction analyses, which we are constructing by systematically carrying out calculations of various chemical species adsorbed on metal surface models.

Our script program utilizes a semi-automatic and systematic quantum chemical calculation with SIESTA. Three-layer fcc(111), (100), and (211) slab models are used as typical metal surfaces and chemical species including H, C, and O atoms are adsorbed on the surface.

As an application, we evaluate the catalytic activity for the methane steam reforming reaction by using sparse modeling techniques. We first predicted the conversion ratio of methane on clean metal surfaces. The computational results for one- and two-atom adsorbed surfaces were used as the descriptor as well as the results for the surface itself. The predicted conversion ratio by the MC_+ method, a linear sparse modeling method, shows good agreement with the experimental value as shown in the Figure below. Looking at the survived descriptors, it was found that the adsorption energy of C_2 negatively correlates with the conversion ratio. Furthermore, these techniques were also applied to the experimental results of multiple articles. Here, the doping, support, and temperature effects were additionally considered.



Development of QSPR Machine Learning Algorithms to Predict voltaic Properties

IC046

Dr Nastaran Meftahi

RMIT University, Melbourne, Australia

Machine learning algorithms are applying to select excitonic materials with desired chemical properties, from a large range of possible candidate. By this method we can develop algorithms to predict quantum based electronic properties in the shortest time. In this respect, the Harvard organic photovoltaic dataset has been taken from literature. This dataset consist of 350 small molecules and polymers with experimental properties of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbitals (LUMO), electrochemical gap, optical gap, power conversion efficiency (PVC), open circuit potential (Voc) and short circuit current density (Jsc). Then very sparse variable selection methods can choose the most relevant descriptors for modelling the aforementioned electronic/optical properties. By applying quantitative structure property relationship (QSPR) machine learning we will be capable of making quantitative models linking molecular and physicochemical properties of materials to their photovoltaic and electronic performance. Essentially this uses machine learning to 'fill in the gaps' between more rigorous quantum chemical calculations, allows rapid and accurate prediction of the properties of very large virtual library.

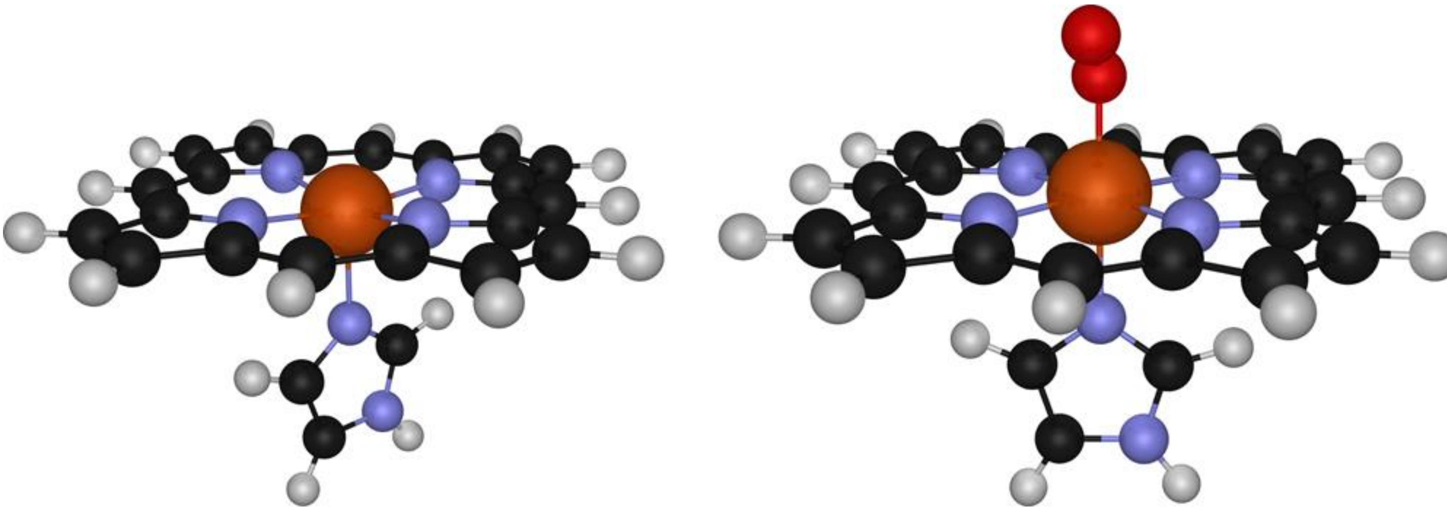
A Brief Account of My Encounters with Exchange in Computational Chemistry

IC047

Prof. Russell J. Boyd

Dalhousie University, Halifax, Canada

My interest in electron correlation in atomic systems at the outset my career took me on a fascinating journey that I could not have foreseen. The many highlights included the relative spin-state energies of atoms and molecules and the interpretation of Hund's multiplicity rule in atomic and molecular systems. My journey ended with some detailed studies of metalloporphyrins, heterocyclic macrocycles containing a metal centre, that are frequently incorporated into proteins via coordination to an amino acid residue and play a critical role in a vast array of chemical processes including oxygen transport, catalysis, electron transfer and active membrane transport. Hemoglobin, the iron-containing, oxygen-transport metalloprotein found in our red blood cells, is the best known example. Our results indicate that predicting the correct ground-state multiplicity for iron (II) porphyrin, a high-spin quintet, remains a significant challenge for electronic structure methods, including commonly employed density functionals.



The Molecular Mechanisms of Oxygen Activation and Hydrogen Peroxide Formation in Lytic Polysaccharide Monooxygenases

IC048

Professor Binju Wang[1], Professor Paul Walton[2], Professor Carme Rovira[3]

[1]Xiamen University, Xiamen, China. [2]University of York, York, United Kingdom. [3]Universitat de Barcelona, Barcelona, Spain

The recently discovered lytic polysaccharide monooxygenases (LPMOs) are copper-dependent enzymes for the degradation of recalcitrant polysaccharides such as chitin and cellulose. Unlike classical hydrolytic enzymes (cellulases), LPMOs catalyze the cleavage of the glycosidic bond via an oxidative mechanism using oxygen and a reductant. The full enzymatic molecular mechanisms, starting from the initial electron transfer from a reductant to oxygen activation and hydrogen peroxide formation, are not yet understood. Using QM/MM metadynamics simulations, we have uncovered the complete oxygen activation mechanisms by LPMO in the presence of ascorbic acid, one of the most used reductants in LPMOs assays. Our simulations capture the sequential formation of $Cu(II)-O_2^-$ and $Cu(II)-OOH^-$ intermediates via facile H-atom abstraction from ascorbate. By investigating all the possible reaction pathways from the $Cu(II)-OOH^-$ intermediate, we ruled out $Cu(II)-O\bullet^-$ formation via direct O-O cleavage of $Cu(II)-OOH^-$. Meanwhile, we identified the exclusive pathway in which the proximal oxygen atom of $Cu(II)-OOH^-$ abstracts a hydrogen atom from ascorbate, leading to Cu(I) and H_2O_2. The “in situ” generated H_2O_2 either converts to LPMO-$Cu(II)-O\bullet^-$ via a homolytic reaction, or diffuses into the bulk water in an uncoupled pathway. The competition of these two pathways is strongly dependent on the binding of the carbohydrate substrate, which plays a role in barricading the “in situ” generated H_2O_2 molecule, preventing its diffusion from the active site into the bulk water. Based on the present results, we propose a new catalytic cycle of LPMOs that is consistent with the experimental information available. In particular, it explains the enigmatic substrate-dependence of the reactivity of the LPMO with H_2O_2.

Understanding the Ultrafast Qx to Qy Transition in Chlorophylls

IC049

Ms. Petra Shih, Prof. Yuan-Chung Cheng

National Taiwan University, Taipei, Taiwan

Radiationless relaxation in molecular excited states plays significant roles in many photophysical and photochemical processes. In particular, the ultrafast dynamics of $Q_x \rightarrow Q_y$ internal conversion in chlorophylls is crucial to the high efficiency of light harvesting in photosynthesis. In this work, we investigate the $Q_x \rightarrow Q_y$ transition in chlorophyll *a* and bacteriochlorophyll *a* theoretically by evaluating the vibronic couplings and electronic couplings to construct a diabatic effective Hamiltonian that can be used to describe the non-adiabatic internal conversion dynamics. This first principle study is achieved by combining time-dependent density functional theory (TD-DFT) and a diabatization method through enforcement of configuration uniformity. Coupling parameters under harmonic approximations are obtained using TD-DFT calculations, leading to excellent agreement between experimental and simulated absorption and high-resolution fluorescence line narrowing spectra. The relaxation rate calculated using Fermi's Golden rule suggests that the sub-100 fs $Q_x \rightarrow Q_y$ process is fully described by weak vibronic couplings, and the energy gap between Q_x and Q_y states explains the strong solvent and chemical-substituent dependence of chlorophyll radiationless relaxations. The methodology developed in this work should be generally applicable to describe internal conversion processes in a broad range of photoactive organic molecules.

Development of Large-Scale Time-Dependent Density Functional Theory Code Based on Massively-Parallel Sparse-Matrix Library

IC050

Prof. Muneaki Kamiya[1,2], Dr. William Dawson[2], Dr. Takahito Nakajima[2]

[1]Faculty of Regional Studies, Gifu University, Gifu, Japan. [2]RIKEN Center for Computational Science, Kobe, Japan

The computational prediction for the chemical reactivity and electronic properties in large-scale molecules composed of several thousands to ten thousands of atoms such as supramolecules and biomolecules plays an important role in drug discovery and nanomaterial design. For example, the light function of a protein depends, of course, on the light functionality of the dye itself contained in the protein, but in many cases the intermolecular interaction between the excited state of the dye and the surrounding amino acids is essentially important. Therefore, an algorithm is needed to calculate large molecular excited states with high accuracy. Time-dependent density functional theory (TDDFT) is becoming a popular methodology for computing excited states for large molecules because of its reasonable cost and relatively high accuracy. Hybrid DFT, which includes a fraction of the Hartree-Fock exchange energy in the exchange-correlation functional, is particularly promising as it provides more robust calculations of biological molecules, an improved descriptions of molecular environments like liquid water and ionic solutions, and more accurate excited state properties. Nevertheless, this inherent cubic scaling still limits the accessible system sizes to some hundred atoms, and routine TDDFT calculations are usually only done in this regime.

In this work, we have developed a memory-partitioned parallel time-dependent density functional theory (TDDFT) calculation program for the purpose of carrying out excited electronic state calculations for large-scale molecules with modern HPC systems. Our implementation is based on an iterative method for solving linear systems. Since the array size of the trial vector itself increases dramatically as the molecular size increases, these trial vectors are calculated based on atomic orbitals, not molecular orbitals, and are distributed across processes. All the matrix multiplications are performed using NTPoly library, which is a massively parallel library for computing the functions of sparse and symmetric matrices.

A Density Functional and Wave Function Theory-based Study on the Mechanism of Oxygen Atom Attack on Polycyclic Aromatic Hydrocarbon

IC051

Dr. Aulia S Hutama

Department of Chemistry, Universitas Gadjah Mada, Yogyakarta, Indonesia. Austrian-Indonesian Center for Computational Chemistry, Yogyakarta, Indonesia

Potential energy curves (PECs) and energy profiles of atomic O attack on some polycyclic aromatic hydrocarbons (PAHs) as models for graphene/graphitic surface have been computed at the density functional theory level of theory to elucidate the mechanism of O attack and chemisorption to PAHs as graphene models. The PECs were obtained by scanning the O atom distance to the nearest carbon atom on "top" and "bridge" positions in coronene, while the energy profile was obtained from the fully relaxed geometries in triplet states. The possibility of an intersystem crossing from triplet to singlet state will be verified by the multireference wave function theory calculations. We proposed a mechanism of O attack and chemisorption reaction on PAHs starting from the non-interacting O and PAHs systems into the chemically bound O on PAHs.

Exploration of the Differences between Amine and Thiolate Addition to Acetylenedicarboxylates.

IC052

Dr Renate L Griffith[1], Dr Robyn L Crumbie[2]

[1]School of Chemistry, UNSW Sydney, Sydney, Australia. [2]School of Science and Health, Western Sydney University, Sydney, Australia

Nucleophilic addition of thiolates to diethyl acetylenedicarboxylate in chloroform at room temperature affords solely the meso dithioaddition product, whereas the addition of amines in ethanol gives only the corresponding (Z)-enamine, as confirmed by X-ray crystal analysis. The monoaddition product of thiolate addition, prepared and isolated at lower temperatures, also exhibited (Z)-stereochemistry. Our computational study on simplified model systems explains the reasons for the observed stereochemistry and why the acetylene dicarboxylate readily undergoes two addition reactions with thiolate nucleophiles, whereas the (Z)-enamine is much less reactive towards addition of thiolate or amine nucleophiles. Gibbs free energy values (G^o) of reactants, intermediates, products and transition states were obtained after a final geometry optimisation at DFT level (ωB97X-D/6-31G*)[1] in a C-PCM implicit solvent model[2,3], followed by calculation of the IR spectra and thermodynamic quantities as implemented in the Spartan software (wavefun.com).

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Molecular Modelling Studies as a Complementary Approach to Experiments to Elucidate the Interfacial Bio-Nano Interactions of Biomaterials

IC053

Dr Nevena Todorova[1], Prof. Irene Yarovsky[1], Prof. Molly M. Stevens[2]

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Nanoparticles exhibit a unique set of size-dependent physicochemical properties that can be easily tailored through functionalisation with biologically relevant chemistries. This has inspired the development of many innovative biomedical applications including colorimetric biosensors and drug-delivery agents. In order to rationally design and optimise these nanoparticles for incorporation and efficiency within biomedical devices and *in vivo*, there is a need to thoroughly understand the fundamental interactions at the bio-nano interface, and how these properties adjust in biological media. Computer simulations present a virtual microscope to assist in gaining such understanding through molecular insights into the structure and dynamics of these bioconjugated nanoparticle systems.[1]

Here, we present recent studies where we have employed classical molecular dynamics to provide theoretical insights into the functional interface of bio-conjugated nanoparticle systems used in drug-delivery,[2] biosensing,[3] and teranostic[4] applications. These works demonstrate that simulations offer a powerful complementary approach to experiments to assists in the design of novel biomedical agents.

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Development of the Large-Scale GW+Bethe-Salpeter Equation Method Based on Fragment Molecular Orbital Method for Applications to Organic Materials

IC054

Dr Takatoshi Fujita

Institute for Molecular Science, Okazaki, Japan

Organic electronics based on π-conjugated molecules or polymers have attracted considerable attention due to their attractive features. Predicting the charged-transport levels or optical excitations is essential for understanding the electronic processes governing the device operation and for rationally designing novel materials. The successful theoretical descriptions of charged and neutral excited states require an accurate quantum mechanical method: in addition, the effects of polarizable environment must be properly taken into account. Here, we present a large-scale GW implementation based on the fragment molecular orbital method. The implementation is based on the fragmentation approximation of the polarization function and the combined GW and Coulomb-hole plus screened exchange approximations for self-energies. Our fragment-based method can describe the state-specific polarization effect and the delocalization of charge and excited states on the same footing. The fragment-based GW is demonstrated by applications to an organic semiconductor thin film and a donor/acceptor interface structure. We highlight the impact of the induced polarization effects on the charged and neutral excitations in the organic semiconductors.

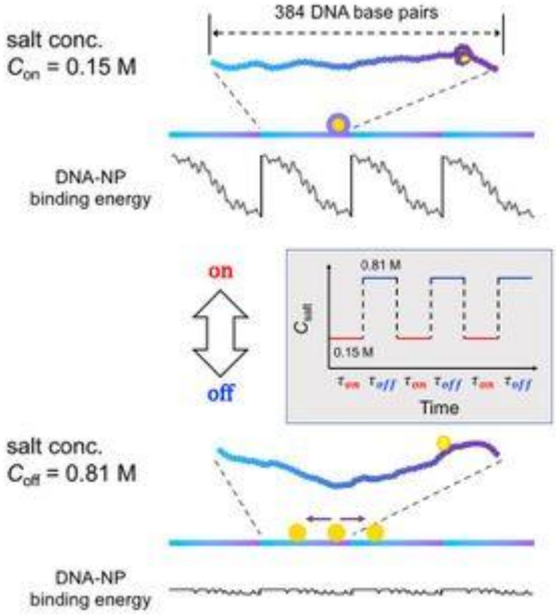
DNA-Based Brownian Motor for Directional Nanoparticle Delivery – Computational Design

IC055

Prof Jun Soo Kim

Ewha Womans University, Seoul, Korea, Republic of

Recently, we proposed a DNA-based Brownian motor for directional transport of positively charged nanoparticles along a single, long double-stranded DNA (dsDNA) with elaborately designed flexibility variation [1]. A periodic and asymmetry potential for nanoparticle binding is constructed along a single dsDNA by a novel strategy that utilizes variation in sequence-dependent DNA flexibility. Directional and processive motion of nanoparticles is achieved by changing salt concentration repetitively over several cycles to switch the asymmetric potential on and off. Results from Brownian dynamics simulations with coarse-grained models will be presented. Results suggest that dsDNA molecules with elaborately designed flexibility variation can be used as a molecule-scale guide for spatial and dynamic control of nanoparticles.



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Search for Conformers Using the Number of Molecular Independent Variables Reduction Method by Specifying Discrete Atoms

IC056

Prof. Hideo Yamakado[1,2], Mr. Yoshitomo Kodaya[2], Mr. Yuuki Midoro[2], Mr. Takuto Oki[2], Dr. Hiroaki Tokoyama[3]

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The authors have been trying to explore crystal structures using the SHS method, which was developed by K. Ohno and S. Maeda and using the GSHS method, which was developed by K. Ohno, Y. Osada and S. Maeda. In this presentation, we propose a new method to search equilibrium structures of molecules: The number of Molecular Independent Variables Reduction Method by Specifying Discrete Atoms. For example, for $C_9H_{17}O_4N_3$ (a kind of dehydrated condensates of alanine) as shown below, six atoms of the 33 atoms in total were designated as the atoms to be searched upward in energy using *μ-ADDF* method, which was developed by S. Maeda, K. Ohno and K. Morokuma. In this case, for now, we have obtained seven equilibrium structures (EQs) and four transition structures (TSs) using the Research Center for Computational Science, Okazaki, Japan.

Structural and Thermochemical Investigation of New Compounds for Hydrogen Storage

IC057

Associate Professor Sarah L Masters[1], Mr Aliyu M Ja'o[1], Dr Derek A Wann[2], Mr Conor Rankine[2]

[1]University of Canterbury, Christchurch, New Zealand. [2]University of York, York, United Kingdom

Climate change is causing immediate changes to the planet, largely due to greenhouse gases produced by fossil fuel use in transportation, thus establishing a demand for clean energy. Hydrogen offers a suitable fuel alternative, however, current physical storage options are inefficient. Chemical storage, particularly amine boranes, provide a hydrogen source, but challenges remain in the search for ideal compounds with high hydrogen capacity and good generation/regeneration cycles.

We have been investigating potential hydrogen storage materials, studying the physicochemical properties of small, hydrogen-dense molecules for their ability to release hydrogen using gas-phase experimental and computational methods. We have been looking in particular at the importance of the formation of dihydrogen bonds in the gaseous hydrogen release process for hydrogen storage materials.

This presentation will focus on piperazine-diborane, which has the potential to release two equivalents of H_2 during the dehydrogenation process. We will present experimental data supported by high-level theoretical calculations, whilst computed thermochemical parameters and the potential energy profiles for hydrogen release pathways will also be highlighted.

When are *cis* Isomers more Stable than *trans* Isomers? A Combinatorial *in Silico* Investigation on Cyclopropane and A_1=A_2 where A_1, A_2 are C, N, P

IC058

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Geometrical isomerism exists when there are two possibilities to arrange functional groups on the same side or the opposite side in a chemical compound with a double bond or a ring. The relative stability of 30 halodiazenes (αN=Nβ), 30 halodiphosphenes (αP=Pβ), 175 haloethenes (αβC=Cγδ), 125 haloimines (αβC=Nγ), 50 haloiminophosphines (αN=Pβ), 125 halomethylphosphines (αβC=Pγ), and 325 halocyclopropanes (1,1-α,β-2,2-γ,δ-cyclopropane) where α, β, γ, δ are H, F, Cl, Br and I were investigated using quantum chemical methods. Results were reported in terms of anomalies where *cis* isomers are predicted to be more stable than *trans* and trends in certain geometrical features of these molecules. Computational results were compared to all available experiment reports.

Topology-Driven Molecular Electronics Lacking π-Conjugation

IC059

Dr Ganna Gryn'ova[1], Prof Dr Clémence Corminboeuf[2]

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Is π-conjugation necessary to achieve efficient transport in molecular electronics? In this work we use Non-Equilibrium Green's Functions technique coupled with Density Functional Theory to demonstrate how molecular topology can be used to boost the tunneling transport in single-molecule junctions featuring saturated hydrocarbon bridges.[1] Specifically, caged saturated hydrocarbons offering multiple s-conductance channels afford transmission far beyond what could be expected based upon conventional superposition laws, particularly if these pathways are composed entirely from quaternary carbon atoms. Computed conductance of molecular bridges based on carbon nanothreads, *e.g.*, polytwistane, is not only of appreciable magnitude; it also shows a very slow decay with increasing nanogap, similarly to π-conjugated wires.

Conventional approaches to highly conductive single-molecule junctions involve π-conjugated systems with appropriately tuned energy levels of the frontier molecular orbitals. Our findings put forward an alternative strategy for modulating the transport in unimolecular electronics that is based on molecular topology and succeeds even in systems completely lacking π-conjugation, e.g., carbon nanothreads, diamondoids and graphane derivatives.

Learning the Art of Chemical Synthesis with Deep Neural Networks and Discipline Scale Data

IC060

Professor Mark P Waller

University of Wollongong, North Wollongong, Australia. Pending.AI, North Wollongong, Australia

Since E. J. Corey first proposed to use a computer to assist in traversing deep synthetic trees in the 1960s, chemists have tried to algorithmically discover the rules of chemistry. We recently demonstrated how well modern methods could perform when planning complex retrosynthetic routes.1 This accomplishment was built on top of two key technologies: firstly, we showed that single step reactions could be quickly predicted using a neural network.2,3 Secondly, the other key component was an algorithm known as Monte Carlo Tree Search (MCTS). We validated our approach on 497 randomly selected targets, and performed double blind AB testing.

We have also developed a novel method for reaction prediction and retrosynthesis based on link prediction.4 This means we are not limited to rules based approaches, so we can effectively discover brand new reactions that have no precedence in the literature.5

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In Silico Design of Sorbents for Selective Capture of CO_2 from Industrial Flue Gases

IC061

Dr. Soujanya Yarasi, Mrs. Akshintala Parameswari

CSIR-IICT, Hyderabad, India

There is growing concern worldwide to cut down CO_2 emissions in an attempt to reduce the rate of global warming.[1] CO_2 capture by means solid adsorption process is receiving increasing attention due to its advantages over conventional technologies based on aqueous amine solvents.[2] The major challenges to achieve superior sorbents are, 1)High CO_2 adsorption capacity, 2)Fast adsorption kinetics, 3)High CO_2 selectivity 4)Mild conditions for regeneration 5)High stability 6)Tolerance to impurities and the cost. Computational screening has been an effective and pragmatic tool in designing a large number of materials and understanding the fundamental structure−function relationship in selection of adsorbents for CO_2 capture, thereby shortening the time from discovery to practical use. A number of computational methods and tools at different spatio-temporal scales are now well established, ranging from electronic structure calculations based on density functional theory, atomic molecular dynamics and Monte Carlo techniques to continuum macroscopic approaches. These techniques are widely adopted in interpreting experimental data and in designing new materials. I shall present in this talk various examples from a wide variety of materials tested and computational methodologies that we adopted in our group in understanding and fine-tuning the binding affinities of potential solid sorbents with the CO_2 molecules.[3-6]

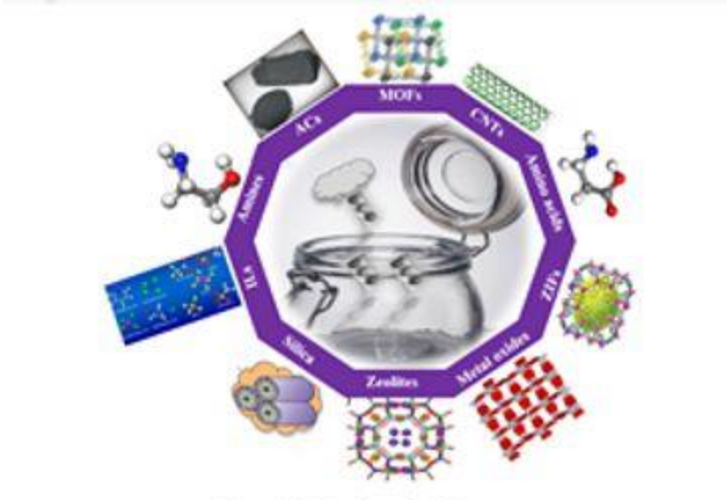

Figure 1. Solid sorbents for CO_2 capture.

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In Situ 2:1 “Sandwich-Type” Complex Formation and Interwire Crosstalk in Single-Molecule Junctions

IC062

Dr Jingxian Yu[1], Ms Feng Yan[2], Ms Fang Chen[3], Ms Xiao-Hui Wu[2], Ms Jing Luo[2], Mr Lin-Qi Pei[2], Ms Shu-Li Qian[2], Prof Andrew D Abell[1], Prof Xiaoshun Zhou[3], Prof Shan Jin[2]

[1]The University of Adelaide, Adelaide, Australia. [2]Central China Normal University, Wuhan, China. [3]Zhejiang Normal University, Jinhua, China

Molecular junction devices offer unparalleled opportunities to address intrinsic intermolecular interactions through probing the changes in electric conductance of single-molecule junctions. Here, we present experimental evidence for the formation of crown ether supramolecular complexes with alkali cations (Li^+, Na^+, K^+ and Rb^+) at the single-molecule level. A rigid and structurally well-defined oligo(phenyleneethynylene) (OPE) molecular wire functionalized with a 15-crown-5 ether moiety (**1**) was synthesized to provide a binding facility for alkali cations. Notably, the formation of a supramolecular 2:1 K^+ sandwich-type complex is observed, which induces a significant increase in the conductance (more than three-fold) compared to **1**. In contrast, the conductance of **1** with either Li^+, Na^+ or Rb^+ follows a linear ascending trend with the increasing effective ionic charge (*ze*/*r*) of these cations, but was found to be considerably lower than that of **1** with K^+. Quantum transport calculations reveal that the ‘4-anchor’ binding mode is the most favored configuration for the 2:1 K^+ sandwich-type junction. The K^+ center popularizes the overlap of electron wave functions between the two molecular wires, and enhances the electron transport. The 1:1 complexation of **1** with either Li^+, Na^+ or Rb^+ promotes a delocalized distribution of HOMOs, which brings the frontier orbitals closer to the Fermi level. These findings not only advance our fundamental knowledge of supramolecular complex formation and charge transport mechanisms, but also provide a basis for the design of new functional devices.

Base-flipping Dynamics from an Intrahelical to an Extrahelical State Exerted by Thymine DNA Glycosylase during DNA Repair Process

IC063

Dr Lintai Da

Shanghai Center for Systems Biomedicine, Shanghai JiaoTong University, Shanghai, China

Thymine DNA glycosylase (TDG) is a DNA repair enzyme that excises a variety of mismatched or damaged nucleotides (nt), e.g., dU, dT, 5fC, and 5caC. TDG is shown to play essential roles in maintaining genome integrity and correctly programming epigenetic modifications through DNA demethylation. After locating the lesion sites, TDG employs a base-flipping strategy to recognize the damaged nucleobases, thereby the interrogated nt is extruded from the DNA helical stack and binds into the TDG active site. The dynamic mechanism of the base-flipping process at an atomistic level, however, remains elusive and challenging to be probed by current experimental techniques. Here, we employed the Markov State Model (MSM) constructed from extensive all-atom molecular dynamics (MD) simulations to reveal the base-flipping mechanism in the presence of TDG at tens of microsecond timescales. We capture several critical intermediate states of the mispaired dT nt during its extrusion process and identify several key TDG residues that are directly involved in the inter-state transitions. Moreover, our studies reveal the atomistic-level details of how TDG participates in sculpturing the DNA backbone and penetrates into the DNA minor groove. Notably, our comparative simulations of the naked and TDG-bound DNA systems indicate that the key intercalated residue Arg275 is critical to stabilize the partially flipped nt by forming a cation-π interaction, most likely via an active recognition scenario. The subsequent base eversion process is shown to be actively promoted by TDG. Finally, we extended our studies to three additional TDG substrates (dU, 5fC, and 5caC) to evaluate the substituent effects of various chemical modifications of the pyrimidine rings on the base-flipping dynamics.

Unveiling the Catch-bond Mechanism Used by FimH to Tackle Antibiotic Resistance in Uropathogenic *E.coli*

IC064

Dr Katie A Wilson, A/Prof Megan L O'Mara

Australian National Univeristy, Canberra, Australia

Urinary tract infections (UTI) are one of the most common bacterial infections with ~150 million cases/year worldwide. Indeed, ~50% of women and 5% of men will develop a UTI during their lifetime and these infections are commonly reoccurring. Uropathogenic *E.coli* (UPEC) causes ~80% of UTI infections. Multi-drug resistance in UPEC is on the rise indicating the need for new treatments. A promising drug target is FimH, which allows UPEC to adhere to the host cell. FimH uses a catch-bond mechanism, which means it undergoes a conformational change upon exposure to mechanical stress (such as flowing fluids) that leads to tighter adherence to the host cell (though binding to a mannose located on the host cell surface). This prevents the bacteria from being flushed from the body. Nevertheless, the structural basis of the FimH catch-bond mechanism is currently unknown and therefore designing antibiotics that target the conformational change that occurs under mechanical stress is difficult. To further complicate matters, FimH has been observed to exist in at least 15 different functional alleles that differ in the amino acid sequence at positions throughout the protein and the atomic level effects of these mutations has not yet been determined. My research uses unrestrained molecular dynamics simulations and adaptive biased steered molecular dynamics simulations to elucidate the structural basis of the catch-bond mechanism employed by FimH (Figure 1) and determines the structural effects of mutations present in the functional alleles of FimH.

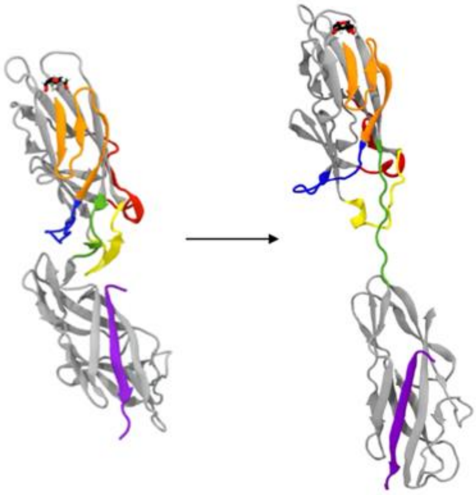

Figure 1. Conformational change modeled for FimH catch-bond mechanism

Machine-Learned Electron Correlation Model for Accurate Reproduction of Correlation Energy at the Basis-Set Limit

IC065

Dr. Yasuhiro Ikabata[1], Mr. Takuro Nudejima[1], Dr. Junji Seino[1,2], Dr. Takeshi Yoshikawa[1], Prof. Hiromi Nakai[1,3]

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An accurate calculation of the electron correlation energy is essential for quantitative evaluation of chemical properties. Recently, machine learning is noticed as a mean of developing a new method to obtain energies such as the exchange-correlation energy in density functional theory and the correlation energy in wavefunction theory. Here, we propose a machine-learned correlation model built using a regression between density variables and the correlation energy density. The correlation energy density of coupled cluster singles, doubles, and perturbed triples (CCSD (T)) was derived based on grid-based energy density analysis [Imamura and Nakai, J. Comput. Chem. 29, 1555 (2008)]. The composite method for the CCSD(T) correlation energy at the complete basis set (CBS) limit [Seino and Nakai, J. Comput. Chem. 37, 2304 (2016)] was extended to the correlation energy density. Numerical assessments revealed that the correlation energy density at the CCSD(T)/CBS level is suitable for the response variable of machine learning. In addition to the density variables commonly used in the exchange-correlation functional, the Hartree−Fock exchange energy density and electron density based on the fractional occupancy of molecular orbitals were used as explanatory variables. The performance of the correlation model was investigated on the basis of machine leaning using about 1% of total grid points in 15 small molecules. The neural network was employed as a method of machine learning. The constructed correlation model reproduced CCSD(T)/CBS reaction energies within a mean absolute deviation of 1 kcal/mol, which is superior to a number of exchange-correlation functionals. The computational time to calculate the total energy was significantly reduced from that of the CCSD(T)/CBS level of calculation based on the extrapolation or composite approach.

A Reduced-Scaling Multireference Perturbation Theory using DMRG Reference Function

IC066

Dr. Masaaki Saitow, Dr. Takeshi Yanai

Nagoya University, Nagoya, Japan

The 2nd-order multireference perturbation theory (CASPT2) originally pioneered by Roos et al. [1] has been known to deliver an accurate description on the complex electronic structures by achieving well-balanced treatment of both static and dynamic correlations. Despite its widespread use in the computational model chemistry, due to its high computational costs in the full configuration interaction treatment in the active space (CAS-CI) for generating the reduced-density matrices, applicability of CASPT2 method has been limited only up to active space composed of 16 electrons in 16 orbitals (CAS(16e,16o)). Later, to overcome this limitation in the size of the active space, in 2011, Kurashige and Yanai developed a CASPT2 approach using *ab initio* density-matrix renormalization algorithm (DMRG-CASPT2) [2]. The DMRG-CASPT2 can treat larger active space with more than 30 active orbitals and has been applied to various challenging multireference problems. However, still, applicability of the DMRG-CASPT2 method has been limited to molecules with approximately 1,000 atomic orbital functions.

In this talk, we show our recent progress on development of a reduced-scaling version of the DMRG-CASPT2 method in the so-called pair-natural orbital (PNO) framework [3]. The PNOs are a set of pair-specific virtual natural orbitals and have been successfully used to reduce the computational costs of various wave function theories such as Coupled-Cluster [4], N-electron Valence-state Perturbation Theory (NEVPT2) [5] and CASPT2 [6]. Derivation of our PNO-DMRG-CASPT2 equations and development of the computational code were carried out using our code generator framework [7].

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Systematic Exploration of Conical Intersection Geometries Between the Ground and First Excited Electronic States Based on Time Dependent Density Functional Theory: Application to reactions

IC067

Dr. Yu Harabuchi[1,2,3], Prof. Satoshi Maeda[1,3,4]

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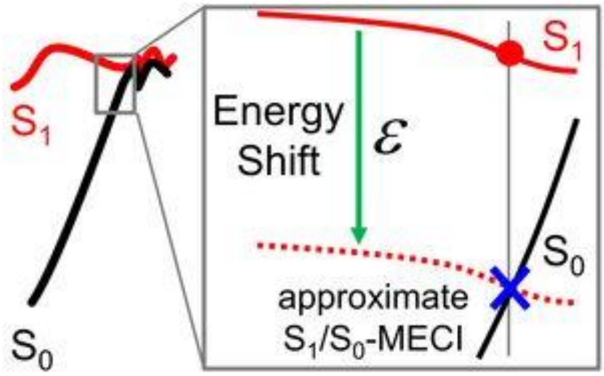
Importance of conical intersections (CIs) in photoreactions is widely known, and a minimum energy CI (MECI) which is the energetically most preferred point in the intersection seam is optimized as the representative geometry of a CI region. Recently, several methods to search for MECI geometries were proposed, and molecular fluorescence has been discussed by exploring S_1/S_0-MECIs and non-radiative decay paths to reach them. Time dependent density functional theory (TDDFT) is a method that describes excited electronic states with reasonable accuracy and cost. However, the potential energy surface (PES) around an S_0/S_1-CI is discontinuous because the reference state, which is normally the ground state, becomes the excited state. Thus, TDDFT is not used to optimize S_1/S_0-MECIs.

In this study, a method is proposed to optimize approximate S_0/S_1-MECI geometries at TDDFT levels using the energy shift (ES) method [1]. The ES method was developed to calculate $4f^N$ excited states of lanthanide compounds [1]; it was employed to avoid discontinuities on TDDFT-PES in this study. Approximate S_0/S_1-MECIs of benzene and naphthalene at the ES/TDDFT level were optimized using the gradient projection (GP) method [2]. The obtained approximate S_0/S_1-MECI geometries and energies well reproduced the true S_0/S_1-MECI geometries and energies at the TDDFT level. Also, the approximate S_0/S_1-MECI geometries were explored using one of automated MECI search methods, the GP/SC-AFIR method [3], at the ES/TDDFT level. All the S_0/S_1-MECI geometries of benzene and naphthalene were found in the automated search [4].



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Decoding Electron Structure of Nicotine, Nicotinamide and Nicotinic Acid from XPS and NMR: Theory and Experiment

IC068

Mr Frederick Backler[1], Dr Hanna Saadeh[2,3], Dr Alessandra Ciavardini[4], Dr Susanna Picciril[5], Dr Marcello Coreno[3], Dr Robert Richter[3], Dr Kevin Prince[3], Professor Feng Wang[1]

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We report results on three biologically and pharmacologically important derivatives of pyridine: nicotine, nicotinic acid and nicotinamide.

XPS probes the chemical state of the molecule because the binding energy shifts depend on the chemical environment of the atom that is ionized, while NMR provides complementary information about the site specific chemical environment [6]. The ionization potentials and outermost valence ionic states of nicotinic acid and nicotinamide [1, 2] as well as calculations of the valence bands [2, 3] have been reported. No gas phase core level spectra are available so far and we study their electron structure using combined XPS(PES) and NMR measurements with computational spectroscopy of their low-lying conformers and trans-/cis-isomers.

We have measured valence band photoelectron spectra, as well as core level C1s, N1s and O1s XPS, which validate our quantum chemical methods and further OVGF calculations for the valence bands [4]. Measurements were performed at the GasPhase Photoemission Beamline of Elettra-Sincrotrone Trieste, Italy.

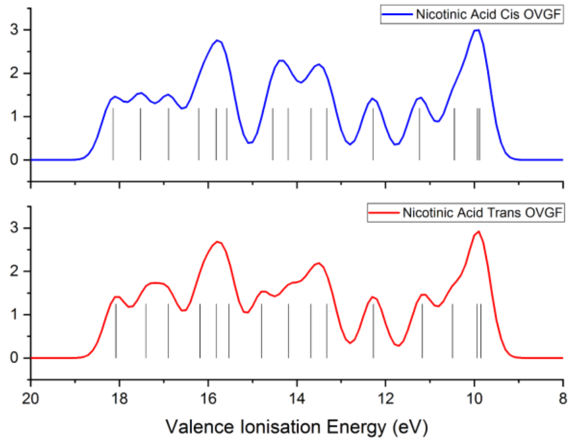

Figure 1 Simulated valence PES of trans- and cis-nicotinic acid [5].

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Giant Caloric Effects in Fast-Ion Conductors: A Promising Route Towards Ambient Solid-State Cooling

IC069

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Solid-state cooling is a sustainable and energy efficient refrigerant technology that exploits field-induced reversible phase transformations in materials. Solid-state cooling is a promising alternative to traditional refrigeration technologies based on compression cycles of greenhouse gases, which in addition to their obvious environmental threats cannot be scaled to small sizes (e.g., microchip dimensions). Nevertheless, most caloric materials known to date (ferroelastic, ferroelectric, and magnetic compounds) display only modest refrigeration performances and/or operate at temperatures far from ambient conditions.

Recently, we have predicted by means of classical and quantum simulation methods that giant caloric effects occur in fast-ion conductors [1-3], a class of materials with high ionic conductivity below their fusion points that commonly are exploited in electro-chemical devices. The giant caloric effects disclosed in fast-ion conductors can be understood in terms of field-driven changes on their ionic conductivity, which are highly reversible and responsive to external fields. A giant cooling effect of ~20 K has been just measured directly in the archetypal superionic compound AgI [4]. We argue that solid-state cooling can benefit immensely from the intensive research already undertaken for solid-sate batteries and oxide fuel cells.

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On the Negative Thermal Expansion of the EDI Zeolitic Ice

IC070

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Regardless of its simple molecular structure, pure water is known to exhibit many anomalous properties. Amongst those properties are the rich crystalline phases and the unusual thermal expansivity as observed both in its liquid and solid phase. The recent discovery of ice XVI, whose network structure is the same as MTN zeolitic framework, and ice XVII are of particular interest because of their low density and stability under negative pressure. Prior to experimental evidence, the stability of those porous ice structures has been predicted theoretically and their properties were surveyed by computer simulations. Here we predict the presence of negative thermal expansion (NTE) characteristic in low density ice having EDI zeolitic-framework using only the evaluation of intermolecular interaction potentials. The thermodynamic stability is quantified in term of free energy that is expressed as the sum of intermolecular potential energy of the quenched-structure at 0 K, the harmonic free energy, and the residual entropy arising from the disordered nature of protons in the studied ice structures. We show that the negative thermal expansion at low temperature arises from the unusual negative Grüneisen parameter and the large heat capacity from the low frequency modes.

Multiscale Method to Calculate the Entropy of Protein Assemblies

IC071

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Entropy and energy combine to give the free energy and thereby govern molecular stability. While much progress has been made in calculating energy by electronic-structure methods and force fields, the ability to calculate entropy still lags far behind. This limitation is a problem for many chemical systems, but is particularly acute for biomolecular assemblies which are typically large and complex. Building on previous work for liquids,[1,2,3] solutions,[4] and isolated flexible molecules,[5] we present new theory to calculate the entropy from a trajectory generated in a molecular dynamics simulation for a series of protein dimers. Entropy is calculated at a hierarchy of structural levels, namely united atoms, residues, proteins, and assembly. The vibrational entropy is derived from covariance matrices of force and torque at each level while the topographical entropy is computed from the distributions of conformers. The method with its multiscale nature provides an insightful decomposition of entropy over all degrees of freedom and is readily scalable to large systems, making it widely applicable to many kinds of molecular systems encountered in chemistry and biology.

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Markov State Models for Understanding Ligand Binding to G Protein-coupled Receptors

IC072

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Monash Institute of Pharmaceutical Sciences, Parkville, Australia

Molecular dynamics (MD) simulation is a powerful tool for studying processes at the molecular level. However, the timescale of the events that can be modelled is conventionally limited by the lengths of the MD simulations being performed. Studying longer timescale processes, such as the binding of a ligand to a receptor is difficult. One efficient approach to studying slow events is the use of Markov state models (MSMs) or hidden Markov models (HMMs) to create statistical models of the overarching long-timescale processes. We have been using MSMs to study the binding of small molecule ligands to G protein-coupled receptors, including the dopamine d3 receptor and the a1A adrenergic receptors. To date, we have developed a model for the binding of the antipsychotic drug haloperidol to the dopamine d3 receptor and models of the conformational changes induced by the binding of adrenaline to the a1A adrenergic receptor. These models provide new insight into the mechanism of action of these important drug targets and can potentially assist the development of new ligands for these receptors.

A Molecular Simulation Study of Carbon Dioxide Adsorption in Two Interpenetrated Metal-Organic Frameworks: LMOF-201 and 202

P001

Mr. Ankit Agrawal[1], Mr. Mayank Agrawal[2], Dr. Donguk Suh[1], Professor Yunsheng Ma[3], Professor Ryotaro Matsuda[3], Dr. Wei-Lun Hsu[1], Professor Hirofumi Daiguji[1]

[1]University of Tokyo, Tokyo, Japan. [2]Georgia Institute of Technology, Atlanta, USA. [3]Nagoya University, Nagoya, Japan

Anthropogenic carbon dioxide (CO_2) emissions are a major contributor to rising global temperatures. The adsorption of CO_2 inside Metal-organic frameworks (MOFs), a type of porous material, is a promising way to reduce atmospheric CO_2 levels. Here, we study two MOFs; LMOF-201 and LMOF-202. Previous studies on both Zn-LMOF-202 and Zn-LMOF-201 reveal that both are isostructural, but Zn-LMOF-202 is rigid, whereas Zn-LMOF-201 is flexible. The change in MOFs' properties by manipulation of their metal cations, organic linkers, and functional groups maintaining the structure topology, makes them highly suitable for CO_2 adsorption. In this work, we propose a novel methodology to enhance the adsorption of CO_2 in MOFs by post-synthetic metal exchange employing Grand Canonical Monte Carlo (GCMC) simulations. Using this computational method, we show that the CO_2 adsorption capacity and selectivity can be magnified by a factor of about 1.5 by changing the metal ion from Zn to In in M-LMOF-202 at 1 bar and 298K. Furthermore, in past, it was found that slight modifications in the ligand part of the LMOF-202 framework by incorporating one oxygen atom into the structure, resulted in flexible LMOF-201. Due to this flexibility, the CO_2 adsorption amount doubled at saturation compared to that of LMOF-202 at 195K. We introduce an approach combining Reactive force field (ReaxFF) and Molecular Dynamics (MD) simulations to capture the structural flexibility of LMOF-201 in presence of CO_2 adsorption. We reproduce the experimental adsorption isotherms of CO_2 in LMOF-201 and observe the existence of two different structures at low and high CO_2 loading respectively. The results of this work show that both LMOF-201 and LMOF-202 have the requisite properties to merit further consideration as a carbon capture adsorbent

Investigating Luminescent Metal Complexes using Computational Methods

P002

Mr. Johnny Agugiaro, Assoc. Prof. David J. D. Wilson

La Trobe University, Melbourne, Australia

Phosphorescent metal complexes continue to play a large role in the design and development of luminescent materials, with a wide range of applications including sensing and display technologies. This is in part due to their long-lived luminescent lifetimes, as well as their ability to harvest both singlet and triplet excitations, leading to theoretical quantum efficiencies of 100%. These factors continue to drive research into improving their photophysical properties.

We have used DFT methods to explore and benchmark a plethora of luminescent iridium and ruthenium metal complexes, utilizing a variety of alterations in order to modify and enhance their photophysical properties. The character of the frontier orbitals of the complexes, as well as the transitions from TDDFT and socTDDFT calculations have been benchmarked against model complexes, $Ir(ppy)_3$ and $Ru(bpy)_3$, in order to determine general rules for modifying and improving the photophysical properties of luminescent metal complexes.

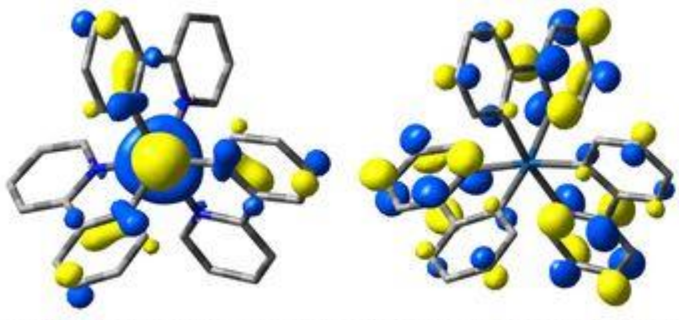


Figure 1: Density plots for the HOMO (left) and LUMO (right) of $Ir(ppy)_3$.

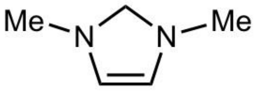
Theoretical Investigation of Ring-Expansion of N-Heterocyclic Carbenes (NHCs) Containing C, P, O, S Heteroatoms

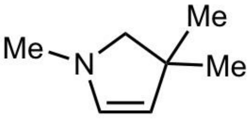
P003

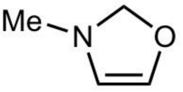
Mrs Khalidah Hamel Mnati Al-Furaiji, Mr David J. D. Wilson

La Trobe Institute for Molecular Science, Melbourne, Australia

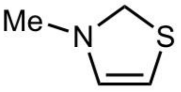
Recently, several groups have investigated ring expansion reactions (RER) of *N*-heterocyclic carbenes (NHCs) with element hydrides, both experimentally[1-2]and theoretically.[3-4]Ring expansion involves insertion of the element into the C–N bond of the NHC with formation of an expanded six-membered ring. By investigating the energetics of reaction pathways,[5]we have explored whether RER can be expected for a variety of heteronuclear NHCs (shown below) that are produced by substitution of one nitrogen atom by carbon (CN, cAAC), phosphorus (PN), oxygen (ON) or sulphur (SN). The insertion pathway involved reaction with silane (SiH_4), which readily participates in RER with NHC (NN). We also explored the preference for silane insertion into the nitrogen-carbon bond (N–C) or element-carbon bond (E−C).


NN


CN


ON


PN


SN

The final products from all of the modelled species are thermodynamically favourable, however, barriers (kinetics) determine the possibility of RER being observed. Our calculations indicate that CN and PN analogues allow facile hydride transfer from the silicon hydride to the carbene carbon, but that subsequent RER is kinetically unfavorable due to large barriers. For both ON and SN, ring expansion is predicted to be experimentally feasible.

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Roby-Gould Bond Indices as a Tool in Chemistry

P004

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There is an absence of a simple procedure that can produce, from a wavefunction, bond indices between well-defined ``atomic'' entities. Here we further develop and evaluate the Roby-Gould bond index method (RGBI) [Gould et al., Theor. Chem. Acc., 2008, 119, 275] which is based on atomic projection operators representing atoms.

We report for the first time bond indices obtained using the occupied pre-natural atomic orbitals (NAOs) of natural bond orbital (NBO) theory, and compare these to those previously obtained using the occupied atomic natural orbitals (ANOs) for a dataset of about 400 molecules comprising first-row atoms, and which include a variety of chemical bonds. While the separate covalent and ionic indices from each method are widely different, remarkably, the total bond indices are essentially the same except for molecules which are usually usually termed ``hypervalent''.

We also describe and exhibit a new bond dial diagram to visually display the information from the RGBI method. The dial diagram easily shows when ``back bonding'' occurs.

Toroidal States in an Isosceles Spin Triangle Without Spin-Orbit Coupling: Applications in a Molecular Spintronics Device

P006

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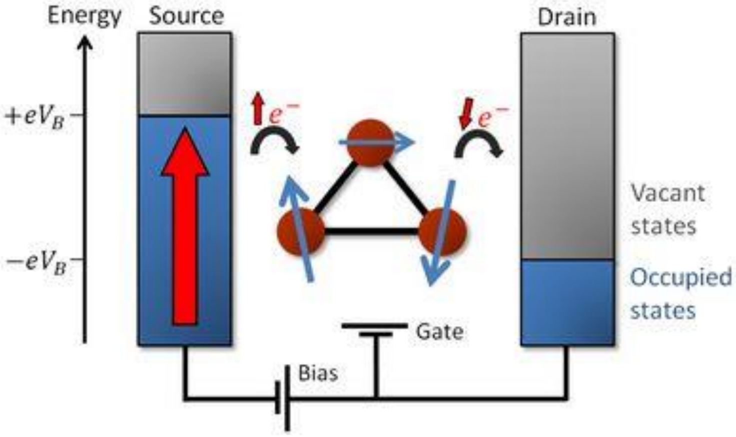
In molecular spintronics devices based on dipolar nanomagnets, unwanted environmental perturbations easily alter the spin state, corrupting the quantum information. Alternatively, toroidal moments, $\boldsymbol{\tau} = g\,\mu_B \sum_q \mathbf{r}_q \times \mathbf{S}_q$, only interact with the curls of external magnetic fields [1], so toroidal states ought to be less affected than dipolar states by homogeneous magnetic fields or nearby nanomagnets, thus allowing for closer packing in technological devices [2]. Building on previous work [3,4], we discuss how the populations of clockwise and anticlockwise toroidal states would be split if a spin current passed through a spin-frustrated triangular nanomagnet, and discuss why this effect could be monitored by measuring the accompanying change in the spin current's polarisation [5]. This phenomenon has been previously predicted in strong [3] and weak [4] spin-orbit coupling regimes, and now in the zero spin-orbit coupling regime [5]. Aside from molecular spintronics, our work is also of fundamental importance to the field of molecular magnetism, as we show that spin-frustration alone can lead to a ground manifold with four distinct, degenerate toroidal states.

Figure: Spintronics device based on a triangular nanomagnet with isosceles spin-coupling. Electrons sequentially tunnel from the up-polarised source lead, to the triangle, then to the unpolarised drain lead. The electrons' spins may be switched by exchange coupling with the triangle's spins, also inducing a net toroidal magnetisation on the triangle.



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Valence and Core Electron Spectroscopy for the Conformational Study of Bio-active Pyridine Derivatives

P007

Mr Fred Backler[1], Dr Hanan Sa'adeh[2,3], Prof. Kevin C Prince[3], Prof. Feng Wang[1]

[1]Swinburne University of Technology, Melbourne, Australia. [2]The University of Jordan, Amman, Jordan. [3]Elettra Sincrotrone, Trieste, Italy

Synopsis: Recent combined theoretical and experimental photoelectron spectroscopic study of biologically significant pyridine derivatives, nicotine, nicotinic acid and nicotinamide, provides insights to intramolecular bonding effects, revealed through rotational conformation. Core Electron Binding Energies (CEBE), Outer Valence Green's Function (OVGF) and Nuclear Magnetic Resonance (NMR) backed by experimental synchrotron based X-ray studies explore details of symmetry and conformation.

The pharmacological activity of many organic molecules can be understood through their conformational properties. In order to better understand the structure-property relationship of bio-active species, it is important to monitor changes to electronic structure through subtle structural differences. We provide highlights from our recently submitted paper [1] which reports on the complete electronic spectra of nicotine, nicotinic acid and nicotinamide. Combining theoretical spectra with highly accurate synchrotron sourced X-ray photoelectron Spectroscopy (XPS), we continue to monitor the impact of flexible bond angles on core level energies, expanding on the insights into rotational conformation as a core event gained from our recent Nuclear Magnetic Resonance (NMR) study [2]. While NMR is sensitive to chemical environment, particularly to changes in Hydrogen bonding due to rotational conformation, XPS results found there to be a negligible impact on the core electron structures. The rotation of functional groups was observed to produce a greater impact on valence electron structures, confirmed by OVGF calculations. By dissecting the sigma versus pi electron character of these species on a theoretical level and compare to real-world measurements we can continue to make advancements towards high throughput drug development. Measurements were obtained at the Gas Phase Photoemission beamline at Elettra-Sincrotrone Trieste, Italy

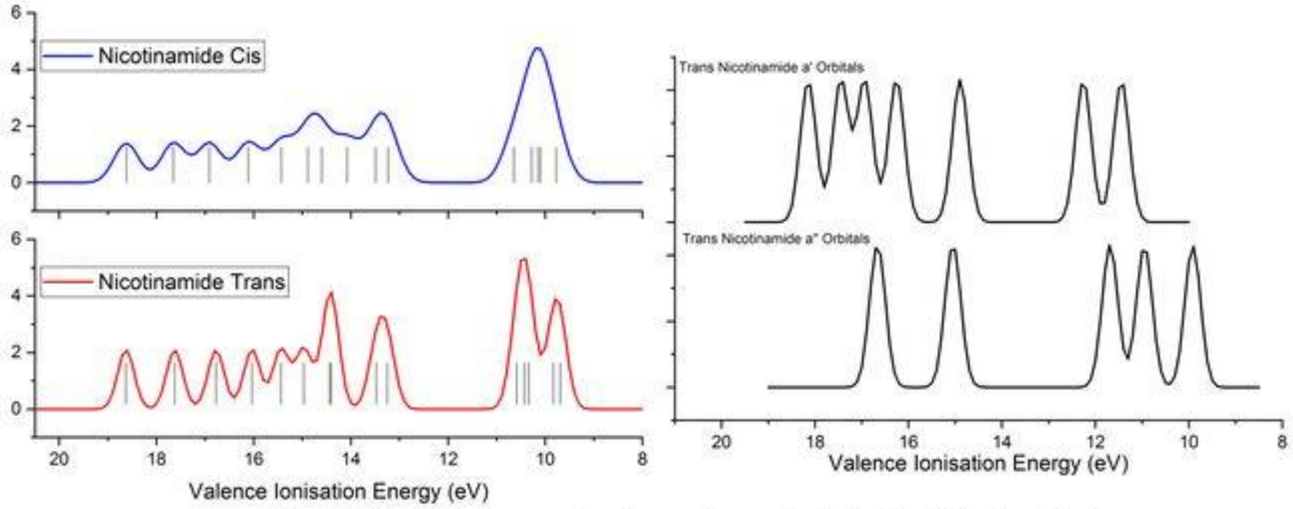

Figure 1: Calculated valence spectra of two conformers of nicotinamide (left) and contributions to valence spectra of trans nicotinamide by a' and a'' orbitals. (right)

[1] Sa'adeh H et al submitted (2019). [2] Backler F et al submitted (2019).

Effect of Ca-Dopant on Lithium Ion Conductivity in $Li_7P_3S_{11}$ and Li_3PS_4 Solid Electrolytes

P008

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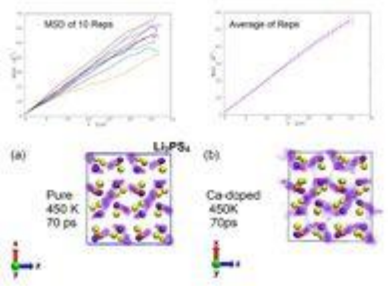


One of the main challenges in the production of all solid state batteries is to fabricate new electrolytes with high ionic conductivities; comparable to traditional liquid electrolytes. $Li_7P_3S_{11}$ and Li_3PS_4 electrolytes are examples of solid electrolytes with high ionic conductivities. It has been experimentally shown that Ca-doping can improve the ionic conductivity of $Li_7P_3S_{11}$. However, studying the mechanism of the diffusivity of the pure and Ca-doped samples at the atomic level is still a challenge due to the relatively low ionic conductivity of solid electrolytes and due to the limitations of numerical methods. To study the conductivity and diffusivity of lithium ions in $Li_7P_3S_{11}$ at the atomic level, we used *ab initio* molecular dynamics (AIMD) simulations at different temperatures.

In contrast to $Li_7P_3S_{11}$ are not studies of the effect of a Ca-dopant on the diffusion mechanism in Li_3PS_4. Using AIMD simulations we studied the ionic conductivity of pure Li_3PS_4 and compared the results with the literature. Also, we studied the effect of the dopant on the conductivity of the material and estimated the ionic conductivity of Ca-doped Li_3PS_4 at room temperature.

Towards an Understanding of Field Effects in the G-Quadruplex/Hemin DNAzyme Peroxidation Catalysis.

P009

Ms Clare Birch, A/Prof Meredith Jordan

The University of Sydney, Sydney, Australia

The promise of DNA-based catalysts is an exciting one: cheap, largely non-toxic, and easily manipulable, they present as strong competitors to traditional catalysts. One such system, the guanine quadruplex/hemin DNAzyme, catalyses the peroxidation of various substrates and has been the subject of extensive optimisation attempts. Between the agnosticism of catalytic enhancement and the numerous competing steric and energetic factors in the G4/hemin DNAzyme, the catalytic behaviour may have any number of causes. Though the role of the quadruplex is uncertain, recent work[1] has proposed a mechanism in which a necessary, but not sufficient, condition for the peroxidation to occur is the presence of a proximal aryl nitrogen in an overhanging substituent at the 5' end of the quadruplex. The site functions analogously to histidine in horseradish peroxidase, facilitating a rate-determining proton transfer step from a "traditional" hydrogen-bonded O-H- - -N to the ion pair O^{-}- - -H-N^{+}. Here we show through DFT studies on a simplified system that directed long-range electrostatics may enhance the rate of this proton transfer process. By applying a series of small electric fields along the proton transfer axis, we see significant variation in the topology of reaction paths. Until now, the quadruplex has been treated entirely as a steric contributor, holding the substrates in appropriate arrangements for the enhanced peroxidation. Our work, by contrast, points to the field generated by the quadruplex—namely the cationic backbone, a proximal localisation of positive charge—as a driving factor in the peroxidation enhancement. This aligns with recent shifts towards an understanding of enzymatic catalysis as the provision of a facilitatory preorganised electrostatic environment. By extending our understanding of the role of the quadruplex in the G4/hemin peroxidase mimic to consider electrostatics, we believe that this work may open a new line of inquiry within quadruplex-based DNAzyme chemistry.

Theoretical Progress Towards pH-Switchable Electrostatic Catalysis

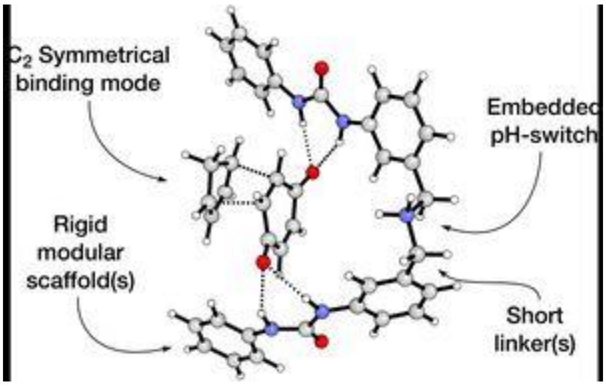
P010

Mr. Mitchell T. Blyth, Prof. Michelle L. Coote

Research School of Chemistry, Australian National University, Canberra, Australia

We have recently demonstrated both theoretically and experimentally that electrostatic fields can catalyse non-redox reactions such as the Diels-Alder [4+2]-cycloaddition. The basis of this observation lies in the ability of electrostatic fields to attenuate or strengthen the dipole moment along a reaction coordinate, and in so doing selectively stabilise charge-separated delocalisation contributors and influence reaction outcomes. However, electrostatic catalysis – the ability of electrostatic fields to catalyse non-redox chemical processes – is still relatively unknown in traditional synthesis due to the strong directional dependence of electric fields and their attenuation in polar solvents.

Using quantum chemistry and kinetic modelling, we have recently developed a proof-of-concept catalyst that is theoretically capable of using pH-dependent electrostatic fields to provide general catalysis to a broad range of Diels-Alder reactions. All reactions showed significant enhancements in catalysis (10–32 kJ mol^{-1} in barrier lowering) when the catalyst was protonated, consistent with electrostatic stabilization of the transition state. The successful catalyst design addresses the problems of field orientation, and catalytic effects remain significant in nonpolar solvents.



Fine Tuning of Ligand Field Splitting in Iron(II) Complexes

P011

Mr Luca Bondì[1,2], Prof Federico Totti[2], Dr Paul Jerabek[3], Dr Anna Garden[1], Prof Sally Brooker[1]

[1]University of Otago, Dunedin, New Zealand. [2]University of Florence, Florence, Italy. [3]Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany

The properties of many materials and enzymes/catalysts are based on those of the central metal ions – and these are in turn related to the coordination environment provided by the ligands. To tune these properties, we therefore need to better understand the parameters which affect the size of the ligand field splitting (Δ_o). Spin crossover (SCO) active complexes are perfect for reporting on the fine-tuning of the metal ion environment.

We recently reported a method to predict the switching temperature $T_{1/2}$ of SCO for two different families of iron(II) complexes in solution using the ^{15}N chemical shift of the coordinating nitrogen (Fig. 1).[1] In order to more clearly understand how the interaction between the metal ion and its coordination sphere occurs, we have since performed a range of theoretical studies on these families of complexes, aiming to predict the effect of ligand substituent modifications on the ligand field experienced. The ultimate aim is to enable prediction of spin state in solution[1-2]/solid state[3] in advance of synthesis. In this presentation our recent theoretical developments and findings will be described.

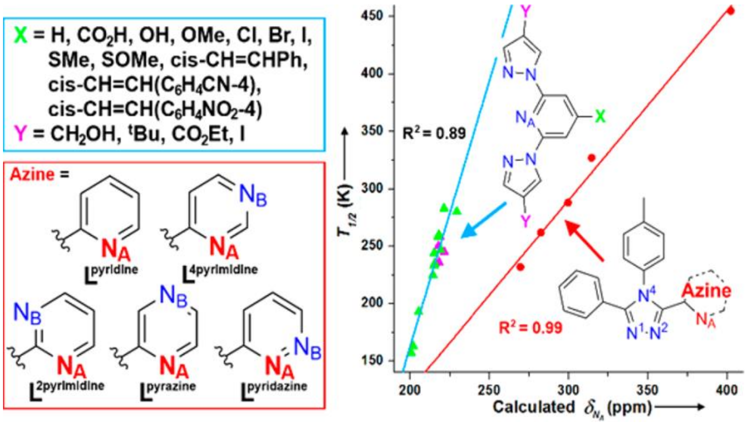


Fig. 1. Correlation of observed $T_{1/2}$ for SCO-active complex with calculated ligand $^{15}N_A$ NMR signal for: (**red**, R^2=0.99) five Fe^{II}(**L**^{azine})$_2$($NCBH_3$)$_2$ complexes in $CDCl_3$; and (**blue**, R^2=0.89) sixteen Fe^{II}(**bpp**^{X,Y})$_2$(Z)$_2$ complexes in $(CD_3)_2CO$ (Z = BF_4 for all but one case where it is PF_6).

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Microscopic Mechanism of SEI Film Formation in Highly Concentrated Electrolytes Based on Nonflammable Trimethyl Phosphate Solvent

P012

Dr Amine Bouibes[1], Dr Norio Takenaka[2], Dr. Soumen Saha[3], Prof. Masataka Nagaoka[1]

[1]Nagoya University, Nagoya, Japan. [2]University of Tokyo, Tokyo, Japan. [3]Kyoto University, Nagoya, Japan

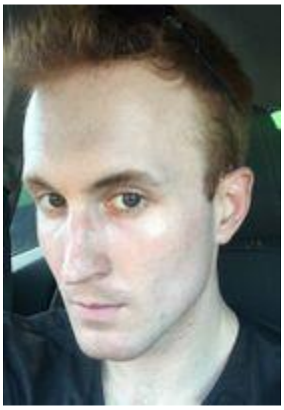
The microscopic understanding of the formation process of the solid electrolyte interphase (SEI) film is an important challenge to design the safe lithium-ion battery (LIB). Attractively, the highly salt-concentrated (HC) electrolyte based on trimethyl-phosphate (TMP) as a unique solvent exhibited a self-extinguishing property in addition to its excellent charge-discharge performance. However, the microscopic mechanism of its SEI layer formation still remains an open question. To investigate such SEI film formation, we used Red Moon (RM) methodology which is the atomistic reaction simulation method recently applied successfully to several secondary battery systems. In the present study, the experimental observations were successfully reproduced where the SEI layers were formed in the “bottom-up” manner resulting in a thinner and denser SEI layer mainly produced through the salt reduction in HC electrolyte. It was revealed that a large amount of salt anions is localized on the SEI surface in HC electrolyte, enhancing the network formation of a dense inorganic layer with SEI salt-derived species. In addition, it was shown that the size of TMP molecule prevents itself from entering in SEI layer, leading to the formation of a pure dense inorganic SEI layer, which should considerably improve the stability of SEI layer and would bring about a long lifetime of advanced safe LIB.

On the Application of the Hubbard-U Correction in Modelling Semiconductors for Solar Water Splitting

P013

Mr Joshua J Brown, A/Prof Alister J Page

The University of Newcastle, Newcastle, Australia



Metal oxide and oxynitride photocatalysts are commonly of a d0 or d10 configuration such as TiO_2, TaON or ZnO and $(GaN)_{1-x}(ZnO)x$ are studied extensively for solar water splitting applications.[1] In simulating these materials there are main steps of the photocatalytic process to consider: (i) light absorption to generate photogenerated charge carriers; (ii) separation and transfer of charge carriers; and (iii) utilization of charge carriers during surface catalytic reactions.[2]

Computational studies on light active devices have provided insight into band engineering with dopants, surface structure, stability, defects recombination and adsorption of catalytic species.[3] However, in order to accurately simulate such photoactive materials, hybrid and/or range-separated exchange correlation functionals (e.g. HSE06) or GW method are typically required to reproduce experimental bandgaps and intrinsic defects levels. Unfortunately, such methods incur a prohibitive computational cost, this cost often puts severe constraints on the system size that can be modelled.[4] As such the Hubbard-U correction is often applied to LDA and GGA functionals (e.g. PBE, PW91, PBEsol etc.) to recover some degree of accuracy with regards to mitigating the self-interaction error and electron localization.[4]

Herein, we detail the influence tuning a multi-site Hubbard-U correction to provide a better bonding centered view of optical properties, reaction energy, defect formation and migration. We highlight the strengths and pitfalls this method applied to screening and providing quantitative insight on d0 and d10 metal semiconductors for solar water splitting

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Effect of Magnetic Anisotropy on Direct Chiral Discrimination in Paramagnetic NMR Spectroscopy

P014

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[1]The University of Melbourne, Melbourne, Australia. [2]Australia's Nuclear Science and Technology Organisation, Sydney, Australia

In the absence of suitable chiral additives, Nuclear Magnetic Resonance (NMR) spectroscopy is blind to chirality due to the space-parity of the shielding and spin-spin coupling tensors. Recently, a theory of chiral discrimination for diamagnetic systems has shown that the space-odd shielding polarizability tensor, a molecular property which accounts for the appearance of a macroscopic electric polarization in the presence of the NMR magnetic field and a rotating nuclear magnetic dipole moment, has opposite sign for two enantiomers. Based on recent work on the theory of paramagnetic NMR, we present and analyze a complete analytic expression for the generalized shielding polarizability tensor, whose isotropic average is proportional to a chiral macroscopic electric polarization measurable in a pulsed NMR experiment probing molecules with an arbitrarily degenerate ground state, providing working expressions for the explicit accurate ab initio calculation of all contributions to the tensor. We recently predicted that this tensor can be measured at room temperature for chiral paramagnetic molecules with a strong magnetic anisotropy (as featured e.g. in lanthanide complexes). We apply our theory by performing ab initio multiconfigurational calculations of all contributions to the tensor for a set of ten trivalent dysprosium complexes which are characterized by a strongly axial ground Kramers doublet and thermally accessible excited Kramers doublets at room temperature. The results show that contributions from thermally populated excited states, while generally reducing the value of the tensor calculated on the assumption of a thermally isolated ground state, do not hinder room temperature detectability of this property for all studied complexes. Trends on the relative sign of dominant contributions are then discussed on the basis of a crystal field model electrostatic potential splitting a ground spin–orbit multiplet, which provides an insight into the properties of the generalized shielding polarizability tensor for open shell species.

The Full Potential Energy Surface for N-H Tautomerisation in Free-Base Porphyrin

P015

Mr Peter J Canfield[1,2,3], Professor Jeffrey R Reimers[4,3], Professor Maxwell J Crossley[1]

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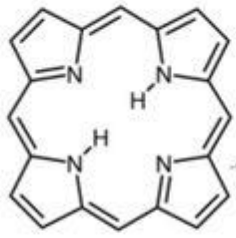
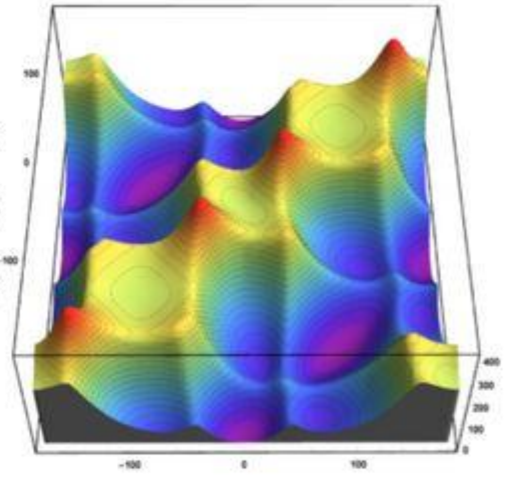
Early theoretical investigations[1] into the tautomerisation of free-base porphyrin were restricted to considering the atomic motions within the plane of the macrocycle. The recent advances in both computing power and the density functional theory treatment of dispersion forces provides the opportunity to revisit this subject in a more comprehensive manner. By devising a sophisticated coordinate system to describe the annular positions of the H-atoms, and explicitly addressing "cross-bonded" structures, we have generated the full potential energy surface for the tautomerisation of free-base porphyrin and identify novel minima and transitions structures of various orders. A new and compact notation derived from consideration of the symmetry perturbation properties of the system is introduced in order to uniquely and systematically describe these stationary points, and doubles as check for the completeness of the set of structures. Of broader relevance, these act as structural prototypes for other porphyrin systems and provide inspiration for synthesis.





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Long-Range Corrected Double Hybrid Density Functionals Optimised for Electronic Excitations

P016

Mr. Marcos Casanova-Páez, Dr. Lars Goerigk

The University of Melbourne, Melbourne, Australia

Double-hybrid density functionals (DHDFs) are nowadays the most accurate and robust functionals in density functional theory (DFT) for ground-state[1,2] and excited-state properties[3,4,5], positioned on the highest rung on the Jacob's Ladder of DFT approximations. DHDFs made a major step forward including not only occupied orbitals, as previous approaches, but also unoccupied ones to better describe non-local electron-correlation effects. Nevertheless, the lack of a long-range correction scheme makes them unreliable when it comes to long-range interactions, a flaw that they share with every non long-range corrected functionals. For this reason, we recently proposed the first two double-hybrid functionals with correct asymptotic long-range behaviour optimised for excited states named ωB2PLYP and ωB2GPPLYP[6]. Herein, we review their excellent performance and show that they are the most accurate and robust density functional theory methods for electronic excitation energies, as they provide a balanced description of local-valence, Rydberg and charge-transfer states. They are also able to tackle the difficult first two transitions in polycyclic aromatic hydrocarbons and show very promising results in a preliminary study on transition metal compounds, which is exemplified for titanium dioxide clusters. We then conclude with an overview of other strategies to further improve time-dependent double hybrids and the insights that we gained from them[7].

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Towards an Accurate Description of Solvent Effects

P017

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Accurate modelling of solute-solvent interactions is crucial for reliable prediction of the outcomes of condensed phase reactions. In this poster, we present a general approach to systematically improve molecular mechanics explicit solvent simulations through an end-point correction scheme for a simple yet fundamental organic reaction.[1] As part of this effort, we have further carried out an extensive assessment of a range of high-level ab initio composite methods and DFT methods, from the lower to upper rungs of Jacob's DFT Ladder, against benchmark DLPNO-CCSD(T)/CBS solute-solvent interaction energies of neutral and charged solutes. This poster will highlight several strategies for the development of a systematically improvable and cost-effective solvent model for condensed phase simulations.

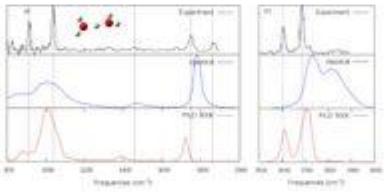
(1) Chen, J.; Shao, Y.; Ho, J. Are Explicit Solvent Models More Accurate than Implicit Solvent Models? A Case Study on the Menschutkin Reaction. *J. Phys. Chem. A* **2019** *123* (26), 5580-5589. DOI: 10.1021/acs.jpca.9b03995

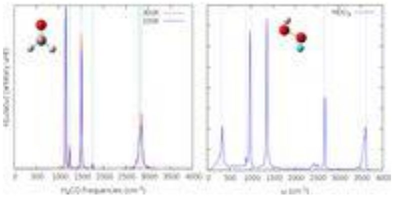
Molecular Vibrational Spectroscopy Study by Path Integral Liouville Dynamics

P018

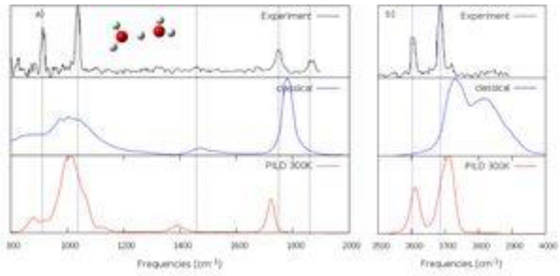
Mr Zifei Chen, Dr Zhijun Zhang, Mr Xinzijian Liu, Mr Kangyu Yan, Mr Haifeng Zheng, Prof Jian Liu

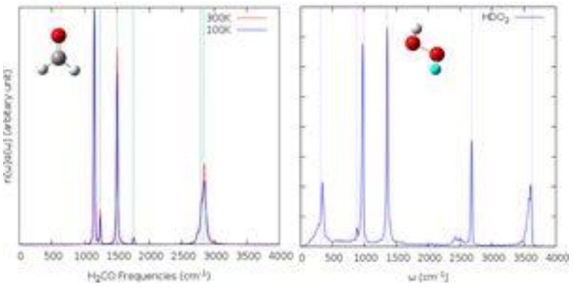
Institute of Theoretical and Computational Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, China





The infrared (IR) spectrum is related to the Fourier transform of the dipole (or dipole-derivative) correlation function, whose quantum version in principle leads to exact vibrational frequencies. Hence, there is then a great deal of effort focus on developing accurate real time quantum dynamics methods. Path integral Liouville dynamics (PILD), a novel imaginary time path integral-based dynamics approach that we have recently developed [2], can reproduce exact results in the harmonic limit for correlation functions (even with nonlinear operators) as well as conserve the equilibrium distribution of quantum canonical ensemble. PILD has been shown to give accurate vibrational spectra for real molecules, e.g. OH, H2O, NH3, and CH4[3]. In this work we study several molecules that are often used as benchmark calculations, including H2O2, CH2O, and H5O2+. By employing the “Middle” scheme [4] that we have developed recently, PILD can use larger time steps without loss of accuracy during the evolution of the real time trajectory. Comparison to exact vibrational frequencies demonstrates that PILD produces a reasonably accurate peak position with a relatively small full width at half maximum.





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Computational Insights into the Role of BINOL-Derived Catalysts in Asymmetric Nazarov Cyclisations

P019

Miss Yuk Ping Chin, Associate Professor Elizabeth H Krenske

[1]School of Chemistry and Molecular Biosciences, The University of Queensland, Australia.

The Nazarov cyclisation is the 4π-electron conrotatory cyclisation of a 3-hydroxypentadienyl cation. Asymmetric catalysts are commonly used to induce enantioselectivity in these reactions. BINOL-derived catalysts have gained special popularity for this purpose in recent years.

This study examines asymmetric Nazarov cyclisations mediated by two BINOL-derived catalysts: a BINOL phosphoric acid and an H_8-BINOL phosphorodithioic acid. Despite their similar chemical structures, these two catalysts give very different enantioselectivities in the cyclisation of **1**. BINOL-derived phosphoric acid **3** gave 81% *ee*[1] while H_8-BINOL phosphorodithioic acid **4** gave only 9% *ee*[2] This presentation will describe the results of DFT calculations of the catalytic mechanism and chiral induction mechanism of the two BINOL-derived catalysts.

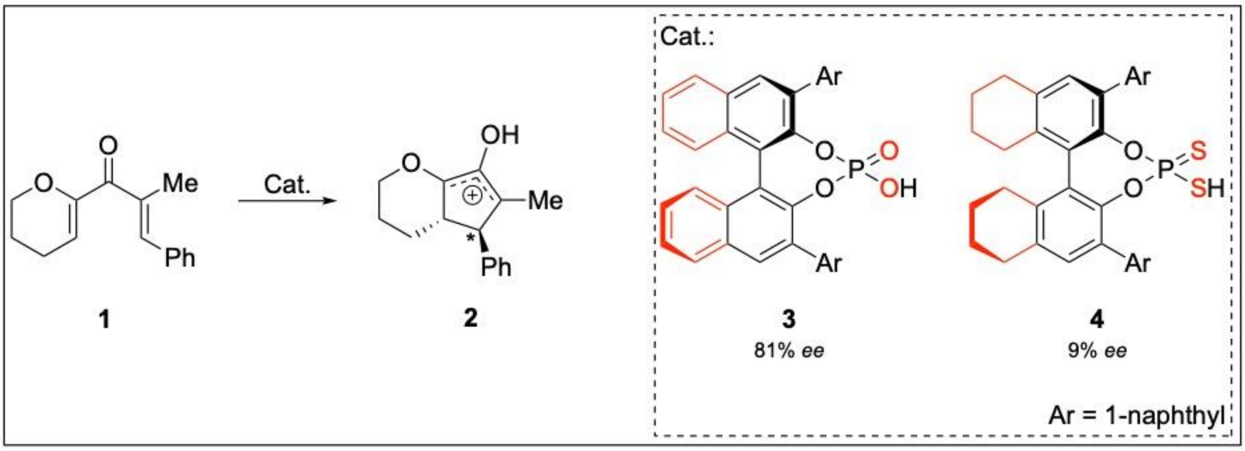

Figure 1. Asymmetric Nazarov cyclisation

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2. Tetrahedron **2009**, 65 (51), 10617–10622

An In-Silico Investigation of Menthol Metabolism

P020

Assoc. Prof. Taweetham Limpanuparb, Ms. Wanutcha Lorpaiboon, Mr. Kridtin Chinsukserm

Mahidol University, Salaya, Thailand

Prevalence of mentholated products for consumption has brought great importance to studies on menthol's metabolic pathways to ensure safety, design more potent derivatives, and identify therapeutic benefits. This *in silico* study supplements previous studies by constructing tentative metabolic pathways of (-)-menthol based on metabolites found experimentally in previous work by Yamaguchi, Caldwell & Farmer, Madyastha & Srivatsan and Hiki et al. The reactions involved in the pathways are conjugation to glucuronide & sulfate, oxidation to alcohol, aldehyde & carboxylic acid, and formation of four/five-membered ring. Gas-phase structures, the standard Gibbs energies and SMD solvation energies at B3LYP/6-311++G(d,p) level were obtained for 102 compounds in the pathways. This study provides a more complete picture by filling the gaps within menthol metabolism as previously proposed.

Recent Development of Automatized Density-Functional Tight-Binding Parameterization for Metal-Containing Systems

P021

Dr. Chien-Pin Chou[1], Dr. Aditya Wibawa Sakti[2], Prof. Hiromi Nakai[1,2,3]

[1]Waseda Research Institute for Science and Engineering (WISE), Waseda University, Tokyo, Japan. [2]Element Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto, Japan. [3]Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, Tokyo, Japan

The density-functional tight-binding (DFTB) method is an approximated DFT method with careful approximations. It uses pre-computed parameters either directly computed from DFT or optimized from reference ab initio or DFT calculations, which makes it robust and suitable for treating large systems. In the past decades, several general or specific parameterization sets have been developed. The recently developed DFTB parameterization set for organic and bio-organic systems, 3ob, has been extensively tested and successfully applied to many applications. It has also been extended to cover several metal elements including Mg, K, Ca, Zn, Ni, and Cu. However, those metal parameters were parameterized mainly for the biochemical systems and the performance for other metal-containing systems are not clear. In this poster, we are presenting the use of the previously developed automatized parameterization scheme for metal-containing systems, including metal-organic frameworks (Cd, Al, and Cu), metal cluster (Pt, Pd, and Rh) and metal oxide (Al) surfaces, and lithium-ion battery electrolyte solutions. We believe that the automatized parameterization scheme and the newly developed parameterizations would enhance the availability of employing the DFTB method to more various systems.

Collisional Energy Transfer Between Hot CH_3CHO/CH_2CHOH and N_2

P022

Ms Maggie E Corrigan, Ms Isabella C Russell, A/Prof Meredith JT Jordan

School of Chemistry, the University of Sydney, Sydney, Australia

The phototautomerisation of acetaldehyde, CH_3CHO, to vinyl alcohol, CH_2CHOH, occurs in tropospheric conditions. Subsequent reaction of CH_2CHOH with OH radicals produces formic acid, HCOOH; this reaction accounts for 7% of global atmospheric HCOOH.

The tautomerisation of CH_3CHO to CH_2CHOH occurs on the highly vibrationally exited ('hot') electronic ground state of CH_3CHO, S_0. As such, the yield of CH_2CHOH in the atmosphere from this process depends on the energy-dependent intersystem crossing rates returning photoexcited CH_3CHO to S_0, the rate of tautomerisation on S_0, and the rate and magnitude of collisional energy transfer (CET) between hot CH_3CHO/CH_2CHOH and N_2. While there is theoretical data describing the intersystem crossing and tautomerisation rates, no direct experimental or theoretical data exists for the CET. A previous study of this tautomerisation reaction in the atmosphere modelled CET by fitting an exponential-down model with a single, energy independent, parameter, to CH_3CHO photodissociation yields at various pressures and wavelengths; this same model and parameter were used to describe CET for both CH_3CHO and CH_2CHOH with N_2.

This work seeks to improve upon the model of CET between CH_3CHO/CH_2CHOH and N_2. Is an exponential down model, with a single, energy-independent parameter, appropriate to describe CET in this system? Is it valid to use the same model and/or parameters for both CH_3CHO and CH_2CHOH? To answer these questions, we use classical trajectory simulations to model collisions between hot CH_3CHO/CH_2CHOH and N_2, with conditions as close as possible to those in the atmosphere. We define internal potential energy surfaces (force fields) for each collision partner, and an interaction potential between CH_3CHO/CH_2CHOH and N_2, considering both the Lennard-Jones potential and a modified exponential-6 formulation. We find that the single parameter exponential model is not appropriate in this system, and that the CET is both energy dependent and different for each tautomer.

Predicting NMR Spectra Using Mixed Pseudoramp-Gaussian Basis Sets

P023

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[1]UNSW, Sydney, Australia. [2]Universidad Icesi, Cali, Colombia

Nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful and versatile spectroscopic tools for chemical analysis and structural determination. However, it is often impractical to interpret and assign NMR spectra for complex molecules by hand and computational methods are often introduced. *Ab initio* NMR calculations are often accurate and have high sensitivity to structural and electronic changes, allowing regioiosmers to be distinguished. However, *ab initio* NMR has issues with diminished accuracy for some molecules such as fluororganics, which can be attributed to the inability of Gaussian basis functions to describe the electron-nuclear cusp.

This study involves a novel type of basis set, called the mixed ramp-Gaussian basis set[1] which involve a new kind of primitive function – the ramp, which has an electron-nuclear cusp. In initial tests with low angular momentum basis functions, mixed ramp-Gaussian basis sets have been shown to be as fast as conventional all-Gaussian basis sets[2] for moderate sized molecules, and to reproduce the electron density at the nucleus far better[3]. For further testing, we have developed a set of pseudoramps, which model ramp functions as a large linear combination of Gaussians. These pseudoramps can be used to predict the calculation results which can be obtained using newly derived mixed ramp-Gaussian basis sets based on parent all-Gaussian basis sets, without full coding and interfacing of the mixed ramp-Gaussian integral package.

We present details of the new mixed ramp-Gaussian basis sets for elements up to Ar, as well as parameters for the pseudorampification for these elements. We also present initial results of using the pseudorampified basis sets to predict NMR chemical shifts.

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(3) – *J. Chem. Theory Comput.*, **2015**, 11, 3679.

fragHAR: Towards Ab Initio Quantum Crystallographic X-Ray Structure Refinement for Polypeptides and Proteins

P024

Mr Justin Bergmann[1], Mr Max L Davidson[2], Dr. Esko Oksanen[3], Professor Ulf Ryde[1], Professor Dylan Jayatilaka[2]

[1]Lund University, Lund, Sweden. [2]University of Western Australia, Perth, Australia. [3]European Spallation Source, Lund, Sweden

We describe the first *ab initio* aspherical X-ray structure refinement for polypeptides and proteins, using a fragmentation approach to break up the protein into residues and solvent, and thereby speed up the quantum-crystallographic Hirshfeld atom refinement (HAR). We find that the geometric and atomic displacement parameters from the new fragHAR method are essentially unchanged from a HAR refinement on the complete unfragmented system when tested on di-, tri- and hexapeptides. The largest changes are for parameters describing hydrogen atoms involved in hydrogen-bond interactions, but we show that these discrepancies can be removed by including the interacting fragments as a single larger fragment in the fragmentation scheme. Significant speedups are observed for the larger systems. With this approach we are able to perform a highly parallelized HAR in reasonable times for large systems. The method is implemented in the TONTO software.

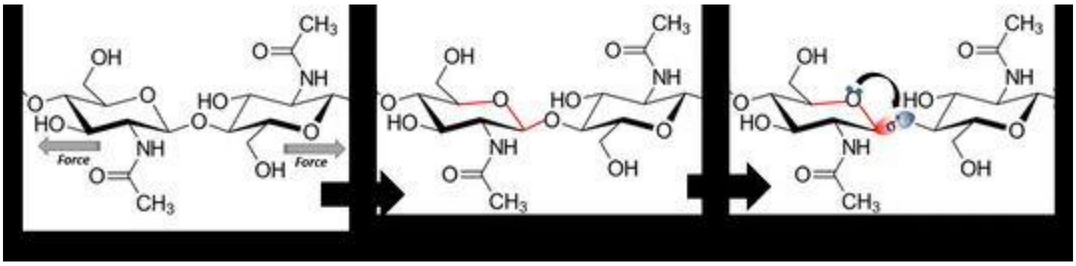
Electronic Structure Understanding of the Mechanically Induced Selectivity in Acid Catalyzed Chitin Hydrolysis

P025

Mr. Danjo P. De Chavez[1], Dr. Horikazu Kobayashi[2], Professor Atsushi Fukuoka[2], Professor Jun-ya Hasegawa[2]

[1]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Japan. [2]Institute for Catalysis, Hokkaido University, Sapporo, Japan

Mechanical ball milling has been used for chitin depolymerization to N-acetylglucosamine (GlcNAc) in which acid requirement have been reduced significantly. The synergy of mechanical activation and acid catalysis afforded higher selectivity of glycosidic bond cleavage over amide bond breakage in lower acid concentrations. Hence, the bioactive GlcNAc monomer was preferentially produced over glucosamine while maintaining lower acid wastes. In this regard, the force dependent mechanochemical activation-deactivation in relaxed and pulled GluNAc dimer undergoing deacetylation and depolymerization reactions have been studied. Relaxed depolymerization and deacetylation reactions have been studied with GlcNAc dimer in a protonated (+1) mixed implicit/explicit water environment using an in-house Modified Gaussian09 at B3LYP/6-311g(d,p) level. Activation Energies (E_A) of Rate Determining Steps (RDS) proved that the two reactions could occur simultaneously. Force Modified Potential Energy Surfaces (FMPES) were then sampled. Mechanical force was introduced explicitly in the rate determining steps of both reactions. Force modifications were done with magnitudes up to 3.0 nN in three unique pulling directions. In general, as applied pulling force increases, the E_A of the RDS of deacetylation increases while that of depolymerization decreases. This result agrees to the selectivity found in the experiment. Energy and structural analyses for the depolymerization showed that activation can be attributed to conformational change of the reactant which leads to a decrease interaction with water. The active site showed a significant change in glycosidic dihedral which leads to e^- donation to the σ^* orbital of the glycosidic bond leading to the activation. Consequently, the Bronsted-Løwry basicity of the glycosidic oxygen also increased which would lead to acid catalysis.

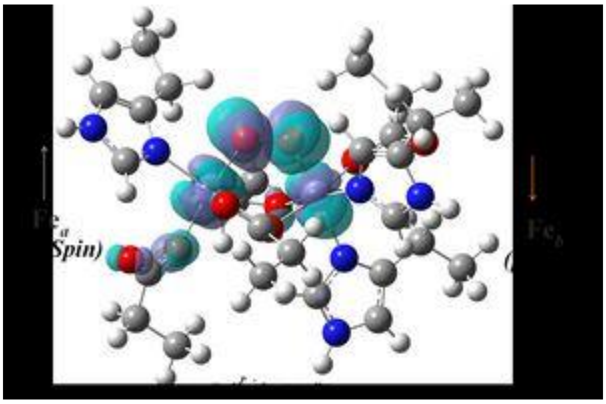


Studies of Peroxide Intermediate Structure and Mechanism of the Aryl Nitration Reaction in Nonheme N-Oxygenase CmlI – A Theoretical Study

P026

Research Scholar Salai Kalaiselvi Dhanasekaran, Dr Senthilnathan Dhurairajan

Centre for Computational Chemistry, CRD, PRIST Deemed to be University, Thanjavur, India



The oxidation of aryl-amine substrate to aryl-nitro product catalyzed by the N-oxygenase (CmlI) is the final step of antibiotic chloramphenicol biosynthesis. The binuclear non-heme iron centers of CmlI, activate O_2 molecular oxygen to initiate the reaction through making of bridged Fe-O bond, followed by oxygenation of aryl-amine substrate and hydrogen atom abstraction. The shuttling of electrons from two iron centers to the substrate is the key factor for the entire reactions. This computational study is dedicated to elucidate the mechanism of the catalytic conversion of aryl-amine substrate to the aryl-nitro product and electronic structure of intermediate of the bi-nuclear iron enzyme. The influences of different spin states of iron centers are also studied for the entire schemes. Density functional theory computations on the structure and mechanism established here show that the initial Proton-Coupled Electron transfer (PCET) steps activate by peroxide intermediate through single electron transfer (SET) reactivity. The spin variation on the reactive iron centers relatively influenced the activation energy of PCET steps. The DFT study with reductionist approach CmlI shows that its electronic and geometric structures are poised to react speedily with the O_2 molecule. Based on the study of the previous computations of peroxy biferric model complexes, UB3LYP functional and the 6-31G* basis set for geometry optimizations and frequency calculations and the 6-311G* basis set for single-point energy calculations were opted with the Gaussian 09 package

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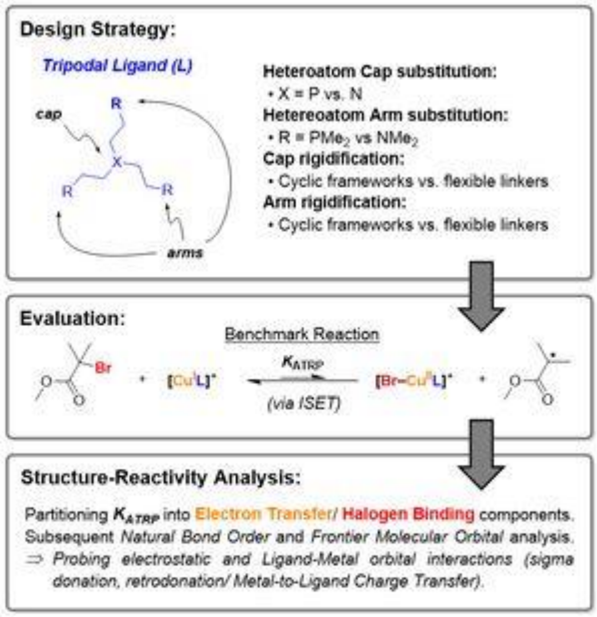
Computational Design of Highly Activating Ligands for Atom Transfer Radical Polymerisation

P027

Mr Phuong H. Doan, Dr Benjamin B. Noble, Mr Alfred K.K. Fung, Prof Michelle L. Coote

ARC Centre of Excellence for Electromaterials Science, Research School of Chemistry, Australian National University, Canberra, Australia

Atom Transfer Radical Polymerisation (ATRP) has revolutionised polymer synthesis; enabling the precise construction of sophisticated macromolecules under mild conditions. In ATRP, a redox active metal mediator (usually Cu) activates a 'dormant' organohalide initiator, generating carbon-based radicals that can be harnessed for polymer chain growth. Crucially, this reaction is reversible and so 'living' polymerisations can be achieved by carefully balancing this activation/deactivation equilibrium (K_{ATRP}). While current ATRP methodology can polymerise a wide-array of monomers, activation of less-stabilised alkenes remains problematic. Indeed, for monomers such as vinyl chloride and vinyl acetate, the N-based ligands usually employed in Cu-base d ATRP are not sufficiently activating. In this work, we use high-level computational theory to assess the performance of P-based ligands in Cu-based ATRP. First, we examine how structural features of a diverse set of ligands affect K_{ATRP}. Next, we establish rational design criteria based on electrostatic arguments and ligand-field theory. Finally, using these design criteria, we propose a range of 'next-generation' ATRP ligands that are predicted to have unprecedented activity.



Partitioning K_{ATRP} into Electron Transfer/ Halogen Binding components.
Subsequent Natural Bond Order and Frontier Molecular Orbital analysis.
⇒ Probing electrostatic and Ligand-Metal orbital interactions (sigma donation, retrodonation/ Metal-to-Ligand Charge Transfer).

Effect of Liquid Phase on Heterogeneous Catalytic Reactions

P028

Mr. Swarit Dwivedi[1], A/Prof. Samir H. Mushrif[2], Prof. Alan Chaffee[1], A/Prof. Akshat Tanksale[1]

[1]Monash University, Melbourne, Australia. [2]University of Alberta, Edmonton, Canada

Liquid phase heterogeneous catalytic reactions have gained popularity as an alternative method of forming products which are otherwise not feasible in gas-phase. Stability of products in the liquid phase is extremely important for a high extent of reaction. Our group has recently developed a liquid phase catalytic reaction for formaldehyde synthesis using syn-gas [1]. CO and H_2 react at the surface of Ni-Ru catalyst particles suspended in methanol-water mixtures to produce formaldehyde. Formaldehyde yield is significantly affected by the composition of methanol-water mixture (Fig. 1a) [1]. To understand the effect of liquid phase, we performed classical molecular dynamics simulations. We observed that the strength of hydrophobic and hydrophilic interactions changes on changing methanol-water mixture composition. In pure methanol, solvated formaldehyde (methoxymethanol) is stabilised in an 8-10 membered methanol ring/chain structure (Fig. 1b). However, at low methanol compositions, hydrophobic clustering of methanol around solvated formaldehyde (methanediol and/or methoxymethanol) is observed (Fig. 1c). These clusters stabilise formaldehyde in the liquid phase and hence a higher yield of formaldehyde is observed experimentally (Fig. 1a). At near equimolar compositions, the strong hydrophilic nature of water prevents the formation of ring/chain structures and, also, hydrophobic clustering is not favoured (Fig. 1d). Consequently a lower yield of formaldehyde is observed at near equimolar compositions. This changing micro-phase structure can potentially explain various other thermodynamic anomalies of formaldehyde-methanol-water mixtures.

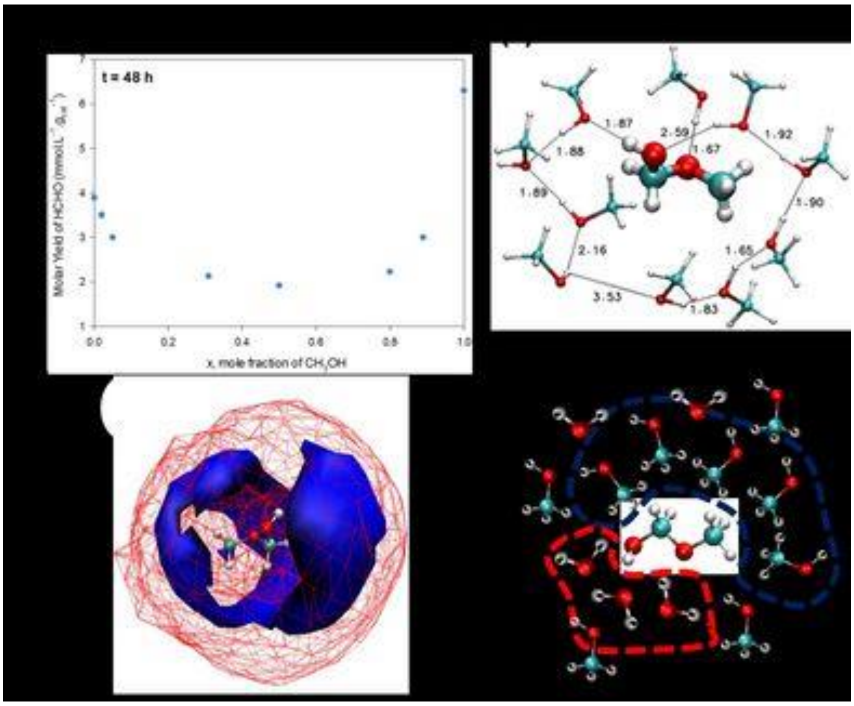


Figure: (a) Formaldehyde yield on varying methanol concentration [1], (b) methoxymethanol surrounded by ring/chain structure in pure methanol [1], (c) spatial distribution function at 0.3 methanol mole-fraction (blue iso-surface represents methanol whereas red wireframe represents water), (d) schematic of hydrophobic (blue enclosure) and hydrophilic (red enclosure) molecular arrangement at near equimolar methanol-water mixture compositions.

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Exploring the Structure and Mechanism of Transport of the Human Sodium Proton Exchanger Isoform One (NHE1)

P029

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Sodium proton exchanger isoform 1 (NHE1) is a ubiquitously expressed integral transmembrane glycoprotein that controls the electroneutral exchange of a single intracellular proton for one extracellular sodium ion across the plasma membrane in all mammalian cells and thus elevating the intracellular pH [1]. NHE1 protects cells from intracellular acidification, and plays key roles in regulating the cell volume and proliferation [2]. Elevated NHE1 levels were found to trigger metastasis especially in breast cancer. [3] The complete crystal structure of NHE1 hasn't been resolved so far. Understanding the mechanism of Na^+/H^+ exchange across NHE1 is important for the future development of clinically useful NHE1 inhibitors.

In this work, three-dimensional homology models for the inward-facing and outward-facing NHE1 states were built based on the crystal structures of *Methanocaldoccocus jannaschii* (*Mj*NhaP1). *Mj*NhaP1 is the most similar Na^+/H^+ antiporter to NHE1 with 20% sequence identity and 38% similarity. Molecular dynamics (MD) simulations, steered molecular dynamics (SMD) simulations potential of mean force (PMF) calculations and molecular docking studies were performed in order to predict the structure of NHE1, understand the mechanism of Na^+/H^+ transport across the membrane and inhibitor binding. Our computational studies have provided detailed mechanistic interpretation to experimental data and serve the basis of future structure-based inhibitor design.

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Molecular Dynamics Simulations of Specific Ion Effects at Interfaces

P030

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The ability to predict specific ion effects (SIEs) in different systems is still an unresolved problem in physics, biology and chemistry. This is due to the fact that ions will interact in systems ranging from simple solvents, to large proteins in unique ways that are dependent on the identity of the ion, and cannot be fully described by electrostatics or concentration models. Until recently it was thought that SIEs were limited to water, however recent experiments by Mazzini et. al., [1] as well as computational work by Gregory et. al. [2] have shown that SIEs are exhibited in non-aqueous systems. In conjunction, Andersson et. al. [3,4] have probed experimentally the vacuum-liquid interface for glycerol solutions of different ions (Cl^- ,Br^- ,I^- ,Na^+) with and without surfactants, revealing that local ionic concentrations, and hence the potential for SIEs to occur, are markedly different at the interface, compared to the bulk liquid. On this basis, this work investigates the structure of vacuum-liquid interfaces in the presence of dissolved salt, to provide new structural insight into ion-ordering and SIEs at liquid interfaces.

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Predicting the Basicity of *N*-Heterocyclic Carbenes

P031

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N-heterocyclic carbenes (NHCs) are an important and widely used class of organocatalysts. Singlet carbenes of NHCs serve as both ligands for organometallic catalysts as well as catalysts in their own right, more prominently as nucleophilic species in *Umpolung* chemistry, but also as Brønsted bases in organic transformations. The basicity of these compounds is inevitably linked to their reactivity and is important for their ability to mediate a broad range of complex chemical transformations[1]. However, there have been few systematic studies (experimental or computational) of the basicity of NHCs.

In this poster, we present a comprehensive and systematic benchmarking study, assessing the performance of a range of high-level *ab initio* methods, density functional theory (DFT) and semi-empirical QM methods. The study covers the 5 main classes of carbenes; imidizoles, triazoles, thiazoles, oxazoles and saturated systems and provides quantitative insight on the structure-basicity relationship of these compounds. Finally, we propose several cost-efficient methods for accurate prediction of gas phase basicity that may be used to help guide the design of better catalysts.

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Accurate Approach in Simulating the Electronic Absorption Cross Section of Small to Medium Molecules

P032

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The electronic absorption spectra of some small sulfur-containing molecules of atmospheric importance have been simulated using a nuclear ensemble approach with the Newton-X package. The ensemble is based on Wigner sampling of vibrational frequencies calculated at the CCSD(T) level of theory with the aug-cc-pV(T+d)Z basis set. The electronic excited state transition energies and oscillator strengths of each geometry in the ensemble are calculated with the EOM-CCSD, RI-CC2 and ADC(2) methods using correlation consistent basis sets with additional diffuse basis functions, denoted aug-cc-pV(X+d)Z+3.

We find very good agreement between our calculated spectra and the available experimental spectra of sulfur dioxide (SO_2), sulfur trioxide (SO_3), hydrogen sulfide (H_2S), carbonyl sulfide (OCS) and carbon disulde (CS_2). We show that computational cost of these simulated spectra can be substantively reduced with negligible loss of accuracy by using a combination of results obtained with the aug-cc-pV(D+d)Z+3 and aug-cc-pV(T+d)Z+3 basis sets.

Sulfuric acid (H_2SO_4) is the dominant form of atmospheric sulfur in the stratosphere and plays an important role in terms of aerosol formation. However, despite its atmospheric significance, the experimental spectrum of H_2SO_4 is not yet known, although there have been multiple attempts to record it. We apply our simulation approach to calculate the electronic absorption spectrum of H_2SO_4, considering the two low-energy conformers that are abundant under atmospheric conditions. Above 6.4 eV, we find that our calculated spectrum for H_2SO_4 is generally in agreement with the experimental upper limits for the absorption cross-section. However, below this energy there is more uncertainty and we suggest that further experimental investigation is needed.

Energy-Based Automatic Fragmentation in the Linear-Scaling Divide-and-Conquer Electron Correlation Calculations

P033

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[Introduction] For treating large systems such as proteins, a lot of fragmentation-based electronic structure methods have been developed. These methods, however, introduce the errors associated with the fragmentation. In addition, especially in proteins, the weak interactions (e.g., dispersion force) usually play important roles to stabilize the higher-order structure. We have developed the divide-and-conquer (DC) method [1] and reported the automatic fragmentation scheme in the DC-SCF calculation [2]. In this study, we extend this scheme to the DC-MP2 electron correlation calculation [3].

[Theory] Each fragment of the DC method consists of the disjoint central region and its neighboring region called the buffer region. In the DC method, the energy error can systematically be decreased by increasing the size of the buffer region. However, the appropriate size of the buffer region depends on the system. In this study, based on the atomic orbital Laplace MP2 method [4] and Schwarz inequality, we derived the upper bound of the electron correlation energy contribution for each atom in the buffer regions. We developed a method to automatically determine the buffer region in the DC-MP2 calculation by establishing energy threshold for this upper bound.

[Numerical assessment] The present method was applied to 100 water molecules. The energy error and the fragment size with respect to the energy threshold is showed in Figure. The energy error decreased and the average fragment size <*r*> increased systematically as the energy threshold e_{thresh} decreased. Therefore, it is conformed that the appropriate size of the buffer region can be selected in each fragment based on the DC-MP2 energy.

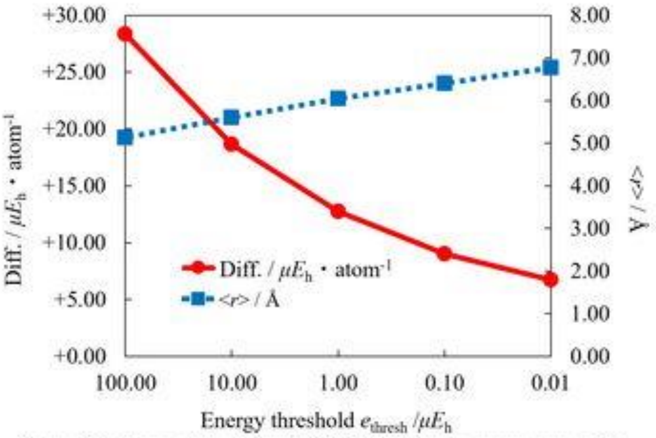

Figure. Dependence of the automated DC-MP2 correlation energy error and the average major axis radius <*r*> on the energy threshold in 100 water molecule calculation with 6-31G(d) basis set.

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Machine Learning Study for Optimization of Reaction Conditions Including Discrete Variables with Small Number of Experiments

P034

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An optimization of reaction condition is one of the most important but highly costing tasks in experiments to obtain desirable results. To realize the rational optimization, it is necessary to control various kinds of chemical conditions including continuous and discrete variables. Recently, optimization schemes for continuous reaction conditions such as reaction time, temperature, concentration, and scale, have successfully been developed with the advances of flow reactor equipment. However, there are still a few practical rational optimizing examples for discrete reaction conditions such as solvents, reductant, and catalysts. In addition, an optimization in small number of experiments is desired because individual batch reactions are performed by human hands in usual laboratories. In this study, we investigated the optimization of reaction conditions for two different organic reaction systems including discrete conditions with small number of experiments. Machine learning was utilized to analyze relationships between reaction conditions and yields of chemical reactions. In the first reaction system, an optimization of high dimensional reaction conditions including discrete variables was investigated [1]. The discrete conditions were represented in binary vectors for machine learning. The scheme reasonably performed to reduce the experimental attempts. In the second reaction system, a solvent selection scheme was investigated in the reaction conditions because the reaction is highly sensitive to the solvent [2]. The characteristics of solvents were numerically represented in their physical properties. The scheme showed a potential to predict chemical yields for solvents before performing experiments.

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Mechanism and Optimisation of Nitroxide Mediated polymerisation

P035

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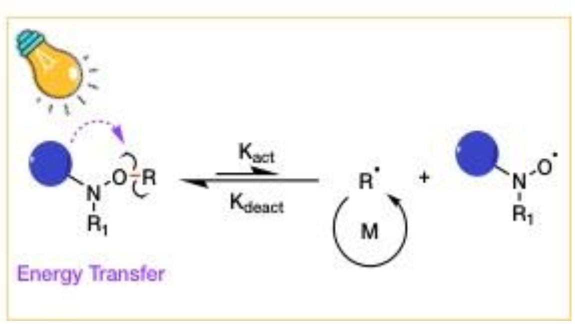
Nitroxide mediated polymerization (NMP) confers living characteristics on radical polymerization through reversible deactivation. Despite the advantages of a “living” mechanism, NMP requires elevated temperatures (above 100 °C) for the reaction to occur in a reasonable time frame. An alternative is nitroxide mediated photopolymerisation (NMP^2) where a chromophore is added, enabling photocleavage of the alkoxyamine bond from the energy provided by light in the U.V range [1]. However, a good photoiniferter is proving difficult to design. Previous work has shown that the choice of chromophore, its position in the molecule, competitive pathways for cleavage and energy dissociation all need to be considered when developing an NMP^2 initiator [2 3]. In the present work, we use high-level quantum chemistry to explore potential photocleavage mechanisms of a wide array of NMP^2 initiators with the aim to correlate their structure and reactivity. The influence of potential side reactions is also investigated.



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Parallel MP2 by Quadrature

P036

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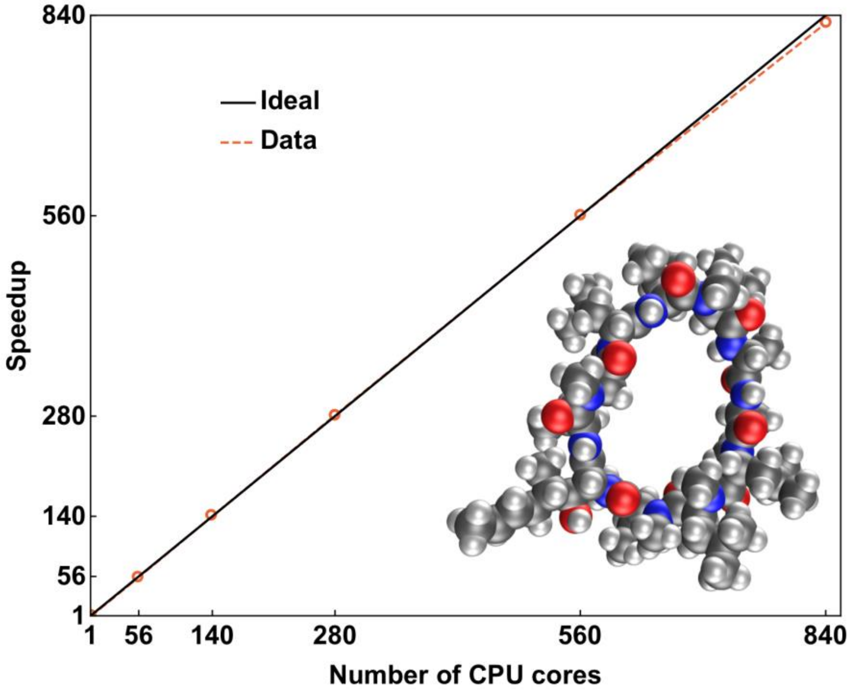
Australian National University, Canberra, Australia

Modern computers are increasingly relying on parallelism for performance gains and it is crucial that quantum chemists keep abreast of these changes by developing algorithms that can exploit these new architectures. We present one such algorithm, Q-MP2-OS, for computing the opposite-spin MP2 energy. Our quadrature-based algorithm uses Almlöf's approach to transform the orbital energy denominators, and uses the same Becke partitioning of the molecule that is used in density functional theory. The resulting atomic domains are interacted pair-wise, and completely independently, leading to an embarrassingly parallel algorithm.



Speedup of the Q-MP2-OS implementation with respect to the number of CPU cores. Calculations were performed for the cyclosporine molecule ($C_{62}H_{111}N_{11}O_{12}$).

We have implemented Q-MP2-OS in a development version of the Q-Chem quantum chemistry package and demonstrated close to ideal speedups for up to 840 cores. Furthermore, the judicious use of cut-offs reduces the scaling of the algorithm from $O(N^4)$ to $O(N^2)$ whilst still maintaining sub kcal mol^{-1} accuracy.

Decomposing Specific-Ion Interactions

P038

Mr Kasimir P Gregory, Prof. Erica J Wanless, A. Prof. Grant B Webber, A. Prof. Alister J Page

The University of Newcastle, Callaghan, Australia

Specific-ion effects (SIEs) induce or influence physicochemical phenomena in a way that is determined by the identity of the ions present, and not merely by charge or concentration. Such effects have been known since the seminal work of Hofmeister and are often categorised according to the well-known Hofmeister series. Examples of SIEs are ubiquitous throughout chemistry and biology, and are traditionally explained in terms of the influence ions have on the structure of water. However, this explanation is unsatisfactory as it is unable to adequately explain and predict frequently-observed series reversals and anomalies. By modelling solvated ion-N-isopropylacrylamide (NIPAM) complexes with GKS-EDA, we show that ion-NIPAM interaction free energies are predominantly independent of the counterion, even in ion-pairs. However, ion-pairing can modulate repulsive ion-NIPAM interactions and thus induce a Hofmeister series reversal.

Molecular Modelling of Non-Ionic Surfactant ($C_{12}E_6$) Aqueous Phase Behaviour

P039

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Non-ionic surfactants containing polyethylene oxide (PEO) head groups are widely used in drug formulations, paints, cosmetics, textiles and detergents. In our research, we are interested in PEO surfactants as excipients in lipid-based drug formulations. Molecular dynamics (MD) simulation is a useful tool for obtaining atomic scale information, which helps to understand the colloidal structure formation of these PEO surfactants. However, many existing force fields do not reproduce the experimental phase behaviour of PEO due to the poor parameterisation of oxy functional groups and vicinal ethylene oxide groups, thus MD simulations with PEO molecules lag behind. The present study was carried out to identify a whether the recently released GROMOS force fields, 2016H66 developed to model the ‘gauche effect’ of PEO and $53A6_{DBW}$ developed to model interactions between water and ethylene oxide chains adequately models PEO surfactants. In this work, we performed extensive MD simulations using those two force fields to model the aqueous phase behaviour of the simple non-ionic surfactant, hexaethylene glycol monododecyl ether ($C_{12}E_6$), and then compared the simulated phase behaviour with experimental observation. From these simulations, we found that 2016H66 force field reproduced the experimental phase behaviour of $C_{12}E_6$/water systems better than $53A6_{DBW}$. In conclusion, our study showed that spontaneous aggregation of PEO surfactants into different colloidal structures can be successfully modelled with 2016H66 force field.

Influence of Sugar and Bases on the Stretching Vibrations of PO_2^- of DNA: A Computational Study with FMO/FDD.

P040

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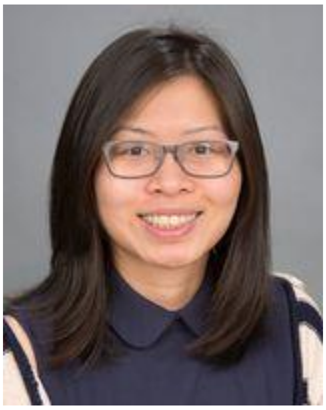

DNA is able to change its conformation when exposed to different conditions.[1] Infrared (IR) spectroscopy, a technique that studies the interaction of light and bonds and functional groups present in a sample, has been utilised to study the structural changes when DNA is exposed to different conditions.[1] B-DNA has been shown to convert to A-DNA when the hydration level falls below 75%., resulting in a shift in $\nu_{asym}PO_2^-$ from 1240 to 1220 cm^{-1}.[2, 3] In addition, the $\nu_{sym}PO_2^-$ peak at 1080 cm^{-1} becomes more intense after hydration.[2, 3] With the ability to accurately characterise DNA conformation, this opens the possibility of using IR spectroscopy as a tool to study DNA-drug interactions. To explain the shifts in $\nu(PO_2^-)$, Fragment Molecular Orbital (FMO) with Frozen Dimer Domains (FMO/FDD) is used.[4]

FMO, a method that fractions large systems into smaller fragments, is a cost efficient and accurate theory, a suitable method to study large biomolecule.[4] FMO/FDD allows for frequency calculations to be performed on the fragments of interest, decreasing computational cost while not compromising on the accuracy of the calculation.[4]

In this study, we utilised the FMO approach to study DNA models, in particular single-stranded models that comprises of 1 and 2 nucleobase pairs. The effect of a varying degree fragmentation on IR spectra was explored and the calculated results were compared with experimental data. In addition, the inclusion of both implicit and explicit solvation models, on the prediction of IR frequencies is also investigated.

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Theoretical Study of Ni Catalysts for H_2 Oxidation and Production via the Minimum Energy Intersystem Crossing Point

P041

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In this study, the mechanism of H_2 oxidation and production reactions using homogeneous Ni catalysts with the different R and R' substituent groups of ligand complexes on the singlet and triplet states were investigated using DFT calculations. The potential energy profiles of four $[Ni(P^{R}_{2}N^{R'}_{2})_{2}]^{2+}$ complexes when (R, R') substituent groups of ligands which consist of (H, H), (Me, H), (Me, Me) and (Cy, Me) were compared. The results revealed that the bare active site, the singlet state was calculated to be more stable than the triplet sate. Moreover, we found that the energy between the singlet and triplet states depend on geometry of complex. For calculated potential energy pathway involved the minimum-energy intersystem crossing point (MEICP) between the singlet and triplet states, there are two MECPs (MECP1 and MECP2) have been observed around TS1. The MECP1 geometry is similar to hydride-proton intermediate, and the geometry of MECP2 is H_2 complex. Therefore, analysis of the reaction coordinate of MECP structure showed that the energy gap between the singlet and triplet states significantly depends on distortion of geometry. This knowledge could be useful for ligand design to develop more efficient catalysts.

Electronic Transport Investigation of Redox-Switching Azulenequinones/Hydroquinones via First-Principles Studies

P042

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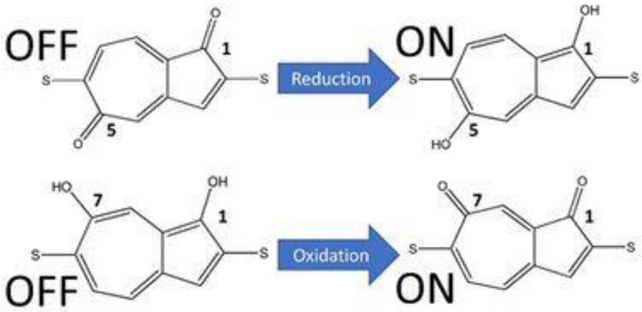
Azulenequinone/hydroquinone molecules, known as non-alternant hydrocarbon compounds, can achieve promising moletronic applications due to the advantageous tunability of azulene via its conversion to its quinone. Given 1,5- and 1,7-azulenequinones are already synthesized and considered the most stable forms of azulenequinones, we investigate such promising candidates for molecular electronic miniaturization using first principles density functional theory and non-equilibrium Green's function theory. The current-voltage characteristics of these molecules display a switching behaviour, with a switching ratio of 35, at low bias, in the 1,5-stable hydroquinone over quinone 2,6-azulene dithiolate, thus showing a redox molecular switch function. To understand the reason for current switching, we analyse the molecular orbitals obtained from first principles calculations and compare them with diagrammatic quantum interference calculations. Exploring multiple theoretical DQI models [3,4] allowed us to examine whether destructive quantum interference (DQI) plays a role or not [1,2] in our electronic transport study. The different theoretical models yielded contradicting results on the existence of DQI in 1,5-azulenequinone. Our work provides a theoretical foundation from a DQI perspective which predicts electron-transport properties for organic redox switching components in nano-electronics circuits.



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Normal Mode Analysis for Vibrational Motions in Liquid Water

P043

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Understanding behaviors and properties of liquid water has been a long-standing topic in both experimental and computational chemistry. Atomic level simulations for water molecules under different circumstances depict microscopic pictures to tackle the problems. We use the normal modes of the optimal structure of a single water molecule as the reference to construct the coordinate systems and then the effective potential energy surfaces of the molecular in the bulk water environment. We use thousands of uncorrelated structures sampled by path integral molecular dynamics. In each structure, we collect the exact frequencies obtained from the effective potential energy surface for each vibrational normal mode. The results hint that the frequency of the symmetric stretching mode is often lower than that of the asymmetric stretching mode. We will also show its implication in the IR and Raman spectra.

Transport Properties of Ionic Liquids from MD Simulations with a Self-Consistent Atomic Charge Determination

P044

Dr.Sc. Lukman Hakim[1,2,3], Dr. Yoshiki Ishii[2], Prof. Nobuyuki Matubayasi[2]

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Ionic liquids are recognized as the third group of solvents and considered to be environmentally friendly electrolytes due to their nonvolatility, high thermal stability, and high ionic conductivity. Ionic liquid electrolytes based on the pyridinium cation and bis-(fluorosulfonyl)amide anion have been reported to exhibit a good performance for the next generation sodium-ion battery. Here we report a systematic investigation on the influence of counter-cation species to the transport properties of sodium-ion in ionic liquid system using a self-consistent MD/DFT combination to account the strong effect charge transfer and polarization while enabling the simulation to be carried out at ns order. The results suggest that the diffusion of sodium ion is considerably higher in [Na, C_1Pip][FSA] system compared to [Na, C_1Pyr][FSA] owing to the higher charge transfer that effectively reduces the total charges of ionic liquid cation and anion.

Ab Initio Examination of Nitrogen Gas Solubility in Fluorinated Ionic Liquid Clusters

P045

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Monash University, Clayton, Australia

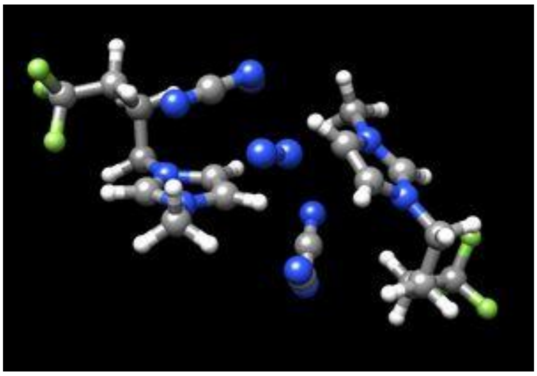
Presently, ammonia production is performed by the energy intensive Haber-Bosch process, requiring high temperatures and pressures. While it is possible to electrochemically produce ammonia from nitrogen gas in ambient conditions, the low solubility of nitrogen gas in traditional electrolytes and the competing hydrogen evolution reaction act as two barriers.

Ionic liquids are suitable electrolytes to counteract both barriers, displaying higher gas solubilities and as a non-aqueous electrolyte, allowing control over reactive hydrogen sources, increasing Faraday efficiencies.[1] Furthermore, the versatility of ionic liquids allows constituent ions to be tweaked for specific properties.

It has been observed that the fluorination of ionic liquids increases their gas solubility.[2] However, reasons as to why this is are yet to be fully elucidated. In this work, nitrogen gas solvation is simulated in ionic liquid clusters. In particular, imidazolium and pyrrolidinium based cations C_4mim^+ and C_4mpyr^+ are contrasted against their fluorinated counterparts $C_FC_3mim^+$ and $C_FC_3mpyr^+$, by being paired with dicyanamide anions.

The Fragment Molecular Orbital (FMO) method is combined with the recently developed spin ratio scaled second order Møller–Plesset perturbation theory (SRS-MP2)[3] is used to construct minimum energy two ion pair structures of each ionic liquid. Then, nitrogen gas is inserted into these clusters, allowing an quantitative energetic comparison between each ionic liquid.

The interaction energy between the ionic liquid and nitrogen gas and the deformation of each ionic liquid upon gas insertion separately do not correlate with solubility trends. Instead, the sum of these observables, the binding energy of gas insertion correlates with solubility. Ultimately, this provides a theoretical framework to assess the capacity of ionic liquids to dissolve small gases.



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[2] Almantariotis et al., *J. Phys. Chem. B*, 2017, **121**, 426
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Assessing Noncovalent Interactions in Electronic Excited States

P046

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Time-dependent density functional theory (TD-DFT) is the most accessible method for computationally treating electronic excited states of medium- to large-sized molecular systems. Known limitations inherent in traditional Kohn-Sham DFT unfavourably translate directly into TD-DFT, including poor treatment of noncovalent interactions. Techniques to appropriately treat noncovalent interactions in DFT are well-developed for the electronic ground state but remain largely untested for excited states.

In this work, we assess the performance of time-dependent density functional approximations (TD-DFA) in treating noncovalent interactions for electronically excited states by the study of excimer and exciplex binding energies. Excimer and exciplex systems are studied specifically, as they combine both excited-state properties and fundamental noncovalent interactions. Consequently, any computational method applied to such systems must be able to describe both.

While there have been studies of older methods [1]—often based on various experimental or computational reference data—we establish a common reference for all systems against which older and newer methods are benchmarked. A modern wavefunction reference of SCS-CC2/def2-TZVP is established, showing agreement with CCSDR(3) estimated to the complete-basis-set limit. Binding energies and equilibrium distances for a set of selected excimers and exciplexes are thoroughly investigated against this reference for various TD-DFAs. The TD-DFAs studied span across global hybrids, range-separated hybrids, double-hybrids, and newly developed range-separated double-hybrids [2]. We hope this study provides valuable insights for further method development to address noncovalent interactions in electronic excited states.

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Finding and Analyzing Interfacial Amorphous Carbon Structures in CNT-Based Functional Materials by Artificial Force Induced Reaction Method

P047

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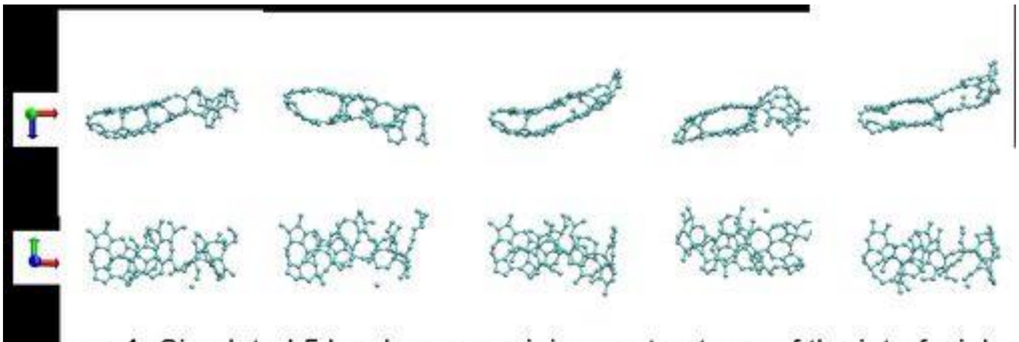
Many types of CNT-based functional materials are being developed and are now applied to various devices, such as nano chemical sensors, efficient and durable electrodes for secondary batteries, and flexible organic thermoelectric devices. Their functional properties depend on the properties of CNTs, e.g. length, size, chirality, and number of walls, contained in CNT-based materials, such as CNT yarns, CNT films, or CNT nano-composites. In addition to that, the interface carbon structures in CNT-based materials also determine the properties of their functionalities. However, there are difficulties in direct experimental measurements of the interfacial carbon structure in CNT-based materials because of their structural complexities. Therefore, the theoretical simulation of the interfacial structure is required to predict and design such functional materials. To this end, we here report the multiscale kinetic simulation scheme for interfacial systems to predict their structure and properties and show its application to the interfacial amorphous carbon in CNT-based materials. In our scheme, the energy and gradient calculations are done with the Self-consistent charge density functional tight-binding method and the structural searches are performed by the artificial force induced reaction method combined with the rate constant matrix contraction method which are implemented in the developer version of the GRRM program. The calculated structural transitions of amorphous carbons are then mapped onto the structural transition route map (STRMs) composed of local energy minima (nodes) and transition paths (edges). The constructed STRMs allows us to predict and analyze the interfacial structures relaxation mechanism and resulting functional properties. From the simulations, we found that the interfacial steric constraints have a non-negligible effect on structural relaxation processes of amorphous carbons and discussed the guiding principle of the interfacial structure control. We also discuss the applicability and limits of our simulation scheme.



ure 1: Simulated 5 local energy minimum structures of the interfacial

Understanding the Extent of Ionicity in Diamine Protic Ionic Liquids

P048

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Protic ionic liquids (PILs) are synthesised via a simple Brønsted acid-Brønsted base proton transfer reaction. In this work, we study the degree of proton transfer in diamine PILs as a means of quantifying the ionicity of these PILs by using thermodynamic cycles. We focus on four PILs, which are, dimethylethylenediamine acetate [DMEDAH][Ac], dimethylethylenediamine formate [DMEDAH][Form], dimethylethylenediamine propionate [DMEDAH][Prop] and dimethylethylenediamine nitrate [DMEDAH][Nitrate]. We propose an alternative measure, $\Delta pKa^{IL,}$ where we consider the ions of ILs as single molecular entities rather than individual ions. Single and double ion-pairs of PILs were studied to understand the importance of cooperativity effects on influencing the extent of proton transfer. It was found that the single ion-pair model was insufficient to reflect accurate ΔpKa^{IL} values. Increasing the cluster size from 1 to 2 led to improved ΔpKa^{IL}. The relative basicity of the anion was found to be a significant factor in including the role of the solvation model as well as the preferred protonation site. PILs consisting of strongly basic anions such as [Ac] or [Form] showed that protonation of both primary and tertiary amine centres was possible to the same degree. Conversely, [Nitrate]-based PILs preferred the tertiary amine centre instead. We argue that the implementation of a solvation model for studying the extent of ionicity in PILs is dependent on the charge distribution of the resulting ionic liquid. We find that gas phase calculations are sufficient to reflect the extent of ionicity in primary protonated PILs.

Tuning of the Dielectric Constant to Correct for Delocalisation Error: Development and Preliminary Testing of a Novel Computational Method

P049

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It is well known that the majority of density-functional approximations (DFAs) suffer from delocalisation error which can be characterised by concave-down fractional charge behaviour (Cohen, Mori-Sanchez & Yang 2008). In 2015, Dale and Johnson observed that DFA calculations conducted with polarizable continuum solvent models (PCM) result in concave-up fractional charge behaviour, interpreted as localisation error (Dale & Johnson 2015). It was suggested that a carefully chosen dielectric constant could return the linear fractional charge behaviour expected of an exact density-functional, consistent with Koopmans' theorem (Perdew et al. 1988). The goal of this work is to construct a procedure for finding an optimised dielectric constant which closely approximates this expected linear behaviour. The optimisation routine is based on the bisection method, converging to linear from both a concave-up and -down fractional charge curves as the dielectric constant is modified. Once the dielectric tuning method was implemented it was tested on the relevant testing sets, specifically the vertical ionisation energy (VIE) set published by McKechnie, Booth, Cohen and Cole (2015). This method shows promise in the linear correction of DFT plots in most cases - particularly hybrid cases where neither delocalisation nor localisation error was extreme. The method, however, tended to return poor results compared to published energetic approximations of VIE using coupled-cluster methods. These results and potential applications of this dielectric tuning method will be discussed.

Internal Oriented Electric Fields as a Strategy for Selectively Modifying chemical Reactivity

P050

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Recent work in our group has been focused on studying the effect of static electric fields on reaction kinetics and thermodynamics, and to what extent these effects are general and applicable. Up to now, however, the application of electric fields to electronic excited states has been largely confined to Stark spectroscopy, rather than as a usable strategy for deliberately altering excited states. Here, we present a proof-of-concept study into the feasibility of applying static electric fields as a way of tuning photochemical behavior, using charged functional groups (acid/base groups) as the means by which the electric field is applied. We demonstrate that, with acetophenone, the electric field effects are large, usable, and persistent in high-polarity solvents.

Importance of Li Distribution on High Li Conductivity in $Li_x(Ge,P)_3S_{12}$

P051

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$Li_x(GeP)_2S_{12}$ (LGPS) is a lithium superionic conductor, where an important potential application is an electrolyte for all-solid-state batteries that could be safer and have higher power compared to conventional batteries using liquid electrolytes. $Li_{10}GeP_2S_{12}$ shows an exceptionally high conductivity of 12 mS/cm at room temperature [1], and doubling of the conductivity to 25 mS/cm was attained in the related compound $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ [2]. The structure of LGPS is complicated. The backbone is a framework of GeS_4 and PS_4 tetrahedra where there are (Ge,P) shared sites and P-only sites. Li is four-folded coordinated with S and occupy four types of sites, Li1 to Li4. $(Li1)S_4$ and $(Li3)S_4$ form a one-dimensional chain and this is considered to be the primary Li diffusion route. The original article [1] claimed that the Li1 site is clearly double-split while the other Li sites are not split. However, in our presentation we show that the Li3 site is actually double-split at room temperature and triple-split at 10K.

The consequence of Li splitting is more local minima for Li, which in turn results in increased complexity in Li migration paths. Understanding and controlling of Li splitting is crucial to further enhance Li conductivity. Both Li1 and Li3 sites, which are found to split, take part in the primary Li conduction path and therefore the intriguing high Li conductivity of LGPS should be strongly influenced by fine details of the Li potential. Our first principles calculations show that that neither Li1 nor Li3 sites splits in $Li_{12}Ge_3S_{12}$ where all Li sites are occupied. Therefore, reducing the Li concentration, or introducing Li vacancies, was found to be necessary for splitting of these Li sites.

[1] Nat. Mater. 10, 682 (2011). [2] Nat. Energy, 1, 16030 (2016).

Effect of Protonation on the Reaction Mechanism of Fragmentation and 1,3-Rearrangement *via* Breslow Intermediates

P052

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Breslow intermediates, the key intermediates in *N*-heterocyclic carbene (NHC)-catalyzed reactions, can break the C–N bonds of thiamin and other NHCs, leading to the fragmentation and the 1,3-rearrangement. Distinct reaction pathways, in terms of radical and ionic channels, have been proposed in the literature.[1,2] In this study, we investigate the reaction mechanism of thiamin analogue with density functional theories. Three different protonation states, including the neutral amine, the N1-protonated amine, and the imine, are located. Computational results show that the Breslow intermediate in the protonation states of the neutral amine and of the N1-protonated amine could only undergo the radical route. On the contrary, Breslow intermediate in the imine state could proceed through both of the radical and the ionic channels. Among all of the reaction pathways, the ionic route of the imine state exhibits the lowest free energy barrier ($\Delta G^{\ddagger}$ = 22.4 kcal/mol, SMD model[3]). In the ionic mechanism, however, the C5α–N3' bond cleavage is coupled with a proton transfer from the 4-amine group to the O2'' atom. The reaction mechanism of thiamin with the 4-amine group is therefore concluded ionic, while that of NHCs without a nearby amine group is radical. In addition, the neutral phosphate buffer employed in experiments[2] tends to facilitate the interchange between the aforementioned tautomers and further affects the reaction pathway afterwards.

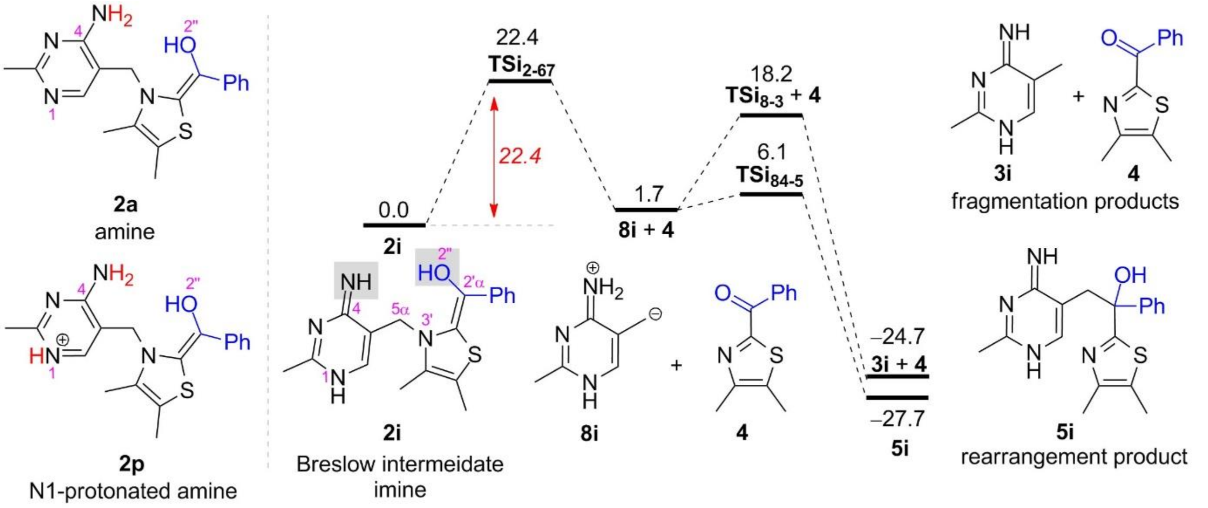

Figure 1. Different protonation states (left), and energy profile (right) of the lowest-energy pathway calculated at M06-2X/6-311+G(d,p) level with the SMD model.

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Without Compromising Efficiency and Accuracy: Solving the Nuclear Schrödinger Equation Using Path Integral Monte Carlo Simulation with Modified Shepard Interpolation

P053

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The University of Sydney, Sydney, Australia

Feynman's path integral formalism describes nuclei in a quantum system as ”ring polymers”, which describe the closed quantum paths the system can take. Thermodynamic properties, described in terms of the thermal density matrix, are calculated by sampling all possible paths using Monte Carlo simulation, which are weighted by their action. The convergence of the method, that is, the number of beads for each ring polymer and the number of Monte Carlo steps taken, can be improved by using more accurate description of the action (Symplectic schemes). We compare the convergence efficiency between four current existing action formalisms, primitive approximation (PA), Takahashi-Imada (TI), Suzuki factorisation (SF), and Chin formalisms. We further numerically optimised the parameters for SF and CA schemes, by doing so, lower order commutators roughly cancel in order to achieve higher order numerical accuracy and improve the computational efficiency. We apply the resulting schemes to three realistic systems, H_2O, HCN-HNC, and CH_4. The first two systems adopted relatively inexpensive however spectroscopically accurate PESs in order to demonstrate the convergence efficiency between four formalisms. The PES of methane was constructed by using modified Shepard interpolation, that is, as a weighted sum of second order Taylor expansion about a set of PES data points at regions of interest, calculated at a given level of electronic structure theory, the technique for combining modified Shepard interpolation and path integrals formalisms is novel, and we intend to demonstrate that it is efficient and potentially accurate to calculate the total internal energy for systems larger than four atoms.

Molecular Spintronics with Single-Molecule Magnets Under Irradiation

P054

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The University of Melbourne, Melbourne, Australia

Single molecule magnets (SMMs) are a broad class of strongly anisotropic inorganic complexes that are promising candidates for use in spintronic devices[1]. SMMs adsorbed to sp^2 surfaces impart hysteresis fingerprints on local electric currents, providing evidence for an exchange interaction between the giant spin of the SMM and the spin of electrons in the medium[2,3]. Injecting spin polarised current into SMM-based devices is the next pivotal step towards the realisation of nanomagnet-based spintronics and has become feasible since (i) efficient spin injection in graphene has now been achieved[4] and (ii) coupling between terbium-based SMMs and quantum dot devices has been demonstrated[2,3].

We present here[5] a theoretical investigation of a spintronic device consisting of a SMM grafted to a quantum dot in contact with metallic leads. The SMM is perturbed along its easy axis by the magnetic component of a coherent resonant radiation. We explore the spin dynamics of the SMM and the electric and spin currents flowing through the device when the source electrode is spin polarised. Even at zero bias voltage, we find a net current is pumped through the device and the spin current injected in the ferromagnetic source is switched in the drain lead. Additionally, the source spin current is not only reversed but also amplified in the drain lead. We show that the pumping and related effects can be explained by spin transitions in the SMM induced by the applied radiation and subsequent relaxation via spin asymmetric charge transfer processes.

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A Systematic Study on Bond Activation Energies of NO, N_2, and O_2 Catalyzed by Eight Transition Metal Hexamers

P055

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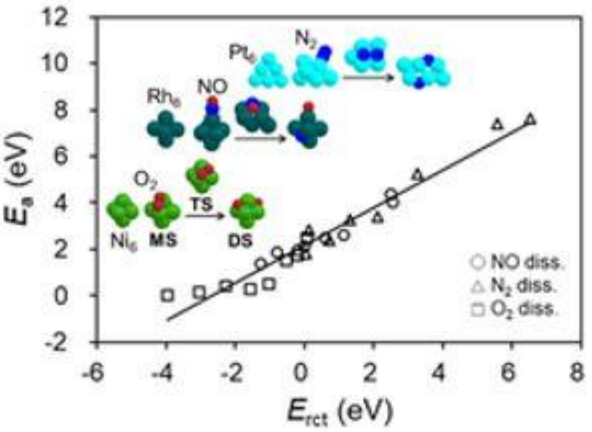
Nanoclusters of transition metals often exhibit different reactivities from bulk surfaces. For example, sub-nanometric metal clusters have attracted much attention as candidates of alternatives for conventional heterogeneous catalysts. It has been demonstrated that metal clusters can take various isomeric forms under mild conditions. Recently, in several small metal cluster catalysis, the importance of reactivities of metastable isomers has been discussed.

Here, the next interest would be generality of the importance of metastable isomers. To discuss the relation between these structures and reactivities in various reaction systems, we have systematically investigated catalytic bond activation of NO, N_2, and O_2 on hexamers M_6 of eight transition metals (M = Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au) by density functional theory calculations. For all the 24 cases, the lowest energy structures at the molecular-adsorption state, bond dissociation transition state (TS), and dissociative-adsorption state were identified by a systematic procedure. Furthermore, using the obtained dataset, a simple linear regression analysis was made to explore the applicability of the Brønsted–Evans–Polanyi (BEP) principle to flexible metal cluster catalysts. The computational details are described in our recent paper (T. Ichino et al., *ChemCatChem* **2019**, *11*, 1346-1353).

The bare M_6 clusters considered here took various geometries (e.g., octahedron for Rh_6, triangular prism for Ir_6, and planar triangle in Au_6). At TS of 20/24 cases, the M_6 moiety changed to similar shapes to metastable isomeric structures in the bare state. The results will expand the generality of the recent discussion that metastable isomers play significant roles in metal cluster catalysis. As the results of simple linear regression analysis, the bond activation energies correlated linearly with the reaction energy changes, demonstrating that the BEP relation exists in the present systems. This result will expand the applicability of the BEP principle to flexible systems.



Key Factor of the S_0/S_1 Minimum Energy Conical Intersection

P056

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The minimum energy conical intersection (MECI) geometries play an important role in photophysics and photochemistry. Especially, the MECI between the singlet ground (S_0) and lowest singlet excited (S_1) states are essential to understand the decay process of photoexcited molecules such as a radiative process emitting fluorescence and a transition to the lowest triplet state via intersystem crossing. Quantum chemical calculations provide various types of S_0/S_1 MECI geometries such as ring strain, ring opening, π-bond rotation, and σ-bond dissociation. Contrary to the equilibrium geometries in the ground and excited states, which can be well understood by the chemical bond theory, the chemical interpretation of MECI geometries is still far from comprehensive understanding.

In this study, a systematic analysis was performed on the S_0/S_1 MECI of organic molecules.[1] The frozen orbital analysis, which approximates the excited states with minimal main configurations, was adopted to analyze the excitation energy components at the S_0/S_1 MECI geometries as well as the S_0 and S_1 equilibrium geometries. At the S_0/S_1 MECI geometries, the HOMO−LUMO gaps decreased as expected, but did not vanish. The remaining gaps were balanced with the HOMO−LUMO Coulomb integrals. Furthermore, we discovered that the HOMO−LUMO exchange integrals became approximately zero. Based on the features, we examine a methodology to obtain the molecular geometries of MECI. The new optimization scheme and performance will be explained in the presentation.

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The Production of Formic Acid and Formaldehyde From CO_2 Using Boron-Doped Diamond: A Theoretical Study

P057

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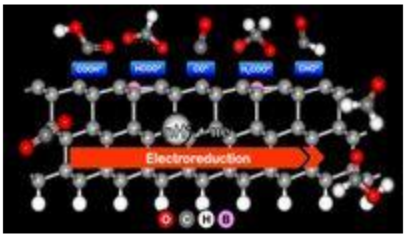

Graphical abstract

Electrochemical synthesis holds significant promises in the carbon dioxide conversion to fine and commodity chemicals. Many different electrode materials have been used, with varies product selectivities to alcohols, aldehydes, and hydrocarbons. Boron doped diamond (BDD) is regularly used in redox reactions because it is a metal-free electrode with a wide potential window and low background current. Nevertheless, the stability of the BDD surface as a function of hydroxyl, oxygen and hydrogen coverage at different electro-potentials have not been studied, and therefore, the reasons for its tendency to convert CO_2 towards low molecular weight aldehydes is unidentified. This work presents the electronic properties of the BDD surface terminated with H, OH, and O species at different coverages in the vacuum and aqueous phase. Additionally, minimum energy pathways of the reaction of CO_2 towards formic acid and formaldehyde were investigated using periodic density functional theory. It will be shown that oxygen species is in average 80 kJ mol^{-1} more strongly bound to the surface than H and OH, and that solvation increases the stability of the oxygen covered BDD surface. Therefore, the kinetics of water and hydroxyl dissociation at the BDD surface will play an important role in the CO_2 activation. Additionally, CO_2 reactions at selected oxidised BDD surfaces via formate ($CO_2^* + H^+ + e^- \rightarrow HCOO^*$), carboxylate ($CO_2^* + H^+ + e^- \rightarrow COOH^*$) and CO hydrogenation ($CO_2^* \rightarrow CO^* + O^*$) will be shown in detail.

The Role of Solvation in Predicting Protein-Ligand Binding Affinities: Validating the Automated Topology Builder

P058

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University of Queensland, Brisbane, Australia

The calculation of protein-ligand binding affinities using classical molecular dynamic simulation techniques has the potential to significantly accelerate the drug discovery process. The affinity of a ligand binding to a specific protein is directly related to the difference in free energy between the solvated ligand and the protein-ligand complex. The Automated Topology Builder (ATB, atb.uq.edu.au) has been shown to be able to accurately reproduce the solvation free energies of small molecules. However, the ability of the ATB to accurately predict protein-ligand binding free energies remains to be determined. A set of 8 protein-ligand systems that had been used previously to validate the OPLS and GAFF force fields was selected. Before computing interactions between the ligands and protein the extent to which the experimental binding affinities reflect interactions with the protein, as opposed to simply differences in solvation, was investigated to determine the utility of the test set. This was done by comparing the protein-binding affinities to the ΔGhydration and ΔGpartitionH2O→Hexane. It was found that in some cases the systems selected are not a valid test of differences in protein-ligand interactions. For example, in the case of CDK2 the differences in solvation using the ATB parameters are just as predictive as the ligand-protein binding calculations using either OPL3 or GAFF. An analysis of the appropriateness of these test systems will be presented together with the discussion of other challenges associated with the validation of ligand force fields.

An Exploration of Bifurcation on a Reaction Route Network of a Diels-Alder Reaction Based on the AFIR Method

P059

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Bifurcation is a reaction that gives two products because of a reaction path branching after passing through a transition state [1]. Although intrinsic reaction coordinate (IRC) is widely used in analyses of chemical reactions, bifurcations cannot be described using IRC. It is known that when a bifurcation occurs, the shape of the potential energy surface perpendicular to the reaction path changes from a valley to a ridge, which is called valley-ridge transition (VRT). In the previous studies, bifurcations were discussed using *ab initio* molecular dynamics simulations. Computing frequencies of vibrational modes perpendicular to an IRC path was done to investigate the occurrence of VRT. However, the computational costs of these methods are high. Recently, several automated reaction path search methods have been reported, and analyses of chemical reactions using reaction path networks in which minima and transition states are connected by IRC paths have become possible. In the artificial force induced reaction (AFIR) method [2], one of the automated reaction path search methods, a reaction path is traced by minimizing the model energy function called the AFIR function in which artificial force term between fragments is added to the potential energy function. The minimization path on an AFIR function is called an AFIR path. In the present study, a method to explore bifurcations on a reaction route network by investigating the AFIR paths is proposed. The present method was applied to a Diels-Alder reaction of 2-vinylfuran and 3-methoxycarbonylcyclopentadienone, which has been reported as a reaction accompanying a bifurcation. It was shown that the previously reported bifurcation could be detected using the present method. In addition, some other bifurcations were newly found in the reaction route network of the Diels-Alder reaction.

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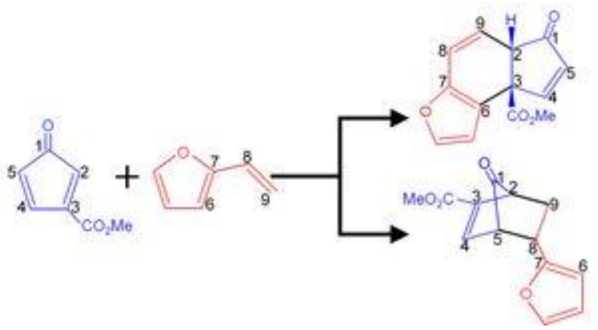

Investigating the Mechanism of High Performing Dielectric Materials

P060

Miss Lilit Jacob, Dr Terry Frankcombe

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Colossal permittivity (CP) dielectric materials have emerging applications in microelectronics and high-density storage materials. High permittivity and low dielectric loss are the desired characteristics of an optimal performing dielectric material. Achieving both colossal permittivity and low dielectric loss remained a challenge for many years. Nevertheless, a new class of materials were discovered recently which have the ideal dielectric material properties. The discovery of this highly efficient In + Nb doped TiO2 material (INTO) triggered extensive research on new CP materials. However, the applications of these materials are restricted due to the extreme synthetic conditions at the industrial level as compared to small scale laboratory preparation conditions. Therefore, it is necessary to understand the mechanism leading to the colossal permittivity and low loss characteristics of the corresponding materials, in order to achieve the practical applications.

Initially we are focusing on the mechanism of INTO materials, which will be further extended to other CP materials. In fact, a mechanism called Electron Pinned Defect Dipole has already been proposed for the CP behaviour of INTO material. Even though this mechanism seems like a reasonable fit to the nature of the material, there is not much evidence supporting the claim. We are carrying out detailed investigation of the structural and electronic characteristics of the INTO materials out using Density Functional Theory. Band structure calculations and projected charge density analysis depicts the electron hopping over localized states as the origin of the low dielectric loss in these materials.

Identifying Binding Modes of Neurosteroids at an Intra-subunit Pocket on $GABA_A$ Receptors

P061

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Type A gamma-aminobutyric acid ($GABA_A$) receptors belong to the Cys-loop receptor superfamily of ligand gated chloride channels. Various drug design campaigns have succeeded in developing pharmacologically and clinically important drugs that modulate the inhibitory effects of the neurotransmitter GABA on $GABA_A$ receptors. Neurosteroids binding at the transmembrane region of $GABA_A$ have an established therapeutic role in treating behavioural disorders. In order to develop more effective compounds based on the neurosteroid scaffold, we aimed to characterise their binding mode in detail. A recent publication (Chen et al., 2018), points to a neurosteroid binding-site within the alpha1 subunit not previously observed in resolved $GABA_A$ structures. The binding mode of these compounds was studied using carefully equilibrated molecular dynamics simulations performed on the OpenMM GPU-accelerated platform. We calibrated flat-bottom restraints through a series of simulations to establish the balance necessary to maintain the compounds at the binding-site while allowing unbiased sampling. Stable binding modes were identified for the compounds studied herein and we report the important interactions observed during the simulation. This will form the basis for experimental validation of the important binding residues and refinement of the neurosteroid scaffold.

Implications of Hybrid Organic-Inorganic Functionalized Dodecaborane Dianions in Lithium and Magnesium Ion Batteries

P062

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For the development of magnesium ion batteries the search for a better electrolyte anion is one of the highly challenging tasks. Recently the boron cluster anion, viz., $CB_{11}H_{12}^-$, has been experimentally shown to have excellent properties as a halogen free anionic component of the electrolyte for Mg ion batteries.[1] Moreover, highly stable inorganic derivatives of the dodecaborane dianion, namely, $B_{12}(CN)_{12}^{2-}$ [2] and $B_{12}(SCN)_{12}^{2-}$ [3] are theoretically predicted to be excellent electrolytes for lithium and magnesium ion batteries.

In this context, we have theoretically proposed hybrid organic-inorganic derivatives of $B_{12}H_{12}^{2-}$, viz., $B_{12}X_{12}^{2-}$ (X = -C≡C-CN and -C≡C-BO) using density functional theory.[4] Both $B_{12}(C{\equiv}C\text{-}CN)_{12}^{2-}$ and $B_{12}(C{\equiv}C\text{-}BO)_{12}^{2-}$ possess high stability in the gas phase. The presence of the organic-inorganic functional group in the $B_{12}H_{12}^{2-}$ increases the solubility of $B_{12}X_{12}^{2-}$ in low polarity solvents. Both $B_{12}(C{\equiv}C\text{-}CN)_{12}^{2-}$ and $B_{12}(C{\equiv}C\text{-}BO)_{12}^{2-}$ are found even more suitable electrolyte anions than that of the $B_{12}(CN)_{12}^{2-}$ and $B_{12}(SCN)_{12}^{2-}$ because Li^+/Mg^{2+} salt of the former two dianions require less energy to dissociate into corresponding cation and anion in the solvent. In addition, the oxidation potential of $B_{12}(C{\equiv}C\text{-}CN)_{12}^{2-}$ and $B_{12}(C{\equiv}C\text{-}BO)_{12}^{2-}$ vs Mg^{2+}/Mg is very high (12.58 and 12.91 V). Therefore, these dianions are proposed as better electrolytes for reversible Li and Mg ion batteries. Thus the present work shows the possibility of designing desired multiply charged stable anions for appropriate applications through suitable organic-inorganic functionalization.

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Computational Insights into the Origin of Enantioselectivity in a Palladium Catalyzed Dynamic Kinetic Asymmetric Transformation of Racemic Biaryls

P063

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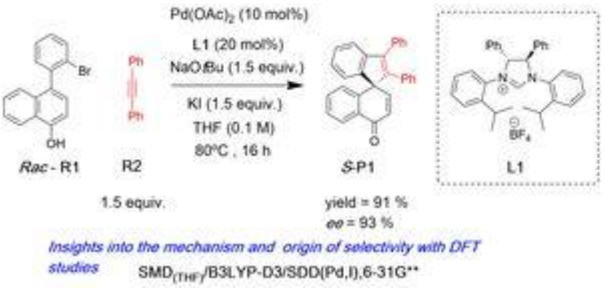
Dynamic Kinetic Asymmetric Transformation (DYKAT) involves the conversion of a mixture of enantiomers or a diastereomeric mixture of enantiomers to a single enantiomeric product with quantitative yield and highest enantiomeric excess (>99%). We became interested in addressing the energetic issues of DYKAT of racemic biaryls accomplishing axial-to-centre chirality transfer.[i] The reaction involves catalytic spiroannulation of 4-(2-bromophenyl)naphthalen-1-ol with diphenylacetylene leading to one of the enantiomeric product with a quaternary stereocenter in high selectivity. We became curious to learn this dual catalytic example[ii] consisting of $Pd(OAc)_2$ and a chiral N-heterocyclic carbene, along with NaO^tBu and KI in THF as solvent.To gain insights into origin of stereoselectivity, mechanistic investigation was carried out by using the B3LYP-D3 functional. An iodide bound anionic Pd(0)-NHC species with THF-bound Na ion as the counter ion was found to be the most likely active catalyst. The process of dearomatization of phenol ring leading to the formation of a quaternary stereocentre is found to be barrierless when it proceeds through the intermediate formed entirely from the *R*-biaryl. It was found that intermediate formed from the *S*-biaryl after migratory insertion is converted to the corresponding intermediate in the *R*-biaryl pathway through a rotation along C−C biaryl bond.



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Stabilising Molecular Fragments of Group 13, 15 Heteronuclear Diatomics

P064

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The donor-acceptor approach has now been extensively used to stabilise molecular fragments (atoms or molecules) of the main group elements to form “molecular materials”. These molecular materials may or may not be stable in their material form. We present here a theoretical investigation to stabilise group 13-15 heteronuclear diatomics with the help of donor ligands (cAAC, NHC). Group 13-15 diatomics are well known in their bulk material form for their use in electronics as semiconductor materials. Stabilising them in their molecular form opens up the potential for possibly a new route of their synthesis (which at present requires very harsh reaction conditions). These molecular materials can also act as a soluble form of the otherwise insoluble bulk material. Our results from a DFT investigation suggests that these diatomics can be stabilised by the use of one donor ligand (there are previously reported studies when these fragments have been stabilised by the use of two donor ligands, which suggests they have a different bonding model as well). The bonding and electronic structures of these systems have been explored by the aid of MO, NBO and EDA analysis. Multireference methods were employed to investigate AlN, which has a multiconfigurational character.

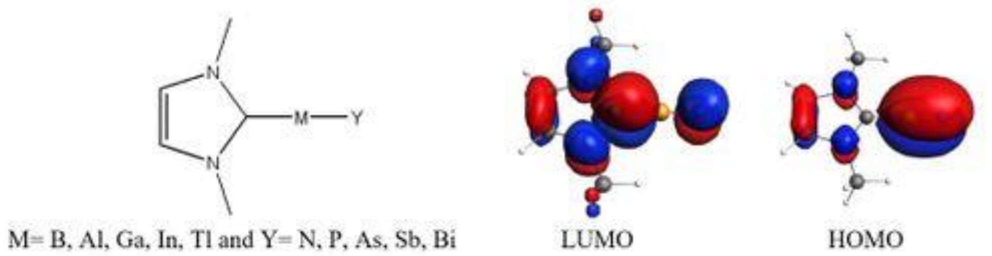

Fig. 1 Ligand-stabilised diatomics, with plots of molecular orbitals of NHC-BN.

Examination of Statistical Methods for Analyzing Fragment Molecular Orbital Calculation Results on Ligand-Protein Interactions.

P065

Mr Yusuke Kawashima[1], Ms Nanami Mori[1], Dr Hirotomo Moriwaki[2], Dr Norihito Kawashita[3], Dr Yu-Shi Tian[1], Dr Tatsuya Takagi[1]

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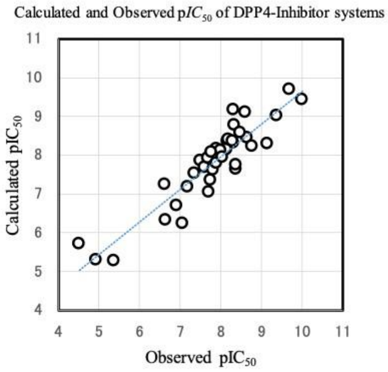
Fragment Molecular Orbital1) (FMO) method is one of the powerful computational methods for assisting Structure-Based Drug Design (SBDD). FMO method is considered to give more accurate protein-ligand interaction energies than classical molecular mechanics. FMO also gives Inter-Fragment Interaction Energies (IFIE) easily. Thus, we can explain the interaction energy results easily using IFIE values.

Although FMO gives plenty of information with regard to interaction energies, analyzing methods are still under development. For example, usually, large numbers of IFIE values are obtained against a smaller number of protein-ligand experimental free energy changes, which presents a so-called n<p problem. Thus, advanced statistical methods are required for solving the problem.

In this study, we applied some statistical methods (PLS and Sparse PLS) to analyze FMO calculation results of DPP4-inhibitor systems, which is one of the antidiabetic drugs and has sufficient PDB data for analyzing the relationships. Using the Sparse PLS, a better correlation coefficient between calculated and experimental pIC50s of the inhibitors were obtained. As a result of this statistical compensation for FMO results, charged amino acids were corrected more than other amino acids. Although this result shows a sufficient correlation between the observed and calculated pIC50s, some of the coefficients of the multiple regression type PLS expression are unexplainable. Thus, we are trying to compensate for the FMO results by SCIFIE2), which corrects overestimated long-range electrostatic interactions. Their details are going to be shown in the presentation.



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HACA Accelerated: The Role of the Submerged Barrier in the Rate of Radical-Acetylene Addition Reactions

P066

Mr Patrick D Kelly[1], Mr Oisin J Shiels[1], Mx Aislinn J Turner[1], Mr Brett R Burns[1], Mr Cameron C Bright[1], Prof Stephen J Blanksby[2], Dr Gabriel da Silva[3], A/Prof Adam J Trevitt[1]

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Acetylene is known to be a key reactant in molecular weight growth chemistry of combustion environments. In the well-studied HACA reaction (H loss, C_2H_2 addition), two acetylene molecules add sequentially to a phenyl radical, to form naphthalene. The HACA reaction is observed only at high temperatures, owing to the positive energy barrier to the first acetylene addition. However, low-temperature molecular weight growth reactions are known to be significant in extraterrestrial chemistry, particularly in the interstellar medium and in Titan's atmosphere. Key formation mechanisms for nitrogen-substituted polycyclic aromatic hydrocarbons (NPAHs) are currently under scrutiny, but could involve the molecular weight growth reactions of both ions and radical species.

Acetylene addition to pyridine- and aniline-based distonic radical cations is reported at room temperature, using ion-trap mass spectrometry. These reactions occur with efficiencies between 0.1% and 40%, with the 3- and 4-dehydroanilinium radical cations reacting 2 orders of magnitude more slowly with acetylene than the 2-dehydroanilinium radical cation, and all three dehydropyridinium radical cations. Preliminary calculations with M06-2X-D3(0)/6-31++G(2df,p) indicate that the energy of the inner, adduct-forming transition state is correlated with the reaction efficiency – acetylene reacts with 3- and 4-dehydroanilinium radical cations through an inner transition state with energy within 0.3 kcal/mol of the separated reactants, whereas the other radical cations react with inner transition states approximately 5 kcal/mol below the energies of the separated reactants. To what extent the inner transition state is 'submerged' relative to the reactants may therefore prove critical in identifying reactions that may occur in the low temperature conditions of Titan's atmosphere.

Control of Ziegler-Natta Catalyst Activity by the Structural Design of External Donor

P067

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We present the laboratory synthesized two new cycloalkoxysilanes which have been evaluated as external donors in heterogeneous Ziegler-Natta catalyst for the synthesis of polypropylene. Polymerization of propylene was carried out using 4th generation Ziegler-Natta (ZN) catalyst containing diisobutylphthalate (DIBP) as an internal donor in conjunction with triethylaluminium (TEAL) as cocatalyst. To exploit the experimental behavior and structural aspects of these new external donors *i.e.* control of the tacticity and productivity of polypropylene polymer, quantum mechanical calculations (DFT) using B3LYP (Becke-3-parameters,Lee-Yang-Parr) functional were performed on known commercial alkoxysilanes to generate the electronic and structural aspects of external donors then these were implemented over newly synthesized external donors. The theoretical binding energies of complex formed between the external donors and the co-catalyst were found to have a fair correlation with the experimentally measured productivity of polypropylene. The comparative results confirmed that certain essential structural characteristics are required to achieve high activity of catalyst and stereospecificity of polypropylene.

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Size-Dependent Level Alignment Between Anatase and Rutile TiO_2 Nanoparticles

P068

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It is well known that conventional local-density approximation (LDA) and generalized gradient approximation (GGA) based functionals severely underestimate the band gap of oxides including TiO_2 materials. The broadly used hybrid functionals such as PBE0 and B3LYP give too large calculated band gap values for TiO_2. To avoid so-called band gap problem in DFT and to describe the electronic structure of TiO_2 materials properly, we proposed a modified hybrid functional containing 12.5 % of non-local Fock exchange called as PBEx [1]. Based on this PBEx functional, the prediction of size dependent band alignment in anatase and rutile nanoparticles was investigated [2]. A predictive map of how the anatase-rutile level alignment varies from the smallest nanoparticles to the bulk was provided on the basis of vacuum-referenced electronic levels. In agreement with most recent works, a staggered type II anatase level alignment is predicted for the bulk, which we further find to persist into the regime of large NPs. Our results also suggest that other level alignments which are less favorable for photocatalysis will emerge when the diameter of the TiO_2 NPs is reduced below ~15 nm.

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Practical Excited-State Simulation of Thousands of Atoms

P069

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Excited-state dynamics is attracting much attention in various fields such as bio- and nano-science, for example, from the viewpoint of light-energy conversions and emission processes. In addition to experimental studies, various theoretical approaches have been performed from the microscopic point of view. However, simulations of excited-state dynamical process of practical bio- and/or nano-systems might not be feasible due to the large computational costs. Our research group has developed divide-and-conquer density functional tight-binding molecular dynamics (DC-DFTB-MD) method in order to perform the large-scale simulations in the ground state. The present study extended the DC-DFTB-MD method to time-dependent (TD) theory, as denoted by DC-TDDFTB-MD, to treat excited-state dynamics.

In the presentation, theoretical background, implementation, and illustrative applications will be explained. Photoactive yellow protein (PYP) (~2000 atoms) exhibits an absorption maximum at 2.78 eV, while the absorption maximum of chromophore occurs at 4.37 eV in water. Thus, the red-shift is 1.59 eV. The excitation energy shift could be reasonably reproduced by the present method as well as the correlation method, namely, DC-TDDFTB (1.46 eV), DC-TDDFT (1.43 eV), DC-SACCI (1.63 eV), respectively. On the other hand, the wall time of DC-TDDFTB was drastically short, i.e., DC-TDDFTB (1.87 seconds), DC-TDDFT (~3 hours), DC-SACCI (~11 hours). The lifetime of 2-acetylindan-1,3-dione (AID) in acetonitrile solvent following the fluorescence could be also demonstrated by the DC-TDDFTB-MD simulations with the use of the all-atom model (~900 atoms) of AID and explicit 150 acetonitrile molecules.

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Catalysis by Pure Graphene - From Supporting Actor to Protagonist through π-π Interactions

P070

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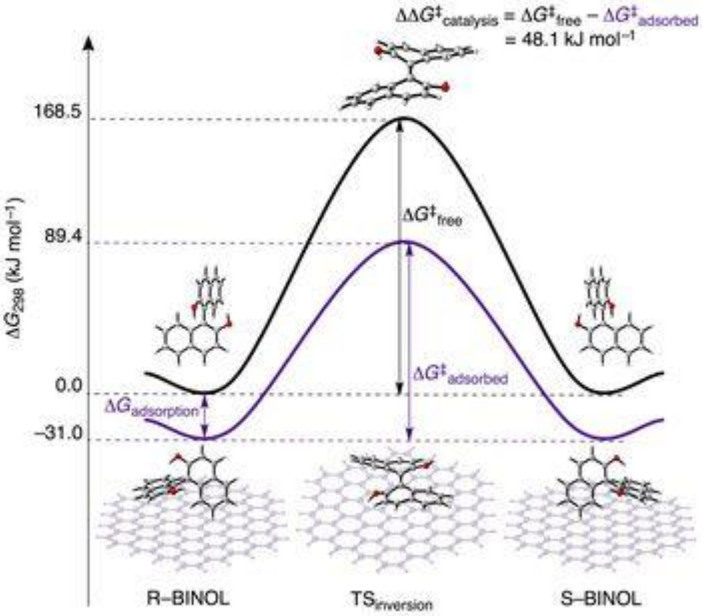
Since its first isolation in 2004, graphene has been extensively studied for its numerous exceptional properties such as its conductivity and mechanical strength.[1] While its ability to non-covalently bind molecules has been well studied for applications in sensors and extraction devices,[2] this principle remains surprisingly unexplored for the sake of stabilizing transition structures. Given the current interest in metal-free catalysis,[3] expanding the application of this concept to transition structures has the potential to open up opportunities for applications of graphene as a catalyst. Herein, we explore the possibility to lower the activation energy of a chemical process purely through stabilizing π-π interactions between transition structure and graphene using density functional theory methods. On the simple example of binaphthyl racemizations we find a significant catalytic effect originating from π-π interactions and shape-complementarity between catalyst and transition structure indicating the potential for applications of pure graphene in catalysis beyond its use as a catalyst support.



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Role of Atmospheric Molecular Clusters in the Atmosphere

P071

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Formation of aerosols or clouds in the atmosphere significantly affect climate weather but also human health. We focus on the study of new particle formation in the atmosphere from single molecules. Colliding molecules might form clusters. If those clusters are stable enough, they then grow into aerosol particles. To perform molecules-clusters-aerosol population analysis, precise quantum chemistry calculations are required (calculations of clusters stability). We explain how we deal with obstacles such as proper configurational sampling of atmospheric molecular clusters, performing computationally exhausting quantum chemistry calculations or numerical solving of differential equations for clusters evolution where the concentration of molecules differs by several orders of magnitude. In the end, we present our research in the context of several important molecules/clusters in the atmosphere, e.g., clusters containing sulphuric acid, ammonia, guanidine, water, and other molecules.

Towards Selective nAChR Therapeutics: Identifying the Binding Mode of CMPI and NS9283 in α4β2 nAChRs

P072

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[1]Sydney School of Pharmacy, Faculty of Medicine and Health, The University of Sydney, Sydney, Australia. [2]Brain and Mind Centre, The University of Sydney, Sydney, Australia

Development of selective therapeutics targeting neuronal nicotinic acetylcholine receptors (nAChRs) is a long-sought goal which has been inspired by their established role in devastating neurodegenerative diseases. nAChRs assembled in a 3α:2β stoichiometry contain a third agonist binding site at the α4α4 interface which offers a unique opportunity to develop selective therapeutics. Compounds targeting this site seem to possess a desirable modulatory profile analogous to benzodiazepines targeting GABAA receptors. Two such compounds, CMPI and NS9283 have been proven to bind at the α4α4 agonist binding site using site-directed mutagenesis, yet their precise binding mode is yet to be revealed. We conducted molecular dynamics simulations and free energy perturbation (FEP) calculations to characterise the binding modes of CMPI and NS9283. Carefully equilibrated all-atom simulations, revealed an overlapping binding mode between CMPI and NS9283 at the α4α4 binding site with stable interactions to residues of established importance. For further validation and to establish a platform for future lead optimisation, we attempted to correlate experimentally derived potencies with the relative binding free energies of CMPI and NS9283 analogues calculated using FEP. The findings and protocols reported herein should contribute to the development selective nAChR therapeutics.

Calculating the Exact Ground State Wave Function of Two-Electron Atoms via Analytic Perturbation Theory

P073

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National Chiao Tung University, Hsinchu, Taiwan

The exact wave function of two-electron atoms can, as proposed by Fock[1], be expressed as a series expansion in the hyperradius r as

$$\Psi = \Sigma_h r^h \cdot \Psi_h(\ln(r),\alpha,d) = \Sigma_h r^h \Sigma_p \ln(r)^p \cdot \psi_{hp}(\alpha,d).$$

The challenge lies in deriving the Fock coefficients $\psi_{hp}(\alpha,d)$, which depend on the hyperangle α and the scaled interelectron distance d, as well as - parametrically - on the electron and nucleus charges, Y and Z, and the energy E.

Assuming that the ground state energy E can be expressed as a power series in the parameter Y, $E = \varepsilon_0 Y^0 + \varepsilon_1 Y^1 + \varepsilon_2 Y^2 + \ldots$, turns the Fock coefficients into power series in Y (and, less importantly, Z), and thus opens the possibility of calculating the terms of the exact wave function following the ideas of perturbation theory. Treating the components ε_y of the energy separately allows for a massive simplification of the analytical expression of the wave function.

This presentation demonstrates the methods for obtaining the terms of the exact wave function which correspond to the first-order perturbation correction and shows how the coefficients of the pure Fock expansion can be derived using the tools of perturbation theory.

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Insights into $MoTe_2$ Intrinsic Defects from Ab Initio Calculations

P074

Dr. Martina Lessio[1], Mr. Alexander Kerelsky[2], Prof. Abhay Pasupathy[2], Prof. David R Reichman[2]

[1]University of Sydney, Sydney, Australia. [2]Columbia University, New York, USA

Recent experimental results show that intrinsic defects are present even in high quality semiconducting transition metal dichalcogenides (TMDs) such as $MoTe_2$. Some of the defects manifest themselves as true atomic lattice distortions with a several nanometer spatial extent, an unexpected finding in semiconducting TMDs. Additionally, these defects appear to be associated with magnetic properties and might thus be desirable for specific applications such as spintronics. However, the nature of the defects and the origin of the several nanometer-scale lattice distortions remains unknown. In this contribution, we use periodic density functional theory calculations to gain insights into the features of these defects. In particular, by comparing computed local density of states plots to experimental scanning tunneling microscopy images, we find that the defects are likely to be antisite defects in which Mo atoms replace chalcogen atoms. Additionally, we compute phonon spectra of the defective structures and compare them to the phonon spectrum of the pristine material to determine whether the hypothesized defects can be responsible for the lattice distortions observed in the experiments.

Scaffold-based Molecular Design Using Graph Generative Model

P075

Mr Jaechang Lim, Mr Sang-Yeon Hwang, Mr Seungsu Kim, Mr Seokhyun Moon, Prof Woo Youn Kim

KAIST, Daejeon, Korea, Republic of

Scaffolds of molecules play a critical role in determining their molecular properties. Thus, generating molecules retaining a specific scaffold as a substructure has practical advantages in molecular design, for instance, in drug discovery. Accordingly, we developed a scaffold-based molecular graph generative model. The model generates new molecular graphs by extending the graph of a scaffold through successive additions of atoms and bonds. In contrast to previous related models, our model guarantees that the generated molecules have the scaffold as a substructure.

The model showed high validity, uniqueness, and novelty of generated molecules, showing that the model can learn chemical rules of adding atoms and bonds rather than simply memorizing the training set. We also tested that our model can generate molecules with desirable properties. Despite the fact that the scaffold restricts the search space, our model successfully generated new molecules with a desirable molecular property while retaining a scaffold. Moreover, the model can simultaneously control multiple molecular properties of generated molecules. We further tested that scaffold-based generation strategy is applicable for designing epidermal growth factor receptor inhibitor (EGFR) where only a small amount of labeled data is available. We trained the model with both a small amount of labeled data and a large amount of unlabeled data in a semi-supervised manner. As a result, the model designed new potential EGFR inhibitors whose predicted binding affinity is about 1.5 higher than those of their scaffolds in terms of pIC50.

Investigating the Effects of Membrane Lipid Composition on Neurotransmitter Transport Function

P076

Miss Yiechang Lin, Dr Katie A Wilson, A/Prof Megan L O'Mara

Australian National University, Canberra, Australia

Mutations in neurotransmitter transporters in the SLC6 family have been implicated in a range of psychiatric disorders including ADHD, depression, Parkinsons and addiction, rendering them attractive targets for studies into mental disorders. Interactions between these lipids and embedded membrane proteins are known to play a regulatory role with regards to protein activity, localisation and trafficking. Due to the complexity of natural membranes, most membrane proteins have been investigated in the context of simplified model bilayers containing only a few key lipid species. While this reduces the complexity of system set up, it is unclear whether the omitted lipid species play critical roles in protein modulation.

Using coarse grained molecular dynamics simulations of the dopamine, serotonin and glycine transporter proteins in a complex model of the neuronal membrane, and in a two-component POPC-cholesterol membrane, we investigated how lipid composition affects physical membrane properties such as membrane thickness and fluidity. In addition, analysis of how different lipid species cluster around the protein through density calculations provides pertinent information on the kind of lipid-proteins taking place within these simulated systems.

Finding Electrons: Transforming Chemical Thought by Analysing Wavefunctions

P077

Dr Yu Liu

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Localized valence bond theory and the delocalized molecular orbital theory are always being discussed in terms of which is the better description of electronic structure. Molecular orbital theory is preferred by most theoretical chemists. However, the chemical sense of the practising chemist is based on valence bond theory. What is missing is an intuition-free method to inspect the high dimensionality electronic wavefunction to recover chemical intuition from MO calculation.

A method is aimed to visualise the many-electron wavefunction into hyper-regions related by permutation symmetry. These hyper-regions represent "tiles" of the wavefunction from which the wavefunction may be regenerated in its entirety upon application of the set of permutations of electrons from one spin. A Voronoi diagram is constructed from a complete set of even permutations of the average position of Monte Carlo walkers sampling Ψ^2. When one of the identical 3N-dimensional Voronoi sites is projected onto each electron, chemical motifs are naturally revealed, including single, double and triple bonds.

The structures of some molecules such as N_2 and F_2 give connections with the double-quartet of Linnett. Molecules such as CH_4 and C_2H_4 show the corresponding chemical bonds which are satisfied by common chemical sense. C_2's structure, which is in terms of a near triple bond with singlet-coupled outer electrons, is arrived by this method with a conguration interaction calculation.

Despite being one of the most important discussions of chemical thought, the "curly-arrow" notation of reaction mechanisms has been treated with suspicion: the connection with rigorous molecular quantum mechanics is still unclear. The analysis of the wavefunction tile along a reaction coordinate is demonstrated to reveal the electron movements depicted by the canonical "curly-arrow" notation for several reactions such as S_N2 and the 4 + 2 Diels-Alder reaction. It is a breakthrough in connecting traditional depictions of chemical mechanism with state-of-the-art quantum chemical calculations.

Spin Crossover Induced by Non-covalent Interaction of a Metal-Organic Complex with N-Doped Graphene

P078

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Controlling the electronic and magnetic states of single molecules represents a big challenge towards miniaturization of electronic devices to the molecular scale. So far, modification of spin states of single molecules was achieved by applying various external stimuli including temperature, light, and magnetic/electric fields. Here, we demonstrate a way to control the spin state of a single iron(II) phthalocyanine molecule by its positioning on N-doped graphene.[1] By means of the high-resolution scanning probe microscopy with functionalized tips, we observe distinct sub-molecular contrast over molecules located on bare graphene and in the vicinity of nitrogen dopants. The spin transition was explained using state-of-the-art theoretical methods, from which it is evident that the weak intermixing between the z-component orbitals of N-graphene (p_z of N-dopant) and of FePc (d_{xz}, d_{yz}, d_{z^2}) result in the reordering of the Fe d-orbitals leading to spin-crossover. Moreover, it presents a method for triggering spin state transition and tuning the electronic properties of molecules through weak non-covalent interaction with suitably functionalized graphene.

1. Bruno de la Torre[†], Martin Švec[†], Prokop Hapala, Jesus Redondo, Ondřej Krejčí, **Rabindranath Lo**[†], Debashree Manna, Amrit Sarmah, Dana Nachtigallová, Jiří Tuček, Piotr Błoński, Michal Otyepka, Radek Zbořil, Pavel Hobza, Pavel Jelínek, *Nat. Commun*, **2018,** *9*, 2831 ([†]The authors are co-first authors)

The One-Electron Self-Interaction Error in 50 Density Functional Approximations

P079

Mr Dale R Lonsdale, Dr Lars Goerigk

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Spurious electron self-interaction has been one of the major failings of Density Functional Theory (DFT) to date, causing a myriad of poor results for a variety of calculations including barrier heights, bond fragmentation, metallic clusters, band gaps and charge transfer processes. One-electron corrections have been developed [1], but do not lead to systematic improvements in general thermochemistry [2] and are most useful in cases where fractional charges occur e.g. in transition states.

The self-interaction error (SIE) is present in every DFT calculation to varying degree, and therefore an in-depth study on how it manifests itself in different density functional approximations (DFAs) is warranted. The SIE presents itself as the one-electron and many-electron varieties. Herein, we focus on the first and present an investigation into its behaviour on 50 DFAs that were chosen based on their popularity, established accuracy, or novelty [3]. Our model systems are one-electron atomic and dinuclear ions, which allow us to assess the one-electron SIE directly from the energies of these calculations. We establish trends upon change of atomic-orbital basis set, DFA, inter-nuclear distance, and type of nuclei and split the SIE into density and functional contributions to establish parallels with related studies [4].

Our results reaffirm literature findings on the nature of the one-electron SIE and aid the user to choose the right DFAs for SIE. Surprisingly, many range-separated hybrid DFAs do not automatically outperform global hybrids [3]. Our study provides insights into an old problem from new angles and we hope this data can guide future method development.

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The Effect of Ionic Liquids on the H_2 Splitting Capacity of Frustrated Lewis Pairs: Computational Insights

P080

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Frustrated Lewis pairs (FLPs), Lewis acid-base adducts which are sterically hindered from forming a dative bond, have shown great potential in metal-free catalysis including hydrogen splitting. Since their conception by Stephan *et al.*[1], FLPs have been intensively scrutinised from an experimental and computational perspective to understand the mechanism of H_2 splitting in FLPs. The reaction proceeds via a bimolecular pathway in which the Lewis acid and Lewis base form a pre-organised 'encounter complex'. However, as only *ca* 2% of the total molecules are believed to be complexed at a time, the stabilisation of the FLP encounter complex is essential for enhanced kinetics of hydrogen activation.

Ionic liquids were shown to increase the proportion of complexed molecules in an FLP when compared to conventional molecular solvents,[2] but the mechanism through which this enhanced stability is achieved is unknown. This work investigates the electronic and orbital effects of the $[C_2mim][NTf_2]$ ionic liquid on the prototypical intermolecular FLP, $tBu_3P/B(C_6F_5)_3$. Hydrogen splitting by the FLP in the presence of the ionic liquid was studied via DFT to compare the effect of molecular and ionic liquid solvents on reaction kinetics and thermodynamics. Interaction energy between the FLP and ionic liquids ions/benzene is also examined to note any differences between ionic liquids and conventional molecular solvents.

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Effect of Factors on Ethylene Epoxidation by Oxoiron(IV) Porphyrin π-Cation Radical Complex in High Spin States: A DFT Study

P081

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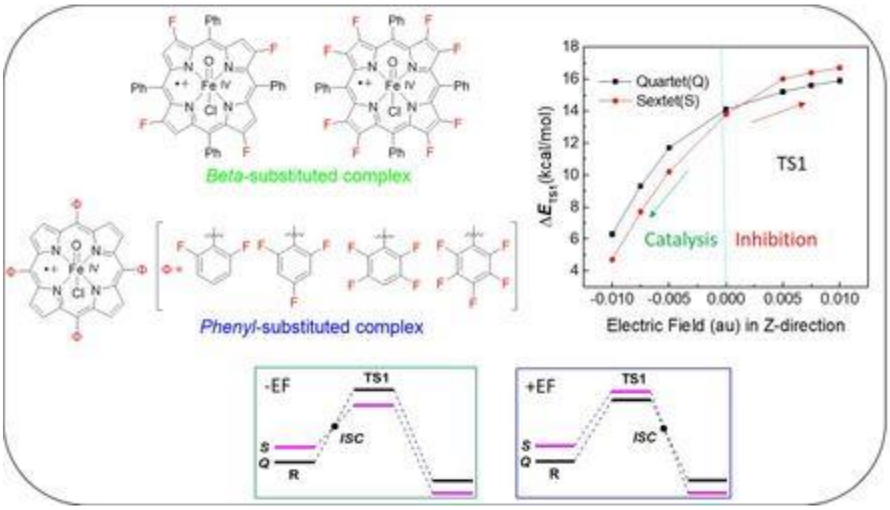
The effects of peripheral fluorine atoms and external electric field on the ethylene epoxidation by the oxoiron(IV) porphyrin cation radical complex (Compound I) in the quartet and sextet spin-multiplicities were systematically investigated using the density functional theory (DFT) method. The overall routes of epoxidation reaction were determined using a model system of ethylene and Fe(IV)OCl-porphyrin with substituted fluorine atoms under with/without external electric field. Showing the energy diagrams and contour maps of electron density difference for the transition states, we confirmed that the electron-withdrawing by peripheral fluorine atoms enhances the reactivity with more the number of fluorine atoms as observed experimentally, moreover, the direction of external electric field greatly affects reactivity. We also analyzed the behavior of the electron shift for transition state by electron density difference, and the intersystem crossing (ISC) between the quartet and sextet spin-multiplicities was discussed by means of the intrinsic reaction coordinate method. Finally, we concluded that the rate-determining step is located at the first transition state (TS1) for the activation of C=C and Fe=O bonds, and the ground electronic state changes from quartet state to sextet state around the TS1.



Determining the Mechanism of a Novel Class of Mitochondrial Uncoupler

P082

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ANU, Canberra, Australia

Targeting of the elevated transmembrane potential of the cancerous mitochondria is an attractive option for inducing cellular apoptosis. A novel family of long chain fatty acid uncouplers containing a substituted phenylurea head and carboxylic acid tail have recently been developed to this effect. We present an *in silico* investigation to determine the mechanism of experimentally determined uncoupling. Quantum chemical pKa values of protonatable sites were determined at the G3MP2(+) level of theory in aqueous solution using an isodesmic proton exchange method. Observed pKa values for the studied compounds lie outside the range at which they could be expected to reversibly deprotonate *in vivo* as part of a protonophoric uncoupling mechanism. Electrogenic trans-bilayer transport of anions was then investigated as a possible mechanism for observed uncoupling activity. Quantum chemistry calculations were conducted to determine the propensity of aryl urea uncouplers to bind carboxylate, hydroxyl or chloride anions at the M062X/6-31(+)G* level of theory. Anion binding energetics determined from quantum chemistry calculations suggest reversible binding and release of anions is a possible mechanism by which uncoupling activity can be rationalised. Correlation was also found between experimentally observed mitochondrial depolarisation of active uncouplers and a water to n-pentadecane free energy of solvation, indicating that the ability to distribute the charge of a bound anion are crucial determinants of activity for this class of compound. Molecular dynamics simulations were conducted to further examine the in-bilayer conformational space of the most potent uncoupler in relevant protonation states. The carboxylic acid form of the most potent derivative was seen to readily penetrate a GROMOS 54A7 DOPC bilayer in microsecond timescale united-atom molecular dynamics simulations. In summary, we have provided robust justification for the initially puzzling SAR for this set of compounds and have determined a mechanism for uncoupling activity observed *in vivio*.

Theoretical Insights into CO2 Hydrogenation to Methanol by a Mn–PNP Complex

P083

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The catalytic activity of PNP-based Mn(I), Fe(II) and Ru(II) homogeneous complexes for CO_2 hydrogenation to methanol has been explored. The hydrogenation occurs in the presence of a morpholine co-catalyst via a formamide intermediate. DFT calculations performed on the demonstrative reaction pathway allow us to suggest a complete reaction mechanism. The present study reports the multistep transformation of CO_2 to methanol. We propose that following initial CO_2 hydrogenation to HCOOH by metal catalysts, amidation of HCOOH to N-formylmorpholine occurs in the presence of morpholine, which further undergoes hydrogenation reaction for the formation of methanol by metal catalysts. The highly exergonic nature of the amidation step increases the overall rate of the reaction. Remarkably, the N-formylmorpholine hydrogenation step may follow two different pathways (C=O vs. C–N bond hydrogenation) and both the pathways involve comparable reaction free energy barriers for hydrogenation, i.e., both the considered reaction mechanisms are competitive in nature. Furthermore, our microkinetic modelling results agree well with previous experimental studies, which confirm that the proposed reaction mechanism is the most plausible mechanism for CO_2 hydrogenation to methanol.

Correlation Effects in the electron Spectrum and ionization Dynamics of OsO_4

P084

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Indian Institute of Technology Kharagpur, Kharagpur, India

The experimentally recorded photoelectron spectra of OsO_4 exhibit five distinct bands with varying intensities. Correct assignment of these vibronic bands requires an accurate treatment of the electronic structure and correlation in the cationic species. In this presentation, we would present a comparative account of different electronic structure methods (such as, EOM-CCSD and CASSCF) in the presence of spin-orbit coupling to provide an assignment of the experimental photoelectron bands. While both EOM-CCSD and CASSCF methods could describe the low-lying electronic states of the cation accurately, the high-energy excited states demand a multi-reference treatment with an expanded active space. That apart, the origin of spin-orbit coupling in different electronic states and their consequence in the experimental spectra will be discussed. By analyzing the state of the ejected photoelectron, the photo-ionization cross-sections have been calculated for all photo-ionization channels that adequately explain the variation of cross-section with photon energy and the resonant structures in the experimental findings. The resonant structures have been explained by calculating the asymmetry parameters and from the wave function analysis of the ejected photoelectron. It will be shown that the resonant structures are prominent when the molecular orbitals are contributed by both metal and ligand orbitals.

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Investigating the Effect of Protonation Site on stability

P085

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Protomers are protonation isomers. The effects of changing protonation site on photostability is of fundamental interest. Gas phase experiments on isolated populations of specific protomers are emerging, providing an excellent reference point for computational analysis and benchmarking. Experimental results are shown where separation of protonation isomers of protonated quinazoline and protonated nicotine is achieved and validated by comparison to computationally simulated vibronic spectra.

Reliable results for the assignment of protomer populations is calculations of excitation energies with CC2. However, description of the Frank-Condon region is possible using CC2, TD-DFT, CASSCF or CASPT2//CASSCF—each providing varying benefits and drawbacks. Finding the driving factors in the non-radiative decay pathways of protomers remains a challenge, however, these pathways appear to be modelled well using CASPT2//CASSCF or NEVPT2//CASSCF.

Polarisation of Water in Hydrated Choline Dihydrogen Phosphate and Related Ionic Liquids

P086

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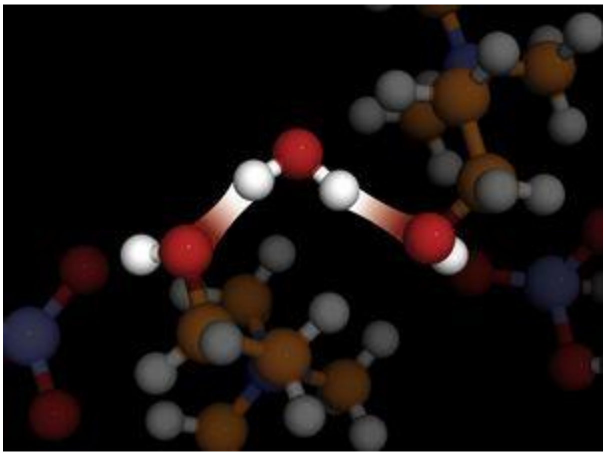
Here we investigate experimental research into the solvation of *cytochrome C* by hydrated choline dihydrogen phosphate, offering alternatives to cryogenic protein storage.[1] The interaction of water with the ionic liquid is crucial to facilitate protein solvation, with *cyt C* insoluble in the neat IL.[2]

We demonstrate that water interacts favourably with the choline cation, contrary to popular belief of strong interactions between anions and water. Hydrogen bonding is crucial in lowering the free energy of the systems studied, with a fully hydrogen-bonded network present in favourable configurations.

We propose the use of a free energy of interaction, ΔG^{INT}, quantifying the effects of intermolecular hydrogen bonding on the overall stability of the IL-water cluster, with the change in structure of water also investigated. Configurations with the largest increase in O-H bond length of water also show the largest reduction in ΔG^{INT}, suggesting that increased polarisation of water is key to enabling protein solvation.

Predicted infrared spectra demonstrate that the use of choline polarises water, indicated by a reduction in vibrational frequencies and longer intramolecular bonds. In contrast, water is depolarised in imidazolium-based ILs that do not solubilise *cyt C*. Electronic effects are also present here, with a large distribution of dipole moments present in the constituent ions of hydrated [ch][dhp], with the addition of water resulting in a redistribution of electron density throughout the entire molecular cluster, facilitating interactions with biomolecules.



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MP2-Q-F12-SOS: A Novel Efficient Method to Compute the MP2-F12 Correlation Energy

P087

Mr Simon C McKenzie, Prof. Peter M W Gill

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A major limitation of traditional ab initio methods is that we approximate the wave function as a linear combination of products of one-electron functions, which cannot accurately describe the Coulomb hole or the electron-correlation cusp. Explicitly correlated F12 methods improve this approximate description by introducing a two-electron basis function and are considered the current state-of-the-art for highly accurate ab initio calculations.

Unfortunately, the cost of an explicitly correlated method, such as MP2-F12 theory, is several times more expensive than its traditional counterpart, MP2 theory. Taking inspiration from Head-Gordon's MP2-SOS and our recent Q-MP2-SOS theories, we develop a novel efficient method for computing the MP2-F12 correlation energy that we term MP2-Q-F12-SOS.

In MP2-SOS theory, the correlation energy is approximated by a simple scaling of the opposite spin MP2 energy. The advantage of MP2-SOS is its lower formal quartic cost in comparison to the quintic cost of full MP2. We have discovered that a similar scaling of the opposite spin MP2-F12 energy can accurately reproduce the correlation energy.

In a recent work, we have reformulated the MP2-SOS energy using numerical quadrature, which we term Q-MP2-SOS. The advantage of this approach is to reduce the cost of the MP2-SOS energy from formally quartic to quadratic and expose massive parallelism. We can use similar techniques to efficiently compute the MP2-F12-SOS energy.

stability of Protonated Pyridine Derivatives in the Gas-Phase

P088

Mr Benjamin I. McKinnon[1], Mr Samuel J.P. Marlton[1], Mr James P. Bezzina[1], Professor Stephen J. Blanksby[2], Associate Professor Adam .J. Trevitt[1]

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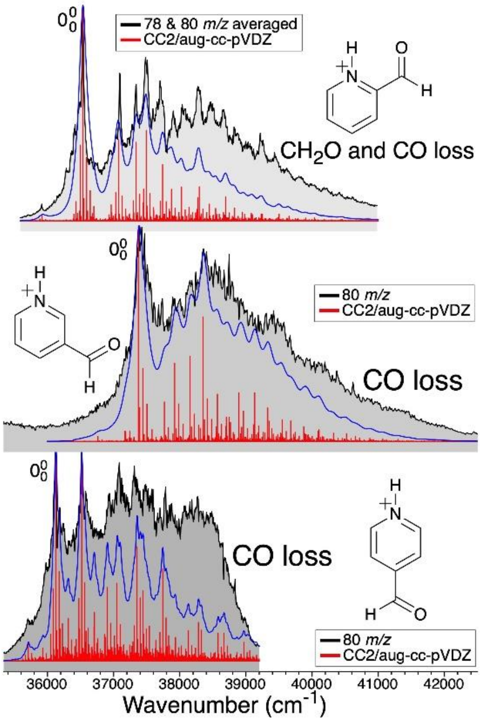
Predicting the effect of protonation on the spectroscopy and dynamics of pyridine derivatives in the gas-phase remains problematic as experimental and theoretical data are scarce. Protonated formylpyridine is the simplest aromatic aldehyde and is of importance due to containing the four atoms common to all biological life. Understanding the photostability of fundamental, protonated, *N*-heteroaromatics in gas-phase isolation will provide vital benchmark data for theoretical methods. The photostability of protonated formylpyridine is investigated experimentally within the 35000-46500 cm^{-1} (285-215 nm) energy range using an ion trap mass spectrometer coupled with a tuneable UV laser. Such experiments allow the Franck-Condon region for the initially prepared singlet excited-state due to ππ* transitions and resultant photoproducts to be observed.

Analysis of key spectral features within the investigated Franck-Condon region, including assignment of the origin, is made possible through CC2 and CASSCF methods. Experimentally observing photoproducts allows plausible potential energy diagrams to be constructed, which explain deactivation from the excited-state manifold and ultimately mechanisms leading to dissociation on the ground-state. Norrish-type I chemistry due to intersystem crossing to the triplet manifold is also observed.



Boron Nitride Nanotube Nucleation During Ni-catalysed Chemical Vapour Deposition: Non-equilibrium Molecular Dynamics

P089

Mr Ben McLean, A/Prof. Grant B Webber, A/Prof. Alister J Page

University of Newcastle, Callaghan, Australia

The catalytic chemical vapour deposition (CVD) growth of carbon nanotubes (CNTs) has been studied extensively both experimentally and theoretically, with a well understood growth mechanism. In contrast, boron nitride nanotubes (BNNTs) have been synthesised successfully via CVD though little is known regarding the catalytic pathways to BNNT nucleation and growth.[1] Here we present mechanisms detailing the nucleation and growth of BNNTs during Ni-catalysed ammonia borane CVD and Ni-catalysed boron oxide CVD (BOCVD), using ReaxFF molecular dynamics simulations, that are strikingly different to that for CNTs. Our simulations reveal that during ammonia borane CVD, the Ni catalyst activates B-H bonds to produce H_2, and subsequently frees BN fragments to form BN chains and rings on the Ni catalyst surface. Ultimately, we observe adjacent BN ring networks that grow perpendicular to the surface fusing together via B-N bonds to form BNNT caps, comprising entirely of hexagonal BN rings. For BOCVD, we observe reaction chemistry markedly different to that previously assumed from experiment.[2] We observe the Ni-catalysed production of H_2 far exceeding that of H_2O and subsequently, O hindering the formation of BN ring networks. Further, we propose future potential catalysts for BNNT growth based on density functional theory (DFT) interfacial energy calculations.

A Mirror-Image Approach to Spin Contamination in Single-Determinant Wave Functions

P090

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Wave functions constructed from spin-unrestricted orbitals are susceptible to contamination through the artificial mixing of states of higher spin multiplicity. This spin contamination results in a poor quality wave function with distorted properties such as spin density and energy. Spin contamination is common when using low-levels of theory (single-determinant methods) to model processes that involve breaking an electron pair, such as singlet excitations and homolytic bond cleavage. It is desirable to have inexpensive computational methods that are suitable for describing these states without suffering from such deficiencies.

We have developed the Mirror-Image (MI) method, which is capable of describing spin-contaminated states, while preserving the low computational cost and intuitive simplicity of single-determinant methods. The MI wave function is constructed from a linear combination of a single-determinant reference and its “mirror-image”. The mirror-image determinant is a spin-exchanged version of the reference determinant, where all the α and β electrons are interchanged.

MI wave functions have very clean $\langle S^2 \rangle$ values and provide improved energies over a single determinant, without an increased computational cost. We report excitation energies for a variety of systems, using both the MI approach and perturbative models based on it.

Exploring the Applicability of Density Functional Approximations: The Most Comprehensive Benchmark Study of Double Hybrids and Application of Low-Cost DFT to Clam-Like Cyclotricatechylene Capsules

P091

Ms Nisha Mehta, PROF Brendan F. Abrahams, DR Lars Goerigk

The University of Melbourne, Melbourne, Australia

Double-hybrid density functionals (DHDFs) are the most accurate and robust density functional approximations (DFAs) for a variety of properties. Over the past years, a large number of such DHDFs have been developed, each with their own advantages and disadvantages, but with limited cross-validation that compares different DHDFs directly with one another. In the first half of this presentation, we present our recent efforts in making the ``jungle'' of DHDFs more accessible to the user and developer communities. We present an assessment of more than 115 variations of dispersion-corrected and -uncorrected DHDFs with the help of the large GMTKN55 benchmark database. To the best of our knowledge, this is the largest DHDF benchmark study in terms of the size of the benchmark database and range of DHDFs assessed. We will address some of the risks and misconceptions in the field and address the most accurate DHDFs that will benefit the general chemistry community [1].

In the second half of this presentation, we apply reliable low-cost DFAs to gain computational insights into macrocyclic compounds that have been shown to be able to encapsulate group I metal cations. The isolation of such ions—especially from aqueous solution—is challenging due to their high hydration enthalpy but can be facilitated by the macrocyclic compound cyclotricatechylene (CTC), which is rigid bowl-shaped and can form clam-like units that can be used selectively bind metal cations. We present a detailed analysis of the factors that stabilize such CTC-based capsules at different protonation states and their interaction with various encapsulated guests [2]. These results will provide an insightful understanding and useful guidance for future synthesis of these systems.

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Full Atomistic Simulation of Ethylene/1-Octene Copolymerization Reaction Process Catalyzed by (Pyridylamido)Hf(IV) Complex

P092

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(Pyridylamido)Hf(IV) complex is a cationic catalyst (Hf-cat) which has a strong potential to incorporate α-olefin monomers, thus attracting attention as an ethylene/1-octene copolymerization catalyst. The two types of borate counteranions (CAs), $MeB(C_6F_5)_3^-$ and $B(C_6F_5)_4^-$, are widely used as co-catalysts for Hf-cat. It is well-known that the polymerization reaction proceeds faster with $B(C_6F_5)_4^-$ than with $MeB(C_6F_5)_3^-$, however, the role of these CAs in insertion reactions has not been fully elucidated. Therefore, we focused on 1-octene insertion and theoretically investigated their electronic effects by quantum mechanical (QM) calculation and dynamic effects by replica exchange molecular dynamics (REMD) calculation. As a result, we have found that both the energetics and the kinetics are totally different between the two CAs. That is, $MeB(C_6F_5)_3^-$ has a strong electronic effect to lower the transition state energy, coordinating to the Hf center by methyl moiety during the insertion process, while $B(C_6F_5)_4^-$ has a weak electronic effect, staying away from the Hf center (Fig. 1).

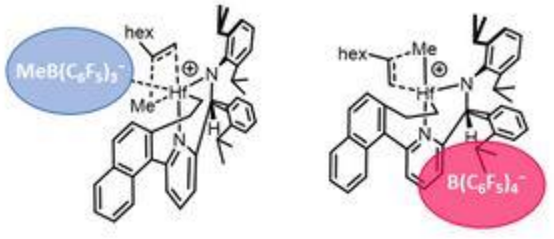

Fig. 1. Transition state structures of 1-octene insertion.

On the basis of these findings, we have also performed full atomistic simulations of 1-octene homopolymerization and ethylene/1-octene copolymerization processes using Red Moon (RM) method, a novel molecular simulation method developed by our group to simulate complex chemical reaction systems, in order to analyze their microscopic mechanisms. The RM simulation result of 1-octene homopolymerization process has reproduced the tendency of the faster reaction rate with $B(C_6F_5)_4^-$ than with $MeB(C_6F_5)_3^-$. In addition, the RM simulation result of ethylene/1-octene copolymerization process was in good agreement with the experimentally obtained ratio of 1-octene to ethylene incorporated in the generated copolymer. The details of the theoretical analysis by QM, REMD calculations and RM simulations will be provided in the presentation.

Molecular Level Explanation of the Conversion of Regio-specificity (8R to 12S) in Lipoxygenase by a Single Mutation L434F

P093

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Indian Institute of Technology, Kharagpur, India

Lipoxygenases are a family of non-haem, non-sulphur iron-containing lipid peroxidising enzymes that catalyse stereo- and regio-specific formation of hydroperoxy derivatives from poly-unsaturated fatty acids in the presence of molecular oxygen[1,2]. Lipoxygenases are found in plants, animals and fungi. Their catalytic action has important consequences in a range of inflammatory and associated diseases. In this presentation, we would discuss the presence of a multi-channel network of oxygen migration pathways that allow an effective transfer of oxygen from bulk to the active site. We will discuss the relation between oxygen population in different migration channels and formation of different stereo and regio-specific products in wild-type as well as several mutants of lipoxygenases. The results indicate a possibility of evolutionarily optimized migration channels in lipoxygenases that allow accumulation of oxygen density at certain regions to attain regio-and stereo-specificity. In particular, we will highlight the effect of a single point mutation (L434F) on the conformational dynamics in the active site and consequent change in oxygen migration channels resulting in a complete change of the regio- and stereo-specificity of the products.

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pH-Switchable Electrostatic Catalysis of Organo-SOMO Reactions

P094

Dr Ahmed Elaaf Mohamed, Professor Michelle L Coote

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Density functional theory using the M06-2X/6-31+G(d, p) level of theory was used to investigate the effectiveness of charged functional groups in producing a localised electric field to promote electrostatic catalysis in organo-SOMO catalysed reactions. The specific reactions being studied and presented here is an intramolecular α-arylation, and α-vinylation of an aldehyde as catalysed by a SOMO-activated species, generated through one-electron oxidation of an enamine intermediate. Both positively and negatively charged functional groups such as carboxylic acid and tertiary amine moieties are fixed on the enamine intermediate in an orientation to produce a local field which interacts with the dipole moment of the key transition state. Additionally, the effect of the functional group modifications on the initial formation of the enamine intermediate that undergoes SOMO-activation was also investigated.

For the above reactions, the effect of the charged functional groups will be quantified through changes in the activation energy barrier in both gas and solution phase as well as through analysis of changes in regio- and stereo- selectivity of the products due to the pH-switchable catalysis.

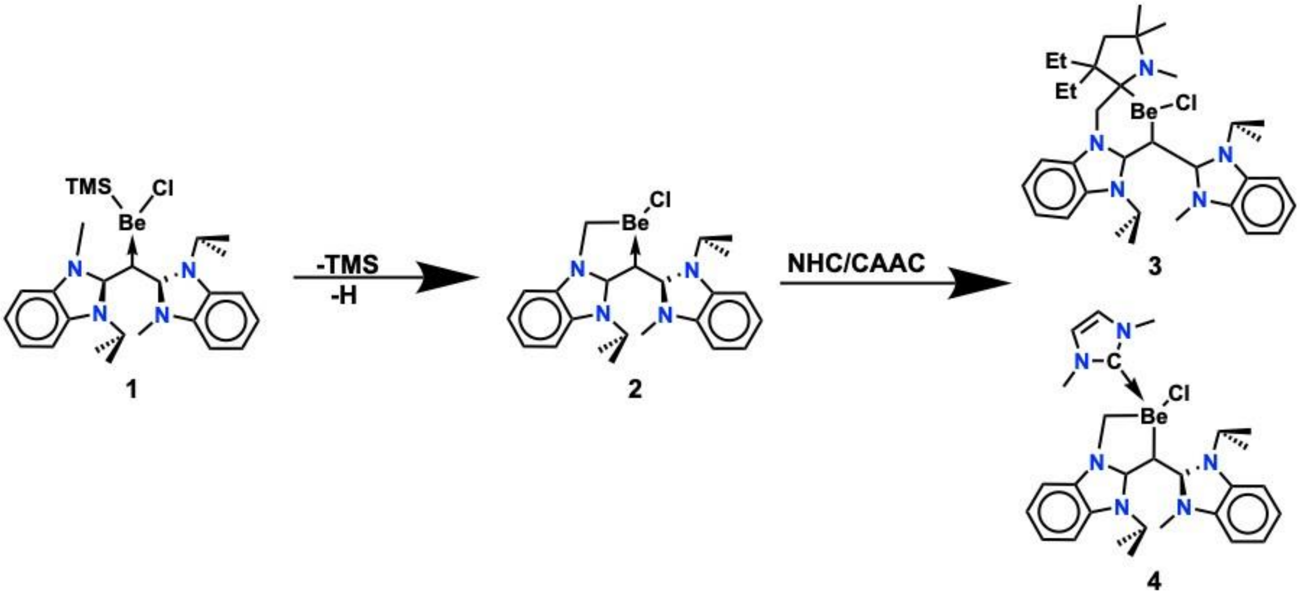
Theoretical Insights to Novel Beryllium Reactivity

P095

Mr Andrew Molino, Associate Professor David J. D. Wilson

La Trobe University, Melbourne, Australia

Recent reports have found beryllium to facilitate the activation of relatively inert chemical bonds. Therefore, interest in beryllium chemistry has grown significantly in recent years with a number of beryllium compounds stabilised by N-heterocyclic carbene (NHCs) and cyclic (alkyl) (amino) carbene (CAACs). We report results of theoretical investigations for a series of novel beryllium carbodicarbenes (CDC) in collaboration with synthetic studies.[1-3] We have utilized Atoms in Molecules (AIM) calculations and Energy Decomposition Analysis (EDA) to determine the local electronic environment of **1** and **2**. Further we have undertaken mechanistic studies to understand different reactivity to form **3** and **4**.[4]



1. J. E. Walley, G. Breiner, G. Wang, D. A. Dickie, A. Molino, J. L. Dutton, D. J. D. Wilson and R. J. Gilliard Jr, *ChemComm*, 2019, **55**, 1967-1970. 2. K. J. Iversen, D. J. D. Wilson and J. L. Dutton, *Organometallics*, 2013, **32**, 6209-6217. 3. L. A. Freeman, J. E. Walley, A. D. Obi, G. Wang, D. A. Dickie, A. Molino, D. J. D. Wilson and R. J. Gilliard, Jr., *Inorg. Chem.*, 2019, DOI: 10.1021/acs.inorgchem.9b01058. 4. J. E. Walley, A. D. Obi, G. Breiner, G. Wang, D. A. Dickie, A. Molino, J. L. Dutton, D. J. D. Wilson, R. J. Gilliard. Jr., ***Submitted***.

Colloidal Stability of Apolar Nanoparticles

P096

Miss Debora Monego[1], Mr Thomas Kister[2], Mr Nicholas Kirkwood[3], Mr Tobias Kraus[2], Mr Paul Mulvaney[3], Mr Asaph Widmer-Cooper[1]

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Metal and semiconductor nanoparticles exhibit unique properties that enable their use in a wide range of applications. In order to prevent them from randomly aggregating in solution, stabilizing agents are often chemically attached to the NPs surface. Experiments and simulations indicate that nanoparticles stability and assembly are strongly dependent on how these ligands order on their surface. We use a combination of small-angle X-ray scattering and molecular dynamics simulations to study the relationship between the temperature-dependent colloidal stability of gold nanoparticles in alkane solution and the order-disorder transition gone through by ligands coating these particles. Our results indicate that the interaction between gold nanoparticles in solution is markedly affected by the structure of the ligand shell, changing from repulsive to attractive as the ligands align with one another to form ordered bundles on their surfaces. In this work, we show how the ability of the ligand shell to order (or not) can explain a diverse range of surprising phenomena, including an inversion of the effect of ligand length on particle stability when increasing nanoparticles size, solvent effects that run opposite to the rule of “like dissolves like”, and stabilities to aggregation that increase by >3 orders of magnitude upon the addition of a single methyl group to the tail of the ligands. These changes are not accounted by existing theories such as Flory-Huggins solution theory, which may explain why they often fail to predict the stability of such systems and shows the need for improved models that include them.

A Computational Study of the Mechanism for the Enantiomerization of Tröger's Bases

P097

Miss Alyssa Dwight, Miss Sooin Byeon, Dr Damian Moran

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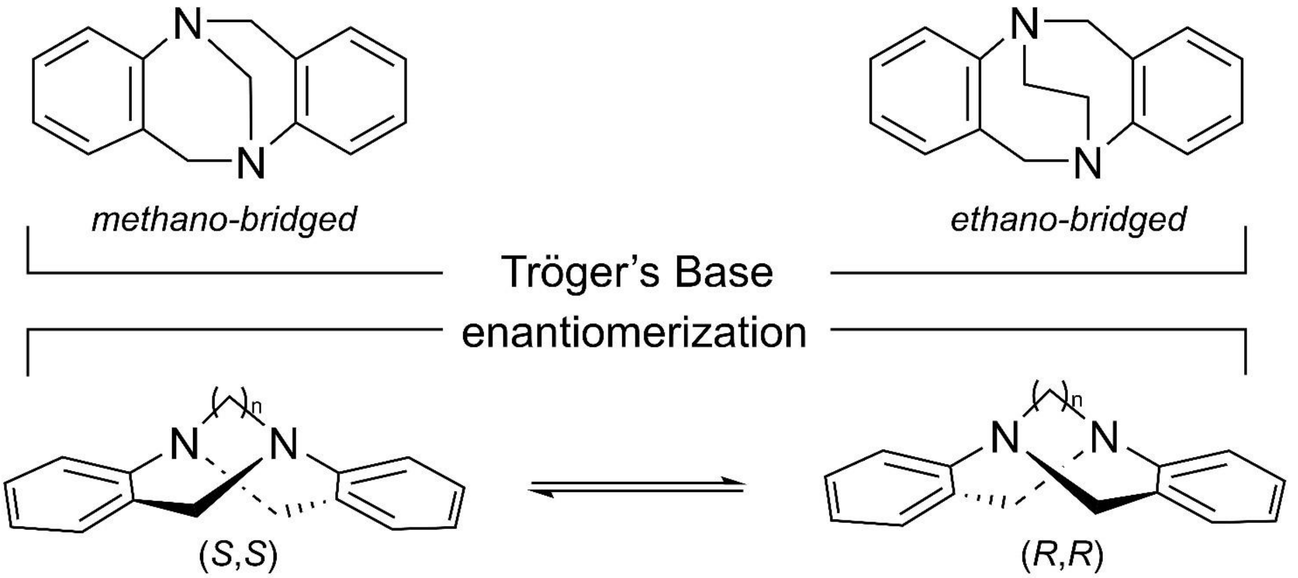
Since they were first reported late in the 19th century, Tröger's bases (TBs) have been the subject of many studies owing to their synthetic accessibility and conformationally rigid molecular framework. TB have a bicyclic structure that consists of a diazocine ring with bridged nitrogens. Pyramidal nitrogens are not generally stable to inversion of configuration, leading to a 50:50 mixture of stereoisomers under equilibrium conditions. As TBs have trivalent nitrogens locked in a rigid framework, they are configurationally stable. Interestingly, while Lewis acids promote the enantiomerization of methano-bridged TB, ethano-bridged structures retain their configuration. In this poster, we will present results from our computational investigation of the mechanism for the interconversion of TB enantiomers. We have considered the enantiomerization of both the methano- and ethano-bridged TBs via a proton-catalysed ring opening mechanism, as well as a retro-Diels–Alder mechanism. Our results agree with the available experimental data.



Molecular Dynamics Simulations on DNA Behaviour on Graphene Oxide and Reduced Graphene Oxide-PEG-NH2 in the Presence of Mg^{2+} and Cl^- ions

P098

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Introduction

Graphene is an excellent material for biosensor development, for example in nucleic acid detection. We investigate the process of adsorption of double stranded and single stranded DNA on two different graphenic species, through Molecular Dynamics (MD) simulations. The two graphene species are Graphene Oxide (GO) and reduced graphene oxide functionalized with polyethylene glycol amino groups (rGO-PEG-NH2). Furthering previous studies we factor in the presence of magnesium (Mg2+) and chloride (Cl-) ions, resulting in both dsDNA and ssDNA adsorption on the GO and rGO-PEG-NH2 surfaces.

Method

MD simulations were performed using GROMACS with the parmbsc1 forcefield containing slight charge parameter modifications in the case of ssDNA molecules.

Results

In the case of GO and either dsDNA or ssDNA, Mg^{2+} ions could act as a bridge between the GO surface and DNA molecules and encouraged adsorption through electrostatic interactions. However, in the case of rGO-PEG-NH_2 the ions remained predominantly in solution, away from the graphenic surface. For dsDNA, the oligonucleotide was principally adsorbed on rGO-PEG-NH_2 by electrostatic forces, however for ssDNA, π–π stacking interactions could contribute to an occasional anchoring of the oligonucleotide to the graphenic surface. Electrostatic interactions were found to be the predominant forces influencing adsorption, followed by hydrogen bonds and subsequently, π–π stacking interactions when applicable. Graphene functionalization in the presence of ions could introduce force differences for biosensor descrimination between single or double-stranded DNA.

This work was supported by a grant of the Ministry of Research and Innovation, Operational Program Competitiveness Axis 1 - Section E, Program co-financed from European Regional Development Fund under the project number 154/25.11.2016, P_37_221/2015, "A novel graphene biosensor testing osteogenic potency; capturing best stem cell performance for regenerative medicine" (GRABTOP).

Systematic Search for Crystal Structures of Dioxides of Group 14 Elements (CO_2, SiO_2, GeO_2) under Ultrahigh Pressure

P099

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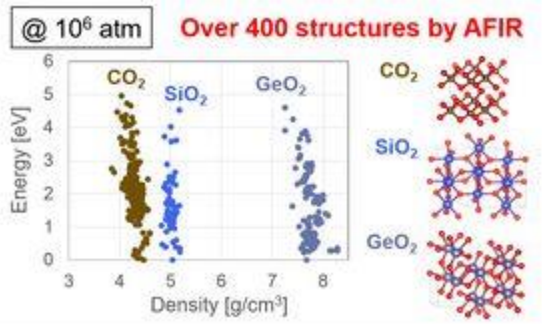
Crystal structures under ultrahigh pressure attract attention in terms of chemistry and geology. SiO_2 is a compound of the two most abundant elements in Earth's crust, silicon and oxygen, and it is well-known SiO_2 shows a variety of crystal polymorphs. GeO_2 is a chemical analogue of SiO_2 and several polymorphs have been reported. In ultrahigh pressure environments, as the interior of the earth, the most stable structure might be completely different from that under normal pressure. For example, carbon is a group 14 element and solid CO_2 (dry ice) forms a molecular crystal under normal pressure. However, it has recently been studied that CO_2 can form non-molecular crystal structures like SiO_2 in ultrahigh pressure environment of several hundreds of thousands of atm. In this study, we focused on the effect of pressure on the crystal structures of dioxides of group 14 elements, SiO_2, GeO_2, and CO_2. Systematic searches for crystal structures of each dioxide were performed by using the artificial force induced reaction (AFIR) method under 1 and 10^6 atm, respectively. A number of crystal structures including known structures have been obtained by our systematic searches. At 1 atm, over 1000 structures were obtained in various densities. On the other hand, at 10^6 atm, over 400 structures were obtained in relatively high densities. At 1 atm of SiO_2, cristobalite-like, quartz, anatase-like, and stishovite were stable structures. On the other hand, at 10^6 atm, stishovite and $CaCl_2$ type of structures were relatively stable. A similar tendency was observed in GeO_2 crystal. At 1 atm of CO_2, molecular crystal was most stable. However, quartz-like and cristobalite-like structures were obtained as stable structures at 10^6 atm. We used the AFIR method implemented in the GRRM program and electronic state calculations (PBE-D2/DZP level) with periodic boundary conditions were carried out by using SIESTA program.



Coordination Chemistry of Carbon

P100

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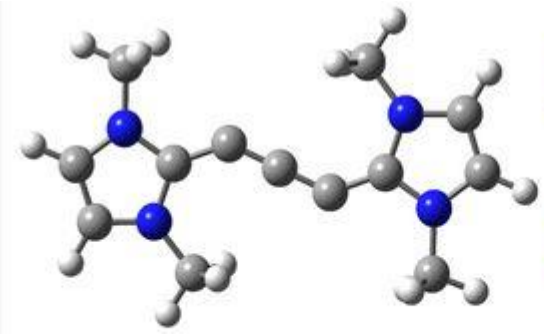
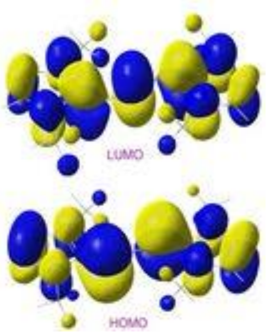
La Trobe Institute for Molecular Sciences (LIMS), La Trobe University, Melbourne, Australia

Over the last few decades, there has been a growing interest in the potential of considering coordination bonding within carbon-based molecules. Recent reports of new theoretical and experimental studies of ligand stabilised main group species in the donor-acceptor framework further extends the number and range of L-E_n-L molecules.[1,2]

Previously, Bestmann *et al.* (1989)[3] had hypothesised that the ligand stabilising C_n chain with odd value of *n* could only be achieved by two donor molecules, but even number of *n* required one donor and one acceptor ligand. The synthesis of ligand stabilised C_3 was reported by Bestmann in 1993 using the conventional phosphine ligands. Since then, the C_1 and C_2 molecules have been studied extensively with the aid of new models and new understanding of bonding. The synthesis of C_2 specie stabilised by two carbene donor ligands, appears to contradicted Bestmann's hypothesis.[4]

Here we present results of a theoretical study exploring ligands stabilised C_3 fragment coordinating by modern carbene ligands (such as NHC and cAAC). We will report results from our computational study, including molecular orbital (MO), natural bond order (NBO), energy decomposition analysis (EDA) and bond dissociation energy (BDE) analysis, in order to probe the fundamental nature of bonding, thermodynamic stability and electronic structure of the novel C_3 molecules.





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Analytic First-Order Derivatives of Partially Contracted *N*-Electron Valence State Second-Order Perturbation Theory (PC-NEVPT2)

P101

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A balanced treatment of dynamic and static electron correlation is important in computational chemistry, and multireference perturbation theory (MRPT) is able to do this at a reasonable computational cost. In this study, analytic first-order derivatives, specically gradients and dipole moments, are developed for a particular MRPT method, state-specic partially contracted n-electron valence state second-order perturbation theory (PC-NEVPT2) [1]. Only one linear equation needs to be solved for the derivative calculation if the Z-vector method is employed, which facilitates the practical application of this approach. Comparison of the calculated results with experimental geometrical parameters of O_3 indicates excellent agreement, although the calculated results for O_3^- are slightly outside the experimental error bars. The 0–0 transition energies of various methylpyrimidines and *trans*-polyacetylene are calculated by performing geometry optimizations and seminumerical second-order geometrical derivative calculations. In particular, the deviations of 0–0 transition energies of *trans*-polyacetylene from experimental values are consistently less than 0.1 eV with PC-NEVPT2, indicating the reliability of the method. These results demonstrate the importance of adding dynamic electron correlation on top of methods dominated by static electron correlation and of developing analytic derivatives for highly accurate methods [2].

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[2] Y. Nishimoto *submitted* (ChemRxiv: https://doi.org/10.26434/chemrxiv.8298776.v1)

Development of Second-Order Perturbation Theory with Low-Rank Approximation to CAS Wavefunctions of Molecular Aggregates

P102

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Kyoto University, Kyoto, Japan

An efficient low-rank approximation to complete active space (CAS) wavefunctions of molecular aggregates is presented. Based on this ansatz, we have developed an efficient CASSCF level calculation and have been developing a second-order perturbation theory (CASPT2). We also present several results including excitation energies of an anthracene decamer approximately equivalent to CASSCF with CAS(100,100).

In the method, low-lying electronic states of molecular aggregates are efficiently expanded by a small number of 'rank-one basis states' that are direct products of constituent mono-molecular CAS wavefunctions. The complexities raised by strong intra-molecular entanglement are therefore encapsulated by rank-one basis states and eliminated from the degree of freedom of the effective Hamiltonian for molecular aggregates. Each monomer states within the rank-one basis states is optimized iteratively. If the basis states are chosen effectively, low-lying excited states of aggregates, including such as Frenkel exciton, charge separation, or singlet fission, are calculated accurately with moderate costs.

We calculated the monomeric excited states of an anthracene dimer. Each mono-molecular wave function was constructed with CAS(10,10), and thus this calculation was equivalent to CAS(20,20) for the dimer. Only 16 rank-one basis states (i.e., S_0S_0, S_0S_n, S_nS_0 (n = 1,2,3,4), C^+A^-, A^-C^+, $^1(T_1T_1)$) well reproduced the excitation energies obtained with exact diagonalization by DMRG-CASCI (CAS(20,20), M=1024, 17 state-averaged). We also calculated an anthracene decamer with CAS(10,10) for each molecule and compared the results with those of the dimer.

In order to consider the dynamical correlation, which is not described at CASSCF level, we have been developing a second order perturbation theory (CASPT2). The representation of the rank-one basis allows us to compute 3-RDMs with affordable costs. The development of CASPT2 based on rank-one basis states and some results will be presented.

Anion Dependences in Solution Structure and Ion Conduction Mechanism in Superconcentrated Electrolyte Solution for Na-Ion Batteries

P103

Dr Masaki Okoshi[1,2,3], Prof Hitoshi Washizu[2,3], Prof Hiromi Nakai[3,4,5]

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Superconcentrated electrolyte solutions are receiving increasing attention as a novel class of liquid electrolyte for secondary batteries because of their unusual and favorable characteristics [1]. Recently, we have performed theoretical analysis on the superconcentrated electrolyte solution for Na-ion batteries [2] on the basis of large-scale quantum molecular dynamics simulations, that is divide-and-conquer density-functional tight-binding molecular dynamics (DC-DFTB-MD) method [3]. We have found the unique solution structure with network-like connections between all carrier ions that prohibits the conventional vehicular-type diffusion of carrier ions. Instead, ligand-exchange reactions of solvents/anions around carrier ions maintain diffusion of carrier ions.

In the present study, we examine the anion dependences in solution structures and ion conduction properties: 40% NaFSA (sodium bis(fluorosulfonyl)amide))-DME (dimethoxyethane) and NaTFSA (sodium bis(trifluoromethylsulfonyl)amide)-DME solutions are investigated. Although local interactions (geometric structure, binding energy, and so forth) between Na and FSA/TFSA are similar to each other, the solution properties such as electron conductivity are quite different [1].

We observe the network-like structures that are common in NaFSA- and NaTFSA-DME solutions, while the degrees of coordination of solvents/anions to Na^+ ions are different: multi-coordinate characters of solvents/anions are more obvious in NaFSA-DME solution than in NaTFSA-DME solution. This is attributed to the steric effects caused by the bulky trifluoromethyl ($-CF_3$) groups in TFSA. As for the diffusion properties, we observe ligand-exchange reactions with dynamical rearrangements of the network structures. The rate of ligand-exchange reaction of NaFSA-DME solution (0.018 ± 0.004 ps^{-1}) is ca. 40% more frequent than that of NaTFSA-DME solution (0.013 ± 0.002 ps^{-1}), reflecting the more ligand-carrier ion connections.

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An AFIR Study on the Mechanism of the C-C Coupling Reaction of Borepin Derivatives via Oxidative Deborylation

P104

Dr. Cihan Ozen[1], Assist.Prof Yoshiaki Shoji[2], Prof. Takanori Fukushima[2], Prof. Satoshi Maeda[1]

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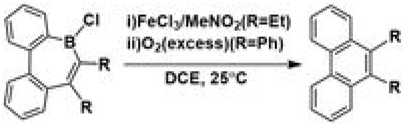

The C-C bond formation is a fundamental transformation in organic chemistry. In 2016, the Fukushima group discovered a new C-C bond formation method in which the borepin derivatives are employed. The reaction can take place not only with transition metal compounds but also with oxidants such as O_2. Although a great experimental effort has been spent, the mechanism of this transformation is still ambiguous to date. In order to elucidate the mechanism of this reaction, a systematic theoretical approach, namely artificial force induced reaction method, has been utilized. In this study, two reaction systems have been chosen: ethyl substituted borepin with $FeCl_3/MeNO_2$ and phenyl substituted borepin with O_2. According to the calculations, the mechanism consists of four basic steps a) quaternization of the boron via the coordination of oxidant b) intersystem crossing c) skeletal rearrangement d) elimination of a boron moiety.

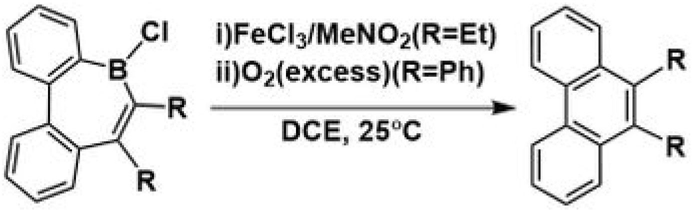

Figure 1. The deborylation/C-C coupling reactions of borepin derivatives

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2) Maeda, S.; Y. Harabuchi.; M. Takagi.; K. Saita.; K. Suzuki.; T. Ichino.; Y. Sumiya.; K. Sugiyama.; Y. Ono. *J. Comput. Chem*. **2018**, 39, 233-251.

EPHI - An Embarrassingly Parallel Code for Calculating Molecular Hessians via PBS Queues

P105

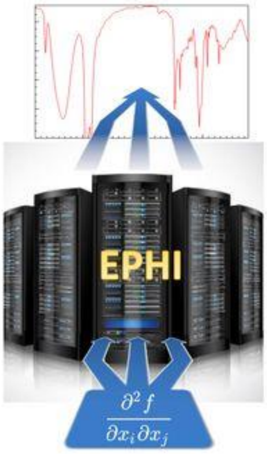
Mr Gareth Elliott, Mr Kas Gregory, A/Prof. Alister Page, Miss Simone Waite

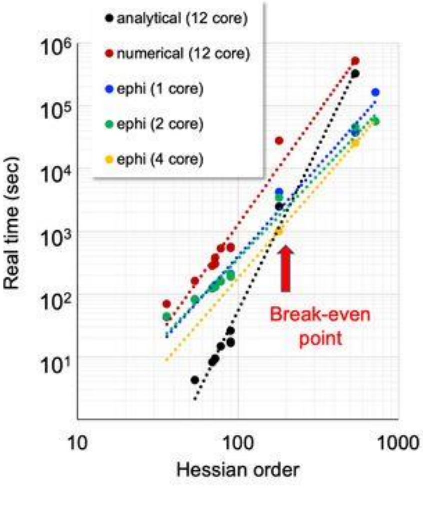
The University of Newcastle, Callaghan, Australia

Calculating the Hessian is important for many aspects of modern computational chemistry; it enables the characterisation of transition states vs local minima, and the estimation of thermochemical corrections and molecular spectra within the harmonic approximation (e.g. IR, Raman, VCD etc.).

The 3*N* x 3*N* elements of the Hessian can be calculated analytically or numerically. On traditional computing architectures, the former is undoubtedly the most efficient method. However, with increasing molecular size, overheads in memory and disk required for analytical 2nd derivatives quickly become prohibitive, particularly with accurate correlated wave function methods. On the other hand, calculating the Hessian matrix numerically requires modest memory and disk, but is extremely inefficient because 3*N* x 3*N* individual force calculations must be calculated sequentially. However, if these 3*N* x 3*N* elements are distributed over a large number of independent calculations, it is in principle possible to assemble the Hessian in an embarrassingly parallel fashion. Such an approach is well suited to modern cluster/supercomputing environments running PBS queues, which often have a large number of idle cores.

Here we report a code that takes this approach. “EPHI” (Embarrassingly Parallel Hessians and Intensities) calculates individual elements of the Hessian matrix via forward finite differences of nuclear forces in Cartesian coordinates via a distributed array of independent calculations. Each calculation is performed as an independent PBS job, and this provides substantial real-time speedup for large molecules, even with a single core per job. Currently, EPHI is interfaced to Gaussian, GAMESS, Turbomole, ORCA and DFTB+. We will discuss the dependence of EPHI's “break-even point” (i.e. the point at which EPHI is more time-efficient than analytical 2nd derivatives, shown below for HF/6-31G), as a function of the model chemistry. We will also demonstrate the suite of backend utilities in EPHI that enable calculation of thermochemical corrections, IR spectra and Raman spectra.





Gas Phase Structures of Alanine

P106

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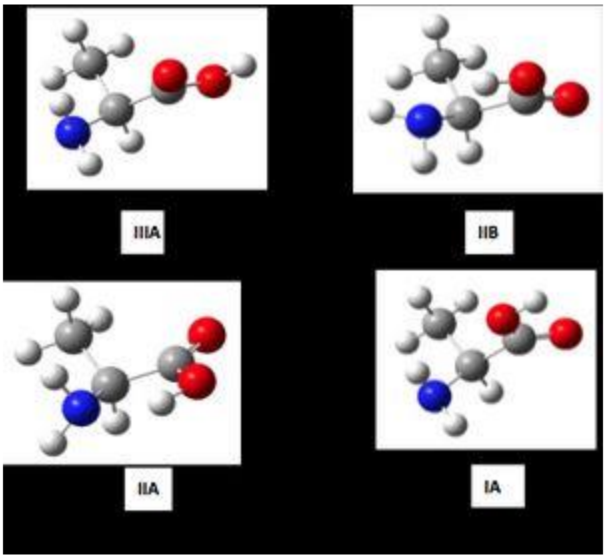
The gas-phase study of the conformational landscape of biomolecules provides fundamental understanding of structure. Alanine, the simplest chiral amino acid, is an ideal biomolecule to explore the ability of computational methods to identify and characterise conformers. In our research we have identified two new conformers that have not previously been noticed. As a result, we have explored a range of methods and basis sets to identify an appropriate approach to study the conformations and properties of flexible molecules in the gas phase. We will present results of an investigation of various methods including HF, DFT, MP2 and coupled-cluster, to account for the conformational flexibility of alanine including the identification of all minima. We have benchmarked relative energies of isomers with CCSD(T)-F12/CBS methods.

While 15 unique minima have been identified in theoretical studies, only 4 conformers have been identified experimentally. Calculated rotational barriers (transition states) enable us to rationalise experimental observations.



Molecular Dynamics Simulations of the Frequency Dielectric Response of Water

P107

Mr Joshua Owen Pryor, Dr Stephen Bosi, Dr Erica Smith

University of New England, Armidale, Australia

The dielectric response of water is of great importance, not only due to the general abundance of water, but also because of the importance of water in countless industrial, environmental, and biological functions. Molecular dynamics simulations allow for investigation of this response on a molecular level in a specified environment. However, any molecular dynamics simulation is limited by the models utilised. In this work, the influence of external oscillating electric fields, ranging in frequency from 2 - 16000 GHz, on particular water models was investigated using molecular dynamics simulations and compared to experimental data of real water. Four water models, SPC/E, SPC/ε, SPC/ε_1 and SPC/fw, were investigated for the accuracy of each model's frequency dielectric response, and the ability to reproduce dynamics which contribute to the dielectric response at high frequencies. All simulations were conducted in a constant temperature of 300 K and under a constant pressure of 1 atmosphere. The SPC/fw model is more complex than the other three models in that it allows for flexible bond lengths and angles. Consequently, better agreement with experiment at high frequencies was hypothesised. The SPC/E and SPC/fw models were accurate in reproducing the low frequency contribution to the dielectric function, the main Debye peak, that is characteristic of water. All four models reproduced the dynamics of the very high frequency dielectric response, which is attributed to libration modes, with SPC/fw most closely reproducing experimental results. However, none of the models accurately reproduced the high frequency contributions to the dielectric function, which are the main contributors to the deviation from Debye behaviour over the high GHz and low THz regions.

Evaluating Classical Force Fields to Study Dissolution and Crystallisation of Hybrid Organometallic Halide Perovskites.

P108

Mr Madhuranga Rathnayake[1], Dr. Stefano Bernardi[1], Dr. Asaph Widmer-Cooper[1,2]

[1]ARC Centre of Excellence in Exciton Science, School of Chemistry, The University of Sydney, Sydney, Australia. [2]The University of Sydney Nano Institute, Sydney Nanoscience Hub, The University of Sydney, Sydney, Australia

Organometallic halide perovskites show a promising future as an efficient and low-cost alternative for conventional photovoltaics. Devices with power conversion efficiencies over 20% have already been reported. Solution processability, high absorption coefficient and tunable bandgap make hybrid perovskites a promising alternative to silicon-based photovoltaics. However, further development is necessary before perovskite solar cells can be widely adopted by industry. For instance, they cannot currently be printed at scale. Even though a wide variety of specific fabrication methods exist to make hybrid perovskites with desired properties and composition, a molecular-level understanding of how they crystallise from solution is still lacking. Ab initio molecular dynamics simulations have been used to obtain atomistic insight into some of these processes, but are limited to timescales of the order of 10s of ps. In contrast, processes on much longer timescales have been successfully studied using classical force fields for both organic and inorganic systems. A couple of attempts have been made recently to parameterise force fields for studying organometallic halide perovskites, with some success at reproducing solid-state properties. However, a force field that can accurately describe dissolution and crystallisation is still lacking. In this work, we evaluate the ability of contemporary force fields to describe both solid-state and solution-state properties of organometallic halide perovskites, ranging from simple non-polarisable force fields through to more complex polarisable ones.

Acknowledgement:
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Effect of A6-A11 Linkage Modifications on the Conformational Dynamics of Insulin

P109

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Insulin is a key hormone in the treatment of diabetes, but existing insulin treatments have pharmacokinetic issues[1]. Insulin analogues in which the integral A6-A11 disulfide linkage is replaced with a dicarba linkage (either a C=C linkage or a C≡C linkage) have substantially altered biological activity; double bonded *cis*-dicarba analogues have more rapid biological activity, whereas double bonded *trans*-dicarba analogues and triple bonded dicarba analogues have minimal biological activity[1,2]; for this reason, these analogues are of interest for diabetes treatments. In this work the effect of these substitutions on the structure and dynamics of insulin are examined through the use of Molecular Dynamics simulations. Differentiation of these analogues is visible in the helical character of the A-chain N-terminal alpha-helix; in the *cis*-dicarba and *trans*-dicarba analogues, helical character is significantly reduced – the alpha-helical content assigned using DSSP drops from 45.9% to 10.18% and 0.11% for the *cis* and *trans* analogues respectively. Conformational differences in analogues can be seen, with the *trans* analogue noticeably different, but differences are more prominent at the A6-A11 linkage site. Fig 1. demonstrates this through analysis of His^{B5}-$\mathrm{Cys}^{A6/A11}$ interactions, with compatable *cis*-isomer and native interactions, and a substantially closer His^{B5}-$\mathrm{Cys}^{A6/A11}$ interaction observed for the alkyne and *trans* isomers. This combination of increased N-terminal A-chain alpha-helix flexibility and reduced His^{B5}-$\mathrm{Cys}^{A6/A11}$ interactions facilitates the activity of the *cis*-dicarba analogue over the *trans* and alkyne variants; building on these insights offers the potential for improved treatments for diabetic individuals.

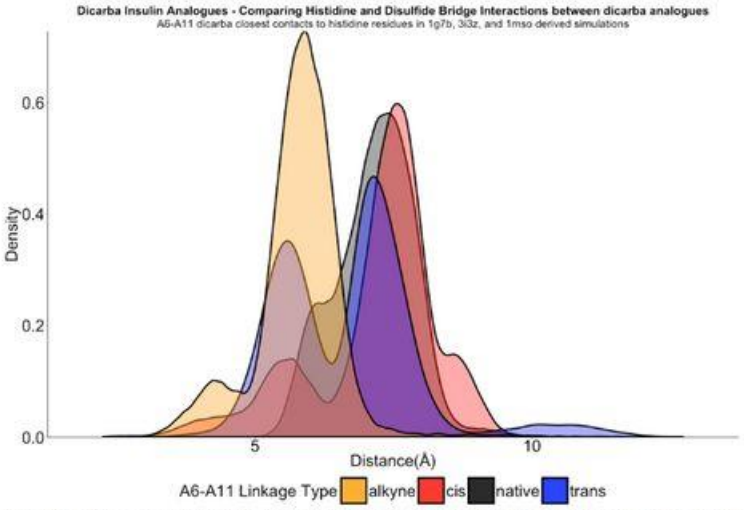

Figure 1. A density plot of His^{B5}-$\mathrm{Cys}^{A6/A11}$ distances in native insulin (black) simulations compared to the *cis*-dicarba insulin analogue (red), *trans*-dicarba insulin analogue (blue), and the alkyne-dicarba insulin analogue (orange)

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Optimizing Stable Free Radicals for the Electrochemical Generation of Reactive Intermediates

P110

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The use of electrochemistry in place of traditional chemical reagents, or other exogenous controls, has been widely advocated in recent years. To expand the scope for carbon-centered radical generation by electrochemical activation of adducts based on stable free radicals, a test set of 12 simple electron-rich Kuhn verdazyl and triazinyl derivatives in conjunction with nine different alkyl leaving groups have been computationally assessed. Electrochemical oxidation was found to reduce the bond-dissociation Gibbs free energy (298K in acetonitrile) by 70 kJ mol-1 on average, when comparing the homolytic cleavage pathway of the unoxidized adduct, to the preferred mesolytic pathway of the oxidized adduct (i.e. to form either a stable radical and a carbocation, or a heterocyclic cation and a carbon-centered radical). Adducts of derivatives functionalized with electron donating substituents favored mesolytic cleavage to carbon-centered radicals under mild electrochemical potentials (-0.7 to -0.2 V. vs Fc+/Fc), opening scope for a new facile and clean source of reactive intermediates for synthesis and polymer chemistry. Considering the full thermochemical cycle, we illustrate that all the relevant free energy changes can be reduced to differences between the oxidation potentials of adducts and radicals, defining a series of criterion that govern the rational design of suitable candidates for this form of chemistry.

Designer Polymers: Predicting Viscosity from Molecular Simulation

P111

Dr. Tanglaw Roman[1,2], Dr. James C. Reid[2], Prof. Debra J. Searles[2,3]

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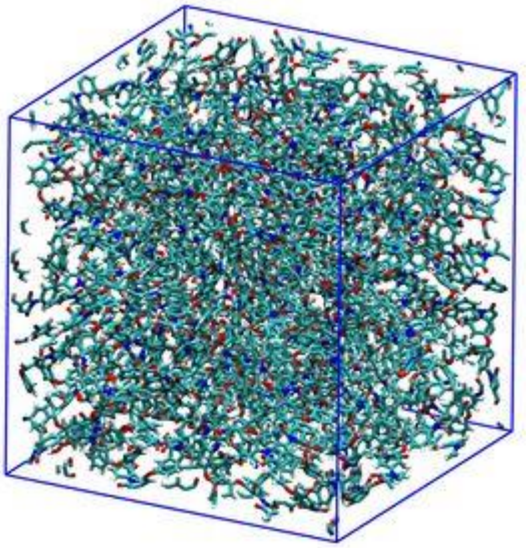
Molecular dynamics simulations are an important approach to assist in understanding of polymers in general, and can be used to determine the viscosity of polymer melts applicable to additive manufacturing. The viscosity has implications on the behaviour of a melt during processing, and its potential suitability for 3D printing. This project considers how well different molecular simulation methodologies perform: simulations involve systems that are not at thermodynamic equilibrium. Bulk systems of phenylethynyl-terminated polyimide with 1,3 bis(3-aminophenoxy)benzene of different chain lengths are modelled in periodic simulation cells, where atomic interactions are described with classical models. Relaxation times and convergence of the viscosity results and their ability to reproduce experimental trends and values at a range of typical temperatures will be discussed in this presentation.

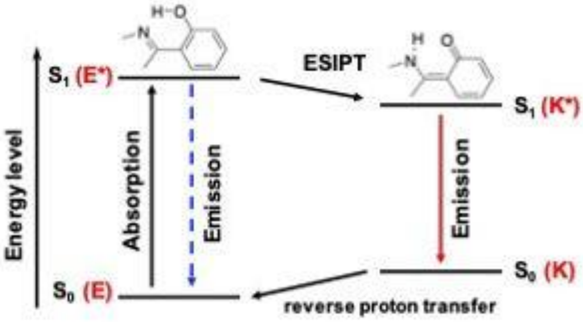


Computational Insight into the Excited-State Intramolecular Proton Transfer Mechanism of HPI Dyes

P112

Miss Ras Baizureen Roseli, Miss Ilene Allison, Mr Atul Shukla, Associate Professor Ebinazar Namdas, Associate Professor Shih-Chun Lo, Associate Professor Elizabeth Krenske

The University of Queensland, Brisbane, Australia



Excited-state intramolecular proton transfer (ESIPT) has attracted much attention for the development of highly fluorescent materials. ESIPT is a photoinduced enol-to-keto tautomerisation via proton transfer in the excited state. In the ground state, absorption takes place in the enol (E) tautomer while in the excited state, emission occurs from the keto (K*) tautomer, inducing a large Stokes shift which is a desirable property for optoelectronic applications.

ESIPT, like many other excited-state processes, is difficult to predict *a priori*. In this study, linear and non-linear response time-dependent density functional theory (TD-DFT) techniques have been employed to investigate the ESIPT mechanism of hydroxy-substituted tetraphenyl imidazole (HPI) dyes. This work aims to obtain insight into the molecular level processes as a key step in the design of new optoelectronic materials.

Rationalising the chemistry of Atmospherically Important Carbonyls Through Theory and Structure

P113

Mr. Keiran N Rowell[1], Prof. Scott H. Kable[1], A/Prof. Meredith J. T. Jordan[2]

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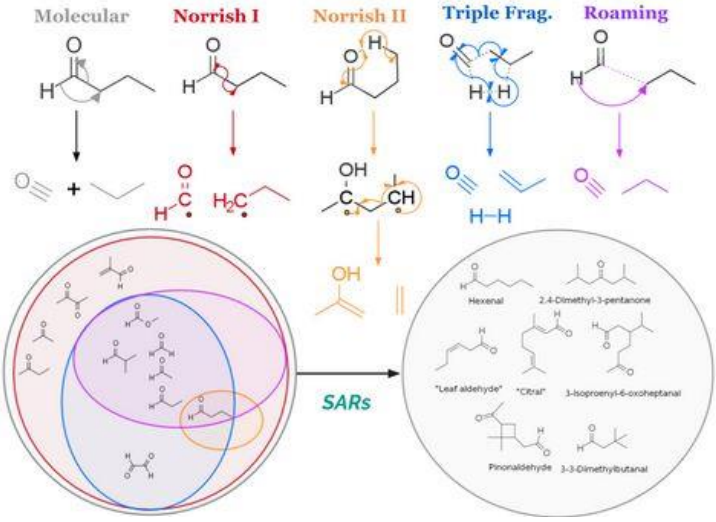
Carbonyls are among the most abundant and photoactive volatile organic compounds (VOCs) in the atmosphere. Their varied, complex structures pose a challenge to atmospheric chemistry models. Experimental photolysis paramaters are available for small prototypical molecules, however this data does not cover all reaction channels and is missing larger abundant species.

Atmospheric models circumvent this lack of data by applying the same photolysis parameters from one molecule to all other molecules of that type (e.g. the photolysis rate of butanal is used for all linear aldehydes). Such approaches do not account for the complex photochemistry of the carbonyl moiety, where small structural changes can dramatically alter photolysis rates, accessible electronic surfaces, or even which reaction products are formed.

In this work theoretical chemistry is used to explore the photophysics of the carbonyl moiety as a whole, on relevant electronic states (S_1, T_1, & S_0), and derive fundamental structure activity relationships (SARs) to rationalise the photochemistry of diverse carbonyl species (*see figure)*. This is accomplished with combined TD-DFT and coupled cluster methods, which are found to predict photochemical quantities with mean absolute deviations of ~5-7 kJ/mol in comparison to experimental data.



Trends in excitation energies are be explained by the nature of each carbonyl's frontier orbitals. Intrinsic barriers to dissociation on each electronic state are explained in terms of competing effects—hyperconjugation in the incipient radicals lowers reaction barriers, while delocalisation across the dissociating bond raises barriers.

The calculated photochemical quantities in this work are the quantities required for the theoretical prediction of photolysis rate coefficients. These quantities can be coupled in a master equation model to provide theoretical photolysis rates to supplement photolysis parameters missing from atmospheric models, and provide a chemically rationalised framework to modify existing photolysis data to more appropriately model the diversity of carbonyls in the atmosphere.

Potential-Dependent Rates of Reaction for Hydrogen Evolution on MoS_2 Electrocatalysts

P114

Mr Charlie Ruffman[1], Mr Calum K Gordon[1], Dr Egill Skúlason[2], Dr Anna L Garden[1]

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Hydrogen (H_2) is becoming increasingly established as a promising alternative to traditional fossil fuels, yet it relies on a cheap and clean method of production. This may be accomplished *via* the electrocatalytic splitting of water, of which a key component is the hydrogen evolution reaction (HER). In the HER an appropriate catalyst is used to combine protons to form H_2.[1] Emerging nanoscale MoS_2 materials have been identified as promising catalysts as they are both Earth-abundant and show high activity towards H_2 production.[2] However, there has been limited work elucidating the mechanism for the HER on MoS_2,[3] and the factors that influence the rate of H_2 production are not fully understood.

This presentation will explore results from mechanistic density functional theory calculations for the HER on MoS_2. It will discuss a method of modelling the electrochemical cell to include electrolyte, charged species, and applied potential within periodic density functional theory,[4] and show how this can be used to calculate reaction rates as a function of potential. We use this methodology to demonstrate how the potential-dependent rate of hydrogen evolution may be tuned by placing MoS_2 catalysts on different supporting materials. Our calculated potential-dependent rates allow a more comprehensive mechanistic understanding of the HER on MoS_2, which in turn will inform the rational design of new MoS_2-based catalysts.

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Theoretical Study of Manganese Melilites and Related Structures

P115

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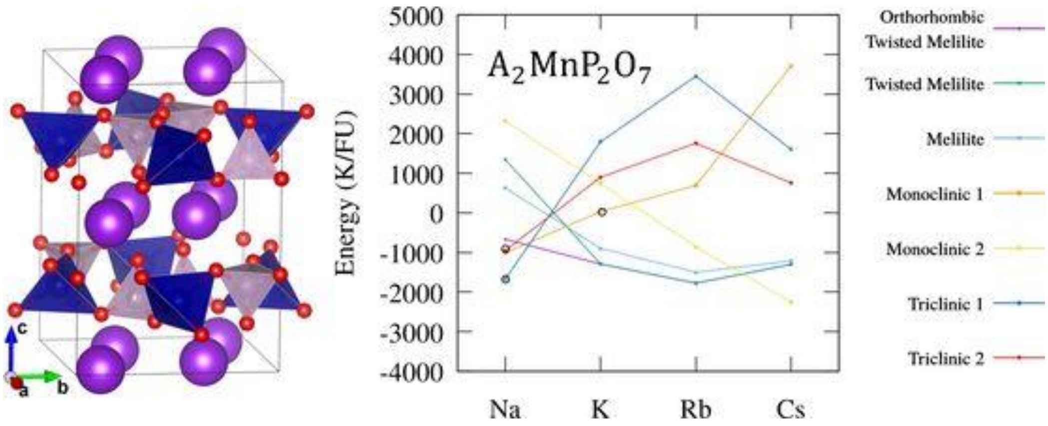
Manganese melilites and related compositions[1-8] with chemical formulae $A_2MnC'_2O_7$ (A^{1+}: Na, K, Rb, Cs; C'^{5+}: As, V, P and A^{2+}: Ca, Sr, Ba; C'^{4+}: Si, Ge) were studied theoretically using density functional theory. The relative stability of different phases was approximated by comparing relaxed crystal structure energies. Further calculations of the magnetic structure and super-super exchange parameters of selected melilite structures were also performed. The calculated results mostly agree with the limited set of experimentally measured magnetic and crystal structures[5,8-10] and suggest interesting pathways for further research.



Left: $K_2CoP_2O_7$ twisted melilite crystal structure[1], $P4_2/mnm$ (#136), a=b≈7.5Å, c≈10.0Å, Right: relaxed structural energies for a variety of different compositions potentially compatible with the $A_2MnP_2O_7$ chemical formula from literature[1-8]. All data points have been normalised per composition to the average energy, experimental structures indicated with small black circle

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Combining Modern Force Fields with ONIOM(QM:MM): the SICTWO Interface

P116

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[1]Hokkaido University, Sapporo, Japan. [2]Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain

Quantum mechanics/molecular mechanics (QM/MM) methods are very popular in multiscale modelling of complex molecular systems. QM/MM calculations give accurate structures and energies at a low computational cost. ONIOM(QM:MM) is a popular QM/MM approach.[1][2] However, the commonly used ONIOM(QM:MM) implementations support for few force fields. In order to overcome this limitation, we have developed the SICTWO interface.[3] SICTWO is a user-friendly interface, giving access to the force fields in the Tinker molecular mechanics program from a Gaussian09 or a Gaussian16 calculation.

ONIOM(QM:MM)

We have used SICTWO to study of complex molecular systems; (a) ONIOM(QM:MM3) method rationalised the selectivity of transition metal homogeneous catalysis,[3][4] (b) ONIOM(QM:OPLS-AA) and ONIOM(QM:MMFF) methods described the molecular structure of RESVAN, where dispersion interactions play a key role,[3][5] (c) ONIOM(QM:AMOEBA09) method explained the binding preference of the radicals on interstellar ices,[6] (d) ONIOM(QM:MM3) method rationalised the origin of emission of $[Cu_2(dmp)_2(\mu\text{-}dppa)_2]^{2+}$complex.[7] These examples evidence that the SICTWO interface is a useful tool for the computational chemistry community.

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Anion Binding Affinity – Acidity versus Conformational Effects

P117

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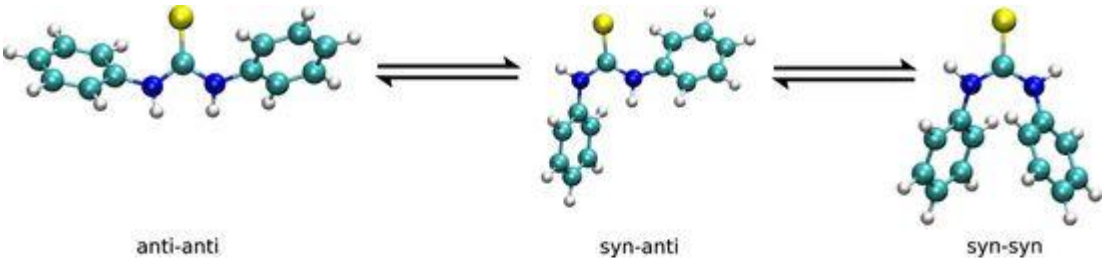
Anion receptors, small molecules that can bind to anions and transport them across cell membranes, show promise for the treatment of cystic fibrosis and as novel anticancer agents[1]. An example for anion receptors with a dual-hydrogen bond donor motif are (thio)ureas, (thio)squaramides[2] and croconamides. The acidity of the N-H protons is usually used to estimate the anion binding affinity of these receptors. While ureas and squaramides show an increasing chloride binding affinity with increasing acidity of the N-H protons, thioureas, thiosuaramides and croconamides do not exhibit this trend[3]. For anion receptors with low pK_a values this unexpected behaviour is thought to be a consequence of a larger proportion of molecules existing in their deprotonated form. However, the conformational preferences of these receptors may also play an important role.

In this poster, we present high-level quantum chemical calculations in conjunction with hybrid implicit-explicit solvent model simulations to elucidate the conformational equilibria of some common dual hydrogen bonding anion receptors. Our results suggest that conformational effects play an important role in determining the binding affinity of anion receptors and that investigations into the possibility of pre-organising them into suitable conformations could aid in designing novel anion transporters with higher activity.



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Locating Minimum Energy Structures of Materials

P118

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That physical properties are a consequence of the system's interactions is not disputed. However, their interrelation is not well understood; how can properties be extracted if the structural arrangements are known? This question has been a main focus of theoretical chemistry for the last few decades. [1] Meanwhile, a secondary focus lies within this desirable goal. How can we systematically find the numerous configurations that exist in a material?

Traditional algorithms (e.g. genetic algorithms) solve this problem by limiting the phase space observed and the creation of candidates is not guided by the system's potential energy surface (PES). [2] Algorithms like this are used because it is extremely costly to survey the complete potential surface and for larger clusters – where governing interaction energies are adequately represented – it become essential to find a more cost effective way than full geometry screening with wavefunction-based methods.

A new process is presented that attempts to marry molecular dynamics (MD) and theoretical chemistry to locate all minimum energy structures contributing to bulk properties. MD is used on a large set of starting configurations to find low energy candidates which are filtered using clustering algorithms and finally *ab initio* techniques. [3]

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Semi-Local Machine-Learned Kinetic Energy Density Functional for Orbital-Free Density Functional Theory

P119

Dr. Junji Seino[1,2], Mr. Ryo Kageyama[1], Mr. Mikito Fujinami[1], Dr. Yasuhiro Ikabata[1], Prof. Hiromi Nakai[1,3]

[1]Waseda University, Tokyo, Japan. [2]JST-PRESTO, Saitama, Japan. [3]ESICB, Kyoto University, Kyoto, Japan

Density functional theory (DFT) is one of the most popular schemes for obtaining electronic states and their properties in molecules and materials. The total energy can be written as a functional of the electron density. The kinetic and exchange-correlation energies, which are components in the total energy, have approximate formulae because the exact expressions are unknown. For the kinetic energy (KE), the majority use the Kohn−Sham (KS) expression, which introduces a set of KS orbitals instead of using the explicit functional in terms of electron density. This is because the development of a practical KE density functional (KEDF) has been a difficult task both for isolated and bulk systems. However, the continuous developments toward practically accurate KEDF have been done because of the low computational cost.

The present study attempts to construct the KEDF using machine learning (ML). The present scheme adopts electron densities and their gradients as descriptors, and the KE density of KS as the objective value in atoms and molecules. A multi-layer neural network was adopted here for ML. The results showed that the ML KEDF provides closer KEs with the KS expression than 37 conventional KEDFs [Seino, Kageyama, Fujinami, Ikabata, Nakai, J. Chem. Phys. 148, 241705 (2018)]. Furthermore, the ML procedure was applied to a construction of KS potential functional, which is the derivative of KEDF in terms of electron density. The ML KEDF and potential functional are utilized for the optimization of electron density in the OF-DFT framework. The procedure in details and accuracy will be discussed in the presentation.

Theoretical Study on the Optical Properties of Multichromophoric Systems Based on an Exciton Analysis: Modification Guidelines

P120

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Designability of supramolecular and polymer design has been enhanced by recent advances in experimental techniques. In particular, optical properties of multichromophoric systems drastically change depending on molecular compositions and structure, where design guidelines are demanded for development of efficient optical materials. In the present study, we propose modification strategy of emission and circularly polarized luminescence (CPL) of the multichromophoric systems based on an excitonic analysis [1, 2].

Generation and annihilation mechanisms of the emission and CPL have been analyzed for an achiral crystal of 2,5-diphenyl-1,4-distyrylbenzene (*trans*-DPDSB) molecules as an example. The emission is predominantly caused by a local transition of a structurally relaxed chromophore due to the weak exciton coupling. The interactions between this chromophore and the surrounding ones positively contribute to the emission intensity. The decomposed CPL components with strong intensities originate from the interactions of the exciton electric transition dipole moments (ETDMs) between the chromophore and its adjacent monomers, which cancels out each other in enantiomeric pairs of the achiral system. Based on these findings, we propose the guidelines toward the improvement in the photofunctions. The modification guidelines suggested that it is most effective to improve the ETD strength for the first excited state of the relaxed chromophore. Moreover, the CPL signal is generated by the control of the relative orientations of the ETDMs of the surrounding chromophores. In practice, it is possible to implement these modifications by manipulating the molecular species and conformations of the multichromophoric system. The Frenkel-exciton decomposition analysis (FEDA) [1] which reveals the contributions of components of the supramolecular system provides new possibilities for utilizing the potentials of multichromophoric systems.

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Activation of a Non-Redox Isomerisation Using Static Electricity

P121

Mrs Catherine D Simpson[1], Mrs Heather M Aitken[1], Dr Naomi L Haworth[1], Dr Nadim Darwish[2], Dr Simone Ciampi[2], Professor Michelle L Coote[1]

[1]ARC Centre of Excellence for Electromaterials Science, Research School of Chemistry, Australian National University, Canberra, Australia. [2]Nanochemistry Research Institute, Department of Chemistry, Curtin University, Perth, Australia

Despite electrolytes and electrostatic interactions being ubiquitous in chemical, material and biological sciences, there is still much to learn about the impact of static electric fields on the reaction rates and equilibrium positions of non-redox chemical systems. Recently there have been developments in experimental and computational methods to investigate electrostatic catalysis[1].

This work uses computational chemistry to study the effect of oriented electric fields on the ring opening of spiropyrans. Spiropyrans can undergo the ring opening reaction when exposed to various stimulants such as UV light or heat. Here we show that static electric fields can also yield measurable changes to the equilibrium between a ring-closed spiropyran molecule and its merocyanine ring-opened form, due to its increased polarity. The electric field effects are found to be strongly directional, but concurrent experimental studies suggest that the spiropyran can self-align to the electric field thus removing one of the practical barriers to scaling up electrostatic catalysis. This poster presentation will focus on our theoretical results but make reference to supporting experimental data.

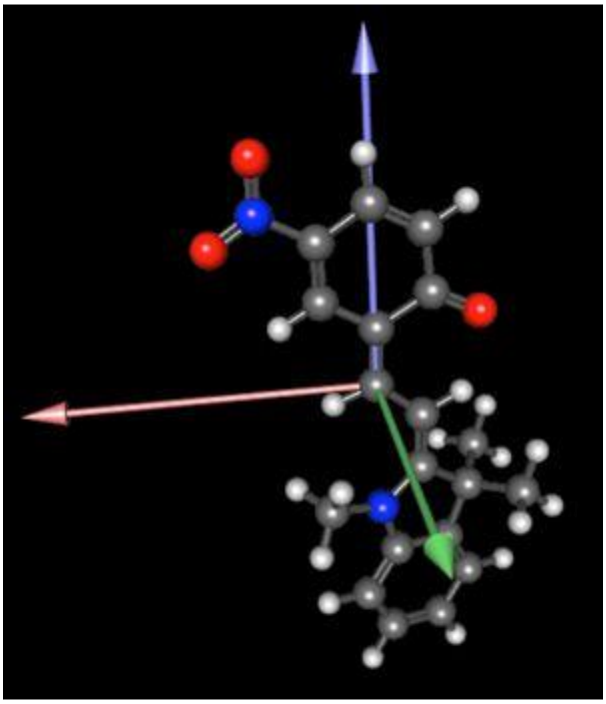

Figure 1. One of the ring opened isomers of spiropyran.

Acknowledgements: Financial support from the ARC (CE140100012 and FL170100041) and supercomputing time on the National Facility of the National Computational Infrastructure are gratefully acknowledged.

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Understanding the Mechanism of Oxidative Polymerisation of Phenols

P122

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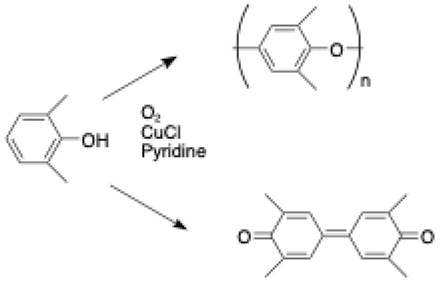
Regioselective polymerisation of 2,6-dimethyl phenol leads to an important engineering thermoplastic (PPO) with outstanding characteristics, such as resistance to high temperatures and is a major constituent of Noryl^{TM}[1]. However, the mechanism of the reaction has been the subject of much discussion over the last 60 years and it is still debated whether the coupling happens through a radical pathway or by ionic mechanism[2]. The metal catalyst in the presence of oxygen is considered as an indispensable part of reaction (scheme 1) but their roles are not well understood. DFT calculations have been performed with the ωB97X-D functional to gain more insight into the mechanism of phenol polymerisation. All the possible reaction pathways resulting from the oxidation of phenol and subsequent polymerisation have been considered and underpinned with calculations of Gibbs free energies. Implicit and explicit solvent models, with benzene and water as solvents, were incorporated in the calculations. Recently ionic liquids have shown significant potential to stabilise radicals[3] and these have been tested as phenoxyl radical stabilisers both experimental and theoretically. If successful, this new pathway will eliminate the use of metal catalysts currently used to perform controlled polymerisation, with the view of achieving more regioselectivity in the oxidation of phenol without the need to protect ortho-sites.



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Machine Learning Protocol for Asymmetric Hydrogenation Catalysis

P123

Ms Sukriti Singh, Ms Monika Pareek, Mr Avtar Changotra, Mr Sayan Banerjee, Mr Bangaru Bhaskararao, Prof Palaniappan Balamurugan, Prof. Raghavan B. Sunoj

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Design of asymmetric catalysts often involves tedious trial and error cycles driven by chemical intuition. Molecular insights on stereocontrol in transition states, obtained using modern electronic structure computations, have also contributed to this goal, although such methods are generally resource intensive.[1] In view of the steady increase in interest toward efficient catalytic asymmetric reactions and the rapid growth in the field of Machine Learning (ML) in the recent years, we envisaged dovetailing these two important domains. We selected a set of quantum chemically derived molecular descriptors from five different asymmetric binaphthyl-derived catalyst families with the propensity to impact the enantioselectivity of asymmetric hydrogenation of alkenes and imines. The chosen parameters are then used in random forest (RF) as well as other ML algorithms, which are well known for their predictive capabilities. The predictive power of the *random forest* (RF) built using the molecular parameters of a set of 368 substrate-catalyst combinations is found to be impressive, with a root mean square error (RMSE) in the predicted %*ee* of about 8.4±1.8 as compared to the experimentally known values. The accuracy of RF is found to be superior to other ML methods such as convolutional neural network, decision tree and eXtreme Gradient Boosting as well as stepwise linear regression. The trained ML models are also tested for prediction of unseen samples drawn from different axially chiral catalysts. Interestingly, very good predictions with an RMSE of 8.5±0.0 could be obtained for these new sets of catalysts. The proposed method is expected to provide a leap forward in the design of catalysts for asymmetric transformations.

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Microscopic Explanation of the Enantiomeric Excess in S_N1 Reaction in Solution: A Full Atomistic Simulation Study

P124

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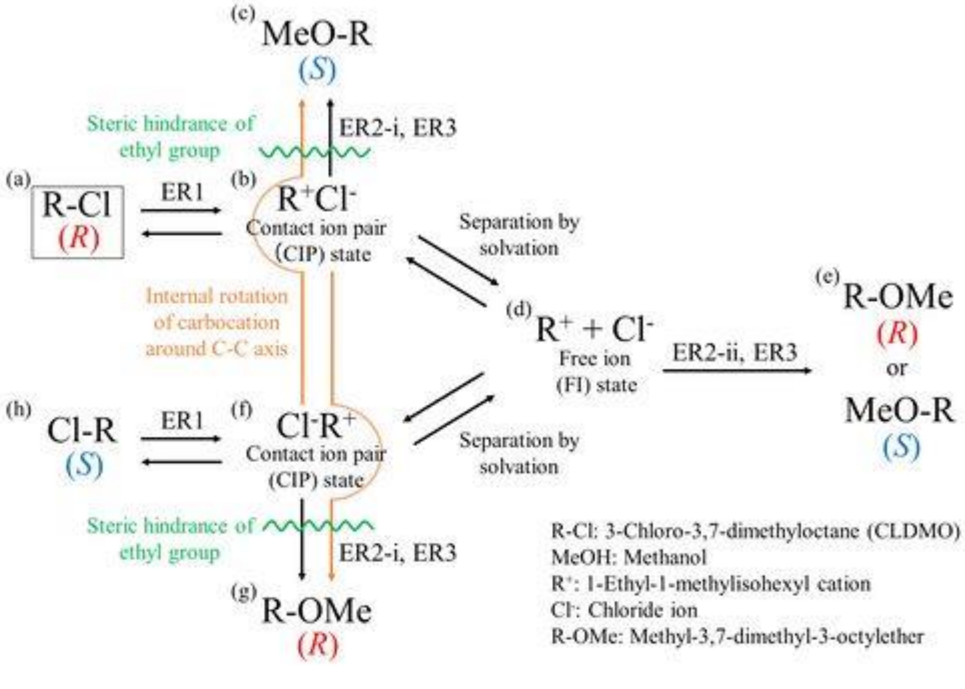
In general, S_N1 reaction of tertiary alkyl halide solutes in protic polar solvents consist of three elementary reactions; (i) spontaneous dissociation of a halogen atom (ER1), (ii) nucleophilic attacks of solvent molecules to the generated planar carbocation (ER2), and (iii) deprotonation (ER3). In particular, the reaction of chiral tertiary ones can yield, through these elementary ones, two kinds of enantiomers, (*R*)- and (*S*)- enantiomers, resulting in the excess state of one enantiomer stereochemically inverted from the original reactant. So far, this phenomenon has been explained by the shielding effect in ER2 at contact ion pair (CIP) states. However, it has not been enough taken to include the influence of structural characteristics of solute or solvent molecules on their enantiomer formation mechanisms. In the present study, to understand the microscopic reaction mechanism of the enantiomeric excess (ee), we have theoretically studied S_N1 reaction of (*R*)-3-chloro-3,7-dimethyloctane in methanol using quantum mechanics (QM) method. Then, based on the mechanism obtained, we have tried to perform full atomistic simulation of the enantiomer formation process using Red Moon (RM) method.



From the QM calculation results of the present S_N1 reaction mechanism including the shielding effect, we suggest a possible enantiomer formation mechanism (Figure), where, due to the structural characteristics of the solute molecule, the internal rotation of the ethyl group of carbocation (R^+) at a CIP state (b) (or (f)) should have a decisive role of transition to a free ion state (d), contributing to racemization (e). In addition, we suggest the internal rotation about the carbon C-C bond of R^+ at a CIP state can lead to retention of stereochemical configuration of the reactant in the final product, shown as (b) to (g) (or (f) to (c)). The computational method, etc. with RM simulation result will be provided in the presentation.

Computational Molecular Spectroscopy Leading the Way to New Physics

P125

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There is a divide in physics, a chasm between the physics of the small (quantum mechanics and the Standard Model of Matter) and the heavy (general relativity). Unifying these theories, and explaining dark matter and dark energy, requires new fundamental physics theories[1,2]. Many of these new theories predict a variation of one or more fundamental constants[3] such as the proton-to-electron mass ratio, over time. Being able to more accurately measure the variation of the proton-to-electron mass ratio could revolutionise physics[4] by allowing us to filter through the currently competing fundamental physics theories.

The most sensitive tests of temporal or spatial variation in the proton-to-electron mass ratio relies on the fact that changing this ratio changes the frequency of spectral transitions, a measurable quantity. Therefore, by comparing the frequency of molecular spectral transitions from distant astrophysical sources to their frequency today, scientists can perform high accuracy tests for variations in the proton-to-electron mass ratio, which have (with assumptions) currently constrained the variation to less than 1 part in 10^{-17}/yr.

To improve on existing measurements, we are aiming to systematically look at spectral transitions from a large number of molecules found in space and identify those transitions most likely to allow a very high sensitivity measurement of variation in the proton-to-electron mass ratio. Based on existing and new spectroscopic models of astrophysically-relevant molecules[5], we will utilise high level variational nuclear-motion calculations to simulate the effect of a small shift in the proton-to-electron mass ratio on the molecule's transition frequencies and thereby identify promising candidate transitions.

Our ultimate goal is to determine the optimal molecules and spectral transitions to test astrophysically whether the proton-to-electron mass ratio has changed over cosmological time.

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Crystal Structure Prediction by Artificial Force Induced Reaction Method: Applications to Silicon Carbide

P126

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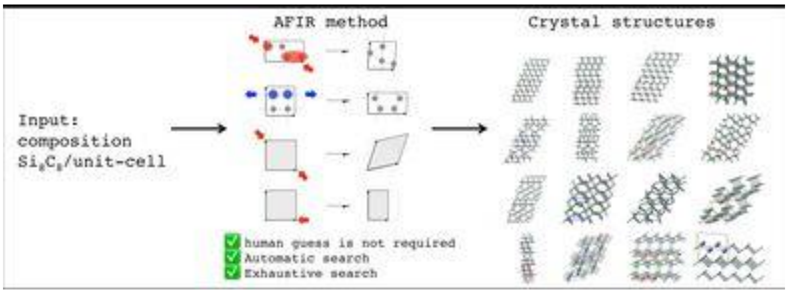
Silicon carbide (SiC) is a crystal in which carbon and silicon are combined with 1:1 ratio, and is also widely used industrially as a wide-gap semiconductor. It is reported that silicon carbide can take more than 40 polymorphs, including diamond type (3C-SiC) and wurtzite type (2H-SiC). Crystal structures of SiC are important because the band gap of SiC depends on it. For example, 3C-SiC has the smallest band gap of 2.36 eV among polymorphs, while 2H-SiC has the largest one of 3.39 eV. However, it is difficult to create specific crystal structures separately in experiments, and theoretical calculations are indispensable for crystal structure prediction. It corresponds to searching for minimum points on the potential energy surfaces (PES). Since there are huge numbers of minimum points on the PES, an efficient crystal structure search methods are desired.

On the other hand, we have developed artificial force induced reaction (AFIR) method for automated exploration of chemical reaction pathways. Recently, AFIR method has been extended to perform the global search for low-lying crystal structures, by combining with the periodic boundary conditions (PBCs). In this study, thus, we performed a systematic search for SiC crystal structures by the PBC/AFIR method.

Crystal structure prediction calculations were carried out by utilizing a local developmental version of the GRRM program. Energies, gradients, and lattice stresses were computed by self consistent charge density functional tight binding (SCC-DFTB) method using DFTB+ program with pbc-0-3 parameter. Band structures were computed by density functional theory (DFT) using the SIESTA program (PBE+D2/DZP level). As a result, more than 10,000 crystal structures were generated. These data include structures such as 3C-SiC and 2H-SiC as already reported. We have also found relatively stable new structures that have a small band gap than 3C-SiC.



Computational Studies of Adsorption and SERS Spectra of 2,2'-Bipyridyl on Au, Ag, and Au-Ag Nanoalloy

P127

Mr Masato Takenaka[1], Mr Yoshikazu Hashimoto[2], Dr Takeshi Iwasa[1,3,4], Prof Tetsuya Taketsugu[1,3,4], Dr Gediminas Seniutinas[5,6], Dr Armandas Balcytis[5,6], Prof Saulius Juodkazis[5,6,2], Prof Yoshiaki Nishijima[2]

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In this study, SERS of 2,2'–bipyridyl (22BPY) on Au, Ag, and Au–Ag alloy nanodisc arrays was experimentally and theoretically investigated. Experimental SERS spectra from Au and Ag nanodiscs show similar peaks, whereas those from Au–Ag alloy reveal new spectral features. To understand SERS spectral variations between Au, Ag and its alloy Au–Ag systems, plasmonic field variations are numerically analyzed using finite difference time domain (FDTD) simulations for considering the physical enhancement effects, whereas structural and electronic properties of Au, Ag, and Au–Ag alloy 20-atom tetrahedral clusters and adsorption of 22BPY to these clusters are investigated by means of the density functional theory (DFT) computations for considering the chemical enhancement effects.The DFT results indicate that 22BPY prefers a coplanar adsorption on a (111) face with trans-conformation having close energy difference to cis-conformation. Adsorption to the pure Au cluster is stronger than to the pure Ag or Au–Ag alloy clusters. The adsorption on Au–Ag alloy surface can induce deformations (i.e., roughness) of the surface due to different affinity of the analyte molecule to Au and Ag, as well as different bonding strength between metal atoms. One strong peak at around 800 cm–1 can be reproduced by calculating coplanar adsorption geometry where one side of the analyte molecule is supported by the surface breaking the inherent symmetry of this vibrational mode making the mode Raman active. This work provides insight into 3D character of SERS on nanorough surfaces due to different binding energies and bond length of nanoalloys.

Computational Studies into Enantioconvergent Guanidine-Copper Complex Catalysed Reactions

P128

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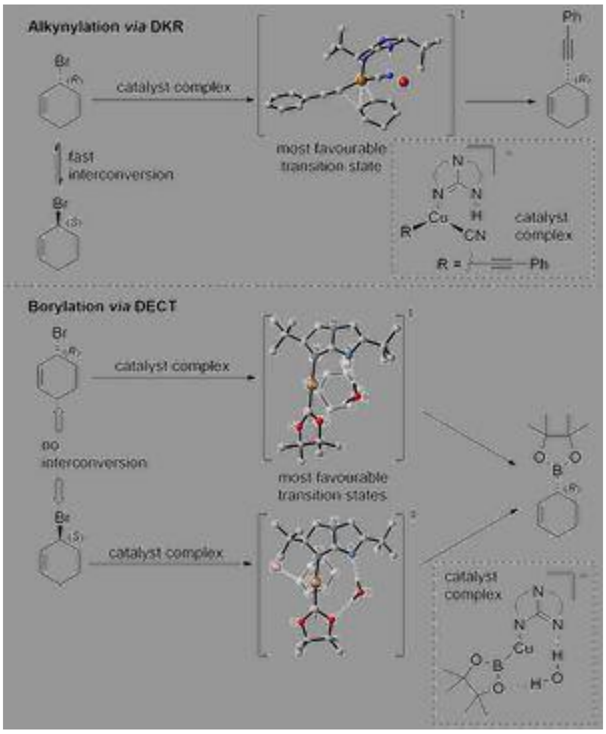
Singapore University of Technology and Design, Singapore, Singapore

Enantioconvergent reactions convert both enantiomers of a racemic starting material into an enantio-enriched product. There are several ways through which enantioconvergence may occur such as dynamic kinetic resolution (DKR) where the starting enantiomers rapidly interconvert and one of the enantiomers forms the product faster than the other or direct enantio-convergent transformation (DECT) where each enantiomer undergoes a different reaction pathway to form the product.

This poster will detail the quantum chemical studies of two enantioconvergent reactions, alkynylation[1] and borylation[2] of racemic allyl bromides catalysed by a guanidinium-copper complex, using density functional theory. These studies showed that the alkynylation reaction proceeded via a DKR pathway whereas the borylation reaction proceeded via a DECT pathway.



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The Origin of the Anelasticity of Zinc Oxide Nanowires: a Density Functional Theory Study

P129

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School of Science, RMIT University, Melbourne, Australia

A solid that is subjected to elastic deformation will immediately recover its original shape when strain is removed. However, in some solids the recovery takes time, a property known as anelasticity.[1] The ability of anelastic materials to temporarily retain this change in volume has been widely applied in mechanical noise damping systems for a broad range of applications. Anelasticity of nanowires has recently attracted attention as an interesting property for high efficiency mechanical damping materials. While the mechanism of anelasticity has so far been analysed using continuum mechanical models based on defect diffusion, the investigation of the mechanisms behind anelasticity have not yet been approached through quantum mechanical modelling. Such an approach could unravel the energy dissipation mechanisms at the level of individual Zn-O bonds within the crystal. Here we examine the potential mechanism of anelasticity in narrow zinc oxide nanowires[2] based on density functional theory. By analysing the bond stretching and compression within the nanowire structure (Figure 1), we unravel potential mechanisms behind anelasticity in these nanowires. Our approach sheds light on various local-minimum structures of the nanowire, and can be applied to other nanowire materials for the prediction of their potential anelasticity.

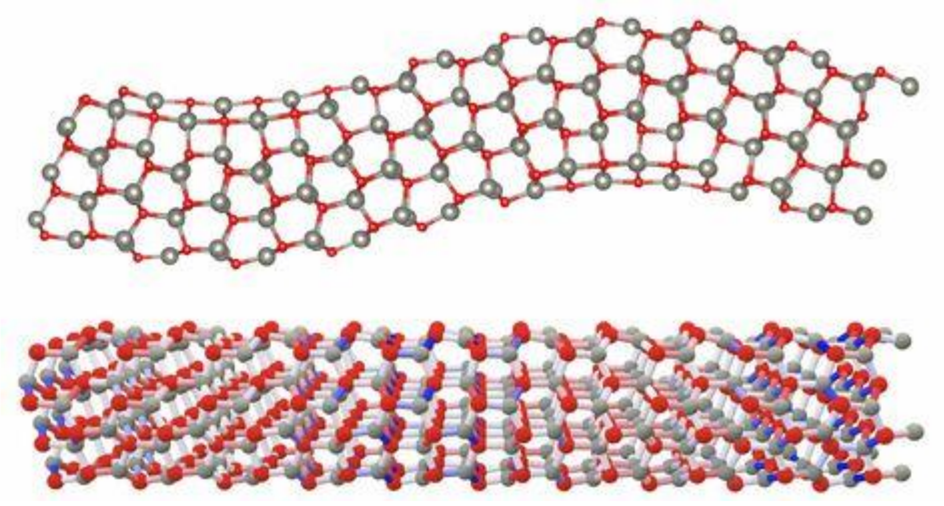

Figure 1: (Top) The structure of the ZnO nanowire with a sinusoidal bending structure. (Bottom) The ZnO bond stretch-strain patterns projected on the pristine ZnO nanowire.

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Effect of Adsorption and Surface Strain on the Light-Harvesting Properties and Carrier Mobility of Phosphorene

P130

Mr Patrick D. Taylor, Dr Sherif A. Tawfik, Associate Professor Michelle J. S. Spencer

RMIT University, Melbourne, Australia

Two-dimensional (2D) materials, such as boron nitride (BN), silicene, molybdenum disulphide (MoS_2) and phosphorene, have become increasingly popular owing to their potential for transforming the future of electronics [1]. Monolayer black phosphorus (phosphorene) displays electronic properties that are highly suitable for both nano- and optoelectronics and tuning these properties will greatly expand the applications of phosphorene [2-4]. In this work, the effects of adsorption of fluorine, chlorine, bromine, and iodine on the electronic and structural properties of phosphorene are investigated using density functional theory. We find that adsorption of these atoms on the phosphorene surface causes it to transition from being a direct to an indirect semiconductor and introduces a spin polarised defect state (see Figure 1). Importantly, we find that the effective electron and hole masses in these systems are not only tunable by applying mechanical strain but also vary with the direction of strain across the structure. This work shows that these modifications have promising properties for enhancing the light harvesting abilities of phosphorene, giving it potential applications in gas sensors and storage devices, as well as other areas of nano- and optoelectronics.

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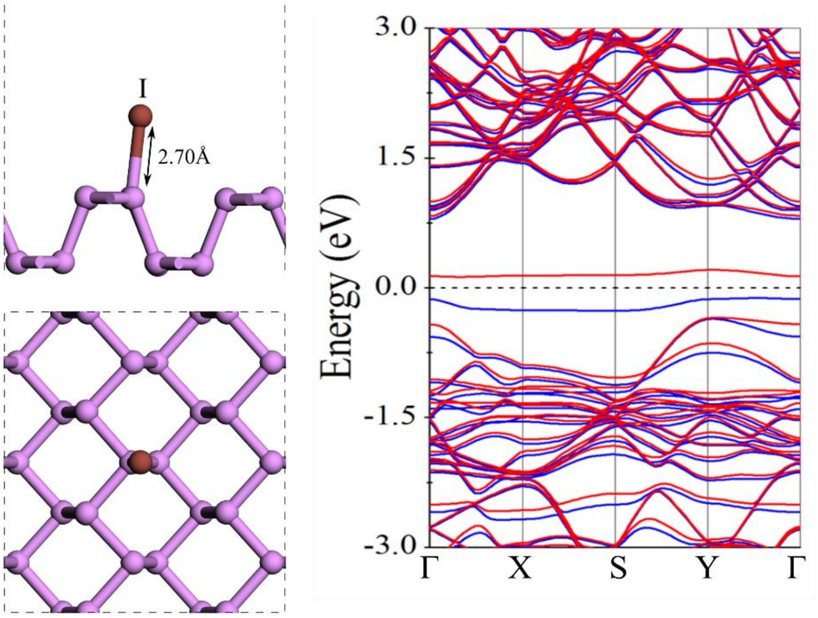

Figure 1 - Optimised structure of iodine adsorbed on phosphorene (left) and band structure (right)

Theoretical Study on the Reaction Mechanism of Zn(OTf)$_2$-Mediated Annulations of *N*-Propargylated Tetrahydrocarboline

P131

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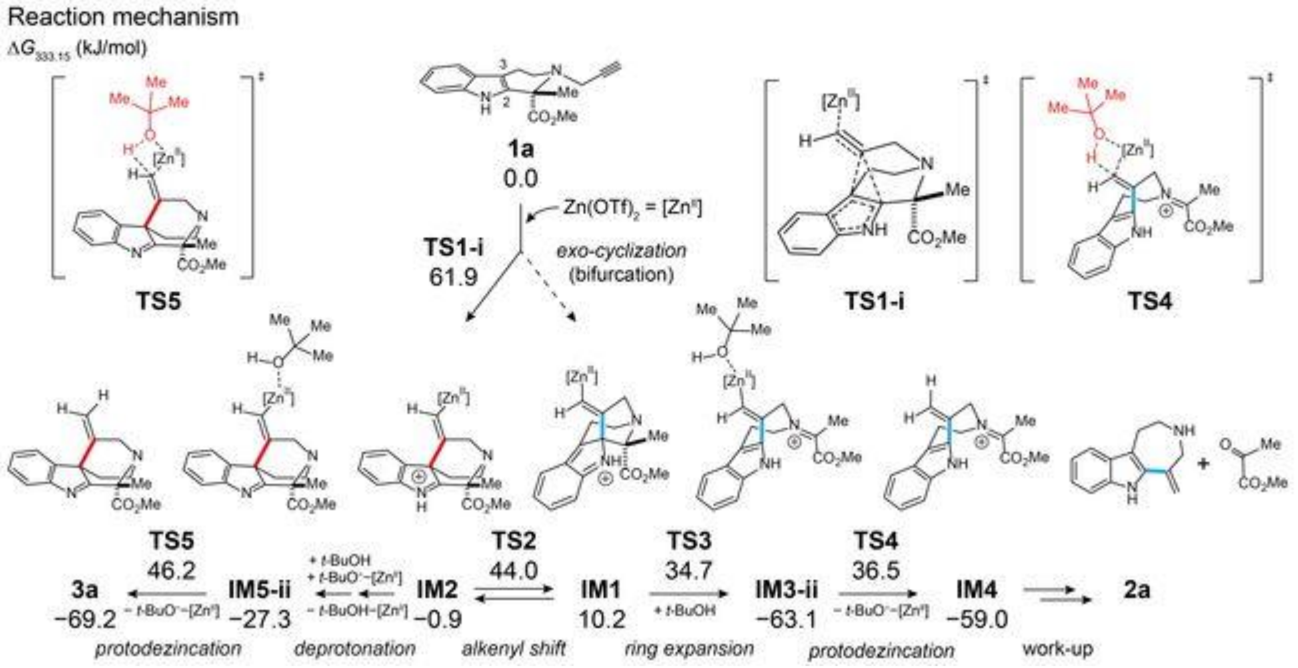
Bioactivities of indole alkaloids have attended much attention in the field of drug discovery. Alkaloidal scaffolds are generally complicated, and thus developments of synthetic processes for desired scaffolds would be important. Recently, Oguri and co-workers developed new processes that *N*-propargylated tetrahydrocarbolines as a common reactant converted to products with distinct scaffolds [1]. For example, reactant **1a** converted to three products **2a/3a/4a** under mild condition (Zn(OTf)$_2$ catalyst, *t*-BuOH solvent, and 60 °C). We have investigated reaction mechanisms from **1a** to **2a/3a/4a** by density functional theory (DFT) method combined with a systematic reaction path search method to provide mechanistic insights into the selectivity. The computational details were mentioned in our recent paper [1]. Free energies were evaluated at the ωB97X-D/Def2-SVP level with the SMD (*t*-BuOH) method.

Initially, Zn(OTf)$_2$ catalyst coordinates to the propargyl group of **1a**. As mentioned in our paper [1], at **IM0**, the intramolecular cyclization of **1a** proceeds: the *exo*-cyclization affords either **2a** or **3a**, and the *endo*-cyclization gives **4a**. The *exo*-cyclization via **TS1-i** is kinetically preferred over the *endo*-cyclization via **TS1-ii**. An intrinsic reaction coordinate calculation from **TS1-i** provided **IM1** and **IM2** as the two endpoints (see Figure). **IM2** can isomerize to **IM1** through the relatively low barrier **TS2**. **IM3-ii** is then generated through a C–C bond scission and subsequent solvent coordination. **IM3-ii** could be a resting state since it has the lowest energy of any structure along this path. **IM3-ii** undergoes protodezincation to yield **IM4** and *t*-BuO–[Zn^{II}]. **IM4** is expected to be hydrolyzed to **2a** in the workup procedure. Based on the free energy profile, a kinetic simulation was examined to illustrate the time evolution of the population of each species. Their simulated population was qualitatively consistent with the experimental yields.



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Large-Scale Quantum Mechanical Molecular Dynamics Simulations of Polaron Formation Process in a Lead Halide Perovskite Material Using Divide-and-Conquer Type Density-Functional Tight-Binding Method

P132

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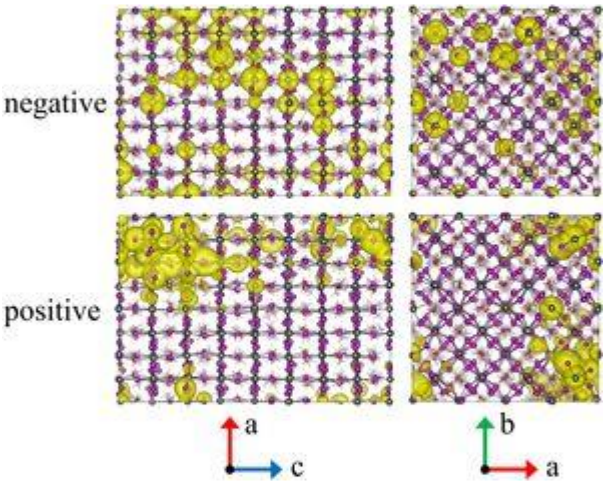
Polarons, which are charges in solids wearing structural deformation, play a key role in photo-electronic devices such as solar cells. In particular, in order to understand the extremely long charge carrier lifetime and diffusion length in perovskite solar cells, which are photovoltaics composed of lead halide perovskites (LHPs), the polaron formation process in LHPs is desired to be clarified. To obtain the atomistic information of the polaron formation process, quantum-mechanical (QM) molecular dynamics (MD) simulations are promising ways. However, because the polaron formation phenomenon in LHPs is expected to have the spatial scale of nanometers and time scale of hundreds of femtoseconds, conventional first-principles techniques such as Kohn-Sham DFT have severe difficulties because of their computational cost. For this reason, we employed divide-and-conquer type density-functional tight-binding (DC-DFTB), which is a linear-scaling quantum mechanical calculation method capable of QM-MD simulations of systems composed of (tens of) thousands of atoms.

In this study, the most typical LHP for solar cells, $MAPbI_3$ (MA = CH_3NH_3), is the target of discussion. The polaron formation process was tracked by NVE-MD simulations with additional -1 or +1 charge in the model system. The employed model system is a 4 * 4 * 4 supercell of $MAPbI_3$, whose size is 3.7 nm * 3.7 nm * 5.4 nm, composed of 3,072 atoms. The calculations were performed under periodic boundary condition, using Dcdftbmd code.

The obtained snapshots of spatial charge carrier distributions are shown by yellow isosurfaces in the figure, where the radii of the negative and positive charge carriers are estimated at 1.1 and 0.9 nm, respectively, suggesting the importance of the large model system for the simulations. On the basis of the simulation results, the relationship between the structural deformation and the charge localization were discussed. Further details will be presented in the poster.



Cyclohexane Oxidation in Zeolites: Molecular Mechanism and Energetics

P133

Mr Rahul Verma[1], Mr Shilendra Kumar Sharma[2,3], Ms Shilpi Saxena[2,3], Mr Raj Ganesh Pala[2,3], Mr sri sivakumar[2,3], Mr Nisanth N Nair[1]

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The catalytic transformation of alkane C-H bond by microporous crystalline solids acids are widely used in the oil and petrochemical industries in the process of cracking of hydrocarbons [1]. Understanding the reaction mechanism of these hydrocarbon cracking over acidic zeolite [2] [3] is of great importance. For this purpose mechanism of the oxidation of cyclohexane over acidic zeolites i.e. Na-ZSM-5 and MCM-22, is studied using density functional theory (DFT) calculations. Experimental studies have revealed that a combination of these two zeolites (dual zeolite) gives a higher rate of conversion from cyclohexane to cyclohexanone and cyclohexanol (KA-oil), along with a substantial decrease in the amount of byproducts released [4]. In our theoretical study, we observed that the conformation of cyclohexane changes during the C-H bond activation at the transition state. This activation process triggers the reaction and a cyclohexyl peroxide compound is formed which is subsequently converted into KA-oil.

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Spectroscopic Investigation of 2-Phenylcyclobutanamine and Ethylbenzene Derivatives in the Gas-Phase

P134

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The ability for a molecule such as a neurotransmitter to bind to a receptor is determined by the functional groups present in the molecule. While functional groups play a large role in this binding, the molecular conformation preference plays a significant role.

The conformational preference of the neurotransmitter analogue 2-Phenylcyclobutanamine in the gas-phase was investigated. With the use of one colour R2PI, the electronic spectrum was recorded and subsequently the infrared spectrum by IR-UV ion depletion. Water clusters were also observed and theoretical calculations and spectra were used aid in assignment of conformational preference.

An anharmonic model shown to have improved accuracy in predicting aliphatic CH stretches in comparison to computed IR spectra was implemented to aid in conformational assignment. The anharmonic model was also applied to number of haloethylbenzenes showing significant agreement with experimental spectra. As a result anti and gauche conformational assignments were made for a number of haloethylbenzene molecules.

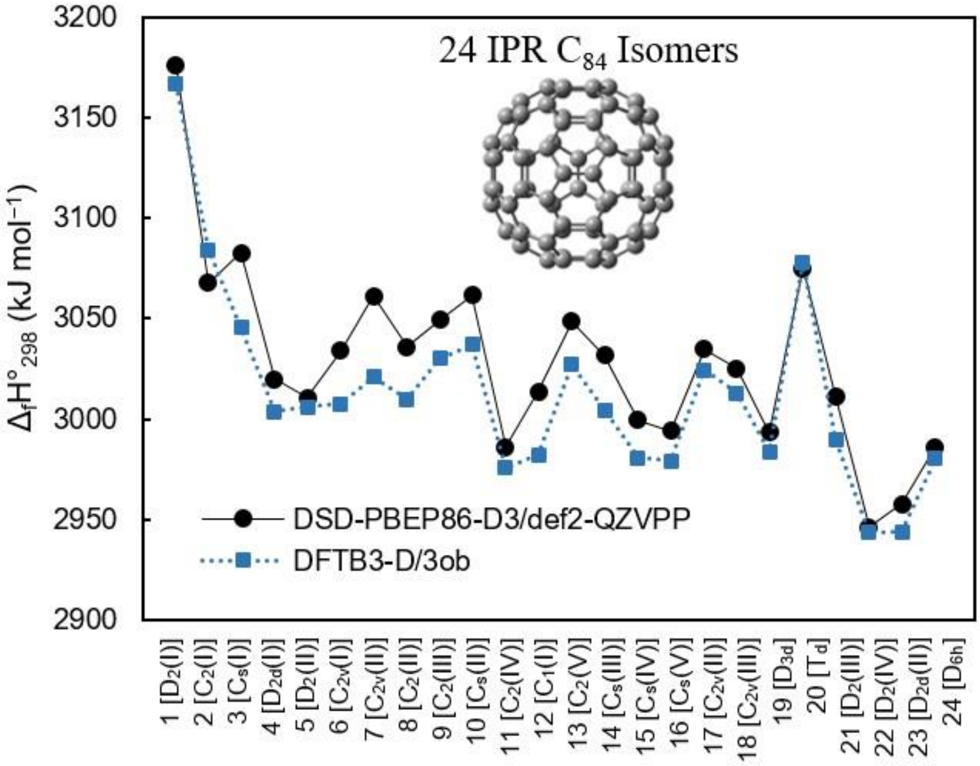
Thermochemical and Kinetic Stabilities of Giant Fullerenes Using Density Functional Tight Binding Theory with Isodesmic Reactions

P135

Miss Simone L Waite, Dr Alister J Page

University of Newcastle, Newcastle, Australia

Carbon-based nanomaterials (fullerenes, nanotubes, graphene, etc) have attracted particular interest due to their unique electronic, optical, thermal, mechanical and chemical properties. In 1985 the first of these carbon nanostructures to be discovered and characterized was buckminsterfullerene, $(I_h)C_{60}$.[1] Despite the wealth of investigation into this remarkable molecule, the Δ_fH for C_{60} (2560 kJ mol^{-1} according to NIST[2]) remained uncertain, with experimental values spanning ±100 kJ mol^{-1}. Recently, double hybrid density functional theory and W1h theory[3] have been employed to obtain an accurate Δ_fH for C_{60} (2520.0 ± 20.7 kJ mol^{-1})[4] and some higher fullerenes[5] via isodesmic reaction schemes. However, such high-level approaches are impractical for comprehensively studying giant fullerenes, due to their size and the huge number of cage isomers. Here we demonstrate the utility of dispersion-corrected 3rd-order density functional tight binding (DFTB3-D/3ob) method for predicting Δ_fH in larger fullerenes using isodesmic reactions. We show that DFTB3-D/3ob performs well for all 24 IPR C_{84} isomers to benchmark DSD-PBEP86/def2-QZVPP Δ_fH values[6] (Figure). This gives the opportunity for further application of DFTB3-D/3ob to a wider range for fullerene systems, including larger fullerenes and carbon nano onions.



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Machine Learning for Predicting Electron Transfer Coupling in Organic Semiconductors

P136

Dr. Chun-I Wang[1], Dr. Chao-Ping Hsu[1], Dr. Gil C. Claudio[2], Dr. Ignasius Joanito[1], Mr. Chang-Feng Lan[1], Mr. Mac Kevin E. Braza[2]

[1]Institute of Chemistry, Academia Sinica, Taipei, Taiwan. [2]Institute of Chemistry, University of the Philippines Diliman, Quezon City, Philippines

Electron transfer coupling is a critical factor in determining electron transfer rates. This coupling strength can be sensitive to details in molecular geometries, especially inter-molecular configurations. Thus, studying charge transporting behavior with full first principles methods demands a large amount of computation resources. To address this issue, we developed a machine learning (ML) approach to evaluate electronic coupling. The kernel-based and neural-networks-based ML models with Coulomb matrix representation were built for ethylene, naphthalene, carbazole and fluorine systems. The ML models achieved a reasonable mean absolute error and high accuracy in phase prediction. The distance and orientation dependence of electronic coupling was successfully captured. Most importantly, bypassing QC calculation, the ML model could save 10 to 10^4 times the computation cost. With the help of ML, reliable charge transport models and mechanisms can be further developed.

Establishing Design Principles for Dendronised Polymer Systems for CRISPR Construct Delivery

P137

Ms Lily Wang, A/Prof Megan O'Mara

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Dendronised polymers are a promising solution to the ongoing problem of non-viral delivery of CRISPR constructs for genome engineering. Computational characterization of polymers can be challenging because of the non-linear nature of many polymers. We introduce PolyTop, a molecular dynamics topology builder for non-linear polymers. Using PolyTop, we simulate polymers with polyamidoamine (PAMAM) dendrons to explore the effect of structural changes on transfection efficiency. Properties such as solvent-accessible surface area are correlated with experimental trends in packaging and delivery efficiency.

Toward a Quantum-Chemical Benchmark Set for Enzymatically Catalyzed Reactions: Important Steps and Insights.

P138

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Benchmarking is an essential tool in quantum chemistry for both method developers and general users, but often benchmark sets focus on smaller molecules due to the high computational cost of dealing with larger systems. In this work, we present steps toward the construction of a benchmark set for five enzymatically-catalyzed reactions using active site models, ranging in size from 27 to 112 atoms [1]. Our work is inspired by a study of semi-empirical molecular-orbital theory methods against B3LYP-based structures and energies [2]. Using the same model systems used in that study, we first explore the structural differences between the popular B3LYP/6-31G(d,p) level of theory and newer methods that include adequate treatments of London dispersion and basis-set superposition error. We then investigate different strategies to obtain either exact or estimated complete-basis-set (CBS) barrier heights (BHs) and reaction energies (REs) with the help of the DLPNO-CCSD(T) approach, which offers an exciting and more affordable path into exploring larger biochemically relevant structures at the coupled cluster level. Based on our analysis, we present three strategies for obtaining reliable values. These recommendations constitute our main findings, and can be used by others as guidelines for their own analyses. We also conduct a preliminary benchmark study of 35 density functionals on 16 BHs and 12 REs across the five reactions, which we use as an indicator for the validity of our approach toward generating such a benchmark set, as we are able to reproduce major recommendations in the field of modern DFT.

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Optimisation of Free Energy Calculations for Use in Structure-based Drug Design

P139

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Despite a rigorous theoretical framework and the potential for high accuracy calculations based on free energy perturbation or integration methods have not found routine use in structure-based drug design. One of the main challenges is transferring methodology optimized for small, generally rigid ligands carrying a most a single charged group to larger (> 40 atoms) flexible systems containing a range of diverse chemical moieties, the type of molecule increasingly of interest in structure-based drug design. This is further complicated by desire to develop automated high throughput protocols that can efficiently exploit advances in hardware. In this work the suitability of a range of protocols involving single and dual topologies, various soft core potentials and different ways to combine ligands have been compared exploiting a series of molecules used to validate the OPLS[1], GAFF[2] and ATB[3] force fields.

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3. (a) Malde, A. K.; Zuo, L.; Breeze, M.; Stroet, M.; Poger, D.; Nair, P.C.; Oostenbrink, C.; Mark, A. E. *J. Chem. Theory Comput.* **2011**, *7*, 4026-4037. (b) Koziara, K. B.; Stroet, M.; Malder, A. K.; Mark, A. E. *J. Comput. Aided Mol. Des*. **2014**, *28*, 221-233. (c) Stroet, M.; Caron, B.; Visscher, K.; Geerke, D.; Malde, A. K.; Mark, A. E. *J. Chem. Theory Comput*. **2018**, *14*, 5834-5845.

Directing the Self Assembly of Nanorods with Depletion Interactions

P140

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Colloidal nanorods made of semiconductors or noble metals exhibit useful and tuneable properties that depend on their dimensions and on how they are ordered on larger scales. How they assemble is highly dependent on how the rods interact with one another and with their environment. One way to drive the assembly of nanorods into an ordered structure is via the addition of a polymer depletant. Adding this depletant applies an osmotic pressure to the rods causing them to aggregate into liquid-like droplets or ordered assemblies (nematic, smectic or crystal), depending on the dimensions and the concentrations of the two components.

To better understand the forces driving assembly in such systems, we have used SAXS experiments together with Monte-Carlo simulations to study rod assembly in dispersions of CdSe nanorods and polystyrene depletants of different molecular weights. We find that, depending on the polymer size, some types of order do not form, different types of order may coexist over large concentration ranges and the dimensions of an assembly can change the order present. Our results indicate that this is due to interfacial contributions to the free energy, which strongly affect the order and shape of the assemblies that form.

Finally, we have used umbrella sampling to characterise assembly pathways for a range of different polymer concentrations and sizes, and show that monolayer nucleation and growth can be the optimal pathway even when starting from a dense liquid state.

Nitroxide Radical All-Organic Batteries in Ionic Liquid Electrolytes

P141

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Currently, the predominant storage type for solar cells are the expensive, non-renewable vanadium flow and lithium-ion batteries. An alternative are all-organic, radical based batteries, with the reaction of these radicals providing a competitive capacity and voltage. One such example of a potential battery is based on a nitroxide radical in a neat ionic liquid (IL). ILs have previously shown an ability to stabilise radicals comprised of both carbon and oxygen radical centres as well as increasing their redox potential and making the redox process reversible. The effect of the ILs is seen to vary greatly between different IL structures, with both the anion and the cation playing a pivotal role in the stability of radicals. The total interaction energy between IL and radical can be up to -86.6kJ mol^{-1} for the 1,3-dimethylimidazolium triflate IL solvent.[1] This computational result was correlated with experimental data where the rotational diffusion of the radical was measured using EPR to determine there was a direct correlation between rotational hindrance of the radical and interaction energy between the radical and IL. Therefore, the most likely IL to stabilise the radical was determined to be those containing triflate. This knowledge was then applied to a TEMPO flow battery, in which the TEMPO radical underwent both reduction and oxidation processes. Our quantum chemical calculations demonstrated that the redox potential could be significantly improved compared to traditional aqueous electrolytes.[2] Equally important, the aminoxy anion (see Fig. 1) produced upon the reduction of the nitroxide radical, was shown to be stabilised by IL ions allowing us to make the reduction process reversible. This is the first report of such reversibility of nitroxide radicals in any media.

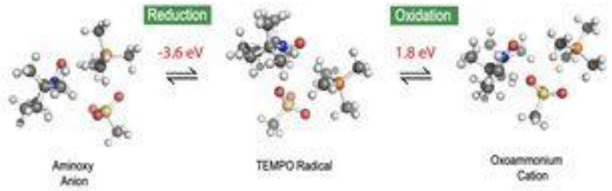

Figure 1: Potential reactions and redox potential involved in a TEMPO/TEMPO redox flow battery.

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2. L.Wylie, K.Oyaizu, A.Karton, M.Yoshizawa-Fujita, E.I.Izgorodina, *ACS Sustainable Chemistry & Engineering* **2019**, *7*, 5367-5375.

Methods to Improve the Calculations of SMD Solvation Free Energies and Associated pKa Values: Comparison between Choosing an Optimal Theoretical Level, Solute Cavity Scaling and Using Explicit Solvent Molecules

P142

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Many approaches have been used to improve the accuracy of implicit solvent models. Here we compare three strategies in title using a large test set of pK_a values for amines, nucleobases, carboxylic acids, thiols, peptide carbon acids, alcohols and anilines, as calculated using different protocols for calculating Gibbs free energies of solvation using SMD within the framework of a thermodynamic cycle. The gas-phase component is consistently calculated via the high-level CBS-QB3 method so as to minimize other sources of error. Two protocols without explicit solvent molecules were first evaluated with the finding that using protocol 1 in this work is more accurate than using the best compromise level of theory, M052X/6-31G(d) (protocol 2), especially for methyl substituted nucleic acid bases. Two further protocols were tested, in which an explicit solvent molecule was included and SMD solvation energies were calculated using either M052X/cc-PVTZ (protocol 3) or M062X/6-31G(d) (protocol 4). It was found that the results with protocol 3 were superior to protocol 4, and that both out-performed protocols 1-2 for acids, but showed larger errors for bases. In other words, the anions benefit from explicit solvation but the cations do not, which indicates that using explicit solvent does not always improve results. Our recommended protocols (1 for bases and 3 for acids) were compared with results obtained via solute cavity scaling. Our results suggest that solute cavity scaling does not significantly improve the SMD results for the C, H, N, O compounds tested when the correct theoretical level is employed and explicit solvent effects are correctly calculated, and that solute cavity scale factors for one class of compounds in one solvent cannot be directly applied to other solute/solvent combinations.

Relativistic Effects in the K-Shell ionization Differential Cross Sections of Heavy Elements with the Complex Basis Function Method

P143

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Various relativistic effects become important in the K-shell photoionization differential cross sections (DCS) of heavy elements. The large and small components of the initial bound state have different orbital angular momenta. In addition, at a high photon energy, the multipole effects beyond the dipole approximation become important. Their significance has been well-known for a long time, but their theoretical studies are rather limited. In this study, we try to calculate the DCSs including these effects with the complex basis function (CBF) method[1], hoping future applications to molecular systems.

The relativistic DCS can be calculated by extending the corresponding non-relativistic CBF treatment[2]. The first-order perturbed wave function (FOPwf) induced by a light irradiation satisfies the relativistic inhomogeneous equation consisting of the unperturbed Dirac Hamiltonian and the inhomogeneous perturbation term of the vector potential times the initial bound state. The regular continuum wave function is derived from the FOPwf.

We approximate the potential of the uranium K-shell electron by a pure Coulomb potential, and express the FOPwf by a linear combination of real and complex STOs[2]. Fig 1 shows the DCS at 279 keV. Our result (this work), almost identical to previous numerical relativistic values by Pratt *et al.*[3], is compared with Sujkowski's experimental values[4], and the results derived by the relativistic and non-relativistic Born approximations, all of which included multipole effects. We also show the DCS in the non-relativistic dipole approximation. The detailed comparisons will be given in the presentation.

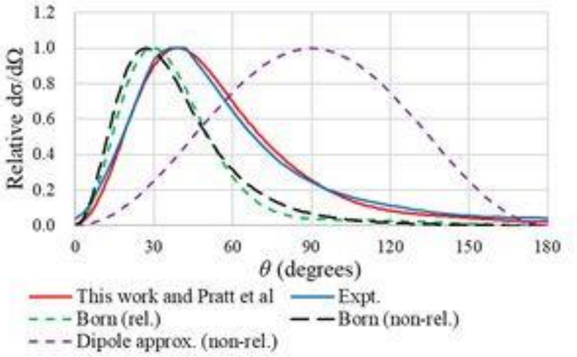

Fig 1. Uranium K-shell differential cross sections at 279keV. The maxima of DCSs are normalized to unity

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Competition Between Charge Migration and Charge Transfer Induced by Nuclear Motion Following Core Ionization: Model Systems and Application to Li_2^+

P144

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Attosecond spectroscopy presents opportunities for the control of chemical reaction dynamics and products, as well as for quantum information processing; we address the somewhat unique situation of core-ionization spectroscopy which, for dimeric chromophores, leads to strong valence charge localization and hence tightly paired potential-energy surfaces of very similar shape. Application is made to the quantum dynamics of core-ionized Li_2^+, with Li_2 being the simplest stable molecule facilitating both core ionization and valence ionization. First, the quantum dynamics of some model surfaces are considered, with the surprising result that subtle differences in shape between core-ionization paired surfaces can lead to dramatic differences in the interplay between charge migration and charge transfer induced by nuclear motion. Then, equation-of-notion coupled-cluster (EOM-CCSD) calculations are applied to determine potential-energy surfaces for 8 core-excited state pairs, calculations believed to be the first of their type for other than the lowest-energy core-ionized pair. While known results for the lowest-energy pair suggest that Li_2^+ is unsuitable for studying charge migration, higher-energy pairs are predicted to yield results showing competition between charge migration and charge transfer. Highlighted is a focus on the application of Hush’s 1975 theory for core-ionized X-ray photoelectron spectroscopy (XPS) to understand the shapes of the potential-energy surfaces and hence predict key features of attosecond charge migration.

Linear-Scaling Divide-and-Conquer Finite-Temperature Self-Consistent Field for Static Correlation Systems

P145

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The efficient evaluation of electron correlation has been a key issue in quantum chemical calculations. Electron correlation is typically categorized into dynamical and static contributions, although these contributions are inseparable in principle. For treating the dynamical electron correlation of large systems, many multilayer techniques or fragmentation-based linear-scaling methods exist. However, only a few attempts have been conducted to combine the fragmentation-based method with static correlation theories other than the multilayer schemes. For systems with static correlation effects, several multiconfiguration and multireference theories have been used widely. These theories require the manual determination of the active space before calculations. Although using the automated active space selection scheme is practical, attempts to combine the fragmentation-based method are lacking owing to difficulties in the automated active space selection of each fragment.

Other approaches for static correlation based on single-reference theories have been developed. These single-reference-based schemes can effectively describe the bond-breaking reactions, double bond rotation, diradicals, and conjugated polymers with smaller computational costs. The finite-temperature (FT) schemes can incorporate static correlation effects by introducing the concept of fractional occupation number with a fictitious temperature and electronic entropy.

In this study, we extended the FT scheme to the divide-and-conquer (DC) self-consistent-field (SCF) calculations. The DC method proposed by Yang and Lee is a fragmentation-based method. The authors' group has reported the development of the DC-based Hartree-Fock, hybrid density functional theory electron-correlation, and excited-state methods. The DC method originally utilizes the fractional occupation number for each fragment for wide applicability to systems with delocalized electrons and/or spins and to improve the SCF convergence. DC-based approaches are highly compatibility with the FT schemes. Test calculations of various systems demonstrate the high accuracy and efficiency of FT-DC-SCF.

Re-Examination of Proline-Catalyzed Intermolecular Aldol Reaction: A Theoretical Study of the Mechanism and Stereoselectivity

P146

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Full catalytic cycle of proline-catalyzed intermolecular aldol reaction of acetone and p-nitrobenzaldehyde in acetone solvent has been investigated by G3(MP2,CC)//M062X/6-31+G(d) level of theory. The SMD solvent model was used to calculated the solvation Gibbs free energies at M062X/6-31+G(d) level of theory. Proline catalyzes the aldol reaction according to the enamine mechanism. The initial reaction between proline and acetone was reinvestigated. The stereoselectivities of reactions of enamine with syn- and anti-arrangement and the re and si attack modes of p-nitrobenzaldehyde have been analyzed. Finally, the electrostatic effects on the barrier heights and reaction energies were also studied.

Mechanistic Investigation of the Intramolecular C-H Bond Silylation by Silacyclobutane

P147

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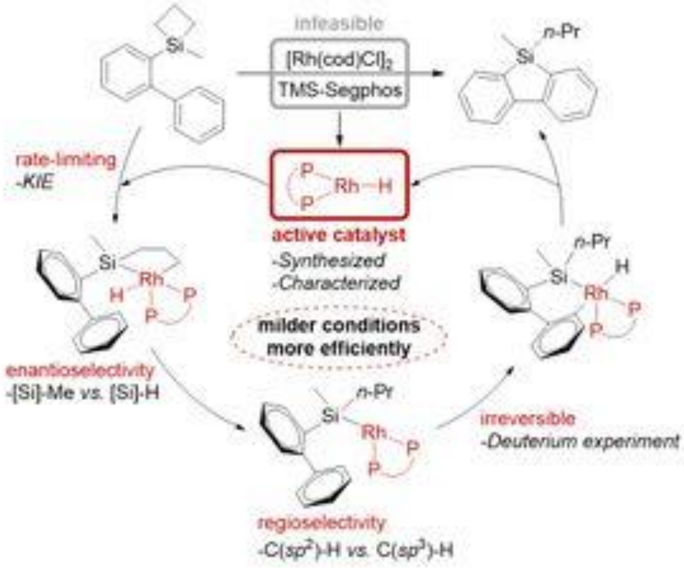
The mechanism of intramolecular C-H bond silylation *via* silacylcobutane (SCB) was studied combining both experiments and DFT computations. The DFT calculations revealed that a Rh(I)-hydride species was the active catalyst which requires a high energy barrier to generate from the Rh(I)-chloride precatalyst. The active catalyst was synthesized, characterized by NMR spectrum, and the reactions proceed efficiently under much milder conditions catalyzed by the active catalyst because the high energy requiring generation of active catalyst step was avoided. The rate-limiting step in the catalytic cycle is the oxidative insertion of [Rh]-H into the SCB ring, while the C-H bond activation step was irreversible but not rate-limiting. Results of kinetic isotope effects, deuterium labeling experiments, and kinetic analysis are consistent with the theoretical studies. The DFT studies also demonstrated that C(sp^2)-H bond activation was slightly favored over C(sp^3)-H bond by comparing corresponding energy barriers. Meanwhile, the calculations of the asymmetric reactions were performed to explain the enantioselectivity of different substrates.



Reaction Paths for Methacrolein with Low Energy Barriers

P148

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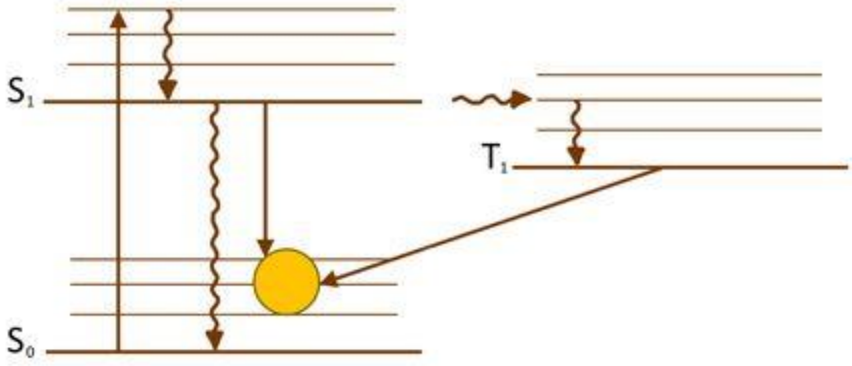
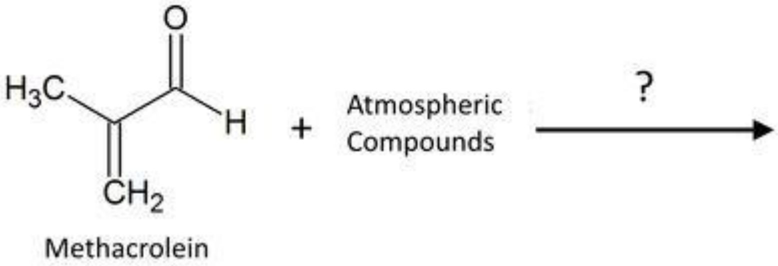
Despite being produced in substantial amounts, methacrolein's reaction fate is not fully known, leaving atmospheric models used to predict air quality excluding potential key pathways. Methacrolein is a major product of isoprene, the predominant reactive hydrocarbon emitted into the atmosphere. It absorbs solar irradiation strongly however, photolysis is slow, with a significant portion of photoexcited methacrolein expected to relax to the vibrationally excited ground state, available for reactions. We examine whether methacrolein in such states reacts with major atmospheric gases: nitrogen and oxygen. The threshold energies of the reactions in ground and excited states are being calculated using Density Functional Theory to examine feasibility. Product studies are also being made via Fourier transform infrared spectroscopy. Preliminary calculations support the feasibility of a reaction with oxygen, with an energy threshold from the ground state well within energy gained through solar irradiation. Initial experimental results support this, with different products formed at energies below that of known reaction pathways. By further clarifying the reaction's properties, a new degradation pathway for methacrolein may be elucidated, bringing atmospheric model predictions to more closely reflect reality.





Bimetallic Alloys for CVD growth of Graphene and Carbon Nanotubes

P149

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Low dimensional carbon nanomaterials such as graphene/carbon nanotubes (CNTs) have been the focus of research interest due to their remarkable physicochemical properties and potential industrial applications. Bimetallic alloy catalysts are novel materials for chemical vapour deposition growth of graphene and CNTs, due to their heteronuclear metal-metal bonding, geometrical structure and catalytic properties. In this work, first principles calculations were performed to examine the strength of the graphene-catalyst interaction for bimetallic transition metal alloy catalysts (Figure 1). Results indicate that alloys composed of a strongly interacting metal and a weakly interacting metal produce yield alloys with ideal graphene interaction strengths, and vice-versa. We show also that the surface layer structure plays a major role in determining the overall graphene-metal interaction for these alloy catalysts. These findings will assist in the future experimental development of new alloy CVD catalysts for more controlled carbon nanostructure growth.

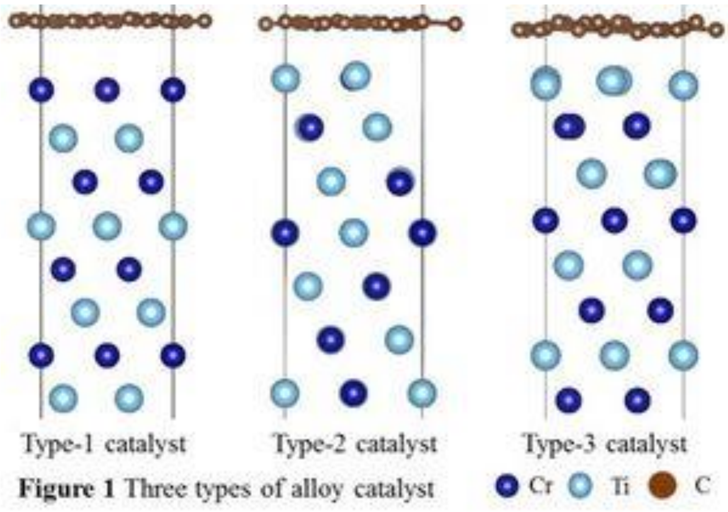

Figure 1 Three types of alloy catalyst