

28th Canadian Symposium on Theoretical and Computational Chemistry

Program and Book of Abstracts

Windsor, Ontario, July 15–19, 2018



Welcome



<http://cstcc2018.catc.ca>

The Canadian Symposium on Theoretical and Computational Chemistry (CSTCC) is the largest regularly occurring meeting of theoretical chemists in Canada. Held every two years, the CSTCC is the merged successor of two conference series: Canadian Symposium on Theoretical Chemistry (1965–2010) and Canadian Computational Chemistry Conference (1992–2009). Since the merger, the CSTCC has been held in Guelph, Ontario (2012), Montreal (2014), and Regina, Saskatchewan (2016). The 28th CSTCC, hosted at the downtown campus of the University of Windsor, continues the long-standing tradition of bringing together researchers from Canada and around the world. The CSTCC program covers the full scope of theoretical and computational chemistry, including methodological advances and high-level applications.

It is our great pleasure to welcome you in Southern Ontario. We hope that you will enjoy both the scientific and social programs of the Symposium as well as your stay in the area.

Sincerely,

James W. Gauld, University of Windsor

Viktor N. Staroverov, The University of Western Ontario

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Molecules



Special thanks go to Prof. Mark Thachuk who helped us with the CSTCC website.

Symposium Venues

Registration / Check-in

Sunday, July 15, 4:00 pm – 7:30 pm
School of Social Work Building (167 Ferry St.)

From Monday to Thursday, badges may be picked up near the lecture hall

Opening mixer

Sunday, July 15, 6:00 pm – 7:30 pm
School of Social Work Building

Talks

Monday, July 16, 8:50 am – Thursday, July 19, 5:10 pm
School of Social Work Building

Poster sessions

School of Social Work Building

Session A (presenters whose last names begin with the letters A–L):
Monday, July 16, 5:00 pm – 6:30 pm

Session B (presenters whose last names begin with the letters M–Z):
Wednesday, July 18, 5:00 pm – 6:30 pm

CATC business meeting (lunch will be provided)

Wednesday, July 18, 12:30 pm – 2:00 pm
School of Social Work Building

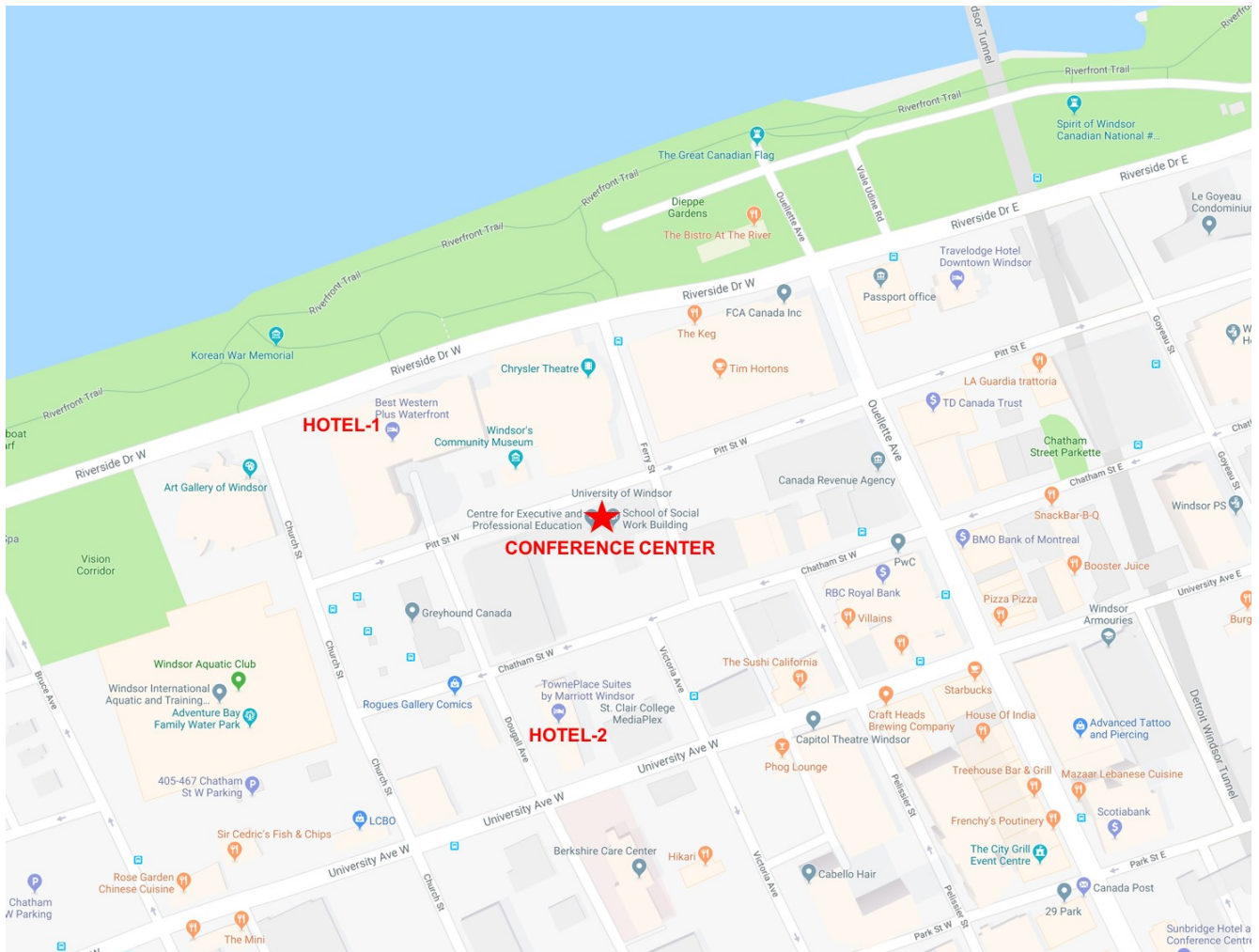
Banquet

Wednesday, July 18, 7:00 pm – 9:00 pm
The Windsor Club (2072 Riverside Dr. East)
<http://www.windsor-club.com>

Shuttle buses will be provided

Map of symposium venues and local restaurants

Downtown Windsor, Ontario



Conference Center: School of Social Work Building (167 Ferry St.)

Hotel 1: Best Western Plus Waterfront Hotel (277 Riverside Dr. West)

Hotel 2: TownePlace Suites by Marriott Windsor (250 Dougall Ave.)

SCHEDULE OF ORAL PRESENTATIONS

Monday, July 16

Session Chair: James Gault

- 8:50 – 9:00 Introductory remarks
- 9:00 – 9:30 **Raymond Kapral**, University of Toronto
Molecular machines and synthetic motors: Active motion on nanoscales
- 9:30 – 10:00 **Artur Izmaylov**, University of Toronto Scarborough
Constrained quantum variational eigensolver: Quantum computer search engine in the Fock space
- 10:00 – 10:30 **Nicholas Mosey**, Queen's University
Periodic quantum chemistry using contracted plane-wave basis functions
- 10:30 – 11:00 Break

Session Chair: Arvi Rauk

- 11:00 – 11:30 **H. Bernhard Schlegel**, Wayne State University
Computational simulation of molecules interacting with intense laser fields
- 11:30 – 12:00 **Ksenia Bravaya**, Boston University
Multireference perturbation theory for metastable electronic states
- 12:00 – 12:30 **Alex Brown**, University of Alberta
Two-photon absorption in biofluorophores
- 12:30 – 14:00 Lunch break
- 14:00 - 15:00 **2017 CATC Honorary Lecture: Axel Becke**, Dalhousie University
Localization/delocalization errors in density-functional theory
- 15:00 – 15:30 Break

Session Chair: Paul Ayers

- 15:30 – 16:00 **Weitao Yang**, Duke University
Localized orbital scaling correction for systematic elimination of delocalization and static/strong correlation error in density-functional approximations
- 16:00 – 16:30 **Matthias Ernzerhof**, Université de Montréal
Surface plasmon polariton-controlled molecular switch
- 16:30 – 17:00 **Alex Wang**, University of British Columbia
Functional differentiability and derivatives in DFT: The whole story thus far

Tuesday, July 17

Session Chair: Dennis Salahub

- 9:00 – 9:30 **Peter Tieleman**, University of Calgary
Challenges in simulations of biological membranes
- 9:30 – 10:00 **Sarah Rauscher**, University of Toronto Mississauga
Molecular simulations of intrinsically disordered proteins
- 10:00 – 10:30 **Justin MacCallum**, University of Calgary
Solving protein structures by iterating between computation and experiment
- 10:30 – 11:00 Break

Session Chair: Styliani Consta

- 11:00 – 11:30 **Stacey Wetmore**, University of Lethbridge
Modeling the structure, repair and replication of damaged DNA
- 11:30 – 12:00 **Sergei Noskov**, University of Calgary
*Electronic polarization effects in the molecular confinements:
Next frontier for bio-molecular simulations*
- 12:00 – Bus tour / Free time

Wednesday, July 18

Session Chair: Mark Thachuk

- 09:00 – 09:30 **Aurora Clark**, Washington State University
Advanced graph-theory methods for characterizing and exploring condensed-phase organization, dynamics, and reactivity
- 09:30 – 10:00 **Tao Zeng**, Carleton University
Our recent studies on vibronic coupling: applications in singlet fission and derivation of (pseudo-)Jahn–Teller formalisms
- 10:00 – 10:30 **Jason Pearson**, University of Prince Edward Island
Electron pair distributions as a predictive tool in chemistry
- 10:30 – 11:00 Break

Session Chair: Marcel Nooijen

- 11:00 – 11:30 **Piotr Piecuch**, Michigan State University
Toward exact quantum chemistry: High-level coupled-cluster energetics by Monte Carlo sampling and moment expansions
- 11:30 – 12:00 **Joshua Hollett**, University of Winnipeg
The ΔNO method: A hybrid approach to the correlation problem
- 12:00 – 12:30 **Paul Johnson**, Université Laval
Model wavefunctions for strongly correlated systems
- 12:30 – 14:00 Lunch break / CATC Business Meeting
- 14:00 – 15:00 **Plenary Lecture: Peter Gill**, Australian National University
New ways to think about electronic excited states
- 15:00 – 15:30 Break

Session Chair: Erin Johnson

- 15:30 – 16:00 **Roman Krems**, University of British Columbia
Applications of machine learning for quantum dynamics
- 16:00 – 16:30 **Gabriel Hanna**, University of Alberta
An efficient solution of the quantum-classical Liouville equation without surface hopping
- 16:30 – 17:00 **Aaron Kelly**, Dalhousie University
Trajectory-based approaches to quantum dynamics: Wavefunctions, density matrices and master equations

Thursday, July 19

Session Chair: Allan East

- 09:00 – 09:30 **Andreas Götz**, University of California San Diego & Scripps Research Institute
Insights into oxygen activation and proton pumping of cytochrome c oxidase from DFT and molecular dynamics
- 09:30 – 10:00 **Martin Field**, Laboratoire Chimie et Biologie des Métaux, CEA, Grenoble
Adaptive hybrid potential simulations of condensed phase systems
- 10:00 – 10:30 **Rustam Khaliullin**, McGill University
Ab initio molecular dynamics on nanoscale

10:30 – 11:00 Break

Session Chair: Russell Boyd

- 11:00 – 11:30 **Seiji Mori**, Ibaraki University
Mechanistic insights into metal-catalyzed highly selective organic transformation reactions
- 11:30 – 12:00 **Gilles Peslherbe**, Concordia University
Computational investigation of biologically viable pathways for thionitrate decomposition in model compounds and enzymes
- 12:00 – 12:30 **Christopher Rowley**, Memorial University of Newfoundland
Molecular mechanical force fields with higher-order dispersion terms using the exchange-hole dipole moment model
- 12:30 – 14:00 Lunch break
- 14:00 – 15:00 **2018 CATC Honorary Lecture: Ajit Thakkar**, University of New Brunswick
Reflections on forty-seven years in theoretical and computational chemistry
- 15:00 – 15:30 Break

Session Chair: Viktor Staroverov

- 15:30 – 16:00 **Anguang Hu**, DRDC Suffield Research Centre
Multiresolution non-equilibrium simulations of ultrafast selective reactions under thermomechanical compression using quantum solid-state chemistry
- 16:00 – 16:30 **Nelaine Mora-Diez**, Thompson Rivers University
Deuterium isotope effects on acid-base equilibria
- 16:30 – 17:00 **Gino DiLabio**, University of British Columbia Kelowna
Development and application of atom-centered potentials for accurate modeling of large systems
- 17:00 – 17:10 Closing remarks

POSTER PRESENTATIONS

Poster Session A (Monday, July 16, 5:00 pm – 6:30 pm)

- A1 **Ahmad I. Alrawashdeh**
A practical model to predict the correlation energy of molecules
- A2 **James S. M. Anderson**
Truncating FCI using the mathematics of complexity for solving the electronic structure and nuclear structure Schrödinger equations
- A3 **Philippe Archambault**
Density-functional theory studies of vanadium oxide clusters and their reactions with fluorocarbons
- A4 **Samantha L. Bidwell**
Models for analyzing three-center two-electron bonds
- A5 **Stephen G. Dale**
Assessing the performance of the “B05” density functional on densities
- A6 **Allan L. L. East**
Hydrolysis mechanisms via semicontinuum modelling
- A7 **Amer M. El-Samman**
Ionization potentials from ab initio ground-state wave functions
- A8 **Carlos Enriquez-Victorero**
The behaviour of hydroxyl radical in aqueous systems: Complexes with halide anions
- A9 **Rebecca Evans**
Evaluation of hybrid and pure DFT methods for the binding of novel ligands in the tyrosine hydroxylase enzyme
- A10 **Alexandre Giguère**
Surface plasmon polariton controlled molecular switch
- A11 **Kyle W. Hall**
Molecular-level correlations in entangled polymer melts: Insights from molecular dynamics simulations
- A12 **Hrant P. Hratchian**
Efficient methods for studying electron detachment of metal oxide clusters
- A13 **Mu-Jie Huang**
Chemotactic clustering of chemically-powered Janus motors

- A14 **Hang Hu**
Electronic structure and properties of ZnO crystals and nanotubes
- A15 **Seifollah Jalili**
Molecular dynamics simulation of water transport through bilayer graphyne membranes
- A16 **Jaspreet Kaur**
TDDFT excitation energies from accurate exchange-correlation potentials
- A17 **Michael Kilgour**
Interplay of coherence and decoherence effects in quantum absorption refrigerators
- A18 **Roman Korol**
Charge transport in DNA: From comprehensive simulations to key principles
- A19 **Mike Lecours**
Alternative treatment of symmetry for use with local coupled-cluster approaches to molecules and solids
- A20 **Zhenfei Liu**
Efficient calculation of level alignment at weakly coupled molecule-metal interfaces using substrate screening within the GW approach

POSTER PRESENTATIONS

Poster Session B (Wednesday, July 18, 5:00 pm – 6:30 pm)

- B1 **Steven M. Maley**
How does the amount of Hartree–Fock exchange affect the observation of the pseudo-Jahn–Teller effect?
- B2 **Margot E. Mandy**
State-specific dissociation rate coefficients for $H_2(v,j) + H_2(v',j')$
- B3 **Nelaine Mora-Diez**
Modelling the repair of damaged proteins by antioxidants
- B4 **Egor Ospadov**
Construction of Fermi potentials for many-electron systems
- B5 **Irina Paci**
Theoretical evaluation of the dielectric response in metal/metal oxide nanocomposites
- B6 **Raymond A. Poirier**
Atoms in molecule density approach: A novel way of computing molecular energies and properties
- B7 **Alastair J. Price**
Dispersion-corrected density-functional theory applied to amino-acid adsorption on model quartz surfaces
- B8 **Cory C. Pye**
An ab initio investigation of the hydration of the d^0 transition-metal tetraoxo complexes. II. 5th and 6th period metals
- B9 **Arvi Rauk**
Copper(I) chelators for a trifunctional attack on Alzheimer's disease
- B10 **Neil Raymond**
Thermodynamic properties of nonadiabatic systems using Gaussian mixture distributions
- B11 **Angel Reyes Figueroa**
Evaluation of Martini coarse-grained model for microcanonical ensemble
- B12 **Bryan Robertson**
Dynamics of many chemically propelled nanomotors near reactive walls

- B13 **Shahin Sowlati-Hashjin**
Molecular dynamic investigation of mechanism of action of cationic PHMB on bacterial membranes
- B14 **S. Maryamdokht Taimoory**
Mechanistically well-designed furans-maleimides Diels-Alder approach in preparation of a materials raging from thermally-labile end-caps for self-immolative polymers to hydrogels for cell culture
- B15 **S. Maryamdokht Taimoory**
High-affinity and selective detection of pyrophosphate in water by a resorcinarene salt receptor
- B16 **Ruijie Darius Teo**
A single AT-GC exchange can modulate charge-transfer-induced p53-DNA dissociation
- B17 **Mark Thachuk**
Equations of motion for generalized coarse-grained particles obtained from Mori–Zwanzig projection
- B18 **Rodrigo Wang**
Correlation factor models for strong correlation
- B19 **Jian-Xiong Yang**
The longest C–C single bond and a potential new way to conduct electrons
- B20 **Chou-Hsun Yang**
Approximate DFT-based methods for generating diabatic states and calculating electronic couplings: Models of two and more states
- B21 **Shuyang Ye**
Quantum particle moving in a circular ring with potentials

**Abstracts
of
Oral Presentations**

Molecular machines and synthetic motors: Active motion on nanoscales**Raymond Kapral¹** and Pierre Gaspard²¹*Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada*²*Department of Physics, Université Libre de Bruxelles, Brussels, Belgium*

Molecular machines operate under nonequilibrium conditions and extract chemical energy from their environment to perform a variety of transport and other biological functions in the cell. Synthetic nanomotors without moving parts also operate under nonequilibrium conditions using chemical energy to move in solution, and are able to transport cargo and perform other functions. The mechanisms that lead to directed motion of chemically-powered motors and molecular machines will be discussed. Since both of these active objects must respect the basic laws of microscopic reversibility while functioning under nonequilibrium conditions, it will be shown that their theoretical descriptions have much in common, although they use very different mechanisms to move [1,2]. This link can be exploited in potential applications of synthetic nanomotors.

[1] P. Gaspard and R. Kapral, *J. Chem. Phys.* **147**, 211101 (2017).

[2] P. Gaspard and R. Kapral, *J. Chem. Phys.* **148**, 134104 (2018).

Constrained quantum variational eigensolver: Quantum computer search engine in the Fock space

Artur F. Izmaylov^{1,2}

*¹Department of Physical and Environmental Sciences, University of Toronto Scarborough
Toronto, Ontario M1C 1A4, Canada*

²Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

Quantum variational eigensolver (QVE) is an efficient computational method providing chemical accuracy in electronic structure calculations on a universal-gate quantum computer. However, such a simple task as computing the energy of a hydrogen molecular cation, H_2^+ is not possible for a general QVE protocol because the calculation will invariably collapse to the lower energy of the corresponding neutral form, H_2 . The origin of the problem is that QVE effectively performs an unconstrained energy optimization within the Fock space of the original electronic problem. We show how this can be avoided by introducing necessary constraints directing QVE to the electronic state of interest. The proposed constrained QVE can find an electronic state with a certain number of electrons, spin, or any other property. The new algorithm does not require any additional quantum resources.

Periodic quantum chemistry using contracted planewave basis functions

Nicholas J. Mosey

Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

Quantum chemical calculations of the electronic structures of condensed-phased systems play important roles in chemistry, physics, materials science, and engineering. While many approaches for representing the electronic structure in the condensed-phase exist, most popular methods employ periodic boundary conditions and expand the electronic states in a set of planewave basis functions to perform density functional theory (DFT) calculations. The large number of planewave basis functions required to describe the electronic states in conjunction with the poor scaling of the construction of the exact exchange operator in a planewave basis has precluded the use of modern density functionals that include exact exchange in these calculations. This limitation impacts the accuracy of such calculations, with problems ranging from relatively large errors in energies to completely erroneous descriptions of the electronic structure.

We have recently developed an approach for performing quantum chemical calculations of periodic systems that includes exact exchange in a manner that is much more efficient than approaches using planewave basis sets. Our method is based on using a set of localized atom-centered basis functions that are then represented by Fourier series expansions. The resulting functions, called contracted planewave basis functions (CPWBFs), are used as the basis functions in quantum chemical calculations. The localized nature of the CPWBFs allows the electronic structure to be represented accurately with a relatively small number of basis functions and facilitates the efficient evaluation of the exchange operator. As such, this approach is a promising means of performing DFT calculations of periodic systems using density functionals that include exact exchange, with recent calculations demonstrating that this approach is approximately 1 to 2 orders of magnitude faster than modern approaches for evaluating exact exchange with planewave basis sets. In this presentation, I will discuss the details of this method and describe approaches we have developed to increase the efficiency of this technique.

Computational simulation of molecules interacting with intense laser fields

H. Bernhard Schlegel

*Department of Chemistry, Wayne State University
Detroit, Michigan 48202, USA*

The availability of short, intense laser pulses has opened up new frontiers in chemistry and physics. Attosecond laser pulses can directly explore electron dynamics, image molecular orbitals and probe bond making and breaking processes. Intense femtosecond laser pulses can act as photonic reagents by selectively altering the nuclear and electronic dynamics of molecules. The response of molecules to short, intense laser pulses cannot be treated by the perturbative methods used for ordinary spectroscopy. Direct simulation of the dynamics is needed to understand the behaviour of molecules under these extreme conditions.

Short, intense laser pulses in the optical range cause rapid ionization. We have used time-dependent configuration interaction with absorbing boundaries to simulate the ionization and find that strong field ionization rates depend markedly on the conjugation length of the molecule and the orientation of the molecule in the laser beam. The shapes of the ionization yield for linearly polarized light can be understood primarily in terms of the nodal structure of the highest occupied orbitals. Depending on the orbital energies, ionization from lower lying orbitals may also make significant contributions to the shapes. The shapes of the ionization yield for circularly polarized light can be readily explained in terms of the shapes for linearly polarized light.

In the mid IR range, short intense laser pulses can rapidly deposit substantial amounts of vibrational energy into specific parts of a molecule. Such highly energized molecules can undergo fast rearrangements and selective dissociations. We have used ab initio classical trajectory calculations in time-varying electric fields to examine the fragmentation of molecules in intense IR laser pulses.

Multireference perturbation theory for metastable electronic states

Ksenia Bravaya

*Department of Chemistry, Boston University
Boston, Massachusetts 02446, USA*

Electronic states metastable with respect to electron ejection are ubiquitous in highly energetic environment, chemical, and biological systems, and often lead to chemical decomposition. Predicting the energetics and lifetimes of the metastable states, resonances, is crucial for understanding the processes of electron capture and the resulting chemical conversion. In this talk, two models extending multiconfigurational quasidegenerate perturbation theory of second order (XMCQDPT2) to metastable electronic states will be introduced. XMCQDPT2 combined with complex absorbing potential (CAP) formalism, CAP-XMCQDPT2, enables treatment of both shape and Feshbach resonances and yields accurate width and lifetimes [1]. Importantly, the model allows one to extract resonance position and width at a cost of single electronic structure calculation. Alternative approach is based on using XMCQDPT2 in the context of Feshbach projection formalism. The model also yields resonance position and width at a cost of a single calculation, and moreover, does not require computing and analyzing so-called eta-trajectory, dependence of energies and widths on the strength of the absorbing potential. The results of benchmark calculations for shape and Feshbach resonances will be presented.

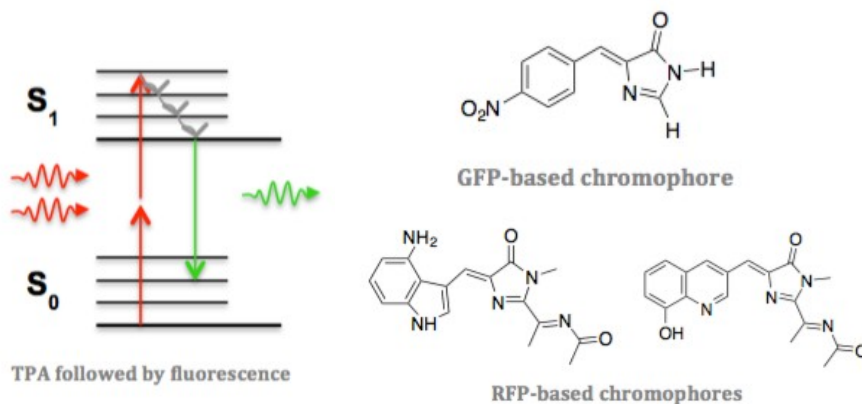
- [1] A. A. Kunitsa, A. A. Granovsky, and K. B. Bravaya, “CAP-XMCQDPT2 method for molecular electronic resonances”, *J. Chem. Phys.* **146**, 184107 (2017).

Two-photon absorption in biofluorophores

Alex Brown

*Department of Chemistry, University of Alberta
Edmonton, Alberta T6G 2G2, Canada*

I will discuss our recent research examining the photophysical properties of biofluorophores, with an emphasis on the determination of two-photon absorption (TPA) cross-sections. I will introduce TPA, including the use of two- (or few-) level models for interpreting TPA cross-sections, based on transition dipole moments (oscillator strengths), permanent dipole moments, and excitation energies. I will highlight our recent work computationally exploring TPA in (1) families of emissive RNA analogues and (2) fluorescent protein (FP) chromophores, including those incorporating non-canonical amino acids (ncAAs). In (1), the effects of conformational flexibility (including attachment of the sugar ring), tautomerization, and base-pairing/base-stacking on the TPA have been considered as these can impact the interpretation and prediction of experimental measurements. In (2), possible green FP(GFP)- and red FP(RFP)-like chromophores, built from ncAAs, with large intrinsic TPA as compared to known FP chromophores, have been proposed and the strong effect of conformation on TPA explored.



Localization/delocalization errors in density-functional theory

Axel D. Becke, Stephen G. Dale, and Erin R. Johnson

*Department of Chemistry, Dalhousie University
Halifax, Nova Scotia, Canada*

Local DFT approximations, such as GGAs and exact-exchange-GGA hybrids with a small exact-exchange fraction, have a propensity to (over)delocalize charge in, e.g., charge-transfer complexes and in charge transfer excitations. This “delocalization” error has been a challenge in DFT for at least two decades and remains fundamentally unsolved. The underlying locality/non-locality effects will be discussed in two contexts: classic charge-transfer complexes, and exciton energy/size in extended polyenes as models of polyacetylene. Both of these display the problem dramatically. A non-local pure correlation functional of Becke [1] may offer a solution.

[1] A. D. Becke, *J. Chem. Phys.* **122**, 064101 (2005).

Localized orbital scaling correction for systematic elimination of delocalization and static/strong correlation error in density functional approximations

Weitao Yang

*Department of Chemistry and Department of Physics
Duke University, North Carolina, USA*

The delocalization and static correlation error of popular density functional approximations (DFAs) lead to diversified problems in present-day density functional theory calculations. For achieving a universal elimination of these two errors, we develop a localized orbital scaling correction (LOSC) framework, which unifies our previously proposed global and local scaling approaches. The LOSC framework accurately characterizes the distributions of global and local fractional electrons and spins, and is thus capable of correcting system energy, energy derivative and electron density in a self-consistent and size-consistent manner. Our approach introduces the explicit derivative discontinuity and largely restores the flat-plane behavior of electronic energy at fractional charges and fractional spins. The LOSC–DFAs lead to systematically improved results, including the dissociation of ionic species, single bonds, multiple bonds without breaking space or spin symmetry, the band gaps of molecules and polymer chains, the energy and density changes upon electron addition and removal, and photoemission spectra.

[1] C. Li, X. Zheng, N. Q. Su, and W. Yang, “Localized orbital scaling correction for systematic elimination of delocalization error in density functional approximations”, *Natl. Sci. Rev.* **5**, 203 (2018).

[2] N. Q. Su, C. Li, and W. Yang, “Describing strong correlation with fractional-spin correction in density functional theory”, submitted.

Surface plasmon polariton-controlled molecular switch

Matthias Ernzerhof

*Department of Chemistry, University of Montreal
Montréal, Québec, Canada*

Molecular electronic devices are studied extensively to explore their potential use in electronics and also to gain an understanding of the mechanisms of electron transport at the molecular scale. Recent experiments show that molecules can be strongly coupled to surface plasmon polaritons (SPPs) and that the resulting, so called dressed molecular states, are entanglements of electrons and SPPs. Here we propose molecular electronic devices that are derived from dressed molecules. We present a simple, analytical theory that shows how SPP's can provide complete control of the molecular conductance. In a suggested device, the SPP couples a localized excited state to the continuum wave function of the molecular conductor and the details of this coupling, i.e., frequency and field strength of the SPP, are the parameters that modulate the molecular conductance. In addition to the molecular switch, we also design a photovoltaic cell that harvests the SPP energy to generate a photo current. The proposed, SPP-controlled devices represent a novel type of opto-electronic circuitry that significantly enlarges the potential of molecular electronics.

Functional differentiability and derivatives in DFT: The whole story thus far

Yan Alexander Wang

*Department of Chemistry, University of British Columbia
Vancouver, British Columbia V6T 1Z1, Canada*

In this talk, I will review the concepts of functional differentiability and the proper procedures to obtain functional derivatives in density-functional theory [1–6]. Particular emphasis will be put on the analysis of kinetic-energy density functionals and their functional derivatives. In the end, we will gain a deeper appreciation of chemical potential, $\mu = \frac{\delta E_v[\rho_0]}{\delta \rho_0}$, in both electron-number constrained Hilbert space and electron-number unconstrained Fock space.

- [1] F. E. Zahariev and Y. A. Wang, *Phys. Rev. A* **70**, 042503 (2004).
- [2] Y. A. Zhang and Y. A. Wang, *Int. J. Quantum Chem.* **109**, 3199 (2009).
- [3] Y. A. Wang and P. Xiang, in *Recent Advances in Orbital-Free Density Functional Theory*, edited by T. A. Wesolowski and Y. A. Wang (World Scientific, Singapore, **2013**), Chap. 1, pp. 3-12.
- [4] P. Xiang and Y. A. Wang, *Prog. Theor. Chem. Phys.* **31**, Chap. 18 (2018).
- [5] Y. A. Zhang and Y. A. Wang, “Asymptotic Behavior of Finite-System Wave Functions and Physical Interpretation of the Kohn-Sham Orbital Energies,” to be submitted.
- [6] S.-Y. Ye and Y. A. Wang, “Asymptotic Behavior of Functional Derivatives of Kinetic-Energy Density Functionals,” to be submitted.

Challenges in simulations of biological membranes

D. Peter Tieleman

*Department of Biological Sciences and Centre for Molecular Simulation
University of Calgary, Calgary, AB T2N 1N4, Canada*

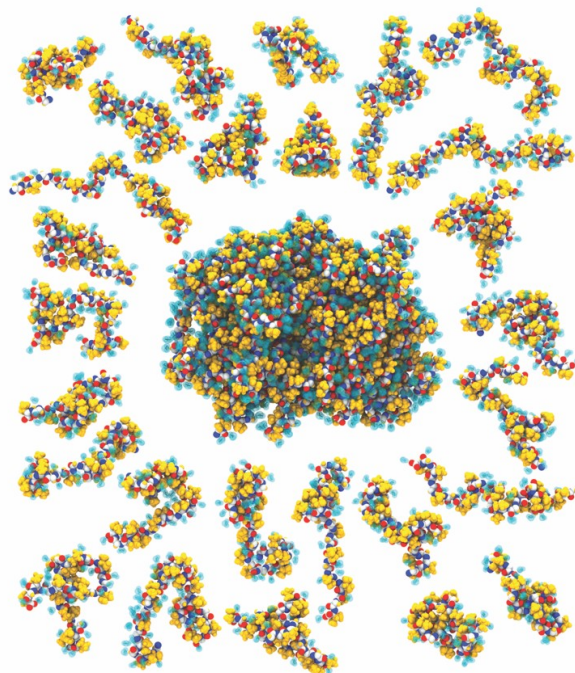
Biological membranes have a complex composition with hundreds of different lipids and a high protein concentration. The nature of the lateral structure of membranes is hotly debated as experiments reach increasingly higher spatial and temporal resolution. Computer simulations give detailed insight in lipid properties but the time and length scales involved in processes such as domain formation and domain dynamics remain a challenge. Coarse-grained simulations with the Martini model have enabled a significant jump in time and length scale, and currently can reach of the order of 100 microseconds on systems of *ca.* 100×100 nm size on relatively available computers. Atomistic simulations on smaller systems can reach tens of microseconds, which is beginning to be useful to study non-trivial lipid mixtures. I will describe recent work on mixtures at both atomistic and coarse-grained levels. We are also interested in the interactions between lipids and membrane proteins. The local environment around membrane proteins is uniquely shaped by the protein surface, resulting in a local composition and membrane properties that differ significantly from the average properties of the lipids that make up the membrane model. This may play an important role in shaping the lateral structure of biological membranes.

Molecular simulations of intrinsically disordered proteins

Sarah Rauscher

*Department of Chemical and Physical Sciences, University of Toronto Mississauga
Mississauga, Ontario L5L 1C6, Canada*

Intrinsically disordered proteins (IDPs) are abundant in all kingdoms of life and fulfill many critical functions. Despite their biological importance, IDPs are poorly understood relative to the wealth of structural information available for folded proteins. The structural description of IDPs poses formidable challenges to both theory and experiment: IDPs do not have a stable structure, but rather a structural ensemble consisting of many interconverting conformational states. Molecular simulations can be used to obtain structural ensembles of IDPs, but are currently limited by the accuracy of their energy functions (force fields). To address this challenge, we have carried out a systematic comparison of state-of-the-art force fields for the specific case of IDPs [1] and developed an improved force field suitable for both IDPs and folded proteins [2]. Accurate simulations of IDPs open up new possibilities for the detailed structural characterization of this important class of proteins. As a prototypic example of the insight afforded by molecular simulations of IDPs, I will describe our work on the structure of elastin [3], the protein responsible for the elasticity of skin, lungs, and arteries.



- [1] S. Rauscher, V. Gapsys, M.J. Gajda, M. Zweckstetter, B.L. de Groot, H. Grubmüller, *J. Chem. Theor. Comput.* **11**, 5513 (2015).
- [2] J. Huang, S. Rauscher, G. Nawrocki, T. Ran, M. Feig, B.L. de Groot, H. Grubmüller, A.D. MacKerell Jr., *Nat. Methods* **14**, 71 (2017).
- [3] S. Rauscher and R. Pomès, *eLife* **6**, e26526 (2017).

Solving protein structures by iterating between computation and experiment

Kari Gaalswyk,¹ Christopher Jaroniec,² and **Justin L. MacCallum**¹

¹*Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada*

²*Department of Chemistry, Ohio State University, Columbus, Ohio, USA*

Integrative structural biology [1] is an emerging field that combines computation with sparse experimental data to infer the structure of biomolecules and their complexes. The MacCallum lab has developed a Bayesian approach to integrative structural biology called Modeling Employing Limited Data (MELD), that leverages the strength of physics-based modeling to resolve the ambiguity inherent in sparse data [2,3].

A number of experimental techniques require the incorporation of one or more probes into the biomolecule under study. Some probe locations are far more informative than others, and when the structure is known, good probe locations can be identified by visual inspection. But when the structure is unknown, there is currently no principled way to choose probe locations and we are largely reduced to guessing. A strategy to predict which probe locations are most informative would reduce the time, cost, and experimental effort required to solve a structure by focusing on the most valuable probe locations. We have developed a computational approach called Rational Probe Mutagenesis (RPM) that iterates between computation and experiment. Initially, a conformational ensemble is generated using all information currently available. Next, the ensemble is analyzed to predict which probe location is most likely to be informative. Essentially, RPM is looking for a probe location that maximally distinguishes between the various structures that have been sampled. After the most promising probe location is identified, the experiments are carried out, and the results are used to generate an updated conformational ensemble.

We demonstrate the application of MELD to solid-state NMR experiments using the paramagnetic relaxation enhancement technique [4]. We show that MELD is able to generate accurate models using only a small number of paramagnetic labels and that RPM can identify the most valuable probe locations. The combination of MELD and RPM is able to generate more accurate models than conventional approaches and is able to reduce the experimental effort by two-thirds.

[1] A. B. Ward, A. Sali, I. A. Wilson, *Science* **339**, 913 (2013).

[2] J. L. MacCallum, A. Perez, K. A. Dill, *PNAS* **112**, 6985 (2015).

[3] A. Perez, J. L. MacCallum, K. A. Dill, *PNAS* **112**, 11846 (2015).

[4] I. Sengupta, P. S. Nadaud, J. J. Helmus, C. D. Schwieters, C. P. Jaroniec, *Nat. Chem.* **4**, 410 (2012).

Modeling the structure, repair and replication of damaged DNA

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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 and direct repair processes. Computer modeling can provide detailed molecular level information about the structure of modified DNA and its interactions with enzymes that replicate or repair damaged DNA. This talk will highlight recent work from my group that employs a multi-pronged computational approach (i.e., 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.

**Electronic polarization effects in the molecular confinements:
Next frontier for bio-molecular simulations**

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Explicit treatment of electronic polarizability in empirical force fields offers the potential to significantly improve the accuracy of molecular simulations of macromolecules in condensed phases with particular importance for studies of metal ions interactions with protein hosts and subsequent transport across cell or artificial membranes. Towards achieving this we have developed a novel polarizable force field based on the classical Drude oscillator model and improved computationally efficient DFT3-TB scheme for studies of ion interactions with membrane proteins used as part of a biotechnology devices (LeuT transporter, gA channel for lipid packing sensing or rapid assessment of drug interactions with membranes). The developed Drude model is computationally accessible allowing for microsecond simulations of macromolecules as well as the application of enhanced sampling and free energy simulations methodologies. Improvements in the model over the additive CHARMM36 force field on the selective ion permeation in model channels and physiologically relevant membrane proteins show the utility of explicit treatment of electronic polarizability in a force field. An overview of the models with explicit treatment of polarization response will be presented along with discussion on the ongoing developments in the force field including soluble metalloproteins, nanosurfaces, ion channels and membrane-localized nanosensors [1–4].

[1] Wheatley, R. W.; Juers, D. H.; Lev, B. B.; Huber, R. E.; Noskov, S. Y. Elucidating factors important for monovalent cation selectivity in enzymes: *E. coli* β -galactosidase as a model. *Phys. Chem. Chem. Phys.* **17**, 10899 (2015).

[2] Ngo, V.; da Silva, M.C.; Kubillus, M.; Li, H.; Roux, B.; Elstner, M.; Cui, Q.; Salahub, D.R.; Noskov, S.Y. Quantum Effects in Cation Interactions with First and Second Coordination Shell Ligands in Metalloproteins. *J. Chem. Theor. Comp.* **11**, 4992 (2015).

[3] Li, H.; Ngo, V.; Da Silva, M. C.; Salahub, D. R.; Callahan, K.; Roux, B.; Noskov, S. Y. Representation of ion–protein interactions using the drude polarizable force-field. *J. Phys. Chem. B* **119**, 9401 (2015).

[4] Zhekova, H.; Ngo, V.; Da Silva, M.; Salahub, D.R.; Noskov, S.Y. Selective Ion Binding and Transport by Membrane Proteins – A Computational Perspective, *Coord. Chem. Rev.* **345**, 108 (2017).

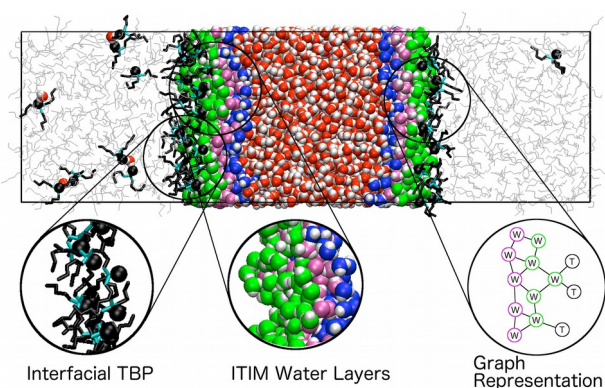
Advanced graph-theory methods for characterizing and exploring condensed-phase organization, dynamics, and reactivity

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Graph-theoretical approaches for characterizing the structure and dynamics of condensed phase systems have rapidly expanded in the last five years [1]. Such methods utilize network analysis algorithms to study the behavior of covalent or intermolecular interactions and can include a large array of algorithms including Google's PageRank [2], and the Dijkstra algorithm that underpins nearly all routing software [3]. Applications of these methods



have helped reveal new correlating relationships in many complex systems, including concentrated electrolytes [4–5], liquid:liquid phase boundaries [5–6], and in solvent confinement [7–8]. More recent advances leverage the topological patterns of these chemical networks as new collective variables for potential of mean force simulations—increasing the tools available to study highly dimensional energy surfaces and reaction mechanisms.

- [1] Clark, A. E. Intermolecular network theory: A general approach for understanding the structural and dynamic properties of liquids and solutions. *Annu. Rep. Comput. Chem.* **2015**, *11*, 313.
- [2] Hudelson, M.; Mooney, B. L.; Clark, A. E. Determining polyhedral arrangements of atoms using PageRank, *J. Math. Chem.* **2012**, *50*, 2342.
- [3] Ozkanlar, A.; Clark, A. E. *ChemNetworks*: A complex network analysis tool for chemical systems, *J. Comput. Chem.* **2014**, *35*, 495.
- [4] Kelley, M.; Donley, A.; Clark, S.; Clark, A. E. Structure and dynamics of NaCl ion pairing in solutions of water and methanol *J. Phys. Chem. B* **2015**, *119*, 15652.
- [5] Ghadar, Y.; Christiansen, S. L.; Clark, A. E. Influence of aqueous ionic strength upon liquid:liquid interfacial structure and dynamics, *Fluid Phase Equil.* **2016**, *407*, 126.
- [6] Ghadar, Y.; Parmar, P.; Samuels, A.; Clark, A. E. Solutes at the liquid:liquid phase boundary—Solubility and solvent conformational response alter interfacial microsolvation reactions, *J. Chem. Phys.* **2015**, *142*, 104707.
- [7] Wang, C.; Bai, P.; Siepmann, I.; Clark, A. E. Deconstructing hydrogen bond networks of solvents confined in nanoporous materials: Implications for alcohol-water separation *J. Phys. Chem. C* **2014**, *118*, 19723.
- [8] Zhou, T.; McCue, A.; Ghadar, Y.; Bako, I.; Clark, A. E. On the behavior of capillary wave fronts and their role in defining interfacial regions of water, *J. Phys. Chem. B*, **2017**, DOI: 10.1021/acs.jpcc.7b07406

Our recent studies on vibronic coupling: applications in singlet fission and derivation of (pseudo-)Jahn-Teller formalisms

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Singlet fission (SF) converts one short-lived singlet exciton to two long-lived triplet excitons. It can potentially enhance the power conversion efficiency in photovoltaic devices. In the new concept of intramolecular singlet fission (iSF), chromophore units are covalently bonded and it is easier to adjust intermolecular morphology to facilitate SF. However, the detailed iSF mechanism is still unclear. In this presentation, our recent works in SF are discussed. Through performing quantum chemistry calculations and quantum dynamics simulations, we investigated the small size effects in iSF and presented a step-by-step picture for the through-liner iSF [1,2]. With the new understanding, we proposed a strategy to enhance the iSF efficiency by making appropriate substitution on the linker. We also explored the significance of azaborine substitution in designing SF chromophores [3].

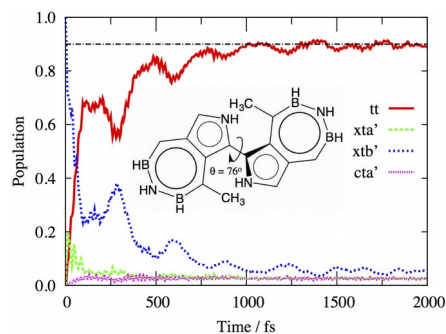


Fig. 1. Evolutions of populations of relevant states in intramolecular singlet fission.

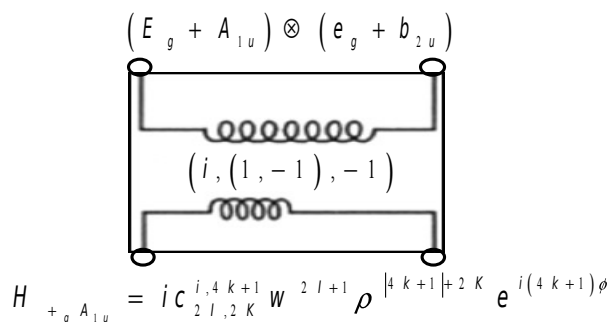


Fig. 2. Symmetry eigenvalues play essential roles in obtaining (p)JT Hamiltonian expansion formulas.

In the second half of the talk, we will present our recent works on deriving general formalisms of Jahn-Teller and pseudo-Jahn-Teller Hamiltonians. A growing number of studies reveal the limitations of the standard 2nd order expansions of (p)JT Hamiltonians in vibrational coordinates. Although some case-specific high-order expansion formulas had been derived, general (p)JT Hamiltonian formalisms up to arbitrary order were still unavailable. We endeavor to derive such general formalisms. Employing the root-branch approach and the modularized approach, we have successfully derived general expansion formulas for trigonal [4], tetrahedral and octahedral [5], and tetragonal [6] (p)JT Hamiltonians. The trigonal formulas are used to study photodetachment spectrum of CO₃²⁻. New insight into this problem is obtained.

[1] T. Zeng and P. Goel, *J. Phys. Chem. Lett.* **7**, 1351 (2016).

[2] T. Zeng, *J. Phys. Chem. Lett.* **7**, 4405 (2016).

[3] T. Zeng, S. K. Mellerup, D.-T. Yanget al., *J. Phys. Chem. Lett.* **9**, 2919 (2018).

[4] T. Zeng and I. Seidu, *Phys. Chem. Chem. Phys.* **19**, 11098 (2017).

[5] T. Zeng, R. J. Hickman, A. Kadri, and I. Seidu, *J. Chem. Theory Comput.* **13**, 5004 (2017).

[6] R. J. Hickman, R. A. Lang, and T. Zeng, *Phys. Chem. Chem. Phys.* **20**, 12312 (2018).

Electron pair distributions as a predictive tool in chemistry

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For over a century [1] chemists have been enamored with Lewis's concept of a localized electron pair to represent the now intuitive features of electronic structure such as the so-called lone pair and even the chemical bond itself. Despite its simplicity, the Lewis model yields an impressive wealth of predictive ability in terms of molecular structure [2] and chemical properties and is ubiquitous in chemical literature. Of course, it is rather unfortunate that the Lewis model is entirely qualitative and yields no information regarding how any specific electron pair is distributed.

In this talk, I will survey our efforts to use electron pair distributions as the feedstock for a series of computational techniques that seek to explicitly characterize and quantify electronic structure and molecular properties [3,4]. By determining electron pair distribution functions for the interelectronic separation and center-of-mass coordinates of localized molecular orbitals, one is able to glean insight on the nature and strength of a wide variety of covalent and non-covalent interactions [5]. Furthermore, recent work in our group has shown that electron pair distributions are able to rationalize a wide variety of chemical reactivity.

I will also show that interelectronic distribution functions may be reliably mapped to correlation energies and other properties using statistical machine learning techniques. Owing to their invariance with molecular translation and rotation, and their compact representation of pairwise electronic interactions, electronic distribution functions are excellent candidates for molecular representations in statistical techniques such as kernel ridge regression models and artificial neural networks. These and other recent work will be highlighted.

[1] G. N. Lewis, *J. Am. Chem. Soc.* **38**, 762 (1916).

[2] R. J. Gillespie and E.A. Robinson, *Angew. Chem. Int. Ed.* **35**, 495 (1996).

[3] D. C. Hennessey, B. J. H. Sheppard, D. E. C. K. Mackenzie, J. K. Pearson, *Phys. Chem. Chem. Phys.* **16**, 25548 (2014).

[4] A. J. Proud, D. E. C. K. Mackenzie, J. K. Pearson, *Phys. Chem. Chem. Phys.* **17**, 20194 (2015).

[5] A. J. Proud, B. J. Sheppard, and J. K. Pearson, *J. Am. Chem. Soc.* **140**, 219 (2018).

Toward exact quantum chemistry: High-level coupled-cluster energetics by Monte Carlo sampling and moment expansions

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One of the main goals of electronic structure theory is precise *ab initio* description of increasingly complex polyatomic systems. It is widely accepted that size extensive methods based on the exponential wave function ansatz of coupled-cluster (CC) theory are excellent candidates for addressing this goal. Indeed, when applied to molecular properties and chemical reaction pathways, the CC hierarchy, including CCSD, CCSDT, CCSDTQ, etc., rapidly converges to the limit of the exact, full configuration interaction (CI) diagonalization of the Hamiltonian, allowing one to capture the relevant many-electron correlation effects in a conceptually straightforward manner through particle-hole excitations from a single Slater determinant. One of the key challenges has been how to incorporate higher-than-two-body components of the cluster operator, needed to achieve a quantitative description, without running into prohibitive computational costs of CCSDT, CCSDTQ, and similar schemes, while eliminating failures of the more practical perturbative approximations of the CCSD(T) type in multi-reference situations, such as chemical bond breaking.

In this talk, we examine a radically new way of obtaining accurate energetics equivalent to high-level CC calculations, even when electronic quasi-degeneracies and higher-than-two-body clusters become significant, at the small fraction of the computational cost, while preserving the black-box character (minimum input information) of conventional single-reference computations. The key idea is a merger of the deterministic formalism, abbreviated as CC(*P;Q*) [1–5], with the stochastic CI [6,7] and CC [8–10] Monte Carlo approaches [11,12]. The advantages of the proposed methodology will be illustrated by a few molecular examples, where the goal is to recover highly accurate full CCSDT and CCSDTQ energetics, including bond breaking in F₂ and H₂O and the automerization of cyclobutadiene.

- [1] J. Shen and P. Piecuch, *Chem. Phys.* **401**, 180 (2012).
- [2] J. Shen and P. Piecuch, *J. Chem. Phys.* **136**, 144104 (2012).
- [3] J. Shen and P. Piecuch, *J. Chem. Theory Comput.* **8**, 4968 (2012).
- [4] N.P. Bauman, J. Shen, and P. Piecuch, *Mol. Phys.* **115**, 2860 (2017).
- [5] I. Magoulas, N.P. Bauman, J. Shen, and P. Piecuch, *J. Phys. Chem. A* **122**, 1350 (2018).
- [6] G.H. Booth, A.J.W. Thom, and A. Alavi, *J. Chem. Phys.* **131**, 054106 (2009).
- [7] D. Cleland, G.H. Booth, and A. Alavi, *J. Chem. Phys.* **132**, 041103 (2010).
- [8] A.J.W. Thom, *Phys. Rev. Lett.* **105**, 263004 (2010).
- [9] R.S.T. Franklin, J.S. Spencer, A. Zocante, and A.J.W. Thom, *J. Chem. Phys.* **144**, 044111 (2016).
- [10] J. S. Spencer and A. J. W. Thom, *J. Chem. Phys.* **144**, 084108 (2016).
- [11] J.E. Deustua, J. Shen, and P. Piecuch, *Phys. Rev. Lett.* **119**, 223003 (2017).
- [12] J.E. Deustua, J. Shen, and P. Piecuch, in preparation.

The Δ NO method: A hybrid approach to the correlation problem

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Recently, we introduced an approach to modelling electronic structure that treats the static and dynamic components of electron correlation in different manners [1]. Static correlation is captured by a cumulant functional (CF), while dynamic correlation is captured by an on-top density (ODF). Such a partitioning of electron correlation between a CF and an ODF plays to the strengths of each of the related electronic structure methods. The development of a new ODF for short-range dynamic correlation [2], the extension of the method to open-shells, the treatment of double-counting of electron correlation, and the development of an effective optimization algorithm for the two-electron density matrix, will be discussed.

[1] J. W. Hollett, C. Menzies and H. Hosseini, *J. Chem. Phys.* **145**, 084106 (2016).

[2] J. W. Hollett and N. Pegoretti, *J. Chem. Phys.* **148**, 164111 (2018).

Model wavefunctions for strongly correlated systems

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Established methods of quantum chemistry are based on the orbital picture: electrons occupy orbitals and interact with the average field of the other electrons. The wavefunction is a Slater determinant of the occupied orbitals. This picture is convenient when it is possible to unambiguously label orbitals as occupied or unoccupied. Systems of this type are weakly correlated and generally well-described by existing methods. When it's difficult to classify orbitals as occupied or unoccupied, the wavefunction cannot be described by a Slater determinant, and the number of important Slater determinants grows exponentially with the system size. Systems of this type are strongly correlated. The goal of our work is to develop affordable variational techniques for strongly correlated systems. Our approach uses wavefunctions from integrable models, which will serve as starting points for perturbation theories. This approach will be outlined with the eigenvectors of Richardson-Gaudin models.

New ways to think about electronic excited states

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As the pioneers of our field — Pauling, Lennard-Jones, Mulliken, Pople and others — investigated the systematic application of quantum mechanics to chemistry, their initial focus was on ground electronic states. This is unsurprising, because that is where the majority of high-quality experimental data were found and because the mathematical difficulties are least overwhelming for the lowest eigenvalue of a Hamiltonian. However, times have changed. Following brilliant advances in the experimental characterization and manipulation of short-lived excited-state species, the development of exquisitely tunable lasers, and the advent of alarmingly fast computers, we stand on the brink of a major disruption in chemistry, where we will shake off the shackles of the ground state and freely explore “excited-state chemistries” in which molecular personalities differ dramatically from their ground-state alter egos.

Unfortunately, for historical reasons, the ground state still retains a privileged position in many descriptions of excited states and I will argue that this bias is unhelpful, both conceptually and computationally. To remedy the situation, we are pursuing a hierarchy of excited-state models which are rooted, like their ground-state analogs, in the mean-field, orbital-based picture that has proven so fertile for chemists of all persuasions. I will introduce two Maximum Overlap Methods (MOM) that enable us to compute such state-specific models and I will use low-lying excited states of several atoms to demonstrate both the strengths and weaknesses of the approach [1–4].

What am I asserting if I claim that a molecule is in a “singly-excited electronic state” state? Or, for that matter, a doubly- or triply-excited state? Do these descriptions correspond to an experimentally observable feature of the molecule? If not, do they correspond to a universally agreed theoretical definition? If not, which definition have we been using and are we confident that it’s a good one?

I will argue that these questions have been either ignored or treated superficially by many researchers and that, as a result, it is likely that some states have been incorrectly classified in the past.

I will propose a simple definition [5] of an excitation number η that is easy to calculate and easy to interpret for electronic excited states which have been obtained using the MOM approach. We have computed η for a variety of excited states of a selection of organic and inorganic molecules and we find that it is almost always close to an integer. The rounded form of η provides clean and compelling answers to the questions above in all the cases that we have investigated.

- [1] A. T. B. Gilbert, N. A. Besley and P. M. W. Gill, *J. Phys. Chem. A* **112**, 13164 (2008).
- [2] N. A. Besley, A. T. B. Gilbert and P. M. W. Gill, *J. Chem. Phys.* **130**, 124308 (2009).
- [3] G. M. J. Barca, A. T. B. Gilbert and P. M. W. Gill, *J. Chem. Phys.* **141**, 111104 (2014).
- [4] G. M. J. Barca, A. T. B. Gilbert and P. M. W. Gill, *J. Chem. Theory Comput.* **14**, 1501 (2018).
- [5] G. M. J. Barca, A. T. B. Gilbert and P. M. W. Gill, *J. Chem. Theory Comput.* **14**, 9 (2018).

Applications of machine learning for quantum dynamics

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Machine learning is becoming a new powerful tool for physics and chemistry research. This presentation will discuss how quantum theory of molecular dynamics can benefit from machine learning [1]. In particular, it will be argued that combining machine learning with quantum dynamics calculations allows one to ask new questions and may help solve problems generally considered unfeasible. To illustrate this, we will consider two important problems.

The first part of this talk will be on the inverse scattering problem in chemical reaction dynamics [2]. Any quantum reactive scattering calculation requires an accurate potential energy surface (PES). For typical reactive systems of three atoms or more, such potential energy surfaces are constructed by computing the potential energy at thousands of points in the configuration space and fitting the computed points by an analytical function or a neural network. Computing and fitting the potential energy points is a very laborious and time-consuming task. We will illustrate a machine-learning approach, which makes feasible a feedback loop, allowing for the gradual improvement of PES based on results of rigorous quantum dynamics calculations. Such feedback loops produce accurate global PES with only 30 *ab initio* energies for the three-dimensional $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction and 290 *ab initio* energies for the six-dimensional $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ reaction. These surfaces are obtained automatically by a Bayesian optimization algorithm and do not require fitting the *ab initio* energies with analytical functions. By construction, these potentials reproduce accurately the reaction probabilities in a wide range of energies.

In the second part of the talk, we will discuss the feasibility of applying machine learning for extrapolation of properties of complex quantum systems [3]. Our focus will be on predicting sharp transitions in the phase diagram of a lattice Hamiltonian. We will present a method capable of extrapolating across the transition lines. The method is based on Gaussian Process regression with a combination of kernels chosen through an iterative procedure maximizing the predicting power of the kernels. The calculations within a given phase can be used to predict not only the closest sharp transition, but also a transition removed from the available data by a separate phase. This makes this approach particularly valuable for searching phase transitions in the parts of the parameter space that cannot be probed experimentally or theoretically.

For our other recent work on applications of Gaussian Process regression to problems in molecular dynamics, see Refs. 4–6.

- [1] J. Cui and R. V. Krems, *Phys. Rev. Lett.* **115**, 073202 (2015).
- [2] R. Vargas-Hernandez, Y. Guan, D.H. Zhang, and R. V. Krems, arXiv: 1711.06376 (2018).
- [3] R. Vargas-Hernandez, J. Sous, M. Berciu, and R. V. Krems, arXiv: 1803.08195 (2018).
- [4] J. Cui, Z. Li and R. V. Krems, *J. Chem. Phys.* **143**, 154101 (2015).
- [5] J. Cui and R. V. Krems, *J. Phys. B* **49**, 224001 (2016).
- [6] D. Vieira and R. V. Krems, *Astrophys. J.* **835**, 255 (2017).

An efficient solution of the quantum-classical Liouville equation without surface hopping

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We propose a highly efficient mixed quantum-classical molecular dynamics scheme based on a solution of the quantum-classical Liouville equation (QCLE) [1]. By casting the equations of motion for the quantum subsystem and classical bath degrees of freedom onto an approximate set of coupled first-order differential equations for c -numbers, this scheme propagates the composite system in time deterministically in terms of independent classical-like trajectories. To demonstrate its performance, we apply the method to the spin-boson model [2], a photo-induced electron transfer model [3], and a Fenna-Matthews-Olsen complex model [4], and find excellent agreement out to long times with the numerically exact results, using several orders of magnitude fewer trajectories than the surface-hopping solutions of the QCLE. Owing to its accuracy and efficiency, this method promises to be useful for studying the dynamics of mixed quantum-classical systems.

- [1] R. Kapral and G. Ciccotti, *J. Chem. Phys.* **110**, 8919 (1999).
- [2] A. J. Leggett et al., *Rev. Mod. Phys.* **59**, 1 (1987).
- [3] H. Wang and M. Thoss, *Chem. Phys. Lett.* **389**, 43 (2004).
- [4] R. E. Fenna and B. W. Matthews, *Nature* **258**, 573 (1975).

**Trajectory-based approaches to quantum dynamics:
Wavefunctions, density matrices and master equations**

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I will present recently developed trajectory-based approaches for treating nonequilibrium quantum dynamics in molecular and condensed-phase systems. Rooted in mean-field theory, these methods employ statistical ensembles of trajectories to simulate the real-time dynamics of nonadiabatic processes like charge and energy transfer. We will explore the performance of selected techniques of this type in a variety of scenarios, including proton-coupled electron transfer reactions, photosynthetic energy transfer, and the relaxation of photo-generated charge carriers in molecular wires.

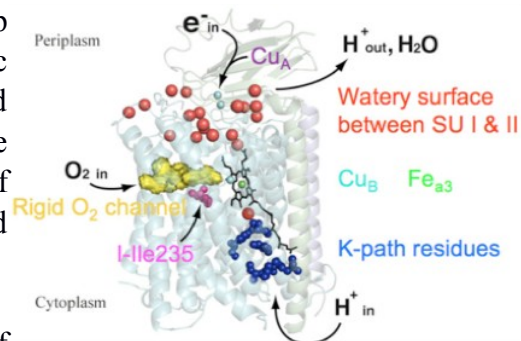
Insights into oxygen activation and proton pumping of cytochrome c oxidase from DFT and molecular dynamics

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Cytochrome c oxidase (CcO) is the last enzyme in the respiratory electron transport chains of mitochondria and many aerobic bacteria [1]. Its function is to catalyze the reduction of molecular oxygen to water and utilize the resultant energy to pump protons across the inner mitochondrial or bacterial cytoplasmic membrane, forming an electrochemical potential that is utilized by the cell in numerous ways, most prominently for the synthesis of ATP [2]. The catalytic proton pumping cycle of CcO is driven by redox events, molecular oxygen binding, and O₂ activation in the dinuclear heme Fe_{a3}-Cu_B complex (DNC).



We employ classical molecular dynamics (MD) simulations of the entire *ba*₃-type enzyme embedded in its membrane and density functional theory (DFT) calculations of large DNC cluster models to explore this redox-coupled proton transport mechanism [3-6]. Here we present our latest refinements of the reaction mechanism, considering different protonation states and tautomers [3-5]. We focus on structural changes within the DNC upon going from state P_R to F in the catalytic cycle and demonstrate how water molecules can influence pK_a values of residues that are crucial for proton uptake and proton pumping. We further show that calculated vibrational frequencies of iron-oxo-, peroxy-, and hydroperoxy-species compare well to resonance Raman experiments of experimentally accessible intermediates for the entire reaction cycle. Using long-time scale MD simulations we were able to identify water exit pathways, which may also act as proton transport pathways [6]. This work is supported by NIH grant R01 GM100934 and computer time via NSF award ACI-1548562 (allocation TG-CHE130010).

[1] O. M. H. Richter and B. Ludwig, *Rev. Physiol. Biochem. Pharmacol.* **147**, 47 (2003).

[2] D. G. Nicholls and S. J. Ferguson, *Bioenergetics 3*. Academic Press Ltd.: London (2002).

[3] L. Noodleman, W.-G. Han Du, J. A. Fee, A. W. Götz, R. C. Walker, *Inorg. Chem.* **53**, 6458 (2014).

[4] W.-G. Han Du, A. W. Götz, L. Yang, R. C. Walker, L. Noodleman, *Phys. Chem. Chem. Phys.* **18**, 21162 (2016).

[5] W.-G. Han Du, A. W. Götz, L. Noodleman, *Inorg. Chem.* **57**, 1048 (2018).

[6] L. Yang, Å. A. Skjevik, W.-G. Han Du, L. Noodleman, R. C. Walker, A. W. Götz, *Biochim. Biophys. Acta – Bioenergetics* **1857**, 1594 (2016).

Adaptive hybrid potential simulations of condensed phase systems

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Hybrid quantum chemical (QC)/molecular mechanical (MM) potentials are widely employed in molecular simulation, finding particular utility in the study of chemical reactions in enzymes and other condensed phase systems. In the simplest application of these techniques, the atoms in a system are divided into two regions consisting of a small central core, which is treated with a precise QC method, and a larger environment, surrounding the core, which is described with a more approximate MM method. Traditionally the partitioning of atoms between QC and MM regions has been fixed, and chosen beforehand. This is sufficient for many classes of problem, but becomes troublesome when there are mobile groups in the system that can diffuse readily between the two regions. To overcome this deficiency, adaptive algorithms have been developed, in which the partitioning of the atoms between different regions is allowed to change during a simulation. A number of such algorithms have been proposed, but they all have shortcomings, either because they are significantly more expensive than fixed-partitioning approaches, or because they introduce numerical approximations that severely limit their applicability.

Recently the *scaled interaction single partition adaptive* (SISPA) hybrid potential algorithm was introduced [1]. In contrast to previously proposed adaptive methods, the SISPA approach has a computational cost comparable to fixed-partitioning methods and yet has consistent energies and forces making it suitable for a wide range of simulation types, including geometry optimization and molecular dynamics within the microcanonical ensemble. This talk will discuss adaptive hybrid potential simulations, with an emphasis on the SISPA algorithm, describe some current developments, and outline directions for future work.

[1] M. J. Field, *J. Chem. Theor. Comput.* **9**, 2342 (2017).

Ab initio* molecular dynamics on nanoscale**Hayden Scheiber, Yifei Shi, and **Rustam Z. KhaliullinDepartment of Chemistry, McGill University
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Despite remarkable recent progress in linear-scaling density function theory, the computational cost of existing methods remains too high for routine *ab initio* molecular dynamics (AIMD) simulations. We developed a new linear-scaling AIMD method with an extremely low computational overhead by assuming that electrons in materials are strictly localized within predefined radii. High efficiency of the method is achieved without sacrificing its accuracy with a combination of two techniques: (1) fast but only approximate description of localized electrons and (2) the stochastic treatment of nuclear motion, fine-tuned to retain stable dynamics even with imperfect forces. A remarkable feature of the implemented method is that it remains efficient for challenging condensed phase systems even if large accurate basis sets are used. We demonstrated that, for systems well-represented by localized electrons, the new AIMD method enables simulations on previously inaccessible time and length scales.

Mechanistic insights into metal-catalyzed highly selective organic transformation reactions

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Modern density functional theory is very useful to analyze mechanistic insights into metal-catalyzed highly-selective conversion reactions. Rh(I)BINAP-catalyzed isomerization of allylic amines was examined by using DFT, QM/MM calculations, and the Artificial Force Induced Reaction (AFIR) method, which enables us to perform automatic reaction pathway search [1]. Graph theory approach for this complicated reaction pathways by using Prim's algorithm is very useful to find the most economical reaction pathway (Fig. 1). The dissociative mechanisms which do not involve two allylic amine molecules are preferred over the associative mechanisms, which was proposed by previous model studies by ab initio and DFT calculations. We also reported DFT studies on Ni-catalyzed Suzuki–Miyaura coupling through C–O bond activations of methoxynaphthalene with phenyl boronic acid [2]. This reaction goes through rate-determining oxidative addition of the C–O bond followed by transmetalation and reductive elimination to lead a coupling product. Electron donating nature of the ICy N-heterocyclic (NHC) carbene ligand makes the activation energy of the oxidative addition more feasible. In addition to those studies, importance of non-covalent interaction on second-sphere coordination of indole group on one-electron oxidized Cu(II)-salen complexes [3] and origin of high enantioselectivity in Cu(I)-catalyzed alkynylation of α -ketoester (see equation). In the latter studies, interactions between a cyclohexyl group of the α -ketoester and cyclohexylphosphine were found [4].

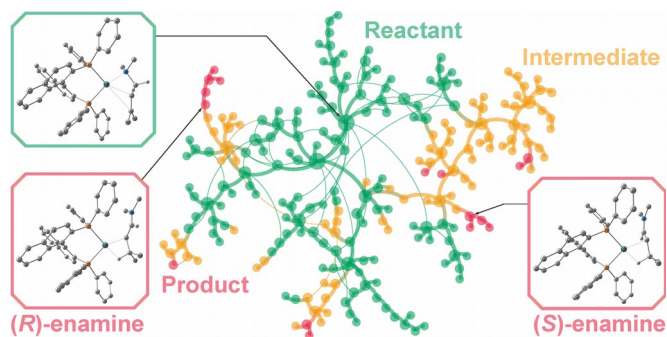


Figure 1. Dissociative mechanism network graphs of Rh(I)-catalyzed proton transfer of allylic amine. The bold line denotes the minimum span tree in the network.

- [1] T. Yoshimura, S. Maeda, T. Taketsugu, M. Sawamura, K. Morokuma, S. Mori, *Chem. Sci.* **8**, 4475 (2017).
- [2] M. C. Schwarzer, R. Konno, T. Hojo, A. Ohtsuki, K. Nakamura, A. Yasutome, H. Takahashi, T. Shimasaki, M. Tobisu, N. Chatani, S. Mori, *J. Am. Chem. Soc.* **139**, 10347 (2017).
- [3] H. Oshita, T. Yoshimura, S. Mori, F. Tani, Y. Shimazaki, O. Yamauchi, *J. Biol. Inorg. Chem.* **23**, 51 (2018).
- [4] M. C. Schwarzer, A. Fujioka, T. Ishii, H. Ohmiya, S. Mori, M. Sawamura, *Chem. Sci.* **9**, 3484 (2018).

Computational investigation of biologically viable pathways for thionitrate decomposition in model compounds and enzymes

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Organic thionitrates (RSNO_2) can release vasoactive nitrite and nitric oxide and are key intermediates in the biotransformation of organic nitrates such as glyceryl trinitrate (GTN). However, mechanisms of NO_2^- and NO release from RSNO_2 have been poorly studied and remain a matter of much debate. To address this, we performed a comprehensive high-level quantum chemistry investigation of RSNO_2 decomposition by homolysis (following or not a possible concerted rearrangement), hydrolysis and thiolysis using CH_3SNO_2 as a model compound. The postulated mechanisms of NO formation from RSNO_2 via bond homolysis is found to exhibit a large activation barrier and to be decidedly unfavorable. Gas-phase hydrolysis of CH_3SNO_2 to release NO_2^- when examined with three explicit water molecules is substantially more favorable. Nonetheless, the most favorable pathways for CH_3NO_2 decomposition involve reaction with OH^- or CH_3S^- to release NO_2^- . These reactions model attack by an activated water or a neighboring cysteinate on an enzyme-bound RSNO_2 (E-Cys-NO_2), which is implicated in GTN enzymatic bioactivation. In sum, the model calculations predict biologically viable pathways for RSNO_2 decomposition with NO_2^- but not with NO release. Following these model calculations, decomposition pathways are under investigation in the glyceraldehyde-3-phosphate dehydrogenase (GAPDH) protein active site using the quantum mechanics/molecular mechanics (QM/MM) approach to include the effect of the protein environment on its reactivity. GAPDH is a well-known glycolytic enzyme that exhibits various moonlighting functions, and it was recently shown to catalyze glyceryl trinitrate (GTN) to nitrite via a hypothesized E-Cys-NO_2 thionitrate intermediate [English and co-workers, Nitric Oxide, 2013].

Molecular mechanical force fields with higher-order dispersion terms using the exchange-hole dipole moment model

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Molecular mechanical forces generally include dispersion interactions through the $-C_6/r^6$ term of the Lennard-Jones potential. The C_6 coefficients are assigned empirically, so different force fields have widely different parameters for the same atom type. Atomic dispersion coefficients can be calculated accurately using the eXchange-hole-Dipole Moment (XDM) model, providing an ab initio check of these parameters. Comparison of the XDM and force field coefficients shows that the dispersion coefficients are systematically 50% higher than the XDM values, which compensates the neglect of sizable $-C_8/r^8$ and $-C_{10}/r^{10}$ dispersion interactions. To correct this issue, we have implemented an improved non-bonded potential into OpenMM, which describes Pauli repulsion using a Buckingham-type exponential term and includes $-C_8/r^8$ and $-C_{10}/r^{10}$ dispersion terms. The dispersion coefficients are assigned from a simple molecular DFT calculation, while the repulsive parameters are fit empirically using the ForceBalance automated parameterization code. We have successfully parameterized a new water model using this procedure, which predicts that $-C_8/r^8$ and $-C_{10}/r^{10}$ dispersion is a significant component of the liquid cohesive energy. These terms also account for roughly 30% of the solute-solvent attraction of aqueous methane. Using this procedure, we are developing a new force field that describes dispersion with systematic, QM-derived parameters and the correct distance dependence.

- [1] M. Mohebifar, E. Walters, E. R. Johnson, and C. N. Rowley, *J. Chem. Theory Comput.* **13**, 6146 (2017).

Reflections on forty-seven years in theoretical and computational chemistry

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I will use this honorary lecture to share some thoughts on recurring themes and motifs in my career that began with a stint as a research assistant in the summer of 1971. The topics covered will range over the usual domains of an academic career: research, community service, and teaching. The research motifs will include asymptotic analysis [1], interaction with experiments [1,2], and simple models [3]. The community service motif will be “giving back”.

[1] A. J. Thakkar, *Z. Phys. Chem.* **230**, 633 (2016).

[2] A. J. Thakkar and T. Wu, *J. Chem. Phys.* **143**, 144302 (2015).

[3] S. A. Blair and A. J. Thakkar, *Chem. Phys. Lett.* **610**, 163 (2014).

Multiresolution non-equilibrium simulations of ultrafast selective reactions under thermomechanical compression using quantum solid-state chemistry

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In this talk, I will present our recent developments on multiresolution non-equilibrium simulations of ultrafast selective reactions under thermomechanical compression using quantum solid-state chemistry. These developments also include molecular integrals of quantum chemistry using solid harmonics with a speed-up factor up to three orders of magnitude faster than conventional molecular integrals of Cartesian Gaussian functions [1–2]. Our simulations mainly mimic pressure jump experimental technique to capture non-equilibrium chemical bonding pathways under the enthalpy minimum condition using quantum solid-state chemistry calculations in which major contributions to mechanical stress tensor components are direct products of bond force and bond length vectors. Consequently, non-equilibrium bond breaking and forming processes are directly correlated to changes of mechanical stress components together with transformations of crystal structures, changes of energy and enthalpy and thermomechanically selective reaction modes. This leads to multiresolution non-equilibrium simulations regarding lowest resolution for structures, intermediate resolution for energy and enthalpy and highest resolution for reaction modes. Figure 1 shows simulation results about a transformation of hexagonal diamond under shock dynamic compression.

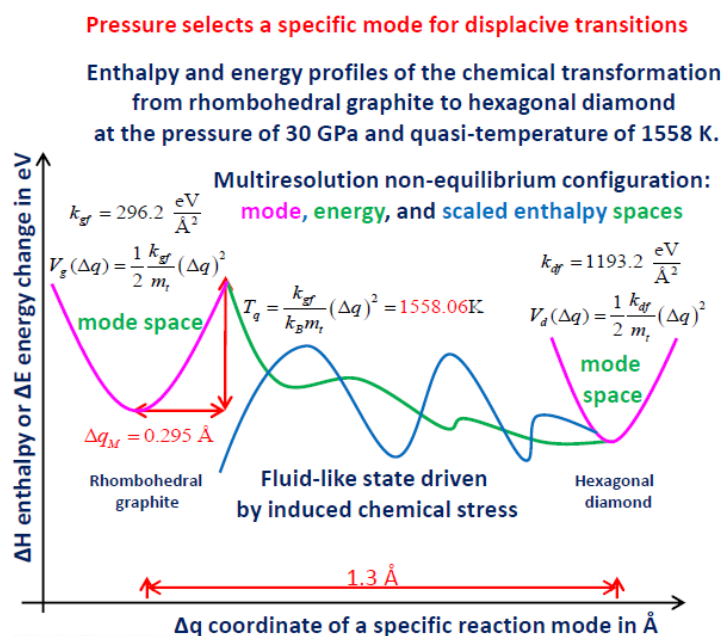


Figure 1. Transformation of hexagonal diamond under shock compression.

[1] A. Hu and B. I. Dunlap, *Can. J. Chem.* **91**, 907 (2013).

[2] A. Hu, N. Chan, and B. I. Dunlap, *J. Chem. Phys.* **148**, 074102 (2017).

Deuterium isotope effects on acid-base equilibria

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Heavy water (D₂O) plays an important role as a neutron moderator and coolant in CANDU (Canada Deuterium Uranium) nuclear reactors, allowing unenriched uranium to be used as a fuel. The lifetime of these reactors is compromised by corrosion of the D₂O-carrying pipes because acidic species present are chemically altered by deuterium isotope exchange. Established corrosion mitigation techniques are insufficient to deal with this problem as they are based on data generated from light water since very little data (i.e., p*K_a* values) is available for heavy water under hydrothermal conditions. Our research involved the computational determination of p*K_a* values of 74 weak organic and inorganic acids in both H₂O and D₂O at ambient (25 °C, 101.3 kPa) and hydrothermal (250 °C, 20.0 MPa) conditions using DFT and continuum solvation methods. The calculated difference of p*K_a* between D₂O and H₂O at ambient conditions for the studied acids is in very good agreement with experimental values, which provides confidence in the calculated p*K_a* difference at hydrothermal conditions, for which little experimental data is available. In addition, both p*K_a* differences follow a very interesting pattern depending on temperature and pressure which is further investigated [1].

[1] N. Mora-Diez, Y. Egorova, H. Plommer, P. Tremaine, *RSC Adv.* **5**, 9097 (2015).

Development and application of atom-centered potentials for accurate modeling of large systems

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We have developed 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, our 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 [1–4].

- [1] V. K. Prasad, A. Otero de la Roza and G. A. DiLabio, *J. Chem. Theory Comput.* **14**, 726 (2018).
- [2] A. Otero de la Roza and G. A. DiLabio, *J. Chem. Theory Comput.* **13**, 3505 (2017).
- [3] G. A. DiLabio, “Atom-centered potentials for noncovalent interactions and other applications”, in *Non-Covalent Interactions in Quantum Chemistry and Physics: Theory and Applications*, ed. by A. Otero de la Roza and G. A. DiLabio (Elsevier, 2017).
- [4] J. D. Holmes, A. Otero de la Roza and G. A. DiLabio, *J. Chem. Theory Comput.* **13**, 4205 (2017).

Abstracts of Posters

A practical model to predict the correlation energy of molecules

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In both wavefunction and density functional electronic structure theories, the accurate prediction of the electron correlation energy is of a great importance. The methods that account for the correlation energy accurately are impractical and computationally expensive. Herein, we provide a practical model that is computationally efficient for predicting CCSD(T) correlation energies for large molecules. In this model, the electron correlation energy for molecules is described as a function of differences between atoms in molecule densities (AIMD) and isolated atomic densities (IAD) calculated for both at the nuclei. The correlation energies are fitted to the CCSD(T)/6-31++G(d,p)//HF/6-31++G(d,p) values. The performance of this model was evaluated by comparing correlation energies for 700 molecules using the root mean square deviation (RMSD) and R^2 . The model is found to give very encouraging results.

[1] D. P. O'Neill, P. M. W. Gill, *Mol. Phys.* **103**, 763 (2005).

[2] Z. Ištvanová, R. A. Poirier, J. W. Hollett, *Comput. Theor. Chem.* **1074**, 136 (2015).

[3] Z. Ištvanová, V. Grandy, R. A. Poirier, C. D. Keefe, J. W. Hollett, *Comput. Theor. Chem.* **1067**, 64 (2015).

Truncating FCI using the mathematics of complexity for solving the electronic structure and nuclear structure Schrödinger equations

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An important goal of contemporary electronic and nuclear structure is to be able obtain a desired accuracy from approximate solutions to the Schrödinger equation in the least time. The full configuration interaction (FCI) method provides the best possible wave-function within a basis set. The approach proposed here involves selecting a subset of the solutions used in FCI (typically a subset of all possible Hartree-Fock solutions within a basis set). Results from Griebel and others [1–4] in the mathematics of complexity literature show that if the analytic solutions to a given Schrödinger equation have mixed bound derivatives then it is possible to obtain FCI accuracy with polynomial scaling (at least in the large basis set limit). The theorems from Griebel and others [1–4] indicate which solutions to include based on the number of nodes in each solution. We refer to this approach as the GK-CI method. This truncation of the FCI method does not require any physical intuition of orbitals (e.g. the Hartree-Fock solutions) and is not constructed from the typical excitation-hierarchy approach. In this presentation I will describe the method as well as provide preliminary results from both electronic structure and nuclear structure calculations [5].

[1] M. Griebel and S. Knapek, *Constr. Approx.* **16**, 525 (2000).

[2] H. Bungartz and M. Griebel, *Acta Numer.* **13**, 147 (2001).

[3] G. W. Wasilkowski and H. Wozniakowski, *Found. Comput. Math.* **5**, 451 (2005).

[4] S. A. Smolyak, *Dokl. Akad. Nauk.* **4**, 240 (1963).

[5] J. S. M. Anderson and P. W. Ayers, *J. Chem. Phys.* Submitted (2018).

Density-functional theory studies of vanadium oxide clusters and their reactions with fluorocarbons

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Vanadium oxide species have been the subject of extensive experimental and theoretical studies as they are important catalysts in many industrial processes [1], such as the selective oxidation and functionalization of hydrocarbons. Gas-phase studies of neutral and ionic vanadium oxide clusters are useful because they allow us to better understand the nature of the reactive sites on catalyst surfaces by investigating small cluster models [2]. Castleman and co-workers, through extensive experimental studies have worked towards characterizing vanadium oxide clusters and their reactivity. However, it is a cumbersome and expensive process to describe the structural and electronic properties directly by experimental techniques [3]. As an alternative, quantum chemistry calculations offer an efficient way to obtain a large amount of information, such as molecular geometries, electronic properties, binding energies and the description of bonding in these systems. While transition metal-containing species may at times remain a challenge for quantum chemistry calculations, previous reports [4–6] demonstrate that density-functional theory (DFT) is a powerful tool for investigating transition metal-containing clusters. We therefore present a systematic DFT study of the structural and electronic properties of V_xO_y and $V_xO_y^+$ ($x = 1-4$, $y = 1-10$) clusters. Various basis sets and functionals were tested to determine an appropriate model chemistry aimed at investigating vanadium oxide cluster cations and their reactivity towards fluorocarbons, more specifically the reaction mechanisms of $V_2O_4^+$ with CH_2F_2 and CH_3CF_3 with a focus on possible cluster structure-activity relations.

- [1] B. M. Weckhuysen and D. E. Keller, *Catal. Today* **78**, 25 (2003).
- [2] R. C. Bell, K. A. Zemski, D. R. Justes and A. W. Castleman Jr., *J. Chem. Phys.* **114**, 798 (2001).
- [3] J. M. Thomas and W. J. Thomas, *Principles and Practices of Heterogeneous Catalysis*; VCH (1996).
- [4] M. Calatayud, J. Andrés and A. Beltrán, *J. Phys. Chem. A* **105**, 9760 (2001).
- [5] S. Vyboishchikov and J. Sauer, *J. Phys. Chem A* **105**, 8588 (2001).
- [6] S.-C. Qi, J.-I. Hayashi and L. Zhang, *RSC Adv.* **6**, 77375 (2016).

Models for analyzing three-center two-electron bonds

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Three-center two-electron bonds play an important role in a rich array of chemistries. Despite a large volume of studies of such systems using molecular orbital theory, a simple-to-use quantitative model is still absent in the computational chemistry toolbox. We have developed such a model based third order perturbational molecular orbital theory. This model has been applied to a set of compounds that include three-center two-electron bonds.

Assessing the performance of the “B05” density functional on densities

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In two papers [1, 2], Becke introduced Kohn-Sham density-functional approximations for static and dynamic correlation to be partnered with 100 percent exactly-computed (Hartree-Fock) exchange. Known as “B05”, this was the first functional specifically designed to model the non-local properties of exchange and correlation simultaneously. Non-locality issues, often referred to as "delocalization error", have emerged as one of the most vexing problems in DFT today. The physics of non-locality is built into the B05 functional in a natural way and one wonders, therefore, if B05 might provide accurate treatment of delocalised charges. However, implementation challenges have prevented the B05 functional from being widely available. We recently proposed a procedure, “B05min” [3], circumventing the need for a self-consistent implementation, and assessed its efficacy on dipole moments. We expand this assessment to a subset of challenging charge transfer systems and recent, controversial, density error studies.

[1] A. D. Becke, *J. Chem. Phys.* **119**, 2972 (2003).

[2] A. D. Becke, *J. Chem. Phys.* **122**, 064101 (2005).

[3] S. D. Dale, E. R. Johnson, A. D. Becke *J. Chem. Phys.* **147**, 154103 (2017).

Hydrolysis mechanisms via semicontinuum modelling

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Our use of semicontinuum (cluster + continuum) modelling of solvation effects has quantified large errors in continuum modelling (and demonstrated appropriate cures) for reactions involving aqueous H_3O^+ or OH^- . This poster will first show results for the reaction Gibbs energy of the water autoionization reaction ($2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$), where traditional continuum models make astounding errors of 50 kcal mol^{-1} . With this problem cured, the poster will then show our results for the multistep energy profiles for the hydrolysis of amide, ether, and lignin models. The more accurate modelling tidies up the known mechanisms and identifies the rate-determining steps.

Ionization potentials from *ab initio* ground-state wave functions

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We present a new method for extracting the first ionization potential, I , of a given many-electron system from its ground-state *ab initio* wave function. The method is based on the fact that the average local ionization energy (ALIE), a quantity that can be constructed from the two-electron reduced density matrix, approaches I in the $r \rightarrow \infty$ limit. This limit can be determined either graphically or analytically using basis-set representations of the generalized Fock matrix and the electron density. The principal difference between the proposed method and the extended Koopmans theorem (EKT) is that the former does not require any matrix inversion or diagonalization. The ALIE-based method was implemented in the *Gaussian 09* program and its performance was compared to that of the EKT.

The behaviour of hydroxyl radical in aqueous systems: Complexes with halide anions

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Despite the very important roles that hydroxyl radical (OH^\cdot) plays across a diverse range of fields such as atmospheric chemistry, water treatment, and some key biomolecular mechanisms, the reactivity of this species has posed immense challenges to experimental and theoretical investigations. Halide anions are ubiquitous and the interaction of OH^\cdot with those halide anions, particularly with Cl^- and Br^- , is relevant to key biological, atmospheric, and even industrial water treatment processes. In this study, we utilize *ab initio* molecular dynamics (MD) simulations to characterize extensively the formation of two-centre three-electron interactions called hemibonds between OH^\cdot and halide anions in aqueous systems. The focus is in understanding the structure, behavior, and solvation structure of the XOH^\cdot complexes ($\text{X}=\text{Cl}, \text{Br}$) in water. We investigate how the presence of the halide anion modifies the properties of OH^\cdot . We also investigate what is the influence of the counterion over the XOH^\cdot - complex by adding Na^+ in some simulations, and perform free energy calculations to characterize the stretching of the X-O^\cdot distance. Car-Parrinello Molecular Dynamics (CPMD) [1] as implemented in the *CPMD* software and Density Functional Theory for the evaluation of the forces, specifically the density functional HCTH [2], are employed. After studying the possibility of system size effects, we decided to use a system containing 96 water molecules in addition to the halide anion and the hydroxyl radical. In the systems containing Na^+ as a counterion we substitute one of the water molecules by the Na^+ cation. Both, relatively long CPMD simulations and Constrained MD simulations have been used to study the behavior of the XOH^\cdot complex, the strength of the halide-radical interaction along the X-O distance, and elucidate the role of the solvating molecules in the way the system evolves. The complex structure, both atomic and electronic, and the free energy along the stretching of the O-X distance are analyzed and show that the complex has a marked electron transfer character that is even more accentuated for Br^- than for Cl^- . This partial electron transfer or electron sharing changes the nature of the OH^\cdot first solvation shell considerably. Counterion effects have been found to be minimal and only of electrostatic nature without any apparent impact on the nature of the complex. These results have potential implications in regulating OH^\cdot activity in biological or industrial processes.

[1] R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

[2] A. D. Boese *et al.*, *J. Chem. Phys.* **112**, 1670 (2000).

Evaluation of hybrid and pure DFT methods for the binding of novel ligands in the tyrosine hydroxylase enzyme

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The Minnesota 2006 density functional methods include both pure and hybrid models, each of which benefitting different aspects of various systems. The Tyrosine Hydroxylase (TyrOH) enzyme contains a Fe^{2+} in the center of the active site. M06-2X, M06-L, and M06 have all been used to evaluate the binding strength of novel ligands in the TyrOH active site. TyrOH is the rate determining enzyme in the synthesis of the catecholamine, dopamine. TyrOH converts tyrosine to L-DOPA, which is administered in the treatment of Parkinson's patients, as dopamine cannot cross the blood brain barrier. The inhibition of TyrOH reduces dopamine in the brain to undetectable levels. A crystal structure of the active site of Tyrosine Hydroxylase with a known inhibitor bound was obtained from the protein data bank (PDB ID: 2TOH). In this work, dopaminergic derivatives were inserted into the enzymatic active site in silico in order to test the strength of the interactions between the substrate and active site, to determine if any of these derivatives could be effective inhibitors. M06-2X is a hybrid functional, while M06-L and M06 are both pure; all of these functionals were used to optimize structures and to analyze interaction energies. While all the methods are suited for large complexes, such as the active site of an enzyme, M06-2X is stated to be best for interaction energies, M06-L best when a transition metal is present, and M06 as an intermediate between the two. The novel dopaminergic derivatives were optimized with implicit solvent with either M06-2X, M06-L, or M06 and 6-31G with relaxed amino acid side-chains. Interaction energies between the ligands and protein were determined using the same DFT methods as mentioned above with the 6-311+G* basis set. M06-2X and M06 are hybrid functionals, while M06-L is pure; all of these functionals were used to optimize structures and to analyze interaction energies. Preliminary results show significant differences between the methods within the same complex, as well as potential in determining a well-suited derivative, that has seeded other promising ligands.

[1] Y. Zhao, D. G. Truhlar, *Chem. Phys Lett.* **502**, 1 (2011).

Surface plasmon polariton controlled molecular switch

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Molecular electronic devices are studied extensively to explore their potential use in electronics and also to gain an understanding of the mechanisms of electron transport at the molecular scale. Recent experiments [1,2] show that molecules can be strongly coupled to surface plasmon polaritons (SPPs) and that the resulting, so called dressed molecular states, are entanglements of electrons and SPPs. Here we propose molecular electronic devices that are derived from dressed molecules. We present a simple analytical theory, based on Hückel Hamiltonian and the Source-Sink potential method [3], that shows how SPPs can provide complete control of the molecular conductance. In a suggested device made from azulene, the SPP couples a localized excited state to the continuum wave function of the molecular conductor and the details of this coupling, i.e. frequency and field strength of the SPP, are the parameters that modulate the molecular conductance. In addition to the molecular switch, we also design a photovoltaic cell that harvests the SPP energy to generate a photo current. The proposed, SPP-controlled devices represent a novel type of opto-electronic circuitry that significantly enlarges the potential of molecular electronics.

- [1] R. Chikkaraddy, B. de Nijs, F. Benz, S. J. Barrow, O. A. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, and J. J. Baumberg, *Nature* **535**, 127 (2016).
- [2] B. de Nijs, F. Benz F. , S. J. Barrow, D. O. Sigle. R. Chikkaraddy, A. Palma, C. Carnegie, M. Kamp, R. Sundararaman, P. Narang, O. A. Scherman, and J. J. Baumberg, *Nat. Commun.* **8**, 994 (2017).
- [3] F. Goyer, M. Ernzerhof, and M. Zhuang, *J. Chem. Phys.* **126**, 144104 (2007).

Molecular-level correlations in entangled polymer melts: Insights from molecular dynamics simulations

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An increasing number of studies are probing the molecular-level details of important polymer-based materials and polymer processes, such as polymer crystallization. However, molecular-level scientific understanding of entangled polymer melts, and associated chain dynamics, remains incomplete. To address this, we have conducted long coarse-grain simulations (e.g., > 35 μ s) for large-scale, well-entangled polymer systems (e.g., containing hundreds of C₉₆₀H₁₉₂₂ chains). Through detailed analysis and visualization of these systems, we reveal several new facets of polymer dynamics in entangled polymer melts. For example, new connections are made between entanglement lengths and molecular-level correlations, thus affording new interpretations of polymer entanglements. In addition to advancing scientific understanding of polymer melts, this work provides insights relevant to future work probing and rationalizing polymer dynamics during complex phenomena, including polymer crystallization.

Efficient methods for studying electron detachment of metal oxide clusters

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Photoelectron spectroscopy is a well-developed technique providing rich structural, reactivity, and dynamical information of chemical systems. Critically, full assessment of the resulting spectra often requires corroborating theoretical and computational analysis. Our group is particularly interested in modeling anion photoelectron spectroscopy of metal oxide clusters, which serve as molecular models of surface defect sites. Such calculations can be complicated by the presence of unpaired and strongly correlated electrons, and the standard computational tool box lacks a full complement of practical tools for efficient exploration of this problem class. This presentation will describe our lab's efforts to develop new efficient models for treating these complicated electronic structures and qualitatively identifying the nature of detached electrons. Recent application studies modeling anion photoelectron spectra of metal oxide clusters using these models will also be described.

Chemotactic clustering of chemically-powered Janus motors

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Chemotaxis is the directional movement of cells in response to gradients of chemical signals. Synthetic motors are also able to respond to chemical gradients and mimic such chemotactic motions. Here we investigate the motion of Janus motors in gradient fields of fuel (A) and product (B) particles. The Janus motor comprises catalytic (C) and noncatalytic (N) hemispheres, and each hemisphere may interact differently with the A and B particles. For a given specification of interaction strengths, a Janus motor is able to reorient and move in gradient fields, thus displaying a chemotactic response to the gradient. The dynamics of a collection of active Janus motors is also considered. The Janus motors are found to form clusters through interactions mediated by chemotaxis.

Electronic structure and properties of ZnO crystals and nanotubes

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Density-functional theory, namely LDA+1/2, is used to predict the electronic properties of the bulk ZnO wurtzite crystal, as well as armchair, zigzag, and chiral ZnO nanotubes. The predicted band gap for ZnO wurtzite is 3.20 eV, which agrees well with the reported experimental values of 3.30 to 3.55 eV. From X-ray crystallographic simulations of the ZnO wurtzite, the d-spacings, i.e. the vector lengths along the 100 plane (d1), the 002 plane (d2) and the 101 plane (d3) were determined to be 5.48, 5.16 and 5.01 Å. As for ZnO nanotubes, in addition to changes in configuration, different sizes of ZnO (n,m) were explored, with n ranging from 3 to 7, and the bandgap for ZnO nanotubes was found to remain fairly consistent regardless of nanotube size and configuration, ranging from 3.02 eV for ZnO (3,0) to 3.38 eV for ZnO (6,6). This slight difference is likely due to the cut-off error which naturally exist within the LDA+1/2 implementation [1]. The fact that ZnO nanotubes have a similar band gap as the wurtzite crystal indicates that they most likely exhibit the same orbital interactions, and indeed density of states analysis shows similar binding patterns for the crystal and nanotubes, where the d-orbital of zinc interacts with the p-orbital of oxygen, in contrast to previous theoretical predictions that ZnO nanotubes and wurtzite crystal involve an sp^2 hybridization bonding pattern [2].

[1] L. G. Ferreira, M. Marques, and L. K. Teles. *AIP Advances* **1**, 032119 (2011).

[2] B. Wang *et al.* *Nanotechnology* **18**, 345706 (2007).

Molecular dynamics simulation of water transport through bilayer graphyne membranes

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With increasing global population growth and changes in climate caused by industrialization, the development of low-cost and energy-efficient methods for obtaining fresh water from the saline water of seas and oceans is among the most attractive scenarios for combating against water scarcity. Currently, membrane-based technologies such as reverse osmosis (RO) nanofiltration, which uses the pressure difference across a membrane as a driving force to filter impurities, are widely used throughout the world for water treatment and desalination and much scientific activity has been devoted to improve the efficiency of RO processes by designing novel membrane materials

It has been shown that nanoporous materials are good candidates for water desalination membranes. Water can flow through nanopores due to its small size, while the passage of ions is blocked because of the larger size of ionic hydration shell. Carbon nanotubes and graphene monolayers containing artificial nanoscale pores have been proposed as effective structures for this purpose [1,2].

In this project, Non-equilibrium molecular dynamics simulations of water-salt solutions driven through single and double-layer graphyne membranes by a pressure difference created by rigid pistons are carried out to determine the relative performance of the membranes as filters in a reverse osmosis desalination process. γ -graphyne is a new family of carbon allotrope with phenyl rings connected by acetylene bonds, exhibiting triangular pores. The pore size can be adjusted by changing the number of acetylene bonds (n) between adjacent phenyl rings. γ -graphyne (or graphyne- n) structures, with their natural pores have been shown to be good candidates for water desalination [3,4].

It is found that the flow rate of water through a graphyne-4 membrane is twice that of a graphyne-3 membrane for both single and double-layer membranes. Although the addition of a second layer to a single-layer membrane reduces the membrane permeability, the double-layer graphyne membranes are still two or three orders of magnitude more permeable than commercial reverse osmosis membranes. The minimum reduction in flow rate for double-layer membranes occurs at a layer spacing of 0.35 nm with an AA stacking configuration, while at a spacing of 0.6 nm the flow rate is close to zero due to a high free energy barrier for permeation. The distribution of residence times of water molecules in the interlayer region suggests that at the critical layer spacing of 0.6 nm, a cross-over occurs in the mechanism of water flow from the collective movement of hydrogen-bonded water sheets to the permeation of individual water molecules. All membranes are demonstrated to have a high salt rejection fraction and the double-layered graphyne-4 membranes can further increase the salt rejection by trapping ions that have passed through the first membrane from the feed solution in the interlayer space.

[1] B. Corry, *Energy Environ. Sci.* **4**, 751 (2011).

[2] D. Cohen-Tanugi and J. C. Grossman, *Nano Lett.* **12**, 3602 (2012).

[3] S. Lin and M. J. Buehler, *Nanoscale* **5**, 11801 (2013).

[4] J. Kou *et al.*, *Nanoscale* **6**, 1865 (2014).

TDDFT excitation energies from accurate exchange-correlation potentials

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The quality of Kohn-Sham orbitals and orbital energies used in adiabatic linear-response time-dependent density-functional theory (TDDFT) calculations is an important factor determining the accuracy of the resulting valence and Rydberg excitation energies [1]. Recently, our group has developed a method for generating accurate exchange-correlation potentials from *ab initio* electronic wave functions [2–4]. Here we employed the Kohn-Sham orbitals and orbital energies obtained by this method from Hartree-Fock and CASSCF wave functions, along with four approximate exchange-correlation kernels (LDA, PBE, PBE0 and TPSS), to calculate vertical excitation energies of 14 molecules of the benchmark test set of Leang *et al.* [5]. The results are significantly more accurate than those obtained using standard local and semilocal functionals, but not much better than those obtained with hybrid density functionals such as PBE0. We also find that the choice of the kernel has a considerable effect on the accuracy of excitation energies for a fixed set of Kohn-Sham orbitals and orbital energies, in agreement with previous studies [6,7].

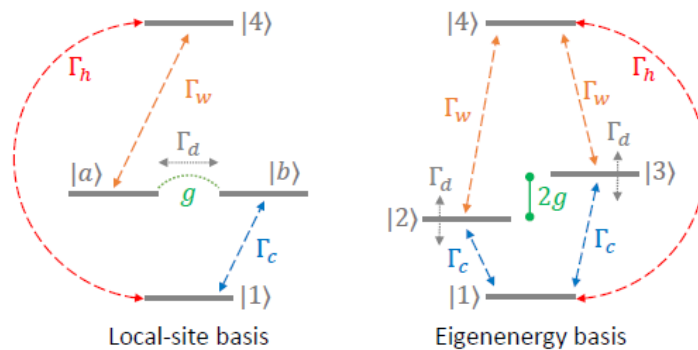
- [1] R. van Meer, O. V. Gritsenko, and E. J. Baerends, *J. Chem. Theory Comput.* **10**, 4432 (2014).
- [2] I. G. Ryabinkin, S. V. Kohut, and V. N. Staroverov, *Phys. Rev. Lett.* **115**, 083001 (2015).
- [3] R. Cuevas-Saavedra, P. W. Ayers, and V. N. Staroverov, *J. Chem. Phys.* **143**, 244116 (2015).
- [4] I. G. Ryabinkin, E. Ospadov, and V. N. Staroverov, *J. Chem. Phys.* **147**, 164117 (2017).
- [5] S. S. Leang, F. Zahariev, and M. S. Gordon, *J. Chem. Phys.* **136**, 104101 (2012).
- [6] P. Bleiziffer, A. Heßelmann, C. J. Umrigar, and Andreas Gorling, *Phys. Rev. A* **88**, 042513 (2013).
- [7] Y. Jin, Y. Yang, D. Zhang, D. Peng, and W. Yang, *J. Chem. Phys.* **147**, 134105 (2017).

Interplay of coherence and decoherence effects in quantum absorption refrigerators

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We present a quantum thermal machine where the device operation hinges on the presence or absence of steady-state, eigenbasis coherences. Absorption refrigerators mediate energy transfer from a cold thermal reservoir to a hot one, using energy input from a “work” reservoir. In our model, the working medium of the refrigerator comprises a discrete 4-level system coupled to 4 baths.



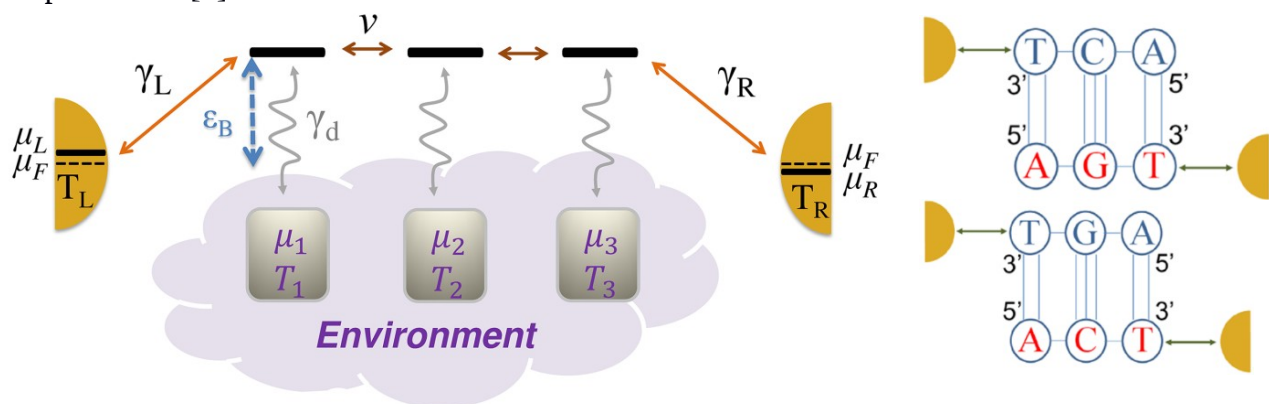
In this model, bath-induced coherences from the “cold” and “work” baths, compete with environmental effects from a “decoherence bath”. We find that eigenbasis coherences generally suppress the current, while having a minimal effect on the device coefficient of performance (cooling efficiency). We further demonstrate very clearly the shortcomings of secular-type quantum master equations, and the necessity of retaining population-coherence couplings to for certain thermodynamical systems.

Charge transport in DNA: From comprehensive simulations to key principles

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Double helical DNA can support charge carrier transfer for up to 30 nm, yet their use in nanoelectronic circuits is questionable, and a full understanding of transport mechanisms is still missing given the complexity of the system. We adapt the Landauer-Büttiker probe method, a quantum scattering technique that mimics elastic and inelastic scattering effects, and model coherent and incoherent charge transport behavior in DNA molecular junctions. Our code is implemented in MATLAB and is available as open source [1].



We reproduce and interpret tunneling to hopping crossover [2] in both the conductance and the thermopower in AT-rich DNA sequences of varying lengths [3]. Moreover, based on the comprehensive simulations, we reveal that most sequences with 3 to 7 base pairs conduct via a mixed, coherent-incoherent mechanism due to the influence of the surrounding thermal environment. The model allows us to identify exceptional DNA molecules predicted to be excellent and robust conductors of electric current over a wide range of physical conditions [4]. Finally, we show that key conductance features of the model can be captured with a reasonable accuracy in a deep neural network, trained on a small part of the sequence space.

[1] R. Korol, M. Kilgour and D. Segal, *Comp. Phys. Comm.* **224**, 396 (2018).

[2] Y. Li, L. Xiang, J. Palma, Y. Asai, and N. Tao, *Nature Comm.* **7**, 11294 (2016).

[3] R. Korol, M. Kilgour and D. Segal, *J. Chem. Phys.* **145**, 224702 (2016).

[4] R. Korol and D. Segal, *J. Phys. Chem. C* **122**, 4206 (2018).

Alternative treatment of symmetry for use with local coupled-cluster approaches to molecules and solids

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Canonical orbitals, transforming according to their irreducible representations (point groups), reflect the symmetry of the molecule, but are often delocalized across the molecule and they are not suitable for local correlation approaches [1]. To combine the use of symmetry with local correlation approaches we aim to construct *congruent localized* orbitals that reflect the symmetry of the molecule by their repeating shapes, which can be used in symmetry adapted local coupled-cluster calculations, by only calculating the unique amplitudes.

An alternative to using point groups to describe the symmetry of a molecule is to view the molecule in terms of small repeating subgroups or “unit cells”, as shown in the figure below for a complex molecule. By constructing local orbitals for a single unit cell, we can use symmetry operators to generate congruent localized orbitals for the rest of the molecule. A potential complication arises as the set of congruent occupied orbitals may be linear dependent. For example, in benzene with a six-fold axis we get 6 occupied *congruent* π -orbitals, rather than the canonical 3.

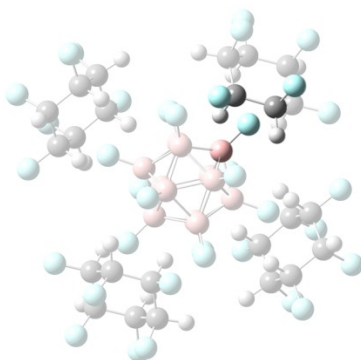


Figure 1. The unit cell of a complicated molecule [96 atoms reduced to a unit-cell of 8].

The molecular unit cells are analogues to crystalline unit cells in the solid state, but require rotation-like operators to map the nuclear coordinates between unit cells. The constructed local orbitals can also be rotated between unit cells using the derived symmetry operators. Crystalline unit cells are related by a translational operator, but the general approach is the same. The symmetry analysis to be discussed here is a vital component to the development of symmetry adapted local correlation approaches.

[1] C. Riplinger and F. Neese, *J. Chem. Phys.* **138**, 034106 (2013).

Efficient calculation of level alignment at weakly coupled molecule-metal interfaces using substrate screening within the *GW* approach

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The physics of level alignment at molecule-metal interfaces can often be accurately captured by the *ab initio GW* approach. However, the computational cost for such *GW* calculations for typical interfaces is significant, given their large system size and chemical complexity. In the past, approximate self-energy corrections constructed from image-charge models have been used to compute level alignment with good accuracy. However, this approach neglects dynamical effects of the polarizability and requires the definition of an image plane. In this work, we propose a new approximation for *GW* calculations of molecule-metal interfaces, where we greatly simplify the evaluation of the polarizability of the combined system. This is done by first computing the non-interacting polarizability of each individual system, without the use of large supercells, followed by folding and interpolation techniques to efficiently combine these quantities. Overall, this approach greatly reduces the computational cost for conventional *GW* calculation of level alignment without sacrificing the accuracy. Moreover, this approach captures both dynamical and nonlocal polarization effects without the need to invoke a classical image charge expression or to define an image plane. We benchmark our approximation for the case of a benzene molecule physisorbed on graphite.

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How does the amount of Hartree–Fock exchange affect the observation of the pseudo-Jahn–Teller effect?

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Potential energy surfaces are a concept at the heart of computational chemistry. Previous studies have detailed the effect of both integration grid size and exact exchange on various properties including the nature of stationary points (i.e., transition structure vs. minimum) on potential energy surfaces but none have addressed the root cause of such discrepancies. In this work we introduce a catastrophe theory approach to the problem and examine two contentious stationary points belonging to planar disilene and 2Si TCNQ from the perspective of the pseudo-Jahn–Teller (pJT) effect using DFT methods. First the planar stationary points are characterized using a variety of model chemistries and integration grids. The effect of the amount of Hartree–Fock exchange is then studied and the usage of DFT for assessing pJT parameters is explored.

State-specific dissociation rate coefficients for $\text{H}_2(v,j) + \text{H}_2(v',j')$

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Dissociation of molecular hydrogen is an important cooling mechanism in regions of the interstellar medium associated with star formation. Full dimensional quasiclassical trajectories were calculated for all combinations of (v,j) with internal energy below 1 eV. Using the chemically accurate BMKP2 interaction potential with a minimum of 80000 trajectories at each translational energy, cross sections were calculated. Since the values of rate coefficients can exhibit high sensitivity to the values of the cross sections near threshold, additional large batches of trajectories were calculated to achieve the desired precision. State-specific rate coefficients were calculated at temperatures between 100 K and 100000 K using a piecewise linear excitation function. The resulting state-specific rate coefficients, γ , are parametrized as a function of temperature over the range 600– 10000 K using:

$$\log_{10} \gamma(t) = a + bz + cz^2 + d(1/t - 1)$$

where $t = T/4500$ K and $z = \log_{10} t$. It was found that the values of the resulting rate coefficients were sensitive to the internal energy of both molecules with initial vibrational energy having a slightly greater effect than rotational energy. This effect diminished as temperature increased.

Modelling the repair of damaged proteins by antioxidants

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Free radicals are very reactive species that can damage proteins and other biomolecules. One of the first products of these reactions are carbon-centred protein radicals, which may subsequently become other species. Certain molecules, known as antioxidants, can scavenge free radicals by several mechanisms, including hydrogen atom transfer (HAT) and single electron transfer. This way antioxidants could repair damaged proteins. A particularly interesting group of antioxidants are those with thiol groups in their structure. Dihydrolipoic acid (DHLA) and glutathione (GSH) are examples of these antioxidants in which the S-H bond is weak enough to efficiently repair protein carbon-centred radicals by the HAT mechanism. GSH is a natural tripeptide (L-glutamate, L-cysteine and L-leucine) which takes part in many biochemical reactions that regulate the levels of free radicals. Phenolic compounds, such as α -tocopherol (vitamin E) or its water soluble analogue Trolox, are also known for their antioxidant activity. Trolox is commonly used as a reference molecule against which the antioxidant capacity of other species and mixtures is assessed.

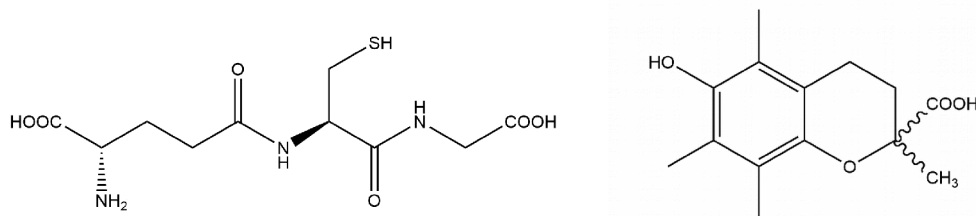


Figure 1. Antioxidants used in this study: GSH (left) and Trolox (right)

In this work, we have used the M06-2X functional with the 6-31++G(d,p) basis set and the SMD solvation model to study the thermodynamics and the kinetics of the HAT repair reactions between the antioxidants GSH and Trolox and four N-formyl leucinamide radicals (centred at the α , β , γ and δ carbons). Calculations have been performed in water and in pentyl ethanotate, to mimic the effect of the microenvironment (hydrophobic or hydrophilic) of the damaged amino acid within the protein. The protein model N-formyl-leucinamide was recently used to study the antioxidant capacity of DHLA following a similar repair mechanism [1,2]. The results obtained in this work allow the antioxidant activity comparison between Trolox, GSH and DHLA.

[1] R. Castañeda-Arriaga, N. Mora-Diez, J. R. Alvarez-Idaboy, *RSC Adv.* **5**, 96714 (2015).

[2] R. Castañeda-Arriaga, A. Dominguez-Castro, J. R. Alvarez-Idaboy, N. Mora-Diez, *Can. J. Chem.* **94**, 1119 (2016).

Construction of Fermi potentials for many-electron systems

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The Fermi potential, $v_F(\mathbf{r})$, is the nonclassical part of the multiplicative effective potential appearing in the Kohn-Sham-type equation for the square root of the electron density. The conventional method of constructing $v_F(\mathbf{r})$ by inverting that equation produces unsatisfactory results when applied to electron densities expanded in Gaussian basis sets. We describe a different approach which is based on an exact formula for $v_F(\mathbf{r})$ in terms of the interacting one- and two-electron reduced density matrices of the system. The proposed method produces accurate approximations to the basis-set-limit $v_F(\mathbf{r})$ when applied to generate potentials using finite Gaussian basis sets [1]. We showcase applications of our method to atomic and molecular wave functions generated at various levels of *ab initio* theory.

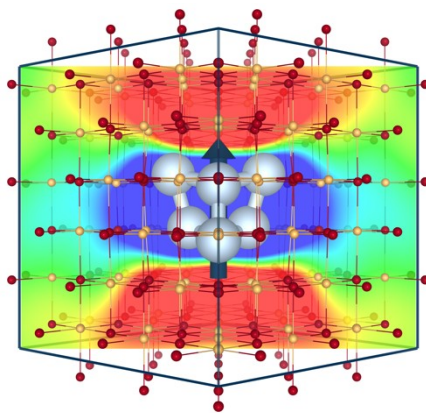
[1] E. Ospadov and V. N. Staroverov, *J. Chem. Theory Comput.*, in press.

Theoretical evaluation of the dielectric response in metal/metal oxide nanocomposites

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Inclusions of Ag and Au are an effective way to enhance the permittivity of high- κ oxides; however, the scale of many modern devices pushes inclusion dimensions below the metal–insulator transition at ~ 2 nm. We describe the implementation of a methodology within the modern theory of polarization, by which the dielectric response in these molecular-scale nanocomposites can be obtained from first-principles calculations. Our methodology also allows partitioning of the response into inclusion and matrix contributions. The method was applied by our group to a series of nanocomposite materials, starting with Ag_8/MgO [1]. We find that the major contributions to the enhanced response in the nanocomposite, over the initial dielectric oxide, come from both the Ag–O interaction at the inclusion–matrix interface, and the molecular structure of the composite.



[1] D. Hally and I. Paci, *Nanoscale* **10**, 9583 (2018).

**Atoms in molecule density approach:
A novel way of computing molecular energies and properties**

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Computing properties of large molecules from its atoms (atomic basins) or from small building blocks is a challenging problem in quantum chemistry. For example, properties of proteins may be computed from properties of their amino acids. For this purpose, the electron density and some other properties of atoms-in-molecules have been stored in a database. The electron density for the molecule of interest is then built using this database. As a result, the molecular properties (such as number of electrons, potential energy, etc.) can be computed.

- [1] J. E. Besaw, P. L. Warburton, and R. A. Poirier. Atoms and bonds in molecules: Topology and properties. *Theor. Chem. Acc.* **134**, 115 (2015).
- [2] P. L. Warburton, R. A. Poirier, and D. Nippard. Atoms and bonds in molecules from radial densities. *J. Phys. Chem. A* **115**, 852867 (2011).

Dispersion-corrected density-functional theory applied to amino-acid adsorption on model quartz surfaces

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Controlled growth of enantiopure biomolecules is an important area of development for modern chemistry. Hydroxylated quartz surfaces are chiral surfaces with many possible hydrogen bonding sites, making them potentially promising substrates to seed enantiospecific separations. We extend the current understanding of the interaction of amino acids with this surface, focusing on alanine, serine, and aspartic acid. Dispersion-corrected density-functional theory (DFT) was used, specifically the B86bPBE functional [1,2] with the exchange-hole dipole moment (XDM) dispersion model [3]. This work can be used as a stepping stone to provide further insight into how amino acid crystals will interact with this surface.

[1] A. D. Becke, *J. Chem. Phys.* **85**, 7184 (1986).

[2] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

[3] A. Otero de la Roza, and E. R. Johnson, *J. Chem. Phys.* **136**, 174109 (2012).

An *ab initio* investigation of the hydration of the d^0 transition-metal tetraoxo complexes. II. 5th and 6th period metals

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The aqueous solution chemistry of simple oxometalates can be very complex and extremely important to understand experimentally and to describe computationally. The solvated oxometalate anion is considered to be surrounded by successive layers of the solvent water molecules creating a series of hydration shells, or spheres [1–3]. This study is an examination of the first (innermost) hydration sphere of oxometalate species and the effect of the hydration sphere on the structure of the oxoanion. *Ab initio* calculations, using HF, MP2, and B3LYP levels of theory and extended basis sets including polarization and diffuse functions, were systematically performed to calculate the optimized geometries and vibrational spectra of the hydrated species: NbO_4^{3-} , TaO_4^{3-} , MoO_4^{2-} , WO_4^{2-} , TcO_4^- , ReO_4^- , RuO_4 , OsO_4 . The results of the calculations were compared to experimental values where possible.

- [1] C. C. Pye and W. W. Rudolph, *J. Phys. Chem. A* **105**, 905 (2001) [SO_4^{2-}].
- [2] C. C. Pye and W. W. Rudolph, *J. Phys. Chem. A* **107**, 8746 (2003) [PO_4^{3-}].
- [3] C. C. Pye and V. E. J. Walker, *J. Phys. Chem. A* **115**, 13007 (2011) [ClO_4^- , BrO_4^- ; SeO_4^{2-} , AsO_4^{3-} , VO_4^{3-}]

Copper(I) chelators for a trifunctional attack on Alzheimer's disease

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Two components of the neurotoxicity of the amyloid beta ($A\beta$) peptide of Alzheimer's disease are its ability to bind reducible copper to generate reactive oxygen species (ROS) and its ability to increase its toxicity through aggregation. We describe here the design of several copper complexes that 1) will out-compete the $A\beta$ peptide for the reduced copper, 2) be redox-inactive toward dissolved oxygen, and 3) prevent the aggregation of $A\beta$ when attached to a suitable inhibitor ligand. The methodology involves a combination of *ab initio* DFT and empirical molecular dynamics calculations.

Thermodynamic properties of nonadiabatic systems using Gaussian mixture distributions

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Our focus is on obtaining time-independent properties at thermal equilibrium of electronically nonadiabatic systems. Nonadiabatic systems are of importance in numerous fields such as photochemistry, biology, quantum information processing, and electro-chemistry. Properties of interest include: the partition function Z , internal energy U , heat capacity C_V , and Gibbs energy G . Efficient calculation of G and ΔG enables high-throughput screening for catalytic materials.

Only nonadiabatic systems that can be described by a vibronic Hamiltonian, obtained through electronic structure calculations, are investigated. In our most recent work we introduced our path integral Monte Carlo (PIMC) method using Gaussian mixture distributions (GMD) for investigating these precalculated vibronic Hamiltonians [1]. Hamiltonians are evaluated in a product basis of nuclear and electronic degrees of freedom, without employing any mapping schemes such as the Meyer–Miller–Stock–Thoss (MMST) representation [2,3].

The partitioning of the full vibronic Hamiltonian into a harmonic oscillator operator and a coupling operator is a key step in our methodology. Using this form of the Hamiltonian, the partition function of the full system can then be expressed as the product of two factors: the normalization factor of a distribution (that is evaluated analytically) and a Monte Carlo estimator (of the coupling contribution to the partition function).

The advantage of this formulation is computational efficiency. We stochastically evaluate the Monte Carlo estimator using a Gaussian mixture model (GMM). A powerful property of GMMs is the ability to form smooth approximations to arbitrarily-shaped densities. Our partitioning of the Hamiltonian is therefore motivated by the computational benefits provided by GMMs.

We are currently investigating the application of machine learning algorithms to optimize the GMM's used in our method. In the future we aim to accelerate the calculations for larger systems with the use of graphics processing units (GPU's).

[1] N. Raymond, D. Iouchtchenko, P.-N. Roy, and M. Nooijen, *J. Chem. Phys.* **148**, 023819 (2018).

[2] H.-D. Meyer and W. H. Miller, *J. Chem. Phys.* **70**, 3214 (1979).

[3] G. Stock and M. Thoss, *Phys. Rev. Lett.* **78**, 578 (1997).

Evaluation of Martini coarse-grained model for microcanonical ensemble

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Molecular dynamics simulations have been an important tool in the biological field, used as a computational microscopy to get insights of complex systems. The Martini forcefield is one of the most widely used model for coarse-grained simulations of biomolecular systems. Therefore it is important to analyze the physical behavior of this model. In the present work, we analyze the energy conservation of a hydrated lipid bilayer and water in the microcanonical ensemble as a function of the time step, the size of the system, and the parameters “common” and “new” from the Martini’s website. The results suggest worse energy conservation for the systems using the Verlet list against the group, independent of the size of the system. The difference in the total energy is less than 1% for the common parameters, but for the new set achieved approximately 90% using a time step of 30 fs for the bilayer system. The preliminary conclusion points to use a time step of 20 fs for the best relation between accuracy and performance.

Dynamics of many chemically propelled nanomotors near reactive walls

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The collective motion of active matter is a complex phenomenon encompassing a large class of systems, ranging from flocks of animals on the macroscopic level to colonies of bacteria and self-propelled particles on the micron- and nano-scale. While these systems all operate out of equilibrium, the mechanisms by which collective phenomena occur may be quite different and, apart from the interactions between active entities, the influences of the environment play a crucial role in the resulting dynamics. Here we present a system of many chemically-propelled sphere-dimer motors driven by self-diffusiophoresis in the presence of a reactive wall. Using a hybrid molecular dynamics-reactive multiparticle collision dynamics (MD-RMPC) algorithm we investigate the influence of a reactive wall, whose reaction matches the reaction driving the motion of each individual motor, on the collective motion of sphere-dimers. In essence the chemical gradients produced by the reaction at the wall act by influencing the chemical gradients, generated by each motor, which are responsible for the propulsion and collective behaviour of sphere-dimers. Understanding the behaviour of such systems will lead to a further understanding of external influences on collective phenomena of active systems, particularly in those involving chemistry.

Molecular dynamic investigation of mechanism of action of cationic PHMB on bacterial membranes

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Cationic polymers such as polyhexamethylene biguanide (PHMB) are of a great interest due to their high antibacterial activity and low toxicity to humans. PHMB and similar polymers have been successfully used as topical anti-infective solutions in ophthalmology, as disinfectants and biocides in water systems, in topical wound, on cotton and environments. PHMB has been generally believed to kill bacteria through disrupting their membrane. In contrary, it has been recently proposed that PHMB enters cells and condenses bacterial chromosomes in a selective fashion. In the present study, we have employed classical molecular dynamics and umbrella sampling methods to investigate the behavior of PHMB polymers and gram-negative membranes in order to shed lights on the potential PHMB mechanism of action on the bacterial membrane. Specifically, various properties (e.g., RMSD, area per lipid, and hydrogen bonding occupancies) of several systems including the membrane (made up with POPG and POPE with a 1:3 ratio), PHMB, PHMB-membrane (inserted and separated), were examined. Furthermore, membrane penetration by PHMB was examined using umbrella sampling approach. Our results suggest that while PHMB molecules can slightly affect the surface of the membrane, a single PHMB molecule has a negligible structural effect on the membrane, while it can penetrate and pass through the membrane with a relatively low free energy barrier.

[1] G. Müller and A. Kramer, *J. Antimicrob. Chemother.* **61**, 1281 (2008).

[2] G. Müller, T. Koburger, and A. I. Kramer, *Chem. Biol. Interact.* **201**, 58 (2013).

[3] S. Wessels, and H. Ingmer, *Regul. Toxicol. Pharmacol.* **67**, 456 (2013).

[4] P. Gilbert, J. R. Das, M. V. Jones, and D. G. Allison, *J. Appl. Microbiol.* **91**, 248 (2001).

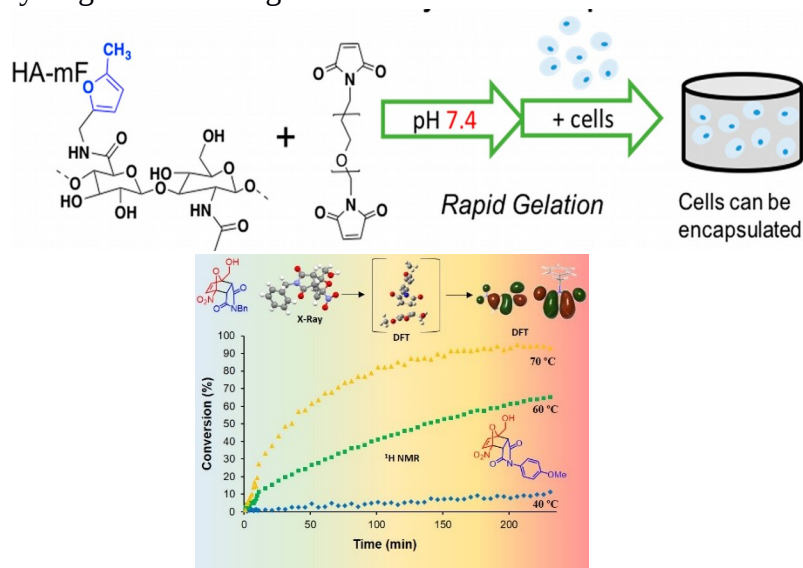
Mechanistically well-designed furans-maleimides Diels-Alder approach in preparation of a materials raging from thermally-labile end-caps for self-immolative polymers to hydrogels for cell culture

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The Diels-Alder reaction between furans and maleimides has recently proven highly useful for (bio)chemists and material chemists due to its controllable reversibility. This makes it an efficient tool for applications ranging from self-healing materials, to self-immolative polymers, to engineered hydrogels for 3D cell culture and tissue engineering. However, when we sought to use this technology for either crosslinking biopolymers to create hydrogels for 3-D cell culture (Figure 1a), or for applications in our self-immolative polymer systems (Figure 1b), we found that there were no investigations developing variably-temperature sensitive systems. Consequently, we designed and evaluated a small library of end-caps for this application and analyzed the behaviour of these systems computationally. We used similar calculations to explain the differential results obtained when different furans were used in hydrogel crosslinking.



This presentation will discuss the experimental and computational results from both of these studies, providing further insight into the mechanistic, kinetic, and thermodynamic behaviour of these highly useful cycloadducts.

- [1] S. M. Taimoory, S. I. Sadraei, R. Fayoumi, S. Nasri, M. Revington, J. F. Trant, *J. Org. Chem.* **83**, 4427 (2018).
 [2] L. J. Smith, S. M. Taimoory, R. Y. Tam, A. E. G. Baker, N. B. Mohammad, J. F. Trant, M. S. Shoichet, *Biomacromolecules* **19**, 926 (2018).

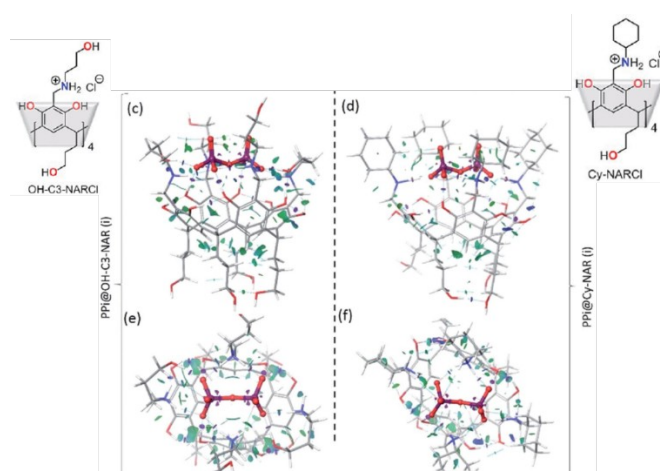
High-affinity and selective detection of pyrophosphate in water by a resorcinarene salt receptor

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Design and study of novel receptors being able to detect different biologically relevant ions (phosphate, PPI, ATP, ADP etc.) under physiological conditions shows promise as a future diagnostic paradigm [1]. Due to the high hydration energies of anions in water, designing receptors with high specific preferences for particular anion species requires a careful conceptual design. Among other factors that define this strong affinity, the rational design of multiple attractive interactions arising from H-bonding and/or other non-covalent interactions is particularly important.



This presentation will highlight our work in preparing and evaluating high-affinity receptors specific for PPI in water. The *N*-alkyl ammonium resorcinarene chloride (NARCl; Figure 1a) receptors were evaluated using a range of different experimental analysis tools. These results were predicted and explained using computational analyses. This presentation will focus on a discussion of the combination of conformational searches, non-covalent interaction (NCI) analysis and density functional theory (DFT) calculations (Figure 1b) describe the factors that control the observed high binding affinity and selectivity of NARXs for PPI [2].

- [1] A. E. Hargrove, S. Nieto, T. Zhang, J. L. Sessler and E. V. Anslyn, *Chem. Rev.* **111**, 6603 (2011).
[2] N. K. Beyeh, Isabel Diez, S. M. Taimoory, D. Meister, A. I. Feig, J. F. Trant, R. H. A. Ras, K. Rissanen. *Chem. Sci.* **9**, 1358 (2018).

A single AT-GC exchange can modulate charge-transfer-induced p53-DNA dissociation

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The tumor suppressor protein p53 prevents tumor formation by responding to cellular stress signals via selective transcription of key target genes. Using molecular dynamics simulations and density functional theory, we shed light on p53 differential interaction with p21 and Gadd45 genes and, in particular, on the observed preferential dissociation from the Gadd45 promoter sequence under oxidative stress [1]. We show that a change from the AT (p21) to the GC (Gadd45) nucleobase pair in the DNA region proximal to the redox-active cysteine of p53 attenuates through-DNA hole transfer in favor of hole transfer to cysteine, thus promoting disulfide formation and consequent DNA dissociation from the protein.

[1] Augustyn, K. E., Merino, E. J. and Barton, J. K. A Role for DNA-mediated Charge Transport in Regulating p53: Oxidation of the DNA-bound Protein from a Distance. *Proc. Natl. Acad. Sci. USA* **104**, 18907 (2007).

Equations of motion for generalized coarse-grained particles obtained from Mori–Zwanzig projection

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The common strategy for producing a coarse-grained (CG) description of an atomistic system is to designate groups of atoms as CG particles, and then determine which variables will be used to describe the latter. Typically, the center of mass of the atom groups is used to describe the position and momentum of the CG particle. Once a CG mapping is prescribed, a number of methods are available to obtain a potential describing the interactions in the CG variable space. In many cases, such CG potentials are used in molecular dynamics simulations employing the same methodology used for atomistic systems, namely applying Newton's Laws with the appropriate boundary conditions. This is fundamentally an approximation, because it ignores the dissipative and random forces that arise in the equations of motion due to the coarse-graining procedure. Further, in virtually all cases reported in the literature, the CG mapping is fixed, so that a given atomistic particle is always assigned in the same way to the same CG particle(s) (in fact, the usual situation is that an atomistic particle is assigned to precisely one CG particle only).

In the present work, a generalized CG mapping procedure is presented that allows for atomistic particles to be assigned to more than a single CG particle at the same time, and allows for this mapping to change in time. Mori-Zwanzig projection operator techniques are then used to derive the equations of motion corresponding to this generalized mapping. It produces a generalized Langevin equation with the appropriate dissipative and random forces, along with a prescription for obtaining the correct CG potential. In addition to familiar terms, the generalized equation also has forces arising from the mapping itself. That is, the change of the mapping with time produces forces that in turn affect the particle motions. Examples of different applications of the generalized mapping are given. In particular, it should be very useful for describing solvents, since many independent solvent molecules can be grouped together to form larger, fluid-like CG particles, with individual molecules being allowed to flow into and out of particular CG particles as time progresses.

The generalized equation forms a fundamental basis upon which a wide variety of CG mapping schemes can be systematically described, all the while producing a correct formulation for evaluating the corresponding CG potentials, and the dissipative and random forces necessary for obtaining the correct dynamical description of the CG system.

Correlation factor models for strong correlation

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Despite the great success of the Kohn-Sham method in calculations of molecular properties, the accurate treatment of strong or static correlation is still challenging. An important step towards the solution of this problem is provided by the B13 [1,2] density functional of Becke. Recently, Přecechtělová *et al.* [3,4] constructed accurate, non-empirical correlation factor models based on exact exchange. In this approach, a correlation factor $f_c(\mathbf{r},\mathbf{u})$ turns a model exchange hole $\rho_x(\mathbf{r},\mathbf{u})$ into an exchange-correlation hole according to

$$\rho_{xc}(\mathbf{r},\mathbf{u}) = f_c(\mathbf{r},\mathbf{u}) \rho_x(\mathbf{r},\mathbf{u}).$$

Here, we advance this approach further by introducing corrections to the correlation factor models to account for strong correlation.

[1] A. D. Becke, *J. Chem. Phys.* **138**, 074109 (2013).

[2] A. D. Becke, *J. Chem. Phys.* **138**, 161101 (2013).

[3] J. Přecechtělová, H. Bahmann, M. Kaupp, and M. Ernzerhof, *J. Chem. Phys.* **141**, 111102 (2014).

[4] J. Pavlíková Přecechtělová, H. Bahmann, M. Kaupp, and M. Ernzerhof, *J. Chem. Phys.* **143**, 144102 (2015).

The longest C–C single bond and a potential new way to conduct electrons

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A drum-like molecular structure [1] is designed to hold two C atoms in sp^2 hybridization and force them to form an unconventional σ bond with each other using their unhybridized p_z orbitals (Fig. 1). If we carefully design the side of the drum-like structure, we can elongate the C–C single σ bond to an extreme length of *ca.* 2.8 Å, achieving the longest C–C single bond in record [2].

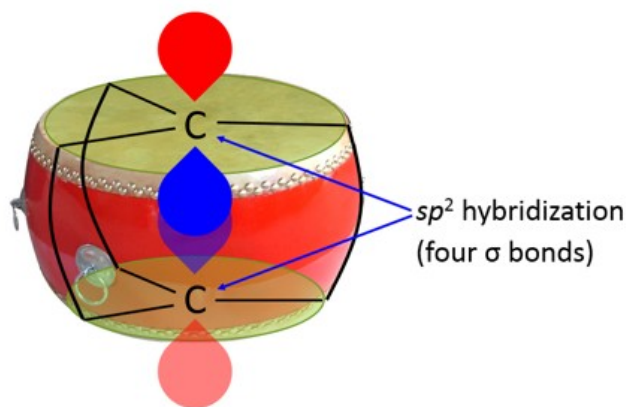


Figure 1. The drum-like structure that contains an extremely long C–C single bond.

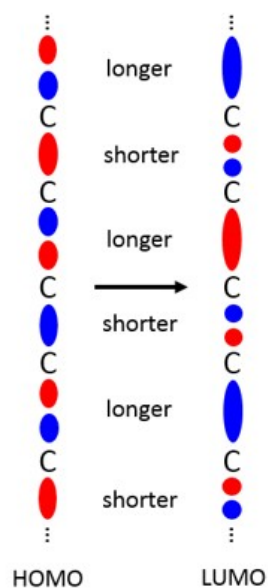


Figure 2. The conducting mechanism of the infinite drum-like structure.

We can further build an infinitely long polymer using the drum-like molecule as the monomer. Because each C atom in the long C–C bond of the infinite structure can readily vibrate above and below the drum surface, the polymer should exhibit a novel electronic conductivity through the saturated long C–C covalent bond network (Fig. 2). Preliminary band structure calculations have predicted the band gap of the conducting polymer to be around 2 eV, already achieving similar conductance to those conventional organic conducting polymers based on unsaturated conjugation framework [3].

[1] D. Feller and E. R. Davidson, *J. Am. Chem. Soc.* **109**, 14 (1987).

[2] T. Suzuki, Y. Uchimura, Y. Ishigaki, T. Takeda, R. Katoono, H. Kawai, K. Fujiwara, A. Nagaki, and J. Yoshida, *Chem. Lett.* **41**, 5 (2012).

[3] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, *Rev. Mod. Phys.* **60**, 3 (1988).

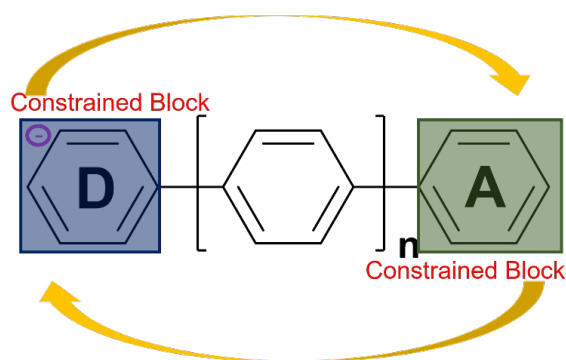
Approximate DFT-based methods for generating diabatic states and calculating electronic couplings: Models of two and more states

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Four types of density functional theory (DFT)-based approaches are assessed in this work for the approximate construction of diabatic states and the evaluation of electronic couplings between these states. These approaches include the constrained DFT (CDFT) method, the constrained noninteracting electron (CNE) model to post-process Kohn–Sham operators, the approximate block-diagonalization (BD) of the Kohn–Sham operators, and the generalized Mulliken–Hush method. It is shown that the first three approaches provide a good description for long-distance intermolecular electron transfer (ET) reactions. On the other hand, inconsistent results were found when applying these approaches to intramolecular ET in strongly coupled, mixed-valence systems. Model analysis shows that this discrepancy is caused by the inappropriate use of the two-state model rather than the defects of the approaches themselves. The situation is much improved when more states are included in the model electronic Hamiltonian. The CNE and BD approaches can thus serve as efficient and robust alternatives for building ET models based on DFT calculations.



[1] Chou-Hsun Yang, ChiYung Yam and Haobin Wang, *Phys. Chem. Chem. Phys.* **20**, 2571 (2018).

Quantum particle moving in a circular ring with potentials

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A free quantum particle moving in a circular ring has well defined energies and angular momenta with integer quantum numbers [1]. However, after a potential is introduced into the circular orbit, the behavior of the quantum particle will have some drastic changes. For example, its angular momentum might allow non-integer (including half-integers) quantum numbers. In this poster, I will fully explain the intricate patterns of motion for a quantum particle moving in a circular ring with potentials.

[1] D. J. Griffiths, *Introduction to Quantum Mechanics* (Cambridge University Press, 2016).

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