## 52nd Midwest Theoretical Chemistry Conference

The Ohio State University Columbus, Ohio June 2–4, 2022 (mwtcc.osu.edu)

<image>

## Organizers

John Herbert Sherwin Singer Alexander Sokolov Steffen Lindert

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# **REU Opportunity in 2023**

Experimental & Computational Spectroscopy: Fundamental Probes of Molecules, Molecular Interactions, and Materials

(Ohio State University, June 2023)





**PI:** John Herbert (Quantum Chemistry)



**Co-PI:** Bern Kohler (Ultrafast Photochemistry)



ionization energy

Heather Allen (Interface Science)



Abraham Badu-Tawiah (Mass Spectrometry)



Robert Baker (Ultrafast X-Ray)



Anne Co (Electrocatalysis)



Philip Grandinetti Solid-State NMR



Steffen Lindert (Computational Biochemistry)



Zachary Schultz (Surface-Enhanced Raman)



Alexander Sokolov (Quantum Chemistry)



Claudia Turro (Inorganic Photochemistry)

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Chemical and Biomolecular Engineering & Chemistry Building (CBEC)

# **Campus Map**



The following numbered items are labeled on the map above.

### • <u>Conference Locations</u>:

- 1. Jones Tower (on-campus housing), 123 W. Lane Ave.
- 2. Blackwell Inn (conference banquet), 2110 Tuttle Park Place
- 3. Physics Research Building (Thursday poster sessions), 191 W. Woodruff Ave.
- 4. CBEC lobby (Friday lunch), 151 W. Woodruff Ave.
- 5. Evans/Newman-Wolfrom Lab (Friday & Saturday talks), 100 W. 18th Ave.
- Parking: We suggest either of the following two surface lots:
  - 6. Closest to housing: St. John's Arena, 108 W. Lane Ave.
  - 7. Backup/overflow option: Lot B, Tuttle Park Pl.

Note that the Lane Ave. Garage (across from the Blackwell Inn) will be closed June 3–4. Additional parking instructions can be found on the next page.

# **Parking Information**

- The nearest garage (Lane Ave. Garage, across from the Blackwell Inn) will close at 19:00 on June 1 and will remain closed June 3–4.
- On weekdays, Arps Garage (18th & College, near Evans Lab) is open to visitors only after 16:00.
- We recommend the St. John's Arena lot (location #6 on the campus map).
- The front entrance of Jones Tower is accessible by vehicle but free temporary parking while you check in and unload, as you would expect at a hotel, is not available. You could be ticketed unless you register your license plate to allow surface parking using the ParkMobile app (see below). If you are not driving alone, you can drop off your passenger(s) and luggage and park in a surface lot.
- There are two ways to pay for parking:
  - ParkMobile App: This is a downloadable app that lets you pay for parking directly from your phone. Create a ParkMobile account at parkmobile.io, via the ParkMobile iOS or Android app, or via their automated phone system at 877-727-5009. After setting up an account, follow ParkMobile's prompts to pay for parking. One benefit of ParkMobile is that parking sessions can be extended via the app or online.
  - Pay-By-Plate: Pay-by-Plate machines are located throughout campus. Upon parking, walk to the nearest Pay-by-Plate machine (clearly marked by directional signs). Enter your license plate number and select the form of payment and amount of parking time desired, as indicated by printed instructions on the Pay-by-Plate machine. Since verification of payment is done via license plate, it is important to enter your license plate information correctly. Please note: Machines only accept credit card payments and do not provide refunds.
- A full list of alternative parking options can be found on the CampusParc website, but we are unaware of better options than the one we have suggested.

## **Schedule of Events & Presentations**

Thursday, June 2 (Atrium, Physics Research Building)

- 16:30–17:00: Check-in and poster setup
- 17:00–19:00: Poster Session 1 (odd numbered posters)
- $\sim 18:45$ : Pizza
- 19:00–21:00: Poster Session 2 (even numbered posters)

Friday, June 3 (Room 1008, Evans Lab, 100 W. 18th Ave.)

- 07:30-08:00: Coffee and breakfast boxes
- 08:00–08:10: Welcome remarks
- Session 1: Biomolecules (Presider: Yang Yang)
  - 08:10–08:30: Peter Kekenes-Huskey (Loyola University)
  - 08:30-08:45: Jaehoon Yang (Ohio State)
  - 08:45-09:40: Benoît Roux (University of Chicago)
  - 09:40-09:55: Diego Becerra (Ohio State)
  - 09:55–10:10: Nils Strand (Northwestern)
  - 10:10-10:30: Yirong Mo (UNC Greensboro)
  - 10:30–10:45: Gregory Rassolov (University of Chicago)
- 10:45–11:00: Coffee break
- Session 2: Complex Systems (Presider: Jason Goodpaster)
  - 11:00-11:15: Ryan Szukalo (Penn State)
  - 11:15-11:35: Shane Parker (Case Western)
  - 11:35-11:50: Debadrita Saha (Indiana)
  - 11:50-12:25: Noa Marom (Carnegie Mellon)
- 12:25–13:30: Lunch (boxed lunches delivered to CBEC Lobby)
- Session 3: Quantum Chemistry (Presider: Hans Lischka)
  - 13:30–13:45: Rajat Majumder (Ohio State)
  - 13:45-14:05: Yang Yang (Wisconsin-Madison)
  - 14:05-14:20: Guarav Harsha (Michigan)
  - 14:20–14:35: Arnab Chakraborty (Michigan State)
  - 14:35–15:10: Ka Un Lao (Virginia Commonwealth)
  - 15:10-15:25: Sarah Maier (Indiana)
  - 15:25–15:40: Alexander Rusakov (Oakland U.)
- 15:40–16:00: Coffee break
- Session 4: Statistical Mechanics (Presider: Peter Kekenes-Huskey)
  - 16:00–16:20: Jonathan Brown (Ohio State)

- 16:20–16:35: Anderson Duraes (Notre Dame)
- 16:35-16:50: Zhongyi Wan (Wisconsin-Madison)
- 16:50-17:25: Todd Gingrich (Northwestern)
- 18:00-18:30: Social (drinks): Blackwell Inn, Plaza Level foyer\*
- 18:30–20:00: Banquet (Blackwell Inn ballroom)

#### Saturday, June 4 (Room 1008, Evans Lab, 100 W. 18th Ave.)

- 07:45–08:10: Coffee and breakfast boxes
- Session 5: Quantum Chemistry (Presider: Ari Chakraborty)
  - 08:10-08:25: Ericka Miller (Case Western)
  - 08:25-08:45: Jason Goodpaster (Minnesota)
  - 08:45–09:00: Eric Collins (Indiana)
  - 09:00-09:15: Montgomery Gray (Ohio State)
  - 09:15-09:50: Lasse Jensen (Penn State)
  - 09:50-10:05: Sasha North (Michigan State)
  - 10:05-10:25: Hans Lischka (Texas Tech)
  - 10:25–10:40: Alejandro Blanco-Gonzalez (Bowling Green State)
  - 10:40–10:55: Daniel Sadowsky (University of Pittsburgh–Bradford)
- 10:55-11:15: Coffee break
- Session 6: General Quantum Mechanics (Presider: Shane Parker)
  - 11:15–11:35: Ari Chakraborty (Syracuse)
  - 11:35-11:50: Yanze Wu (Penn)
  - 11:50-12:05: Maximilian Saller (Michigan)
- 12:05–12:30: Awards and closing remarks

<sup>\*</sup>Participants will each receive one ticket redeemable for a wine, beer, or soft drink

## **Poster Presenters & Number Assignments**

List is alphabetical by family name, except for some late additions. Presenters assigned odd numbers should stand by their posters during Session 1 and those with even numbers during Session 2.

- 1. Vibin Abraham (Michigan)
- 2. Lucas Aebersold (Central Michigan)
- 3.
- 4. Abdelrahman Ahmed (Ohio State)
- 5. Majed Aljohani (University of Toledo)
- 6. Vishikh Athavale (Penn)
- 7. Semiha Bali (Michigan State)
- 8. Francisco Ballesteros (Virginia Commonwealth)
- 9. John Barber (West Virginia)
- 10. Suhita Basumallick (Michigan State)
- 11. Lokesh Baweja (Illinois Institute of Technology)
- 12. Pawan Bhatta (University of Toledo)
- 13. Kyle Billings (West Virginia)
- 14. Dulat Bostan (Marquette)
- 15. Paige Bowling (Ohio State)
- 16. Caitlin Bresnahan (Environmental Lab, U.S. Army ERDC)
- 17. Dustin Broderick (Ohio State)
- 18. Mark Bronson, Jr. (Penn State)
- 19. Arnab Chakraborty (Michigan State)
- 20. Sruthy Chandy (Indiana)
- 21. Minwei Che (Indiana)
- 22. Junhan Chen (Penn)
- 23. Soumik Das (Michigan)
- 24. Carlos de Moura (Ohio State)
- 25. Diksha Dhawan (Michigan)
- 26. Brendan Dutmer (Highland Community College)
- 27. Anurag Dwivedi (Indiana)
- 28. Mengdi Fan (Ohio State)
- 29. Nicolas Frazee (West Virginia)
- 30. Shahed Haghiri (Purdue)
- 31.
- 32. Alex Hanes (Ohio State)

- 33. Eric Hantz (Ohio State)
- 34. Benjamin Harless (Notre Dame)
- 35. Dalia Hassan (Michigan)
- 36. Gaohe Hu (Penn State)
- 37. Nathan Jansen (Michigan State)
- 38. Glen Jenness (Environmental Lab, U.S. Army ERDC)
- 39. Carolin Joy (Marquette)
- 40. Sumit Kale (Purdue)
- 41. William Kattner (Case Western)
- 42. Katherine Kidder (Penn State)
- 43. Anup Kumar (Indiana)
- 44. Jack Lawrence (Purdue)
- 45. Narasimhan Loganathan (Michigan State)
- 46. Miguel Angel Lopez-Ruiz (Indiana)
- 47. James MacLean (Oakland University)
- 48. Aniket Mandal (Ohio State)
- 49. Zaheer Masood (Southern Illinois)
- 50. Ilia Mazin (Ohio State)
- 51. Timothé Melin (Michigan State)
- 52. Hayden Moran (West Virginia)
- 53. Duyen Nguyen (Central Michigan)
- 54. Felipe Pacci Evaristo (Ohio State)
- 55. Taylor Parsons (Kansas)
- 56. Alexander Pixler (Northern Illinois)
- 57. Timothy Ricard (Indiana)
- 58. Christina Schumm (Michigan State)
- 59. Timothy Schutt (Environmental Lab, U.S. Army ERDC)
- 60. Hannah Scott (West Virginia)
- 61. Yi Shi (Purdue)
- 62. Yuming Shi (Purdue)
- 63. Vinit Singh (Purdue)
- 64. Terrence Stahl (Ohio State)
- 65. Zachary Stewart (Michigan State)
- 66. Asia Sykes (Indiana University East)
- 67. Thomas Testoff (Southern Illinois)

- 68. Vikrant Tripathy (Indiana)
- 69. Corentin Villot (Virginia Commonwealth)
- 70. Yuchen Wang (Purdue)
- 71. Jared Weidman (Michigan State)
- 72. Hepeng Ye (Penn State)
- 73. Adil Yermek (Marquette)
- 74. Yuanhao Zhang (Ohio State)
- 75. Zehao Zhou (Case Western)
- 76. Xiao Zhu (Indiana)

77.

78. Safa Ahad (Purdue)

# **Abstracts for Oral Presentations**

These are listed on the following pages in the order that they appear in the schedule.

Mechanisms of calmodulin-dependent activation of myofilament targets Xuan Fang and Peter <u>Kekenes-Huskey</u>

The protein calmodulin (CaM) is essential to cell development and adaptation. Although CaM is known for regulating protein targets in a calcium-dependent manner, its function is modulated by post-translational modifications (PTMs). As such, CaM integrates myriad signaling pathways utilized cells. To better understand the molecular bases of CaM's target regulation, we simulated its complexes with calcineurin, a phosphatase, and myosin light chain kinase. These simulation data suggest that CaM utilizes its solvent-exposed surface to activate targets, as part of a multi-dentate interaction with calmodulin-binding motifs. PTMs may in turn modify how CaM's solvent-exposed surface interfaces its targets. These findings provide insights into molecular mechanisms of cell regulation driven by CaM/target interactions.

#### New algorithm to compute free energy differences

Jaehoon Yang, Sherwin J. Singer Department of Chemistry and Biochemistry The Ohio State University

Extraction of the free energy difference (FED) between thermodynamic states from statistical simulations provides a crucial point of contact with experiment. However, free energy calculations, challenged by the need to sample otherwise rarely accessed configurations, require a far greater computational burden compared to simulation under a single set of thermodynamic variables and have spurred significant effort aimed at making FED calculation more efficient.

Ultimately free energy estimation requires the estimation of differences among  $a_i = -\ln[\int dR \exp[-U_i(R)]$ 

where R represents the system variables and the multiple potentials  $U_j(R)$  may be the system at different temperatures  $U_j(R) = \beta_j V(R)$ , different umbrella potentials, or different particle composition as in "alchemical" transformations. Methods in current use, such Bennett acceptance ratio (BAR), multi-state Bennet acceptance ratio (MBAR), or weighted histogram analysis method (WHAM), require solution of non-linear equation that are notoriously slow to converge.

We introduce a method to treat the multiple potential problem which eliminates non-linear equations. Instead, free energies follow from solution of linear equations. For the two-potential problem, our method can be shown analytically to match the performance of BAR. We present numerical evidence that our method matches previously known methods for model problems, and for a more realistic calculations such as the free energy of analine dipeptide conformers where our method can replace MBAR or WHAM with comparable accuracy and far greater efficiency.

Using Computer Simulations to Advance our Understanding of Biological Systems at the Atomic Level

#### **Benoit Roux**

# Department of Biochemistry and Molecular Biology, Department of Chemistry, The University of Chicago, 929 East 57<sup>th</sup> St, Chicago, Illinois 60637, USA

Classical molecular dynamics (MD) simulations based on atomic models play an increasingly important role in a wide range of applications in physics, biology and chemistry. The approach consists of constructing detailed atomic models of the macromolecular system, and, having described the microscopic forces with a potential function, using Newton's classical equation, F=MA, to literally "simulate" the dynamical motions of all the atoms as a function of time. The calculated trajectory, though an approximation to the real world, provides detailed information about the time course of the atomic motions, which is impossible to access experimentally. While great progress has been made, producing genuine knowledge about biological systems using MD simulations remains enormously challenging. Among the most difficult problems is the characterization of large conformational transitions occurring over long-time scales. Issues of force field accuracy, the neglect of induced polarization, in particular, are also a constant concern. A powerful paradigm for mapping the conformational landscape of biomolecular systems is to combine free energy methods, transition pathway techniques and stochastic Markov State Model based massively distributed simulations. These concepts will be illustrated with a few recent computational studies of Src tyrosine kinases,<sup>1-5</sup> K<sup>+</sup> channels,<sup>6-10</sup> and the P-type ion pumps.<sup>11-14</sup>

#### References

- 1 Shukla, D., Meng, Y., Roux, B. & Pande, V. S. Activation pathway of Src kinase reveals intermediate states as targets for drug design. *Nat Commun* **5**, 3397, (2014).
- 2 Meng, Y., Pond, M. P. & Roux, B. Tyrosine Kinase Activation and Conformational Flexibility: Lessons from Src-Family Tyrosine Kinases. *Acc. Chem. Res.* **50**, 1193-1201, (2017).
- 3 Meng, Y. *et al.* Predicting the Conformational Variability of Abl Tyrosine Kinase using Molecular Dynamics Simulations and Markov State Models. *J. Chem. Theo. Comp.* **14**, 2721-2732, (2018).
- 4 Paul, F., Meng, Y. & Roux, B. Identification of Druggable Kinase Target Conformations Using Markov Model Metastable States Analysis of apo-Abl. *J. Chem. Theo. Comp.* **16**, 1896-1912, (2020).
- 5 Paul, F., Thomas, T. & Roux, B. Diversity of Long-Lived Intermediates along the Binding Pathway of Imatinib to Abl Kinase Revealed by MD Simulations. *J Chem Theo Comp.* **16**, 7852-7865, (2020).
- 6 Ostmeyer, J., Chakrapani, S., Pan, A. C., Perozo, E. & Roux, B. Recovery from Slow Inactivation in K+ Channels Controlled by Water Molecules. *Nature* **501**, 121-124, (2013).
- 7 Li, J., Ostmeyer, J., Cuello, L. G., Perozo, E. & Roux, B. Rapid constriction of the selectivity filter underlies C-type inactivation in the KcsA potassium channel. *J. Gen. Physiol.* **150**, 1408-1420, (2018).
- Li, J., Shen, R., Reddy, B., Perozo, E. & Roux, B. Mechanism of C-type inactivation in the hERG potassium channel. *Sci Adv* **7**, eabd6203, (2021).
- 9 Li, J. *et al.* Computational study of non-conductive selectivity filter conformations and C-type inactivation in a voltage-dependent potassium channel. *The Journal of general physiology* **153**, (2021).
- 10 Rohaim, A. *et al.* A distinct mechanism of C-type inactivation in the Kv-like KcsA mutant E71V. *Nat Commun* **13**, 1574, (2022).
- 11 Castillo, J. P. *et al.* Mechanism of potassium ion uptake by the Na(+)/K(+)-ATPase. *Nat. Comm.* **6**, 7622, (2015).
- 12 Das, A., Rui, H., Nakamoto, R. & Roux, B. Conformational Transitions and Alternating-Access Mechanism in the Sarcoplasmic Reticulum Calcium Pump. *J. Mol. Biol.* **429**, 647-666, (2017).
- 13 Rui, H., Das, A., Nakamoto, R. & Roux, B. Proton Countertransport and Coupled Gating in the Sarcoplasmic Reticulum Calcium Pump. *J. Mol. Biol.* **430**, 5050-5065, (2018).
- 14 Thirman, J., Rui, H. & Roux, B. Elusive Intermediate State Key in the Conversion of ATP Hydrolysis into Useful Work Driving the Ca(2+) Pump SERCA. *J. Phys. Chem. B* **125**, 2921-2928, (2021).

#### A Coarse-Grained Model for Side-Chain Liquid Crystalline Linear Polymers

#### Diego Becerra and Lisa M. Hall

William G. Lowrie Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, Ohio 43210, USA.

Liquid crystals (LCs) are self-organizing molecules that can be attached to linear polymer chains either within the backbone or in an end-on or side-on configuration along the backbone. Polymers with two types of LC moieties can be designed to exhibit complex deformation behavior in response to heat. When this type of polymers with properly attached mesogenic groups are slightly crosslinked, the resulting liquid crystal elastomers are excellent candidates to be implemented in applications such as soft robotics.

In particular, we have developed a coarse-grained model for side-chain liquid crystalline polymers (SCLCPs) inspired by an elastic rod model for semi-flexible polymers that accounts for bending, orientational and twisting interactions. The model comprises a polymer backbone and pendant side chains with a terminal mesogenic group. Each site exhibits 12 degrees of freedom; six describe position and orientation, and six describe momentum. The modeled bonded interactions prevent spherical and aspherical sites from having non-physical rotations.

The SCLCP model is implemented in the multi-purpose LAMMPS simulation package. Regarding performance, it maintains the computational efficiency to permit long-scale molecular dynamics simulations that are typically required to understand the complex phase behavior of these materials.

#### Using tensor network states for time-periodic nonequilibrium systems

Nils E. Strand, Hadrien Vroylandt, Todd R. Gingrich

# Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA

Single-particle Brownian ratchets subject to a time-periodic drive have been thoroughly studied but ratcheting phenomena in interacting many-body systems offer new challenges. Even with interactions as simple as volume exclusion, the mean steady-state current tends to respond dramatically to changes in carrier density. We present a novel approach for computing these currents for a time-periodic 1D ratchet discretized on a periodic-boundary-condition lattice. The approach leverages the time-dependent variational principle (TDVP) method of evolving binary tree tensor network states to compute the response of steady-state currents to particle density, the frequency of the ratchet drive, and the diffusion constant governing thermal motion. The TDVP approximation is controllable and provided the tensor network's maximal bond dimension is sufficiently large, we demonstrate agreement with brute force Gillespie sampling. The method shows promise for studying classical many-body stochastic systems subject to time-dependent external forces, particularly when rare fluctuations play a crucial role.

#### Activations of Small Molecules by Main-Group Compounds: Insights from Computations

#### Yirong Mo

(Department of Nanoscience, University of North Carolina at Greensboro, Greensboro, North Carolina; Department of Chemistry, Western Michigan University, Kalamazoo, Michigan)

#### Abstract

The adsorption and activation of small molecules like CO and N<sub>2</sub> generally require transition metals. Currently, there is a trend to explore multi-bonded and unsaturated main group compounds that can interact with small molecules, in order to find non-metal catalysts. Significantly, Braunschweig et al. not only showed that diboryne (B=B) stabilized by N-heterocyclic carbenes (B<sub>2</sub>(NHC<sup>R</sup>)<sub>2</sub>) can bind and activate CO molecules to forge C-C bonds, but also found that borylene (CAAC)DurB, where CAAC is a cyclic alkyl(amino) carbene and Dur refers to 2,3,5,6-tetramethylphenyl, can bind and activate N<sub>2</sub>. Thus, we explored the activation mechanisms in both cases using our developed block-localized wavefunction (BLW) method. The BLW method is the simplest variant of ab initio valence bond (VB) theory, and able to derive strictly electron-localized states self-consistently and thus probe the inter- or intramolecular electron transfer.

For  $B_2(NHC^R)_2$ , although the ground state of  $B_2({}^{3}\Sigma_{g}{}^{-})$  is of a single bond, the strong electrostatic attraction from NHC<sup>R</sup> excites  $B_2$  to its third excited state  $({}^{1}\Sigma_{g}{}^{+})$  of a triple bond. But among the two BB  $\pi$  bonds, only one of the two  $\pi$  bonds (HOMOs) fits to one of the degenerate LUMOs of CO. Analyses showed that the strong steric repulsion between the HOMO of CO and the other HOMO of  $B_2(NHC^R)_2$  leads to the HOMO-LUMO swap in the latter. Subsequently, both HOMO and HOMO-1 of  $B_2(NHC^R)_2$  can effectively interact with the two  $\pi^*$  anti-bonding orbitals of CO, resulting in substantial electron back-donation and the ultimate activation of CO.

In the activation of N<sub>2</sub> by two (CAAC)HB molecules, our study revealed a bonding scheme for the end-on bridging borylene-N<sub>2</sub> complex where the  $\sigma$  donation mainly comes from the  $\pi$  orbitals of N<sub>2</sub> and thus there are two opposite and perpendicular push-pull channels. It is the push-pull interaction that governs the enhanced activation of N<sub>2</sub>. Further studies show that replacing the substituents bonded to the boron atom can modulate the strength of the push-pull interaction and lead to different geometries of end-on bridging borylene-N<sub>2</sub> complexes.

#### **References:**

- 1. Mo, Y.; Song, L.; Lin, Y. J. Phys. Chem. A 111, 8291-8301 (2007).
- 2. Zhang, H., Cao, Z., Wu, W., Mo, Y., Angew. Chem. Int. Ed., 57(40), 13076-13081 (2018).
- 3. Zhang, H., Yuan, R., Wu, W., Mo, Y., Chem. Eur. J., 26(12), 2619-2625 (2020).
- 4. Tang, C.-K.; Li, Y.-Z.; Ma, F.; Cao, Z.; Mo, Y., J. Phys. Chem. Lett. 12(31), 7545-7552 (2021).

#### Static structure of active fluids reflects energy dissipation

<u>Gregory Rassolov</u>, University of Chicago Laura Tociu, University of Chicago Étienne Fodor, University of Luxembourg Suriyanarayanan Vaikuntanathan, University of Chicago

The University of Chicago Department of Chemistry 5735 S. Ellis Ave Chicago, IL 60637

Active matter systems are driven out of equilibrium by local non-conservative forces, giving rise to unique behaviors and novel structures as these systems dissipate the energy injected by driving. However, the relationship between structure, dissipation, and driving forces is only partially understood even for simple active matter systems, presenting obstacles for controllably achieving novel or desirable behaviors. In this talk, I will outline our efforts to overcome this by using tools from liquid-state theories and machine learning. Our main result is a non-equilibrium mean field framework which elucidates a connection between dissipation and the static structure with no temporal or polarization information included. We show how this dissipation-structure connection may be generally applicable to many systems, including isotropic active Ornstein-Uhlenbeck particles and more complex anisotropic active rotors, across several regimes of behavior. Finally, we demonstrate that a neural network can both learn this connection and generalize it to contexts where our theoretical framework breaks down, even with no access to information about the underlying dynamics. Our results outline a new perspective on the underlying relationship between system organization and dissipation in far-from-equilibrium systems and point towards the use of similar techniques for more complex and physically relevant systems, such as active nematics.

#### Energetic and entropic contributions to effective coarse-grained potentials Ryan J. Szukalo<sup>1</sup>, Will G. Noid<sup>1</sup>

<sup>1</sup> Penn State University, Chemistry Department. 77 Pollock Rd, State College, PA 16801

Coarse-grained (CG) models provide the necessary increased efficiency for molecular dynamics simulations to investigate length- and time-scales that are unattainable with traditional all-atom models. The effective potentials which govern the CG interactions are configuration-dependent free energies that contain significant entropic contributions. Consequently, these effective potentials can vary strongly with thermodynamic state point, which severely limits the transferability and thermodynamic representability of the model. Thus, model reparameterization is often necessary to accurately study multiple state points. Here, we employ a recently developed "dual potential" approach that provides a rigorous framework to decompose effective potentials into energetic and entropic components. Specifically, we consider CG models for orthoterphenyl (OTP), a small glass former. First, we employ a structure-based variational principle to determine an effective interaction potential that accurately models the underlying structure. Subsequently, we employ an energy-matching variational principle to determine an energetic operator which accurately models energetics. We demonstrate that this dual approach accurately describes the structure and thermodynamics of the underlying atomic model and accurately predicts the temperature-dependence of the CG potentials. With this predictive reference model, CG simulations can then be performed at state points for which a specific model has not been parameterized, realizing an even greater increase in computational efficiency.

### Accelerating TDDFT with semiempirical preconditioning

Zehao Zhou and Shane M. Parker

Department of Chemistry, Case Western Reserve University, 10900 Euclid Ave., Cleveland, Ohio 44106, USA

Time-dependent density functional theory (TDDFT) has become the workhorse for first-principles simulations of excited-state molecular properties such as one- and multi-photon absorption spectra, dynamic (hyper)polarizabilities, and excited-state absorption spectra. Implementations based on linear and nonlinear response theory enable calculations of spectra using hybrid density functionals for molecules with up to about 500 atoms. However, the relatively high computational expense of first-principles methods has led to the development of semiempirical models that attempt to approximate the TDDFT results at significantly reduced computational expense, such as the simplified TDDFT (sTDDFT) model by Grimme and co-workers[J. Chem. Phys. 2013, 138, 244104]. Here, we show how semiempirical models can instead be used to accelerate first-principles calculations, rather than replace them. In particular, we use the sTDDFT model as a preconditioner during the iterative calculation of excited states in TDDFT. The sTDDFT preconditioner speeds up TDDFT calculations by a factor of 1.4 on average and up to a factor of 3 without any loss of accuracy. Our approach is part of a general strategy for accelerating guantum chemistry calculations by attempting to combine the accuracy of first-principles methods with the low cost of semiempirical models.

# Quantum simulation and Quantum computation of chemical dynamics on ion-trap quantum computers

### <u>Debadrita Saha<sup>†</sup></u>, Philip Richerme<sup>†</sup>, Jeremy M. Smith<sup>†</sup>, Amr Sabry<sup>†</sup>, Srinivasan S. Iyengar<sup>†</sup>

The accurate computational study of chemical, materials, biological, and atmospheric problems has critical impact on a wide range of health and environmental problems. But such studies are deeply limited by the steep algebraic scaling of electron correlation methods, and the exponential scaling in studying quantum nuclear dynamics, especially since many of these problems involve the coupled behavior of hydrogen nuclei in conjunction with correlated electronic structure. Recently, with the experimental and algorithmic developments in quantum computing, considerable progress has been made on the study of electronic structure on quantum hardware. However, the development of quantum algorithms for describing nuclear dynamics and the simulation of vibrational spectra of fluxional molecular systems has received less attention. In Refs. [1,2], we provide a framework, along with the experimental verification, that allows for the solution of quantum nuclear dynamics on ion-trap quantum devices.

The quantum nuclear dynamics Hamiltonian on a single Born-Oppenheimer potential surface is mapped in Ref. [1] to the Hamiltonian that describes the evolution of coupled spin states that are localized on a lattice, as is



in case of an ion-trap quantum computer. As shown in the figure, we find that the Born-Oppenheimer potential surface may be used to compute the spin-state coupling elements such that the spin lattice dynamics exactly reproduces the dynamics of a shared proton on a shortstrong hydrogen bonded system. Thus, in a sense we have derived a general purpose "quantum compiler" to perform analogue computations on all quantum hardware where such lattice Hamiltonians (and more precisely an Ising Hamiltonian) can be implemented. Approximations involved in this map will also be described as part of this talk.

Additionally, we have used Sandia National Lab's Quantum Scientific Computing Open User Testbed (QSCOUT) ion-trap quantum computing device to emulate the quantum trajectory of the shared proton's wavepacket in a short-strong hydrogen bonded system [2]. This allows us to then extract the vibrational frequencies and eigenspectrum for the shared proton motion from the spin lattice dynamics. Indeed, we find that the error in such a simulation is of the order of ~3.3 cm<sup>-1</sup> in the vibrational frequencies when we compare the spin-lattice evolution with the corresponding classical calculations of vibrational spectra. Thus, our approach offers a new paradigm for studying the quantum chemical dynamics and vibrational spectra of molecules on quantum hardware.

 <sup>1</sup>Saha, D.; Iyengar, S. S.; Richerme, P.; Smith, J. M.; Sabry, A. <u>Mapping Quantum Chemical Dynamics</u> <u>Problems to Spin-Lattice Simulators.</u> J. Chem. Theory Comput. 2021, 17, 6713–6732.
<sup>2</sup>Richerme, P.; Revelle, M. C.; Saha, D.; Norrell, S. A.; Yale, C. G.; Lobser, D.; Burch, A. D.; Clark, S. M.; Smith, J. M.; Sabry, A; Iyengar, S. S. <u>Quantum Computation of Hydrogen Bond Dynamics and Vibrational</u> <u>Spectra.</u> arXiv:2204.08571.

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#### Many-Body Perturbation Theory Meets Machine Learning to Discover Singlet Fission Materials

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Singlet fission (SF), the conversion of one singlet exciton into two triplet excitons, could significantly enhance solar cell efficiency. Molecular crystals that undergo SF are scarce. Computational exploration may accelerate the discovery of SF materials. We have used many-body perturbation theory (MBPT) within the GW approximation and the Bethe-Salpeter equation (GW+BSE) to identify several potentially promising candidate materials [1-4]. However, GW+BSE calculations of the excitonic properties of molecular crystals are impractical for large-scale materials screening. In recent years, machine learning (ML) algorithms have been used increasingly in conjunction with first-principles simulations to accelerate computational design and discovery of materials. We use the sure-independence-screening-and-sparsifying-operator (SISSO) machine-learning algorithm to generate computationally efficient models that can predict the MBPT thermodynamic driving force for SF for a dataset of 101 polycyclic aromatic hydrocarbons (PAH101) [5]. SISSO generates models by iteratively combining physical primary features. The best models are selected by linear regression with cross validation. The SISSO models successfully predict the SF driving force with errors below 0.2 eV. Based on the cost, accuracy, and classification performance of SISSO models, we propose a hierarchical materials screening workflow. Three potential SF candidates are found in the PAH101 set.

[1] X. Wang, X. Liu, C. J. Cook, B. Schatschneider, and N. Marom "On the Possibility of Singlet Fission in Crystalline Quaterrylene", J. Chem. Phys. 148 184101 (2018)

[2] X. Wang, X. Liu, R. Tom, C. J. Cook, B. Schatschneider, and N. Marom "Phenylated Acene Derivatives as Candidates for Intermolecular Singlet Fission", J. Phys. Chem. C 123, 5890 (2019)

[3] X. Liu, R. Tom, X. Wang, C. J. Cook, B. Schatschneider, and N. Marom "Pyrene-Stabilized Acenes as Intermolecular Singlet Fission Candidates: Importance of Exciton Wave-Function Convergence", J. Phys.: Condens. Matter, 32 184001 (2020)

[4] X. Liu, R. Tom, S. Gao, and N. Marom "Assessing Zethrene Derivatives as Singlet Fission Candidates Based on Multiple Descriptors", J. Phys. Chem. C 124, 26134 (2020)

[5] X. Liu, X. Wang, S. Gao, V. Chang, R. Tom, M. Yu, L. Ghiringhelli, N. Marom, npj Computational Materials, DOI: 10.1038/s41524-022-00758-y (2022)

### Implementation of Spin-Orbit Coupling Effects in Quasi-Degenerate N-electron Valence Perturbation Theory

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Spin-orbit interactions play a major role in understanding the magnetic properties of matter and describing the hyperfine structure of molecules and atoms. Accurate theoretical treatment of these effects has garnered significant interest, especially in modelling single-molecule magnets and molecular spintronic devices. Though significant progress has been made in simulating the spin-orbit interactions of molecular systems, accurate and efficient description of spin-orbit coupling for heavy metal compounds including electron correlation effects is still lacking. In this talk, I will present the implementation of exact spin-orbit (Breit-Pauli formulation) and spin-orbit mean field approximation (SOMF) in partially contracted quasi-degenerate N-electron valence perturbation theory (QD-NEVPT2) and demonstrate the capabilities and shortcomings of the implementation for several systems of interest. I will present a benchmark of spin-orbit coupling splitting in diatomic radicals along with my results for 3d and 4d transition metal ions. Finally, I will present results for lanthanide and actinide systems where spin-orbit coupling effects are crucial to understanding the electronic structure.

Title: Direct Incorporation of Nuclear Quantum Effects in ab initio Molecular Dynamics

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Abstract: Nuclear quantum effects play an important role in a variety of chemical and biological processes, but it remains challenging to accurately include nuclear quantum effects in large-scale molecular simulations. Herein we developed a new approach named constrained nuclear–electronic orbital molecular dynamics (cNEO-MD) for the accurate and efficient incorporation of nuclear quantum effects in molecular simulations. This new MD approach is a combination of our recently developed constrained nuclear–electronic orbital density functional theory (cNEO-DFT) and constrained minimized energy surface molecular dynamics (CMES-MD). We employed cNEO-MD to calculate the vibrational spectra of a series of small molecules and the results are compared to those from conventional *ab initio* molecular dynamics (AIMD) as well as from experiments. With the same formal computational scaling, cNEO-MD greatly outperforms conventional AIMD in describing the vibrational modes with a significant hydrogen motion character. This work opens the possibility of using cNEO-MD in the study of static and dynamic properties of systems with significant nuclear quantum effects.

#### Wave function theories for finite-temperature electronic structure

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Wave function methods have offered a robust, systematically improvable means to study the ground-state properties in quantum many-body systems. Theories like coupled cluster and their derivatives provide highly accurate approximations to the energy landscape at a reasonable computational cost. Analogs of such methods to study thermal properties, though highly desirable, have been lacking because evaluating thermal properties involve a trace over the entire Hilbert space. Approximating every state in the Hilbert space is an impossible task. Besides, excited-state theories are not as well studied as ground-state ones.

In this talk, I will introduce our recently developed framework to overcome these difficulties by employing the theory of thermofield dynamics, a theory that allows us to construct a single wave function that encodes the equilibrium thermal behavior of the system. Ensemble averages become expectation values over this so-called thermal state. Around this thermal state, we have developed a framework to extend ground-state wave function theories to non-zero temperatures.

I will discuss explicit formulations of mean-field, configuration interaction, and coupled cluster theories for thermal properties of fermions in the grand canonical ensemble. To assess the quality of these approximations, we will show benchmark studies for both model and small atomic and molecular, while comparing against exact results.

We will see that the thermal methods perform similarly to their ground-state counterparts, while merely adding a pre-factor to the computational cost. They also inherit all the properties, good or bad, from the ground-state methods, signifying the robustness of our formalism and the scope for future development.

## Benchmarking the Semi-Stochastic CC(*P*;*Q*) Approach for Singlet–Triplet Gaps in Biradicals

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We recently developed a semi-stochastic approach to converging high-level coupled-cluster (CC) energetics, such as those obtained in the CC calculations with singles, doubles, and triples (CCSDT), in which the deterministic CC(P;Q) framework is merged with the stochastic configuration interaction Quantum Monte Carlo (CIQMC) propagations [J. E. Deustua, J. Shen, and P. Piecuch, *Phys. Rev. Lett.* **119**, 223003 (2017); *J. Chem. Phys.* **154**, 124103 (2021)]. In this presentation, we investigate the ability of the semi-stochastic CC(P;Q) methodology, which we extended to open-shell states, to recover the CCSDT energies of the lowest singlet and triplet states and the corresponding singlet–triplet gaps of biradical systems, including methylene, (HFH)<sup>-</sup>, cyclobutadiene, cyclopentadienyl cation, and trimethylenemethane. We demonstrate that the semi-stochastic CC(P;Q) calculations are capable of generating the results of the CCSDT quality and improving the singlet–triplet gaps obtained with the triples corrections to CCSD defining the CR-CC(2,3) approach out of the early stages of the CIQMC propagations.

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## Accelerating Quantum Chemistry Calculations via Fragmentation Approaches

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Accuracy in the initial guess is important in self-consistent field (SCF) calculations, not only to accelerate the calculation, but also to avoid its oscillation or divergence. The many-body expansion (MBE) has recently been used to build high-quality density matrices (DMs) in our group. Such MBE-DM approaches combined with purification and distance-based cutoff schemes provide high-quality DMs as initial guesses to largely reduce the SCF cycles necessary for convergence and perform up to 40% speedup for a wide range of systems as compared with traditional initial guesses including superposition of atomic densities, superposition of atomic potentials, and basis set projection. In addition, MBE-DM can be used to derive energy directly via one Fock build with mean absolute deviation (MAD) per monomer within the so-called "dynamical accuracy" at the three-body expansion. Recently, we move forward one more step to build DMs using the generalized many-body expansion (GMBE) with intersecting fragments. This newly developed GMBE-DM approach shows promising results for the direct energy prediction with MAD per monomer still within the "dynamical accuracy" but using only the one-body expansion and 2 Angstrom minimum-distance cutoff. The number of subsystem calculations in GMBE1-DM is at least one order of magnitude smaller than MBE3-DM. As compared with the corresponding energy-based GMBE1 approach, the performance of GMBE1-DM is at least one order of magnitude better. Thus, preliminary applications of GMBE-DM to molecular and ionic clusters suggest that this is a route to achieve very high accuracy and low cost in fragment-based calculations.

# Models incorporating molecular fragmentation, error cancellation and machine learning for the prediction of redox potentials

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While accurate wavefunction theories like CCSD(T) are capable of modelling redox processes, steep computational scaling renders them intractable for treating large systems or extensive databases. In contrast, density functional theory (DFT) is more computationally feasible, yet often fails to quantitatively describe redox processes. Over the last decade our group has developed the Connectivity-Based Hierarchy (CBH), an error correction approach based on systematic molecular fragmentation protocols that offers significant improvements to DFT performance. Here we report an efficient delta machine learning ( $\Delta$ -ML) model that builds on CBH and achieves coupled cluster accuracy by correcting for deficiencies in DFT. Emphasizing systematic improvements to low levels of theory via corrections to local molecular units, CBH represents a suitable foundation for improved molecular feature attribution in  $\Delta$ -ML.

Our project design integrates concepts from molecular fragmentation, systematic error cancellation, and deep learning. First, we show that by using an electrostatic difference map, ionization sites within a molecule may be identified, and CBH correction schemes for ionization processes may be automated. As a central focus of our work, we employ our "FragGraph" QM/ML model, which embeds atom-centered, fragment-wise fingerprints taken from CBH into a computational graph to further increase accuracy in the prediction of ionization potentials. CBH fingerprints systematically capture portions of the molecular environment, making them a useful tool in molecular property prediction. Highlighting a new feature of our  $\Delta$ -ML framework, we show that the incorporation of electronic descriptors from DFT improves model performance. In summary, we present a progression of methods aimed at systematically improving low-level redox calculations, and we assess their performance on a large test set of ionization potentials.

## The Earth's Rarest Element Astatine and Its Remarkable Medical Isotope At-211: a Quantum-Chemical Tale

## Alexander A. Rusakov

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Astatine-211 is an especially promising alpha-emitter for targeted radiotherapy of cancer. Besides superheavy elements, astatine's chemistry is among the least understood due to extremely low amounts available and relatively short half-life. Reliable quantum-chemical predictions of astatine's properties are essential for the successful design of At-211-based radiopharmaceuticals. Such qualitative predictions require the simultaneous treatment of the effects of relativity, including massive spin-orbit interaction, electronic correlations, and a significant adaptation of the existing quantum-chemical methods. We report the results of modeling a wide range of At-containing molecules ranging from diatomics to drugs and outline the routes for developing the existing computational strategies to address the challenges identified in these studies.

# An open-source code for classical fluids density functional theory for polymers and associating liquids

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Many material properties of polymer and other small molecule systems can be understood at the classical level. To model these systems, we implement coarse-grained models using classical density functional theory (or fluids density functional theory, fDFT) in an open-source, publicly available code. The effects of polymer connectivity are modelled with inhomogeneous statistical associating fluid theory (iSAFT). The general iSAFT formulation assumes infinitely strong bonds, but we have also implemented an extension of that theory to include strong (but breakable) particle-particle associations. Unbonded interactions can be included with simple pairwise potentials, or they can be including using the direct correlation function, if available (e.g., from simulation, theory, or numerical calculation).

This code was originally developed to study ion-containing block copolymers, which have potential application as solid-state, nonflammable battery electrolytes and in other charge transport applications. In these systems, the two polymer types tend to microphase separate, and ions are preferentially solvated by the microphase with the higher dielectric constant. This effect and ion correlations can strongly affect the polymer phase behavior; even a small amount of salt can significantly increase the effective segregation strength between the blocks. Additionally, lithium ions can strongly complex with the ether oxygens (EO) in polymers such as polyethylene oxide. For such systems, ion correlation effects can be included using the direct correlation function of a reference fluid of unbonded monomers and salt, obtained by solving the Ornstein-Zernike equation with the hypernetted-chain closure, and Li-EO complexation can be modeled with breakable strong associations. By turning these individual effects on and off, we show how each contributes to the phase behavior of these polymer systems.

#### Separation of Enantiomers: A Screw Model Mechanism

Authors: <u>Anderson D. S. Duraes</u> and J. Daniel Gezelter

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Enantiomers are two compounds with the same structural formula that are non-superimposed mirror images. Because enantiomers have identical physical and chemical properties in an achiral media such as water, the separation of the two compounds is expensive and not general.

In this work, we present a general model to separate enantiomers without performing any chemical reaction: employing local rotational motion in a fluid. The principle behind the local rotation is that it couples the compounds' translation and rotation motion, sending enantiomers in opposite directions.

We explore the translation-rotation coupling of enantiomers through hydrodynamics, and a molecular equivalent of the pitch of a screw is introduced to describe the degree of translation-rotation coupling. Molecular pitch is a structural feature of the molecules and can be easily computed, allowing rapid estimation of the pitch of 85 drug-like molecules. Carrying out simulations of enantiomeric mixtures in a range of fluids such as  $\Lambda$ - and  $\Delta$ -[Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in water and (R, R)- and (S, S)-atorvastatin (a drug molecule) in methanol support predictions made using the molecular pitch values.

In an Engineering part of this work, we predict the separation of realistic racemic mixtures through a competition model and coupled drift diffusion equations. We find that enantiomeric separation on a centimeter length scale can be achieved in hours, using experimentally-achievable local rotational motion.

Because our work relies on a first-principle approach, *i.e.*, without data fitting, we can apply the same theory to objects that are larger than molecules. In this sense, we mathematically show that certain achiral objects can also exhibit a non-zero molecular pitch.



Figure 1: Like the left- (blue) and right-handed (yellow) screws, the enantiomers move to opposite directions under a local rotational motion.

Reference: Anderson D. S. Duraes and J. Daniel Gezelter, "Separation of Enantiomers through Local Vorticity: A Screw Model Mechanism", J. Phys. Chem. B, 125 (42), pp. 11709–11716 (2021). DOI: 10.1021/acs.jpcb.1c07127

#### Atomistic Insights into Phase Selection during Epitaxial Growth in Polymorphic System: A Case Study of Al<sub>2</sub>O<sub>3</sub>

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Molecular dynamics (MD) simulation has been long applied to study crystallization. Our goal is to use MD simulations to explore the mechanism of crystallization in systems with multiple metastable crystal polymorphs. One such example is aluminum oxide, Al<sub>2</sub>O<sub>3</sub>. The metastable cubic  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which can be used as substrate for growing other cubic materials, has been reported to be the first phase formed during both homogeneous and heterogeneous crystallization. In a previous work, we proposed that the structural similarity of Al atoms arrangement between amorphous Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> lead to its formation. More recently, we have been examining the kinetics and mechanism of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystallization to ultimately bring atomistic insights into phase selection during epitaxial growth. We begin by benchmarking our Al<sub>2</sub>O<sub>3</sub> force field for various structural and thermodynamic properties. An averaged Steinhardt bond order parameter is then applied to monitor the velocity of amorphous-y interface under different growth temperatures. The rate can be fit with an Eyring type model to decompose the resulting activation free energy into enthalpic and entropic components, yielding  $\Delta H^{\ddagger}=2.6 \text{ eV}$ and  $\Delta S^{\ddagger}=17$  R at 900K. Such large entropy of activation is also reported by experimental measurements in the epitaxial growth of Silicon and Germanium, which we propose that arises from reorientation in medium-range order during crystallization.

## Nonequilibrium steady states: principles, simulations, and rates

#### Todd R. Gingrich

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Chemical systems can deviate from equilibrium for a variety of reasons: because they are kinetically trapped, because they are subject to a time-varying drive, or because they are simultaneously in contact with multiple incommensurate reservoirs. This last scenario, which generates a nonequilibrium steady state (NESS), yields a stationary distribution over microstates that is not Boltzmann and that sustains currents. I will discuss three parallel efforts to better understand the chemical dynamics of such steady states. First, I will introduce a thermodynamic uncertainty relationship constraining the magnitude of fluctuations in currents. Next, I will discuss my group's efforts to elucidate structure-function relationships in model molecular motors by simulating the NESS with a mixture of Langevin dynamics and Grand Canonical Monte Carlo chemostats. Finally, I will show how tensor network methods, popular for electronic structure and quantum dynamics, can be repurposed to compute rates for nonequilibrium reaction-diffusion processes. Balanced Description of Excited States with State Averaged Resonating Hartree-Fock

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Nonadiabatic molecular dynamics (NAMD) simulations provide atomistic insights into photochemical processes, rendering them essential to the progression of the field. However, a major challenge for NAMD simulations lies in obtaining balanced representations of diverse excited states without sacrificing computational affordability. We present Resonating Hartree-Fock (ResHF) as a promising electronic structure theory candidate for NAMD simulations. We hypothesize that ResHF's nonorthogonal Slater determinant manifold will allow for balanced representation of both conical intersections and charge transfer states, all the while boasting mean field scaling. Some exciting work on generating excited state energies with state averaged (SA) ResHF has already been done by Nite and Jiménez-Hoyos in 2019. However, many questions remain concerning the assembly of the nonorthogonal Slater determinant manifold. In this talk, we present our explorations of these questions, describing our novel approach to building excited SA-ResHF wavefunctions out of restricted determinants derived from linear combinations of natural transition orbitals.

Advancements in Machine Learning and Quantum Embedding for Large Scale Simulations

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Large, periodic, and condensed phase systems impose a challenge for theoretical studies due to the compromise between accuracy and computational cost in their calculations. We present two methods that show exciting promise for treating this compromise: machine learning and quantum embedding. We exploit machine learning methods to solve the trade-off between the accuracy and computational cost by leveraging large data sets to train on highly accurate calculations using small molecules and then apply them to larger systems. We are developing a method to train a neural network potential with high-level wavefunction theory on targeted systems of interest that can describe bond breaking. We combine density functional theory calculations and higher-level ab initio wavefunction calculations, such as CASPT2, to train our neural network potentials. We first trained our neural network at the DFT level of theory. Using an adaptive active learning training scheme, we retrained the neural network potential to a CASPT2 level of accuracy. Quantum embedding methodology exploits the locality of chemical interactions to allow for accurate yet computationally efficient calculations to be performed on complex systems. Quantum embedding allows for the partitioning of the system into two regions. One is treated at a highly accurate level of theory using wave function theory methods, and the other is treated at the more computationally efficient level of DFT. We discuss our recent advancements for quantum embedding, specifically for systems with complicated electronic structure such as metal organic frameworks. Together, we believe both methodologies can allow for complex systems to be studied at a significantly reduced computational cost.
#### Interpretable Graph-Network-Based Machine Learning Models via Molecular Fragmentation for Chemical Accuracy at DFT Cost

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#### Abstract

The failure of approximate methods, e.g., density functional theory (DFT), to compute accurate electronic structures and energies for complex systems is well documented. While the newest collection of dispersion corrected and long-range corrected density functionals offer improved results, the errors in thermochemical properties computed with DFT are often greater than 5 kcal/mol for many chemical processes. In this talk, we discuss a new fragmentation-based molecular representation framework "FragGraph" involving embedding fragment-wise fingerprints onto molecular graphs. Our QM/ML model is specifically designed for delta machine learning ( $\Delta$ -ML) which learns the difference between properties calculated at two levels of theory. We aim to correct the deficiencies of approximate methods such as DFT to calculate molecular properties with an accuracy comparable to the most sophisticated and computationally intensive methods such as coupled cluster theory.

Our framework is based on many of the ideas from machine learning, fragmentation, and errorcancellation. Broadly, we combine the advantages of existing error-cancellation methods with standard molecular featurization techniques to develop a general framework for quantifying the molecular structure. More specifically, our method uses a molecular graph attributed with a collection of vectors representing each of the local environments of atoms based on fragments from the Connectivity-Based Hierarchy (CBH) of error cancellation schemes. The utility of our FragGraph representation is showcased in a QM/ML framework by using a state-of-the-art deep learning model to predict a variety of molecular properties. Each of the fragment-wise fingerprints are augmented by surrounding fragments through message-passing within a Graph Neural Network. Similar to standard fragmentation-based correction methods, each fragment ultimately provides a correction which, when summed, gives a total correction for a system. One of the key advantages of this approach is the inherent interpretability which allows the breakdown of the total  $\Delta$ -ML corrections into individual group contributions elucidating the deficiencies of approximate levels of theory based on molecular fragments.

#### **Basis Set Effects on Methods Used to Calculate Noncovalent Interactions**

#### Montgomery Gray and John M. Herbert

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**Abstract:** To understand the role that basis sets have when calculating noncovalent interactions, we have performed a systematic study of different basis sets in conjunction with several different methods used to study noncovalent interactions and evaluated their performance. This study includes Pople basis sets (6-31G(d) through 6-311++G(2df,2pd)), Karlsruhe basis sets (def2-SVP through def2-QZVPD), and Dunning basis sets (jun-cc-pVDZ through aug-cc-pVQZ) with several different methods: symmetry-adapted perturbation theory (SAPT), "Extended"-SAPT (XSAPT), and supramolecular DFT. We have found that diffuse functions play a vital role in achieving benchmark quality interaction energies and that convergence in these methods is typically achieved when triple-z basis sets are used. Results show that contrary to conventional wisdom, the larger Pople basis sets with adequate diffuse and polarization functions provide interaction energies of similar quality to that of the more sophisticated Dunning and Karlsruhe basis sets.

Relevant work:

- 1. Montgomery Gray and John M. Herbert J. Chem. Phys. 155, 034103 (2021)
- Montgomery Gray and John M. Herbert *Journal of Chemical Theory and Computation* 18, 4, 2308-2330 (2022)

#### Chemical and Electromagnetic Effects in Surface-enhanced Raman Imaging of Single Molecules

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Surface-enhanced Raman scattering (SERS) can be used to detect and image individual molecules. Experimentally and theoretically it has been shown that it is possible to resolve molecule vibrations using the highly confined electric near-field at the surface of plasmonic metal nanoparticles. Understanding the specific interactions between the molecules and the plasmonic nanoparticles becomes important for correctly interpreting the images. However, atomistic simulations of surfaceenhanced spectroscopes remains a challenge due the necessity of bridging the different length scale of the molecule and the metal nanoparticle. Here we present our recent progress on developing a reliable and efficient hybrid computational method that bridges classical electrodynamics and electronic structure theory. Focus will be on understanding chemical, resonance, and inhomogeneous electric fields in surfaceenhanced spectroscopies. Specifically, we will discuss how a first-principles Raman bond model can be used to gain insights into the chemical enhancements in SERS. Finally, we will discuss our latest results focusing on understanding the effects of near-field localizations, field gradient, substrate effects on the resolution in Raman scattering images.

# *Ab initio* composite strategies and multireference approaches for lanthanide sulfides and selenides

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Though thermodynamic properties such as enthalpies of formation, bond dissociation energies (BDEs), and reaction enthalpies, are of paramount importance in understanding reactivity, they can be difficult to describe for heavy element species. Recently, the *f*-block *ab initio* correlation consistent composite approach (*f*-ccCA) was introduced to provide energetic predictions of heavy element species, but at much reduced computational cost as compared with traditional treatment for heavy element species. Here, the method is demonstrated for a number of lanthanide sulfides and selenide species. The multireference character of the molecules is also assessed. The theoretically determined BDEs are compared to the BDEs recently obtained by the Morse group using a predissociation-based two-photon ionization (R2PI) method, providing a gauge of the theoretical methods with unprecedented accuracy. [1,2]

[1] J.J. Sorensen, E. Tieu, and M.D. Morse, J. Chem. Phys. 154, 124307 (2021).

[2] M.D. Morse, Acc. Chem. Res. 52, 119 (2019).

#### Assessment and tuning of the polyradicaloid character of Polycyclic Aromatic Hydrocarbons

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Polycyclic Aromatic Hydrocarbons (PAHs) with singlet biradicaloid character attract strong interest because of their use in many applications such as organic semiconductors, in singlet fission processes, in nonlinear optics and as energy storage devices. The characterization of the electronic structure of these compounds by means of quantum chemical methods and the investigation of ways how to tune their properties provide important information toward the development of improved materials. The theoretical calculation of biradicaloids poses substantial theoretical problems because of the inherent open shell character which requires multireference calculations for a completely satisfactory treatment. In this presentation, the results of multireference averaged quadratic coupled cluster calculations (MR-AQCC) are reported for different sets of compounds including Kekulé and non- Kekulé structures such as acenes, diindenoacenes, zethrenes and triangulenes. As descriptors for the biradicaloid character natural orbital occupations, number of unpaired electrons and singlet/triplet splittings are used. These benchmark data are compared with density functional theory (DFT) results in terms of spin contamination and the fractional occupation number weighted density (FOD).

# Torsionally broken symmetry assists infrared excitation of biomimetic charge-coupled nuclear motions in the electronic ground state

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#### Abstract

The concerted interplay between reactive nuclear and electronic motions in molecules actuates chemistry. Here, we demonstrate that out-of-plane torsional deformation and vibrational excitation of stretching motions in the electronic ground state modulate the charge-density distribution in a donor-bridge-acceptor molecule in solution. The vibrationally-induced change, visualized by transient absorption spectroscopy with a mid-infrared pump and a visible probe, is mechanistically resolved by *ab-initio* multiconfigurational quantum mechanics/molecular mechanics (QM/MM) simulations. Mapping the potential energy landscape attributes the observed charge-coupled coherent nuclear motions to the population of the initial segment of a double-bond isomerization channel, also seen in biological molecules. Our results illustrate the pivotal role of pre-twisted molecular geometries in enhancing the transfer of vibrational energy to specific molecular modes, prior to thermal redistribution. This motivates the search for synthetic and catalytic strategies towards achieving potentially new infrared-mediated chemistry.

Universal Anharmonic Potential Energy Surfaces for XY<sub>2</sub>-Type Molecules

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An approach to generate anharmonic potential energy surfaces for both linear and bent XY<sub>2</sub>-type molecules from their equilibrium geometries, Hessians, and total atomization energies alone is presented. Two key features of the potential energy surfaces are that (a) they reproduce the harmonic behavior around the equilibrium geometries exactly, and (b) they have the correct limiting behavior with respect to total bond dissociation. The potentials are constructed from two diatomic potentials, for which both the Morse or Varshni potentials are tested, and a triatomic potential, for which modified forms of the Anderson-n potential are tested. Potential energy surfaces for several linear and bent molecules are constructed from ab initio data, and the third-order derivatives of these surfaces at their equilibrium geometries are compared to the results of finite difference computation. For bent molecules, the vibrational spectra predicted by vibrational configuration interaction calculations on these surfaces are compared to experiment. A modified version of the Anderson-n potential, in combination with the Varshni potential, is demonstrated predict vibrational frequencies associated with bond angle bending an average of 20 cm<sup>-1</sup> below the harmonic oscillator approximation and with a fourfold reduction in the root-mean-square deviation from experiment compared to the harmonic oscillator approximation.

A tale of three particles: Generation of entangled-photon pair from biexcitonic-toexciton cascade decay in semiconductor nanoparticles

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Motivation and significance: This work aims to investigate the generation of entangled

photon pairs in quantum dots. Entangled photon pairs (EPP) are important in quantum optics and are essential for quantum information, quantum teleportation, quantum key distribution, and controlled logic operations. Semiconductor nanoparticles such as quantum dot (QD) are especially well suited for EPP generation and have been proven to have high-entanglement fidelity, extraction efficiency, and photon indistinguishability.

**Theoretical and computational strategy**: Accurate description of biexcitonic and exciton states are crucial for accurate prediction of generation of EPPs. In this work, we have used the frequency-dependent geminal-screened electron-hole interaction kernel method (FD-GSIK) for treating the excitonic and biexcitonic states. The FD-GSIK is a first-principles, explicitly-correlated, real-space method that avoids using unoccupied orbitals to construct the electron-hole interaction kernel by performing a complete infinite-order diagrammatic summation of particle-hole excitations and deriving a



renormalized R12 real-space electron-hole correlator operator. The FD-GSIK method also bypasses the computationally expensive AO-to-MO integral transformation step by computing all integrals directly in the real-space numerically using Monte Carlo integration. The frequency-dependent component of the FD-GSIK method implements the necessary quasiparticle screening needed for describing biexcitonic states. We have used a time-dependent diagrammatic approach for treating light-matter interactions. Specifically, light-matter interaction is treated using the dressed-atom representation, and the time-propagation is performed diagrammatically using Feynman-Goldstone formulation using field-dependent single-particle states.

**Results and future directions**: In this work, the combination of dressed-atom and FD-GISK method was applied to investigate exciton binding energies and biexciton binding energies for large quantum dots (Pb<sub>140</sub>S<sub>140</sub>, Pb<sub>140</sub>Se<sub>140</sub>, Cd<sub>144</sub>Se<sub>144</sub>). Chemical insights from biexciton binding energies, exciton binding energies, fine-structure splitting, oscillator strengths, degree of entanglement, and time-dependent electron-hole recombination probability for these quantum dots will be presented. The results from these calculations demonstrate the efficacy of the FD-GSIK method for capturing electron-hole correlation and treating 2-electron 2-hole excitation in large clusters and nanoparticles. Future and ongoing work in this direction include enhancing photon-entanglement characteristics by optimizing surface ligands and adding core/shell heterojunctions will be discussed.

**Reference:** <u>McLaughlin, P.F. and Chakraborty, A., 2020. Compact Real-Space Representation of Excited States Using</u> Frequency-Dependent Explicitly Correlated Electron–Hole Interaction Kernel. Journal of Chemical Theory and Computation, 16(9), pp.5762-5770. Spin-dependent Reaction Through Coupled Nuclear-Spin Dynamics

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Nonadiabatic dynamics plays a crucial role in various chemical relaxation phenomena, including photochemistry and electron transfer processes. In a nonadiabatic system with a complex-valued Hamiltonian (e.g., with spin-orbit coupling (SOC) or external magnetic field), the nuclei experience a Lorentz-like force (Berry force) in a direction perpendicular to their velocity. Since the sign of the Berry force depends on the electronic spin direction, the nuclei associated with opposite electronic spins may undergo different reaction pathways. In particular, such effects could be very strong near an avoided conical intersection (CI) with SOC, where the Berry force becomes huge and will dramatically alter the motion of the nuclei.

We investigate a two-state model Hamiltonian with two nuclear degrees of freedom, one incoming channel and two outgoing channels of nuclei. The model has an 'avoided' CI: a CI from diabatic couplings eliminated by a small electronic SOC. By using two-dimensional scattering calculations, we find that the nuclei have a huge spin-dependent selectivity on the outgoing reaction channel. For certain incoming energies (0.63 eV) and SOC (5.4 meV), the selectivity can approach unity. Considering the small magnitude of SOC and the richness of avoided conical intersections, such spin polarization should not be uncommon in molecules. Our discovery may help understanding many important spin-related reactions, such as chiral induced spin selectivity (CISS) or magnetochemical reactions.

# Accurate and cost-effective cavity-modified quantum dynamics from classical-like trajectories

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#### Abstract

Recent experimental observations of strong coupling between photonic cavity modes and molecular matter placed inside the cavity have highlighted potentially exciting new routes for controlling chemical processes. Elucidating the underlying physics and supporting the development of new experimental studies of such systems calls for accurate, flexible and cost-effective theoretical methods for calculating cavity-modified quantum dynamics. Methods based on the linearized semiclassical (LSC) approach show great potential in this respect due to their linear scaling with systems size and ability to interface with higher levels of theory in order to increase the accuracy of results. We have demonstrated two examples of LSC based approaches yielding highly accurate results for cavity modified quantum dynamics without incurring the prohibitively high computational costs associated with numerically exact methods.

We have shown that a recently proposed set of modified LSC approaches, which use a modified form of the identity operator, considerably outperform traditional LSC without increasing computational cost.<sup>1</sup> These methods yield accurate results for a series of benchmark systems modelling atomic systems placed inside cavities, highlighting their potential as a general purpose tool for simulating cavity-modified dynamics of complex chemical systems.

We have also demonstrated that for charge transfer systems inside cavities, using LSC in conjunction with the Fermi's Golden Rule approach for calculating rate constants constitutes another powerful tool for the study of quantum dynamics inside cavities.<sup>2</sup> This method for calculating cavity-modified rate constants can in fact yield quantum mechanically exact results for a commonly studied class of light-matter Hamiltonians.

#### **References:**

- [1] M.A.C. Saller, A. Kelly and E. Geva, J. Phys. Chem. Lett., 12, 3163-3170 (2021)
- [2] M.A.C. Saller, Y. Lai and E. Geva, J. Phys. Chem. Lett., 13, 2330-2337 (2022)

## **Abstracts for Poster Presentations**

These are listed on the following pages in the order that they appear in the list of poster presenters.

### Compact wavefunctions for ground and excited states using tensor product state representations

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For strongly interacting many-electron systems, a full configuration interaction (FCI) calculation is necessary to obtain accurate results. However, the exponential scaling of FCI limits its application to larger systems. With improved computing facilities, a lot of alternate methods like selected CI (SCI) and DMRG (density matrix renormalization group) have been able to solve larger systems but have their own limitations. The variational space for SCI becomes intractable when the active space is larger and the amount of strong correlation increases. And DMRG is most applicable for pseudo 1D systems. In this work, we present an alternate wavefunction representation: the tensor product state (TPS) representation. We divide the active space into smaller strongly interacting clusters and solve the exact solution within that space. The final wavefunction of the system is represented in the basis of tensor products of these cluster states. We use the selected CI method in this cluster basis to represent the final wavefunction and hence call this method tensor product selected CI (TPSCI). The number of variational degrees of freedom required is drastically reduced compared to traditional determinant based selected CI over a range of different types of systems like bond breaking in diatomics and  $\pi$ -conjugated systems. We present a description of the TPSCI method, along with a more recent extension to excited states.

### A detailed study of the Green's function approach for the calculation of isotropic exchange couplings

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Computation of magnetic exchange coupling constants is important for a growing number of areas, including spintronics, magnetic memory storage, and novel molecular magnet design. Determining exchange coupling for high-nuclearity complexes is not possible experimentally, and thus, computational methods are needed to make predictions. The most widely used methods compute the differences in total energies of a set of magnetic configurations, but the cost and difficulty increase steeply as more centers are added. Thus, it is desirable to have a black-box method that involves only a single state. Recent work[1] has adapted the use of approximate Green's functions from the solid-state community for use on molecules. The Green's function approach provides a far more efficient route to calculate isotropic magnetic exchange coupling, as it only requires the calculation of one state. However, large-scale tests have not yet been performed. Thus, we assess the ability of the Green's function approximation for exchange coupling calculations to reproduce the standard broken-symmetry energy difference approach for transition metal complexes. To accomplish this, we have selected a variety of heterodinuclear, homodinuclear and polynuclear systems containing *3d* transition metal centers and computed the couplings with both the Green's function and energy difference methods.

We found that the Green's function approach is shown to have mixed results for the cases tested. For dinuclear complexes with larger strength couplings the Green's function method is unable to reliably reproduce the energy difference values. However, for weaker dinuclear couplings, the Green's function approach reproduces broken-symmetry energy difference couplings. In polynuclear cases, the Green's function approximation worked remarkably well for oxo-Fe complexes, but not so well for other complexes.

#### References

[1] Steenbock, T.; Tasche, J.; Lichtenstein, A. I.; Herrmann, C., J. Chem. Theory Comput., 2015, 11, 5651-5664.

### A Comparative Study of Core-Valence Separation Approximation Schemes for Simulating Core-Level Ionization

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X-ray spectroscopy is a powerful tool for studying the electronic structure and dynamics of matter. Accurate simulations of experimental X-ray spectra is critical for their reliable interpretation and assignment. However, simulation of core-level excited states can be challenging. One of the primary challenges is that corelevel excited states are embedded in a continuum of valence-level excited states, making convergence onto the states of interest difficult. One widely used solution to this problem is to invoke the Core-valence Separation (CVS) approximation. Despite its widespread use, many different CVS schemes exist. For example, the CVS approximation can include different classes of excitations, and may or may not introduce the frozen-core approximation. Furthermore, while CVS has been widely used and studied for K-edges (i.e. ionizations from 1s orbitals), its performance for L-edges (2s and 2p ionizations) is less understood. In this work, we analyze the performance of various CVS schemes for simulating K- and Ledge core-level ionization energies and spectra within the framework of singlereference Algebraic Diagrammatic Construction theory. We demonstrate that the choice of CVS scheme can yield appreciably different ionization energies, and discuss the role of various approximations.

#### A quantum chemical investigation of molecular recognition of the highly infectious SARS-CoV-2 Omicron variant by the human ACE2 receptor

#### Majed Aljohani, Pawan Bhatta and Xiche Hu

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Omicron (B.1.1.529) has emerged as the latest SARS-CoV-2 variant of concern (VOC) that features enhanced transmissibility, immune escape, and pathogenicity. Omicron carries upwards of 50 mutations in its genome, 30 of which exist in the gene encoding the S protein. Strikingly, as many as 15 of those mutations occurred in the Omicron receptor-binding domain (RBD) that binds with the human angiotensin-converting enzyme 2 (ACE2) receptor. Since S protein's binding to the human ACE2 receptor is the initial key step for host cell entry, it is necessary to assess the effects of Omicron VOC mutations on the S affinity for the ACE2 receptor. Here, we have carried out a comparative analysis of the molecular recognition of the RBDs of the wild type (WT) and Omicron by the human ACE2 based on x-ray crystal structures of their respective complexes. First, we systematically examined the binding pocket of both crystal structures to identify all non-bonded intermolecular interactions that are responsible for S protein's molecular recognition by ACE2. Subsequently, the strengths of interaction energies between all interface residues in WT and Omicron and their interacting residues in ACE2 were quantified by means of the supermolecular approach using quantum mechanics method at the B2PLYP level. It was found that Omicron binds to ACE2 with higher affinity. Several hot spot residues from the mutated S protein are identified as the molecular determinants for the enhanced binding. The intermolecular interaction energy of mutated residues N477, R493, R498 and Y501 with ACE2 are -1.8, -6.3, -8.2 and -8.3 kcal/mol, respectively. In contrast, the intermolecular interaction energy for the corresponding WT residues S477, Q493, Q498 and N501 are -0.02, -0.4, -3.1 and -4.1 kcal/mol, respectively. This increase in binding affinity is ascribed to new hydrogen bonds formed by N477, salt bridge and CH- $\pi$ interactions formed by R493, salt bridge, cation- $\pi$  and CH- $\pi$  interactions formed by R498, and  $\pi$ - $\pi$  and CH- $\pi$  interactions formed by Y501. The results also reveal that the contribution of nonmutated residues to the overall binding affinity is enhanced in Omicron. This enhancement of nonmutated residues can be attributed to the allosteric influence of the large number of mutations at the interface of Omicron. This quantification of binding affinity enhancement for the heavily mutated Omicron, at an advanced level of electronic structure calculation, provides a molecular level explanation for the observed rapid transmission and severe pathogenicity of the Omicron VOC. Moreover, the unravelling of molecular determinants for binding of the highly infectious SARS-CoV-2 Omicron variant to the human ACE2 receptor may be valuable in future for the molecular development of targeted therapies against current and future variants of Covid-19.

# TDDFT-1D: DFT based configuration interaction method with a lone doubly excited configuration

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The combination of Kohn-Sham (KS) Density Functional Theory (DFT) and Time Dependent Density functional theory (TDDFT) provides an inexpensive yet accurate way to calculate potential energy surfaces of interest for simulating photochemical and photophysical processes. However, in the region around a conical intersection (CI) between the ground state  $(S_0)$  and the first excited state  $(S_1)$ , where static correlation is key, DFT/TDDFT fails. It does not predict the correct dimensionality of the CI manifold seam.

TDDFT-1D is an electronic structure ansatz that utilize the fictitious DFT/TDDFT wave functions in the framework of a larger configuration interaction Hamiltonian. The configuration interaction space includes the reference KS state, all singly excited configurations, and one doubly excited configuration. The orbitals of the reference state are rotated such that that energy a double excitation from the HOMO to the LUMO is minimized. This method can produce physically meaningful potential energy surfaces near  $S_1/S_0$  avoided crossings and CIs. Initial benchmarking also shows that the vertical excitation energies are as accurate as those from TDDFT. We derive and implement analytical gradients and derivative couplings for TDDFT-1D, which should lead to the immediate application of this method in nonadiabatic simulations.

#### Effect of PFAS on human Thyroglobulin Protein: An in-silico approach

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Per- and polyfluoroalkyl substances (PFASs) are a family of compounds that are environmentally persistent and difficult to degrade. These compounds have been used in food packaging, water-repellent clothing, and non-stick cookware due to their water-repellent properties. However, PFAS molecules can interfere with metabolic pathways in humans and in animals, including but not limited to the thyroid system, cholesterol regulation, plasma proteins, and certain nuclear hormone receptors. The toxicity and the bioaccumulation of the PFAS compounds for these proteins correlate with their interactions as well as the binding strength.

The adverse effects associated with PFAS are thought to be both chain length and the functional group dependent. In this work, we have investigated the effect of three PFAS compounds (PFOS, PFOA, PFNA) with various lengths and functional groups on the human thyroglobulin protein. Thyroglobulin is the precursor protein in synthesizing the thyroid hormones, T3 and T4, through a reaction between Tyrosine residues located at specific sites on the protein. The binding as well as the interactions with the surroundings of three PFAS compounds were studied using Molecular Dynamics and binding energy calculations to understand the potential effects of the selected PFAS molecules on thyroid hormone synthesis.

#### Acceleration of Self Consistent Field Calculations via Many-Body Expansions

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(Dated: May 16, 2022)

**ABSTRACT**: In spite of the monumental advances made in the fields of computer science spanning the last 40 years, even the most fundamental methods of approximating solutions of the Schrödinger equation, such as the Hartree-Fock equations and Kohn-Sham implementations of Density Functional Theory, scale non-linearly in terms of computational cost. This cost conundrum is all the more harrowing, given that it is incurred at every cycle in the construction and subsequent diagonalization of the Fock-Matrix which scale biquadratically and cubically, respectively. Indeed, methods such as integral screening and parallel processing algorithms have mitigated the costs to some extent; however, a frequently overlooked concept is the quality at which the SCF protocol is initiated, the initial guess. The quality of the initial guess not only dictates the speed at which the process converges but also whether or not the protocol converges at all. In this way, garnering the highest quality initial guesses is of paramount importance for the success of the SCF algorithm and also provides an indication of the stability of the information it offers. Chemical fragmentation allows the solution to both accuracy and efficiency concerns. One such technique is the Many-Body Expansion (MBE), through which a system of interest is partitioned into subsystems which may or may not be disjoint. The MBE has been shown to be a robust method for different cluster types namely, water clusters and ion pair clusters both of which showed energy prediction improvements of several orders of magnitude when compared to the default initial guess method, SAD (Superposition of Atomic Density), which is the standard method in all popular quantum chemistry software programs. The Mean Absolute Deviation for the neutral water clusters in direct energy prediction using the third order MBE was a mere 2 kcal/mol, which pales in comparison to the error seen in SAD, which was 149 kcal/mol at the HF (Hartree-Fock) level of theory and using Def2-TZVPPD basis set. The generalized version of the MBE, GMBE, has been able to predict energy at a more efficient level. For example, testing, as a proof of concept, on a cluster of 100 water molecules, the error in energy prediction was as small as 0.044 kcal per monomer (about 0.0001 % water monomer energy)using B3LYP level of theory and cc-pVDZ basis set. It is worth noting the GMBE implementation required only 270 subsystem calculations based on the set theoretical principle of inclusion and exclusion, a concept from foundational mathematics. For comparison, the MBE version would have required a minimum of thousands of subsystems (trimers, dimers, etc.) even when using distance screening to exclude some superfluous calculations. The conquering of a relatively large water cluster with such marginal error at such a small cost in terms of number of calculations speaks to the accuracy and efficiency of the set theory decomposition. Preliminary testing on chaotrope and kosmotrope containing ionic clusters of differing charges has also shown very promising results.

Utilizing Multi-Scale Modeling and Machine Learning Approaches to Characterize the Structure-Function Relationship of the Platelet-Activating Factor Receptor

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The platelet-activating factor receptor (PAFR) is a G protein-coupled receptor (GPCR) that is implicated in multiple inflammatory response pathways as well as bacterial infection in the airway and several types of cancer. Thus, discovery of an effective antagonist against PAFR would lead to numerous therapeutic applications. However, the structure-function relationship of PAFR is poorly understood. In this project, we used a combination of docking, machine learning, and molecular dynamics (MD) simulations to characterize the structure-function relationship of PAFR and identify trends in formation of stable receptor-ligand complexes. MD simulations used Gaussian accelerated MD, in order to access conformations associated with the transition from the inactive to active state of PAFR. Small molecule docking was used with machine learning to massively reduce the computational time needed to screen ligand-receptor complexes. In particular, docking results utilized the Bag of Bonds (BoB) data feature to predict binding affinities, utilizing 20% of total data for training and subsequent testing against the rest of the ligand library. The top 5% of results predicted from BoB were cross-validated by running docking simulations on PAFR. Predicted docking energies were competitive with results from brute force docking. In combination with insights obtained from our MD simulations, we are able to show that ring-containing ligands are a necessary prerequisite for optimization of synthetic antagonists. Our approach holds promise for widespread application to other GPCRs.

#### Development and Implementation of Semi-Stochastic Double Electron Attachment and Double Ionization Potential Equation-of-Motion Coupled-Cluster Approaches

<u>Suhita Basumallick</u>,<sup>1</sup> Arnab Chakraborty,<sup>1</sup> Jun Shen,<sup>1</sup> and Piotr Piecuch<sup>1,2</sup> <sup>1</sup>Department of Chemistry, Michigan State University, East Lansing, MI 48824 <sup>2</sup>Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824

Our group has recently developed a novel way of converging high-level coupled-cluster (CC) [1-3] and equation-of-motion (EOM) CC [4,5] energetics by identifying dominant higherthan-doubly excited determinants with the help of stochastic configuration interaction Quantum Monte Carlo (CIQMC) wave function propagations. We have also started developing the analogous approaches that enable high-level particle-nonconserving EOMCC computations for open-shell systems within the electron attachment (EA) and ionization potential (IP) formulations of EOMCC [6]. In this presentation, we extend the semistochastic, CIQMC-driven, EOMCC methods to the double electron attachment (DEA) and double ionization potential (DIP) regimes by using the CIQMC wave function propagations to identify the dominant 4-particle-2-hole (4p-2h) and 4-hole-2-particle (4h-2p) components of the relevant electron attaching and ionizing operators. By examining methylene and trimethylenemethane biradicals as representative molecular examples, we demonstrate that the resulting semi-stochastic DEA- and DIP-EOMCC approaches are capable of recovering total electronic energies and singlet-triplet gaps obtained in the high-level, fully deterministic, DEA-EOMCC(4p-2h) and DIP-EOMCC(4h-2p) computations at the small fraction of the cost.

#### References

- [1] J. E. Deustua, J. Shen, and P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017).
- [2] J. E. Deustua, J. Shen, and P. Piecuch, J. Chem. Phys. 154, 124103 (2021).
- [3] A. Chakraborty, S. H. Yuwono, J. E. Deustua, J. Shen, and P. Piecuch, to be submitted to *J. Chem. Phys.*
- [4] J. E. Deustua, S.H. Yuwono, J. Shen, and P. Piecuch, J. Chem. Phys. 150, 111101 (2019).
- [5] S. H. Yuwono, A. Chakraborty, J. E. Deustua, J. Shen, and P. Piecuch, *Mol. Phys.* 118, e1817592 (2020).
- [6] A. Chakraborty, J. Shen, and P. Piecuch, to be presented at the 52<sup>nd</sup> Midwest Theoretical Chemistry Conference (MWTCC), Columbus, Ohio, June 2-4, 2022.

### Conformational and Thermodynamic Differences Underlying Wild-type and Mutant YEATS Domain Specificity for Epigenetic Marks

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#### Abstract

Histone post-translational modifications (PTMs) form an organized "code" that are interpreted by multiple reader domains and proteins to regulate gene expression. The YEATS domain is a prototypical PTM reader that recognizes multiple lysine acetylation marks on the histone H3 tails as a way of recruiting chromatin remodellers. Two YEATS mutations have been identified which have been linked with leukemia, Wilms tumor, and other forms of cancer and result in either an insertion or deletion of residues in the loop connecting beta sheets distant from the protein active site. In vitro experiments have shown that these mutations modulate the selectivity of YEATS domains for various lysine actylation marks, although different experiments have provided contrasting views on the ability of the insertion and deletion mutants to discern specific PTMs. Here, we have performed multiple molecular dynamics simulations of wild-type, insertion, and deletion mutant YEATS domains free from and in complex with two PTM mimicking peptides: one that mimics acetylation on residue K9 of H3 and the other that mimics acetylation on residue K27 of H3. Results show that these two peptides have distinct flexibilities and binding energetics when bound to YEATS domains, and that these properties are affected by interactions both local to and distant from the PTM being recognized. Furthermore, these properties are modulated by the YEATS insertion and deletion mutants, which results in disparate binding affects in these systems. Together, these results suggest that only the partial exposure of histone tails is sufficient in the context of nucleosomes for YEATS-mediated recognition of acetylation marks on histone tails. They also caution against the over-interpretation of the results obtained from experiments on reader domain-histone peptide binding in isolation and not in the full-length nucleosome context.

# The N501Y mutation in SARS-CoV-2 Variants of Concern enhances their hACE2 receptor binding affinity

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The N501Y mutation found in a series of SARS-CoV-2 Variants of Concern (VOCs), including the highly infectious alpha-, beta-, gamma- and omicron-strains, has been linked to increased transmission and immune escape. There is an urgent need to understand this mutation at the molecular level so that effective antibody therapies and vaccines against the new emerging variants can be developed. Here, we carried out a comparative analysis of the molecular recognition of the spike proteins of the wild type and the mutant strains by the human cell surface receptor ACE2 (hACE2) based on x-ray crystal structures of their respective complexes. The latter are hydrated with water using a constrained equilibration MD simulation protocol in the NPT ensemble. The binding pocket of Y501 was thoroughly examined to identify all non-bonded intermolecular interactions that are responsible for its molecular recognition by ACE2, and compared with that of N501. Subsequently, the strengths of interaction energies between Y501/N501 and its interacting residues in ACE2 were quantified by means of the supermolecular approach quantum mechanically at the B2PLYP level. It was found that Y501 and N501 bind to ACE2 with intermolecular interaction energy of -6.11 and -4.11 kcal/mol, respectively. This gain in binding energy was attributed to the  $\pi$ - $\pi$  and CH- $\pi$  interactions enabled by the aromatic phenyl ring of Y501. Furthermore, as revealed in the figure, a network of water molecules around Y501 facilitated the formation of a hydrogen bond with the hydroxyl group of Y501. This finding of enhanced binding affinity of the N501Y mutants may explain partly the increased transmissibility of the VOCs with N501Y mutation. Moreover, the unraveling of molecular determinants responsible for the enhanced binding affinity of Y501 to ACE2 in this work lays the foundation for the molecular design of targeted therapies against current and future variants of Covid-19.



Figure 1. Stereo diagrams of Y501 with its interacting residues in ACE2, and the water network.

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# Using Modeling and Regression Approaches to Predict the Photocycle of a Canonical Microbial Rhodopsin

Fine-tuning of the spectral bandwidth of microbial rhodopsins is necessary to design robust platforms for applications in optogenetics. Experimental approaches to optimization (e.g., point mutations in proteins, incorporation of modified retinal chromophores) are often time-consuming and do not always lead to a viable application. In addition, computational approaches like guantum mechanical calculations are intensive and often provide relative scales of absorption spectra. Recently, molecular dynamics (MD) simulations in combination with linear regression techniques have been successful in predicting the effect of point mutations on ground state absorption of squid rhodopsins. Predictions are obtained by measuring the dynamics of the retinal chromophore and using linear regression to identify a subset of variables that are fit to a two-component model for spectral absorption. To date, this technique has focused solely on the ground state of retinal proteins; prediction of higher-energy conformations associated with the rest of the photocycle has yet to be accomplished. To address this issue, we carried out MD simulations on the photointermediates of bacteriorhodopsin (bR), the canonical microbial rhodopsin. Dynamics of the retinal binding pocket (dihedrals of the retinal backbone, orientation of retinal methyl groups, and bending angle) were used as variables for testing our regression model. K-fold cross-validation was carried out on 10% of our data set for training, using the remaining 90% of data for testing. The generated model was then validated against MD simulations of three mutants of bR. Our results show good agreement with spectroscopic data of the bR photocycle. This robust method of linear regression is instrumental in the modification and tuning of retinal proteins in a high throughput manner as well as providing a framework for modeling and validating the photocycle of newly-discovered microbial rhodopsins.

#### Quantum Effects in Vibrational–Rotational Energy Transfer Simulated Using Mixed Quantum/Classical Theory

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Vibrational–rotational energy transfer plays an important role in the atmospheric studies of Earth, stars, and other planets.<sup>1,3</sup> Since experimental studies are difficult at extreme energies, computational simulations can be a useful tool to describe vibrational transitions at high temperatures. Our research is focused on testing the Mixed Quantum/Classical theory (MQCT) approach, where vibration and rotation are treated quantum mechanically, whereas the scattering process is described classically.<sup>1</sup> Several papers published by our research group show that for the systems which involve only rotational motion, MQCT results are in good agreement with full quantum results.<sup>1,2</sup> However, systems that have vibrational motion, in addition to rotational, were not examined in detail. For this reason, we carried out calculations for vibrating diatom + atom systems (N<sub>2</sub> + O, CO + H, and CO + He) using a rovibrational basis set. Overall, our results are in good agreement with full quantum results. In particular, using MQCT code we were able to reproduce the quantum glory effect observed in the total cross section of the N<sub>2</sub> + O system.<sup>3</sup>

#### **References:**

[1] A. Semenov, B. Mandal, and D. Babikov. "MQCT: User-ready program for calculations of inelastic scattering of two molecules." *Computer Physics Communications* 252 (2020): 107155.

[2] B. Mandal, A. Semenov, and D. Babikov. "Calculations of differential cross sections using mixed quantum/classical theory of inelastic scattering." *The Journal of Physical Chemistry* A 122.30 (2018): 6157-6165.

[3] Q. Hong, M. Bartolomei, F. Esposito, C. Coletti, Q. Sun, and F. Pirani. "Reconciling experimental and theoretical vibrational deactivation in low-energy O+ N<sub>2</sub> collisions." *Physical Chemistry Chemical Physics* 23.29 (2021): 15475-15479.

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TITLE: Application of Multiscale Fragmentation Approaches to Enzymatic Barrier Heights BODY: This talk will explore the different aspects of fine-tuning multiscale fragmentation approaches for protein systems and then we will discuss its application for calculating enzymatic barrier heights. Recent work has shown that QM models with hundreds of atoms may be required to obtain convergence, which limits the levels of theory that can be applied. By using a multiscale fragmentation approach, we are able to push to the *ab initio* limit in systems with hundreds of atoms. Through sequential testing of distance-based thresholding, many-body expansion truncation, and different combinations of levels of theory for high-/low-level layers we have been able to establish a protocol for completing energetic calculations on protein systems. Here we have considered the methyl transfer by human catechol O-methyltransferase (COMT) to test our procedures capability to predict accurate enzymatic barrier heights.

#### Multi-faceted Approaches to the Advancement of PFAS treatment

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Given their ideal properties, PFAS have widely been used in applications including non-stick coatings, cleaning supplies, makeup, fire-fighting foams, fast-food packaging, and more. However, these materials are quite recalcitrant to natural degradation and can accumulate in nature and within the human body. Given the wide range of expertise our team possesses, we are uniquely suited to perform a multi-pronged approach to determine pathways in which to tackle the PFAS problem. Thousands of PFAS exist making it difficult to classify and regulate the material. Here, our team is able to apply machine learning techniques to generate novel classification schemes. These schemes allow for intelligent subset selection of PFAS and fluorinated compounds that are then subjected to high throughput workflows for the generation of good quality 3-D structures, which are then used in a database of computed physical and chemical properties. Our team is also actively involved in understanding at the atomistic level (using density functional theory) how carborane anion ([HCB11H5F6]–)/silylium (Et3SiH/Et3Si+) chemistry can be used as a pseudo-catalyst to aid in the degradation of PFAS. Furthermore, our team has employed molecular dynamics to examine materials for the removal of PFAS from clays, to pores, and functionalized graphene.

**Title:** Addressing the Growing Pains of the Many-Body Expansion for Large Systems

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#### Abstract:

The many-body expansion (MBE) is an effective tool for side-stepping the exponential CPU and memory requirements of conventional quantum mechanical methods by systematically reducing chemical systems to combinations of fragments. Three and four-body MBE terms are required to accurately capture many-body polarization effects but combinatorics makes the unfiltered MBE unfeasible for large systems. We have shown that a minority of the three and four-body terms make meaningful contributions to the predicted super-system energy and that energy screening using semi-empirical methods can be used to predict unneeded calculations. The energy-screened four-body MBE has been applied to challenging proton-ordered water isomers to achieve sub-kcal/mol fidelity relative to super-system Hartree-Fock calculations; however the use of the MBE with post Hartree-Fock methods results in the accumulation of basis set superposition effects. To resolve this issue we build upon previous work with the energy screened MBE and counterpoise corrections schemes to extend the MBE for use with large systems and correlated methods.

Title: A Recursive Cell Multipole Method for use in Atomistic Electrodynamics Models

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We present an extension of the recursive implementation of a cell multipole method (CMM) to go beyond the quasistatic approximation. In this method, the higher order electrodynamic interaction tensors used for the CMM are calculated recursively, thus greatly reducing the implementation complexity of the CMM. By pairing this new method with an atomistic electrodynamics simulation, it allows for the efficient simulation of systems with over a million atoms. Using this method we study the effects that retardation has the near and far field properties of large plasmonic nanoparticle systems. To study SERS, both the near and far field properties need to be modeled accurately, thus this method can be employed to model the surface allowing us to capture the effects that confined electric and magnetic fields have on the Raman scattering.

#### Quantum-Monte-Carlo-Driven Equation-of-Motion Coupled-Cluster Approaches for Electron Attachment and Ionization: Implementation and Applications

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The recently proposed idea of identifying the most important higher-than-doubly excited determinants in coupled-cluster (CC) [1–3] and equation-of-motion (EOM) CC [4,5] calculations with the help of stochastic configuration interaction Quantum Monte Carlo (CIQMC) wave function propagations is extended to the electron attachment (EA) and ionization potential (IP) EOMCC frameworks. We demonstrate that the CIQMC wave function propagations, despite their particle-conserving character, are very efficient in identifying the dominant 3-particle–2-hole (3p-2h) and 3-hole–2-particle (3h-2p) components of the respective particle-nonconserving electron attaching and ionizing operators without having to resort to the previously utilized active-space concepts [6,7]. By using the CH and OH radicals and the C<sub>2</sub>N, CNC, N<sub>3</sub>, and NCO open-shell systems as representative examples, we demonstrate that the semi-stochastic, CIQMC-driven, EA-and IP-EOMCC approaches are capable of converging total and excitation energies equivalent to those obtained in the fully deterministic EA-EOMCC(3p-2h) and IP-EOMCC(3h-2p) calculations in an automated manner and at the small fraction of the computational cost.

#### References

- [1] J. E. Deustua, J. Shen, and P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017).
- [2] J. E. Deustua, J. Shen, and P. Piecuch, J. Chem. Phys. 154, 124103 (2021).
- [3] A. Chakraborty, S. H. Yuwono, J. E. Deustua, J. Shen, and P. Piecuch, to be submitted to *J. Chem. Phys.*
- [4] J. E. Deustua, S.H. Yuwono, J. Shen, and P. Piecuch, J. Chem. Phys. 150, 111101 (2019).
- [5] S. H. Yuwono, A. Chakraborty, J. E. Deustua, J. Shen, and P. Piecuch, *Mol. Phys.* 118, e1817592 (2020).
- [6] J. R. Gour, P. Piecuch, and M. Włoch, J. Chem. Phys. 123, 134113 (2005).
- [7] J. R. Gour and P. Piecuch, J. Chem. Phys. 125, 234107 (2006).

### Computational Investigations of Supramolecular Interactions: Anion Binding with Macrocyclic and Cage Receptors

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Density functional (DFT) theory including dispersion corrections has been widely used for the investigation of supramolecular interactions involving medium-sized and large molecules. In this work, we present a thorough investigation using DFT methods for the study of supramolecular receptors, viz., macrocycles and cages. In particular, we focus on receptors where the anion binding is via non-conventional C-H hydrogen bond donors. With a series of atomic, molecular, and novel designer anions of different sizes and shapes, we explore the effects of preorganization and complementarity on selective binding of anions with receptors involving different cavity sizes. Importantly, solvent effects in a variety of nonpolar as well as polar solvent environments are evaluated using the conductor-like polarizable continuum model (CPCM) to calculate the binding affinities of a range of macrocycle-anion and cage-anion complexes. Furthermore, we design a series of cage receptors with tunable chloride affinity by functionalizing a triazolo cage receptor. Finally, we investigate the application of cages as liquid-liquid extractants of aqueous chloride into an organic solvent. This work provides a foundation for the development and application of computational models for anion binding and computer-aided design of anion-receptors.

Electronic Structure for Multielectronic Molecules Near a Metal Surface

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We analyze a model problem representing a multi-electronic molecule sitting on a metal surface. Working with a reduced configuration interaction Hamiltonian, we show that one can extract very accurate ground state wavefunctions as compared with the numerical renormalization group theory (NRG) -- even in the limit of weak molecule-molecule coupling strength  $t_d$  but strong intramolecular electron-electron repulsion U. Moreover, we extract what appear to be meaningful excitation energies as well. Our findings should lay the groundwork for future *ab initio* studies of charge transfer processes and bond making/breaking processes on metal surfaces.

# A Computational Investigation on the Origin of Stereoselectivity in Photochemical Reactions

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#### Abstract

Photochemical reactions provide alternatives to ground-state chemistries, opening up new routes for desired product formation. At the same time, photochemistry is not well known for achieving high selectivity, in particular stereoselectivity. This presentation will show how an asymmetric photocatalyst having a chiral phosphoric acid backbone can achieve diastereoselectivity in a photoexcited [2+2] cycloaddition. Examination of this reaction using quantum chemical reaction path finding shows that strong interactions between catalyst and substrate in the excited state are instrumental in the reaction outcome, providing a template for stereoselective product formation. The growing string method and molecular dynamics sampling of the conformation space are used to arrive at our overall mechanistic picture, providing an efficient means to sample the reaction pathways on the excited state reaction landscape. The latest results show that intersystem crossing (ISC) may play a key role as well in determining the stereoselectivity.

#### References

1. Alonso, R.; Bach. T. Angew. Chem., Int. Ed. 2014, 53, 4368.

2. Maturi, M. M.; Bach. T. Angew. Chem., Int. Ed. 2014, 53, 7661.

3. Tröster, A.; Alonso, R.; Bauer, A.; Bach, T. J. Am. Chem. Soc. 2016, 138, 7808.

4. Pecho, F.; Zou, Y. Q.; Gramüller, J.; Mori, T.; Huber, S. M.; Bauer, A.; Gschwind, R. M.; Bach, T. *Chem. Eur. J.* **2020**, *26*, 5190.

5. Pecho, F.; Sempere, Y.; Gramüller, J.; Hörmann, F. M.; Gschwind, R. M.; Bach, T. J. Am. Chem. Soc. 2021, 143, 9350.

# Multireference algebraic diagrammatic construction theory for simulating X-ray photoelectron spectroscopy

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X-ray spectroscopic techniques have been widely developed and applied to investigate electronic structure and dynamics in molecules and materials. However, new ab initio methods to simulate core-level excited states are essential to understanding the core electron phenomena in chemical systems with various strengths of electron correlation. I will present the algebraic diagrammatic construction (ADC) in the multireference (MR) framework for calculating core ionization energies and X-ray photoelectron spectra. The MR-ADC method uses a multiconfigurational wavefunction as a reference (e.g., CASCI or CASSCF), from which the excited states are calculated. In contrast to conventional multireference methods, MR-ADC can simulate excitations from all molecular orbitals, including inner-shell and core, and does not require the inclusion of these orbitals in the active space. To access the high-energy core ionized states, we implemented the Core-Valence Separation (CVS) approximation to the IP-MR-ADC framework, which enables direct access to the inner-shell excitations by decoupling them from the valence configurations. The resulting CVS-IP-MR-ADC method enables the investigation of core ionized states in multireference electronic problems. I will demonstrate the accuracy of the CVS-IP-MR-ADC approach by showing its applications for bond-breaking processes and open-shell systems, such as biradicals and coordination complexes.

### Dynamical Self-energy Mapping (DSEM) for Creation of Sparse Hamiltonians Suitable for Quantum Computing

Diksha Dhawan, Mekena Metcalf, Dominika Zgid

May 1, 2022

We present a two step procedure called the dynamical self-energy mapping (DSEM) that allows us to find a sparse Hamiltonian representation for molecular problems. In the first p art of t his p rocedure, t he a pproximate s elf-energy of a molecular system is evaluated using a low level method and subsequently a sparse Hamiltonian is found that best recovers this low level dynamic self-energy. In the second step, such a sparse Hamiltonian is used by a high level method that delivers a highly accurate dynamical part of the self-energy that is employed in later calculations. The tests conducted on small molecular problems show that the sparse Hamiltonian parametrizations lead to very good total energies. DSEM has potential to be used as a classical-quantum hybrid algorithm for quantum computing where the sparse Hamiltonian containing only O(n2) terms in a Gaussian orbital basis, where n is the number of orbitals in the system, could reduce the depth of the quantum circuit by at least an order of magnitude when compared with simulations involving a full Hamiltonian.

#### Additivity of Diene Substituent Gibbs Free Energy Contributions for hetero-Diels–Alder Reactions between (F<sub>3</sub>C)<sub>2</sub>B=N(CH<sub>3</sub>)<sub>2</sub> and Substituted Cyclopentadienes

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Systematic computational studies of pericyclic hetero-Diels–Alder reactions between aminoborane  $(F_3C)_2B=N(CH_3)_2$ , **1**, and all permutations of substituted cyclopentadienes *c*- $C_5R^1R^2R^3R^4R^{5a}R^{5b}$  (R = H, CH<sub>3</sub>, CF<sub>3</sub>, F) allow isolation of substitutional effects on free energy barrier heights and reaction free energies. The effects appear to be additive in all cases. Substitution at positions 5a and 5b always increases barriers and reaction energies, an effect explained by steric interactions between substituents and the aminoborane moiety. For cases R = CH<sub>3</sub>, regioselectivities differ from those expected from canonical organic chemistry predictions. Frontier molecular orbital calculations suggest this arises from the extreme polarization of the  $\pi$  interaction in **1**. For cases R = CF<sub>3</sub>, the 2/3-substitution comparison accords with canon, but the 1/4-substitution comparison does not. This appears to arise from a combination of electronic and steric issues. For cases R = F, many of the reactions are exergonic, in contrast to the cases R = CH<sub>3</sub>, CF<sub>3</sub>. Additionally, fluorine substitution at positions 2 and 4 have a barrier lowering effect. Frontier molecular orbital calculations support an orbital calculations support an orbital-based preference for formation of 2- and 4-substituted "*meta*" products rather than "*ortho/para*" products.

### Mapping Multidimensional Chemical Dynamics Problems to a Family of Hybrid Quantum and Classical Computing Environments

Anurag Dwivedi\*, Miguel Angel Lopez-Ruiz\*, Debadrita Saha\*, Philip Richerme\*, Srinivasan S. Iyengar\*

Chemical dynamics simulations are central to Theoretical and Computational Quantum Chemistry that help to understand and accurately predict the molecular properties of chemical systems underlying a wide range of chemical, material, biological and atmospheric processes. However, the computational cost incurred in solving a chemical dynamics problem grows exponentially with the number of degrees of freedom of a chemical system, limiting a classical computer to only specific chemical systems. A chemical dynamics problem involves quantum treatment of nuclear degrees of freedom which requires accurate time evolution of nuclear wavefunctions on precisely computed potential energy surfaces. These often need accurate electronic structure calculations to be performed on an exponentially growing set of nuclear configurations. The complexity of quantum nuclear dynamics problems is further compounded by the need to propagate the wavefunction, which again scales exponentially with the number of dimensions involved.

With the advantage of  $2^n$  dimensional exponential Hilbert space for n qubit system, quantum computers are seen as a potential to solve exponential scaling chemical dynamics problems. However, low-fidelity, noisy operations, and low-qubit counts of the currently available NISQ computers due to the scaling in the CNOT gates and the circuits' length still hinder the progress. One way to mitigate this issue is to use hybrid computing by preprocessing the problem on a classical computer before mapping it to a quantum computer.

In the same direction, our algorithm decomposes the multidimensional unitary operator and wavefunction into independent, parallel streams of one-dimensional propagators and wavefunctions using Tensor Networks, as shown in the given figure. These one-dimensional propagators and wavefunctions are weighted by an

entanglement parameter that depicts the entanglement between any two neighboring dimensions. The one-dimensional propagators are then simplified so that an effective Hamiltonian for each dimension can be derived from it. Recently, quantum nuclear dynamics on a one-dimensional Born-Oppenheimer potential energy surface have been mapped to a spin-lattice quantum simulator where the spin dynamics are governed by local magnetic fields and coupling between the spin-states localized at lattice sites<sup>1</sup>.

Our next step is to map these independent one-dimensional effective Hamiltonians to the spin-lattice quantum simulator where the governing parameters needed to operate the quantum simulator are determined by the effective one-dimensional



molecular Hamiltonians<sup>1</sup>. These effective one-dimensional subsystems can then be propagated simultaneously and efficiently on the quantum simulator. To investigate the performance of the method, a shared proton dynamics of a short-strong hydrogen-bonded system on a two-dimensional potential surface has been implemented on IonQ quantum computing hardware, and results are awaited.

<sup>1</sup>Saha, Debadrita, et al. "Mapping Quantum Chemical Dynamics Problems to Spin-Lattice Simulators." *Journal of Chemical Theory and Computation* 17.11 (2021): 6713-6732. \*Indiana University, Bloomington, Indiana 47405, USA
#### **Comparing Single-ion and Salt-doped Polymer Electrolytes via Coarse-grained Simulations**

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Block copolymers (BCP) are promising as solid-state electrolytes due to the combination of ion conductivity and mechanical robustness. Salt-doped block copolymers with free cations and anions are widely explored in experiments and simulations. Besides the relatively lower ionic conductivity of polymer electrolytes versus liquid electrolytes, another disadvantage of salt-doped BCPs is the generally lower lithium-ion transference number  $(t_+)$ .  $t_+$  represents the fractional contribution of cations to overall conductivity, assessing the efficiency of lithium-ion conduction. One approach to achieve higher  $t_+$  is to use a single-ion structure that limits anion motion by tethering anions to the relatively immobile polymer backbone. We use coarse-grained molecular dynamics simulations to compare ion structure and dynamics in salt-doped versus single-ion BCPs at various ion concentration and polarity conditions. Specifically, we calculate the profiles of cation distribution, cation velocity and monomer relaxation rate within each lamella, as well as the overall cation diffusivity and conduction. We find cation mobility is higher in single-ion systems especially at lower ion concentrations when ionic aggregation is problematic for the salt-doped systems.

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Characteri ation of the conformational landscape of lariat peptides via molecular dynamics simulations

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Development of targeted therapies that are orally available remains a prominent challenge in the pharmaceutical industry. Cyclic peptides have emerged as a viable alternative to small molecule drugs, as they can passively diffuse across the cell membrane and retain target specificity. However, characteri ation of their behavior in different phases (aqueous solvent and the plasma membrane) remains challenging for a number of reasons. Lariat cyclic peptides (i.e., depsipeptides) form a significant fraction of naturally-occurring cyclic peptides, but little is known about their mechanism of permeation and action [1]. We hypothesi ed that an increase in N-methylation and heterochirality (substitution of D-amino acids for L-amino acids) will lead to improved passive permeability of lariat peptides. In order to test this hypothesis, we carried out molecular dynamics (MD) simulations on a small library of lariat peptides in various environments. This involved developing and validating force field parameters consistent with the CHARMM force field. Our next step was to carry out Gaussian accelerated MD (GaMD) simulations on lariat peptides in aqueous and hydrophobic (octanol or chloroform) solvents to determine the change in conformation of the cyclic backbone as a function of solvent. Finally, we performed umbrella sampling (US) simulations to capture the free energy of permeation across a

1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) bilayer for the best-performing lariat peptides. Our results show that MD-based techniques can successfully characteri e the interconversion between hydrophilic and hydrophobic conformations of lariat peptides, and in combination with high-resolution permeability studies, provide the framework for prediction of larger peptide libraries via machine learning approaches. [1] Kelly et al. J. Amer. Chem. Soc. 2021, 143, 705-714.

#### EFP meets ANI: Modeling macroscopic systems with neural network potentials

#### Shahed Haghiri (Purdue University)

Machine learning has made its way into many scientific fields as a powerful problem-solving tool. In chemistry Neural Network Potentials (NNPs) have been created to circumvent expensive quantum mechanical calculations. ANI is one of the general-purpose deep learning NNPs that rivals accuracy of CCSD(T) with only a fraction of the computational cost. One of the remaining challenges of local NNPs such as ANI is an accurate description of long-range interactions and, as a result, larger errors in modeling extended molecular systems. The Effective Fragment Potential (EFP) is a QM based method for modeling non-covalent interactions. EFP decomposes the non-covalent interaction energy into electrostatic, polarization, dispersion, exchange-repulsion and charge transfer terms by using perturbative expansions. Here, we propose a combination of EFP and ANI, which makes ANI suitable for modeling extended molecular systems. In this ANI/EFP neural network, long-range interactions are modeled via electrostatic potentials from EFP that are used as additional input parameters for ANI. Thus, the long-range interactions in the molecular system are described with EFP, while ANI takes care of the short-range interactions. The developed computer codes will contribute to the open-source LibEFP and TorchANI software libraries.

#### Excitonic Coupling in Melanin: Consequences of Chemical and Geometric Disorder

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#### ABSTRACT

Melanin is a ubiquitous natural pigment characterized by broadband absorption, ultrafast nonradiative deactivation (sunscreening), and radical scavenging abilities. The origins of these functions are obscure because the precise chemical structure of any melanin is still unknown. Buehler and co-workers (Chen et al., Nat. Commun. 2014, 5, 3859) postulated that structurally disordered aggregates of excitonically coupled chromophores can explain the unusual absorption spectrum of melanin, which increases monotonically and exponentially with decreasing wavelength. They supported their conclusion using calculations that included just a single type of chromophore, but it has been proposed that melanin has sufficiently many chromophores to absorb continuously throughout the UV, visible, and near-IR. Here, we explore the consequences of geometric disorder and chemical disorder on melanin's electronic absorption spectrum using Frenkel exciton theory and coupling strengths typically encountered in organic aggregates. Orientational disorder strongly localizes excitonic states even in the absence of disorder due to randomization of the intermolecular couplings. To explore the effects of chemical disorder, a model based on dimers composed of distinct chromophores was formulated. It is shown that the dimer absorption spectra remain largely unchanged compared to the uncoupled monomer spectra due to poor excitonic mixing. Further, we show that cooperative, intensity-borrowing effects due to the presence of additional monomer transitions that preferentially increase the absorption intensity in the blue and decrease oscillator strength in the red are only expected in highly ordered, H aggregates, which are unlikely to be present in melanin. Our simulations suggest that excitonic coupling only modestly reshapes absorption by an ensemble of absorbers with geometric and chemical disorder and is unlikely to produce a melanin-like absorption spectrum from chromophores that have a significantly different spectrum in the zero-coupling limit.

Chen, C. T.; Chuang, C.; Cao, J. S.; Ball, V.; Ruch, D.; Buehler, M. J. Excitonic Effects from Geometric Order and Disorder Explain Broadband Optical Absorption in Eumelanin. *Nat. Commun.* **2014**, *5*, 3859. <u>https://doi.org/10.1038/ncomms4859</u>.

#### Measuring the calcium sensitivity of cardiac troponin C site II

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Calcium-dependent cardiac muscle contraction is regulated by the troponin protein complex (cTn), which consists of three subunits: troponin C (cTnC) the calcium binding subunit, troponin I (cTnI) which inhibits actomyosin interaction, and troponin T (cTnT) which anchors the protein complex to tropomyosin. The regulatory domain (N-terminal domain) of cTnC (cNTnC) has been a target of substantial interest for the treatment of congestive heart failure via two main approaches: computer-aided drug discovery and gene therapy. Both tactics possess great promise for treating the disease. As part of the drug discovery approach, small drug-like molecules that increase Ca<sup>2+</sup> sensitivity without altering the concentration of systolic Ca<sup>2+</sup> are of particular interest <sup>1</sup>. Gene therapy has proven to be a viable approach, as previous studies have demonstrated the effectiveness of calcium sensitizing mutations to regain myocyte contractility and functionality post an induced myocardial infarction event in mouse models <sup>2, 3</sup>. We investigate the effects of altering calcium sensitization through a variety of computational approaches aimed at characterizing a potentially important new class of calcium sensitizer small molecules and measuring the  $\Delta\Delta G$  between wildtype and known calcium sensitivity altering mutants of cNTnC. We utilize knowledge of known calcium sensitizers for virtual screenings of extensive chemical libraries and employ the free energy method of Adaptive Steered Molecular Dynamics (ASMD) to characterize known calcium cNTnC sensitizing and desensitizing mutations.

(1) Perrone, S. V.; Kaplinsky, E. J. Calcium sensitizer agents: a new class of inotropic agents in the treatment of decompensated heart failure. *Int J Cardiol* **2005**, *103* (3), 248-255. DOI: 10.1016/j.ijcard.2004.12.012.

(2) Shettigar, V.; Zhang, B.; Little, S. C.; Salhi, H. E.; Hansen, B. J.; Li, N.; Zhang, J.; Roof, S. R.; Ho, H.-T.; Brunello, L.; et al. Rationally engineered Troponin C modulates in vivo cardiac function and performance in health and disease. *Nature Communications* **2016**, *7* (1), 10794. DOI: 10.1038/ncomms10794.

(3) Feest, E. R.; Steven Korte, F.; Tu, A. Y.; Dai, J.; Razumova, M. V.; Murry, C. E.; Regnier, M. Thin filament incorporation of an engineered cardiac troponin C variant (L48Q) enhances contractility in intact cardiomyocytes from healthy and infarcted hearts. *J Mol Cell Cardiol* **2014**, *72*, 219-227. DOI: 10.1016/j.yjmcc.2014.03.015.

Authors: Benjamin M. Harless, Jasmine Sindelar, J. Daniel Ge elter

## Title: Residue-specific Structure and Dynamics of water around the insect antifreeze protein, DAFP-1: A Molecular Dynamics Study

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Antifree e proteins (AFPs) are proteins characteri ed by their ability to depress the free ing point of water without af fecting the melting point, called thermal hysteresis. The mechanisms by which these proteins accomplish this are not fully characteri ed. DAFP-1, the protein of study, is a hyperactive beetle protein from the species Dendroides canadensis and can exhibit up to 8°C of free ing point depression when isolated. DAFP-1 is modeled using the amber99 force field in TIP4P-Ice and SPCE and simulated utili ing OpenMD. We isolate water structure and dynamics around residues of interest, the ice binding sites (IBS) and the non ice binding sites (NIBS), to investigate the tetrahedrality order parameter and the hydrogen bond jump times. The tetrahedrality order parameter, *q*(*r*), represents the degree of local orientational ordering of water molecules in a tetrahedral network. Hydrogen bond jump time,  $\tau(\mathbf{r})$ , are the characteristic times required to break hydrogen bonds after they form. We study both the local structural ordering as well as dynamic ordering as a function of distance from specific protein residues. We find differences in both tetrahedrality and jump times when comparing residues in the IBS vs the NIBS at close ranges. The IBS had longer hydrogen jump times and lower tetrahedrality order parameter. This indicates that the water is slowed around the IBS and is slightly less organi ed than that of water around the NIBS. We compare these values to that of small molecule cryoprotectants, eq., DMSO, formate, formic acid, methanediol, that share functional groups to amino acids. The behavior between the protein and cryoprotectants is different which indicates the importance of the collective effect of the amino acids. By comparing these two we will characteri e and describe the structural and dynamic contributions to the environment from the amino acid functional groups of antifree e proteins to cause thermal hysteresis.

# Accurate and cost-effective quantum dynamics of complex systems

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#### Abstract:

The focus of our work lies in developing accurate and cost-effective theoretical methods for simulating molecular quantum dynamics in complex chemical and biological systems. Theoretical approaches are key both in interpreting experimental results and gaining a deeper understanding of the underlying physics as well as in guiding the development of new experiments. While quantum mechanically exact dynamics methods exist, their prohibitive exponential scaling with system size makes them unsuitable for the study of large and complex molecular systems.

The linearized semiclassical (LSC) approach provides an excellent alternative, due to their linear scaling with system size and rigorous derivation. We have shown that the accuracy of the well-established quasiclassical mapping Hamiltonian (QC/MH) class of methods, which constitutes one application of LSC, can be considerably improved by using an alternative definition of the electronic population operator.

A variety of important chemical processes, ranging from photosynthesis to photovoltaics, involve energy or charge transfer (CT). We have demonstrated a general-purpose strategy for calculating charge transfer rate constants in complex molecular systems, by applying LSC methods to the Fermi s golden rule (FGR) approach for calculating CT rate constants. We have shown that this approach can yield highly accurate and even analytical results for a number of benchmark systems, including examples of cavity modified CT.

Another approach for improving and extending the LSC class of methods involves their use as an input to the generalized quantum master equation (GQME). Considerable progress has been made in developing this approach, which uses short-time approximate inputs to generate highly accurate long-time electronic dynamics by encoding the effect of the environment into a memory Kernel. We have demonstrated that LSC methods show considerable promise as an approximate input for the GQME, yielding highly accurate results for complex molecular environments, including biological light-harvesting systems. This approach also shows considerable promise for further improving the performance of LSC for cavity modified dynamics, which we have already shown to be accessible using QC/MH methods. We are also developing a comprehensive library of projection based dynamics methods, tailored for simulating a wide range of quantum dynamical effects.

### An Exact Frozen Density Embedding Method for Calculation of Polarizability

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#### May 10, 2022

Frozen Density Embedding(FDE) with freeze-and-thaw cycles is a formally exact embedding scheme, but in practice, it is limited to weakly overlapping subsystems due to requirement of approximate non-additive kinetic energy density functionals. We previously reported that approximate nonadditive kinetic energy density functionals are not necessary when external orthogonality(EO) if enforced between subsystems, and FDE can then be generalized to strongly overlapping subsystems. In this work, we correct our previous implementation of EO in TDDFT regime and show that supermolecular polarizabilities can be exactly reproduced. We further discuss the limitation of exact FDE in interpreting interactions between subsystems due to non-unique partitioning of total density. We demonstrate the origin of non-uniqueness by showing how subsystems electrons are polarized differently in freeze-and-thaw cycles and such polarization is also dependent on how subsystems are polarized. Moreover, we show that when excitations are localized within one subsystem, they are stable with respect to the ways of polarization. It thus sheds light on possible approach to minimizing impacts from non-unique nature of FDE on subsystem properties.

#### Shannon and von Neumann entropies of multi-qubit Schrödinger's cat states

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We used IBM's publicly accessible quantum computers [1,2] to evaluate the von Neumann entropy [3] and the Shannon entropy [4,5] for n-qubit Schrödinger's "cat" states.[6] An n-qubit cat state is a maximally entangled wavefunction of the form,

$$|\Psi_n\rangle = \frac{|0_0\rangle \otimes \dots |0_{n-1}\rangle + |1_0\rangle \otimes \dots |1_{n-1}\rangle}{\sqrt{2}}$$

For a pure cat state and with a fault-free measurement, the Shannon entropy of the distribution over measurement outcomes should equal one, and the von Neumann entropy should equal zero. Deviations from these values indicate decoherences and faults in either the preparation or measurement of the qubit states. The Shannon entropy in a case with  $2^n$  outcomes takes the the form,

$$S_{S_o} = \sum_{j=1}^{2^n} P_j \log_2 P_j$$

where  $P_j$  is the probability for the qubits to be found in the state  $|j\rangle = |q_0q_1...q_{n-1}\rangle$ ,  $q_i \in \{0, 1\}$  upon measurement. The von Neumann entropy is derived from the density matrix,  $\rho$ , in the form,

$$S_{vN} = -Tr(\rho \log_2 \rho)$$

Quantum state tomography was performed on 2-5 qubit cat states to determine the density matrix of the states as they reside on the quantum computers. Two kinds of circuits were constructed to determine Shannon entropy. We found a near linear relationship between the number of qubits in the state and the Shannon entropy. We developed a two-parameter model that reproduces the near-linearity of the entropy vs. the number of qubits, based on the probabilities of observing 0 when a qubit is set to  $|0\rangle$  and 1 when it is set to  $|1\rangle$ . The slope of the entropy vs. number of qubits provides an index of the quality a quantum computer that is more sensitive than the current "Quantum Volume" measure.[7]

This work has been supported in part by NSF grant CHE-1900399.

[1] N. Jansen, M. Loucks, S. Gilbert, C. Fleming-Dittenber, J. Egbert, and K. L. C. Hunt, *Phys. Chem. Chem. Phys.* 24, 7666 (2022).

[2] IBM Q Experience is a trademark of International Business Machines Corporation, registered in many jurisdictions worldwide. See quantum-computing.ibm.com.

[3] J. von Neumann, *Göttingen Nachrichten* **1927**, 273 (1927).

- [4] C. E. Shannon, Bell System Technical Journal 27, 379 (1948).
- [5] C. E. Shannon, Bell System Technical Journal 27, 623 (1948).
- [6] D. Greenberger, M. Horne, and A. Zeilinger, Bell's Theorem, *Quantum Theory, and Conceptions of the Universe* (Kluwer Academic, Dordrecht, 1989), p. 73.

[7] A. W. Cross, L. S. Bishop, S. Sheldon, P. D. Nation, and J. M. Gambetta *Phys. Rev. A* **100**, 032328 (2019).

#### Achieving an Atomistic Understanding of our Environment

#### <u>Glen R. Jenness</u>, Harley R. McAlexander, Timothy C. Schutt, Caitlin G. Bresnahan, Michael Roth, Manoj K. Shukla

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As part of its mission, the United States Army Corps of Engineers (USACE) has a keen interest in tracking the environmental fate of various chemicals and materials. However, the natural environment is an extremely heterogeneous system, with many components acting in tandem to change chemicals that come into contact with it. Consequently, determining the fate of chemical compounds and their associated risk to population centers is a daunting prospect.

The Computational Chemistry Team of USACE's Engineer Research and Development Center (ERDC) has spent the decade developing tools and expertise that will enable policy makers to determine potential threats to our civilian population. In this presentation, we will discuss some of our techniques and methodologies, which range from the application of standard DFT and wave-function methods, to the development of novel tools and algorithms including, but not limited to, automatic DFTB parameterization, machine learning, and conformational sampling techniques.

### Rotational energy transfer in intermolecular collisions using Mixed Quantum/Classical theory

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The study of rotational energy transfer in the intermolecular collisional processes is pivotal in probing and discerning molecular interactions. Notably, in bimolecular collisions the energy transfer can occur between both collisional partners owing to the excitation of one molecule accompanied by the simultaneous quenching of another. Experimental studies of rotational energy transfer become challenging as the rotational energy spacing is small and high image resolution is required. Computational studies of rotational energy transfer using full quantum treatment becomes unachievable and expensive for larger molecules having numerous rotational energy transfer in inter-molecular collisions, where translational motion (scattering) is treated classically whereas internal motion (rotation and/or vibration) is treated quantum mechanically. MQCT is computationally inexpensive concomitantly accurate.

Ammonia is an abundant molecule in the Inter stellar medium (ISM) and a practical gas thermometer of the medium. The study of collision energy transfer in ammonia/deuterated ammonia aids in estimating molecular abundance in ISM. A detailed study of rotational energy transfer between ND<sub>3</sub> and D<sub>2</sub> (molecules with very different rotational constants)- simulated by both full quantum method and MQCT were carried out to illustrate the accuracy and scope of our method.

#### References

- 1. Semenov, A., Mandal, B., & Babikov, D. (2020). *Computer Physics Communications*, 252, 107155.
- 2. Gao, Z., Loreau, J., Van Der Avoird, A., & Van De Meerakker, S. Y. (2019). *Physical Chemistry Chemical Physics*, 21(26), 14033-14041.
- 3. Walmsley C. M., Ungerechts H., 1983, A&A, 122, 164

#### **Constructive Quantum Interference in a Photo-Chemical Reaction**

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Interferences emerge when multiple pathways coexist together, leading toward the same result. In this talk I will present a theoretical study for a reaction scheme that leads to constructive quantum interference in a photoassociation (PA) reaction of a <sup>87</sup>Rb Bose–Einstein condensate where the reactant spin state is prepared in a coherent superposition of multiple bare spin states. This is achieved by changing the reactive scattering channel in the PA reaction. As the origin of coherent control comes from the spin part of the wavefunction, we showed that it is sufficient to use radio frequency (RF) coupling to achieve the superposition state. We simulate the RF coupling on a quantum processor (IBMQ Lima), and our results show that interferences can be used as a powerful resource for the coherent control of photochemical reactions. The approach is general and can be employed to study a wide spectrum of chemical reactions in the ultracold regime.

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A systematic study of effects of oxygen vacancies from pure and N-doped reduced Titanium nanoparticles with potential application in nanoscience Authors: <u>Kattner, William;</u> Bhandari, Srijana; Parker, Shane. Case Western Reserve University, 10900 Euclid Ave, Cleveland, OH 44106

The energetic and optical properties of titanium oxide (titania) nanoparticles with oxygen vacancies have been analyzed extensively due to their tremendous potential in nanomedicine, and photocatalysis<sup>1,2</sup>. The electronic structure and exciton binding energies for pure titania nanoparticles were analyzed previously<sup>1</sup>, finding that for small particles, the electronic structure depends more on the structure of the titania nanoparticle than its size. As such, various isomers were systematically analyzed for their energetic and optical properties for both pure titania nanoparticles, and defected nanoparticles. Here, we use density functional theory (DFT) and time-dependent DFT (TDDFT) to investigate how oxygen vacancies and single-point nitrogen doping affect the electronic and optical properties of titania nanoparticles. Single-point nitrogen defects in particular have been shown to decrease the fundamental and optical gaps of titania nanoparticles<sup>2</sup>. More specifically, we investigate the optical properties of single oxygen vacancies and single nitrogen doping at various sites for the n=35 type nanoparticle. We find that internal sites are most likely to form oxygen vacancies or nitrogen defects and in both cases we reproduce the experimentally observed blue shift upon defect formation.

#### References

- Cho, D.; Ko, K.; Lamiel-Garcia, O.; Bromley, S.; Lee, J.; Illas, F. Effect of Size and Structure on the Ground-State and Excited-State Electronic Structure of TiO2 Nanoparticles. *J. Chem Theor and Comp tation*. 2016 12 3751 3763. DOI: 10.1021/acs.jctc.6b00519
- Xiaobo Chen and Clemens Burda Journal of the American Chemical Society 2008 130 (15), 5018-5019 DOI: 10.1021/ja711023z

#### **Electrocatalytic CO<sub>2</sub> Reduction using Metal-Nanographene Complexes**

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#### Abstract

The reduction or conversion of CO<sub>2</sub> into fuel or other value-added products is a topic of active research interest. Recent experimental work has demonstrated that a large Renanographene-diimine complex with 18 fused aromatic rings has the least negative potential measured to date for the electrocatalytic reduction of CO<sub>2</sub> to CO. A decrease in overpotential of 0.8 V was observed relative to a previous generation catalyst due to the incorporation of the nanographene ligand. This suggests that the size and composition of the nanographene can affect the onset potential substantially. In this study, we use DFT computations to investigate the properties of the Re-nanographene complex to tune its performance as an electrocatalyst for CO<sub>2</sub> reduction. In particular, we investigate how the catalytic property of metal complexes with nanographene ligands are associated with the stability and reactivity of the polyaromatic hydrocarbon ligands attached, the properties of the metal center, and the effects of heteroatoms in the ligand center. A rigorous analysis is carried out with a test set of metal-nanographene complexes containing 5 to 28 fused aromatic rings to investigate the effects of the ligand center. In addition, alternative metal centers such as Mo and Mn are investigated for understanding the role of the metal center in catalysis. We report our results on the dependence of catalytic properties of the complex with (a) the number of fused rings, (b) the topological arrangement for the same number of rings, and (c) cheaper earth-abundant alternatives to replace the Re metal center.

Investigation of the space of coarse-grained representations

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All-atom molecular dynamics simulations are a powerful tool for gaining insights into chemical systems. However, due to the computational cost, low-resolution coarse-grained (CG) models are widely adopted for studying larger, longer length scale systems such as polymers and biomolecules. However, there exist many unanswered questions regarding the first step in constructing a CG model - i.e., how best to represent a system in reduced detail. In this study, we developed a statistical physics framework for investigating these questions. We adopt the Gaussian Network Model (GNM) as a simple model for proteins. Given the GNM, we can analytically evaluate all properties of a CG model constructed using any reduced resolution representation. We assess the quality of each CG representation using a variety of metrics which describe the preservation of different aspects of the underlying high-resolution model.

We implement Monte Carlo (MC) sampling to sample the space of possible CG representations of the system with a fixed number of CG sites. We adopt a new sampling algorithm which we prove to be ergodic, which allows us to sample a more general set of representations in which the number of atoms in each CG site is allowed to fluctuate, while the number of sites remains fixed. We find that allowing the number of atoms of the CG sites to fluctuate allows for the discovery of higher quality representations. We also find that the ability of the model to preserve the slow-low frequency modes is anti-correlated with the amount of information preserved by the model at low resolutions, but that these metrics become uncorrelated at higher resolutions.

#### <u>Graph-theoretic molecular fragmentation for potential surfaces yields</u> <u>tensor network representations for efficient quantum dynamics</u>

#### Anup Kumar, Indiana University

Molecular potential energy surfaces have a critical role in the study of quantum nuclear effects. reaction pathways, and vibrational properties for anharmonic systems. But these calculations are severely hindered due to the potentially exponential number of electronic energy calculations needed as a function of nuclear dimensions. In addition, post-Hartree-Fock accuracy for each such electronic energy adds steep algebraic cost.

Molecular fragmentation-based approaches been have recently developed to simplify the electronic problem. Nevertheless, their application to produce general multidimensional potential surfaces poses additional challenges. For example, a molecular meaningfully system may be represented using multiple fragmentation strategies simultaneously within one



potential energy calculation. We have developed a graph-theory-based molecular fragmentation methodology that has close connections to many-body expansion and ONIOM. We treat the potential surfaces obtained from graph-theoretic fragmentation as diabatic states and combine multiple such diabatic states to arrive at surfaces that have shown post-Hartree-Fock accuracy but at DFT cost.

In addition, when these graph-theory-based potential surfaces are used to compute the quantum propagator for nuclear dynamics, the propagator reduces to a series of lower-dimensional operators (or lower rank tensors) leading to a general tensor-network decomposition of quantum nuclear propagation. This greatly reduces the complexity of quantum propagation. Both approaches are discussed with demonstrations on a protonated water wire system where the coupled quantum behavior of nuclear degrees of freedom is known to have a critical role.

## First-Principles Modelling of excitonic interactions and spectroscopic signatures of single point mutants of the Fenna-Matthews-Olson (FMO) photosynthetic protein

#### Jack Lawrence (Purdue University)

The Fenna-Matthews-Olson (FMO) pigment protein complex serves as a conduit that transfers the energy from the chlorosomal antenna to the reaction center of photosynthetic green sulfur bacteria. FMO employs excitonic behavior to achieve high efficiency in energy transfer. The protein is trimeric, with each monomer unit containing eight bacteriochlorophyll-a (BChl *a*) pigments active in the excitonic mechanism. Recently, we have developed a computational procedure based on the polarizable quantum mechanical/effective fragment potential (QM/EFP) method that produces quantitative agreement with experimental absorption and circular dichroism (CD) spectra of FMO. In this work, we compare absorption and CD spectra of the wildtype FMO and several single-point FMO mutants. We find that the mutations introduce both local and long-range changes in solvatochromic and geometric environments of BChl *a* pigments, intricately affecting excitonic structure and absorption and CD spectra of the protein.

#### Molecular Level Insight about the Adsorption and Diffusion of Poly- and Perfluoroalkyl Substances in Near- and Sub-surface Environments

#### Narasimhan Loganathan, Angela K. Wilson

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Poly- and perfluoroalkyl substances (PFAS) are important emerging contaminants of concern as categorized by the United States Environmental Protection Agency (U.S. EPA). This is primarily due to the linkage between exposure to a number of PFAS species with detrimental health impacts including carcinogenesis, immunotoxicity, developmental, and reproductive disorders. At the same time, the widespread use of PFAS in a myriad of industrial, domestic and commercial applications over six decades has resulted in their ubiquitous presence in natural settings including soils, sediments, surface water, and ground water. With increasing bioaccumulation and potential toxicity of PFAS, a molecular level understanding of the behavior of PFAS in each of those environments is important, particularly as these settings represent the essential exposure pathways of PFAS for humans and animals.

Classical molecular dynamics (MD) simulations were performed to provide critical insight into the adsorption and dynamics of PFAS in kaolinite pores, an important constituent of soils and sediments. A broad range of short- and long-chain PFAS molecules that vary in functionalities were examined. All of the simulations were performed at near neutral pH conditions where the active functional groups were deprotonated. These studies clearly highlight that the interfacial adsorption properties of PFAS are strongly influenced by the length of the hydrocarbon backbone and the terminal functionalities. Furthermore, the nature of prevalent metal cations with varying hydration properties on the fate and transport properties of PFAS has been considered. These results provide critical insight underlying the adsorption mechanisms of PFAS at water-saturated mineral surfaces and may be useful in the design and validation of effective in-situ or site-specific mitigation techniques of soils and sediments.

#### Controlled quantum nuclear dynamics of tensor network states.

Miguel Angel Lopez-Ruiz, Anurag Dwivedi, and Srinivasan S. Iyengar Department of Chemistry, and the Indiana University Quantum Science and Engineering Center (IU-QSEC),

Indiana University, Bloomington, IN-47405

A comprehensive knowledge of the dynamics of quantum many-body systems is possibly the cornerstone for the study of chemical systems. In spite of the great success that quantum theory has had since its inception, the so-called "course of dimensionality", i.e., the exponential scaling of the system degrees of freedom with its size, still poses a major computational challenge. The full description of an arbitrary quantum state can become virtually intractable due to the immense dimension of the system's Hilbert space. In an effort to tackle this issue, tensor networks (TN) have emerged as a general data compression scheme which allow the truncation of the Hilbert space, by exploiting the intrinsic entanglement structure of physical states. Moreover, with the emergent interest in quantum information, a demand for hybrid (quantum-classical) algorithms that are suitable for future NISQ devices is on the rise, and TN methods are considered to be compelling candidates.

Using a TN approach, we present a mechanism for the controlled quantum propagation of the nuclear degrees of freedom of general multi-configurational chemical systems at a reduced computational complexity. In particular, we propose a novel algorithm to suppress the potentially exponential growth of non-physical entanglement that could render simulations intractable; a well known issue in TN methods. The algorithm is then probed using a symmetric hydrogen-bonded system, namely, the protonated 2,2'-bipyridine, and its results are compared to those obtained via direct diagonalization.

#### Towards predictive ab initio models of astatine compounds

#### James MacLean, Jacob Adamski, Vincent Casetti, and Alexander Rusakov Department of Chemistry, Oakland University, Rochester, MI 48309

The element astatine is a highly promising agent for targeted cancer radiotherapy. Its isotope At-211 has a half-life of 7.2 hours and undergoes pure alpha decay into relatively non-toxic products. It can destroy malignant tissue and be expelled quickly from the system with minimal complications. The major obstacle in developing efficacious astatine-based therapeutic agents is its understudied chemistry leading to the *in vivo* loss of At-211.

Computational quantum-chemical studies of astatine are instrumental in bringing down this barrier. Because astatine is a heavy element, adequate computational methods to simulate its chemistry must account for the intertwined effects of spin-orbit interactions and electron correlations. We present state-of-the-art models of small astatine molecules (At<sub>2</sub>, HAt, and AtAu) based on relativistic coupled-cluster theory to establish the most reliable theoretical reference. Based on these results, we determine appropriate relativistic DFT-based schemes for large At-containing molecules. Finally, we apply these findings to complex At species from multivalent halides to precursors of therapeutic agents.

## Spin-adapted spin-flip DFT: TDDFT, but better

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#### May 2022

Time-dependent density functional theory (TDDFT), is an affordable way to carry out non-adiabatic simulations and excited state calculations. TDDFT falls short in certain cases to predict the correct topology of potential energy surfaces. This has lead to spin-flip time-dependent density functional theory (SF-TDDFT) being developed as a qualitatively correct and very efficient method for describing electronic excitation en ergies, conical intersections, excited state reaction pathways, and excited state nonadiabatic molecular dynamics (MD) simulations. Despite having multiple advantages, SF-TDDFT has one major drawback in the form of serious spincontamination, which is why the spin-adapted spin-flip DFT (SA-SF-DFT) method has been introduced as an improvement over traditional TDDFT. The spin-adapted nature of SA-SF-DFT allows it to generate all necessary determinants and hence avoiding the topology problem faced by TDDFT. In addition to this, SA-SF-DFT accurately accounts for the majority of the electron-electron correlation present in a system due to a small semi-empirical modification m ade t o t he fi nal Ha miltonian ma trix. This is si milar to the work of Grimme et al. on DFT/MRCI, where the DFT treatment of dynamic correlation was combined with the static correlation obtained from the multireference configuration interaction (MRCI) m ethod. SA-SF-DFT has been implemented in the QChem software package, and has produced highly accurate results at much lower cost. I will be presenting a poster demonstrating the accuracy and efficiency of this method, and thus showcasing its superiority over traditional TDDFT calculations.

#### Electrochemical reduction of CO<sub>2</sub> at the earth-abundant transition metaloxides/copper interfaces

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62901, USA.

#### Abstract

Electrochemical reduction of CO<sub>2</sub> to value-added fuels and chemicals suffers from high overpotentials and poor product selectivity due in part to lack of high-performance catalysts. In this study, we investigated CO<sub>2</sub> reduction to C<sub>1</sub> products at the metal-oxide/copper interface, focusing on the earth-abundant transition metals, including Fe, Co and Ni, based on the results of density functional theory (DFT) calculations. Our results indicate that CO<sub>2</sub> reduction to CO<sub>(g)</sub>, HCOOH<sub>(l)</sub> and H<sub>2</sub>CO<sub>(l)</sub> is not favorable at the interfacial sites, modeled as (MO)<sub>4</sub>/Cu(100). CO<sub>2</sub> reduction on (FeO)<sub>4</sub>/Cu(100) leads to the formation of CH<sub>4(g)</sub> at a low limiting potential of -0.18 V. On (CoO)<sub>4</sub>/Cu(100), CO<sub>2</sub> can be reduced to CH<sub>4(g)</sub> at a limiting potential of -0.48 V but a solvent with permittivity constant ( $\varepsilon_r$ ) less than 70 (e.g. in propylene carbonate) can steer the reaction to produce CH<sub>3</sub>OH<sub>(l)</sub>. On (NiO)<sub>4</sub>/Cu(100), CH<sub>3</sub>OH<sub>(l)</sub> is the most favorable product at a limiting potential of -0.28 V. These results demonstrate that the presence of the metal oxide/Cu interface lowers significantly the limiting potentials of electrochemical CO<sub>2</sub> reduction from that on Cu. Furthermore, the activity and product selectivity can be regulated by tuning the nature of (MO)<sub>4</sub>/Cu(100) and selecting appropriate solvent.

## Multireference algebraic diagrammatic construction theory for accurate simulations of UV/Vis and X-ray absorption spectra of strongly correlated molecules

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*Ab initio* computational methods serve a critical role in the interpretation of many experimental photochemical processes, with the aim of understanding how the physical properties of molecules may change in response to absorbing light of a particular wavelength. Algebraic diagrammatic construction (ADC) theory is a routinely used class of many such theoretical methods, as it achieves a good balance of computational cost and accuracy in calculating the excited state properties of molecules. However, ADC theory has been shown to be unreliable when simulating excitation energies of molecules that are known to exhibit strong electron correlation in their ground and excited states. In this work, we present the strict and extended second-order formulations of multireference ADC (MR-ADC(2) and MR-ADC(2)-X), which combine the descriptions of static and dynamical electron correlation to accurately predict the excitation energies and excited state properties of strongly-correlated molecules. We describe the theoretical framework of these implementations and present an extensive benchmark of these methods for calculating the UV/Vis and X-ray absorption spectra of many weakly- and strongly correlated systems.

Complex electronic structure of LuF and its spectroscopic and thermochemical properties

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Ab initio methods including both scalar and spin-orbit relativistic effects were used to investigate the bond dissociation energies (BDEs) of LuF. Since the 1960s, experimental BDE measurements many lanthanide diatomics including lanthanide fluoride molecules such as LuF have varied mainly due to the use of empirical models and the lack of direct measurements. Thus, computational approaches can provide new insight about these species. Here, a number of single-and multireference wavefunctions methods have been utilized, and a total of 132 states, including four dissociation channels  $Lu(^{2}D) + F(^{2}P)$ ,  $Lu(^{2}P) + F(^{2}P)$ , and two  $Lu(^{4}F) + F(^{2}P)$  have been described.

#### Theoretical Investigation of Cyclic Ketone Reactions with OH Radicals: Effects of Conjugation

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Free radicals found in the combustion environments, such as the OH radical, propagate chemical schemes and initiate chemical reactions. The reaction of OH with conjugated ketone molecules may lead to the formation of resonance stabilized products. Such resonance-stabilized adduct comparatively much more stable than other possible radical intermediates and may play an important role during the combustion scheme by affecting reaction progress with comparatively lower relative energy values. In this study, we examine the reaction of two biofuel combustion intermediates, cyclohex-2-en-1-one and cyclohex-3-en-1-one with the OH radical with geometry optimization using B3LYP/CBSB7 and energy calculations and transition state optimization using CBS-QB3 methods. The entrance channel for both reactions was examined with geometry optimization using  $M062X/6-311++G^{**}$  with energy calculations using CCSD(T)/cc-pVTZ. All calculations were preformed using Gaussian 16 and the West Virginia University Thorny Flat Cluster under National Science Foundation Major Research Instrumentation Grant #1726534. The effects of stereochemical addition are considered in the formation of intermediates and final products. It is found that there is a higher energetic barrier in the transition state upon isomerization from the van der Waal's complex to the resonancestabilized adducts when compared to formation of non-resonance-stabilized adducts.

#### Assessment of the Influence of Self-interaction Error on predicting Magnetic Exchange Coupling Constants using Three Self-interaction Correction Methods

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Accurate theoretical determination of magnetic exchange couplings (J) is necessary to describe the strength and nature of the coupling, especially for large, multicenter magnetic complexes where experimental measurements become challenging. Although density functional theory (DFT) is among the most popular methods used in computational studies, self-interaction error (SIE) could impact the accurate prediction of J couplings. Here, the role of removing SIE in evaluating J couplings is benchmarked using three self-interaction correction (SIC) methods, namely, Perdew-Zunger-SIC (PZ-SIC) [1], the orbitalwise scaled SIC (OSIC) [2], and the local scaling (LSIC) [3] methods. Both spin-projected and non-projected Js for representative cases of different magnetic interactions, including H-He models, organic radical molecules, and chlorocuprate, are evaluated. Our results reveal that PZ-SIC performs well for systems dominated by single-electron regions, while the overcorrection of the J is observed in most complexes. In contrast, LSIC shows better predictions than PZ-SIC in the set of organic systems and chlorocuprate. Besides, both density and energy corrections are needed to improve the J prediction. Finally, SIC methods must be used with care since each method shows different performances in different cases.

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[1] Perdew, J. P.; Zunger, A., *Phys. Rev. B*, **1981**, 23(10), 5048.

[2] Vydrov, O. A. et al., J. Chem. Phys., 2006, 124(9), 094108.

[3] Zope, R. R. et al., J. Chem. Phys., 2019, 151(21), 214108.

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Submit as contributed presentation

#### Studying Interparticle Interactions of Polymer-Grafted Nanoparticles in Solution via Coarse-Grained Molecular Dynamics Simulations

By grafting polymer chains onto nanoparticles (creating PGNs), one can precisely control interparticle interactions. PGNs are typically synthesized and processed in solution before use in applications such as flexible electronics where a precise spacing of inorganic particles in a robust and flexible matrix is desirable. Understanding their solubility and interactions in solution is crucial to control their structure during deposition and drying. We use coarse-grained molecular dynamics (MD) simulations to study the effective interactions between two PGNs in implicit solvent. Specifically, we use a Kremer-Grest type of model for graft chains and attach these to the surface of spherical nanoparticles ten times the monomer size. Monomers interact via mixed Lennard-Jones potentials; the repulsive part is kept constant while an attractive part is added with adjustable strength to consider various solvent strengths. Nanoparticle interactions are of an integrated form as though they are composed of a uniform melt density of monomers. We analyze polymer conformations around individual PGNs and the overlap between polymer canopies for pairs of PGNs at different solvent strengths. We also calculate the potential of mean force between PGNs and find a relatively sudden onset of a deep attractive well with increasing solvent strength, due to the collective interactions of many chains; the implications for solution behavior will be discussed.

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#### Basis Set Dependence of Optical Rotation Calculations with Different Choices of Gauge

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#### Abstract

In this work, the basis set dependence of optical rotation (OR) calculations is examined for various choices of gauge/level of theory. The OR is calculated for a set of 50 molecules using B3LYP and CAM-B3LYP, and 17 molecules using coupled cluster with single and double excitations (CCSD). The calculations employ the correlationconsistent basis sets, aug-cc-pV $\zeta$ Z with  $\zeta = D, T, Q$ . An inverse-power extrapolation formula is then utilized to obtain OR values at the complete basis set (CBS) limit. We investigate the basis set convergence for these methods and three choices of gauge: length gauge (with gauge-including atomic orbitals, LG(GIAOs), for DFT), the origin-invariant length gauge [LG(OI)], and the modified velocity gauge (MVG). The results show that all methods converge smoothly to the CBS limit and that the LG(OI) approach has a slightly faster convergence rate than the other choices of gauge. While the DFT methods reach gauge invariance at the CBS limit, CCSD does not. The significant difference between the MVG and LG(OI) results at the CBS limit, 26%, indicates that CCSD is not quite at convergence in the description of electron correlation for this property. On the other hand, gauge invariance at the CBS limit for DFT does not lead to the same OR values for the two density functionals, which is also due to electron correlation incompleteness. A limited comparison to gas-phase experimental OR values for the DFT methods shows that CAM-B3LYP seems more accurate than B3LYP. Overall, this study shows that the LG(OI) approach with the augcc-pVTZ basis set for DFT, and with the CBS(DT) extrapolation for CCSD, provides a good cost/accuracy balance.

Title: Aromaticity and η<sup>8</sup> Actinide Complexation of Cyclooctapnictogen Dianions
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**Abstract:** Complexation of aromatic rings to metal centers forms the foundation of both organotransition metal and organoactinide chemistry. Ferrocene,  $(\eta^5-C_5H_5)_2Fe$ , represents a landmark example of the former, while uranocene,  $(\eta^8-C_8H_8)_2U$ , was the first example of the latter when reported in 1968. Since then, a multitude of different sandwich complexes have been synthesized; however, organic rings have largely dominated the space due to the availability of myriad aromatic organic ring systems. This has not prevented chemists from coordinating inorganic ring systems to metals; for example, complexation of the aromatic P<sub>5</sub><sup>-</sup> fragment to iron to form the mixed-ring sandwich compound  $(\eta^5-C_5Me_5)(\eta^5-P_5)Fe$  was demonstrated in 1987.

To expand the area, we undertook computational studies of the aromaticities and complexation abilities of cyclic octapnictogen dianions ( $Pn_8^{2-}$ ). Theoretically isolobal with cyclooctatetraenyl dianion ( $COT^{2-}$ ), these rings represent actinocene-compatible analogues of the  $P_5^-$  ligand. All permutations of  $Pn_8^{2-}$  were investigated to determine their structures, aromaticities, and stabilities toward distortion/decomposition. Optimizations of the rings typically gave planar configurations, which frequency analyses showed were energetic minima. NICS<sub>zz</sub> calculations for several  $Pn_8^{2-}$  rings showed ring currents consistent with aromaticities similar to that of  $COT^{2-}$ .

Optimizations of mixed-ring actinocene analogues ( $\eta^{8}$ -C<sub>8</sub>H<sub>8</sub>)( $\eta^{8}$ -Pn<sub>8</sub>)An (An = Th, U, Pu) showed that the complexes adopted sandwich-style structures. Loewdin and molecular orbital analyses for several examples indicated bonding with covalent character between the actinides and Pn<sub>8</sub><sup>2–</sup> rings. The degrees of covalency varied with the actinide and with the components of the inorganic ring. Inclusion of relativistic effects proved key in examining stabilities and covalencies.

Efficiently capturing Post-Hartree-Fock and large basis set effects in *ab initio* molecular dynamics using graphical decomposition of molecular structure

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We present a graph-theoretic approach to adaptively compute local many-body approximations in an efficient manner to perform (a) accurate post-Hartree–Fock (HF) ab initio molecular dynamics (AIMD) at density functional theory (DFT) cost for medium- to large-sized molecular clusters, (b) hybrid DFT electronic structure calculations for condensed-phase simulations at the cost of pure density functionals, and (c) reduced-cost on-the-fly basis extrapolation for gas-phase AIMD and condensed phase studies. The salient features of our approach are ONIOM-like in that (a) the full system (cluster or condensed phase) calculation is performed at a lower level of theory (pure DFT for condensed phase or hybrid DFT for molecular systems), and (b) this approximation is improved through a correction term that captures all many-body interactions up to any given order within a higher level of theory (hybrid DFT or CCSD for condensed phase; CCSD or MP2 for molecular clusters), combined through graph-theoretic methods. Specifically, a region of chemical interest is partitioned into a set of nodes and these nodes are then connected to form edges based on a given definition of local envelope (or threshold) of interactions. The nodes and edges together define a graph, which forms the basis for developing the many-body expansion. The methods are demonstrated through *ab initio* dynamics studies on protonated water clusters and poly-peptide fragments, and conformational stabilization and lattice energy studies on homogeneous and heterogeneous surfaces of water with organic adsorbates using two-dimensional periodic boundary conditions. A critical hallmark of our approach is the simultaneously invoking of multiple electronic structure packages to assemble the energy and forces for the full system. Indeed, in this presentation we illustrate this utility with the mixing of Quantum Espresso, Psi4, and Gaussian16 for the evaluation of each time-step in the computation of AIMD simulations and also the energetic benchmarks. This approach works in parallel with an adaptive, dynamic scheduler which can run simultaneous calculations across computational nodes on multiple supercomputer clusters.

#### Influence of the Clay Structure and Composition on the Adsorption and Dynamics of PFAS – A Molecular Dynamics Investigation

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Soil and sediments represent pathways for the near- and sub-surface transport of poly- and perfluorinated alkyl substances (PFAS) – substances which have been linked to a number of significant health concerns including developmental and autoimmune disorders. Because of the potential exposure to humans and animals, it is important to understand the fate and transport of PFAS in the environment. Clay minerals are important mineral fractions of soils and sediments and the presence of nano- and meso-confined pores present in clays makes them an ideal substrate to adsorb and limit the transport of PFAS in near-surface regions. Thus, in this study, the interactions of a PFAS alternative with critical mineral components of soils have been examined using classical molecular dynamics (MD) simulations. Our studies will clearly demonstrate how structures, mineralogical composition, and surface charge distribution can be responsible for the adsorption behavior of PFAS in the meso-confined pores of these minerals. This is one of the first studies to provide molecular level insight on PFAS molecules/alternatives in soil environments.

#### The Environment of Theoretical Chemistry at the Nexus of Army and Civil Works Research

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This poster will highlight the research expertise of the Computational Chemistry Team (CCT), located at the U.S. Army Corps of Engineers (USACE) Engineer Research and Development Center (ERDC), Vicksburg, Mississippi. We will present the capabilities available in the team, the project environment the team operates in, and potential ways to get involved. The CCT is uniquely situated to support applied solutions to our nation's military and infrastructure requirements, and provides premiere research and development into materials, the environment, and arctic domains. The team currently consists of 11 PhD computational chemists with expertise in electronic structure and excited state modeling, reaction pathways, surface interactions and reactivity, approximated methods for quantum chemistry (including, but not limited to, DFTB and machine learning), molecular dynamics of solvation phenomena, partitioning, shock and materials properties, and coarse-grain models. This expertise fuels success in projects ranging from basic research of fundamental phenomena up through prototype technologies for applied use in the field. Recent projects to highlight include PFAS degradation and removal, environmental contaminant modeling, polymer nanocomposite materials, sensors based on molecular imprinting polymers, de novo peptide design, and ionic-liquid-mediated topological effects.

Computational predictions of a modified Wimley-White scale to account for anionic lipids

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Understanding the thermodynamics of how membrane-active peptides (MAPs) partition into membrane surfaces has been an ongoing challenge since Wimley and White (WW) characterized their residue-specific free energy scale almost 30 years ago. This fundamental understanding is a critical component in being able to design MAPs with tunable binding affinities to specific membrane environments (e.g., bacterial, eukaryotic, cancerous). However, it is clear that once the WW scale is applied to membrane environments that are more complex than containing only phosphatidylcholine (PC), the direct correlation between theory and experiment no longer holds true. In particular, electrostatics and surface potential penalize the free energy gain of the process of partitioning into the membrane. We hypothesize that the inclusion of charge effects in the WW scale can be accounted for by a linear relationship that is non-additive with respect to hydrophobic interactions. To test this hypothesis, we conducted umbrella sampling (US) simulations to model the partitioning of a pentapeptide into bilayers with increasing anionic lipid compositions. The central amino acid residue in the pentapeptide was substituted for all 20 amino acids to calculate the residue-specific free energy of partitioning. Our results show that as the fraction of anionic lipids increases, electrostatic effects are less significant for the partitioning of charged and/or polar residues. The data obtained here creates the framework for a modified WW scale that accounts for electrostatic effects in addition to hydrophobicity. This framework can then be used for intelligent design of membrane active peptides that are effective in a range of biological membrane environments.

#### Strong Electron Correlation from Standard Density Functional Approximations via Partition-DFT

#### Yi Shi and Adam Wasserman

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Standard approximations for the exchange-correlation (XC) functional in Kohn-Sham-DFT (KS-DFT) typically lead to unacceptably large errors when applied to strongly- correlated electron systems. Partition-DFT is a formally exact reformulation of KS-DFT in which the ground-state density and energy of a system is obtained through self-consistent calculations on isolated fragments. Here we show how the typical errors of the standard approximations in KS-DFT can be largely avoided through Partition-DFT even when the same approximations are applied to the fragments. Our method is illustrated with Partition-DFT calculations on simple models of "strongly-correlated" hydrogen chains, for which numerically exact results are available. With a simple "overlap approximation" (OA) for the partition energy, the binding curves of the hydrogen chains are significantly improved. We are also exploring whether the OA gives a quantitatively correct description of the quasi-longrange antiferromagnetic correlations observed in stretched strongly-correlated hydrogen chains.

## Suppressing exchange-correlation errors through a Generalized Overlap Approximation in Partition-DFT

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Quantum embedding methods can in principle lead to linear scaling and multilevel-accuracy calculations (beyond standard Kohn-Sham approximations) of electronic properties of molecules and materials. Partition Density Function Theory (P-DFT), a density-based embedding method, features a unique interaction potential and in many cases fragments with fractional numbers of electrons. An "overlap approximation" (OA) for the partition energy of P-DFT has been shown to eliminate energy and density errors caused by the underlying exchange-correlation approximations, such as delocalization and static-correlation errors. We have revised the OA and demonstrated its applicability to challenging systems of strong fragment interaction such as N<sub>2</sub> and Cr<sub>2</sub>. As part of the revised OA, a neural-network based overlap-functional has been trained to improve over the conventional error-function based functional.

## Quantum Neural Networks for Analyzing X-Ray Scattering Data

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Determining the chemical structures of molecules from scattering cross-sections has been a long-standing problem in chemistry. To date, it is accomplished by performing molecular dynamics simulations that are extensively resource-consuming and often give unphysical structures. Moreover, with the advent of ultrafast-pulsed X-ray free-electron lasers (XFELs), which provide high-resolution images of molecules undergoing structural and electronic changes, the data size is growing rapidly that would soon render classical approaches incapable. In this project, we are looking for a solution to this data deluge using Quantum Machine Learning (QML). QML has shown great potential in dealing with such problems while using exponentially smaller resources. We demonstrate here the working of a Hybrid Quantum-Classical Neural Network (HQCNN) architecture on a Noisy Intermediate-Scale Quantum (NISQ) processor. The aim is to predict the molecular coordinates (like bond length and bond angle) of N-Methylmorpholine using the X-ray scattering cross-section data.

First, the n-dimensional classical data is mapped onto O(log n)-qubits using Amplitude Encoding in O(n) time. Then the parametrized quantum circuit maps the input data into output. The parameters of the QNN are optimized on a classical computer via gradientbased methods. The cost function evaluated using quantum circuits can be parallelized to get massive speed-ups, and the state preparation scheme can be made more efficient in the future with access to a qRAM. Ultimately, we benchmark the QML model on current NISQ computers. Interestingly, the QML algorithm gets insights into the mapping using only a few qubits and small datasets. For models of comparable sizes, QNN even performs better than a classical NN. The results demonstrate the advantages of quantum computing and machine learning in discovering trends in big data. We can reveal fundamental principles of molecular reactions by efficiently predicting the molecular structures from the X-ray scattering data.
# Quantifying and reducing spin contamination in algebraic diagrammatic construction theory of charged excitations

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Many electronic structure methods rely on Hartree-Fock (HF) theory to provide reference orbitals for calculating accurate electron affinities (EA) and ionization potentials (IP). One of those methods is algebraic diagrammatic construction theory (ADC), which provides a computationally efficient approach for calculating accurate EAs and IPs. For open-shell systems specifically, ADC relies on an unrestricted HF (UHF) reference that can be plagued with spin contamination (SC) error, in which the wavefunction is not a true eigenfunction of the spin squared operator,  $\hat{S}^2$ . In this work, we assess the accuracy of ADC by calculating EAs and IPs for many open-shell molecules with different degrees of SC in the ground electronic state. Following this assessment, we benchmark the accuracy of ADC combined with other types of reference orbitals, such as: 1) orbital-optimized Møller-Plesset perturbation theory (OMP) and 2) restricted open-shell HF (ROHF). Our results demonstrate that for strongly spin contaminated systems, both OMP and ROHF reference orbitals reduce the spin contamination and energy errors in the electron-attached and ionized states simulated using ADC.

## Time-Dependent Configuration Interaction Applications for the Attosecond Scale

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Time-dependent quantum methods can be used to provide an accurate description of electron dynamics at the femtosecond/subfemtosecond time scale. By modeling interactions under the influence of a strong electric field, and using a time-dependent configuration interaction (TDCI) approach[1], high harmonic spectra for diatomic systems can be obtained and predictions can be made about the electronic motion of systems, from main group to transition metal species. The latter is accomplished with Orbkit[2], a Python utility program, which can use configuration state occupancies to model the electron flux of systems.

#### References

- [1] Ulusoy, Inga S. and Stewart, Zachary and Wilson, Angela K., J. Chem. Phys. 148, 014107 (2018)
- [2] Hermann, Gunter and Pohl, Vincent and Tremblay, Jean Christophe and Paulus, Beate and Hege, Hans-Christian and Schild, and Axel, *J. Comp. Chem.* **37**, 1511-1520 (2016)

### Nuclear Quantum Effects Are Important in Studying the Conformer Distributions of RNA Building Blocks

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Nuclear quantum effects have been shown to modulate the distribution of various organic compounds and protein model compounds. However, this is not well studied in the case of RNA or DNA, which are critical to life. Ring polymer molecular dynamics was used to incorporate nuclear quantum effects into the simulation of dinucleotides, and results were compared to those from analogous classical molecular dynamics simulations where quantum uncertainty of the position of the nucleus is not incorporated. We found that the conformer distribution was affected significantly when nuclear quantum effects were incorporated at room temperature; however, these become less significant at higher temperatures where the systems approach the classical limit. Comparison with existing NMR and thermodynamical data suggests greater agreement between experiment and simulated results.

AMOEBA Force Field Calculated Exciton Polarization Energy of Bulk Aromatic Hydrocarbons

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#### Abstract:

Development of organic semiconductors and light sensitizers for organic photovoltaics (OPVs) has gained interest as an alternative to traditional metallic and rare metal materials for semiconductors and PVs. For traditional metals and semiconductors with large dielectric constants and weak exciton binding, dissociation of the electron from the hole is relatively facile. However, in systems where the exciton is more tightly bound or localized (Frenkel or Charge Transfer Excitons) and binding energy is in orders of magnitude greater, charge separation and charge transport have a significant impact on device efficiency. Intermolecular interactions play a large role in the more tightly bound excitonic systems, of which organic molecular solids are included. Chief among these interactions is the polarization energy. The magnitude of polarization energy in relation to intermolecular interactions has an adverse effect on charge mobility, charge separation and semiconductor efficiency. Additionally, exciton polarization energy plays a role in the energy of exciton splitting. This can have an adverse effect on the band structure of organic thin films; potentially changing the type of Kasha aggregation being ascribed to differing intermolecular conformations.

In this work, the state specific atomic polarizability (SSAP) was utilized to calculate the polarization energy of small oligoacenes in order to take into account electron density and molecular orientation. Here, we calculate the polarization energy of the positive and negative charge carriers, as well as the exciton polarization energy utilizing the SSAPs and the AMOEBA force field in order to assess how bulk conformation effects charge mobility and energy of charge transfer. By calculating the bulk polarization energy of small aromatic hydrocarbons such as benzene and anthracene in their crystal and amorphous conformations, we can explore the relationship between molecular disorder and charge mobility. Calculation of the exciton polarization energy will allow us to examine disorder's effect on the energy of charge transfer.

# **EE-ONIOM-CT** method to efficiently account for the missing interactions in ONIOM: Energies and Analytic Gradients

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#### Abstract

Hybrid methods such as ONIOM are widely used for the study of local processes in large systems. However, the intrinsic need for system partition leads to less-than-desirable performance for many chemical processes. This is due to the missing interactions in the chemically important model region (i.e., active site) at the high-level theory. The missing interactions can be categorized into two classes, viz. charge transfer (i.e., charge reorganization between regions) and long-range electrostatic interactions. Our group has presented two entirely different methods to treat these deficiencies individually. ONIOM-CT and ONIOM-EE methods have been demonstrated to improve the performance of ONIOM by incorporating charge transfer and missing electrostatic interactions, respectively.

In general, the separation of missing interactions into two individual categories may not be sufficient to reach high accuracy. Thus, it is highly desirable to develop a method to correct both deficiencies simultaneously. Our new method aims at connecting the methods ONIOM-CT and ONIOM-EE for a more comprehensive treatment. We employ a stepwise procedure by first satisfying ONIOM-CT condition for charge balance before accounting for the electrostatic interactions from the rest of the system while keeping the model region density unchanged. We will demonstrate our method using embedding charges determined from a Mulliken population analysis. The analytic gradient expressions for this method have been derived and implemented. They require solving three sets of z-vector self-consistent equations, one for the full system at the low-level, and one each for the model system at low-level and high-level. Nevertheless, our implementation is efficient, and is assessed against full system calculations at high-level theory for sample problems involving proton transfer and other reactive processes.

### Machine Learning Corrections for Dispersion Interactions in Symmetry-Adapted Perturbation Theory

Corentin Villot and Ka Un Lao

Department of Chemistry, Virginia Commonwealth University 1001 W Main St, Richmond, VA 23284 May 16, 2022

The highly non-local nature of the dispersion component of interaction energy has proven difficult to efficiently model. To overcome this challenge, several correction schemes, including D3 and many-body dispersion (MBD), have been developed for density functional theory, and more recently used as the replacement of the dispersion component in (extended) symmetry-adapted perturbation theory [(X)SAPT]. The empirical nature of these replacements necessitates careful parametrization with high-quality data, and a re-parameterization of MBD and D3 was proposed using thousands of benchmark dispersion values calculated at the level of SAPT2+(3)(CCD)/aug-cc-pVTZ. The MBD model of dispersion is further improved using machine learning (ML) models, increasing its accuracy by at least a factor of two with good transferability in various types of systems. The proposed (X)SAPT+MBD-ML model provides an efficient and accurate way to obtain the dispersion contribution in (X)SAPT calculations.

# A quantum algorithm for evolving open quantum dynamics on quantum computing devices

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#### Abstract

Designing quantum algorithms for simulating quantum systems has seen enormous progress, yet few studies have been done to develop quantum algorithms for open quantum dynamics despite its importance in modeling the system-environment interaction found in most realistic physical models. In this work we propose and demonstrate a general quantum algorithm to evolve open quantum dynamics on quantum computing devices. The superoperators that govern the time evolution can be converted into unitary matrices with minimal dilation guaranteed by the Sz.-Nagy theorem. This allows the evolution of the initial state through unitary quantum gates, while using significantly less resource than required by the conventional Stinespring dilation. We demonstrate the algorithm on an amplitude damping channel and a spin-boson two level system using the IBM Qiskit quantum simulator and the IBM Q quantum devices. The proposed algorithm does not require particular models of dynamics or decomposition of the quantum channel, and thus can be easily generalized to other open quantum dynamical models.

# Light-induced spin flipping in transition metal complexes via *ab initio* real-time electron dynamics

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Spin transitions in transition metal complexes have a number of important applications including solar energy conversion, sensing, and information technology. Theoretical treatments of these processes have proven challenging due to the complex static and dynamic correlation inherent to transition metal systems which generally require the use of multiconfigurational wavefunctions. The time-dependent spin-orbit configuration interaction (TDSOCI) method [1] is a real-time electron dynamics method for simulating spin transitions of molecules in an external time-dependent electric field. The inclusion of spin-orbit coupling allows for a mapping between spin-mixed and spin-pure states in an explicitly time-dependent manner. The method is applied to study the effects of ultrafast laser pulses on spin transitions in Fe-containing complexes.

#### References

[1] I.S. Ulusoy and A.K. Wilson, Phys. Chem. Chem. Phys. 21, 7265 (2019).

**Title:** Modeling near-field effect on molecular excited states using the Discrete Interaction Model/Quantum Mechanical Method.

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Abstract: Strong light-matter interactions can drastically change molecular optical properties. The growing demand to understand such optical behavior motivates theoretical studies on single molecule and multiple molecules in the strong coupling regimes. Here, we use the discrete interaction model/quantum mechanical (DIM/QM) method. This hybrid method offers QM level description for the molecule and classical electrodynamics description for the larger nanoparticle. In this work, we extend the DIM/QM method to include the local field effects on the molecular excited states. We perform a study on how multiple electronic transitions couple to the local field. We find that the inclusion of more electronic transitions will be essential when the molecular resonance is off-resonance with the surface plasmon. We also look at the light-matter coupling strength when intermolecular interaction is present. We notice that the intermolecular interaction will lower the coupling strength through detuning the molecular resonances from the surface plasmon.

#### Pressure dependence of ozone forming reaction

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The process of ozone (O<sub>3</sub>) formation was a topic of intense experimental and theoretical studies over several last decades. Detailed understanding of the mechanism of this reaction is important for many aspects of atmospheric chemistry, geosciences and even for geo-biology. Recombination reactions, like the one that forms ozone, are often described by the Lindeman mechanism (the energy-transfer mechanism) that works through a broad range of pressure values.<sup>1,2</sup> In the first step, the metastable ozone molecule (O<sub>3</sub><sup>\*</sup>) are formed from oxygen atoms and molecules. The second step is stabilization of the metastable complex to a stable ozone by collision with bas gas [M] (e.g. Ar, N<sub>2</sub>):

$$0 + 0_2 \rightarrow 0_3^*$$
  
 $0_3^* + [M] \rightarrow 0_3 + [M]^*$ 

As it can be seen from Fig. 1, experimental rate coefficient is roughly constant (~ $6 \times 10^{-34}$  cm<sup>6</sup>/s) in the low pressure limit.<sup>3</sup> However, when pressure is above 1 bar (high-pressure range) it starts deacreasing.<sup>4,5</sup> Therefore, the main goal of this research is development of a model which predicts a "plateau" at low pressure and some "fall-off" at high pressure, and fits the available experimental data. For the model, we use as input the energies and lifetimes of rotational-vibrational states accurately computed in our group. Bound states and scattering resonances above dissociation threshold are both included. Good agreement with experiment is obtained if the state-to-state transition cross sections are used as fitting parameters.



Figure 1. Pressure dependence of the third-order recombination rate coefficient. Green line corresponds to our theoretical model, while colored symbols illustrate experimental data.

#### **References:**

- <sup>1</sup> A. Teplukhin, D. Babikov. J. Phys. Chem. A 122, 9177-9190 (2018).
- <sup>2</sup> A. Teplukhin , I. Gayday, D. Babikov. J.Phys. Chem. 149, 164302 (2018).
- <sup>3</sup>Lin, C. L., M. T. Leu. Int. J. Chem. Kin. 14.4, 417-434 (1982).
- <sup>4</sup> De Cobos, AE Croce, J. Troe. Int. J. Chem. Kin. 16.12, 1519-1529 (1984).
- <sup>5</sup> Hippler, H., R. Rahn, J. Troe. J. Chem. Phys. 93.9, 6560-6569, (1990).

### Local Analysis of Ion Structure and Dynamics in Coarse-Grained

### Simulations of Block Copolymer Electrolytes with Homopolymer

### Additives

#### Yuanhao Zhang; Mengdi Fan; Lisa M. Hall

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Salt-doped block copolymers (BCP) are promising solid electrolytes because of their ability to form two distinct microphases which allow for ionic conductivity along with significant mechanical strength. Recent study has shown that the addition of relatively high molecular weight (MW) homopolymers of the same chemistry as the conductive phase will form a relatively mobile homopolymer-rich region with higher ion concentration in the center of conducting microphase, leading to a higher overall ion conductivity. We use coarse-grained molecular dynamics simulations to understand the correlation between the distribution of each component (influenced by the chain length and concentration of ions and additives) and the local motion of ions or ion conductivity. We use a simple bead-spring model with Lennard-Jones (LJ) interactions between all beads, Coulomb interactions between ions, and additional solvation interactions of the form  $-1/r^4$  between ions and the beads of the conducting block. Microphase separation is driven by relatively unfavorable LJ interactions between conducting and non-conducting type beads, and the dynamics of the nonconducting beads are slowed (T<sub>g</sub> is increased) by increasing the like-like LJ interaction strength for those beads. We analyze the distribution of ions and homopolymers with different MWs. We also calculate the local ion mobility as a function of distance across the microphase domain, showing clear differences in the dynamic behavior of ions based on on their location. The local polymer relaxation time and number of ion neighbors around a given ion will also be discussed to explain the mobility distribution.

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award DE-SC0014209

### Accelerating ab-initio calculations using semiempirical methods <u>Zehao Zhou</u><sup>1</sup>, Shane M. Parker<sup>1</sup> 1.Case Western Reserve University, Cleveland, 44016, Ohio

We report a general strategy to speedup Time-Dependent Density Functional Theory (TDDFT) calculations of molecular response properties by leveraging semiempirical models. Instead of replacing expensive ab-initio methods with cheap semiempirical methods, we use the semiempirical methods to accelerate the ab-initio calculations. As an example, we use a semi-empirical preconditioner in the iterative Davidson algorithm to accelerate the TDDFT excitation energy calculation, acquiring a cost reduction of 37-70%. The crucial advantage of using the semi-empirical preconditioner is that the converged result is unchanged, so there is no tradeoff between accuracy and speedup. Moreover, the preconditioner can be further improved by tuning the empirical parameters that define the semiempirical model, leading to an additional cost reduction of 10 to 20%. A promising application of our work is non-adiabatic molecular dynamics, where significant cost reduction should be expected since excitation energies are computed millions of times.

### Funding acknowledgment

This work was supported by a startup fund from Case Western Reserve University. This work made use of the High Performance Computing Resource in the Core Facility for Advanced Research Computing at Case Western Reserve University.

# Graph theoretic molecular fragmentation augmented with machine learning for multi-dimensional electronic potential energy surfaces

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#### Abstract

Accurate electronic structure calculation and molecular dynamics calculations have steep and in many cases exponential, computational cost. This work discusses new approaches that utilize machine learning and graph theory, and will be generalized to include quantum computing algorithms as part of future developments, to address these key challenges. To overcome the steep algebraic complexity of electronic structure calculations, many fragmentation methods have been developed. In our case, the Ivengar group has also introduced a graph-theoretic description for molecular fragmentation that has connections to dynamic programming in computer science. Here, a system is divided into a set of nodes, or vertices, that are then connected through edges, faces and higher order graph theoretic objects known as simplexes, to represent a collection of asynchronous, but locally interacting sub-systems. Each such sub-system is treated in our case at two levels of electronic structure theory, and the result is used to construct perturbative many-body expansions. These expansions converge rapidly with many-body order (or graphical rank) of subsystems and have been previously used for molecular dynamics calculations, and for computing multi-dimensional potential energy surfaces. Specifically, in all these cases we have shown that coupled cluster level dynamics trajectories and potential surfaces may be obtained at DFT cost. The approach has been demonstrated for gas-phase dynamics studies, for condensed phase electronic structure calculations, and also for basis set extrapolation based dynamics.

In this poster, we will introduce a *family of neural networks* (NN) from machine learning, that are asynchronous and act in parallel, to represent efficiently, the post-Hartree-Fock electronic structure energy contributions for all simplexes (fragment sub-systems). The approach is particularly useful when coupled cluster accuracy is desired. Towards this, we use a unique multi-dimensional tessellation/clustering algorithm where the multi-dimensional molecular space is treated as a learning space that is then tessellated based on some pre-determined density measures. This tessellation/clustering scheme is used to determine our training data used for machine learning. These are then used to extrapolate, through fully connect dense neural networks, the energies for molecular dynamics trajectories at one-tenth the cost as compared to a regular fragmentation-based dynamics calculation. A molecular aggregate (water cluster in this case) is treated as a graph and each node, edge, triangle, tetrahedron, etc. in the graph have an independent machine learning model. For future work, given that our neural networks are constructed for molecular fragments that may be part of larger systems, we probe the potential for this approach to allow the construction of a transfer-learning approach where we "learn" from a smaller system and predict for a similar larger system. These methods will be used to study organic reactions on water surfaces.

# PigmentHunter: An online graphical computational tool for excitonic calculations on chlorophyll proteins

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We report the development of an online application called PigmentHunter that enables "pointand-click" simulation of excitonic spectra of chlorophyll proteins based on PDB structures. PigmentHunter uses the nanoHUB.org science gateway to link a graphical user interface to a high-performance computing backend. The application automates the process of:

- Importing structural data from PDB files and classifying recognized photosynthetic pigments (chlorophylls, bacteriochlorophylls, and pheophytins)
- Calculating inter-pigment coupling values using point-dipole coupling (PDC) and transition electrostatic potential (TrESP) methods
- Calculating site energy values using normal-coordinate structural decomposition (NSD) calculations
- Introducing point mutations into the protein structures
- Preparing and running molecular dynamics (MD) simulations
- Predicting pigment site energies using the charge density coupling (CDC) method
- Simulating absorption and circular dichroism (CD) spectra of the protein complex

Mutation induced frequency shifts calculated using the PigmentHunter application agree well with experimental values for a series of point mutants of the water-soluble chlorophyll protein from *Lepidium virginicum*.

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The following is a list of all registered participants, alphabetical by family name.

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- 99. Emmeline Riendeau (Purdue)
- 100. Benoît Roux (University of Chicago)
- 101. Alexander Rusakov (Oakland University)
- 102. Daniel Sadowsky (University of Pittsburgh-Bradford)

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- 104. Manas Sajjan (Purdue)
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# **Conference History**

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51.	2019	University of Notre Dame	25.	1992	Michigan State University
50.	2018	University of Chicago	24.	1991	Northern Illinois University
49.	2017	Michigan State	23.	1990	University of Wisconsin, Madison
48.	2016	University of Pittsburgh	22.	1989	Indiana UPurdue U. Indianapolis
47.	2015	University of Michigan, Ann Arbor	21.	1988	Argonne National Laboratory
46.	2014	Northwestern University	20.	1987	University of Pittsburgh
45.	2013	University of Illinois at Urbana-Champaign	19.	1986	Indiana University at Bloomington
44.	2012	University of Wisconsin, Madison	18.	1985	Marquette University
43.	2011	University of Notre Dame	17.	1984	Southern Illinois University
42.	2010	Purdue University	16.	1983	Northwestern University
41.	2009	Southern Illinois University	15.	1982	Michigan State University
40.	2008	University of Michigan	14.	1981	University of Chicago
39.	2007	Indiana University	13.	1980	University of Minnesota
38.	2006	Ohio State University	12.	1979	Purdue University
37.	2005	University of Missouri, Columbia	11.	1978	Battelle's Columbus Laboratories
36.	2004	Michigan State University	10.	1977	Argonne National Laboratory
35.	2003	Iowa State University	9.	1976	Northern Illinois University
34.	2001	University of Minnesota	8.	1975	University of Wisconsin, Madison
33.	2000	University of Iowa	7.	1974	University of Kentucky, Lexington
32.	1999	University of Notre Dame	6.	1972	Michigan State University
31.	1998	Purdue University	5.	1971	Indiana University at Bloomington
30.	1997	University of Illinois at Urbana–Champaign	4.	1970	Iowa State University
29.	1996	Indiana UPurdue U. Indianapolis	3.	1969	University of Minnesota
28.	1995	Northwestern University	2.	1968	University of Wisconsin, Madison
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