Crawford Research Group

Department of Chemistry, Virginia Tech

The Group

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Advanced Research Computing

General
- 20k cores
- 1.8 PFLOPS
- 4 major compute clusters

Capacity
- Hundreds of concurrent jobs
- Additional long-term storage
- Data publication with VTData

Specialization
- Large-scale CPU nodes
- GPU acceleration
- "Big data" nodes (>TB scratch)
- High-MEM (128GB) nodes
- IBM "Minsky" for Deep Learning

Psi4 Quantum Chemistry Suite

Psi4 Features

- Arbitrarily high angular momentum in integrals and derivative integrals.
- New coupled cluster codes including RHF, ROHF, UHF, and Brueckner references with CCSD and CCSD(T) methods.
- Excitation energy methods, including RPA, CIS(D), EOM-CCSD, CC2, and CC3.
- Coupled cluster linear response for dipole polarizabilities and optical rotation.
- Determinant-based CI methods, including CASSCF, RASSCF, RAS-CI, Full CI.
- Integral-direct SCF, MP2, and MP2-R12 energies.
- Diagonal Born-Oppenheimer correction for SCF and CI wave functions.
- Written in C++ with modern standards.
- Interoperability with Python.

Psi4NumPy Features

- Rapid prototyping through Python interface.
- Direct access to integrals, wave function parameters, and optimizations.
- Reference implementations of >20 electronic structure theories.
- Interactive Jupyter Notebook Tutorials covering >25 unique subjects.

"**Psi4 1.4: Open-Source Software for High-Throughput Quantum Chemistry**," D. G. A. Smith *et al.*, *ChemRxiv* (https://chemrxiv.org/s/bc41e8fe7ebc56c18fec)

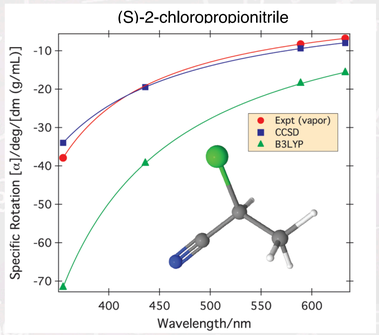
"**Psi4NumPy: An Interactive Quantum Chemistry Programming Environment for Reference Implementations and Rapid Development**," D. G. A. Smith *et al.*, *J. Chem. Theory Comput.* **14**(7), 3504-3511 (2018).

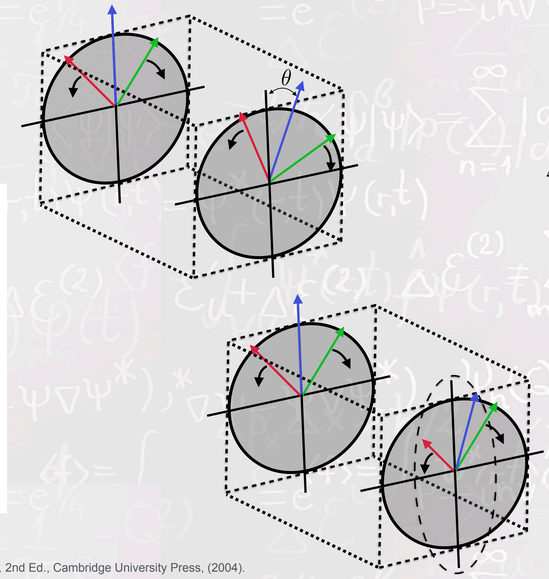
Chiroptical Properties

Optical Rotation

$$\langle \mu \rangle = \alpha \mathbf{E} + \frac{1}{\omega}\mathbf{G}'\frac{\partial \mathbf{B}}{\partial t}$$

$$\mathbf{G}'(\omega) = -\frac{2\omega}{\hbar}\mathrm{Im}\sum_{n\neq 0}\frac{\langle 0|\mu|n\rangle\langle n|m|0\rangle}{\omega_{n0}^2 - \omega^2}$$

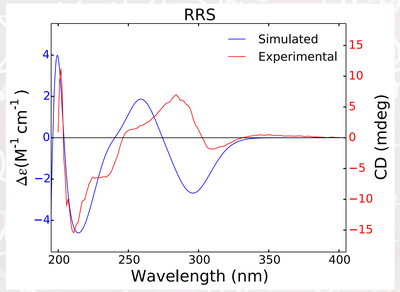




Circular Dichroism

$$\mathrm{R}_{n0} = \mathrm{Im}\langle 0|\mu|n\rangle\langle n|m|0\rangle$$

$$\Delta\epsilon(\tilde{\nu}) = \frac{1}{k\sigma}\sum_n \tilde{\nu}_{n0}\mathrm{R}_{n0}\exp\left(-\left[\frac{\tilde{\nu}-\tilde{\nu}_{n0}}{\sigma}\right]^2\right)$$



L. Rosenfeld, *Z. Physik* **52**, 161 (1928).
L. D. Barron, *Molecular Light Scattering and Optical Activity,* 2nd Ed., Cambridge University Press, (2004).
T. D. Crawford, *Theo. Chem. Acc.* **115**, 227-245 (2006).

Y. Du, K. C. Pearce, Y. Dai, P. Krai, S. Dalal, M. Cassera, M. Goetz, T. D. Crawford, and D. G. I. Kingston, *J. Nat. Prod.* **80**, 1639-1647 (2017).

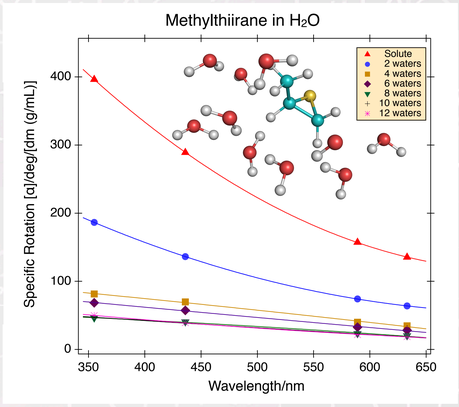
Solvation Models

Implicit Solvent

$$\nabla \cdot [\epsilon(\mathbf{r})\nabla V^{NPE}(\mathbf{r})] = -4\pi\rho_{\mathrm{tot}}(\mathbf{r})$$

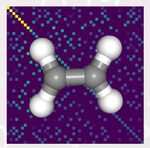
$$\epsilon[\rho(\mathbf{r})] = 1 + \frac{\epsilon_\infty - 1}{2}\left[1 + \frac{1-(\rho(\mathbf{r})/\rho_0)^{2\beta}}{1+(\rho(\mathbf{r})/\rho_0)^{2\beta}}\right]$$

Explicit Solvent



J. C. Howard, J. Womack, J. Dziedzic, C.-K. Skylaris, B. P. Pritchard and T. D. Crawford, *J. Chem. Theory Comput.*, **13**(11), 5572-5581 (2017).
R. D'Cunha and T. D. Crawford, *in preparation* (2020).

Rise of the Machines



Featurization

$$\nu(x) = \sum_{i<N} g(d_i, \sigma, x)$$

$$\frac{\partial E}{\partial x} = D_{pq}\frac{\partial h_{pq}}{\partial x} + \Gamma_{pqrs}\frac{\partial g_{pqrs}}{\partial x}$$

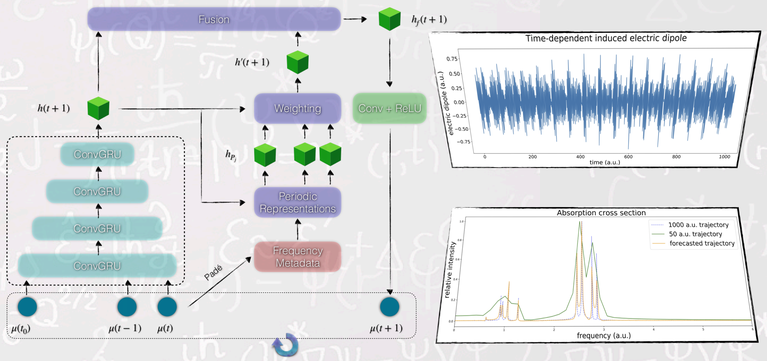
$$\mu_\alpha^{\mathrm{ind}} = \sum_\beta \mathrm{Tr}\left[\mathbf{P}_\beta \mathbf{D}_\alpha(t)\right] - \mathrm{Tr}\left[\mathbf{P}_\alpha \mathbf{D}_\alpha(t=0)\right]$$

$$y(\boldsymbol{\nu}) = \sum_i^M k(\boldsymbol{\nu}'_i, \boldsymbol{\nu})\alpha_i$$

QCArchive
A MolSSI Project

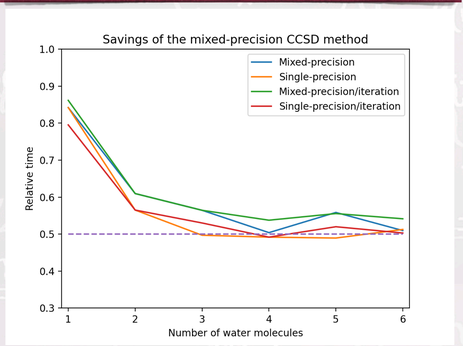
Training Data

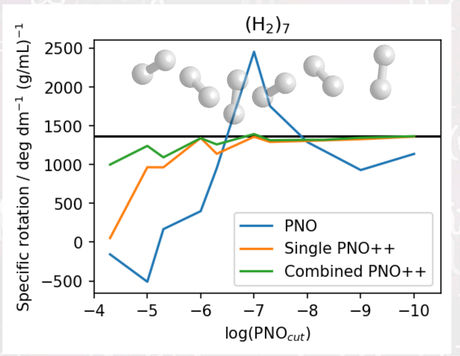
$$\sigma(\omega) = \frac{4\pi\omega}{3c}\sum_\alpha \mathrm{Im}\left[\frac{\tilde{\mathbf{E}}(\omega)\cdot\tilde{\mu}_\alpha^{\mathrm{ind}}(\omega)}{|\tilde{\mathbf{E}}(\omega)|^2}\right]$$



B. G. Peyton, C. Briggs, J. T. Margraf, T. D. Crawford, *in preparation* (2020).
A. Bazanté, H. E. Kristiansen, T. B. Pederson, and T. D. Crawford, *in preparation* (2020).

Computational Efficiency





R. D'Cunha, A. Kumar, T. D. Crawford, *in preparation* (2020).

Recent Publications

"**Structure Elucidation and Confirmation of Phloroglucinols from the Roots of *Garcinia dauphinensis* by Comparison of Experimental and Calculated ECD Spectra**", K. C. Pearce, R. G. Fuentes, S. Calderon, R. Marolikar, D. G. I. Kingston, and T. D. Crawford, *in preparation* (2020).

"**PNO++: Perturbed Pair Natural Orbitals for Coupled-cluster Linear Response Theory**", R. D'Cunha, A. Kumar, and T. D. Crawford, *in preparation* (2020).

"**Explicit Solvation Effects on the Optical Rotations of Chiral Compounds**", R. D'Cunha and T. D. Crawford, *in preparation* (2020).

"**Forecasting Real-Time Coupled-Cluster with Machine Learning**", A. Bazanté, H. E. Kristiansen, T. B. Pedersen, and T. D. Crawford, *in preparation* (2020).

"**Real-Time Coupled-Cluster Theory: A Compendium on Various Integrators**", A. Bazanté and T. D. Crawford, *in preparation* (2020).

"**Machine-Learning Coupled Cluster Properties through a Density Based Representation**", B. G. Peyton, C. Briggs, J. T. Margraf, and T. D. Crawford, *in preparation* (2020).

"**Tensor Representations and Symmetry in Many-Electron Wave Functions**", T.D. Crawford and R. Di Remigio, Annual Reports in Computational Chemistry 15, Ch. 4, 2019.

"**Basis Set Superposition Errors in the Many-Body Expansion of Molecular Properties**", B. G. Peyton and T. D. Crawford, *J. Phys. Chem. A* **123** (20), 4500-4511 (2019).

"**Diagrammatic Coupled Cluster Monte Carlo**", C. J. C. Scott, R. Di Remigio, T. D. Crawford, and A. J. W. Thom, *J. Phys. Chem. Lett.* **10**, 925-935 (2019).

"**Reduced-Scaling Coupled Cluster Response Theory: Challenges and Opportunities**", T.D. Crawford, A. Kumar, A. Bazanté and R. Di Remigio, *WIREs Comput Mol Sci* **e1406**, 1-25 (2019).

"**Frontiers of Coupled Cluster Chiroptical Response Theory**", T.D. Crawford in *Frontiers of Quantum Chemistry*, M. J. Wójcik et al., eds., Springer Nature, Singapore, Ch.3, (2018).

"**On the Performance of Property-Optimized Basis Sets for Optical Rotation With Coupled Cluster Theory**", J. C. Howard, S.S.V. Sowndarya, I. Ansari, T. J. Mach, A. Baranowska-Laczkowska, and T. D. Crawford, *J. Phys. Chem. A* **122** (28), 5962–5969 (2018).

"**Phloroglucinols from the Roots of *Garcinia dauphinensis* and their Antiproliferative and Antiplasmodial Activities**", R. G. Fuentes, K. C. Pearce, Y. Du, A. Rakotondrafara, A. L. Valenciano, M. B. Cassera, V. E. Rasamison , T. D. Crawford, and D. G. I. Kingston, *J. Nat. Prod.* **82**, 431-439 (2018).

Oh, The Places You'll Go