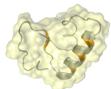




# Valeev Research Group

## Objectives

To solve the electronic Schrödinger equation with controlled precision and accuracy, but fast enough to treat systems (100s of atoms) and explore dynamics.



With sparse electronic structure methods, the electronic structure of entire proteins can be computed accurately!

## Research Interests

- Novel numerical representations for quantum mechanics of large systems, especially condensed phase
- Fundamental development of electronic structure theory to reach high precision and accuracy for prediction (not rationalization)
- Create high-performance implementations of electronic structure methods for execution on massively-parallel computers of today and tomorrow

## Software Development



Massively Parallel Quantum Chemistry

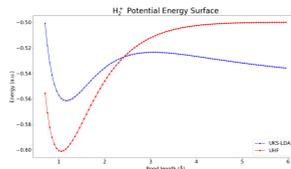
Tiled Array Tensor Framework

Libint Gaussian Integral Engine

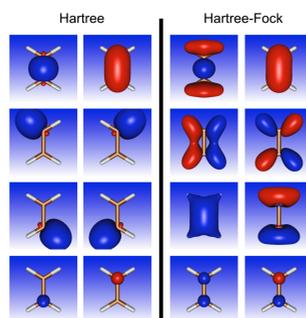
ORCA Quantum Chemistry Program

## Self-Interaction Free DFT

Density Functional Approximations (DFAs) often suffer from self-interaction error (SIE) that results from incomplete cancellation of the coulomb self-interaction and the approximate exchange-correlation functional. In the local density approximation, even the very simple one-electron system,  $H_2^+$  shows signs of SIE.



Starting with a Hartree Product *ansatz*, we propose to model the "genuine" exchange and correlation energy with a new type of DFA.



Total energy (a.u.) for small molecules

Molecule*	Hartree-Fock	Hartree	Difference
CH <sub>4</sub>	-40.2133	-39.9773	0.2360
HF	-100.0582	-99.1806	0.8776
HCN	-92.9049	-92.2330	0.6719
CO	-112.7789	-111.9110	0.8679
N <sub>2</sub>	-108.9778	-108.1638	0.8140
H <sub>2</sub> CO	-113.9110	-113.0748	0.8362

### Hartree orbitals:

- Have no SIE, like Hartree-Fock
- Are required to be localized
- Always have higher energy than Hartree-Fock

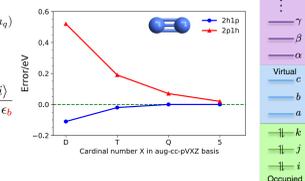
## Explicitly-Correlated Many-Body Methods

All many-body methods suffer from slow convergence of with respect to the basis set size. Explicitly Correlated R12/F12 methods improve basis set convergence and allow to attain optimal performance, as demonstrated here for the single-particle self-energy methods that yield correlated ionization potential (IP) and electron affinity (EA)

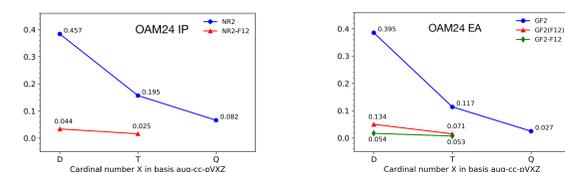
$$[\mathbf{F} + \Sigma(E)]c = E c$$

$$\Sigma_{pa}(E) = (a_p | \hat{H}^{(1)} | a_a) (a_a | (E - \hat{H}^{(1)})^{-1} | a_a) + (a_p | \hat{H}^{(1)} | (1 + T_2^{(1)}) a_a) + (a_p | \hat{H}^{(1)} | a_a) (a_a | (E - \hat{H}^{(1)})^{-1} | a_a) (a_a | \hat{H}^{(1)} | a_a)$$

$$\Sigma_{pq}^{(2)}(E) = \frac{1}{2} \sum_{i,j} \frac{\langle pa || ij \rangle \langle ij || qa \rangle}{E + \epsilon_a - \epsilon_i - \epsilon_j} + \frac{1}{2} \sum_{i,a,b} \frac{\langle pi || ab \rangle \langle ab || qi \rangle}{E + \epsilon_i - \epsilon_a - \epsilon_b}$$



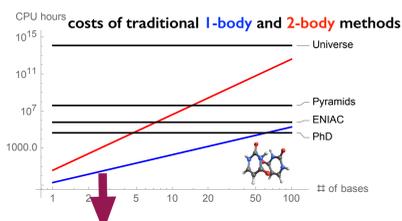
Reduced basis-set error in NR2-F12 enables calculation of accurate electron binding at lower cost compared to conventional NR2 method.



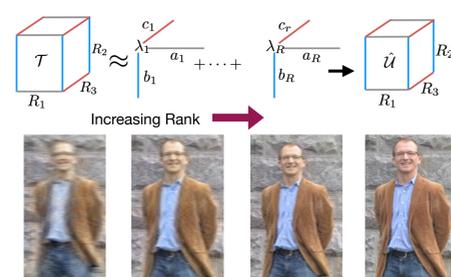
Pavošević, F.; Peng, C.; Ortiz, J. V.; Valeev, E. F. *J. Chem. Phys.* **2017**, *147* (12), 121101.  
 Teke, N. K.; Pavošević, F.; Peng, C.; Valeev, E. F. *J. Chem. Phys.* **2019**, *150* (21) 214103.

## Reduced Complexity Methods via Tensor Compression

Many-body electronic structure methods, in their canonical formalism, suffer from high polynomial scaling with respect to the system size due to the highly delocalized nature of the reference orbitals. Tensor compression strategies like pair natural orbitals, canonical polyadic decompositions etc, attempt to lower the scaling through a compact representation of the wavefunction.



### Canonical Polyadic Decomposition (CP)

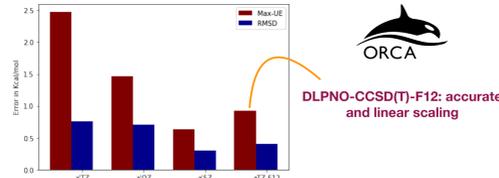


All many-body electronic structure methods suffer from large basis set errors that stem from an incorrect description of the wave function at short e-e distances. R12/F12 theory introduces terms that describe the e-e cusp explicitly. Combined with the linearly scaling algorithms, one can get near CBS results for large systems.



PSII enzyme (565 atoms)  
~ 3 days, 4 CPU cores

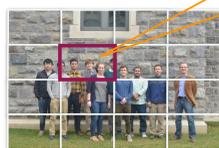
### Errors in heats of formation



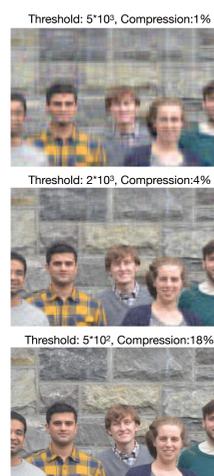
DLPNO-CCSD(T)-F12: accurate and linear scaling

### Pair Natural Orbitals

Pair natural orbitals (PNOs) are obtained by the diagonalization of the pair-specific 1-electron reduced density matrix.



PNO generation procedure is analogous to a blocked singular value decomposition of our group photo.



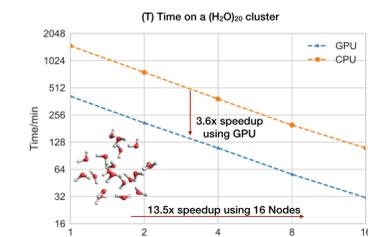
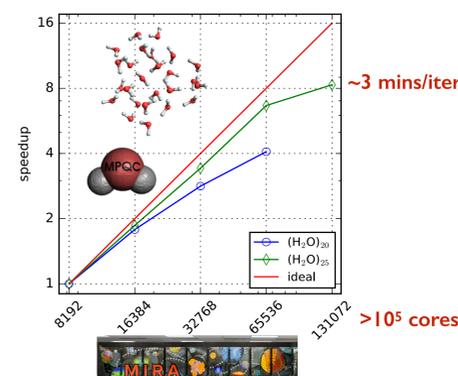
Threshold: 5\*10<sup>3</sup>, Compression:1%

Threshold: 2\*10<sup>3</sup>, Compression:4%

Threshold: 5\*10<sup>2</sup>, Compression:18%

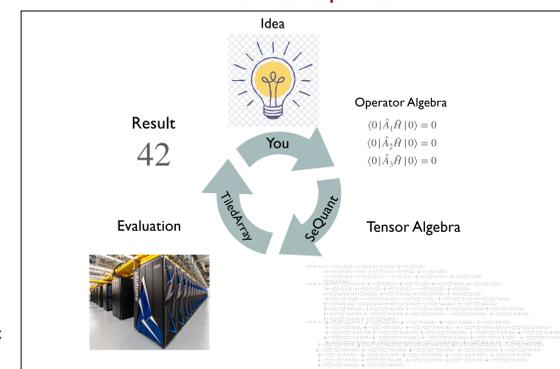
## High Performance Computing for Electronic Structure Theory

### Massively-Scalable Explicitly-Correlated Coupled-Cluster Methods



efficient execution on graphical processing units

### Near Future: Near-Complete Automation of Theoretical Exploration



### Efficient PNO-MP2 Method Implementation

Performance (sec) vs. state-of-the-art PNO-MP2 in Molpro\*

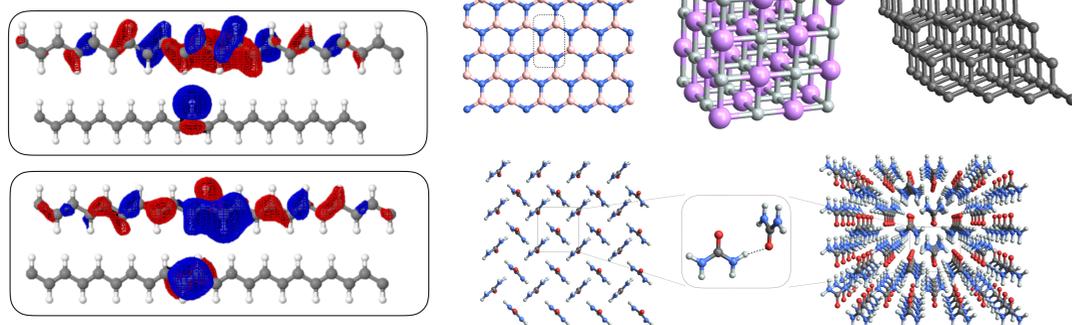
Step	Molpro	MPQC
orbital domains (OSV)	43	54
integral transform	161	139
PNO generation	37	91
LMP2 solver	54	21
<b>Total</b>	<b>265</b>	<b>341</b>

20 cores x 2.8 GHz AVX      24 cores x 2.5 GHz AVX  
 conventional DF-MP2 solver: 579 seconds

## Efficient Electronic Structure Theory for Periodic Systems

Reduced-scaling methods are an efficient way to treat not only molecules but also infinite periodic systems, such as a crystal bulk or surface. In solids each unit cell interacts with an "infinite" number of its replicas the "infinite sum may converge", making computational costs significantly higher than in molecular cases. Reduced-scaling approximations and parallel computing can be used to reduce the costs.

### orbital localization in periodic systems: (C<sub>2</sub>H<sub>2</sub>)<sub>n</sub>



## Valeev Research Group Spring 2020



(L-R) Yue, Nakul, Bimal, Sam, Marjory, Karl, Conner, Ashutosh, Andrey and Prof. Valeev



## Former Members

Dr. Varun Rishi (Caltech)      Dr. Xiao Wang (Flatiron Institute)

Dr. Chong Peng (J. P. Morgan)      Dr. Fabijan Pavosevic (Yale University)

Dr. Drew Lewis, Dr. David Hollman (Sandia National Laboratories)

Dr. Jinmei Zhang (Lawrence Berkeley National Laboratories)

Mr. Justus Calvin (Apple Inc.)      Dr. Ligo Kong (Oracle Inc.)

Dr. Florian Bischoff (Humboldt Universität zu Berlin)