Scaling Quantum Mechanics and First Principles Dynamics for Accuracy and Efficiency

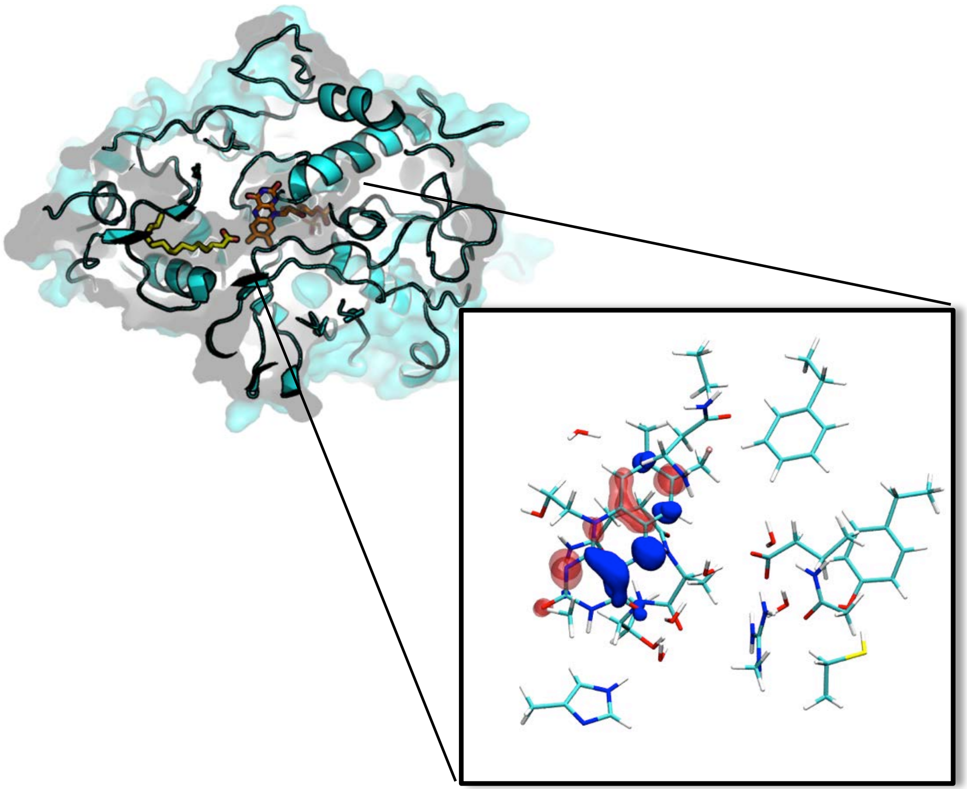
Todd J. Martínez
SLAC National Accelerator Laboratory
Stanford University

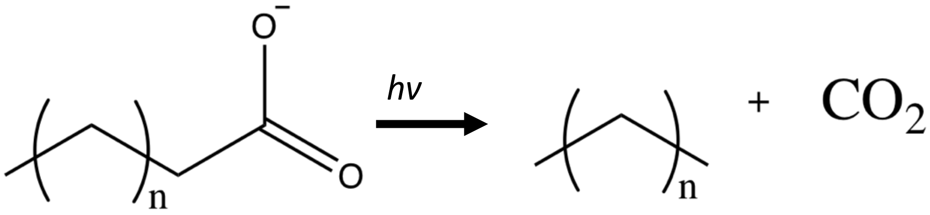
SciDAC4 Project: Designing Photocatalysts Through Scalable Quantum Mechanics and Dynamics

Project Overview

- Improve computational modeling tools for modern architectures to enable design of improved photocatalysts
- Major Thrusts
  - Enable Rapid Prototyping and deployment of multi-level parallel algorithms (Alex Aiken, Kunle Olukotun, Lexing Ying)
    - Legion/Regent for high-level parallel expression
    - DeLite to build domain specific languages for quantum chemistry and first principle dynamics
  - Develop and implement modular library frameworks for large-scale atomistic simulations (Ed Hohenstein, Todd Martínez, Robert Parrish)
    - Lightspeed framework to build electronic structure from highly tuned primitives
  - Design of photoactivated enzymes (Ron Dror, Possu Huang, TJ Lane, Henry van den Bedem)
    - Protein design with novel cofactors
    - QM/MM investigations of photoenzymes

FAP: CO_2 Photochemistry in Nature



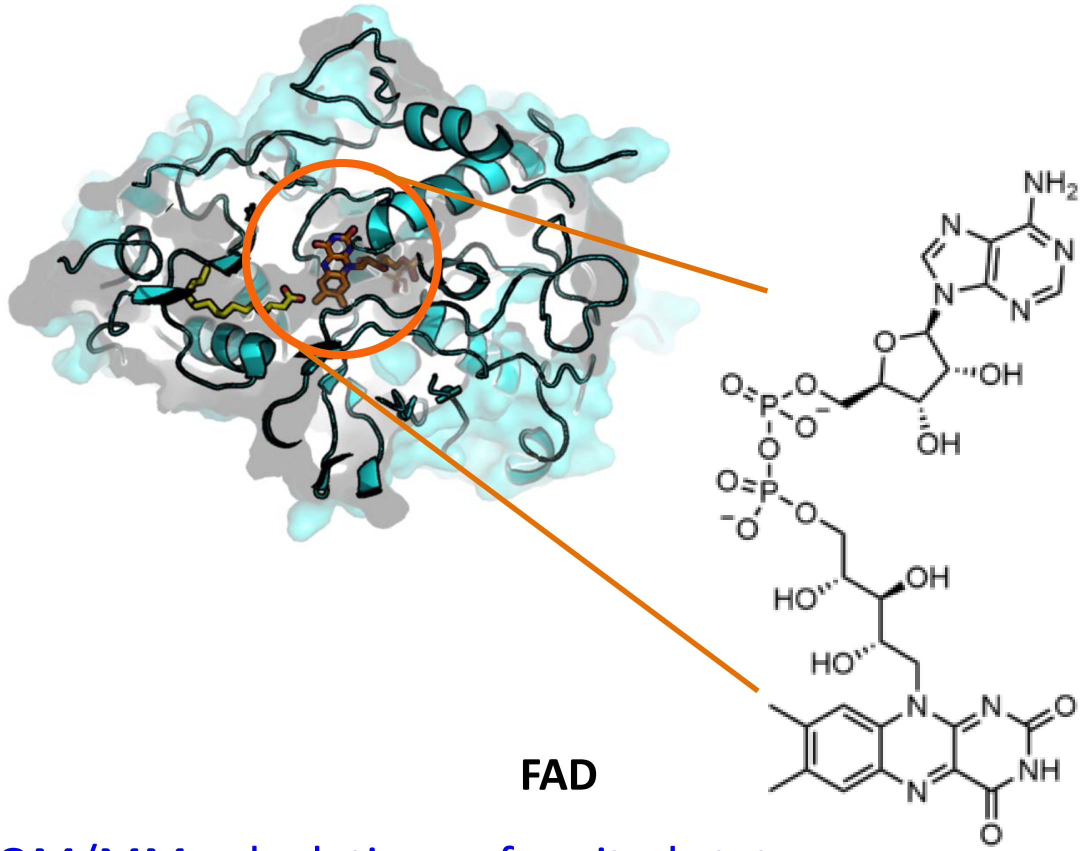


Fatty Acid Photodecarboxylase

- Photo-activated production of alkanes
- Requirement for light: not yet clear
- Mechanism: not known
- **Project goal**: QM calculations to predict mechanism, verify by comparing to spectroscopy, crystallography

Chromophore in FAP

Like all photoenzymes, FAP contains an “antenna” molecule (**cofactor**) that absorbs photons and plays a key role in the chemistry

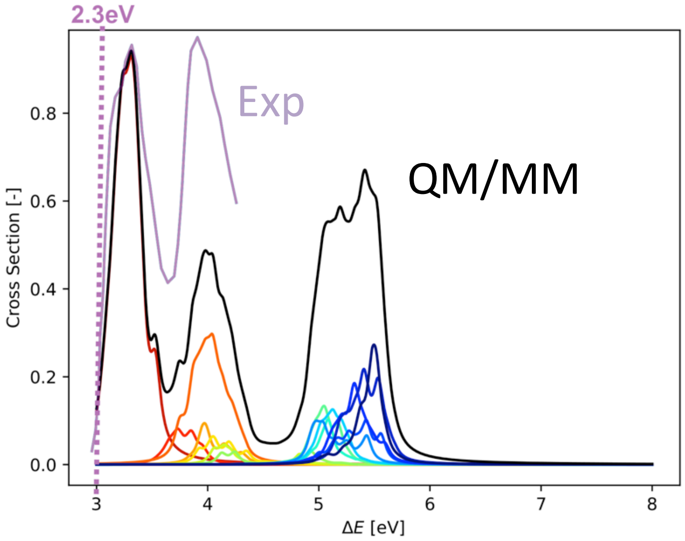


FAD

QM/MM calculations of excited state mechanism are in progress

Large QM regions: Need fast and accurate QM!

Absorption Spectrum



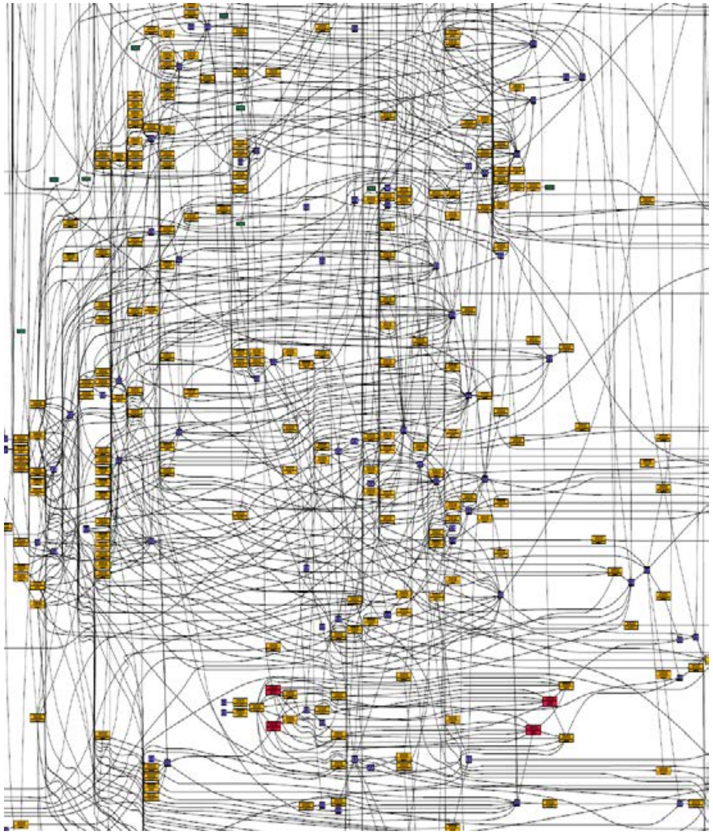
See Poster by TJ Lane

Legion

- Task-based programming model
  - Heterogeneous machines
  - Distributed memory

- Key features
  - Programs are written without specifying where computations will run and where data will be placed
  - Separate *mapping* phase allows program to be tuned to a particular machine

- Currently working to apply Legion to electron repulsion integral generation



Task graph for one time step of a simple application

DeLite

- DeLite framework allows for easy specification of domain specific languages
  - Domain specific optimizations
  - Structure computation and data
  - Optimize mapping to different hardware targets such as GPUs or FPGAs
- Working to develop DSL for J/K matrix build
- Using DeLite multiscale neural network DSL to machine learn better exchange-correlation functionals

$$\underbrace{\left[-\frac{1}{2}\nabla^2 + V_{KS}[\rho]\right]}_{H[\rho]}\psi_i(r) = \lambda_i\psi_i(r), \qquad \rho(r) = \sum_{i=1}^{N_e}|\psi_i(r)|^2$$

Learn the nonlinear map from potential to density

Primitives for Electronic Structure?

SCF Energy

Electron Repulsion Integrals (ERIs)

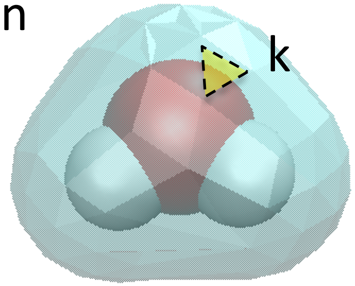
$$J^{(\mathbf{D})}_{\mu\nu} = \sum_{\rho\sigma} (\mu\nu|\rho\sigma) D_{\rho\sigma} \qquad K^{(\mathbf{D})}_{\mu\nu} = \sum_{\rho\sigma} (\mu\rho|\nu\sigma) D_{\rho\sigma}$$

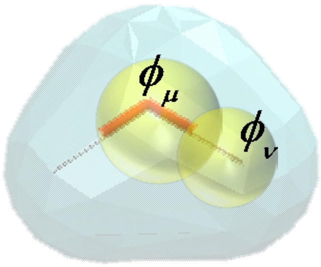
Density Matrix

SCF Gradients

$$J(A,B)^{\xi} = \sum_{\mu\nu\rho\sigma} (\mu\nu|\rho\sigma)^{\xi} A_{\mu\nu} B_{\rho\sigma} \qquad K(A,B)^{\xi} = \sum_{\mu\nu\rho\sigma} (\mu\rho|\nu\sigma)^{\xi} A_{\mu\nu} B_{\rho\sigma}$$

Continuum Solvation
and QM/MM

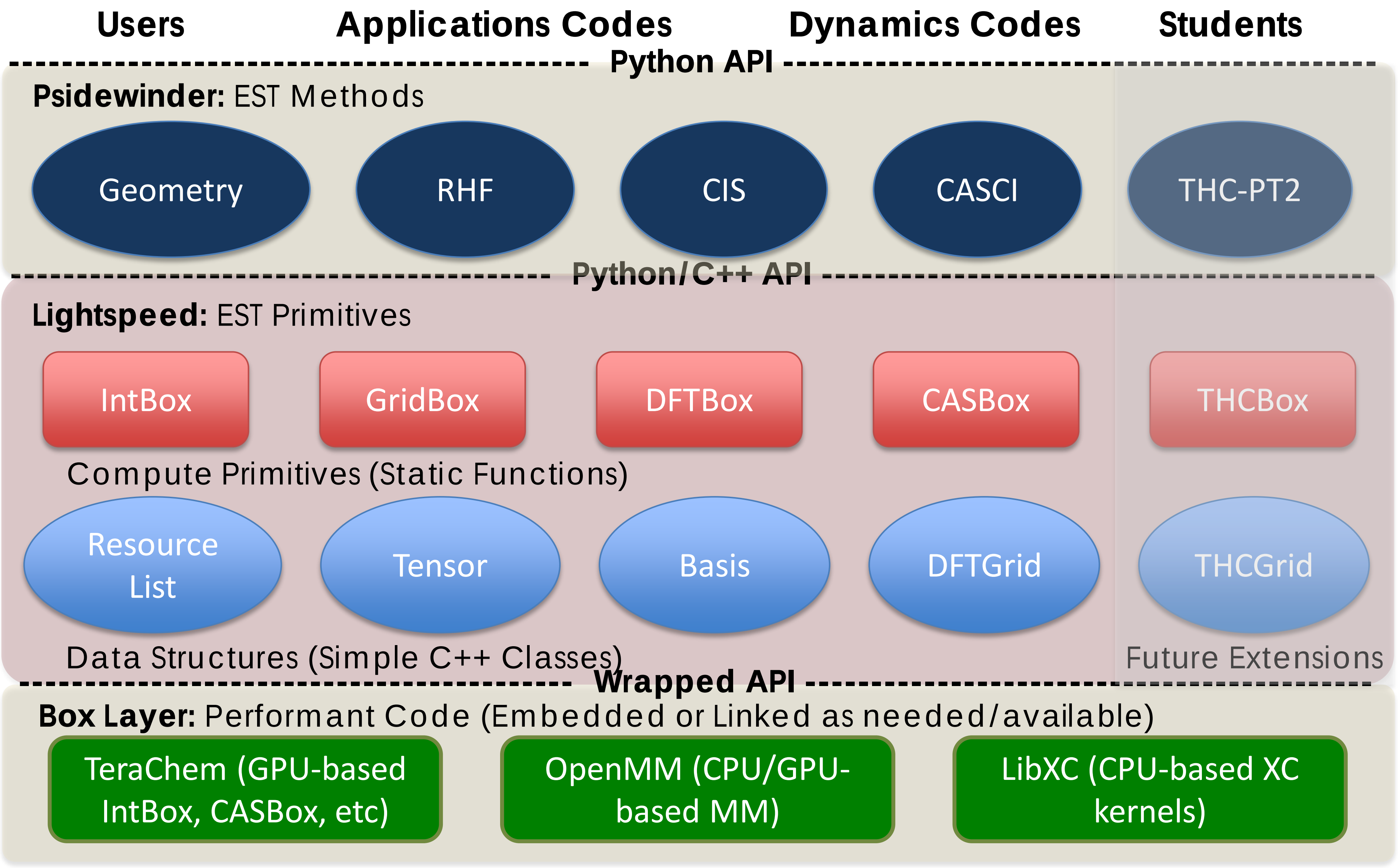




$$V_k = \sum_{\mu\nu} P_{\mu\nu} (\mu\nu|k) \qquad \Delta F^S_{\mu\nu} = \sum_k q_k (\mu\nu|k)$$

We built fast GPU versions of these primitives
Build a framework that allows easy reuse?

Lightspeed: Library Layout



Users

Applications Codes

Dynamics Codes

Students

Python API

Psidewinder: EST Methods

Geometry

RHF

CIS

CASCI

THC-PT2

Python/C++ API

Lightspeed: EST Primitives

IntBox

GridBox

DFTBox

CASBox

THCBox

Compute Primitives (Static Functions)

Resource List

Tensor

Basis

DFTGrid

THCGrid

Data Structures (Simple C++ Classes)

Future Extensions

Wrapped API

Box Layer: Performant Code (Embedded or Linked as needed/available)

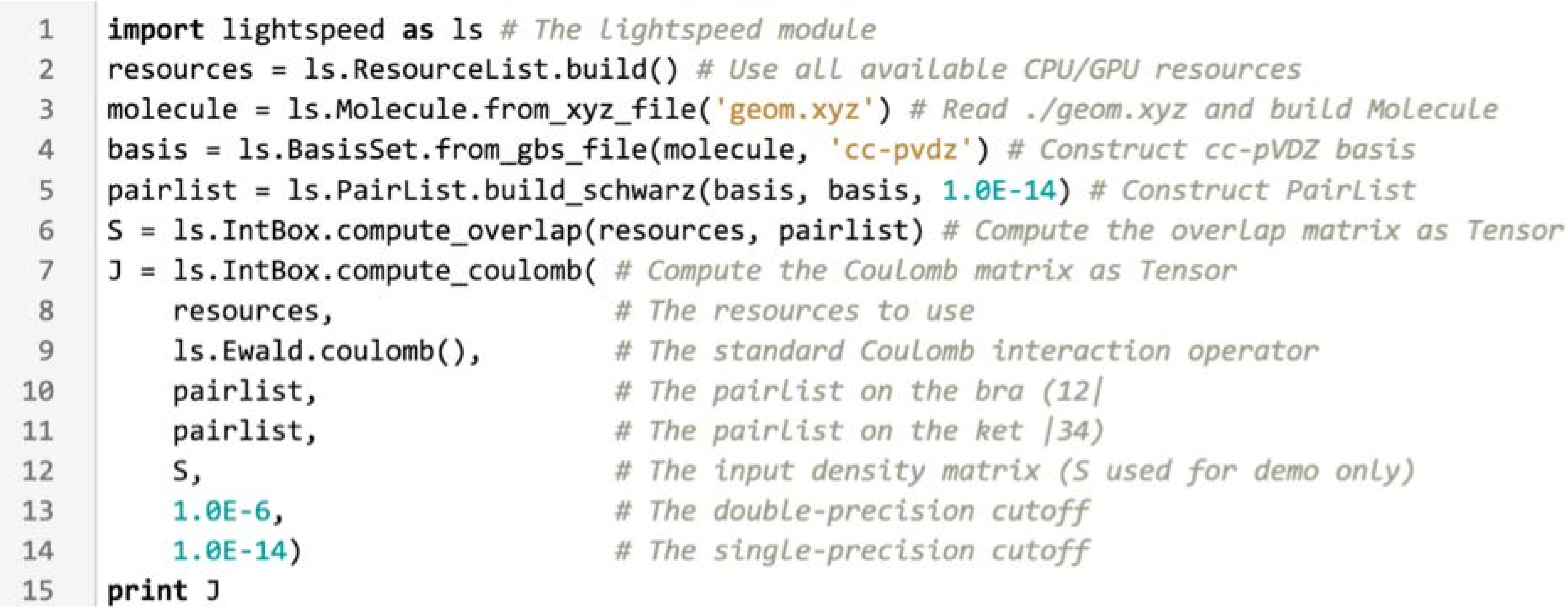
TeraChem (GPU-based IntBox, CASBox, etc)

OpenMM (CPU/GPU-based MM)

LibXC (CPU-based XC kernels)

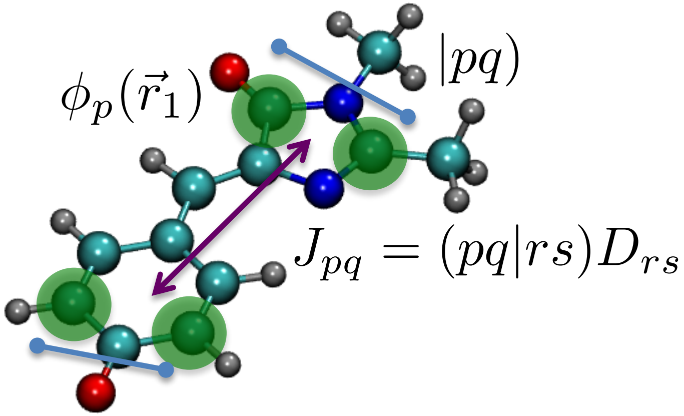
R.M. Parrish, T.J. Martinez and co-workers, *in preparation.*

Lightspeed



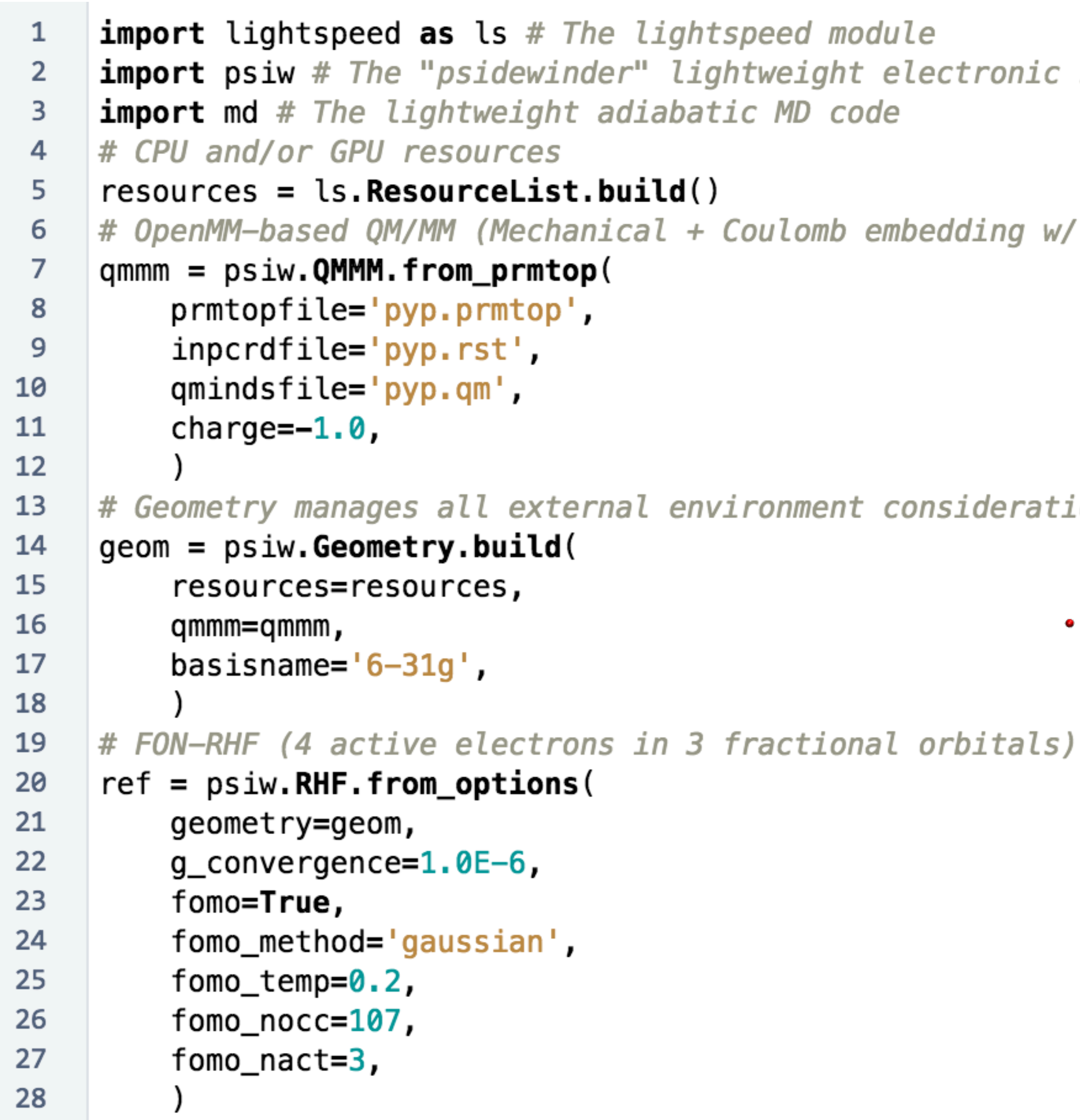
```
import lightspeed as ls # The Lightspeed module
resources = ls.ResourceList.build() # Use all available CPU/GPU resources
molecule = ls.Molecule.from_xyz_file('geom.xyz') # Read ./geom.xyz and build Molecule
basis = ls.BasisSet.from_gbs_file(molecule, 'cc-pvdz') # Construct cc-pVDZ basis
pairlist = ls.PairList.build_schwarz(basis, basis, 1.0E-14) # Construct PairList
S = ls.IntBox.compute_overlap(resources, pairlist) # Compute the overlap matrix as Tensor
J = ls.IntBox.compute_coulomb( # Compute the Coulomb matrix as Tensor
    resources,                 # The resources to use
    ls.Ewald.coulomb(),        # The standard Coulomb interaction operator
    pairlist,                  # The pairlist on the bra (12|
    pairlist,                  # The pairlist on the ket |34)
    S,                         # The input density matrix (S used for demo only)
    1.0E-6,                    # The double-precision cutoff
    1.0E-14)                   # The single-precision cutoff
print J
```

+

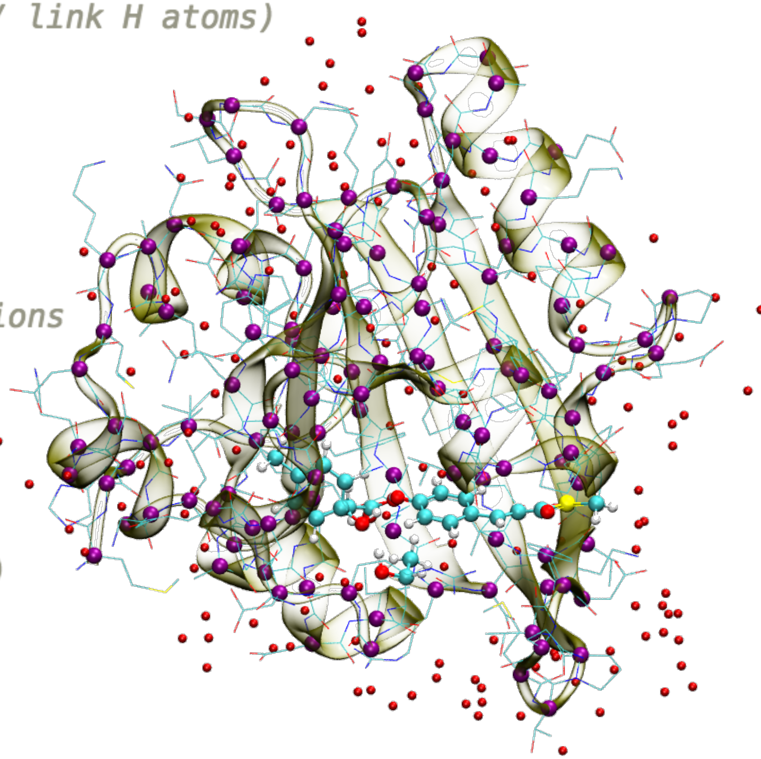


R.M. Parrish, T.J. Martinez and co-workers, *in preparation.*

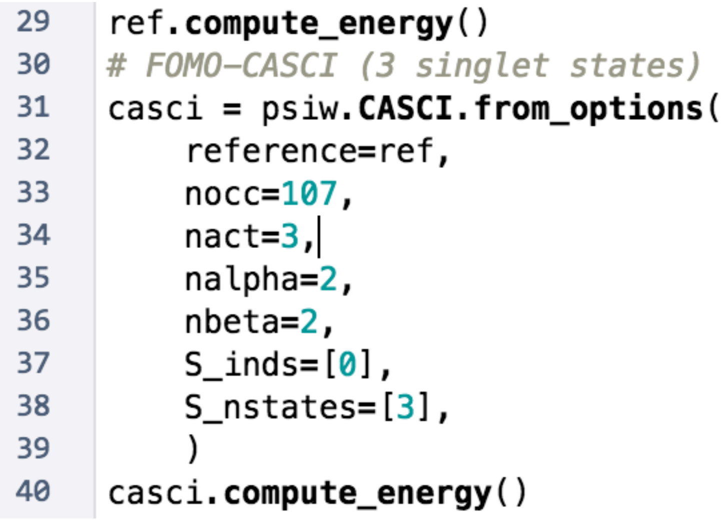
Lightspeed Example: QM/MM FOMO-CASCI



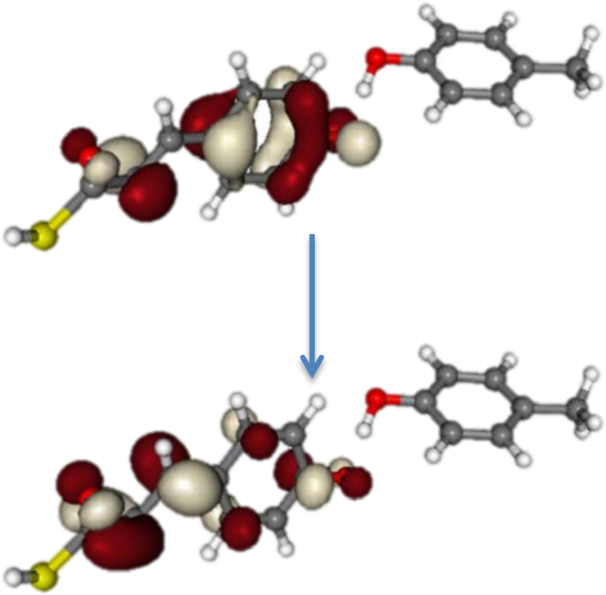
```python
import lightspeed as ls # The lightspeed module
import psiw # The "psidewinder" lightweight electronic structure module
import md # The lightweight adiabatic MD code
# CPU and/or GPU resources
resources = ls.ResourceList.build()
# OpenMM-based QM/MM (Mechanical + Coulomb embedding w/ link H atoms)
qmmm = psiw.QMMM.from_prmtop(
    prmtopfile='pyp.prmtop',
    inpcrdfile='pyp.rst',
    qmindsfile='pyp.qm',
    charge=-1.0,
    )
# Geometry manages all external environment considerations
geom = psiw.Geometry.build(
    resources=resources,
    qmmm=qmmm,
    basisname='6-31g',
    )
# FON-RHF (4 active electrons in 3 fractional orbitals)
ref = psiw.RHF.from_options(
    geometry=geom,
    g_convergence=1.0E-6,
    fomo=True,
    fomo_method='gaussian',
    fomo_temp=0.2,
    fomo_nocc=107,
    fomo_nact=3,
    )
```



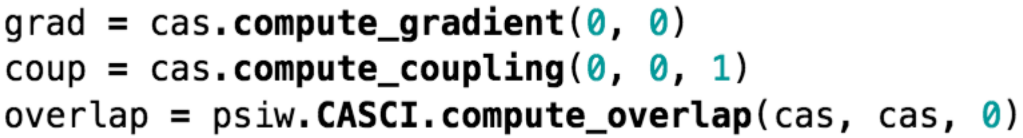
Lightspeed Example: QM/MM FOMO-CASCI (continued)



```python
ref.compute_energy()
# FOMO-CASCI (3 singlet states)
casci = psiw.CASCI.from_options(
    reference=ref,
    nocc=107,
    nact=3,
    nalpha=2,
    nbeta=2,
    S_inds=[0],
    S_nstates=[3],
    )
casci.compute_energy()
```



Key Methods:

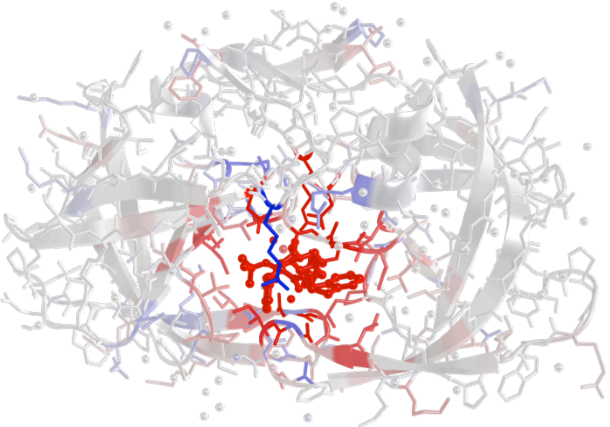


```python
grad = cas.compute_gradient(0, 0)
coup = cas.compute_coupling(0, 0, 1)
overlap = psiw.CASCI.compute_overlap(cas, cas, 0)
```

And another dozen lines to production-scale AIMD (see Parrish poster)...

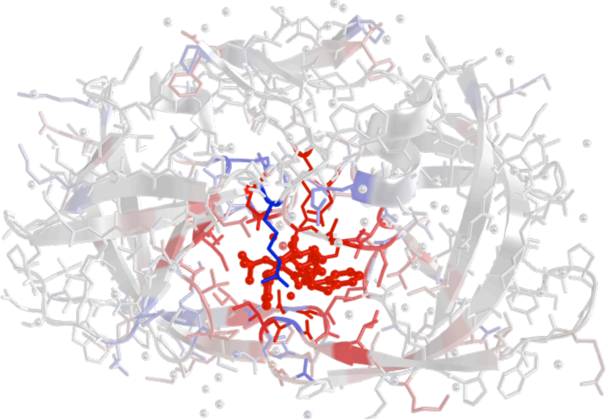
Lightspeed Enables Rapid Prototyping:
Parallax – Neglect of Fragment Differential Overlap (NFDO)

Current State of the Art:



Single Points

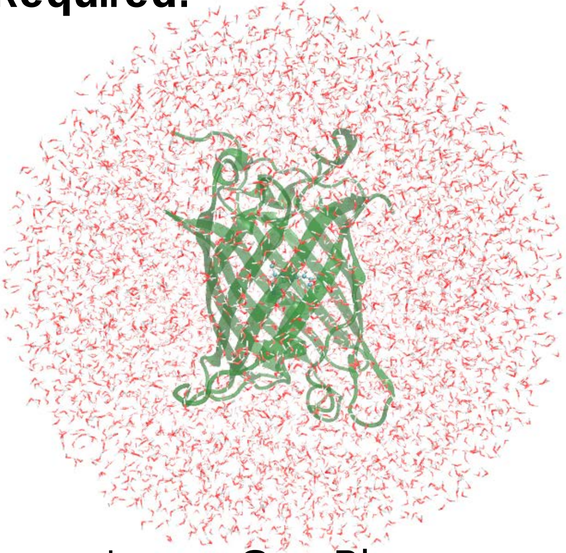
Next Target:



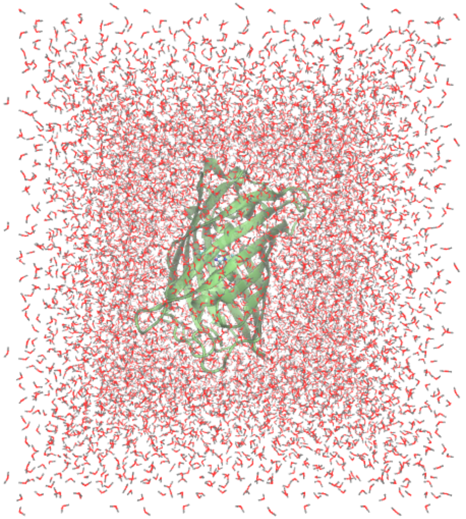
Dynamics

At the Least, Coulomb Embedding is Required:
=> Parallax Idea:

$$E \equiv \sum_{A} E_{\mathrm{A}}^{\mathrm{SCF}} + \frac{1}{2} \sum_{A} \sum_{B'} E_{\mathrm{AB'}}^{\mathrm{Coulomb}} + \frac{1}{2} \sum_{A} \sum_{B'} E_{AB'}^{6-12}$$

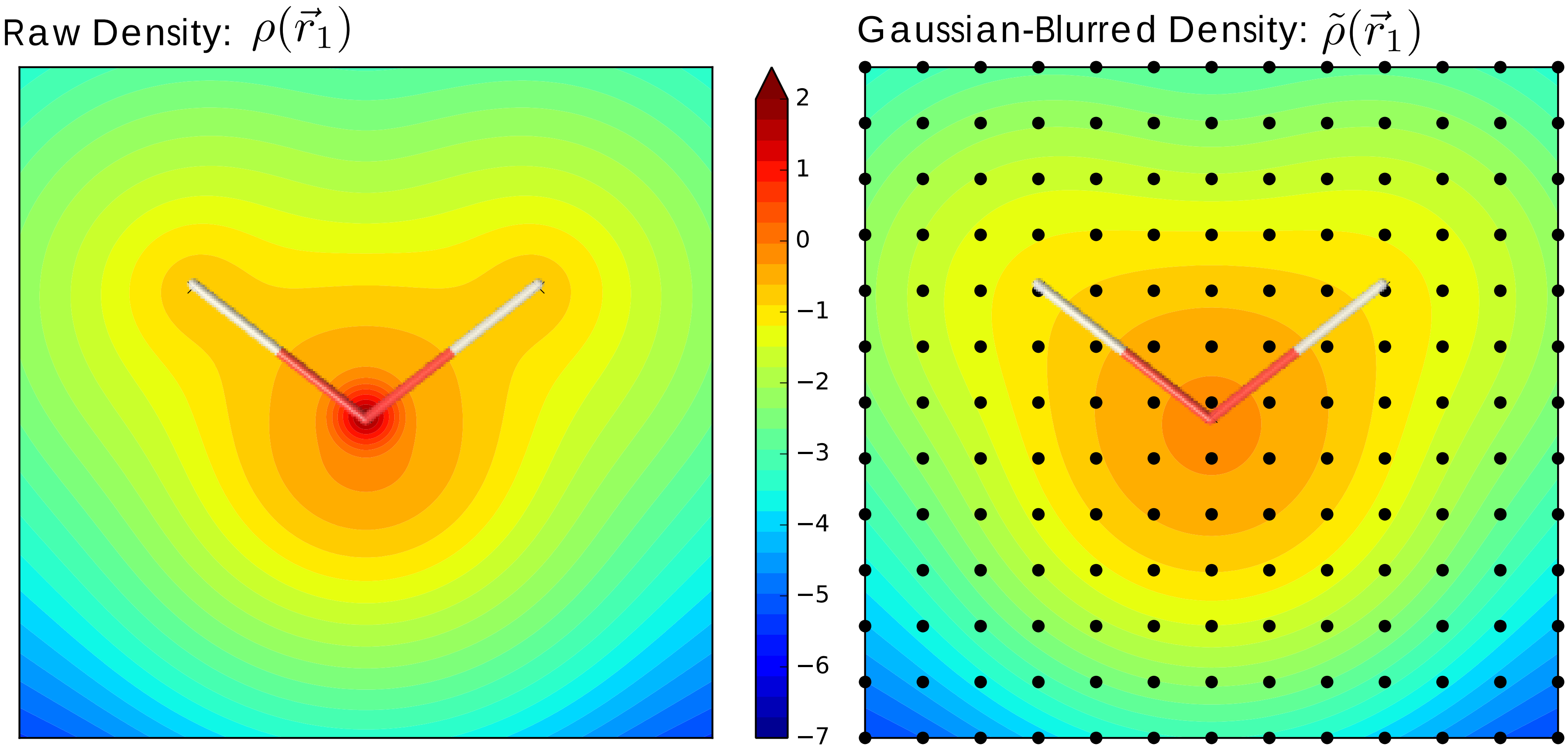


Large Gas-Phase



Large PBC

Parallax: PME Approach



Raw Density: $\rho(\vec{r}_1)$

Gaussian-Blurred Density: $\tilde{\rho}(\vec{r}_1)$

Not Fourier Representable

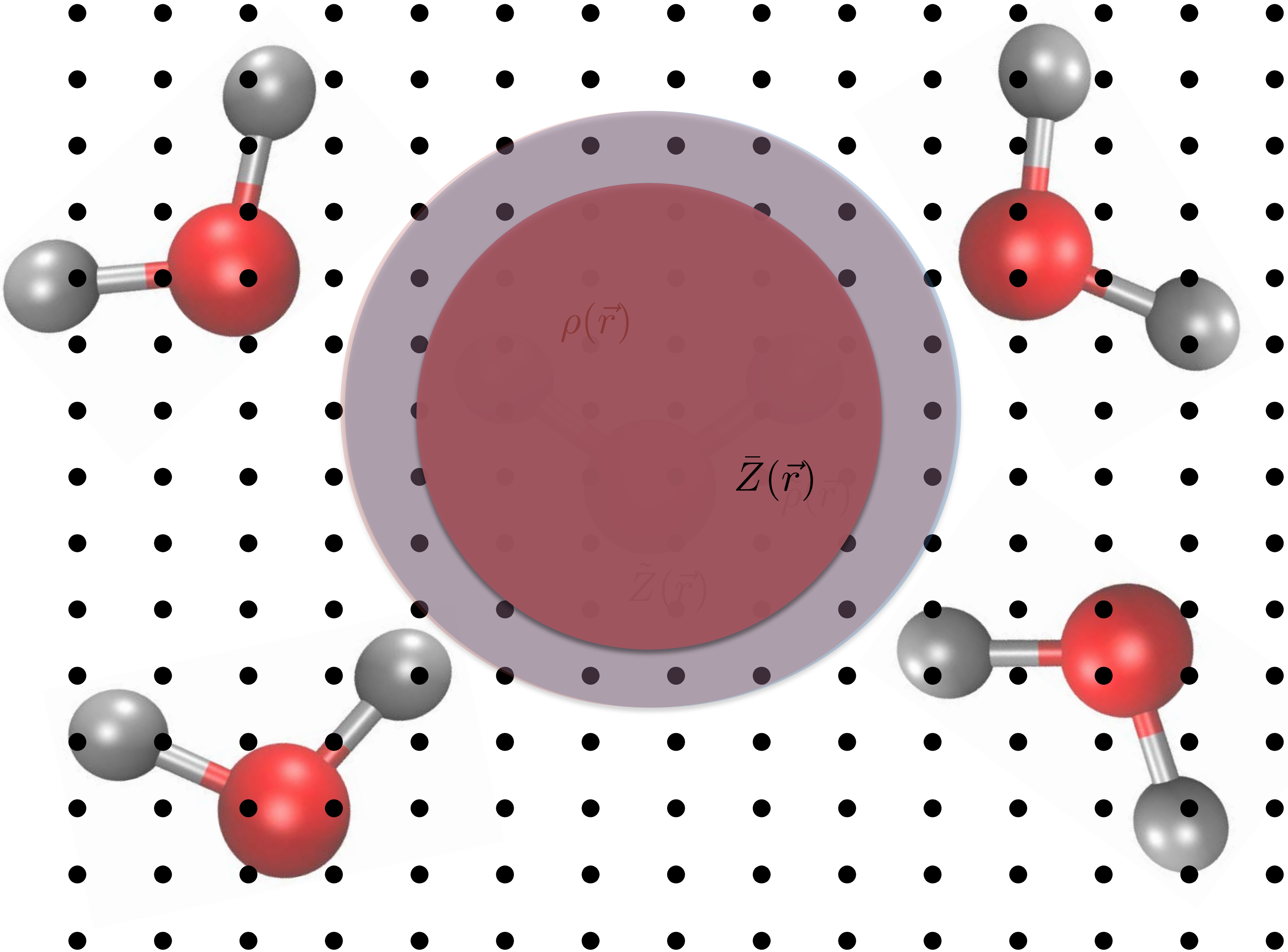
Fourier Representable

ESP of blurred density (long-range Ewald ESP):

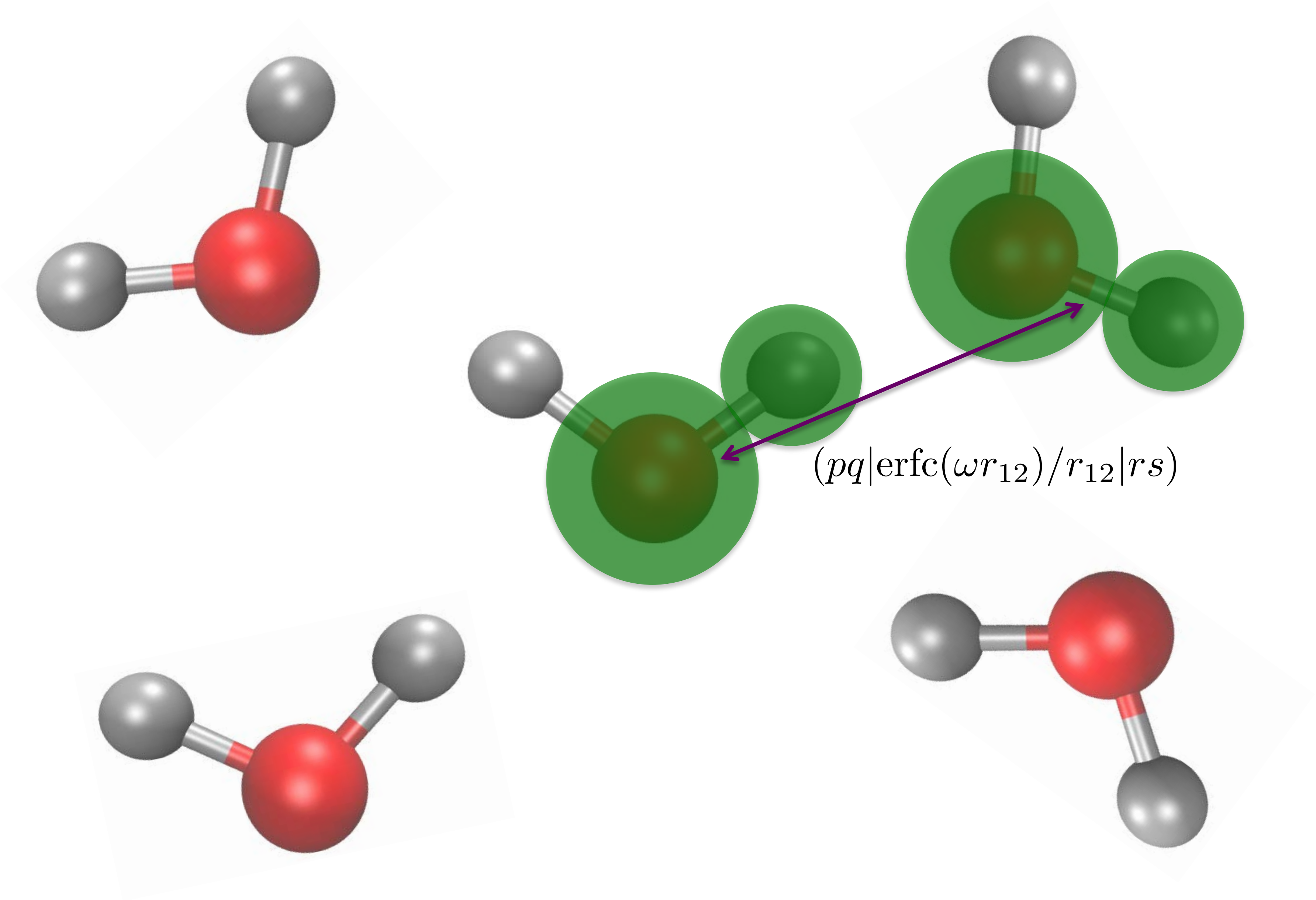
$$\tilde{\rho}(\vec{r}_1) \xrightarrow{\mathrm{FFT}} \hat{\rho}(\vec{k}) \xrightarrow{4\pi/k^2} \hat{Z}(\vec{k}) \xrightarrow{\mathrm{IFFT}} \tilde{Z}(\vec{r}_1)$$

T. Darden, D. York, and L. Pedersen, J. Chem. Phys., 98, 10089 (1993).
L. Füsti-Molnár and Peter Pulay, J. Chem. Phys., 117, 7827 (2002).
C.-M. Chang, Y. Shao, and J. Kong, J. Chem. Phys., 136, 114112 (2012).

Parallax: Full Coulomb Embedding (Long Range)



Parallax: Full Coulomb Embedding (Short Range)

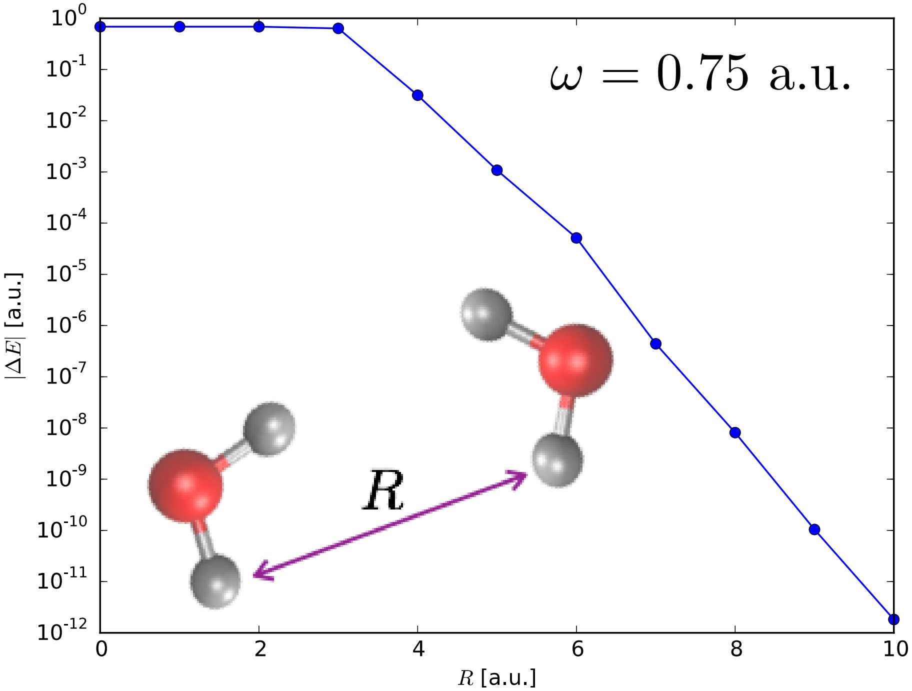


$(pq|\mathrm{erfc}(\omega r_{12})/r_{12}|rs)$

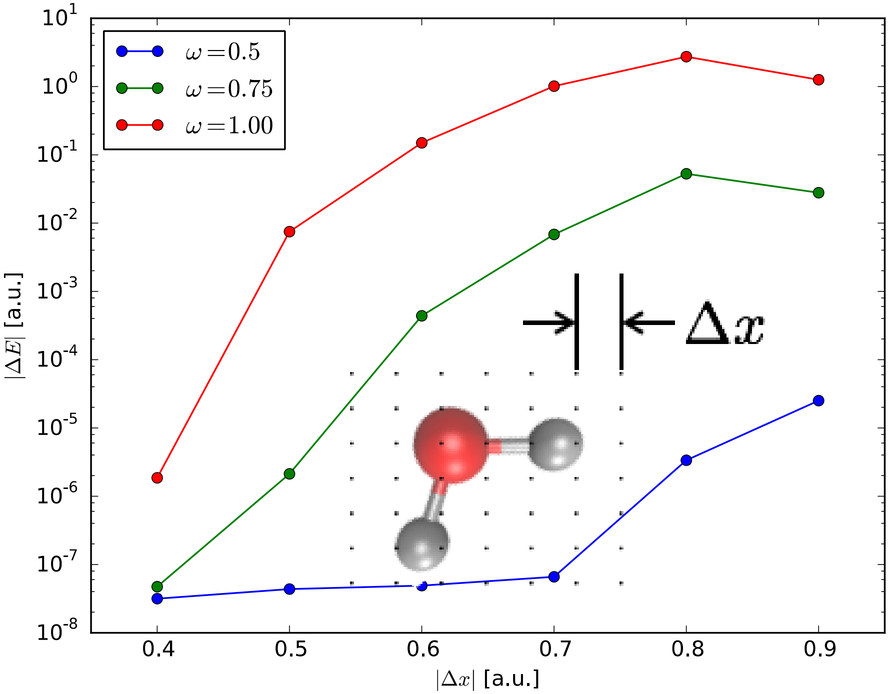
=> Linear Scaling, highly but not embarrassingly parallel.

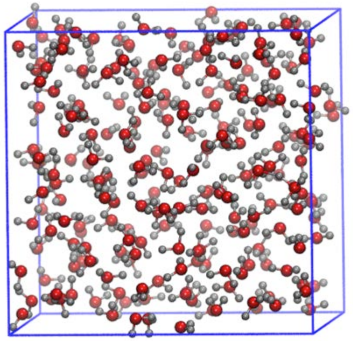
Parallax: Sensitivity to Grid/Ewald Parameters

Short-Range Cutoff Distance:



Fourier Grid Spacing:

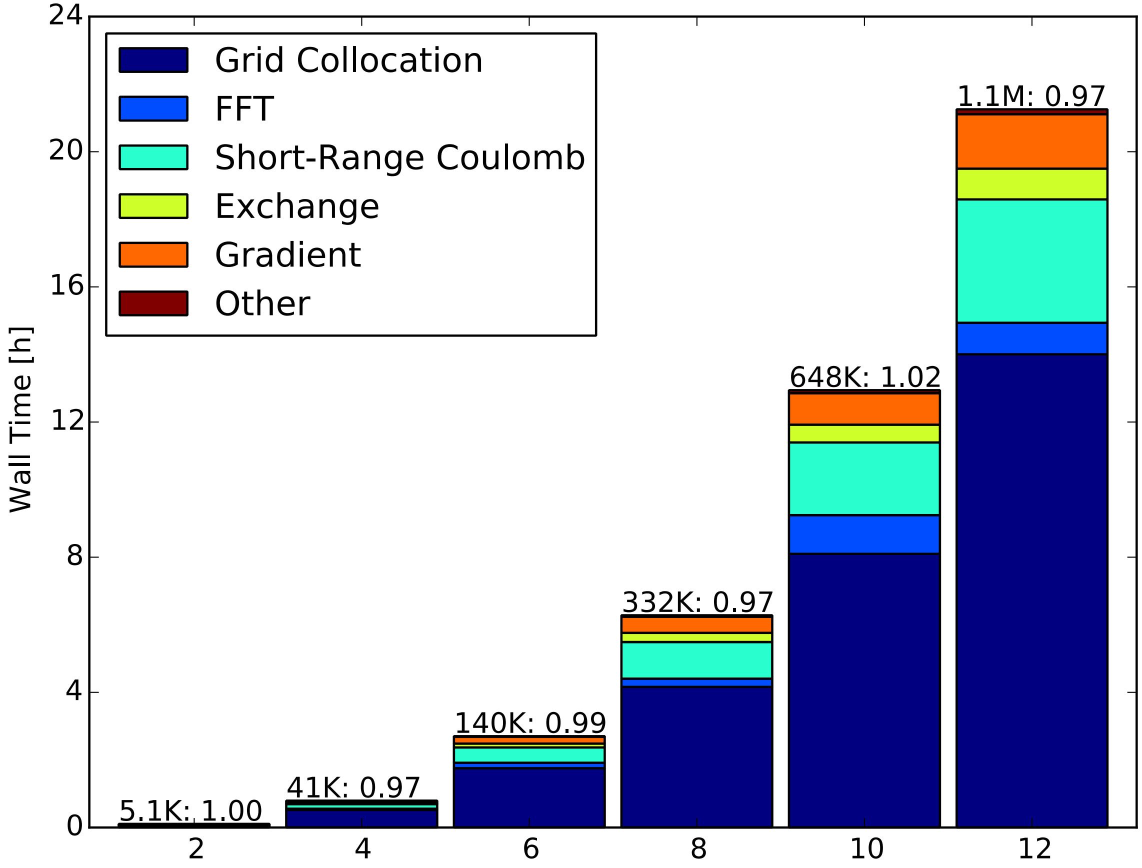


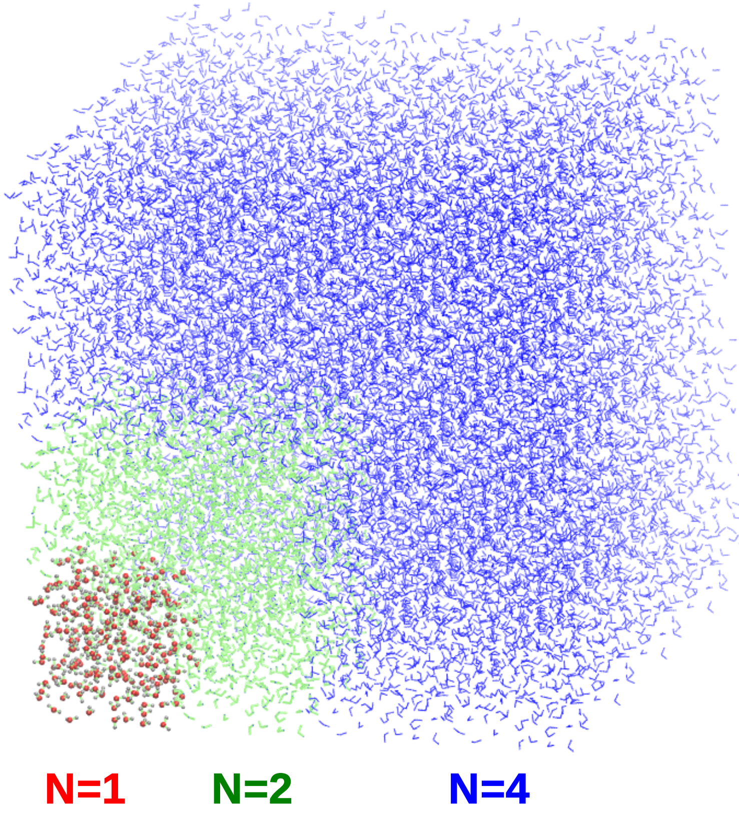


Parallax: RHF/STO-3G
648-Atom Unit Cell
-1.6x10^4 E_h SCF Energy

Parallax: Scaling for Simple Water Box

Parallax: RHF/STO-3G Timings on PBC Water Boxes (10 SCF Iterations + Gradient)



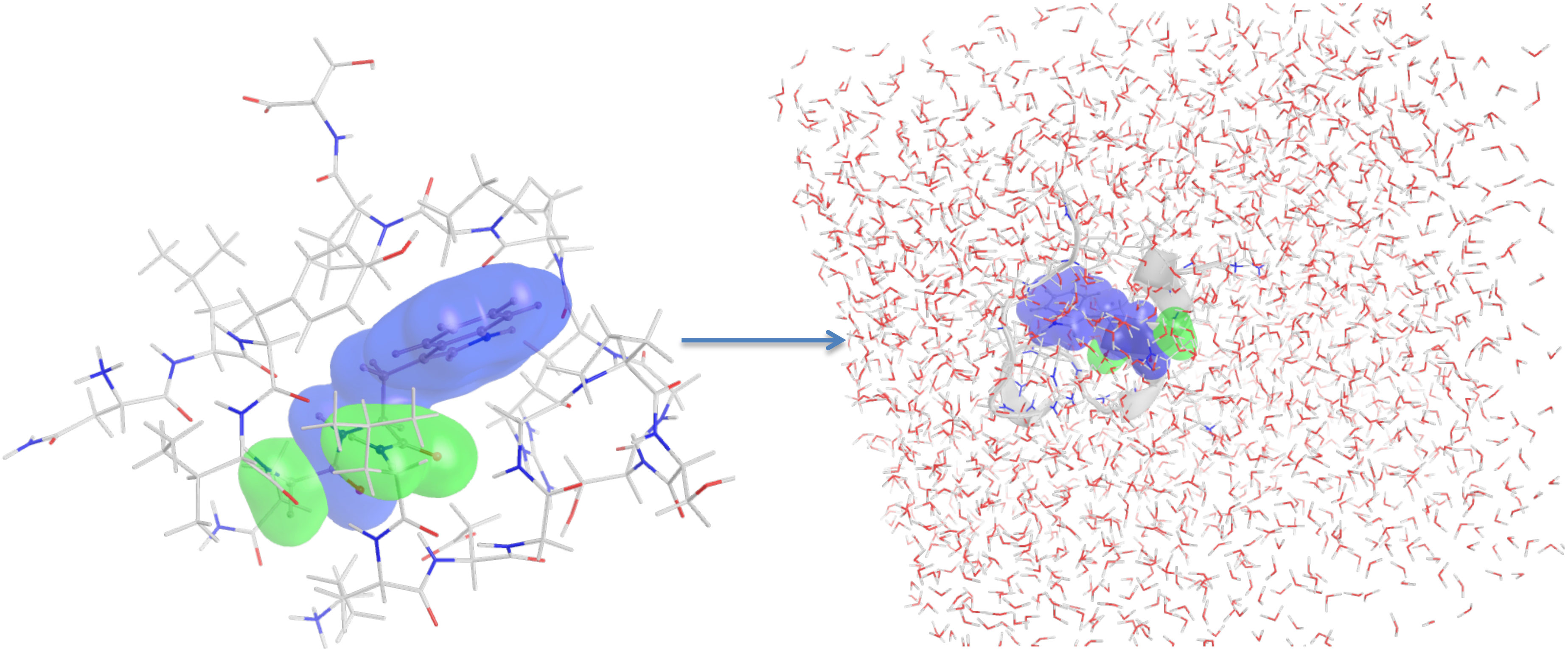


$$N_{\text{atom}} = 648N^3$$

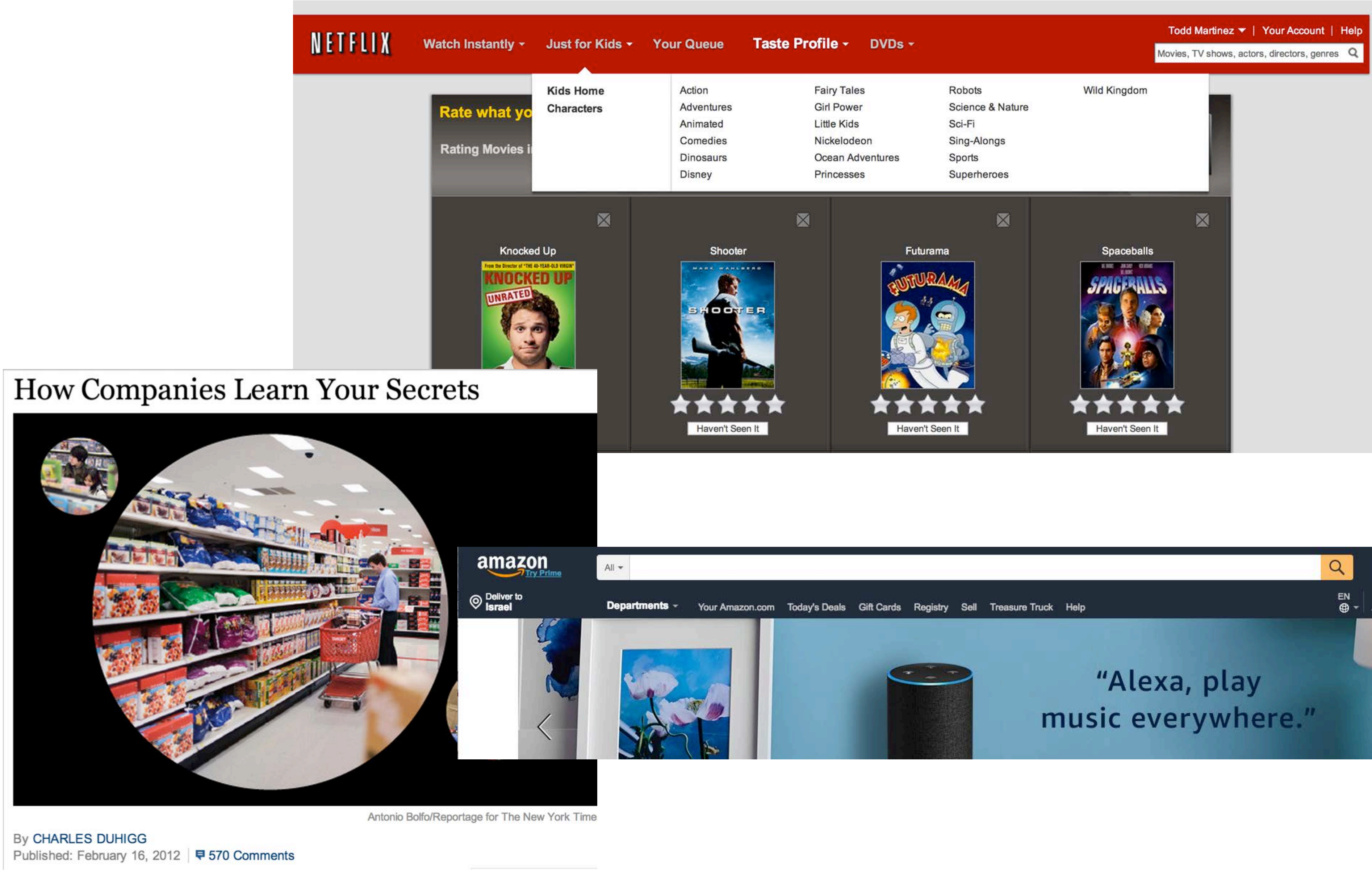
12-Core Intel E5-2640@2.5 GHz/400 GB RAM

Parallax – Next Steps

- Benchmark accuracy of approach
- Application to chemical reactions in solution
  - Reacting system treated as a single fragment
- Extend to allow for fragmentation across covalent bonds
- Extend to allow for dynamic fragmentation



Recommendation Systems



How Companies Learn Your Secrets

Antonio Bolfo/Reportage for The New York Time

By CHARLES DUHIGG
Published: February 16, 2012 | 570 Comments

Recommendation Systems

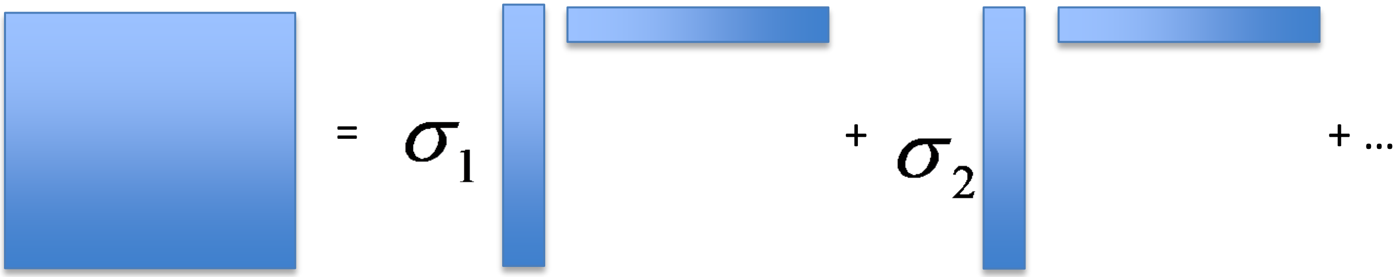
	Dark City	Star Wars	Zero Dark Thirty	Steel Magnolias
Joe	1	?	2	1
Fred	5	5	1	1
Jane	?	?	5	?
Alex	?	3	?	?
Sara	1	?	?	5

Need to complete the matrix…
Is this possible?
Only if the matrix does not have much information!

Machine learning strategy: ASSUME the problem is well-posed

In example above – 10 numbers out of 20, assume this is enough to determine remaining 10 numbers…

Singular Value Decomposition



$$\mathbf{A} = \mathbf{U\Sigma V}$$

Diagonal
Rank = number nonzero diagonal elements

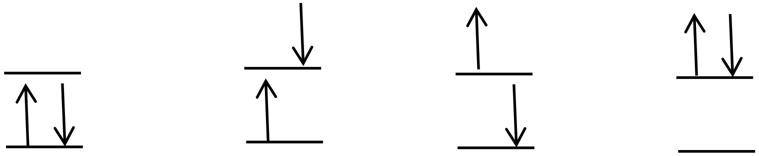
Assume rank is small and find best low rank approximation that reproduces known entries in the matrix…

Full CI

Full Configuration Interaction:

$$\psi = \sum_I c_I \left| I \right\rangle$$

All possible arrangements of
N electrons in M orbitals



$$c_1\, \varphi_1\overline{\varphi}_1 + c_2\, \varphi_1\overline{\varphi}_2 + c_3 \varphi_2\overline{\varphi}_1 + c_4 \varphi_2\overline{\varphi}_2$$

Need matrix-vector products **Hc**, vector length N_I is *factorial* in N,M

Formal cost: $O\left(N_I^2\right)$

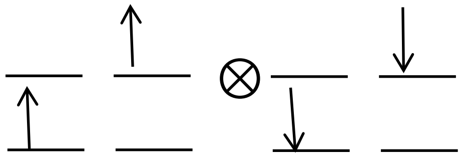
Accounting for sparsity of **H**: $O\left(N_I\right)$

Rank Sparsity in Full CI?

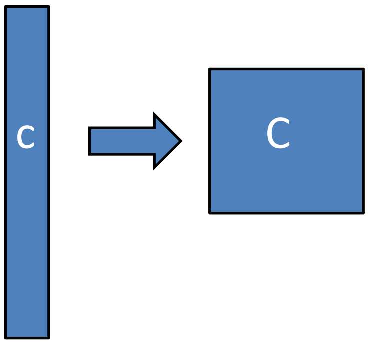
How can we reveal noninformative nature of CI vector?

Rearrange vector to a matrix:

$$\{\varphi_1,\varphi_2\}\otimes\{\bar{\varphi}_1,\bar{\varphi}_2\}$$



"α-string" "β-string"



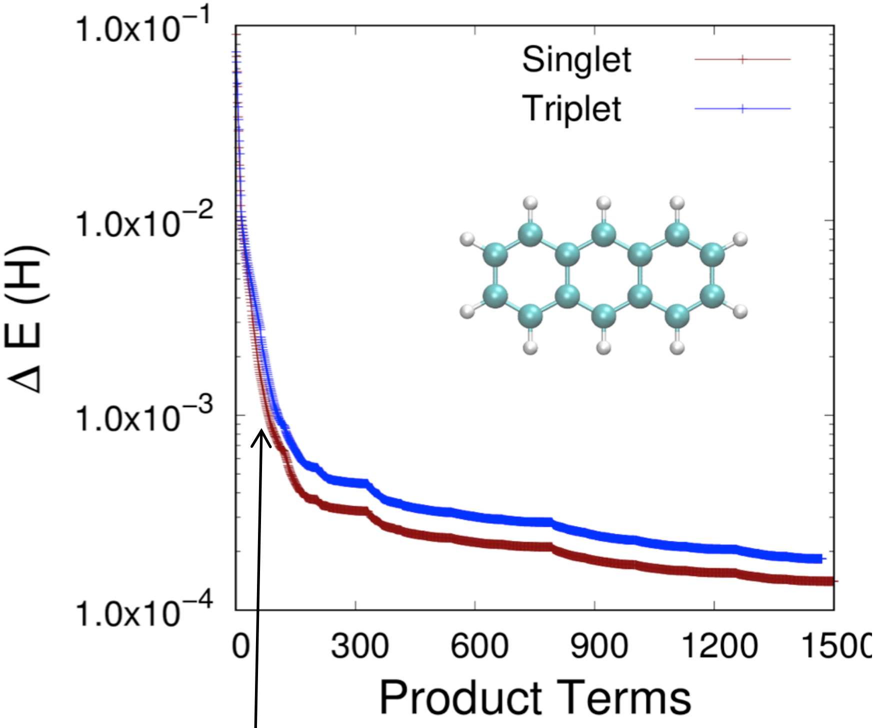
$$\psi=\sum_{IJ}C_{IJ}\left|\alpha_I\beta_J\right\rangle$$

Now, play same trick from recommendation systems: $\mathbf{C}=\sum_{r}^{N_r}\lambda_r P_r Q_r^T$

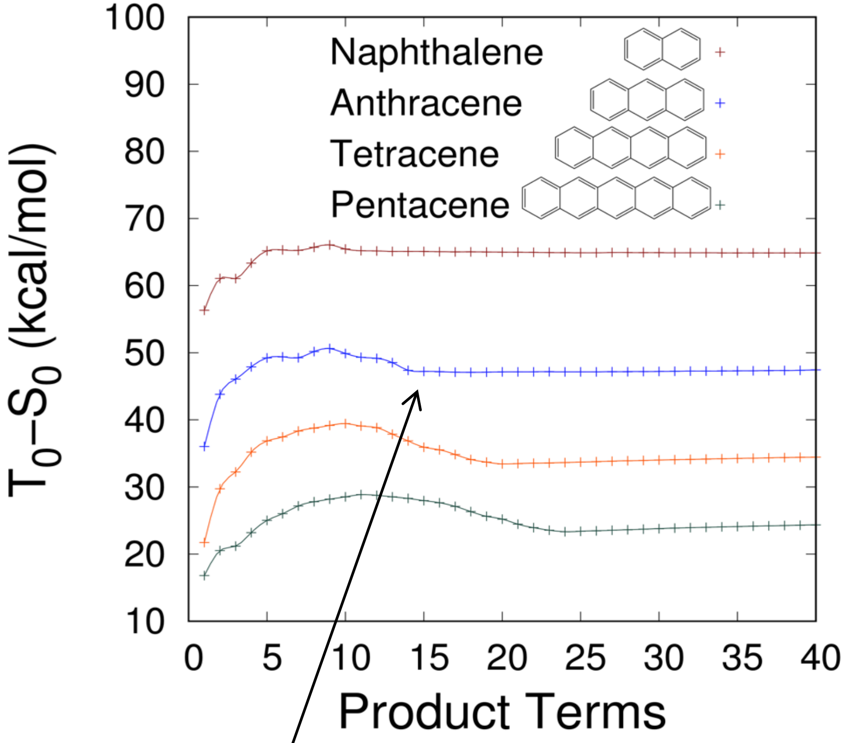
Memory requirement, Computational cost: $O\left(\sqrt{N_I}\right)$

Note early work by Koch and later also Taylor…

Are Electronic Wavefunctions Informative?



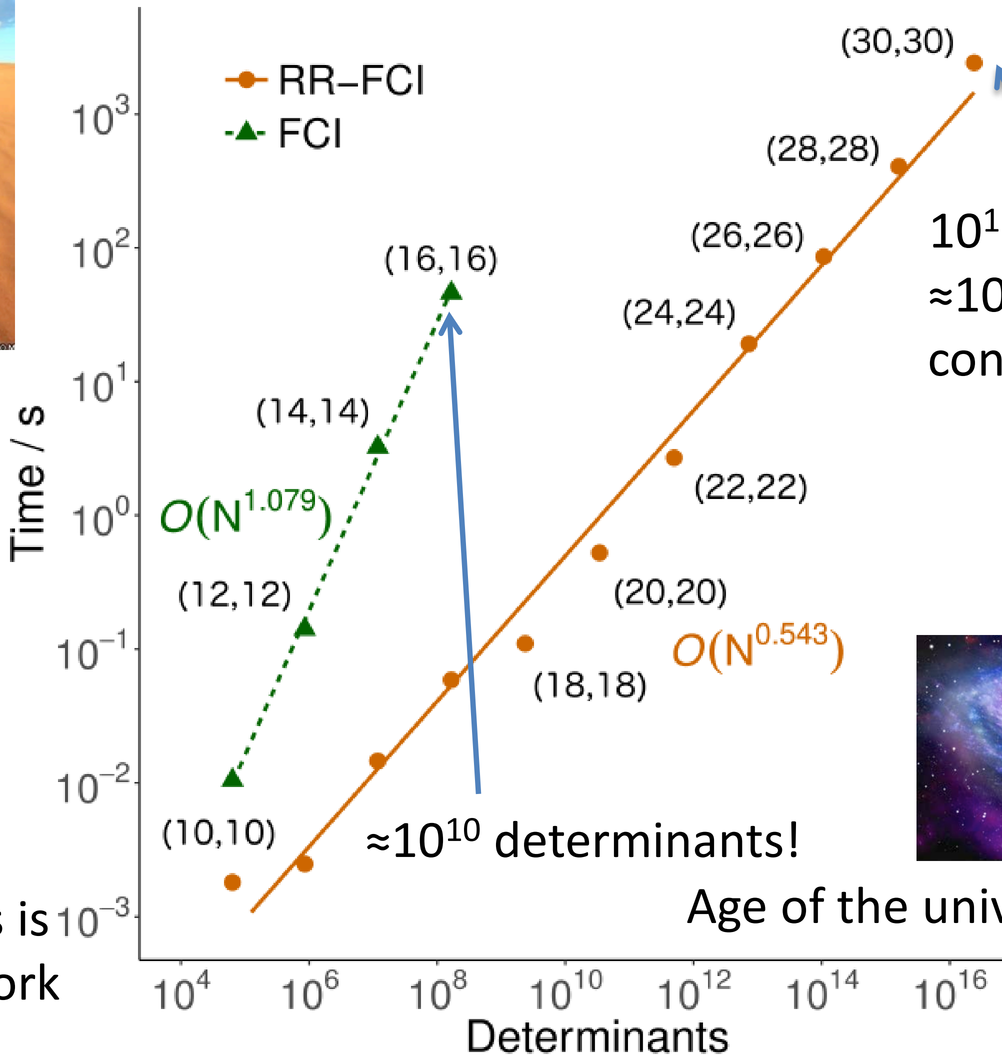
50 terms (out of 10^4) are enough for kcal/mol accuracy!



Even fewer terms needed for accurate energy differences!

rr-FCI Performance

Number of grains of sand on Earth: 10^{18}



10^{16} determinants $\approx 10^{15}$ seconds w/ conventional FCI

$\approx 10^{10}$ determinants!

Even the “conventional” FCI timings here are FAR faster than expected – this is because of Fales-Levine work on GPU-based Full CI

Age of the universe: 10^{17} sec

rr-FCI

- Renaissance in selected CI methods – exploiting element sparsity of CI vector (Evangelista, Head-Gordon, Umrigar, Alavi): FCI-QMC, Heat Bath-CI, Adaptive Sampling CI
- These also increase the efficiency of full CI – some are deterministic (ASCI) and others are stochastic (FCI-QMC, HBCI)
- rr-FCI exploits *rank* sparsity of CI vector
  - There is an rr-FCI value for *every* element of the CI vector
  - This is qualitatively different from approximations which neglect small elements
- Deterministic, so gradient is straightforward for dynamics
- Working to improve convergence and to exploit mixed precision

Tensor Hypercontraction

Applying decomposition techniques to 4th order tensor:

$$(ij\,|\,kl) = \sum_{PQ} X_{iP} X_{jP} Z_{PQ} X_{kQ} X_{lQ}$$

P,Q indices have approx. same range as basis

i,j,k,l are *unpinned*! Can sum over any of these without carrying along the others…

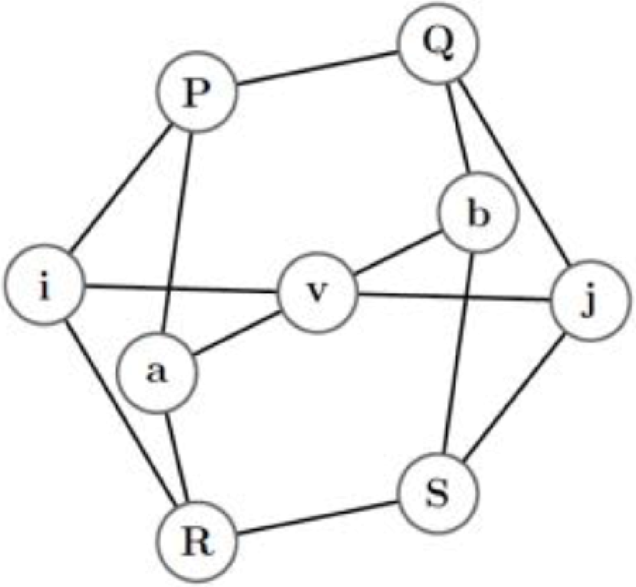
Numerical methods to determine X and Z simultaneously…
Analytic formulas to determine Z, given X
Numerical methods to determine X, given Z

Formal scaling of all pair methods reduced to O(N^4)!

Implementation of THC

$$E_{\mathrm{MP2}} = \sum_{ijab} t_{ij}^{ab} \left[2(ia|jb) - (ib|ja) \right]$$

$$E_{\mathrm{THC-MP2}} = \sum_{\nu} \sum_{ijab} \sum_{PQRS} \tau_i^{\nu} \tau_j^{\nu} \tau_a^{\nu} \tau_b^{\nu} \cdot X_i^P X_a^P Z^{PQ} X_j^Q X_b^Q \times$$
$$\left[2 \cdot X_i^R X_a^R Z^{RS} X_j^S X_b^S - X_i^R X_b^R Z^{RS} X_j^S X_a^S \right]$$

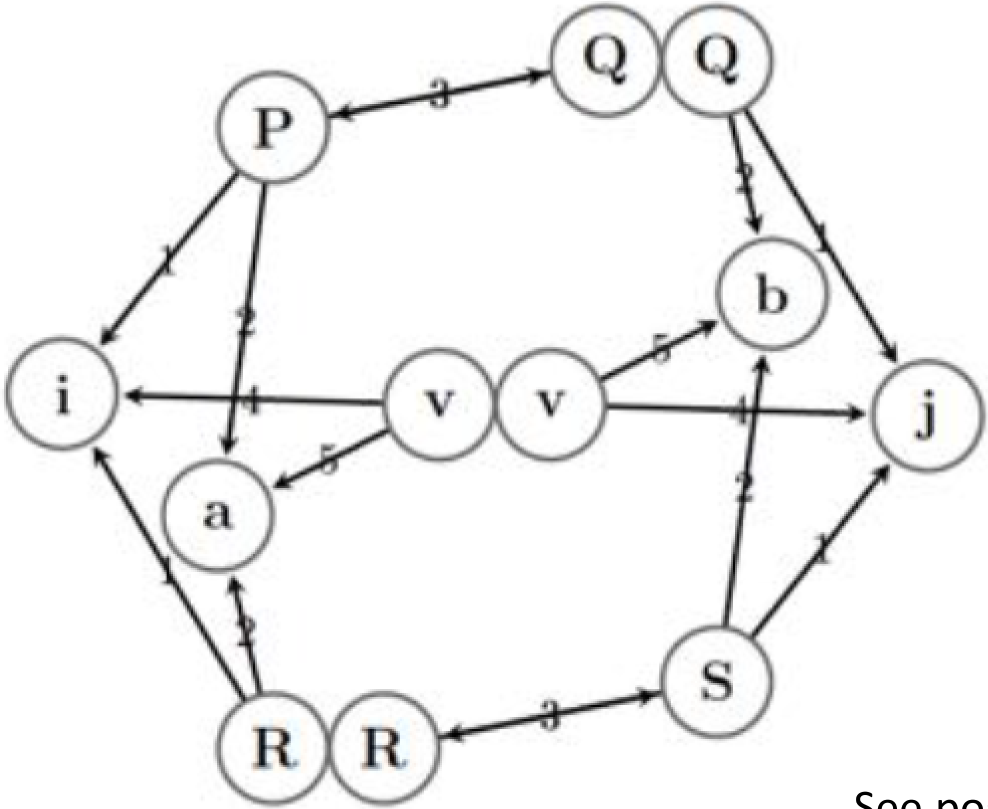


Graphical Representation of J-like term

$$E \leftarrow 2 \sum_{\nu} \sum_{ijab} \sum_{PQRS} \tau_i^{\nu} \tau_j^{\nu} \tau_a^{\nu} \tau_b^{\nu} \cdot X_i^P X_a^P Z^{PQ} X_j^Q X_b^Q \cdot X_i^R X_a^R Z^{RS} X_j^S X_b^S$$

Where to put parenthesis?

Automatic Factorization for THC



See poster by Ed Hohenstein

$$E \leftarrow 2 \sum_{\nu QR} \underbrace{\left(\sum_{P} \underbrace{\left(\sum_{i} \tau_i^{\nu} X_i^P X_i^R \right)}_{O^{\nu}_{PR}} \underbrace{\left(\sum_{a} \tau_a^{\nu} X_a^P X_a^R \right)}_{V^{\nu}_{PR}} Z^{PQ} \right)}_{A^{\nu}_{RQ}} \underbrace{\left(\sum_{S} \underbrace{\left(\sum_{j} \tau_j^{\nu} X_j^Q X_j^S \right)}_{O^{\nu}_{QS}} \underbrace{\left(\sum_{b} \tau_b^{\nu} X_b^Q X_b^S \right)}_{V^{\nu}_{QS}} Z^{RS} \right)}_{A^{\nu}_{RQ}}$$

Conclusions

- Lightspeed framework being developed to rapidly prototype new algorithms: will provide lessons for more flexible DSLs and implementation of core “boxes” in Legion
- NFDO method being developed using the Lightspeed framework – demonstrates ability to rapidly prototype in this environment
- Rank reduced Full CI leverages low complexity of CI wavefunctions
- Rank reduction techniques can also be used for electron repulsion integrals with tensor hypercontraction – we are exploring automated code generation and optimization to implement THC algorithms
- Simulations of photoenzyme activity in FAP are underway and will be enabled/facilitated by quantum chemistry and first principles dynamics developments

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