Reliable approximation in electronic structure methods:

from real space partitioning to quantum Monte Carlo approaches

Amanda Dumi Seminar at Oak Ridge National Laboratory

When is DFT not enough?

- DFT citation/publications demonstrate it's applicability and often reliable performance
- In strongly correlated regimes, or when functional and system physics do not agree

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Reduce cost through various system reductions

Sampling Configurations Quantum Monte Carlo: applications and developments

Hilbert Space

selected CI as approximate trial wave functions

Real Space

Determining molecular fragments with unsupervised machine learning (UML)

QMC application: periodic absorption[1]

H on graphene

Method	Binding energy (meV)
DMC	-691 $\pm$ 19
PW91	-810 to -830, -870
PBE	-790, -840, -980

- functional dependent binding energy
- a need for benchmark values

[1] A. Dumi et al, 'The Binding of Atomic Hydrogen on Graphene from Density Functional Theory and Diffusion Monte Carlo Calculations', *The Journal of Chemical Physics*, 156.14 (2022), 144702DOI:10.1063/5.0085982.

Diffusion Monte Carlo

- Recast the Schrodinger equation in imaginary time

$$\frac{\partial \left|\Psi\right\rangle}{\partial \tau} = -\hat{H}\left|\Psi\right\rangle$$

  - A formal soltuion to this:

$$\left|\psi\left(\tau_1 + \delta\tau\right)\right\rangle = e^{-\hat{H}\delta\tau}\left|\psi\left(\tau_1\right)\right\rangle$$

Anything non-orthogonal to the ground state is going to decay out exponentially

$$\lim_{\tau\to\infty}\left|\psi(\tau)\right\rangle = c_0 e^{-\epsilon_0\tau}\left|\phi_0\right\rangle$$

$$-\frac{\partial\psi(\mathbf{R},\tau)}{\partial\tau} =$$

$$\left[\sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2\psi(\mathbf{R},\tau)\right] \text{ diffusion term}$$

$$+$$

$$\left(V(\mathbf{R}) - E_T\right)\psi(\mathbf{R},\tau) \text{ branching term}$$

Importance sampling

- use of trial wavefunction for efficient sampling.

Fixed-node approximation

- Antisymmetry of fermions causes sampling problems
- Solution: fix nodes of trial wavefunction
- necessitates accurate nodal surface of trial wavefunction

QMC application: periodic absorption

H on graphene

Method	Binding energy (meV)
PBE	-820
PBE	-871
PBE0	-851 (-800)
HSE	-794 (-743)
DMC	-691 $\pm$ 19
PW91	-810 to -830, -870
PBE	-790, -840, -980

- QMCPACK binding energies provide benchmark.
- Hybrid functionals are very close.
- Even with close binding energies, density seems to disagree in bonding region.

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QMC application: non-valence correlation bound anion[2]

NVCB rely on accurate description of correlation to bind

$$E_{corr} = E_{true} - E_{HF}$$

model system: H_2O_4

Radial integration of Hartree-Fock orbital density, $R = 4$ Angstroms

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Selected-CI

$\Psi_n = \sum c_I^{(n)} |D_I\rangle$

$e_\alpha = \frac{\langle \Psi^{(n)} | \hat{H} | \alpha \rangle^2}{E^{(n)} - \langle \alpha | \hat{H} | \alpha \rangle}$.

$\{|\alpha\rangle\}$

single & double excitations

$\{|\alpha\rangle\}_*^{(n)}$

Ψ_n

Ψ_{n+1}

H_2O_4 Results

wave function	basis set	EBE (meV)
D/HF	aug-cc-pVDZ+7s7p	183 ± 10
SD/HF	aug-cc-pVDZ	176 ± 12
SD/HF	cc-pVDZ	-528 ± 25
SD/B3LYP	aug-cc-pVDZ+7s7p	212 ± 11
SD/HF(N)//SD/NO SDCI(A)	aug-cc-pVDZ+7s7p	205 ± 10
SD/HF(N)//MD/NO SDCI(A)	aug-cc-pVDZ+7s7p	202 ± 12

[2]S. Upadhyay et al, 'The Role of High-Order Electron Correlation Effects in a Model System for Non-Valence Correlation-Bound Anions', *The Journal of Chemical Physics*, 153.22 (2020), 224118DOI:10.1063/5.0030942.

wave function	basis set	EBE (meV)
MD/CIPSI NO	aug-cc-pVDZ+3s1p	190 ± 9

- Summary of selected-CI success/challenges and overall performance of other methods.

$R = 7$

- HF binds electron -> correlation not essential
- still orbital shape has noticeable changes
- DFT can recover those changes.

$R = 4$

- NCVB regime
- HF does not bind
- CIPSI shape changes slight, impacts energy.
- SDCI shape seems wrong

Follow-up Questions Ongoing projects at Sandia National Laboratories

- Can various selected CI approaches or later optimizations improve the compactness and quality of the trial wave function?
- Is there a balance in how well we are capturing dynamic vs static correlation in these systems? Especially in cases of energy differences.

↪ Aluminum systematic study: exploring various multideterminant generation and optimization schemes

- Selected CI captures static correlation, but should we take a second look at how dynamic correlation is captured?

↪ Jastrow form study

Jastrow Factor forms

$$\Psi(\{r_i\}\{r_I\}) = exp(\mathcal{J})D(\{r_i\})$$

standard: parameterize separate 1,2, and 2-body terms. optimize parameters with VMC

A possible alternative form:

- Using framework of SNAP atomic potential
- represent the particle densities as bispectrum components.[3] [4]
- A perspective of particle neighborhoods which require fewer parameters for VMC optimization

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Projection of the ρ particle density on the surface of the 4-D sphere:

$$E^i_{SNAP}\left(\mathbf{B}^i\right) = \beta_0^{\alpha_i} + \sum_{k=1}^{K} \beta_k^{\alpha_i} B_k^i = \beta_0^{\alpha_i} + \beta^{\alpha_i} \cdot \mathbf{B}^i$$

$$B_{j_1,j_2,j} = \sum_{m_1',m_1=-j_1}^{j_1} \sum_{m_2',m_2=-j_2}^{j_2} \sum_{m',m=-j}^{j} \left(c^j_{m'm}\right)^* C^{jm}_{j_1 m_1 j_2 m_2} \times C^{jm'}_{j_1 m_1' j_2 m_2'} c^{j_1}_{m_1' m_1} c^{j_2}_{m_2' m_2}$$

TO DO:

initial python sandbox for testing unit tests ensure single and multiple species work accessing LAMMPS API object interface with QMCPack

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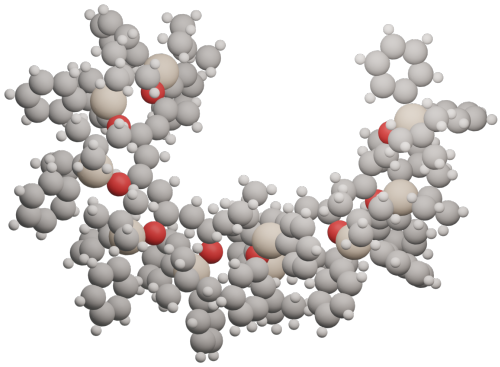
[3] A. P. Bartók, R. Kondor, and G. Csányi, 'On Representing Chemical Environments', *Phys. Rev. B*, 87 (2013), 184115DOI:10.1103/PhysRevB.87.184115.

[4] ,A. P. Thompson et al, 'Spectral Neighbor Analysis Method for Automated Generation of Quantum-Accurate Interatomic Potentials', *Journal of Computational Physics*, 285 (2015), 316–30DOI:https://doi.org/10.1016/j.jcp.2014.12.018.

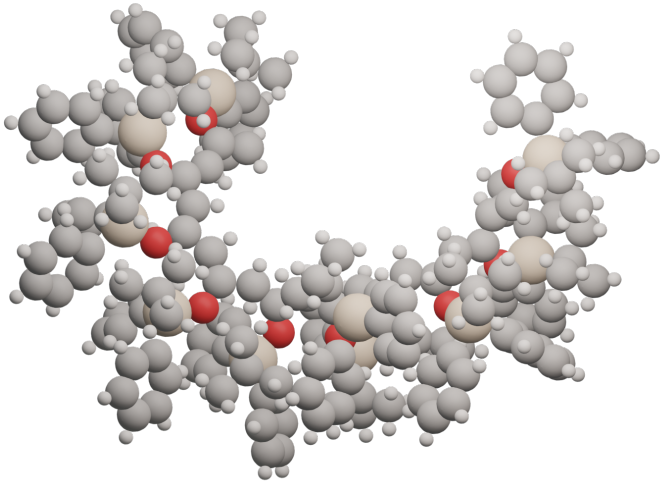
Fragmenting with unsupervised machine learning

Problem

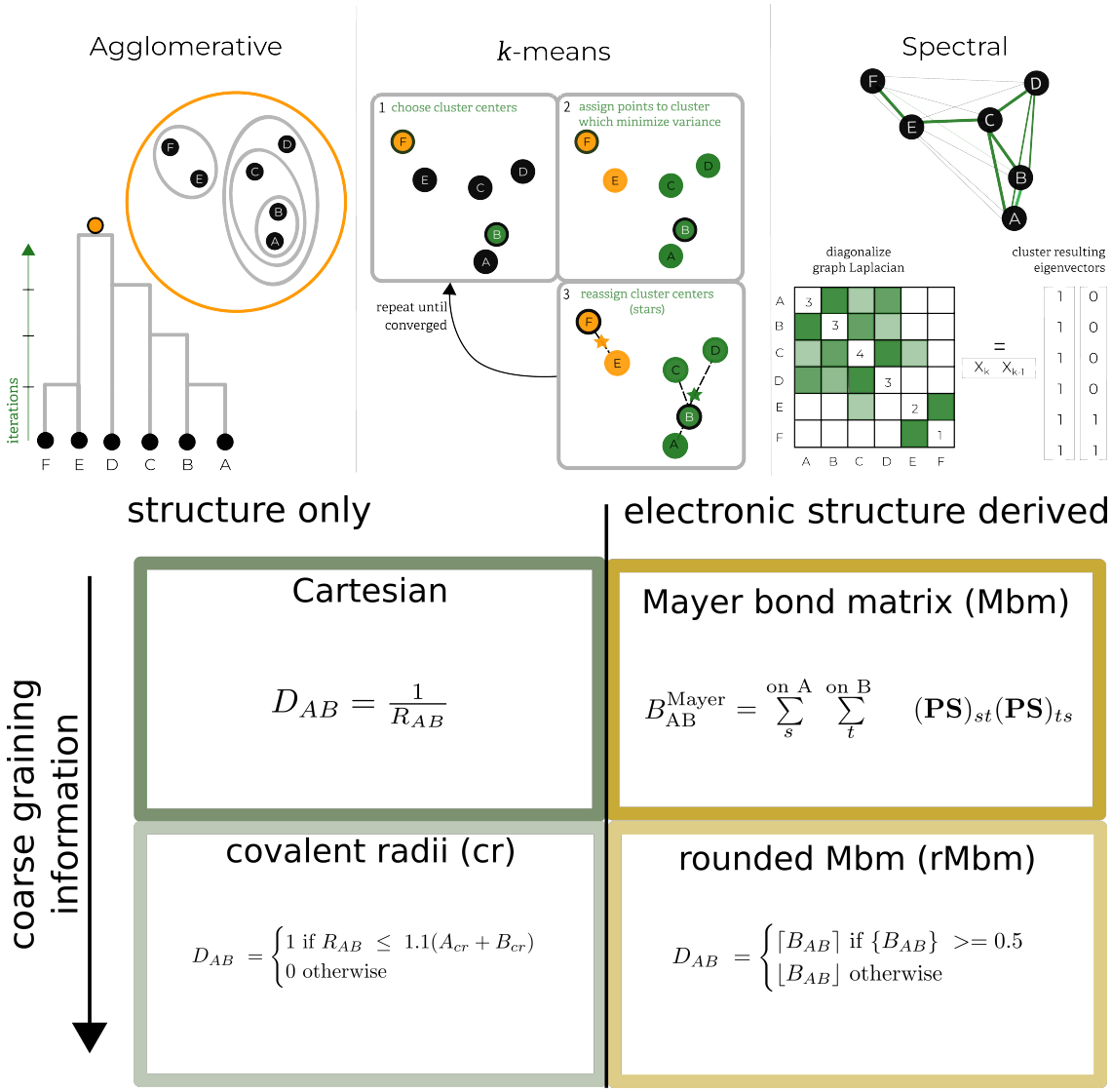


Fragmenting with unsupervised machine learning

Problem



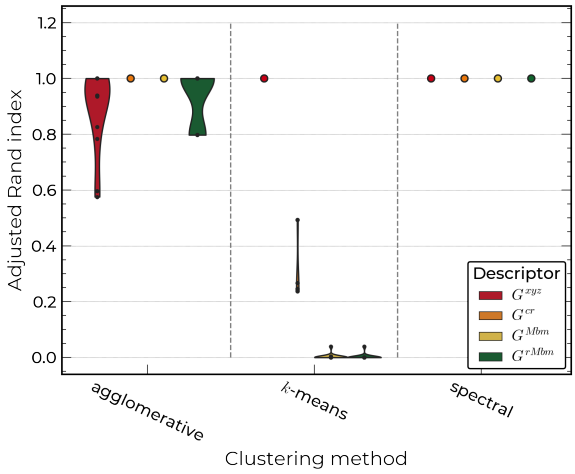
Approach



Performance

Systems:

- water clusters
- methylthiophenes
- small polymer systems



Performance:

Summary:

- UML methods are able to resolve fragments
- spectral clustering performs well and is insensitive to descriptor

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Conclusions

In regimes of strong electron correlation, mean field methods may be problematic and require need alternatives

Presented on three approaches:

- QMC: application to H_2O_4 and H on graphene ↪ systems where DFT varies.
- SCI methods in H_2O_4 as trial wave function
- UML MF: offer an approach to determining molecular fragmentation automatically, with very little information

References

Albert P. Bartók, Risi Kondor, & Gábor Csányi, 'On Representing Chemical Environments', *Phys. Rev. B*, 87 (2013), 184115DOI:10.1103/PhysRevB.87.184115

Amanda Dumi, Shiv Upadhyay, Leonardo Bernasconi, Hyeondeok Shin, Anouar Benali, & Kenneth D. Jordan, 'The Binding of Atomic Hydrogen on Graphene from Density Functional Theory and Diffusion Monte Carlo Calculations', *The Journal of Chemical Physics*, 156.14 (2022), 144702DOI:10.1063/5.0085982

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Shiv Upadhyay, Amanda Dumi, James Shee, & Kenneth D. Jordan, 'The Role of High-Order Electron Correlation Effects in a Model System for Non-Valence Correlation-Bound Anions', *The Journal of Chemical Physics*, 153.22 (2020), 224118DOI:10.1063/5.0030942