

# Reliable approximation in electronic structure methods: from real space partitioning to quantum Monte Carlo approaches

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# 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

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  
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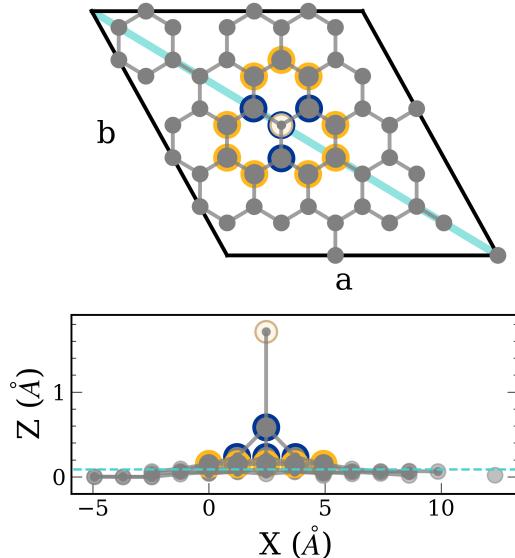
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# QMC application: periodic absorption<sup>1</sup>

## 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), 144702 DOI:10.1063/5.0085982 .

# Diffusion Monte Carlo

- Recast the Schrodinger equation in imaginary time

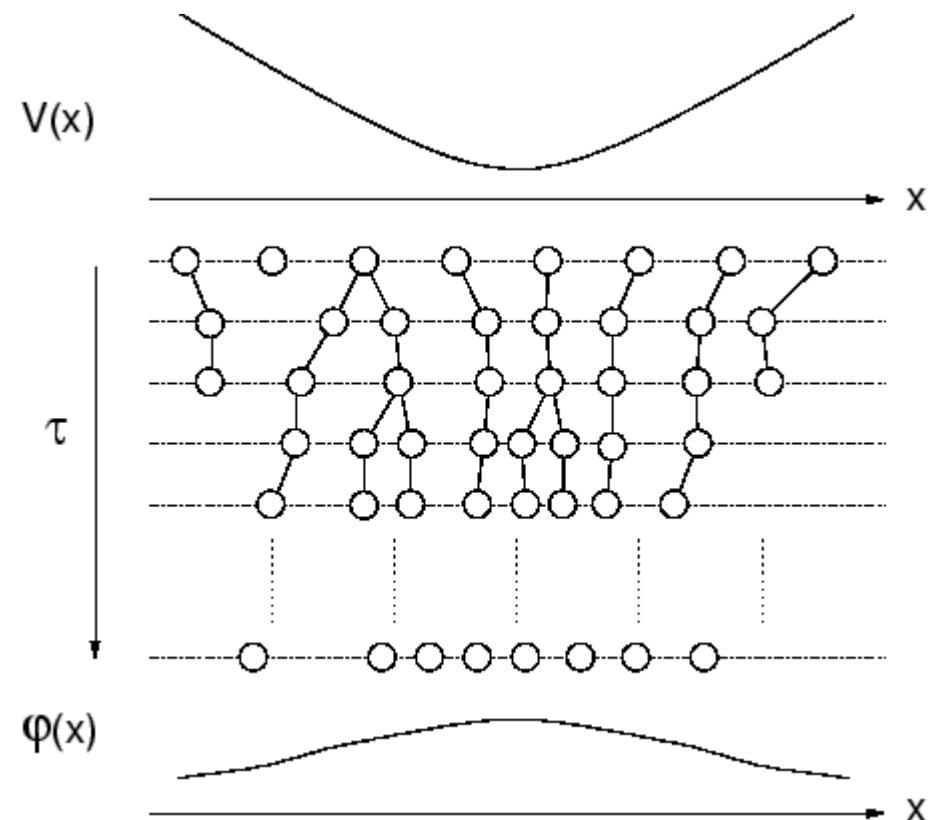
$$\frac{\partial |\Psi\rangle}{\partial \tau} = -\hat{H} |\Psi\rangle$$

- A formal solution to this:

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

Anything non-orthogonal to the ground state decays exponentially

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



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

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

+

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

# Importance sampling

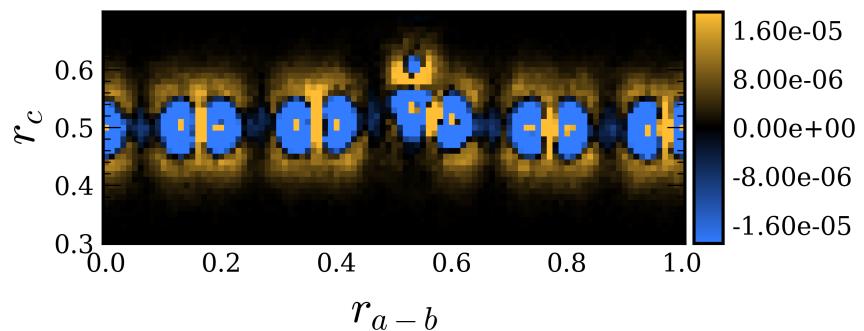
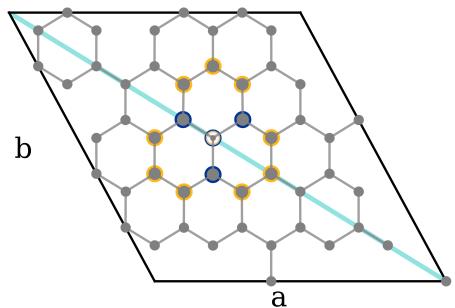
- use of trial wavefunction for efficient sampling.

# 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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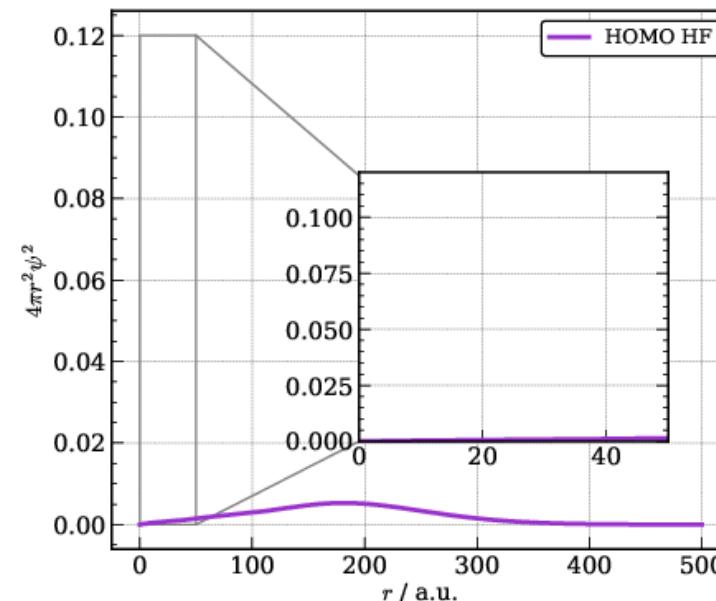
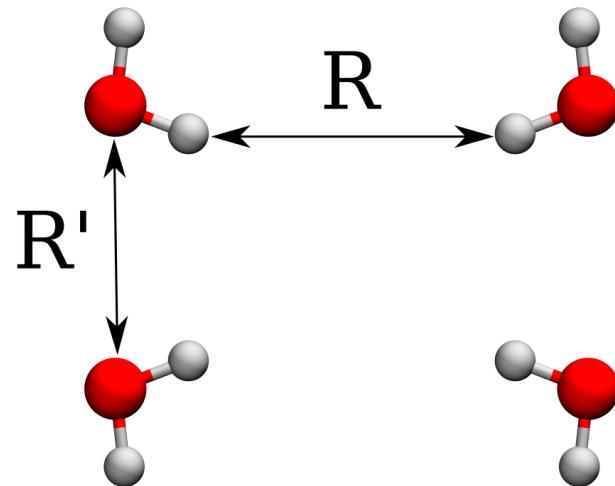
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# QMC application: non-valence correlation bound anion<sup>1</sup>

NVCB rely on accurate description of correlation to bind

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



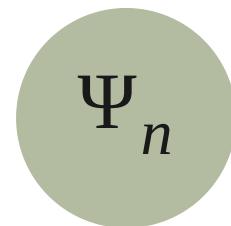
1. S. Upadhyay et al, “The Role of High-Order Electron Correlation Effects in a Model System for Non-Valence Correlation-Bound Anions,” *The Journal of Chemical Physics*, 153.22 (2020), 224118 DOI:10.1063/5.0030942 .

# Selected-Cl

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

# Selected-CI

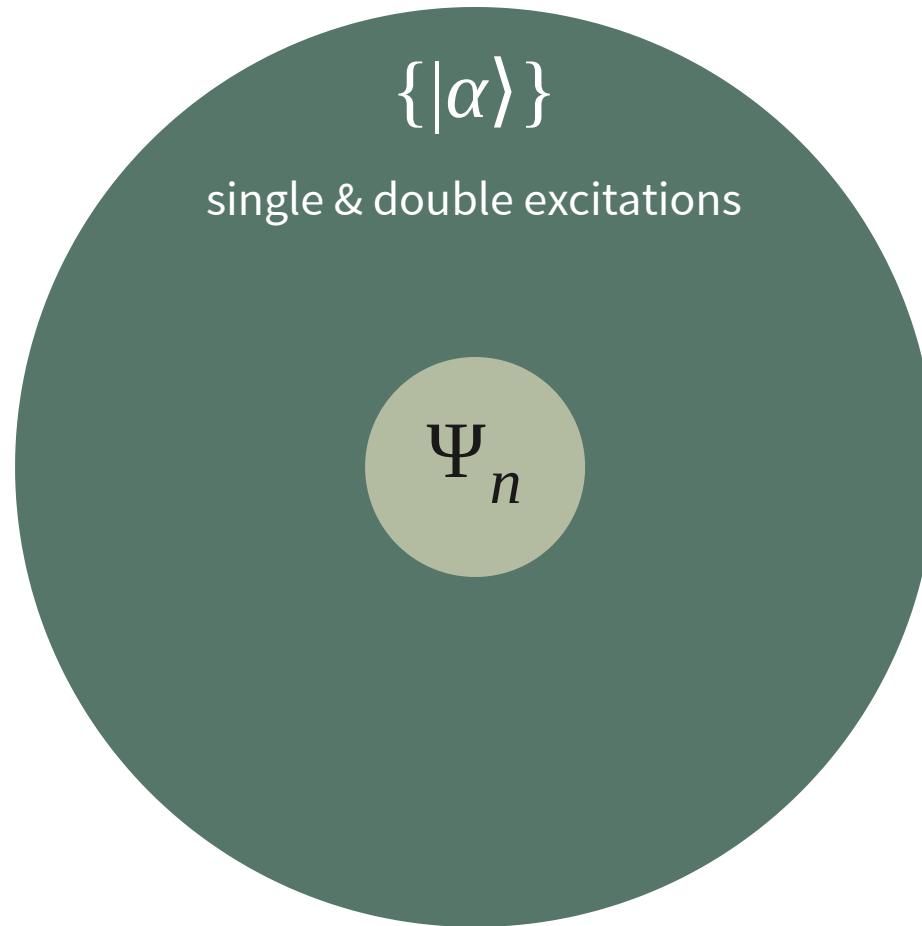
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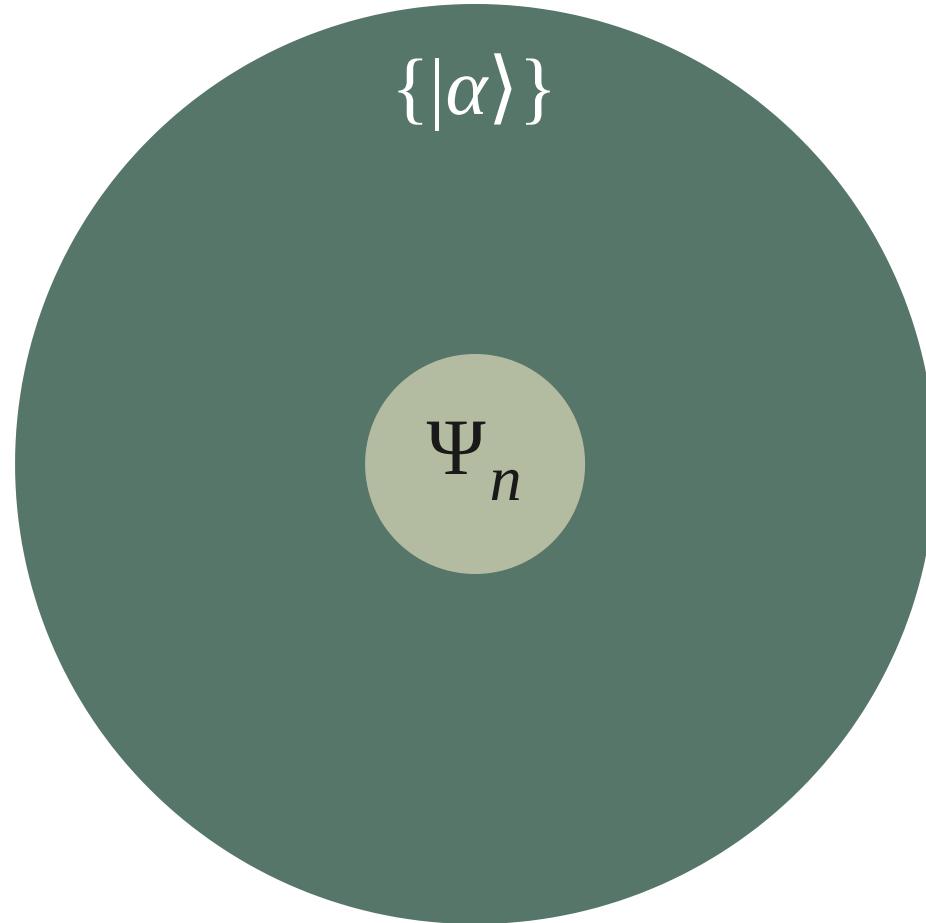
$$e_\alpha = \frac{\langle \Psi^{(n)} | \hat{H} | \alpha \rangle^2}{E^{(n)} - \langle \alpha | \hat{H} | \alpha \rangle}.$$



# Selected-CI

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

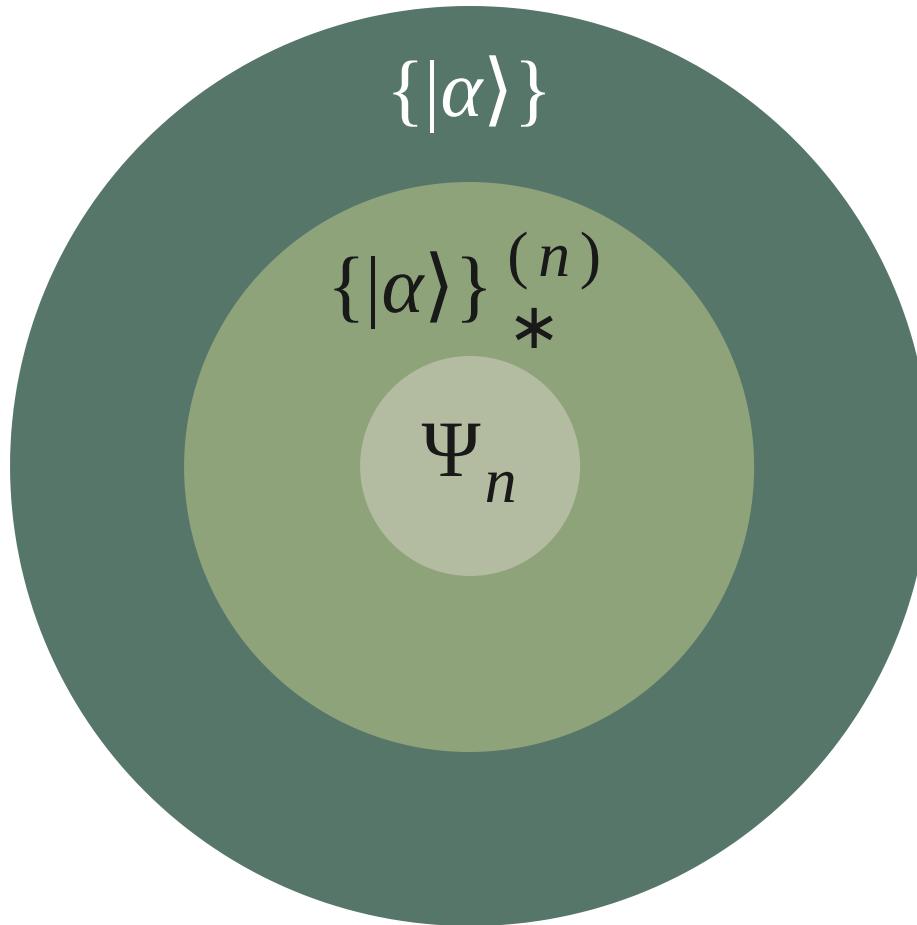
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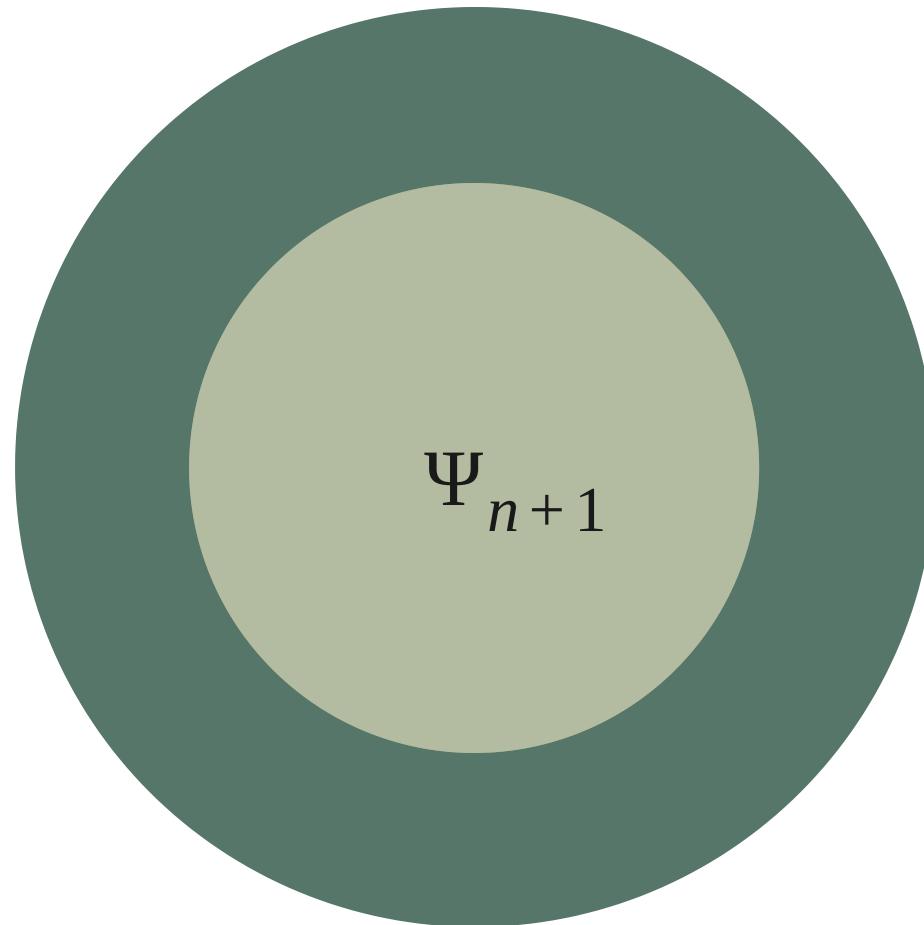
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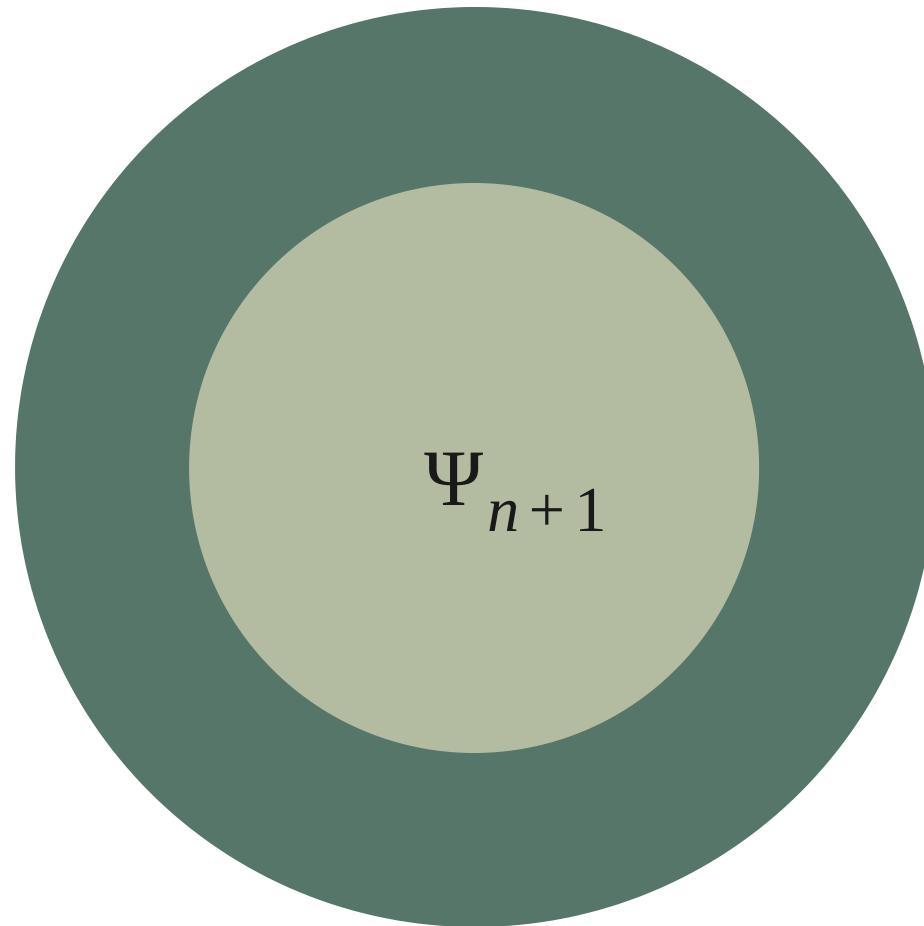
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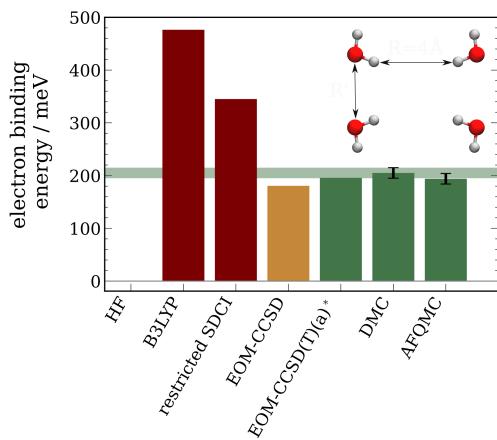
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# $\text{H}_2\text{O}_4$ Results

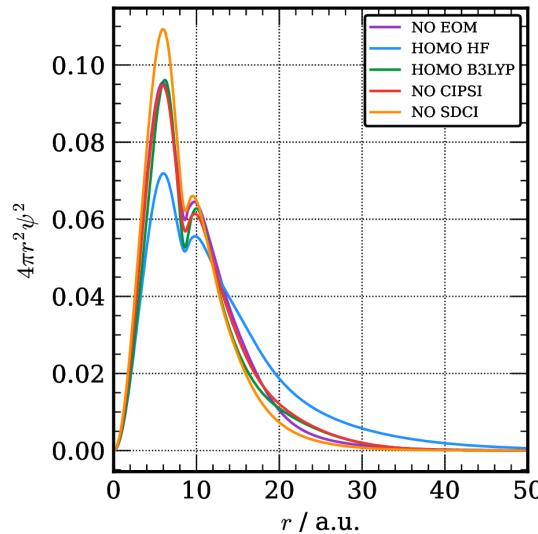
## QMC for weak $e^-$ binding



wave function	basis set	EBE (meV)
D/HF	aug-cc-pVDZ+7s7p	$183 \pm 10$
SD/HF	aug-cc-pVDZ	$176 \pm 12$
SD/HF	cc-pVDZ	$-528 \pm 25$
SD/B3LYP	aug-cc-pVDZ+7s7p	$212 \pm 11$
SD/HF(N)//SD/NO SDCI(A)	aug-cc-pVDZ+7s7p	$205 \pm 10$
SD/HF(N)//MD/NO SDCI(A)	aug-cc-pVDZ+7s7p	$202 \pm 12$
MD/CIPSI NO	aug-cc-pVDZ+3s1p	$190 \pm 9$

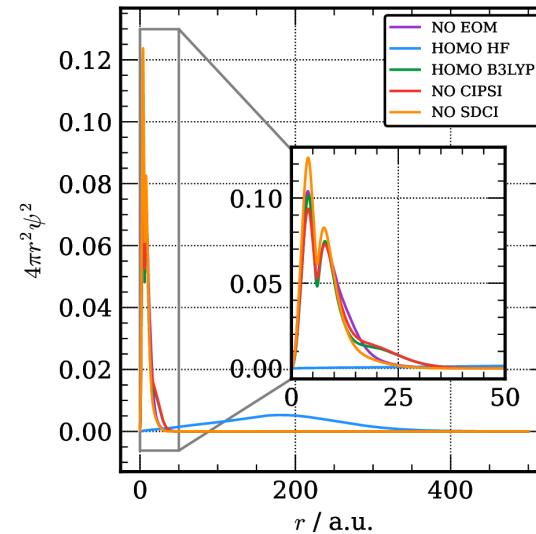
- Summary of selected-Cl success/challenges and overall performance of other methods.

$R = 7$



- 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



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- Is there a balance in how well we are capturing dynamic vs static correlation in these systems? Especially in cases of energy differences.



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Ongoing projects at Sandia National Laboratories

- Can various selected CI approaches or later optimizations improve the compactness and quality of the trial wave function?
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  - ↳ Aluminum systematic study: exploring various multideterminant generation and optimization schemes



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- 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.<sup>1 2</sup>
- A perspective of particle neighborhoods which require fewer parameters for VMC optimization



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

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

Projection of the  $\rho$  particle density on the surface of the 4-D sphere:

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

$$\begin{aligned} B_{j_1, j_2, j} = & \sum_{m'_1, m_1 = -j_1}^{j_1} \sum_{m'_2, m_2 = -j_2}^{j_2} \sum_{m', m = -j}^j \left( c_{m'm}^j \right)^* C_{j_1 m_1 j_2 m_2}^{jm} \\ & \times C_{j_1 m'_1 j_2 m'_2}^{jm'} C_{m'_1 m_1}^{j_1} C_{m'_2 m_2}^{j_2} \end{aligned}$$

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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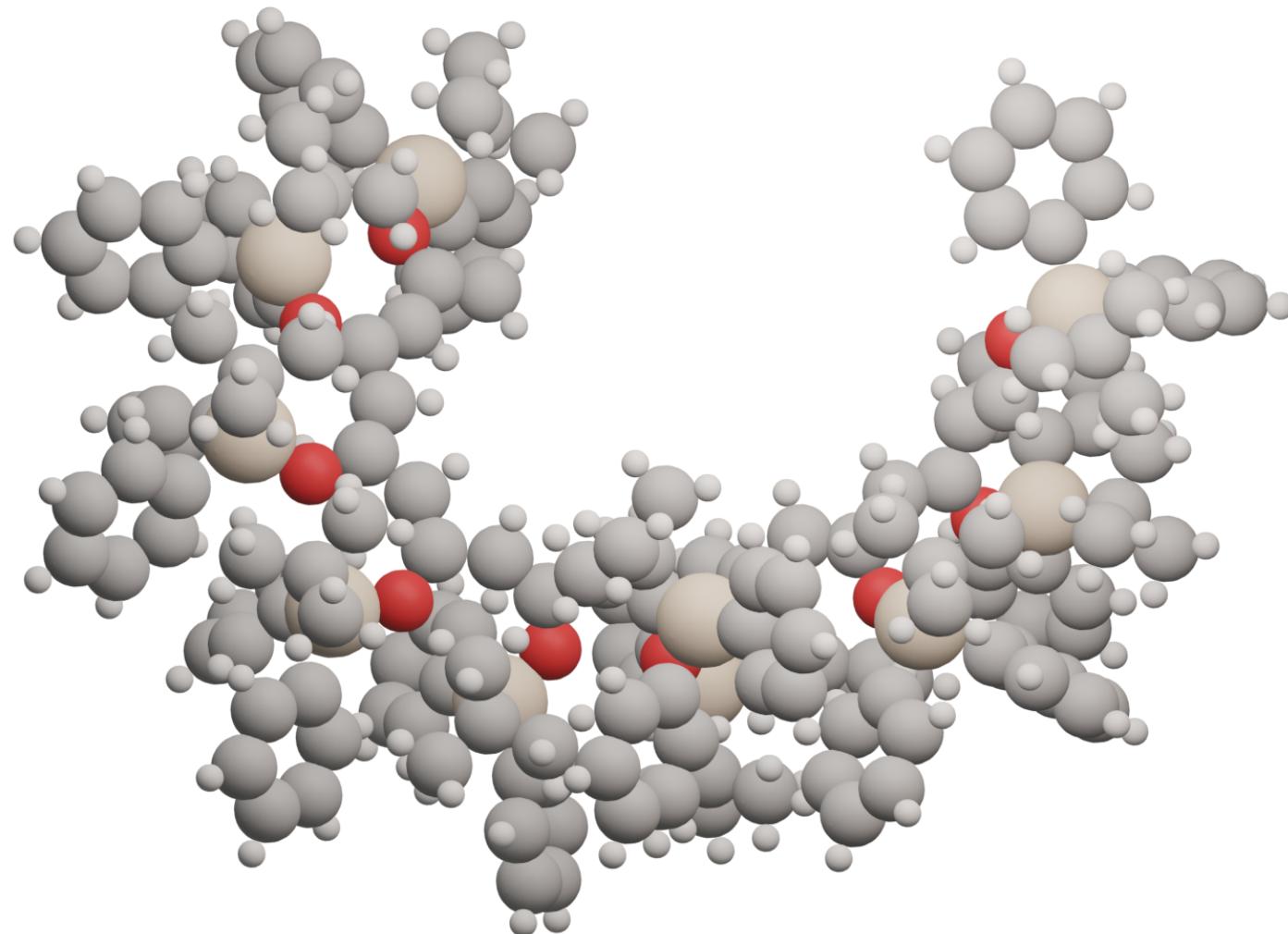
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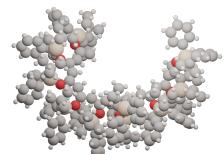
# Fragmenting with unsupervised machine learning

## Problem

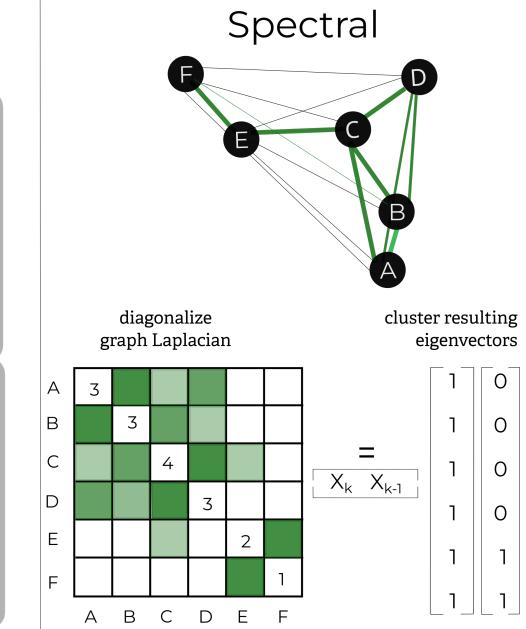
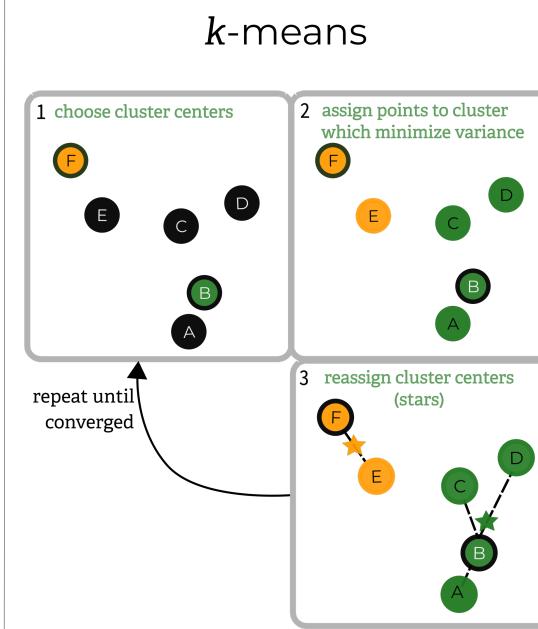
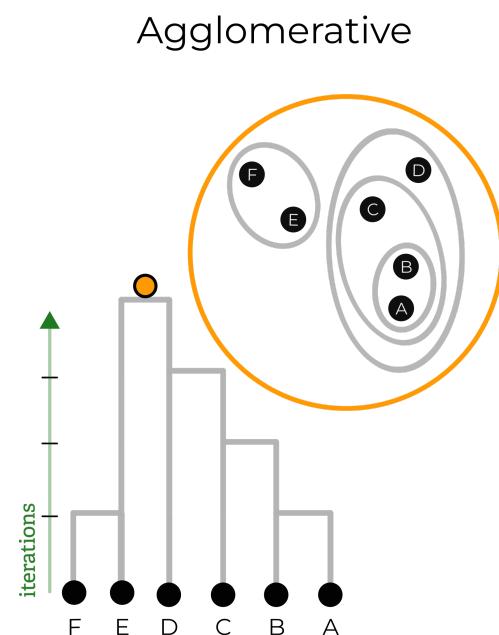


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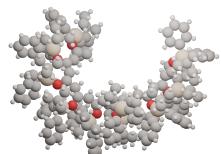


Approach



# Fragmenting with unsupervised machine learning

Problem



Approach

structure only

Cartesian

$$D_{AB} = \frac{1}{R_{AB}}$$

electronic structure derived

Mayer bond matrix (Mbm)

$$B_{AB}^{\text{Mayer}} = \sum_s^{\text{on A}} \sum_t^{\text{on B}} (\mathbf{PS})_{st} (\mathbf{PS})_{ts}$$

covalent radii (cr)

$$D_{AB} = \begin{cases} 1 & \text{if } R_{AB} \leq 1.1(A_{cr} + B_{cr}) \\ 0 & \text{otherwise} \end{cases}$$

coarse graining  
information

rounded Mbmm (rMbm)

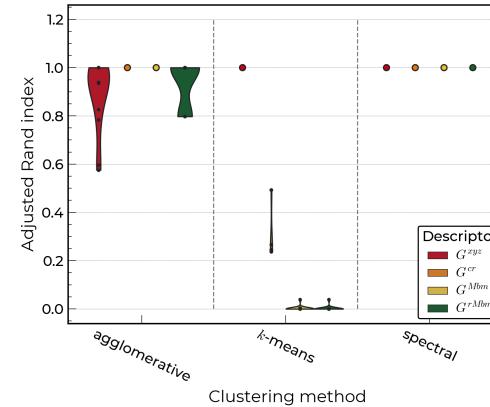
$$D_{AB} = \begin{cases} \lceil B_{AB} \rceil & \text{if } \{B_{AB}\} \geq 0.5 \\ \lfloor B_{AB} \rfloor & \text{otherwise} \end{cases}$$

# 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

# Acknowledgements

- Dr. Kenneth D. Jordan
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- Argonne Leadership Computing Facility
- Sandia National Laboratories

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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  $\text{H}_2\text{O}_4$  and H on graphene  
    → systems where DFT varies.
- SCI methods in  $\text{H}_2\text{O}_4$  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](https://doi.org/10.1103/PhysRevB.87.184115)
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