

Partitioning electronic structure problems when DFT isn't enough

Amanda Dumi
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Why deviate from the norm?

- DFT citation/publications
- DFT works well when
- DFT fails when

Reduce cost through various system reductions

Sampling Configurations

Quantum Monte Carlo:
applications and
developments

Hilbert Space

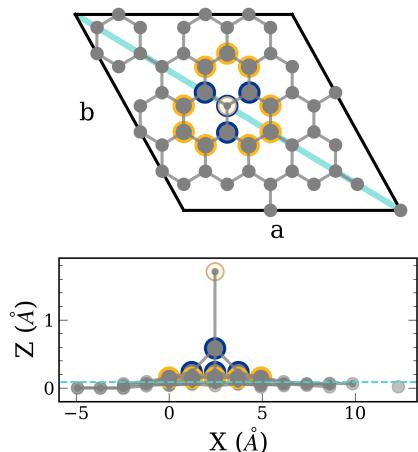
selected CI as approximate
trial wave functions

Real Space

Determining molecular
fragments with
unsupervised machine
learning (UML)

QMC application: periodic absorption¹

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

Diffusion Monte Carlo

- Recast the Schrodinger equation in imaginary time

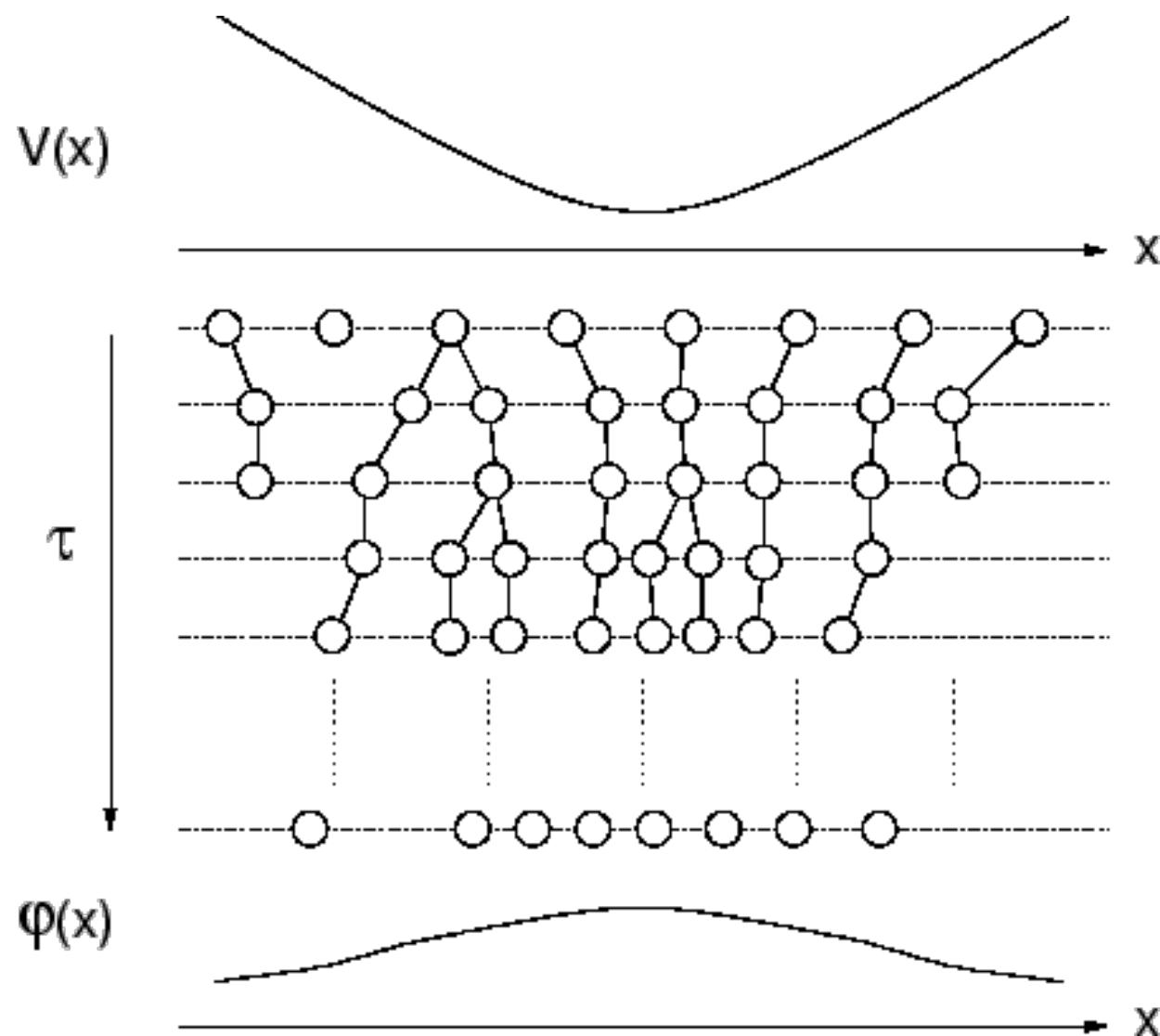
$$\frac{\partial |\Psi\rangle}{\partial \tau} = -\hat{H} |\Psi\rangle$$

- 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 is going to decay out exponentially

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



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

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

+

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

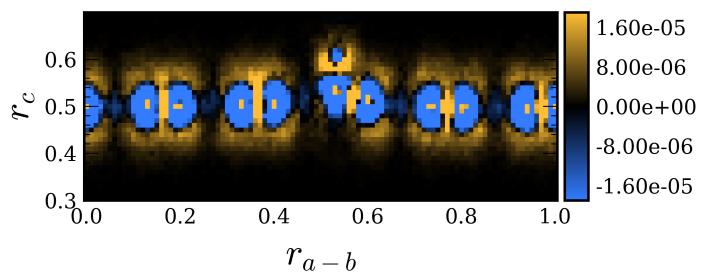
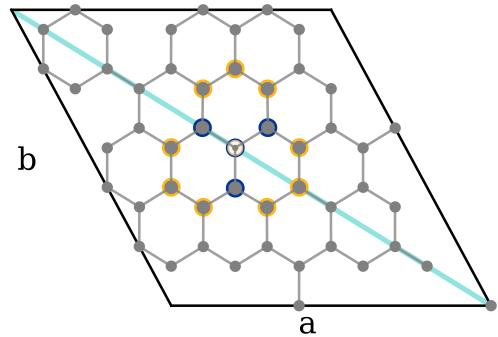
Importance sampling

- 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
PBEO	-851 (-800)
HSE	-794 (-743)
DMC	-691 ± 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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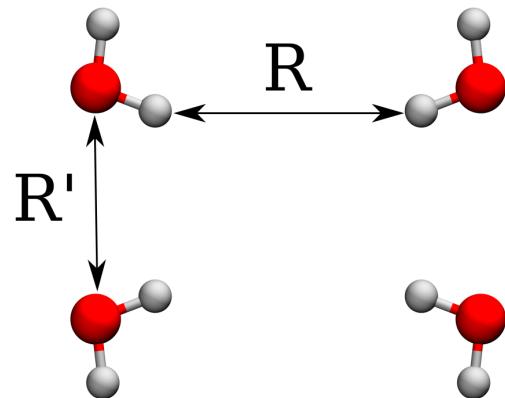
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QMC application: non-valence correlation bound anion¹

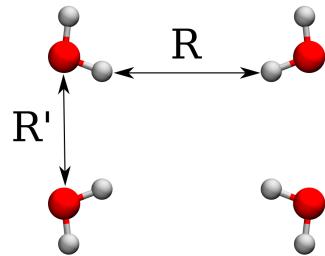
NVCB rely on accurate description of correlation to bind

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



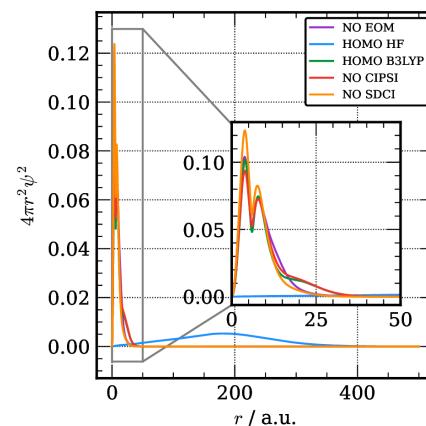
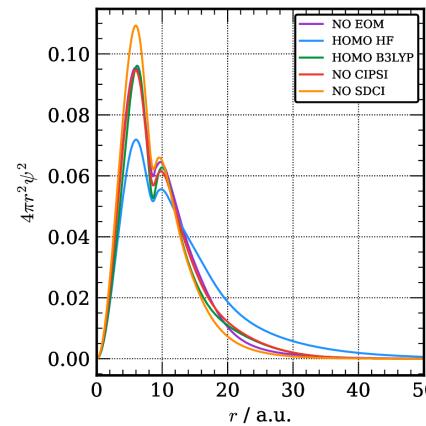
model system: H_2O_4

H₂O₄ 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
MD/CIPSI NO	& aug-cc-pVDZ+3s1p	190 ± 9

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



Follow-up Questions

Ongoing projects at Sandia National Laboratories

- Can various SCI approaches or later optimization 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 optimizaiton schemes
- SCI 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.¹²
- A perspective of partical neighborhoods which require fewer parameters for VMC optimization



Projection of the ρ 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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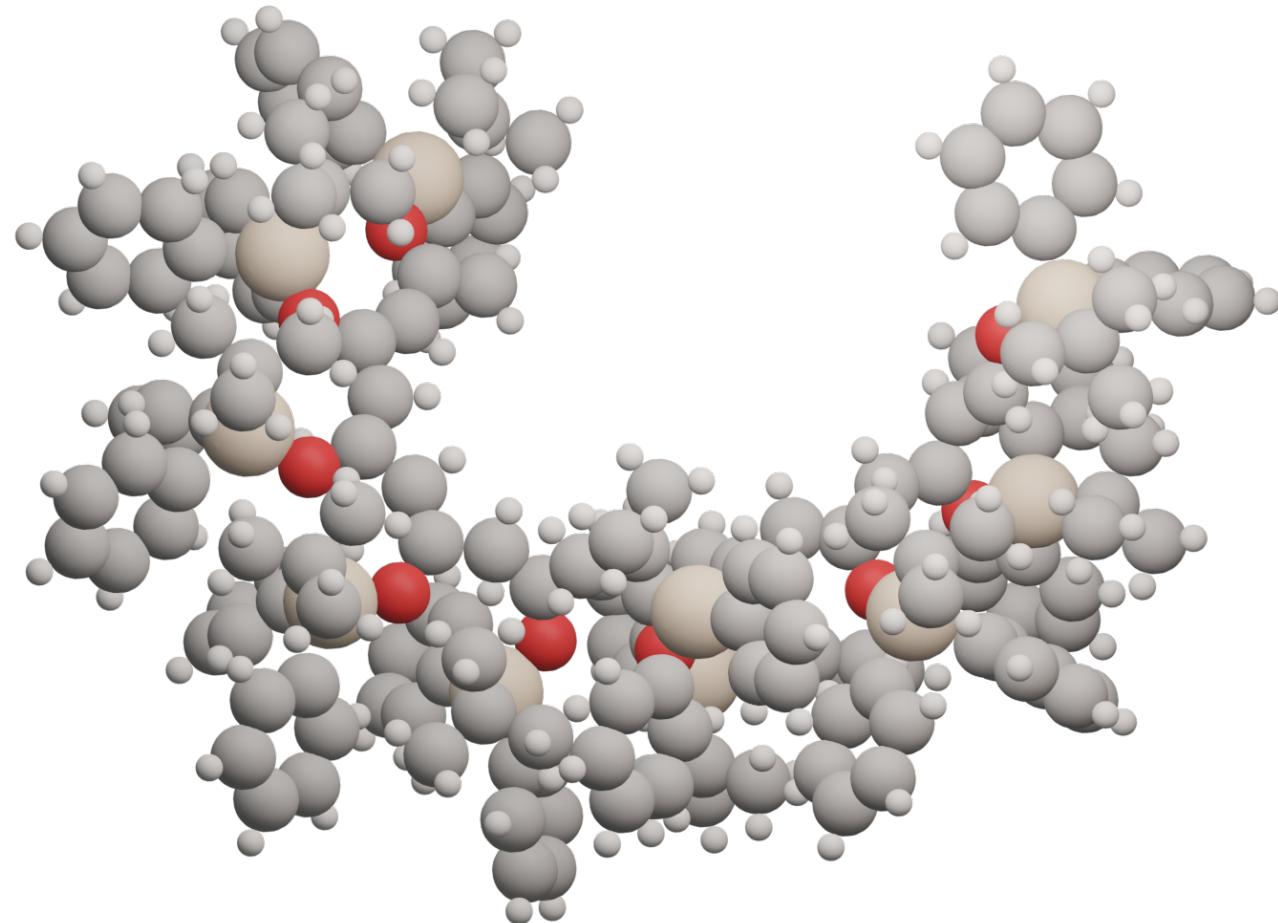
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Fragmenting with unsupervised machine learning

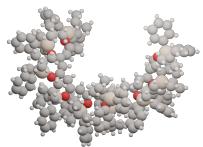
Problem



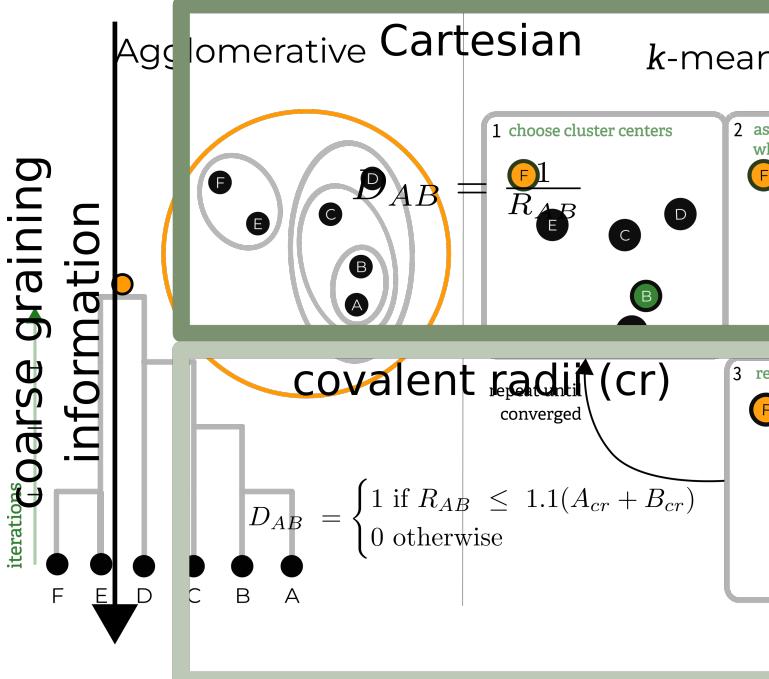
Fragmenting with unsupervised machine learning

Problem

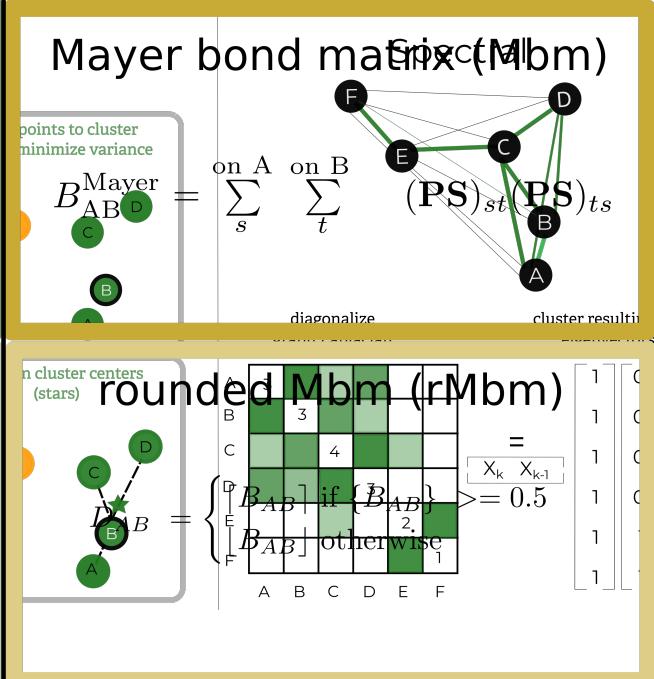
Approach



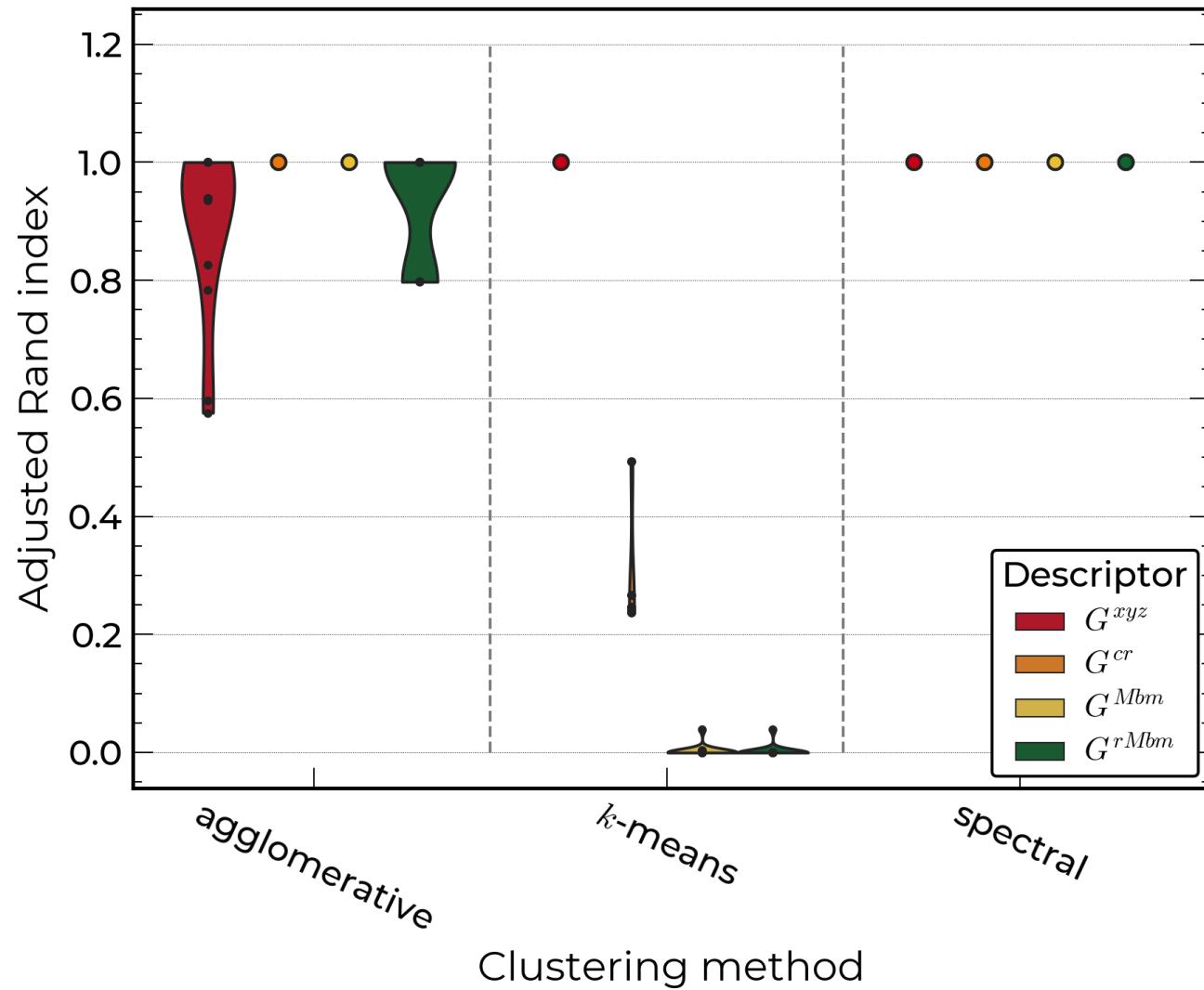
structure only



| electronic structure derived



Performance



Acknowledgements

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Computational Resources

- Pitt center for research computing
- Argonne Leadership Computing Facility

Funding: - Need to add this



Sandia
National
Laboratories



Argonne
NATIONAL LABORATORY



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

Presented on three:

- UML MF: offer an approach to determining molecular fragmentation automatically, with very little information.
- QMC: application to H₂O₄ and H on graphene.
→ systems where DFT varies.
- SCI methods in H₂O₄ as trial wave function.

References

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