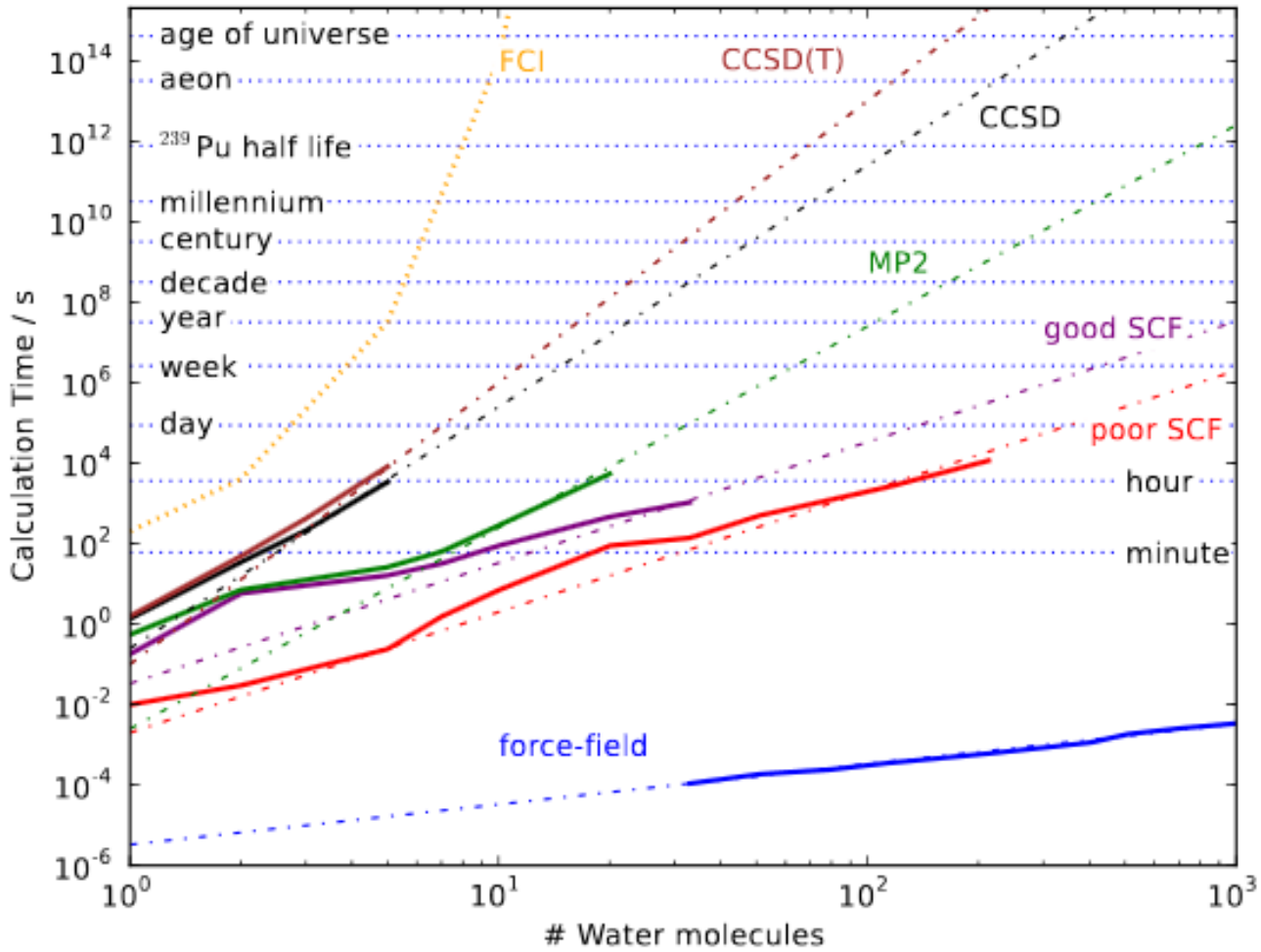
Extrapolation techniques to improve the scaling of electronic structure

Ankit Mahajan

Department of Physics,
IIT Bombay

Outline

More is difficult!



Source: Thom, A. ECIQMC, (Un)linked Stochastic Coupled Cluster Theory and Other Animals.

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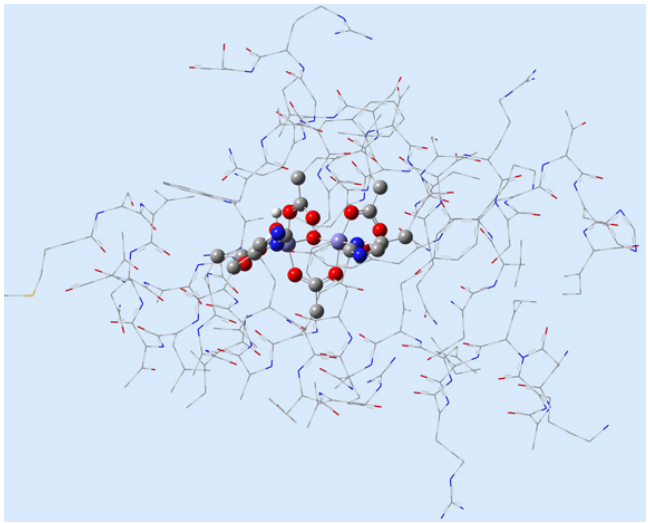
What is PIE-ONIOM?

Hybrid methods
Divide into layers



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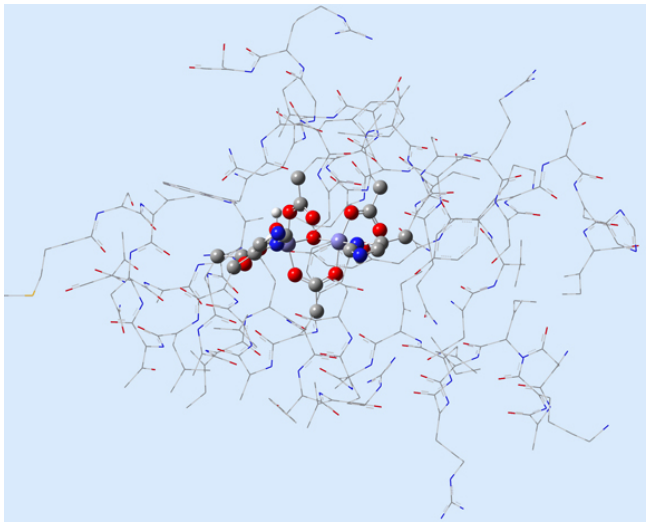
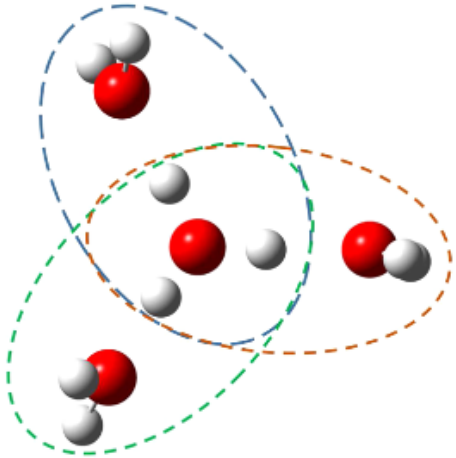


+

Frgament methods
Divide into fragments



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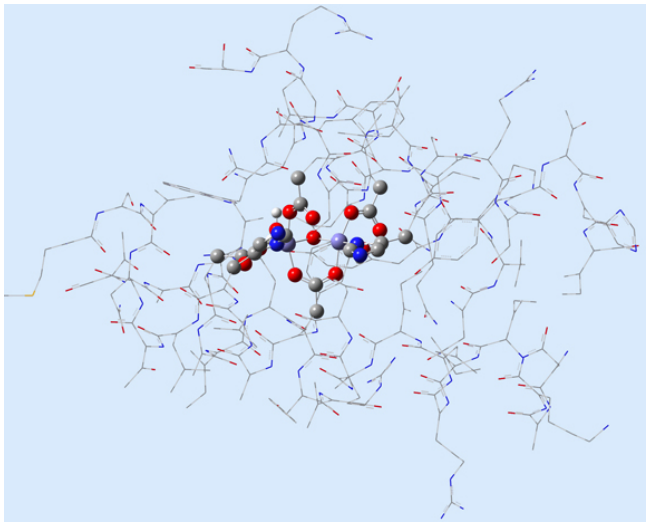

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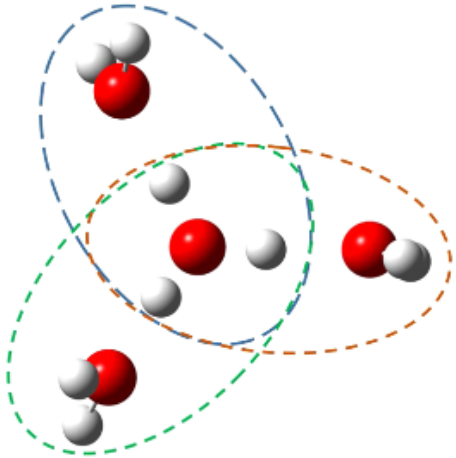

PIE-ONIOM
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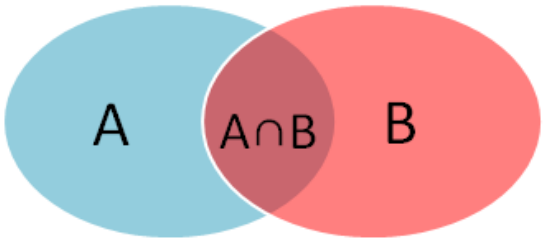
What is PIE-ONIOM?



$$E_{PIE-ONIOM} = [E^{high}(A) + E^{high}(B) - E^{high}(A \cap B)]$$

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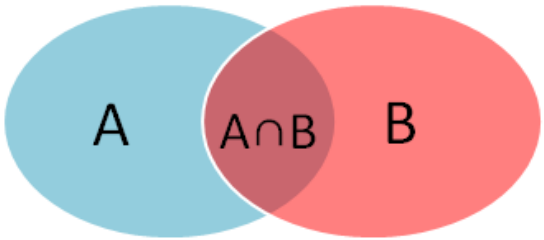

$$E_{PIE-ONIOM} = [E^{high}(A) + E^{high}(B) - E^{high}(A \cap B)] + E^{low}(A \cup B) - [E^{low}(A) + E^{low}(B) - E^{low}(A \cap B)]$$

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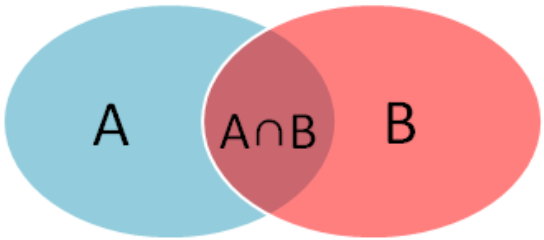

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Generalize with the principle of inclusion-exclusion

How is it implemented?

Calculate fragments

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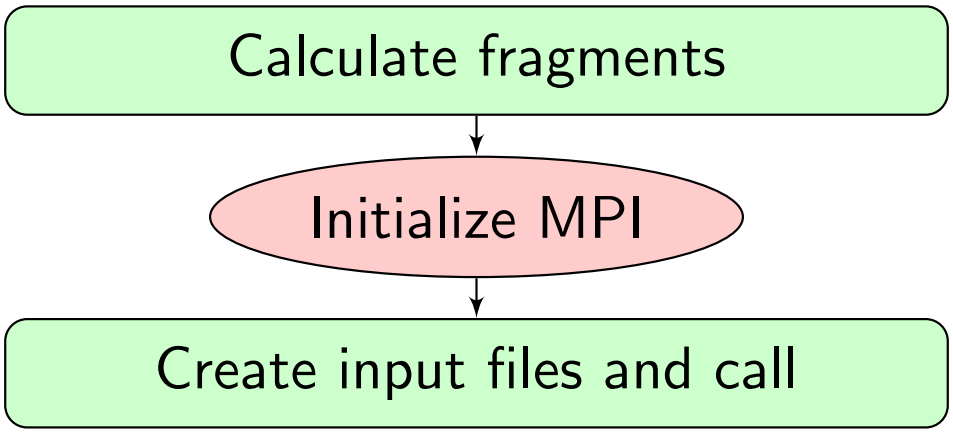

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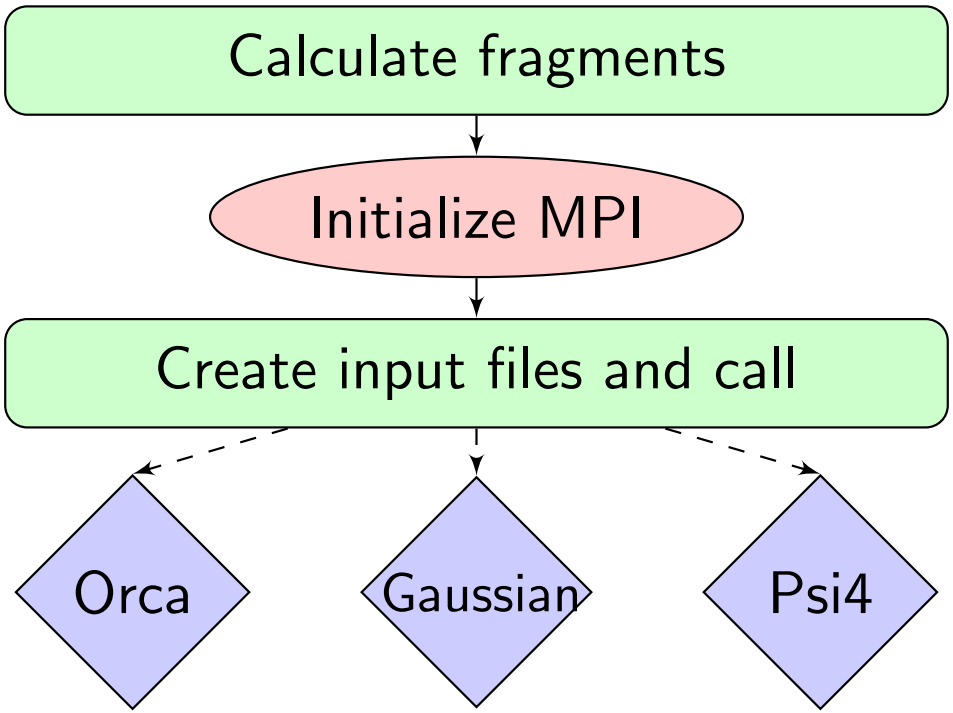

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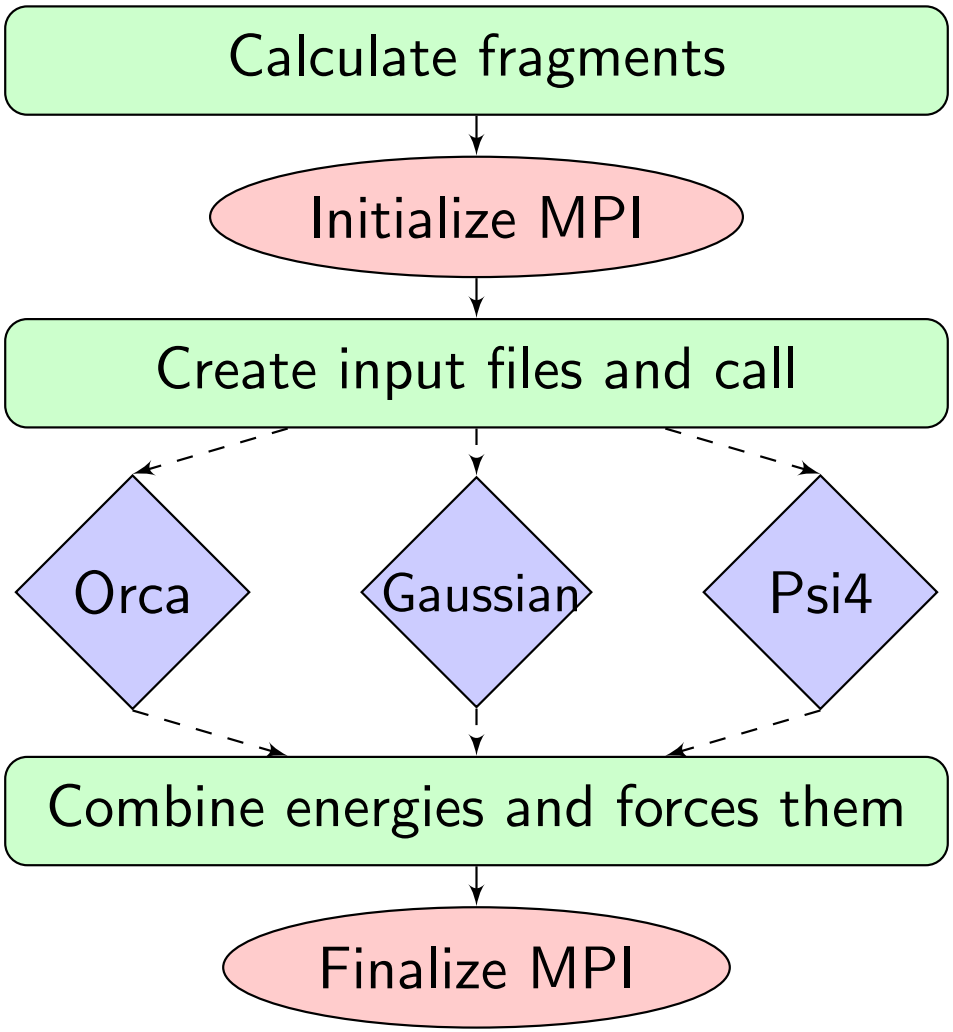
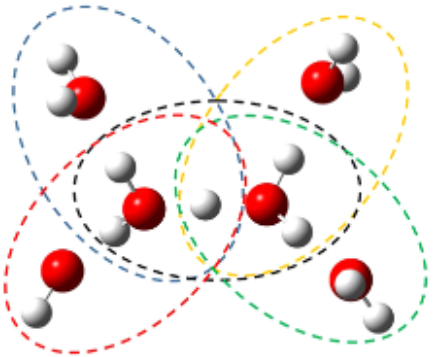


Born Oppenheimer Molecular Dynamics



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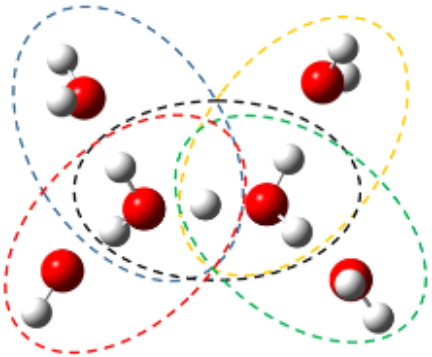

$$M_I \ddot{\mathbf{R}}_\mathbf{I}(t) = -\nabla_I min\{\int \Psi^* \hat{H} \Psi d\mathbf{r}\}$$

$$\hat{H}\Psi_0 = E_0\Psi_0$$

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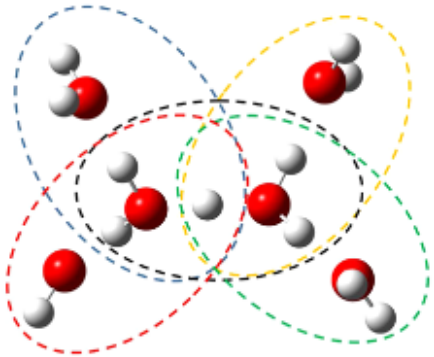

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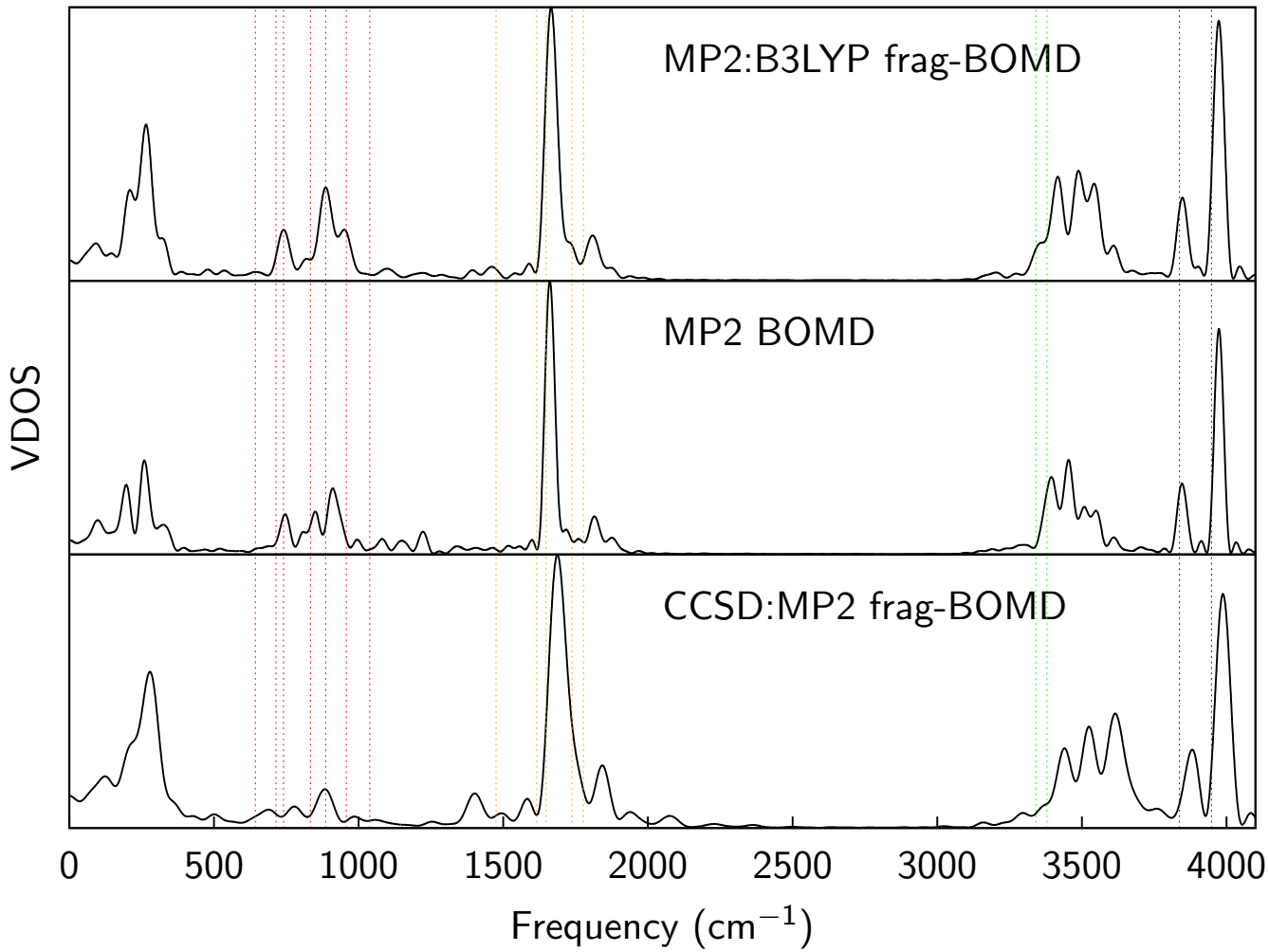
$$I_V(\omega) = \lim_{T\to\infty} \int_{t=0}^{t=T} exp(-i\omega t)\langle \mathbf{V}(0).\mathbf{V}(t)\rangle dt$$

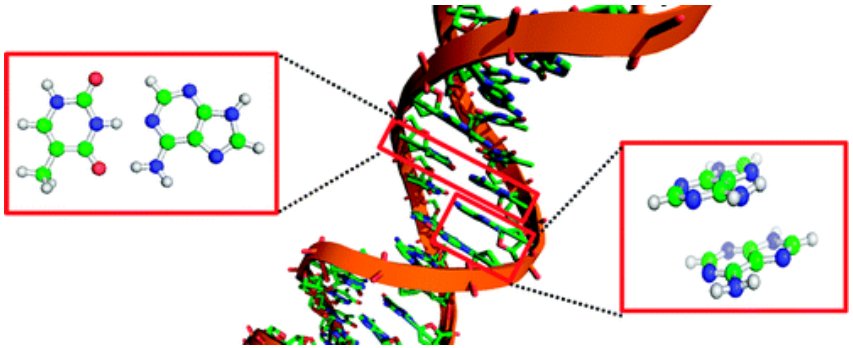
Vibrational density of states



Outline

Introduction

- Weak but important: found in proteins, DNA molecules, drugs, enzymes, etc., govern processes like condensation, crystallization, catalysis, solvation, etc.



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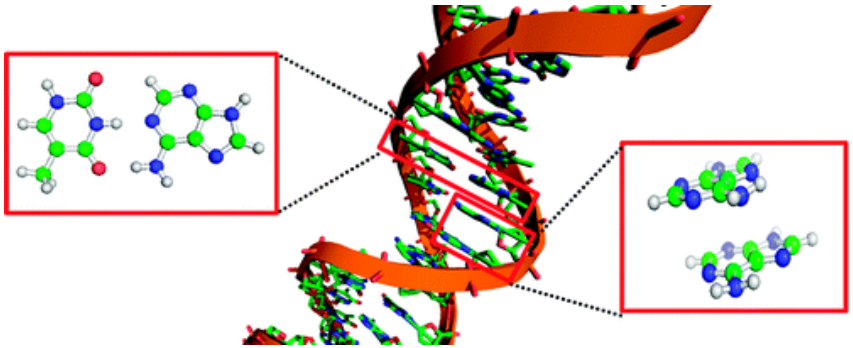

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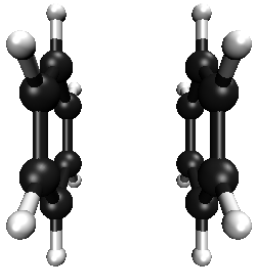
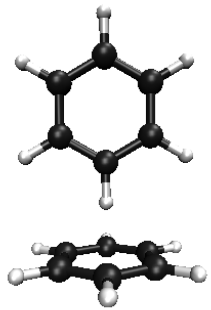
- Not amenable to mean field treatments; non-local, correlated methods necessary

Dimers



(a) Sandwich (D_{2h})



(b) T-shaped (C_{2v})

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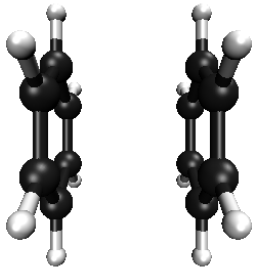

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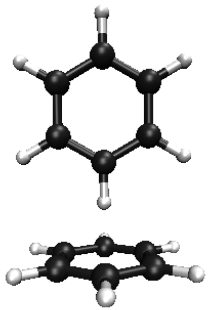


(d) T-shaped (C_{2v})

Rigid monomers

Method dependence

$$E_{int} = E(AB;AB) - E(A;A) - E(B;B)$$

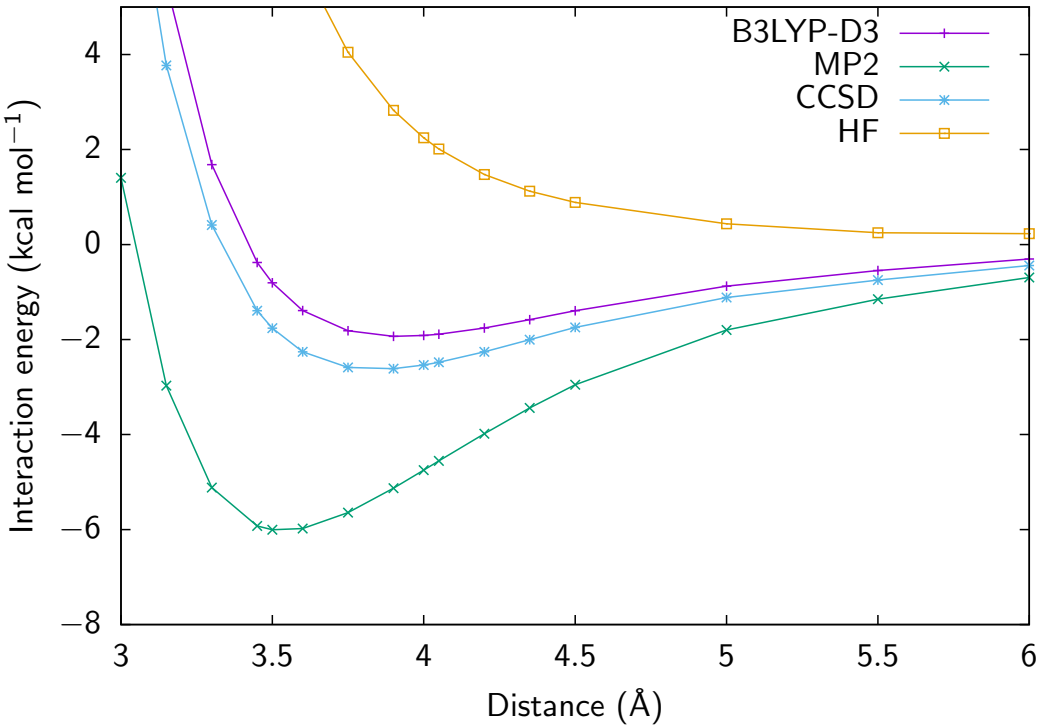


Figure: Sandwich Dimer PES scans (using aug-cc-pVDZ basis set, not CP corrected)

Basis dependence

$$E_{int}^{CP} = E(AB;AB) - E(A;AB) - E(B;AB)$$

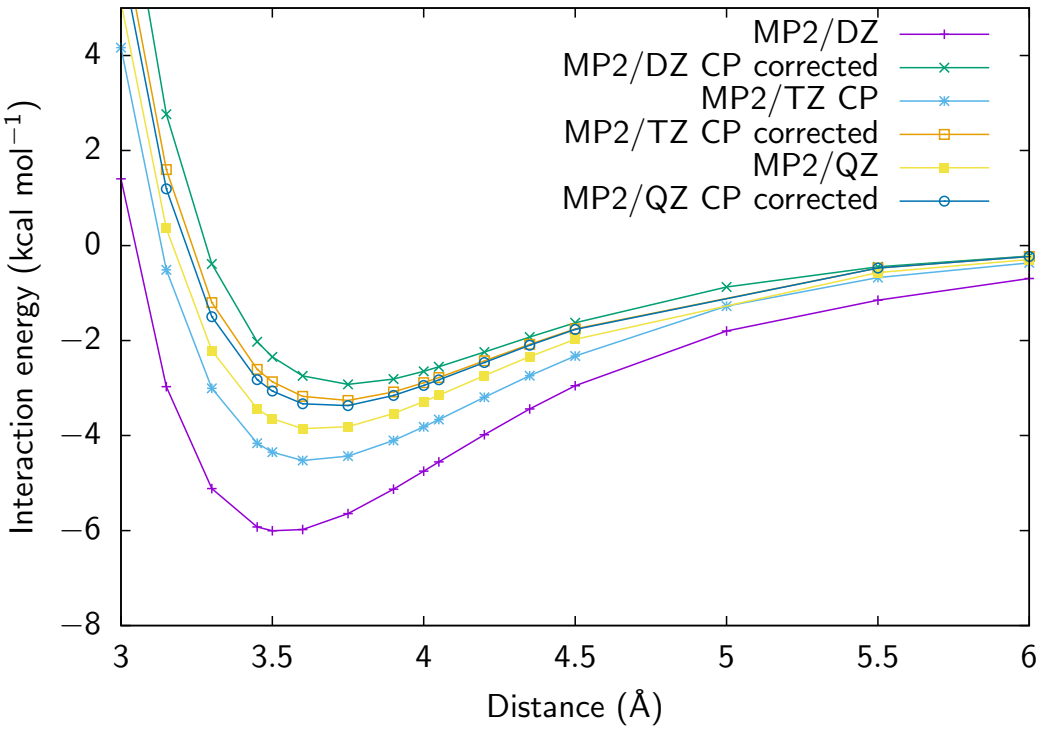
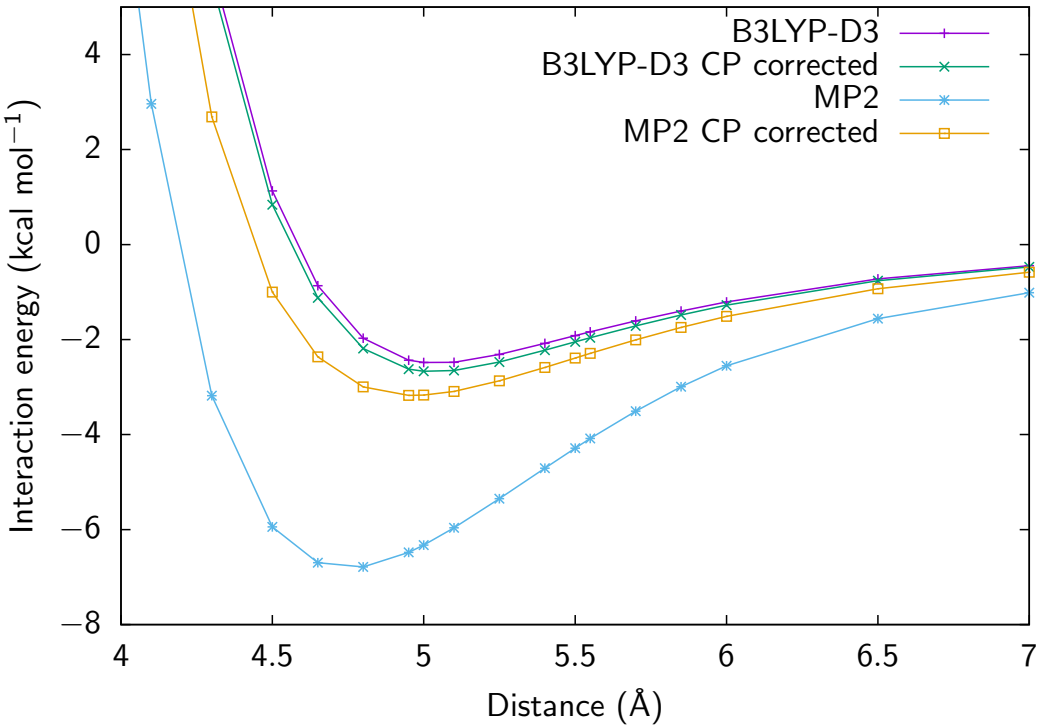


Figure: Sandwich Dimer PES scans ('XZ' denotes aug-cc-pVXZ basis set)

T-shaped



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Many body decomposition

Interaction energy of the cluster $f_1 f_2 \ldots f_n$:

$$E_{int} = [E_1 + E_2 + \cdots + E_n] - \sum_{i=1}^{N} E[f_i]$$

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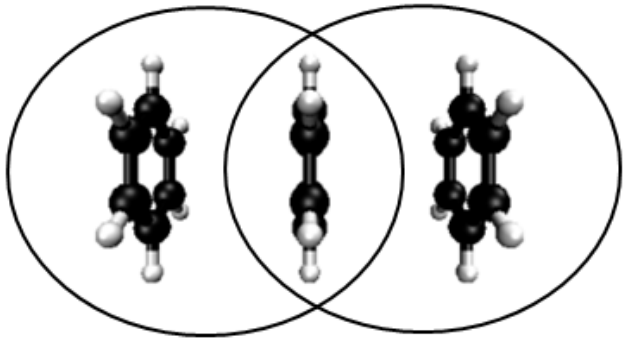
Trimer



- Tauer et al. showed that in benzene π clusters neighboring two-body terms dominate the interaction energy

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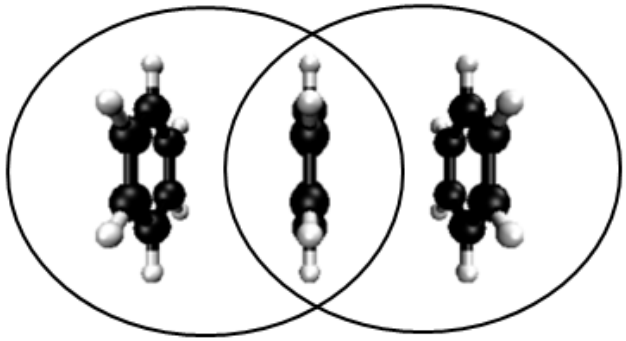

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- PIE-ONIOM approach with overlapping dimer fragments could be effective

Trimer PES

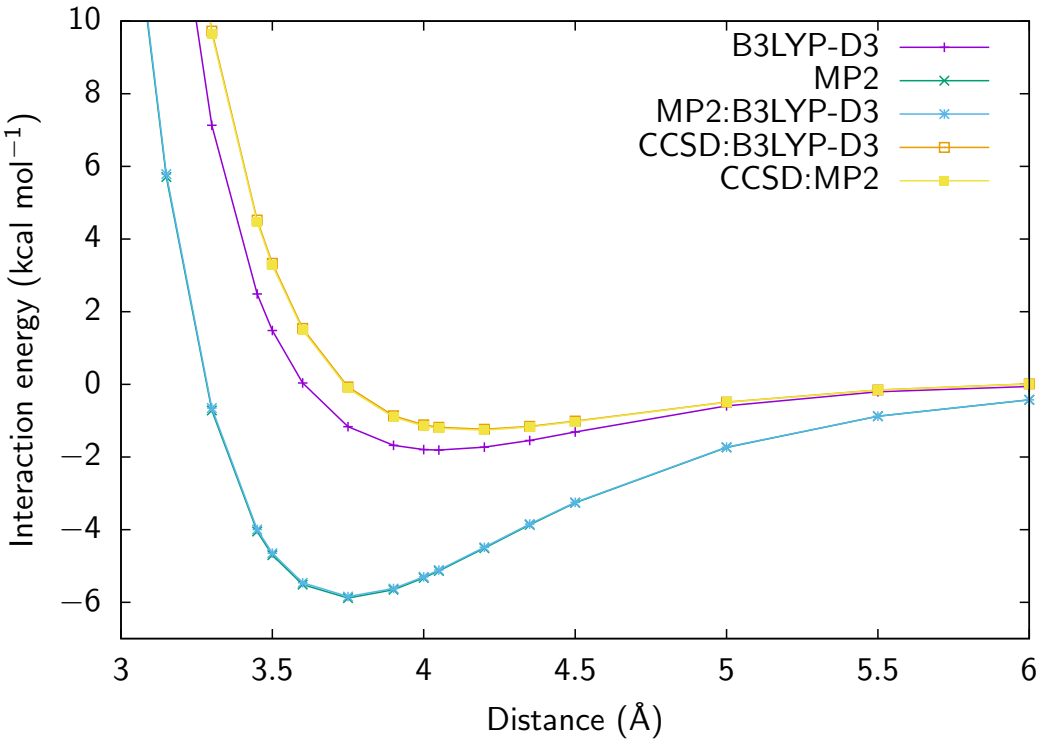
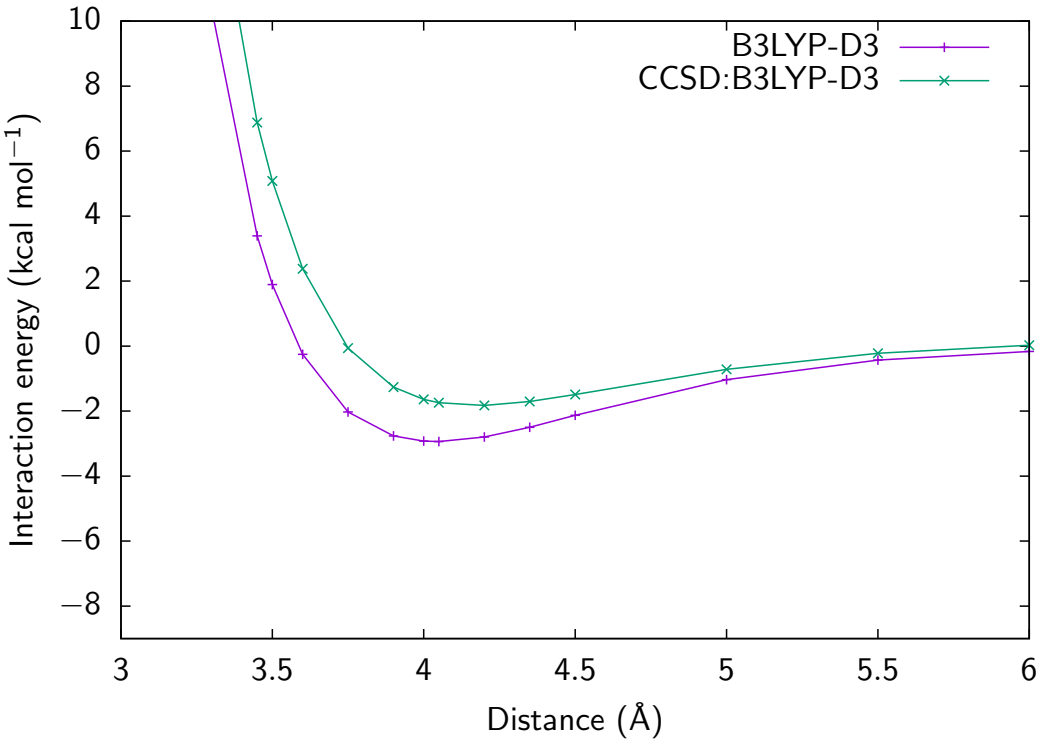


Figure: Trimer PES scans for the sandwich geometry

Tetramer



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Outline

Matrix product states

- A general state of a multi-electron system can be written as

$$|\psi\rangle = \sum_{n_{j\sigma}} C_{n_{1\uparrow} n_{1\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}} |n_{1\uparrow} n_{1\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}\rangle$$

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- DMRG variationally optimizes this matrix product with truncated virtual dimensions

Extrapolation

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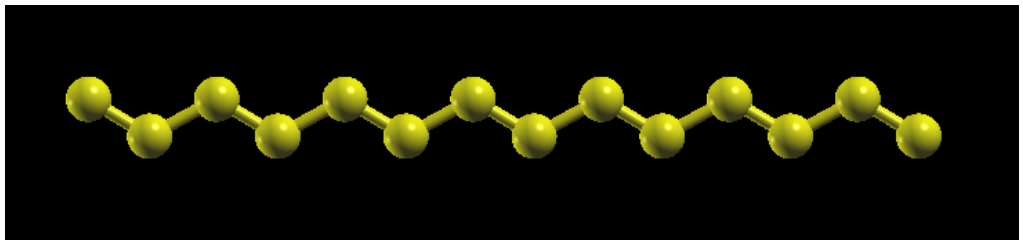
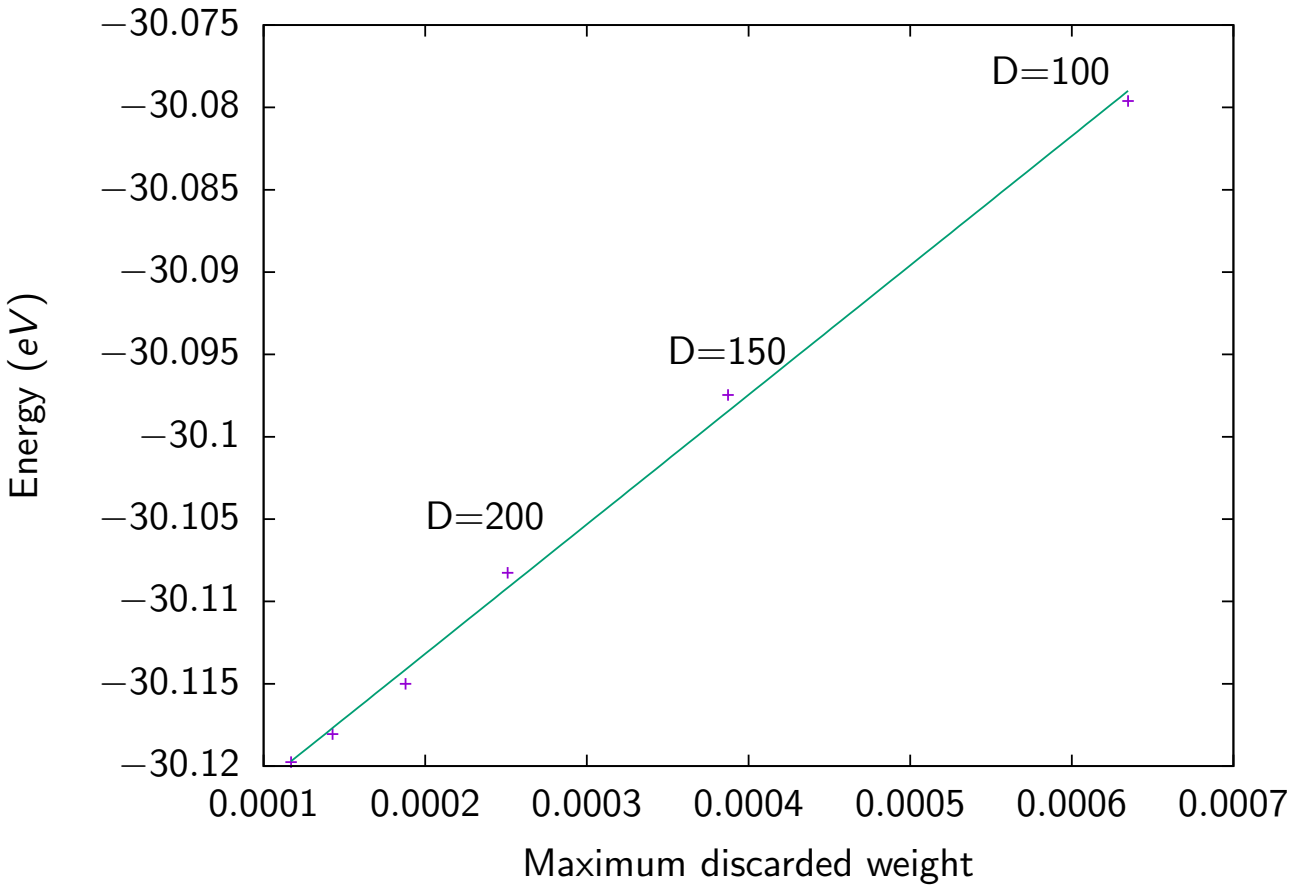
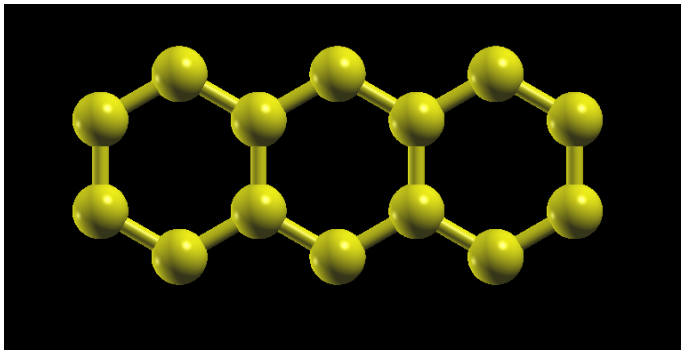
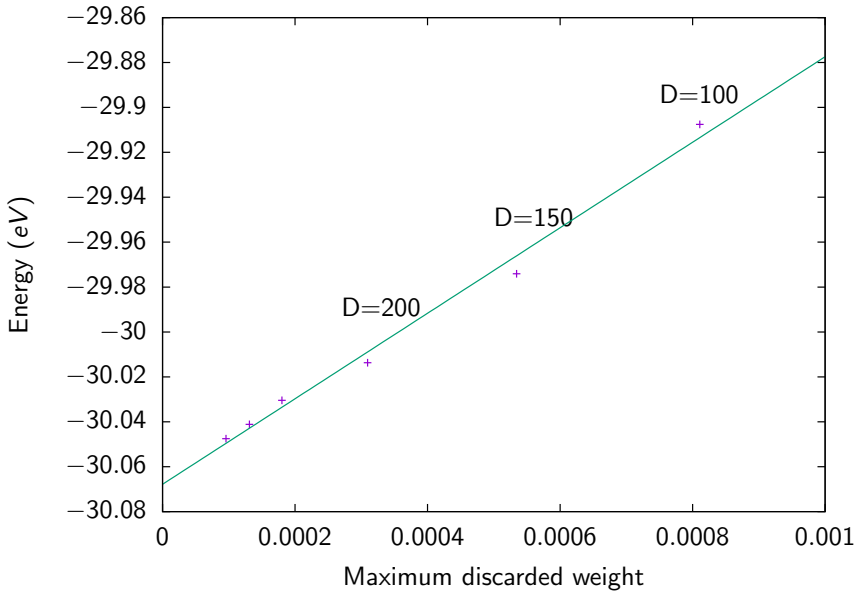


TPA


−30.075
−30.08
−30.085
−30.09
−30.095
−30.1
−30.105
−30.11
−30.115
−30.12
Energy (eV)
0.0001
0.0002
0.0003
0.0004
0.0005
0.0006
0.0007
Maximum discarded weight
D=100
D=150
D=200

Acene




−29.86
−29.88
−29.9
−29.92
−29.94
−29.96
−29.98
−30
−30.02
−30.04
−30.06
−30.08
Energy (eV)
0
0.0002
0.0004
0.0006
0.0008
0.001
Maximum discarded weight
D=100
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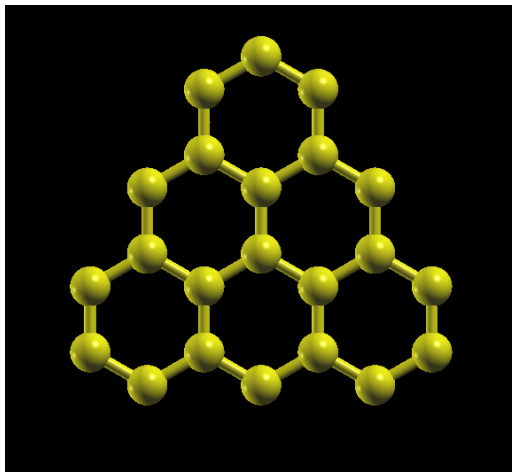
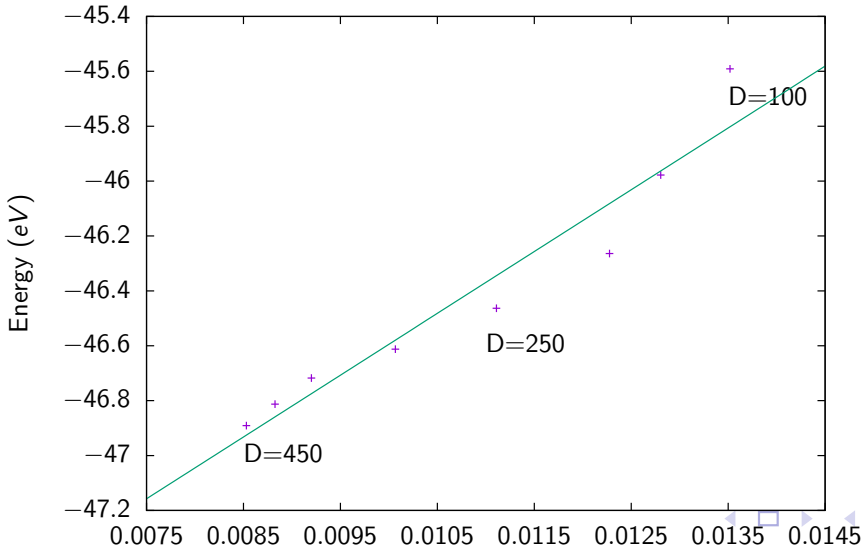
D=200

TZGND2




−45.4
−45.6
−45.8
−46
−46.2
−46.4
−46.6
−46.8
−47
−47.2
Energy (eV)
0.0075
0.0085
0.0095
0.0105
0.0115
0.0125
0.0135
0.0145
D=100
D=250
D=450