Ab Initio Molecular Dynamics using Fragment-Based Electronic Structure Calculations

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Outline

The scaling conundrum

- "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

  Source: Paul AM Dirac. "Quantum mechanics of many-electron systems". In: *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. Vol. 123. 792. The Royal Society. 1929, pp. 714–733

- Unfavorable scaling of computational time with system size of accurate electronic structure methods makes large systems intractable:
  DMRG: $\Omega(N^4)$, MP2: $O(N^5)$, CCSD(T): $O(N^6)$
- Composite approach: A series of smaller calculations to extrapolate to an accurate final result

Composite approaches

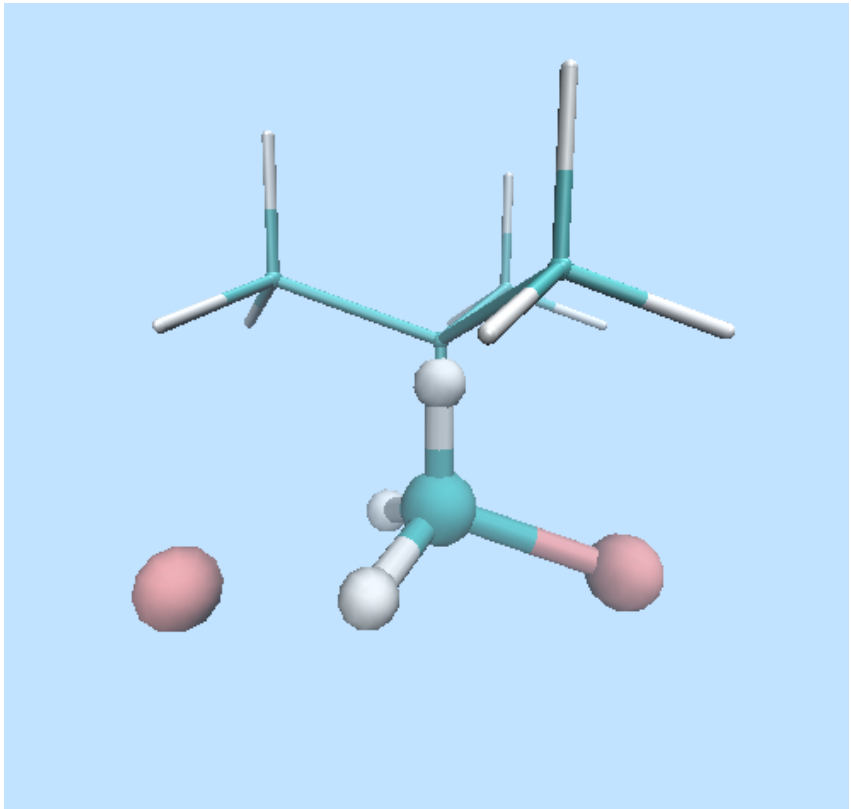
- Hybrid methods: Only chemically active parts of the system need to be treated accurately
  Large system divided into layers which are treated at different levels of theory
  Examples: QM/MM, ONIOM
- Fragment methods: Breaking up a large system into smaller fragments
  Based on the fundamental principle of near-sightedness of electronic interactions[1]
  Examples: MTA, FMO
- PIE-ONIOM: A way of combining these two approaches

[1] There do exist systems where long-range delocalized interactions are important. Fragmentation-based approaches cannot be applied in such cases.

Outline

QM/MM

- MM methods are fast, but cannot account for reactive phenomena like formation or breaking of bonds



- The system is divided into two parts: a QM region, which contains the chemically active part of the large system, and a MM region, which contains the remaining atoms

QM/MM contd.

$$\hat{H}_{eff} = \hat{H}_{QM} + \hat{H}_{MM} + \hat{H}_{QM-MM} \tag{1}$$

$$\hat{H}_{QM} = -\frac{1}{2}\sum_{i}\nabla_i^2 + \sum_{ij}\frac{1}{r_{ij}} - \sum_{i\alpha}\frac{Z_\alpha}{r_{i\alpha}} + \sum_{\alpha\beta}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \tag{2}$$

$$\hat{H}_{MM} = E_{MM}(R_M) \tag{3}$$

$$\hat{H}_{QM-MM} = -\sum_{iM}\frac{q_M}{r_{iM}} - \sum_{\alpha M}\frac{Z_\alpha q_M}{r_{\alpha M}} + \sum_{\alpha M}\left(\frac{A_{\alpha M}}{R_{\alpha M}^{12}} - \frac{B_{\alpha M}}{R_{\alpha M}^{6}}\right) \tag{4}$$

$$\begin{aligned} E_{QM/MM} &= \langle\psi|\hat{H}_{QM} - \sum_{iM}\frac{q_M}{r_{iM}} + \sum_{\alpha M}\frac{Z_\alpha q_M}{r_{\alpha M}}|\psi\rangle + E_{MM} + E_{QM-MM} \\ &= E_{QM} + E_{MM} + E_{QM-MM} \end{aligned} \tag{5}$$

- IMOMM: Extrapolative scheme

$$E_{IMOMM} = E_{QM,model} + E_{MM,real} - E_{MM,model} \quad (6)$$

- $E_{MM,real} - E_{MM,model} = E_{MM} + E_{QM-MM} \implies E_{IMOMM} = E_{QM/MM}$
- Energy calculations of chemically realistic systems $\implies$ low level calculations can be done using QM methods
- IMOMO: Less accurate, fast QM methods employed for low level calculations

$$E_{IMOMO} = E_{QM-high,model} + E_{QM-low,real} - E_{QM-low,model} \quad (7)$$

- ONIOM: Generalized method with n layers treated at different levels of theory.

Outline

Cardinality Guided Molecular Tailoring Approach (CG-MTA)

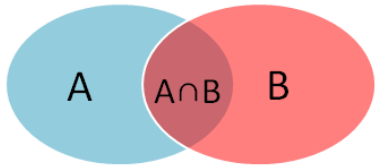
- Divide-and-Conquer: A large system broken into smaller *overlapping* fragments
- Principle of Inclusion-Exclusion:

$$|\bigcup_{i=1}^{n} A_i| = \sum_{i=1}^{n} |A_i| - \sum_{1 \le i < j \le n} |A_i \cap A_j| + \ldots + (-1)^{n-1} |A_1 \cap A_2 \cap \cdots \cap A_n| \tag{8}$$

$$E_{MTA} = \sum_{i=1}^{n} E(A_i) - \sum_{1 \le i < j \le n} E(A_i \cap A_j) + \ldots + (-1)^{n-1} E(A_1 \cap A_2 \cap \cdots \cap A_n) \tag{9}$$

- Interactions between fragment not included

- Using ONIOM on top of MTA to account for inter-fragment interactions. These are calculated at the low level of theory.



$$E^{high}_{MTA} = E^{high}(A) + E^{high}(B) - E^{high}(A \cap B) \tag{10}$$

$$\begin{aligned} E^{low}_{frag-int} &= E^{low} - E^{low}_{MTA} \\ &= E^{low} - \{E^{low}(A) + E^{low}(B) - E^{low}(A \cap B)\} \end{aligned} \tag{11}$$

$$\begin{aligned} E_{PIE-ONIOM} &= E^{high}_{MTA} + E^{low}_{frag-int} \\ &= E^{low} + \sum_{X=A,B} \{E^{high}(X) - E^{low}(X)\} \\ &\quad - \{E^{high}(A \cap B) - E^{low}(A \cap B)\} \end{aligned} \tag{12}$$

- General expression for n fragments

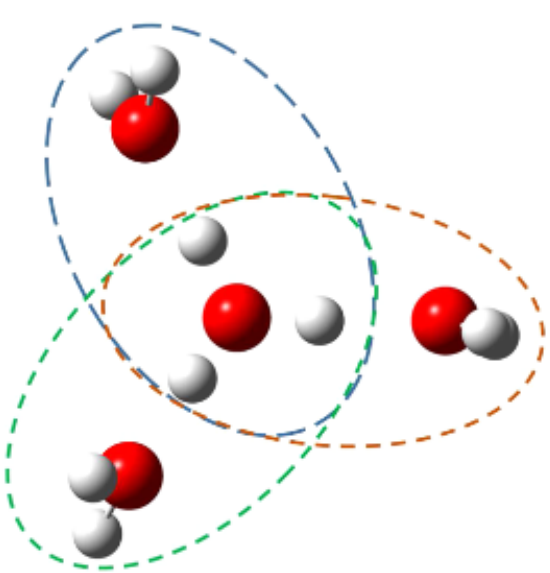
$$E_{PIE-ONIOM} = E^{level,0}(0) + \sum_{i=1}^{n} S(i) - \sum_{1 \le i < j \le n} S(i \cap j) + \cdots + (-1)^{n-1} S(1 \cap 2 \cap \cdots \cap n) \tag{13}$$

$$S(X) = E^{level,1}(X) - E^{level,0}(X) \tag{14}$$

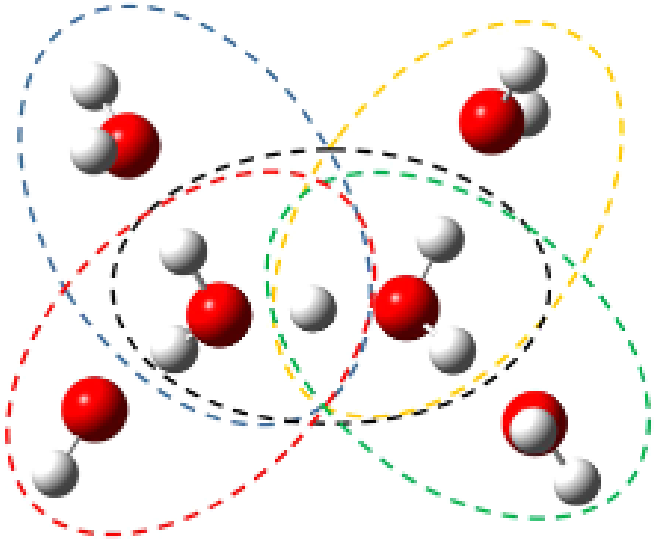
- Analytical gradients are calculated as

$$\frac{\partial E_{PIE-ONIOM}}{\partial \mathbf{R}} = \frac{\partial E^0}{\partial \mathbf{R}} + \sum_{i=1}^{n} \frac{\partial S(i)}{\partial \mathbf{R}} - \sum_{1 \le i < j \le n} \frac{\partial S(i \cap j)}{\partial \mathbf{R}} + \cdots + (-1)^{n-1} \frac{\partial S(1 \cap 2 \cap \cdots \cap n)}{\partial \mathbf{R}} \tag{15}$$

Fragmentation procedure



(a) $H_9O_4^+$



(b) $H_{13}O_6^+$

Source: Junjie Li and Srinivasan S Iyengar. "Ab Initio Molecular Dynamics Using Recursive, Spatially Separated, Overlapping Model Subsystems Mixed within an ONIOM-Based Fragmentation Energy Extrapolation Technique". In: *Journal of chemical theory and computation* 11.9 (2015), pp. 3978–3991

- Automated fragmentation: All hydrogen bond interactions treated accurately

Outline

Original implementation and modifications

- C++ wrapper code: Creates fragments $\rightarrow$ calculates overlaps $\rightarrow$ makes subsystems $\rightarrow$ delegates ES calculations to 'Gaussian' $\rightarrow$ extracts results and puts them together
- Can calculate energies, forces and dipole moments; can do electronically embedded calculations; exploits massive parallelizability inherent to fragment methods, using MPI
- Multiplatform capability: Added functionality to use 'ORCA' and 'PSI4' for ES calculations
- Increases the number of methods that can be used in the PIE-ONIOM calculation (e.g. allows DMRG)
  Calculations at different levels of theory can be done with different packages, based on their efficiency

Details of a SP calculation

Table: Details of a $H_{13}O_6^+$ MP2:B3LYP PIE-ONIOM calculation with PSI4. This calculation was done with the aug-cc-pVDZ basis

Entity	B3LYP	MP2
Whole system	-459.092029386	-
Primary Fragment 1	-153.2081112394	-152.8379018167
Primary Fragment 2	-153.1305816997	-152.7609535409
Primary Fragment 3	-153.1367243127	-152.7668477484
Primary Fragment 4	-153.1941978610	-152.8245727860
Primary Fragment 5	-153.1925218134	-152.8231040857
Derivative Fragment 1	-76.6532226680	-76.4673705372
Derivative Fragment 2	-76.7044716652	-76.5192670148
PIE-ONIOM energy	-457.985386	

PES

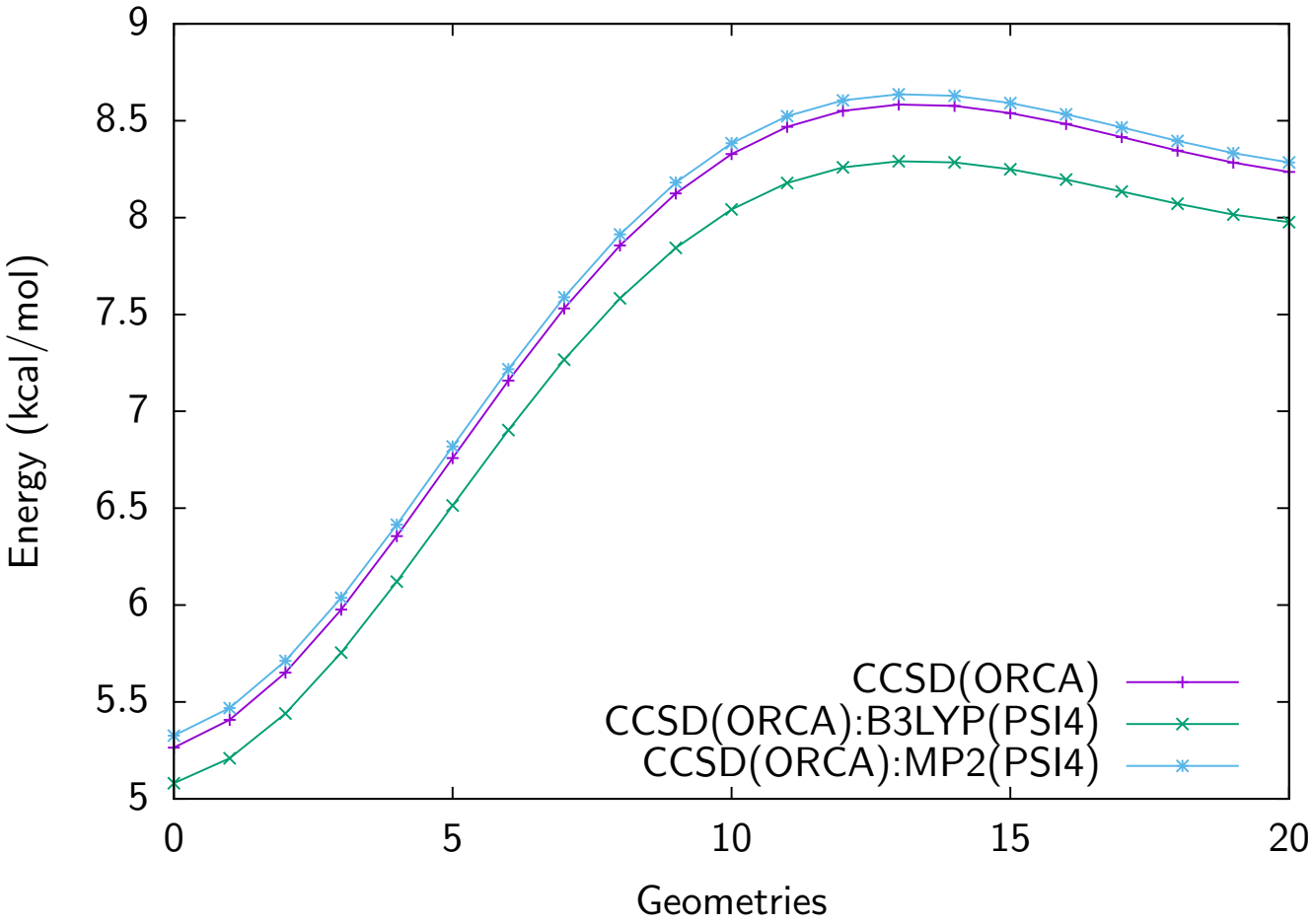


Figure: Sampling of the PES of the solvated Zundel cation. All calculations were done using aug-cc-pVDZ

Outline

Ehrenfest and BOMD

$$\hat{H}|\Psi\rangle = i\hbar\frac{\partial}{\partial t}|\Psi\rangle \tag{16}$$

- Ehrenfest:

$$M_I\ddot{\mathbf{R}}_\mathbf{I}(t) = -\nabla_I \int \Psi^* \hat{H}\Psi d\mathbf{r} \tag{17}$$

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}_e\Psi \tag{18}$$

- BOMD:

$$M_I\ddot{\mathbf{R}}_\mathbf{I}(t) = -\nabla_I min\{\int \Psi^* \hat{H}\Psi d\mathbf{r}\} \tag{19}$$

$$E_0\Psi_0 = \hat{H}\Psi_0 \tag{20}$$

Extended Lagrangian Molecular Dynamics

- Car and Parrinello: Fictitious electron dynamic variables

$$\mathcal{L} = \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \sum_i \mu \langle \dot{\phi} | \dot{\phi} \rangle - \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle + \text{constraints} \quad (21)$$

- ADMP: Use electron density instead of MOs

$$\begin{aligned} \mathcal{L} = & \frac{1}{2} Tr(\mathbf{V}^T \mathbf{M} \mathbf{V}) + \frac{1}{2} Tr \left[\{ \mu^{1/4} \mathbf{W} \mu^{1/4} \}^2 \right] - E(\mathbf{R}, \mathbf{P}) \\ & - Tr \left[\mathbf{\Lambda} (\mathbf{P}\mathbf{P} - \mathbf{P}) \right] \end{aligned} \quad (22)$$

$$\mathbf{M} \frac{d^2 \mathbf{R}}{dt^2} = - \frac{\partial E(\mathbf{R}, \mathbf{P})}{\partial \mathbf{R}} \quad (23)$$

$$\mu^{1/2} \frac{d^2 \mathbf{P}}{dt^2} \mu^{1/2} = - \left[\frac{\partial E(\mathbf{R}, \mathbf{P})}{\partial \mathbf{P}} + \mathbf{\Lambda P} + \mathbf{P \Lambda} - \mathbf{\Lambda} \right] \quad (24)$$

PIE-ONIOM applications

- Short trajectories only: Fragment topology may change during dynamics, which would require dynamic fragmentation (not implemented yet)
- BOMD: Ground state energy and gradients can be calculated using PIE-ONIOM
- ADMP: The lower level electronic structure propagated using ADMP while the fragments treated using BOMD, which allows the use of pHF methods.
- Vibrational DOS: Fourier transform of the velocity autocorrelation

$$I_V(\omega) = \lim_{T\to\infty} \int_{t=0}^{t=T} dt exp(-i\omega t)\langle \mathbf{V}(0).\mathbf{V}(t)\rangle \qquad (25)$$

Contd.

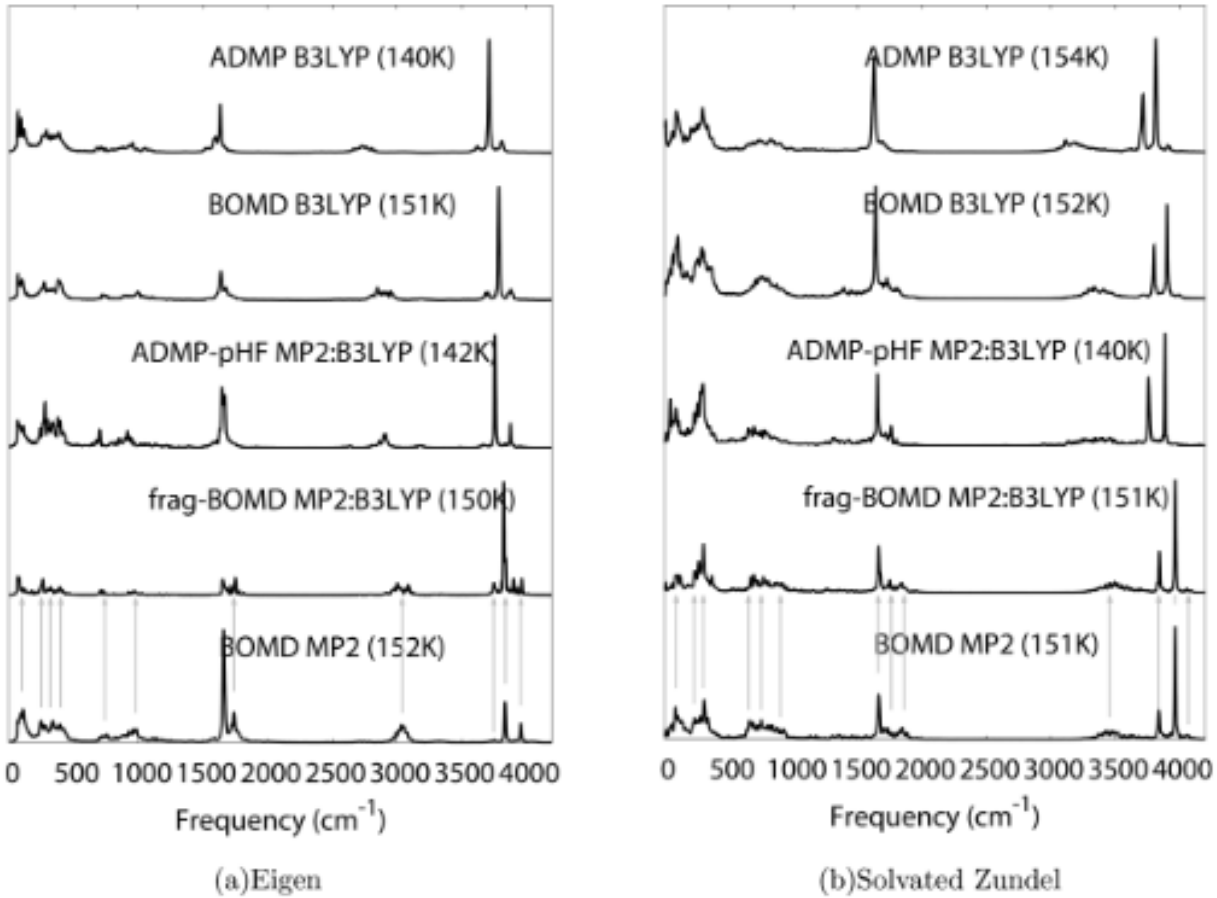


Figure: Vibrational density of states of (a)$H_9O_4^+$, (b)$H_{13}O_6^+$ at 150K

Source: Junjie Li, Cody Haycraft, and Srinivasan Sesha Iyengar. "Hybrid extended Lagrangian, post-Hartree-Fock Born-Oppenheimer ab initio molecular dynamics using fragment-based electronic structure". In: *Journal of chemical theory and computation* (2016)

Outline

Future work

- Doing dynamics with DMRG: Analytic DMRG gradients available in ORCA
  Focus on strongly correlated systems
- Pi-stacking systems: Accounting for non-covalent bonded interactions
  Benzene trimers, tetramers, etc.