Outline

- Accurate Ab initio molecular dynamics (AIMD) simulations require accurate electronic structure with dense and diffuse basis sets at every time step.
- This is prohibitive and hence direct application of AIMD is often limited to DFT with modest basis sets.
- True for clusters and condensed phase.
- Condensed phase: limited to small bases, and 2\textsuperscript{nd} or 3\textsuperscript{rd} rung (pseu) DFT methods
- The figure on the left shows the electronic structure gold standard of basis set and correlation.
- The figure on the right shows the situation when nuclear dynamics, classical and quantum, are included.

Adaptive Many-body expansions

Simplex decomposition of molecular structure, when combined with the ONIOM method allows an adaptive many-body expansion that can be used for AIMD and for accurate potential energy surface calculations.

For such a graph, \( G \), the Euler characteristic is given by

\[
\chi = n_0 - n_1 + n_2 - \ldots + (-1)^r n_r = \sum_{r=0}^\infty (-1)^r n_r
\]

where \( n_r \) is the number of geometric entities (or simplexes) of rank-\( r \). For example, \( n_0 \) is the number of nodes, and so on. We replace the appearance of each rank-\( r \), numbered using the index \( \alpha \), by an energy correction analogous to that in ONIOM and in many-body expansions:

\[
\eta_\alpha \rightarrow \eta_\alpha + \sum_{s=r+1}^\infty \Delta \eta_r (\alpha, \beta) \left( \prod_{m=0}^{r-1} \eta_m \right)
\]

with \( \Delta \eta_r (\alpha, \beta) = E_{\alpha}(R) - E_{\alpha}(R^\beta) \), the square bracketed term contains the over counting correction, where \( \eta_\alpha \) is the number of times the \( \alpha \)\textsuperscript{th} rank-\( r \) simplex appears in all \( n_r \)-rank simplexes.

The graph-theoretic energy expression that includes all embedded simplexes yields a generalized (geometric) description of many-body interactions

\[
E_{\alpha}(R) = E_{\alpha}(R^0) + \sum_{m=0}^{\infty} (-1)^m \eta_{\alpha}^m
\]

We have shown that this last expression is a generalized, adaptive, many body expansion.

Efficient algorithms for Clusters and condensed phase

Post-Hartree-Fock AIMD at DFT cost

- Born-Oppenheimer as well as Extended Lagrangian treatment
- For the first time, Car-Parrinello-like simulations with CCSD accuracy[3]; dynamics and spectroscopy of water, small molecules, and peptide fragments
- MP2 and Large basis DFT dynamics of peptide fragments
- Trajectories are in the microcanonical regime, and we observe energy deviations with the order of tens of a kcal/mol. Drift of similar order.

Continuous topology morphing (CTM) for potential surfaces

- Our C++ module allows the use of multiple electronic structure packages for every dynamics step.
- The Extended Lagrangian treatment: Car-Parrinello-like treatment with from Refs. [2] but with atom-centered Gaussian basis functions and the single particle electronic density matrix, that is the Atom Density Matrix Propagation with Post-Hartree-Fock accuracy (ADMP-pHF):

\[
L = \frac{1}{2} Tr(V^T M V) + \frac{1}{2} Tr \left( \left( \frac{1}{3} \rho \right)^{1/4} \left( \frac{1}{3} \rho \right)^{1/4} \right)^2 = \rho_{\alpha}^{1/4}(R) = \frac{1}{2} Tr \left( \left( \frac{1}{3} \rho \right)^{1/4} \left( \frac{1}{3} \rho \right)^{1/4} \right)
\]

- In the extended Lagrangian, ADMP-pHF; the electronic density matrices that determine \( \left( \frac{1}{3} \rho \right)^{1/4} \) are propagated with nuclear degrees of freedom
- Basis set extrapolated dynamics is also carried out using this same extended Lagrangian.

References


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