Accelerated Quantum Molecular Dynamics

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Outline

- Quantum MD
  - Current approaches
  - Challenges
- Extended Lagrangian Born–Oppenheimer MD
- Accelerated MD
- Coupling XL–BOMD and AMD
  - Vacancies in graphene
Quantum based MD

Integrate the equations of motion of classical molecular trajectories

\[ M_I \ddot{R}_I = -\frac{\partial U(R; \rho_{sc})}{\partial R_I} \]

with the forces calculated on the fly from a self-consistent quantum mechanical description of the electronic structure:

\[ H[\rho] \Psi_i = \varepsilon_i \Psi_i \]

\[ \rho = \sum_{\text{occ.}} |\Psi_i|^2 \]

\( \#\text{SCF} \times \mathcal{O}(N^3) \)

Goal: To develop a unique computational capability based on a new generation quantum based molecular dynamics that overcomes current limitations allowing design and prediction of materials and processes on time and length scales multiple orders of magnitude beyond current capacity.
Quantum based MD

Born-Oppenheimer MD (1973)
- Accurate and reliable
- General, any material
- Long time steps
  - Energy drift
  - Expensive, SCF cost

Car-Parrinello MD (1985)
- Parameter dependence
- Material dependent
- Short time steps
  + Small energy drift
  + Fast, no SCF required

The best of both worlds

New Generation Quantum Mechanical Molecular Dynamics
XL-BOMD
The Challenge

Quantum Molecular Dynamics

- \(O(N^3)\) Diagonalization
- \(O(N)\) Regular linear scaling
- \(O(N)\) Low pre-factor

Significant pre-factor reduction is required for practical large scale QMD!
LATTE: Self-Consistent Charge Density Functional based Tight-Binding Theory

“Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties”

\[
U_{\text{DFTB}}(\mathbf{R}; \rho) = 2Tr[\rho h] + \frac{1}{2} \sum_{i,j} q_i q_j \gamma_{ij} + E_{\text{pair}}[\mathbf{R}]
\]

\[
H_{i\alpha,j\beta}[\mathbf{q}] = h_{i\alpha,j\beta} + \sum_l q_l \gamma_{il} \delta_{ij} \delta_{\alpha\beta}
\]

\[
q_i = 2 \sum_{\alpha} \rho_{i\alpha,i\alpha}
\]

\[
\rho = \theta (\mu I - H[\mathbf{q}])
\]

Maybe the simplest and most efficient approach to electronic structure theory that still covers the relevant features of “exact” ab initio Kohn-Sham DFT.

Typically two orders of magnitude in speed up (w.r.t. DFT)!
Potential energy surface at the SCF optimized electronic ground state

Potential energy surface of a non-optimized electronic state

Potential energy surface of a shadow H is very close to the exact SCF optimized electronic ground state

New Fast “SCF-free” GXL-BOMD

Car-Parrinello MD

dt_{CP} \ll dt_{BO}
SCF-free Generalized XL-BOMD

Niklasson & Cawkwell, JCP 141, 164123 (2014)

\[
\mathcal{L}_{\text{Shadow}}^{\text{XBO}} = \sum_I \frac{M_I \dot{R}_I^2}{2} - \mathcal{U}(R, n) + \frac{\mu}{2} \int \dot{n}^2 \, dr - \frac{\mu \omega^2}{2} \int (\rho - n) \dagger K \dagger K (\rho - n) \, dr
\]

\[
\mathcal{L}_{\text{XBO}}^{\text{Shadow}} = \mathcal{L}_{\text{BO}}^{\text{KS}}, \quad \{ \sim \text{BO approx.} \lim \omega \to \infty, \lim \mu \to 0, \lim \mu \omega \to \text{constant} \}
\]

\[
M_I \dot{R}_I = -\frac{\partial \mathcal{U}(R, n)}{\partial R_I} \bigg|_{n}
\]

\[
\ddot{n}(r) = -\omega^2 \int K(r, r') (\rho[n](r') - n(r')) \, dr'
\]

\[
E_{\text{Tot}} = \frac{1}{2} \sum_I M_I \dot{R}_I^2 + \mathcal{U}(R, n) \quad \text{Shadow Hamiltonian}
\]

\[
K(r, r') \sim \left( \frac{\delta \rho[n](r)}{\delta n(r')} - \delta (r - r') \right)^{-1}
\]

\[
\mathcal{U}(R, n) = \min_{\rho} \left\{ E_{\text{DFT}}^{(1)}(R, \rho, n) \left| \rho = \sum_{\text{occ}} |\Psi_i|^2, \langle \Psi_i | \Psi_j \rangle = \delta_{ij} \right\} + V_{nn}(R)
\]

\[
\rho[n] = \arg \min_{\rho} \left\{ E_{\text{DFT}}^{(1)}(R, \rho, n) \left| \rho = \sum_{\text{occ}} |\Psi_i|^2, \langle \Psi_i | \Psi_j \rangle = \delta_{ij} \right\}
\]

\[
E_{\text{DFT}}^{(1)}(R, \rho, n) = E_{\text{DFT}}(R, n) + \int \frac{\delta E_{\text{DFT}}(R, n)}{\delta \rho} \bigg|_{\rho=n} (\rho[n](r) - n(r)) \, dr
\]
SCF-free Generalized XL-BOMD Canonical Ensemble

Isocyanic acid (HNCO)$_{24}$

NVE ensemble

NVT ensemble

Nose thermostat

Is the XL-BOMD compatible with the thermostats? Does it help?
SCF-free Generalized XL-BOMD Canonical Ensemble

Average temperature and the square-root of its second moment

XL-BOMD converges faster with the right fluctuations
Infrequent Events

Can we accelerate the transition without perturbing the probabilities for the system to escape? **AMD**
Parallel Replica Dynamics

The properties of the exponential allow us to parallelize time, by having many processors seek the first escape event. The procedure:

- **Replicate**
- **Dephase**
- **Parallel time**
- **Allow correlated events**

**Formula:**
\[ \tau_{corr} \]

(overhead) 

**Procedure:**
- **Add all these times together** \( t_{sum} \) **when first event occurs on any processor**

**Note:**
- Must detect every transition.

**Equation:**
\[ \tau_{rxn} / n_{proc} \gg 2\tau_{corr} \]

**Reference:**
XL-BOMD + Accelerated Molecular Dynamics

AMDF
(BES program)

Master

Replica 1
Replica 2
...  
Replica n

Python script

LATTE: Tight Binding Order N
Parallel Implementation MultiThreads
We have studied 1 and 2 vacancy diffusion.

Temperature distribution of a graphene sheet containing 1V at 2500 and 3000 K in the NVT using Langevin Dynamics run for 100 ps.

We have analyzed the normal modes to pick the dephasing time ~5ps. There are some slow modes perpendicular to the sheet plane.
Application: Vacancies in graphene

1V diffusivities in NVT ensemble ParRep-LATTE, reaching on the order of hundreds of ns

\[ D = \nu \lambda^2 \exp(-\Delta E / k_B T) \]

\[ \lambda = 1.54 \times 10^{-10} \text{ m} \]

\[ \nu = 9.44 \times 10^{12} \text{ s}^{-1} \]

\[ \Delta E = 0.54 \text{ eV} \]

\[ \Delta E = 1.16 \text{ eV} \]

Migration barriers in agreement with recent DFT calculations
Competing events at higher temperatures
Application: Vacancies in graphene

2V configurations at 3500 K in NVT ensemble ParRep–LATTE

Net translation of the center of mass
Application: Vacancies in graphene

Mobility and configurational distribution compatible with experiments

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Conclusions

- We have developed a tool coupling XL-BOMD and AMD that reaches ~2–3 orders of magnitude speedup with respect to traditional methods.
- We have calculated single vacancy mobilities in graphene reaching hundreds of ns.
- We have also studied the very stable 2V-complex migration.