Car-Parrinello molecular dynamics

Shiwu Gao
Tillämpad Fysik, Chalmers/GU
Outline

• Time dependent phenomena

• Molecular dynamics (GW lecture)

• Ab initio molecular dynamics (AIMD)
  - Born-Oppenheimer MD
  - Car-Parrinello MD

• Electronic dynamics – TDDFT

• Illustrative examples
Time-dependent phenomena

- Time-dependent phenomena in nature
  - breathing while you sit
  - up and go
- Scattering
  - energy exchange (cold and warm)
- Reaction
  - particle exchange: \( AB+C=A+BC \)
- Time-dependent spectroscopy
  - 2PPE (pump-probe)
- Electronic dynamics?
Classical MD with model potentials

\{\mathbf{R}_i\} = \{\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N\} \quad \text{— atom positions}

\(V(\{\mathbf{R}_i\})\) — an educated construction

\[
V_e^E \approx V_e^{\text{approx}}(\{\mathbf{R}_I\}) = \sum_{I=1}^{N} v_1(\mathbf{R}_I) + \sum_{I<J}^{N} v_2(\mathbf{R}_I, \mathbf{R}_J) \\
+ \sum_{I<J<K}^{N} v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \cdots
\]

Equations of motion

\[
M_I \ddot{\mathbf{R}}_I(t) = - \nabla_I V_e^{\text{approx}}(\{\mathbf{R}_I(t)\})
\]

Force
Limitations of model potentials

• The potential form is predetermined

• It does not account for any contributions from electronic polarization/transfer (in the dynamically changing environment)

• Unknown for new/complex systems
Ab initio molecular dynamics (AIMD)

\[ V(\vec{R}) = \min_{\Phi} E[\Phi, \vec{R}] \]

- **Empirical QM Potentials**
  - Tight binding Hamiltonians
  - Semi-empirical quantum chemistry methods

- **Ab Initio Potentials**
  - Quantum chemistry, wavefunction methods
  - Density functional theory

Kohn-Sham DFT

\[ V(\vec{R}) = \min_{\Phi} E_{KS}[\Phi, \vec{R}] \]
- Starting from a geometry $\mathbf{R}(t) = (\mathbf{R}_1(t), \mathbf{R}_2(t), \ldots, \mathbf{R}_N(t))$
- Find the adiabatic ground state for $\mathbf{R}(t)$

$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r}) \right] \Phi_i = \varepsilon_i \Phi_i$$

$$\rho(\vec{r}) = \sum_i \Phi_i^*(\vec{r}) \Phi_i(\vec{r})$$

$$E[\rho] = T[\rho] + E_{\text{coulomb}}[\rho] + E_{xc}[\rho]$$

$$V_{\text{eff}}(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \frac{\delta E_{xc}[\rho]}{\delta \rho} + V_{\text{ext}}$$

- Updating force from $V(\vec{R}) = \min_{\Phi} E_{KS}[\Phi, \vec{R}]$
- Update atom positions $\mathbf{R}(t+ \Delta t) = \mathbf{R}(t) + \ldots$

Time consuming! Electrons reach the adiabatic ground state!
Car-Parrinello MD (CPMD)

Lagrangian

\[
\mathcal{L}_{\text{CP}} = \mu \sum_i \int |\Phi_i|^2 dr + \frac{1}{2} \sum_k M_k \ddot{R}_k^2 - E_{KS}[\Phi, R] \\
+ \sum_{ij} \Lambda_{ij} \left( \int dr \Phi_i^* \Phi_j - \delta_{ij} \right)
\]

- The electrons—classical particle
- Timescale gap between electrons and molecules
  - electron $10^{-15}$ s
  - molecules $10^{-12}$s
- The $\Lambda_{ij}$ introduced to assure orthonormalization
Equation of motion

Lagrangian equation

\[ \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}} \right) - \frac{\partial L}{\partial q} = 0 \]

CP equations of motion

\[ M_k \ddot{R}_k = -\frac{\partial E_{KS}[\Phi, R]}{\partial R_k} \]
\[ \mu \ddot{\Phi}_i = -\frac{\partial E_{KS}[\Phi, R]}{\partial \Phi_i} - \sum_j \Lambda_{ij} \Phi_j \]
Implementation in PW-PP

- The wave function
  \[ \Phi_i = \sum c_i(G)e^{iG \cdot r} \]

\[ \mathcal{L} = \mu \sum_i \sum_G |\dot{c}_i(G)|^2 + \frac{1}{2} \sum_I M_I \dot{R}_I^2 - E_{KS} \{\{G\}, \{R_I\}\} \\
+ \sum_{i,j} \Lambda_{ij} \left( \sum_G c_i^*(G)c_j(G) - \delta_{ij} \right) , \]

\[ \mu \ddot{c}_i(G) = -\frac{\partial E}{\partial c_i^*(G)} + \sum_j \Lambda_{ij} c_j(G) \]

\[ M_I \ddot{R}_I = -\frac{\partial E}{\partial R_I} . \]

- Velocity Verlet algorithm

\[ \dot{R}_I(t + \delta t) = \dot{R}_I(t) + \frac{\delta t}{2M_I} F_I(t) \]

\[ R_I(t + \delta t) = R_I(t) + \delta t \dot{R}_I(t + \delta t) \]

\[ \dot{c}_I(t + \delta t) = \dot{c}_I(t) + \frac{\delta t}{2\mu} f_i(t) \]

\[ \ddot{c}_I(t + \delta t) = c_i(t) + \delta t \dot{c}_I(t + \delta t) \]

\[ c_i(t + \delta t) = \ddot{c}_i(t + \delta t) + \sum_j X_{ij} c_j(t) \]

calculate \( F_I(t + \delta t) \)

calculate \( f_i(t + \delta t) \)

\[ \dot{R}_I(t + \delta t) = \dot{R}_I(t + \delta t) + \frac{\delta t}{2M_I} F_I(t + \delta t) \]

\[ \dot{c}_I(t + \delta t) = \dot{c}_I(t + \delta t) + \frac{\delta t}{2\mu} f_i(t + \delta t) \]

\[ \ddot{c}_I(t + \delta t) = c_i(t + \delta t) + \sum_j Y_{ij} c_j(t + \delta t) \]
Features of CPMD

- Electrons and atoms evolved simultaneously in each timestep $\delta t$
- Electron dynamics is not realistic
- Molecular dynamics is physical in the proper regime (adiabaticity), by controlling timestep $\delta t$, and electron mass $\mu$
CPMD-a revolution to MD simulations

- Number of publications vs years
- CPMD dominating AIMD since 1985

Ref. D. Marx, J. Hutter
NIC series, 3, 329 (200)
Applications

- **Solid State Applications**
  - Melting of silicon
  - Molecular solids (HBr, Ice)

- **Surfaces**
  - Surface reconstruction (silicon)
  - Molecules on Surfaces (CO on Pt)

- **Liquids**
  - Water, ions in water, ammonia, HF