CT 5: Car Parrinello Molecular Dynamics

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Genesis

Motivation

- Propagation of wavefunction without minimizing at each step
- Long time step set by nuclear motion (not electronic)

Basic Idea

- Classical–mechanical energy–scale separation: time seperation between fast electrons & slow nuclei
- Two component quantum/classical system $\rightarrow$ two purely classical problem
- Classical evolution of Ψ destroys their true time dependance

Equations of Motion

Lagrangian

$$\mathcal{L}_{\mathrm{CP}} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2} \mu_i \left\langle \dot{\psi}_i | \dot{\psi}_i \right\rangle - \left\langle \Psi_0 | \hat{H}_{\mathrm{e}} | \Psi_0 \right\rangle + \sum_i \sum_j \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij})$$

Euler Lagrange Equations

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I}$$

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\psi}_i^*} = \frac{\partial \mathcal{L}}{\partial \dot{\psi}_i^*}, \quad \dot{\psi}_i^* = \langle \psi_i |$$

Equations of Motion ($\cdots$ cont)

$$
\begin{aligned}
M_I \ddot{\mathbf{R}}_I(t) &= -\nabla_I \left\langle \Psi_0 | \hat{H}_e | \Psi_0 \right\rangle + \nabla_I \left[\sum_i \sum_j \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij}) \right] \\
\mu_i \ddot{\psi}_i(t) &= -\frac{\partial}{\partial \psi_i^*} \left\langle \Psi_0 | \hat{H}_e | \Psi_0 \right\rangle + \frac{\delta}{\delta \psi_i^*} \left[\sum_i \sum_j \Lambda_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right) \right]
\end{aligned}
$$

Tricks

- Starting from B.O. surface
- Cold wavefunction (thermostats)
- μ_i and Δt has to be appropriately

Issues

- Degenerate electronic states
- Zero band–gap
- Orthogonalization needed