Car-Parrinello molecular dynamics

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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

$\{\mathbf{R}_I\}=\{\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N\}$ — atom positions

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

$$V_{\mathrm{e}}^{\mathrm{E}} \approx V_{\mathrm{e}}^{\mathrm{approx}}(\{\mathbf{R}_I\}) = \sum_{I=1}^{N} v_1(\mathbf{R}_I) + \sum_{I\langle J}^{N} v_2(\mathbf{R}_I, \mathbf{R}_J) + \sum_{I\langle J\langle K}^{N} v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \cdots$$

Equations of motion

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I V_{\mathrm{e}}^{\mathrm{approx}}(\{\mathbf{R}_I(t)\})$$

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

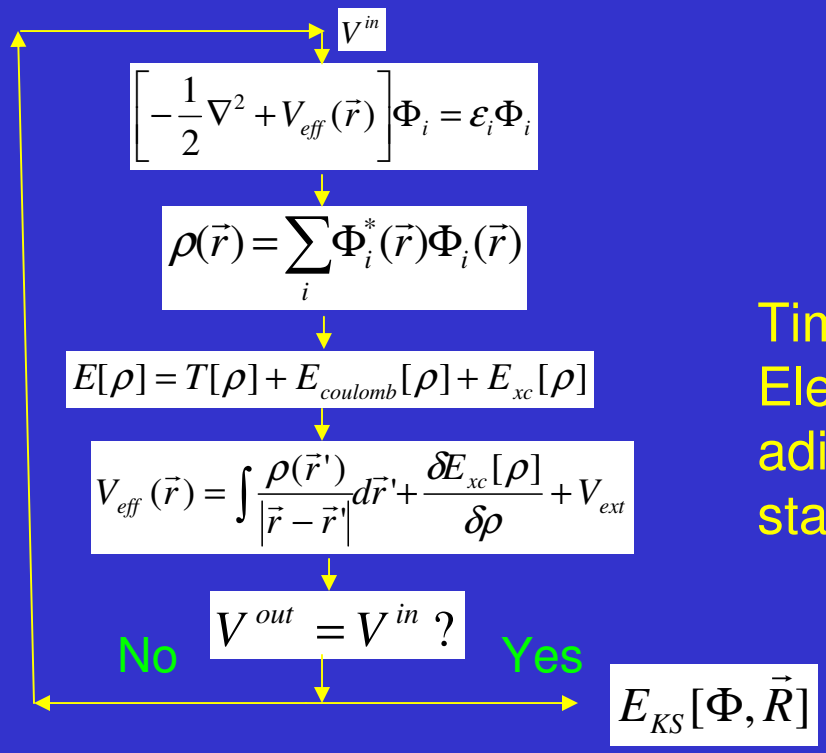
Kohn-Sham DFT

$$V(\vec{R}) = \min_{\Phi} E_{KS}[\Phi, \vec{R}]$$

Born-Oppenheimer MD

-Starting from a geometry **R**(t)=(**R**$_1$(t), **R**$_2$(t), …, **R**$_N$(t))

-Find the adiabatic ground state for **R**(t)



Time consuming! Electrons reach the adiabatic ground stae!

- Updating force from $V(\vec{R}) = \min_{\Phi} E_{KS}[\Phi, \vec{R}]$

- Update atom positions **R**(t+ Δ t)= **R**(t)+…

Car-Parrinello MD (CPMD)

Lagrangian

$$\mathcal{L}_{\mathrm{CP}} = \mu \sum_i \int |\dot{\Phi}_i|^2 d\mathbf{r} + \frac{1}{2} \sum_k M_k \dot{\mathbf{R}}_k^2 - E_{\mathrm{KS}}[\Phi, \mathbf{R}] + \sum_{ij} \Lambda_{ij} \left(\int d\mathbf{r} \Phi_i^* \Phi_j - \delta_{ij} \right)$$

- The electrons--classical particle
- Timescale gap between electrons and molecules

  electron 10^{-15} s molecules 10^{-12}s
- The Λ_{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

$$\begin{aligned} M_k\ddot{\mathbf{R}}_k &= -\frac{\partial E_{\mathsf{KS}}[\Phi,\mathbf{R}]}{\partial \mathbf{R}_k} \\ \mu\ddot{\Phi}_i &= -\frac{\partial E_{\mathsf{KS}}[\Phi,\mathbf{R}]}{\partial \Phi_i}-\sum_j \Lambda_{ij}\Phi_j \end{aligned}$$

Implementation in PW-PP

- The wave function

$$\Phi_i = \Sigma\, c_i(G) e^{iG\cdot r}$$

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

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

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial E}{\partial \mathbf{R}_I}.$$

- Velocity Verlet algorithm

$$\dot{\tilde{R}}_I(t+\delta t) = \dot{\mathbf{R}}_I(t) + \frac{\delta t}{2M_I}\mathbf{F}_I(t)$$

$$\mathbf{R}_I(t+\delta t) = \mathbf{R}_I(t) + \delta t\, \dot{\tilde{R}}_I(t+\delta t)$$

$$\dot{\tilde{c}}_I(t+\delta t) = \dot{\mathbf{c}}_I(t) + \frac{\delta t}{2\mu}\mathbf{f}_i(t)$$

$$\tilde{\mathbf{c}}_i(t+\delta t) = \mathbf{c}_i(t) + \delta t\, \dot{\tilde{c}}_i(t+\delta t)$$

$$\mathbf{c}_i(t+\delta t) = \tilde{\mathbf{c}}_i(t+\delta t) + \sum_j \mathbf{X}_{ij}\, \mathbf{c}_j(t)$$

calculate $\mathbf{F}_I(t+\delta t)$

calculate $\mathbf{f}_i(t+\delta t)$

$$\dot{\mathbf{R}}_I(t+\delta t) = \dot{\tilde{R}}_I(t+\delta t) + \frac{\delta t}{2M_I}\mathbf{F}_I(t+\delta t)$$

$$\dot{\mathbf{c}}'_i(t+\delta t) = \dot{\tilde{c}}_i(t+\delta t) + \frac{\delta t}{2\mu}\mathbf{f}_i(t+\delta t)$$

$$\dot{\mathbf{c}}_i(t+\delta t) = \dot{\mathbf{c}}'_i(t+\delta t) + \sum_j \mathbf{Y}_{ij}\, \mathbf{c}_j(t+\delta t)$$

Features of CPMD

- Electrons and atoms evolved simultaneously in each timestep δ t
- Electron dynamics is not realistic
- Molecular dynamics is physical in the proper regime (adiabadicity), by controlling timestep δ t, and electron mass μ

CPMD-a revolution to MD simulations

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

Ref. D. Marx, J. Hutter
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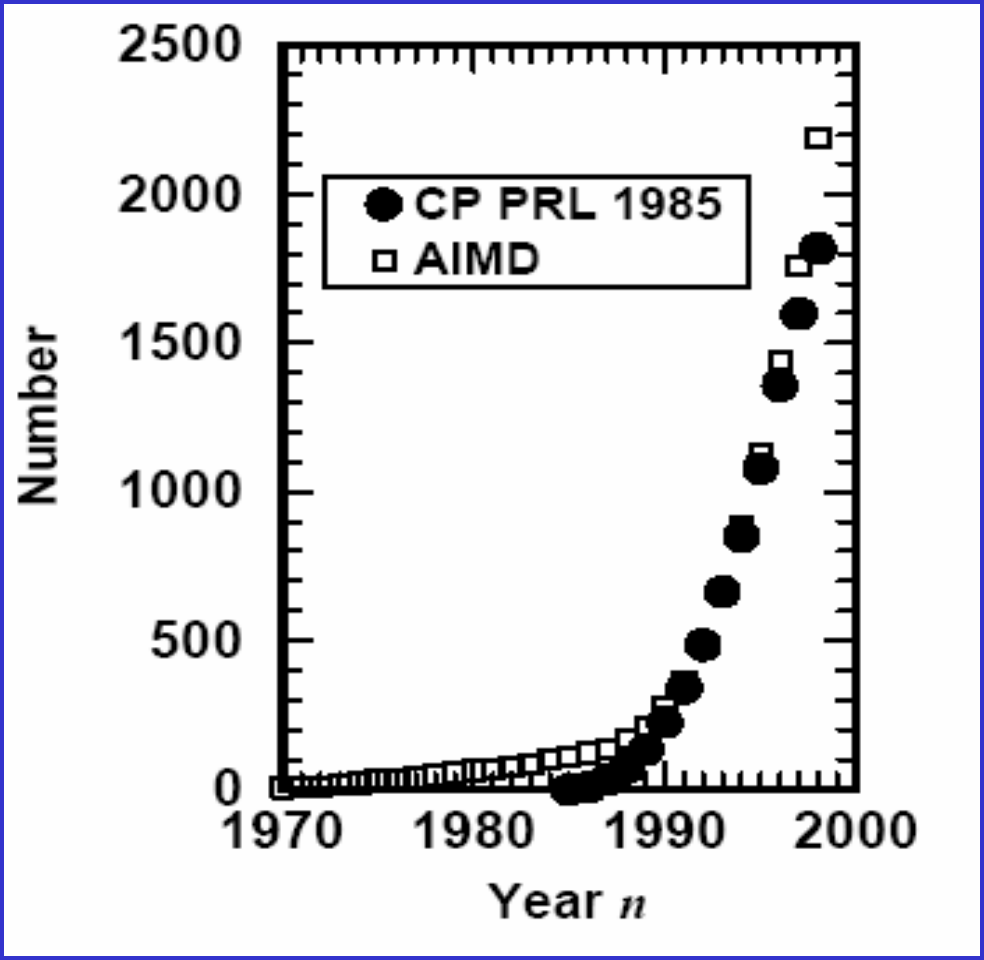

Applications

- 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