Ab Initio MD: Born-Oppenheimer and Car-Parrinello

This lecture explores ways to simplify the computationally expensive Ehrenfest dynamics by making further approximations, leading to the two most common ab initio MD methods.

Born-Oppenheimer Dynamics (BOD)

The first major simplification is to consider only the electronic **ground state**. Instead of solving the full time-dependent Schrödinger equation for the electrons, we assume that the electrons react instantaneously to the motion of the nuclei.

This is the core of **Born-Oppenheimer Dynamics (BOD)**. At every single time step in the simulation:

1. The nuclear positions, $\underline{R}(t)$, are considered fixed.
2. The **time-independent** Schrödinger equation is solved for the electrons to find the ground state wavefunction, $\phi_0(\underline{r}|\underline{R}(t))$, and its corresponding energy, $E_0(\underline{R}(t))$.
3. The force on each nucleus is then calculated as the negative gradient of this ground state energy: $F_\alpha = -\nabla_{R_\alpha} E_0(\underline{R}(t))$.
4. The nuclei are moved according to this force using Newton's equations of motion, and the process repeats.

The coupled equations for BOD are:

- **For the nuclei (classical):** $M_\alpha \ddot{R}_\alpha = -\nabla_{R_\alpha} E_0(\underline{R}(t))$
- **For the electrons (quantum):** $\hat{H}_r(\underline{r}|\underline{R}(t))\phi_0(\underline{r}|\underline{R}(t)) = E_0(\underline{R}(t))\phi_0(\underline{r}|\underline{R}(t))$

In practice, solving the electronic structure problem at every time step involves a computationally expensive self-consistency loop (like in DFT or Hartree-Fock).

Car-Parrinello Dynamics (CPD)

Car-Parrinello Dynamics (CPD) was developed to avoid the costly self-consistency calculation at every single MD step. The clever idea is to treat the electronic orbitals as classical fields that have their own dynamics.

A **fictitious mass**, μ, is assigned to the orbitals, and a fictitious kinetic energy term is added to the system's Lagrangian. This creates an extended Lagrangian that describes both the real dynamics of the nuclei and the fictitious dynamics of the orbitals.

$$L_{CP} = \underbrace{\sum_\alpha \frac{1}{2} M_\alpha \dot{R}_\alpha^2}_{\text{Nuclear K.E.}} + \underbrace{\sum_i \frac{1}{2} \mu \langle \dot{\rho}_i | \dot{\rho}_i \rangle}_{\text{Fictitious Orbital K.E.}} - \langle \phi_0 | \hat{H}_r | \phi_0 \rangle + \text{constraints}$$

Summary and Problems with Ehrenfest Dynamics

Key Features:

- It's a fully self-consistent coupling of quantum electrons and classical nuclei.
- The total energy of the system is strictly conserved.
- It describes a single, unique nuclear trajectory that evolves on an optimal average potential. For this reason, it's often called the **"best average path method"**.

Major Problem:

- The system always evolves on this average potential, even in regions where the quantum system would split into different states. For example, after passing through a region of strong non-adiabatic coupling, the Ehrenfest trajectory will follow an unphysical average path instead of choosing one of the physically meaningful potential energy surfaces. This leads to incorrect behavior, especially for processes like chemical dissociation.

Comparison of Methods

Method	Nuclear Dynamics	Electronic Dynamics	Solves El. Structure	Typical Time Step
EFMD	Classical, in an average field	Quantum, time-dependent	For each nuclear position and electron state	Very Small
BOD	Classical, on the ground state PES	Instantaneous ground state (time-independent SE)	For each nuclear position	~0.5 fs
CPD	Classical, on a "close to" ground state PES	Fictitious classical dynamics	Once at the beginning	~0.1 fs

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From this, we get a new set of coupled equations of motion. The key difference compared to BOD is in the electronic part:

- **In BOD:** The electronic system is forced to be at the exact ground state minimum at every step. This is expressed as: $-\hat{H}_r^{SCF}\rho_i + \sum_j \lambda_{ij}\rho_j = 0$
- **In CPD:** The orbitals are allowed to evolve in time according to a fictitious Newtonian dynamic. This is expressed as: $-\hat{H}_r^{SCF}\rho_i + \sum_j \lambda_{ij}\rho_j = \mu\ddot{\rho}_i$

This means CPD only requires one full, self-consistent electronic structure calculation at the very beginning. After that, the orbitals are simply propagated forward in time along with the nuclei.

The fictitious mass μ is a crucial control parameter. To ensure the system stays close to the true Born-Oppenheimer surface, the fictitious orbital dynamics must be much faster than the real nuclear dynamics. This requires a small μ, which in turn necessitates using a much smaller time step in CPD compared to BOD.