

Ehrenfest Dynamics

Ehrenfest dynamics is a specific flavor of ab initio molecular dynamics that provides a semi-classical approximation for the interaction between quantum electrons and classical nuclei. It starts from the Time-Dependent Self-Consistent Field (TD-SCF) equations derived in the previous lecture.

From Quantum to Classical Nuclei

The key step is to take the TD-SCF equation for the nuclear wavefunction (Ω) and analyze it in the classical limit ($\hbar \rightarrow 0$). The nuclear wavefunction is expressed in its polar form:

$$\Omega(\underline{R}, t) = A(\underline{R}, t) e^{\frac{i}{\hbar} S(\underline{R}, t)}$$

where A is the amplitude and S is the phase. Substituting this into the nuclear Schrödinger equation splits it into two parts:

1. **The real part**, which gives the **Quantum Hamilton-Jacobi (QHJ) equation**. In the classical limit where $\hbar = 0$, the quantum potential term vanishes, and this equation becomes the classical Hamilton-Jacobi equation. It describes a fluid of classical particles (the nuclei) moving in an average potential created by the quantum electrons.
2. **The imaginary part**, which gives the **Quantum Continuity Equation (QCE)**. This equation ensures that the probability density of the nuclei ($|\Omega|^2 = A^2$) is locally conserved.

The QHJ and QCE together are fully equivalent to the original time-dependent Schrödinger equation for the nuclei.

The Coupled Equations of Motion

By taking the classical limit of the QHJ equation, we can derive a Newtonian equation of motion for the nuclei. This is the **Ehrenfest equation of motion for the nuclei (ED_R)**:

$$M_\alpha \ddot{R}_\alpha = -\nabla_{R_\alpha} \left\{ \int d\underline{r} \Phi^* \hat{H}_r \Phi \right\} = -\nabla_{R_\alpha} V_{\text{Ehrenfest}}$$

Here, the nuclei move according to a classical force ($F = -\nabla V$) derived from an effective potential, $V_{\text{Ehrenfest}}$. This potential is the expectation value of the electronic Hamiltonian, averaged over the electronic wavefunction Φ . This potential can be calculated using various ab initio methods like DFT, HF, MP2, etc.

To complete the picture, we need an equation for the electronic wavefunction's time evolution. In the classical limit, the nuclear density $|\Omega|^2$ becomes a delta function located at the classical trajectory $\underline{R}(t)$. This simplifies the electronic Schrödinger equation to the **Ehrenfest equation of motion for the electrons (ED_r)**:

$$i\hbar\dot{\Phi} = -\frac{\hbar^2}{2m} \sum_{\beta} \nabla_{r_{\beta}}^2 \Phi + V_{rR}(r, \underline{R}(t))\Phi$$

Ehrenfest dynamics, therefore, consists of simultaneously solving these two coupled equations ($ED_R + ED_r$).

Ehrenfest Dynamics in an Adiabatic Basis

For situations involving multiple electronic states (like in photochemistry), the electronic wavefunction can be expanded in a basis of adiabatic states, $\Phi(t) = \sum_i c_i(t) \Phi_i(r|\underline{R})$.

This transforms the nuclear equation of motion. The force on the nuclei now has two components:

1. An **average force** derived from a weighted average of the potential energy surfaces of the electronic states.
2. An additional **non-adiabatic force** that arises from the coupling between different electronic states. This term is responsible for driving transitions between potential energy surfaces, for example, at a conical intersection.

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.