

Lecture 1: Ab Initio MD & Time-Dependent Self-Consistent Field

The goal is to derive molecular dynamics (MD), which is based on Newton's equations, from a quantum mechanical foundation based on the Schrödinger equation. This leads to the **Time-Dependent Self-Consistent Field (TD-SCF)** method.

The core idea is based on the separation of timescales: electrons are light and fast, while nuclei are heavy and slow. This allows us to use a **product ansatz** to separate their equations of motion.

The molecular Hamiltonian operator is:

$$\hat{H}(\underline{r}, \underline{R}) = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_{R_{\alpha}}^2 - \frac{\hbar^2}{2} \sum_{\beta} \frac{1}{m} \nabla_{r_{\beta}}^2 + V_{rR}(\underline{r}, \underline{R})$$

This Hamiltonian is used in the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \Psi(\underline{r}, \underline{R}, t)}{\partial t} = \hat{H} \Psi(\underline{r}, \underline{R}, t)$$

The Mean-Field Ansatz

To solve this, we propose a separation of the total wavefunction Ψ into electronic (Φ), nuclear (Ω), and phase (F_T) components. This is a **mean-field** or Self-Consistent Field (SCF) approximation.

$$\Psi(\underline{r}, \underline{R}, t) = \Phi(\underline{r}|\underline{R}, t) \Omega(\underline{R}, t) F_T(t)$$

The wavefunctions are normalized such that $\langle \Omega | \Omega \rangle_R = 1$ and $\langle \phi | \phi \rangle_r = 1$. This is an approximation because it uses a single determinant for the wavefunction; a more general approach would be a multi-configuration expansion ($\Psi = \sum_i c_i \phi_i \Omega$).

The total energy of the system is given by the expectation value of the Hamiltonian:

$$E_T(t) = \int d\underline{r} d\underline{R} \Phi^* \Omega^* \hat{H}_T \Phi \Omega$$

Deriving the TD-SCF Equations

By substituting the ansatz into the time-dependent Schrödinger equation and requiring that the total energy is conserved ($\frac{dE}{dt} = 0$), we can derive two symmetric, coupled Schrödinger equations—one for the electrons and one for the nuclei.

This process separates the original, fully coupled problem into two equations that are coupled through an averaging process. These are the **Time-Dependent Self-Consistent Field (TD-SCF) equations**.

Equation for the electrons (Φ):

$$i\hbar \dot{\Phi} = -\frac{\hbar^2}{2} \sum_{\beta} \frac{1}{m} \nabla_{r_{\beta}}^2 \Phi + \left\{ \int d\underline{R} \Omega^* V_{rR} \Omega \right\} \Phi$$

Equation for the nuclei (Ω):

$$i\hbar \dot{\Omega} = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_{R_{\alpha}}^2 \Omega + \left\{ \int d\underline{r} \Phi^* \left[-\frac{\hbar^2}{2} \sum_{\beta} \frac{1}{m} \nabla_{r_{\beta}}^2 + V_{rR} \right] \Phi \right\} \Omega$$

Interpretation

The TD-SCF equations describe a system where:

- The slow variables (nuclei) move in an average field, or potential, created by the fast variables (electrons).
- Simultaneously, the fast variables (electrons) move in an average field created by the slow variables (nuclei).

This establishes a full feedback loop between the electronic and nuclear motion. The achievement of this method is the successful separation of the full Schrödinger equation into two coupled equations. However, further approximations are needed to make this approach practical.