Summary last lecture

2 Approximations to the full electron-nuclear Schrödinger equation:

- Born-Oppenheimer approximation: (i) electronic ground state only
  (ii) mass nuclei >> mass electron

  full electron-nuclear Schrödinger equation $\rightarrow [\hat{T}_n(\mathbf{R}) + E^0_{\mathbf{R}}]\Phi(\mathbf{R}) = E_{\text{tot}}\Phi(\mathbf{R})$ (1)

- Classical Approximation of nuclear motion: valid at high temperature, high mass of nuclei

$$i\hbar\frac{\partial}{\partial t}\Phi(\mathbf{R},t) = [\hat{T}_n(\mathbf{R}) + E^0_{\mathbf{R}}]\Phi(\mathbf{R}) \rightarrow \mathbf{f}_I = M_I\ddot{\mathbf{R}}_I \quad (2)$$

  where $\mathbf{f}_I = \mathrm{d}\mathbf{p}_I/\mathrm{d}t$ is the force on atom I, given by $\mathbf{f}_I = -\frac{\partial E^0_{\mathbf{R}}}{\partial \mathbf{R}_I}$.

Solving Newton's Equations of motion for molecular systems is generally referred to as Molecular Dynamics (MD) simulation.

Time-stepping algorithms: Verlet, Velocity Verlet and Leap Frog

Born-Oppenheimer Molecular Dynamics (BOMD)

Remember: to go from $\mathbf{R}(t) \rightarrow \mathbf{R}(t+\delta t)$ we need the force $\mathbf{f}_I(\mathbf{R}(t))$

In BOMD $\mathbf{f}_I(\mathbf{R}(t))$ is obtained from static electronic structure calculations on the nuclear configuration at time t, $\mathbf{R}'=\mathbf{R}(t)$. How? Using the varational principle,

$$E_{\mathbf{R}'} = \min_{\{\Psi_{\mathbf{R}'}\}} \langle \Psi_{\mathbf{R}'} | \hat{H}_{\rm e}(\mathbf{R}') | \Psi_{\mathbf{R}'} \rangle = \langle \Psi^0_{\mathbf{R}'} | \hat{H}_{\rm e}(\mathbf{R}') | \Psi^0_{\mathbf{R}'} \rangle \quad (3)$$

$$\hat{H}_{\rm e} = \hat{T}_e(\mathbf{r}) + V_{en}(\mathbf{R}', \mathbf{r}) + V_{ee}(\mathbf{r}) + V_{nn}(\mathbf{R}'). \quad (4)$$

Note that Eq. 3 is equivalent with solving the ground state of the Schrödinger equation $\hat{H}_{\rm e}\Psi^0_{\mathbf{R}'} = E^0_{\mathbf{R}'}\Psi^0_{\mathbf{R}'}$.

The forces on the nuclei are equal to minus the gradient of the ground state energy with respect to the nuclear coordinates,

$$\mathbf{f}_I(\mathbf{R}') = -\nabla_{\mathbf{R}_I} \langle \Psi^0_{\mathbf{R}} | \hat{H}_{\rm e} | \Psi^0_{\mathbf{R}} \rangle |_{\mathbf{R}=\mathbf{R}'}. \quad (5)$$

Hellmann-Feynman theorem

The nuclear force on the electronic ground state potential energy surface reads:

$$\mathbf{f}_I(\mathbf{R}') = -\nabla_{\mathbf{R}_I} \langle \Psi^0_{\mathbf{R}} | \hat{H}_\mathrm{e} | \Psi^0_{\mathbf{R}} \rangle |_{\mathbf{R}=\mathbf{R}'}. \tag{6}$$

The force in Eq. 6 can be calculated using the Hellmann-Feynman theorem.

Consider

- a general Hamiltonian that depends on a parameter λ, $\hat{H}(\lambda)$
- an eigenfunction of this Hamiltonian, Ψ_λ (not necessarily the ground state)
- the corresponding eigenvalue E_λ.

The Hellmann-Feynman theorem states that

$$\frac{\mathrm{d}}{\mathrm{d}\lambda} \langle \Psi_\lambda | \hat{H}(\lambda) | \Psi_\lambda \rangle = \langle \Psi_\lambda | \frac{\mathrm{d}}{\mathrm{d}\lambda} \hat{H}(\lambda) | \Psi_\lambda \rangle \tag{7}$$

Proof:

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\Psi_\lambda|\hat{H}(\lambda)|\Psi_\lambda\rangle = \langle\frac{\mathrm{d}}{\mathrm{d}\lambda}\Psi_\lambda|\hat{H}(\lambda)|\Psi_\lambda\rangle + \langle\Psi_\lambda|\hat{H}(\lambda)|\frac{\mathrm{d}}{\mathrm{d}\lambda}\Psi_\lambda\rangle \tag{8}$$

$$+\langle\Psi_\lambda|\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{H}(\lambda)|\Psi_\lambda\rangle \tag{9}$$

$$= E_\lambda\langle\frac{\mathrm{d}}{\mathrm{d}\lambda}\Psi_\lambda|\Psi_\lambda\rangle + E_\lambda\langle\Psi_\lambda|\frac{\mathrm{d}}{\mathrm{d}\lambda}\Psi_\lambda\rangle \tag{10}$$

$$+\langle\Psi_\lambda|\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{H}(\lambda)|\Psi_\lambda\rangle \tag{11}$$

$$= E_\lambda\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\Psi_\lambda|\Psi_\lambda\rangle + \langle\Psi_\lambda|\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{H}(\lambda)|\Psi_\lambda\rangle \tag{12}$$

$$= \langle\Psi_\lambda|\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{H}(\lambda)|\Psi_\lambda\rangle \tag{13}$$

Equation 13 follows from Eq. 12 because the norm of Ψ_λ is invariant with respect to a change in λ, $\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\Psi_\lambda|\Psi_\lambda\rangle = 0$.

The Hellmann-Feynman theorem is valid for any Hamiltonian (incl. Hartree-Fock, Kohn-Sham) as long as Ψ_λ is an exact eigenfunction of this Hamiltonian.

Brief review: Kohn-Sham Density Functional Theory (KS-DFT)

- Electron density $\rho(\mathbf{r})$ expressed in terms of KS-orbitals $(\phi_1, \ldots, \phi_n)$:

$$\rho(\mathbf{r}) = \sum_i |\phi_i|^2, \tag{14}$$

- Ground state Energy for a given nuclear configuration $\mathbf{R}'$, $E^{\mathrm{KS}}_{\mathbf{R}'}$:
  Minimize functional

$$E_{\mathbf{R}'}[\rho(\{\phi_i\})] = -\frac{1}{2}\sum_i \langle\phi_i|\nabla^2|\phi_i\rangle + \int \mathrm{d}\mathbf{r} V_{en}(\mathbf{R}')\rho(\mathbf{r}) \tag{15}$$

$$+\frac{1}{2}\int \mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}\frac{\rho(\mathbf{r_1})\rho(\mathbf{r_2})}{\mathbf{r_{12}}} + E_{\mathrm{xc}}[\rho] + V_{nn}(\mathbf{R}') \tag{16}$$

  with respect to all electron densities ρ integrating to N electrons,

$$E^{\mathrm{KS}}_{\mathbf{R}'} = \min_{\rho(\{\phi_i\})} E_{\mathbf{R}'}[\rho(\{\phi_i\})], \tag{17}$$

- $E^{\mathrm{KS}}_{\mathbf{R}'} = E^{0}_{\mathbf{R}'}$ if the exact exchange correlation functional (E_{xc}) was known.

- Equivalently, minimization can be carried out wrt KS-orbitals

$$0 = -\frac{\delta}{\delta \phi_i^*} E_{\mathbf{R}'}\left[\rho(\{\phi_i\})\right] + \sum_j \Lambda_{ij}\phi_j \quad \forall i, \tag{18}$$

  where Λ_{ij} is a matrix of Lagrange undetermined multipliers.

- Equation 18 leads to the Kohn-Sham equations,

$$\hat{H}^{\mathrm{KS}}\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}). \tag{19}$$

BOMD using KS-DFT

Use KS-DFT as electronic structure method in BOMD.

- At each time step or nuclear configuration $\mathbf{R}'$ solve for KS-orbitals and nuclear forces:

$$0 = -\frac{\delta}{\delta\phi_i^*} E_{\mathbf{R}'}\left[\rho(\{\phi_i\})\right] + \sum_j \Lambda_{ij}\phi_j \tag{20}$$

$$\mathbf{f}_I(\mathbf{R}') = -\nabla_{\mathbf{R}_I} \min_{\rho(\{\phi_i\})} E_{\mathbf{R}}[\rho(\{\phi_i\})]|_{\mathbf{R}=\mathbf{R}'} = -\nabla_{\mathbf{R}_I}\langle\Psi_{\mathbf{R}}^{\mathrm{KS}}|\hat{H}^{\mathrm{KS}}|\Psi_{\mathbf{R}}^{\mathrm{KS}}\rangle|_{\mathbf{R}=\mathbf{R}'}, \tag{21}$$

  where $\Psi_{\mathbf{R}}^{\mathrm{KS}}$ is the KS determinant obtained from the KS-orbitals.

- Use Hellmann-Feynman theorem to calculate the force Eq. 21.
  Identify λ with the coordinate of nucleus I, $\mathbf{R}_I$:

$$\mathbf{f}_I(\mathbf{R}') = -\nabla_{\mathbf{R}_I}\langle\Psi_{\mathbf{R}}^{\mathrm{KS}}|\hat{H}^{\mathrm{KS}}|\Psi_{\mathbf{R}}^{\mathrm{KS}}\rangle|_{\mathbf{R}=\mathbf{R}'} = -\langle\Psi_{\mathbf{R}}^{\mathrm{KS}}|\nabla_{\mathbf{R}_I}\hat{H}^{\mathrm{KS}}|\Psi_{\mathbf{R}}^{\mathrm{KS}}\rangle|_{\mathbf{R}=\mathbf{R}'}. \tag{22}$$

  $\rightarrow$ fortunately, no need to calculate nuclear derivative of wavefunction :)

- Use force in one of the time stepping algorithms discussed to propagate nuclei.

Scheme is called density functional theory-based MD (DFT-MD) or *ab-initio* MD (AIMD).