Nuclear dynamics and the adiabatic approximation (A and P ch. VIII)

- Up until now we have considered the nuclei (or ions if they include some core electrons) as a fixed external potential

- However, they have dynamics like electrons. Also, the interaction between electrons and nuclei is what determines the equilibrium position of nuclei

- Let's start with the full many-body Hamiltonian:

$$H_{tot} = T_N + T_e + V_{ee} + V_{eN} + V_{NN}$$

Kinetic energy of nuclei: $-\sum_I \frac{\hbar^2 \nabla_I^2}{2 m_I}$

* Partition into: $H_{tot} = T_N(R) + T_e(r) + V(r, R)$

$R = \{\vec{R}_I\}$, all nuclear coordinates

All Coulomb interactions

$r = \{\vec{r}_i\}$, all electronic coordinates

* Many-body Schrödinger equation is:

$$[T_N(R) + T_e(r) + V(r,R)]\,\Psi(r,R) = \underbrace{W\,\Psi(r,R)}$$

vibronic wavefunction / energy of combined electron / nuclear system

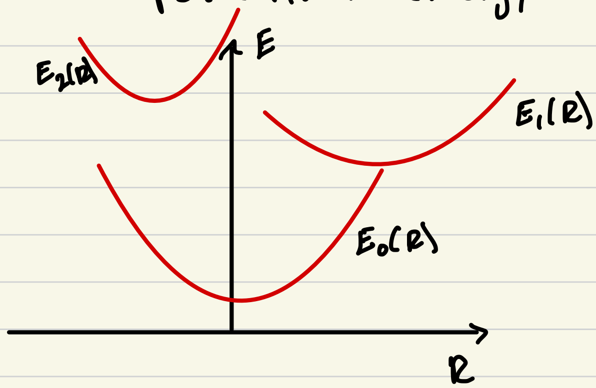
* $T_N \propto \frac{1}{m_I}$, $T_e \propto \frac{1}{m_i}$, so we expect $T_N \ll T_e$, hence the "static lattice" approximation we have been using.

* Electronic "adiabatic" Hamiltonian:

$$H_e(r;R) = T_e + V(r,R) \longrightarrow H_e(r;R)\,\psi_n(r;R) = E_n(R)\,\psi_n(r;R)$$

parametric dependence on R, i.e., R is a parameter, not a variable

- If we solve for $E_n(R)$ versus R, we get a multidimensional potential energy surface



- Consider $\Psi_0(r;R)$ for ground-state nondegenerate potential energy surface [i.e., far from any other $E_n(R)$]

* Define classical forces on nuclei:

$$M_I \ddot{R}_I = -\frac{\partial E_0(\{R_J\})}{\partial R_I}$$ ← Forces are negative gradients of potential energy surfaces determined from electronic energies at fixed R

- If we treat nuclei as classical, these EOM give their dynamics

- What if we treat the nuclei quantum mechanically?

* Still assuming nondegenerate adiabatic potential energy surface

* Approximate full vibronic wavefunction with:

$$\Psi_{trial}(r,R) = \chi(R)\,\Psi_m(r;R)$$

nuclear part ↑ ↑ electronic part at fixed R

- This partitioning assumes electrons are in instantaneous ground state for every R, even if nuclei are allowed to move

- This is the "adiabatic" approximation

* Now take the expectation value of H_{tot} with Ψ_{trial}:

$$\langle\langle \chi\psi_m | T_N + H_e | \chi\psi_m \rangle\rangle$$

where $\langle\langle \psi|\phi\rangle\rangle = \iint \psi^*(r;R)\,\phi(r;R)\,dr\,dR$

$\langle \psi|\phi\rangle = \int \psi^*(r;R)\,\phi(r;R)\,dr$

result is a function of R

$$= \langle\langle \chi\psi_m | \overset{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}}{T_N} | \chi\psi_m \rangle\rangle + \overbrace{\langle\langle \chi\psi_m | H_e | \chi\psi_m \rangle\rangle}^{=\langle \chi | E_m(R) | \chi\rangle}$$

$$= \langle \chi | -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2} | \chi \rangle - \frac{\hbar^2}{2M}\langle\langle \chi\psi_m | \chi \frac{\partial^2 \psi_m}{\partial R^2}\rangle\rangle - \frac{\hbar^2}{m}\langle\langle \chi\psi_m | \frac{\partial \chi}{\partial R}\frac{\partial \psi}{\partial R}\rangle\rangle$$
$$+ \langle \chi | E_m(R) | \chi \rangle$$

- Now we minimize this quantity WRT χ under the constraint that χ is normalized:

$$\left[-\frac{\hbar^2}{2M} + E_m(R)\right]\chi(R) + \Lambda(R)\chi(R) = W\chi(R)$$

contains all of the terms involving $\frac{\partial \psi}{\partial R}$.

can often be chosen to vanish if ψ is real

- Dropping Λ gives equation for χ:

$$\left[-\frac{\hbar^2}{2M} + E_m(R)\right]\chi(R) = W\chi(R)$$ ⇐ Born-Oppenheimer approx

⇒ Nuclear dynamics described by Schrödinger equation with effective potential $E_m(R)$, i.e., adiabatic PES