Nuclear Dynamics and adiabatic approximation

- So far we considered nuclei fixed. They just provide a fixed external potential

- However nuclei move, like e^-. Their eq. obey schroedinger eq. it is the interaction between e^- & nuclei what determines the eq. positions of nuclei.

→ 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: $H_{T.T} = T_N(R) + T_e(r) + V(r, R)$

$R = \{R_I\}$ all nuclear coords

$r = \{r_i\}$ all e^- coords

all coulomb interactions

* Many body Sch. eq:

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

W: energy of combined e^- & nuclear system

Ψ: vibronic wave fn.

$\star\star$ $T_N \propto \frac{1}{M_I}$ $T_e \propto \frac{1}{m_e}$ so $T_N \ll T_e$, hence the static lattice approx. we have been using.

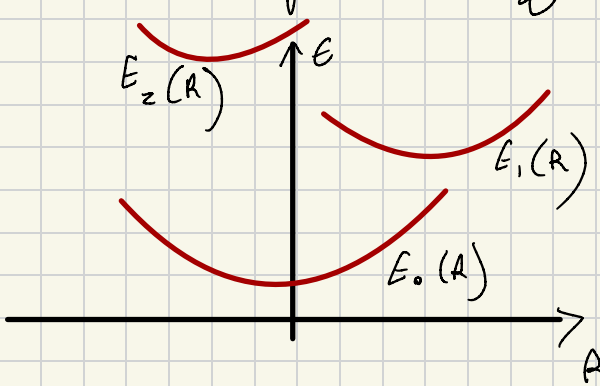
$\star$ Electronic "adiabatic" Hamiltonian:

$$H_e(r;R) = T_e + V(r,R)$$

$$H_e(r;R)\,\Psi_n(r;R) = E_n(R)\,\Psi_n(r;R)$$

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 PES. (potential energy surface)



→ Consider $\Psi_0(r;R)$ for ground state non degenerate PES far from other $E_n(R)$. Here we can define the classical

forces on nuclei: $M_I \ddot{R}_I = -\frac{\partial E_0(\{R_I\})}{\partial R_I}$

↳ Forces are the 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 a non degenerate PES
  + Approximate full vibronic wave fn with

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

$\chi(R)$: nuclear part; $\Psi_m(r;R)$: ↳ electronic part at fixed R

→ This partitioning assumes that e^- are in instantaneous ground state for every R, even if nuclei are allowed to move

→ Adiabatic approximation.

* Take expectation value of H_{Total} with ψ_{trial}

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

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

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

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

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

$$= \left\langle \chi \left| \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial R^2} \right| \chi \right\rangle - \frac{\hbar^2}{2M}\langle\langle \chi\psi_m | \chi \frac{\partial^2\psi_m}{\partial R^2} \rangle\rangle$$

$$- \frac{\hbar^2}{M}\langle\langle \chi\psi_m | \frac{\partial\chi}{\partial R}\frac{\partial\psi}{\partial R} \rangle\rangle$$

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

↑ Contains all terms involving $\frac{\partial\psi}{\partial R}$ which can often be chosen to vanish if ψ is real

Dropping Λ gives Born-Oph. approx.

⇒ Nuclear dynamics described By sch. eq. with effective potential $E_m(R)$

Lattice Vibrations and Phonons

- Now we are going to "ignore" e^- and concentrate on the lattice of ions.

But everything we have learned so far still applies $\Rightarrow$ e^- in a crystal are Bloch states, which are quantized waves with the translational symmetry of the lattice.

→ Phonons $\Rightarrow$ Quantized lattice vibrations, quasiparticle excitations of the harmonic lattice.

- They must obey Bloch's Theorem $\Rightarrow$ they have a wave vector $\Rightarrow$ wave packets can be constructed, which travel with group velocity $\frac{\partial \omega_q}{\partial q} = v_q$. They carry heat (often very efficiently)

$\frac{\partial \varepsilon_k}{\partial \hbar} = v_k$ → e^- velocity in crystals.

- Probes of Phonons:

A: $q = 0$ (center of Brillouin zone)

1- Infrared absorption

2- Light scattering (Raman)

B. q out of Γ (within the 1st BZ)

1.- Inelastic neutron scattering

2.- Inelastic x-Ray scattering (x-Ray Raman)

3.- Inelastic e^- scattering (usually used for surfaces)

4.- Inelastic atom scattering (surface vibrations)

- Back to the full Hamiltonian:

$$H = \sum_\alpha \frac{P_\alpha^2}{2M_\alpha} + \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{\alpha\neq\beta} \frac{Z_\alpha Z_\beta e^2}{|R_\alpha - R_\beta|}$$

$$+ \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|r_i - r_j|} - \sum_{i\alpha} \frac{Z_\alpha e^2}{|R_\alpha - r_i|}$$

$$\Rightarrow H\{P_\alpha, p_i, R_\alpha, r_i\}$$

- We have solved the the Sch. eq. for e^- within the independent e^- approximation.

- In electronic scales room T ($T = 300$ K, $k_B T \sim 25$ meV) is very small $\Rightarrow$ e^- in ground state ($E_F \sim 1$-10 eV).

· let's now look at the ionic hamiltonian, treating ions classically = { classical nuclei approximation ≠ Adiabatic or Born-Oppenheimer approximation.

$$H_\alpha = \sum_\alpha \frac{P_\alpha}{2M_\alpha} + \sum_{k,n} \mathcal{E}_n(k,R)$$

Potential energy, e^- in ground state

$T=0$ all ions (nuclei + core e^-) sit at lattice points (equilibrium)

$$\vec{r}(R_{n,\alpha}) = \vec{R}_{n,\alpha} + \vec{u}(r_{n,\alpha})$$

small ⇒ harmonic approximation

→ Taylor expansion of $V(R_{n,\alpha})$ in powers of $U(r_{n,\alpha})$

→ stop at second order.

→ Assume (ex.) The atomic potential is a Lennard-Jones.

$V(R)$ (pair-like potential) $V(R_{1,1} \dots R_{n,\alpha}) =$

$$\frac{1}{2} \sum_{\substack{n\,n' \\ \alpha\,\alpha'}} V(\vec{R}_{n,\alpha} - \vec{R}_{n',\alpha'}) +$$