

Chap 2. Transitions in Molecular Systems

Molecular degrees of freedom : Nuclei $\{R_I\}$, electrons $\{r_i\}$, spins $\{\sigma_i\}$

$$[\text{Molecular wavefunction}] \simeq \chi(R)\varphi(r; R)\Theta(\sigma)$$

quantum numbers = (Nuclei, electrons, spins)

• Molecular transitions

- $\chi \rightarrow \chi'$: vib. rot. spectra, relaxation
- $\chi\varphi \rightarrow \chi'\varphi'$: electronic (vibronic) spectra, internal conversion
- $\chi\varphi\Theta \rightarrow \chi'\varphi'\Theta'$: intersystem crossing ($S_n \rightarrow T_m$)

• Interactions inducing molecular transitions

- photon (light-matter interaction)
- external fields (external degrees of freedom, heat baths)
- nonadiabatic coupling
- spin-orbit interaction (& other higher-order interactions)

- Summary

$$\begin{cases} \Phi(r, R) = \sum_n \chi_n(R) \varphi_n(r; R) \\ H\Phi = E\Phi \end{cases}$$

$$\begin{aligned} \Rightarrow [T_N + E_k(R) + L_{kk}(R)]\chi_k(R) \\ + \sum_{n \neq k} [W_{kn}(R) + L_{kn}(R)]\chi_n(R) = E\chi_k(R) \end{aligned}$$

Coupled differential equations for $\chi_n(R)$

$$L_{kn} \equiv \langle \varphi_k | T_N | \varphi_n \rangle - \sum_I (\hbar^2 / M_I) \langle \varphi_k | \nabla_I | \varphi_n \rangle \cdot \nabla_I$$

$$\left[\begin{array}{l} \text{Note: For real } \varphi_n, \langle \varphi_n | \nabla_I | \varphi_n \rangle = 0, \text{ thus } L_{nn} = \langle \varphi_n | T_N | \varphi_n \rangle \\ \text{Proof: Take } \nabla_I \text{ of } \langle \varphi_n | \varphi_n \rangle = 1 \\ \Rightarrow \langle \nabla_I \varphi_n | \varphi_n \rangle + \langle \varphi_n | \nabla_I \varphi_n \rangle = 2\text{Re} \langle \varphi_n | \nabla_I | \varphi_n \rangle = 0 \end{array} \right]$$

• Three approximations

1. Born-Huang approx. (= Adiabatic approx.)

- $\{\varphi_n\}$... adiabatic electronic, ie, $W_{kn}(R) = \delta_{kn}E_n(R)$
- Neglect off-diagonals
- Retain the diagonals $L_{kk}(R)$

2. Born-Oppenheimer approx.

- Born-Huang AND neglect diagonal $L_{kk}(R)$

3. Crude-adiabatic approx.

- electronic basis φ at particular nuclear geometry R_0
(usually equilibrium in ground state)

$$\Phi(r, R) \simeq \sum_n \chi_n(R) \varphi_n(r; R_0)$$

- Neglect off-diagonals

• Crude Adiabatic Approx.

$$\Phi(r, R) \simeq \sum_n \chi_n(R) \varphi_n(r; R_0)$$

Electronic basis φ obtained at a particular nuclear geometry R_0 :

$$H_e(r; R_0) \varphi(r; R_0) = E(R_0) \varphi(r; R_0)$$

Nuclear coordinate dependence is represented by ΔU :

$$H_e(r; R) = H_e(r; R_0) + \Delta U(r, R)$$

Here, $L_{kn} = 0$ (because R_0 is constant)

$$\Rightarrow [T_N + E_k(R_0) + \Delta U_{kk}(R)] \chi_k(R) + \sum_{n \neq k} \Delta U_{kn}(R) \chi_n(R) = E \chi_k(R)$$

$$\text{where } \Delta U_{kn}(R) = \int dr \varphi_k^*(r; R_0) \Delta U(r, R) \varphi_n(r; R_0)$$

In Crude-Adiab approx. off-diagonals are further neglected

$$\boxed{[T_N + E_k(R_0) + \Delta U_{kk}(R)] \chi_k(R) = E \chi_k(R)}$$