

CHEMISTRY 273

BORN-OPPENHEIMER APPROXIMATION AND SPECTROSCOPIC TRANSITIONS

For a single electron interacting with an electromagnetic wave, we showed that the interaction Hamiltonian was:

$$1. \quad H'(t) = -\frac{e}{2mc} [\vec{A}(r) \cdot \vec{p} + \vec{p} \cdot \vec{A}(r)]$$

gave, in the dipole approximation, the transition probability:

$$2. \quad P_{\alpha\beta} = \frac{2}{3} \frac{\pi}{c\hbar^2} |\vec{\mu}_{\alpha\beta}|^2 \quad \text{where} \quad \vec{\mu}_{\alpha\beta} = \int \psi_{\alpha}(-e\vec{r}) \psi_{\beta} d\vec{r}$$

For a system of charged nuclei (charges eZ_I) and electrons, the Hamiltonian and transition dipole are:

$$3. \quad H'(t) = \frac{e}{2mc} \left\{ \sum_I Z_I [(\vec{A}(\mathbf{R}_I) \cdot \vec{p}_I + \vec{p}_I \cdot \vec{A}(\mathbf{R}_I))] - \sum_i [(\vec{A}(\mathbf{r}_i) \cdot \vec{p}_i + \vec{p}_i \cdot \vec{A}(\mathbf{r}_i))] \right\}$$

$$4. \quad \mu_{\alpha\beta} = \int \psi_{\alpha} \left[\underbrace{\sum_I eZ_I \vec{R}_I}_{(\hat{\mu}_N)} - \underbrace{\sum_i e\vec{r}_i}_{(\hat{\mu}_{el})} \right] \psi_{\beta} d\vec{R} \, d\vec{r}$$

To evaluate these results we utilized the Born-Oppenheimer Approximation:

$$5. \quad \psi(\mathbf{r}, \mathbf{R}) \approx \psi_{el}(\mathbf{r}; \mathbf{R}) \chi_{NUC}(\mathbf{R})$$

Steps 6-10 derive the equation for $\chi(\mathbf{R})$ and illustrate the Hamiltonian terms that are neglected (approximated as zero) when (5) is utilized.

$$6. \quad \text{Separate } \mathcal{H} \text{ as } \mathcal{H} = H_{NUC} + H_{el} \text{ where } H_{NUC} = \sum_I -\frac{\hbar^2}{2M_I} \nabla_I^2$$

$$7. \quad \text{and } H_{el} = (\text{kinetic energy of } e's) + (e - e \text{ repulsion}) \\ + (e - Z \text{ attraction}) + (Z - Z \text{ repulsion})$$

$$8. \quad \psi_{el} \text{ is defined by} \quad H_{el} \psi_{el} = E(\mathbf{R}) \psi_{el}$$

$$\text{for the } k^{\text{th}} \text{ electronic state} \quad H_{el} \psi_k = E_k(\mathbf{R}) \psi_k$$

NOTE: H_{el} affects χ only multiplicatively $\Rightarrow H_{el} \psi \chi = \chi H_{el} \psi$ (see (7) above).

$$9. \quad \mathcal{H} \psi_k \chi = \chi \underbrace{H_N}_{\text{approximate as } 0} \psi_k + \psi_k H_N \chi + \chi H_{el} \psi_k = \mathcal{E}_T \psi_k \chi$$

$$\psi_k H_N \chi + \chi E_k(\mathbf{R}) \psi_k + \mathcal{E}_T \psi_k \chi$$

$$\psi_k [H_N \chi + E_k(\mathbf{R}) \chi] = \mathcal{E}_T \chi$$

where \mathcal{E}_T = Total energy (electronic and nuclear motion)

$$10. \quad H_N \chi + E_k(\mathbf{R}) \chi = \mathcal{E}_T \chi \text{ determines } \chi$$

$$H_N \chi_{k,v} + E_k(\mathbf{R}) \chi = \mathcal{E}_{k,v} \chi_{k,v}$$

$$\psi(\mathbf{r}, \mathbf{R}) = \psi_{k,v}(\mathbf{r}, \mathbf{R}) \approx \psi_k(\mathbf{r}; \mathbf{R}) \chi_{k,v}(\mathbf{R})$$

The electronic energy of the k^{th} state, $E_k(\mathbf{R})$, provides the potential function for the motion of the nuclei. The quantum number v refers to the nuclear states associated with the k^{th} electronic level.

Evaluating $\vec{\mu}_{\alpha\beta}$ in the B.O. approximation

$$\Psi_\alpha = \psi_{k_1} \chi_{k_1, v_1} \quad \Psi_\beta = \psi_{k_2} \chi_{k_2, v_2}$$

$$\vec{\mu}_{\alpha\beta} = \int \Psi_\alpha (\vec{\mu}_N + \vec{\mu}_{el}) \Psi_\beta d\mathbf{R} d\mathbf{r}$$

$$= \int \chi_{k_1, v_1} \vec{\mu}_N \chi_{k_2, v_2} d\mathbf{R} \int \psi_{k_1} \psi_{k_2} d\mathbf{r} + \int \chi_{k_1, v_1} \chi_{k_2, v_2} d\mathbf{R} \int \psi_{k_1} \vec{\mu}_{el} \psi_{k_2} d\mathbf{r}$$

I. Electronic transitions ($k_1 \neq k_2$)

$$\int \psi_{k_1} \psi_{k_2} d\mathbf{r} = 0$$

$$\vec{\mu}_{\alpha\beta} = \underbrace{\int \chi_{k_1, v_1} \chi_{k_2, v_2} d\mathbf{R}}_{\text{Franck-Condon factor}} \underbrace{\int \psi_{k_1} \vec{\mu}_{el} \psi_{k_2} d\mathbf{r}}_{\text{electronic transition moment integral}}$$

II. Nuclear transitions ($v_1 \neq v_2$) in same electronic state ($k_1 = k_2 = k$)

$$\vec{\mu}_{\alpha\beta} = \int \chi_{k, v_1} \vec{\mu}_N \chi_{k, v_2} d\mathbf{R} + \int \chi_{k, v_1} \chi_{k, v_2} d\mathbf{R} \int \psi_k(\mathbf{r}; \mathbf{R}) \vec{\mu}_{el}(\mathbf{r}; \mathbf{R}) \psi_k(\mathbf{r}; \mathbf{R}) d\mathbf{r}$$

$$\vec{\mu}_{\alpha\beta} = \int \chi_{k,v1} \chi_{k,v2} d\vec{R} \int \underbrace{\left[\sum_I eZ_I \vec{R}_I - \sum_i e\vec{r}_i \right]}_{\vec{\mu}_k(\mathbf{R}) \text{ is dipole moment of } k^{\text{th}} \text{ electronic state as a function of } \mathbf{R}.} \psi_k(\mathbf{r}; \mathbf{R}) \psi_k(\mathbf{r}; \mathbf{R}) d\mathbf{r}$$

$$\vec{\mu}_{\alpha\beta} = \int \chi_{k,v1} \vec{\mu}_k(\mathbf{R}) \chi_{k,v2} d\vec{R}$$

↑

$\vec{\mu}_k(\mathbf{R})$ must be a function of \mathbf{R} or otherwise intergral is zero.