

6.2: Nonadiabatic Effects

Even without the BO approximation, we note that the nuclear-electronic product states form a complete basis in which to express the total vibronic wavefunction:

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{i,J} c_{i,J} \Phi_{i,J}(\mathbf{R}) \psi_i(\mathbf{r}, \mathbf{R}) \quad (6.2.1)$$

We can therefore use this form to investigate the consequences of the BO approximation. For a given vibronic state, the action of the Hamiltonian on the wavefunction in the TISE is

$$\hat{H}\Psi_{i,J} = \left(\hat{T}_N(\mathbf{R}) + \hat{H}_{el}(\mathbf{R}) \right) \Phi_{i,J}(\mathbf{R}) \psi_i(\mathbf{R}) \quad (6.2.2)$$

Expanding the Laplacian in the nuclear kinetic energy via the chain rule as

$$\nabla^2 AB = (\nabla^2 A) B + 2(\nabla A) \nabla B + A \nabla^2 B,$$

we obtain an expression with three terms

$$\begin{aligned} \hat{H}\Psi_{i,J} &= \Phi_{i,J}(\mathbf{R}) \left(\hat{T}_N(\mathbf{R}) + U_i(\mathbf{R}) \right) \psi_i(\mathbf{R}) \\ &\quad - \sum_J \frac{\hbar^2}{M_J} \nabla_R \Phi_{i,J}(\mathbf{R}) \nabla_R \psi_i(\mathbf{R}) \\ &\quad - \sum_J \frac{\hbar^2}{2M_J} \Phi_{i,J}(\mathbf{R}) \nabla_R^2 \psi_i(\mathbf{R}) \end{aligned} \quad (6.2.3)$$

This expression is exact for vibronic problems, and is referred to as the **coupled channel Hamiltonian**. Note that if we set the last two terms in Equation 6.2.3 to zero, we are left with

$$\hat{H} = \hat{T}_N + U \quad (6.2.4)$$

which is just the Hamiltonian we used in the Born-Oppenheimer approximation, Equation 6.1.7. Therefore, the last two terms describe deviations from the BO approximation, and are referred to as nonadiabatic terms. These depend on the spatial gradient of the wavefunction in the region of interest, and act to couple adiabatic Born-Oppenheimer states. The coupled channel Hamiltonian has a form that is reminiscent of a perturbation theory Hamiltonian in which the Born-Oppenheimer states play the role of the zero-order Hamiltonian being perturbed by a nonadiabatic coupling

$$\hat{H} = \hat{H}_{BO} + \hat{V} \quad (6.2.5)$$

To investigate this relationship further, it is helpful to write this Hamiltonian in its matrix form. We obtain the matrix elements by sandwiching the Hamiltonian between two projection operators and evaluating

$$\hat{H}_{i,I,J} = \iint d\mathbf{r} d\mathbf{R} \Psi_{i,I}^*(\mathbf{r}, \mathbf{R}) \hat{H}(\mathbf{r}, \mathbf{R}) \Psi_{j,J}(\mathbf{r}, \mathbf{R}) \quad (6.2.6)$$

Making use of Equation 6.2.3 we find that the Hamiltonian can be expressed in three terms

$$\hat{H}_{i,I,j,J} = \int d\mathbf{R} \Phi_{i,I}(\mathbf{R}) \left(\hat{T}_N(\mathbf{R}) + U_j(\mathbf{R}) \right) \Phi_{j,J}(\mathbf{R}) \delta_{i,j} \quad (6.2.7)$$

$$- \sum_I \frac{\hbar^2}{M_I} \int d\mathbf{R} \Phi_{i,I}(\mathbf{R}) \nabla_R \Phi_{j,J}(\mathbf{R}) \cdot \mathbf{F}_{ij}(\mathbf{R}) \quad (6.2.8)$$

$$- \sum_I \frac{\hbar^2}{2M_I} \int d\mathbf{R} \Phi_{i,I}(\mathbf{R}) \Phi_{j,J}(\mathbf{R}) \mathbf{G}_{ij}(\mathbf{R}) \quad (6.2.9)$$

$$- \sum_I \frac{\hbar^2}{2M_I} \int d\mathbf{R} \Phi_{i,I}(\mathbf{R}) \Phi_{j,J}(\mathbf{R}) \mathbf{G}_{ij}(\mathbf{R}) \quad (6.2.10)$$

where

$$\mathbf{F}_{ij}(\mathbf{R}) = \int d\mathbf{r} \psi_i^*(\mathbf{r}, \mathbf{R}) \nabla_{\mathbf{R}} \psi_j(\mathbf{r}, \mathbf{R}) \quad (6.2.11)$$

$$\mathbf{G}_{ij}(\mathbf{R}) = \int d\mathbf{r} \psi_i^*(\mathbf{r}, \mathbf{R}) \nabla_{\mathbf{R}}^2 \psi_j(\mathbf{r}, \mathbf{R}) \quad (6.2.12)$$

The first term in Equation 6.2.10 gives the BO Hamiltonian. In the latter two terms, \mathbf{F} is referred to as the nonadiabatic, first-order, or derivative coupling, and \mathbf{G} is the second-order nonadiabatic coupling or diagonal BO correction. Although they are evaluated by integrating over electronic degrees of freedom, both depend parametrically on the position of the nuclei. In most circumstances the last term is much smaller than the other two, so that we can concentrate on the second term in evaluating couplings between adiabatic states. For our purposes, we can write the nonadiabatic coupling in Equation 6.2.5 as

$$\hat{V}_{i,I,j,J}(\mathbf{R}) = - \sum_I \frac{\hbar^2}{M_I} \int d\mathbf{R} \Phi_{i,I}(\mathbf{R}) \nabla_{\mathbf{R}} \Phi_{j,J}(\mathbf{R}) \cdot \mathbf{F}_{ij}(\mathbf{R}) \quad (6.2.13)$$

This emphasizes that the coupling between surfaces depends parametrically on the nuclear positions, the gradient of the electronic and nuclear wavefunctions, and the spatial overlap of those wavefunctions.

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