5. <u>THE ADIABATIC APPROXIMATION</u>

In quantum mechanics, the adiabatic approximation refers to those solutions to the Schrödinger equation that make use of a time-scale separation between fast and slow degrees of freedom, and use this to find approximate solutions as product states in the fast and slow degrees of freedom. Perhaps the most fundamental and commonly used version is the Born–Oppenheimer (BO) approximation, which underlies much of how we conceive of molecular electronic structure and is the basis of potential energy surfaces. The BO approximation assumes that the motion of electrons is much faster than nuclei due to their large difference in mass, and therefore electrons adapt very rapidly to any changes in nuclear geometry. That is, the electrons "adiabatically follow" the nuclei. As a result, we can solve for the electronic state of a molecule for fixed nuclear configurations. Gradually stepping nuclear configurations and solving for the energy leads to a potential energy surface, or adiabatic state. Much of our descriptions of chemical reaction dynamics is presented in terms of propagation on these potential energy surfaces. The barriers on these surfaces are how we describe the rates of chemical reactions and transition state. The trajectories along these surfaces are used to describe mechanism.

More generally, the adiabatic approximation can be applied in other contexts in which there is a time-scale separation between fast and slow degrees of freedom. For instance, in the study of vibrational dynamics when the bond vibrations of molecules occur much faster than the intermolecular motions of a liquid or solid. It is also generally implicit in a separation of the Hamiltonian into a system and a bath, a method we will often use to solve condensed matter problems. As widely used as the adiabatic approximation is, there are times when it breaks down, and it is important to understand when this approximation is valid, and the consequences of when it is not. This will be particularly important for describing time-dependent quantum mechanical processes involving transitions between potential energy sources.

5.1. Born–Oppenheimer Approximation

As a starting point, it is helpful to review the Born–Oppenheimer Approximation (BOA). For a molecular system, the Hamiltonian can be written in terms of the kinetic energy of the nuclei (N) and electrons (e) and the potential energy for the Coulomb interactions of these particles.

$$
\begin{aligned}
\hat{H} &= \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{NN} + \hat{V}_{eN} \\
&= -\sum_{i=1}^{n} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{J=1}^{N} \frac{\hbar^2}{2M_J} \nabla_J^2 \\
&\quad + \frac{1}{4\pi\varepsilon_0} \sum_{\substack{i,j=1 \\ j>i}}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{4\pi\varepsilon_0} \sum_{\substack{I,J=1 \\ J>I}}^{N} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{n} \sum_{J=1}^{N} \frac{Z_J e^2}{|\mathbf{r}_i - \mathbf{R}_J|}
\end{aligned}
\tag{5.1}
$$

Here and in the following, we will use lowercase variables to refer to electrons and uppercase to nuclei. The variables n, i, $\boldsymbol{r}$, ∇_r^2, and m_e refer to the number, index, position, Laplacian, and mass of electrons, respectively, and N, J, $\boldsymbol{R}$, and M refer to the nuclei. e is the electron charge, and Z is the atomic number of the nucleus. Note, this Hamiltonian does not include relativistic effects such as spin-orbit coupling.

The time-independent Schrödinger equation is

$$\hat{H}\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right)\Psi\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right) = E\Psi\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right) \tag{5.2}$$

$\Psi\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right)$ is the total vibronic wavefunction, where "vibronic" refers to the combined electronic and nuclear eigenstates. Exact solutions using the molecular Hamiltonian are intractable for most problems of interest, so we turn to simplifying approximations. The BO approximation is motivated by noting that the nuclei are far more massive than an electron ($m_e \ll M_l$). With this criterion, and when the distances separating particles is not unusually small, the kinetic energy of the nuclei is small relative to the other terms in the Hamiltonian. Physically, this means that the electrons move and adapt rapidly—adiabatically—in response to shifting nuclear positions. This offers an avenue to solving for Ψ by fixing the position of the nuclei, solving for the electronic wavefunctions ψ_i, and then iterating for varying $\boldsymbol{R}$ to obtain effective electronic potentials on which the nuclei move.

Since it is fixed for the electronic calculation, we proceed by treating $\boldsymbol{R}$ as a parameter rather than an operator, set $\hat{T}_N$ to 0, and solve the electronic TISE:

$$\hat{H}_{el}\left(\hat{\mathbf{r}},\mathbf{R}\right)\psi_i\left(\hat{\mathbf{r}},\mathbf{R}\right) = U_i\left(\mathbf{R}\right)\psi_i\left(\hat{\mathbf{r}},\mathbf{R}\right) \tag{5.3}$$

U_i are the electronic energy eigenvalues for the fixed nuclei, and the electronic Hamiltonian in the BO approximation is

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} \tag{5.4}$$

In (5.3), ψ_i is the electronic wavefunction for fixed $\boldsymbol{R}$, with $i = 0$ referring to the electronic ground state. Repeating this calculation for varying $\boldsymbol{R}$, we obtain $U_i(\boldsymbol{R})$, an effective or mean-field potential for the electronic states on which the nuclei can move. These effective potentials are known as Born–Oppenheimer or adiabatic potential energy surfaces (PES).
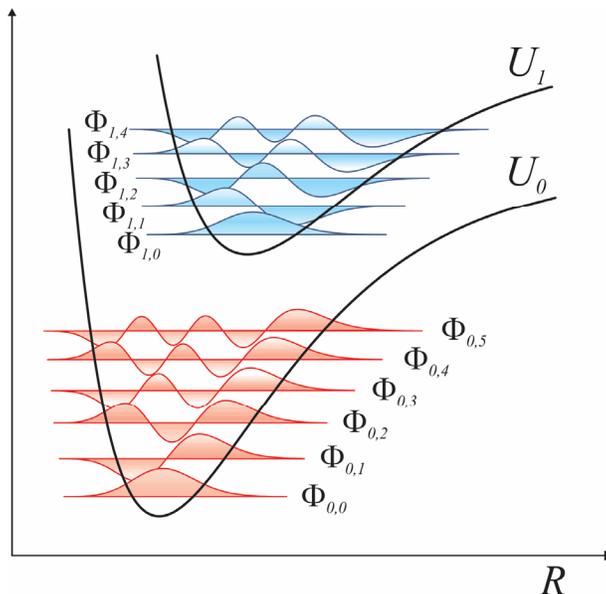
For the nuclear degrees of freedom, we can define a Hamiltonian for the ith electronic PES:

$$\hat{H}_{Nuc,i} = \hat{T}_N + U_i(\hat{R}) \tag{5.5}$$

which satisfies a TISE for the nuclear wave functions $\Phi(R)$:

$$\hat{H}_{Nuc,i}\Phi_{iJ}(R) = E_{iJ}\Phi_{iJ}(R) \qquad (5.6)$$

Here J refers to the Jth eigenstate for nuclei evolving on the ith PES. Equation (5.5) is referred to as the BO Hamiltonian.

The BOA effectively separates the nuclear and electronic contributions to the wavefunction, allowing us to express the total wavefunction as a product of these contributions $\Psi(\mathbf{r},\mathbf{R}) = \Phi(\mathbf{R})\psi(\mathbf{r},\mathbf{R})$ and the eigenvalues as sums over the electronic and nuclear contribution: $E = E_N + E_e$. The BOA does not treat the nuclei classically. However, it is the basis for semiclassical dynamics methods in which the nuclei evolve classically on a potential energy surface, and interact with quantum electronic states. If we treat the nuclear dynamics classically, then the electronic Hamiltonian can be thought of as depending on $\mathbf{R}$ or on time as related by velocity or momenta. If the nuclei move infinitely slowly, the electrons will adiabatically follow the nuclei and systems prepared in an electronic eigenstate will remain in that eigenstate for all times.

5.2. 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:

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_{i,J} c_{i,J}\Phi_{i,J}(\mathbf{R})\psi_i(\mathbf{r},\mathbf{R}) \qquad (5.7)$$

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

$$\hat{H}\,\Psi_{i,J} = \left(\hat{T}_N(\mathbf{R}) + \hat{H}_{el}(\mathbf{R})\right)\Phi_{i,J}(\mathbf{R})\psi_i(\mathbf{R}) \tag{5.8}$$

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

$$\hat{H}\,\Psi_{i,J} = \Phi_{i,J}(\mathbf{R})\left(\hat{T}_N(\mathbf{R}) + U_i(\mathbf{R})\right)\psi_i(\mathbf{R})$$
$$-\sum_J \frac{\hbar^2}{M_J}\nabla_R\Phi_{i,J}(\mathbf{R})\nabla_R\psi_i(\mathbf{R}) \tag{5.9}$$
$$-\sum_J \frac{\hbar^2}{2M_J}\Phi_{i,J}(\mathbf{R})\nabla_R^2\psi_i(\mathbf{R})$$

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 (5.9) to zero, we are left with $\hat{H} = \hat{T}_N + U$, which is just the Hamiltonian we used in the Born-Oppenheimer approximation, eq. (5.5). 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 ay a nonadiabatic coupling V:

$$\hat{H} = \hat{H}_{BO} + \hat{V} \tag{5.10}$$

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

$$\hat{H}_{i,I,j,J} = \iint dr d\mathbf{R}\,\Psi_{i,I}^*(\mathbf{r},\mathbf{R})\hat{H}(\mathbf{r},\mathbf{R})\Psi_{j,J}(\mathbf{r},\mathbf{R}). \tag{5.11}$$

Making use of eq. (5.9) we find that the Hamiltonian can be expressed in three terms

$$\hat{H}_{i,I,j,J} = \int d\mathbf{R}\,\Phi_{i,I}(\mathbf{R})\left(\hat{T}_N(\mathbf{R}) + U_j(\mathbf{R})\right)\Phi_{j,J}(\mathbf{R})\delta_{i,j}$$
$$-\sum_I \frac{\hbar^2}{M_I}\int d\mathbf{R}\,\Phi_{i,I}(\mathbf{R})\nabla_R\Phi_{j,J}(\mathbf{R})\cdot\mathbf{F}_{ij}(\mathbf{R}) \tag{5.12}$$
$$-\sum_I \frac{\hbar^2}{2M_I}\int d\mathbf{R}\,\Phi_{i,I}(\mathbf{R})\Phi_{j,J}(\mathbf{R})\mathbf{G}_{ij}(\mathbf{R})$$

where

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

$$\mathbf{G}_{ij}(\mathbf{R}) = \int d\mathbf{r}\, \psi_i^*(\mathbf{r}, \mathbf{R}) \nabla_R^2 \psi_j(\mathbf{r}, \mathbf{R})$$
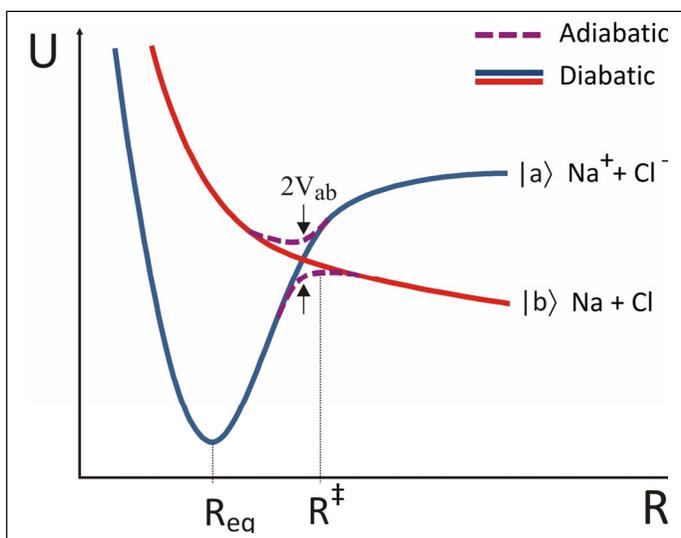
(5.13)

The first term in eqn. (5.12) 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 (5.10) as

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

(5.14)

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.

5.3. Diabatic and Adiabatic States

Although the Born–Oppenheimer surfaces are the most straightforward and commonly calculated, they may not be the most chemically meaningful states. As an example consider the potential energy curves for the diatomic NaCl. The chemically distinct potential energy surfaces one is likely to discuss have distinct atomic or ionic character at large separation between the atoms. These "diabatic" curves focus on physical effects, but are not eigenstates. In the figure, the ionic state $|a\rangle$ is influenced by the Coulomb attraction between ions that draws them together, leading to a stable configuration at R_{eq} once these attractive terms are balanced by nuclear repulsive forces. However, the neutral atoms (Na^0 and Cl^0) have a potential energy surface $|b\rangle$ which is dominated by repulsive interactions. The adiabatic potentials from the BO Hamiltonian will reflect significant coupling between the diabatic electronic states. BO states of the same symmetry will exhibit an avoided crossing where the electronic energy between corresponding diabatic states is equal. As expected from our earlier discussion, the splitting at the crossing for this one-dimensional system would be $2V_{ab}$, twice the coupling between diabatic states.

The adiabatic potential energy surfaces are important in interpreting the reaction dynamics, as can be illustrated with the reaction between Na and Cl atoms. If the neutral atoms are prepared on the ground state at large separation and slowly brought together, the atoms are weakly repelled until the separation reaches the transition state $R^{\ddagger}$. Here we cross into the regime where the ionic configuration has lower energy. As a result of the nonadiabatic couplings, we expect that an electron will transfer from Na^0 to Cl^0, and the ions will then feel an attractive force leading to an ionic bond with separation R_{eq}.

Diabatic states can be defined in an endless number of ways, but only one adiabatic surface exists. In that respect, the term "nonadiabatic" is also used to refer to all possible diabatic surfaces. However, diabatic states are generally chosen so that the nonadiabatic electronic couplings in eq. (5.13) are zero. This can be accomplished by making the electronic wavefunction independent of R.

As seen above, for coupled states with the same symmetry the couplings repel the adiabatic states and we get an avoided crossing. However, it is still possible for two adiabatic states to *cross*. Mathematically this requires that the energies of the adiabatic states be degenerate ($E_\alpha = E_\beta$) *and* that the coupling at that configuration be zero ($V_{\alpha\beta}=V_{\beta\alpha}=0$). This isn't possible for a one-dimensional problem, such as the NaCl example above, unless symmetry dictates that the nonadiabatic coupling vanishes. To accomplish this for a Hermitian coupling operator you need two independent nuclear coordinates, which enable you to independently tune the adiabatic splitting and coupling. This leads to a single point in the two-dimensional space at which degeneracy exists, which is known as a conical intersection (an important topic that is not discussed further here).

5.4. Adiabatic and Nonadiabatic Dynamics

OK, so what does the discussion above mean for dynamics? The BO approximation never explicitly addresses electronic or nuclear dynamics, but neglecting the nuclear kinetic energy to obtain potential energy surfaces has implicit dynamical consequences. As we discussed for our NaCl example, moving the neutral atoms together slowly allows electrons to completely equilibrate about each forward step, resulting in propagation on the adiabatic ground state. This is the essence of the adiabatic approximation. If you prepare the system in Ψ_α, an eigenstate of H at the initial time t_0, and propagate slowly enough, that Ψ_α will evolve as an eigenstate for all times:

$$H(t)\Psi_\alpha(t) = E_\alpha(t)\Psi_\alpha(t) \tag{5.15}$$

Equivalently this means that the nth eigenfunction of $H(t_0)$ will also be the nth eigenfunction of $H(t)$. In this limit, there are no transitions between BO surfaces, and the dynamics only reflect the phases acquired from the evolving system. That is the time propagator can be expressed as

$$U(t,t_0)_{adiabatic} = \sum_\alpha |\alpha\rangle\langle\alpha| \exp\left(-\frac{i}{\hbar}\int_{t_0}^t dt' \, E_\alpha(t')\right) \qquad (5.16)$$

In the opposite limit, we also know that if the atoms were incident on each other so fast (with such high kinetic energy) that the electron did not have time to transfer at the crossing, that the system would pass smoothly through the crossing along the diabatic surface. In fact it is expected that the atoms would collide and recoil. This implies that there is an intermediate regime in which the velocity of the system is such that the system will split and follow both surfaces to some degree.
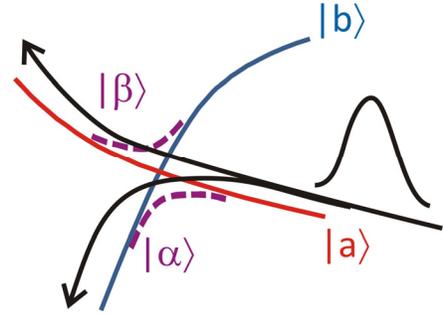
In a more general sense, we would like to understand the criteria for adiabaticity that enable a time-scale separation between the fast and slow degrees of freedom. Speaking qualitatively about any time-dependent interaction between quantum mechanical states, the time-scale that separates the fast and slow propagation regimes is determined by the strength of coupling between those states. We know that two coupled states exchange amplitude at a rate dictated by the Rabi frequency Ω_R, which in turn depends on the energy splitting and coupling of the states. For systems in which there is significant nonperturbative transfer of population between two states a and b, the time scale over which this can occur is approximately $\Delta t \approx 1/\Omega_R \approx \hbar/V_{ab}$. This is not precise, but is provides a reasonable starting point for discussing "slow" versus "fast". "Slow" in an adiabatic sense would mean that a time-dependent interaction act on the system over a period such that $\Delta t \ll \hbar/V_{ab}$. In the case of our NaCl example, we would be concerned with the time scale over which the atoms pass through the crossing region between diabatic states, which is determined by the incident velocity between atoms.

Adiabaticity criterion

Let's investigate these issues by looking more carefully at the adiabatic approximation. Since the adiabatic states $\Psi_\alpha(t) \equiv |\alpha\rangle$ are orthogonal for all times, we can evaluate the time propagator as

$$U(t) = \sum_\alpha e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} |\alpha\rangle\langle\alpha| \qquad (5.17)$$

and the time-dependent wavefunction is

$$\Psi(t) = \sum_\alpha b_\alpha(t) e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} |\alpha\rangle \qquad (5.18)$$

Although these are adiabatic states we recognize that the expansion coefficients can be time-dependent in the general case. So, we would like to investigate the factors that govern this time-

dependence. To make the notation more compact, let's define the time-rate of change of the eigenfunction as

$$|\dot{\alpha}\rangle = \frac{\partial}{\partial t}|\Psi_\alpha(t)\rangle \tag{5.19}$$

If we substitute the general solution eq. (5.18) into the TDSE, we get

$$i\hbar \sum_\alpha \left(\dot{b}_\alpha |\alpha\rangle + b_\alpha |\dot{\alpha}\rangle - \frac{i}{\hbar} E_\alpha b_\alpha |\alpha\rangle \right) e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} = \sum_\alpha b_\alpha E_\alpha |\alpha\rangle e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} \tag{5.20}$$

Note, the third term on the left hand side equals the right hand term. Acting on both sides from the left with $\langle\beta|$ leads to

$$-\dot{b}_\beta e^{-\frac{i}{\hbar}\int_0^t E_\beta(t')dt'} = \sum_\alpha b_\alpha \langle\beta|\dot{\alpha}\rangle e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} \tag{5.21}$$

We can break up the terms in the summation into one for the target state $|\beta\rangle$ and one for the remaining states.

$$-\dot{b}_\beta = b_\beta \langle\beta|\dot{\beta}\rangle + \sum_{\alpha\neq\beta} b_\alpha \langle\beta|\dot{\alpha}\rangle \exp\left[-\frac{i}{\hbar}\int_0^t dt'\, E_{\alpha\beta}(t') \right] \tag{5.22}$$

where $E_{\alpha\beta}(t) = E_\alpha(t) - E_\beta(t)$.

The adiabatic approximation applies when we can neglect the summation in eq. (5.22), or equivalently when $\langle\beta|\dot{\alpha}\rangle \ll \langle\beta|\dot{\beta}\rangle$ for all $|\alpha\rangle$. In that case, the system propagates on the adiabatic state $|\beta\rangle$ independent of the other states: $\dot{b}_\beta = -b_\beta \langle\beta|\dot{\beta}\rangle$. The evolution of the coefficients is

$$b_\beta(t) = b_\beta(0)\exp\left[-\int_0^t \langle\beta(t')|\dot{\beta}(t')\rangle dt' \right]$$
$$\approx b_\beta(0)\exp\left[\frac{i}{\hbar}\int_0^t E_\beta(t')\,dt' \right] \tag{5.23}$$

Here we note that in the adiabatic approximation $E_\beta(t) = \langle\beta(t)|H(t)|\beta(t)\rangle$. Equation (5.23) indicates that in the adiabatic approximation the population in the states never changes, only their phase.

The second term on the right in eq. (5.22) describes the nonadiabatic effects, and the overlap integral

$$\langle\beta|\dot{\alpha}\rangle = \left\langle \Psi_\beta \left| \frac{\partial\Psi_\alpha}{\partial t} \right. \right\rangle \tag{5.24}$$

determines the magnitude of this effect. $\langle\beta|\dot{\alpha}\rangle$ is known as the nonadiabatic coupling (even though it refers to couplings between adiabatic surfaces), or as the geometrical phase. Note the

parallels here to the expression for the nonadiabatic coupling in evaluating the validity of the Born-Oppenheimer approximation, however, here the gradient of the wavefunction is evaluated in time rather than the nuclear position. It would appear that we can make some connections between these two results by linking the gradient variables through the momentum or velocity of the particles involved.

So, when can we neglect the nonadiabatic effects? We can obtain an expression for the nonadiabatic coupling by expanding

$$\frac{\partial}{\partial t}\left[H|\alpha\rangle = E_\alpha|\alpha\rangle\right] \tag{5.25}$$

and acting from the left with $\langle\beta|$, which for $\alpha \neq \beta$ leads to

$$\langle\beta|\dot{\alpha}\rangle = \frac{\langle\beta|\dot{H}|\alpha\rangle}{E_\alpha - E_\beta} \tag{5.26}$$

For adiabatic dynamics to hold $\langle\beta|\dot{\alpha}\rangle << \langle\beta|\dot{\beta}\rangle$, and so we can say

$$\frac{\langle\beta|\dot{H}|\alpha\rangle}{E_\alpha - E_\beta} << -\frac{i}{\hbar}E_\beta \tag{5.27}$$

So how accurate is the adiabatic approximation for a finite time-period over which the systems propagates? We can evaluate eq. (5.22), assuming that the system is prepared in state $|\alpha\rangle$ and that the occupation of this state never varies much from one. Then the occupation of any other state can be obtained by integrating over a period τ as

$$\dot{b}_\beta = \langle\beta|\dot{\alpha}\rangle \exp\left[-\frac{i}{\hbar}\int_0^\tau dt' E_{\alpha\beta}(t')\right]$$

$$b_\beta \approx i\hbar\frac{\langle\beta|\dot{H}|\alpha\rangle}{E_{\alpha\beta}^2}\left\{\exp\left[-\frac{i}{\hbar}E_{\alpha\beta}\tau\right]-1\right\} \tag{5.28}$$

$$= 2\hbar\frac{\langle\beta|\dot{H}|\alpha\rangle}{E_{\alpha\beta}^2}e^{-\frac{i}{\hbar}E_{\alpha\beta}\tau}\sin\left(\frac{E_{\alpha\beta}\tau}{2\hbar}\right)$$

Here I used $e^{i\theta} - 1 = 2i\,e^{i\theta/2}\sin(\theta/2)$. For $|b_\beta| << 1$, we expand the *sin* term and find

$$\left\langle\Psi_\beta\left|\frac{\partial H}{\partial t}\right|\Psi_\alpha\right\rangle \ll E_{\alpha\beta}/\tau \tag{5.29}$$

This is the criterion for adiabatic dynamics, which can be seen to break down near adiabatic curve crossings where $E_{\alpha\beta} = 0$, regardless of how fast we propagate through the crossing. Even away from curve crossing, there is always the possibility that nuclear kinetic energies are such that $(\partial H / \partial t)$ will be greater than or equal to the energy splitting between adiabatic states.

5.5. Landau–Zener Transition Probability

Clearly the adiabatic approximation has significant limitations in the vicinity of curve crossings. This phenomenon is better described through transitions between diabatic surfaces. To begin, how do we link the temporal and spatial variables in the curve crossing picture? We need a time-rate of change of the energy splitting, $\dot{E} = dE_{ab} / dt$. The Landau–Zener expression gives the transition probabilities as a result of propagating through the crossing between *diabatic* surfaces at a constant $\dot{E}$. If the energy splitting between states varies linearly in time near the crossing point, then setting the crossing point to $t = 0$ we write

$$E_a - E_b = \dot{E}t \tag{5.30}$$

If the coupling between surfaces V_{ab} is constant, the transition probability for crossing from surface a to b for a trajectory that passes through the crossing is

$$P_{ba} = 1 - \exp\left[-\frac{2\pi V_{ab}^2}{\hbar |\dot{E}|} \right] \tag{5.31}$$

and $P_{aa} = 1 - P_{ba}$. Note if $V_{ab} = 0$ then $P_{ba} = 0$, but if the splitting sweep rate $\dot{E}$ is small as determined by

$$2\pi V_{ab}^2 >> \hbar |\dot{E}| \tag{5.32}$$

then we obtain the result expected for the adiabatic dynamics $P_{ba} \approx 1$.

We can provide a classical interpretation to eq. (5.31) by equating $\dot{E}$ with the velocity of particles involved in the crossing. We define the velocity as $v = \partial R / \partial t$, and the slope of the diabatic surfaces at the crossing, $F_i = \partial E_i / \partial R$. Recognizing

$$(E_a - E_b)/t = v(F_a - F_b) \tag{5.33}$$

we find

$$P_{ba} = 1 - \exp\left[-\frac{2\pi V_{ab}^2}{\hbar v |F_a - F_b|} \right] \tag{5.34}$$

In the context of potential energy surfaces, what this approximation says is that you need to know the slopes of the potentials at their crossing point, the coupling and their relative velocity in order to extract the rates of chemical reactions.
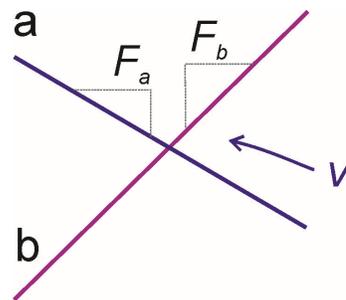
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