6.1. The States Between Which Transitions Occur

To understand the mechanisms by which a molecule can undergo a radiationless transition (Yardley, 1980; Lin, 1980) from one potential energy surface to another, the Schrödinger equation for combined electronic and nuclear motion given in Chapter 1 is needed. The electronic wavefunctions $|\phi_e(r|R)|$ corresponding to the two interacting states between which transitions occur obey the equations

$$\hbar c \phi_{s_0} = E_{s_0}(R)\phi_{s_0}$$  \hspace{1cm} (6.1)

and

$$\hbar c \phi_x = E_x(R)\phi_x \quad (x = S_1 \text{ or } T_1).$$  \hspace{1cm} (6.2)

Within the Born-Oppenheimer approximation, the internal (vibrational-rotational) wavefunctions belonging to the $S_0$ and excited potential surfaces obey the equations

$$(D_R^2 + E_{s_0})x_\nu^0 = \epsilon_\nu^0 x_\nu^0$$  \hspace{1cm} (6.3)

and

$$(D_R^2 + E_x)x_\nu^x = \epsilon_\nu^x x_\nu^x,$$  \hspace{1cm} (6.4)

in which $D_R^2$ is the kinetic energy operator for all of the nuclear vibration and rotation. The energies $\epsilon_\nu^0$ and $\epsilon_\nu^x$ are the total Born-Oppenheimer energies of $\phi_{s_0} x_\nu^0$ and $\phi_x x_\nu^x$, respectively. $\epsilon_\nu^0$ can be decomposed into the electronic energy at the minimum of the $S_0$ surface plus the $x_\nu^0$ internal energy ($\epsilon_\nu^0$)

$$\epsilon_\nu^0 = E_{s_0} (\text{min}) + e_\nu^0.$$  \hspace{1cm} (6.5)
An analogous expression can be written for $\varepsilon^x$:

$$\varepsilon^x = E_x (\text{min}) + \varepsilon^x$$  \hspace{1cm} (6.6)

where $E_x (\text{min})$ is the electronic energy at the minimum of the excited-state surface. $E_x (\text{min}) - E_{S0} (\text{min})$ gives the adiabatic electronic energy difference for the $S_0 \rightarrow X$ excitation; $\varepsilon^0$ and $\varepsilon^x$ are simply the vibration/rotation energies (labeled by the quantum number $v$) on the $S_0$ and $x$ surfaces, respectively.

In the approximation that the internal vibrations and rotations may be uncoupled, the functions $\chi^0_x$ and $\chi^x_x$ consist of products of appropriate rotational functions and of $3N - 6$ vibrational wavefunctions—one for each of the normal or local vibrational coordinates (Yardley, 1980) including the reaction coordinate $Q_r$. As pointed out in Chapter 1, motion along coordinates orthogonal to $Q_r$ can often be thought of as involving approximately harmonic vibration. However, the components of $\chi^0_x$ and $\chi^x_x$ that describe motion along $Q_r$ cannot be approximated by harmonic motion except near local minima. In regions of $Q_r$ space in which $S_0$ has negative curvature, the $Q_r$ component of $\chi^0_x$ looks like a continuum wavefunction rather than a bound vibrational wavefunction.

We now consider the transitions used when a molecule hops from $S_1$ or $T_1$ to $S_0$. The $S_1$ or $T_1$ state has been populated by the mechanism $S_0 + h\nu \rightarrow S_n \rightarrow (S_1, T_1)$. In the Born-Oppenheimer approximation, the wavefunction of this excited state is given by

$$\psi_x = \phi_x (r | R) \chi^x_x (R).$$  \hspace{1cm} (6.7)

The vibrational energy level $\varepsilon^x$ may be high or quite low (e.g., in condensed-phase situations). Although $\varepsilon^x$ also contains rotational and, perhaps, relative translational energy, we will, for brevity, speak of this energy as being vibrational. If the density of states (states per cm$^{-1}$ of energy) in the $S_0$ manifold is high at this energy level ($\varepsilon^x$), it is likely that there is a state of the $S_0$ manifold

$$\psi_0 = \phi_{S0} (r | R) \chi^0_x (R)$$  \hspace{1cm} (6.8)

that is nearly degenerate with $\psi_x$. These two zeroth-order states will be coupled by the terms in the true Hamiltonian that give rise to non-Born-Oppenheimer corrections. This coupling will be strong if the off-diagonal matrix elements $\langle \psi_x | H | \psi_0 \rangle$ are nonnegligible when compared to the energy difference $\varepsilon^x - \varepsilon^0$ (Yardley, 1980). Therefore, in this situation the non-Born-Oppenheimer coupling is said to give rise to transitions between $\psi_x$ and $\psi_0$, and these transitions are the hopping that has been discussed. If the excited state is a triplet, the non-Born-Oppenheimer terms alone would not couple $\psi_x$ and $\psi_0$; $H$ must
6.2. Rates of Transitions

To evaluate rates of such transitions, the conventional Fermi "golden rule" can be used (Yardley, 1980; Lin, 1980); this rule states that transitions starting in \( \phi_x \chi^0_x \) and going to \( \phi_s \chi^0_s \) and caused by the non-Born-Oppenheimer parts of \( H - h_e \) occur at a rate given in sec\(^{-1}\) by

\[
W = \frac{2\pi}{\hbar} \sum_v |\langle \phi_{s_0} \chi^0_{s_0} | H - h_e | \phi_x \chi^0_x \rangle|^2 \delta(\epsilon^0_v - \epsilon^0_s). \tag{6.9}
\]

The \( \delta \) function guarantees that the states \( \phi_{s_0} \chi^0_{s_0} \) contributing to the total radiationless transition rate have the same Born-Oppenheimer energy as \( \phi_x \chi^0_x \). When many vibrational or rotational modes are present, there may be many \( \chi^0_s \) functions, each having the same energy \( \epsilon^0_v \). The number of such states is referred to as the density of states \( \rho \) at this total energy \( \epsilon^0_v \)

\[
\rho(\epsilon^0_v) = \sum_v \delta(\epsilon^0_v - \epsilon^0_s). \tag{6.10}
\]

If there is reason to believe that all of the states \( \{ \phi_{s_0} \chi^0_{s_0} \} \) in this degenerate manifold couple to the same extent with the initial state \( \phi_x \chi^0_x \), then the sum over \( v \) in the above expression for \( W \) can be replaced by the appropriate state density

\[
W = \frac{2\pi}{\hbar} |\langle \phi_{s_0} \chi^0_{s_0} | H - h_e | \phi_x \chi^0_x \rangle|^2 \rho(\epsilon^0_v) \tag{6.11}
\]

in which \( \chi^0_x \) is any one of the degenerate states. Modern research on the behavior of electronically excited molecules indicates that, even for systems with high state densities, often only a small fraction of the modes play an active role in the radiationless transition. As a result, it may not be wise to use equation 6.11 when trying to understand radiationless transition rates; it is probably more appropriate to think in terms of equation 6.9.

**Internal Conversion Rates**

We now consider how equation 6.9 depends on the electronic energy difference and the vibrational wavefunctions \( \chi^0_x \) and \( \chi^0_s \) for the internal conversion case in which \( \phi_x \) is a singlet state. The terms in \( H - h_e \) that couple the initial state \( \phi_{s_1} \chi^0_{s_1} \) to the final state \( \phi_{s_0} \chi^0_{s_0} \) are the non-Born-Oppenheimer terms, and the off-diagonal coupling matrix element described in Chapter 1 is

\[
\langle \phi_{s_0} \chi^0_{s_0} | H - h_e | \phi_x \chi^0_x \rangle \quad \text{(6.12)}
\]
As discussed in Chapter 1, the second term in this expression is usually larger than the first (except when the second term vanishes, owing to symmetry); hence, the analysis will proceed using only this term. The analysis of the first term can be performed in analogous fashion (Berry, 1966); to do so would not shed further light on the physical origins of internal conversion.

An expression for the above coupling matrix element that is more physically useful can be obtained by applying the $D_R$ operator to the Born-Oppenheimer Schrödinger equation, which $\phi_s$, obeys:

$$D_R(h_c\phi_{S_1} - E_{S_1}\phi_{S_1}) = 0. \tag{6.13}$$

Multiplying on the left by $\phi_{S_0}$ and integrating over the electronic coordinates only yields

$$\langle \phi_{S_0} | D_R h_c | \phi_{S_1} \rangle + \langle \phi_{S_0} | h_c D_R \phi_{S_1} \rangle - D_R E_{S_1} \langle \phi_{S_0} | \phi_{S_1} \rangle - E_{S_1} \langle \phi_{S_0} | D_R \phi_{S_1} \rangle = 0. \tag{6.14}$$

Equation 6.14 can be solved for $\langle \phi_{S_1} | D_R \phi_{S_1} \rangle$, which can then be used to reexpress the coupling matrix element and, therefore, to write the transition rate as

$$W = \frac{2\pi}{\hbar} \sum \delta(\epsilon^0_{\nu} - \epsilon^0_{\nu'}) \left| \langle \chi^0_{\nu} | [E_{S_1} - E_{S_0}]^{-1} \langle \phi_{S_0} | D_R h_c | \phi_{S_1} \rangle \cdot 2D_R \chi^0_{\nu'} \rangle \right|^2 \tag{6.15}$$

This analysis shows that $W$ is likely to be large if regions of nuclear configuration space ($R$) exist for which the electronic energy gap is small ($E_{S_1}(R) \approx E_{S_0}(R)$) and the product $\chi^0(R)D_R \chi^0(R)$ is nonvanishing. Therefore, molecular deformations that bring the two singlet-state potential surfaces close to one another should be sought. If $\chi^0$ and $D_R \chi^0$ have appreciable overlap in the region in which $E_{S_0} \approx E_{S_1}$, then internal conversion is likely. However, the electronic force matrix element $\langle \phi_{S_0} | D_R h_c | \phi_{S_1} \rangle$ must also be substantial; this integral will be large if (in the orbital-following sense introduced in Chapter 4) the distortion tends to evolve the orbital structure of $\phi_{S_1}$ into that of $\phi_{S_0}$. Where symmetry is present, the direct product of the $S_0$ and $S_1$ symmetries must match that of $D_R h_c$. For example, in $H_2CO$, the $n\pi^*$ state is achieved by excitation from an occupied $b_2(n)$ orbital to the vacant $b_1(\pi^*)$ orbital. The kind of motion that is symmetry-consistent with $b_1 \times b_2$ is $a_2$. $H_2CO$ does not have any vibration with $a_2$ symmetry. As a result, the $\langle \phi_{S_0} | D_R h_c | \phi_{S_1} \rangle$ matrix element should be small for $n\pi^*$ states in $C_{2v}$ symmetry. In contrast, $\pi\pi^*$ $S_1$ states have $b_1 \times b_1 = a_1$ symmetry and, hence, $D_R$ can be $a_1$ because $S_1$ is also $a_1$. $H_2CO$ has these $a_1$ vibrations (symmetric CH
expected to have the largest effect on mapping the \( \pi^* \) orbital into the \( \pi \) orbital because the nature of these two orbitals is affected by the distance from C to O.

Let us review the procedure developed so far. If a coordinate exists along which \( E_{S_0} \) approaches \( E_{S_1} \), the hopping rate for internal conversion is increased. Near this avoided crossing or near approach of the \( S_0 \) and \( S_1 \) surfaces, one considers whether symmetry or physical force are likely to make \( \langle \phi_{S_0} | D_R h | \phi_{S_1} \rangle \) significant for deformations either along \( Q_r \) \((D_R = D_{Q_r})\) or along some direction perpendicular to \( Q_r \). Directions in which both this electronic force matrix element is large and the vibrational product \( \chi^*_0 D_R \chi^*_e \) is substantial will play important roles as modes that digest the excess electronic energy \( E_{S_0} - E_{S_1} \). That is, the direction along which \( E_{S_0} \) and \( E_{S_1} \) come close is important because this motion brings the molecule to the funnel geometry. Once the molecule is near the funnel, it can use other degrees of freedom (orthogonal to \( Q_r \)) to digest the excess electronic energy.

**Energy-Digesting Modes**

Two extreme cases of how the \( E_{S_0} \) and \( E_x \) surfaces might appear may be distinguished. The first case pertains to situations in which \( E_{S_0} \) and \( E_x \) do not approach one another closely—in other words, within an energy gap that is approximately equal to a non-Born-Oppenheimer matrix element. The shapes of two such surfaces are shown in Figure 6-1. Efficient internal conversion may still be possible by transfer of electronic energy to internal vibrational energy. To analyze the rates of such processes in this case, note first that the energy-denominator factor in equation 6.15—\( |E_{S_0}(Q) - E_{S_1}(Q)|^{-1} \)—is small and never undergoes rapid growth near some critical geometry as it would, for example, in the near-crossing situations (a second special case that will be treated shortly). Therefore, \( E_{S_0} - E_{S_1} \) is approximated as a part that depends on the reaction coordinate \( Q_r \), plus a part that describes the (approximately harmonic) motion perpendicular to \( Q_r \):}

![Figure 6-1](https://via.placeholder.com/150)  
*Energy surfaces that do not approach closely.*
Furthermore, the shapes of $E_{S_0}(R)$ and $E_{S_1}(R)$ are assumed to be sufficiently similar that $E_{S_0}(R) - E_{S_1}(R)$ can be neglected relative to the presumed large value of $E_{S_0}(Q_r) - E_{S_1}(Q_r)$ splitting.

To continue the analysis, two additional assumptions are made: (1) Only one mode, whose spatial coordinate is $R_a$, plays an active role as an energy acceptor (Yardley, 1980). (2) In the initial $S_1$ state, the active mode is in its $\nu' = 0$ level. Assumption 2 is by no means fully justified or even necessary. In condensed media situations, it might be more justified, since vibrational energy would probably have been dissipated to the surroundings prior to the internal conversion process. This assumption is made only so the resulting integral containing $x^0_a(R_a)$ and $D_{R_a}x^\pm_a(R_a)$ can be physically interpreted more easily. We will then argue that essentially the same physical picture would be obtained, after more tedious algebraic manipulation, if the more general ($\nu' \neq 0$) case were analyzed (see Yardley, 1980). Under the above outlined limitations, the rate expression (equation 6.15) becomes

$$W = \frac{2\pi}{\hbar} \sum_\nu \delta(\epsilon^0_\nu - \epsilon^\pm_\nu) \langle \chi^0_\nu(Q_r)|E_{S_0}(Q_r) - E_{S_1}(Q_r)|^{-1}\chi^\pm_\nu(Q_r)\rangle$$

$$\left( \prod_{b \neq a} \langle \chi^0_{\nu_b}|\chi^\pm_{\nu_b}\rangle \right) \langle \phi_{S_0}|D_{R_a}h_e|\phi_{S_1}\rangle_{eq} 2\langle \chi^0_{\nu_a}|D_{R_a}|\chi^\pm_{\nu_a}\rangle|^2.$$  (6.17)

Here the product $\Pi_b$ extends over all modes other than $Q_r$ and the active $R_a$ and gives rise to simple Franck-Condon overlap factors for the passive modes. If these modes are fully passive, then the shapes of the $S_0$ and $S_1$ surfaces along these directions should be identical, in which case the $\langle \chi^0_{\nu_b}|\chi^\pm_{\nu_b}\rangle$ overlap factors would reduce to products of simple $\delta$-functions $\Pi_b \delta_{\nu_b \nu_b}$. In writing the above expression for $W$, we assumed that the electronic force matrix element is rather insensitive to $R_a$. Consequently, $\langle \phi_{S_0}|D_{R_a}h_e|\phi_{S_1}\rangle_{eq}$ was evaluated at the equilibrium value of the $S_1$ state of $R_a (R_a = R_{a0}^0)$, which was denoted by the subscript "eq" in this integral. The vibrational quantum numbers appearing in $\epsilon^0_\nu$ and $\epsilon^\pm_\nu$ are underlined because they contain the quantum numbers of all modes (for example, $\nu = \nu_{Q_r}, \nu_a, \nu_b; b = 1 \ldots$).

With all of these observations, $W$ reduces to

$$W = \frac{2\pi}{\hbar} \sum_{\nu_a \nu_r \nu_r} \delta(\epsilon^0_{\nu_a} + E_{S_0}(\text{min}) + \epsilon^0_{\nu_r} - \epsilon^\pm_{\nu_a} - E_{S_1}(\text{min}) - \epsilon^\pm_{\nu_r})$$

$$\left| \langle \chi^0_{\nu_r}(Q_r)|E_{S_0}(Q_r) - E_{S_1}(Q_r)|^{-1}\chi^\pm_{\nu_r}(Q_r)\rangle \right|^2$$
in which $e_r^0$ and $e_r^x$ are the internal energies in the $Q_r$ mode in the two states. The energy-conservation $\delta$-function requires that the excess energy

$$E_{s_0}(\text{min}) - E_{s_1}(\text{min}) + e_r^0 - e_r^x = \Delta E_r,$$

which is equal to an adiabatic electronic energy difference plus the amount of energy along $Q_r$ that has to be "digested," is balanced by the change in vibrational energy of the energy-accepting mode. This modified energy gap is shown in Figure 6-2.

If $x_{v_0}^0$ and $x_{v_0}^x$ are approximated by simple harmonic oscillator functions having identical frequencies $\omega$ but equilibrium bond lengths that differ by $\Delta R_a$, the evaluation of the $\langle x_{v_0}^0 | D_{R_a} | x_{v_0}^x \rangle$ integral is straightforward. For the case of $v_0' = 0$ (Yardley, 1980)

$$\langle x_{v_0}^0 | D_{R_a} | x_{v_0}^x \rangle = \sqrt{\frac{\omega}{\hbar}} \left[ \sqrt{\frac{v_0}{2}} \left( -\sqrt{X} \right)^{v_a-1}((v_a - 1)!)^{-1/2} 

- \frac{v_a + 1}{2} \left( -\sqrt{X} \right)^{v_a+1}((v_a + 1)!)^{-1/2} \right] \exp \left( -X/2 \right) \tag{6.19}$$

is obtained, in which $X = \omega/(2\hbar)\Delta R^2$. Substitution of this result into equa-
\[ W = \frac{4\pi\omega}{\hbar^2} \sum_{\nu,\nu'} |\langle \phi_{S_0} | D_{R_s} \phi_{S_1} \rangle_{eq}|^2 \]

\[ |\langle \chi_{\nu'}^0(Q_r) | E_{S_0}(Q_r) - E_{S_1}(Q_r) \rangle|^{-1} \chi_{\nu'}^0(Q_r) \rangle|^2 \]

\[ e^{-x} \frac{\Delta E_r^2}{2\pi\hbar\omega(\Delta E_r - \hbar\omega)} \]

\[ \exp \left[ - \frac{\Delta E_r - \hbar\omega}{\hbar\omega} \left( \ln \left( \frac{\Delta E_r - \hbar\omega}{\hbar\omega} \right) - 1 \right) \right] \]  

(6.20)

in which \( \Delta E_r \) is the excess energy or gap defined earlier.

Notice that \( \Delta E_r \) depends upon \( e_{\nu_r}^0 - e_{\nu_r}^1 \), the energy change along the mode \( Q_r \). Since for this special case \( E_{S_0}(Q_r) - E_{S_1}(Q_r) \) does not become small for any value of \( Q_r \), the element \( \langle \chi_{\nu_r}^0 | (E_{S_0} - E_{S_1})^{-1} \chi_{\nu_r}^0 \rangle \) is likely to be small unless \( \chi_{\nu_r}^0 \) and \( \chi_{\nu_r}^1 \) have very similar shapes. This will not be the case if \( \Delta E_r \equiv 0 \), since then \( \chi_{\nu_r}^0 \) would correspond to a wave packet having high kinetic energy and a short de Broglie wavelength (as in Figure 6-2). This function could have little overlap with any low-energy \( \chi_{\nu_r}^1 \). Hence, the dominant contribution is for \( \nu_r' = 0 \) and small \( \nu_r \), and therefore it is reasonable to set \( \nu_r' = \nu_r = 0 \) in equation 6.20.

Notice that equation 6.20 leads to the conclusion that high frequency vibrational modes should be most effective in digesting the excess energy. For such modes, \( (\Delta E_r - \hbar\omega)/\hbar\omega \) is as small as possible. The exponential dependence of \( W \) on the energy gap \( \Delta E_r \) is thought to give rise to the observations leading to the Kasha rule. For most molecules the \( S_0 - S_1 \) spacing (near the \( S_0 \) equilibrium geometry populated in the Franck-Condon absorption process) is larger than the \( S_1 - S_2, S_2 - S_3, \ldots \) splittings. Hence, internal conversion from \( S_1 \) to \( S_0 \) is slower than between higher states, since \( \Delta E_r \) is larger for the \( S_1 \rightarrow S_0 \) transition.

Equation 6.20 also shows that if experimentally one desired to modify the rate of internal conversion by isotopic substitution, the high frequency variations should be modified. For example, substitution of deuterium for hydrogen should produce substantial changes in the rate of internal conversion.

In the other extreme case (see Figure 6-3) in which \( E_{S_0}(Q_r) - E_{S_1}(Q_r) \) becomes small along \( Q_r \) (of the order of magnitude of the non-Born-Oppenheimer matrix elements), we assume for motion along directions perpendicular to \( Q_r \) that \( E_{S_0} - E_{S_1} \) can be written as two components—one consisting of motion along \( Q_r \) and a second comprised of harmonic segments (having the same geometries and frequencies). These harmonic potentials are assumed to be identical on \( S_0 \) and \( S_1 \) and, hence, cancel yielding

\[ E_{\nu} - E_{\nu'} \approx E_{\nu}(Q_r) - E_{\nu'}(Q_r) \]  

(6.21)
In this case, $Q_r$ itself is the energy-digesting mode.

The treatment in this section of the special case in which $E_{S_0}$ and $E_{S_1}$ do not approach closely can also be made for this case in Figure 6-3 to the point at which

$$ W = \frac{2\pi}{\hbar} \sum_{v_r} \delta(E_{S_0}(min) + e^0_{v_r} - E_{S_1}(min) - e^*_{v_r}) $$

$$ 4|\langle x^0_{v_r}(E_{S_0}(Q_r) - E_{S_1}(Q_r))^{-1} \langle \phi_{S_0, h_e} | \phi_{S_1, h_e} | D_{Q_r} \langle x^*_{v_r} | x^*_{v_r} \rangle |^2 \) (6.22)$$

Because $(E_{S_0} - E_{S_1})^{-1}$ enhances contributions to the integral over $Q_r$ near the point of closest-approach $Q^c$, the electronic force matrix element and the energy difference can be approximated by their values at $Q^c$ to obtain

$$ W = \frac{8\pi}{\hbar} \sum_{v_r} \delta(E_{S_0}(min) + e^0_{v_r} - E_{S_1}(min) - e^*_{v_r}) $$

$$ |[E_{S_0}(Q^c) - E_{S_1}(Q^c)]^{-2} |\langle \phi_{S_0, h_e} | D_{Q_r} \langle x^*_{v_r} | x^*_{v_r} \rangle |^2 \langle x^0_{v_r} | D_{Q_r} \langle x^0_{v_r} | x^*_{v_r} \rangle |^2 \) (6.23)$$

Unfortunately, an energy-gap law is not easily obtained for this case because the $\langle x^0_{v_r} | D_{Q_r} \langle x^*_{v_r} \rangle$ integral does not include two bound harmonic oscillator functions; $x^0_{v_r}$ describes free (unbound) motion along the $S_0$ surface. However, transitions will be favored if the electronic energy gap $E_{S_0}(Q^c) - E_{S_1}(Q^c)$ is small and the electronic-force matrix element is large. Moreover, the kinetic energy of motion along $Q_r$ in the product $S_0$ state is $E_{S_1}(min) + e^*_{v_r} - E_{S_0}(Q^c)$, at $Q = Q^c$.

**The Landau-Zener Point of View**

Before discussing the rates of intersystem crossing, it is useful to point out the
looking at rates of surface hopping (Eyring, Walter, and Kimball, 1944), a method that pertains only to the second case treated above (the close approach of $S_0$ and $S_1$ depicted in Figure 6-3). In the Landau-Zener approach the near crossing of the $S_0$ and $S_1$ surfaces is parameterized by the slopes ($f_0$ and $f_1$) of the surfaces near their avoided crossing and the closest-approach energy $2\varepsilon_{10} = 2(E_{S_1}(Q_r) - E_{S_0}(Q_r))$. The probability of a surface hop (per vibration along $Q_r$, as dictated by $x_{\phi_r}$) is then expressed as

$$P = 1 - \exp\left[-(4\pi^2\varepsilon_{10}^2/hv|f_0 - f_1|)^{-1}\right]$$

(6.24)

in which $v$ is the velocity of the nuclei as they pass through the avoided-crossing region. The dependence of $P$ on the vibrational level ($x_{\phi_r}$) of the initial $S_1$ state comes from this velocity—if $v$ is large, the velocity is high. Equation 6.24 shows that three things—a close approach (small $\varepsilon_{10}$), fast-moving nuclei (high frequency vibration), and a small difference in slope (small change in force)—favor surface hopping. This influence of the change in slope (which is the change in the forces felt by the nuclear framework of the molecule along the $Q_r$ direction) is obscured somewhat in the earlier expression for $W$ (equation 6.23). This force effect is contained in the $x_{\phi_r}(Q_r)D_{Q_r}x_{\phi_r}(Q_r)$ factor. If $S_0$ and $S_1$ have very different slopes near $Q_r$, the wavefunctions $x_{\phi_r}$ and $x_{\phi_r}$ will have greatly different local de Broglie wavelengths in this region, and $x_{\phi_r}$ and $x_{\phi_r}$ are not likely to have large local overlap. In contrast, similar slopes of $S_0$ and $S_1$ near $Q_r$ will lead to large overlap of $x_{\phi_r}$ and $x_{\phi_r}$ (i.e., similar shapes in $x_{\phi_r}$ and $x_{\phi_r}$).

### 6.3. Intersystem Crossing Rates

In intersystem crossing rates the electronic wavefunctions $\phi_0$ and $\phi_x$ are singlet and triplet, respectively. However, the spin-orbital operator

$$h_{SO} = \frac{e^2\hbar}{2m^2c^2} \left\{ \sum_{\alpha} Z_{\alpha} (r_{i\alpha} \times P_i) \cdot S_i + \sum_{i \neq j} \left[ \frac{(2P_j - P_i) \times r_{ij}}{r_{ij}^3} \right] \cdot S_i \right\}$$

(6.25)

couples $\phi_0$ and $\phi_x$ to give perturbed wavefunctions $\tilde{\phi}_0$ and $\tilde{\phi}_x$ that contain both singlet and triplet components. Intersystem crossing is viewed as occurring between these perturbed functions by a mechanism similar to that just discussed for internal conversion. The perturbed electronic wavefunctions are approximated by

$$\tilde{\phi}_{S_0} = \phi_{S_0} + \langle \phi_{S_0} | h_{SO} | \phi_{T_1} \rangle (E_{S_0} - E_{T_1})^{-1} \phi_{T_1}$$

(6.26)
and

$$\Phi_{T_1} = \Phi_{T_1} + \langle \Phi_{T_1} | h_{SO} | \phi_{S_0} \rangle (E_{T_1} - E_{S_0})^{-1} \phi_{S_0}$$  \hspace{1cm} (6.27)$$

(Eyring, Walter, and Kimball, 1944; Pilar, 1968). These functions can now be used in the Fermi golden-rule formula to evaluate $W$ for intersystem crossing. In doing so, the electronic-force matrix element (or even the second non-Born-Oppenheimer factor $\langle \phi_{S_0} | D_{Q} h_{e} | \phi_{T_1} \rangle$ that was not analyzed earlier) is modified because $\Phi_{S_0}$ and $\Phi_{T_1}$ are now of mixed spin character:

$$\langle \phi_{S_0} | D_{Q} h_{e} | \phi_{T_1} \rangle = \langle \phi_{S_0} | D_{Q} h_{e} | \phi_{T_1} \rangle$$

$$+ \langle \phi_{S_0} | D_{Q} h_{e} | \phi_{S_0} \rangle \langle \phi_{T_1} | h_{SO} | \phi_{S_0} \rangle (E_{T_1} - E_{S_0})^{-1}$$

$$+ \langle \phi_{S_0} | h_{SO} | \phi_{T_1} \rangle \langle \phi_{T_1} | D_{Q} h_{e} | \phi_{T_1} \rangle (E_{S_0} - E_{T_1})^{-1}$$

$$+ \text{terms second order in } h_{SO}.$$  \hspace{1cm} (6.28)$$

The first term vanishes because of spin orthogonality since $D_{Q} h_{e}$ contains no spin-dependent terms. The other two terms contain electronic-force expectation values, $E_{S_0} - E_{T_1}$ energy denominators, and spin-orbit matrix elements. When squared and substituted into the expression for $W$ (equation 6.23), these integrals give an expression for the rate of intersystem crossing. The treatment of digesting modes other than $Q_r$ (if $S_0$ and $T_1$ remain far apart) and the treatment of the case of $Q_r$ accepting the excess energy (when $S_0$ and $T_1$ cross or come very close) proceed in the same way as that for intersystem crossing; therefore, we need not repeat the analysis of the dependence of this radiationless rate on the energy gap, accepting-mode frequencies, and so forth.

The primary difference between the expressions for internal conversion ($W_{IC}$) and intersystem crossing ($W_{ISC}$) is contained in the spin-orbit integrals $\langle \phi_{S_0} | h_{SO} | \phi_{T_1} \rangle$ whose squares enter into $W_{ISC}$. These integrals require further discussion (Turro, 1978). The spin-orbit operator $h_{SO}$ consists of the dot product ($L_{+} S_{+} + L_{-} S_{-} + 2L_{z} S_{z}$) of a spatial electronic angular-momentum operator and an electric spin operator. Clearly, it is the spin-operator components ($S_{+}, S_{-}$, but not $S_{z}$) that map the triplet spin function into the singlet spin function in the $\langle \phi_{S_0} | h_{SO} | \phi_{T_1} \rangle$ integral. When operating on $\phi_{T_1}$, the corresponding spatial angular-momentum operator components can alter the angular characteristics of the spatial wavefunction in $\phi_{T_1}$. More specifically, since the components $L_{x}, L_{y}, L_{z}$ (or $L_{+}, L_{-}, L_{z}$) of the angular-momentum operator transform like rotation operators under point-group symmetry (see Appendix C or Cotton, 1963), the direct product of the spatial symmetries of $\phi_{S_0}$ and $\phi_{T_1}$ must match that of
at least one of the components $L_x$, $L_y$ or $L_z$ for the spin-orbit matrix element to be nonvanishing. This is another important factor to keep in mind when deciding when intersystem crossing is likely to occur. For example, in H$_2$CO, the intersystem crossing transitions $(\pi\pi^*)^1 \rightarrow (n\pi^*)^3$ or $(n\pi^*)^3 \rightarrow n^2$ are spin-orbit favored because they utilize transitions between $\pi(b_1)$ and $n(b_2)$ orbitals or $\pi^*(b_1)$ and $n(b_2)$ orbitals whose direct product $a_2$ has the symmetry of a rotation about the symmetry axis of the molecule. Pictorially, this is represented by noting that a 90° rotation of the $n(b_2)$ orbital maps it into a $\pi$-like $b_1$ orbital. Likewise, the intersystem crossing rates $(\pi\pi^*)^1 \rightarrow (\pi\pi^*)^3$ and $(n\pi^*)^1 \rightarrow (n\pi^*)^3$ should be smaller because they are forbidden by first-order perturbation analysis—that is, the molecule has no rotation having $b_1 \times b_1 = a_1$ or $b_2 \times b_2 = a_1$ symmetry.

In the Landau-Zener method, which applies only to two surfaces ($T_1$ and $S_0$) that intersect or approach closely, the probability of intersystem crossing is given as before (equation 6.24) except that now the energy splitting $2\epsilon_{01}$ is caused by the spin-orbit coupling and is given by

$$\epsilon_{01} = \langle \phi_{S_0} | h_{SO} | \phi_{T_1} \rangle_{Q^2}. \quad (6.29)$$

Hence, the same conditions that favor internal conversion also favor intersystem crossing, except that the rate of intersystem crossing also includes the spin-orbit matrix element in a multiplicative manner. This element will be small unless heavy atoms are present and the two states can be connected by any of $L_x$, $L_y$, or $L_z$. 