Herschbach Notes
on Molecular Collisions

2.0 Archtypical Inelastic Collisions

A. Electronically Inelastic Collisions: Curve Crossing

B. Vibrationally Inelastic Collisions: Impulsive Energy Transfer
Electronically Inelastic Collisions: Curve Crossing

Typically, at thermal collision energies molecular collision processes take place on a potential energy surface for a particular electronic state. This holds when surfaces corresponding to different electronic states are widely separated in energy (compared with the collision energy), so the Born-Oppenheimer approximation holds well throughout and the nuclear and electronic motion can be treated separately. However, for many systems the potential energy curves or surfaces for different electronic states come close together. Electronically inelastic transitions can then occur even at modest collision energies. These involve a transfer of the nuclear motion from one potential energy surface to another. To treat such nonadiabatic nuclear motion, we must go beyond the B-O approximation by including the coupling of electronic states by the nuclear momenta operators. Here, after some qualitative preliminary comments, we shall derive the Landau-Zener approximation for the probability of transition between a pair of electronic potential curves that "cross" in zeroth-order.

From the uncertainty principle, the time required to distinguish between a pair of electronic states separated by $\Delta E$ is of the order $\tau = h/\Delta E$. For instance, this is 4 femtoseconds ($1 \text{ fsec} = 10^{-15} \text{ sec}$) for $\Delta E = 1 \text{ eV}$. If the collision time is much longer than $\tau$, the dynamics will be almost entirely adiabatic; the system will remain almost solely on one or the other surface throughout the collision. If the collision duration is much less than $\tau$, however, the process will be mostly nonadiabatic; the adiabatic surfaces then have no special significance for the nuclear motion. For example, for a pair of H atoms colliding at 10 eV and interacting over a range of 4 Å the collision time is about 10 fs. Thus, even in such a hyperthermal collision, nonadiabatic transitions will be improbable for electronic surfaces separated by more than 1 eV.

If $L$ is the length of the interaction region, which is crossed with relative velocity $v$, the collision time is of the order $L/v$. Thus the ratio of this time to $\tau$ is given by $L\Delta E/hv$; this is often called the Massey parameter. Only when this ratio is small, corresponding to an impulsive interaction, will transitions become highly probable.

Curve-Crossing. The "crossing" of ionic and covalent potential curves for alkali halide molecules, illustrated in Fig. 1, is the prototype case for transitions between potential curves of different electronic states. The solid curves represent the adiabatic potentials, denoted here by $E_{\pm}$,
that correspond to eigenfunctions $\psi_\pm$ which diagonalize the electronic Hamiltonian, $\mathbf{H}$. The dashed curves labelled $H_{ii}$ and $H_{cc}$ correspond, respectively, to the diatomic "zeroth-order" potentials. These arise from ion-pair and covalent functions, $\phi_i$ and $\phi_c$, that serve as basis states for computing matrix elements of the Hamiltonian; since $\mathbf{H}$ is not diagonal in this basis there is an off-diagonal element $H_{ic}$ that represents coupling between the ionic and covalent configurations. Asymptotically, at large internuclear distances $r$, $E_+$ and $H_{ii}$ correlate with the ion-pair configuration, $M^+ + X^-$, and $E_-$ and $H_{cc}$ correlate with the homopolar or covalent configuration, $M + X$. In the asymptotic region, the ion-pair energy is higher than the covalent energy by $\Delta = \text{IP}(M) - \text{EA}(X)$, the difference between the ionization potential of the alkali metal and the electron affinity of the halogen. However, because of the Coulombic attraction between the ions, as $r$ decreases the $H_{ii}$ potential curve drops rapidly, crosses $H_{cc}$ at some distance $r_X$, and descends further below to make the ionic configuration dominant at the equilibrium internuclear distance of the molecule. Since for alkali halides the crossing radius $r_X$ is quite large (in the range 6-18 Å), the covalent potential $H_{cc}$ is still quite flat at that distance. Hence the crossing radius can be found from $e^2/r_X = \Delta$, simply equating the attractive Coulombic energy attained at the crossing to that required to form the ion-pair.

If for simplicity we neglect the nonorthogonality of $\phi_i$ and $\phi_c$, in the region near the crossing (not a bad approximation since $r_X$ is large), the adiabatic potentials are related to the diabatic zeroth order ones by

$$E_\pm = \frac{1}{2} \left( H_{ii} + H_{cc} \right) \pm \frac{1}{2} \left[ \left| H_{ii} - H_{cc} \right| + \frac{4}{|H_{ic}|^2} \right]^{1/2}$$

(1)

Evident here is the "non-crossing rule," which states that for a diatomic molecule potential curves of the same symmetry cannot cross. If the zeroth order states (and hence the adiabatic ones too) have the same symmetry, then $H_{ic}$ cannot vanish except perhaps at a particular $r$. Therefore, since the separation between the $E_\pm(r)$ curves depends on both $H_{ii} - H_{cc}$ and $H_{ic}$, both of which in general will not vanish at the same $r$, the adiabatic curves will never intersect. Their closest approach will occur at the crossing radius of the zeroth order curves, where

$$E_\pm(r_X) = \pm H_{ic}(r_X) \quad \text{since there} \quad H_{ii}(r_X) = H_{cc}(r_X)$$

(2)

Thus the separation of the adiabatic curves at the crossing point is given by $\Delta E(r_X) = 2H_{ic}(r_X)$. According to the Landau-Zener approximation, the
probability of a transition from $E_-$ to $E_+$ or vice versa in a collision traversing $r_X$ with relative velocity $v$ is given by

$$ P = e^{-2\pi \Gamma}, \quad \text{with} \quad \Gamma = \frac{|\hat{H}_{ic}|^2}{\hat{H}_{ic} \left[ \frac{\partial \hat{H}_{ii}}{\partial r} - \frac{\partial \hat{H}_{cc}}{\partial r} \right]} $$  \hspace{1cm} (3)

This depends on the energy separation of the adiabatic curves at $r_X$, the difference in slopes of the diabatic curves there, and the collision velocity. Note that $\Gamma$ is just the Massey parameter with an effective interaction length given by

$$ L = \frac{|\hat{H}_{ic}|}{2\left| \frac{\partial \hat{H}_{ii}}{\partial r} - \frac{\partial \hat{H}_{cc}}{\partial r} \right|} $$ \hspace{1cm} (4)

In effect, if the electron transfer that switches between the ionic and covalent configurations occurs, it does so in a region of length $L$ in the neighborhood of $r_X$. Since the probability that a transition does not occur is $1 - P$, and the crossing region is traversed on both the incoming and outgoing portion of the collision trajectory, the net probability that electron transfer occurs is given by:

$$ P(1 - P) + (1 - P)P = 2P(1 - P), $$ \hspace{1cm} (5)

corresponding to (yes in)(no out) + (no in)(yes out).

**Landau-Zener Derivation.** Many variants of the derivation can be found in the literature; we consider a simple one that serves to exhibit the essential features. Generalizing slightly the notation, we label the zeroth order basis states 1 and 2 (rather than $i$ and $c$). Then the wavefunction can be written as

$$ \psi(r, t) = c_1(t) \exp(H_{11}t/\hbar)\phi_1(r) + c_2(t) \exp(H_{22}t/\hbar)\phi_2(r) $$ \hspace{1cm} (6)

At any time $t$, there are $|c_1(t)|^2$ systems in the state $\phi_1$ and $|c_2(t)|^2$ in the state $\phi_2$. On substituting this into the time-dependent Schrödinger equation, $\hat{H}\psi = (\hbar/\imath)\partial\psi/\partial t$, we obtain a pair of first-order coupled equations,

$$ \begin{align*}
\dot{c}_1 &= \frac{i}{\hbar} H_{12} c_2 - \frac{1}{\hbar} (H_{11} - H_{22}) \frac{\dot{c}_1}{\dot{t}} \\
\dot{c}_2 &= \frac{i}{\hbar} H_{12} c_1 - \frac{1}{\hbar} (H_{11} - H_{22}) \frac{\dot{c}_2}{\dot{t}}
\end{align*} $$ \hspace{1cm} (7)

These must be solved simultaneously subject to the boundary conditions specifying that the system is initially in $\phi_2$: 
\[ c_1(-\infty) = 0 \text{ and } |c_2(-\infty)| = 1 \]  

(8)

The probability we wish to evaluate is then given by

\[ P = |c_2(\infty)|^2 = 1 - |c_1(\infty)|^2 \]  

(9)

Note that this is the probability that the system, having started in \( \phi_2 \), is still in \( \phi_2 \) after traversing \( r_X \); that means that a transition will have occurred between the adiabatic curves. The coupled equations (7) need be solved only for asymptotic values of \( c_1 \) and \( c_2 \). On eliminating \( c_2 \), we obtain a second order equation,

\[ \dot{c}_1 + \frac{\bar{t}}{\hbar} (H_{11} - H_{22}) - \frac{i}{\hbar} \frac{\partial H_{12}}{\partial t} c_1 + \frac{(H_{12})^2}{\hbar} c_1 = 0 \]  

(10)

The key Landau-Zener approximations are now introduced:

(a) the interaction matrix element \( H_{12}(r_X) \) at the crossing radius is assumed to be much smaller than the relative kinetic energy;

(b) the transition region is assumed short enough so that we may regard \( H_{11} - H_{22} \) as a simply proportional to the the time, \( \alpha t \), and take \( H_{12} \) as constant in the region near \( r_X \) where transitions occur.

With these approximations and the substitutions

\[ f = H_{12}/\hbar \quad \text{and} \quad c_1 = \text{Uexp}[-i(H_{11} - H_{22})t/\hbar] \]

Eq.(10) is reduced to a known form, the Weber equation,

\[ \ddot{u} + \left( f^2 - \frac{i\alpha}{2} + \frac{\alpha^2 t^2}{4} \right) u = 0 \]  

(11)

and the solution subject to the boundary conditions gives for the asymptotic value of \( |c_1(\infty)|^2 \) the result \( 1 - \exp(-2\pi\Gamma) \) and hence yields the Landau-Zener formula.

**Energy Separation at the Crossing Point.** According to the L–Z approximation, the transition probability is an exponential function of the square of \( \Delta E(r_X) = 2H_{12}(r_X) \), the separation between the adiabatic
curves at the crossing radius of the diabatic zeroth order curves. Particularly when \( r_X \) is large, \( \Delta E \) can often be determined fairly well from either theoretical or experimental data. This is nicely exemplified by the long-range ionic-covalent interactions in alkali halides and alkali hydrides. As seen in Fig. 2, for these systems \( \Delta E \) is simply a decreasing exponential function of the crossing radius. The data shown were computed by Grice (1974) using simple asymptotic wavefunctions. Good agreement was found with values of \( \Delta E \) derived from spectroscopic potential-curves for an excited state of \( \text{H}_2 \) which corresponds to curve crossing of \( \text{H}^*(2s,2p) + \text{H}(1s) \) and \( \text{H}^+ + \text{H}^- \), and similar experimental results for \( \text{LiH}, \text{KH}, \) and \( \text{RbH} \).

In deriving these \( \Delta E \) values, it is necessary to take into account the nonorthogonality of the basis functions (neglected above and in almost all accounts of curve-crossing). On solving the \( 2 \times 2 \) secular equation including the overlap integral, \( S = \langle \phi_i | \phi_C \rangle \) we find the separation of the adiabatic curves \( E_\pm \) at the crossing radius is given by

\[
\Delta E(r_X) = 2(H_{ij}S - H_{iC})/(1 - S^2)
\]  

(12)

Also, it is easy to show that in terms of the adiabatic curves this separation is given by

\[
\Delta E(r_X) = \pm 2E_\pm(r_X)/(1 \pm S)
\]  

(13)

if the zero of energy is chosen such that \( H_{CC} = 0 \) as \( r \to \infty \). When spectroscopic data permit, the requisite \( E_\pm(r_X) \) values can be obtained from Rydberg-Klein-Rees curves determined directly from vibrational and rotational level spacings.

References

Fig. 1 Potential energy curves for LiI. Dashed lines indicate "zeroth-order" ionic & covalent states which intersect at $R_c$. Solid lines denote adiabatic potential curves.
Fig. 2. Reduced variable plot of the ratio of adiabatic splitting to crossing radius versus crossing radius. From Mol. Phys. 27, 159 (1974).

\[ V^*(R_c) = \left( \frac{2}{V^2} \right) \Delta V(R_c) \]

\[ R_c^* = \frac{1}{2} \left( \gamma + \psi \right) R_c \]

where \( \gamma = (2E)^{1/2} \), \( E = \text{electron affinity} \)