

16.2: Multichannel Problems

When excited electronic states are involved, couplings between two or more electronic surfaces may arise. Dynamics occurring on an excited-state surface may evolve in a way that produces flux on another surface. For example, collisions between an electronically excited $1s2s(^3S)$ He atom and a ground-state $1s^2(^1S)$ He atom occur on a potential energy surface that is repulsive at large R (due to the repulsive interaction between the closed-shell $1s^2$ He and the large $2s$ orbital) but attractive at smaller R (due to the $\sigma^2\sigma^{*1}$ orbital occupancy arising from the three $1s$ -derived electrons). The ground-state potential energy surface for this system (pertaining to two $1s^2(^1S)$ He atoms) is repulsive at small R values (because of the $\sigma^2\sigma^{*2}$ nature of the electronic state). In this case, there are two Born-Oppenheimer electronic-nuclear motion states that are degenerate and thus need to be combined to achieve a proper description of the dynamics:

$$\Psi_1 = |\sigma^2\sigma^{*2}|\Psi_{\text{ground.}}(R, \theta, \phi)$$

pertaining to the ground electronic state and the scattering state $\Psi_{\text{ground.}}$ on this energy surface, and

$$\Psi_2 = |\sigma^2\sigma^{*1}2\sigma^1|\Psi_{\text{ex.}}(R, \theta, \phi)$$

pertaining to the excited electronic state and the nuclear-motion state $\Psi_{\text{ex.}}$ on this energy surface. Both of these wavefunctions can have the same energy E ; the former has high nuclear-motion energy and low electronic energy, while the latter has higher electronic energy and lower nuclear-motion energy.

A simple model that can be used to illustrate the two-state couplings that arise in such cases is introduced through the two one-dimensional piecewise potential surfaces shown below.

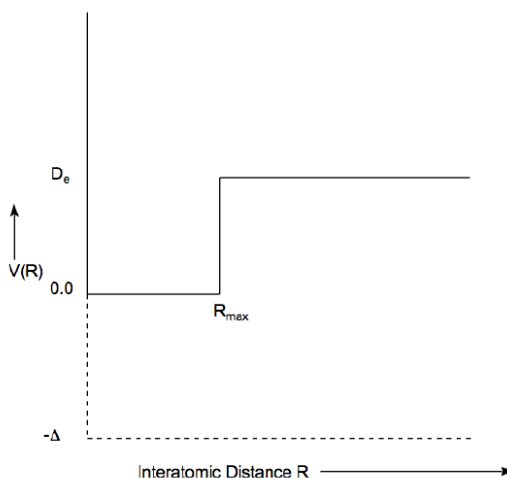


Figure 16.2.1: Insert Caption here!

The dashed energy surface

$$V(R) = -\Delta \text{ for } 0 \leq R < \infty$$

provides a simple representation of a repulsive lower-energy surface, and the solid-line plot represents the excited-state surface that has a well of depth D_e and whose well lies Δ above the ground-state surface.

In this case, and for energies lying above zero (for $E < 0$, only nuclear motion on the lower energy dashed surface is "open" (i.e., accessible)) yet below D_e , the nuclear motion wavefunction can have amplitudes belonging to both surfaces. That is, the total (electronic and nuclear) wavefunction consists of two portions that can be written as:

$$\Psi = A\phi\sin(kR) + \phi''A''\sin(k''R) \text{ (for } 0 \leq R \leq R_{\text{max}})$$

and

$$\Psi = A\phi\sin(kR_{\text{max}})e^{\kappa R_{\text{max}}}e^{-\kappa R} + \phi''A''\sin(k''R) \text{ (for } R_{\text{max}} \leq R < \infty),$$

where ϕ and ϕ'' denote the electronic functions belonging to the upper and lower energy surfaces, respectively. The wavenumbers k and k'' are defined as:

$$k = \sqrt{\frac{2\mu E}{\hbar^2}}$$

$$k'' = \sqrt{\frac{2\mu(E + \Delta)}{\hbar^2}}$$

and κ is as before

$$\kappa = \sqrt{\frac{2\mu(D_e - E)}{\hbar^2}}.$$

For the lower-energy surface, only the $\sin(k''R)$ function is allowed because the $\cos(k''R)$ function does not vanish at $R=0$.

The Coupled Channel Equations

In such cases, the relative amplitudes (A and A'') of the nuclear motion wavefunctions on each surface must be determined by substituting the above "two-channel" wavefunction (the word channel is used to denote separate asymptotic states of the system; in this case, the ϕ and ϕ'' electronic states) into the full Schrödinger equation. In Chapter 3, the couplings among Born-Oppenheimer states were so treated and resulted in the following equation:

$$[(E_j(R) - E)\Xi_j(R) + T\Xi_j(R)] = - \sum_i \left[\langle \Psi_j | T | \Psi_i \rangle (R) \Xi_i(R) + \sum_{a=1, M} \left(\frac{-\hbar^2}{m_a} \right) \langle \Psi_j | \nabla_a | \Psi_i \rangle (R) \cdot \nabla_a \Xi_i(R) \right]$$

where $E_j(R)$ and $\Xi_j(R)$ denote the electronic energy surfaces and nuclear-motion wavefunctions, Ψ_j denote the corresponding electronic wavefunctions, and the ∇_a represent derivatives with respect to the various coordinates of the nuclei. Changing to the notation used in the one-dimensional model problem introduced above, these so-called **coupled-channel** equations read:

$$\left[(-\Delta - E) - \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \right] A'' \sin(k''R) = - \left[\langle \phi'' | -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} | \phi'' \rangle A'' \sin(k''R) + \left(-\frac{\hbar^2}{\mu} \right) \langle \phi'' | \frac{d}{dR} | \phi \rangle \frac{d}{dR} A \sin(kR) \right]$$

(for $0 \leq R \leq R_{\max}$),

$$\left[(-\Delta - E) - \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \right] A'' \sin(k''R) = - \left[\langle \phi'' | -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} | \phi'' \rangle A'' \sin(k''R) + \left(-\frac{\hbar^2}{\mu} \right) \langle \phi'' | \frac{d}{dR} | \phi \rangle \frac{d}{dR} A \phi \sin(kR_{\max}) e^{\kappa R_{\max}} e^{-\kappa R} \right]$$

(for $0 \leq R < \infty$),

when the index j refers to the ground-state surfaces ($V(R) = -\Delta$, for $(0 < R < \infty)$), and

$$\left[(0 - E) - \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \right] A \sin(kR) = - \left[\langle \phi | -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} | \phi \rangle A \sin(kR) + \left(-\frac{\hbar^2}{\mu} \right) \langle \phi | \frac{d}{dR} | \phi'' \rangle \frac{d}{dR} A'' \sin(k''R) \right]$$

(for $0 \leq R \leq R_{\max}$)

$$\left[(D_e - E) - \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \right] A \sin(kR_{\max}) e^{\kappa R_{\max}} e^{-\kappa R} = - \left[\langle \phi | -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} | \phi \rangle A \sin(kR_{\max}) e^{\kappa R_{\max}} e^{-\kappa R} - \left(\frac{\hbar^2}{\mu} \right) \langle \phi | \frac{d}{dR} | \phi'' \rangle \frac{d}{dR} A'' \sin(k''R) \right]$$

(for $R_{\max} \leq R < \infty$)

when the index j refers to the excited-state surface (where $V(R) = 0$, for $0 < R \leq R_{\max}$ and $V(R) = D_e$ for $R_{\max} \leq R < \infty$).

Clearly, if the right-hand sides of the above equations are ignored, one simply recaptures the Schrödinger equations describing motion on the separate potential energy surfaces:

$$\left[(-\Delta - E) - \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \right] A'' \sin(k''R) = 0$$

(for $0 \leq R \leq R_{\max}$),

$$\left[(-\Delta - E) - \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \right] A'' \sin(k''R) = 0$$

(for $0 \leq R < \infty$);

that describe motion on the lower-energy surface, and

$$\left[(0 - E) - \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \right] A \sin(kR) = 0$$

(for $0 \leq R \leq R_{\max}$),

$$\left[(D_e - E) - \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \right] A \sin(kR_{\max}) e^{\kappa R_{\max}} e^{-\kappa R} = 0$$

(for $R_{\max} \leq R < \infty$)

describing motion on the upper surface on which the bonding interaction occurs. The terms on the right-hand sides provide the couplings that cause the true solutions to the Schrödinger equation to be combinations of solutions for the two separate surfaces.

In applications of the coupled-channel approach illustrated above, coupled sets of second order differential equations (two in the above example) are solved by starting with a specified flux in one of the channels and a chosen energy E . For example, one might specify the amplitude A to be unity to represent preparation of the system in a bound vibrational level (with $E < D_e$) of the excited electronic-state potential. One would then choose E to be one of the eigenenergies of that potential. Propagation methods could be used to solve the coupled differential equations subject to these choices of E and A . The result would be the determination of the amplitude A' of the wavefunction on the groundstate surface. The ratio A'/A provides a measure of the strength of coupling between the two Born-Oppenheimer states

Perturbative Treatment

Alternatively, one can treat the coupling between the two states via time dependent perturbation theory. For example, by taking $A = 1.0$ and choosing E to be one of the eigenenergies of the excited-state potential, one is specifying that the system is initially (just prior to $t = 0$) prepared in a state whose wavefunction is:

$$\begin{aligned} \Psi_{\text{ex}}^0 &= \phi \sin(kR) \text{ (for } 0 \leq R \leq R_{\max} \text{)} \\ \Psi_{\text{ex}}^0 &= \phi \sin(kR_{\max}) e^{\kappa R_{\max}} e^{-\kappa R} \text{ (for } R_{\max} \leq R \leq \infty \text{)}. \end{aligned}$$

From $t = 0$ on, the coupling to the other state

$$\Psi_{\text{ground}}^0 = \phi' \sin(k'R) \text{ (for } 0 \leq R < \infty$$

is induced by the "perturbation" embodied in the terms on the right-hand side of the coupled-channel equations

Within this time dependent perturbation theory framework, the rate of transition of probability amplitude from the initially prepared state (on the excited state surface) to the ground-state surface is proportional to the square of the perturbation matrix elements between these two states:

$$\begin{aligned} \text{Rate} \propto & \left| \int_0^{R_{\max}} \sin(kR) e^{\kappa R_{\max}} e^{-\kappa R} \left\langle \phi \left| \frac{d}{dR} \right| \phi' \right\rangle \left(\frac{d}{dR} \sin(k'R) \right) dR + \int_{R_{\max}}^{\infty} \sin(kR_{\max}) e^{\kappa R_{\max}} e^{-\kappa R} \right. \\ & \left. \left\langle \phi \left| \frac{d}{dR} \right| \phi' \right\rangle \left(\frac{d}{dR} \sin(k'R) \right) dR \right|^2 \end{aligned}$$

The matrix elements occurring here contain two distinct parts:

$$\langle \phi | \frac{d}{dR} | \phi'' \rangle$$

has to do with the electronic state couplings that are induced by radial movement of the nuclei; and both

$$\sin(kR) \frac{d}{dR} \sin(k'R)$$

relate to couplings between the two nuclear-motion wavefunctions induced by these same radial motions. For a transition to occur, both the electronic and nuclear-motion states must undergo changes. The initially prepared state (the bound state on the upper electronic surface) has high electronic and low nuclear-motion energy, while the state to which transitions may occur (the scattering state on the lower electronic surface) has low electronic energy and higher nuclear-motion energy.

Of course, in the above example, the integrals over R can be carried out if the electronic matrix elements $\langle \phi | \frac{d}{dR} | \phi'' \rangle$ can be handled. In practical chemical applications (for an introductory treatment see **Energetic Principles of Chemical Reactions**, J. Simons, Jones and Bartlett, Portola Valley, Calif. (1983)), the evaluation of these electronic matrix elements is a formidable task that often requires computation intensive techniques such as those discussed in Section 6.

Even when the electronic coupling elements are available (or are modelled or parameterized in some reasonable manner), the solution of the coupled-channel equations that govern the nuclear motion is a demanding task. For the purposes of this text, it suffices to note that:

1. couplings between motion on two or more electronic states can and do occur;
2. these couplings are essential to treat whenever the electronic energy difference (i.e., the spacing between pairs of Born-Oppenheimer potential surfaces) is small (i.e., comparable to vibrational or rotational energy level spacings);
3. there exists a rigorous theoretical framework in terms of which one can evaluate the rates of so-called radiationless transitions between pairs of such electronic, vibrational, rotational states. Expressions for such transitions involve (a) electronic matrix elements that depend on how strongly the electronic states are modulated by movement (hence the $\frac{d}{dR}$) of the nuclei, and (b) nuclear-motion integrals connecting the initial and final nuclear-motion wavefunctions, which also contain $\frac{d}{dR}$ because they describe the "recoil" of the nuclei induced by the electronic transition.

Chemical Relevance

As presented above, the most obvious situation of multichannel dynamics arises when electronically excited molecules undergo radiationless relaxation (e.g., internal conversion when the spin symmetry of the two states is the same or intersystem crossing when the two states differ in spin symmetry). These subjects are treated in some detail in the text **Energetic Principles of Chemical Reactions**, J. Simons, Jones and Bartlett, Portola Valley, Calif. (1983)) where radiationless transitions arising in photochemistry and polyatomic molecule reactivity are discussed.

Let us consider an example involving the chemical reactivity of electronically excited alkaline earth or $d^{10}s^2$ transition metal atoms with H_2 molecules. The particular case for $Cd^* + H_2 \rightarrow CdH + H$ has been studied experimentally and theoretically. In such systems, the potential energy surface connecting to ground-state $Cd(^1S) + H_2$ becomes highly repulsive as the collision partners approach (see the depiction provided in the Figure shown below). The three surfaces that correlate with the $Cd(^1P) + H_2$ species prepared by photo-excitation of $Cd(^1S)$ behave quite differently as functions of the Cd-to- H_2 distance because in each the singly occupied 6p orbital assumes a different orientation relative to the H_2 molecule's bond axis. For (near) C_{2v} orientations, these states are labeled 1B_2 , 1B_1 , and 1A_1 ; they have the 6p orbital directed as shown in the second Figure, respectively. The corresponding triplet surfaces that derive from $Cd(^3P) + H_2$ behave, as functions of the Cd-to- H_2 distance (R) in similar manner, except they are shifted to lower energy because $Cd(^3P)$ lies below $Cd(^1P)$ by ca. 37 kcal/mol.

Collisions between $Cd(^1P)$ and H_2 can occur on any of the three surfaces mentioned above. Flux on the 1A_1 surface is primarily reflected (at low collision energies characteristic of the thermal experiments) because this surface is quite repulsive at large R . Flux on the 1B_1 surface can proceed in to quite small R (ca. 2.4 Å) before repulsive forces on this surface reflect it. At geometries near $R = 2.0$ Å and $r_{HH} = 0.88$ Å, the highly repulsive 3A_1 surface intersects this 1B_1 surface from below. At and near this intersection, a combination of spin-orbit coupling (which is large for Cd) and non-adiabatic coupling may induce flux to evolve onto the 3A_1 surface, after which fragmentation to $Cd(^3P) + H_2$ could occur.

In contrast, flux on the 1B_2 surface propagates inward under attractive forces to $R = 2.25 \text{ \AA}$ and $r_{HH} = 0.79 \text{ \AA}$ where it may evolve onto the 3A_1 surface which intersects from below. At and near this intersection, a combination of spin-orbit coupling (which is large for Cd) and non-adiabatic coupling may induce flux to evolve onto the 3A_1 surface, after which fragmentation to $Cd(^3P) + H_2$ could occur. Flux that continues to propagate inward to smaller R values experiences even stronger attractive forces that lead, near $R = 1.69 \text{ \AA}$ and $r_{HH} = 1.54 \text{ \AA}$, to an intersection with the 1A_1 surface that connects to $Cd(^1S) + H_2$. Here, non-adiabatic couplings may cause flux to evolve onto the 1A_1 surface which may then lead to formation of ground state $Cd(^1S) + H_2$ or $Cd(^1S) + H + H$, both of which are energetically possible. Processes in which electronically excited atoms produce groundstate atoms through such collisions and surface hopping are termed "electronic quenching".

The nature of the non-adiabatic couplings that arise in the two examples given above are quite different. In the former case, when the 1B_1 and 3A_1 surfaces are in close proximity to one another, the first-order coupling element:

$$\langle \Psi(^1B_1) | \nabla_j | \Psi(^3A_1) \rangle$$

is non-zero only for nuclear motions (i.e., ∇_j) of $b_1 x a_1 = b_1$ symmetry. For the CdH_2 collision complex being considered in (or near) C_{2v} symmetry, such a motion corresponds to rotational motion of the nuclei about an axis lying parallel to the H-H bond axis. In contrast, to couple the 3A_1 and 1B_2 electronic states through an element of the form

$$\langle \Psi(^1B_2) | \nabla_j | \Psi(^3A_1) \rangle,$$

the motion must be of $b_2 x a_1 = b_2$ symmetry. This movement corresponds to asymmetric vibrational motion of the two Cd-H interatomic coordinates.

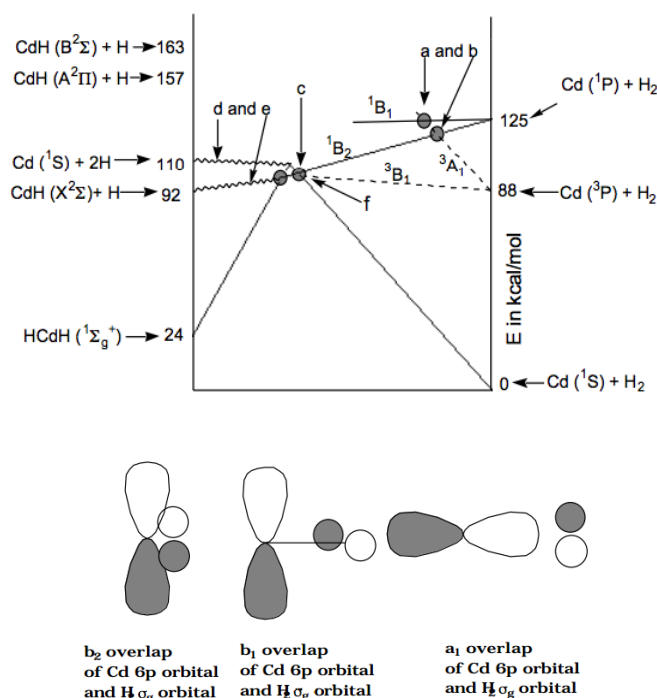
The implications of these observations are clear. For example, in so-called halfcollision experiments in which a van der Waals CdH_2 complex is probed, internal rotational motion would be expected to enhance $^1B_1 \rightarrow ^3A_1$ quenching, whereas asymmetric vibrational motion should enhance the $^1B_2 \rightarrow ^3A_1$ process.

Moreover, the production of ground-state $Cd(^1S) + H_2$ via $^1B_2 \rightarrow ^1A_1$ surface hopping (near $R = 1.69 \text{ \AA}$ and $r_{HH} = 1.54 \text{ \AA}$) should also be enhanced by asymmetric vibrational excitation. The 1B_2 and 1A_1 surfaces also provide, through their non-adiabatic couplings, a "gateway" to formation of the asymmetric bond cleavage products $CdH(^2\Sigma) + H$. It can be shown that the curvature (i.e., second energy derivative) of a potential energy surface consists of two parts: (i) one part that is always positive, and (ii) a second that can be represented in terms of the non-adiabatic coupling elements between the two surfaces and the energy gap ΔE between the two surfaces. Applied to the two states at hand, this second contributor to the curvature of the 1B_2 surface is:

$$\frac{|\langle \Psi(^1B_2) | \nabla_f | \Psi(^1A_1) \rangle|^2}{E(^1B_2) - E(^1A_1)}.$$

Clearly, when the 1A_1 state is higher in energy but strongly non-adiabatically coupled to the 1B_2 state, negative curvature along the asymmetric b_2 vibrational mode is expected for the 1B_2 state. When the 1A_1 state is lower in energy, negative curvature along the b_2 vibrational mode is expected for the 1A_1 state (because the above expression also expresses the curvature of the 1A_1 state).

Therefore, in the region of close-approach of these two states, state-to-state surface hopping can be facile. Moreover, one of the two states (the lower lying at each geometry) will likely possess negative curvature along the b_2 vibrational mode. It is this negative curvature that causes movement away from C_{2v} symmetry to occur spontaneously, thus leading to the $CdH(^2\Sigma) + H$ reaction products.



Coupled-state dynamics can also be used to describe situations in which vibrational rather than electronic-state transitions occur. For example, when van der Waals complexes such as HCl...Ar undergo so-called vibrational predissociation, one thinks in terms of movement of the Ar atom relative to the center of mass of the HCl molecule playing the role of the R coordinate above, and the vibrational state of HCl as playing the role of the quantized (electronic) state in the above example.

In such cases, a vibrationally excited HCl molecule (e.g., in $v = 1$) to which an Ar atom is attached via weak van der Waals attraction transfers its vibrational energy to the Ar atom, subsequently dropping to a lower (e.g., $v = 0$) vibrational level. Within the twocoupled-state model introduced above, the upper energy surface pertains to Ar in a bound vibrational level (having dissociation energy D_e) with HCl in an excited vibrational state (Δ being the $v = 0$ to $v = 1$ vibrational energy gap), and the lower surface describes an Ar atom that is free from the HCl molecule that is itself in its $v = 0$ vibrational state. In this case, the coordinate R is the Ar-to-HCl distance.

In analogy with the electronic-nuclear coupling example discussed earlier, the rate of transition from HCl ($v=1$) bound to Ar to HCl($v=0$) plus a free Ar atom depends on the strength of coupling between the Ar...HCl relative motion coordinate (R) and the HCl internal vibrational coordinate. The $\langle \phi | \frac{d}{dR} | \phi' \rangle$ coupling elements in this case are integrals over the HCl vibrational coordinate x involving the $v = 0$ (ϕ) and $v = 1$ (ϕ') vibrational functions. The integrals over the R coordinate in the earlier expression for the rate of radiationless transitions now involve integration over the distance R between the Ar atom and the center of mass of the HCl molecule.

This completes our discussion of dynamical processes in which more than one Born-Oppenheimer state is involved. There are many situations in molecular spectroscopy and chemical dynamics where consideration of such coupled-state dynamics is essential. These cases are characterized by

1. total energies E which may be partitioned in two or more ways among the internal degrees of freedom (e.g., electronic and nuclear motion or vibrational and ad-atom in the above examples),
2. Born-Oppenheimer potentials that differ in energy by a small amount (so that energy transfer from the other degree(s) of freedom is facile).

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