

Summation and Outlook

Irradiation of $\text{N}_2\text{F}_4(\text{NF}_2)$ provides a convenient source of atomic fluorine which can be used to introduce F into substrates and/or to form radicals which readily yield products containing the NF_2 moiety. Vibrationally excited intermediates may be generated by this procedure at low pressures and a number of interesting unimolecular decomposition pathways studied. Fluoronitrene, NF , the fragment formed concomitantly with F in the photolysis of NF_2 , is isoelectronic with O_2 . How closely the chemistry of NF parallels that of O_2 remains an intriguing chal-

lenge.³³ The photochemistry of *N*-fluorimines, analogs of ketones, promises to be a fruitful area of study. Uncovering evidence for alkylfluorodiazenes, RN_2F , suggests that other routes to these species should be sought, for they may well play a key role in the development of new fluorination methods.

We are grateful to the National Science Foundation and the North Carolina State University Engineering Foundation for generous financial support.

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The Geometry of Intersecting Potential Surfaces

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The notion of a potential function for the motion of the nuclei in a molecular system takes different forms from different points of view.

For the classical idealist, the potential function is simply the work which must be done to bring the constituent atoms from infinite separation to some specified conformation. This definition gives no assurance that a potential function exists, or is unique, and it is sadly lacking in operational significance.

For the experimentalist, a potential function is that function which, when inserted into the appropriate quantum mechanical description of the nuclear motion, reproduces his data within their scatter. It is to be hoped that the same function is consistent with the results of more than one kind of experiment.

For the theoretician, a molecular potential function is a creature of the Born-Oppenheimer separation, and attention tends to focus on the limitations of this remarkably useful approximation.

A potential energy function is the basic premise, or the object of the game, in many different endeavors with small molecules. Many phenomena are thought of as being controlled by a single potential function and provide data for determining that function. Examples are vibrational energy levels of diatomic^{1,2} and polyatomic³ molecules, elastic scattering of atoms,⁴ transport phenomena and gas imperfections,^{5,6} and product energy distributions in atom-transfer reactions.⁷⁻⁹ There are, however, other processes of a fundamentally different sort, which cannot be explained in terms of a single potential function. Examples are perturbations in bound states,^{10,11} predissociation in small molecules,^{12,13} collisional transfer of electronic energy,^{14,15} and

electronic chemiluminescence.^{8,16} These phenomena must be described in terms of the interaction of two (or more) electronic states or potential functions.

Comparing problems tractable in terms of a single electronic state with those which must involve two states is, quite literally, like comparing a line to a plane. In view of this great increase in complexity, I have chosen to isolate a small, but well-defined and fundamental, part of the problem. This Account is devoted to a discussion of the geometrical properties of triatomic potential functions in the neighborhood of an intersection. The intersection of electronic states raises fundamental questions about the precise definition of potential functions, their validity, and above all their usefulness.

Definitions of Potential Functions

To begin with, there are the coordinates of the electrons, lumped together in the set q . The coordinates specifying the shape of the system or conformation¹⁷ of the nuclei are $(Q_1, Q_2, Q_3) \equiv Q$. They

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will often be normal mode displacements from some reference conformation, but there are other useful ways to choose them. We use only these molecule-fixed coordinates, omitting angular momentum effects. Since spin-orbit interaction is neglected, the electronic Hamiltonian operator $\hat{H}(q, Q)$ may be taken as real. It operates on the electronic coordinates only; the Q 's are merely parameters.

This operator is tractable only when it is represented as a matrix in terms of a complete orthonormal set of electronic wave functions, $\phi(q, Q)$, which may depend parametrically on the set of nuclear displacements Q . The matrix elements are

$$H_{ij}(Q) = \int \phi_i^* \hat{H} \phi_j dq \quad (1)$$

The diagonal element $H_{ii}(Q)$ is the expectation value of the energy of a system represented by the wave function ϕ_i . This function, $H_{ii}(Q) \equiv E_i(Q)$, is by definition the potential energy function for the i th electronic state. This magnificently general but somewhat formal definition produces a pair of potential functions corresponding to any chosen pair of electronic states, the basis states under consideration. There are several physically meaningful ways to choose these pairs of basis states. The *adiabatic* states ψ_1, ψ_2 , which diagonalize H , are a possible choice. The resulting adiabatic potential functions are often considered to be *the* potential functions of the molecule. In many cases, however, these adiabatic states are not the most useful or natural,¹⁸⁻²² since they sometimes undergo an abrupt change of character in the neighborhood of an intersection, as we shall see. In such a case, it is much more natural to work with states having a definite electronic configuration or orbital occupancy, which does not change as the molecule is distorted in the neighborhood of some conformation of interest. Anticipating a bit, we refer to these as *crossing states*, ϕ_1, ϕ_2 .

It is important to establish the relationship between these crossing states and the adiabatic states, and between the corresponding potential functions. These pairs of states must be related by a transformation which takes one complete orthonormal set into another (eq 2). Here the transformation matrix

$$\begin{aligned} \psi_1 &= (\cos \theta)\phi_1 - (\sin \theta)\phi_2 \\ \psi_2 &= (\sin \theta)\phi_1 + (\cos \theta)\phi_2 \end{aligned} \quad (2)$$

which mixes the states ϕ has geometric significance as a rotation through the angle θ of an arbitrary point in plane polar coordinates. The mixing is completely determined by the single parameter θ , the mixing angle. In order to relate the potential surfaces for the states ϕ to those for the adiabatic states ψ , we need the relationship between the Hamiltonian matrix in the ϕ basis, \mathbf{H}_ϕ , and the corresponding matrix \mathbf{H}_ψ in the ψ basis

$$\mathbf{H}_\psi = U^+ \mathbf{H}_\phi U \quad (3)$$

where U is the transpose of the matrix which transforms $\phi \rightarrow \psi$ in eq 2. Starting with the ϕ states and

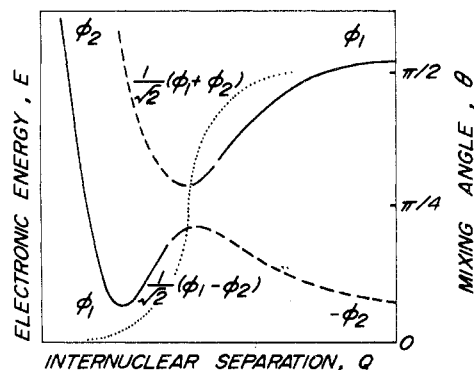


Figure 1. Two adiabatic potential curves with an avoided intersection. The adiabatic states are the indicated linear combinations of the crossing states ϕ_1, ϕ_2 each of which has a definite orbital occupancy. The dotted line represents the mixing angle, eq 2 and 4.

using the fact that H_ψ is diagonal, the mixing angle θ is determined by

$$\tan 2\theta = \frac{2H_{12}}{H_{22} - H_{11}} \quad (4)$$

and separation of the adiabatic energies is

$$E_2 - E_1 = [(H_{22} - H_{11})^2 + 4|H_{12}|^2]^{1/2} \quad (5)$$

These equations involve matrix elements in the ϕ basis, as defined in eq 1. Consider for a minute the application of these equations to the crossing of diatomic potential curves. Suppose we have, at some particular internuclear separation Q_0 , $0 < H_{12} \ll H_{11} = H_{22}$, and H_{12} is a slowly varying function of Q . Then as Q passes through the value Q_0 , the denominator in (4) goes through zero and of course changes sign. The mixing angle θ switches from nearly 0 to nearly $\pi/2$, with $\theta = \pi/4$ at Q_0 (see Figure 1).

Intersections of Potential Energy Hypersurfaces

In the previous section we have talked about potential energy *functions*, avoiding geometrical language. Geometry needs a space, and several spaces are useful. There is the four-space $E3Q$ in which the coordinates are potential energy and the three Q 's. Then there is the three-dimensional conformation space $3Q$. In addition there are three spaces EQ_iQ_j which appear as sections of the $E3Q$ space with Q_k held constant.

It is often most convenient to define curves and surfaces parametrically. With this in mind, define a *curve* as a one-parameter locus, *i.e.*, a correspondence between values of a single parameter and points in a space. A surface is a two-parameter locus or a family of curves. A hypersurface is a three-parameter locus or a family of surfaces. In $E3Q$, one relation among the four variables determines a hypersurface, two independent constraints determine a surface, and three determine a curve.

The word intersection will be used, for the present,²³ to refer to the situation in which two adiabatic potential hypersurfaces in $E3Q$ have one or more points in common, and we consider properties of the two surfaces at and near these points. By *intersection locus* is meant the set of all points in $3Q$ for which the two potential functions have the same

(23) The distinction between intersections and contact will be introduced later.

(17) The term conformation is used in order to reserve the term configuration for an assignment of electrons to orbitals, *e.g.*, $\dots (\pi_u)^4 \pi_g$.

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energy. The intersection locus is simply the projection onto $3Q$ of the intersection in $E3Q$.

The intersection of the adiabatic states is defined by $E_2 - E_1 = 0$ in eq 5. This is equivalent to two conditions (eq 6 and 7). We will make the traditional

$$H_{22}(Q) - H_{11}(Q) = 0 \quad (6)$$

$$H_{12}(Q) = 0 \quad (7)$$

assumption²⁴ that conditions 6 and 7 are independent and sufficient, although it has been suggested that further conditions distinguishing contact from intersection should be imposed.²⁵ Each condition defines a surface in $3Q$ space, and their common points define the intersection locus. Since it is intersections we want, we ignore cases in which no intersection occurs, and assume that we are dealing with states ϕ for which condition 6 is satisfied on some set of points in $3Q$. There will be an intersection if condition 7 is also satisfied at some of these points.

The Role of Symmetry

According to eq 1, condition 7 is simply an integral which must be zero. Considerations of symmetry provide a powerful tool for deciding whether or not an integral is zero, and we assume that H_{12} will not be zero unless this is required by symmetry. We can make the maximum use of symmetry by choosing the coordinates Q_1, Q_2, Q_3 to be normal mode displacements from some reference conformation Q_0 on an intersection locus. These displacements will belong to one or another of the symmetry types (irreducible representations) of the point group corresponding to the Q_0 conformation. For a triatomic molecule, the possible point groups are $D_{\infty h}$ (linear with a center of symmetry), $C_{\infty v}$ (linear), D_{3h} (equilateral), C_{2v} (isosceles), and C_s (planar, *i.e.*, no symmetry element but the plane of the molecule). Only the first three of these point groups can have degenerate electronic (or vibrational) states with orbital (or vibrational) angular momentum.

Since we are primarily interested in the immediate neighborhood of an intersection, it is natural to expand the Hamiltonian operator $\hat{H}(q, Q)$ in a power series^{10, 26, 27} in the Q 's, centered on Q_0

$$\hat{H}(q, Q) = \hat{H}(q, Q_0) + \sum_i \hat{H}_i(q, Q_0) Q_i + \frac{1}{2} \sum_{ij} \hat{H}_{ij}(q, Q_0) Q_i Q_j + \dots \quad (8)$$

where, for example

$$\hat{H}_i(q, Q_0) = \left(\frac{\partial \hat{H}(q, Q)}{\partial Q_i} \right)_{Q=Q_0} \quad (9)$$

Derived from this expansion of the operator, there will be corresponding expansions of its matrix elements using an appropriate pair of electronic basis states. Here, and in the rest of the article, it is most convenient to use basis states which diagonalize the Hamiltonian at Q_0 , but which are independent of displacements Q from that point.²⁸ Therefore they

will not in general diagonalize H at arbitrary conformations in the neighborhood of Q_0 . They will belong to one or another of the symmetry types of the point group of Q_0 . With basis states of this type, the linear terms in eq 1 have the form

$$H_{12}(Q) = \sum_i Q_i \int \psi_1^*(q, Q_0) \hat{H}_i(q, Q_0) \psi_2(q, Q_0) dq \quad (10)$$

in which the integral itself is independent of Q . The symmetry properties of the derivatives \hat{H}_i can be deduced from the symmetry of the corresponding Q_i .²⁷ The symmetry properties of the \hat{H}_i , along with those of $\psi_1(q, Q_0)$ and $\psi_2(q, Q_0)$, allow one to identify those integrals of form 10 which must be zero, *i.e.*, for which the integrand is not totally symmetric. In this way we identify the first terms in the expansion of the Hamiltonian matrix.

Types of Intersections

The various types of intersections which can arise are most conveniently cataloged according to the symmetry or point group of the molecule at the intersection point.²⁹

(A) In the isosceles (C_{2v}) point group we take for example electronic basis states belonging to the representations A_1 and B_2 (Herzberg's¹⁰ notation), both of which are symmetric with respect to the plane of the molecule, but which have different symmetry with respect to the other operations of the group. The symmetric stretch, Q_1 , and bending, Q_2 , belong to the A_1 representation and do not distort the isosceles symmetry. The antisymmetric stretch Q_3 reduces the symmetry to C_s . It is Q_3 which breaks the symmetry and mixes A_1 and B_2 . The intersection is *allowed* only when $Q_3 = 0$. The Hamiltonian matrix for electronic states of A_1 and B_2 symmetry therefore has the form,³⁰ to first order in Q_1

$$H = \begin{bmatrix} aQ_1 + bQ_2 & Q_3 \\ Q_3 & cQ_1 + dQ_2 \end{bmatrix} \quad (11)$$

This matrix determines, by means of eq 4 and 5, the mixing of the basis states and the splitting of the two adiabatic hypersurfaces in the neighborhood of an intersection locus in the full $EQ_1Q_2Q_3$ space. In the $Q_3 = 0$ section, there is no mixing and we see the intersection of two planes, each associated uniquely with one of the basis states. In a section in which Q_1 is zero, the surfaces form a double cone, and the mixing varies smoothly with Q_2 and Q_3 as indicated in Figure 2. Because of its appearance in this section, this intersection of A_1 and B_2 (or A_2 and B_1) states allowed in C_{2v} is commonly called a conical intersection.^{24, 29}

A conical intersection also occurs in D_{3h} (equilateral), involving the components of a degenerate E' state,²⁷ which splits into A_1 and B_2 states when the system is distorted into C_{2v} (isosceles). In terms of the normal mode displacements, the matrix has the form of (11) with $a = c = d = 1$ and $b = -1$. The normal modes Q_2 and Q_3 are degenerate in this case.

A conical intersection is of interest in connection with the electron jump reaction (eq 12). This involves a change in electronic configuration from $K +$

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(29) T. Carrington, *Faraday Discuss. Chem. Soc.*, **53**, 27 (1972).

(30) All these coordinates Q_i are understood to be multiplied by a constant scale factor with dimensions of energy.

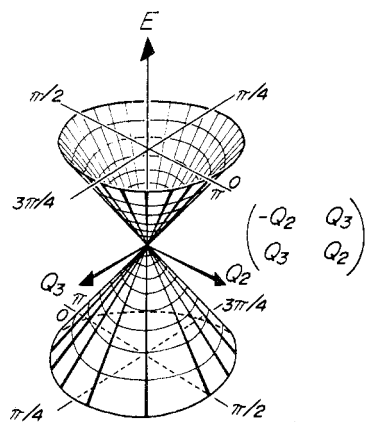
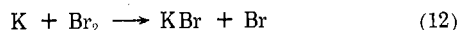


Figure 2. A conical intersection of A_1 and B_2 states in C_{2v} . The mixing of the basis states on the two sheets of the cone is indicated by the mixing angle θ . The Hamiltonian matrix is indicated schematically, showing only the first-order dependence on normal mode displacements. The cone is not in general circular. See eq 11.



Br_2 to $K^+ + Br_2^-$ as the reactants approach.³¹ In C_{2v} , the 2A_1 surface correlating with neutral reactants crosses the strongly attractive 2B_2 surface correlating with $K^+ + Br_2^-$. In the unlikely event that K approaches Br_2 along the perpendicular bisector, there can be no electron jump, since there is no interaction of the two surfaces in C_{2v} . However, in C_s conformations in the neighborhood of the intersection, the interaction will be strong, and there will be an abrupt change in character of the adiabatic surface, covalent to ionic, as the reactants approach. This electron jump will be less sudden for trajectories which do not come so close to the intersection, and the attraction between the reactants caused by mixing in of ionic character will extend to longer range.

The discussion just given, based on *state* correlations, has a more primitive but qualitatively similar version based on *orbital* correlations. The electron jumps from a σ_g orbital on K to a σ_u orbital on Br_2 , forbidden in the broadside approach.³² Arguments based on orbital correlations are much used, and, it must be observed, useful³³ much of the time.³⁴

(B) Another common type of intersection involves the components of a Π state of a linear ($C_{\infty v}$) molecule. When the molecule is bent, the degenerate Π state splits into two states, A' and A'' , symmetric and antisymmetric with respect to the plane of the molecule, as indicated in Figure 3. The splitting is proportional to the square of the bending coordinate, but there is no mixing of the states due to a static displacement, since they are always of different symmetry. The ground state of NO_2 , 2A_1 , and the first excited state, 2B_1 , are components of the ${}^2\Pi_u$ state which correlates with ground states of $O + NO$.³⁵ Although A_1 and B_1 are not mixed by simply bending the molecule, they can be mixed by rotation or

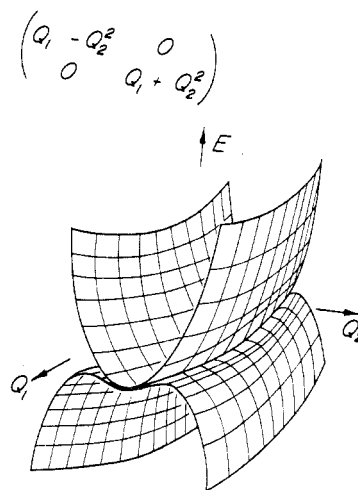


Figure 3. A glancing intersection of the components of a Π state. There is no mixing of the basis states. Q dependence of the Hamiltonian matrix is indicated.

spin-orbit coupling. This may occur in the radiative recombination,³⁶ $O + NO \rightarrow NO_2^*$.

(C) For a linear molecule with a center of symmetry ($D_{\infty h}$), a quite different type of intersection can occur, between a Σ_g^+ and a Σ_u^+ state. Though this intersection is not very common, it provides a particularly striking illustration of the fact that an intersection may have three very different forms in its three different sections. The Hamiltonian matrix takes the form

$$H = \begin{bmatrix} -Q_1 - Q_2^2 & Q_3 \\ Q_3 & Q_1 + Q_2^2 \end{bmatrix} \quad (13)$$

Here for simplicity we have omitted the coefficients of the Q 's, retaining only the qualitative features of the lowest order Q dependence. In the $Q_2 = 0$ section (EQ_1Q_3 space) we have a double cone with variable mixing, as in Figure 2. In the $Q_3 = 0$ section (EQ_1Q_2 space) there is no mixing, and the surfaces are intersecting parabolic cylinders. In the $Q_1 = 0$ section, the surfaces meet at a point. They separate linearly in the Q_3 direction with mixing, but quadratically in the Q_2 direction without mixing, as indicated schematically in Figure 4.

(D) Even in C_s conformations, intersections and near-intersections are of interest. If the two states have different symmetry with respect to the plane (A' and A'' states), they will not interact as a result of any static deformation, since H_{12} will be zero everywhere. Any section of the intersection will be, to first order in the displacements, two intersecting planes, with no mixing. The states may be mixed by spin-orbit coupling or rotation, however, and this mixing will be significant only in the neighborhood of the intersection. Thus the intersection of A' and A'' states in C_s , while uninteresting from the point of view of static displacements, can be quite important in real collisions.

If the two states have the same symmetry with respect to the plane, H_{12} will not be zero in any finite bent conformation. The two hypersurfaces may approach more or less closely, but will not actually in-

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(33) B. H. Mahan and J. S. Winn, *J. Chem. Phys.*, 57, 4321 (1972).

(34) Not always useful however. For H_2 , the state $1\sigma_g 1\sigma_u^2 \Sigma_u^+$ has a dissociation energy of 80 kcal/mol, greater than that of H_2^+ , and dissociates adiabatically to $H(1^2S) + H(2^2P)$.

(35) R. A. Gangi and L. Burnelle, *J. Chem. Phys.*, 55, 851 (1971).

(36) F. Kaufman, in "Chemiluminescence and Bioluminescence," J. Lee, D. M. Hercules, and M. Cormier, Plenum Press, New York, N. Y., 1973, p. 83.

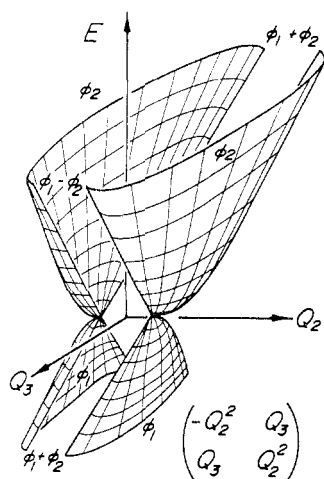


Figure 4. Intersection and mixing of Σ_g^+ and Σ_u^+ states, ϕ_1 and ϕ_2 .

tersect. This type of avoided intersection is responsible for many electron jump reactions, including some of the alkali-halogen systems³⁷ and, for example, ${}^3\text{H} + \text{Li}_2 \rightarrow \text{HLi} + \text{Li}$.

A special type of avoided intersection in C_s is an asymptotic intersection, in which the two surfaces coalesce as one atom is removed to infinity, leaving the other two as a diatomic molecule. The splitting and mixing are similar to that shown in Figure 1, with the separation between the two curves decreasing as the third atom is pulled away.²⁹ Intersections of this type occur for H_3^+ ³⁹ and H_3 .⁴⁰

Properties of the Intersection Locus

The intersection locus is the set of all points in the $3Q$ space (or any conformation space) for which the two adiabatic potential functions are equal. More formally, it is the projection onto the $3Q$ space of the intersection in the $E3Q$ space.

The intersection locus in the $3Q$ space is determined by two conditions, (6) and (7). In general, each of these conditions defines a surface in $3Q$, and their intersection defines the intersection locus, a curve in $3Q$. It may happen, however, that condition 7 is satisfied everywhere in $3Q$, *i.e.*, when the basis states have different symmetry with respect to the plane of the three-atom system. The intersection locus is then a surface in $3Q$ rather than a curve.

The locus may or may not extend to infinity. If it is possible to pull one atom completely away from the other two without leaving the intersection, the locus will be called infinite in extent; otherwise it is finite. The simplest example of a locus which is an infinite surface is the intersection of the A' and A'' components of a Π state. On the locus linear displacements Q_1 and Q_3 can take any values, defining an infinite surface in the $3Q$ space. On the other hand, in the intersection of A' and A'' states in C_s , the locus may be a finite surface. As an example,^{8,35} consider the first two excited states of NO_2 . When N is removed from O_2 starting at the equilibrium conformation of ground state NO_2 , the lower state,

${}^2\text{B}_1(A'')$, correlates with excited $\text{N}({}^2\text{D})$ and ground-state O_2 . The higher excited state, ${}^2\text{B}_2(A')$, correlates with ground-state products. Therefore the hypersurfaces must cross as the N atom is removed, and this will be true in C_s as well as C_{2v} , since the states have different symmetry with respect to the plane of the molecule. It is clear, however, that the hypersurfaces must separate eventually when the N is withdrawn, since in the limit they are separated by the excitation energy of the N atom.

When the intersection locus is a curve, there are again the two possibilities, infinite or finite extent. An example of a locus curve of finite extent is also provided by NO_2 , this time the ground-state ${}^2\text{A}_1(A')$ and the ${}^2\text{B}_2(A')$ state mentioned above.²⁹ It remains to discuss a locus which is an infinite curve. In the simplest example of this, we have a diatomic molecule X_2 with two states of different symmetry, for example, Σ_g^+ and Σ_u^+ , with potential curves which cross. As the third atom, with S_g symmetry, for example, approaches X_2 in C_{2v} , we have electronic states A_1 and B_2 for the three-atom system. These states do not interact in C_{2v} , so the approach of the third atom does not split the intersection originally present in the diatomic curves. Conversely, as the third atom recedes to infinity in C_{2v} , the states do not separate and the intersection extends to infinity. In C_s , however, both A_1 and B_2 become A' , and the locus is a curve rather than a surface.

A locus curve (or surface) of finite extent may have an end point (or edge), or instead may be a closed loop (or closed surface). A simple continuity argument indicates that a finite locus must be closed, without end or edge. The electronic Hamiltonian operator is a completely continuous function of nuclear displacements, *i.e.*, all derivatives are continuous for all Q . Its matrix elements, using electronic basis states which are themselves completely continuous functions of the nuclear displacements, and its eigenvalues will also be completely continuous. Thus the potential energy functions are completely continuous and so are the surfaces, eq 6 and 7, which define the locus curve in $3Q$, which must also be completely continuous. To see that this curve must be closed, consider the following counter-example. Suppose that the two surfaces (6) and (7) intersect along a curve of finite length. A section through this curve would have the form shown in Figure 5. Since the curves C_1 and C_2 coincide over the range a - b , they cannot separate outside this range without having a discontinuity in at least one derivative. Since this violates the condition that the locus is completely continuous, we have the result that the finite locus curve cannot have an end point, and therefore must be a closed curve. When the intersection locus is a finite surface, it must be a closed surface, as one can show by arguments like those just presented, applied to hypersurfaces in $E3Q$.

The Classification of Intersections

The various types of intersections can be classified according to the role of symmetry, the dimensionality of the locus, its extent, and the order of contact of the surfaces.

As regards the role of symmetry, three cases arise. An *enforced* intersection involves the components of

(37) D. R. Herschbach in ref 36, p 29.

(38) Y. T. Lee, R. J. Gordon, and D. R. Herschbach, *J. Chem. Phys.*, **54**, 2410 (1971).

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a degenerate electronic state (two-dimensional representation) such as $\Pi(A' + A'')$ in $C_{\infty v}$ or $\Pi_u(A_1 + B_1)$ in $D_{\infty h}$ for linear molecules and $E'(A_1 + B_2)$ in D_{3h} for equilateral. In these cases one knows *a priori* precisely where the surfaces will intersect. The intersection is enforced in all linear or equilateral conformations. In the system ABA in bent conformations, symmetry plays a weaker role. Consider states of $A_1 B_2$ symmetry in C_{2v} (isosceles), both A' symmetry when distorted into C_s . Symmetry will *allow* an intersection only in C_{2v} conformations, but it does not enforce the existence of an intersection, nor can it tell us precisely where the locus will occur in the Q_1, Q_2 plane. In the ABC system in bent conformations, symmetry plays no role. Two states, A' and A'' in C_s , can intersect anywhere, and symmetry provides no restrictions. An intersection is purely *accidental*.

The most important properties of the locus in $3Q$ are its *dimensionality* (it can be a surface or a curve) and its *extent* (finite or infinite). For an enforced intersection, the locus is infinite. In an allowed intersection, the locus is a curve which may be finite or infinite in extent. In an accidental intersection, the locus will be a surface, which may or may not extend to infinity. In addition to these general properties, the behavior of the hypersurfaces in the neighborhood of the intersection is of interest. They may separate linearly, quadratically, or even as some higher power of normal mode displacement, so that the degree, or *order of contact*, becomes another descriptive property.

In addition to these geometrical properties, the manner of mixing of the basis states in the neighborhood of an intersection is a characteristic property with a rich variety of expressions.

Conclusion

The classification of intersections of adiabatic potential hypersurfaces reveals several quite different types, and it is a pleasant endeavor to explore their geometrical properties and electronic character. It is tempting to regard a potential function as an end in itself, something to be produced and admired. I would not be the first to take that view, but it would

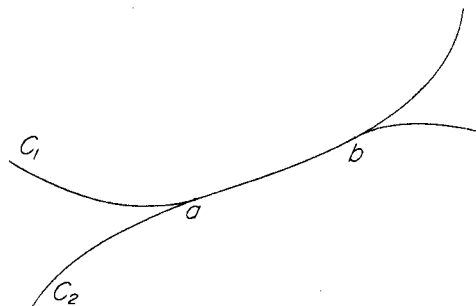


Figure 5. Two curves which coincide over a finite interval cannot separate outside this interval without a discontinuity in at least one derivative.

be irresponsible to end this article without turning outward for a moment.

Does it really matter, as far as observable quantities are concerned, what type of intersection we have? In view of the great success of classical trajectory calculations on a single potential surface,^{7,8} it is natural to try to extend this approach to the case of intersecting surfaces, and an excellent beginning in this direction has been made.⁴¹⁻⁴³ It is clear that the dynamics of the nuclear motion near an intersection will play a crucial role,¹⁸⁻²¹ and the Landau-Zener model should be qualitatively useful. Slow collisions will tend to stay on a single adiabatic surface, if they do not pass too close to an intersection. Fast collisions will tend to stay on one of the crossing surfaces. Motion perpendicular to the reaction coordinate will also be important.^{32,44} Dynamical effects will tend to blur distinctions made on the basis of geometry alone. Nevertheless, the geometrical properties of an intersection provide the logical starting point for a discussion of dynamics.

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