

Locating Electronic Degeneracies of Polyatomic Molecules: A General Method for Nonsymmetric Molecules

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A general method for finding all electronic degeneracies lying on the ground-state potential surface of a molecular system is proposed. The method is based on the idea that the spin pairing of the valence electrons is the major factor determining the topology of the potential surface. The number of different spin-pairing arrangements (anchors) that can be constructed from the constituent atoms determines the number of critical points (minima, transition states) on the ground-state surface. It is shown that whereas the interaction between two states leads in general to an avoided crossing of potential surfaces the interactions in a three-state system (consisting of three anchors) lead in general to a 2-fold degeneracy (conical intersection) and in a four-state system to a 3-fold degeneracy. It is further shown that in a 3D world the highest degree of nonaccidental electronic degeneracy is 3. Since the number of anchors in a polyatomic system can be large, in general numerous 3-fold degeneracies exist in the system, *independent of nuclear symmetry*. The whole topology of the potential surface can be constructed around the degeneracies since minima and transition states are directly accessible from them via a monotonic declining route. A practical procedure for establishing the approximate structures of the 3-fold degenerate “points” and also those of the more familiar 2-fold degeneracies (conical intersections) is proposed.

I. Introduction

Conical intersections are now considered to be important loci in the potential energy surfaces of polyatomic molecules.^{1–10} Since their introduction as efficient funnels for the radiationless transition between different electronic states,^{11,12} their properties have been the subject of continuous interest. Nonetheless, there still seems to be no general procedure for determining the nature of conical intersections in a given system or even just their number. The search for them is sometimes quite arduous and often has to be helped by chemical intuition.

Teller¹² discussed conical intersections in terms of a two-state system. Realizing that a conical intersection is not possible in a 1D space, he noted that at least one more parameter must be introduced, using perturbation theory. This approach was followed by most subsequent workers^{4–7,13,14} who introduced various parameters to describe the interactions between the two states. We present a model based on the concept of a chemical reaction as a two-state system, a concept that is now extensively used in the description of ground-state chemical reactions.^{14–16} An extension to higher dimensions (namely, to a k -state system where $k \geq 3$) leads naturally to electronic degeneracies. It is shown that the highest (nonaccidental) degeneracy in an n atomic system ($n \geq 4$) is 3-fold: three electronic states having the same energy. These, as well as the more familiar 2-fold degenerate conical intersections, can be located by considering different spin-paired structures composed of the same n atoms.

II. Model

The method is based on the assumption that stationary points on the ground-state potential surface may be found by consider-

ing the spin pairing of valence electrons.^{17,18} This is an extension of Lewis' idea that a pair of electrons creates a chemical bond:¹⁹ a local minimum on the potential surface is determined to a large extent by the chemical bonding between neighboring atoms. Two electrons of opposite spins create a chemical bond so that each minimum is defined by a set of electron pairs with different spins.^{17,18} The term “anchor”^{10,20,21} is used to define a particular spin-pairing scheme that may exist in many different nuclear configurations.²²

Our prime interest is in understanding the topology of the ground-state potential energy surface and the role of degeneracies in chemical systems. The crossing of potential surfaces (actual or avoided) is conveniently introduced using a two-state model for reacting systems,^{15,23–25} which can be expanded to the more general k -fold state system. Consider a system consisting of two species P and R that differ only by their spin-pairing schemes (anchors^{20–22}). Within the Born–Oppenheimer approximation, the corresponding electronic wave functions are ϕ_P and ϕ_R , respectively. ϕ_P and ϕ_R are different but not necessarily orthogonal to each other. At certain nuclear configurations Q_P and Q_R , respectively, they lie at local minima on the ground-state potential surface. If motion along the coordinate connecting the two species (the reaction coordinate) involves a single local maximum, then the reaction $P \rightarrow R$ is an elementary one.

The electronic wave function of the system along the reaction coordinate may be written as the linear combination^{15,16,21}

$$|\phi\rangle_{\text{reaction}} = k_P|\phi_P\rangle \pm k_R|\phi_R\rangle$$

Here, k_P and k_R are coefficients such that $k_P = 1$ and $k_R = 0$ at Q_P whereas $k_P = 0$ and $k_R = 1$ at Q_R . As the system moves along the reaction coordinate, k_P varies smoothly from unity to

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zero, and k_R , from zero to unity. At a certain point along the coordinate, $k_P = k_R$, and the potential surfaces of P and R cross. If the two states interact at this point, which is the usual case, then the degeneracy is lifted:²³ two adiabatic potential surfaces are formed—a ground state and an excited state. This is a standard quantum mechanical problem.^{23,24} The wave functions of these adiabatic states are formed by linear combinations of the original wave functions; one is the in-phase combination $|\phi_P\rangle + |\phi_R\rangle$, and the other, the out-of-phase one $|\phi_P\rangle - |\phi_R\rangle$. As shown elsewhere,^{21,25} the in-phase combination is the ground state if the number of exchanged electron pairs is odd (3,5, ...) whereas in cases where that number is even (2, 4, ...) the *out-of-phase* combination is the ground state. (If the total number of electrons is odd, then one electron pair consists of a single electron.) The nuclear configuration at the avoided crossing vicinity, Q_{RP} , has a stationary point (local maximum or minimum) on the ground-state surface.^{15,26} Reactions for which the wave function $|\phi\rangle_{\text{reaction}}$ is the in-phase combination are labeled as phase-preserving reactions, and those for which $|\phi\rangle_{\text{reaction}}$ is the out-of-phase combination, phase-inverting reactions. The other combination of the two original states (with the opposite sign) is an electronically excited state, which has a local minimum at Q_{RP} .^{25–27}

The secular matrix describing the system using ϕ_P and ϕ_R as basis functions is in general not symmetric: at most nuclear configurations, the matrix elements are all different. At the crossing point Q_{RP} , the matrix is symmetric and may be written as

$$\begin{Bmatrix} A - E & B \\ B & A - E \end{Bmatrix} \quad (\text{II.1a})$$

where $A = \langle \phi_P | H | \phi_P \rangle = \langle \phi_R | H | \phi_R \rangle$ and $B = \langle \phi_P | H | \phi_R \rangle = \langle \phi_R | H | \phi_P \rangle$. Diagonalization leads to eq II.1b:

$$\begin{Bmatrix} A - B - E & 0 \\ 0 & A + B - E \end{Bmatrix} \quad (\text{II.1b})$$

The resulting adiabatic wave functions at Q_{RP} are the in-phase and out-of-phase combinations $|\phi_P + \phi_R\rangle$ and $|\phi_P - \phi_R\rangle$, whose energies are $A - B$ and $A + B$, respectively. The energy separation between the two states is $2B$. Note that the interaction could be defined along a single coordinate—this is a 1D problem.

Consider now a system consisting of *three* different anchors (species differing by their spin pairing)—P, R, and S—all connected pairwise by elementary reactions. This system is a triad of two-state systems. Taken separately, each pair interacts along a single coordinate, as discussed above for the two-state system. If the pairs were independent of each other, then six states would result. However, interactions cannot be neglected, and a general treatment of three anchors involves a 2D surface, namely, two independent coordinates. (The third reaction coordinate may be expressed as a linear combination of the other two.) The original three wave functions will combine (at any nuclear configuration) to form *three linearly independent wave functions*. It is always possible to find a nuclear arrangement Q_{PRS} at which the potential surfaces of the three anchors cross, as will be shown using a geometric analogy.

The three anchors are defined by their spin-pairing arrangement. The infinite number of nuclear configuration of each anchor makes it possible to find configurations at which their energies are equal (i.e., $\langle P | H | P \rangle = \langle R | H | R \rangle = \langle S | H | S \rangle$). For the Hamiltonian matrix to be symmetric, the off-diagonal elements must also be equal, a condition that can be satisfied.^{28–30} The

physical distance separating two different atoms determines the strength of the interaction between them. In a plane defined by two independent reaction coordinates, three anchors may be thought of as being placed at the apices of a triangle. Equal interactions mean that the triangle can be equilateral. This is always possible in principle: the point at which the interactions between the three species are equal is equivalent to the point at which the medians of the triangle cross.

This point may be reached along many trajectories—for instance, by using a path connecting the transition state between P and R with anchor S at its local minimum. The matrix (II.2a) describing the system at Q_{PRS} is written with ϕ_P , ϕ_R , and ϕ_S as basis functions:

$$\begin{Bmatrix} A - E & B & B \\ B & A - E & B \\ B & B & A - E \end{Bmatrix} \quad (\text{II.2a})$$

This is possible, as both the diagonal integrals, A , and the off-diagonal elements, B , are equal to each other at this geometry.²⁸ Matrix II.2a is diagonalized to yield II.2b:

$$\begin{Bmatrix} A - B - E & 0 & 0 \\ 0 & A - B - E & 0 \\ 0 & 0 & A + 2B - E \end{Bmatrix} \quad (\text{II.2b})$$

Thus, *two* electronic energy levels are found at Q_{PRS} , supporting, however, *three* independent wave functions, two of which are degenerate. (Note that if one of the wave functions of the original anchors were a linear combination of the other two, then the matrix becomes a 2×2 one.) This is the origin of a conical intersection. The energy separation between the ground and the excited states is $3B$.

The energy ordering of the states remains to be determined. The Longuet-Higgins phase-change rule^{1,2,10,20,21} can be used for this purpose: if all reactions connecting P, R, and S are phase-inverting, then the degeneracy is on the electronic ground state. This is also the case if two reactions are phase-preserving and one is phase-inverting (an ip^2 loop^{10,20,21,29}). The nondegenerate state is a higher-lying electronic state.

However, if all of the reactions are phase-preserving (a p^3 loop) or if two are phase-inverting and one is phase-preserving (an i^2p loop), then the loop encircles a single-valued point, and the wave function maintains its sign. Under these conditions, the ground-state potential surface at Q_{PRS} has either a global minimum or a saddle point (second-order transition state): motion away from this point leads smoothly to all three anchors at their respective minima without encountering a barrier. The doubly-degenerate state is an electronically excited state.

Consider next a system consisting of four different anchors, P, R, S, and T, all connected pairwise by elementary reactions. This is a sextet of two-state systems. If they were all independent of each other, then 12 states could be formed from interactions between 6 pairs. However, since they are all connected to each other, the geometric analogy can be extended to a 3D space: the potential surfaces of all four anchors will cross at a certain nuclear configuration, Q_{PRST} . This point is the crossing point of the four medians connecting the apices of a tetrahedron with the center of the opposite plane. At this point, all diagonal elements of the energy matrix are equal since the four anchors can be arranged at the apices of a perfect tetrahedron. Therefore, a 4×4 matrix can be written of the form:

$$\begin{pmatrix} A-E & B & B & B \\ B & A-E & B & B \\ B & B & A-E & B \\ B & B & B & A-E \end{pmatrix} \quad (\text{II.3a})$$

which diagonalizes to eq II.3b.

$$\begin{pmatrix} A-B-E & 0 & 0 & 0 \\ 0 & A-B-E & 0 & 0 \\ 0 & 0 & A-B-E & 0 \\ 0 & 0 & 0 & A+3B-E \end{pmatrix} \quad (\text{II.3b})$$

Two electronic levels are obtained at Q_{PRST} , a ground state and an electronic excited state now separated by $4B$. One of them is nondegenerate (energy $A + 3B$), and the other, *3-fold degenerate* (energy $A - B$). The energy ordering of these states is determined by the nature of the elementary ground-state reactions around the point Q_{PRST} in a manner analogous to that of the three-anchor case.

In general, for $m = 2, 3$, or 4 , two states are formed: one is nondegenerate, and the other is $(m - 1)$ -fold degenerate. Mathematically, this procedure can be extended to any whole number m : a symmetric matrix of any order can be constructed. Diagonalization leads to $m - 1$ equal roots whose values are $A - B$, and one root is equal to $A + (m - 1)B$.

However, the extension of the procedure is *physically* unfeasible: in a 3D space, the off-diagonal matrix elements cannot be made equivalent for these larger systems. The geometric analogue would be a perfect m -fold polyhedron ($m \geq 5$) in which *all* distances between *any* two apices are the same—obviously an absurdity. A 3-fold degeneracy is thus the highest that can be attained by this procedure.³⁰

The prescription for finding *all* 3-fold degeneracies in a given molecular system follows directly from this analysis. All possible four-anchor combinations (quartets) need to be considered, leading to 4×4 matrices of the form of eq II.3a. The degeneracies are found by diagonalization.

Two-fold degeneracies are found by a similar procedure: starting with the 3-fold degeneracy, nuclear motions distort the system so that three of the anchors that are isoenergetic are sought. There are four possible ways to do this for any quartet of anchors. Each separates the 4×4 matrix blockwise into a 3×3 and a 1×1 matrix. At the nuclear configuration at which, say, the three anchors P, R, and S are equivalent, Q'_{PRS} , the resulting 3×3 submatrix, is symmetric (as is eq II.2a). In it, $A' = \langle \phi_{\text{P}} | \text{H} | \phi_{\text{P}} \rangle = \langle \phi_{\text{R}} | \text{H} | \phi_{\text{R}} \rangle = \langle \phi_{\text{S}} | \text{H} | \phi_{\text{S}} \rangle$ is the diagonal matrix element at that nuclear geometry. The matrix element $A_{\text{TT}'} = \langle \phi_{\text{T}} | \text{H} | \phi_{\text{T}'} \rangle$ has a different value, and $B_{\text{TP}'} = B_{\text{TR}'} = B_{\text{TS}'} = 0$. By the same reasoning as applied above, the off-diagonal elements B' are equal (except for those involving T):

$$B' = \langle \phi_{\text{P}} | \text{H} | \phi_{\text{R}} \rangle = \langle \phi_{\text{P}} | \text{H} | \phi_{\text{S}} \rangle = \langle \phi_{\text{R}} | \text{H} | \phi_{\text{S}} \rangle$$

The 3×3 symmetric submatrix can be diagonalized, leading to a doubly degenerate state whose energy is $A' - B'$ and a nondegenerate state (energy $A' + 2B'$) at each Q'_{PRS} . This case has been dealt with above so that in sum the system has one doubly degenerate electronic ground state and two nondegenerate electronic states at this nuclear configuration, for each of the possible three-way interactions. If two or more of the original anchors are equivalent, then the resulting states are isoenergetic and may further interact.

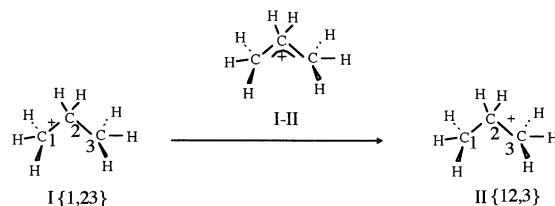


Figure 1. Two basic anchors of the propane⁺ radical cations are I and II. The reaction connecting them was found²⁶ to proceed via an out-of-phase transition state (I-II) obtained by the out-of-phase combination of I and II. The spin-pairing schemes of the electrons of anchors I and II exchanged in the reaction are shown.

III. Examples

Simple systems that demonstrate the ideas of this paper are singly charged radical cations derived from neutral molecules having single chemical bonds only. Removing a single electron from a bond connecting two atoms results in a positive charge on the bond, leading to an anchor with a well-defined spin-pairing arrangement. The number of distinct anchors that can be prepared in this way equals the number of chemical bonds in the parent molecule.

The general procedure has been applied to the methane, ethane, propane, isobutane, and neopentane radical cations and is discussed in a separate paper.³¹ The results obtained for $\text{CH}_3\text{CH}_2\text{CH}_3^{+\bullet}$ are briefly reported here without proof, for completeness. This example was chosen because the point group to which propane⁺ belongs contains no degenerate irreducible representations. Notwithstanding, a 3-fold degeneracy and two 2-fold degeneracies do exist for the ground state in this system, as shown below.

The propane radical cation was previously discussed as a two-state system.³² This choice is based on experiment—ESR data were interpreted as showing two equivalent minima³³ in which the charge is situated on one of the two C—C bonds. The transition state between these two minima (of $C_{2v}(^2B_2)$ symmetry) is formed by an out-of-phase combination of the wave functions corresponding to the two minima;³² see Figure 1. This transition state is very low lying and was thought to be a minimum by some workers.³⁴ This result, which was derived on the basis of symmetry considerations, is also obvious using the spin-paired approach, as three electrons (grouped in two electron pairs) are repaired in the reaction converting them (Figure 1).

Even if the discussion is limited only to the intact molecule (as done in the previous work³²), it is clear from section II that the complete characterization of the ground-state potential surface requires the consideration of other anchors (in addition to I and II). Figure 2 shows the 10 different anchors resulting from the removal of an electron from a single bond of propane. Of all of these possible spin-pairing structures, only anchors I and II exist in a nuclear configuration that lies at an energy minimum. Nonetheless, other anchors must have an impact on the ground-state topology that is expressed by stationary points. Recalling that a three-state system necessarily leads to a degeneracy, the search is begun by looking for a third anchor that together with I and II will form a phase-inverting loop. If such a loop is found, then a conical intersection will be encircled by it. The reaction depicted in Figure 1 is phase-inverting. In the absence of a third minimum on the ground-state potential surface, a simple three-anchor loop cannot be formed. This search is therefore directed at a *second* transition state between I and II that is phase-preserving and involves one of the anchors III—X. A natural choice is either III or IV: by symmetry, only these

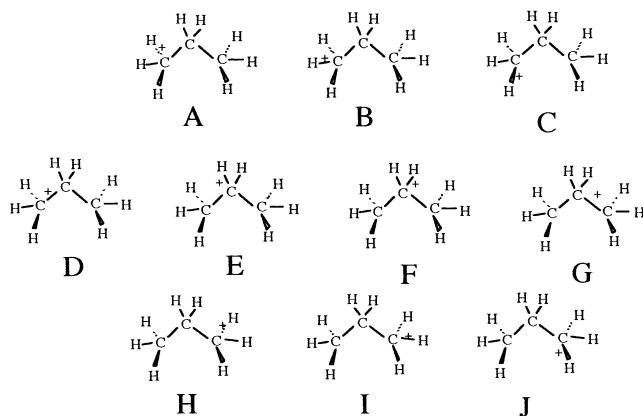


Figure 2. Ten anchors of the propane radical cation system considering only the parent ion (no fragments).

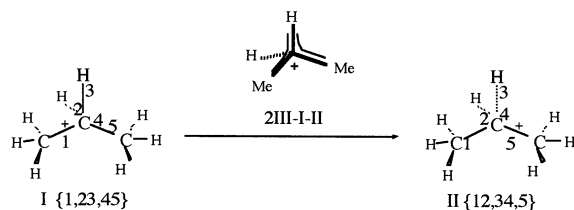


Figure 3. Different elementary reaction connecting I with II. In the transition state, the charge is distributed over two CC bonds and one of the CH bonds. An equivalent transition state involves the other H atom. The reaction is phase-preserving, and three electron pairs are exchanged. The spin-pairing schemes of the electrons of anchors I, II, and III relevant to the reaction are also shown. The wave function of this transition state is formed by the in-phase combination of III-I and III-II. (Note that the out-of-phase combination is I-II, namely, the out-of-phase transition state of Figure 1.) The ground-state nuclear configurations of the two transition states are quite different.

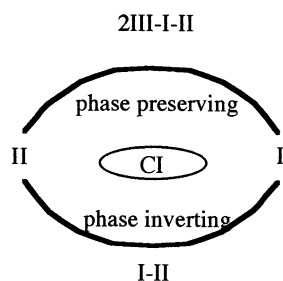


Figure 4. Two-anchor loop encircling a conical intersection. The two minima are connected by two different reaction coordinates: one is phase-inverting, and the other, phase-preserving.

two can have equal interactions with I and II. A transition state constructed from I, II, and III involves five electrons (two of which form the CH bond) and lies along a phase-preserving route, as shown in Figure 3.

This transition state is a stationary point on the ground potential surface, reflecting the existence of anchor III.

The phase-inverting loop formed by the two reactions is shown schematically in Figure 4. Extension to a 3-fold degeneracy is now straightforward: the four anchors leading to it are I, II, III, and IV. Further details are discussed in a separate publication.³¹

All species predicted by the model were located by high-level quantum chemical calculations.³¹ The computed energies and structures of these species agreed with the qualitative predictions of the model. Further details and numerical results are reported in ref 31.

It was stated in section II that in a large system (more than four anchors) the diagonal matrix elements in the secular matrix

may be equal whereas the off-diagonal elements cannot be equalized. This can be demonstrated in a symmetric radical cation such as bipyramidal PH_5^+ : the positive charge can be placed on any of the five P-H bonds, leading to five equivalent anchors. All diagonal elements of the 5×5 matrix analogous to II.3a are equal, but obviously the off-diagonal elements are not all equal. Thus, in this system, the highest degree of electronic degeneracy is 3-fold.

IV. Discussion

The original idea of Teller was that in a two-state system¹² an electronic degeneracy cannot be obtained by varying only one parameter. When magnetic effects can be neglected (as is the case for light atoms), no more than two parameters are required. His approach was based on perturbation theory; the strength of the perturbation was assumed to depend linearly on the parameters (nuclear coordinates).¹⁴ A further development of this view uses the concept of vibronic coupling^{4,35,36}—one looks for the most effective vibration that couples two electronic states. Herzberg and Longuet-Higgins¹ noted that the electronic wave function changes sign when carried in a complete loop around an electronic degeneracy. Salem emphasized the role of biradicaloid structures in polyatomic molecules.³⁷ Gerhartz and Michl used a similar approach in their well-known paper on the H_4 system.³⁸ These workers recognized the perfect tetrahedral geometry as a touching “point” of S_1 and S_0 .

Following Teller’s idea of a perturbed two-state system, Robb, Bernardi, and Olivucci³⁹ define two vectors based on the concept of two states Ψ_1 and Ψ_2 (Ψ_1 and Ψ_2 are the eigenfunctions of the molecular Hamiltonian). One is the gradient difference vector $\mathbf{x}_1 = \partial(E_1 - E_2)/\partial\mathbf{q}$ where E_1 and E_2 are the energies of the two electronic states and $d\mathbf{q}$ is a vector of nuclear displacement. The other (\mathbf{x}_2) is parallel to the direction \mathbf{g} of the diabatic coupling matrix $\mathbf{g} = \langle \Psi_1 | \partial\Psi_2 / \partial\mathbf{q} \rangle$. Yarkoni⁵ developed further the perturbative approach.⁴⁰ He also defined two vectors $\mathbf{g}(\mathbf{Q}_x)$ and $\mathbf{h}(\mathbf{Q}_x)$ in the vicinity of the nuclear configuration \mathbf{Q}_x at which an intersection occurs. The problem of locating the conical intersection reduces to finding the two vectors.

In this paper, a nonperturbative approach is proposed. The basic assumption is that a central role is played by spin pairing in determining molecular structures or proper combinations of them in defining stationary points (minima, transition states) on the ground-state potential surface. At these points, the Born–Oppenheimer approximation is valid.

To consider electronic degeneracies, the two-state model is extended to three- and four-state models. In other words, rather than introducing parameters to a two-state problem, the dimensionality of the system is increased. The coordinates leading to the electronic degeneracies (where the BO approximation breaks down) are constructed from the reaction coordinates leading from one anchor to another. Extending the two-state concept to a three- or four-state concept results in the natural appearance of the electronic degeneracies, regardless of nuclear symmetry. The emphasis is on the *region* in which the degeneracy is to be found, which is defined by the three anchors, rather than on the *point* of degeneracy.

The highest possible degree of electronic degeneracy is 3-fold, a limit imposed by the 3D character of all molecular systems. A pertinent issue is the total number of such degeneracies in a given system. By the arguments of section II, in a large system, half of the 4×4 matrices that can be constructed lead on average to ground-state 3-fold degeneracies. Thus, the maximum number of these species equals one-eighth of the independent anchors that exist in the system (provided they are connected by elementary reactions).

The 3-fold degeneracy serves as a reference point for the construction of the potential surface. Starting from the geometry of the triple degeneracy, one 2-fold degeneracy results from each of the “3 + 1” distortions that discern one anchor from the other three (section II). It follows that each triple degeneracy generates four distinct conical intersections in its vicinity. (Because of symmetry restrictions, in some cases only two different conical intersections are formed.³¹ In any case, the 2-fold degeneracies are formed in pairs—an odd number is not possible). The whole system may be considered to be an ensemble of quartets of anchors that determine the nature of the electronic degeneracies.

In the special case of the propane radical cation, we have seen that two-anchor loops can be formed (instead of the more common three-anchor ones). This is due to the fact that in this system anchors III and IV do not occupy an energy minimum at any nuclear geometry. Their impact is revealed by the existence of phase-inverting transition states between the stable geometries of anchors I and II: they are formed by out-of-phase combinations of III (or IV) with I and II (Figure 4). In this case, two phase-inverting loops and one phase-preserving loop surround the 3-fold degeneracy. (See ref 31.)

In large molecules, it may be possible to observe higher degeneracies because of the coexistence of several noninteracting identical groups. Accidental multiple degeneracies may occur in large systems such as C₆₀, in which the distance between different parts is large enough to minimize interaction,⁴¹ or if the overall symmetry leads to orthogonal wave functions. Such higher degeneracies are found, for instance, in free atoms (d, f, and higher orbitals)—these orbitals are orthogonal to each other and do not interact. Another example is the icosahedral group that has irreducible representations of degrees 4 and 5.

A point that must be addressed is whether the predicted 3-fold degeneracies do in fact exist in a real system. A prerequisite is the partitioning of the secular matrix into noninteracting 4 × 4 units. Therefore, 3-fold degeneracies should be found at molecular geometries in which the bond angles and distances minimize interactions with other anchors. The computed results obtained for propane⁺ and other radical cations³¹ show that this condition is indeed satisfied.

An analysis of the properties of open-shell systems such as radical cations shows that the reaction leading from one isomer to another (sometimes referred to as electromers³²) may proceed along two different reaction coordinates. Potential surfaces supporting two different reaction routes between two molecules are not commonly encountered in closed-shell system. They seem to be common in open-shell ones.

V. Summary

A general procedure for finding all electronic degeneracies in nonsymmetric molecular systems has been presented. The electronic degeneracies due to interactions between atoms bound to the same atom are either 2-fold (conical intersections) or 3-fold degenerate but are not of a higher dimension. The 3-fold degeneracy is a general property of all molecular systems having four or more atoms. The highest possible degree of degeneracy due to this mechanism is 3-fold, which upon proper distortions yields an even number of 2-fold ones (conical intersections). A corollary of this result is that there is no solitary conical intersection—there is at least one more in its neighborhood. The number of different spin-paired options that can be constructed governs the maximum number of degeneracies. Teller’s description¹² of electronic curve-crossing (conical intersections) was based on a single coordinate and a perturbative approach—in

essence, a two-state model. In this paper, electronic degeneracies were discussed in terms of two or three coordinates, extending the model to three or four basic states. The added states are most readily recognized as being derived from different chemical species, and the coordinates connecting them are reaction coordinates. The complete ground-state potential surface may be constructed from quartets of spin-paired species. These “parent” four-state systems connect smoothly with three-state and two-state subsystems, which lead to minima (i.e., stable chemical species). Higher degeneracies, such as those appearing in much larger molecules or if the point symmetry is very high (the icosahedral group), are “accidental” in the sense of the present treatment (they do not arise from interactions between neighboring atoms).

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- (22) For a discussion of anchors, see refs 20 and 21. Anchors are most easily visualized as valence bond species in which all possible structures of a given spin-pairing arrangement are included. In particular, it includes both covalent and ionic structures. An anchor may have a minimum, but quite often a minimum is obtained only if a combination of several anchors is constructed (e.g., benzene). See also Coulson, C. A. *Valence*, 2nd ed. Oxford University Press: London, 1961; Chapter 5.
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- (28) The diagonal terms are equal by construction. Any normalized combination of the three basic functions ϕ_p , ϕ_R , and ϕ_S is also an eigenfunction of the Hamiltonian at this point, with the same eigenvalue.

The off-diagonal terms of the matrix are also equal. Consider, for instance, the combinations $\phi_P + \phi_R - \phi_S$, $\phi_P - \phi_R - \phi_S$, and $-\phi_P + \phi_R + \phi_S$. The matrix elements $\langle \phi_P + \phi_R - \phi_S | H | \phi_P + \phi_R - \phi_S \rangle$ and $\langle \phi_P - \phi_R - \phi_S | H | \phi_P - \phi_R - \phi_S \rangle$ are both equal to A. Expanding, we get $H_{PS} = H_{RS}$, where $H_{PS} = \langle \phi_P | H | \phi_S \rangle$.

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(30) Consider the case of three anchors P, R, and S. The reactions that convert one anchor to another run along a reaction coordinate Q_{PR} , Q_{PS} , and Q_{RS} that consists of combinations of the internal coordinates. Only two of them are independent; the third can be constructed from a linear combination of the other two. The diagonal matrix elements $\langle n | H | n \rangle$ ($n = P, R, \text{ or } S$) can be made equal to each other by varying the values of the internal coordinates of the anchors. This can be done for an arbitrary number of anchors. The interaction energy between any two anchors depends on the location along the reaction coordinate connecting them. In the space spanned by the three anchors, the interaction between any two anchors can be varied only along the two independent coordinates. Therefore, there can be only *one* point at which the three interactions are equal. For the fourth anchor, T, to interact equally with any other two, say P and R, a different plane must be used. That plane is defined by the reaction coordinates that connect P, R, and T. It follows that in a 2D world, the same pairwise

interactions can be realized only for three anchors. The extension to three dimensions is clear.

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