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. Since their introduction as efficient funnels for the radiationless transition between different electronic states, 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.

Teller 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 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. An extension to higher dimensions (namely, to a k-state system where k ≥ 3) leads naturally to electronic degeneracies. It is shown that the highest (nonaccidental) degeneracy in an n atomic system (n ≥ 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 considering the spin pairing of valence electrons. This is an extension of Lewis’ idea that a pair of electrons creates a chemical bond: 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. The term “anchor” is used to define a particular spin-pairing scheme that may exist in many different nuclear configurations.

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 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). Within the Born–Oppenheimer approximation, the corresponding electronic wave functions are \( \phi_P \) and \( \phi_R \), respectively. \( \phi_P \) and \( \phi_R \) 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

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

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 \( k_B \), 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
\(|\psi_P\rangle + |\psi_R\rangle\), and the other, the out-of-phase one \(|\psi_P\rangle - |\psi_R\rangle\).
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, \( Q_{PR} \), has a stationary point (local maximum or
minimum) on the ground-state surface.\(^{15,26}\) Reactions for which
the wave function \(|\psi\rangle_{\text{reaction}}\) is the in-phase combination are
labeled as phase-preserving reactions, and those for which
\(|\psi\rangle_{\text{reaction}}\) 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 \( Q_{RS} \).\(^{25-27}\)

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

\[
\begin{pmatrix}
A - E & B \\
B & A - E
\end{pmatrix}
\]  

(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:

\[
\begin{pmatrix}
A - B - E & 0 \\
0 & A + B - E
\end{pmatrix}
\]  

(II.1b)

The resulting adiabatic wave functions at \( Q_{PR} \) are the in-phase
and out-of-phase combinations \(|\psi_P + \psi_R\rangle\) and \(|\psi_P - \psi_R\rangle\), 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 arrange-
ment. 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 \( \phi_P \), \( \phi_R \), and \( \phi_S \) as
basis functions:

\[
\begin{pmatrix}
A - E & B & B \\
B & A - E & B \\
B & B & A - E
\end{pmatrix}
\]  

(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:

\[
\begin{pmatrix}
A - B - E & 0 & 0 \\
0 & A - B - E & 0 \\
0 & 0 & A + 2B - E
\end{pmatrix}
\]  

(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 \( 2 \times 2 \) 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-preserving, 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 \( p^3 \) loop\(^{10,20,21,29}\)). The nonde-
generate 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 \( 4 \times 4 \) matrix can be written of the form:
which diagonalizes to eq II.3b.

\[
\begin{pmatrix}
A - B & 0 & 0 & 0 \\
0 & A - B & 0 & 0 \\
0 & 0 & A - B & 0 \\
0 & 0 & 0 & A + 3B - E
\end{pmatrix}
\]  

(II.3b)

Two electronic levels are obtained at \(Q_{\text{PRST}}\), a ground state and an electronic excited state now separated by 4\(B\). 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 \(Q_{\text{PRST}}\) 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 \(4 \times 4\) 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 \(4 \times 4\) matrix blockwise into a \(3 \times 3\) and a \(1 \times 1\) matrix. At the nuclear configuration at which, say, the three anchors \(P, R,\) and \(S\) are equivalent, \(Q_{\text{PRST}}\), the resulting \(3 \times 3\) submatrix, is symmetric (as is eq II.2a). In it, \(A' = \langle \phi_1 | H | \phi_1 \rangle = \langle \phi_2 | H | \phi_2 \rangle = \langle \phi_3 | H | \phi_3 \rangle\) is the diagonal matrix element at that nuclear geometry. The matrix element \(B' = \langle \phi_1 | H | \phi_1 \rangle\) has a different value, and \(B' = B_{TS} = B_{TS} = 0\). By the same reasoning as applied above, the off-diagonal elements \(B'\) are equal (except for those involving \(T\):

\[
B' = \langle \phi_1 | H | \phi_2 \rangle = \langle \phi_1 | H | \phi_3 \rangle = \langle \phi_1 | H | \phi_4 \rangle
\]

The \(3 \times 3\) symmetric submatrix can be diagonalized, leading to a doubly degenerate state whose energy is \(A' + 2B'\) and a nondegenerate state (energy \(A' + 2B'\)) at each \(Q_{\text{PRST}}\). 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.

### 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 \(\text{CH}_3\text{CH}_2\text{CH}_3^+\) 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 minima\(^{33}\) in which the charge is situated on one of the two \(\text{C} - \text{C}\) bonds. The transition state between these two minima (of \(C_2\left(2\text{B}_2\right)\) 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 work\(^{32}\)), 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. Thesearch 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
may be equal whereas the off-diagonal elements cannot be equalized. This can be demonstrated in a symmetric radical cation such as bipyramidal Ph$_3^+$: 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 system 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). A further development of this view uses the concept of vibronic coupling—one looks for the most effective vibration that couples two electronic states. Herzberg and Longuet-Higgins 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. Gerhartz and Michl used a similar approach in their well-known paper on the H$_4$ system. 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 Olivucci define two vectors based on the concept of two states $\Psi_1$ and $\Psi_2$ ($\Psi_2$ and $\Psi_3$ are the eigenfunctions of the molecular Hamiltonian). One is the gradient difference vector $x_1 = \partial E_1/\partial q$ where $E_1$ and $E_2$ are the energies of the two electronic states and $q$ is a vector of nuclear displacement. The other ($x_2$) is parallel to the direction of the diabatic coupling matrix $g = \langle \Psi_1 | \partial \Psi_2/\partial q \rangle$. Yarkoni developed further the perturbative approach. He also defined two vectors $g(Q_0)$ and $h(Q_0)$ in the vicinity of the nuclear configuration $Q_0$ 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 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 the electronic degeneracies. (12) (Because of symmetry restrictions, in some cases only two 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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References and Notes

(11) von Neumann, I.; Wigner, E. Phys. Z. 1929, 30, 467.
(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.
(28) The diagonal terms are equal by construction. Any normalized combination of the three basic functions , and 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 \( P + R - S \), \( P - R - S \), and \( -P + R + S \). 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 \( H_{PS} = \langle \phi_P | H | \phi_S \rangle \).


(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 \( \langle n | H | n \rangle \) (\( n = P, R, \) 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.


