Symmetry and degeneracy manifolds in Jahn-Teller molecules

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Abstract: We consider problems in dealing with molecular systems of \( n \) identical nuclei. One problem is that of finding suitable internal coordinates. For \( n \leq 4 \), these can be simply the internuclear distances. For \( n > 4 \), it is shown that, with perhaps one exception, there is no internal coordinate system that treats all nuclei equivalently. We also consider the properties of conical intersections between two Born-Oppenheimer electronic energy surfaces, in particular the problem of identifying the two coordinates that remove the degeneracy to first order in the near neighborhoods of symmetry manifolds.

1. Introduction

In this article, we consider the description of Born-Oppenheimer electronic energies and wave functions in molecular systems containing \( n \) identical nuclei. Section 2 considers the problem of finding an internal coordinate system (dimension \( 3n - 6 \), apart from overall translation and rotation) that, as much as possible, treats the nuclei equivalently. It will be shown that, apart from one possible exception, no completely satisfactory such solution exists for \( n > 4 \). Section 3 considers the behavior of conical intersections between pairs of energy surfaces, concentrating on the case of symmetry-determined \((C_n)\) degeneracy, and for this case, out of the \((3n - 7)\) coordinates that break the degeneracy, identifying the two that make the intersection truly conical, i.e., that break the degeneracy in first order. There is also a brief discussion of other symmetries. There is a brief discussion in Section 4. We wish to emphasize that we are not claiming to give an exhaustive review of the literature, only mentioning a few relevant references, while acknowledging that there are also others. We are also presenting little that is actually new, much of the article being a sort of review, hopefully with new insights into known problems, and emphasizing aspects that are not considered in most treatments.

2. Internal coordinate system

Apart from center-of-mass location and orientation in space, there are \( 3n - 6 \) “internal” coordinates for a system of \( n \) identical nuclei, and naturally it is desirable to choose these coordinates in such a way that all \( n \) nuclei are treated equivalently. This is easily solved if \( n \) is 3 or 4, since for these numbers, and these only, the number of internuclear distances equals the number of desired coordinates [1]:

\[
n(n-1)/2 = 3n - 6 \text{ for } n = 3, 4
\]
Moreover, since permutations of identical nuclei also permute the internuclear distances, the coordinates can be decomposed into subsets belonging to irreducible representations of the permutation groups $S_3$ and $S_4$, as follows:

$n = 3$:

|   |   |   |   |   | dim |
|---|---|---|---|---|-----|
| # | # | # |   |   | (3)  |
| # | # |   |   |   | (2,1) |
| # |   |   |   |   | (1)  |

$n = 4$:

|   |   |   |   |   | dim |
|---|---|---|---|---|-----|
| # | # | # | # |   | (4)  |
| # | # | # |   |   | (3,1) |
| # |   |   |   |   | (2,2) |

In the above table, the Young diagrams for the representations are shown symbolically with # standing for a box, the numbers in parentheses are the numbers of boxes in the rows of the diagrams, and “dim” of course stands for the dimension of the representation.

For more general $n$, we can ask whether there might be a set of symmetric functions of 2 or more nuclei that might serve as coordinates, e.g. $f(a,b)$, a symmetric function of the positions of nuclei $a$ and $b$ (such as the internuclear distance), or $f(a,b,c)$, a symmetric function of nuclei $a$, $b$, and $c$ (such as the area of the triangle formed by the three). Perhaps other types of coordinates may be imagined, but the author has been unable to think of any, so we will restrict ourselves to potential coordinates of this type. For $n > 4$, as we know, the number of such functions is not equal to the number of desired coordinates, $d = 3n - 6$, but we may hope that, when the functions are broken up into combinations belonging to irreducible representations of $S_n$, some one of these, or some combination, might do the trick.

To consider this question, we first observe that there must be some combination of the internal coordinates that is totally symmetric in the nuclei and that represents the overall size of the system, i.e. that belongs to the irreducible representation $(n)$. So our task is to find other irreducible representations whose dimensions add up to $d - l = 3n - 7$. This is also the number of symmetry-breaking coordinates for $C_{nv}$ and other symmetries in which all nuclei are equivalent.

The irreducible representations for symmetric functions of $\nu$ nuclei are:

$(n), (n-1,1), (n-2,2), \ldots, (n-\nu,\nu)$. 
Table 1 shows relevant numbers for symmetric functions of 2 and 3 nuclei, and for \( n \) up to eight.

| \( n \) | \( f(a,b) \) | \( f(a,b,c) \) | \( d-1 \) | \( (n-1,1) \) | \( (n-2,2) \) | \( (n-3,3) \) |
|-------|------------|-------------|---------|-------------|-------------|-------------|
| \( n \) | \( n(n-1)/2 \) | \( n(n-1)x(n-2)/6 \) | \( 3n-7 \) | \( n-1 \) | \( n(n-3)/2 \) | \( n(n-1)x(n-5)/6 \) |
| 3     | 3          | 1           | 2       | 2           | -           | -           |
| 4     | 6          | 4           | 5       | 3           | 2           | -           |
| 5     | 10         | 10          | 8       | 4           | 5           | -           |
| 6     | 15         | 20          | 11      | 5           | 9           | 5           |
| 7     | 21         | 35          | 14      | 6           | 14          | 14          |
| 8     | 28         | 56          | 17      | 7           | 20          | 28          |

Table 1: Data for symmetric functions decomposed into irreducible representations of the permutation groups. Columns 2 and 3 show the number of symmetric functions of the two types, column 4 gives the desired dimension \( d - 1 \), the last three give the dimensions of the three included irreducible representations. Row 2 gives general formulas, the other rows the results for each \( n \).

Perusal of Table 1 shows that, in general, the dimensions of the irreducible representations for \( n > 4 \) do not add up. A possible exception might be for \( n = 5 \) using two different, but independent, symmetric functions, and choosing \((4,1)\), dimension 4, for both. But any such function must be a function only of the relative positions of the two particles, and there does not seem to be any such function that is independent of the internuclear distance.

Much more interesting is the case of \( n = 7 \), for which both \((5,2)\) and \((4,3)\) have dimension 14, exactly what is desired! So for this case it would seem to be feasible to define such a coordinate system, made up of symmetric functions of two or three nuclei, and with all treated equivalently. This would seem to be worthy of further investigation.

Beyond 7, the dimensions of the irreducible representations rapidly become too large, and the same holds if one considers symmetric functions of more than three nuclei. We conclude that \( n = 7 \) is the only reasonably promising possibility.
3. Intersections of Born-Oppenheimer electronic energy surfaces

3a. General considerations

The properties of intersections between Born-Oppenheimer electronic energy surfaces, especially conical intersections, have been the subject of many studies, going back to the classic paper by Jahn and Teller [2] and including those of Longuet-Higgins et al (“LHOPS”) [3] and Herzberg and Longuet-Higgins [4]. Mead and Truhlar [5] have further studied the matter, which turns out to be closely related to the so-called geometric, or Berry, phase [6]. The author has published a review article [7], and more recently there has been one by Wittig [8]. An elegant purely group-theoretical analysis of some aspects of the problem has been given by Ceulemans and Linjen [9].

Throughout this paper, we assume that time-reversal invariance holds, i.e. that there is no external magnetic field, and throughout most of this section we also assume that the total electronic spin is integer, which is equivalent to the possibility of choosing electronic wave functions to be real [10]. A final subsection will present some brief comments on the half-odd integer spin case.

For a system of \( n \) nuclei, the number of internal degrees of freedom (apart from overall translation and rotation) is \( d = 3n - 6 \). As is well known [11], degeneracy of two electronic energy levels requires that two conditions must be satisfied, from which it follows that a degeneracy manifold (the submanifold of the \( d \)-dimensional internal configuration space where degeneracy holds) will be of dimension \( d - 2 = 3n - 8 \), and there will be two coordinates (degeneracy-removing coordinates) that describe the distance of a point in the \( d \)-dimensional space from the degeneracy manifold. For configurations with symmetry, there may be symmetry-determined degeneracy, but the symmetry manifold is in nearly all cases a lower-dimensional submanifold of the degeneracy manifold. For example, for \( C_{nv} \) and regular polyhedron symmetry, the only symmetry-preserving coordinate is the totally symmetrical breathing one, so the dimension of the symmetry manifold is just one.

An intersection is conical if the difference in energy \( \Delta E = E_1 - E_2 \) between the two states depends linearly on the degeneracy-removing coordinates in the infinitesimal neighborhood of the degeneracy; otherwise it is a glancing intersection. For a glancing intersection, not only must the two degeneracy conditions be satisfied, but also all \( d \) components of the gradient of \( \Delta E \) must vanish, a total of \( d + 2 \) conditions. Since the number of conditions for a glancing intersection exceeds the number of available coordinates, this means that intersections must necessarily be conical, except possibly within a symmetry submanifold, where perhaps the gradient may be required by symmetry to vanish. From this point of view, the classic result of Jahn and Teller [2] may be regarded as simply removing this last hope, except for linear configurations.

3b. The Herzberg-Longuet-Higgins sign change

Consider two electronic states, \( \varphi_1 \) and \( \varphi_2 \) which are degenerate at a given point (or manifold) in nuclear configuration space, and define coordinates along the gradients at the degeneracy point of \( (H_{11} - H_{22})/2 \) and \( H_{12} \):

\[
x = r \cos \theta; \quad y = r \sin \theta.
\]  

\( (2) \)
In the near neighborhood of the intersection, the Hamiltonian is proportional to

\[ \hat{H} \propto r \begin{pmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{pmatrix} \]  

(3)

with eigenvalues \( \pm r \) and eigenfunctions

\[ \begin{pmatrix} \frac{\cos \theta}{2} \\ \frac{\sin \theta}{2} \end{pmatrix}, \begin{pmatrix} -\frac{\sin \theta}{2} \\ \frac{\cos \theta}{2} \end{pmatrix}. \]  

(4)

Thus, it is seen that the eigenfunctions undergo a sign change (the Herzberg-Louguet-Higgins, HLH sign change [4]) when the coordinates traverse a full circuit around the intersection, meaning that the real-valued electronic wave functions are not single-valued. The consequences of the HLH sign change have been the subject of many studies [5,6,7].

However, in the case of degeneracies required by symmetry, which are the ones most often studied, one has to be careful about what symmetry-breaking coordinates to use, since not all symmetry-breaking coordinates break the degeneracy in first order, and hence not all generate an HLH sign change. Moreover, the angle \( \theta \) appearing in eq. (1) is not always the same as the natural angle in the coordinate system, and though there may be more than one pair of coordinates with the proper symmetry to remove the degeneracy, only one such pair actually does so.

A simple example is shown in Figure 1.

\[ \begin{align*}
\text{a} & \\
\text{b} & \\
\text{c} \\
\uparrow \\
\end{align*} \]

Figure 1: Triangular pyramid, viewed from above, with the apex atom displaced toward corner \( a \), breaking the \( C_{3v} \) symmetry.

In fig. 1, we define the \( x \) direction as pointing from the baseline \( bc \) to corner \( a \), the \( y \) direction as from corner \( c \) to corner \( b \), and \( z \) perpendicular to the base. The degenerate states are taken to be atomic \( p \) states centered at the center of the base triangle, \( |x\rangle \) and \( |y\rangle \).
the apex moved toward $a$ as in the figure, there is still a plane of symmetry $xz$, so the eigenfunctions will be just $|x>$ and $|y>$, and the effective hamiltonian will be proportional to

$$\hat{h}_a = |x><x| - |y><y|.$$

Similarly, we can define kets rotated through an arbitrary angle $\varphi$:

$$|x_\varphi> = |x\rangle \cos \varphi + |y\rangle \sin \varphi, \quad |y_\varphi> = -|x\rangle \sin \varphi + |y\rangle \cos \varphi$$

and corresponding operators $\hat{h}_\varphi$, also $\hat{h}_b, \hat{h}_c$ for kets rotated toward corners $b, c$, i.e. through angles $\pm 2\pi/3$.

Now, the degeneracy-removing coordinates for this case must belong to irreducible representation (irrep) $E$ of $C_{3v}$, but there are two pairs of coordinates that have this symmetry: the pseudorotation of the atoms at the base, and the $x, y$ coordinates describing the displacement of the apex. Assuming for the present that the base remains equilateral, consider the following possibilities for the apex displacement: First, if the base is very large and the $p$ functions concentrated in a small place, then the wave functions will barely notice the base atoms, and will mainly just follow the apex displacement, so if the apex is displaced at an angle $\theta$ from the $x$ direction, the effective hamiltonian will be proportional to

$$\hat{h}_\theta = \begin{pmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{pmatrix},$$

so the wave function is rotated through half of $2\theta$, or just $\theta$. There is no HLH sign change for the apex displacement, the intersection is glancing with respect to apex displacement, and the degeneracy is removed in first order just through the base pseudorotation.

On the other hand, an equally plausible Hamiltonian for the apex rotation, showing a preference for the nearest base corner to the displaced apex, might be:

$$\hat{h} = \hat{h}_a \cos \theta + \hat{h}_b \cos \left(\theta - \frac{2\pi}{3}\right) + \hat{h}_c \cos \left(\theta + \frac{2\pi}{3}\right)$$

$$= \frac{1}{2} \begin{pmatrix} \cos \theta & -\sin \theta \\ -\sin \theta & -\cos \theta \end{pmatrix}.$$ 

In this case, the wave function is rotated through $\textit{minus}$ one half $\theta$, and there is an HLH sign change. Since base pseudorotation also presumably removes the degeneracy, the true degeneracy-removing coordinate pair is a reinforcing combination of pseudorotation and apex rotation, while they cancel each other in the other combination.

The moral of this is that, when there are two or more coordinate pairs that have the correct symmetry for degeneracy removal, finding the right combination will nearly always require calculation; there will be no purely group-theoretical way to find it.

We now take up the symmetry- and degeneracy-removing combinations for the near neighborhoods of $C_{nv}$ configurations.
3c. *Systems of n identical nuclei near C_{nv} configurations*

In this subsection, we consider systems of \( n \) nuclei distorted slightly from \( C_{nv} \) symmetry. Higher symmetries, such as \( O_h \), have subgroups \( C_{kv} \), so these are really the only groups that need to be considered. The next subsection will contain a brief discussion of other possible symmetries. We emphasize that there is no need to assume that any \( C_{nv} \) configuration is rigid or stable, but only that such configurations exist in the configuration space, which they obviously do. The dimension of the \( C_{nv} \) manifold is just unity. Of the \((3n - 7)\) symmetry-breaking coordinates, we seek to identify the two that break the degeneracy in first order. For this purpose, we need the character tables for the \( C_{nv} \) groups, which are given in Tables 2 and 3:

| \( C_{2v+1,v} \) | \( E \) | \( 2C_{2v+1} \) | \( 2C^2_{2v+1} \) | \( ... \) | \( 2C^{v}_{2v+1} \) | \( (2v+1)\sigma \) |
|------------------|-------|----------------|----------------|-------|----------------|----------------|
| \( A_1 \)        | 1     | 1             | 1             | ...   | 1              | 1              |
| \( A_2 \)        | 1     | 1             | 1             | ...   | 1              | -1             |
| \( E_1 \)        | 2     | 2 cos \( \tau \) | 2 cos 2\( \tau \) | ...   | 2 cos \( \nu \tau \) | 0              |
| \( E_2 \)        | 2     | 2 cos 2\( \tau \) | 2 cos 4\( \tau \) | ...   | 2 cos 2\( \nu \tau \) | 0              |
| \( ... \)        | \( ... \) | \( ... \) | \( ... \) | \( ... \) | \( ... \) | \( ... \) |
| \( E_j \)        | 2     | 2 cos \( j\tau \) | 2 cos \( 2j\tau \) | ...   | 2 cos \( \nu j\tau \) | 0              |
| \( ... \)        | \( ... \) | \( ... \) | \( ... \) | \( ... \) | \( ... \) | \( ... \) |
| \( E_{\nu} \)    | 2     | 2 cos \( \nu \tau \) | 2 cos \( 2\nu \tau \) | ...   | 2 cos \( \nu^2\tau \) | 0              |

...
Table 2: Character table for $C_{nv}$ with $n$ odd, $2\nu + 1$. In the table, $\tau = 2\pi/(2\nu + 1)$.

| $C_{2\nu,v}$ | $E$ | $2C_{2\nu}$ | ... | $2C_{2\nu^{-1}}$ | $C_2$ | $\nu\sigma_v$ | $\nu\sigma_d$ |
|------------|-----|-------------|-----|-----------------|------|--------------|--------------|
| $A_1$      | 1   | 1           | ... | 1               | 1    | 1            | 1            |
| $A_2$      | 1   | 1           | ... | 1               | 1    | -1           | -1           |
| $B_1$      | 1   | -1          | ... | (-1)$^{\nu^{-1}}$ | (-1)$^\nu$ | 1           | -1           |
| $B_2$      | 1   | -1          | ... | (-1)$^{\nu^{-1}}$ | (-1)$^\nu$ | -1          | 1            |
| $E_1$      | 2   | $2\cos \rho$ | ... | $2\cos (\nu^{-1}\rho)$ | -2   | 0           | 0            |
| $E_{\nu^{-1}}$ | 2   | $2\cos (\nu^{-1}\rho)$ | ... | $2\cos (\nu^{-1})^2\rho$ | $2(-1)^{\nu^{-1}}$ | 0           | 0            |

Table 3: Character Table for $C_{nv}$ with $n$ even, $2\nu$. In the table, $\rho = \pi/\nu$.

For most cases, it suffices to restrict ourselves to prime values of $(2\nu + 1)$, since for two primes $p$ and $q$, $C_{pqv}$ can be distorted into $C_{pv}$ or $C_{qv}$ and degeneracy will remain. An exception occurs, e.g. for $E_{nq}$ when distorted to $C_{pv}$. Here the character for the element $C_p$ becomes

$$2\cos\frac{2\pi npq}{qp} = 2$$

and the degeneracy splits into $A_1$ and $A_2$.

For degenerate electronic states with symmetry $E_j$ in $C_{nv}$, the nuclear displacement coordinates that can have nonvanishing matrix elements are those contained in $E_j \times E_j$, for which the characters are:

$$\chi(E) = 4; \chi(C_n^j) = 2 + 2\cos\frac{2\pi (2kj)}{n}; \chi(\sigma) = 0.$$ (9)

This decomposes into $A_1 + A_2 + E_{2j}$. $A_1$ is simply a scalar, shifting both energies equally; $A_2$ is the antisymmetric “cross product” $x_2y_b - x_by_a$, which vanishes for components of the same vector. The potentially degeneracy-removing coordinates in first order are therefore those of $E_{2j}$. But now we have to determine exactly what “$E_{2j}$” means in this context.
For \( n = 2\nu + 1 \), \( \nu \) even: For \( j = 1, 2, 3, \ldots, \nu/2 \), \( 2j \) of course is just \( 2, 4, 6, \ldots, \nu \). For \( j = 1 + \nu/2 \), \( 2j \) is \( \nu + 2 = (2\nu + 1) - (\nu - 1) \), so the effective “\( 2j \)” is \( (\nu - 1) \). For successive \( j \) after this, we get \( \nu - 3, \nu - 5, \) etc.

For \( n = 2\nu + 1 \), \( \nu \) odd: Now we get \( 2, 4, 6, \ldots (\nu - 1) \), then \( (\nu + 1) = (2\nu + 1) - \nu \), so the next ones are \( \nu, \nu - 2, \) etc.

For \( n = 2\nu \), \( \nu \) even, we get \( 2j = 2, 4, 6, \ldots (\nu - 2) \). Next is “\( E_\nu \)”, which is actually \( B_1 + B_2 \). Then the same ones over again: \( \nu - 2, \nu - 4, \) etc.

For \( n = 2\nu \), \( \nu \) odd, we obtain \( 2, 4, 6, \ldots (\nu - 1) \), then \( \nu + 1 = 2\nu - (\nu - 1) \), so we again get the same ones over again, \( \nu - 1, \nu - 3, \) etc.

Now, for each degeneracy, we know the symmetry of the potentially first-order degeneracy-removing coordinates. We must now determine which coordinates have this symmetry, and if there are more of these than are needed, which ones actually do lift the degeneracy in first order.

The coordinates for small deviations from \( C_{nv} \) can be considered to be of three types: Out-of-plane (OP), and in-plane stretch (ST), directly away from or toward the center, and rotation (RO), in plane perpendicular to ST. We first consider \( n = 2\nu + 1 \).

For both OP and ST, the characters are:

\[
\chi(E) = 2\nu + 1; \quad \chi(C) = 0; \quad \chi(\sigma) = 1
\]

\[
\rightarrow A_1 + E_1 + E_2 + \ldots + E_\nu
\]

For RO, it’s the same except that \( \chi(\sigma) = -1 \), so its representations are

\[
A_2 + E_1 + E_2 + \ldots + E_\nu,
\]

and for all the coordinates we have

\[
2A_1 + A_2 + 3(E_1 + E_2 + \ldots + E_\nu). \]

Of these, the OP \( A_1 \) is translation, the OP \( E_1 \) is rotation, and in plane the \( A_2 \) is rotation and one \( E_1 \) is translation, so the remaining true internal coordinates belong to the representations

\[
A_1 + E_1 + 3(E_2 + E_3 + \ldots + E_\nu).
\]

For \( n = 2\nu \), a similar analysis gives for the internal coordinates

\[
A_1 + B_1 + 2B_2 + E_1 + 3(E_2 + E_3 + \ldots + E_{\nu-1}).
\]
The A1 coordinates are symmetry-preserving “breathing” coordinates. Potentially degeneracy-removing are all the E coordinates for odd \( n \), the \( E_{2k} \) for even \( n \), and also \( B_1 \) and \( B_2 \) when \( n \) is a multiple of 4. For odd \( n = 2\nu + 1 \), the \( E_1 \) coordinates are uniquely identified as degeneracy-removing for electronic states degenerate with \( E_\nu \) symmetry, but for all other E symmetries there are three apparent contenders.

The situation is helped somewhat in that we can eliminate the OP E coordinates. These are “folding” coordinates, where the \( n \)-gon is being folded along a diagonal line. A positive fold as viewed from above is the same as a negative one viewed from below, so the lower-energy state is the same for both directions and the intersection is a glancing one with respect to these coordinates.

This still leaves two \( E_j \) coordinate pairs, \( j > 1 \), for each symmetry, and there is no general way to decide which combination is the degeneracy-removing one. For any particular pair of degenerate wave functions, one combination of the two pairs will cancel each other out, the other will remove the degeneracy. Unfortunately, this must be calculated.

We have discussed the determination of degeneracy-removing coordinates in first order, the coordinates that make the intersection truly conical. Relatively little can be said about the global nature of the degeneracy manifolds, but still something can be ascertained. There are \( (n-1)!/2 \) different \( C_{nv} \) configurations, differing by permutations of the nuclei around the ring. Each has its own degeneracy manifold, which we have determined in principle in the near neighborhood of the \( C_{nv} \) configuration. Further away, by continuity, it can be stated that the coordinates of each degeneracy manifold will transform in the same way under \( C_{nv} \), now considered as a subgroup of the permutation group.

3d. Other symmetries

Of course, symmetries other than \( C_{nv} \) are possible. These include octahedral and icosahedral symmetries for appropriate \( n \), and for general \( n \), for example, there is \( C_{kv} \), \( k < n \), for which the dimensionality is \( 1 + n - k \), with \( k \) nuclei forming a regular \( k \)-gon and the others located on the axis through the center of the polygon. The polygon has a breathing degree of freedom, and each of the \( n - k \) other nuclei is allowed to move up and down the axis. For \( n = 2\nu \), for example, there is also the prism-shaped \( C_{vv} \), which has dimension 3, since both \( v \)-gons can breath independently and the height of the prism can change.

3e. Note on half-odd integral spin

In the case where time-reversal invariance holds and the electronic spin is half-odd integer, there is always the two-fold Kramers degeneracy. For an intersection of two Kramers doublets, five conditions are required [10], so here there are cases, such as \( T_d \) symmetry for \( n = 4 \), in which the dimensions of symmetry and degeneracy manifolds are identical. The analog of the HLH sign change is a unitary transformation in the space of a doublet upon being taken along a closed path [7].

4. Discussion

We have discussed two problems connected with systems of \( n \) identical nuclei: The problem of constructing an internal coordinate system treating the nuclei equivalently, as nearly as possible, and that of determining the coordinates that lift a symmetry-determined degeneracy
to first order, thus making the intersection truly conical. The results are not of a sensational nature, but still we hope that our treatment will be somewhat useful.

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