

Chapter 9

Permutational Symmetry and Role of Nuclear Spin in Vibrational Spectra. The Alkali Metal Trimers

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9.1 Introduction

The full quantum mechanical study of nuclear dynamics in molecules has received considerable attention in recent years. An important example of such developments is the work carried on the prototypical systems H_3 ,¹⁻³ Li_3 ,⁴⁻⁷ Na_3 ,^{8,9} and HO_2 .¹⁰⁻¹³ In particular, for the alkali metal trimers, the possibility of a conical intersection between the two lowest doublet potential energy surfaces introduces a complication that makes their theoretical study fairly challenging. Thus, alkali metal trimers have recently emerged as ideal systems to study molecular vibronic dynamics, especially the so-called geometric phase (GP) effect^{8,14,15} (also known as the molecular Aharonov-Bohm effect¹⁴ or Berry's phase effect¹⁶); for further discussion on this topic see Refs. 17, 18, and references therein. The same features turn out to be present too in the case of HO_2 , and their exact treatment assumes even further complexity.¹³

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For Li_3 , Gerber and Schumacher⁴ reported the lowest vibrational levels and have shown that vibronic coupling is essential to describe the electronic ground state giving rise to the so-called dynamic Jahn-Teller effect. In turn, Mayer and Cederbaum⁵ have studied the rovibronic coupling in the electronic A system of Li_3 . Most recently, Kendrick⁹ reported quantum mechanical calculations on the vibrational spectrum of Na_3 using a generalized Born-Oppenheimer treatment. However, a question emerges when we carry out quantum mechanical calculations using, *e.g.*, the efficient MINRES filter diagonalization (MFD) technique.^{6,19} For example, for the $J = 0$ vibrational states of the $^1\text{H}_3$ electronic ground state, one may compute the full spectrum of the corresponding Hamiltonian, and hence, the problem arises of whether all calculated eigenfunctions are “true” molecular vibrational states. We will provide an answer to this question in the following sections of this Chapter.

Symmetry considerations have long been known to be of fundamental importance for an understanding of molecular spectra.^{20–22} Since electrons and nuclei have distinct statistical properties, the total molecular wave function must satisfy appropriate symmetry requirements. In this Chapter, we discuss the permutational symmetries of the total wave function and its various components for a molecule under the permutation of identical particles. Double group theory will be used as a powerful tool to analyze the molecular states, and an extension of Kramers’ theorem^{20,22} to its most general form presented. The significant role of nuclear spin will then be emphasized, and some severe consequences demonstrated. Thus, the material presented in this Chapter may be helpful for a detailed understanding of molecular spectra and collisional dynamics.

9.2 Total molecular wave function

The molecular time-independent nonrelativistic Schrödinger equation assumes the form

$$\hat{H}_{tot}(\mathbf{x}, \mathbf{r}, \mathbf{i}, \mathbf{s})\Psi_{tot}(\mathbf{x}, \mathbf{r}, \mathbf{i}, \mathbf{s}) = E\Psi_{tot}(\mathbf{x}, \mathbf{r}, \mathbf{i}, \mathbf{s}) \quad (9.1)$$

where $\hat{H}_{tot}(\mathbf{x}, \mathbf{r}, \mathbf{i}, \mathbf{s})$ is the total molecular Hamiltonian operator, and E the total energy. In turn, $\Psi_{tot}(\mathbf{x}, \mathbf{r}, \mathbf{i}, \mathbf{s})$ is the total molecular wave function and \mathbf{x} and \mathbf{r} denote collectively the spatial coordinates of the nuclei and electrons, while \mathbf{i} and \mathbf{s} denote the corresponding nuclear and electronic spin coordinates, respectively. For a system consisting of N nuclei and n electrons, there are $3N$ nuclear spacial coordinates and $3n$ electronic ones. Besides these, there are intrinsic coordinates, namely the spin coordinates of every particle. Considering triatomic molecules, the six nuclear coordinates relative to the center of mass consist of three internal and three external coordinates. The former may be taken as the hyperspherical coordinates^{2,23–27} (ρ, θ, ϕ) , while the external or orientational coordinates may be chosen to be the usual Euler angles (α, β, γ) . As illustrated in Figure 9.1, these define the orientation of the body-fixed (BF) frame relative to the space-fixed (SF) frame. In the following sections, we differentiate between these two types of coordinates by expressing $\mathbf{x} = (x, \hat{x})$, where $x = (\rho, \theta, \phi)$ and $\hat{x} = (\alpha, \beta, \gamma)$.

In the strictest meaning, the total wave function cannot be separated since there are many kinds of interactions between the nuclear and electronic degrees of freedom

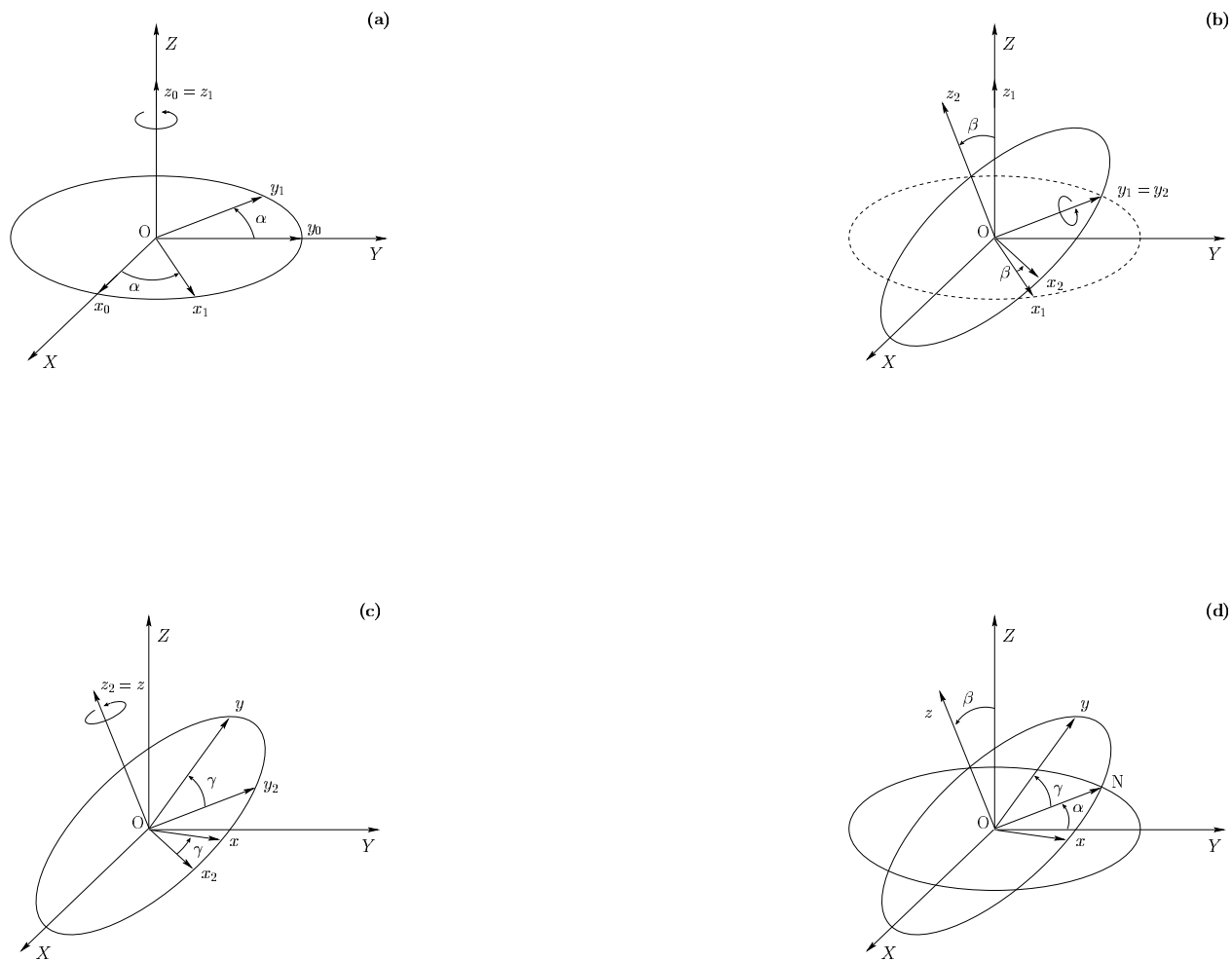


Figure 9.1: The space-fixed (XYZ) and body-fixed (xyz) frames. Any rotation of the coordinate system (XYZ) to (xyz) may be performed by three successive rotations, denoted by the Euler angles (α, β, γ) , about the coordinate axes as follows: (a) rotation about the Z -axis through an angle α ($0 \leq \alpha < 2\pi$), (b) rotation about the new y_1 -axis through an angle β ($0 \leq \beta \leq \pi$), (c) rotation about the new z_2 -axis through an angle γ ($0 \leq \gamma < 2\pi$). The relative orientations of the initial and final coordinate axes are shown in panel (d).

(see later). However, for practical purposes, one can separate the total wave function partially or completely, depending on considerations relative to the magnitude of the various interactions. The most popular separation arises when one ignores all but the coulombic interactions involving the nuclei and electrons. Accordingly, the total molecular wave function is divided in two parts: one, refers to the electronic wave function $\Psi_e(\mathbf{r}, \mathbf{s}; x)$, the other to the nuclear wave function $\Psi_{nuc}(\mathbf{x}, \mathbf{i})$. Of course, one must consider vibronic or rovibronic states when the interactions between electronic and vibrational or rovibrational states cannot be ignored. Regarding the nuclear wave function, it is reasonable to separate the translational part if the interaction between the translational and the other (rotational and vibrational) nuclear degrees of freedom can be ignored. This is typically the case in studies of spectroscopy and collisional dynamics where the measured properties depend on the motions of the interacting species relative to each other but not on the motion of the system as a whole, *i.e.*, the space is assumed to be isotropic. In this case, after separation of the centre of mass² motion, the total Hamiltonian operator can be written in SF coordinates as

$$\hat{H}_{tot} = -\frac{\hbar^2}{2\mu}\nabla^2 + \hat{H}_e(\mathbf{r}, \mathbf{s}; x) \quad (9.2)$$

where, *e.g.*, for a triatomic molecule, ∇^2 is the six-dimensional Laplacian with respect to the six nuclear coordinates \mathbf{x} , μ is the three-body reduced mass $\mu = (m_A m_B m_C / M)^{1/2}$, $\hat{H}_e(\mathbf{r}, \mathbf{s}; x)$ is the electronic Hamiltonian which depends parametrically on the x coordinates, m_A, m_B , and m_C are the masses of nuclei A, B, and C, and $M = m_A + m_B + m_C$.

One then assumes that the electronic part of the problem has been solved for the electronic energy eigenvalues $V_k(x)$ and eigenfunctions φ_k in BF coordinates

$$\hat{H}_e(\mathbf{r}, \mathbf{s}; x)\varphi_k(\mathbf{r}, \mathbf{s}; x) = V_k(x)\varphi_k(\mathbf{r}, \mathbf{s}; x) \quad (9.3)$$

where \mathbf{r} denotes all the electronic coordinates relative to the BF system of coordinates. As already stated, we ignore all magnetic interactions and consider only those of coulombic nature between the various particles. Thus, *e.g.*, for a triatomic molecule, both the eigenvalues and eigenfunctions depend parametrically on the three internal nuclear coordinates.

The total molecular wave function can now be expanded in terms of a complete set of electronic eigenfunctions as follows

$$\Psi_{tot}(\mathbf{x}, \mathbf{r}, \mathbf{i}, \mathbf{s}) = \Psi_{ns}(\mathbf{i}) \sum_{k=0} \Psi_{vr,k}(\mathbf{x})\varphi_k(\mathbf{r}, \mathbf{s}; x) \quad (9.4)$$

where the $\Psi_{vr,k}(\mathbf{x})$ and $\Psi_{ns}(\mathbf{i})$ are the rovibrational and nuclear spin wave functions, respectively; the separation of the spin part from the spatial part of the nuclei wave function can be justified as usual based on the order of magnitude of the associated energies (see later for the electrons case). The Coriolis interaction is a well known rovibrational interaction. However, if we neglect the interaction between the vibrational and rotational degrees of freedom, the rovibrational wave function can be further partitioned as the product of a pure vibrational, $\Psi_v(x)$, and a pure rotational, $\Psi_r(\hat{x})$, wave functions. On

²The problem of separating the centre-of-mass motion in a molecular system is an intricate one which has no implications on the present work; the interested reader is referred to Ref. 28 for details.

the other hand, for low energies, and a nondegenerate ground electronic state, one can neglect the coupling to excited electronic states and truncate the sum in Eq. (9.4) to only one term. This leads to the standard Born-Oppenheimer approximation.

Unfortunately, in the presence of a conical intersection (for further details, see section 9.10.4) the Born-Oppenheimer approximation described in the previous paragraph becomes invalid. As first pointed by Herzberg and Longuet-Higgins,²⁹ due to the conical intersection, a real electronic wave function changes sign when traversing a nuclear path which encircles the conical intersection. Since the total electronuclear wave function must be continuous and single-valued, the nuclear wave function must change sign to compensate that of the electronic wave function. Mead and Truhlar^{14,30,31} have shown that the required sign change in the nuclear wave function can be accounted for by introducing a vector potential into the nuclear Schrödinger equation. For a X_3 -type molecule, the same result can be achieved by multiplying the real double-valued electronic wave function by a complex phase factor which changes sign on encircling the conical intersection which arises for D_{3h} geometries such that the resulting complex electronic wave function becomes single-valued.³²⁻³⁴ The complex phase factor leads then to the vector potential. Billing and Markovic³⁵ adopted hyperspherical coordinates within the complex phase factor approach to include such a GP effect in X_3 molecules which have a single D_{3h} conical intersection, since in this coordinate system the GP effects concern only the ϕ hyperangle. A similar approach has been utilized by Varandas and Yu² to study the transition state resonances and bound vibrational states of H_3 using a time-dependent wavepacket method. Because all the above methods still use only one electronic state, they can be said to be based on a generalized Born-Oppenheimer approximation.³⁶ As our recent studies on the electronically ground doublet state⁶ (and ongoing calculations for the first excited doublet state⁷) of 7Li_3 have shown, the GP effect plays a significant role for this system too.

9.3 Group theoretical considerations

As it is well known, when the electronic spin-orbit interaction is small, the total electronic wave function $\Psi_e(\mathbf{r}, \mathbf{s}; x)$ can be written³ as the product of a spatial wave function $\Psi'_e(\mathbf{r}; x)$ and a spin wave function $\Psi_{es}(\mathbf{s})$. For this, we can use either the SF or the BF coordinate systems. As shown below, it is more appropriate to use BF spin wave functions, since they will be affected by molecular symmetry operations and hence must belong to one of the irreducible representations of the symmetry point group of the molecule. For example, for integral spin values, the transformation $\exp(im_S\varphi)$ for rotation by $\varphi = 2\pi$, where $m_S = S, S-1, \dots, -S$, leads to a retrieval of the spin wave function to itself.²⁰ However, when the spin is half-integral, such a transformation (*i.e.*, a rotation by 2π) will lead to a sign change of the spin wave function. Indeed, if $\varphi' = \varphi + 2\pi$ and $m_S = l/2$ where l is an integer, one has $\exp(im_S\varphi') = -\exp(im_S\varphi)$. The spin wave function will then be double-

³Although for a Slater-type determinant wave function this is true for only two-particle systems, the following discussion is independent of such a restriction.

valued: a rotation by 2π will not bring the system to its starting point, which can only be achieved through a 4π rotation. A rotation by 2π is therefore a new symmetry element, called R (to denote the corresponding operator we use \hat{R} ; such a hat-notation is generally used in this work also for other operators), with respect to which any spin function may be either symmetric or antisymmetric. As a result there are new symmetry elements $\hat{R}Y_i$, where Y_i stands for any of the original symmetry elements (*e.g.*, C_2 , σ , C_3 , ...). Such extended point groups are commonly referred to as double groups,²⁰ and we give some examples in Table 9.1; the lines indicate the separation between the traditional point group and its extension. Note that, for twofold axes (C_2) and planes of symmetry (σ), the new elements ($\hat{R}C_2$ and $\hat{R}\sigma$) belong to the same class as the original elements and cause only a doubling of the class. For axes more than twofold and the centre of symmetry, they cause a doubling of the number of classes. For example, the class designed $2\hat{C}_3$ of the ordinary point group \mathbf{D}_{3h} has two elements C_3 and C_3^2 , while the double group has two extra elements C_3^4 and C_3^5 in the class $2\hat{C}_3^2$, since $\hat{R}C_3 = C_3^4$ and $\hat{R}C_3^2 = C_3^5$. Similarly, one has $\hat{R}S_3 = S_3^5$; for further details, the reader is referred to Herzberg's²⁰ book.

It should also be noted that on reducing the symmetry of a system, the spin wave functions for integral spin are resolved by reducing degeneracies.²⁰ In simple words, this means that by reducing the symmetry, the degenerate spin states in the high-symmetry group split into different states in the lower-symmetry group. However, the spin wave functions for half-integral spin are at most resolved into functions which are still doubly degenerate. Indeed, we may see from Table 9.2 that, for integral S or I , on going from \mathbf{D}_{3h} to \mathbf{C}_{2v} the E'' representation transforms to $B_1 + B_2$. Conversely, for S or I half-integral, the same resolution maintains the E -type degenerate representation. This remaining degeneracy is usually called Kramers' degeneracy to honour the author who first discovered it.^{20,22} According to Kramers' theorem, provided that no external magnetic field is present, the degeneracy of a system consisting of an odd number of identical particles with half-integral spin (fermions) is even. Equivalently, Kramers' theorem states that the electronic (nuclear) wave functions of systems with total electronic (nuclear) spin half-integral are evenly degenerate. This is due to the fact that, as long as no magnetic field is present, there is in all atomic and molecular systems an additional symmetry element that corresponds to the antilinear time reversal operator \hat{T} (see Appendix 9.13): the evolution of a system (classical or quantum) is invariant when the time t is replaced by $-t$. In fact, an extension of Kramers' theorem will be demonstrated to be valid also for systems with a half-integral total angular momentum quantum number J .

Table 9.1: Species and characters of the extended C_2 , C_{2v} , C_{3v} and D_{3h} point groups.

| \mathbf{C}_2 | \hat{I} | $\hat{C}_2(z)$ | \hat{R} | | |
|-----------------|-----------|----------------|-----------|----|--|
| A | 1 | 1 | | 1 | |
| B | 1 | -1 | | 1 | |
| $E_{1/2}^{(a)}$ | 2 | 0 | | -2 | |

| \mathbf{C}_{2v} | \hat{I} | $\hat{C}_2(z)$ | $\hat{\sigma}_v(xz)$ | $\hat{\sigma}_v(yz)$ | \hat{R} |
|-------------------|-----------|----------------|----------------------|----------------------|-----------|
| A_1 | 1 | 1 | 1 | 1 | 1 |
| A_2 | 1 | 1 | -1 | -1 | 1 |
| B_1 | 1 | -1 | 1 | -1 | 1 |
| B_2 | 1 | -1 | -1 | 1 | 1 |
| $E_{1/2}$ | 2 | 0 | 0 | 0 | -2 |

| \mathbf{C}_{3v} | \hat{I} | $2\hat{C}_3$ | $3\hat{\sigma}_v$ | \hat{R} | $2\hat{C}_3^2$ |
|-------------------|-----------|--------------|-------------------|-----------|----------------|
| A_1 | 1 | 1 | 1 | 1 | 1 |
| A_2 | 1 | 1 | -1 | 1 | 1 |
| E | 2 | -1 | 0 | 2 | -1 |
| $E_{1/2}$ | 2 | 1 | 0 | -2 | -1 |
| $E_{3/2}$ | 2 | -2 | 0 | -2 | 2 |

Table 9.1: (cont.)

| \mathbf{D}_{3h} | \hat{I} | $2\hat{S}_3(z)$ | $2\hat{C}_3(z)$ | $\hat{\sigma}_h$ | $3\hat{C}_2$ | $3\hat{\sigma}_v$ | \hat{R} | $2\hat{S}_3^5$ | $2\hat{C}_3^2$ |
|-------------------|-----------|-----------------|-----------------|------------------|--------------|-------------------|-----------|----------------|----------------|
| A'_1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| A'_2 | 1 | 1 | 1 | 1 | -1 | -1 | 1 | 1 | 1 |
| A''_1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 |
| A''_2 | 1 | -1 | 1 | -1 | -1 | 1 | 1 | -1 | 1 |
| E'' | 2 | 1 | -1 | -2 | 0 | 0 | 2 | 1 | -1 |
| E' | 2 | -1 | -1 | 2 | 0 | 0 | 2 | -1 | -1 |
| $E_{1/2}$ | 2 | $\sqrt{3}$ | 1 | 0 | 0 | 0 | -2 | $-\sqrt{3}$ | -1 |
| $E_{3/2}$ | 2 | 0 | -2 | 0 | 0 | 0 | -2 | 0 | 2 |
| $E_{5/2}$ | 2 | $-\sqrt{3}$ | 1 | 0 | 0 | 0 | -2 | $\sqrt{3}$ | -1 |

^{a)} As usual, the indices 1/2, 3/2, and 5/2 which appear in the doubly degenerate E representation indicate the values of the projection of the angular momentum vector, $m_J = \pm 1/2, \pm 3/2, \pm 5/2$.

Table 9.2: Species of spin functions for some important double groups.

| S or I | \mathbf{C}_2 | \mathbf{C}_{2v} | \mathbf{C}_{3v} | \mathbf{D}_{3h} |
|------------|----------------|--------------------------|----------------------|-------------------------------|
| 0 | A | A_1 | A_1 | A'_1 |
| 1/2 | $E_{1/2}$ | $E_{1/2}$ | $E_{1/2}$ | $E_{1/2}$ |
| 1 | $A + 2B$ | $A_2 + B_1 + B_2$ | $A_2 + E$ | $A'_2 + E''$ |
| 3/2 | $2E_{1/2}$ | $2E_{1/2}$ | $E_{1/2} + E_{3/2}$ | $E_{1/2} + E_{3/2}$ |
| 2 | $3A + 2B$ | $2A_1 + A_2 + B_1 + B_2$ | $A_1 + 2E$ | $A'_1 + E' + E''$ |
| 5/2 | $3E_{1/2}$ | $3E_{1/2}$ | $2E_{1/2} + E_{3/2}$ | $E_{1/2} + E_{3/2} + E_{5/2}$ |

Consider then the total angular momentum \mathbf{J} defined by

$$\mathbf{J} = \mathbf{S} + \mathbf{I} + \mathbf{L} + \mathbf{N} \quad (9.5)$$

where \mathbf{S} , \mathbf{I} , \mathbf{L} , and \mathbf{N} are the total electronic spin, nuclear spin, electronic orbital angular momentum, and nuclear orbital angular momentum. For this general case, we can prove that Kramers' theorem still applies since spin and orbital angular momenta must obey the same time-reversal properties (see Appendix 9.14), namely

$$\hat{T}\hat{S}\hat{T}^{-1} = -\hat{S}; \quad \hat{T}\hat{L}\hat{T}^{-1} = -\hat{L} \quad (9.6)$$

$$\hat{T}\hat{I}\hat{T}^{-1} = -\hat{I}; \quad \hat{T}\hat{N}\hat{T}^{-1} = -\hat{N} \quad (9.7)$$

where \hat{A} represents as usual the operator corresponding to the angular momentum (vector) \mathbf{A} , while the quantum number A defines the eigenvalue $A(A+1)$ of \hat{A}^2 . Thus,

$$\hat{T}(\hat{S} + \hat{L})\hat{T}^{-1} = -(\hat{S} + \hat{L}); \quad \hat{T}(\hat{I} + \hat{N})\hat{T}^{-1} = -(\hat{I} + \hat{N}) \quad (9.8)$$

$$\hat{T}(\hat{S} + \hat{I})\hat{T}^{-1} = -(\hat{S} + \hat{I}); \quad \hat{T}(\hat{L} + \hat{N})\hat{T}^{-1} = -(\hat{L} + \hat{N}) \quad (9.9)$$

and hence

$$\hat{T}\hat{J}\hat{T}^{-1} = -\hat{J} \quad (9.10)$$

Eq. (9.6) to Eq. (9.10) imply that all types of angular momenta have the same time-reversal properties. In fact, it is well known^{37,38} that quantities such as energy, coordinates, electric field strength and so on are invariant under time-reversal: the corresponding operators must be time-invariant. In turn, the velocity, linear momentum, angular momentum, magnetic field strength and so on change sign under time-reversal: the corresponding operators must reflect the same property.

Moreover, as also shown in Appendix 9.14 for the electronic spin, one has

$$\hat{T}_S^2 = (-\hat{1})^{2S} \quad (9.11)$$

where hereafter the operator \hat{T}_A stands for a time-reversal operation on the \mathbf{A} variable. Similarly, for the nuclear spin, one has

$$\hat{T}_I^2 = (-\hat{1})^{2I} \quad (9.12)$$

Thus,

$$\hat{T}_I^2 \hat{T}_S^2 = (-\hat{1})^{2(I+S)} \quad (9.13)$$

and finally

$$\hat{T}_J^2 = (-\hat{1})^{2J} \quad (9.14)$$

since

$$\hat{T}_L^2 = (-\hat{1})^{2L} = \hat{1}; \quad \hat{T}_N^2 = (-\hat{1})^{2N} = \hat{1} \quad (9.15)$$

Note that \hat{T}_S , \hat{T}_I , \hat{T}_L , and \hat{T}_N operate on the corresponding degrees of freedom, and hence mutually commute. Note especially that L and N assume always integer values.

At this stage we are ready to prove that Kramers' theorem holds also for the total angular momentum \mathbf{J} . We will do it by *reductio ad absurdum*. Let then $|\Psi_E\rangle$ be the eigenvector of \hat{H} with eigenvalue E ,

$$\hat{H}|\Psi_E\rangle = E|\Psi_E\rangle \quad (9.16)$$

where we use hereafter the Dirac bra-ket notation. Since \hat{T} commutes with \hat{H} , one gets

$$\hat{H}\hat{T}|\Psi_E\rangle = E\hat{T}|\Psi_E\rangle \quad (9.17)$$

Suppose now that the total wave function (state) is nondegenerate, and J is half-integral. From Eq. (9.17) it then follows

$$\hat{T}|\Psi_E\rangle = c|\Psi_E\rangle \quad (9.18)$$

where c is a constant, and hence

$$\hat{T}^2|\Psi_E\rangle = \hat{T}c|\Psi_E\rangle = c^*\hat{T}|\Psi_E\rangle = |c|^2|\Psi_E\rangle \quad (9.19)$$

Note that the third equality in Eq. (9.19) holds due to the fact that \hat{T} is anti-unitary (see Appendix 9.13), and hence can be expressed as

$$\hat{T} = \hat{U}\hat{K} \quad (9.20)$$

where \hat{U} is an unitary operator and \hat{K} the complex conjugate operator. Clearly, Eq. (9.19) is in contradiction with the initial hypothesis that $\hat{T}^2 = -\hat{1}$. The eigenstates of a system with half-integral J must therefore be degenerate, as we wished to demonstrate.

We now prove that the degeneracy must be even. For this, we should first demonstrate two Lemmas: 1) $|\Psi_E\rangle$ is orthogonal to $\hat{T}|\Psi_E\rangle$ if $\hat{T}^2 = -\hat{1}$; 2) $\hat{T}|\Psi'_E\rangle$, $|\Psi_E\rangle$ and $\hat{T}|\Psi_E\rangle$ form a set of mutually orthogonal functions, provided that $|\Psi'_E\rangle$ is orthogonal both to $|\Psi_E\rangle$ and $\hat{T}|\Psi_E\rangle$. Considering first Lemma 1, one has

$$\langle\Psi_E|\hat{T}|\Psi_E\rangle = -\langle\Psi_E|\hat{T}^{\dagger 2}\rangle\langle\hat{T}|\Psi_E\rangle \quad (9.21)$$

$$= -\left[\langle\Psi_E|\hat{T}^\dagger\rangle\langle\hat{T}^\dagger\hat{T}|\Psi_E\rangle\right]^* \quad (9.22)$$

$$= -\left[\langle\Psi_E|\hat{T}^\dagger\rangle|\Psi_E\rangle\right]^* \quad (9.23)$$

$$= -\langle\Psi_E|\hat{T}|\Psi_E\rangle \quad (9.24)$$

where the first equality is obtained owing to the fact that $\hat{T}^2 = -\hat{1}$; the second to the fact that \hat{T} is antilinear, and hence obeys the property $\langle\psi|\hat{T}|\varphi\rangle = \left[\langle\psi|\hat{T}|\varphi\rangle\right]^*$ (see Appendix 9.13); the third results from the anti-unitary property of \hat{T} (*i.e.*, $\hat{T}^\dagger\hat{T} = \hat{1}$); finally, Eq. (9.24) follows from applying again the fact that \hat{T} is antilinear, and hence $\langle\varphi|\hat{T}|\psi\rangle = \left[\langle\psi|\hat{T}^\dagger|\varphi\rangle\right]^*$. Thus, Eq. (9.21) to Eq. (9.24) imply that $\langle\Psi_E|\hat{T}|\Psi_E\rangle = 0$, which completes the proof of Lemma 1.

Let us now prove Lemma 2. One has

$$\langle T\Psi'_E|\Psi_E\rangle = \left(\langle\Psi'_E|\hat{T}^\dagger\rangle|\Psi_E\rangle\right) \quad (9.25)$$

$$= \left[\langle\Psi'_E|\hat{T}^\dagger|\Psi_E\rangle\right]^* \quad (9.26)$$

$$= \left[\langle\Psi'_E|\hat{T}^{\dagger 2}\hat{T}|\Psi_E\rangle\right]^* \quad (9.27)$$

$$= -\left[\langle\Psi'_E|\hat{T}|\Psi_E\rangle\right]^* \quad (9.28)$$

$$= 0 \quad (9.29)$$

and

$$\langle T\Psi'_E | (\hat{T}|\Psi_E\rangle) = (\langle \Psi'_E | \hat{T}^\dagger) (\hat{T}|\Psi_E\rangle) \quad (9.30)$$

$$= [\langle \Psi'_E | (\hat{T}^\dagger \hat{T}|\Psi_E\rangle)]^* \quad (9.31)$$

$$= [\langle \Psi'_E | \Psi_E \rangle]^* \quad (9.32)$$

$$= 0 \quad (9.33)$$

which completes the desired proof.

Finally, we can demonstrate that the degeneracy is even when the total angular momentum quantum number J is half-integral, again via a *reductio ad absurdum* method. Suppose that the degeneracy of the eigenstates is k , then we have k degenerate states $|\Psi_{E,i}\rangle$ ($i = 1, \dots, k$), which have in common the same eigenvalue E . One can then form orthogonal pairs of such states such as $|\Psi_E\rangle$ and $\hat{T}|\Psi_E\rangle$. If k is odd, there will be a single state, *e.g.*, $|\phi\rangle$ which has no pair. However, as mentioned above, $\hat{T}|\phi\rangle$ will be orthogonal to all the k states, and $\hat{T}|\phi\rangle$ is nonzero. This implies that the number of total states of the same eigenvalue E is $(k + 1)$, which contradicts our initial hypothesis. Thus, we conclude that k must be even, and hence proved the generalized Kramers' theorem for total angular momentum.

An inevitable deduction from the generalized Kramers' theorem is that the rotational states of a system with half-integral quantum number J must be evenly degenerate. Note that half-integral total angular momentum quantum numbers only originate from half-integral electronic spin or half-integral nuclear spin, but not when they are both half-integral. Note also that the pure rotational part of the Hamiltonian involves the square of an angular momentum, and hence satisfies the property $\hat{T}\hat{H}_{rot}\hat{T}^{-1} = \hat{H}_{rot}$ (*i.e.*, \hat{H}_{rot} commutes with \hat{T}). However, this result does not rule out the possibility of having degenerate rotational states for integer J values. Indeed, our previous demonstration refers only to the half-integral case with $\hat{T}^2 = -\hat{1}$. In any case, the implication is that we can use double groups as a powerful means to study the rotation of molecular systems, since they become subgroups of the 3D rotation group $\mathbf{SO}(3)$. Thus, we may use Table 9.2 and Table 9.3 (or more extended versions of them²⁰) to analyse the symmetry of the rotational wave function for molecules belonging to any symmetry point group.

9.4 Permutational symmetry of total wave function

The total Hamiltonian operator \hat{H}_{tot} must commute with any permutations \hat{P}_X among identical particles (X) due to their indistinguishability. For example, for a system including three types of distinct identical particles like ${}^7\text{Li}_2 {}^6\text{Li}_2$ with a T_d conformation, one must satisfy the following commutative laws

$$\left[\hat{P}_e, \hat{H}_{tot} \right] = 0; \quad \left[\hat{P}_{7\text{Li}}, \hat{H}_{tot} \right] = 0; \quad \left[\hat{P}_{6\text{Li}}, \hat{H}_{tot} \right] = 0 \quad (9.34)$$

Table 9.3: Resolution of species of symmetric point groups into some point groups of lower symmetry.

| \mathbf{K}_h | \mathbf{D}_{3h} | \mathbf{C}_{3v} | \mathbf{C}_{2v} | \mathbf{C}_s |
|--------------------|--------------------|-------------------|--------------------------|----------------|
| $D_g^0 \equiv S_g$ | A'_1 | A_1 | A_1 | A' |
| $D_u^0 \equiv S_u$ | A''_1 | A_2 | A_2 | A'' |
| $D_g^1 \equiv P_g$ | $A'_2 + E''$ | $A_2 + E$ | $A_2 + B_1 + B_2$ | $A' + 2A''$ |
| $D_u^1 \equiv P_u$ | $A''_2 + E'$ | $A_1 + E$ | $A_1 + B_1 + B_2$ | $2A' + A''$ |
| $D_g^2 \equiv D_g$ | $A'_1 + E' + E''$ | $A_1 + 2E$ | $2A_1 + A_2 + B_1 + B_2$ | $3A' + 2A''$ |
| $D_u^2 \equiv D_u$ | $A''_1 + E' + E''$ | $A_2 + 2E$ | $A_1 + 2A_2 + B_1 + B_2$ | $2A' + 3A''$ |

and hence \hat{P}_X ($X = e, {}^7\text{Li}, {}^6\text{Li}$) are conservative quantities. For a system with N distinct sets of identical particles, there must be N such commutative laws similar to those in Eq. (9.34) which are relative to the various kinds of permutations; thus, there will be N permutational restrictions on the total wave function $\Psi_{tot}(\mathbf{x}, \mathbf{r}, \mathbf{i}, \mathbf{s})$. It must be noted from Figure 9.1(d) and Figure 9.2 that under the permutation of two identical nuclei, the hyperspherical coordinates transform as $(\rho, \theta, \phi, \alpha, \beta, \gamma) \rightarrow (\rho, \theta, -\phi, \alpha, \beta, \gamma + \pi)$.

We will now explain the meaning of the word “identical” used above. Physically, it is meant for particles which possess the same intrinsic attributes, *e.g.*, static mass, charge, spin, parity, and so on. If such particles possess the same intrinsic attributes (as many as we know so far), then we refer to them as physically identical. There is also another kind of identity, which is commonly referred to as chemical identity.³⁹ As discussed in the next paragraph, this is an important concept which must be stressed when discussing the permutational properties of nuclei in molecules.

Let us then first examine ${}^7\text{Li}_3$ in a D_{3h} structure. In this molecule, the three nuclei have not only the same intrinsic attributes but also the same molecular environments due to the fact that they are in chemically equivalent positions. Thus, the three nuclei can be exchanged by rotations of the molecule and the permutational symmetry requirement must be satisfied. Consider now a molecule like CH_3OH with four physically identical hydrogens. For any conformation, the methyl hydrogens will be distinguishable from one another through their positions relative to that of the hydroxyl hydrogen. However, the barrier for internal rotation of CH_3 around the CO axis is low, and tunneling from one equivalent conformation to another may occur. Thus, the permutational symmetry requirement must be applied to the methyl hydrogens. A third example is the linear conformation of NNO , with two physically identical nitrogen nuclei. In principle, the permutational symmetry requirement should also be applied to the two ${}^{14}\text{N}$ nuclei since they are physically identical. However, the two nuclei are placed at different molecular

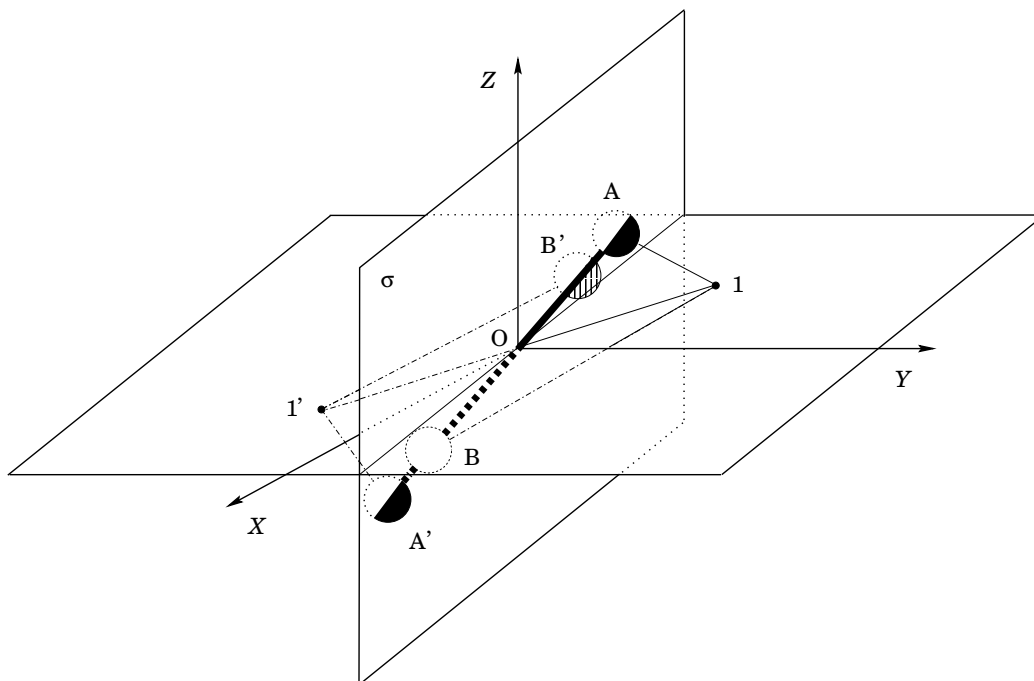


Figure 9.2: The space-fixed (XYZ) and body-fixed (xyz) frames in a diatomic molecule AB . The nuclei are at A and B , and 1 represents the location of a typical electron. The results of inversions of their SF coordinates are $A \rightarrow A'$, $B \rightarrow B'$ and $1 \rightarrow 1'$, respectively. After one executes only the reinversion of the electronic SF coordinates, one obtains $1' \rightarrow 1$. The net effect is then the exchange of the SF nuclear coordinates alone.

environments, *i.e.*, one lies adjacent to the oxygen nucleus while the other does not. Since their permutation involves an extremely high energy process, we may regard such nitrogen nuclei as distinguishable. They can then be said to be chemically nonequivalent,³⁹ and hence not subject to the permutational symmetry requirement in low-energy spectroscopic studies. We should note though that, if their interchange becomes feasible by increasing the energy, the potential energy surface must satisfy the full permutational symmetry requirement dictated by the physical identity alone; this is typically the case in reaction dynamics studies. Another example is the molecule $\text{H}^{12}\text{C} \equiv ^{13}\text{CH}$ where two hydrogen atoms have nonequivalent chemical environments. Again, although the two hydrogen atoms may be distinguishable from the spectroscopic point of view, the corresponding full potential energy surface must generally be symmetric with respect to their permutation; note that in the Born-Oppenheimer approximation, the potential energy surface does not depend on the mass of the nuclei, and hence it is the same as for $\text{H}^{12}\text{C} \equiv ^{12}\text{CH}$. In summary, the permutational symmetry requirement should be applied only to identical particles which are both physically and chemically indistinguishable. In this case, chemical identity implies physical identical particles which have equivalent environments in the molecule and can be brought about by proper rotations of the nuclear framework, or else physically identical particles which may have equivalent chemical environments through some feasible dynamical process. Thus, the concept of chemical identity depends on the

energy regime under consideration. Ideally, one should therefore carry out the nuclear dynamics studies using a global potential energy surface^{40,41} which has built-in the full permutational symmetry implied by the physical identity of the atoms. Of course, if the equivalent minima are separated from each other by high energy barriers, then it may be an excellent approximation to have just the representation for one of the equivalent minima if one assumes that underbarrier tunneling is negligible. In other words, the concept of chemical identity delimits the nuclei motion to a part of the molecule configuration space. Hereafter, we will refer to identical particles with the above understanding.

Let us examine a special but more practical case where the total molecular Hamiltonian, \hat{H}_{tot} , is partitioned into a sum of a nuclear part, $\hat{H}_{nuc}(\mathbf{x})$, and an electronic part, $\hat{H}_e(\mathbf{r}, \mathbf{s}; x)$, as it is the case in the usual Born-Oppenheimer approximation. As a result, the total molecular wave function $\Psi_{tot}(\mathbf{x}, \mathbf{r}, \mathbf{i}, \mathbf{s})$ is given by the product of a nuclear wave function $\Psi_{nuc}(\mathbf{x}, \mathbf{i})$ and an electronic wave function $\Psi_e(\mathbf{r}, \mathbf{s}; x)$. Thus, we may talk separately about the permutational properties of the subsystem consisting of electrons, and the subsystem(s) consisting of identical nuclei. Accordingly, the following commutative laws $[\hat{P}_e, \hat{H}_e] = 0$ and $[\hat{P}_X, \hat{H}_N] = 0$ must be satisfied; $X = A, B, \dots$, and all other symbols have their usual meaning.

As pointed out in the previous paragraph, the total wave function of a molecule consists of an electronic and a nuclear parts. The electrons have a different intrinsic nature from nuclei, and hence can be treated separately when one considers the issue of permutational symmetry. Let us consider first the case of electrons. These are fermions with spin 1/2, and hence the subsystem of electrons obeys the Fermi-Dirac statistics: the total electronic wave function must be antisymmetric under permutation of any two electrons (both their spatial and spin coordinates). This requirement implies the Pauli exclusion principle, which states that two electrons cannot occupy the same spin orbital.

Commonly, nuclear dynamics treatments in molecules neglect the interactions between the nuclear spin and the other nuclear and electronic degrees of freedom in the system Hamiltonian. As a result, the eigenenergies become independent of the nuclear spin. In this case, one must impose the requirements that the symmetry properties of the nuclear spin on the total wave function are satisfied, since the nuclei in the molecule have their specific statistical properties. As it is well known, nuclei having zero or integral nuclear spin quantum numbers are bosons and must obey the Bose-Einstein statistics: the nuclear wave function must therefore be symmetric under permutation of any two identical bosonic particles. On the other hand, nuclei having half-integral spin quantum numbers are fermions and must obey the Fermi-Dirac statistics: the nuclear wave function must in this case be antisymmetric with respect to the permutation of any two fermionic nuclei. For example, ${}^7\text{Li}$ is a fermion with nuclear spin 3/2, and ${}^6\text{Li}$ is a boson with nuclear spin 1. Thus, the total wave function of ${}^7\text{Li}_3$ must be antisymmetric under the permutation of the three identical nuclei (note that this involves a three-pair change); see the corresponding \mathcal{S}_3 permutational group in Table 9.4. Conversely, the total wave function of ${}^6\text{Li}_3$ must be symmetric under the permutation of the three identical nuclei. In turn, the total wave

function of ${}^7\text{Li}_2 {}^6\text{Li}$ must be antisymmetric under the permutation \mathcal{S}_2 of the two identical ${}^7\text{Li}$ nuclei (see also Table 9.4 for the \mathcal{S}_2 permutational group). Following the same reasoning, the total wave function of ${}^6\text{Li}_2 {}^7\text{Li}$ must be symmetric under the permutation of the two identical ${}^6\text{Li}$ nuclei.

Table 9.4: Species and characters of the \mathcal{S}_2 and \mathcal{S}_3 permutational groups.

| | | | |
|-----------------|-------------------|--------|-------|
| | | | |
| \mathcal{S}_2 | (1) | (12) | |
| | | | |
| | [2] | 1 | 1 |
| | [1 ²] | 1 | -1 |
| | | | |
| | | | |
| \mathcal{S}_3 | (1) | 2(123) | 3(12) |
| | | | |
| | [3] | 1 | 1 |
| | [1 ³] | 1 | -1 |
| | [21] | 2 | 0 |
| | | | |

Let us discuss further the permutational symmetry properties of the nuclei subsystem. Since the electronic spatial wave function $\Psi'_e(\mathbf{r}; x)$ depends parametrically on the nuclear coordinates, it must take into account the correct permutational properties of the identical nuclei. Of course, the spin part of the electronic wave function is independent of the permutational properties of the nuclei. This implies that one does not need to take care of the electronic spin wave function when dealing with the permutational properties of the nuclei. However, as it will be further discussed in section 9.8, the electronic spin \mathbf{S} will influence the permutational symmetry properties through the total angular momentum \mathbf{J} . Without loss of generality, we address in the following sections the consequences of such rules based on the premise that the total wave function $\Psi_{tot}(\mathbf{x}, \mathbf{r}, \mathbf{i}, \mathbf{s})$ may be written as

$$\Psi_{tot}(\mathbf{x}, \mathbf{r}, \mathbf{i}, \mathbf{s}) = \Psi_e(\mathbf{r}, \mathbf{s}; x) \Psi_v(x) \Psi_r(\hat{x}) \Psi_{ns}(\mathbf{i}) \quad (9.35)$$

where $\Psi_e(\mathbf{r}, \mathbf{s}; x)$, $\Psi_v(x)$, $\Psi_r(\hat{x})$ and $\Psi_{ns}(\mathbf{i})$ are the electronic, vibrational, rotational and nuclear spin wave functions, respectively.

9.5 Permutational symmetry of nuclear spin wave function

As discussed before, the nuclear spin wave functions must belong to one of the irreducible representations of the double group of the molecule. For example, ${}^6\text{Li}_3$ may have nuclear spin quantum numbers I equal to 0, 1, 2 and 3, and hence the permutational symmetries under \mathcal{S}_3 will be given according to Table 9.2: A'_1 for $I = 0$; $A'_2 + E''$ for $I = 1$; $A'_1 + E' + E''$ for $I = 2$, and so on. For a molecule with half-integral nuclear spin, all the irreducible representations are double-valued due to the Kramers' degeneracy. For example, for ${}^7\text{Li}_3$, the nuclear spin quantum numbers I are half-integral ranging in steps of 1 from $1/2$ up to $9/2$. Thus, according to Table 9.2, the permutation symmetries under \mathcal{S}_3 will be: $E_{1/2}$ for $I = 1/2$; $E_{1/2} + E_{3/2}$ for $I = 3/2$; $E_{1/2} + E_{3/2} + E_{5/2}$ for $I = 5/2$, and so on.

For a nucleus with spin quantum number $I \neq 0$, there are $(2I + 1)$ values of the z -component m_I of the nuclear spin angular momentum, with $m_I = -I, -I + 1, \dots, I - 1, I$. For two such nuclei, the total number of m_I combinations will then be $(2I + 1)^2$. Assuming that $\chi_{m_I}(1)$ is the nuclear spin wave function of nucleus 1 with quantum number m_I , there are $(2I + 1)$ spin wave functions of the form $\chi_{m_I}(1)\chi_{m_I}(2)$ which are symmetric. Of the remaining $(2I + 1)^2 - (2I + 1)$ wave functions, half can be combined in symmetric states

$$\Psi_{ns}^S(1, 2) = \frac{1}{\sqrt{2}} \left[\chi_{m_I}(1)\chi_{m'_I}(2) + \chi_{m'_I}(1)\chi_{m_I}(2) \right], \quad m_I \neq m'_I \quad (9.36)$$

and the other half in antisymmetric ones

$$\Psi_{ns}^A(1, 2) = \frac{1}{\sqrt{2}} \left[\chi_{m_I}(1)\chi_{m'_I}(2) - \chi_{m'_I}(1)\chi_{m_I}(2) \right], \quad m_I \neq m'_I \quad (9.37)$$

The total number of symmetric states is then

$$2I + 1 + \frac{1}{2} [(2I + 1)^2 - (2I + 1)] = (2I + 1)(I + 1) \quad (9.38)$$

and the total number of antisymmetric states is

$$\frac{1}{2} [(2I + 1)^2 - (2I + 1)] = (2I + 1)I \quad (9.39)$$

In summary, for a homonuclear diatomic molecule there are generally $(2I + 1)(I + 1)$ symmetric and $(2I + 1)I$ antisymmetric nuclear spin wave functions. For example, from Eq. (9.38) and Eq. (9.39), the statistical weights of the symmetric and antisymmetric nuclear spin wave functions of ${}^7\text{Li}_2$ will be $5/8$ and $3/8$, respectively. This is also true when one considers ${}^7\text{Li}_2$ ${}^6\text{Li}$ and ${}^6\text{Li}_2$ ${}^7\text{Li}$. For the former, the statistical weights of the symmetric and antisymmetric nuclear spin wave functions are $5/8$ and $3/8$, respectively; for the latter, they are $2/3$ and $1/3$ in the same order.

For a homonuclear triatomic molecule there are similarly²¹ $(2I + 1)(2I + 3)(I + 1)/3$ symmetric, $(2I + 1)(2I - 1)I/3$ antisymmetric, and $(2I + 1)(I + 1)(8I)/3$ degenerate nuclear spin wave functions. For ${}^7\text{Li}_3$, one has therefore 20 symmetric, 4 antisymmetric, and 40

degenerate nuclear spin wave functions. The corresponding statistical weights will then be 5/16, 1/16, and 10/16. Following a similar reasoning for ${}^6\text{Li}_3$ one finds 10 symmetric, 1 antisymmetric, and 16 degenerate nuclear spin wave functions. Thus, the corresponding statistical weights are 10/27, 1/27, and 16/27.

Consider now a linear polyatomic molecule. If this is of the type $Z \cdots \text{BAAB} \cdots Z$ with $D_{\infty h}$ geometry, a \hat{C}_2 rotation about an axis perpendicular to the molecular axis at its midpoint will exchange pairs of identical nuclei. If the nuclei A, B, \cdots , Z contain an odd number of fermions, the \hat{C}_2 rotation leads to a change of sign of the total wave function; otherwise, it will remain unchanged. By repeated application of the two identical nuclei case, the total number of possible nuclear spin wave functions will be given by $(2I_A + 1)^2(2I_B + 1)^2 \cdots (2I_Z + 1)^2$, where I_X denotes the nuclear spin of X ($X = A, B, \cdots, Z$). Similarly, the number of possible symmetric and antisymmetric nuclear spin wave functions can be obtained by an extension of the method used for diatomic molecules. The total number of symmetric states is then given by³⁹

$$(2I_A + 1)(2I_B + 1) \cdots (2I_Z + 1) [(2I_A + 1)(2I_B + 1) \cdots (2I_Z + 1) + 1] / 2 \quad (9.40)$$

and the total number of antisymmetric states is³⁹

$$(2I_A + 1)(2I_B + 1) \cdots (2I_Z + 1) [(2I_A + 1)(2I_B + 1) \cdots (2I_Z + 1) - 1] / 2 \quad (9.41)$$

which represent the corresponding nuclear statistical weights. For molecules of the form $Z \cdots \text{BARAB} \cdots Z$ with $D_{\infty h}$ symmetry, the corresponding numbers must each be multiplied by³⁹ $(2I_R + 1)$.

9.6 Permutational symmetry of electronic wave function

In considering the nuclear permutational properties of the total wave function we must have in mind the corresponding properties of the electronic wave function, since this depends parametrically on the nuclear geometry. The permutational properties of $\Psi_e(\mathbf{r}, \mathbf{s}; x)$ under identical-nuclei exchange are determined by those of $\hat{H}_e(\mathbf{r}, \mathbf{s}; x)$ and hence of $V_k(x)$. Since this represents the potential energy of the electrons in the field of the fixed nuclei, it must have the symmetry of the molecule in its k -th electronic state. The electronic eigenfunctions for nondegenerate states can therefore only be symmetric or antisymmetric with respect to each symmetry operation which is allowed by the symmetry of the molecule in its equilibrium geometry. For degenerate states, a symmetry operation can only transform an eigenfunction into a linear combination of the degenerate eigenfunctions such that the electron density remains unaltered.

Let us begin by considering a homonuclear diatomic molecule. Clearly, permutation of the nuclei does not affect the internuclear distance, but it does affect the electronic spatial coordinates, since they are defined with respect to the BF axes. To find the effect of interchanging nuclei on the electronic wave function, we invert first the SF coordinates of the

nuclei and electrons, and then carry out a second inversion of the SF electronic coordinates alone. The net effect will be the exchange of the SF coordinates of the two nuclei as illustrated in Figure 9.2. The first inversion leaves the electronic wave functions unchanged for Σ^+, Π^+, \dots electronic states, while it changes their sign for Σ^-, Π^-, \dots electronic states. This is due to the fact that reflection in the plane containing the nuclei changes (leaves unchanged) the sign of wave function for $- (+)$ states. Because only the Σ^+ and Σ^- have different energies,³⁹ it is often omitted the \pm sign for degenerate states such as $\Pi, \Delta \dots$ provided that Λ -type doubling is ignored. The second of the above mentioned inversion operations inverts the electron BF coordinates and therefore the electronic wave functions can be classified as g or u states according to whether such inversion of the electronic BF coordinates changes or leaves unchanged the sign of the electronic wave function. In summary, $\Sigma_g^+, \Sigma_u^-, \Pi_g^+, \Pi_u^- \dots$ electronic states have wave functions which are symmetric under the permutation of identical nuclei, whereas $\Sigma_g^-, \Sigma_u^+, \Pi_g^-, \Pi_u^+ \dots$ electronic states are antisymmetric under such a permutation. The permutational symmetry for linear polyatomics follows similar arguments.

Consider now nonlinear molecules, and let us focus on the electronic wave function of ground state Li_3 . This is known to have B_2 symmetry at its equilibrium geometry in the \mathbf{C}_{2v} point group, and hence will be antisymmetric in \mathcal{S}_3 . In fact, in the B_2 irreducible representation of \mathbf{C}_{2v} , the wave function changes sign under a \hat{C}_2 operation. As seen from Table 9.4, the equivalent operation in \mathcal{S}_3 will be the permutation of two particles, say (12), which transforms as $[1^3]$ (this corresponds to the A_2 irreducible representation in the isomorphic \mathbf{D}_{3h} or \mathbf{C}_{3v} symmetry point groups; see Table 9.1). In turn, the electronic wave function at the lowest point of the conical intersection on the upper sheet of the Li_3 potential energy surfaces has degenerate character under \mathcal{S}_3 , since this geometry transforms as E' in the \mathbf{D}_{3h} symmetry point group. Consider next the isotopomer ${}^7\text{Li}_2 {}^6\text{Li}$. With the substitution of ${}^7\text{Li}$ by the isotope ${}^6\text{Li}$, the permutational symmetry group of the system has been reduced from \mathcal{S}_3 to \mathcal{S}_2 . Thus, if existing, the spatial degeneracy upon permutation of the nuclei can be removed in part or completely, since J is an integer. This is indeed the case for the ground state of ${}^7\text{Li}_2 {}^6\text{Li}$, with the electronic wave function at the minimum of the lower sheet of the potential energy surface being antisymmetric under \mathcal{S}_2 . Similarly, the electronic wave function at the lowest point of the conical intersection on the upper sheet of the ${}^7\text{Li}_2 {}^6\text{Li}$ potential energy surface will be symmetric or antisymmetric⁴ under \mathcal{S}_2 . The spatial degeneracy of the electronic wave function has therefore been removed when resolving \mathbf{D}_{3h} into \mathbf{C}_{2v} , since the E' state of the lowest energy structure has been resolved into $A_1 \oplus B_2$ (see Table 9.3, where the same axis convention as in Ref. 20 has been followed: the highest order proper axis always coincides with the z -axis.) which correspond to symmetric and antisymmetric wave functions in \mathcal{S}_2 .

⁴This and the previous statements can be understood from Table 9.11 and Table 9.12, which will be discussed in more detail in subsequent sections.

Table 9.5: The symmetric properties of wave functions of ${}^7\text{Li}_2 {}^6\text{Li}$ electronically ground state in \mathcal{S}_2 permutation group.

| Total | Nuclear spin | Rovibronic | Vibronic | Electronic ^{a)} | Rotational ^{b)} | Vibrational |
|----------|--------------|------------|----------|--------------------------|--------------------------|-------------|
| <i>B</i> | <i>A</i> | <i>B</i> | <i>A</i> | <i>B</i> | <i>B</i> | <i>B</i> |
| <i>B</i> | <i>A</i> | <i>B</i> | <i>B</i> | <i>B</i> | <i>A</i> | <i>A</i> |
| <i>B</i> | <i>B</i> | <i>A</i> | <i>A</i> | <i>B</i> | <i>A</i> | <i>B</i> |
| <i>B</i> | <i>B</i> | <i>A</i> | <i>B</i> | <i>B</i> | <i>B</i> | <i>A</i> |

^{a)} At minimum of the lower sheet of potential energy surface.

^{b)} Rotation about the axis through the ${}^6\text{Li}$ and perpendicular to the ${}^7\text{Li}_2$.

9.7 Permutational symmetry of rovibronic and vibronic wave functions

Since the total wave function must have the correct symmetry under the permutation of identical nuclei, we can determine the symmetry of the rovibronic wave function from consideration of the corresponding symmetry of the nuclear spin wave function. We begin by looking at the case of a fermionic system for which the total wave function must be antisymmetric under permutation of any two identical particles. If the nuclear spin wave function is symmetric then the rovibronic wave function must be antisymmetric; conversely, if the nuclear spin wave function is antisymmetric, the rovibronic wave function must be symmetric under permutation of any two fermions. Similar considerations apply to the case of a bosonic system: the rovibronic wave function must be symmetric when the nuclear spin wave function is symmetric, and the rovibronic wave function must be antisymmetric when the nuclear spin function is antisymmetric. This warrants that the total wave function is totally symmetric under permutation of any two indistinguishable bosons.

As it will be shown in the foregoing discussion (see section 9.8 and section 9.9), the rovibronic wavefunctions for a homonuclear diatomic molecule under the permutation of identical nuclei are: symmetric for even J rotational quantum numbers in Σ_g^+ and Σ_u^- electronic states; antisymmetric for odd J values in Σ_g^+ and Σ_u^- electronic states; symmetric for odd J values in Σ_g^- and Σ_u^+ electronic states; antisymmetric for even J values in Σ_g^- and Σ_u^+ electronic states. Note that the vibrational ground state is symmetric under permutation of the two nuclei. The most restrictive result arises therefore when the nuclear spin quantum number of the individual nuclei is 0. In this case, the nuclear spin function is always symmetric with respect to interchange of the identical nuclei, and hence only

Table 9.6: The symmetric properties of wave functions of ${}^7\text{Li}_2{}^6\text{Li}$ electronically first-excited state in \mathcal{S}_2 permutation group.

| Total | Nuclear spin | Rovibronic | Vibronic | Electronic ^{a)} | Rotational ^{b)} | Vibrational |
|-------|--------------|------------|----------|--------------------------|--------------------------|--------------|
| B | A | B | A | $A \oplus B$ | B | $A \oplus B$ |
| B | A | B | B | $A \oplus B$ | A | $B \oplus A$ |
| B | B | A | A | $A \oplus B$ | A | $A \oplus B$ |
| B | B | A | B | $A \oplus B$ | B | $B \oplus A$ |

^{a)} At minimum of the conical intersection on the upper sheet of potential energy surface.

^{b)} Rotation about the axis through the ${}^6\text{Li}$ and perpendicular to the ${}^7\text{Li}_2$.

totally symmetric rovibronic states are allowed since the total wave function must be symmetric for bosonic systems.

Let us now examine the features of the nuclear probability density of a X_3 molecule (X is an 2S atom) in its electronically ground and first-excited doublet states. For the lowest vibronic A_1 states such nuclear probability density must clearly concentrate⁵ at the regions where the potential energy surface itself has A_1 symmetry, which correspond in the case of homonuclear trimeric 2S systems to the saddle points of the potential energy surface having 2A_1 symmetry in \mathbf{C}_{2v} . Instead, the nuclear probability density of the lowest A_2 vibronic states will concentrate at regions where the potential energy surface has A_2 symmetry; note that the potential energy surface at the minima has 2B_2 symmetry in \mathbf{C}_{2v} , and hence A_2 in \mathcal{S}_3 . Both the A_1 and A_2 probability densities display threefold symmetries on a relaxed triangular plot such as that employed in Figure 9.3 to represent the Li_3 potential energy surface. Although the nuclear probability density of each component for the E vibronic state has twofold symmetry, their sum must also have threefold symmetry.

9.8 Permutational symmetry of rotational wave function

The permutational symmetry of the rotational wave function is determined by the total angular momentum \mathbf{J} which is the resultant of the electronic spin \mathbf{S} , nuclear spin \mathbf{I} , electronic orbital \mathbf{L} , and nuclear orbital \mathbf{N} angular momenta. For a molecule with both integral electronic spin quantum number S and nuclear spin quantum number I , the total

⁵Of course, for highly excited states, the density is expected to cover wide portions of the molecular configuration space.

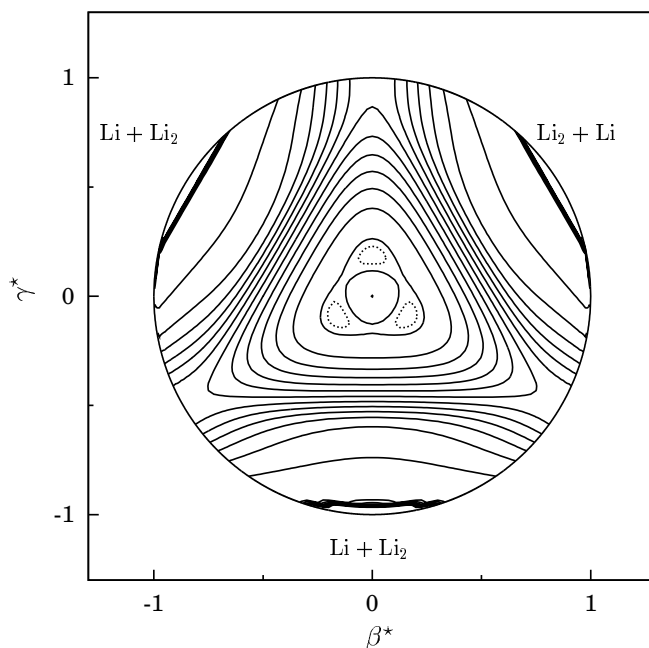


Figure 9.3: Relaxed triangular plot⁴⁷ of the Li_3 ground state potential energy surface using hyperspherical coordinates. Contours, are given by the expression $E_n/\text{eV} = -0.56 + 0.045(n - 1)$ with $n = 1, 2, \dots$, with the dashed line indicating the level -0.565eV . The dissociation limit indicated by the dense contouring implies $\text{Li}_2 (X^1\Sigma_g^+) + \text{Li}$.

angular quantum number J will be an integer or zero, since L and N are always integers or zero. For a molecule with half-integral quantum numbers both for S and I , J will also be an integer or zero. However, for a molecule with integral electronic spin quantum number S and half-integral nuclear spin quantum number I (or *vice versa*), J will be half-integral. For example, for the electronically ground-state of ${}^7\text{Li}_3$, the quantum number I assume half-integral values ranging from $1/2$ (in steps of 1) up to $9/2$, and $S = 1/2$. Thus, J can be an integer or zero, with the lowest rotational state corresponding to $J = 0$. In turn, for the electronic ground-state of ${}^6\text{Li}_3$, the quantum number I will assume integral values ranging from 0 (in steps of 1) up to 3, and $S = 1/2$. As a result, J will be half-integral, with the lowest rotational state being associated to $J = 1/2$. In their work, Gerber and Schumacher⁴ do not refer to this $J = 1/2$ state, which leads us to the conclusion that their calculations refer to ${}^7\text{Li}_3$.

We will now examine the permutational symmetry of the rotational wave functions. Two important remarks must first be made. The first refers to the $J = 0$ rotational state, which must always be totally symmetric. The second emerges from the extended Kramers' theorem, which imposes half-integral J rotational states to be degenerate. Thus, the lowest rotational state for the electronic ground state of ${}^7\text{Li}_3$ corresponds to $J = 0$, and hence must be symmetric. Similarly, the lowest rotational state for the electronic ground state of ${}^6\text{Li}_3$ must be degenerate, since $J = 1/2$.

We address next some simple cases, beginning with homonuclear diatomic molecules. The rotational wave functions are in this case the well known spherical harmonics: for even J values, $\Psi_r(\hat{x})$ is symmetric under permutation of the identical nuclei; for odd J values, $\Psi_r(\hat{x})$ is antisymmetric under the same permutation. A similar statement applies for any $D_{\infty h}$ molecule. Consider now a homonuclear triatomic molecule, and let m_J be the quantum number for the rotational angular momentum component perpendicular to the plane defined by the three atoms. The rotational contribution to the permutational symmetry⁴² is then symmetric if $m_J = 0$, symmetric or antisymmetric if m_J is a nonzero integer multiple of three, and degenerate if m_J is not an integer multiple of three (this includes the half-integral cases referred to above).

We now turn to some well established cases where severe consequences arise due to the nuclear spin quantum number of the individual nuclei being 0 or 1/2. Consider the simplest case of spinless nuclei such as ${}^{16}\text{O}_2$. Since the total wave function must be symmetric, it follows that only even rotational states are allowed for the ground vibrational state (this is always symmetric; see section 9.9) when the electronic wave function is symmetric; conversely, only odd rotational states are allowed if the electronic wave function is antisymmetric. Since the ground electronic state of ${}^{16}\text{O}_2$ is ${}^3\Sigma_g^-$, and hence antisymmetric, it then follows that its lowest rotational state must have $J = 1$, with half of the expected levels being absent in the corresponding Raman spectrum. Similarly, for transitions involving Σ electronic states in homonuclear diatomic molecules with $I = 0$, alternating lines will be missing in the rotational fine structure spectrum. If the nuclei are not identical (*e.g.*, if one is ${}^{16}\text{O}$ and the other is ${}^{17}\text{O}$), the above missing transitions will be restored.

A second well known example is ${}^1\text{H}_2$. Since the nuclear spin quantum number of ${}^1\text{H}$ is 1/2, the total nuclear spin quantum number I can be 0 or 1. When $I = 0$ the nuclear spin wave function is antisymmetric with respect to the interchange of the two protons. Conversely, the spin functions with $I = 1$ are symmetric under the same operation. Since transitions between the $I = 0$ and $I = 1$ states are forbidden, one may view the hydrogen molecule as consisting of two distinct species: para- H_2 with $I = 0$, and ortho- H_2 with $I = 1$. The electronic ground state of H_2 is a ${}^1\Sigma_g^+$ state, and hence para- H_2 can only possess rotational states with even or zero J values in order to preserve the antisymmetric nature of the total wave function; on the other hand, ortho- H_2 will have only odd J rotational states. Of course, in statistical equilibrium at room temperature, there will be three times as many H_2 molecules in ortho states than in para states. As a result, the alternating lines in the rotational fine structure spectrum show a 3:1 intensity ratio. Such

a ratio in the intensities of the rotational fine structure lines for a general homonuclear diatomic with nuclear spin quantum number I is $(I + 1)/I$: for bosons, it represents the relative statistical weight of symmetric to antisymmetric states; for fermions, the relative statistical weight of antisymmetric to symmetric states. Clearly, the nuclear statistical weights of rotational levels will affect the rotational partition function and hence have implications in various fields such as thermodynamics and reaction kinetics. For linear molecules with identical nuclei that are interchangeable by rotation, the nuclear statistical weights can be calculated by the methods discussed in section 9.5.

Finally, let us consider molecules with identical nuclei which are subject to \hat{C}_n ($n \geq 2$) rotations. For C_{2v} molecules in which the \hat{C}_2 rotation exchanges two nuclei of half-integral spin, the nuclear statistical weights of the symmetric and antisymmetric rotational levels will be one and three, respectively. For molecules where \hat{C}_2 exchanges two spinless nuclei, half of the rotational levels (odd or even J values, depending on the vibrational and electronic states) will be missing. For symmetric and spherical tops, there are three or more identical nuclei interchangeable by rotation. For example, for the symmetric top CH_3Cl , the $m_J = 0, 3, 6, \dots$ rotational levels have twice the statistical weight of the $m_J = 1, 2, 4, \dots$ rotational levels for the symmetric vibronic states.³⁹ The rotational levels with different nuclear statistical weights must be summed over separately. However, for sufficiently high temperatures, it may be a good approximation to calculate the rotational partition function by giving to each rotational level an average statistical weight equal to the total spin multiplicity $(2I_A + 1)(2I_B + 1) \dots (2I_Z + 1)$ divided by a symmetry number which represents the number of different indistinguishable orientations obtained by proper rotations of the nuclear framework. For example, the symmetry numbers of $C_{\infty v}$ and $D_{\infty h}$ molecules are one and two, respectively. For nonlinear molecules, the symmetry number is equal to the order of the rotational subgroup, *e.g.*, 12 both for C_6H_6 and CH_4 .

9.9 Permutational symmetry of vibrational wave function

We now consider the permutational properties of the vibrational wave function. Similar to the discussion on the permutational symmetry for homonuclear diatomic molecules (and, in general, $D_{\infty h}$ molecules), in order to find the effect of interchanging the nuclei on the vibrational wave function we first invert the SF coordinates of the nuclei and all displacement vectors, and then carry out a back-inversion of the SF displacement vector coordinates alone. The net effect is therefore just the exchange of the SF coordinates of the nuclei. For $D_{\infty h}$ molecules, such an inversion of the nuclear coordinates exchanges all pairs of identical nuclei. Thus, the first inversion leaves the sign of the vibrational wave function unchanged for Σ^+, Π^+, \dots vibrational states, while it changes its sign for Σ^-, Π^-, \dots vibrational states. The second inversion classifies the vibrational wave functions in g or u according to whether the back-inversion of the displacement vectors leaves the wave function unchanged (the corresponding operator has a +1 eigenvalue) or changes its sign (eigenvalue -1). We conclude that the vibrational wave functions are symmetric for

$\Sigma_g^+, \Sigma_u^-, \Pi_g^+, \Pi_u^-, \dots$ vibrational states while being antisymmetric under permutation of identical nuclei for $\Sigma_g^-, \Sigma_u^+, \Pi_g^-, \Pi_u^+, \dots$ vibrational states. Finally, we note that the ground vibrational states of homonuclear diatomics and, in general, $D_{\infty h}$ molecules are always symmetric under permutation of identical nuclei.

It can be shown that, for ${}^7\text{Li}_2 {}^6\text{Li}$ and ${}^6\text{Li}_2 {}^7\text{Li}$, there are symmetric ($A \cong [2]$ irreducible representation in the \mathcal{S}_2 permutation group) and antisymmetric ($B \cong [1^2]$ in \mathcal{S}_2) vibrational states which are allowed by the symmetry requirement, and hence can be observed spectroscopically. However, drastic consequences may arise if the nuclear spin is 0 or 1/2. In these cases, some rovibronic states cannot be observed since they are symmetry forbidden. For example, in the case of ${}^{12}\text{C}{}^{16}\text{O}_2$, the nuclei are spinless and the nuclear spin wave function is symmetric under permutation of the oxygen nuclei. Since the ground electronic state is Σ_g^+ , only even values of J can then be observed for the ground vibrational level $(v_1, v_2^{l_2}, v_3) = (00^00)$, where (v_1, v_2, v_3) are the quantum numbers of symmetric stretching (ν_1), degenerate bending (ν_2), and antisymmetric stretching (ν_3) normal modes, respectively. As usual, l_2 denotes the quantum number for vibrational angular momentum around the internuclear axis of the linear molecule in the degenerate vibrational mode ν_2 , which can be shown to assume the values $l_2 = v_2, v_2 - 2, \dots, 1$ or 0 (see Appendix 9.15). Similarly, the vibrational mode ν_1 is Σ_g^+ , and hence the odd J rotational levels of the (10^00) vibrational state are missing, since they are antisymmetric. Following the same reasoning, the even J rotational levels of the (00^01) vibrational state will be missing due to the fact that the vibrational mode ν_3 has Σ_u^+ symmetry. Most severe consequences arise also when the total nuclear spin quantum number is 1/2. For example, for the ground electronic state of ${}^1\text{H}_3$ and ${}^3\text{H}_3$ at $J = 0$, the vibrational states of A_1 symmetry will not be allowed and only the vibrational states of A_2 and E symmetry can be observed.

As discussed above, the permutational symmetry of the total wave function requires the proper combination of its various contributions. These are summarized in Table 9.7 to Table 9.14 for all isotopomers of Li_3 . Note that the conclusions hold provided that the various wave functions have the appropriate symmetries. If, for some reason, one of the components fails to meet such a requirement then the symmetry of the total wave function will fail too. For example, even if the vibrational wave functions are properly assigned, the total wave function of systems with conical intersections such as Li_3 may have no physical significance due to failure of the electronic wave function to meet the requirement of single-valuedness (*i.e.*, not change sign when traversing a path that encircles the crossing point). In other words, one needs to include GP effects or treat more accurately the dynamics (*e.g.*, by solving the 2×2 coupled state dynamics problem) in order to warrant the correct symmetry properties of the total wave function. This will be further discussed in the following section.

Table 9.7: The symmetric properties of wave functions of ${}^7\text{Li}_3$ electronically ground state in \mathcal{S}_3 permutation group.

| Total | Nuclear spin | Rovibronic | Vibronic | Electronic ^{a)} | Rotational ^{b)} | Vibrational |
|-------|--------------|------------|----------|--------------------------|---------------------------|-------------|
| A_2 | A_1 | A_2 | A_1 | A_2 | A_2 | A_2 |
| A_2 | A_1 | A_2 | A_2 | A_2 | A_1 | A_1 |
| A_2 | A_1 | A_2 | E | A_2 | E | E |
| A_2 | A_2 | A_1 | A_1 | A_2 | A_1 | A_2 |
| A_2 | A_2 | A_1 | A_2 | A_2 | A_2 | A_1 |
| A_2 | A_2 | A_1 | E | A_2 | E | E |
| A_2 | E | E | A_1 | A_2 | E | A_2 |
| A_2 | E | E | A_2 | A_2 | E | A_1 |
| A_2 | E | E | E | A_2 | $A_1 \oplus A_2 \oplus E$ | E |

^{a)} At minimum of the lower sheet of potential energy surface.

^{b)} Rotation about the axis perpendicular to the plane of the molecule.

9.10 Case studies: 2S systems

9.10.1 Potential energy surfaces

H_3 (and its isotopomers) and the alkali metal trimers (denoted generally for the homonuclears by X_3 , where X is an 2S atom) are typical Jahn-Teller systems where the adiabatic potential energy surfaces of the two lowest electronic states conically intersect. Since such manifolds of electronic states have recently been discussed⁴³ in some detail, we review in this section only the diabatic representation of such surfaces and their major topographical details. The relevant 2×2 diabatic potential matrix \mathbf{W} may be written as⁴⁴

$$\mathbf{W} = \begin{bmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{bmatrix} \quad (9.42)$$

Table 9.8: The symmetric properties of wave functions of ${}^7\text{Li}_3$ electronically first-excited state in \mathcal{S}_3 permutation group.

| Total | Nuclear spin | Rovibronic | Vibronic | Electronic ^{a)} | Rotational ^{b)} | Vibrational |
|-------|--------------|------------|----------|--------------------------|---------------------------|---------------------------|
| A_2 | A_1 | A_2 | A_1 | E | A_2 | E |
| A_2 | A_1 | A_2 | A_2 | E | A_1 | E |
| A_2 | A_1 | A_2 | E | E | E | $A_1 \oplus A_2 \oplus E$ |
| A_2 | A_2 | A_1 | A_1 | E | A_1 | E |
| A_2 | A_2 | A_1 | A_2 | E | A_2 | E |
| A_2 | A_2 | A_1 | E | E | E | $A_1 \oplus A_2 \oplus E$ |
| A_2 | E | E | A_1 | E | E | E |
| A_2 | E | E | A_2 | E | E | E |
| A_2 | E | E | E | E | $A_1 \oplus A_2 \oplus E$ | $A_1 \oplus A_2 \oplus E$ |

^{a)} At minimum of the conical intersection on the upper sheet of potential energy surface.

^{b)} Rotation about the axis perpendicular to the plane of the molecule.

where $W_{12} = W_{21}$. Specifically, for H_3 and Li_3 , two systems which we discuss in detail in this Chapter, the matrix elements in Eq. (9.42) assume the form⁴⁴

$$W_{11} = \sum_{i=1}^3 \mathcal{Q}'_i + X_{\text{EHF}}^{(3)} + \frac{1}{2} (2\mathcal{J}'_1 - \mathcal{J}'_2 - \mathcal{J}'_3) + V_{\text{dc}} \quad (9.43)$$

$$W_{22} = \sum_{i=1}^3 \mathcal{Q}'_i + X_{\text{EHF}}^{(3)} - \frac{1}{2} (2\mathcal{J}'_1 - \mathcal{J}'_2 - \mathcal{J}'_3) + V_{\text{dc}} \quad (9.44)$$

$$W_{12} = W_{21} = \frac{\sqrt{3}}{2} (\mathcal{J}'_2 - \mathcal{J}'_3) \quad (9.45)$$

where the \mathcal{Q} 's and \mathcal{J} 's are the well known Coulomb and exchange integrals which can be obtained semi-empirically from the lowest singlet and triplet diatomic potential curves, $X_{\text{EHF}}^{(3)}$ a three-body extended Hartree-Fock type energy, and V_{dc} the total dynamical correlation energy. Note that the prime in the \mathcal{Q} 's and \mathcal{J} 's expresses the fact that such quantities are calculated from the extended Hartree-Fock diatomic curves alone.

Diagonalization of \mathbf{W} then leads to the two adiabatic surfaces

$$V_{\pm} = \frac{1}{2} \left[(W_{11} + W_{22}) \pm \sqrt{(W_{11} - W_{22})^2 + 4W_{12}^2} \right] \quad (9.46)$$

which may cross when $W_{11} = W_{22}$ and $W_{12} = 0$. For X_3 systems, such a crossing seam is representative of a so-called conical intersection: for a fixed perimeter of the molecule, the

Table 9.9: The symmetric properties of wave functions of ${}^6\text{Li}_3$ electronically ground state in \mathcal{S}_3 permutation group.

| Total | Nuclear spin | Rovibronic | Vibronic | Electronic ^{a)} | Rotational ^{b)} | Vibrational |
|-------|--------------|------------|----------|--------------------------|---------------------------|-------------|
| A_1 | A_1 | A_1 | A_1 | A_2 | A_1 | A_2 |
| A_1 | A_1 | A_1 | A_2 | A_2 | A_2 | A_1 |
| A_1 | A_1 | A_1 | E | A_2 | E | E |
| A_1 | A_2 | A_2 | A_1 | A_2 | A_2 | A_2 |
| A_1 | A_2 | A_2 | A_2 | A_2 | A_1 | A_1 |
| A_1 | A_2 | A_2 | E | A_2 | E | E |
| A_1 | E | E | A_1 | A_2 | E | A_2 |
| A_1 | E | E | A_2 | A_2 | E | A_1 |
| A_1 | E | E | E | A_2 | $A_1 \oplus A_2 \oplus E$ | E |

^{a)} At minimum of the lower sheet of potential energy surface.

^{b)} Rotation about the axis perpendicular to the plane of the molecule.

crossing seam corresponds to the apex of the double cone defined by the two adiabatic potential energy surfaces V_+ and V_- . Although these become non-degenerate due to the so-called Jahn-Teller effect (see subsection 9.10.2), the degeneracy at the locus of conical intersection remains. The location of this crossing seam is defined by the conditions $r_{AB} = r_{BC} = r_{AC}$, where r_{AB} , r_{BC} , and r_{AC} are the interatomic distances. Thus, for homonuclear systems such as Li_3 , the conical intersection occurs for D_{3h} symmetries but, for the heteronuclear systems, they may arise at lower symmetries or even do not occur at all.^{45,46} Clearly, the potential matrix defined in Eq. (9.42) has the correct asymptotic behavior in the vicinity of the conical intersection (see Appendix 9.16).

In the remaining of this subsection we focus on the two lowest doublet states of Li_3 . Figure 9.3 and Figure 9.4 show relaxed triangular plots⁴⁷ of the lower and upper sheets of the Li_3 DMBE III^{48,49} potential energy surface using hyperspherical coordinates. Each plot corresponds to a stereographic projection of the surface of an upper half sphere. The β^* coordinate is associated to $\sin(\theta/2) \cos \phi$, while γ^* denotes $\sin(\theta/2) \sin \phi$. The hyperangle θ runs from zero at the north pole (center of plot) to $\pi/2$ at the equator (the outside circle). The hyperangle ϕ is measured from the positive γ^* axis and grows on going counterclockwise. For the lower sheet, it is noted that the lowest point along the D_{3h} conical intersection seam is located at the origin of the plot and corresponds to an equilateral triangular configuration. As it can be seen, the threefold symmetry gives rise to three wells which are equally spaced by 120 deg intervals around the origin. The minimum energy of the barrier for pseudorotation relative to the bottom of such wells (*i.e.*, the height

Table 9.10: The symmetric properties of wave functions of ${}^6\text{Li}_3$ electronically first-excited state in \mathcal{S}_3 permutation group.

| Total | Nuclear spin | Rovibronic | Vibronic | Electronic ^{a)} | Rotational ^{b)} | Vibrational |
|-------|--------------|------------|----------|--------------------------|---------------------------|-------------|
| A_1 | A_1 | A_1 | A_1 | A_2 | A_1 | A_2 |
| A_1 | A_1 | A_1 | A_2 | A_2 | A_2 | A_1 |
| A_1 | A_1 | A_1 | E | A_2 | E | E |
| A_1 | A_2 | A_2 | A_1 | A_2 | A_2 | A_2 |
| A_1 | A_2 | A_2 | A_2 | A_2 | A_1 | A_1 |
| A_1 | A_2 | A_2 | E | A_2 | E | E |
| A_1 | E | E | A_1 | A_2 | E | A_2 |
| A_1 | E | E | A_2 | A_2 | E | A_1 |
| A_1 | E | E | E | A_2 | $A_1 \oplus A_2 \oplus E$ | E |

^{a)} At minimum of the conical intersection on the upper sheet of potential energy surface.

^{b)} Rotation about the axis perpendicular to the plane of the molecule.

of the saddle points between the three wells), and the energy of the lowest point along the conical intersection seam are⁶ 0.4 meV and 0.0542 eV, respectively. Note that the motion along the hyperradius ρ corresponds to the symmetric stretching mode. Moreover, at the bottom of the well just above the origin, motion along the γ^* axis corresponds to the bending mode while motion along the β^* axis corresponds to the antisymmetric stretching mode. In addition, motion along the hyperangle ϕ about the origin corresponds to the pseudorotational motion. Finally, it should be noted that the origin in the plot of the upper sheet corresponds to an equilateral triangular geometry.

9.10.2 Static Jahn-Teller effect

We examine now the effect of vibronic interactions on the two adiabatic potential energy surfaces of non-linear molecules which belong to a degenerate electronic state, known as the static Jahn-Teller effect.

For a X_3 molecule in the \mathbf{D}_{3h} symmetry point group, we have a totally symmetric A'_1 and a doubly degenerate E' vibrational normal modes in the harmonic-oscillator approximation as illustrated in Figure 9.5. However, for a real molecule which vibrates anharmon-

⁶Units conversion factors are: a.u. of energy = $E_h = 27.211652 \text{ eV} = 4.3598 \text{ aJ} = 2.194746 \times 10^5 \text{ cm}^{-1}$; a.u. of bond length = $a_0 = 0.529177 \text{ \AA} = 0.529177 \times 10^{-10} \text{ m}$.

Table 9.11: The symmetric properties of wave functions of ${}^7\text{Li}_2 {}^6\text{Li}$ electronically ground state in \mathcal{S}_2 permutation group.

| Total | Nuclear spin | Rovibronic | Vibronic | Electronic ^{a)} | Rotational ^{b)} | Vibrational |
|-------|--------------|------------|----------|--------------------------|--------------------------|-------------|
| B | A | B | A | B | B | B |
| B | A | B | B | B | A | A |
| B | B | A | A | B | A | B |
| B | B | A | B | B | B | A |

^{a)} At minimum of the lower sheet of potential energy surface.

^{b)} Rotation about the axis through the ${}^6\text{Li}$ and perpendicular to the ${}^7\text{Li}_2$.

ically, we must consider the effects due to anharmonicity. As discussed in Appendix 9.15, we must then use the set of quantum numbers (v_1, v_2, l_2) instead of (v_1, v_{2a}, v_{2b}) , and employ the notation $(v_1, v_2^{l_2})$ to label the vibrational levels; l_2 is the vibrational angular momentum quantum number with respect to the symmetry axis. Table 9.15 gives the assignments of the lowest vibrational levels for Li_3 in the \mathbf{D}_{3h} symmetry point group. From the assignment one can determine the symmetry of the level. For example, the ground vibrational state $(0, 0^0)$ is A'_1 and the level $(1, 1^1)$ is E' , since v_1 is totally symmetric and $A'_1 \otimes E' = E'$. In turn, for multiply excited degenerate vibrations,^{20,42} the symmetry A'_1 corresponds to $l_2 = 0$, $A'_1 \oplus A'_2$ to $l_2 = 3, 6, \dots$ and E' to $l_2 = 1, 2, 4, 8, \dots$; note that l_2 is a good quantum number, and hence can be used to specify the symmetry of the vibrational level. For example, the level $(0, 3^1)$ has E' symmetry while $(0, 3^3)$ is $A'_1 \oplus A'_2$. It should also be noted that anharmonicity splits the degeneracy of the vibrational levels obtained in the harmonic approximation.²⁰

We now take vibronic interactions into account. In this case, we must determine vibronic states rather than the electronic and vibrational ones. For example, if X_3 in a degenerate E' vibration is singly excited in an E' electronic state, we obtain the vibronic states ${}^{ev}A'_1 \oplus {}^{ev}A'_2 \oplus {}^{ev}E'$, since ${}^vE' \otimes {}^eE' = {}^{ev}A'_1 \oplus {}^{ev}A'_2 \oplus {}^{ev}E'$. If the same vibration is doubly excited (*e.g.*, if $v_2 = 2$, with the symmetric product being $\{{}^vE' \otimes {}^vE'\} = A'_1 \oplus {}^vE'$: note that the associated antisymmetric product is ${}^vA'_2$), we get the vibronic species $({}^vA'_1 \oplus {}^vE') \otimes {}^eE' = {}^{ev}A'_1 \oplus {}^{ev}A'_2 \oplus 2{}^{ev}E'$. Table 9.15 shows the symmetries of the lowest 25 vibrational and vibronic states. In turn, the lowest 26 levels calculated for Li_3 using the Li_3 double many-body expansion^{41,50} potential energy surface (DMBE III^{48,49}) are shown in Table 9.16 and Table 9.17.

We now consider the splitting of the potential energy surface for non-totally symmetric (*i.e.*, ${}^vE'$ in \mathbf{D}_{3h}) displacements of the nuclei. For such geometries the symmetry is lower,

Table 9.12: The symmetric properties of wave functions of ${}^7\text{Li}_2{}^6\text{Li}$ electronically first-excited state in \mathcal{S}_2 permutation group.

| Total | Nuclear spin | Rovibronic | Vibronic | Electronic ^{a)} | Rotational ^{b)} | Vibrational |
|-------|--------------|------------|----------|--------------------------|--------------------------|--------------|
| B | A | B | A | $A \oplus B$ | B | $A \oplus B$ |
| B | A | B | B | $A \oplus B$ | A | $B \oplus A$ |
| B | B | A | A | $A \oplus B$ | A | $A \oplus B$ |
| B | B | A | B | $A \oplus B$ | B | $B \oplus A$ |

^{a)} At minimum of the conical intersection on the upper sheet of potential energy surface.

^{b)} Rotation about the axis through the ${}^6\text{Li}$ and perpendicular to the ${}^7\text{Li}_2$.

and in general the electronic states become non-degenerate (*e.g.*, ${}^eA_1 \oplus {}^eB_2$ in \mathbf{C}_{2v}) instead of being doubly degenerate (${}^eE'$ in \mathbf{D}_{3h}). Thus, for displaced positions of the nuclei, we obtain two non-degenerate electronic states of different energy. Jahn and Teller⁵¹ have been the first to show that, for a nonlinear molecule, there is always one non-totally symmetric normal mode at least which causes a splitting of the potential energy surface such that the minima do not occur at the most symmetric geometry. They are rather at a certain distance from the most symmetric configuration, with the distance increasing with the magnitude of the vibronic interaction. As a result, several equivalent minima arise on the potential energy surface for unsymmetric molecular conformations. If the vibronic interaction is strong, a significant amount of vibrational energy may then be required to bring the molecule from one minimum to another, and hence one must regard the molecule as nonsymmetric. Conversely, for weak vibronic interactions, only a small amount of vibrational energy may suffice to make the system flow from one minimum to another. In this case, the molecule may be regarded as symmetric, and the vibronic interaction treated as a perturbation. Appendix 9.16 gives a proof of the Jahn-Teller theorem for a X_3 molecule following Moffitt and Liehr.⁵²

The treatment of the Jahn-Teller effect for more complicated cases is similar. The general conclusion is that the appearance of a linear term in the off-diagonal matrix elements H_{+-} and H_{-+} leads always to an instability at the most symmetric configuration due to the fact that integrals of the type $\langle \Psi_+ | \hat{h}_1^+ | \Psi_- \rangle$ do not vanish there when the product $\Psi_+^* \Psi_-$ has the same species as a non-totally symmetric vibration (see Appendix 9.16). If Γ is the species of the degenerate electronic wave functions, the species of $\Psi_+^* \Psi_-$ will be that of Γ^2 which is the symmetric product of Γ with itself. For example, for a D_{3h} molecule, we have the symmetric product $\{ {}^eE' \otimes {}^eE' \} = {}^eA'_1 \oplus {}^eE'$ (the associated antisymmetric product is $[{}^eE' \otimes {}^eE'] = {}^eA'_2$) and hence it is the ${}^vE'$ degenerate normal mode that causes the instability since it has the same symmetry as the ${}^eE'$ term which arises from the

Table 9.13: The symmetric properties of wave functions of ${}^6\text{Li}_2 {}^7\text{Li}$ electronically ground state in \mathcal{S}_2 permutation group.

| Total | Nuclear spin | Rovibronic | Vibronic | Electronic ^{a)} | Rotational ^{b)} | Vibrational |
|----------|--------------|------------|----------|--------------------------|--------------------------|-------------|
| <i>A</i> | <i>A</i> | <i>A</i> | <i>A</i> | <i>B</i> | <i>A</i> | <i>B</i> |
| <i>A</i> | <i>A</i> | <i>A</i> | <i>B</i> | <i>B</i> | <i>B</i> | <i>A</i> |
| <i>A</i> | <i>B</i> | <i>B</i> | <i>A</i> | <i>B</i> | <i>B</i> | <i>B</i> |
| <i>A</i> | <i>B</i> | <i>B</i> | <i>B</i> | <i>B</i> | <i>A</i> | <i>A</i> |

^{a)} At minimum of the lower sheet of potential energy surface.

^{b)} Rotation about the axis through the ${}^7\text{Li}$ and perpendicular to the ${}^6\text{Li}_2$.

symmetric product. For a D_{4h} molecule, we have the symmetric product $\{{}^eE_g \otimes {}^eE_g\} = {}^eA_{1g} \oplus {}^eB_{1g} \oplus {}^eB_{2g}$ (note that the associated antisymmetric product is $[{}^eE_g \otimes {}^eE_g] = {}^eA_{2g}$), and hence it is either the ${}^vB_{1g}$ or ${}^vB_{2g}$ normal modes that cause the instability, since they have the same non-totally symmetric behavior as the ${}^eB_{1g}$ and ${}^eB_{2g}$ terms which arise from the symmetric product.

9.10.3 Dynamic Jahn-Teller and the geometric phase effect

We begin by discussing the energy levels which arise when a Jahn-Teller instability is present, *i.e.*, the dynamic Jahn-Teller effect and the related GP effect. This stems from the observation made by Herzberg and Longuet-Higgins²⁹ that a real-valued electronic wave function changes sign when the nuclear coordinates traverse a closed path encircling a conical intersection. This result has been shown⁵³ to be valid even for systems which show no symmetry such as LiNaK. Indeed, it has been rediscovered in a wider context by Berry,¹⁶ and hence it is often referred to as the Berry's phase effect. As pointed out in the Introduction, a further designation¹⁴ is molecular Aharonov-Bohm effect since such an effect appears also in the treatment of a charged particle moving in the presence of a magnetic solenoid.

To be specific, we focus the present discussion on studies of the vibrational spectrum of ground state Li_3 which we have carried out using the DMBE III^{48,49} Li_3 potential energy surface. All the eigenvalues of the system Hamiltonian have been calculated using the MINRES filter diagonalization technique.¹⁹ In turn, the action of the Hamiltonian operator on the nuclear wave function has been evaluated by the spectral transform method in hyperspherical coordinates by using a fast Fourier transform for ρ and ϕ and a DVR-FBR

Table 9.14: The symmetric properties of wave functions of ${}^6\text{Li}_2{}^7\text{Li}$ electronically first excited state in \mathcal{S}_2 permutation group.

| Total | Nuclear spin | Rovibronic | Vibronic | Electronic ^{a)} | Rotational ^{b)} | Vibrational |
|-------|--------------|------------|----------|--------------------------|--------------------------|--------------|
| A | A | A | A | $A \oplus B$ | A | $A \oplus B$ |
| A | A | A | B | $A \oplus B$ | B | $B \oplus A$ |
| A | B | B | A | $A \oplus B$ | B | $A \oplus B$ |
| A | B | B | B | $A \oplus B$ | A | $B \oplus A$ |

^{a)} At minimum of the conical intersection on the upper sheet of potential energy surface.

^{b)} Rotation about the axis through the ${}^7\text{Li}$ and perpendicular to the ${}^6\text{Li}_2$.

transformation for θ .² In such studies, GP effects have also been taken into consideration. Thus, six separate sets of calculations have been performed, which include: (1) no consideration of GP effects using a basis set of A_1 symmetry; (2) no consideration of GP effects using a basis set of A_2 symmetry; (3) no consideration of GP effects using a basis set of E symmetry; (4) consideration of GP effects using a basis set of A_1 symmetry; (5) consideration of GP effects using a basis set of A_2 symmetry; (6) consideration of GP effects using a basis set of E symmetry. The total number of calculated eigenvalues amounted to 3524 without consideration of GP effects, and 3211 with consideration of GP effects. The full spectra have therefore been calculated, which cover the full range of energies up to the threshold for $\text{Li}_2(\text{X } {}^1\Sigma_g^+) + \text{Li}$ dissociation. Of the total number of calculated vibrational levels, 953 (920), 750 (817), and 1621 (1474) have been found to belong to A_1 , A_2 , and E symmetries when GP effects were not (were) taken in consideration. Figure 9.6 to Figure 9.8 show the lowest 40 calculated levels of A_1 , A_2 , and E symmetries and the corresponding assignments. As one would expect, each vibrational level is associated to three different vibronic levels, *e.g.*, the (0,0,0) vibrational level in \mathbf{C}_{2v} is related to the ${}^vA'_1(0,0,0)$, ${}^vA'_2(0,0,0)$ and ${}^vE'(0,0,0)$ levels in \mathbf{D}_{3h} . Note that in an obvious correspondence the vibrational states ${}^vA'_1(v_1, v_2, v_3)$, ${}^vA'_2(v_1, v_2, v_3)$, and ${}^vE'(v_1, v_2, v_3)$ are associated to the vibronic states ${}^{ev}A'_2(v_1, v_2, v_3)$, ${}^{ev}A'_1(v_1, v_2, v_3)$, and ${}^{ev}E'(v_1, v_2, v_3)$; see Table 9.15 to Table 9.17. Note also that the notation (v_1, v_2, v_3) implies that the quantum numbers are associated to the symmetric stretching, bending, and asymmetric stretching vibrational modes in \mathbf{C}_{2v} . They are of A_1 , A_1 , and B_2 symmetries, respectively; the correlation between the assignments in \mathbf{D}_{3h} and \mathbf{C}_{2v} is given in Table 9.15.

For very small vibronic coupling, the quadratic terms in the power series expansion of the electronic Hamiltonian in normal coordinates (see Appendix 9.16) may be considered to be negligible, and hence the potential energy surface has rotational symmetry but shows no separate minima at the bottom of the moat. In this case, the pair of vibronic levels A_1

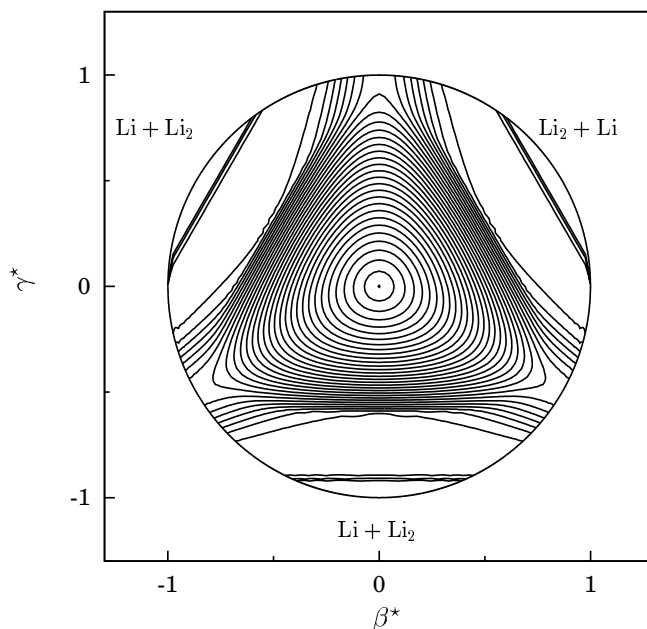


Figure 9.4: Relaxed triangular plot⁴⁷ of the Li_3 first-excited state potential energy surface using hyperspherical coordinates. Contours, are given by the expression $E_n/\text{eV} = -0.56 + 0.045(n - 1)$ with $n = 2, 3, \dots$. The dissociation limit indicated by the dense contouring implies $\text{Li}_2 (b^3\Sigma_u^+) + \text{Li}$.

and A_2 in \mathcal{S}_3 become degenerate by accident, and the D_{3h} quantum numbers (v_1, v_2, l_2) may be used to label the vibronic levels of the X_3 molecule. When the coupling of the vibrational and electronic motions is strong, (v_1, v_2, l_2) are no longer a good set of quantum numbers. In this case, it is more reasonable to think of the vibronic motion as a result of a vibration of an oscillator with C_{2v} symmetry and a rotation corresponding to the motion on the potential valley around the D_{3h} symmetry axis. Such motion may also be viewed as arising from the circular motion of each Li nucleus around their equilibrium positions in the D_{3h} geometry. As we have noted, there is a vibrational angular momentum on the symmetry axis, and hence the rotation of the molecule as a whole is allowed even when the total angular momentum vanishes; indeed, for $l_2 \neq 0$, the molecule must possess a genuine rotation to compensate the vibrational angular momentum such that $J = 0$.

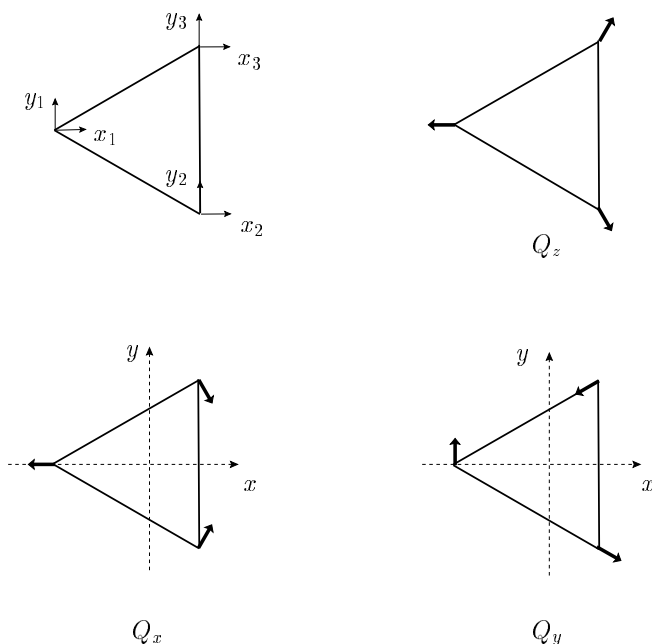


Figure 9.5: Definition of the normal mode coordinates for a D_{3h} X_3 molecule.

The spectra of floppy molecules such as Li_3 may therefore have different interpretations. For example, the spectra of specific symmetries have been fitted⁶ to within a few per cent of error using the simple vibrational normal mode formula

$$\begin{aligned}
 E(v_1, v_2, v_3) &= \sum_{i=1}^3 \left(v_i + \frac{1}{2} \right) \omega_i + \sum_{j \geq i=1}^3 \left(v_i + \frac{1}{2} \right) \left(v_j + \frac{1}{2} \right) x_{ij} \\
 &+ \sum_{k \geq j \geq i=1}^3 \left(v_i + \frac{1}{2} \right) \left(v_j + \frac{1}{2} \right) \left(v_k + \frac{1}{2} \right) y_{ijk} \quad (9.47)
 \end{aligned}$$

where v_i are the vibrational quantum numbers, ω_i are (in energy units) the harmonic frequencies, and x_{ij} and y_{ijk} are higher-order anharmonic corrections. Alternatively, Eq. (9.47) may be interpreted in terms of pseudorotational energies. According to this interpretation, the first and part of the second summations would represent the pseudorotational energy of a S_3 molecule, while the remaining terms would contain the second-order and higher-order coupling pseudorotational terms; the pseudorotational quantum numbers are now defined by $j_i = (v_i + \frac{1}{2})$ for $i = 1, 2, 3$. For X_3 molecules, $j_i = 1/2, 5/2, 7/2, \dots$

Table 9.15: Vibronic species of the vibrational states of Li_3 with consideration of geometric phase effects^{a)}.

| Assignment (v'_1, v'_2) in \mathbf{D}_{3h} | Symmetry of vibrational states | Symmetry of vibronic states | Assignment ^{b)} (v_1, v_2, v_3) in \mathbf{C}_{2v} |
|---|-----------------------------------|--------------------------------|--|
| (0, 0 ⁰) | A'_1 | E' | $E'(0, 0, 0)$ |
| (0, 1 ¹) | E' | $A'_1 \oplus A'_2 \oplus E'$ | $A'_2(0, 0, 0), A'_1(0, 0, 0), E'(0, 0, 1)$ |
| (1, 0 ⁰) | A'_1 | E' | $E'(0, 1, 0)$ |
| (1, 1 ¹) | E' | $A'_1 \oplus A'_2 \oplus E'$ | $A'_2(0, 0, 1), E'(1, 0, 0), A'_1(0, 0, 1)$ |
| (0, 2 ⁰) | A'_1 | E' | $E'(0, 0, 2)$ |
| (0, 2 ²) | E' | $A'_1 \oplus A'_2 \oplus E'$ | $A'_2(0, 1, 0), E'(0, 1, 1), A'_1(0, 1, 0)$ |
| (1, 2 ⁰) | A'_1 | E' | $E'(0, 2, 0)$ |
| (1, 2 ²) | E' | $A'_1 \oplus A'_2 \oplus E'$ | $A'_2(1, 0, 0), E'(1, 0, 1), A'_1(1, 0, 0)$ |
| (0, 3 ¹) | E' | $A'_1 \oplus A'_2 \oplus E'$ | $A'_2(0, 0, 2), E'(0, 0, 3), A'_1(0, 0, 2)$ |
| (0, 3 ³) | $A'_1 \oplus A'_2$ | $2E'$ | $E'(1, 1, 0), E'(0, 1, 2)$ |
| (2, 2 ⁰) | A'_1 | E' | $E'(2, 0, 0)$ |
| (2, 2 ²) | E' | $A'_1 \oplus A'_2 \oplus E'$ | $A'_2(0, 1, 1), E'(0, 2, 1), A'_1(0, 1, 1)$ |

^{a)}For simplicity, the left superscripts v and ev are omitted in denoting the vibrational and vibronic states.

^{b)}In this assignment we keep the symmetry species of the vibronic state in \mathbf{D}_{3h} but indicate the vibrational quantum numbers for the \mathbf{C}_{2v} normal modes. The energy increases from left to right, and up to down.

will belong to E species, while $j_i = 3/2, 9/2, 15/2 \dots$ to A_1 or A_2 ²⁰ (see also the discussion later about the quantum number m).

Since there are potential barriers along the pseudorotational path, one must also consider the effects due to tunneling. Each specified level splits then into three owing to such tunneling effects. In fact, we have now distinct zero-point energies for each of the three vibronic states, with their energy differences being determined by the pseudorotational motion which includes the tunneling effects.

The vibronic motion may be described using the (ρ, θ, ϕ) coordinates. In particular, the wave functions for the pseudorotational motion along the hyperangle ϕ which encircles the origin in a \mathbf{X}_3 system may assume the form⁶

$$\Psi_{pr}(\phi) = f(\rho, \theta) \exp\left(i\frac{l\phi}{2}\right) \exp(in\phi) \quad n = 0, \pm 1, \pm 2, \dots; \quad l = 0, 1 \quad (9.48)$$

where $l = 0(1)$ for the case without (with) consideration of the GP effect. Clearly, they

Table 9.16: The lowest 26 energy levels (in eV) for ground state Li_3 without consideration of geometric phase effects.

| Number | E_n/eV | Symmetry of vibration | Assignment (v_1, v_2, v_3) in \mathbf{C}_{2v} |
|--------|-----------------|-----------------------|---|
| 1 | -0.52816464978 | A_1 | (0,0,0) |
| 2 | -0.52086641058 | E | (0,0,0) |
| 3 | -0.50562197957 | E | (0,0,1) |
| 4 | -0.50240784221 | A_1 | (0,0,1) |
| 5 | -0.48957138875 | A_2 | (0,0,0) |
| 6 | -0.48950339062 | E | (0,0,2) |
| 7 | -0.48710210168 | A_1 | (0,1,0) |
| 8 | -0.48054432662 | A_1 | (1,0,0) |
| 9 | -0.47611328568 | E | (0,1,0) |
| 10 | -0.47273766106 | A_1 | (0,0,2) |
| 11 | -0.47267009384 | E | (0,0,3) |
| 12 | -0.46728845390 | E | (1,0,0) |
| 13 | -0.46008142773 | E | (0,1,1) |
| 14 | -0.45726050697 | A_1 | (0,1,1) |
| 15 | -0.45698549489 | E | (0,0,4) |
| 16 | -0.45570955951 | A_2 | (0,0,1) |
| 17 | -0.45041884404 | A_1 | (1,0,1) |
| 18 | -0.44765547757 | E | (1,0,1) |
| 19 | -0.44399503522 | E | (0,1,2) |
| 20 | -0.44373568206 | A_1 | (0,0,3) |
| 21 | -0.44362378636 | A_2 | (0,1,0) |
| 22 | -0.43949743434 | E | (0,0,5) |
| 23 | -0.43945450351 | A_1 | (0,2,0) |
| 24 | -0.43472274424 | A_1 | (1,1,0) |
| 25 | -0.43394121998 | E | (1,0,2) |
| 26 | -0.43100452644 | E | (0,2,0) |

Table 9.17: The lowest 26 energy levels (in eV) for ground state Li_3 with consideration of geometric phase effects.

| Number | E_n/eV | Symmetry of vibration | Assignment (v_1, v_2, v_3) in \mathbf{C}_{2v} |
|--------|-----------------|-----------------------|---|
| 1 | -0.52524282512 | E | (0,0,0) |
| 2 | -0.51783314253 | A_1 | (0,0,0) |
| 3 | -0.50903972588 | A_2 | (0,0,0) |
| 4 | -0.50128197060 | E | (0,0,1) |
| 5 | -0.49188205106 | E | (0,1,0) |
| 6 | -0.48752020977 | A_1 | (0,0,1) |
| 7 | -0.48169581419 | E | (1,0,0) |
| 8 | -0.47506737423 | E | (0,0,2) |
| 9 | -0.47429223744 | A_2 | (0,0,1) |
| 10 | -0.47257962805 | A_1 | (0,1,0) |
| 11 | -0.47109350982 | E | (0,1,1) |
| 12 | -0.46486144408 | A_2 | (0,1,0) |
| 13 | -0.45992435398 | A_1 | (1,0,0) |
| 14 | -0.45743322309 | E | (0,2,0) |
| 15 | -0.45609295233 | A_1 | (0,0,2) |
| 16 | -0.45572118311 | E | (1,0,1) |
| 17 | -0.45380222742 | A_2 | (1,0,0) |
| 18 | -0.44725687996 | E | (0,0,3) |
| 19 | -0.44322850657 | E | (1,1,0) |
| 20 | -0.44211312570 | A_1 | (0,1,1) |
| 21 | -0.44025040532 | E | (0,1,2) |
| 22 | -0.44004503298 | A_2 | (0,0,2) |
| 23 | -0.43625851187 | E | (2,0,0) |
| 24 | -0.43557972347 | E | (0,2,1) |
| 25 | -0.43004385753 | A_2 | (0,1,1) |
| 26 | -0.42970907209 | A_1 | (1,0,1) |

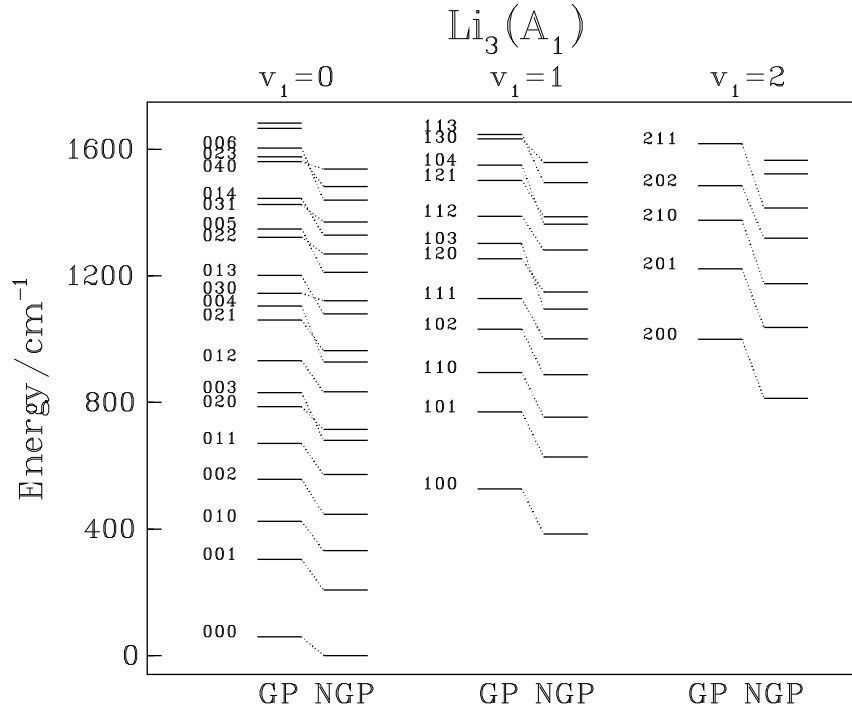


Figure 9.6: The vibrational levels of the lowest forty bound states of A_1 symmetry for ${}^7\text{Li}_3$ calculated without consideration and with consideration of GP effects.

are eigenfunctions of the kinetic energy operator⁶ \hat{K}_ϕ with eigenvalues given by

$$m = \left(n + \frac{l}{2}\right)^2 \quad (9.49)$$

Thus, we can use the approximate quantum number m to label such levels. Moreover, it may be shown⁶ that: 1) \sqrt{m} is half integer for the case with consideration of the GP effect, while it is an integer or zero for the case without consideration of the GP effect; 2) the lowest level must have $m = 0$ and be a singlet with A_1 symmetry in \mathcal{S}_3 when the GP effect is not taken in consideration, while the first excited level has $m = 1$ and corresponds to a doublet E ; conversely, with consideration of the GP effect, the lowest level must have $m = 1/4$ and be a doublet with E symmetry in \mathcal{S}_3 , while the first excited level corresponds to $m = 9/4$ and is a singlet A_1 . Note that such a reversal in the ordering of the levels has been discovered previously by Hancock *et al.*⁴² We further note that $j_\phi = \sqrt{m}$ has a meaning similar to the j_i quantum numbers described after Eq. (9.47): the full set of

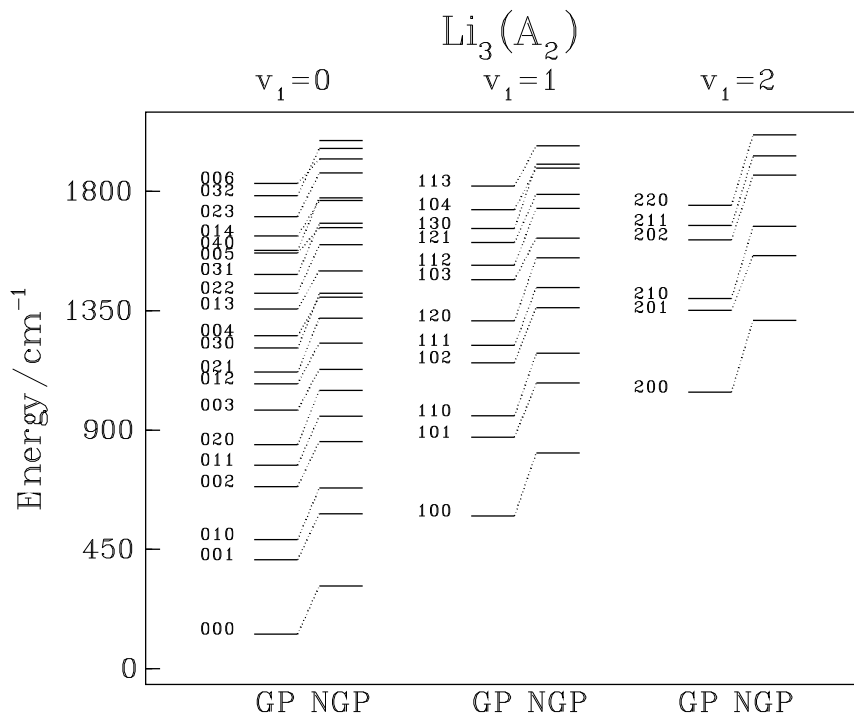


Figure 9.7: As in Figure 9.6 for the lowest forty bound states of A_2 symmetry.

quantum numbers would then be $(j_\rho, j_\theta, j_\phi)$. To complete the description of the vibronic motion, we may then suggest using the set of quantum numbers $(j_\rho, j_\theta, j_\phi)$. The energies of the vibronic levels will then assume the form

$$E(j_\rho, j_\theta, j_\phi) = \sum_{i=\rho,\theta,\phi} j_i \omega_i + \sum_{j \geq i} j_i j_j x_{ij} + \sum_{k \geq j \geq i} j_i j_j j_k y_{ijk} \quad (9.50)$$

where ω_i are the frequencies, x_{ij} is a pseudorotational constant for the i -th motion in energy units, and so on for x_{ij} and y_{ijk} ($i, j, k \equiv \rho, \theta, \phi$).

Since Li_3 in its electronic ground doublet state is a very floppy molecule and the vibrational levels are dense, one may expect the vibrational spectrum to be irregular. To understand such a behavior, the Li_3 vibrational spectrum has been analyzed statistically with basis on random matrix theory.⁵⁴ It has been found⁶ that the full spectrum is more regular than each symmetry block *per se*. This can be understood by recalling that the levels can interact with each other within a symmetry block, while the full spectrum

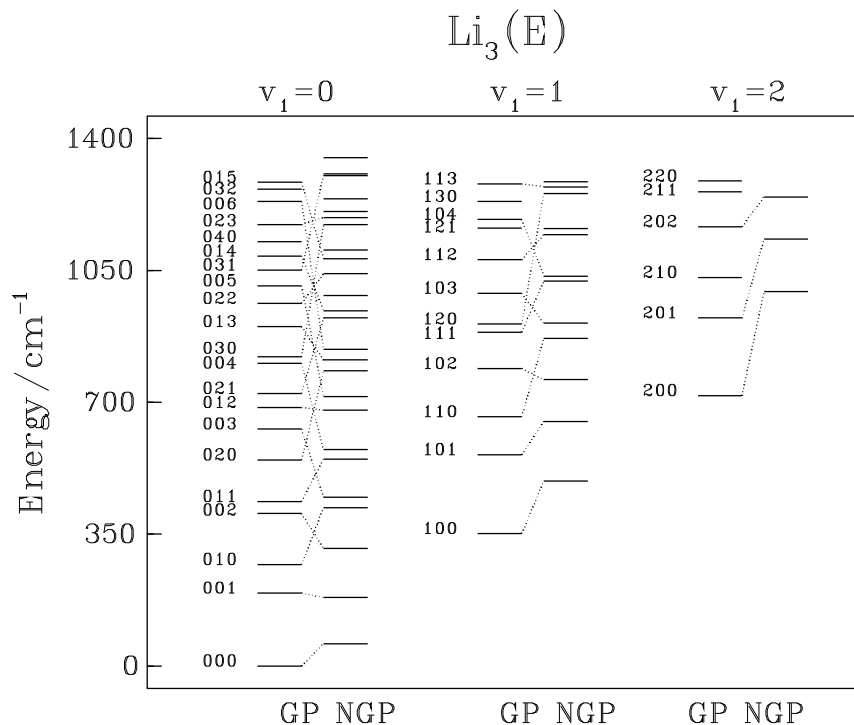


Figure 9.8: As in Figure 9.6 for the lowest fourty bound states of E symmetry.

consists of a random superposition of unrelated sequences of energy levels belonging to different symmetries. As discussed in detail elsewhere,⁶ the spectrum is found to be quasi-regular in short-range and quasi-irregular in long-range. It should also be mentioned that the interactions among the levels of the same symmetry result mainly from the so-called Fermi resonances which occur when two or more levels become nearly degenerate and have the same symmetry. Fermi resonances are produced by the anharmonicity of the potential energy surface and make near-degenerate levels (in the harmonic-oscillator approximation) to repel each other. Thus, they originate extra irregularity in the spectrum of a specific symmetry.

One may think that the dynamic Jahn-Teller effect is equivalent to take in consideration the GP effect which arises, *e.g.*, due to the conical intersection in X_3 -type systems formed from 2S atoms. We find it pedagogical from our calculations for Li_3 to distinguish three situations. The first corresponds to the calculations in sets (1) to (3) mentioned above, *i.e.*, using only one electronic adiabatic Born-Oppenheimer potential energy surface without

consideration of the GP effect. The second refers to the generalized Born-Oppenheimer treatment in which the GP effect is also considered. Finally, one has the exact (or nearly exact) solution which is obtained by solving the multistate quantum dynamical (vibronic) problem; see also subsection 9.10.4. If one thinks of the first approach as corresponding to include the dynamic Jahn-Teller effect alone, then Table 9.16 shows that such an effect has a remarkable importance on the vibrational levels as it may be seen by comparing states with equal sets of quantum numbers (v_1, v_2, v_3) in the C_{2v} point group. In turn, the calculations of sets (4) to (6) would include both the dynamic Jahn-Teller and the GP effects. The difference between the above two sets of results were then attributable to the GP effect alone; see Figure 9.6 to Figure 9.8. This is found⁶ to lead to further shifts of the energy levels, while playing a significant role in the bound vibrational states of Li_3 , not only quantitative but also qualitative.

It must be noted that all genuine vibronic degeneracies remain no matter how strong the vibronic interaction is. This is due to the fact that the permutation-inversion symmetry is unchanged, and hence the potential function retains its original symmetry. For example, the degenerate ${}^{ev}E'$ vibronic levels cannot split even when large amplitude motions are possible. Only the interaction with rotation can produce such a splitting.²⁰

9.10.4 Nonadiabatic coupling effects

Nonadiabatic coupling between adiabatic (Born-Oppenheimer) potential energy surfaces leads to a breakdown of the Born-Oppenheimer approximation. The proper treatment requires then a coupled multistate calculation, which would lead to the exact vibronic levels. For X_3 -type systems such as Li_3 , we have two adiabatic potential energy surfaces which intersect originating an upper sheet, which has the shape of a cone, and a lower sheet, which looks like a trough. If one carries out only single surface generalized Born-Oppenheimer calculations (*i.e.*, by including the GP effect), one obtains either the cone or trough states. For Li_3 , the cone states are genuine bound states. However, we must distinguish two cases for the cone states, depending on whether or not the states of interest have energies which exceed the dissociation energy of the lower surface. If they lie above the dissociation threshold, then they are imbedded in a continuum and would show up as resonances in reactive scattering or as long-lived complexes in studies of unimolecular decomposition. As a result, such states (which are pseudo-bound states in the single surface calculations) are truly resonance states. If the energies of the cone states are not above the dissociation limit on the lower surface, then they are imbedded in the discrete spectrum of the trough states. In this case, they are genuine bound states. Moreover, they have strong interactions with the trough states of the same symmetry. The levels of these states as well as of the states which are near the conical intersection seam would further shift in the nonadiabatic coupling treatment of the problem. Of course, a quantitative assessment of those shifts would require the knowledge of the observed frequencies or rigorous nonadiabatic calculations carried out on the same potential energy surface.

Unfortunately, such comparisons cannot be done at present.

9.10.5 Effects of electron spin and nuclear spin

For molecules with an even number of electrons, the spin wave function has only single-valued representations just as the spatial wave function. For these molecules, any degenerate spin-orbit state is unstable in the symmetric conformation since there is always a non-totally symmetric normal coordinate along which the potential energy depends linearly. For example, for an 3E state of a C_{3v} molecule, the spin wave function has species ${}^{es}A_2$ and ${}^{es}E$ which upon multiplication by the species ${}^{eo}E$ of the orbital wave function leads to total electronic wave functions of species $({}^{es}A_2 \oplus {}^{es}E) \otimes {}^{eo}E = {}^eA_1 \oplus {}^eA_2 \oplus 2{}^eE$. Thus, the 3E state splits into four states of which only two eE states will be unstable. Similarly, for a 3A_1 state which is orbitally stable, a splitting into ${}^eA_2 \oplus {}^eE$ will occur due to the spin-orbit coupling, of which only the first term is stable (the second, eE , is unstable). However, the eE component is only slightly unstable since in an orbitally non-degenerate state the spin-orbit coupling is always very small.²⁰

The situation is different for an electronic system with an odd number of electrons. By Kramers' theorem, the vibronic coupling cannot remove the degeneracy caused by the half-integral spin S . Moreover, as Jahn⁵⁵ has shown, the antisymmetric product of the species of the spin-orbit wave function with itself must have the same species as one of the non-totally symmetric normal vibrations in order to make the Jahn-Teller instability possible. For all axial point groups, the antisymmetric product of any doubly degenerate two-valued representation with itself is totally symmetric; *i.e.*, $E_{1/2}$, $E_{3/2}$, \dots states cannot be split by vibronic coupling. Therefore, for all axial point groups when spin-orbit interaction is strong, there is no Jahn-Teller instability. Only a magnetic field such as that connected with a rotation can remove the degeneracy. As it follows from the previous discussion, for an 2E state, the orbital part of the degeneracy will lead to a Jahn-Teller instability if the spin-orbit coupling is weak. For a strong spin-orbit interaction, 2E will split into two states ${}^{eo}E \otimes {}^{es}E_{1/2} = {}^eE_{1/2} \oplus {}^eE_{3/2}$, with each doublet component remaining doubly degenerate for arbitrary displacements of the nuclei. The general conclusion is that spin-orbit coupling for half-integral spin reduces the instability caused by orbital degeneracy. The above discussion can be applied to the nuclear spin if we consider the nucleus-spin electron-orbit coupling. But since this coupling is generally smaller than the electron spin-orbit coupling, it may be necessary to take it into account only in special cases, *e.g.*, for large values of J .

9.10.6 Other alkali metal trimers

In this subsection, we extend the above discussion to the isotopomers of X_3 systems, where X stands for an alkali metal atom. For the lowest two electronic states, the permutational

properties of the electronic wave functions are similar to those of Li_3 . Their potential energy surfaces show that the barriers for pseudorotation are very low,⁵⁶ and we must regard the concerned particles as identical. ^{23}Na has a nuclear spin $3/2$; ^{39}K , ^{40}K , and ^{41}K have nuclear spins $3/2$, 4 , and $3/2$; ^{85}Rb and ^{87}Rb have nuclear spins $5/2$ and $3/2$; and ^{133}Cs has a nuclear spin $7/2$. From the above discussion, it follows that the permutation properties of molecules consisting of nuclei with individual half-integral spins will be similar to those of molecules involving ^7Li ; conversely, the permutational properties of molecules consisting of individual integral spin nuclei will be similar to those containing ^6Li .

9.10.7 $^1\text{H}_3$ and its isotopomers

We discuss now briefly the molecule $^1\text{H}_3$ and its isotopomers, while highlighting also their differences with respect to $^7\text{Li}_3$. For the title systems, there have been many investigations, *e.g.*, Refs. 2, 42, and references therein. Similarly to Li_3 , H_3 and its isotopomers are important Jahn-Teller systems where the ${}^vE'$ normal coordinates cause instability and lead to the splitting of the potential energy in the form of a conical intersection between the two involved adiabatic potential energy surfaces. The difference between the H_3 and Li_3 potential energy surfaces lie in the fact that the lower sheet is of hat-type and can support only resonance states. Moreover, these resonance states are mainly located in the collinear saddle-point region which is far from the conical intersection; thus, the GP effect calculated on the accurate H_3 DMBE potential energy surface⁵⁷ has been shown² to play a minor role on such transition-state resonances.

As we have discussed in preceding sections, it should also be noted that ^1H and ^3H have nuclear spin $1/2$, which may have drastic consequences on the vibrational spectra of the corresponding trimeric species. In fact, the nuclear spin wave functions can only have A_1 (quartet state) and E (doublet) symmetries. Since the total wave function must be antisymmetric, A_1 rovibronic states cannot therefore be allowed. For $J = 0$, only resonance states of A_2 and E symmetries are permitted. Similarly, only E -symmetric pseudo-bound states are allowed for $J = 0$. Indeed, even when vibronic coupling is taken into account, only A_2 and E vibronic states are allowed. Table 9.18 to Table 9.20 summarize the symmetry properties of the wave functions for $^1\text{H}_3$ and its isotopomers.

9.11 Concluding remarks

In this Chapter, we have discussed the permutational symmetry properties of the total molecular wave function and its various components under permutation of identical particles. We started by noting that most nuclear dynamics treatments carried out so far neglect the interactions between the nuclear spin and the other nuclear and electronic degrees of freedom in the system Hamiltonian. Due to such a neglect, one must impose

Table 9.18: Symmetry properties of $^1\text{H}_3$ and $^3\text{H}_3$ wave functions in the \mathcal{S}_3 permutation group.

| Total | Nuclear spin ^{a)} | Rovibronic | Rotational ^{b)} | Pseudorotational |
|-------|----------------------------|------------|--------------------------|---------------------------|
| A_2 | A_1 | A_2 | A_1 | A_2 |
| A_2 | A_1 | A_2 | A_2 | A_1 |
| A_2 | A_1 | A_2 | E | E |
| A_2 | E | E | A_1 | E |
| A_2 | E | E | A_2 | E |
| A_2 | E | E | E | $A_1 \oplus A_2 \oplus E$ |

^{a)} Nuclear spin $I = \frac{1}{2}$.

^{b)} Total angular momentum quantum number $J = 0, 1, 2, \dots$

the symmetry properties of the nuclear spin in the total wave function. This requires that the total wave function for identical fermions (bosons) must be antisymmetric (symmetric) under the permutation of the identical particles. From a generalization of Kramers' theorem to total angular momentum \mathbf{J} , it has then been shown that the rotational states of a system with half-integral total angular momentum quantum number J must be degenerate. Because molecular double groups are subgroups of the three-dimensional spatial rotation group $\mathbf{SO}(3)$, the former can be used as a powerful means to study the rotational properties of any molecular system. Based on the permutational symmetry requirements of the total wave function and the extended Kramers' theorem, some severe consequences have then been demonstrated for cases where the nuclear spin quantum number is half or zero. The theory has been illustrated by considering in detail the vibrational spectra of the alkali metal trimers where vibronic coupling has been shown to dominate. In this context, we have also reviewed the static and the dynamic Jahn-Teller effects, the GP effect, nonadiabatic coupling, and electron and nuclear spin effects in X_3 (2S) systems. Although the discussion on $^1\text{H}_3$ and its isotopomers has been brief, it has been pointed out that, for $^1\text{H}_3$, A_1 rovibronic states will not be allowed. Moreover, for $J = 0$, only resonant states (hat states) of A_2 and E symmetries are permitted, while only E -states are allowed for the pseudo-bound states (cone states). The implication is that after computing the full spectrum by solving Schrödinger's equation without consideration of nuclear spin effects, one must carefully distinguish the physically allowed solutions from the unphysical (mathematical) ones. For brevity, no attempt has been made to discuss transition selection rules; the interested reader is referred to Ref. 20. Although the material presented in this Chapter focused on H_3 and Li_3 , the theory which has been reviewed and in some occasions extended is general and should be of interest to understand a wider class of systems.

Table 9.19: Symmetry properties of ${}^2\text{H}_3$ wave functions in the \mathcal{S}_3 permutation group.

| Total | Nuclear spin ^{a)} | Rovibronic | Rotational ^{b)} | Pseudorotational |
|-------|----------------------------|------------|--------------------------|---------------------------|
| A_1 | A_1 | A_1 | E | E |
| A_1 | A_2 | A_2 | E | E |
| A_1 | E | E | E | $A_1 \oplus A_2 \oplus E$ |

^{a)} Nuclear spin $I = 1$.

^{b)} Total angular momentum quantum number $J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$

Table 9.20: Symmetry properties of ${}^2\text{H} {}^1\text{H}_2$, ${}^3\text{H} {}^1\text{H}_2$, ${}^2\text{H} {}^3\text{H}_2$ and ${}^1\text{H} {}^3\text{H}_2$ wave functions in the \mathcal{S}_2 permutation group.

| Total | Nuclear spin ^{a)} | Rovibronic | Rotational ^{b)} | Pseudorotational |
|-------|----------------------------|------------|--------------------------|------------------|
| B | A | B | A | B |
| B | A | B | B | A |
| B | B | A | A | A |
| B | B | A | B | B |

^{a)} Nuclear spins are: $I = \frac{1}{2}$ for ${}^1\text{H}$ and ${}^3\text{H}$, and $I = 1$ for ${}^2\text{H}$.

^{b)} Total angular momentum quantum number $J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$

9.12 Update to recent work

After this work has been completed (1998), several articles on multivalued potential energy surfaces and/or the GP effect have been published. Since it would not appear viable at this stage giving a detailed coverage of such work, we list^{43,58–61} here only those papers referring to our own group from which the reader may access other published work through cross referencing.

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Appendix

9.13 Antilinear operators and their properties

In this Appendix we review some important properties of antilinear operators which are used in the text and Appendix 9.14. Let us then consider an operator \hat{O} which acts on a state $|\psi\rangle$ to give $\hat{O}|\psi\rangle$, with the original state being restored after acting twice, *i.e.*, $\hat{O}^2|\psi\rangle = c|\psi\rangle$. Clearly, the space-inversion operator \hat{I} is a well known example of such an operator. Moreover, as it will be shown the time-reversal \hat{T} and complex conjugate \hat{K} operators provide further examples of such operators.

By the very meaning of a physical state, we must require that

$$\langle \hat{O}\psi | \hat{O}\psi \rangle = \langle \psi | \psi \rangle \quad (9.51)$$

This should apply both to linear and antilinear operators hereafter denoted by $\hat{\mathcal{L}}$ and $\hat{\mathcal{A}}$, respectively. For a linear operator, the action on a general state $c_1|\psi_1\rangle + c_2|\psi_2\rangle$ is expressed by

$$\hat{\mathcal{L}}(c_1|\psi_1\rangle + c_2|\psi_2\rangle) = c_1\hat{\mathcal{L}}|\psi_1\rangle + c_2\hat{\mathcal{L}}|\psi_2\rangle \quad (9.52)$$

while, for an antilinear operator,⁶² it assumes the form

$$\hat{\mathcal{A}}(c_1|\psi_1\rangle + c_2|\psi_2\rangle) = c_1^*\hat{\mathcal{A}}|\psi_1\rangle + c_2^*\hat{\mathcal{A}}|\psi_2\rangle \quad (9.53)$$

where c_i ($i = 1, 2$) are complex numbers. As for linear operators (where we have the definition of Hermitian conjugate of $\hat{\mathcal{L}}|\psi\rangle$ to be $\langle \psi | \hat{\mathcal{L}}^\dagger$), we define the Hermitian conjugate of $(\hat{\mathcal{A}}|\psi\rangle)$ as $(\langle \psi | \hat{\mathcal{A}}^\dagger)$; recall that the parenthesis is necessary. Examples are the linear operator \hat{I} , and the antilinear operator \hat{T} . Note that Eq. (9.51) implies that the norm of a vector cannot be altered both for linear and antilinear operators. More generally, a linear operator cannot change the internal product of two vectors and hence must be unitary. Conversely, antilinear operators change the internal product to its complex conjugate, and hence are called anti-unitary.³⁷ Thus, one has

$$\langle \psi | \phi \rangle = \langle \phi | \psi \rangle^* \quad (9.54)$$

which indicates that the unit operator is linear with respect to the ket and antilinear with respect to the bra. In general, a linear operator is linear with respect to the ket and

antilinear with respect to the bra. Regarding the action of an antilinear operator, we have by definition

$$\langle \psi | (\hat{\mathcal{A}} | \phi \rangle) = [(\langle \psi | \hat{\mathcal{A}}) | \phi \rangle]^* \quad (9.55)$$

where the parentheses in $\langle \psi | (\hat{\mathcal{A}} | \phi \rangle)$ indicate the order of the action, with $(\hat{\mathcal{A}} | \cdot)$ being antilinear with respect to both the bra and the ket. In turn, $(\cdot | \hat{\mathcal{A}})$ is linear with respect to both the bra and the ket.

From the definition of Hermitian conjugate and Eq. (9.55), one then gets

$$\langle \psi | (\hat{\mathcal{A}} | \phi \rangle) = \langle \phi | (\hat{\mathcal{A}}^\dagger | \psi \rangle) \quad (9.56)$$

This implies that the Hermitian conjugate of an antilinear operator is also antilinear. It should also be pointed out that the product of two antilinear operators is linear, while the product of a linear and an antilinear operators is antilinear. In general, an antilinear operator may be expressed as a product of a linear and an antilinear operators. From Eq. (9.55), we also have

$$[(\langle \psi | \hat{\mathcal{A}}^\dagger) (\hat{\mathcal{A}} | \psi \rangle)]^* = \langle \psi | (\hat{\mathcal{A}}^\dagger \hat{\mathcal{A}} | \psi \rangle) = \langle \psi | \psi \rangle^* = \langle \psi | \psi \rangle \quad (9.57)$$

Thus,

$$\hat{\mathcal{A}}^\dagger \hat{\mathcal{A}} = \hat{\mathcal{A}} \hat{\mathcal{A}}^\dagger = \hat{1} \quad (9.58)$$

a property which is also satisfied by unitary operators.

9.14 Proof of Eq. (9.6) and Eq. (9.11)

Let us consider the time evolution of a quantum system, which satisfies the time-dependent Schrödinger equation³⁸

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \quad (9.59)$$

where \hat{H} does not depend explicitly on time. Defining now the time-reversal state $|\psi_{rev}(-t)\rangle$ as

$$|\psi_{rev}(-t)\rangle = \hat{T} |\psi(t)\rangle \quad (9.60)$$

such a state must satisfy the corresponding time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial(-t)} |\psi_{rev}(-t)\rangle = \hat{H} |\psi_{rev}(-t)\rangle \quad (9.61)$$

Consider now the complex conjugate of Eq. (9.59),

$$i\hbar \frac{\partial}{\partial(-t)} |\psi(t)\rangle^* = \hat{H} |\psi(t)\rangle^* \quad (9.62)$$

If there is an unitary operator \hat{U} such that

$$\hat{U} \hat{H} \hat{U}^\dagger = \hat{H} \quad (9.63)$$

one has, after the action of \hat{U} on Eq. (9.62),

$$i\hbar \frac{\partial}{\partial(-t)} \hat{U}|\psi(t)\rangle^* = \hat{U}\hat{H}|\psi(t)\rangle^* \quad (9.64)$$

$$= \hat{H}\hat{U}|\psi(t)\rangle^* \quad (9.65)$$

By comparing Eq. (9.64) with Eq. (9.60) and Eq. (9.61), the time-reversal operator can be expressed as a product of an unitary and a complex conjugate operators as follows

$$\hat{T} = \hat{U}\hat{K} \quad (9.66)$$

Thus, the time-reversal state can be written as

$$|\psi_{rev}(-t)\rangle = \hat{T}|\psi(t)\rangle = \hat{U}\hat{K}|\psi(t)\rangle = \hat{U}|\psi(t)\rangle^* \quad (9.67)$$

It is now required for observable quantities that the expectation value of any operator \hat{O} taken with respect to $|\psi_{rev}(-t)\rangle$ must be the same as that of the operator \hat{O}_{rev} taken relative to $|\psi(t)\rangle$, *i.e.*,

$$\langle \psi_{rev}(-t) | \hat{O} | \psi_{rev}(-t) \rangle = \langle \psi(t) | \hat{O}_{rev} | \psi(t) \rangle \quad (9.68)$$

Since

$$\langle \psi_{rev}(-t) | \hat{O} | \psi_{rev}(-t) \rangle = \langle \hat{U}\psi(t) | \hat{O} | \hat{U}\psi(t) \rangle \quad (9.69)$$

$$= \langle \psi(t) | \hat{U}^\dagger \hat{O} \hat{U} | \psi(t) \rangle \quad (9.70)$$

a comparison with Eq. (9.68), and the fact that any operator associated to an observable quantity is Hermitian, leads to

$$\hat{O}_{rev}^T = \hat{U}^\dagger \hat{O} \hat{U} \quad (9.71)$$

where the superscript T in the time-reversal operator \hat{O}_{rev}^T denotes the transpose.

Consider now the case of spinless particles not subject to external electronic and magnetic fields. We may now choose the unitary operator \hat{U} as the unit operator, *i.e.*, $\hat{T} = \hat{K}$. For the coordinate and momentum operators, one then obtains

$$\hat{T}\hat{r}\hat{T}^{-1} = \hat{K}\hat{r}\hat{K}^{-1} = \hat{r} \quad (9.72)$$

$$\hat{T}\hat{p}\hat{T}^{-1} = \hat{K}\hat{p}\hat{K}^{-1} \quad (9.73)$$

$$= \hat{K}(-i\hbar\nabla)\hat{K}^{-1} \quad (9.74)$$

$$= i\hbar\nabla = -\hat{p} \quad (9.75)$$

As a result, the orbital angular momentum operator satisfies the relation

$$\hat{T}\hat{L}\hat{T}^{-1} = \hat{T}(\hat{r} \times \hat{p})\hat{T}^{-1} \quad (9.76)$$

$$= -(\hat{r} \times \hat{p}) = -\hat{L} \quad (9.77)$$

Let us address next the case of half-spin particles. One has

$$\hat{S} = \hat{S}_x \cdot \mathbf{i} + \hat{S}_y \cdot \mathbf{j} + \hat{S}_z \cdot \mathbf{k} \quad (9.78)$$

where

$$\hat{S}_i = \frac{1}{2} \hbar \sigma_i \quad (9.79)$$

with the matrices σ_i ($i = x, y, z$) being the Pauli matrices

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (9.80)$$

If we now choose the unitary operator to be real, then it may assume the form

$$\hat{U} = i\sigma_y \quad (9.81)$$

Applying Eq. (9.71) to the spin operators \hat{S}_i and using Eq. (9.80), one then gets after some matrix multiplications

$$\hat{U}^\dagger \hat{S}_x \hat{U} = -\hat{S}_x, \quad \hat{U}^\dagger \hat{S}_y \hat{U} = \hat{S}_y, \quad \hat{U}^\dagger \hat{S}_z \hat{U} = -\hat{S}_z \quad (9.82)$$

We are now ready to prove that

$$\hat{T} \hat{S} \hat{T}^{-1} = -\hat{S} \quad (9.83)$$

since we have

$$\hat{T} \hat{S}_x \hat{T}^{-1} = i\sigma_y \hat{K} \hat{S}_x \hat{K} \sigma_y^{-1} i^{-1} \quad (9.84)$$

$$= \sigma_y \hat{K} \hat{S}_x \hat{K} \sigma_y \quad (9.85)$$

$$= -\sigma_y \hat{K} \hat{S}_x \sigma_y \quad (9.86)$$

$$= -\frac{1}{2} \hbar \sigma_y \hat{K} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad (9.87)$$

$$= -\frac{1}{2} \hbar \sigma_y \hat{K} \begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix} \quad (9.88)$$

$$= -\frac{1}{2} \hbar \sigma_y \begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix} \quad (9.89)$$

$$= -\frac{1}{2} \hbar \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix} \quad (9.90)$$

$$= -\frac{1}{2} \hbar \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (9.91)$$

$$= -\hat{S}_x \quad (9.92)$$

and, similarly,

$$\hat{T} \hat{S}_y \hat{T}^{-1} = -\hat{S}_y, \quad \hat{T} \hat{S}_z \hat{T}^{-1} = -\hat{S}_z \quad (9.93)$$

Clearly, the above equations and Eq. (9.78) prove Eq. (9.83).

Finally, we demonstrate that

$$\hat{T}_S^2 = (-\hat{1})^{2S} \quad (9.94)$$

From Eq. (9.66) and Eq. (9.81), we have for $S = 1/2$

$$\hat{T}_S^2 = (i\sigma_y \hat{K})^2 = -\sigma_y^2 = -\hat{1} \quad (9.95)$$

where $\hat{1}$ is the unit operator in a 2×2 vector space. Note that, for spinless particles, we have chosen \hat{U} to be the unit operator in a 1×1 vector space (and hence $\hat{T} = \hat{K}$), which leads to

$$\hat{T}_S^2 = \hat{K}^2 = \hat{1} \quad (9.96)$$

and hence proves Eq. (9.94).

The above discussion is now generalized to arbitrary spin values. First, we note that twice application of the time-reversal operator leads the system back to its original state ψ , *i.e.*, $\hat{T}^2\psi = c\psi$. Thus, we have $\hat{T}^2 = c\hat{1}$. Consider next the following two relations

$$\langle \hat{T}\phi | \hat{T}^2\psi \rangle = \left(\langle \phi | \hat{T}^\dagger \right) \left(\hat{T}^2 | \psi \rangle \right) = \left[\langle \phi | \left(\hat{T}^\dagger \hat{T}^2 | \psi \rangle \right) \right]^* = \left[\langle \phi | \hat{T}\psi \rangle \right]^* = \langle \hat{T}\psi | \phi \rangle \quad (9.97)$$

$$\langle \hat{T}\phi | \hat{T}^2\psi \rangle = c \langle \hat{T}\phi | \psi \rangle \quad (9.98)$$

Thus, we have

$$\langle \hat{T}\psi | \phi \rangle = c \langle \hat{T}\phi | \psi \rangle \quad (9.99)$$

Similarly we can show that

$$\langle \hat{T}\psi | \hat{T}^2\phi \rangle = \langle \hat{T}\phi | \psi \rangle \quad (9.100)$$

$$\langle \hat{T}\phi | \psi \rangle = c \langle \hat{T}\psi | \phi \rangle \quad (9.101)$$

from Eq. (9.99) and Eq. (9.101) we can obtain

$$\langle \hat{T}\psi | \phi \rangle = c^2 \langle \hat{T}\psi | \phi \rangle \quad (9.102)$$

and hence

$$c^2 = 1 \quad (9.103)$$

which proves that $\hat{T}^2 = \pm\hat{1}$. By substituting now Eq. (9.66) in $\hat{T}\hat{r}\hat{T}^{-1}$, $\hat{T}\hat{p}\hat{T}^{-1}$, and $\hat{T}\hat{S}\hat{T}^{-1}$, we may show that \hat{U} satisfies equations similar to Eq. (9.82) and Eq. (9.83).

As a first application, consider the case of a single particle with spin quantum number S . The spin wave functions will then transform according to the irreducible representations $D^{(S)}(\alpha)$ of the three-dimensional rotational group $\mathbf{SO}(3)$, where α is the rotational vector, written in the operator form as⁶³

$$\hat{D}^{(S)}(\alpha) = \exp\left(-\frac{i}{\hbar}\hat{S} \cdot \alpha\right) \quad (9.104)$$

The spin operator \hat{S} is an irreducible tensor of rank one with the following transformational properties

$$\hat{D}^{(S)}(\alpha)\hat{S}\hat{D}^{(S)}(\alpha)^{-1} = \hat{g}(\alpha)\hat{S} \quad (9.105)$$

where $\hat{g}(\alpha)$ is an operator of $\mathbf{SO}(3)$. Let us then take $\hat{g}(\alpha)$ to be a rotation by π around the y axis. Thus, from Eq. (9.104) and Eq. (9.105), one gets

$$\exp\left(-\frac{i}{\hbar}\hat{S}_y\right)\hat{S}_x\exp\left(-\frac{i}{\hbar}\hat{S}_y\right) = -\hat{S}_x \quad (9.106)$$

$$\exp\left(-\frac{i}{\hbar}\hat{S}_y\right)\hat{S}_y\exp\left(-\frac{i}{\hbar}\hat{S}_y\right) = \hat{S}_y \quad (9.107)$$

$$\exp\left(-\frac{i}{\hbar}\hat{S}_y\right)\hat{S}_z\exp\left(-\frac{i}{\hbar}\hat{S}_y\right) = -\hat{S}_z \quad (9.108)$$

Comparing Eq. (9.106) to Eq. (9.108) with Eq. (9.82), one obtains

$$\hat{U} = \exp\left(-\frac{i}{\hbar}\pi\hat{S}_y\right) \quad (9.109)$$

Since $\hat{S}_y^T = -\hat{S}_y$, we then have

$$\hat{U}^\dagger = \exp\left(-\frac{i}{\hbar}\pi\hat{S}_y^T\right) \quad (9.110)$$

$$= \exp\left(\frac{i}{\hbar}\pi\hat{S}_y\right) \quad (9.111)$$

$$= \exp\left(-\frac{i}{\hbar}2\pi\hat{S}_y^T\right)\exp\left(-\frac{i}{\hbar}\pi\hat{S}_y\right) \quad (9.112)$$

$$= \hat{D}^{(S)}(2\pi\mathbf{j})\hat{U} \quad (9.113)$$

$$= (-1)^{2S}\hat{U} \quad (9.114)$$

where $2\pi\mathbf{j}$ indicates a 2π rotation about the y axis. Thus, we have

$$\hat{T} = \exp\left(-\frac{i}{\hbar}\pi\hat{S}_y\right)\hat{K} \quad (9.115)$$

and finally, by comparing with Eq. (9.109), one gets

$$\hat{T}^2 = (-\hat{1})^{2S} \quad (9.116)$$

Finally, for a system of n identical particles, the result is

$$\hat{U} = \exp\left(-\frac{i}{\hbar}\pi\hat{S}_{y,1}\right)\exp\left(-\frac{i}{\hbar}\pi\hat{S}_{y,2}\right)\cdots\exp\left(-\frac{i}{\hbar}\pi\hat{S}_{y,n}\right) \quad (9.117)$$

and hence

$$\hat{T}^2 = (-\hat{1})^{\sum_{i=1}^n 2S_i} = (-\hat{1})^{2S} \quad (9.118)$$

9.15 Degenerate and near-degenerate vibrational levels

We discuss here the motion of a system of three identical nuclei in the vicinity of the D_{3h} configuration. The conventional coordinates for the in-plane motion are employed, as shown in Figure 9.5. The normal coordinates (Q_x, Q_y, Q_z), the plane polar coordinates (ρ, φ, z), and the Cartesian displacement coordinates (x_i, y_i, z_i) of the three nuclei ($i = 1, 2, 3$) are related by¹⁵

$$Q_x = \rho \cos \varphi = \frac{1}{\sqrt{3}} \left\{ -x_1 + \left(\frac{1}{2}x_2 + \frac{\sqrt{3}}{2}y_2 \right) + \left(\frac{1}{2}x_3 - \frac{\sqrt{3}}{2}y_3 \right) \right\} \quad (9.119)$$

$$Q_y = \rho \sin \varphi = \frac{1}{\sqrt{3}} \left\{ y_1 + \left(\frac{\sqrt{3}}{2}x_2 - \frac{1}{2}y_2 \right) + \left(-\frac{\sqrt{3}}{2}x_3 - \frac{1}{2}y_3 \right) \right\} \quad (9.120)$$

$$Q_z = z = \frac{1}{\sqrt{3}} \left\{ -x_1 + \left(\frac{1}{2}x_2 - \frac{\sqrt{3}}{2}y_2 \right) + \left(\frac{1}{2}x_3 + \frac{\sqrt{3}}{2}y_3 \right) \right\} \quad (9.121)$$

where the coordinates (Q_x, Q_y) are the doubly degenerate modes belonging to E' irreducible representation in D_{3h} , and Q_z belongs to the A'_1 one. Note that Q_x is symmetric with respect to the xz plane, while Q_y is antisymmetric.

The coordinates of interest to us in the following discussion are Q_x and Q_y , which describe the distortion of the molecular triangle from D_{3h} symmetry. In the harmonic-oscillator approximation, the factor in the vibrational wave function due to the two degenerate modes is then (except for a normalization constant and dependence on Q_z) given by

$$\Psi(v_1, v_{2a}, v_{2b}) \simeq H_{v_{2a}}(\sqrt{\alpha_2}Q_x) H_{v_{2b}}(\sqrt{\alpha_2}Q_y) \exp[-\alpha_2(Q_x^2 + Q_y^2)/2] \quad (9.122)$$

where $H_{v_{2a}}$ and $H_{v_{2b}}$ are Hermite polynomials of order v_{2a} and v_{2b} , respectively; v_{2a} and v_{2b} are the vibrational quantum numbers, and $\alpha_2 = 2\pi\nu_2/\hbar$, with ν_2 being the frequency of the degenerate mode.

Let us then consider the case where the degenerate mode is doubly excited. In this case, $v_2 = v_{2a} + v_{2b} = 2$ and the corresponding vibrational energy level will be triply degenerate with the associated wave functions being given by

$$\Psi_1 = \Psi(v_1, 2, 0) \sim 4\alpha_2 Q_x^2 - 2 \quad (9.123)$$

$$\Psi_2 = \Psi(v_1, 1, 1) \sim 4\alpha_2 Q_x Q_y \quad (9.124)$$

$$\Psi_3 = \Psi(v_1, 0, 2) \sim 4\alpha_2 Q_y^2 - 2 \quad (9.125)$$

Note that only the polynomial factors have been given, since the exponential parts are identical for all wave functions. Of course, any linear combination of the wave functions in Eq. (9.123) to Eq. (9.125) will still be an eigenfunction of the vibrational Hamiltonian, and hence a possible state. There are three such linearly independent combinations which

assume special importance, namely

$$\Psi'_1 = \Psi_1 - \Psi_3 + 2i\Psi_2 \sim 4\alpha_2 (Q_x^2 - Q_y^2 + 2iQ_xQ_y) \quad (9.126)$$

$$\Psi'_2 = \Psi_1 + \Psi_3 \sim 4\alpha_2 (Q_x^2 + Q_y^2) - 4 \quad (9.127)$$

$$\Psi'_3 = \Psi_1 - \Psi_3 - 2i\Psi_2 \sim 4\alpha_2 (Q_x^2 - Q_y^2 - 2iQ_xQ_y) \quad (9.128)$$

Using the plane polar coordinates defined in Eq. (9.119), one obtains

$$\Psi'_1 \simeq 4\alpha_2\rho^2 \exp(-\alpha_2\rho^2/2) \exp(2i\varphi) \quad (9.129)$$

$$\Psi'_2 \simeq 4(\alpha_2\rho^2 - 1) \exp(-\alpha_2\rho^2/2) \quad (9.130)$$

$$\Psi'_3 \simeq 4\alpha_2\rho^2 \exp(-\alpha_2\rho^2/2) \exp(-2i\varphi) \quad (9.131)$$

These new wave functions are eigenfunctions of the z -component of the angular momentum $\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$ with eigenvalues $m_{v_2} = +2, 0, -2$ in units of \hbar . Thus, Eq. (9.129) to Eq. (9.131) represent states in which the vibrational angular momentum of the nuclei about the molecular axis has a definite value. When treating the vibrations as harmonic, there is no reason to prefer them to any other linear combinations which can be obtained from the original basis functions in Eq. (9.123) to Eq. (9.125). However, when perturbations occur due to anharmonicity, the wave functions in Eq. (9.129) to Eq. (9.131) will provide the correct zeroth-order ones. The quantum numbers v_{2a} and v_{2b} are therefore not physically significant, while v_2 and m_{v_2} or v_2 and $l_2 = |m_{v_2}|$ are. It should also be pointed out that the degeneracy in the vibrational levels will be split due to anharmonicity.²⁰

Consider now the general case of a v_2 -multiply excited degenerate vibrational level where $v_2 > 2$. This is dealt by solving the Schrödinger equation for the isotropic 2D harmonic oscillator with the Hamiltonian assuming the form⁶⁴

$$\hat{H}_v = \frac{\hbar\sqrt{\lambda}}{2} \left(-\frac{\partial^2}{\partial q_x^2} - \frac{\partial^2}{\partial q_y^2} + q_x^2 + q_y^2 \right) \quad (9.132)$$

where we have used the dimensionless normal coordinates $q_i = \sqrt{\alpha_2}Q_i$ ($i = x, y$), with $\alpha_2 = 2\pi\nu_2/\hbar = \sqrt{\lambda}/\hbar$. The transformation of such a Hamiltonian into polar coordinates leads to

$$\hat{H}_v = -\frac{\hbar\sqrt{\lambda}}{2} \left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho} \frac{\partial}{\partial\rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial\varphi^2} - \rho^2 \right) \quad (9.133)$$

Separation of variables can then be achieved by using

$$\Psi_v = R(\rho)\Phi(\varphi) \quad (9.134)$$

where

$$R(\rho) = F(\rho) \exp(-\rho^2/2) \quad (9.135)$$

and

$$F(\rho) = \rho^s \sum_{n=0}^{\infty} a_n \rho^n \quad (9.136)$$

Assuming now that the power series expansion in $F(\rho)$ can be terminated to keep $R(\rho)$ well behaved at large ρ values, it may be shown⁶⁴ that

$$\Phi(\varphi) = (2\pi)^{-1/2} \exp(im_{v_2}\varphi) \quad m_{v_2} = \pm v_2, \pm(v_2 - 2), \dots, \pm 1 \text{ or } 0 \quad (9.137)$$

$$R(\rho) = N_{v_2 l_2} \rho^{l_2} L_n^{l_2}(\rho^2) \exp(-\rho^2/2) \quad l_2 = |m_{v_2}|, \quad n = (v_2 + l_2)/2 \quad (9.138)$$

where $L_n^{l_2}(\rho^2)$ are the associated Laguerre polynomials of order n , and the normalization factor assumes the form

$$N_{v_2 l_2} = \sqrt{\frac{2[(v_2 - l_2)/2]!}{\{[(v_2 + l_2)/2]!\}^3}} \quad (9.139)$$

Let us now examine the case of a 3D harmonic oscillator possessing three degenerate normal coordinates (Q_1, Q_2, Q_3) , with the degenerate mode being v -multiply excited; $v = v_1 + v_2 + v_3$. There are then $(v + 1)(v + 2)/2$ degenerate vibrational wave functions and energy levels for each value of v , corresponding to the possible different combinations of v_1, v_2 , and v_3 . It is now convenient to define the polar coordinates (ρ, θ, φ) by the corresponding dimensionless normal coordinates (q_1, q_2, q_3) according to

$$\begin{aligned} q_1 &= \rho \sin \theta \cos \varphi \\ q_2 &= \rho \sin \theta \sin \varphi \\ q_3 &= \rho \cos \theta \end{aligned} \quad (9.140)$$

In such coordinates, the Hamiltonian assumes the form⁶⁴

$$\hat{H}_v = \frac{\hbar\sqrt{\lambda}}{2} \left(-\frac{\partial^2}{\partial q_1^2} - \frac{\partial^2}{\partial q_2^2} - \frac{\partial^2}{\partial q_3^2} + q_1^2 + q_2^2 + q_3^2 \right) \quad (9.141)$$

Transformation of the Hamiltonian into polar coordinates then leads to

$$\hat{H}_v = -\frac{\hbar\sqrt{\lambda}}{2} \left\{ \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\rho^2} \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} - \rho^2 \right\} \quad (9.142)$$

while the vibrational wave equation assumes the form

$$\left\{ \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\rho^2} \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \left(\frac{2E}{\hbar\sqrt{\lambda}} - \rho^2 \right) \right\} \Psi_v = 0 \quad (9.143)$$

Separation of variables may now be obtained by using

$$\Psi_v = R(\rho)\Theta(\theta)\Phi(\varphi) \quad (9.144)$$

which upon insertion into Eq. (9.143) leads to

$$\left\{ \frac{d^2}{d^2\varphi} + m^2 \right\} \Phi = 0 \quad (9.145)$$

$$\left\{ \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) + \left[l(l+1) - \frac{m^2}{\sin^2 \theta} \right] \right\} \Theta = 0 \quad (9.146)$$

$$\left\{ \frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{d}{d\rho} \right) + \left[\frac{2E}{\hbar\sqrt{\lambda}} - \rho^2 - \frac{l(l+1)}{\rho^2} \right] \right\} R = 0 \quad (9.147)$$

These have as solutions

$$\Phi(\varphi) = (2\pi)^{-1/2} \exp(im\varphi) \quad (9.148)$$

$$\Theta(\theta) = N_{l|m|} P_l^{|m|}(\cos \theta) \quad (9.149)$$

$$R(\rho) = N_{vl} \rho^l L_\tau^{l+\frac{1}{2}}(\rho^2) \exp(-\rho^2/2) \quad (9.150)$$

where

$$l = v, v-2, v-4, \dots, 1 \text{ or } 0 \quad (9.151)$$

$$m = 0, \pm 1, \pm 2, \dots, \pm l \quad (9.152)$$

$$\tau = (v+l+1)/2 \quad (9.153)$$

The functions $P_l^{|m|}$ are associated Legendre polynomials of order $|m|$ and degree l , and $L_\tau^{l+\frac{1}{2}}(\rho^2)$ are associated Laguerre polynomials of degree $(v-1)/2$ in ρ^2 . In turn, the normalization factors are found to be

$$N_{l|m|} = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} \quad (9.154)$$

$$N_{vl} = \sqrt{\frac{2[(v-1)/2]!}{\{(v+l+1)/2\}!^3}} \quad (9.155)$$

In the configuration space spanned by (q_1, q_2, q_3) , we may then define the vibrational angular momentum M through its classical components, *i.e.*,

$$M_1 = q_2 p_3 - q_3 p_2 \text{ and its (123) cyclic permutations} \quad (9.156)$$

where p_i are the conjugate momenta associated to q_i ($i = 1, 2, 3$). The operators associated with $M^2 = M_1^2 + M_2^2 + M_3^2$ and its projection M_z (denoted M_3 in Ref. 64) along the z axis assume in polar coordinates the form

$$\hat{M}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \quad (9.157)$$

$$\hat{M}_z = -i\hbar \frac{\partial}{\partial \varphi} \quad (9.158)$$

As for the 2D case, it can be shown that Ψ_v in Eq. (9.144) are eigenfunctions of both \hat{M}^2 and \hat{M}_z defined by

$$\hat{M}^2 \Psi_v = l(l+1)\hbar^2 \Psi_v \quad (9.159)$$

$$\hat{M}_z \Psi_v = m\hbar \Psi_v \quad (9.160)$$

Thus, l and m quantize the vibrational angular momentum and its z -component.

So far, we have considered interactions which are degenerate at the harmonic-oscillator level of approximation. For two levels that are nearly degenerate by accident in such an

approximation, large perturbations may arise due to anharmonicity which are known as Fermi resonances. It should be noted that Fermi resonances occur only between states of the same symmetry. Thus, they cannot occur between two levels with different values of the vibrational angular momentum quantum number l . As usual, Fermi resonances increase the energy of the upper level while decreasing that of the lower one (in common language, they repel each other). Thus, the spectrum of a specific symmetry tends to be more irregular in the presence of Fermi resonances.

9.16 Potential and derivative coupling between adiabatic states in the vicinity of a conical intersection

9.16.1 Jahn-Teller theorem

Following Moffitt and Liehr,⁵² we give in this Appendix a proof of the Jahn-Teller theorem for X_3 molecules pertaining to the D_{3h} point group. Let Ψ_1 and Ψ_2 be the two electronic eigenfunctions which belong to the degenerate electronic states of E' symmetry (denoted ${}^eE'$). The two degenerate normal coordinates are Q_x and Q_y , the former being symmetric and the latter antisymmetric with respect to the xz plane (see Appendix 9.15). Defining complex normal coordinates and electronic eigenfunctions as

$$Q_+ = Q_x + iQ_y = \rho \exp(i\varphi) \quad (9.161)$$

$$Q_- = Q_x - iQ_y = \rho \exp(-i\varphi) \quad (9.162)$$

and

$$\Psi_+ = \Psi_1 + i\Psi_2 \quad (9.163)$$

$$\Psi_- = \Psi_1 - i\Psi_2 \quad (9.164)$$

the electronic energy of the system is in degenerate-state perturbation theory obtained by solving the secular equation

$$\begin{vmatrix} H_{++} - W & H_{+-} \\ H_{-+} & H_{--} - W \end{vmatrix} = 0 \quad (9.165)$$

where the matrix elements are given by

$$H_{++} = \langle \Psi_+ | \hat{H}_e | \Psi_+ \rangle, \quad H_{--} = \langle \Psi_- | \hat{H}_e | \Psi_- \rangle \quad (9.166)$$

$$H_{+-} = \langle \Psi_+ | \hat{H}_e | \Psi_- \rangle, \quad H_{-+} = \langle \Psi_- | \hat{H}_e | \Psi_+ \rangle \quad (9.167)$$

and the integrations are defined with respect to all the electronic coordinates. Then, by developing \hat{H}_e in a power series expansion of the normal coordinates, one gets

$$\hat{H}_e = \hat{h}_0 + \hat{h}_1^+ Q_- + \hat{h}_1^- Q_+ + \hat{h}_2^+ Q_-^2 + \hat{h}_2^- Q_+^2 + \dots \quad (9.168)$$

where we have considered only the dependence on the degenerate complex normal coordinates Q_+ and Q_- . Substitution of Eq. (9.168) in Eq. (9.166) and Eq. (9.167) gives

$$\begin{aligned} H_{++} &= \langle \Psi_+ | \hat{h}_0 | \Psi_+ \rangle + \langle \Psi_+ | \hat{h}_1^+ | \Psi_+ \rangle Q_- + \langle \Psi_+ | \hat{h}_1^- | \Psi_+ \rangle Q_+ \\ &+ \langle \Psi_+ | \hat{h}_2^+ | \Psi_+ \rangle Q_-^2 + \langle \Psi_+ | \hat{h}_2^- | \Psi_+ \rangle Q_+^2 + \dots \end{aligned} \quad (9.169)$$

$$\begin{aligned} H_{+-} &= \langle \Psi_+ | \hat{h}_0 | \Psi_- \rangle + \langle \Psi_+ | \hat{h}_1^+ | \Psi_- \rangle Q_- + \langle \Psi_+ | \hat{h}_1^- | \Psi_- \rangle Q_+ \\ &+ \langle \Psi_+ | \hat{h}_2^+ | \Psi_- \rangle Q_-^2 + \langle \Psi_+ | \hat{h}_2^- | \Psi_- \rangle Q_+^2 + \dots \end{aligned} \quad (9.170)$$

with similarly expressions for H_{--} and H_{-+} .

For a \hat{C}_3 rotation, Q_+ , Ψ_+ and Ψ_-^* are multiplied by $\omega = \exp(2\pi i/3)$ while Q_- , Ψ_- and Ψ_+^* are multiplied by $\omega^* = \exp(-2\pi i/3)$. Since the Hamiltonian must be totally symmetric, it follows that \hat{h}_1^+ , \hat{h}_1^- , \hat{h}_2^+ , and \hat{h}_2^- are multiplied by ω , ω^* , ω^2 and ω^{*2} , respectively. The integrals in Eq. (9.169) and Eq. (9.170) will then be different from zero only if the integrands are invariant under all symmetry operations allowed by the symmetry point group, in particular under \hat{C}_3 . It is readily seen that the linear terms in Q_+ and Q_- vanish in H_{++} and H_{--} . In turn, the first term in H_{+-} and H_{-+} vanishes while one of the linear terms (Q_+ for H_{+-} , and Q_- for H_{-+}) does not vanish. Thus, neglecting quadratic (and higher-order) terms, one obtains

$$H_{++} = H_{--} = W_0, \quad H_{+-} = cQ_+, \quad H_{-+} = cQ_- \quad (9.171)$$

Substitution of Eq. (9.171) in Eq. (9.165), leads to

$$W_{\pm} = W_0 \pm c\sqrt{Q_+Q_-} = W_0 \pm c\rho \quad (9.172)$$

Clearly, Eq. (9.172) shows that to a first approximation the electronic energy varies linearly with displacements in ρ , increasing for one component state while decreasing for the other. Thus, the potential minimum cannot be at $\rho = 0$. This is the statement of the Jahn-Teller theorem for a X_3 molecule belonging to the \mathbf{D}_{3h} point group.

9.16.2 Invariant operators

We follow Thompson and Mead⁸ to discuss the behavior of the electronic Hamiltonian, potential energy, and derivative coupling between adiabatic states in the vicinity of the D_{3h} conical intersection. Different letters will be used to distinguish operators which give to an abstract element A of a point group G one of two possible realizations: \hat{A} if it transforms the nuclear coordinates only; \hat{A} if it acts on the electronic degrees of freedom, including those which depend parametrically on the nuclear coordinates.

It can readily be shown that the electronic Hamiltonian satisfies

$$(\hat{A}\hat{H}_e)\hat{A}\psi = \hat{A}\hat{H}_e\psi \quad (9.173)$$

Indeed, if ψ is an eigenfunction of \hat{H}_e , Eq. (9.173) just expresses the fact that $\hat{A}\psi$ is an eigenfunction of the transformed Hamiltonian with the same eigenvalue. For an arbitrary ψ , it also follows upon its expansion in eigenfunctions of \hat{H}_e . Thus,

$$(\hat{A}\hat{H}_e)\hat{A} = \hat{A}\hat{H}_e \quad (9.174)$$

An electronic operator satisfying Eq. (9.174) for all elements \hat{A} of some point group G will be called an invariant operator. Note that the sum of two invariant operators is still an invariant operator, and so is their product. Similarly, the Hermitian conjugate of an invariant operator is also an invariant operator.⁸

An invariant operator can be expanded in the form⁸

$$\hat{H}_e = \sum_{\mu,s,j} \hat{h}_j^{\mu s} Q_j^{\mu s} \quad (9.175)$$

where $Q_j^{\mu s}$ is a nuclear coordinate transforming as the j th component of the μ -th irreducible representation of G , the index s refers to different occurrences of the same irreducible representation, and $\hat{h}_j^{\mu s}$ is an electronic operator which is independent of the nuclear coordinates. The requirement of Eq. (9.174) thus becomes

$$\sum_{j,k,\mu,s} \left[\hat{h}_j^{\mu s} D_{jk}^\mu(A) Q_k^{\mu s} \right] \hat{A} = \hat{A} \sum_{k,\mu,s} \hat{h}_k^{\mu s} Q_k^{\mu s} \quad (9.176)$$

This must hold independently of the values of the coordinates, and so it must hold term by term for each coefficient $Q_k^{\mu s}$. One has

$$\sum_j \hat{h}_j^{\mu s} D_{jk}^\mu(A) \hat{A} = \hat{A} \hat{h}_k^{\mu s} \quad (9.177)$$

or, equivalently,

$$\hat{A} \hat{h}_k^{\mu s} \hat{A}^{-1} = \sum_j \hat{h}_j^{\mu s} D_{jk}^\mu(A) \quad (9.178)$$

According to Eq. (9.178), the operators $\hat{h}_k^{\mu s}$ transform under $\hat{A} \cdots \hat{A}^{-1}$ according to the irreducible representation μ of G .

Consider now the subgroup \mathbf{C}_{3v} of \mathbf{D}_{3h} . For the former, Eq. (9.175) contains only four symmetry types of electronic operators: \hat{h}_{A_1} , \hat{h}_{A_2} , \hat{h}_x , and \hat{h}_y . Having in mind the direct product representation for the appropriate group (Table 57 of Ref. 20), the direct product decompositions for \mathbf{C}_{3v} may be shown to assume the form

$$u_{A_1} v_{A_1} \propto A_1; \quad u_{A_1} v_{A_2} \propto A_2; \quad u_{A_1} v_x \propto x; \quad u_{A_1} v_y \propto y; \quad (9.179)$$

$$u_{A_2} v_{A_2} \propto A_1; \quad u_{A_2} v_x \propto y; \quad u_{A_2} v_y \propto -x; \quad (9.180)$$

$$u_x v_x + u_y v_y \propto A_1; \quad u_x v_y - u_y v_x \propto A_2; \quad (9.181)$$

$$-u_x v_x + u_y v_y \propto x; \quad u_x v_y + u_y v_x \propto y \quad (9.182)$$

where the symbol \propto means “transforms under \mathbf{C}_{3v} as”, and v_x and v_y are arbitrary functions with the transformation properties of the corresponding subscripts (similarly for A_1 and A_2). Thus one has, *e.g.*, for $\langle E|\hat{h}_{A_2}|E\rangle$,

$$\langle x|\hat{h}_{A_2}|y\rangle = \langle x|u_{A_2}v_y\rangle = -1 \quad (9.183)$$

$$\langle x|\hat{h}_{A_2}|x\rangle = \langle x|u_{A_2}v_x\rangle = 0 \quad (9.184)$$

etc. Similarly, for $\langle E|\hat{h}_x|E\rangle$, one gets

$$\langle x|\hat{h}_x|y\rangle = \langle x|u_xv_y\rangle = 0 \quad (9.185)$$

$$\langle x|\hat{h}_x|x\rangle = \langle x|u_xv_x\rangle = -1 \quad (9.186)$$

Thus, the nonzero submatrices are

$$\langle A_1|\hat{h}_{A_1}|A_1\rangle = 1; \quad \langle A_2|\hat{h}_{A_1}|A_2\rangle = 1; \quad (9.187)$$

$$\langle E|\hat{h}_{A_1}|E\rangle = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (9.188)$$

$$\langle A_1|\hat{h}_{A_2}|A_2\rangle = 1; \quad \langle A_2|\hat{h}_{A_2}|A_1\rangle = 1; \quad (9.189)$$

$$\langle E|\hat{h}_{A_2}|E\rangle = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \quad (9.190)$$

$$\langle A_1|\hat{h}_x|E\rangle = [1 \ 0]; \quad \langle A_1|\hat{h}_y|E\rangle = [0 \ 1] \quad (9.191)$$

$$\langle A_2|\hat{h}_x|E\rangle = [0 \ 1]; \quad \langle A_2|\hat{h}_y|E\rangle = [-1 \ 0] \quad (9.192)$$

$$\langle E|\hat{h}_x|A_1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}; \quad \langle E|\hat{h}_y|A_1\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (9.193)$$

$$\langle E|\hat{h}_x|A_2\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}; \quad \langle E|\hat{h}_y|A_2\rangle = \begin{bmatrix} -1 \\ 0 \end{bmatrix} \quad (9.194)$$

$$\langle E|\hat{h}_x|E\rangle = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}; \quad \langle E|\hat{h}_y|E\rangle = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (9.195)$$

9.16.3 Functional form of the energy

Since the potential energy matrix \mathbf{W} is invariant and restricted to E space, it must assume the form

$$\mathbf{W} = W_{A_1} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + W_{A_2} \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} + W_x \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} + W_y \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (9.196)$$

where W_{A_1} , and so on, are functions of the nuclear coordinates transforming under \mathbf{C}_{3v} as indicated by their subscripts. \mathbf{W} must be Hermitian, and in our case, can be real, from which it follows that $W_{A_2} = 0$.

The exact energies which reduce to the degenerate pair at the reference configuration are just the eigenvalues of \mathbf{W} , which are

$$W_{\pm} = W_{A_1} \pm W_R \quad (9.197)$$

where

$$W_R = \sqrt{W_x^2 + W_y^2} \quad (9.198)$$

To all orders, the general form for functions with transformation properties u_{A_1} , and so on, may be shown⁸ to be

$$u_{A_1} = f_1 [z; \rho^2, \rho^3 \cos(3\varphi)] \quad (9.199)$$

$$u_{A_2} = \rho^3 \sin(3\varphi) f_2 [z; \rho^2, \rho^3 \cos(3\varphi)] \quad (9.200)$$

$$u_x = \rho \cos \varphi f_3 [z; \rho^2, \rho^3 \cos(3\varphi)] + \rho^2 \cos(2\varphi) f_4 [z; \rho^2, \rho^3 \cos(3\varphi)] \quad (9.201)$$

$$u_y = \rho \sin \varphi f_3 [z; \rho^2, \rho^3 \cos(3\varphi)] - \rho^2 \sin(2\varphi) f_4 [z; \rho^2, \rho^3 \cos(3\varphi)] \quad (9.202)$$

Indeed, through third order in ρ , it is a straightforward matter to verify that the above relations hold. We therefore assume that they also hold through n -th order in ρ , and construct functions of the $(n+1)$ -st order in ρ by multiplying those of n -th order by x and/or y . For example, the function of order $(n+1)$ transforming as A_1 will be given by

$$U_{A_1} = xu_x + yu_y = \rho^2 f_3 + \rho^3 \cos(3\varphi) f_4 \quad (9.203)$$

which shows that the same form applies to the $(n+1)$ -st order in ρ . By induction it then holds for all orders. The functions f_i ($i = 1, 2, 3, 4$) are all formally representable as a double power series in their arguments other than z , with the coefficients being constant or functions of z . Thus, from Eq. (9.199) to Eq. (9.202), one obtains

$$W_{A_1} = W_{A_1} [z; \rho^2, \rho^3 \cos(3\varphi)], \quad (9.204)$$

$$W_R = \rho \sqrt{f^2 + \rho^2 g^2 + 2\rho fg \cos(3\varphi)}, \quad (9.205)$$

$$\rightarrow \rho w [z; \rho^2, \rho \cos(3\varphi)] \quad (\rho \rightarrow 0) \quad (9.206)$$

9.16.4 Functional form of the derivative coupling

The two new basis functions which reduce to the degenerate pair (Ψ_1, Ψ_2) at the reference configuration are

$$\Psi_x = \mathbf{S}\Psi_1 \quad (9.207)$$

$$\Psi_y = \mathbf{S}\Psi_2 \quad (9.208)$$

where \mathbf{S} is an unitary transformation matrix. Defining an angle λ by

$$W_x = W_R \cos \lambda, \quad W_y = W_R \sin \lambda \quad (9.209)$$

the eigenfunctions of Eq. (9.196) are

$$\Psi_+ = \Psi_x \sin(\lambda/2) + \Psi_y \cos(\lambda/2), \quad (9.210)$$

$$\Psi_- = \Psi_x \cos(\lambda/2) - \Psi_y \sin(\lambda/2) \quad (9.211)$$

which are not single-valued due to the appearance of $(\lambda/2)$. An appropriate choice of single-valued eigenfunctions is

$$\tilde{\Psi}_{\pm} = \Psi_{\pm} \exp(3i\varphi/2) \quad (9.212)$$

with the derivative coupling being the vector

$$F = \langle \tilde{\Psi}_- | \nabla \tilde{\Psi}_+ \rangle = -\langle \tilde{\Psi}_+ | \nabla \tilde{\Psi}_- \rangle \quad (9.213)$$

Using now Eq. (9.210) to Eq. (9.213), one finds⁸

$$F = F_r + F_{nr} \quad (9.214)$$

where the “removable” and “non-removable” parts of the derivative couplings are in an obvious correspondence given by

$$F_r = \frac{1}{2} \nabla \lambda \quad (9.215)$$

$$F_{nr} = \langle \Psi_x | \nabla \Psi_y \rangle \quad (9.216)$$

From Eq. (9.199) and Eq. (9.209), it then follows

$$\tan \lambda = \frac{f \sin \varphi - \rho g \sin(2\varphi)}{f \cos \varphi + \rho g \cos(2\varphi)} \quad (9.217)$$

Defining now an angle ϵ by $\lambda = \varphi + \epsilon$, one may see that

$$\tan \epsilon = -\frac{\rho g \sin(3\varphi)}{f + \rho g \cos(3\varphi)} \quad (9.218)$$

while the removable part assumes the form

$$F_r = \frac{1}{2} \nabla \left\{ \varphi + \tan^{-1} \left[-\frac{\rho g \sin(3\varphi)}{f + \rho g \cos(3\varphi)} \right] \right\} \quad (9.219)$$

For further details concerning the non-removable part, the reader is referred to the original literature.^{15,57}

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