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THE $H \otimes h_2$ JAHN–TELLER EFFECT IN ICOSAHEDRAL SYMMETRY

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Abstract. The linear $H \otimes h_2$ Jahn–Teller effect in icosahedral symmetry is investigated. The interaction Hamiltonian is diagonalized through a sequence of unitary transformations, where each transformation produces a rotation in the five-dimensional coordinate space. Applying these transformations to the entire Hamiltonian uncouples the motion on the three middle adiabatic surfaces, leaving the highest and lowest surfaces coupled. Approximate solutions to motion on the lowest surface are outlined and briefly discussed.

Key words: icosahedral symmetry, linear Jahn–Teller effect, electronic quintet.

1. INTRODUCTION

The discovery of the C_{60} molecule has increased interest in Jahn–Teller systems with icosahedral symmetry. Almost all of the electronic and vibrational states of C_{60} are highly degenerate due to the high symmetry of the icosahedral group (I_h). The Jahn–Teller interaction, because it involves cases of electronic degeneracy, is thus a fundamental consideration in unravelling the structural and electronic properties of this and other icosahedral complexes. The range of Jahn–Teller interactions within the various I_h irreducible representations adds a new and rich domain to the older on-going areas of Jahn–Teller research.

The earliest theoretical work on icosahedral Jahn–Teller systems was performed by Khlopin, Polinger, and Bersuker [1] who analysed the topology of the adiabatic potential energy surfaces (APES) for the $T \otimes h$, $G \otimes g$, and $H \otimes h_2$ systems. (T, G, and H represent an electronic triplet, quartet, and quintet, respectively). Pooler [2] subsequently studied and catalogued the continuous group invariances of various linear Jahn–Teller systems with icosahedral symmetry, and Judd [3] has discussed additional

group theoretical aspects. More recently, Ceulemans and Fowler [4, 5] have derived the static distortion modes of various icosahedral systems.

In the present work, we report on recent theoretical investigations into the linear Jahn–Teller system $H \otimes h_2$: an electronic quintet coupled to five vibrational modes which transform as a set of $J=2$ states. (A second five-dimensional irreducible representation, h_4, is derivable from a set of $J=4$ states.) Firstly, we diagonalize the linear interaction matrix through a series of unitary transformations to obtain the adiabatic basis states; secondly, we discuss the ground-state solutions to the oscillator Hamiltonian; thirdly, we briefly discuss how these combine to form a strong-coupling wave function.

2. BASIS STATES AND THE HAMILTONIAN

The $J=2$ representation reduces exactly to H in the reduction of the angular momentum states into irreducible representations of the icosahedral group. This means that the states which transform according to H may be written as a set of d states. The following list gives the basis states we will use:

$$\begin{aligned} q_1 &= 2z^2 - x^2 - y^2, \\ q_2 &= zx, \\ q_3 &= xy, \\ q_4 &= x^2 - y^2, \\ q_5 &= yz. \end{aligned} \tag{2.1}$$

These are even and thus can be used as bases for both the electronic and vibrational states. We will denote the electronic and vibrational basis sets by $\{ |i\rangle \}$ and $\{q_i\}$, respectively.

The interaction matrix for $H \otimes h_2$ is defined in terms of the elements

$$V_{ij} = \sum_k \langle i | q_k | j \rangle q_k$$

with the result

$$V = K \begin{bmatrix} 2q_1 & q_2 & -2q_3 & -2q_4 & q_5 \\ q_2 & (q_1 + \sqrt{3}q_4) & \sqrt{3}q_5 & \sqrt{3}q_2 & \sqrt{3}q_3 \\ -2q_3 & \sqrt{3}q_5 & -2q_1 & 0 & \sqrt{3}q_2 \\ -2q_4 & \sqrt{3}q_2 & 0 & -2q_1 & -\sqrt{3}q_5 \\ q_5 & \sqrt{3}q_3 & \sqrt{3}q_2 & -\sqrt{3}q_5 & (q_1 - \sqrt{3}q_4) \end{bmatrix}, \tag{2.2}$$

with the electronic basis vectors ordered $\{ |1\rangle, |2\rangle, |3\rangle, |4\rangle, |5\rangle \}$. The ionic motion is represented by the kinetic energy term

$$H_0 = -\left(\frac{\hbar}{2m}\right)\nabla^2 + \frac{1}{2}m\omega^2 q^2, \tag{2.3}$$

where ∇^2 is the cartesian Laplacian written in terms of the $\{q_i\}$ and $\frac{1}{2}m\omega^2 q^2$ is an harmonic potential energy term, assuming linear restoring forces on ions. In (2.3), m is the ionic mass and

$$q^2 = \sum_i q_i^2$$

and ω is an effective frequency which can be interpreted in terms of the cluster models of O'Brien [6] and Fletcher, et al. [7]. Equations (2.2) and (2.3) allow us to define the total Hamiltonian,

$$H = H_0 + V. \tag{2.4}$$

3. COORDINATE TRANSFORMATION

The normal-mode coordinate system $\{q_i\}$ used in §2 is convenient for expressing H_0, the oscillator part of H; however, it does not fully represent the symmetry of V, the electron–phonon interaction. To better represent this symmetry, we will apply a coordinate transformation introduced by O'Brien [8, 9]. Writing the normal-mode coordinates $\{q_1,q_2,q_3,q_4,q_5\}$ in terms of the new coordinates $\{Q,\alpha,\gamma,\theta,\phi\}$

$$q_1 = Q\left[\frac{1}{2}(3\cos^2(\theta) - 1)\cos(\alpha) + \frac{\sqrt{3}}{2}\sin^2(\theta)\sin(\alpha)\cos(2\gamma)\right],$$

$$q_2 = Q\left[\frac{\sqrt{3}}{2}\sin(2\theta)\cos(\phi)\cos(\alpha) - \frac{1}{2}\sin(2\theta)\cos(\phi)\sin(\alpha)\cos(2\gamma)\right] +$$

$$+ Q[\sin(\theta)\sin(\phi)\sin(\alpha)\sin(2\gamma)],$$

$$q_3 = Q\left[\frac{\sqrt{3}}{2}\sin^2(\theta)\sin(2\phi)\cos(\alpha) +\right.$$

$$\left. + \frac{1}{2}(1+\cos^2(\theta))\sin(2\phi)\sin(\alpha)\cos(2\gamma)\right] +$$

$$+ Q[\cos(\theta)\cos(2\phi)\sin(\alpha)\sin(2\gamma)],$$

$$q_4 = Q\left[\frac{\sqrt{3}}{2}\sin^2(\theta)\cos(2\phi)\cos(\alpha) + \right.$$

$$\left. + \frac{1}{2}(1+\cos^2(\theta))\cos(2\phi)\sin(\alpha)\cos(2\gamma)\right] -$$

$$- Q[\sin(\theta)\sin(2\phi)\sin(\alpha)\sin(2\gamma)],$$

$$q_5 =$$

$$= Q\left[\frac{\sqrt{3}}{2}\sin(2\theta)\sin(\phi)\cos(\alpha) - \frac{1}{2}\sin(2'\theta)\sin(\phi)\sin(\alpha)\cos(2\gamma)\right] -$$

$$- Q[\sin(\theta)\cos(\phi)\sin(\alpha)\sin(2\gamma)], \qquad (3.1)$$

where $0 \le Q < \infty, 0 \le \alpha < \pi/3, 0 \le \gamma < \pi, 0 \le \theta < \pi$, and $0 \le \phi < \pi$ in order to cover the domain of the normal-mode coordinates, and $Q^2 = \Sigma_i q_i^2$.

These coordinates will show their utility when we need to express the unitary transformations which reduce the interaction Hamiltonian. However, the $\{Q, \alpha, \gamma, \theta, \phi\}$ form a nonorthogonal coordinate system, and this complicates the expression of the kinetic Hamiltonian. Even so, the oscillator Hamiltonian takes a surprisingly simple form [9, 10]:

$$H_0 = -\frac{\hbar^2}{2m}\left[Q^{-4}\frac{\partial}{\partial Q}\left(Q^4\frac{\partial}{\partial Q}\right) + (Q^2\sin(3\alpha))^{-1}\frac{\partial}{\partial\alpha}\left(\sin(3\alpha)\frac{\partial}{\partial\alpha}\right)\right] +$$

$$+ \frac{\hbar^2}{8mQ^2}\left[\frac{\lambda_x^2}{\sin^2(\alpha - 2\pi/3)} + \frac{\lambda_y^2}{\sin^2(\alpha + 2\pi/3)} + \frac{\lambda_z^2}{\sin^2\alpha}\right] + \frac{1}{2}m\omega^2Q^2, \qquad (3.2)$$

where $\{\lambda_x, \lambda_y, \lambda_z\}$ are the three components of an angular momentum operator λ within the phonon space. Explicitly,

$$\lambda_x = i(\cos\gamma)\left((\cot\theta)\frac{\partial}{\partial\gamma} - (\csc\theta)\frac{\partial}{\partial\phi}\right) + i(\sin\gamma)\frac{\partial}{\partial\theta},$$

$$\lambda_y = -i(\sin\gamma)\left((\cot\theta)\frac{\partial}{\partial\gamma} - (\csc\theta)\frac{\partial}{\partial\phi}\right) + i(\cos\gamma)\frac{\partial}{\partial\theta}, \qquad (3.3)$$

$$\lambda_z = i\frac{\partial}{\partial\gamma}.$$

Transforming to the new coordinates separates H_0 into a vibrational term involving variables Q and α and a rotational part associated with λ. Bohr and Mottelson [11] have dealt with a Hamiltonian identical to H_0 in their analysis of quadrupole oscillations in nuclei. Pooler [2] has shown that the total Hamiltonian, $H = H_0 + V$, has SO(3) symmetry – a fact we will use in reducing H.

The eigenvalues of the interaction Hamiltonian, V, are surprisingly easy to express, given the complexity of the coordinates: $\{+2, 2\cos(\alpha - \pi/3), -2\cos(\alpha), -2, 2\cos(\alpha + \pi/3)\}$, ordered from top left in the matrix, with each multiplied by KQ. In the adiabatic approximation, solutions to H involve one of five potential energy surfaces, given by the eigenvalues of V with the addition of the restoring term $m\omega^2 Q^2/2$. The lowest of these is

$$U_0 = \frac{1}{2}m\omega^2 Q^2 - 2KQ. \tag{3.4}$$

It is a function of Q only and has a minimum value at $Q = Q_0 = 2K/(m\omega^2)$. The lowest APES thus forms a four-dimensional hypersphere of a radius Q_0 in the five-dimensional space of the vibrational coordinates $\{Q, \alpha, \gamma, \theta, \phi\}$. The APES corresponding to the $-2\cos(\alpha)$ eigenvalue,

$$U_1 = \frac{1}{2}m\omega^2 Q^2 - 2KQ\cos(\alpha), \tag{3.5}$$

is at its minimum value for $Q = Q_0$ and $\alpha = 0$. The minimum values of U_0 and U_1 thus are both $-2K^2/(m\omega^2)$, and the two APES will be degenerate over a three-dimensional subspace of the hypersphere defined by $\alpha = 0$.

4. UNITARY TRANSFORMATIONS

The interaction Hamiltonian can be exactly diagonalized as follows:

$$A^{-1}(\alpha)B^{-1}(\gamma)C^{-1}(\theta)D^{-1}(\phi)[V]D(\phi)C(\theta)B(\gamma)A(\alpha) = [E], \tag{4.1}$$

where

$$A(\alpha) = \begin{bmatrix} \cos(\alpha/2) & 0 & 0 & \sin(\alpha/2) & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ -\sin(\alpha/2) & 0 & 0 & \cos(\alpha/2) & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \tag{4.2}$$

$$B(\gamma) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \cos(\gamma) & 0 & 0 & -\sin(\gamma) \\ 0 & 0 & \cos(2\gamma) & \sin(2\gamma) & 0 \\ 0 & 0 & -\sin(2\gamma) & \cos(2\gamma) & 0 \\ 0 & \sin(\gamma) & 0 & 0 & \cos(\gamma) \end{bmatrix}, \tag{4.3}$$

$$C(\theta) = \begin{bmatrix} (3c^2-1)/2 & -\sqrt{3}sc & 0 & \sqrt{3}s^2/2 & 0 \\ \sqrt{3}sc & (2c^2-1) & 0 & -sc & 0 \\ 0 & 0 & c & 0 & s \\ \sqrt{3}s^2/2 & sc & 0 & (1+c^2)/2 & 0 \\ 0 & 0 & -s & 0 & c \end{bmatrix}, \tag{4.4}$$

using $s = \sin(\theta)$ and $c = \cos(\theta)$, and

$$D(\phi) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \cos(\phi) & 0 & 0 & -\sin(\phi) \\ 0 & 0 & \cos(2\phi) & \sin(2\phi) & 0 \\ 0 & 0 & -\sin(2\phi) & \cos(2\phi) & 0 \\ 0 & \sin(\phi) & 0 & 0 & \cos(\phi) \end{bmatrix}. \tag{4.5}$$

Note that $A^{-1}(\phi) = A(-\phi)$, $B^{-1}(\gamma) = B(-\gamma)$, etc. The diagonalized interaction matrix, $[E]$, takes the form

$$[E] = 2KQ \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \cos(\alpha-\pi/3) & 0 & 0 & 0 \\ 0 & 0 & -\cos(\alpha) & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & \cos(\alpha+\pi/3) \end{bmatrix}. \tag{4.6}$$

The column vectors of the $[D][C][B][A]$ matrix give the eigenvectors of V. In expressing them, we will use $s = \sin(\theta)$, $c = \cos(\theta)$, $b = \cos(\alpha/2)$, and $d = \sin(\alpha/2)$.

For the $+2KQ$ eigenvalue,

$$|u_1\rangle = \begin{bmatrix} \frac{1}{2}(3c^2-1)\,b - \frac{\sqrt{3}}{2}s^2 d\cos(2\gamma) \\ (\sqrt{3}b + d\cos(2\gamma))\,sc\cos(\phi) - sd\sin(2\gamma)\sin(\phi) \\ \left(\frac{\sqrt{3}}{2}s^2 b - \frac{1}{2}(1+c^2)\,d\cos(2\gamma)\right)\sin(2\phi) - cd\sin(2\gamma)\cos(2\phi) \\ \left(\frac{\sqrt{3}}{2}s^2 b - \frac{1}{2}(1+c^2)\,d\cos(2\gamma)\right)\cos(2\phi) + cd\sin(2\gamma)\sin(2\phi) \\ (\sqrt{3}b + d\cos(2\gamma))\,sc\sin(\phi) + sd\sin(2\gamma)\cos(\phi) \end{bmatrix}. \tag{4.7}$$

Likewise, for the $+2KQ\cos(\alpha-\pi/3)$ eigenvalue, the eigenvector is

$$|u_2\rangle=\begin{bmatrix} -\sqrt{3}sc\cos(\gamma) \\ (2c^2-1)\cos(\gamma)\cos(\phi)-c\sin(\gamma)\sin(\phi) \\ s\sin(\gamma)\cos(2\phi)+sc\cos(\gamma)\sin(2\phi) \\ sc\cos(\gamma)\cos(2\phi)-s\sin(\gamma)\sin(2\phi) \\ (2c^2-1)\cos(\gamma)\sin(\phi)+c\sin(\gamma)\cos(\phi) \end{bmatrix}. \tag{4.8}$$

The eigenvector for the $-2KQ\cos(\alpha)$ eigenvalue is

$$|u_3\rangle=\begin{bmatrix} -\frac{\sqrt{3}}{2}s^2\sin(2\gamma) \\ sc\sin(2\gamma)\cos(\phi)+s\cos(2\gamma)\sin(\phi) \\ c\cos(2\gamma)\cos(2\phi)-\frac{1}{2}(1+c^2)\sin(2\gamma)\sin(2\phi) \\ -c\cos(2\gamma)\sin(2\phi)-\frac{1}{2}(1+c^2)\sin(2\gamma)\cos(2\phi) \\ sc\sin(2\gamma)\sin(\phi)-s\cos(2\gamma)\cos(\phi) \end{bmatrix}. \tag{4.9}$$

The lowest eigenvalue of the interaction matrix, $-2KQ$, has

$$|u_4\rangle = \begin{bmatrix} \frac{1}{2}(3c^2-1)d+\frac{\sqrt{3}}{2}s^2b\sin(2\gamma) \\ (\sqrt{3}d-b\cos(2\gamma))sc\cos(\phi)+sb\sin(2\gamma)\sin(\phi) \\ cb\sin(2\gamma)\sin(2\phi)+\left(\frac{\sqrt{3}}{2}s^2d+\frac{1}{2}(1+c^2)b\cos(2\gamma)\right)\sin(2\phi) \\ -cb\sin(2\gamma)\sin(2\phi)+\left(\frac{\sqrt{3}}{2}s^2d+\frac{1}{2}(1+c^2)b\cos(2\gamma)\right)\cos(2\phi) \\ (\sqrt{3}d-b\cos(2\gamma))sc\sin(\phi)-sb\sin(2\gamma)\cos(\phi) \end{bmatrix} \tag{4.10}$$

as its corresponding eigenvector, and the eigenvector corresponding to $+2KQ\cos(\alpha+\pi/3)$ is

$$|u_5\rangle = \begin{bmatrix} \sqrt{3}sc\sin(\gamma) \\ -(2c^2-1)\sin(\gamma)\cos(\phi) - c\cos(\gamma)\sin(\phi) \\ s\cos(\gamma)\cos(2\phi) - sc\sin(\gamma)\sin(2\phi) \\ -s\cos(\gamma)\sin(2\phi) - sc\sin(\gamma)\cos(2\phi) \\ -(2c^2-1)\sin(\gamma)\sin(\phi) + c\cos(\gamma)\cos(\phi) \end{bmatrix}. \quad (4.11)$$

Note that the three eigenvalues with an α-dependence have eigenvectors without any such dependence. Similarly, the eigenvectors corresponding to the $-KQ\cos(\alpha)$ and $-KQ$ eigenvalues likewise have a γ-dependence even though the APES lack any such dependence.

Within H_0 only the λ_i operators will be affected by the $D(\phi)C(\theta)B(\gamma)$ series of transformations. These transformations represent a rotation through the Euler angles (ϕ, θ, γ) on a set of d states. The effect on H_0 of a similar transformation, a rotation on a set of p states, has been considered by Chancey and O'Brien [12]. The result of now forming

$$B^{-1}(\gamma)\,C^{-1}(\theta)\,D^{-1}(\phi)\,H_0 D(\phi)\,C(\theta)\,B(\gamma)$$

is the same as in the earlier case: the phonon angular momentum operator λ is replaced by $\lambda + \boldsymbol{d}$, where $\boldsymbol{d}$ is the orbital angular momentum operator. One angular momentum operator $\boldsymbol{J} = \lambda + \boldsymbol{d}$ thus replaces another. In interpreting $\boldsymbol{J}$ in the oscillator Hamiltonian, we can forget its antecedents and need only to remember it as an angular momentum. The physical effect of the $D(\phi)C(\theta)B(\gamma)$ transformation is to couple the rotational motion of the ligands to the rotation of the electronic state.

The remaining transformation, $A(\alpha)$, affects only the α-dependent term in H_0. Forming $A^{-1}(\alpha)H_0A(\alpha)$ produces the following additional term in the Hamiltonian:

$$\begin{bmatrix} 0&0&0&1&0 \\ 0&0&0&0&0 \\ 0&0&0&0&0 \\ -1&0&0&0&0 \\ 0&0&0&0&0 \end{bmatrix} \left[\frac{3}{2}\cot(3\alpha) + \frac{\partial}{\partial\alpha}\right] - \frac{1}{4}\boldsymbol{I}, \quad (4.12)$$

where $\boldsymbol{I}$ is the unit matrix.

The total transformed Hamiltonian,

$$A^{-1}(\alpha)\,B^{-1}(\gamma)\,C^{-1}(\theta)\,D^{-1}(\phi)\;\; H\; A(\alpha)\,B(\gamma)\,C(\theta)\,D(\phi),$$

thus takes the following form:

$$-\hbar\omega\left[q^{-4}\frac{\partial}{\partial q}\left(q^4\frac{\partial}{\partial q}\right) + (Q^2\sin(3\alpha))^{-1}\frac{\partial}{\partial\alpha}\left(\sin(3\alpha)\frac{\partial}{\partial\alpha}\right)\right] +$$

$$+\frac{\hbar\omega}{4q^2}\left[\frac{J_x^2}{\sin^2(\alpha-2\pi/3)}+\frac{J_y^2}{\sin^2(\alpha+2\pi/3)}+\frac{J_z^2}{\sin^2\alpha}\right]+\frac{1}{2}\hbar\omega q^2+$$

$$+\hbar\omega kq\begin{bmatrix}1 & 0 & 0 & 0 & 0\\ 0 & \cos(\alpha-\pi/3) & 0 & 0 & 0\\ 0 & 0 & -\cos(\alpha) & 0 & 0\\ 0 & 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 0 & \cos(\alpha+\pi/3)\end{bmatrix}-$$

$$-\hbar\omega\begin{bmatrix}0&0&0&1&0\\0&0&0&0&0\\0&0&0&0&0\\-1&0&0&0&0\\0&0&0&0&0\end{bmatrix}\left[\frac{3}{2}\cot(3\alpha)+\frac{\partial}{\partial\alpha}\right]+\frac{\hbar\omega}{4}I \qquad (4.13)$$

(scaling the energy in units of $\hbar\omega$) with $q = Q(m\omega/\hbar)^{1/2}$ and $k\hbar\omega = K(\hbar/m\omega)^{1/2}$. The effect of the α-dependent unitary transformation has been to simplify V at the expense of H_0: the new off-diagonal terms couple the motions on the APES associated with the $+2KQ$ and $-2KQ$ eigenvalues (the highest and lowest of the five energy sheets).

5. SOLUTIONS OF THE FIVE-DIMENSIONAL OSCILLATOR EQUATION

Ignoring the coupling between the adiabatic sheets (i.e., dropping the off-diagonal terms in α) reduces the transformed Hamiltonian to the one that is diagonal in the adiabatic basis states (Eqs. (4.7) to (4.11)). The oscillator Hamiltonian that remains has been analysed previously by Chancey and O'Brien [12]:

$$H_0 = -\hbar\omega\left[q^{-4}\frac{\partial}{\partial q}\left(q^4\frac{\partial}{\partial q}\right)+(q^2\sin(3\alpha))^{-1}\frac{\partial}{\partial\alpha}\left(\sin(3\alpha)\frac{\partial}{\partial\alpha}\right)\right]+$$

$$+\frac{\hbar\omega}{4q^2}\left[\frac{J_x^2}{\sin^2(\alpha-2\pi/3)}+\frac{J_y^2}{\sin^2(\alpha+2\pi/3)}+\frac{J_z^2}{\sin^2\alpha}\right]+\frac{1}{2}\hbar\omega q^2. \qquad (5.1)$$

Solutions are classified by their angular momentum values, with the simplest case being $J = 0$. For $J = 0$, the solutions (Ψ) have the form

$$\Psi(Q, \alpha;\ 0,\ A_1) =$$

$$= \exp[-Q^2/2] Q^{3n} L_N^{3n+3/2}(Q^2) P_n(\cos 3\alpha) \, |0, A_1\rangle$$

in terms of Laguerre and Legendre polynomials. N and n are positive integers or zero, and the energies are given by $E = 2N + 3n + 5/2$. There are no $J = 1$ states and the next highest states in angular momentum have $J = 2$ [12].

For $J = 0$, the lowest energy is given by $N = n = 0$, giving a combined energy of

$$\frac{E}{\hbar\omega} = \frac{5}{2} - 2kq + \frac{1}{4}$$

for a wave function

$$\Psi_{\text{Total}} = \Psi(Q, \alpha; 0, A_1) \, |u_4\rangle.$$

6. DISCUSSION

The four unitary transformations defined in Eqs. (4.2) through (4.5) have a combined effect of almost completely diagonalizing the linear $H \otimes h_2$ Hamiltonian. Only the off-diagonal terms in α remain to couple motions on the highest and the lowest APES. Work remains to be done on this system, and we close with observations under the following headings:

Uniqueness of the lowest eigenvector. There is an ambiguity in the choice of eigenvectors when the roots go degenerate at $\alpha = 0$, but it is clear that the eigenvectors are properly orthogonal and that they change continuously through $\alpha = 0$ and through $\gamma = 0$. Hence, if we continue to ignore any breakdown of the adiabatic approximation where the surfaces meet, the vibronic Hamiltonian can be solved separately on each surface.

The SO(5) surfaces. For the lowest (and the highest) roots the simple substitution of $\alpha \to \alpha/2$ in going from the q-s to the corresponding terms in the electronic eigenvector means that there is a Berry phase change of π that occurs as a point in the q space going once round a closed circuit. It is easy to show that this will select the five-dimensional d-like representation (1,0) of SO(5) as the ground state instead of the one-dimensional s-like representation (0,0) which would have a smaller contribution to the energy from the angular momentum.

REFERENCES

1. Khlopin, V. P., Polinger, V. Z., and Bersuker, I. B. Theoret. Chim. Acta (Berl.), 1978, **48**, 87–101.
2. Pooler, D. R. J. Phys. C: Solid State Phys., 1980, **13**, 1029–1042.
3. Judd, B. R. – In: Perlin, Yu. E. and Wagner, M. (eds.). Modern Problems in Condensed Matter Sciences. North-Holland, Amsterdam, 1984, **7**, 87.
4. Ceulemans, A. and Fowler, P. W. Phys. Rev. A, 1989, **39**, 481–493.
5. Ceulemans, A. and Fowler, P. W. J. Chem. Phys., 1990, **93**, 1221–1234.

6. O'Brien, M. C. M. J. Phys. C: Solid State Phys., 1972, **5**, 2045–2063.
7. Fletcher, J. R., O'Brien, M. C. M., and Evangelou, S. J. Phys. A: Math. Gen., 1980, **13**, 2035–2047.
8. O'Brien, M. C. M. Phys. Rev., 1969, **187**, 407–418.
9. O'Brien, M. C. M. J. Phys. C: Solid State Phys., 1971, **4**, 2524–2536.
10. Judd, B. R. – In: Rice, S. A. and Prigogine, I. (eds.). Advances in Chemical Physics. Wiley, New York, 1984, **57**, 247–309.
11. Bohr, A. and Mottelson, B. R. Nuclear Structure, Vol. 2. Benjamin, Reading, Massachusetts, 1975.
12. Chancey, C. C. and O'Brien, M. C. M. J. Phys. C: Condens. Matter, 1989, **1**, 47–68.

$(H \otimes h_2)$-TÜÜPI JAHNI–TELLERI EFEKT IKOSAEEDRILISES SÜMMEETRIAS

C. Clifton CHANCEY, Mary C. M. O'BRIEN

On uuritud lineaarset $(H \otimes h_2)$-tüüpi Jahni–Telleri efekti ikosaeedrilises sümmeetrias. Interaktsiooni hamiltoniaan on diagonaliseeritud mitmete unitaarteisenduste abil, kus iga teisendus teostab pöörde viiemõõtmelises koordinaatruumis. Nende teisenduste rakendamine koguhamiltoniaanile eraldab liikumised kolmel keskmisel adiabaatilisel pinnal, aga jätab kõrgeima ja madalaima pinna seotuks. On välja eraldatud lähendlahend liikumise tarvis madalaimal pinnal ja lühidalt selle üle diskuteeritud.

ЭФФЕКТ ЯНА–ТЕЛЛЕРА ТИПА $H \otimes h_2$ ИКОСАЭДРИЧЕСКОЙ СИММЕТРИИ

С. Клифтон ЧАНСИ, Мэри С. М. О'БРАЙАН

Исследован линейный эффект Яна–Теллера типа $H \otimes h_2$ в икосаэдрической симметрии. Гамильтониан взаимодействия диагонализован рядом унитарных преобразований, где каждое преобразование осуществляет вращение в пятимерном координатном пространстве. Применение этих преобразований к полному гамильтониану разделяет движение на трех промежуточных адиабатических поверхностях, оставив связанными наивысшую и наинизшую поверхности. Выделено и продискутировано приближенное решение для движения на наинизшей поверхности.