Remarks on phase choices for the electronic wavefunctions when carrying out vibronic or rovibronic energy level and intensity calculations for molecules exhibiting a Jahn–Teller effect

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ABSTRACT

In this pedagogical paper, material already in the Jahn–Teller literature is recast in a way that emphasizes how vibronic wavefunctions for the XY_3 Jahn–Teller problem can conveniently be calculated using electronic and vibrational basis set functions that do not transform into their negatives upon going once around the conical intersection and do transform as irreducible representations of the ordinary C_{3v} point group. We give as an explicit example, a recalculation of the pseudorotational energy levels and wavefunctions near the bottom of a deep Jahn–Teller moat that does not make use of half-integral quantum numbers. A brief discussion, also recast somewhat from material in the literature, is given of how the basis functions used here are related to the more frequently discussed electronic and vibrational basis functions for the Jahn–Teller problem, which transform into their negatives upon going once around the conical intersection.

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1. Introduction

In the classic paper of Longuet-Higgins et al. [1] discussing vibronic consequences of the Jahn–Teller effect in a doubly degenerate electronic state, it was pointed out that the real electronic wavefunction components obtained by diagonalizing the 2×2 electronic Hamiltonian matrix for fixed nuclear positions transform into their negatives when the nuclear positions are adiabatically varied so as to make a complete revolution around the conical intersection of the two electronic potential surfaces. This point was emphasized again in three publications soon afterwards [2–4], and further discussed in numerous publications during the five decades up to the present time (see, e.g., Refs. [5–12]).

After a brief definition of the symmetry operations used here, we turn in Section 3 to the well-known fact [1–12] that this property of the fixed-nuclei Born–Oppenheimer electronic wavefunctions transforming into their negatives arises only when those wavefunctions are chosen to be real. Other transformation properties are obtained [1–12] if complex phase factors for the electronic wavefunctions are chosen after diagonalizing the 2×2 electronic Hamiltonian matrix for fixed nuclear positions. In particular, phases can be chosen so that the two electronic wavefunctions transform into themselves with no sign change when the nuclear configuration makes one revolution around the conical intersec-

tion. If one uses signs in parentheses (±) to indicate how a given electronic $\psi_e(\pm)$ or vibrational $\psi_v(\pm)$ basis function transforms when the vibrational coordinates are taken once around the conical intersection, then the discussion in this paper can be described symbolically as a comparison of calculations using vibronic basis functions of the form $\psi_e(+)\psi_v(+)$ with calculations using vibronic basis sets of the form $\psi_e(-)\psi_v(-)$, where basis functions of the latter type are the overwhelming favorite in the theoretical literature [1–12].

Vibronic basis sets of the form $\psi_e(-)\psi_v(-)$ have a significant mnemonic advantage [1–12] because quantized levels for the pseudo-rotational vibrational motion very near the bottom of the lower Jahn–Teller potential surface having energies proportional to j^2 with j half-integral can be seen as arising when the analog of particle-on-a-ring basis functions $e^{+ij\alpha}$ with $\psi_v(-)$ transformation properties, and therefore half-integer j values, are used to derive these energies. In Section 4 we rederive these energy levels for a C_{3v} molecule: (i) using electronic wavefunctions with $\psi_e(+)$ transformation properties, and (ii) using an $e^{+il\alpha}$ basis set for the pseudorotation problem with only integer l values. One of the advantages of such a calculation is that the electronic, vibrational, and vibronic symmetry properties can be handled relatively simply using the A_1, A_2 and E representations of the permutation–inversion (PI) group isomorphic to the ordinary C_{3v} point group. The half-integer-squared behavior of the energy expression arises with this choice of basis functions because one must average two particle-on-a-ring integer-squared contributions to the energy,

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namely an l^2 contribution from one component of the electronic wavefunction, and an $(l + 1)^2$ contribution from the other, yielding a final energy proportional to $(l + \frac{1}{2})^2 + \frac{1}{4}$.

In Section 5, an attempt is made to relate some of the slightly different language, notation, and ideas in Refs. [1–12] to their analogs in the present calculation.

2. Specification of group-theoretical operations and some sign conventions

It was pointed out in a footnote on p. 64 of [4] that some change in signs of the coordinates defined in [1] was desirable to bring certain results into conventional form. Since the totality of sign choices, atom labels, transformation conventions, etc. determines whether the electronic coordinate expression $(x + iy)$, for example, transforms as $e^{+2\pi i/3}$ or as $e^{-2\pi i/3}$ under the permutation–inversion operation (123), and since we want to make detailed use of such group theoretical transformations, we digress briefly to specify the various sign and transformation conventions used below.

For simplicity, we consider a four-atomic pyramidal C_{3v} molecule, represented symbolically by XY_3, sitting on its base with the X atom pointing upward in the positive z direction, with the Y atoms numbered 1, 2, 3 in a counter-clockwise sense when viewed from the X atom, and with Y_1 lying in the xz plane. The character table for the C_{3v} point-group, involving the classes E, $2C_3$ and $3\sigma_v$ and the symmetry species A_1, A_2 and E, is well-known and fully standardized, so we will not repeat it here.

We imagine the doubly degenerate E electronic state to be caused by a single $p\pi$ electron outside closed shells (located on the X atom), whose two-component wavefunction is represented (in common diatomic notation) by $|\Lambda = \pm 1\rangle$. A vibrational state of a doubly degenerate vibrational fundamental is represented (in common notation) by $|v = 1, l = \pm 1\rangle$. The transformation properties for these functions and for operators involving the variables in these functions are determined as specified in Refs. [13,14]. Briefly, the operation C_3^{-1}, when considered as a rotation matrix for Cartesian x, y, z coordinates, is defined as the matrix obtained by setting $\chi = 2\pi/3$, $\theta = \phi = 0$ on the right of Eq. (6) of [14]. Following Section 11 of [14], this causes the Y_i atom numbering given above to satisfy $C_3^{-1}\boldsymbol{a}_i = \boldsymbol{a}_{i+1}$ (where $i = 1, 2, 3$ modulo 3). Following the arguments in [13,14], we find that the PI operation (123) then causes the following transformations of the variables in any rovibronic wavefunction: (i) The rotational angles (χ, θ, ϕ) are replaced by $(\chi + 2\pi/3, \theta, \phi)$. (ii) The molecule-fixed Cartesian coordinates $\boldsymbol{r}_e$ of the $p\pi$ electron are replaced by $C_3 \boldsymbol{r}_e$. (iii) The infinitesimal vibrational displacement vector $\boldsymbol{d}_i$ of Y_i is replaced by $C_3 \boldsymbol{d}_{i+1}$, and $\boldsymbol{d}_X$ for the X atom is replaced by $C_3 \boldsymbol{d}_X$. Similarly, the PI operation $(23)^*$ causes the following variable transformations: (i) The rotational angles (χ, θ, ϕ) are replaced by $(\pi - \chi, \pi - \theta, \pi + \phi)$. (ii) The molecule-fixed Cartesian coordinates $\boldsymbol{r}_e$ of the $p\pi$ electron are replaced by $\sigma(xz) \boldsymbol{r}_e$. (iii) The infinitesimal vibrational displacement vector $\boldsymbol{d}_i$ of Y_i is replaced by $\sigma(xz) \boldsymbol{d}_{5-i}$, and $\boldsymbol{d}_X$ for the X atom is replaced by $\sigma(xz) \boldsymbol{d}_X$.

If we consider cylindrical polar coordinates for the electron (subscript e), defined by

$$\boldsymbol{r}_e = \boldsymbol{i}r_e \cos\theta_e + \boldsymbol{j}r_e \sin\theta_e + \boldsymbol{k}z_e \qquad (1)$$

then replacing $\boldsymbol{r}_e$ by $C_3 \boldsymbol{r}_e$ corresponds to replacing θ_e by $\theta_e - 2\pi/3$, so that the electronic wavefunction $|\Lambda\rangle \sim e^{+i\Lambda\theta e}$ has the transformation property

$$(123)|\Lambda\rangle = e^{-2\pi i\Lambda/3}|\Lambda\rangle \qquad (2)$$

We can choose similar definitions for the polar coordinates (Q_v, ϕ_v) for a doubly degenerate vibration (subscript v)

$$Q_\pm \equiv Q_x \pm iQ_y \equiv Q_v e^{\pm i\phi_v} \qquad (3)$$

(for example $Q_\pm \equiv \delta r_1 + e^{\pm 2\pi i/3}\delta r_2 + e^{\mp 2\pi i/3}\delta r_3$ for the degenerate XY stretching vibration), which then gives the transformation properties (since Q_v, ϕ_v are replaced by Q_v, $\phi_v - 2\pi/3$)

$$(123)Q_\pm = e^{\mp 2\pi i/3} Q_\pm$$

$$(123)|v, l\rangle = e^{\mp 2\pi il/3}|v, l\rangle. \qquad (4)$$

It can be shown that phase factors can always be chosen so that $(23)^*$, which requires the angles θ_e and ϕ_v to be replaced by their negatives, gives rise to the following transformations

$$(23)^*|\Lambda\rangle = +|-\Lambda\rangle$$

$$(23)^*|v, l\rangle = +|v, -l\rangle \qquad (5)$$

One reason for choosing the set of conventions above is to simplify visual checking of the symmetry properties of various operators and eigenfunctions. A basis-set or operator expression of the general form $A_+B_-C_+ \cdots Z_-$ is of species A (i.e., is not E) in C_{3v} if the number of + subscripts (or more accurately, the total number of $+i\theta_e$ and $+i\phi_v$ exponents) minus the number of − subscripts (total number of $-i\theta_e$ and $-i\phi_v$ exponents) is 0 mod 3. If this 0 mod 3 criterion is satisfied, an expression of the form $(A_+B_-C_+ \cdots Z_-) \pm (A_-B_+C_- \cdots Z_+)$ is A_1 (+ sign) or A_2 (− sign), respectively.

3. Born–Oppenheimer components of a doubly degenerate electronic state that do not change sign when going around a conical intersection

The simplified time-independent Hamiltonian that we consider contains a purely electronic term, a purely vibrational term, and a vibronic interaction term, with subscripts e, v, and ev, respectively,

$$H = H_e + H_v + H_{ev}. \qquad (6)$$

In high-resolution molecular spectroscopy we are normally interested in calculating the stationary rovibronic states of the molecular Hamiltonian, but for the present paper we restrict attention to the stationary vibronic states of the Hamiltonian in Eq. (6). If m and k are used for the effective mass and the quadratic force constant of the doubly degenerate harmonic oscillator Hamiltonian in H_v, and k_{JT} is used for the coefficient of the linear Jahn–Teller interaction term in H_{ev}, we have [1]

$$H_v = (1/2m)(P_x^2 + P_y^2) + (k/2)(Q_x^2 + Q_y^2)$$

$$H_{ev} = k_{JT}(Q_+ e^{+2i\theta} + Q_- e^{-2i\theta}) \qquad (7)$$

H_e is left unspecified, and serves only to put the degenerate electronic state at some particular energy E_e. (From this point forward, the subscripts v and e will not be written, so that Q_v, ϕ_v, and θ_e become Q, ϕ, and θ, respectively.)

For fixed nuclear coordinates, the 2×2 Hamiltonian matrix in the basis set $|\Lambda = -1\rangle$ and $|\Lambda = +1\rangle$ takes the well-known [1] form

$$\begin{bmatrix} E_e + (1/2)kQ^2 & k_{JT}Qe^{-i\phi} \\ k_{JT}Qe^{+i\phi} & E_e + (1/2)kQ^2 \end{bmatrix} \qquad (8)$$

with the well-known eigenvalues [1]

$$E_e + (1/2)kQ^2 + k_{JT}Q \qquad (9a)$$

$$E_e + (1/2)kQ^2 - k_{JT}Q \qquad (9b)$$

corresponding to two potential surfaces with a conical intersection at the point with $Q = 0$ and energy E_e. Column eigenvectors (unnormalized) for the matrix in Eq. (8) belonging to the eigenvalues in Eqs. (9a) and (9b) can be taken to have the form [5,6,8,10]

$$\begin{bmatrix} 1 \\ e^{+i\theta} \end{bmatrix} \begin{bmatrix} 1 \\ -e^{+i\theta} \end{bmatrix} \tag{10}$$

We note in passing that for this simple model, the eigenvalues in Eq. (9) do not depend on ϕ, while the eigenvectors in Eq. (10) do not depend on Q.

The eigenvectors in Eq. (10) lead to normalized electronic wavefunctions for fixed vibrational coordinates Q, ϕ of the form

$$(1/\sqrt{2})[|\Lambda = -1\rangle + e^{+i\phi}|\Lambda = +1\rangle]$$
$$\rightarrow (1/2\sqrt{\pi})[e^{-i\theta} + e^{+i\theta}e^{+i\phi}] \tag{11a}$$

$$(1/\sqrt{2})[|\Lambda = -1\rangle - e^{+i\phi}|\Lambda = +1\rangle]$$
$$\rightarrow (1/2\sqrt{\pi})[e^{-i\theta} - e^{+i\theta}e^{+i\phi}] \tag{11b}$$

In the schematic expressions following the arrows only the θ-dependent parts of the purely electronic basis functions are explicitly indicated. Both of the vibronic wavefunctions in Eq. (11) (and in fact each of the two individual parts of each vibronic wavefunction) transform under the (1 2 3) operation as

$$(1\,2\,3)(1/2\sqrt{\pi})[e^{-i\theta} + e^{+i\theta}e^{+i\phi}]$$
$$= e^{+2\pi i/3}(1/2\sqrt{\pi})[e^{-i\theta} + e^{+i\theta}e^{+i\phi}], \tag{12a}$$

$$(1\,2\,3)(1/2\sqrt{\pi})[e^{-i\theta} - e^{+i\theta}e^{+i\phi}]$$
$$= e^{+2\pi i/3}(1/2\sqrt{\pi})[e^{-i\theta} - e^{+i\theta}e^{+i\phi}], \tag{12b}$$

i.e., these wavefunctions transform as E_- functions in the C_{3v} point group. They also do not go into their negatives when ϕ is increased by 2π [5,6,8,10].

In the fixed-nuclei electronic wavefunctions of Eqs. (11a) and (11b), the vibrational coordinate ϕ is just a parameter, so we can choose [5–12] to multiply each wave function by some arbitrary phase factor of the form $e^{+if(\phi)}$. Choosing the exponentials $e^{-i\phi/2}$ and $e^{-i(\phi-\pi)/2}$ as phase factors for Eqs. (11a) and (11b), respectively, leads to real wavefunctions of the form $(1/\sqrt{\pi})\cos(\theta + \phi/2)$ and $(1/\sqrt{\pi})\sin(\theta + \phi/2)$. These are the functions that were chosen for discussion in [1], and in much of the later theoretical literature [5–12]. They transform into their negatives when ϕ is increased by 2π.

4. Calculation of vibronic energies for states near the bottom of the lower Jahn–Teller potential surface without introducing half-integer quantum numbers

We repeat almost exactly the calculation from Ref. [1], where basis functions with the transformation properties $\psi_e(-)\psi_{vt}(-)$ were used, except that here basis functions with transformation properties $\psi_e(+)\psi_{vt}(+)$ are used. This allows us to avoid the introduction of half-integer quantum numbers, and thus to keep all necessary symmetry considerations within the ordinary C_{3v} point group. Consider for simplicity the case where $k_{JT} > 0$, so that the electronic wavefunction given in Eq. (11b) belongs to the lower Jahn–Teller potential energy surface given in Eq. (9b). Following [1] we wish to solve the eigenvalue problem associated with

$$H\{(1/2\sqrt{\pi})[e^{-i\theta} - e^{+i\theta}e^{+i\phi}][e^{+il\phi}f(Q)]\}$$
$$= E\{(1/2\sqrt{\pi})[e^{-i\theta} - e^{+i\theta}e^{+i\phi}][e^{+il\phi}f(Q)]\} \tag{13}$$

From Eqs. (7) and (9a) and (9b), H takes the form

$$H = (-\hbar^2/2m)[(\partial^2/\partial Q^2) + (1/Q)(\partial/\partial Q)] + (-\hbar^2/2mQ^2)$$
$$\times (\partial^2/\partial\phi^2) + [E_e - (k_{JT}^2/2k)] + (1/2)k[Q - (k_{JT}/k)]^2 \tag{14}$$

when the kinetic energy part of H_v from Eq. (7) is written in polar vibrational coordinates and the potential energy part of Eq. (9b) is

rewritten in the form appropriate for a Harmonic oscillator in the vibrational coordinate Q centered at k_{JT}/k.

Following Ref. [1], we note that when the Jahn–Teller effect is large enough that the depth D of the minimum below the conical intersection is much greater than the radial vibrational quantum $\hbar\omega_r$, i.e., when $D = (k_{JT}^2/2k) \gg \hbar\sqrt{(k/m)} = \hbar\omega_r$, then in the lowest radial vibrational state $|v_r = 0\rangle$, Q will oscillate in a small interval around its equilibrium value $Q_{eq} = k_{JT}/k$. Following a procedure common in the treatment of diatomic molecules, we replace Q in the diatomic-rotational-energy-like operator $(\hbar^2/2mQ^2)(\partial^2/\partial\phi^2)$ by its equilibrium value, and then apply this operator to the wavefunction in Eq. (13) to determine the pseudorotational energy associated with the vibrational angular coordinate ϕ in the present problem.

$$(-\hbar^2/2mQ_{eq}^2)(\partial^2/\partial\phi^2)\{(1/2\sqrt{\pi})[e^{-i\theta} - e^{+i\theta}e^{+i\phi}][e^{+il\phi}f(Q)]\}$$
$$= (+\hbar^2/2mQ_{eq}^2)(1/2\sqrt{\pi})[l^2 e^{-i\theta} - (l+1)^2 e^{+i\theta}e^{+i\phi}][e^{+il\phi}f(Q)]$$
$$= (+\hbar^2/2mQ_{eq}^2)\{[(l+1/2)^2 + 1/4](1/2\sqrt{\pi})[e^{-i\theta} - e^{+i\theta}e^{+i\phi}]$$
$$- (l+1/2)(1/2\sqrt{\pi})[e^{-i\theta} + e^{+i\theta}e^{+i\phi}]\}[e^{+il\phi}f(Q)]. \tag{15}$$

As pointed out in [1] the $(1/2\sqrt{\pi})[e^{-i\theta} + e^{+i\theta}e^{+i\phi}]$ term after the second equality in Eq. (15) involves the electronic wavefunction associated with the upper potential surface in Eq. (9a), which by hypothesis is a long way away from the lower surface, so that the second-order perturbation correction arising from this term (and therefore also this term itself) can be neglected. This yields an apparent pseudorotational energy at this point of $(\hbar^2/2mQ_{eq}^2)[(-l+\frac{1}{2})^2 + \frac{1}{4}]$. As Eq. (15) shows, the dependence of the pseudorotational energy on the half-integer expression $(l+\frac{1}{2})^2$ arises in the present calculation because the l^2 dependence from the $|\Lambda = -1\rangle$ part of the vibronic wavefunction must be averaged with the $(l+1)^2$ dependence from the $|\Lambda = +1\rangle$ part.

Again following [1], the part of the Hamiltonian operator involving terms in Q and $\partial/\partial Q$ can be converted to a form almost identical to that for the ordinary one-dimensional harmonic oscillator, by setting $f(Q) = Q^{-1/2}g(Q)$. This gives, from Eqs. (13) and (14),

$$\{(-\hbar^2/2m)[(\partial^2/\partial Q^2) + (1/Q)(\partial/\partial Q)] + (k/2)[Q - (k_{JT}/k)]^2\}f(Q)$$
$$= Q^{-1/2}\{(-\hbar^2/2m)(\partial^2/\partial Q^2) + (k/2)[Q - (k_{JT}/k)]^2\}g(Q)$$
$$- (1/4)(\hbar^2/2mQ^2)f(Q). \tag{16}$$

The last term in Eq. (16) just cancels a similar term in Eq. (15), and the substitution $q = Q - (k_{JT}/k)$ then yields the equation for a harmonic oscillator centered at $q = 0$, so that the final wavefunction and energy expression becomes

$$\Psi = (1/2\sqrt{\pi})[e^{-i\theta} - e^{+i\theta}e^{+i\phi}][\psi_v(q)e^{+il\phi}] \tag{17a}$$

$$E = E_e - (k_{JT}^2/2k) + (v+1/2)\hbar\sqrt{(k/m)} + (\hbar^2/2mQ_{eq}^2)(l+1/2)^2. \tag{17b}$$

The energy expression in Eq. (17b) agrees with that in Ref. [1], except for notational changes (some of which are caused by setting a number of constants equal to unity there). The wavefunction in Eq. (17a), with transformation properties $\psi_e(+)\psi_{vt}(+)$ under $\phi \rightarrow \phi + 2\pi$, also agrees with that in Ref. [1], though the discussion there requires a factor of $e^{+i\phi/2}$ to be moved from the electronic part in Eq. (17a) to the pseudorotational part, i.e., requires thinking in terms of an expression for Ψ of the form

$$\Psi = (1/2\sqrt{\pi})[e^{-i\theta}e^{-i\phi/2} - e^{+i\theta}e^{+i\phi/2}][\psi_v(q)e^{+i(l+1/2)\phi}], \tag{18}$$

where both the electronic part $[e^{-i\theta}e^{-i\phi/2} - e^{+i\theta}e^{+i\phi/2}]$ and the vibrational part $[\psi_{vt}(q)e^{+i(l+\frac{1}{2})\phi}]$ of the vibronic wavefunction now transform into their negatives, i.e., transform as $\psi_e(-)\psi_{vt}(-)$, when the nuclear coordinates go once around the conical intersection.

It can be seen that the electronic factor in square brackets in the wavefunction of Eq. (17a) transforms as an E_- function under the PI-group operation (123), while the pseudorotational (vibrational) factor $e^{+il\phi}$ at the end transforms as A, E_+, or E_-, respectively when $l = 0$, 1, or 2 mod 3. The complete vibronic wavefunction Ψ in Eq. (17a) then transforms as E_-, A, or E_+, respectively, when $l = 0$, 1, or 2 mod 3.

The complete vibronic wavefunction Ψ in Eq. (18), which is in fact identical to that in Eq. (17a), also transforms as E_-, A, or E_+ when $l = 0$, 1, or 2 mod 3, but the transformation properties of the individual electronic and pseudorotational vibrational factors cannot be described by any symmetry species in C_{3v}. Their description requires more complicated group theoretical considerations [5,6].

5. Discussion

In Section 3, the transformation of the fixed-nuclei electronic wavefunctions into their negatives upon going once around the conical interaction in vibrational space was described as being caused by choosing the fixed-nuclei electronic factor of the total wavefunction to be real. For high-resolution molecular spectroscopists, the choice of real electronic wavefunctions in the case of orbital degeneracy is not universal. For example, many Hund's coupling case problems in diatomic molecules in $\Lambda \neq 0$ states are treated theoretically using the orbital basis set $e^{\pm i\Lambda\theta}$, rather than the real basis set $\cos(\Lambda\theta)$, $\sin(\Lambda\theta)$. Similarly, many Renner–Teller vibronic coupling problems are treated using the basis set $e^{+i\Lambda\theta}e^{+il\phi}$ (with signed Λ and l), rather than the real basis set $\cos(\Lambda\theta + l\phi)$, $\sin(\Lambda\theta + l\phi)$.

On the other hand, calculations in the theoretical chemical reaction literature are often carried out [5,6] after simplifying them by requiring the expectation value (obtained by integration only over the electronic coordinates r) of the gradient of the fixed-nuclei electronic wavefunction $\psi(r,R)$ with respect to the nuclear coordinates R to vanish, i.e., after requiring

$$F(R) \equiv \langle \psi(r,R) | \nabla_R \psi(r,R) \rangle = 0 \qquad (19)$$

(The reader is referred to Refs. [5,6] for precise notational definitions and further details.) For our present purposes, it is sufficient to note that Eq. (19) is satisfied by requiring [5,6] that phases of the electronic wavefunctions $\psi(r,R)$ be chosen so that the $\psi(r,R)$ are real. The assumption of the validity of Eq. (19) is apparently so common in the reaction dynamics literature, that a warning is given at the end of Section 3-A of [5] against arbitrarily tampering with the phases of $\psi(r,R)$ while at the same time presuming that Eq. (19) remains valid. This mathematical inconsistency is much less likely to arise in vibronic calculations in high-resolution molecular spectroscopy papers, however, since Eq. (19) is not normally taken as a universally agreed upon starting point. Instead the effects of H_v acting on $\psi(r,R)$ are explicitly taken into account as needed, as, for example, in Section 4 above.

Eq. (19) is also very frequently taken as the starting point for theoretical discussions of the transformation properties of the fixed-nucleus Born–Oppenheimer electronic wavefunctions [7–12]. In some sense, the pedagogical point of the present paper is to reemphasize that vibronic and rovibronic stationary states for Jahn–Teller molecules can conveniently be calculated without making this assumption.

It has been pointed out [5,6,10–12] that when H_v acts on a $\psi(r,R)$ not satisfying Eq. (19), then the extra terms arising are formally analogous to those that would arise by introducing a magnetic interaction and its associated vector potential. Such an analogy is quite useful for making the connection between the mathematics of the Jahn–Teller problem and the mathematics in other fields of physics [12]. Again, however, an understanding of this instructive analogy is not necessary for vibronic or rovibronic energy level calculations in molecular spectroscopy, since it is sufficient to just take the extra terms into account as needed.

It is not uncommon [8–12] to invoke the concept of Berry phase [15] (also called geometric phase) in discussions of the sign change acquired by electronic wavefunctions in Jahn–Teller problems when the degenerate vibration is taken around a closed loop enclosing the origin. In the present paper we recall the fact that when the vibronic basis functions are chosen to have the form $\psi_e(+)\psi_v(+)$, then neither the electronic part $\psi_e(+)$ nor the vibrational part $\psi_v(+)$ changes sign when $\gamma \to \gamma + 2\pi$, whereas when the vibronic basis functions are chosen to have the form $\psi_e(-)\psi_v(-)$, then both the electronic part $\psi_e(-)$ and the vibrational part $\psi_v(-)$ change sign when $\gamma \to \gamma + 2\pi$. The author was certainly under the impression that Berry phase is related in a rather simple way to whether the electronic basis functions change sign or not, which then led him to the conclusion that the Berry phase for $\psi_e(-)$ would be different from that for $\psi_e(+)$. However, one of the referees points out that geometric phase denotes a phase independent quantity in [15] and most of the other literature on the topic, and recommends making a distinction between sign change and geometric phase. A potentially lengthy discussion of the precise relationship between Berry phase and wavefunction sign change can be terminated at this point by noting that the main purpose of the present paper is to show that authors interested in computing vibronic or rovibronic energies in Jahn–Teller molecules can (if they wish) completely avoid working with electronic and vibrational basis functions $\psi_e(-)$ and $\psi_v(-)$ that change sign when going around a closed loop in vibrational space. An alternative choice of basis functions with factors of the form $\psi_e(+)$ and $\psi_v(+)$ leads (in the author's opinion) to a gain in group-theoretical simplicity and to no loss in computational convenience. In addition, the electronic and vibrational factors in such basis functions exhibit no unusual sign changes, and thus require no additional explanation via the concept of Berry phase.

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