

The relativistic $E \times E$ Jahn–Teller effect revisited

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Abstract

The vibronic Hamiltonian describing linear Jahn–Teller coupling as well as spin–orbit coupling in systems of trigonal symmetry is derived in the diabatic spin–orbital representation, employing the microscopic (Breit–Pauli) spin–orbit coupling operator in the single-electron approximation. The analysis generalizes previous treatments based on more phenomenological models of spin–orbit coupling. It is shown that an alternative time-reversal symmetry adapted diabatic representation exists, in which the 4×4 Jahn–Teller spin–orbit vibronic Hamiltonian is block-diagonal. The adiabatic electronic wave functions are obtained in explicit form. The topological phases (Berry's phases) of all four adiabatic electronic basis states are calculated. As found previously for the special case of systems with D_{3h} symmetry, the topological phases depend on the radius of the loop of integration.

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1. Introduction

The interplay of Jahn–Teller (JT) and spin–orbit (SO) interactions in degenerate electronic states of molecular systems has extensively been studied since decades, beginning with a paper by Jahn in 1938 [1]. The most common case is the $E \times E$ JT effect, where a doubly degenerate vibrational mode lifts the degeneracy of a doubly degenerate electronic state in first order [2–6]. It has been shown by many authors that the JT coupling and the SO coupling tend to quench each other, see, e.g. [6,8].

A particular interesting aspect of JT systems (or, more generally, of conical intersections) is the nontrivial topological phase (also referred to as Berry's phase) carried by the adiabatic electronic wave functions [9–11]. The first analysis of the effect of SO coupling on the topological phase of a JT system has been given by Stone within a phenomenological model of the JT and SO interactions of a single electron in the field of three nuclei arranged in an equilateral triangle

[12]. Mead [13] and Yarkony and collaborators [14–18] have extended this analysis to the more general case of conical intersections. Matsika and Yarkony and Han and Yarkony have given a comprehensive analysis of conical intersections with inclusion of SO coupling in the general case of no symmetry [17,18]. The most detailed analysis of geometric phases in the special case of $E \times E$ JT–SO systems has been given by Koizumi and Sugano [19] as well as Schön and Köppel [20].

It seems that the explicit analysis of geometric phase effects in $E \times E$ JT–SO systems has so far been restricted to systems which exhibit an additional (horizontal) plane of symmetry of the nuclear frame, such as systems with three identical nuclei forming an equilateral triangle [12,13,19,20]. The significance of such a plane of symmetry for the existence of conical intersections and geometric phases has first been pointed out by Mead [13,21] and Yarkony [14–18]. While in general five conditions must be fulfilled to have an exact degeneracy of adiabatic terms in SO-coupled systems, the number of conditions reduces to three when a plane of symmetry exists [14–21]. The plane of symmetry simplifies the JT–SO problem, since certain matrix elements of the SO operator with nonrelativistic electronic wave functions vanish in this case [13].

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It has been shown that the $E \times E$ JT–SO problem, which in general involves four coupled electronic states, decouples into two identical two-state subproblems if the plane of symmetry exists [19–21]. The Kramers degeneracy of the energy levels of odd-electron systems, which in general is the consequence of time-reversal symmetry of the Hamiltonian, reduces to spin degeneracy in this special case, that is, the z -axis projections of the spin of the unpaired electron are good quantum numbers [19,20].

In the absence of a plane of symmetry, the electronic angular momentum and spin projections are not conserved, and Kramers degeneracy is nontrivial in the sense that it arises solely from time-reversal symmetry. It has been pointed out by Mead [22] that interesting geometric phase factors associated with non-Abelian gauge groups are expected in this case.

In the present work, we consider the $E \times E$ JT effect with inclusion of SO coupling in molecular systems with a single threefold symmetry axis, which do not possess a horizontal plane of symmetry. Examples are four-atomic radicals or radical cations with C_{3v} symmetry, such as CH_3S , CH_3I^+ or PF_3^+ . We restrict ourselves to linear JT coupling (the effects of quadratic JT coupling on the geometric phases has been analyzed, for example, in [20]). Unlike the previous investigations, where simplified models of the SO interaction of the type

$$H_{\text{SO}} = AL_zS_z, \quad (1)$$

where L_z , S_z are the z -axis projections of the orbital and spin angular momentum and A is a phenomenological constant, have been assumed, we base our analysis on the “microscopic” Breit–Pauli SO operator in the single-electron approximation [23,24]. We shall derive the 4×4 JT–SO Hamiltonian matrix in a time-reversal symmetry adapted (in short, T-adapted) basis of nonrelativistic diabatic spin–orbital electronic states. It will be shown that alternative T-adapted diabatic basis states can be introduced, which render the JT–SO Hamiltonian block-diagonal. In this new basis, the electronic angular momentum and spin projections are no longer good quantum numbers. The adiabatic electronic wave functions of the 4×4 JT–SO problem and their geometric phase factors will be obtained in closed analytic form.

2. The vibronic Hamiltonian in the diabatic representation

Let us consider, as an example of an odd-electron molecular system with a threefold symmetry axis, a pyramidal molecule with C_{3v} symmetry of the nuclear frame. We describe the unpaired electron in an effective single-particle picture. The three identical nuclei are arranged in the x, y plane. The fourth atom is located above or below the origin of the x, y plane.

The electronic Hamiltonian consists of an electrostatic and a SO part

$$\mathcal{H}_{\text{el}} = \mathcal{H}_{\text{es}} + \mathcal{H}_{\text{SO}}, \quad (2)$$

$$\mathcal{H}_{\text{es}} = -\frac{1}{2}\nabla^2 - \sum_{n=1}^3 \frac{Q}{r_n} - \frac{Q_4}{r_4}, \quad (3)$$

$$\mathcal{H}_{\text{SO}} = A_x\sigma_x + A_y\sigma_y + A_z\sigma_z. \quad (4)$$

Here $Q(=Q_1=Q_2=Q_3)$ and Q_4 are effective nuclear charges. The r_n , $n=1\dots 4$, are the electron–nuclei distances

$$r_n = \left[(x - X_n)^2 + (y - Y_n)^2 + z^2\right]^{\frac{1}{2}}, \quad n=1, 2, 3 \quad (5)$$

$$r_4 = \left[x^2 + y^2 + (z - Z_n)^2\right]^{\frac{1}{2}},$$

and the σ_x , σ_y , σ_z are the Pauli spin matrices. The A_x , A_y , A_z are differential operators in electronic coordinate space. Their explicit form is given in Appendix A. The operator \mathcal{H}_{SO} in Eq. (4) is the well-known Breit–Pauli operator for a single electron moving in the field of four nuclear centers [23,24].

The electronic Hamiltonian specified by Eqs. (2)–(4) commutes with the operator C_3 of the C_{3v} point group as well as with the time-reversal operator,

$$T = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \hat{c}c, \quad (6)$$

where $\hat{c}c$ denotes the operation of complex conjugation,

$$[\mathcal{H}_{\text{el}}, C_3] = 0 \quad (7)$$

$$[\mathcal{H}_{\text{el}}, T] = 0. \quad (8)$$

Note that the vertical symmetry planes ($3\sigma_v$) are symmetry elements of the electrostatic Hamiltonian, but not of the SO operator (\mathcal{H}_{SO} is antisymmetric with respect to σ_v).

When an electron moving in the field of three identical nuclei is considered, as in [12,13,19], the electrostatic Hamiltonian commutes with the reflection operation with respect to the molecular plane (σ_h). As can be seen from the explicit expressions given in Appendix A, A_x and A_y are antisymmetric with respect to σ_h , while A_z is symmetric. As a result, the matrix elements of A_x and A_y with a given orbital of \mathcal{H}_{es} vanish by symmetry. Only matrix elements of A_z are nonzero. For this reason, the four-atomic model considered here, which lacks the symmetry element σ_h , is more general than the previously considered models of three identical nuclei [12,13,19].

Let us next introduce atom-centered basis functions

$$\begin{aligned} \chi_n &= \chi(\vec{r}_n), \quad n=1, 2, 3, 4; \\ \vec{r}_n &= \vec{r} - \vec{R}_n, \quad n=1, 2, 3; \\ \vec{r}_4 &= \vec{r} - \vec{R}_4, \\ \vec{R}_n^T &= (X_n, Y_n, 0), \quad n=1, 2, 3; \\ \vec{R}_4^T &= (0, 0, Z_4). \end{aligned} \quad (9)$$

To take advantage of the C_{3v} symmetry of the electrostatic Hamiltonian, we introduce the symmetry-adapted linear combinations

$$\begin{aligned}
\psi_{E_1} &= 6^{-\frac{1}{2}}[2\chi(\vec{r}_1) - \chi(\vec{r}_2) - \chi(\vec{r}_3)], \\
\psi_{E_2} &= 2^{-\frac{1}{2}}[\chi(\vec{r}_2) - \chi(\vec{r}_3)], \\
\psi_A^{(1)} &= 3^{-\frac{1}{2}}[\chi(\vec{r}_1) + \chi(\vec{r}_3)], \\
\psi_A^{(2)} &= \chi(\vec{r}_4).
\end{aligned} \tag{10}$$

ψ_{E_1} and ψ_{E_2} span the Hilbert space of a degenerate electronic state of E symmetry. In the following, only this 2E state is considered, assuming that is sufficiently separated in energy from the other electronic states.

Following Longuet-Higgins [25], we introduce complex-valued electronic basis functions

$$\begin{aligned}
\psi_+ &= 2^{-\frac{1}{2}}(\psi_{E_1} + i\psi_{E_2}) \\
&= 3^{-\frac{1}{2}}\left[\chi(\vec{r}_1) + e^{\frac{2\pi i}{3}}\chi(\vec{r}_2) + e^{-\frac{2\pi i}{3}}\chi(\vec{r}_3)\right] \\
\psi_- &= 2^{-\frac{1}{2}}(\psi_{E_1} - i\psi_{E_2}) \\
&= 3^{-\frac{1}{2}}\left[\chi(\vec{r}_1) + e^{-\frac{2\pi i}{3}}\chi(\vec{r}_2) + e^{\frac{2\pi i}{3}}\chi(\vec{r}_3)\right].
\end{aligned} \tag{11}$$

These functions transform as follows under C_3

$$\begin{aligned}
C_3\psi_+ &= e^{-\frac{2\pi i}{3}}\psi_+ \\
C_3\psi_- &= e^{\frac{2\pi i}{3}}\psi_-.
\end{aligned} \tag{12}$$

Including the spin function of the electron, we have the following nonrelativistic basis states

$$\begin{aligned}
\psi_1 &= \psi_+|\alpha\rangle, \\
\psi_2 &= \psi_-|\alpha\rangle, \\
\psi_3 &= \psi_+|\beta\rangle, \\
\psi_4 &= \psi_-|\beta\rangle,
\end{aligned} \tag{13}$$

where α (β) denotes the spin projection $+\frac{1}{2}$ ($-\frac{1}{2}$) of the unpaired electron. These electronic basis functions are T-adapted in the sense of Mead [21]

$$\begin{aligned}
T\psi_1 &= \psi_4 \quad T\psi_4 = -\psi_1, \\
T\psi_2 &= \psi_3 \quad T\psi_3 = -\psi_2.
\end{aligned} \tag{14}$$

Consider next symmetry-adapted nuclear displacements from the C_{3v} equilibrium geometry. The bond-stretching coordinates, for example, are given by

$$\begin{aligned}
\delta R_{E_1} &= 6^{-\frac{1}{2}}(2\delta R_1 - \delta R_2 - \delta R_3), \\
\delta R_{E_2} &= 2^{-\frac{1}{2}}(\delta R_2 - \delta R_3), \\
\delta R_A &= 3^{-\frac{1}{2}}(\delta R_1 + \delta R_2 + \delta R_3).
\end{aligned} \tag{15}$$

As is well known, normal modes are obtained by the diagonalization of the F and G matrices [26]. According to the JT theorem [27], only the normal modes of E symmetry are relevant for the vibronic coupling within the 2E electronic state. We consider here a single E mode with dimensionless normal coordinates Q_x , Q_y . It is convenient to introduce the complex-valued combinations

$$Q_{\pm} = Q_x \pm iQ_y = \rho e^{\pm i\varphi}, \tag{16}$$

where ρ and φ are polar coordinates in the Q_{E_1} , Q_{E_2} plane. The transformation properties of Q_{\pm} under C_3 are

$$\begin{aligned}
C_3Q_+ &= e^{-\frac{2\pi i}{3}}Q_+ \\
C_3Q_- &= e^{\frac{2\pi i}{3}}Q_-.
\end{aligned} \tag{17}$$

The vibronic Hamiltonian is obtained by expanding \mathcal{H}_{el} of Eqs. (2)–(4) in a Taylor series up to first order in Q_{\pm} and evaluating matrix elements with the diabatic basis states (Eq. (13)), taking account of the symmetry properties of Eqs. (7), (8), (12), (14) and (17). The result is

$$\mathcal{H}_{\text{el}} = \mathcal{H}_{\text{es}} + \mathcal{H}_{\text{SO}}, \tag{18}$$

$$\mathcal{H}_{\text{es}} = \begin{pmatrix} 0 & \kappa\rho e^{i\varphi} & 0 & 0 \\ \kappa\rho e^{-i\varphi} & 0 & 0 & 0 \\ 0 & 0 & 0 & \kappa\rho e^{i\varphi} \\ 0 & 0 & \kappa\rho e^{-i\varphi} & 0 \end{pmatrix}, \tag{19}$$

$$\mathcal{H}_{\text{SO}} = \begin{pmatrix} \Delta_z & 0 & \Delta_x - i\Delta_y & 0 \\ 0 & -\Delta_z & 0 & -\Delta_x + i\Delta_y \\ \Delta_x + i\Delta_y & 0 & -\Delta_z & 0 \\ 0 & -\Delta_x - i\Delta_y & 0 & \Delta_z \end{pmatrix}. \tag{20}$$

The energy E_0 of the doubly degenerate electronic state at the reference geometry has been set to zero. The (real) parameter κ in Eq. (19) is the well-known coupling constant of the (nonrelativistic) linear $E \times E$ JT effect [2–7]. The parameters Δ_x , Δ_y , Δ_z are matrix elements of the SO operator and are real numbers. Their definition is given in Appendix A. They are independent of the nuclear coordinates (ρ , φ) up to first order in ρ . Note that the zeros in the cross-diagonal of Eq. (20) are a consequence of the time-reversal invariance of the T-adapted electronic basis functions (Eq. (14)). It should also be noted that the Breit–Pauli SO operator is not diagonal in the nonrelativistic diabatic basis (13). Including only its diagonal elements [28] is an approximation.

Including the harmonic part of the potential-energy surface with vibrational frequency $\hbar\omega$ (which arises from the spin-paired electrons not explicitly considered here) and the nuclear kinetic-energy operator, we have the final vibronic Hamiltonian

$$\mathcal{H} = \left(T_N + \frac{\hbar}{2}\omega\rho^2\right)\mathbf{1} + \mathcal{H}_{\text{es}} + \mathcal{H}_{\text{SO}}. \tag{21}$$

Here $\mathbf{1}$ denotes the four-dimensional unit matrix and T_N is given by

$$T_N = -\frac{\hbar\omega}{2}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2}\right). \tag{22}$$

As mentioned above, the SO matrix elements Δ_x , Δ_y vanish if \mathcal{H}_{es} possesses a horizontal plane of symmetry. The SO coupling is then characterized by the single parameter Δ_z and the vibronic Hamiltonian is block diagonal.

$$\mathcal{H}_{\text{es}} + \mathcal{H}_{\text{SO}} = \begin{pmatrix} \Delta_z & \kappa\rho e^{i\varphi} & 0 & 0 \\ \kappa\rho e^{-i\varphi} & -\Delta_z & 0 & 0 \\ 0 & 0 & -\Delta_z & \kappa\rho e^{i\varphi} \\ 0 & 0 & \kappa\rho e^{-i\varphi} & \Delta_z \end{pmatrix}. \tag{23}$$

In this special case, considered previously in [6–8,12,19,20], for example, the spin projections are good quantum numbers; the upper-left (lower-right) block of Eq. (23) corresponds to the spin projections $+\frac{1}{2}$ ($-\frac{1}{2}$).

3. Transformation of the vibronic Hamiltonian to block-diagonal form

At the reference geometry ($\rho = 0$), the electrostatic part \mathcal{H}_{es} of the vibronic potential-energy matrix vanishes. The remaining matrix \mathcal{H}_{so} of Eq. (20) can be diagonalized, by the following constant (that is, independent of ρ and φ) unitary transformation matrix

$$S = \begin{pmatrix} 0 & 0 & e^{-\frac{i\gamma}{2}} \sin \gamma & e^{-\frac{i\gamma}{2}} \cos \gamma \\ e^{-\frac{i\gamma}{2}} \sin \gamma & e^{-\frac{i\gamma}{2}} \cos \gamma & 0 & 0 \\ 0 & 0 & e^{\frac{i\gamma}{2}} \cos \gamma & e^{\frac{i\gamma}{2}} \sin \gamma \\ e^{\frac{i\gamma}{2}} \cos \gamma & e^{\frac{i\gamma}{2}} \sin \gamma & 0 & 0 \end{pmatrix}, \quad (24)$$

where

$$\begin{aligned} \cos \gamma &= \frac{1}{\sqrt{2}} \left(1 + \frac{\Delta_z}{\Delta} \right)^{\frac{1}{2}} \\ \sin \gamma &= \frac{1}{\sqrt{2}} \left(1 - \frac{\Delta_z}{\Delta} \right)^{\frac{1}{2}} \end{aligned} \quad (25)$$

$$\chi = \arg(\Delta_x + i\Delta_y)$$

and

$$\Delta^2 = \Delta_x^2 + \Delta_y^2 + \Delta_z^2. \quad (26)$$

The transformed Hamiltonian reads

$$S^\dagger \mathcal{H} S = \left(T_N + \frac{\hbar}{2} \omega \rho^2 \right) \mathbf{1} + \begin{pmatrix} \Delta & 0 & \kappa \rho e^{-i\varphi} & 0 \\ 0 & -\Delta & 0 & \kappa \rho e^{-i\varphi} \\ \kappa \rho e^{i\varphi} & 0 & -\Delta & 0 \\ 0 & \kappa \rho e^{i\varphi} & 0 & \Delta \end{pmatrix}. \quad (27)$$

Reordering rows and columns, we obtain the Hamiltonian in block-diagonal forms (see also [11], Appendix C)

$$\mathcal{H}' = \left(T_N + \frac{\hbar}{2} \omega \rho^2 \right) \mathbf{1} + \begin{pmatrix} \Delta & \kappa \rho e^{i\varphi} & 0 & 0 \\ \kappa \rho e^{-i\varphi} & -\Delta & 0 & 0 \\ 0 & 0 & -\Delta & \kappa \rho e^{i\varphi} \\ 0 & 0 & \kappa \rho e^{-i\varphi} & \Delta \end{pmatrix}. \quad (28)$$

Note that the electronic basis states corresponding to the vibronic Hamiltonian matrix (28) are diabatic states, since the unitary transformation S is independent of ρ and φ . They are related to the original spin-orbital diabatic electronic basis states ψ_k (Eq. (13)) as follows:

$$\begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \end{pmatrix} = \begin{pmatrix} e^{-\frac{i\gamma}{2}} \cos \gamma & 0 & e^{\frac{i\gamma}{2}} \sin \gamma & 0 \\ 0 & e^{-\frac{i\gamma}{2}} \cos \gamma & 0 & e^{\frac{i\gamma}{2}} \sin \gamma \\ -e^{-\frac{i\gamma}{2}} \sin \gamma & 0 & e^{\frac{i\gamma}{2}} \cos \gamma & 0 \\ 0 & -e^{-\frac{i\gamma}{2}} \sin \gamma & 0 & e^{\frac{i\gamma}{2}} \cos \gamma \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}. \quad (29)$$

Eq. (29) reveals that the new diabatic basis states involve linear combinations of the original basis states (Eq. (13)) with different orbital angular momentum and spin projections. Thus, neither the electronic angular momentum projections ($\Lambda = \pm 1$) nor the spin projections ($m_s = \pm 1/2$) are good quantum numbers in the basis which block-diagonalizes the vibronic Hamiltonian. The block-diagonal structure is a consequence of the time-reversal symmetry of the Hamiltonian.

The basis states ϕ_k are T-adapted in the same manner as the original basis states

$$\begin{aligned} T\phi_1 &= \phi_4 & T\phi_4 &= -\phi_1, \\ T\phi_2 &= \phi_3 & T\phi_3 &= -\phi_2. \end{aligned} \quad (30)$$

Note that the operator T does not mix the pairs (ϕ_1, ϕ_4) and (ϕ_2, ϕ_3) . The formal substitution $\Delta \rightarrow -\Delta$ interchanges the pairs (ϕ_1, ϕ_4) and (ϕ_2, ϕ_3) .

The relativistic linear $E \times E$ JT Hamiltonian (28) has the same form as that derived previously for trigonal molecules with a horizontal symmetry plane [19,20]. The SO parameter Δ_z of the latter case is replaced by the parameter Δ defined in Eq. (26).

4. Adiabatic potential-energy surfaces and adiabatic electronic wave functions

It is trivial to diagonalize the Hamiltonian (28) in the fixed-nuclei limit ($T_N \rightarrow 0$). The adiabatic terms are

$$\begin{aligned} U_{1,4}(\rho) &= \frac{\hbar}{2} \omega \rho^2 + \sqrt{\kappa^2 \rho^2 + \Delta^2}, \\ U_{2,3}(\rho) &= \frac{\hbar}{2} \omega \rho^2 - \sqrt{\kappa^2 \rho^2 + \Delta^2}. \end{aligned} \quad (31)$$

Note that the adiabatic terms are determined by the single parameter Δ defined in the Eq. (26), rather than by the individual matrix elements $\Delta_x, \Delta_y, \Delta_z$. Eq. (31) represents two rotationally symmetric hyperboloids in $\mathcal{Q}_{E_1}, \mathcal{Q}_{E_2}$ space. The degeneracy of the nonrelativistic eigenvalue at $\rho = 0$ is lifted by the SO splitting 2Δ . Each adiabatic term is doubly degenerate (Kramers degeneracy).

The unitary matrix which diagonalizes the upper-left block of the potential matrix reads

$$W_+ = \begin{pmatrix} e^{\frac{i\varphi}{2} + i\eta_1} \cos \theta & e^{\frac{i\varphi}{2} + i\eta_2} \sin \theta \\ -e^{-\frac{i\varphi}{2} + i\eta_1} \sin \theta & e^{-\frac{i\varphi}{2} + i\eta_2} \cos \theta \end{pmatrix}, \quad (32)$$

where

$$\begin{aligned} \cos \theta &= \frac{\kappa \rho}{\sqrt{(\sqrt{\kappa^2 \rho^2 + \Delta^2} - \Delta)^2 + \rho^2 \kappa^2}} \\ \sin \theta &= -\frac{U_{1,4} - \Delta}{\sqrt{(\sqrt{\kappa^2 \rho^2 + \Delta^2} - \Delta)^2 + \rho^2 \kappa^2}} < 0 \end{aligned} \quad (33)$$

and η_1, η_2 are arbitrary phases. For the lower-right block of the potential matrix, the unitary transformation matrix is

$$W_- = \begin{pmatrix} -e^{\frac{i\varphi}{2} + i\eta_3} \cos \theta & -e^{\frac{i\varphi}{2} + i\eta_4} \sin \theta \\ -e^{-\frac{i\varphi}{2} + i\eta_3} \sin \theta & e^{-\frac{i\varphi}{2} + i\eta_4} \cos \theta \end{pmatrix}, \quad (34)$$

where η_3, η_4 again are arbitrary phases. The adiabatic electronic functions are thus given in the following form

$$\begin{aligned} \phi_1^{\text{ad}} &= e^{i\eta_1} \left(e^{\frac{i\varphi}{2}} \cos \theta \phi_1 - e^{-\frac{i\varphi}{2}} \sin \theta \phi_2 \right), \\ \phi_2^{\text{ad}} &= e^{i\eta_2} \left(e^{\frac{i\varphi}{2}} \sin \theta \phi_1 + e^{-\frac{i\varphi}{2}} \cos \theta \phi_2 \right), \\ \phi_3^{\text{ad}} &= e^{i\eta_3} \left(-e^{\frac{i\varphi}{2}} \cos \theta \phi_3 - e^{-\frac{i\varphi}{2}} \sin \theta \phi_4 \right), \\ \phi_4^{\text{ad}} &= e^{i\eta_4} \left(-e^{\frac{i\varphi}{2}} \sin \theta \phi_3 + e^{-\frac{i\varphi}{2}} \cos \theta \phi_4 \right). \end{aligned} \quad (35)$$

These adiabatic electronic wave functions have to be T-adapted, that is, we require

$$\begin{aligned} T\phi_1^{\text{ad}} &= \phi_4^{\text{ad}} & T\phi_4^{\text{ad}} &= -\phi_1^{\text{ad}}, \\ T\phi_2^{\text{ad}} &= \phi_3^{\text{ad}} & T\phi_3^{\text{ad}} &= -\phi_2^{\text{ad}}. \end{aligned} \quad (36)$$

The adiabatic functions $\phi_1^{\text{ad}}, \phi_4^{\text{ad}}$ belong to the upper adiabatic potential-energy sheet $U_{1,4}(\rho)$ and are transformed into each other by time reversal. The functions $\phi_2^{\text{ad}}, \phi_3^{\text{ad}}$ are likewise associated with the lower potential-energy sheet $U_{2,3}(\rho)$. The conditions (36) determine the phase angles $\eta_1 \cdots \eta_4$, with the result

$$\begin{aligned} \phi_1^{\text{ad}} &= \left(e^{\frac{i\varphi}{2}} \cos \theta \phi_1 - e^{-\frac{i\varphi}{2}} \sin \theta \phi_2 \right), \\ \phi_2^{\text{ad}} &= i \left(e^{\frac{i\varphi}{2}} \sin \theta \phi_1 + e^{-\frac{i\varphi}{2}} \cos \theta \phi_2 \right), \\ \phi_3^{\text{ad}} &= -i \left(e^{\frac{i\varphi}{2}} \cos \theta \phi_3 + e^{-\frac{i\varphi}{2}} \sin \theta \phi_4 \right), \\ \phi_4^{\text{ad}} &= \left(-e^{\frac{i\varphi}{2}} \sin \theta \phi_3 + e^{-\frac{i\varphi}{2}} \cos \theta \phi_4 \right). \end{aligned} \quad (37)$$

The adiabatic electronic wave functions (37) are double-valued functions of the angular coordinate φ (because of the phase angle $e^{\frac{i\varphi}{2}}$). They can alternatively be written as single-valued functions

$$\begin{aligned} \tilde{\phi}_1^{\text{ad}} &= (e^{i\varphi} \cos \theta \phi_1 - \sin \theta \phi_2), \\ \tilde{\phi}_2^{\text{ad}} &= i(e^{i\varphi} \sin \theta \phi_1 + \cos \theta \phi_2), \\ \tilde{\phi}_3^{\text{ad}} &= -i(\cos \theta \phi_3 + e^{-i\varphi} \sin \theta \phi_4), \\ \tilde{\phi}_4^{\text{ad}} &= (-\sin \theta \phi_3 + e^{-i\varphi} \cos \theta \phi_4). \end{aligned} \quad (38)$$

The dependence of the ϕ_k^{ad} on the nuclear coordinates ρ , φ gives rise to nondiagonal matrix elements of T_N and thus to nonadiabatic couplings.

The single-valued form (38) of the adiabatic wave function is most suitable for the calculation of the topological phase according to the expression [29]

$$\gamma_n(C) = i \oint_C d\vec{R} \langle n(\vec{R}) | \nabla_R n(\vec{R}) \rangle, \quad (39)$$

where $n(\vec{R})$ is a single-valued adiabatic wave function which depends parametrically on the nuclear coordinate \vec{R} . The integral is to be evaluated over a closed path in parameter space ρ, φ which encloses the origin $\rho = 0$.

Let us illustrate the calculation of the topological phase for the wave function $\tilde{\phi}_1^{\text{ad}}$ (Eq. (38)). Integrating over a circle of radius R around the origin, we have

$$\gamma_1 = i \int_0^{2\pi} R d\varphi \left[(e^{-i\varphi} \cos \theta, -\sin \theta) \frac{1}{R} \frac{\partial}{\partial \varphi} \begin{pmatrix} e^{i\varphi} \cos \theta \\ -\sin \theta \end{pmatrix} \right]_{\rho=R} \quad (40)$$

$$\gamma_1 = -\pi \left(1 + \frac{\Delta}{\sqrt{R^2 \kappa^2 + \Delta^2}} \right). \quad (41)$$

The topological phases of the other three adiabatic states are

$$\gamma_2 = -\pi \left(1 - \frac{\Delta}{\sqrt{R^2 \kappa^2 + \Delta^2}} \right), \quad (42)$$

$$\gamma_3 = -\gamma_2, \quad (43)$$

$$\gamma_4 = -\gamma_1. \quad (44)$$

The two components of an adiabatic electronic Kramers doublet thus have geometric phases of opposite signs. As found previously for planar triatomic systems [12,13,19,20], the geometric phases depend on the radius of the integration contour when SO coupling is included. In the nonrelativistic case ($\Delta = 0$), on the other hand, we have $\gamma = \pm \pi$, independent of R . In the limit $\kappa R \gg \Delta$, that is, for a large radius of the integration contour, Eq. (41) yields $\gamma_1 = \gamma_2 \approx -\pi$, $\gamma_3 = \gamma_4 \approx \pi$ like in the nonrelativistic case. In the opposite limit $\kappa R \ll \Delta$, we find $\gamma_4 = -\gamma_1 \approx 2\pi$ and $\gamma_2 = \gamma_3 \approx 0$, that is, the absence of a nontrivial geometric phase. This result indicates that the whole area enclosed by the integration contour contributes to the geometric phase in the general case, while in the nonrelativistic case the source of the geometric phase is exclusively the conical intersection at $\rho = 0$ [13].

5. Conclusions

We have derived the Hamiltonian of the linear $E \times E$ JT effect in trigonal systems with the inclusion of SO coupling, employing the microscopic (Breit–Pauli) SO operator in the single-electron approximation. This analysis generalizes previous derivations for planar triatomic systems, where the existence of a plane of symmetry eliminates some of the SO coupling elements.

When the usual diabatic spin orbitals are employed as electronic basis functions, the vibronic Hamiltonian is a 4×4 matrix, that is, four electronic basis states are coupled by the vibronic and SO interactions. We have shown that the linear JT–SO Hamiltonian can be transformed to block-diagonal form by a constant (geometry-independent) unitary transformation.

The electronic angular momentum and spin projections are no longer good quantum numbers in this transformed basis. These basis states, like the original spin orbitals, are T-adapted, that is, they form two pairs which are mapped onto each other by the time-reversal operator.

The adiabatic electronic states, which diagonalize the JT–SO Hamiltonian in the fixed-nuclei approximation, have been obtained in explicit form. It has been shown that they can be made T-adapted like the diabatic electronic basis states. Each of the two sheets of the adiabatic potential-energy surfaces is doubly degenerate. This is a (nontrivial) consequence of the time-reversal symmetry of the Hamiltonian.

The geometric phases of the adiabatic electronic wave functions have been calculated for the four-state system. The geometric phases of the two adiabatic electronic states within a Kramers doublet have opposite signs. If the radius of the integration contour encircling the origin of the nuclear coordinate phase is sufficiently large, the geometric phases of the JT–SO effect are $\pm\pi$, like in the nonrelativistic case. In the opposite limit, the geometric phases tend towards zero or 2π . The latter results agree with those obtained previously for planar triatomic systems [12,13,19,20].

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Appendix A

The differential operators A_x , A_y , A_z are

$$A_x = -ig\beta^2 \sum_{n=1}^3 \frac{Q}{r_n^3} \left(y_n \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) - ig\beta^2 \frac{Q_4}{r_4^3} \left(y \frac{\partial}{\partial z} - z_4 \frac{\partial}{\partial y} \right), \quad (\text{A1})$$

$$A_y = -ig\beta^2 \sum_{n=1}^3 \frac{Q}{r_n^3} \left(z \frac{\partial}{\partial x} - x_n \frac{\partial}{\partial z} \right) - ig\beta^2 \frac{Q_4}{r_4^3} \left(z_4 \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right),$$

$$A_z = -ig\beta^2 \sum_{n=1}^3 \frac{Q}{r_n^3} \left(x_n \frac{\partial}{\partial y} - y_n \frac{\partial}{\partial x} \right) - ig\beta^2 \frac{Q_4}{r_4^3} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right),$$

where

$$x_n = x - X_n,$$

$$y_n = y - Y_n,$$

$$r_n = \sqrt{x_n^2 + y_n^2 + z^2}, \quad n = 1, 2, 3, \quad (\text{A2})$$

$$z_4 = z - Z_4,$$

$$r_4 = \sqrt{x^2 + y^2 + z_4^2}.$$

X_n , Y_n , Z_n are coordinates of the nuclei, $g \simeq 2.0023$ is g -factor of the electron and $\beta = \frac{e\hbar}{2m_e c}$ is the Bohr magneton.

The expressions for A_x , A_y , A_z are given below

$$\begin{aligned} A_x &= \frac{1}{2} \int \psi_+^* A_x \psi_+ d^3r = -\frac{1}{2} \int \psi_-^* A_x \psi_- d^3r, \\ A_y &= \frac{1}{2} \int \psi_+^* A_y \psi_+ d^3r = -\frac{1}{2} \int \psi_-^* A_y \psi_- d^3r, \\ A_z &= \frac{1}{2} \int \psi_+^* A_z \psi_+ d^3r = -\frac{1}{2} \int \psi_-^* A_z \psi_- d^3r. \end{aligned} \quad (\text{A3})$$

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