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A theoretical study of time-dependent dynamical Jahn-Teller effect in an impurity center in a solid is presented. We are considering the relaxation of excited states in the E\textsuperscript{e}–e problem through the conical intersection of the potential energy. A strict quantum-mechanical treatment of vibronic interactions with both the main Jahn-Teller active vibration and the nontotally symmetric phonons causing the energy loss is given. The applied method enables us to calculate the time-dependence of the distribution function of the basic configurational coordinate. We have performed a series of numerical calculations allowing us, among other relaxation features, to visualise the details of the relaxation through the conical intersection. In particular, we elucidate how the Slonczewski quantization of the states in the conical intersection affects the relaxation. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4903814]

I. INTRODUCTION

In many cases the dynamics of excited molecules in solutions and impurity centers in crystals is governed by the Jahn-Teller (JT) or pseudo-Jahn-Teller (PJT) effect.\textsuperscript{1–9} Quite often the potential surfaces of these states have conical intersections (called also as molecular funnels or diabolic points) - the seam-type crossing points of two sheets of potential energy in the space of two leading configurational coordinates. In the vicinity of such intersections the electronic states are strongly mixed with vibrational states. It has commonly been assumed that this mixing facilitates nonadiabatic transitions and therefore essentially affects the speed of chemical and photochemical reactions and the rate of non-radiative de-excitation transitions from excited electronic states to the ground electronic state (see, e.g., Refs. 10–12).

To describe nonadiabaticity effects in the vicinity of a conic intersection one should consider the vibronic interaction of valence electrons with few main JT active vibrations. At the same time, one needs to take into account the vibronic interaction with \( N \sim N_A \) bath modes (phonons) responsible for the energy loss and relaxation through the conical intersection (\( N_A = 6.022 \times 10^{23} \) is the Avogadro’s number). In the last years the multi-configurational time-dependent Hartree (MCTDH) method has been developed,\textsuperscript{13–18} which allows one to describe the quantum dynamics of Jahn-Teller systems with several vibrational degrees of freedom. However, because of the fast growth of the required amount of calculations and the diminishing of their accuracy with the increasing of the number of contributing coordinates and the calculating time, this method does not allow one to describe the vibronic dynamics involving the bath modes (phonons) causing the relaxation through a conical intersection.

Recently, a new method\textsuperscript{19–22} was proposed, which allows one to describe the JT and PJT effects taking non-totally symmetric phonons (bath modes) into account. At the basis of the method lies the observation of O’Brien\textsuperscript{23} that in harmonic approximation it is always possible to present the potential energy of arbitrary number (\( N \)) vibrations as a quadratic form of a chosen (in this case the JT-active) configurational coordinate and of all other coordinates. This means that in principle there exists a possibility to replace the linear vibronic interaction with an arbitrary number of vibrations by that with the single (degenerate) vibration if instead to the potential energy of the independent normal modes to use the properly found quadratic non-diagonal potential energy in the representation of configurational coordinates. In Ref. 23 a set of \( N \) equations for the parameters of the corresponding effective quadratic interaction was proposed. However, it remained unclear how these equations could be solved in the case of \( N \sim N_A \). Besides, to make the idea of O’Brien useful, one not only needs to find the explicit equation for this interaction but also to give the method how to perform the required calculations by using this non-diagonal form which depends on \( \sim N_A \) coordinates of the bulk. In Ref. 19 (see also Refs. 20 and 21) both these problems have been solved supposing that vibronic interaction with phonon continuum is relatively weak.

In Ref. 19 it was shown that in this approximation quadratic interaction, which replaces the linear vibronic interaction with phonons, is a product of the coordinate of the main Jahn-Teller active non-totally symmetric mode and the configurational coordinate of the bulk mode of the same representation; the latter coordinate is a definite linear combination of phonon coordinates. The derived interaction of the main Jahn-Teller-active mode(s) with phonons allows one to perform calculations in two steps. First, seed vibronic states, taking into account only the vibronic interaction with the main mode(s), are calculated numerically. Then, by using the found eigenstates as a basis, the derived quadratic interaction of the Jahn-Teller mode with phonons is taken into account by applying the cumulant expansion of the evolution operator. Note that to perform the first step calculations the MCTDH method\textsuperscript{13–18} can be used.

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In Refs. 19–21 the proposed method was applied for the calculation of the optical (absorption and Raman excitation) spectra of impurity centers in crystals with the JT and PJT effect in the excited state. In Ref. 22 it was used for calculations of time dependence of vibrational coordinates contributing to PJT effect. The model considered in Ref. 22 corresponds to the problem of dimer interacting with the environment. In Ref. 22 the master equation for the vibronic levels of a JT- and PJT-system was found taking into account the derived quadratic interaction of the (P)JT-active mode with phonons. This equation was numerically solved for a number of vibronic interaction parameters. This allowed the authors to describe the non-adiabatic irreversible evolution of the JT-active vibration due to the emission of the non-totally symmetric phonons to the bulk.

In this study we are using the method for quantum-mechanical description of the relaxation of a vibronic system through the conical intersection. We are considering the simplest relevant system, the well-known E⊗σ-problem with the conical intersection in the Mexican hat-type adiabatic potential. The essential feature of this case is the existence of the Berry phase, which leads to the existence of the momentum quantum number of vibrionic levels. In the energy relaxation, being under consideration here, the Berry phase manifests itself as the nonzero momentum of emitted phonons (the latter belong to e-representation, as the main mode). To describe the effect of this emission, we derived the master equation for the populations of vibronic levels. The applied method enables us to find a density matrix describing the time evolution of the populations of vibronic levels. Knowing this matrix, one can calculate the time dependence of any quantity of the vibronic subsystem. Here we are considering the time-dependence of the distribution function of the basic configurational coordinate in the case of the optical excitation of the centre by a spectrally selective and non-selective light pulses. We have performed a series of numerical calculations allowing us, among other relaxation features, to visualise the details of the system passing through the conical intersection. In particular, we elucidate that the Slonczewski quantization of the states in the conical intersection affects the systems passing through the conical intersection.

II. E⊗σ PROBLEM FOR LOCAL MODE AND PHONONS

We are considering a twofold degenerate electronic state of E-representation of a trigonal optical centre in a crystal. The E-state interacts, besides totally-symmetric modes, with doubly-degenerate modes of e-representation. The latter interaction causes the Jahn-Teller effect—the corresponding vibronic problem is called as the E⊗σ-problem. Our goal is to study the time-dependence of the Jahn-Teller effect in this case.

In the basis of the electronic states |x⟩ and |y⟩ of the E-representation (these states transform as x and y components of the polar vector, respectively) the vibronic Hamiltonian of the system reads

\[ H = H \cdot I + V, \]

where \( H \) is the Hamiltonian of vibrations, \( I \) is 2 × 2 unit matrix, \( V \) is the 2 × 2 matrix of the vibronic interaction with \( e \) vibrations. In harmonic approximation

\[ H = \sum_{j>0} \alpha_j a_j^+ a_j \]

(up to the not important here zero-point energy) with \( a_j^+ \) being the annihilation and creation operators; the index \( j \) stands here for the normal modes, while the index \( \alpha = 1, 2 \), for the rows of symmetry representations. In the linear approximation vibronic interaction reads

\[ V = k \sum_{\alpha=x,y} \sigma_{\alpha} Q_{\alpha}, \]

where \( Q_x \) and \( Q_y \) are the configurational coordinates of e-representation, \( \sigma_x \) and \( \sigma_z \) are the Pauli matrices, and \( k \) is the constant of vibronic coupling. If one takes two components of the excited state as \( |+\rangle = (|x\rangle + i|y\rangle)/\sqrt{2} \) and \( |-\rangle = (|x\rangle - i|y\rangle)/\sqrt{2} \), then \( V \) gets the form

\[ V = \kappa Q \begin{pmatrix} 0 & e^{-i\varphi} \\ e^{i\varphi} & 0 \end{pmatrix}, \]

where \( Q \) is the radial and \( \varphi \) is the angular variable of the main e-mode \( Q_e = Q \cos \varphi, Q_x = Q \sin \varphi \).

We are considering the case when the configurational coordinates \( Q_\alpha \) are the linear combinations of a number of normal coordinates \( x_\mu \). Under consideration is the case when the main contribution to \( Q_\alpha \) is given by one normal coordinate \( x_\alpha \) describing the local mode; the contribution of other modes is supposed to be small. In this case \( Q_\alpha \) can be presented in the form

\[ Q_\alpha = (1 + \lambda^2)^{-1/2} \left( x_{\alpha 0} + \lambda \sum_{j \geq 1} e_j x_{\alpha j} \right), \]

where \( \lambda \) is a dimensionless parameter, \( e_j \) are the normalized polarization vectors \( \sum_j e_j^2 = 1 \). The number of the contributing phonons is considered to be arbitrary. Besides, we are also considering the case when the coordinate \( x_0 \) corresponds to a narrow wave packet of phonons, i.e., it describes the pseudolocal mode. In the model under consideration the vibronic interaction can also be presented in the form

\[ V = (1 + \lambda^2)^{-1/2} \sum_{j \geq 0} e_j Q_j \begin{pmatrix} 0 & e^{-i\varphi_j} \\ e^{i\varphi_j} & 0 \end{pmatrix}, \]

where \( Q_j \) is the radial and \( \varphi_j \) is the angular variable of the e-mode \( j \). This vibronic interaction as well as the full Hamiltonian \( H_{JT} \) commutes with the operator of the pseudo-momentum

\[ \hat{j} = -i \sum_{j \geq 0} \frac{\partial}{\partial \varphi_j} + \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \]

This means that the eigenvalues of this operator \( J = \pm 1/2, \pm 3/2, \pm 5/2, \ldots \) are conserving quantities also in a multi-coordinate case.
III. TRANSFORMED INTERACTION WITH PHONONS

In Ref. 19 it was shown that if the vibronic interaction with non-totally symmetrical phonons,

\[ V_{ph} = \lambda k \sum_{a,s,y} \sigma_a \sum_j e_j x_{ja}, \]

is weak, then it can be replaced, up to \( \lambda^2 \) terms included, by the following quadratic interaction of the JT-active mode with phonons:

\[ H' = \lambda \sum_{a,s,y} \sum_j (\alpha_0^2 - \alpha_j^2) e_j x_{0a} x_{ja}. \]  (8)

In this approximation

\[ H_{JT} = H + H' \cdot I, \]  (9)

where

\[ H = (H_0 + H_{ph}) \cdot I + V_0. \]  (10)

Here \( H_0 = \omega_0 \sum_{a,s,y} a_0^+ a_0 \) is the vibrational Hamiltonian of the main mode, \( V_0 = k \sum_{a,s,y} \sigma_a e_j x_{0a} \) is the vibronic interaction of this mode, \( H_{ph} = \sum_{j \geq 1} \omega_j a_{0j}^+ a_{0j} \) is the Hamiltonian of phonons. \( H' \) can also be presented in the form

\[ H' = \lambda \sum_{a,s,y} \sum_j v_j (a_{0a}^+ a_{0a} + a_{0a} a_{0a}^+) \]  (11)

or in the form

\[ H' = \lambda \sum_{j \geq 1} v_j (a_{0-}^+ a_{0+} + a_{0+}^+ a_{0-}) + H_c, \]  (12)

where \( a_{0-} \) and \( a_{0+} \) are the destruction and creation operators of phonons, \( a_{0\pm} = (a_{0j} \pm ia_{0j})/\sqrt{2} \) are the operators of the destruction of phonons with the non-zero momentum \( \pm 1 \). As it should be, this Hamiltonian conserves the pseudo-momentum \( J \). Note also another characteristic feature of this interaction:

\[ \vert j \rangle = \sum_n C_{2n+J} \vert 2n + J - 1/2, J - 1/2 \rangle \pm \rangle + C_{2n+J} \vert 2n + J + 1/2, J + 1/2 \rangle - \rangle. \]  (14)

The amplitudes \( C_{j \pm} \) and the energies \( E_{\pm} \) are the solutions of the matrix equation

\[ \begin{pmatrix} J + 1/2 & \sqrt{2(J+1)D} & 0 & 0 & 0 & \ldots \\ \sqrt{2(J+1)D} & J + 3/2 & \sqrt{2D} & 0 & 0 & \ldots \\ 0 & \sqrt{2D} & J + 5/2 & \sqrt{2(J+3)D} & 0 & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \\ C_2 \\ \ldots \end{pmatrix} = E \begin{pmatrix} C_0 \\ C_1 \\ C_2 \\ \ldots \end{pmatrix}. \]  (15)

Here \( D = \kappa^2 / 2 \omega_0 \) (the subscript \( J \) is omitted for simplicity). Equation (15) can easily be solved numerically, taking into account many hundreds\(^{28-30}\) or even thousands of basic vibrational states.\(^{20,21}\)

IV. VIBRONIC BASIS

If one neglects the weak interaction term \( H' \), then, as it follows from Eq. (9), the problem under consideration is reduced to the problem of the JTE with a single twofold degenerate mode contributing to the vibronic coupling. This allows one to use the vibronic states \( \vert v \rangle \) and the energies \( E_v \) of the JTE in the case of a single doubly-degenerate mode as the basis, and to take into account the interaction with phonons \( H' \) approximately by means of the methods of the many-body theory.

The eigenstates of \( H_0 I + V_0 \) can be presented as the superposition of the products of the electronic states \( \vert \pm \rangle \) and the eigenstates of the Hamiltonian \( H_0 \) describe the two-dimensional harmonic oscillator. The eigenstates of this Hamiltonian \( \vert n, m \rangle \) have two quantum numbers. The integer quantum number \( n \) determines the energy \( \omega_0 (n + 1) \) of the two-dimensional oscillator, while the sign-alternative \( m \) determines the projection of the rotational momentum on the symmetry \( (z) \)-axis \( \langle m \vert n \rangle \leq n \). Correspondingly, the eigenstates of the vibronic Hamiltonian \( H_0 I + V_0 \) have two quantum numbers: \( v \) and \( J = m - \frac{1}{2} = \pm \frac{1}{2}, \pm \frac{3}{2}, \ldots \) — the projection of the full (electronic \( s = 1/2 \) and vibrational \( r \)) rotational momentum of the vibronic motion on the \( z \) \((C_y)\)-axis. The states with the same \( \vert J \rangle \) are degenerate (Kramers degeneracy). For \( J > 0 \) the eigenstates of \( H_0 I + V_0 \) read
V. ACCOUNT OF PHONONS: DENSITY OPERATOR

To calculate the time evolution of the excited state of JT-system interacting with phonons we apply the density operator $\hat{\rho}$ of the vibronic subsystem. The matrix elements of this operator read

$$\hat{\rho}_{\nu\nu'} = \langle 0_{ph} | e^{-i(tH + H^\prime)} | \nu \rangle \langle \nu' | e^{i(tH + H^\prime)} | 0_{ph} \rangle, \quad (16)$$

where $|0_{ph} \rangle$ is the zero-point state of phonons. Below we shall use the density operator in the interaction representation $\hat{\rho}(t) = e^{iH^\prime} \hat{\rho} e^{-iH}$. In this representation the time derivative of the density operator reads $\dot{\hat{\rho}} = -i[\hat{\rho}, [H^\prime, \hat{\rho}]] | 0_{ph} \rangle$. Up to the second order, with respect to the interaction parameter $\lambda$, it can be presented in the form

$$\dot{\hat{\rho}}(t) = -\int_0^t dt' \langle 0_{ph} | [\hat{H}^\prime(t), [\hat{H}^\prime(t'), \hat{\rho}(t')] | 0_{ph} \rangle. \quad (17)$$

Inserting here Eq. (11) we get

$$\dot{\hat{\rho}}(t) = \lambda^2 \int_0^t d\tau G(\tau) \sum a_{\alpha\nu}(t)a_{\alpha\nu}^\dagger(t - \tau)\hat{\rho}(t)$$

$$-\hat{\rho}(t - \tau)a_{\alpha\nu}^\dagger(t - \tau) + \hat{H}, \quad (18)$$

where

$$G(\tau) = \sum_j e_j^2 \langle 0_{ph} | a_{\alpha j}(\tau)a_{\alpha j}^\dagger(0_{ph}) \rangle = \sum_j v_j^2 e^{-i\omega_j \tau}, \quad (19)$$

$$e_j^2 \rightarrow v_j^2.$$ 

The correlation function $G(t)$ describes phonon excitations. This function differs essentially from zero only for $\tau \leq t_0$, where $t_0^{-1}$ is the characteristic width of phonon spectrum.

A. Master equation

We are interested in the case of strong vibronic coupling with the main mode and weak coupling with phonons. In this case the time dependence of the diagonal and non-diagonal elements of the density matrix is different. The non-diagonal elements change (decay) very fast in time with the characteristic reciprocal time $\sim \sqrt{D} \omega_0$, where $D \gg 1$. The time dependence of diagonal elements, however, is determined only by the interaction with phonons, which in our case is weak. The corresponding characteristic reciprocal time is at least $\lambda^2$ times smaller than $\sqrt{D} \omega_0$.

Let us consider the diagonal elements $\rho_{\nu\nu}$. For $t \gg t_0$ one can replace $\hat{\rho}(t - \tau)$ in Eq. (18) by $\hat{\rho}(t)$. Then Eq. (18) reduces to the master equation in the Lindblad form. Inserting Eq. (14) into this equation and taking into account that $H^\prime$ conserves the rotation momentum $J$, we get the master equation in the following standard form:

$$\dot{\rho}_{\nu\nu} \approx -\gamma_{\nu} \rho_{\nu\nu} + \sum_{\nu' \neq \nu} \gamma_{\nu\nu'} \rho_{\nu'\nu'}, \quad (20)$$

where $\rho_{\nu'\nu'}$ describes other diagonal elements of the density matrix with the same $J$ as $\rho_{\nu\nu}$.

$$\gamma_{\nu\nu'} = \lambda^2 |A_{\nu\nu'}|^2 \int_t^\infty d\tau G(\tau)e^{i(E_{\nu'} - E_{\nu})\tau} \quad (21)$$

is the rate of the phonon-induced transitions from the state $|\nu\rangle$ to the state $|\nu'\rangle$, $\gamma_{\nu} = \sum_{\nu'} \gamma_{\nu\nu'}$ is the decay rate of the state $|\nu\rangle$,

$$A_{\nu\nu'} = \langle \nu' | (a_{0_+} + a_{0_-}^\dagger)|\nu\rangle + \langle \nu' | (a_{0_-} + a_{0_+}^\dagger)|\nu\rangle \quad (22)$$

is the matrix element of the interaction Hamiltonian $H^\prime$ between the states $|\nu\rangle$ and $|\nu'\rangle$,

$$|\nu_-⟩ = (+|\nu⟩ = \sum_n C_{2n,\nu}|2n, J - 1/2⟩,$$

$$|\nu_+⟩ = (-|\nu⟩ = \sum_n C_{2n+1,\nu}|2n + 1, J + 1/2⟩ \quad (23)$$

(in Eqs. (20)–(23) the index $J$ is omitted for simplicity). The first term in the right-hand side of Eq. (20) describes the decay rate of the state $|\nu⟩$ due to the phonon-assisted transitions from this level to other levels, the second term describes the transitions from all other levels to the level $\nu$).

To calculate $A_{\nu\nu'}$ we take into account the relations

$$|n + l, l⟩ = |n + 1⟩ \pm |n⟩, \quad l = 0, 1, 2, ..., a_{0\pm} |n⟩ = \sqrt{n + 1}|n + 1⟩ \pm, \quad a_{0\pm} |n⟩ = \sqrt{n}|n - 1⟩ \pm, \quad (24)$$

where $|n⟩ \pm$ is the state of $n$ phonons with the projection of the momentum $m = \pm n$ (this state can be presented in the form $a_{0\pm}^\dagger |0, 0⟩ / \sqrt{n + 1}$). Using the above-given equations, we get

$$A_{\nu\nu', J} = \sum_n \left[ C_{2n+1,\nu, J}(\sqrt{n + J} + 1/2) + C_{2n,\nu, J}(\sqrt{n + J} + 1/2) C_{2n, \nu, J} + \sqrt{n + 1} C_{2n+1,\nu, J} \right] \quad (25)$$

where $C_{n,\nu, J}$ are the solutions of the Eq. (15) for $J = 1/2, 3/2, 5/2, ...$ and for the eigenvalue $E_{\nu}$. As it should be, $A_{\nu\nu', J}$ is symmetric: $A_{\nu\nu', J} = A_{\nu', \nu, J}$. In the important case $J = 1/2$

$$A_{\nu\nu'} = \sum_n \left[ \sqrt{n + 1} C_{2n+1,\nu, J}(C_{2n,\nu} + C_{2n+2,\nu}) + C_{2n+1,\nu, J}(C_{2n,\nu} + C_{2n+2,\nu}) \right]. \quad (26)$$

In the large $t$ limit

$$\gamma_{\nu\nu'} = 2\pi \lambda^2 |A_{\nu\nu'}|^2 \nu^2 (E_{\nu'} - E_{\nu}), \quad (27)$$

where $\nu^2(\omega)$ is the Fourier transform of $G(t)$. For every $\nu$ this function differs from zero only for the nearest $\nu'$. Therefore, the transition from the level $\nu$ takes place only to one lower level $\nu'$. Analogously, transitions to the level $\nu$ take place only from one higher level $\nu'$. This essentially simplifies the solution of the master equation (20).
VI. RELAXATION OF THE CONFIGURATIONAL COORDINATE

Here we are studying the time-dependence of the distribution function of the configurational coordinate $Q = \sqrt{x_0^2 + x_1^2}$ in the case of the optical excitation of the centre. We suppose that the temperature is zero ($T = 0$). Two cases of optical excitation are considered: (1) excitation by a spectrally non-selective light pulse, (2) quasi-monochromatic excitation, when initially only one vibronic state $|\nu_0\rangle$ is populated. In the first case, different states with $J = \pm 1/2$ are initially excited with a relative probability $\rho_{\nu\nu}(t = 0) = C_{0,\nu}^2$. (28)

In the second case

$\rho_{\nu\nu}(t = 0) = \delta_{\nu0}$. (29)

This case can be considered due to the fact that for a small $\lambda$ the relaxation rates $\gamma_{\nu}$ are smaller than the energy differences $E_{\nu + 1} - E_{\nu} \sim \omega_0$ of the nearest vibronic levels. Therefore, the excitation with the duration $\sim \omega_0^{-1}$ on the one hand is sufficiently monochromatic to excite one level or a small group of levels and, on the other hand, it is sufficiently short to allow one to study the time-dependence of the relaxation.

By using the initial value of the diagonal elements of the density operator one can solve the master equation (20) step by step and to find these elements for different times. After that one can calculate the time dependence $P(Q, t)$ of the distribution of the radial coordinate $Q$ by using the equation

$$P(Q, t) = \sum_{\nu} \rho_{\nu\nu}(t)(|+\rangle_{\nu}\langle +|_{\nu} + |-\rangle_{\nu}\langle -|_{\nu})$$

$$= \sum_{\nu} \rho_{\nu\nu}(t)(|\Psi_{\nu+}(Q)|^2 + |\Psi_{\nu-}(Q)|^2),$$ (30)

FIG. 1. Some examples of wave functions of 2D isotropic harmonic oscillator. (Configurational coordinate $Q$ is dimensionless.)

FIG. 2. (Left) The scheme of potentials and electronic transitions in the configurational coordinate space. The upper potential corresponds to the Jahn-Teller effect, $E\oplus e$-problem. (Right) A graph of relaxation in case of quasi-monochromatic excitation; intensity axis corresponds to the value of the distribution function $P(Q, t)$. 

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FIG. 3. The time dependence of the distribution function of the configurational coordinate $Q$. Spectrally non-selective excitation. $D = 10$, $\omega_M = 1.3$, $\lambda^2 = 0.1$.

where $|\nu_Q\rangle$ is the wave function of the vibrations of the vibronic state $\nu$ in the coordinate representation,

$$
\Psi_{\nu+}(Q) = \sum_n C_{2n,\nu}\psi_{2n,0}(Q),
$$

$$
\Psi_{\nu-}(Q) = \sum_n C_{2n+1,\nu}\psi_{2n+1,1}(Q).
$$

$\psi_{2n,0}(Q)$ is the wave function of the two-dimensional oscillator for the level with the energy $2n\hbar\omega_0$ and the momentum $m = 0$, $\psi_{2n+1,1}(Q)$ is the radial (i.e., $\varphi = 0$) part of the wave function of this oscillator for the level with the energy $(2n+1)\hbar\omega_0$ and the momentum $m = 1$ (the energy of the zero-point state is considered to be equal to zero). These functions satisfy the following recurrent relations (see the Appendix):

$$
\psi_{2n,0}(Q) = \frac{1}{2^n\sqrt{n!}}e^{Q^2/2}\left(\frac{d^2}{dQ^2} + \frac{1}{Q}\frac{d}{dQ}\right)^n e^{-Q^2},
$$

$$
|\psi_{2n+1,1}(Q)| = \frac{e^{i\varphi}}{2\sqrt{n+1}}\left(Q - \frac{d}{dQ}\right)\psi_{2n,0}(Q).
$$

Using these relations, we have calculated a few hundred wave functions $|2n,0\rangle$ and $|2n+1,1\rangle$ by means of the Maple program package (when performing calculations for $n > 10$ quantum numbers high-precision calculations are required). For example, the $Q$-dependence of the functions $|0,0\rangle$, $|1,1\rangle$, $|100,0\rangle$, and $|101,1\rangle$ are presented in Fig. 1.

VII. NUMERICAL RESULTS AND DISCUSSION

A. Spectrally non-selective excitation

Let us start with the excited state of the JT system, which can be obtained in the case of spectrally non-selective excitation of the $|A_1\rangle \rightarrow |E\rangle$ electronic transition ($|A_1\rangle$ is the initial electronic state of $A_1$ representation). In Fig. 2 vibronic potential is depicted. In the case of such excitation the initial distribution function is the sum of the distribution functions of all levels $|\nu\rangle$ excited at spectrally nonselective excitation.

According to Fig. 3 the distribution function at small times is situated mainly inside the inner potential depicted in Fig. 2 (see also Fig. 5(a) for a detailed potential). However, a notable small distribution intensity exists also near the surface of the outer potential (in Fig. 3(b) right “branch”). At large times, as a result of relaxation, the distribution function is situated in the potential well. In Fig. 4 the relaxation of a system similar to the one in Fig. 3 is depicted, only the interaction with phonons is stronger, as is expected and displayed in the graph, the relaxation in the case of a stronger phonon interaction takes place faster. Calculations were also performed with different vibronic interaction strengths starting from $D = 5$ up to $D = 20$, but the qualitative shape of the relaxation graph remains the same. It is interesting to note that the peak at small coordinates first increases and then
FIG. 5. Relaxation in the case of quasi-monochromatic excitation \( D = 10, \omega_M = 1.3, \lambda^2 = 0.1 \). (a) Potential and vibronic levels. (Zero level of potential energy is taken to intersect the conical intersection.) (b) Diagonal elements of density matrix (vibronic level population). (c) Time dependence of the distribution function of the configurational coordinate \( Q \) in case of relaxation from \( \nu = 7 \), and (d) in case of relaxation from \( \nu = 23 \). (e) and (f) Functions \( \Psi_{\nu-}^0(Q) \) and \( \Psi_{\nu+}^0(Q) \). Note, that the lower the vibronic level is, the more the functions \( \Psi_{\nu-}^0(Q) \) and \( \Psi_{\nu+}^0(Q) \) overlap.

B. Spectrally selective excitation

As a second case, we are considering the relaxation when only one vibronic level is excited. This case corresponds to the optical excitation of the \( |A_1 \rangle \rightarrow |E \rangle \) electronic transition with quasi-monochromatic light being in resonance with the corresponding vibronic transition. In Fig. 5(a) the vibronic potential is depicted. Here we are considering two cases — the
relaxation from a vibronic level which is situated below the conical intersection and the relaxation from a vibronic level which is situated above the conical intersection.

Fig. 5(b) shows the time-dependency of the diagonal elements of the density matrix, i.e., the population density of vibronic levels if level $\nu = 23$ is excited. Note that considering the relaxation process above the conical intersection, the change of population density is not smooth—it is obvious, that each vibronic level couples with phonons differently. It is also evident that the relaxation close but above the conical intersection takes place relatively faster than below it. This demonstrates the expected effect of a non-adiabatic mixing of vibronic states, which is maximal in this region of energy.

Fig. 5(c) shows the relaxation from the vibronic level $\nu = 7$, in this case there is no relaxation through the conical intersection, the peak of the distribution function is shifted away from configurational coordinate’s zero. This peak corresponds to the turning “point” of the left (smaller $Q$ part) branch of the lower potential in Fig. 5(a), shifting this peak towards higher values in the course of time corresponds to relaxation towards the minimum of the potential. As was in the case of spectrally non-selective excitation, it is also notable in the present case—the distribution intensity near the surface of outer potential—the rim at higher $Q$ corresponds to the turning points from this outer branch of the potential. In the case of excitation to the vibronic level below the conical intersection at small times the structure of the distribution functions of the corresponding vibronic level (Eq. (31)) is detectable. Compare, for example, Fig. 5(c) and graph of $\Psi_7^2(Q)$ and $\Psi_7(Q)$ in Fig. 5(e).

Fig. 5(d) shows the relaxation from the vibronic level $\nu = 23$, which is situated above the conical intersection. The upper left corner of the graph describes the relaxation in the inner potential area and through the conical intersection, note the non-trivial shape of the distribution function in this area.

C. Quantum features of relaxation through conical intersection

Finally, let us have a closer look at the relaxation process through the conical intersection. The states in the conical intersection can be approximately described if to take into account only the central cone part of the potential energy. Quantization of states in such a truncated potential leads to the quantum levels called as the Slonczewski resonances. In Fig. 6, the vibronic spectra of the optical transition $|A_i\rangle \rightarrow |E\rangle$ in the case $D = 20$ are presented. The Slonczewski resonances are observed in that spectra as spectral line groups in higher energy parts of these spectra (the line groups around the lines 26 and 31 in case of $D = 20$). For example, the group of lines near $\nu = 26$ corresponds to the zero-point Slonczewski level, while the group of lines near $\nu = 31$ corresponds to the first excited Slonczewski level.

In Fig. 7, some cases of the relaxation of distribution function in the case of quasi-monochromatic excitation are depicted. The Slonczewski resonances are manifested also in relaxation graphs as a non-monotonous dependence of the distribution functions at small $Q$ on time. For example, there is a detectable pattern that if excited is the level left from the most intense vibronic line in the Slonczewski group, the maximum of the distribution function is situated at zero time at configurational coordinate zero (e.g., Figs. 7(a), and 7(b), and 7(f) and 7(g)). If excited is the most intense line and the first line from right (in case of $D = 10$) or the most intense line and the first and second line from right (in case of $D = 20$), the distribution function at small times is spread wider and the maximum of distribution function is achieved later (e.g., Figs. 7(c)–7(e) and 7(h)–7(j)).

To elucidate the reason of such time dependence we present here the distribution functions of the levels close to levels 26 and 31 in Fig. 8. As it follows from these figures the distribution functions of plus-states below the mentioned levels have well-pronounced peaks at $Q = 0$. These peaks

![Fig. 6. (Left) Vibronic potential in case of $D = 20$. (Right) Vibronic spectra in case of $D = 20$, here are clearly noticeable Slonczewski resonances–spectral line groups around $\nu = 26$ and $\nu = 31$ vibronic levels.](image-url)
FIG. 7. The time dependence of the distribution function of the configurational coordinate $Q$ in case of quasi-monochromatic excitation $D = 20$, $\omega_M = 1.3$, $\lambda^2 = 0.1$, fragments of graphs near the origin of coordinates (area around conical intersection). (a)–(e) Relaxation from levels, which belong to zero-point Slonczewski level. (f)–(j): Relaxation from levels, which belong to first-point Slonczewski level. Note that graphs bear similarities row-wise, i.e., the shape of relaxation graph depends on level’s position in Slonczewski resonance.
correspond to the Slonczewski states in the conical intersection with $+1/2$ electronic momentum quantum number and with the zeroth vibrational momentum. The levels higher than levels 25 and 30 have analogous but reduced peaks, which mean that the contribution of the Slonczewski resonances to these levels is diminished. The minus-states depend on $Q$ and on the deviation from main levels 26, 31 differently. These states have peaks at non-zero, however, at small $Q$ values. These peaks correspond to the Slonczewski states with $-1/2$ electronic momentum quantum number and $+1$ vibrational momentum quantum number. The strongest peaks have the levels above (not below, as in the case of plus-states) the main levels. The minus-states below levels 26 and 31 are essentially reduced, except in the case of main levels and one or two levels above the main levels; the rule is that minus-states are considerably weaker than plus-states at small $Q$ values.

In the case of excitation above levels 26 and 31, the plus-states relax to the nearest minus states with lower energy and vice versa. This leads to a non-monotonous dependence of the distribution function on time.

VIII. CONCLUSION

We have presented a novel, strictly quantum-mechanical method to describe a long-time energy relaxation through the conical intersection of the surfaces of the potential energy in the case of $E\otimes e$-problem, caused by the emission of phonons to the bulk. The description is based on a numerically exact consideration of vibronic states of the main Jahn-Teller mode and an approximate analytical consideration of vibronic interaction with nontotally symmetric phonons. The method enabled us to find a time-dependent density matrix, which describes the time evolution of the population of vibronic levels. Knowing this matrix, we calculated the time dependence of the distribution function of the configurational coordinate in the case of the optical excitation of the centre by a spectrally non-selective short light pulse and also in the case of a selective light pulse if only one certain vibronic level was excited. Several cases of various vibronic interaction strength, phonon interaction strength and optical excitation types (spectrally selective and non-selective) were studied. The calculated time evolution of the distribution function allows one to observe...
the details of the relaxation of the system towards the conical intersection and its passing through the conical intersection. This time evolution also shows the quantum features of the process of passing through the conical intersection. This is clearly seen as the oscillatory dependence of the distribution function at small coordinates in time being governed by the interaction of the Slonczewski resonances with phonons.

In our calculations we took into account only the acoustic phonons which were described in the Deby-Van Hove model. However, the theory allows one to easily consider real phonon spectra which fully account for both, the short- and long-range interactions of the crystal lattice.

Here the case was considered when the main vibronic interaction is given by the single twofold degenerate local or pseudolocal mode. However, the basic transformation of the vibronic interaction with phonons used in this theory works for an arbitrary number of local (or pseudolocal) modes. Therefore, the presented theory can be directly generalized to the case of the vibronic interaction with several leading modes and phonons. The difference as compared to the considered case is in the vibronic basis, which should be used for consideration of phonons. To solve the problem, one needs first to find the required vibronic basis in the case of several leading modes using, e.g., diagonalization of vibronic matrix. After that, when using the quadratic interaction of the leading modes with phonons, derived in Refs. 20 and 21, in the same way as it was done here, one can find the effects of relaxation caused by the emission of phonons to the bulk. The transformation of the vibronic interaction with phonons works also for Jahn-Teller systems of other symmetry and an arbitrary number of local (or pseudolocal) modes. Therefore, the described algorithm can be used for any Jahn-Teller system.

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APPENDIX: WAVE FUNCTIONS OF 2D ISOTROPIC HARMONIC OSCILLATOR WITH MOMENTUM \( m = 0 \) AND \( m = 1 \)

Let us find the wave functions of 2D isotropic harmonic oscillator. The Hamiltonian of this oscillator in the units \( \omega_0 = 1 \) reads

\[
H = \frac{1}{2} \left( -\frac{d^2}{dx_1^2} - \frac{d^2}{dx_2^2} + x_1^2 + x_2^2 \right).
\]

In polar coordinates \( x_1 = Q \cos \varphi, \ x_2 = Q \sin \varphi, \)

\[
H = -\frac{1}{2} \left( \frac{d^2}{dQ^2} + \frac{1}{Q} \frac{d}{dQ} + \frac{1}{Q^2} \frac{d^2}{d\varphi^2} + Q^2 \right).
\]

We are interested in the eigenstates of this Hamiltonian which (1) do not have the rotation momentum (i.e., \( m = 0 \) or (2) have a small momentum \( m = 1 \). The first states do not depend on \( \varphi \); the \( \varphi \)-dependence of the latter states is given by the factor \( e^{i\varphi} \).

Using creation and destruction operators

\[
a_i = \frac{1}{\sqrt{2}} \left( \frac{d}{dx_i} + x_i \right), \quad a_i^\dagger = \frac{1}{\sqrt{2}} \left( -\frac{d}{dx_i} + x_i \right) \quad (A3)
\]

we get \( H = \sum_{i=1,2} a_i^\dagger a_i + 1 \).

Let us introduce the operators \( a_k^\pm = \alpha(k \pm ia_0^2) \) of the creation of phonon with the orbital momentum \( m = \pm 1 \). The phonon excitations with the total momentum \( m = 0 \) can be obtained from the zero-point state by applying the operator \( a_k^+ a_k^- \). For example, such state with \( 2n \) quanta equals

\[
|2n, 0\rangle = \frac{1}{n!} a_k^+ a_k^- |0, 0\rangle
\]

\[= \sum_{k=0}^{n} \frac{n!}{k!(n-k)!} |0, 0\rangle.
\]

Taking into account the well-known relations for the harmonic oscillator

\[
a^{\pm} |0\rangle = \sqrt{k!} |k\rangle = \frac{1}{\sqrt{2\pi} \sqrt{k}} e^{-x^2/2} H_k(x),
\]

\[H_k(x) = (-1)^k e^{x^2} \frac{d^k}{dx^k} e^{-x^2},
\]

we get

\[|2n, 0\rangle = \frac{1}{2^n \sqrt{\pi} n!} e^{(x_1^2 + x_2^2)/2} \]

\[\times \sum_{k=0}^{n} \frac{1}{k!(n-k)!} \left( \frac{d^{2k}}{dx_1^{2k}} \frac{d^{2(n-k)}}{dx_2^{2(n-k)}} \right) e^{-x_1^2-x_2^2}. \]

The sum in Eq. (A6) can be easily calculated. We get

\[|2n, 0\rangle = \frac{1}{2^n \sqrt{\pi} n!} e^{(x_1^2 + x_2^2)/2} \left( \frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} \right)^n e^{-x_1^2-x_2^2}. \]

Using polar coordinates and taking into account that

\[
\frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} = \frac{d^2}{dQ^2} + \frac{1}{Q} \frac{d}{dQ} + \frac{1}{Q^2} \frac{d^2}{d\varphi^2}
\]

and that the factor \( e^{-x_1^2-x_2^2} = e^{-Q^2} \) does not depend on \( \varphi \), we get

\[|2n, 0\rangle = \frac{1}{2^n \sqrt{\pi} n!} e^{Q^2/2} \left( \frac{d^2}{dQ^2} + \frac{1}{Q} \frac{d}{dQ} \right)^n e^{-Q^2}. \]

Analogously, one can find the state with momentum \( m = 1 \):

\[|2n+1, 1\rangle \equiv |n+1\rangle_+ |n\rangle_- = \frac{1}{\sqrt{n+1}} a_{k}^+ |2n, 0\rangle. \]

Taking into account the relation

\[a_{k}^+ = \frac{1}{2} \left( x_1 + i x_2 - \frac{d}{dx_1} - \frac{i}{Q} \frac{d}{dx_2} \right) \]

\[= \frac{1}{2} e^{i\varphi} \left( Q - \frac{d}{dQ} - i \frac{1}{Q} \frac{d}{d\varphi} \right), \]

(A10)
we get

\[ |2n + 1, 1\rangle = \frac{e^{i\phi}}{2\sqrt{(n + 1)}} \left( Q - \frac{d}{dQ} \right) |2n, 0\rangle. \quad (A11) \]

Analogously, one can calculate the states with higher rotational momentum.

Remark: calculations of the wave functions \(|2n, 0\rangle\) and \(|2n + 1, 1\rangle\) can be done by using, e.g., Maple or Mathematica.