Dynamical pseudo-Jahn-Teller effect: time evolution of quantum states above avoided crossing of electronic levels

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Abstract. Quantum states above the avoided crossing of electronic levels of a vibronic system with pseudo-Jahn-Teller effect are considered both analytically and numerically. Equations for energies and wave functions of the states are derived. Expansions of these functions over numerically exact vibronic states are obtained and time evolution of the states is found by applying the Fock-Krylov theorem.

1. Introduction
Avoided crossing of energy levels plays an important role in many phenomena of physics, chemistry and biology. First time this problem was addressed in connection with Landau-Zener effect [1,2] – the transition between levels with energy separation being a linear function of time and with coupling in the diabatic Hamiltonian being independent of time. At present we know a number of phenomena governed by avoided crossing: energy exchange, charge exchange, mixed valence, predissociation, associative recombination (see e.g. [3-8] and references therein). Note also strong entanglement between electronic and nuclear degrees of freedom in systems with avoided levels crossing which could be exploited in the nascent field of quantum computation [9-11].

In molecular systems avoided crossing is usually considered in terms of pseudo-Jahn-Teller effect (PJTE) [12,13]. In the simplest such a system - dimer [14,15] the main motion above the avoided crossing can be considered in terms of vibrations at the upper branch of the adiabatic potential energy surface (APES). See in this connection the 1979 study of Loorits [16] (published in Russian as a preprint of Institute of Physics, Tartu, Estonia; translated to English in [17], this issue). In this work it was shown that the higher-energy part of the optical spectrum of the system with strong PJTE in excited state consists of series of groups of lines. This result was interpreted in favour of existence of vibrations at the upper branch of the APES: every group of lines corresponds to creation of a particular quantum vibrational state at optical transition in this branch of the APES. Non-adiabatic transitions to another branch of the APES show up in this spectrum as components in groups. A year later analogous groups of spectral lines were numerically found in the optical $E\times e$ problem [18-20]. Corresponding levels in the upper branch of the APES in this case are known as Slonczewski resonances [21].

Although direct evidence of existence of vibrations at the upper branch of the APES of PJTE have been obtained long ago, as far as we know the properties of these vibrations were not clarified until now. Here these properties are considered. We derive analytical equations describing the energies and the wave functions of these states (see also Ref. [22] where analogous description of Slonczewski resonances in $E\times e$ problem is given). We also find the expansion of these states over the exact vibronic states of the problem. This allows us to get time dependence of the states under consideration by applying the Fock-Krylov theorem [23].
If calculated in this way, time dependence of the states under consideration holds for short times – shorter than or comparable with the period of the main mode in the diabatic basis. At large time one needs to take into account the interaction of the system with the vibrational continuum of the environment (phonons in crystals) causing the transfer of the energy to the bulk. This can be done by applying the theory [22, 24-26] allowing one to consider interaction of the Jahn-Teller and pseudo-Jahn-Teller systems with phonons. Using this theory one can calculate rates of decay of the basic vibronic states due to emission of phonons to the bulk. In the current study we use results obtained in Ref. [24] for description of time evolution of the states under consideration. This allows one to find evolution of these PJTE systems also for long times.

Note that the short time-scale dynamics of the PJTE can be also calculated by means of numerical solution of time-dependent Schrödinger equation; see in this connection the multi-configurational time-dependent Hartree method developed in Refs. [27-32]. This method allows one to calculate dynamics of vibronic systems with several (usually up to ten) vibrational degrees of freedom. However, this theory does not allow one to consider long time-scale evolution of vibronic systems which is determined by their interaction with the phonon continuum.

2. Pseudo-Jahn-Teller effect. Quantum states above the avoided crossing

In the simplest case the Hamiltonian of the systems describing PJTE and a dimer can be presented in the form [12-17] \( H = H_I + H_{el} \), where

\[
H_I = \left( d^2/dx^2 + \omega^2 x^2 \right)/2, \\
H_{el} = \mathcal{E} \sigma_x + k x \sigma_z.
\]

Here \( H_I \) is the Hamiltonian of one-dimensional vibrations in harmonic approximation, \( H_{el} \) is the vibronic interaction, \( x \) is the reduced displacement of the vibrating system from the equilibrium position (dynamical variable), \( I \) is the \( 2 \times 2 \) unit matrix, \( \sigma_x \) and \( \sigma_z \) are the Pauli matrices, \( \omega \), \( \mathcal{E} \) and \( k \) are the parameters of the model (\( \mathcal{E} \) gives the splitting of the levels at \( x = 0 \), \( k \) is the strength of the vibronic coupling; units with \( \hbar = 1 \) are used). In case of deep minima of the crossing potentials (with energy \( -D \), where \( D = k^2/2\omega^2 \) is the vibronic stabilization energy) the parameters of the model satisfy the conditions \( D \gg \mathcal{E} \gg \omega \). For \( \omega < \mathcal{E} \) this Hamiltonian is used for description of the PJTE [13].

The eigenstates \( |\psi\rangle \) of the Hamiltonian \( H \) (called vibronic states) can be found by numerical solving of the stationary Schrödinger equation using the eigenstates \( |n\rangle \) of the Hamiltonian \( H_0 \) of the active mode as the basis [14-17]. The latter states \( |n\rangle \) have a quantum number - the integer \( n = 0, 1, 2, ... \) which determines the energies of the levels of the mode \( \omega(n + 1/2) \). There are even (+) and odd (-) solutions of the stationary Schrödinger equation \( H|\psi\rangle = E|\psi\rangle \) which have the form

\[
|\psi_+\rangle = \sum_n (c_{2n,n}^+ |2n\rangle |0\rangle_x + c_{2n+1,n}^+ |2n+1\rangle |1\rangle_x),
\]

\[
|\psi_-\rangle = \sum_n (c_{2n,n}^- |2n\rangle |1\rangle_x + c_{2n+1,n}^- |2n+1\rangle |0\rangle_x)
\]

where \( c_{n,v}^\pm \) are the solutions of two matrix equations with tridiagonal matrices (see equations (15) in Ref. [17]). Solutions of these equations can be easily found numerically; see Ref. [17] where these solutions were found for rather large values of the vibronic stabilization energy \( D \).

The Hamiltonian \( H \) in the adiabatic approximation gets the form (see equations. (27) and (28) in Ref. [17])
\[ H_+ = \frac{1}{2} \left( -\frac{d^2}{dx^2} + x^2 + k^2 \varepsilon^2 \right) \cdot \left( \frac{k^2 \varepsilon^2}{4} \right) \cdot \left( -\frac{d}{dr^2} + 2 \varepsilon \right) \cdot \sigma \]  

(3)

Here \( H_+ \) describes in this approximation the motion of the system in the upper branch of the potential surfaces, while \( H_- \) describes the motion of it in the lower branch of the potential surfaces. We are interested in the eigenstates of Hamiltonian \( H_+ \) describing the quantum states above the avoided crossing. Using the dimensionless coordinate \( r = x \sqrt{2D} \) the Hamiltonian \( H_+ \) gets the form

\[ H_+ = -d^2/dr^2 + \sqrt{r^2 + \varepsilon^2} + \Omega^2 r^2 + \varepsilon^2 \left[ \frac{k^2 \varepsilon^2}{4} \right] \]  

(4)

where \( D = k^2/2 \), \( \Omega = 1/2D^{1/3} \), \( \varepsilon = \varepsilon / D^{1/3} \). We consider the case when \( \Omega \ll \varepsilon \ll 1 \) and restrict ourselves to the consideration of states with the characteristic values of \( r > \varepsilon \). In this case in the zeroth approximation one can neglect the terms \( \propto \Omega^2 \) and \( \propto \varepsilon^2 \). Then Hamiltonian \( H_+ \) gets the following simple form: \( H_+^{(0)} = -d^2/dr^2 + |r| \). The solution of this equation is the Airy function \([2] \):

\[ \psi_i (|r|) = \text{Ai} (|r| + E_i), \quad \psi_i (-|r|) = (-1)^n \psi_i (|r|) \]  

(5)

where \( \text{Ai}(r) \) is the Airy function, \( E_i = E_i / D^{1/3} \), \( E_i \) is the energy of the level number \( l \), \( \mu_i \) are the normalization factors:

\[ \mu_0 = 1.31, \quad \mu_1 = 1.01, \quad \mu_2 = 0.936, \quad \mu_3 = 0.880, \quad \mu_4 = 0.847, \quad \mu_5 = 0.817, \quad \mu_6 = 0.796 \]  

(6)

The energies \( E_i \) are determined by the boundary conditions. The first order corrections can be found by applying the equation

\[ \delta E_i = \langle \psi_i | (H_+ - E_i) | \psi_L \rangle = \frac{2}{\pi} \int_0^\infty d\rho \psi_i (\rho) (H_+ - E_i) \psi_i (\rho) \]  

(7)

2.1 Even states

Let us consider first the even states. These states satisfy the boundary condition \( d\psi(r)/dr \big|_{r=0} = 0 \). Using this condition we get the following energies of the first five even levels above the avoided crossing in zeroth approximation: \( E_0 = 1.02 \), \( E_2 = 3.25 \), \( E_4 = 4.82 \), \( E_6 = 6.16 \), \( E_8 = 7.37 \). Let us consider now the first-order corrections. The term \( \sqrt{r^2 + \varepsilon^2} - |r| \) gives rather weakly dependent on \( n \) correction \( \delta E_{2l} = \zeta_{2l,n} \varepsilon \), where \( \zeta_{2l,n} \approx 1 \). The term \( \left( \varepsilon^2 / 8D^{2/3} \right) \left( \left( r^2 + \varepsilon^2 / D^{2/3} \right)^2 \right) \) gives even smaller corrections. However, the term \( \Omega^2 r^2 \) gives rapidly growing with \( l \) corrections \( \delta E_{2l} = \alpha_{2l} / D^{3/2} \) with \( \alpha_0 = 0.22 \), \( \alpha_2 = 5.69 \), \( \alpha_4 = 8.67 \), \( \alpha_6 = 12.43 \), \( \alpha_8 = 20.29 \). Consequently, one can present energies of the even states in the form

\[ E_{2l} \approx D^{1/3} \left( E_{2l} + \zeta_{2l,n} \varepsilon + \zeta_{2l} D^{2/3} \right) \]  

(8)

2.2 Odd states

Now we consider the odd states. These states satisfy the condition \( \psi(r) \big|_{r=0} = 0 \). This condition gives in zeroth approximation the following energies of the levels in the upper branch of the potential surface: \( E_1 = 2.34 \), \( E_3 = 4.09 \), \( E_5 = 5.52 \), \( E_7 = 6.79 \), \( E_9 = 7.95 \). The first-order corrections of the energies of these states with respect to \( \sqrt{r^2 + \varepsilon^2} - |r| \) give \( \varepsilon^2 \eta_{2n+1} \): the first-order corrections stemming from the term \( \Omega^2 r^2 / 2 \) equal \( \xi_{2n+1} D^{2/3} \), where first 5 values of \( \eta_{2n+1} \) and \( \xi_{2n+1} \) are:
\[ \eta_1 = 0.160, \quad \eta_3 = 0.063, \quad \eta_5 = 0.026, \quad \eta_7 = 0.020, \quad \eta_9 = 0.016, \quad \text{and} \quad \zeta_1 = 1.087, \quad \zeta_3 = 2.162, \quad \zeta_5 = 3.212, \quad \zeta_7 = 4.249, \quad \zeta_9 = 5.279. \]

Consequently, the energies of odd terms approximately given by the equation

\[ E_{2l+1} \approx D^{1/3} \left( E_{2l+1} + \varepsilon^2 \eta_{2l+1} + \zeta_{2l+1} D^{-2/3} \right) \]  

(9)

The wave functions of the first 6 levels (3 even and 3 odd) are depicted in figure 1.

Figure 1. Adiabatic potential energy surfaces in case of PJTE (thick black curves) and first six vibrational states above the avoided crossing (energies \( E_n \) – straight black lines, wave functions are shown by curves); \( D = 27, \ \varepsilon = 1 \).

3. Time evolution of vibrational levels in the upper states

The wave functions \( \psi_n(x) \) describe only dependence of full wave functions on the vibrational coordinates. The electronic part of the wave functions in the adiabatic approximation above the avoided crossing for \( E > 0 \) equals \( |e_x\rangle = \left( |0\rangle_x + |1\rangle_x \right)/\sqrt{2} \). The full states in this approximation read \( |\tilde{\psi}_l\rangle = |\psi_l\rangle |e_x\rangle \). These states are not the stationary ones; they can be presented as the wave-packets of the stationary states:

\[ |\tilde{\psi}_l\rangle = \sum_v \left( S^{+}_{v,l} |\Psi_{v+}\rangle + S^{-}_{v,l} |\Psi_{v-}\rangle \right) \]  

(10)

where

\[ S^{\pm}_{v,2l} = 2^{-1/2} \sum_n c^{\pm}_{2n,2l} \langle 2n | \psi_{2l+1} \rangle, \]

\[ S^{\pm}_{v,2l+1} = 2^{-1/2} \sum_n c^{\pm}_{2n+1,2l+1} \langle 2n+1 | \psi_{2l+1} \rangle \]  

(11)

The amplitudes \( c^{\pm}_{n,v} \) (see equations (2)) are found at the diagonalization of the vibronic matrix; see Ref. [17]. The overlapping integral \( \langle n | \psi_{2l} \rangle \) of the wave function of the harmonic oscillator with the wave function of the state under consideration differs from zero if both, \( l \) and \( n \) are even or odd. It equals

\[ \langle n | \psi_{2l} \rangle = 2 \sqrt{1/2^n n! \sqrt{2\pi} D^{1/2}} \mu_l \int_0^\infty dr H_n(r) \sqrt{2D} e^{-r^2/4D} \text{Airy}(r-r_l) \]

where \( H_n \) is the Hermite polynomials. This integral can be easily calculated for any given \( D \) and \( r_l \).

The density function

\[ \rho_l(E) = \sum_v \left( |S^{+}_{v,l}|^2 \delta(E - E_{v+}) + |S^{-}_{v,l}|^2 \delta(E - E_{v-}) \right) \]  

(12)
gives the spectrum of these states. According to the Fock-Krylov theorem, the square root of the absolute value of its Fourier transform

\[ L(t) = \sum_{\nu} |S_{\nu,\nu'}|^2 e^{iE_{\nu'} t} + |S_{\nu',\nu}|^2 e^{iE_{\nu'} t} \]  

(13)

describes the time evolution (decay) of this state. Thus, to find the time evolution mentioned one needs to calculate the amplitudes \( S_{\nu,\nu'} \). This can be done using equations (5) and (11). Equation (13) does not account for the decay of the vibronic levels caused by the interaction with phonons. This decay will be taken into account by adding the imaginary summands \( i\gamma_{\nu,\nu'} \) to the energies \( E_{\nu,\nu'} \) in equation (13). The method of calculations of the decay factors \( \gamma_{\nu,\nu'} \) was developed in [24].

4. Numerical results

Presented here analytical theory of the quantum states above the avoided crossing of APESs allows one to calculate the functions \( L_n(t) \) describing the decay of the population probability of these levels. Using given above equations (2), (5), (11) and (13) we performed calculations of \( L_n(t) \) for six lowest levels of the system with \( D = 25, \epsilon = 0.5, \epsilon = 5 \) and \( D = 50, \epsilon = 0.5, \epsilon = 5 \) (we use units \( \hbar = \omega = 1 \)). In our calculations we used 2000 x 2000 and 2500 x 2500 vibronic matrices with no remarkable differences in the results. To calculate amplitudes \( S^\pm_{\nu,\nu'} \) (see equations (11)), we took into account 61 and 71 lowest states \( |n\rangle \) also with no remarkable difference in the results. The calculated decay-functions \( L(t) \) are presented in figures 2 – 4. Several characteristic features of the decays should be noted.

First, the fastest stages of the time evolutions under consideration have characteristic time \( \lesssim 0.1 \). For usual parameters of molecular systems this corresponds to femtosecond times. At this stage, the larger is the vibronic interaction \( D \) the faster is the short time-scale dynamics (see figures 2 and 3). These conclusions are in agreement with the result obtained in [27-32] by means of the multi-configurational time-dependent Hartree method.

Another essential characteristic of the decay laws is the presence of the oscillatory features in the \( t \lesssim 1 \) region for all levels except the lowest ones. This-type oscillatory time-dependence of the probability of population of a quantum state is characteristic for systems with discrete energy spectrum weakly interacting with quasi-continuum of states. Physically such regime of decay corresponds to the situation when the energy transferred from one sub-system to another can return back. The quasi-continuum mentioned corresponds here to the exact vibronic states with almost equidistant energy levels with the mean energy quantum being close to unity. The probability to return back increases with the level number: the higher is the level the more states below exist from which the system can return back. The reason of absence of the oscillatory features for the lowest levels is the following: when the system leaves this level it leaves also the upper branch of the APES and cannot return back.
Figure 2. Short-time evolution of the states: $L(t)$ for levels $n = 0 - 6$ at $\varepsilon = 0.5$, $\gamma = 0.05$.

Figure 3. Effect of $\varepsilon$ in short time evolution is small: $L(t)$ for levels $n = 0$ and $1$, $\gamma = 0.05$.

Figure 4. Long time evolution of the states with $n=0...5$ for $\varepsilon = 0.5$, $D = 50$, $\gamma = 0.05$. 
One more characteristic feature of decays of the population probability is the repeating of the probability maxima with the mean period close to $2\pi$ corresponding to the period of the main vibration. This period appears due to the broad almost equidistant energy spectrum of the highly excited vibronic system with large $D$. It is a consequence of the Floquet’s theorem which in this case tells us that the periodically time-dependent system has periodic energy spectrum. The decay of the periodicity at large time in our case corresponds to the violation of the equidistant levels. This violation is essential for large $\epsilon$ but it is rather small in case of small $\epsilon$. Therefore the decay mentioned is quite small in last case and it is remarkable in the first case. Due to the same reason the repeating period for large $\epsilon$ differ from $2\pi$. One more reason of the decay in the long-time-scale is the vibronic interaction with phonons, which in our case is taken into account by the factor $e^{-\gamma t}$, where $\gamma$ is the decay constant (for calculation of $\gamma$ see Ref. [24]).

5. Summary

Pseudo-Jahn-Teller effect (PJTE) in a simplest vibronic system with two quasi-degenerate electronic states and a single non-totally symmetric vibrational mode (with the frequency $\omega$) is considered. An analytical theory of the quantum states above the avoided crossing of the electronic levels in this system is proposed. It is found that in case of large PJTE stabilization energy and small or moderate electronic splitting energy the wave functions of these quantum states are approximately given by Airy functions. The knowledge of these functions allows us to calculate the time evolutions of the probability of population of these states. To this end the equations describing decomposition of these functions over numerically exact vibronic states are derived. This allows us to calculate these time evolutions by applying the Fock-Krylov theorem.

A remarkable features of the found time dependencies is existence of three different time scales: 1) the primary dephasing decay with femtosecond ($t \sim 0.1\omega^{-1}$) characteristic duration, 2) the oscillatory stage for $t \lesssim 1/\omega$ corresponding to energy transfer forth and back between the states under consideration and the vibronic states and 3) the repeating of the probability maxima with relatively long mean period $\sim 2\pi$ – a consequence of the Floquet’s theorem. At longer times the decrease of the probabilities under consideration is determined by the vibronic interaction with phonons.

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