Vibronic states in conical intersections: manifestations of centrifugal energy and non-adiabaticity in optical spectra of Jahn-Teller systems

V. Hizhnyakov¹, K. Pae¹, V. Boltrushko¹, H. Köppel²

¹Institute of Physics, University of Tartu, W. Ostwaldi Str 1, 50411, Tartu, Estonia
²Theoretische Chemie Physikalisch-Chemisches Institut, Universität Heidelberg, Neuenheimer Feld 229 D-69120 Heidelberg, Germany

hizh@ut.ee

Abstract. Quantum states in conical intersections of adiabatic potentials in Jahn-Teller systems, known as Slonczewski resonances, are considered. It is shown that centrifugal forces associated with the rotation of the Jahn-Teller deformation (pseudorotation) play an important role in these resonances causing appearance of gaps in the energy spectrum of these states. In addition, the decay of these states, caused by non-adiabaticity, decreases with increasing angular momentum of the pseudorotation. As a result, states with a large momentum acquire a long lifetime. The optical spectra of the $A_1 \rightarrow E$ electronic transition with different values of the pseudorotational angular momentum are presented. In these spectra, centrifugal energy gaps and the stabilization of levels with a large pseudorotation momentum are clearly identified.

1. Introduction
An essential feature of a vibronic system (molecule, impurity center in crystals) with electronic degeneracy is the existence of conical intersections of the adiabatic potential energy surfaces (APES). The presence of these intersections is crucial for the time evolution of the electronic excitations: the behavior of a system in the vicinity of a conical intersection is governed by strong non-adiabaticity, causing fast transitions between crossing branches of APES. This results in the appearance of specific resonant states, which strongly affect the time evolution of the excited states. In the $E \otimes e$ Jahn-Teller system, the simplest system with the conical intersection, these states are known as Slonczewski resonances. Originally, these states were considered in Ref. [1], where it was found that these states may have a rather small decay rate.

Impressive manifestations of resonance states in $E \otimes e$ systems with a strong Jahn-Teller effect (JTE) in the excited state were numerically found in Refs [2-4], where it was shown that the higher-energy part of the optical spectra of such systems consists of series or groups of lines. Analogous groups of lines were also numerically found in optical spectra of vibronic systems with strong pseudo-Jahn-Teller effect in the excited state [5]. The authors of Refs. [2-5] have interpreted these groups of lines as a manifestation of the quasi-stationary (resonance) states in the upper branch of the APES: every group of lines in the spectrum corresponds to excitation of a particular resonance state in this branch of the APES. The reason for the existence of a number of lines in every group is given by the non-adiabaticity: due to non-adiabatic interactions, the resonance states in the conical intersection are not stationary; i.e.
they are the wave packets (of the stationary states). This non-stationarity of the resonance states has its effect in the dynamics: according to the Fock-Krylov theorem [6], the energy spectrum of a wave-packet determines its time evolution and characterizes the decay rate $\Gamma$, being determined by the width of the envelope of the spectrum.

While the short-range evolution of resonant states in time is govern by non-adiabatic processes, a longer evolution in time is essentially determined by other processes that result from the interaction of the vibronic system with phonons of the bulk: this interaction leads to the emission of phonons, which leads to a finite lifetime of the vibronic states. The phonon emission mentioned was studied in detail in Refs. [7-9]. Because of this emission, evolution becomes irreversible in time: as a result of emission, energy is lost, and the system passes through a conical intersection from the upper to the lower branch of the APES. This makes it impossible to restore the system in its original state. Instead, this will lead to the relaxation of the system to the thermal equilibrium state. Both relaxation processes mentioned above - the non-adiabaticity-induced and the phonon-induced relaxation of the resonant states were studied in [10] for a pseudo-Jahn-Teller system. Here we will extend this study to the $E \otimes e$ Jahn-Teller system.

A specific aspect of the dynamics of the $E \otimes e$ Jahn-Teller system is participation of the pseudorotation: the motion towards and away from the conical intersection includes rotation of the Jahn-Teller deformation of the system around its centre, which in its turn, affects the deformation and the radial motion through the centrifugal forces. The rotation mentioned is characterized by the half-odd integer quantum number $j = \pm 1/2, \pm 3/2, \pm 5/2, \ldots$; the larger is $|j|$ the stronger are centrifugal forces and the stronger is the additional deformation. Hence, Slonczewski resonance states essentially depend on the centrifugal forces and on the value of $j$. In the present communication, we study these dependences. We will show that centrifugal forces lead to appearance of gaps in the energy spectra of the Slonczewski resonance states. In addition, the states with large $|j|$ have small decay rate $\Gamma_{j,n}$ (here $n$ is the quantum number of the radial motion). The physical meaning of this effect is as follows: for larger $j$ the dominant motion of the vibronic system takes place farther away from the crossing point of the conical intersection and the non-adiabaticity becomes correspondingly weaker. As a result, the decay rates $\Gamma_{j,n}$ of the Slonczewski resonances decrease with increasing $j$. Here we derive the analytical equation for the non-adiabaticity-induced rate $\Gamma_{j,n}$ and perform numerical calculations of $\Gamma_{j,n}$ for resonances with different angular ($j$) and radial ($n$) quantum numbers. We also present optical spectra of the electronic transition $A \rightarrow E$ with different values of the pseudorotational angular momentum $j$, calculated by Kaja Pae in her Bachelor's thesis [11]. Analogous spectra have been calculated by Horst Köppel. These spectra clearly demonstrate the importance of the non-adiabaticity and of the centrifugal forces for the Slonczewski resonances. They show the existence of centrifugal gaps in the spectra and the decrease of the rate $\Gamma_{j,n}$ of the non-adiabaticity-induced decay of the Slonczewski resonances with increasing $|j|$ and $n$.

2. Vibronic states

Using a matrix representation for the $E$ electronic state, the vibronic Hamiltonian in case of linear interaction of the optical electrons of this state with double degenerate vibrations of the $e$ -representation can be presented as the following sum of the vibronic Hamiltonians of the double degenerate $e$ -modes:

$$\hat{H} = \hat{H}_v \cdot \hat{I} + \hat{V} .$$ (1)

Here $\hat{I}$ is the $2 \times 2$ unit matrix,
\[ H_v = \frac{1}{2} \left( \omega^2 r^2 - \frac{\partial^2}{\partial r^2} - \frac{\partial}{\partial r} - \frac{1}{r^2} \frac{\partial^2}{\partial \varphi^2} \right) \]  

is the vibrational Hamiltonian of the vibrational \( e \)-mode, \( \omega, r \) and \( \varphi \) are the frequency, radial and angular variables of this mode,

\[ \hat{V} = k r \left( \hat{\sigma}_x \cos \varphi + \hat{\sigma}_y \sin \varphi \right) \]

is the vibronic interaction of optical electrons of the \( E \)-state with the \( e \)-mode, \( k \) is the interaction parameter, \( \hat{\sigma}_a \) are the Pauli matrices. The Hamiltonian \( \hat{H} \) commutes with the operator of the pseudo-rotational angular momentum \( \hat{J} = \hat{\sigma}_z / 2 - i \partial / \partial \varphi \), which means that these two operators have common eigenstates. Therefore the eigenstates of the \( \hat{H} \) can be classified according to the eigenvalues \( j = \pm 1/2, \pm 3/2, \ldots \) of \( \hat{J} \). These states for \( j > 0 \) can be presented in the form \[12\]

\[ |\psi^{(j)}_v \rangle = e^{-i \varphi} \sum_{n=0}^{\infty} \left( C_{2n,v}^{(j)} e^{-i \varphi/2} |n + l \rangle \right)_x |n \rangle \]

where \( |n \rangle_x \) are the stationary states of the circular quantum oscillator with the rotational momentum \( \pm n, l = j \pm 1/2 \), the \( C_{n,v}^{(j)} \) in Eq. (4) satisfy the eigenvalue equation for the tridiagonal matrix \[12\]

\[ \begin{pmatrix} j + 1/2 & \sqrt{(2j + 1)D} & 0 & \cdots \\ \sqrt{(2j + 1)D} & j + 3/2 & \sqrt{2D} & \cdots \\ 0 & \sqrt{2D} & j + 5/2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} C_{0,v}^{(j)} \\ C_{1,v}^{(j)} \\ C_{2,v}^{(j)} \\ \vdots \end{pmatrix} = E_v \begin{pmatrix} C_{0,v}^{(j)} \\ C_{1,v}^{(j)} \\ C_{2,v}^{(j)} \\ \vdots \end{pmatrix} \]

and \( D = k^2 / 2 \omega^3 \) is the dimensionless Jahn-Teller stabilization energy. This equation can be solved numerically.

3. Adiabatic approximation

To describe the quantum states of conical intersections, we need to apply the adiabatic approximation. There are various possibilities for introducing such an approximation. The simplest and best known possibility is to use an orthogonal transformation of the Hamiltonian, which diagonalizes the matrix of the vibronic interaction \( \hat{V}_v \) \[12-14\]. However, in this approximation \( j \) is not a good quantum number. Therefore, it is preferable to use an approximation that takes the conservation law of the half-odd integer rotational momentum \( J \) into account. This approximation can be conveniently introduced using as the basis states the functions

\[ |\psi^{(j)}_v(r, \varphi) \rangle = e^{-i \varphi} r^{-1/2} \begin{pmatrix} e^{-i \varphi/2} \chi_v(r) \\ e^{+i \varphi/2} \psi_v(r) \end{pmatrix} \]

Then the stationary Schrödinger equation reduces to the following one-dimensional equation of radial vibronic motion:

\[ (\hat{H}_J - E) \begin{pmatrix} \chi(r) \\ \psi(r) \end{pmatrix} = 0. \]
Here \( H_j = T + U^{(j)} \) is the Hamiltonian of radial motion with rotational quantum number \( j \), and
\[
T = -2^{-1} d^2/dr^2, \quad U^{(j)} = 2^{-1} \left( \omega^2 r^2 + j^2 / r^2 \right) - \hat{\sigma}_z \cdot j / 2r^2 + \hat{\sigma}_x \cdot kr
\]
are operators of kinetic \((T)\) and potential \((U^{(j)})\) energies of the radial motion (the unit matrix is omitted). Thus, the use of basis states (7) makes it possible to separate angular and radial variables and reduce the problem of vibronic states to the consideration of only the radial vibronic motion. The angular part of the kinetic energy is here taken into account by the operator of the potential energy of centrifugal forces \( j(j + \hat{\sigma}_z) / 2r^2 \).

Performing now orthogonal transformations \( \tilde{T} = OTO^T \) and \( \tilde{U}^{(j)} = OU^{(j)}O^T \) with \( \hat{O} = \cos \alpha + i\hat{\sigma}_y \cdot \sin \alpha \) and \( \alpha = -(1/2) \arctan (2kr / j) \), one gets [2]
\[
\tilde{T} = T + \alpha' \alpha^2 / 2 + \hat{K}, \quad \hat{K} = \left( \alpha' d/dr + \alpha'' / 2 \right) \cdot i\hat{\sigma}_y,
\]
\[
\tilde{U}^{(j)} = 2^{-1} \left( \omega^2 r^2 + j^2 / r^2 \right) + \sqrt{\left( j / 2r^2 \right)^2 + k^2 r^2} \cdot \hat{\sigma}_z.
\]
where \( \alpha' \equiv d\alpha / dr = 3 jkr^2 / \left( j^2 + (2kr)^2 \right) \) and \( \alpha'' = d^2\alpha / dr^2 \). The non-diagonal radial operator \( \hat{K} \) serves here as the non-adiabaticity operator. Neglecting this operator corresponds to the adiabatic approximation.

4. Quantum states of conical intersection
To consider the quantum states of conical intersection, it is convenient to use the dimensionless coordinate \( \tilde{\xi} = (2k)^{1/3} r \) and to use \( 2D^{2/3} \omega \) as the energy unit. Then the transformed Hamiltonian takes the form
\[
H_j = -\frac{1}{2} \frac{d^2}{d\tilde{\xi}^2} + \frac{j^2}{2\tilde{\xi}^2} + \tilde{\xi} \sqrt{1 + \left( \frac{j}{\tilde{\xi}} \right)^2} \cdot \hat{\sigma}_z + \frac{9}{8} \frac{j^2 \tilde{\xi}^4}{\left( j^2 + \tilde{\xi}^2 \right)^2} + \frac{\tilde{\xi}^2}{8D^{2/3}} + iK_j \hat{\sigma}_y,
\]
where
\[
K_j = -\frac{3\tilde{\xi} j^2}{2 \left( j^2 + \tilde{\xi}^6 \right)} \left( \frac{j^2 - 2\tilde{\xi}^6}{j^2 + \tilde{\xi}^6} + \tilde{\xi} \frac{d}{d\tilde{\xi}} \right)
\]
is the dimensionless non-adiabaticity operator. The remarkable property of the Hamiltonian (11) is that only the term \( \tilde{\xi}^2 / 8D^{2/3} \) depends on the value of the vibronic interaction parameter \( D \). In the large \( D \) limit this term can be neglected and the \( D \)-dependence will disappear.

The resonance states are the solutions of the stationary Schrödinger equation which one gets upon neglect of the non-adiabaticity operator \( K_j \). Then, using the dimensionless energy \( \varepsilon = E / D^{2/3} \), this equation gets the form
\[
\left( -\frac{d^2}{d\tilde{\xi}^2} + 2 \left( U_j - \varepsilon_{j,n} \right) \right) \chi_{j,n}^{(\varepsilon)} = 0,
\]
where \( U_j = \omega^2 r^2 + j^2 / r^2 \) is the Hamiltonian of radial motion with rotational quantum number \( j \), and \( T = -2^{-1} d^2/dr^2, \quad U^{(j)} = 2^{-1} \left( \omega^2 r^2 + j^2 / r^2 \right) - \hat{\sigma}_z \cdot j / 2r^2 + \hat{\sigma}_x \cdot kr \) are operators of kinetic \((T)\) and potential \((U^{(j)})\) energies of the radial motion (the unit matrix is omitted). Thus, the use of basis states (7) makes it possible to separate angular and radial variables and reduce the problem of vibronic states to the consideration of only the radial vibronic motion. The angular part of the kinetic energy is here taken into account by the operator of the potential energy of centrifugal forces \( j(j + \hat{\sigma}_z) / 2r^2 \).

Performing now orthogonal transformations \( \tilde{T} = OTO^T \) and \( \tilde{U}^{(j)} = OU^{(j)}O^T \) with \( \hat{O} = \cos \alpha + i\hat{\sigma}_y \cdot \sin \alpha \) and \( \alpha = -(1/2) \arctan (2kr / j) \), one gets [2]
\[
\tilde{T} = T + \alpha' \alpha^2 / 2 + \hat{K}, \quad \hat{K} = \left( \alpha' d/dr + \alpha'' / 2 \right) \cdot i\hat{\sigma}_y,
\]
\[
\tilde{U}^{(j)} = 2^{-1} \left( \omega^2 r^2 + j^2 / r^2 \right) + \sqrt{\left( j / 2r^2 \right)^2 + k^2 r^2} \cdot \hat{\sigma}_z.
\]
where \( \alpha' \equiv d\alpha / dr = 3 jkr^2 / \left( j^2 + (2kr)^2 \right) \) and \( \alpha'' = d^2\alpha / dr^2 \). The non-diagonal radial operator \( \hat{K} \) serves here as the non-adiabaticity operator. Neglecting this operator corresponds to the adiabatic approximation.

4. Quantum states of conical intersection
To consider the quantum states of conical intersection, it is convenient to use the dimensionless coordinate \( \tilde{\xi} = (2k)^{1/3} r \) and to use \( 2D^{2/3} \omega \) as the energy unit. Then the transformed Hamiltonian takes the form
\[
H_j = -\frac{1}{2} \frac{d^2}{d\tilde{\xi}^2} + \frac{j^2}{2\tilde{\xi}^2} + \tilde{\xi} \sqrt{1 + \left( \frac{j}{\tilde{\xi}} \right)^2} \cdot \hat{\sigma}_z + \frac{9}{8} \frac{j^2 \tilde{\xi}^4}{\left( j^2 + \tilde{\xi}^2 \right)^2} + \frac{\tilde{\xi}^2}{8D^{2/3}} + iK_j \hat{\sigma}_y,
\]
where
\[
K_j = -\frac{3\tilde{\xi} j^2}{2 \left( j^2 + \tilde{\xi}^6 \right)} \left( \frac{j^2 - 2\tilde{\xi}^6}{j^2 + \tilde{\xi}^6} + \tilde{\xi} \frac{d}{d\tilde{\xi}} \right)
\]
is the dimensionless non-adiabaticity operator. The remarkable property of the Hamiltonian (11) is that only the term \( \tilde{\xi}^2 / 8D^{2/3} \) depends on the value of the vibronic interaction parameter \( D \). In the large \( D \) limit this term can be neglected and the \( D \)-dependence will disappear.

The resonance states are the solutions of the stationary Schrödinger equation which one gets upon neglect of the non-adiabaticity operator \( K_j \). Then, using the dimensionless energy \( \varepsilon = E / D^{2/3} \), this equation gets the form
\[
\left( -\frac{d^2}{d\tilde{\xi}^2} + 2 \left( U_j - \varepsilon_{j,n} \right) \right) \chi_{j,n}^{(\varepsilon)} = 0,
\]
where $\chi_{j,n}^{(+)}(\xi) \equiv \chi_{j,n}^{(+)}(\xi)$ is the wave function of the state at the conical intersection with the dimensionless energy $\varepsilon_{j,n}$, $n$ is the quantum number of radial motion, and

$$U_j^{(+)} = j^2/2\xi^2 + (\xi/2)\sqrt{1 + j^2/\xi^6} + 9j^2\xi^4/8(j^2 + \xi^6)^2 + \xi^2/8D^{3/2}$$

is the potential energy of the upper APES (Fig. 1).

Fig. 1. Adiabatic potentials for $j = 1/2, 3/2, 5/2, 7/2, 9/2$ (from down to up).

The effect of non-adiabaticity is small when the dominant motion of the system takes place far away from the conical intersection with $\xi = 0$ and $\varepsilon = 0$. For states above the conical intersection this may happen in two cases: 1) $\xi^3 \gg j$, and 2) $j \gg \xi^3$, where $\bar{\xi}$ is the mean value of the radial coordinate $\xi$. The first case (considered earlier in Ref. [10]) corresponds to small energy of rotation (small $j$) but large energy of the radial motion (large $n$). In this case for $D \gg 1$ one can take $U_j^{(+)} \approx \xi/2$ which does not depend on $j$. Then in the zeroth approximation one gets for the eigenfunctions $\chi_{j,n}^{(+)}(\xi)$ the Airy functions

$$\chi_{j,n}^{(+)}(\xi) \approx z_n^{-1/2}Ai(\xi - \varepsilon_n).$$

Here $\varepsilon_n$ are the zeros of the Airy function, $z_m$ are the normalization factors. First-order corrections with respect to $j$ - dependent terms lead to the dependence of the eigenvalues and the eigenfunctions on $j$. However, for large $n$ and small $j$ these dependences are weak. For the five lowest levels one gets $\bar{\xi}_1 \approx 1.7$, $\bar{\xi}_2 \approx 3$, $\bar{\xi}_3 \approx 4$, $\bar{\xi}_4 \approx 5$, $\bar{\xi}_5 \approx 5.8$ (see also Ref. [10], where the energy corrections caused by the centrifugal and elastic forces are also given). Consequently the condition $|j| \ll \xi^3$ is indeed fulfilled for the levels with large $n$ and relatively small $|j|$.

In the second case the last to last term in Eq. (14) can be neglected. Then for $D \gg 1$ one gets $U_j^{(+)} \approx j^2/\xi^2 + \xi\sqrt{1 + j^2/\xi^6}$. This potential energy has its minimum at

$$\xi_{0,j} = \left(2j^2(j^2 - 1)/\left(j\sqrt{3 + j^2 - j^2 - 1}\right)^{3/2}\right)^{1/6}$$

(16)
manifesting the balance between the repulsive centrifugal and attractive vibronic forces. Near this minimum

\[ U^{(+)}_j \approx U^{(+)}_{0,j} + \Omega_j^2 \left( \xi - \xi_{0,j} \right)^2 / 2, \tag{17} \]

where \( U^{(+)}_{0,j} \approx j^2 / 2 \xi_{0,j}^2 + \left( \xi_{0,j} / 2 \right) \sqrt{1 + j^2 / \xi_{0,j}^6} \) is the value of \( U^{(+)}_j \) at the minimum, and

\[ \Omega_j \approx j \xi_{0,j}^{-2} \sqrt{3 + 7.5 \left( j^2 + \xi_{0,j}^6 \right)} / \sqrt{2} - 4.5 j^2 / \left( j^2 + \xi_{0,j}^6 \right)^{3/2} \tag{18} \]

is the frequency of the vibrations at the minimum (see Fig. 2).

![Fig. 2. Parameters of upper APES in dependence on the rotation quantum number \( j \): energy of the \( U_0 \) (solid line), equilibrium position \( \xi_{0,j} \) (dash-dot line) and frequency \( \Omega \) (dash line) of the upper adiabatic potential; energy \( U_1 \) of lower potential (long dash line) and force \( F \) (dot line) of the lower adiabatic potential at coordinate \( \xi = \xi_{0,j} \).](image)

In this case the energy levels in the potential (17) describe the quantum states of the conical intersection. The wave functions are the eigenfunctions of harmonic oscillator

\[ \psi^{(+)}_{j,n}(\xi) \approx \chi^{(+)}_{j,n}(\xi) \approx \left( 2^n n! \right)^{-1/4} \left( \Omega_j / \pi \right)^{1/4} H_n \left( \sqrt{\Omega_j} \left( \xi - \xi_{0,j} \right) \right) e^{-\Omega_j/2 \left( \xi - \xi_{0,j} \right)^2}. \tag{19} \]

The energies of the states with radial number \( n \) and rotational quantum number \( j \) equal \( \varepsilon_{j,n} \approx U^{(+)}_{0,j} + \Omega_j \left( n + 1/2 \right) \). These energies exceed the energy of the conical intersection and they strongly depend on \( |j| \) (increase with \( |j| \)). This means that energy spectrum of the states in the conical intersection with given \( j \) has a gap of centrifugal origin.

5. Decay of the resonance states

Resonance states are stationary only in the adiabatic approximation; with account of non-adiabaticity they become non-stationary. Therefore, these states manifest themselves as groups of lines in optical spectra [2-5]. To characterize quantitatively this effect of non-adiabaticity, we consider transitions from the resonance states of the upper branch of the APES to the lower branch of the APES. We take into account that in the strong vibronic coupling limit \( D \gg 1 \) the spacing of the vibronic levels \( \sim \omega \) is small as compared to the characteristic Jahn-Teller energy \( \omega D \). In the dimensionless units used here,
this spacing is \( \sim (8D)^{-1/3} \) and in case \( D \gtrsim 1 \) is indeed small. This allows us to consider transitions from resonance state to the states of the lower sheet of the APES taking into account only the repulsive part
\[
U_j^{(-)}(\xi) \approx U_{1,j} - F_j \cdot (\xi - \xi_{0,j})
\]  
(20)
of the potential having a continuous energy spectrum. Here \( U_{1,j} \approx 2^{-1} \left( j^2 / \xi_{0,j}^2 + \sqrt{\xi_{0,j}^2 + j^2 / \xi_{0,j}^4} \right) \) is the energy of the lower sheet of the APES at \( \xi = \xi_{0,j} \), \( F_j \equiv j^2 / \xi_{0,j}^3 + (1/2 - j^2 / \xi_{0,j}^6) \sqrt{1 + j^2 / \xi_{0,j}^6} \) is the force corresponding to this sheet of the APES at this coordinate. The wave function of the final (lower) state with the potential energy (20), total energy \( E_{n,j} \approx U_{0,j}^{(+)} + \Omega_j (n + 1/2) \) and coordinates close to \( \xi_{0,j} \) is given by the Airy function [15]:
\[
\chi_{j,n}^{(-)}(\xi) \equiv \sqrt{2/\pi} \left( F/2 \right)^{1/6} Ai\left(\left(\xi - \xi_{0,j} + x_{j,n}\right)\left(2F_j\right)^{1/3}\right).
\]  
(21)
Here \( x_{j,n} = (E_{n,j} + U_{0,j} - U_{1,j})/F_j \) is the difference in the coordinate \( \xi_{0,j} \) of the minimum of the upper branch of the APES and the coordinate of the zero of the Airy function \( \chi_{j,n}^{(+)}(\xi) \).

To find the rate \( \Gamma_{n,j} \) of the transitions, we use Fermi’s Golden rule. Taking into account that in the dimensionless units the density of the final states equals \( F_j^{-1} \), and that the dimensionless energy unit corresponds to energy \( 2D^{1/3} \hbar \omega \) one gets
\[
\Gamma_{j,n} = 4\pi D^{1/3} \omega F_j^{-1} \left| \int d\xi \chi_{j,n}^{(-)}(\xi) K_j \chi_{j,n}^{(+)}(\xi) \right|^2.
\]  
(22)
Note that the rate \( \Gamma_{j,n} \) was also considered in Ref [1]. However in [1] the force \( F_j \) was ignored and the plane wave approximation \( \chi_{j,n}^{(+)}(r) \propto e^{iK_jr} \) was used for the finite wave function. This approximation is too rough: it does not take into account the remarkable change of the lower APES for coordinates \( \xi - \xi_{0,j} \pm \sqrt{(n+1/2)/\Omega_j} \) of the initial state \( \chi_{j,n}^{(+)}(\xi) \) essentially contributing to the integral in Eq. (22) . In contrast, our equation (22) takes this change into account: here \( \chi_{j,n}^{(-)} \) is given by the Airy function, which essentially differs from a simple plane wave. One more remark that should be made about calculations of the rate of transitions in Ref. [1] is the use of a simple adiabatic approximation that does not allow the author of Ref. [1] to separate the radial and angular variables. This significantly complicates numerical calculations of the rate.

Here we are interested in the effects of centrifugal forces on non-adiabaticity-induced decay \( \Gamma_{j,n} \) of resonance states. To this end we consider the rates given by Eq. (22) in case of large \( j \) corresponding to the second case. In this case
\[
\xi_{0,j} \approx (2j^2)^{1/3}, \quad x_{j,n} \approx (2j^2)^{1/3} + \sqrt{3} (4j)^{-1/3} (n+1/2),
\]
\[
\Omega_j \approx \sqrt{3} (4j)^{-1/3}, \quad F_j \approx 1, \quad K_j \approx (3/2)(4j)^{-2/3} \left( d/d\xi_j' + \xi_{0,j}' \left( \xi_j' d/d\xi_j' - 2 \right) \right),
\]
where \( \xi_j' = \xi_j - \xi_{0,j} \). We also take into account the relations
\[
d\chi_{j,n}^{(+)}/d\xi = \sqrt{\Omega_j/2} \left( \sqrt{n} \chi_{j,n-1}^{(+)} - \sqrt{n+1} \chi_{j,n+1}^{(+)} \right),
\]
\[
\xi' d\chi_{j,n}^{(+)} / d\xi' = 2^{-1} \left( \sqrt{n(n-1)} \chi_{j,n-2}^{(+)} - \chi_{j,n}^{(+)} - \sqrt{(n+1)(n+2)} \chi_{j,n+2}^{(+)} \right).
\]

This gives

\[
\Gamma_{j,n} \approx \frac{3^{9/4} D^{1/3} \omega}{\sqrt{\pi} 2^{n-2} n^{3/2}} |W_{j,n}|^2,
\]

where

\[
W_{j,n} = -\int dx e^{-x^2/2} Ai\left(x/\Omega_j^{(1)} + x_{j,n}\right) [n H_{n-2}(x) - H_{n+1}(x) + \sqrt{2/\Omega_j} \xi_{50j}^{-1} (n(n-1)H_{n-2}(x) - 5H_n(x)/2 - H_{n+2}(x)/4)].
\]

The results of numerical calculations of the normalized dimensionless rate \( \gamma_{j,n} = \log_{10} \left( \Gamma_{j,n}/\omega D^{1/3} \right) \) are given in Table 1.

| \( n \) | \( j \) | 3/2 | 5/2 | 7/2 | 9/2 | 11/2 | 13/2 | 15/2 |
|-------|-------|-----|-----|-----|-----|-------|-------|-------|
|   0   | 0.28  | 2.20 | 3.47 | 3.14 | 3.39 | 3.76  | 4.19  |
|   1   | 0.41  | 1.84 | 4.33 | 3.54 | 3.51 | 3.74  | 4.08  |
|   2   | 0.80  | 1.93 | 3.46 | 4.29 | 3.83 | 3.93  | 4.17  |
|   3   | 1.35  | 2.19 | 3.35 | 6.48 | 4.31 | 4.23  | 4.39  |
|   4   | 2.05  | 2.58 | 3.47 | 5.09 | 4.99 | 4.64  | 4.69  |
|   5   | 2.90  | 3.08 | 3.73 | 4.82 | 6.15 | 5.17  | 5.08  |

From this table one can see that the decay rates for large \( j \) and \( n \) are small, as is expected from general considerations. However for moderate \( j = 3/2 \) they are comparable with \( \omega \). E.g. for \( D = 400 \) one gets from Table 1 \( \Gamma_{3/2,0} = 3.9 \omega \), \( \Gamma_{3/2,1} = 2.9 \omega \), \( \Gamma_{3/2,2} = 1.2 \omega \). Note the decrease of \( \Gamma_{j,n} \) with increasing \( j \). This narrowing is the result of the shift of the main amplitude of the resonance wavefunction from the point of conical intersection that reduces the non-adiabaticity. This decrease in the decay rate of the resonant levels with increasing rotational angular momentum is a phenomenon that may be important for photochemical processes in molecular systems and in solids.

It should be noted that the harmonic approximation used here for the description of the resonance states works satisfactorily only for relatively small \( |j| \) and \( n \). For large \( |j| \) and \( n \) the high-energy part of the potential of the upper sheet of the APES is important, which is essentially asymmetric and strongly deviates from simple parabola. Besides, the linear approximation used for description of the dependence of the lower potential sheet on radial coordinate is also rather rough. Therefore the presented values of \( \gamma_{j,n} \) should be considered only as estimates of these quantities, becoming less correct for large values of \( |j| \) and \( n \).

Eq. (23) for \( \Gamma_{j,n} \) does not take into account the decay due to vibronic interactions with phonons of \( e \)-representation caused by emission of phonons to the bulk. The rate of this phonon emission was studied in detail in Refs. [7-9] and was found to be commonly much smaller than \( \omega \). Both relaxation processes mentioned above - the non-adiabaticity induced and the phonon-induced relaxation of the resonant states - were studied in [10] for a pseudo-Jahn-Teller system.
6. Optical spectra

From the equation for $\Gamma_{j,n}$ derived above one can conclude, that if the energy $\varepsilon_{j,n}$ of the rotational and radial motion is large then non-adiabaticity only weakly affects the resonance states in the conical intersection; i.e. these states are almost stationary. Besides, due to the centrifugal forces, the states above the conical intersection with small energy and large rotational momentum $j$ are absent. The last effect is called here the centrifugal gap.

These results are in good agreement with our calculations of the optical spectra of $A_1 \rightarrow E$ electronic transitions. In these calculations it was assumed that only the lowest level $|l\rangle, |0\rangle$ is occupied initially, and the transitions to the states $|\Psi_k^{(j)}\rangle$ with $j = l \pm 1/2$ were considered. In this case the spectra are given by the equation

$$F^{(j)}(E) = \sum_n C_{2n,k}^{(j)} \delta\left(E - E_k^{(j)} - j + 1/2\right)$$

with $j = l \pm 1/2$. Spectra with $j = l - 1/2$ have an analogous structure. The results of calculations for $D = 10$ and $D = 400$ and $j = 1/2, 3/2, 5/2, 9/2$ are presented in Figs 3 and 4.

![Fig. 3. Spectra of $A_1 \rightarrow E$ electronic transition from the lowest vibrational state with $l = j - 1/2$ for $j = 1/2$ (top left), $j = 3/2$ (top right), $j = 5/2$ (lower left), $j = 9/2$ (lower right); $D = 10$. Peaks for $E > 0$ correspond to Slonczewski resonances. The energy of the lowest resonance increases with $j$.](image-url)
Fig. 4. The same as in Fig. 3, but for $D = 400$. Comparison of the spectra in Figs. 3 and 4 shows an increase of the gap at the center of the spectrum with increasing $j$ and $D$, which indicates the disappearance of lower resonances.

In these spectra, in the high-frequency regions one can see strong oscillations of line intensities, so that the lines are assembled in groups of lines. The appearance of these groups of lines is due to the Slonczewski resonances. Attention is drawn to the middle part of the spectra, where there are no lines. This energy region corresponds to optical transitions to the lower part of the upper branch of the conical intersection. It is clearly seen that this "empty" region of the spectrum increases with increasing $j$. This means that the width of the energy region in the lower part of the conical intersection, where there are no resonances, increases with $j$. This is expected: the greater $j$, the stronger are centrifugal forces causing the centrifugal gap in the spectrum. Besides, one can see that, indeed, the larger is $j$ and $n$ the smaller is the width of the spectrum of the group; for very large $j$ and $n$ the satellite lines disappear showing that the corresponding states are almost stationary. In the figures, it is also seen that the energy region in which there are no resonances increases with increasing $D$. This increase is a consequence of the dependence of the vibronic Hamiltonian on $\sqrt{D}$, which represents an increased steepness of the upper cone.

Note finally that the presented spectra confirm, at least qualitatively, the calculations presented here for the rate of non-adiabatic decay of resonant states. To verify this, one should take into account that the half-width of the group of lines corresponding to a given resonance state equals $2\Gamma_{j,n}$. E.g. for $D = 400$ one gets $2\Gamma_{3/2,0} = 7.8\omega$, $2\Gamma_{3/2,1} = 5.8\omega$, $2\Gamma_{3/2,2} = 2.4\omega$. These values really agree with the half-widths of the envelopes of the first three groups of lines in the upper right-hand spectrum, shown in Fig. 4.

7. Concluding remarks
In present communication, we have studied quantum states in conical intersections of adiabatic potentials in a prototypical Jahn-Teller system, known as Slonczewski resonances. We have found that rotation of the Jahn-Teller deformation (pseudorotation) plays an important role for these resonances. We derived an analytical equation for the decay rates $\Gamma$ of these states caused by the non-adiabaticity and performed numerical calculations of the rates for different values of momentum of the rotation $j$ and radial quantum numbers $n$. We have found that the rotation of the Jahn-Teller deformation causes the appearance of gaps in the energy spectrum of the resonance states and a decrease of their non-adiabatic decay rate. As a result, the states with a large rotational quantum number $j$ acquire a long lifetime and became almost stationary. This stabilization of the resonance states for large $j$ is the result of a shift of their dominant motion away from the point of conical intersection, caused by the centrifugal forces and resulting in the decrease of the effects of non-adiabaticity. The decrease in the decay rate of the resonant levels for fast rotation may be important for photochemical processes in molecular systems and in solids.

We also calculated the optical spectra of the electronic transition $A_1 \rightarrow E$ with different values of the rotational angular momentum $j$. The resonance states are clearly manifested in these high-energy parts of these spectra as series of groups of lines. E.g. in these spectra one can clearly see the centrifugal gaps and the decrease of the rates $\Gamma_{j,n}$ of the non-adiabaticity-induced decay of the Slonczewski resonance states with increasing $|j|$ and $n$.

Finally, we recall that the present consideration focus on the linear $E \otimes e$ JT-problem, where the APES depend only on the radial coordinate and not on the pseudorotational angle $\varphi$. When including higher-order JT couplings this symmetry and the quantum number $j$ is lost and the optical spectra become much more irregular and complex. It may be a challenge to find other system parameters that play a similar role as the angular momentum in these more general situations, or at least establish scenarios how the present findings are modified for systems with weak breaking of the pseudorotational symmetry. Another useful extension may be that to multimode JT systems where a collective pseudorotational motion continues to exist. Here, even the existence of the Slonczewski resonances appears to be hardly addressed in the literature.

8. Acknowledgement
This work was supported by institutional research funding (IUT2-27) of the Estonian Ministry of Education and Research.

References
This work was supported by institutional research funding (IUT2-27) of the Estonian Ministry of Education and Research.
Bakalaureusetöö, Tartu (2009); (K. Pae, Electronic transitions in symmetrical systems with strong vibronic interaction, Bachelor thesis, Tartu, 2009).

[12] H.C. Longuet-Higgins, U. Öpik, M.H. Pryce, and R.A. Sack, Proc. R. Soc. London, Ser. A 244, 1 (1958).

[13] Y. Toyozawa, Optical Processes in Solids, Cambridge University Press, (2003).

[14] I.B. Bersuker, The Jahn–Teller Effect, Cambridge University Press, Cambridge (2006)

[15] K. Pae and V. Hizhnyakov, J.Chem. Phys. 145, 064108 (2016)

[16] L.D. Landau and E.M. Lifshits, Quantum Mechanics: Non-Relativistic Theory, § 24 Motion in a homogeneous field, Pregamon Press (1977).

[17] V. Hizhnyakov, H. Kaasik, T. Vaikjärv, Proc. JTS (2016).