large stationary magnetic fields, in the case $\varepsilon/m = 10^3$, we have the parameter $\chi \sim 10^{-5}$, whereas in modern lasers it appears that fields can be obtained with values $\xi = 0.1$ at $\omega \sim 10^{15}$ sec^{-1}. For the values given above, a contribution to the anomalous magnetic moment of the electron, due to the electromagnetic wave, can exceed the contribution from the constant magnetic field by two orders of magnitude. When account is taken of the contribution to the anomalous moment of the vacuum corrections in the next higher approximations in α ($\sim \alpha^2, \alpha^3$), it turns out that the corrections obtained here generally speaking make a smaller contribution than the term $\sim \alpha^2$, but a larger one than the term $\sim \alpha^3$.[19]

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Quasi-classical dynamics of symmetric molecules

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We study the vibronic problem in the simplest Jahn–Teller and Renner–Teller systems in the quasi-classical energy and momentum range. The method developed in this paper leads to a transcendental equation for the levels, which includes the action in the adiabatic terms, the interference phase, and the probability for non-adiabatic transitions. We discuss the consequences and possible generalizations of the theory.

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The basic features of the nuclear motion in symmetric molecules are caused by the existence of those surfaces in the nuclear coordinate configuration space on which the molecular electronic terms are degenerate. The adiabatic approximation is violated near the corresponding symmetric configurations and the motion of the nuclei on any one of the degenerate potential surfaces becomes coupled with the motion on the others.

These features of the nuclear dynamics manifest themselves strongly in the electronic-vibrational spectra of Jahn-Teller and Renner-Teller molecules. Optical transitions connecting electronic terms in the regions of adiabatic nuclear motion are collected in relatively wide bands with a simple Franck-Condon structure, while anamolous spectra arise for transitions between terms in symmetric nuclear configurations. The data from spectral studies at those frequencies, which give information about the dynamical coupling of electronic states, cannot be understood without a detailed study of the dynamics of the nuclear motion in the appropriate regions of space. Meanwhile all calculations of electronic-vibrational wavefunctions and energy levels performed for symmetric molecules up to the present[1–4] refer to low-lying excitations corresponding to initial values of the series of quantum numbers m and n (see Figs. 1 and 2 below). In those states the nuclear motion of real molecules is localized close to stable molecular configurations which are far from being completely symmetric. Completely symmetric configurations are reached only in states with large quantum numbers when the motion of the nuclei along connected potential surfaces is complicated.

Notwithstanding the complexity of such a motion the conditions $m \gg 1$ and $n \gg 1$ give us the possibility of ap-

plying a quasi-classical approximation and to overcome the basic difficulty in the study of nuclear dynamics in the region where terms get close to one another—a significant interaction of the electronic states.

1. SEMI-CLASSICAL APPROXIMATION FOR JAHN-TELLER MOLECULES

The main features of the dynamics of the nuclear motion in Jahn-Teller molecules appear in the simplest $E-e$ model[1] which corresponds to the following Schrödinger equation for the nuclear amplitudes ($\hbar = M = 1$):

$$\begin{pmatrix} T(\rho,\varphi)+U_1(\rho,\varphi)-E, & \frac{1}{2\rho^2}\frac{\partial}{\partial\varphi} \\ -\frac{1}{2\rho^2}\frac{\partial}{\partial\varphi}, & T(\rho,\varphi)+U_2(\rho,\varphi)-E \end{pmatrix}\Psi=0. \qquad (1)$$

Here T is the kinetic energy operator and U_1 and U_2 are the adiabatic electron potentials. Neglecting the angular dependence of U_1 and U_2 we can split off the angular part of Ψ.

After rotating the vector (Ψ_1, Ψ_2) through $\pi/4$ we are led to the following set of equations for the radial nuclear amplitudes with half-odd-integral angular momentum:

$$\begin{pmatrix} -\frac{1}{2}\frac{d^2}{d\rho^2}+\frac{m^2}{2\rho^2}+U_1(\rho)-E, & \frac{m}{2\rho^2} \\ \frac{m}{2\rho^2}, & -\frac{1}{2}\frac{d^2}{d\rho^2}+\frac{m^2}{2\rho^2}+U_2(\rho)-E \end{pmatrix}\Phi=0. \qquad (2)$$

The most popular model of adiabatic potentials

$$U_{1,2}={}^1/_2\omega^2\rho^2\pm F\rho \qquad (3)$$

corresponds to the conic section, typical of two-dimensional problems. The set (2) must be solved with the boundary conditions $\Phi_{1,2}\to 0$ as $\rho\to 0, \infty$. The principal interest then is the search for the energy levels characterizing the position of the spectral lines.

We introduce a dimensionless variable and dimensionless parameters

$$x=\frac{(2E)^{1/2}}{m}\rho, \quad \delta=\frac{Fm}{2^{1/2}E^{3/2}}, \quad \Omega=\omega\frac{m}{2^{1/2}E} \qquad (4)$$

and we shall look for the solution of the basic set (2) in the quasi-classical form:

$$\Phi_1=\frac{a_{1+}}{p_1^{1/2}}\exp\left(i\int_{x_1^0}^{x}p_1\,dx\right)+\frac{a_{1-}}{p_1^{1/2}}\exp\left(-i\int_{x_1^0}^{x}p_1\,dx\right), \qquad (5)$$

$$\Phi_2=\frac{a_{2+}}{p_2^{1/2}}\exp\left(i\int_{x_2^0}^{x}p_2\,dx\right)+\frac{a_{2-}}{p_2^{1/2}}\exp\left(-i\int_{x_2^0}^{x}p_2\,dx\right),$$

$$p_{1,2}=m\left(1-\frac{1}{x^2}-\frac{\Omega^2}{2}x^2\pm\delta x\right)^{1/2}. \qquad (6)$$

Here $x_{1,2}^0$ are the external turning points (which are close to zero) on the adiabatic terms, while the coefficients satisfy the following set of first-order equations:

$$\frac{d\mathbf{a}}{dx}=\begin{pmatrix} 0 & -\frac{p_1'}{2p_1}e^{-2iS_1}, & \frac{iv}{2(p_1p_2)^{1/2}}e^{-i(S_1-S_2)}, & \frac{iv}{2(p_1p_2)^{1/2}}e^{-i(S_1+S_2)} \\ -\frac{p_1'}{2p_1}e^{2iS_1}, & 0 & \frac{-iv}{2(p_1p_2)^{1/2}}e^{i(S_1+S_2)}, & \frac{-iv}{2(p_1p_2)^{1/2}}e^{i(S_1-S_2)} \\ \frac{iv}{2(p_1p_2)^{1/2}}e^{i(S_1-S_2)}, & \frac{iv}{2(p_1p_2)^{1/2}}e^{-i(S_1+S_2)}, & 0 & -\frac{p_2'}{2p_2}e^{-2iS_2} \\ \frac{-iv}{2(p_1p_2)^{1/2}}e^{i(S_1+S_2)}, & \frac{-iv}{2(p_1p_2)^{1/2}}e^{-i(S_1-S_2)}, & -\frac{p_2'}{2p_2}e^{2iS_2}, & 0 \end{pmatrix}\mathbf{a}, \qquad (7)$$

in which

$$S_{1,2}=\int_{x_{1,2}^0}^{x}p_{1,2}\,dx, \quad v=\frac{m}{x^2}, \quad \mathbf{a}=\begin{pmatrix} a_{1+} \\ a_{1-} \\ a_{2+} \\ a_{2-} \end{pmatrix}. \qquad (8)$$

We can simplify Eq. (7) if we bear in mind that when $S_{1,2}\gg 1$ the matrix elements connecting the incident and the reflected wave in one adiabatic channel can be omitted if we guarantee the correct boundary conditions at the turning points $x_{1,2}^0$. Moreover, if $S_{1,2}\gg|S_1-S_2|$, and this condition is satisfied when $\delta\ll 1$ everywhere except in the immediate vicinity of $x_{1,2}^0$ the set (2) can be split into two:

$$\frac{da_{1\pm}}{dx}=\pm\frac{iv}{2(p_1p_2)^{1/2}}e^{\mp i(S_1-S_2)}a_{2\pm},$$
$$\frac{da_{2\pm}}{dx}=\pm\frac{iv}{2(p_1p_2)^{1/2}}e^{\pm i(S_1-S_2)}a_{1\pm}, \qquad (9)$$

which are connected only through the requirement that the wavefunction is damped under the barrier ($x\to 0$):

$$a_{1+}(x_1^0)e^{-i\pi/4}=-a_{1-}(x_1^0)e^{i\pi/4},$$
$$a_{2+}(x_2^0)e^{-i\pi/4}=-a_{2-}(x_2^0)e^{i\pi/4}.$$

If we change to a new variable

$$t=\pm\int^{x}\left(1-\frac{1}{x^2}-\frac{\Omega^2}{2}x^2\right)^{-1/2}dx$$

(t is negative in the incident wave and positive in the reflected one) and bear in mind that

$$S_1-S_2=m\delta\int_0^t x(t)\,dt, \quad (p_1p_2)^{1/2}=m\left(1-\frac{1}{x^2}-\frac{\Omega^2}{2}x^2\right)^{1/2},$$

we find for amplitudes which are continuous at $t=0$

$$b_{1,2+}=a_{1,2+}e^{-i\pi/4}, \quad b_{1,2-}=a_{1,2-}e^{i\pi/4} \qquad (10)$$

the equations

$$\frac{db_1}{dt}=-\frac{i}{2x^2(t)}\exp\left(-im\delta\int_0^t x(t)\,dt\right)b_2,$$
$$\frac{db_2}{dt}=-\frac{i}{2x^2(t)}\exp\left(im\delta\int_0^t x(t)\,dt\right)b_1. \qquad (11)$$

In this semi-classical system the motion along a single trajectory is determined by the following equation:

$$x(t)=\frac{1}{2^{1/2}\Omega}(1-(1-4\Omega^2)^{1/2}+2(1-4\Omega^2)^{1/2}\sin^2\Omega t)^{1/2}. \qquad (12)$$

The requirement that the radial motion is quasi-classical ($n\gg 1$) and the condition that there exists a single

trajectory in both electronic states ($\delta \ll 1$) impose restrictions on the dimensionless frequency Ω. To find those we consider first of all the rough asymptotic behavior of the spectrum $E_{n,m}$ in weak and strong Jahn-Teller fields. It is of the form

$$\begin{aligned} &E_{n,m}=\omega(n+m+1), && F^{2/3}\ll\omega,\\ &E_{n,m}={}^1/_2(3\pi Fn)^{2/3}, && n\gg m,\quad F^{2/3}\gg\omega,\\ &E_{n,m}={}^3/_2(Fm)^{2/3}, && m\gg n,\quad F^{2/3}\gg\omega \end{aligned} \tag{13}$$

and they represent the levels of a two-dimensional oscillator and a conical well.[6] We get then for δ and Ω the following order-of-magnitude expressions:

$$\begin{aligned} &\delta=\frac{F}{\omega^{3/2}}\frac{m}{(m+n)^{1/2}}, && \Omega=\frac{m}{m+n}, && F^{2/3}\ll\omega,\\ &\delta=\frac{m}{n}, && \Omega=\frac{\omega}{F^{2/3}}\frac{m}{n^{1/2}}, && n\gg m,\quad F^{2/3}\gg\omega,\\ &\delta=1, && \Omega=\frac{\omega}{F^{2/3}}m^{1/2}, && m\gg n,\quad F^{2/3}\gg\omega. \end{aligned}$$

When $n \gg m$ the requirements $n \gg 1$ and $\delta \ll 1$ turn out to be satisfied for any value of the parameter $F^{2/3}/\omega$. Moreover, this condition leads to the restriction $\Omega \ll 1$ which allows us to reduce Eqs. (11) to the form

$$\begin{aligned} &\frac{dc_1}{dt}=\frac{1}{2(1+t^2)}\exp\left(-2i\mu\int_0^t(1+t^2)^{1/2}dt\right)c_2,\\ &\frac{dc_2}{dt}=\frac{-1}{2(1+t^2)}\exp\left(2i\mu\int_0^t(1+t^2)^{1/2}dt\right)c_1,\\ &c_1=b_1,\quad c_2=-ib_2,\quad \mu=m\delta\frac{1-(1-4\Omega^2)^{1/2}}{2\Omega^2(1-4\Omega^2)^{1/2}}. \end{aligned} \tag{14}$$

Physically, the condition $\Omega \ll 1$ means that the method used allows us to find those levels of Jahn-Teller molecules which correspond to an almost straight-line motion of the nuclei in the region where the terms approach one another. The set of Eqs. (14) can be solved in terms of parabolic cylinder functions for the amplitudes:

$$\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}=\begin{pmatrix}\cos g, & -\sin g\\ \sin g, & \cos g\end{pmatrix}\begin{pmatrix}c_1\exp\left(-i\mu\int_0^t(1+t^2)^{1/2}dt\right)\\ c_2\exp\left(i\mu\int_0^t(1+t^2)^{1/2}dt\right)\end{pmatrix}, \tag{15}$$

$$g=-\frac{1}{2}\operatorname{arctg}\frac{1}{t}.$$

The solution has the form

$$\begin{aligned} \psi_1&=-\frac{2A}{(1+i)\mu^{1/2}}D_{p+1}((1+i)z)+\frac{2B}{(1+i)\mu^{1/2}}D_{p+1}(-(1+i)z),\\ \psi_2&=AD_p((1+i)z)+BD_p(-(1+i)z),\\ z&=\mu^{1/2}t,\quad p=-1-i\mu/2, \end{aligned} \tag{16}$$

where A and B are arbitrary constants. Equations (15) and (16) lead to the following asymptotic behavior for the $c_{1,2}$ ($\varphi = \frac{1}{4}\mu(1-\ln\frac{1}{2}\mu)$):

$$\begin{aligned} c_1&=\frac{2e^{i\varphi}}{(1+i)\mu^{1/2}}(Be^{\pi\mu/4}-Ae^{-\pi\mu/4}),\\ c_2&=A(2\pi)^{1/2}e^{-i\varphi}\Gamma^{-1}(1+i\mu/2), && t\to-\infty;\\ c_1&=B(2\pi)^{1/2}e^{-i\varphi}\Gamma^{-1}(1+i\mu/2),\\ c_2&=\frac{2e^{i\varphi}}{(1+i)\mu^{1/2}}(Ae^{\pi\mu/4}-Be^{-\pi\mu/4}), && t\to+\infty, \end{aligned} \tag{17}$$

and, hence the formula for the coupling of the amplitudes of the quasi-classical waves (5) has the form

$$\begin{pmatrix}a_{1+}\\ a_{2+}\end{pmatrix}=\begin{pmatrix}-i(1-e^{-\pi\mu})^{1/2}e^{-i\Psi}, & -e^{-\pi\mu/2}\\ -e^{-\pi\mu/2}, & -i(1-e^{-\pi\mu})^{1/2}e^{i\Psi}\end{pmatrix}\begin{pmatrix}a_{1-}\\ a_{2-}\end{pmatrix} \tag{18}$$

$$\Psi=\frac{\mu}{2}-\frac{\mu}{2}\ln\frac{\mu}{2}-\frac{\pi}{4}+\arg\Gamma\left(1+\frac{i\mu}{2}\right).$$

To find now the energy levels of a molecule it is necessary to use the second boundary condition for Eq. (2). It specifies the exponential damping of Φ_1 and Φ_2 beyond the turning points x_1 and x_2. When we use a quasi-classical description this imposes a well known connection on the coefficients $a_{1,2+}$, $a_{1,2-}$ in the turning points:

$$a_{i+}=ae^{i(\pi/4-\Omega_i)},\quad a_{i-}=ae^{-i(\pi/4-\Omega_i)}, \tag{19}$$

where the Ω_i are the actions in the adiabatic terms. The condition that the sets (18), (19) are simultaneously soluble:

$$\cos(\Omega_1+\Omega_2)+(1-e^{-\pi\mu})^{1/2}\cos(\Omega_1-\Omega_2-\psi)=0 \tag{20}$$

is the required equation for the energy levels of a Jahn-Teller molecule in the quasi-classical sector $n \gg m$. The limiting forms of this equation correspond to the quasi-classical quantization in a combined well when there is a weak coupling of almost degenerate states ($\mu \to 0$, $\cos(\Omega_1+\Omega_2)=0$) and the quantization in isolated wells in the strong coupling region ($\mu \to \infty$, $\cos\Omega_1 \cos\Omega_2 = 0$).

A detailed picture of the levels can be obtained through a numerical solution of Eq. (20). A comparison of the results of the corresponding calculations with all the data from[1-4] (a numerical solution of the set of coupled Eqs. (2) for m between $\frac{1}{2}$ and $\frac{9}{2}$, $n \leq 20$) shows good agreement (accuracy of 0.01 in units of ω) even in the quantum region $m, n \sim 1$. When $n \sim 10$ the accuracy is 0.001. Part of the comparison of the data is given in Fig. 1.

In the quasi-classical region $m, n > 10$ a solution of the set (2) through an expansion in a limited base for weak[1-4] or strong[7,8] coupling of the states would lead to considerable computational difficulties as the coupling parameter μ changes for such values of m and n within

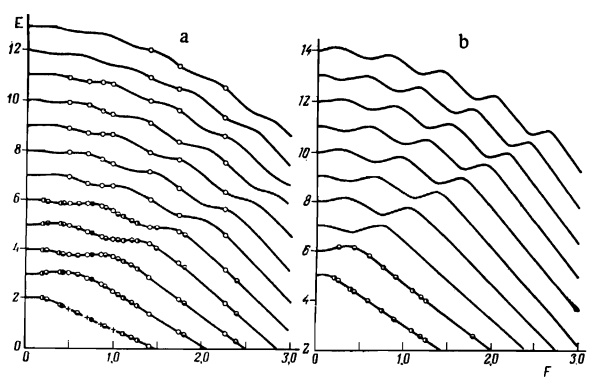

FIG. 1. Energy levels of a Jahn-Teller molecule for $m = \frac{3}{2}$ (a) and for $m = \frac{9}{2}$ (b) found from Eq. (20) and found in [1](○), [2](◒), [3](●), and [4](+). E and F in units ω and $\omega^{3/2}$.

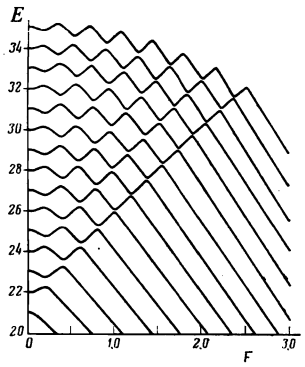

FIG. 2. Energy levels of a Jahn-Teller molecule for $m = \frac{41}{2}$ found by using Eq. (20). E and F in units ω and $\omega^{3/2}$.

very wide limits while F changes in a small range. An example of the calculation of the levels in that region, using Eq. (20) is shown in Fig. 2.

One can apply Eq. (20) to calculate the electron-vibrational levels of the NH_3 molecule in the electronic $\tilde{B}'E''$ state of symmetry D_{3h}, interacting with a ν_3 e'-type vibration, for

$$CH_3(\tilde{C}^2E''(D_{3h})+\nu_3(e')),\quad CH_3I(\tilde{B}'E(c_{3v})+\nu_6(e)),$$
$$CF_3I(\tilde{C}'E(c_{3v})+\nu_6(e)),\quad VCl_4(\tilde{X}^2E(T_d)+\nu_2(e)),$$

and for a number of other simple molecules and radicals. The best results are in that case possible for relatively high levels with $n>10$, identified in spectral experiments.[9]

2. SEMI-CLASSICAL APPROXIMATION FOR RENNER-TELLER MOLECULES

The simplest Renner-Teller molecule is described by a set of coupled equations for the nuclear amplitudes which is similar to the set (2) with integral values of the angular momentum and adiabatic potentials:

$$U_{1,2}=U^0(\rho)\pm\varepsilon^2\rho^2/2, \tag{21}$$

where $U^0(\rho)$ takes in the general case the anharmonicity of the oscillations into account while ε^2 is Renner's parameter. The semi-classical amplitude method of the preceding section can immediately be generalized to this case. For a model with $U^0=\frac{1}{2}\omega^2\rho^2$ the corresponding semi-classical equations have for $n\gg m$ the form

$$\frac{dc_1}{dt}=\frac{1}{1+t^2}\exp\left(-2i\gamma\int_0^t(1+t^2)dt\right)c_2,$$
$$\frac{dc_2}{dt}=\frac{-1}{1+t^2}\exp\left(2i\gamma\int_0^t(1+t^2)dt\right)c_1, \tag{22}$$

where

$$\gamma=\frac{m\lambda}{2}\frac{(1-(1-4\Omega^2)^{1/2})^{3/2}}{2^{3/2}\Omega^3(1-4\Omega^2)^{1/4}}$$
$$\lambda=\varepsilon^2m^2/2E^2,\quad \Omega=\omega m/2^{1/2}E.$$

This set has four singularities—the zeroes of the adiabatic splitting—and can be studied rather completely for small and large γ.

When $\gamma\ll 1$ one can use perturbation theory for the functions

$$\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}=\begin{pmatrix}\cos g, & -\sin g\\ \sin g, & \cos g\end{pmatrix}\begin{pmatrix}c_1\exp\left(-i\gamma\int_0^t(1+t^2)dt\right)\\ c_2\exp\left(i\gamma\int_0^t(1+t^2)dt\right)\end{pmatrix},$$

which satisfy the set of equations

$$d\psi_1/dt-i\gamma(t^2-1)\psi_1+2i\gamma t\psi_2=0,$$
$$d\psi_2/dt+i\gamma(t^2-1)\psi_2+2i\gamma t\psi_1=0. \tag{23}$$

To first order in the off-diagonal and to second order in the diagonal elements of the S-matrix this leads to the following coupling of the amplitudes of the quasi-classical waves[6]:

$$\begin{pmatrix}a_{1+}\\ a_{2+}\end{pmatrix}=\begin{pmatrix}i(1-p_0^2)^{1/2}e^{-i\psi_0}, & p_0\\ p_0, & i(1-p_0^2)^{1/2}e^{i\psi_0}\end{pmatrix}\begin{pmatrix}a_{1-}\\ a_{2-}\end{pmatrix}, \tag{24}$$

where

$$p_0=\frac{\pi}{\Gamma(^4/_3)}\left(\frac{2}{3}\right)^{4/3}\gamma^{1/2},\quad \psi_0=\frac{p_0^2}{2\cdot 3^{1/2}}. \tag{25}$$

For large values of the basic Renner parameter $\gamma\gg 1$ the splitting off of the fastest oscillations in Eqs. (22) through the substitution

$$\Sigma=c_1(1+t^2)^{1/2}\exp\left(i\gamma(^1/_3t^3+t)\right),$$
$$\Delta=c_2(1+t^2)^{1/2}\exp\left(-i\gamma(^1/_3t^3+t)\right) \tag{26}$$

leads to the following second-order equation for the function Σ:

$$d^2\Sigma/dt^2+(\gamma^2(1+t^2)^2-4i\gamma t)\Sigma=0 \tag{27}$$

with a paired distribution of the zeroes of the adiabatic splitting:

$$t_{1,2+}=i(1\pm\gamma^{-1/2}),\quad t_{1,2-}=-i(1\pm\gamma^{-1/2}). \tag{28}$$

This makes it possible to connect the asymptotic behavior $\Sigma(-\infty)$ with the asymptotic behavior $\Sigma(+\infty)$ as follows. It is necessary to analytically continue the quasi-classical representation of Σ from $-\infty$ along the adjoint Stokes line entering the region $t_{1,2+}$ (or $t_{1,2-}$) and to join it on that line with the exact solution of (27) in that region. After that we must change in the exact solution to the adjoint Stokes line which emerges from the region $t_{1,2+}$ (or $t_{1,2-}$), join this solution onto the quasi-classical representation of Σ, and continue the latter to $t\to+\infty$. As a result we get the coupling formula:

$$\begin{pmatrix}a_{1+}\\ a_{2+}\end{pmatrix}=\begin{pmatrix}i(1-p^2)^{1/2}e^{-i\psi}, & p\\ p, & i(1-p^2)^{1/2}e^{i\psi}\end{pmatrix}\begin{pmatrix}a_{1-}\\ a_{2-}\end{pmatrix}. \tag{29}$$

Here

$$p=2^{1/2}e^{-4/3\gamma}.$$

The small phase ψ turns out to be undefined but it will become clear in what follows that this does not prevent us from establishing the main features in the behavior of the energy levels.

If we now use (24), (29), and the boundary conditions in the external turning points which are similar to (19) we get finally the following equations for the levels of Renner-Teller molecules in the quasi-classical sector $n \gg m$:

$$\begin{aligned} &\cos(\Omega_1+\Omega_2)-(1-p_0^2)^{1/4}\cos(\Omega_1-\Omega_2-\psi_0)=0, \quad \gamma\ll 1,\\ &\cos(\Omega_1+\Omega_2)+(1-p^2)^{1/4}\cos(\Omega_1-\Omega_2-\psi)=0, \quad \gamma\gg 1. \end{aligned} \tag{30}$$

One can simplify these equations bearing in mind that p_0 and p are small and introducing into our considerations the complete actions taking into account the additional phases in the transition region

$$\tilde{\Omega}_{1,2}=\Omega_{1,2}\pm\psi/2.$$

In that case

$$\begin{aligned} &\sin\tilde{\Omega}_1\sin\tilde{\Omega}_2=\pm 1/4 p_0^2, \quad \gamma\ll 1,\\ &\cos\tilde{\Omega}_1\cos\tilde{\Omega}_2=\pm 1/4 p^2, \quad \gamma\gg 1. \end{aligned} \tag{31}$$

When the states are weakly coupled ($\gamma \to 0$) the quantitation conditions lead to narrow doublets $E = \omega(m+n+1)$ with a splitting of the order of ωp_0.

One can use Eqs. (31) and their generalizations to find the vibronic levels of many Renner molecules and radicals. Examples of this are $C_3(\tilde{A}'\Pi_u)$, $CNC(\tilde{X}^2\Pi_g)$, $BO_2(\tilde{A}^2\Pi_u)$, $NH_2(\tilde{X}^2B_1, \tilde{A}^2A_1)$, $BH_2(\tilde{X}^2A_1, \tilde{A}^2B_1)$. For some of them the number of identified levels reaches 50.[9]

3. QUASI-CLASSICAL APPROXIMATION FOR SYMMETRY MOLECULES

When $m \gg n$ and $n \sim m \gg 1$ it is impossible to use the semi-classical approximation of the preceding sections. In those cases the trajectories in the adiabatic electronic states are circular or elliptic and they differ appreciably from one another. The quasi-classical approximation remains, however, applicable. In particular, for the set (2) with $U^0_{1,2} = \pm F_\rho$ which will be used below one can find the quasi-classical asymptotic behavior of Φ_1 and Φ_2 as follows.

Using the integral transformation ($\rho \equiv r$)

$$\begin{aligned} \Phi_1&=\int_0^\infty dp\, p^{1/4}(\Sigma(p)K_1(pr)+\Delta(p)K_2(pr)),\\ \Phi_2&=\int_0^\infty dp\, p^{1/4}(\Sigma(p)K_2(pr)+\Delta(p)K_1(pr)), \end{aligned} \tag{32}$$

where the combinations of Bessel functions $K_{1,2}(x) = J_{m+1/2}(x) \mp iJ_{m-1/2}(x)$ satisfy the equations

$$\begin{aligned} &\left(\frac{d}{dx}-i\right)(x^{1/4}K_1)+\frac{m}{x}(x^{1/4}K_2)=0,\\ &\left(\frac{d}{dx}+i\right)(x^{1/4}K_2)+\frac{m}{x}(x^{1/4}K_1)=0, \end{aligned} \tag{33}$$

the set (2) with $U^0_{1,2}$ can be reduced to the following one:

$$\begin{aligned} &\frac{d\Sigma}{dp}-i\varepsilon(p)\Sigma+\frac{m}{p}\Delta=0, \quad \frac{d\Delta}{dp}+i\varepsilon(p)\Delta+\frac{m}{p}\Sigma=0,\\ &\varepsilon(p)=p^2/2-E. \end{aligned} \tag{34}$$

In the quasi-classical region one can introduce the following representation for the solutions (33) and (34):

$$\begin{pmatrix}\Sigma\\ \Delta\end{pmatrix}=\begin{pmatrix}\cos g, & \sin g\\ -\sin g, & \cos g\end{pmatrix}\begin{pmatrix}c_1\exp\left(i\xi\int^p\omega(p)\,dp\right)\\ c_2\exp\left(-i\xi\int^p\omega(p)\,dp\right)\end{pmatrix},$$

where $\omega(p) = (\varepsilon^2 - m^2/p^2)^{1/2} > 0$ has the meaning of the adiabatic splitting,

$$\xi=\operatorname{sign}\varepsilon, \quad g=-1/2\operatorname{arctg}(im/p\varepsilon),$$

$$\begin{pmatrix}x^{1/4}K_1\\ x^{1/4}K_2\end{pmatrix}=\left(\frac{2}{\pi}\right)^{1/4}\begin{pmatrix}\cos g_1, \sin g_1\\ -\sin g_1, \cos g_1\end{pmatrix}\begin{pmatrix}\exp\left(i\int^x\left(1-\frac{m^2}{x^2}\right)^{1/4}dx-i\frac{\pi}{2}\right)\\ \exp\left(-i\int^x\left(1-\frac{m^2}{x^2}\right)^{1/4}dx+i\frac{\pi}{2}\right)\end{pmatrix},$$

$$g_1=-\frac{1}{2}\operatorname{arctg}\frac{im}{x}.$$

They enable us to integrate in (32) using the saddlepoint method around the points $p^\pm = (2(E \pm r))^{1/2}$. The calculations lead to the following results:

$$\begin{aligned} \Phi_1(r)&=\frac{2i}{(2(E-r)-m^2/r^2)^{1/4}}(-c_1^-e^{iS_1-i\pi/4}+c_2^-e^{iS_1+i\pi/4}),\\ \Phi_2(r)&=\frac{2i}{(2(E+r)-m^2/r^2)^{1/4}}[c_1^+e^{-iS_2+i\pi/4}-c_2^+e^{iS_2-i\pi/4}), \end{aligned} \tag{35}$$

$$S_1=\int_{r_1^0}^r\left(2(E-r)-\frac{m^2}{r^2}\right)^{1/2}dr, \quad S_2=\int_{r_2^0}^r\left(2(E+r)-\frac{m^2}{r^2}\right)^{1/2}dr,$$

where we have used for obtaining them the exact equations

$$\int_{p_1}^{p^\pm}\omega(p)\,dp-\int_m^{x^\mp}\left(1-\frac{m^2}{x^2}\right)^{1/2}dx=-\int_{r_{1,2}^0}^r\left(2(E\mp r)-\frac{m^2}{r^2}\right)^{1/2}dr$$

$$(x^\mp = rp^\mp).$$

In Eqs. (35) $c^\mp_{1,2}$ are the quasi-classical amplitudes to the right and to the left of the hump of $\omega(p)$ in the p-representation and, thus, the solution of the problem (34) determines the asymptotic behavior of the functions Φ_1 and Φ_2 in the r-representation.

The conditions for the applicability of the quasi-classical formulae for Σ, Δ, and $K_{1,2}$ determine the region where these asymptotic expressions are applicable in the form $r_0 \ll r \ll E$. For very low energies in the lower well (35) is applicable up to its boundaries; as $E \to -\infty$, $r_0 \to E^{1/4}$. Thus, the non-adiabatic transitions turn out to be localized in a narrow region around the interior turning points and this makes it possible to consider the Jahn-Teller problem (2) using asymptotic expressions of the following form:

$$\begin{aligned} \Phi_1&=\frac{1}{(2(E-U_1))^{1/4}}(-c_1^-e^{i\tilde{S}_1}+c_2^-e^{-i\tilde{S}_1}),\\ \Phi_2&=\frac{1}{(2(E-U_2))^{1/4}}(c_1^+e^{-i\tilde{S}_2}-c_2^-e^{i\tilde{S}_2}),\\ \tilde{S}_{1,2}&=\int^r(2(E-U_{1,2}))^{1/2}dr-\pi/4. \end{aligned} \tag{36}$$

If the motion is quasi-classical in the upper and the lower wells the solution of the set (34) gives the following coupling formulae:

$$\begin{pmatrix} c_1^+ \\ c_2^+ \end{pmatrix} = e^D \begin{pmatrix} 1, & -(1-e^{-2D})^{1/2} e^{i\varphi} \\ -(1-e^{-2D})^{1/2} e^{-i\varphi}, & 1 \end{pmatrix} \begin{pmatrix} c_1^- \\ c_2^- \end{pmatrix}, \quad (37)$$

$$D = \left| \int_{p_1}^{p_2} \omega(p)\, dp \right|,$$

which are suitable for straight-line ($n \gg m$) and elliptic ($n \sim m \gg 1$) trajectories. In that case φ is the same as ψ for $n \gg m$ and is a small, undetermined quantity when $n, m \gg 1$.

To find the energy levels it is now sufficient to guarantee the boundary conditions for $\Phi_{1,2}$ around the external turning points $r_{1,2}$ which are similar to (19). As a result one obtains a transcendental equation which for $n \gg m$ is the same as Eq. (20):

$$\operatorname{ctg} \Omega_1 \operatorname{ctg} \Omega_2 = \frac{1-(1-e^{-2D})^{1/2}}{1+(1-e^{-2D})^{1/2}}. \quad (38)$$

If the classical trajectories are elliptic, $D \gg 1$ and Eq. (38) simplifies to

$$\cos \Omega_1 \cos \Omega_2 = \pm 1/4 e^{-2D}.$$

A special case is that of the circular motion, $m \gg n$, when the quasi-classical representation of $\Phi_1(r)$ may turn out to be inapplicable as the radial nuclear motion in the upper electronic state may in that case correspond to a purely quantal value $n \sim 1$. In that case, however, the quasi-classical picture is applicable for the motion in the lower state and Eqs. (34) lead to the following coupling:

$$c_1^+ = e^{i\chi} c_2^+,$$

$$\chi = -2\arctg\,(2^{-1/2}\pi^{-1/2}\Gamma(-\nu)\exp(-2D+\nu+1/2-(\nu+1/2)\ln(\nu+1/2))\cos\pi\nu),$$

$$\nu = -\frac{1}{2} + \frac{3^{1/2}}{2} m \frac{E-E_0}{E_0}, \quad E_0 = \frac{3}{2} m^{2/3}.$$

Taking into account the sole boundary condition for $\Phi_2(r)$ we get for the energy levels the following result:

$$\cos(\pi(\nu+1/2))\cos\Omega_2 = \pm 2^{-1/2}\pi^{-1/2} \frac{\exp(-2D-(\nu+1/2)+(\nu+1/2)\ln(\nu+1/2))}{\Gamma(1+\nu)}. \quad (39)$$

The necessary condition for the applicability of this equation, apart from $m \gg n$, $\Omega \ll 1$ corresponds to a rather strong Jahn-Teller effect.

The results obtained in this section for exponentially small splittings of the quasi-classical levels can be written in the form

$$\cos \Omega_1 \cos \Omega_2 = \pm W_{1,2}/4,$$

where $W_{1,2}$ is the probability for a non-adiabatic transition. This representation makes it possible to study Renner-Teller molecules in levels corresponding to elliptic trajectories by using Landau's method for finding the transition probability.[10] The role of the special momentum point $p_{1,2}$ is in that case performed by the origin so that

$$D = \int_0^{r_1} (2(U_1-E))^{1/2}\, dr - \int_0^{r_2} (2(U_2-E))^{1/2}\, dr.$$

In particular, for circular trajectories

$$D = m(\pi/8 - 1/4 \ln 2).$$

CONCLUSION

Of most interest in experimental studies of symmetric molecules is the determination of the electron-vibrational interaction constants F and ε. They are found as the result of a spectral determination of the position of the molecular energy levels. The set of levels studied must then be sufficiently large as one must usually determine not only F and ε but also the frequencies of the symmetric oscillations in the excited states. A study of a large number of levels can not be done correctly without knowing their interaction. In the quasi-classical energy region the appropriate results are given in the basic sections 1 to 3. In this sense the widest application must be for the asymptotic relations for small or exponentially small level splittings.

We note in conclusion that the method for determining the energy spectrum of symmetric molecules proposed here can be applied to a study of more complicated cases of a Jahn-Teller degeneracy.

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