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The intersection of vibronic levels

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Abstract

The basic one-dimensional vibronic problem has been solved exactly in an analytical form for degenerate configurations. The solution using the intermediate *p*-representation and the Heun functions expansion on the Gauss basis set has indicated the existence of dynamic symmetry. The direct solution in *x*-representation has specified an effective method for the calculation of vibronic problems. Conical intersection parameters have been obtained and analyzed for a few lower levels.

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1. Introduction

The intersection of levels stays among basic problems of quantum mechanics for a long time. This problem is a direct consequence of the dependence of the Schrödinger equation on the parameters and therefore it occurs in various fields of quantum physics. In particular, the amplitude of the external field can be considered as the parameter in the laser molecular dynamics, the amplitude of interaction is the parameter for the spin-boson problem, the nuclear coordinates are the parameters for electronic dynamics of molecular systems.

The intersections of molecular electronic potentials are the most studied. These intersections are subjected to the famous Wigner–Neuman theorem for the adiabatic potentials of the same symmetry [1] and form a multi-sheeted nuclear potential surface with seams at the degenerate configurations. The conventional approach to this problem is comprehensively represented in [2, 3].

The degeneracy of molecular levels is induced by the geometric symmetry of nuclear configuration (see, for example [4–7]) or by the dynamic symmetry owing to the characteristic separation of variables [8–11]. Many authors have studied the geometric degeneracy, but the dynamic degeneracy has been discussed much rarely and sometimes it is considered as 'accidental'. The most known examples of the dynamic symmetry have been found in exactly solvable quantum-mechanical models [8–12], but the exact analytical solutions to vibronic

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equations remain unknown even for the simplest models. The impressive Moffitt–Thorson 'nodal' intersection of vibronic levels [13] is, probably, the example of such a type. However, its analytical reconstruction given by Judd [14] is approximate only.

Undoubtedly, the geometry of intersections of vibronic levels satisfies the general principles of conical intersections [15], but the relevant analytical confirmations are still lacking since corresponding calculations must be based on exact results for the dynamics in degenerate configurations.

In this work, we present the exact solution for the simplest vibronic model in an analytical form. The paper is organized as follows: section 2 includes the mathematical formulation of the problem and its p-representation reducing to the Heun equation. This equation is solved in section 3 where the spectrum and the conditions for the existence of degenerate solutions are found. Section 4 deals with the coordinate representation and section 5 with the geometry of vibronic surfaces in the vicinity of lower intersections. Section 6 summarizes the results.

2. Formulation of the problem: the p-representation

The basic one-dimensional vibronic model is defined by the following Schrödinger system of equations (see, for example [16]):

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_1}{\mathrm{d}x^2} + \left(\frac{m\Omega^2x^2}{2} - F_1x\right)\psi_1 + V\psi_2 = E\psi_1, \\ -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_2}{\mathrm{d}x^2} + \left(\frac{m\Omega^2x^2}{2} - F_2x\right)\psi_2 + V\psi_1 = E\psi_2. \end{aligned} \tag{1}$$

Introduction of the new variable, functions and parameters

$$x = \left(\frac{\hbar}{m\Omega}\right)^{\frac{1}{2}}\zeta, \tag{2}$$

$$\psi = \mathrm{e}^{-\zeta^2/2}\chi, \tag{3}$$

$$a, b = (\Omega^3 m\hbar)^{-\frac{1}{2}}F_{1,2}, \qquad \nu = \frac{V}{\hbar\Omega}, \qquad \varepsilon = \frac{E}{\hbar\Omega} + \frac{1}{2} \tag{4}$$

leads to the equations

$$\begin{aligned} \frac{1}{2}\frac{\mathrm{d}^2\chi_1}{\mathrm{d}\zeta^2} - \zeta\frac{\mathrm{d}\chi_1}{\mathrm{d}\zeta} + (a\zeta + \varepsilon - 1)\,\chi_1 - \nu\chi_2 = 0, \\ \frac{1}{2}\frac{\mathrm{d}^2\chi_2}{\mathrm{d}\zeta^2} - \zeta\frac{\mathrm{d}\chi_2}{\mathrm{d}\zeta} + (b\zeta + \varepsilon - 1)\,\chi_2 - \nu\chi_1 = 0. \end{aligned} \tag{5}$$

We transfer equation (5) into the p-representation by using the contour Fourier transformation

$$\chi_{1,2}(\zeta) = \int_L \varphi_{1,2}(p)\,\mathrm{e}^{\mathrm{i}p\zeta}\,\mathrm{d}p, \tag{6}$$

where the complex plane contour L is subjected to the following increment conditions:

$$\varphi_{1,2}(p)\,\mathrm{e}^{\mathrm{i}p\zeta}|_L = 0, \qquad p\varphi_{1,2}(p)\,\mathrm{e}^{\mathrm{i}p\zeta}|_L = 0. \tag{7}$$

The amplitudes $\varphi_{1,2}(p)$ satisfy two coupled differential equations of first order

$$\begin{aligned} (p + \mathrm{i}a)\frac{\mathrm{d}\varphi_1}{\mathrm{d}p} - \left(\frac{p^2}{2} - \varepsilon\right)\varphi_1 - \nu\varphi_2 = 0, \\ (p + \mathrm{i}b)\frac{\mathrm{d}\varphi_2}{\mathrm{d}p} - \left(\frac{p^2}{2} - \varepsilon\right)\varphi_2 - \nu\varphi_1 = 0. \end{aligned} \tag{8}$$

We define two new functions ϕ_1 and ϕ_2 as follows:

$$\begin{aligned}\varphi_1 &= \phi_1 \exp\left(\int \frac{p^2/2-\varepsilon}{p+\mathrm{i}a}\,\mathrm{d}p\right),\\ \varphi_2 &= \phi_2 \exp\left(\int \frac{p^2/2-\varepsilon}{p+\mathrm{i}b}\,\mathrm{d}p\right),\end{aligned} \tag{9}$$

and obtain the second-order differential equation for the function ϕ_1:

$$(p+\mathrm{i}a)(p+\mathrm{i}b)\frac{\mathrm{d}^2\phi_1}{\mathrm{d}p^2}+\left[p+\mathrm{i}b+\mathrm{i}\left(\frac{p^2}{2}-\varepsilon\right)(b-a)\right]\frac{\mathrm{d}\phi_1}{\mathrm{d}p}-\nu^2\phi_1=0. \tag{10}$$

Transformation from the variable p to the new independent variable z,

$$p=\mathrm{i}[(a-b)z-a], \tag{11}$$

reduces equation (10) to the confluent Heun equation (see [17])

$$z(z-1)\frac{\mathrm{d}^2}{\mathrm{d}z^2}\phi_1+[\gamma(z-1)+\delta z-\beta z(z-1)]\frac{\mathrm{d}}{\mathrm{d}z}\phi_1+q\phi_1=0 \tag{12}$$

with parameters

$$\begin{aligned}\beta &= -(a-b)^2/2, & \gamma &= 1-a^2/2-\varepsilon,\\ \delta &= \varepsilon+b^2/2, & q &= -\nu^2.\end{aligned} \tag{13}$$

3. Degenerate solutions

As is already clear in [17], we take the partial solution of equation (10) in the form of the following Gauss hypergeometric functions expansion:

$$\phi_1=\sum_m d_m\,{}_2F_1(m,\omega-m,\gamma,z), \tag{14}$$

where the parameter ω is given by

$$\omega=\gamma+\delta-1=\frac{b^2-a^2}{2}. \tag{15}$$

Substitution of the expansion equation (14) into equation (12) leads to the three-term recurrence relation for the coefficients d_m

$$C_{m-1}d_{m-1}+B_m d_m+A_{m+1}d_{m+1}=0 \tag{16}$$

with

$$\begin{aligned}A_m &= -\beta\frac{m(m-\omega)\,(m-\gamma)}{(2m-\omega)\,(2m-\omega-1)},\\ B_m &= q+m(m-\omega)+\beta\frac{m(m-\omega)\,(\omega-2\gamma+1)}{(2m-\omega+1)\,(2m-\omega-1)},\\ C_m &= \beta\frac{m(m-\omega)(m-\omega+\gamma)}{(2m-\omega)(2m-\omega+1)}.\end{aligned} \tag{17}$$

These coefficients can also be obtained by the confluence procedure in the solution of the general Heun equation (see [17]). Finally, calculating the integrals in equation (9), we obtain the amplitude $\psi_1(\zeta)$ in the form

$$\psi_1=\mathrm{e}^{-\zeta^2/2}\sum_m d_m\int_L \mathrm{e}^{\beta z^2/2+a(a-b)z}\,\mathrm{e}^{[a-(a-b)z]\zeta}\,z^{\gamma-1}\,{}_2F_1(m,\omega-m,\gamma,z)\,\mathrm{d}z. \tag{18}$$

The solutions of the recurrence relation in equation (16) are specified by two adjacent coefficients d_m. Taking into account the equality $A_0 = 0$, we can put $d_m = 0$ for all negative m and recast equation (16) for $m \geqslant 0$ in the form

$$d_0 = 1, \quad d_1 = -B_0/A_1, \ldots, d_{m+1} = -(C_{m-1}d_{m-1} + B_m d_m)/A_{m+1}, \ldots. \tag{19}$$

Employing the two additional conditions,

$$C_{k-1} = 0 \tag{20}$$

and

$$\det(\mathbf{M}) = 0, \tag{21}$$

where $\mathbf{M}$ is a three-diagonal $k \times k$ matrix

$$\mathbf{M} = \begin{pmatrix} B_0 & A_1 & & & & & & \\ C_0 & B_1 & A_2 & & & & & \\ & C_1 & B_2 & & & & & \\ & & C_2 & . & . & . & & \\ & & & . & . & . & A_{k-3} & \\ & & & & & & B_{k-3} & A_{k-2} \\ & & & & & & C_{k-3} & B_{k-2} & A_{k-1} \\ & & & & & & & C_{k-2} & B_{k-1} \end{pmatrix} \tag{22}$$

and k is a positive integer, all the coefficients d_m with $m \geqslant k$ are equal to zero. In this case, we obtain the accurate solution to equation (12) as a finite sum of k hypergeometric functions.

In consequence of the equalities $C_0 = 0$ and $B_0 = q \neq 0$, the condition of equation (21) can be rewritten in the form

$$\det(\tilde{\mathbf{M}}) = 0, \tag{23}$$

where the matrix $\tilde{\mathbf{M}}$ is obtained by removing the first row and the first column from matrix $\mathbf{M}$. The matrix $\tilde{\mathbf{M}}$ has dimension $(k-1) \times (k-1)$. Thus, nontrivial solutions in the form of equation (14) contain at least two hypergeometric functions:

$$k \geqslant 2. \tag{24}$$

Equation (20) leads to the energy spectrum

$$\varepsilon = k - b^2/2. \tag{25}$$

Interchanging parameters a and b, we find also the additional levels

$$\varepsilon = \tilde{k} - a^2/2. \tag{26}$$

The spectrum of analytically solvable cases, equations (25) and (26), coincides with the energy levels of diabatic potentials. Equation (23) defines the eigenvalues of the accessory parameter $q = -\nu^2$.

In particular, for the lowest level of the spectrum in equation (25) we obtain

$$k = 2, \qquad \varepsilon = 2 - b^2/2, \qquad \nu^2 = 1 - b^2 + ab, \qquad d_1 = (\omega - 1 - \beta)\frac{d_0}{\beta}. \tag{27}$$

The energy level $\varepsilon = 2 - b^2/2$ coincides with the first excited vibrational level in the diabatic potential $m\Omega^2 x^2/2 - F_2 x$ and the wavefunction equation (14) is a sum of two Gauss hypergeometric functions

$$\phi_1 = {}_2F_1(0, \omega, \omega - 1, z) + \frac{\omega - 1 - \beta}{\beta}\,{}_2F_1(1, \omega - 1, \omega - 1, z) = \frac{\beta z - \omega + 1}{\beta(z-1)}. \tag{28}$$

For solvable cases, the product $z^{\gamma-1}\,{}_2F_1(m,\omega-m,\gamma,z)$ in the integrand of equation (18) can be simplified as follows (see [18]):

$$z^{\gamma-1}\,{}_2F_1(m,\omega-m,\gamma,z) = z^{\omega-k}\,{}_2F_1(m,\omega-m,\omega+1-k,z) = \frac{(-1)^l\Gamma(p)}{\Gamma(p+l)}\frac{\mathrm{d}^l}{\mathrm{d}z^l}[z^{-p}(1-z)^{-m}], \tag{29}$$

where

$$p = m+1-\omega, \qquad l = k-1-m. \tag{30}$$

Calculating the integrals in equation (18) by parts, we obtain

$$\psi_1 = \mathrm{e}^{a^2-a\zeta+\zeta^2/2}\sum_m d_m\frac{(-1)^m\Gamma(p)}{\Gamma(p+l)}\int_L z^{-p}(z-1)^{-m}\frac{\mathrm{d}^l}{\mathrm{d}z^l}[\mathrm{e}^{-\alpha^2(z-z_0)^2}]\,\mathrm{d}z, \tag{31}$$

with

$$\alpha = \frac{a-b}{2}, \qquad z_0 = \frac{a-\zeta}{\alpha}. \tag{32}$$

Generally, the point $z=0$ is the branching point for the integrand in equation (31), and the only possible integration contour L is a closed contour winding around the pole $z=1$. Calculating the residue in the point $z=1$ and using the definition of Hermitian polynomials

$$H_n(x) = (-1)^n\,\mathrm{e}^{x^2}\frac{\mathrm{d}^n}{\mathrm{d}x^n}\,\mathrm{e}^{-x^2}, \tag{33}$$

we finally find the amplitude ψ_1 in the coordinate representation

$$\psi_1^{(1)} = 2\pi\mathrm{i}(-\alpha)^{k-2}\,\mathrm{e}^{a^2-(a+b)^2/4+b\zeta-\zeta^2/2} \times\sum_m d_m\frac{(-1)^m}{\Gamma(p+l)}\sum_{n=0}^{m-1}\frac{\Gamma(p+n)\alpha^{-n}}{\Gamma(n+1)\Gamma(m-n)}H_{k_1}\left(\zeta-\frac{a+b}{2}\right), \tag{34}$$

where

$$k_1 = k-2-n. \tag{35}$$

When the parameter ω is a negative integer or zero, the parameter p is a positive integer and the additional integration contour winding around the pole $z=0$ becomes available. This contour generates the second, linearly independent physical solution

$$\psi_1^{(2)} = 2\pi\mathrm{i}\,\mathrm{e}^{a\zeta-\zeta^2/2}\sum_m d_m\frac{\Gamma(p)}{\Gamma(p+l)\Gamma(m)}\sum_{n=0}^{p-1}\frac{\Gamma(m+n)(-\alpha)^{k-1-\omega-n}}{\Gamma(n+1)\Gamma(p-n)}H_{k_2}(\zeta-a), \tag{36}$$

where

$$k_2 = k-1-\omega-n. \tag{37}$$

The energy level in equation (25), $\varepsilon = k-b^2/2$, is degenerate in this case (it coincides with the level $\tilde{k} = k-\omega$ in equation (26)).

The second components, $\psi_2^{(1)}$ and $\psi_2^{(2)}$, of the diabatic vectors are obtained from $\psi_1^{(1)}$, $\psi_1^{(2)}$ and equations (3)–(5) by the formal substitutions

$$H_{k_1} \Rightarrow \frac{1}{\nu}\left[([a-b]\,\zeta+k-1)\,H_{k_1}+2k_1\,(b-\zeta)\,H_{k_1-1}+2k_1(k_1-1)H_{k_1-2}\right], \tag{38}$$

$$H_{k_2} \Rightarrow \frac{1}{\nu}\left[\left(\frac{a^2-b^2}{2}+k-1\right)H_{k_2}+2k_2\,(a-\zeta)\,H_{k_2-1}+2k_2(k_2-1)H_{k_2-2}\right]. \tag{39}$$

This completes the proof that double degeneracy and therefore dynamic symmetry in the basic vibronic problem, equation (1), exists.

4. Calculation ansatz: the x-representation

The global form of the amplitudes $\psi_{1,2}^{(1,2)}$, which has been found above, indicates the way to find the solutions of the problem equation (1) directly in x-representation, which proves to be an effective calculation procedure. With this goal we introduce the new functions $h_{1,2}(\zeta)$ and the new variable y according to the equations

$$h_{1,2}(\zeta) = \chi_{1,2}(\zeta)\exp(-b\zeta), \qquad y = \zeta - b \tag{40}$$

and rewrite equation (5) in the form

$$[\hat{\Lambda} + (a-b)(y+b)]h_1(y) - \nu h_2(y) = 0, \tag{41}$$

$$\hat{\Lambda}h_2(y) - \nu h_1(y) = 0, \tag{42}$$

where $\hat{\Lambda}$ is the second-order differential operator

$$\hat{\Lambda} = \frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}y^2} - y\frac{\mathrm{d}}{\mathrm{d}y} + k - 1 \tag{43}$$

and the parameter k is introduced according to equation (25).

The system of equations (41) and (42) results in the fourth-order differential equation for the function h_2

$$\mathcal{L}h_2(y) = 0, \tag{44}$$

where the operator $\mathcal{L}$ has the form

$$\mathcal{L} = [\hat{\Lambda} + (a-b)(y+b)]\hat{\Lambda} - \nu^2. \tag{45}$$

For the solvable cases we take the solution to equation (44) in the form of an expansion in Hermitian polynomials $H_m(y)$

$$h_2(y) = \sum_m q_m H_m(y). \tag{46}$$

Substitution of the expression in equation (46) into equation (44) leads to the following three-term recurrence relation for the coefficients q_m

$$c_{m-1}q_{m-1} + b_m q_m + a_{m+1}q_{m+1} = 0 \tag{47}$$

with

$$\begin{aligned} a_m &= m(m-k+1)(b-a), \\ b_m &= (m-k+1)(m-k+b^2-ab+1) - \nu^2, \\ c_m &= (m-k+1)(b-a)/2. \end{aligned} \tag{48}$$

The properties of the recurrence relation (47) are similar to the properties of relation (16). Because of the equality $a_0 = 0$, the sum in equation (46) begins from $m = 0$. At integer values of parameter k ($k \geqslant 2$), parameter $c_{k-1} = 0$ and the sum on the right-hand side of equation (46) is truncated at $m = k-1$ provided that the additional condition is fulfilled

$$\det(\mathbf{m}) = 0, \tag{49}$$

where **m** is a three-diagonal $k \times k$ matrix with the structure exactly the same to that given in equation (22)

$$\mathbf{m} = \begin{pmatrix} b_0 & a_1 & & & & & & & \\ c_0 & b_1 & a_2 & & & & & & \\ & c_1 & b_2 & & & & & & \\ & & c_2 & . & . & . & & & \\ & & & . & . & . & a_{k-3} & & \\ & & & & & & b_{k-3} & a_{k-2} & \\ & & & & & & c_{k-3} & b_{k-2} & a_{k-1} \\ & & & & & & & c_{k-2} & b_{k-1} \end{pmatrix}. \tag{50}$$

Because of the equalities $a_{k-1} = 0$, $b_{k-1} = -\nu^2 \neq 0$, the last column and the last row can be removed from the matrix **m**.

For the case $k = 2$, we obtain the following solutions to equation (49) and recurrence relation (47):

$$\nu^2 = 1 - b^2 + ab, \qquad q_1 = \frac{a-b}{2\nu^2} q_0. \tag{51}$$

As a result, the function $h_2(y)$ is given by

$$h_2(y) = q_0 H_0(y) + q_1 H_1(y) = q_0 \left(1 + \frac{a-b}{\nu^2} y\right) \tag{52}$$

and using equation (42) we immediately get

$$h_1(y) = \frac{q_0}{\nu}. \tag{53}$$

Finally, the wavefunctions ψ_1 and ψ_2 are obtained in the form

$$\begin{aligned} \psi_1(\zeta) &= \frac{q_0}{\nu} \exp(-\zeta^2/2 + b\zeta), \\ \psi_2(\zeta) &= \frac{q_0}{\nu^2} \exp(-\zeta^2/2 + b\zeta)[1 + (a-b)\zeta]. \end{aligned} \tag{54}$$

In the diabatic limit $\nu \to 0$ (i.e. $a \to (b^2 - 1)/b$), the normalized function ψ_2 coincides with the wavefunction of the first excited vibrational level of the diabatic potential $\zeta^2/2 - b\zeta$, while the normalized function ψ_1 approaches zero.

Thus we found the analytical solution for the portion of energy spectrum of the two-component Schrödinger equation at special values of interaction parameter ν. Ordinarily, such situations are said to be quasi-exactly solvable [19, 20]. The important feature of the states found is that they belong to the degenerate levels and, therefore, stand out against the other ones. We believe that the spectrum of the system considered does not contain any other degenerate levels. To confirm this statement, the dynamic symmetry of the system should be analyzed completely and we are planning to work in this direction aiming to find the symmetry operators which could clarify the origin of degeneration.

5. Conical intersection of vibronic levels

In the three-dimensional space $\{a, b, \nu\}$, vibronic levels are degenerate along the line

$$\nu = \nu(a, b), \qquad \frac{b^2 - a^2}{2} = k - \tilde{k} = \omega. \tag{55}$$

Here $\nu(a, b)$ is the solution to equation (21). Vibronic levels intersect each other along this line and form the double cone surface in the vicinity of the intersection. To get the shape of the

conical intersection in the infinitely close vicinity of degenerate configurations we follow the up-to-date version of perturbation theory for degenerate levels of Schrödinger operator [21]. We specify the perturbation $\delta\hat{\mathbf{H}}$ in the following matrix form:

$$\delta\hat{\mathbf{H}} = \begin{pmatrix} \delta a\zeta, & -\delta\nu \\ -\delta\nu, & \delta b\zeta \end{pmatrix}. \tag{56}$$

Here δa, δb and $\delta\nu$ stand for the increments of parameters a, b and ν respectively while moving away from the degenerate configuration.

Now, we shall find the parameters of the lowest intersection at the energy equation (27) for the geometrically symmetric case

$$b = -a, \qquad \nu(a,b) \equiv \nu(a) = \sqrt{1-2a^2}. \tag{57}$$

As a first unperturbed solution we take the function given by equation (54)

$$\psi^{(1)} = \begin{pmatrix} \psi_1(\zeta) \\ \psi_2(\zeta) \end{pmatrix}. \tag{58}$$

The second solution can be immediately obtained using the symmetry of the Hamiltonian

$$\psi^{(2)} = \begin{pmatrix} \psi_2(-\zeta) \\ \psi_1(-\zeta) \end{pmatrix}. \tag{59}$$

Orthogonal solutions $\mathbf{\Psi}_1$ and $\mathbf{\Psi}_2$ can be obtained as symmetrized combinations of functions $\psi^{(1)}$ and $\psi^{(2)}$

$$\mathbf{\Psi}_1 = \psi^{(1)} + \psi^{(2)}, \qquad \mathbf{\Psi}_2 = \psi^{(1)} - \psi^{(2)}. \tag{60}$$

The normalizing coefficients for these functions, N_1 and N_2, are equal to the integrals below

$$\begin{aligned} N_1 &= \int_{-\infty}^{+\infty} \mathbf{\Psi}_1^T \mathbf{\Psi}_1 \,\mathrm{d}\zeta = \frac{4q_0^2\sqrt{\pi}e^{a^2}}{1-4a^2+4a^4}\left(1-2a^2+2a^4+e^{-a^2}\sqrt{1-2a^2}\right), \\ N_2 &= \int_{-\infty}^{+\infty} \mathbf{\Psi}_2^T \mathbf{\Psi}_2 \,\mathrm{d}\zeta = \frac{4q_0^2\sqrt{\pi}e^{a^2}}{1-4a^2+4a^4}\left(1-2a^2+2a^4-e^{-a^2}\sqrt{1-2a^2}\right). \end{aligned} \tag{61}$$

Matrix elements of the perturbation $\delta\hat{\mathbf{H}}$ are given by

$$\begin{aligned} \delta H_{11} &= \frac{1}{N_1}\int_{-\infty}^{+\infty} \mathbf{\Psi}_1^T \delta\mathbf{H}\mathbf{\Psi}_1 \,\mathrm{d}\zeta \\ &= -a\sigma + \frac{4q_0^2\sqrt{\pi}\left(e^{a^2}\sqrt{1-2a^2}+1\right)}{A_\Sigma(1-2a^2)} w_\eta \eta, \end{aligned} \tag{62}$$

$$\begin{aligned} \delta H_{22} &= \frac{1}{N_2}\int_{-\infty}^{+\infty} \mathbf{\Psi}_2^T \delta\mathbf{H}\mathbf{\Psi}_2 \,\mathrm{d}\zeta \\ &= -a\sigma + \frac{4q_0^2\sqrt{\pi}\left(e^{a^2}\sqrt{1-2a^2}-1\right)}{A_\Delta(1-2a^2)} w_\eta \eta, \end{aligned} \tag{63}$$

$$\begin{aligned} \delta H_{12} = \delta H_{21} &= \frac{1}{\sqrt{N_1 N_2}}\int_{-\infty}^{+\infty} \mathbf{\Psi}_1^T \delta\mathbf{H}\mathbf{\Psi}_2 \,\mathrm{d}\zeta \\ &= \frac{8q_0^2\sqrt{\pi}e^{a^2}a^5}{\sqrt{A_\Sigma A_\Delta}(1-2a^2)^2} w_\tau \tau, \end{aligned} \tag{64}$$

where we introduced the symmetrized increments σ, τ and η

$$\begin{aligned}\delta a &= w_\tau \tau + \sigma,\\ \delta b &= w_\tau \tau - \sigma,\\ \delta \nu &= 2a(1-2a^2)^{-1/2}\sigma + w_\eta \eta,\end{aligned} \tag{65}$$

and the scaling factors w_τ and w_η

$$w_\tau = \frac{e^{-a^2}}{2a^5}\sqrt{(1-2a^2+2a^4)e^{2a^2}-1+2a^2}, \tag{66}$$

$$w_\eta = \frac{e^{-a^2}[(1-2a^2+2a^4)e^{2a^2}-1+2a^2]}{2a^4(1-2a^2)}. \tag{67}$$

The corrections for the vibronic levels in the vicinity of the intersection are the eigenvalues of matrix $\delta\mathbf{H}$

$$\delta\varepsilon = \overline{\delta\varepsilon} \pm \sqrt{\tau^2+\eta^2}, \tag{68}$$

where

$$\overline{\delta\varepsilon} = -a\sigma + \frac{(1-2a^2+2a^4)e^{a^2}-e^{-a^2}}{2a^4}(1-2a^2)^{1/2}\eta. \tag{69}$$

That visualizes the double cone shape of the intersection.

The excited level with $k = 3$ has two degenerate configurations which are defined by two solutions of equation (49):

$$\nu = \tfrac{1}{2}\sqrt{10-12a^2 \pm 2\sqrt{9+4a^2+4a^4}}. \tag{70}$$

The components $\psi_1(\zeta)$ and $\psi_2(\zeta)$ of the first unperturbed solution for the wavefunction are obtained in the form

$$\begin{aligned}\psi_1(\zeta) &= \frac{2q_0(\nu^2+4a^2-1+2a\zeta)}{\nu(\nu^2+2a^2-1)}\exp(-\zeta^2/2+b\zeta),\\ \psi_2(\zeta) &= \frac{q_0[8a^2\zeta^2+(4a^2+\nu^2)(4a\zeta+\nu^2+2a^2-1)]}{\nu^2(\nu^2+2a^2-1)}\exp(-\zeta^2/2+b\zeta).\end{aligned} \tag{71}$$

The normalized solutions, the splitting of degenerate levels and the cone's shape are calculated by analogy with the case $k = 2$, however they are highly tedious.

The characteristic behavior of a few levels for the basic vibronic model calculated numerically is shown in figure 1. The levels are drawn as a function of the force parameter b at a fixed value of interaction $\nu = 0.95$, with $\omega = 0$ for thick lines and $\omega = -2$ for thin lines. The force parameter a is changed as $-\sqrt{b^2-2\omega}$. The dashed lines are $\varepsilon = k - b^2/2$ for $k = 2, 3$ and 4. These lines intersect the energy levels in degenerate configurations. In full agreement with the analytical treatment, the positions of intersections of all levels coincide with the energy levels of diabatic potentials. In the close vicinity of intersections these levels coincide with that given by the perturbation theory approach.

The number of degenerate configurations of individual level is equal to the number of physical solutions of equation (49). This number depends on the value of the interaction parameter ν. The critical values ν_i of the parameter ν are given by

$$\nu_i = \sqrt{(i-k)(i-k+\omega)}, \tag{72}$$

where

$$i = 1, 2, \ldots, k-1. \tag{73}$$

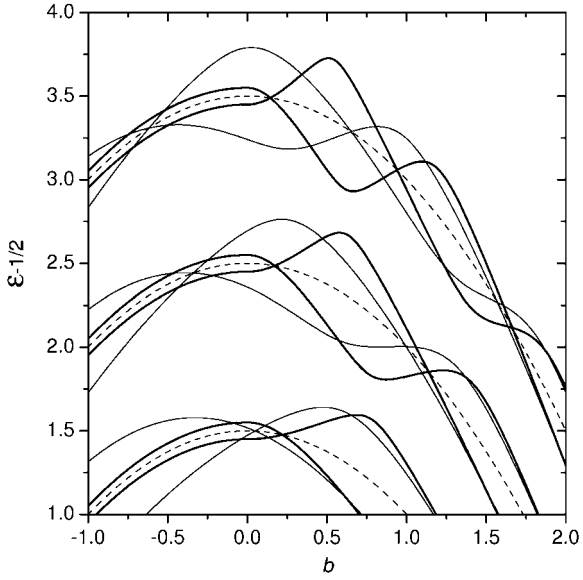

Figure 1. Energy levels as a function of the force parameter b at a fixed value of interaction $\nu = 0.95$. $a = -\sqrt{b^2 - 2\omega}$. Thick lines are for $\omega = 0$, thin lines are for $\omega = -2$. Dashed lines are $\varepsilon = k - b^2/2$ with $k = 2$, 3 and 4.

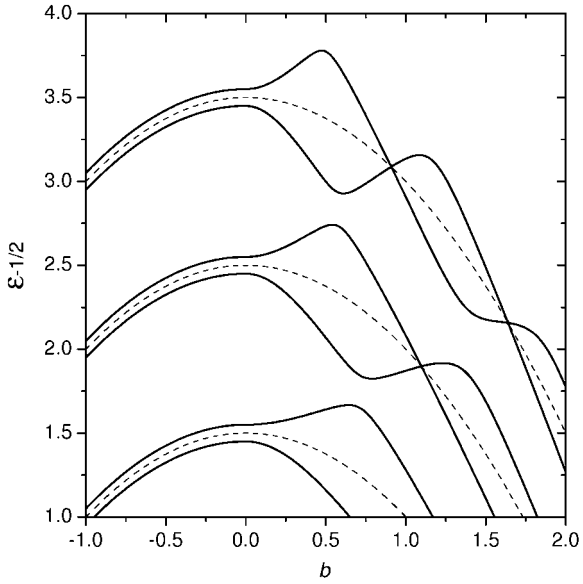

Figure 2. As figure 1. $\omega = 0$, $\nu = 1.05$.

In particular, for the geometrically symmetric case $b = -a$, the number of intersections of levels is changed at integer values of the parameter ν. Comparison of figures 1 and 2 demonstrates the disappearance of degenerate configurations when the parameter ν is changed from 0.95 to 1.05.

6. Conclusion

The one-dimensional vibronic problem may have degenerate solutions, which are deduced in this paper in an analytically exact form. The corresponding levels form a harmonic sequence presenting the conical intersections over the manifold $\{a, b, \nu\}$ in the degeneracy vicinities. The degeneracy conditions are the resonance displacement of the diabatic potentials and the special value of interaction generating the dynamic symmetry. These conditions restrict the conventional semiclassical quantization conditions essentially.

The basis set for degenerate levels is generated by the contours connecting p- and x-representations that gives rise to the dynamic symmetry group. Finding the group operators in x-representation will be a worthwhile target for a subsequent study.

The conical intersection parameters found in an exact analytical form as the functions on the parameters of the molecular system can be used to check the numerically obtained potential surfaces in the intersection vicinity.

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