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# Quasiclassical and exact quantization of simple two-level model systems

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**Abstract.** The Laplace method is considered in application to one-dimensional two-state eigenvalue problems in the example of simple models, including that of coupled parabolic terms and radial oscillators with quadratic, linear and constant coupling (basic models of Renner, pseudo-Jahn–Teller effects etc.). In all cases, the solution can be presented either as a two-state analogue of the Bohr–Sommerfeld quasiclassical quantization rule, or in more general form. Compared with the semiclassical picture of inelastic collisions in the momentum-space representation, the contour of integration of ‘trajectory equations’ for the case of bound states is finite, and any desired degree of accuracy can easily be achieved. Because no convergence problems arise, the need to compute the equation possessing ‘physical sense’ (e.g. for adiabatic amplitudes) is circumvented, suggesting that the method would be applicable also to complicated potentials and to many-state problems. Numerical tests for the energy level positions and calculations of eigenfunctions are presented; practical applications and generalizations are outlined.

## 1. Introduction

The role which nuclear motion plays in the coupling of electronic states, and various manifestations of this coupling, excite permanent interest. In this paper, we are primarily interested in the effects of vibronic coupling on the details of the vibrational structure in electronic absorption and emission spectra. Consideration of simple models gives a good basis for understanding the problem. The models usually used are, in general, of two categories. The first assume the electrons to follow the nuclei adiabatically [1, 2]. Because the electronic functions become dependent on nuclear coordinates, the nuclear motion results in so-called non-adiabatic coupling, which becomes stronger the faster the nuclei move. The second use a set of electronic wavefunctions for some fixed nuclear configuration as a basis [3, 4]. All quantities in the coupled equations which result from allowing nuclei to move are expanded in a power series about this fixed configuration. Typically, only the lower-order terms are retained, those presumed to give a reasonable approximation to potential curves and coupling terms.

Some interesting models belonging to the first category can be found in the literature [5, 6], but those of the second type are seemingly simpler for theoretical treatment and practical use. In this and previous papers [7–9], we also deal with models having two diabatic potentials and some coupling function as a starting point. Analytical methods, usually in quasiclassical approximation, result, for the eigenvalue problem in coupled potentials, in rather simple quantization formulae. They have

clear physical meaning and replace, for this case, the Bohr–Sommerfeld quantization rule. In [9], on the basis of experimental vibronic levels and by use of quasiclassical quantization conditions, the diabatic description of the valence-Rydberg states of diatomics was suggested. The method proves very convenient practically, and rather accurate, i.e. the method is accurate when experimental data are abundant (the simultaneous fit to 70 vibronic levels of four isotopic species of dihydrides [10–14] enables one to reproduce the *ab initio* EF adiabatic double-minimum potential [15, 11–12] very well). Unfortunately, the results for the *b'c'*-states of the nitrogen molecule [16–17] were less impressive. It was appreciated, later, that the use of a more precise quantization function in the least squares fitting procedure would result in appreciable improvement of the method.

In attempts to improve the two-state quantization formulae (section 2), our attention was first attracted to the fact that some intermediate quasiclassical quantization forms in the high energy region are actually exact, not asymptotic. It can be shown for all models under consideration, i.e. that of two parabolic electronic potentials with equal frequencies and constant coupling (section 3), and a family of three problems having as particular cases the simplified Renner and Jahn–Teller models (section 4). The important point is that in all cases the system of two second-order differential equations describing the model can be reduced, by taking the Laplace transformation, to a pair of coupled first-order differential equations.

Some of our first-order equations (e.g. for diabatic and adiabatic amplitudes, and provided the independent variable is chosen in some special way) may be considered as the trajectory time-dependent equations. Compared with exact [18–19] and approximate [20–21] trajectory equations in the momentum–space representation, the Laplace transforms describe motion rather in the phase space. Certainly, the model of the linear terms with constant coupling [18] (inelastic two-channel scattering) and the linear Jahn–Teller model [19] (resonance elastic scattering) are special cases of equation (5) ( $\omega=0$ ,  $k>1$ ) and equation (29) ( $\Lambda=1/2$ ,  $E_+=E_-=E$ ,  $\omega_+=\omega_-=0$ ) of this paper, but many other ‘exactly solvable’ models of scattering are also possible (cf equation (29) with imaginary frequencies). The contours of integration of the Laplace transforms lie, in general, in the complex plane, but no special complications, compared with the integration of the trajectory equations along the real axis in momentum space [20–23], arise. In scattering problems (elastic or inelastic), all difficulties originate from the infiniteness of motion in the mean adiabatic term. The integrations should be performed, strictly speaking, over infinite limits. Because this is impossible, the precision of numerical calculations is limited. Simplifications are achieved only for the case of bound states. Due to finite and strongly defined limits of integration, calculations can be highly accurate. Most important, no convergence problem arises, and computations can be performed with any convenient and single-valued in the complex plane equations, not necessarily possessing ‘physical sense’ (sections 3, 5).

The models of coupled oscillators with equal frequencies, equation (5), and the special case of the pseudo-Jahn–Teller model,  $\Lambda=\frac{1}{2}$  and  $\omega_+=\omega_-$  in equation (29), can also be treated by use of Bargmann’s method [24, 25] (i.e. in the coherent states representation [26]). The resulting system of linear first-order differential equations of [24, 25] can be successfully integrated along the conjectured contour (section 5), and the quantization condition for vibronic levels can also be written (it replaces the requirement for eigenfunctions to belong to the space of entire functions in Bargmann’s approach). In general, the Laplace method seems easily applicable to

various models. Besides that, a very simple expression for eigenfunctions in the coordinate representation is available in its frames.

In section 5 the results of numerical tests are presented. In section 6 some details of practical applications of our approach are considered, and possible generalizations are mentioned.

## 2. Two-level quasiclassical quantization

In order to obtain a complete idea of the subject of the paper, let us look at the quasiclassical formulae available at present for describing the two-state quantization problem. Hereafter,  $\mathcal{A}_{1,2}$  denote the actions in the lower and upper adiabatic potentials ( $\mathcal{A}_1 > \mathcal{A}_2$ ), and  $\mathcal{P}$  has the meaning of the transition probability between adiabatic terms. The 'tunneling' action  $\mathcal{D}$ , if not stated, correlates at high energies with the Landau-Zener factor.

The quantization form

$$\cos(\mathcal{A}_1 + \mathcal{A}_2) + (1 - \mathcal{P})^{1/2} \cos(\mathcal{A}_1 - \mathcal{A}_2 - \varphi) = 0 \quad (1)$$

where  $\mathcal{P} \sim \exp(-2\mathcal{D})$  and  $\varphi$  is the non-adiabatic (Landau-Zener) phase, was first announced [7] as characteristic of rather high levels ( $\mathcal{A}_1 \gg 1$ ,  $\mathcal{A}_2 > 0$  or  $\mathcal{A}_2 \approx 0$ ) of the simplest Jahn-Teller vibronic problem (cf (29) of this paper with  $\Lambda = \frac{1}{2}$ ,  $E_+ = E_-$  and  $\omega_+ = \omega_-$ ). The limiting cases of (1) are the usual Bohr-Sommerfeld conditions of quantization in the separate,  $\cos \mathcal{A}_1 \cos \mathcal{A}_2 = 0$  (when no non-adiabatic transitions occur and  $\mathcal{P} = \varphi = 0$ ), and united,  $\cos(\mathcal{A}_1 + \mathcal{A}_2) = 0$  ( $\mathcal{P} = 1$ ) adiabatic potential wells. Equation (1) reproduces the high numerical energy levels of [27-30] very well [7], but near and below the bottom of the upper adiabatic term,  $\mathcal{A}_2 \leq 0$ , especially at not too large  $\mathcal{D}$ , the precision of (1) is reasonable only (typically within a few per cent).

Next, the well-founded expression

$$(1 - \mathcal{P}) \cos(\mathcal{A}_1 + \varphi) \cos(\mathcal{A}_2 - \varphi) + \mathcal{P} \cos \mathcal{A}_+ \cos \mathcal{A}_- = 0 \quad (2)$$

where  $\mathcal{A}_+$  and  $\mathcal{A}_-$  are the actions in diabatic potentials, is characteristic of quantization in the high-energy region ( $\mathcal{A}_2 \geq 0$ ) [8-9] in systems of two coupled diabatic terms involving crossing. As limiting cases, it has quantization in adiabatic,  $\cos \mathcal{A}_1, \cos \mathcal{A}_2 = 0$  ( $\mathcal{P} = \varphi = 0$ ), and diabatic,  $\cos \mathcal{A}_+ \cos \mathcal{A}_- = 0$  ( $\mathcal{P} = 1$ ), potentials.

In [9] the quasiclassical treatment of some two-state models was extended to the situations where the lower adiabatic potential becomes double-well. At energies below the bottom of the upper adiabatic term, it was found that the quantization condition could be presented as the product of two terms:

$$\cos(\mathcal{A}' + \mathcal{A}'' - \psi) + \mathcal{R}^{1/2} \cos(\mathcal{A}' - \mathcal{A}'') = 0 \quad (3a)$$

describing the quantization in the double-minimum potential (here  $\mathcal{A}'$  and  $\mathcal{A}''$  are two complementary parts of the action  $\mathcal{A}_1$  in the lower double-well adiabatic potential,  $\mathcal{R}$  is the reflection probability related to the potential hump, and  $\psi$  is the corresponding phase correction; due to pre-exponential corrections in  $\mathcal{R}$  [9], equation (3a) describes well both weak and strong coupling limits), and

$$\cos(\mathcal{A}_2 + \psi) - \mathcal{R}^{1/2} = 0 \quad (3b)$$

defines the so-called false spectrum [31]. (The conditions (1) and (2) also possess a false spectrum. At energies below the bottom of the upper adiabatic term and in the weak coupling limit, it is  $\cos \mathcal{A}_2 + 0(\mathcal{P}) = 0$ ,  $\mathcal{A}_2 < 0$ .)

The quantization formulae (2)–(3) are very convenient for use in the least squares fitting procedure [9], but the quantization forms (2) and (3) do not fit each other exactly in a common region of applicability, i.e. in the energy gap between adiabatic terms. Unfortunately, further essential progress seems impossible in this ‘quasiclassical’ way. Besides restricted precision, the results which can be obtained for the more realistic models discussed in section 4 are either coincident with those for parabolic terms or would have doubtful practical value because of mismatches between various limiting cases.

For purposes of the present paper, let us consider the findings from another point of view. First, equation (1) and (2) are special cases of the more universal and straightforward quantization form

$$Q = \cos(\mathcal{A}_1 + \mathcal{A}_2) + \text{mod } T_{11} \cos(\mathcal{A}_1 - \mathcal{A}_2 - \arg T_{11}) = 0 \quad (4)$$

where the matrix  $T$  (obeying the system of trajectory equations) describes transitions between adiabatic terms. The only difference between the expressions (1) and (2) is in the character of the model used. Namely, these expressions appear when the non-adiabatic transitions take place once or twice during one period of classical motion, respectively. (For the relationship between  $\mathcal{P}$ ,  $\varphi$ , and the  $T$ -matrix in the case of equation (2) compare with (5.8) of [8].) Second, equation (4) itself is exact for all models under consideration, in spite of the fact that the actions  $\mathcal{A}_{1,2}$  entering it are quasiclassical. In this way, the precision of (4) depends only on the precision of the calculation of the  $T$ -matrix. All previously used  $T$ -matrices [8, 9] were asymptotic in the main large parameter of the quasiclassical treatment of bound states,  $\mathcal{L} = \mathcal{A}_1 - \mathcal{A}_2 \gg 1$ . (That is, the  $T$ -matrix used was just the transition matrix [31] for the corresponding resonance or inelastic scattering problem  $\mathcal{A}_1 = \infty$ ; in the latter case the  $T$ -matrix turns out also to be the scattering matrix [23, 31], which is some special case of the transition matrix.) As a result, some error is introduced in the quantization conditions. This error becomes smaller as the difference  $\mathcal{L}$  becomes larger. (Under favorable conditions,  $\mathcal{L} = 50$ – $100$ , the quantization formulae (2) and (3) guarantee a residual mean-square deviation of about 1% of the smaller frequency [9].) In the presently proposed numerical approach, due to restricted  $\mathcal{A}_1 - \mathcal{A}_2$ , the equations describing the  $T$ -matrix can easily be resolved to any desired degree of accuracy.

It should be stressed here that the numerical  $T$ -matrix, in contrast to its asymptotic form, is not defined unambiguously. All possible pairs of  $(\text{mod } T_{11}, \arg T_{11})$  satisfying (4) can be obtained in calculations by use of different contours and equations (section 5).

### 3. Basic model and exact quantization

The simplest problem, and most elaborated quasiclassically, is the quantization problem of two coupled parabolic potentials with equal frequencies [8, 9]

$$\frac{d^2\Psi}{dx^2} + l^2 \left[ \varepsilon - \frac{x^2}{2} + kx + \begin{pmatrix} x & v \\ v & -x \end{pmatrix} \right] \Psi = 0 \quad (5)$$

where  $l = (F_1 F_2)^2 / 4\hbar\mu\omega^3$  ( $F_{1,2}$  are the forces at the crossing point  $x = 0$ ,  $\varepsilon = 0$ ) is the main large parameter of quasiclassical treatment, approximately equal to the difference of the quantum numbers  $\Delta N = (\mathcal{A}_1 - \mathcal{A}_2) / \pi$ , where  $\mathcal{A}_{1,2}$  are the adiabatic actions, the

energy  $\varepsilon$  and the coupling constant  $v$  are given in units  $\hbar\omega$ ,  $x$  in  $(\hbar/\mu\omega)^{1/2}$  and the reduced mean force  $k = (F_1 + F_2)/(F_1 - F_2)$ .

This model should be considered as four-parametric. Including the full energy, there are four parameters (and four independent actions) which give the full description of the  $T$ -matrix in (4).

Problem (5) has a solution [8]

$$\Psi(x) = \exp\left(\frac{-lx^2}{2}\right) \int_{\Gamma} \exp(lqx) G(q) dq \quad (6)$$

where the functions  $G_{1,2}$  obey the coupled first-order differential equations

$$\begin{pmatrix} d_1(d/dq) + l\varepsilon + 1/2 & v \\ v & d_2(d/dq) + l\varepsilon + 1/2 \end{pmatrix} G = 0 \quad (7)$$

$$d_{1,2} = q - (k \pm 1) \quad \varepsilon = q^2/2 + \varepsilon$$

and the contour  $\Gamma$  is chosen such that the increments of the out-of-integral terms along the contour are zero:

$$\{d_n G_n \exp(lqx)\}_{\Gamma} = 0 \quad n = 1, 2. \quad (8)$$

In particular, this condition is satisfied when the contour begins and ends at  $q = \pm \infty$  [8], but the four independent solutions (6) of such a kind rise exponentially either at  $x \rightarrow -\infty$  or at  $x \rightarrow +\infty$  at any energy and cannot describe the bound states. A good prompt for the contours is the locus of the saddle points in (6) in the classically accessible regions (the phase curves)

$$q_{1,2}^* = x \pm ip_{1,2}$$

where

$$p_{1,2} = [2(\varepsilon + kx \pm (x^2 + v^2)^{1/2}) - x^2]^{1/2} \quad (9)$$

are quasiclassical adiabatic impulses. The phase curves (9) are closed, but in other coordinate systems (as defined below by relations (11)) they are periodic only.

The first-order equations we will deal with, for the auxiliary function  $C$  (the column of  $C_1, C_2$ ), defined by

$$G = \exp\left(-1 \int \tilde{Q} dq\right) \begin{pmatrix} 1/s_1 & 0 \\ 0 & 1/s_2 \end{pmatrix} C$$

where

$$\begin{aligned} s_{1,2} &= (d_{1,2})^{1/2} & \tilde{Q} &= (q - k)\varepsilon/s^2 \\ s &= (d_1 d_2)^{1/2} = ((q - k)^2 - 1)^{1/2} \end{aligned} \quad (10)$$

and after introducing the time-like variable  $\tau$

$$s(d/dq) = d/d\tau$$

so that

$$q - k = \cosh \tau \quad \text{and} \quad s = \sinh \tau \quad (11)$$

become in the most simple Landau-Zener form

$$\frac{dC}{d\tau} + l \begin{pmatrix} \chi & v \\ v & -\chi \end{pmatrix} C = 0 \quad \text{where} \quad \chi = \varepsilon/s. \quad (12)$$

Previously [8, 9], this equation was treated by various approximate analytical methods. It was also shown [8] how the quasiclassical quantization arises from the conditions (8). Now we have attempted to consider this and similar quantization problems exactly, combining analytical and numerical approaches. As a preliminary, let us specify transformation to the adiabatic basis in (12) as

$$C = U^{-1}Da \quad D = \begin{pmatrix} e^- & 0 \\ 0 & e^+ \end{pmatrix} \quad U^{-1} = \begin{pmatrix} \cos \beta & -\sin \beta \\ \sin \beta & \cos \beta \end{pmatrix} \quad (13)$$

where

$$\tan \beta = v/\chi, \quad e^\pm = \exp(\pm l \int Q \, dq) = \exp(\pm l \int \theta \, d\tau) \quad (14)$$

$Q = (\chi^2 + v^2)^{1/2}/S$  is the adiabatic potential in 'q-representation', and  $\theta = Qs, s \, d\tau = dq$  (cf equation (11)). The adiabatic amplitudes  $a_{1,2}$  obey the equation

$$\left\{ \frac{d}{dz} + \beta' \begin{pmatrix} 0 & -(e^+)^2 \\ (e^-)^2 & 0 \end{pmatrix} \right\} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0. \quad (15)$$

Here  $\beta' = d\beta/dz, z$  signifies  $q$  or  $\tau$ .

Let also

$$e^0 = \exp(-l \int \bar{Q} \, dq) = \exp(-l \int \bar{\theta} \, d\tau) \quad \bar{\theta} = \bar{Q}s. \quad (16)$$

The conditions (8) in the notation introduced become

$$\begin{aligned} \{(d_1)^{1/2} \exp(lqx) e^0 (a_1 \cos \beta e^- - a_2 \sin \beta e^+)\}_\Gamma &= 0 \\ \{(d_2)^{1/2} \exp(lqx) e^0 (a_1 \sin \beta e^- + a_2 \cos \beta e^+)\}_\Gamma &= 0. \end{aligned} \quad (17)$$

Let us specify some matrix  $T$  describing changes in coefficients  $a_{1,2}$  along the contour  $\Gamma$  (the initial and final points are chosen through one period of classical motion and, particularly, are coincident in the  $q$ -plane):

$$a_{(f)} = T a_{(i)} \quad \text{where } a_{(i), (f)} = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}_{\text{initial, final}}. \quad (18)$$

Note that each column of the  $T$ -matrix and the matrix in total obey (15). That is, each equation in the form

$$a' + Ma = 0 \quad (19a)$$

where  $a$  is the column of two coefficients and  $M$  is some  $2 \times 2$  matrix, denotes simultaneously the equation

$$T' + MT = 0 \quad (19b)$$

for the  $T$ -matrix, assuming  $T=1$  at the initial point of the contour. It is fully equivalent to two integrations of (19a) described by the following scheme

$$a_{(i)} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \rightarrow a_{(f)} = \begin{pmatrix} T_{11} \\ T_{21} \end{pmatrix} \quad \text{and} \quad a_{(i)} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \rightarrow a_{(f)} = \begin{pmatrix} T_{12} \\ T_{22} \end{pmatrix}.$$

The use of (19b) instead of (19a) is justified because the  $T$ -matrix always possesses some useful properties. Typical are

$$\det T = 1 \quad (20)$$

resulting, provided  $\text{Tr } M = 0$ , from  $T = 1$  at the initial point, and the 'reversibility in time' property [8]

$$T^* = T^{-1} \quad (21)$$

which enables one to halve the interval of integration.

The quantization condition is really the condition of resolvability of the system of linear algebraic equations (17). In terms of the  $T$ -matrix and bearing in mind that for the case where the factors  $(d_{1,2})^{1/2}$  change sign upon circumventing the contour  $\Gamma$ , but  $\exp(iqx)$ ,  $\cos\beta$  and  $\sin\beta$  return to initial values, this condition becomes<sup>1</sup>

$$\det T + e_{\Gamma}^0(T_{11}e_{\Gamma}^- + T_{22}e_{\Gamma}^+) + (e_{\Gamma}^0)^2 = 0. \quad (22)$$

In contrast to definitions (14) and (16),  $e_{\Gamma}^{\pm}$  include definite integrals along the contour. Because the conditions (20) and (21) are fulfilled, we come to the quantization form (4) with

$$\mathcal{A}_{1,2} = \frac{l}{2i} \oint_{\Gamma} (\bar{Q} \pm Q) dq = \frac{l}{2i} \int_{\Gamma} (\bar{\theta} \pm \theta) d\tau = \frac{l}{2} \oint p_{1,2} dx. \quad (23)$$

The last equality in (23) is exact, because the impulses  $p_{1,2}$  are taken in the quasiclassical form in accordance with expression (9) for the saddle points. In such a way, the quantization condition (4) turns out to be exact for the model (5) provided the elements of the  $T$ -matrix are found exactly.

Consider now the modifications needed if the Landau-Zener-like system (12) of first-order equations is not available (this is so for some of the models of section 4), the second-order equation only. The latter for the  $C_2$  function can be written as

$$\left( \frac{d^2}{d\tau^2} - l^2\theta^2 - l\chi' \right) C_2 = 0 \quad (24)$$

where  $\theta^2 = \chi^2 + v^2$  and  $\chi' = d\chi/d\tau$ . If we look for a solution in the form

$$C_2 = \theta^{-1/2} [b_1 \exp(-l \int \theta d\tau) + b_2 \exp(l \int \theta d\tau)]$$

we obtain the equations

$$\left\{ \frac{d}{d\tau} - \frac{1}{2\theta} \begin{pmatrix} -\chi' & (\theta' - \chi')(e^+)^2 \\ (\theta' + \chi')(e^-)^2 & \chi' \end{pmatrix} \right\} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = 0 \quad (25)$$

(The redefinition  $b_1 = a_1\theta^{1/2} \sin\beta$ ,  $b_2 = a_2\theta^{1/2} \cos\beta$ , with  $\beta$  from (14), which would return us to (15), is impossible in the general case of non-constant  $v$ ).

In terms of the coefficients  $b_{1,2}$  we have

$$C = RDb \quad R = \frac{1}{v\theta^{1/2}} \begin{pmatrix} \chi + \theta & \chi - \theta \\ v & v \end{pmatrix} \quad (26)$$

with the diagonal matrix  $D$  from (13). Introducing the alternative  $\tilde{T}$ -matrix which, like (18), describes changes in the coefficients  $b_{1,2}$  along the contour  $\Gamma$  (and, according to the above, obeys equation (25)), one can again obtain a quantization condition in the

<sup>1</sup> It is necessary in this consideration that the contour  $\Gamma$  is either coincident with the phase curve or equivalent to it, i.e. circumvents the singularities of (15), including the branching points of the adiabatic potential, in just the same manner and has the initial and final points coincident in the  $q$ -plane.



form (4), but with the elements of the  $\tilde{T}$ -matrix. Naturally, this condition will describe just the same energy levels. Mathematically it is due to the similarity transformation (equations (13) and (26) were used)

$$(UR)^{-1}D_{\Gamma}TUR = D_{\Gamma}\tilde{T}, \quad D_{\Gamma} = \begin{pmatrix} e_{\Gamma}^{-} & 0 \\ 0 & e_{\Gamma}^{+} \end{pmatrix},$$

which conserves the trace of the product  $D_{\Gamma}\tilde{T}$  entering equation (22):

$$\begin{aligned} \text{Tr}(D_{\Gamma}T) &= 2 \bmod T_{11} \cos(\mathcal{A}_1 - \mathcal{A}_2 - \arg T_{11}) \\ &= \text{Tr}(D_{\Gamma}\tilde{T}) = 2 \bmod \tilde{T}_{11} \cos(\mathcal{A}_1 - \mathcal{A}_2 - \arg \tilde{T}_{11}). \end{aligned}$$

In such a way, equation (25) and (15) (provided the Landau-Zener-like form (12) is available) lead to different  $T$ -matrices,  $\tilde{T} \neq T$ , even on the same contour.

The most natural and analytical contour for computing the  $T$ -matrix is the phase curve  $q_1^*$  in the lower adiabatic term. When the lower adiabatic potential is single-well, this contour exists at all energies of physical interest. Unfortunately, this contour falls into two parts when the lower adiabatic potential becomes double-minimum, the energy being below the potential hump, and this is really the only parameter region where the quantization condition cannot be written in form (4).

Further generalizations can be considered as follows. Because the equations for the  $T$ -matrix in the eigenvalue problem should be integrated over restricted limits, no convergence problems exist, and the need to compute the trajectory equations for adiabatic amplitudes is circumvented. This enables us to avoid computations with branching functions and remove 'quasiclassical' restrictions on the contour of integration. As a result, the quantization function  $Q$  can be extended over the whole parameter region. These generalizations lead to significant simplifications of the method, suggesting that it may also be applicable to more complicated problems. For the example of the basic model, one can define a matrix describing, as (18), the changes in the column of functions  $G$  in (7) upon circumscribing the contour,  $G_{(t)} = TG_{(0)}$ . The system of linear differential equations  $G' + MG = 0$  (and  $T' + MT = 0$ ,  $T = 1$  initially), can easily be integrated numerically along the finite contour. The quantization condition becomes, in most general form

$$Q_C = \det T + 1 - \text{Tr} T = 0. \quad (27a)$$

For the case of equation (7)  $\text{Tr} M \neq 0$ , and  $\det T = \exp(2i(\mathcal{A}_1 + \mathcal{A}_2)) \neq 1$ . The complex quantization function  $Q_C = Q \exp(i(\mathcal{A}_1 + \mathcal{A}_2))$  is less convenient than the real one in a search for the energy levels, but computations of eigenfunctions are simplified, because (6) can be formulated directly in terms of the corresponding  $T$ -matrix (section 5). In order to have the quantization function in a real form, one must obtain (19b) with  $\text{Tr} M = 0$ . Besides (15) and (25) leading to (4), it may be an equation in the Landau-Zener form (12), but in general such a matrix  $M$  turns out to be asymmetric. The following real forms were also met in our calculations:

$$Q = \cos(\mathcal{A}_1 + \mathcal{A}_2) - \text{Tr} T/2 = 0 \quad (27b)$$

when  $T^* = T^{-1}$  and, as a consequence,  $T_{11} = T_{22}^*$ , and sometimes

$$Q = \cos(\mathcal{A}_1 + \mathcal{A}_2) - (T_{12} - T_{21})/2 = 0 \quad (27c)$$

provided the  $T$ -matrix satisfies some symmetry property (distinctive from the reversibility in time), so that  $T_{21} = -T_{12}^*$ .

For all models under consideration, the sum of adiabatic actions in (4) and (27b, c) is equal to the sum of diabatic actions:

$$\mathcal{A}_1 + \mathcal{A}_2 = \frac{i}{\hbar} \oint_{\Gamma} Q dq = \frac{i}{\hbar} \int_{\Gamma} \bar{\theta} d\tau = \mathcal{A}_+ + \mathcal{A}_-. \quad (28)$$

In turn, the latter can always be expressed through the full energy and the parameters of diabatic potentials. In particular, for the model (5) it is  $\mathcal{A}_+ + \mathcal{A}_- = \pi(E_1 + E_2)$ , where  $E_{1,2} = \epsilon_{1,2}$  are the energies with respect to the bottom of the diabatic terms.

#### 4. Other models

The three models available can be represented in the most obvious form of coupled radial oscillators by the equations ( $\hbar = \mu = 1$ )

$$\begin{pmatrix} \frac{d^2}{d\rho^2} + \frac{1}{\rho} \frac{d}{d\rho} + 2E_+ - \frac{(K+\Lambda)^2}{\rho^2} - \omega_+^2 \rho^2; 2V\rho^{2\Lambda} \\ 2V\rho^{2\Lambda}; \frac{d^2}{d\rho^2} + \frac{1}{\rho} \frac{d}{d\rho} + 2E_- - \frac{(K-\Lambda)^2}{\rho^2} - \omega_-^2 \rho^2 \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = 0 \quad (29)$$

where  $\Lambda = 0, \frac{1}{2},$  or  $1$ , and  $E_{\pm} = E \pm A$ ,  $\omega_{\pm}^2 = \omega^2 \pm \Delta$ . Among other numerous forms of this equation, that with coupled Morse-like potentials seems also of interest. Assuming  $\rho = \exp(-x/2)$  we have

$$\begin{pmatrix} \frac{d^2}{dx^2} + 2(\mathcal{E}_1 - \mathcal{U}_1(x)); 2\mathcal{V}_{12}(x) \\ 2\mathcal{V}_{21}(x); \frac{d^2}{dx^2} + 2(\mathcal{E}_2 - \mathcal{U}_2(x)) \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = 0 \quad (30)$$

where

$$\mathcal{E}_{1,2} = -(K \pm \Lambda)^2/8, \quad \mathcal{U}_{1,2} = (\omega_{\pm}^2/8) \exp(-2x) - E_{\pm}/4 \exp(-x)$$

and

$$\mathcal{V}_{12} = \mathcal{V}_{21} = (V/4) \exp(-x - \Lambda x)$$

in terms of the parameters of (29). Most general applications of the models are associated with the form (30). Because of the three different types of coupling possible in the system of diabatic potentials involving possible crossing, one can choose a model which leads to better results.

In applications, the models described by (29) and (30) should be considered in general as five-parametric. Compared to the model (5), the fifth additional independent parameter may be considered as arising due to the restricted number of bound states in Morse potentials. Some specific three-parameter cases  $\Delta = 0$ ,  $A = 0$ , at  $\Lambda = \frac{1}{2}, 1$  are also of physical interest and widely known: they represent, respectively, the simplest Jahn-Teller and Renner (for linear molecules) quantization problems. In more general form, equation (29) may serve as a starting point for a precise description of non-adiabatic effects in systems exhibiting pseudo-Jahn-Teller and Renner splitting. In particular, the application to Renner molecules looks very promising. The well-tried Hamilton equations of [32] (cf equation (12), (15) and (33)

therein) allowing for the effects of electron spins and the non-integral nature of the orbital angular momentum, upon neglecting  $\rho^4$  and higher terms, are just (29) at  $\Lambda=1$ . Depending on whether the adiabatic frequencies  $\omega_{1,2}=(\omega^2 \pm \varepsilon)^{1/2}$  (where  $\varepsilon=(\varepsilon_0^2 + \Delta^2)^{1/2}$ ,  $\varepsilon_0 \equiv 2V$ ) are: (i) both real; (ii)  $\omega_1$  is imaginary, and (iii) both are imaginary, equation (29) presents a simplified model of the linear, the linear in upper and bent in lower, and the bend in both adiabatic states molecule. In spite of our equation (29) describe in cases (ii) and (iii) the resonance and two-channel scattering processes, respectively, the transition (scattering) matrix can be estimated precisely by means of integration over a large enough portion of the infinite contour. Then the matrix may be used in the usual quasiclassical way [7] to describe bound states in modified potentials.

Assuming the definitions

$$r = \rho^2/2 \quad \Psi_+ = r^{(K+\Lambda)/2} \tilde{\Psi}_+ \quad \Psi_- = r^{(K-\Lambda)/2} \tilde{\Psi}_- \quad (31)$$

we rewrite (29) as

$$\begin{pmatrix} r(D^2 - \omega_+^2) + (K+1+\Lambda)D + E_+; 2^\Lambda V \\ 2^\Lambda V r^{2\Lambda}; r(D^2 - \omega_-^2) + (K+1-\Lambda)D + E_- \end{pmatrix} \begin{pmatrix} \tilde{\Psi}_+ \\ \tilde{\Psi}_- \end{pmatrix} = 0 \quad D = d/dr.$$

Looking for the solution as the integrals

$$\tilde{\Psi}_\pm = \int_r \exp(qr) G_\pm(q) dq \quad (32)$$

we come to the equations

$$\begin{pmatrix} s_+ D - W - A + (1-\Lambda)q; -2^\Lambda V \\ -2^\Lambda V (-D)^{2\Lambda}; s_- D - W + A + (1+\Lambda)q \end{pmatrix} \begin{pmatrix} G_+ \\ G_- \end{pmatrix} = 0 \quad (33)$$

where

$$s_\pm = q^2 - \omega_\pm^2 = s_0 \pm \Delta \quad s_0 = q^2 - \omega^2 \quad W = Kq + E$$

which are valid provided the increments of the out-of-integral terms along the contour are zero. The first of these is

$$\{\exp(qr) s_+ G_+\}_r = 0$$

but the second is

$$\{\exp(qr) s_- G_-\}_r = 0 \quad \Lambda = 0$$

or

$$\{\exp(qr) [s_- G_- + 2^{1/2} V G_+]\}_r = 0 \quad \Lambda = 1/2, \quad (34)$$

or

$$\{\exp(qr) [s_- G_- + 2V(rG_+ - dG_+/dq)]\}_r = 0 \quad \Lambda = 1.$$

System (33) is equivalent to one second-order equation for the function  $G_+$ . It looks simpler upon introducing the new function  $G$

$$G_+ = G \exp\left(\int (\bar{Q} - (1-\Lambda)q\Delta s^{-2}) dq\right)$$

where

$$\tilde{Q} = \begin{cases} s^{-2}(Ws_0 + A\Delta) & s^2 = s_0^2 - \Delta^2 & \text{when } \Lambda = 0 \\ s^{-2}(Ws_0 + A\Delta - F^2) & s^2 = s_0^2 - \Delta^2 & F \equiv V & \text{when } \Lambda = 1/2 \\ s^{-2}(Ws_0 + A\Delta) & s^2 = s_0^2 - \varepsilon_0^2 - \Delta^2 & \varepsilon_0 \equiv 2V & \text{when } \Lambda = 1 \end{cases}$$

and a new variable according to

$$d/d\tau = s^{1+\Lambda} d/dq. \tag{35}$$

This equation is again equation (24) ( $l=1$ ):

$$\left( \frac{d^2}{d\tau^2} - \theta^2 - \chi' \right) G = 0. \tag{36}$$

Here a prime signifies differentiation with respect to  $\tau$ , and

$$\theta^2 = s^{2(1+\Lambda)} Q^2 = \chi^2 + v^2 \quad \chi = (W\Delta + As_0)/s^{1-\Lambda} \tag{37}$$

where

$$v^2 = \begin{cases} V^2 & \Lambda = 0 \\ [F^4 - 2F^2(Ws_0 + A\Delta)]/s & \Lambda = 1/2 & F \equiv V \\ \varepsilon_0^2(W^2 - A^2) & \Lambda = 1 & \varepsilon_0 \equiv 2V. \end{cases} \tag{38}$$

We have also

$$Q = \begin{cases} (\tilde{Q}^2 + s^{-2}(A^2 - W^2 + V^2))^{1/2} & \Lambda = 0, \\ (\tilde{Q}^2 + s^{-2}(A^2 - W^2))^{1/2} & \Lambda = 1/2, 1. \end{cases} \tag{39}$$

At  $\Lambda = \frac{1}{2}, 1$ , the coupling parameter is contained either in  $\tilde{Q}^2$ , or in  $s^2$ .

Looking for the solution of (36) as

$$G = \theta^{-1/2}(b_1 e^- + b_2 e^+)$$

where

$$e^\pm = \exp\left(\pm \int \theta d\tau\right),$$

we come to (25) for coefficients  $b_{1,2}$  (and the  $T$ -matrix, remembering (19a, b)). The relations (34) are more complicated than (8) at  $\Lambda = \frac{1}{2}, 1$ , but the route to the quantization condition differs only in detail, and we come again to (4). It should be stressed once more that this is so until the 'phase curves' (which are the solutions of the equations for the saddle points,  $r + \tilde{Q} \pm Q = 0$ ).

$$q_{1,2}^* = -K/\rho^2 + iP_{1,2}/\rho \tag{40}$$

where

$$P_{1,2} = \left( 2(E \pm R(\rho)) - \frac{K^2}{\rho^2} - \omega^2 \rho^2 \right)^{1/2} \tag{41}$$

and

$$R(\rho) = \left( V^2 \rho^{4\Lambda} + \left( A - \frac{\Delta \rho^2}{2} \right)^2 \right)^{1/2}$$

or more general (but 'quasiclassically' equivalent) hand-made contours of integration

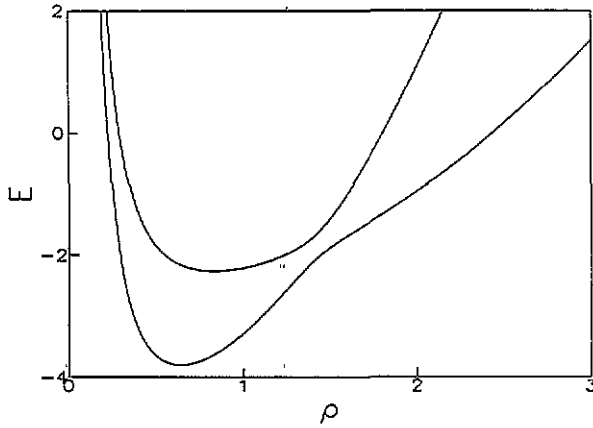


Figure 1. Adiabatic potential curves involving quasicrossing at  $E=2$ ,  $A=K=\Delta=0.5$ ,  $\omega=1$ , and  $V=0.1$  in equation (29). The case  $\Lambda=0, \frac{1}{2}$  and  $1$  are visually undistinguished.

are possible (cf sections 3 and 5).

Typical adiabatic potential curves involving quasi-crossing and described by (29) behave as shown in figure 1. The corresponding zeros and poles of the adiabatic potentials (39) in the  $q$ -representation are shown in figure 2. Note that the left part of figure 2 ( $\mathcal{A}_2^* = \infty$ , the two right poles are absent) corresponds to the four-parametric model of section 3. When the energy falls to the bottom of the upper adiabatic potential (i.e. the action  $\mathcal{A}_2$  becomes zero and then negative), the inner zeros 2 and 3 reach the segment  $[p_1, p_2]$  [8], and all further events are moved near it [9].

In the Renner case  $\Lambda=1$ , the four zeros of the adiabatic potential (39) are placed qualitatively as shown in figure 2, but at small  $A$  the zeros are grouped in pairs near

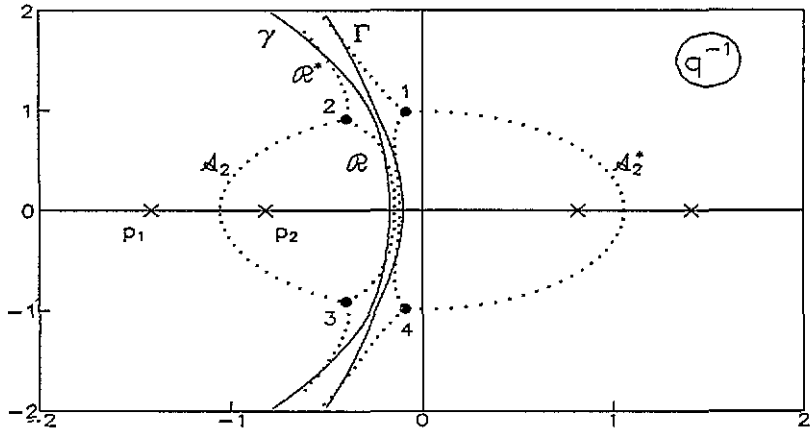


Figure 2. Pattern of zeros (1-4) and poles of adiabatic potential (39) (parameters the same as in figure 1), and anti-Stokes lines (dotted). The latter are labelled according to the four independent classical actions; the fifth one is the tunnelling factor  $\mathcal{D}$  calculated between the zeros 1-2 (or 3-4). The phase curves  $\Gamma$  (the locus of saddle points  $q_1^*$ , of equation (40)) and  $\gamma$  (that of  $q_2^*$ ) reveal quasicrossings.

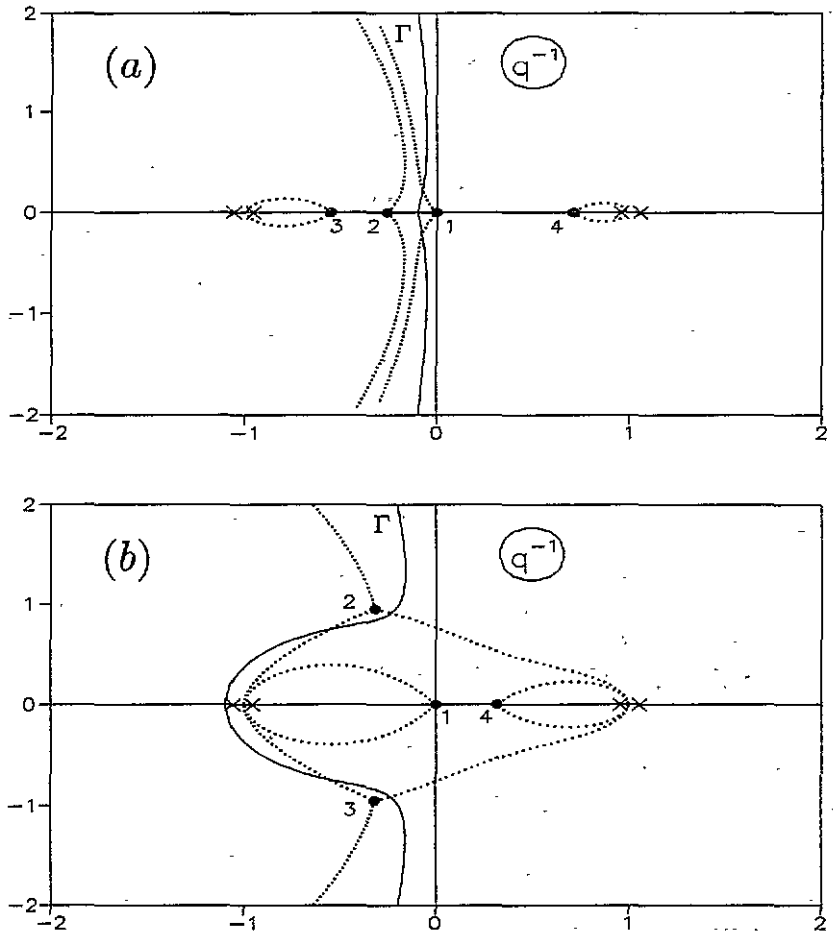


Figure 3. Typical Jahn-Teller ( $\Lambda = \frac{1}{2}$ ) patterns of zeros of the potential (39) for the case of high (a) and very deep (b) levels. Parameters the same as for 143th and 140th levels from [28], respectively, except small  $\Delta = 0.1$  introduced to split, visually, the poles.

$q^{-1} = K/E$  and  $q^{-1} = 0$ . The outer pair of poles or all the poles may lie on the imaginary  $q^{-1}$ -axis (resonance and two-channel scattering, respectively), then one or both contours  $\Gamma$  and  $\gamma$  become infinite. Note that the full potential in (36) involves, in general, six zeros in the  $q$ -plane (whereas its adiabatic part only four), and the treatment by means of comparison equations becomes too complicated and irrelevant to accuracy. Practically,  $A = \Delta = 0$  ( $\mathcal{R} = 0$ , cf figure 2) is the only parameter region where (36) may be considered analytically. We can expect in (1)  $\varphi \approx 0$  (unfortunately, undefined) and  $\mathcal{P} = \mu \exp(-2\mathcal{D})$ , where  $\mathcal{D} \approx \epsilon K^3/6E^2$  is a specific (non-Landau-Zener) factor, and  $\mu \approx 1$  should depend weakly on the actions  $\mathcal{A}_2$  and  $\mathcal{A}_2^*$  (cf [7] where at  $\mathcal{R} = 0$  and  $\mathcal{A}_2, \mathcal{A}_2^* \gg 1$  this result was obtained semi-classically, with  $\mu = 2$ ).

The specific Jahn-Teller ( $\Lambda = \frac{1}{2}$ ) schemes of zeros and poles for high and very deep levels (see section 5) are presented in figure 3. The action between the zeros 1-4,  $\mathcal{A}_2 + \pi K$ , is not the independent value for the simplest case  $A = \Delta = 0$  tested below.

## 5. Numerical tests

Unfortunately, only a few energy levels (to 2–3 decimal places in units  $\omega$ ) are available in the literature [33] for the four-parameter case of coupled parabolic terms. These and numerous levels [34] (to 1–2 decimal places) in the special three-parametric case  $k=0$  of equation (5) (i.e. in the symmetric potentials) are well described by asymptotic formulae [8] and cannot confirm unambiguously the exact expression (4). To test quantization formulae (4) and (27*a–c*), we have used numerous data from [28] and [29] (most to four decimal places) and [35] (to eight decimal places) obtained in the three different computational ways for the simplified two- and three-dimensional Jahn–Teller system. The corresponding radial equations are just equations (29) with  $\Lambda = \frac{1}{2}$ ,  $A = \Delta = 0$ ,  $\omega = 1$ , and the angular momentum  $K \equiv m$  [28] or  $K \equiv j + 1/2$  [35], respectively. Our parameter  $F \equiv V$  is related to  $a$  and  $a'$  of [28] and [29], respectively, as  $a = 2^{3/4}F$  and  $a' = 2F$ , and to the first-order coupling parameter  $D$  of Longuet-Higgins and Moffitt as  $D = F^2/2$ .

Although special estimations of actions  $\mathcal{A}_{1,2}$  in (4) are not needed for the model problems (for the case the sum  $\mathcal{A}_1 + \mathcal{A}_2$  is  $\pi(E + K + F^2/2)$  exactly and the difference  $\mathcal{A}_1 - \mathcal{A}_2$  is estimated simultaneously with the integration of (25) along the analytically given contours), the quasi-classical picture is rather instructive. It is also very convenient, especially in applications, to use the actions along the finite anti-Stokes and Stokes lines as the independent parameters characterizing the  $T$ -matrix. For the two-state quantization problem, the simplest possible set of such independent parameters consists of two classical actions,  $\mathcal{A}_1$  and  $\mathcal{A}_2$ , and the ‘tunneling’ factor  $\mathcal{D}$ . In terms of two actions,  $\mathcal{A}_2$  and  $\mathcal{D}$ , a rather general specification of the parameter regions can be given ( $\mathcal{A}_1 > 0$  for all levels). We will call the vibronic levels *high* ( $\mathcal{A}_2, \mathcal{D} > 0$ ), *low* ( $\mathcal{A}_2 < 0, \mathcal{D} > 0$ ) or *deep* ( $\mathcal{A}_2, \mathcal{D} < 0$ ).

For the Jahn–Teller problem, some of these cases were illustrated by figure 3. In the case of *low* levels, the zeros 2 and 3 are complex conjugate and the contour  $\lambda$  does not exist in the classically accessible region. For *deep* levels, when compared with figure 3(b), the contour  $\Gamma$  circumvents the poles from another ‘usual’ side. The quasiclassical contour  $\Gamma$  (phase curve) for *very deep* levels becomes, strictly speaking, invalid<sup>2</sup>. Nevertheless, some hand-drawn contours (cf. footnote in section 3) leading to the quantization condition in the ‘quasiclassical’ form (4) are possible. This is so because the outer zeros of the adiabatic potential in figures 2 and 3 are never fused in the case of single-well lower adiabatic potentials.

Practically, the integrations of (25) with elements of (37) and (38) were performed in the  $q$ -plane. All possible contours of integration lead to just the same energy levels, in spite of the fact that the  $T$ -matrices obtained may be quite unlike each other. Whereas the ‘middle’ anti-Stokes line (halving  $\mathcal{D}$ -factor) used as a contour (and possible for *high* and *low* levels only) results in the elements of the  $T$ -matrix being coincident qualitatively with the quasiclassical ones (of equation (1)), the contours along the phase curves  $q_1^*$  lead sometimes to very large mod  $T_{11}$  (more than 100 for the *very deep* 150th and 154th levels of [28]). The symmetry of the  $T$ -matrix in the high-energy region,  $T_{12} = T_{21}$  (which is equivalent to unitarity,  $T^+ = T^{-1}$ , characteristic of the scattering matrix), is only approximate. It is violated most strongly on the phase curves (as compared to anti-Stokes lines), and for lower levels. All  $T$ -matrices satisfying the equality (4),  $Q(E) = 0$ , can be obtained if to move the ‘matching point’

<sup>2</sup>In particular, it falls in some coordinate systems into two parts for motion ‘forward’ and ‘back’, in contrast to the ‘right’ and ‘left’ parts in the case of *deep* levels in the double-well potential (cf. section 3).

(that is the initial and final points of the contour) along the 'matching' line. But really, no numerical matching is needed: all matchings were performed analytically, the quantization condition being the result.

Most of our levels are coincident with those from [28] and [29] within the quoted precision, figure 4. Except the 26th level from [28] (perhaps misprinted), appreciable discrepancies appear at larger values of coupling parameter, where the differences  $\mathcal{A}_1 - \mathcal{A}_2$  are the largest and other methods fall down in precision [28]. Certainly, the difficulties in our method also rise with the increase of limits of integration in the equation for the  $T$ -matrix. Nevertheless, a guaranteed accuracy of at least  $10^{-12}$  at  $\mathcal{A}_1 - \mathcal{A}_2 \approx 10^2$  (i.e. at about 30 levels below the bottom of the upper adiabatic term [9]) is possible for the elements of the  $T$ -matrix and the energy levels in calculations with 16-byte complex numbers (about  $10^3$  steps of the Runge-Kutta procedure with local precision  $10^{-15}$  is needed). In particular, we have easily computed the exact energy levels  $E = 1$  ( $D = 1.5$ ) and  $E = -0.5$  ( $D = 2$ ) from [35] lying on Judd's base line [36] correct to 13 decimal figures. Attention was also paid to the last part of table 1 from [35] ( $D = 2.1-2.5$ ), where the largest errors in the level positions should be expected. Nevertheless, only sparse discrepancies with our results in the 8th decimal place were found (except for the few evident misprints, the following two being the most obvious).

Besides (25), the following equations were used ( $s = q^2 - \omega^2$ ,  $W = Kq + E$ ):

$$\frac{dT}{dq} + \frac{1}{s} \begin{pmatrix} -W + q/2, -2^{1/2}F \\ 2^{1/2}F(W - q/2)/s, -W + 2F^2/s + 3q/2 \end{pmatrix} T = 0 \quad (42)$$

fully equivalent to (33), and

$$\frac{dT}{dq} + \frac{1}{s} \begin{pmatrix} -F^2/s - q/2, -2^{1/2}F \\ 2^{1/2}F(W - q/2)/s, F^2/s + q/2 \end{pmatrix} T = 0 \quad (43)$$

obtained after eliminating the mean term. The contour of integration should circumvent the two left poles (of figures 2 and 3) (in the general case, the Laplace transforms of (29) possess five regular singular points). Besides that, equations (2.15 and 16) of [24] (or equation (3) and (4) of [25]) in the coherent states representation (and valid

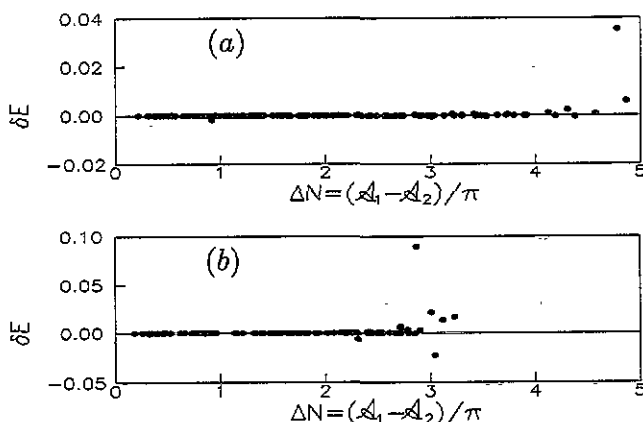


Figure 4. The energy level positions according to [28] (a) and [29] (b) in comparison with present results.



Table 1.

Level,	[35], table 1:	$D=2.1, n=5$	$D=2.2, n=23$
Energy,	[35]	0.44653700	3.34236908
	Present value:	0.44563700	3.24326908

also for the three-dimensional pseudo-Jahn-Teller problem) were used. For convenience, they can be rewritten as

$$\frac{dT}{dz} + \frac{1}{z(z-\kappa^2)} \begin{pmatrix} -(\varepsilon-\delta+\kappa^2)z, \kappa z(z+\varepsilon+\delta+j+1) \\ \kappa(z+\varepsilon-\delta), -(\varepsilon+\delta)z-\kappa^2(z+j+1) \end{pmatrix} T=0 \quad (44)$$

where

$$\delta=\frac{1}{4} \quad j=K-\frac{1}{2} \quad \varepsilon=(E-K-1)/2 \quad \kappa=F/2$$

in terms of our parameters, or (after excluding the mean term)

$$\frac{dT}{dz} + \frac{1}{z(z-\kappa^2)} \begin{pmatrix} \delta z + \kappa^2(j+1)/2, \kappa z(z+\varepsilon+\delta+j+1) \\ \kappa(z+\varepsilon-\delta), -\delta z - \kappa^2(j+1)/2 \end{pmatrix} T=0. \quad (45)$$

These equations should be integrated along any contour circumventing the two poles<sup>3</sup>.

Equations (42) and (44) result in the complex quantization condition (27a), whereas (43) and (45) lead to the real quantization function (27b). Because (42)–(45) are single-valued in the complex plane, calculations are extremely simple. It is sufficient to perform integrations either in the upper, or in the lower half-plane only.

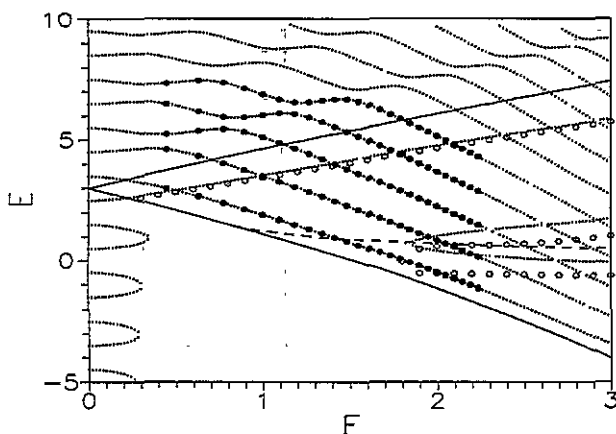


Figure 5. Pattern of energy levels (dotted) in the three-dimensional Jahn-Teller system described by radial equations (29) with  $\Lambda=\frac{1}{2}$ ,  $\omega=1$ ,  $A=\Delta=0$ ,  $K=j+\frac{1}{2}=3$ ,  $V=F$ . Solid lines: the bottom of upper ( $\mathcal{A}_2=0$ ) and lower ( $\mathcal{A}_1=0$ ) adiabatic terms; dashed line corresponds to  $\mathcal{Q}=0$ . Full circles: energy levels from [35]. Open circles: quasiclassical interpretation of the false energy levels, see the text.

<sup>3</sup> Just this same character of singularities (i.e. the two poles and irregular singular point in infinity) possess the Bessel transforms of (29) with  $\Lambda=\frac{1}{2}$  and  $\omega_+=\omega_-$ , which can be obtained combining the approaches of [7] and [8]. Besides the 'circle-like' contours, 'eight-like' contours are also possible. The two types of contour correspond to double degeneration of the energy levels in the simplest Jahn-Teller problem.

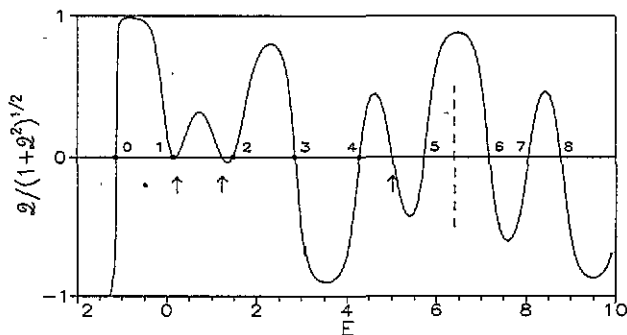


Figure 6. Quantization function (4), (27b, c) (reduced to unity interval). The parameters ( $D=2.5, j=2.5$ ) same as in the last column of data [35] in figure 5. Full circles: the zeros of  $Q$  corresponding to 'true' levels from [35]; Arrows: false levels. Dashed line indicates the bottom of upper adiabatic term.

The full  $T$ -matrix can be reconstructed by use of symmetry properties (the reversibility in time for the case of (42)–(45)).

The full pattern of energy levels is shown in figure 5, and in figure 6 typical example of the real quantization function is presented. Unfortunately, besides the familiar pattern of the 'true' energy levels [7, 37], all the quantization forms possess non-physical solutions, described qualitatively by (3b) with  $\mathcal{B} = (1 + \exp(2\mathcal{D}))^{-1}$  and  $\psi = \delta - \delta \ln |\delta| + \arg \Gamma(1/2 + \delta)$ ,  $\delta = \mathcal{D}/\pi$  (cf [9]). That is, the exact quantization forms reveal obviously quasiclassical properties.

False levels can be recognized easily on diagrams like figure 5: they are approximately parallel to the bottom of the upper adiabatic term, but the most straightforward way is to compute the eigenfunctions. Those corresponding to false levels are extremely depressed (see figure 7 where the overlap integrals  $\langle \Psi | \Psi \rangle = \langle \Psi_1 | \Psi_1 \rangle + \langle \Psi_2 | \Psi_2 \rangle$ ,  $\Psi_{1,2} = \Psi_{\pm} \pm \Psi_{\mp}$  were obtained immediately from (32) by use of (31)). The weakening is larger as the precision of calculations becomes higher, suggesting that the 'false' eigenfunctions are really equal to zero. Practically, it is sufficient in most cases to compare the non-normalized wavefunctions (32) near the turning points. The normalized adiabatic wavefunctions in the coordinate representation are shown in figure 8 and behave just as expected.

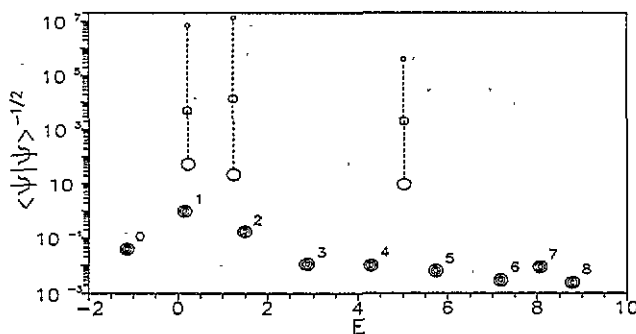
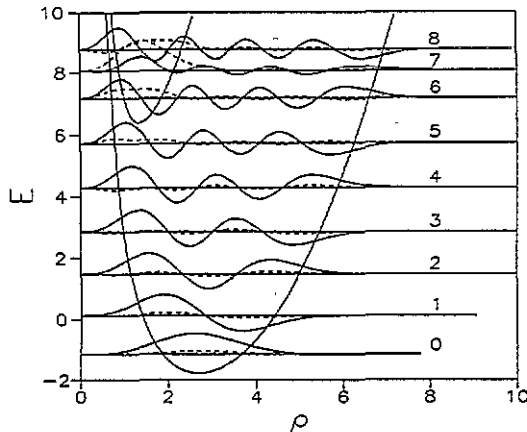


Figure 7. The behaviour of normalization factors for 'true', 0–8, and 'false' eigenfunctions depending on the precision of calculation:  $\delta E = 10^{-2}\omega$  (the largest circles) to  $\delta E = 10^{-6}\omega$ . Parameters same as in figure 6.



**Figure 8.** Adiabatic potential curves and normalized wavefunctions in the lower and upper adiabatic terms (solid and dashed lines, respectively; parameters same as in figures 6 and 7). The seventh function reveals evident membership of the lowest vibrational state in the upper adiabatic term.

## 6. Conclusion

The proposed method is extremely simple for model problems and can be used for testing other computational approaches. In practical applications of the method in its present form, some complications arise compared with use of the asymptotic quantization forms (1)–(2) because intermediate iterations are needed to bring into conformity the parameters of potentials and independent actions. Besides that, some uncertainty exists in identification of the parameters (independent actions) of real and model systems. In particular, this is because the relation  $\mathcal{A}_1 + \mathcal{A}_2 = \mathcal{A}_+ + \mathcal{A}_-$  between adiabatic and diabatic actions which takes place for all the models under consideration, is violated for arbitrarily chosen potentials etc. Nevertheless, an improvement of the earlier proposed approach [9] to the reconstruction of potential curves is possible by use of numerical  $T$ -matrices in the quantization conditions. Our preliminary estimations show that a mean square deviation in the energy level positions not worse than  $10^{-3}\omega$  is achievable in practice (remember that a value of about  $10^{-1}\omega$  corresponds to the initial approximation, whereas  $10^{-2}\omega$  provides a rather precise description of essentially coupled states [9]). Further progress is associated with the quantization form (27a) involving only the general characteristics of the  $T$ -matrix and seemingly applicable to more complicated problems which cannot be reduced to a pair of coupled first-order differential equations.

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