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On the quantisation of the two-dimensional harmonic oscillator with 2:1 resonance

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Abstract. Exact eigenfunctions, which simultaneously diagonalise the Hamiltonian of a 2:1 resonant, two-dimensional harmonic oscillator and an additional constant of the motion, cubic in the cartesian displacement coordinates and momenta, are found by direct solution of the Schrödinger equation in parabolic coordinates. The connection with the usual harmonic-oscillator cartesian basis is established and used in the formulation of a second-order perturbation theory for the oscillator with a particular form of non-linear coupling. Uniform semiclassical quantisation of the unperturbed oscillator is discussed.

1. Introduction

The two-dimensional anisotropic harmonic oscillator with 2:1 frequency ratio is the starting point for the investigation of vibrational motion in many molecular systems such as CO_2 (Fermi 1931). CO_2 is characterised by the so-called Fermi resonance between the two vibrational degrees of freedom. Model Hamiltonians (Noid *et al* 1979, Eaker and Schatz 1984) include various types of non-linear couplings, but in order to treat them, either perturbationally or semiclassically, a detailed understanding of quantum properties of the zero order, i.e. uncoupled, degenerate, system is necessary.

The Hamiltonian under consideration is of the form (we use the units in which $m = \hbar = \omega_y = 1$)

$$H = \tfrac{1}{2}(p_x^2 + p_y^2 + 4x^2 + y^2). \tag{1}$$

The corresponding Schrödinger equation is separable in (x, y) coordinates, reflecting the fact that the energies associated with each separable degree of freedom are integrals of motion. The wavefunctions $\psi_{n_x n_y}(x, y) = \psi_{n_x}(x)\psi_{n_y}(y)$ $(n_x, n_y = 0, 1, 2, \ldots)$ are the products of the usual one-dimensional harmonic oscillator eigenfunctions (Landau and Lifshitz 1977). The degeneracy of each energy level

$$E_n = 2n_x + n_y + \tfrac{3}{2} \equiv n + \tfrac{3}{2}, \qquad n = 0, 1, 2, \ldots, \tag{2}$$

is equal to $[n/2]+1$ ([ ] denotes the integer part of the number). As the analysis of the SU(2) symmetry of the problem suggests (Demkov 1963) it is more convenient to label the eigenfunctions $\psi_{n_x n_y}$ belonging to the same n-subspace by $\psi_{n,\mu}$, where

$$\mu = n_x - j, \qquad j = \tfrac{1}{2}[\tfrac{1}{2}n], \tag{3}$$

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so that for given n, μ takes on the values

$$\mu = -j, -j+1, \ldots, +j. \tag{4}$$

Note that for n of the form $n = 4l$, $4l+1$ (l integer), j is an integer, whereas for $n = 4l+2$, $4l+3$, j is a half-integer.

It has been shown by Noid *et al* (1979) that the Hamilton-Jacobi equation for the classical analogue of (1) allows for separation of variables in parabolic coordinates. The corresponding separation constant can then easily be expressed in terms of displacement coordinates and momenta in order to obtain an additional (classical) integral of motion. The (properly symmetrised) quantum analogue is given by

$$K = 2x(y^2 - p_y^2) + p_x(yp_y + p_y y). \tag{5}$$

If, in addition, one introduces creation and annihilation operators via relations

$$x, y = (2\omega_{x,y})^{-1/2}(a^+_{x,y} + a_{x,y}), \qquad p_{x,y} = \mathrm{i}(\tfrac{1}{2}\omega_{x,y})^{1/2}(a^+_{x,y} - a_{x,y}),$$

(in our units $\omega_x = 2$, $\omega_y = 1$) then the operators H and K can be written in the form

$$H = 2a_x^+ a_x + a_y^+ a_y + \tfrac{3}{2}, \tag{1a}$$

$$K = 2[a_x(a_y^+)^2 + a_x^+ a_y^2]. \tag{5a}$$

Thus, H and K form another pair of commuting operators and can be diagonalised simultaneously. The corresponding eigenfunctions can be found by solving the Schrödinger equation in parabolic coordinates. This is done in § 2. In § 3 the connection with the cartesian basis is established. This is then used in § 4 to find the perturbed spectrum of the oscillator with a particular small non-linear coupling. Section 5 contains remarks concerning the semiclassical quantisation of the unperturbed oscillator.

2. Solution of the Schrödinger equation in parabolic coordinates

Let us define the parabolic coordinates as

$$\begin{aligned} \eta &= [(x^2+y^2)^{1/2} - x]^{1/2}, \qquad 0 \leqslant \eta < +\infty, \\ \xi &= \operatorname{sgn} y[(x^2+y^2)^{1/2} + x]^{1/2}, \qquad -\infty < \xi < +\infty, \end{aligned} \tag{6}$$

where sgn y is the sign of y. There is a two-to-one correspondence between the points $(\xi, 0)$, $(-\xi, 0)$ in (ξ, η) configurational space and the points $(x, 0)$ $(x > 0)$ in (x, y) space. As such, for well behaved potentials, any wavefunction $\psi(\xi, \eta)$ in order to be uniform and smooth on the positive x axis should satisfy the following conditions:

$$\psi(\xi, 0) = \psi(-\xi, 0), \qquad \nabla\psi|_{(\xi,0)} = \nabla\psi|_{(-\xi,0)}, \tag{7}$$

for any ξ.

The time-independent Schrödinger equation for Hamiltonian (1) in parabolic coordinates reads

$$-\frac{1}{2(\xi^2+\eta^2)}\left(\frac{\partial^2}{\partial\xi^2} + \frac{\partial^2}{\partial\eta^2} - \xi^6 - \eta^6\right)\psi(\xi, \eta) = E\psi(\xi, \eta). \tag{8}$$

By representing the wavefunction in the form $\psi(\xi, \eta) = \phi_1(\xi)\phi_2(\eta)$, the variables can be separated in (8) with the resulting two one-dimensional equations

$$\mathrm{d}^2\phi_1(\xi)/\mathrm{d}\xi^2 + (2E\xi^2 - \xi^6 + k)\phi_1(\xi) = 0, \tag{9a}$$

$$\mathrm{d}^2\phi_2(\eta)/\mathrm{d}\eta^2 + (2E\eta^2 - \eta^6 - k)\phi_2(\eta) = 0. \tag{9b}$$

The separation constant k represents the eigenvalues of operator (5), whose differential form in parabolic coordinates is given by

$$K = \frac{1}{(\xi^2+\eta^2)}\left(\xi^2\frac{\partial^2}{\partial\eta^2} - \eta^2\frac{\partial^2}{\partial\xi^2} + \xi^6\eta^2 - \xi^2\eta^6\right). \tag{10}$$

The conditions imposed on functions $\phi_1(\xi)$ and $\phi_2(\eta)$ follow from the square integrability of $\psi(\xi, \eta)$ and conditions (7). The former demands that $\phi_1(\xi)\to 0$ when $\xi\to\pm\infty$ and $\phi_2(\eta)\to 0$ when $\eta\to+\infty$, whereas the latter for separable wavefunctions are equivalent to

$$[\phi_1(\xi) - \phi_1(-\xi)]\phi_2(0) = 0, \tag{11a}$$

$$(\mathrm{d}\phi_1/\mathrm{d}\xi|_\xi + \mathrm{d}\phi_1/\mathrm{d}\xi|_{-\xi})\phi_2(0) = 0, \tag{11b}$$

$$[\phi_1(\xi) + \phi_1(-\xi)]\,\mathrm{d}\phi_2/\mathrm{d}\eta|_0 = 0. \tag{11c}$$

It can be seen that (11b) follows from (11a), so that (11a) and (11c) are independent conditions which should be satisfied simultaneously. Since the symmetric double-well 'potential' in equation (9a) (k is assumed to be a spectral parameter) can support only eigenstates of even or odd parity, equations (11a) and (11c) immediately give the respective boundary conditions for $\phi_2(\eta)$ at $\eta = 0$; i.e. $\mathrm{d}\phi_2/\mathrm{d}\eta|_0 = 0$ or $\phi_2(0) = 0$. This result also reflects the fact that in defining the parabolic coordinates (6), the domains of variation of ξ and η can be interchanged (together with the factor sgn y).

Moreover, since in our case (9a) and (9b) formally differ only by the sign of the parameter k, the problem is reduced to solving for the eigenvalues k of one of the two one-dimensional boundary-value problems (say that associated with (9a)). In principle, one should solve for all the eigenvalues $k_q(E)$ ($q = 0, 1, \ldots$ is the number of zeros of the eigenfunction) of the one-dimensional problem as a function of E. Then the conditions

$$k_q(E) = -k_{q'}(E) \tag{12}$$

(where indices q and q' correspond to eigenfunctions of the same parity) would give the eigenvalues of both H and K. Actually, as shown below, due to the specifically simple form of the solutions of the one-dimensional problem which satisfy (12), they can be found in a more direct way.

One-dimensional problems of the type defined by (9a) have been investigated by many authors (see, e.g., Chaudhuri and Mukherjee (1984) and references therein). Following the usual scheme we look for the eigenfunctions of the form (hereafter we drop the index 1 in $\phi_1(\xi)$)

$$\phi(\xi) = u^{p/2}f(u)\exp(-u^2/4) \tag{13}$$

where $u = \xi^2$, $p = 0$ (1) for even (odd) states, and $f(u)$ is a function regular at $u = 0$. Substituting expression (13) in (9a) one finds the differential equation for $f(u)$:

$$4uf'' + 2(2p + 1 - 2u^2)f' + [(2E - 2p - 3)u + k]f = 0. \tag{14}$$

In principle, $f(u)$ should be sought in the form of an infinite power series of u. Here we will investigate under what conditions this series can be truncated, i.e. we look for $f(u)$ in the form of a polynomial:

$$f(u) = \sum_{s=0}^{N} a_s u^s. \tag{15}$$

By substituting (15) in (14), one finds that necessarily

$$E = 2N + p + \tfrac{3}{2} \tag{16}$$

and that the coefficients a_s satisfy the recurrence relations

$$4(N-s+1)a_{s-1} + ka_s + 2(s+1)(2s+2p+1)a_{s+1} = 0, \tag{17}$$

$$0 \leqslant s \leqslant N, \qquad a_{-1} = a_{N+1} = 0.$$

Note first that by setting $n = 2N + p$, equation (16) is equivalent to (2). Secondly, (17) defines a system of linear homogeneous equations, which has a non-trivial solution if the corresponding tridiagonal determinant is equal to zero:

$$D_{N+1} \equiv \begin{vmatrix} k & 2(2p+1) & 0 & & & \cdots & & & 0 \\ 4N & k & 4(2p+3) & 0 & & \cdots & & & 0 \\ 0 & 4(N-1) & k & 6(2p+5) & 0 & & \cdots & & 0 \\ 0 & & \cdots & & & 0 & 8 & k & 2N(2p+2N-1) \\ 0 & & \cdots & & & & 0 & 4 & k \end{vmatrix} = 0. \tag{18a}$$

The above polynomial equation for determining the eigenvalues k is of the form

$$k^{N+1} - b_{N-1}k^{N-1} + b_{N-3}k^{N-3} - \ldots = 0 \tag{18b}$$

with $b_i \geqslant 0$. As they are eigenvalues of a Hermitian operator, all the roots of (18b) are real. For given $n = 2N + p$, there are exactly $N + 1 = [n/2] + 1 = 2j + 1$ real eigenvalues, with the property that if k is an eigenvalue then so is $-k$, i.e. condition (12) is fulfilled. We see therefore that the problem of quantisation in parabolic coordinates is solved.

In analogy with (3) and (4) it is convenient to label the eigenvalues k_λ^n belonging to the same n-subspace by 'quantum numbers' λ:

$$\lambda = -j, -j+1, \ldots, +j. \tag{19a}$$

For given n there is a one-to-one correspondence between the numbers λ and eigenvalues k_n^λ, with the properties

$$k_{-j}^n < k_{-j+1}^n < \ldots < k_j^n, \qquad k_{-\lambda}^n = -k_\lambda^n. \tag{19b}$$

Similarly, from (13), we define

$$\phi_{n\lambda}(\xi) = \xi^p f_{n\lambda}(\xi^2) \exp(-\xi^4/4). \tag{20}$$

Note that for given n both $N = 2j$ and p are uniquely defined; in particular, $p = 0$ for n even, $p = 1$ for n odd. The real functions (20), being the eigenfunctions of the one-dimensional symmetric double-well problem, for fixed n, satisfy the orthogonality condition

$$\int_0^{+\infty} \phi_{n\lambda}(\xi)\phi_{n\lambda'}(\xi)\, \mathrm{d}\xi = c\delta_{\lambda\lambda'} \tag{21}$$

where c is a constant dependent on normalisation.

The simultaneous eigenfunctions of H and K can now be written as

$$\psi_{n\lambda}(\xi, \eta) = \phi_{n\lambda}(\xi)\phi_{n-\lambda}(\eta) \tag{22}$$

and satisfy the orthogonality condition

where the normalisation to unity is assumed.

All eigenvalues k_λ^n for $n < 10$ can be found analytically from (18*b*). They are given in table 1 and shown in figure 1, where in addition, their relation to the eigenvalues $k_q(E)$ of the one-dimensional double-well problem is indicated. Thus, the spectrum of the operator K is discrete, extends from $-\infty$ to $+\infty$ and is symmetric with respect to the infinitely degenerate eigenvalue $k = 0$. For $n \geqslant 10$, equation (18*b*) can easily be solved numerically.

With known eigenvalues k_λ^n, all the coefficients of the polynomials $f_{n\lambda}(u)$ can be expressed in closed form. This is shown in the appendix, where in addition the explicit expressions for the first few polynomials are given. From (14) simple expressions follow for polynomials corresponding to eigenvalues $k_0^n = 0$ (in that case $j = N/2$ is an integer):

$$f_{n0}(u) = \text{constant} \times L_j^{(\gamma)}(u^2/2) \tag{24}$$

where $\gamma = (2p-1)/4$ and $L_j^{(\gamma)}(z)$ are generalised Laguerre polynomials (Abramowitz and Stegun 1964).

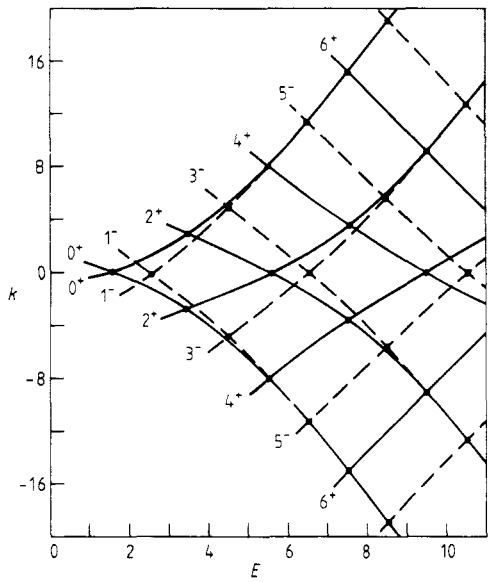

Figure 1. Coordinates of heavily marked dots give the quantised values of the energy $E = E_n$ and separation constant $k = k_\lambda^n$. Schematically also shown are the eigenvalues $\pm k_q(E)$ of the symmetric double-well problem (9*a*) corresponding to even (full lines) and odd (broken line) eigenstates. The labels $q^\mp (q = 0, 1, \ldots)$ denote the number of nodes and the parity of the corresponding eigenfunction.

Table 1. Eigenvalues k_λ^n for $n = 0, 1, \ldots, 9$. See also relations (19*a*, *b*).

n	j	$\lvert\lambda\rvert$	$(k_\lambda^n)^2/8$	n	j	$\lvert\lambda\rvert$	$(k_\lambda^n)^2/8$
0	0	0	0	5	1	0, 1	0, 16
1	0	0	0	6	$\frac{3}{2}$	$\frac{1}{2}, \frac{3}{2}$	$3(5 \mp 2\sqrt{5})$
2	$\frac{1}{2}$	$\frac{1}{2}$	1	7	$\frac{3}{2}$	$\frac{1}{2}, \frac{3}{2}$	$25 \mp 2\sqrt{109}$
3	$\frac{1}{2}$	$\frac{1}{2}$	3	8	2	0, 1, 2	$0, 4(10 \mp \sqrt{54})$
4	1	0, 1	0, 8	9	2	0, 1, 2	$0, 12(5 \mp \sqrt{11})$

3. Connection between the two bases

The normalised wavefunctions $\{\psi_{n\lambda}(\xi, \eta)\}$ and $\{\psi_{n\mu}(x, y)\}$, $(\lambda, \mu = -j, \ldots, +j)$ span the same n-subspace of the Hamiltonian H and are connected by the unitary $(2j+1)\times(2j+1)$ matrix $\boldsymbol{C}^n$:

$$|n\lambda\rangle = \sum_{\mu'=-j}^{+j} C^n_{\lambda\mu'}|n\mu'\rangle. \tag{25}$$

By acting with the operator K on both sides of (25) and projecting on the states $|n\mu\rangle$ one finds the system of equations determining the matrix elements of $\boldsymbol{C}^n$:

$$\sum_{\mu'}[\langle n\mu|K|n\mu'\rangle - k^n_\lambda \delta_{\mu\mu'}]C^n_{\lambda\mu'} = 0, \qquad \mu = -j, \ldots, +j. \tag{26}$$

The non-zero matrix elements of operator (5) or (5a) can be directly calculated by using standard one-dimensional harmonic oscillator matrix elements (Landau and Lifshitz 1977):

$$\langle n\mu|K|n\mu-1\rangle = \langle n\mu-1|K|n\mu\rangle = 2[(j+\mu)(n-2j-2\mu+1)(n-2j-2\mu+2]^{1/2}. \tag{27}$$

The tridiagonal determinant associated with the system (26) should be equal to zero. If one assumes that k^n_λ are unknown, this just gives another way to calculate the eigenvalues of operator K. In particular, the results of table 1 can be rederived. Note that here, unlike in (18a), the corresponding matrix is symmetric (real Hermitian).

Apart from being unitary the matrices $\boldsymbol{C}^n$ possess an additional symmetry which follows from the transformation properties of the two bases $\{|n\lambda\rangle\}$ and $\{|n\mu\rangle\}$ under reflections with respect to the x and y axes. Let us define the parity operators:

$$\Pi_1[(x, y)\to(-x, y)] = \Pi_1[(\xi, \eta)\to(\operatorname{sgn}\xi\eta, |\xi|)], \tag{28a}$$

$$\Pi_2[(x, y)\to(x, -y)] = \Pi_2[(\xi, \eta)\to(-\xi, \eta)], \tag{28b}$$

$$\Pi[(x, y)\to(-x, -y)] = \Pi_1\Pi_2. \tag{28c}$$

The action of these operators on the eigenfunctions is given by

$$\Pi_1|n\mu\rangle = (-1)^{j+\mu}|n\mu\rangle, \qquad \Pi_1|n\lambda\rangle = |n-\lambda\rangle, \tag{29a}$$

$$\Pi_2|n\mu\rangle = (-1)^n|n\mu\rangle, \qquad \Pi_2|n\lambda\rangle = (-1)^n|n\lambda\rangle, \tag{29b}$$

$$\Pi|n\mu\rangle = (-1)^{n+j+\mu}|n\mu\rangle, \qquad \Pi|n\lambda\rangle = (-1)^n|n-\lambda\rangle. \tag{29c}$$

Note that only Π_2 commutes with K. Of course, one can form symmetric and antisymmetric combinations of the vectors $|n\lambda\rangle$ and $|n-\lambda\rangle$ in order to construct the common basis of H, K^2 and Π.

Upon acting with Π_1 on both sides of (25) one derives the above-mentioned symmetry property:

$$C^n_{-\lambda\mu} = (-1)^{j+\mu}C^n_{\lambda\mu}. \tag{30}$$

Hence, it is sufficient to solve for $C^n_{\lambda\mu}$ with $\lambda \geqslant 0$ in order to obtain the matrix $\boldsymbol{C}^n$. For given n and k^n_λ closed-form expressions can be derived for the matrix elements $C^n_{\lambda\mu}$. These are given in the appendix together with the explicit form of the first few matrices $\boldsymbol{C}^n$.

4. Application to perturbation theory

In a number of papers (Noid *et al* 1979, Sanders 1981, Eaker and Schatz 1984) the quantum mechanical spectrum of the classically non-integrable Hamiltonian

$$\tilde{H} = H + \alpha V, \tag{31}$$

with H given by (1) and

$$V = x(y^2 + \beta x^2), \tag{32}$$

has been investigated by employing the various semiclassical methods of quantisation. Using the results of the preceding sections we derive below the quantum mechanical perturbation theory result up to second order in the coupling constant α. Of course, due to the cubic terms in (32) one can talk only about the quasi-stationary quantum states. For the present consideration of the low-lying part of the spectrum, we assume that all effects associated with the tunnelling into the continuum can be neglected.

Direct calculations show that the only non-zero matrix elements of the perturbation V in the $|n\mu\rangle$ basis are

$$\langle n\mu|V|n-6\mu-\tfrac{3}{2}\rangle = \langle n-6\mu-\tfrac{3}{2}|V|n\mu\rangle = \tfrac{1}{8}\beta[(j+\mu)(j+\mu-1)(j+\mu-2)]^{1/2}, \tag{33a}$$

$$\langle n\mu|V|n-4\mu\rangle = \langle n-4\mu|V|n\mu\rangle = \tfrac{1}{4}[(j+\mu)(n-2j-2\mu)(n-2j-2\mu-1)]^{1/2}, \tag{33b}$$

$$\langle n\mu|V|n-2\mu-\tfrac{1}{2}\rangle = \langle n-2\mu-\tfrac{1}{2}|V|n\mu\rangle = \tfrac{1}{4}(j+\mu)^{1/2}(2n-4j-4\mu+1)+\tfrac{3}{8}\beta(j+\mu)^{3/2}, \tag{33c}$$

$$\langle n\mu|V|n\mu-1\rangle = \langle n\mu-1|V|n\mu\rangle = \tfrac{1}{4}[(j+\mu)(n-2j-2\mu+1)(n-2j-2\mu+2)]^{1/2}. \tag{33d}$$

By comparing (33d) with (27) one concludes that within the given n-subspace operator equality holds: $V = K/8$ and therefore V is diagonal in the $\{|n\lambda\rangle\}$ basis. Hence perturbed energies can be labelled by

$$\tilde{E}_{n\lambda} = E_n + \alpha E^{(1)}_{n\lambda} + \alpha^2 E^{(2)}_{n\lambda} \tag{34}$$

and the first-order correction is given simply by

$$E^{(1)}_{n\lambda} = \tfrac{1}{8}k^n_\lambda. \tag{35}$$

Once the 'proper' basis of the degenerate zero-order Hamiltonian is known, the second-order energy shift is given by (Landau and Lifshitz 1977)

$$E^{(2)}_{n\lambda} = \sum_{n'\neq n} \frac{\Sigma_{\lambda'}|\langle n\lambda|V|n'\lambda'\rangle|^2}{E_{n'} - E_n}. \tag{36}$$

By substituting (25), (33a)-(33c) in (36) and using the unitarity properties of the matrix elements $C^n_{\lambda\mu}$ one derives the closed form result

$$E^{(2)}_{n\lambda} = -\tfrac{1}{64}\sum_{\mu=-j}^{+j} |C^n_{\lambda\mu}|^2 W(n,\mu) \tag{37a}$$

where

$$\begin{aligned} W(n,\mu) = {} & 15\beta^2(j+\mu)^2 + 9(n-2j-2\mu)^2 + 4(6\beta+1)(j+\mu)(n-2j-2\mu) \\ & + (15\beta^2+12\beta+2)(j+\mu) \\ & + (12\beta+11)(n-2j-2\mu) + \tfrac{11}{2}\beta^2 + 6\beta + 4. \end{aligned} \tag{37b}$$

By using the averaging method of classical mechanics (Bogoliubov and Mitropolsky 1961) and second quantisation, Sanders (1978) has derived an effective Hamiltonian (up to second order in α) which he then diagonalises in a given n-subspace in order to obtain the approximate eigenvalues of (31). By using the representation (5*a*) of the operator K one can conclude that the first-order result of Sanders is equivalent to ours, i.e. equation (35). The second-order term in the effective Hamiltonian of Sanders contains a factor of the form (37*b*). The only difference is that in the case of Sanders the last term in (37*b*) reads $15\beta^2/4+6\beta+13/4$. Obviously, the method based on classical mechanics fails to reproduce this term correctly. For large quantum numbers the difference is insignificant.

In tables 2 and 3, the energy levels, as calculated from equations (34) and (37*a*, *b*), are shown for two sets of parameters α and β. For comparison, also shown are the

Table 2. Energy levels of Hamiltonian (31) as predicted by various methods. E_0, unperturbed levels; E_p, present perturbational results; E_q, present quantum-variational results; E_{av}, results of Sanders (1981). Results are given in units used by Sanders (1981), so that $E_p = \omega\tilde{E}_{n\lambda}$, where $\omega = 0.7$ and $\tilde{E}_{n\lambda}$ is given by (34)-(37) with $\alpha = -0.04\omega^{-5/2}$, $\beta = -0.04$.

n	λ	E_0	E_q	E_p	E_{av}
0	0	1.050	1.0496	1.0496	1.0488
1	0	1.75	1.7476	1.7476	1.7409
2	$\frac{1}{2}$	2.45	2.4221	2.4224	2.4223
	$-\frac{1}{2}$	2.45	2.4709	2.4707	2.4709
3	$\frac{1}{2}$	3.15	3.1001	3.1007	3.1005
	$-\frac{1}{2}$	3.15	3.1847	3.1843	3.1846
4	1	3.85	3.7694	3.7706	3.7700
	0	3.85	3.8444	3.8445	3.8446
	−1	3.85	3.9081	3.9072	3.9079
5	1	4.55	4.4350	4.4370	4.4362
	0	4.55	4.5367	4.5369	4.5370
	−1	4.55	4.6316	4.6301	4.6311
6	$\frac{3}{2}$	5.25	5.0959	5.0990	5.0978
	$\frac{1}{2}$	5.25	5.2050	5.2065	5.2054
	$-\frac{1}{2}$	5.25	5.2683	5.2672	5.2685
	$-\frac{3}{2}$	5.25	5.3587	5.3565	5.3579

Table 3. Same as table 2, but for $\alpha = -0.08\omega^{-5/2}$, $\beta = -0.08$. E_{FT} are the results of the Fourier-transform based semiclassical method (Eaker and Schatz 1984).

n	λ	E_0	E_q	E_p	E_{av}	E_{FT}
0	0	1.050	1.0485	1.0485	1.0497	1.049
1	0	1.750	1.7404	1.7406	1.7476	1.745
2	$\frac{1}{2}$	2.45	2.3859	2.3883	2.3873	2.391
	$-\frac{1}{2}$	2.45	2.4863	2.4849	2.4865	2.477
3	$\frac{1}{2}$	3.15	3.0316	3.0371	3.0354	3.030
	$-\frac{1}{2}$	3.15	3.2070	3.2044	3.2067	3.209
4	1	3.85	3.6584	3.6702	3.6659	3.654
	0	3.85	3.8275	3.8285	3.8285	3.828
	−1	3.85	3.9495	3.9434	3.9487	3.946
5	1	4.55	4.2729	4.2928	4.2862	4.269
	0	4.55	4.4960	4.4988	4.4991	4.517
	−1	4.55	4.6884	4.6792	4.6863	4.683

present results of converged 'exact' quantum calculations (diagonalisation in the $|n\mu\rangle$ harmonic oscillator basis of 72 eigenfunctions), the above-discussed results of Sanders (1981) and the semiclassical results based on quantisation of classical action variables by means of the fast-Fourier transform method (Eaker and Schatz 1984). It can be seen that the agreement between the present perturbation results and 'exact' quantum calculations is very good for low-lying states. The largest improvement, as compared with the results of Sanders, is, as expected, for the ground and first excited states. At higher excitations the perturbational results are less accurate.

In the work of Noid *et al* (1979) there is a misprint which alters the sign of the parameter β in perturbation (29) (see the footnote in Wardlaw *et al* (1984)). Therefore, the results given in their tables I and II correspond respectively to $\beta = 0.08$ and $\beta = 0.04$ and should not be compared with the results shown in tables 2 and 3 (similarly to Sanders (1981) and Eaker and Schatz (1984)).

5. Semiclassical quantisation

Complete information on semiclassical spectra of both H and K can be obtained by considering one of the one-dimensional boundary value problems (9*a*, *b*), together with the additional condition (12). When applied to the symmetric double-well problem (9*a*), uniform semiclassical quantisation conditions (Child 1974) result in the following equation for determination of the eigenvalues k, corresponding, respectively, to even and odd eigenfunctions:

$$\gamma(E,k)-\tfrac{1}{2}\nu[-(2/\pi)\delta(E,k)]\pm\tfrac{1}{2}\tan^{-1}\{\exp[-2\delta(E,k)]\}=(n_{e,o}+\tfrac{1}{2}) \tag{38}$$

where $n_{e,o}=0, 1, 2, \ldots$ and

$$\nu(x)=-\nu(-x)=\arg\Gamma(\tfrac{1}{2}+\mathrm{i}x)+x(1-\ln|x|). \tag{39}$$

In equation (38) the phase integrals are defined as

$$\gamma(E,k)=\int_{\mathrm{Re}\,\xi_1(E,k)}^{\xi_2(E,k)} p(E,k,\xi)\,\mathrm{d}\xi, \tag{40a}$$

$$\delta(E,k)=\mathrm{i}\int_{0}^{\xi_1(E,k)} p(E,k,\xi)\,\mathrm{d}\xi, \tag{40b}$$

with

$$p(E,k,\xi)=(2E\xi^2-\xi^6+k)^{1/2}. \tag{41}$$

Above, $\xi_2>0$ is the turning point which is real for both $k\gtrless 0$, and ξ_1 satisfies $0<\xi_1<\xi_2$ for $k<0$ and $\mathrm{Re}\,\xi_1=0$, $\mathrm{Im}\,\xi_1>0$ for $k>0$. That branch of (41) is chosen which renders $\delta>0$ for $k<0$ and $\delta<0$ for $k>0$.

By noting that

$$\mathrm{i}p(E,k,\xi)=p(E,-k,\mathrm{i}\xi), \tag{42a}$$

$$\mathrm{i}\xi_1(E,k)=\xi_1(E,-k), \tag{42b}$$

one can prove the important relations

$$\delta(E,k)+\delta(E,-k)=0, \tag{43}$$

$$\gamma(E,k)+\gamma(E,-k)=\tfrac{1}{2}\pi E. \tag{44}$$

Equation (43) directly follows from (42*a*, *b*) and (41*b*), whereas the proof of (44) is more involved. By using contour integration in the complex ξ-plane one can show that the partial derivative with respect of k of the left-hand side of (44) vanishes for any k. Then $\gamma(E, 0)$ is easily calculated from (40*a*) to obtain the right-hand side of (44). As will be mentioned below, relation (44) also follows from other considerations.

Turning back to condition (12), we demand that if k is an solution of (38) for given E and $n'_{e,o}$ then $-k$ should also be the solution for the same E and some other $n''_{e,o}$. By using now (43) and (44) and the identity

$$\tan^{-1}[\exp(-x)]+\tan^{-1}[\exp(x)]=\tfrac{1}{2}\pi, \tag{45}$$

valid for any real x, one finds again the exact quantisation condition for the energy:

$$E = E_n = n+\tfrac{3}{2} \tag{46}$$

where $n=2(n'_e+n''_e)$ for even states and $n=2(n'_o+n''_o)+1$ for odd states.

Thus, semiclassical approximations of the eigenvalues k_λ^n of the operator K can be found from (38) in which $E=E_n$ and $n_{e,o}=j+\lambda=0, 1, \ldots, 2j$. Note that, whenever n is of the form $4l$, $4l+1$ (l integer), equation (38) gives the exact eigenvalue $k_0^n=0$.

Various approximate formulae can be derived from (38) (Child 1974, Bhattacharya 1985). For example, when $n \gg 1$ and k is not too close to zero, eigenvalues for say $\lambda<0$ are given by

$$k_\lambda^n = \tilde{k}_\lambda^n + (-1)^{n+1}\Delta_\lambda^n \tag{47}$$

where $\tilde{k}_\lambda^n$ is the solution of the equation

$$\tilde{\gamma}(E_n, k) \equiv \gamma(E_n, k) - \tfrac{1}{2}\nu[-(2/\pi)\delta(E_n, k)] = (j+\lambda+\tfrac{1}{2}) \tag{48}$$

and

$$\Delta_\lambda^n = \tfrac{1}{2}\exp[-2\delta(E_n, \tilde{k}_\lambda^n)][\partial\tilde{\gamma}/\partial k|_{k=\tilde{k}_\lambda^n}]^{-1}. \tag{49}$$

Note that here, since for given n all states are of well defined parity Π_2, one can talk only about the exponential shifts (49) rather than about the familiar exponential splittings in the one-dimensional symmetric double-well problem (see also figure 1).

Concluding this section we make a few remarks on 'quantising trajectories' of Hamiltonian (1) corresponding to quantised values of classical integrals of motion E and K. The analysis of these trajectories has been used by Noid *et al* (1979) as a starting point for quantisation of the near-integrable Hamiltonian (31). Noid *et al* define the classical action variables $I_\xi(E, k)$ and $I_\eta(E, k)$ based upon the separation of variables in the Hamilton–Jacobi equation in parabolic coordinates. These action variables are simply related to the phase integrals of the form (40*a*). In particular the relation (44) follows from the canonical invariance of the total action (Noid *et al* 1979)

$$I = (2\pi)^{-1}\oint_C \sum_i p_i\,\mathrm{d}q_i = E$$

where (p_i, q_i) is any set of canonically conjugate momenta and coordinates and C is, in this degenerate case, the trajectory. The action variables $I_\xi(E, k)$ and $I_\eta(E, k)$ have been quantised by applying the combination of approximate quantisation conditions of the form (48) (without the correction $\nu(x)$) and exact quantisation conditions for trajectories with $k=0$. As can be seen from figure 1 this is not a bad approximation even for small values of n. Actually, in situations like this when the exact quantised values of both $E=E_n$ and $k=k_\lambda^n$ are known, it is more correct to define the quantised

action variable simply as $I_\xi(E_n, k_\lambda^n)$ and $I_\xi(E_n, k_\lambda^n)$. In this way the quantum effects of tunnelling and over barrier reflection, present in the zero-order Hamiltonian, are effectively accounted for.

6. Concluding remarks

Some of the approaches used in the present work can be generalised to any two-dimensional harmonic oscillator with commensurate frequencies. Thus in the case $\omega_x/r = \omega_y/s = 1$ (r, s integers) the analogues of (1a) and (5b) would be

$$H = ra_x^+ a_x + sa_y^+ a_y + \tfrac{1}{2}(r+s),$$

$$K = \text{constant}[a_x^s (a_y^+)^r + (a_x^+)^s (a_y)^r].$$

One can then use the method of § 3 to derive the eigenvalues of K and the unitary transformation connecting the cartesian basis and the common eigenbasis of H and K.

On the other hand, the coordinate systems, different from cartesian, which allow the separation of variables in the Schrödinger equation seem to be known only when $r = s = 1$ (polar coordinates) and $r = 2$, $s = 1$ (parabolic coordinates).

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Appendix

For given $n = 2N + p$ and $k = k_\lambda^n$ all coefficients a_s of the polynomial (15) can be expressed from equation (17) in terms of a_0 (see also Chaudhuri and Mukherjee 1984):

$$a_s = (-1)^s [D_s/(2s+p)!] a_0, \qquad s = 1, 2, \ldots, N, \tag{A1}$$

where D_s is an $s \times s$ tridiagonal determinant with non-zero matrix elements

$$D_{i,i-1} = 4(N+2-i), \qquad D_{ii} = k, \qquad D_{i,i+1} = 2i(2i+2p-1), \qquad i = 1, 2, \ldots, s. \tag{A2}$$

D_s is obtained from D_{N+1}, equation (18a), by retaining the first s rows and s columns. From (17), the following recurrence relations can be derived:

$$D_s = kD_{s-1} - 4(N-s+2)(2s+p-2)(2s+p-3)D_{s-2} \tag{A3}$$

with $D_{-1} = 0$, $D_0 = 1$. The first few polynomials $f_{n\lambda}(u)$ are given in table 4.

The unitary matrices $\boldsymbol{C}^n$, connecting the $\{|n\lambda\rangle\}$ and $\{|n\mu\rangle\}$ bases, can be obtained by solving equations (26). For given n and $k = k_\lambda^n$ all coefficients $C_{\lambda\mu}^n$, $\mu = -j, \ldots, j-1$, can be expressed in terms of $C_{\lambda j}^n$:

$$C_{\lambda\mu}^n = (-\tfrac{1}{2})^{j-\mu} \left(\frac{(j+\mu)!}{(2j)!(n-2j-2\mu)!} \right)^{1/2} \Delta_{j-\mu} C_{\lambda j}^n \tag{A4}$$

Table 4. Polynomials $f_{n\lambda}(u)$, for $n = 0, 1, \ldots, 5$. Polynomials are normalised so that $a_0 = 1$ for each (n, λ).

n	j	λ	$f_{n\lambda}(u)$	n	j	λ	$f_{n\lambda}(u)$
0	0	0	1	4	1	0	$1-\frac{2}{3}u^2$
1	0	0	1			± 1	$1\mp 4u+2u^2$
2	$\frac{1}{2}$	$\pm\frac{1}{2}$	$1\mp\sqrt{2}u$	5	1	0	$1-\frac{2}{5}u^2$
3	$\frac{1}{2}$	$\pm\frac{1}{2}$	$1\mp\frac{1}{3}\sqrt{6}u$			± 1	$1\mp\frac{4}{3}\sqrt{2}u+\frac{2}{3}u^2$

where $\Delta_{j-\mu}$ is the $(j-\mu)\times(j-\mu)$ determinant obtained from the determinant of the homogeneous system of equations (26) by retaining the last $j-\mu$ columns and $j-\mu$ rows. The coefficient $C^n_{\lambda j}$ is fixed up to a phase by the unitarity condition

$$|C^n_{\lambda j}| = \left(\sum_{\mu=-j}^{+j} \frac{(j+\mu)!(\Delta_{j-\mu})^2}{2^{2j-2\mu}(2j)!(n-2j-2\mu)!} \right)^{-1/2} \tag{A5}$$

with the convention $\Delta_0 = 1$. From (A4) and (26) one derives the recurrence relations

$$\Delta_{j-\mu} = -k\Delta_{j-\mu-1} - 4(j+\mu+2)(n-2j-2\mu-3)(n-2j-2\mu-2)\Delta_{j-\mu-2} \tag{A6}$$

with $\Delta_{-1} = 0$. By identifying $n = 2N+p$, $2j = N$, $\mu = j-s$ and comparing with (A3) one finds that

$$\Delta_{j-\mu} = (-1)^s D_s. \tag{A7}$$

For $n = 0, 1, \ldots, 6$ the matrices $\boldsymbol{C}^n$ are listed below. Columns correspond to $C^n_{\lambda\mu}$ with $\mu = -j, \ldots, j$ and rows to $C^n_{\lambda\mu}$ with $\lambda = -j, \ldots, j$. Phases have been fixed so that $C^n_{\lambda -j} > 0$.

$$\boldsymbol{C}^0 = \boldsymbol{C}^1 = 1, \qquad \boldsymbol{C}^2 = \boldsymbol{C}^3 = \begin{bmatrix} \frac{1}{2}\sqrt{2} & -\frac{1}{2}\sqrt{2} \\ \frac{1}{2}\sqrt{2} & \frac{1}{2}\sqrt{2} \end{bmatrix},$$

$$\boldsymbol{C}^4 = \begin{bmatrix} \frac{1}{4}\sqrt{6} & -\frac{1}{2}\sqrt{2} & \frac{1}{4}\sqrt{2} \\ \frac{1}{2} & 0 & -\frac{1}{2}\sqrt{3} \\ \frac{1}{4}\sqrt{6} & \frac{1}{2}\sqrt{2} & \frac{1}{4}\sqrt{2} \end{bmatrix}, \qquad \boldsymbol{C}^5 = \begin{bmatrix} \frac{1}{4}\sqrt{5} & -\frac{1}{2}\sqrt{2} & \frac{1}{2}\sqrt{3} \\ \frac{1}{4}\sqrt{6} & 0 & -\frac{1}{4}\sqrt{10} \\ \frac{1}{4}\sqrt{5} & \frac{1}{2}\sqrt{2} & \frac{1}{4}\sqrt{3} \end{bmatrix},$$

$$\boldsymbol{C}^6 = \begin{bmatrix} \frac{1}{2} & -1/2r_1 & \frac{1}{2} & -1/2r_2 \\ \frac{1}{2} & -1/2r_2 & -\frac{1}{2} & 1/2r_1 \\ \frac{1}{2} & 1/2r_2 & -\frac{1}{2} & -1/2r_1 \\ \frac{1}{2} & 1/2r_1 & \frac{1}{2} & 1/2r_2 \end{bmatrix}, \tag{A8}$$

where $r_{1,2} = (5\mp 2\sqrt{5})^{1/2}$.

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