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Semiclassical quantization and resonance in spin tunnelling*

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Abstract. We derive a semiclassical quantization for a spin, study it for not too small a spin quantum number ($S \geqslant 5$), and compute the $2S+1$ eigenvalues of a Hamiltonian exhibiting resonant tunnelling as the magnetic field parallel to the anisotropy axis is increased. Special attention is paid to the resonance condition. As a corollary we prove that semiclassical quantization and quantum-mechanical perturbation theory agree there where they should.

1. Introduction

Resonance has revived the experimental interest in spin quantum tunnelling. The idea is both fascinating and simple [1–4]. Each molecule in, e.g. a Mn_{12} acetate crystal carries a spin of fixed angular momentum $10\,\hbar$ and experiences a constant magnetic field $\boldsymbol{H}$. The corresponding Hamiltonian is given by

$$\mathcal{H} = -\gamma S_z^2 - g\mu_B \boldsymbol{H}\cdot\boldsymbol{S}. \tag{1}$$

The first term on the right is a magnetic anisotropy. Now let $\boldsymbol{H} = (\alpha, 0, \delta)$ and absorb $g\mu_B$ into α and δ so that equation (1) reduces to

$$\mathcal{H} = -[\gamma S_z^2 + \delta S_z] - \alpha S_x \equiv -F(S_z) - \alpha S_x. \tag{2}$$

Here $\gamma > 0$ and we may assume $\alpha, \delta \geqslant 0$. By putting $\gamma := -\gamma$ we encounter a situation whose tunnelling physics and mathematics hardly changes and therefore need not be treated separately. In this paper, S_x and S_z have the dimension of angular momentum, to be measured in units $\hbar$. For the moment we suppose that the spin quantum number S is an integer.

The term αS_x tries to generate a rotation about the x-axis and thus aims at inducing a tunnelling transition. It certainly does so for $\delta = 0$. For arbitrary nonzero δ the degeneracy in the spectrum of S_z^2 is lifted and no tunnelling can occur *unless* a special choice of δ is made that restores the degeneracy. For $\alpha = 0$ a degeneracy exists, if $F(m\hbar) = F(n\hbar)$ for some integers m and n, i.e. putting $\gamma\hbar = \Gamma$,

$$\Omega_m^{(0)} \equiv -m^2\Gamma - m\delta = -n^2\Gamma - n\delta \equiv \Omega_n^{(0)}. \tag{3}$$

In passing we note that both Γ and δ have the dimension of frequency. Equation (3) tells us

$$(m^2 - n^2)\Gamma + (m-n)\delta = 0 \tag{4}$$

* Dedicated to Heinz Horner on the occasion of his 60th birthday.

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so that with $-S \leqslant m \neq n \leqslant S$ we are left with

$$(m+n)\Gamma + \delta = 0 \Rightarrow m + n = -\delta/\Gamma = -k \tag{5}$$

where $k \geqslant 1$ is chosen to be a positive integer. Hence $m = -n - k$. The remarkable aspect of this condition is that it can be realized for *all* n in the ballpark $-S \leqslant n \leqslant S - k$. Furthermore, degeneracy can be realized by a single choice, namely, $\delta = k\Gamma$. Here one has exploited the fact that the anisotropy is *quadratic* in S_z. The variable parameter δ is at the disposal of the experimentalist and the corresponding magnetic field is usually increased from minus to plus a few tesla. One then finds [1–4] several resonances inbetween. It is fair to say that the above set-up is indeed elegant. It is a corollary of semiclassical quantization, as treated in this paper, that the resonance condition (5) also holds for $\alpha \neq 0$. The (tiny) level splitting is a consequence of quantum mechanics.

Meanwhile resonance has been studied intensively. Those who invented it already initiated a first attempt [1] at its theoretical understanding. In an admirable tour de force, Chudnovsky and Garanin [5, 6] were able to fully analyse the influence of the heat bath provided by the surroundings of the spins on the tunnelling process if $\delta = 0$, and there is little doubt that their arguments can be generalized to the $\delta \neq 0$ case. Here we assume a much lower temperature so that the heat bath can be neglected. The analysis of semiclassical quantization, including resonance, is the main theme of this paper. It yields the energy eigenvalues of the Hamiltonian (2) to a good approximation and thus completes our earlier work [7–9] on the Wentzel, Kramers and Brillouin (WKB) formalism for spins; we refer the reader to the excellent review [10] for additional information regarding the experimental and theoretical context. In section 2 we reconsider the WKB formalism and indicate the use of the WKB wavefunctions in computing the level splitting at resonance. We then treat semiclassical spin quantization (section 3) and determine (section 4) the energy eigenvalues for arbitrary external field, i.e. δ. In section 5 we extend the results to half-integer spin quantum numbers and Hamiltonians in which the term αS_x is replaced by αS_x^l with $l > 1$. The conclusion is that semiclassical quantization holds here too, but that for even l the condition (3) may correspond to true degeneracy; that is, no resonance and no tunnelling. We end the paper with a discussion (section 6).

2. WKB and resonance

The eigenvalues and eigenvectors of the Hamiltonian (2) are solutions of the eigenvalue equation $\mathcal{H}\psi = E\psi$. The S_z axis being the main anisotropy axis, it is natural to write this equation in a representation with S_z diagonal. Then S_z is simply $s = n\hbar$, a multiplication operator on the spectrum of S_z. Furthermore, let $T_{\pm\hbar}$ induce a translation by $\pm\hbar$ so that $(T_{\pm\hbar}\psi)(s) = \psi(s \pm \hbar)$. Then S_x reads

$$S_x = \tfrac{1}{2}(S_+ + S_-) = \tfrac{1}{2}\left[a\left(\sqrt{s(s+\hbar)}\right)T_{\hbar} + a\left(\sqrt{s(s-\hbar)}\right)T_{-\hbar}\right] \tag{6}$$

where $a(s) = [\sigma(\sigma+\hbar) - s^2]^{1/2}$. As a consequence, the Schrödinger equation assumes the form of a second-order difference equation,

$$h_{n,n-1}\psi_{n-1} + h_{n,n+1}\psi_{n+1} + (h_{nn} - E)\psi_n = 0. \tag{7}$$

The matrix elements and the vector components are taken in the basis of the eigenvectors of S_z, and (7) is valid for $-S+1 \leqslant n \leqslant S-1$. Disregarding the remaining two equations, relation (7) has two linearly independent solutions for *any* value of E; they are determined

by fixing, e.g. ψ_0 and ψ_1. The $2S+1$ eigenvalues of $\mathcal{H}$ are singled out by requiring that ψ satisfy the boundary conditions

$$h_{\pm S,\pm(S-1)}\psi_{\pm(S-1)} + (h_{\pm S,\pm S} - E)\psi_{\pm S} = 0. \tag{8}$$

Equivalently, we can extend (7) to $n = \pm S$ by defining arbitrary real $h_{\pm S,\pm(S+1)} = h_{\pm(S+1),\pm S}$ and imposing the boundary conditions $\psi_{\pm(S+1)} = 0$.

If $\alpha = 0$, the eigenvectors are those of S_z and the eigenvalues equal $\overline{h}\Omega_n^{(0)}$ with n ranging from $-S$ to S; cf equation (3). It is interesting to note that, unless degeneracy (3) occurs, with increasing energy the eigenvectors are alternately localized on the 'right' ($n > 0$) or on the 'left' ($n < 0$). Far from degeneracy an approximate localization on alternating sides remains true for a nonvanishing α, if $\alpha \ll \Gamma S + \delta$, which is supposed throughout the paper.

By varying δ, neighbouring eigenvalues can get very close to each other, although true degeneracy cannot occur [11]. As we discuss below, the mechanism of the avoided level crossing is spin tunnelling. When two eigenvalues become as close as possible, we speak of a *quantum-mechanical resonance*. This has to be distinguished from what we call a *semiclassical resonance*, which we understand to be the coincidence of semiclassical eigenvalues. We shall prove in section 4 that the condition for a semiclassical resonance remains (3). Apart from the resonance at $\delta = 0$, we cannot expect that the two definitions predict the same 'resonant' values for δ. Because, however, semiclassical eigenvalues nicely approximate the true ones, only a small 'fine tuning' of δ may be necessary to pass from semiclassical to true, quantum-mechanical, resonance. In the remaining part of this section we explain how one can estimate the level splitting at resonance.

Let us choose δ close to a resonant value and let $E_1 < E_2$ be two (unknown) neighbouring, nearly degenerate, eigenvalues. Let us also imagine that we are given two linearly independent vectors $\eta(E)_n$ and $\vartheta(E)_n$ which depend continuously on E and solve (7). To avoid all confusion, we emphasize that no linear combination of them satisfies the boundary conditions (8) and, hence, the eigenvalue equation, if E is not an eigenvalue. On the other hand, the eigenvector belonging to E_1 is a linear combination of $\eta(E_1)$ and $\vartheta(E_1)$, and its analogue holds for E_2. Let $E_1^{(\mathrm{sc})}$ and $E_2^{(\mathrm{sc})}$ be the semiclassical eigenvalues corresponding to E_1 and E_2, respectively. Because all four energies are now close to each other, we can replace $\eta(E_1)$ and $\eta(E_2)$ by $\eta(E_1^{(\mathrm{sc})})$, and $\vartheta(E_1)$ and $\vartheta(E_2)$ by $\vartheta(E_2^{(\mathrm{sc})})$, or *vice versa*. In this way, finding E_1 and E_2 *and* the corresponding eigenvectors reduces to good approximation to diagonalizing $\mathcal{H}$ in a two-dimensional subspace. In so doing, we can use the WKB method to obtain $\eta(E)$ and $\vartheta(E)$.

Though WKB never considered spins, their idea is also applicable here, provided one generalizes the formalism appropriately [7–9] so as to take care of the discrete nature of a spin and its different commutation relations, as compared with a particle. A semiclassical analysis formally means that we take the limit $\overline{h} \to 0$ and at the same time $S \to \infty$ in such a way that $\overline{h}S = \sigma$ remains constant. In this limit we are left with a continuum description with s ranging in the interval $[-\sigma, \sigma]$. In the spirit of WKB we now make the ansatz $\psi = \exp(\mathrm{i}\mathcal{S}/\overline{h})$ with

$$\mathcal{S} = \mathcal{S}_0 + \sum_{n=1}^{\infty} \left(\frac{\overline{h}}{\mathrm{i}}\right)^n \mathcal{S}_n \tag{9}$$

for the wavefunction we are looking for, expand everything in powers of $\overline{h}$, and usually stop after the first-order term, the zeroth-order one being dominant. So *de facto* we use a continuum description, even though $\overline{h}$ is still finite.

The dominant contribution to tunnelling comes from the classically forbidden region, say, between the inner turning points $b_1 < b_2$. In this interval the two linearly independent

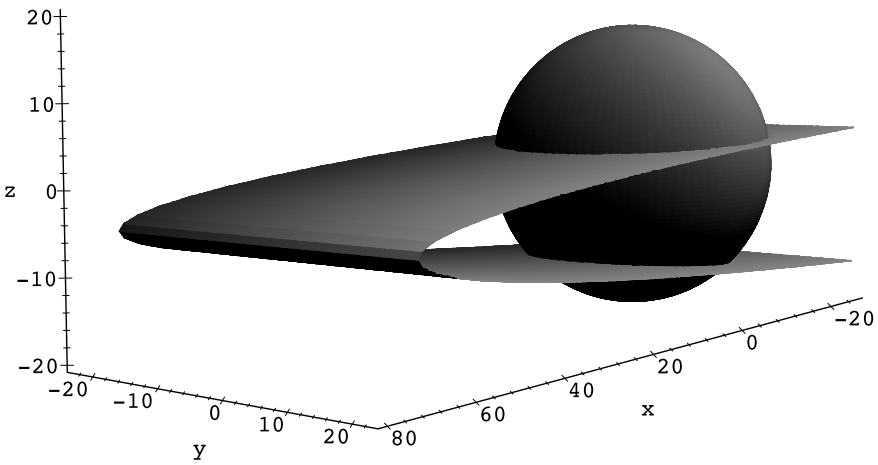

Figure 1. Classical orbits of the Hamiltonian $\mathcal{H} = -\gamma S_z^2 - \delta S_z - \alpha S_x$ are the intersection(s) of the energy surface $E = -\gamma S_z^2 - \delta S_z - \alpha S_x$ and the sphere $S_x^2 + S_y^2 + S_z^2 = \sigma^2$, here plotted for $S = 20$, $\hbar = \alpha = \gamma = 1$, $\delta = 10$, and $E = -50$.

WKB wavefunctions read [7–9]

$$\phi_{E,l}(s) = C_l \exp -\frac{1}{\hbar} \int_{b_1}^{s} \mathrm{d}s' \ \operatorname{arccosh}\left(\frac{-E - F(s')}{\alpha a(s')}\right) \tag{10}$$

and

$$\phi_{E,r}(s) = C_r \exp -\frac{1}{\hbar} \int_{s}^{b_2} \mathrm{d}s' \ \operatorname{arccosh}\left(\frac{-E - F(s')}{\alpha a(s')}\right). \tag{11}$$

Here $C_{l,r}$ are normalization constants and the arccosh expression stems from $\mathcal{S}_0$ in (9). As can be seen from figures 1 and 2, there are four turning points on the $s := S_z$ axis, two inner ones, b_1 and b_2, and two outer ones, a_1 and a_2. The inner turning points, b_1 and b_2, are boundaries of the classically allowed motion to the left and right of them, respectively, such that here the argument of the hyperbolic cosine equals 1. The functions depend continuously on the (classical) energy E. By using appropriate connection formulae, both can be extended to the whole interval $[-\sigma, \sigma]$, and the functions obtained in this way are almost perfectly localized on the left and on the right, respectively. Indeed, between b_1 and b_2 equations (10) and (11) define, respectively, a rapidly decaying and a rapidly increasing function. Localization of the extended solutions then follows from $\phi_{E,l}(b_1) \gg \phi_{E,l}(b_2)$ and $\phi_{E,r}(b_1) \ll \phi_{E,r}(b_2)$. For later use we note that the two functions are not orthogonal to each other and, because of the localization, their tiny overlap comes essentially from the classically forbidden region.

If we restrict $\phi_{E,l}(s)$ and $\phi_{E,r}(s)$ to the discrete values $s = n\hbar$ with integer n between $-S$ and S, we obtain the two vectors $\eta(E)$ and $\vartheta(E)$. Our earlier discussion shows that, if E happens to be an eigenvalue far enough from other eigenenergies, then $\phi_{E,l}$ or $\phi_{E,r}$ alone is a good approximation of the corresponding eigenvector. Returning to the problem of resonance, we can find E_1 and E_2 by diagonalizing $\mathcal{H}$ in the subspace spanned by, say, $\phi_{E_1^{(\mathrm{sc})},l}$ and $\phi_{E_2^{(\mathrm{sc})},r}$. Close to the semiclassical resonance (3) there exist integers $m < 0 < n$ such that these functions are localized near $m\hbar$ and $n\hbar$, respectively. We shall use the shorthand ϕ_m and ϕ_n for them. Let χ denote the matrix of $\mathcal{H}$ so that $\chi_{ij} = \langle\phi_i|\mathcal{H}|\phi_j\rangle$, and let o be the overlap matrix with elements $o_{ij} = \langle\phi_i|\phi_j\rangle$, where $i, j \in \{m, n\}$. We recall that

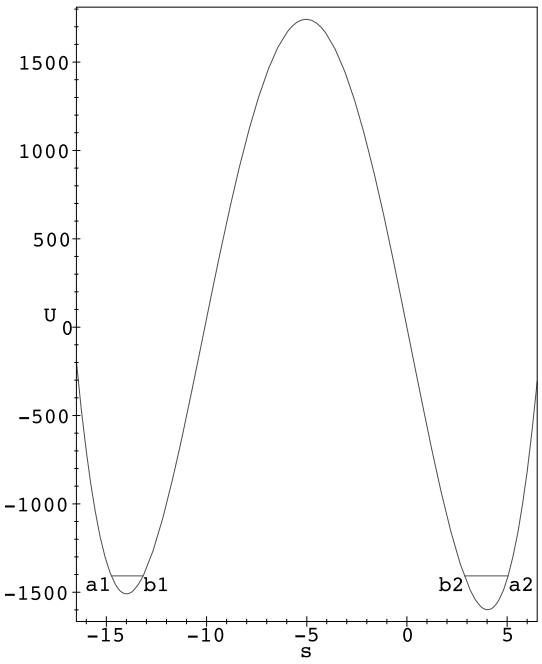

Figure 2. The effective, quartic double-well potential $U(s)$ given by equation (21) has been plotted for $\hbar = \alpha = \gamma = 1$, $\delta = 10$, and $E = -56.7$. For $S = 20$, $E = E_{-14} = E_4$; that is, the levels -14 and 4 are at resonance. The two horizontal segments are located at the 'energy' level $\mathcal{E} = (S^2 - E^2)/2$. They end up in the turning points, which limit the classical motion. U'' is about 1% bigger in the minimum on the right than in the minimum on the left.

o_{mn} is nonvanishing, although very small; we shall estimate it below. There is no harm in supposing ϕ_m and ϕ_n to be normalized.

We now turn to an explicit calculation of the quantum-mechanical level splitting. To a good approximation [7–9], E_1 and E_2 agree with the eigenvalues E_- and E_+ of the 2×2 matrix

$$o^{-1}\chi = \frac{1}{1 - o_{mn}^2} \begin{pmatrix} \chi_{mm} - \chi_{mn}o_{mn} & \chi_{mn} - \chi_{nn}o_{mn} \\ \chi_{mn} - \chi_{mm}o_{mn} & \chi_{nn} - \chi_{mn}o_{mn} \end{pmatrix}. \tag{12}$$

Namely, expand the eigenfunctions in terms of ϕ_m and ϕ_n and take matrix elements. For the eigenvalues we find

$$E_\pm = \frac{1}{2(1 - o_{mn}^2)}(\chi_{mm} + \chi_{nn} - 2\chi_{mn}o_{mn} \pm D) \tag{13}$$

where

$$D = [(\chi_{mm} - \chi_{nn})^2 + 4(\chi_{mn} - \chi_{mm}o_{mn})(\chi_{mn} - \chi_{nn}o_{mn})]^{1/2}. \tag{14}$$

Let $(x_\pm, y_\pm)$ denote the eigenvectors of $o^{-1}\chi$ corresponding to $E_\pm$. That is, the approximate eigenvectors of $\mathcal{H}$ are $x_\pm\phi_m + y_\pm\phi_n$. For $r_\pm = x_\pm/y_\pm$ an elementary computation yields

$$r_\pm^2 = \frac{\chi_{nn} - E_\pm}{\chi_{mm} - E_\pm} \tag{15}$$

and, by orthogonality, $r_+r_- = -1 - (r_+ + r_-)o_{mn}$. Near resonance equations (13) and (15) provide improved eigenvalues and eigenvectors as compared with the semiclassical ones.

We now have to tune δ to quantum-mechanical resonance. Supposing χ_{mn} is of the order of the overlap, the second term under the square root in (14) is of order o_{mn}^2. The overlap is a smooth function of δ and remains uniformly small in the small region where we vary δ. So the minimal distance between E_+ and E_- is reached when $\Delta_{mn} = \chi_{mm} - \chi_{nn}$ vanishes (or is also of order o_{mn}). Thus we conclude that the quantum-mechanical level splitting is of order o_{mn}. The order of magnitude of o_{mn} is easily inferred from equations (10), (11). For this estimate we may suppose $E = E_1^{(\mathrm{sc})} = E_2^{(\mathrm{sc})}$. Then

$$o_{mn} = C \exp -\frac{1}{\hbar} \int_{b_1}^{b_2} \mathrm{d}s \ \operatorname{arccosh}\left(\frac{-E - F(s)}{\alpha a(s)}\right) \tag{16}$$

where C is a constant of order 1. The exponential factor in o_{mn} can be interpreted as a transition probability. This suggests to write the level splitting $\Delta E = E_+ - E_-$ in the form

$$\Delta E = \frac{\pi\hbar}{\tau_0} \exp -\frac{1}{\hbar} \int_{b_1}^{b_2} \mathrm{d}s \ \operatorname{arccosh}\left(\frac{-E - F(s)}{\alpha a(s)}\right) \tag{17}$$

where $1/\tau_0$ is an attempt frequency. Recalling the expression of the hyperbolic cosine in terms of a natural logarithm and using $b_1 \approx m\hbar$ and $b_2 \approx n\hbar$, we find the order-of-magnitude estimate

$$\Delta E = \frac{\pi\hbar}{\tau_0} \left[\frac{\alpha S}{\Gamma(m^2 + n^2) + \delta(m + n)}\right]^{n-m} . \tag{18}$$

By identifying τ_0 with the time period of the classical motion—see equation (22) below—equations (17) and (18) become fully explicit. For δ_0 and $n = -m = S$ they agree, respectively, with formulae (C.11) and (C.12) in appendix C of our earlier work [8]. In that case (17) leads to a remarkably precise result, as can be seen in table 1 of [8]. Equation (17) was also obtained [9] by an independent argument.

Of course δ can be chosen to let Δ_{mn} vanish. The reason is that $\chi_{mm} \approx E_1^{(\mathrm{sc})}$ and $\chi_{nn} \approx E_2^{(\mathrm{sc})}$ (the small deviation coming from the fact that ϕ_m and ϕ_n do not satisfy the boundary conditions (8)), and *semiclassical* eigenvalues do cross each other at resonance. Thus $\Delta_{mn} = 0$ for a δ close to $-(m+n)\Gamma$. In particular, because of a reflexion symmetry of the Hamiltonian, the level pairs $\{m = -n, n\}$ are at semiclassical *and* quantum-mechanical resonance, once $\delta = 0$.

The origin of the level splitting is spin tunnelling. At quantum-mechanical resonance $|r_\pm| = 1$ and thus the approximate eigenfunctions are $\psi_\pm = (\phi_m \pm \phi_n)/\sqrt{2}$. If we start on the left, we take $\phi_m = (\psi_+ + \psi_-)/\sqrt{2}$. This state evolves under the influence of the dynamical evolution generated by $\exp(\mathrm{i}t\mathcal{H}/\hbar)$. After a time T given by equation (17) through $T\Delta E = \pi\hbar$, the system is in $\phi_n = (\psi_+ - \psi_-)/\sqrt{2}$, i.e. on the right. All this is exactly as in the case with a reflection symmetry $S_z \leftrightarrow -S_z$ such as when $\delta = 0$. In the corresponding classical problem an approximate reflection symmetry survives for remarkably high values of δ ($\delta \leqslant 10\Gamma$) with a shifted center of symmetry; cf figure 2. Because of this approximate symmetry and for low enough energies, the attempt frequencies in the two, now different, orbits centred at m and n are hardly different; see equation (22) below. This fact is crucial for the interpretation of τ_0 in the level splitting formula (17).

3. Semiclassical quantization

Semiclassical quantization of a single spin can be handled straightforwardly since we always find closed orbits—if any—as the intersection of the energy surface $\mathcal{H} = -[\gamma S_z^2 + \delta S_z] - \alpha S_x \equiv E$ and the sphere $\boldsymbol{S}^2 = S_x^2 + S_y^2 + S_z^2 \equiv \sigma^2$; cf figure 1. Here the classical

equations of motion associated with the Hamiltonian $\mathcal{H} = -F(S_z) - \alpha S_x$ can be reduced to a second-order differential equation [12] for S_z,

$$\ddot{S}_z = -F(S_z)F'(S_z) - EF'(S_z) - \alpha^2 S_z = -\frac{\mathrm{d}}{\mathrm{d}s}U(s)\bigg|_{s=S_z} \tag{19}$$

where

$$U(s) = \tfrac{1}{2}F^2(s) + EF(s) + \tfrac{1}{2}\alpha^2 s^2. \tag{20}$$

In this case, $F(s) = \gamma s^2 + \delta s$ so that

$$U(s) = \tfrac{1}{2}\gamma^2 s^4 + \gamma\delta s^3 + [\gamma E + \tfrac{1}{2}(\alpha^2 + \delta^2)]s^2 + \delta E s. \tag{21}$$

Equation (19) describes the motion of a unit 'mass' with coordinate $s = S_z$ in a 'potential' $U(s)$ so that its 'energy' $\mathcal{E} = \frac{1}{2}\dot{s}^2 + U(s)$ is conserved. The true dimension of $\mathcal{E}$, which is called ε in [8], is (energy)^2. In principle, we fix $\mathcal{E}$ by specifying $s(0)$ and $\dot{s}(0)$. In practice [8, section 2.2] there are only two independent constants of the three-dimensional motion of a spin, namely, the energy E and $\boldsymbol{S}^2 = \sigma^2$, so that $\mathcal{E}$ is bound to be a function of both of them: $\mathcal{E} = \frac{1}{2}(\alpha^2\sigma^2 - E^2)$. This is most easily verified by using (20), computing E^2, and realizing that $\dot{E} = -F(s) - \alpha S_x$ while $\dot{s} = -\alpha S_y$.

For E negative enough, U is a double-well potential, which is asymmetric in s for $\delta \neq 0$ and we have two disjoint closed orbits, as is brought out by figures 1 and 2. Figure 2 shows that the asymmetry develops much more slowly than the shift of the maximum; this latter is roughly at $-\delta/2$. The turning points $a_1 < b_1 < b_2 < a_2$ are solutions of the equation $U(s) = \mathcal{E}$. Given E, classically allowed motion is between a_i and b_i, with $i = 1, 2$, so either on the left or on the right. The period of this motion and, thus, implicitly the attempt frequency is

$$T_i(E) = \left|2\int_{a_i}^{b_i} \mathrm{d}s[2(\mathcal{E} - U(s))]^{-1/2}\right|. \tag{22}$$

If $\mathcal{E}$ is close enough to the bottom of the potential well, $U(s)$ is nearly parabolic in the domain of integration of (22) and $T_i(E) \approx 2\pi/\sqrt{U''(s_i)}$, where s_1 and s_2 are the locations of the minima. Because $U(s)$ is independent of the spin quantum number S, the attempt frequency will also be (nearly) independent of S.

Once an orbit exists, any E is classically acceptable. Quantum mechanically, however, only $2S + 1$ energy eigenvalues survive. Determining the allowed eigenvalues to fair approximation and in closed form is what semiclassical quantization is (or should be) good for.

Handling a single spin, we have only a single pair of canonically conjugate variables q and p, which are related through the Poisson bracket $\{q, p\} = 1$. Since in a Hamiltonian formalism q and p are handled on an equal footing there is no harm in interchanging them by putting $q_{\mathrm{new}} := -p$ and $p_{\mathrm{new}} := q$ so that the new variables have the same Poisson bracket $\{q_{\mathrm{new}}, p_{\mathrm{new}}\} = 1$ as the old ones. Instead of declaring $q = S_z$ and $p = -\phi$ to be canonical coordinates [7–9], with ϕ as the azimuth, we now find it advantageous to put

$$q = \phi \qquad \text{and} \qquad p = S_z. \tag{23}$$

Semiclassical quantization is a condition on the action integral,

$$\oint p\,\mathrm{d}q = \oint S_z\,\mathrm{d}\phi = nh \qquad n \in \mathbb{Z} \tag{24}$$

where the integral is to be taken over a classical, closed orbit, h is Planck's constant, and n is an integer; cf Messiah [13]. Along a closed orbit S_z can often, certainly in this case,

be specified as a function of $0 \leqslant \phi \leqslant 2\pi$; cf figure 1. We write $S_z = \sigma\cos\theta$, with θ as the polar angle, and arrive at the condition which we will use in the spin problem below,

$$\sigma\langle\cos\theta\rangle \equiv \frac{\sigma}{2\pi}\oint \mathrm{d}\phi\ \cos\theta = n\bar{h} \qquad n \in \mathbb{Z}. \tag{25}$$

Of course $\cos\theta$ is to be given as a function of ϕ. The fact that n is a positive *or negative* integer, restricted to $|n| \leqslant S$, is typical to spins.

To verify that all this makes sense, we take the limit $\alpha \to 0$ so that the paraboloid $-[\gamma S_z^2 + \delta S_z] - \alpha S_x \equiv E$ becomes very steep and, consequently, S_z in (24) is more or less constant as the spin tracks its orbit. Hence we find $2\pi S_z = nh$, which is equivalent to saying $S_z = n\bar{h}$, as should be the case on the spectrum of S_z.

As an application of the semiclassical quantization condition (25) we study the Hamiltonian (2) with vanishing δ. The energy as given in polar coordinates,

$$E = -\gamma S_z^2 - \alpha S_x = -\gamma\sigma^2\cos^2\theta - \alpha\sigma\sin\theta\cos\phi \tag{26}$$

leads to a quadratic equation for $y := x^2$ with $x = \cos\theta$; this only happens when $\delta = 0$. Here we assume $E < 0$, which is typical to tunnelling. In view of considerations to come in section 4, we introduce the dimensionless parameters

$$a = \frac{\alpha}{2\gamma\sigma} \qquad Q^2 = -\frac{E}{\gamma\sigma^2} \qquad \text{and} \qquad \epsilon = \frac{a\cos\phi}{Q^2}. \tag{27}$$

Here a is supposed to be small; in the Mn_{12} case, $a = 0.3$.

The quantity y obeys the equation $y^2 - 2Q^2(1 - 2\epsilon^2Q^2)y + (1 - 4\epsilon^2)Q^4 = 0$ so that

$$y_\pm = Q^2\{(1 - 2\epsilon^2Q^2) \pm 2\epsilon[1 - Q^2 + \epsilon^2Q^4]^{1/2}\} \geqslant 0. \tag{28}$$

In view of $y_-(\phi) = y_+(\phi + \pi)$, it suffices to consider y_+ and, thus,

$$x_\pm = \pm Q\{(1 - 2\epsilon^2Q^2) + 2\epsilon[1 - Q^2 + \epsilon^2Q^4]^{1/2}\}^{1/2} \equiv \pm Qf(Q,\epsilon). \tag{29}$$

That is, we are left with a 'positive' branch, $x_+(\phi)$, and a 'negative' one, $x_-(\phi)$, symmetrically positioned with respect to the S_x–S_y plane. Both x_+ and x_- have to be inserted into (25). They correspond to $n > 0$ and $n < 0$, respectively, and yield the same energy. Indeed, (25) and (29) imply

$$\left(\frac{n}{S}\right)^2 = Q^2\langle f\rangle^2. \tag{30}$$

As a matter of fact, f is a function of Q^2 so that the solution of (30) for E only depends on $|n|$. It then remains to calculate the quantum-mechanical splitting of the levels $-n$ and n as indicated in section 2.

In this case, semiclassical quantization is a straightforward integration giving up to second order in a (see appendix A)

$$\langle\cos\theta\rangle = \frac{1}{2\pi}\int_0^{2\pi}\mathrm{d}\phi x_\pm(\phi) = \pm Q\left[1 - \frac{a^2}{4}(Q^{-2} + Q^{-4})\right] = \frac{n\bar{h}}{\sigma} = \frac{n}{S}. \tag{31}$$

The dependence of $x_\pm(\phi)$ on ϕ is a dependence upon $\cos\phi$. If desired, one can change variables through $z := \exp(\mathrm{i}\phi)$ and obtain a contour integral in the complex z plane.

What we are after is the energy E as it appears in Q. First we solve (31), a fourth-order equation in Q. Recalling that it already contains an error term of the order of a^4, it suffices to find $Q = Q(a)$ up to second order, which can be done by iteration. To this end we rewrite (31) in a form that is easy to iterate,

$$Q = \frac{|n|}{S} + \frac{a^2}{4}(Q^{-1} + Q^{-3}). \tag{32}$$

Iterating once, i.e. replacing Q in the right-hand side of (32) by $|n|/S$, we obtain Q up to second order in a:

$$Q = \frac{|n|}{S}\left\{1 + \frac{a^2}{4}\left(\frac{S}{n}\right)^2\left[1 + \left(\frac{S}{n}\right)^2\right]\right\}. \tag{33}$$

Because $E = -\gamma\sigma^2 Q^2$, squaring (33) and dropping terms of order a^4 we obtain the second-order expression for the frequencies ($|n| \leqslant S$),

$$\Omega_n \equiv E_n/\hbar = -n^2\Gamma - \frac{\alpha^2}{8\Gamma}\left[1 + \left(\frac{S}{n}\right)^2\right]. \tag{34}$$

Here, and in the next section, we have dropped the superscript 'sc', and E_n denotes a semiclassical eigenvalue. As announced, the degeneracy of E_n and E_{-n} is not lifted. It has to be borne in mind that (34) has been obtained under the assumption that we may drop everything beyond second order in a^2, an assumption that may, but need not, hold. In appendix A we derive an exact expression of $\langle\cos\theta\rangle$ in terms of a power series in a. Using this power series one can obtain semiclassical energies up to any order.

As equation (34) is second-order in a, it is instructive to compare it with second-order quantum-mechanical perturbation theory [14],

$$E_n^{(2)}/\hbar = -n^2\Gamma - \frac{\alpha^2}{8\Gamma}\left[\frac{n^2 + S(S+1)}{n^2 - 1/4}\right]. \tag{35}$$

The correction to $-n^2\Gamma$ is slightly bigger in absolute value than in (34) but the agreement is excellent, except for, say, $|n| \leqslant 2$ and $S \leqslant 4$. For the ground state with $|n| = S$, equation (34) yields $E_{\pm S} = -\gamma\sigma^2 - \alpha^2/4\gamma$ which agrees with the minimal classical energy, cf [8, equation (2.6)]. Table 1 of [8] shows that, for $\alpha = \gamma = \hbar = 1$ and $S \geqslant 8$, the ground state has $\Omega_S + S^2\Gamma = -0.26$, which is indeed near the predicted $-\frac{1}{4}$. In fact, it is slightly less, as we would expect. Under the proviso $S \geqslant 5$ and $|n| \geqslant 3$, the deviation of the 'shift' $E_n^{(2)}/\hbar + n^2\Gamma$ from that given by numerically exact eigenvalues E_n is less than 15%.

4. Determining the energies for nonzero δ

We proceed in analogy to the $\delta = 0$ case. In the argument below we are looking for solutions of a fourth-order equation $P_4(x) = 0$ in dependence upon a given combination a of the coefficients of the polynomial P_4. Instead of attempting to obtain an exact solution, which would not provide much insight, we rewrite $P_4(x) = 0$ in the form of a fixed-point equation $x = f(x, a)$, and, supposing the smallness of a, find the solution $x = x(a)$ by iteration, up to a given order in a. We have already applied this procedure once, namely, to (32).

The energy as given in polar coordinates and to be compared with (26) reads

$$E = -\gamma S_z^2 - \delta S_z - \alpha S_x = -\gamma\sigma^2\cos^2\theta - \delta\sigma\cos\theta - \alpha\sigma\sin\theta\cos\phi. \tag{36}$$

As before, we put $x = \cos\theta$ but do not get a quadratic equation in $y := x^2$ once $\delta \neq 0$,

$$\gamma\sigma^2 x^2 + \delta\sigma x + \alpha\sigma\sqrt{1 - x^2}\cos\phi + E = 0. \tag{37}$$

In agreement with (27) we now define the dimensionless quantities

$$a = \frac{\alpha}{2\gamma\sigma} \qquad d = \frac{\delta}{2\gamma\sigma} \qquad Q^2 = -\frac{E}{\gamma\sigma^2} + d^2 \qquad \epsilon = \frac{a\cos\phi}{Q^2} \tag{38}$$

which reduce to (27) whenever $\delta = 0$. Here too, $E < 0$ will be assumed.

The two solutions $x = x_\pm$ of (37) obey the equation

$$x = -d \pm Q(1 - 2\epsilon\sqrt{1-x^2})^{1/2}. \tag{39}$$

According to what has been outlined at the beginning of this section, we assume $\epsilon < \frac{1}{2}$ so that the outer square root can be expanded. Then (39) can be solved by iteration to any order in a. The algebra has been relegated to appendix B. After an integration with respect to ϕ one finds, to second order in a,

$$\langle x\rangle \equiv \frac{1}{2\pi}\int_0^{2\pi} \mathrm{d}\phi\, x(\phi) = x_0 + \frac{a^2}{2Q^4}[x]_2 \tag{40}$$

where $x_0 = -d \pm Q$ and

$$[x]_2 = \mp Q\left[\pm Q x_0 + \frac{1}{2}(1 - x_0^2)\right] = \mp\frac{Q}{2}(Q^2 + 1 - d^2). \tag{41}$$

Unless stated otherwise, we will not repeat that henceforth we have to add a term $\mathcal{O}(a^4)$ to all right-hand sides of the equations in this section.

Semiclassical quantization means, in complete analogy to (31), that $\langle x\rangle$ is to be equal to n/S with $-S \leqslant n \leqslant S$. Realizing that $n > 0$ corresponds to the upper and $n < 0$ to the lower sign in (41) and $\pm n = |n|$, we combine (41) with (40) and obtain

$$\frac{n}{S} = \langle x\rangle = \pm Q - d \mp \frac{a^2}{4Q}[1 + Q^{-2}(1 - d^2)] \tag{42}$$

and thus

$$\frac{\pm n}{S} = \frac{|n|}{S} = Q - \mathrm{sgn}(n)d - \frac{a^2}{4Q}[1 + Q^{-2}(1 - d^2)]. \tag{43}$$

We now rewrite this in a form that is apt to iteration,

$$Q = Q_0 + \frac{a^2}{4Q}[1 + Q^{-2}(1 - d^2)] \qquad Q_0 = \frac{|n|}{S} + \mathrm{sgn}(n)d. \tag{44}$$

To obtain Q to second order in a, we iterate once,

$$Q = Q_0 + \frac{a^2}{4Q_0}[1 + Q_0^{-2}(1 - d^2)]. \tag{45}$$

For $\delta = d = 0$ we recover (33). Squaring (45), dropping terms of order a^4 and taking advantage of (38) we obtain

$$\Omega_n \equiv E_n/\hbar = -n^2\Gamma - n\delta - \frac{\alpha^2}{8\Gamma}\left[\frac{S^2 + n^2 + n\delta/\Gamma}{(n + \delta/2\Gamma)^2}\right] + \mathcal{O}(a^4\Gamma S^2). \tag{46}$$

Plainly, this is identical with (34) for $\delta = d = 0$. On the other hand, second-order perturbation theory gives

$$E_n^{(2)}/\hbar = -n^2\Gamma - n\delta - \frac{\alpha^2}{8\Gamma}\left[\frac{S(S+1) + n^2 + n\delta/\Gamma}{(n + \delta/2\Gamma)^2 - 1/4}\right] \tag{47}$$

see also [14]. The above expression agrees with equation (35) when δ vanishes, and with (46) whenever n and S are sufficiently large and $a \ll 1$. The latter condition is quite reasonable since we have used quantum-mechanical perturbation theory and, thus, compared the 'perturbation' $-\alpha S_x$ with the 'rest', namely, $-\gamma S_z^2 - \delta S_z$.

Once we know the semiclassical energies E_n, we can tune δ so as to get semiclassical resonance $E_m = E_n$ for some $m \neq n$. Despite being obtained for $\alpha = 0$, the resonance condition (3) remains valid for $\alpha \neq 0$ as well. Both (46) and (47) depend on n through

the expression $n^2 + n\delta/\Gamma$. Therefore (3) directly implies $E_m = E_n$ for each couple $\{m, n\}$ satisfying $m + n = -k = -\delta/\Gamma$.

A closer inspection shows that (3) implies degeneracy, to *any* order, of semiclassical eigenvalues. To see why, we return to equation (39). Let us start by averaging it, namely,

$$\frac{n}{S} = -d \pm Q\left\langle\left(1 - 2\epsilon\sqrt{1-x^2}\right)^{1/2}\right\rangle. \tag{48}$$

We now add d on the right and on the left, multiply both sides by S, and square the result so as to find

$$n^2 + n\delta/\Gamma = -(\delta/2\Gamma)^2 + \left[SQ\left\langle\left(1 - 2\epsilon\sqrt{1-x^2}\right)^{1/2}\right\rangle\right]^2. \tag{49}$$

The right-hand side does not show any n-dependence. It is obtained by taking x as a solution to the fourth-order equation (39), depending on $E, \alpha, \delta, \Gamma$, and ϕ. After integration with respect to ϕ, we are left with (49), an implicit equation for E. Solving it for E, the solution $E = E_n$ will depend on n through the combination $n^2 + n\delta/\Gamma$, as it shows up in (49). Hence $E_m = E_n$ whenever $m^2 + m\delta/\Gamma = n^2 + n\delta/\Gamma$.

5. Extensions

The extension of the above results to half-integer spins is straightforward. All that we have to do is to interprete m and n as half-integers whenever they refer to eigenvalues of S_z. In particular, m and n are half-integers in the resonance condition (3)–(5) and in the quantization condition (24), (25), and the semiclassical eigenvalues are also labelled by half-integers. At semiclassical resonance δ/Γ is still an integer.

The case when in the Hamiltonian S_x is replaced by S_x^l with $l > 1$ brings nothing new, if l is an odd integer. For positive integer l semiclassical quantization is essentially unchanged. In the definition (38) of ϵ, $\cos\phi$ is replaced by $\cos^l\phi$ and in equations (39), (48) and (49) ($\sqrt{1-x^2}^{\,l}$) is substituted for $\sqrt{1-x^2}$. The upshot is that the semiclassical eigenvalues still depend on n through the expression $n^2 + n\delta/\Gamma$ and therefore (3) still implies $E_m^{(\mathrm{sc})} = E_n^{(\mathrm{sc})}$. If l is odd, spin tunnelling splits the semiclassical degeneracy.

For even l, however, the meaning of equations (3)–(5) changes. Depending on the parity of k, (5) may refer to resonance or to true degeneracy. Let us recall that (3) gives the condition for degeneracy when $\alpha = 0$. In the case of integer spins, if k is odd then $n - m = -k - 2m$ is odd for each m and n such that $m + n = -k$. As a consequence, the αS_x^l term does not split the degeneracy of all these level pairs. In the case of half-integer spins the same happens if k is even. Therefore $E_m = E_n$ holds for the true eigenvalues, even if not *exactly* at, but only very close to, the field $\delta = k\Gamma$ at which $E_m^{(\mathrm{sc})} = E_n^{(\mathrm{sc})}$.

An explanation of this generalized Kramers degeneracy can be found in section 8 of [9], but for the reader's convenience we repeat the argument here. We write the matrix of $\mathcal{H}$ (for l even) in the basis of the S_z-eigenvectors $|n\rangle$. By noticing that $\langle m|\mathcal{H}|n\rangle = 0$ whenever $n-m$ is odd, we can permute the elements of the basis so as to transform the matrix into a block-diagonal form containing two blocks: the first is formed with $n = -S, -S+2, -S+4, \ldots$, the second with $n = -S+1, -S+3, -S+5, \ldots$. Both can be diagonalized independently, so the von Neumann–Wigner argument [11] about the avoided level crossing does not apply.

For a degenerate energy level there is no tunnelling. That is to say, a left-localized initial state remains approximately left-localized during time evolution. The reason is that in the corresponding two-dimensional eigensubspace of the Hamiltonian there exists an approximately left-localized state which is dominant in the eigenfunction expansion of the

initial state. Therefore, if in an experimental situation the tranverse anisotropy fields are a combination of even powers only, measurements à la [1, 2] of the quantum decay of magnetization in an increasing longitudinal external magnetic field would ideally yield a fast decay (a step), only when δ/Γ passes every other integer value. In other words, every second (expected) step would be missing. Unfortunately, an experiment in an applied magnetic field usually has a transverse component that induces steps at the remaining integer values.

6. Discussion

We have defined semiclassical resonance to be the degeneracy $E_m = E_n$ for energy levels as they follow from semiclassical quantization. The ensuing level splitting is a purely quantum-mechanical phenomenon. Both can be handled straightforwardly by the WKB formalism [7–9]. The resonance experiments as set up for spin tunnelling in Mn_{12} acetate [1–4] and Fe_8 magnetic crystals [15] are both elegant and quite promising since they provide a detailed test of the physics of spin quantum tunnelling and the crossover from the regime of thermal activation to that of quantum behaviour. This paper's considerations on tunnelling resonance are valid, if the temperature is low enough; say [5, 6] below 1 K in the Mn_{12} case.

If so, one could apply semiclassical quantization section 3 to arbitrary numerical precision but the amount of insight thus obtained is fairly restricted. We have chosen a different way out and derived an explicit expression for the energy levels and, hence, for semiclassical resonance through an external field $-\delta S_z$ under the assumption that $\alpha/(2\Gamma S Q^2) \ll 1$ where $Q^2 = (\delta^2/4 - \gamma E)/(\Gamma S)^2$ is dimensionless; cf (38). For the ground state of Mn_{12} with $S = 10$, we have $Q \approx 1$ and the considerations apply. In fact, we have also derived the energy levels for $\delta = 0$ under slightly less restrictive conditions and found that the shift of the ground state energy is well-predicted by $-\alpha^2/4\Gamma$. In some resonance experiments one would like to focus on states with m and n closer to zero since, in resonance, the tunnelling frequency is much higher. As a consequence, the aforementioned assumption may, but need not, hold. It mainly depends on Q^2. If $E \approx -n^2\hbar\Gamma$, then $Q^2 \approx (n/S)^2$ and it is the smaller the closer n is to 0.

Whenever δ is tuned to the degeneracy of some energy levels of the Hamiltonian $\mathcal{H}_0 = -\gamma S_z^2 - \delta S_z$, this degeneracy is not lifted by semiclassical quantization of the system with $\alpha \neq 0$. Only quantum mechanics lifts it, and only in high orders of $\alpha/\Gamma S$. At first sight rather surprisingly—but at a first sight only (section 2)—the mathematics underlying tunnelling for $\delta \neq 0$, when the Hamiltonian's symmetry of a rotation through π about the S_x axis is broken, is identical to that of the case $\delta = 0$. That is to say, the very same formalism, whether WKB or otherwise, can be applied to both cases.

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Appendix A. Semiclassical quantization for $\delta = 0$

We have to integrate $x = \cos\theta$ relative to ϕ, i.e. average the expression $\{\ldots\}^{1/2}$ in (29) and below,

$$x_\pm = \pm Q\{1 - 2\epsilon^2 Q^2 + 2\epsilon[1 - Q^2 + \epsilon^2 Q^4]^{1/2}\}^{1/2} \tag{50}$$

where $\epsilon = Q^{-2} a \cos\phi$. For $\delta = 0$, there are two disjoint classical orbits once $E < -\alpha\sigma$. Exactly in this energy range one finds $\{\ldots\} \geqslant 0$ so that taking the square root in (50) is well-defined. For the moment we suppose that a and thus ϵ is small enough to perform a series expansion of the outer square root. It is of the form

$$(1 - 2y)^{1/2} = 1 - \sum_{n \geqslant 1} b_n y^n \qquad \text{where} \quad b_n = \frac{(2n-3)!!}{n!}. \tag{51}$$

The series converges for $|y| < \frac{1}{2}$ while $b_1 = 1, b_2 = b_3 = \frac{1}{2}$. Introducing the shorthand $r = [1 - Q^2 + (\epsilon Q^2)^2]^{1/2}$ we see that we have to average

$$\{1 - 2\epsilon(\epsilon Q^2 - r)\}^{1/2} = 1 - \sum_{n \geqslant 1} b_n \epsilon^n (\epsilon Q^2 - r)^n. \tag{52}$$

We now concentrate on the series, insert the definition of ϵ and apply the binomial theorem to (52) so as to find

$$\sum_{n \geqslant 1} \sum_{m=0}^{n} b_n Q^{-2n} a^{m+n} (-1)^{n-m} \binom{n}{m} r^{n-m} \cos^{m+n}\phi. \tag{53}$$

At this point we observe that r depends on ϕ through $\cos^2\phi$. Hence, $\langle g(r)\cos^\ell\phi\rangle$ vanishes for ℓ odd, whatever the function g may be. Thus, when averaging (53), only terms with $\ell = m + n$ even will survive. For these terms $n - m = (n + m) - 2m$ is also even and we can apply the binomial theorem to r^{n-m} as well. Furthermore, averaging a cosine is equivalent to a contour integration over the unit circle C_1 in the complex z plane,

$$\langle\cos^\ell\phi\rangle = \frac{2^{-\ell}}{2\pi \mathrm{i}} \oint_{C_1} \frac{\mathrm{d}z}{z} (z + z^{-1})^\ell = 2^{-\ell} \binom{\ell}{\ell/2}. \tag{54}$$

Finally, we are left with

$$\begin{aligned}\langle\cos\theta\rangle &= \pm Q\Bigg[1 - \sum_{n \geqslant 1} \sum_{m=0}^{n} \sum_{l=0}^{(n-m)/2} b_n Q^{-2n} (1 - Q^2)^{\frac{n-m}{2} - l} \\ &\qquad \times \left(\frac{a}{2}\right)^{2l+m+n} \binom{n}{m} \binom{\frac{1}{2}(n-m)}{l} \binom{2l+m+n}{l + \frac{1}{2}(m+n)}\Bigg] \\ &\equiv \pm Q\Bigg[1 - \sum_{k=1}^{\infty} \mathcal{C}_k(Q^2) \left(\frac{a}{2}\right)^{2k}\Bigg]\end{aligned} \tag{55}$$

where it is understood that $m + n$ is even. If it were not because of the third binomial coefficient in (55) we could directly resum the series. In the style of Borel [16, 17], however, we could, by noting $n! = \Gamma(n + 1)$ and taking an Eulerian integral representation of the second kind [18, 19] for the Gamma function in conjunction with Hankel's contour integral [18, 19] for its inverse,

$$\frac{1}{\Gamma(t)} = \frac{\mathrm{i}}{2\pi} \int_{C_2} \frac{\mathrm{d}z}{z} \mathrm{e}^{-z} (-z)^{-t} \tag{56}$$

where C_2 is a counter-clockwise infinite contour around the positive real axis. We will not pursue this idea here. Collecting terms of order a^2 we find $\mathcal{C}_1 = Q^{-2} + Q^{-4}$ and arrive at (31), as shown.

How good is all this? Since we interchange the series (51) and averaging, namely, $\oint \mathrm{d}z \ldots$, we have to prove uniform convergence of the series and thus, in view of (51), uniform boundedness of $y = \epsilon(\epsilon Q^2 - r)$ as $\cos\phi$ varies between 1 and -1. The upshot appears in (55). Plainly, the series in (55) is convergent for a small enough so that, for a given a, Q and, thus, the energy has to stay away from zero. The series in (55) certainly diverges at energies for which the two classical orbits merge into a single one. One can handle divergent series through, e.g. Borel summation [16, 17] as above, but this is not the topic of this paper.

Appendix B. Quantizing to second order in ϵ

In this appendix we consider ϵ as a 'small' parameter and sketch how one can perform semiclassical quantization up to second order in ϵ. As we will see, the method can be generalized and the considerations of appendix A concerning the validity of the approximations involved apply here as well.

We denote the two branches $x_\pm$ of (39), namely,

$$x = -d \pm Q\left[1 - 2\epsilon\sqrt{1-x^2}\right]^{1/2} \tag{57}$$

simply by x. Keeping in mind that $x = \cos\theta$ depends on ϕ, we fix ϕ for the moment and study x's dependence upon $\epsilon = aQ^{-2}\cos\phi$. In view of (57) it is clear that $x = x(\epsilon)$ is analytic in a neighbourhood of $\epsilon = 0$. Defining the nth partial 'Taylor sum' of $x(\epsilon)$ to be

$$x_n = \sum_{k=0}^{n} \frac{x^{(k)}(0)}{k!}\epsilon^k \equiv \sum_{k=0}^{n} [x]_k \epsilon^k \tag{58}$$

with $x_0 = x(0) = -d \pm Q$, using (51), and expanding the outer square root of (57), we can rewrite (57) in the form

$$x = x_0 \mp Q \sum_{n\geqslant 1} b_n \epsilon^n (1-x^2)^{n/2}. \tag{59}$$

Up to and including terms of order two we then find

$$x = x_0 \mp Q[\epsilon(1-x^2)^{1/2} + \epsilon^2(1-x^2)/2] + \mathcal{O}(\epsilon^3) \tag{60}$$

whence

$$x_1 = x_0 \mp Q(1-x_0^2)^{1/2}\epsilon = x_0 + [x]_1\epsilon \tag{61}$$

because $\sqrt{1-x^2} = \sqrt{1-x_0^2} + \mathcal{O}(\epsilon)$.

In order to obtain x_2, we observe that (60) implies

$$[x]_2 = \mp Q\left\{\left[\sqrt{1-x^2}\right]_1 + [1-x^2]_0/2\right\}. \tag{62}$$

In analogy to (58), we have used the notation $[f]_n = f^{(n)}(0)/n!$.

As for the entries of (61), a simple calculation gives

$$\begin{aligned}\left[\sqrt{1-x^2}\right]_1 &= \left.\frac{\mathrm{d}\sqrt{1-x^2}}{\mathrm{d}\epsilon}\right|_{\epsilon=0} = -x_0(1-x_0^2)^{-1/2}x'(0) \\ &= -x_0(1-x_0^2)^{-1/2}[x]_1 = \pm Q x_0.\end{aligned} \tag{63}$$

Since $[1-x^2]_0 = 1 - x_0^2$ we end up with

$$x_2 = x_1 + [x]_2\epsilon^2 = x_0 \mp Q\epsilon\sqrt{1-x_0^2} - Q\epsilon^2[Qx_0 \pm (1-x_0^2)/2]. \tag{64}$$

It is x_2 that is to be averaged with respect to ϕ. Inserting $\langle\epsilon\rangle = 0$ and $\langle\epsilon^2\rangle = a^2/2Q^4$ into $\langle x_2\rangle$ we obtain equation (40).

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