Semiclassical Quantization and Resonance in Spin Tunneling†

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Abstract

We derive semiclassical quantization for a spin, study it for not too small a spin quantum number \(S \geq 5\), and compute the \(2S+1\) eigenvalues of a Hamiltonian exhibiting resonant tunneling 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.

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†Dedicated to Heinz Horner on the occasion of his 60th birthday.
1 Introduction

Resonance has revived the experimental interest in spin quantum tunneling. The idea is both fascinating and simple [1–3]. 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 \( \mathbf{H} \). The corresponding Hamiltonian is given by

\[ \mathcal{H} = -\gamma S_z^2 - g\mu_B \mathbf{H} \cdot \mathbf{S} . \]  

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

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

Here \( \gamma > 0 \) and we may assume \( \alpha, \delta \geq 0 \). By putting \( \gamma := -\gamma \) we encounter a situation whose tunneling physics and mathematics hardly changes and therefore need not be treated separately. In the present 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 \( \alpha S_x \) tries to generate a rotation about the \( x \)-axis and thus aims at inducing a tunneling transition. It certainly does so for \( \delta = 0 \). For arbitrary nonzero \( \delta \) the degeneracy in the spectrum of \( S_z^2 \) is lifted and no tunneling can occur unless a special choice of \( \delta \) 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 \( \gamma\hbar = \Gamma \),

\[ \Omega_m^{(0)} = -m^2\Gamma - m\delta = -n^2\Gamma - n\delta = \Omega_n^{(0)} . \]  

In passing we note that both \( \Gamma \) and \( \delta \) have the dimension of frequency. Equation (3) tells us

\[ (m^2 - n^2)\Gamma + (m - n)\delta = 0 \]  

so that with \( -S \leq m \neq n \leq S \) we are left with

\[ (m + n)\Gamma + \delta = 0 \Rightarrow m + n = -\delta/\Gamma = -k \]  

where \( k \geq 1 \) 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 \(-S \leq n \leq S-k \). Furthermore, degeneracy can be realized by a single choice, viz., \( \delta = k\Gamma \). Here one has exploited the fact that the anisotropy is quadratic in \( S_z \).

The variable parameter \( \delta \) 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 [1–5] several resonances in between. In passing we note that both \( \Gamma \) and \( \delta \) may correspond to true degeneracy; that is, no resonance and no tunneling. We finish the paper with a discussion (§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 \( S_z \) reads

\[
S_z = \frac{1}{2} (S_+ + S_-) = \frac{1}{2} \left[ a \left( \sqrt{s(s + \hbar)} \right) T_{\hbar} + a \left( \sqrt{s(s - \hbar)} \right) T_{-\hbar} \right]
\]

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,

\[
h_{n,n-1}\psi_{n-1} + h_{n,n+1}\psi_{n+1} + (h_{nn} - E)\psi_n = 0.
\]

(7)

The matrix elements and the vector components are taken in the basis of the eigenvectors of \( S_z \), and (7) is valid for \(-S + 1 \leq n \leq S - 1\). Disregarding the remaining two equations, relation (6) has two linearly independent solutions for any value of \( E \); they are determined by fixing, e.g., \( \psi_0 \) and \( \psi_1 \). The \( 2S + 1 \) eigenvalues of \( \mathcal{H} \) are singled out by requiring that \( \psi \) satisfy the boundary conditions

\[
h_{\pm S,\pm(S-1)}\psi_{\pm(S-1)} + (h_{\pm S,\pm S} - E)\psi_{\pm S} = 0.
\]

(8)

Equivalently, we can extend (6) 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 \( \hbar \Omega_n^{(0)} \) with \( n \) ranging from \(-S \) to \( S \); cf. Eq. (6). It is interesting to note that, as the energy increases while avoiding accidental degeneracies (6), 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 \( \alpha \), if \( \alpha \ll \Gamma S + \delta \), which is supposed throughout the paper.

By varying \( \delta \), neighbouring eigenvalues can get very close to each other, although true degeneracy cannot occur (2). As we discuss below, the mechanism of the avoided level crossing is spin tunneling. 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 §4 that the condition for a semiclassical resonance remains (6). Apart from the resonance at \( \delta = 0 \), we cannot expect that the two definitions predict the same ‘resonant’ values for \( \delta \). Because, however, semiclassical eigenvalues nicely approximate the true ones, only a small ‘fine tuning’ of \( \delta \) 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 \( \delta \) 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 (6). To avoid all confusion, we emphasize that no linear combination of them satisfies the boundary conditions (6) 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 analog holds for \( E_2 \). Let \( E_1^{(sc)} \) and \( E_2^{(sc)} \) 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 \( \eta(E_1) \) by \( \eta(E_1^{(sc)}) \) and \( \vartheta(E_1) \) by \( \vartheta(E_1^{(sc)}) \), 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 Wentzel, Kramers, and Brillouin (WKB) never considered spins, their idea is applicable here too, provided one generalizes the formalism appropriately (6) so as to take care of the discrete nature of a spin and its different commutation relations as compared to a particle. A semiclassical analysis formally means that we take the limit \( \hbar \to 0 \) and at the same time \( S \to \infty \) in such a way that
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 $E = -50$.

$hS = \sigma$ 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 $\psi = \exp(iS/\hbar)$ with $S = S_0 + \sum_{n=1}^{\infty} \left( \frac{\hbar}{i} \right)^n S_n$ for the wave function we are looking for, expand everything in powers of $\hbar$, and usually stop after the first-order term, the zeroth-order one being dominant. So de facto we use a continuum description, even though $\hbar$ is still finite.

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

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

and

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

Here $C_{l,r}$ are normalization constants and the arccosh expression stems from $S_0$ in (3). As can be seen from Figs. 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, and 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 $b_2$ Eqs. (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 $\nu(E)$. 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...
Figure 2: The effective, quartic double-well potential $U(s)$ given by Eq. (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.
$\mathcal{H}$ in the subspace spanned by, say, $\phi_{E_1^{(sc)},j}$ and $\phi_{E_2^{(sc)},i}$. Close to the semiclassical resonance (8) there exist integers $m < 0 < n$ such that these functions are localized near $m\hbar$ and $n\hbar$, respectively. We shall use the shorthand $\phi_m$ and $\phi_n$ for them. Let $\chi$ 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 $o_{mn}$ is nonvanishing, although very small; we shall estimate it below. There is no harm in supposing $\phi_m$ and $\phi_n$ to be normalized.

We now turn to an explicit calculation of the quantum-mechanical level splitting. To a good approximation (8, 9, 10), $E_1$ and $E_2$ agree with the eigenvalues $E_-$ and $E_+$ of the $2 \times 2$ matrix

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

To see it, expand the eigenfunctions in terms of $\phi_m$ and $\phi_n$ and take matrix elements. For the eigenvalues we find

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

where

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

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

$$r_{\pm}^2 = \frac{\chi_{nn} - E_{\pm}}{\chi_{mm} - E_{\pm}}$$ \hspace{1cm} (15)

and, by orthogonality, $r_+r_- = 1 - (r_+ + r_-)o_{mn}$. Near resonance Eqs. (13) and (14) provide improved eigenvalues and eigenvectors as compared to the semiclassical ones.

We now have to tune $\delta$ to quantum-mechanical resonance. Supposing $\chi_{mn}$ 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 $\delta$ and remains uniformly small in the small region where we vary $\delta$. 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 Eqs. (10, 17). For this estimate we may suppose $E = E_1^{(sc)} = E_2^{(sc)}$. Then

$$o_{mn} = S \exp -\frac{1}{\hbar} \int_{b_1}^{b_2} ds \arccosh \left( \frac{-E - F(s)}{a(s)} \right)$$ \hspace{1cm} (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 $\Delta E = E_2 - E_1$ in the form

$$\Delta E = \frac{\pi \hbar}{\tau_0} \exp -\frac{1}{\hbar} \int_{b_1}^{b_2} ds \arccosh \left( \frac{-E - F(s)}{a(s)} \right)$$ \hspace{1cm} (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

$$\Delta E \approx \frac{\pi \hbar}{\tau_0} \left[ \frac{aS}{\Gamma(m^2 + n^2) + \delta(m + n)} \right]^{n-m}.$$ \hspace{1cm} (18)

By identifying $\tau_0$ with the time period of the classical motion – see Eq. (22) below –, Eqs. (17) and (18) become fully explicit. For $\delta = 0$ and $n = -m = S$ they agree, respectively, with formulas (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 (3). Equation (17) was obtained (10) also by an independent argument.

Of course $\delta$ can be chosen to let $\Delta_{mn}$ vanish. The reason is that $\chi_{mm} \approx E_1^{(sc)}$ and $\chi_{nn} \approx E_2^{(sc)}$ (the small deviation coming from the fact that $\phi_m$ and $\phi_n$ do not satisfy the boundary conditions (8)), and
semiclassical eigenvalues do cross each other at resonance. Thus \( \Delta_{mn} = 0 \) for a \( \delta \) 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 tunneling. 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 \( \phi_n = (\psi_+ + \psi_-)/\sqrt{2} \). It evolves under the influence of the dynamical evolution generated by \( \exp(i\mathcal{H}/\hbar) \). After a time \( T \) given by Eq. (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 \( \delta \) (\( \delta \leq 10\Gamma \)) 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 centered at \( m \) and \( n \) are hardly different; see Eq. (22) below. This fact is crucial for the interpretation of \( \tau_0 \) 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 \( S_z^2 = S_x^2 + S_y^2 + S_z^2 = \sigma^2 \); cf. Fig. 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 (13) for \( S_z \),

\[
\dot{S}_z = -F(S_z)F'(S_z) - EF'(S_z) - \alpha^2 S_z = -\frac{d}{ds} U(s) \bigg|_{s=S_z}
\]

(19)

where

\[
U(s) = \frac{1}{2} F^2(s) + EF(s) + \frac{1}{2} \alpha^2 s^2.
\]

(20)

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

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

(21)

Equation (14) describes the motion of a unit ‘mass’ with coordinate \( s = S_z \) in a ‘potential’ \( U(s) \) so that its ‘energy’ \( \mathcal{E} = \frac{1}{2}s^2 + U(s) \) is conserved. The true dimension of \( \mathcal{E} \), which is called \( \varepsilon \) in Ref. 1, is (energy). In principle, we fix \( \mathcal{E} \) by specifying \( s(0) \) and \( \dot{s}(0) \). In practice [3 §2.2] there are only two independent constants of the three-dimensional motion of a spin, viz., the energy \( E \) and \( S^2 = s^2 \), so that \( \mathcal{E} \) is bound to be a function of both of them: \( \mathcal{E} = \frac{1}{2}(\alpha^2 s^2 - E^2) \). This is most easily verified by using (20), computing \( E^2 \), and realizing that \( E = -F(s) - \alpha S_x \) 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 Figs. 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

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

(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 \( q_{\text{new}} := -p \) and \( p_{\text{new}} := q \) so that the new variables have the same Poisson bracket \( \{q_{\text{new}}, p_{\text{new}}\} = 1 \) as the old ones. Instead of declaring \( q = S_z \) and \( p = -\dot{\phi} \) to be canonical coordinates \([8, 9, 10]\), with \( \phi \) as the azimuth, we now find it advantageous to put

\[
q = \phi \quad \text{and} \quad p = S_z .
\]  

(23)

Semiclassical quantization is a condition on the action integral,

\[
\oint p \, dq = \oint S_z \, d\phi = n\hbar, \quad n \in \mathbb{Z} ,
\]

(24)

where the integral is to be taken over a classical, closed orbit, \( \hbar \) is Planck’s constant, and \( n \) is an integer; cf. Messiah [14]. Along a closed orbit \( S_z \) can often, certainly in the present case, be specified as a function of \( 0 \leq \phi \leq 2\pi \); cf. Fig. 1. We write \( S_z = \sigma \cos \theta \), with \( \theta \) as the polar angle, and arrive at the condition which we will use in the spin problem below,

\[
\sigma \langle \cos \theta \rangle \equiv \frac{\sigma}{2\pi} \int \! d\phi \cos \theta = n\hbar, \quad n \in \mathbb{Z} .
\]

(25)

Of course \( \cos \theta \) is to be given as a function of \( \phi \). The fact that \( n \) is a positive or negative integer, restricted to \(|n| \leq S\), is typical to spins.

To verify that all this makes sense, we take the limit \( \alpha \to 0 \) so that the paraboloid \(-\gamma S_z^2 + \delta S_x - \alpha S_x \equiv E \) becomes very steep and, consequently, \( S_z \) in (23) is more or less constant as the spin tracks its orbit. Hence we find \( 2\pi S_z = n\hbar \), which is equivalent to saying \( S_z = n\hbar \), as should be the case on the spectrum of \( S_z \).

As an application of the semiclassical quantization condition (23) we study the Hamiltonian (2) with vanishing \( \delta \). The energy as given in polar coordinates,

\[
E = -\gamma S_z^2 - \alpha S_x = -\gamma \sigma^2 \cos^2 \theta - \alpha \sigma \sin \theta \cos \phi ,
\]

(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 tunneling. In view of considerations to come in §4, we introduce the dimensionless parameters

\[
a = \frac{\alpha}{2\gamma \sigma}, \quad Q^2 = -\frac{E}{\gamma \sigma^2} \quad \text{and} \quad \epsilon = \frac{a \cos \phi}{Q^2} .
\]

(27)

Here \( a \) is supposed to be small; in the Mn12 case, \( a = 0.3 \).

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

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

(28)

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

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

(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 (23). They correspond to \( n > 0 \) and \( n < 0 \), respectively, and yield the same energy. Indeed, (23) and (24) imply

\[
\left( \frac{n}{S} \right)^2 = Q^2 \langle f \rangle^2 .
\]

(30)
As a matter of fact, \( f \) is a function of \( Q^2 \) so that the solution of (31) for \( E \) only depends on \(|n|\). It then remains to calculate the quantum-mechanical splitting of the levels \(-n\) and \(n\) as indicated in §2.

In the present case, semiclassical quantization is a straightforward integration giving up to second order in \( a \) (see Appendix A)

\[
\langle \cos \theta \rangle = \frac{1}{2\pi} \int_0^{2\pi} d\phi \, x_\pm(\phi) = \pm Q[1 - \frac{a^2}{4}(Q^{-2} + Q^{-4})] = \frac{n\hbar}{\sigma} = \frac{n}{S}.
\]

(31)

The dependence of \( x_\pm(\phi) \) on \( \phi \) is a dependence upon \( \cos \phi \). If desired, one can change variables through \( z := \exp(i\phi) \) 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,

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

(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 \( a \):

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

(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 (\(|n| \leq S\)),

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

(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.

Equation (34) being second-order in \( a \), it is instructive to compare it with second order quantum-mechanical perturbation theory \[15\],

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

(35)

The correction to \(-n^2\Gamma\) is slightly bigger in absolute value than in (34) but the agreement is excellent, except for, say, \(|n| \leq 2\) and \(S \leq 4\). For the ground state with \(|n| = S\), Eq. (34) yields \(E_{\pm S} = -\gamma\sigma^2 - \alpha^2/4\gamma\) which agrees with the minimal classical energy, cf. \[4\] Eq. (2.6)]. Table I of Ref. \[9\] shows that, for \(\alpha = \gamma = \hbar = 1\) and \(S \geq 8\), the ground state has \(\Omega_S + S^2\Gamma = -0.26\), which is indeed near the predicted \(-1/4\). In fact, it is slightly less, as we would expect. Under the proviso \(S \geq 5\) and \(|n| \geq 3\), 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 \(\delta\)

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
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, viz., to (32).

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

\[
E = -\gamma S^2 - \delta S - \sigma x = -\gamma \sigma^2 \cos^2 \theta - \delta \sigma \cos \theta - \alpha \sigma \sin \theta \cos \phi ,
\]

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

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

\[
a = \frac{\alpha}{2\gamma \sigma} \quad d = \frac{\delta}{2\gamma \sigma} \quad Q^2 = -\frac{E}{\gamma \sigma^2} + d^2 \quad \epsilon = \frac{a \cos \phi}{Q^2}
\]

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

\[
x = -d \pm Q \left( 1 - 2\epsilon \sqrt{1 - x^2} \right)^{1/2} .
\]

According to what has been outlined at the beginning of this section, we assume \( \epsilon < 1/2 \) so that the outer square root can be expanded. Then (37) can be solved by iteration to any order in \( a \). The algebra has been relegated to Appendix B. After an integration with respect to \( \phi \) one finds, to second order in \( a \),

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

where \( x_0 = -d \pm Q \) and

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

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 \( -S \leq n \leq S \). Realizing that \( n > 0 \) corresponds to the upper and \( n < 0 \) to the lower sign in (41) and \( \pm n = |n| \), we combine (11) with (40) and obtain

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

and thus

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

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

\[
Q = Q_0 + \frac{a^2}{4Q_0} \left[ 1 + Q^{-2}_0(1 - d^2) \right] , \quad Q_0 = \frac{|n|}{S} + \sgn(n) d .
\]

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

\[
Q = Q_0 + \frac{a^2}{4Q_0} \left[ 1 + Q^{-2}_0(1 - d^2) \right] .
\]
For $\delta = d = 0$ we recover (33). Squaring (33), dropping terms of order $a^4$ and taking advantage of (38) we obtain

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

(46)

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

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

(47)

see also [13]. The above expression agrees with Eq. (35) when $\delta = 0$ 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 Eq. (33). Let us start by averaging it, viz.,

$$\bar{n} / S = -d \pm Q \langle (1 - 2 \epsilon \sqrt{1 - x^2})^{1/2} \rangle .$$

(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

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

(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 (49), depending on $E$, $\alpha$, $\delta$, $\Gamma$, and $\phi$. After integration with respect to $\phi$, 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 interpreting $m$ 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 (11) and in the quantization condition (13,14), and the semiclassical eigenvalues are also labelled by half-integers. At semiclassical resonance $\delta / \Gamma$ is still an integer.

The case where in the Hamiltonian $S_z$ is replaced by $S_z^l$ with $l > 1$ brings nothing new, if $l$ is an odd integer. For positive integer $l$ semiclassical quantization is essentially unchanged. In the definition (18) of $\epsilon$, $\cos \phi$ is replaced by $\cos \phi$ and in Eqs. (18), (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 $E_m^{(sc)} = E_n^{(sc)}$. If $l$ is odd, spin tunneling splits the semiclassical degeneracy.

For even $l$, however, the meaning of Eqs. (3)-5 changes. Depending on the parity of $k$, (5) may refer to resonance or to true degeneracy. Let us recall that (5) 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 $\alpha L^4 \Omega_x$ 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 $E_m^{(sc)} = E_n^{(sc)}$.

An explanation of this generalized Kramers degeneracy can be found in §8 of [14], 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\textsubscript{z}-eigenvectors \ket{n}. 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 \[12\] about the avoided level crossing does not apply.

For a degenerate energy level there is no tunneling. 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 transverse anisotropy fields are a combination of even powers only, measurements \textit{à la} \[3, 10\] of the quantum decay of magnetization in an increasing longitudinal external magnetic field would ideally yield a fast decay (a step), only when \( \delta/\Gamma \) 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 \[3, 10\]. The resonance experiments as set up for spin tunneling in Mn\textsubscript{12} acetate \[1, 2\] and Fe\textsubscript{8} magnetic crystals \[10\] are both elegant and quite promising since they provide a detailed test of the physics of spin quantum tunneling and the crossover from the regime of thermal activation to that of quantum behavior. The present paper’s considerations on tunneling resonance are valid, if the temperature is low enough; say \[2, 3\] below 1 K in the Mn\textsubscript{12} case.

If so, one could apply semiclassical quantization (§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. \[13\].

For the ground state of Mn\textsubscript{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 tunneling frequency is much higher. As a consequence, the afore mentioned 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 \( \delta \) is tuned to 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 does lift it, and only in high orders of \( \alpha/\Gamma S \). At a first sight rather surprisingly – but at a first sight only (§2) – the mathematics underlying tunneling for \( \delta \neq 0 \), when the Hamiltonian’s symmetry of a rotation through \( \pi \) about the \( S_z \) 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 \( \phi \), i.e., average, the expression \( \{\ldots\}^{1/2} \) in \[23\] and below,
\[
x_{\pm} = \pm Q\{1 - 2\epsilon^2 Q^2 + 2\epsilon \left[1 - Q^2 + \epsilon^2 Q^4\right]^{1/2}\}^{1/2},
\]
(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 $\{\ldots\} \geq 0$ so that taking the square root in (44) is well-defined. For the moment we suppose that $a$ and thus $\epsilon$ is small enough to perform a series expansion of the outer square root. It is of the form

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

(51)

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

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

(52)

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

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

(53)

At this point we observe that $r$ depends on $\phi$ through $\cos^2 \phi$. Hence, $\langle g(r) \cos^\ell \phi \rangle$ vanishes for $\ell$ 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,

$$\langle \cos^\ell \phi \rangle = \frac{2^{-\ell}}{2\pi i} \oint_{C_1} \frac{dz}{z} (z + z^{-1})^\ell = 2^{-\ell} \left( \frac{\ell}{2} \right).$$  

(54)

Finally, we are left with

$$\langle \cos \theta \rangle = \pm Q \left[ 1 - \sum_{n \geq 1} \sum_{m=0}^{(n-m)/2} b_n Q^{-2n} (1 - Q^2)^{\frac{m-n}{2}} \left( \frac{a}{2} \right)^{2l+m+n} \binom{n}{m} \binom{\frac{l}{2} (n-m)}{l} \binom{2l + m + n}{l + \frac{1}{2} (m+n)} \right] = \pm Q \left[ 1 - \sum_{k=1}^\infty C_k(Q^2) \left( \frac{a}{2} \right)^{2k} \right]$$  

(55)

where it is understood that $m + n$ is even. If not we were not because of the third binomial coefficient in (55) we could directly resum the series. In the style of Borel [17, 18], however, we could, by noting $n! = \Gamma(n+1)$ and taking an Eulerian integral representation of the second kind [19, 20] for the Gamma function in conjunction with Hankel’s contour integral [19, 20] for its inverse,

$$\frac{1}{\Gamma(t)} = \frac{i}{2\pi} \int_{C_2} \frac{dz}{z} e^{-z} (-z)^{-t},$$  

(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 $C_1 = Q^{-2} + \frac{Q^{-4}}{2}$ and arrive at (31), as advertised.

How good is all this? Since we interchange the series (41) and averaging, viz., $\frac{1}{\Gamma(t)}$, we have to prove uniform convergence of the series and thus, in view of (55), uniform boundedness of $y = \epsilon(\epsilon Q^2 - r)$ as $\cos \phi$ varies between 1 and $-1$. The upshot appears in (54). Plainly, the series in (55) is convergent for $\epsilon$ 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 [17, 18] as above, but this is not the topic of the present paper.
Appendix B: Quantizing to Second Order in $\epsilon$

In this appendix we consider $\epsilon$ as a ‘small’ parameter and sketch how one can perform semiclassical quantization up to second order in $\epsilon$. 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), viz.,
\[ x = -d \pm Q \sqrt{1 - x^2}^{1/2} , \] (57)
simply by $x$. Keeping in mind that $x = \cos \theta$ depends on $\phi$, we fix $\phi$ 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 neighborhood of $\epsilon = 0$. Defining the $n$th partial ‘Taylor sum’ of $x(\epsilon)$ to be
\[ x_n = \sum_{k=0}^{n} \frac{x^{(k)}(0)}{k!} \epsilon^k \equiv \sum_{k=0}^{n} [x]_k \epsilon^k , \] (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
\[ x = x_0 \mp Q \sum_{n \geq 1} b_n \epsilon^n (1 - x^2)^{n/2} . \] (59)
Up to and including terms of order two we then find
\[ x = x_0 \mp Q \epsilon (1 - x^2)^{1/2} + \epsilon^2 (1 - x^2)/2 + O(\epsilon^3) , \] (60)
whence
\[ x_1 = x_0 \mp Q (1 - x_0^2)^{1/2} \epsilon = x_0 + [x]_1 \epsilon \] (61)
because $\sqrt{1 - x^2} = \sqrt{1 - x_0^2} + O(\epsilon)$.

In order to obtain $x_2$, we observe that (60) implies
\[ [x]_2 = \mp Q \{ [\sqrt{1 - x^2}]_1 + [1 - x^2]_0/2 \} . \] (62)
In analogy to (58) we have used the notation $[f]_n = f^{(n)}(0)/n!$.

As for the entries of (58), a simple calculation gives
\[ [\sqrt{1 - x^2}]_1 = \left. \frac{d \sqrt{1 - x^2}}{d \epsilon} \right|_{\epsilon=0} = -x_0 (1 - x_0^2)^{-1/2} x'(0) \]
\[ = -x_0 (1 - x_0^2)^{-1/2} [x]_1 = \mp Q x_0 . \] (63)
Since $[1 - x^2]_0 = 1 - x_0^2$ we end up with
\[ x_2 = x_1 + [x]_2 \epsilon^2 = x_0 \mp Q \epsilon \sqrt{1 - x_0^2} - Q \epsilon^2 Q x_0 \pm (1 - x_0^2)/2 \] (64)
It is $x_2$ that is to be averaged with respect to $\phi$. Inserting $\langle \epsilon \rangle = 0$ and $\langle \epsilon^2 \rangle = a^2/2Q^4$ into $\langle x_2 \rangle$ we obtain Eq. (40).

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