A discrete WKB method is developed for calculating tunnel splittings in spin problems. The method is then applied to the issue of how nuclear spins affect the macroscopic quantum coherence of the total magnetic moment in small magnetic particles. The results are compared with numerical work, and with previous instanton based analytic approaches.

1 Motivation for this Work

Small magnetic particles have now been investigated as good candidates for experimental observation of macroscopic quantum tunneling (MQT) and coherence (MQC). This is because at first sight the main criteria for a system to be a good candidate for seeing MQP (P for phenomena) are met. One of these is that the energy barrier through which the system must tunnel be microscopic, even though the tunneling variable itself is macroscopic. This demand is met for the physical reason that the anisotropy energy barrier originates in spin-orbit or spin-spin interactions at the microscopic level, both of which are relativistic effects, and hence small. A second criterion is that there be a well defined macrovariable, whose dynamics can, to a first approximation, be isolated from those of other microscopic degrees of freedom. This criterion can be met by working at temperatures sufficiently below the equivalent anisotropy energy gap, as spin wave excitations are then frozen out, and we may focus on the net magnetic moment of the particle as the macrovariable.

There are also extremely good reasons to believe, however, that MQP are very hard to observe in general. Chief among these reasons is that the couplings of the macrovariable to the microscopic degrees of freedom give rise to decoherence. This effect can be especially severe in the case of macroscopic quantum coherence, even when the coupling is so small that the semiclassical dynamics of the macrovariable are significantly underdamped. The best studied example which provides a detailed illustration of this point is that of the spin-boson problem. Further support for this point is provided by the scantiness of observational evidence for quantum coherence even in systems that one
would regard as microscopic. Thus, we know of only a few dozen or so “flexible” molecules like NH$_3$ which display coherent flip-flop between different nuclear configurations. The frequency of flip-flop is generally in the 0.1–100 GHz range. Given the vast range of molecular structures, and bonding strengths, there must surely be many naturally occurring molecules whose energy barriers and attempt frequencies are such as to put the flip-flop frequency at about 1 Hz. Yet such flip-flop has never been seen. The reason almost certainly is that such molecules are never naturally encountered in isolation by themselves, and collisions and other environmental interactions are very effective in wiping out the quantum coherence.

It is thus important to identify mechanisms for decoherence in the magnetic particle system, and several have been put forth (phonons, magnons, Stoner excitations). The most critical, however, is the spin of the nuclei in the particle. The hyperfine coupling between the nuclear and electronic spins in magnetic solids is of order 100 MHz or more (in frequency units) per nucleus, which is rather high on the scale of the expected MQC frequencies. At the same time this frequency is rather low on the scale of the attempt frequencies associated with the electronic moments. Nuclear spins are therefore likely to be extremely efficient decoherers or “observers” of the direction of the moment of a small particle. This expectation is confirmed by theoretical calculations for both MQT and MQC. It is the latter that I wish to focus on and revisit in this article, for several reasons. First is that this decoherence mechanism falls outside the scope of the harmonic oscillator bath, so one cannot rely on previous results. The calculations in Ref. 9 are done using an instanton technique with many physically motivated approximations about the trajectories likely to give the dominant contribution to some path integral. It is not obvious even to me that this calculation is done in strict adherence with the Rheinheitsgebot. On the occasions that I have given seminars on the subject, the quizzical looks on the faces of my audience make it clear to me that it does not fully believe or understand my approach. It is therefore desirable to study this problem using different methods, and we shall do so in this article using the discrete WKB method. Although this method itself is quite old (see Braun’s review for references), it does not appear to have been used in spin tunneling problems except for some work by van Hemmen and Sütő. These authors have not fully exploited the power of this method, however. We shall see that calculations which have traditionally been done by instanton methods can be done much more simply to the same accuracy using this method. The opportunity to present the technical aspects of this method in a tutorial volume devoted to tunneling in complex systems is greatly welcome, and provides me with another reason for writing this article.
It should be noted that the same subject has also been studied by Prokof'ev and Stamp in several papers. The first of these correctly notes that the tunneling amplitude is suppressed by nuclear spins, but fails to recognize the implications of this fact for the nature of the tunneling spectrum. See footnote d for more on this. Subsequent papers purport to make detailed calculations of the tunneling spectrum including lineshapes, and also to include a host of other physical effects, such as spin diffusion, the Suhl-Nakamura interaction, and others with less familiar names such as “topological decoherence”, “orthogonality blocking”, and “degeneracy blocking”. I cannot comment on the later work, simply because I do not understand much of it, especially some of the more mathematically specific and detailed conclusions, about lineshapes, for example. My goal in this article will be much more modest. It was argued in Refs. 3 and 9 that in the presence of nuclear spins the tunneling spectrum is broken into several resonance lines. A physical interpretation was attached to this broken-up spectrum, and formulas were presented for their frequencies and spectral weights. This article corroborates these claims. As in the previous papers, I have not attempted to model or calculate the details of the relaxation, i.e., the lineshapes. To this extent, I am only prepared to claim a qualitative understanding for the very low frequency part of the tunneling spectrum. Fortunately, it is the high frequency end that is most likely to be experimentally relevant if at all, and here the situation is much better.

The plan of this article is as follows. In Sec. 2, I will give a brief introduction to the physical problem and the models studied in this paper. Sec. 3 contains a general discussion of the discrete WKB method. This is used to calculate the bare tunnel splitting, i.e., without nuclear spins, in Sec. 4. Nuclear spins are added to the problem in Sec. 5. This section has the bulk of the new results in this article. The results for the tunnel splitting(s) obtained via the discrete WKB method are checked against those from exact numerical diagonalization of model Hamiltonians. I also compare them with those from the instanton approach, and identify which features of the latter appear to be quantitatively robust, and which are only qualitatively correct. I conclude in Sec. 6 with a summary of the effects of nuclear spins, and some general remarks on the observability of MQC in magnetic particles.

2 Introduction to Physical Problem and Models

2.1 Physical System

The physical system is a small insulating magnetic particle, about 50 Å in diameter, at millikelvin temperatures. The anisotropy energy gap is much larger than this, so spin wave excitations are frozen out, and the individual atomic
spins are orientationally locked together. Furthermore, at this size the particle typically contains only one magnetic domain. Thus the magnitude of the total spin or magnetic moment of the particle is essentially fixed proportional to the number of atomic spins (assuming one magnetic species for simplicity), and the only relevant dynamical variable is its direction. (It may be useful to think of the system in terms of a Heisenberg-like model, with additional single-ion anisotropy terms.) The existence of anisotropy implies that some directions are energetically favored over others, and we wish to investigate whether the spin orientation can display quantum mechanical behavior, in particular tunneling and/or coherent oscillation between different energy minima.

A model Hamiltonian which incorporates the above features is:

$$H_0 = -k'_1 S^2_z + k'_2 S^2_x$$

Here $S_x$, $S_y$, and $S_z$ are the components of our large spin, and $k'_i$ are phenomenological anisotropy coefficients. This particular Hamiltonian is time-reversal invariant, which should be the case if our particle is not subject to any external magnetic fields. We take $k'_1 > 0$, $k'_2 > 0$, so that in classical language, $\pm \hat{z}$ are easy directions, and $\pm \hat{x}$ are hard directions. Quantum mechanically, the two classical ground states $\pm \hat{z}$ will be split by tunneling. A generally valid approximate expression for the tunnel splitting can be obtained by writing

$$\Delta_0 \simeq \omega_e \exp(-S \mu/\omega_e).$$

[A more exact expression is given in Eq. (24) below.] In this formula,

$$\omega_e = 2(k_1 k_{12})^{1/2}$$

is the oscillation (or precession) frequency for small deviations of the spin orientation from the classical equilibrium directions $\pm \hat{z}$ and we have also defined

$$k_1 = S k'_1, \quad k_2 = S k'_2, \quad k_{12} = k_1 + k_2.$$  

Further, $S \mu$ is a quantity proportional to the energy barrier, of order $S k_{12}$. We work throughout in units such that $\hbar = 1$.

We next wish to consider the influence of nuclear spins. To model this let us suppose that $N_n$ of the atoms have nuclei with spins $I_i$, and take all of these to be of magnitude $1/2$. Let us further simplify the problem and assume that the hyperfine interaction for each of these atoms is of identical strength and of the form $s_i \cdot I_i$, where $s_i$ is the electronic spin on atom $i$. All the assumptions

\[\text{This result may be derived by writing down the Heisenberg equation of motion for } S, \text{ and linearizing it in small deviations from } S = S \hat{z}.\]
except that of identical interaction strength are immaterial, and even this is a rather good approximation. The effects of relaxing it will be briefly discussed in Sec. 5.3. The total hyperfine contribution to the Hamiltonian can then be written as

$$H_{hf} = -\frac{\omega_n}{S} \sum_{i=1}^{N_n} s_i \cdot I_i = -\frac{\omega_n}{S} \mathbf{S} \cdot \mathbf{I}_{tot}, \quad (5)$$

where we have expressed the coupling constant in terms of $\omega_n$, the nuclear Larmor frequency that would be obtained if the electronic spin orientation were fixed. The first expression in Eq. (5) is just the sum of the interactions for the individual atoms, and the second follows from assuming that the atomic spins are all parallel to one another, which permits one to write $s_i = (s/S)\mathbf{S}$ for all $i$. The remaining sum equals $\sum_i \mathbf{I}_i$, which we call $\mathbf{I}_{tot}$, the total nuclear spin. For any given value of $N_n$, $\mathbf{I}_{tot}$ can take on values ranging in integer steps from $N_n/2$ to either 0 (if $N_n$ is even) or 1/2 (if $N_n$ is odd), with multiplicities that can easily be found. (See below.) Since $H_{hf}$ commutes with $I_{tot}^2$, we can consider the problem for one value of $I_{tot}$ at a time. Writing $I$ instead of $I_{tot}$ henceforth, we arrive at a model Hamiltonian obtained by adding Eqs. (1) and (5), i.e.,

$$H_I = \frac{1}{S} \left(-k_1 S_z^2 + k_2 S_x^2 - \omega_n \mathbf{S} \cdot \mathbf{I}\right). \quad (6)$$

[For completeness, we give here the formula for the multiplicity, i.e., the number of times a given value of $I_{tot}$ appears when $N_n$ spins of magnitude 1/2 are added together. For $I_{tot} = (N_n/2) - k$, the multiplicity is given by

$$\binom{N_n}{k} - \binom{N_n}{k - 1}. \quad (7)$$

As an example, if $N_n = 6$, multiplets with $I_{tot} = 3, 2, 1, \text{and } 0, \text{occur } 1, 5, 9, \text{and } 5 \text{times respectively}.\]

It should be noted at this point that for a particle of diameter 50 Å, which corresponds to $S = O(10^4)$, and typical material or anisotropy parameters, the tunnel splitting $\Delta_0$ as given by Eq. (2) is unobservably small. Of course the splitting goes up if $S$ is decreased, but particles much smaller than 50 Å seem difficult to attain controllably and reproducibly with present day technology.\[^{b}\]

\[^{b}\]The last few years have seen some very interesting work\[^{16,17,18}\] on systems with much smaller values of $S$, of order 10. These systems are based on magnetic molecules, where the value of $S$ is highly reproducible, but it is my belief that the interesting questions here are quite different, and have little to do with MQP. Interestingly, semicalssical methods, such as those developed in this paper, are likely to be quite valuable in analyzing these systems. For particles with intermediate values of $S$, say about 100, on the other hand, it will probably be necessary to devise new ways of treating the environment because the law of large numbers will no longer be applicable.
MQC is a more likely proposition in antiferromagnetic particles\textsuperscript{19, 20, 21} where the two states involved differ in the orientation of the Néel vector, or the spins on one of the sublattices.\textsuperscript{c} The essential aspects of the earlier papers,\textsuperscript{3, 9} in which the influence of nuclear spins was studied using instantons, hold equally for ferro- and antiferro-magnetic particles. My goal in this article is to try and verify the predictions of the instanton approach as quantitatively as possible. It is simpler to do this using a ferromagnetic model, and I shall therefore limit myself to that in this article.

I also do not wish to discuss at length the experimental observability of the reversal phenomenon. In addition to the values of the physical parameters mentioned above, this hinges on a number of other issues such as the temperature, the signal size, stray magnetic fields, the nature of the substrate, etc. We refer readers to previous papers\textsuperscript{3, 9, 22, 23} for detailed discussions of these points. For the purposes of this article, we will only note that the ratio $\omega_n/\omega_e$ is of order $10^{-3}$ to $10^{-2}$ in antiferromagnets, and is about one order of magnitude higher in ferromagnets. Throughout this article therefore, we shall assume that $\omega_n/\omega_e \ll 1$, and work to leading order in this ratio. We shall further assume that $\Delta_0/\omega_n \ll 1$, which, by virtue of the exponentially small WKB or Gamow factor, is almost certain to be the case for values of $S$ of interest to us.

2.2 What to Calculate; Preliminary Arguments

Having settled on a theoretical model, let us ask what physical quantity we should calculate. One way the dynamical behaviour of the moment can be described is in terms of a time dependent probability to find it along some direction given an initial state in which it was prepared.\textsuperscript{4, 5} This description best applies to experiments on a single system. Another way is to find the appropriate frequency-dependent dynamical susceptibility $\chi(\omega)$. This description better applies to an assembly of identical or nearly identical systems, such as is obtained in an NMR experiment. We will adopt the second approach.

Let us suppose then that we wish to calculate $\chi''(\omega)$ for our magnetic particle. Since the Hamiltonian (6) describes a closed system, $\chi''$ can only consist of a set of delta functions. The real system is of course not closed, and has means of energy relaxation such as phonons, with which the spins can interact in a variety of ways. These will lead to line widths and broadening in the usual way. Now in a setup such as NMR, the resonance frequencies are few in number and usually known quite accurately to begin with. Interest\textsuperscript{c} The reason for this is quite simple. The tunnel splitting can still be written in the form $\Delta_0$. The energy barrier $Su$ is of the same order of magnitude, but the electronic spin attempt frequency, $\omega_e$, is about 100 times higher for antiferromagnets than ferromagnets, being given by the geometric mean of an exchange energy and an anisotropy energy in contrast to Eq. (3).
Figure 1: Structure of low lying energy levels of coupled electron and nuclear spin systems. The states $|\pm 0\rangle$ are electronic spin ground states with $S$ localized along $\pm \hat{z}$ in the absence of the nuclear spins. The corresponding first two excited states are $|\pm 1\rangle$ and $|\pm 2\rangle$. The central part of the figure shows how the ground electronic levels are modified by the nuclear spins, still ignoring tunneling. The ratio $\omega_e/\omega_n \gg 1$ and is not accurately represented in the figure. If $\omega_n \gg \Delta_0$, only states joined by dashed lines mix with each other to any appreciable extent once tunneling is turned on.
by $| + 0, p \rangle$, and $| - 0, p \rangle$, where $p = 2I_z$, will be split into $2I + 1$ Zeeman levels with a spacing $\omega_n$. (The higher states $| \pm 1 \rangle, | \pm 2 \rangle, \ldots$, will also be similarly split, but we do not consider that for the moment.) As long as $I$ is small enough so that $2I\omega_n \ll \omega_e$, our basic assumption that $\omega_n \gg \Delta_0$ combined with the physically obvious but important fact that significant resonance is only possible between states that are degenerate to within the matrix element connecting them implies that the state $| + 0, p \rangle$ will resonantly tunnel only to the state $| - 0, -p \rangle$. Since this tunneling now involves a change in the nuclear spin state in addition to that of the electronic spin, the splitting should in general be different from $\Delta_0$. We denote the magnitude of this splitting by $\Delta(I, p)$, i.e.,

$$\Delta(I, p) = \pm (E_{g(0,p)} - E_{u(0,p)}),$$

where $E_{g(0,p)}$ and $E_{u(0,p)}$ denote the energies of the antisymmetric and symmetric linear combinations $(|0, p\rangle \mp |0, p\rangle)/\sqrt{2}$. Note that the antisymmetric state need not be the one with higher energy.

To orient further discussion, let us summarize the results of the instanton approach. In this approach too the starting point is that the nuclear spins spoil the degeneracy between the $| \pm 0 \rangle$ states. An instanton connecting degenerate states must involve the flipping over of a certain number of nuclear spins along with that of $S$. Since the nuclear spins can only respond on a time scale $\omega_n^{-1}$ to any perturbation, and the instanton has a temporal width of order $\omega_e^{-1}$, perturbation theory shows that each nuclear spin coflip reduces the tunneling amplitude by a factor $\sim (\omega_n/\omega_e)$. The amplitude for $p$ nuclear spin coflips was found (in the case of an antiferromagnetic particle) to be

$$\Delta_p = (\pi \omega_n / 2 \omega_e)^{|p|} \Delta_0.$$  

In other words, the tunneling amplitude decreases geometrically with the number of units by which $I_z$ must change. If this is so (and we will find here that by and large it is), then clearly the more interesting problem is find the tunneling frequencies $\Delta(I, p)$ themselves, and the associated spectral weight to be assigned to each frequency. The issue of linewidths and relaxation becomes secondary. As stated in the previous section, however, the calculation on which these conclusions are based is not totally satisfactory. It is with this viewpoint that we focus in this article on calculating the splittings as carefully as possible.

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\[d\]This reduction of tunneling amplitudes due to nuclear spin coflips was also found by Prokof’ev and Stamp. The highly chopped-up nature of the $\chi''$ spectrum was missed by them, however, and the mechanism for decoherence initially studied by them is rather different from mine.
It should be clarified that the amplitudes $\Delta_p$ are not to be identified with the tunnel splittings themselves. To see this, consider a multistate trajectory that starts and ends at a specific state with $S_z = S$ and $I_z = p/2$. The intermediate states with a long residence time in this trajectory are those with $S_z = S$, $I_z = p/2$, and $S_z = -S$, $I_z = -p/2$. Since $p$ spins can be chosen from $N_n$ in many ways, there can be several such intermediate states, and the amplitudes for all the corresponding trajectories must be added together. This leads to interference effects. When the combinatoric factors are added together, it is found that the splittings are given by

$$\left( \begin{array}{c} n \\ |p| \end{array} \right) \Delta_p, \quad n = |p|, |p| + 1, \ldots, (N_n + |p|)/2. \quad (10)$$

In this article we will try and see how correct these results are. The main flaw in the previous work is the conclusion that $\Delta_p = \Delta_{-p}$, i.e., that the $|0, p\rangle \leftrightarrow |-0, -p\rangle$ and $|0, -p\rangle \leftrightarrow |-0, p\rangle$ splittings are the same. In yet more words, the splittings for $p$ co-flips are independent of whether the co-flipping spins are parallel or antiparallel to the large electronic spin $S$. We will see that this is no longer true. Further, the geometric dependence $(\omega_n/\omega_e)^{|p|}$ seems to be only approximately correct. Finally, we will show in Sec. 5 that the binomial factor in Eq. (10) follows from a simple effective tunneling Hamiltonian connecting the states $|0, p\rangle$ and $|-0, -p\rangle$, which holds as long as $\omega_n/\omega_e \ll 1$.

One trivial point should be noted and disposed of once and for all. Since the Hamiltonian (6) is time-reversal invariant, the bare tunnel splitting vanishes unless $S$ is an integer, and all the splittings $\Delta(I, p)$ vanish unless $S + I$ is an integer. For the purposes of interpreting the relation (10) (or a more accurate replacement) it is useful to define $\Delta_0$ for all $S$ by Eq. (2) or its more accurate version, Eq. (24) below.

3 The Discrete WKB Method

Like its continuous counterpart, the discrete WKB method is applicable to a wide variety of settings. (See the review by Braun for examples.) We will only give an overview and physically motivated discussion of this method using the Hamiltonian (1) as an illustrative example.

Let us write a general eigenfunction of $H_0$ as $\sum_m a_m |m\rangle$, where as usual $S_z |m\rangle = m |m\rangle$. Schrödinger’s equation then becomes a three-term recursion relation for the coefficients $a_m$:

$$w_m a_m + t_{m,m+2} a_{m+2} + t_{m,m-2} a_{m-2} = E a_m, \quad (11)$$

where $w_m = \langle m | H_0 | m \rangle$, and $t_{m,m+2} = \langle m | H_0 | m \pm 2 \rangle$. Now for large $S$, the differences $w_{m+2} - w_m$ and $t_{m,m+2} - t_{m-2,m}$, etc., are of order $1/S$ relative
Figure 2: Mapping of spin problem onto an electron hopping on a lattice. The diagram is drawn for a case such as Eq. (11) with only second neighbour hopping. It is evident that the sites connected by dashed and solid lines then belong to two disjoint subspaces of the Hamiltonian.

to $w_m$ and $t_{m,m+2}$ themselves. It is thus extremely useful to view Eq. (11) as arising from a tight-binding model for an electron on a one-dimensional lattice with sites labeled by $m$, on-site energies $w_m$, and hopping energies $t_{m,m±2}$, that vary slowly with position. (See Fig. 2.) This viewpoint immediately suggests the approximation of semiclassical electron dynamics, and indeed this approximation is identical to discrete WKB.

To apply semiclassical dynamics, we define local $m$-dependent functions $w(m)$ and $t(m)$ by

$$w(m) = w_m, \quad t(m) = (t_{m,m+2} + t_{m,m-2})/2,$$

which we extend to continuous values of $m$ by demanding that they be smooth, and that $dw/dm$ and $dt/dm$ be of relative order $S^{-1}$ with $m$ formally regarded as a quantity of order 1. A particle of energy $E$ can be assigned a local, $m$-dependent, wavevector $q(m)$ in complete analogy with the continuous WKB approach. The only difference is that the kinetic energy is given by $2t(m)\cos q(m)$ instead of $q^2(m)/2\mu$ ($\mu$ being the mass). We thus obtain

$$q(m) = \cos^{-1} \left( \frac{E - w(m)}{2t(m)} \right).$$

The general solution to (11) is given by linear combinations of

$$a_m \sim \frac{1}{\sqrt{v(m)}} \exp \left( \pm i \int^m q(m') \frac{dm'}{2} \right).$$

For the Hamiltonian (11), the hopping connects sites differing by $\Delta m = 2$, so that the eigenvalue problem divides into two subspaces depending on whether $S - m$ is even or odd. This point is of no consequence for application of the discrete WKB method itself, as the problem can be recast as one of nearest-neighbor hopping in each subspace.
Figure 3: Discrete WKB method potential energy diagram for a symmetric double-well problem. The functions $U_{\pm}(m) = w(m) \pm 2t(m)$ are the local band edges. For a particle with energy $E$ as shown, the regions $m_1 \leq m \leq m_2$, and $m_3 \leq m \leq m_4$ are classically accessible, and represent the two wells. The particle must tunnel across the classically forbidden region between $m_3$ and $m_4$.

In this equation,

$$v(m) = -2t(m) \sin q(m)$$  \hspace{1cm} (15)

is the local particle velocity (equal to $\partial E/\partial q$), and the factor $[v(m)]^{-1/2}$ fixes the normalization so that the probability current is conserved. Also, the factor of $1/2$ in the integrand reflects the step length $\Delta m = 2$ in Eq. (11).

We conclude here our general discussion of the discrete WKB method, and continue the illustration with the Hamiltonian (1) in the next section. Braun's review\cite{12} contains a proper proof of the above approximations, as well as connection formulas at turning points, Bohr-Sommerfeld quantization rules, etc. Most of these are physically apparent, and the chief novelty arises from the fact that for particle in a periodic potential (or a tight-binding model), the allowed energies lie in a band, and are bounded both above and below. This gives rise to turning points when the energy equals the local upper band edge $w(m) + 2|t(m)|$, in addition to those that occur when the energy equals $w(m) - 2|t(m)|$. These features are illustrated in Fig. 3. Braun refers to the first kind of turning point as “unusual”, but the associated formulas are easily derived from those for a “usual” turning point by making a gauge transformation which changes the sign of every other coefficient $a_m$. The associated bookkeeping can be fairly cumbersome, however, and it is easy to make mistakes.
4 Tunnel Splitting for the Hamiltonian

We now turn to applying the discrete WKB method to finding the ground state wavefunction and tunnel splitting $\Delta_0$ for the Hamiltonian (1). (We can also find the higher splittings and wavefunctions.\footnote{See Eq. (23) below. This formula is analogous to one that appears in the solution to Problem 3, Sec. 50, in the famous text by Landau and Lifshitz.\footnote{However, it is not the final formula in that solution! We have found it preferable to use the unnumbered intermediate equation in which the splitting is given as a product of the wavefunction and its derivative at the symmetry point of the potential. The three dimensional analog of the latter formula is often named after C. Herring who first used it find the splitting of the electron terms in the $H^+_2$ ion. This problem is also discussed by Landau and Lifshitz in the solution to the problem accompanying Sec. 81.}}) There are three steps in finding the wavefunction itself: (i) find it in the classically allowed region, (ii) find it in the classically forbidden region $|m| \ll S$, (iii) match the two parts of the wavefunction using the connection formulas or otherwise. The splitting is then obtainable by a textbook formula.

To find the wavefunction in the classically allowed region near $m = -S$, e.g., it is advantageous to write $C_n = a_{-S+n}$, with $n = 0, 1, \ldots$. It is generally necessary to obtain the functions $u(m)$ and $t(m)$ to an accuracy such that the first two terms in an expansion in powers of $S^{-1}$ are correctly given; if only the leading term is kept, then retention of the $\left(\frac{u(m)}{v(m)}\right)^{-1/2}$ factor in Eq. (14) can not be justified. In carrying out this exercise near the ends of the chain, as is the case now, it is necessary to treat $n = S + m$ rather than $m$ as a quantity of order $S^0$. It is also useful to add a constant $k'_1 S(S + 1)$ to the Hamiltonian. The Schrödinger equation then reads

$$\left(2k_1 + k_2\right) \left(n + 1\right) C_n + \frac{1}{2} k_2 \sqrt{n(n-1)} C_{n-2} + \frac{1}{2} k_2 \sqrt{(n+1)(n+2)} C_{n+2} = E C_n. \quad (16)$$

This equation, however, can be solved exactly. It is that for the harmonic oscillator Hamiltonian

$$\mathcal{H}_{ho} = (2k_1 + k_2) a^\dagger a + \frac{1}{2} k_2 (a^2 + a^\dagger)^2, \quad (17)$$

where $a^\dagger$ and $a$ are raising and lowering operators for the number eigenstates $|n\rangle$ obeying $a^\dagger a |n\rangle = n |n\rangle$, and $C_n = \langle n | \psi \rangle$ for an energy eigenfunction $|\psi\rangle$. We can diagonalize $\mathcal{H}_{ho}$ by writing $a = (x + ip)/2^{1/2}$, $a^\dagger = (x - ip)/2^{1/2}$, where $x$ and $p$ are canonical position and momentum operators obeying $[x, p] = i$ as usual. This yields

$$\mathcal{H}_{ho} = k_{12} x^2 + k_1 p^2. \quad (18)$$
The wavefunction $C_n$ (automatically normalized to unity) is now easily obtained by evaluating the overlap $\langle n|\psi \rangle$ in the $x$ representation. We quote the final result for the ground state. $C_n$ vanishes for odd $n$, and for even $n$ it equals

$$C_n = \sqrt{\text{sech} \theta} \left( \frac{n}{n/2} \right)^{1/2} \left( -\frac{\tanh \theta}{2} \right)^{n/2},$$

(19)

where

$$\theta = (1/4) \ln(k_{12}/k_1).$$

(20)

It is also useful to note the relations $\sinh 2\theta = k_2/\omega_e$, $\cosh 2\theta = (2k_1+k_2)/\omega_e$, and $\tanh 2\theta = k_2/(2k_1+k_2)$, with $\omega_e = 2(k_1k_{12})^{1/2}$ as defined in Eq. (3). That $\omega_e$ is the small precession frequency for the electronic moments is now obvious from Eq. (18).

We mention for completeness that the above results also follow from making a Bogoliubov transformation

$$a = \cosh \theta b - \sinh \theta b^\dagger,$$

(21)

$$a^\dagger = -\sinh \theta b + \cosh \theta b^\dagger,$$

which, with $\theta$ given by Eq. (20), diagonalizes $\mathcal{H}_{\text{lo}}$. The coefficients $C_n$ follow from an obvious two-term recursion relation connecting $C_n$ and $C_{n-2}$.

The only constraint used in deriving Eq. (19) was $n \ll S$. In particular, the result holds for $S \gg n \gg 1$. Thus it actually extends out into part of the classically forbidden region. This is a great advantage as it allows us to match to the quasiclassical form of the wavefunction on the other side of the turning point directly, obviating the need for connection formulas.

The wavefunction in the classically forbidden region is directly found using the formulas (14) and (15). Under the conditions $n/2 \gg 1$, $S - n/2 \gg 1$, we find that for even $n$

$$C_n = \left( \frac{n}{2} \left( 1 - \frac{n}{2S} \right)^3 \right)^{-1/4} \left( \text{sech} \theta \right)^{1/2} \left( -\tanh \theta \right)^{n/2}.$$

(22)

$C_n$ continues to vanish for odd $n$.) We have already adjusted the multiplicative constant in this result, so as to agree with Eq. (19) when $S \gg n \gg 1$.

The tunnel splitting is generally given by the formula (see footnote $f$)

$$\Delta_0 = \begin{cases} 2t_{2,0}|a_0(a_2 - a_{-2})|, & \text{even } S, \\ 2t_{1,-1}|a_1^2 - (a_{-1})^2|, & \text{odd } S. \end{cases}$$

(23)

(It is also easily shown that the antisymmetric state is lower in energy for odd $S$, and higher for even $S$.) Applying this formula to the problem at hand, we
Table 1: Comparison between numerical and analytical [Eq. (24)] results for the tunnel splitting without nuclear spins. The parameters are $k_1 = 5.0$, $k_2 = 20.0$.

| $S$  | $\Delta_0$ (numerical) | $\Delta_0$ (analytic) | Error(%) |
|------|------------------------|------------------------|----------|
| 10   | $9.282 \times 10^{-3}$  | $9.749 \times 10^{-3}$  | 5.0      |
| 11   | $3.738 \times 10^{-3}$  | $3.906 \times 10^{-3}$  | 4.5      |
| 12   | $1.497 \times 10^{-3}$  | $1.558 \times 10^{-3}$  | 4.1      |
| 13   | $5.974 \times 10^{-4}$  | $6.195 \times 10^{-4}$  | 3.7      |
| 14   | $2.375 \times 10^{-4}$  | $2.455 \times 10^{-4}$  | 3.4      |
| 15   | $9.412 \times 10^{-5}$  | $9.708 \times 10^{-5}$  | 3.1      |
| 16   | $3.721 \times 10^{-5}$  | $3.830 \times 10^{-5}$  | 2.9      |
| 17   | $1.468 \times 10^{-5}$  | $1.508 \times 10^{-5}$  | 2.7      |
| 18   | $5.778 \times 10^{-6}$  | $5.927 \times 10^{-6}$  | 2.6      |
| 19   | $2.271 \times 10^{-6}$  | $2.326 \times 10^{-6}$  | 2.4      |
| 20   | $8.910 \times 10^{-7}$  | $9.115 \times 10^{-7}$  | 2.3      |

obtain

$$\Delta_0 = 4\omega_e \left(\frac{S}{\pi}\right)^{1/2} \text{sech} \theta \tanh S \theta.$$  \hspace{1cm} (24)

Since $\tanh \theta < 1$, the last factor in this result can be rewritten as a WKB or Gamow factor $\exp(-S|\ln \tanh \theta|)$. For $k_1/k_12 \ll 1$, this is approximately equal to $\exp(-4Sk_12/\omega_e)$, which is of the same form as Eq. (2).

It is of interest to note that the only previous calculations of $\Delta_0$ to the same accuracy (and with which we agree completely) are by Enz and Schilling, and by Belinicher, Provdencia, and Providencia, both of whom employ methods of much greater complexity. Other tunnel splitting calculations either find an incorrect prefactor, or not at all. In Table 1, we compare the formula with exact answers for the splitting obtained by numerical diagonalization of $H_0$ for $S$ ranging from 10 to 20, for parameters $k_2 = 20.0$, and $k_1 = k_2/4 = 5.0$. This choice yields $\omega_e = 22.36$, $\tanh \theta = 0.3820$, and $\text{sech} \theta = 0.9242$. As can be seen, the errors are quite small and the results improve steadily with increasing $S$. Note further that Eq. (24) consistently overestimates the splitting. These results are in keeping with previous numerical studies.

5 Inclusion of Nuclear Spins

5.1 One-Configurational Splittings

The results of the previous section enable us to calculate the tunnel splitting $\Delta(I,p/2)$ for small values of $I$ and $p$. Let us begin with the simplest possible
Figure 4: Lattice diagram for MQC problem with one nuclear spin coflip. The $k_z S_z^2$ and $S_z I_z$ bonds are shown by heavy solid and dashed lines respectively. The division into two subspaces is again evident.

case, when $I = 1/2$, and $p = \pm 1$. Then as discussed in Sec. 2, it is necessary to take $S$ to be a half integer. We will write $S = N + 1/2$, where $N$ is an integer.

In the language developed in the last section, the problem is now equivalent to that of an electron hopping on a lattice with two rows, corresponding to $I_z = \pm 1/2$, and $2S + 1 = 2(N + 1)$ lattice points per row. The problem is represented pictorially in Fig. 4, where the various non-zero off-diagonal elements of the Hamiltonian (6) are shown as bonds connecting the corresponding lattice points. The bonds connecting alternate sites in the same row arise from the $k_z S_z^2$ term, while the bonds connecting sites in different rows arise from the terms $S_z I_z$ and $S_\pm I_\mp$. It is apparent that the sites form two groups that are disconnected from each other, or in proper mathematical language, that the Hamiltonian divides into two disjoint subspaces. In particular the splitting of the two lowest states in the space that contains the state $| - S, -1/2 \rangle$ equals $\Delta(1/2, 1)$, while the splitting in the space containing $| - S, +1/2 \rangle$ equals $\Delta(1/2, -1)$.

Let us first calculate $\Delta(1/2, -1)$ [which equals $\Delta_1$ as we will show in Eq. (46) below]. The lattice diagram for this is shown in Fig. 5, where we have thrown away the states in the other subspace, and we have relabeled the sites as explained below. We will obtain the splitting by finding a suitable effective two-state Hamiltonian. To this end, let us first ignore the $S_\pm I_\mp$ terms in $H_I$. The two lowest energy states are then $| + 0, p = -1 \rangle \equiv | I \rangle$ and $| - 0, p = +1 \rangle \equiv | II \rangle$. These states live on different rows of the lattice, with $| I \rangle$ and $| II \rangle$ being localized near the right edge of the lower row, and the left

---

It is necessary in this section to refer to two different types of states with similar labels: the states $| S_z, I_z \rangle$, and the states $| \pm n, p \rangle$, where $n$ is the harmonic-oscillator-like excitation index used in Sec. 2.2. We shall avoid notational confusion by referring to the second type of state as $| 0, p = 1 \rangle$, $| - 0, p = 1 \rangle$, etc., in which the label $p$ is explicitly identified.
edge of the upper row, respectively. It should be carefully noted that neither state is large near both ends. The state which is large near \( S_z = -S + 1 \) and \( I_z = -1/2 \) (lower left corner), for example, is approximately equal to \( | -1, p = -1 \rangle \) which is higher in energy than \( | I \rangle \) or \( | II \rangle \) by \( \omega_e \). The additional bias in the on-site energy due to the term \( \omega_n S_z I_z / S \) is not large enough to offset this energy difference since \( \omega_n \ll \omega_e \). For the same reason, the wavefunctions of the states \( | I \rangle \) and \( | II \rangle \) are very well approximated by the wavefunction found in the previous section. It is necessary only to redefine the position coordinate appropriately. We do this by labelling the sites in Fig. 5 by \( j = 0, 1, \ldots, N \), where \( j \) runs from left to right for the upper row, and in the opposite direction for the lower row. Then

\[
\langle S - 2j, -1/2|I\rangle = \langle -S + 2j, +1/2|II\rangle = C'_j. \tag{25}
\]

Further, \( C'_j = C_{2j} \) where \( C_{2j} \) is given by Eqs. (14) and (22).

The effective two-state Hamiltonian can be written as

\[
\mathcal{H}_{\text{eff}} = \begin{pmatrix} E_0 & V \\ V & E_0 \end{pmatrix}, \tag{26}
\]

where \( E_0 = \langle I|\mathcal{H}_I|I\rangle = \langle II|\mathcal{H}_I|II\rangle \), and \( V = \langle I|\mathcal{H}_I|II\rangle = \langle II|\mathcal{H}_I|I\rangle \). The value of \( E_0 \) is clearly immaterial, while the tunnel splitting is given by \( 2|V| \). The off-diagonal element \( V \) arises from the \( S_+ I_- \) and \( S_- I_+ \) terms and can be directly evaluated because \( \omega_n \ll \omega_e \). We have

\[
V = \sum_{j=0}^{N} C'_j C'_{N-j} \left( -S + 2j + 1, -\frac{1}{2} \left| \frac{\omega_n}{2S} S_+ I_- \right| - S + 2j, \frac{1}{2} \right),
\]

\[
= -\left( \frac{\omega_n}{2S} \right) \sum_{j=0}^{N} C'_j C'_{N-j} \left( (2j + 1)(2S - 2j) \right)^{1/2}. \tag{27}
\]
The dominant contribution to the sum arises from the middle of the chains, i.e., from values of \( j \) such that \( (N - j), j \gg 1 \). Using Eq. (22) and neglecting terms of order unity in comparison with \( j \) and \( N - j \), we obtain

\[
V = -(-1)^N 2 \omega_n (S/\pi)^{1/2} \text{sech} \theta \tanh \theta \sum_j [(j + 1/2)(N - j + 1/2)]^{-1/2}.
\]

(28)

For \( N \gg 1 \) the sum may be approximated by an integral, which is easily shown to equal \( \pi \). Making use of Eq. (24), and recalling that \( S = N + 1/2 \), we can write the tunnel splitting (which equals \( 2|V| \)) as

\[
\Delta = \Delta(1/2, 1) = \frac{\pi \omega_n}{2 \omega_c} (\tanh \theta)^{-1/2} \Delta_0.
\]

(29)

The splitting \( \Delta(1/2, 1) \) (\( = \Delta_1 \)) can be found in the same way. The appropriate lattice diagram is drawn in Fig. 6. This time the two low energy states are \(| + 0, p = 1 \rangle \) and \(| - 0, p = -1 \rangle \), and the wavefunctions are given by the same \( C_j' \) as above with the sites labeled as shown. The key quantity is again the off-diagonal element. It is obvious from the figure that this is again given by a sum as in Eq. (23). The only change required is that we replace the product of wave functions in that summand by \( C_j' C_{N+1-j}' \). The sum is again dominated by the central region, and since \( C_j' \approx -\tanh \theta C_j' \) in this region, the change in the summand has the effect of multiplying each term in the sum by \(-\tanh \theta\). The final result for the splitting is, therefore,

\[
\Delta_1 = \Delta(1/2, 1) = \frac{\pi \omega_n}{2 \omega_c} (\tanh \theta)^{1/2} \Delta_0.
\]

(30)

We thus see that apart from the factors of \((\tanh \theta)^{\pm 1/2}\), the results (29) and (30) agree with the instanton answer, Eq. (9). This agreement shows that...
The hyperfine coupling term in the H̃_10 approach by exercising a little more care. These factors can also be found from the instanton method is basically sound, and although it cannot not in its simplest version give the prefactors in ∆_0 correctly, the overall picture it provides is correct. In fact, the ( tanh θ) ±1/2 factors can also be found from the instanton approach by exercising a little more care. These origin of these factors is actually very easy to understand. They reflect the fact that the state with antiparallel alignment of the electronic and nuclear spins has greater quantum fluctuations or zero point motion than the state with parallel alignment. An- other way to say this is that the state ∣S_z = S, I_z = I⟩ is an eigenstate of the hyperfine coupling term in H̃_1, while ∣S_z = S, I_z = −I⟩ is not. This difference in zero point fluctuations shows up as a higher tunneling rate for coflips in which the nuclear spins are oppositely aligned to the electronic ones.

### Table 2: Comparison between numerical and analytical [Eqs. (29) and (30)] results for one-coflip tunnel splitting. The parameters are k_1 = 5.0, k_2 = 20.0, and ω_0 = 0.1. For each value of S, the entry in the upper row is ∆_1, and that in the lower row ∆_{−1}.

| S   | ∆_{±1} (numerical) | ∆_{±1} (analytic) | Error(%) |
|-----|--------------------|-------------------|----------|
| 10  | 2.576 × 10^{-5}    | 2.681 × 10^{-5}   | 4.1      |
|     | 6.661 × 10^{-5}    | 7.018 × 10^{-5}   | 5.4      |
| 11  | 1.034 × 10^{-5}    | 1.072 × 10^{-5}   | 3.6      |
|     | 2.674 × 10^{-5}    | 2.805 × 10^{-5}   | 4.9      |
| 12  | 4.134 × 10^{-6}    | 4.267 × 10^{-6}   | 3.2      |
|     | 1.069 × 10^{-5}    | 1.117 × 10^{-5}   | 4.5      |
| 13  | 1.646 × 10^{-6}    | 1.694 × 10^{-6}   | 2.9      |
|     | 4.257 × 10^{-6}    | 4.435 × 10^{-6}   | 4.2      |
| 14  | 6.534 × 10^{-7}    | 6.705 × 10^{-7}   | 2.6      |
|     | 1.689 × 10^{-6}    | 1.755 × 10^{-6}   | 3.9      |
| 15  | 2.587 × 10^{-7}    | 2.648 × 10^{-7}   | 2.4      |
|     | 6.688 × 10^{-7}    | 6.933 × 10^{-7}   | 3.7      |
| 16  | 1.022 × 10^{-7}    | 1.044 × 10^{-7}   | 2.2      |
|     | 2.641 × 10^{-7}    | 2.732 × 10^{-7}   | 3.5      |
| 17  | 4.024 × 10^{-8}    | 4.105 × 10^{-8}   | 2.0      |
|     | 1.041 × 10^{-7}    | 1.075 × 10^{-7}   | 3.3      |
| 18  | 1.583 × 10^{-8}    | 1.612 × 10^{-8}   | 1.9      |
|     | 4.092 × 10^{-8}    | 4.221 × 10^{-8}   | 3.2      |
| 19  | 6.217 × 10^{-9}    | 6.322 × 10^{-9}   | 1.7      |
|     | 1.608 × 10^{-8}    | 1.655 × 10^{-8}   | 3.0      |
| 20  | 2.438 × 10^{-9}    | 2.476 × 10^{-9}   | 1.6      |
|     | 6.303 × 10^{-9}    | 6.482 × 10^{-9}   | 2.9      |
We also remind readers that in Eqs. (29) and (30), $\Delta_0$ is not the tunnel splitting for the bare problem without nuclear spins (which vanishes because $S$ is half-integral), but rather the pseudo-splitting formally given by Eq. (24).

In Table 2, we show the comparison between the above formulas and exact answers from numerical diagonalization of $H_I$ with $I = 1/2$. We choose $k_1 = 5.0$ and $k_2 = 20.0$ as before, and $\omega_n = 0.1$. Since $\omega_e = 22.36$, the condition $\omega_n \ll \omega_e$ is well obeyed. Again the agreement is very satisfactory, and improves with increasing $S$. In particular, the inclusion of the $(\tanh \theta)_{\pm 1/2}$ factors seems to be required.

### 5.2 Two-Coflip Splittings

Let us proceed to calculate the two-coflip splittings, $\Delta(1, \pm 2) (= \Delta_{\pm 2})$, by studying the Hamiltonian (1) for $I = 1$ and integer $S$. As before, we carry out the calculation by including the $S_z I_z$ term in the unperturbed Hamiltonian along with $H_0$, and treating the $S_+ I_-$ and $S_- I_+$ terms as a perturbation.

Suppose we wish to find $\Delta(1, 2)$. The appropriate lattice diagram is shown in Fig. 7. This tunneling process requires making a transition from the state $| -1, p = -2 \rangle \equiv | I \rangle$ to the state $| 0, p = 2 \rangle \equiv | IV \rangle$. However, there is no direct matrix element of $H_I$ between these states, and we must go through intermediate states. The lowest energy intermediate states are $| -1, p = 0 \rangle \equiv | II \rangle$ and $| 1, p = 0 \rangle \equiv | III \rangle$. Keeping only these we obtain a four-state effective Hamiltonian

$$H_{\text{eff}} = \begin{pmatrix} E_0 & V & 0 & 0 \\ V & E_1 & \Delta(1)/2 & 0 \\ 0 & \Delta(1)/2 & E_1 & V \\ 0 & 0 & V & E_0 \end{pmatrix},$$

(31)
where the equality of various elements is assured by symmetry. Here, \( E_0 = \langle I|H_I|I \rangle = \langle IV|H_I|IV \rangle \), \( E_1 = \langle II|H_I|II \rangle = \langle III|H_I|III \rangle \), \( V = \langle II|H_I|I \rangle \), and \( \Delta^{(1)} \) is the tunnel splitting between the states \( |II \rangle \) and \( |III \rangle \). This splitting is identical to the splitting between the first excited states of the Hamiltonian \( H_0 \) without nuclear spins, and is given by \[ \Delta^{(1)} = \frac{2S}{\sinh \theta \cosh \theta} \Delta_0. \] (32)

Secondly, the energy difference \( E_1 - E_0 = \omega_c + O(\omega_n) \).

The key quantity in calculating \( \Delta_2 \) is thus the matrix element \( V \) as before. This is given by a sum involving the lattice site wavefunctions of the states \( |I \rangle \) and \( |II \rangle \) and a \( I-IS_+ \) matrix element. Refering to Fig. 7, consider the contribution of the bond connecting site \( n \) in the lower row to site \( n-1 \) in the middle row. The matrix element for this bond equals

\[ -\frac{\omega_n}{2S} (-S+n-1, I_z = 0|S_+ I_- - S+n, I_z = -1) = -\frac{\omega_n}{\sqrt{2}S} (n(2S-n+1))^{1/2}. \] (33)

The wavefunctions at the two ends of this bond, on the other hand, are given by \( \langle n|\psi_0 \rangle \) and \( \langle n-1|\psi_1 \rangle \), where \( |\psi_0 \rangle \) and \( |\psi_1 \rangle \) are the ground and first excited state of the harmonic oscillator Hamiltonian \( H_{ho} \), Eq. (17), and \( |n \rangle \) are the eigenstates of the number operator \( a^\dagger a \). Thus,

\[
V = -\frac{\omega_n}{\sqrt{2}S} \sum_{n=0}^{\infty} (n(2S-n+1))^{1/2} \langle \psi_1|n-1\rangle \langle n|\psi_0 \rangle \\
= -\frac{\omega_n}{\sqrt{S}} \sum_{n=0}^{\infty} n^{1/2} \langle \psi_1|n-1\rangle \langle n|\psi_0 \rangle \\
= -\frac{\omega_n}{\sqrt{S}} \sum_{n=0}^{\infty} \langle \psi_1|a|n\rangle \langle n|\psi_0 \rangle \\
= -\frac{\omega_n}{\sqrt{S}} \langle \psi_1|a|\psi_0 \rangle \\
= \frac{\omega_n}{\sqrt{S}} \langle \psi_1|a|\psi_0 \rangle = -\sinh \theta. \] (34)

The second equality in this chain follows from noting that the sum is dominated by values of \( n \) of order unity, which allows us to neglect \( n \) in comparison to \( S \). The final equality follows if one makes use of the Bogoliubov transformation \[ (21) \). Then, \( \langle \psi_1|a|\psi_0 \rangle = -\sinh \theta \langle \psi_1|b^\dagger|\psi_0 \rangle = -\sinh \theta. \]
Table 3: Comparison between numerical and analytical results for two-coflip tunnel splittings, for $k_1 = 5.0$, $k_2 = 20.0$, $\omega_n = 0.5$, $S = 15$, and $I = 1$. In the column labeled ‘ratio’ we give the ratio of the numerically obtained splittings to those given by the instanton method, i.e., to Eqs. (36) and (39), but with a numerical factor of $\pi^2/4$ instead of 2.

| Numerical | Ratio |
|-----------|-------|
| $\Delta_2$ | $2.559 \times 10^{-8}$ |
| $\Delta_{-2}$ | $3.488 \times 10^{-7}$ |

To leading order in $\omega_n$, the energy splitting of the lowest two states of the effective Hamiltonian (31) is easily shown to be given by

$$\frac{V^2}{E_1 - E_0 - \Delta^{(1)}/2} - \frac{V^2}{E_1 - E_0 + \Delta^{(1)}/2} \approx \frac{V^2}{(E_1 - E_0)^2} \Delta^{(1)}. \quad (35)$$

Combining Eqs. (32), (34), and using the fact that $E_1 - E_0 = \omega + \mathcal{O}(\omega_n)$, we finally obtain

$$\Delta_2 = \Delta(1, 2) \approx 2 \frac{\omega_n^2}{\omega_e} \tanh \theta \Delta_0. \quad (36)$$

The calculation of $\Delta(1, -2)$ proceeds very similarly. The effective Hamiltonian has the same structure as Eq. (31), except that this time the states $|I\rangle$ and $|IV\rangle$ must be taken as $|-0, p = 2\rangle$ and $|+0, p = -2\rangle$ respectively, while the states $|III\rangle$ and $|IV\rangle$ are unchanged. This time the bonds connect site $n$ in the upper row with site $n + 1$ in the lower row, and the matrix element is

$$-\frac{\omega_n}{2S} (-S + n + 1, I_z = 0 | S, I_+ = S + n, I_z = 1 \rangle \approx -\frac{\omega_n}{\sqrt{S}} (n + 1)^{1/2} \quad (37)$$

instead of Eq. (33). Using the same technique as before, the transition matrix element $V$ is found to be

$$V = -\frac{\omega_n}{\sqrt{S}} \sum_{n=0}^{\infty} (n + 1)^{1/2} \langle \psi_1 | n + 1 \rangle \langle n | \psi_0 \rangle = -S^{-1/2} \omega_n \cosh \theta. \quad (38)$$

Substituting this in Eq. (33), we obtain the splitting as

$$\Delta_{-2} = \Delta(1, 2) \approx 2 \frac{\omega_n^2}{\omega_e} (\tanh \theta)^{-1} \Delta_0. \quad (39)$$

The results (36) and (39) are very close to but not exactly what one would expect from the instanton method, even after the fluctuational factors of $\tanh \theta$.
have been included. If we define $\eta_\pm = (\pi \omega_n / 2\omega_e) (\tanh \theta)^{\pm 1/2}$, then an instanton argument would lead us to expect

$$\Delta_{\pm 2} = \eta_0^2 \Delta_0.$$  \hfill (40)

This would require the numerical factors in Eqs. (36) and (39) to be $\pi^2/4$ instead of 2. Could this really be the case, and if so, what is the source of the discrepancy in our present calculation? One possible answer is that we have ignored the contribution of higher energy intermediate states in the calculation of $\Delta_{\pm 2}$. In fact, it can be shown that these states' contribution is also formally of order $(\omega_n/\omega_e)^2 \Delta_0$, but with different numerical prefactors, which decrease rapidly with increasing intermediate state energy. The accurate calculation of these numerical factors is difficult. Similarly, we neglected the terms of higher order in $S^{-1}$ in expanding the matrix element (33). Terms of such higher order are also present in the contributions from the higher intermediate states, and it is not clear that the sum of all these terms will continue to be of higher order in $S^{-1}$. When these approximations are taken into account, we cannot exclude the possibility that Eq. (40) holds exactly.

We show a comparison between our theoretical and numerical results in Table 3. The quality of agreement is still fairly good, though not as impressive as for the one-coflip splittings. We have not carried out this numerical work as extensively as in the previous cases, and so can not comment on the behavior with increasing $S$.

5.3 Higher Coflip Processes; Effective Hamiltonian

It is evident that the discrete WKB method is increasingly ill suited to the calculation of higher coflip processes. Systematic numerical investigation of this problem runs into the difficulty that the splittings necessarily decrease with increasing coflip number $p$, requiring the numerical diagonalization to be carried out to increasing precision. My own numerical studies are very limited, and while it is undoubtedly possible to improve on them, that would require substantially greater time and effort than I am prepared to commit!

There is, however, one aspect of the higher coflip problem, which can be understood quite simply. [We have alluded to this earlier; see the discussion immediately preceding Eq. (10).] This is that splittings $\Delta(I, p)$ for different $I$ but equal $p$ can be related to each other. To see this, let us consider the problem in terms of $N_n$ nuclear spins each with spin 1/2 rather than the model (3). There are then a large number of states in the $|+0, p\rangle$ group that are degenerate with one another, and with an equally large number of mutually degenerate states in the $|-0, -p\rangle$ group. (Recall that $p = 2I_{z}^{\text{rot}}$.) A $p$-coflip
process can take us from any of the states in the first group to several states in the second group. A convenient algebraic method for keeping track of which states are connected is as follows. To avoid cluttering up the formulas, it is best to treat the cases $p > 0$ and $p < 0$ separately. Let us do the $p > 0$ case first. Let $\pi_{\pm p}$ be projection operators onto the set of states with $I^\text{tot}_z = \pm p/2$, irrespective of the value of $I$. Further, let

$$
\sigma_+ = |+0\rangle \langle -0|,
\sigma_- = |-0\rangle \langle +0|,
$$

be transition operators for the large electronic spin between the two states involved in the MQC process. Finally, let $\Delta_p$ be the amplitude for the transition between any two of the states in the groups with opposite $I_z$. Then, an effective Hamiltonian that describes all the coflip processes of order $p$ is

$$
H_{\text{cf}}^p = \Delta_p \left( \sigma_+ \pi_p Q_+^p \pi_{-p} + \text{h.c.} \right);
$$

$$
Q_+^p = \sum_{j_1, j_2, \ldots, j_p} I_{j_1}^+ I_{j_2}^+ \cdots I_{j_p}^+;
$$

where $I^\pm = I_x \pm i I_y$ as usual, and the sum in Eq. (43) is over all distinct $p$-tuplets of indices chosen from the indices $1, 2, \ldots, N_n$.

Let us check that Eq. (42) does what it is supposed to. Consider the first term on the right, and let it operate on a ket. The projection operator $\pi_{-p}$ ensures that this term is only relevant when we operate on a state with $I_z = -p/2$. The operator $Q_+^p$ then raises (or flips) $p$ nuclear spins leading to a state with $I_z = p/2$. The projection operator $\pi_p$ in this term is added to ensure that the result is sensible when we operate on a bra. The second term in (42) ensures hermiticity and describes processes in which $I_z$ is lowered.

It is now very easy, however, to find the $I$ dependence of the matrix elements of $H_{\text{cf}}^p$. We first note that because $(I_j^+)^2 = 0$ for any $j$, we can write

$$
Q_+^p = \frac{1}{p!} (I_1^+ + I_2^+ + \cdots + I_{N_n}^+)^p = \frac{1}{p!} (I^+)^p.
$$

The only non-zero matrix element of $H_{\text{cf}}^p$ between states of given $I$ is thus equal to

$$
\frac{\Delta_p}{p!} \left( I, m = \frac{1}{2} p \mid (I^+)^p \mid I, m = -\frac{1}{2} p \right) = \Delta_p \left( I + \frac{1}{2} p \right).
$$

The case $p < 0$ is now easily treated by minor changes of notation. We simply change $Q_+^p$ in the first term in Eq. (42) to its hermitean adjoint $Q_+^p$. 

23
Table 4: Numerical results for higher coflip tunnel splittings. The parameters are \(k_1 = 5.0, k_2 = 20.0, \omega_n = 0.5, S = 15,\) and \(I = 0, 1, 2, 3.\) The table shows \(\Delta(I, p)\) divided by the combinatoric factor in Eq. (46). This combinatoric number is shown next to the result in parentheses.

| \(p\) | \(I = 0\) | \(I = 1\) | \(I = 2\) | \(I = 3\) |
|-------|-----------|-----------|-----------|-----------|
| 0     | 9.412 \times 10^{-5}(1) | 9.435 \times 10^{-5}(1) | 9.479 \times 10^{-5}(1) | 9.546 \times 10^{-5}(1) |
| -2    | 3.488 \times 10^{-7}(1) | 3.497 \times 10^{-7}(3) | 3.507 \times 10^{-7}(6) |          |
| 2     | 2.559 \times 10^{-8}(1) | 2.586 \times 10^{-8}(1) | 2.628 \times 10^{-8}(6) |          |
| -4    | 2.134 \times 10^{-9}(1) | 2.138 \times 10^{-9}(5) |          |          |
| 4     | 2.655 \times 10^{-11}(1) | 2.580 \times 10^{-11}(5) |          |          |
| -6    | 1.735 \times 10^{-11}(1) |          |          |          |
| 6     | 3.624 \times 10^{-13}(1) |          |          |          |

with the sum in the analog of Eq. (13) being over all \(|p|\)-tuplets. Thus \(Q_{p}^{-} = (I^{-})^{|p|}/|p|!\) for \(p < 0,\) and the matrix element analogous to (13) is identically evaluated. The upshot is that we can write

\[
\Delta(I, p) = \left(I + \frac{1}{2}|p|\right) \Delta_{p}
\]

(46)

for all \(p,\) positive or negative.

We show in Tables 4 and 5 some numerical results for tunnel splittings involving up to 6 nuclear spin coflips. Instead of tabulating \(\Delta(I, p)\) itself, we have divided it by the combinatorial factor in Eq. (15). We expect that the resultant quantities will be independent of \(I,\) and we can see from the tables that indeed they are. In all the cases, the spread in the values of \(\Delta_{p}\) so deduced is less than 2%.

Table 5: Same as Table 4 for odd numbers of coflips. Now \(S = 31/2,\) and \(I = 1/2, 3/2, 5/2.\) The other parameters are unchanged.

| \(p\) | \(I = 1/2\) | \(I = 3/2\) | \(I = 5/2\) |
|-------|-----------|-----------|-----------|
| -1    | 3.265 \times 10^{-6}(1) | 3.272 \times 10^{-6}(2) | 3.284 \times 10^{-6}(3) |
| 1     | 1.327 \times 10^{-6}(1) | 1.326 \times 10^{-6}(2) | 1.323 \times 10^{-6}(3) |
| -3    | 1.619 \times 10^{-8}(1) | 1.623 \times 10^{-8}(4) |          |
| 3     | 2.305 \times 10^{-9}(1) | 2.306 \times 10^{-9}(4) |          |
| -5    |          | 1.136 \times 10^{-10}(1) |          |
| 5     |          | 6.457 \times 10^{-12}(1) |          |
The fact that $\Delta(I, p)$ grows with $I$ may make one wonder if this might not be a way to boost the resonance frequency for some of the tunneling processes. In fact, the result (46) only applies to the ideal case where the hyperfine couplings are identical for all the nuclei. This limits the relevance of this result for actual systems to small values of $p$ or $I$. Real particles typically possess some small spread in these couplings. This spread spoils the degeneracy of all the states in the $|0, p\rangle$ group (and likewise for the states $|-0, -p\rangle$). When the spread starts to equal $\Delta p$, then the constructive interferences which give rise to the large combinatoric factors in Eq. (46) are no longer possible. The spectral weight in $\chi''$ is then shifted from the higher frequency peaks in a given coflip group to lower frequencies. Secondly, we have neglected incoherent processes involving the nuclear spins. MQC is destroyed by a single such process, and since the likelihood that at least one such process will occur in a given time grows linearly with $N_n$, the number of nuclear spins, it is evident that it does not pay to increase this number.

6 Conclusions

The main purpose of this article has been to verify previous calculations of the coflip tunneling frequencies without using instanton methods. We find that by and large, the instanton calculations lead to correct answers.

Our discussion up to this point has treated the system as closed, with no means for energy to flow in and out. If this were strictly true, this would imply that $\chi''$ consisted of a sum of delta functions at the frequencies $\Delta(I, p)$. This is of course an idealization. To complete the discussion of the problem, we must also consider relaxation. If we put in broadening by hand, the qualitative picture of the $\chi''$ spectrum is as shown in Fig. 8. A proper investigation of the physical mechanisms behind this would take us into very different territory. Two obvious mechanisms which may be mentioned in passing are phonons and dipolar magnetic fields due to other nuclei such as protons which may be present in the material. It does not seem worthwhile to develop a quantitative theory of the relaxation due to even these processes in the absence of experimental impetus, but certain broadly valid comments can nevertheless be made. By appealing to the general principles laid down in Refs. 11 and 29, it is quite plausible that the relaxation can be treated by coupling the resonating variable (which we would regard as different for each coflip line) to a phenomenological harmonic oscillator bath (which would also be different for each coflip line). Broadly speaking, such a bath has two effects. First, it leads to a pulling down or downward renormalization of the bare coherence frequency $\Delta_b$ to $\tilde{\Delta}_b$. At the simplest level this renormalization can be understood in terms
of a multiplicative Franck-Condon factor. Second, it gives rise to true damping of the resonance, i.e., an intrinsic broadening or linewidth. (There may of course be additional inhomogeneous broadening arising from a spread in $\Delta_0$.)

The general point which is noteworthy is that as the bare frequency $\Delta_b$ of the coherence phenomenon under study decreases, the environment suppresses it even further. This is especially so if the environment has any subohmic or ohmic component. Environmental degrees of freedom that might not have been relevant if $\Delta_b$ had been higher by a factor of 10, say, gang up on the system, as it were, and do start to matter. Further, degeneracy is broken by weaker and weaker stray fields and drifts, effectively eliminating the resonance altogether.

All this implies that the higher coflip resonances in our problem are highly likely to be overdamped and unobservable. This point can be seen even in the simplistic model introduced in Ref. 9, and briefly touched upon at the end of the previous section. If a single nuclear spin undergoes an incoherent transition from $I_z = 1/2$ to $I_z = -1/2$ or vice versa at a rate $1/\tau$, then any MQC in the particle as a whole is damped at a rate $N_n/\tau$. All the lines in $\chi''(\omega)$ thus acquire a width of order $N_n/\tau$ irrespective of the number of coflips involved, and the higher coflip lines with $\Delta(I, p) < N_n/\tau$ essentially merge into a mushy continuous background with no clear feature that could be identified as a resonance. This in turn means that while an accurate calculation of $\Delta(I, p)$ for large $|p|$ would still have theoretical interest, the unlikelihood of its relevance to experiment reduces the urgency of this calculation considerably. The most interesting remaining problem at this stage appears to be that of broadening of the very low order coflip lines.

Let us therefore summarize our conclusions about how MQC in small mag-
netic particles is affected by nuclear spins. The effect is severe, and the spectrum of $\chi'$ is broken up into a large number of lines which can be grouped by the number of nuclear spin coflips required to maintain degeneracy, or more conveniently by the nuclear spin polarization

$$p = \frac{2}{s} \sum_i s_{iz} I_{iz},$$

(47)

where $s_i$ and $I_i$ are the electronic and nuclear spins on atom $i$. The frequency of a line decreases quasi-geometrically with the number of coflips $|p|$, and there is a further distinction between $p > 0$ and $p < 0$, with the latter having a higher frequency. Within each polarization group, there is a fine structure to the tunneling spectrum controlled by interference between the different ways in which $p$ nuclear spins can coflip. The total spectral weight in a given polarization block is therefore given by $f_p$, the probability that a particle will have polarization $p$. This probability can be controlled by thermostatstical factors. For example, if we assume that the nuclear spins are in equilibrium with the electronic spin, then the Boltzmann weights for $I_i$ parallel and antiparallel to $s_i$ are in the ratio $1 : \exp(-\beta \omega_n)$, where $\beta = 1/k_B T$. This leads to

$$f_p = (2\pi \sigma_p^2)^{-1/2} e^{-(p-\bar{p})^2/2\sigma_p^2},$$

(48)

where $\bar{p} = N_n \tanh(\beta \omega_n/2)$, and $\sigma_p = N_n^{1/2} \text{sech}(\beta \omega_n/2)$. The dominant resonance line is thus that with zero polarization, and has a weight $f_0$.

Finally, we note that the effect of nuclear spins on magnetic particle MQC is completely different from that of an oscillator bath. While unlike the latter, the present problem does not seem to lend itself to the study of elegant mathematical questions such as renormalization group connections with the Kondo problem, it provides a novel and interestingly different example of how interaction with the environment suppresses MQC.

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