Quantum Coherence in Small Antiferromagnets

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An antiferromagnetic particle with an excess spin $\vec{j}$ has 2 degrees of freedom. The one associated with $\vec{j}$ is ferromagnetic, while the antiferromagnetic behavior involves Néel vector $\vec{n}$. It is shown that the spin-parity effect described by Loss *et al.* has to do with the ferromagnetic degree of freedom and does *not* imply the localization of $\vec{n}$ for small enough particles for half-integer spin. It is also shown that the tunnel splitting associated with $\vec{n}$ is insensitive to applied fields. [S0031-9007(97)03553-9]

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The possibility of quantum tunneling in mesoscopic magnetic systems is of fundamental interest since this tests our understanding of the transition between classical and quantum physics [1]. Within the past year or so has emerged the first strong evidence for quantum tunneling in very small molecular *ferromagnets* [2]. However, what is observed is the relaxation from a higher to a lower quantum well, the analogy of alpha decay. In order to observe *quantum coherence*, a symmetric double well potential is needed (but see below for coherence in excited states). The ground state has equal probability of being in each well, and, if the system is started in one well, it will tunnel back and forth between wells. Evidence for such quantum coherence effects in magnetic systems is highly controversial [3]. The realization of symmetric double wells for a ferromagnet is *very* delicate since the two wells correspond to time reversal conjugate states and the symmetry is easily destroyed by external fields. Here it is shown that the tunneling of the Néel vector $\vec{n}$ in an antiferromagnet [4] avoids this problem since it can occur between wells which are unaffected by weak external fields.

Interference involving the Berry phase [5] is the origin of a number of interesting effects. The Haldane conjecture [6] that integer spin chains have gaps while similar half-integer system do not can be interpreted in terms of this phase. Loss *et al.* [7] have examined the role of such interference effects on the quantum tunneling of $\vec{n}$. They identify tunneling with the amplitude for the *complete* reversal of $\vec{n}$, and show, if the *total* or excess spin $\vec{j}$ is half-integer, interference destroys this amplitude. This is *interpreted* [7] as an absence of tunneling for $\vec{n}$. In fact, this zero amplitude implies rather a degenerate ground state. Here, as is more usual, the absence of tunneling is taken to imply $\vec{n}$ is localized in one or the other quantum well. It is *not* implied that Berry phase interference effects are absent, but rather that the resulting doublet ground state for the spin half-integer does not have as a direct consequence the localization of $\vec{n}$.

On the other hand, the results presented here *do* confirm, for larger antiferromagnets, there are important differences between the cases of excess whole and half-integer spin, j.

The nature of the anisotropy energy is also of considerable importance [4]. This energy is the origin of the double well potential. Invariably there is a uniaxial-anisotropy $-K_{\|}\cos^2\theta$, or $-AS_z^2$, here assumed to correspond to an *easy axis*. This suffices for antiferromagnetic tunneling. *If* there is also an energy $K_{\perp}\sin^2\theta\sin^2\phi \equiv BS_y^2$, there is also a tunnel effect associated with excess spin $\vec{j}$ and this and $\vec{n}$ are coupled. Here, unless stated otherwise, it will be assumed that $K_{\perp} = 0$.

The problem will be formulated using the auxiliary particle method [8]. This replaces *exactly* the spin problem with one which involves the tunneling of a *single* auxiliary particle described by a tight binding model in which the number of sites is determined by the spin value.

Following earlier work [4,9], it will be assumed that the essentials of the problem are contained in a model which comprises two large spins $\vec{S}_1$ and $\vec{S}_2$ which reflect the two sublattice magnetizations of the antiferromagnet. The value of the excess spin $j = |S_1 - S_2|$. The effective Hamiltonian contains the exchange and a suitable anisotropy energy, i.e.,

$$\mathcal{H} = J\vec{S}_1 \cdot \vec{S}_2 - A[(S_{1,z})^2 + (S_{2,z})^2]. \qquad (1)$$

If H_e and H_a are the basic exchange and anisotropy fields, then the Hamiltonian parameters scale as $J \sim H_e/N$ and $A \sim H_a/N$, where N is the total number of spins. The quantity A reflects the $K_{\|}$ anisotropy.

In general, $m = S_{1z} + S_{2z}$, $S_1 + S_2 \geq m \geq 0$, is a good quantum number, and the solution is a linear combination of $|n + m, -n> \equiv |S_1, S_2; S_{1z} = n + m, S_{2z} = -n\rangle$. The auxiliary particles $a_{n,m}$ create single particle states $|n, m> \equiv a_{n,m}^{\dagger}|>$ which map to the $|n + m, -n>$. The constraint is $Q_m = \sum_n a_{n,m}^{\dagger}a_{n,m} = 1$. *No mean-field approximation is to be made.* The auxiliary particle Hamiltonian is

$$\mathcal{H}_m = \sum_{n=-n_b}^{n_t}\left[\epsilon_n a_{n,m}^{\dagger}a_{n,m} + t_n^{n+1}(a_{n+1,m}^{\dagger}a_{n,m} + \text{H.c.})\right], \qquad (2)$$

where the upper limit n_t is the smaller of S_2 and $S_1 - m$ while n_b is the lesser of S_2 and $S_1 + m$, and where the diagonal energies are

$$\epsilon_n = -J(n + m)n - A[(n + m)^2 + n^2] \quad (3)$$

and the hopping matrix elements

$$t_n^{n+1} = \frac{J}{2} M_{n+m}^{n+m+1}(S_1) M_n^{n+1}(S_2), \quad (4)$$

and where the

$$M_n^{n+1}(S) = [S(S + 1) - n(n + 1)]^{1/2} \quad (5)$$

are the usual matrix elements of the raising operators. A uniform external field adds a constant term $m(g\mu H)$ and can be neglected, *thus reflecting the insensitivity of the present results to an external field*. The time independent Schrödinger equation for such a tight binding model is

$$(\epsilon_n - \epsilon) f(n) = -t_n^{n+1} f(n + 1) - t_n^{n-1} f(n - 1), \quad (6)$$

where $f(n)$ is the wave function amplitude for site n.

For large spin values, the continuum approximation requires $|t_n^{n+1}| \gg |\epsilon_n - \epsilon_{n+1}|$, which is equivalent to $J \gg A$. When the excess spin $j = 0$, the ground state will have $m = 0$. The result for this value of m is

$$[E + 2S^2 A(1 - x^2)] f = \frac{d}{dx}(1 - x^2)\frac{df}{dx}, \quad (7)$$

where $E = -S(S + 1) - 2S^2(A/J) - (\epsilon/J)$ and where $x = n/S$. A very similar continuum limit approach which maps certain spin problems to that of a particle in a potential has been developed [10] by others. If now $A = 0$, the solutions are $f = P_n(x)$, the Legendre polynomials. The energies $\epsilon = \frac{J}{2}[k(k + 1) - 2S(S + 1)]$, and are *exact*. The wave functions, superimposed on the barrier, are shown in Fig. 1(a). The localization of the Néel vector $\vec{n}$ is equivalent to a wave function peaked near either $n = \pm S$. If j is finite, the degenerate ground state will have $m = j$, and directly, the solutions of Eq. (6) are just the Clebsch-Gordon coefficients, Figs. 1(b), 1(c). Clearly, for finite j there is only a weak tendency to localize near $\pm S$, *and this is independent of the integer or half-integer nature of* j. The ground state is determined by the value of the excess spin, i.e., the smallest possible value of $k = j$, and the first excited states lie an energy $(j + 1)J$ higher. For finite A, the matrix elements to these excited states are $\sim S^2 A$ and the $P_n(x)$ (or Clebsch-Gordon coefficients) remain a good approximation provided $S^2 A < (j + 1)J$. The barrier height is $B_a = S^2 A$ while the spin-flop energy $\omega_0 = S\sqrt{JA}$ so that this is equivalent to $B_a < (j + 1)^{1/2}\omega_0$ or $\omega_0 < (j + 1)^{1/2} H_e/N$ *and implies a small magnet*. The quantity $(j + 1)^{1/2} H_e/N$ is the exchange only zero point energy appropriate to this regime.

For a larger magnet, $\omega_o > (j + 1)^{1/2} H_e/N$ (but still $A \ll J$) the exchange remains responsible for the "stiffness" of the wave function. Again, consider first $j = 0$. It might be anticipated, for a state localized in a *single* well, the wave function is $f(x) = e^{\pm\lambda x} P_n(x)$. In fact, assuming the wave functions are *strongly* localized near either $x = \pm 1$, and using $J \ll S^2 A$, the properties of the P_n permit the wave function for nth excited state to be written as $e^{\pm\lambda x} \sum_{k \le n} a_k P_k(x)$, and the energies are

$$\epsilon_n = \frac{J}{2}[n(n + 1) - 2S(S + 1)] - 2S^2 A + 2(n + 1)S\sqrt{JA}, \quad (8)$$

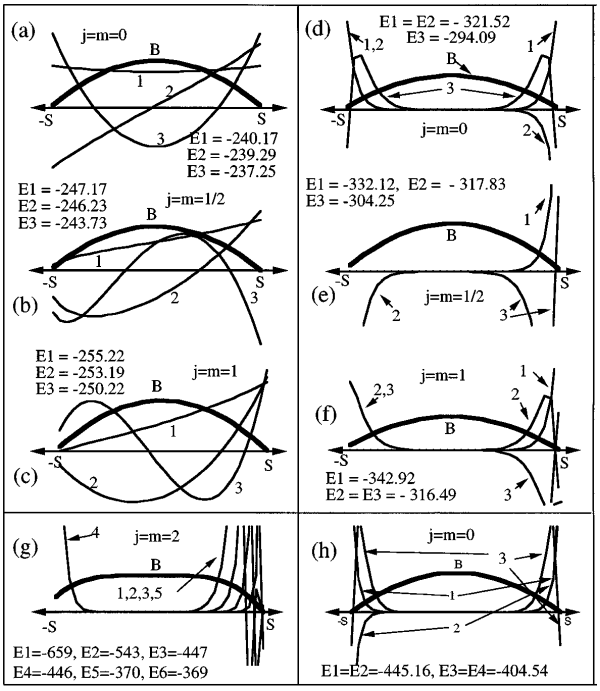

FIG. 1. Shown are the barrier $B(n)$ and the wave functions, $f(n)$, labeled $1, 2, 3 \ldots$ by ascending order in energy. The excess spin j and m are given along with the energies En. When the energies are indicated as being equal, this is only approximate. There is always a small tunnel splitting of the order of Eq. (9). All states *are* strictly doubly degenerate ($m \to -m$) except $m = 0$. The calculations are all for $S = 15$ but are typical. When $(j + 1)^{1/2}(H_e/N) > \omega_0$ (anisotropy energy $A = 0.001J$), the system is *small*, and, (a)–(c), the wave function for $\vec{n}$ is delocalized. In (a) the excess spin is zero, while for (b) it is half-integer and for (c) integer. The existence of an excess spin *does* induce a weak tendency to localize $\vec{n}$; however, this tendency is determined by the fractional excess spin and is *independent* of the integer or half-integer nature of j. For the sequence, (d)–(f), $\omega_0 > (j + 1)^{1/2} H_e/N$ ($A = 0.2J$) corresponding to a *midsized* particle. With no excess spin, (d), all states, including the ground state, are delocalized. When, (e), the excess spin is half-integer all states are well localized with alternate states, in energy, being on opposite ($\pm S$) sides of the barrier. For integer excess spin, (f), the ground state is well localized but the excited states are delocalized. In (g) are shown results for a $B(S_z)^4$ anisotropy with $j = m = 2$ and $B = 0.003J$. All states are localized with the first three being on the same side ($+S$) of the barrier. Higher states alternate sides with energy. The last panel (h) illustrates the crossover to the *large* particle limit $\omega_0 > H_e/N^{1/2}$ when the fluctuations in $\vec{n}$ are suppressed.

with $\lambda = 2S\sqrt{A/J}$. Notice, the zero point energy is greater than interlevel spacing; i.e., this energy is over twice that appropriate for a harmonic oscillator. Numerically, the spacing decreases with increasing n, consistent with the weakening of the strong localization assumption. For the same regime, wave functions which account for tunneling are of the form $(e^{\lambda x} \pm e^{-\lambda x}) \sum_{k \le n} a_k P_k(x) = e^{\lambda x}(1 \pm e^{-2\lambda x}) \sum_{k \le n} a_k P_k(x)$, and at the same level of approximation the tunnel splitting is

$$4S\sqrt{JA}e^{-4S\sqrt{(A/J)}}, \tag{9}$$

which conforms with the usual wisdom that this must be the zero point energy times a WKB exponential [4].

In the same midsize regime, but now with an excess spin, $j \ll S$, the wave functions remain localized near $x = \pm 1$, and the wave equation becomes

$$\left[E + 2S^2 A(1 - x^2) + \frac{(j \pm \frac{m}{2})^2}{1 - x^2} \right] f = \frac{d}{dx}(1 - x^2)\frac{df}{dx}. \tag{10}$$

where the positive (minus) sign corresponds to localization near $x = -1$ ($x = +1$). The solutions involve associated Legendre polynomials, P_n^μ, with energies given by Eq. (8), if $\mu = (j \pm m)/2$ is an integer. For half-integer μ the energies lie roughly halfway between those of Eq. (8). The important physics lies in the restrictions on the P_n^μ, i.e., that $\mu \le n$. Consider, e.g., $j = 2$, if $m = 2$ the ground state has $\mu = n = 0$ and lies near $x = +1$, while the first excited state has $n = 1$. The lowest lying state near $x = -1$ has $\mu = 1$ and therefore $n = 1$, which is degenerate with the first excited state near $+1$. Tunneling states can be constructed by taking the sum and difference of these degenerate states, and, within the present strong localization approximation, the tunnel splitting is again given by Eq. (9). The numerical results show delocalization causes the tunnel splitting to increase fairly rapidly as the states mount in energy.

The situation changes for half-integer spins. If, e.g., $j = 1/2$, the ground state with $m = 1/2$ is still localized near $x = +1$. However, the lowest state in the $x = -1$ well has $\mu = 1/2$, and this corresponds to a state which is roughly halfway between the ground state and the first excited state in the $+1$ well, and indeed, numerically, Fig. 1(e), with mounting energy, the states alternate between the $x = \pm 1$ wells.

In this midsize regime there is a clear difference between integer and half-integer total spin. Only the former exhibits the small tunnel splitting Eq. (9) and has well delocalized excited states. However, in both cases the *ground state* is essentially localized. There is a simple scaling argument by which to understand this phenomena. With increasing A the energy levels must evolve without crossing (for fixed m) from the $A = 0$ limit to a fixed point associated with $A \to \infty$. At the fixed point, the eigenenergies are

$$\epsilon_n = -J(n + m)n - A[(n + m)^2 + n^2], \tag{11}$$

and, for j integer and fixed m, the j lowest energy states are singlets with the rest doublets. For j half-integer, all the states are singlets consistent with the above. However there is no assurance, for integer j, the states are delocalized, and indeed, the numerical results, Fig. 1(g), for an anisotropy term $A[(n + m)^4 + n^4]$, which has an equivalent fixed point structure, exhibit wave functions which are strongly localized even though the levels form relatively close pairs. For j integer and $m = 0$ the wells are *always* symmetric and states always delocalized.

The decay length $\Delta x \equiv \lambda^{-1} = (1/S)\sqrt{J/A}$ or $\Delta n = \sqrt{J/A}$. This represents an uncertainty in the magnitude of the Néel vector, and is small when it is less than the quantum uncertainly $S^{1/2}$ in the transverse parts of the same vector; i.e., there is a *crossover* which occurs when $\sqrt{J/A} \sim S^{1/2}$ or $\omega_0 \sim H_e/N^{1/2}$. The field $H_e/N^{1/2}$ drives the longitudinal fluctuation in the Néel vector. Only when $\omega_0 > H_e/N^{1/2}$, Fig. 1(h), is the system *macroscopic* with a fully developed classical order parameter, $\vec{n}$. This final characteristic energy corresponds to a zero point energy of the bulk Néel state. Consider, e.g., a hypothetical linear chain with a fully developed Néel state $|\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow \ldots >$. This trivially has $\langle S^2 \rangle \sim N$ which implies an exchange energy cost $\sim H_e/N^{1/2}$. This estimate is independent of dimension and essentially unaltered by corrections due to spin-wave zero-point motion.

Turning now to experimental consequences. At least for the small excess moments and larger particles, it must be recognized that there are two energies associated with the reversal of the excess spin j, these corresponding to the distinct possibilities of reversing $\vec{j}$ with or without the Néel vector $\vec{n}$. The barrier $B_a \sim S^2 A = SH_a$, *proportional to the size of the system*, must be surmounted when $\vec{n}$ is reversed. The *ground states* with $m = \pm j$ are on opposite sides of this barrier and to pass from one to the other the B_a barrier is relevant. However, there is another state with $m = -j$ which is on the *same* side of this barrier as $m = +j$, *but* at an energy $j\omega_0$ higher. *This* latter energy has the size dependence of j. Thus *if* $SH_a > j\omega_0$, it costs less energy to reverse $\vec{j}$ with $\vec{n}$ *fixed*, and there is a *unidirectional* anisotropy field of magnitude $H_A \sim \omega_0$ and which is very much bigger that the bare anisotropy field H_a.

In connection with ferritin [3], measurements in the classical regime are fitted to an Arrhenius law $f = \tau_0 e^{-E_b/kT}$ and imply a barrier height $E_b \sim 235$ T and a $\tau_0 \sim 10^{-11}$–10^{-13} s (~ 3 T–3×10^2 T). *However*, the dependence of E_b on volume, while linear, *does not* extrapolate to zero as it should if it is the barrier B_a. Thus that the barrier height $\sim J$ and that τ_0 is *very* large, begs the interpret of this relaxation as being of purely exchange origin, with the barrier being that required to reverse a single spin in the exchange field.

If the experiment is to be interpreted in terms of tunneling, then the action $S_{\mathrm{AFM}} \equiv 4S\sqrt{H_a/H_e} \sim 7.5$. The Néel temperature is about 240 K, and it is estimated

that $H_e \sim 130$ T. For the S state Fe $+3$, it is difficult to imagine the single ion anisotropy, H_{a1}, much greater than a few times 10^{-2} T. The anisotropy in the exchange scales with that in the g factor. This latter is typically less than 10^{-3} and implies an $H_{a2} \sim H_{a1}$. The sum $H_a = H_{a1} + \frac{1}{2}H_{a2}$ determines S_{AFM}. The spin per sublattice $S \sim (5/2) \times (N/2) = 5000$, and would imply an H_a which is $\sim 10^{-6}$ T and an incredible cancellation accident.

However, potential tunneling data *should*, perhaps surprisingly, be interpreted in terms of the small particle limit. With $j \sim 150$ the energy $(j + 1)(H_e/S) \sim 4$ T while, with $H_a \sim 10^{-3}$ T, $SH_a \sim 5$ T, placing the system on the edge of the small regime. Numerical studies show, when first $SH_a > (j + 1)(H_e/S)$, the absolute ground states has $m = \pm j$ and is $\sim jH_a \sim 0.15$ T lower than the states with $m = 0$ which are the lowest to exhibit a tunnel splitting. The $H_a = 0$ splitting $\sim (j + 1)(H_e/S)$ between the first two states with $m = 0$ decreases dramatically to approach a value given by the tunnel formula (9), *but* with a much smaller coefficient before $\sqrt{A/J}$ in the exponential consistent with the observation of tunneling [3]. The dependence of S_{AFM} on particle size should be faster than linear. Notice with an iron loading of 1000, $H_e/S \sim 0.05\mathrm{T} \sim 1.5 \times 10^8$ Hz, which is the order of magnitude of the observed splitting [3]. This puts smaller particles truly in the small particle limit.

Since they *are* excited states, the $m = 0$ levels must be populated if tunneling is to be observed. Since jH_a is a smallish faction of 1 K, these levels will have an appreciable equilibrium population. In addition, for $T < 200$ mK and dilute ferritin it is difficult to imagine a sizable relaxation mechanism which can change the quantum number m and a slow relaxation of the amplitude might be expected for a modestly rapid cooling protocol.

There is the possibility that the anisotropy energy for the total moment $\vec{j}$ has the opposite sign, corresponding to an easy plane, to that relevant for the dynamics of $\vec{n}$, i.e., and easy axis. In this case $m = 0$ is the ground state and there is no slow relaxation of the signal.

There are no magnetic dipole matrix elements between the $m = 0$ levels, and hence no coupling to a strictly uniform field. When the Néel vector $\vec{n}$ is reversed, the up and down dipoles are displaced by one lattice spacing and so *any* antiferromagnet has a quadrupole moment. Particles with an excess spin can have much larger such moments. The measuring system [3] comprises flat loops for both the detection and applied ac and dc fields, and hence there *will* be both a dynamic and static coupling to the tunnel levels, although the precise magnitude is difficult to estimate.

In connection with these experiments, Garg [3] has argued that the hyperfine field of $\sim 2\%$ Fe^{57} would destroy the coherence. However, the analysis of tunneling *with* nuclear spin flips corresponds to the presently defined midsized regime. The hyperfine field, H_{hf}, is, at least, comparable with the presently suggested small value for H_a, and with the present small particle interpretation of experiment the relevant "reduction factor" depends on H_{hf}/H_a and *not* H_{hf}/ω_0, and, depending upon the precise numbers, might not lead to a reduction at all. In fact, involving nuclear spin flips has the *advantage* of giving the tunneling signature a much larger strength. A more detailed analysis of this will be presented elsewhere.

If $K_\perp$ is finite, ferromagnetic tunneling "turns on" and n is coupled to $\vec{j}$. For integer spin all remaining degeneracies will be lifted; *however*, for small $K_\perp$ the new ferromagnetic tunnel splitting will be very much smaller than those discussed above. For a midsized particle, it is necessary to *add* a ferromagnetic exponential factor [11], $e^{-j \ln(4K_A/K_\perp)} = (K_\perp/4K_A)^j$. For ferritin with $j \sim 150$, this is most probably a *very* small quantity. Furthermore, this splitting is *very* sensitive to an applied magnetic field.

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[9] Loss *et al.* use a central spin model which is somewhat different, but contains the same basic physics.

[10] See J. L. Van Hemmen and A. Suto in Ref. [1] and references therein.

[11] See, e.g., the first part of Ref. [4].