Have Resonance Experiments Seen Macroscopic Quantum Coherence in Magnetic Particles? The Case from Power Absorption

Anupam Garg

Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208

(Received 8 March 1993)

Recent magnetic resonance experiments on ferritin and nanofabricated magnetic dots of $Fe(CO)_5$ have been interpreted in the framework of macroscopic quantum coherence (MQC). The power absorption in MQC is calculated and shown to be exceeded by a factor of 50 to 150 in the ferritin experiments. Alternative microscopic causes for the resonance are suggested. In the $Fe(CO)_5$ experiments, MQC predicts no resonance at all at the ac fields involved, and the power absorbed is 10^{18} times larger than expected.

PACS numbers: 75.60.Jp, 03.65.Bz, 76.20.+q, 76.30.Fc

Whether or not quantum superpositions of *macroscopically* distinct states exist in nature has been actively investigated in the last decade [1]. The observation of tunneling between such states would be an especially clear signature of quantum mechanics. In discussing this, it is essential to distinguish between "macroscopic quantum tunneling" (MQT), the decay of a metastable state, and "macroscopic quantum coherence" (MQC), the resonance between two or more nearly degenerate states. Both MQT and MQC are hard to see because (among other reasons), if one imagines preparing a macrovariable in a superposition of states, the coupling between such a variable and its environment rapidly destroys the phase coherence between these states. Phase coherence must be maintained for much longer for MQC than MQT, and MQC is thus far more susceptible to environmental suppression [2,3] than MQT [4], and thus much harder to observe.

The most sustained experiments have been on current biased Josephson junctions and SQUIDs. To date, there is evidence only for MQT and energy level quantization [5], but not for MQC despite committed efforts [6]. MQC is clearly the more dramatic effect, and Awschalom *et al.* claim to have seen just this in a recent resonance experiment on ferritin particles [7]. A similar resonance was seen earlier [8] in $Fe(CO)_5$ particles, but its origin was not clear. It is the purpose, in part, of this paper to ask whether these resonances could be due to MQC. See also Ref. [9].

To understand the phenomena in question, let us consider a small (~ 50 Å radius), single domain ferromagnetic particle at $T=0$ [10], with an easy direction $\hat{\mathbf{z}}$ for the total moment $\mathbf{M}_0$ in the absence of any applied magnetic field. By time reversal, $-\hat{\mathbf{z}}$ is a degenerate easy direction. The resonance of $\mathbf{M}_0$ between $\pm\hat{\mathbf{z}}$ is an example of MQC. Similarly, for an antiferromagnetic particle, the Néel vector l has two classically degenerate orientations, again denoted $\pm\hat{\mathbf{z}}$, between which it can resonate [11]. Because of its finite size, the particle may possess a net uncompensated moment, $\mathbf{M}_0$, which also switches between opposite directions, which we may also take as $\pm\hat{\mathbf{z}}$.

The tunnel splitting Δ can be estimated using instanton methods, assuming model forms for the anisotropy energy [10,11]. The key feature of the answers is that the WKB exponent is proportional to the particle volume. As a result, even with typical ranges of material parameters, Δ varies over a huge range. The tunneling frequency $\omega_r = \Delta/\hbar \sim 10^2$–$10^6$ sec^{-1} for the antiferromagnetic case. For the ferromagnetic case, the WKB exponent is $(K_2/K_1)^{1/2} M_0/\mu_B$, where K_1 and K_2 are the hard and medium axis energies (measured from that of the easy direction). Since $M_0/\mu_B \sim 500$–5000, unless $K_2/K_1 \ll 10^{-4}$, i.e., unless the anisotropy is extremely close to that of the easy plane type, ω_r is expected to be unobservably small [12]. Because of finite size effects and uncertainties about the moments, exchange couplings, and anisotropies near the particle surface, these results provide only very broad estimates for Δ, but the phenomena do not seem totally unobservable.

In this paper, however, we are not so much concerned with the intrinsic observability of MQC. Rather, supposing that a situation close to the idealized ones described above can be attained, we wish to understand the resonant excitation of the transition between the two tunnel split energy levels by an ac magnetic field, and to obtain estimates for the power absorption in this process.

Let us denote the states (for either particle, ferromagnetic, or antiferromagnetic) with $\mathbf{M}_0 \| \pm\hat{\mathbf{z}}$ by $|\pm\rangle$. The tunneling can be represented by a Hamiltonian $\Delta\sigma_x/2$, where the σ's are the usual Pauli matrices in the $|\pm\rangle$ space, and not real spins. Let an ac field $\mathbf{H}(t)$ be applied at an arbitrary angle with respect to $\hat{\mathbf{z}}$. The moments in the particle experience a local anisotropy field H_a. Typically, $H_a \sim 0.01$–1 T $\gg H(t)$. The components of $\mathbf{H}(t)$ transverse to $\hat{\mathbf{z}}$ then have negligible effect on the tunneling matrix element Δ, and cannot directly induce transitions between the $|+\rangle$ and $|-\rangle$ states. The mixing to the higher energy states is also negligible, and the largest effect of $\mathbf{H}(t)$ is to shift the energies of the $|\pm\rangle$ states via the dipolar coupling to the component $H_z(t)$. Thus, we can take the Hamiltonian for our system as

0031-9007/93/71(25)/4249(4)$06.00

$$\mathcal{H} = (\Delta/2)\sigma_x - M_0 H_z(t)\sigma_z . \quad (1)$$

If $H_z(t) = H_z \sin\omega t$, and $M_0 H_z \ll \Delta$, Eq. (1) is the classical NMR Hamiltonian for a spin-$\frac{1}{2}$ system, excluding explicitly the couplings which lead to T_1 and T_2 processes, which we assume to be moderate. If we have N identical particles, then neglecting inhomogeneous broadening, the steady state power absorption is given by the standard result (see Ref. [13], e.g.)

$$P = \frac{\hbar\omega}{2}\frac{N'_{eq}}{T_1}\left\langle \frac{T_1 T_2 (M_0 H_z/\hbar)^2}{1+(\delta T_2)^2 + T_1 T_2 (M_0 H_z/\hbar)^2} \right\rangle , \quad (2)$$

where $\delta = \omega - \omega_r$ is the detuning, $N'_{eq} = N\tanh(\Delta/2k_BT)$ is the thermal equilibrium population difference between the two energy levels, and the angular brackets denote an average over the orientations of the easy axes of the particles. If we take these as completely random, then the small H_z limit yields the imaginary part of the dynamic susceptibility as

$$\chi''(\omega) = \frac{N'_{eq} M_0^2}{3\hbar}\frac{T_2}{1+(\delta T_2)^2} . \quad (3)$$

We can also get a gross upper bound on P from Eq. (2),

$$P \le P_{sat} = N'_{eq}\Delta/2T_1 , \quad (4)$$

which can be easily understood as saying that in steady state the rate of excitation cannot exceed that of decay. The bound itself is attained at zero detuning near saturation, i.e., for $M_0 H_z \gg 2\hbar/(T_1 T_2)^{1/2}$. (Of course, we must still satisfy $M_0 H_z \ll \Delta$.)

We can now apply these results to the experiments of Awschalom *et al.* on ferritin [7]. Ferritin is an iron oxyhydroxide complex, related to the mineral ferrihydrite [14], and is found in many animals, encased in a protein shell (apoferritin). The core has a diameter of $\sim$75 Å, and is believed to be antiferromagnetic. Awschalom *et al.* estimate that of the 4500 Fe^{3+} moments in a ferritin grain, about 43 are uncompensated, giving a net moment $M_0 \simeq 217\mu_B$ per grain. They measure the dynamic susceptibility of $N \simeq 38000$ ferritin grains in solution at $T < 200$ mK, and see a resonance at 940 kHz. (They also measure the power spectrum, and establish that the fluctuation dissipation theorem is well obeyed, showing that the experiments are in the linear response regime.) They claim that this resonance is due to a simultaneous reversal of all 4500 moments in a grain, i.e., due to precisely the type of antiferromagnetic MQC described above.

Figure 1(b) of Ref. [7] shows a resonance at $\nu_r = 940$ kHz, of FWHM $\simeq 50$ kHz, at $T = 29.5$ mK. In the MQC interpretation, we must take $\Delta = 2\pi\hbar\nu_r$, and since $\Delta \ll k_BT$, $N'_{eq} = N\Delta/2k_BT \simeq 29.1$. From the FWHM, we obtain $2T_1^{-1} < 2\pi(5\times10^4\ \mathrm{sec}^{-1})$, giving $P_{sat} < 1.5\times10^{-21}$ W. The actual power is given by $P = \pi\nu_r\chi''(\nu_r)\times H_{ac}^2$, where $H_{ac} = 10^{-5}$ G is the applied ac field. Taking $\chi''(\nu_r) = 3.4\times10^{-11}$ emu/G, we obtain $P = 1.0\times10^{-21}$ W. [Note (i) that the scales in Figs. 1(b) and 2(b) of Ref. [7] are inconsistent, so I have used the smaller value for $\chi''(\nu_r)$ deduced from Fig. 2(b); (ii) the correct value for H_{ac} is 10^{-5} G, and not 10^{-4} G as stated in Fig. 1(b).] This is dangerously close to the estimated upper bound, and leaves practically no room for inhomogeneous broadening. Indeed, taking $2T_2^{-1} = 2\pi(5\times10^4\ \mathrm{sec}^{-1})$ from the FWHM, the estimated peak power from Eq. (3) is 7.0×10^{-24} W, 150 times smaller than the measured value, which is a little too much in our view. This discrepancy can be reduced to 50 if we assume that all the easy axes are perfectly aligned normal to the substrate.

Note that by the thermodynamic sum rule,

$$\chi_{res}(T) \equiv \int_0^\infty d\omega\,\chi''(\omega) \approx \frac{\pi N M_0^2 \omega_r}{6k_BT} . \quad (5)$$

Thus, the above disagreement can be restated as an equal disagreement for the product $N'_{eq}M_0^2$, and cannot be linked to the use of phenomenological Bloch equations for the pseudospin. The MQC interpretation simply does not provide enough oscillators (50 to 150 times too few) to account for the absorption seen. In fact, Awschalom *et al.* effectively make use of this sum rule, but conclude that $M_0 \simeq 640\mu_B$, which is not so far off their direct estimate of $217\mu_B$. To do this, however, they use the smaller quantity $-T\chi_{res}/dT$ and not χ_{res} itself, a step for which we see no basis. They also omit the factor of $\frac{1}{3}$ arising from the particle orientation average. Without these two steps, one would obtain $M_0 \simeq 2600\mu_B$, in line with the power discrepancy.

Further doubts that MQC is occurring arise from the sharpness of the resonance. MQC gives a formula of the type $\nu_r = k\nu_0\exp(-k'U/h\nu_0)$ for the tunneling frequency, where ν_0 is an attempt frequency, U is the barrier height, and k and k' are constants of order unity. We must have $\nu_0 \gtrsim k_BT/h \sim 10^9$–$10^{10}$ Hz to reduce incoherent transitions. This implies that $k'U/h\nu_0 \sim 5$–10, as $\nu_r \sim 1$ MHz. Assigning the entire FWHM $\delta\nu_0 = 50$ kHz to variations in U_0, we are forced to conclude that the barrier heights are very uniform: $\delta U/U \lesssim (0.5$–$1)\%$. It is not known if the particle volumes are so uniform, but even if this is granted the surface areas and shapes need not be so, and it is rather unlikely that the barrier heights are equally uniform. About a fourth of the Fe^{3+} spins are at the surface in a single ferritin grain, and variations of the surface contributions to the anisotropy energy well in excess of 1% can be expected.

Let us therefore ask if the resonance can be microscopic in origin. The only obvious magnetic species in sufficient numbers are protons (H nuclei), and Fe^{3+} ions in the ferritin cores, and would require effective or local fields of 220 and 0.34 G, respectively, to yield $\nu_r = 940$ kHz. Although a 220 G field at the protons could be of dipolar origin, like that seen in $CuCl_2\cdot 2H_2O$ [15], it is difficult to obtain a signal of the size seen because (i)

there seem to be many inequivalent H sites in the proposed ferritin core structure [14] so that only a small fraction would see the same 220 G field, and (ii) unusually large Gossard-Portis enhancement factors [16] would be needed to offset the small proton moment.

If we attribute the resonance to Fe^{3+} ions, then with 4500 ions per ferritin core, and $M_0^2 = 35\mu_B^2$, the discrepancy in the sum rule is reduced to 15 to 45, but the required local field of 0.34 G would seem to be at odds with the large antiferromagnetic exchange fields. The general belief that ferritin is antiferromagnetic is based on the appearance and sharpening of the hyperfine split lines in ^{57}Fe Mossbauer spectra at low temperatures, which is then ascribed to superparamagnetism, and can be traced to Ref. [17]. These same authors do not see any clear sign of a Néel point from 4.2 to 300 K in their susceptibility measurements, however. It is not at all clear that the Mossbauer data could not be explained by *paramagnetic* relaxation of single spins or small clusters of spins [18], with relaxation times changing from 1 to 10 ns, say. We have not been able to find reports of investigations of magnetic ordering by more direct means such as neutron diffraction or NMR on ^{57}Fe enriched ferritin, or by antiferromagnetic resonance (AFMR). We urge such experiments, as they would obviously help in understanding ferritin for its own sake, and the lattermost would bear directly on MQC, as it would provide a value for v_0. Even if we accept the antiferromagnetism, if the anisotropy is of the easy-plane type the AFMR frequency is the geometric mean of the exchange and in-plane anisotropy fields. The latter can be as small as 1 G, but the required local field is still about a hundred times smaller than what typical exchange constants give.

Yet a third possibility arises from the fact that Fe^{3+} binds to apoferritin with a stoichiometry of 12 Fe/apoferritin [14,19]. The precise binding site is uncertain, but extended x-ray absorption fine-structure spectroscopy measurements reveal that the Fe^{3+} is sixfold coordinated by O (and possibly N) 2.0 Å away. The Fe-O octahedra are similar to but distinct from the octahedra in the ferritin core and α-Fe_2O_3. Since the resonance in Ref. [7] is seen in samples diluted with apoferritin by 1000:1, there are potentially enough Fe^{3+} ions in the Fe^{3+}-apoferritin complexes (2.5 times the number in the cores) to provide the signal size seen. The ground state of Fe^{3+} consists generally of three Kramers doublets. A nuclear moment (^{14}N?) on one or more of the ligands would provide a small magnetic field of just the right magnitude to split the doublets by about 1 MHz, and could account for the observations of Awaschalom *et al.* [20]. In this view, the undiluted samples do not show a resonance as there is no apoferritin. Further investigation of the Fe^{3+} spin Hamiltonian in the Fe-apoferritin complex by electron spin resonance would be very welcome, both for understanding the results in Ref. [7], and for the nature of the complex itself, which seems to play an important role in iron uptake by ferritin.

We next turn to the experiments in Ref. [8]. These are performed on arrays of dots of $Fe(CO)_5$, believed to be ferromagnetic. Data are presented for three arrays, each with 100 dots at 1.0 μm interparticle spacing, with diameters of 15 nm, and heights of 38, 50, and 70 nm, which display a resonance peak in $\chi''(\omega)$ at $\omega_r \simeq 400$, 200, and 50 sec^{-1}, respectively, at a temperature $T = 22.5$ mK. The resonance height shown is $\sim 3\times 10^{-12}$ emu/G. Although the authors conclude (correctly, in our view) that a comparison of the data with MQC is beset with "fundamental discrepancies," we do not believe that they have identified the most serious of these. This is that their ac magnetic field is so large as to make the energy of the supposedly degenerate states with $\mathbf{M}_0 \| \pm \hat{\mathbf{z}}$ swing up and down with an amplitude far exceeding the assumptive tunnel splitting [21]. We shall see that as a result one should expect *no* resonance at all, i.e., no peak in the susceptibility.

Let us focus on the sample that displays a resonance at $\omega_r = 400$ sec^{-1}. We estimate the moment from other data given in [8] as $M_0 \simeq 10^{-15}$ emu. The ac magnetic field has an amplitude $H_z = 30$ mG, giving $M_0 H_z \simeq 3 \times 10^{-17}$ erg, which is $\sim 10^8$ times the assumptive tunnel splitting $\Delta = \hbar\omega_r \simeq 4\times 10^{-25}$ erg. This is an extreme limit for NMR, which is usually not analyzed. The ac field is the exact opposite of a small perturbation in this case, so the picture of transitions between Zeeman split levels in the static field and Eqs. (2)–(4) are completely invalid. It is better to work in the $|\pm\rangle$ basis, and view the situation as a level crossing or Landau-Zener-Stuckelberg problem [22] (Fig. 1). A particle in the $|+\rangle$ state has a time dependent energy $-M_0 H_z(t)$ and would stay in that state were it not for the term $\Delta\sigma_x/2$ in Eq. (1). Taking $H_z(t) = H_z \sin\omega t$, the usual adiabaticity parameter is given by $\gamma = \Delta^2/8\hbar\omega M_0 H_z$. The parameter values of Ref. [8] clearly correspond to the fast-passage limit, $\gamma \ll 1$. In one cycle of the ac field, the particle crosses the

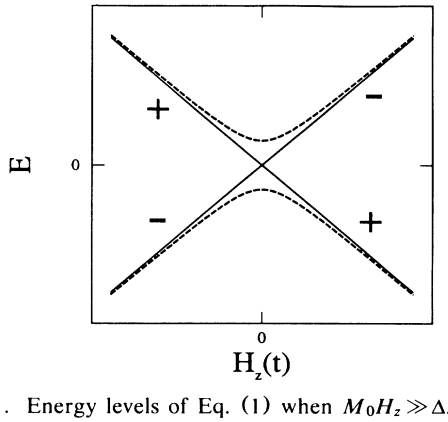

FIG. 1. Energy levels of Eq. (1) when $M_0 H_z \gg \Delta$. The system moves up and down the curves marked + and − as H_z varies, and makes transitions between them in the vicinity of the crossing. The dashed lines are the adiabatic energy curves followed by the system when H_z varies very slowly.

transition region in Fig. 1 twice. For a single passage, the probability for the spin to flip is given by $2\pi\gamma$. It is thus apparent that as long as $M_0H_z \gg \Delta, \hbar\omega$, there is nothing special about the case $\omega = \Delta/\hbar$; i.e., there is no resonant absorption.

To calculate the power absorption, let us assume that random fluctuations in the field $H_z(t)$ are correlated over a time $t_{\rm coh} \gg \omega^{-1}$. Then successive passages of the transition region are correlated, and one cannot use the single passage result [22] *a priori*. If we write the state as

$$|\psi(t)\rangle = \sum_{j=\pm} a_j(t) e^{-i\phi_j(t)} |j\rangle , \tag{6}$$

with

$$\phi_\pm(t) = \pm \hbar^{-1} \int^t M_0 H_z(t')dt' , \tag{7}$$

then in the $a_\pm$ basis, we get a reduced Hamiltonian

$$H_1(t) = (\Delta/2)[\cos 2\phi(t)\sigma_x - \sin 2\phi(t)\sigma_y] , \tag{8}$$

with $\phi(t) = \phi_+(t)$. This is a very rapidly rotating magnetic field, with an oscillating sense of rotation. The pseudospin precesses in opposite directions at different times, the net result being nearly zero. The nonzero contributions arise from the points of stationary phase $\dot\phi(t_j) = 0$, i.e., $t_j = j\pi/\omega$. The time scale over which a transition can occur is that over which the phase difference $\phi_+ - \phi_-$ has advanced by $\sim\pi$ from its value at t_j, and is given by $(\pi\hbar/2M_0H_z\omega)^{1/2} \equiv \eta^{-1}$. (We assume that $M_0H_z \gg \hbar\omega$, so successive t_j's are well separated. Note that η^{-1} is not the usual "Landau-Zener time" $\Delta/2M_0H_z\omega$.) The corresponding energy transfer is $\sim 2M_0H_z\omega/\eta \sim \hbar\eta$. Since there are $\omega/2\pi$ passages of the transition region per unit time, and since in steady state, the power must be proportional to the inversion, we expect the power to vary as $N'_{\rm eq}\gamma\omega\hbar\eta$. A longer calculation, to be published elsewhere, gives the final answer for the power as

$$P = \frac{N'_{\rm eq}}{2} \frac{\Delta^2\omega}{(2\pi\hbar\omega M_0H_z)^{1/2}} . \tag{9}$$

The actual power absorbed in the experiments [8] is again given by $\omega\chi''(\omega)H_{\rm ac}^2/2$, which exceeds Eq. (9) by $\sim 10^{18}$. Note that the fact noted by the authors, $\hbar\omega_r/k_bT = 10^{-8}$, is not the sole reason for expecting a small signal, for even if $N'_{\rm eq}$ is replaced by the total particle number N in Eq. (9), the absorbed power is still 10^{10} times too large. Thus, we strongly suspect that the resonance in this experiment, too, is of some microscopic origin.

I am indebted to Dr. V. Chandrasekhar and Dr. W. P. Halperin for many useful discussions, and to the latter for translating Ref. [17]. This work is supported by the National Science Foundation through Grant No. DMR-9102707.

[1] For a review, see A. J. Leggett, in *Chance and Matter*, edited by J. Souletie, J. Vannimenus, and R. Stora (North-Holland, Amsterdam, 1987).

[2] A. O. Caldeira and A. J. Leggett, Phys. Rev. Lett. **46**, 211 (1981); Ann. Phys. (N.Y.) **149**, 374 (1984); **153**, 445(E) (1984).

[3] S. Chakravarty and A. J. Leggett, Phys. Rev. Lett. **52**, 5 (1984).

[4] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).

[5] J. M. Martinis, M. H. Devoret, and J. Clarke, Phys. Rev. Lett. **55**, 1543 (1985); M. H. Devoret, J. M. Martinis, and J. Clarke, *ibid.* **55**, 1908 (1985). See J. Clarke *et al.*, Science **239**, 992 (1988), for a review of this work.

[6] S. Han, J. Lapointe, and J. Lukens, Phys. Rev. Lett. **66**, 810 (1991). This experiment does not attain low enough dissipation to see MQC; the results nevertheless display nontrivial quantitative features in the incoherent relaxation of the trapped flux that were predicted in Refs. [3,4].

[7] D. D. Awschalom, J. F. Smyth, G. Grinstein, D. P. DiVincenzo, and D. Loss, Phys. Rev. Lett. **68**, 3092 (1992).

[8] D. D. Awschalom, M. A. McCord, and G. Grinstein, Phys. Rev. Lett. **65**, 783 (1990).

[9] Anupam Garg, in Proceedings of the XX International Conference on Low Temperature Physics, Eugene, Oregon, 4–11 August 1993 (to be published), paper G3-10.

[10] E. M. Chudnovsky and L. Gunther, Phys. Rev. Lett. **60**, 661 (1988).

[11] B. Barbara and E. M. Chudnovsky, Phys. Lett. A **145**, 205 (1990); I. V. Krive and O. B. Zaslavskii, J. Phys. Condens, Matter **2**, 9457 (1990).

[12] The rate for ferromagnetic MQC can be increased by applying a field $\mathbf{H} \perp \hat{\mathbf{z}}$, which decreases the barrier height, and the angle through which M must tunnel. Likewise, if $\mathbf{H}$ is applied along $-\hat{\mathbf{z}}$, one obtains an MQT setup, and the escape rate can be made large (10^6–10^8 sec^{-1}) by having H approach within a few percent of the classical coercive field required to render the $\hat{\mathbf{z}}$ direction unstable.

[13] L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Wiley, New York, 1975), see Chap. 6.

[14] See P. M. Harrison and T. H. Lilley, in *Iron Carriers and Iron Proteins*, edited by T. M. Loehr (VCH, New York, 1989), for an up to date review on ferritin.

[15] N. J. Poulis, G. E. G. Hardeman, W. van der Lugt, and W. P. A. Haas, Physica (Utrecht) **23**, 907 (1957).

[16] A. C. Gossard and A. M. Portis, Phys. Rev. Lett. **3**, 164 (1959); A. Narath, Phys. Rev. **131**, 1929 (1963).

[17] A. Blaise, J. Chappert, and J.-L. Girardet, C.R. Acad. Sci. Paris **261**, 2310 (1965).

[18] See, e.g., H. H. Wickman, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum, New York, 1966), Vol. 2.

[19] D. E. Sayers, E. C. Theil, and F. J. Rennick, J. Biol. Chem. **258**, 14076 (1983); N. D. Chasteen and E. C. Theil, *ibid.* **257**, 7672 (1982).

[20] The field dependence of ν_r is still puzzling, but no more so than in the MQC interpretation.

[21] The same qualitative point is made by P. C. E. Stamp, E. M. Chudnovsky, and B. Barbara, Int. J. Mod. Phys. B **6**, 1355 (1992), see pp. 1453–1454.

[22] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon, New York, 1977), 3rd ed., Sec. 90.