Tunneling in Mesoscopic Magnetic Molecules

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We present a theoretical study of magnetic relaxation of big molecules, $Mn_{12}O_{12}$, at low temperature, when the relaxation time τ is temperature independent. If the magnetic field h_z is not too low, tunneling can only take place if energy is exchanged with phonons. Then, $1/\tau \sim h_z^3$ for weak h_z. A steeper increase is expected for higher h_z. The effect of a transverse field h_x is small. The maximum of $\tau(h_z)$ observed experimentally at $h_z = 0.2$ T might be due to tunneling without phonons in low field, with a relaxation rate reduced by hyperfine interactions.

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Recently discovered big magnetic molecules [1–4] are of interest because of the gigantic relaxation time τ of their magnetization [4], which reaches two months in zero magnetic field at 2 K in the $Mn_{12}O_{12}$ molecule (often called "Mn_{12}") combined with acetate ions. A theory of this relaxation time has been recently proposed [5] in the case of thermally excited relaxation, and τ was shown to be given by an Arrhenius law, in agreement with experiments above 2 K. However, recent experiments [6] show that the Arrhenius law is not satisfied below 2 K, and that τ goes to a finite limit when the temperature T goes to zero. The purpose of the present Letter is to calculate τ in terms of microscopic parameters and predict its dependence on tunable parameters such as the external magnetic field.

The experimental fact that τ is the same in the periodic crystal and in a dilute solution [7] shows that molecules are not magnetically coupled to each other. In the absence of magnetic field, each molecule has a double, Kramers degeneracy in its ground state. The transition from one ground state to the other is possible only if the molecule jumps over a potential barrier Δ or tunnels through it. Jumps over the barrier are efficient processes above 2 K and were studied in Ref. [5]. Tunneling through the barrier is the subject of the present work. The spin s of the molecule will be assumed to be fixed and equal to 10, in agreement with electron paramagnetic resonance (EPR) [3] and inelastic neutron scattering [8] experiments, which show that the lowest excited multiplicity corresponds to $s = 9$ and lies rather high, about $\delta = 30$ K above the multiplicity $s = 10$ in the $Mn_{12}O_{12}$ molecule combined with acetate ions. The energy barrier Δ can be deduced from the Arrhenius law, and is about 61 K in the same material. It may be associated with a spin Hamiltonian H_a, which can be derived from a perturbative treatment of the spin orbit interaction $\mathbf{L} \cdot \mathbf{S}$. The molecule is embedded in a tetragonal crystal; and, within second order perturbation theory, the form allowed by the tetragonal symmetry is

$$H_a = -AS_z^2. \tag{1}$$

An apparent paradox of the present model should be pointed out: The energy difference δ between the multiplicities $s = 10$ and $s = 9$ is replaced by infinity although it is lower than Δ, which is not replaced by infinity. This is paradoxical, but at least qualitatively correct, because the effect which impedes the transition between the two degenerate ground states of (1) is (in the case of thermal activation) the height of the potential barrier, which is the energy $\Delta = 100A$ of the state ($s = 10$, $m = 0$). Taking states $s = 9$ into account would increase the number of relaxation paths in the phase space, but would not modify the barrier.

One might expect tunneling between states ($s = 10$, $m = 10$) and ($s = 10$, $m = -10$) to occur as a consequence of a spin Hamiltonian which does not commute with S^z, e.g.,

$$H_a^1 = -C[S_+^4 + S_-^4]. \tag{2}$$

which is the lowest order form allowed by tetragonal symmetry. Tunneling as a consequence of (2) or similar perturbations has been studied by many authors in the case of mesoscopic systems [9–12]. However, this kind of tunneling is possible only if the magnetic field h_z in the z direction is so weak that the Zeeman splitting $4\mu_B h_z s$ is lower than the zero-field tunneling splitting $\hbar\omega_T^0$. This is a consequence of energy conservation and can be seen as follows: For $h_z = 0$, there are two low-lying eigenstates $|\text{sym}\rangle$ and $|\text{ant}\rangle$ of the total Hamiltonian, which is the sum of (1) and (2). Let their energy be 0 and $\hbar\omega_T^0$, respectively. In the space of the eigenvalues m of S^z, the wave functions $|\text{sym}\rangle$ and $|\text{ant}\rangle$ may be written as real, symmetric, and antisymmetric functions of m, so that $\langle\text{sym}|S^z|\text{sym}\rangle = \langle\text{ant}|S^z|\text{ant}\rangle = 0$

and $\langle \mathrm{ant}|S^z|\mathrm{sym}\rangle = \langle \mathrm{sym}|S^z|\mathrm{ant}\rangle \cong s$. If a field h_z is now applied, which is small with respect to the energy of the higher levels, the eigenstates may be approximated within lowest-order perturbation theory by $|\mathrm{sym}\rangle\cos\varphi + |\mathrm{ant}\rangle\sin\varphi$, where $\tan 2\varphi = -2\mu_B h_z \times \langle \mathrm{ant}|S^z|\mathrm{sym}\rangle/\hbar\omega_T^0 \approx -2\mu_B h_z s/\hbar\omega_T^0$. If $\mu_B h_z s \gg \hbar\omega_T^0$, $\tan\varphi$ is close to 1 or -1. This means that the eigenstates of the Hamiltonian are localized in the regions $m > 0$ and $m < 0$, respectively. If the system is prepared at time $t = 0$ in the state $S^z = -s$, the probability that it is still in this state two centuries later is close to 1. Thus, there is no tunneling if $\mu_B h_z s \gg \hbar\omega_T^0$. The elementary case of a spin 1/2, subject to the Hamiltonian $\tilde{H} = -h_z S_z - h_x S_x$, is a good illustration of this property. In that case, $\hbar\omega_T^0 = h_x$. As will be seen, for large s values, $\hbar\omega_T^0$ is much smaller.

Now, the tunnel frequency is, according to experiment, extremely low (less than 1 month^{-1}); and, since a magnetic field of 1 T is equivalent to $2\mu_B s/k_B = 13.4$ K and to a frequency $\omega = 2\mu_B s/\hbar \approx 2.8 \times 10^{11}$ s^{-1}, practically any magnetic field (that of the Earth or the demagnetizing field) would destroy the tunnel effect, if it were produced by the above mechanism.

In trying to explain the observed tunneling, two phenomena have to be taken into account: hyperfine interactions [13,14] and phonons [15]. The latter are the main objects of the present study, where the importance of energy conservation will be emphasized. The former will be naively described here as a random field, which is mainly produced by Mn nuclear spins. The hyperfine field seen by an electronic spin is [15] about 0.02 T. The resulting random field seen by the total spin S has, therefore, a distribution of half-width 0.02 T. For higher fields, direct tunneling can be expected to be negligible, and energy conservation requires interactions with phonons of the large surrounding system. These will be investigated in the rest of this Letter. Note that angular momentum conservation also requires interaction with a large surrounding system [16].

We consider an experiment in which the sample is in equilibrium in a negative field parallel to z at $t = 0$, so that it is in the spin state $|-s\rangle$. At $t = 0$, the field is reversed, and we want to investigate the state of the system at a positive time t. The transition to a spin state $|m\rangle$ (with $S_z|m\rangle = m|m\rangle$) is possible if a phonon of wave vector q is created, the energy of which allows energy conservation:

$$E_m + \hbar\omega_q = E_{-s}\,. \tag{3}$$

In this formula, E_m is an eigenvalue of the spin Hamiltonian

$$H_{\mathrm{sp}} = -AS_z^2 - 2\mu_B h_z S_z - C[S_+^4 + S_-^4]\,. \tag{4}$$

In view of the weakness of the experimental tunneling frequency, C is expected to be small, so that

$$E_m \cong -Am^2 - 2\mu_B h_z m\,. \tag{5}$$

If the field satisfies $h_z < A$, (3) can, therefore, only be satisfied for $m = s$ and reads

$$\hbar\omega_q = 2h_z s\,. \tag{6}$$

In practice, (6) can only be satisfied by acoustic phonons. For the sake of simplification, only one phonon mode will be taken into account. Extension to three modes is straightforward.

In this Letter, we consider a single spin (a single molecule) in an otherwise periodic crystal. Experimentally [7], the relaxation time in such a system is the same as in the perfectly periodic medium. The spin-phonon interaction will be assumed to be linear with respect to the local strain, which is $(1/\sqrt{N})\sum_q i\mathbf{q}\cdot\mathbf{u}_q$, where $\mathbf{u}_q$ is the Fourier transform of the displacement and N is the number of unit cells. In terms of phonon creation and destruction operators, $c_q^\dagger$ and c_q, the spin-phonon interactions should, therefore, have the form

$$H_{\mathrm{sp\text{-}ph}} = \sum_q \sqrt{\frac{\hbar}{2NM\omega_q}}\,[iqV_q(\mathbf{S})c_q^\dagger - iqV_q^\dagger(\mathbf{S})c_q]\,, \tag{7}$$

where V_q is a function of the spin to be specified later, which depends weakly on $|\mathbf{q}|$ for a given orientation $\mathbf{q}/|\mathbf{q}|$, and M is the mass per unit cell.

In order to discuss the effect of the spin-phonon interaction, it is convenient to introduce the eigenstate $|m^*\rangle$ of the spin Hamiltonian (4), as well as the states $|m^*, q\rangle$, where there is one phonon of well-defined wave vector q, and the molecule is in state $|m^*\rangle$.

At time $t = 0$, the system is in the state $|-s, \mathrm{vac}\rangle$, with no phonons and $S_z = -s$. This state may be approximated conveniently by the state $|-s^*, \mathrm{vac}\rangle$, where the molecule is in state $|-s^*\rangle$ and there is no phonon. The interaction (7) induces transitions from this state to states $|m^*, q\rangle$. The transition probability per unit time is given by the "golden rule"

$$p(-s^*, \mathrm{vac} \to m^*, q) = \frac{2\pi}{\hbar}\,|m^*, q|H_{\mathrm{sp\text{-}ph}}|-s^*, \mathrm{vac}|^2 \times \delta(E_m + \hbar\omega_q - E_{-s})\,,$$

where the delta function corresponds to the requirement of energy conservation, the central point of this Letter. Substituting (7), one obtains

$$p(-s^*, \mathrm{vac} \to m^*, q) = \frac{\pi q^2}{NM\omega_q}\,|\langle m^*|V_q|-s^*\rangle|^2 \times \delta(E_m + \hbar\omega_q - E_{-s})\,. \tag{8}$$

Summing (8) over q, one obtains the transition probability per unit time from the spin state $|-s^*\rangle$ to the spin state $|m^*\rangle$, namely,

$$p(-s^* \to m^*) = \frac{\pi}{NM}\sum_q \frac{q^2}{\omega_q}\,|\langle m^*|V_q|-s^*\rangle|^2 \times \delta(E_m + \hbar\omega_q - E_{-s})\,.$$

The tunneling rate ω_T is obtained by summing this expression over m. Transforming the sum into an integral and introducing the specific mass ρ, one finds

$$\hbar\omega_T = \frac{\hbar}{8\pi^2\rho}\sum_m \int \frac{q^2}{\omega_q} d^3q\, |\langle m^*|V_q|-s^*\rangle|^2 \times \delta(E_m + \hbar\omega_q - E_{-s}). \quad (9)$$

For the sake of simplification, an isotropic dispersion law, $\omega_q = cq$, will be assumed; and the spin-phonon interaction, $V_q = V$, will be assumed to be independent of q. Following Abragam and Bleaney [15], we also multiply by the number 3 of acoustic phonon modes and obtain the following formula, identical to Eq. (10.49) of Ref. [15]:

$$\hbar\omega_T = \frac{3}{2\pi\hbar^3c^5\rho}\sum_m |\langle m^*|V|-s^*\rangle|^2 (E_{-s} - E_m)^3. \quad (10)$$

In moderate field ($2\mu_B h_z < A$, i.e., 0.45 T for $Mn_{12}O_{12}$) only the value $s = m$ is consistent with (3), and one can write (10) as

$$\hbar\omega_T = \frac{3}{2\pi\hbar^3c^5\rho} |\langle s^*|V|-s^*\rangle|^2 (E_{-s} - E_s)^3. \quad (11)$$

Using (3) and (5), one obtains

$$\hbar\omega_T = \frac{12}{\pi\hbar^3c^5\rho} |\langle s^*|V|-s^*\rangle|^2 (h_z s)^3. \quad (12)$$

The phonon-assisted tunneling frequency is *proportional to the cube of the applied field* h_z when $2\mu_B h_z < A$. This result is independent of the approximations which, for the sake of simplicity, have been made (a single phonon mode, isotropic dispersion, and V independent of q).

We now have to worry about the structure of the states $|m^*\rangle$. We shall first discuss the case $2\mu_B h_z < A$ when only the states $|s^*\rangle$ and $|-s^*\rangle$, which are close to the eigenstates $|s\rangle$ and $|-s\rangle$ of (1), are to be taken into account. The perturbation due to the last term of (4) couples spin states $|m\rangle$ and $|m'\rangle$ with $|m - m'| = 4$, so that $|s^*\rangle$ and $|-s^*\rangle$ have the form

$$|s^*\rangle = \sum_p \lambda_{s-4p}|s - 4p\rangle,$$

$$|-s^*\rangle = \sum_p \mu_{-s+4p}|-s + 4p\rangle. \quad (13)$$

For the molecule $Mn_{12}O_{12}$, s is an even integer (actually 10). Then, it follows from (13) that the only terms of V_q which contribute to (12) are those which shift S_z by an integer multiple of 4. Such a lowest order term is

$$V_q^{(4)}(\mathbf{S}) = g_{xq}^{(4)}S_x^4 + g_{yq}^{(4)}S_y^4. \quad (14)$$

Thus, the second-order anisotropy has no effect. The fourth-order anisotropy (14) is presumably much smaller, so that a very small tunneling rate is expected. The situation should change for magnetic fields h_z sufficiently larger than A/μ_B. If $A < 2\mu_B h_z < 2A$, the values $m = s$ and $s - 1$ should be taken into account in (10), and relation (12) is to be replaced by

$$\hbar\omega_T = \frac{3}{2\pi\hbar^3c^5\rho}\Big[|\langle s^*|V_q|-s^*\rangle|^2 (2h_z s)^3 + |\langle (s-1)^*|V_q|-s^*\rangle|^2 (h_z - A)^3(2s-1)^3\Big]. \quad (15)$$

Now, the lowest-order terms of (7) contribute. If, in the spirit of Abragam and Bleaney [15], we assume that they are due to the modulation of the ligand field by phonons, they have the form

$$V_q^{(1)}(\mathbf{S}) = g_{xq}^{(1)}(S_xS_z + S_zS_x) + g_{yq}^{(1)}(S_yS_z + S_zS_y). \quad (16)$$

The coefficients $g^{(1)}$ are expected to be larger than the $g^{(4)}$'s in (14), so that an abrupt increase of the tunneling rate is expected when $2\mu_B h_z$ becomes larger than A. The existence of terms linear in S_x and S_y in the spin-phonon interaction has also been suggested [16]. They would not modify our analysis since they can also be inserted into (15).

In order to go further, it is necessary to specify the coefficients of the expansions (13). This will be done only in the case $2\mu_B h_z < A$. The coefficients μ, for instance, satisfy the equations

$$\begin{aligned}[A(s-4p)^2 - h_z(s-4p) + E_B]\mu_{-s+4p} &= -C\langle -s+4p|S_+^4|-s+4p-4\rangle\mu_{-s+4p-4} \\ &\quad -C\langle -s+4p|S_+^4|-s+4p+4\rangle\mu_{-s+4p+4},\end{aligned} \quad (17)$$

which for $1 \le p \le s/2 - 1$, can alternately be written in the form

$$\frac{\mu_{-s+4p-4}}{\mu_{-s+4p}} = K_{-s+4p}(E) - L_{-s+4p}\frac{\mu_{-s+4p+4}}{\mu_{-s+4p}}, \quad (18)$$

where $E = E_{-s}$, and the coefficients K and L can easily be deduced from (17). It is easily seen that L_{-s+4p} is of order unity (actually comprised between 0.1 and 10), while K_{-s+4p} is much larger than 1 for $1 \le p \le s/2 - 1$ if $2\mu_B h_z$ and Cs^2 are much smaller than A. A rough approximation is $K_{-s+4p}(E) \approx A/Cs^2$. If $2\mu_B h_z \ll A$, then $\mu_{-s+4p+4}/\mu_{-s+4p}$ is expected to be small. Neglecting L in (18), μ_{-s+4p} is seen to be of order $(Cs^2/A)^p$.

The matrix elements which appear in (9) when (13) is inserted are

$$\langle s^*|S_+^4|-s^*\rangle = \sum_{p=1}^{s/2} \lambda_{s-4p}^*\mu_{s-4p+4} \times \langle s-4p|S_+^4|s-4p-4\rangle$$

and a similar expression for $\langle s^*|S_+^4|-s^*\rangle$. Each term of this sum is roughly of order $s^4(Cs^2/A)^{s/2-1}$, so that the sum should be of order $s^5(Cs^2/A)^{s/2-1}$. A more careful calculation, taking into account the dependence of K on p in (18), yields

$$|\langle s^*|S_+^4|-s^*\rangle| \approx |\langle s^*|S_+^4|-s^*\rangle| \approx s^{9/2}\left[\frac{4Cs^2}{Ae^2}\right]^{s/2-1}. \tag{19}$$

This result does not depend on h_z, but is only valid for $\mu_B h_z \ll A$. Collecting formulas (12), (14), and (19), one concludes that in moderate fields ($\mu_B h_z < A$) the phonon-assisted tunneling rate is of order

$$\hbar\omega_T \approx \frac{384 g_4^2 s^9}{\pi^2 e^4 \hbar^3 c^5 \rho}\left[\frac{4Cs^2}{Ae^2}\right]^{s-2}(4\mu_B h_z s)^3, \tag{20}$$

where g_4 is the order of magnitude of the coefficients g in (14). If a q-independent interaction $V_q^{(4)}(\mathbf{S}) = g_4(S_+^4 + S_-^4)$ is assumed in (7), the perturbative result is given exactly by (20) with an "=" sign instead of "≈" (of the order of magnitude of).

The zero-field tunneling frequency ω_T^0 can be shown to be approximately equal to (19) multiplied by $4C/\hbar s$. Thus, it depends on the anisotropy as $(Cs^2/A)^{s/2-1}$, as already shown by Van Hemmen and Sütö [10]. This result is analogous to a formula obtained previously in a slightly different case by Kornblitt and Shender [9]. The much more abrupt decrease with increasing s, obtained by Chudnovsky and Gunther [17], does not correspond to the present situation. The maximum value h_0 of h_z which allows for tunneling without phonons, given by $4\mu_B h_0 s \approx \hbar\omega_T^0$, is

$$\mu_B h_0 \approx Cs^{5/2}\left[\frac{4Cs^2}{Ae^2}\right]^{s/2-1}.$$

An applied transverse field h_x can also, in principle, induce tunneling. The tranverse field-induced, phonon-assisted tunneling rate decreases with increasing spin s as $(h_x/As)^{4s-2}$, a formula analogous to (20). For a field of 0.8 T (or $2\mu_B h_z/k_B = 1.07$ K) along the x axis, and for $As = 6$ K, this factor is very small (about 10^{-26}), *so* that transverse field-induced tunneling is not observable. Transverse field-induced tunneling without phonons would only be possible for unphysical values of h_z. We conclude that a transverse field has no observable effect. On the contrary, assuming g_4 to be of order C, the observed tunneling is compatible with (20) if $4Cs^2/Ae^2$ is about 0.03.

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Note added.—As we were preparing the revised version of this Letter, we received a preprint [18] reporting a detailed experimental investigation of the tunneling time τ as a function of the external field h_z. It was found that τ increases with decreasing h_z for $h_z > h_M = 0.2$ T in agreement with (20), but then τ has a maximum and a slight decrease for smaller fields. A tentative explanation is the following: (a) The above theory is a correct description of the model constituted by Eqs. (4) and (7). (b) It describes experiments in $Mn_{12}O_{12}$, at least qualitatively, for $h_z > 0.2$ T. (c) In weaker fields, tunneling without phonons occurs; but, because of hyperfine interactions, the tunneling rate is much lower than the distance ω_T^0 between the states $S_z = -10$ and $S_z = 10$. The value $h_M = 0.2$ T is about ten times as large as expected from our knowledge of hyperfine interactions. This discrepancy will be examined in a future article.

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