Quantum Forces in Molecular Magnets

Eugene M. Chudnovsky\textsuperscript{1,2}, Javier Tejada\textsuperscript{1}, Ricardo Zarzuela\textsuperscript{1}
\textsuperscript{1}Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain
\textsuperscript{2}Physics Department, Lehman College, The City University of New York,
250 Bedford Park Boulevard West, Bronx, NY 10468-1589
(Dated: May 11, 2014)

Two-state systems may exhibit mechanical forces of purely quantum origin that have no counterpart in classical physics. We show that the such forces must exist in molecular magnets due to quantum tunneling between classically degenerate magnetic states. They can be observed in the presence of a microwave field when the magnet is placed in a static magnetic field with a gradient.

PACS numbers: 75.50.Xx; 75.45.+j; 03.65.-w

Forces of quantum nature are known in physics. One example is a Casimir force between two surfaces in a close proximity to each other. It is caused by the quantization of the fields in the space between the surfaces \cite{4}. Casimir forces have been extensively discussed in relation to a number of condensed matter systems \cite{2} see, e.g., recent applications to topological insulators \cite{3}. In this Letter we will discuss the force of a purely quantum origin of another kind: The force that is pertinent to the two-state systems. Such systems are very common in nature. They correspond to a situation when the lowest energy doublet of a quantum system is separated from the rest of the spectrum by a large gap, making only that doublet relevant in low-energy experiments. We will focus our attention on molecular magnets, although our conclusions will apply to any two-state system for which the energy distance $\Delta$ between the two states of the doublet can be controlled by the external field. Quantum Hamiltonian of a non-interacting two-state system is

$$\mathcal{H} = -\frac{1}{2}\Delta \sigma_z$$

where $\sigma_z$ is a Pauli matrix. Its eigenstates, $|\pm\rangle$, correspond to $\sigma_z = \pm 1$ and have energies $E_{\pm} = \mp \Delta/2$, with $|+\rangle$ being the ground state and $|-\rangle$ being the excited state. The general form of the normalized wave function is a superposition of the $|\pm\rangle$ states:

$$|\Psi\rangle = C_+ e^{-iE_+t/\hbar}|+\rangle + C_- e^{-iE_-t/\hbar}|-\rangle$$

with $|C_+|^2 + |C_-|^2 = 1$.

The Hamiltonian (1) is equivalent to the Hamiltonian of a spin-1/2 particle in the magnetic field. In the presence of the field gradient, there is a force on the particle that was used at the dawn of quantum physics to separate particles in beams according to their spin projection \cite{4}. The effect we are after has the same origin. However, here we are particularly interested in the situation when $\sigma_z$ describing the two-state system has nothing to do with the real spin 1/2, and the magnetic moment associated with it, is rather related to the tunnel splitting of classically degenerate states.

Let us consider a crystal containing a macroscopic number of non-interacting two-state particles. The occupation numbers of the states with $\sigma_z = \pm 1$ are $n_{\pm} = |C_{\pm}|^2$. The corresponding one-particle density matrix operator is $\rho = |\Psi(t)\rangle\langle\Psi(t)|$. In the presence of the gradient of $\Delta$ created by the gradient of the external field, the force on the crystal is

$$\mathbf{F} = \sum_n Tr \left[ (-\nabla \mathcal{H}) \rho \right] = \frac{1}{2} \sum_n (n_+ - n_-) (\nabla \Delta)$$

where summation is over occupation numbers of the particles. Note that $\mathbf{F}$ depends only on the gradient of $\Delta$ and on the occupation numbers, but not on the choice of the quantization axis for the effective spin 1/2.

The physical origin of the above force is clear. The particles with $\sigma_z = 1$, occupying the ground state level with energy $E_+ = -\Delta/2$, are attracted to the area where $\Delta$ is higher, while the particles with $\sigma_z = -1$, occupying the excited level with energy $E_- = \Delta/2$ are attracted to the area where $\Delta$ is lower. If for all particles $\Delta \ll k_BT$ the two states are almost equally occupied, $n_+ \approx n_-$, and the force is close to zero but at $k_BT \ll \Delta$ one has $n_+ \approx 1$, $n_- \approx 0$, and the net force is non-zero.

In molecular magnets this force must exist as a consequence of quantum tunneling between classically degenerate magnetic states \cite{5}. According to Eq. (3) at $k_BT \ll \Delta$ (that is, at $n_+ \approx 1$, $n_- \approx 0$) and the gradient of the tunnel splitting $|\nabla \Delta| \sim 1K/cm$, the force on a small crystal containing $10^{16}$ magnetic molecules would be of order $10^{-5}N$. On increasing temperature above $\Delta/k_B$ the force must disappear due to the equilibration of the populations of the two levels.

Another interesting situation is when the populations $n_{\pm}$ oscillate in time, causing mechanical oscillations of the crystal. This could be measured with the help of a mechanical resonator, a force microscope or a tunneling microscope. Such a situation can be achieved by placing the crystal in the ac field that provides Rabi oscillations of the populations of the two levels \cite{5}. Some complication comes from the gradient of $\Delta$ that makes it impossible to satisfy the condition of the resonance, $\hbar \omega = \Delta$, by the ac field of a fixed frequency $\omega$, for all particles of
the crystal. Below we compute the oscillating force on the crystal of a molecular magnet and study conditions under which it can be experimentally detected.

The exact form of the spin Hamiltonian is not important for our purpose but to explain the concept we will stick for the moment to a toy model of a crystal of uniaxial high-spin magnetic molecules in a strong transverse magnetic field. We choose the easy magnetization axis in the Y-direction. The field, \( B(z) \), is applied in the X-direction, with the field gradient being in the Z-direction. The Hamiltonian of an individual molecule is

\[
H_M = -DS_y^2 - g\mu_BBS_x
\]

where \( D \) is the anisotropy constant, \( g \) is the gyromagnetic factor, and \( \mu_B \) is the Bohr magneton. Non-commutation of \( H_M \) with \( S_y \) provides tunneling between degenerate classical energy minima, \( S_y = \pm S \). When \( B \) is small compared to the anisotropy field \( 2DS/(g\mu_B) \) the tunnel splitting can be computed with the help of the perturbation theory. At higher fields \( \Delta \) can be obtained by exact diagonalization of the spin Hamiltonian. In the last 20 years this has been done for a number of molecular magnets with account of all terms in the Hamiltonian that are dictated by symmetry. High-field cavity and EPR experiments in spin-10 Fe-8 and Mn-12 molecular magnets agree well with theoretical values of \( \Delta \). Strong dependence of \( \Delta \) on \( B \) makes it relatively easy to create a significant gradient of \( \Delta \) inside the sample.

Note that at the classical level the magnetic field applied perpendicular to the easy magnetization axis of the crystal creates a finite magnetic moment \( \mathbf{M} \) in the direction of the field. The gradient of the field then creates a constant classical force on the paramagnet, \( \mathbf{F} = \nabla (\mathbf{M} \cdot \mathbf{B}) \). Unlike this force, the quantum force we are after appears due to the tunnel splitting \( \Delta \). To measure this force one should exploit its dependence on the populations, \( n_\pm \), of the tunneling doublet. With an eye on resonant experiments we are interested in the situation where the change in \( \Delta \) across the sample of thickness \( a \) is small compared to \( \Delta \) itself, that is, \( |a\nabla\Delta| \ll \Delta_0 \), where \( \Delta_0 \) is the tunnel splitting in the middle of the sample. According to Eq. (5) this translates into the condition \( Su[\partial B/\partial z] \ll B_0 \), where \( B_0 \) is the transverse field in the middle of the sample. Writing \( B = B_0(1 + z/l) \), where \( l \) is the characteristic length describing the field gradient, the above conditions can be reduced to \( a \ll l/S \). The dependence of \( \Delta \) on \( z \) is then given by

\[
\Delta(z) = \Delta_0 \left( 1 + \frac{2Sz}{l} \right), \quad -a/2 < z < a/2
\]

Let now a weak ac field of amplitude \( h_{ac} \) and frequency \( \omega = \Delta_0/\hbar \) be applied along the Y-axis. Classically, such a field does not generate any magnetic moment and, therefore, it cannot be responsible for any classical force. In the presence of the ac field the truncated two-state Hamiltonian for an individual molecule becomes

\[
\mathcal{H} = -\frac{1}{2}\Delta \sigma_z - W\sigma_y \cos(\omega t)
\]

where

\[
W = g\mu_BSh_{ac}
\]

For the moment we will focus on the detuning from the resonance solely due to the field gradient,

\[
\delta(z) = \frac{\Delta(z)}{\hbar} - \omega = \frac{2Sz}{l} - \omega
\]

and will comment on the detuning due to dipolar and hyperfine fields later on.

Close to the resonance, solution of the Schrödinger equation with the Hamiltonian \( \mathcal{H} \) and the wave function \( \psi \) permits the rotating wave approximation, yielding the famous Rabi result

\[
C_- = i \frac{W}{\hbar\Omega_R} e^{i\delta t/2} \sin \left( \frac{\Omega_R t}{2} \right)
\]

\[
C_+ = e^{-i\delta t/2} \left[ \cos \left( \frac{\Omega_R t}{2} \right) + i \frac{\delta}{\Omega_R} \sin \left( \frac{\Omega_R t}{2} \right) \right]
\]

where

\[
\Omega_R(z) = \sqrt{\delta^2(z) + \left( \frac{W}{\hbar} \right)^2}
\]

As has been discussed above, at \( T = 0 \) the force acting on the molecules is proportional to

\[
n_+ - n_- = |C_+|^2 - |C_-|^2 = \frac{\delta^2}{\Omega_R^2} + \frac{W^2}{(\hbar\Omega_R)^2} \cos(\Omega_R t)
\]

which is now a function of coordinates due to the field gradient. Switching from summation to integration in Eq. (5), we have

\[
F(t) = \frac{1}{2} N \nabla (\nabla \Delta) \int_{-a/2}^{a/2} dz \left[ |C_+(z,t)|^2 - |C_-(z,t)|^2 \right]
\]

where \( N \) is the number of molecules in the crystal. When \( W \to 0 \), one has \( n_+ - n_- \to 1 \) and the problem reduces to the one of a constant force. Here we are interested in the oscillating part of the force due to the second term in Eq. (12),

\[
F_{osc} = NS \Delta_0 \int_{-a/2}^{a/2} dz \frac{W^2}{(\hbar\Omega_R(z))^2} \cos(\Omega_R(z)t)
\]

We shall introduce notation

\[
\Omega_0 = \Omega_R(0) = \frac{W}{\hbar} = S \left( g\mu_Bh_{ac} \right)
\]

where

\[
\Delta_{osc} = \int_{-a/2}^{a/2} dz \left( \frac{W^2}{(\hbar\Omega_R(z))^2} \right) \cos(\Omega_R(z)t)
\]
for the Rabi frequency at $z = 0$. The condition $\delta(z = a/2) \ll \Omega_0$ is needed to insure that contributions of molecules belonging to different layers of the crystal do not cancel for a substantial period of time. It is equivalent to

$$\frac{S_0}{\ell} \frac{1}{\omega} \ll \Omega_0 \tag{16}$$

With this condition Eq. (14) becomes

$$F_{osc} = NS \frac{S_0 \hbar}{a} \int_0^\infty d\xi \cos \left( \frac{\Omega_0 t \xi^2}{2} \right) \frac{1 + \xi^2}{1 + \xi^2} \tag{17}$$

where

$$\epsilon = \left( \frac{S_0}{\ell} \right) \left( \frac{\omega}{\Omega_0} \right) \ll 1 \tag{18}$$

Smallness of $\epsilon$ allows one to replace $\sqrt{1 + \xi^2}$ with $1 + \xi^2/2$ and to reduce the integral in Eq. (17) to the sum of Fresnel integrals

$$\cos(\Omega_0 t) \int_0^\epsilon d\xi \cos \left( \frac{\Omega_0 t \xi^2}{2} \right) - \sin(\Omega_0 t) \int_0^\epsilon d\xi \sin \left( \frac{\Omega_0 t \xi^2}{2} \right) \tag{19}$$

There are two regimes in the temporal behavior of this expression. At $\Omega_0 t \ll 2/\epsilon^2$, it reduces to $\epsilon \cos(\Omega_0 t)$, resulting in

$$F_{osc} = NS \frac{S_0}{\ell} \cos(\Omega_0 t) \tag{20}$$

At $\Omega_0 t \gg 2/\epsilon^2$, recalling that $\int_0^\infty dx \cos x^2 = \int_0^\infty dx \sin x^2 = \sqrt{\pi/8}$, one obtains

$$F_{osc} = NS \frac{\hbar \Omega_0}{a} \sqrt{\frac{\pi}{2\Omega_0 t}} \cos \left( \frac{\Omega_0 t}{4} \right) \tag{21}$$

that is, the force that goes down as a square root of time. Interpretation of the two regimes is straightforward. Initially all molecules oscillate in phase due to the small variation in the Rabi frequency. With time, however, molecules belonging to different layers of the crystal accumulate large phase differences and the forces acting on them begin to cancel.

To solve the problem for an arbitrary microwave pulse and arbitrary $\epsilon$, without relying on the rotating wave approximation, we replace $W$ in Eq. (7) with $WF(t)$, where $W$ is the same constant as before and $F(t)$ is an arbitrary function of time representing the time dependence of the amplitude of the ac field. Schrödinger equation generates the following equations for $C_{\pm}$:

$$i \frac{d}{d\tau} C_{\pm}(\tilde{z}, \tau) = \frac{1}{2} e^{2i\epsilon \tilde{z} \tau} F(\tau) \left[ 1 + e^{2i(\omega/\Omega_0)\tau} \right] C_{\mp}(\tilde{z}, \tau) \tag{22}$$

where $\tau \equiv \Omega_0 t$ and $\tilde{z} \equiv z/a$. The solution depends on two parameters: $\epsilon$ and $\omega/\Omega_0$. We solve Eqs. (22) numerically and compute the force given by Eq. (13). The oscillating part of the force for $F(t) = 0$ at $t < 0$ and $F(t) = 1$ at $t > 0$, in the case of $\epsilon = 0.1$ and $\omega/\Omega_0 = 100$, is shown in Fig. [1]. For small $\epsilon$ the deviation of numerical results from the analytical formulas (20) and (21), obtained for the two limiting cases of short and long times, is small. The envelope curve in Fig. [2] follows the asymptotic analytical result at long times, $F_{osc}(t)/F_{osc}(0) = (1/\epsilon) \sqrt{\pi/(2\Omega_0 t)}$.

**FIG. 1:** Oscillating force normalized by its value at $t = 0$ for $\epsilon = 0.1$ and $\omega/\Omega_0 = 100$. The inset shows oscillations. The envelope line shows analytical result for the amplitude of the force at long times.

**FIG. 2:** Oscillating force normalized by its value at $t = 0$ for $\epsilon = 1.0$ and $\omega/\Omega_0 = 10$.

Note that a sizable force may also exist in the case of a strong detuning due to a strong field gradient, when the condition $\epsilon \ll 1$ is not fulfilled. For instance, the ratio of $F_{osc}(0)$ at $\epsilon = 1$ to $F_{osc}(0)$ at $\epsilon = 0.1$ is 0.788 and the decrease of the amplitude with time is rather slow.
This occurs due to the coherent contribution to the force of the central layer of the crystal where the detuning is still small. Fig. 2 shows the time dependence of the normalized oscillating force for $\epsilon = 1$ and $\omega/\Omega_0 = 10$.

We shall now focus on the conditions needed to observe the oscillating force. Most of these conditions are the same as the ones needed for detecting Rabi oscillations. Firstly, the spread of $\Delta$ due to dipole-dipole and hyperfine interactions should be small to provide near-resonance condition for all molecules apart from broadening due to the gradient of the transverse field. Local stray field $H_L$ along the anisotropy axis would change $\Delta_0$ to $\Delta = \sqrt{\Delta_0^2 + W_L^2}$ where $W_L = gS\mu_B H_L$. Small spread of $\Delta$ occurs when $W_L \ll \Delta_0$, in which case $\Delta = \Delta_0[1 + W_L^2/(2\Delta_0)]$. For $H_L \sim 10^5$G small spread of $\Delta$ requires $\omega = \Delta_0/\hbar$ in the GHz range. Some molecular magnets have $\Delta$ in this range or higher at $B = 0$ due to the symmetry of the Hamiltonian [14–15]. For the transverse field to dominate $\Delta$ of that magnitude the field must be in the tesla range. For $B_0 = 1T$ and the field gradient of 1T/cm (which can be easily achieved in a quadrupole magnet) the parameter $l = B_0/|\nabla B|$ is 1 cm.

Secondly, a significant number of Rabi cycles should occur before the phase of the wave function of an individual molecule is destroyed by decoherence. Studies of decoherence [13–15] suggest that the decoherence time in molecular magnets can hardly exceed one hundred nanosecond. Thus, the Rabi frequencies involved must be in the excess of 10MHz, which requires $h_{ac}$ of a few gauss or greater. To date Rabi oscillations have been observed in the $S = 5$ Fe-5 molecular magnet [20] and in the $S = 1/2$ V-15 molecular magnet [21, 22].

For $\omega \sim 10$GHz and $\Omega_0 \sim 100$MHz, the condition [18] at $l \sim 1$ cm and $S \sim 1$, gives $a \ll 0.1$mm. Molecular magnet of such dimensions would typically have less than 10$^{15}$ molecules. Substituting $N = 10^{14}$, $\omega = 10$GHz, $l = 1$ cm, $S = 1$ into Eq. (20), we get the amplitude of the oscillating force of order $10^{-8}$N, which is comparable to the weight of the crystal. The force of that magnitude should be powerful enough to generate surface acoustic waves in the substrate to which the sample is fixed. It could also be measured by placing the sample on a micro-cantilever and measuring the deflection of the cantilever as a function of temperature. Since the Rabi frequency is proportional to the amplitude of the ac field, the resonance with the mechanical mode of the cantilever can be achieved by varying $h_{ac}$. Given the magnitude of the computed force the effect may be detectable even when only a small fraction of the molecules is near resonance with the ac field due to a large field gradient or because of dipolar, hyperfine, and other stray fields in the crystal. This may also be true for a system that is artificially diluted to reduce dipole-dipole interactions.

In conclusion, we have shown that two-state systems can exhibit forces of purely quantum origin. Forces related to quantum tunneling of the magnetic moment have been computed. High magnitude of such forces and their strong dependence on temperature and field gradient should make them detectable in molecular magnets.

The work of EMC has been supported by the University of Barcelona and by the NSF Grant No. DMR-1161571. The work of JT and RZ has been supported by the Spanish Government Project No. MAT2011- 23698.

[1] H. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948).
[2] M. Kardar and R. Golestanian, Rev. Mod. Phys. 71, 1233 (1999).
[3] A. G. Grushin and A. Cortijo, Phys. Rev. Lett. 106, 020403 (2011).
[4] W. Gerlach and O. Stern, Zeitschrift für Physik 9, 353 (1922).
[5] E. M. Chudnovsky and J. Tejada, Macroscopic Quantum Tunneling of the Magnetic Moment (Cambridge University Press, Cambridge, England, 1998).
[6] I. I. Rabi, Phys. Rev. 51, 652 (1937).
[7] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. 76, 3830 (1996).
[8] D. A. Garanin, J. Phys. A 24, L61 (1991).
[9] E. M. Chudnovsky and J. Tejada, Lectures on Magnetism (Rinton Press, Princeton, NJ, 2006).
[10] E. del Barco, J. M. Hernandez, J. Tejada, N. Biskup, R. Achey, I. Rutel, N. Dalal, and J. Brooks, Phys. Rev. B 62, 3018 (2000).
[11] F. Luis, F. L. Mettes, J. Tejada, D. Gatteschi, and L. J. de Jongh, Phys. Rev. Lett. 85, 4377 (2000).
[12] S. Takahashi, R. S. Edwards, J. M. North, S. Hill, and N. S. Dalal, Phys. Rev. B 70, 094429 (2004).
[13] S. Takahashi, I. S. Tupitsyn, J. van Tol, C. C. Beedle, D. N. Hendrickson, and P. C. E. Stamp, Nature 476, 76 (2011).
[14] O. Waldmann, C. Dobe, H. Mutka, A. Furrer, and H. U. Güdel, Phys. Rev. Lett. 95, 057202 (2005).
[15] G. de Loubens, A. D. Kent, V. Krymov, G. J. Gerfen, C. C. Beedle, and D. N. Hendrickson, J. Appl. Phys. 103, 07B910 (2008).
[16] S. Hill, R. Edwards, N. Aliaga-Alcaino, and G. Christou, Science 302, 1015 (2003).
[17] E. Del Barco, A. Kent, E. Yang, and D. Hendrickson, Phys. Rev. Lett. 93, 157202 (2004).
[18] W. Wernsdorfer, D. Mailly, G. A. Timco, and R. E. P. Winpenny, Phys. Rev. B 72, 064409 (2005).
[19] A. Ardavan, O. Rival, J. J. L. Morton, S. J. Blundell, A. M. Tyryshkin, G. A. Timco, and R. E. P. Winpenny, Phys. Rev. Lett. 98, 057201 (2007).
[20] C. Schlegel, J. van Slageren, M. Manoli, E. K. Brechin, and M. Dressel, Phys. Rev. Lett. 101, 147203 (2008).
[21] S. Bertaina, S. Gambarelli, T. Mitra, B. Tsukerblat, A. Müller, and B. Barbara, Nature (London) 453, 203 (2008); ibid 466, 1006 (2010); J. H. Shim, S. Bertaina, S. Gambarelli, T. Mitra, A. Müller, E. I. Baikulov, B. Z. Malkin, B. Tsukerblat, and B. Barbara, Phys. Rev. Lett. 109, 050401 (2012).
[22] J. Yang, Y. Wang, Z. Wang, X. Rong, C.-K. Duan, J.-H. Su, and J. Du, Phys. Rev. Lett. 108, 230501 (2012).