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How to Cross an Energy Barrier at Zero Kelvin without Tunneling Effect

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This Letter deals with the broad class of magnetic systems having a single or collective spin S with an energy barrier, such as rare-earth elements and their compounds, single molecule magnets with uniaxial anisotropy, and more generally any other anisotropic quantum system made of single or multiple objects with discrete energy levels. Till now, the reversal of the magnetization of such systems at zero kelvin required making use of quantum tunneling with a significant transverse field or transverse anisotropy term, at resonance. Here, we show that another very simple method exists. It simply consists in the application of a particular sequence of electromagnetic radiations in the ranges of optical or microwave frequencies, depending on the characteristics of the system (spin and anisotropy values for magnetic systems). This produces oscillations of the Rabi type that pass above the barrier, thus extending these oscillations between the two energy wells with mixtures of all the $2S+1$ states. In addition to its basic character, this approach opens up new directions of research in quantum information with possible breakthroughs in the current use of multiple quantum bits.

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The magnetic properties of systems with uniaxial anisotropy are dominated by the presence of an energy barrier separating the spin-up and spin-down states. The reversal between an up–spin state and a down–spin state requires, either a sufficient temperature for thermal activation above the barrier [$T > T_B = \Delta E/\ln(t/\tau_0)$, where ΔE is the energy barrier, τ_0 the usual prefactor of the Arrhenius law, and t the time] or the application of a sufficient transverse field to induce resonant tunneling through the barrier.

Demonstrated for the first time at the mesoscopic scale, this effect led to a stepwise hysteresis in the single molecule magnet Mn_{12}-ac [1]. Later it was confirmed in many other mesoscopic systems (Fe_8 [2], the lanthanides double-deckers [3,4], etc.). These results paved the way to the new field of magnetism at the mesoscopic scale (see, e.g., [5]).

In this Letter, we demonstrate the existence of a third possibility to pass a barrier as a simple consequence of the application of a special protocol of ac-magnetic fields, a method which is valid with or without an applied magnetic field. This protocol is purely quantum mechanical and aims to realize the control of the whole $2S+1$ states of a uniaxial spin S without thermal excitation or quantum tunneling. In particular, it shows that the coincidence of levels, required in quantum tunneling, is not required here.

The dynamics of a spin S of uniaxial anisotropy in a magnetic field H_z, is described by

$$\mathcal{H} = -DS_z^2 - H_z S_z, \qquad S_z = S, S-1, \ldots, -S, \quad (1)$$

where D is the anisotropy constant. The energy of the state $S_z = m$, given by

$$E_m = -Dm^2 - H_z m, \quad (2)$$

enables to plot the energy barrier,

$$E_m - E_{\min}, \qquad E_{\min} = -DS^2 - H_z S, \quad (3)$$

which is shown in Fig. 1 for $S = 10$ and $H_z = 0$.

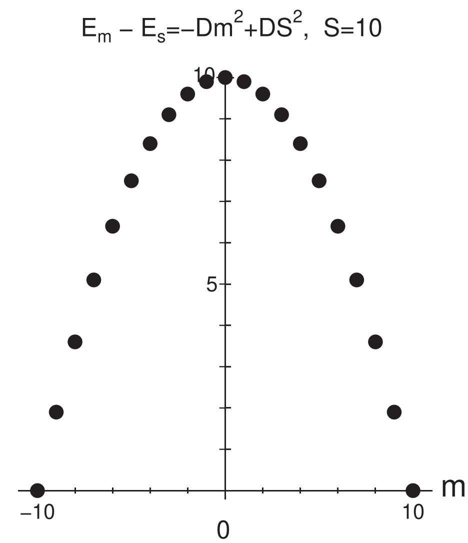

FIG. 1. Energies of states E_m [Eq. (2)] for $S = 10, D = 0.1$, and $H_z = 0$. We plot $E_m - E_{\min}, E_{\min} = E(\pm S) = -DS^2$, showing the energy barrier between the states $m > 0$ and $m < 0$.

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When $D \neq 0$, the energy difference between the states of $S_z = m - 1$ and $S_z = m$ for a given field H_z is given by (for simplicity we take the Planck constant $\hbar = 1$):

$$\omega_{m\to m-1} \equiv E_{m-1} - E_m = H_z + D(2m-1),\quad m = S, S-1, \ldots, -S+1. \tag{4}$$

If we add the circularly polarized frequency $\omega_{m\to m-1}$, the Hamiltonian (1) must be complemented by

$$\mathcal{H}_{\mathrm{acm}} = -h_{\mathrm{ac}}[\sin(\omega_{m\to m-1}t)S_x + \cos(\omega_{m\to m-1}t)S_y], \tag{5}$$

and the z-spin component oscillates between m and $m-1$. Note that, in the past, such state oscillations were used to prove the effect of photon-assisted quantum tunneling [6].

It is well known that in the limit $D = 0$, the application of such a resonance ac field in the xy plane induces periodic spin oscillations between $S_z = S$ and $-S$, a motion which is usually called Rabi oscillations [see Sec. I in Supplemental Material (SM) [7]]. However, in the presence of an energy barrier DS_z^2, the Rabi oscillations are not possible because the level separations between the states m and $m-1$ given by (4) are all different. As we will see below, we will still create oscillations, applying several frequencies simultaneously between the states of $S_z = m$ and $m-1$ for each separation (Sec. II in SM [7]).

In the presence of a longitudinal field H_z, the energy levels, calculated for $S = 10$ and $D = 0.1$, are depicted (Fig. 2). The transition between each consecutive level (E_m and E_{m-1}) is induced by the application of a resonance field with the frequency $\omega_{m\to m-1}$ given by (4).

When we include the ac fields up to $\omega_{S'\to S'-1}$, the Hamiltonian becomes

$$\mathcal{H} = -DS_z^2 - H_zS_z - h_{\mathrm{ac}}\left(\sum_{m=S}^{S'}\sin(\omega_{m\to m-1}t)S_x + \sum_{m=S}^{S'}\cos(\omega_{m\to m-1}t)S_y\right). \tag{6}$$

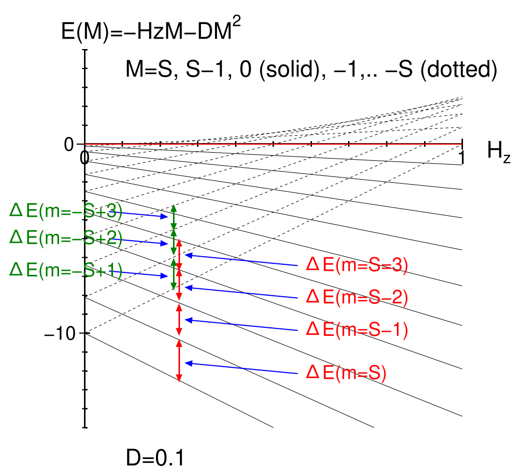

FIG. 2. Energy levels of the spin $S = 10$ as a function of positive H_z for $D = 0.1$. Some of the energy differences between the states are depicted by arrows.

First, let us consider the case with a single ω_S, which causes the oscillation between S and $S-1$ [that is, $S' = S$ in (6)] as shown in Fig. 3. As expected, the result is a slow oscillation of S_z between $m = S$ and $S-1$ with a rapid precession of the x component around the z axis. In the particular case where the $S-1$ level is in coincidence with a level on the other side of the barrier, photon-activated tunneling should be observed, as this was confirmed experimentally in [6].

If we now include one more ac field, i.e., $\omega_{S-1\to S-2}$ on the top of $\omega_{S\to S-1}$, we find the superposition of two successive resonances: one between the levels $m = S$ and $S-1$ and one between $S-1$ and $S-2$ [Fig. 4(a)]. This leads to more complex oscillations of S_z between $m = S$ and $S-2$, together with a rapid precession of the x component around the z axis. Interestingly, such a spin motion corresponds to nothing else but an incomplete Rabi oscillation, in which the xy components are modulated with an envelope corresponding to the period of the z component.

Taking now all the ac fields of one side of the barrier (from $\omega_{S\to S-1}$ to $\omega_{S-9\to S-10}$), we find similar oscillations of the x and z components with, however, larger amplitudes and modulations. In particular, S_z oscillates between the ground state $S_z = 10$ and the top of the barrier [Fig. 4(b)]. (All cases of $S' = S, S-1, \ldots, -S+1$ are shown Fig. 3 of SM [7]).

Finally, if we include all the resonance fields given by $\omega_{m\to m-1}$ (4), i.e., $S' = -S+1$, we find that the spin oscillations extend above the barrier between the states S and $-S$ [Fig. 4(c)]. The interferences between the corresponding oscillations associated with all the x, y, and z spin components of each one of the 21 states of our spin $S = 10$,

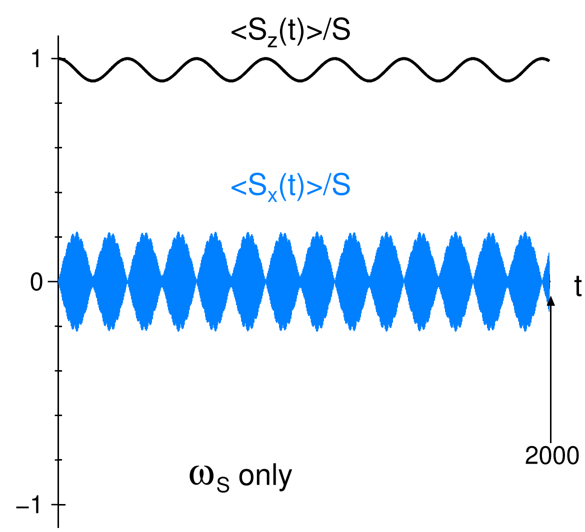

FIG. 3. Time dependence of the reduced spin components $S_x(t)/S$ (below, thin line) and $S_z(t)/S$ (above, bold line) under the ac field of $\omega_{S\to S-1}$ only. $h_{\mathrm{ac}} = 0.005$. (In the figure ω_S denotes $\omega_{S\to S-1}$.) The initial state is $(S_x/S, S_y/S, S_z/S) = (0,0,1)$. As we have $S = 10$, this scheme shows that S_x oscillates between $+2$ and -2 and S_z between $S = 10$ and $S-1 = 9$.

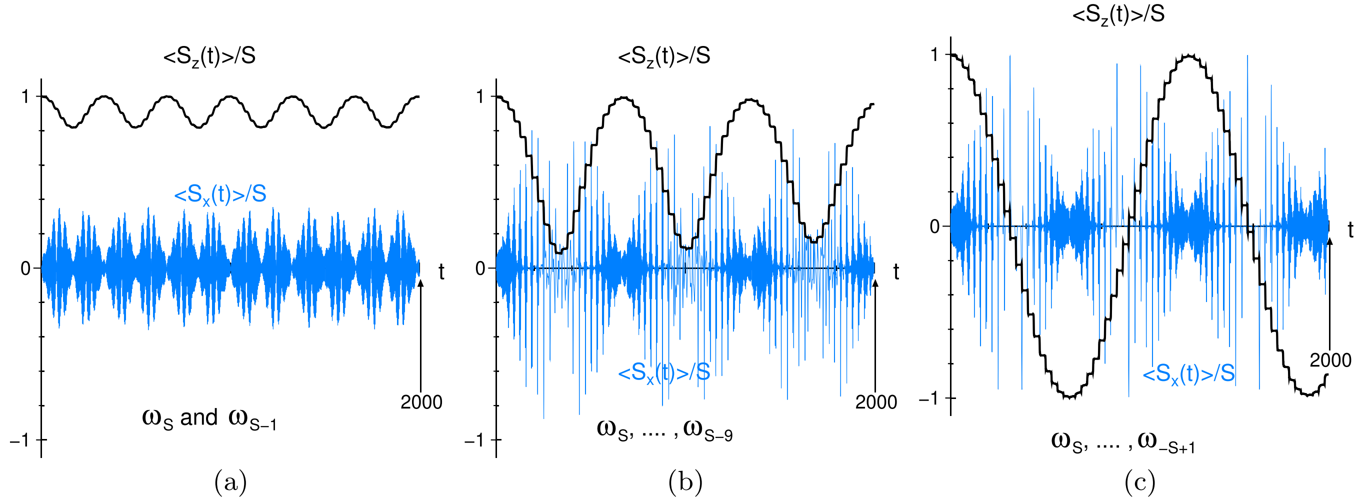

FIG. 4. Time dependence of the reduced spins components $S_x(t)/S$ (below, thin line) and $S_z(t)/S$ (above, bold line) under the ac field with $h = 0.005$ and $H_z = 0$. (a) $\omega_{S\to S-1}$ and $\omega_{S-1\to S-2}$ and (b) $\omega_{S\to S-1}, \ldots, \omega_{S-9\to S-10}$. (c) $\omega_{S\to S-1}, \ldots, \omega_{-S+1\to S}$. In all the cases, the initial state is $(S_x, S_y, S_z) = (0, 0, 1)$.

lead to rather fast in-plane spin oscillations with much slower, and also almost complete perpendicular oscillations between S and $-S$. Even if it is purely quantum, this motion is rather similar to, but quite different from a classical Rabi oscillation. We call it "giant quantum oscillations above the barrier" (GQOAB). Note that the present oscillations from one well to the other one differ from those resulting from quantum tunneling because the application of a significant transverse field and the coincidence of the spin-up and spin-down levels are not required.

In order to show some more details regarding the properties of our GQOAB, we write the Schrödinger equation in the rotating frame (Sec. III-A in SM [7]):

$$i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle = \left(-DS_z^2 - h_{\rm ac}\frac{f(t)}{2i}(S^+ - S^-)\right)|\Phi(t)\rangle, \quad (7)$$

where the sinusoidal functions of (6) can be written

$$f(t) = \frac{\sin(2DSt)}{\sin(Dt)}, \quad (8)$$

which is depicted in SM (Fig. 4 of SM [7]). These equations do not depend on H_z, contrary to the case of quantum tunneling where the spin-up and spin-down states must be in coincidence (see Fig. 5 of SM [7]).

This new mechanism induces spin reversal above the barrier as this is the case with thermal activation, but here the activation is coherent and associated with the application of a particular time-dependent electromagnetic field $f(t)$ at zero kelvin.

Clearly enough, these calculations performed with the example of a spin $S = 10$, which corresponds to the case of Mn_{12}-ac, could be done with any spin size. For example, as the calculations are done at zero kelvin, we could also have taken the smallest possible spin with a barrier, $S = 1$. However, on the experimental side, this would be more tricky because the height of the barrier being DS^2, the use of very small spins would require extremely low temperatures, often not available. Regarding the high spins side, the limitation comes from the fact that the spin levels become very close to each other making difficult the applications of the adapted microwaves frequencies. We have shown that this GQOAB is also valid for any other integer and also noninteger spin, even if the energy structure is slightly different for the noninteger case (see Fig. 5 for $S = 19/2$ as an example in noninteger case, and also Sec. III-B in SM [7] for $S = 5$).

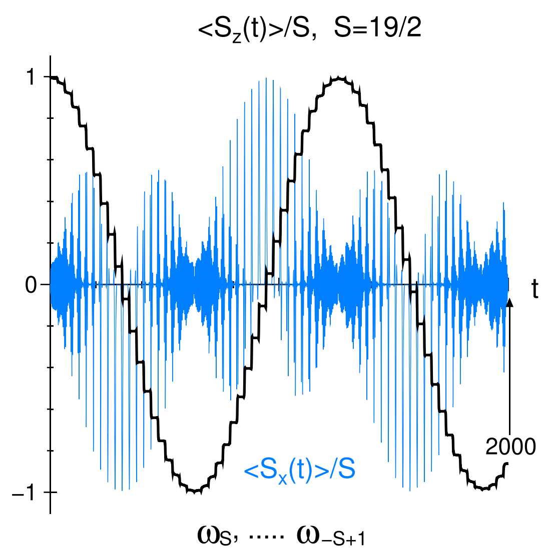

FIG. 5. Time dependence of the reduced spin components $S_x(t)/S$ (below, thin line) and $S_z(t)/S$ (above, bold line) under the ac field of $\omega_{S\to S-1}, \ldots, \omega_{-S+1\to -S}$ for a noninteger spin $S = 19/2$. $H_z = 0$ and $h_{\rm ac} = 0.005$. (In the figure ω_S represents $\omega_{S\to S-1}$, and so on.) The initial state is $(S_x, S_y, S_z) = (0, 0, 1)$.

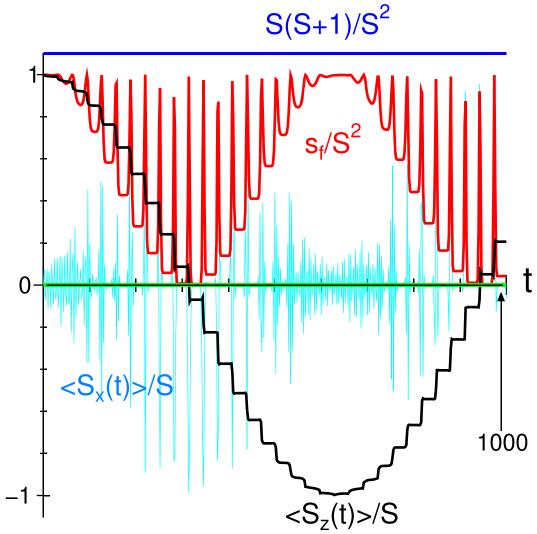

FIG. 6. Motions of spin $S = 10$ for $H_z = 0.1$, $h_{ac} = 0.005$, and the driving ac field $f(t)$ given by Eq. (8). The amplitude $h_{ac} = 0.005$. $\langle S_x(t) \rangle$ (thin curve) and $\langle S_x(t) \rangle$ (bold curve) are normalized by S, The normalized spin length (spin fidelity s_f) is given by the bold line (above). The total spin $S(S+1)$ normalized by S^2 is given by the blue line.

Despite their similarities, our GQOAB and the classical Rabi oscillations are obviously very different, the first being quantum with finite D while the second can be classical with $D = 0$ (Fig. 2 in SM [7]). For example, in our GQOAB, the spin fidelity [8,9]

$$s_f = \langle S_x \rangle^2 + \langle S_y \rangle^2 + \langle S_z \rangle^2 \tag{9}$$

is not conserved, which is obviously in opposition with the case of classical Rabi oscillations (see Fig. 6 and Sec. I of SM [7]). In contrast, the total spin $\langle S_x^2 \rangle + \langle S_y^2 \rangle + \langle S_z^2 \rangle = S(S+1)$ is conserved in both cases.

It is also noted that when $D = 0$, all the resonance frequencies become the same, i.e., $\hbar\omega_{m\to m-1} = H_z$. In this case, the amplitude of the ac field is $2Sh_{ac}$, and $\langle S_z \rangle$ shows usual Rabi oscillations with a period proportional to $1/2Sh_{ac}$. Conversely, for large D this period is simply proportional to $1/h_{ac}$ showing that, when D approaches 0, the period of GQOAB oscillations changes very rapidly in a complicated manner especially when S is large [see Fig. 9(c) in Sec. III-D in SM [7]].

Our very simple procedure to create quantum oscillations going through all the states from one side of the barrier to the other one, could be realized with single molecule magnets or $3d$ or $4f$ elements, highly diluted in a nonmagnetic matrix single crystal. Single-domain nanoparticles could also be used, if the required important set of frequencies is available. As an example, we might suggest the case of Ho^{3+} ions diluted in the matrix of $YLiF_4$ [10] in which a barrier evidenced by a Mn_{12}-like stepwise hysteresis loop was observed. Furthermore, this system offers the possibility to extend our approach when the electronic levels on each side of the barrier are split by hyperfine interactions.

In conclusion, through the application of a particular protocol of experimentally accessible electromagnetic radiations, we found a new method to reverse a spin above a barrier at zero kelvin, whatever its parity is. This mechanism, which does not require the application of a transverse field or the coincidence of spin-up and spin-down states, is not a tunneling effect, even if it shows similar quantum oscillations between the ground spin-up and spin-down states. In our case, the frequency of these oscillations is proportional to the amplitude of the applied electromagnetic radiation field. We have demonstrated the method with $S = 10$. In this case, we need 20 different frequencies while a spin $S = 20$ would require 40. Using an electron paramagnetic resonance spectrometer generating the so-called "shaped pulses" [11], we are currently performing experiments that will enable us to elucidate what the limitations on the size of large spins are.

Together with its basic interest, which gets back to the early days of magnetism by showing how to pass a barrier at zero kelvin without using the tunnel effect, GQOAB opens new possibilities in quantum information through very simple spin manipulations in the presence of a barrier. This procedure is "active" as it leads to controllable oscillations over the barrier between two arbitrary states, unlike the quantum tunneling effect where, since the levels must coincide, there is no way to monitor the quantum oscillations. In the present method, all the transitions between any pair of the $2S + 1$ states are possible. The energies of the initial state and the target state are not necessarily the same as it is the case with quantum tunneling. Furthermore, parasitic magnetic fields will not have any influence in, e.g., decoherence as the transitions do not depend on the external magnetic field H_z.

Even if this was not our main motivation, this approach enabling the superposition of the whole $2S + 1$ states of a spin on both sides of the energy barrier, should pave the way to new methods of quantum manipulations for quantum computing, transfer between different states, contiguous, noncontiguous, in a same barrier well or in different barrier wells.

During the last decade, qubit manipulations of single-spin magnets with or without rare earths, or with or without nuclear spins (see e.g., [10]) have been extensively investigated together with other materials, such as single-electron quantum dots in superconducting circuits (see the review [12] and references therein). More recently, special integrations mixing electronuclear spin qubits and quantum circuits have been realized [13–18] enabling the implementation of various error corrections quantum algorithms [19–23]. In particular the multibit spin manipulations that are currently under way [24] involve quantum states connection through the creation or annihilation of the ladder operators, as in our approach, but in the absence of a barrier which greatly reduces the possibilities of manipulation, in particular, because in the presence of an energy barrier, the entanglements are restricted to the pair of states which is in coincidence. By contrast, the use of the precisely shaped microwave frequencies proposed in this Letter, should permit the simultaneous quantum mechanical control of the $2S + 1$ states in the presence of a barrier and should therefore provide a novel generic strategy for the integration of various quantum magnetic systems. Furthermore, the populations of the states separated by a barrier are expected to be more stable against decoherence, which is particularly true here, as the Hamiltonian is independent of H_z.

In order to obtain GQOAB at finite temperature, the temperature must be sufficiently low for the microwave-induced jump probability to be much higher than the thermal activation jump probability. Taking the example of Mn_{12}-ac with $S = 10$ and $D \simeq 0.6$ K, we find $T \ll 15$ K which is more than acceptable. In addition, decoherence effects [25,26] should be lower than with Rabi oscillations because GQOAB are (i) nonsensitive to external magnetic fields and (ii) continuously supported by applied microwaves. And, as the Rabi oscillations are now reaching coherence times of the order of the microseconds [27,28] and even of the dozen microseconds [29] (in the example of CaWO4:Gd) we expect that the use of GQOAB will not be limited by decoherence effects.

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