Spin tunneling in magnetic molecules: Quantitative estimates for Fe8 clusters

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Abstract

Spin tunneling in the particular case of the magnetic molecular cluster octanuclear iron(III), Fe8, is treated by an effective Hamiltonian that allows for an angle-based description of the process. The presence of an external magnetic field along the easy axis is also taken into account in this description. Analytic expressions for the energy levels and barriers are obtained from a harmonic approximation of the potential function which give results in good agreement with the experimental results. The energy splittings due to spin tunneling is treated in an adapted WKB approach and it is shown that the present description can give results to a reliable degree of accuracy.

Key words: Spin tunneling, Fe8 cluster

1 Introduction

In the last decades, tunneling in mesoscopic systems has attracted a great deal of interest [1,2,3]. This physical process corresponds in a standard quantum description to the tunneling of the collective degree of freedom associated with the angular momentum direction through a potential barrier separating two minima of an effective potential associated with the spatial orientation. Besides the interest in this new class of processes due to the wide domain of investigations and possible applications, it also draws attention because it can shed light on several aspects of our understanding of the transition from quantum to classical physics [3]. From the theoretical point of view, spin tunneling has been treated mainly by the use of a WKB method adapted to

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spin systems [4, 5, 6], by using Feynman’s path integral treatment of quantum mechanics [7, 8], and also by using $su(2)$ coherent states [9] in order to establish a correspondence between the spectrum of the spin system with the energy levels of a particle moving in an effective potential [10].

In more recent years a renewed interest in the study of spin tunneling has emerged mainly motivated by the discovery of magnetic molecules that can stand for a decisive testing ground for the basic ideas proposed before. From the experimental point of view, among the several advantages the magnetic clusters present, it has been recognized that they are well defined crystalline materials with the same shape, size and orientation. Furthermore, the determination of their fundamental parameters which play an essential role in the study of the dynamics of the magnetization, such as the spin of the cluster, its magnetic anisotropy, the intra- and inter-clusters interactions can be accurately carried out. In this connection, the discovery of the Mn$_{12}$ac-manganese acetate [11] paved the way for a series of works discussing the possibility of identifying a spin tunneling process [12, 13, 14, 15, 16, 17] at sufficiently low temperatures such that the pure quantum contributions become important. Due to the great uniaxial magnetic anisotropy of the cluster, the first approximation phenomenological Hamiltonian for describing this molecule is

$$H = -D J_z^2,$$

where $D/k_B \approx 0.7 K$ and $k_B$ is the Boltzmann constant. Since it is immediately seen that it does not contain terms responsible for transitions between the energy levels, this Hamiltonian is not sufficient to afford for a sound starting point for the desired study of the spin tunneling process if only pure quantum contributions are to be considered. Of course the thermally-assisted transitions can always be taken into account and their role in the spin tunneling has also been emphasized as an important component in the whole process [16]. Along this line sophisticated theoretical approaches have been put forth so as to treat these important processes when temperature plays a dominant role [18, 19]. In this way, in what concerns this molecule, the introduction of additional terms in the Hamiltonian has already been discussed in the literature [20], where the symmetry of the cluster only allows a small transverse anisotropy of fourth-order. A more complete Hamiltonian is then

$$H = -D J_z^2 + B J_z^4 + C \left( J_x^4 + J_y^4 \right),$$

where $B/k_B = -1.1 \times 10^{-3} K$ and $C/k_B = \pm 3 \times 10^{-5} K$.

The discovery of the Fe$_8$ magnetic cluster (octanuclear iron cluster) [21] pointed to a new scenario in the spin tunneling discussions since its proposed
basic phenomenological Hamiltonian,

\[ H = -D J_z^2 + \frac{E}{2} \left(J_x^2 + J_y^2\right), \]

with \( D/k_B = 0.275 \text{ K} \) and \( E/k_B = 0.046 \text{ K} \), already can account for a quantum description whose results can be compared with the experimental ones. In fact the quantum effects in the dynamics of the magnetization can be better investigated in this magnetic cluster mainly because the parameters characterizing it were carefully measured, and also because the presence of the important transverse term is clearly seem to induce tunneling effects. Also, it has been reported that this cluster has an experimentally observed barrier of ca. 22−24 K, and that below 0.35 Kelvin the relaxation of magnetization becomes temperature independent \[22,23\], thus suggesting that, under this circumstance, this temperature corresponds to the crossover to the regime where quantum effects dominate the spin tunneling processes. Furthermore, it was also verified that when an external magnetic field is applied along the easy axis of the Fe8 cluster the hysteresis loops present well-defined steps at integer multiples of \( \Delta H_{\parallel} \approx 0.22 T \)[22,23,24]; this also suggests, in the same way that occurs in the Mn12ac cluster, that an energy matching of states then takes place \[22,23,24\]. In this perspective, the Fe8 magnetic cluster is a good candidate to be studied in order to verify the importance of the pure quantum contributions to the spin tunneling when temperature effects can be neglected.

In a previous paper \[25\] one of the authors has presented an angle-based approach which allows an effective Hamiltonian to be obtained that can be reliably used in the description of general quantum spin tunneling processes, and in particular it was also shown that it can be used to describe the magnetic molecules, for instance the Fe8 cluster. In this case, the numerical diagonalization of the corresponding effective Hamiltonian associated with the Fe8 cluster leads us to get the energy spectrum and the ground state energy barrier in a direct way. Since the value of the calculated energy barrier is in good agreement with the experimental one, we want now to start from the proposed effective Hamiltonian to get other results related to measurable properties of that magnetic molecule. In this connection, we will be interested mainly in the ground state and barrier energies, as well as in the energy splitting that is directly associated with the spin tunneling. However, instead of directly obtaining those results by a numerical calculation, here we intend to show that some approximations based on well established quantum grounds can be used that allow us to express them in analytic form. We then propose a direct use of an adapted version of the WKB approximation \[26\] for the calculation of the energy splitting of low-lying energy levels, as well as we can also verify that the energy splitting can be obtained for energy levels at the top of the potential barrier if, in this case, use is made of the Kemble, Hill-Wheeler, and
Miller-Good expression [27,28,29] for the barrier tunneling probability.

This paper is organized as follows. In section 2 we present our previous results concerning the effective Hamiltonian related to the magnetic molecules and some basic assumptions. In section 3 we apply these assumptions to the case of the Fe8 magnetic cluster, and we compare the results obtained with the ones coming from the direct diagonalization of the phenomenological starting Hamiltonian of the model. The effects of the presence of an external magnetic field oriented parallel to the easy axis on the energy splitting is also discussed. Finally, section 4 contains our final comments and conclusions.

2 Effective Hamiltonians for spin tunneling

The starting point of the proposed approach, as discussed in Refs. [25,30,31], is the introduction of a quantum phenomenological Hamiltonian describing the spin system, written in terms of angular momentum operators obeying the standard commutation relations, being that its form reflects the structural symmetries of the system. It may also contain terms taking into account external applied magnetic fields. The degree of freedom that undergoes tunneling is considered a particular collective manifestation of the system, and it is assumed to be the only relevant one. At the same time, the temperature of the system is assumed so conveniently low that possible related thermally assisted processes are not taken into account so that only quantum effects are considered. For instance, the general quantum Hamiltonian

$$H = AH_{||}J_z - DJ_z^2 + \frac{E}{2} \left(J_z^2 + J_2^2\right)$$

(1)

can be used to study some systems of interest. In particular, for $A = g\mu_B$ this Hamiltonian describes the octanuclear iron cluster, Fe8, in the presence of an external magnetic field along the z axis (easy axis); clearly, $A = 0$ denotes the absence of an external field. This spin system has a $j = S = 10$ ground state and a suggested dominant quantum spin tunneling below 0.35 $K$; furthermore, $D/k_B = 0.275 K$ and $E/k_B = 0.046 K$ [22,24]. On the other hand, from a pure algebraic model point of view, it is interesting to see that the Lipkin quasi-spin model Hamiltonian [32], of wide use in many-body physics, can also be obtained by just considering $D = 0$, being that the interest in this model resides in the fact that it stands for a valuable testing ground for checking the validity of approximations in treating collective degrees of freedom.

Now, it has been already shown [25,31] that a new approximate Hamiltonian – written in terms of an angle variable – can be extracted from (1) which allows for a good description of spin systems when $2S \gtrsim 10$, where $S$ is the
total spin value of the physical system. In its general form, the new effective Hamiltonian for such a system is written as

\[ H = -\frac{1}{2} \frac{d}{d\phi} \frac{1}{M(\phi)} \frac{d}{d\phi} + V(\phi), \]

where

\[ V(\phi) = V_1 \cos^2 \phi + V_2 H_\parallel \cos \phi + V_3 \] (2)

is the potential energy function with \( V_1 = -(D - E) S (S + 1), \)
\( V_2 = -A \sqrt{S(S + 1)} \) and \( V_3 = -ES (S + 1). \) The effective “inertia” associated with the spin system is given by

\[ \frac{1}{M(\phi)} = M_1 \cos^2 \phi + M_2 H_\parallel \cos \phi + M_3, \] (3)

where \( M_1 = 2(D - E), M_2 = A/S \) and \( M_3 = 4E. \) Figure 1 depicts the potential and effective mass functions when \( A = 0 \) for the \( Fe_8 \) cluster. It is clearly seen two deep minima in the potential, characterizing the trapping wells, as well as the maxima. At the same time, we observe that the effective mass function presents a similar behaviour, being that the minima of both functions occur at \( \phi = 0 \) and \( \pi. \)

![Fig. 1. The potential and the effective mass functions for the \( Fe_8 \) cluster in the absence of an external magnetic field in the direction of the easy axis, \( H_\parallel = 0. \)]

The corresponding Schrödinger equation associated with the \( Fe_8 \) molecule

\[ H \psi_k(\phi) = \mathcal{E}_k \psi_k(\phi) \] (4)

can then be directly solved by just performing a Fourier analysis so that the resulting wave function

\[ \psi_k(\phi) = \sum_n c_{kn} e^{in\phi} \]
and energy eigenvalues are readily obtained. A test can then be immediately carried out by comparing the eigenvalues \( \mathcal{E}_k \) coming from the solutions of Eq. (1) with those obtained by diagonalizing Eq. (1) within the set of eigenstates \( \{|Sm\rangle\} \) of the \( J_z \) operator – the results coming from the diagonalisation of Eq. (1) will be hereafter called the reference values. As already verified in the past, the spectra in both cases are in good agreement for \( 2S \gtrsim 10 \) \cite{25}, being the deviation of the order of 0.5% for the ground state energy and 14.7% for the energy splitting of the lowest doublet. At the same time, we can also estimate the height of the potential barrier: since we have obtained numerically \( \mathcal{E}_{gs} \simeq -27.6447 \, K \) from Eq. (4), and verified that the top of the potential barrier is given by

\[
V_{\text{max}}(\phi) = -ES(S+1),
\]

then

\[
h_b = -ES(S+1) - \mathcal{E}_{gs}
\]

measures the ground state energy barrier that gives \( h_b \simeq 22.58 \, K \) which is only 1.7% higher than the experimental result, namely, 22.2 \( K \), as presented in \cite{22}.

These results then allow us to apply our approach in the description of spin tunneling in a reliable way. Here, however, instead of focusing our attention on the numerical procedures and results directly obtained from Eq. (4), we want to show that some assumptions based on well-established quantum grounds can be taken for granted so that we can get analytic expressions for the ground state and barrier energy, as well as the energy splitting associated with spin tunneling.

### 3 Application

#### 3.1 Ground state and barrier energies \( (H_\parallel = 0) \)

Let us first consider the case when no external paralel magnetic field is applied, i.e., \( A = 0 \). In this case we see that a simple approximate analytic expression of the ground state energy barrier for the Fe8 cluster can be obtained from the proposed effective Hamiltonian, Eqs. (2) and (3). To this end, we first take into account the fact that the potential function presents deep minima at \( \phi = 0 \) and \( \pi \), and maxima at \( \phi = \pi/2 \) and \( 3\pi/2 \), respectively, so that

\[
\mathcal{E}_{\text{min}} = V(\phi = 0) = -DS(S+1) = -30.25 \, K.
\]
We can now consider that the lowest part of the spectrum can be well described by a harmonic approximation so that the ground state energy can be written as \( \mathcal{E}_{gs} \simeq \mathcal{E}_{\text{min}} + \omega/2 \). To obtain an approximate expression for \( \omega \) we have to consider the potential minimum at \( \phi_{\text{min}} = 0 \), and verify that the effective mass can also be taken at that angle as a good approximation in order to write

\[
M (\phi = \phi_{\text{min}}) \omega^2 = \left. \frac{d^2V(\phi)}{d\phi^2} \right|_{\phi_{\text{min}}},
\]

from which we obtain

\[
\omega = 2 \sqrt{(D^2 - E^2) S (S + 1)}.
\]

It is then direct to see that the ground state energy in this approximation is

\[
\mathcal{E}_{gs} = -DS (S + 1) + \sqrt{(D^2 - E^2) S (S + 1)} \simeq -27.41 \, K,
\]

and, recalling that \( h_b = -ES(S + 1) - \mathcal{E}_{gs} \), the barrier energy is written as

\[
h_b = (D - E) S (S + 1) - \sqrt{(D^2 - E^2) S (S + 1)} \simeq 22.35 \, K.
\]

The deviation from the reference value for the ground state energy is then of the order of 0.5% while for the barrier height it is 0.7%. It is interesting to verify that the analytic expression for the barrier height can give a better approximation than the numerical calculations do. Furthermore, since we are considering two separate potentials, tunneling is not taken into account, but we still get good approximations to those quantities because the change in energy due to tunneling is several orders of magnitude smaller than the energy values of the spin states.

### 3.2 Energy splitting \( (H_\parallel = 0) \)

In what concerns the energy splitting associated with tunneling, let us assume from the outset the validity of the main ideas supporting the WKB approximation for the present case\[\text{[4,5,6]}\]. We will consider this without a formal demonstration, but in what follows we intend to show that it is a sound starting working background. From this standpoint, if we take advantage of the symmetric character of both the potential function and effective “inertia” when \( A = 0 \), we may go one step further and consider the WKB energy
splitting expression [26]

\[ \Delta E \simeq \frac{\omega_b}{\pi} \exp \left[ -\sqrt{2M} \int_{\phi_i}^{\phi_s} \sqrt{V(\phi) - E} \, d\phi \right] , \]  

(5)

where \( \omega_b \) is the frequency associated with the minimum of the symmetric potential and \( \phi_{i,s} \) are the classical turning points respectively. It is important to stress that this approximation is tailored to be used in calculating splittings in energy levels far from the top of the potential barrier. Now, from the operational point of view we have to observe that the mass \( M \) appearing in Eq. (5) is constant, whereas we have an angle-dependent effective mass function instead. Therefore, if we want to use the WKB approximation, we have to introduce a conveniently chosen averaging procedure in such a way that the effective mass is then substituted by an appropriate constant value.

In order to implement all the approximations let us first consider that we may use the approximate average value for the constant mass

\[ M = \frac{\int_{\phi_i}^{\phi_s} M(\phi) \, d\phi}{\int_{\phi_i}^{\phi_s} d\phi} , \]  

(6)

in the barrier region while, on the other hand, we will assume the frequency at the minimum of the potential as before. Based on these results, we will use the proposed approximations for the calculation of the energy splittings associated with tunneling occuring in the energy spectrum of the Fe8 cluster.

First let us consider the lowest energy doublet since we are considering that the temperature regime is such that the quantum effects dominate, i.e., the temperatures are below the cross-over value. Since the energy levels are far from the barrier top, we will directly use the WKB expression, Eq. (5), where we take explicitly

\[ \omega_b = 2\sqrt{(D^2 - E^2)S(S + 1)} \]

at the \( \phi = 0 \) minimum as before, and we assume expression (6) to be valid here too. With these considerations we get \( \Delta E \simeq 8.9 \times 10^{-10}K \), while the reference value obtained is \( \Delta E_{\text{ref}} \simeq 6.8 \times 10^{-10}K \), thus showing that, in spite of the introduced approximations, the WKB approximation is a useful expression to estimate the energy splitting for the Fe8 cluster. It is important to stress that the numerical precision plays an essential role in the study of the energy splitting associated with tunneling. However, instead of focusing exclusively on our results, although they were obtained from double precision calculations, we will study their deviations from the reference values since they measure the
quality of our approach. Now, considering that the next two energy doublets are also far from the barrier top, we can go one step further and apply the WKB approximation to them. Using the expressions for $\omega_b$ and $M$ we get the results for the deviations

| Doublets | Diagonalization method | WKB approximation |
|----------|------------------------|-------------------|
| first    | 31%                    | 14.7%             |
| second   | 8%                     | 9%                |
| third    | 5%                     | 8%                |

It is clearly seen that the obtained deviations are higher in the lowest energy levels due to the precision of the calculations and approximations involved.

On the other hand, if we also consider that the higher energy states can be of importance for the transitions of the magnetic moment, we can directly use the Kemble [27], Hill-Wheeler [28], and Miller-Good [29] (KHW/MG) expression for the barrier penetrability to describe the energy splitting occurring in those states that are just at the top of the barrier, that is,

$$ P(\mathcal{E}) = \frac{1}{1 + \exp\left[\frac{\omega_t}{\pi} (V_0 - \mathcal{E})\right]} $$

where $\omega_t$ denotes the frequency associated with the concavity at the top of the barrier, and $V_0 = V(\phi = \phi_{\text{top}})$. It is important to see that $\mathcal{E} = V_0$ implies in $P = 0.5$ instead of the usual WKB value $P = 1.0$, thus assuring us that the KHW/MG expression is a better approximation for this particular kind of situation.

Now, a first approximation for $\omega_t$ can be proposed as in the previous case, i.e.,

$$ \omega_t = \sqrt{\frac{1}{M(\phi = \phi_{\text{top}})} \left| \frac{d^2V(\phi)}{d\phi^2}\right|_{\phi = \phi_{\text{top}}}}. $$

Since the barrier presents a maximum at $\phi = \pi/2$ where $V_0 = -5.06 K$, as already seen, and the reference results show that there is a doublet in this energy region, then we are allowed, in the same way we did before, to use the KHW/MG approximation to estimate the corresponding energy splitting. Thus, at the barrier top the frequency is given by

$$ \omega_t = 2\sqrt{2E(D - E)S(S + 1)}, $$
and the effective mass at the maximum is
\[ M \left( \phi = \frac{\pi}{2} \right) = \frac{1}{4E} , \]

so that
\[ \Delta E \simeq \frac{2\sqrt{(D^2 - E^2)S(S+1)}}{\pi} \left\{ 1 + \exp \left[ \frac{\pi (|E| - ES(S+1))}{\sqrt{2E(D - E)S(S+1)}} \right] \right\}^{-1} \]
is an estimate to the energy splitting at the barrier top. In this way, for the energy levels at \(|\mathcal{E}| \simeq 5.34 \, K\) we get \(\Delta \mathcal{E} \simeq 0.65 \, K\), being the reference result \(\Delta \mathcal{E}_{ref} \simeq 0.72 \, K\). These results indicate that the KHW/MG approximation can be trustfully used in estimating the energy splitting at the top of the Fe8 cluster energy barrier. However, its use for the next lower doublet already presents a great deviation from the reference value. For those doublets close to (but not at) the barrier top, a parabolic approximation is much more adequate. In this case, the energy splitting expression takes the form
\[ \Delta \mathcal{E}_{par} \simeq \frac{\omega_p}{\pi} \exp \left[ -\frac{\pi (|\mathcal{E}| - V_0)}{2\sqrt{2Eh_p}} \right] , \]

where

\[ h_p = V(\phi_{max}) - V(\phi_{min}) \]
is the total potential energy barrier depth. Applying this expression to the levels near \(|\mathcal{E}| \simeq 7.5 \, K\) we get \(\Delta \mathcal{E}_{par} \simeq 0.14 \, K\), whereas \(\Delta \mathcal{E}_{ref} \simeq 0.13 \, K\).

### 3.3 Low-lying Energies and Energy splitting (\(H_{||} \neq 0\))

We can discuss now the role of an applied external magnetic field along the \(z\) direction (easy axis) on the Fe8 cluster. In this case, if such an external magnetic field is applied we start from Eqs. (2) and (3) with \(A = g\mu_B\), with fixed \(g = 2\).

It is immediate to see that the presence of the magnetic field does not change the positions of the potential extrema at \(\phi = 0\) and \(\pi\), but it introduces a shift in energy at these points so that the difference in the height between the two minima will be \((H_{||} > 0)\)
\[ V(\phi = \pi) - V(\phi = 0) = 2\sqrt{S(S+1)g\mu_BH_{||}} . \]
This means that for some particular values of $H_{\parallel}$ a degeneracy in the energy spectrum will occur such that the state with quantum number, for instance, $n$, will match its energy with that of the state with $-n + k$, as it is indeed expected. Figure 2 exhibits the potential and effective mass for some values of $H_{\parallel}$. The pictures depict the effects of the external field on the potential and effective mass functions, both for a weak field (that produces the first matching) as well as for a value near that producing an diverging behaviour of the effective mass. Let us first discuss weak external magnetic $H_{\parallel}$ fields, below the first matching value. Following the same procedure developed above, where use was made of a harmonic approximation, we see that the energy of the ground state in the deeper/shallower potential well is given by

$$\mathcal{E}_{gs}(H_{\parallel}) \simeq \mathcal{E}_{gs}(H_{\parallel} = 0) \pm$$

$$\left\{ \frac{V_2}{2} \sqrt{-2V_1(M_1 + M_3)} \left[ \frac{V_2}{4V_1} + \frac{M_2}{2(M_1 + M_3)} \right] \right\} H_{\parallel}.$$

Fig. 2. The potential and the effective mass functions for the Fe8 cluster for some values of the external magnetic field in the direction of the easy axis. In case (a) the magnetic field corresponds to that of the first matching of the energy levels, while, in case (b), the magnetic field is close to the saturation value. It is to be noted that the effective mass in case (b) exhibits values already showing the trend to divergence that occurs when the magnetic field attains the saturation value.

It is important to see that in this approximation, since we are considering two separate potentials, there is no tunneling at all, so that the two levels coincide for $H_{\parallel} = 0$. Therefore, the energy gap as a function of the external magnetic
field $H_\parallel$ can be directly obtained, and reads

$$\Delta \mathcal{E} (H_\parallel) \simeq \Delta \mathcal{E} (H_\parallel = 0) +$$

$$\left\{ 2V_2 + \sqrt{-2V_1 (M_1 + M_3)} \left[ \frac{V_2}{4V_1} + \frac{M_2}{2(M_1 + M_3)} \right] \right\} H_\parallel$$

(7)

if we also take into account now the tunneling. This result can be immediately compared with the reference values obtained from Eq. (11). Our result for the coefficient of the linear dependence is 26.79 $KT^{-1}$, while the reference result, which also exhibits a linear dependence, is 26.85 $KT^{-1}$, thus showing a good agreement with a deviation of 0.22%.

In what concerns specifically the discussion of the change of the energy splitting associated with the tunneling due to the presence of an external magnetic field of this kind, we have to point that a new expression, still based on the WKB approximation, must be introduced because of the field-induced asymmetry of the potential and effective mass (see figure 2). It can be shown that the new expression is given by

$$\Delta \mathcal{E} (H_\parallel) \simeq \frac{\sqrt{\omega_1 \omega_2}}{\pi} \exp \left( -\sqrt{2M} \int_{\phi_i}^{\phi_s} \sqrt{V_1 \cos^2 \phi + V_2 H_\parallel \cos \phi + |\mathcal{E}| + V_3} \, d\phi \right),$$

where $\omega_{1,2} (H_\parallel)$ are the frequencies at the minima of the two potential wells and the effective mass can be treated in the same way as before. If we perform a harmonic approximation for both $\omega_1$ and $\omega_2$ we can readily conclude that related factor is nearly constant for weak $H_\parallel$. In the same way, an analysis of the behaviour of the effective mass as a function of small $H_\parallel$ also shows that it is also almost constant. In fact the dominant contribution comes from the exponential factor – the tunneling probability factor – which can be given in an approximated form as

$$\exp \left[ -\sqrt{2M} \int_{\phi_i}^{\phi_s} \sqrt{V_1 \cos^2 \phi + V_2 H_\parallel \cos \phi + |\mathcal{E}| + V_3} \, d\phi \right] \simeq$$

$$\exp \left[ \left( -\sqrt{2M} \int_{\phi_i}^{\phi_s} \sqrt{V_1 \cos^2 \phi + |\mathcal{E}| + V_3} \, d\phi \right) \left( 1 + \chi H_\parallel^2 \right) \right],$$

(8)

where $\chi$ is a constant and the integral in the rhs corresponds to the tunneling probability factor in the absence of the magnetic field. Therefore we see that the total energy separation of doublets tends to increase linearly (as can be
seen from Eq. (7) with small $H_\parallel$ – thus removing degeneracies that would occur when $H_\parallel = 0$ if no tunneling is considered – because of the asymmetry of the potential wells, at the same time that the tunneling probability factor tends to decrease with small $H_\parallel$ mainly due to the widening of the barrier to be tunneled, Eq. (8).

Another interesting result that can be still obtained with the harmonic approximations is the numerical value of the external magnetic field that result in the matching of the energy levels in the two separate potential wells. In fact, by imposing that the first excited state in the deeper potential must match the lowest energy level in the shallower one, we get an expression that gives that particular value of the external magnetic field. Therefore, since we already know the expressions for $E_{\text{min}}$ and $\omega$, we write

$$E_{\text{deep}}(H_\parallel) \simeq E_{\text{min}}(H_\parallel) + \frac{3}{2} \omega(H_\parallel)$$

and

$$E_{\text{shallow}}(H_\parallel) \simeq E_{\text{min}}(H_\parallel) + \frac{1}{2} \omega(H_\parallel).$$

Now, imposing that the two levels match their energies, we get

$$H_0^\parallel = \frac{-\sqrt{-2V_1(M_1 + M_3)}}{2 \left\{ \sqrt{-2V_1(M_1 + M_3)} \left[ \frac{V_2}{4V_1} + \frac{M_2}{2(M_1 + M_3)} \right] + V_2 \right\}}.$$

The estimated magnitude of the field is then $H_0^\parallel \approx 0.2239 \, T$ which is in good agreement with the experimental value of 0.22 T as presented in [22,24].

From another perspective, it is interesting to observe that the particular value of the magnetic field intensity $H_0$, whose multiples $kH_0$ lead to the matching of the energy levels, can be obtained without any reference to the harmonic approximation at all. In fact, we can also extract an expression for that particular value of the magnetic field from an analysis of the effective mass expression. Realizing that the presence of zeroes in the function $I(\phi) = 1/M(\phi)$ (infinites of the effective mass) indicates that tunneling cannot occur, we look for the expression of the strength of $H_\parallel$ beyond which tunneling will not take place. A direct calculation shows that the limit - the saturation value - is given by

$$H_{\parallel,\text{lim}} = \frac{4Sk_B}{g\mu_B} \sqrt{2E(D - E)} \simeq 4.32 \, T \quad (9)$$
so that

\[ H_\parallel^0 = \frac{H_\parallel^{\text{lim}}}{2S} = \frac{2k_B}{g\mu_B} \sqrt{2E(D - E)} \simeq 0.216 \, T \]  \tag{10}

for \( g = 2 \). This result is also in good agreement with the experimental value.

It is important to verify that for this value of the external parallel magnetic field the original minimum at \( \phi = \pi \) and the maxima at \( \phi = \pi/2 \) and \( 3\pi/2 \) have turned into a single maximum of the potential function, while the only surviving minimum is the one at \( \phi = 0 \) \((= 2\pi)\). This means that, in this particular situation, there is only one direction along which the spin can be directed at.

4 Conclusions

Based on a quantum angle-based description of spin tunneling developed before and briefly reviewed here, in this paper we addressed the problem of obtaining quantitative results for the \( \text{Fe}_8 \) cluster in what concerns the barrier, low-lying energy doublets and their energy splittings associated with spin tunneling. Although numerical calculations are direct, and the results are in very good agreement with those coming from the diagonalization of the starting phenomenological Hamiltonian – written in terms of the angular momentum operators –, we have shown that analytic expressions can be obtained that allow us to see how the quantities of interest of the \( \text{Fe}_8 \) cluster depend on its anisotropy constants. This construction can be seen to be very simple in the case of no external magnetic field, when a harmonic approximation for the potential energy function around its minimum, together with the introduction of the corresponding frequency at that point, is proposed. Analytic expressions for the ground state and barrier energies are then directly written. In what regards the energy splitting associated with the spin tunneling in this case, we have shown that an adapted WKB expression for symmetric potentials can be directly used and that the results are of the same order of those coming from the numerical calculations. Thus, we verify that the WKB expression can be reliably used in the description of tunneling occurring in the \( \text{Fe}_8 \) cluster.

We also have shown that we can still obtain the relevant results if an external magnetic field parallel to the easy axis is applied. In this case, besides the expressions for the low-lying energy spectrum, we also obtained an analytic expression for the rule governing the spacing between the energy doublets as a function of the intensity of the magnetic field. The linear dependence thus obtained can be seen to come from the asymmetry of the potentials induced by the external magnetic field. It is also clear that this effect is several orders of magnitude higher than the energy splitting associated with tunneling. This
quantum effect, by its turn, can also be described in the case of a slightly asymmetric potential through an extended WKB expression, and it was shown that the energy splitting increases with the intensity of the external magnetic field, as it should be, mainly due to the widening of the potential barrier.

Experimentally, the value of the external magnetic field whose multiples produce well-defined steps in the hysteresis loops was determined, and it was also suggested that such effect corresponds to the energy matching of states in the two wells of an energy barrier. In the present quantum angle-based approach, we have shown that this is a consistent picture of the process, and that the experimental value $H_0 = 0.22 \, T$ is obtained through a simple approximation proposed to describe the low-lying energy levels of the spectrum of the Fe8 cluster. In fact, we also have shown that the result thus obtained is not fortuitous; regarding the expression for the effective mass as another valuable source of information about the tunneling process, we obtained almost the same value for $H_0$ by simply looking for the intensity of the field at which the effective mass diverges, thus blocking the tunneling process.

The agreement between the results presented in this paper and the experimental data concerning the Fe8 cluster properties seems to corroborate the usefulness of our quantum angle-based proposed approach indicating that it can be reliably used in the description of tunneling of spin systems.

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