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Magnetic tunneling told to ignorants by two ignorants

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Abstract. Magnetic tunneling of a large spin subject to the Hamiltonian $\mathcal{H} = -DS_z^2 + BS_x^2 - g\mu_\mathrm{B}\mathbf{H}\cdot\mathbf{S}$ is investigated by elementary methods for weak fields $\mathbf{H}$. In zero field ($\mathbf{H} = 0$) the tunnel frequency in the ground state is found to be equal to $Ds[1 + (2D/B) + 2\sqrt{(1 + D/B)D/B}]^{-s}$ multiplied by a quantity whose variation with s is slower than exponential. This result coincides with that of path integral methods [16]. For the values of the longitudinal field which allow tunneling, the tunnel frequency ω_T is shown to vanish when $H_y = 0$ for certain "diabolic" values of $g\mu_\mathrm{B}H_x/\sqrt{B(D+B)}$, in qualitative agreement with experiments by Wernsdorfer and Sessoli. The particular case $H_z = 0$ was already obtained by Garg by means of path integrals. The diabolic values of $g\mu_\mathrm{B}H_x/\sqrt{B(D+B)}$ are in agreement with numerical results but, as already noticed by Wernsdorfer and Sessoli, they disagree with the experimental ones. This may be an effect of higher order anisotropy terms, which is briefly addressed in the conclusion.

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1 Introduction

Tunneling in magnetic systems is the subject of a considerable literature, especially because of the discovery in the eighties of high spin molecular groups which form good crystals. Those spins are just large enough to have a ground state splitting which is sufficiently small to deserve the name of tunnel splitting, but is yet observable in a time reasonably short with respect to the duration of a Ph.D. thesis.

The best example is presently the compound $[(\mathrm{tacn})_8\mathrm{Fe}_8\mathrm{O}_8(\mathrm{OH})_8]^{8+}$ (where tacn is 1-4-7-triazacyclononane), where tunneling is observable at temperatures $T < 0.4$ K [1–3]. In this material, hereafter called "Fe_8", the molecular groups can be with a fairly good approximation treated as spins of modulus $s = 10$ in an anisotropy field. The Hamiltonian resulting from this anisotropy and an external magnetic field H is

$$\mathcal{H} = -DS_z^2 + BS_x^2 - g\mu_\mathrm{B}H_xS_x - g\mu_\mathrm{B}H_yS_y - g\mu_\mathrm{B}H_zS_z. \quad (1)$$

We are interested in the Ising case, $D > 0$, $B > 0$ which corresponds to Fe_8. The spin s will be assumed to be integer and even except if a different hypothesis is specified. Extension to odd spins would be straightforward. The field is assumed to be weak. In particular, the longitudinal component H_z satisfies the condition

$$|H_z| \ll Ds \quad (2)$$

so that the low energy regions $S_z \approx -s$ and $S_z \approx s$ are separated by a potential barrier of the order of Ds^2, which ensures a long relaxation time. For most of the values of H_z, the low energy eigenstates of (1) are localized in the region $S_z < 0$ or in the region $S_z > 0$. Such states will be called negative-localized and positive-localized, respectively. For particular values of H_z, they are delocalized. An initially negative-localized spin subject to Hamiltonian (1) oscillates between the two wells $S_z \approx -s$ and $S_z \approx s$ with the "tunnel frequency" ω_T. The calculation of ω_T can easily be performed numerically if the spin is not too large. For large s, say $s > 40$ if $B/D \approx 1$, it becomes difficult. In the present work, the limit $s \gg 1$ is studied by analytic methods.

For $H_z = 0$, $2\hbar\omega_\mathrm{T}$ can also be interpreted as the "tunnel splitting" of the "ground doublet", *i.e.* between the delocalized ground state of (1) and the lowest excited state. A way to measure ω_T is to initially apply a strongly negative longitudinal field $H_z(t)$, so that the ground state is negative-localized. Then, $H_z(t)$ is slowly raised until it becomes slightly positive and the change in magnetization ΔM is measured. At low temperature, demagnetization occurs only when tunneling is possible, *i.e.* for $H_z \approx 0$,

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and ΔM is directly related to $\omega_{\rm T}$ which can thus be determined [4].

Tunneling can also occur for positive values of H_z (see formula (5) below). The tunnel frequency can be measured in a similar way except that the longitudinal field is abruptly switched from a strongly negative value to a positive one, which is slightly smaller than that which permits tunneling. The spin is then in the negative-localized state of lowest energy. This state will be called the "pseudo-ground state". As $H_z(t)$ is slowly raised, tunneling becomes possible between this pseudo-ground state and a positive-localized state. When delocalization is greater (*i.e.* 50%), the distance between levels is minimal and equal to the tunnel splitting $2\hbar\omega_{\rm T}$ which we want to calculate.

A particularly interesting feature of Fe_8 is the recent experimental observation [4] that, for $H_y = H_z = 0$ and for particular values of H_z, in particular $H_z = 0$, the tunnel frequency has minima when the transverse field H_x is varied. This is in agreement with theoretical predictions [5–8] that the tunnel splitting vanishes for certain values of H_x. This exact degeneracy is so exceptional [9] that it is sometimes qualified [10] "diabolic". This property will be studied in Section 7 and extended to certain nonvanishing values of H_z, in agreement with experiment [4].

In practice, a spin is also subject to hyperfine interactions, dipole-dipole interactions and spin-phonon interactions [11–13]. As a result, the minima of $\omega_{\rm T}$ do not vanish. However, their location is probably not strongly affected [13]. Since the value of $\omega_{\rm T}$ far from the minima is probably not strongly modified by the interaction with the rest of the world, this interaction will be ignored in the present work.

The fields which allow tunneling between the pseudo-ground state and a state which roughly corresponds to $S_z = m_0 > 0$ can be obtained as follows if the coefficients B, $g\mu_{\rm B}H_x$, $g\mu_{\rm B}H_y$, responsible for tunneling, are small in comparison with D. Then the approximate energies of the two tunneling states are

$$E^0_{-s} = -Ds^2 + g\mu_{\rm B}H_z s \tag{3}$$

and

$$E^0_{m_0} = -Dm_0^2 - g\mu_{\rm B}H_z m_0. \tag{4}$$

The field H_z which allows tunneling between the pseudo-ground state and a state with $S_z \approx m_0$ is given by the "level-crossing" condition $E^0_{-s} = E^0_{m_0}$ or

$$g\mu_{\rm B}H_z = D(s - m_0). \tag{5}$$

Relations (3–5) also hold with a good approximation if B, $g\mu_{\rm B}H_x$, $g\mu_{\rm B}H_y$ are not very small with respect to D, provided s is large, so that classical mechanics are almost valid and S_x and S_y are small in the ground state and in the pseudo-ground state.

Although a spin 10 can easily be treated numerically as seen in Section 7.3, it is of interest to rely on analytic treatments which can be done of course for very small spins ($s = 1/2$, $s = 1$...) but also for large spins.

Large spins are often treated by path integral methods [14–18] which require elaborate mathematical techniques (coherent spin states, Berry phase, instantons, ...). As a typical example, the "Wess-Zumino term", which introduces the Berry phase in the Lagrangian of a spin, is not required in the elementary quantum theory although it is "crucial to describe the Kramers degeneracy" [16] when one wants to apply the path integral method. In other words, it is a trick to avoid missing Kramers' symmetry. These "freely invented ideas and concepts", these "creations of the human mind" [21], are, as Einstein said, essential ingredients of theoretical physics. However, it may be of interest to try (as much as possible) to avoid such artificial concepts which involve a long conceptual detour before contact with the physical reality is reached. We hope that ignorant readers will be as happy to avoid this detour, as the ignorant authors are.

In the present work, we apply elementary manipulations to the wave function. This approach can be compared to the WKB theory of van Hemmen and Sütö [19,20] (who did not derive diabolic points) and to Garg's [22] recent article in which, independently of the present work, "diabolic points" are addressed by means of the "discrete WKB method" [23,24]. Our treatment is more self-contained than Garg's one, and it does not use the $\hbar \to 0$ limit implied in the WKB method.

2 The Schrödinger equation

It is convenient to introduce the eigenvectors $|m\rangle$ of S_z defined by $S_z|m\rangle = m|m\rangle$, and to write the eigenvectors of $\mathcal{H}$ as

$$|E\rangle = \sum_{m=-s}^{s} \mu_m(E)|m\rangle \cdot \tag{6}$$

Inserting (6) into (1) one obtains

$$\sum_{m'} \langle m|\mathcal{H}|m'\rangle \mu_{m'} = E\mu_m \tag{7}$$

where the summation over m' is from $m-2$ to $m+2$ except for $m = \pm s$ and $m = \pm(s-1)$, with obvious modifications in these cases.

Relation (7) can be regarded as a Schrödinger equation for the "wave function" μ_m which depends on the one-dimensional, discrete variable m.

All eigenvalues E are real since the Hamiltonian $\mathcal{H}$ is Hermitian. One can choose basis vectors $|m\rangle$ such that the matrix elements

$$\begin{aligned}\langle m|S^-|m+1\rangle = \langle m+1|S^+|m\rangle &= \sqrt{s(s+1) - m(m+1)} \\ &= \sqrt{(s-m)(s+m+1)}\end{aligned} \tag{8}$$

are real.

Using relations $S_x = (S^+ + S^-)/2$ and $S_y = -\mathrm{i}(S^+ - S^-)/2$, equation (7) can be written as

$$B\mu_{m-2}\langle m|S_+^2|m-2\rangle - 2g\mu_B(H_x - \mathrm{i}H_y)\mu_{m-1}\langle m|S_+|m-1\rangle + 4\mu_m\langle m|\mathcal{H} - E|m\rangle - 2g\mu_B(H_x + \mathrm{i}H_y)\mu_{m+1}\langle m|S_-|m+1\rangle + B\mu_{m+2}\langle m|S_-^2|m+2\rangle = 0. \quad (9)$$

We are particularly interested in the pseudo-ground state wave function, which corresponds to a value of E close to (3) and is concentrated in the region $m \approx -s$. For a particular value of H_z, approximately given by (5), there is tunneling between this wave function and a wave function concentrated in the region $m \approx m_0$. Between these two regions, there is a "tunneling region" where both wave functions are small. In, particular, when $\mathbf{H} = 0$, an elementary calculation given in Section 5 and in Appendix A shows that in the tunneling region (defined in that case by $s - |m| \gg 1$) the wave function is a sum of exponential functions $\exp(\pm\kappa_0 m)$. From an analogy with the elementary theory of quantum tunneling, one can guess that the tunnel splitting is dominated by a factor $\exp(-2\kappa_0 s)$. This is actually the formula (35) given in the abstract and derived in Section 5. However, there are corrections which depend on the behaviour of the wave function in the regions $m \approx \pm s$. In the forthcoming analysis, it will be argued that these corrections have a slower variation than an exponential.

In vanishing transverse field ($H_x = H_y = 0$), (9) has two types of solutions: i) those which vanish for odd values of m, ii) those which vanish for even values of m. These solutions will be called, respectively, "even-valued", and "odd-valued".

In weak transverse field (see formula (11) below), the eigenfunctions are still approximately even-valued or odd valued (Fig. 1) in the sense that the ratio

$$\text{average oddness} = \sum_p |\mu_{2p+1}|^2 \Big/ \sum_p |\mu_{2p}|^2 \quad (10)$$

is either large or small with respect to 1. This statement holds if the matrix elements of $\mathcal{H}$ between odd and even values of m are small with respect to the difference between successive diagonal elements. The former are, for low-lying states ($|m| \approx s$) of the order of $g\mu_B H_x\sqrt{s}$ and $g\mu_B H_y\sqrt{s}$ according to (9, 8), while the latter are of order $Ds^2 - D(s-1)^2 \approx 2Ds$. Therefore the "average oddness" (10) is large or small with respect to 1 if

$$\begin{cases} g\mu_B|H_x| \ll D\sqrt{s} & \text{(a)} \\ g\mu_B|H_y| \ll D\sqrt{s}. & \text{(b)} \end{cases} \quad (11)$$

The field will be called "weak" if it satisfies (2, 11). The present work is restricted to weak fields.

Equation (9) will be called $\mathcal{E}(m)$. The $(2s+1)$ equations $\mathcal{E}(-s)$, $\mathcal{E}(-s+1)$, ... $\mathcal{E}(s)$ define the components μ_m and the eigenvalue E. The eigenvalues E can in principle be obtained by writing that the determinant of the coefficients vanishes. This yields an algebraic equation of degree $(2s+1)$ in E which, for large s, is not easy to handle. To overcome this difficulty, we shall, in a first step, ignore a part of the equations (9), so that the remaining set can be solved for any value of E. This is the program of the next section.

3 Basis vectors

The advantage of considering large values of s is that, the variation of the matrix elements (8) with m is slow in the major part of the interval $[-s, s]$. More precisely, $d\langle m|S^-|m+1\rangle/dm \ll \langle m|S^-|m+1\rangle$ if

$$s - |m| \gg 1. \quad (12)$$

If (12) is fulfilled, one can hope to find solutions of (9) which are such that $\mu_m/\mu_{m-1} = \xi(m)$ varies slowly with m. Neglecting this variation, each equation (9) becomes an algebraic equation of degree 4 in $\xi(m)$, which has 4 solutions for each value of m, and is explicitly written and solved in Section 5 and in Appendix A. These 4 solutions generate 4 solutions $\varphi_1(m)$, $\varphi_2(m)$, $\varphi_3(m)$, $\varphi_4(m)$ of a subset of the system (9), to be precised below. Even though $\mu_m/\mu_{m-1} = \xi(m)$ is only approximately independent of m in only a part of the interval $[-s, s]$, the 4 functions $\varphi_r(m)$ can be defined as exact solutions of this subset of equations (9). The maximum number of elements of this subset can be deduced from the fact that the total number of equations (9) is $(2s+1)$ and the subset should have 4 independent solutions. It can therefore not contain more than $(2s+1) - 4 = (2s-3)$ equations. It is thus possible to define 4 functions $\varphi_1(m)$, $\varphi_2(m)$, $\varphi_3(m)$, $\varphi_4(m)$ which satisfy $\mathcal{E}(-s+2)$, $\mathcal{E}(-s+3)$, ... $\mathcal{E}(s-2)$. The complete definition of these 4 functions will be specified below in this section. The system of $(2s-3)$ equations $\mathcal{E}(-s+2)$, $\mathcal{E}(-s+3)$, ... $\mathcal{E}(s-2)$ will be called "truncated Schrödinger equation".

The true solution of the full system of $(2s+1)$ equations (9) will then be obtained by inserting

$$\mu_m = \sum_{r=1}^{4} u_r \varphi_r(m) \quad (13)$$

into the 4 remaining equations $\mathcal{E}(-s)$, $\mathcal{E}(-s+1)$, $\mathcal{E}(s-1)$ and $\mathcal{E}(s)$, which, together with the normalization condition, determine the 5 variables u_r and E. According to (13), the four functions $\varphi_r(m)$ may be regarded as "basis functions" or basis vectors of a 4 dimensional vector space $\mathcal{V}(E)$ which depends on E, but this inconvenience is not a dramatic one because the value of E of interest is approximately known, and given by (3).

Insertion of (13) into (7) yields

$$\sum_{m'} \langle m|\mathcal{H}|m'\rangle \sum_{r=1}^{4} u_{r'}\varphi_{r'}(m') = E \sum_{r=1}^{4} u_{r'}\varphi_{r'}(m). \quad (14)$$

This equation is automatically satisfied for $-s+2 \le m \le s-2$. It is satisfied for $m = -s,\ -s+1,\ s-1,\ s$ if $E,\ u_1,\ u_2,\ u_3,\ u_4$ have appropriate values. Multiplying

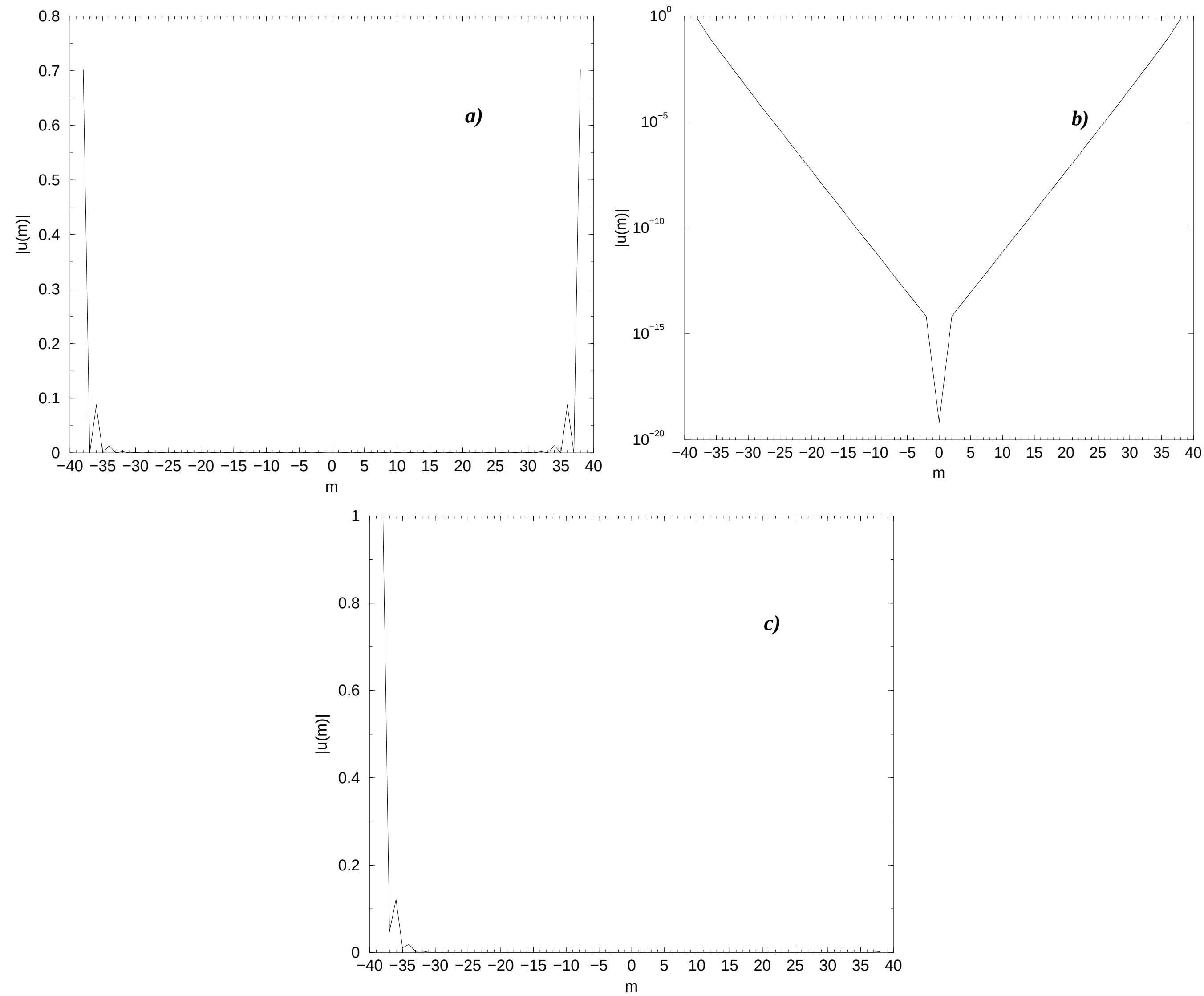

Fig. 1. Ground state function μ_m for $s = 38$ and $B = C$ in vanishing field (a) and its logarithm (b), and for $H_z = H_y = 0$ and $2g\mu_{\rm B}H_x = \sqrt{B(D+B)}$ (c). Curve (b) corresponds to even values of m, while $\mu_m = 0$ if m is odd.

both sides of (14) by $\varphi_r^*(m)$ and summing over m', one obtains

$$\sum_{r=1}^{4} u_{r'} \sum_{mm'} \varphi_r^*(m)\langle m|\mathcal{H}|m'\rangle\varphi_{r'}(m') = E\sum_{r=1}^{4} u_{r'} \sum_{m} \varphi_r^*(m)\varphi_{r'}(m) \quad (15)$$

or

$$\begin{pmatrix} \mathcal{A}_{11} & \mathcal{A}_{12} & \mathcal{A}_{13} & \mathcal{A}_{14} \\ \mathcal{A}_{21} & \mathcal{A}_{22} & \mathcal{A}_{23} & \mathcal{A}_{24} \\ \mathcal{A}_{31} & \mathcal{A}_{32} & \mathcal{A}_{33} & \mathcal{A}_{34} \\ \mathcal{A}_{41} & \mathcal{A}_{42} & \mathcal{A}_{43} & \mathcal{A}_{44} \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix} = 0 \quad (16)$$

where the elements of the 4×4 Hermitian matrix $\mathcal{A}$ are

$$\mathcal{A}_{rr'} = \sum_{mm'} \varphi_r^*(m)\langle m|\mathcal{H}|m'\rangle\varphi_{r'}(m') - E\sum_{m}\varphi_r^*(m)\varphi_{r'}(m) \quad (17)$$

which directly depend on E and also indirectly because the components $\varphi_r(m)$ do.

Equations $\mathcal{E}(-s+2)$ to $\mathcal{E}(s-2)$ define unambiguously the vector space $\mathcal{V}(E)$ of the 4 functions $\varphi_r(m)$, the choice of these 4 functions inside $\mathcal{V}(E)$ is still arbitrary. Most of this ambiguity can be removed by the requirements that, with a good approximation (Fig. 2),

– $\varphi_1(m)$ and $\varphi_2(m)$ are negative-localized,
– $\varphi_3(m)$ and $\varphi_4(m)$ are positive-localized,

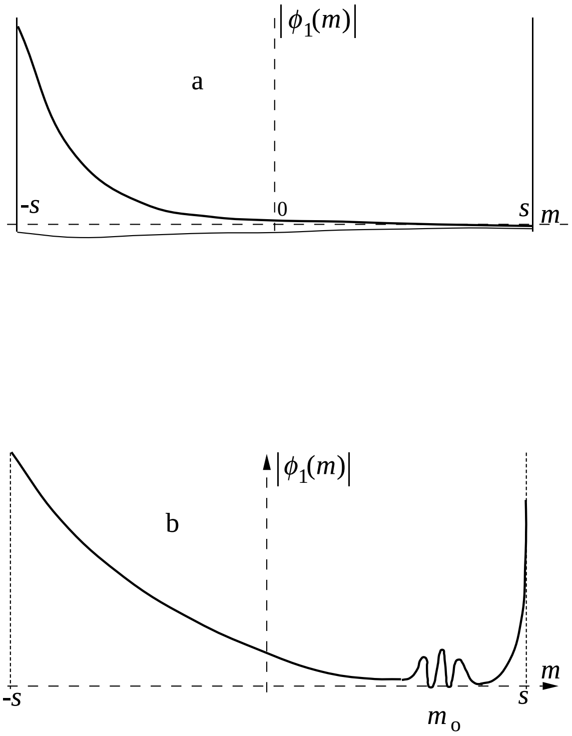

Fig. 2. a) Modulus of $\varphi_1(m)$ in vanishing field for an even value of s. Thick line: even values of m. Thin line: odd values of m (the sign has been changed to ensure legibility). b) Schematic representation of $\varphi_1(m)$ for $H_x = H_y = 0$ and $H_z \neq 0$ for even values of m.

and by the orthogonality relations

$$\sum_{mm'} \varphi_1^*(m)\langle m|\mathcal{H}|m'\rangle\varphi_2(m') = \sum_m \varphi_1^*(m)\varphi_2(m)$$
$$= \sum_{mm'} \varphi_3^*(m)\langle m|\mathcal{H}|m'\rangle\varphi_4(m') = \sum_m \varphi_3^*(m)\varphi_4(m) = 0. \tag{18}$$

The ambiguity in the choice of the basis functions inside $\mathcal{V}(E)$ can be completely removed by optimizing the localization. However, this optimization is only approximately possible. We shall come back to this point at the end of Section 5.

When $H_x = H_y = 0$, relations (18) are satisfied if φ_1 and φ_4 are chosen even-valued and φ_2 and φ_3 odd-valued. The effect of a weak transverse field is to transform these exact properties into approximate ones. Thus, as shown more precisely in Appendix A.3

– $\varphi_1(m)$ and $\varphi_4(m)$ are approximately even-valued,
– $\varphi_2(m)$ and $\varphi_3(m)$ are approximately odd-valued.

The orthogonality relations (18) imply

$$\begin{cases} \mathcal{A}_{12} = 0 & \text{(a)} \\ \mathcal{A}_{34} = 0. & \text{(b)} \end{cases} \tag{19}$$

The basis functions are generally not eigenfunctions of $\mathcal{H}$. However, the following theorem holds.

Theorem. If tunneling is neglected, a basis function $\varphi_r(m')$ is an eigenfunction of $\mathcal{H}$ for the eigenvalue E if and only if

$$\mathcal{A}_{rr}(E) = 0. \tag{20}$$

Proof. Assume $r = 1$. The quantities

$$Y(m) = \sum_{m'}\langle m|\mathcal{H}|m'\rangle\varphi_1(m') - E\varphi_1(m) \tag{21}$$

vanish for $m \neq \pm s$ or $\pm(s-1)$ because of the definition of φ_1. The 4 quantities $Y(-s)$, $Y(-s+1)$, $Y(s)$, $Y(s+1)$ satisfy the relations $\sum_m \varphi_{r'}(m)^* Y(m) = 0$ for $r' = 3$ and 4 because tunneling is neglected, for $r' = 2$ because of (19a), and for $r' = 1$ as a consequence of (20). These 4 relations are easily seen to be independent, so that $Y(m) = 0$ for any m and φ_1 is an eigenvector of $\mathcal{H}$ for the eigenvalue E.

4 Tunneling

In this section, we establish the general formulae which yield ω_{T} when the matrix elements $\mathcal{A}_{rr'}$ are known.

We first stress the relation between basis functions $\varphi_r(m)$, which are solutions of the truncated Schrödinger equation, and wave functions, solutions of the full Schrödinger equation. If the energy E is not appropriately chosen, the basis functions are not wave functions. But our goal is to find the right eigenvalues E, so that some basis functions are wave functions. How many? The case of interest is that of level-crossing. Then, for $E = E^0_{-s}$, two basis functions are solutions of the full Schrödinger equation with a very good approximation (*i.e.* neglecting tunneling). Which ones? Since s is an even integer, the ground state or pseudo-ground state is, at least approximately, even-valued. Since the spin is initially in the negative region, we identify its wave function with the negative-localized, approximately even-valued basis function φ_1. We wish to describe tunneling of this state with a positive-localized state, which must have almost the same energy, and therefore have a wave function almost identical with φ_4 (if it is almost even-valued) or φ_3 (if it is almost odd-valued). In the former case, the theorem of the previous section yields the level-crossing condition, ignoring tunneling:

$$\mathcal{A}_{11} = \mathcal{A}_{44} = 0. \tag{22}$$

These two equations are enough to obtain E and H_z if H_x and H_y are given. The condition on H_z should be approximately equivalent to (5), where m_0, or $(s - m_0)$, should be even since φ_4 is even-valued. Odd values of $s - m_0$ correspond to the case

$$\mathcal{A}_{11} = \mathcal{A}_{33} = 0. \tag{23}$$

Since the beginning of this section, tunneling has been ignored. The tunnel splitting is the difference between two eigenvalues, which are given, according to (16), by $\det \mathcal{A} = 0$. In this determinant, $\mathcal{A}_{11}$ and $\mathcal{A}_{44}$ are small, but $\mathcal{A}_{22}$ and $\mathcal{A}_{33}$ are not, so that $\mathcal{A}_{23}$, $\mathcal{A}_{24}$, $\mathcal{A}_{31}$ and $\mathcal{A}_{32}$ can be neglected and the energy is given with a good approximation, according to (19), by

$$\begin{vmatrix} \mathcal{A}_{11} & 0 & \mathcal{A}_{13} & \mathcal{A}_{14} \\ 0 & \mathcal{A}_{22} & 0 & 0 \\ 0 & 0 & \mathcal{A}_{33} & 0 \\ \mathcal{A}_{41} & \mathcal{A}_{42} & \mathcal{A}_{43} & \mathcal{A}_{44} \end{vmatrix} = 0$$

or

$$\mathcal{A}_{11}\mathcal{A}_{44} = \mathcal{A}_{14}\mathcal{A}_{41}. \qquad (24)$$

If a solution $(H_z^0, E^{(0)})$ of (22) is known, one can look for solutions $(H_z^0 + \delta H_z, E^{(0)} + \delta E)$ of (24). Inserting the expansions $\mathcal{A}_{11} = \lambda(\delta E + K\delta H_z)$ and $\mathcal{A}_{44} = \lambda'(\delta E - K'\delta H_z)$ into (24) one obtains for each value of H_z two solutions δE^+ and δE^- whose difference is $\sqrt{(K+K')^2\delta H_z^2 + 4\mathcal{A}_{14}\mathcal{A}_{41}/(\lambda\lambda')}$. The minimum, obtained for $\delta H_z = 0$, is the tunnel splitting

$$2\hbar\omega_{\rm T} = E^+ - E^- = 2|\mathcal{A}_{14}|/\sqrt{\lambda\lambda'}. \qquad (25)$$

In the case of tunneling between φ_1 and φ_3, which corresponds to odd values of $(s - m_0)$, the tunnel splitting is given by an analogous formula with $\mathcal{A}_{14}$ replaced by $\mathcal{A}_{13}$,

$$2\hbar\omega_{\rm T} = {\rm Const} \times |\mathcal{A}_{13}|. \qquad (26)$$

We shall generally consider even values of $(s - m_0)$, when (25) applies.

Formula (25) can only be useful if $\mathcal{A}_{14}$ is at least approximately known. In the next section, we give a simple example.

5 The zero-field case

In this section, the leading factor of the tunneling frequency is calculated for large, even s in the absence of a field.

If $\mathbf{H} = 0$, the Schrödinger equation (7) can be rewritten as a recursion formula for the ratio $X_m = \mu_m/\mu_{m-2} = \xi(m)\xi(m-1)$, namely

$$X_{m+2} = -K_m(E) - \frac{L_m}{X_m} \qquad (27)$$

where the expressions of $K_m(E)$ and L_m are easily deduced from the textbook formulae (8) and are given in Appendix C. In this section, we shall use the approximate expressions for $s - |m| \gg 1$, namely

$$\begin{cases} K_m(E) = \frac{4}{B(s^2-m^2)}\left[- Dm^2 + \frac{B}{2}(s^2 - m^2) - E\right] & \text{(a)} \\ L_m = 1. & \text{(b)} \end{cases} \qquad (28)$$

Replacing E by (3), and making the approximation $X_{m+2} = X_m$, (27) yields $X_m = X$, a value independent of m given by $X^2 + 2(1 + 2D/B)X + 1 = 0$, or

$$X = \xi^2 = -{\rm e}^{\pm 2\kappa_0} = -[1 + (2D/B) + 2\sqrt{(1 + D/B)D/B}]^{\pm 1} \qquad (29)$$

where we have introduced the notation

$${\rm e}^{\pm\kappa_0} = \sqrt{1 + \frac{D}{B}} \pm \sqrt{\frac{D}{B}}\,\cdot \qquad (30)$$

In this approximation, we have obtained 4 independent solutions $\mu_m^{(a)}$, $\mu_m^{(b)}$, $\mu_m^{(c)}$, $\mu_m^{(d)}$, of (7), which all have a constant ratio $\mu_m/\mu_{m-1} = \xi = \sqrt{X}$. The values of ξ corresponding to the 4 solutions are

$$\xi_a = {\rm i}{\rm e}^{-\kappa_0}, \quad \xi_b = -{\rm i}{\rm e}^{-\kappa_0}, \quad \xi_c = {\rm i}{\rm e}^{\kappa_0}, \quad \xi_d = -{\rm i}{\rm e}^{\kappa_0}. \qquad (31)$$

Since these values are independent of m, the assumption of a slowly varying ratio $\mu_m/\mu_{m-1} = \xi(m)$ is justified, but of course only if (12) is fulfilled, otherwise the approximation (28) would not be correct.

From the above values of ξ one can deduce 4 basis functions of the form $\exp[-\kappa_0 m \pm {\rm i}\pi/2]$ and $\exp[\kappa_0 m \pm {\rm i}\pi/2]$, but it is more convenient to choose the real linear combinations

$$\begin{aligned} \varphi_1(m) &= {\rm e}^{-\kappa_0(s+m)}\cos(m\pi/2), \\ \varphi_2(m) &= {\rm e}^{-\kappa_0(s+m)}\sin(m\pi/2), \\ \varphi_3(m) &= {\rm e}^{-\kappa_0(s-m)}\cos(m\pi/2), \\ \varphi_4(m) &= {\rm e}^{-\kappa_0(s-m)}\sin(m\pi/2). \end{aligned} \qquad (32)$$

These expressions can be multiplied by a normalization factor when appropriate. The factor ${\rm e}^{\pm\kappa_0 s}$ ensures that the normalization factor has a finite limit for infinite s.

Formulae (32) show that, in agreement with the prescription of Section 3

- $\varphi_1(m)$ is negative-localized (with just a small tail in the region $m > 0$) and strictly even-valued.
- $\varphi_2(m)$ is negative-localized and strictly odd-valued;
- $\varphi_3(m)$ is positive-localized and strictly odd-valued;
- $\varphi_4(m)$ is positive-localized and strictly even-valued.

Although expressions (32) are only valid if (12) is fulfilled, functions $\varphi_r(m)$ are strictly even- and odd-valued, for the reasons explained in Section 2. It follows from this fact and the definition (17) that off-diagonal elements $\mathcal{A}_{rr'}$ vanish except if φ_r and $\varphi_{r'}$ have the same parity, *i.e.* only $\mathcal{A}_{14} = \mathcal{A}_{41}$ and $\mathcal{A}_{23} = \mathcal{A}_{32}$ do not vanish. Therefore, the equation $\det \mathcal{A} = 0$, which yields the eigenvalues E, exactly reduces to (24), which in the general case is but approximate.

To put (24) and the equivalent formula (25) into a more transparent form, one can write the definition (17) as $\mathcal{A}_{41} = \sum_m \varphi_4^*(m)Y(m)$. The quantity $Y(m)$ defined by (21) vanishes for $-(s-1) < m < s-1$. It also vanishes (with a very good approximation) for $m = -s$ and

$-(s-1)$ if E and $\varphi_1(m)$ are such that $\mathcal{A}_{11} = 0$ (this is relation (20) and the corresponding theorem). Finally, for $\mathbf{H} = 0$, $\varphi_1(m)$ is strictly even-valued and $Y(s-1)$ vanishes, so that

$$\mathcal{A}_{41} = \varphi_4^*(s)Y(s) = \varphi_4^*(s)(\langle s|\mathcal{H}|s\rangle - E)\varphi_1(s) + \varphi_4^*(s)\langle s|\mathcal{H}|s-2\rangle\varphi_1(s-2). \quad (33)$$

In this expression, $\varphi_4^*(s)$ is of order unity and, in the limit of large spins, just contributes a constant, s-independent factor in the expression (25) of ω_{T}. The factor $\sqrt{\lambda\lambda'}$ in that expression is also a constant factor. Furthermore, the energy E is the ground state energy, which should not be very different from $\langle s|\mathcal{H}|s\rangle$, so that a correct order of magnitude is obtained by dropping the first term of (33). With these approximations (25, 33) yield

$$2\hbar\omega_{\mathrm{T}} \approx \mathrm{Const} \times Bs|\varphi_1(s-2)|. \quad (34)$$

Insertion of (29, 32) into (34) yields the tunnel splitting

$$2\hbar\omega_{\mathrm{T}} \approx 2Ds\left[1 + (2D/B) + 2\sqrt{(1+D/B)D/B}\right]^{-s} \quad (35)$$

but formula (32), which has been applied to $m = s-1$, is only valid in the tunneling region. In reality, the ratio $X_r(m) = \varphi_r(m)/\varphi_r(m-2) = \xi(m)\xi(m-1)$ deduced from (27) is not constant. It differs from (29) by a factor which is appreciably different from 1 in a narrow region near $m = -s$ and $m = s$. Taking these regions into account would just contribute to the constant in (34). However, as seen in Appendix C, even in the tunneling region, the weak correction to $X_r(m)$ yields a divergent factor in the function $\varphi_r(m) = \mathrm{Const} \times \prod_q X_r(q)$. The divergence, however, is a power of s, weaker than exponential. Thus, our calculation correctly gives the dominant contribution to the tunnel splitting for large s. This dominant factor is in agreement with the result obtained by path integrals, as can be seen for instance from formula (31a) of Schilling [16].

The basis functions out of the tunneling regions can be derived from (27). The energy E could be obtained by perturbation theory, but expression (3) is already a good approximation. For instance $X_4(m)$ can be most conveniently deduced from $X_4(-s+2)$. If B/D is not too large, *e.g.* $B/D < 1$) and if $-X_4(-s+2)$ is large enough (*e.g.* $X_4(-s+2) < -1$, it is easy to prove recursively from (27) that $X_4(m) < -1$ for any m. This is done in Appendix E. The resulting value of $|\varphi_4(m)|$ is therefore an increasing function of m. On the other hand, in the tunneling region, it is a linear combination $\mathrm{e}^{\kappa_0 m} + k\mathrm{e}^{-\kappa_0 m}$. The fact that it is an increasing function of m implies that k is very small, so that the resulting function $\varphi_4(m)$ satisfies the required conditions in spite of the ambiguity on the starting point $X_4(-s+2)$ of the recursion procedure. In practice, a possible choice is $X_4(-s+2) = \infty$. Numerical solution of (27) with this starting point shows a regular convergence to $X_4 = \mathrm{e}^{2\kappa_0}$.

6 Weak fields

6.1 The tunneling region

In this section, the results given in the previous sections in zero field are extended to the case of weak fields which satisfy (2) and (11). One can look for solutions of the truncated Schrödinger equation (7) in the tunneling region, for which the ratio $\mu_m/\mu_{m-1} = \xi(m)$ varies slowly with m. The resulting equation is of the fourth degree and can be solved approximately for small fields. The calculation is given to lowest order in Appendix A. One thus finds 4 (complex) solutions $\mu_m^{(a)}$, $\mu_m^{(b)}$, $\mu_m^{(c)}$, $\mu_m^{(d)}$, with ratios $\xi_a(m)$, $\xi_b(m)$, $\xi_c(m)$, $\xi_d(m)$ which are close to the values (31). In the case $H_y = 0$, these functions can be combined to obtain real basis functions as in Section 5. The results, which generalize (32), are

$$\varphi_r(m) = \mathrm{Const} \times \mathrm{e}^{-\kappa_0(s+m)} \exp[-h_z\Psi(m/s)] \times \cos[m\pi/2 - h_x\Phi(m/s) + \alpha_r] \quad (r = 1,2) \quad (36)$$

and

$$\varphi_r(m) = \mathrm{Const} \times \mathrm{e}^{-\kappa_0(s-m)} \exp[h_z\Psi(m/s)] \times \cos[m\pi/2 - h_x\pi + h_x\Phi(m/s) + \alpha_r] \quad (r = 3,4) \quad (37)$$

where the reduced fields are

$$h_x = \frac{g\mu_{\mathrm{B}}H_x}{2\sqrt{B(B+D)}}, \quad (38)$$

and

$$h_z = \frac{g\mu_{\mathrm{B}}H_z}{2\sqrt{D(B+D)}}, \quad (39)$$

and the meaning of the various functions is explained below. The most important one is Φ, which is a sum of phase shifts corresponding to the various values of m. The typical phase shift value is small with respect to unity, as seen in Appendix A, if

$$|h_x| \ll s. \quad (40)$$

If this inequality is satisfied, the sum of the phase shifts can be replaced by an integral, and one obtains, as seen in Appendix A,

$$\Phi(v) = \int_{-1}^{v} \frac{\mathrm{d}u}{\sqrt{1-u^2}} \cdot \quad (41)$$

The function Ψ is a sum of corrections to κ_0. If the sum is replaced by an integral, one finds

$$\Psi(v) = \int_{0}^{v} \frac{\mathrm{d}u}{1-u} \cdot \quad (42)$$

We now discuss the phases α_r. In agreement with the requirements of Section 3, $\varphi_1(m)$ and $\varphi_4(m)$ must have a small average oddness, and therefore be almost even-valued in the region where these functions are large, but also on the corresponding edge of the tunneling region. Thus, $h_x \Phi(-1) + \alpha_1$ and $\pi - h_x \Phi(1) + \alpha_4$ should be close to 0 or (since $\Phi(-1) = 0$ and $\Phi(1) = \pi$)

$$\alpha_1 \approx \alpha_4 \approx 0. \tag{43}$$

Similarly, since $\varphi_2(m)$ and $\varphi_3(m)$ are approximately odd-valued,

$$\alpha_2 \approx \alpha_3 \approx \pi/2. \tag{44}$$

These relations are consistent with (19). They can also be obtained by noticing that, for $\mathbf{H} = 0$, (36, 37) should reduce to (32), and this implies $\alpha_1 = \alpha_4 = 0$ and $\alpha_2 = \alpha_3 = \pi/2$.

Relations (43, 44) hold only if (11) is satisfied. For fixed values of B and D, this condition is more stringent than (40) in the limit $s \to \infty$.

In the case $H_y \neq 0$, (36) is replaced, for $r = 1$, by the following expression derived in Appendix A.

$$\begin{aligned}\varphi_1(m) = \mathrm{Const} \times \exp\left[-\kappa_0(s+m) + h_z \Psi(m/s)\right] \\ \times \{\cos\left[m\pi/2 - h_x\Phi(m/s) + \alpha_1\right] \cosh\left[h_y \Phi(m/s)\right] \\ + \mathrm{i}\sin\left[m\pi/2 - h_x\Phi(m/s) + \alpha_1\right] \sinh\left[h_y\Phi(m/s)\right]\}\end{aligned} \tag{45}$$

where

$$h_y = \frac{g\mu_{\mathrm{B}} H_y}{2\sqrt{BD}} \cdot \tag{46}$$

Formulae analogous to (45) can easily be obtained for $r = 2, 3, 4$.

The remarkable feature in formulae (36, 37) is the phase $h_x \Phi(m/s)$. Even if H_x satisfies (11a), this phase can be locally large. In particular, it can be equal to $\pi/2$ for some value of m, so that φ_1, for instance, is locally odd-valued although it has been defined as having a small average oddness.

In particular, if one applies formula (34) for the tunnel frequency, and if $\varphi_1(s-2)$ is calculated from (36), ω_{T} is found to vanish for $h_x \Phi(1) = (2n+1)\pi/2$. In the next section, this conclusion will be seen to be correct although a more elaborate proof is necessary, since (36) is not applicable outside the tunneling region, and in particular for $m = s - 2$.

6.2 Tunnel frequency

The tunnel splitting is related, through (25), to $\mathcal{A}_{41}$. This quantity is approximately given by (33). An exact expression would include additional terms containing $\varphi_4^*(s-1)$, but these terms are small because $\varphi_4(s-1)$ is almost even-valued for weak fields, and $(s-1)$ is odd.

To exploit (33), one needs the expression of $\varphi_1(m)$ outside the tunneling region, for $m \approx s$. In weak field, the tunneling region includes almost the whole interval $-s < m < s$, the excluded region is very narrow and the field can be treated as a weak perturbation in this region. This strategy is applied below.

Let m_2 be the upper boundary of the tunneling region, which is somewhat arbitrary and can therefore be assumed to be an even integer. For $m \leq m_2$, $\varphi_1(m)$ is given by (45). For $m > m_2$, it is not, but is is in principle given by equations $\mathcal{E}(m_2-1)$ $\mathcal{E}(m_2-1)$, $\mathcal{E}(m_2)$ $\mathcal{E}(m_2+1)$, ... $\mathcal{E}(s-2)$ defined in Section 2. Since these equations depend on $\mathbf{H}$, any solution $\varphi(m)$ of $\mathcal{E}(m)$ for $m_2 - 3 \leq m < s-1$ depends on $\mathbf{H}$. It also depend on the energy $(E - E_s^{(0)})$ counted from the ground state energy. Finally it depends on the initial conditions and, for given values of $\varphi(m_2-2)/\varphi(m_2)$, $\varphi(m_2-3)/\varphi(m_2-1)$ and $\varphi(m_2-1)/\varphi(m_2)$, it is proportional to $\varphi(m_2)$ since equations $\mathcal{E}(m)$ are linear. Thus

$$\begin{aligned}\varphi(m) = \varphi(m_2) f_m\Big(\frac{\varphi(m_2-2)}{\varphi(m_2)}, \frac{\varphi(m_2-3)}{\varphi(m_1)}, \\ \frac{\varphi(m_2-1)}{\varphi(m_2)}, H_x, H_y, H_z, E - E_s^{(0)}\Big)\end{aligned} \tag{47}$$

where f_m is a function of m, E, $\mathbf{H}$ and the initial conditions.

In weak field, we shall replace H_x, H_y, H_z by 0. This is a rather poor approximation, which will be refined in the next sections. The ratios $\varphi(m_2-2)/\varphi(m_2)$ and $\varphi(m_2-3)/\varphi(m_2-1)$ are both approximately equal to $\mathrm{e}^{2\kappa_0}$ according to (45). Since the interest is focussed on tunneling at low temperature, the energy of interest is that of the pseudo-ground state, $E = E_{-s}^{(0)}$. Thus, (47) reads

$$\begin{aligned}\varphi(m) = \varphi(m_2) \\ \times f_m\left(\mathrm{e}^{2\kappa_0}, \mathrm{e}^{2\kappa_0}, \frac{\varphi(m_2-1)}{\varphi(m_2)}, 0, 0, 0, E_{-s}^{(0)} - E_s^{(0)}\right).\end{aligned} \tag{48}$$

Let f_m^{ev} be the even-valued solution of $\mathcal{E}(m_2)$, $\mathcal{E}(m_2+2)$, ... $\mathcal{E}(s-2)$ for $\mathbf{H} = 0$, $\varphi(m_2) = 1$ and $\varphi(m_2-2)/\varphi(m_2) = \mathrm{e}^{2\kappa_0}$. Let f_m^{odd} be the odd-valued solution of $\mathcal{E}(m_2-1)$, $\mathcal{E}(m_2+1)$, ... $\mathcal{E}(s-2-1)$ for $\mathbf{H} = 0$, $\varphi(m_2-1) = 1$ and $\varphi(m_2-3)/\varphi(m_2-1) = \mathrm{e}^{2\kappa_0}$. It is easily seen that $\varphi(m)$ is a linear combination of f_m^{ev} and f_m^{odd}, so that (48) takes the form

$$\begin{aligned}\varphi(m) = \varphi(m_2) f_m^{\mathrm{ev}}\left(E_{-s}^{(0)} - E_s^{(0)}\right) \\ + \varphi(m_2-1) f_m^{\mathrm{odd}}\left(E_{-s}^{(0)} - E_s^{(0)}\right).\end{aligned} \tag{49}$$

This formula can be applied to function $\varphi_1(m)$ and inserted into (33). The contribution of the second, odd-valued term of (49) vanishes and one obtains

$$\mathcal{A}_{41} = F\left(E_{-s}^{(0)} - E_s^{(0)}\right) \varphi_1(m_2) \tag{50}$$

where $F(E)$ is a real function. Expression (45) can be substituted for $\varphi_1(m_2)$, where $\Phi(m_2/s)$ can be replaced by $\Phi(1) = \pi$. Replacing α_1 by 0, one obtains

$$\begin{aligned}\mathcal{A}_{41} = (-1)^{m_2/2} \mathrm{e}^{-\kappa_0(s+m_0)} \tilde{G}_s\left(E_{-s}^{(0)} - E_s^{(0)}\right) \\ \times \left[\cos(h_x\pi)\cosh(h_y\pi) - \mathrm{i}\sin(h_x\pi)\sinh(h_y\pi)\right]\end{aligned} \tag{51}$$

where $\tilde{G}_s(E)$ is a real quantity, whose behaviour as a function of s for large s is smoother than an exponential. Insertion of (51) into (25) yields

$$2\hbar\omega_{\rm T} = {\rm e}^{-\kappa_0(s+m_0)} G_s\left(E_{-s}^{(0)} - E_s^{(0)}\right) \times \left|\cos(h_x\pi)\cosh(h_y\pi) - {\rm i}\sin(h_x\pi)\sinh(h_y\pi)\right| \quad (52)$$

where $G_s(E)$ differs from $\tilde{G}_s(E)$ by the factor $\sqrt{\lambda\lambda'}$ which is independent on s. The argument $(E_{-s}^{(0)} - E_s^{(0)})$ is approximately equal to $2H_z s$. The dependence on H_x and H_y is thus contained in the last factor of (52). The consequences will be seen in the next section.

7 Diabolic fields

7.1 Approximate argument

"Diabolic fields" have been defined in Section 1 as those for which the pseudo-ground state is exactly degenerate with a positive-localized state. This implies two conditions. The first one is a level-crossing condition, which is essentially a condition on H_z, approximately given by (5), or more precisely by (22) if m_0 is even and by (23) if m_0 is odd. Usually, there is a non-vanishing coupling $\mathcal{A}_{41}$ (in the former case) or $\mathcal{A}_{31}$ (in the latter case) between the negative- and positive-localized wave functions, and there is a tunnel splitting which is proportional to this coupling, as seen, in the former case, from (25), and in the latter case, from (26). It is said that "levels repel each other".

However, if this coupling vanishes,

$$\mathcal{A}_{41} = 0 \quad (53)$$

the tunnel splitting vanishes and the degeneracy of two states is perfect. According to (52), this occurs for even values of m_0 if the "zero-coupling conditions"

$$H_y = 0 \quad (54)$$

and

$$g\mu_{\rm B}H_x = (2n+1)\sqrt{B(B+D)} \quad (55)$$

are simultaneously satisfied, together with the level-crossing condition (22).

If m_0 is odd, the level-crossing condition is (23) and the zero-coupling condition is

$$\mathcal{A}_{31} = 0 \quad (56)$$

which is easily found to be approximately equivalent to (54) again, together with

$$g\mu_{\rm B}H_x = 2n\sqrt{B(B+D)}. \quad (57)$$

Both families of diabolic fields are displayed in Figure 3.

Formula (55) has been obtained for the first time by Garg [6]. The existence of diabolic fields has also been predicted by Chudnovsky and Di Vicenzo [25], Kalatski

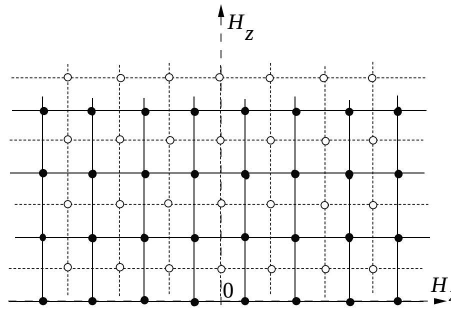

Fig. 3. Diabolic points in the plane (H_x, H_z). They consist of two families. i) The intersections (full dots) of curves (full lines) approximately given by (55, 5), where $(s-m_0)$ is an even integer. ii) The intersections (empty dots) of curves (dotted lines) approximately given by (57, 5), where $(s-m_0)$ is an odd integer. The component H_y is zero.

et al. [26], Tupitsyn *et al.* [27]. Formulae (55, 57) are consistent with (11) if $n \ll \sqrt{Ds/B}$.

The derivation of (55) given in the previous section is approximate, and does not warrant that the tunnel splitting $2\hbar\omega_{\rm T}$ exactly vanishes. Instead, it might just have minima. In the next subsection, we show that $\omega_{\rm T}$ does vanish for values of $\mathbf{H}$ which are close to those given above in the present subsection.

7.2 Does the tunnel frequency exactly vanish?

In the previous subsection, the "diabolic" fields which allow perfect degeneracy have been determined by means of approximate relations. It is easy to obtain under which *exact* conditions the matrix $\mathcal{A}$ has two eigenvectors for the eigenvalue 0. This is done in Appendix D, where exact, necessary and sufficient conditions of diabolic degeneracy of (16) are shown to be

$$\mathcal{A}_{11} - \frac{\mathcal{A}_{31}\mathcal{A}_{13}\mathcal{A}_{22}}{\mathcal{A}_{22}\mathcal{A}_{33} - \mathcal{A}_{32}\mathcal{A}_{23}} = 0, \quad (58)$$

$$\mathcal{A}_{41} + \frac{\mathcal{A}_{42}\mathcal{A}_{23}\mathcal{A}_{31}}{\mathcal{A}_{22}\mathcal{A}_{33} - \mathcal{A}_{32}\mathcal{A}_{23}} = 0, \quad (59)$$

and

$$\mathcal{A}_{44} - \frac{\mathcal{A}_{42}\mathcal{A}_{24}\mathcal{A}_{33}}{\mathcal{A}_{22}\mathcal{A}_{33} - \mathcal{A}_{32}\mathcal{A}_{23}} = 0. \quad (60)$$

If $\mathcal{A}_{22}$ and $\mathcal{A}_{33}$ are not small, the second term of the denominator can be neglected with a very good approximation, and (22, 53) are obtained as approximate forms of (58, 60). Similarly, if $\mathcal{A}_{22}$ and $\mathcal{A}_{44}$ are not small (23, 56) are obtained as approximate forms of the same equations (58–60). We shall focus on the former case and assume $H_y = 0$.

In the following of this subsection, we assume $H_y = 0$. The three left hand sides of (58–60) are real, as seen from the definition (17). Thus, there are 3 equations for 3 parameters E, H_x and H_z. It will be shown below that these equations have exact solutions in the vicinity of the approximate ones found in the previous subsection.

To first order in ω_{T} (58, 60) are identical with (22). These two equations have a solution for the same value of E on surfaces of the (H_x, H_y, H_z) space which are roughly planes defined by (5), where $(s - m_0)$ is an even integer. The small additional term absent in (22), which appears in (58, 60), cannot alter this statement. In particular, these surfaces include the plane $H_z = 0$. That one is exactly a plane, for symmetry reasons.

To first order in ω_{T}, (59) is identical with (53). Instead of showing, as is the previous subsection, that $\mathcal{A}_{41}$ is very small for $h_x = n+1/2$, one can show that $\mathcal{A}_{41}$ changes sign when h_x goes continuously from n to $n+1$. This property follows from (51) which, for $H_y = 0$, reads

$$\mathcal{A}_{41} = (-1)^{m_2/2} \mathrm{e}^{-\kappa_0 (s+m_0)} \tilde{G}_s \left(E_{-s}^{(0)} - E_s^{(0)} \right) \times \cos(h_x \pi) \cosh(h_y \pi) . \quad (61)$$

While that formula is not accurate enough to warrant a strictly vanishing value of $\mathcal{A}_{41}$ for a well-defined field, it is precise enough to show that $\mathcal{A}_{41}$ has different signs for $h_x = n$ and $h_x = n+1$. The left hand side of (59), which only differs from $\mathcal{A}_{41}$ by a tiny amount, has the same property. Since this variation from a positive to a negative value is continuous, there is a value of h_x where (59) is exactly satisfied.

The conclusion is that, for $H_y = 0$ and any value of H_z satisfying (2), $\mathcal{A}_{41} = \mathcal{A}_{14}$ vanishes on curves of the (H_x, H_z) space which are roughly straight lines defined by (55). The intersections of these curves with the surfaces defined by (58, 60) are the "diabolic" fields for which the negative-localized pseudo-ground state has exactly the same energy as a positive-localized state (Fig. 3).

The other diabolic family, approximately given by (57, 5) with odd values of m_0, can be treated in a similar way and level degeneracy is found to be exact.

7.3 Small spins

Our derivation of (55, 57) is approximate, and only valid for large spins. It is of interest to test the results for small spins. The case $s = 1$ is easily treated analytically (Appendix B). The tunnel frequency vanishes for a single value of $|H_x|$, which is exactly given by (55) with $n = 0$. We have calculated numerically the tunneling frequency of (1) for $H_y = H_z = 0$, a ratio $B/D = 0.19$, and all integer values of s from 1 to 10. Our numerical results (Fig. 4) are in agreement with those of Wernsdorfer and Sessoli and suggest that (55) might actually be exact. So far as we understand, there is no explanation of this. Our treatment is obviously approximate, and more elaborate calculations, for instance by Garg [6] are not exact either.

The number n_d of zeros of the tunnel frequency when H_x goes from 0 to ∞ is obviously not infinite. According to our numerical study, $n_d = 2s$ (*i.e.* s for each sign) for $H_z = 0$. In view of condition (40), this is not in disagreement with our analytic argument results. Moreover, this coincides with the analytic result derived by Garg [28] in the case $D \ll B$.

8 Conclusion

Elementary, approximate methods have been used to calculate the tunnel frequency of large spins. In vanishing field, the dominant factor (35) is that obtained by path integrals [16] and the first correction, as shown in Appendix C, is a power s^Q, in agreement with path integral methods [16]. We did not check the value of the exponent Q, which is $3/2$ according to Schilling, but probably depends on B/D in our treatment.

We have rederived Garg's result that the tunnel frequency of model (1) for $H_y = H_z = 0$ vanishes for certain values of H_x.

In addition, we have argued that the tunnel frequency in weak fields can completely vanish for $H_y = 0$ when H_x satisfies (55) or (57), and H_z satisfies the usual level-crossing condition, *not only* for $H_z = 0$. These results are in agreement with experiments of Wernsdorfer and Sessoli, but the present theoretical derivation is, to our knowledge, the first one. Our derivation is based on the impossibility of matching an even-valued wave function with an odd-valued one. It should be stressed that our analysis in the case $H_z \neq 0$ is not so complete as for $H_z = 0$. In particular, the behaviour of the wave function and basis functions out of the tunneling region is much more complicated than the behaviour described in Section 5 and in Appendix E.

The present attempt to derive the tunnel frequency by elementary methods is moderately successful. Our argument is not so simple as we had wished, and our argument holds only for weak fields which satisfy (2, 11). In contrast, numerical calculations reported in the present work or before [4,6,8] show that the diabolic conditions (55, 57) also hold for fields which do not satisfy (11). To our knowledge, there is no analytic explanation of this fact, except for $D \ll B$. Another point which has not been clarified in the case $B/D \leq 1$ is the number n_d of diabolic values of H_x.

Our method consists in analyzing the properties of the spin wave function, which is written as a sum of two localized wave functions $\varphi_1(m)$ and $\varphi_4(m)$. It turns out that a rather poor knowledge of $\varphi_1(m)$ and $\varphi_4(m)$ is sufficient to provide satisfactory informations on the tunnel frequency. More precisely, the tunneling frequency is dominated by a factor which can be deduced from the study the tunneling region $s - |m| \gg 1$ alone. In that region, the behaviour of the wave function is simple and does not depend very much on the energy E, so that the study is rather easy.

The limit of large spins is not adequate to a comparison with experiments in molecular magnets of spin $s = 10$. Numerical methods are much more efficient in practice. They lead to large deviations of the tunnel frequency from formula (35) and even from improved forms derived from more quantitative calculations [16]. In contrast, the values of diabolic fields obtained from numerical methods, in the present paper of by other authors [4,8], are even for small

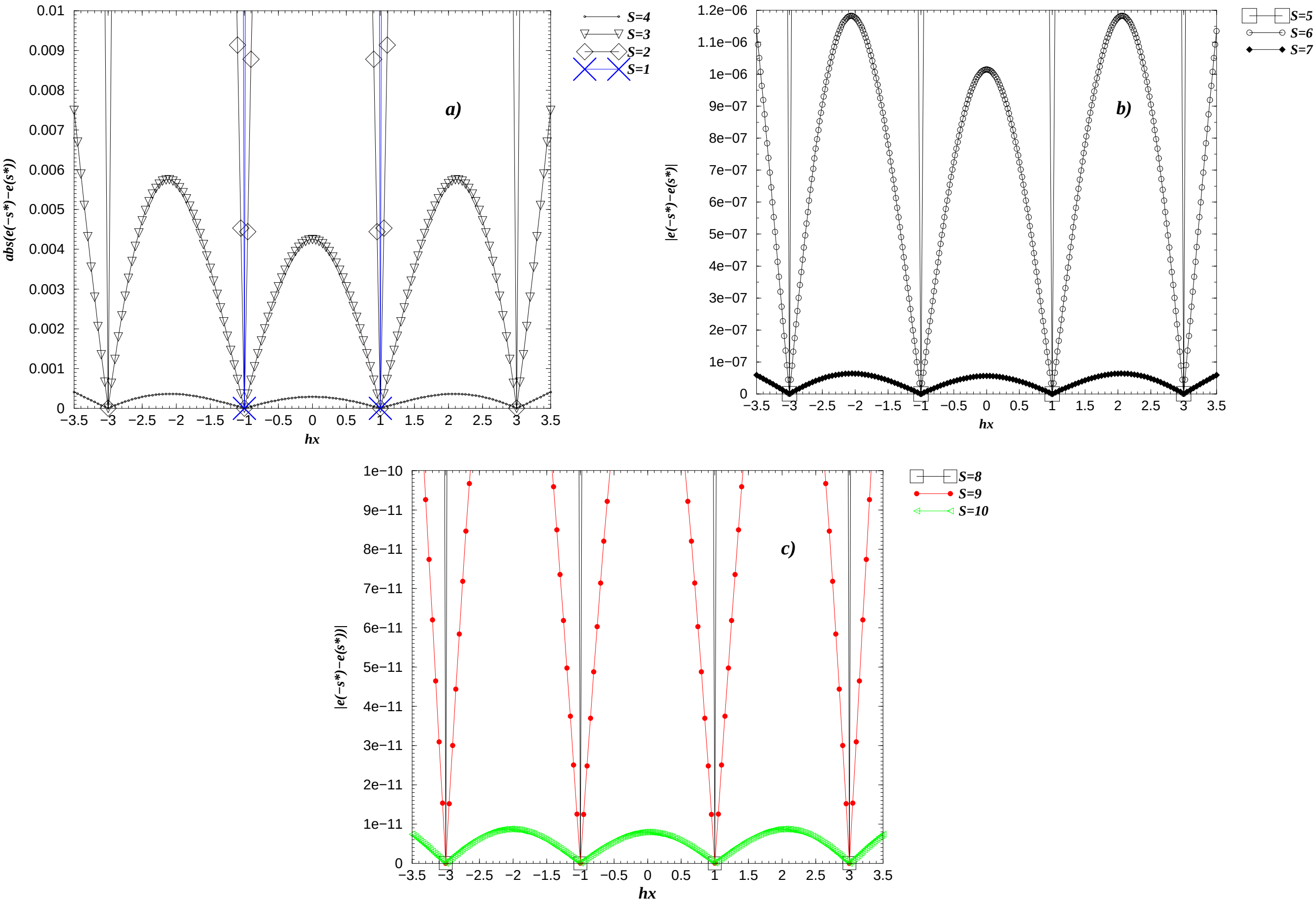

Fig. 4. Tunnel splitting, in Kelvin, as a function of $2h_x = g\mu_B H_x/\sqrt{B(B+D)}$ for the Hamiltonian $\mathcal{H} = -DS_z^2 + BS_x^2 - g\mu_B H_x S_x$ in the neighbourhood of the first three zeros for $s = 1, 2, 3, 4$ (a), $s = 5, 6, 7$ (b), and $s = 8, 9, 10$ (c).

spins in surprisingly good agreement with (55). The explication has been quite recently given by Keçecioğlu and Garg [29].

This agreement is not so good with experimental data. According to experiments [4], the "diabolic" fields which allow perfect degeneracy are almost equidistant, in agreement with (55), but the distance is different by a factor $\sqrt{2}$. This discrepancy has been attributed to higher order terms. The consequences of fourth order terms, for instance, is briefly discussed in Appendix A.4. The 4 independent solutions of the Schrödinger equation in the tunneling regions, described by (31) would be replaced by 8 solutions, given by an equation of degree 8, and the corresponding ratios $\xi_\alpha(m)$ would depend on m. The equidistance of the diabolic fields should be destroyed.

If higher order terms are small and if s is large, they can be treated pertubatively, as seen in Appendix A.4, by a slight extension of the methods used in the present work. In the case of Fe_8, the spin $s = 10$ may not be large enough to warrant the correctness of the perturbative treatment. The pretty large discrepancy of a factor $\sqrt{2}$ between formula (55) and the experimental data suggests that perturbation theory can be only qualitatively successful. On the other hand, the approximate equidistance of the diabolic fields, which is experimentally observed, suggests that higher order terms have no dramatic effect. The algebra related to higher order terms is heavy, and their investigation is left for future investigation. Anyway, for $s = 10$, the precise determination of diabolic fields is best done numerically.

Another goal for future work could be the extension of the present method to antiferromagnets, where diabolic points have been detected, using coherent spin states and the Berry phase, by Golyshev and Popkov [30].

Before Wernsdorfer and Sessoli [4] published their experiments on Fe_8, the search for diabolic points was perhaps discouraged by the experimental observation of *maxima* of the relaxation rate in $Mn_{12}O_{12}$-acetate as a function of the longitudinal field H_z when (5) is satisfied for odd values of $(s - m_0)$ and a "nominally" vanishing transverse field. This is surprising, because level crossing occurs between the even-valued vave function φ_1 and the odd-valued vave function φ_3, so that (56) holds and the tunnel splitting should vanish. The maximum which is experimentally observed may be a result of hyperfine interactions, which are much stronger in $Mn_{12}O_{12}$ than in Fe_8.

It is a pleasure to acknowledge illuminating discussions with A. Garg, R. Sessoli and W. Wernsdorfer.

Appendix A: Behaviour of the wave function

A.1 General properties

In this appendix we study the behaviour of the wave function μ_m for

$$s - |m| \gg 1 \tag{A.1}$$

when E is close to the energy of the pseudo-ground state, approximately given by (4), or a weakly excited state. It follows that

$$\langle m|\mathcal{H} - E|m\rangle = D(s^2 - m^2) - H_z(s+m) + B\langle m|S_x^2|m\rangle \tag{A.2}$$

or, according to (A.1),

$$\langle m|\mathcal{H} - E|m\rangle = D(s^2 - m^2) - H_z(s+m) + \frac{B}{2}(s^2 - m^2). \tag{A.3}$$

The wave function has usually a large amplitude only in a localized region of the interval $-s < m < s$, except if tunneling occurs. In that case, which is of interest for us, there are two regions where the amplitude is large. One corresponds to $m < 0$ and the other one to $m > 0$. These regions will be called "regions of high probability" and are separated by a broad region called "tunneling region" where the wave function has a low amplitude.

A.2 Behaviour of the wave function in the tunneling region

We now look for solutions of (9) which, if (A.1) is satisfied, are such that $\mu_m/\mu_{m-1} = \xi(m)$ varies slowly with m. Neglecting this variation between $(m-2)$ and $(m+2)$, (9) can be written with the help of (A.3) and (8) as

$$F(\xi) = -\frac{4D}{B} + \eta \tag{A.4}$$

where

$$F(\xi) = \left(\xi + \xi^{-1}\right)^2 \tag{A.5}$$

and

$$\eta = \frac{2H_x}{B}\frac{\xi + \xi^{-1}}{\sqrt{s^2 - m^2}} + \frac{2\mathrm{i}H_y}{B}\frac{\xi - \xi^{-1}}{\sqrt{s^2 - m^2}} + \frac{4H_z}{B(s-m)}\cdot \tag{A.6}$$

Since the fields are assumed to be small (relations (2, 11)), it is of interest to solve first the zero field case, when $\eta = 0$ and (A.4) reduces to *i.e.* $\xi^2 \pm 2\mathrm{i}\xi\sqrt{D/B} + 1 = 0$. The solution of this second degree equation yields the 4 solutions (31) which can be written as

$$\xi_{0r} = \mathrm{i}\epsilon_r \mathrm{e}^{\kappa_0 \epsilon_r} \tag{A.7}$$

where κ_0 is given by (30) and

$$\epsilon_a = -\epsilon_b = \epsilon_c = -\epsilon_d = -\epsilon'_a = -\epsilon'_b = \epsilon'_c = \epsilon'_d = 0. \tag{A.8}$$

In weak, but nonvanishing field, one can replace ξ by ξ_{0r} in (A.6), thus obtaining 4 values

$$\eta_r = \frac{2H_x}{B}\frac{\xi_{0r} + \xi_{0r}^{-1}}{\sqrt{s^2 - m^2}} + \frac{2\mathrm{i}H_y}{B}\frac{\xi_{0r} - \xi_{0r}^{-1}}{\sqrt{s^2 - m^2}} + \frac{4H_z}{B(s-m)}\cdot \tag{A.9}$$

Inserting

$$\xi_r = \xi_{0r}\exp(\delta\kappa_r) \tag{A.10}$$

into (A.4) yields, to first order in $\delta\kappa_r$

$$\delta\kappa_r = \frac{\eta_r}{\xi_{0r}F'(\xi_{0r})} \tag{A.11}$$

or, using (A.5),

$$\delta\kappa_r = \frac{\eta_r}{\xi_{0r}^2 - \xi_{0r}^{-2}}\cdot \tag{A.12}$$

Formulae (A.10, A.12, A.9, A.7) yield the four solutions of (A.4)

$$\xi_r(m) = \exp\Big[\epsilon'_r\kappa_0 + \mathrm{i}\epsilon_r\pi/2 - \mathrm{i}\epsilon_r\frac{H_x}{2\sqrt{B(B+D)(s^2-m^2)}} - \epsilon_r\epsilon'_r\frac{H_y}{2\sqrt{BD(s^2-m^2)}} - \epsilon'_r\frac{H_z}{2(s-m)\sqrt{D(B+D)}}\Big]\cdot \tag{A.13}$$

It is convenient to introduce solutions of the truncated Schrödinger equation (9) (for $m \neq \pm s, \pm(s-1)$) which reduce to (32) when the field vanishes. For instance

$$\begin{aligned}\tilde{\varphi}_1(m) &= \mathrm{Const}\times\left\{\prod_{p=-s}^{m}\xi_a(p) + \prod_{p=-s}^{m}\xi_b(p)\right\}\\ &= \mathrm{Const}\times\mathrm{e}^{-\kappa_0(s+m)}\Big\{\exp\Big[\mathrm{i}m\pi/2 - \mathrm{i}\sum_{p=-s}^{m}\frac{h_x}{\sqrt{s^2-p^2}} + \sum_{p=-s}^{m}\frac{h_y}{\sqrt{s^2-p^2}} + \sum_{p=-s}^{m}\frac{h_z}{s-p}\Big]\\ &\quad + \exp\Big[-\mathrm{i}m\pi/2 + \mathrm{i}\sum_{p=-s}^{m}\frac{h_x}{\sqrt{s^2-p^2}} - \sum_{p=-s}^{m}\frac{h_y}{\sqrt{s^2-p^2}} + \sum_{p=-s}^{m}\frac{h_z}{s-p}\Big]\Big\}\end{aligned} \tag{A.14}$$

where h_x, h_y, h_z are defined by (38, 46, 39). A function $\tilde{\varphi}_2(m)$ can be defined by replacing the sum of exponentials in (A.14) by their difference. Functions $\tilde{\varphi}_3(m)$

and $\tilde{\varphi}_4(m)$ can be defined analogously to $\tilde{\varphi}_1(m)$ and $\tilde{\varphi}_2(m)$ by replacing ξ_a and ξ_b by ξ_c and ξ_d.

The typical term in the sums between brackets in (A.14) is of the order of h_α/s, so that the replacement of the sums by integrals is allowed if $h_\alpha \ll s$. In the discussion of the phase of the wave function, this leads to (40).

A.3 Orthogonality relations

Because $\tilde{\varphi}_1$ and $\tilde{\varphi}_4$ are almost even-valued and $\tilde{\varphi}_2$ and $\tilde{\varphi}_3$ are almost odd-valued, they almost satisfy the orthogonality relations (18). These relations are exactly satisfied by functions $\varphi_1(m) = \tilde{\varphi}_1(m) + \lambda\tilde{\varphi}_2(m)$, $\varphi_2(m) = \mu\tilde{\varphi}_1(m)+\tilde{\varphi}_2(m)$, $\varphi_3(m) = \tilde{\varphi}_3(m)+\lambda'\tilde{\varphi}_4(m)$ and $\varphi_4(m) = \mu'\tilde{\varphi}_3(m)+\tilde{\varphi}_4(m)$, where the small corrections λ, μ, λ', μ' can be obtained by inserting these relations into (18).

When s goes to ∞, the sums in (A.14) can be replaced by the integrals (41, 42), so that (A.14) reads

$$\begin{aligned}\tilde{\varphi}_1(m) = \text{Const} \times \exp\left[-\kappa_0(s+m) + h_z\Psi(m/s)\right]\\ \times \left\{\cos\left[m\pi/2 - h_x\Phi(m/s)\right]\cosh\left[h_y\Phi(m/s)\right]\right.\\ \left.+\,\mathrm{i}\sin\left[m\pi/2 - h_x\Phi(m/s)\right]\sinh\left[h_y\Phi(m/s)\right]\right\}\cdot\end{aligned}$$

A similar expression can be obtained for $\tilde{\varphi}_2$. Insertion into $\varphi_1(m) = \tilde{\varphi}_1(m) + \lambda\tilde{\varphi}_2(m)$ yields (45), with $\tan\alpha_1 = -\lambda$.

Similar expressions of $\varphi_2(m)$, $\varphi_3(m)$ and $\varphi_3(m)$ can be derived. These expressions are only valid in the tunneling region. However the functions $\varphi_r(m)$ can in principle be deduced for all values of m from the truncated Schrödinger equation if their form is known in the tunneling region.

A.4 Higher order terms

The above formalism can be extended to spin Hamiltonians which contain a fourth order term $\mathcal{H}_4 = -AS_z^4 - A'(S_-^4 + S_+^4) - A''S_x^4$. Assuming $A'' = 0$, formula (A.5) is modified as

$$\begin{aligned}F(\xi) = \left(\xi+\xi^{-1}\right)^2 - \frac{4A}{B}(s^2+m^2)\\ - \frac{4A'}{B}(s^2-m^2)\left(\xi^4+\xi^{-4}\right).\qquad \text{(A.15)}\end{aligned}$$

For $A = A' = A'' = 0$, the tunneling frequency was found to be dominated by a factor which can be deduced from the study of the tunneling region $s - |m| \gg 1$ alone, which was done in the second part of this appendix. The fourth order terms probably do not alter this property.

If $A' = 0$, but $A \neq 0$, the methods of this appendix can be transposed at the cost of minor algebraic complications. In particular, the solutions $\xi_0(m)$ of (A.4) depend on m. It follows that the basis functions $\varphi_r(m)$ are given by formulae which are appreciably more complicated than (45). The dependence in m is not exponential even for $H_z = 0$. The expression of the tunnel frequency is more complicated than (35). However, for $H_y = 0$ and weak fields, the basis functions $\varphi_r(m)$ still depend on H_x through the single factor $\cos\left[m\pi/2 - h_x\Phi(m/s) + \alpha_r\right]$, so that diabolic fields are still given by a condition on $h_x\Phi(1)$. The same analysis as above shows that this condition is still $h_x\Phi(1) = (2n+1)\pi/2$. The expression of $\Phi(m/s)$ is modified, so that (55) does not hold, but the zeros of the tunneling frequency are still equidistant.

The term in A' in (A.15) has a more severe effect because $\xi_0(m)$ is now given by an algebraic equation of degree 8, not 4. Thus, 8 basis functions are needed. The expected effect are that the zeros of the tunneling frequency are no longer equidistant, and this expectation is confirmed by numerical simulations. However, if A' is not very large, there are 4 basis functions which decay very rapidly and give a negligible contribution to the tunnel frequency. The 4 other basis functions can be treated perturbatively, replacing $\left(\xi^4+\xi^{-4}\right)$ by $\left(\xi_0^4+\xi_0^{-4}\right)$ in (A.15). The resulting complications are the same as those which result from the AS_z^4 term.

Appendix B: Diabolic point of a spin 1

In this appendix, model (1) is considered in the case $s = 1$ and $H_y = H_z = 0$. Using (8), the matrix $\langle m|\mathcal{H}|m'\rangle$ is found as

$$\mathcal{H} = \begin{bmatrix} -D+B' & -H' & B' \\ -H' & 2B' & -H' \\ B' & -H' & -D+B' \end{bmatrix} \qquad \text{(B.1)}$$

with $H' = g\mu_\mathrm{B}H/\sqrt{2}$ and $B' = B/2$. The antisymmetric eigenvector $(1, 0, -1)$ has obviously the eigenvalue $-D$. The symmetric eigenvectors (u, v, u) are given by

$$\begin{bmatrix} -D+B'-E & -H' & B' \\ -H' & 2B'-E & -H' \\ B' & -H' & -D+B'-E \end{bmatrix}\begin{bmatrix} u \\ v \\ u \end{bmatrix} = 0 \qquad \text{(B.2)}$$

or

$$\begin{bmatrix} -D+2B'-E & -H' \\ -2H' & 2B'-E \end{bmatrix}\begin{bmatrix} u \\ v \end{bmatrix} = 0$$

hence

$$\begin{aligned}&\begin{vmatrix} -D+2B'-E & -H' \\ -2H' & 2B'-E \end{vmatrix}\\ &= (-D+2B'-E)(2B'-E) - 2H'^2 = 0. \qquad \text{(B.3)}\end{aligned}$$

Exact degeneracy occurs if the antisymmetric eigenvalue $E = -D$ is solution of (B.3), *i.e.* $2B'(2B'+D) - 2H'^2 = 0$. Substitution of $H' = g\mu_\mathrm{B}H/\sqrt{2}$ and $B' = B/2$ yields

$$g\mu_\mathrm{B}H_x = \sqrt{B(D+B)} \qquad \text{(B.4)}$$

which is identical with (55) with $n = 0$.

Appendix C: Corrections

In this appendix, the form of the dominant correction to (35) for large s will be obtained in zero field. One can use (27) with the exact values

$$K_m(E)=\frac{\langle m|\mathcal{H}-E|m\rangle}{B\,\langle m|BS_y^2|m+2\rangle}$$
$$=\frac{2(B+2D)(s^2-m^2)-4\epsilon s}{B\sqrt{(s-m)(s-m-1)(s+m+1)(s+m+2)}} \quad \text{(C.1)}$$

and

$$L_m=\frac{\langle m|S_+^2|m-2\rangle}{\langle m|S_-^2|m+2\rangle}$$
$$=\sqrt{\frac{(s-m+1)(s-m+2)(s+m)(s+m-1)}{(s-m)(s-m-1)(s+m+1)(s+m+2)}}, \quad \text{(C.2)}$$

where the notation

$$\epsilon s=E-\frac{Bs}{2}+Ds^2, \quad \text{(C.3)}$$

has been introduced

For $s-|m|\gg 1$, (C.1, C.2) can be approximated by

$$K_m(E)\simeq {K_m}^{(0)}+\frac{{K_m}^{(1)}}{s-m}+\frac{{K'_m}^{(1)}}{s+m} \quad \text{(C.4)}$$

and

$$L_m\simeq 1+\frac{{L_m}^{(1)}}{s-m}+\frac{{L'_m}^{(1)}}{s+m} \quad \text{(C.5)}$$

where $K_m^{(0)}$, etc., are constants.

Inserting (C.4, C.5) into (27), the solutions are seen to have the form

$$X^{\pm}(m)\simeq -\mathrm{e}^{\pm 2\kappa_0}\left[1+\frac{A^{\pm}}{s-m}+\frac{B^{\pm}}{s+m}\right] \quad \text{(C.6)}$$

where $A^{\pm}$ and $B^{\pm}$ are constants. Therefore, for an even spin s,

$$\varphi_1(2q)=(-1)^q\varphi_1(-s)\prod_{p=-s/2+1}^{q}X^-(2p)$$
$$=(-1)^q\varphi_1(-s)\exp\left[\sum_{p=-s/2+1}^{q}\ln X^-(2p)\right]$$

or, using (C.6) and replacing the sums by integrals,

$$\varphi_1(2q)\simeq(-1)^q\varphi_1(-s)\exp\Big[-\kappa_0(2q+s)+\frac{1}{2}\int_{-s}^{2q}\frac{A^-\mathrm{d}u}{s-u}+\frac{1}{2}\int_{-s+2}^{2q}\frac{B^-}{s+u}\Big]$$
$$=(-1)^q\varphi_1(-s)\exp\Big[-\kappa_0(2q+s)+\frac{A^-}{2}\ln\frac{s-2q}{2s}+\frac{B^-}{2}\ln(s+2q)\Big]. \quad \text{(C.7)}$$

The quantity $\mathcal{A}_{41}$, which appears in the expression of the tunnel splitting, is dominated by the factor

$$\varphi_1(s)\simeq\varphi_1(-s)\exp\left[-2\kappa_0 s-\frac{A^-}{2}\ln(2s)+\frac{B^-}{2}\ln(2s)\right]$$
$$\approx\exp(-2\kappa_0 s)s^{(B^--A^-)}. \quad \text{(C.8)}$$

It follows that

$$\hbar\omega_{\mathrm{T}}=\mathrm{Const}\times\exp(-2\kappa_0 s)s^Q \quad \text{(C.9)}$$

where $Q=B^--A^-$

The factor $\mathrm{e}^{-2\kappa_0 s}$ corresponds to (35) and the next factor is a correction which, as expected, has a slower variation than an exponential.

The calculation of the constant in (C.9) would require an analysis of the region $m\approx\pm s$. This might be expected to be unavoidably numerical, but Garg [31] seems to have found an analytic way.

Appendix D: Condition for total degeneracy

In this appendix, it is shown that (16) can has two independent eigenvectors for the eigenvalue 0 if certain conditions are satisfied. The two vectors can be written as $(u_1,u_2,1,0)$ and $(v_1,v_2,0,1)$. Equation (16) will be split into 2, namely

$$\begin{pmatrix}\mathcal{A}_{11}&0&\mathcal{A}_{13}&\mathcal{A}_{14}\\0&\mathcal{A}_{22}&\mathcal{A}_{23}&\mathcal{A}_{24}\end{pmatrix}\begin{pmatrix}u_1\\u_2\\1\\0\end{pmatrix}=\begin{pmatrix}\mathcal{A}_{11}&0&\mathcal{A}_{13}&\mathcal{A}_{14}\\0&\mathcal{A}_{22}&\mathcal{A}_{23}&\mathcal{A}_{24}\end{pmatrix}\begin{pmatrix}v_1\\v_2\\0\\1\end{pmatrix}=0 \quad \text{(D.1)}$$

and

$$\begin{pmatrix}\mathcal{A}_{31}&\mathcal{A}_{32}&\mathcal{A}_{33}&0\\\mathcal{A}_{41}&\mathcal{A}_{42}&0&\mathcal{A}_{44}\end{pmatrix}\begin{pmatrix}u_1\\u_2\\1\\0\end{pmatrix}=\begin{pmatrix}\mathcal{A}_{31}&\mathcal{A}_{32}&\mathcal{A}_{33}&0\\\mathcal{A}_{41}&\mathcal{A}_{42}&0&\mathcal{A}_{44}\end{pmatrix}\begin{pmatrix}v_1\\v_2\\0\\1\end{pmatrix}=0. \quad \text{(D.2)}$$

The solution of (D.1) is

$$u_1=-\mathcal{A}_{13}/\mathcal{A}_{11},\quad u_2=-\mathcal{A}_{23}/\mathcal{A}_{22},\quad v_1=-\mathcal{A}_{14}/\mathcal{A}_{11},\quad v_2=-\mathcal{A}_{24}/\mathcal{A}_{22}. \quad \text{(D.3)}$$

Insertion of (D.3) into (D.2) yields

$$\mathcal{A}_{31}\mathcal{A}_{13}\mathcal{A}_{22}+\mathcal{A}_{32}\mathcal{A}_{23}\mathcal{A}_{11}-\mathcal{A}_{11}\mathcal{A}_{22}\mathcal{A}_{33}=0, \quad \text{(D.4)}$$

$$\mathcal{A}_{41}\mathcal{A}_{13}\mathcal{A}_{22}+\mathcal{A}_{42}\mathcal{A}_{23}\mathcal{A}_{11}=0, \quad \text{(D.5)}$$

$$\mathcal{A}_{41}\mathcal{A}_{14}\mathcal{A}_{22} + \mathcal{A}_{42}\mathcal{A}_{24}\mathcal{A}_{11} - \mathcal{A}_{11}\mathcal{A}_{22}\mathcal{A}_{44} = 0 \quad \text{(D.6)}$$

and

$$\mathcal{A}_{31}\mathcal{A}_{14}/\mathcal{A}_{22} + \mathcal{A}_{32}\mathcal{A}_{24}/\mathcal{A}_{11} = 0. \quad \text{(D.7)}$$

However (D.7) is the complex conjugate of (D.5), and therefore a consequence of (D.5). We are left with two real equations (D.4, D.6) and a complex equation (D.5). In other words, there are 4 real equations for 4 real parameters E, H_z, H_x and H_y.

It is convenient to rewrite (D.4) in the form (58). Insertion of (58) into (D.5) yields (59). Equation (60) can be deduced from (58, 59), but is more easily obtained from (58) by a permutation of the indices (1234) into (4321).

Appendix E: The zero-field ground state out of the tunneling region

For large s, and $\epsilon = 0$, (C.1) and (C.2) read for $m < 0$

$$K_m(E) = \frac{2(1+2D/B)}{\sqrt{1-1/(s+m)}} L_m \quad \text{(E.1)}$$

and

$$L_m = \sqrt{\frac{(s+m)(s+m-1)}{(s+m+1)(s+m+2)}}\,. \quad \text{(E.2)}$$

Formula (27) now reads

$$|X_{m+2}| = K_m(E) - \frac{L_m}{|X_m|} = L_m\left[\frac{2(1+2D/B)}{\sqrt{1-1/(s+m)}} - \frac{1}{|X_m|}\right]\cdot \quad \text{(E.3)}$$

If $|X_m| > 1$, (E.3) implies

$$|X_{m+2}| > L_m\left[2(1+2D/B) - 1\right] = (1+4D/B)L_m. \quad \text{(E.4)}$$

The values of L_m are $L_s + 2 = 0.41$, $L_s + 4 = 0.63$, $L_s + 6 = 0.73$, $L_s + 8 = 0.79$, with a regular convergence to 1. Thus, if D/B is large enough, *e.g.* $D/B > 1$, (E.4) implies $|X_{m+2}| > 1$. If X_{-s+2} is arbitrarily chosen to satisfy $X_{-s+2} < -1$, then (27) generates an increasing function $\varphi(m)$ which can be identified with $\varphi_4(m)$ as stated in Section 5.

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