Diabolical points in the magnetic spectrum of Fe₈ molecules

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(received 1 October 1999; accepted in final form 8 March 2000)

PACS. 75.10.Dg – Crystal-field theory and spin Hamiltonians.
PACS. 75.50.Xx – Molecular Magnets.
PACS. 03.65.Bz – Foundations, theory of measurement, miscellaneous theories (including Aharonov-Bohm effect, Bell inequalities, Berry’s phase).

Abstract. – The magnetic molecule Fe₈ has been predicted and observed to have a rich pattern of degeneracies in its spectrum as an external magnetic field is varied. These degeneracies have now been recognized to be diabolical points. This paper analyzes the diabolicity and all essential properties of this system using elementary perturbation theory. A variety of arguments is given to suggest that an earlier semiclassical result for a subset of these points may be exactly true for arbitrary spin.

The molecular cluster [Fe₈O₂(OH)₁₂(tacn)₆]⁸⁺ (or just Fe₈ for short) has a total spin \( J = 10 \) at low temperatures, and is described to a first approximation by the spin Hamiltonian [1–3]

\[
\mathcal{H} = k₁J_x^2 + k₂J_y^2 - gμ_B \mathbf{J} \cdot \mathbf{H},
\]

where \( k₁ > k₂ > 0 \), and \( \mathbf{H} \) is an external magnetic field. Thus the axes \( x, y, \) and \( z \) are hard, medium, and easy, respectively. EPR measurements indicate \( k₁ ≈ 0.33 \) K, \( k₂ ≈ 0.22 \) K.

In the absence of any applied magnetic field, the spin of the molecule has degenerate classical minima along the \( ±\hat{z} \) directions. Application of a field cant the minima away from \( ±\hat{z} \), but the degeneracy is preserved if \( \mathbf{H} \) is in the \( x-y \) plane. This degeneracy is lifted by quantum-mechanical tunnelling between the low-energy orientations. It is of some interest to calculate the tunnel splitting \( Δ \), since tunnelling plays an important role in the low-temperature dynamics. A few years ago, without knowledge of the relevance of eq. (1) to Fe₈, it was predicted [4] that, for \( \mathbf{H} \parallel \hat{x} \), \( Δ \) would oscillate as a function of \( H \), with perfect zeros at certain values, and this effect was explained in terms of interference arising from a Berry phase in the spin path integral. These oscillations have now been seen by Wernsdorfer and Sessoli [5] using a clever technique which enables Landau-Zener-Stückelberg (LZS) transitions between the levels in question. The underlying value of \( Δ \) can be extracted from the observed LZS transition rate.

In addition to the predicted oscillations, however, Wernsdorfer and Sessoli have also observed oscillations for certain non-zero values of \( H_z \) as \( H_x \) is swept. Villain and Fort [6] have noted that if \( H_z \) is chosen properly, these oscillations also represent perfect degeneracy, i.e.,
\(\Delta\) again vanishes exactly at isolated points in the \(H_x-H_z\) plane (or the full three-dimensional \((H_x, H_y, H_z)\) space). Thus, all the zeros of \(\Delta\) are, in fact, "diabolical points" in the magnetic field space. (This coinage is due to Berry and Wilkinson [7], as the shape of the energy surface when plotted against two parameters in the Hamiltonian — \(H_x\) and \(H_z\) in our case — is a double elliptic cone joined at the vertex, which resembles an Italian toy called diavolo.) Formulas for these points have been found by Villain and Fort, and independently by the author [8] (see below).

Diabolical points are of interest because of their rarity in real-life physical systems. Indeed, the von Neumann-Wigner theorem states that as a single parameter in a Hamiltonian is varied, an intersection of two levels is infinitely unlikely, and that level repulsion is the rule. It is useful to review the argument behind this theorem. Let the energies of the levels in question be \(E_1\) and \(E_2\), which we suppose to be far from all other levels. Under an incremental perturbation \(V\), the secular matrix is

\[
\begin{pmatrix}
E_1 + V_{11} & V_{12} \\
V_{21} & E_2 + V_{22}
\end{pmatrix},
\]

with \(V_{21} = V_{12}^\ast\). The difference between the eigenvalues of this matrix is given by

\[
[(E_1 - E_2 + V_{11} - V_{22})^2 + 4|V_{12}|^2]^{1/2},
\]

which vanishes only if

\[
E_1 + V_{11} = E_2 + V_{22}, \quad V_{12} = V_{12}^\ast = 0.
\]

Hence, for a general Hermitian matrix, three conditions must be satisfied for a degeneracy, which in general requires at least three tunable parameters. If the matrix is real and symmetric, the number of conditions and tunable parameters is reduced to two [9].

An exception to this rule occurs when the Hamiltonian has some symmetry, when levels transforming differently under this symmetry can intersect. For the \(\text{Fe}_8\) problem, the intersections when \(H \parallel \hat{x}\) or \(H \parallel \hat{z}\) can be understood in terms of symmetry [10], but those with both \(H_x\) and \(H_z\) non-zero cannot.

The results reported in ref. [8] are based on a generalization [11] of the discrete phase integral (or WKB) method [12,13], and are asymptotically accurate as \(J \to \infty\). Villain and Fort use an approximate version of the same method, with the additional condition \(k_1 - k_2 \ll k_1\). These calculations while involving only elementary methods of analysis, still entail the development of considerable calculational machinery, and are quite long. Surprisingly, the full global structure of the energy spectrum can be obtained by a much simpler method — textbook perturbation theory in \(k_2/k_1\) and the field components \(H_y, H_z\). This is an extension of an earlier calculation by Weigert [14], who analysed the problem for \(H_y = H_z = 0\). In particular, one can rigorously establish the existence of diabolical points, and find formulas for their locations via a series of small calculations. It is hoped that the simplicity of this approach will make the subject accessible to a wide readership.

Before proceeding further, it is useful to develop a scheme for labelling the eigenstates of \(\mathcal{H}\). Suppose first that \(H = 0\), and \(k_2 = k_1\). The states can then be labelled by the eigenvalue \(m\) of \(J_z\), and the ground states are \(m = \pm J\). If \(k_2\) is now decreased, states with \(m\) differing by an even integer will mix. If \(k_1 - k_2 \ll k_2\), or \(J\) is large, the barrier between \(m = -J\) and \(m = +J\) is large (see fig. 1), tunnelling is negligible, and we can find states \(|m^\ast\rangle\) which evolve continuously from \(|m\rangle\), such that \(\{m^\ast\}\) are eigenstates of \(\mathcal{H}\) to a good approximation. This approximation will continue to hold if the field \(H\) is turned on, as long as \(|H| \ll H_c = 2k_1J/g\mu_B\).
The first set of diabolical points lies on the line $H_y = H_z = 0$, because $\mathcal{H}$ is then invariant under a 180° rotation about $\hat{\mathbf{x}}$. Levels with different parity under this operation can intersect as $H_x$ is varied. In particular, the pseudo-ground states $m^* = \pm J$ are exactly degenerate at a sequence of $H_x$ values as found in ref. [4]. Since the symmetry is destroyed if either $H_y \neq 0$ or $H_z \neq 0$, so are the intersections, and the points are indeed diabolical. The same is true of intersections of levels with $m^* = \pm (J - \ell)$, where $\ell$ is an integer.

A similar argument applies when $\mathbf{H} \parallel \hat{\mathbf{z}}$, so another set of diabolical points is expected when $H_x = H_y = 0$. In terms of fig. 1, the states which are degenerate are no longer symmetrically located, and it is possible for, say, $m^* = -J$ to be degenerate with $m^* = J - 1$. The new discovery by Wernsdorfer and Sessoli is that the tunnel splitting between these states also oscillates as $H_x$ is now varied. As mentioned above, these oscillations are also perfect, and the corresponding diabolical points are not associated with any obvious symmetry of $\mathcal{H}$. (A similar situation holds in the spectrum of a particle confined to a two-dimensional triangular region [7]. Apart from an overall size, which only affects the overall energy scale in a trivial manner, a triangle is parametrized by two angles. Two sets of diabolical points arise when the triangles are isosceles, but the rest appear when the triangles are scalene with no special symmetry.)

We can thus classify the diabolical points by the $m^*$ numbers of the levels which are degenerate. Let the state with predominantly negative values of $m$ be labelled by $m_1^*$, and the other state by $m_2^*$. We define $k = m_1^* + J$, and $k' = m_2^* - J$. In other words, counting from 0, the $k$-th level in the left well is degenerate with state number $k'$ in the right well. When $k, k' \ll J$, the semiclassical analysis gives the location of the diabolical point as ($H_y = 0$ always)

$$h_x = \frac{\sqrt{1 - \lambda}}{J} \left[ J - \ell - \frac{1}{2} (k + k' + 1) \right],$$

$$h_z \approx \frac{\sqrt{\lambda}}{2J} (k - k').$$

Here, $h = \mathbf{H}/H_c$ is a reduced field with $H_c = 2k_1 J/g\mu_B$, $\lambda = k_2/k_1$, and $\ell$ is an integer.

Another way to label the degeneracies is to number the levels in order of increasing energy, starting with 1 for the lowest level, and then simply give the numbers of the two crossing levels. Thus if the lowest two levels are degenerate ($k = k' = 0$), we will say that levels 1 and 2 cross, while for $k = 0, k' = 1$, or $k = 1, k' = 0$, we would say that levels 2 and 3 cross. This labelling is not unique, but we will find it convenient.

Fig. 1 – Schematic energy level diagram when $k_2 \approx k_1$. 
With this background, we now turn to our calculations. Following Weigert [14] we regard the $k_2$ term in eq. (1) as the perturbation, along with the $y$ and $z$ components of $\mathbf{H}$. It is convenient to divide all energies by $k_1$, and write $\bar{\mathcal{H}} = \mathcal{H}/k_1 = \mathcal{H}_0 + \mathcal{H}_1$, where
\begin{align}
\mathcal{H}_0 &= J_x^2 - 2Jh_x J_x, \\
\mathcal{H}_1 &= \lambda J_y^2 - J(h_- J_+ + h_+ J_-),
\end{align}
where $J_\pm = J_y \pm iJ_z$, $h_\pm = h_y \pm ih_z$. These notations for $J_\pm$ are unconventional, but they are now convenient, as we will take the quantization axis to be $x$, not $z$. We will label the eigenvalue of $J_x$ by $n$. To zeroth order, the energy of state $n$ is given by
\begin{equation}
E^{(0)}_n = n^2 - 2Jh_x n.
\end{equation}
Levels $n$ and $n'$ are approximately degenerate if $Jh_x = (n + n')/2$. To see if they are exactly degenerate when $\bar{\mathcal{H}}_1$ is included, we find the secular matrix $V$ to an appropriate order in perturbation theory, and examine the conditions (4). We do this for a number of different cases.

**Case 1: levels 1 and 2 cross.** – Let the degenerate levels be $n_0$ and $n_0 + 1$, so that $Jh_x \approx (n_0 + 1/2)$. For brevity, we label the states by A and B, and denote the matrix elements $\langle n_0 + 1|J_-|n_0\rangle$ etc. by $a_1$, $a_2$, $a_3$, etc., as indicated in fig. 2. Note that all $a_i$ can be chosen as real. To first order in $\lambda$ and $h_\pm$,
\begin{align}
V_{AA} &= \lambda[J(J + 1) - n_0^2]/2, \\
V_{BB} &= \lambda[J(J + 1) - (n_0 + 1)^2]/2, \\
V_{AB} &= -Jh_+ a_2.
\end{align}
The conditions for diabolicity are thus
\begin{equation}
Jh_x = (n_0 + 1/2)(1 - \frac{1}{2}\lambda), \quad h_y = h_z = 0.
\end{equation}
Writing $n_0 = J - \ell - 1$, this is identical to eqs. (5) and (6) with $k = k' = 0$, once we recognize that $(1 - \lambda/2) = (1 - \lambda)^{1/2} + O(\lambda^2)$. Since $-J \leq n_0 \leq J - 1$, there are $2J$ such points.
The conclusion that these points lie on the line \( h_y = h_z = 0 \) is unchanged if we go to higher order. The relevant condition is clearly that for off-diagonal elements. Contributions to the AB element of the second-order secular matrix arise from intermediate states \( n_0 + 1 \) and \( n_0 - 1 \). A short calculation gives \( V_{AB}^{(2)} = \lambda a_2 J(a_1^2 + a_0^2)h_{-}/8 \). Adding this to eq. (12) and setting the sum to zero, we again obtain the conditions \( h_y = h_z = 0 \).

**Case 2: levels 2 and 3 cross.** Let the lowest energy level be \( n_0 \), and let \( n_0 \pm 1 \) be approximately degenerate. This requires \( Jh_x \approx n_0 \). Again, we denote the states \( n_0 \pm 1 \) by A and B, and the various matrix elements of \( J_\pm \) by \( a_1 \) to \( a_4 \) as in fig. 3. To \( O(\lambda) \), \( V_{AA} \) and \( V_{BB} \) are given by \( \lambda[J(J+1) - (n_0 \pm 1)^2]/2 \). The order \( h_\gamma^2 \), \( h_\epsilon^2 \) contributions to the diagonal terms of the second-order secular matrix are found to be both equal to \( 4J^2(h_\gamma^2 + h_\epsilon^2)[J(J+1) - n_0^2 + 1]/3 \). The interesting terms are \( V_{AB} \) and \( V_{BA} \). Including first-order pieces from \( \lambda J_y^2 \), and second order pieces from \( h_\pm \), we get
\[
V_{AB} = (\frac{1}{4} \lambda + J^2 h_\pm^2) a_2 a_3.
\]

For a diabolical point, therefore, the vector \( h \) must have components
\[
h = \frac{1}{J} \left[ n_0 \left( 1 - \frac{1}{2} \lambda \right), 0, \frac{1}{2} \sqrt{\lambda} \right].
\]

With \( n_0 = J - \ell - 1 \), these are exactly the lowest-order terms in an expansion in \( \lambda \) of eqs. (5) and (6) with \( k = 1 \). Since \( -J \leq n_0 \leq J - 1 \), there are \( 2J - 1 \) such points.

**Case 3: levels 3 and 4 cross.** This case can arise either with \( k = k' = 1 \), or with \( k = 2 \), \( k' = 0 \), but we shall be able to distinguish between these. Referring to fig. 2 again, the degenerate levels are \( n_0 - 1 \) (C) and \( n_0 + 2 \) (D). Equality of \( E_C \) and \( E_D \) again requires \( Jh_x \approx (n_0 + \frac{1}{2}) \). To first order in \( \lambda \), \( V_{CC} - V_{DD} = -3\lambda(n_0 + 1) \), so that the diagonal elements are equal when
\[
Jh_x = (n_0 + 1)(1 - \frac{1}{2} \lambda).
\]

As in case 2, it is the off-diagonal term which is of greater interest. The secular matrix is now diagonal in first order, and off-diagonal terms only arise in second and higher orders. Second-order terms arise from the combination of one \( h_\pm J_\pm \) term and one \( \lambda J_y^2 \) term, while third-order terms arise from three \( h_\pm J_\pm \) terms. The net result is
\[
V_{CD} = -\frac{1}{4}(h_\pm^2 J^2 + \lambda)h_+Ja_1a_2a_3.
\]

This can vanish in two ways. The first is to have \( h_y = h_z = 0 \), in which case the diabolical field is given by eq. (13) again. This case corresponds to \( k = k' = 1 \).

The second way for \( V_{CD} \) to vanish is for the factor in parentheses in eq. (17) to vanish. This happens when
\[
h_y = 0, \quad h_z = \sqrt{\lambda}/J.
\]

In conjunction with eq. (16), this is seen to be the same as eqs. (5) and (6) with \( k = 2 \), \( k' = 0 \), and \( n_0 = J - \ell - 2 \).

It is clear that this procedure gets rapidly more tedious if we apply it to cases with larger \( k \) and \( k' \). It is more useful to consider higher-order perturbative corrections for the cases treated above. In the argument leading to eq. (16), e.g., we have only gone up to \( O(\lambda) \). It is obvious that inclusion of higher-order terms can at best alter the value of \( h_x \) at the diabolical point by terms of order \( \lambda^2 \), \( h_\gamma^2 \), and \( h_\epsilon^2 \), but cannot destroy the existence of a perfect degeneracy.

The same argument applies in all the other cases, and constitutes a constructive proof of the existence of diabolical points.
It is particularly interesting to investigate the subset of diabolical points on the line $H_y = H_z = 0$ in greater depth. As noted before, these points correspond to $k = k'$, and the degenerate levels have $n$ quantum numbers differing by an odd integer. Thus they can never be coupled by the remaining perturbation $H_\perp = \lambda J_y^2$, and the problem is effectively one of non-degenerate perturbation theory. Let us consider case 1 first. The second-order correction to the energy of state A arises from the intermediate states $n_0 \pm 2$, and to that of state B from $n_0 - 1$ and $n_0 + 3$. It suffices to find the energy denominators assuming that $Jh_x = (n_0 + \frac{1}{2})$. A short calculation gives

$$
\begin{pmatrix}
V_{AA}^{(2)} \\
V_{BB}^{(2)}
\end{pmatrix} = \frac{-2}{3} \lambda^2 \left[ (J(J+1) - (n_0^2 + n_0 + 1))^2 + 2n_0^2 + \left( -n_0 - \frac{1}{5n_0 + 2} \right) \right].
$$

Along with eqs. (9)-(11), this means that to $O(\lambda^2)$, the states are degenerate when

$$
Jh_x = (n_0 + \frac{1}{2})(1 - \frac{1}{2} \lambda - \frac{1}{8} \lambda^2),
$$

which is precisely what eq. (5) also gives.

In the same way, for the subcase $k = k' = 1$ of case 3, we obtain

$$
\begin{pmatrix}
V_{CC}^{(2)} \\
V_{DD}^{(2)}
\end{pmatrix} = \frac{-1}{40} \lambda^2 \left[ (J(J+1) - (n_0^2 + n_0 + 1))^2 - 6n_0^2 + \left( \frac{9n_0 - 4}{21n_0 - 19} \right) \right].
$$

Including lower-order terms, the condition for degeneracy is found to be identical to eq. (20).

The fact that the two pairs of states $k = k' = 0$, and $k = k' = 1$ are simultaneously degenerate (at least to order $\lambda^2$), is very striking. Calculations to $O(\lambda^2)$ were in fact done by Weigert [14], but he did not perform them sufficiently explicitly, and reached the opposite conclusion, i.e., that the degeneracy conditions would be different. It is clear, however, that this equality is a result of the simple form of $\mathcal{H}$, and is violated when higher anisotropies such as $(J_x \pm iJ_y)^4$ are included.

The second striking feature about the result (20) is that there are no terms like $\lambda^2 J^2$ or $\lambda^2 n_0^4$, etc. on the right-hand side, and that it agrees precisely with the semiclassical answer. Since the latter is obtained in a very different limit, namely, $J \to \infty$, it begins to raise the suspicion that it might be exact. To test this suspicion, we have carried the calculation for case 1 to order $\lambda^3$. For this, not only must we find $V_{AA}^{(3)}$ and $V_{BB}^{(3)}$, but we must also keep $O(\lambda)$ corrections in the energy denominators in the calculations for $V_{AA}^{(2)}$ and $V_{BB}^{(2)}$, since $Jh_x$ depends on $\lambda$ at the diabolical point. The resulting calculation is lengthy, but is efficiently done using MAPLE. Almost miraculously, all powers of $J$ multiplying $\lambda^3$ cancel, as do terms $\lambda^3 n_0^j$, with $j \geq 2$, and the contribution to $E_A - E_B$ is just $\lambda^3 (2n_0 + 1)/16$. The condition for degeneracy thus becomes

$$
Jh_x = (n_0 + \frac{1}{2})(1 - \frac{1}{2} \lambda - \frac{1}{8} \lambda^2 - \frac{1}{16} \lambda^3).
$$

It will not have escaped the reader that the last factor equals $(1 - \lambda)^{1/2}$ to $O(\lambda^3)$!

It is useful to consider the structure of the perturbation series to higher order in $\lambda$. It is clear that we cannot get negative powers of $J$ in the formula for $Jh_x$; instead it generates positive powers. Although the low-order analysis suggests otherwise, in principle we should expect terms such as $\lambda^N J^K (J + 1)^K$, with $0 < K < N - 1$ in $N$-th order. Such terms would be reminiscent of an asymptotic series, and would signal a zero radius of convergence. Such a situation would be very odd in our problem since the perturbation $\lambda J_y^2$ does not appear to
be singular. Although plausible, this is far from a complete argument that such terms are in fact absent, since we have not excluded terms such as $\lambda^N n_0^{N-1}$ in $N$-th order.

Further evidence that the result (5) is exact comes from looking at low values of $J$. We have done this for $J$ up to 2. For $J = 1/2$, there is nothing to prove as the only degeneracy is at $h_x = 0$, which is also guaranteed by Kramers’s theorem. For $J = 1$, the energies are directly found to be $E_{\pm 1} = 1 + \frac{1}{4} \lambda \mp (4h_x J^2 + \frac{1}{4} \lambda^2)^{1/2}$, and $E_0 = \lambda$, so $E_1 = E_0$ when $Jh_x = (1 - \lambda)^{1/2}/2$. For $J = 3/2$, $\mathcal{H}$ separates into two $2 \times 2$ matrices in the $J_x$ basis, which we call $M_1$ and $M_2$. Both eigenvalues of $M_1$ coincide with those of $M_2$ at $h_x = 0$. This is again Kramers’s degeneracy. In addition, one eigenvalue of $M_1$ coincides with one of $M_2$ precisely when $h_x = 2(1 - \lambda)^{1/2}/3$. For $J = 2$, $\mathcal{H}$ separates into a $3 \times 3$ matrix ($M_1$) and a $2 \times 2$ matrix ($M_2$). The expected degeneracies are at $h_x = (1 - \lambda)^{1/2}/4$ and $3(1 - \lambda)^{1/2}/4$. At the second value of $h_x$, one eigenvalue of $M_1$ indeed coincides with one of $M_2$. At $h_x = (1 - \lambda)^{1/2}/4$, however, two distinct $M_1$ eigenvalues coincide with two $M_2$ eigenvalues. Thus we again see the simultaneous degeneracy of two sets of levels ($k = k' = 0$, and $k = k' = 1$), leading us to believe that this feature is also generally true. A rigorous proof of these conjectures remains an open problem.

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This work is supported by the National Science Foundation through Grant No. DMR-9616749.

REFERENCES

[1] Barra A.-L. et al., Europhys. Lett., 35 (1996) 133.
[2] Sangregorio C. et al., Phys. Rev. Lett., 78 (1997) 4645.
[3] Caciuffo R. et al., Phys. Rev. Lett., 81 (1998) 4744.
[4] Garg A., Europhys. Lett., 22 (1993) 205.
[5] Wernsdorfer W. and Sessoli R., Science, 284 (1999) 133.
[6] Villain J. and Fort A., preprint, July 1999.
[7] Berry M. and Wilkinson M., Proc. R. Soc. London, Ser. A, 392 (1984) 15.
[8] Garg A., Proceedings of the 22nd International Conference on Low Temperature Physics, August 4–11, 1999, Helsinki, to appear in Physica B.
[9] Arnold V. I., Mathematical Methods of Classical Mechanics (Springer-Verlag, New York) 1978. See Appendix 10.
[10] Garg A., Phys. Rev. B, 51 (1995) 15161.
[11] Garg A., Phys. Rev. Lett., 83 (1999) 4385.
[12] Dingle R. B. and Morgan G. J., Appl. Sci. Res, 18 (1967) 221.
[13] van Hemmen J. L. and Sütő A., Europhys. Lett., 1 (1986) 481; Physica B, 141 (1986) 37.
[14] Weigert S., Europhys. Lett., 26 (1994) 561.