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A group theoretical study of planar methyl rotation

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Abstract. Most papers on methyl group tunnelling use a model in which the motion of a rigid rotator is hindered by a potential of threefold symmetry. There are a number of difficulties with such a description and, in this paper, the model is replaced by one which describes the motion of three protons, which have mutual interactions and which are hindered by an external potential. The analysis makes considerable use of symmetry ideas and arrives at conclusions which are substantially different from those of the previous model. A comparison of the two models shows that, in the absence of dipolar interactions, both will have an orbital singlet level with spin of $\frac{3}{2}$, but that the level described as ^{2}E in the rigid-rotator model will not occur in the present model and that there will be no corresponding level with fourfold degeneracy. Instead there will be two separated orbital singlets, each with spin $\frac{1}{2}$. The inclusion of the dipolar interaction splits the quartet into two doublets, so that finally there are four separated low-lying energy levels, each being doubly degenerate.

1. Introduction

Many papers concerned with the hindered rotation of methyl groups have used a Hamiltonian of the form

$$(-\hbar^2/2I)(\partial^2/\partial\varphi^2) + V(\varphi)$$

where the first term describes a free rotor and the second a hindering potential of threefold symmetry. It then follows that the low-lying single-particle energy levels consist of a singlet and a doublet so that, with three protons, the low-lying many-particle states should consist of a spin quartet, labelled ^{4}A and two doubly degenerate spin-$\frac{1}{2}$ states, labelled ^{2}E. The use of such a Hamiltonian is, at first sight, surprising, for the protons in a methyl group can hardly be regarded as free, the coordinate φ is not usually defined, and in most cases the hindering potential does not have threefold symmetry. In an attempt to understand why this model is, apparently, so successful, a specific model of three protons interacting through a mutual interaction, in the presence of a hindering potential, was considered by one of us (Stevens 1983, hereafter referred to as I). It was found that a Hamiltonian of the above form could be obtained if φ was identified with a specific variable, but even then it was necessary to use different boundary conditions for the two types of solution: those with spin-$\frac{1}{2}$ and those with spin-$\frac{3}{2}$. It is also apparent,

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although it was not stressed, that the description ^{2}E of one of the levels is inappropriate, for the eigenstates are not direct products of spin and orbital variables. In parallel with this investigation, which was entirely algebraic, Clough and McDonald (1983) carried out a numerical study and concluded that, although the E doublet is not split, its long-standing symmetry description is incorrect. The same conclusion was reached in I. The purpose of this paper is to show that, using general arguments, the doublet can be expected to be split, which suggests that both the models were insufficiently general.

The model to be discussed has similarities to that of I, the main difference being that the emphasis will be placed on symmetry considerations. An additional feature will be the inclusion of magnetic dipolar interactions between the nuclear spins, which is found to produce a splitting of the otherwise degenerate quartet levels and so is of experimental interest.

The Hamiltonian is taken to be

$$(-\hbar^2/2m_0r_0^2)(\partial^2/\partial\varphi_1^2 + \partial^2/\partial\varphi_2^2 + \partial^2/\partial\varphi_3^2) + U(\varphi_1 - \varphi_2) + U(\varphi_2 - \varphi_3) + U(\varphi_3 - \varphi_1) + V(\varphi_1) + V(\varphi_2) + V(\varphi_3) + W_{12} + W_{23} + W_{31}. \tag{1}$$

It is intended to represent three protons which can move on a circle of radius r_0, with the φ-variables describing their angular positions on the circle. $U(\varphi_1 - \varphi_2)$ describes a mutual potential energy between particles 1 and 2, and $V(\varphi_1)$ describes the potential energy of particle 1 in a hindering potential of no particular symmetry. W_{12}, which is given specifically below, is the dipolar interaction between particles 1 and 2. It takes the form

$$W_{12} = \{\gamma_N^2\beta_N^2/r_0^3[2 - 2\cos(\varphi_1 - \varphi_2)]^{3/2}\} \times \left\{\boldsymbol{I}^1\cdot\boldsymbol{I}^2 - \frac{\frac{3}{4}[I_+^1\exp(-i\varphi_1) + I_-^1\exp(i\varphi_1)][I_+^2\exp(-i\varphi_2) + I_-^2\exp(i\varphi_2)]}{[2 - 2\cos(\varphi_1 - \varphi_2)]}\right\}.$$

After some rearrangement this can be written as

$$W_{12} = \{\gamma_N^2\beta_N^2/r_0^3[2 - 2\cos(\varphi_1 - \varphi_2)]^{3/2}\}[\tfrac{1}{2}(2I_z^1I_z^2 - I_x^1I_x^2 - I_y^1I_y^2) + \tfrac{3}{2}\sin(\varphi_1 + \varphi_2)(I_x^1I_y^2 + I_y^1I_x^2) + \tfrac{3}{2}\cos(\varphi_1 + \varphi_2)(I_x^1I_x^2 - I_y^1I_y^2)]. \tag{2}$$

As the emphasis throughout is on symmetry it is an important requirement, with identical particles, that the Hamiltonian is invariant under their interchanges. It then follows that $U(\varphi_1 - \varphi_2) = U(\varphi_2 - \varphi_1)$, showing that U is invariant under reversals of the φ-values. In the absence of the W interactions no spin variables occur in H; so all eigenstates can be taken to be eigenstates of total spin (either $I = \frac{1}{2}$ or $I = \frac{3}{2}$). Inclusion of the W potentials produces a coupling between spins and orbital motion and so reduces the overall symmetry. In particular, W is not invariant under reversal of the φ-values, although the loss in symmetry can be partially restored by requiring that, on reversal of the φ-values, $I_+(I_x + iI_y)$ and $I_-(I_x - iI_y)$ interchange. The potentials V may or may not be invariant under reversal of the φ-values but, as will emerge, there is little loss in generality if it is assumed that the V are invariant. This will therefore be generally assumed, and the case where they are not invariant will be discussed separately.

Because of the contrast with the rigid-rotator theory it is convenient, at this point, to stress that all the symmetry operations are performed on the form of the Hamiltonian.

No geometrical types of argument about the shape of the molecule or the effects of physically interchanging particles are used.

Finally it will be assumed that all the potentials contain parameters which, on changing their values, alter the potentials without changing their symmetry properties. Among the various possibilities will be that of eliminating some particular interaction. It can then be argued that, if a given eigenvalue has eigenstates which transform irreducibly under the symmetry operations of the appropriate symmetry group of the Hamiltonian for a particular choice of parameters, then, on changing the parameters, the corresponding eigenvalues and eigenstates may alter, but in such a way that the irreducible representation stays unaltered.

2. The symmetry elements

To obtain the symmetry group of the Hamiltonian and then its irreducible representations it is first necessary to define some basic symmetry operators. These will now be listed, with $\alpha(1)$ denoting one of the $I = \frac{1}{2}$ spin components of particle 1 and $\beta(1)$ denoting its other component, the axis of quantisation being taken as in the z direction, i.e. perpendicular to the plane of the proton triangle. (This is already implied by the form of W.)

Thus the operation C has the following property:

$$\begin{array}{lccc} & \varphi_1 \to \varphi_2 & \alpha(1) \to \alpha(2) & \beta(1) \to \beta(2) \\ C: & \varphi_2 \to \varphi_3 & \alpha(2) \to \alpha(3) & \beta(2) \to \beta(3) \\ & \varphi_3 \to \varphi_1 & \alpha(3) \to \alpha(1) & \beta(3) \to \beta(1). \end{array}$$

Similarly,

$$\begin{array}{lccc} & \varphi_1 \to \varphi_2 & \alpha(1) \to \alpha(2) & \beta(1) \to \beta(2) \\ \sigma: & \varphi_2 \to \varphi_1 & \alpha(2) \to \alpha(1) & \beta(2) \to \beta(1) \\ & \varphi_3 \to \varphi_3 & \alpha(3) \to \alpha(3) & \beta(3) \to \beta(3) \end{array}$$

and

$$\begin{array}{lccc} & \varphi_1 \to -\varphi_1 & \alpha(1) \to \mathrm{i}\beta(1) & \beta(1) \to \mathrm{i}\alpha(1) \\ T: & \varphi_2 \to -\varphi_2 & \alpha(2) \to \mathrm{i}\beta(2) & \beta(2) \to \mathrm{i}\alpha(2) \\ & \varphi_3 \to -\varphi_3 & \alpha(3) \to \mathrm{i}\beta(3) & \beta(3) \to \mathrm{i}\alpha(3). \end{array}$$

It immediately follows that $C^3 = E = \sigma^2 = T^4$, where E is the unit operator. Also, T is equivalent to $\mathrm{i}(I_+ + I_-)$ within $I = \frac{1}{2}$; so $T^{-1}(I_+)T = (I_+ + I_-)I_+(I_+ + I_-) = I_-$, and vice versa, which shows that the operation on the Hamiltonian by T leaves it invariant, even when the dipolar interaction is included. T has the further property that it commutes with C and σ and so with all the elements of the subgroup to which they give rise, which is the permutation group on three symbols. Since this group has six elements and three classes, it follows that the symmetry group of the Hamiltonian has 24 elements and 12

Table 1. Irreducible representations of the group.

	E	$2C$	3σ	T	$2TC$	$3T\sigma$	T^2	$2T^2C$	$3T^2\sigma$	T^3	$2T^3C$	$3T^3\sigma$
Γ_1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	−1	−1	−1	1	1	1	−1	−1	−1
Γ_3	1	1	1	i	i	i	−1	−1	−1	−i	−i	−i
Γ_4	1	1	1	−i	−i	−i	−1	−1	−1	i	i	i
Γ_5	1	1	−1	1	1	−1	1	1	−1	1	1	−1
Γ_6	1	1	−1	−1	−1	1	1	1	−1	−1	−1	1
Γ_7	1	1	−1	i	i	−i	−1	−1	1	−i	−i	i
Γ_8	1	1	−1	−i	−i	i	−1	−1	1	i	i	−i
Γ_9	2	−1	0	2	−1	0	2	−1	0	2	−1	0
Γ_{10}	2	−1	0	−2	1	0	2	−1	0	−2	1	0
Γ_{11}	2	−1	0	2i	−i	0	−2	1	0	−2i	i	0
Γ_{12}	2	−1	0	−2i	i	0	−2	1	0	2i	−i	0

classes. Its character table is given in table 1. An important requirement is that any state of physical significance must be reversed on interchanging two particles. The operator which does this is σ. In the one-dimensional irreducible representations, only Γ_5, Γ_6, Γ_7 and Γ_8 have character -1; so of the one-dimensional representations these are the only four relevant ones. Coming now to the two-dimensional irreducible representations the following argument shows that they are irrelevant. With any chosen two-dimensional representation it is possible to choose the basis pair so that the matrix of σ is diagonal. Its diagonal elements are therefore 1 and -1. The member of the pair which goes with 1 is invariant under σ, whereas the member with -1 reverses. However, since the representation is irreducible, it must be possible to choose elements of the group which admix the basis states, and these are neither invariant nor reversed by σ. So the states in a two-dimensional representation are not all reversed by σ and therefore do not satisfy the antisymmetry requirement.

3. Special case

It is now convenient to examine once more the model used in I, which is a special case of the Hamiltonian obtained by choosing the parameters in it so that W and V are absent and U describes a potential which is everywhere large except when $\varphi = 2\pi/3$. New variables

$$X = (\varphi_1 - \varphi_2)/\sqrt{2}$$

$$Y = (\varphi_1 + \varphi_2 - 2\varphi_3)/\sqrt{6}$$

and

$$Z = (\varphi_1 + \varphi_2 + \varphi_3)/\sqrt{3}$$

are introduced, and the Hamiltonian becomes

$$H \equiv (-\hbar^2/2m_0r_0^2)(\partial^2/\partial X^2 + \partial^2/\partial Y^2 + \partial^2/\partial Z^2) + U(\sqrt{2}\,X) + U(\sqrt{\tfrac{3}{2}}\,Y - \sqrt{\tfrac{1}{2}}\,X) + U(-\sqrt{\tfrac{3}{2}}\,Y - \sqrt{\tfrac{1}{2}}\,X).$$

It separates into

$$H_Z + X_{XY}$$

where

$$H_Z = (-\hbar^2/2m_0r_0^2)(\partial^2/\partial Z^2)$$

and

$$H_{XY} = (-\hbar^2/2m_0r_0^2)(\partial^2/\partial X^2 + \partial^2/\partial Y^2) + U(\sqrt{2}\,X) + U(\sqrt{\tfrac{3}{2}}\,Y - \tfrac{1}{2}X) + U(-\sqrt{\tfrac{3}{2}}\,Y - \sqrt{\tfrac{1}{2}}\,X).$$

The eigenstates of H_Z are of the form $\exp(i\lambda Z)$. Those of H are found by examining the form of

$$U(\sqrt{2}\,X) + U(\sqrt{\tfrac{3}{2}}\,Y - \sqrt{\tfrac{1}{2}}\,X) + U(-\sqrt{\tfrac{3}{2}}\,Y - \sqrt{\tfrac{1}{2}}\,X)$$

in the (X, Y) plane, where it is found that there are deep minima at six points which lie on a hexagon, and which are equivalent to a lattice of points because the whole Hamiltonian is invariant under the increase in any φ by a multiple of 2π. If the U potential is supposed to be a delta function, it can be assumed that the eigenstates of H_{XY} are highly localised in these wells and each will be orthogonal to the other five. This assumption was made in I, although it was also pointed out that, if they are not orthogonal, then group theoretical arguments can be used to obtain six mutually orthogonal states. It is this idea that we now pursue, except that in general it is necessary to consider 12 states. Under the symmetry elements of the group, as applied to H_{XY}, the six states corresponding to the six minima in the (X, Y) plane give a reducible representation with the characters, in the order of the classes, being 6 0 0 0 0 2 6 0 0 0 0 2. It is, however, not the properties of H_{XY} which are of interest, but those of H, and to study these it is necessary to multiply the states of H_{XY} by those of H_Z. For the case when λ is zero this is simply a numerical multiple; so the above characters are the appropriate ones. They give rise to the representations $\Gamma_1 + \Gamma_6 + \Gamma_9 + \Gamma_{10}$. However, when λ is non-zero, each state of H_{XY} is multiplied by either $\exp(i\lambda Z)$ or by $\exp(-i\lambda Z)$, which doubles the number of states and produces the character sequence 12 0 0 0 0 0 12 0 0 0 0 0 0, which is equivalent to $\Gamma_1 + \Gamma_2 + \Gamma_5 + \Gamma_6 + 2\Gamma_9 + 2\Gamma_{10}$. It is then necessary to take the spin into account, and with three spins of $\frac{1}{2}$ there are eight possible spin states, which give the character sequence 8 2 4 0 0 0 −8 −2 −4 0 0 0, or $2\Gamma_3 + 2\Gamma_4 + \Gamma_{11} + \Gamma_{12}$. Alternatively, the states with total spin $\frac{3}{2}$ give the sequence 4 4 4 0 0 0 −4 −4 −4 0 0 0, or $2\Gamma_3 + 2\Gamma_4$, and the two families with spin $\frac{1}{2}$ give the sequence $\Gamma_{11} + \Gamma_{12}$. To obtain the overall set of irreducible representations the irreducible representations for the orbital states must be multiplied by those for the spin states and reduced to irreducible form. In so doing, only those of Γ_5, Γ_6, Γ_7 and Γ_8 type need be retained, for these are the only ones of physical importance. The final results are that with $\lambda = 0$ and $I = \frac{3}{2}$ the states transform as $2\Gamma_7 + 2\Gamma_8$. With $\lambda = 0$ and $I = \frac{1}{2}$ the states transform as $2\Gamma_7 + 2\Gamma_8$. With $\lambda \neq 0$ and $I = \frac{3}{2}$ the states transform as $4\Gamma_7 + 4\Gamma_8$, and with $\lambda \neq 0$ and $I = \frac{1}{2}$ the states transform as $4\Gamma_7 + 4\Gamma_8$.

With the delta function for U the lowest states will have $\lambda = 0$ and the six orbital states can be combined with the $I = \frac{3}{2}$ spin manifold to give four states, transforming as $2(\Gamma_7 + \Gamma_8)$, but Γ_7 and Γ_8 are conjugate representations and so can be expected to have the same energies. Also there is higher symmetry in the spin space than has been assumed in the symmetry group used, because the spin is not coupled to the orbital variables; so the four states are actually degenerate and form a spin quartet. This particular level can be described as ${}^4\Gamma_6$, for all the spin parts are symmetric under σ and the overall

antisymmetry is entirely due to an orbital part of Γ_6 symmetry. Similarly the six orbital states can, alternatively, be combined with the $I = \frac{1}{2}$ spin manifolds, of which there are two. The result, $2(\Gamma_7 + \Gamma_8)$, is again a pair of conjugate irreducible representations. A Γ_7 will always be degenerate with a Γ_8, because they are conjugate representations, but there is no *a priori* reason why one (Γ_7, Γ_8) pair should be degenerate with another such pair. However, in the present example, with the delta function for U, this can be expected to occur, and indeed it can be expected that they will coincide in energy with the quartet. This is the point which was overlooked in I, that in arriving at the conclusion that there would be a ^{4}A and a 'doublet E' (using the incorrect description) it should also have been found that they would not be separated in energy. The fact that they are, experimentally, implies that something is wrong with the Hamiltonian, and the obvious correction is to use a modified U. In fact the experimental evidence appears to be that the splitting (or splittings?) of the ground states are more determined by the hindering potential than by the internal interaction of the methyl group; so it would seem preferable to include V as well.

4. General model

Once V is included, the Hamiltonian no longer separates into an H_Z and an H_{XY} part and the determination of the eigenstates and eigenvalues becomes an even more difficult problem. However, the symmetry of H is unaltered; so, provided that any extra splittings are small, the low-lying energy levels should be spanned by the same irreducible representations as found for the special case. Thus all that should happen is that the energy levels and states will change retaining any basic degeneracies. It may be noted that all the representations of the special case are of the type $\Gamma_7 + \Gamma_8$, where the two have been associated because they are conjugate representations and so must remain degenerate. This degeneracy can also be regarded as an example of Kramers' degeneracy, an essential degeneracy associated with an odd number of particles with spin $\frac{1}{2}$. However, with W omitted, there is nothing to couple spins with orbits; so there must be more degeneracy than the above for the states with $I = \frac{3}{2}$. The upshot must be that the low-lying levels consist of two separated spin doublets and a spin quartet, with similar conclusions for the excited levels. This conclusion has been reached by symmetry arguments, using a V such that $V(\varphi) = V(-\varphi)$. All possible degeneracies have now been lifted; so adding another term to V of odd symmetry can have no further effect on the degeneracies. In fact the only remaining question is can the spin quartet be split by an interaction which couples spin and orbits together? W is such an interaction. Also from the form of (2) it is apparent that in the spin space the operators in it transform like second-rank tensors and they cannot split spin doublets, either because $D_{1/2} \times D_{1/2} = D_0 + D_1$ does not contain D_2, or from Kramers' theorem. They can, however, split a spin quartet, as is seen because

$$D_{3/2} \times D_{3/2} = D_0 + D_1 + D_2 + D_3$$

contains D_2, or by using equivalent operators. The only possible reservation to this can arise because the reduced matrix element depends on the expectation value of the orbital part of W taken over the orbital wavefunction. There is no reason to suppose that this is zero.

5. Discussion

The use of the symmetry properties of a general model of the motion of hindered methyl rotation has shown that far from ^4A and ^2E being a correct description of the low-lying levels it is much more likely that there are four low-lying energy levels each with twofold degeneracy. The $I = \frac{3}{2}$ is split by the dipolar interaction and the two $I = \frac{1}{2}$ levels should not have been described as ^2E in the first place. In fact all the levels should be regarded as Kramers' degenerate levels, or given the description $\Gamma_7 + \Gamma_8$. Once this is realised, it seems hardly necessary to go through a detailed theory for a glance at the character table (table 1) shows all that is really needed. There are only four irreducible representations which give antisymmetric many-particle states—$\Gamma_5, \Gamma_6, \Gamma_7$ and Γ_8—and only two of these produce twofold degeneracy, as required by Kramers' theorem. These are Γ_7 and Γ_8. No other degeneracy is to be expected except in special cases where there is more symmetry.

As an illustration of the effect of higher symmetry it is of interest to consider the case when the parameters in H are chosen so that U and W are zero. The particles then move independently. The lowest single-particle level can be expected to be similar to the $J = 0$ state of a free rotator and the first excited states, instead of being doubly degenerate as is the free rotator level, with $J = 1$, will be split by the potential V, unless it has threefold symmetry. The lowest states for three particles will have two spin-paired protons in $J = 0$, with the remaining proton in one or other of the split $J = 1$ states. This will produce two closely spaced doublet levels as the ground states. However, if V has threefold symmetry, they will coincide in energy. The quartet state is produced by putting a proton in each of $J = 0, +1$ and -1, with their spins parallel.

It will have been noticed that no specific reference has been made to the experimental position, except that the hindering seems to cause splittings. There are several reasons why the experiments give little guidance. It is not easy to determine the low-lying energy spectrum and to establish the nature of their states, primarily because of selection rule difficulties. So the techniques which have been employed are, for the most part, quite complicated in nature, and there is then the question of how to interpret them. In many cases this has been done using, as a framework, the ^4A and ^2E picture, which is probably incorrect (see Wurger (1989), Heidemann *et al* (1989), Vuorimaki and Punkkinnen (1989) and Horsewill and Aibout (1989), which are good reference sources for work using this scheme). We are thus unable to claim that experiment supports the conclusions which follow from our analysis. A further complication arises because the experiments seem to show that, in any case, the splittings are temperature dependent, and there is no way in which such an effect can arise in the context of the present model. So while our model would seem to be an improvement in so far as it replaces a commonly used model it is still inadequate. It probably needs extension along the lines introduced by Hewson (1982) and Whittall and Gehring (1987).

Finally it is perhaps of interest to see how the ^4A, ^2E notation can arise. If three protons are placed at the corners of an equilateral triangle it may be assumed that they occupy orbitals φ_A, φ_B and φ_C, which transform into one another under rotations of the triangle. With these three orbitals, eight Slater determinantal functions can be formed, for at each site there are two possible spin orientations. The Dirac (1947) treatment can be used to show that their energy levels can be obtained from an effective Hamiltonian

$$J(\boldsymbol{I}^1 \cdot \boldsymbol{I}^2 + \boldsymbol{I}^2 \cdot \boldsymbol{I}^3 + \boldsymbol{I}^3 \cdot \boldsymbol{I}^1).$$

This Hamiltonian is invariant under interchanges of the spin labels and its eigenstates

can be given the labelling ^{4}A and ^{2}E. If, however, the triangle is distorted, H_{eff} takes the form

$$J_{12}\boldsymbol{I}^1 \cdot \boldsymbol{I}^2 + J_{23}\boldsymbol{I}^2 \cdot \boldsymbol{I}^3 + J_{31}\boldsymbol{I}^3 \cdot \boldsymbol{I}^1.$$

The symmetry for interchanges is reduced, if not eliminated, and the ^{2}E is split into two spin doublets. The antisymmetric nature of the wavefunctions remains unaltered. It seems that in a number of papers it is assumed that the antisymmetry under interchanges of particles is equivalent to interchanges of sites, and that this in turn has led to the assumption that they each appear to be in a hindering potential of threefold symmetry. Neither assumption is correct, in general. Rather it appears that the hindering potential produces a distortion of the equilateral triangle of protons so that there are, in general, two separated spin-$\frac{1}{2}$ doublets and, in the absence of spin–orbit coupling, a quartet. The latter will be split by the dipolar interaction; so the low-lying levels can be expected to consist of four Kramers' doublets.

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