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Rotational tunnelling of three coupled molecules

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Abstract. By means of both the variational method and the pocket-state formalism the energy levels of three coupled methyl or ammine groups are calculated for a wide range of potential parameters. In particular the case of a small one-particle potential is investigated where the energy spectrum is governed by the E^a–E^b splitting. The effects of different symmetries of the Hamiltonian on the spectrum are studied.

1. Introduction

Rotational tunnelling is a probe well suited to studying the inter-atomic potential between the various constituents of molecular crystals. The energy spectrum of a methyl or ammine group is in most cases well described by a Hamiltonian containing a simple static potential (Press 1981)

$$H = -\partial^2/\partial\varphi^2 - V\cos(3\varphi). \tag{1}$$

φ denotes the average angle of the three protons; the energies are given in units of the rotational constant B, which has values of about 650 μeV. Different crystal environments are accounted for by a variation in the parameter of the one-particle potential V.

There are two physical situations which require us to go beyond the static one-particle potential approximation. The thermal motion of the lattice leads to an additional time-dependent potential. The resulting temperature-dependent level shift and lifetime effects have been tackled in various approaches (Hüller 1980, 1989, Clough 1981, Hewson 1982, Würger 1989). The other case which the single-particle picture in equation (1) fails to describe is where there is a strong rotation–rotation coupling between adjacent molecules.

Then the potential cannot be separated and a rotational hindering barrier as in (1) is a bad representation of the inter-molecular interactions. As a consequence of the two-body forces the state vector for neighbouring molecules cannot be written as a product of one-particle states; in direct space this corresponds to a coherent rotational motion of adjacent molecules. There are two different effects of the surrounding groups on a given molecule.

(i) The E states are more strongly localised; thus an E-symmetric neighbour provides a higher molecular field than the A-symmetric one and the tunnelling splitting depends on the symmetry of the surrounding molecules.

(ii) An E-symmetric neighbour removes the degeneracy of the E^a and E^b states, i.e. right- and left-handed rotation correspond to different energies. An equivalent statement is that the Hamiltonian is not invariant under time reversal of the coordinate of a single molecule. Clearly, the total Hamiltonian does exhibit this symmetry, as there is no magnetic field.

In the great majority of experiments, rotational tunnelling seems to be a single-particle effect. There are, however, a few exceptions. The observed spectrum of LiAc (Clough *et al* 1984) could be explained by the assumption of coupled pairs. In $Pb(CH_3)_4$ and in various hexammine salts the environment of the methyl groups and the ammine molecules exhibits a high symmetry; hence the low-order Fourier components of the single-particle potential are expected to be small and the rotational barrier is mainly due to the rotor–rotor coupling. Finally, solid methane and the two-dimensional layers of methyl groups in $Sn(CH_3)_2F_2$ (Press 1981) provide examples of infinite systems of coupled molecules. In general, the coupling leads to several tunnelling lines with a characteristic temperature dependence.

Contrary to the problem of coupled oscillators which can be solved by Fourier transformation, there is no such method to calculate the energy levels of coupled methyl groups. So far only the problem of two coupled rotors has been treated exactly by diagonalising or inverting the Hamiltonian matrix (Clough *et al* 1984, Häusler and Hüller 1985). In this paper, we extend these calculations to three coupled groups. There are two new features with respect to previous work on two coupled rotors. The addition of a third molecule changes the symmetry properties and, as a consequence, the energy spectrum of the Hamiltonian drastically. Furthermore we focus on the case of strong coupling and small one-particle potential; this parameter range has been neglected so far. The symmetry of the potential in this work is of the kind relevant for the tetrahedral or octahedral coordination of the ligands in $Pb(CH_3)_4$ and in the hexammine salts. Besides a possible application to two sets of three ammine molecules each in $Ni(NH_3)_6I_2$ (Blank and Kearley 1987, Bates and Stevens 1969), the formalism is to be extended to the interesting cases of four or six coupled groups. From such calculations, one could obtain insight into the spectrum of an infinity of coupled tunnelling systems.

The organisation of the paper is as follows. In section 2 we introduce the model Hamiltonian and we discuss some symmetry properties. Then in section 3 we present numerical results for a wide range of parameters obtained by a variational treatment. In a complementary approach we reformulate the problem by means of Bloch states and we rederive the characteristics of the energy scheme. Section 4 is devoted to a discussion of the results.

2. The model Hamiltonian

We look at three molecular groups, each of which consists of a central atom and three protons. Exchange symmetry of the protons requires the Hamiltonian to be invariant under rotations $\varphi_i \rightarrow \varphi_i + 2\pi/3$, where φ_i is the average angle of the three protons of the ith molecule $\varphi_i \equiv \frac{1}{3}(\varphi_i^{(1)} + \varphi_i^{(2)} + \varphi_i^{(3)})$:

$$H(\varphi_i) = H(\varphi_i + 2\pi/3) \qquad i = 1, 2, 3. \tag{2}$$

For simplicity, we assume the molecular sites to be identical and for the coupling constants to be equal; a more general formulation would render the spectra more complicated without changing the essential features which we are interested in. When retaining only the lowest-order components of a Fourier expansion of the potential energy, we obtain the Hamiltonian

$$H = -\sum_i \left(\frac{\partial^2}{\partial\varphi_i^2} + V\cos(3\varphi_i)\right) - \sum_{i,j} W\cos(3\varphi_i + 3\varphi_j). \tag{3}$$

The Hilbert space splits into 27 irreducible subspaces which can be classified by symmetry quantum numbers for the three molecules: $\boldsymbol{k} = (k_1, k_2, k_3)$, where $k_i = 1$, 0 and -1 correspond to symmetries $\mathrm{E^a}$, A and $\mathrm{E^b}$, respectively. Owing to the identical potential parameters and the time reversal symmetry of (3) the 27 representations yield only six different level schemes.

For $V = 0$ we have in addition to the symmetry due to proton (2) an inversion centre at $\varphi_\mathrm{I} \equiv (\pi/6)(1, 1, 1)$ with respect to $\varphi \equiv (\varphi_1, \varphi_2, \varphi_3)$:

$$H(\varphi) = H(2\varphi_\mathrm{I} - \varphi). \tag{4}$$

This corresponds to the existence of two degenerate configurations of the three molecules. In contrast to the invariance under proton permutation, this is not an exact symmetry of the physical system. For molecular sites fulfilling (4), one expects a spontaneous symmetry breaking due to a static phonon. The situation described by (4) is analogous to that of a particle in a double-minimum potential.

3. Results

3.1. Variational treatment

We denote the eigenstates of (3) by their symmetry $\boldsymbol{k}$ and by a band index α (Matuschek and Hüller 1988). The former labels the 27 irreducible subspaces, and the latter enumerates the states therein, beginning with the ground-state multiplet $\alpha = 0$.

For the numerical work an expansion in a product basis of angular momentum eigenstates is most convenient:

$$|\alpha\boldsymbol{k}\rangle = \sum_{m,n,p} c_{mnp}^{(\alpha\boldsymbol{k})} |m\rangle\, |n\rangle\, |p\rangle. \tag{5}$$

The one-particle states $|m\rangle$ are defined by

$$\langle \varphi_i | m \rangle \equiv (1/\sqrt{2\pi}) \exp(\mathrm{i} m \varphi_i). \tag{6}$$

Owing to the symmetry of the Hamiltonian (2) the expansion coefficients in (5) vanish unless $(m - k_1)/3$, $(n - k_2)/3$ and $(p - k_3)/3$ are integers; these are the periodic boundary conditions in the angles φ_i for the wavefunction.

By means of the variational method we obtain the lowest energy level of symmetry $\boldsymbol{k}$ by minimising

$$E_{0\boldsymbol{k}}(\{c_{mnp}\}) \equiv \langle 0\boldsymbol{k}|H|0\boldsymbol{k}\rangle / \langle 0\boldsymbol{k}|0\boldsymbol{k}\rangle \tag{7}$$

with respect to the expansion coefficients. Higher levels $E_{\alpha\boldsymbol{k}}$ can be calculated by imposing orthogonality on the lower-lying states

$$\langle \beta\boldsymbol{k} | \alpha\boldsymbol{k} \rangle = 0 \qquad \text{for } 0 \leqslant \beta < \alpha. \tag{8}$$

In figures 1 and 2 we show the two lowest multiplets for various parameters. We distinguish four qualitatively different level schemes.

Regime I is the strong-coupling regime with zero bias ($W > 10$ and $V = 0$). The 54 levels of the two lowest bands are arranged in five groups with equal spacings Δ. Between the two A-symmetric groups there are two levels with the states which contain one, two or three E labels of the same type and the middle level with the states exhibiting at least one $\mathrm{E^a}$–$\mathrm{E^b}$ pair.

Regime II is the weakly biased regime ($W > 10$ and $\Delta \leqslant V < C$). C denotes some critical value of the one-particle potential which roughly equals unity. The non-zero bias splits the two bands by an energy of about $6V$; the arrangement of the various states is similar to that in regime II. The spacings are no longer equal; their ratio is about 1 : 3.

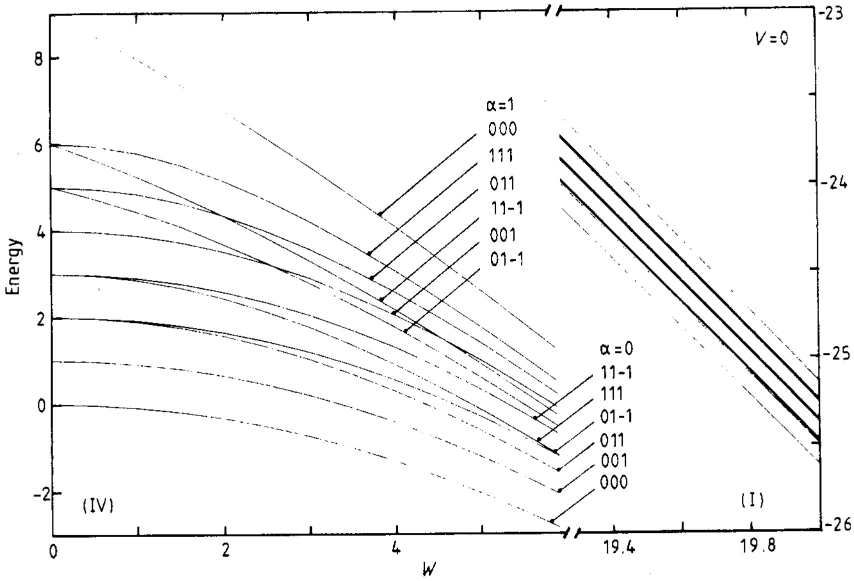

Figure 1. The two lowest-lying bands $\alpha = 0, 1$ for $0 \leqslant W \leqslant 20$ and $V = 0$.

Regime III is the strongly biased regime ($V \gg C$). The distribution of the 27 states in each band is very different from that described above. The energy spectrum is governed by the number of E-symmetric molecules with a negligibly small E^a–E^b splitting. The level spacings decrease with increasing number of E labels; for $V > W$ they become equal.

Regime IV is the free-rotor regime ($W < 1$ and $V < 1$): the spectrum is that of three almost free rotors; it contains states for which the total angular momentum (i.e. the sum of the squares of the individual angular momenta) does not exceed nine.

The calculation is confined to a Hilbert space Ω^3 of dimension 33^3, where $\Omega \equiv \{|m\rangle: -16 \leqslant m \leqslant 16\}$. This space separates into 27 subspaces of dimension 1331; for $V = 0$ these split further into two parts each. Hence the stationary solutions of (7) are determined by looking for the minimum of a function of 1330 variables, which is done numerically by means of library routines.

The variational treatment is exact in this finite-dimensional space. The results are most sensitive to the dimension for strong coupling; we have performed calculations in irreducible subspaces of dimension 2197 instead of 1331 and found deviations smaller than 10^{-4} which is negligible.

It is quite a difficult task to find the minimum of a function in such high-dimensional spaces. We have tested the computer program by starting the search from different initial values; it always discovered the correct minimum. The accord with the results from Bloch theory of § 3.2 assures that there is no systematic neglect of a lower-energy solution. Moreover, the energy spectra for the free-rotor regime IV and the strongly biased regime III agree with those obtained by perturbation theory and in the Hartree approximation, respectively.

3.2. *Pocket-state formalism*

In this section we give a complementary treatment of the tunnelling spectrum by setting up the state vector of pocket states localised in the various minima of the potential

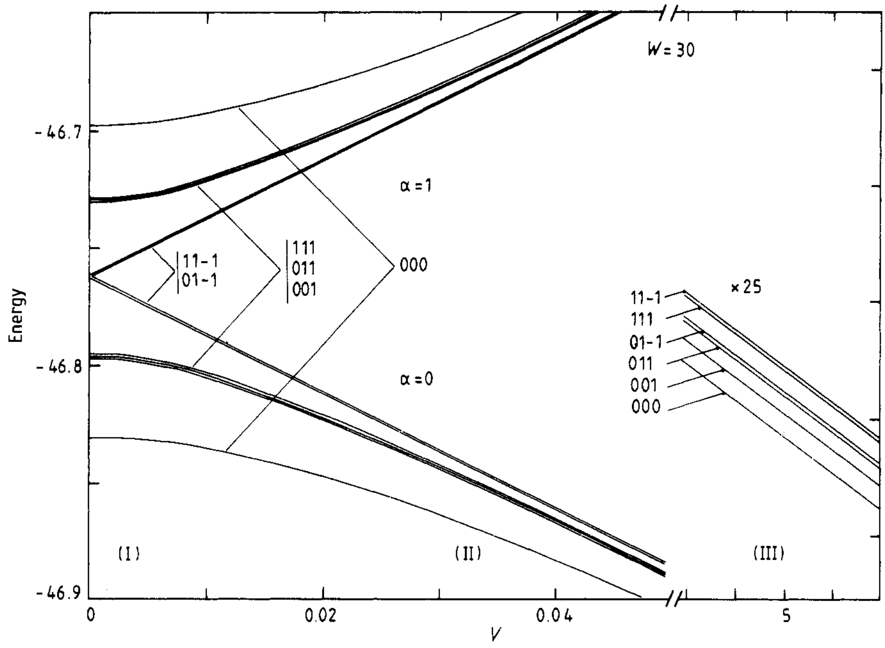

Figure 2. The two lowest-lying bands $\alpha = 0, 1$ for $W = 30$ and finite V.

energy. This method is analogous to the calculation of electronic energy bands starting from Wannier functions; it has been applied previously to the rotation of a single molecule (Hüller and Kroll 1975, Hüller 1980).

For $W > 0$ and $V = 0$ there are two sets of 27 minima at the sites of two simple cubic lattices $\varphi_{mnp} \equiv (\pi/3)(m, n, p)$: one with m, n, p even, and the other with m, n, p odd. A non-zero bias, $V > 0$, removes the degeneracy of the two sets; they are then separated by an energy of $6V$.

For strong coupling and vanishing one-particle potential the state vector can be written as a superposition of pocket states. We separate the phases corresponding to the symmetries (2) and (4); for $\alpha = 0, 1$ we have

$$|\alpha \boldsymbol{k}\rangle = \sum_{m,n,p} (1 - 2\alpha)^m \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\varphi}_{mnp}) \, |mnp\rangle. \tag{9a}$$

For large V we construct states from the two sets separately; they read, for $\alpha = 0, 1$,

$$|\alpha \boldsymbol{k}\rangle = \sum_{m,n,p} (1 + (-1)^{\alpha+m}) \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\varphi}_{mnp}) |mnp\rangle. \tag{9b}$$

By $|mnp\rangle$ we denote a state localised in the potential minimum at $\boldsymbol{\varphi}_{mnp}$.

As soon as one knows the Hamilton matrix in the pocket-state basis, i.e.

$$a_{mnp;m'n'p'} \equiv \langle mnp|H|m'n'p'\rangle \tag{10}$$

the energy spectrum is easily calculated by means of

$$E_{\alpha k} = \langle \alpha \boldsymbol{k}|H|\alpha \boldsymbol{k}\rangle / \langle \alpha \boldsymbol{k}|\alpha \boldsymbol{k}\rangle. \tag{11}$$

Obviously the main difficulty is to work out the matrix elements (10). We are interested in the level scheme rather than in absolute energies; thus we may make quite a crude approximation in estimating the non-diagonal elements of the Hamiltonian.

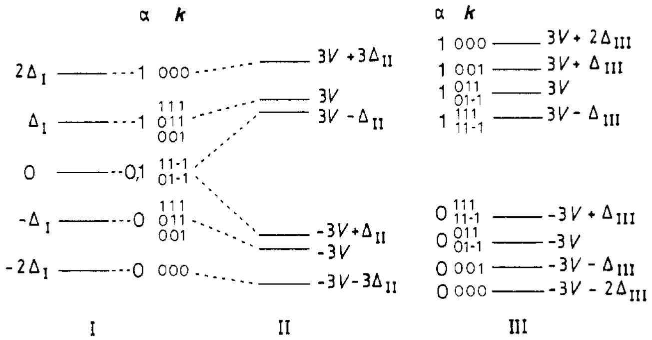

Figure 3. The level scheme obtained by means of equation (11) for strong coupling and three different ranges of the bias. As ±1 corresponds to E^a and E^b symmetry, levels differing in one sign display the E^a–E^b splitting.

We retain only elements between neighbouring minima, and we approximate them by means of the WKB exponent

$$\exp\left(-\int \mathrm{d}\eta \sqrt{D - U(\eta)}\right) \tag{12}$$

where D is the diagonal element in (10) and U is the barrier along a straight line between adjacent pockets. This is the simplest version of the WKB approximation, but it is sufficient for our purpose. We need not even compute the quantities (12) explicitly, because the dominant tunnelling paths can be determined from the distance between the pockets and the height of the barrier separating them.

We distinguish the following ranges for the potential parameters.

In the zero-bias range or regime I, owing to the lower barrier of $2W$ the matrix elements between pockets along space diagonals (with distance $\pi/\sqrt{3}$) are the most important; the state vector is given by (9*a*).

In the small-bias range or regime II, for $\Delta < V < C$ the state is restricted to 27 pockets as in (9*b*), but the tunnelling occurs via the other set of minima.

In the large-bias range or regime III, if V exceeds some critical value C, the matrix elements connecting pockets along a coordinate axis dominate the spectrum; their distance equals $2\pi/3$, and the barrier height is $4W + 2V$.

These ranges correspond to those discussed in § 3.2. By means of equations (9) and (11) the level schemes for the different values of the bias V are easily calculated; they are shown in figure 3.

This section was mainly motivated by a wish to confirm the validity of the numerical results of § 3.2. On the other hand, the pocket-state formalism in itself provides a powerful tool for the calculation of the energy spectrum of strongly coupled rotors, because it applies to higher coordination numbers as well, where the methods using an angular momentum basis are unsuitable because of the numerical expense. Clearly, then, a more thorough computation of the matrix elements (10) is required; the evaluation of (3) between harmonic oscillator states should be a reliable approach.

3.3. *The effect of a collective free-rotor coordinate*

The potential in (3) is incomplete in so far as we have neglected the one-particle sine component as well as the coupling term with the minus sign between the angles. Taking into account the latter, we obtain the coupling Hamiltonian

$$H = -\sum_i \frac{\partial^2}{\partial \varphi_i^2} - W^{(+)} \sum_{i,j} \cos(3\varphi_i + 3\varphi_j) - W^{(-)} \sum_{i,j} \cos(3\varphi_i - 3\varphi_j). \tag{13}$$

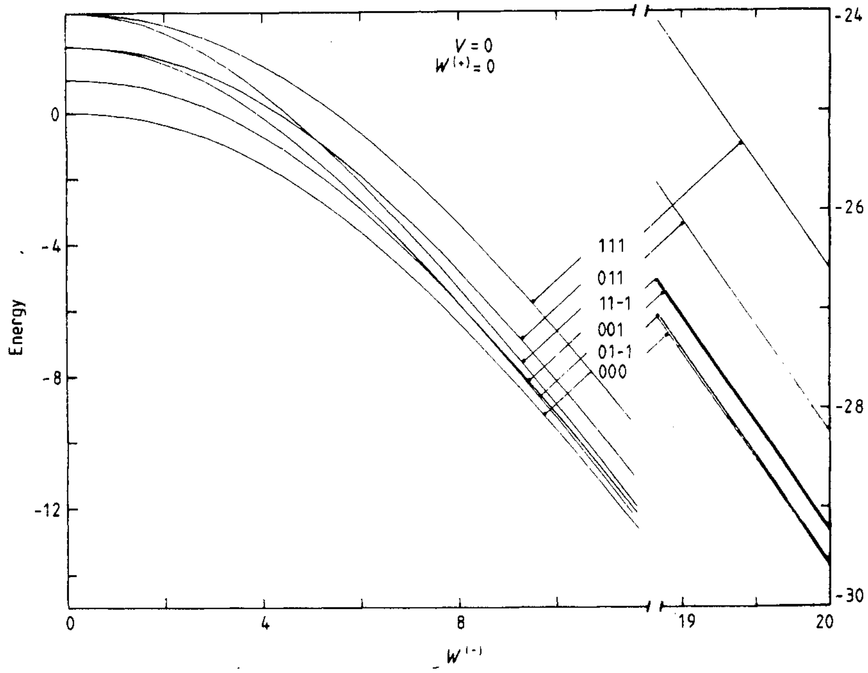

Figure 4. The levels of the lowest multiplet of the Hamiltonian (13) for $V = 0$ and $W^{(+)} = 0$.

This potential energy is minimum in a finite number of points in configuration space. For $W^{(+)} = 0$ these minima degenerate to lines, i.e. one can single out a collective coordinate which corresponds to a free rotor; then the Hamiltonian exhibits a continuous symmetry with respect to a collective rotation of the three molecules which corresponds to translational invariance along the principal diagonal in φ-space:

$$H(\varphi) = H[\varphi + t(1, 1, 1)] \qquad t \text{ real}, \quad W^{(+)} = 0. \tag{14}$$

In figure 4 we show the lowest-energy band as a function of $W^{(-)}$. For $W^{(-)} = 0$ the spectrum is that of three independent free rotors, whereas for strong coupling one obtains the levels of a single rotor with the triple moment of inertia as it is to be expected from the symmetry (14). For large $W^{(-)}$, the spectrum is described by

$$E_k = \text{constant} + \tfrac{1}{3}(k_1 + k_2 + k_3)^2. \tag{15}$$

A similar result has been derived for two coupled rotors (Häusler and Hüller 1985, Häusler 1988); there the rotational constant of the collective coordinate is $\frac{1}{2}$ instead of $\frac{1}{3}$ as in our case.

Figure 5 displays the behaviour of the energy spectrum when passing continuously from $W^{(-)} = 0$ to $W^{(+)} = 0$ and keeping $W^{(+)} + W^{(-)}$ constant. Besides these limiting cases, the parameter set $W^{(+)} = W^{(-)}$ is somewhat particular. The coupling potential then reads $2W^{(+)}\Sigma_{\langle ij\rangle} \cos(3\varphi_i) \cos(3\varphi_j)$; owing to the missing sine terms there is no E^a–E^b splitting.

4. Discussion

In the preceding sections we derived a variety of possible spectra for three coupled rotors. There are two different causes for the deviation from the usual scheme which is

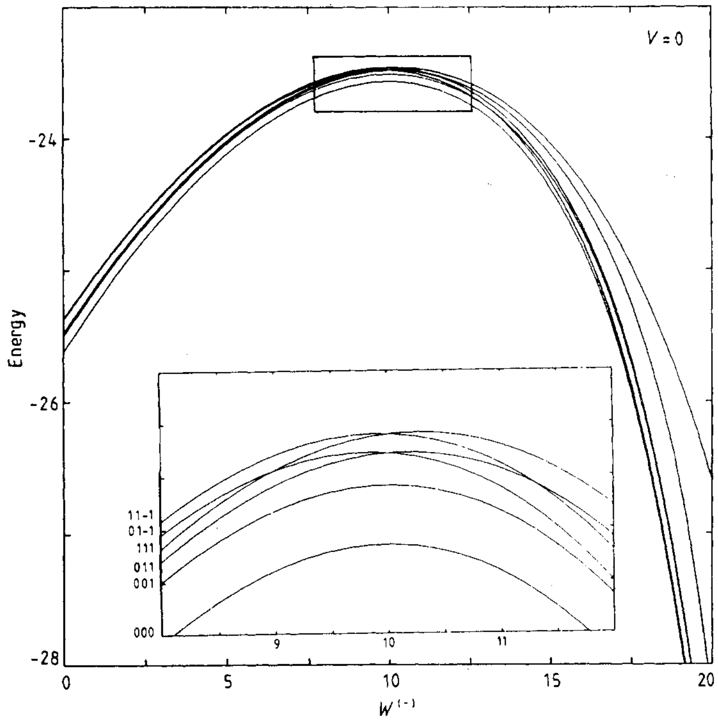

Figure 5. The levels of the lowest multiplet for $V = 0$ and $W^{(+)} + W^{(-)} = 20$.

governed by the A–E splitting of the one-particle states, namely the presence of a collective free-rotor coordinate as in (13) with $W^{(+)} \equiv 0$ and the existence of two degenerate configurations as in (3). In previous work on two coupled rotors (Clough *et al* 1984, Häusler and Hüller 1985) The ensuing effects have not been separated; there both vanish simultaneously with increasing one-particle potential V.

This is different in the present case. Whereas the consequences of a collective zero-potential coordinate can be seen in figure 5 or by comparing figures 1 and 4, the effects of an increasing bias are displayed in figure 2. This separation seems quite important, because the existence of a collective free-rotor coordinate is rather an unphysical artefact. In general the Fourier expansion of the coupling potential contains terms with both plus and minus signs. As the calculation for a simple point charge model indicates (Würger (1988); the connection to the notation used there is made by putting $W^{(\pm)} = -V_s \pm V_c$), the latter are relatively small; hence they may be neglected, if the remainder of the Hamiltonian then does not exhibit a continuous symmetry.

For a similar reason we have neglected higher-order contributions and the sine term in the one-particle potential. Being compatible with the symmetries (2) and (4), they do not affect the energy spectrum significantly. Only the one-particle cosine terms of odd order break the symmetry (4) and hence act as a bias separating the two sets of minima of the potential energy.

It is noteworthy that the expectation values of the operators $\cos(3\varphi_i)$ and $\sin(3\varphi_i)$ vanish for zero bias, whereas $\cos(6\varphi_i)$ has quite a large diagonal element. In physical terms that corresponds to the absence of a well defined preferential orientation of the molecules; we emphasise the analogy of the two sets of minima of the potential in (3) with a double-minimum potential. The present case is more complicated in so far as we

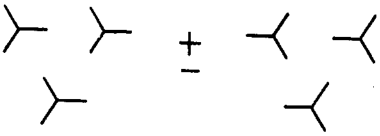

Figure 6. Illustration of the states for zero bias; the two signs correspond to $\alpha = 0, 1$.

deal with three coupled molecules instead of a single particle; the strongly coherent motion is reflected by the large expectation value of $\cos(3\varphi_i + 3\varphi_j)$. This situation is illustrated in figure 6.

The most intriguing feature seems to us the difference between the spectra for zero and finite bias as displayed in figures 2 and 3. For $V = 0$ the two lowest bands overlap; the level scheme is dominated by the E^a–E^b splitting. With increasing coupling strength the bands become narrower, but their structure remains unchanged. A non-zero bias splits the first librational multiplet from the ground states and alters the level scheme substantially; with larger V, one approaches the region where the system can be described by a product of one-particle states. For the range of parameters investigated, this crossover occurs at a bias of about one rotational constant; it is not clear whether this remains true for still stronger coupling.

The condition of such a small one-particle potential is most likely to be fulfilled for small complexes with several ammine or methyl ligands. Examples are the metal hexammine salts which cover the whole range from almost free rotation to low-frequency tunnelling (Blank and Kearley 1987, Kearley *et al* 1987); the different inelastic transitions observed by neutron scattering have so far escaped understanding. A very recent investigation of the central peak (Kearley 1989) excludes the interpretation of the tunnelling spectra of $Ni(NH_3)_6I_2$ as inter-band transition as in figure 2 with $V = 30B$ and $W = 0.016B$; the high-resolution spectra of the quasi-elastic intensity do not show the fine structure predicted by the model. When assuming the tunnelling lines to be due to intra-band transitions, we obtain the correct line positions, but the observed temperature dependence of the intensities is in manifest contradiction with such an explanation. For a comparison with the experimental data available for $Co(NH_3)_6(PF_6)_2$ it seems indispensable to deal with six coupled molecules; owing to the shallow potential the ligands are not supposed to lock in an orientation separating them into two groups of three molecules each.

5. Conclusion

We have dealt with a Hamiltonian exhibiting two symmetries of quite different origin; the invariance under proton exchange entails the coherent rotational tunnelling, whereas the (approximate) crystal symmetry (4) leads to the situation of a biased double well, the two minima corresponding to different collective orientations of the molecular groups. The main results are as follows.

(i) For a small one-particle potential the energy spectrum is dominated by the E^a–E^b splitting; this novel feature is in contrast to the situation described by (1), where the E-symmetric states are degenerate.

(ii) The transition to the strongly biased regime, where the energy difference between A- and E-symmetric states governs the level scheme, occurs at about one rotational constant. This relatively small value might render difficult the search for compounds showing the weak-bias behaviour.

(iii) It is essential whether the interaction part of the Hamiltonian exhibits a continuous symmetry. For a zero one-particle potential such a symmetry results in the energy spectrum of a free rotor with a moment of inertia which is the sum of the moments of the coupled molecules; in the absence of a continuous symmetry the coupling leads to a tunnelling spectrum which becomes exponentially narrow with increasing coupling strength. We believe the Hamiltonian (3) to be generic for coupled molecules rather than that for two rotors studied previously.

Strong rotor–rotor coupling provides an interesting variety of rotational tunnelling; the general aspects of our results for three groups are expected to be valid for larger systems as well.

Acknowledgments

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