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Tunneling of Coupled Methyl Groups

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A method is developed which allows the calculation of tunneling frequencies for coupled methyl groups in strong or weak orientational potentials to any desired accuracy. The method is applied to two coupled methyl groups and the results of the calculation are compared with a recent experiment. The comparison allows conclusions on the strength and symmetry of the potential. A further important point is the prediction of coupling effects in rotational tunneling also in the limit of strong potentials.

Rotational tunneling has been observed in systems containing methane molecules, ammonium ions or methyl side groups [1]. Tunneling transitions occur between the energy levels of the librational ground state multiplet of the molecules performing small angular oscillations around the minima of the orientational potential. For the majority of the experimental results a single particle description seems to be sufficient for a complete understanding of the low temperature spectra. Exceptions are methane [2] where the line width has been explained in terms of coupled tunneling, lithium acetate [3] where the coupling is responsible for a splitting of the tunneling lines, manganese acetate [4], lead tetramethyl [5] and $(NH_4)_2PF_6$ [6] where certain features of the spectrum are not yet fully understood, but may well turn out to be a consequence of intermolecular couplings.

It has been presumed [7] that coupling effects are unobservable for strong single particle potentials. In the following we develop a method that allows to calculate tunneling frequencies for coupled methyl groups. For shallow potentials it repeats the calculations of Clough et al. [3]. We have, however, extended the range of parameters to the frustrated regime where single particle potential and interactions tend to counteract. Our method, furthermore, allows to include relatively strong potentials. Contrary to earlier statements we have found that the former presumption about this limit is not true. For strong potentials the relative splitting caused by coupling effects does not go to zero when single particle potential and interactions are increased proportionally – it tends towards a constant.

For the purpose of clarifying the method of our calculation we start with a single rotor in a threefold cosine potential of strength V_3. The Schrödinger equation for this problem reads:

$$\left[-\frac{\partial^2}{\partial\alpha^2}-\frac{V_3}{2}(e^{3i\alpha}+e^{-3i\alpha})-E\right]\psi(\alpha)=0. \tag{1}$$

where all energies are measured in units of $B=\hbar^2/2\theta$ and θ is the moment of inertia. The equation is solved by the ansatz:

$$\psi(\alpha)=\sum_n a_n^s e^{i(3n+k)\alpha}. \tag{2}$$

If $k=0$, $\psi(\alpha)$ is a symmetric A-type function. For $k=\pm 1$ it is one of the two degenerate E-type solutions. The symmetry label A, E_a or E_b is denoted by s. On inserting (2) into (1) one obtains an infinite series of equations for the coefficients a_n^s:

$$V_3\, a_{n+1}^s+2[E-(3n+k)^2]\, a_n^s+V_3\, a_{n-1}^s=0. \tag{3}$$

For finite values of the potential strength parameter V_3 the coefficients a_n^s have appreciable values only in a small region around $n=0$, say for $-N<n<N$ and N depends on the value of V_3. For $|n|>N$ the a_n^s are insignificantly small. Putting these coefficients to zero, there remain $2N+1$ equations for $2N+1$ coefficients which together with the eigenvalue E could be found by the diagonalization of the $(2N+1)\times(2N+1)$ matrix. It is much easier, however, to choose a fixed value, say e.g. 1, for one of the coefficients so that the system of $2N+1$ homogeneous equations for $2N+1$ coefficients is transformed into an inhomogeneous system of $2N+1$ equations for $2N$ coefficients. We discard one of the equations for the moment. The $2N$ remaining coefficients can now be obtained from an inversion of the matrix rather than by its diagonalization. Of course, the discarded equation is not fulfilled, but if we choose E such that it is, we obtain an excellent solution. This way, the problem represented by (1) can be solved on a pocket calculator. One choose $a^s_{-N}=1$, iterates Eq. (3) $2N$ times to calculate a^s_N and then adjusts E such that $a^s_{N+1}=0$ follows from the next iteration. For larger and larger N the accuracy with which the eigenvalue E can be determined becomes better and better until it reaches the accuracy of the calculator. For $V_3=30$ (a value which corresponds to a tunneling splitting of 0.005 B or 3 µeV) and a 10 digit calculator this happens for $N=6$. A comparison with tabulated eigenvalues shows full agreement within the accuracy of these tables.

The main advantage of the method is the replacement of a matrix diagonalization by a matrix inversion which is much quicker. Also the matrix to be inverted is a sparse matrix. In fact, in the one-dimensional example of this paragraph the matrix contains nonvanishing elements only in the diagonal and in two adjacent parallels. The inversion is therefore trivial and can be performed on pocket calculator. In cases of practical interest to be presented in the following, more than 90% of the elements may be zero which greatly reduces the number of operations to be performed. As inversions are so easy to perform there are almost no limits to the number of coefficients included, whereas a diagonalization procedure comes to the limits of capability of a computer fairly quickly. A disadvantage of the method is that one has to iterate the inversion process several times to find the energy eigenvalue and the wave function, but with 20 iterations one is able to reduce the distance between the upper and the lower limit of an energy eigenvalue by 6 orders of magnitude. A further disadvantage is that only one eigenvalue together with the corresponding wave function is calculated at one time whereas a set of eigenvalues comes out of a single diagonalization.

The method can be generalized to problems with more than one degree of freedom. The field of applications would include the rotational tunneling of tetrahedral molecules where the Hamiltonian, if written in terms of quaternions, acts on functions depending on the 4 coordinates τ_1, τ_2, τ_3, and τ_4. A suitable expansion would be

$$\psi(\tau_1, \tau_2, \tau_3, \tau_4) = \sum_{m_1, m_2, m_3, m_4} a_{m_1, m_2, m_3, m_4} \tau_1^{m_1} \tau_2^{m_2} \tau_3^{m_3} \tau_4^{m_4} \tag{4}$$

where the m_i run over non-negative integers only. $L=(m_1+m_2+m_3+m_4)/2$ has the property of an angular momentum and thus only integer values of L are allowed and for a given orientational potential only terms up to a maximum value of L will contribute appreciably.

The potential is a polynomial in the quaternions itself, the kinetic energy contains only differentiations w.r.t. the quaternions and multiplications with them. Therefore application of the Hamiltonian only couples a finite number of polynomials and Schrödinger's equation can be written as a recursion relation between the coefficients a_{m_1, m_2, m_3, m_4}.

Interactions of a finite number of particles as e.g. the four methyl groups in $Pb(CH_3)_4$ or two methyl groups in lithium acetate or manganese acetate are examples which can also be treated using the method outlined above. The interaction of many tunnelling molecules which manifests itself in very interesting phenomena in solid methane [2] is a quantum manybody problem for which we only expect approximate solutions. This is beyond the reach of our method which provides solutions which, in principle, are exact.

In this paper we will concentrate on two interacting methyl groups with the Hamiltonian:

$$H=-\frac{\partial^2}{\partial\alpha_1^2}-\frac{\partial^2}{\partial\alpha_2^2}+V(\alpha_1, \alpha_2). \tag{5}$$

We immediately specialize the potential to the form

$$V(\alpha_1, \alpha_2)=-V_3(\cos 3\alpha_1-\cos 3\alpha_2) - W_3\cos(3\alpha_1-3\alpha_2). \tag{6}$$

This amounts to the following simplifications:

(i) The single particle potential for the two groups is the same *(ii)* only one Fourier component has been included *(iii)* also the interaction is reduced to a single Fourier component *(iv)* the relative phase between the single particle potential and the interaction can only have two values depending on the sign of W_3. As the substitution $V_3 \to -V_3$ corresponds to an exchange of the two groups, only $V_3 \geqq 0$ will be considered. We distinguish two cases: *A)* If the angles α_1 and α_2 are measured relative to the same direction in the crystal, then the minima of the single particle potentials are $\pi/3$ apart, and the two groups tend to localize in staggered orien-

tations. Negative values of W_3 enhance this tendency, positive values reduce it. For $W_3>0$ the interaction counteracts the single particle potential – this will be called the frustrated case. *B)* If the origin of the scale for measuring the second angle is shifted by $2\pi/3$ such that α_2 is replaced by $\alpha_2+\pi/3$ then the single particle potential tends to orient the two groups parallel. Now the interaction prefers the staggered orientation for positive W_3. Thus $W_3>0$ again corresponds to the frustrated case.

The direct interaction between two groups rotating around a common axis as it is in Li-acetate certainly prefers the staggered orientation. This is true for electrostatic multipole-multipole forces as well as for the shortrange repulsion of the two groups. The following analysis shows that the frustrated case cannot be reconciled with the experimental data - it therefore seems that case *A)* with $W_3<0$ is realized where the interaction and the single particle potential cooperate to localize the two groups in the staggered orientation.

$-V_3(\cos 3\alpha_1-\cos 3\alpha_2)$ represents the potential energy of the two methyl groups with all the other atoms fixed at their equilibrium positions. In lithium acetate the two methyl groups rotate around a common axis which lies in two mirror planes. Therefore the single particle potential should have a sixfold symmetry. Following Clough et al. [3] we assume that this sixfold symmetry is lifted by the polaron effect, i.e. by local lattice relaxations which remove one of the mirror planes and thus permit the appearance of the threefold term which then dominates the tunneling. In principle the distortion is different for the different quantum states of the methyl groups under consideration. For the states within the ground state tunneling multiplet, however, the proton distribution function is almost the same leading to similar distortions of the lattice. As long as we deal with the states in the ground state multiplett and with transitions between them we may therefore consider the displacements as rigid. Two cases are conceivable:

1) The two closely spaced groups create a common long range distortion field which would tend to orient them parallel. *2)* The direct interaction forces the two groups into the staggered orientation and each of them creates a corresponding distortion field in its own backyard which supports the staggered orientation. Anticipating our later discussion of the experimental data it seems that the second alternative is realized in Li-acetate. An independent check of the assertion that the two methyl groups are in staggered orientations by coherent elastic neutron diffraction on deuterated Li-acetate would be very desirable.

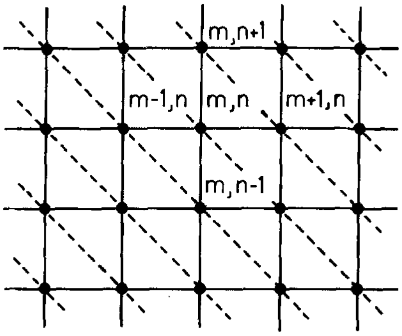

Fig. 1. The "lattice" of coefficients a^{rs}_{mn}. Full lines denote "interactions" due to the single particle potential V_3, broken lines denote "interactions" due to the two particle potential W_3

The Schrödinger equation $(H-E)\psi(\alpha_1,\alpha_2)=0$ with the Hamiltonian (5) is solved by the Ansatz:

$$\psi(\alpha_1,\alpha_2)=\sum_{m,n} a^{rs}_{mn}\, e^{i(3n+k_1)\alpha_1}\, e^{i(3m+k_2)\alpha_2} \tag{7}$$

k_1 and k_2 assume the values $0, +1$, and -1 for the A, E_a, and E_b symmetry species respectively, r and s denote the symmetry labels. The coefficients a^{rs}_{mn} fulfill the recursion relation:

$$a^{rs}_{mn}[(3m+k_1)^2+(3n+k_2)^2-E)] + \frac{V_3}{2}(a^{rs}_{m-1,n}+a^{rs}_{m+1,n}+a^{rs}_{m,n-1}+a^{rs}_{m,n+1}) + \frac{W_3}{2}(a^{rs}_{m+1,n-1}+a^{rs}_{m-1,n+1})=0 \tag{8}$$

which is represented graphically on the "lattice" of coefficients in Fig. 1. The potentials V_3 and W_3 introduce "interactions" between the lattice points. The single particle potential couples coefficients along rows or along columns only. Restriction to one Fourier component in the potential means nearest neighbours interaction only. A $\cos 6\alpha$ potential would induce next nearest neighbour interactions and so on. A $\sin 3n\alpha$ term would make interactions to right and left (up and down) neighbours different. The two particle potential introduces interactions along one of the diagonals. A contribution of the type $\cos(3\alpha_1+3\alpha_2)$ would be found on the other diagonal and again higher Fourier coefficients would introduce "interactions" of longer range.

Now we truncate (8) by demanding that all coefficients with $n^2+m^2>K^2$ are zero. The size K of the field of nonzero coefficients is determined by the strengh of the potentials V_3 and W_3. This leaves us with a number of nonzero coefficients. Call that number N. There are N homogeneous linear equations between them:

$$\sum M^{rs}_{m'n',mn}\, a^{rs}_{mn}=0 \tag{9}$$

which could be solved by a diagonalization procedure. We have again chosen a fixed value for one of the a^{rs}_{mn}. Then we have N inhomogeneous equations for $N-1$ coefficients. We solve $N-1$ of them by inversion and then adjust the energy such that the remaining equation is also fulfilled. There are the same advantages as in the one dimensional example. With "interactions" to six neighbour coefficients only, seven elements in each row and column of M are nonzero. In a typical example with $K=8$ there are 200 coefficients a^{rs}_{mn} to be determined. M is a 200×200 matrix with 40,000 elements of which only 1,300 are nonzero. This corresponds to a sparsity of 97%. A further reduction of the problem is achieved by consideration of the symmetries of the coefficients a^{rs}_{mn}.

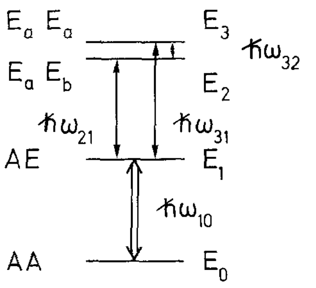

Fig. 2. The energy levels of two coupled methyl groups in the librational groundstate tunneling multiplet together with the symmetry labels and the transition frequencies

The ground state multiplet contains four levels: The non degenerate AA level with energy E_0, the fourfold AE level with energy E_1, the twofold E_aE_b level with energy E_2 and the twofold E_aE_a level with energy E_3. Four transitions are possible with energies $\hbar\omega_{10}=E_1-E_0, \hbar\omega_{21}=E_2-E_1, \hbar\omega_{31}=E_3-E_1$, and $\hbar\omega_{32}=E_3-E_2$. This is shown in Fig. 2. Our main results are shown in Figs. 3, 4, and 5. All three figures show the same region of the parameter space (V_3, W_3). Positive and negative V_3 are physically identical so the pictures are restricted to $V_3>0$.

Figure 3 represents the basic tunelling energy $\hbar\omega_{10}$. When W_3 is negative the single particle potential and the interaction cooperate: much smaller values of V_3 are needed for more negative W_3 to produce a given tunnel splitting. On the side of positive W_3 the contrary is the case. Figure 4 is a plot of the ratio $v=\omega_{21}/\omega_{10}$. The energy $\hbar\omega_{10}$ is absorbed when both groups are in the A-state and one of them is lifted into the E-state, $\hbar\omega_{21}$ is absorbed when the second group is lifted up, too. With no interaction the two energies are, of course, equal. So the deviation of v from 1 is a measure of the importance of the interaction. For very strong interactions it makes a difference if the two groups end up in different E-states (E_aE_b) or in the same (E_aE_a) state. Figure 5 is a plot of $\Delta=\omega_{32}/\omega_{10}$ which is a dimensionless measure of this splitting.

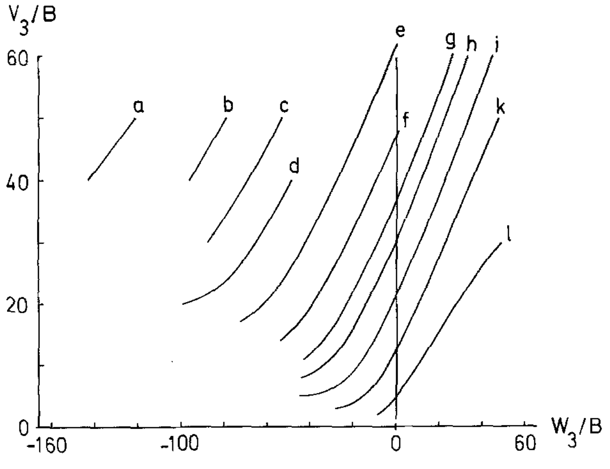

Fig. 3. Lines of equal tunneling energy $\hbar\omega_{10}$ in the (V_3, W_3) parameter space. Negative values of V_3 only correspond to a shift of the origin of α_1 and α_2 by $\pi/3$. Negative W_3 amplify the influence of V_3, positive W_3 diminish it (all energies in units of B)

a: $1\cdot10^{-7}$
b: $1\cdot10^{-6}$
c: $5\cdot10^{-6}$
d: $2\cdot10^{-5}$
e: $1\cdot10^{-4}$
f: $5\cdot10^{-4}$
g: $2\cdot10^{-3}$
h: $5\cdot10^{-3}$
i: $2\cdot10^{-2}$
k: $1\cdot10^{-1}$
l: $5\cdot10^{-1}$

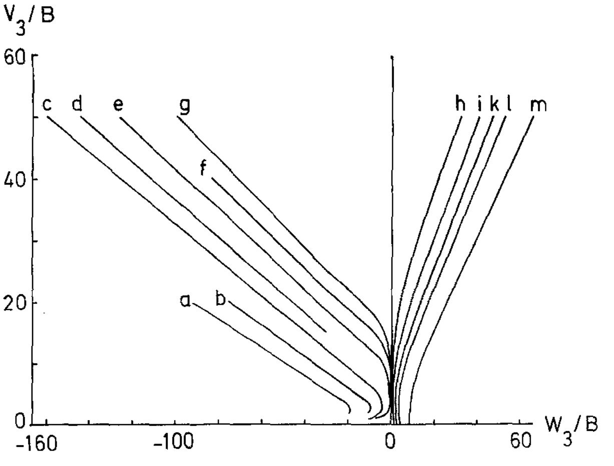

Fig. 4. Contours of $v=\omega_{21}/\omega_{10}$ in the same region of parameter space as Fig. 3. In the limit $W_3\to0$ the two groups are independent, leading to $v=1$.

a: $v=0.5$
b: $v=0.75$
c: $v=0.909$
d: $v=0.952$
e: $v=0.980$
f: $v=0.990$
g: $v=0.995$
h: $v=1.005$
i: $v=1.020$
k: $v=1.053$
l: $v=1.111$
m: $v=1.429$

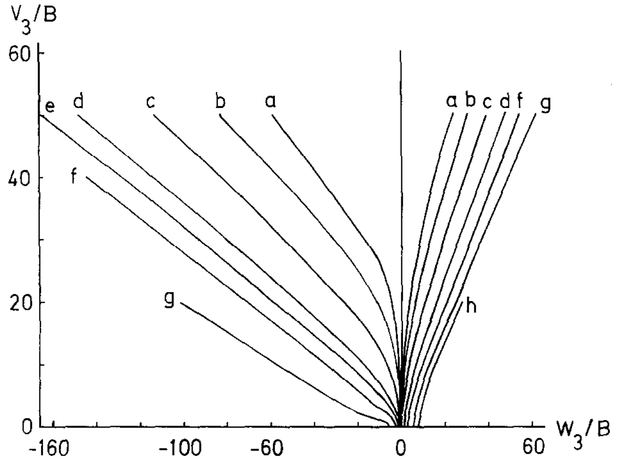

Fig. 5. Same as Fig. 4, but contours of $\Delta = \omega_{32}/\omega_{10}$ are plotted. With the contours approximately parallel to those of Fig. 4 they can only be used for a consistency check, but not as an independent information to determine the potential parameters.

a: $\Delta = 0.0005$
b: $\Delta = 0.002$
c: $\Delta = 0.01$
d: $\Delta = 0.05$
e: $\Delta = 0.1$
f: $\Delta = 0.2$
g: $\Delta = 0.6$
h: $\Delta = 1.0$

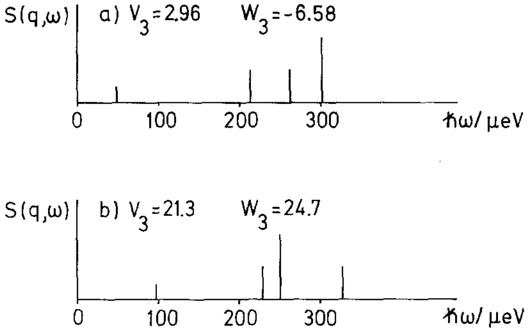

Fig. 6. Tunneling spectrum as expected for positive and negative values of W_3. $W_3 < 0$: values used by Clough et al. to describe the tunneling spectrum of Li-acetate; $W_3 > 0$: values of (V_3, W_3) leading to a tunneling lines with a similar mean-energy and width

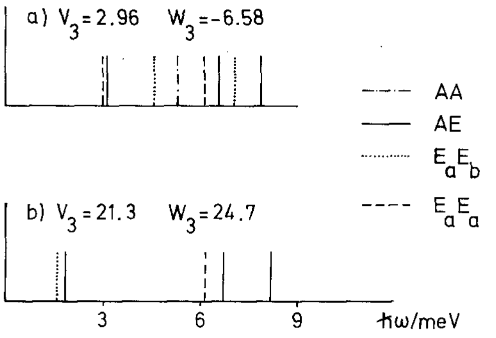

Fig. 7. Librational spectrum for the same values of V_3 and W_3 as in Fig. 6. The plotted lines denote the energy for a transition from a librational excited state with specified symmetry to the mean-energy of the librational ground state multiplett

It has been suggested that interaction effects in rotational tunneling would only be visible for relatively shallow single-particle potentials. The argument is as follows: In a deep potential the modulus of the A und E-species wave functions is almost the same, therefore the neighboring molecules will not notice the difference and their energy levels should not be influenced. Our calculations show that this is not the case. On the contrary – in the limit of strong potentials the frequency ratios v and Δ tend towards functions of the ratio W_3/V_3 only, independent of the strength V_3 itself. The flaw in former arguments [7] is connected to the extreme sensibility of the tunneling frequencies to changes of the potential. It is true that the influence of the coupling on the tunneling frequencies becomes smaller and smaller with increasing localization, but as the frequencies themselves become very small the effect on their ratios is still noticeable.

In lithium acetate a group of transitions is found around $260\,\mu V = 0.4\,B$ with a splitting that suggests a frequency ratio *a)* $v = 0.85$ or *b)* $v = 1.30$. From Figs. 3 and 4 we find the corresponding potential parameters (V_3, W_3) in units of B: *a)* (2.96, −6.58) and *b)* (21.3, 24.7). In Fig. 6 we show the calculated tunneling spectra for both cases. Case *a)* is the one considered by Clough et al. in their analysis. Comparing both calculated spectra with the experimental result [3] we are lead to confirm this choice because it describes better the position of the most intensive peak within the tunnel line and the position of the low energy peak. Figure 7 shows the librational spectra calculated for the cases *a)* and *b)*. They both do not agree well with the measured spectra [3]. This cannot be improved by a different choice of (V_3, W_3) because of the mentioned sensibility of the tunneling spectrum with respect to changes of the potential in the overlap-region between the equilibrium orientations [8]. On the other hand the librational spectrum is sensitive to the shape of the potential in the region of the minima. Additional Fourier components to better characterise the potential might improve the calculation. For excited librational states the proton density distribution deviates from the ground state distribution. Therefore also the local lattice distortion, the polaron effect and the corresponding threefold potential are different in excited states. The importance of this effect can only be examined in a quantum mechanical calculation which takes the lattice degrees of freedom into account. Our calculated tunneling splittings differ slightly from those calculated in [3] for the same parameter values. More noticeable deviations occur for the librational spectra. The origin of these discrepancies is unknown to us.

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