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Rotational tunneling of orientationally coupled methyl groups: Molecular field approximation versus numerically exact solution

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The orientational coupling of methyl groups leads to a split rotational tunneling line. We study the dependence of this splitting on the type and strength of the interaction. Two types of pair potentials are considered (M1) $\cos 3\varphi_i \cos 3\varphi_j$ and (M2) $\cos 3(\varphi_i+\varphi_j)$. The tunneling spectra are calculated numerically exact for $N=2$ and $N=3$ rotors by using a sparse matrix method (SMM). For model M1 we also probe the molecular field approximation (MFA). For both, $N=2$ and $N=3$, not even qualitative agreement is found between MFA and SMM. But a trend can be seen towards MFA-like behavior; with increasing N, the dependence of the splitting on the coupling strength *qualitatively* resembles the MFA prediction. However, by our SMM results, we are led to the conjecture, that for moderate coordination numbers a considerable splitting should occur within a much broader range of coupling strengths than predicted by MFA.

I. INTRODUCTION

The classically forbidden tunneling through potential barriers is one of the most striking features of quantum mechanics. For single particles and rigid potentials this phenomenon is well understood and there exist powerful numerical or Wentzel–Kramers–Brillouin (WKB) methods to approximate the tunneling rates. However, a coupling between various degrees of freedom may strongly influence the tunneling behavior. One example is the coupling to lattice vibrations, cf. Ref. 1, which establishes a microscopic description of dissipation and temperature dependence. In the present paper we concentrate on the effect of coupling between different tunneling coordinates on the tunneling spectra. We will consider coordinates confined to finite regions in space.

Due to tunneling multiply degenerated classical ground state energies split and the corresponding levels determine the lowest excitation energies of the system. In absence of even the slightest differences in the depth of the potential minima this splitting decreases exponentially to arbitrarily small values with increasing height of the potential barriers separating the classical ground state configurations. This distinguishes physical systems, where some internal symmetry assures equivalence between the various potential minima; they can exhibit extremely small tunneling energies. Outstanding examples are the *rotational tunneling systems*, where tunneling between the minima are accompanied by an exchange of identical particles. The hydrogen molecule H_2 is famous for its *ortho* and *para* symmetry species being stable over times many orders of magnitude longer than the inverse energy difference between the two eigen energies. There, a rotation of 180° corresponds to an (odd) permutation of identical atoms.

Let us focus our attention onto systems like CH_3 and CH_4. The CH_3 molecule is a one-dimensional symmetrical rotor. Due to its invariance under 120° rotations, any nonvanishing rotational potential must have at least three equivalent minima. The tetrahedral symmetry of the three-dimensional symmetrical rotor CH_4 enforces that its orientational potential has at least 12 equivalent minima. In molecular crystals containing these types of rotors, tunneling energies in the μeV range or below can be found experimentally.[2]

Suppose that the environment has no symmetry at all. Then the symmetry group of the CH_3-Hamiltonian is the point group C_3, and the eigenfunctions can be classified according to the irreducible representations $\Gamma \in \{A, E^a, E^b\}$ of that group. For CH_4 the eigenfunctions are classified with respect to the irreducible representations of the tetrahedral group T, whence $\Gamma \in \{A, T, E^a, E^b\}$.

The equivalence of the potential minima in rotational tunneling systems is not destroyed by coupling the rotational degree(s) of freedom to any set $\{x_k\}$ of other spatial coordinates, including rotations. For a single methyl rotor with angle coordinate φ the total potential energy V always has the periodicity property

$$V\left(\varphi+\frac{2\pi}{3},\{x_k\}\right)=V(\varphi,\{x_k\}). \tag{1}$$

Therefore, Γ remains a good quantum number, e.g., even in presence of dissipation. An immediate physical consequence is the sharpness of the tunneling line(s) in rotational systems at temperatures many orders of magnitude higher than the tunneling energy itself.[2] This is a profound dissimilarity to translational tunneling systems. For hydrogen atoms, which tunnel to a crystallographically equivalent and empty neighboring site,[3] the tunneling lines are only observable at temperatures below the tunneling energy.[4] Only operators that can change the nuclear spin state of the symmetrical rotor are able to induce rotational tunneling transitions, thereby

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changing Γ. An example is the neutron scattering operator. Hence, rotational tunneling energies are directly observable by inelastic neutron scattering.

Orientational coupling by interatomic forces between closely situated rotors complicates the rotational tunneling spectrum, because the tunneling lines split. This has been found experimentally[5,6] and theoretically[5,7] for coupled pairs of rotors. On the other hand in solid methane yet no clear evidence is found for a splitting of the tunneling lines caused by interactions between adjacent CH_4 molecules,[8] which are expected to dominate by far all other potential contributions. This system seems to be very well described within an effective single particle description which takes into account nothing but the molecular field of the surrounding rotors.[2,9] This molecular field approximation (MFA) provides the simplest way for treating many body effects. For the reasons given below, we have been interested in the question, for which cases MFA is really applicable. Our most sensitive probe to quantify correlations will be the splittings of tunneling lines, i.e., the *differences of the differences* between the lowest few eigenvalues of the Hamiltonian.

The vanishing of the *relative* splittings of the tunneling lines (on the scale of the tunneling energy itself) in the *strong coupling limit* turns out to be a salient property of the MFA, independent of the number of coupled rotors. And the reliability of MFA is expected to grow with increasing coordination number. On the other hand it is known from numerical calculations, performed for systems containing two,[7] three,[10] or four[11,12] rotors, that increasing coupling strengths usually lead to an increase of the relative splitting of the tunneling line. The question arises, which scenario will be the correct one for a system of strongly coupled rotors with moderate to large coordination number.

We analyze the situation in terms of more precise numerical data and a considerably extended range of coupling strengths for up to three equivalently coupled rotors. The numerical results are also very useful to test the reliability of simpler calculational schemes, e.g. Ref. 12, which, in turn, allow us to calculate the spectra of more than three coupled rotors.

Only the one-dimensional CH_3 rotors are examined to study the influence of orientational interactions on the tunneling spectra. Rotors of higher dimensionality, like CH_4, would require a much larger Hilbert subspace.[13,14]

We have investigated two types of pair potentials between the ith and the jth methyl group (M1) $\cos 3\varphi_i \cos 3\varphi_j$ and (M2) $\cos 3(\varphi_i+\varphi_j)$. Only the second model is capable of different eigenvalues for states which differ only by substitution of some E^a by E^b symmetry lables or vice versa. MFA cannot, in principle, reproduce this $E^a \leftrightarrow E^b$ splitting and therefore MFA is not applied to model M2.

The organization of the paper is as follows: In Sec. II, the two models are explained. Within the pocket state picture (Sec. III) the splitting of the tunneling lines can be understood qualitatively. The calculational scheme of the self-consistent molecular field approximation is explained in Sec. IV A. Numerically exact eigenvalues are obtained by the sparse matrix method (SMM),[7,15] which is described in Sec. IV B. The various results are presented in Sec. V. In Sec. VI the conclusion is drawn.

II. MODELS

From Eq. (1) it can be seen that orientational coupling of N different rotors (enumerated by i) does not mix their symmetries $\Gamma_i \in \{A, E^a, E^b\}$. Therefore, the full Hilbert space can be conceived as the direct sum of 3^N irreducible subspaces named by the N-tuples $\{\Gamma_1 \ldots \Gamma_N\}$ of symmetry labels. Within each irreducible subspace there exists a unique eigenstate having the respectively lowest eigenvalue; all together these "ground states" of different symmetry form the tunneling multiplet into which we are interested here.

Two model Hamiltonians for N coupled methyl rotors are investigated,

$$H^{(1)} \equiv \sum_{i=1}^{N} BL_i^2 + \frac{W/2}{N-1} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \cos 3\varphi_i \cos 3\varphi_j \tag{2}$$

and

$$H^{(2)} \equiv \sum_{i=1}^{N} (BL_i^2 + V \cos 3\varphi_i) + \frac{W/2}{N-1} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \cos 3(\varphi_i + \varphi_j). \tag{3}$$

Here, L_i is the angular momentum of the ith rotor, φ_i is its angular coordinate, and $B \approx 650$ μeV is the rotational constant.

The term $\sim \cos 3\varphi_i \cos 3\varphi_j$ in Eq. (2) dominates in the Fourier expansion of the interaction, if the six protons of two methyl groups i and j are rotating in a common plane around parallel axes. On the other hand, the coupling between two methyl groups rotating around a common axis is $\sim \cos 3(\varphi_i + \varphi_j)$ in lowest nontrivial order and is described by Eq. (3).

The single-particle potential is not included in $H^{(1)}$ in order to pronounce the influence of coupling, and because the type of interaction in $H^{(1)}$ cannot show frustration. On the other hand, the influence of cooperative or noncooperative relationship between interaction and single-particle potential can be studied for the type of interaction in $H^{(2)}$ (see Sec. V B). In the above sense, the Hamiltonian $H^{(1)}$ describes a maximally coupled system, which is well suited to test the reliability of the MFA results.

The use of equivalent neighbor models may appear unrealistic. Physically, a large number of coupled rotors can only be realized by arrays of rotors, each interacting with only a few nearest neighbors; examples are one-dimensional chains (e.g., Gamma-picoline[16]), two-dimensional planes [e.g., $SnF_2(CH_3)_2$ (Ref. 17)], or even a three-dimensional network (e.g. solid methane[18,9]). However, knowing the properties of equivalent neighbor models (2) and (3) for various N, conclusions can be drawn about infinite lattices of coupled rotors with *finite* coordination and with equal coupling strengths.[19]

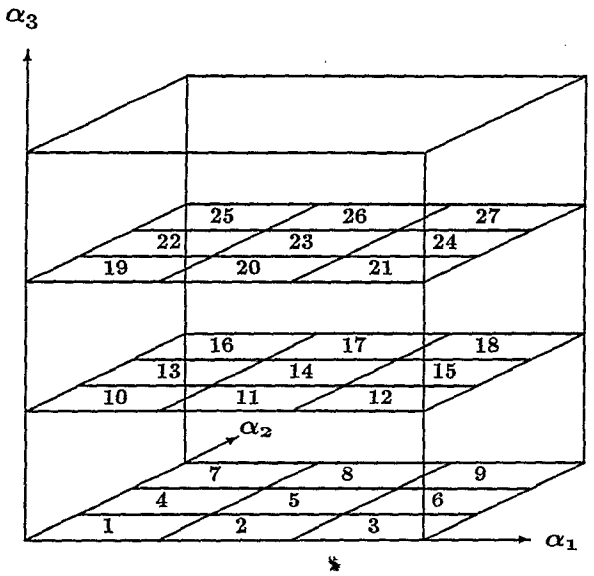

FIG. 1. Enumeration of the 27 equivalent parts in the configuration space of three (interacting) methyl groups, as used in Eq. (4). φ_1, φ_2, and φ_3 are the angular coordinates. Pocket state $|j\rangle$ is localized around minimum j.

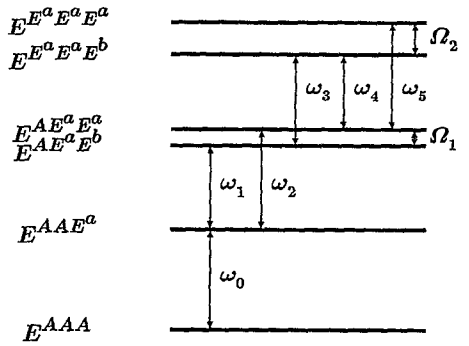

FIG. 2. Tunneling levels for the general, equivalently coupled 3-methyl system. Transitions, which involve the symmetry change of a *single* rotor are observable by inelastic neutron scattering and are indicated by arrows. The various transition energies can be estimated in terms of pocket state matrix elements, cf. Eq. (6). For zero coupling, all ω_i are equal to the single particle tunneling energy, and $\Omega_i=0$.

III. TUNNELING SPECTRUM IN TERMS OF POCKET STATES

The tunneling spectrum is qualitatively well described within the pocket state picture.[20] Consider the case of *three* coupled methyl groups; no special potential is assumed. Still, the symmetry of the CH_3 rotor enforces that the positions of the potential minima form a three-dimensional periodic array in configuration space $[0,2\pi]^3$ with lattice constant $2\pi/3$. The boundary condition for the wave functions leads to 27 values for the quasimomenta (k_1,k_2,k_3), where $k_i\in\{-1,0,1\}$; they are one to one related to the 27 three-tuples $(\Gamma_1,\Gamma_2,\Gamma_3)$ of irreducible representations $(\Gamma_i\in\{E^a,A,E^b\})$ of the product group $C_3\otimes C_3\otimes C_3$, e.g., $(E^a,A,E^b)\Leftrightarrow(-1,0,1)$.

In order to construct ansatz functions of correct symmetry, we start with a single pocket state.[20,13] For high barriers between the potential minima, this is a highly localized wave function centered at the position of some potential minimum. The pocket state does not crucially depend on the symmetry $(\Gamma_1,\Gamma_2,\Gamma_3)$. By applying to this pocket state all symmetry operations which commute with the Hamiltonian, we obtain copies, each of which is centered in one of the other minima of the potential. Suitable linear combinations of this set $\{|1\rangle,\ldots,|27\rangle\}$ (enumeration according to Fig. 1) of pocket states belong each to one of the irreducible representations of the product group $C_3\otimes C_3\otimes C_3$; their coefficients are known from elementary group theory. Hence we restrict ourselves to the 27-dimensional Hilbert space which is spanned by these pocket states. For sufficiently high potential barriers, Wannier states of this periodic problem appear to be suitable pocket states. Note that the pocket state basis is nonorthogonal. By symmetry, there are five different nonvanishing overlaps and six different matrix elements $\langle i|H|j\rangle$ of the Hamiltonian

$$
\begin{aligned}
&D\equiv\langle 1|H|1\rangle \quad 1=\langle 1|1\rangle,\\
&t\equiv\langle 1|H|2\rangle \quad t'\equiv\langle 1|2\rangle,\\
&a\equiv\langle 1|H|5\rangle \quad a'\equiv\langle 1|5\rangle,\\
&b\equiv\langle 1|H|8\rangle \quad b'\equiv\langle 1|8\rangle,\\
&c\equiv\langle 1|H|15\rangle \quad c'\equiv\langle 1|15\rangle,\\
&d\equiv\langle 1|H|14\rangle \quad d'\equiv\langle 1|14\rangle.
\end{aligned}
\tag{4}
$$

By $|\Psi^{\Gamma_1\Gamma_2\Gamma_3}\rangle$ and $E^{\Gamma_1\Gamma_2\Gamma_3}$ we denote the approximate eigenvectors and eigenvalues as calculated from the Hamilton *matrix*. Consequently, the eigenenergies $E^{\Gamma_1\Gamma_2\Gamma_3}_{\text{true}}$ of the Hamilton *operator* are approximated from above by

$$
E^{\Gamma_1\Gamma_2\Gamma_3}=\frac{\langle\Psi^{\Gamma_1\Gamma_2\Gamma_3}|H|\Psi^{\Gamma_1\Gamma_2\Gamma_3}\rangle}{\langle\Psi^{\Gamma_1\Gamma_2\Gamma_3}|\Psi^{\Gamma_1\Gamma_2\Gamma_3}\rangle}\geqslant E^{\Gamma_1\Gamma_2\Gamma_3}_{\text{true}},
$$

which, in terms of the elements (4), leads to six different values[15]

$$
\begin{aligned}
E^{AAA}&=\frac{D+6t+6a+6b+6c+2d}{1+6t'+6a'+6b'+6c'+2d'},\\
E^{AAE^a}&=\frac{D+3t-3c-d}{1+3t'-3c'-d'},\\
E^{AE^aE^b}&=\frac{D-3b+2d}{1-3b'+2d'},\\
E^{AE^aE^a}&=\frac{D-3a+3c-d}{1-3a'+3c'-d'},\\
E^{E^aE^aE^b}&=\frac{D-3t+3a-d}{1-3t'+3a'-d'},\\
E^{E^aE^aE^a}&=\frac{D-3t-3a+6b-3c+2d}{1-3t'-3a'+6b'-3c'+2d'}.
\end{aligned}
\tag{5}
$$

Since suitable linear combinations of the lowest 27 eigenfunctions appear to be perfect pocket functions, we may safely assume for our qualitative reasoning that the approximative eigenvalues equal the true ones. The typical spectrum

for not too strong coupling is shown in Fig. 2. Note that the matrix elements $t,a,\ldots,d$ are negative due to the kinetic energy contribution.

For strong potential we can well neglect the primed elements, i.e., $\langle i|j\rangle$ for $i\neq j$, of the overlap matrix (Gram matrix) in Eqs. (5) as compared to the normalization $\langle 1|1\rangle=1$.[21] A qualitatively simple picture of the level scheme arises. The t matrix element appears to be the main contribution to the tunneling energy and all splittings of the tunneling line (Fig. 2) are given by linear combinations of a, b, c, and d,

$$\begin{aligned}
\omega_0&\approx -3t-6(a+b)-9c-3d,\\
\omega_1&\approx -3t-3b+3(c+d),\\
\omega_2&\approx -3t-3a+6c,\\
\omega_3&\approx -3t+3(a+b)-3d,\\
\omega_4&\approx -3t+6a-3c,\\
\omega_5&\approx -3t+6b-6c+3d,\\
\Omega_1&\approx -3(a-b)+3(c-d),\\
\Omega_2&\approx -6(a-b)-3(c-d).
\end{aligned} \tag{6}$$

In Eqs. (6) only those energy differences are listed, which are observable in an inelastic neutron scattering experiment, where the symmetry of a *single* rotor can be changed, only.

For small c and d, corresponding to high single particle potentials, an approximative ratio of $\Omega_2/\Omega_1\approx 2$ is found for the $E^a\leftrightarrow E^b$ splittings. In the case of $c=d$ and comparatively small t,a,b, which corresponds to a strong $\cos 3\varphi_i \cos 3\varphi_j$ interaction, the tunneling spectrum can be characterized by $|\omega_0|:|\omega_1|:|\omega_3|\approx 4:2:1$ and $\Omega_1=\Omega_2\approx 0$, obtained from Eq. (6). Both properties are found in the exact calculations of Sec. V B.

IV. CALCULATIONAL METHODS

The tunneling energies are the differences of the eigenvalues of the eigenstates in the lowest librational multiplet. The basic difficulty in their numerical determination is the extreme precision required. The eigenvalues have to be accurate on a scale several orders of magnitude below the smallest differences of the *librational* energies, i.e., the smallest differences of the eigenvalues for each fixed set $(\Gamma_1,\ldots,\Gamma_N)$ of symmetries. Moreover, every additional interacting rotor drastically extends the amount of numerical work to be done. Here, these problems are further enhanced, because we need to calculate small differences of the already very tiny tunneling energies to get the splitting of tunneling lines.

The molecular field approximation (MFA) is an effective single particle description. It offers an intuitive understanding for the occurrence of the splitting of tunneling lines (Sec. IV A) and its applicability would simplify the task enormously. However, with respect to the extreme precision required, the question is: For which cases does MFA yield sufficiently precise *quantitative* results? This will be studied in Sec. V as a function of both the number of interacting rotors (coordination number) and the coupling strength.

A. Molecular field approximation

Within the MFA, the effective orientational potential for a given rotor depends on the molecular field generated by all neighboring rotors. Note that E-symmetric neighbors are stronger localized and thus cause higher effective fields than A-symmetric neighbors. Consequently, neighborhoods with unlike symmetry yield different effective potentials and the tunneling line splits.

MFA is applied only to model M1 Eq. (2). The $E^a\leftrightarrow E^b$ splitting, only present in model M2 Eq. (3), cannot be obtained from MFA (see below), hence the MFA results for model M2 are necessarily worse than those for model M1. Model M1 is an equivalent neighbour model, therefore the eigenvalues of Eq. (2) depend only on the *number* n of A-symmetric rotors ($0\leq n\leq N$) but not on their sites i. The ground state energy of $H^{(1)}$ in molecular field approximation can be written as

$$nE_0^A+(N-n)E_0^E, \tag{7}$$

where E_0^A and E_0^E are the lowest eigenvalues of the n-dependent effective single-particle Hamiltonians H_{eff}^{Γ},

$$H_{\text{eff}}^A \equiv BL^2+W\left(\frac{n-1}{N-1}\,c^A+\frac{N-n}{N-1}\,c^E\right)(\cos 3\varphi-c^A/2),$$

$$H_{\text{eff}}^E \equiv BL^2+W\left(\frac{n}{N-1}\,c^A+\frac{N-n-1}{N-1}\,c^E\right)(\cos 3\varphi-c^E/2),$$

$$c^{\Gamma}\equiv\langle 0\Gamma|\cos 3\varphi|0\Gamma\rangle \quad \text{with } \Gamma\in\{A,E\}.$$

For a given number n of A-symmetric rotors, the lowest eigenstates $|0\Gamma\rangle$ have to be determined selfconsistently for all symmetries Γ,

$$H_{\text{eff}}^{\Gamma}|0\Gamma\rangle=E_0^{\Gamma}|0\Gamma\rangle.$$

The MFA-ground state is the product state formed from the single-rotor ground states $|0\Gamma\rangle$. In MFA, the splitting of the tunneling line results merely from the inequality $|c^E|\geq|c^A|$, which is due to the different shape of the eigenfunctions of A- and E-symmetry. Since the states $|0E^a\rangle$ and $|0E^b\rangle$ are complex conjugate to each other, it holds that $c^{E^a}=c^{E^b}$. Consequently there cannot be any $E^a\leftrightarrow E^b$ splitting within MFA.

B. Sparse matrix method

Let $|l_i\rangle$ denote the eigenstates of the kinetic energy operator L_i^2 of the ith rotor

$$L_i^2|l_i\rangle=l_i^2|l_i\rangle \ (l_i\in\{\ldots,-2,-1,0,1,2,\ldots\},1\leq i\leq N). \tag{8}$$

In the basis $\{|l_1\rangle|l_2\rangle\ldots|l_N\rangle\}$ of products of free rotor states, the Hamiltonian matrix has only a few nonvanishing elements per row; it is a *sparse matrix*. Because of the ladder operator structure of all potential operators ($e^{i3\varphi}\pm e^{-i3\varphi}$) in the models (2) and (3), we find

$$\langle l'|e^{\pm i3\varphi}|l\rangle=\delta_{l',l\pm 3}.$$

Hence, the number of nonvanishing elements per row is independent of the size of the basis considered; it is equal to $1-2N+2N^2$ for $H^{(1)}$, and for $H^{(2)}$ it is $1+N+N^2$.

On first view, the free rotor basis may look inconvenient and, in particular for model (3), the eigenfunctions of the single-methyl Hamiltonian $BL^2+V\cos 3\varphi$ (Mathieu basis) might appear to be better adapted. However, for strong coupling it turns out that the number of required basis functions does not differ much if the Mathieu- or the free rotor basis is taken. The reason lies in the high accuracy which is needed for the determination of the eigenvalues; it necessitates to take into account highly excited states, whose energies are much above the top of the potential barriers. But the Mathieu eigenstates with high eigenvalues are almost equal to free rotor eigenstates.

The eigenstates $|\Psi^{k_1,k_2,k_3}\rangle$ with quasimomentum (k_1,k_2,k_3), $k_i\in\{-1,0,1\}$, correspond to a certain symmetry $(\Gamma_1,\Gamma_2,\Gamma_3)$. We expand them into products of free rotor states (8), for which $l_i=3p_i+k_i$ and $p_i\in\mathscr{Z}$, i.e., p_i being a whole number,

$$|\Psi^{k_1,k_2,k_3}\rangle=\sum_{p_1,p_2,p_3} C^{k_1,k_2,k_3}_{p_1,p_2,p_3} \times|3p_1+k_1\rangle|3p_2+k_2\rangle|3p_3+k_3\rangle.$$

Inserting this into the stationary Schrödinger equation yields a recursion relation for the expansion coefficients $C^{k_1,k_2,k_3}_{p_1,p_2,p_3}$,

$$\begin{aligned}0=&\left[\sum_{i=1}^{3}(3p_i+k_i)^2-E\right]C^{k_1,k_2,k_3}_{p_1,p_2,p_3}+\frac{V}{2}\,(C^{k_1,k_2,k_3}_{p_1-1,p_2,p_3}\\&+C^{k_1,k_2,k_3}_{p_1+1,p_2,p_3}+C^{k_1,k_2,k_3}_{p_1,p_2-1,p_3}+C^{k_1,k_2,k_3}_{p_1,p_2+1,p_3}\\&+C^{k_1,k_2,k_3}_{p_1,p_2,p_3-1}+C^{k_1,k_2,k_3}_{p_1,p_2,p_3+1})+\frac{W}{4}\,(C^{k_1,k_2,k_3}_{p_1,p_2-1,p_3-1}\\&+C^{k_1,k_2,k_3}_{p_1,p_2+1,p_3+1}+C^{k_1,k_2,k_3}_{p_1-1,p_2,p_3-1}+C^{k_1,k_2,k_3}_{p_1+1,p_2,p_3+1}\\&+C^{k_1,k_2,k_3}_{p_1-1,p_2-1,p_3}+C^{k_1,k_2,k_3}_{p_1+1,p_2+1,p_3}).\end{aligned}\tag{9}$$

Together with the normalizability requirement

$$\langle\Psi^{k_1,k_2,k_3}|\Psi^{k_1,k_2,k_3}\rangle=\sum_{p_1,p_2,p_3}|C^{k_1,k_2,k_3}_{p_1,p_2,p_3}|^2=\text{finite},$$

Eq. (9) can only be satisfied, if the energy parameter E is equal to an eigenvalue of the Schrödinger equation. The lowest eigenvalue E^{k_1,k_2,k_3} for each quasimomentum belongs to the tunneling multiplet. Numerically, the eigenenergy is found by recasting the homogeneous linear system of Eqs. (9) into a truncated inhomogeneous system (one coefficient C can be fixed to 1) which is treated by matrix *inversion*. And E must be adjusted such that the truncated equation is fulfilled (cf. Ref. 7).

The Hilbert subspace is determined by choosing a sphere of radius R around the coefficient $C^{k_1,k_2,k_3}_{0,0,0}$,

$$\sum_{i=1}^{3} p_i^2\leqslant R^2.$$

Most of our results were obtained using $R=9$; only for some potential parameters, which lead to very low tunneling energies, $R=11$ has been needed. This method is very well adapted to the high sparsity of the problem (more than 99%), because it saves computer memory as compared to a diagonalization. It therefore allows a substantial enlargement of the size of the accessible Hilbert subspace and thus an extension of the range of potential parameters, in particular coupling strengths. A further reduction in required computer memory and computation time was achieved by taking advantage of symmetry relations between the coefficients in case of those symmetries (k_1,k_2,k_3) where two or more k_i are equal; for $\{A,A,A\}$ symmetry, only about 1/16 of the full sphere of $C^{0,0,0}_{p_1,p_2,p_3}$ is relevant. The gain in computer time is considerable, particularly for large R. A diagonalization requires an execution time proportional to R^9, whereas our method takes time proportional to R^3 only. A minimization of the ground state energy still needs time at least proportional to R^6. This was perhaps the reason why the variational approach[10] has been restricted to merely $R=5$. We find, that this is not sufficient to correctly determine the *differences* of tunneling energies from the μeV region (in Ref. 10 only eigenvalues are given).

V. RESULTS

A. $\cos 3\varphi_i \cos 3\varphi_j$ type interaction

Consider the tunneling energy of a given methyl group. When the symmetry of i surrounding rotors is changed from A to E, the tunneling energy changes $\propto\delta_i$, which is defined in units of the average tunneling frequency (Fig. 2), e.g.,

$$\delta_1\equiv 2\,\frac{\omega_0-\omega_1}{\omega_0+\omega_1}.\tag{10}$$

The relative splitting δ_i can be used to quantify the reliability of MFA results. For $N=\infty$, we obtain an upper bound $\delta_\infty^{\mathrm{MFA}}$ for the MFA-variation of the tunneling line caused by a complete switch of the symmetry of the surrounding rotors from all-A to all-E.

Figure 3 compares numerically exact values of δ_1 for $N=2$ and 3 with MFA results from Eq. (7); the dashed line shows $\delta_\infty^{\mathrm{MFA}}$. The following trends can be seen:

(1) For $N=2$ and $N=3$ the exact splittings approach $\delta_1\to 2/3$ as $W/B\to\infty$; this limiting value was already obtained in the discussion of the pocket state method (Sec. III) and can be understood in terms of tunneling matrix elements.[19]

(2) On the contrary, MFA predicts a vanishing relative splitting of the tunneling line in the strong coupling limit and for *all* particle numbers.

(3) The δ_1 splittings at low values of $W/B\lesssim 5$ are better reproduced by perturbation theory with respect to the interaction (starting from the free rotor basis), than by self-consistent MFA. Here, both for $N=2$ and $N=3$, the lowest eigenfunctions are poorly approximated by single particle product states.

(4) The numerically exact calculations reveal slight modifications with increasing number of rotors, going from

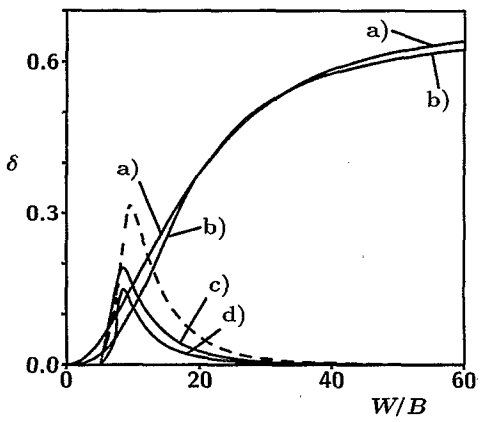

FIG. 3. Relative splitting δ of the tunneling line on the scale of the tunneling energy according to model M1 Eq. (2). The continuous lines show δ_1, as defined in Eq. (10) (a) $N=2$, SMM; (b) $N=3$, SMM; (c) $N=2$, MFA; (d) $N=3$, MFA. The dashed line refers to $\delta_\infty^{\mathrm{MFA}}$ for the infinite system treated in MFA. The tunneling energy for a complete E-symmetric surrounding is compared with the tunneling energy for complete A-symmetric surrounding.

$N=2$ to $N=3$: reduced δ_1 splittings at low $W/B\lesssim 20$; also reduced values at high $W/B\gtrsim 40$; a weak indication for the development of a "peak" between $W/B=20$ and 30 as compared to the $N=2$ behavior.

We tried to improve the MFA approximation by additionally using second-order perturbation theory for the calculation of the correlation energy, starting from the best self-consistent single-rotor states. The only noticeable effect was an improvement for the $W/B\lesssim 5$ splittings. This again confirmes our conjecture that for $N=2$ and $N=3$ the correlations are the dominant origin for the splitting of the tunneling line.

On the other hand, for $N\gtrsim 5$ equivalently coupled rotors, δ_i approaches zero as $W/B\to\infty$ for all i.[19] Insofar the MFA result for the splitting of the tunneling line is becoming exact in the limiting cases of $W/B=0$ and $W/B=\infty$. The properties of item (4) above can be interpreted as the first hint for the evolution of a maximum in δ_1, as it is obtained in MFA for all numbers of rotors.

If MFA described the splitting of tunneling lines correctly, the peak structure for the δ_1-splitting around $W\approx 10B$, would imply

(i) Split tunneling lines should occur only for coupling strengths W roughly ranging from $6B$ to $30B$. This corresponds to tunneling energies between 600 and 10 μeV.

(ii) Only for systems within this range of coupling strengths (or tunneling energies) a shifting of the tunneling line can take place when the concentration of rotors of a given symmetry is changed. In experiments[22,23] the tunneling energies are larger than 140 μeV when such a shifting has been observed for the transition into complete A-symmetric samples (by cooling below the tunneling energy and waiting sufficiently long compared to the nuclear spin conversion time[24]). For this shifting, $\delta_\infty^{\mathrm{MFA}}$ in Fig. 3 would be an upper bound.

It is still unknown, whether or not MFA is capable to correctly describe the splitting of tunneling lines over the *whole range* of interaction strengths in case of (moderately) large numbers of rotors. However, the exact δ_1 curves (Fig. 3) indicate that the peak for $N\gtrsim 5$ ought to be situated around $25B$ and considerable splitting, say $\delta_1\gtrsim 0.05$, should occur within a much broader range of coupling strengths than predicted by MFA. Therefore, MFA yields only *qualitatively* correct δ_1 curves.

B. cos 3($\varphi_i+\varphi_j$) type interaction

Model M2 Eq. (3) combines a single particle potential $\sim V\cos 3\varphi_i$ $(V>0)$ with a pair-interaction $\sim W\cos 3(\varphi_i+\varphi_j)$. Two cases can be distinguished. For the *nonfrustrated* type of coupling $(W<0)$ the interaction deepens the 27 potential minima of the single particle potential, whereas for the *frustrated* type of coupling $(W>0)$, the interaction weakens these minima. For $W>|V|/2>0$, 54 equivalent potential minima appear at shifted positions. All relative splittings of the tunneling lines turn out to be much larger for frustrated coupling.

In this section the quantities

$$v\equiv\frac{\omega_0-\omega_1}{\omega_0} \tag{11}$$

and

$$\Delta_i\equiv\frac{\Omega_i}{\omega_0} \tag{12}$$

[cf. Eq. (6)] are used to measure the splittings of the tunneling lines on the scale of the tunneling energy ω_0.

In Fig. 4 the results for two and three rotors are presented; $V=30B$ and relatively weak coupling is taken. In the case $N=3$ two possible types of $E^a\leftrightarrow E^b$ splittings, Δ_1 and Δ_2 (cf. Fig. 2), exist. From Fig. 4(b) it can be seen that their ratio is approximately $\Delta_2/\Delta_1\approx 2$ for any interaction strength, which is in accordance with Sec. III. The general behavior of v and Δ looks similar. At any coupling strength, the splitting is reduced with increasing number N of particles [this trend can be extrapolated to larger numbers of N (Ref. 12)]. For $N>2$ on the *non*frustrated side, $W<0$, the splitting starts to vanish after an extremum, e.g., for $V=20B$, the extremum in v occurs at $\approx -10B$ respectively at $\approx -50B$ in Δ_2 (Fig. 5). The insets of Fig. 5 show a magnification of the $N=3$ data.

As compared to the $N=2$ behavior, the appearance of extrema of the splittings of the tunneling lines for $N=3$ is a qualitatively new feature. We emphasize the following alterations as compared to the $N=2$ case: The splittings v and Δ (Fig. 5) start to decrease for very large nonfrustrating interactions $(W<0)$. There is a pronounced difference between frustrated and nonfrustrated type of coupling; for $N=3$, the Δ_2 values for the two types of coupling differ by three orders of magnitude [Fig. 5(b)]. Going from $N=2$ to $N=3$, Δ_2 is reduced by two orders of magnitude for $W<0$, and v by one order; for $W>0$ the reduction in the splitting Δ_2 is less pronounced.

Unfortunately it was not possible to clarify, whether or not the relative splittings decrease to zero as $|W|/B\to\infty$. If

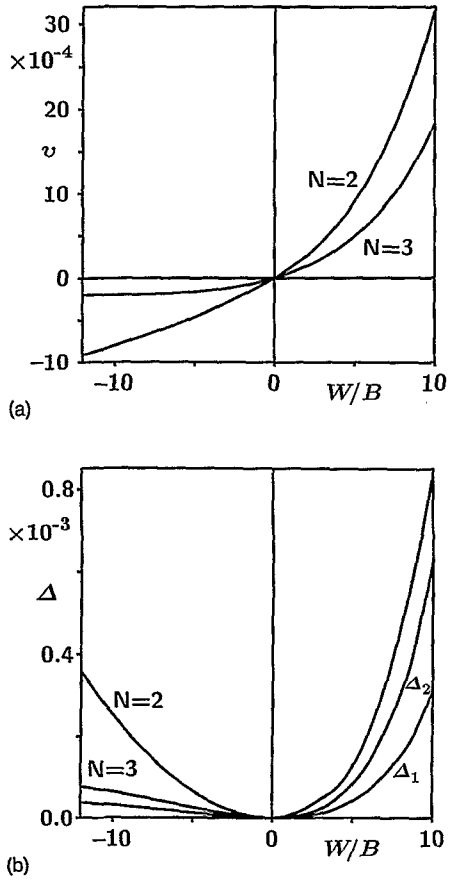

FIG. 4. Influence of the coupling W on the splitting of the tunneling spectrum according to model M2 Eq. (3) for $V=30B$, as calculated by means of the sparse matrix method. In (a), v [cf. Eq. (11)], in (b) Δ [cf. Eq. (12)] is shown, both for $N=2$ and $N=3$ coupled rotors.

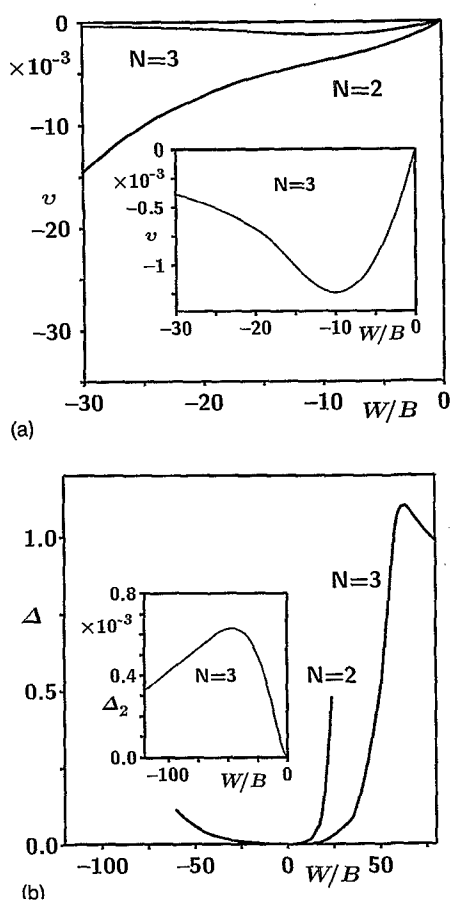

FIG. 5. Same as Fig. 4, but for higher values of W/V; here $V/B=20$ is chosen. The insets show a magnification of the $N=3$ data for nonfrustrated coupling ($W/B<0$). In (b) only Δ_2 is shown for $N=3$.

this was the case, the $\cos 3(\varphi_i+\varphi_j)$ interaction in this respect would be qualitatively different from a $\cos 3\varphi_i \cos 3\varphi_j$ type interaction in case of $N=3$.[19] At least for the nonfrustrated type of coupling $W<0$, the splitting Δ_2 is already close to zero, which is the intrinsic MFA value.

VI. CONCLUSION

We have calculated with extreme precision the tunneling level schemes for two and three orientationally interacting methyl groups. Numerically, a sparse matrix method (SMM) was used which takes advantage of the ladder operator structure of the Hamiltonians. Two types of pair potentials have been considered, (M1) $\cos 3\varphi_i \cos 3\varphi_j$ and (M2) $\cos 3(\varphi_i+\varphi_j)$. The splitting of the tunneling line is of course the most sensitive quantity to test MFA, i.e., the effective single particle description.

For model M1, MFA does not even yield qualitative agreement with the properties of the exact level scheme from SMM for both $N=2$ and $N=3$. However, it is possible to interpret the data as being evidence for a development towards a MFA-like behavior when the number of rotors increases up to more than some value N_c; Ref. 19 indicates $N_c \geq 4$. But the qualitative agreement with MFA for large N is contrasted by the quantitative differences indicated in Fig. 3; the range of coupling strengths where splitting can be expected (Sec. V A) should be much broader than the MFA prediction $6...30B$, which corresponds to tunneling energies between $600...10$ μeV. Therefore, in many systems, the linewidth would be much smaller, if MFA were quantitatively correct; typically, the correlation of the rotors is responsible for the linewidth.

For model M2, where we study a $\cos 3(\varphi_i+\varphi_j)$ pair interaction, relative splittings of the tunneling line and relative $E^a \leftrightarrow E^b$ splittings are calculated with very high precision by SMM. Generally both are reduced for $N=3$ as compared to $N=2$. This is much more pronounced for the nonfrustrated type of coupling, where the single particle potential and the interaction cooperate. In particular the Δ_2 splittings turn out to be smaller than $\approx 10^{-3}$, and therefore they are already close to the intrinsic MFA value $\Delta_2^{\mathrm{MFA}}=0$. Contrary to the $N=2$ case, a qualitatively new feature for $N=3$ is obtained; there are extrema (Fig. 5) of the relative splittings of the tunneling line. With further increased coupling strengths, the splitting and, in accordance with the MFA picture, the correlating influence of the orientational coupling decreases.

Let Z be the coordination number of every rotor in a finitely coordinated infinite network of rotors;[19] for simplicity, we assume equivalent coupling. In order to draw conclusions about the validity of the MFA description of the rela-

tive splittings of the tunneling lines, we estimate $N=1+Z$ to be the relevant particle number in the sense of the present paper. Tentatively applying our results to three-dimensional CH_4 rotors, we do understand the success of explaining rotational tunneling in solid methane phase II by means of MFA.[9] The coordination number among the "ordered" rotors in that case is $Z=8$. This explains *qualitatively* that single particle behavior[25] is observed, despite the fact that the interaction is by far dominant as compared to the single-rotor potential (the latter, originating mainly from the interaction between the hydrogens of one rotor with the carbon atom of an adjacent rotor, is expected to be weak). This maintains the nomenclature to distinguish between "ordered" and "freely rotating" molecules. The observed finite linewidth for the $A \leftrightarrow T$ transition is (at least mainly) attributed to the variation in the symmetry species distribution among different neighborhoods.[8]

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