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Rotational tunnelling of N coupled methyl groups

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Abstract. The influence of orientational coupling between rotational tunnelling molecular groups on the tunnelling spectrum is studied in the limit of strong coupling. In previous work contradicting results were obtained depending on the calculation methods: exact numerical computations for two or three rotors find an increasing relative splitting of the tunnelling lines (i.e. measured on the scale of the tunnelling energy itself) with increasing coupling strength, whereas Hartree approximations always yield a vanishing splitting in this limit. In order to clarify this point, a model of N equivalently coupled XH_3 groups is investigated. The relative splitting is calculated for two types of tunnelling matrix elements prevailing in the strong coupling limit. One of the matrix elements is connected with the motion of only one rotor and is shown to lead to unsplit tunnelling lines. The other matrix element involves the collective motion of all rotors and it is demonstrated that it causes the relative splittings of the tunnelling lines. Within a WKB-type argument the importance of these two matrix elements for the tunnelling spectrum are compared; for $N \leq 3$ a dominance of the coupling influence, and for $N \geq 5$ a dominance of the single-particle influence is found. The case $N = 4$ turns out to be marginal, insofar as neither the contributions from the classical paths nor the contributions from the quadratic fluctuations around the classical paths distinguish between both matrix elements. Therefore even in the strong coupling limit a finite relative splitting of the tunnelling line should remain observable for $N = 4$.

1. Introduction

Since it was discovered that tunnelling lines may split due to the orientational coupling between near-lying rotational tunnelling molecular groups [1], as was found by means of inelastic neutron scattering in lithium acetate [2] (attributed to the interaction between neighbouring pairs of CH_3 groups), the question arose of how this splitting would behave in the case of more than two rotors. Experimentally, split tunnelling lines could only be observed unambiguously when the coupling strength between *two* rotors dominates over the coupling between different pairs of rotors [3]; one exception is the almost freely rotating hexamine systems [4]. Solid methane for example, where the single particle potential contribution can be neglected, compared to the octupol–octupol interaction between neighbouring CH_4 rotors, is very suitably described by an *effective* single particle potential due to the quantum mechanically averaged octupol moments of all neighbouring rotors [5]; a description that results in unsplit tunnelling lines, in accordance with the observation [6]. On the other hand, it is found from numerical calculations, performed at systems containing two [7], three [8, 9], or four

[10] rotors, that an increasing coupling strength always yields an increasing relative splitting of the tunnelling line.

The very suggestive Hartree picture [11] is often used to explain tunnelling splittings: the effective orientational potential of a given rotor depends on the molecular field of the neighbouring rotors, which itself depends on the symmetry state of the neighbours; this results in an effective potential contribution depending on the given symmetry species distribution of the surroundings. This distribution varies between different sites, resulting in different effective potentials, and hence split tunnelling lines. This picture, when taken seriously for self-consistent numerical calculations of, for example, two rotors, leads to completely wrong relative splittings [8]. Moreover, the Hartree picture is inherently incapable of reproducing $E^a \leftrightarrow E^b$ splittings, because complex-conjugate wavefunctions produce equal molecular fields. A salient prediction of Hartree calculations is the vanishing of the relative splittings in the strong coupling limit, independent on the number of coupled rotors; insofar as the Hartree result is capable of explaining the observations on CH_4 [5, 6].

One aim of the present paper is to illuminate the origin of the splitting of the tunnelling line and the role of the particle number. An estimate should be given for the possible range of reliability of Hartree-type calculations. As representatives for rotational tunnelling systems methyl groups are considered, assuming a certain model for the pair potential. Orientational coupling in more complicated systems, like diluted CH_4 [12], is not yet observed unambiguously and computations are of course much more complicated [13]. The relevant tunnelling matrix elements, depending on the particle number, are calculated approximately in section 3. Using these matrix elements, the tunnelling spectrum of N rotors will be calculated in section 4.

2. The model

The following model Hamiltonian for N equivalently coupled methyl groups is considered:

$$H = -B \sum_{i=1}^N \partial_{\hat{\phi}_i} - \frac{W/2}{N-1} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \cos 3\hat{\phi}_i \cos 3\hat{\phi}_j. \quad (1)$$

$B \approx 650 \mu\text{eV}$ is the rotational constant and W the strength of the methyl-methyl coupling. H has threefold symmetry with respect to all angle operators $\hat{\phi}_i$, due to the identity of the hydrogen atoms. The factor $1/(N-1)$ ensures an extensive ground-state energy. This model may describe experimental situations for $N = 2$ (coupled pairs), $N = 3$ and $N = 4$ (e.g. tetrahedral $\text{Me}(\text{CH}_3)_4$ compounds, as they are studied in tin or lead tetra methyl [14]). Note, however, that for infinite N it does not represent lattices of coupled rotational tunnelling groups, like one-dimensional chains, two-dimensional planes (as in $\text{SnF}_2(\text{CH}_3)_2$ [15]) or three-dimensional lattices (such as methane), all being characterized by a finite coordination of every rotor. Some tentative conclusions even for these systems will be drawn in section 5.

The pair interaction, chosen here, differs from the one considered in other papers [2, 7] dealing with orientational coupling, even though it represents quite well, for example, the situation of methyl groups rotating in a common plane with parallel axes. A coupling $\sim \cos 3\hat{\phi}_i \cos 3\hat{\phi}_j$ guarantees the degeneracy of all E^a - and E^b -symmetric

eigen-energies and is therefore most consistent with a Hartree calculation. All eigenvalues of (1) are just determined by the number of rotors being in E-symmetric states. As already mentioned, the Hartree approximation predicts, for $W/B \rightarrow \infty$, a zero relative splitting (i.e. when measured on the scale of the mean tunnelling frequency) of the tunnelling line, independently of the particle number N .

3. Dominant tunnelling matrix elements

In the limit $W/B \rightarrow \infty$, the probability amplitudes of the ground states are well localized at the positions of the potential minima, forming pocket states [16, 17] at every minimum. For high potential barriers and a suitable choice for the pocket states, the matrix elements of the Hamiltonian between adjacent pocket states allow the tunnelling energy to be determined quite well. With increasing W , all overlaps die out exponentially so that finally one type of matrix element t will dominate the tunnelling energy.

3.1. The potential

Before estimating the tunnelling integrals t , a short discussion of the potential should be given. For all N there are two minima per unit cell of volume $(2\pi/3)^N$: they correspond to $\cos 3\varphi_i = +1$ and $\cos 3\varphi_i = -1$ for all $1 \leq i \leq N$. These 2×3^N equivalent minima form a body-centred cubic lattice (of dimension N), as illustrated in figure 1 for $N = 3$. Every minimum is surrounded by two types of next-neighbouring minima: (a) along the $2N$ edges of the $(2\pi/3)^N$ unit cell and (b) along the half length of its 2^N space diagonals. The distances of the neighbours are $2\pi/3$ and $\sqrt{N}\pi/3$. The $(\frac{N}{\text{int}(N/2)})$ potential maxima (only for $N = 3$, the maxima form a continuous net over the unit cell) have a height of $W/2$ for odd numbers N or $\frac{W}{2} \frac{N}{N-1}$ for even numbers N . The maxima are located at the centres of all $(N+1)/2$ - or $N/2$ -dimensional hypersquares, surrounding the unit cell. In consequence, for both types of neighbourhoods (i) and (ii), a straight line in configuration space, connecting two adjacent potential minima, crosses a saddle point of the potential (with the exception of $N = 2$); the structure of the potential is such that just the straight lines are the classical paths of *minimal* action, that start and end in adjacent minima. The barrier heights are (i) $2W$ and (ii) $NW/2$ respectively.

The curvatures of the potential are characterized by the eigenvalues of the Hesse matrix (also in case (ii) the Hesse matrix can be diagonalized easily, as it is a cyclic matrix). These eigenvalues along the straight lines (i) and (ii) are given by:

(i) $9W \cos 3\varphi_1$ in the direction of a path (here along φ_1) of type (i) and $9W(1 - \frac{1 - \cos 3\varphi_1}{N-1})$ in all orthogonal directions.

(ii) $9W \cos 6\alpha_0$, with $\alpha_0 := (1/N) \sum_{i=1}^N \varphi_i$, along a path of type (ii) and $9W(1 - \frac{(N-2)(1 - \cos 6\alpha_0)}{2(N-1)})$ in all orthogonal directions.

Note, that in both cases the eigenvalues related to directions orthogonal to the paths and are non-negative for $N \geq 3$ and that all curvatures are equal for $N = 4$ ($\varphi_1 \in [0, 2\pi/3]$ and $\alpha_0 \in [0, \pi/3]$).

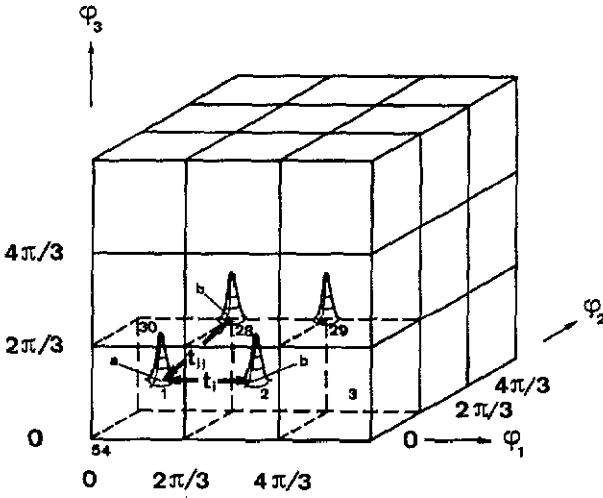


Figure 1. Structure of the potential in case of three particles $N = 3$; a suitable choice for the enumeration of the 2×3^N minima is indicated. a and b denote the two relevant types of next-neighbouring potential minima, which are connected along paths (i) i.e. the edges or along paths (ii) i.e. the space diagonals of every $(2\pi/3)^N$ unit cell.

3.2. Classical action

The tunnelling integrals t may be approximated by

$$t_{i,ii} \sim A \exp(-S_E/\hbar) \tag{2}$$

where S_E is the Euclidian action along a classical one instanton path [18] between two adjacent minima, say a and b of type (i) or (ii) (cf figure 1) and A is the prefactor, which is determined by the quadratic fluctuations around the classical paths. This relation can be derived from the long-time behaviour of the matrix elements of the time evolution operator in (Wick-rotated) imaginary time representation between position eigenstates, which are localized at a and b respectively, as is shown for example in [18, 19] for one-dimensional systems. As the prefactor generally depends only weakly on the potential barrier height (according to a power law only), the part which is exponentially dependent on W (2), determines which matrix element dominates in the large W limit. The Euclidian action is given by

$$S_E = \int_{-\infty}^{\infty} d\tau \left[\frac{\hbar^2}{4B} (\dot{\vec{\varphi}}^{Cl}(\tau))^2 + U(\vec{\varphi}^{Cl}(\tau)) \right] \tag{3}$$

where $\hbar^2/2B$ is the moment of inertia of *one* rotor, $\vec{\varphi} \equiv \{\varphi_1, \dots, \varphi_N\}$, the dot denotes the derivative with respect to τ and

$$U(\vec{\varphi}) := -\frac{W}{N-1} \sum_{i=1}^N \sum_{j=i+1}^N \cos 3\varphi_i \cos 3\varphi_j + \frac{WN}{2}$$

is the potential energy (the additive constant fixes the ground state energy to zero). $\vec{\varphi}^{Cl}(\tau)$ obeys the classical equation of motion in the inverted potential $-U$

$$(\hbar^2/2B)\ddot{\vec{\varphi}}^{Cl}(\tau) = +\text{grad}\{U(\vec{\varphi}^{Cl}(\tau))\}.$$

The boundary conditions are $\bar{\varphi}^{\text{Cl}}(\tau = -\infty) = a$, $\bar{\varphi}^{\text{Cl}}(\tau = +\infty) = b$ and it is required that $\bar{\varphi}^{\text{Cl}}(\tau)$ should monotonously approach b , i.e. that they are the one-instanton solutions corresponding to the potential $-U$. According to the previous section, the classical paths are just straight lines in configuration space connecting the minima a and b . For the two types of path the multi-dimensional instanton solution is therefore given by $\bar{\varphi}_i^{\text{Cl}}(\tau) = \{\varphi_1^{\text{Cl}}(\tau), 0, \dots, 0\}$ and $\bar{\varphi}_{ii}^{\text{Cl}}(\tau) = \{\alpha_0^{\text{Cl}}(\tau), \dots, \alpha_0^{\text{Cl}}(\tau)\}$, $\varphi_1^{\text{Cl}}(\tau)$ and $\alpha_0^{\text{Cl}}(\tau)$ being one-dimensional instantons.

After substitution of the integration variable, the tunnelling matrix elements become

$$t_i \sim \exp -\frac{1}{\hbar} \int_0^{2\pi/3} d\varphi_1 \sqrt{\frac{W}{B}(1 - \cos 3\varphi_1)} = e^{-(4/3)\sqrt{2W/B}} \quad (4a)$$

$$t_{ii} \sim \exp -\frac{1}{\hbar} \int_0^{\pi/3} d\alpha_0 \sqrt{N^2 \frac{W}{2B}(1 - \cos^2 3\alpha_0)} = e^{-(N/3)\sqrt{2W/B}} \quad (4b)$$

In the case of (4a) the result just corresponds to the WKB integral of a one-dimensional threefold Mathieu problem $-B\partial_\varphi^2 + W(1 - \cos 3\varphi)$. The N -dependence in (4b) is firstly due to the increasing mass of N rotors moving simultaneously along the space diagonal of the unit cube. A second contribution comes from the height of the barrier being proportional to N .

For $N = 4$, no exponential difference between t_i and t_{ii} appears; the much weaker W -dependence of one of the two prefactors A in (3) should determine which of the two tunnelling-matrix elements dominates. The prefactor is given by the determinant of some operator, which depends solely on the second derivatives of the potential along the classical path. But all the curvatures along both types of path are found in section 3.1 to be equal in the case of $N = 4$ and therefore even the contributions from the quadratic fluctuations around the classical paths to the tunnelling-matrix element are equal for (i) and (ii). The considered approximation up to second-order in the fluctuations around the classical paths is known [20] to be sufficient for a quantitative determination of tunnelling frequencies of the threefold Mathieu problem in the $W/B \rightarrow \infty$ limit, i.e. just on the energy scale on which the splitting of tunnelling lines are characterized here.

For the other particle numbers a dominant coupling behaviour is found if $N \leq 3$, and a dominant single-particle behaviour if $N \geq 5$. The important prediction is therefore a vanishing relative splitting of the tunnelling line according to model (1) if the particle number exceeds 4.

4. Energy spectra resulting from t_i and t_{ii}

The Hamiltonian matrix may be written in the basis of 2×3^N pocket states, each corresponding to a highly localized probability amplitude at a certain potential minimum [16, 17]. Symmetrized linear combinations of good representatives of pocket states, with respect to the symmetry group of the rotor, approximate to the eigenstates of H quite well in cases of high potential barriers. These pocket states define a finite-dimensional basis of the most relevant part of the Hilbert space. Accordingly, the eigenvalues of the corresponding Hamiltonian matrix approximate to the vibrational ground state energies, the differences being the tunnelling energies.

For a given number n of A-symmetric rotors ($1 \leq n \leq N$, the number of E-symmetric rotors is $N - n$), the eigenvalues are given by

$$\begin{aligned} & \left[2n + \left(e^{i2\pi/3} + e^{-i2\pi/3} \right) (N - n) \right] t_i \\ & + \left(\prod_{j=1}^N \Gamma_j \right)^{-1/2} \left[1 + \sum_{1 \leq j_1 \leq N} \Gamma_{j_1} \right. \\ & \left. + \sum_{1 \leq j_1 < j_2 \leq N} \Gamma_{j_1} \Gamma_{j_2} + \sum_{1 \leq j_1 < j_2 < j_3 \leq N} \Gamma_{j_1} \Gamma_{j_2} \Gamma_{j_3} + \dots + \prod_{j=1}^N \Gamma_j \right] t_{ii}. \end{aligned} \quad (5)$$

Here $\Gamma_j := (e^{i2\pi/3})^{k_j}$, $\{k_1, \dots, k_N\}$ characterizing the symmetry state of the corresponding eigenvector (i.e. $k_j = 0$ if the j th rotor is in an A-symmetric state and $k_j = \pm 1$ for an E^s-symmetric state respectively). Equation (5) may be interpreted as follows: all eigenvectors of H are Bloch states (the $\{k_1, \dots, k_N\}$ form the reciprocal lattice corresponding to the $(2\pi/3)^N$ unit cells) which gain a phase factor of $(e^{i2\pi/3})^{k_j}$ when φ_j is increased by $2\pi/3$. In order to find the eigenvalue corresponding to a given $\{k_1, \dots, k_N\}$, we have to sum up all next-neighbour phase contributions starting from a certain potential minimum say, for example, of number 1, for $2N$ neighbours of type (i) and 2^N neighbours of type (ii). The phase relation to neighbours of the first type is simply $(e^{\pm i2\pi/3})^{k_j}$ depending on the Bloch phase exponent k_j along the corresponding edge. The relation to the minima of the second type is found as follows: minimum number 1 and minimum number 2×3^N (the one lying across the half-space diagonal) are related by a phase factor $(\prod_{j=1}^N \Gamma_j)^{-1/2}$; this phase factor is common to all the 2^N corners of the cube surrounding minimum number 1. Now the phase relation between the corner 2×3^N and all other corners is determined by the number of edges which have to be passed in order to reach them respectively, starting from the corner 2×3^N , e.g. the minimum on the space diagonally opposite side to 1 (which is $1 + 3^N$), is reached after passing N edges. Different sums in the second square brackets of (5) classify different types of corners.

The eigenvalues (5) are real; for the terms $\sim t_{ii}$ this is because every single term is a complex number of modulus 1 and, together with the common factor $(\prod_{j=1}^N \Gamma_j)^{-1/2}$, the first and the last, the second and the second last terms etc. form mutually reciprocal complex values.

The eigenvalues (5) can be calculated for given numbers n of A-symmetric rotors as is shown in the appendix. They are

$$E^{\{k_1, \dots, k_N\}} = (3n - N)t_i + 2^n t_{ii}.$$

This energy spectrum is illustrated in figure 2.

Three cases must be distinguished:

(i) t_i is the dominant matrix element; then the resulting tunnelling spectrum is equidistant with tunnelling energy $3|t_i|$ and the rotors behave as being effectively uncoupled. This was shown in section 3.2 to be the case if the particle number N exceeds 4. The case of a vanishing splitting of the tunnelling line agrees at least qualitatively with the result of a Hartree-type calculation; the wavefunction can be

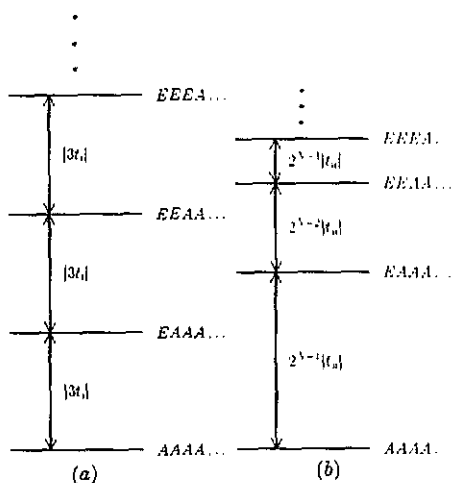


Figure 2. Energy level scheme for N coupled rotors according to model (1) in the large W limit. (a) shows the spectrum for dominant tunnelling-matrix element t_i and (b) for dominant t_{ii} . The equidistant spectrum of (a) corresponds to an effective single-particle problem with potential $W \cos 3\varphi$. The negative sign of the $t_{i,ii}$ is due to the kinetic energy part of the Hamiltonian.

represented by a suitable product of single-particle wavefunctions and the correlations become unimportant in the strong coupling limit. It would be worthwhile to check the quantitative validity of the Hartree approximation for weaker coupling strengths and $N \geq 5$.

(ii) t_{ii} is the dominant matrix element; then the spectrum may be characterized by the following relative splittings of the tunnelling line, measured on the scale of the mean tunnelling frequency

$$\frac{(E^{EAAA\dots} - E^{AAAA\dots}) - (E^{EEEE\dots} - E^{AEEE\dots})}{\frac{1}{2}[(E^{EAAA\dots} - E^{AAAA\dots}) + (E^{EEEE\dots} - E^{AEEE\dots})]} = 2 \frac{2^{N-1} - 1}{2^{N-1} + 1} \quad (6)$$

if complete A- and complete E-symmetric surroundings are compared, or

$$\frac{(E^{EAAA\dots} - E^{AAAA\dots}) - (E^{EEAA\dots} - E^{EAAA\dots})}{\frac{1}{2}[(E^{EAAA\dots} - E^{AAAA\dots}) + (E^{EEAA\dots} - E^{EAAA\dots})]} = \frac{2}{3} \quad (7)$$

if the second tunnelling line is compared with the first one.

Both relations are also found in exact numerical calculations for $N = 2$ and $N = 3$ in the strong-coupling limit [8]. They can also be found in figure 5 of [9] for intermediate values of the coupling strength within the numerical accuracy.

(iii) t_i and t_{ii} are of comparable size; then at least the energy difference between the lowest tunnelling states is dominated by t_{ii} and therefore a split tunnelling line should be observable. For the quantity (7) one now obtains $\frac{2}{3}$. This was estimated to be the case for $N = 4$.

5. Conclusion

The tunnelling spectrum for a system of N coupled XH_3 rotors has been calculated for an equivalent-neighbour model (1) in the limit of strong coupling, when only two possible types of tunnelling integral dominate. No single-particle potential has been

taken into account for the rotors, because such a potential would not modify any result for $W \rightarrow \infty$ and, for finite W , it would lead to reduced values for the relative splittings of the tunnelling line.

Within a WKB-type argument it turns out, that a split tunnelling line is only expected if less than 5 rotors are mutually coupled. Otherwise the matrix element t_i , corresponding to uncoupled $2\pi/3$ rotations of a single rotor, dominates and the wavefunction approaches a product of single-particle states. This suggests strongly that for $N \geq 5$, Hartree-type calculations should become reliable, eventually also for weaker coupling strengths. One consequence would be that split tunnelling lines in coupled $N \geq 5$ systems should occur only within a certain limited range of (relatively large) tunnelling frequencies [8]. The observed splitting of the tunnelling lines in the hexamine systems would fall into this category. Note that the reason for the vanishing of the relative splitting of the tunnelling line for $N \geq 5$ is not the decreasing of the relative fluctuation in the probability distribution of the surrounding rotors with respect to a given rotor; the tunnelling frequency should not even vary as the symmetry of the surrounding is changed from complete E-symmetry into complete A-symmetry.

The N dependence of the matrix element t_{ii} , corresponding to simultaneous $\pi/3$ rotations of all rotors, results from the N -dependent mass which is involved when moving between two adjacent potential minima of type (ii), and from the N -dependent height of the barrier to be surmounted; finally, the infinite system will show a spontaneous symmetry-breaking and localize into one half of the minima.

Real physical systems are indeed often infinite, but not all rotors are equivalently coupled. In order to also draw conclusions about the relative splittings also for finitely coordinated networks with equal coupling strengths between all next neighbours, it is suggested that a cluster expansion is imagined and attention is focused on the lowest-order terms. The single-particle contribution corresponds to an averaged Hartree result, which reproduces the mean of the tunnelling frequency. The term including the next-neighbour sphere of rotors, when the boundary conditions are suitably modified, corresponds to the equivalent-neighbour model presented here. This correspondence is of course not quantitatively correct, since contributions to the inter-cluster interaction are replaced by intra-cluster interactions. The relative splittings of the tunnelling line expected from an equivalent-neighbour model are therefore to be considered as upper bounds for the splittings in the corresponding infinite network. In consequence, only the one-dimensional chains of coupled methyl groups are expected to show a split tunnelling line (in the limit of strong coupling), as only they correspond in that sense to the case $N = 3$. This is in qualitative agreement with the result of a recent investigation [21], where for chains of mutually strongly coupled methyl groups a split tunnelling feature was deduced, albeit in a system allowing a collective free-rotor mode (with interaction potential $\sim W \cos 3(\varphi_i - \varphi_j)$). All higher-dimensional lattices (with the rather academic exception of a honeycomb lattice in two-dimensions, which is related to $N = 4$) should exhibit unsplit tunnelling lines. In particular, solid methane in the low-temperature phase II would be considered an $N = 9$ case, which makes the observed single-particle behaviour understandable. Some caution is advisable concerning predictions for the diluted rotational tunnelling systems in rare gas matrices [22], which contain small, orientationally coupled clusters of various sizes. These systems often are almost freely rotating and only if the two-particle interaction is strong enough to reduce the tunnelling frequency severely, the results of this paper should be applicable. In the weak coupling limit, it is known from a perturbational treatment that those systems should exhibit split tunnelling lines [23].

In order to confirm the results presented here, numerical calculations for particle numbers $N = 3, 4, 5$ would be desirable. Moreover, exact calculations of tunnelling spectra of long chains could test the prediction of a tunnel-split ground state in such systems of coordination 2. The hope is that only the small systems escape the relatively easy-to-use single-particle description for the orientational coupling phenomenon.

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Appendix. Evaluation of the eigenvalues

The expression in the first square brackets of (5) is equal to $3n - N$, using $e^{i2\pi/3} + e^{-i2\pi/3} = -1$.

In order to prove the identity

$$\left(\prod_{j=1}^N \Gamma_j \right)^{-1/2} \left(1 + \sum_{1 \leq j_1 \leq N} \Gamma_{j_1} + \sum_{1 \leq j_1 < j_2 \leq N} \Gamma_{j_1} \Gamma_{j_2} + \sum_{1 \leq j_1 < j_2 < j_3 \leq N} \Gamma_{j_1} \Gamma_{j_2} \Gamma_{j_3} + \dots + \prod_{j=1}^N \Gamma_j \right) = 2^n \quad (\text{A1})$$

where n denotes the number of A-symmetric rotors and $\Gamma_j = (e^{i2\pi/3})^{k_j}$, $k_j \in \{-1, 0, +1\}$, $j \in \{1, \dots, N\}$, it should be recalled that the eigenvalues only depend on the number of A-symmetric rotors. The first factor is therefore

$$\prod_{j=1}^N \Gamma_j = (e^{i2\pi/3})^{N-n}. \quad (\text{A2})$$

The second factor can be written as

$$\sum_{l=0}^N \sum_{1 \leq j_1 < j_2 < \dots < j_l \leq N} \prod_{\kappa=1}^l \Gamma_{j_\kappa} = \sum_{l=0}^N \sum_{\lambda=0}^l (e^{i2\pi/3})^\lambda \binom{n}{l-\lambda} \binom{N-n}{\lambda}.$$

The identity can be seen as follows. Without loss of generality let

$$\{k_1, \dots, k_N\} = \underbrace{\{0, \dots, 0\}}_n \underbrace{\{1, \dots, 1\}}_{N-n}.$$

Then for a certain l , λ of the l j s may be larger than n ($0 \leq \lambda \leq l$, $1 \leq j_{l-\lambda} \leq n < j_{l-\lambda+1} \leq N$) and the corresponding Γ_j are equal to $e^{i2\pi/3}$. For fixed λ there are $\binom{n}{l-\lambda}$ terms with $j \leq n$ and $\binom{N-n}{\lambda}$ terms with $j > n$.

Now it remains to calculate the double sum over the binomials:

$$\begin{aligned}
 & \sum_{l=0}^N \sum_{\lambda=0}^l (e^{i2\pi/3})^\lambda \binom{n}{l-\lambda} \binom{N-n}{\lambda} \\
 &= \sum_{\lambda=0}^N (e^{i2\pi/3})^\lambda \binom{N-n}{\lambda} \underbrace{\sum_{l=\lambda}^N \binom{n}{l-\lambda}}_{\sum_{l=0}^{N-\lambda} \binom{n}{l}} \\
 & \sum_{l=0}^{N-\lambda} \binom{n}{l} = \begin{cases} 2^n & \text{if } \lambda \leq N-n \\ 2^n - \sum_{l=N-\lambda+1}^n \binom{n}{l} & \text{if } \lambda > N-n \end{cases} \\
 &= \sum_{\lambda=0}^{N-n} (e^{i2\pi/3})^\lambda \binom{N-n}{\lambda} 2^n = 2^n (1 + e^{i2\pi/3})^{N-n}. \quad (\text{A3})
 \end{aligned}$$

The last but one sign of equality is valid because the terms with $\lambda > N - n$ vanish due to the properties of the binomial coefficients. Equation (A1) follows from (A2) and (A3).

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