Theory of the Temperature Dependence of Rotational Tunnelling Phenomena of Coupled Pairs of CH$_3$ Groups

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A discussion of the need to go beyond the single-isolated-molecular group approximation for the temperature dependence of rotational tunnelling properties is given. As a simple model calculation the case of a coupled-pair of methyl groups is considered in the Hewson [8] approximation. Some recent experimental results on lithium acetate [1] are discussed in the framework of the model.

I. Introduction

Quantum coherence phenomena are of some current interest [2]. In particular there has been considerable theoretical interest in the effect of coupling to other degrees of freedom. Rotational tunnelling of molecular groups in solids provides us with a quantum coherence system that is experimentally quite easy to investigate and which exhibits interesting temperature dependent phenomena. Press [3] has reviewed much of the experimental work and the theoretical interpretation of the results. The theory is very successful in explaining experimental data at the very lowest temperatures but, however, is rather unsuccessful in accounting for the temperature dependent effects. It is the latter problem that is the subject of this and another later paper.

Until recently theoretical efforts have concentrated on the problem of a single molecular group coupled to a continuum of boson states (phonons). Hewson [8] obtained the lowest order perturbational result for the neutron spectrum using the Green function equation of Motion technique. Agreement with experiment was found in several cases to be unsatisfactory [6]. This strongly suggests that for many systems we are not dealing with a weak-coupling problem and we must either find another starting point or sum certain terms in the perturbation series to infinite order. Clough et al. [4] attempted the former in a theory which treats the lattice as a heat bath. This theory raises many interesting points but has been shown [6] to be based on a use of non-rigorous quantum mechanics which makes its value difficult to assess. Huggins et al. [6, 7] have argued that the main difficulty lies in the most common Ansatz: one considers a single molecular group in an average (static) potential well (static well approximation SWA) and treats the interactions as perturbations. He has argued that the temperature dependence can be better understood in many cases by including from the beginning the dispersed nature of the torsional motion. That is the SWA is not universally applicable. As a (more extreme) example consider a simple Bravais lattice. If we used as a basis set the Einstein oscillator states for the average potential we would have great difficulty in explaining experiments using perturbation theory. In molecular tunnelling systems with closely-spaced molecular groups the Einstein oscillator approach does not adequately allow for the coherent propagation of torsional excitations (librons).

An important question then arises: the Einstein oscillator approximation for a Bravais lattice would fail to explain the $T=0$ neutron scattering spectrum so why is the SWA so successful in explaining the neutron spectrum [5, 9] at very low temperatures? This is a consequence of a molecular group's symmetry and can be seen in the calculation of Gehring et al. [7] where the most important symmetry-allowed matrix elements result in no renormalization of the SWA tunnel splittings at $T=0$.

In this paper we consider the simplest possible model which goes beyond the SWA in the simplest possible approximation i.e. the Hewson model [8] ex-
tended to a pair of coupled methyl groups. Then in a later paper we shall give a discussion of the temperature dependent properties in real crystals with closely-spaced methyl groups and to discuss possible experiments to investigate this point of view. We wish to use the simple model in the present paper to illustrate differences from the results of SWA theories. In addition, recent neutron scattering experiments [1] have suggested that lithium acetate contains coupled pairs of methyl groups which interact only weakly with other pairs and the rest of the lattice. We apply our results to this system and find that the theory is not in contradiction with experiment. Unfortunately, the methyl group pairs are close to freely-rotating pairs which means there are many low-lying excited states and hence several coupling coefficients appear in the theoretical formulae which cannot be calculated or measured. This prevents our formulae being useful as far as a good fit to experiment is concerned but nevertheless they give insight into the mechanism responsible for the temperature dependence. More important is the possibility that other systems far from the freely-rotating-pair limit may be discovered and since the extra coupled-pair tunnel splittings [1] would not be resolvable by neutron scattering some of the temperature dependent properties would appear anomalous in a SWA picture. Lithium acetate does give a clear example of the limitations of the SWA approach. It is not universal although it can be expected to be satisfactory for some systems.

II. Coupled Pairs of Methyl Groups

As a first step beyond the static well approximation we consider a pair of methyl groups which interact strongly between themselves but are essentially isolated from other pairs of groups in the crystal. It is assumed that the pairs interact weakly with the surrounding lattice so that this interaction may be treated as a perturbation. It is then fairly straightforward to generalize Hewson’s model [8-1 to this more complicated case. This problem is not purely academic since it has recently been found that lithium acetate crystallizes with paired methyl groups [1] with apparently only weak interpair interactions. Clough et al. [1] have calculated the energy levels for the Hamiltonian

\[ \mathcal{H} = \frac{\hbar^2}{2I} \left( \frac{\partial^2}{\partial \theta_1^2} + \frac{\partial^2}{\partial \theta_2^2} \right) + V(\cos 3\theta_1 + \cos 3\theta_2) + W \cos 3(\theta_1 - \theta_2) \]  

(1)

\( \theta_1, \theta_2 \) are orientations of the two methyl groups, \( I \) is the moment of inertia of a single-methyl group and \( V \) is the interaction parameter between a single group and the surrounding lattice. \( W \) is the intermethyl group interaction parameter. More general Hamiltonians are clearly possible but Clough et al. [1] found that Eq. (1) was adequate to describe the energy levels of lithium acetate. If \( W = 0, V \neq 0 \) we recover the usual SWA solutions while if \( V = 0, W \neq 0 \) we may make the transformation \( \xi_1 = \theta_1 + \theta_2 \) and \( \xi_2 = \theta_1 - \theta_2 \) and separate the Schrödinger equation into a free rotor part and an oscillator part. In this case the ground state splittings take the form shown in Fig.1. We have labelled the eigenstates in the same way as [1] by making use of the correspondence with the total nuclear spin quantum number \((3/2 \leftrightarrow A, \text{one of the 1/2 states} \leftrightarrow E_a, \text{the other} E_b)\). In the more interesting case \( 0 < W < V \) Clough et al. found the ground state splittings shown in Fig.2. We wish to discuss both the case of almost free rotation and strongly-hindered rotation. It is convenient to use a different notation for eigenvalues and eigenstates of (1) for these two limiting cases. For the nearly free rotor we define \([n s's']\), where \( s, s' \) are the nuclear spin states by

\[ \phi_{nss'} = \langle nss' | \mathcal{H} | nss' \rangle = E_{nss'} | nss' \rangle. \]  

(2)

Here the number \( n \) indicates the \( n \)th excited state with nuclear spin state \( ss' \). \([nss']\) is always degenerate with the state \([ns's']\). In the oscillator-like case, where both \( W \) and \( V \) are large, we know that the excited states must resemble tunnel-split coupled-oscillator states. The total wavefunction of a pair of coupled oscillators is a product of a symmetric mode (in phase) and an antisymmetric mode (anti-phase). In the symmetric mode the two methyl