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COMMENT

## Rotational tunnelling and Kramers degeneracy

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**Abstract.** The E-symmetric states of rotational tunnelling systems are shown to exhibit Kramers degeneracy; we demonstrate how the corresponding time-reversal symmetry could be broken by a more general coupling to phonons. The physical relevance of this is discussed and we comment on a paper by Clough that appeared in *New Scientist* in March 1988.

There has been controversy concerning the proper treatment of the coupling of a tunnelling particle to lattice vibrations (Clough 1985, Gunn 1985). Recently, Clough (Clough 1988, Clough *et al* 1988) has argued that conventional quantum mechanics does not correctly account for the interaction of a methyl rotor with its crystal environment, and in particular for the removal of the degeneracy of the E-symmetric states. Furthermore, he claims that the only escape is to use a multi-valued rotational wavefunction  $\psi(\varphi) \neq \psi(\varphi + 2\pi)$  in connection with what has become known as Berry's phase (Berry 1984).

A methyl group may be looked at as a one-dimensional rotor subject to the potential caused by the neighbouring atoms; the three protons being indistinguishable, the Hamiltonian must be invariant under rotations of  $2\pi/3$  in the collective angle  $\varphi \equiv \frac{1}{3}(\varphi_1 + \varphi_2 + \varphi_3)$ . When we describe the crystal environment using a single harmonic oscillator of frequency  $\omega$  and retain only the lowest-order components of a Fourier expansion of the potential energy, we obtain the Hamiltonian operator

$$H_0 = -\partial^2/\partial\varphi^2 + V \cos(3\varphi) + 4\hbar\omega b^+ b + g \sin(3\varphi + \delta)(b^+ + b). \quad (1)$$

The phase  $\delta$  governs the relative coupling strength to the sine or shaking mode and to the cosine or breathing mode.

Now we look at the behaviour of the Hamiltonian under time reversal; the corresponding operator for a system of three fermions reads (Kittel 1963)

$$\theta = (-i\sigma_y^{(1)})(-i\sigma_y^{(2)})(-i\sigma_y^{(3)})C. \quad (2)$$

$C$  is the operator of complex conjugation and  $\sigma_y^{(v)}$  are usual Pauli matrices.  $\theta$  commutes with the position operator and anti-commutes with the angular momentum.

The Hamiltonian being quadratic in the angular momentum and real, its commutator with the time-reversal operator vanishes. Therefore the four lowest-lying E-symmetric states are degenerate; the second pair of them, as given in the Appendix, may be constructed by applying  $\theta$  to the first one.

The generalisation of (1) with many harmonic oscillators is the usual starting point for a treatment of temperature effects in rotational tunnelling (Hewson 1982, Würger 1989). The condition for Kramers degeneracy given above is satisfied by any coupling term derived from a potential energy, i.e. that is a function of the rotor and bath coordinates only.

A different situation may arise from the more general interaction

$$H_1 = \bar{g}(l_- b^+ + l_+ b) \quad (3)$$

where  $l_{\pm} \equiv \exp(\pm i3\varphi)$  are ladder operators in the angular momentum basis. This coupling term represents a rotor driven by the bath around its axis in a definite sense. To avoid misunderstanding, we stress that (3) is not an equivalent of the rotating wave approximation commonly made in the treatment of damping phenomena of a harmonic oscillator coupled to a heat bath (Lindenberg and West 1984) and that is assumed to preserve the main features of a coupling linear in the oscillator displacements.

The commutator of  $H_1$  with the time-reversal operator is easily calculated:

$$[H_1, \theta] = 2i \bar{g} \sin(3\varphi)(b^+ - b). \quad (4)$$

It is non-vanishing for the eigenstates of the Hamiltonian  $H_0$ . Thus an additional coupling term, such as that given in (3) removes the degeneracy of the  $E^a$ - and  $E^b$ -symmetric states. Bearing in mind that the  $E$  states have finite angular momenta of equal modulus and opposite sign, one should not be surprised by this result. Note that the commutator (4) is proportional to the momentum of the bath oscillator.

Up to now there is no experimental evidence to show that this effect is of physical relevance; in fact, we believe that the coupling of a methyl rotor to its crystal environment is correctly described by a Hamiltonian of type (1), the potential energy of which is a function of the particle coordinates only. In the recent discussion some confusion seems to have arisen from a mixing of quantum mechanical and classical concepts. The picture of a rotor being pushed back and forth is borrowed from classical mechanics and it is difficult to see how to implement it properly in a quantum theoretical frame. Although the description of the coupling by random impulses has its merits in the context of the numerical simulation of molecular dynamics, it invariably leads to *ad hoc* assumptions concerning the exact form of the coupling.

In conclusion, we have clarified that the degeneracy of the  $E$ -symmetric states is of Kramers type and we have shown that, contrary to Clough's claim, ordinary quantum mechanics is well suited to account for the lifting of this degeneracy due to a more general coupling. Finally, we have argued that such a splitting due to a velocity-dependent potential, and thus Clough's attack on quantum mechanics, is not relevant for the case of a methyl rotor interacting with its crystal environment.

## Appendix

We now give explicitly the four  $E$ -symmetric states of lowest energy; the arrows indicate the  $z$  component of the proton spins and  $\varepsilon$  equals  $\exp(i2\pi/3)$

$$\begin{aligned} & (1/\sqrt{3})(|\uparrow\uparrow\downarrow\rangle + \varepsilon|\downarrow\uparrow\uparrow\rangle + \varepsilon^*|\uparrow\downarrow\uparrow\rangle)\psi_a(\varphi) \\ & (1/\sqrt{3})(|\downarrow\downarrow\uparrow\rangle + \varepsilon|\uparrow\downarrow\downarrow\rangle + \varepsilon^*|\downarrow\uparrow\downarrow\rangle)\psi_a(\varphi) \\ & (1/\sqrt{3})(|\downarrow\downarrow\uparrow\rangle + \varepsilon^*|\uparrow\downarrow\downarrow\rangle + \varepsilon|\downarrow\uparrow\downarrow\rangle)\psi_b(\varphi) \\ & (1/\sqrt{3})(|\uparrow\uparrow\downarrow\rangle + \varepsilon^*|\downarrow\uparrow\uparrow\rangle + \varepsilon|\uparrow\downarrow\uparrow\rangle)\psi_b(\varphi). \end{aligned}$$

For the Hamiltonian (1),  $\psi_a$  and  $\psi_b$  are complex conjugates.

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## Reply by S Clough

Dr Würger raises an old problem (Clough and Poldy 1972, Clough 1972). The question though does not concern the rules of quantum mechanics so much as the proper way to describe experiments. The Kramers degeneracy of Würger's title is an undoubted property of the eigenstates of a conservative system—the whole sample, sample holder, cryostat etc. Experiments, however, do not report on the whole system, but only on a small part of it. The decomposition of the total system into two non-conservative parts, an experimentally observed subsystem and a driving thermal environment is a necessary and indeed crucial step in modelling experiments.

It is not possible to divide a system into two parts which act on each other and at the same time preserve the purity of the separated coordinates. The state function of each part depends on the coordinates of the other part. The Born–Oppenheimer approximation is a well known example. In his equation (1), Würger allows the rotor wavefunction to be driven by the lattice, but nowhere does he allow the lattice state to be driven by the rotor wavefunction. By this omission he discards those motions of the environment which are correlated with the motions of the rotor. The physical consequence of this is that he loses the mechanism by which the rotor and its environment exchange angular momentum, i.e. the thermally driven rotation which is actually measured.

There are essentially two ways of dealing with these correlations. The more difficult way is to incorporate them into the description of the lattice phonons. The better way, because we are not really interested in the phonons, is to modify the decomposition into system and heat bath by making such local coordinate transformations as are necessary to remove the observable correlations from the heat bath and transfer them into the rotor Hamiltonian. With the total system now divided into two parts which can for practical purposes be regarded as uncorrelated, the larger heat bath part can properly be described by a temperature. With this decomposition though, the one-dimensional coordinate  $\varphi$  can no longer be identified with the pure rotational coordinate of the rotor since it incorporates correlated lattice displacements. The variation of these admixtures means that the  $\varphi$  subspace, embedded in the total coordinate space, is curved.

The curvature of the  $\varphi$  axis then enters the kinetic energy part of the one-dimensional Hamiltonian in the form of a gauge potential  $A(\varphi)$  because differentiating along a curved axis requires the covariant differential operator  $(\partial/\partial\varphi + iA(\varphi))$  instead of  $\partial/\partial\varphi$  as in Würger's equation (1). The appearance of  $i$  shows that in general there is no time reversal symmetry for the one-dimensional Hamiltonian, because the curvature of the  $\varphi$  axis and