Reply to `Rotational tunnelling and Kramers degeneracy'

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For the Hamiltonian (1), ψ_a and ψ_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 φ 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 φ subspace, embedded in the total coordinate space, is curved.

The curvature of the φ 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 $(\partial/\partial\varphi + \mathrm{i}A(\varphi))$ 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 φ axis and its variation with φ depend on the particular thermal state of the heat bath. The Hamiltonian of the total system exhibits time-reversal symmetry, but a particular thermal state does not. It causes either clockwise or anticlockwise methyl rotation, just as a ferromagnet is polarised in one of two equally probable directions. The sign of A depends on the particular thermal state, and determines the sense of rotation. In breaking the time-reversal symmetry it lifts the E degeneracy of the one dimensional subsystem.

It is evidently necessary to distinguish carefully between two different pairs of E levels, that pertaining to the system as a whole and that pertaining only to the rotor subsystem. The former pair is degenerate because the total system is isolated and the latter pair is not degenerate because the subsystem is not isolated. There is an important connection with the topological (Berry's) phase (Berry 1984). The topological phase is not a property of a conservative system, but of part of a conservative system. Each part is driven by the other and the wavefunction of each acquires an extra phase dependent on the details of the driven trajectory. The observed splitting is just the time rate of change of this phase. The phase is also related to the fact that angular momentum is conserved for the system as a whole and not conserved for the two parts into which it is divided.

The alternative way of dealing with the correlated motions of the lattice is to elaborate the descriptions of the phonon scattering processes. This allows one to choose φ to be the pure rotation coordinate of the rotor. The subspace is then flat and the one-dimensional Hamiltonian has time-reversal symmetry. Then the two E states of the rotor subsystem diverge in time, not now because of the φ-dependent part of the one-dimensional Hamiltonian, but because they are affected differently by the phonons. This is the path which Würger embarks upon, indeed demonstrating in his equations (3) and (4) how the E splitting arises. This is where he might have introduced the dependence of these rotation-inducing lattice processes on the rotor wavefunction, thereby dealing with the coherence and the transfer of angular momentum. At this point though he abandons the new terms with the remark that 'there is no experimental evidence for this effect (the E splitting) to be of physical relevance'. This is the point at which we disagree, and the disagreement is very substantial. Because the E splitting is thermally driven, it is observable as a broadening of the motional spectrum, a broadening which has been studied in thousands of experiments over the last 50 years and attributed to the reciprocal of the correlation time for thermally excited rotation.

The nature of the disagreement is illuminated by Würger's remark about 'mixing quantum mechanical and classical concepts' which he evidently regards as inadmissable. If the concepts of torque and rotation, being certainly classical in Würger's sense, were to be excluded from quantum mechanics by fundamental postulate, then there would be no room for discussion. The gauge potential A which is related to the torque (Clough 1985) and the E splitting which is the rate of rotation (Beckmann and Clough 1977) would be zero by definition. The existence of the belief that classical concepts have no place in quantum mechanics (though this is not what the Copenhagen interpretation says) explains why this controversy was not resolved long ago, and it also explains why Würger describes me as attacking quantum mechanics. In fact it is only the quantum mechanics of isolated systems which has difficulty with concepts like torque and rotation.

Since Berry's work (at first using the adiabatic approximation but subsequently generalised) and the numerous developments which have followed it, the quantum mechanics of driven quantum systems has been thoroughly elucidated. Whether the systems are driven by an experimenter as in most of the experimental papers on the subject, or driven by a thermal heat bath is not important. In all cases a gauge potential structure is to be found guiding the evolution of the driven system (Wilczek and Zee 1984), and a topological phase in the evolution of the wavefunction. In our case these relate to the integral of the torque exerted by the lattice on the group and the angle through which the rotor rotates. Thus the classical concepts are part of the quantum mechanics of driven systems which is completely orthodox quantum mechanics. That this must be so can also be inferred from the correspondence principle and the reasonable requirement that the theory should be capable of describing classical cylinders tossing on a stormy sea as well as the motions of methyl groups in hot crystals.

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