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## Thermal gauge potentials and coherent thermally assisted tunnelling

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**Abstract.** It is commonly assumed that thermal excitation of a vibration leads to an incoherent mixture of vibrational states. We show, using the excitation of a violin string by a steadily driven bow as a model, that the new gauge theory of driven dynamical systems implies coherence. This means that the thermally excited state is a pure one in a representation that moves with the vibrations. This gives rise to a new and very simple description of thermally assisted tunnelling through the barriers of a periodic potential. It explains why there is only a single transport process, not one for each vibrational level. The real and imaginary parts correspond to the free bidirectional tunnelling frequency and to the thermally driven monodirectional tunnelling rate. A simple statistical mechanical assumption enables both of these to be easily obtained as weighted averages of overlap integrals of vibrational states located in adjacent potential wells. As the coherent tunnelling frequency declines with increasing temperature and the thermally driven rate rapidly increases, a smooth transition occurs from the quantum tunnelling regime to a quasi-classical thermal ‘hopping’ regime. The predictions are in good agreement with a large body of experimental data on quantum tunnelling and thermally activated rotations of methyl groups. The general assumptions are expected to apply to some degree to other transport phenomena.

### 1. Introduction

A harmonic oscillator like a pendulum can be excited, or sustained in an average state of excitation against frictional damping, by a series of small impulses. At one extreme (incoherence) the impulses occur at random times and have random directions; in the coherent case they are synchronised with the vibration and all have the same direction. The excitation of a violin string by a steadily drawn bow is a model for coherent excitation. A simple description of this process is that the string and bow only stick momentarily when they happen to be moving at the same speed. As a result an impulse is transmitted in each cycle to sustain the oscillations. The mechanism is similar to an electronic oscillator drawing power from a steady voltage.

A particle moving on a sinusoidal surface, and excited from rest by incoherent impulses, may eventually acquire enough energy to pass over the crests of the surface. Its direction of motion though is predictable only if the full history of the impulses is known. A particle experiencing coherent impulses will cross a crest while moving in the direction of the impulses. The usual assumptions of incoherent time-dependent perturbation theory correspond to the first case and lead to a description of a thermally excited quantum oscillator in terms of an incoherent mixture of ground and excited

states. This implies that all observable effects of phase coherence between different vibrational states are lost in the process of excitation. This is one extreme assumption, the other being that perfect coherence is retained. This paper is about this second assumption. The nature of thermal excitation is most clearly revealed by the way the wavefunction penetrates a potential barrier between two potential wells, so we shall go on to explore this property. The key assumption we make here is that there is also perfect coherence between excitations in neighbour wells. For coherent excitation and coherence between adjacent wells, the process of barrier penetration is extremely simple. All aspects of the process may be predicted from simple statistically weighted averages of overlap integrals of the vibrational states on the two sides of the barrier, the vibrational states merely providing the basis for our description of the coherently excited state.

The main motivation for this paper is to explain a large body of experimental data (Clough *et al* 1982, Clough and McDonald 1982) on the quantum tunnelling and thermally activated rotation rates of methyl groups. The outstanding feature of these data is their extreme simplicity and the ease with which they may all be described by a universal expression involving no adjustable parameters (Clough *et al* 1981). The clear message of the data is that thermally assisted tunnelling is a very simple process dependent only on the temperature and not on the phonon spectrum of the host lattice. The only problem has been that it apparently required coherent thermal excitation which is quite incompatible with the usual perturbation theory descriptions.

There is a simple reason why coherent excitation with all its attendant simplicity has been largely ignored. The mechanism by which the coherent excitation is generated and sustained has been missing from quantum descriptions of dynamical processes. This missing element is a gauge potential which represents the coherent motion of the thermal environment (Clough *et al* 1984, Wilczek and Zee 1984, Clough 1985). The introduction of the gauge potential represents a substantial revolution in the quantum mechanics of the solid state. The startling fact is that most time integrals in most quantum mechanical theories are incorrect because of the omission of what has become known as the topological phase. Many aspects of condensed matter physics will therefore need reassessment. The new approach recognises that all experiments involve driven systems rather than freely evolving isolated ones, and it leads to a switch from dealing with a single Hamiltonian to dealing with a sequence of Hamiltonians. This revolution was launched by Berry (1984) who proved that a quantum system slowly (adiabatically) driven around a loop in parameter space acquires an extra quantum phase related to the topology of the trajectory. The adiabatic restriction was removed subsequently (Berry 1987, Aharonov and Anandan 1987). The appearance of a phase angle connected with a system following a circuital path recalls the well known Aharonov–Bohm effect (Aharonov and Bohm 1959) and, generally, the structure of gauge theory in electromagnetism and particle physics. It was by pursuing this line of thought that Mead (1980) had introduced the vector potential in the context of the Born–Oppenheimer approximation and Wilczek and Zee (1984), following Berry, found the (generally non-Abelian) gauge structure implicit in the dynamics of all driven systems. Since isolated systems are only an abstraction, gauge potentials are ubiquitous in dynamical problems.

A completely different line of reasoning led to the same conclusion. The behaviour of isolated quantum systems is incompatible with the assumptions of classical mechanics (Clough and Poldy 1972, Clough 1972), and thus with the correspondence principle. The gauge potential is just what is required to put this matter right (Clough *et al* 1984, Clough 1985). A simple example of this is a toy elastic-powered aeroplane. A rotation

of the propeller through 360 degrees is accompanied by a twist in the elastic, so it is not a symmetry operation. On the other hand it is commonly assumed that the rotation through 360 degrees of a methyl group in a crystal is a symmetry operation, as if nothing corresponded to the elastic. The effect of the twist in the elastic on the propeller corresponds to a change in the gauge potential. Leaving it out leads to the loss of its coherent effects and, perhaps worse still, introduces a false rotational symmetry.

## 2. The origin of the thermal gauge potential

In describing methyl rotation, most authors require the one-dimensional rotational Hamiltonian to exhibit threefold symmetry and time-reversal symmetry and its wavefunctions to satisfy  $2\pi$  periodicity and to be perfectly correlated with the nuclear spin states. All this follows if the one-dimensional coordinate is the pure rotation coordinate of the methyl group. We depart from this. Our coordinate  $\varphi$  is never pure rotation, but is always slightly admixed with lattice displacements. Our prime concern is to decompose the total system into a one-dimensional subsystem and a random heat bath. That this is possible we regard as an empirical fact, but it is unreasonable to suppose that one can simultaneously choose the single coordinate arbitrarily. Either the projected coordinate is allowed to float and the heat bath is random, or the coordinate is fixed and the heat bath is non-random. The important interactions between system and environment are described in one case by the way the coordinate varies and in the other by correlations in the heat bath. Since we choose the former way, the Hamiltonian is not subject to the symmetry restrictions that apply in the latter case.

Generally we assert that any decomposition into a subsystem and random heat bath leaves the embedded subsystem space curved into the larger space of the total system. The variation of the curvature is responsible for the force (or torque) on the subsystem, just as the variation of the curvature of spacetime is responsible for gravitational force. It is convenient to treat the curvature as a local coordinate (or set of coordinates) whose variation with  $\varphi$  then becomes a gauge potential  $A$  (or potentials). The operator  $\partial/\partial\varphi$  has to be replaced by the covariant derivative ( $\partial/\partial\varphi + iA$ ), thus introducing the gauge potential in the usual way. Since we deal with a one-dimensional rotor, a single one-dimensional gauge potential is sufficient.

It is important to emphasise that the Hamiltonian containing a vector potential does not describe an isolated subsystem, but one driven by the heat bath, so it contains some information about the driven trajectory in the form of the history of the gauge potential. This information is transmitted to the evolving wavefunction. From our point of view, the important information is whether the methyl group is being driven in a clockwise or anticlockwise sense, and the strength of the driving effect. We may anticipate that the latter depends on the temperature. The former can be regarded as a kind of spontaneous symmetry breaking because the excited lattice states fall into two classes according to the direction in which they drive the methyl group.

A considerable simplification is achieved by considering only the trajectory of the subsystem itself in its own projective Hilbert space. This is the point of view adopted by Aharonov and Anandan (1987) and it is the simplest possible representation of the observable effects. By considering only the lowest two levels of a harmonic oscillator, we reduce the appropriate space to a simple sphere. The ground state and the first excited vibrational states are represented by two points at opposite ends of a diameter, and any mixed state can be represented by a point elsewhere on the sphere. Conventionally, a

thermal state would be represented by an axially symmetric density function. The axial symmetry means that there is no preference for right- or left-handed motion. This is the picture that emerges from ordinary perturbation theory, and it comes from neglecting the non-random character of the heat bath. It is consequently incorrect. Since we have transferred the non-randomness to the gauge potential, we can trace the effect on the trajectory, and find a strong departure from axial symmetry. This then has important consequences for tunnelling rotation.

### 3. Coherent excitation

To describe coherent excitation we introduce a time-dependent gauge potential  $A$  into the harmonic oscillator Hamiltonian:

$$\mathcal{H} = (i\hbar \partial/\partial x + A)^2 + kx^2 \quad (1)$$

and describe the state function in terms of the eigenfunctions  $|u_i\rangle$  of the  $A = 0$  Hamiltonian. We refer to these functions as the vibrational states. For simplicity we consider only the lowest two vibrational states, separated by the energy  $\hbar\omega$  where  $\omega$  is the harmonic angular frequency. The term in (1) that is linear in  $A$  couples these two states, the matrix elements being imaginary. Recalling the model of the violin string, we assume that  $A$  consists of a series of impulses synchronised with the oscillation. Picking out the resonant (or nearly resonant to allow for thermal fluctuations) Fourier component of  $A$ , we can make use of an analogy with the motion of a spin in a static magnetic field proportional to  $\omega$  along the  $z$  axis and a nearly resonant magnetic field along the  $y$  axis. For the oscillator the  $x$  and  $y$  axes correspond to displacement and momentum. The field along  $y$  may be decomposed in the usual way into two components rotating about  $z$  in opposite directions, and the one rotating counter to the motion of the oscillator discarded as non-resonant. A transformation into a rotating frame now removes the time dependence of the field perpendicular to  $z$  and reduces the effective  $z$  field to a value dependent on the small departure from resonance. It also removes the relative time dependence of  $|u_0\rangle$  and  $|u_1\rangle$ . The fields can be combined into an effective field tilted at an angle  $\theta$  to  $z$  and the stationary states in the rotating frame have the form

$$|v_0\rangle = \cos \theta |u_0\rangle + i \sin \theta |u_1\rangle \quad |v_1\rangle = \sin \theta |u_0\rangle - i \cos \theta |u_1\rangle. \quad (2)$$

As  $\theta$  varies, the state  $|v_0\rangle$  follows a trajectory from  $|u_0\rangle$  along a particular plane in the projective Hilbert space. If  $|u_0\rangle$  and  $|u_1\rangle$  are visualised as the south and north poles, then  $|v\rangle$  lies on a particular longitude and the direction in which it moves depends on the sign of  $A$ . We assume the mean excitation is given by statistical mechanics:

$$\langle \sin^2 \theta \rangle / \langle \cos^2 \theta \rangle = \exp(-\hbar\omega/kT). \quad (3)$$

A matrix can be constructed from the coefficients of  $|v_0\rangle$ :

$$\rho = \begin{bmatrix} \cos^2 \theta & i \sin \theta \cos \theta \\ -i \sin \theta \cos \theta & \sin^2 \theta \end{bmatrix}. \quad (4)$$

An ensemble average of this matrix gives the populations of the vibrational states on the diagonal, as is clear from (3). The off-diagonal elements only survive the averaging procedure, though, if we use a particular representation (or rotating frame) for each oscillator, dependent on the particular history of the gauge potential at that site. Unless

we can compare two or more oscillators that experience similar excitation histories, we can expect the off-diagonal elements to have no effect on experiments conducted on macroscopic samples, and this is why they are usually ignored. The barrier penetration problem, though, may depend on a comparison of this kind. In this case therefore it is of cardinal importance to retain these off-diagonal terms.

#### 4. Thermally assisted rotation of methyl groups

The usual Hamiltonian used to discuss the hindered rotation of methyl groups is

$$\mathcal{H} = -(\hbar^2/2I)\partial^2/\partial\varphi^2 - V \cos 3\varphi. \tag{5}$$

This can be regarded as approximately equivalent to three harmonic oscillators in potential wells centred at  $\varphi = 0$ ,  $\varphi = 2\pi/3$ ,  $\varphi = 4\pi/3$ . The wavefunctions in adjacent potential wells overlap beneath the potential barriers and so give rise to tunnelling rotation at a rate governed by overlap integrals, which may be obtained numerically. For simplicity we again limit the discussion to only two vibrational states in each potential well. There are therefore four overlap integrals  $\Delta_{00}$ ,  $\Delta_{11}$ ,  $\Delta_{01}$ , and  $\Delta_{10}$ , arising respectively from the overlap of two ground states, two excited states, and one of each. Because the excited vibrational state is an odd function,  $\Delta_{00}$  and  $\Delta_{11}$  have opposite signs and  $\Delta_{01} = -\Delta_{10}$ .

We assume that the three harmonic oscillator states localised in the three wells are identically excited, having experienced identical gauge potentials. The overlap integral connecting states in potential wells  $m$  and  $n$  is

$$W_{nm} = \Delta_{00}\cos^2\theta + \Delta_{11}\sin^2\theta + i\Delta_{01}\sin 2\theta \tag{6}$$

$$W_{mn} = W_{nm}^*. \tag{7}$$

The effect of the overlap is to lift the threefold degeneracy. The eigenvalues and eigenfunctions are easily found by diagonalisation of the matrix

$$\begin{bmatrix} 0 & W_{12} & W_{13} \\ W_{21} & 0 & W_{23} \\ W_{31} & W_{32} & 0 \end{bmatrix} = \Delta_m \begin{bmatrix} 0 & \exp(i\alpha) & \exp(-i\alpha) \\ \exp(-i\alpha) & 0 & \exp(i\alpha) \\ \exp(i\alpha) & \exp(-i\alpha) & 0 \end{bmatrix}. \tag{8}$$

$$\Delta_m = [(\Delta_{00}\cos^2\theta + \Delta_{11}\sin^2\theta)^2 + (\Delta_{01}\sin 2\theta)^2]^{1/2} \tag{9}$$

$$\sin \alpha = (\Delta_{01}\sin 2\theta)/\Delta_m. \tag{10}$$

The secular equation

$$(x/\Delta_m)^3 - 3(x/\Delta_m) - 2\cos 3\alpha = 0 \tag{11}$$

yields the eigenvalues  $2\Delta_m \cos \alpha$ ,  $2\Delta_m \cos(\alpha + 2\pi/3)$ ,  $2\Delta_m \cos(\alpha + 4\pi/3)$ . The eigenfunctions have the form of Bloch waves with wavenumbers 0,  $2\pi/3$  and  $-2\pi/3$ .

At low temperature when  $\theta$  is small,  $W_{nm}$  is real and  $\alpha$  is small. Because  $\Delta_{00}$  and  $\Delta_{11}$  have opposite signs, the real part of the overlap  $W_{nm}$  decreases with increasing temperature, while the imaginary part increases steadily in magnitude. This progressive change makes an important change in the character of the rotational motion. On superimposing the three Bloch wave eigenfunctions, a wavepacket that is initially located in one of the three potential wells is set up. The subsequent evolution is governed by the

eigenvalues, whose differences therefore characterise the motion. At low temperature the eigenvalues are  $2\Delta_m$ ,  $-\Delta_m$ ,  $-\Delta_m$ . The wavepacket evolves bidirectionally, leaving the potential well in which it was initially localised and appearing distributed symmetrically in the other two wells, before returning to the original well. This is an oscillatory motion with a frequency related to the splitting  $3\Delta_m$ , which is approximately  $3\Delta_{00}$  at low temperature.

At high temperature  $\alpha$  approaches  $\pi/2$  in magnitude and the eigenvalues are 0,  $3^{1/2}\Delta_m$  and  $-3^{1/2}\Delta_m$ . In this case the wavepacket evolves in a monodirectional way, appearing successively in wells 1, 2, 3, 1, etc, and therefore the motion corresponds to the usual meaning of rotation. The direction of the rotation depends on the sign of  $\alpha$  and therefore on the sign of the gauge potential that created the thermal excitation. This is driven or thermally assisted tunnelling rotation, and the origin of its monodirectional character is in the breaking of the time-reversal symmetry by the gauge potential term. At intermediate temperatures, the bidirectional free tunnelling and the monodirectional rotation coexist, with the frequency of the former declining as the rate of the latter increases.

The temperature-dependent tunnel frequency is simply given by the real part of  $\Delta_m$ . From (3) and (9) this is

$$\Delta_m \cos \alpha = [\Delta_{00} + \Delta_{11} \exp(-\hbar\omega/kT)]/[1 + \exp(-\hbar\omega/kT)]. \quad (12)$$

This thermal average of the splittings of different vibrational states was proposed long ago by Allen (1974) to account for the observed reduction in the tunnel frequency of methyl groups with rising temperature (Clough and Hill 1974). It has been frequently used (Johnson and Mottley 1973, Punkkinen *et al* 1975, Prager *et al* 1977, Müller-Warmuth *et al* 1978) and has proved remarkably reliable. The problem has been to understand why it works, starting from an incoherent mixture of vibrational states. Attempts to account for its success in terms of rapid transitions between the vibrational states (Allen 1974) were not successful, failing to explain simultaneously the observed broadening of the tunnel spectrum. It was indeed appreciated quite early that the expression (12) required a coherent mixture of vibrational states (Johnson and Mottley 1973) but the mechanism that could maintain this coherence was not apparent. The gauge potential therefore resolves this old problem.

The thermally activated rotation rate corresponds to the imaginary part of  $\Delta_m$ . Generalised to include higher excited vibrational levels, it is

$$2 \sum_i |\Delta_{i,i+1}| \exp[-(E_i + E_{i+1})/2kT] / \sum_j \exp(-E_j/kT). \quad (13)$$

Since it grows with increasing temperature, it first acts to damp the coherent tunnel frequency and then swamps it at higher temperatures. In this case a realistic description must involve more than the first two vibrational states. The rate can be calculated from the model as a weighted average of overlap integrals without the use of any adjustable parameters. A procedure of this kind was used by Das (1956, 1957) and by Stejskal and Gutowsky (1958), but using the diagonal overlaps  $\Delta_{i,i}$  as in (12) rather than  $\Delta_{i,i+1}$  as in (13). (The overall temperature dependence obtained, though, is not so very different from (13)). A more serious problem seemed to be an underlying inconsistency with the symmetry constraints of quantum theory (Freed 1965), and this held back the development of the theory for several years. Now it is clear that this was a misapprehension due to the absence of the symmetry-breaking gauge term. The idea that the transport rate is a simple thermal average was revived by Clough *et al* (1981) who

also demonstrated that it accounted for all of a considerable amount of data collected on methyl rotation (Clough *et al* 1982, Clough and McDonald 1982, McDonald *et al* 1986). Similar conclusions were reached by other workers (Montjoie and Müller-Warmuth 1985, Montjoie *et al* 1988), again on the basis of studies of many different compounds. The present discussion shows though that the actual expressions that have been used

$$\sum_{i>0} |\Delta_{ii}| \exp(-E_i/kT) / \sum_j \exp(-E_j/kT) \quad (14)$$

need to be modified. They have involved thermal averages of the moduli of the tunnel splittings of the vibrational levels calculated from the Hamiltonian (5). Two defects of (14) are remedied in (13). In using (14) it was necessary to omit the  $i = 0$  term in the numerator because the thermally assisted transport rate must approach 0 as  $T \rightarrow 0$ , and the reason for using the moduli of  $\Delta_{ii}$  was unclear. In (13) no terms are omitted and all have the same sign selected by the direction associated with the gauge potential.

When the vibrational states in adjacent potential wells are assumed to be incoherent (see, for example, Holstein (1959) on the diffusion of small polarons) the contribution to the transport rate is found to depend on the square of the overlap integral  $\Delta_{i,i+1}$  divided by a denominator which is a measure of the incoherence of the vibrational states. The simplicity of coherent thermally assisted transport derives from the fact that no mismatch occurs. There are consequently no adjustable parameters, making the predictions very testable and the experiments unambiguous. There is only one rate constant, not one for each vibrational state. Now the problem of the false symmetry constraints is resolved, a simple picture emerges for the thermally assisted transport and in particular for the transition from free quantum tunnelling to thermally driven rotation as the magnitude of the fluctuating gauge potential rises with increasing temperature.

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