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COMMENT

Semiclassical approximation for methyl-group rotation

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Abstract. Methyl-group rotation is a one-dimensional example of molecular rotational tunnelling. The tunnel splitting of the methyl-group torsional ground state is obtained using a path integral formulation and semiclassical approximation.

Methyl-group rotation is a simple one-dimensional example of the phenomenon of molecular rotational tunnelling which has attracted considerable attention in recent years, both theoretical (Hewson 1982a, b, Clough *et al* 1984, Clough 1985) and experimental (Press 1981, Clough and Heidemann 1979). Theoretical interest has concentrated on the temperature dependence of methyl-group rotational energy levels, which are seen experimentally by inelastic neutron scattering techniques to shift and broaden as temperature increases.

We feel it is desirable to treat the interaction of the methyl group with a lattice using a path integral formulation. In this comment we use a path integral formulation to obtain the ground-state energy levels of the methyl group in the absence of interactions with the lattice, using the semiclassical approximation to evaluate the path integrals. This corresponds to the physical situation at very low temperatures at which the lattice is quiet, although it is recognised that an interaction with the lattice may cause effects at zero temperature which are not included here.

The motivation for this comment is twofold. First, we would like to obtain the tunnel splitting of the methyl-group torsional ground state neglecting interactions with the lattice using a path integral treatment as a preliminary to the full treatment of the problem including the effects of the interactions with the lattice (Whittall and Gehring 1987). Second, the work presented here will serve as another example of the use of trajectories in complex time to evaluate path integrals, which has been of interest recently with respect to the double-well problem (Holstein 1986, Radosz 1985).

Using Feynman and Hibbs' (1965) formulation of statistical mechanics the density matrix for a quantum mechanical system is given by the path integral

$$\rho(x_f, x_i; U) = \int_{x(0)=x_i}^{x(U)=x_f} Dx(\tau) \exp\left(-\frac{1}{\hbar} S[x(\tau)]\right)$$

where

$$S[x(\tau)] = \int_0^U L_E(x, \dot{x}) d\tau. \quad (1)$$

$S[x(\tau)]$ is the Euclidean action as a functional of the path $x(\tau)$, τ is an imaginary time variable, $L_E(x, \dot{x})$ is the Euclidean Lagrangian and $\dot{x} \equiv dx/d\tau$. We are said to be

working in imaginary time because the expression (1) for the density matrix, ρ , in terms of the path integral is obtained by substituting an imaginary time interval proportional to inverse temperature into the real-time path integral of Feynman's (1948) formulation of quantum mechanics, such that the endpoint $U = \hbar/kT$, where k is Boltzmann's constant and T is temperature.

We shall evaluate the density matrix for the methyl group using the semiclassical approximation (Coleman 1977). The Euclidean action for the methyl group neglecting interactions is given by

$$S = \int_0^U (\frac{1}{2} I \dot{\phi}^2 - V_0(\phi)) d\tau \quad (2)$$

where ϕ is the angular coordinate of the methyl group with respect to rotation about its axis of symmetry and I is the moment of inertia of the methyl group. The potential $V_0(\phi)$ must be a threefold periodic potential. Experimentally it has been found that the energy levels of the methyl group at zero temperature are well described by the potential

$$V_0(\phi) = V_0(1 - \cos 3\phi). \quad (3)$$

To evaluate (1) in the semiclassical approximation we must find the path $\bar{\phi}(\tau)$ which is a stationary point of the effective action, such that

$$-\frac{I d^2 \bar{\phi}}{d\tau^2} + \frac{dV_0(\bar{\phi})}{d\phi} = 0. \quad (4)$$

The path $\bar{\phi}(\tau)$ must satisfy the boundary conditions

$$\phi(U) = \phi_f \quad \phi(0) = \phi_i. \quad (5)$$

One solution to (4) is termed an instanton and this is discussed in Coleman (1977). Coleman uses instantons to solve for the ground-state energy levels of a particle in a double-well potential and in an infinite periodic potential. We will use the same technique for the methyl-group problem which is equivalent to that of a particle in a threefold periodic potential. For this case the paths $\bar{\phi}(\tau)$ consist of strings of instantons and anti-instantons (for which the direction of rotation is opposite to that for the instanton). For the boundary conditions $\phi_f = \phi_i = 0$, the paths are subject to the restriction

$$n - \bar{n} = 3m \quad m \text{ integer} \quad (6)$$

where n and \bar{n} are the numbers of instantons and anti-instantons, respectively.

Applying the semiclassical approximation using the instanton method we obtain the result

$$\begin{aligned} \rho(0, 0, U) &= \int_{\phi(0)=0}^{\phi(U)=0} D\phi(\tau) \exp\left(-S \frac{[\phi(\tau)]}{\hbar}\right) \\ &= \left(\frac{\nu}{\pi\hbar}\right)^{1/2} \exp\left(\frac{-\nu U}{2}\right) \sum_{n=0}^{\infty} \sum_{\bar{n}=0}^{\infty} \frac{1}{n! \bar{n}!} (K \exp(-S_1/\hbar) U)^{n+\bar{n}} \\ &\quad \times (\delta(n - \bar{n}) + \delta(n - \bar{n} - 3) + \delta(n - \bar{n} + 3) + \delta(n - \bar{n} - 6) + \dots) \end{aligned} \quad (7)$$

where $\nu = (9V_0/I)^{1/2}$, S_1 is the Euclidean action for the path consisting of a single instanton and K is a constant which depends on V_0 and I .

Using the identities

$$\delta_{ab} = \int_0^{2\pi} \frac{d\theta}{2\pi} \exp i\theta(a-b) \quad (8)$$

and

$$\delta(\theta) + \delta(\theta - 2\pi/3) + \delta(\theta + 2\pi/3) = 3(1 + \exp i3\theta + \exp(-i3\theta) + \exp i6\theta + \dots) \quad (9)$$

we obtain our final result:

$$\rho(0, 0, U) = \frac{1}{3}(\nu/\pi\hbar)^{1/2}(\exp(-\frac{1}{2}\nu U)/2\pi) \times [\exp(2KU \exp(-S_1/\hbar)) + 2 \exp(-KU \exp(-S_1/\hbar))] \quad (10)$$

where $U = \hbar/kT$.

In the low-temperature limit, the density matrix projects out the lowest energy levels of the system. Thus the energies of the ground torsional levels of the methyl group are given by

$$\begin{aligned} E_A &= \frac{1}{2}\hbar\nu - 2\hbar K \exp(-S_1/\hbar) \\ E_{E^{a,b}} &= \frac{1}{2}\hbar\nu + \hbar K \exp(-S_1/\hbar). \end{aligned} \quad (11)$$

The labels A , E^a and E^b are symmetry labels referring to the irreducible representation of the CH_3 symmetry group.

There is a tendency in the literature when referring to the tunnel splitting of the methyl group (e.g. Hewson 1982a, b) to imply that the effect is to raise the E states and lower the A states by equal amounts. This is not supported by our derivation of the energies of the methyl-group ground torsional levels using a path integral formulation and the semiclassical approximation. Our results indicate that the energy shifts of the E and A states are of differing magnitudes. In another paper (Whittall and Gehring 1987) we have shown how a path integral formulation can be used to derive the energy levels of the methyl group interacting with a lattice.

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