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1989 J. Phys. A: Math. Gen. 22 1941

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COMMENT

Ground-state tunnel splitting of the methyl group in a three-fold potential

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Received 28 November 1988

Abstract. An approximate value of tunnel splitting of the methyl-group torsional ground state is obtained using the traditional methods of wave mechanics.

The calculation of energy levels of methyl groups in single-particle potentials does not present any substantial problem and as such it has been discussed thoroughly in the past (Press 1981). It is also generally agreed that approximate methods have little practical importance in the case of one-dimensional rotational motion. However, the existence of good approximate results is nevertheless useful for further understanding of rotational tunnelling.

Recently Whittall and Gehring (1987) presented an interesting calculation of the methyl-group ground-state tunnelling frequency using a path-integral formulation. We would like to supplement their derivation by showing how one can obtain the WKB equivalent of their result by an almost trivial application of the method described by Landau and Lifshitz (1977) for the case of the double well.

The solution of the Schrödinger equation for a CH_3 group in a three-fold potential $V(\gamma) = V_3(1 + \cos 3\gamma)$, neglecting the possibility of tunnelling, can be approximated with the quasiclassical wavefunction $\phi_0(\gamma - \gamma_c)$ which describes the motion with a certain energy E_0 localised in a well corresponding to a minimum of the potential $V(\gamma)$ at $\gamma = \gamma_c$. $\phi_0(\gamma - \gamma_c)$ is exponentially damped on both sides of the well and is also assumed to be normalised so that

$$\int_{\gamma_c - \pi/3}^{\gamma_c + \pi/3} d\gamma \phi_0^2(\gamma - \gamma_c) = 1.$$

When the possibility of tunnelling is taken into account, the three-fold degenerate ground state E_0 splits into a doubly degenerate level $E_{E_{a,b}}$ and a non-degenerate ground state E_A . The subscript A, E_a, E_b are symmetry labels denoting irreducible representations of the point group C_3 . The correct zero-order approximation for the wavefunctions corresponding to these levels can be written in terms of $\phi_0(\gamma - \gamma_c)$ as:

$$\psi_A = \frac{1}{\sqrt{3}} [(\phi_0(\gamma - \pi/3) + \phi_0(\gamma - \pi) + \phi_0(\gamma + \pi/3))] \quad (1)$$

$$\psi_{E_a} = \frac{1}{\sqrt{3}} [\phi_0(\gamma - \pi/3) + \varepsilon \phi_0(\gamma - \pi) + \varepsilon^* \phi_0(\gamma + \pi/3)] \quad (2)$$

where $\varepsilon = e^{i2\pi/3}$ and $\psi_{E_b} = \psi_{E_a}^*$. The product $\phi_0(\gamma - \gamma_c)\phi_0(\gamma - \gamma'_c)$ is vanishingly small everywhere ($\gamma_c \neq \gamma'_c$) and the functions ψ_A and $\psi_{E_{a,b}}$ can be taken as normalised to unity on the interval $[-\pi, \pi]$. The relevant Schrödinger equations are

$$\frac{d^2}{d\gamma^2} \phi_0(\gamma - \pi/3) + \frac{2J}{\hbar^2} (E_0 - V) \phi_0(\gamma - \pi/3) = 0 \quad (3)$$

$$\frac{d^2}{d\gamma^2} \psi_A + \frac{2J}{\hbar^2} (E_A - V) \psi_A = 0 \quad (4)$$

$$\frac{d^2}{d\gamma^2} \psi_{E_a} + \frac{2J}{\hbar^2} (E_E - V) \psi_{E_a} = 0 \quad (5)$$

and there is a similar equation for ψ_{E_b} . J is the moment of inertia of the methyl group around its symmetry axis. If we multiply (4) by $\phi_0(\gamma - \pi/3)$ and (3) by ψ_A , and subtract the corresponding terms, we obtain after integration over γ from 0 to $2\pi/3$,

$$E_A - E_0 = -\frac{2\hbar^2}{J} \phi_0(\gamma - \pi/3) \phi'_0(\gamma - \pi/3) \Big|_{\gamma=0} \quad (6)$$

where $\phi'_0 \equiv d\phi_0/d\gamma$. To obtain this result we used

$$\int_0^{2\pi/3} d\gamma \phi_0(\gamma - \pi/3) \psi_A(\gamma) \approx 1/\sqrt{3}$$

$\psi_A(\gamma=0) = \psi_A(\gamma=2\pi/3) \neq 0$, $\psi'_A(\gamma=0) = \psi'_A(\gamma=2\pi/3) = 0$, and the fact that $\phi_0(\gamma - \pi/3)$ is an even function with respect to the point $\gamma = \pi/3$. By an identical manipulation of (3) and (5) we can also show that

$$E_E - E_0 = \frac{\hbar^2}{J} \phi_0(\gamma - \pi/3) \phi'_0(\gamma - \pi/3) \Big|_{\gamma=0} \quad (7)$$

Subtracting (6) from (7), setting $E_0 = \frac{1}{2}\hbar\omega_0$, and using the wkb results given in Landau and Lifshitz (1977) for $\phi_0(\gamma - \pi/3)|_{\gamma=0}$ and its derivative, we can write

$$E_E - E_A \approx \hbar\omega_T = 3\hbar \frac{\omega_0}{2\pi} \exp\left(-\frac{2}{\hbar} \int_0^{\gamma_0} d\gamma [2J(V - \frac{1}{2}\hbar\omega_0)]^{1/2}\right) \quad (8)$$

Using the relation $\omega_0^2 = 9V_3/J$ and the expression $V(\gamma) = V_3(1 + \cos 3\gamma)$, enables us to rewrite (8) as the tunnelling frequency:

$$\omega_T = 3 \frac{\omega_0}{2\pi} \exp\left(-\frac{J\omega_0}{\hbar} \int_0^{\gamma_0} d\gamma \left[\frac{8}{9}(1 + \cos 3\gamma) - 4\hbar/J\omega_0\right]^{1/2}\right) \quad (9)$$

and γ_0 is determined by

$$\gamma_0 = \frac{1}{3} \cos^{-1}\left(\frac{9}{2} \frac{\hbar}{J\omega_0} - 1\right) \quad (10)$$

The tunnelling frequency ω_T calculated with the help of (9) is listed for various values of $(J\omega_0/\hbar)$ in table 1, which also includes values obtained for the 'Gaussian pocket state approximation' (Peternelj *et al* 1987) based on the formula

$$\omega_T = \frac{3}{2} \omega_0 \exp\left(-\frac{\pi^2 J\omega_0}{9\hbar}\right) \left[\frac{J\omega_0}{\hbar} \left(\frac{\pi^2}{9} - \frac{4}{9}\right) + 1 + \dots\right] \quad (11)$$

Table 1. Tunnelling frequency ω_T/ω_0 for a methyl group in a three-fold potential $V_3(1 + \cos 3\gamma)$, calculated by different methods

$J\omega_0/\hbar$	Exact calculation	wKB method	Gaussian pocket state app.
5.55	2.91×10^{-2}	3.79×10^{-2}	1.58×10^{-2}
7.85	5.04×10^{-3}	5.76×10^{-3}	1.68×10^{-3}
11.10	3.53×10^{-4}	3.77×10^{-4}	6.39×10^{-5}
13.59	4.36×10^{-5}	4.54×10^{-5}	4.99×10^{-6}
15.70	7.26×10^{-6}	7.46×10^{-6}	5.62×10^{-7}

The result (8) can also be derived by the following heuristic argument, advocated recently by Dekker (1987) for a double well. Assuming that at $t = 0$, the methyl group is in a pure state $\psi_i(\gamma)$, the density matrix in the coordinate representation is

$$\rho(\gamma, \gamma', t) = \sum_{m,n} \exp(-i\omega_{mn}t) \varphi_m(\gamma) \varphi_n^*(\gamma') \langle \varphi_m | \psi_i \rangle \langle \psi_i | \varphi_n \rangle \quad (12)$$

where E_m and φ_m are the eigenvalues and eigenfunctions, respectively, of the Hamiltonian

$$H = -(\hbar^2/2J)(d^2/d\gamma^2) + V_3(1 + \cos 3\gamma)$$

and where $\omega_{mn} \equiv (E_m - E_n)\hbar$, and $\langle \varphi_m | \psi_i \rangle \equiv \int_{-\pi}^{\pi} d\gamma \varphi_m^* \psi_i$. The probability that the methyl group is in the state ψ_f at time t , is:

$$P_{\psi_f}(t) = \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} d\gamma d\gamma' \psi_f^*(\gamma) \rho(\gamma, \gamma', t) \psi_f(\gamma'). \quad (13)$$

Choosing $\psi_i(\gamma) = \phi_0(\gamma + \pi/3)$, $\psi_f(\gamma) = \phi_0(\gamma \pm \pi/3)$ or $\phi_0(\gamma - \pi)$, we obtain, considering only the lowest three eigenstates (1) and (2) in the sum (12),

$$P(-\pi/3|t) = 1 - \frac{8}{9} \sin^2(\frac{1}{2}\omega_T t)$$

and

$$P(\pi/3|t) = P(\pi|t) = \frac{4}{9} \sin^2(\frac{1}{2}\omega_T t).$$

If we denote the corresponding probability amplitudes as $P(t) = |\chi(t)|^2$, then we notice that

$$\lim_{t \rightarrow 0} \frac{d}{dt} |\chi(\pi/3|t)| = \frac{1}{3}\omega_T \lim_{t \rightarrow 0} |\chi(-\pi/3|t)|.$$

On the other hand, since at $t = 0$ the methyl group is localised in the well centred at $\gamma_c = -\pi/3$, we can imagine, within the framework of quasiclassical approximation, that during unit time, the CH_3 group executing classical torsional oscillations, approaches each classical turning point corresponding to energy E_0 , a number $\omega_0/2\pi$ of times. Therefore we can also write

$$\lim_{t \rightarrow 0} \frac{d}{dt} |\chi(\pi/3|t)| = \frac{\omega_0}{2\pi} |T(E_0)| \lim_{t \rightarrow 0} |\chi(-\pi/3|t)|$$

where

$$|T(E_0)| = \exp\left(-\frac{1}{\hbar} \int_{-\gamma_0}^{\gamma_0} d\gamma [2J(V - E_0)]^{1/2}\right)$$

is the familiar wkb amplitude for barrier transmission. Comparing the two expressions we recover the result (8).

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