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Dynamics of a Pair of Interacting Rotors†

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Abstract—As a preliminary investigation of coupled rotation relevant to plastic crystals, the dynamics of two rigid-molecule rotors with parallel fixed axes is studied for a cosine potential of interaction. The problem is separable in terms of the sum and difference of the molecular angular displacements, and is soluble exactly; both quantum-mechanical and classical solutions are obtained. Owing to the form of the potential, the sum of the angles executes free rotation. The relative motion given by the difference of the angles corresponds to harmonic libration of the molecules in opposite senses at the lowest energies, and to uniform rotation in opposite senses at the highest energies. The classical behaviour is examined in some detail at intermediate energies.

1. Introduction

A considerable body of evidence suggests that in many molecular crystals the molecules rotate more or less freely at some temperatures.$^{(1,2)}$ Molecular rotation in solids has received particularly detailed attention in the hydrogens$^{(3)}$ and the methanes,$^{(4)}$ where rotation persists to low temperatures and nuclear spin effects provide valuable extra information on the nature of the phenomenon. An aspect of molecular rotation in solids which has received much less theoretical attention is the nature of the rotator phase of plastic crystals, particularly where details of the coupled rotations are concerned. Many globular (quasi-spherical) molecules give crystals which undergo a solid-state transition to a high-temperature cubic phase which is very soft mechanically. In this plastic crystalline phase it appears that the molecules are rotating rather freely, whence the alternative name, rotator phase. In some crystals the transition to a cubic phase is preceded at lower temperatures by a transition

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to an axial phase in which the molecules are believed to rotate freely about a fixed axis. Free rotation arises because thermal expansion results in an increase in the centre-of-mass separation between molecules, which reduces the anisotropic forces constraining the molecules to librate about various equilibrium orientations. One may thus contrast plastic crystals, where weakly anisotropic intermolecular forces allow rotation before melting, with liquid crystals, where strongly anisotropic forces orient the molecules even after melting.(5)

An early treatment of rotation in molecular crystals was given by Pauling,(6) who considered a diatomic molecule rotating in a plane subject to the simple hindering potential

$$V = V_0(1 - \cos 2\theta), \tag{1}$$

where θ is the angle the molecule makes with some fixed direction. The eigenfunctions of the Schrödinger equation are then Mathieu functions,(7) which for large V_0 behave like linear combinations of oscillator functions and for small V_0 like free rotor functions, in accord with physical expectations. This work was extended to an octahedral potential by Devonshire.(8) The main feature of more recent work on rotational phase transitions has been the use of some effective one-molecule potential to replace that given by Eq. (1). For example, Martin and Walmsley(9) obtained a good qualitative description of the phase transition in solid hydrogen, and Casey and Runnels(10) showed that a phase transition occurs in a chain of hard squares at the smallest separation permitting rotation when both neighbours cooperate fully. The transitional and librational modes of molecular crystal models were studied in the self-consistent-phonon approximation(11) by Raich and Etters,(12) who showed that the librational modes became unstable as the temperature rose. Work on the time-dependence of the molecular motion has also concentrated on single molecules, for instance in Lechner's model,(13) where a molecule is treated as undergoing rotational diffusion with occasional large-angle reorientations.

The present paper is a preliminary study of coupled rotors. It is a modest extension of Pauling's work,(6) and deals with a pair of diatomic molecules interacting through a cosine potential. This problem has the advantage of being exactly soluble in terms of special functions, and permits the collective and time-dependent aspects of the motion to be studied. The quantum-mechanical solution is outlined; it does not differ essentially from the solution of Pauling's problem. The classical dynamics is dealt with in more detail: a classical treatment is not inappropriate at high temperatures, and is useful in treating the time dependence.

2. Analysis of the Model

The model consists of two identical coplanar diatomic molecules rotating about fixed parallel axes perpendicular to the plane. The molecules make angles θ_1 and θ_2 with a fixed direction in the plane, and interact through a potential

$$V(\theta_1, \theta_2) = -J \cos 2(\theta_1 - \theta_2). \tag{2}$$

This could be the angle-dependent part of a dipole–dipole interaction. The moment of inertia of each molecule is I. The hamiltonian for the system is then

$$H = -(\hbar^2/2I)[\partial^2/\partial\theta_1^2 + \partial^2/\partial\theta_2^2] + V(\theta_1, \theta_2), \tag{3}$$

and the lagrangian is

$$L = \tfrac{1}{2}I[(\partial\theta_1/\partial t)^2 + (\partial\theta_2/\partial t)^2] - V(\theta_1, \theta_2). \tag{4}$$

2.1. Quantum-Mechanical Treatment

In terms of the new variables

$$\psi = \theta_1 + \theta_2, \tag{5}$$

$$\phi = \theta_1 - \theta_2, \tag{6}$$

the hamiltonian becomes

$$H = -(\hbar^2/4I)[\partial^2/\partial\psi^2 + \partial^2/\partial\phi^2] + V(\phi), \tag{7}$$

and the Schrödinger equation is separable. The wavefunction can then be written as the product of functions $\Psi(\psi)$ and $\Phi(\phi)$ which satisfy

$$\mathrm{d}^2\Psi/\mathrm{d}\psi^2 + (4IW/\hbar^2)\Psi = 0, \tag{8}$$

$$\mathrm{d}^2\Phi/\mathrm{d}\phi^2 + (4I/\hbar^2)(E - W + J\cos 2\phi)\Phi = 0. \tag{9}$$

Here E is the total energy and W is a separation constant having the dimensions of energy.

The probability amplitude for the angle sum ψ given by Eq. (8) is that of a free rotor of energy W and moment of inertia $2I$. The normalized solution is

$$\Psi = (2\pi)^{-1/2} \exp (im\phi), \tag{10}$$

where

$$W = m^2\hbar^2/4I, \tag{11}$$

and the boundary conditions require m to be an integer.

Equation (9) giving the probability amplitude for the angle difference ϕ is an example of Mathieu's equation,⁽⁷⁾ like that obtained by Pauling.⁽⁶⁾ For $E - W \gg J$ the eigenvalues and eigenfunctions approach those of a free rotor of energy $E - W$ and moment of inertia $2I$. For $E - W + J \ll J$ the eigenvalues are

$$E - W + J = (n + \tfrac{1}{2})\hbar\omega_0, \tag{12}$$

where n is an integer and

$$\omega_0 = (2J/I)^{1/2}. \tag{13}$$

The eigenfunctions occur in degenerate pairs

$$\Phi_n{}^{\pm} = 2^{-1/2}\{H_n[\phi/\phi_0] \pm H_n[(\phi - \pi)/\phi_0]\}, \tag{14}$$

where $H_n(x)$ is a Hermite function⁽⁷⁾ and

$$\phi_0{}^2 = \hbar/(8IJ)^{1/2}. \tag{15}$$

In this limit, values of ϕ differing significantly from 0 or π have a low probability, and ϕ librates about these equilibrium values. It can be verified that the amplitude ϕ_0 is related to ω_0 by

$$\phi_0{}^2 = \hbar/2I\omega_0, \tag{16}$$

as required for a harmonic librator of moment of inertia $2I$, and that the frequency ω_0 is that given by a Taylor series expansion of the potential to second order about either minimum.†

2.2 CLASSICAL TREATMENT

The Lagrangian equations of motion are

$$I\,\mathrm{d}^2\theta_1/\mathrm{d}t^2 = -2J \sin 2(\theta_1 - \theta_2), \tag{17}$$

$$I\,\mathrm{d}^2\theta_2/\mathrm{d}t^2 = 2J \sin 2(\theta_1 - \theta_2). \tag{18}$$

† In Pauling's paper⁽⁶⁾ the frequencies corresponding to the energy, amplitude and small-angle expansion of the potential are all different. Examination of the appropriate asymptotic solutions of Mathieu's equation⁽¹⁴⁾ shows that the frequency given by Pauling for the energy is too large by a factor π and that his $\phi_0{}^2$ is too large by a factor 2π.

They too are separated by introducing the variables ψ and ϕ, with the result

$$d^2\psi/dt^2 = 0, \tag{19}$$

$$d^2\phi/dt^2 + (4J/I)\sin 2\phi = 0. \tag{20}$$

As in the quantum-mechanical treatment, the sum of the angles rotates freely. The solution of Eq. (19) is

$$\psi = \psi_0 + \omega t \tag{21}$$

where ψ_0 and ω are constants determined by the boundary conditions.

The relative motion is described by Eq. (20). The standard first step in solving such equations$^{(15)}$ gives

$$(d\phi/dt)^2 = \Omega^2 + \Omega_0^2 \cos 2\phi, \tag{22}$$

where Ω^2 is a constant and

$$\Omega_0^2 = 4J/I. \tag{23}$$

The condition that $d\phi/dt$ must be real places no restriction on ϕ provided $\Omega^2 > \Omega_0^2$, but when $\Omega^2 < \Omega_0^2$ certain values of ϕ are excluded and ϕ thus oscillates rather than rotates. This result at once indicates that Ω^2 is a measure of the energy of the system, E. In fact

$$E = (I/2)[(d\theta_1/dt)^2 + (d\theta_2/dt)^2] + V(\theta_1, \theta_2) \tag{24}$$

$$= (I/4)[(d\psi/dt)^2 + (d\phi/dt)^2] + V(\phi) \tag{25}$$

$$= (I/4)(\omega^2 + \Omega^2), \tag{26}$$

and if we write the energy of free rotation as W, by analogy with the quantum-mechanical treatment, then†

$$\Omega^2 = 4(E - W)/I. \tag{27}$$

So ϕ can take all values for $E - W > J$, but oscillates for $E - W < J$ until at the minimum of the potential $E - W = -J$ and ϕ is fixed at 0 or π. As expected from a classical treatment, then, rotation gives way to libration as the energy falls below the barrier height. The formal solution of Eq. (22) is

$$\int_0^{\phi} (\Omega^2 + \Omega_0^2 \cos 2\phi')^{-1/2} d\phi' = t_0 \pm t, \tag{28}$$

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† The constant Ω^2 is so written because it has the dimensions of frequency squared, by analogy with Ω_0^2. However, it should be noted that the energy of the minimum of the potential is $-J$, so that Ω^2 may be negative. This gives rise to no unphysical results, since Ω appears alone only when $\Omega^2 > 0$.

which has now to be evaluated in the two regions of motion. The quantity t_0 is a constant of integration fixing the relative orientation at $t = 0$ and hence may be neglected, while the ambiguity of sign arises from the two possible senses of rotation and so can also be neglected.

For $\Omega^2 > \Omega_0^2$, i.e. $E - W > J$, integration of Eq. (28) gives$^{(16)}$

$$F(\phi, k) = (\Omega^2 + \Omega_0^2)^{1/2} t \tag{29}$$

where F is an elliptic integral of the first kind,$^{(7,16)}$ and the parameter k is given by

$$k^2 = 2\Omega_0^2/(\Omega^2 + \Omega_0^2) = 2J/(E - W + J). \tag{30}$$

The explicit solution for ϕ is then

$$\phi = \sin^{-1}[\mathrm{sn}(2^{1/2}\Omega_0/k)t] \tag{31}$$

where sn u is a Jacobian elliptic function,$^{(7,16)}$ which depends on k as a parameter, the argument u being the right-hand side of Eq. (29) rewritten in terms of k instead of Ω^2. In this limit ϕ rotates in a constant sense. The period of this rotation follows from that of sn u, namely $4K(k)$, where $K(k) \equiv F(\pi/2, k)$ is a complete elliptic integral of the first kind.$^{(7,16)}$ The value of ϕ therefore increases by 2π with a frequency $\Omega_0/2^{3/2}kK(k)$. In the limit of high energies, $k \to 0$ and $K \to \pi/2$, and the angular frequency becomes simply Ω, as follows directly from Eq. (22).

The uniformity of the rotation can be examined via the angular velocity $\mathrm{d}\phi/\mathrm{d}t$. In Eq. (22) $\cos 2\phi$ is written in terms of $\sin\phi$, which by Eq. (31) is sn u, with the result

$$(\mathrm{d}\phi/\mathrm{d}t)^2 = \Omega^2 + \Omega_0^2 - 2\Omega_0^2\,\mathrm{sn}^2 u. \tag{32}$$

Since $0 \leqslant \mathrm{sn}^2 u \leqslant 1$, the maximum relative angular velocity is $(\Omega^2 + \Omega_0^2)^{1/2}$ and the minimum $(\Omega^2 - \Omega_0^2)^{1/2}$. Hence at the lower limit of this region where $\Omega = \Omega_0$ the angular velocity varies between zero and $2^{1/2}\Omega_0$, while at high energies where $\Omega \gg \Omega_0$ the angular motion is practically uniform with a frequency Ω as already found. The angular velocity is shown as a function of time in Fig. 1. This shows that when the energy equals the barrier height the motion is critically damped. At higher energies the angular velocity oscillates about Ω, the amplitude of the oscillation decreasing with increasing energy.

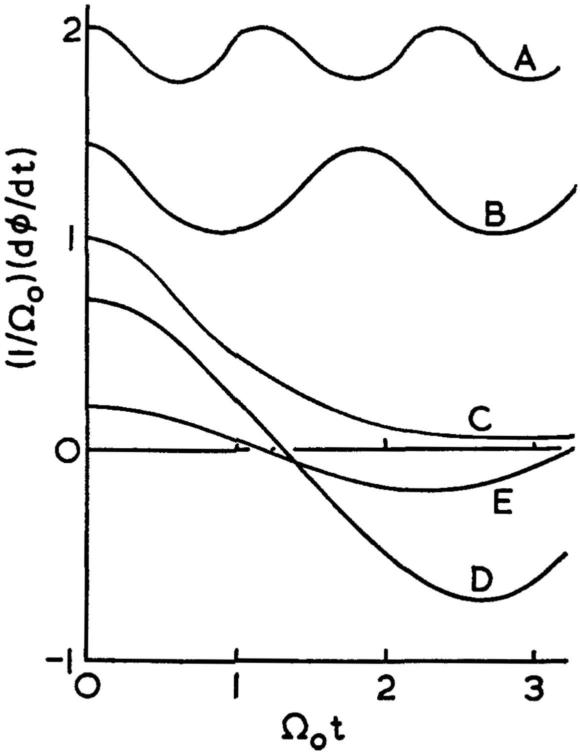

Figure 1. The classical angular velocity of relative motion as a function of time for different values of $(E-W)/J$. Curves A, B, C, D and E correspond to $(E-W)/J = 7$, 3, 1, 0 and -0.96 respectively.

For $\Omega^2 < \Omega_0{}^2$, i.e. for $E-W<J$, integration of Eq. (28) gives[(16)]

$$F(\alpha,\, 1/k) = 2^{1/2}\Omega_0 t \tag{33}$$

where k is defined by Eq. (30) and

$$\alpha = \sin^{-1}(k \sin\phi). \tag{34}$$

The explicit solution is then

$$\phi = \sin^{-1}[(1/k)\mathrm{sn}(2^{1/2}\Omega_0 t)], \tag{35}$$

where the parameter of $\mathrm{sn}\, v$ is $1/k$. Since $k>1$ and $\mathrm{sn}^2 v \leqslant 1$, ϕ is confined to the regions $n\pi \pm \sin^{-1}(1/k)$, where n is an integer and $\sin^{-1}(1/k)$ is taken in the first quadrant. Only in these regions is the angular velocity real. The angular frequency of oscillation follows from the periodicity of sn v as $\pi\Omega_0/2^{1/2}K(1/k)$. In the limit as $E - W \rightarrow -J$, where $k^2 \gg 1$, the semi-amplitude of libration decreases as $1/k$ but the frequency becomes the constant $2^{1/2}\Omega_0$. Replacement of Ω_0 from Eq. (23) confirms that this is the same frequency ω_0 as in the quantum-mechanical libration. It is also found that the parameter k deduced from the ground-state energy ($n = 0$ in Eq. (12)) is the inverse of the semi-amplitude ϕ_0, just as in the classical harmonic limit. The classical angular velocity is shown as a function of time in Fig. 1. The libration shows as an oscillation of the velocity about zero, the amplitude decreasing with decreasing energy. At the lowest energies, the angular velocity varies sinusoidally with time, as appropriate to harmonic libration.

3. Discussion

Both in the quantum-mechanical and in the classical treatment, the sum of the angular displacements ψ undergoes free rotation, essentially because the forces on the rotors are equal and opposite. A similar result holds for the sum of the angular displacements of a linear chain of rotors interacting through potentials $V(\theta_n - \theta_{n+1})$ if cyclic boundary conditions are assumed. Such potentials are not entirely realistic since there are no space-fixed equilibrium orientations as would be expected in crystals: equilibrium corresponds to any parallel orientation of adjacent molecules, whatever angle each makes with the vector joining them. However, this defect of the potential need not obscure the essential physical results, and would in any case be less serious for the molecules of higher symmetry encountered in plastic crystals. For present purposes a space-fixed equilibrium orientation of the molecules can be simulated by setting to zero the energy of free rotation W, whereupon the sum of the angular displacements is fixed and can be taken to represent parallel molecules perpendicular to their line of centres. With this convention, the relative angular motion corresponds to equal and opposite motions of the two molecules, behaviour reminiscent of the cogwheel modes proposed(17) for the benzene crystal.

At energies below the barrier height libration begins, but the two treatments have the expected differences that classically there is a sudden change to libration about one of the equilibrium orientations, whereas quantum-mechanically there is a gradual change to libration in which both orientations are accessible. At sufficiently low energies the libration is harmonic. The treatments concur in finding uniform rotation at sufficiently high energies. The classical results show that at lower energies the molecules accelerate when parallel or anti-parallel, and decelerate when perpendicular.

The extrapolation from this study to a full-scale model of a plastic crystal is a long one. Collective antiphase motion of molecules probably occurs subject to geometrical constraints: for example, it can occur in a ring of molecules each interacting with the two neighbours only if the number of molecules is even. It seems likely that such collective modes could not readily be detected by inelastic neutron scattering, since the asymmetric part of the potential is necessarily weak in plastic crystals, so that the modes it governs will have short lifetimes. An extension of self-consistent methods(9–12) to study collective modes of coupled rotation would be of interest, although caution would be needed since such treatments can give spurious phase transitions.(18) At the same time, the present work suggests that a classical treatment might give more easily visualized results. Perhaps a compromise can be effected by the use of the angular momentum coherent states,(19) which are particularly useful for describing the transition from quantum to classical angular momentum.

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