The Torsion Oscillator-Rotator in the Quantum Mechanics

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The theory of a symmetric rotator which in addition to the usual three degrees of rotational freedom has about the axis of symmetry also a degree of torsional freedom between two of its principal parts, is treated quantum mechanically. The potential energy is taken to be expressible in the form: $V = L(1-\cos m\phi')$ where L is proportional to the restoring torque, ϕ' is the angle of displacement, and m the number of minima of the potential energy curve as ϕ' increases from zero to 2π. The Schrödinger equation is found to be separable into two differential equations, one being the quantum mechanical equation for an ordinary symmetric rotator, and the other being of the form of Mathieu's equation: $d^2M/dx^2 + (a+16q\cos 2x)\,M = 0$ in which a is proportional to the energy parameter of the oscillator, q proportional to the restoring torque, and x to ϕ'. It is found that the solutions to this equation must satisfy the condition: $M(x-m\pi) = (\exp -2\pi iKA_z'/A_z)\,M(x)$ where K is the quantum number of angular momentum about the axis of symmetry, A_z' and A_z the moments of inertia of the lower part of the top and of the whole of the top respectively about the axis of symmetry. This ordinarily demands a general non-periodic solution to Mathieu's equation which, however, degenerates like the ordinary Mathieu functions to an exponential function as $q \to 0$. A qualitative discussion is given about the manner in which the energy states in the limiting case where $q=0$ go over into the other limiting case where $q=\infty$, and the calculation of the intensities and the selection rules for the rotator are finally determined where $q=0$ and where $q=\infty$. These it is believed will also be valid at least in first approximation in the neighborhoods of these limiting cases where q no longer is quite zero and not quite equal to infinity.

THE problem of the symmetric rotator has been subjected to detailed quantum mechanical treatment by several writers[1] and expressions derived for the energies of various quantum states as well as the probabilities of transition from one state to another. An interesting modification of this is one where in addition to the three degrees of rotational freedom there exists also a degree of torsional freedom between two principal parts of the rotator about the axis of symmetry. This seems of interest especially since certain molecules, the simplest of which probably are ethylene (C_2H_4) and ethane (C_2H_6), are thought to behave in this manner.

The motion of the top is best described by the aid of the Eulerean angles θ, ϕ and ψ where θ denotes the angle between the space fixed axis z and the axis of symmetry z' of the top, ϕ and ψ are respectively the angles between the line of nodes and the x' axis and the x axis. In this case where the upper part of the top may twist with respect to the lower part, two angles, ϕ_1 and ϕ_2 are required, denoting respectively the angles between the line of nodes and the x'' axis fixed in the lower part of the top and the x''' axis fixed in the

[1] D. M. Dennison, Phys. Rev. **28**, 318 (1926); F. Reiche and H. Rademacher, Zeits. f. Physik **39**, 444 (1926); F. Reiche and H. Rademacher, Zeits. f. Physik **41**, 453 (1927); R. de L. Kronig and J. J. Rabi, Phys. Rev. **29**, 262 (1927); C. Mannebeck, Phys. Zeits. **28**, 262 (1927).

upper part of the top. For convenience of calculation the following change of variable is made:

$$\phi = \frac{A_z'\phi_1 + A_z''\phi_2}{A_z' + A_z''}, \quad \phi' = \phi_2 - \phi_1 \tag{1}$$

where A_z' and A_z'' are the moments of inertia of the lower and upper parts of the top about the axis of symmetry. Taking A_x as the moment of inertia about the x' axis and letting $A_z = A_z' + A_z''$ one may write the kinetic energy:

$$2T = A_x(\dot{\theta}^2 + \dot{\psi}^2 \sin^2\theta) + A_z(\dot{\phi}^2 + \dot{\psi}^2 \cos^2\theta + 2\dot{\psi}\dot{\phi}\cos\theta) + (A_z'A_z''/A_z)\dot{\phi}'^2. \tag{2}$$

Unlike the symmetric rotator, the potential energy will not here be equal to zero, but may be expected to have approximately the form:

$$V = L(1 - \cos m\phi')$$

where L is proportional to the restoring torque and m denotes the number of minima of the potential energy curve as ϕ' increases from zero to 2π.

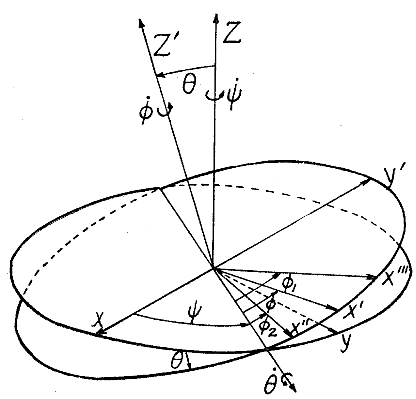

Fig. 1.

The Schrödinger equation, when obtained from the kinetic energy function by methods which are well known[2] and which are tantamount to using the Laplacian in generalized coordinates, becomes:

$$\begin{aligned} &\partial^2 U/\partial\theta^2 + \cot\theta\,\partial U/\partial\theta + (A_x/A_z + \cot^2\theta)\partial^2 U/\partial\phi^2 \\ &\quad - (2\cot\theta/\sin^2\theta)\partial^2 U/\partial\phi\partial\psi + (1/\sin^2\theta)\partial^2 U/\partial\psi^2 \\ &\quad + (A_xA_z/A_z'A_z'')\partial^2 U/\partial\phi'^2 + (8\pi^2 A_x/h^2)(E + L\cos m\phi')U = 0. \end{aligned} \tag{3}$$

As in the problem of the symmetric rotator, ϕ and ψ occur only as ignorable coordinates and if we put:

$$U = \Theta(\theta)e^{i(N\psi + K\phi)}M(m\phi'/2) \tag{4}$$

where $\Theta(\theta)$ and $M(m\phi'/2)$ are functions of θ and ϕ' alone and where because of the single valuedness of U, N and K must be integers or zero, it is found

[2] E. Schrödinger, Ann. d. Physik **79**, 748 (1926).

that (3) consists of two parts, one depending only on θ and another depending only on ϕ'. As is well known this condition can exist only when each part is a constant, say $8\pi^2 A_x W_1/h^2$. Equation (3) may now be separated into two differential equations, one a function only of θ and the other a function of ϕ' only. These two differential equations are:

$$d^2\Theta/d\theta^2 + \cot\theta d\Theta/d\theta - [(N - K\cos\theta)^2/\sin^2\theta]\Theta + (J(J+1) - K^2)\Theta = 0 \quad (5)$$

where:

$$\begin{aligned} J(J+1) - K^2 &= (8\pi^2 A_x/h^2)(E - W_1) - K^2 A_x/A_z \\ &= (8\pi^2 A_x W/h^2) - K^2 A_x/A_z \end{aligned} \quad (6)$$

and:

$$d^2M(x)/dx^2 + (a + 16q\cos 2x)M(x) = 0 \quad (7)$$

where:

$$x = m\phi'/2, \quad a = 32\pi^2 A_z' A_z'' W_1/A_z m^2 h^2, \quad q = 2\pi^2 A_z' A_z'' L/A_z m^2 h^2. \quad (8)$$

Solutions of the differential equations.

A. The solution to equation (5) is just that for an ordinary symmetrical rotator and has been carried out by Reiche and Rademacher, and Kronig and Rabi who by introducing the substitutions:

$$s = |K + M|, \; d = |K - M|, \; t = (\tfrac{1}{2})(1 - \cos\theta), \; \Theta = t^{d/2}(1-t)^{s/2}F,$$

were able to write equation (5) in the form of the hypergeometric equation:

$$t(1-t)F'' + [\gamma + (\alpha + \beta + 1)t]F' - \alpha\beta F = 0 \quad (9)$$

where:

$$\gamma = 1 + d, \quad \alpha = (d+s)/2 + J + 1, \quad \beta = (d+s)/2 - J.$$

The solution to (9) is the hypergeometric function:

$$F = 1 + (\alpha\beta/\gamma)t + (\alpha(\alpha+1)\beta(\beta+1)/2!\gamma(\gamma+1))t^2 + \cdots$$

which in order that the wave function: remain everywhere finite demands that α be equal to a negative integer, $\alpha = -p$, $(p = 0, 1, 2, \cdots)$. To obtain the equation for the energies, one solves equation (6) which gives:

$$W = (h^2/8\pi^2)[J(J+1)/A_x - K^2(1/A_x - 1/A_z)]. \quad (10)$$

B. Equation (7) is Mathieu's equation in the usual form. The common solutions are those which have a period of 2π in x and these are known as Mathieu's functions, denoted by $\mathrm{ce}_n(x, q)$ and $\mathrm{se}_n(x, q)$. Condon[3] has found that equation (7) is just that for the physical pendulum in the quantum mechanics and that in this case the required solutions were those where:

$$M(x + \pi) = M(x)$$

and that these were the Mathieu functions of *even* order. Similarly in treating

[3] E. U. Condon, Phys. Rev. **31**, 891 (1928).

the problem of rotation in diatomic crystals, Pauling[4] found the quantum mechanical equation to be of the form (7) where now the required solutions satisfy:

$$M(x + 2\pi) = M(x)$$

a condition which is fulfilled by the Mathieu functions of both *even* and *odd* order.

There now remains to investigate which of the solutions $M(x)$ are the required ones in our cases. We have the condition to comply with, that the wave function must be single valued, i.e., when the original configuration of the system has been restored, the wave function must assume its initial value. This interests us only in so far as it concerns the variable ϕ', defined as the difference between ϕ_2 and ϕ_1 which describe the positions of the lower and upper parts of the top relative to the line of nodes. We must inquire how the original configuration of the rotator may be restored by variation of the angles ϕ_1 and ϕ_2. This may be accomplished by letting ϕ_1 and ϕ_2 independently increase by an integral number (τ and σ respectively) of times 2π. The necessary and sufficient condition for single valuedness is, therefore, using equation (1):

$$U\{\theta, \psi, \phi + 2\pi(\tau A_z' + \sigma A_z'')/A_z, \phi' - 2\pi(\tau - \sigma)\} = U(\theta, \psi, \phi, \phi')$$

where by (4) this leads to the requirement:

$$M[(m/2)(\phi' - 2\pi(\tau - \sigma))] = e^{-2\pi i K(\tau A_z' + \sigma A_z'')/A_z} M(m\phi'/2).$$

Since $A_z' + A_z'' = A_z$ and $e^{-2\pi i K\sigma} = 1$ this becomes:

$$M[(m/2)(\phi' - 2\pi(\tau - \sigma))] = e^{-2\pi i K(\tau-\sigma)A_z'/A_z} M(m\phi'/2). \tag{11}$$

Now τ and σ were taken as integers, consequently their differences, $\tau - \sigma$ must be integral, and since (11) must hold for all values of $\tau - \sigma$ we may without loss of generality set this difference equal to unity, in which case we may write:[5]

$$M[(m/2)(\phi' - 2\pi)] = e^{-2\pi i K A_z'/A_z} M(m\phi'/2). \tag{12}$$

In general this demands general and non-periodic solutions to Mathieu's equation which in the limiting case where $q = 0$ degenerate, as do the ordinary Mathieu functions, to exponential functions. When $q = 0$ Mathieu's equation has solutions:

$$M(x) = e^{i(a)^{1/2}x}, \tag{13}$$

a condition which when inserted into (12) gives, after some simplification:

$$\tfrac{1}{2}m(a)^{1/2} - KA_z'/A_z = s \quad s = \cdots - r, \cdots - 2, -1, 0, 1, 2, \cdots r, \cdots .$$

[4] Linus Pauling, Phys. Rev. **36**, 430 (1930).

[5] Solutions to Mathieu's equation which must conform to conditions similar to (12) have long been known and been of importance to astronomers. Whittaker and Watson (Modern Analysis, p. 413) briefly treat solutions subject to the condition: $F(z+2\pi) = (\exp 2\pi\mu)\ F(z)$ where $\mu \neq 0$. The equations give to a first approximation the departure of an orbit from a periodic orbit, which is certainly unstable unless the exponents μ occurring in pairs of opposite sign, are purely imaginary (Analytical Dynamics, E. T. Whittaker, 3rd ed., p. 397).

Hence the solutions to Mathieu's equation required in our case become, when $q=0$,

$$M(x) = e^{(2i/m)(s+KA_z'/A_z)}. \tag{14}$$

An interesting case arises where $A_z'=A_z''$ which occurs in such molecules as ethane where the upper and lower parts of the top are identical. When this is so the condition (11) becomes:

$$M[(m/2)(\phi' - 2\pi(\tau - \sigma))] = e^{-iK(\tau-\sigma)\pi}M(m\phi'/2) \tag{11'}$$

which by inspection reveals that the required solutions are of two kinds, namely, such that:

$$M(x + m\pi) = \pm M(x), \tag{15}$$

the plus sign being taken for K even, and the minus sign for K odd.

To the knowledge of the writer, tables of such solutions to Mathieu's equation have never been computed, but in analogy to the ordinary Mathieu functions we may expect them to degenerate to sin nx and cos nx as $q \rightarrow 0$ where because of (11′), n need no longer be an integer. Letting $q=0$ in (7) it is quickly seen that the solutions satisfying the conditions set forth in (11′) and (15) are the following:

K even:

$$1,\ e^{\pm 2xi/m},\ e^{\pm 4xi/m},\ e^{\pm 6xi/m},\ \cdots$$

K odd:

$$e^{\pm xi/m},\ e^{\pm 3xi/m},\ e^{\pm 5xi/m},\ \cdots. \tag{14'}$$

This suggests the necessity in many physical problems of finding solutions to Mathieu's equation which are not the usual ones periodic in x by π and 2π, but more general ones periodic in x by $m\pi$, where m is an integer greater than 2.

As has been pointed out by other writers, there are two limiting cases of Mathieu's equation, namely; when $q=0$ where it is the quantum mechanical equation for a simple rotator; and secondly when x is small so that higher order terms in the expansion of the cosine may be neglected, where it becomes the wave equation for the harmonic oscillator. In the first instance the energy is given by the expression:

$$W_1 = (2s + 2KA_z'/A_z)^2h^2A_z/32\pi^2A_z'A_z'' \tag{16}$$

while in the second case the energy is of the form:

$$W_1 = (j + \tfrac{1}{2})h\nu_0. \tag{16'}$$

With the aid of Goldstein's tables[6] for the ordinary Mathieu functions, Condon has made a chart showing how for the physical pendulum (i.e., where $m=1$) the levels in one limiting case go over into the other limiting case. In the problem of rotation in diatomic crystals (i.e., where $m=2$), Pauling has pointed out that where x is small so that higher orders of x in the expansion

[6] S. Goldstein, Trans. Cambr. Phil. Soc. **23**, 303 (1927).

of cos $2x$ in Eq. (7) may be neglected and one effectively has the harmonic oscillator to deal with, there is a two-fold degeneracy of the levels, i.e., each level is double, one component corresponding to vibration about the position of equilibrium $\theta=0$, and the other to vibration about the position of equilibrium $\theta=\pi$. When $q=0$, and one has free rotation, then as is well known there exists also a two-fold degeneracy of all the levels except the first one. Pauling, also using the tables of Goldstein, has traced how as q becomes different from zero and this latter degeneracy is removed, the levels go over to the double degeneracy of the other limiting case.

This we should like also to do here for cases where $m>2$, but are confronted by two difficulties. The first of these arises when we consider the general case where the two parts of the rotator are not alike, for as we have seen, general solutions to Mathieu's equation are then required. If we consider the case where both parts of the rotator are identical, we are still confronted with the fact that tables of the functions which degenerate to (14′) as $q\rightarrow 0$ have never been computed for cases where $m>2$. While it is therefore not at present possible to give charts which are quantitatively right for $m>2$, one may nevertheless, show qualitatively how this transition takes place from the one extreme where $q=0$ to the other extreme where q is infinite. For simplicity we consider $m=3$, but the reasoning may equally well be made to embrace higher values of m. When $m=3$, functions (14′) become:

K even:

$$1,\ e^{\pm 2xi/3},\ e^{\pm 4xi/3},\ e^{\pm 2xi},\ \cdots$$

with the characteristic values:

$$0,\ 4h^2/8\pi^2A_z,\ 16h^2/8\pi^2A_z,\ 36h^2/8\pi^2A_z,\ \cdots$$

K odd:

$$e^{\pm xi/3},\ e^{\pm xi},\ e^{\pm 5xi/3},\ \cdots$$

with the characteristic values:

$$h^2/8\pi^2A_z,\ 9h^2/8\pi^2A_z,\ 25h^2/8\pi^2A_z,\ \cdots.$$

If $q\neq 0$, the corresponding functions are in the first place solutions of Eq. (7) in the range from zero to 3π with the boundary conditions (15). The equation, however, has coefficients periodic in the period π, so the solutions must be solutions of Eq. (7) in the range zero to π with exponents 0, $\pm 2\pi i/3$ for K even, and $\pm\pi i/3$, πi for K odd. Since the equation is real, solutions with exponents $\pm 2\pi i/3$ are conjugate complex functions with the same real characteristic values; likewise the solutions with exponents $\pm\pi i/3$ have the same real characteristic value. The solutions with exponents zero and πi are just the ordinary Mathieu functions of even and odd order, the characteristic values of which may be taken from Goldstein's tables. These are indicated in Fig. 2 as solid lines.

All of these functions, however, may be regarded as solutions of Eq. (7) in the interval from zero to 6π subject to the simple periodic boundary condition so that by the oscillation theorem for Sturm-Liouville systems with periodic boundary conditions,[7] when the characteristic values are arranged in order, the lowest is single and its characteristic function has no zeros; the next term is double and its characteristic functions each have two zeros; the third term is also double and the characteristic functions each have four zeros, etc. It follows that the double characteristic values will fall into order according to the number of zeros of their characteristic functions so that the graphs of these can never cross one another. Neither can they cross the graphs of any of the ordinary Mathieu functions, and they must therefore lie as de-

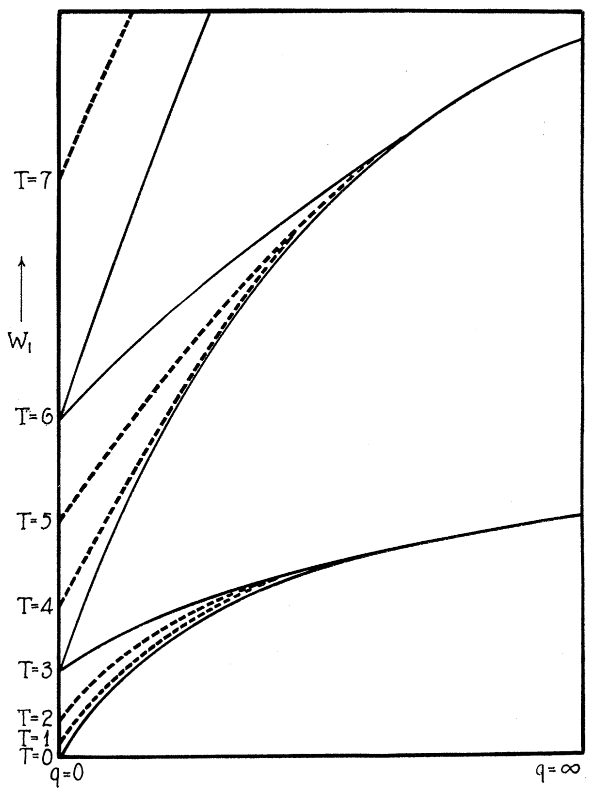

Fig. 2.

picted by the broken lines in Fig. 2, reducing to their limiting values for $q=0$ and $q=\infty$.

This result may easily be verified in the simple case of potential energy functions such as are used by Kronig and Penny[8] and then applying directly their Eq. (6) which here would be written:

$$P(\sin z)/z + \cos z = \cos 2\pi k/6$$

where k is an integer and P a parameter proportional in our problem to the

[7] E. L. Ince, Ordinary Differential Equations, p. 246.

[8] R. de L. Kronig and W. A. Penny, Proc. Roy. Soc. **130**, 499 (1931).

restoring torque. Determining the roots of this equation for values of P between zero and infinity, one arrives at exactly the same conclusions as indicated in Fig. 2.

It is possible now also to write solutions to Eq. (7) for our problem where q is large, i.e., where x is small so that higher order terms in the expansion of $\cos 2x$ may be neglected, and where consequently this equation then becomes the quantum mechanical equation for a harmonic oscillator. We shall again for the sake of simplicity let $m=3$ in which case the functions are nearly zero everywhere except close to $\phi'=0$, $\phi'=2\pi/3$, and $\phi'=4\pi/3$. Each level, as we have seen, shows a three-fold degeneracy for K even and K odd, and the characteristic functions may now to a good approximation be taken to be expressible by:

$$\Psi_{n,j} = (\tfrac{1}{3})^{1/2}\left\{X_j\left(\frac{\phi'}{\phi_0'}\right) + \omega^n X_j\left(\frac{\phi' - 2\pi/3}{\phi_0'}\right) + \omega^{2n} X_j\left(\frac{\phi' - 4\pi/3}{\phi_0'}\right)\right\} \tag{17}$$

where n is 0, 2 or 4 for K even, and 1, 3 or 5 for K odd, the X_j's are the Hermite orthogonal functions of the indicated arguments, ϕ_0' is equal to $(h\nu_0/2q)^{1/2}$, ω, ω^2, $\cdots$ and ω^5 are the five complex sixth roots of unity. It has been pointed out that the degeneracy can not entirely be removed, but while one of the components splits away, the other two components remain degenerate throughout for all values of q. Where K is even, that component which splits away is characterized by $n=0$, while the other two components which remain degenerate have the characteristic functions with $n=2$ and $n=4$; when K is odd, that component which splits away is characterized by $n=3$, while the components which remain degenerate for all values of q have $n=1$ and $n=5$. The index j represents the torsional, or as it may here appropriately be called, the vibrational quantum number.

The complete wave function U may now be written:

$$U = Rt^{d/2}(1-t)^{s/2}F(-p, 1+d+s+p, 1+d, t)e^{i(N\psi+K\phi)}M(x)$$

R being a normalizing factor so chosen that:

$$\int UU^*dv = 1 \tag{18}$$

where dv is an element of volume in coordinate space which in the example we are considering is:

$$dv = (g)^{1/2}d\theta d\psi d\phi d\phi' = A_x(A_z'A_z'')^{1/2}\sin\theta d\theta d\psi d\phi d\phi'.$$

Calculation of intensities

The matrix elements of a coordinate q_i are:

$$q^i(k, l) = \int q^i U_k U_l dv \tag{19}$$

where U_k and U_l are the characteristic functions belonging to states k and l respectively and where as in (18) dv is an element of volume in coordinate space.

Following Kronig and Rabi, considering charges fixed in the lower and the upper parts of the top with coordinates $(x'', y'', z'') = (a_1, 0, c_1)$, and $(x''', y''', z''') = (a_2, 0, c_2)$, one obtains as coordinates in free space, where β_1 and β_2 are substituted for A_z'/A_z and A_z''/A_z respectively and where:

$$\phi_1 = \phi - \beta_1\phi', \ \phi_2 = \phi + \beta_2\phi', \ \beta_1 + \beta_2 = 1$$

$$x_i = c_i \sin\theta \sin\psi + a_i \cos\psi \cos(\phi \mp \beta_i\phi') - a_i \cos\theta \sin\psi \sin(\phi \mp \beta_i\phi')$$

$$y_i = -c_i \sin\theta \cos\psi + a_i \sin\psi \cos(\phi \mp \beta_i\phi') - a_i \cos\theta \cos\psi \sin(\phi \mp \beta_i\phi')$$

$$z_i = c_i \cos\theta + a_i \sin\theta \sin(\phi \mp \beta_i\phi')$$

where $i = 1$ takes the upper sign and $i = 2$ takes the lower sign.

For the case where $q = 0$ we proceed in the manner outlined by Kronig and Rabi, by putting these coordinates into (19) together with the characteristic functions appropriate for this extreme case and evaluating the resulting definite integrals. We shall first consider those amplitudes for the component of the electric moment lying along the axis of symmetry z'. It is apparent that Eqs. (19) integrated over the variable θ and ψ will have identically the same value as in the case of the ordinary symmetric rotator. Setting this part of the integral equal to C, noting that this component of the electric moment does not depend on β_i, the integrals we shall have to evaluate will be of the kind:

$$I = C\int_0^{2\pi}\int_0^{2\pi} e^{iK\phi}e^{-iK'\phi}e^{i(s/\beta_i \pm K)\beta_i\phi'}e^{-i(s'/\beta_i \pm K')\beta_i\phi'}d\phi d\phi'.$$

In order for this integral not to vanish K must be equal to K', i.e., $\Delta K = 0$ which it will be seen carries with it the requirement that $s = s'$ in order for the integration over ϕ' not to vanish also. We have thus the additional selection rule that $\Delta s = 0$ which if we set $T = (s/\beta_i \pm K)$ where T is to be interpreted as the torsional quantum number may more advantageously be written: $\Delta T = 0$. Carrying out the integrations, the amplitudes are found to be identically those obtained by Dennison in the case of the ordinary symmetric rotator.[1]

Turning now to consider the amplitudes where the component of the electric moment lying in the $x'y'$ plane is involved, it is clear that as before the integration of the expressions (19) over θ and ψ must be exactly the same as for the ordinary symmetric rotator. Setting this part of the integral equal to C', the integrations which we shall have to carry out will all be of the kind:

$$I = C'\int_0^{2\pi}\int_0^{2\pi} e^{i(\phi \pm \beta_i\phi')}e^{iK\phi}e^{-iK'\phi}e^{i(s/\beta_i \pm K)\beta_i\phi'}e^{-i(s'/\beta_i \pm K')\beta_i\phi'}d\phi d\phi'.$$

In order that these integrals are not to vanish, we see that K' must be equal to $K \pm 1$, i.e., $\Delta K = \pm 1$, a condition which here just as before carries with it the requirement that $s = s'$. We have consequently the selection rule here also that $\Delta s = 0$, which, however, if we again adopt the notation $T = (s/\beta_i \pm K)$ may be expressed: $\Delta T = \pm 1$. We have then to evaluate the integrals which lead here as before to identically the amplitudes of the ordinary symmetric rotator.[1]

As we have seen, each of the energy states except the first exhibits a two-fold degeneracy. If for simplicity we consider a model where the upper and lower parts of the rotator are identical and apply on it a slight perturbation, this degeneracy may be removed for those states which have as their characteristic functions the ordinary Mathieu functions, while for the other levels, the degeneracy persists, as we have seen, for all values of q. To each of the components of these levels whether they split apart or not may be ascribed a characteristic function, and it may readily be seen that the correct wave functions are $\cos T\phi'/2$ and $\sin T\phi'/2$, and when $\Delta T = \pm 1$, that the probability of transition between two energy states, the one with an even characteristic function and the other with an odd characteristic function will be the same as that between two energy states where the characteristic functions are both even or both odd. When, however, $\Delta T = 0$ the transitions must be between energy states both of which are characterized by even wave func-

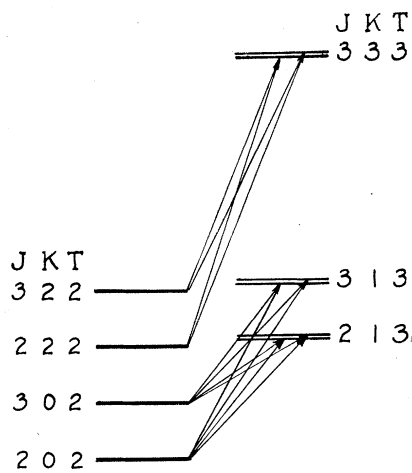

Fig. 3.

tions or both by odd wave functions (e.g., $\cos T\phi'/2 \to \cos T\phi'/2$; $\sin T\phi'/2 \to \sin T\phi'/2$). To illustrate what are some of the permitted transitions, a few energy values ($J=2$, $J=3$, $T=2$, $T=3$) have been computed, for a model where the upper and lower parts of the top are alike (i.e., $A_z' = A_z''$) and where A_x has been taken equal to $2A_z$. In Figure 3 are shown the corresponding energy levels, and the transitions are indicated where $\Delta J = 0$, ± 1, $\Delta K = \pm 1$, $\Delta T = \pm 1$.

To determine the amplitudes and the transition rules at the other extremity where q is very large we are obliged as before to construct and evaluate a set of definite integrals like those indicated in (19) using the same coordinates as before, but now using the characteristic functions (17) which are the appropriate ones in this region. We consider first those amplitudes where the electric moment along the axis of symmetry is involved. As before we shall denote the integration over θ and ψ by C, and bearing in mind that this component of the electric moment is independent of ϕ_i, the integrals we must solve will be of the kind:

$$I_{n',j'}^{n,j} = C\int_0^{2\pi}\int_0^{2\pi} e^{iK\phi}e^{-iK'\phi}\Psi_{n,j}\Psi_{n',j'}{}^{*}d\phi d\phi',$$

which vanishes except where $K=K'$, $n=n'$, and $j=j'$. We consequently have where the component of the electric moment along the z' axis is concerned, selection rules and amplitudes which are identically the same as where $q=0$.

We turn now to where the electric moment lies in the $x'y'$ plane and set the integration over θ and ψ as before equal to C', which enables us to write the integrals to be evaluated as follows:

$$I_{n',j'}^{n,j} = C'\int_0^{2\pi} e^{\pm i\phi}e^{iK\phi}e^{-iK'\phi}d\phi\int_0^{2\pi} e^{\pm i\phi},e^{\pm i\phi'/2}\Psi_{n,j}\Psi_{n',j'}{}^{*}d\phi'.$$

In order for this not to vanish we must set $K=K'\pm1$, and now replacing $\Psi_{n,j}$ and $\Psi_{n'},_{j'}{}^{*}$ by their appropriate values, remembering that one of these must correspond to even values of K and the other to odd values of K, the integrals become expressible as:

$$\begin{aligned}I_{n',j'}^{n,j} = (C''/3)\int_0^{2\pi} e^{\pm i\phi'/2}\Big\{ & X_j\Big(\frac{\phi'}{\phi_0'}\Big)X_{j'}\Big(\frac{\phi'}{\phi_0'}\Big)\\ & + \omega^{(x)}X_j\Big(\frac{\phi'-2\pi/3}{\phi_0'}\Big)X_{j'}\Big(\frac{\phi'-2\pi/3}{\phi_0'}\Big)\\ & + \omega^{(y)}X_j\Big(\frac{\phi'-4\pi/3}{\phi_0'}\Big)X_{j'}\Big(\frac{\phi'-4\pi/3}{\phi_0'}\Big)\Big\}d\phi\end{aligned}$$

or which is equivalent:

$$I_{n',j'}^{n,j} = (C''/3)\int_0^{2\pi} X_j\Big(\frac{\phi'}{\phi_0'}\Big)X_{j'}\Big(\frac{\phi'}{\phi_0'}\Big)e^{\pm i\phi},e^{\pm i\phi'/2}\big\{1+\omega^{(x)}e^{\pm\pi i/3}+\omega^{(y)}e^{\pm 2\pi i/3}\big\}d\phi'.$$

In the above integrals, when the exponents are taken positive, the sums within the brackets may be seen always to be equal to three or to zero, and when the exponents are taken negative, those sums which previously were found equal to three now become zero and vice versa, except $n=n'\pm3$, in which case the sums always vanish. Since the actual coordinates over which we are integrating are cosines and sines, one must take sums and differences of these integrals, where the exponentials have exponents of different sign. Consequently the probability of transition between any two levels belonging to sets with quantum numbers j and j' respectively will be the same where $n\neq n'\pm3$. When $n=n'\pm3$ the transition cannot take place. We obtain when we expand the term $e^{i\phi'/2}$ into a series:

$$\begin{aligned}I_{n',j'}^{n,j} = (C''/3)\int_0^{2\pi} X_j\Big(\frac{\phi'}{\phi_0'}\Big)X_{j'}\Big(\frac{\phi'}{\phi_0'}\Big)\big\{&[1+\omega^{(x)}e^{\pi i/3}+\omega^{(y)}e^{2\pi i/3}][1+i\phi'/2\\ &-\phi'^2/8+\cdots]\pm[1+\omega^{(x)}e^{-\pi i/3}+\omega^{(y)}e^{-2\pi i/3}][1-i\phi'/2-\phi'^2/8-\cdots]\big\}d\phi'.\end{aligned}$$

From this it is apparent that there will be several transitions allowed depending upon changes of j to various values of j'. These may be determined by evaluation of the components of these integrals of which we shall consider only the first two:

$$I^{n,j}_{n',j'} = C'' \int_0^{2\pi} X_j\left(\frac{\phi'}{\phi_0'}\right) X_j\left(\frac{\phi'}{\phi_0'}\right)\left\{ \left[1 + \omega^{(x)} e^{\pi i/3} + \omega^{(y)} e^{2\pi i/3}\right] \right.$$
$$\left. \pm \left[1 + \omega^{(x)} e^{-\pi i/3} + \omega^{(y)} e^{-2\pi i/3}\right] \right\} d\phi'$$

which of course vanishes except where $j = j'$, where it takes the value C''.

$$I^{n,j}_{n',j'} = \frac{C''}{6} \int_0^{2\pi} X_j\left(\frac{\phi'}{\phi_0'}\right) X_{j'}\left(\frac{\phi'}{\phi_0'}\right)\left\{ i\phi'/2\left[1 + \omega^{(x)} e^{\pi i/3} + \omega^{(y)} e^{2\pi i/3}\right] \right.$$
$$\left. \mp i\phi'/2\left[1 + \omega^{(x)} e^{-\pi i/3} + \omega^{(y)} e^{-2\pi i/3}\right] \right\} d\phi'.$$

which has a value only when $j = j' \pm 1$. Here it takes the value $C''/8(q)^{1/2}$.

It is thus proved that the appropriate amplitudes are the same expressions as before, only that here they will in general be multiplied by some definite constant, and while these amplitudes and transition rules are valid only where q is very large and the levels are completely degenerate, they should serve to indicate what will be the important transitions where q is still large, but where the degeneracy has been partly removed and the one component has begun to split away. It should be noticed that in the region of large q, the only transition which is of importance is the first one we have just discussed above where $j = j'$. This is of course what is to be expected from the problem of the ordinary symmetric rotator since it is the limiting case of our rotator when q becomes infinite.

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