The Rotation of Molecules in Crystals

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Citation: The Journal of Chemical Physics **3**, 189 (1935); doi: 10.1063/1.1749630
View online: http://dx.doi.org/10.1063/1.1749630
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/3/3?ver=pdfcov
Published by the AIP Publishing

The Rotation of Molecules in Crystals

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(Received December 14, 1934)

The problem of the rotation of molecules in crystals has been generalized to embrace also polyatomic configurations. Two models, of which the homo- and heteropolar diatomic molecules are special cases, are considered. The potential energy expressions are taken to be harmonic functions of the coordinates, satisfying the symmetry of the model under consideration. Two limiting cases exist; one where the crystal fields are small and effecting the motion of the top only slightly; the other where the crystal fields are large, restraining the top to rotate principally about its axis of symmetry, which will oscillate isotropically about its position of equilibrium. The eigenvalues of the problem are approximated for small fields by applying Schrödinger perturbation theory to the rotator and for large fields by applying Schrödinger perturbation theory to the isotropic oscillator in two dimensions. The connection of the eigenvalues for extreme values of the field is considered in detail. The eigenfunctions may on the rotator side be expanded in terms of the hypergeometric functions, and on the oscillator side in terms of associated Laguerre polynomials.

I. INTRODUCTION

THE interpretation of the specific heat measurements made on many crystals requires an assumption that there exists a critical temperature above which it is possible for the molecular configurations within the crystal to rotate. The problem has been discussed by several authors, but the only real attempts at a dynamical description of the phenomenon are those of Pauling[1] and Sterne[2] on rotation of diatomic molecules in crystals. While Pauling in reality treats the two dimensional model, Sterne has considered the actual three dimensional model of the spherical oscillator, pointing out that the Schrödinger equation is of the form of one of those encountered in studying the hydrogen molecule ion. Adopting a method for determining the eigenvalues for this equation developed by Wilson,[3] he is able to show diagrammatically how the energy level scheme varies as the crystal fields increase in magnitude.

While the problem of the spherical oscillator does not yield an exact quantum mechanical solution, the two limiting cases, where the crystal fields approach zero, thus effecting the motion of the top only slightly, and where the crystal fields approach infinity, so that the axis of symmetry oscillates isotropically about its position of equilibrium, are examples which may be solved exactly. These limiting cases shall henceforth be known as the *rotator* and *isotropic oscillator* sides respectively. The rather obvious implication is that the general case where the crystal fields take values intermediate between zero and infinity should lend itself to a solution by a perturbation method much like that used by Koenig[4] to solve Hill's equation. Since, however, no additional difficulties are encountered, the problem may as readily be generalized to embrace rotation also of polyatomic configurations in crystals. We shall, however, here confine ourselves to two particular polyatomic configurations which probably are among the most representative of those likely to rotate in the crystal form,[5] namely, the tetrahedral XY_3 configuration and the coplanar XY_3 configuration.

In Section II we shall adopt potential energy functions appropriate for our problem and set up the quantum mechanical Hamiltonian. In Section III we shall proceed to approximate the eigenvalues for the spherical oscillator in the region of small fields by applying Schrödinger perturbation theory to the limiting case of the rotator, the corresponding eigenfunctions being expandable in terms of the eigenfunctions of the symmetric rotator. In Section IV we shall develop asymptotic expansions to the eigenvalues in the region of strong crystal fields by applying perturbation theory to the other limiting case, the corresponding eigenfunctions here being expandable in terms of the eigenfunctions of the

[1] Linus Pauling, Phys. Rev. **36**, 430 (1930).
[2] T. E. Sterne, Proc. Roy. Soc. **A130**, 551 (1930).
[3] A. H. Wilson, Proc. Roy. Soc. **A118**, 628 (1928).
[4] Harold D. Koenig, Phys. Rev. **44**, 657 (1933).
[5] The homo- and heteropolar diatomic molecules in crystals may be thought of as special cases of these models, where the moment of inertia about the axis of symmetry has been shrunk to zero and where the angular momentum about this axis is zero.

isotropic oscillator in two dimensions. In Section V we shall consider the connection of the eigenvalues for extreme values of the crystal fields, while Section VI will be devoted to a discussion of the selection rules.

II. The Schrödinger Equation

In describing the motion of the top, it is customary to make use of two sets of coordinates; one set x, y and z fixed in space and another set, x', y' and z' fixed in the rotator. These two sets of coordinates may then be related to each other by the Eulerean angles θ, φ and ψ where θ denotes the angle between the space fixed z axis and the axis of symmetry z' of the top; φ denotes the azimuth angle and ψ the precession angle. The quantum mechanical expression for the kinetic energy of the rotator in these coordinates is well known, it having been determined by several writers.[6]

The potential energy function must represent some average value of the interactions of the rotator with the other components in the crystal lattice. It will in general be a function periodic in θ and φ, the periodicity being such that it will fulfill the symmetry requirements of the molecule; i.e., it must repeat itself every time the molecule assumes its initial position or one indistinguishable from it. We shall, in fact, assume that the potential energy function may quite well be represented by a sum of terms which are harmonic functions of the coordinates. The two particular models which we here wish to study, namely the tetrahedral XY_3 and coplanar XY_3 configurations will be referred to as model A and model B respectively[7] and their potential energy expressions will be considered individually.

Model A

The tetrahedral XY_3 configuration has the three Y particles located at the corners of an equilateral triangle and the X particle located at some distance d from their plane along the axis of symmetry. Referring this configuration to the Eulerean system it is seen that the required boundary conditions are: $V(\theta, \varphi)=V(\theta+2\pi, \varphi+2\pi/3)$. We shall adopt a potential energy function consisting of harmonic terms satisfying these conditions, breaking it off after the second term. Such a one is: $V(\theta, \varphi)=-2\mu_1 \cos\theta+\mu_2 \cos 3\varphi$, where μ_1 and μ_2 are parameters of magnitude depending upon the crystal fields. In this function the first term represents a torque restraining the top to rotate principally about its axis of symmetry while the second term limits the free rotation of the top also about z'.

Model B

The co-planar XY_3 model is a special case of Model A where $d=0$. Referring this to the Eulerean system one sees that because of its coplanarity, the required boundary conditions will this time be: $V(\theta, \varphi)=V(\theta+\pi, \varphi+\pi/3)$. A potential energy function broken off as before at the second term, made up of harmonic functions satisfying these boundary conditions may be taken to be: $V(\theta, \varphi)=\mu_1(1-\cos^2\theta)+\mu_2 \sin^2\theta \cos 2\varphi$, where as before μ_1 and μ_2 are parameters of magnitude. Here as before the first term depends only upon θ and seeks to make the rotator spin principally about its axis of symmetry while the second, a function of both θ and φ, limits the free rotation also about this axis.

It is now possible to write the complete quantum mechanical Hamiltonian. It is:

$$(1/\sin\theta)\,\partial/\partial\theta(\sin\theta\,\partial\Psi/\partial\theta)+(A/C+\cos^2\theta/\sin^2\theta)\partial^2\Psi/\partial\varphi^2+1/\sin^2\theta\,\partial^2\Psi/\partial\psi^2$$
$$-2(\cos\theta/\sin\theta)\partial^2\Psi/\partial\psi\partial\varphi+(8\pi^2A/h^2)\{E+\mu_1V_1(\theta)-\mu_2V_2(\theta,\varphi)\}\Psi=0, \quad (1)$$

[6] 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 **51**, 453 (1927); R. de L. Kronig and J. J. Rabi, Phys. Rev. **29**, 262 (1927); C. Mannebach, Phys. Zeits. **28**, 72 (1927).

[7] The regular tetrahedral XY_4 configuration is another typical case where rotation is apt to occur. This interesting model has its four Y particles at corners of a regular tetrahedron and its X particle at their center of gravity. It is especially interesting in that its symmetry prevents any definite choice of axis of symmetry. The potential energy function here must consequently depend upon both θ and φ, but contain no term in θ alone. In fact it is readily seen that a function conforming to the symmetry requirements for this model would be: $\mu_1 \cos\theta \sin^2\theta \sin^2\varphi$.

where A and C are the two principal moments of inertia (C being that about the axis of symmetry) and $V_1(\theta)$ and $V_2(\theta, \varphi)$ the two terms comprising the potential energy functions. Eq. (1), except for the last term ($\mu_2 V_2(\theta, \varphi)$) may become separable by the substitution:

$$\Psi = Y(\theta) \exp(i(K\varphi + M\psi)), \tag{2}$$

where as usual in such problems, the single-valuedness requirements demand that K and M be integers. In order to make (1) exactly separable, we make the restriction that μ_2 (i.e., the forces preventing free rotation about the axis of symmetry z') shall be small so that this term may be thought of as a perturbation term merely. While this limits the generality of the problem, it seems probable that in a great many cases the rotation about the axis of symmetry is only slightly restricted.

After substitution of (2) into (1) (where the term in μ_2 has been neglected) and dividing through by Ψ, we obtain as our unperturbed equation to be solved:

$$(1/\sin\theta)\, d/d\theta(\sin\theta\, dY/d\theta) + \{(8\pi^2 A/h^2)(E + \mu_1 V_1(\theta)) - K^2 A/C - (M - K\cos\theta)^2/\sin^2\theta\} Y = 0. \tag{3}$$

III. Characteristic Values and Functions Where μ_1 Is Small

In this section we shall approximate the characteristic values of Eq. (3) where μ_1 is small. We follow Sterne, making the following substitutions:

$$x = \cos\theta, \qquad \lambda^2 = 8\pi^2 A \mu_1/h^2, \qquad \Lambda = 8\pi^2 AE/h^2 - K^2(A/C - 1) \quad \text{(for model } A\text{)},$$

$$\Lambda = (8\pi^2 A/h^2)(E - \mu_1) - K^2(A/C - 1) \quad \text{(for model } B\text{)}.$$

in Eq. (3) and obtain:

$$(1 - x^2) Y'' - 2xY' + (\Lambda + \lambda^2 V(x) - (M - Kx)^2/(1 - x^2)) Y = 0. \tag{4}$$

When $\lambda = 0$, Eq. (4) reduces to the equation of the top, which when the substitutions:

$$Y = t^{a/2}(1 - t)^{b/2} F, \qquad t = 1/2(1 - x), \qquad a = |K + M|, \qquad b = |K - M|,$$

be made, may be written in the form of the hypergeometric equation. This has as a solution the hypergeometric function, and it may readily be shown that for this to be a suitable solution for the physical problem it is necessary that $\Lambda = J(J+1)$ where J is a positive integer. Thus, to obtain the eigenvalues of Eq. (3) when λ is a small quantity different from zero, we apply the Schrödinger perturbation theory to the equation of the rotator, interpreting $\lambda^2 V(x)$ as a perturbing potential which for models A and B will be, respectively, $((2)^{\frac{1}{2}}\lambda)^2 x$ and $\lambda^2 x^2$. The eigenvalues are evaluated to fourth approximation and the eigenfunctions to third approximation. The Schrödinger theory leads to the following well-known relations for the energies and the eigenfunctions:

$$E_k^{(n)} = \int H^{(n)} \Psi_k^{(0)} \bar{\Psi}_k^{(0)} dv + \sum_{i=1}^{n-1} \sum_{\tau=1}^{\infty} \int (H^{(n-i)} - E_k^{(n-i)}) A_{k\tau}^{(i)} \Psi_\tau^{(0)} \bar{\Psi}_k^{(0)} dv$$

and

$$\Psi = \sum_m \left(\sum_s \lambda^{(s)} A_{km}^{(s)} \Psi_m^{(0)}\right)$$

where

$$A_{k\tau}^{(i)}(E_k^{(0)} - E_\tau^{(0)}) = \int H^{(i)} \Psi_k^{(0)} \bar{\Psi}_\tau^{(0)} dv + \sum_{s=1}^{i-s} \sum_{j=1}^{\infty} \int (H^{(i-s)} - E_k^{(i-s)}) A_{kj}^{(s)} \Psi_j^{(0)} \bar{\Psi}_\tau^{(0)} dv.$$

For crystals belonging to model A, the problem is identically that of the Stark effect of polyatomic molecules. This has been discussed by Mannébach[8] who has carried the eigenvalues to second approximation. We restate his results, adding our own third and fourth approximations:

[8] C. Mannebach, reference 6. Mannebach has shown in this discussion of the Stark effect how the matrix components here encountered may readily be evaluated.

$$\lambda^2\Lambda^{(1)}{}_{J,K,M}=-\lambda^2KM/J(J+1), \qquad \lambda^4\Lambda^{(2)}{}_{J,K,M}=4\lambda^4(\Phi_{J,K,M}-\Phi_{J+1,K,M}),$$

$$\lambda^6\Lambda^{(3)}{}_{J,K,M}=64\lambda^6KM(\Xi_{J+1,K,M}-\Xi_{J,K,M}),$$

$$\lambda^8\Lambda^{(4)}{}_{J,K,M}=\lambda^8\{(32KM)^2(\Theta_{J,K,M}-\Theta_{J+1,K,M})+8(P_{J,K,M}-P_{J+2,K,M})\},$$

where:

$$\begin{aligned}\Phi_{J,K,M}&=(J^2-K^2)(J^2-M^2)/(2J+1)(2J)^3(2J-1),\\ \Xi_{J,K,M}&=(1/(2J-2)(2J)^2(2J+2))\Phi_{J,K,M},\\ \Theta_{J,K,M}&=(1/(2J-2)(2J)^2(2J+2))\Xi_{J,K,M},\\ P_{J,K,M}&=((2J-2)/(2J)(2J-1))\Phi_{J,K,M}\Phi_{J-1,K,M}.\end{aligned} \tag{5}$$

The coefficients $A_{k\tau}{}^{(i)}$ in the expansions of the eigenfunctions up to third approximation have been computed, but will not be tabulated here since whenever they are needed they may quite readily be computed.

For crystals belonging to model B, the procedure is identically the same. The energies have been determined here also to a fourth approximation, but only three approximations are listed here since the fourth is entirely too long and unwieldy to be of interest. In this case also the coefficients $A_{k\tau}{}^{(i)}$ in the expansions of the eigenfunctions will be omitted. The results are summarized below:

$$\lambda^2\Lambda^{(1)}{}_{J,K,M}=-\lambda^2\{\Phi_{J,K,M}+(KM)^2/J^2(J+1)^2+\Phi_{J+1,K,M}\},$$

$$\lambda^4\Lambda^{(2)}{}_{J,K,M}=8\lambda^4\{P_{J,K,M}-P_{J+2,K,M}+32(KM)^2(\Xi_{J,K,M}-\Xi_{J+1,K,M})\},$$

$$\begin{aligned}\lambda^6\Lambda^{(3)}{}_{J,K,M}=4\lambda^6\{&(8KM)^2(R_{J,K,M}-R_{J+1,K,M})+(S_{J,K,M}-S_{J+2,K,M})\\ &+(16KM)^2[((2J+4)/(2J+3))Q_{J+1,K,M}Q_{J+2,K,M}-2Q_{J,K,M}Q_{J+1,K,M}\\ &+((2J-2)/(2J-1))Q_{J,K,M}Q_{J-1,K,M}]\},\end{aligned} \tag{6}$$

where:

$$\begin{aligned}\Phi_{J,K,M}&=(J^2-K^2)(J^2-M^2)/(2J-1)(2J)^2(2J+1),\\ \Xi_{J,K,M}&=(1/(2J-2)^2(2J)(2J+2)^2)\Phi_{J,K,M},\\ P_{J,K,M}&=(1/(2J-1))(\Phi_{J,K,M}\Phi_{J-1,K,M}),\\ R_{J,K,M}&=((\Lambda^{(1)}{}_{J-1,K,M}-\Lambda^{(1)}{}_{J,K,M})/2J)\Xi_{J,K,M},\\ S_{J,K,M}&=((\Lambda^{(1)}{}_{J-2,K,M}-\Lambda^{(1)}{}_{J,K,M})/(2J-1)^2)P_{J,K,M},\\ Q_{J,K,M}&=(1/(2J-2)(2J)(2J+2))\Phi_{J\ K,M}.\end{aligned}$$

IV. Characteristic Functions and Values When μ_1 Is Large

It has been pointed out in Section I that when μ_1 is large we have what corresponds to the classical case of the rotator constrained to rotate primarily about its axis of symmetry, which in turn oscillates isotropically with simple harmonic motion about the space fixed z axis. Under these conditions the Eulerean angle θ will be small, and consequently we may replace the trigonometric function in θ in Eq. (3) by their expansions in terms of θ. Then making the substitutions:

$$\begin{aligned}x&=(8\pi^2A\mu_1/h^2)^{\frac{1}{4}},\\ \epsilon^{(0)}&=(8\pi^2A/h^2\mu_1)^{\frac{1}{2}}W=2(V+1),\end{aligned} \tag{7}$$

where:

$$8\pi^2AW/h^2=8\pi^2AE/h^2-K^2A/C+16\pi^2A\mu_1/h^2, \quad \text{(for model } A\text{)}$$

$$8\pi^2AW/h^2=8\pi^2AE/h^2-K^2A/C, \quad \text{(for model } B\text{)}$$

and disregarding all but first order terms we have:

$$d^2Y/dx^2+(1/x)dY/dx+\{2(V+1)-(L^2/x^2)-x^2\}Y=0. \tag{8}$$

Eq. (8) is the quantum mechanical equation for the isotropic oscillator in two dimensions, and has been carefully studied in connection with the carbon dioxide molecule by Dennison[9] who has shown that the solution must be of the form $Y(x)=\exp(-x^2/2)\,Z(x)$ where $Z(x)$ is the associated Laguerre polynomial which in order to remain everywhere finite requires that V must be an integer and that L take the values $V, V-2, V-4, \cdots$. This limitation on L leads in our problem to certain interesting relations between the quantum numbers K and M. We shall consider this point more in detail in Section V. The energy of the isotropic oscillator in two dimensions is then determined and by referring to (7) it is readily seen that for our problem it is:

$$E^{(0)}{}_{V,K}=(V+1)h\omega+K^2h^2/8\pi^2C,$$

where $\omega=(\mu_1/2\pi^2A)^{\frac{1}{2}}$.

To obtain asymptotic expansions for the eigenvalues where μ_1 is large we proceed to apply the Schrödinger perturbation theory to this limiting case, using as perturbation operators successively higher and higher order terms. To second approximation these are:

$$\lambda' H=(\lambda'/3)(xd/dx+(M^2+KM-2K^2)-ax^4),$$

$$\lambda'^2 H=(\lambda'^2/15)((x^3/3)d/dx+(M^2+7KM/4+K^2)+2bx^6/3),$$

where for model A, $a=1/4$, $b=1/16$ and for model B, $a=b=1$, and $\lambda'=(h^2/8\pi^2A\mu_1)^{\frac{1}{2}}$.

The procedure followed in obtaining eigenvalues and functions for model A, where the potential energy function is periodic in θ with a period of 2π, is identically the same as that of Section III.[10] The eigenvalues were actually evaluated to third approximation, but only the first and second are reproduced here, the third becoming entirely too unwieldy for use. Here as in Section III we shall omit the coefficients $A_{k\tau}{}^{(i)}$ in the expansions of the wave functions. The first and second approximations to the eigenvalues are given below:

$$\begin{aligned}\epsilon^{(1)}{}_{V,L}&=(\lambda'/3)\{(M^2+KM-2K^2-1)-(1/4)(\alpha_{V+2,L}+(V+1)^2+\alpha_{V,L})\},\\ \epsilon^{(2)}{}_{V,L}&=(\lambda')^2\{(1/15)[((3V-3)/24)\alpha_{V+2,L}+((3V-7)/24)\alpha_{V,L}+(M^2+7KM+K^2-1/3)(V+1)\\ &\quad+(V+1)^3/24]+(1/12)(\beta_{V,L}-\beta_{V+2,L})+(1/96)(\rho_{V,L}-\rho_{V+4,L})\},\end{aligned}\tag{9}$$

where $\alpha_{V,L}=(V^2-L^2)/4$,

$\beta_{V,L}=((V^2-4)/4)\alpha_{V,L}$,

$\rho_{V,L}=\alpha_{V,L}\alpha_{V-2,L}$.

To approximate to the eigenvalues for model B where μ_1 is large, after the method we have been using, one should take into account that this model may oscillate isotropically about two positions of equilibrium, namely $\theta=\theta_0$ and $\theta=\theta_0+\pi$. Replacing θ by $\theta+\pi$ in Eq. (3) one sees that it again leads to Eq. (6) except that now L must be redefined as $|K+M|$. There will then be two independent solutions to the unperturbed Eq. (7) which we shall denote as $Y_{V,L}(x)$ and $Y_{V,L}(x+\gamma\pi)$ where $\gamma=2\pi(A\omega/h)^{\frac{1}{2}}$, corresponding to this twofold degeneracy. To obtain asymptotic expansions for the eigenvalues one should then use Schrödinger perturbation theory for degenerate systems; the first order perturbation contributions to the characteristic values occurring as roots of the secular determinant $|H^{(1)}{}_{k,l}-E\delta_l{}^k|=0$. The stabilized unperturbed wave function will then be seen to be $Y^{(0)}{}_{V,L}{}^i=(1/2)^{\frac{1}{2}}\{Y_{V,L}(x)\pm Y_{V,L}(x+\gamma\pi)\}$ where i takes values one and two, respectively, associated with the plus and minus signs.

Now in all cases except where either or both K and M are zero, will the above secular determinant yield identical roots so that in only a few cases will the degeneracies in θ be removed. This is readily seen since (1) by the symmetry of the problem, the two diagonal terms will be alike and, (2) the integrals which determine the values

[9] D. M. Dennison, Rev. Mod. Phys. 3, 294 (1931).

[10] The matrix components here encountered have been evaluated by means of a method entirely similar to that used by Mannebach referred to under Section III. It is possible to expand $H^{(i)}\,Y_{V,L}(x)$ by means of a recurrence relation where the coefficients may be obtained by the method of undetermined coefficients.

of the non-diagonal elements will always contain periodic factors because of the restriction that $L=|K\pm M|$ which when integrated between the proper limits will vanish. Moreover since the wave functions have values only in the immediate neighborhood of $\theta=\theta_0$ and $\theta=\theta_0+\pi$, it is readily seen that for states where K or M are zero, the non-diagonal elements of the above determinant will be very small in the region of large μ_1. Hence the roots will also here be nearly alike; the splitting of the terms becoming appreciable only with increasing V and as μ_1 decreases to relatively small values. If we confine ourselves to the lower eigenvalues, i.e. for values of V not over two or three, we may to a good approximation ignore the splitting of the terms and here adopt a set of expressions similar to (9). For model B these are:

$$\begin{aligned}\epsilon^{(1)}{}_{V,\,L}&=(\lambda'/3)\{(M^2\pm KM+K^2-1)-(\alpha_{V+2,\,L}+(V+1)^2+\alpha_{V,\,L})\},\\ \epsilon^{(2)}{}_{V,\,L}&=(\lambda'^2)\{(1/15)[(2V+3)\alpha_{V+2,\,L}+(2V+1)\alpha_{V,\,L}+(M^2\pm 7KM/4+K^2-1/3)(V+1)\\ &\quad+(2/3)(V+1)^3]+(1/36)(\sigma_{V,\,L}-\sigma_{V+2,\,L})+(1/72)(\rho_{V,\,L}-\rho_{V+4,\,L})\},\end{aligned}\tag{10}$$

where α and ρ are defined as before and where $\sigma=(4V^2-1)\alpha_{V,\,L}$. The plus or minus signs are used accordingly as we define L to be $|K-M|$ or $|K+M|$. These expressions are similar to those developed by Wilson[11] and used by Sterne. These also show no splitting of the eigenvalues, but yield what might be termed mean values of the very closely lying components of the oscillator levels.

V. Connection of the Eigenvalues for Extreme Values of μ_1

Having now obtained expressions which approximate the eigenvalues in the region where μ_1 takes small values and asymptotic expansions for these in the region of large μ_1 values, it is possible to calculate and draw diagrams showing how these vary with μ_1. This has been done in Figs. 1 and 2 for models A and B, respectively. It is of interest, however, quite independently to investigate the connection of the eigenvalues for one extreme case with another, especially since it might serve to confirm our earlier work. It is possible to predict how this connection must take place by observing the nature of the degeneracies of each eigenvalue in the two limiting cases; by observing the restrictions placed upon the values of K, M and L for any value of V by the requirement of finiteness and by the relation $|K\pm M|=L$; and finally observing that Eq. (7) is of the Sturm-Liouville type with periodic coefficients concerning which, for given values of K and M, the oscillation theorem[12] states that the graphs of any two eigenvalues when plotted against μ_1 can never cross each other.

We consider first model A. In the extreme case of μ_1 equal to zero, the eigenvalues are those of the symmetric rotator and each is $2(2J+1)$ fold degenerate except for $K=0$ where the degeneracy is $(2J+1)$ fold. In the other extreme case where μ_1 is infinite, the eigenvalues are those of an isotropic oscillator plus a plane rotator. Now the requirement that the wave function remain finite fixes the values that L may take for a given value of V. Thus for example when $V=0$, L must also take the value zero. Hence by the condition $|K-M|=L$, K is always equal to M. Since, however, K (and M) may take either plus or minus values, all characteristic values where $V=0$ are twofold degenerate, except where $K=M=0$ which is single. Where $V=1$, L also must be unity, and the restriction $|K-M|=L$ establishes that $M=K\pm 1$. Thus since here again K takes either plus or minus values, eigenvalues with $V=1$ are fourfold degenerate. For higher values of V, analogous relations hold, so that in general we may say that any eigenvalue characterized by a quantum number V is $2(V+1)$ fold degenerate except where $K=0$ which has a $(V+1)$ fold degeneracy, and those where K assumes such values that $M=0$ which have a $(2V+1)$ fold degeneracy. Thus observing the requirements of the oscillation theorem that no two characteristic values of a given K and M

[11] A. H. Wilson, reference 3; T. E. Sterne, reference 2.

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

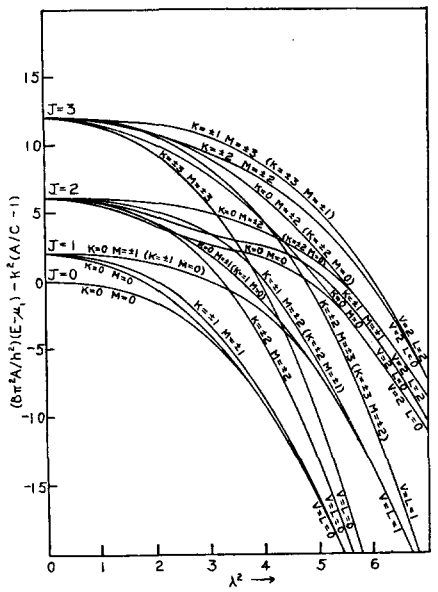

FIG. 1.

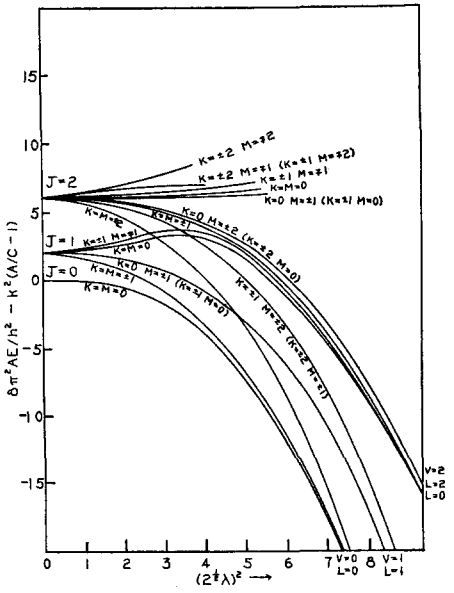

FIG. 2.

may ever cross, and observing that each component level in one limiting case must be consummated by one in the other limiting case, it is possible without ambiguity to join the eigenvalues in the two extreme cases. This is shown in Fig. 1.

For model B we proceed much as before. In the extreme case of $\mu_1=0$ the characteristic values are again those for the symmetric rotator with its characteristic degeneracies, and where μ_1 is infinite the eigenvalues are again those of the isotropic oscillator, but this time with somewhat different degeneracies. These differences, we know, arise because of the two positions of equilibrium $\theta=\theta_0$ and $\theta=\theta_0+\pi$, about which the molecule here may oscillate. Replacing θ by $\theta+\pi$ in Eq. (3) we have seen that L must be redefined as $|K+M|$. Thus taking for example $V=0$, and consequently also $L=0$, we have the restriction $K=\pm M$ always. Hence since K may take both plus or minus values, all levels where $V=L=0$ are fourfold degenerate, except in the instance where $K=M=0$ which is twofold degenerate. When for example, $V=1$ and $L=1$, this requirement becomes $K=\pm(M\pm1)$ and such eigenvalues, since K may take both plus and minus values will be eightfold degenerate except when $K=0$ which is only fourfold degenerate, and for such cases where K takes a value making $M=0$, which are sixfold degenerate. In general one may say that on the oscillator side, characteristic values have a degeneracy of $4(V+1)$ except those where $K=0$ which are only $2(V+1)$ fold degenerate, and those where K takes such values that $M=0$ which are $2(2V+1)$ times degenerate. As before, observing the oscillation theorem and noting that all component levels in each limiting case are accounted for, one may as before without ambiguity join the characteristic values of the extreme case of $\mu_1=0$ to those of the other extreme case of $\mu_1=\infty$. It is shown in Fig. 2 how these join.

VI. Selection Rules

We conclude our discussion of the spherical oscillator with a few remarks concerning the selection rules and the transition probabilities. Formally these may of course be determined in the usual manner by examining which of the matrix components are different from zero, but

since the problem is not exactly soluble, a general formulation cannot readily be given. By again considering limiting cases, however (i.e., where $\mu_1=0$ and where $\mu_1=\infty$) and observing how the characteristic values in these limiting cases connect, it is possible to predict which transitions will be the important ones.

A matrix component $q_{k,\,l}$ may be determined from the integral $q_{k,\,l}=\int\Psi_k q\Psi_l dv$ where q is the classical coordinate, Ψ_k and Ψ_l are the wave functions of the k-th and the l-th states, respectively, and dv is an element of-volume in configuration space.

Kronig and Rabi[13] have considered the matrix components for the symmetric rotator (i.e., our problem where $\mu_1=0$) and have found that for the electric moment parallel to z', these vanish always except where $\Delta J=\pm1$, or 0; $\Delta K=0$; $\Delta M=\pm1$, or 0; and for the electric moment in the $x'y'$ plane they vanish unless $\Delta J=\pm1$, or 0; $\Delta K=\pm1$; $\Delta M=\pm1$, or 0.

We wish also to consider them when $\mu_1=\infty$. Our problem differing from that of Kronig and Rabi only in that the potential energy function is here different from zero the classical coordinates will be identically those used by them, which as is well known, are expressible in terms of trigonometric functions of the Eulerean angles. When $\mu_1=\infty$, θ, however, will be small so that we may as before replace the trigonometric functions in θ by their expansions in θ. Without actually setting up the integrals which lead to the matrix components, we shall state the results. When the electric moment is parallel to z', all matrix components will vanish except where $\Delta V=\Delta K=\Delta M=0$. When the electric moment is in the $x'y'$ plane, all matrix components are zero in first approximation unless $\Delta V=0$, $\Delta K=\Delta M=\pm1$. To investigate the selection rules to higher order approximations it is necessary to make use of the perturbed wave functions.

Now by referring to Fig. 1, it is seen that the only selection rule which remains of first order importance throughout all values of μ_1 when the electric moment is parallel to z', is the one $\Delta J=0$, $\Delta K=0$, $\Delta M=0$, where $J=K=M$. All matrix components arising from other transitions become of higher order importance only on the oscillator side, and as μ_1 becomes infinite go to zero.

When the electric moment is in the $x'y'$ plane, there are two sets of transitions of first order importance throughout all values of μ_1. These are $\Delta J=\pm1$, $\Delta K=\Delta M=\pm1$; $\Delta J=0$, $\Delta K=\pm1$, $\Delta M=\mp1$. All other transitions become of higher order importance as μ_1 increases and in the limit yield nothing.

These conclusions concerning the selection rules are strictly speaking, drawn from considerations of the limiting cases of model A only. Nevertheless these same are applicable also to model B since here again matrix components will vanish unless these are observed. This is true only insofar as transitions between levels characterized by solutions $Y_{V,\,L}(x)$ and $Y_{V,\,L}(x+\gamma\pi)$ may be neglected. These latter are however, of negligible significance in the region of large μ_1 and become of real importance only as the rotator side is approached. Even here these transitions in general offer no problem since as we have seen, only in the special cases where K or M are zero is this degeneracy removed so that transitions from an initial level to one component of a final level will be indistinguishable experimentally from transitions to both components or to the other component. Hence the same selection rules will be seen to be applicable to both models.

[13] Kronig and Rabi, reference 6.