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Internal Molecular Motions of Large Amplitude Illustrated by the Symmetrical Vibration of Ammonia

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A general method is developed for separating slow internal motions of molecules from their rapid vibrations, with the rotational motion. The zero approximation for the slow motion can be obtained by Schrödinger's rule from the classical motion in which the rapid vibrations are replaced by constraints.

The theory is applied to the symmetrical double-minimum vibration of ammonia, the combined vibration-rotation energy levels being evaluated as characteristic numbers of a Sturm-Liouville equation in one variable. The microwave absorption frequencies of $N^{14}H_3$ and $N^{15}H_3$ are computed, also the pure rotation frequencies in the far infra-red.

PART 1. THE GENERAL THEORY OF VIBRATION AND ROTATION OF MOLECULES WITH INTERNAL MOTIONS OF LARGE AMPLITUDE

1. Introduction

AS far as vibration and rotation are concerned, a molecule may be regarded as a system of mass points, the atoms, moving in a field of force derived from a potential energy which depends on their relative positions. The atoms have a stable position of relative equilibrium, and the motion may usually be considered in a good first approximation as made up of normal vibrations about this configuration together with a translation and rotation of the configuration as a whole. In quantum mechanics this separation follows closely the way in which the problem would be treated in classical mechanics.³

In some interesting cases this picture does not furnish a good first approximation because vibrations of so large an amplitude must be considered that the interaction between vibration and rotation becomes large or that more than one equilibrium configuration may be within their limits. It is still usually true that the motion can be considered as made up of rapid vibrations

about a configuration which changes more slowly, and which depends on only a few varying parameters.

2. The Form of the Schrödinger Equation

For a system of N mass points moving in a field of force derived from a potential energy V , we may use any coordinates in configuration space. When we express the motion of the system in terms of l slowly varying coordinates q_1, \dots, q_l , and λ rapidly varying coordinates v_1, \dots, v_λ , where

$$l + \lambda = 3N, \quad (2.1)$$

the classical kinetic energy may be derived first of all in terms of the corresponding velocities $\dot{q}_1, \dots, \dot{q}_l$, and $\dot{v}_1, \dots, \dot{v}_\lambda$, and, being a positive definite form, may always be expressed as

$$T = \frac{1}{2} \sum_a \sum_b a_{ab} \dot{q}_a \dot{q}_b + \frac{1}{2} \sum_\alpha \sum_\beta c_{\alpha\beta} (\dot{v}_\alpha + \sum_a b_{\alpha a} \dot{q}_a) (\dot{v}_\beta + \sum_b b_{\beta b} \dot{q}_b), \quad (2.2)$$

where the cross terms between \dot{q} 's and \dot{v} 's have been taken into the quadratic form of the \dot{v} 's.

We may then transform to the momenta in two stages. Firstly, the momentum u_α corresponding to v_α is given by

$$u_\alpha = \sum_\beta c_{\alpha\beta} (\dot{v}_\beta + \sum_a b_{\beta a} \dot{q}_a), \quad (2.3)$$

and, if $C_{\alpha\beta}$ are the coefficients reciprocal to $c_{\alpha\beta}$,

¹ This paper includes part of work done for a Ph.D. thesis at Ohio State University.

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³ E. B. Wilson and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).

we have

$$\dot{v}_\alpha + \sum_a b_{\alpha a} \dot{q}_a = \sum_\beta C_{\alpha\beta} u_\beta \quad (2.4)$$

so that

$$T = \frac{1}{2} \sum_a \sum_b a_{ab} \dot{q}_a \dot{q}_b + \frac{1}{2} \sum_\alpha \sum_\beta C_{\alpha\beta} u_\alpha u_\beta.$$

Secondly, the momentum p_a corresponding to q_a is given by

$$p_a = \sum_b a_{ab} \dot{q}_b + \sum_\alpha b_{\alpha a} u_\alpha \quad (2.5)$$

and if A_{ab} are the coefficients reciprocal to a_{ab} , we have

$$\dot{q}_a = \sum_b A_{ab} (p_b - \sum_\alpha b_{\alpha b} u_\alpha), \quad (2.6)$$

so that

$$T = \frac{1}{2} \sum_a \sum_b A_{ab} (p_a - \sum_\alpha b_{\alpha a} u_\alpha) (p_b - \sum_\beta b_{\beta b} u_\beta) + \frac{1}{2} \sum_\alpha \sum_\beta C_{\alpha\beta} u_\alpha u_\beta, \quad (2.7)$$

where the cross terms between p 's and u 's are taken into the quadratic form of the p 's.

Further, the discriminant of this quadratic form for T is just the product of the determinants of the A 's and the C 's, so that if we integrate over configuration space with volume element $d\rho d\sigma$, where

$$d\rho = dq_1 \cdots dq_l / \left(\begin{vmatrix} A_{11} & \cdots & A_{1l} \\ \vdots & \ddots & \vdots \\ A_{l1} & \cdots & A_{ll} \end{vmatrix} \right)^{\frac{1}{2}} \quad (2.8)$$

and

$$d\sigma = dv_1 \cdots dv_\lambda / \left(\begin{vmatrix} C_{11} & \cdots & C_{1\lambda} \\ \vdots & \ddots & \vdots \\ C_{\lambda 1} & \cdots & C_{\lambda\lambda} \end{vmatrix} \right)^{\frac{1}{2}}, \quad (2.9)$$

the Schrödinger equation for the problem is given by the condition that

$$E = \int \int \left[\frac{\hbar^2}{8\pi^2} \left(\sum_a \sum_b A_{ab} \left(\frac{\partial \psi}{\partial q_a} - \sum_\alpha b_{\alpha a} \frac{\partial \psi}{\partial v_\alpha} \right) \times \left(\frac{\partial \psi}{\partial q_b} - \sum_\beta b_{\beta b} \frac{\partial \psi}{\partial v_\beta} \right) + \sum_\alpha \sum_\beta C_{\alpha\beta} \frac{\partial \psi}{\partial v_\alpha} \frac{\partial \psi}{\partial v_\beta} \right) + V \psi^2 \right] d\rho d\sigma \quad (2.10)$$

is stationary, subject to

$$\int \int \psi^2 d\rho d\sigma = 1. \quad (2.11)$$

In these transformations we may use freely velocities and momenta corresponding to quasi-

⁴ E. Schrödinger, Ann. d. Physik 79 (4), 376 (1926).

coordinates, such as angular velocities and momenta,⁵ provided that we take account of their nature when we carry out the variation.

3. Choice of Variables

Consider a system of N particles of mass m_s and Cartesian coordinates ξ_s, η_s , and ζ_s , $s=1, \dots, N$, in a field of force derived from a potential energy function V . Suppose that ξ_s, η_s , and ζ_s , can be expressed in terms of $3N$ variables q_1, \dots, q_l , and v_1, \dots, v_λ , such that variations of v_1, \dots, v_λ , from zero cause increases in V large, in a manner to be specified below, compared to changes caused by any variations in q_1, \dots, q_l . We shall use geometrical language with respect to a $3N$ dimensional Euclidean space of line element

$$ds^2 = \sum_{s=1}^N m_s (d\xi_s^2 + d\eta_s^2 + d\zeta_s^2), \quad (3.1)$$

the configuration space with volume element $d\rho d\sigma$ ((2.8), (2.9)).

We can specify precisely the part of this space corresponding to $v_\alpha=0, \alpha=1, \dots, \lambda$, as follows. There must be one or more points of unstable equilibrium ($dV=0$) at which d^2V expressed as a sum of squares of differentials in perpendicular directions has just λ of them with (large) positive coefficients, the coefficients of the remaining l being negative or zero. The lines of greatest slope leading to lower values of V from one of these equilibrium points mark out a definite l dimensional sub-space (A) containing the line of greatest slope through each point of itself.⁶ This sub-space can be continued through the points of stable equilibrium, and q_1, \dots, q_l , may be any l variables describing its points. The existence of coordinates specifying the position of the center of mass and the orientation of the molecule, which do not enter at all into V , does not essentially alter this procedure. Thus

$$\begin{aligned} \xi_r &= \xi_r^0(q_1, \dots, q_l) \\ \eta_r &= \eta_r^0(q_1, \dots, q_l) \\ \zeta_r &= \zeta_r^0(q_1, \dots, q_l) \end{aligned} \quad r=1, \dots, N \quad (3.2)$$

for points of the sub-space (A).

⁵ L. Boltzmann, Wien. Sitzungsberichte (1902). See also E. T. Whittaker, *Analytical Dynamics* (Cambridge University Press, London, 1927), p. 41.

⁶ This is essentially the argument by which water-courses are defined as lines of greatest slope down from forks or passes. A. Cayley, Phil. Mag. 18 (4), 264 (1859).

At each point, P , of this sub-space construct the normal (perpendicular) flat sub-space (B_P) . In this normal region take v_1, \dots, v_λ to be given as an orthogonal Cartesian coordinate system with the point of intersection P as origin, and with axes in the directions of the principal axes of d^2V at P in the region (B_P) , but with scales to be specified below. Since the l dimensional sub-space (A) contains the line of greatest slope, or direction of the gradient of V , through each point of itself, we must have, near $v_\alpha=0$, $\alpha=1, \dots, \lambda$,

$$V = V_0 + K^2 \left(\sum_\alpha \frac{1}{2} V_\alpha v_\alpha^2 + 0[v_\alpha^3] \right), \quad (3.3)$$

where $V_0, V_1, \dots, V_\lambda$, are functions of q_1, \dots, q_l and our assumption about the potential energy is precisely that K is large, when the v_α are expressed in atomic units, and the V_α are of order unity.

Then q_1, \dots, q_l , and v_1, \dots, v_λ , specify position uniquely sufficiently near to $v_1=0, \dots, v_\lambda=0$,⁷ and we shall have

$$\left. \begin{aligned} \xi_r &= \xi_{r^0} + \sum_\alpha \xi_{r\alpha} v_\alpha \\ \eta_r &= \eta_{r^0} + \sum_\alpha \eta_{r\alpha} v_\alpha \\ \zeta_r &= \zeta_{r^0} + \sum_\alpha \zeta_{r\alpha} v_\alpha \end{aligned} \right\} r=1, \dots, N, \quad (3.4)$$

where $\xi_{r\alpha}, \eta_{r\alpha}$, and $\zeta_{r\alpha}$, $\alpha=1, \dots, \lambda$, as well as ξ_{r^0}, η_{r^0} , and ζ_{r^0} , are functions of q_1, \dots, q_l , only, and for each set of values of q_1, \dots, q_l ,⁸

$$\sum_r m_r \left(\frac{\partial \xi_{r^0}}{\partial q_a} \xi_{r\alpha} + \frac{\partial \eta_{r^0}}{\partial q_a} \eta_{r\alpha} + \frac{\partial \zeta_{r^0}}{\partial q_a} \zeta_{r\alpha} \right) = 0, \quad a=1, \dots, l, \alpha=1, \dots, \lambda, \quad (3.5)$$

since (B_P) is normal to (A) , and

$$\sum_r m_r (\xi_{r\alpha} \xi_{r\beta} + \eta_{r\alpha} \eta_{r\beta} + \zeta_{r\alpha} \zeta_{r\beta}) = 0, \quad \alpha, \beta = 1, \dots, \lambda, \alpha \neq \beta, \quad (3.6)$$

since v_1, \dots, v_λ , are orthogonal coordinates in the normal sub-space (B_P) .

⁷ The region in which this is so will be bounded by loci of intersection of sub-spaces (B_P) for adjacent points P of (A) , and to cover, as would be necessary for an exact theory, the whole of configuration space just once, we should have to define the coordinates in a more complicated way.

⁸ These are the extensions of the Eckart conditions for the case of separation of translation and rotation from vibration. C. Eckart, Phys. Rev. **47**, 552 (1935).

Finally, for any arbitrary K , we may choose the scales of v_1, \dots, v_λ , so that

$$\sum_r m_r (\xi_{r\alpha}^2 + \eta_{r\alpha}^2 + \zeta_{r\alpha}^2) = 1/V_\alpha. \quad (3.7)$$

Then the classical kinetic energy in terms of the velocities is

$$\begin{aligned} & \sum_a \sum_b \frac{1}{2} \sum_r m_r \left[\sum_\xi \left(\frac{\partial \xi_{r^0}}{\partial q_a} + \sum_\alpha \frac{\partial \xi_{r\alpha}}{\partial q_a} v_\alpha \right) \right. \\ & \quad \times \left. \left(\frac{\partial \xi_{r^0}}{\partial q_b} + \sum_\beta \frac{\partial \xi_{r\beta}}{\partial q_b} v_\beta \right) \right] \dot{q}_a \dot{q}_b \\ & + \sum_a \sum_\beta \sum_r m_r \left[\sum_\xi \left(\frac{\partial \xi_{r^0}}{\partial q_a} + \sum_\alpha \frac{\partial \xi_{r\alpha}}{\partial q_a} v_\alpha \right) \xi_{r\beta} \right] \dot{q}_a \dot{v}_\beta \\ & \quad + \sum_\alpha \sum_\beta \frac{1}{2} \sum_r m_r \sum_\xi \xi_{r\alpha} \xi_{r\beta} \dot{v}_\alpha \dot{v}_\beta, \end{aligned}$$

where \sum_ξ means the sum of similar terms in ξ, η , and ζ . The second term of this is just

$$\sum_a \sum_\beta \sum_r m_r \sum_\xi \sum_\alpha \frac{\partial \xi_{r\alpha}}{\partial q_a} v_\alpha \xi_{r\beta} \dot{q}_a \dot{v}_\beta$$

by (3.5), and the last term is just $\frac{1}{2} \sum_\alpha (\dot{v}_\alpha^2 / V_\alpha)$ by (3.6) and (3.7), so that we may write the whole in the form of (2.2)

$$\frac{1}{2} \sum_a \sum_b a_{ab} \dot{q}_a \dot{q}_b + \frac{1}{2} \sum_\alpha \frac{1}{V_\alpha} (\dot{v}_\alpha + \sum_a b_{a\alpha} \dot{q}_a)^2, \quad (3.8)$$

where

$$b_{a\alpha} = V_\alpha \sum_r m_r \sum_\xi \sum_\beta \frac{\partial \xi_{r\beta}}{\partial q_a} v_\beta \xi_{r\alpha}, \quad (3.9)$$

and

$$\begin{aligned} a_{ab} &= \sum_r m_r \sum_\xi \left(\frac{\partial \xi_{r^0}}{\partial q_a} + \sum_\alpha \frac{\partial \xi_{r\alpha}}{\partial q_a} v_\alpha \right) \\ & \quad \times \left(\frac{\partial \xi_{r^0}}{\partial q_b} + \sum_\beta \frac{\partial \xi_{r\beta}}{\partial q_b} v_\beta \right) \\ & - \sum_\alpha V_\alpha \sum_r m_r \sum_\xi \sum_\beta \frac{\partial \xi_{r\beta}}{\partial q_a} v_\beta \xi_{r\alpha} \\ & \quad \times \sum_s m_s \sum_\xi \sum_\gamma \frac{\partial \xi_{s\gamma}}{\partial q_b} v_\gamma \xi_{s\alpha}. \quad (3.10) \end{aligned}$$

Then, by (2.7), the kinetic energy in terms of the

momenta is

$$T = \frac{1}{2} \sum_a \sum_b A_{ab} (p_a - \sum_\alpha b_{a\alpha} u_\alpha) \times (p_b - \sum_\beta b_{b\beta} u_\beta) + \frac{1}{2} \sum_\alpha V_\alpha u_\alpha^2, \quad (3.11)$$

where A_{ab} are the coefficients reciprocal to a_{ab} .

4. Translation and Rotation

It is convenient in practice to use a moving frame of reference with origin at the center of mass of the molecule and rotating with it. If x_s, y_s , and $z_s, s=1, \dots, N$ are the Cartesian coordinates of the N nuclei relative to this moving frame, we write

$$\begin{cases} \xi_s = \xi + l_{\xi x} x_s + l_{\xi y} y_s + l_{\xi z} z_s \\ \eta_s = \eta + l_{\eta x} x_s + l_{\eta y} y_s + l_{\eta z} z_s \\ \zeta_s = \zeta + l_{\zeta x} x_s + l_{\zeta y} y_s + l_{\zeta z} z_s \end{cases}, \quad (4.1)$$

where ξ, η , and ζ , are the coordinates of the center of mass relative to the fixed frame, and $l_{\xi x}, \dots, l_{\zeta z}$, are the direction cosines of the moving axes, functions in general of three Eulerian angles θ, φ , and ψ .⁹ $\xi, \eta, \zeta, \theta, \varphi$, and ψ , are then six of the slowly varying coordinates, the remainder being q_1, \dots, q_m , say, where

$$6 + m + \lambda = 3N. \quad (4.2)$$

We have now

$$\begin{cases} x_r = x_r^0 \\ y_r = y_r^0 \\ z_r = z_r^0 \end{cases}, \quad (4.3)$$

for the sub-space (A), and for general points of configuration space,

$$\begin{cases} x_r = x_r^0 + \sum_\alpha x_{r\alpha} v_\alpha \\ y_r = y_r^0 + \sum_\alpha y_{r\alpha} v_\alpha \\ z_r = z_r^0 + \sum_\alpha z_{r\alpha} v_\alpha \end{cases}, \quad (4.4)$$

where x_r^0, y_r^0, z_r^0 , and $x_{r\alpha}, y_{r\alpha}, z_{r\alpha}, \alpha=1, \dots, \lambda$, are functions only of the remaining slowly varying coordinates q_1, \dots, q_m .

We can express the components of linear velocity, $u_s, v_s, w_s, s=1, \dots, N$, of the N particles in the instantaneous directions of the rotating axes in terms of u, v, w , the components of the

velocity of the center of mass in these directions, $\omega_x, \omega_y, \omega_z$, the components of the angular velocity of rotation of the axes about these directions, $\dot{q}_1, \dots, \dot{q}_m$, and $\dot{v}_1, \dots, \dot{v}_\lambda$. Thus, in vector notation, with \mathbf{r} for (x, y, z) , \mathbf{v} for (u, v, w) , and $\boldsymbol{\omega}$ for $(\omega_x, \omega_y, \omega_z)$,

$$\mathbf{v}_s = \mathbf{v} + [\boldsymbol{\omega} \times (\mathbf{r}_s^0 + \sum_\alpha \mathbf{r}_{s\alpha} v_\alpha)] + \sum_\alpha \left(\frac{\partial \mathbf{r}_s^0}{\partial q_\alpha} \dot{q}_\alpha + \sum_\alpha \frac{\partial \mathbf{r}_{s\alpha}}{\partial q_\alpha} \dot{q}_\alpha v_\alpha \right) + \sum_\alpha \mathbf{r}_{s\alpha} \dot{v}_\alpha, \quad (4.5)$$

and the kinetic energy is

$$\sum_{s=1}^N \frac{1}{2} m_s \mathbf{v}_s^2, \quad (4.6)$$

while from the properties of the center of mass,

$$\sum_s m_s (\mathbf{v}_s - \mathbf{v}) = 0, \quad (4.7)$$

and

$$\sum_s m_s [\mathbf{r}_s^0 \times \mathbf{r}_{s\alpha}] = 0, \quad (4.8)$$

$$\sum_s m_s \left(\frac{\partial \mathbf{r}_s^0}{\partial q_\alpha} \cdot \mathbf{r}_{s\alpha} \right) = 0, \quad (4.9)$$

(4.7), (4.8), and (4.9), replacing the extended Eckart conditions, (3.5) above, with

$$\sum_s m_s (\mathbf{r}_{s\alpha} \cdot \mathbf{r}_{s\beta}) = 0, \quad (4.10)$$

and

$$\sum_s m_s \mathbf{r}_{s\alpha}^2 = \frac{1}{V_\alpha}, \quad (4.11)$$

replacing (3.6) and (3.7).

When the classical kinetic energy in terms of the velocities is found, we see that there will be no cross terms between the components of the velocity of the center of mass and any others, or between the various \dot{v}_α , while the cross terms between angular velocity components and \dot{v}_α reduce to

$$\sum_s m_s \left([\boldsymbol{\omega} \times \sum_\alpha \mathbf{r}_{s\alpha} v_\alpha] \cdot \sum_\beta \mathbf{r}_{s\beta} \dot{v}_\beta \right) = (\boldsymbol{\omega} \cdot \sum_s m_s [\sum_\alpha \mathbf{r}_{s\alpha} v_\alpha \times \sum_\beta \mathbf{r}_{s\beta} \dot{v}_\beta]) \quad (4.12)$$

where

$$\sum_s m_s [\sum_\alpha \mathbf{r}_{s\alpha} v_\alpha \times \sum_\beta \mathbf{r}_{s\beta} \dot{v}_\beta], \quad (4.13)$$

is just the so-called "internal angular momen-

⁹ E. T. Whittaker, *Analytical Dynamics* (The Cambridge University Press, London, 1927), p. 41.

tum." The cross term between \dot{q}_α and \dot{v}_α takes the form

$$\sum_s m_s \left(\sum_\beta \frac{\partial \mathbf{r}_{s\beta}}{\partial q_\alpha} v_\beta \cdot \mathbf{r}_{s\alpha} \right) \dot{q}_\alpha \dot{v}_\alpha. \quad (4.14)$$

There is in general no reason why cross terms between angular velocity components and \dot{q}_α should vanish, though symmetry may sometimes require this.

The classical kinetic energy in terms of the momenta will take the form (3.11) simplified in that terms in the total linear momentum are separate, while the terms $\sum_\alpha b_{\alpha\alpha} u_\alpha$ for the components of angular momentum are just the internal angular momentum in terms of the u_α , from (4.12), exactly as in the usual vibration rotation theory,

$$\sum_s m_s \left[\sum_\alpha \mathbf{r}_{s\alpha} v_\alpha \times \sum_\beta \mathbf{r}_{s\beta} V_\beta u_\beta \right], \quad (4.15)$$

while the corresponding terms for the p_α are

$$\sum_s m_s \left(\sum_\alpha \frac{\partial \mathbf{r}_{s\alpha}}{\partial q_\alpha} v_\alpha \cdot \sum_\beta \mathbf{r}_{s\beta} V_\beta u_\beta \right). \quad (4.16)$$

5. The Zero-Order Approximation

In the potential energy we neglect the higher order terms, writing

$$V = V_0 + \frac{1}{2} \sum_\alpha K^2 V_\alpha v_\alpha^2. \quad (5.1)$$

In the kinetic energy we neglect the terms in $b_{\alpha\alpha}$ and in the coefficients a_{ab} the terms in v_α , so that if

$$a_{ab}^0 = \sum_r m_r \left(\frac{\partial \mathbf{r}_{r^0}}{\partial q_a} \cdot \frac{\partial \mathbf{r}_{r^0}}{\partial q_b} \right), \quad (5.2)$$

we have

$$T = \frac{1}{2} \sum_a \sum_b A_{ab}^0 p_a p_b + \frac{1}{2} \sum_\alpha V_\alpha u_\alpha^2, \quad (5.3)$$

where A_{ab}^0 are the coefficients reciprocal to a_{ab}^0 .

The coordinates v_α are separable in the Schrödinger equation arising from (5.1) and (5.3), and if $\psi_n(w)$ is the n th harmonic oscillator wave function, making

$$(n + \frac{1}{2}) = \int \left[\frac{1}{2} \left(\frac{\partial \psi_n}{\partial w} \right)^2 + \frac{1}{2} w^2 \psi_n^2 \right] dw \quad (5.4)$$

stationary subject to

$$\int \psi_n^2 dw = 1, \quad (5.5)$$

and if we take

$$\psi = \chi \prod_\alpha V_\alpha^{\frac{1}{2}} \left(\frac{2\pi K}{h} \right)^{\frac{1}{2}} \psi_{n\alpha} \left(\left(\frac{2\pi K}{h} \right)^{\frac{1}{2}} v_\alpha \right), \quad (5.6)$$

(2.10) and (2.11) give that

$$E = \int \left[\frac{h^2}{8\pi^2} \sum_a \sum_b A_{ab}^0 \frac{\partial \chi}{\partial q_a} \frac{\partial \chi}{\partial q_b} + \left[V_0 + \sum_\alpha \left(n + \frac{1}{2} \right) \frac{hK V_\alpha}{2\pi} \right] \chi^2 \right] d\rho_0 \quad (5.7)$$

is stationary subject to

$$\int \chi^2 d\rho_0 = 1, \quad (5.8)$$

where

$$d\rho_0 = dq_1 \cdots dq_l / \left(\begin{vmatrix} A_{11}^0 & \cdots & A_{1l}^0 \\ \vdots & \ddots & \vdots \\ A_{l1}^0 & \cdots & A_{ll}^0 \end{vmatrix} \right)^{\frac{1}{2}}. \quad (5.9)$$

This is just what would be obtained by applying Schrödinger's rule to the classical problem got by introducing Eqs. (3.2) or (4.3) as equations of constraint, and adding the energy of the quantized rapid oscillations to the potential energy V_0 .

When we go to first-order perturbation theory, the anharmonic terms in the rapid vibrations give rise to terms of order 1 as compared with the terms of order K kept in. If there are no degenerate solutions for the rapid vibrations, the terms multiplying A_{ab} and involving u_α will all vanish except those in $u_\alpha^2 v_\beta^2$, which will be of order 1. When A_{ab} are expanded in powers of v_α , the linear terms vanish on the average, and the terms in v_α^2 will be of order $1/K$. If some of the rapid vibrations are degenerate, zero-order perturbation theory may be necessary, and some of the terms multiplying A_{ab} and involving u_α , given by (4.15) and (4.16), may need to be retained as sometimes happens with the internal angular momentum in the usual vibration-rotation theory.¹⁰ In this case we can get the zero-order approximation by keeping in only these terms in $b_{\alpha\alpha}$, while replacing A_{ab} by A_{ab}^0 .

¹⁰ E. Teller and L. Tisza, *Zeits. f. Physik* **73**, 791 (1932).

PART II. THE ROTATION-VIBRATION ENERGIES OF PYRAMIDAL XY_3 MOLECULES INCLUDING THE EFFECT OF THE DOUBLE MINIMUM

1. Introduction

The potential energy of a pyramidal XY_3 molecule is a minimum for two configurations which cannot be brought into coincidence by rotation of the molecule. The determining of the energy values of such a system is called the double minimum problem.

Shaffer¹¹ has given a treatment of the energies of a pyramidal XY_3 molecule to the second order of approximation, but ignoring the presence of the double minimum. His results therefore apply only to those XY_3 molecules for which the height of the potential hill between the two minima is great, but not to a molecule such as ammonia for which the hill is low. Manning,¹² Morse and Stuckelberg,¹³ and Rosen and Morse,¹⁴ have computed the energy levels of a system having a double minimum, but having only one degree of freedom. Their results do not readily extend to a system which can rotate. Dennison and Uhlenbeck¹⁵ have given a method by which the splitting of an originally single level, which is caused by the double minimum, may be estimated. This method originally applied to a system with one degree of freedom, but Fermi,¹⁶ and later Sheng, Barker, and Dennison,¹⁷ showed how to include the effects of rotation. Hadley and Dennison studied the effect of various changes in size of the hydrogen triangle as the nitrogen moves through it.

In this part, the wave equation for the pyramidal XY_3 molecular model is set up so that all degrees of freedom may be considered, following the method of Part I. In the zero approximation, in which all vibrations except that with the double minimum are rapid, a Sturm-Liouville equation in one variable is derived. The simplest potential energy with a double minimum, and

which can be readily combined with the rotational energy, leads to the associated Mathieu equation. A method is given for computing the characteristic values, and the method is applied to the ammonia molecule.

2. Derivation of the Wave Equation in Zero Approximation

Suppose the molecule has a symmetrical configuration of unstable equilibrium with the three Y nuclei, each of mass m , at the vertices of an equilateral triangle, while the X nucleus, of mass M , lies at the centroid of this triangle. Suppose that this configuration is stable for displacements in the plane, but unstable for a displacement of the X nucleus perpendicular to the plane. Suppose further that there are two positions of stable equilibrium, in which the three Y nuclei lie at the corners of an equilateral triangle (in general of a different size) and the X nucleus lies on the normal to the plane of this triangle through its centroid, on one or other side. Then the lines of greatest slope from the unstable point to the stable points correspond to motion of the X nucleus along the normal while the equilateral triangle varies in size; and this locus can be continued along the lines of greatest slope with the same direction through the points of stable equilibrium.

Thus we may take (4.3) with

$$\left. \begin{aligned} x_{10} &= s, & y_{10} &= 0, & z_{10} &= \frac{M}{3m+M}r \\ x_{20} &= -\frac{1}{2}s, & y_{20} &= \frac{\sqrt{3}}{2}s, & z_{20} &= \frac{M}{3m+M}r \\ x_{30} &= -\frac{1}{2}s, & y_{30} &= -\frac{\sqrt{3}}{2}s, & z_{30} &= \frac{M}{3m+M}r \\ x_{40} &= 0, & y_{40} &= 0, & z_{40} &= \frac{3m}{3m+M}r \end{aligned} \right\}, \quad (7.1)$$

where r , the height of the pyramid, can be regarded as a seventh slowly varying coordinate, in addition to the coordinates of the center of mass and the Eulerian angles; and s , the distance from the centroid of the triangle to any of the three Y nuclei, is a function of r fixed by the form of the potential energy. The coefficients of r in

¹¹ W. H. Shaffer, *J. Chem. Phys.* **9**, 607 (1941).

¹² M. F. Manning, *J. Chem. Phys.* **3**, 136 (1935).

¹³ P. M. Morse and E. C. L. Stuckelberg, *Helv. Phys. Acta* **4**, 337 (1931).

¹⁴ N. Rosen and P. M. Morse, *Phys. Rev.* **42**, 210 (1932).

¹⁵ D. M. Dennison and C. E. Uhlenbeck, *Phys. Rev.* **41**, 313 (1932).

¹⁶ E. Fermi, *Nuovo Cimento* **9**, 277 (1932).

¹⁷ H. Sheng, E. F. Barker, and D. M. Dennison, *Phys. Rev.* **60**, 786 (1941). See also L. N. Hadley and D. M. Dennison, *Phys. Rev.* **70**, 780 (1946).

z_{10}, \dots, z_{40} , have been adjusted so that the origin is the center of mass.

Leaving out the motion of the center of mass, we have in zero approximation,

$$T = \frac{1}{2} \left[\left(3ms'^2 + \frac{3mM}{3m+M} \right) \dot{r}^2 + \left(\frac{3}{2}ms^2 + \frac{3mM}{3m+M} r^2 \right) \times (\omega_x^2 + \omega_y^2) + 3ms^2\omega_z^2 \right], \quad (7.2)$$

where s' stands for ds/dr , so that, in terms of the momenta,

$$T = \frac{1}{2} \left[\frac{R^2}{\left(3ms'^2 + \frac{3mM}{3m+M} \right)} + \frac{1}{\left(\frac{3}{2}ms^2 + \frac{3mM}{3m+M} r^2 \right)} (\Omega_x^2 + \Omega_y^2) + \frac{1}{3ms^2} \Omega_z^2 \right], \quad (7.3)$$

and, putting

$$\Omega_x = \Phi, \quad \Omega_x^2 + \Omega_y^2 = \Theta^2 + \left(\frac{\Phi - \Psi \cos \theta}{\sin \theta} \right)^2,$$

we have

$$d\rho_0 = \left(\left[3ms^2 \left(3ms'^2 + \frac{3mM}{3m+M} \right) \right] \right)^{\frac{1}{2}} \times \left(\frac{3}{2}ms^2 + \frac{3mM}{3m+M} r^2 \right) \sin \theta dr d\theta d\varphi d\psi, \quad (7.4)$$

where φ , θ , and ψ , are Eulerian angles giving the x , y , and z directions relative to a fixed set, and Φ , Θ , and Ψ are the conjugate momenta.

Thus

$$E = \int \left[\frac{h^2}{8\pi^2} \left(\left(3ms'^2 + \frac{3mM}{3m+M} \right)^{-1} \left(\frac{\partial \chi}{\partial r} \right)^2 + \left(3ms^2 + \frac{3mM}{3m+M} r^2 \right)^{-1} \times \left(\left(\frac{\partial \chi}{\partial \theta} \right)^2 + \frac{1}{\sin^2 \theta} \left(\frac{\partial \chi}{\partial \varphi} - \cos \theta \frac{\partial \chi}{\partial \psi} \right)^2 \right) + (3ms^2)^{-1} \left(\frac{\partial \chi}{\partial \psi} \right)^2 \right] d\rho_0 \quad (7.5)$$

is stationary, subject to

$$\int \chi^2 d\rho_0 = 1, \quad (7.6)$$

where

$$V(r) = V_0(r) + \sum_{\alpha} (n_{\alpha} + \frac{1}{2}) h \frac{K V_{\alpha}(r)}{2\pi} \quad (7.7)$$

depends on the form of the original potential energy.

The Schrödinger equation arising from (7.5) is separable, and if we take

$$\chi = f(r) \psi_{jlk}(\theta) \frac{e^{2\pi i(l\varphi + k\psi)}}{2\pi}, \quad (7.8)$$

where $\psi_{jlk}(\theta)$ is the normalized function of the symmetrical rotator, we shall have

$$E = \int \left[\frac{h^2}{8\pi^2} \left[\frac{1}{\left(3ms'^2 + \frac{3mM}{3m+M} \right)} \left(\frac{df}{dr} \right)^2 + \frac{j(j+1) - k^2}{\left(\frac{3}{2}ms^2 + \frac{3mM}{3m+M} r^2 \right)} f^2 + \frac{k^2}{3ms^2} f^2 \right] + V f^2 \right] \times \left(\left[3ms^2 \left(3ms'^2 + \frac{3mM}{3m+M} \right) \right] \right)^{\frac{1}{2}} \times \left(\frac{3}{2}ms^2 + \frac{3mM}{3m+M} r^2 \right) dr \quad (7.9)$$

stationary, subject to

$$\int f^2 \left(\left[3ms^2 \left(3ms'^2 + \frac{3mM}{3m+M} \right) \right] \right)^{\frac{1}{2}} \times \left(\frac{3}{2}ms^2 + \frac{3mM}{3m+M} r^2 \right) dr = 1. \quad (7.10)$$

The problem thus reduces to a Sturm-Liouville equation¹⁸ containing two parameters, j and k , in addition to E .

3. The Choice of Special Forms for $s(r)$ and $V(r)$

In order to simplify the wave equation, we assume, as a rough approximation, that s is

¹⁸ E. L. Ince, *Ordinary Differential Equations* (Longmans, London, 1927), p. 217.

independent of r . This means that the X -nucleus is regarded as moving in a straight line through the centroid and perpendicular to the plane of a rigid equilateral triangle of Y -nuclei. In this particular case the wave equation could have been obtained from the usual theory for a plane XY_3 molecule,¹⁹ allowing the coordinate ' r ' to be large before separation.

Writing

$$r = \left(\frac{3m + M}{2M} \right)^{\frac{1}{2}} sx, \quad (8.1)$$

(7.9) and (7.10) become, multiplying f by a constant factor,

$$E = \int \left[\frac{h^2}{8\pi^2} \frac{2}{3ms^2} \left[\left(\frac{df}{dx} \right)^2 + \left(\frac{j(j+1) - k^2}{1+x^2} + \frac{k^2}{2} \right) f^2 \right] + V f^2 \right] \times (1+x^2) dx \quad (8.2)$$

is stationary, subject to

$$\int f^2 (1+x^2) dx = 1, \quad (8.3)$$

giving the wave equation

$$\frac{1}{1+x^2} \frac{d}{dx} \left[(1+x^2) \frac{df}{dx} \right] + \left[\frac{8\pi^2}{h^2} \frac{3ms^2}{2} (E - V(x)) - \frac{j(j+1) - k^2}{1+x^2} - \frac{k^2}{2} \right] f = 0, \quad (8.4)$$

or in normal form with

$$g = f(1+x^2)^{\frac{1}{2}}, \quad (8.5)$$

$$\frac{d^2 g}{dx^2} + \left[\frac{8\pi^2}{h^2} \frac{3ms^2}{2} (E - V(x)) - \frac{j(j+1) - k^2}{1+x^2} - \frac{k^2}{2} - \frac{1}{1+x^2} + \frac{x^2}{(1+x^2)^2} \right] g = 0. \quad (8.6)$$

In order to deal with various values of j and k without change in the form of the differential equation, we may conveniently take, for all n_α

¹⁹ W. H. Shaffer, J. Chem. Phys. 3, 127 (1935).

zero,

$$V(x) = \frac{h^2}{8\pi^2} \frac{2}{3ms^2} \frac{(a - bx^2)^2}{(1+x^2)^2}. \quad (8.7)$$

Here $V(x)$ is a function of x^2 with a maximum

$$V = \frac{h^2}{8\pi^2} \frac{2}{3ms^2} a^2$$

for $x=0$, a minimum $V=0$ for $x=(a/b)^{\frac{1}{2}}$, which rises asymptotically to the value

$$V = \frac{h^2}{8\pi^2} \frac{2}{3ms^2} b^2$$

as x tends to ∞ . Physically, this is the right kind of behavior,¹² but an arbitrary shape has been introduced for $V(r)$ for the convenience of a comparatively simple equation.

Now write

$$\sum_\alpha n_\alpha \frac{hK V_\alpha}{2\pi} = \frac{h^2}{8\pi^2} \frac{2}{3ms^2} \times [\epsilon_0 + \epsilon_1 x^2 + \epsilon_2 x^4 + \dots], \quad (8.8)$$

where ϵ_0 , ϵ_1 , and ϵ_2 , depend linearly on the quantum numbers of the rapidly varying vibrational coordinates, and

$$V(x) \approx \frac{h^2}{8\pi^2} \frac{2}{3ms^2} \left[\frac{(a^2 + \epsilon_0) - (2ab - \epsilon_1 - 2\epsilon_0)x^2 + (b^2 + \epsilon_2 + 2\epsilon_1 + \epsilon_0)x^4}{(1+x^2)^2} \right]. \quad (8.9)$$

(8.6) now becomes

$$\frac{d^2 g}{dx^2} + \left[\lambda - \frac{A + Bx^2 + Cx^4}{(1+x^2)^2} \right] g = 0, \quad (8.10)$$

where

$$A = j(j+1) - \frac{1}{2}k^2 + 1 + a^2 + \epsilon_0, \quad (8.11)$$

$$B = j(j+1) - 2ab + \epsilon_1 + 2\epsilon_0, \quad (8.12)$$

$$C = \frac{1}{2}k^2 + b^2 + \epsilon_2 + 2\epsilon_1 + \epsilon_0, \quad (8.13)$$

$$\lambda = \frac{8\pi^2}{h^2} \frac{3ms^2}{2} E. \quad (8.14)$$

4. Calculation of the Energy Values

We must find those solutions of (8.10) which, for real values of x , are single-valued, with continuous first and second derivatives, and which vanish exponentially at $x = \pm \infty$. A method of constructing such solutions, and computing the characteristic energy values, is given in a forthcoming paper by the present writers. This method involves the evaluation of a certain infinite determinant; to obtain satisfactory convergence in applications to the ammonia molecule, it turns out that one must use several hundred rows and columns.

Instead of using this method, we use a modification of the WKB method²⁰ for the calculation of the energy values. The method used here is suggested by the discussion in Appendix D II of *Fundamental Principles of Quantum Mechanics* by Kemble.²¹

Write (8.10) in the form

$$g'' + (p/\hbar)^2 g = 0. \quad (9.1)$$

Define ρ/\hbar and ξ by

$$(\rho/\hbar)^2 = (p/\hbar)^2 + (1+x^2)^{-2}, \quad (9.2)$$

$$\xi = \int_{x_1}^x (\rho/\hbar) dx. \quad (9.3)$$

Then the two functions

$$\left. \begin{aligned} U_1 &= (\rho/\hbar)^{-1/2} \exp(i\xi) \\ U_2 &= (\rho/\hbar)^{-1/2} \exp(-i\xi) \end{aligned} \right\} \quad (9.4)$$

are solutions of

$$U'' + (p/\hbar)^2 U + QU = 0, \quad (9.5)$$

where

$$Q = (\rho''/2\rho) - \frac{3}{4}(\rho'/\rho)^2 + (1+x^2)^{-2}. \quad (9.6)$$

If Q is small compared with $(p/\hbar)^2$, the functions (9.4) are approximate solutions of (9.1). Considering x as a complex variable, Q is small for pure imaginary values of x , for the four lowest vibrational energy levels of the ammonia molecule, which are the only levels we shall compute.

²⁰ G. Wentzel, *Zeits. f. Physik* **38**, 518 (1926); H. A. Kramers, *Zeits. f. Physik* **39**, 828 (1926); M. L. Brillouin, *J. de phys. et rad.* **7**, 353 (1926).

²¹ E. G. Kemble, *Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937).

Let functions α_1 and α_2 be defined by the relations

$$\left. \begin{aligned} g &\equiv \alpha_1 U_1 + \alpha_2 U_2 \\ 0 &= \alpha_1' U_1 + \alpha_2' U_2 \end{aligned} \right\}. \quad (9.7)$$

The differential equations for α_1 and α_2 are

$$\left. \begin{aligned} \alpha_1' &= -iQ(\hbar/2\rho)[\alpha_1 + \alpha_2 \exp(-2i\xi)] \\ \alpha_2' &= iQ(\hbar/2\rho)[\alpha_1 \exp(2i\xi) + \alpha_2] \end{aligned} \right\}. \quad (9.8)$$

ρ and ξ are multiple-valued functions of x ; to define the branches which we shall use, let the zeros of ρ be $\pm x_1, \pm x_2$, where $x_1^2 < x_2^2$. For the levels we are considering, x_1 and x_2 are real. We define the desired branches by writing

$$\left. \begin{aligned} (\rho/\hbar) &= (C-\lambda)^{1/2}(1+x^2)^{-1} \\ &\quad \times \exp(-i\pi/2)(x^2-x_1^2)^{1/2}(x^2-x_2^2)^{1/2}, \\ \xi &= \int_{x_1}^x (\rho/\hbar) dx, \end{aligned} \right\} \quad (9.9)$$

$$\left. \begin{aligned} -\pi &< \arg(x+x_1) < \pi, & 0 > \arg(x-x_1) > 2\pi, \\ -\pi &< \arg(x+x_2) < \pi, & 0 > \arg(x-x_2) > 2\pi. \end{aligned} \right\}$$

With these conventions, the real part of $i\xi$ increases without limit as $x \rightarrow \infty$.

To obtain boundary conditions for (9.8), we apply the condition that allowed solutions of (9.1) are either even or odd. Evaluating (9.7) at $x=0$, we have, for odd solutions:

$$g(0) = \alpha_1(0)U_1(0) + \alpha_2(0)U_2(0) = 0, \quad (9.10)$$

and for even solutions:

$$g'(0) = \alpha_1(0)U_1'(0) + \alpha_2(0)U_2'(0) = 0. \quad (9.11)$$

Only the ratio $\alpha_1(0)/\alpha_2(0)$ is of importance; taking, arbitrarily, $\alpha_2(0)=1$, we see that the boundary condition for α_1 is

$$\alpha_1(0) = \pm \exp[-2i\xi(0)], \quad (9.12)$$

the upper sign leading to even solutions.

(9.8) can be solved by repeated integrations. The required solution for α_2 is

$$\begin{aligned} \alpha_2(x) &= e^{iF} \left[1 \pm i \int_0^x \frac{Q\hbar}{2\rho} e^{2i(\xi-F)} dy \right. \\ &\quad \left. + \int_0^x \frac{Q\hbar}{2\rho} e^{2i(\xi-F)} dy \right. \\ &\quad \left. \times \left[\int_0^y \frac{Q\hbar}{2\rho} e^{-2i(\xi-F)} dz \right] dy \pm \dots \right], \quad (9.13) \end{aligned}$$

where y and z are dummy variables of integration, and

$$\left. \begin{aligned} F &= \int_0^x \frac{Qh}{2\rho} dy \\ \zeta &= \xi - \xi(0) = \int_0^x \frac{\rho}{h} dy \end{aligned} \right\} \quad (9.14)$$

If $Qh/2\rho$ is sufficiently small along the path of integration, we can write:

$$\alpha_2(x) = \exp \left[i \int_0^x \frac{Qh}{2\rho} \times [1 \pm \exp(2i\zeta - 2iF)] dy \right]. \quad (9.15)$$

We obtain another condition by the requirement that g shall vanish at $x = \infty$. Since the real part of $i\xi$ increases without limit as $x \rightarrow \infty$, and it can be shown that Q vanishes as x^{-2} , we see that α_1 must vanish more rapidly than $\exp(-2i\xi)$ as $x \rightarrow \infty$. (9.8) then shows that $\alpha_1 \rightarrow 0$, and α_2 approaches a constant, for any point on a large quarter-circle of radius X , drawn from the positive real axis to either end of the imaginary axis, as $X \rightarrow \infty$.

Finally, g must be a single-valued function of x . If $f(x+i0)$ denotes the limiting value of a function $f(x)$ as x approaches the real axis from above, and $f(x-i0)$ the value as x approaches real values from below, this condition is

$$g(x+i0) = g(x-i0). \quad (9.16)$$

From (9.15) and the following remark, we have, for very large x ,

$$\left. \begin{aligned} \alpha_2(x+i0) &= \exp \left[i \int_0^{i\infty} \frac{Qh}{2\rho} \times [1 \pm \exp(2i\zeta - 2iF)] dy \right] \\ \alpha_2(x-i0) &= \exp \left[i \int_0^{-i\infty} \frac{Qh}{2\rho} \times [1 \pm \exp(2i\zeta - 2iF)] dy \right] \end{aligned} \right\} \quad (9.17)$$

From the restrictions on the arguments of the factors of ρ , if $x_1 < x < x_2$; $\rho(x-i0) = e^{\pi i} \rho(x+i0)$, $\xi(x-i0) = e^{\pi i} \xi(x+i0)$; if $x > x_2$; $\rho(x-i0)$

$= e^{2\pi i} \rho(x+i0)$, $\xi(x-i0) = \xi(x+i0) - 2\xi(x_2+i0)$. Substituting in (9.16), we obtain the condition

$$\int_0^{i\infty} \frac{Qh}{2\rho} [1 \pm e^{2i(\zeta-F)}] dy = 2 \left[\xi(x_2+i0) - \frac{\pi}{2} \right] + \int_0^{-i\infty} \frac{Qh}{2\rho} [1 \pm e^{2i(\zeta-F)}] - 2n\pi. \quad (9.18)$$

Since Q and ρ are even functions of x , we obtain, inserting the value of $\xi(x_2+i0)$, the condition in real form,

$$\int_{x_1}^{x_2} \frac{\rho}{h} dx = \int_0^{i\infty} \frac{Qh}{2\rho} \times [1 \pm \cos(2\zeta - 2F)] dx + (n + \frac{1}{2})\pi, \quad (9.19)$$

where n is any integer. Negative values of n correspond to changing the sign of ρ , and lead to no new values of the energy. We may therefore take $n \geq 0$.

5. Application to the Ammonia Molecule

The problem is, for given values of the potential constants, to find the values of the energy for which (9.19) is satisfied. The solution requires successive trials, but a method will be outlined by which both members of a pair of levels can be found within an accuracy of about 1 part in 1000 by essentially one approximation.

The first step is to compute the left member of (9.19) for several values of the energy parameter λ , until the value $(n + \frac{1}{2})\pi$, for the desired value of n , is bracketed. An increment of unity in λ is convenient. Usually there is enough advance information for only two values of λ to have to be used. Denoting the value of the left member of (9.19) by Φ , the value of $d\Phi/d\lambda$ is given accurately enough by the differences of Φ over the range of λ needed.

The integral

$$\int_0^{i\infty} \frac{Qh}{2\rho} dx$$

is next computed by numerical integration. This integral is so small compared with π that the range used need not extend far. It is also insensitive to changes in λ and the potential constants, so that its value is known for an entire set of calculations from one preliminary calculation.

By interpolation, a value λ_m of λ can now be found such that

$$\int_{x_1}^{x_2} \frac{\rho}{h} dx = (n + \frac{1}{2})\pi + \int_0^{i\infty} \frac{Qh}{2\rho} dx. \quad (10.1)$$

Using $\lambda = \lambda_m$, the remaining integral in (9.19) is now computed. This can be done by numerical integration until ρ becomes large, when the integrand begins to oscillate rapidly. When this happens, the integral over the remaining range can be evaluated as a rapidly converging series obtained by integration by parts. The consideration of this integral changes λ by such a small amount from λ_m that the value of the integral does not change sensibly if λ_m is replaced by a more accurate value of λ . Denoting this integral by $\Delta\Phi$, we see that there are two slightly separated values of λ given by $\lambda_m \pm \Delta\lambda$, where $\Delta\lambda = \Delta\Phi/(d\Phi/d\lambda)$. Thus $2\Delta\lambda$, the splitting of a pair of levels, is given to more decimal places than λ_m or than an allowed value of λ .

We use Birge's 1941 values for the fundamental constants.²² Thus $h/8\pi^2c = 27.99 \times 10^{-40}$ g cm, $m = 1.673 \times 10^{-24}$ g, $M(\text{N}^{14})/m = 13.90$, $M(\text{N}^{15})/m = 14.88$. The final adopted parameters for the lowest vibrational state of N^{14}H_3 are

$$\frac{3ms^2}{2} = 2.210 \times 10^{-40} \text{ g cm}^2, \quad a = 13.26, \text{ and } b = 50.02. \quad (10.2)$$

These correspond to a barrier height between the minima of 2225 cm^{-1} , an equilibrium height of the pyramid of $0.377 \times 10^{-8} \text{ cm}$, and an H-H separation of $1.626 \times 10^{-8} \text{ cm}$ ($s = 0.939 \times 10^{-8} \text{ cm}$); a and b for N^{15}H_3 were chosen to give the same barrier height and dimensions.

Four pairs of energy levels for N^{14}H_3 were computed, as given in Table I, and three pairs for N^{15}H_3 . Perhaps the most interesting use to which these values can be put is the interpretation of

TABLE I. Computed energy levels of ammonia.

n	j	k	$E \pm \Delta E (\text{cm}^{-1})$	
			N^{14}H_3	N^{15}H_3
0	0	0	496.5 ± 0.397	492.7 ± 0.378
0	3	0	616.9 ± 0.361	612.7 ± 0.340
0	0	4	436.9 ± 0.453	433.4 ± 0.429
1	0	0	1441.0 ± 11.14	

²² R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941).

the microwave absorption band lying near 1 cm^{-1} . This band was originally located, but not resolved, by Cleeton and Williams.²³ More recently, Bleaney and Penrose,²⁴ Good,²⁵ and Townes,²⁶ have resolved this band using the isotope N^{14}H_3 . Good and Coles²⁷ have reported measurements using N^{15}H_3 . The data can be fitted approximately by the formulas:

$$\left. \begin{aligned} \nu (\text{cm}^{-1}) &= 0.7935 - 0.00502j(j+1) \\ &\quad + 0.00698k^2 + \dots \text{ for } \text{N}^{14}\text{H}_3, \\ \nu (\text{cm}^{-1}) &= 0.7575 - 0.00473j(j+1) \\ &\quad + 0.00659k^2 + \dots \text{ for } \text{N}^{15}\text{H}_3. \end{aligned} \right\} \quad (10.3)$$

From Table I we obtain the formulas

$$\left. \begin{aligned} \nu (\text{cm}^{-1}) &= 0.794 - 0.0060j(j+1) \\ &\quad + 0.0069k^2 \text{ for } \text{N}^{14}\text{H}_3, \\ \nu (\text{cm}^{-1}) &= 0.756 - 0.0062j(j+1) \\ &\quad + 0.0064k^2 \text{ for } \text{N}^{15}\text{H}_3. \end{aligned} \right\} \quad (10.4)$$

The agreement for these levels is about the same as that obtained by Hadley and Dennison,¹⁷ who allowed the hydrogen triangle to expand as the nitrogen approaches. They obtain

$$-0.0047j(j+1) + 0.0059k^2 \quad (10.5)$$

for the variation with j and k in N^{14}H_3 .

For the pure rotation spectrum of N^{14}H_3 , we obtain from the first two entries in Table I, the formula

$$\nu (\text{cm}^{-1}) = 20.1j', \quad (10.6)$$

where j' is the value of j for the upper state. Dennison²⁸ gives

$$\nu (\text{cm}^{-1}) = 19.890j' - 0.00178j'^3. \quad (10.7)$$

For the two fundamental lines of N^{14}H_3 corresponding to this mode of vibration (the transitions $0+, 0, 0 \rightarrow 1-, 0, 0$ and $0-, 0, 0 \rightarrow 1+, 0, 0$), we find the values 933 cm^{-1} and 956 cm^{-1} , while the experimental values given by Herzberg²⁹ are 931.58 cm^{-1} and 968.08 cm^{-1} . While the general position is about right, the splitting is only 23 cm^{-1} instead of 36.5 cm^{-1} . The results are comparable in accuracy with those of Manning,¹² who

²³ C. E. Cleeton and N. H. Williams, Phys. Rev. **46**, 235 (1934).

²⁴ B. Bleaney and R. D. Penrose, Nature **157**, 339 (1946).

²⁵ W. E. Good, Phys. Rev. **69**, 339 (1946).

²⁶ C. H. Townes, Phys. Rev. **70**, 665 (1946).

²⁷ W. E. Good and D. K. Coles, Phys. Rev. **71**, 383 (1947).

²⁸ D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

²⁹ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 295.

computes a splitting of 0.83 cm^{-1} for the ground levels, and 27 cm^{-1} for the splitting of the fundamental frequency.

6. Conclusions

The potential function assumed is capable of yielding the vibrational energies and the interaction with rotation, within reasonable error. The agreement with experiment could probably be improved slightly by using a larger equilibrium height of the pyramid.

The potential function assumed is apparently too sharp near the maximum, but has nearly the correct form near the minima. A function in form something like the error function should perhaps be subtracted from the assumed potential. This would reduce the height of the barrier near the origin, and thus increase the splitting of the levels $n=1$ without seriously affecting the position of these levels or the splitting of the ground levels.

The term in the microwave spectrum mentioned by Townes,³⁰ of the form $|j^2 + j - 1.56k^2|^{\frac{1}{2}} \times (j^2 + j - 1.56k^2)$ does not occur in a more exact treatment.

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APPENDIX

7. The Energy in Zero Approximation, Including the Rapidly Changing Variables and the Retained Part of the Internal Angular Momentum

We extend the expressions (7.1) corresponding to (4.3) to include the rapidly varying coordinates as in (4.4), in terms first of "intermediate

coordinates," w_1, w_2, w_3, w_4 , and w_5 . These are chosen so that small changes in them give coordinate displacements orthogonal, with respect to the kinetic energy, to motion of the center of mass, to rotation, and to change in the coordinate r . Taking

$$\begin{aligned} x_1 &= s + w_1 + w_2 & + w_4 \\ x_2 &= -\frac{1}{2}s - \frac{1}{2}w_1 + w_2 & - \frac{1}{2}w_4 - \frac{\sqrt{3}}{2}w_5 \\ x_3 &= -\frac{1}{2}s - \frac{1}{2}w_1 + w_2 & - \frac{1}{2}w_4 + \frac{\sqrt{3}}{2}w_5 \\ x_4 &= & -\frac{3m}{M}w_2 \\ y_1 &= & w_3 & - w_5 \\ y_2 &= \frac{\sqrt{3}}{2}s + \frac{\sqrt{3}}{2}w_1 & + w_3 - \frac{\sqrt{3}}{2}w_4 + \frac{1}{2}w_5 \\ y_3 &= -\frac{\sqrt{3}}{2}s - \frac{\sqrt{3}}{2}w_1 & + w_3 + \frac{\sqrt{3}}{2}w_4 + \frac{1}{2}w_5 \\ y_4 &= & -\frac{3m}{M}w_3 \\ z_1 &= \frac{r}{1 + (3m/M)} - s'w_1 + \frac{2r}{s}w_2 \\ z_2 &= \frac{r}{1 + (3m/M)} - s'w_1 - \frac{r}{s}w_2 + \frac{\sqrt{3}r}{s}w_3 \\ z_3 &= \frac{r}{1 + (3m/M)} - s'w_1 - \frac{r}{s}w_2 - \frac{\sqrt{3}r}{s}w_3 \\ z_4 &= -\frac{3mr}{M + 3m} + \frac{3m}{M}s'w_1, \end{aligned} \quad (12.1)$$

approximate equations for the components of velocity of the particles are

$$\begin{aligned} \dot{x}_1 &= u + \frac{Mr}{M + 3m}\omega_y + s'\dot{r} + \dot{w}_1 + \dot{w}_2 + \dot{w}_4 \\ \dot{x}_2 &= u + \frac{Mr}{M + 3m}\omega_y - \frac{\sqrt{3}}{2}s\omega_z - \frac{1}{2}s'\dot{r} - \frac{1}{2}\dot{w}_1 + \dot{w}_2 - \frac{1}{2}\dot{w}_4 - \frac{\sqrt{3}}{2}\dot{w}_5 \end{aligned}$$

³⁰ See reference 26, p. 669.

$$\begin{aligned}
\dot{x}_3 &= u + \frac{Mr}{M+3m}\omega_y + \frac{\sqrt{3}}{2}s\omega_z - \frac{1}{2}s'\dot{r} - \frac{1}{2}\dot{w}_1 + \dot{w}_2 - \frac{1}{2}\dot{w}_4 + \frac{\sqrt{3}}{2}\dot{w}_5 \\
\dot{x}_4 &= u - \frac{3mr}{M+3m}\omega_y - \frac{3m}{M}\dot{w}_2 \\
\dot{y}_1 &= v - \frac{Mr}{M+3m}\omega_x + s\omega_z + \dot{w}_3 - \dot{w}_5 \\
\dot{y}_2 &= v - \frac{Mr}{M+3m}\omega_x - \frac{1}{2}s\omega_z + \frac{\sqrt{3}}{2}s'\dot{r} + \frac{\sqrt{3}}{2}\dot{w}_1 + \dot{w}_3 - \frac{\sqrt{3}}{2}\dot{w}_4 + \frac{1}{2}\dot{w}_5 \\
\dot{y}_3 &= v - \frac{Mr}{M+3m}\omega_x - \frac{1}{2}s\omega_z - \frac{\sqrt{3}}{2}s'\dot{r} - \frac{\sqrt{3}}{2}\dot{w}_1 + \dot{w}_3 + \frac{\sqrt{3}}{2}\dot{w}_4 + \frac{1}{2}\dot{w}_5 \\
\dot{y}_4 &= v + \frac{3mr}{M+3m}\omega_x - \frac{3m}{M}\dot{w}_3 \\
\dot{z}_1 &= w - s\omega_y + \frac{M}{M+3m}\dot{r} - s'\dot{w}_1 + \frac{2r}{s}\dot{w}_2 \\
\dot{z}_2 &= w + \frac{\sqrt{3}}{2}s\omega_x + \frac{1}{2}s\omega_y + \frac{M}{M+3m}\dot{r} - s'\dot{w}_1 - \frac{r}{s}\dot{w}_2 + \sqrt{3}\frac{r}{s}\dot{w}_3 \\
\dot{z}_3 &= w - \frac{\sqrt{3}}{2}s\omega_x + \frac{1}{2}s\omega_y + \frac{M}{M+3m}\dot{r} - s'\dot{w}_1 - \frac{r}{s}\dot{w}_2 - \sqrt{3}\frac{r}{s}\dot{w}_3 \\
\dot{z}_4 &= w - \frac{3m}{M+3m}\dot{r} + \frac{3m}{M}s'\dot{w}_1.
\end{aligned} \tag{12.2}$$

These form an orthogonal set with respect to the kinetic energy, giving, in zero approximation for (7.2),

$$\begin{aligned}
T &= \frac{1}{2} \left((M+3m)(u^2 + v^2 + w^2) \right. \\
&\quad + \left(\frac{3mM}{M+3m}r^2 + 3ms^2 \right) (\omega_x^2 + \omega_y^2) \\
&\quad + 3ms^2\omega_z^2 + \left(\frac{3mM}{M+3m} + 3ms'^2 \right) \dot{r}^2 \\
&\quad + \left(3m \left[1 + \frac{3m}{M} \right] s'^2 + 3m \right) \dot{w}_1^2 \\
&\quad \times \left(3m \left[1 + \frac{3m}{M} \right] + 6m \frac{r^2}{s^2} \right) \\
&\quad \times (\dot{w}_2^2 + \dot{w}_3^2) + 3m(\dot{w}_4^2 + \dot{w}_5^2) \Big). \tag{12.3}
\end{aligned}$$

Further, the internal angular momentum about the z axis, $\sum m_r(x_r\dot{y}_r - y_r\dot{x}_r)$, reduces to

$$\begin{aligned}
&3m \left(1 + \frac{3m}{M} \right) (w_2\dot{w}_3 - w_3\dot{w}_2) \\
&\quad - 3m(w_4\dot{w}_5 - w_5\dot{w}_4). \tag{12.4}
\end{aligned}$$

In a rotation through $2\pi/3$ about the z axis, and in a reflection in the x - z -plane, w_2 and w_3 behave like the x and y components of a vector; and so do w_4 and w_5 ; while w_1 is invariant. Since the symmetry must be preserved, the normal coordinates may be taken to be v_1 involving only w_1 ; and v_2 and v_4 connected with w_2 and w_4 , and v_3 and v_5 connected by the same equations with w_3 and w_5 . v_2 and v_3 form a degenerate pair, and so do v_4 and v_5 . The terms in the normal coordinates in the kinetic energy are to take the form

$$\frac{1}{2}(\dot{v}_1^2/V_1 + (\dot{v}_2^2 + \dot{v}_3^2)/V_2 + (\dot{v}_4^2 + \dot{v}_5^2)/V_4).$$

Thus we may take

$$\begin{aligned}
 \left(3m\left(1+\frac{3m}{M}\right)s'^2+3m\right)^{\frac{1}{2}}w_1 &= \frac{1}{(V_1)^{\frac{1}{2}}}v_1 \\
 \left(3m\left(1+\frac{3m}{M}\right)+6m\frac{r^2}{s^2}\right)^{\frac{1}{2}}w_2 &= \frac{1}{(V_2)^{\frac{1}{2}}}\cos\gamma v_2 + \frac{1}{(V_4)^{\frac{1}{2}}}\sin\gamma v_4 \\
 \left(3m\left(1+\frac{3m}{M}\right)+6m\frac{r^2}{s^2}\right)^{\frac{1}{2}}w_3 &= \frac{1}{(V_2)^{\frac{1}{2}}}\cos\gamma v_3 + \frac{1}{(V_4)^{\frac{1}{2}}}\sin\gamma v_5 \\
 (3m)^{\frac{1}{2}}w_4 &= -\frac{1}{(V_2)^{\frac{1}{2}}}\sin\gamma v_2 + \frac{1}{(V_4)^{\frac{1}{2}}}\cos\gamma v_4 \\
 (3m)^{\frac{1}{2}}w_5 &= -\frac{1}{(V_2)^{\frac{1}{2}}}\sin\gamma v_3 + \frac{1}{(V_4)^{\frac{1}{2}}}\cos\gamma v_5,
 \end{aligned} \tag{12.5}$$

where γ , as well as s , V_0 , V_1 , V_2 , and V_4 , is an even function of r .

The degeneracy of v_2 and v_3 requires us to keep in (12.4) the term in $v_2\dot{v}_3 - v_3\dot{v}_2$, namely,

$$\left[3m\left(1+\frac{3m}{M}\right)\frac{\cos^2\gamma}{\left[3m\left(1+\frac{3m}{M}\right)+6m\frac{r^2}{s^2}\right]} - \frac{\sin^2\gamma}{3m}\right]\frac{1}{V_2}(v_2\dot{v}_3 - v_3\dot{v}_2)$$

or, in terms of the momenta,

$$\left[\frac{(M+3m)\cos^2\gamma}{(M+3m)+2M\frac{r^2}{s^2}} - \sin^2\gamma\right](v_2u_3 - v_3u_2)$$

as well as a similar term in $v_4u_5 - v_5u_4$.

Thus, if Ξ , H , and Z are the components of total linear momentum of the molecule referred to the fixed frame, the whole zero order Hamiltonian is

$$\begin{aligned}
 &\frac{1}{2}\left\{\frac{1}{M+3m}(\Xi^2+H^2+Z^2) + \frac{R^2}{\left(3ms'^2+\frac{3mM}{3m+M}\right)}\right. \\
 &\quad + \frac{1}{\left(\frac{3}{2}ms^2+\frac{3mM}{3m+M}\right)}(\Omega_x^2+\Omega_y^2) + \frac{1}{3ms^2} \\
 &\quad \times \left[\Omega_z - \frac{(M+3m)\cos^2\gamma}{(M+3m)+2M\frac{r^2}{s^2}} - \sin^2\gamma\right](v_2u_3 - v_3u_2) \\
 &\quad - \left[\frac{(M+3m)\sin^2\gamma}{(M+3m)+2M\frac{r^2}{s^2}} - \cos^2\gamma\right](v_4u_5 - v_5u_4) \\
 &\quad \left. + V_1u_1^2 + V_2(u_2^2+u_3^2) + V_4(u_4^2+u_5^2)\right\} \\
 &\quad + V_0 + \frac{1}{2}K(V_1v_1^2 + V_2(v_2^2+v_3^2) \\
 &\quad + V_4(v_4^2+v_5^2)). \tag{12.6}
 \end{aligned}$$

This reduces to the form given by Shaffer¹¹ if r is allowed to vary only slightly from an equilibrium value.