

On the Vibrations of Polyatomic Molecules

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An exact solution of the wave equation is found for a form of one-dimensional potential energy which may be of use in discussing polyatomic molecular vibrational energies. An example of its use is given in an analysis of the vibration of the nitrogen in the ammonia molecule. The potential energy for this atom has two minima a distance $2x_m$ apart, separated by a "hill" of height H . The values of x_m and H are not known directly from band spectral data, and are needed for a full analysis of the spectrum. By joining two potential curves of the sort dealt with in the first part of this paper in a symmetric manner, a curve simulating that for the nitrogen atom in ammonia was formed. It was found that for certain values of the constants fixing this curve, the allowed vibrational energies were the same as the experimentally determined values for ammonia. The corresponding value of x_m was 0.38A, and that of H was $\frac{1}{4}$ electron-volt. These values are probably near the correct values of x_m and H for ammonia.

IN THE course of the study of polyatomic molecules one encounters potential functions of a form considerably different from those used in atomic or diatomic molecular problems. A perturbation method using any of the usual exact solutions of the Schrödinger equation would usually involve perturbation energies too large to give good results.

One method of obviating this difficulty is the use of the Wentzel-Kramers-Brillouin method. Another is to develop new exact solutions of the wave equation for potential fields more nearly like those usually encountered in polyatomic molecular problems.

One such exact solution, for a potential field with two minima,¹ has already been developed. Another solution, for a different form of potential field is described in this paper, and an example of its application to the vibrational states of NH_3 is given.

THE EXACT SOLUTION

The potential field² which is amenable of exact solution is

$$V(x) = B \tanh(x/d) - C \operatorname{sech}^2(x/d). \quad (1)$$

If $|B| < 2C$ this potential has a minimum value at $x_0 = -\tanh^{-1}(B/2C)$. The second derivative at this point is

$$(d^2V/dx^2)_{x=x_0} = (1/8d^2C^3)(4C^2 - B^2)^2 \quad (2)$$

and

$$V(x_0) = -(4C^2 + B^2)/4C.$$

¹ Morse and Stueckelberg, *Helv. Phys. Acta* **4**, 337 (1931).

² The continuous energy spectrum for a potential field somewhat like this has been discussed by Eckart, *Phys. Rev.* **35**, 1303 (1930).

The wave equation for such a potential is

$$d^2\psi/dz^2 + (-\epsilon - \beta \tanh z + \gamma \operatorname{sech}^2 z)\psi = 0 \quad (3)$$

where $z=x/d$, and $(\epsilon, \beta, \gamma) = (8\pi^2 M d^2/h^2)(-E, B, C)$. E is the allowed energy of the system. Now set $\psi = e^{az} \cdot \cosh^{-bz} \cdot F(z)$. The equation becomes

$$F'' + 2(a - b \tanh z)F' + [\gamma - b(b+1)] \operatorname{sech}^2 z \cdot F = 0$$

and ψ/F is finite in the range $-\infty \leq z \leq \infty$, if

$$a = -\frac{1}{2}[(\epsilon + \beta)^{1/2} - (\epsilon - \beta)^{1/2}] \text{ and } b = \frac{1}{2}[(\epsilon + \beta)^{1/2} + (\epsilon - \beta)^{1/2}] \quad (4)$$

where both square roots are taken as positive quantities.

Now let $u = \frac{1}{2}(1 + \tanh z)$. The equation for F in terms of u is

$$u(1-u)F'' + [a+b+1-2(b+1)u]F' + [\gamma - b(b+1)]F = 0. \quad (5)$$

The solution of this equation which remains finite at $u=0$ is the hypergeometric function

$$F = F\left([b + \frac{1}{2} - (\gamma + \frac{1}{4})^{1/2}, b + \frac{1}{2} + (\gamma + \frac{1}{4})^{1/2}; a + b + 1; u\right).$$

This series approaches infinity³ in the same manner as $\exp[2(b-a)z]$ as u approaches unity, unless $b + \frac{1}{2} - (\gamma + 1/4)^{1/2}$ is a negative integer. In this case the function is a Jacobi polynomial. Therefore ψ will not be finite everywhere unless

$$b = (\gamma + \frac{1}{4})^{1/2} - n - \frac{1}{2}. \quad (6a)$$

Referring to Eq. (4) we see that the other constant a becomes

$$a = -\beta/[(4\gamma + 1)^{1/2} - 2n - 1]. \quad (6b)$$

The allowed values of the energy E are

$$\begin{aligned} -E_n &= (h^2/8\pi^2 M d^2)(a^2 + b^2) \\ &= \frac{1}{4}[(4C + g^2)^{1/2} - g(2n+1)]^2 + B^2/[(4C + g^2)^{1/2} - g(2n+1)]^2. \end{aligned} \quad (6c)$$

The quantum number n can be zero or any positive integer less than or equal to $(\gamma + 1/4)^{1/2} - (\beta/2)^{1/2} - 1/2$. The constant $g^2 = h^2/8\pi^2 M d^2$.

Therefore the solution of the wave Eq. (2) is the wave function

$$\psi_n = N_n e^{ax/d} \cosh^{-b}(x/d) F\left(-n, (4\gamma + 1)^{1/2} - n; a + b + 1; \frac{1}{2}[1 + \tanh(x/d)]\right) \quad (7)$$

where the values of a and b are given in Eqs. (6a) and (6b). The normalizing factor is obtained from the following equation

$$N_n = 1/2^b [d \cdot G(a + b + 1, b - a - 1, 2(\gamma + \frac{1}{4})^{1/2}, a + b + 1; n)]^{1/2}$$

³ Whittaker and Watson, *Modern Analysis*, page 299.

where

$$\begin{aligned}
 G(k, \lambda, \mu, \nu; n) &= 2 \int_0^1 u^k (1-u)^\lambda [F(-n, \mu-n; \nu; u)]^2 du \\
 &= 2\Gamma(\lambda+1) \sum_{s=0}^{2n} (-1)^s [\Gamma(k+s+1)/\Gamma(k+\lambda+s+2)] \\
 &\quad \cdot \sum_t \frac{\Gamma(t+\mu-n)\Gamma(s-t+\mu-n)[\Gamma(\nu)n!]^2}{[\Gamma(\mu-n)]^2 \Gamma(t+\nu)\Gamma(s+\nu-t)(n-t)!(n+t-s)!t!(s-t)!}
 \end{aligned}$$

where the limits of the summation over t are fixed by the factorials.

The allowed energy levels for a typical form of Eq. (1) are given in Fig. 1.

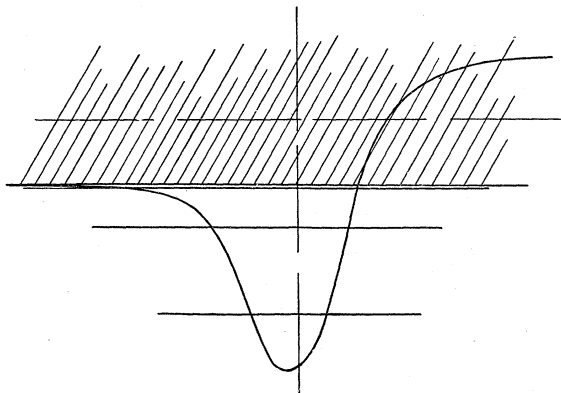


Fig. 1. Allowed energy levels for a potential function of form corresponding to Eq. (1).

When γ is much larger than unity then the allowed values of the energy become

$$E_n = V(x_m) + h\omega_0(n + \frac{1}{2}) - (h^2/8\pi^2Md^2)(1 + 3B^2/8C^2)(n + \frac{1}{2})^2 + \dots \quad (8)$$

for small values of n . Here ω_0 is the classical frequency of oscillation about the minimum point, $x = x_m$.

$$\omega_0 = (4C^2 - B^2)/4\pi d(2MC^3)^{1/2}.$$

APPLICATION TO THE AMMONIA MOLECULE PROBLEM

An example of the use of these wave functions can be taken from the treatment of the vibrations of the ammonia molecule.

The equilibrium configuration of the ammonia molecule⁴ has a pyramidal structure with the three hydrogen atoms at the vertices of an equilateral triangle for the base, and the nitrogen atom along a perpendicular line through the center of the base. Due to the symmetry of the molecule there will be two equivalent positions of equilibrium for the nitrogen, at equal distances above and below the plane of the hydrogens. This equivalence of the

⁴ See the discussion and references given in the article of Dennison and Hardy, *Phys. Rev.* **39**, 938 (1932).

two minima makes every vibrational level a doublet, a result which is found experimentally.

To analyze the vibrational behavior we first separate off the coordinates of the center of gravity of the molecule and the Eulerian angles fixing its orientation in space, and deal only with the coordinates fixing the relative positions of the atoms. One of these coordinates is x , the distance of the nitrogen atom from the plane of the hydrogens. The other five coordinates, z_1, z_2, z_3, z_4, z_5 , can be chosen that the positions of the two equilibrium configurations are at $z_1 = \dots = z_5 = 0, x = \pm x_m$. The potential function $V(x, z_1, z_2, z_3, z_4, z_5)$ therefore has its two minima at these two points.

Classically, the problem of small vibrations about either of these minima would be straightforward. The potential V near each minima has six mutually orthogonal principal axes, such that the kinetic energy becomes a sum of squares of velocities and the potential energy becomes a sum of squares of coordinates. These coordinates, which we can call y_0, \dots, y_5 , make up a so-called normal set of coordinates: by their means we can separate the problem and find the six fundamental modes of vibration. For ammonia, x almost coincides with one of the normal coordinate axes. Classically therefore x can be used as one of the normal coordinates with fair accuracy for small vibrations.

This analysis is valid for a classical consideration of small amplitude vibrations, but for large amplitudes the concept of normal coordinates is not valid; in general the energy equation cannot be separated. Quantum mechanically, the use of normal coordinates for the ammonia problem is never valid, for we can never have the equivalent of small vibrations (i.e., have the wave function all concentrated near one point) since there must be as much of the wave function about one minimum as about the other.

However, we can justify our use of x as a "normal" coordinate (i.e., our approximate splitting off from the general six-dimensional problem a one-dimensional problem in x alone) by the following method.

The general, vibrational equation, in six coordinates, will not be separable; but we can say a few things about the wave functions which satisfy it. From considerations of symmetry we know that all the wave functions will either be symmetric or antisymmetric about the nodal hypersurface $x=0$. The function for the lowest state will be symmetric, having no nodes at all, and having two maxima near the two points $x = \pm x_m, z_1 = \dots = z_5 = 0$. The function for the next lowest state will be antisymmetric, its only nodal surface being the hypersurface $x=0$. In fact all the wave functions can be separated into pairs, one function in each pair being similar to the other except for the addition of a nodal surface at $x=0$.

The wave functions for the higher states will have other nodal surfaces as well. These surfaces will have quite complicated forms in general, and cannot be separated into clear-cut families of surfaces, as can be done in a separable problem. Nevertheless we will find that some of our wave functions will fall into an easily classified family. These functions will represent states where one type of oscillation is excited and the others are not; the nodal surfaces of

this family will be a one-parameter set of surfaces which will be orthogonal to the x axis. This family of wave functions is the set we wish to study. They will only be large near the x axis. Therefore, for these wave functions, we will not introduce much error if we consider their variation along the x axis to satisfy a one-dimensional wave equation, using for potential field $V(x, 0, 0, 0, 0, 0)$ (called hereafter $V(x)$ for short), and their corresponding energies to be given by the allowed energies of this one-dimensional problem.

Perhaps we could find other "normal coordinates" in a similar manner. In the other cases they might be curvilinear lines joining the two minimum points and they would each be tangent to one of the classical normal coordinates at these points. However, the reasoning is not as clear cut for these other cases, and since we do not need them for our problem, we will not digress further.

The problem of the vibrations along the x axis is clear cut and the behavior of the wave functions along the x axis and the corresponding energy values can be obtained by solving the wave equation

$$d^2\psi/dx^2 + (8\pi^2M/h^2)(W - V(x))\psi = 0. \quad (9)$$

From the discussion above we know that V must have two minima symmetrically placed at $x = \pm x_m$, separated by a potential "hill." As $|x|$ becomes large, V approaches some asymptotic value whose height above the minima gives the energy of dissociation of ammonia for this type of vibration.

In studying the behavior of ammonia it would be very useful to know the value of x_m , the height H of the hill between the minima and the general shape of the potential curve. The data for determining these quantities are obtained from the analysis of the molecule's infrared spectrum. Presumably by analyzing the rotational structure of the bands one could obtain values of the moments of inertia of the molecule about its major axes, and thence obtain the value of x_m . The moment of inertia about the x axis has been obtained⁴ in this manner, but this alone cannot give us any of the properties of $V(x)$. It seems that the best way to determine these properties is to assume a form of the potential field and then see whether the values of the vibrational energies computed for this field check with the experimentally determined levels. This method will not give us a unique answer, particularly since we know the values of only a few of the lowest vibrational energies. In general, a whole family of curves could be devised whose energy levels check with the observed levels. However, we are helped out of this difficulty by our knowledge of the general shape of V , and so we can rule out many potential forms as being unreasonable. From the results to appear later in this paper it seems probable that all those potential forms which appear reasonable and which check the data differ very little in their essential properties, and all give about the same value of x_m and H . If this is actually the case, then the values of x_m and H which are obtained in this paper are fairly close to the correct values.

A form of potential field which would satisfy our preconceptions of its form would be made by joining two potential fields $V(x)$ of the form given in Eq. (1) in a symmetric manner.

$$V(x) = \begin{cases} B \tanh(x/d - k) - C \operatorname{sech}^2(x/d - k), & x \geq 0 \\ -B \tanh(x/d + k) - C \operatorname{sech}^2(x/d + k), & x \leq 0. \end{cases} \quad (10)$$

This would make the half distance between minima, $x_m = kd - \tanh^{-1}(B/2C)$. The height of the intermediate hill, H , can also be found.

It can be shown¹ that as long as the energy level considered is below the top of the intermediate hill the difference between the level for the single minimum problem (such as for Eq. (1)), and that for the corresponding double minimum problem (such as for Eq. (10)), can be fairly accurately given by a perturbation calculation.

The wave functions for the double minimum problem become

$$\Psi_n^\pm(x) = K[\psi_n(x - dk) \pm \psi_n(-x - dk)] \quad (11a)$$

where the ψ 's are given in Eq. (7). The constant K is a normalization constant. The energies become

$$\begin{aligned} W_n^\pm = E_n + & \int_0^\infty [\psi_n(x + dk)]^2 V(x) dx \\ & \pm \int_0^\infty \psi_n(x - dk) V(x) \psi_n(-x - dk) dx. \end{aligned} \quad (11b)$$

This shows that for each level of the one minimum problem there is a pair of levels for the double minimum case.

The actual shift of the center of gravity of the levels, given by the first integral, is not particularly important, since its value is small compared to the distance between levels for different values of n . But the second integral is of importance since twice its value gives the separation between the levels in a pair. This separation is small compared to the energy difference between different pairs as long as the levels are below the top of the intermediate hill.

The integral

$$\Delta W_n = 2 \int \psi(x - dk) V(x) \psi(-x - dk) dx \quad (11c)$$

giving the inter-doublet separation can be computed since we know the functions ψ_n .

From Eq. (6c) the separation between the lower two pairs is

$$E_1 - E_0 = 2g(C + g^2/4)^{1/2} - 2g^2 - B^2/4 \frac{g(4C + g^2)^{1/2} - g^2}{C + g^2 - g(4C + g^2)^{1/2}}. \quad (12a)$$

The inter-pair separations turn out to be

$$\begin{aligned} \Delta W_0 &= \frac{4\Gamma(2b)e^{-2ak}}{\Gamma(b+a)\Gamma(b-a)(2 \cosh k)^{2b}} \left[\frac{2C \tanh k}{b+1} - \frac{B}{b} \right] \\ \Delta W_1 &= \frac{2\Gamma(2b+2)}{\Gamma(b+a)\Gamma(b-a)(2 \cosh k)^{2b}} \frac{e^{-2ak}}{[(2a^2+b)(b+1)^2 + a^2b(1+2b)]}. \end{aligned} \quad (12b)$$

$$\left. \left\{ 2C \left[\left(\frac{a^2 - (b+1)^2}{b+1} + \frac{(b+1)^2}{b+2} \right) \tanh k + \frac{2a(b+1)}{b+2} \tanh^2 k \right. \right. \right. \right. \\ \left. \left. \left. + \frac{(b+1)^2}{b+2} \tanh^3 k \right] \right. \right. \\ \left. \left. - B \left[\frac{a^2 - b - 1}{b} + 2a \tanh k + (b+1) \tanh^2 k \right] \right\} \right\} \quad (12c)$$

where from Eqs. (6a) and (6b) we have

$$b = (C/g^2 + \frac{1}{4})^{1/2} - n - \frac{1}{2}, \quad a = -B/2g^2b. \quad (12d)$$

The value of n for (12b) is zero and that for (12c) is unity.

The data by which we seek to obtain values for the constants in Eq. (10), representing a possible form for the potential field in ammonia are obtained from the paper by Dennison and Hardy.⁵ They are the separations between the two lowest pairs of levels, $E_1 - E_0 = 950 \text{ cm}^{-1}$ and the inter-pair separations $\Delta W_0 = 0.8 \text{ cm}^{-1}$, $\Delta W_1 = 33 \text{ cm}^{-1}$.

One difficulty is at once apparent, for there are four constants to determine in Eq. (10), B , C , d and k , and only three experimental values available

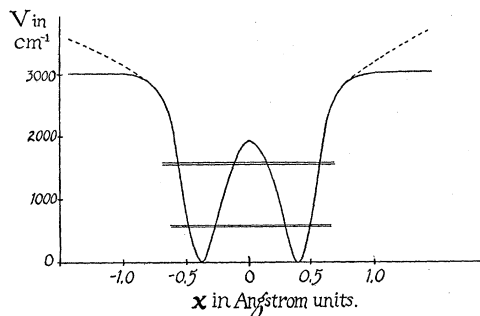


Fig. 2. Energy levels and potential function for the nitrogen atom in the ammonia molecule.

to make the fit. It would seem that even for this form of potential there would be a whole family of possible curves which would fit the data. This actually is true, a range of values of B , C , d and k was found which would fit. However this range of values is considerably curtailed if we require that V be reasonable in shape; that $|B|$ cannot be greater than $2C$, that the second level must be below the center hill, and that the hill should not be higher than the value of V at $x = \infty$.

These requirements limit the range of allowed values of C to between 2200 and 3000 cm^{-1} , that of B to between zero and 1000 cm^{-1} ; but that of d is between 0.16 and 0.185 \AA and that of k is between 2.24 and 2.20. This means that the possible values of x_m lie between 0.365 and 0.390 \AA , and those of H lie

⁵ Dennison and Uhlenbeck, Phys. Rev. 41, 313 (1932), obtain, by different methods, a result in exact agreement with this.

between 1950 and 2100 cm^{-1} . One of the potential curves for an intermediate set of values of the constants is shown in Fig. 2, with its corresponding energy levels.

The fact that all possible forms of potential of the form of Eq. (10) giving energy levels which fit the data give values of x_m and H which differ at most by eight percent, makes it seem probable that any form of V which would fit the data and have a reasonable form would give values of x_m near 0.38A and of H near 2050 cm^{-1} (a quarter volt). This seems likely, for the value of $E_1 - E_0$ will more or less fix the curvature upward about the two minima, while the values of ΔW_0 and ΔW_1 will more or less fix the curvature downward about the central hill and the height of this hill, while the joining of the curves about the minima and the curve about the hill will more or less fix x_m .

The value of the dissociation energy $V(\infty) = V(x_m)$, however, is not closely fixed by our data, for it varies from 2200 to 4000 cm^{-1} . This is to be expected, since the energy levels we have used to fix our curves are very little effected by a change in the form of V for large values of x . In fact a potential curve of the form given by the dotted line in Fig. 2 would have very nearly the same values of allowed energies as the curve given by the solid line for Eq. (10). For this reason our analysis can tell us nothing about the value of the dissociation energy for this type of vibration (except that it cannot be less than 2200 cm^{-1} !).

However the value of x_m is the important value to be fixed, for a complete analysis of the ammonia spectrum requires a knowledge of its value. It seems likely that its value should be about 0.38A, which makes the moment of inertia about the axis of symmetry $4.41 \cdot 10^{-40}$ gm-cm².⁵ The range of possible values of x_m introduces in this last result an uncertainty of only about 1 percent.