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The Two-Minima Problem and the Ammonia Molecule

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The system of a particle moving in a potential field containing two equal minima is treated by the Wentzel-Kramers-Brillouin method of approximation. The energy levels are grouped in pairs and the object of the computation is to find the separation between two levels forming a pair. This is accomplished by connecting the oscillatory and exponential approximate solutions of the wave equation by means of the Kramers connection formulae. If Δ is the separation of a pair and $h\nu$ the distance between two pairs $\Delta/h\nu=1/\pi A^2$ where $A=\exp\left[(2\pi/h)\int_0^{x_1}[2m(V-E)]^{1/2}dx\right]$. A particular potential curve is chosen consisting of two equal parabolae connected by a straight line. The expression for Δ may then be evaluated explicitly as a function of the length of the joining line, $2(x_0-\alpha)$ and the distance between two minima, $2x_0$. These formulae may be applied to determining the form of the ammonia molecule. Substituting the experimental values for Δ_0 and Δ_1, it is found that $x_0=3.161$ and $\alpha=1.916$. An exact solution for this particular potential curve may be found by joining Weber's function $D_n(x-x_0)$ and $D_n(x+x_0)$ to a hyperbolic sine or cosine. This process also leads to expressions for Δ which may be equated to the experimental values yielding $x_0=3.182$ and $\alpha=1.930$, in good agreement with the earlier determination. Finally x_0 is used to compute $2q_0=0.760\times10^{-8}$ cm, the distance between the two potential minima, and the following dimensions of the ammonia molecule, $\mathrm{H-H}=1.64\times10^{-8}$, $\mathrm{N-H}=1.02\times10^{-8}$ cm.

§1.

THE one-dimensional system of a particle moving in a potential field consisting of two equal minima was first treated qualitatively by Hund[1] who showed that the vibrational energy levels which lie below the potential maximum will occur in pairs. The distance between two pairs is roughly equal to $h\nu_0$ where ν_0 is the normal frequency of oscillation, while the separation of the two levels forming a pair depends upon the height and nature of the barrier between the minima and is in general very small. We propose to compute the level separation using the Wentzel-Kramers-Brillouin method of approximation and then to compare this solution with an exact solution based on a particular potential field. Finally an application of the results will be made to the ammonia molecule.

§2.

The W. K. B. method yields an approximate solution of the wave equation whose form depends essentially upon whether the region being considered lies within or without the region in which the classical motion might take place, that is, the region where the kinetic energy is positive. In the first case the solution is oscillatory and has the form

$$\psi_{(x)}=(c/P^{1/2})\cos\left[(2\pi/h)\int^{x}Pdx+\gamma\right]$$

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[1] F. Hund, Zeits. f. Physik **43**, 805 (1927).

where x is the coordinate of the system, c and γ are arbitrary constants, and

$$P = +\left[2m\left|E - V\right|\right]^{1/2}.$$

In the second or non-classical region the solution consists of a linear combination of an increasing and a decreasing exponential[2] which has the form

$$\psi_{(x)} = (a/P^{1/2}) \exp\left[(2\pi/h)\int^{x} Pdx\right]$$
$$+ (b/P^{1/2}) \exp\left[-(2\pi/h)\int^{x} Pdx\right].$$

At each boundary or critical point there will exist two conditions upon the arbitrary constants c, γ, a and b which arise from the fact that each function must approximate the *same* exact solution of the wave equation. These relations between the constants are the so-called Kramers connection formulae.[3] The increasing exponential connects with the oscillatory solution so that $c=a$ and $\gamma=+\pi/4$ while for the decreasing exponential $c=2b$ and $\gamma=-\pi/4$.

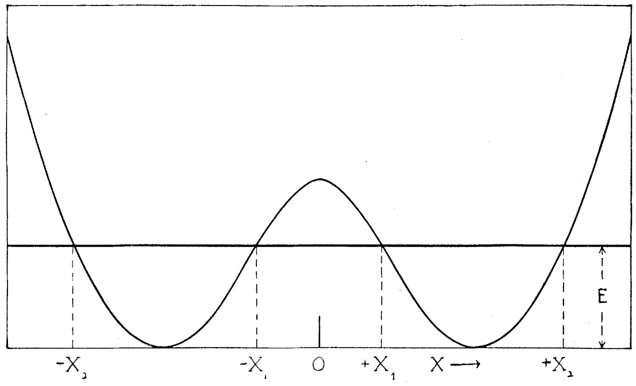

Fig. 1.

These formulae furnish a method by which we may approximate to any solution of the wave equation. When however one wishes to approximate the *eigenfunctions*, namely those functions for which $\int_{-\infty}^{+\infty}\tilde{\psi}\psi dx$ is finite, one must let ψ be represented only by the *decreasing* exponential as x approaches + or − infinity. Thus in a region from $+\infty$ to $-\infty$ which has n critical points, there will exist $2n+2$ conditions arising from the connection formulae.

The $n+1$ regions will furnish $2n+2$ constants but one of these, the multiplicative one, must be kept arbitrary in order later to normalize the wave

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[2] By increasing or decreasing exponential we will always mean increasing or decreasing when we proceed *away* from the boundary point between the classical and non-classical regions *into* the non-classical region.

[3] H. A. Kramers, Zeits. f. Physik **39**, 828 (1926), H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **58**, 217 (1929), A. Zwaan, Utrecht Diss., 1929. These formulae are collected in a paper by L. A. Young and G. Uhlenbeck, Phys. Rev. **36**, 1154 (1930).

function. Thus there is one condition remaining and this just serves to fix the value of E, that is to determine the eigenvalues of the problem. When we have a system in which the potential has only a single minimum this procedure leads to the well-known half integer quantization of the phase integral.

$$\oint Pdx = (n + \tfrac{1}{2})h. \tag{1}$$

§3.

Let us now consider the case of two equal minima, (illustrated in Fig. 1) where the energy level E is assumed to lie below the potential barrier at $x=0$. Since the potential is an even function of x the wave functions will be divided into two classes, those which are even functions of x and those which are odd functions. We begin by assuming that the level in question corresponds to an even eigenfunction, ψ_+, and we denote the energy by E_+.

In the region from $-x_1$ to $+x_1$ the wave function will have the character of an hyperbolic cosine and may be written in the following manner where C is the multiplicative constant mentioned earlier.

$$\psi_+ = (C/P^{1/2}) \cosh\left[(2\pi/h)\int_0^x Pdx\right] \quad -x_1 < x < x_1.$$

It is now convenient to write $\int_0^x Pdx = \int_0^{x_1} Pdx - \int_x^{x_1} Pdx$. Further let $A = \exp[(2\pi/h)\int_0^{x_1} Pdx]$. We may then express ψ_+ as

$$\psi_+ = (C/2P^{1/2})\left\{A \exp\left[-(2\pi/h)\int_x^{x_1} Pdx\right] + (1/A)\exp\left[(2\pi/h)\int_x^{x_1} Pdx\right]\right\}$$
$$-x_1 < x < x_1.$$

Applying now the connection formulae between the regions $-x_1$ to x_1 and x_1 to x_2, we obtain the following oscillatory solution for the latter region.

$$\psi_+ = R_+ C \cos\left[(2\pi/h)\int_{x_1}^x Pdx - \theta_+\right] \tag{2}$$

where

$$\tan\theta_+ = (2A^2 - 1)/(2A^2 + 1) \tag{3}$$

and

$$R_+ = (4A^4 + 1)^{1/2}/2A.$$

Now in the region $x > x_2$ we must have the decreasing exponential, that is,

$$\psi_+ = (\alpha C/P^{1/2}) \exp\left[-(2\pi/h)\int_{x_2}^x Pdx\right]$$

where α is a new constant as yet undetermined. This connects in the region x_1 to x_2 with

$$\psi_+ = (2\alpha C/P^{1/2}) \cos\left[(2\pi/h)\int_x^{x_2} Pdx - \pi/4\right]. \tag{4}$$

Eqs. (2) and (4) must give identical values for ψ_+ as a function of x and consequently also of the first derivative of ψ_+. We may thus eliminate α by requiring that ψ_+'/ψ_+ as determined from (2) shall be the same as ψ_+'/ψ_+ determined from (4). This gives immediately

$$\tan\left[(2\pi/h)\int_{x_1}^{x} Pdx - \theta_+\right] = \tan\left[(2\pi/h)\int_{x_2}^{x} Pdx + \pi/4\right].$$

The two angles whose tangents are equal must differ by $n\pi$ where n is an integer and this leads to the result,

$$\oint Pdx = (n + \tfrac{1}{4} + \theta_+/\pi)h. \tag{5}$$

From (3) one sees that $\theta_+ < \pi/4$ and in the limit of an infinite barrier where $A \rightarrow \infty$, $\theta_+ \rightarrow \pi/4$ and (5) reduces to (1).

The foregoing calculation is appropriate for a discussion of one of the levels E_+ where ψ_+ is an even function of x. For the remaining levels E_- where ψ_- is an odd function of x we must start in the region $-x_1$ to x_1 with the hyperbolic sine. We obtain in a similar manner,

$$\oint Pdx = (n + \tfrac{1}{4} + \theta_-/\pi)h \tag{6}$$

where

$$\tan\theta_- = (2A^2 + 1)/(2A^2 - 1),$$

thus $\theta_- \geq \pi/4$.

Let us now consider a pair of levels E_+ and E_- which are defined by the same value of n. Subtracting (6) from (5) and writing out $\oint Pdx$ we find.

$$2\int_{x_1}^{x_2} \{[2m(E_- - V)]^{1/2} - [2m(E_+ - V)]^{1/2}\}dx = (\theta_- - \theta_+)h/\pi. \tag{7}$$

A is usually a large quantity and when this is the case it will be seen that θ_+ is nearly equal to θ_- and consequently we may develop both and obtain to a high degree of approximation,

$$\theta_- - \theta_+ = 1/A^2.$$

Where $\theta_- - \theta_+$ is small, both E_- and E_+ must lie very close to the energy E of a corresponding one minimum potential system. Calling the difference $E_- - E_+$ for the nth pair of levels Δ_n, we find by developing (7)

$$\Delta_n = h/2\pi m A_n^2 \int_{x_1}^{x_2} \frac{dx}{[2m(E_n - V)]^{1/2}}.$$

This expression may be somewhat simplified by remembering that

$$2m\int_{x_1}^{x_2}\frac{dx}{[2m(E-V)]^{1/2}}=\oint dt=\frac{1}{\nu}$$

where ν is the classical frequency of oscillation. When the potential V between x_2 and x_1 does not deviate too greatly from a parabolic form, $h\nu$ may be identified with the distance between neighboring pairs of levels.

$$\Delta_n/h\nu = 1/\pi A_n{}^2 \tag{8}$$

where

$$A_n = \exp\left[+(2\pi/h)\int_0^{x_1}[2m(V-E_n)]^{1/2}dx\right].$$

The expression (8) shows that the relative separation of a pair of levels does not depend upon the form of the curve but only upon a square root area

$$(2\pi/h)\int_0^{x_1}[2m(V-E_n)]^{1/2}dx$$

in the non-classical region. This result might have been expected from considerations analogous to the Gamow, Condon, Gurney theory of radioactive disintegration.

§4.

The infrared spectrum of the ammonia molecule exhibits features which may be directly related to the one dimensional problem of two equal minima. The parallel type vibration bands for example are observed to be composed of two nearly superimposed bands; a phenomenon whose existence depends upon the fact that there are two equivalent positions of equilibrium for the nitrogen nucleus. This problem has been treated by Dennison and Hardy,[4] who show that the normal coordinate x_3 which is to be correlated with the band at 10.5μ, may be identified with the coordinate x which we have been using. (For a more exact discussion, see the paper just cited.)

The experimental work so far done on the ammonia spectrum presents us with three data, the frequency ν_0 and the separation between the two lowest pairs of levels.

$$\nu_0 = 950\ \text{cm}^{-1},\quad \Delta_0 = 0.8\ \text{cm}^{-1},\quad \Delta_1 = 32.2\ \text{cm}^{-1}.$$

The estimated error of ν_0 and Δ_1 is less than a percent but the error in Δ_0 may be as high as 10 or 20 percent.

We should of course like to be able to reconstruct the potential V as a function of x using the known experimental data. Of the three facts we possess, ν_0 is needed to determine the curvature in the region of the minima which we designate by $x=\pm x_0$. Formula (8) now shows that if we know Δ_0 and Δ_1 we can impose two and only two conditions on the curve, namely we can de-

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[4] D. M. Dennison and J. D. Hardy, Phys. Rev. **39**, 938 (1932).

termine the square root area from $x=0$ to $x=(x_1)_0$ and from $x=0$ to $x=(x_1)_1$ where $(x_1)_0$ and $(x_1)_1$ are the critical points for the two states $n=0$ and 1 respectively.

We shall therefore choose a very simple curve with two parameters which will allow us to correlate the observed data. Let this curve be formed by two equal parabolae joined by a straight line as illustrated in Fig. 2. The two pairs of levels corresponding to $n=0$, 1 are shown in the figure but since the drawing is to scale the separations Δ_0 and Δ_1 are much too small to be represented. The two parameters are $(x_0-\alpha)$, half the length of the joining line and x_0, half the distance between the two minima. We do not mean that this curve represents very closely the actual potential function, but it must possess the two properties as to square root area mentioned before, and these are the only features of the potential curve which we can at present learn. The parameter x_0 is of great physical interest and it turns out that this is very insensitive to the exact shape of V, provided only V has the general form indicated in Figs. 1 or 2.

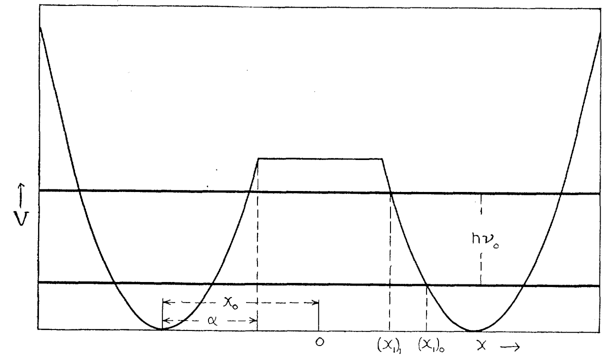

Fig. 2.

By use of this particular curve the quantities A and Δ may be readily computed as functions of α and x_0.

$$\frac{\Delta_n}{h\nu_0}=\left(\frac{1}{\pi}\right)\left[\frac{\alpha+[\alpha^2-2n-1]^{1/2}}{(2n+1)^{1/2}}\right]^{2n+1}\exp\left[-(2x_0-\alpha)(\alpha^2-2n-1)^{1/2}\right]. \quad (9)$$

Equating Δ_0 and Δ_1 to their observed values we obtain a transcendental equation which yields the values,

$$\alpha = 1.916$$

$$x_0 = 3.161.$$

The physical significance of these will be discussed later.

§5.

One reason for choosing the potential function illustrated in Fig. 2 is that for this particular curve we may also obtain an exact solution and thus we are able to test, for one case at least, the accuracy of the foregoing computation. There are two reasons why we might doubt its validity. In the first place the W. K. B. approximation is designed to hold best for energy states where n, the quantum number is a large integer. We wish to apply the formulae however to the two lowest states where $n=0$ and 1. In the second place the W. K. B. method becomes inapplicable when the potential at the critical point is too nearly equal to the potential throughout the non-classical region. This obtains because in this case $P^{1/2}$ becomes very small and the W. K. B. expression for ψ does not satisfy the wave equation at all accurately. Fig. 2 is drawn to scale using the values for α and x_0 obtained for ammonia and it is seen that the highest critical point does not lie very far beneath the potential in the non-classical region.

The exact solution is obtained in the following manner. The wave equation may be written,

$$(d^2\psi/dx^2) + (2n + 1 - 2V/h\nu_0)\psi = 0$$

where x and $2n+1$ are proportional to the displacement coordinate q and to the energy E respectively. (n is not necessarily an integer here although it will be nearly equal to one when the potential barrier is sufficiently high.)

$$q = [h/4\pi^2\mu\nu_0]^{1/2}x, \quad E = (2n + 1)h\nu_0/2. \tag{10}$$

The potential may be expressed as follows

$$\begin{aligned} 2V/h\nu_0 &= (x - x_0)^2 \text{ from } x = (x_0 - \alpha) \text{ to } +\infty \\ &= (x + x_0)^2 \text{ from } x = (\alpha - x_0) \text{ to } -\infty \\ &= \alpha^2 \qquad\quad \text{ from } x = (x_0 - \alpha) \text{ to } (\alpha - x_0). \end{aligned}$$

In the region of the joining line, from $x=(x_0-\alpha)$ to $(\alpha-x_0)$ the differential equation is satisfied by any linear combination of a hyperbolic sine or cosine. (Assume that $2n+1<\alpha^2$.) It is known that the solutions of the total wave equation may be divided into the two classes, ψ_+ which are even functions of x and ψ_- which are odd functions. It is clear that these must just correspond to the hyperbolic cosine and sine respectively.

Thus from $x=(x_0-\alpha)$ to $(\alpha-x_0)$

$$\begin{aligned} \psi_+ &= A \cosh (\alpha^2 - 2n_+ - 1)^{1/2}x \\ \psi_- &= B \sinh (\alpha^2 - 2n_- - 1)^{1/2}x. \end{aligned}$$

Now in the region from $x=(x_0-\alpha)$ to $+\infty$, one set of solutions of the differential equation will be Weber's functions, $D_n(x-x_0)$. These functions[5] converge properly for large values of x while for small values of x (i.e., $(x-x_0)$ large and negative) we may fit them by means of the parameter n to any curve we please. Now if we join $D_{n+}(x-x_0)$ to ψ_+ or $D_{n-}(x-x_0)$ to ψ_- so that their values and first derivatives agree at the point $x=x_0-\alpha$, we shall have a complete and continuous solution to the wave equation, throughout this region. A similar process may be carried out for nega-

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[5] See for example E. T. Whittaker and G. N. Watson, Modern Analysis, 4th Edition, p. 347 (1927).

tive values of x using $D_n(x+x_0)$. The conditions necessary for joining these curves will determine the n_+ or n_- and hence the energy difference Δ_n. The computation is straightforward and makes use of the asymptotic expression for $D_n(y)$ given by Whittaker and Watson, for large *negative* values of y.

$$\begin{aligned} D_{n(y)} = {} & e^{-y^2/2}(2^{1/2}y)^n\left[1 - n(n-1)/4y^2 + n(n-1)(n-2)(n-3)/32y^4 \cdots\right] \\ & - \left[(2\pi)^{1/2}e^{n\pi i}e^{y^2/2}/\Gamma(-n)(2^{1/2}y)^{n+1}\right]\left[1 + (n+1)(n+2)/4y^2 \right. \\ & \left. + (n+1)(n+2)(n+3)(n+4)/32y^4 + \cdots\right]. \end{aligned}$$

It does not seem possible to give Δ_n as an explicit function of n but the two quantities we need Δ_0 and Δ_1 have been computed,[6]

$$\begin{aligned} \Delta_0/h\nu_0 &= (2\alpha/\pi^{1/2}) \exp\left[-\alpha^2 - 2(x_0-\alpha)(\alpha^2-1)^{1/2}\right] \\ \Delta_1/h\nu_0 &= \left[(4\alpha^3-4\alpha)/\pi^{1/2}\right] \exp\left[-\alpha^2 - 2(x_0-\alpha)(\alpha^2-3)^{1/2}\right]. \end{aligned} \tag{11}$$

It is interesting to compare formulae (9) and (11). When x_0 and α are sufficiently large, the two values of Δ_0 agree to within 7 percent and the values of Δ_1 to within 3 percent. This result is in accord with the work of Young and Uhlenbeck[3] who found that the W. K. B. approximation for the hydrogenic wave functions was surprisingly good even for the low quantum states. The agreement of (9) and (11) for the particular values of x_0 and α found for ammonia is somewhat poorer, being about 10 percent for both Δ_0 and Δ_1. On the other hand we may equate (11) to the experimental data Δ_0 and Δ_1 when we find,

$$\alpha = 1.930 \quad x_0 = 3.182. \tag{12}$$

Thus the error in the determination of the constants α and x_0 is in each case about 0.7 percent.

We shall adopt the values (12) and from these may compute the actual distance between the two minima in the ammonia molecule. Substituting the appropriate values for ν_0 and μ, the reduced mass, into (10) we obtain $2q_0 = 0.760 \times 10^{-8}$ cm.

The moment of inertia, A, about an axis perpendicular to the symmetry axis is known from band spectrum measurements to be $A = 2.80 \times 10^{-40}$. Combining this datum with the value for q_0 we may find C, the moment of inertia about the figure axis and hence the normal distances between two hydrogen nuclei and between a hydrogen and nitrogen nucleus.

$$\begin{aligned} C &= 4.42 \times 10^{-40} \\ H - H &= 1.64 \times 10^{-8} \text{ cm} \\ N - H &= 1.02 \times 10^{-8} \text{ cm}. \end{aligned}$$

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[6] These expressions have been calculated from the asymptotic expansion for $D_n(y)$ and are consequently only asymptotically correct. The next order term would change 2α to $2\alpha + a/\alpha^3$ and $4\alpha^3 - 4\alpha$ to $4\alpha^3 - 4\alpha + 3/4\alpha + b/\alpha^3$ in the numerators of Δ_0 and Δ_1 respectively. These corrections are insignificant in the case of ammonia.

These values for C and the molecular dimensions are of considerable importance since because of the interaction between vibration and rotation it appears to be impossible to determine them from an investigation of the fine structure of the infrared bands themselves. We feel that the value of C is accurate to within 2 percent. The chief error in its determination probably lies in the uncertainty with which Δ_0 is known.

The results we have obtained may be compared with an exact solution of a two minima problem by Morse and Rosen.[7] The potential used by them has the same general form as shown in Fig. 1 in the region between the minima. For large positive and negative values of x however the potential rapidly approaches a constant asymptote in a manner which is unlikely to represent the true curve since it would predict far too low a heat of dissociation for the molecule. In spite of this difference between their potential and the one used by us, they obtain $2q_0 = 0.73 \times 10^{-8}$ cm, a value differing from ours by only 4 percent. This agreement illustrates the qualitative result of the W. K. B. approximation, namely that the magnitude of the splitting of the levels depends only upon the potential curve between the two minima. It shows also how insensitive q_0 is to the exact form of the curve in this region providing only it has the general shape of Figs. 1 or 2 and contains a sufficient number of disposable parameters which may be used to fit the observed data Δ_0 and Δ_1 with their theoretical values.

[7] P. M. Morse and N. Rosen, Phys. Rev. **40**, 1039(A) (1932).