The Double Minimum Problem Applied to the Ammonia Molecules[1]

F. T. WALL AND GEORGE GLOCKLER

University of Minnesota, Minneapolis, Minnesota

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A simple quantum-mechanical calculation has been made to obtain the doublet separations for the parallel type frequencies of the ammonias. The calculated values for the separations are: NH_2D (21), NHD_2 (11) and ND_3 (5.8) cm^{-1}, which compare favorably with observed values: NH_2D (20), NHD_2 (10) and ND_3 (3.4) cm^{-1}.

THE symmetrical double minimum problem such as arises in the consideration of the vibrations of the ammonia molecule has been studied by a number of authors.[2] The treatment given by Manning was an exact one which he applied successfully to the molecules NH_3 and ND_3. In the present paper there will be outlined a simple although approximate method of treating the problem and the results will be applied to calculate the doublet separations for the molecules NH_2D, NHD_2 and ND_3. The particular mode of vibration here considered is that in which the nitrogen atom of the ammonia molecule oscillates through the plane of the hydrogens.

A simple potential energy function for such a double minimum problem is given by the expression

$$V = \tfrac{1}{2}k(|x| - l)^2,$$

where $2l$ equals the distance between the minima and k is a force constant. The corresponding potential energy curve consists of portions of two parabolas, and except for the sharp point in the middle, the function should represent fairly well the potential energy of an actual system (see Fig. 1). If we regard the sharp point as a perturbation to the true potential function whatever it may be, it is seen that its contribution to the total energy is small, because the wave functions are small in this region.

A particle subject to the above type of potential energy would behave in the neighborhood of the minima very much like a harmonic oscillator. Accordingly for the lowest pair of energy levels, the wave functions can be approximated by

$$\psi_{0\pm} = N_{0\pm}\{e^{-b(x-l)^2} \pm e^{-b(x+l)^2}\}.$$

The wave function with the positive sign is a symmetric function whereas that with the negative sign is an antisymmetric function. $N_{0\pm}$ is the normalizing factor and b, which for a harmonic oscillator equals $(\pi/h)(km)^{\frac{1}{2}}$, could be taken as a variation parameter. It was found in the calculations, however, that although varying b produced some lowering of the energy levels, very little difference was produced in the separations of the levels, so the above given value of b was retained throughout.

For the next lowest pair of energy levels, the wave functions assumed were

$$\psi_{1\pm} = N_{1\pm}\{(x-l)e^{-b(x-l)^2} \pm (x+l)e^{-b(x+l)^2}\},$$

where the positive sign now corresponds to the *antisymmetric* function and the negative sign to the *symmetric* function. Each of the symmetric functions is, of course, orthogonal to each of the antisymmetric ones, but any one of the functions
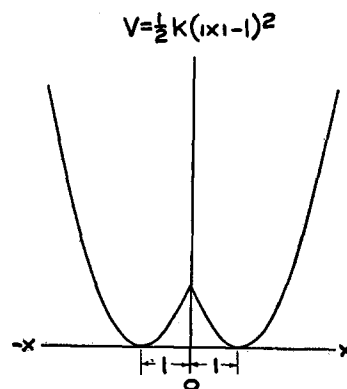

FIG. 1. Potential energy curve for the double minimum for the ammonias. Parallel type frequency ν_3.

[1] This article is based upon part of a thesis to be presented to the faculty of the Graduate School of the University of Minnesota by F. T. Wall in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Morse and Stueckelberg, Helv. Phys. Acta. **4**, 337 (1931); Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932); Rosen and Morse, Phys. Rev. **42**, 210 (1932); M. F. Manning, J. Chem. Phys. **3**, 136 (1935).

TABLE I.

COMPOUND	ν_0(mean)	q^2	$a_0 - s_0$	$a_1 - s_1$	$\Delta\nu$ (calc.)	$\Delta\nu$ (obs.)
NH$_3$	944.5 cm^{-1}	7.02	2.52 cm^{-1}	30.4 cm^{-1}	(33) cm^{-1}	33 cm^{-1}
NH$_2$D	884	7.51	1.49	19.5	21	20
NHD$_2$	813	8.16	.76	10.7	11	10
ND$_3$	747.5	8.88	.35	5.46	5.8	3.4

is not exactly orthogonal to the other function of the same symmetry. To make the orthogonality complete, one could add to $\psi_{1\pm}$ (without the normalizing factor) the term

$$\frac{\mp le^{-2bl^2}}{1 \mp e^{-2bl^2}}\{e^{-b(x-l)^2} \mp e^{-b(x+l)^2}\}.$$

It turns out, however, that $2bl^2 > 7$ and hence the correction for complete orthogonality is very small. Such a refinement is unwarranted by the approximate nature of the problem and so the additional term was omitted.

The energies of the two pairs of lowest levels have been calculated by using the above functions and evaluating the integral

$$W = \int \psi H \psi d\tau,$$

$$H = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + \tfrac{1}{2}k(|x| - l)^2.$$

Making the substitutions

$$b = (\pi/h)(km)^{\frac{1}{2}}, \quad 2bl^2 = q^2$$

and

$$1/2\pi(k/m)^{\frac{1}{2}} = \nu_0,$$

there result the following expressions for the energies:

$$W_{0S} = \frac{h\nu_0}{2}\left\{1 + \frac{2q^2 - 4q^2/(\pi)^{\frac{1}{2}}\int_0^q e^{-n^2}dn - 4/(\pi)^{\frac{1}{2}}qe^{-q^2}}{1 + e^{-q^2}}\right\},$$

$$W_{0A} = \frac{h\nu_0}{2}\left\{1 + \frac{2q^2 - 4q^2/(\pi)^{\frac{1}{2}}\int_0^q e^{-n^2}dn}{1 - e^{-q^2}}\right\},$$

$$W_{1S} = \frac{3h\nu_0}{2}\left\{1 + \frac{2q^2 - 4q^2/(\pi)^{\frac{1}{2}}\int_0^q e^{-n^2}dn - 4q^3/(\pi)^{\frac{1}{2}}e^{-q^2}}{3[1 - (1 - 2q^2)e^{-q^2}]}\right\},$$

$$W_{1A} = \frac{3h\nu_0}{2}\left\{1 + \frac{2q^2 - 4q^2/(\pi)^{\frac{1}{2}}\int_0^q e^{-n^2}dn - 8/(\pi)^{\frac{1}{2}}qe^{-q^2} + 4q^3/(\pi)^{\frac{1}{2}}e^{-q^2}}{3[1 + (1 - 2q^2)e^{-q^2}]}\right\}.$$

The subscripts S and A refer, respectively, to symmetric and antisymmetric states. The quantity q multiplied by $(1/2\pi)(h/\nu_0)^{\frac{1}{2}}$ represents half the "normal coordinate" separation of the minima.

The height of the potential hill is given by $V_{x=0} = (h\nu_0/2)q^2$. Assuming that this height is the same for each of the molecules NH$_3$, NH$_2$D, NHD$_2$ and ND$_3$, there is obtained a relationship between ν_0 and q, namely:

$$\nu_0 q^2 = \text{const.}$$

Using the mean values of the observed frequencies[3] and finding the value of q^2 that gives the correct separation for NH$_3$, it is then possible to compute the other separations. The results are given in Table I. The agreement of the calculated frequency differences $\Delta\nu$ is acceptable, while the calculation of the energy level differences $(a_0 - s_0)$

is not satisfactory in the case of ammonia (NH$_3$) where the experimental value[4] is 0.67 cm^{-1} in comparison with a calculated value of 2.52 cm^{-1}.

The calculated height of the potential hill is 3317 cm^{-1} which is about 50 percent too high since the actual function does not go up to a sharp point as here assumed. In addition to the errors introduced by the approximations made, there is some inaccuracy involved in assuming that the potential hill has the same height for each of the molecules. The height of the hill probably increases with increasing mass because the more massive particles will spread out less when the nitrogen atom penetrates the potential barrier. The effect of increasing the height would be to lower the calculated separation, a change which would be favorable especially in the case of ND$_3$.

[3] Migeotte and Barker, Phys. Rev. 50, 418 (1936).

[4] Wright and Randall, Phys. Rev. 44, 391 (1933).