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INVERSION-VIBRATION AND INVERSION-ROTATION INTERACTIONS IN THE AMMONIA MOLECULE

William T. Weeks

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Doctoral Committee:

Assistant Professor Karl T. Hecht, Chairman
Instructor R. Stephen Berry
Professor David M. Dennison
Assistant Professor William C. Meecham
Associate Professor C. Wilbur Peters

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (CONT'D)

LIST OF FIGURES

I. INTRODUCTION

The vibration-rotation spectrum of ammonia, NH_3, has been the subject of many investigations, both experimental and theoretical, during the course of the past thirty years.(1) Consequently, the main features of this spectrum and the main features of the molecular structure are well understood. Ammonia is a pyramidal molecule (symmetry group C_{3v}) with the N atom approximately 0.38×10^{-8} cm above the plane of the three hydrogen atoms, the N-H distance being approximately 1.02×10^{-8} cm. Its vibrational spectrum shows four fundamentals, two totally symmetric (species A_1), and two doubly degenerate (species E). The rotational structure is that of a symmetric top, the two totally symmetric fundamentals having a parallel band structure and the two doubly degenerate fundamentals having a perpendicular band structure.

Probably the most striking feature of the ammonia spectrum is that every line consists of two components. In the two doubly degenerate fundamentals ν_3 and ν_4 and in the totally symmetric fundamental ν_1 the separation of the two components is small (of the order of 1 cm^{-1}). The two components of the symmetric fundamental ν_2, however, show a much greater splitting (36.6 cm^{-1}). Similarly, the components of the overtones of ν_3, ν_4, and ν_1 are only slightly split whereas the components of the overtones of ν_2 are very widely split. It is well known that the doubling of the ammonia spectrum can be attributed to the existence of two equilibrium configurations for the molecule. Indeed, starting from one equilibrium configuration, the other can be obtained by inverting the nitrogen atom through the plane of the three hydrogen atoms. If the potential energy of the molecule is plotted as a function of the distance of the nitrogen atom from the plane of the hydrogen atoms a curve of the form shown in Figure 2 is obtained. The curve possesses two symmetrically placed minima at the equilibrium configurations, separated by a central maximum at the point where the nitrogen atom passes through the plane of the hydrogen atoms. The energy levels of a particle moving through such a double minimum potential occur in pairs. The lowest lying pair of levels has the smallest separation while the separation of the remaining pairs increases rapidly with increasing energy. Since the potential energy is symmetrical with respect to inversion through the plane of the hydrogen atoms the wave functions corresponding to the energy levels must be either even or odd functions of the inversion coordinate. The even wave functions correspond to the lower members of each pair (+ levels), whereas the odd wave functions correspond to the upper members (- levels). The energy levels are labelled by a quantum number $n_{2\pm}$, where $n_2 = 0, 1, \ldots,$ and so on. The doubling of the ammonia spectrum is interpreted by associating the widely split fundamental ν_2 with a vibrational motion which carries the molecule from one equilibrium configuration to another. Since ammonia has six vibrational degrees of freedom one needs, besides the quantum number $n_{2\pm}$, five other quantum numbers to describe completely the vibrational energy levels. Following the notation used by Benedict, Plyler, and Tidwell$^{(6-9)}$, a vibrational level will be described by the sextet of numbers $(n_1, n_2^{\pm}, n_3^{\ell_3}, n_4^{\ell_4})$. A molecule in a given vibrational state can, of course, be in any one of a number of rotational states. In order to specify an energy level completely, one must give, besides the vibrational quantum numbers, the total angular momentum quantum number J and the quantum number K associated with the component of angular momentum along the symmetry axis of the molecule. Thus an energy level of ammonia is specified completely by the octet of quantum numbers (n_1, $n_2\pm$, $n_3^{\ell_3}$, $n_4^{\ell_4}$, J, K).

Infrared selection rules are determined by the dipole moment vector of the molecule. Since the dipole moment changes sign when the molecule is reflected through its center of mass, it follows that infrared transitions are allowed only between states of opposite parity. The parity of the level (n_1, $n_2\pm$, $n_3^{\ell_3}$, $n_4^{\ell_4}$, J, K) is given by $\pm (-1)^K$ where the plus sign is taken for n_2+ (+ levels) and the minus sign for n_2- (- levels). Thus, for parallel bands ($\Delta K = 0$), transitions between two + levels or between two - levels are forbidden. For perpendicular bands ($\Delta K = \pm 1$), transitions from + to - levels or - to + levels are forbidden. The action of this selection rule in the formation of inversion doublets in the frequency spectrum of ammonia is illustrated in Figure 1.

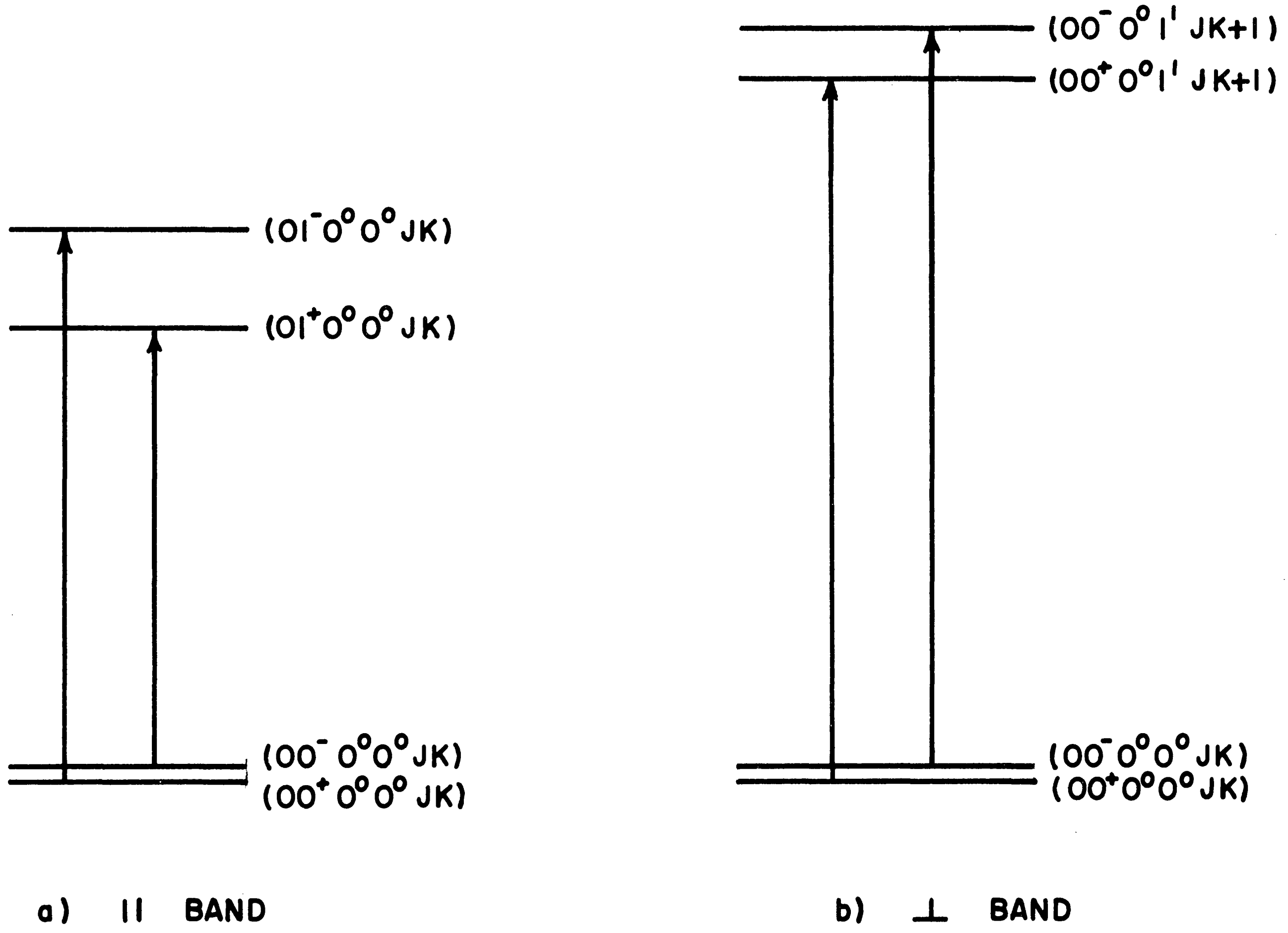
The problem of a particle moving in a double minimum potential was first solved by Dennison and Uhlenbeck.(2) Using the WKB method these authors found, for energy levels lying below the central maximum (c.f. Figure 2)

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

where

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

In Equation (1), $\Delta_n = E_n- - E_n+$, ν is the classical frequency of oscillation in one of the potential minima, and $E_n = \frac{1}{2}[E_n- + E_n+]$. X_n is the smallest positive value of x satisfying the equation $V_{(x)} = E_n$



a) || BAND

b) ⊥ BAND

Figure 1. Formation of Inversion Doublets.

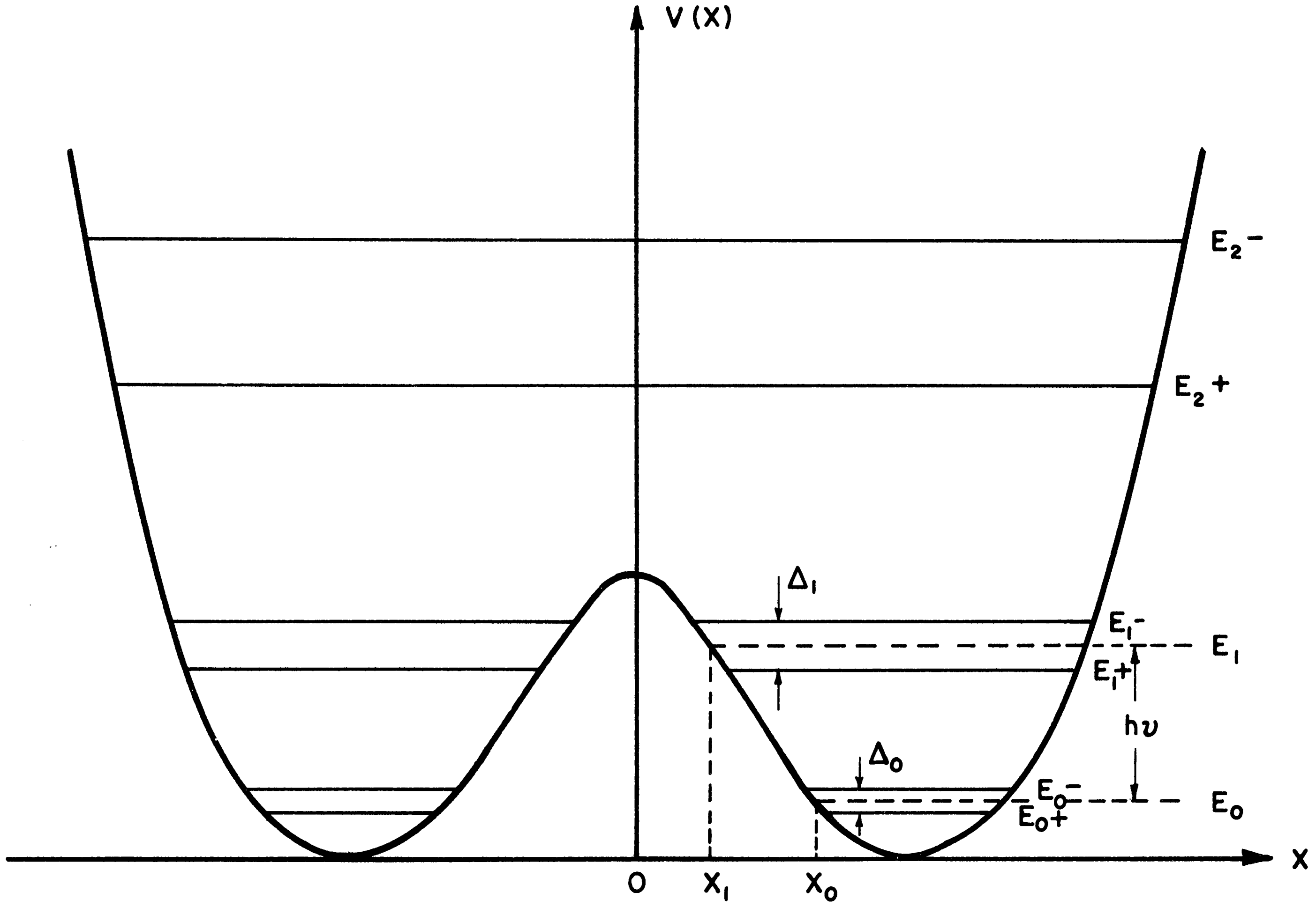


Figure 2. Double Minimum Potential.

(inner classical turning point). Using as data the values of Δ_0, Δ_1, and $h\nu$ obtained from experimental work on the ammonia spectrum, Dennison and Uhlenbeck were able to determine the values of the parameters in a simple potential curve consisting of two equal parabolae joined by a horizontal straight line. The values they obtained correspond to a potential barrier height of 1769 cm^{-1} and a distance of 0.38×10^{-8} cm between the nitrogen atom and the plane of the hydrogen atoms.

The double minimum problem was considered also by Manning(3) who showed that the one dimensional Schroedinger equation could be solved numerically with a potential of the form

$$\frac{V}{hc} = a \operatorname{sech}^4(X/2\rho) - b \operatorname{sech}^2(X/2\rho) \quad . \tag{2}$$

The constants obtained by Manning from the data for ammonia are $a = 66{,}551 \text{ cm}^{-1}$, $b = 109{,}619 \text{ cm}^{-1}$, and $\rho = 0.04793\,(h/c\mu)^{1/2}$ where μ is the reduced mass for the vibration. By taking appropriate values for the reduced mass, Manning was able to calculate the energy levels for both NH_3 and ND_3. His results are given in Table I.

A theoretical treatment of the dependence of the inversion splitting on the rotational quantum numbers J and K has been given by Sheng, Barker, and Dennison.(4) Their method is based on the WKB splitting formula, Equation (1). They begin by noting that in the lowest order ammonia Hamiltonian

$$H = T + V_0 + \frac{1}{2I_B}(P_x^2 + P_y^2) + \frac{1}{2I_C} P_z^2$$

the moments of inertia I_B and I_C will be strongly dependent on the inversion coordinate. Here P_x, P_y and P_z are the three components of the total angular momentum of the molecule. T is the vibrational kinetic energy and V_0 the potential energy. Since the rotational part of H is diagonal in J and K they obtain a Hamiltonian

$$H = T + V_0 + \frac{\hbar^2}{2I_B^e}\left[J(J+1)-K^2\right] + \frac{\hbar^2}{2I_C^e}K^2$$
$$+ \frac{\hbar^2}{2}\left(\frac{1}{I_B} - \frac{1}{I_B^e}\right)\left[J(J+1)-K^2\right] + \frac{\hbar^2}{2}\left(\frac{1}{I_C} - \frac{1}{I_C^e}\right)K^2$$

where I_B^e and I_C^e are the equilibrium values of the moments of inertia. Regarding V_0 as depending only on the inversion coordinate x, they obtain an effective one dimensional potential energy function

$$V(x) = V_0(x) + \delta V(x) \tag{3}$$

where

$$\delta V(x) = \frac{\hbar^2}{2}\left(\frac{1}{I_B} - \frac{1}{I_B^e}\right)\left[J(J+1)-K^2\right] + \frac{\hbar^2}{2}\left(\frac{1}{I_C} - \frac{1}{I_C^e}\right)K^2 .$$

Combining (3) with Equation (1) and expanding the exponential, they obtain

$$\Delta_n = \Delta_n^0 \left[1 - \frac{2\mu}{\hbar}\int_0^{x_n} \frac{\delta V(x)}{\sqrt{2\mu(V_0(x) - E_n)}}\,dx + \ldots\right] \tag{4}$$

for the inversion splitting. In Equation (4), Δ_n^0 is the inversion splitting for the non-rotating molecule and μ is a reduced mass for the inversion motion. Using Manning's potential, Equation (2), for $V_0(x)$, and assuming the inversion motion along a parabolic path which approaches the two equilibrium configurations in the direction required by the appropriate normal coordinate, Sheng, Barker, and Dennison find, in wavenumbers

$$\Delta_1 = \Delta_1^0 - .162\,[J(J+1) - K^2] + .060\,K^2$$

for the first vibrational state of ammonia. This calculation has been repeated by Hadley and Dennison(5) for both the ground state and first excited state of ammonia. Using the same path for the inversion coordinate as Sheng, Barker, and Dennison, they find

$$\Delta_1 = \Delta_1^0 - .156\,[J(J+1) - K^2] + .063\,K^2$$

$$\Delta_0 = \Delta_0^0 - .0035\,[J(J+1) - K^2] + .0018\,K^2 \quad .$$

By modifying the path of the inversion motion Hadley and Dennison found the following alternate set of numbers for Δ_1 and Δ_0.

$$\Delta_1 = \Delta_1^0 - .21\,[J(J+1) - K^2] + .03\,K^2$$

$$\Delta_0 = \Delta_0^0 - .0047\,[J(J+1) - K^2] + .0012\,K^2 \quad .$$

The most recent experimental values of these numbers, as given by Benedict, Plyler and Tidwell(6-9), are

$$\Delta_1 = 35.81 - .1817\,[J(J+1) - K^2] + .0721\,K^2$$

$$\Delta_0 = .7934 - .005054\,[J(J+1) - K^2] + .001998\,K^2 \, .$$

Recent investigations of the ammonia spectrum by Benedict, Plyler, and Tidwell(6-9) and Garing, Nielsen and Rao(10) have uncovered a wealth of new information. Since the theory reviewed above is only a first approximation to the actual situation in ammonia it is to be expected that some extension and refinement of theory will be needed to account for some of the new data. Thus, a re-examination of the theory of the inversion spectrum of ammonia seems pertinent and it is with this objective in mind that the present investigation has been undertaken. Some of the available data on ammonia is summarized in Tables II, III and IV. Examination of these tables reveals some interesting variations in the inversion splittings. From Table III one sees that although the magnitude of the inversion-vibration splitting depends mainly on the quantum number n_2 there is also a significant dependence on the remaining quantum numbers. If the one dimensional models which have been used in the past were strictly valid then all levels with $n_2 = 0$ would have the same splitting, namely .793 cm^{-1} whereas the observed splittings for these levels vary from .35 to 2.24 cm^{-1}. Similarly, all levels with $n_2 = 1$ would have the splittings 35.81 cm^{-1}. Actually, the observed splittings vary from 18.49 to 45.4 cm^{-1}.

The inversion-rotation splittings offer an even greater challenge. The coefficients $B^- - B^+$ and $C^- - C^+$ in the inversion-rotation splitting formula

$$\Delta = \Delta^0 + (B^- - B^+)[J(J+1) - K^2] + (C^- - C^+)K^2$$

are given in Table IV. The main variations in these coefficients are given by the inversion quantum number n_2. In particular, the magnitudes of $B^- - B^+$ and $C^- - C^+$ increase with n_2, as n_2 goes from 0 to 2, but show a marked decrease for $n_2 = 3$. The coefficients of $J(J+1) - K^2$ and K^2 cannot be computed by means of the WKB formula, Equation (4), for levels with n_2 equal to 2 or 3 since these levels lie above the central potential barrier. Furthermore, the coefficients of $J(J+1) - K^2$ and K^2

TABLE I

MANNING'S ENERGY LEVELS (cm^{-1})

	NH_3			ND_3		
Level	Calc.	Obs(1935)	Obs(1959)	Calc.	Obs(1935)	Obs(1959)
$00^+0^00^0$	0	0	0	0	0	0
$00^-0^00^0$	0.83	0.67	0.793	< 0.2		0.053
$01^+0^00^0$	935	932	932.51	746.0	746	745.7
$01^-0^00^0$	961	964	968.32	748.5	755	749.4
$02^+0^00^0$	1610	1600	1597.42	1379	1363	1359
$02^-0^00^0$	1870	1910	1882.16	1434	1437	1429
$03^+0^00^0$	2360	2380	2383.46	1852	1831	1830
$03^-0^00^0$	2840		2895.48	2140		2106.60

TABLE II

VIBRATIONAL LEVELS OF AMMONIA (cm^{-1})

$n_1 n_3^{\ell_3} n_4^{\ell_4}$	$n_2^{\pm} = 0^+$	0^-	1^+	1^-	2^+	2^-	3^+	3^-
				NH_3				
$0\ 0^0\ 0^0$	0.00	0.793	932.51	968.32	1597.42	1882.16	2383.46	2895.48
$0\ 0^0\ 1^1$	1628.26	1629.26	2539.6	2585.0				
$0\ 0^0\ 2^0$	3215.59	3217.83						
$1\ 0^0\ 0^0$	3335.72	3336.71	4294.51	4320.06				
$0\ 1^1\ 0^0$	3443.59	3443.94	4416.91	4435.40				
$1\ 0^0\ 1^1$	4955.94	4956.8						
$0\ 1^1\ 1^1$	5052.61	5053.18	6012.72	6036.40				
$0\ 2^2\ 0^0$	6849.96	6850.39						
$0\ 0^0\ 2^2$	3239.74	3241.16						
				ND_3				
$0\ 0^0\ 0^0$	0.00	0.053	745.7	749.4	1359	1429	1830	2106.60
⎧ $0\ 0^0\ 2^0$	(2359?)		3093.01	3099.46				
⎩ $1\ 0^0\ 0^0$	2420.05	2420.64	3171.89	3175.87				
$0\ 1^1\ 0^0$			3327.94	3329.56				
⎧ $0\ 1^1\ 2^0$	4887.29	4887.67						
⎩ $1\ 1^1\ 0^0$	4938.44							

Level with brackets are in Fermi resonance

TABLE III

VIBRATION-INVERSION SPLITTINGS IN NH_3 (cm^{-1})

n_1	$n_2^{\pm}$	$n_3^{\ell 3}$	$n_4^{\ell 4}$	Inversion Splitting
0	0	0^0	0^0	.793
0	1	0^0	0^0	35.81
0	2	0^0	0^0	284.74
0	3	0^0	0^0	512.02
0	0	1^1	0^0	.35
0	0	2^2	0^0	.43
0	0	0^0	1^1	1.01
0	0	0^0	2^0	2.24
0	0	0^0	2^2	1.42
0	0	1^1	1^1	.57
1	0	0^0	0^0	.99
1	0	0^0	1^1	.86
0	1	1^1	0^0	18.49
0	1	0^0	1^1	45.4
0	1	1^1	1^1	23.68
1	1	0^0	0^0	25.55

TABLE IV

ROTATION-INVERSION SPLITTINGS IN NH_3 (cm^{-1})

$$\Delta = \Delta_n + (B_n^- - B_n^+)[J(J+1) - K^2] + (C_n^- - C_n^+)K^2$$

n_1	$n_2^{\pm}$	$n_3^{\ell 3}$	$n_4^{\ell 4}$	$B^- - B^+$	$C^- - C^+$
0	0	0^0	0^0	-.005054	.001998
0	1	0^0	0^0	-.1817	.0721
0	2	0^0	0^0	-.535	.231
0	3	0^0	0^0	-.3041	.1034
1	0	0^0	0^0	-.012	.003
0	0	1^1	0^0	-.0036	.0007
0	0	0^0	1^1	.048	.011
1	1	0^0	0^0	-.1265	.0470
0	1	1^1	0^0	-.0984	.0429
0	1	0^0	1^1	-.191	.097
0	1	1^1	1^1	-.130	.054

have a significant dependence on the remaining vibrational quantum numbers n_1, $n_3^{\ell_3}$, and $n_4^{\ell_4}$. If a one-dimensional model were strictly valid all states with $n_2 = 1$ would have $B^- - B^+ = -.1817$ cm^{-1} and $C^- - C^+ = .0721$ cm^{-1} whereas for these levels the observed values of $B^- - B^+$ vary from -.0984 to -.191 cm^{-1} while the observed values of $C^- - C^+$ vary from .0429 to .097 cm^{-1}. The dependence of $B^- - B^+$ and $C^- - C^+$ on the vibrational quantum numbers is considerably more striking in the levels with $n_2 = 0$. Whereas a one-dimensional theory would imply that $C^- - C^+ = .001998$ cm^{-1} and $B^- - B^+ = -.005054$ cm^{-1} for all levels with $n_2 = 0$, the observed values of $C^- - C^+$ are seen to vary from .0007 to .011 cm^{-1}. The observed values of $B^- - B^+$ vary from -.0036 cm^{-1} to -.012 cm^{-1} with the exception of the levels $(0, 0^{\pm}, 0^0, 1^1)$ where $B^- - B^+$ changes sign to become .048 cm^{-1}.

Although the inversion splitting is intimately related to the single degree of freedom associated with the normal mode ν_2, the mode in which the pyramid height changes most drastically, it is clear from the new experimental information that there must be strong interactions between the inversion coordinate and the remaining vibrational coordinates. Indeed, it appears that a development of the complete vibration-rotation Hamiltonian is needed to explain the variation of the rotation-inversion constants with the vibrational quantum numbers. In this thesis a scheme is proposed for describing the interaction between the inversion coordinate and the remaining vibrational coordinates. The development of this scheme follows a course roughly parallel to the conventional treatment of molecules. In the usual normal coordinate treatment of molecules the potential energy expansion, in lowest approximation, is equivalent to the potential of a system of uncoupled harmonic oscillators. Interactions between the vibrational motions are contained in the cubic and quartic terms of the potential expansion. Normally, the cubic and quartic part of the potential can be treated as a perturbation. The analogous development for ammonia is obtained by representing the potential, in lowest approximation, by a double minimum potential, involving the inversion coordinate, plus the potential of a system of uncoupled harmonic oscillators involving the five remaining vibration coordinates but not the inversion coordinate. Interactions between the inversion coordinate and the remaining vibrational coordinates are obtained by interpreting the parameters occurring in the double minimum potential as functions of the vibrational coordinates. For example, if Manning's potential were used for the double minimum potential the parameters a, b, and ρ would be interpreted as functions of the vibrational coordinates. The multi-dimensional potential function obtained in this way leads to a Schroedinger equation far too complicated to solve exactly. Indeed, the problem of obtaining solutions seems completely hopeless unless the interaction terms can be written in such a way that perturbation theory can be used. One might expect that this can be done since the inversion splitting, although a drastic function of the inversion quantum number n_2, is a relatively mild function of the quantum numbers n_1, n_3 and n_4. In this thesis the interaction terms are obtained by expanding the parameters appearing in the double minimum potential in a Taylor series in the vibrational coordinates. The interaction terms obtained in this way are roughly analogous to the cubic and quartic terms in the conventional potential expansion and are treated by means of perturbation theory. The real justification for the use of perturbation theory, however, must come a posteriori.

The potential energy function used in this thesis leads to a fair overall description of the "pure inversion" levels $(0, n_{2\pm}, 0^0, 0^0)$ and accounts rather well for the dependence of the inversion-vibration splittings on the quantum numbers n_3 and n_4 belonging to the two doubly degenerate modes. Unfortunately the potential fails to account for the dependence of the inversion-vibration splitting on the quantum number n_1. The rotation-inversion constants $B^- - B^+$ and $C^- - C^+$ have been calculated, in first approximation, for the levels $(0, n_2, 0^0, 0^0)$ where $n_2 = 0$, 1, 2 and 3. The calculated results compare favorably with the observed values. The problem of setting up the complete rotation-vibration Hamiltonian and its development in orders of magnitude is considered. Although a calculation of all the rotation-inversion constants on the basis of this Hamiltonian has not proved practical some insight into the dependence of $B^- - B^+$ and $C^- - C^+$ on the vibrational quantum numbers is gained.

II. INTERNAL COORDINATES AND THE VIBRATIONAL KINETIC ENERGY

Six internal coordinates are required to describe the vibrational motions of the ammonia molecule. In order to introduce the internal coordinates it is convenient to start with a cartesian reference frame attached to the molecule and with origin at the center of mass of the molecule as shown in Figure 3. Let x_i, y_i and z_i be the cartesian coordinates of the i^{th} atom with respect to this reference frame. The subscripts $i = 1, 2,$ and 3 refer to hydrogen atoms and $i = 4$ to the nitrogen atom. Let m be the mass of a hydrogen atom and M the mass of the nitrogen atom. The twelve cartesian coordinates of the four atoms can be replaced by six internal coordinates $u_i (i = 1, \ldots, 6)$ by means of the scheme (c.f. Figure 4).*

$$x_1 = -\frac{\sqrt{3}}{2} u_1 - \frac{\sqrt{3}}{2} u_3 - \frac{1}{2} u_4 - \frac{M}{M+3m} u_6$$

$$y_1 = -\frac{1}{2} u_1 + \frac{1}{2} u_3 - \frac{\sqrt{3}}{2} u_4 - \frac{M}{M+3m} u_5$$

$$z_1 = -\frac{M}{M+3m} u_2 - \frac{M}{M+3m} \left(\frac{u_2}{u_1}\right) u_5 - \frac{\sqrt{3}\, M}{M+3m} \left(\frac{u_2}{u_1}\right) u_6$$

$$x_2 = \frac{\sqrt{3}}{2} u_1 + \frac{\sqrt{3}}{2} u_3 - \frac{1}{2} u_4 - \frac{M}{M+3m} u_6$$

$$y_2 = -\frac{1}{2} u_1 + \frac{1}{2} u_3 + \frac{\sqrt{3}}{2} u_4 - \frac{M}{M+3m} u_5$$

$$z_2 = -\frac{M}{M+3m} u_2 - \frac{M}{M+3m} \left(\frac{u_2}{u_1}\right) u_5 + \frac{\sqrt{3}\, M}{M+3m} \left(\frac{u_2}{u_1}\right) u_6$$

---

* These coordinates are somewhat similar to those used by Slawsky and Dennison.(15)

$$
\begin{aligned}
x_3 &= u_4 - \frac{M}{M+3m} u_6 \\
y_3 &= u_1 - u_3 - \frac{M}{M+3m} u_5 \\
z_3 &= -\frac{M}{M+3m} u_2 + \frac{2M}{M+3m}\left(\frac{u_2}{u_1}\right) u_5 \\
x_4 &= \frac{3m}{M+3m} u_6 \\
y_4 &= \frac{3m}{M+3m} u_5 \\
z_4 &= \frac{3m}{M+3m} u_2 \quad .
\end{aligned}
\qquad (5)
$$

The physical significance of the internal coordinates is easily discovered. Consider first the case where $u_3 = u_4 = u_5 = u_6 = 0$. One then finds that

$$
\begin{aligned}
z_4 - z_1 = z_4 - z_2 = z_4 - z_3 = u_2 \\
y_3 = -2y_1 = -2y_2 = u_1 \quad .
\end{aligned}
$$

Thus u_2 is the physical height of the ammonia pyramid and u_1 is the distance from a hydrogen atom to the center of the hydrogen triangle. All the configurations that arise when $u_3 = u_4 = u_5 = u_6 = 0$ have pyramidal symmetry. That is, the hydrogen atoms form an equilateral triangle and the three N-H bond lengths are equal. The coordinates u_3, u_4, u_5, and u_6 describe motions in which the molecular framework is distorted from pyramidal symmetry. The coordinates u_3 and u_4 describe motions in which the nitrogen atom remains stationary and the hydrogen atoms undergo displacements parallel to the x - y plane.

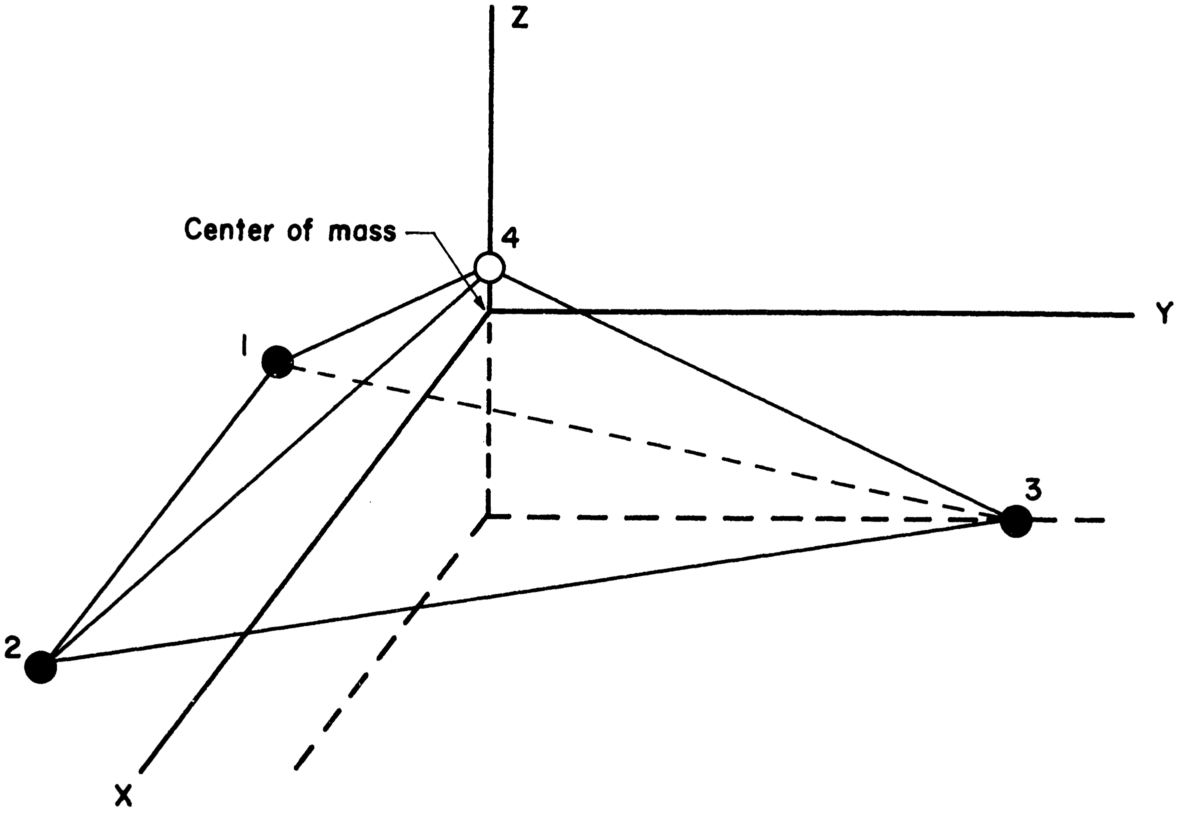


Figure 3. Equilibrium Configuration of Ammonia.

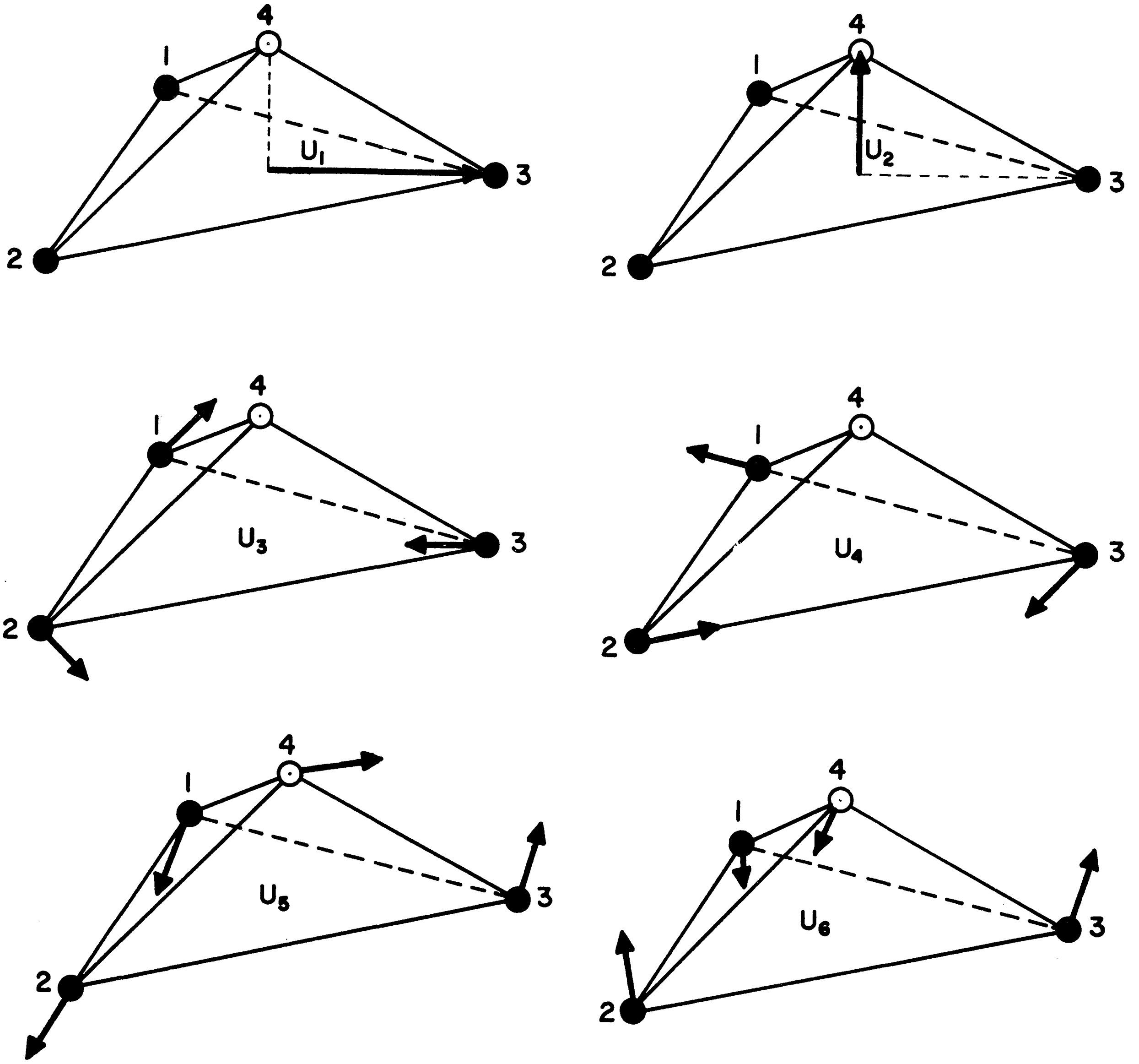


Figure 4. Internal Coordinates.

u_5 represents a displacement of the nitrogen atom parallel to the y-axis with a corresponding tipping of the hydrogen triangle, the motion being parallel to the z-y plane. u_6 represents a displacement of the nitrogen atom parallel to the x-axis with a corresponding tipping of the hydrogen triangle, this time with the motion parallel to the x - z plane. The motions represented by the internal coordinates are illustrated in Figure 4. The two equilibrium configurations of ammonia are given by

$$u_1 = u_1^0 \qquad u_2 = \pm u_2^0 \qquad u_3 = u_4 = u_5 = u_6 = 0$$

where u_1^0 is approximately .94 x 10^{-8} cm and u_2^0 is approximately .38 x 10^{-8} cm. Inversion of the molecule through a plane passing through the center of mass and perpendicular to the symmetry axis is accomplished by means of the transformation

$$u_2 \longrightarrow -u_2 \qquad u_i \longrightarrow u_i \ (i \neq 2)$$

which implies

$$z_i \longrightarrow -z_i \qquad x_i \longrightarrow x_i \qquad y_i \longrightarrow y_i \quad (i = 1, 2, 3, 4) .$$

It is clear that the coordinates u_1 and u_2 are totally symmetric with respect to the six operations of the symmetry point group C_{3v} (A_1 type vibrations). Furthermore u_3 and u_4 transform among themselves under the operations of C_{3v} and are of type E, as are u_5 and u_6.

One may verify quite quickly by means of Equation (5) that the three quantities

$$m(x_1 + x_2 + x_3) + Mx_4$$
$$m(y_1 + y_2 + y_3) + My_4$$
$$m(z_1 + z_2 + z_3) + Mz_4$$

vanish identically. Furthermore the three quantities

$$\sum_{i=1}^{3} m(y_i\dot{z}_i - z_i\dot{y}_i) + M(y_4\dot{z}_4 - z_4\dot{y}_4)$$

$$\sum_{i=1}^{3} m(z_i\dot{x}_i - x_i\dot{z}_i) + M(z_4\dot{x}_4 - x_4\dot{z}_4)$$

$$\sum_{i=1}^{3} m(x_i\dot{y}_i - y_i\dot{x}_i) + M(x_4\dot{y}_4 - y_4\dot{x}_4)$$

vanish for all symmetric pyramidal configurations, that is, whenever $u_3 = u_4 = u_5 = u_6 = 0$. The first triplet of relations shows that the origin of the molecule-fixed reference frame always remains at the center of mass of the molecule. The second triplet of relations shows that the molecule-fixed reference frame is so oriented that the three components of internal angular momentum, as seen in this frame, are always zero whenever the molecule is in a pyramidal symmetry configuration. It should be noted that the condition on the orientation of the molecule-fixed reference frame is a little more stringent than the condition usually applied in molecular physics.*

The vibrational kinetic energy of the molecule can be obtained quite easily. Upon introducing the mass weighted internal coordinates

$$X_1 = \sqrt{3m}\, u_1 \qquad X_2 = \sqrt{\mu}\, u_2$$
$$X_3 = \sqrt{3m}\, u_3 \qquad X_5 = \sqrt{\mu}\, u_5$$
$$X_4 = \sqrt{3m}\, u_4 \qquad X_6 = \sqrt{\mu}\, u_6$$

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* The usual condition is that the internal angular momentum should vanish when the molecule is in its equilibrium configuration.

where

$$\mu = \frac{3mM}{M+3m}$$

one finds

$$\begin{aligned} T_{vib} &= \tfrac{1}{2}(\dot{x}_1^2 + \dot{x}_2^2) + \tfrac{1}{2}(\dot{x}_3^2 + \dot{x}_4^2) \\ &+ \tfrac{1}{2}\left[1 + 2\left(\frac{x_2}{x_1}\right)^2\right](\dot{x}_5^2 + \dot{x}_6^2) \\ &+ 2(x_5\dot{x}_5 + x_6\dot{x}_6)\frac{x_2}{x_1}\frac{d}{dt}\left(\frac{x_2}{x_1}\right) \\ &+ (x_5^2 + x_6^2)\left[\frac{d}{dt}\left(\frac{x_2}{x_1}\right)\right]^2 \end{aligned} \qquad (6)$$

Before introducing the final set of coordinates to be used in this investigation it will be helpful to review briefly the normal coordinate treatment of ammonia. Consider the purely fictitious case where the potential barrier separating the two equilibrium configurations becomes so high that the probability of an inversion from one configuration to another is negligibly small. In this limiting case the molecule would execute small amplitude oscillations about a single equilibrium configuration. Then the coordinates x_3, x_4, x_5, and x_6 would never differ very much from zero and x_1 and x_2 would never differ very much from their equilibrium values x_1^0 and x_2^0. The vibrational kinetic energy would be given to a very good approximation by

$$T_{vib} = \tfrac{1}{2}(\dot{\delta}_1^2 + \dot{\delta}_2^2) + \tfrac{1}{2}(\dot{x}_3^2 + \dot{x}_4^2) + \frac{1}{2\rho_0}(\dot{x}_5^2 + \dot{x}_6^2)$$

where

$$\delta_1 = x_1 - x_1^0$$
$$\delta_2 = x_2 - x_2^0$$

and

$$\frac{1}{\rho_0} = 1 + 2\left(\frac{x_2^0}{x_1^0}\right)^2$$

The potential energy would be replaced by the leading terms in its Taylor expansion about the equilibrium configuration. In view of the symmetry properties of the coordinates, the leading terms in the potential energy expansion would be

$$V = \frac{K_{11}}{2}\delta_1^2 + K_{12}\delta_1\delta_2 + \frac{K_{22}}{2}\delta_2^2 + \frac{K_{33}}{2}(X_3^2 + X_4^2)$$

$$+ K_{35}(X_3X_5 + X_4X_6) + \frac{K_{55}}{2}(X_5^2 + X_6^2) \quad .$$

Upon introduction of the normal coordinates

$$Q_1' = \cos\psi\,\delta_1 + \sin\psi\,\delta_2$$

$$Q_2' = -\sin\psi\,\delta_1 + \cos\psi\,\delta_2$$

$$Q_{3x}' = \cos\tau\,X_4 + \sin\tau\,\frac{X_6}{\sqrt{\rho_0}}$$

$$Q_{4x}' = -\sin\tau\,X_4 + \cos\tau\,\frac{X_6}{\sqrt{\rho_0}}$$

$$Q_{3y}' = \cos\tau\,X_3 + \sin\tau\,\frac{X_5}{\sqrt{\rho_0}}$$

$$Q_{4y}' = -\sin\tau\,X_3 + \cos\tau\,\frac{X_5}{\sqrt{\rho_0}}$$

where

$$\cos 2\psi = \frac{\dfrac{K_{11} - K_{22}}{2}}{\sqrt{\left(\dfrac{K_{11} - K_{22}}{2}\right)^2 + K_{12}^2}}$$

$$\cos 2\tau = \frac{\dfrac{K_{33} - \rho_0 K_{55}}{2}}{\sqrt{\left(\dfrac{K_{33} - \rho_0 K_{55}}{2}\right)^2 + \rho_0 K_{35}^2}} \qquad (7)$$

the kinetic and potential energies assume the simple forms

$$T_{vib} = \frac{1}{2}\left(\dot{Q}_1'^2 + \dot{Q}_2'^2 + \dot{Q}_{3x}'^2 + \dot{Q}_{3y}'^2 + \dot{Q}_{4x}'^2 + \dot{Q}_{4y}'^2\right)$$

and

$$V = \frac{\lambda_1}{2} Q_1'^2 + \frac{\lambda_2}{2} Q_2'^2 + \frac{\lambda_3}{2}\left(Q_{3x}'^2 + Q_{3y}'^2\right) + \frac{\lambda_4}{2}\left(Q_{4x}'^2 + Q_{4y}'^2\right)$$

where

$$\left.\begin{matrix}\lambda_1 \\ \lambda_2\end{matrix}\right\} = \frac{K_{11} + K_{22}}{2} \pm \left[\left(\frac{K_{11} - K_{22}}{2}\right)^2 + K_{12}^2\right]^{1/2} \qquad (8)$$

and

$$\left.\begin{matrix}\lambda_3 \\ \lambda_4\end{matrix}\right\} = \frac{K_{33} + \rho_0 K_{55}}{2} \pm \left[\left(\frac{K_{33} - \rho_0 K_{55}}{2}\right)^2 + \rho_0 K_{35}^2\right]^{1/2} . \qquad (9)$$

The corresponding normal frequencies are given by

$$\omega_i = \frac{1}{2\pi c}\sqrt{\lambda_i}\ (\mathrm{cm}^{-1})\ ;\ i = 1,2,3,4 \ .$$

The quadratic force constants K_{ij} appearing above are mass dependent quantities. However, they are related to the mass independent force constants a, b, c, α, β, and γ used by Dennison.(11)

$$K_{11} = \frac{b}{m} \qquad K_{33} = \frac{\beta}{m}$$

$$K_{12} = \frac{c}{\sqrt{m\mu}} \qquad K_{35} = \frac{\gamma}{\rho_0\sqrt{m\mu}}$$

$$K_{22} = \frac{a}{\mu} \qquad K_{55} = \frac{\alpha}{\rho_0^2\,\mu} \qquad (10)$$

The quadratic force constants are merely the second derivatives of the potential energy function, evaluated at an equilibrium configuration.

It should be born in mind that the quadratic force constants are well defined quantities for any potential energy function possessing a minimum even if the quadratic terms in the Taylor expansion are a very poor approximation to the true potential. The potential energy function of the ammonia molecule cannot be represented by the leading terms in its Taylor expansion. Even so, there is a well defined set of quadratic force constants associated with the ammonia potential. Indeed, if the potential energy function for ammonia were known, the force constants could be calculated by simple differentiation. Because of the symmetry of the potential, evaluation of the derivatives at either of the two equilibrium configurations will lead to the same set of force constants. In practice, complete potential energy functions for molecules are never known. The values of the quadratic force constants must be inferred from observed spectra. This is as true for ammonia as for any other molecule. For the present it is sufficient to note that the constants K_{ij} are meaningful quantities even in the case of ammonia.

The final set of coordinates to be used in the ensuing calculations now can be introduced. Let

$$Q_{3x} = \cos\tau\, X_4 + \sin\tau \frac{X_6}{\sqrt{\rho(X_1, X_2)}}$$

$$Q_{4x} = -\sin\tau\, X_4 + \cos\tau \frac{X_6}{\sqrt{\rho(X_1, X_2)}}$$

$$Q_{3y} = \cos\tau\, X_3 + \sin\tau \frac{X_5}{\sqrt{\rho(X_1, X_2)}}$$

$$Q_{4y} = -\sin\tau\, X_3 + \cos\tau \frac{X_5}{\sqrt{\rho(X_1, X_2)}} \qquad (11)$$

where
$$\rho(x_1, x_2) = \frac{1}{1 + 2\left(\frac{x_2}{x_1}\right)^2}$$

and the constant, τ, is defined by Equation (7). The coordinates Q_{3x}, Q_{3y}, Q_{4x} and Q_{4y} are defined in such a way that they become normal coordinates in the vicinity of the equilibrium configurations of ammonia. Note that in general they depend on the totally symmetric coordinates x_1 and x_2. When expressed in terms of new coordinates, the vibrational kinetic energy, Equation (6), becomes

$$T_{vib} = \frac{1}{2}(\dot{x}_1^2 + \dot{x}_2^2) + \frac{1}{2}(\dot{Q}_{3x}^2 + \dot{Q}_{3y}^2) + \frac{1}{2}(\dot{Q}_{4x}^2 + \dot{Q}_{4y}^2)$$
$$+ \left[\sin\tau\,\vec{R}_3 + \cos\tau\,\vec{R}_4\right]^2 \cdot \left[\frac{x_1\dot{x}_2 - x_2\dot{x}_1}{x_1^2 + 2x_2^2}\right]^2 \qquad (12)$$

where $\vec{R}_3$ is a vector with components Q_{3x}, Q_{3y} and $\vec{R}_4$ a vector with components Q_{4x}, Q_{4y}. Finally, the coordinates x_1 and x_2 are replaced by a pair of coordinates σ and ζ defined by

$$x_1 = a_0 \sinh\sigma \cos\zeta$$
$$x_2 = a_0 \cosh\sigma \sin\zeta$$
$$a_0^2 = (x_2^0)^2 - (x_1^0)^2 + x_1^0 x_2^0\left(\frac{K_{11} - K_{22}}{K_{12}}\right)$$
$$\sigma \geq 0 \quad ; \quad -\frac{\pi}{2} \leq \zeta \leq +\frac{\pi}{2} \quad . \qquad (13)$$

The constant, a_0, in Equation (13) has been defined in such a way that, in the neighborhood of an equilibrium configuration, $\delta\sigma = \sigma - \sigma_0$ and $\delta\zeta = \zeta - \zeta_0$ are proportional to the two totally symmetric normal coordinates of ammonia. In fact, it is easy to show that this choice of a_0 implies

$$\frac{1}{2}(\dot{\delta}_1^2+\dot{\delta}_2^2) = \frac{a_0^2}{2}(\cosh^2\sigma_0 - \sin^2\zeta_0)(\delta\dot{\sigma}^2+\delta\dot{\zeta}^2)$$

$$\frac{K_{11}}{2}\delta_1^2 + K_{12}\delta_1\delta_2 + \frac{K_{22}}{2}\delta_2^2 = \frac{a_0^2}{2}(\cosh^2\sigma_0 - \sin^2\zeta_0)(\lambda_1\,\delta\sigma^2 + \lambda_2\,\delta\zeta^2).$$

Here, σ_0 and $\pm\,\zeta_0$ are the equilibrium values of σ and ζ. From the equations above, one sees that σ and ζ are related to the normal coordinates Q_1' and Q_2' by the relations

$$Q_1' = \left[a_0^2(\cosh^2\sigma_0 - \sin^2\zeta_0)\right]^{1/2}\delta\sigma$$

$$Q_2' = \left[a_0^2(\cosh^2\sigma_0 - \sin^2\zeta_0)\right]^{1/2}\delta\zeta \quad .$$

The physical significance of σ and ζ is best seen by inverting Equations (13) and replacing x_1 and x_2 by their more physical counterparts u_1 and u_2. It will be recalled, that u_2 is the height of the ammonia pyramid and u_1 is the distance from a hydrogen atom to the center of the hydrogen triangle.

One finds,

$$\left(\frac{\mu}{a_0^2\cosh^2\sigma}\right)u_2^2 + \left(\frac{3m}{a_0^2\sinh^2\sigma}\right)u_1^2 = 1$$

$$\left(\frac{\mu}{a_0^2\sin^2\zeta}\right)u_2^2 - \left(\frac{3m}{a_0^2\cos^2\zeta}\right)u_1^2 = 1 \quad .$$

Thus, the family of curves in the u_1 - u_2 plane with σ constant are ellipses and the family of curves with ζ constant are hyperbolas. This is illustrated in Figure 5. The coordinate ζ is to be identified as the inversion coordinate. Indeed, the molecule can be inverted from one equilibrium position to the other by changing ζ continuously from ζ_0 to $-\zeta_0$ while keeping σ fixed at its equilibrium value σ_0. A precise comparison between this inversion coordinate and the one used by Sheng,

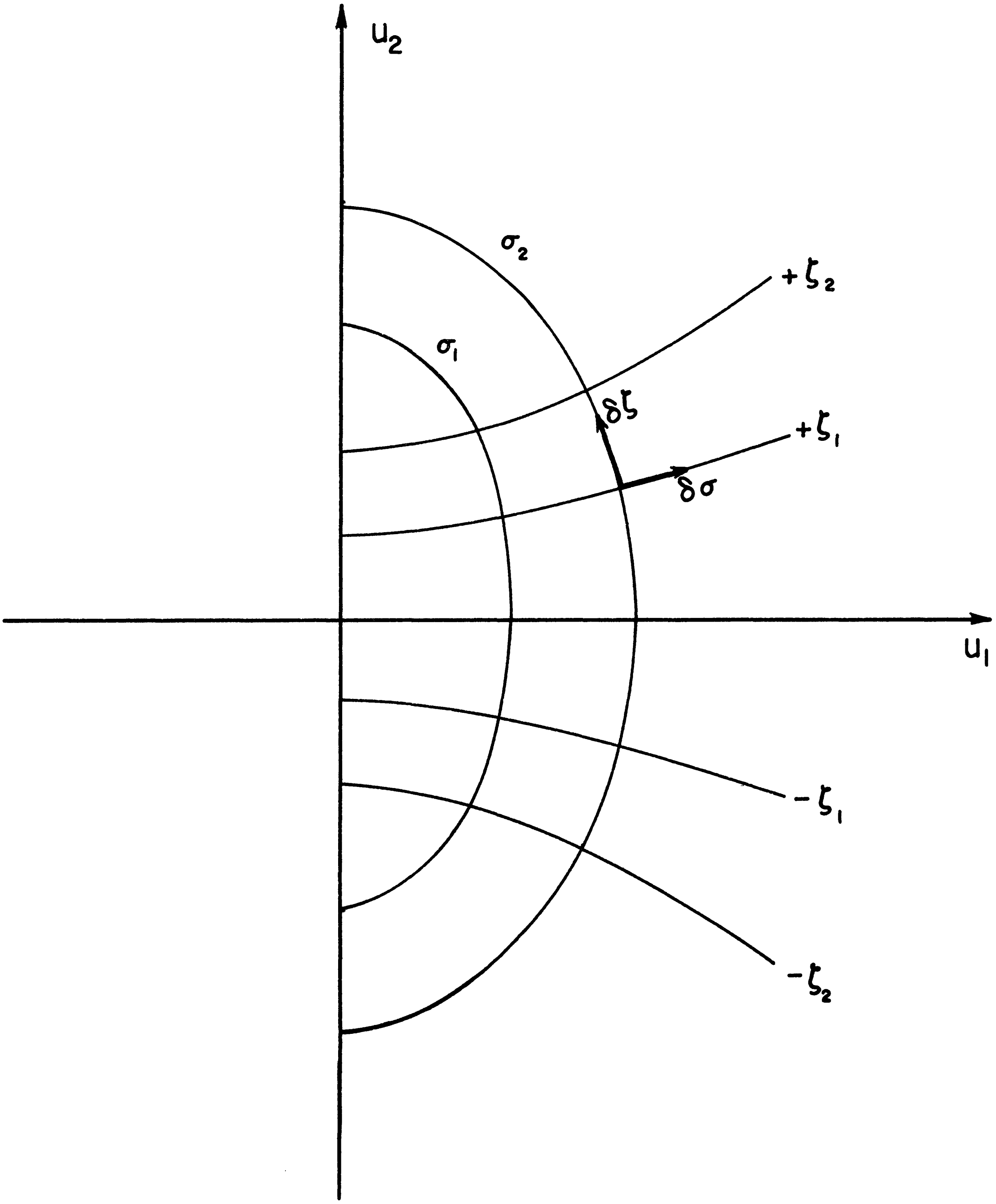

Figure 5. The Coordinates σ and ζ.

Barker, and Dennison(4) (and also by Hadley and Dennison(5)) will be made later when the numerical values of a_0, σ_0, and ζ_0 have been determined. The change to a new form for the inversion coordinate actually has little physical significance and is made mostly for mathematical convenience.

Upon introduction of the coordinates σ and ζ the vibrational kinetic energy, Equation (12), becomes

$$\begin{aligned} T_{vib} &= \frac{a_0^2}{2}(\cosh^2\sigma - \sin^2\zeta)(\dot{\sigma}^2 + \dot{\zeta}^2) \\ &+ \frac{1}{2}\left(\dot{Q}_{3x}^2 + \dot{Q}_{3y}^2\right) + \frac{1}{2}\left(\dot{Q}_{4x}^2 + \dot{Q}_{4y}^2\right) \\ &+ \left[\sin\tau\,\vec{R}_3 + \cos\tau\,\vec{R}_4\right]^2 \cdot \left[\frac{\cosh\sigma\sinh\sigma\,\dot{\zeta} - \sin\zeta\cos\zeta\,\dot{\sigma}}{\sinh^2\sigma\cos^2\zeta + 2\cosh^2\sigma\sin^2\zeta}\right]^2. \end{aligned} \tag{14}$$

So far no approximations have been made. Equation (14) is a completely rigorous expression for the classical vibrational kinetic energy.

III. THE POTENTIAL ENERGY AND THE VIBRATIONAL HAMILTONIAN

The most general form of the potential energy function in the immediate neighborhood of an equilibrium configuration of a molecule can be deduced from symmetry considerations alone. However, there is no straightforward procedure for inferring the form of the potential over a finite region in the configuration space of the molecule. Consequently, whenever a finite potential is needed, as is the case with ammonia, one must lean heavily on intuitive arguments. In this thesis a potential energy function will be proposed in order to describe the inversion-vibration interactions in ammonia. The implications of this potential will be worked out in considerable detail and compared with the observed data.

The relative success of one-dimensional treatments of the ammonia molecule comes from the fact that there is one mode of motion which is primarily involved in its inversion. This mode of motion will be identified with the coordinate ζ of the previous section. It will be recalled that ζ describes a motion in which the hydrogen atoms ride along an elliptic path that can carry the molecule from one configuration to an inverted configuration. It seems reasonable to assume that in spite of the large amplitude of the inversion motion the instantaneous configuration of the molecule never departs very much from the set of configurations having pyramidal symmetry. Consequently it will be assumed that the coordinates u_3, u_4, u_5 and u_6, which describe the distortion of the molecule from pyramidal symmetry, never vary very much from zero. This, in turn, implies that Q_{3x}, Q_{3y}, Q_{4x}, and Q_{4y} never differ much from zero. The family of elliptic paths along which the molecule can invert is obtained by holding σ constant and letting ζ vary. It will be assumed that the only members of this family of paths which are accessible to the molecule are those for which σ differs very little from its equilibrium value σ_0. That is, it is assumed that the accessible paths are those which pass through small neighborhoods of the two equilibrium configurations. This assumption implies that the potential energy depends on σ only through $\delta\sigma = \sigma - \sigma_0$. In effect, $\delta\sigma$, Q_{3x}, Q_{3y}, Q_{4x} and Q_{4y} are considered to describe very small oscillations while ζ describes a motion of very large amplitude. In the subsequent discussion the five small oscillation coordinates will be replaced by their dimensionless counterparts q_1, q_{3x}, q_{3y}, q_{4x}, and q_{4y}, defined by

$$\delta\sigma = \left[\frac{h}{4\pi^2 c\,\omega_1\, a_0^2 (\cosh^2\sigma_0 - \sin^2\zeta_0)}\right]^{1/2} q_1$$

$$Q_{3x} = \left[\frac{h}{4\pi^2 c\,\omega_3}\right]^{1/2} q_{3x}$$

$$Q_{3y} = \left[\frac{h}{4\pi^2 c\,\omega_3}\right]^{1/2} q_{3y}$$

$$Q_{4x} = \left[\frac{h}{4\pi^2 c\,\omega_4}\right]^{1/2} q_{4x}$$

$$Q_{4y} = \left[\frac{h}{4\pi^2 c\,\omega_4}\right]^{1/2} q_{4y} \quad . \qquad (15)$$

The coordinates q_1, q_{3x}, q_{3y}, q_{4x}, and q_{4y} were defined in such a way that they reduce to (dimensionless) normal coordinates in the vicinity of either equilibrium configuration of the molecule. Thus, in the neighborhood of the equilibrium configurations the dependence of the potential energy on these coordinates is given by a sum of harmonic oscillator potentials. It is tempting, then, to assume that in the general case the dominant terms in the ammonia potential will be of the form

$$\frac{V}{hc} = \frac{V_0(\zeta)}{hc} + \frac{C_1}{2} q_1^2 + \frac{C_3}{2}\left(q_{3x}^2 + q_{3y}^2\right) + \frac{C_4}{2}\left(q_{4x}^2 + q_{4y}^2\right)$$

where C_1, C_3, and C_4 are constants and $V_0(\zeta)$ is a double minimum potential of the general form illustrated in Figure 2, with minima at ζ_0 and $-\zeta_0$ and a central maximum at $\zeta = 0$. The potential above is, of course, incomplete. It provides no interaction between the inversion coordinate and the remaining coordinates. Consequently it implies that the inversion splitting depends only on the quantum number n_2 and not on the other quantum numbers. Although the observed inversion splittings are governed mainly by the quantum number n_2 there is also a significant dependence on the remaining quantum numbers. Consequently, the potential above must be supplemented by an interaction term.

The addition of an interaction term will lead to a non-separable Schroedinger equation. However, the observed data for ammonia suggests that a perturbation treatment of the interactions may be valid. The change in the inversion splitting with the quantum number n_2 is much greater than the variation of the splitting within groups of levels having the same value of n_2. This indicates that the inversion splitting is predominantly determined by the one-dimensional "potential" $V_o(\zeta)$, and only midly dependent on the interaction of the inversion coordinate ζ with the remaining vibrational coordinates. One of the major tasks of this thesis will be to justify a perturbation treatment of the inversion-vibration interactions.

Although the inversion splittings are extremely sensitive functions of the inversion potential, the WKB splitting formula, Equation (1), suggests that there may be many mathematical functions $V_o(\zeta)$ which can account, at least approximately, for the observed splittings. Practical considerations, however, limit the form of $V_o(\zeta)$ to those functions for which the energy levels and wave functions can be found with reasonable ease. A possible candidate is Manning's potential, Equation (2). The energy levels for this potential are relatively easy to find. Unfortunately, the wave functions, which are given by a semi-convergent power series in the variable $\tanh^2(x/2\rho)$, would be somewhat cumbersome to use in a perturbation calculation. In order to obtain more manageable wavefunctions, the double minimum potential

$$\begin{aligned}\frac{V_o(\zeta)}{hc} &= -2F\cos\left(\frac{\zeta}{L}\right) + 2G\cos\left(\frac{2\zeta}{L}\right) \quad \text{for } |\zeta| \leq \pi L \\ &= 2(F+G) \quad \text{for } \pi L < |\zeta| \leq \frac{\pi}{2}\end{aligned} \tag{16}$$

will be used in the present investigation. In Equation (16), F and G are positive constants such that $F \leq 4G$ and L is a positive constant such that $L \leq 1/2$. This potential has a central maximum at $\zeta = 0$ and minima at $\zeta = \pm \zeta_o$ where $\cos\left(\frac{\zeta_o}{L}\right) = \frac{F}{4G}$.

It will be seen, after numerical values of F, G, and L have been obtained, that the potential becomes very large at $\zeta = \pm \pi L$ so that the wavefunctions for the low lying energy levels, for all practical purposes, vanish. For $|\zeta| > \pi L$ the wavefunctions are completely negligible.

The potential function, Equation (16), has been chosen mainly for mathematical convenience. It has the general form to be expected of an inversion potential in the neighborhoods of ζ_0 and $- \zeta_0$ and throughout the interval $- \zeta_0 < \zeta < \zeta_0$. For $|\zeta| \gg |\zeta_0|$ it is undoubtedly a very poor approximation to the true ammonia potential. However, one would not expect the low lying energy levels to be affected very much by the behavior of the potential at large values of $|\zeta|$. In the next chapter it will be seen that the wavefunctions belonging to the lowest eight energy levels become negligibly small when $|\zeta| \gg |\zeta_0|$.

Interactions between the inversion coordinate and the remaining vibrational coordinates are obtained by assuming that the parameters F and G are not really constants but mild functions of the coordinates q_1, q_{3x}, q_{3y}, q_{4x} and q_{4y}. Since these coordinates, which represent very small oscillations, never differ very much from zero it should be possible to obtain a very good approximation by expanding F and G in a Taylor series and retaining only the leading terms. In principle, L could be expanded in a Taylor series also. However, an expansion of L, F, and G would yield more unknown constants than can be determined by the available data on ammonia. Thus, in practice, one of the three parameters must be regarded as a genuine constant. The argument for choosing L as the constant can be stated as follows. The inversion splitting is expected to be a very sensitive function of the potential barrier height and the separation of the potential minima. The height of the central barrier for the potential given by Equation (16) is

$$4G\left[1-\frac{F}{4G}\right]^2$$

and is independent of L. Furthermore, the separation of the potential minima can be shown to be very insensitive to the value of L. Thus, if one of the three parameters must be regarded as a true constant then L is probably the best choice.*

Since the potential energy must be invariant under the six operations of the point group C_{3v} the expansions of F and G depend on q_{3x}, q_{3y}, q_{4x}, and q_{4y} only through the combinations

$$r_3^2 = q_{3x}^2 + q_{3y}^2$$

$$r_4^2 = q_{4x}^2 + q_{4y}^2$$

$$\vec{r}_3 \cdot \vec{r}_4 = q_{3x}q_{4x} + q_{3y}q_{4y} \quad .$$

Furthermore, the six vibrational coordinates were defined in such a way that in the vicinity of an equilibrium configuration q_1, q_{3x}, q_{3y}, q_{4x}, q_{4y}, and $\delta\zeta = \zeta - \zeta_0$ are proportional to the normal coordinates of the molecule. This implies that no term linear in q_1 occurs and imposes a relation between the coefficients of $\vec{r}_3 \cdot \vec{r}_4$ in the expansions of F and G. Thus, out to terms quadratic in the coordinates, one finds that

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* The curvature of the potential near the minima is a sensitive function of L. Thus, L controls the mean separation of consecutive inversion doublets.

the most general form of the expansion of F and G is

$$F = F_0 + F_1 q_1^2 + F_3 r_3^2 + F_4 r_4^2 + k\cos\left(\frac{2\zeta_0}{L}\right)\vec{r}_3\cdot\vec{r}_4$$

$$G = G_0 + G_1 q_1^2 + G_3 r_3^2 + G_4 r_4^2 + k\cos\left(\frac{\zeta_0}{L}\right)\vec{r}_3\cdot\vec{r}_4$$

where F_0, F_1, F_3, F_4, G_0, G_1, G_3, G_4 and k are true constants. In order to simplify the computations to follow, k will be set equal to zero. Thus one obtains

$$\begin{aligned}\frac{V}{hc} = {} & \frac{c_1}{2} q_1^2 + \frac{c_3}{2} r_3^2 + \frac{c_4}{2} r_4^2 \\ & -2\left[F_0 + F_1 q_1^2 + F_3 r_3^2 + F_4 r_4^2\right]\cos\left(\frac{\zeta}{L}\right) \\ & +2\left[G_0 + G_1 q_1^2 + G_3 r_3^2 + G_4 r_4^2\right]\cos\left(\frac{2\zeta}{L}\right) \qquad (17)\end{aligned}$$

as a possible approximate potential energy function for the ammonia molecule. Equation (17) is, of course, a very incomplete potential function. Cubic and quartic terms could be added to this potential. However, unless the coefficients of the extra terms are strongly dependent on the inversion coordinate ζ, they will not make an appreciable contribution to the inversion splitting. Since the purpose of this thesis is to describe the inversion splittings these extra terms will not be included. In Appendix I it will be shown that the potential function, Equation (17), contains many of the cubic and quartic terms involving the inversion coordinate that would be found in the general potential expansion. It should be emphasized that the true ammonia potential is unknown and that Equation (17) is no more than a guess concerning the shape of the actual potential. The main task of this thesis is to discover to what extent, if any, Equation (17) can be used to approximate the ammonia potential.

Since q_1, q_{3x}, q_{3y}, q_{4x} and q_{4y} reduce to dimensionless normal coordinates near the equilibrium configurations, the corresponding normal frequencies can be found by evaluating the second derivatives of V/hc at an equilibrium configuration. One finds

$$\begin{aligned}
\omega_1 &= C_1 - 4F_1\cos\left(\frac{\xi_0}{L}\right) + 4G_1\cos\left(\frac{2\xi_0}{L}\right)\\
\omega_3 &= C_3 - 4F_3\cos\left(\frac{\xi_0}{L}\right) + 4G_3\cos\left(\frac{2\xi_0}{L}\right)\\
\omega_4 &= C_4 - 4F_4\cos\left(\frac{\xi_0}{L}\right) + 4G_4\cos\left(\frac{2\xi_0}{L}\right).
\end{aligned}$$

These relations can be used to eliminate the constants C_1, C_3 and C_4 from the potential function. With a slight bit of rearrangement one sees that apart from an additive constant, which can be neglected, Equation (17) can be rewritten as

$$\begin{aligned}
\frac{V}{hc} &= \frac{\omega_1}{2}q_1^2 + \frac{\omega_3}{2}r_3^2 + \frac{\omega_4}{2}r_4^2\\
&+ \left[2G_0' + \frac{F_0'^2}{4G_0'}\right] - 2F_0'\cos\frac{\xi}{L} + 2G_0'\cos\frac{2\xi}{L}\\
&+ \left[-2F_1\left(\cos\frac{\xi}{L} - \cos\frac{\xi_0}{L}\right) + 2G_1\left(\cos\frac{2\xi}{L} - \cos\frac{2\xi_0}{L}\right)\right]\left(q_1^2 - \frac{1}{2}\right)\\
&+ \left[-2F_3\left(\cos\frac{\xi}{L} - \cos\frac{\xi_0}{L}\right) + 2G_3\left(\cos\frac{2\xi}{L} - \cos\frac{2\xi_0}{L}\right)\right]\left(r_3^2 - 1\right)\\
&+ \left[-2F_4\left(\cos\frac{\xi}{L} - \cos\frac{\xi_0}{L}\right) + 2G_4\left(\cos\frac{2\xi}{L} - \cos\frac{2\xi_0}{L}\right)\right]\left(r_4^2 - 1\right) \qquad (18)
\end{aligned}$$

where

$$F_0' = F_0 + \frac{F_1}{2} + F_3 + F_4$$

$$G_0' = G_0 + \frac{G_1}{2} + G_3 + G_4 \quad . \tag{19}$$

It is in this form that the potential will be used in the subsequent calculations. It should be observed that this potential has minima at

$$\zeta = \pm \zeta_0 \qquad q_1 = r_3 = r_4 = 0$$

where

$$\cos\left(\frac{\zeta_0}{L}\right) = \frac{F_0}{4G_0}$$

corresponding to the two equilibrium configurations of the molecule.

Having arrived at expressions for the kinetic and potential energies, one can set up the vibrational Hamiltonian for the molecule. Equation (14), which is a rigorous expression for the kinetic energy, is a bit more general than is needed. Examination of this equation reveals that the term involving $[\sin \tau \vec{R}_3 + \cos \tau \vec{R}_4]^2$ gives contributions to the inversion splittings of the order of $B^- - B^+$, namely of the order of .005 cm^{-1} for states with $n_2 = 0$, and of the order of .2 cm^{-1} for states with $n_2 = 1$. (c.f. Table IV). Consequently this term will be neglected in the treatment of the inversion-vibration splitting which are of the order of .8 cm^{-1} in states with $n_2 = 0$ and 35 cm^{-1} in states with $n_2 = 1$. A further simplification arises from the assumption that σ never differs very much from σ_0. Thus, the vibrational kinetic energy can be approximated by

$$T_{vib} = \frac{a_0^2}{2}(\cosh^2\sigma_0 - \sin^2\zeta)(\delta\dot{\sigma}^2 + \dot{\zeta}^2)$$
$$+ \frac{1}{2}(\dot{Q}_{3x}^2 + \dot{Q}_{3y}^2) + \frac{1}{2}(\dot{Q}_{4x}^2 + \dot{Q}_{4y}^2) \quad .$$

The transcription to quantum mechanics is straight forward. When made in such a way that the volume element in configuration space is simply $d(\xi\sigma)\,d\xi\,dQ_{3x}\,dQ_{3y}\,dQ_{4x}\,dQ_{4y}$ one finds

$$T_{vib} = \frac{-\hbar^2}{2a_0^2}\left[\frac{1}{\sqrt{\cosh^2\sigma_0 - \sin^2\xi}}\frac{\partial^2}{\partial\xi^2}\frac{1}{\sqrt{\cosh^2\sigma_0 - \sin^2\xi}} + \frac{1}{\cosh^2\sigma_0 - \sin^2\xi}\frac{\partial^2}{\partial(\xi\sigma)^2}\right]$$

$$-\frac{\hbar^2}{2}\left[\frac{\partial^2}{\partial Q_{3x}^2} + \frac{\partial^2}{\partial Q_{3y}^2} + \frac{\partial^2}{\partial Q_{4x}^2} + \frac{\partial^2}{\partial Q_{4y}^2}\right].$$

Upon introducing the dimensionless coordinates defined by Equation (15) and letting

$$X = \frac{\xi}{L} \qquad \left(X_0 = \frac{\xi_0}{L}\right) \tag{20}$$

where L is the potential constant appearing in Equations (17) and (18) one finds for the vibrational Hamiltonian

$$\frac{H_{vib}}{hc} = -D\frac{\partial^2}{\partial X^2} - \frac{\omega_1}{2}\frac{\partial^2}{\partial q_1^2} - \frac{\omega_3}{2}\left(\frac{\partial^2}{\partial q_{3x}^2} + \frac{\partial^2}{\partial q_{3y}^2}\right) - \frac{\omega_4}{2}\left(\frac{\partial^2}{\partial q_{4x}^2} + \frac{\partial^2}{\partial q_{4y}^2}\right)$$

$$-D\left[f_1(X)\frac{\partial^2}{\partial X^2} + f_2(X)\frac{\partial}{\partial X}\right] - \frac{\omega_1}{2}f_1(X)\left(\frac{\partial^2}{\partial q_1^2} + \frac{1}{2}\right) + \frac{V_{eff}}{hc}$$

where

$$D = \frac{h}{8\pi^2 c\, a_0^2(\cosh^2\sigma_0 - \sin^2\xi_0)L^2}$$

$$f_1(X) = \frac{(\sin LX)^2 - \sin^2\xi_0}{\cosh^2\sigma_0 - (\sin LX)^2}$$

$$f_2(X) = \frac{2L(\cosh^2\sigma_0 - \sin^2\xi_0)(\sin LX)(\cos LX)}{\left[\cosh^2\sigma_0 - (\sin LX)^2\right]^2} \tag{21}$$

and

$$\frac{V_{eff}}{hc} = \frac{V_{true}}{hc} + \frac{\omega_1}{4} f_1(x) - \frac{DL^2(\cosh^2\sigma_0 - \sin^2\rho_0)}{[\cosh^2\sigma_0 - (\sin Lx)^2]^2}\left[1 - 2(\sin Lx)^2 + \frac{3(\sin Lx)^2(\cos Lx)^2}{\cosh^2\sigma_0 - (\sin Lx)^2}\right].$$

V_{eff} is an "effective" potential for the vibrational motions of the molecule whereas V_{true} is the actual potential. In this thesis, the trial potential function given by Equation (18) will be identified with the effective potential V_{eff}. Upon making this identification, the vibrational Hamiltonian can be written as

$$H_{vib} = H_{vib}^{(0)} + H_{vib}^{(1)} \tag{22}$$

where*

$$\frac{H_{vib}^{(0)}}{hc} = \frac{\omega_1}{2}\left(-\frac{\partial^2}{\partial q_1^2} + q_1^2\right) + \frac{\omega_3}{2}\left(-\frac{\partial^2}{\partial q_{3x}^2} - \frac{\partial^2}{\partial q_{3y}^2} + q_{3x}^2 + q_{3y}^2\right)$$

$$+ \frac{\omega_4}{2}\left(-\frac{\partial^2}{\partial q_{4x}^2} - \frac{\partial^2}{\partial q_{4y}^2} + q_{4x}^2 + q_{4y}^2\right)$$

$$+ \left(-D\frac{\partial^2}{\partial x^2} + 2G_0' + \frac{F_0'^2}{4G_0'} - 2F_0'\cos x + 2G_0'\cos 2x\right) \tag{23}$$

---

* Actually, Equation (23) holds for $-\pi \leq x \leq \pi$. For $\pi < |x| \leq \frac{\pi}{2L}$ the last term in Equation (23) should be replaced by [c.f. Equation (16)]:

$$-D\frac{\partial^2}{\partial x^2} + 2G_0' + \frac{F_0'^2}{4G_0'} + 2(F_0' + G_0')$$

and

$$\frac{H^{(1)}_{vib}}{hc} = h_1(x)\left(q_1^2 - \frac{1}{2}\right) + h_3(x)\left(r_3^2 - 1\right) + h_4(x)\left(r_4^2 - 1\right)$$
$$- D\left[f_1(x)\frac{\partial^2}{\partial x^2} + f_2(x)\frac{\partial}{\partial x}\right] - \frac{\omega_1}{2} f_1(x)\left(\frac{\partial^2}{\partial q_1^2} + \frac{1}{2}\right) \qquad (24)$$

where

$$h_i(x) = -2F_i(\cos x - \cos x_0) + 2G_i(\cos 2x - \cos 2x_0) \qquad (25)$$
$$i = 1, 3, 4.$$

In order to calculate the vibrational energies implied by this Hamiltonian the Schroedinger equation

$$\frac{1}{hc} H_{vib} \Psi_{vib} = E(cm^{-1}) \Psi_{vib}$$

must be solved. In order to facilitate this calculation $H^{(1)}_{vib}$ will be regarded as a perturbation on the "zero-order" Hamiltonian $H^{(0)}_{vib}$.

IV. VIBRATIONAL ENERGIES OF NH_3 IN LOWEST APPROXIMATION

The calculation of the inversion-vibration splittings is begun by finding the eigenvalues and eigenfunctions of the "unperturbed" Schroedinger equation

$$\frac{1}{hc} H^{(0)}_{vib} \Psi^{(0)}_{vib} = E^{(0)}_{vib} \Psi^{(0)}_{vib} .$$

This equation is separable. Indeed, the q_1, q_{3x}, q_{3y}, q_{4x}, q_{4y} dependence of this equation is trivial. One finds

$$E^{(0)}_{vib} = E_{n_2^\pm} + \omega_1(n_1 + \tfrac{1}{2}) + \omega_3(n_3 + 1) + \omega_4(n_4 + 1) \tag{25}$$

$$\Psi^{(0)}_{vib} = \psi_{n_2^\pm}(x)\, \psi_{n_1}(q_1)\, \psi_{n_3 \ell_3}(q_{3x}, q_{3y})\, \psi_{n_4 \ell_4}(q_{4x}, q_{4y}) \tag{26}$$

where ψ_{n_1} is a one-dimensional harmonic oscillator wave function and $\psi_{n_3\ell_3}$ and $\psi_{n_4\ell_4}$ are two-dimensional isotropic harmonic oscillator wavefunctions. $E_{n_2\pm}$ and $\psi_{n_2\pm}$ are the eigenvalues and eigenfunctions of the one-dimensional equation

$$\left[-D\frac{\partial^2}{\partial x^2} + V'(x)\right]\psi(x) = E\,\psi(x) \tag{27}$$

where

$$\begin{aligned} V'(x) &= \left[2G_0' + \frac{F_0'^2}{4G_0'}\right] - 2F_0'\cos x + 2G_0'\cos 2x \\ &\qquad \text{for} \quad -\pi \le x \le +\pi \\ &= \left[2G_0' + \frac{F_0'^2}{4G_0'}\right] + 2(F_0' + G_0') \\ &\qquad \text{for} \quad \pi < |x| \le \frac{\pi}{2L} . \end{aligned}$$

It does not appear possible to obtain exact solutions of Equation (27) in terms of known functions. However, for $E \ll V(\pi)$ it is possible to obtain eigenvalues and eigenfunctions numerically. The proper procedure would be to obtain solutions in the interval $-\pi \leq x \leq +\pi$ and join them, in the usual manner, to the exponential solutions for the intervals $\pi < |x| \leq \frac{\pi}{2L}$. However, for the levels of interest in the present investigation it will be seen that $\psi(x)$, in the interval $-\pi \leq x \leq +\pi$ becomes negligibly small* as $|x| \to \pi$ so that the exponential solutions in the intervals $\pi < |x| \leq \frac{\pi}{2L}$ are negligibly small. Consequently, in the subsequent work only solutions in the interval $-\pi \leq x \leq \pi$ will be considered. That is, the eigenfunction will be treated as if they vanished identically in the intervals $\pi < |x| < \frac{\pi}{2L}$.

The form of $V'(x)$ suggests that one should expand $\psi(x)$ in a Fourier series in the interval $-\pi \leq x \leq +\pi$. Since the operator

$$H^{(2)} = -D\frac{\partial^2}{\partial x^2} + V'(x)$$

is unchanged when x is replaced by -x, the eigenfunctions must be either even functions or odd functions of the coordinate x. The even functions are given by

$$\psi_+ = \frac{a_0}{\sqrt{2\pi}} + \sum_{K=1}^{\infty} \frac{a_K}{\sqrt{\pi}} \cos Kx$$

and the odd functions by

$$\psi_- = \sum_{K=1}^{\infty} \frac{b_K}{\sqrt{\pi}} \sin Kx \quad .$$

---

* For the levels $n_{2\pm} = 3^{\pm}$ it is found that the value of $|\psi(x)|^2$ at $x = \pm\pi$ is less than 10^{-8} of its maximum value. Scale drawings of the wavefunctions are given in Figures 8 through 15.

Substitution of these expansions into Equation (27) yields the two matrix equations

$$\sum_{k=0}^{\infty} \left(H^{(2)+}_{jk} - E_+ \delta_{jk} \right) a_k = 0 \tag{28}$$

$$\sum_{k=1}^{\infty} \left(H^{(2)-}_{jk} - E_- \delta_{jk} \right) b_k = 0 \tag{29}$$

where

$$H^{(2)\pm}_{jk} = \int_{-\pi}^{+\pi} u_j^{\pm} H^{(2)} u_k^{\pm}\, dx$$

$$u_0^+ = \frac{1}{\sqrt{2\pi}}$$

$$\left.\begin{aligned} u_k^+ &= \frac{\cos kx}{\sqrt{\pi}} \\ u_k^- &= \frac{\sin kx}{\sqrt{\pi}} \end{aligned}\right\} k \geq 1 \; .$$

The exact solution of Equations (28) and (29) would involve the diagonalization of the infinite matrices $H^{(2)+}$ and $H^{(2)-}$. However, good approximations to the eigenvalues and eigenvectors can be obtained by retaining only the first N terms in the expansions of the eigenfunctions and diagonalizing the N x N truncations of the infinite matrices $H^{(2)+}$ and $H^{(2)-}$, provided N is chosen to be sufficiently large. This procedure is essentially equivalent to a variational treatment. The form of the matrices, whose matrix elements are given in Table V, indicates that a

TABLE V

NON-VANISHING MATRIX ELEMENTS OF $H^{(2)^+}$ AND $H^{(2)^-}$

$H^{(2)^+}$

$n = 0, 1, 2, 3, \ldots$

$$H_{nn} = 2G_0' + \frac{F_0'^2}{4G_0'} + n^2 D \qquad n \neq 1$$

$$H_{11} = 2G_0' + \frac{F_0'^2}{4G_0'} + 1^2 D + G_0'$$

$$H_{01} = H_{10} = -\sqrt{2}\, F_0'$$

$$H_{02} = H_{20} = \sqrt{2}\, G_0'$$

$$H_{n,n+1} = H_{n+1,n} = -F_0' \qquad n \geq 1$$

$$H_{n,n+2} = H_{n+2,n} = G_0' \qquad n \geq 1$$

$H^{(2)^-}$

$n = 1, 2, 3, \ldots$

$$H_{nn} = 2G_0' + \frac{F_0'^2}{4G_0'} + n^2 D \qquad n \neq 1$$

$$H_{11} = 2G_0' + \frac{F_0'^2}{4G_0'} + 1^2 D - G_0'$$

$$H_{n,n+1} = H_{n+1,n} = -F_0'$$

$$H_{n,n+2} = H_{n+2,n} = G_0'$$

very good approximation can be obtained in this way. The only nonvanishing matrix elements are either on the principal diagonal or on the first or second diagonal above or below the principal diagonal. The off diagonal elements are independent of k while the diagonal elements increase as k^2. By truncating the matrices at a sufficiently large N a very good approximation to the low lying eigenvalues and their eigenfunctions should be obtained. Thus, given numerical values of the constants D, F_o', and G_o', approximate eigenvalues and eigenfunctions of Equation (27) can be found by determining the eigenvalues and eigenvectors of two finite matrices. This can be done quite easily with the aid of a digital computer.*

By trying several different values N for the dimension of the truncated matrices it was found that a value of N equal to 12 was sufficiently large since an increase in N beyond this value leads to insignificant changes in the eigenvalues and eigenvectors corresponding to observed levels in the ammonia spectrum. At least two cycles of computation are required to determine the constants D, F_o', and G_o'. Although the decomposition of the vibrational Hamiltonian into $H_{vib}^{(0)}$ and $H_{vib}^{(1)}$ was made in a way that minimizes the contribution of $H_{vib}^{(1)}$ to the levels $(0, n_2\pm, 0^0, 0^0)$, this contribution is not negligible. A tentative choice of D, F_o' and G_o' is made by neglecting $H_{vib}^{(1)}$ altogether and choosing the three

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* Most of the initial computing was done on the IBM 650 at the University of Michigan Statistical Research Laboratory. Later the investigation was continued on the IBM 704 at General Motors Research Laboratories. Final computations were performed on the IBM 704 at the University of Michigan Computing Center.

potential constants so that the best possible fit to the observed levels $(0, n_{2\pm}, 0^0, 0^0)$ is obtained. Using the resulting eigenfunctions, the approximate contribution due to $H^{(1)}_{vib}$ is calculated. Then the values of D, F_o', and G_o' are adjusted to compensate for the contributions of $H^{(1)}_{vib}$ to the levels $(0, n_{2\pm}, 0^0, 0^0)$. The best values of D, F_o', and G_o' that have been found in this way are

$$\begin{aligned} D &= 64.93 \text{ cm}^{-1} \\ F_o' &= 1894.61 \text{ cm}^{-1} \\ G_o' &= 1288.68 \text{ cm}^{-1} . \end{aligned} \tag{30}$$

It is possible, however, that a better choice of these numbers could be made. The eigenvalues and eigenvectors of the 12 x 12 truncations of the matrices $H^{(2)+}$ and $H^{(2)-}$ have been computed using the above set of potential constants. The results are presented in Tables VI and VII. The calculated energy differences $E_{n_{2\pm}} - E_{0+}$ are given in Table VIII along with the observed differences for the levels $(0, n_{2\pm}, 0^0, 0^0)$. However, comparison between theory and experiment should be made only after the contributions of $H^{(1)}_{vib}$ have been computed and incorporated in the calculated values. In order to indicate the magnitude of the error introduced by replacing the infinite matrices $H^{(2)+}$ and $H^{(2)-}$ by finite N x N matrices, the calculated energy differences are given for N equal to twelve, sixteen, and twenty. The eigenvalues for the 12 x 12 truncations have been computed using two different matrix diagonalizing schemes, Jacobi's method, and Givens' Method. A comparison of the results indicates that the eigenvalues can be computed with an error less than 0.01 cm^{-1}.

A scale drawing of the lower portion of the one-dimensional 'potential" V'(x), showing the positions of the energy levels, is given in Figure 6. The separation of the lowest pair if levels is too small to be shown. Figure 7 shows a scale drawing of the path of the coordinate x through physical space. The path used by Sheng, Barker, and Dennison is shown on the same diagram. The double minimum wavefunctions are depicted in Figures 8 through 15.

TABLE VI

EIGENVALUES AND EIGENVECTORS OF $H^{(2)^+}$
(12 x 12 TRUNCATION)

n_2^+	0^+	1^+	2^+	3^+	4^+
$E_{n_2^+}$ (cm^{-1})	514.55	1451.71	2131.65	2899.49	3925.35
a_0	.647154	.125510	.437270	-.131256	.224109
a_1	.362054	.495878	.307225	.225158	-.131521
a_2	-.447480	.603562	.177672	.357973	-.113213
a_3	-.467819	-.073639	.575400	-.048483	.371143
a_4	-.022430	-.531707	.485977	.269292	.000916
a_5	.160871	-.252730	-.102389	.733106	-.014177
a_6	.062313	.097022	-.304725	.353268	.637748
a_7	-.020628	.110248	-.089206	-.172564	.578506
a_8	-.017838	.009066	.055148	-.188563	-.005545
a_9	-.000387	-.019376	.034769	-.014796	-.192113
a_{10}	.002506	-.005476	-.002021	.034106	-.054597
a_{11}	.000494	.001508	-.005404	.010167	.020004

TABLE VII

EIGENVALUES AND EIGENVECTORS OF $H^{(2)^-}$
(12 x 12 TRUNCATION)

n_2^-	0^-	1^-	2^-	3^-	4^-
$E_{n_2^-}$ (cm^{-1})	515.49	1487.20	2401.77	3387.16	4482.53
b_1	.771718	-.122245	.368526	-.240582	.254615
b_2	.523913	.481142	.004443	.298187	-.266783
b_3	-.148653	.760754	.107159	.188733	.088427
b_4	-.310924	.174758	.695448	-.110052	.307827
b_5	-.072999	-.313068	.539354	.448221	-.151417
b_6	.066367	-.206113	-.085132	.717284	.214791
b_7	.037308	.021520	-.254207	.178893	.728610
b_8	-.003985	.056222	-.064203	-.205890	.352643
b_9	-.007251	.009731	.040722	-.122294	-.129749
b_{10}	-.000800	-.007187	.021746	.011743	-.140729
b_{11}	.000775	-.002637	-.001966	.024031	-.009218
b_{12}	.000206	.000383	-.003106	.003291	.020130

TABLE VIII

ENERGY DIFFERENCES FOR THE LEVELS $(0, n_2^{\pm}, 0^0, 0^0)$
(N x N TRUNCATION)

Level	Energy Difference (cm^{-1})			
	Calculated			
$n_2^{\pm}$	N = 12	N = 16	N = 20	Observed
0^+	0.00	0.00	0.00	0.00
0^-	0.94	0.94	0.94	0.793
1^+	937.16	937.16	937.16	932.51
1^-	972.65	972.65	972.65	968.32
2^+	1617.10	1617.09	1617.09	1597.42
2^-	1887.22	1887.22	1887.22	1882.16
3^+	2384.94	2384.85	2384.85	2383.46
3^-	2872.61	2872.55	2872.55	2895.48
4^+	3410.80	3409.30	3409.30	-
4^-	3967.98	3967.67	3967.67	-

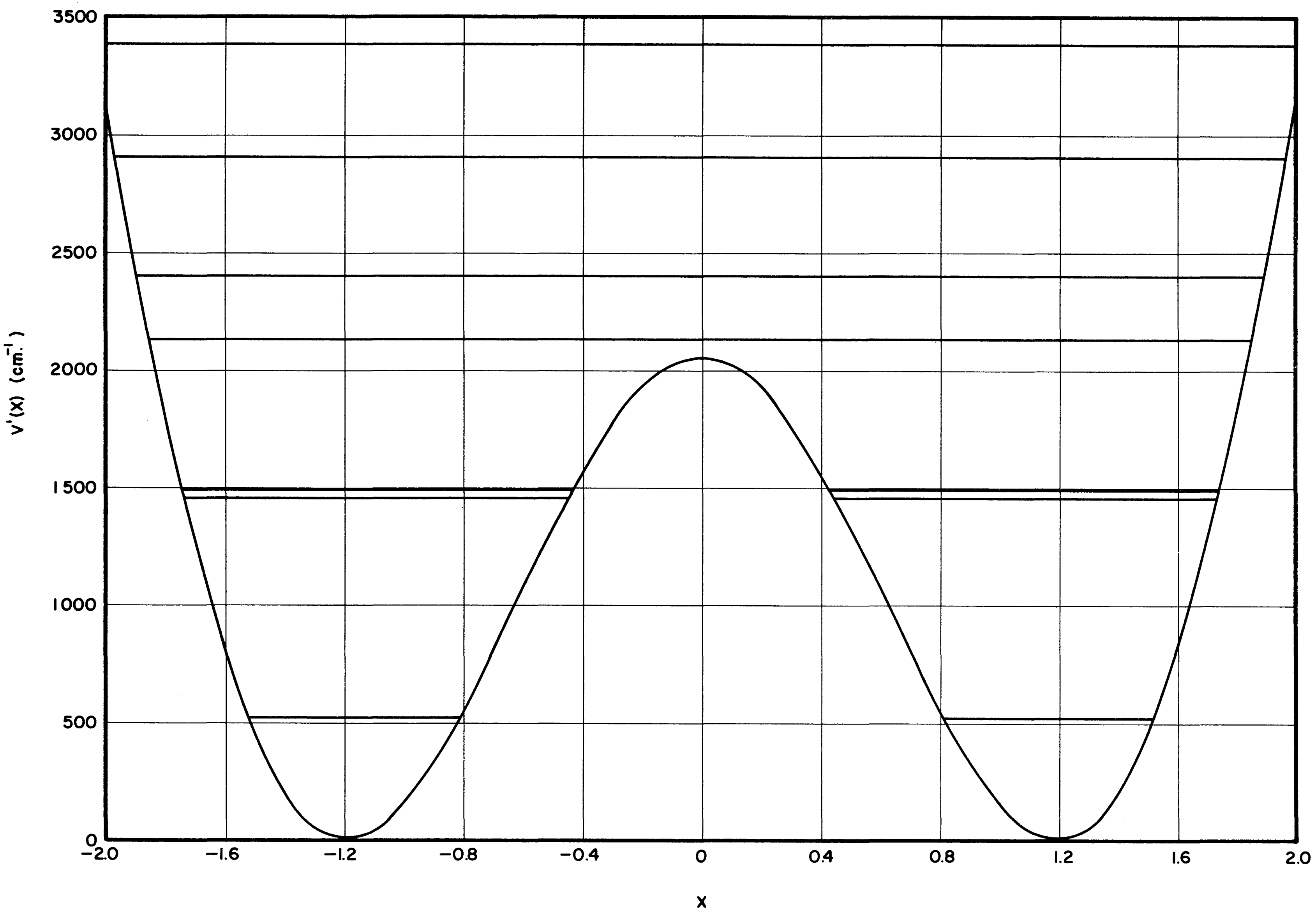

Figure 6. The One-Dimensional Potential V'(x).

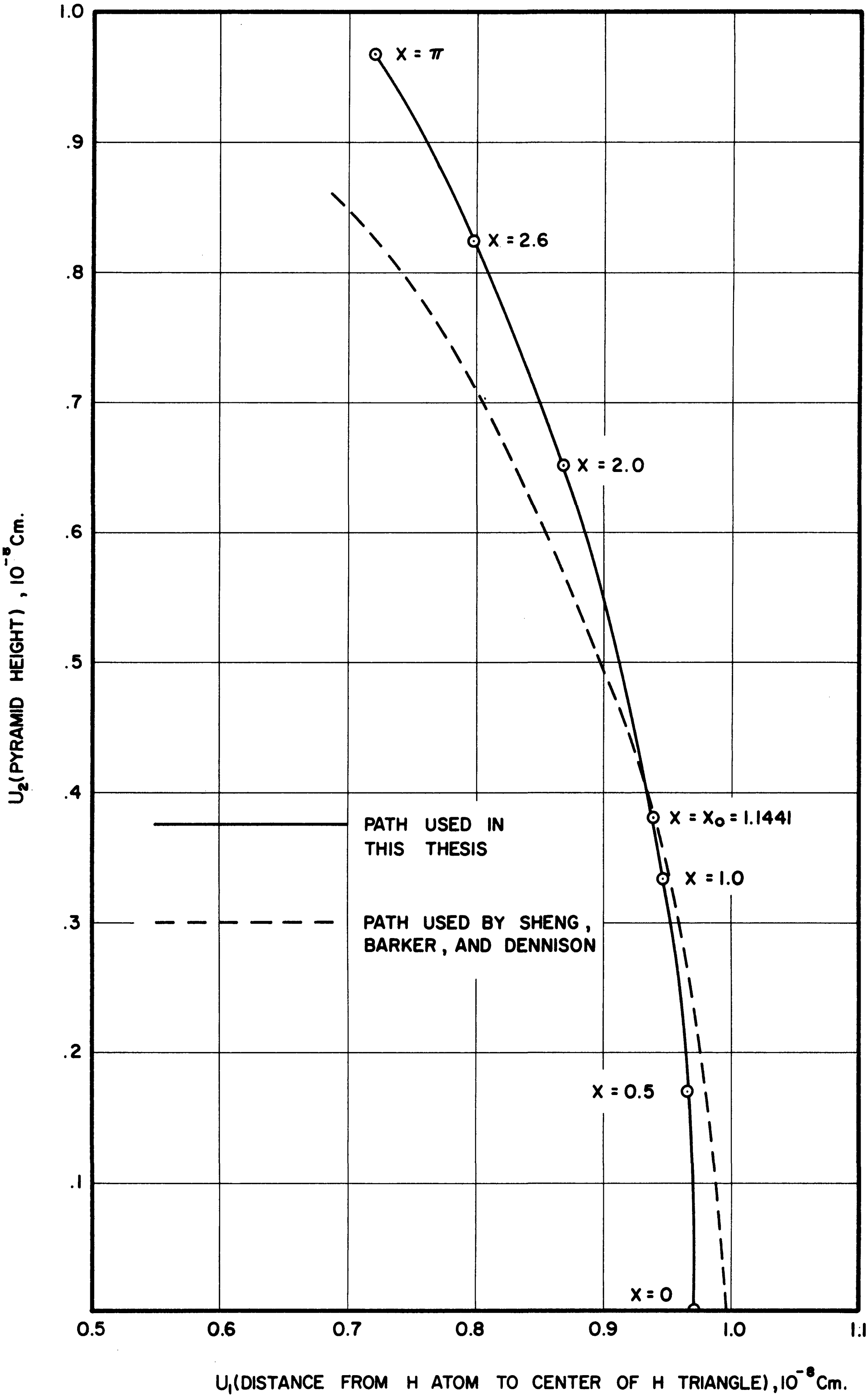

Figure 7. The Inversion Path.

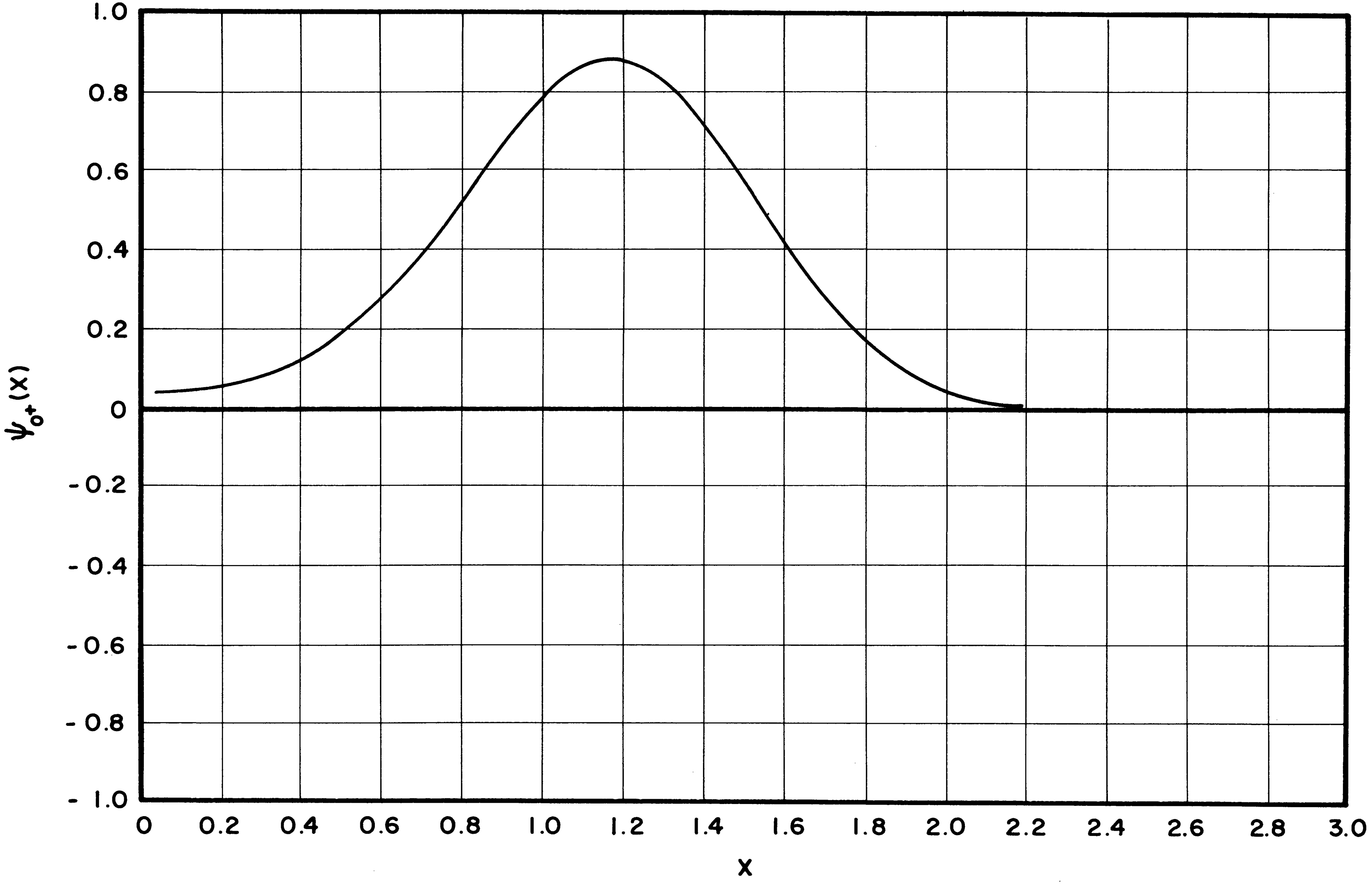

Figure 8. The Wavefunction $\psi_{0^+}(x)$.

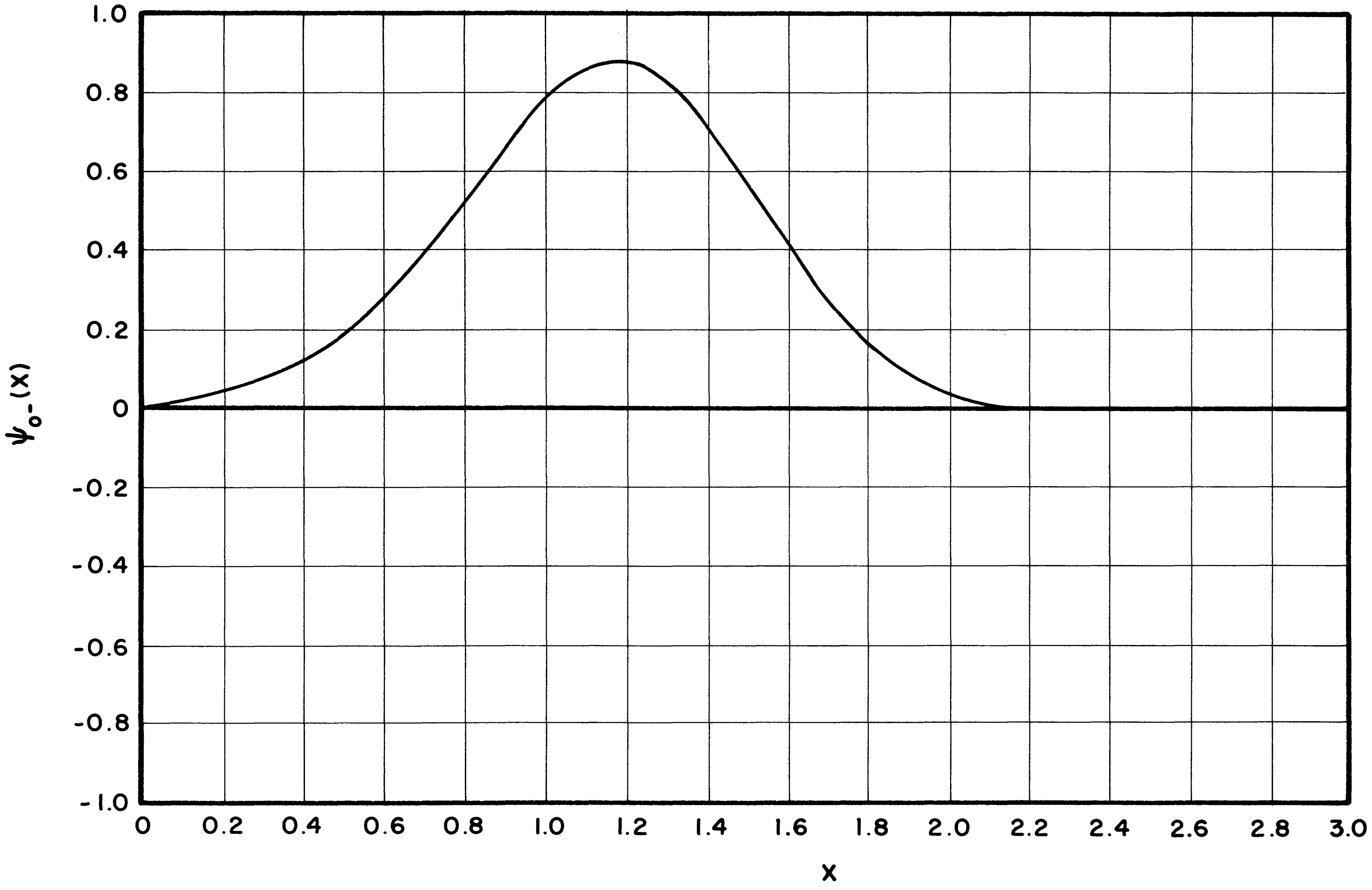

Figure 9. The Wavefunction $\psi_{0^-}(x)$.

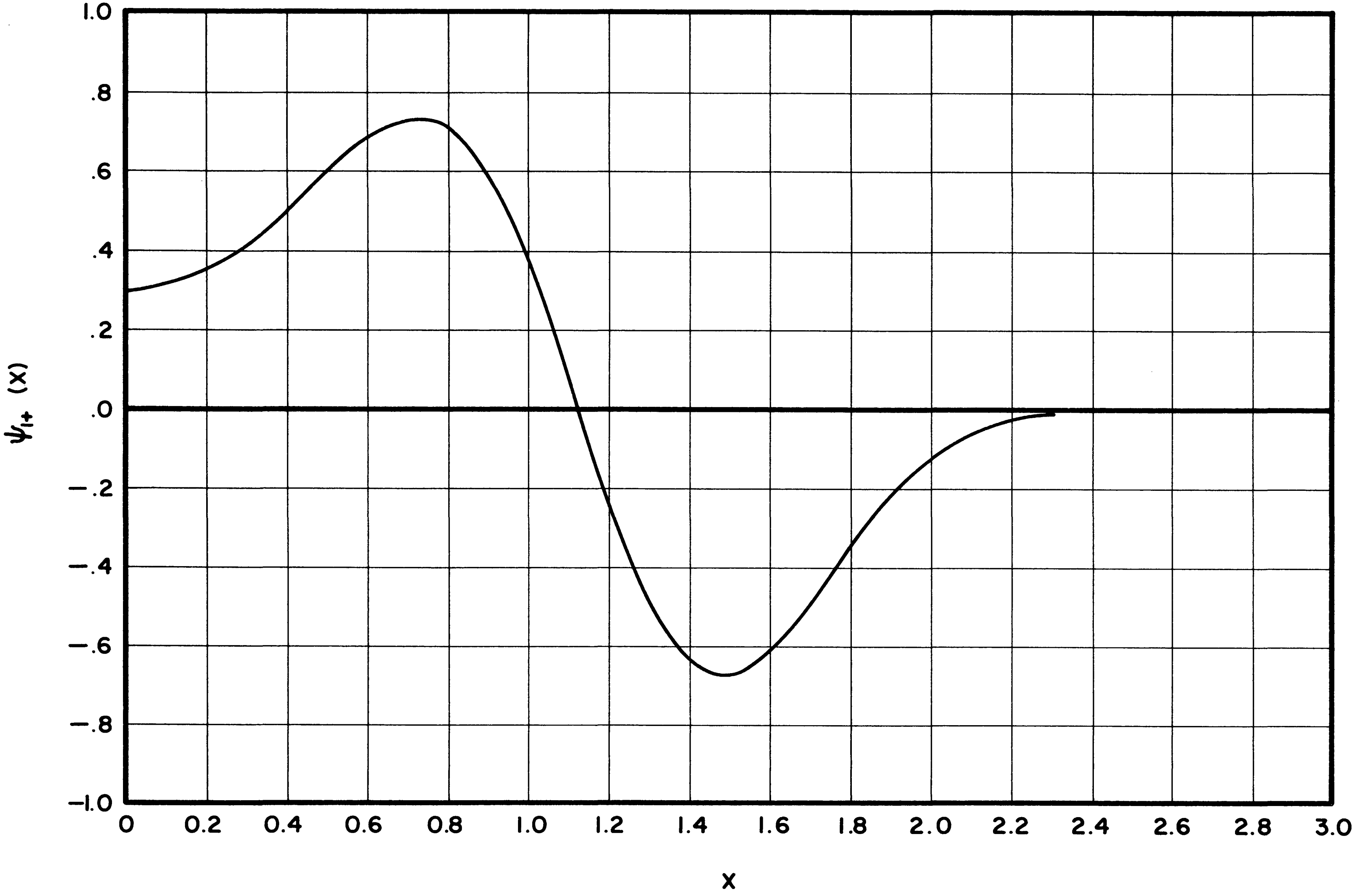

Figure 10. The Wavefunction $\psi_1+(x)$.

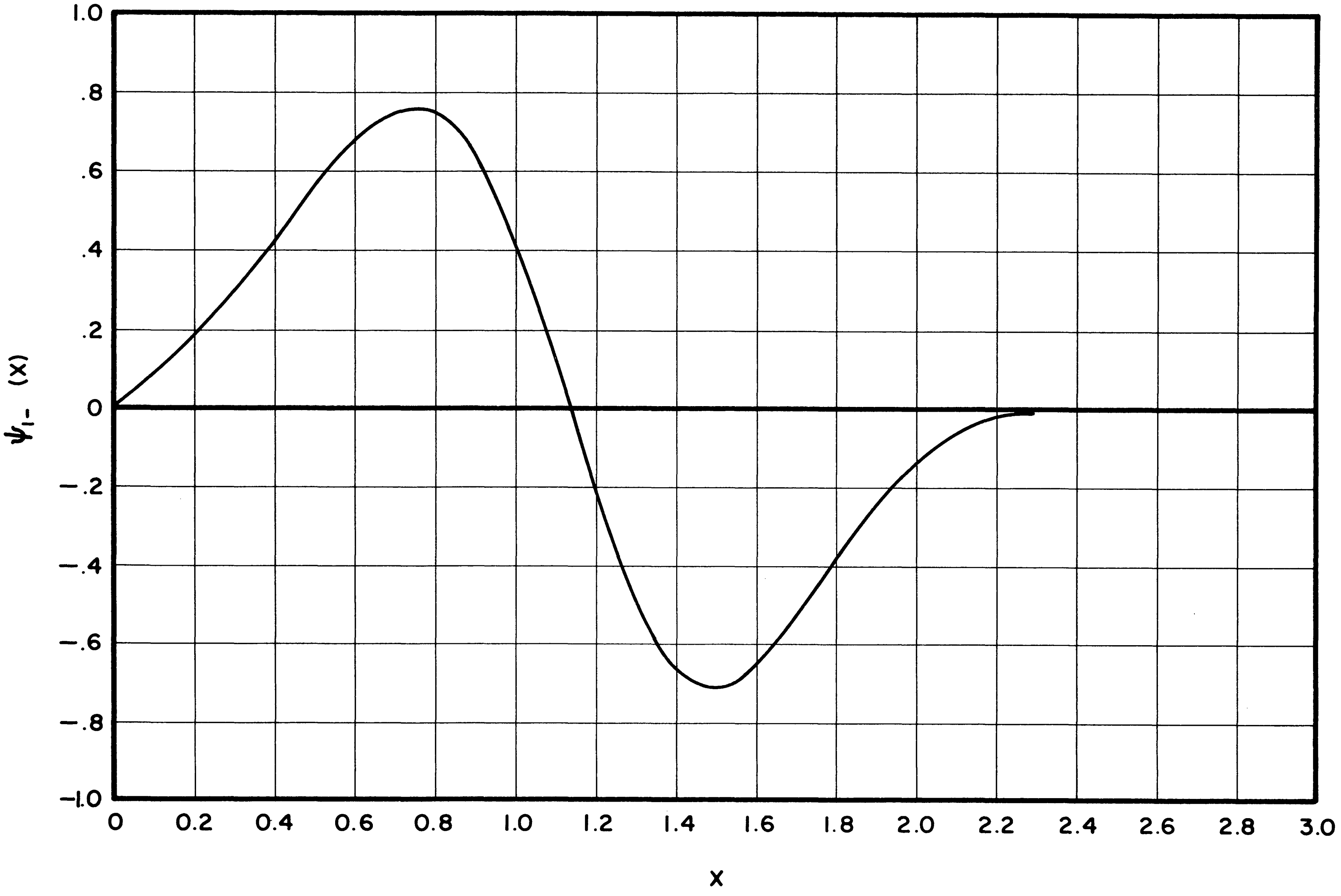

Figure 11. The Wavefunction $\psi_{1^-}(x)$.

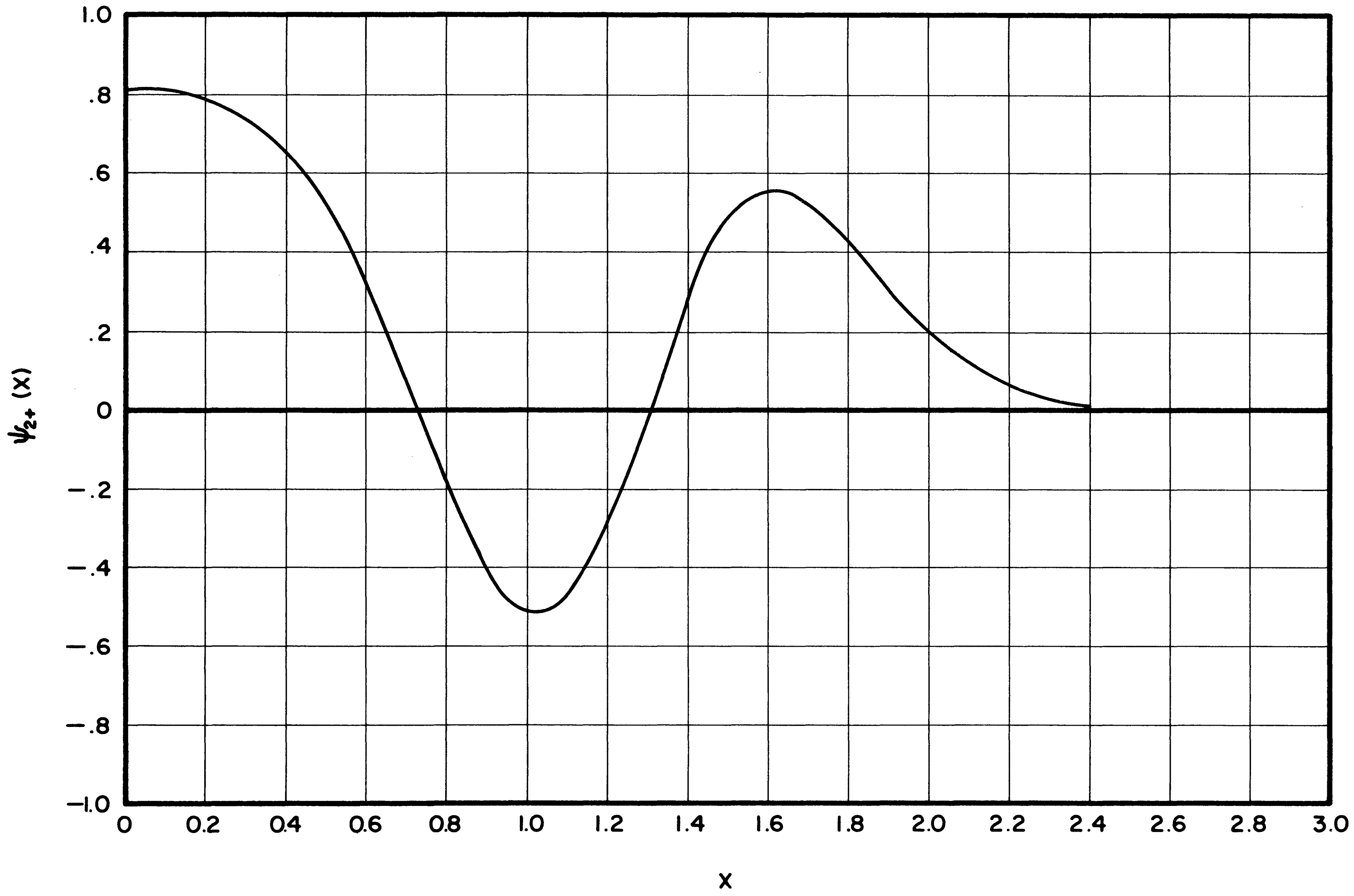

Figure 12. The Wavefunction $\psi_{2^+}(x)$.

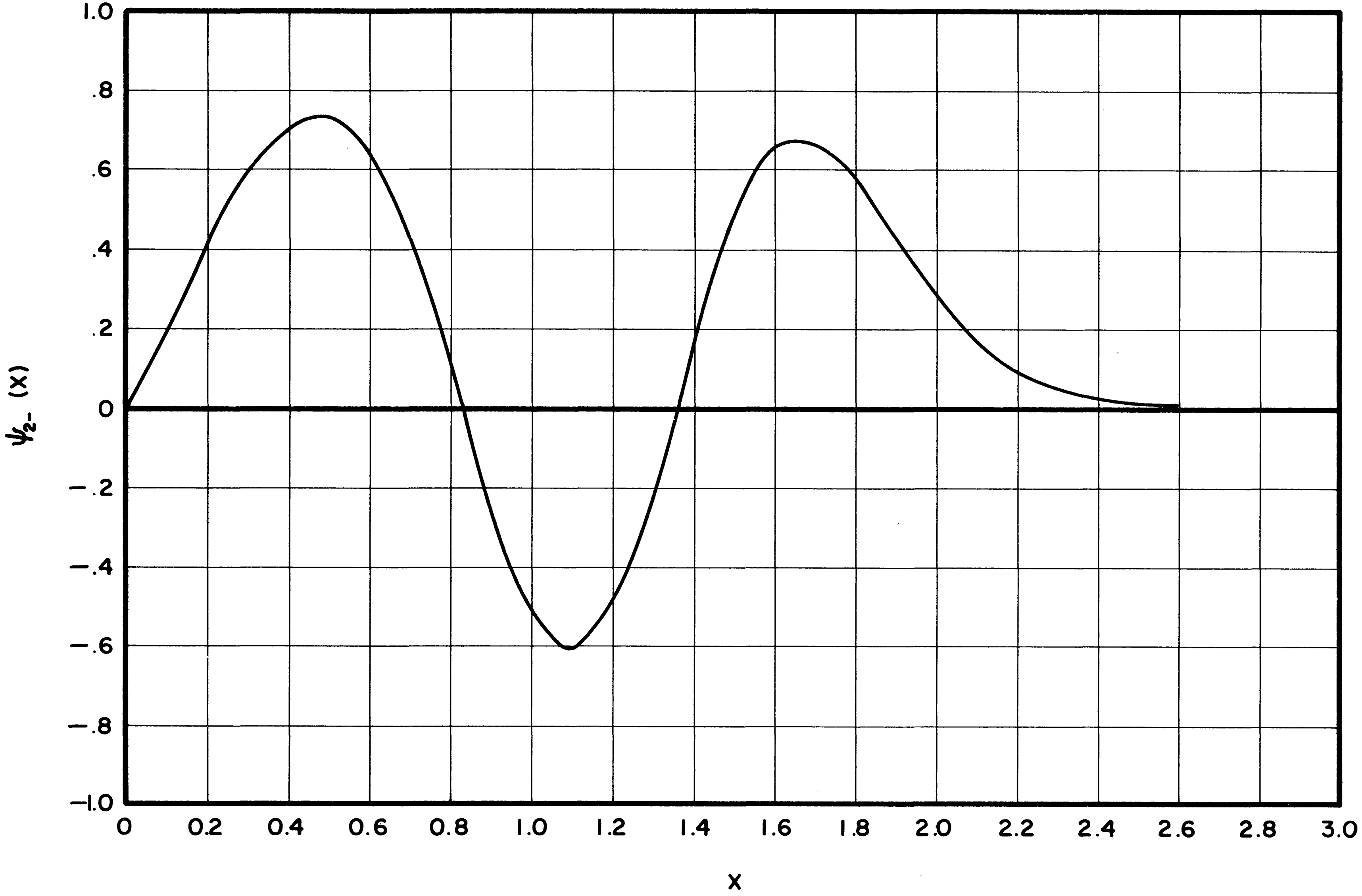

Figure 13. The Wavefunction $\psi_{2-}(x)$.

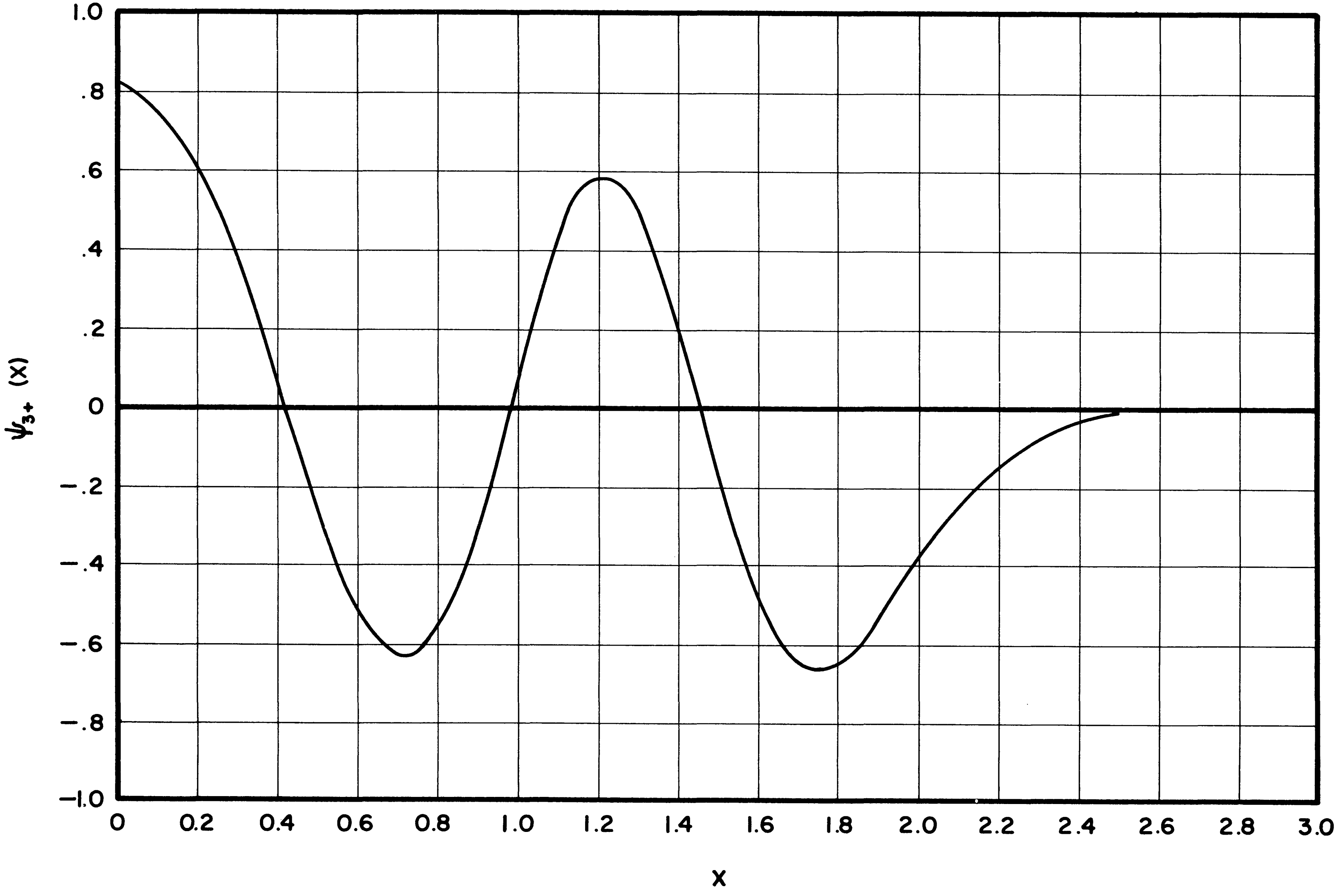

Figure 14. The Wavefunction $\psi_{3^+}(x)$.

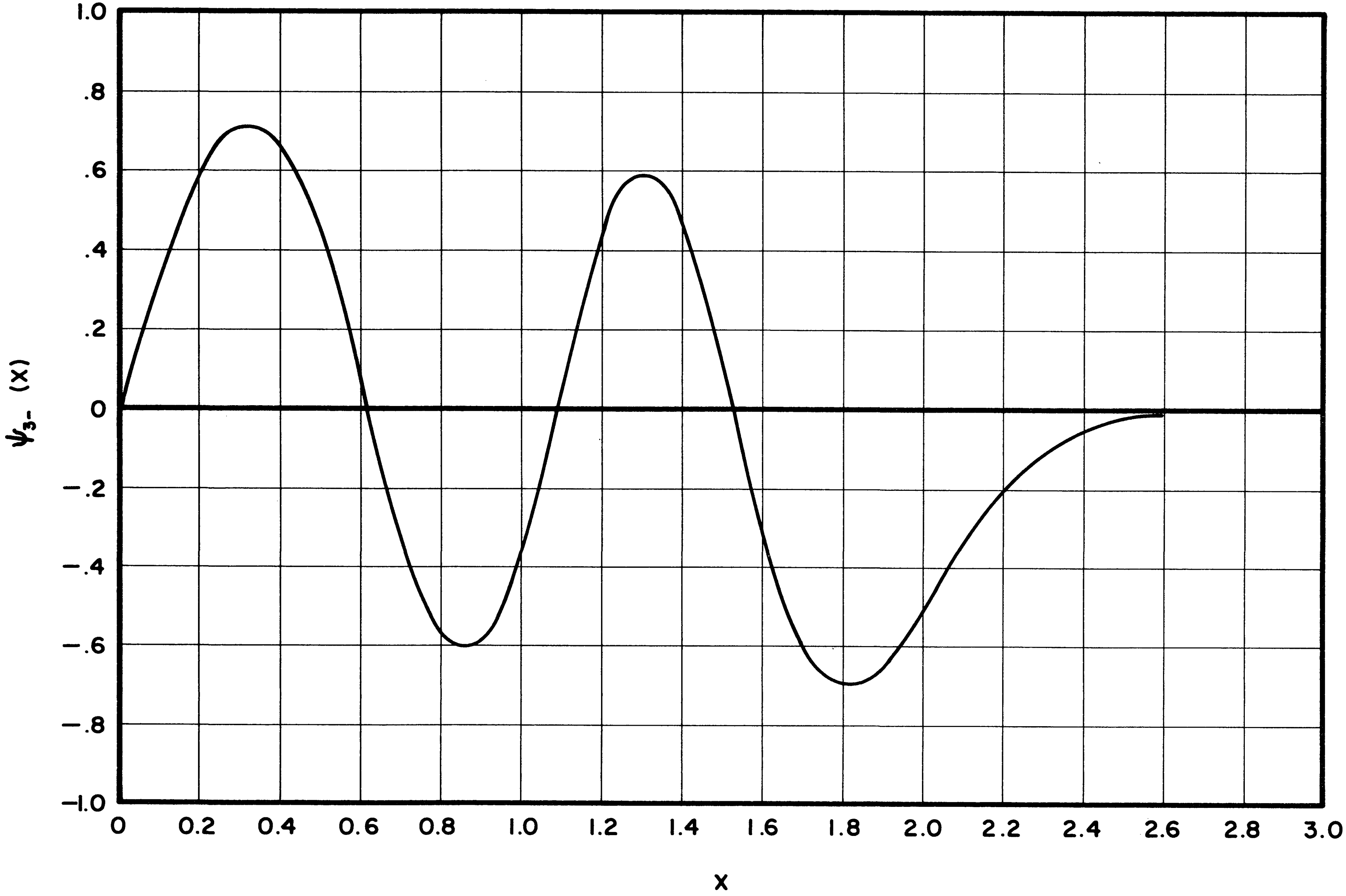

Figure 15. The Wavefunction $\psi_{3-}(x)$.

V. INVERSION-VIBRATION SPLITTINGS

Having obtained zero order energies and wavefunctions it is now possible to compute the contributions due to the perturbation $H^{(1)}_{vib}$. This calculation is done in two steps. First, perturbation theory is used to express the energy corrections as functions of the interaction constants F_i and G_i $(i = 1, 3, 4)$. The second step is to choose numerical values of the interaction constants in such a way that a good overall description of the vibration-inversion splitting is obtained.

The matrix elements of $H^{(1)}_{vib}$ are readily evaluated. The integrals over the harmonic oscillator wavefunctions are well known and give no difficulty. The integrals over the double minimum wavefunctions must, of course, be evaluated numerically. All the non-vanishing matrix elements of $H^{(1)}_{vib}$ are presented in Table IX. It is seen that the matrix of $H^{(1)}_{vib}$ is diagonal in the quantum numbers ℓ_3 and ℓ_4 and has no elements connecting + states with - states. Since there are no matrix elements connecting states of the same unperturbed energy, non-degenerate first and second order perturbation theory can be used to calculate the energy corrections.

In order to achieve the desired goal of expressing the energy corrections as functions of the interaction constants alone it is necessary to know the numerical values of the normal frequencies ω_1, ω_3, and ω_4. Furthermore, in order to do the numerical integrations over the inversion coordinate x it is necessary to assign numerical values to the five parameters, a_0, ζ_0, σ_0, L, and x_0. The most recent estimates of the

TABLE IX

NON-VANISHING MATRIX ELEMENTS OF $H_{vib}^{(1)}$

$$(n_1\ n^{1}_{2\pm}\ n_3\ell_3 n_4\ell_4|\frac{1}{hc}\ H_{vib}^{(1)}|n_1\ n_{2\pm}\ n_3\ell_3 n_4\ell_4) =$$

$$-\ D(n^{1}_{2\pm}\ |f_1\ \frac{\partial^2}{\partial x^2} + f_2\ \frac{\partial}{\partial x}|n_{2\pm}) + (n^{1}_{2\pm}\ |h_1 + \frac{\omega_1}{2}\ f_1|n_{2\pm})n_1$$

$$+\ (n^{1}_{2\pm}|h_3|n_{2\pm})n_3 + (n^{1}_{2\pm}|h_4|n_{2\pm})n_4$$

$$(n_1\text{-}2,\ n^{1\pm}_{2},\ n_3,\ \ell_3 n_4\ell_4|\frac{1}{hc}\ H_{vib}^{(1)}|n_1\ n_2^{\pm} n_3\ell_3 n_4\ell_4)$$

$$= (n_1\ n^{1}_{2\pm}\ n_3\ell_3 n_4\ell_4|\frac{1}{hc}\ H_{vib}^{(1)}|n_1\text{-}2,\ n_{2\pm}\ n_3\ell_3 n_4\ell_4)$$

$$= \frac{1}{2}\ (n^{1}_{2\pm}|h_1 - \frac{\omega_1}{2}\ f_1|n_{2\pm})\ \sqrt{n_1(n_1 - 1)}$$

$$(n_1\ n^{1}_{2\pm}, n_3\text{-}2,\ \ell_3 n_4\ell_4|\frac{1}{hc}\ H_{vib}^{(1)}|n_1\ n_2^{\pm}\ n_3\ell_3 n_4\ell_4)$$

$$= (n_1\ n^{1}_{2\pm}\ n_3\ell_3 n_4\ell_4|\frac{1}{hc}\ H_{vib}^{(1)}|n_1\ n_2^{\pm},\ n_3\text{-}2,\ \ell_3 n_4\ell_4)$$

$$= \frac{1}{2}\ (n^{1}_{2\pm}|h_3|n_{2\pm})\ \sqrt{n_3^{\,2} - \ell_3^{\,2}}$$

$$(n_1\ n^{1}_{2\pm}\ n_3\ell_3,\ n_4\text{-}2,\ \ell_4|\frac{1}{hc}\ H_{vib}^{(1)}|n_1\ n_2^{\pm}\ n_3\ell_3 n_4\ell_4)$$

$$= (n_1\ n^{1}_{2\pm}\ n_3\ell_3 n_4\ell_4|\frac{1}{hc}\ H_{vib}^{(1)}|n_1\ n_{2\pm},\ n_3\text{-}2,\ \ell_3 n_4\ell_4)$$

$$= \frac{1}{2}\ (n^{1}_{2\pm}|h_4|n_{2\pm})\ \sqrt{n_4^{\,2} - \ell_4^{\,2}}$$

$$(n^{1}_{2\pm}|g|n_{2\pm}) = \int_{-\pi}^{+\pi} \psi_{n^{1}_{2\pm}}(x)g(x)\psi_{n_{2\pm}}(x)dx$$

normal frequencies and equilibrium moments of inertia of NH_3 and ND_3 have been made by Benedict and Plyler.$^{(7)}$ Their values for ω_1, ω_3, and ω_4 will be used in the present calculation. The equilibrium dimensions x_1^0 and x_2^0 can be calculated from their estimated values of the equilibrium moments of inertia and will be used also. From Equation (13) it is seen that a_o can be calculated once the quadratic force constants a, b, and c for the symmetric vibrations are known. With the aid of Equations (8) through (10), the constants a, b, and c can be calculated once $(\omega_1)NH_3$, $(\omega_1)ND_3$, and $(\omega_2)NH_3$ are known. For the first two of these frequencies the values given by Benedict and Plyler will be used. The normal frequency $(\omega_2)NH_3$ can be calculated from the potential energy function given by Equations (17) or (18). One finds

$$(\omega_2)^2 = 16\,D\,G_o\left[1 - \left(\frac{F_o}{4G_o}\right)^2\right] . \tag{30}$$

The constants F_o and G_o are as yet unknown. However, the constants $F_o' = F_o + \frac{1}{2} F_1 + F_3 + F_4$ and $G_o' = G_o + \frac{1}{2} G_1 + G_3 + G_4$ are known. Assuming that F_1, F_3, and F_4 are much smaller than F_o, and G_1, G_3 and G_4 are much smaller than G_o, one can obtain an approximation to $(\omega_2)NH_3$ by replacing F_o by F_o' and G_o by G_o' in Equation (30). With the resulting approximate value of $(\omega_2)NH_3$, and the frequencies $(\omega_1)NH_3$ and $(\omega_1)_{ND_3}$, one can obtain approximate values of the quadratic force constants a, b, c and thus an approximate value of a_o. Equation (13) may be used to obtain approximate values of σ_o and ζ_o. The approximate value of L can then be obtained from the constant D. Finally, the equilibrium value x_o of the inversion coordinate is given by ζ_o/L. Thus, the values of ω_1,

ω_3 and ω_4 are known and the values of a_o, ζ_o, σ_o, L, and x_o can be estimated. Consequently, the numerical integrations required to evaluate the matrix elements of $H^{(1)}_{vib}$ can be done and the energy correction expressed as a function of the interaction constants F_i and G_i ($i = 1, 3, 4$) alone.

The improved energies, including the contribution due to $H^{(1)}_{vib}$, will be given by

$$E_{vib} = E^{(0)}_{vib} + E^{(1)}_{vib} \tag{31}$$

where $E^{(0)}_{vib}$ is the zero order energy given by Equation (25). The energy correction $E^{(1)}_{vib}$ will be of the form

$$\begin{aligned} E^{(1)}_{vib} = {} & A_2(n_2^{\pm}) + n_1 A_1(n_2^{\pm}) + n_3 A_3(n_2^{\pm}) + n_4 A_4(n_2^{\pm}) \\ & + n_1^2 A_{11}(n_2^{\pm}) + n_3^2 A_{33}(n_2^{\pm}) + n_4^2 A_{44}(n_2^{\pm}) \\ & + n_3 n_4 A_{34}(n_2^{\pm}) + n_1 n_3 A_{13}(n_2^{\pm}) + n_1 n_4 A_{14}(n_2^{\pm}) \\ & + \ell_3^2 L_3(n_2^{\pm}) + \ell_4^2 L_4(n_2^{\pm}) \end{aligned}$$

where the coefficients A_i, A_{ij}, and L_i depend only upon the interaction constants F_i and G_i and the quantum number $n_{2\pm}$. The problem at hand is to determine the six interaction constants so that Equation (31) will yield the correct inversion vibration splittings.

In order to describe the method by which the interaction constants are determined it is convenient to introduce the notation

$$\Delta E(n_1 n_2 n_3^{\ell_3} n_4^{\ell_4}) = E(n_1 n_2^- n_3^{\ell_3} n_4^{\ell_4}) - E(n_1 n_2^+ n_3^{\ell_3} n_4^{\ell_4})$$

$$\bar{E}(n_1 n_2 n_3^{\ell_3} n_4^{\ell_4}) = \frac{1}{2}\left[E(n_1 n_2^- n_3^{\ell_3} n_4^{\ell_4}) + E(n_1 n_2^+ n_3^{\ell_3} n_4^{\ell_4})\right].$$

ΔE is the splitting of the levels $(n_1\ n_2^{\pm}\ n_3^{\ell_3}\ n_4^{\ell_4})$ and $\bar{E}$ is their mean position. For simplicity, the splittings $\Delta E(0\ n_2\ 0^0\ 0^0)$ will be denoted by Δ_{n_2}. The constants F_3 and G_3 can be determined from the observed shift in splitting

$$\Delta E(0\ 0\ 1^1\ 0^0) - \Delta_0$$

and the observed anharmonicity

$$\bar{E}(0\ 1\ 1^1\ 0^0) - \left[\bar{E}(0\ 1\ 0^0\ 0^0) + \bar{E}(0\ 0\ 1^1\ 0^0)\right]$$

since these two quantities are independent of F_1, G_1, F_4, and G_4. Equating the observed numbers to the calculated expressions, in terms of F_3 and G_3, one obtains a pair of equations of the form

$$C_0 + C_1 F_3 + C_2 G_3 + C_3 F_3^2 + C_4 F_3 G_3 + C_5 G_3^2 = 0$$
$$C_0' + C_1' F_3 + C_2' G_3 + C_3' F_3^2 + C_4' F_3 G_3 + C_5' G_3^2 = 0$$

where the C_i and C_i' are numerical constants. Numerical values of F_3 and G_3 are found by solving this pair of equations. The best values of F_3 and G_3 that have been found, so far, are

$$F_3 = -175.0 \text{ cm}^{-1}$$
$$G_3 = 14.0 \text{ cm}^{-1}.$$

Similarly, the shift in splitting

$$\Delta E(0\ 0\ 0^0\ 1^1) - \Delta_0$$

and the anharmonicity

$$\bar{E}(0\ 1\ 0^0\ 1^1) - \left[\bar{E}(0\ 1\ 0^0\ 0^0) + \bar{E}(0\ 0\ 0^0\ 1^1)\right]$$

yield a pair of equations involving F_4 and G_4 alone. The best values of F_4 and G_4 so far obtained are

$$F_4 = 27.7 \text{ cm}^{-1}$$
$$G_4 = -13.8 \text{ cm}^{-1}$$

The question naturally arises of why the two observed shifts in splitting $\Delta E(0\ 0\ 1^1\ 0^0) - \Delta_0$ and $\Delta E(0\ 1\ 1^1\ 0^0) - \Delta_1$ were not used to determine F_3 and G_3. One finds that the two equations for F_3 and G_3 obtained by using these two experimental numbers are almost constant multiples of each other. Thus, with an interaction of the form postulated in this thesis, the two observed splittings with $n_3 = 1$ are not, effectively, independent pieces of information. Two pieces of information of a distinctly different nature are needed. Thus, the observed anharmonicity and one observed splitting have to be used.

The determination of F_1 and G_1, if at all possible, is subject to much greater uncertainty than the determination of F_3, G_3, F_4 and G_4. Three pairs of levels $(1, 0^{\pm}, 0^0, 0^0)$, $(1, 1^{\pm}, 0^0, 0^0)$, and $(1, 0^{\pm}, 0^0, 1^1)$, involving the excitation of the q_1 mode, have been observed in the spectrum of NH_3. From Table II one sees that

$$E_{vib}(10^{\pm}0^0 0^0) \sim E_{vib}(00^{\pm}0^0 2^0) \quad .$$

A more general potential than the one used in this thesis would contain a term of the form $k_{144}\ q_1\ r_4{}^2$ which has matrix elements connecting the levels $(1, 0^{\pm}, 0^0, 0^0)$ and $(0, 0^{\pm}, 0^0, 2^0)$. Consequently, these levels will be in Fermi resonance with each other. Similarly, the levels $(1, 1^{\pm}, 0^0, 0^0)$ would be in resonance with $(0, 1^{\pm}, 0^0, 2^0)$ and $(1, 0^{\pm}, 0^0, 1^1)$ would be in resonance with $(0, 0^{\pm}, 0^0, 3^1)$. (The levels $(0, 0^{\pm}, 0^0, 3^1)$ and $(0, 1^{\pm}, 0^0, 2^0)$ have not yet been observed in the ammonia spectrum.) In general, one would expect the Fermi resonance to have some effect on the splittings of the levels involved. Similarly, the observed anharmonicity

$$\bar{E}(110^0 0^0) - [\bar{E}(010^0 0^0) + \bar{E}(100^0 0^0)]$$

can be expected to involve a contribution due to the Fermi resonance. In order to make reliable estimates of F_1 and G_1 one must know the values that the anharmonicity, and one splitting, would have in the absence of the Fermi resonance.

Benedict, Plyler, and Tidwell(9) have attempted to estimate the magnitude of the cubic constant k_{144} connecting the resonating levels $(1, 0^{\pm}, 0^0, 0^0)$ and $(0, 0^{\pm}, 0^0, 2^0)$. If their estimate of $-k_{144}/\sqrt{2} = 37.4$ cm^{-1} is correct, then the observed value of $\bar{E}(1, 0, 0^0, 0^0)$ would be 13.15 cm^{-1} higher than the unperturbed value while the observed value of $\bar{E}(0, 0, 0^0, 2^0)$ would be 13.15 cm^{-1} lower than the unperturbed value. The observed splittings of the levels $(1, 0^{\pm}, 0^0, 0^0)$ and $(0, 0^{\pm}, 0^0, 2^0)$ are 0.99 cm^{-1} and 2.24 cm^{-1}, respectively. No matter whether the observed numbers or estimated values of the unperturbed numbers are used*, one has the problem of choosing F_1 and G_1 such that

$$\Delta E(100^0 0^0) > \Delta_0$$
$$\Delta E(110^0 0^0) < \Delta_1 \quad .$$

It appears that there are no values of F_1 and G_1, unless third and higher order perturbations give significant contributions, which will satisfy these inequalities. One can fit the splitting of the levels $(1, 0^{\pm}, 0^0, 0^0)$, in which case the predicted splitting of the levels $(1, 1^{\pm}, 0^0, 0^0)$ is much too large or one can fit the splitting of the levels $(1, 1^{\pm}, 0^0, 0^0)$, in which case the calculated splitting of the levels $(1, 0^{\pm}, 0^0, 0^0)$ will be too small. In order to obtain a rough estimate of the values of F_1 and G_1 the second alternative was chosen. Although

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* Assuming the estimated value of k_{144} in Reference (9) is valid one finds that the Fermi resonance should increase the splitting of the levels $(1, 0^{\pm}, 0^0, 0^0)$ by about .09 cm^{-1} and decrease the splitting of $(0, 0^{\pm}, 0^0, 2^0)$ by an equal amount.

this choice is quite arbitrary it might perhaps be hoped that the Fermi resonance has a smaller percentage influence on the splitting of the levels $(1, 1^{\pm}, 0^0, 0^0)$ than on the splitting of the levels $(1, 0^{\pm}, 0^0, 0^0)$. The values of F_1 and G_1 obtained in this way are

$$F_1 = 144.0 \text{ cm}^{-1}$$
$$G_1 = 25.6 \text{ cm}^{-1}.$$

It should be understood that the numbers for F_1 and G_1 may be very badly in error. Indeed, it is very doubtful whether the form of the postulated interaction between q_1 and the inversion coordinate x is valid.

Since F_o' and G_o' are known, the values of the interaction constants can be used, with the aid of Equation (19), to calculate F_o and G_o. Equation (30) then can be used to obtain an improved value for the normal frequency ω_2 for NH_3, which in turn can be used to obtain improved estimates of the force constants a, b, and c. Improved estimates of the parameters a_o, ζ_o, σ_o, L, and x_o then can be made. The best values so far obtained for these parameters are presented in Table X. As a final step, the corrections to the energy levels due to $H^{(1)}_{vib}$ are re-calculated using the interaction constants and the improved parameters given in Table X. The re-computation yields final values for the coefficients A_i, A_{ij}, and L_i in the energy correction formula. The final values of these coefficients are presented in Table XI. The reliability of the calculated results is limited, of course, by the uncertainty in the interaction constants F_1 and G_1. However, only the coefficients A_1, A_{11}, A_{13} and A_{14} are much affected by this uncertainty. The remaining coefficients are very insensitive to the values of F_1 and G_1.

It should be noticed that the magnitudes of the interaction constants F_i and G_i are sufficiently small to justify the use of perturbation theory. That this would be so was not obvious at the beginning of the calculation. Another point of interest is that $H_{vib}^{(1)}$ contributes a correction to the levels $(0, n_2\pm, 0^0, 0^0)$. It is found that only matrix elements of $H_{vib}^{(1)}$ for which $\Delta n_2 = 0, \pm 1$ make significant contributions to the energy corrections of the lower states. In the calculation of the energy corrections only contributions of matrix elements $(n_2|H_{vib}^{(1)}|n_2')$ with $n_2, n_2' < 4$ were retained, where this limitation was dictated by practical considerations of the available digital computer time. However it is estimated that the contributions of matrix elements with $n_2 \geq 4$ is less important for the lower states than the contributions of third or higher order perturbation terms. The corrected energies for the levels $(0, n_2\pm, 0^0, 0^0)$ for $n_2 = 0, 1,$ and 2 are given in Table XII. The correction for $n_2 = 3$ has not been calculated since it involves matrix elements connecting $n_2 = 3$ levels to $n_2 = 4$ levels. The corrected levels should be compared with the unperturbed levels given in Table VIII. Inclusion of the correction due to $H_{vib}^{(1)}$ is seen to enhance the agreement between the calculated and observed energies. However, the ground state splitting remains too large even after the correction has been applied. Unfortunately, with the simple form of the potential assumed in this investigation, it does not seem possible to decrease the ground state splitting and still retain a good overall description of the remaining $(0, n_2\pm, 0^0, 0^0)$ levels. This matter is discussed more fully in Appendix II.

The calculated inversion splittings, as a function of the vibrational quantum numbers, for levels with n_2 equal to 0 or 1 are given by

$$\begin{aligned}\Delta E(n_1 0 n_3^{\ell_3} n_4^{\ell_4}) = \Delta_0 - .559\, n_1 - .734\, n_3 + .220\, n_4 \\ + .272\, n_1^2 + .283\, n_3^2 + .026\, n_4^2 \\ - .167\, n_3 n_4 + .783\, n_1 n_3 - .176\, n_1 n_4 \\ - .0003\, \ell_3^2 - .0007\, \ell_4^2\end{aligned} \tag{31}$$

and

$$\begin{aligned}\Delta E(n_1 1 n_3^{\ell_3} n_4^{\ell_4}) = \Delta_1 - 16.445\, n_1 - 22.626\, n_3 + 6.749\, n_4 \\ + 5.949\, n_1^2 + 6.213\, n_3^2 + .544\, n_4^2 \\ - 3.687\, n_3 n_4 + 12.164\, n_1 n_3 - 3.599\, n_1 n_4 \\ - .0048\, \ell_3^2 - .0017\, \ell_4^2\end{aligned} \tag{32}$$

In deriving Equation (31) and (32), third and higher order perturbation corrections have been neglected. Although the magnitudes of the interaction constants F_1 and G_1 are much less than the magnitudes of F_0 and G_0, the splittings are such sensitive functions of F_1 and G_1 that terms cubic in the quantum numbers n_i are not completely negligible.

The calculated splittings for levels with $n_1 = 0$ are compared with the observed splittings in Table XIII. These numbers were obtained from Equations (31) and (32) by setting Δ_0 and Δ_1 equal to their observed values 0.793 and 35.81 cm^{-1}, respectively. The numbers in Table XIII are sensitive functions of F_3, G_3, F_4, and G_4 but are essentially independent of F_1 and G_1. It is seen that the calculated and observed results agree reasonably well with the exception of the splitting of the levels $(0, 0^{\pm}, 0^0, 2^0)$. It was pointed out above that this pair of levels is in Fermi resonance with the pair $(1, 0^{\pm}, 0^0, 0^0)$ so that agreement between the calculated and observed splittings perhaps should not be expected. Apart from the exception just mentioned, eleven data have been accounted for with four interaction constants. Differences between the observed and calculated values of the order of 1 to 2 cm^{-1} for the levels $(n_1, 1^{\pm}, n_3^{\ell_3}, n_4^{\ell_4})$ and 0.1 to 0.2 cm^{-1} for the levels $(n\ , 0^{\pm}, n_3^{\ell_3}, n_4^{\ell_4})$ can be expected due to the neglect of third and higher order perturbation corrections, the neglect of cubic and quartic terms in the expansion of the potential parameters F and G, and the approximate nature of the double-minimum wavefunctions $\psi_{n_2\pm}(x)$. The fact that the calculated numbers do not reproduce exactly the data used to determine the interaction constants is due primarily to the fact that these constant were obtained using approximate values of the parameters a_o, ζ_o, σ_o, L, and x_o whereas the numbers given in Table XIII were calculated using improved values for these parameters. Table XIV summarizes the results for the splittings of the states in which the symmetric q_1 vibration has been excited. In this case there is very little agreement between the calculated and observed numbers. The anharmonicity used to determine F_1 and G_1 should be the one corrected for Fermi resonance, namely 20.18 cm^{-1} + $C_{FR}(100^o0^o)$ - $C_{FR}(110^o0^o)$, where C_{FR} is the correction due to Fermi resonance. Benedict, Plyler, and Tidwell(9) have

TABLE X

PARAMETERS FOR NH_3

$\omega_1 = 3516.98 \text{ cm}^{-1}$

$\omega_3 = 3590.51 \text{ cm}^{-1}$

$\omega_4 = 1689.11 \text{ cm}^{-1}$

$x_1^0 = 2.101 \times 10^{-20} \text{ cm} \times \text{gm}^{1/2}$

$x_2^0 = .7757 \times 10^{-20} \text{ cm} \times \text{gm}^{1/2}$

$F_0' = 1894.61 \text{ cm}^{-1}$

$G_0' = 1288.68 \text{ cm}^{-1}$

$D = 64.93 \text{ cm}^{-1}$

$F_0 = 2111.91 \text{ cm}^{-1}$

$G_0 = 1275.68 \text{ cm}^{-1}$

$F_1 = -144.0 \text{ cm}^{-1}$

$G_1 = 25.6 \text{ cm}^{-1}$

$F_3 = -175.0 \text{ cm}^{-1}$

$G_3 = 14.0 \text{ cm}^{-1}$

$F_4 = 29.7 \text{ cm}^{-1}$

$G_4 = -13.8 \text{ cm}^{-1}$

$X_0 = 1.1441$

$\sinh \sigma_0 = 1.1133$

$\sin \zeta_0 = .2648$

$L = .2342$

$a_0 = 1.9574 \times 10^{-20} \text{ cm} \times \text{gm}^{1/2}$

$\omega_2 = 1047.98 \text{ cm}^{-1}$

$a = 2.2712 \times 10^5 \text{ dyne/cm}$

$b = 7.0770 \times 10^5 \text{ dyne/cm}$

$c = 2.0624 \times 10^5 \text{ dyne/cm}$

TABLE XI

COEFFICIENTS IN THE ENERGY CORRECTION FORMULA (cm^{-1})

$A_2(0^+)$	= - .235	$A_2(0^-)$	= - .299
$A_1(0^+)$	= - 1.608	$A_1(0^-)$	= - 2.167
$A_3(0^+)$	= - 5.658	$A_3(0^-)$	= - 6.392
$A_4(0^+)$	= - .997	$A_4(0^-)$	= - .777
$A_{11}(0^+)$	= - 7.188	$A_{11}(0^-)$	= - 6.916
$A_{33}(0^+)$	= - 8.233	$A_{33}(0^-)$	= - 7.950
$A_{44}(0^+)$	= - .541	$A_{44}(0^-)$	= - .515
$A_{34}(0^+)$	= 4.320	$A_{34}(0^-)$	= 4.153
$A_{13}(0^+)$	= -15.525	$A_{13}(0^-)$	= -14.742
$A_{14}(0^+)$	= 4.046	$A_{14}(0^-)$	= 3.870
$L_3(0^+)$	= - .0771	$L_3(0^-)$	= - .0774
$L_4(0^+)$	= - .0250	$L_4(0^-)$	= - .0257
$A_2(1^+)$	= - 4.221	$A_2(1^-)$	= - 4.636
$A_1(1^+)$	= 40.175	$A_1(1^-)$	= 23.730
$A_3(1^+)$	= 40.944	$A_3(1^-)$	= 18.318
$A_4(1^+)$	= -18.831	$A_4(1^-)$	= -12.082
$A_{11}(1^+)$	= -12.792	$A_{11}(1^-)$	= - 6.843
$A_{33}(1^+)$	= -14.078	$A_{33}(1^-)$	= - 7.865
$A_{44}(1^+)$	= - 1.063	$A_{44}(1^-)$	= - .519
$A_{34}(1^+)$	= 7.779	$A_{34}(1^-)$	= 4.092
$A_{13}(1^+)$	= -26.926	$A_{13}(1^-)$	= -14.772
$A_{14}(1^+)$	= 7.435	$A_{14}(1^-)$	= 3.836
$L_3(1^+)$	= - .0562	$L_3(1^-)$	= - .0610
$L_4(1^+)$	= - .0166	$L_4(1^-)$	= - .0183
$A_2(2^+)$	= -10.68	$A_2(2^-)$	= - 9.75

TABLE XII

CORRECTED ENERGY LEVELS $E_{vib}(0, n_2^{\pm}, 0^0, 0^0)$

Level	Calculated (cm^{-1})	Observed (cm^{-1})
$0\ 0^+\ 0^0\ 0^0$	0.00	0.00
$0\ 0^-\ 0^0\ 0^0$	0.88	0.793
$0\ 1^+\ 0^0\ 0^0$	933.20	932.51
$0\ 1^-\ 0^0\ 0^0$	968.29	968.32
$0\ 2^+\ 0^0\ 0^0$	1606.70	1597.42
$0\ 2^-\ 0^0\ 0^0$	1877.78	1882.16

Splitting	Calculated (cm^{-1})	Observed (cm^{-1})
Δ_0	0.88	0.793
Δ_1	35.09	35.81
Δ_2	271.08	284.56

TABLE XIII

INVERSION-VIBRATION INTERACTIONS: DEGENERATE VIBRATIONS

Inversion Splitting			
Level	Calculated (cm^{-1})	Observed (cm^{-1})	
001^10^0	.34	.35	a
002^00^0	.46	-	
002^20^0	.46	.43	
000^01^1	1.04	1.04	b,c
000^02^0	1.34	2.24	
000^02^2	1.33	1.42	
001^11^1	.42	.57	
011^10^0	19.39	18.49	
010^01^1	43.10	45.4	
011^11^1	23.00	23.68	

Anharmonicity	Calculated (cm^{-1})	Observed (cm^{-1})	
$\bar{E}(011^10^0) - [\bar{E}(010^00^0) + \bar{E}(001^10^0)]$	32.32	31.98	a
$\bar{E}(010^01^1) - [\bar{E}(010^00^0) + \bar{E}(000^01^1)]$	-15.28	-14.9	b,d
$\bar{E}(011^11^1) - [\bar{E}(010^00^0) + \bar{E}(001^11^1)]$	19.18	21.24	

a Used to fit F_3 and G_3

b Used to fit F_4 and G_4

c A more recent value is 1.01 cm^{-1} - c.f. Reference (10).

d In view of Reference (10), - 16.88 cm^{-1} is probably better.

TABLE XIV

INVERSION-VIBRATION INTERACTIONS: LEVELS WITH $n_1 = 1$

Inversion Splitting

Level	Calculated (cm^{-1})	Observed (cm^{-1})
$100^0 0^0$	.51	.99
$101^1 0^0$	.84	-
$100^0 1^1$	.58	.86
$110^0 0^0$	25.32	25.55

Anharmonicity	Calculated (cm^{-1})	Observed (cm^{-1})
$\bar{E}(110^0 0^0) - [\bar{E}(010^0 0^0) + \bar{E}(100^0 0^0)]$	30.63	30.18 cm*

* Including a somewhat arbitrary correction of 10 cm^{-1} for Fermi resonance.

estimated that $C_{FR}(100^o0^o)$ is 13.5 cm^{-1}. Since the levels $(0, 1^{\pm}, 0^0, 2^0)$ have not been observed it is difficult to make a reasonable estimate of $C_{FR}(110^o0^o)$. For the purpose of determining F_1 and G_1 a somewhat arbitrary estimate of 10 cm^{-1} was made for the overall contribution of the Fermi resonance to the anharmonicity.

It might be tempting to argue that the discrepancy between the computed and observed splittings for the pair $(1, 0^{\pm}, 0^0, 0^0)$ can be attributed entirely to the Fermi resonance with the pair $(0, 0^{\pm}, 0^0, 2^0)$. It is very easy to show, however, that such an argument is probably incorrect. Suppose there were terms in the potential of the form $f(x)q_1r_4{}^2$ having matrix elements connecting the states $(1, 0^{\pm}, 0^0, 0^0)$ and $(0, 0^{\pm}, 0^0, 2^0)$. Let the matrix elements connecting the two (+) states be V_{12}^{+} and V_{21}^{+} and the matrix elements connecting the two (-) states be V_{12}^{-} and V_{21}^{-}. The symmetry of the perturbing term must be such that it has no matrix elements connecting (+) states with (-) states. The energy shift due to the resonance between the two sets of levels is given by the roots $E_{\pm}$ of the two secular determinants

$$\begin{vmatrix} E^{(0)}_{1\pm} - E_{\pm} & V_{12}^{\pm} \\ V_{21}^{\pm} & E^{(0)}_{2\pm} - E_{\pm} \end{vmatrix} = 0$$

where $E^{(0)}_{1\pm}$ and $E^{(0)}_{2\pm}$ are the energies of the unperturbed levels $(1, 0^{\pm}, 0^0, 0^0)$ and $(0, 0^{\pm}, 0^0, 2^0)$. The perturbed energies are readily shown to be

$$E_{1\pm} = E^{(0)}_{1\pm} + \Delta_{\pm}$$
$$E_{2\pm} = E^{(0)}_{2\pm} - \Delta_{\pm}$$

where

$$\Delta_{\pm} = -\left(\frac{E_{1\pm}^{(0)} - E_{2\pm}^{(0)}}{2}\right) + \left[\left(\frac{E_{1\pm}^{(0)} - E_{2\pm}^{(0)}}{2}\right)^2 + |V_{12}^{\pm}|^2\right]^{1/2} .$$

The effect of the resonance on the inversion splitting is given by

$$E_{1^-} - E_{1^+} = E_{1^-}^{(0)} - E_{1^+}^{(0)} + (\Delta_- - \Delta_+)$$
$$E_{2^-} - E_{2^+} = E_{2^-}^{(0)} - E_{2^+}^{(0)} - (\Delta_- - \Delta_+) .$$

Thus, if the effect of the resonance is to increase the splitting of the pair (1, $0^{\pm}$, 0^0, 0^0) it must also decrease the splitting of the pair (0, $0^{\pm}$, 0^0, 2^0) by an equal amount, and vice versa. However, with the choice of the six interaction constants made in this thesis, the splittings of the levels (1, $0^{\pm}$, 0^0, 0^0) and (0, $0^{\pm}$, 0^0, 2^0) would have to be increased simultaneously in order to account for the observed numbers. Clearly, a simultaneous increase in splitting cannot be achieved by a Fermi resonance alone. Another possibility remains, however. In view of the generally good agreement obtained for splittings involving the degenerate vibrations one could assume that the calculated splitting of 1.34 cm^{-1} for the level (0, $0^{\pm}$, 0^0, 2^0) is correct, in the absence of the Fermi resonance, and that the resonance increases this splitting to the observed 2.24 cm^{-1}. In this case the unperturbed splitting of the levels (1, $0^{\pm}$, 0^0, 0^0) would have to be 1.89 cm^{-1} in order for the resonance to yield the observed splitting of .99 cm^{-1}. However, if F_1 and G_1 are chosen so that the unperturbed splitting of (1, $0^{\pm}$, 0 $^0_,$ 0^0) is 1.89 cm^{-1} then the unperturbed splitting for the levels (1, $1^{\pm}$, 0^0, 0^0) would be of the order of 70 cm^{-1} whereas the observed splitting is 25.55 cm^{-1}. It appears highly unlikely that a Fermi resonance perturbation could reduce the splitting of the levels $(1, 1^{\pm}, 0^0, 0^0)$ by such a large amount. It is highly probable that the actual interaction between the q_1 vibration and inversion is more sophisticated than the simple interaction postulated in this thesis. However, with the limited amount of information available concerning states in which the q_1 vibration is excited there is little hope of guessing an improved form for the interaction.

The discussion above also casts some doubt on whether the discrepancy between the calculated and observed splittings of the levels $(0, 0^{\pm}, 0^0, 2^0)$ can be attributed to Fermi resonance alone. Indeed, the interaction may be strongly ℓ_4 dependent whereas the model used in this investigation is practically independent of ℓ_4. The inclusion of an $\vec{r}_3 \cdot \vec{r}_4$ term in $H^{(1)}_{vib}$, which is allowed by the symmetry of the molecule but was omitted arbitrarily in this work, is of no help in this connection. An $\vec{r}_3 \cdot \vec{r}_4$ term would make contributions to the splitting which are proportional to the products $n_3 n_4$ and $\ell_3 \ell_4$ and consequently could not account for the difference of the splittings of $(0, 0^{\pm}, 0^0, 2^0)$ and $(0, 0^{\pm}, 0^0, 2^2)$. Unfortunately the splitting of the levels $(0, 0^{\pm}, 2^0, 0^0)$ has not been observed so that it is not known whether there is a similar dependence of the inversion splitting on ℓ_3.

The investigation, so far, has attempted to account for 23 observed data from the vibration-inversion spectrum of NH_3. These data are the positions of the seven "pure inversion" levels $(0, n_{2\pm}, 0^0, 0^0)$, the splittings of twelve other pairs of vibrational levels, and four numbers which essentially measure the anharmonicity of the interaction of the vibrational modes with the inversion. It has been shown that the potential energy function postulated in this thesis will account for the "pure inversion" levels, and all but one datum involving the interaction of the degenerate vibrations with the inversion, or a total of 18 data. Of the five data which cannot be accounted for, four are intimately involved with the non-degenerate q_1 vibration and the fifth, the splitting of the levels $(0, 0^{\pm}, 0^0, 2^0)$, is involved with q_1 at least through a Fermi resonance with the levels $(1, 0^{\pm}, 0^0, 0^0)$.

VI. VIBRATIONAL ENERGIES OF ND_3 IN LOWEST APPROXIMATIONS

Now that the potential constants for NH_3 have been determined it is a simple matter to obtain the constants for ND_3. The binding forces in molecules are, to a very good approximation, mass independent. Consequently the potential energy of NH_3 must be identical to the potential energy of ND_3. In order for a potential of the form given by Equation (17) to be valid for ND_3 as well as NH_3 the following relations must hold between the potential constants.

$$(F_0)_{ND_3} = (F_0)_{NH_3}$$

$$(G_0)_{ND_3} = (G_0)_{NH_3}$$

$$\left.\begin{aligned} (F_i)_{ND_3} &= \frac{(\omega_i)_{ND_3}}{(\omega_i)_{NH_3}} (F_i)_{NH_3} \\ (G_i)_{ND_3} &= \frac{(\omega_i)_{ND_3}}{(\omega_i)_{NH_3}} (G_i)_{NH_3} \end{aligned}\right\} i=1,3,4 \qquad (33)$$

$$\frac{(D)_{ND_3}}{(D)_{NH_3}} = \left[\frac{(\omega_2)_{ND_3}}{(\omega_2)_{NH_3}}\right]^2$$

These relations can be obtained by the following arguments. If the potential energies of ND_3 and NH_3 are to be identical then they must be identical at the planar configuration ($\zeta = q_1 = r_3 = r_4 = 0$) and at the equilibrium configurations ($\zeta = \pm\ \zeta_0$, where $\cos (\zeta_0/L) = F_0/4G_0$, and

$q_1 = r_3 = r_4 = 0$). Equating the potential energies of NH_3 and ND_3 at these points, one obtains the two equations

$$-2(F_0)_{ND_3} + 2(G_0)_{ND_3} = -2(F_0)_{NH_3} + 2(G_0)_{NH_3}$$

$$-2(G_0)_{ND_3} - \frac{(F_0)^2_{ND_3}}{4(G_0)_{ND_3}} = -2(G_0)_{NH_3} - \frac{(F_0)^2_{NH_3}}{4(G_0)_{NH_3}}$$

whose solutions are the first two of the Equations (33). From $\cos(\zeta_0/L) = F_0/4G_0$ it follows that

$$\left(\frac{\zeta_0}{L}\right)_{ND_3} = \left(\frac{\zeta_0}{L}\right)_{NH_3} .$$

The interactions constants F_i and G_i are related to the normal frequencies ω_i by relations of the form

$$\omega_i = C_i - 4F_i \cos\left(\frac{\zeta_0}{L}\right) + 4G_i \cos\left(\frac{2\zeta_0}{L}\right) .$$

Hence, the interaction constants of ND_3 must be related to those for NH_3 by the second pair of relations of Equation (33). The last of Equations (33) follows from Equation (30). The normal frequency $(\omega_2)ND_3$ can be obtained by application of the product rule

$$\frac{(\omega_1)_{ND_3}(\omega_2)_{ND_3}}{(\omega_1)_{NH_3}(\omega_2)_{NH_3}} = \frac{m_H}{m_D}\left[\frac{M+3m_D}{M+3m_H}\right]^{1/2}$$

where m is the nitrogen mass, m_H the hydrogen mass, and m_D the deuterium mass. The normal frequencies $(\omega_i)NH_3$ and $(\omega_i)ND_3$ for i = 1, 3, 4 are known from the analysis of the NH_3 and ND_3 spectra by Benedict and Plyler(7), and $(\omega_2)NH_3$ was calculated in the preceding chapter. The values of the constants for ND_3, calculated from Equation (33), are given in Table XV. The constants F_0' and G_0' appearing in the effective one-dimensional potential can be obtained from Equation (19). The three constants needed to solve the one-dimensional problem for ND_3 are found to have the values

$$D = 37.93 \text{ cm}^{-1}$$

$$F_o' = 1953.61 \text{ cm}^{-1}$$

$$G_o' = 1285.08 \text{ cm}^{-1} \quad .$$

Using these values of the constants the eigenvalues of the one-dimensional double minimum problem, Equation (27), have been found for ND_3 according to the method described in Chapter IV of this thesis. In this case, the 0^+ level lies 394.93 cm^{-1} above the minima of the effective one-dimensional potential $V'(x)$. The energy differences $E_{n_2\pm} - E_{0^+}$ are given in Table XVI. A calculation of the contributions to the energies of ND_3 due to the perturbation $H^{(1)}_{vib}$, which would be complicated by the presence of several resonances, will not be given in this work.

TABLE XV

CONSTANTS FOR ND_3 (cm^{-1})

$\omega_1 = 2496.96$

$\omega_3 = 2642.18$

$\omega_4 = 1226.32$

$\omega_2 = 801.01$

$D = 37.93$

$F_o = 2111.91$

$G_o = 1275.68$

$F_1 = -102.2$

$G_1 = 18.2$

$F_3 = -128.8$

$G_3 = 10.3$

$F_4 = 21.6$

$G_4 = -10.0$

TABLE XVI

ENERGY DIFFERENCES FOR THE LEVELS $(0, n_2{\pm}, 0^0, 0^0)$ of ND_3 (N x N TRUNCATION)

Level	Energy Differences (cm^{-1})			
$n_2{\pm}$	Calculated			Observed
	N = 12	N = 16	N = 20	
0^+	0.00	0.00	0.00	0.00
0^-	0.08	0.08	0.08	0.053
1^+	746.90	746.74	746.74	745.7
1^-	751.20	751.18	751.18	749.4
2^+	1359.71	1359.45	1359.45	1359
2^-	1435.70	1435.60	1435.60	1429
3^+	1835.47	1834.98	1834.98	1830
3^-	2115.41	2115.08	2115.07	2106.60
4^+	2495.39	2485.28	2485.28	-
4^-	2873.08	2867.55	2867.55	-

VII. INVERSION-ROTATION SPLITTINGS IN NH_3

The infra red spectrum of ammonia shows the rotational structure of a symmetric top molecule. The effective rotational constants are functions of the vibrational quantum numbers and the symmetry (+ or -) of the inversion state. In other words, the inversion splittings are functions of the rotational quantum numbers and, as indicated in the introduction to this thesis, can be expressed by a formula of the form

$$\Delta_n = \Delta_n^o + (B_n^- - B_n^+)\left[J(J+1) - K^2\right] + (C_n^- - C_n^+)K^2 + \cdots \quad .$$

Although terms quartic in J and K are often added to this type of expression in order to obtain an empirical fit to the experimentally observed splittings, the dominant contribution comes from the quadratic terms. In this investigation no attempt will be made to calculate terms quartic in J and K even though they could be included in the theoretical development. Until the quadratic terms can be accounted for accurately, there seems to be little point in trying to calculate the smaller quartic terms.

For motions in which the degenerate vibrations are not excited the ammonia molecule maintains the geometry of a symmetric pyramid, in which case the two moments of inertia perpendicular to the symmetry axis are equal and the products of inertia vanish. One of the basic assumptions made in this investigation is that in spite of the large amplitude of the inversion motion the instantaneous configuration of the molecule never departs very much from one of pyramidal symmetry. Thus, in lowest approximation, the rotation-vibration Hamiltonian can be regarded as the sum of the vibrational Hamiltonian and a symmetric rotator Hamiltonian

$$H = H_{vib} + \frac{1}{2I_{\parallel}}(P_x^2 + P_y^2) + \frac{1}{2I_{\perp}}P_z^2 \qquad (34)$$

where $I_{\perp}$ is the moment of inertia about the symmetry axis and $I_{\parallel}$ is the moment of inertia about an axis perpendicular to the symmetry axis. P_x, P_y and P_z are the three components of the total angular momentum with respect to a molecule-fixed reference frame. The moments of inertia $I_{\parallel}$ and $I_{\perp}$ will be very sensitive functions of the inversion coordinate, but, in lowest approximation, will be independent of the remaining vibrational coordinates.

In the introduction it was pointed out that the rotation-inversion constants $B^- - B^+$ and $C^- - C^+$, are extremely sensitive functions of the inversion quantum number, n_2, while their dependence on the remaining vibrational quantum numbers is much milder. Thus, one might expect that the main features of the inversion doublet separation are contained in the simple Hamiltonian given above. Indeed, the investigations of Sheng, Barker and Dennison(4) and Hadley and Dennison(5) give ample verification to this expectation. Nevertheless it becomes clear from the experimentally observed data that the higher order terms in the complete vibration-rotation Hamiltonian cannot be neglected entirely. However, since the contributions of the higher order terms are rather difficult to compute and since the Hamiltonian (34) can be expected to give the major contributions to the inversion doublet separations, the following method of attack will be used. First the contributions of the Hamiltonian (34) will be calculated and compared to the observed data.

Then the complete vibration-rotation Hamiltonian will be developed and those terms which can contribute to $B^- - B^+$ and $C^- - C^+$ examined. Before presenting the lengthy development of the complete Hamiltonian it will be profitable to work out in some detail the implications of a Hamiltonian of the form of Equation (34).

For the purpose of computation it is convenient to rewrite Equation (34) as

$$H = H^{(0)} + H^{(1)}$$

where

$$\frac{H^{(0)}}{hc} = \frac{H^{(0)}_{vib}}{hc} + B_e\left[J^2 - J_z^2\right] + C_e J_z^2 \tag{35}$$

$$\frac{H^{(1)}}{hc} = \frac{H^{(1)}_{vib}}{hc} + (B - B_e)\left[J^2 - J_z^2\right] + (C - C_e) J_z^2 \tag{36}$$

where

$$B = \frac{h}{8\pi^2 c\, I_{\parallel}} \qquad C = \frac{h}{8\pi^2 c\, I_{\perp}} \tag{37}$$

B and C are functions of the inversion coordinate. B_e and C_e are the equilibrium values of B and C and are constants.* $J_\alpha = 1/\hbar\, P_\alpha (\alpha = x,y,z)$ are dimensionless angular momentum operators and $J^2 = J_x^2 + J_y^2 + J_z^2$. $H^{(0)}_{vib}$ is given by Equation (23) and $H^{(1)}_{vib}$ is given by Equation (24).

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* $B_e = 9.965$ cm^{-1} and $C_e = 6.341$ cm^{-1}.(7)

If the degenerate frequencies are not excited the moments of inertia are

$$I_{\parallel} = \frac{1}{2}x_1^2 + x_2^2$$
$$I_{\perp} = x_1^2$$

where x_1 and x_2 are the mass weighted internal coordinates introduced in Chapter II. Upon introducing the coordinates σ and ζ defined by Equation (13) and replacing σ by its equilibrium value σ_0, one obtains

$$B - B_e = B_e\left[\frac{\sin^2\zeta_0 - (\sin Lx)^2}{\left(\frac{\cosh^2\sigma_0 - 1}{\cosh^2\sigma_0 + 1}\right) + (\sin Lx)^2}\right] \tag{38}$$

$$C - C_e = C_e\left[\frac{\cos^2\zeta_0 - (\cos Lx)^2}{(\cos Lx)^2}\right] \tag{39}$$

where $x = \zeta/L$ is the inversion coordinate.

The "zero-order" Schroedinger equation

$$\frac{H^{(0)}}{hc}\Psi^{(0)} = E^{(0)}\Psi^{(0)}$$

has solutions

$$\Psi^{(0)} = \Psi^{(0)}_{vib}\,\psi_{JKM} \tag{40}$$

$$E^{(0)} = E^{(0)}_{vib} + B_e\left[J(J+1) - K^2\right] + C_e K^2 \tag{41}$$

where ψ_{JKM} is a symmetric top wavefunction, $\Psi^{(0)}_{vib}$ is the wavefunction given by Equation (26), and $E^{(0)}_{vib}$ is given by Equation (25). The energy correction due to the "perturbation," $H^{(1)}$, is easily obtained. Since the calculation of the vibration-rotation energies will be restricted to terms at most quadratic in the rotational quantum numbers J and K, the corrected energies are found to have the form

$$E = E_{vib} + B(n_1 n_2^{\pm} n_3 n_4)\left[J(J+1) - K^2\right] + C(n_1 n_2^{\pm} n_3 n_4)K^2 \qquad (42)$$

where E_{vib} is given by Equation (31) and

$$B(n_1 n_2^{\pm} n_3 n_4) = B_e + \beta_2(n_2^{\pm}) + n_1\beta_1(n_2^{\pm}) + n_3\beta_3(n_2^{\pm}) + n_4\beta_4(n_2^{\pm})$$

$$C(n_1 n_2^{\pm} n_3 n_4) = C_e + \gamma_2(n_2^{\pm}) + n_1\gamma_1(n_2^{\pm}) + n_3\gamma_3(n_2^{\pm}) + n_4\gamma_4(n_2^{\pm}) \qquad (43)$$

The quantities $\beta_2(n_2\pm)$ and $\gamma_2(n_2\pm)$ are the expectation values of Equations (38) and (39), respectively. The coefficients $\beta_i(n_2\pm)$ and $\gamma_i(n_2\pm)$ with i = 1, 3, or 4 arise from cross terms between the off-diagonal matrix elements of Equations (38) and (39), respectively, and the off-diagonal matrix elements of $H^{(1)}_{vib}$. Numerical values of the $\beta_i(n_2\pm)$ and $\gamma_i(n_2\pm)$ are given in Table XVII.

The quantities of interest in this investigation are the differences of the rotational constants of the (+) and (-) levels, namely

$$B^- - B^+ = B(n_1 n_2^- n_3 n_4) - B(n_1 n_2^+ n_3 n_4)$$

$$C^- - C^+ = C(n_1 n_2^- n_3 n_4) - C(n_1 n_2^+ n_3 n_4) \quad .$$

The calculated values of $B^- - B^+$ and $C^- - C^+$, for the levels (0, $n_2\pm$, 0^0, 0^0, J, K), are compared with the observed values in Table XVIII. The numbers given in Table XVIII are differences of the diagonal matrix elements of the rotational part of Equation (36) and correspond to the quantities calculated by Sheng, Barker and Dennison$^{(4)}$ for $n_2 = 1$ and Hadley and Dennison$^{(5)}$ for $n_2 = 0$ and 1. Although agreement between the observed and calculated numbers is not perfect, and should not be perfect in the present approximation, the calculated numbers do show the correct dependence on the quantum number n_2. The magnitudes of $B^- - B^+$ and $C^- - C^+$ increase with n_2 for n_2 equal to 0, 1, and 2 and decrease when n_2 is equal to 3.

Although the differences of the rotational constants depend mainly on the inversion quantum number, n_2, they have been found to vary significantly with the vibrational quantum numbers n_1, n_3 and n_4. In order to discuss this dependence it is convenient to write

$$B(n_1 n_2^- n_3 n_4) - B(n_1 n_2^+ n_3 n_4)$$

$$= B(0 n_2^- 0 0) - B(0 n_2^+ 0 0) + \Delta B(n_1 n_2 n_3 n_4)$$

$$C(n_1 n_2^- n_3 n_4) - C(n_1 n_2^+ n_3 n_4)$$

$$= C(0 n_2^- 0 0) - C(0 n_2^+ 0 0) + \Delta C(n_1 n_2 n_3 n_4) \; .$$

In the present approximation, ΔB and ΔC depend only on the coefficients $\beta_i(n_2 \pm)$ and $\gamma_i(n_2 \pm)$, i = 1, 3, or 4, of Equation (43) and hence arise from cross terms between off-diagonal matrix elements of $H^{(1)}_{vib}$ and off-diagonal matrix elements of Equations (38) and (39). The calculated values of ΔB and ΔC, for levels with $n_2 = 1$, are compared with the observed values in Table XIX. It is seen from this table that the changes in $B^- - B^+$ and $C^- - C^+$, for levels with $n_2 = 1$, as functions of n_1, n_3, and n_4, are given surprisingly well by the simple Hamiltonian.$^{(34)}$ In all cases the signs of ΔB and ΔC are correct and, with the exception of the level $(0\ 1^{\pm}\ 0^0\ 1^1)$, the calculated magnitudes agree rather well with the observed numbers. The corresponding numbers for levels with $n_2 = 0$ are shown in Table XX. The calculated values of ΔB and ΔC for the levels $(1\ 0^{\pm}\ 0^0\ 0^0)$ undoubtedly should be disregarded since they are strongly dependent on the potential constants F_1 and G_1. It was seen in Chapter V that these constants, which account for the inversion splitting of the levels $(1\ 1^{\pm}\ 0^0\ 0^0)$, were inadequate to describe the splitting of the pure vibrational levels $(1\ 0^{\pm}\ 0^0\ 0^0)$. Hence, they cannot be expected to give the correct inversion-vibration-rotation interaction for the latter. For the levels $(0\ 0^{\pm}\ 1^1\ 0^0)$ the calculated and observed values of ΔC agree well while the calculated and observed values of ΔB agree in sign and only roughly in magnitude. The calculated and observed numbers for the levels $(0\ 0^{\pm}\ 0\ 1^1)$ disagree violently. Indeed, the sign of ΔB is not given correctly.

Complete agreement between the calculated and observed rotation-inversion constants should not be expected on the basis of a Hamiltonian as incomplete as Equation (34). In fact, it is rather remarkable that the calculated and observed numbers agree as well as they do. In order to discuss the possible contributions due to neglected terms in the Hamiltonian it will be convenient to use the symbol $\sim$ to mean "of the order of magnitude of." By numbers of the order of ω or B will be meant numbers of the order of magnitude of $\omega_2 = 1047.98\ \mathrm{cm}^{-1}$ and $B_e = 9.965\ \mathrm{cm}^{-1}$, respectively. The symbol n will be used to represent the collection of six vibrational quantum numbers and J to represent the two rotational

TABLE XVII

COEFFICIENTS IN EQUATION (43)(cm^{-1})

$\beta_2(0^+) = -.039993$	$\beta_2(0^-) = -.045545$
$\beta_1(0^+) = -.080141$	$\beta_1(0^-) = -.075269$
$\beta_3(0^+) = -.122296$	$\beta_3(0^-) = -.118176$
$\beta_4(0^+) = .031764$	$\beta_4(0^-) = .030540$
$\gamma_2(0^+) = .033635$	$\gamma_2(0^-) = .035166$
$\gamma_1(0^+) = .025590$	$\gamma_1(0^-) = .023673$
$\gamma_3(0^+) = .039369$	$\gamma_3(0^-) = .035166$
$\gamma_4(0^+) = -.010136$	$\gamma_4(0^-) = -.009798$
$\beta_2(1^+) = .309620$	$\beta_2(1^-) = .140587$
$\beta_1(1^+) = -.142895$	$\beta_1(1^-) = -.075911$
$\beta_3(1^+) = -.208919$	$\beta_3(1^-) = -.118094$
$\beta_4(1^+) = .057433$	$\beta_4(1^-) = .030428$
$\gamma_2(1^+) = -.032810$	$\gamma_2(1^-) = .015892$
$\gamma_1(1^+) = .043645$	$\gamma_1(1^-) = .024909$
$\gamma_3(1^+) = .064482$	$\gamma_3(1^-) = .039452$
$\gamma_4(1^+) = -.017529$	$\gamma_4(1^-) = -.009972$
$\beta_2(2^+) = .714178$	$\beta_2(2^-) = .145634$
$\gamma_2(2^+) = -.125151$	$\gamma_2(2^-) = .047184$
$\beta_2(3^+) = .147835$	$\beta_2(3^-) = -.106612$
$\gamma_2(3^+) = .065656$	$\gamma_2(3^-) = .160586$

TABLE XVIII

INVERSION-ROTATION SPLITTINGS IN THE LEVELS $(0\ n_2^{\pm}\ 0^0\ 0^0\ J\ K)$

$n_2^{\pm}$	$(B^- - B^+)_{calc}$	$(B^- - B^+)_{obs}$	$(C^- - C^+)_{calc}$	$(C^- - C^+)_{obs}$
$0^{\pm}$	-.005552 (cm^{-1})	-.005054 (cm^{-1})	.001531 (cm^{-1})	.001998 (cm^{-1})
$1^{\pm}$	-.1690	-.1817	.0487	.0721
$2^{\pm}$	-.5685	-.535	.1723	.231
$3^{\pm}$	-.2544	-.3041	.0949	.1034

TABLE XIX

DEPENDENCE OF $B^- - B^+$ AND $C^- - C^+$ ON n_1, n_3, AND n_4 WHEN $n_2 = 1$

Level	ΔB_{calc} (cm^{-1})	ΔB_{obs} (cm^{-1})	ΔC_{calc} (cm^{-1})	ΔC_{obs} (cm^{-1})
$1\ 1^{\pm}\ 0^0\ 0^0$	.0670	.0552	-.0187	-.0251
$0\ 1^{\pm}\ 1^1\ 0^0$	.0908	.0833	-.0250	-.0292
$0\ 1^{\pm}\ 0^0\ 1^1$	-.0270	-.009	.0076	.025
$0\ 1^{\pm}\ 1^1\ 1^1$	.0638	.052	-.0175	-.018

TABLE XX

DEPENDENCE OF $B^- - B^+$ AND $C^- - C^+$ ON n_1, n_3, AND n_4 WHEN $n_2 = 0$

Level	ΔB_{calc}(cm^{-1})	ΔB_{obs} (cm^{-1})	ΔC_{calc} (cm^{-1})	ΔC_{obs} (cm^{-1})
$1\ 0^{\pm}\ 0^0\ 0^0$	.0049	-.007	-.0019	.001
$0\ 0^{\pm}\ 1^1\ 0^0$	.0041	.0015	-.0011	-.0013
$0\ 0^{\pm}\ 0^0\ 1^1$	-.0012	.099	.0003	.009

quantum numbers J and K. For example, one finds

$$(n|\frac{H^{(1)}_{vib}}{hc}|n) \sim \omega\left(\frac{B}{\omega}\right)$$

$$(n|\frac{H^{(1)}_{vib}}{hc}|n'\neq n) \sim \omega\sqrt{\frac{B}{\omega}}$$

$$(n|\frac{H^{(1)}_{rot}}{hc}|n) \sim B\left(\frac{B}{\omega}\right)J^2$$

$$(n|\frac{H^{(1)}_{rot}}{hc}|n'\neq n) \sim B\sqrt{\frac{B}{\omega}}\,J^2$$

where

$$H^{(1)}_{rot} = H^{(1)} - H^{(1)}_{vib} \ .$$

In the calculation of the corrections to the rotational energies, obtained by treating Equation (36) as a perturbation, two kinds of terms have been taken into account. First, the diagonal matrix elements of $H^{(1)}_{rot}$ were calculated. These give a correction of order

$$\frac{B^2}{\omega}J^2 \ .$$

Next, the contribution due to cross terms between the off-diagonal matrix elements of $H^{(1)}_{vib}$ and $H^{(1)}_{rot}$ were calculated. This contribution is of the order

$$\frac{1}{\omega}\left(\omega\sqrt{\frac{B}{\omega}}\right)\left(B\sqrt{\frac{B}{\omega}}J^2\right) = \frac{B^2}{\omega}J^2 \ .$$

Thus, the inversion-rotation splittings calculated above are the differences of two terms of the order of magnitude of $(B^2/\omega)J^2$. However, one knows from the usual molecular theory that there are terms in the rotation-vibration Hamiltonian which have not been included in the present treatment that make contributions of order $(B^2/\omega)J^2$. The main interest in the present investigation is not in the rotational constants themselves but in their differences for the - and + inversion states. Not all terms of order $(B^2/\omega)J^2$ should be expected to give equally important contributions to the inversion-rotation splittings. The dominant contributions should come from those terms which are sensitive functions of the inversion coordinate. Nevertheless, to give a proper treatment of the dependence of the inversion splittings on the rotational quantum numbers one should develop the complete rotation-vibration Hamiltonian and retain all terms which can make contributions of order $(B^2/\omega)J^2$.

The relative success of the calculations based on the incomplete Hamiltonian (34) suggests that the neglected terms make only a very small contribution to the inversion splittings, with the exception, perhaps, of the levels with $n_4 = 1$. One would like to verify this. Also, one would like to see why the calculated and observed splittings for levels with $n_4 = 1$ disagree so badly. The remainder of this chapter will be devoted to obtaining a development of the complete Hamiltonian out to terms which make contributions of order $(B^2/\omega)J^2$ to the rotational energies. The task of diagonalizing this Hamiltonian is complicated by several resonances and has not been accomplished in general. Nevertheless, it has been possible to calculate the contribution to the energies of the levels $(0\ n_2 \pm\ 0^0\ 0^0\ J\ K)$.

The general Hamiltonian for an N-atomic molecule, using a completely arbitrary set of 3N-6 internal (vibrational) coordinates, can be written in the form

$$H = \frac{1}{2}\sum_{i,j}^{x,y,z} \mu^{1/4} g^{-1/4} (P_i - p_i + C_i) \mu^{-1/2} g^{1/2} \mu_{ij} (P_j - p_j) \mu^{1/4} g^{-1/4}$$

$$+ \frac{1}{2}\sum_{\alpha,\beta=1}^{3N-6} \mu^{1/4} g^{-1/4} p_\alpha \mu^{-1/2} g^{1/2} g^{\alpha\beta} p_\beta \mu^{1/4} g^{-1/4} + V \qquad (44)$$

where P_x, P_y, and P_z are the three components of total angular momentum in a molecule-fixed reference frame, p_x, p_y, and p_z are the components of the internal angular momentum, and p_α ($\alpha = 1, 2, \ldots, 3N-6$) are the 3N-6 linear momentum operators conjugate to the 3N-6 internal coordinates. The quantities μ_{ij} are related to the reciprocals of the moments and products of inertia and the quantities C_x, C_y, and C_z, which do not occur in the usual molecular vibration-rotation Hamiltonian, are functions of the internal coordinates. A discussion of the derivation of Equation (44) and the precise definition of all quantities appearing in Equation (44) are given in Appendix III. Equation (44) is a little more general than the usual molecular Hamiltonian in which the internal coordinates are normal coordinates. In Appendix III it is shown that when normal coordinates are chosen for internal coordinates, Equation (44) reduces to the usual molecular Hamiltonian in the form given by Darling and Dennison.(13) The necessity of using the more general Hamiltonian arises from the fact that the inversion coordinate is not a normal coordinate, and, indeed, does not even describe a small oscillation.

Equation (44) will be developed in the five small oscillation coordinates, retaining only those terms which make contributions to the energy of order $(B^2/\omega)J^2$ or larger. Furthermore, terms whose energy contributions are of higher degree than quadratic in the rotational quantum numbers J and K will be discarded. Under these restrictions one obtains

$$H = H^{(0)} + H^{(1)}$$

where $H^{(0)}$ is again given by Equation (35) and

$$
\begin{aligned}
\frac{H^{(1)}}{hc} = {} & \frac{H^{(1)}_{vib}}{hc} + B_e\phi_1(x)\left[J^2 - J_z^2\right] + C_e\phi_2(x)J_z^2 \\
& + A_0\left[\phi_3(x)q_1^2 + \phi_4(x)\left(\frac{10^3}{\omega_3}\right)r_3^2 + \phi_5(x)\left(\frac{10^3}{\omega_4}\right)r_4^2\right]\cdot\left[J^2 - J_z^2\right] \\
& + A_0\left[\phi_6(X)q_1^2 + \phi_7(x)\sin^2\tau\left(\frac{10^3}{\omega_3}\right)r_3^2 + \phi_7(x)\cos^2\tau\left(\frac{10^3}{\omega_4}\right)r_4^2\right]\cdot J_z^2 \\
& + A_0\left[\phi_8(x)(q_{3x}p_{3y} - q_{3y}p_{3x}) + \phi_9(x)(q_{4x}p_{4y} - q_{4y}p_{4x})\right]\cdot J_z \\
& + \frac{A_0}{4i}\tan 2\tau\left[\phi_9(x) - \phi_8(x)\right]\cdot\left[\sqrt{\frac{\omega_3}{\omega_4}}(q_4^{-}p_3^{+} - q_4^{+}p_3^{-}) + \sqrt{\frac{\omega_4}{\omega_3}}(q_3^{-}p_4^{+} - q_3^{+}p_4^{-})\right]\cdot J_z \qquad (45) \\
& + \frac{A_0}{i}\left[\phi_{10}(x)p_1 - \frac{1}{i}\left(\phi_{11}(X)\frac{\partial}{\partial X} + \phi_{12}(X)\right)\right] \\
& X\left[\left(\frac{10^2\sin\tau}{\sqrt{\omega_3}}q_3^{+} + \frac{10^2\cos\tau}{\sqrt{\omega_4}}q_4^{+}\right)(J_x - iJ_y) - \left(\frac{10^2\sin\tau}{\sqrt{\omega_3}}q_3^{-} + \frac{10^2\cos\tau}{\sqrt{\omega_4}}q_4^{-}\right)(J_x + iJ_y)\right] \\
& + A_0\phi_{13}(x)\left[\left(\sqrt{\frac{\omega_3}{\omega_4}}q_4^{-}p_3^{-} - \sqrt{\frac{\omega_4}{\omega_3}}q_3^{-}p_4^{-}\right)(J_x - iJ_y) + \left(\sqrt{\frac{\omega_3}{\omega_4}}q_4^{+}p_3^{+} - \sqrt{\frac{\omega_4}{\omega_3}}q_3^{+}p_4^{+}\right)(J_x + iJ_y)\right]
\end{aligned}
$$

where

$$p_1 = \frac{1}{i}\frac{\partial}{\partial q_1} \qquad p_{jx} = \frac{1}{i}\frac{\partial}{\partial q_{jx}} \qquad p_{jy} = \frac{1}{i}\frac{\partial}{\partial q_{jy}}$$

$$\left.\begin{aligned} p_j^{\pm} &= p_{jx} \pm i\, p_{jy} \\ q_j^{\pm} &= q_{jx} \pm i\, q_{jy} \end{aligned}\right. \qquad (j = 3,4)$$

$$A_0 = \frac{h}{8\pi^2 c\, a_0^2} \ .$$

A discussion of the derivation of Equation (45) and the precise definition of the functions $\phi_j(x)$ are given in Appendix III. If one sets all the $\phi_j(x) = 0$ except $\phi_1(x)$ and $\phi_2(x)$, Equation (45) reduces to Equation (36) with

$$B - B_e = B_e\phi_1(x)$$
$$C - C_e = C_e\phi_2(x) \ .$$

The additional terms are essentially of two types. One type consists of terms quadratic in the total angular momentum operators and quadratic in the small displacement coordinates. The others are the "coriolis" operators, linear in the total angular momentum operators. A third type of term which, in general, could give contributions of order $(B^2/\omega)J^2$ has been omitted. It consists of terms quadratic in the total angular momentum operators but linear in the small displacement coordinates. These terms have matrix elements connecting states for which one of the vibrational quantum numbers differs by unity. They will make contributions to the rotational energies of order $(B^2/\omega)J^2$ only if the potential perturbation has matrix elements between states for which one vibrational quantum number differs by unity. Due to the special form of $H^{(1)}_{\text{vib}}$ used in this thesis the potential perturbation has no matrix elements involving a change in a vibrational quantum number by one unit. It has been pointed out that the potential function used in this work is incomplete since it does not contain any of the terms cubic in the small displacement coordinates, but independent of the inversion coordinate, that normally can be expected to appear. If these missing cubic terms were included then it would be necessary to include the terms quadratic in the total angular momentum operators and linear in the small displacement coordinates. The neglect of these terms can be expected to introduce appreciable errors in the calculation of the rotational constants $B^{\pm}$ and $C^{\pm}$ but should not affect appreciably the differences $B^- - B^+$ and $C^- - C^+$.*

Another term which has not been included in Equation (45) is the ℓ-type doubling operator

$$\frac{\delta H}{hc} = -2A_0\,\phi_\ell(x)\left[\left(\frac{10^3\sin^2\tau}{\omega_3}q_3^{+2} + \frac{10^3\cos^2\tau}{\omega_4}q_4^{+2}\right)\left(J_x - iJ_y\right)^2 + \left(\frac{10^3\sin^2\tau}{\omega_3}q_3^{-2} + \frac{10^3\cos^2\tau}{\omega_4}q_4^{-2}\right)\left(J_x + iJ_y\right)^2\right]$$

where $\phi_\ell(x)$ is defined in Appendix III. Normally this operator gives contributions of order $(B^3/\omega^2)J^3$ only. However, for degenerate levels with $\ell_4 = \pm 1$ and $K = \pm 1$, this operator contributes to the "giant"

---

* Whereas calculations of the differences $B^- - B^+$ and $C^- - C^+$ are relatively successful, calculations of $B^{\pm}$ and $C^{\pm}$ for the individual inversion states are not very successful.

ℓ-type resonance discussed by Garing, Nielsen, and Rao.(10) In the present investigation no attempt will be made to discuss this special case.

Unfortunately, a perturbation treatment of Equation (45) becomes exceedingly complicated due to the presence of several near resonances. For example, the coriolis operator proportional to $\phi_{10}(x)$ has matrix elements connecting the states $(1\ n_2^-\ 0^0\ 0^0\ J\ K)$ and $(0\ n_2^+\ 1^1\ 0^0\ J\ K{+}1)$. The difference between the zero order energies of these two states is

$$E_{n_2^-} - E_{n_2^+} - 73.53 + 3.62(2K+1) \quad \mathrm{cm}^{-1}.$$

This difference is especially small when n_2 is 0 or 1 since $E_{0^-} - E_{0^+} = .94\ \mathrm{cm}^{-1}$ and $E_{1^-} - E_{1^+} = 35.49\ \mathrm{cm}^{-1}$. Another resonance arises from the fact that the coriolis operator proportional to $1/i(\phi_{11}\ \partial/\partial x + \phi_{12})$ has matrix elements connecting the states $(0\ 2^+\ 0^0\ 0^0\ J\ K)$ and $(0\ 0^-\ 0^0\ 1\ J\ K{+}1)$. The energy difference between these levels is

$$-72.96 + 3.62\,(2K+1) \quad \mathrm{cm}^{-1}.$$

Due to these rotational resonance interactions it is not possible for levels where n_1, n_3, and n_4 are not all zero, to compute the corrections to $B^- - B^+$ by ordinary non-degenerate perturbation theory. Such calculations have been tried but the corrections to $B^- - B^+$ so obtained proved too large, due mainly to the presence of resonance denominators. It appears, however, that non-degenerate perturbation theory can be used to calculate the contributions to the energies of the levels $(0,\ 0^{\pm},\ 0^0,\ 0^0,\ J,\ K)$ and $(0,\ 1^{\pm},\ 0^0,\ 0^0,\ J,\ K)$ and the subsequent calculations will be limited to these levels.

The differences of the rotational constants for the levels $(0, 0^{\pm}, 0^0, 0^0)$ and $(0, 1^{\pm}, 0^0, 0^0)$, calculated from Equation (45), are given in Table XXI. It is seen that the calculated values of $C^- - C^+$ differ little from those computed on the basis of the Hamiltonian (34), although the additional contributions do make a slight improvement. The magnitudes of the calculated values of $B^- - B^+$ are now considerably too large whereas formerly they were too small. From a breakdown of the contributions to $B^- - B^+$ from individual terms of Equation (45), presented in Table XXII, it can be seen that the contributions due to the extra terms in Equation (45) are all very small compared to the contribution from the original Hamiltonian (34), with the single exception of the contribution from the cariolis operator

$$A_0\left(\phi_{11}(x)\frac{\partial}{\partial x} + \phi_{12}(x)\right)\left[\left(\frac{10^2\sin\tau}{\sqrt{\omega_3}}q_3^+ + \frac{10^2\cos\tau}{\sqrt{\omega_4}}q_4^+\right)(J_x - iJ_y) - \left(\frac{10^2\sin\tau}{\sqrt{\omega_3}}q_3^- + \frac{10^2\cos\tau}{\sqrt{\omega_4}}q_4^-\right)(J_x + iJ_y)\right].$$

Thus, it is not strictly legitimate to neglect all terms in the rotation-vibration-inversion Hamiltonian except those given by Equation (34).

It has been pointed out that when n_1, n_3, and n_4 are not all zero the rotational constants will be affected by rotational resonance interactions. Thus one should not expect the simple Hamiltonian given by Equation (34) to give correct values of $B^- - B^+$ for these levels. Yet it was seen earlier that with the exception of levels with $n_4 = 1$ Equation (34) leads to reasonable values for the differences of the rotational constants. Thus, resonance interactions must have a much

TABLE XXI

$B^- - B^+$ AND $C^- - C^+$ CALCULATED FROM EQUATION (45)

Level	$(B^- - B^+)_{calc}$	$(C^- - C^+)_{calc}$	$(B^- - B^+)_{obs}$	$(C^- - C^+)_{obs}$
$0\ 0^{\pm}\ 0^0\ 0^0$	-.007189 (cm^{-1})	.001586 (cm^{-1})	-.005054 (cm^{-1})	.001998 (cm^{-1})
$0\ 1^{\pm}\ 0^0\ 0^0$	-.2237	.0504	-.1817	.0721

TABLE XXII

INDIVIDUAL CONTRIBUTIONS TO $B^- - B^+$

Level	Contributions to $B^- - B^+$				
$0\ 0^{\pm}\ 0^0\ 0^0$	-.005552	-.000345	-.000005	-.000006	-.001281
$0\ 1^{\pm}\ 0^0\ 0^0$	-.1690	-.013686	-.000155	-.000186	-.040677
Contributing Terms from Equation (45)	Lowest Order (Same as Table XVIII)	ϕ_3, ϕ_4, ϕ_5 Terms of the form $\phi(x)q^2[J^2-J_z^2]$	ϕ_{10}	ϕ_{13}	$\phi_{11}\frac{\partial}{\partial x} + \phi_{12}$
			Coriolis terms: $\phi(x)qp(J_x \pm i\ J_y)$		

greater effect on the levels, $(0, n_{2\pm}, 0^0, 1^1, J, K)$ than, say, on the levels $(0, n_{2\pm}, 1^1, 0^0, J, K)$. That this should be the case is by no means obvious in the absence of explicit calculations using the complete Hamiltonian, Equation (45).

One of the chief effects of rotational resonances is to alter the dependence of the rotational energies on the rotational quantum numbers. Thus, in bands seriously affected by rotational resonances one cannot expect the inversion splittings to be given by a simple power series in the rotational quantum numbers. It is worthwhile, then, to look at the experimental situation. One finds, that in the bands $(0, 0^{\pm}, 0^0, 1^1)$ and $(0, 1^{\pm}, 0^0, 1^1)$ the inversion pattern is highly irregular(8,9,10) and that the numbers given for the rotation-inversion constants are averages derived from data that can be fitted only very poorly by a power series in the rotational quantum numbers. Similarly, the bands $(1, 0^{\pm}, 0^0, 0^0)$ $(0, 0^{\pm}, 0^0, 2^0)$, and $(0, 0^{\pm}, 0^0, 2^2)$ show a very irregular inversion pattern.(9) The first two of these bands are, of course, further complicated by a Fermi resonance interaction. On the other hand, the bands $(0, 0^{\pm}, 1^1, 0^0)$ and $(0, 1^{\pm}, 1^1, 0^0)$ show a very regular inversion pattern.(6,9) Thus, it is apparent from the observed data that the bands with $n_4 > 0$ are affected by rotational resonances. On the other hand, the observed data for bands with $n_3 = 1$ and $n_4 = 0$ show no evidence of rotational resonance interactions, contrary to what one might expect on the basis of the Hamiltonian given by Equation (45).

Rather lengthy calculations will be required in order to determine whether the Hamiltonian (45) implies results consistent with the observed inversion patterns in the bands $(0, n_{2\pm}, 0^0, 1^1)$ and $(0, n_{2\pm}, 1^1, 0^0)$. These calculations will be considered at a future date. At the present there is some doubt regarding the favorable outcome of further calculations based on this Hamiltonian. Indeed, it may very well be that the model proposed in this thesis is not sufficiently sophisticated to yield the finer details of the inversion doublet separation in the spectrum of ammonia.

APPENDIX I

COMPARISON WITH THE GENERAL POTENTIAL EXPANSION

Let q_1, q_2, q_{3x}, q_{3y}, q_{4x}, and q_{4y} be the six dimensionless normal coordinates of ammonia. The most general expansion of the potential energy about an equilibrium configuration will be of the form

$$V = V^{(2)} + V^{(3)} + V^{(4)} + \ldots$$

where $V^{(2)}$ contains the quadratic terms, $V^{(3)}$ the cubic terms, $V^{(4)}$ the quartic terms, and so on. The quadratic part is given by

$$\frac{V^{(2)}}{hc} = \frac{\omega_1}{2} q_1^2 + \frac{\omega_2}{2} q_2^2 + \frac{\omega_3}{2}\left(q_{3x}^2 + q_{3y}^2\right) + \frac{\omega_4}{2}\left(q_{4x}^2 + q_{4y}^2\right) .$$

The most general form, consistent with the symmetry of ammonia, of the cubic part is

$$\frac{V^{(3)}}{hc} = k_{111} q_1^2 + k_{112} q_1^2 q_2 + k_{122} q_1 q_2^2 + k_{222} q_2^3$$

$$+ k_{233} q_2 (q_{3x}^2 + q_{3y}^2) + k_{244} q_2 (q_{4x}^2 + q_{4y}^2) + k_{234} q_2 (q_{3x} q_{4x} + q_{3y} q_{4y})$$

$$+ k_{133} q_1 (q_{3x}^2 + q_{3y}^2) + k_{144} q_1 (q_{4x}^2 + q_{4y}^2) + k_{134} q_1 (q_{3x} q_{4x} + q_{3y} q_{4y})$$

$$+ k_{333} q_{3y} (q_{3y}^2 - 3 q_{3x}^2) + k_{444} q_{4y} (q_{4y}^2 - 3 q_{4x}^2)$$

$$+ k_{334} \left[q_{4y} (q_{3x}^2 - q_{3y}^2) + 2 q_{3y} q_{3x} q_{4x} \right] + k_{344} \left[q_{3y} (q_{4x}^2 - q_{4y}^2) + 2 q_{4y} q_{3x} q_{4x} \right] .$$

The complete quartic terms will not be given. In the present investigation only the part of the potential involving the normal coordinate

q_2, which is intimately related to the inversion coordinate, is of interest. The quartic terms involving q_2 are

$$\frac{V^{(4)}}{hc} = k_{2111} q_2 q_1^3 + k_{2211} q_2^2 q_1^2 + k_{2221} q_2^3 q_1 + k_{2222} q_2^4$$

$$+ k_{2233} q_2^2 (q_{3x}^2 + q_{3y}^2) + k_{2234} q_2^2 (q_{3x} q_{4x} + q_{3y} q_{4y})$$

$$+ k_{2244} q_2^2 (q_{4x}^2 + q_{4y}^2) + k_{1233} q_1 q_2 (q_{3x}^2 + q_{3y}^2)$$

$$+ k_{1234} q_1 q_2 (q_{3x} q_{4x} + q_{3y} q_{4y}) + k_{1244} q_1 q_2 (q_{4x}^2 + q_{4y}^2)$$

$$+ k_{2333} q_2 q_{3y} (q_{3y}^2 - 3 q_{3x}^2) + k_{2444} q_2 q_{4y} (q_{4y}^2 - 3 q_{4x}^2)$$

$$+ k_{2334} q_2 \left[q_{4y} (q_{3x}^2 - q_{3y}^2) + 2 q_{3y} q_{3x} q_{4x} \right]$$

$$+ k_{2344} q_2 \left[q_{3y} (q_{4x}^2 - q_{4y}^2) + 2 q_{4y} q_{3x} q_{4x} \right] + \cdots ,$$

Of the terms listed above only those having diagonal matrix elements normally would be of interest, namely the therms whose coefficients are k_{2211}, k_{2222}, k_{2233}, and k_{2244}.

If the potential used in this thesis, Equation (17) or (18), is expanded in a Taylor series about an equilibrium configuration one finds

$$\frac{V}{hc} = \frac{\omega_1}{2} q_1^2 + \frac{\omega_2}{2} q_2^2 + \frac{\omega_3}{2} (q_{3x}^2 + q_{3y}^2) + \frac{\omega_4}{2} (q_{4x}^2 + q_{4y}^2)$$

$$+ k_{222} q_2^3 + k_{112} q_1^2 q_2 + k_{233} q_2 (q_{3x}^2 + q_{3y}^2) + k_{244} q_2 (q_{4x}^2 + q_{4y}^2)$$

$$+ k_{2222} q_2^4 + k_{1122} q_1^2 q_2^2 + k_{2233} q_2^2 (q_{3x}^2 + q_{3y}^2) + k_{2244} q_2^2 (q_{4x}^2 + q_{4y}^2) \qquad \text{(I-1)}$$

where

$$q_2 = \sqrt{\frac{\omega_2}{2D}}\ (x - x_0)$$

$$\cos x_0 = \frac{F_0}{4G_0}$$

$$(\omega_2)^2 = 16 D G_0\left[1 - \left(\frac{F_0}{4G_0}\right)^2\right]$$

$$k_{222} = \left(\frac{2D}{\omega_2}\right)^{3/2} F_0 \sin x_0$$

$$k_{112} = \left(\frac{2D}{\omega_2}\right)^{1/2}\left[2F_1 \sin x_0 - 4G_1 \sin 2x_0\right]$$

$$k_{233} = \left(\frac{2D}{\omega_2}\right)^{1/2}\left[2F_3 \sin x_0 - 4G_3 \sin 2x_0\right]$$

$$k_{244} = \left(\frac{2D}{\omega_2}\right)^{1/2}\left[2F_4 \sin x_0 - 4G_4 \sin 2x_0\right]$$

$$k_{2222} = \left(\frac{2D}{\omega_2}\right)^2 \frac{G_0}{3}\left[7\left(\frac{F_0}{4G_0}\right)^2 - 4\right]$$

$$k_{1122} = \left(\frac{2D}{\omega_2}\right)\left[F_1 \cos x_0 - 4G_1 \cos 2x_0\right]$$

$$k_{2233} = \left(\frac{2D}{\omega_2}\right)\left[F_3 \cos x_0 - 4G_3 \cos 2x_0\right]$$

$$k_{2244} = \left(\frac{2D}{\omega_2}\right)\left[F_4 \cos x_0 - 4G_4 \cos 2x_0\right].$$

The potential used in this thesis contains only those cubic and quartic terms which involve q_2. In particular it contains four of the six possible cubic terms involving q_2 and it contains the four quartic terms in q_2 which normally would be of importance. The cubic and quartic constants can be calculated from the values of the potential constants given in Table X. One finds

$$k_{222} = 83.86 \quad cm^{-1}$$

$$k_{112} = -119.4 \quad cm^{-1}$$

$$k_{233} = -127.0 \quad cm^{-1}$$

$$k_{244} = 33.7 \quad cm^{-1}$$

$$k_{2222} = -18.29 \quad cm^{-1}$$

$$k_{1122} = 1.0 \quad cm^{-1}$$

$$k_{2233} = -4.4 \quad cm^{-1}$$

$$k_{2244} = -3.0 \quad cm^{-1}.$$

APPENDIX II

FURTHER DETAILS ABOUT THE POTENTIAL V'(x)

A great deal of attention has been given to the solution of the one-dimensional equation

$$\left[-D\frac{d^2}{dx^2} + V'(x)\right]\psi = E\,\psi \qquad \text{(II-1)}$$

where

$$V'(x) = 2G + \frac{F^2}{4G} - 2F\cos x + 2G\cos 2x \quad .$$

The basic problem is to choose constants D, F, and G so that the eigenvalues of (II-1) will approximate as closely as possible the observed energies of the levels ($0, n_2\pm, 0^0, 0^0$) of ammonia. The initial choice of the potential constants was made by matching the central barrier height, the separation of the minima, and the curvature of V'(x) at the minima with the corresponding quantities for Manning's potential, Equation (2). Equation (II-1) was then solved several times using potential constants slightly different from the initial choice. In this way it was possible to observe the manner in which the eigenvalues depend upon the potential constants. Eigenvalues for twenty-seven sets of potential constants in the neighborhood of

$$\begin{aligned} D &= 64.80\ \text{cm}^{-1} \\ F &= 1890.70\ \text{cm}^{-1} \\ G &= 1286.02\ \text{cm}^{-1} \end{aligned} \qquad \text{(II-2)}$$

are given in Table XXIII. Comparison with the observed numbers, given in Table VIII, shows that values of the potential constants, for which the splitting $E_1- - E_1+$ and the separation $E_1+ - E_0+$ agree well with the observed numbers, imply a ground state splitting $E_0- - E_0+$ considerably larger than the observed value.

Since there are three constants D, F, and G available, one would suspect that it should be possible to fit the three numbers $E_1- - E_1+$, $E_1+ - E_0+$, and $E_0- - E_0+$ exactly. In order to investigate this possibility it is convenient to write Equation (II-1) as

$$\left[-\frac{d^2}{dx^2} + 2B + \frac{A^2}{4B} - 2A\cos x + 2B\cos 2x\right]\psi = W\psi \tag{II-3}$$

where

$$A = \frac{F}{D} \qquad B = \frac{G}{D} \qquad W = \frac{E}{D}\ . \tag{II-4}$$

If one defines the quantities α and β as

$$\alpha = \frac{E_0- - E_0+}{E_1+ - E_0+} = \frac{W_0- - W_0+}{W_1+ - W_0+} \tag{II-5}$$

$$\beta = \frac{E_1- - E_1+}{E_1+ - E_0+} = \frac{W_1- - W_1+}{W_1+ - W_0+} \tag{II-6}$$

then

$$E_1+ - E_0+ = D(W_1+ - W_0+) \tag{II-7}$$

$$E_0- - E_0+ = \alpha D(W_1+ - W_0+) \tag{II-8}$$

$$E_1- - E_1+ = \beta D(W_1+ - W_0+) \tag{II-9}$$

TABLE XXXIII

CALCULATED ENERGY LEVELS

The notation in this table is related to that of the text by the equivalences

$ES0 = E_{0}+ - E_{0}+$ $\qquad$ $EA0 = E_{0}- - E_{0}+$
$ES1 = E_{1}+ - E_{0}+$ $\qquad$ $EA1 = E_{1}- - E_{0}+$
$ES2 = E_{2}+ - E_{0}+$ $\qquad$ $EA2 = E_{2}- - E_{0}+$
$ES3 = E_{3}+ - E_{0}+$ $\qquad$ $EA3 = E_{2}- - E_{0}+$

EGST is the energy difference between $E_{0}+$ and the potential minima.

D = 64.00	F = 1875.70	G = 1276.02	EGST = 508.42
EA0 = 0.91	EA1 = 961.05	EA2 = 1864.21	EA3 = 2836.68
ES0 = 0.	ES1 = 926.53	ES2 = 1599.15	ES3 = 2355.75
D = 64.00	F = 1875.70	G = 1286.02	EGST = 511.31
EA0 = 0.83	EA1 = 966.55	EA2 = 1872.56	EA3 = 2844.54
ES0 = 0.	ES1 = 934.31	ES2 = 1614.96	ES3 = 2365.75
D = 64.00	F = 1875.70	G = 1296.02	EGST = 514.16
EA0 = 0.77	EA1 = 972.05	EA2 = 1881.01	EA3 = 2852.56
ES0 = 0.	ES1 = 941.96	ES2 = 1630.89	ES3 = 2376.01
D = 64.00	F = 1890.70	G = 1276.02	EGST = 507.60
EA0 = 0.96	EA1 = 959.47	EA2 = 1862.80	EA3 = 2837.98
ES0 = 0.	ES1 = 923.25	ES2 = 1592.05	ES3 = 2354.44
D = 64.00	F = 1890.70	G = 1286.02	EGST = 510.50
EA0 = 0.89	EA1 = 964.97	EA2 = 1871.06	EA3 = 2845.71
ES0 = 0.	ES1 = 931.13	ES2 = 1607.77	ES3 = 2364.25
D = 64.00	F = 1890.70	G = 1296.02	EGST = 513.38
EA0 = 0.81	EA1 = 970.46	EA2 = 1879.43	EA3 = 2853.60
ES0 = 0.	ES1 = 938.86	ES2 = 1623.60	ES3 = 2374.30
D = 64.00	F = 1905.70	G = 1276.02	EGST = 506.78
EA0 = 1.02	EA1 = 957.90	EA2 = 1861.44	EA3 = 2839.36
ES0 = 0.	ES1 = 919.92	ES2 = 1585.04	ES3 = 2353.26
D = 64.00	F = 1905.70	G = 1286.02	EGST = 509.69
EA0 = 0.94	EA1 = 963.39	EA2 = 1869.62	EA3 = 2846.96
ES0 = 0.	ES1 = 927.89	ES2 = 1600.64	ES3 = 2362.87
D = 64.00	F = 1905.70	G = 1296.02	EGST = 512.58
EA0 = 0.86	EA1 = 968.88	EA2 = 1877.91	EA3 = 2854.72
ES0 = 0.	ES1 = 935.72	ES2 = 1616.39	ES3 = 2372.73
D = 64.80	F = 1875.70	G = 1276.02	EGST = 511.40
EA0 = 0.96	EA1 = 966.74	EA2 = 1876.52	EA3 = 2857.72
ES0 = 0.	ES1 = 930.60	ES2 = 1605.18	ES3 = 2371.60
D = 64.80	F = 1875.70	G = 1286.02	EGST = 514.31
EA0 = 0.89	EA1 = 972.26	EA2 = 1884.84	EA3 = 2865.54
ES0 = 0.	ES1 = 938.49	ES2 = 1620.95	ES3 = 2381.49

TABLE XXXIII (CONT'D)

CALCULATED ENERGY LEVELS

D = 64.80 F = 1875.70 G = 1296.02 EGST = 517.19
EAO = 0.82 EA1 = 977.77 EA2 = 1893.26 EA3 = 2873.50
ESO = 0. ES1 = 946.22 ES2 = 1636.83 ES3 = 2391.64

D = 64.80 F = 1890.70 G = 1276.02 EGST = 510.58
EAO = 1.03 EA1 = 965.17 EA2 = 1875.16 EA3 = 2859.11
ESO = 0. ES1 = 927.28 ES2 = 1598.13 ES3 = 2370.40

D = 64.80 F = 1890.70 G = 1286.02 EGST = 513.50
EAO = 0.93 EA1 = 970.67 EA2 = 1883.39 EA3 = 2866.79
ESO = 0. ES1 = 935.25 ES2 = 1613.79 ES3 = 2380.10

D = 64.80 F = 1890.70 G = 1296.02 EGST = 516.40
EAO = 0.86 EA1 = 976.18 EA2 = 1891.72 EA3 = 2874.63
ESO = 0. ES1 = 943.07 ES2 = 1629.59 ES3 = 2390.05

D = 64.80 F = 1905.70 G = 1276.02 EGST = 509.75
EAO = 1.08 EA1 = 963.60 EA2 = 1873.85 EA3 = 2860.57
ESO = 0. ES1 = 923.88 ES2 = 1591.16 ES3 = 2369.33

D = 64.80 F = 1905.70 G = 1286.02 EGST = 512.69
EAO = 0.99 EA1 = 969.10 EA2 = 1881.99 EA3 = 2868.12
ESO = 0. ES1 = 931.95 ES2 = 1606.71 ES3 = 2378.83

D = 64.80 F = 1905.70 G = 1296.02 EGST = 515.59
EAO = 0.92 EA1 = 974.60 EA2 = 1890.25 EA3 = 2875.84
ESO = 0. ES1 = 939.87 ES2 = 1622.41 ES3 = 2388.59

D = 65.60 F = 1875.70 G = 1276.02 EGST = 514.37
EAO = 1.02 EA1 = 972.41 EA2 = 1888.80 EA3 = 2878.70
ESO = 0. ES1 = 934.62 ES2 = 1611.21 ES3 = 2387.44

D = 65.60 F = 1875.70 G = 1286.02 EGST = 517.30
EAO = 0.93 EA1 = 977.93 EA2 = 1897.08 EA3 = 2886.47
ESO = 0. ES1 = 942.59 ES2 = 1626.93 ES3 = 2397.24

D = 65.60 F = 1875.70 G = 1296.02 EGST = 520.20
EAO = 0.86 EA1 = 983.45 EA2 = 1905.47 EA3 = 2894.40
ESO = 0. ES1 = 950.42 ES2 = 1642.78 ES3 = 2407.28

D = 65.60 F = 1890.70 G = 1276.02 EGST = 513.54
EAO = 1.08 EA1 = 970.84 EA2 = 1887.48 EA3 = 2880.17
ESO = 0. ES1 = 931.24 ES2 = 1604.21 ES3 = 2386.35

D = 65.60 F = 1890.70 G = 1286.02 EGST = 516.48
EAO = 0.99 EA1 = 976.36 EA2 = 1895.69 EA3 = 2887.81
ESO = 0. ES1 = 939.31 ES2 = 1619.82 ES3 = 2395.95

D = 65.60 F = 1890.70 G = 1296.02 EGST = 519.40
EAO = 0.91 EA1 = 981.87 EA2 = 1903.98 EA3 = 2895.61
ESO = 0. ES1 = 947.22 ES2 = 1635.57 ES3 = 2405.80

D = 65.60 F = 1905.70 G = 1276.02 EGST = 512.70
EAO = 1.15 EA1 = 969.29 EA2 = 1886.23 EA3 = 2881.72
ESO = 0. ES1 = 927.80 ES2 = 1597.29 ES3 = 2385.39

D = 65.60 F = 1905.70 G = 1286.02 EGST = 515.66
EAO = 1.05 EA1 = 974.79 EA2 = 1894.34 EA3 = 2889.23
ESO = 0. ES1 = 935.96 ES2 = 1612.78 ES3 = 2394.79

D = 65.60 F = 1905.70 G = 1296.02 EGST = 518.59
EAO = 0.96 EA1 = 980.30 EA2 = 1902.56 EA3 = 2896.89
ESO = 0. ES1 = 943.96 ES2 = 1628.43 ES3 = 2404.44

The values of α and β computed from the observed energy levels of ammonia are

$$\alpha_{obs} = 0.896564 \times 10^{-3} \qquad \beta_{obs} = 0.384562 \times 10^{-1} .$$

If A and B can be chosen so that the calculated values of α and β agree exactly with the observed values then the constants D, F, and G can be determined from Equation (II-4) so that the eigenvalues of Equation (II-1) agree exactly with the observed energies of ammonia.

By solving Equation (II-3) for many pairs A and B, it was found, empirically, that α and β are given very well by the equations

$$\begin{aligned}\alpha \times 10^{3} = {} & .994387 + .246127(A-A_0) - .644397(B-B_0) \\ & + .203826(A-A_0)^2 + .271413(A-A_0)(B-B_0) \\ & + .712288(B-B_0)^2\end{aligned} \tag{II-10}$$

$$\begin{aligned}\beta \times 10^{2} = {} & 3.78722 + .837883(A-A_0) - 1.86413(B-B_0) \\ & + .0947898(A-A_0)^2 - .393892(A-A_0)(B-B_0) \\ & + .473991(B-B_0)^2\end{aligned} \tag{II-11}$$

where

$$A_0 = 29.1775 \qquad B_0 = 19.8460 .$$

In order to find the values of A and B which yield the observed values of α and β one replaces α by α_{obs} in Equation (II-10) and β by β_{obs} in Equation (II-11) and solves the resulting equations for A and B. The two equations are plotted in Figure 16. Interestingly enough, the two curves do not intersect so that the two equations can not have a real

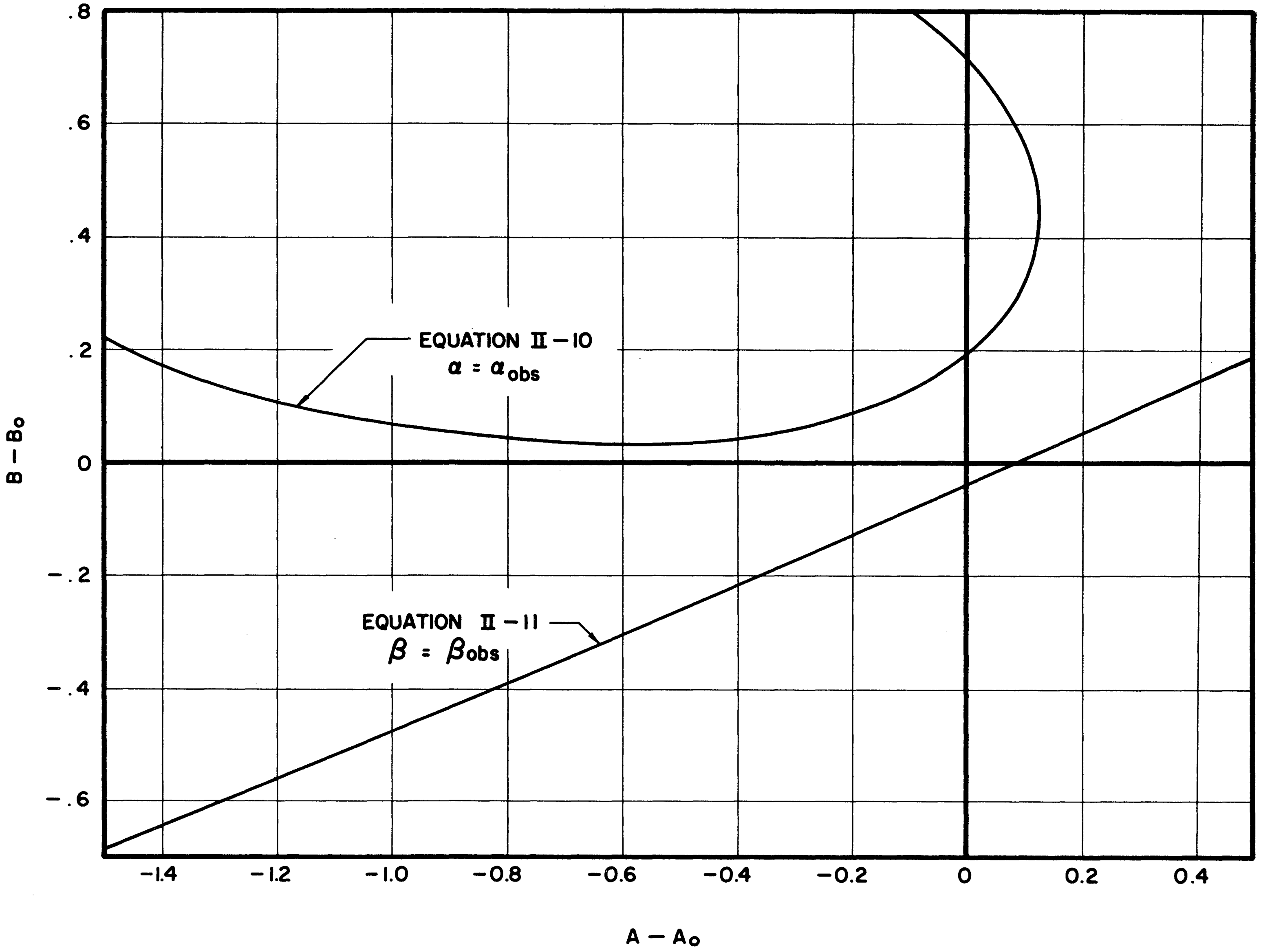

Figure 16. Graphs of Equations (II-10) and (II-11).

solution. Consequently, D, F, and G can not be chosen so that the calculated values of $E_{1-} - E_{1+}$, $E_{1+} - E_{0+}$, and $E_{0-} - E_{0+}$ agree exactly with the observed values. Apparently, the analytic form of V'(x) must restrict the spectrum of Equation (II-1) in such a way that $E_{1-} - E_{1+}$, $E_{1+} - E_{0+}$, and $E_{0-} - E_{0+}$ can not be given completely arbitrary values.

In order to obtain a better fit to the observed energies of the levels $(0, n_2\pm, 0^0, 0^0)$ it is necessary to modify the potential. One possible line of generalization is to regard the potential V'(x), used in this investigation, as the leading terms in a Fourier expansion of the complete potential. The next higher approximation would then be

$$V'(x) = 2G + \frac{F^2}{4G} - 2F\cos x + 2G\cos 2x + \lambda\cos 3x + \mu\cos 4x + \cdots$$

This line of generalization has not been very fruitful. The energy levels obtained by retaining the cos 3x term but not the cos 4x term have been obtained both exactly* and by perturbation theory. The perturbation treatment illustrates the effect of the cos 3x term quite well. Using the wavefunctions obtained with the constants (II-2) one finds

$$E_{0+} = 513.50 - .701916\lambda - .738872\times10^{-4}\lambda^2 \quad \text{cm}^{-1}$$

$$E_{0-} = 514.43 - .704194\lambda - .709932\times10^{-4}\lambda^2 \quad \text{cm}^{-1}$$

$$E_{1+} = 1448.75 - .200503\lambda - 1.92065\times10^{-4}\lambda^2 \quad \text{cm}^{-1}$$

$$E_{1-} = 1484.17 - .286123\lambda - .910978\times10^{-4}\lambda^2 \quad \text{cm}^{-1}.$$

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* By exactly it is meant here that the solution was obtained by the method described in Chapter IV, which is, of course, an approximation method.

Here λ is the coefficient of the cos 3x term. A little study of these energy formulas will reveal that a choice of λ which reduces the splitting $E_{0-} - E_{0+}$ will produce an almost proportional reduction in the splitting $E_{1-} - E_{1+}$. What is needed is a perturbation which decreases $E_{0-} - E_{0+}$ while increasing $E_{1-} - E_{1+}$ slightly. The requirements which must be satisfied by such a perturbation can best be seen from the WKB splitting formula, Equation (1). An examination of this formula reveals that the inversion splitting is controlled mainly by the area under the central maximum of the potential curve. For example, one would like a perturbation which, in the notation of Figure 2, increases the ratio of the area enclosed by E_0 and the central barrier of V(x) to the area enclosed by E_1 and the central barrierof V(x). No attempt has been made to include such a perturbation since it would shed little light on the main problem of this thesis, namely the interaction of the inversion motion with the remaining degrees of freedom of ammonia.

APPENDIX III

DEVELOPMENT OF THE ROTATION-VIBRATION HAMILTONIAN

The Hamiltonian, Equation (44), used in Chapter VII can be drived by methods very similar to those used by Wilson and Howard(12) and Darling and Dennison.(13) The essential difference is that Equation (44) is valid for an arbitrary set of 3N-6 internal (vibrational) coordinates, whereas the Wilson, Howard, Darling, and Dennison Hamiltonian is valid only when normal coordinates are used for internal coordinates. This generalization is necessary since a practical treatment of ammonia inversion requires the introduction of a coordinate which describes a motion of large amplitude. The details of the derivation of Equation (44) will not be given here since there is almost a one-to-one correspondence to the derivation of the usual molecular Hamiltonian as given for example by Wilson, Decius, and Cross.(14) The necessary modifications can be seen at once by comparing the following equations to the corresponding equations in Reference (14). The results are given below for a molecule of N atoms.

Let $r_1, r_2, \ldots, r_N$, be the cartesian position vectors of the N atoms with respect to a molcule-fixed reference frame. This reference frame is defined by specifying the location of its origin and its orientation with respect to the molecule. The origin will be required to be at the center of mass of the molecule so that

$$\sum_{i=1}^{N} m_i \vec{r_i} = 0 \qquad \text{(III-1)}$$

where m_i is the mass of the i^{th} atom. The orientation can be specified by imposing suitable conditions on the internal angular momentum

$$\sum_{i=1}^{N} m_i \vec{r}_i \times \dot{\vec{r}}_i \tag{III-2}$$

as measured with respect to the molecule-fixed frame. The conditions used in this thesis is that the internal angular momentum should vanish whenever the degenerate modes are not excited. Thus six conditions are imposed on the 3N components of the position vectors $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N$. That is, only 3N-6 of these components are independent variables. Let

$$u^\alpha = u^\alpha(\vec{r}_1, \ldots, \vec{r}_N) \qquad \alpha = 1, 2, \ldots, 3N-6 \tag{III-3}$$

be 3N-6 independent internal coordinates. Let x_i, y_i, and z_i be the three components of $\vec{r}_i$. Classically, the vibrational kinetic energy is given by

$$\frac{1}{2} \sum_{i=1}^{N} m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) = \frac{1}{2} \sum_{\alpha,\beta=1}^{3N-6} g_{\alpha\beta} \dot{u}^\alpha \dot{u}^\beta \tag{III-4}$$

In general, the coefficients $g_{\alpha\beta}$ are functions of the internal coordinates. Let $g^{\alpha\beta}$ be the elements of the inverse to the matrix $g_{\alpha\beta}$. That is

$$\sum_{\beta=1}^{3N-6} g_{\alpha\beta} g^{\beta\gamma} = \delta_\alpha^{\ \gamma} \tag{III-5}$$

The internal angular momentum of the molecule is given by

$$\sum_{i=1}^{N} m_i(y_i\dot{z}_i - z_i\dot{y}_i) = \sum_{\alpha=1}^{3N-6} \xi_\alpha \dot{u}^\alpha$$

$$\sum_{i=1}^{N} m_i(z_i\dot{x}_i - x_i\dot{z}_i) = \sum_{\alpha=1}^{3N-6} \eta_\alpha \dot{u}^\alpha \qquad \text{(III-6)}$$

$$\sum_{i=1}^{N} m_i(x_i\dot{y}_i - y_i\dot{x}_i) = \sum_{\alpha=1}^{3N-6} \zeta_\alpha \dot{u}^\alpha$$

The Equations (III-6) define the 3(3N-6) functions ξ_α, η_α, ζ_α. Now define

$$\xi^\alpha = \sum_{\beta=1}^{3N-6} g^{\alpha\beta}\xi_\beta \qquad \eta^\alpha = \sum_{\beta=1}^{3N-6} g^{\alpha\beta}\eta_\beta \qquad \zeta^\alpha = \sum_{\beta=1}^{3N-6} g^{\alpha\beta}\zeta_\beta \qquad \text{(III-7)}$$

for $\alpha = 1$ to 3N-6. Introduce 3N-6 linear momentum operators

$$p_\alpha = \frac{\hbar}{i}\frac{\partial}{\partial u^\alpha} \qquad (\alpha = 1, 2, \ldots, 3N-6) \qquad \text{(III-8)}$$

and define

$$p_x = \sum_{\alpha=1}^{3N-6} \xi^\alpha p_\alpha \qquad \text{(III-9)}$$

$$p_y = \sum_{\alpha=1}^{3N-6} \eta^\alpha p_\alpha$$

$$p_z = \sum_{\alpha=1}^{3N-6} \zeta^\alpha p_\alpha$$

The moments of inertia are defined by

$$I_{xx} = \sum_{i=1}^{N} m_i (y_i^2 + z_i^2)$$

$$I_{yy} = \sum_{i=1}^{N} m_i (z_i^2 + x_i^2)$$

$$I_{zz} = \sum_{i=1}^{N} m_i (x_i^2 + y_i^2) \tag{III-10}$$

and the products of inertia by

$$I_{xy} = \sum_{i=1}^{N} m_i \, x_i y_i$$

$$I_{yz} = \sum_{i=1}^{N} m_i \, y_i z_i$$

$$I_{zx} = \sum_{i=1}^{N} m_i \, z_i x_i \tag{III-11}$$

Modified moments and products of inertia, I'_{ij}, are now defined by

$$I'_{xx} = I_{xx} - \sum_{\alpha=1}^{3N-6} \xi^{\alpha} \xi_{\alpha}$$

$$I'_{yy} = I_{yy} - \sum_{\alpha=1}^{3N-6} \eta^{\alpha} \eta_{\alpha}$$

$$I'_{zz} = I_{zz} - \sum_{\alpha=1}^{3N-6} \zeta^{\alpha} \zeta_{\alpha}$$

$$I'_{xy} = I_{xy} + \sum_{\alpha=1}^{3N-6} \xi^{\alpha} \eta_{\alpha} \tag{III-12}$$

$$I'_{xz} = I_{xz} + \sum_{\alpha=1}^{3N-6} \xi^{\alpha} \zeta_{\alpha}$$

$$I'_{yz} = I_{yz} + \sum_{\alpha=1}^{3N-6} \eta^{\alpha} \zeta_{\alpha}$$

The matrix μ_{ij} ($i, j = x, y, z$) is defined as the inverse of the matrix

$$\begin{pmatrix} I'_{xx} & -I'_{xy} & -I'_{xz} \\ -I'_{yx} & I'_{yy} & -I'_{yz} \\ -I'_{zx} & -I'_{zy} & I'_{zz} \end{pmatrix} \qquad \text{(III-13)}$$

and μ is defined as the determinant of the matrix of the μ_{ij}. Let g be the determinant of the matrix of the $g_{\alpha\beta}$. Let

$$C_x = -\frac{\hbar}{i}\sum_{\alpha=1}^{3N-6}\frac{\partial \xi^\alpha}{\partial u^\alpha}$$

$$C_y = -\frac{\hbar}{i}\sum_{\alpha=1}^{3N-6}\frac{\partial \eta^\alpha}{\partial u^\alpha}$$

$$C_z = -\frac{\hbar}{i}\sum_{\alpha=1}^{3N-6}\frac{\partial \zeta^\alpha}{\partial u^\alpha} \qquad \text{(III-14)}$$

and let P_x, P_y, and P_z be the three components of the total angular momentum of the molecule. Finally, let $V(u^\alpha)$ be the potential energy. Then, the exact Hamiltonian operator of the molecule is

$$H = \frac{1}{2}\sum_{i,j}^{x,y,z}\mu^{1/4}g^{-1/4}(P_i - p_i + C_i)\mu^{-1/2}g^{1/2}\mu_{ij}(P_j - p_j)\mu^{1/4}g^{-1/4}$$
$$+ \frac{1}{2}\sum_{\alpha,\beta=1}^{3N-6}\mu^{1/4}g^{-1/4}p_\alpha\mu^{-1/2}g^{1/2}g^{\alpha\beta}p_\beta\mu^{1/4}g^{-1/4} + V(u^\alpha) \; . \qquad \text{(III-15)}$$

The translational kinetic energy of the center of mass has been discarded since it is of no spectroscopic interest.

Probably the most obvious difference between Equation (III-15) and the usual molecular Hamiltonian is the appearance of the functions C_x, C_y, and C_z. They arise in the following fashion. If the classical kinetic energy of a system of particles is

$$T = \frac{1}{2} \sum_{\alpha,\beta} \Lambda_{\alpha\beta} \dot{q}^{\alpha} \dot{q}^{\beta}$$

then one form of the quantum mechanical Hamiltonian operator is

$$H = \frac{1}{2} w^{-1/2} \gamma^{-1/4} \sum_{\alpha,\beta} p_\alpha \gamma^{1/2} \Lambda^{\alpha\beta} p_\beta \gamma^{-1/4} w^{1/2} + V \tag{a}$$

where $\Lambda^{\alpha\beta}$ is the inverse of $\Lambda_{\alpha\beta}$ and $\gamma = \det \Lambda_{\alpha\beta}$. With this form of the Hamiltonian the wavefunctions are normalized according to

$$\int \psi^* \psi \, w \, dq^1 dq^2 dq^3 \ldots$$

w is a weight factor which can be chosen arbitrarily. Instead of the canonical momenta p_α sometimes it is convenient to use operators P'_α which are not canonical momenta. Suppose the operators are related by

$$p_\alpha = \sum_\mu W_{\alpha\mu} P'_\mu \tag{b}$$

Let the weight factor in Equation (a) be chosen so that $w = \det W_{ij}$. Define

$$G^{\mu\nu} = \sum_{\alpha,\beta} W_{\alpha\mu} \Lambda^{\alpha\beta} W_{\beta\nu} \tag{c}$$

and

$$\frac{1}{G} = \det G^{\mu\nu} .$$

Then

$$\gamma = w^2 G \qquad . \qquad \text{(d)}$$

Now put Equation (b) into Equation (a) to obtain

$$H = \frac{1}{2} w^{-1/2} \gamma^{-1/4} \sum_{\alpha,\beta,\mu,\nu} W_{\alpha\mu} P'_\mu \gamma^{1/2} \Lambda^{\alpha\beta} W_{\beta\nu} P'_\nu \gamma^{-1/4} w^{1/2} + V .$$

Using Equations (c) and (d), H can be re-written

$$H = \frac{1}{2} \sum_{\mu\nu} G^{-1/4} \sum_{\alpha\beta} \{ w^{-1} W_{\alpha\beta} P'_\beta (W^{-1})_{\mu\alpha} w \} G^{1/2} G^{\mu\nu} P'_\nu G^{-1/4} + V .$$

Define

$$C_\mu = \left[w^{-1} \sum_{\alpha\beta} W_{\alpha\beta} P'_\beta (W^{-1})_{\mu\alpha} w \right] - P'_\mu \quad . \qquad \text{(e)}$$

Then the Hamiltonian can be written

$$H = \frac{1}{2} \sum_{\mu\nu} G^{-1/4} (P'_\mu + C_\mu) G^{1/2} G^{\mu\nu} P'_\nu G^{-1/4} + V . \qquad \text{(f)}$$

Equation (f) is the starting point for deriving Equation (III-15). The operators P'_α can be identified with the operators $P_x - p_x$, etc. From Equation (e) one sees that the quantities C_μ vanish classically. However, when the P'_μ are quantum mechanical operators the C_μ do not vanish in general. Equations (III-14) were calculated from Equation (e).

Equation (III-15) is identical to Equation (44) of Chapter VII. It is Hermitian operator. The volume element in configuration space is

$$dV = dV_{vib} \cdot dV_{rot}$$

where

$$dV_{vib} = du_1 du_2 \ldots du_{3N-6}$$

and, if the three Euler angles θ, ϕ, and χ are used as rotational coordinates,

$$dV_{rot} = \sin\theta \, d\theta \, d\phi \, d\chi \, .$$

The total angular momentum operators can be expressed in terms of θ, ϕ, and χ alone while all other quantities appearing in Equation (III-15) are independent of θ, ϕ, and χ.

Before applying Equation (III-15) to ammonia it will be of some interest to examine the limiting case in which the internal coordinates are also normal coordinates. Normal coordinates are related to the cartesian components of the atoms by equations of the form

$$\begin{aligned} x_i &= x_i^0 + \sum_{\alpha=1}^{3N-6} \ell_{i\alpha} Q_\alpha \\ y_i &= y_i^0 + \sum_{\alpha=1}^{3N-6} m_{i\alpha} Q_\alpha \\ z_i &= z_i^0 + \sum_{\alpha=1}^{3N-6} n_{i\alpha} Q_\alpha \\ i &= 1, 2, \ldots, N \end{aligned} \qquad \text{(III-16)}$$

where x_i^o, y_i^o, and z_i^o are the cartesian components of the equilibrium position of the ith atom. The quantities $\ell_{i\alpha}$, $m_{i\alpha}$, and $n_{i\alpha}$ are constants determined so that

$$\frac{1}{2} \sum_{i=1}^{3N-6} m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) = \frac{1}{2} \sum_{\alpha=1}^{3N-6} \dot{Q}_\alpha^2$$

$$V = \frac{1}{2} \sum_{\alpha=1}^{3N-6} \lambda_\alpha \dot{Q}_\alpha^2 \quad + \text{ higher terms.}$$

Thus, $g_{\alpha\beta} = \delta_{\alpha\beta}$ and g = 1. Using the standard condition

$$\sum_{i=1}^{N} m_i \vec{r}_i^{\,0} \times \vec{r}_i = 0$$

on the orientation of the molecular fixed reference frame one finds

$$\xi_\alpha = \sum_{i=1}^{N} \sum_{\beta=1}^{3N-6} m_i (m_{i\beta} n_{i\alpha} - n_{i\beta} m_{i\alpha}) Q_\beta$$

$$\eta_\alpha = \sum_{i=1}^{N} \sum_{\beta=1}^{3N-6} m_i (n_{i\beta} l_{i\alpha} - l_{i\beta} n_{i\alpha}) Q_\beta$$

$$\zeta_\alpha = \sum_{i=1}^{N} \sum_{\beta=1}^{3N-6} m_i (l_{i\beta} m_{i\alpha} - m_{i\beta} l_{i\alpha}) Q_\beta \; . \qquad \text{(III-17)}$$

It follows from Equations (III-17) that

$$C_x = C_y = C_z = 0$$

Thus one sees that, when normal coordinates are used, Equation (III-15) reduces to the usual molecular Hamiltonian as given by Darling and Dennison. Combining (III-9) and (III-17), one sees that the internal angular momentum can be written in the symmetrical form

$$p_x = \sum_{\beta > \alpha} \zeta_{\alpha\beta}^{(x)} (Q_\alpha p_\beta - Q_\beta p_\alpha)$$

$$p_y = \sum_{\beta > \alpha} \zeta_{\alpha\beta}^{(y)} (Q_\alpha p_\beta - Q_\beta p_\alpha)$$

$$p_z = \sum_{\beta > \alpha} \zeta_{\alpha\beta}^{(z)} (Q_\alpha p_\beta - Q_\beta p_\alpha) \qquad \text{(III-18)}$$

where

$$\zeta^{(x)}_{\alpha\beta} = \sum_{i=1}^{N} m_i (m_{i\alpha} n_{i\beta} - n_{i\alpha} m_{i\beta}) \qquad \text{(III-19)}$$

with similar expressions for $\zeta^{(y)}_{\alpha\beta}$ and $\zeta^{(z)}_{\alpha\beta}$.

In the case where general internal coordinates are used ξ_α, η_α, and ζ_α will not be simple linear functions of the internal coordinates. In particular, for ammonia, ξ_α, η_α, and ζ_α will be functions of the inversion coordinate. Consequently it will not, in general, be possible to express the internal angular momentum operators in the symmetrical form given by Equation (III-18). The Hamiltonian about to be written down for ammonia, therefore, will look a little different from the usual Hamiltonian for a symmetric XY_3 molecule.

In order to set up the Hamiltonian for ammonia it is convenient to start with the coordinates x_1, x_2, Q_{3x}, Q_{3y}, Q_{4x}, and Q_{4y} defined in Chapter II. It will be recalled that

$$x_1 = \sqrt{3m}\, u_1 \qquad\qquad x_2 = \sqrt{\mu}\, u_2$$

where u_2 is the pyramid height and u_1 is the distance from a hydrogen atom to the center of the hydrogen triangle. The coordinates Q_{3x}, Q_{3y}, Q_{4x}, and Q_{4y} are defined by Equation (11) and are small displacement coordinates which reduce to normal coordinates in the neighborhoods of the equilibrium configurations.

The development of the μ_{ij}, p_x, p_y, p_z, C_x, C_y, and C_z is straightforward but tedious. Neglecting higher order terms in the small coordinates Q_{3x}, Q_{3y}, Q_{4x}, and Q_{4y}, one finds

$$\mu_{xx} = \frac{1}{I_{\parallel}} + \frac{x_1}{I_{\parallel}^2}(\cos\tau\, Q_{3y} - \sin\tau\, Q_{4y}) + \frac{3}{2}\frac{1}{I_{\parallel}^2}\Big\{(\sin^2\tau + \rho\cos^2\tau)(Q_{3x}^2 + Q_{3y}^2)$$

$$+ (\cos^2\tau + \rho\sin^2\tau)(Q_{4x}^2 + Q_{4y}^2) + 2(1-\rho)\sin\tau\cos\tau(Q_{3x}Q_{4x} + Q_{3y}Q_{4y})$$

$$- \rho\sin^2\tau\,(Q_{3x}^2 - Q_{3y}^2) - \rho\cos^2\tau\,(Q_{4x}^2 - Q_{4y}^2)\Big\}$$

(III-20)

$$\mu_{yy} = \frac{1}{I_{\parallel}} - \frac{x_1}{I_{\parallel}^2}(\cos\tau\, Q_{3x} - \sin\tau\, Q_{4x}) + \frac{3}{2}\frac{1}{I_{\parallel}^2}\Big\{(\sin^2\tau + \rho\cos^2\tau)(Q_{3x}^2 + Q_{3y}^2)$$

$$+ (\cos^2\tau + \rho\sin^2\tau)(Q_{4x}^2 + Q_{4y}^2) + 2(1-\rho)\sin\tau\cos\tau(Q_{3x}Q_{4x} + Q_{3y}Q_{4y})$$

$$+ \rho\sin^2\tau(Q_{3x}^2 - Q_{3y}^2) + \rho\cos^2\tau\,(Q_{4x}^2 - Q_{4y}^2)\Big\}$$

(III-21)

$$\mu_{zz} = \frac{1}{I_{\perp}} + \frac{3\rho(1-\rho)}{I_{\perp}^2}\Big\{\sin^2\tau\,(Q_{3x}^2 + Q_{3y}^2) + \cos^2\tau\,(Q_{4x}^2 + Q_{4y}^2)$$

$$+ 2\sin\tau\cos\tau\,(Q_{3x}Q_{4x} + Q_{3y}Q_{4y})\Big\} \qquad \text{(III-22)}$$

$$\mu_{yz} = \mu_{zy} = \frac{2\sqrt{\rho}\, X_2}{I_{\parallel} I_{\perp}} (\sin\tau\, Q_{3y} + \cos\tau\, Q_{4y})$$

$$+ \frac{2\rho\sqrt{\rho}}{I_{\parallel} I_{\perp}} \left(\frac{X_2}{X_1}\right) \Big\{ (\cos^2\tau - \sin^2\tau)(Q_{3x}Q_{4x} - Q_{3y}Q_{4y})$$

$$+ \sin\tau \cos\tau \,(Q_{3x}^2 - Q_{4x}^2 - Q_{3y}^2 + Q_{4y}^2) \Big\}$$

(III-23)

$$\mu_{zx} = \mu_{xz} = \frac{2\sqrt{\rho}\, X_2}{I_{\parallel} I_{\perp}} (\sin\tau\, Q_{3x} + \cos\tau\, Q_{4x})$$

$$+ \frac{3\rho\sqrt{\rho}}{I_{\parallel} I_{\perp}} \left(\frac{X_2}{X_1}\right) \Big\{ (\cos^2\tau - \sin^2\tau)(Q_{3x}Q_{3y} + Q_{4x}Q_{4y})$$

$$+ 2\sin\tau \cos\tau \,(Q_{3x}Q_{3y} - Q_{4x}Q_{4y}) \Big\}$$

(III-24)

$$\mu_{xy} = \mu_{yx} = \frac{X_1}{I_{11}^2}(\cos\tau\, Q_{3x} - \sin\tau\, Q_{4x})$$

$$- \frac{3\rho}{I_{11}^2}\Big\{ \sin^2\tau\, Q_{3x}Q_{3y} + \cos^2\tau\, Q_{4x}Q_{4y}$$

$$+ \sin\tau\cos\tau\,(Q_{3x}Q_{4y} + Q_{3y}Q_{4x})\Big\} \tag{III-25}$$

$$p_x = -\frac{2\sqrt{\rho}}{X_1}(\sin\tau\, Q_{3y} + \cos\tau\, Q_{4y})\frac{\hbar}{i}\left(X_2\frac{\partial}{\partial X_1} - X_1\frac{\partial}{\partial X_2}\right)$$

$$+ \sqrt{\rho}\,\frac{X_2}{X_1}\frac{\hbar}{i}\left\{\left(Q_{4y}\frac{\partial}{\partial Q_{3y}} - Q_{3y}\frac{\partial}{\partial Q_{4y}}\right) + \left(Q_{3x}\frac{\partial}{\partial Q_{4x}} - Q_{4x}\frac{\partial}{\partial Q_{3x}}\right)\right\} \tag{III-26}$$

$$p_y = \frac{2\sqrt{\rho}}{X_1}(\sin\tau\, Q_{3x} + \cos\tau\, Q_{4x})\frac{\hbar}{i}\left(X_2\frac{\partial}{\partial X_1} - X_1\frac{\partial}{\partial X_2}\right)$$

$$+ \sqrt{\rho}\,\frac{X_2}{X_1}\frac{\hbar}{i}\left\{\left(Q_{4x}\frac{\partial}{\partial Q_{3y}} - Q_{3y}\frac{\partial}{\partial Q_{4x}}\right) + \left(Q_{4y}\frac{\partial}{\partial Q_{3x}} - Q_{3x}\frac{\partial}{\partial Q_{4y}}\right)\right\} \tag{III-27}$$

$$p_z = (\rho\sin^2\tau - \cos^2\tau)\frac{\hbar}{i}\left(Q_{3x}\frac{\partial}{\partial Q_{3y}} - Q_{3y}\frac{\partial}{\partial Q_{3x}}\right)$$

$$+ (\rho\cos^2\tau - \sin^2\tau)\frac{\hbar}{i}\left(Q_{4x}\frac{\partial}{\partial Q_{4y}} - Q_{4y}\frac{\partial}{\partial Q_{4x}}\right)$$

$$+ \frac{\hbar}{i}(1+\rho)\sin\tau\cos\tau\left\{\left(Q_{4x}\frac{\partial}{\partial Q_{3y}} - Q_{3y}\frac{\partial}{\partial Q_{4x}}\right) + \left(Q_{3x}\frac{\partial}{\partial Q_{4y}} - Q_{4y}\frac{\partial}{\partial Q_{3x}}\right)\right\} \tag{III-28}$$

$$C_x = \frac{\hbar}{i} \frac{2x_1x_2}{(2I_{\parallel})^{3/2}} \left(\sin\tau \, Q_{3y} + \cos\tau \, Q_{4y} \right) \tag{III-29}$$

$$C_y = -\frac{\hbar}{i} \frac{2x_1x_2}{(2I_{\parallel})^{3/2}} \left(\sin\tau \, Q_{3x} + \cos\tau \, Q_{4x} \right) \tag{III-30}$$

$$C_z = 0 \tag{III-31}$$

$$I_{\parallel} = \frac{1}{2} x_1^2 + x_2^2 \tag{III-32}$$

$$I_{\perp} = x_1^2 \tag{III-33}$$

$$\rho = \frac{I_{\perp}}{2I_{\parallel}} \tag{III-34}$$

In the development of the Hamiltonian all terms whose energy contributions are of higher degree than quadratic in the rotational quantum numbers J and K will be discarded. Furthermore, terms whose contributions to the energy are of smaller order of magnitude than $(B^2/\omega)J^2$ will be dropped. Let

$$H_{rot} = \frac{1}{2} \sum_{i,j}^{x,y,z} \mu^{1/4} g^{-1/4} (P_i - p_i + C_i) \mu^{-1/2} g^{1/2} \mu_{ij} (P_j - p_j) \mu^{1/4} g^{-1/4} .$$

H_{rot} contains three basic types of terms, namely

(a) $\frac{1}{2} \mu_{ij} P_i P_j$

(b) $\frac{1}{2} (p_i \mu_{ij} + \mu_{ij} p_i + \cdots) P_j$

(c) $\frac{1}{2} p_i \mu_{ij} p_j + \cdots$

where i, j = x, y, z. Consider terms of type (a). Of these terms only those diagonal in the rotational quantum numbers are of interest since the off diagonal terms lead to energy terms of degree higher than quadratic in J and K. Thus, with regard to type (a) terms the only μ_{ij} that need be considered are those for which i = j. In the order of magnitude notation of Chapter VII one finds

$$\mu_{jj} \sim \frac{1}{I} + \frac{1}{I}\sqrt{\frac{B}{\omega}}\, q + \frac{1}{I}\left(\frac{B}{\omega}\right) q^2 + \cdots$$

where I is a moment of inertia and q is any one of the four degenerate vibrational coordinates in dimensionless form. The term linear in q has only off diagonal matrix elements connecting states for which the vibrational quantum numbers change by plus or minus one. The potential perturbation $H^{(1)}_{vib}$, used in this thesis, has no matrix elements connecting states for which the degenerate quantum numbers change by one unit. Thus, the terms in μ_{jj} linear in q cannot connect with the potential perturbation and therefore can be neglected. Of the terms quadratic in q^2 only those which have matrix elements diagonal in the vibrational quantum numbers need be retained since the off diagonal elements make contributions to the energy smaller than $(B^2/\omega)J^2$.

Consider next the type (b), or coriolis, terms. Only the term proportional to the operator $p_z P_z$ has diagonal matrix elements. The remaining coriolis terms contribute only through the squares of their matrix elements. With the exception of μ_{zz} it is necessary to retain only the leading term of μ_{ij} (the term of order 1/I) since higher order terms make energy contributions smaller than $(B^2/\omega)J^2$. This means that the μ_{ij} with $i \neq j$ can be neglected completely since their leading terms are of order $\frac{1}{I}\sqrt{B/\omega}\, q$.

Type (c) terms have matrix elements of order B. They can contribute to the rotational energies only through connections with matrix elements of H_{rot} which are off diagonal in the vibrational quantum numbers. The largest matrix elements, off diagonal in the vibrational quantum numbers, of H_{rot} are of order $B\sqrt{B/\omega}$ so that the contributions from type (c) terms will be of the order of magnitude of $B^2/\omega \sqrt{B/\omega}\, J^2$. Thus, type (c) terms can be neglected altogether. In the derivation of the classical vibrational kinetic energy in Chapter II it will be recalled that a term of the form [cf. Equation (12)]

$$\left[\sin\tau\, \vec{R}_3 + \cos\tau\, \vec{R}_4\right]^2 \cdot \left[\frac{x_1 \dot{x}_2 - x_2 \dot{x}_1}{x_1^2 + 2x_2^2}\right]^2$$

arose and was subsequently neglected. In the transcription to quantum mechanics this term becomes an operator of type (c) with matrix elements of order B and consequently can be neglected in the calculation of rotational energies. Considerable simplification in the form of the kinetic energy is thus obtained since one can take $g_{\alpha\beta} = \delta_{\alpha\beta}$.

With these simplifications, the terms of H_{rot} which can contribute to the inversion-rotation constants $B^- - B^+$ and $C^- - C^+$ are

$$\begin{aligned} H_{rot} = {} & \frac{1}{2I_{\parallel}}\left(P^2 - P_z^2\right) + \frac{1}{2I_{\parallel}} P_z^2 \\ & + \frac{3}{(2I_{\parallel})^3}\left[(X_1^2 + X_2^2 - X_2^2\cos 2\tau) R_3^2 + (X_1^2 + X_2^2 + X_2^2\cos 2\tau) R_4^2\right]\left(P^2 - P_z^2\right) \\ & + \frac{3}{(2I_{\parallel})^2}\left(\frac{X_2}{X_1}\right)^2\left[\sin^2\tau\, R_3^2 + \cos^2\tau\, R_4^2\right] \cdot P_z^2 \\ & + \frac{1}{I_{\perp}(2I_{\parallel})}\Big\{\left[X_2^2 + (X_1^2 + X_2^2)\cos 2\tau\right]\left(Q_{3x}\mathcal{P}_{3y} - Q_{3y}\mathcal{P}_{3x}\right) \\ & + \left[X_2^2 - (X_1^2 + X_2^2)\cos 2\tau\right]\left(Q_{4x}\mathcal{P}_{4y} - Q_{4y}\mathcal{P}_{4x}\right)\Big\} \cdot P_z \end{aligned} \qquad \text{(III-35)}$$

$$- \frac{(x_1^2+x_2^2)\sin 2\tau}{I_{\perp}(2I_{\parallel})}\left[(Q_{4x}\mathcal{P}_{3y}-Q_{3y}\mathcal{P}_{4x})+(Q_{3x}\mathcal{P}_{4y}-Q_{4y}\mathcal{P}_{3x})\right]\cdot P_z$$

$$-\left[\frac{\hbar}{(2I_{\parallel})^{3/2}}\left(x_2\frac{\partial}{\partial x_1}-x_1\frac{\partial}{\partial x_2}\right)+\left(x_2\frac{\partial}{\partial x_1}-x_1\frac{\partial}{\partial x_2}\right)\frac{\hbar}{(2I_{\parallel})^{3/2}}\right]$$

$$\times\left[(\sin\tau\, Q_3^+ + \cos\tau\, Q_4^+)(P_x - iP_y) - (\sin\tau\, Q_3^- + \cos\tau\, Q_4^-)(P_x+iP_y)\right]$$

$$+\frac{x_2}{(2I_{\parallel})^{3/2}}\left[(Q_4^-\mathcal{P}_3^- - Q_3^-\mathcal{P}_4^-)(P_x-iP_y)+(Q_4^+\mathcal{P}_3^+ - Q_3^+\mathcal{P}_4^+)(P_x+iP_y)\right]$$

where

$$\left.\begin{aligned}
\mathcal{P}_{jx} &= \frac{\hbar}{i}\frac{\partial}{\partial Q_{jx}} \qquad \mathcal{P}_{jy} = \frac{\hbar}{i}\frac{\partial}{\partial Q_{jy}}\\
\mathcal{P}_j^{\pm} &= \mathcal{P}_{jx} \pm i\,\mathcal{P}_{jy}\\
Q_j^{\pm} &= Q_{jx} \pm i\, Q_{jy}\\
R_j^2 &= Q_{jx}^2 + Q_{jy}^2
\end{aligned}\right\}\quad j=3,4$$

In order to find the final form of the Hamiltonian one introduces the coordinates σ and ζ defined by Equation (13) of Chapter II and expands the resulting Hamiltonian in powers of the small coordinate $\delta\sigma = \sigma - \sigma_o$. The "volume element", dx_1dx_2, then transforms into $(\cosh^2\sigma_o - \sin^2\zeta)^{1/2}d(\delta\sigma)d\zeta$. It is much more convenient to have $d(\delta\sigma)d\zeta$ for the "volume" element. This can be accomplished by the transformation

$$H \longrightarrow (\cosh^2\sigma_o - \sin^2\zeta)^{1/2} H\,(\cosh^2\sigma_o - \sin^2\zeta)^{-1/2}$$

on the complete Hamiltonian. Upon making this transformation and introducing the dimensionless coordinates defined by Equation (15) of Chapter III, and the inversion coordinate $x = \zeta/L$, one obtains the desired form of the Hamiltonian. The development of the pure vibrational part of the Hamiltonian is not given here since it has been discussed in detail in Chapters II and III. Any terms which involve q_1 and x alone and are independent of the momentum operators are absorbed into the "effective" potential, Equation (17). The resulting Hamiltonian can be written as the sum of an "unperturbed" part, $H^{(o)}$, and a "perturbation", $H^{(1)}$.

$$H = H^{(0)} + H^{(1)} \tag{III-36}$$

where $H^{(o)}$ is given by Equation (35) and $H^{(1)}$ is given by Equation (45) of Chapter VII. The functions $\phi_j(x)$ appearing in $H^{(1)}$ are defined below.

$$\phi_1(x) = \frac{\sin^2\zeta_0 - (\sin Lx)^2}{\left(\frac{\cosh^2\sigma_0 - 1}{\cosh^2\sigma_0 + 1}\right) + (\sin Lx)^2}$$

$$\phi_2(x) = \frac{\cos^2\zeta_0 - (\cos Lx)^2}{(\cos Lx)^2}$$

$$\phi_3(x) = \left(\frac{2DL^2}{\omega_1}\right)\left\{ \frac{2(\sinh 2\sigma_0)^2}{(\cosh^2\sigma_0 + 1)^3} \; \frac{\left[1 + (\sin Lx)^2\right]^2}{\left[\left(\frac{\cosh^2\sigma_0 - 1}{\cosh^2\sigma_0 + 1}\right) + (\sin Lx)^2\right]^3} \right.$$

$$\left. - \frac{2(2\cosh^2\sigma_0 - 1)}{(\cosh^2\sigma_0 + 1)^2} \; \frac{\left[1 + (\sin Lx)^2\right]}{\left[\left(\frac{\cosh^2\sigma_0 - 1}{\cosh^2\sigma_0 + 1}\right) + (\sin Lx)^2\right]^2} \right\}$$

$$\phi_4(x) = \left(\frac{12DL^2}{1000}\right)\left[\frac{\cosh^2\sigma_0 - \sin^2\zeta_0}{(\cosh^2\sigma_0+1)^3}\right]\cdot\left[\frac{\sinh^2\sigma_0 + (1-\cos 2\tau\cosh^2\sigma_0)(\sin Lx)^2}{\left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right) + (\sin Lx)^2\right]^3}\right]$$

$$\phi_5(x) = \left(\frac{12DL^2}{1000}\right)\left[\frac{\cosh^2\sigma_0 - \sin^2\zeta_0}{(\cosh^2\sigma_0+1)^3}\right]\cdot\left[\frac{\sinh^2\sigma_0 + (1+\mathrm{co}2\tau\cosh^2\sigma_0)(\sin Lx)^2}{\left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right) + (\sin Lx)^2\right]^3}\right]$$

$$\phi_6(x) = \left(\frac{2DL^2}{\omega_1}\right)\left(\frac{2\cosh^2\sigma_0 - 1}{\sinh^4\sigma_0}\right)\frac{1}{(\cos Lx)^2}$$

$$\phi_7(x) = \left(\frac{12DL^2}{1000}\right)\left[\frac{\cosh^2\sigma_0(\cosh^2\sigma_0 - \sin^2\zeta_0)}{\sinh^2\sigma_0\,(\cosh^2\sigma_0+1)^2}\right]\cdot\left[\frac{(\sin Lx)^2}{(\cos Lx)^2\left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right)+(\sin Lx)^2\right]^2}\right]$$

$$\phi_8(x) = \left(\frac{2}{\sinh^2\sigma_0(\cosh^2\sigma_0+1)}\right)\cdot\left[\frac{(\cosh^2\sigma_0+\cos 2\tau)(\sin Lx)^2 + \sinh^2\sigma_0\cos 2\tau}{(\cos Lx)^2\left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right) + (\sin Lx)^2\right]}\right]$$

$$\phi_9(x) = \left(\frac{2}{\sinh^2\sigma_0(\cosh^2\sigma_0+1)}\right)\cdot\left[\frac{(\cosh^2\sigma_0-\cos 2\tau)(\sin Lx)^2 - \sinh^2\sigma_0\cos 2\tau}{(\cos Lx)^2\left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right) + (\sin Lx)^2\right]}\right]$$

$$\phi_{10}(x) = \left[\left(\frac{16\omega_1}{1000}\right)\frac{(\cosh^2\sigma_0-\sin^2\zeta_0)}{(\cosh^2\sigma_0+1)^3}\right]^{1/2}\cdot\left[\frac{(\sin Lx)(\cos Lx)}{\left[\cosh^2\sigma_0-(\sin Lx)^2\right]\cdot\left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right)+(\sin Lx)^2\right]^{3/2}}\right]$$

$$\phi_{11}(x) = \left[\left(\frac{8D}{1000}\right)\frac{(\cosh^2\sigma_0-\sin^2\zeta_0)}{(\cosh^2\sigma_0+1)^3}\right]^{1/2}\cdot\left[\frac{\sinh 2\sigma_0}{\left[\cosh^2\sigma_0-(\sin Lx)^2\right]\cdot\left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right)+(\sin Lx)^2\right]^{3/2}}\right]$$

$$\phi_{12}(x) = \left[\left(\frac{8D}{1000}\right)\frac{\cosh^2\sigma_0 - \sin^2\zeta_0}{(\cosh^2\sigma_0+1)^3}\right]^{1/2} \cdot \left[\frac{L\sinh 2\sigma_0\,(\sin Lx)(\cos Lx)}{\left[\cosh^2\sigma_0 - (\sin Lx)^2\right]^2 \cdot \left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right) + (\sin Lx)^2\right]^{3/2}}\right.$$

$$\left. - \frac{3}{2}\,\frac{L\sinh 2\sigma_0\,(\sin Lx)(\cos Lx)}{\left[\cosh^2\sigma_0 - (\sin Lx)^2\right] \cdot \left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right) + (\sin Lx)^2\right]^{5/2}}\right]$$

$$\phi_{13}(x) = \left(\frac{2\cosh\sigma_0}{(\cosh^2\sigma_0+1)^{3/2}}\right) \cdot \left[\frac{(\sin Lx)}{\left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right) + (\sin Lx)^2\right]^{3/2}}\right]$$

$$\phi_\ell(x) = \left[\frac{3A_0\sinh^2\sigma_0}{10^3(\cosh^2\sigma_0+1)^3}\right]\left[\frac{(\cos Lx)^2}{\left[\left(\frac{\cosh^2\sigma_0-1}{\cosh^2\sigma_0+1}\right) + (\sin Lx)^2\right]^3}\right].$$

APPENDIX IV

TABLES OF MATRIX ELEMENTS

Matrix elements involving the double minimum wavefunctions were evaluated numerically using Simpson's rule. With thirty subdivisions between zero and π it was found that the integration error was less than 10^{-7} times the numerical value of the integrand.

The accuracy of the matrix elements is limited by the accuracy to which the wavefunctions are known. Twelve term wavefunctions were used to evaluate the matrix elements given in the following table. In order to test the accuracy of the wavefunctions a few matrix elements were evaluated using fourteen term wavefunctions. The matrix elements agreed to at least six significant figures, with the exception of matrix elements involving $\partial/\partial x$ which agreed to four or five significant figures.

$n_2n'_2$	$(n_2^+\|h_3\|n'^+_2)$	$(n_2^-\|h_3\|n'^-_2)$	$(n_2^+\|h_4\|n'^+_2)$	$(n_2^-\|h_4\|n'^-_2)$
00	$-.467606 \times 10^{1}$	$-.542328 \times 10^{1}$	$-.873123 \times 10^{0}$	$-.655510 \times 10^{0}$
01	$.867375 \times 10^{2}$	$.878445 \times 10^{2}$	$-.228496 \times 10^{2}$	$-.229026 \times 10^{2}$
02	$-.213726 \times 10^{2}$	$-.126225 \times 10^{2}$	$.346734 \times 10^{1}$	$.665662 \times 10^{0}$
03	$.464270 \times 10^{0}$	$-.252747 \times 10^{1}$	$.178068 \times 10^{1}$	$.171871 \times 10^{1}$
11	$.444662 \times 10^{2}$	$.214308 \times 10^{2}$	$-.182366 \times 10^{2}$	$-.115947 \times 10^{2}$
12	$.118434 \times 10^{3}$	$.119915 \times 10^{3}$	$-.327715 \times 10^{2}$	$-.313853 \times 10^{2}$
13	$-.471151 \times 10^{2}$	$-.165911 \times 10^{2}$	$.909685 \times 10^{1}$	$.167909 \times 10^{0}$
22	$.100408 \times 10^{3}$	$.234857 \times 10^{2}$	$-.366790 \times 10^{2}$	$-.151160 \times 10^{2}$
23	$.130042 \times 10^{3}$	$.136849 \times 10^{3}$	$-.350632 \times 10^{2}$	$-.344866 \times 10^{2}$
33	$.244878 \times 10^{2}$	$-.890763 \times 10^{1}$	$-.170506 \times 10^{2}$	$-.902593 \times 10^{1}$

$n_2n'_2$	$(n_2^+\|h_1\|n_2^+)$	$(n_2^-\|h_1\|n'^-_2)$	$(n_2^+\|f_1\|n'^+_2)$	$(n_2^-\|f_1\|n'^-_2)$
00	$-.179351 \times 10^{1}$	$-.252028 \times 10^{1}$	$.198772 \times 10^{-2}$	$.209264 \times 10^{-2}$
01	$.813915 \times 10^{2}$	$.821361 \times 10^{2}$	$-.135438 \times 10^{-1}$	$-.138544 \times 10^{-1}$
02	$-.173895 \times 10^{2}$	$.856668 \times 10^{1}$	$.463384 \times 10^{-2}$	$.360913 \times 10^{-2}$
03	$-.190976 \times 10^{1}$	$-.366937 \times 10^{1}$	$-.133960 \times 10^{-2}$	$-.411220 \times 10^{-3}$
11	$.497647 \times 10^{2}$	$.274422 \times 10^{2}$	$-.303040 \times 10^{-2}$	$.277680 \times 10^{-3}$
12	$.113072 \times 10^{3}$	$.112272 \times 10^{3}$	$-.178044 \times 10^{-1}$	$-.190968 \times 10^{-1}$
13	$-.401257 \times 10^{2}$	$-.103887 \times 10^{2}$	$.948055 \times 10^{-2}$	$.532233 \times 10^{-2}$
22	$.106826 \times 10^{3}$	$.330431 \times 10^{2}$	$-.964387 \times 10^{-2}$	$.190433 \times 10^{-2}$
23	$.123020 \times 10^{3}$	$.126487 \times 10^{3}$	$-.202837 \times 10^{-1}$	$-.229159 \times 10^{-1}$
33	$.360425 \times 10^{2}$	$.565791 \times 10^{1}$	$.285542 \times 10^{-2}$	$.891787 \times 10^{-2}$

$n_2n'_2$	$(n_2^+\|f_1\ \partial^2/\partial x^2 + f_2\ \partial/\partial x\|n'^+_2)$	$(n_2^-\|f_1\ \partial^2/\partial x^2 + f_2\ \partial/\partial x\|n'^-_2)$	$(n_2^+\|\phi_1\|n'^+_2)$	$(n_2^-\|\phi_1\|n'^-_2)$
00	$-.272164 \times 10^{-1}$	$-.260876 \times 10^{-1}$	$-.401377 \times 10^{-2}$	$-.456117 \times 10^{-2}$
01	$.397984 \times 10^{-1}$	$.510165 \times 10^{-1}$	$.639752 \times 10^{-1}$	$.648416 \times 10^{-1}$
02	$-.573596 \times 10^{-1}$	$-.262753 \times 10^{-1}$	$-.163243 \times 10^{-1}$	$-.100948 \times 10^{-1}$
03	$-.609436 \times 10^{-1}$	$-.113582 \times 10^{0}$	$.110208 \times 10^{-2}$	$-.124426 \times 10^{-2}$
11	$-.396541 \times 10^{-1}$	$-.240685 \times 10^{-1}$	$.310743 \times 10^{-1}$	$.141097 \times 10^{-1}$
12	$.614595 \times 10^{-1}$	$.154060 \times 10^{0}$	$.874902 \times 10^{-1}$	$.889947 \times 10^{-1}$
13	$-.145083 \times 10^{0}$	$-.321238 \times 10^{-1}$	$-.358252 \times 10^{-1}$	$-.136784 \times 10^{-1}$
22	$-.256263 \times 10^{-2}$	$.403451 \times 10^{-2}$	$.716768 \times 10^{-1}$	$.146162 \times 10^{-1}$
23	$.183408 \times 10^{0}$	$.324971 \times 10^{0}$	$.966487 \times 10^{-1}$	$.102474 \times 10^{0}$
33	$.166487 \times 10^{-1}$	$-.152486 \times 10^{-1}$	$.148371 \times 10^{-1}$	$-.106999 \times 10^{-1}$

$n_2n'_2$	$(n_2^+\|\phi_2\|n'^+_2)$	$(n_2^-\|\phi_2\|n'^-_2)$	$(n_2^+\|\phi_3\|n'^+_2)$	$(n_2^-\|\phi_3\|n'^-_2)$
00	$.530497 \times 10^{-2}$	$.554653 \times 10^{-2}$	$.930913 \times 10^{-2}$	$.929488 \times 10^{-2}$
01	$-.318863 \times 10^{-1}$	$-.326830 \times 10^{-1}$	$.155256 \times 10^{-2}$	$.156265 \times 10^{-2}$
02	$.115586 \times 10^{-1}$	$.934755 \times 10^{-2}$	$-.301491 \times 10^{-3}$	$-.132347 \times 10^{-3}$
03	$-.387615 \times 10^{-2}$	$-.149748 \times 10^{-2}$	$-.467250 \times 10^{-4}$	$-.644025 \times 10^{-4}$
11	$-.517480 \times 10^{-2}$	$.250653 \times 10^{-2}$	$.103536 \times 10^{-1}$	$.991180 \times 10^{-2}$
12	$-.417493 \times 10^{-1}$	$-.453269 \times 10^{-1}$	$.221296 \times 10^{-2}$	$.216771 \times 10^{-2}$
13	$.234896 \times 10^{-1}$	$.140636 \times 10^{-1}$	$-.727922 \times 10^{-3}$	$-.156253 \times 10^{-3}$
22	$-.197392 \times 10^{-1}$	$.744196 \times 10^{-2}$	$.115175 \times 10^{-1}$	$.100510 \times 10^{-1}$
23	$-.480763 \times 10^{-1}$	$-.551837 \times 10^{-1}$	$.241475 \times 10^{-2}$	$.245316 \times 10^{-2}$
33	$.103554 \times 10^{-1}$	$.253280 \times 10^{-1}$	$.101283 \times 10^{-1}$	$.952609 \times 10^{-2}$

n_2n_2'	$(n_2^+\|\phi_4\|n_2'^+)$	$(n_2^-\|\phi_4\|n_2'^-)$	$(n_2^+\|\phi_5\|n_2'^+)$	$(n_2^-\|\phi_5\|n_2'^-)$
00	$.391918 \times 10^{-1}$	$.391331 \times 10^{-1}$	$.377515 \times 10^{-1}$	$.376891 \times 10^{-1}$
01	$.641152 \times 10^{-2}$	$.645432 \times 10^{-2}$	$.675024 \times 10^{-2}$	$.678951 \times 10^{-2}$
02	$-.125469 \times 10^{-2}$	$-.557873 \times 10^{-3}$	$-.127179 \times 10^{-2}$	$-.529613 \times 10^{-3}$
03	$-.185855 \times 10^{-3}$	$-.262946 \times 10^{-3}$	$-.231754 \times 10^{-3}$	$-.292021 \times 10^{-3}$
11	$.434855 \times 10^{-1}$	$.416642 \times 10^{-1}$	$.423722 \times 10^{-1}$	$.404380 \times 10^{-1}$
12	$.912880 \times 10^{-2}$	$.895037 \times 10^{-2}$	$.966211 \times 10^{-2}$	$.943104 \times 10^{-2}$
13	$-.302028 \times 10^{-2}$	$-.662782 \times 10^{-3}$	$-.310733 \times 10^{-2}$	$-.608598 \times 10^{-3}$
22	$.482731 \times 10^{-1}$	$.422264 \times 10^{-1}$	$.475086 \times 10^{-1}$	$.410947 \times 10^{-1}$
23	$.996364 \times 10^{-2}$	$.101327 \times 10^{-1}$	$.105333 \times 10^{-1}$	$.106584 \times 10^{-1}$
33	$.425384 \times 10^{-1}$	$.400504 \times 10^{-1}$	$.414600 \times 10^{-1}$	$.388456 \times 10^{-1}$

n_2n_2'	$(n_2^+\|\phi_6\|n_2'^+)$	$(n_2^-\|\phi_6\|n_2'^-)$	$(n_2^+\|\phi_7\|n_2'^+)$	$(n_2^-\|\phi_7\|n_2'^-)$
00	$.495847 \times 10^{-2}$	$.495966 \times 10^{-2}$	$.592425 \times 10^{-2}$	$.594098 \times 10^{-2}$
01	$-.157273 \times 10^{-3}$	$-.161203 \times 10^{-3}$	$-.186988 \times 10^{-2}$	$-.188705 \times 10^{-2}$
02	$.570110 \times 10^{-4}$	$.461050 \times 10^{-4}$	$.407712 \times 10^{-3}$	$.213560 \times 10^{-3}$
03	$-.191184 \times 10^{-4}$	$-.738610 \times 10^{-5}$	$.185330 \times 10^{-4}$	$.571212 \times 10^{-4}$
11	$.490678 \times 10^{-2}$	$.494467 \times 10^{-2}$	$.475737 \times 10^{-2}$	$.527668 \times 10^{-2}$
12	$-.205920 \times 10^{-3}$	$-.223566 \times 10^{-3}$	$-.262932 \times 10^{-2}$	$-.261320 \times 10^{-2}$
13	$.115858 \times 10^{-3}$	$.693663 \times 10^{-4}$	$.946625 \times 10^{-3}$	$.276104 \times 10^{-3}$
22	$.483494 \times 10^{-2}$	$.496901 \times 10^{-2}$	$.343713 \times 10^{-2}$	$.517266 \times 10^{-2}$
23	$-.237127 \times 10^{-3}$	$-.272183 \times 10^{-3}$	$-.288712 \times 10^{-2}$	$-.298537 \times 10^{-2}$
33	$.498338 \times 10^{-2}$	$.505723 \times 10^{-2}$	$.511655 \times 10^{-2}$	$.585883 \times 10^{-2}$

n_2n_2'	$(n_2^+\|\phi_8\|n_2'^+)$	$(n_2^-\|\phi_8\|n_2'^-)$	$(n_2^+\|\phi_9\|n_2'^+)$	$(n_2^-\|\phi_9\|n_2'^-)$
00	$-.562704 \times 10^{-1}$	$-.556612 \times 10^{-1}$	$.442474 \times 10^{0}$	$.443031 \times 10^{0}$
01	$-.738568 \times 10^{-1}$	$-.751227 \times 10^{-1}$	$-.687266 \times 10^{-1}$	$-.700248 \times 10^{-1}$
02	$.213379 \times 10^{-1}$	$.147971 \times 10^{-1}$	$.209835 \times 10^{-1}$	$.151915 \times 10^{-1}$
03	$-.369493 \times 10^{-2}$	$-.105624 \times 10^{-3}$	$-.453452 \times 10^{-2}$	$-.796081 \times 10^{-3}$
11	$-.916744 \times 10^{-1}$	$-.726531 \times 10^{-1}$	$.411839 \times 10^{0}$	$.429284 \times 10^{0}$
12	$-.996514 \times 10^{-1}$	$-.103448 \times 10^{0}$	$-.921175 \times 10^{-1}$	$-.965816 \times 10^{-1}$
13	$.454612 \times 10^{-1}$	$.210678 \times 10^{-1}$	$.441598 \times 10^{-1}$	$.219921 \times 10^{-1}$
22	$-.134418 \times 10^{0}$	$-.694600 \times 10^{-1}$	$.373934 \times 10^{0}$	$.433965 \times 10^{0}$
23	$-.111508 \times 10^{0}$	$-.121294 \times 10^{0}$	$-.103731 \times 10^{0}$	$-.114223 \times 10^{0}$
33	$-.675133 \times 10^{-1}$	$-.363974 \times 10^{0}$	$.436772 \times 10^{0}$	$.466467 \times 10^{0}$

n_2^+	n_2^-	$(n_2^+\|\phi_{10}\|n_2^-)$	$(n_2^+\|\phi_{11}\ \partial/\partial x + \phi_{12}\|n_2^-)$	$(n_2^+\|\phi_{13}\|n_2^-)$
0^+	0^-	$.226178 \times 10^{0}$	$.277264 \times 10^{-2}$	$.436201 \times 10^{0}$
0^+	1^-	$-.276350 \times 10^{-1}$	$-.553503 \times 10^{0}$	$-.542808 \times 10^{-1}$
0^+	2^-	$-.539464 \times 10^{-2}$	$.438012 \times 10^{-1}$	$-.988656 \times 10^{-2}$
0^+	3^-	$.134868 \times 10^{-2}$	$.284173 \times 10^{-1}$	$.249894 \times 10^{-2}$
1^+	0^-	$-.300194 \times 10^{-1}$	$.551208 \times 10^{0}$	$-.588229 \times 10^{-1}$
1^+	1^-	$.194907 \times 10^{0}$	$.910707 \times 10^{-1}$	$.376112 \times 10^{0}$
1^+	2^-	$-.333022 \times 10^{-1}$	$-.654567 \times 10^{0}$	$-.654736 \times 10^{-1}$
1^+	3^-	$-.805519 \times 10^{-2}$	$.344760 \times 10^{-1}$	$-.148232 \times 10^{-1}$
2^+	0^-	$-.329941 \times 10^{-2}$	$-.108658 \times 10^{0}$	$-.579365 \times 10^{-2}$
2^+	1^-	$-.730052 \times 10^{-1}$	$.730930 \times 10^{0}$	$-.141703 \times 10^{0}$
2^+	2^-	$.148399 \times 10^{0}$	$.545528 \times 10^{0}$	$.286752 \times 10^{0}$
2^+	3^-	$-.531645 \times 10^{-2}$	$-.412469 \times 10^{0}$	$-.115794 \times 10^{-1}$
3^+	0^-	$.352353 \times 10^{-2}$	$-.225416 \times 10^{-1}$	$.654325 \times 10^{-2}$
3^+	1^-	$-.128605 \times 10^{-2}$	$-.301038 \times 10^{0}$	$-.130456 \times 10^{-2}$
3^+	2^-	$-.131620 \times 10^{0}$	$.959401 \times 10^{0}$	$-.255018 \times 10^{0}$
3^+	3^-	$.145189 \times 10^{0}$	$.104257 \times 10^{1}$	$.281417 \times 10^{0}$

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