# A STUDY OF THE BORN-OPPENHEIMER APPROXIMATION

Thesis for the Degree of M. S.
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Alvin R. Hagler
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# THE BORN-OPPENHEIMER APPROXIMATION

by

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# Abstract

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The Born-Oppenheimer approximation for molecules is presented in detail. Up-to-date terminology and notation are used. Also presented is a survey of work that has been done in molecular physics in which the Born-Oppenheimer approximation is assumed or known to be insufficient.

# ACKNOWLEDGMENT

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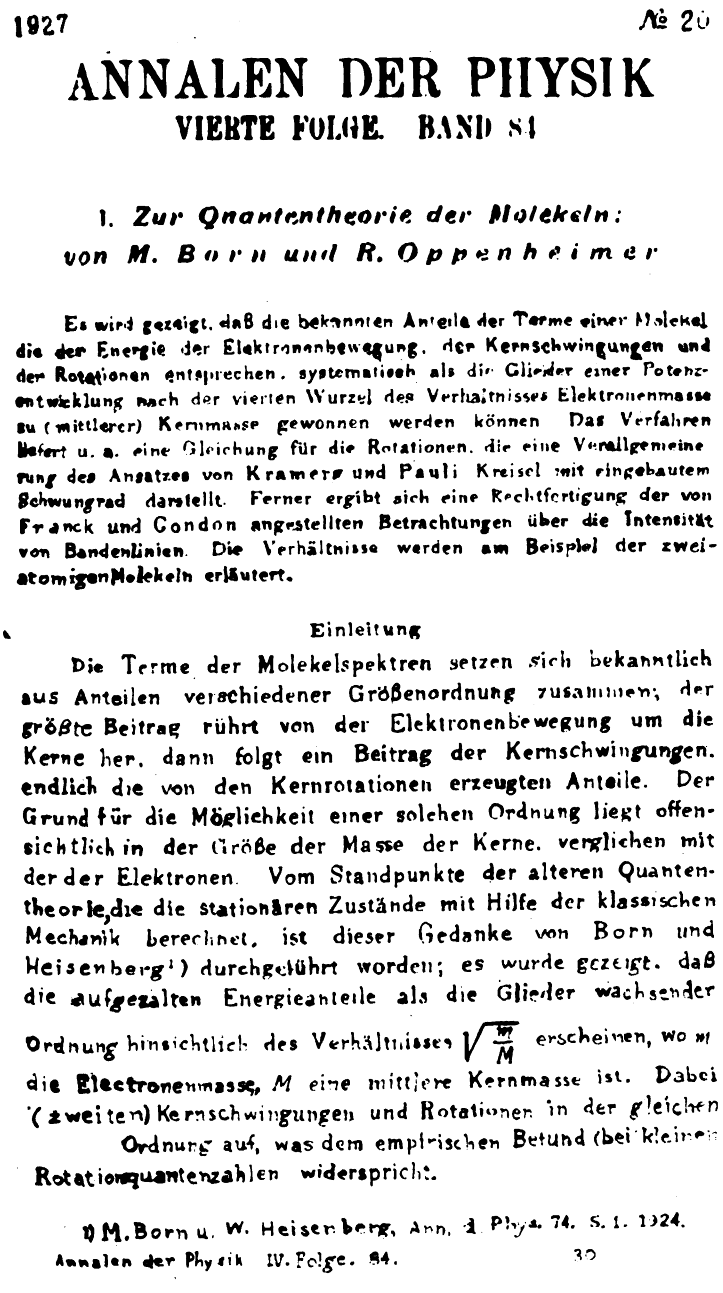
TABLE OF CONTENTS

# LIST OF FIGURES



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## 1. *Zur Quantentheorie der Molekeln;*

### *von M. Born und R. Oppenheimer*

Es wird gezeigt, daß die bekannten Anteile der Terme einer Molekel die der Energie der Elektronenbewegung, der Kernschwingungen und der Rotationen entsprechen, systematisch als die Glieder einer Potenzentwicklung nach der vierten Wurzel des Verhältnisses Elektronenmasse zu (mittlerer) Kernmasse gewonnen werden können. Das Verfahren liefert u. a. eine Gleichung für die Rotationen, die eine Verallgemeinerung des Ansatzes von **Kramers** und **Pauli** Kreisel mit eingebautem Schwungrad darstellt. Ferner ergibt sich eine Rechtfertigung der von **Franck** und **Condon** angestellten Betrachtungen über die Intensität von Bandenlinien. Die Verhältnisse werden am Beispiel der zweiatomigen Molekeln erläutert.

### Einleitung

Die Terme der Molekelspektren setzen sich bekanntlich aus Anteilen verschiedener Größenordnung zusammen; der größte Beitrag rührt von der Elektronenbewegung um die Kerne her, dann folgt ein Beitrag der Kernschwingungen, endlich die von den Kernrotationen erzeugten Anteile. Der Grund für die Möglichkeit einer solchen Ordnung liegt offensichtlich in der Größe der Masse der Kerne, verglichen mit der der Elektronen. Vom Standpunkte der alteren Quantentheorie, die die stationären Zustände mit Hilfe der klassischen Mechanik berechnet, ist dieser Gedanke von **Born** und **Heisenberg**[1]) durchgeführt worden; es wurde gezeigt, daß die aufgezählten Energieanteile als die Glieder wachsender Ordnung hinsichtlich des Verhältnisses $\sqrt{\frac{m}{M}}$ erscheinen, wo $m$ die Electronenmasse, $M$ eine mittlere Kernmasse ist. Dabei (zweiten) Kernschwingungen und Rotationen in der gleichen Ordnung auf, was dem empirischen Befund (bei kleinen Rotationsquantenzahlen widerspricht.

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[1]) M. Born u. W. Heisenberg, Ann. d. Phys. 74. S. 1. 1924.

Fig. 1

# INTRODUCTION

The Born-Oppenheimer approximation was formulated in a famous paper published by Born and Oppenheimer in 1927 Ann. Physik, Vol. 84, page 457 . It is the most fundamental and basic work in molecular physics. The first page of that paper, which is the subject of this study, is reproduced as Figure 1 of this thesis.

The problem that Born and Oppenheimer investigated may be quite simply stated. A molecule consists of a semi-rigid nuclear framework which is free to rotate in inertial space. The nuclei are in vibratory motion about their equilibrium positions. About the nuclei, electrons move in considerably more rapid motion. To compute the allowed energies for the electronic motion along with those of nuclear vibration and rotation from first principles would provide accurate prediction of all molecular parameters as well as the complete emission and absorption spectrum of the molecule. The difficulty, is however, that the Schroedinger wave equation is impossible to solve exactly for all but the most simple molecules.

Born and Oppenheimer, in attempting to find an approximate method of solution of the molecular wave equation, assumed that the electronic part of the wave equation could be solved for various nuclear configurations with the nuclei held fixed. The wave equation for the nuclei could then be solved by successive approximations with the electronic energy making up part of the potential field in which the nuclei move. This procedure is now known as the Born-Oppenheimer approximation.

Theoretical work done in molecular physics can be generally classified as falling into one of a few categories. The main divisions can be taken as electronic structure calculations, vibration-rotation calculations, and vibronic calculations. Among these divisions the number of papers involving electronic structure calculations, (with the nuclear framework fixed in its equilibrium configuration), and those involving vibration-rotation calculations (assuming no direct electronic interaction with the vibration-rotation motion) is vast. These papers are important to the understanding of molecular spectroscopy and structure. This study, however, is limited to papers in which the Born-Oppenheimer approximation is not considered sufficient, i.e., cases that deal with interactions between nuclear and electronic motion which is beyond the scope of the Born-Oppenheimer approximation.

The original paper by Born and Oppenheimer is not readily available in English. It has been translated and a microfilm copy was obtained from the Oak Ridge National Laboratory. The quantum mechanical language and notation used is characteristic of early quantum mechanics and does differ somewhat from modern works in that respect. This difference makes the original paper more difficult to read. In this study modern terminology and notation has been used in presenting the original theory of Born and Oppenheimer. Some typographical errors were located in the original paper and these will be pointed out at the end of this chapter.

As was previously stated, the vast body of work which assumes complete validity of the Born-Oppenheimer approximation will not be considered here. A survey of work which does not assume the Born-Oppenheimer approximation sufficient was made. It is possible to classify this work in several more or less distinct categories. These were taken to be: rotational spin uncoupling, the Jahn-Teller effect, the Renner effect, general vibration-electronic interactions, and miscellaneous improved methods of calculation. Each of these is discussed in this work in turn.

The method used was a library search of physics abstracts from 1926 to 1964. The abstracts were copied on cards and grouped according to category. There is, as might be expected, some overlapping of categories particularly among the Jahn-Teller and Renner effects, and vibration-electronic interactions since it could be argued that the first two are simply special cases of the third.

Definitive or basic papers were identified, separated, and given special emphasis. The most basic papers were then looked up and read, whereas only the abstract was read for the others except when the abstract was not clear or sufficiently explicit for our purpose.

It is hoped that this study will make a contribution toward identifying and clarifying those problems which are connected with the Born-Oppenheimer approximation.

# CHAPTER 1

# THE THEORY OF BORN AND OPPENHEIMER

The theory appearing in the famous paper by Born and Oppenheimer will be presented in this chapter.

One seeks to solve the Schroedinger equation for the motion of the electrons of a molecule located in force free space. Each electron moves in the force field provided by the nuclei and by all the other electrons. The nuclear framework is semi-rigid and thus admits vibratory motion. This in turn provides a non-constant force field for the electronic motion. Also, rotation of the molecule about its center of mass is possible. Occurence of coupling among the various types of motion needs, of course, to be considered as well. The translational motion, as in classical mechanics, separates completely from the other types of motion if one takes the coordinate origin at the instantaneous center of mass. This will be done, and the translational motion will not be considered further.

Since exact solution of the Schroedinger equation is out of the question, an expansion method of approximation is used. In this expansion, the zeroth order of approximation relates to the electronic energy. Terms of the second order correspond to the harmonic portion of the vibrational energy (normal modes portion), and the fourth order of approximation is associated principally with the rotational motion. As will be seen later, energy contributions from orders one and three vanish. The vanishing of terms of first order is due to the existence of an equilibrium position for the nuclei. For this situation the electronic energy of the molecule is a minimum. The vanishing of terms of order three is more difficult to interpret. It is, however, indirectly due to the same fact which is responsible for the vanishing of the first order terms. The theory also shows that in order to determine the complete eigenfunctions in zeroth order (and with them the transition probabilities in zeroth order) one must calculate energies through terms of fourth order. Continuation of the calculation beyond the fourth order has not been carried out. It is neither simple, nor does it yield results of fundamental significance. The diatomic molecule is treated as an example of the general theory.

## 1. Notation and Definitions.

The mass and rectangular coordinates of the elections will be denoted by

$$m, x_k, y_k, z_k, \qquad k = 1, 2, 3, \cdots, n$$

and that of the nuclei by

$$M_l, X_l, Y_l, Z_l, \qquad l = 1, 2, 3, \cdots, N$$

Let $M$ be the average of the nuclear masses $M_l$. Let

$$K = \sqrt[4]{\frac{m}{M}} \tag{1}$$

then

$$M_l = \frac{M}{\mu_l} = \frac{m}{K^4 \mu_l} \tag{2}$$

The $\mu_l$ are dimensionless and on the order of unity.

The potential energy of the system is

$$U(x_1, y_1, z_1, x_2, y_2, z_2, \cdots X_1, Y_1, Z_1, X_2, Y_2; Z_2; \cdots) = U(x, X). \tag{3}$$

Here $x$ denotes the totality of the election coordinates and $X$ that of the nuclei. The potential energy function depends only on the relative positions of the particles, but here no use is made of the particular form (Coulomb's law).

The kinetic energy of the electrons is represented by the operator

$$T_E = -\frac{\hbar^2}{2m}\sum_{k=1}^{n}\left(\frac{\partial^2}{\partial x_k^2}+\frac{\partial^2}{\partial y_k^2}+\frac{\partial^2}{\partial z_k^2}\right), \tag{4}$$

and the kinetic energy operator of the nuclei is

$$T_N = -\frac{\hbar^2 K^4}{2m}\sum_{l=1}^{N}\mu_l\left(\frac{\partial^2}{\partial X_l^2}+\frac{\partial^2}{\partial Y_l^2}+\frac{\partial^2}{\partial Z_l^2}\right). \tag{5}$$

The Hamiltonian is given by

$$H = H_0 + K^4 H_1, \tag{6}$$

where

$$T_E + U = H_0\left(x, \frac{\partial}{\partial x}, X\right) \tag{7}$$

$$T_N = K^4 H_1\left(\frac{\partial}{\partial X}\right). \tag{8}$$

It will be convenient to use the $3N-6$ independent relative nuclear coordinates

$$\xi_i = \xi_i(X), \qquad i = 1, 2, 3, \cdots (3N-6), \tag{9}$$

which specify the instantaneous distances between the nuclei, plus an additional six coordinates:

$$\theta_i = \theta_i(X), \qquad i = 1, 2, 3, 4, 5, 6, \tag{10}$$

which are the three Euler angles $(\theta, \phi, \Psi)$ and the three coordinates of the center of mass $(X_0, Y_0, Z_0)$ , these six coordinates serve to locate the position and orientation of the molecule in inertial space. The new coordinates $\xi$ and $\theta$ are obtained from the nuclear coordinates $X$ by a linear transformation, a fact that has been recognized in writing (9) and (10).

This transformation does not separate the Hamiltonian into translational, rotational, and relative motion. However, $H_1$ - representing the kinetic energy of vibration and rotation - may be written in three parts as follows:

$$H_1 = H_{\xi\xi} + H_{\xi\theta} + H_{\theta\theta}, \tag{11}$$

and developments of general vibration-rotation Hamiltonians$^{(1)}$ show that $H_{\xi\xi}$ is linear and homogeneous in $\partial^2/\partial\xi_i\partial\xi_j$ ; $H_{\xi\theta}$ involves the $\frac{\partial}{\partial\xi_i}$ ; and $H_{\theta\theta}$ is independent of $\xi_i$ . Some general conclusions may be drawn about these operators. If the operator $H_1$ is applied to any function of the relative coordinates $f(\xi)$ , the resulting quantity must be independent of the position in space and therefore independent of the $\theta_i$ . In particular, in $H_{\xi\xi}$ the coefficients of the $\partial^2/\partial\xi_i\partial\xi_j$ cannot depend on $\theta_i$ . On the other hand $\xi_i$ , $\theta_i$, and $\frac{\partial}{\partial\theta_i}$ must appear in $H_{\xi\theta}$ in addition to $\frac{\partial}{\partial\xi_i}$ , $H_{\theta\theta}$ will contain $\frac{\partial}{\partial\theta_j}$, $\xi_i$, and $\theta_i$ in addition to $\partial^2/\partial\theta_i\partial\theta_j$ .

The Schroedinger equation of the molecule is

$$(H_0 + K^4 H_1 - W)\Psi = 0, \tag{12}$$

where the eigenfunctions are denoted by $\Psi$ and the allowed energies by $W$ .

## 2. Electron Motion with Fixed Nuclei.

If in (12) one sets $\kappa = 0$, then a differential equation in the $x_k$ alone is obtained and the $X_l$ appear only as parameters:

$$[H_0(x, \tfrac{\partial}{\partial x}, X) - W]\Psi = 0 \tag{13}$$

This equation represents the motion of electrons about fixed nuclei. The relative nuclear distances and Eulerian angles appear as parameters. We assume that this equation is solved. If we let the origin of coordinates move with the center of mass of the molecule, translational motion will separate off completely from all other types of motion, the center-of-mass coordinates $X_0, Y_0, Z_0$ will be superfluous if translational motion is not of immediate interest, and $\theta_i$ will now represent only the three Eulerian angles $(\theta, \phi, \Psi)$. Translation will be disregarded for our purposes and will no longer be considered explicitly.

Let the $n^{th}$ eigenvalue and its corresponding eigenfunction be denoted by

$$W = V_n(\xi)\,, \quad \Psi = \varphi_n(x, \xi_i, \theta_i). \tag{14}$$

Then (13) becomes

$$[H_0(x, \tfrac{\partial}{\partial x}, \xi, \theta) - V_n(\xi)]\,\varphi_n(x, \xi, \theta) = 0 \tag{15}$$

All $V_n$'s are here assumed to be non-degenerate eigenvalues. This is not usually true for all electronic states of a given molecule, and if it is not so true, then special considerations apply. These degeneracies were not, however, considered by Born and Oppenheimer and will not be considered in this chapter.

It will be shown below that the function $V_n(\xi)$ plays the part of the potential energy for the vibration of the nuclei.

Instead of taking derivatives with respect to $\xi_i$ directly, let us replace $\xi_i$ by $\xi_i + K\zeta_i$ and expand with respect to $K$. The coefficients of a given power of $K$ will then be a homogeneous polynomial in $\zeta_i$ whose coefficients are the derivatives with respect to $\zeta_i$. Thus the expansion starts with a given nuclear configuration specified by $\xi$ and expands about this configuration, the deviations being given by $\zeta$. We have then,

(16) $$V_n(\xi + K\zeta) = V_n^{\circ} + K V_n^{(1)} + K^2 V_n^{(2)} + \cdots ,$$

where

(a) $V_n^{\circ} = V_n(\xi)$,

(17) (b) $V_n^{(1)} = \sum_i \zeta_i \frac{\partial V_n}{\partial \xi_i}$,

(c) $V_n^{(2)} = \frac{1}{2} \sum_{ij} \zeta_i \zeta_j \frac{\partial^2 V_n}{\partial \xi_i \partial \xi_j}$,

This is obtained by taking $\frac{\partial V_n}{\partial K} = \frac{\partial V_n}{\partial(\xi + K\zeta)} \frac{\partial(\xi + K\zeta)}{\partial K} = \zeta \frac{\partial V_n}{\partial(\xi + K\zeta)}$ and evaluating at $K = 0$, etc. Similarly,

(a) $H_\circ = H_\circ^{\circ} + K H_\circ^{(1)} + K^2 H_\circ^{(2)} + \cdots$,

(18)

(b) $\varphi_n = \varphi_n^{\circ} + K \varphi_n^{(1)} + K^2 \varphi_n^{(2)} + \cdots$.

Now we expand the quantities $\varphi_n^{(1)}$ and $\varphi_n^{(2)}$ in terms of the eigenfunction $\varphi_n^{\circ}(x, \xi, \Theta)$ :

(a) $\varphi_n^{(1)} = \sum_{n'} u_{nn'}^{(1)} \varphi_{n'}^{\circ}$,

(19)

(b) $\varphi_n^{(2)} = \sum_{n'} u_{nn'}^{(2)} \varphi_{n'}^{\circ}$,

where $u_{nn'}^{(r)}$ is a homogeneous polynomial of the $r^{\text{th}}$ degree in $\zeta_i$.

For example, multiply (18b) by $(\varphi_{n'}^{0})^*$ and integrate over all electron configuration space:

(20) $$\int (\varphi_{n''}^{0})^* \varphi_n^{(1)}\, dx = \sum_{n'} u_{nn'}^{(1)} \int (\varphi_{n''}^{0})^* \varphi_{n'}^{0}\, dx = \sum_{n'} u_{nn'}^{(1)} \delta_{n'n''},$$

since the $\varphi_n$'s are orthogonal functions. Now

$$\frac{\partial \varphi_n}{\partial K} = \sum_i \frac{\partial \varphi_n}{\partial(\xi_i + K\zeta_i)} \frac{\partial(\xi_i + K\zeta_i)}{\partial K} = \sum_i \frac{\partial \varphi_n}{\partial(\xi_i + K\zeta_i)} \cdot \zeta_i$$ which if evaluated at $K = 0$ becomes $\varphi_n^{(1)} = \sum_i \zeta_i \frac{\partial \varphi_n^0}{\partial \xi_i}$. Making use of this equation (20) becomes:

(21) $$u_{nn'}^{(1)} = \int (\varphi_{n'}^{0})^* \sum_i \zeta_i \frac{\partial \varphi_n^0}{\partial \xi_i}\, dx = \sum_i \zeta_i \int (\varphi_{n'}^{0})^* \frac{\partial \varphi_n^0}{\partial \xi_i}\, dx.$$

By a similar treatment:

(22) $$u_{nn'}^{(2)} = \frac{1}{2} \sum_{ij} \zeta_i \zeta_j \int (\varphi_{n'}^{0})^* \frac{\partial^2 \varphi_n^0}{\partial \xi_i \partial \xi_j}\, dx,$$

Thus as asserted, $u_{nn'}^{(r)}$ is a homogeneous polynomial of degree $r$ in $\zeta_i$. The integrals given here, in which $dx$ represents the volume element in configuration space of the electrons, are independent of the orientation of the nuclei in space and therefore independent of $\Theta_i$. They may be evaluated in the principal axes system.

If $F$ is any operator operating on $x_i$ then we will define

(23) $$\int (\varphi_{n'}^{0})^* F \varphi_n^{r}\, dx \equiv F_{nn'}^{r}$$

as the matrix element of the $r^{th}$ order of $F$. For $r = 0$ this becomes the ordinary matrix element

(24) $$F_{nn'}^{0} = F_{nn'} = \int (\varphi_{n'}^{0})^* F \varphi_n^{0}\, dx$$

In general, according to equation (19), ( $\varphi_n^{(r)} = \sum_{n''} u_{nn''}^{(r)} \varphi_{n''}^{0}$ ),

(25) $$F_{nn'}^{(r)} = \sum_{n''} u_{nn''}^{(r)} F_{n''n'}.$$

Now it follows from (15) for $K=0$, and for $F=(H_0^0-V_n^0)$ that

$$
\begin{aligned}
(H_0^0-V_n^0)^{(r)}_{nn'} &\equiv \int(\varphi_{n'}^0)^*(H_0^0-V_n^0)\,\varphi_n^{(r)}\,dx \\
&= \int(\varphi_{n'}^0)^*(H_0^0-V_n^0)\sum_{n''} u^{(r)}_{nn''}\,\varphi^0_{n''}\,dx \\
&= \sum_{n''} u^{(r)}_{nn''}\left[\int(\varphi^0_{n'})^* H_0^0\,\varphi^0_{n''} - \int(\varphi^0_{n'})^* V_n^0\,\varphi^0_{n''}\right]dx \\
&= \sum_{n''} u^{(r)}_{nn''}\left(V^0_{n''}\,\delta_{nn''} - V_n^0\,\delta_{n'n''}\right) = u^{(r)}_{nn'}(V^0_{n'}-V^0_n).
\end{aligned}
$$

Thus

(26) $$(H_0^0-V_n^0)^{(r)}_{nn'} = u^{(r)}_{nn'}(V^0_{n'}-V^0_n).$$

Now by substituting (16) and (18) into (15) and equating coefficients of similar powers of $K=0$ we obtain

(a) $(H_0^0-V_n^0)\,\varphi_n^0 = 0$

(27) (b) $(H_0^0-V_n^0)\,\varphi_n^{(1)} + (H_0^{(1)}-V_n^{(1)})\,\varphi_n^0 = 0$

(c) $(H_0^0-V_n^0)\,\varphi_n^{(2)} + (H_0^{(1)}-V_n^{(1)})\,\varphi_n^{(1)} + (H_0^{(2)}-V_n^{(2)})\,\varphi_n^0 = 0$

Due to the orthogonality of the eigenfunctions, multiplication by $(\varphi_{n'}^0)^*$ and integration over $x_i$ will, with the use of (25) provide:

(a) $u^{(1)}_{nn'}(V^0_{n'}-V^0_n) + (H_0^{(1)})_{nn'} - V_n^{(1)}\,\delta_{nn'} = 0,$

(28)

(b) $u^{(2)}_{nn'}(V^0_{n'}-V^0_n) + (H_0^{(1)}-V_n^{(1)})^{(1)}_{nn'} + (H_0^{(2)})_{nn'} - V_n^{(2)}\,\delta_{nn'} = 0$

The expansion (18a) for the Hamiltonian may be treated similarly in terms of $(H_0^{(1)})_{nn'}, (H_0^{(2)})_{nn'}$, ... which are the matrix elements

$$\left(\frac{\partial H_0}{\partial \xi_i}\right)_{nn'},\ \left(\frac{\partial^2 H_0}{\partial \xi_i\,\partial \xi_j}\right)_{nn'},\ \cdots.$$

These will be used later.

## 3. The Perturbation Equations.

An arbitrary configuration of electrons and nuclei cannot be dealt with by means of a general perturbation treatment. Only those conditions that conform to a stable molecule can be considered. For the unperturbed system the electron motion will be considered for an arbitrary, but fixed nuclear configuration $\xi_i$ . Next, all quantities will be developed in terms of small variations of $\xi_i$ which will be designated $K\zeta_i$ . We assume that for a stable molecule the amplitudes of vibration go to zero as $K$ goes to zero, an assumption that is justified by the results.

As in paragraph 2, equation (18), we have the expansion

$$H_0\left(x, \frac{\partial}{\partial x}, \xi + K\zeta, \theta\right) = H_0^0 + K H_0^{(1)} + K^2 H_0^{(2)} + \cdots , \tag{29}$$

where

$$H_0^0 = H_0\left(x, \frac{\partial}{\partial x}, \xi\right),$$

$$H_0^{(1)} = \sum_i \zeta_i \frac{\partial H_0}{\partial \xi_i} ,$$

$$H_0^{(2)} = 1/2 \sum_{ij} \zeta_i \zeta_j \frac{\partial^2 H_0}{\partial \xi_i \partial \xi_j} ,$$

and by (11), since $\frac{\partial}{\partial \xi} f(\xi + K\zeta) = \frac{1}{K} \frac{\partial}{\partial \zeta} f(\xi + K\zeta)$, where $f(\xi + K\zeta)$ is some function of $\xi + K\zeta$ :

$$K^4 H_1\left(X, \frac{\partial}{\partial X}\right) = K^4\left(\frac{1}{K^2} H_{\zeta\zeta} + \frac{1}{K} H_{\zeta\theta} + H_{\theta\theta}\right) \tag{30}$$

$$= K^2 H_{\zeta\zeta}^0 + K^3 (H_{\zeta\theta}^0 + H_{\zeta\zeta}^{(1)}) + K^4 (H_{\theta\theta}^0 + H_{\zeta\theta}^{(1)} + H_{\zeta\zeta}^{(2)}) + \cdots ;$$

where

$$(31)\quad \begin{aligned} &\text{(a)}\quad H^{\circ}_{\zeta\zeta} = H^{\circ}_{\zeta\zeta}\left(\xi, \frac{\partial^2}{\partial\zeta_i\,\partial\zeta_j}\right), \\ &\text{(b)}\quad H^{(1)}_{\zeta\zeta} = \sum_i \zeta_i \frac{\partial H^{\circ}_{\zeta\zeta}}{\partial\xi_i}, \end{aligned}$$

$$(32)\quad \begin{aligned} &\text{(a)}\quad H^{\circ}_{\zeta\theta} = H^{\circ}_{\zeta\theta}\left(\xi, \theta, \frac{\partial}{\partial\zeta}, \frac{\partial}{\partial\theta}\right), \\ &\text{(b)}\quad H^{(1)}_{\zeta\theta} = \sum_i \zeta_i \frac{\partial H^{\circ}_{\zeta\theta}}{\partial\xi_i}, \end{aligned}$$

$$(33)\quad \begin{aligned} &\text{(a)}\quad H^{\circ}_{\theta\theta} = H^{\circ}_{\theta\theta}\left(\xi, \theta, \frac{\partial^2}{\partial\theta_i\,\partial\theta_j}\right), \\ &\text{(b)}\quad H^{(1)}_{\theta\theta} = \sum_i \zeta_i \frac{\partial H^{\circ}_{\theta\theta}}{\partial\xi_i}. \end{aligned}$$

The argument $\xi_i$ is from here on to be considered as a constant. The Hamiltonian becomes

$$(34)\quad \begin{aligned} H = H_o + K^4 H_1 = H^{\circ}_{o} + K H^{(1)}_{o} + K^2\left(H^{(2)}_{o} + H^{\circ}_{\zeta\zeta}\right) + K^3\left(H^{(3)}_{o} + H^{\circ}_{\zeta\theta} + \right. \\ \left. + H^{(1)}_{\zeta\zeta}\right) + K^4\left(H^{(4)}_{o} + H^{\circ}_{\theta\theta} + H^{(1)}_{\zeta\theta} + H^{(2)}_{\zeta\zeta}\right) + \cdots, \end{aligned}$$

after substitution and collection of the coefficients of the various powers of $K$.

Now we expand the eigenfunctions and energies in the following manner:

$$(35)\quad \begin{aligned} &\text{(a)}\quad \Psi = \Psi^{\circ} + K\,\Psi^{(1)} + K^2\,\Psi^{(2)} + \cdots, \\ &\text{(b)}\quad W = W^{\circ} + K\,W^{(1)} + K^2\,W^{(2)} + \cdots. \end{aligned}$$

Then, by equating the coefficients of the different powers of $K$, in the resulting wave equation, to zero, the following set of perturbation equations result:

$$\text{(a)}\quad (H_0^0 - W^0)\Psi^0 = 0,$$

$$\text{(b)}\quad (H_0^0 - W^0)\Psi^{(1)} = (W^{(1)} - H_0^{(1)})\Psi^0,$$

$$\text{(36)}\quad \text{(c)}\quad (H_0^0 - W^0)\Psi^{(2)} = (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0)\Psi^0 + (W^{(1)} - H_0^{(1)})\Psi^{(1)},$$

$$\begin{aligned}\text{(d)}\quad (H_0^0 - W^0)\Psi^{(3)} = {} & (W^{(3)} - H_0^{(3)} - H_{\zeta\theta}^0 - H_{\zeta\zeta}^{(1)})\Psi^0 \\ & + (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0)\Psi^{(1)} + (W^{(1)} - H_0^{(1)})\Psi^{(2)},\end{aligned}$$

$$\begin{aligned}\text{(e)}\quad (H_0^0 - W^0)\Psi^{(4)} = {} & (W^{(4)} - H_0^{(4)} - H_{\theta\theta}^0 - H_{\zeta\theta}^{(1)} - H_{\zeta\zeta}^{(2)})\Psi^0 \\ & + (W^{(3)} - H_0^{(3)} - H_{\zeta\theta}^0 - H_{\zeta\zeta}^{(1)})\Psi^{(1)} \\ & + (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0)\Psi^{(2)} + (W^{(1)} - H_0^{(1)})\Psi^{(3)}.\end{aligned}$$

## 4. Solution of the Perturbation Equations of Zero and First Order; Nuclear Equilibrium.

The zeroth order perturbation equation (36a) was presented in paragraph 2 in the discussion of electron motion for fixed nuclei. From the normalized eigenfunctions $\varphi_n^0(x, \xi, \theta)$ introduced in paragraph 2, and the associated eigenvalues $V_n^0 = V_n(\xi)$, one obtains the general solution of (36a) in the form

$$\Psi_n^0 = \chi_n^0(\zeta, \theta)\, \varphi_n^0(x, \xi, \theta), \tag{37}$$

where $\chi_n^0$ is an (as yet) arbitrary function of $\zeta_i, \theta_i$ . These functions are needed to obtain the solutions of the higher perturbation equations. The next perturbation equation (36b) is

$$(H_0^0 - W_n^0)\Psi_n^{(1)} = (W_n^{(1)} - H_0^{(1)})\Psi_n^0. \tag{38}$$

It may be solved if $\Psi_n^{(1)}$ is imagined expanded as a series in $\Psi_n^0$ . Then it may be seen that the left side of the equation is orthogonal to $\Psi_n^0$ . Therefore, for non-trivial solutions to exist the right-hand side must be orthogonal to $\Psi_n^\circ$ with respect to the $x_i$, i.e.,

$$\int (\Psi_n^\circ)^* (W_n^{(1)} - H_o^{(1)}) \Psi_n^\circ \, dx = 0,$$

or

$$\int (\chi_n^\circ)^* (\varphi_n^\circ)^* W_n^{(1)} \chi_n^\circ \varphi_n^\circ \, dx - \int (\chi_n^\circ)^* (\varphi_n^\circ)^* H_o^{(1)} \chi_n^\circ \varphi_n^\circ \, dx = 0,$$

or

$$W_n^{(1)} |\chi_n^\circ|^2 \int (\varphi_n^\circ)^* \varphi_n^\circ \, dx - |\chi_n^\circ|^2 (H_o^{(1)})_{nn} = 0 .$$

Thus,

(39) $$[(H_o^{(1)})_{nn} - W_n^{(1)}] \, |\chi_n^\circ|^2 = 0 ,$$

where $(H_o^{(1)})_{nn}$ is the diagonal element of the operator $H_o^{(1)}(x_i)$ and according to (39) it must be a constant, since for equation (39) to be satisfied, we must have that $(H_o^{(1)})_{nn} = W_n^{(1)}$ ; the function $|\chi_n^\circ|^2$ must be non-zero, otherwise $\Psi_n^\circ$ would be identically equal to zero. It thus follows that

(40) $$W_n^{(1)} = (H_o^{(1)})_{nn} = 0 .$$

Now, from (17) and (28a), and taking $n' = n$, we have that

$$(H_o^{(1)})_{nn} = V_n^{(1)} = \sum_i \zeta_i \frac{\partial V_n}{\partial \xi_i} = 0$$ ; hence

(41) $$\frac{\partial V_n}{\partial \xi_i} = 0 ,$$ for all i.

Equation (41) shows that the relative coordinates $\xi_i$ cannot be arbitrarily chosen but must correspond to an extreme value of the electron energy $V_n(\xi)$. It will later be shown that this extreme value must be a minimum value. The function $\chi_n^\circ(\zeta, \theta)$ is as yet unspecified. If in (38) one sets

$W_n^0 = V_n(\xi) = V_n^0$ , $W_n^{(1)} = 0$ , and $\Psi_n^0 = \chi_n^0 \varphi_n^0$ , then the defining equation for $\Psi_n^{(1)}$ is obtained:

(42) $$(H_0^0 - V_n^0)\Psi_n^{(1)} = -H_0^{(1)} \varphi_n^0 \chi_n^0 .$$

A particular solution according to (27b) is of the form

(43) $$\Psi_n^{(1)} = \chi_n^0 \varphi_n^{(1)} ,$$

where $\varphi_n^{(1)}$ is the function (19a) defined by (18). The general solution of (42) is obtained by the addition of a general solution ( $\varphi_n^0$) of the homogeneous equation with another as yet undefined factor $\chi_n^{(1)}(\xi, \Theta)$ ; thus:

(44) $$\Psi_n^{(1)} = \chi_n^0 \varphi_n^{(1)} + \chi_n^{(1)} \varphi_n^0 .$$

## 5. Solution of the Perturbation Equations to Second and Third Order; Nuclear Vibrations.

The second order perturbation equation (36c) reads:

$$(H_0^0 - W_n^0)\Psi^{(2)} = (W^{(2)} - H_0^{(2)} - H_{\xi\xi}^0)\Psi^0 + (W^{(1)} - H_0^{(1)})\Psi^{(1)}.$$

After introduction of the first order solutions (44) this equation becomes

(45) $$(H_0^0 - V_n^0)\Psi_n^{(2)} = (W_n^{(2)} - H_0^{(2)} - H_{\xi\xi}^0)\chi_n^0 \varphi_n^0 - H_0^{(1)}(\chi_n^0 \varphi_n^{(1)} + \chi_n^{(1)} \varphi_n^0)$$

which has solutions only if the right-hand side is orthogonal to $\varphi_n^0$ . Multiplying by $(\varphi_n^0)^*$ and integrating over $dx$ results in

(46) $$[(H_0^{(2)} + H_{\xi\xi}^0)_{nn} + (H_0^{(1)})_{nn}^{(1)} - W_n^{(2)}]\chi_n^0 = 0 .$$

Now it follows from (28b) for $V_n^{(1)} = 0$ that

(47) $$(H_0^{(2)})_{nn} + (H_0^{(1)})_{nn}^{(1)} = V_n^{(2)} ,$$

and since $H^\circ_{\zeta\zeta}$ is independent of $x_i$ , one has that, $(H^\circ_{\zeta\zeta})_{nn} = H^\circ_{\zeta\zeta}$. Now it follows that

$$[\, H^\circ_{\zeta\zeta} + V^{(2)}_n - W^{(2)}_n \,]\, \chi^\circ_n = 0. \tag{48}$$

Since $H^\circ_{\zeta\zeta}$ is the vibrational Hamiltonian, and since $V^{(2)}_n$ depends on the displacements $\zeta_i$ of the nuclei from their equilibrium positions $\xi_i$ , (48) must represent the equation for nuclear vibration. More explicitly we have for (48),

$$[\, H^\circ_{\zeta\zeta}\left( \xi, \frac{\partial^2}{\partial \zeta_i \partial \zeta_j} \right) + 1/2 \sum_{ij} \zeta_i \zeta_j \frac{\partial^2 V_n}{\partial \xi_i \partial \xi_j} \,]\, \chi^\circ_n = W^{(2)}_n \chi^0_n. \tag{49}$$

It is seen that the second order portion of $V_n(\xi)$ plays the part of the harmonic potential energy of vibration of the nuclei. This provides a further condition for the existence of a stable molecule, viz., that the extreme value of $V_n(\xi)$ defined by (41) must be a minimum; for the quadratic form $V^{(2)}_n(\xi)$ must be positive definite if all normal modes are to be stable and vibrations about the equilibrium point are possible. Equation (49) would be separable if a linear transformation of the $\zeta_i$ to normal coordinates were to be performed: If $\sigma^\circ_{ns}(\zeta)$ is an eigenfunction of (49) with eigenvalue $W^{(2)}_{ns}$ , then the general solution to (49) is

(50)

(a) $W^{(2)} = W^{(2)}_{ns}$ , $\chi^\circ_n = \chi^\circ_{ns}$ , where

(b) $\chi^\circ_{ns} = \rho^\circ_{ns}(\Theta)\, \sigma^\circ_{ns}(\zeta)$.

The index $s$ specifies the set of 3N-6 vibrational quantum numbers. The function $\rho^\circ_{ns}(\Theta)$ is as yet undetermined and must be analyzed when continuing to higher orders of approximation. As is well known, the functions $\sigma^\circ_{ns}(\zeta)$ are linear conbimations of products of Hermite orthogonal functions in the normal coordinates. The property of the Hermite orthogonal functions, that they are either odd or even will be used later.

If $\Phi$ is any operator dependent on $\zeta_i$, then the matrix

$$\Phi_{\substack{nn'\\ ss'}} = \int (\sigma^{0}_{n's'})^{*} \, \Phi \, \sigma^{0}_{ns} \, d\zeta , \tag{51}$$

may be formed, where $d\zeta$ is the volume element in $\zeta_i$ space.

In order to solve equation (45), (48) is substituted into (45) in the form

$$( W^{(2)}_{ns} - H^{0}_{\zeta\zeta} ) \chi^{0}_{ns} = V^{(2)}_{n} \chi^{0}_{ns} ,$$

and then (45) becomes

$$( H^{0}_{0} - V^{0}_{n} ) \Psi^{(2)}_{n} = ( V^{(2)}_{n} - H^{(2)}_{0} ) \chi^{0}_{ns} \varphi^{0}_{n} - H^{(1)}_{0} ( \chi^{0}_{ns} \varphi^{(1)}_{n} + \chi^{(1)}_{ns} \varphi^{0}_{n} ), \tag{52}$$

which has as the solution to the reduced equation $\chi^{(2)}_{ns} \varphi^{0}_{n}$, and the particular solution $\chi^{0}_{ns} \varphi^{(2)}_{n} + \chi^{(1)}_{ns} \varphi^{0}_{n}$. The general solution is therefore;

$$\Psi^{(2)}_{n} = \chi^{0}_{ns} \varphi^{(2)}_{n} + \chi^{(1)}_{ns} \varphi^{(1)}_{n} + \chi^{(2)}_{ns} \varphi^{0}_{n} , \tag{53}$$

where $\chi^{(2)}_{ns}$ is another, as yet unspecified, function of $\zeta_i$ and $\theta_j$, since (53) is the solution to the equation of vibration.

Next, the perturbation equations of third order (36d) may be studied. Introducing functions that have already been determined, (36d) becomes

$$\begin{aligned} ( H^{0}_{0} - V^{0}_{n} ) \Psi^{(3)}_{n} = {} & ( W^{(3)} - H^{(3)}_{0} - H^{0}_{\zeta\theta} - H^{(1)}_{\zeta\zeta} ) \chi^{0}_{ns} \varphi^{0}_{n} \\ & + ( W^{(2)}_{ns} - H^{(2)}_{0} - H^{0}_{\zeta\zeta} )( \chi^{0}_{ns} \varphi^{(1)}_{n} + \chi^{(1)}_{ns} \varphi^{0}_{n} ) \\ & - H^{(1)}_{0} ( \chi^{0}_{ns} \varphi^{(2)}_{n} + \chi^{(1)}_{ns} \varphi^{(1)}_{n} + \chi^{(2)}_{ns} \varphi^{0}_{n} ). \end{aligned} \tag{54}$$

If the right-hand side is considered to be expanded as a series in $\varphi_n^\circ$, (54) may be written

$$(55)\qquad (H_0^\circ - V_n^\circ)\Psi_n^{(3)} = W^{(3)}\chi_{ns}^\circ \varphi_n^\circ - \sum_{n'} F_{nn'}^{(3)}\varphi_{n'}^\circ \ ,$$

where

$$(56)\qquad F_{nn'}^{(3)} = F_{nn'}^{(3,1)}\chi_{ns}^{(2)} + F_{nn'}^{(3,2)}\chi_{ns}^{(1)} + F_{nn'}^{(3,3)}\chi_{ns}^\circ \ .$$

Equating the right-hand side of (54) to the right-hand side of (55) after substituting (56) provides

$$(57)\qquad \sum_{n'}\left( F_{nn'}^{(3,1)}\chi_{ns}^{(2)}\varphi_{n'}^\circ + F_{nn'}^{(3,2)}\chi_{ns}^{(1)}\varphi_{n'}^\circ + F_{nn'}^{(3,3)}\chi_{ns}^\circ\varphi_{n'}^\circ \right)$$
$$= (H_0^{(2)} + H_{\varsigma\theta}^\circ + H_{\varsigma\varsigma}^{(1)})\chi_{ns}^\circ\varphi_n^\circ + (-W_{ns}^{(2)} + H_0^{(2)} + H_{\varsigma\varsigma}^\circ)(\chi_{ns}^\circ\varphi_n^{(1)}$$
$$+ \chi_{ns}^{(1)}\varphi_n^\circ) + H_0^{(1)}(\chi_{ns}^\circ\varphi_n^{(2)} + \chi_{ns}^{(1)}\varphi_n^{(1)} + \chi_{ns}^{(2)}\varphi_n^\circ).$$

From (57) it is seen that

$$\text{(a)}\qquad \sum_{n'} F_{nn'}^{(3,1)}\chi_{ns}^{(2)}\varphi_{n'}^\circ = H_0^{(1)}\chi_{ns}^{(2)}\varphi_n^\circ \ ,$$

$$(58)\quad \text{(b)}\qquad \sum_{n'} F_{nn'}^{(3,2)}\chi_{ns}^{(1)}\varphi_{n'}^\circ = [(-W_{ns}^{(2)} + H_0^{(2)} + H_{\varsigma\varsigma}^\circ)\varphi_n^\circ + H_0^{(1)}\varphi_n^{(1)}]\chi_{ns}^{(1)} \ ,$$

$$\text{(c)}\qquad \sum_{n'} F_{nn'}^{(3,3)}\chi_{ns}^\circ\varphi_{n'}^\circ = [(H_0^{(2)} + H_{\varsigma\theta}^\circ + H_{\varsigma\varsigma}^{(1)})\varphi_n^\circ + (-W_{ns}^{(2)} + H_0^{(2)} + H_{\varsigma\varsigma}^\circ)\varphi_n^{(1)}$$
$$+ H_0^{(1)}\varphi_n^{(2)}]\chi_{ns}^\circ \ ,$$

Multiplying (58a, b, c) from the left by $(\varphi_{n''}^\circ)^*$ and integrating over $dx$ gives

$$\text{(a)}\qquad F_{nn'}^{(3,1)} = (H_0^{(1)})_{nn'} \ ,$$

$$(59)\quad \text{(b)}\qquad F_{nn'}^{(3,2)} = (H_{\varsigma\varsigma}^\circ + H_c^{(2)} - W_{ns}^{(2)})_{nn'} + (H_c^{(1)})_{nn'}^{(1)} \ ,$$

$$\text{(c)}\qquad F_{nn'}^{(3,3)} = (H_0^{(3)} + H_{\varsigma\theta}^\circ + H_{\varsigma\varsigma}^{(1)})_{nn'} - (W_{ns}^{(2)} - H_0^{(2)} - H_{\varsigma\varsigma}^\circ)_{nn'}^{(1)} + (H_0^{(1)})_{nn'}^{(2)}$$

where $F_{nn'}^{(3,3)}$ is a homogeneous operator of odd degree in $\varsigma_i$ and $\frac{\partial}{\partial\varsigma_i}$ (see equations 31 and 32). Multiplication of (55) from the left by $(\varphi^\circ_n)^*$ and integration over $dx$ yields

(60) $$W^{(3)}\chi^\circ_{ns} - F^{(3)}_{nn} = 0.$$

Substituting (59a) into (56) and using (60), we find

(61) $$F^{(3,2)}_{nn}\chi^{(1)}_{ns} = (W^{(3)} - F^{(3,3)}_{nn})\chi^\circ_{ns},$$

and substituting (47) into (59b), we have

(62) $$F^{(3,2)}_{nn} = H^\circ_{\zeta\zeta} + V^{(2)}_n - W^{(2)}_{ns}.$$

Equation (61) is the inhomogeneous equation related to the vibration equation (48) through the functions $\chi^\circ_{ns}$ . Since (48) has solutions $\chi^\circ_{ns} = \rho^\circ_{ns}(\theta)\sigma^\circ_{ns}(\zeta)$ by (50b) with eigenvalues $W^{(2)}_{ns}$, (61) has solutions only when the right-hand side is orthogonal to $\sigma^\circ_{ns}$ with respect to $\zeta$ space. Because of (50b) this provides a differential equation for $\rho^\circ_{ns}(\theta)$,

(63) $$(F^{(3,3)}_{\substack{nn\\ss}} - W^{(3)})\rho^\circ_{ns} = 0.$$

However, as has been established, $F^{(3,3)}_{nn}$ is odd in $\zeta_i$ and $\frac{\partial}{\partial\zeta_i}$ . If $F^{(3,3)}_{nn}$ is transformed to normal coordinates $\eta_i, \frac{\partial}{\partial\eta_i}$ , then it will also be odd in the normal coordinates, because the transformation from $\zeta_i$ to $\eta_i$ is a linear transformation. Furthermore, the $\sigma^\circ_{ns}(\zeta)$, when transformed to $\sigma^\circ_{ns}(\eta)$ will be products of harmonic oscillator wave functions, so that the integrands of

$$F^{(3,3)}_{\substack{nn\\ss}} = \int_{-\infty}^{\infty} \sigma^\circ_{ns}(\eta)\, F^{(3,3)}_{nn}\left(\eta, \frac{\partial}{\partial\eta}\right) \sigma^\circ_{ns}(\eta)\, d\eta$$

will be odd in $\eta_i$ for all $i = 1, 2, 3, \cdots$, 3N-6. Hence, $F^{(3,3)}_{\substack{nn\\ss}} = 0$ for $s = s'$ . Then for (63) to have non-zero solutions $\rho^{\circ}_{ns}(\theta)$ (which we must have in order for the total wave functions $\Psi$ to be non-vanishing), we must have that

$$W^{(3)} = 0 .$$

The functions $\rho^{\circ}_{ns}$ remain undefined. Now (61) becomes

$$F^{(3,2)}_{nn}\,\chi^{(1)}_{ns} = -\,F^{(3,3)}_{nn}\,\chi^{\circ}_{ns} ,$$

and its solution has the form

$$\chi^{(1)}_{ns} = S^{(1)}_{ns}\,\rho^{\circ}_{ns} , \tag{64}$$

where $S^{(1)}_{ns}$ is the following operator (with respect to $\theta_i$):

$$S^{(1)}_{ns} = \sum_{s'}{}' \frac{F^{(3,3)}_{\substack{nn\\ss'}}\,\sigma^{\circ}_{ns'}}{W^{(2)}_{ns} - W^{(2)}_{ns'}} . \tag{65}$$

Equation (65) can be obtained by the following steps:

$$F^{(3,2)}_{nn}\chi^{(1)}_{ns} = -\,F^{(3,3)}_{nn}\,\chi^{\circ}_{ns} = -\,F^{(3,3)}_{nn}\,\rho^{\circ}_{ns}\,\sigma^{\circ}_{ns} ,$$

$$(H^{\circ}_{\zeta\zeta} + V^{(2)}_{n} - W^{(2)}_{ns})\,\chi^{(1)}_{ns} = -\,F^{(3,3)}_{nn}\,\rho^{\circ}_{ns}\,\sigma^{\circ}_{ns} ,$$

$$[W^{(2)}_{ns} - (H^{\circ}_{\zeta\zeta} + V^{(2)}_{n})]\,\chi^{(1)}_{ns} = F^{(3,3)}_{nn}\,\rho^{\circ}_{ns}\,\sigma^{\circ}_{ns} ,$$

we now let $\chi^{(1)}_{ns} = \rho^{\circ}_{ns} \sum\limits_{s''} a_{ns''}\,\sigma^{\circ}_{ns''}$ and have

$$[W^{(2)}_{ns}\,\rho^{\circ}_{ns} \sum_{s''} a_{ns''}\sigma^{\circ}_{ns''} - (H^{\circ}_{\zeta\zeta} + V^{(2)}_{n})\,\rho^{\circ}_{ns} \sum_{s''} a_{ns''}\sigma^{\circ}_{ns''}]$$

$$= [W^{(2)}_{ns}\,\rho^{\circ}_{ns} \sum_{s''} a_{ns''}\sigma^{\circ}_{ns''} - \rho^{\circ}_{ns} \sum_{s''} a_{ns''}\,W^{(2)}_{ns''}\,\sigma^{\circ}_{ns''}] = F^{(3,3)}_{nn}\sigma^{\circ}_{ns}\,\rho^{\circ}_{ns}.$$

We multiply from the left by $(\sigma^{\circ}_{ns'})^{*}$ and integrate over $d\zeta$ to obtain

$$W^{(2)}_{ns}\,a_{ns'} - a_{ns'}\,W^{(2)}_{ns'} = F^{(3,3)}_{\substack{nn\\ss'}} ;$$

thus

$$a_{ns'} = \frac{F^{(3,3)}_{\substack{nn\\ss'}}}{(W^{(2)}_{ns} - W^{(2)}_{ns'})} \quad ; \quad a_{ns} = 0 \tag{66}$$

Since we had $\chi^{(1)}_{ns} = S^{(1)}_{ns}\,\rho^{\circ}_{ns} = \rho^{\circ}_{ns}\sum\limits_{s''} a_{ns''}\sigma^{\circ}_{ns''}$, substitution of

(66) into this establishes (65). Now (55) becomes

(67) $$(H_0^\circ - V_n^\circ)\Psi_n^{(3)} = -\sum_{n'} F_{nn'}^{(3)} \varphi_{n'}^\circ .$$

If $\Psi_n^{(3)}$ is expanded as a series in $\varphi_n^\circ$, then (67) may be multiplied from the left by $(\varphi_{n'}^\circ)^*$ with $n \neq n'$ and integrated over $dx$ to give:

(68) $$\Psi_n^{(3)} = \sum_{n'}{}' \frac{F_{nn'}^{(3)} \varphi_{n'}^\circ}{V_n^\circ - V_{n'}^\circ} ,$$

which can be written as

$$\Psi_n^{(3)} = \sum_{n'}{}' \left( G_{nn'}^{(3,1)} \chi_{ns}^{(2)} \varphi_{n'}^\circ + G_{nn'}^{(3,2)} \chi_{ns}^{(1)} \varphi_{n'}^\circ + G_{nn'}^{(3,3)} \chi_{ns}^\circ \varphi_{n'}^\circ \right).$$

This expression may be treated in a manner similar to (56) and one finds that $G_{nn'}^{(3,1)}$ is a number, $G_{nn'}^{(3,2)} = \frac{F_{nn'}^{(3,2)}}{(V_n^\circ - V_{n'}^\circ)}$, and is a differential operator with respect to $\zeta_i$, whereas $G_{nn'}^{(3,3)}$ is an operator with respect to $\zeta_i, \theta_i$. Now using (28b),

(69) $$\sum_{n'}{}' G_{nn'}^{(3,1)} \chi_{ns}^{(2)} \varphi_{n'}^\circ = \sum_{n'}{}' \frac{(H_0^{(1)})_{nn'} \varphi_{n'}^\circ}{V_n^\circ - V_{n'}^\circ} \chi_{ns}^{(2)} = \sum_{n'}{}' u_{nn'}^{(1)} \varphi_{n'}^\circ \chi_{ns}^{(2)} = \varphi_n^{(1)} \chi_{ns}^{(2)} ;$$

thus finally we can write

(70) $$\Psi_n^{(3)} = \varphi_n^{(1)} \chi_{ns}^{(2)} + \sum_{n'}{}' \left( G_{nn'}^{(3,2)} \chi_{ns}^{(1)} \varphi_{n'}^\circ + G_{nn'}^{(3,3)} \chi_{ns}^\circ \varphi_{n'}^\circ \right).$$

## 6. Solution of the Perturbation Equations of the Fourth and Higher Orders: Rotation and Coupling Effects.

Equation (36e), after substitution of the quantities that have already been found, becomes

(71) $$\begin{aligned}(H_0^\circ - V_n^\circ)\Psi_n^{(4)} &= (W^{(4)} - H_0^{(4)} - H_{\theta\theta}^\circ - H_{\zeta\theta}^{(1)} - H_{\zeta\zeta}^{(2)}) \chi_{ns}^\circ \varphi_n^\circ \\ &\quad - (H_0^{(3)} + H_{\zeta\theta}^\circ + H_{\zeta\zeta}^{(1)})(\chi_{ns}^{(1)} \varphi_n^\circ + \chi_{ns}^\circ \varphi_n^{(1)}) \\ &\quad + (W_{ns}^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^\circ)(\chi_{ns}^{(2)} \varphi_n^\circ + \chi_{ns}^{(1)} \varphi_n^{(1)} + \chi_{ns}^\circ \varphi_n^{(2)}) \\ &\quad - H_0^{(1)} \left[ \varphi_n^{(1)} \chi_{ns}^{(2)} + \sum_{n'}{}' ( G_{nn'}^{(3,2)} \chi_{ns}^{(1)} \varphi_{n'}^\circ + G_{nn'}^{(3,3)} \chi_{ns}^\circ \varphi_{n'}^\circ ) \right].\end{aligned}$$

The right-hand side can be expanded in terms of $\varphi_n^\circ$ to obtain

$$(H_\circ^\circ - V_n^\circ)\,\Psi_n^{(4)} = W^{(4)} X_{ns}^\circ\, \varphi_n^\circ - \sum_{n'} F_{nn'}^{(4)}\, \varphi_{n'}^\circ \tag{72}$$

where

$$F_{nn'}^{(4)} = F_{nn'}^{(4,2)} X_{ns}^{(2)} + F_{nn'}^{(4,3)} X_{ns}^{(1)} + F_{nn'}^{(4,4)} X_{ns}^\circ\,, \tag{73}$$

and where

$$F_{nn'}^{(4,2)} = (\, H_{\zeta\zeta}^\circ + H_\circ^{(2)} - W_{ns}^{(2)}\,)_{nn'} + (H_\circ^{(1)})_{nn'}^{(1)}\,. \tag{74}$$

This is found by multiplying (71) from the left by $(\varphi_n^\circ)^*$ and integrating over $dx$. $F_{nn'}^{(4,2)}$ is identical to $F_{nn'}^{(3,2)}$, (59b), $F_{nn'}^{(4,3)}$ is of odd order in $\zeta_i$ and $\frac{\partial}{\partial \zeta_i}$, and $F_{nn'}^{(4,4)}$ is of even order in $\zeta_i$ and $\frac{\partial}{\partial \zeta_i}$.

Equation (72) has non-trivial solutions only if the right-hand side is orthogonal to $\varphi_n^\circ$. Multiplying (72) from the left by $(\varphi_n^\circ)^*$ and integrating over $dx$ provides

$$W^{(4)} X_{ns}^\circ - F_{nn}^{(4)} = 0.$$

Substituting this into (73) gives

$$F_{nn}^{(4,2)} X_{ns}^{(2)} = (\, W^{(4)} - F_{nn}^{(4,4)})\, X_{ns}^\circ - F_{nn}^{(4,3)} X_{ns}^{(1)}\,. \tag{75}$$

The left side, because of (74), is identical to the vibration equation (48), and therefore the right-hand side must be orthogonal to $\sigma_{ns}^\circ$. If the values of $X_{ns}^\circ$ and $X_{ns}^{(1)}$ from (50b) and (64) are introduced along with the definition

$$(\Phi)_{ss'}^{(1)} = \int (\sigma_{ns'}^\circ)^*\, \Phi\, S_{ns}^{(1)}\, d\zeta = {\sum_{s''}}' \frac{(\, \Phi\, F_{\substack{nn\\ ss''}}^{(3,3)}\,)_{s's''}}{W_{ns}^{(2)} - W_{ns''}^{(2)}} \tag{76}$$

then it follows that

$$[\, F_{\substack{nn\\ ss}}^{(4,4)} + (\, F_{nn}^{(4,3)})_{ss}^{(1)} - W^{(4)}\,]\, \rho_{ns}^\circ = 0. \tag{77}$$

These equations at last define $\rho^{\circ}_{ns}(\theta)$ , and therefore the motion of the principal axes of inertia in inertial space. The most interesting term of the operator in (77) is the one that contains the second derivative with respect to $\theta_i$ ; it is formed from $H^{\circ}_{\theta\theta}\chi^{\circ}_{ns}\varphi^{\circ}_{n}$ as may be seen in (71) and therefore corresponds to the term in $F^{(4,4)}_{nn}$ ,

$$(78) \qquad (\overline{H^{\circ}_{\theta\theta}})_n = \int (\varphi^{\circ}_n)^* H^{\circ}_{\theta\theta} (\varphi^{\circ}_n \cdots) \, dx$$

where in the position of the dots the function on which the operator acts in introduced. Instead of the simple operator $H^{\circ}_{\theta\theta}$ , the more complicated $(\overline{H^{\circ}_{\theta\theta}})_n$ occurs. Physically, this corresponds to the inclusion of a coupling of the rotational motion of the nuclei with the electron motion. This is the effect which Kramers and Pauli(2) attempted to describe in diatomic molecules by mounting a flywheel on the rotating nuclear framework. Then there is in (77) the term which is derived from the operator $H_{\zeta\theta}$ . This corresponds to a coupling of the rotation with the angular momentum which results from the nuclear vibrations. Finally, there is a term that does not affect $\theta_i$ . It gives an additional contribution on the order of $\kappa^4$ to the vibrational energy and represents anharmonic corrections.

We now consider the rotation. If $r$ represents a suitable set of rotational quantum numbers, then one has for the solution of (77)

$$(79) \qquad W^{(4)} = W^{(4)}_{nsr} \; ; \; \rho^{\circ}_{ns} = \rho^{\circ}_{nsr}(\theta).$$

Now (75) and finally (72) can be solved. It is not instructive, for our general considerations however, to write out the solutions explicitly.

The treatment could be carried on, but nothing fundamentally new would result. The higher perturbations describe the coupling between rotation, vibration, and electron motion. No new quantum numbers that have not already been introduced would result.

We now summarize our principal conclusions. It has been demonstrated that to completely define the eigenfunctions, even to zeroth order, the solution of the perturbation equations is required to fourth order, since

(80) $$\Psi_{nsr}(x, \zeta, \theta) = \varphi_n^{\circ}(x, \zeta, \theta)\sigma_{ns}^{\circ}(\zeta)\rho_{nsr}^{\circ}(\theta) + \cdots,$$

where $\varphi_n^{\circ}$ is the eigenfunction of the electronic motion for fixed nuclei, $\sigma_{ns}^{\circ}$ is the eigenfunction for harmonic nuclear vibration, and $\rho_{nsr}^{\circ}$ is the eigenfunction for rotation of the nuclear framework. The vibration coordinates $\zeta_i$ are measured from the equilibrium positions $\xi_i$, which are defined as the positions for which the energy of the electronic motion $V_n(\xi)$ is a minimum. The energy to the fourth order is

(81) $$W_{nsr} = V_n^{\circ} + K^2 W_{ns}^{(2)} + K^4 W_{nsr}^{(4)} + \cdots,$$

where $V_n^{\circ}$ is the minimum value of the electronic energy which is characteristic of a situation in which the nuclear framework is rigid and at rest in inertial space, $W_{ns}^{(2)}$ is the harmonic nuclear vibrational energy, $W_{nsr}^{(4)}$ gives the energy of rotation plus anharmonic corrections to the vibrational energy. Up to and including the fourth order of approximation, the vibration-rotation motion is independent of the motion of the electrons.

## 7. Special Case of Diatomic Molecules.

As an example of the method, a short treatment of diatomic molecules will now be given. Since degeneracies will not be considered, this will be for the special case when the axial component of the angular momentum of the molecule is zero.

In the case of two nuclei there is only one $\xi$ coordinate for the nuclear separation, and five $\theta$ coordinates, which are the coordinates of the center of mass $X_0, Y_0, Z_0$ and the polar coordinates of the orientation of the nuclear axis, $\theta$ and $\omega$.

The kinetic energy of the nuclei is given by

$$T_N = -K^4 \frac{\hbar^2}{2m} \left[ \Delta_0 + \frac{\mu}{\xi^2} \frac{\partial}{\partial \xi}\left( \xi^2 \frac{\partial}{\partial \xi} \right) + \frac{\mu}{\xi} \Delta_\theta \right] \tag{82}$$

where

$$K = \sqrt[4]{\frac{m}{M_1+M_2}} \quad , \quad \mu = \frac{(M_1+M_2)^2}{M_1 M_2} \tag{83}$$

and

$$\text{(84)} \quad \begin{aligned} &\text{(a)} \quad \Delta_0 = \frac{\partial^2}{\partial X_0^2} + \frac{\partial^2}{\partial Y_0^2} + \frac{\partial^2}{\partial Z_0^2} \, , \\ &\text{(b)} \quad \Delta_\theta = \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \omega^2} + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right), \end{aligned}$$

$$\text{(85)} \quad \begin{aligned} &\text{(a)} \quad H_{\xi\xi} = -\frac{\hbar^2}{2m} \mu \frac{\partial^2}{\partial \xi^2} \, , \\ &\text{(b)} \quad H_{\xi\theta} = -\frac{\hbar^2}{2m} \frac{2\mu}{\xi} \frac{\partial}{\partial \xi} \, , \\ &\text{(c)} \quad H_{\theta\theta} = -\frac{\hbar^2}{2m} \left( \Delta_0 + \frac{\mu}{\xi^2} \Delta_\theta \right). \end{aligned}$$

Replacing $\xi$ by $\xi + \kappa\zeta$ and expanding in terms of $\kappa$, we find

(86) (a) $H^{0}_{\zeta\zeta} = -\frac{\hbar^2}{2m}\mu\frac{\partial^2}{\partial\zeta^2}$,

(b) $H^{p}_{\zeta\zeta} = 0$, $p = 1, 2, \cdots$

(87) (a) $H^{0}_{\zeta\theta} = -\frac{\hbar^2}{2m}\frac{2\mu}{\xi}\frac{\partial}{\partial\zeta}$,

(b) $H^{(1)}_{\zeta\theta} = \frac{\hbar^2}{2m}\frac{2\mu}{\xi^2}\zeta\frac{\partial}{\partial\zeta}$,

(88) (a) $H^{0}_{\theta\theta} = -\frac{\hbar^2}{2m}\left(\Delta_0 + \frac{\mu}{\xi^2}\Delta_\theta\right)$,

(b) $H^{(1)}_{\theta\theta} = \frac{\hbar^2}{2m}\frac{2\mu}{\xi^2}\zeta\Delta_\theta$.

The equilibrium nuclear separation is determined by

$$V_{n'} = \frac{dV_n}{d\xi} = 0. \qquad (89)$$

The equations of nuclear vibration (48) are

$$\left[-\frac{\hbar^2\mu}{2m}\frac{d^2}{d\zeta^2} + \tfrac{1}{2}\zeta^2 V_n''(\xi) - W_n^{(2)}\right]\chi_n^0 = 0. \qquad (90)$$

Let

$$a = \frac{m}{\hbar^2\mu}W_n^{(2)}, \quad b = \frac{m}{2\mu\hbar^2}V_n'', \quad \eta \equiv \zeta\sqrt[4]{b};$$

then (90) becomes

$$\left[\frac{d^2}{d\eta^2} + \left(\frac{a}{\sqrt{b}} - \eta^2\right)\right]\chi_n^0 = 0, \qquad (91)$$

with eigenvalues

$$\frac{a}{\sqrt{b}} = 2s + 1, \quad s = 0, 1, 2, \cdots \qquad (92)$$

and eigenfunctions

$$\sigma^0_{ns} = e^{-\frac{1}{2}\eta^2}H_s(\eta) \qquad (93)$$

where $H_s(\eta)$ is the $s^{th}$ hermite polynomial.

The vibrational energy is then;

(94) $$K^2 W^{(2)}_{ns} = a\hbar^2 \frac{K^2\mu}{m} = (2s+1)\, b\, \frac{\hbar^2 K\mu}{m} = (s+\tfrac{1}{2})\frac{h}{4\pi}\sqrt{K^4\frac{\mu}{m}V''_n}$$

or

(95) $$K^2 W^{(2)}_{ns} = (s+\tfrac{1}{2})\, h\nu_0\ ;$$

where

(96) $$\frac{1}{4\pi}\sqrt{K^4\frac{\mu}{m}V''_n} = \frac{1}{4\pi}\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)V''_n} = \nu_0$$

The rotational equation (77) exclusive of the anharmonic correction to the vibrational energy is given in (97). Since $H_{\xi\theta}$ does not contain derivatives with respect to $\theta_j$, according to (85), all terms in (77) except $(\overline{H^0_{\theta\theta}})_n$ will be represented by a constant, $C_{ns}$,

(97) $$[(\overline{H^0_{\theta\theta}})_n + C_{ns} - W^{(4)}]\,\rho^0_{ns} = 0.$$

The translational part of $H_{\theta\theta}$ may be omitted. According to (78) and (88), for an arbitrary function $f(\theta)$:

(98) $$(\overline{H^0_{\theta\theta}})_n\, f(\theta) = -\frac{\hbar^2\mu}{2m\xi^2}\int(\varphi^0_n)^*\Delta_\theta(\varphi^0_n f)\,dx,$$

and by (84)

(99) $$\Delta_\theta(\varphi^0_n f) = \varphi^0_n\,\Delta_\theta f + f\,\Delta_\theta\varphi^0_n + 2\left(\frac{1}{\sin^2\theta}\frac{\partial\varphi^0_n}{\partial\omega}\frac{\partial f}{\partial\omega} + \frac{\partial\varphi^0_n}{\partial\theta}\frac{\partial f}{\partial\theta}\right).$$

Therefore

(100) $$\begin{aligned}(\overline{H^0_{\theta\theta}})_n\, f(\theta) = -\frac{\hbar^2\mu}{2m\xi^2}\Big[\Delta_\theta f + f\cdot\int(\varphi^0_n)^*\Delta_\theta\varphi^0_n\,dx \\ + \frac{2}{\sin^2\theta}\frac{\partial f}{\partial\omega}\int(\varphi^0_n)^*\frac{\partial\varphi^0_n}{\partial\omega}\,dx \\ + 2\frac{\partial f}{\partial\theta}\int(\varphi^0_n)^*\frac{\partial\varphi^0_n}{\partial\theta}\,dx\Big].\end{aligned}$$

Now since

$$\Delta_\theta = \frac{\partial^2}{\partial\theta^2} + \cot\theta\,\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\omega^2},$$

it is convenient to let:

$$\bar{\Theta}_n = \int (\varphi_n^\circ)^* \frac{\partial \varphi_n^\circ}{\partial \theta}\, dx, \qquad \bar{\Omega}_n = \int (\varphi_n^\circ)^* \frac{\partial \varphi_n^\circ}{\partial \omega}\, dx,$$
$$\bar{\Theta}_n^2 = \int (\varphi_n^\circ)^* \frac{\partial^2 \varphi_n^\circ}{\partial \theta^2}\, dx, \qquad \bar{\Omega}_n^2 = \int (\varphi_n^\circ)^* \frac{\partial^2 \varphi_n^\circ}{\partial \omega^2}\, dx. \tag{101}$$

The quantities (101) are the diagonal elements of the matrices of the angular momenta $L_\theta, L_\omega$ as well as $\bar{L}_\theta^2, \bar{L}_\omega^2$ (except for a factor of $\hbar^2$ or $-\hbar^2$), where $\theta$ and $\omega$ are Euler angles, and $\bar{L}_\theta^2, \bar{L}_\omega^2$ are squares of the mean values. Using this notation in (97) provides

$$\Big[\Big(\frac{\partial^2}{\partial \theta^2} + 2\bar{\Theta}_n \frac{\partial}{\partial \theta} + \bar{\Theta}_n^2\Big) + \cot\theta\Big(\frac{\partial}{\partial \theta} + \bar{\Theta}_n\Big)$$
$$+ \frac{1}{\sin^2\theta}\Big(\frac{\partial^2}{\partial \omega^2} + 2\bar{\Omega}_n \frac{\partial}{\partial \omega} + \bar{\Omega}_n^2\Big) + \frac{m\xi^2}{\hbar^2\mu}(W^{(4)} - C_{ns})\Big]\rho_{ns}^\circ = 0. \tag{102}$$

According to (102), the magnitude of $\frac{2m\xi^2}{\hbar^2\mu}W^{(4)}$ is equal to a numerical function of the rotational quantum numbers, $g_{ns}(r)$; for the rotational energy it then follows that

$$K^4 W_{nsr}^{(4)} = \frac{\hbar^2 \mu K^4}{2m\xi^2} g_{ns}(r) = \frac{\hbar^2}{2J} g_{ns}(r), \tag{103}$$

where

$$J = \frac{m}{\mu K^4}\xi^2 = \frac{M_1 M_2}{M_1 + M_2}\xi^2, \tag{104}$$

and is the moment of inertia of the nuclei in the equilibrium configuration.

Higher approximations will not be considered in this section. It will be shown next that the diatomic molecule may also be dealt with by a different perturbation treatment where the unperturbed motion will consist of the electronic motion plus uniform nuclear rotation, rather than nuclei at rest.

## 8. Independent Treatment of the Diatomic Molecule.

Substituting equation (11) into (12) we obtain

(105) $$[H_0 + K^4(H_{\xi\xi} + H_{\xi\theta} + H_{\theta\theta}) - W]\Psi = 0.$$

In the diatomic molecule $H_{\xi\theta}$ is independent of $\theta$, therefore it is again possible to separate translation and rotation. Making use of (85) and omitting the terms corresponding to translational motion we have

(106) $$[H_0 - \frac{\hbar^2\mu}{2m} K^4 (\frac{\partial^2}{\partial\xi^2} + \frac{2}{\xi}\frac{\partial}{\partial\xi} + \frac{1}{\xi^2}\Delta_\theta) - W]\Psi = 0.$$

Now let

(107) $$\Psi = Y_r(\theta,\omega)\,\Psi_r(x,\xi),$$

where $Y_r$ is a spherical harmonic of $r^{th}$ order, i.e. a function which satisfies

$$\Delta_\theta Y_r + r(r+1) Y_r = 0.$$

Then it follows that

(108) $$[H_0 - \frac{\hbar^2\mu}{2m} K^4 (\frac{\partial^2}{\partial\xi^2} + \frac{2}{\xi}\frac{\partial}{\partial\xi} - \frac{r(r+1)}{\xi^2}) - W]\Psi_r = 0.$$

Now we replace $\xi$ by $\xi + K\zeta$ to provide an equation for the vibrations with uniform rotation. The energy of these states is given by

(109) $$R = \frac{\hbar^2\mu K^2}{2m}\frac{r(r+1)}{\xi^2} = \frac{\hbar^2}{2J} r(r+1).$$

Now we set

(110) $$W = E + R$$

and equation (108) becomes

(111) $$(H^0 + K H^{(1)} + K^2 H^{(2)} + \cdots - E)\Psi_r = 0,$$

where

(112)
(a) $$H^{\circ} = H_{\circ}^{\circ},$$
(b) $$H^{(1)} = H_{\circ}^{(1)} + \zeta R',$$
(c) $$H^{(2)} = H_{\circ}^{(2)} + \tfrac{1}{2}\zeta^{2} R'' - \frac{\hbar^{2}\mu}{2m}\frac{\partial^{2}}{\partial\zeta^{2}},$$
(d) $$H^{(3)} = H_{\circ}^{(3)} + \tfrac{1}{6}\zeta^{3} R''' - \frac{\hbar^{2}\mu}{2m}\frac{2}{\zeta}\frac{\partial}{\partial\zeta},$$

and $H_{\circ}^{\circ}, H_{\circ}^{(1)}, \cdots$ are the operators defined earlier in this paper. Following the procedure that has already been established, the perturbation equations are

(113)
(a) $$(H^{\circ} - E^{\circ})\Psi_{r}^{\circ} = 0,$$
(b) $$(H^{\circ} - E^{\circ})\Psi_{r}^{(1)} = (E^{(1)} - H^{(1)})\Psi_{r}^{\circ},$$
(c) $$(H^{\circ} - E^{\circ})\Psi_{r}^{(2)} = (E^{(2)} - H^{(2)})\Psi_{r}^{\circ} + (E^{(1)} - H^{(1)})\Psi_{r}^{(1)}, \cdots.$$

(113a) has the solution

(114) $$E^{\circ} = V_{n}(\xi), \quad \Psi_{r}^{\circ} = \Psi_{rn}^{\circ} = \sigma_{rn}^{\circ}(\zeta)\,\varphi_{n}^{\circ}(x, \xi),$$

where $V_{n}(\xi), \varphi_{n}^{\circ}(x,\xi)$ have been defined previously and $\sigma_{rn}^{\circ}$ is arbitrary. The condition of integrability (making use of orthogonality relations) for (113b) is

$$(E^{(1)} - H_{nn}^{(1)})\,\sigma_{rn}^{\circ}(\zeta) = 0.$$

Now according to (28a), section 2,

(115) $$H_{nn}^{(1)} = (H_{\circ}^{(1)})_{nn} + \zeta R' = V_{n}^{(1)} + \zeta R' = \zeta \frac{d}{d\xi}(V_{n} + R);$$

therefore it follows, as in section 4, that

(116) $$E^{(1)} = 0, \quad \frac{d}{d\xi}(V_{n} + R) = 0.$$

This means that for the undisturbed rotation, the centrifugal force must be equal in magnitude but opposite in direction to the restoring force which is due to electronic motion. The centrifugal force is given by

(117) $$-\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\frac{L_r^2}{\xi^2} = -\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\hbar^2\,\frac{r(r+1)}{\xi^2}\,,$$

where $L_r = \sqrt{r(r+1)}\,\hbar$ is the angular momentum of the system. From (119) the equilibrium displacement $\xi_r$ may be computed in terms of the rotation quantum number $r$. For small values of the rotational energy, $\xi_r$ may be expanded in powers of $\beta$, where

(118) $$\beta = K^4\frac{\mu}{m}\hbar^2 r(r+1) = \left(\frac{1}{M_1}+\frac{1}{M_2}\right)\hbar^2 r(r+1)\,,$$

to provide

(119) $$\xi_r = \xi + \frac{1}{\xi^3 V_n''}\beta - \frac{3}{\xi^7 V_n''^2}\left(1+\xi/6\,\frac{V_n'''}{V_n''}\right)\beta^2+\cdots\,.$$

Since $\beta$ is on the order of $K^4$, only as many terms of this series may be used as will correspond to the degree of the approximation in the perturbation treatment.

Proceeding by the method used to solve (113b), we have

(120) $$\Psi_{rn}^{(1)} = \sigma_{rn}^{0}\,\varphi_n^{(1)} + \sigma_{rn}^{(1)}\,\varphi_n^{0}\,,$$

and the condition of integrability of (112c) is

(121) $$[\,H_{nn}^{(2)} + (H^{(1)})_{nn}^{(1)} - E_n^{(2)}\,]\,\sigma_{rn}^{0} = 0.$$

Now the vibration equation becomes

(122) $$\left[-\frac{\hbar^2\mu}{2m}\frac{\partial^2}{\partial\zeta^2} + \tfrac{1}{2}\,\zeta^2(V_n''+R'') - E_n^{(2)}\right]\sigma_{rn}^{0} = 0.$$

Using the method of section 7, we obtain

(123) $$K^2 E_{rns}^{(2)} = (s+\tfrac{1}{2})\,h\nu_r\,,$$

where the frequency $\nu_r$ is given by

$$\nu_r = \frac{1}{4\pi}\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\left(V_n'' + R''\right)} \tag{124}$$

and is still dependent on the rotation quantum number $r$ that appears in $R$. Further as in section 7,

$$\sigma^{\circ}_{rns} = e^{-\frac{1}{2}\eta^2} H_s(\eta) , \tag{125}$$

where

$$\eta = \zeta\sqrt[4]{b} \quad , \quad b = \frac{m}{\hbar^2 \mu}\left(V_n'' + R''\right) \quad , \text{and } H_s(\eta)$$

is the $s^{th}$ Hermite polynomial.

If this treatment is continued in the manner previously established it will be found that $E^{(3)} = 0$, and $E^{(4)}$ is of the character predicted by the general treatment.

## 9. Errata.

We conclude this chapter with a list of errata that we have found in the Born-Oppenheimer paper. Corrections have been made in this thesis.

In (54) [(51) of the original paper] a superscript in the first part of the last term was corrected.

Equation (59b) [54b of the original paper] $H_0^{(2)}$ should appear with a positive sign.

On page 16, after equation (59), it was stated in the original paper that $F_{nn'}^{(3,3)}$ is of <u>third</u> degree in $\zeta_i, \frac{\partial}{\partial \zeta_i}$. A correct statement is that $F_{nn'}^{(3,3)}$ is of <u>odd</u> degree in . $\zeta_i, \frac{\partial}{\partial \zeta_i}$ In (71) [(63) of the original paper] several errors in both superscripts and signs were corrected.

In (90) [(86) of the original paper] a negative sign was omitted in front of $W_n^{(2)}$.

# CHAPTER 2

# MAGNETIC INTERACTIONS BETWEEN MOLECULAR ROTATION AND ELECTRONIC MOTION

As we have discussed, the Born-Oppenheimer approximation assumes no direct interaction between electronic and nuclear motion. However, when the electronic state is not one of zero angular momentum, then -- aside from generally small electrostatic and gyroscopic interactions of higher than fourth order of approximation -- it is necessary to consider magnetic interactions between the rotating nuclei, orbiting electrons, and electron spins. This will result in vector coupling of various types depending on the relative strength of the predominating interaction. The effect is most pronounced in diatomic molecules. For these, F. Hund in a series of papers from 1926 to 1928 distinguished four ideal cases of coupling. It has been found that molecules usually exhibit predominantly one of these cases. Generally, no actual case corresponds completely to one of the ideal coupling schemes. It is, however, found that most actual cases approximate one of the ideal cases fairly closely. In some molecules one form of coupling may go over into another if the vibration or rotation energy of the molecule is changed.

We describe now the four coupling cases as given by Hund.

Case (a): Here the spin-orbit angular momentum with quantized projection $\Omega\hbar$ along the molecular axis couples with the rotational angular momentum $O\hbar$ of the nuclei to form the total angular momentum $J^*\hbar$ as shown in Fig. 2.

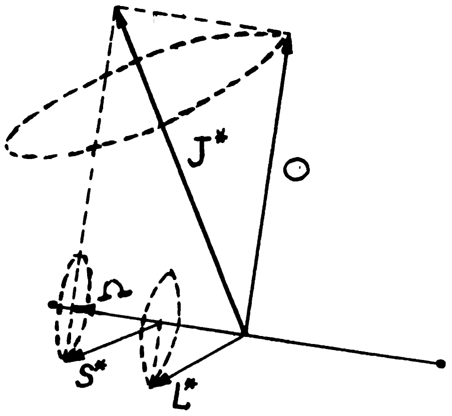

Fig. 2

We have that $S^*\hbar$ is the resultant spin angular momentum of all electrons with quantized projection $\Sigma\hbar$ along the molecular axis, $L^*\hbar$ is the resultant orbital angular momentum of all electrons with quantized projection $\lambda\hbar$ along the molecular axis, and

$$\Omega = \lambda + \Sigma$$

$$L^* = \sqrt{L(L+1)}$$

$$S^* = \sqrt{S(S+1)}$$

$$J^* = \sqrt{J(J+1)}$$

Actually, Oñ is not simply the rotational angular momentum of the nuclei, but it is a sum of this and rapidly fluctuating components of the spin and orbital angular momenta perpendicular to the molecular axis due to their precession about this line. If $\lambda \neq O$ , the electronic states exhibit a two-fold degeneracy which is removed by the rotational-electronic interactions giving rise to a splitting of levels that is called $\lambda$-doubling. (Before 1930, this was called $\sigma$-doubling). The splitting is due to a small difference in the energy depending on the sense of the over-all rotation relative to the electronic motion.

Case (b): If $\lambda = O$ , or if L* is small, then S* cannot be considered as tightly coupled to the molecular axis; then $\lambda$ and O form a resultant N* to which S* couples, forming the total angular momentum vector J*. In this scheme the spin is thus uncoupled from the molecular axis, as shown in Fig. 3. When L* is small but $\lambda \neq O$ , an electronic degeneracy is again removed by the rotational-electronic interactions giving rise to $\lambda$-doubling similar to case (a).

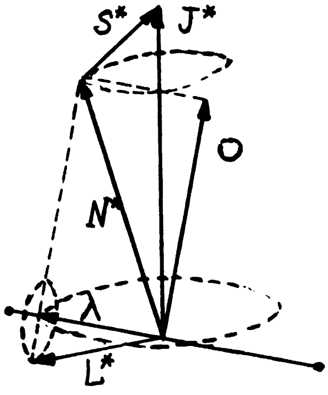

Fig. 3

Case (c): If the axial field is not strong enough to break down the spin-orbit coupling of the individual atoms that form the molecule, then the total angular momenta $J_i^*\hbar$ of the individual atoms will precess about the molecular axis with quantized projections along the molecular axis that add to form $\Omega\hbar = \sum_i J_i^*$ (axial component)$\hbar$ which then is added to the rotational angular momentum $O\hbar$ forming the resultant total angular momentum $J^*\hbar$ of the molecule. Case (c) is illustrated in Fig. 4.

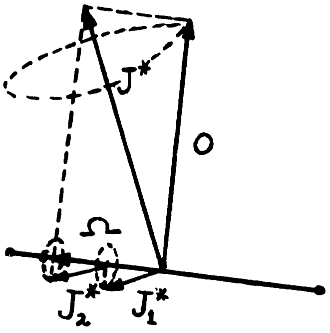

Fig. 4

Case (d): If one electron in a molecule moves in an orbit that is large compared with separation of the nuclei then this electron, which carries most of the orbital angular momentum, will be influenced by axial field polarization, so $L^*$ will not have a quantized projection along the molecular axis but will add to the angular momentum of rotation (with quantized magnitude $R^*$) to form $N^*$ which then adds to

$S^*$ to form the total angular momentum $J^*\hbar$ of the molecule, as in Fig. 5.

Rotational-electronic interactions cause each rotational level to be split into (2L + 1) components. As in case (b) the spin is uncoupled from the molecular axis.

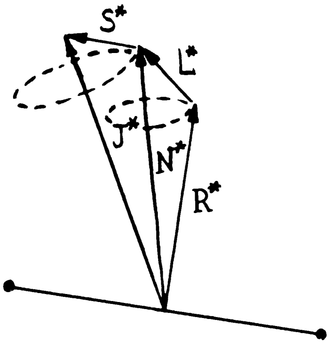

Fig. 5

The development of these ideas is given in a series of papers published by Hund[3,4,5,6,7] in 1926, 1927, and 1928. Experimental work since that time has demonstrated that cases (a) and (b) are the ones which principally occur along with a coupling scheme intermediate between (a) and (b).

Further work was done by Hill and Van Vleck[8] (1928) who developed a theory of $\lambda$-type doubling. They considered the spin-rotation interaction and showed that case (b) can be converted to case (a) with an adiabatic increase in coupling energy. The coupling energy was found to be proportional to the cosine of the angle between S and the molecular axis. The treatment forms the basis of all further work on spin-uncoupling phenomena in coupling intermediate between Hund's cases (a) and (b).

An experiment by Weizel[9] (1928) in which he discovered nine bands in the $He_2$ spectrum consistent with the angular momentum becoming uncoupled from the rotation helped verify Hund's ideas.

The theory of the distortion of spin multiplets produced when the molecule rotates along with $\lambda$-type doubling was developed by Van Vleck[10] (1929). He predicted that singlet $\pi$ states would exhibit $\lambda$-type doubling proportional to $j(j + 1)$ where j is the rotational quantum number, $\lambda$ doubling, he found, is modified by the spin in $^2\pi$ states, while $\rho$ doubling in $^2s$ states is due to rotational coupling with the fluctuating components of spin and orbital angular momentum perpendicular to the molecular axis.

Rotational uncoupling of the orbital angular momentum from the molecular axis was discussed by Watson[11] (1929). He concluded that the rotational energy is limited by rotational instability due to the uncoupling.

Kronig and Fujioka[12] (1930) outline a method by which constants that measure the decoupling may be determined from the spectrum, and the manner in which they affect intensities. Using this method Fujioka[13] developed several intensity expressions.

Mulliken and Christy[14] (1931) reformulated Van Vleck's equation for $\lambda$-type and spin doubling in $^1\pi$, $^2\Sigma$, and $^2\pi$ states; the results were applied to several molecules (including intermediate coupling cases). They found that agreement was particularly good for CaH. They revised some doubtful J values and identified a new branch in the spectrum.

Rotational uncoupling was discussed by Davidson[15] (1932) who found band values and intensities that agree fairly well with theory for bands in the hydrogen molecular spectrum.

From the work of Van Vleck and that of Kronig the conditions for the occurrence of perturbations were investigated in detail by Dieke[16] (1935). He found that when the electronic motion can be described approximately by the precession of a constant angular momentum about the molecular axis, the elements of the perturbation matrix can be calculated completely.

Van Vleck[17] (1936) demonstrated that the coefficient of $J(J + 1)$ and $(v + 1/2)$ in the energy terms of hydrogen or deuterium must contain small corrections due to L uncoupling. The magnitudes were estimated.

The explicit form of the interaction between rotation and spin was given by Kovacs[18] (1961) for cases intermediate between (a) and (b) in the $^2\Pi$ , $^2\Delta$ , $^3\Pi$, $^3\Delta$ , and $^4\Pi$ states. Previously the explicit form of the interaction between rotation and spin was known only for Hund's case (b).

Most of the major theoretical work on Hund's cases was completed in 1936. An outline, again in historical order, of other work done in this area will now be given.

Mulliken[19] (1927) derived equations for the intensity in case (b) doublet states in diatomic molecules.

Hund[20] (1928) showed that rotational uncoupling has only limited application when the molecule is in strong electric or magnetic fields.

Mulliken[21] (1929) published a table summarizing the experimental work that had been done on $\lambda$-type doubling up to that time.

Dieke[22] (1929) discussed the influence of a progression between cases (a) and (b) on the band spectrum of helium.

Mulliken[23] (1930) gave rules for the determination of $\Omega$ values and symmetry properties for case (c) coupling.

Mulliken[24] (1930) published a table of spectroscopic notation proposing some revisions. One change was the decision to give the name $\lambda$-type doubling to the effect that had previously been called $\sigma$-type doubling.

Van Vleck[25] (1951) reviewed the theory of rotational uncoupling in modern formulation relying heavily on angular momentum commutation relations. He then applied this to:

(a) Polyatomic molecules with no internal angular momentum.

(b) Electron spin coupling in diatomic molecules not in $\Sigma$ states.

(c) $\lambda$-type and $\rho$-type doubling.

(d) Coupling of electron spins in polyatomic molecules.

(e) Coupling of nuclear spins in molecules with $S = 0$.

(f) Intensities and behavior in external fields.

Mann and Hause[26] (1960) studied rotational uncoupling by measuring the magnitude of the infrared Faraday rotation (rotation of the plane of polarization of incident plane polarized light) in the NO molecule in $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states.

Hougen[27] (1963) obtained expressions for the rotational energy levels in vibronic states using spin uncoupling concepts.

Chiu[28] (1964) studied predissociation of diatomic molecules in case (b) coupling.

Flygare[29] (1964) derived equations relating spin-rotation constants and magnetic shielding.

Raynes[30] (1964) presented matrix elements for the Hamiltonian of a nonlinear polyatomic molecule in a multiplet electronic state which include magnetic interactions between unpaired electrons when the multiplicity is non-zero.

# CHAPTER 3

# THE JAHN-TELLER EFFECT

Degenerate electronic wave functions are possible only if all the atoms of a molecule lie on a straight line, according to a theorem proved by H. A. Jahn and E. Teller[31] in 1937. In all other cases involving degeneracy of the electronic energy, a more stable configuration will be one in which the nuclear framework is distorted by the electron cloud. This has the effect of removing the orbital electronic degeneracy by the perturbing influence of the distortion. The degenerate states will be split in energy by an amount approximately determined by first order perturbation theory as:

$$E_n' - E_n = \int \Psi^* H \Psi d\tau$$

where H is the perturbation potential, and $E_n' - E_n$ is the amount by which the electronic energy is shifted if it is in state $\Psi_n$ in the absence of the perturbation. The perturbation takes the form of a distortion vibration which is usually called a Jahn-Teller vibration. Since degeneracy in the electronic wave function was ignored in the original work by Born and Oppenheimer, the Jahn-Teller effect lies thus beyond the scope of the Born-Oppenheimer approximation.

A distinction must be made between the so called "static Jahn-Teller effect," and the "dynamical Jahn-Teller effect." The former refers to distortion of the nuclear framework by a given electronic configuration, i.e. the equilibrium configuration of the nuclei is permanently changed by the electronic distortion. The latter, which is the situation that obtains when the electron-nuclear coupling is weak deals with the distortion of the nuclear motion by the electronic motion without the nuclei taking up a new equilibrium position.

The Jahn-Teller theorem holds rigorously only if the wavefunctions considered are for all electrons involved in molecular binding. It can further be shown that spin degeneracy is also necessarily removed by the distortion of the nuclear framework if a stable molecule is to result.

The Jahn-Teller theorem was introduced in 1937. However, further contributions to the basic theory included in the general discussion above were made by H. A. Jahn[32] (1938) and by Sponer and Teller[54] (1941). Further contributions in the area follow below.

Van Vleck[33] (1939) in developing the theory for the structure of a molecular cluster of the form $X \cdot 6H_2O$ ($X = Ti, V, Cr$) found that stability is achieved only if the $H_2O$ groups are distorted from a cubical arrangement in the manner required by the Jahn-Teller theorem.

The ideas of Jahn and Teller were enlarged upon by Öpik and Pryce[34] (1957) in a survey article in which they discuss the linear molecule as well as octahedral complexes.

Moffitt and Liehr[35] (1957) discussed the implications of the Jahn-Teller theorem for the case that the distortion forces tending to lower the electronic symmetry are of the same order of magnitude as the vibrational restoring forces. They show that this leads to direct coupling between electronic motion and nuclear modes of vibration in the dynamical Jahn-Teller effect. Extensive calculations were performed. These are of importance for the general understanding of vibrational effects in the ultraviolet spectra of molecules.

It was found by Thorson[45] (1958) that some forbidden transitions become allowed when the electronic degeneracy is removed by the Jahn-Teller effect.

Longuet-Higgins, Öpik, Pryce, and Sack[37] (1958) provided a survey of the dynamical Jahn-Teller effect and also found that several "forbidden" electronic transitions become allowed transitions when the nuclear framework is distorted to remove electronic degeneracy.

Clinton and Rice[36] (1958) reformulated the Jahn-Teller theorem with the aid of the Hellmann-Feynman theorem (which states that many properties of molecules may be explained by considering the electron cloud as a classical charge distribution rather than relating it to the customary quantum mechanical interpretation). In this way they were able to formulate the problem in terms of forces rather than in terms of the usual energy approach.

Child[49] (1960) found by group theoretical arguments that under certain conditions there is no Jahn-Teller coupling between vibrations of the same symmetry type.

Clinton[38] (1960) outlined a dynamical treatment of the Jahn-Teller effect in which effects in the moving nuclear framework are treated as perturbations on the orientation of the charge density in inertial space. The Hellmann-Feynmann theorem was used.

It was shown by Hobey and McLachlan[50] (1960) that the Born-Oppenheimer calculation can be adapted directly to a degenerate electronic state. They used a dynamical Jahn-Teller treatment to set up the equations of motion and discussed symmetry-forbidden transitions that become allowed through Jahn-Teller distortion.

Clinton and Hamilton[51] (1960) used the results of Clinton and Rice[36] to calculate force curves for $O_2^+$ and NO.

A dynamical Jahn-Teller treatment was used by Liehr[52] (1960) to calculate vibronic intensities in electronically forbidden bands.

Zalewski[39] (1961) presented the results of a study of the static Jahn-Teller effect in the $C_6H_6^+$ ion. Bond lengths were computed.

Child and Longuet-Higgins[40] (1961) developed the theory needed to interpret infrared, Raman, and microwave spectra of molecules in electronic states with orbital degeneracy. Conclusions were drawn about a molecular dipole moment that would be symmetry-forbidden in a non-degenerate electronic state, and Jahn-Teller active vibrations that give rise to overtones.

Child[41] (1962) investigated the general case of a four-fold degenerate octahedral molecule for strong vibronic coupling with a Jahn-Teller vibration and made predictions about the spectra that should result.

The Jahn-Teller effect in the particular case of aromatic ions was studied by Coulson and Golebiewski[42] (1962). They found a potential function more general than that of Moffitt and Liehr[35]. It is in good agreement with theoretical electronic structure calculations for benzene and triphenylene.

Coulson and Strauss[43] (1962) computed potential energy curves for an arbitrary displacement of the atoms in $CH_4^+$, $CF_4^+$, and the excited states of $NH_3^+$ and $NH_3$ by using the Hellmann-Feynman theorem. They were able to make predictions of the magnitude of the displacement of a nucleus in the static Jahn-Teller effect.

Child[44] (1963) developed formulas for vibronic energy levels of electronically degenerate molecules that exhibit a weak Jahn-Teller effect.

The static Jahn-Teller effect in octahedral and tetrahedral molecules was examined by Birman[53] (1963). Several modes of instability were found, and suggestions were made for further work.

Forgman and Orgel[46] (1959) measured the infrared spectra of the tris-acetylacetonates of chromium, manganese, iron and aluminum to 400 $cm^{-1}$. The nature of the bands which they attributed to the vibrational motion of the oxygen atoms relative to the metal was, they concluded, consistent with the operation of the Jahn-Teller mechanism in the manganic compound.

Claasen and Weinstock[47] (1960) failed to detect a Jahn-Teller effect in $IrF_6$ similar to that found in $OsF_6$.

Snyder[48] (1960) attributed poor resolution in the E.S.R.

spectra of aromatic negative ions to the Jahn-Teller effect.

Experimental work done on the Jahn-Teller effect that comes under the general heading of solid state physics is not covered here although much has been done in that area.

Further references to the Jahn-Teller effect will be found in another section dealing with general vibronic interactions.

# CHAPTER 4

# THE RENNER EFFECT

The structure of the $\pi$-term in linear, triatomic molecules was investigated in 1934 by Renner[55]. The two-fold degeneracy in the $\pi$-term could be removed, he found, by a perturbation produced when the molecule was "bent." This bending is produced by two-fold degenerate vibrations, the "bending modes."

A two-fold degenerate electronic wave function of the form $\Psi = \frac{1}{\sqrt{2\pi}} e^{\pm i\lambda\phi}$ describes the $\pi$ state in a linear triatomic molecule when all of the nuclei lie on a straight line. (Where $\phi$ is the azimuthal coordinate) and $\lambda$ is the component of the total electronic angular momentum along the molecular axis. (The angle $\phi$ is measured around the figure axis.) Under the perturbing influence of a distortion vibration, the degeneracy is split such that even (gerade) and odd (ungerade) non-degenerate wave functions result. These may be written:

$$\Psi_g = \frac{1}{2\sqrt{\pi}} \left( e^{i\lambda\phi} + e^{-i\lambda\phi} \right)$$

$$\Psi_u = \frac{1}{2\sqrt{\pi}} \left( e^{i\lambda\phi} - e^{-i\lambda\phi} \right)$$

Renner was able to compute the difference in energy in the $\Psi_g$ and $\Psi_u$ vibronic states.

There was no further work on this effect until Dressler and Ramsay[56] (1957) suggested that the transition between two states with large vibronic splitting in the electronic absorption spectrum of $NH_2$ should be written $^2A_1\ \pi_u$ --$^2B_1$ according to Mulliken's definition of $B_1$. They expected spectra of the same type for HCO, $CH_2^+$, $BH_2$, and $H_2O^+$.

The ideas of Dressler and Ramsay lead to predicted frequencies that are in agreement with experimental observation, according to Pople and Longuet-Higgins[57] (1958). Pople[58] (1960) extended the theory of vibronic interaction in linear triatomic molecules in $\pi$ electronic states to account for coupling between an odd electron spin and orbital angular momentum. He obtained expressions for splittings and shifts in energy.

Hougen[59] (1962) considered the effect of Fermi resonance on the vibronic energy levels of linear triatomic molecules in $\pi$ electronic states when the Renner, and spin-orbit interactions are small compared to the distortion vibration frequency. The results agree with experimental data on the $A^2\pi$ vibronic states of $BO_2$.

Hougen and Jesson[60] (1963) give expressions for anharmonic corrections to the energy of vibration of linear triatomic molecules in $\pi$ electronic states with very small Renner effect and spin-orbit interaction.

# CHAPTER 5

## THE GENERAL INTERACTION BETWEEN ELECTRONIC MOTION AND NUCLEAR VIBRATIONS

In the Born-Oppenheimer approximation, interactions between nuclear and electronic motion are completely neglected. The wave function $\psi$ is assumed separable: $\psi = \psi_e \psi_n$, where $\psi$ is the complete wave function, $\psi_e$ is the purely electronic wave function, and $\psi_n$ is the wave function corresponding to nuclear motion. Actually the wave function $\psi$ contains an interaction term neglected by the Born-Oppenheimer approximation, i.e., $\psi = (\psi_e \psi_n + \psi_{en})$. This function is termed the "vibronic wave function" if $\psi_n \equiv \psi_v$ (vibrational wave function) and $\psi_{en} \equiv \psi_{ev}$ (an interaction term that cannot be factored). The function $\psi$ is termed the "rovibronic wave function" if $\psi_n \equiv \psi_v \psi_r$ and $\psi_{en} \equiv \psi_{evr}$, where $\psi_r$ is the rotational wave function and $\psi_{evr}$ is an interaction term involving vibration, rotation, and electronic terms that cannot be factored.

The Jahn-Teller and Renner effects are seen to be special cases of this more general treatment of interaction terms ignored in the Born-Oppenheimer approximation. At times it is difficult to distinguish cases which should be classified Jahn-Teller effect or Renner effect from the more general vibration-electronic interactions.

The first significant paper published in this area - which remains a very active one to this day - was by Condon[61] (1927) in which he proposed that energy eigenvalues should be the sum of a function depending on electronic quantum numbers and a function depending on vibrational quantum numbers, i.e., $\psi = \psi_{ne}$, where $\psi_{ne}$ is a function of electronic quantum numbers, electronic coordinates, and nuclear coordinates. Little appears in the literature following Condon's contribution until 1956. (Work on the Jahn-Teller effect and Renner effect is not considered here.)

Wu and Bhatia[62] (1956) found it necessary to include the coupling between electronic and nuclear motion when considering Vander Waal's interactions, since these are of the same order of magnitude.

A survey of non-empirical and semiempirical calculations of vibronic interaction was provided by Liehr[63] (1957).

Liehr[64] (1957) showed that the complete molecular wave equation must be modified, if approximate electronic wave functions are used, in order for the Born-Oppenheimer approximation to be applied properly. He provided a reformulation of the Born-Oppenheimer calculation that incorporates the needed modifications.

The interaction between nuclear and electronic motion in degenerate electronic states of octahedral molecules was investigated by Moffitt and Thorson[65] (1957).

Liehr[66,67,68] (1958) performed calculations for several rovibronic intensities. He found, however, poor agreement with experiment at 50,000 $cm^{-1}$. and 39,500 $cm^{-1}$. This paper was followed by another in which he evaluates a number of integrals that appeared in the first. A third paper was published to provide some numerical corrections to the intensities of vibronic transitions previously calculated.

Dressler and Ramsay[69] (1959) measured the electronic absorption spectra of $NH_2$ and $ND_2$ and were able to verify vibronic structure in an excited vibronic state.

Liehr[70] (1960) discussed the variation of electronic energy as the nuclei of the $C_6H_6^+$ molecule are displaced. Vibronic constants for the determination of energies were computed, and also vibronically allowed intensities were calculated. Only fair agreement with experiment was obtained.

Large vibronic interactions in complex molecules should not be expected, but radiationless transitions are highly probable according to El'Yoshevich[71] (1960).

Fulton and Gouterman[72] (1961) presented a general mathematical treatment of the vibronic coupling of two electronic states. They show that spectral distribution in bands differ considerably from the expected if vibronic coupling is present.

Liehr[73] (1961) derived formulae for non-degenerate electron distributions by using the Born-Oppenheimer approximation and first order perturbation theory. He was able to compute vibronic absorption intensities of benzene, the cyclopentadienide ion, and the tropylium ion. Configurational instability is found for these in agreement with the Jahn-Teller theorem. A mathematical and pictorial description of the nuclear dynamics of molecules exhibiting the Jahn-Teller effect is given. Suggestions for future work were made.

An essay concerned with the classification of vibronic interactions in molecular systems was written by Liehr[74] (1962). He used the pictorial model provided by Jahn and Teller[31] and by Sponer and Teller[54].

Second order perturbation theory was used by Bader[75] (1962) to determine the change in electronic charge density due to nuclear vibration. He found a particular type of electronic distortion is energetically favored over other possible distortions.

Merrifield[76] (1963) showed that the vibronic Schroedinger equation may be solved numerically if it is assumed that electronic excitation influences the nuclei only in changing their equilibrium distance but not their frequency of vibration.

Kolos and Wolniewicz[77] were able to compute energies and expectation values for the vibronic ground states and the first vibrational excited states of $H_2$, $D_2$, and $T_2$ using the complete non-relativistic Hamiltonian and 147-term variational wave functions.

Hougen[78] (1964) found that in vibronic interactions in molecules with a fourfold symmetry axis the Jahn-Teller active vibrations are non-degenerate, whereas degenerate vibrations are not Jahn-Teller active. The Renner effect does affect the position of the energy levels, however. In limiting cases of the Jahn-Teller effect and the Renner effect it is possible to write vibronic wave functions as a product of vibrational and electronic wave functions even though there are degenerate electronic states and vibrations capable of removing the degeneracy.

General vibronic equations for the coupling of two electronic states in terms of previously given adiabatic potentials[72], in which the coupling terms depend only on the coordinates, were developed by Gouterman[79] (1965). This is the last major theoretical contribution as of this writing. Other work pertinent to the theory of vibronic coupling will now be presented.

Herzberg and Teller[80] (1933) discussed the selection rules for the vibration quantum numbers during an electronic transition.

Using the fact that with group theoretical calculations it can be shown that all degenerate electronic states in non-linear polyatomic molecules are unstable[31], Narumi and Takano[81] (1950) computed the vibronic interaction energy, with the assumption that it is on the order of the potential energy of the vibration.

McDowell[82] (1954) discussed the formation of different vibronic states in methane under impact of electrons with known energy.

Sidman and McClure[83] (1956) studied the absorption and emission spectra of azulene in which, they decided, one of the transitions is perturbed by a vibrational-electronic interaction.

A theoretical discussion of the weak bands of formaldehyde was presented by Pople and Sidman[84] (1957). They showed that the intensity of the perpendicular bands can be accounted for by vibrationally-induced mixing of excited electronic states.

Witowski and Moffitt[85] (1960) derived the Hamiltonian that represents the vibronic states of a dimer formed by two identical molecules.

Albrecht[86] (1960) suggested that the major part of the electric-dipole allowedness in the phosphoresence of benzene is due to vibronic mixing of $^3B_{1u}$ and $^3E_{1u}$ states.

A formula was derived for line shape contours of a band due to an electronic-vibrational transition by Rebane[87] (1960).

DeVoe[88] (1962) used first order perturbation theory to explain the electronic absorption spectrum of chromophores by considering the interaction between vibronic lines of the same electronic band or others.

In a conference on luminescence the Fourier representation of vibronic bands was discussed by Stepanov[89] (1962).

Albrecht[90] (1963) used second order perturbation theory to bring dipole allowed character into a spin-forbidden transition. He considered spin-vibronic coupling in this treatment.

Hougen[91] (1963) discussed nearly degenerate vibronic states. He points out a loose analogy to the problem of spin uncoupling in the $^2\pi$ state of a diatomic molecule in his treatment.

Read[92] (1964) discussed the effect of vibronic interactions on the differential cross sections for excitation of a molecular state by electron collision.

# CHAPTER 6

## CRITIQUES AND REFINEMENTS OF THE APPROXIMATION

Presented in this final chapter is significant work of fairly recent origin pertaining to (a) critical evaluation of the Born-Oppenheimer approximation, (b) consideration of correction terms neglected in the Born-Oppenheimer approximation, and (c) methods of solution that attempt to not introduce the Born-Oppenheimer approximation at all.

In 1951 Born[93] devised a method which permits the direct inclusion of terms representing interactions between nuclear and electronic motion. It was assumed that $\psi$ total $(\chi,X) = \sum_n \psi_n(X) \cdot \Phi_n(\chi,X)$. Here $\psi$ total is a function of both nuclear and electronic coordinates, X and $\chi$, $\psi_n(X)$ depends on nuclear coordinates (X), and $\Phi_n(\chi,X)$ depends on electronic coordinates ($\chi$) with the nuclear coordinates (X) entering as parameters. This treatment, however, still makes use of the adiabatic approximation in that the nuclei are considered clamped for the computation of $\Phi_n(\chi,X)$, the electronic wave function.

Aroeste[94] (1953) found that expanding the molecular wave function by the Born-Oppenheimer method in terms of the parameter $\kappa = (m/M)^{1/4}$ provides perturbation matrix elements of the first order in $\kappa$. Some of these contain non-adiabatic terms which may, in principle, be calculated.

The coupling between electronic and nuclear motions of two helium atoms has been considered by Wu[95] (1956). He concluded that this interaction is not negligible when compared to the Vander Waal's interaction.

Dalgarno and McCarroll[96] investigated the coupling between electronic and nuclear motion in diatomic molecules, particularly for cases of large nuclear separation. They found that the nuclear-electronic coupling energy is on the order of $\frac{m}{M}$ times the electronic kinetic energy if the molecule were imagined separated adiabatically to two atoms in S states. Hence, for this situation the nuclear-electronic coupling may be ignored. If one or both of the separated atoms are in non-zero orbital angular momentum states, then the coupling cannot be ignored since it will not be negligible compared to the Vander Waal's interaction. Quantitative results are given for the $1S\sigma_g^+$ and $2P\sigma_u$ configurations of $H_2^+$ and the ${}^1\Sigma_g^+$ state of $H_2$. An estimate of the error involved in the use of the Born-Oppenheimer approximation is also given. This work was continued and enlarged upon in a later paper[97].

A variational method was formulated by Kolos and Roothaan[98] (1960) for calculating the exact electronic wave function by explicitly accounting for the interelectronic distance in the hydrogen molecule. Excellent agreement with experiment was attained for energy calculation. A comparison with various approximate methods of solution was made in order to obtain a better evaluation of those methods that must be used for more than two-electron systems.

Jepson and Hirschfelder[99] (1960) present a review of the work that has been done on calculation of the coupling terms neglected in the Born-Oppenheimer approximation. They suggest that more accurate wave functions are attainable if center-of-mass coordinates are used rather than the usual coordinate system fixed in space.

The portion of the binding energy of the hydrogen molecule that may be attributed to interaction between nuclear and electronic motion was calculated by Kolos and Wolniewicz[100] (1961). The correction to the computed binding energy which ignores this interaction cannot be checked directly, however, as it is smaller than the experimental error of the best available value.

Froman[101] (1962) devised a method for the calculation of "reduced electronic energy" which is found by assuming finite nuclear mass for molecules similar to the manner in which it is done for atoms. He uses the Born-Oppenheimer approximation in this calculation and claims to have attained results in slightly better agreement with experiment than heretofore available for $H_2$, HD, and $D_2$. The effect, as expected, is largest for $H_2$.

Kolos and Wolniewicz[102] (1963) discuss the shortcomings and limitations of the Born-Oppenheimer approximation. They assert that greatly improved results will not follow from attempts to improve the approximation. Complete accuracy will come only from exact solution of the complete wave equation for all the particles involved. A variational procedure is formulated which does not at any point introduce separation of nuclear and electronic motion. The wave equation used is the Schroedinger equation.

This equation is, however, not completely satisfactory to the accuracy desired, because such matters as spin effects and relativistic corrections are not included. An extended discussion of these effects and their expected contributions to the energy is given. Application of the procedure to the hydrogen molecule is outlined and gives satisfactory results.

The computational work on the hydrogen molecule is extended and further refined by Kolos and Bolnevich[103] (1963).

The Franck-Condon principle was re-formulated by Tavger[104] (1963) so that it would be more consistent with the quantum mechanics of electronic transitions in polyatomic molecules.

Further calculations on the hydrogen molecule were performed by Kolos and Wolniewicz[105] (1964) by using the methods given in a previous work[102].

The interaction between electronic and nuclear motion was analyzed by Micha[106] (1964) with the aid of time-dependent quantum mechanics in a study of molecular systems. A comparison was made with the results of the Born-Oppenheimer approximation.

Fisk and Kirtman[107] (1964) investigated sources of error involved in the Born-Oppenheimer treatment. An effective potential function for nuclear motion was found in terms of vibrational momentum and the internuclear distance. A method was presented for computing the energy shifts due to nuclear-electronic coupling which was then applied to $H_2$ by obtaining a numerical solution of the Schroedinger wave equation for the effective potential. An energy shift of about 0.2 $cm^{-1}$ was computed due to the interaction.

It is now possible to solve the Schroedinger wave equation to experimental accuracy for the hydrogen molecule, but for more complex molecules for which exact solution is virtually impossible at the present time (even with numerical techniques), the Born-Oppenheimer approximation continues to be of value.

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