A STUDY OF THE RENNER EFFECT
IN THE LINEAR XY₂ MOLECULE

by

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A variational principle is applied to the Schrödinger equation for the $XY_2$ linear molecule. Trial solutions are synthesized from the nuclear eigenstates, which are assumed to be simple harmonic oscillator eigenstates, and from the unperturbed electronic states, whose azimuthal dependence is known because of the cylindrical symmetry of the field of the nuclei. The secular equation is discussed, and an expression for the Renner splitting of the $\pi^+$ state is obtained.
I would like to thank Dr. F.W. Dalby who originally suggested the problem, and whose many comments were always valuable and greatly appreciated. I would also like to thank Dr. L. de Sobrino who made this thesis possible through his constant guidance.

I am also grateful to the National Research Council of Canada for the financial assistance given to me in the form of a Bursary.
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INTRODUCTION

In linear molecules, to the zeroth approximation, the electrons move in the cylindrically symmetric field provided by the fixed nuclei. Hence the projection of the orbital angular momentum along the nuclear axis is conserved, and the electronic states are classified by the absolute value of this projection, usually denoted by $\Lambda \overline{m}$. For

$$\Lambda = 0, 1, 2, \ldots$$

the states are called

$$\Sigma, \Pi, \Delta, \ldots$$

respectively; states higher than $\Delta$ are not usually encountered. The $\Sigma$ or ground state is not degenerate but the other states are two-fold degenerate; that is, the projection of the total angular momentum along the axis can be $\pm \Lambda \overline{m}$.

When certain vibrations of the nuclei are considered, the so-called degenerate vibrations, the cylindrical symmetry of the field seen by the electrons is broken, and hence the degenerate levels of the electronic spectra of linear molecules are split; this is called the Renner splitting or Renner effect.

The method customarily used to obtain expressions for the Renner splitting has been the Born-Oppenheimer approximation. However, this method leads to a pair of second order coupled equations; for non-degenerate states the coupling terms can be neglected and the equations can be simplified, but this is not the case for degenerate states. Moreover, this method is not very practical because it first approximates the electronic states, and this approximation is then used to obtain the nuclear states. But it can be assumed to a very good approximation that the
nuclei undergo harmonic vibrations only, so that the nuclear states are completely known and so is the angular dependence of the unperturbed electronic states because of the cylindrical symmetry of the nuclear field.

In this thesis, these two facts are used to construct trial solutions which are subsequently used to solve the Schrödinger equation by a variational procedure.

The Renner effect is a result of the coupling between the electronic and vibrational motions of the linear molecule. Spin effects are neglected (see reference 3) as are the rotational and translational motions of the molecule. Thus if is the total number of electrons and the total number of nuclei, the number of co-ordinates needed to describe the problem is \( 3N + (3N' - 6) \) for a non-linear molecule or \( 3N + (3N' - 5) \) for a linear molecule. The \( (3N' - 6) \) or \( (3N' - 5) \) co-ordinates are known as the normal co-ordinates of the nuclear vibrations. The classical expression for the kinetic energy of the nuclei contains purely quadratic terms in the time derivative of these normal co-ordinates, that is, if \( S_\alpha \) is the \( \alpha \) th normal co-ordinate of a molecule, then the kinetic energy is

\[
T = \frac{1}{2} \sum_\alpha \left( \frac{1}{m_\alpha} \right) S_\alpha^2,
\]

where \( m_\alpha \) is a reduced mass associated with \( S_\alpha \) (see Chapter I); similarly, the potential energy contains the sum of quadratic terms in \( S_\alpha \).

If harmonic oscillations are considered.

The set of displacements, or modes of vibration \( S_\alpha \), contains for linear molecules displacements both parallel and perpendicular to the molecular axis. The first do not remove the symmetry of the nuclear field, and hence their effect is merely to shift the energy levels; the second do remove the degeneracy and cause the Renner splitting. The latter are
called degenerate vibrations and through them the nuclei have angular
momentum directed along the molecular axis. Thus it is anticipated that
the projection of the total angular momentum along the axis will still
be conserved. That is, letting $\ell \hat{H}$ be the nuclear angular momentum, with
$\ell = 0, \pm 1, \pm 2, \ldots$ then

$$\kappa = |\Lambda + \ell| = 0, 1, 2, \ldots$$

characterizes states comprising the nuclear vibrations and electronic
motion, that is, the vibronic states. Likewise, vibronic states are called
$\Sigma, \Pi, \Delta, \ldots$

states.

The theory developed is applicable to any linear molecule but the
normal co-ordinates depend on the molecule in consideration. The linear
$XY_2$ molecule has been chosen as the subject of this thesis. A similar
treatment can be given to any other linear molecule if its normal
co-ordinates are used. The number of nuclei does not matter. In diatomic
molecules the cylindrical symmetry cannot be removed because vibrations
perpendicular to the axis are really rotations. For triatomic molecules
there is only one degenerate mode of vibration, while for molecules with
more than 3 atoms there are more than one degenerate mode. For example,
the acetylene molecule $C_2H_2$ has two degenerate modes; however, each mode
can be put in the calculations and the Renner splitting of each can be
studied. In short, each molecule has a characteristic set of normal
vibrations but the method remains the same for all of them.
CHAPTER I

Normal Co-ordinates of the XY₂ Linear Molecule

The XY₂ linear molecule has four nuclear degrees of freedom so that four co-ordinates are needed to describe its nuclear vibrations. These are denoted by \( S_1, S_{2a}, S_{2b}, S_3 \); they are illustrated in Figure 1. \( S_{2a} \) and \( S_{2b} \) describe the degenerate mode and they cause the Renner splitting, whereas \( S_1 \) and \( S_3 \) do not remove the cylindrical symmetry of the nuclear field.

In Figure 1, the \( Z \) axis is chosen as the axis of the molecule; \( M_1 \) is the mass of the Y atom, \( M_2 \) that of the X atom. The atoms are labelled 1, 2, 3 from left to right. The origin of the co-ordinate frame coincides with the center of the X atom, that is, the center of mass of the nuclei which is approximately coincident with that of the whole molecule.

Mode 1:

Since \( M_1 = M_3 \), conservation of linear momentum requires the displacement of one Y atom to the right to be equal to the displacement of the other Y atom to the left. These displacements are denoted by \( \pm S_1 \) respectively.

Mode 2a (2b):

If \( \pm S_{2a} (\pm S_{2b}) \) is the displacement of the X atom in the \( y(x) \) direction, then again by conservation of linear momentum, each Y atom must move

\[
\frac{M_2}{2M_1} S_{2a} (S_{2b}).
\]

Mode 3:

If \( \pm S_3 \) is the displacement of atom X in the Z direction, then each Y atom must move \[ -S_3 \frac{M_2}{2M_1} \] in the Z direction.
Figure 1

The four normal modes of the linear $XY_2$ molecule.
Let
\[ u = \frac{M_2}{2M_1} \]
then the total displacement of the \( \text{XY}_2 \) linear molecule can be summarized as in Chart I.

The nuclear kinetic energy is given by

\[
T_n = \frac{1}{2} \left[ M_1 (\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2) + M_2 (\dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2) + M_3 (\dot{x}_3^2 + \dot{y}_3^2 + \dot{z}_3^2) \right]
\]

\[
= \frac{1}{2} \left\{ \left[ (u S_{3b})^2 + (u S_{2a})^2 + (u S_{3a})^2 \right] M_1
+ M_2 \left[ S_{2b}^2 + S_{2a}^2 + S_{3}^2 \right]
+ M_3 \left[ (u S_{2b})^2 + (u S_{2a})^2 + (S_{1} - \mu S_{3})^2 \right] \right\}
\]

\[
T_n = \frac{1}{2} m_1 S_1^2 + \frac{1}{2} m_2\left( S_{2a}^2 + S_{2b}^2 \right) + \frac{1}{2} m_3 S_3^2 \quad \text{(I-1)}
\]

where

\[ m_1 = 2M_1 \]
\[ m_2 = m_3 = M_2 (1 + \mu) \]

Similarly the potential energy is bilinear in the Cartesian co-ordinates, but by definition of the normal co-ordinates,\(^5\) it becomes

\[
V = \frac{1}{2} \lambda_1 S_1^2 + \frac{1}{2} \lambda_2 \left( S_{2a}^2 + S_{2b}^2 \right) + \frac{1}{2} \lambda_3 S_3^2 \quad \text{(I-2)}
\]

It is hereby assumed that the molecule executes simple harmonic oscillations only.
<table>
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<th>$x_1 = -uS_{2b}$</th>
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**Chart 1**

The displacements of the linear $XY_2$ molecule in terms of its normal co-ordinates.

Note: $2\ell$ is the equilibrium distance between the $\gamma$ nuclei (see chapter II).
CHAPTER II

Treatment of the Hamiltonian

The Hamiltonian of a system of $N$ electrons and $N'$ nuclei can be written as

$$\mathcal{H} = T_e + U_{ee} + T_n + U_{nn} + U_{ne}$$  \hspace{1cm} (II-1)

where

- $T_e$ is the electronic kinetic energy,
- $T_n$ is the nuclear kinetic energy,
- $U_{nn}$ is the Coulomb interaction between the nuclei,
- $U_{ee}$ is the Coulomb interaction between the electrons,
- $U_{ne}$ is the Coulomb interaction between the electrons and nuclei.

The static approximation will be used to separate the Hamiltonian (II-1), i.e. it is assumed that the electrons are sensitive only to some equilibrium configuration of the nuclei. In general, the equilibrium position varies for each electronic state but for the molecule of interest, the linear $XY_2$ molecule such as $CO_2$, $CS_2$, this can be neglected. In other words, each electronic state, except the ground state, is two-fold degenerate because the electrons see a cylindrically symmetric field of the nuclei, and the equilibrium configuration of the nuclei remains approximately the same for the first few electronic states.

The eigenstates of the unperturbed Hamiltonian of the static approximation are known; because the electrons move in the cylindrically symmetric field provided by the nuclei the azimuthal dependence of their eigenstates are known, and the eigenstates of the nuclear motion are those of the simple harmonic oscillator. In the adiabatic approximation, the electrons follow the motion of the nuclei very closely rather than being sensitive to one
equilibrium configuration of the nuclei. (See reference \ref{3} for a full discussion.) In this latter approximation the unperturbed eigenstates are not known at all. Only $U_{nn}$ and $U_{ne}$ in (II-1) depend on the internuclear separation $Q$. (Vector quantities will be denoted by a bar under the quantity.) Let

$$V(Q) = U_{nn}(Q) + U_{ne}(Q)$$

In the static approximation, one solves for

$$H_e(Q) |\ell_i(Q)\rangle = \left[ \frac{T_e + V_{ee} + V(Q)}{E_i} \right] |\ell_i(Q)\rangle = E_{ei} |\ell_i(Q)\rangle$$

where $\{Q\}$, the equilibrium position of the nuclei is determined by solving

$$H_e(Q) |\ell_i(Q)\rangle = E_{ei} |\ell_i(Q)\rangle$$

and putting

$$\frac{\partial E_{ei}(Q)}{\partial Q} \bigg|_{Q = Q_0} = 0$$

The $|\ell_i(Q)\rangle$ are the degenerate electronic states and the $Q_0$ dependence will be omitted henceforth. Since the $\{Q_0\}$ are assumed to be independent of the electronic states, which is a very good approximation for the CO$_2$, CS$_2$ molecules, the $|\ell_i\rangle$ form a complete set.

The nuclear Hamiltonian is

$$H_n = T_n + \frac{1}{2} \frac{\partial^2 E_{ei}}{\partial Q_0 \partial Q_0} : \delta \phi : \delta \phi$$

where

$$Q = Q_0 + \delta \phi$$

and

$$H_n |\beta_j\rangle = E_{nj} |\beta_j\rangle$$

(Differential operators are written in their dyadic notation.) Again, $E_{nj}$ depends on the electronic state in general but not for the CO$_2$, CS$_2$ linear molecules.
The interaction Hamiltonian is

\[ H_{en} = V(Q) - V(Q_0) - \frac{1}{2} \sum \frac{\partial^2 E_{i \ell}}{\partial Q_i \partial Q_\ell} \delta Q_i \delta Q_\ell \]

Since the nuclear displacements \( \delta Q \) are much smaller than the equilibrium nuclear separations and the distance from any electron to any nucleus, \( V(Q) \) can be expanded about \( Q_0 \) and

\[ H_{en} = \frac{\partial V}{\partial Q_0} \delta Q + \frac{1}{2} \frac{\partial^2 V}{\partial Q_i \partial Q_\ell} \delta Q_i \delta Q_\ell + \ldots - \frac{1}{2} \frac{\partial^2 E_{i \ell}}{\partial Q_i \partial Q_\ell} \delta Q_i \delta Q_\ell. \]  

(II - 4)

Explicit expressions for \( \frac{\partial V}{\partial Q_i} \) and \( \frac{\partial^2 V}{\partial Q_i \partial Q_\ell} \) will now be obtained for linear molecules such as \( \text{CO}_2, \text{CS}_2 \).

a) Expansion of \( U_{ne} \)

The explicit expression for \( U_{ne} \) is

\[ U_{ne} = - e^2 \sum_{i=1}^{N} \sum_{i'}^{N'} \frac{\mathcal{Z}_{i'i'}}{\mathbf{r}_{ii'}} \]

where

\( \mathcal{Z}_{i'i'} \) is the charge number on the \( i' \)th nucleus,

\( \mathbf{r}_{ii'} \) is the distance between the \( i' \)th nucleus and the \( i \)th electron.

Since the vibration of each nucleus is small, \( \mathbf{r}_{ii'} \) can be expanded about the equilibrium position of each nucleus. That is, retaining the co-ordinate system chosen in Chapter I, and referring to Figure I, let the equilibrium position of the nuclei be

\[ \mathbf{r}_1 = - e \mathbf{\hat{r}}, \quad \mathbf{r}_2 = 0, \quad \mathbf{r}_3 = e \mathbf{\hat{r}}. \]

![Figure I](image)
Let $R_i'$ be the position vector of the $i$th electron from the equilibrium position of the \( i \)'th nucleus. Put

$$a\ R_i' = R_i' = (z_i + r_i) \hat{k} + \rho_i^e$$

where

$$a = \left( \frac{2\pi m_2 \nu_2}{\hbar} \right)^{\frac{1}{2}} \text{ has dimension } L^{-1},$$

(a has been introduced to have all co-ordinates dimensionless)

$\rho_i^e$ is the radial vector from the Z axis to the $i$th electron.

The displacement of each nucleus from its equilibrium position is given by

$$a\ Q_i' = Q_i = -\mu q_1 -(q_1 + \mu q_3) \hat{k}$$

$$a\ Q_2' = Q_2 = q_2 + q_3 \hat{k}$$

$$a\ Q_3' = Q_3 = -\mu q_1 -(q_1 - \mu q_3) \hat{k}$$

where the $q_i'$s are dimensionless normal co-ordinates analogous to the $S_i'$s with

$$q_i = q_{ib} \hat{i} + q_{ia} \hat{j} = a\left(S_{ib} \hat{i} + S_{ia} \hat{j}\right)$$

The interaction potential is

$$U_{me} = -e^2 \sum_i \sum_i \frac{3\ \overset{3}{i}'}{a\ L_i' - Q_i'}$$

$$= -e^2 a \sum_i \sum_i \frac{3\ \overset{3}{i}'}{R_{ii}'} \left[1 - 2 \frac{R_{ii}'}{R_{ii}'} + \left(\frac{Q_i'}{R_{ii}'}\right)^2\right]^{-\frac{1}{2}}$$

$$= -e^2 a \sum_i \sum_i \frac{3\ \overset{3}{i}'}{R_{ii}'} \left[1 - 2 \frac{Q_i'}{R_{ii}'} \cos(Q_{ii}'R_{ii}') + \left(\frac{Q_i'}{R_{ii}'}\right)^2\right]^{-\frac{1}{2}}$$
But \((1 - 2 \lambda z + z^2)^{-\frac{1}{2}}\) is the generating function of the Legendre polynomials \(P_\omega(z)\) if
\[
|2 \lambda z - z^2| < 1 \quad \text{and} \quad |2 \lambda z + z^2| < 1
\]
i.e. \((1 - 2 \lambda z + z^2)^{-\frac{1}{2}} = \sum_{\omega=0}^{\infty} P_\omega(z) \lambda^\omega\)

Since the displacement of the nuclei is much smaller than the distance from the equilibrium position of the nuclei to the electrons,
\[Q_i < R_{\text{eq}}\]
and
\[V_{\text{me}} = -e^2 a \sum_i \sum_i \frac{3 q_i}{R_{ii}} \sum_{\omega=0}^{\infty} P_\omega(\cos(Q_i, R_{ii}))(\frac{Q_i}{R_{ii}})^\omega\]

Let
\[V_{\text{me}}^{(\omega)} = -e^2 a \sum_i \sum_i \frac{3 q_i}{R_{ii}} P_\omega(\cos(Q_i, R_{ii}))(\frac{Q_i}{R_{ii}})^\omega\]

The first few Legendre polynomials \(P_\omega(z)\) are
\[P_0(z) = 1\]
\[P_1(z) = z\]
\[P_2(z) = \frac{1}{2} (3z^2 - 1)\]

Thus,
\[V_{\text{me}}^{(0)} = -e^2 a \sum_i \sum_i \frac{3 q_i}{R_{ii}}\]
\[V_{\text{me}}^{(1)} = -e^2 a \sum \left\{ [(e - z_i) \frac{3 i}{R_{ii}} + (e + z_i) \frac{3 i}{R_{ii}}] g_1 \right.\]
\[+ \left[ u (e - z_i) \frac{3 i}{R_{ii}} + \frac{3 i}{R_{ii}} z_i - u (e + z_i) \frac{3 i}{R_{ii}} \right] g_2 \]
\[+ \left[ \frac{3 i}{R_{ii}} - u \left( \frac{3 i}{R_{ii}} + \frac{3 i}{R_{ii}} \right) \right] P_i^e \left\{ P_2 \cos(\psi_i^e - \psi_i) \right\} \]
where \( \varphi_m \) is the azimuthal angle of \( q_2 \).

Let

\[
\xi^2 a \sum_i \left[ u_1 (l_1 - z_i) \frac{3_i^1}{R_i^{*3}} + (l_1 + z_i) \frac{3_i^3}{R_i^{*3}} \right] = \chi_1^{(1)}
\]

\[
\xi^2 a \sum_i \left[ u_1 (l_1 - z_i) \frac{3_i^1}{R_i^{*1}} + \frac{3_i^2}{R_i^{*2}} z_i - u_1 (l_1 + z_i) \frac{3_i^3}{R_i^{*3}} \right] = \chi_3^{(1)}
\]

\[
\left\{ \left( \sum_i a_i \cos \varphi_i e \right)^2 + \left( \sum_i a_i \sin \varphi_i e \right)^2 \right\} \frac{1}{2} = \chi_2^{(1)}
\]

\[
\tan \varphi_e = \frac{\sum_i a_i \sin \varphi_i e}{\sum_i a_i \cos \varphi_i e}
\]

with

\[
a_i = \xi^2 a \left[ \frac{3_i^2}{R_i^{*2}} - u_1 \left( \frac{3_i^1}{R_i^{*1}} + \frac{3_i^3}{R_i^{*3}} \right) \right] \rho_i e.
\]

Then

\[
U_{me}^{(1)} = - \left[ \chi_1^{(1)} q_1 + \chi_2^{(1)} \cos (\varphi_e - \varphi_m) q_2 + \chi_3^{(1)} q_3 \right]
\]

\[
U_{me}^{(2)} = - \xi^2 a \sum_i \left\{ \frac{3_i^1}{4} \left[ u_1^2 \left( \frac{1}{R_i^{*1}} + \frac{1}{R_i^{*3}} \right) + \frac{3_i^3}{R_i^{*3}} \right] \rho_i e^{\cos (\varphi_i e - \varphi_m)} \frac{1}{2} \left[ \frac{3_i^2}{R_i^{*2}} \frac{z_i e}{R_i^{*2}} + \frac{3_i^3}{R_i^{*3}} \frac{z_i e}{R_i^{*3}} \right] \right\} q_2^2
\]

\[
+ \frac{3}{2} \left\{ 2 u_1^2 \left[ \frac{3_i^1}{R_i^{*1}} + \frac{3_i^3}{R_i^{*3}} \right] q_1 + \left[ \frac{3_i^2}{R_i^{*2}} \frac{z_i e}{R_i^{*2}} + 2 u_1^2 \left[ \frac{3_i^1}{R_i^{*1}} + \frac{3_i^3}{R_i^{*3}} \right] \right] \right\} q_2^2
\]

\[
+ \frac{3}{2} \left\{ 2 u_1^2 \left[ \frac{3_i^1}{R_i^{*1}} + \frac{3_i^3}{R_i^{*3}} \right] q_1 + \left[ \frac{3_i^2}{R_i^{*2}} \frac{z_i e}{R_i^{*2}} + 2 u_1^2 \left[ \frac{3_i^1}{R_i^{*1}} + \frac{3_i^3}{R_i^{*3}} \right] \right] \right\} q_2^2
\]

\[
+ \frac{3}{2} \left\{ 2 u_1^2 \left[ \frac{3_i^1}{R_i^{*1}} + \frac{3_i^3}{R_i^{*3}} \right] q_1 + \left[ \frac{3_i^2}{R_i^{*2}} \frac{z_i e}{R_i^{*2}} + 2 u_1^2 \left[ \frac{3_i^1}{R_i^{*1}} + \frac{3_i^3}{R_i^{*3}} \right] \right] \right\} q_2^2
\]

\[
+ u \left[ 3 g_1 \left( \frac{z_i e}{R_i^{*1}} - \frac{z_i e}{R_i^{*3}} \right) + 3 \left( \frac{1}{R_i^{*1}} - \frac{1}{R_i^{*3}} \right) \right] q_3^2
\]

\[
+ u \left[ 3 g_1 \left( \frac{z_i e}{R_i^{*1}} - \frac{z_i e}{R_i^{*3}} \right) + 3 \left( \frac{1}{R_i^{*1}} - \frac{1}{R_i^{*3}} \right) \right] q_3^2
\]

\[
+ u \left[ 3 g_1 \left( \frac{z_i e}{R_i^{*1}} - \frac{z_i e}{R_i^{*3}} \right) + 3 \left( \frac{1}{R_i^{*1}} - \frac{1}{R_i^{*3}} \right) \right] q_3^2
\]
Alternatively, \( U_{ne}^{(2)} \) can be written as

\[
U_{ne}^{(2)} = -\left( \frac{\hbar}{\pi^2} \lambda_0 \mathcal{Q}_1 + \frac{\hbar}{\pi^2} \lambda_2 \mathcal{Q}_2 + \frac{\hbar}{\pi^2} \lambda_3 \mathcal{Q}_3 + \frac{\hbar}{\pi^2} \lambda_4 \mathcal{Q}_4 \right)
\]

\[
+ \frac{\hbar}{\pi^2} \lambda_5 \mathcal{Q}_5 \cos (\mathcal{Q}_e - \mathcal{Q}_n) + \lambda_{12} \mathcal{Q}_6 \cos (\mathcal{Q}_e - \mathcal{Q}_n) + \lambda_1 \mathcal{Q}_7 \cos (\mathcal{Q}_e - \mathcal{Q}_n) + \lambda_2 \mathcal{Q}_8 \cos (\mathcal{Q}_e - \mathcal{Q}_n) \mathcal{Q}_9 \mathcal{Q}_{10}
\]

where

\[
\tan 2\mathcal{Q}_e = \frac{\sum \left\{ \frac{3}{4} \left[ 3, \lambda_1^2 \left( \frac{1}{R_{\mathcal{Q}_1}} + \frac{1}{R_{\mathcal{Q}_2}} \right) + \frac{3}{2} \frac{1}{R_{\mathcal{Q}_3}} \right] \rho_{\mathcal{Q}_e}^2 \sin 2\mathcal{Q}_e \right\}}{\sum \left\{ \frac{3}{4} \left[ 3, \lambda_2^2 \left( \frac{1}{R_{\mathcal{Q}_1}} + \frac{1}{R_{\mathcal{Q}_2}} \right) + \frac{3}{2} \frac{1}{R_{\mathcal{Q}_3}} \right] \rho_{\mathcal{Q}_e}^2 \cos 2\mathcal{Q}_e \right\}}
\]

\[
\lambda_{22} = e^2 q \left[ \frac{3}{4} \left[ 3, \lambda_1^2 \left( \frac{1}{R_{\mathcal{Q}_1}} + \frac{1}{R_{\mathcal{Q}_2}} \right) + \frac{3}{2} \frac{1}{R_{\mathcal{Q}_3}} \right] \rho_{\mathcal{Q}_e}^2 \sin 2\mathcal{Q}_e \right] + \left[ \frac{3}{4} \left[ 3, \lambda_2^2 \left( \frac{1}{R_{\mathcal{Q}_1}} + \frac{1}{R_{\mathcal{Q}_2}} \right) + \frac{3}{2} \frac{1}{R_{\mathcal{Q}_3}} \right] \rho_{\mathcal{Q}_e}^2 \cos 2\mathcal{Q}_e \right]^2
\]

and similarly for

\[
\tan \mathcal{Q}_e', \tan \mathcal{Q}_e'', \tan \mathcal{Q}_e''', \lambda_{13}, \lambda_{23}, \lambda_1, \lambda_2, \lambda_3.
\]

\( U_{ne}^{(2)} \) represents the interaction between the electrons and the nuclei fixed at their equilibrium position; \( U_{ne}^{(2)} + U_{ne}^{(3)} \equiv \mathcal{V}(\mathcal{Q}_0) \).

Thus, the electronic eigenstates \( \lambda_{1}(\mathcal{Q}_0) \) are the degenerate states of the electrons in the cylindrically symmetric field of the nuclei.

\( U_{ne}^{(1)} \) and \( U_{ne}^{(2)} \) represent the interaction between the electrons and the dipole and quadrupole moments of the nuclei respectively. It has not been found necessary to consider higher moments interaction.

The displacements \( \mathcal{Q}_1 \) and \( \mathcal{Q}_3 \) do not remove the cylindrical symmetry and they will be omitted; similarly the terms involving \( \mathcal{Q}_1 \mathcal{Q}_2 \) and \( \mathcal{Q}_2 \mathcal{Q}_3 \) in \( U_{ne}^{(1)} \) will be omitted because these represent a coupling between the \( \mathcal{Q}_1(\mathcal{Q}_3) \) and \( \mathcal{Q}_2 \) vibration with the electronic motion and will be considered a second order effect. Thus
\[ U_{ne}^{(i)} = -\lambda_2^{(i)} q_{2i} \cos(\varphi_e - \varphi_n) \]
\[ U_{ne}^{(2)} = -\frac{1}{2} \left[ \lambda_2^{(2)} q_{2i}^2 + \lambda_2^{(2)} q_{2i}^2 \cos 2(\varphi_e - \varphi_n) \right] \]

b) Expansion of \( U_{nn} \)

\( U_{nn} \) can be expanded similar to \( U_{ne} \) about the equilibrium position of each nucleus since the equilibrium distance \( l \) between the atoms is much greater than the displacements of the nuclei. Proceeding as in the case of \( U_{ne} \), one finds

\[ U_{nn}^{(0)} = \frac{e^2}{\ell^2} \left( \frac{3}{2} \varphi_1^2 + 3 \varphi_2^2 + 3 \varphi_3^2 + 3 \varphi_1^2 \varphi_2^2 \right) \]

\[ U_{nn}^{(1)} = \frac{e^2}{\ell^2} \left\{ -\left( \frac{3}{2} \varphi_1^2 + 3 \varphi_2^2 + 3 \varphi_3^2 \right) \varphi_1 + (1 + \mu)(3 \varphi_2^2 \varphi_3^2 - 3 \varphi_3^2) \varphi_3 \right\} \]

\[ U_{nn}^{(2)} = \frac{e^2}{\ell^3} \left\{ 2 \varphi_2^2 - 2 (1 + \mu)^2 \varphi_2^2 \right\} \]

Omitting the terms in \( \varphi_1 \) and \( \varphi_3 \),

\[ U_{nn}^{(1)} = 0 \]
\[ U_{nn}^{(2)} = -\frac{e^2 a}{\ell^3} (1 + \mu)^2 \varphi_2^2 \]

c) Explicit expression for \( H_{en} \)

Incorporating into \( \lambda_2^{(2)} \) the coefficient of \( q_{2i}^2 \) from \( U_{nn}^{(2)} \) and also

\[ \frac{\partial^2 E e_i}{\partial q_{2i} \partial q_{2i}} \]

\[ H_{en} = -\lambda_2^{(1)} q_{2i} \cos(\varphi_e - \varphi_n) - \frac{1}{2} \left[ \lambda_2^{(2)} q_{2i}^2 + \lambda_2^{(2)} q_{2i}^2 \cos 2(\varphi_e - \varphi_n) \right] \]

\[ (\Pi - 5) \]
CHAPTER III

Unperturbed Eigenstates

From (II-2), (II-3), (II-5), the Hamiltonian is

(III-1) \[ H = H_e + H_n + H_{en} \]

where

\[ H_e = T_e + U_{ee} + U_{ne}^{(o)} + U_{nn}^{(o)} \]

which contains the electronic co-ordinates and the equilibrium position of the nuclei, and

\[ H_n = T_n + \frac{1}{\hbar^2} \frac{\partial^2 E_{ei}}{\partial q_0 \partial \varphi_0} \delta q \delta \varphi \]

In the Hamiltonian (III-1) the only terms that we would like to retain are those that break the cylindrical symmetry of the nuclear field, that is terms that contain \( \varphi_n \) only; since the energy of the nuclear states does not depend on the electronic states for linear \( XY_2 \) molecules such as \( \text{CO}_2 \), \( \text{CS}_2 \), from (I-1) and (I-2),

(III-2) \[ H_n = \frac{1}{2} \sum (S_n^2 + S_n^2) + \frac{1}{2} \chi_n^2 (S_n^2 + S_n^2) \]

The eigenstates of \( H_e \) and \( H_n \) are known and will be discussed presently.

a) Eigenstates of \( H_e \)

Due to the cylindrical symmetry of the nuclear field, the wave function of the electrons can be written as \( \chi_n e^{\pm i\varphi} \), and the states shall be represented simply as \( | \varphi \pm \rangle \). Here it is assumed that when the electrons are rotated through an angle \( \varphi \), the symmetric \( \chi_n e^{+i\varphi} \) and antisymmetric \( \chi_n e^{-i\varphi} \) wave functions of the degenerate
electronic state transform like $e^{i\Lambda \phi}$ and $e^{-i\Lambda \phi}$ respectively. $\Lambda$ denotes the projection of the total electronic angular momentum on the $Z$ axis and it will be used from now on to characterize the energy of the electronic states, that is

$$(III-3) \quad H_e \mid \Lambda^\pm \rangle = E_{e\Lambda} \mid \Lambda^\pm \rangle$$

b) Eigenstates of $H_n$

The nuclear Hamiltonian is

$$H_n = \frac{1}{2} m_2 (S_{2a}^2 + S_{2b}^2) + \frac{1}{2} \lambda_2 (S_{2a}^2 + S_{2b}^2)$$

where

$$\lambda_2 = 4 \pi^2 m_a \omega_2^2$$

and $\omega_2$ is the observed classical frequency of oscillation.

$$H_n = \frac{P_{2a}^2}{2m_a} + \frac{P_{2b}^2}{2m_a} + 2 \pi^2 m_a \omega_2^2 (S_{2a}^2 + S_{2b}^2)$$

where $P_r$ is the momentum conjugate to $S_r$. In terms of the dimensionless co-ordinates $\xi_{2a}, \xi_{2b},$

$$H_n = a^2 \frac{P_{2a}^2 + P_{2b}^2}{2m_a} + \frac{2 \pi^2 a^2}{a^2} m_a \omega_2^2 (\xi_{2a}^2 + \xi_{2b}^2)$$

By putting $P_r = -i \hbar \frac{\partial}{\partial \xi_r}$ and $E = \frac{2E_n}{\hbar \omega_2},$

$$H_n \psi_n = E_n \psi_n$$

becomes

$$\left[ -(\frac{\partial^2}{\partial \xi_{2a}^2} + \frac{\partial^2}{\partial \xi_{2b}^2}) + \xi_{2a}^2 + \xi_{2b}^2 \right] \psi_n = E_n \psi_n$$
where $\Psi_n$ is the nuclear wave function. From the appendix where the solution to this equation is discussed,

$$\Psi_n(q_2a, q_2b) \equiv \Psi_n(q_2, \varphi_n) \equiv \Psi(p, \varphi_n)$$

and

$$\Psi(p, \varphi_n) = \frac{N_{re}}{\sqrt{2\pi}} e^{i\varphi_n} \rho^{\frac{v_2}{2}} L^{\ell}_{\sigma} (\rho) e^{\pm i\ell \varphi_n} \tag{III-4}$$

where

$$\rho = q_2^2$$

$$\sigma = \frac{v_2 - \ell}{2}$$

$$E_n = \ell \nu_2 (\nu_2 + 1), \quad \nu_2 = 0, 1, 2, \ldots$$

$$\ell = \nu_2, \nu_2 - 2, \ldots, 1 \text{ and } 0 \text{.}$$

$N_{re}$ is a normalizing constant

$L^\ell_{\sigma}$ is the associated Laguerre polynomial.

Once again, the nuclear states will be denoted by $|\nu_2, \ell \pm \rangle$

(or $|\sigma, \ell \pm \rangle$) and

$$H_n |\nu_2, \ell \pm \rangle = E_{\nu_2} |\nu_2, \ell \pm \rangle \tag{III-5}$$
CHAPTER IV

Application of the Variational Principle

The Schroedinger equation for a system of $i$ electrons and $i'$ nuclei is

$$ (\nabla - 1) H(\psi) = E |\psi\rangle $$

where

$$ H = H_e + H_n + H_{e_n}, \text{ from (III-1)} $$

The Hamiltonian $H$ operates in the Hilbert space of both the electrons and the nuclei, and to denote this, the round ket, $\langle\rangle$, has been used.

The usual ket $\langle l|$ denotes a state in the Hilbert space of either the electrons, or the nuclei, that is, $H_e |\lambda^\pm\rangle = E_{e\lambda} |\lambda^\pm\rangle$

$$ H_n |\nabla, e^\pm\rangle = E_{n\nabla} |\nabla, e^\pm\rangle $$

For the purpose of applying the variational principle, the following notation will be used:

$$ |\alpha_{i}\rangle = |\lambda^{(s)}\rangle $$

where the superscript $(s)$ denotes the sign of $\lambda$. The one-to-one correspondence between $\alpha$ and $\lambda^{(s)}$ may be made in the following manner:

$$ |\alpha_{o}\rangle = |0\rangle; \quad |\alpha_{1}\rangle = |1^+\rangle; \quad |\alpha_{2}\rangle = |1^-\rangle $$

$$ |\alpha_{3}\rangle = |2^+\rangle; \quad |\alpha_{4}\rangle = |2^-\rangle $$

etc.
Thus (III-3) becomes

(\text{IV-2}) \quad H_e |\alpha_i\rangle = E_{e i} |\alpha_i\rangle \quad , \quad i = 0, 1, 2 ,

and \quad E_{e i} = E_{e (i+1)} \quad \text{for each odd } i.

Similarly, \quad |\beta_j\rangle = |V_2, \ell^{(s)}\rangle .

Again a one-to-one correspondence may be made in the following way:

|\beta_0\rangle = |0, 0\rangle ;
|\beta_1\rangle = |1, 1^+\rangle ;
|\beta_2\rangle = |1, 1^-\rangle ;
|\beta_3\rangle = |2, 2^+\rangle ;
|\beta_4\rangle = |2, 0\rangle ;
|\beta_5\rangle = |2, 2^-\rangle ;

\text{etc.}

Since \ell \text{ takes on the values } V_2, V_2 - 2, \ldots, 1 \text{ or 0 for each } V_2, \text{ the degeneracy for each nuclear state is easily seen to be } (V_2+1) - \text{ fold, for each value of } E_{e i} .

Thus (III-5) becomes

(\text{IV-3}) \quad H_n |\beta_j\rangle = E_{n j} |\beta_j\rangle \quad , \quad j = 0, 1, 2 ,

and

E_{n1} = E_{n2}
E_{n3} = E_{n4} = E_{n5}
E_{n6} = E_{n7} = E_{n8} = E_{n9} \quad \text{etc.}

The \quad |\alpha_i\rangle, \quad |\beta_j\rangle \quad \text{each form a complete orthonormal set in the Hilbert space of the electrons and nuclei respectively, since for linear molecules such as CO}_2, \text{ CS}_2 \text{ the equilibrium internuclear distance is the same for all electronic states and the nuclear energy is independent of the electronic state.}
Application of the variational principle to (IV-1) gives

\[ \delta \left[ \langle \Psi | H | \Psi \rangle - E \langle \Psi | \Psi \rangle \right] = 0 \quad \delta E = 0 \]

It is now assumed that the \( | \Psi \rangle \) can be synthesized from the \( | \alpha_i \rangle \) and \( | \beta_j \rangle \) in the following manner:

\[
| \Psi \rangle = \sum_i \sum_j a_{ij} \left( | \alpha_i \rangle \times | \beta_j \rangle \right),
\]

\[
| \Psi \rangle = \sum_i \sum_j a_{ij} \left( | \alpha_i \beta_j \rangle \right),
\]

that is, \( | \Psi \rangle \) consists of all the possible linear combinations of the electronic and vibrational states, and hence the secular determinant that will result from applying the variational principle will be most general.

Proceeding to carry through the variational principle,

\[
\left( | \Psi \rangle | H | | \Psi \rangle \right) = \sum_{i,j} \sum_{i',j'} a_{ij}^* a_{i'j'} \left( \langle \alpha_i \beta_j | H e + H m + H e n | \alpha_{i'} \beta_{j'} \rangle \right)
\]

\[
= \sum_{i,j} \sum_{i',j'} a_{ij}^* a_{i'j'} \left[ E_{ei} \delta_{ii'} \delta_{jj'} + E_{nj} \delta_{ii'} \delta_{jj'} + H_{i'j'}^{ii'} \right]
\]

where

\[ H_{i'j'}^{ii'} = \langle \alpha_i \beta_j | H e n | \alpha_{i'} \beta_{j'} \rangle. \]

\[
\left( | \Psi \rangle | \Psi \rangle \right) = \sum_{i,j} \sum_{i',j'} a_{ij}^* a_{i'j'} \delta_{ii'} \delta_{jj'}.
\]

Therefore

\[
\left( | \Psi \rangle | H | | \Psi \rangle \right) - E \left( | \Psi \rangle | \Psi \rangle \right) = \sum_{i,j} \sum_{i',j'} a_{ij}^* a_{i'j'} \left[ H_{i'j'}^{ii'} + \left( E_{ei} + E_{nj} - E \right) \delta_{ii'} \delta_{jj'} \right]
\]

\[
= \sum_{i,j} \sum_{i',j'} a_{ij}^* a_{i'j'} \left[ H_{i'j'}^{ii'} - \Delta E_{ij} \delta_{ii'} \delta_{jj'} \right]
\]

where

\[ \Delta E_{ij} = E - E_{ei} - E_{nj}. \]
Applying a variation with respect to $a_{i,j}$,

$$\sum_{i',j'} a_{i',j'} \left[ H_{i,j}^{i',j'} - \Delta E_{i,j} \delta_{i,i'} \delta_{j,j'} \right] = 0 \quad ; \quad i = 0, 1, 2, \ldots \quad j = 0, 1, 2, \ldots$$

In order to solve for the $a_{i,j}$,

$$\left| H^{i,j'}_{j,j'} - \Delta E \delta_{i,i'} \delta_{j,j'} \right| = 0$$

\(i = 0, 1, 2, \ldots\)

\(j = 0, 1, 2, \ldots\)

\(i = 0, 1, 2, \ldots\)

\(j = 0, 1, 2, \ldots\)

From the determinant (IV-4) all the information about the vibronic states of the linear molecules such as CO\(_2\), CS\(_2\) can be obtained. However, only some of the matrix elements $H_{i,j}^{i',j'}$ are non-vanishing, and before analyzing the determinant (IV-4) the values of the non-vanishing matrix elements $H_{i,j}^{i',j'}$ will have to be found.
CHAPTER V

Non-vanishing Matrix Elements

From \( (II-5) \), the interaction Hamiltonian is

\[
H_{en} = -\frac{1}{2} \lambda_2^{(1)} q_2 \cos (\psi_e - \psi_n) - \frac{1}{2} \lambda_2^{(2)} q_2^2 + \lambda_2^{(2)} q_2^2 \cos 2 (\psi_e - \psi_n)
\]

The electronic states contain the angle \( \psi \) as defined in Chapter III Part (a). Putting

\[
\psi = \psi_e + \psi'
\]

the angular matrix element of the first term in \( H_{en} \) becomes

\[
\int e^{-i \psi_e} e^{-i \psi_n} \cos (\psi_e - \psi_n) e^{i \psi'} e^{i \psi_n'} d \psi_e d \psi_n.
\]

The subscript \( e \) in \( \psi_e \) will be omitted from now on and \( \psi_e' \) will also be put equal to \( \psi \).

Substituting \( q_2 = \rho \), equation \((II-5)\) becomes

\[
\begin{align*}
(\nabla-1) \quad H_{en} &= -\frac{1}{2} \lambda_2^{(1)} \rho \cos (\psi_e - \psi_n) - \frac{1}{2} \left( \lambda_2^{(2)} \rho + \lambda_2^{(2)} \rho \cos 2 (\psi_e - \psi_n) \right)
\end{align*}
\]

The angular part of the matrix elements \( H_{jj'} \) can be obtained from the following integral:

\[
(\nabla-2) \quad \Theta = \frac{1}{(2\pi)^3} \iint \int e^{-i \psi_e - i \psi_n} \cos(\psi_e - \psi_n) \rho^{2n} e^{i \psi' e^{i \psi_n'}} d \psi_e d \psi_n d \psi_{n'}
\]

with \( \lambda, \ell, \lambda', \ell' \) taking on both positive and negative integral values.

The radial matrix elements in the Hilbert space of the nuclei are of the following type:

\[
(\nabla-3) \quad \langle \sigma e | \rho^m | \sigma' e' \rangle = \int e^{-\rho} \rho^{\ell + \ell'} \rho^{n} L_\sigma (\rho) L_\sigma^{e'} (\rho) \frac{d \rho}{\rho^2},
\]

with \( \sigma, \sigma', \ell, \ell' \) always taking on positive integral values.
In both (V-2) and (V-3) \( n \) is a positive multiple of \( \frac{1}{2} \). The value \( 2n \) corresponds to \( \omega \) in \( \mathcal{U}_{\eta, \epsilon}^{(\omega)} \). No matter what \( \omega \) is, \( \mathcal{U}_{j, j'}^{(\omega)} \) always contains products of (V-2) and (V-3) \( \times \mathcal{S}_{\Lambda-\Lambda'} \), where

\[
\mathcal{S}_{\Lambda-\Lambda'} = \begin{cases} 
1 & \Lambda = \Lambda' \\
0 & \Lambda \neq \Lambda'
\end{cases}
\]

Thus, the evaluation of (V-2), (V-3) allows one to go to any order to approximation in \( \mathcal{U}_{\eta, \epsilon}^{(\omega)} \) if it is necessary.
a) Angular part of matrix elements.

It is quite easy to see which of the matrix elements \((V-2)\) are non-vanishing.

\[
\Theta = \frac{1}{(2\pi)^2} \int \int e^{-i(\lambda - \lambda')\Psi} e^{-i(\lambda' - \lambda)\Psi} \cos^{2\nu} (\Psi - \Psi_n) d\Psi d\Psi_n
\]

But

\[
\cos^{2\nu} (\Psi - \Psi_n) = \left[ \frac{e^{i(\Psi - \Psi_n)} + e^{-i(\Psi - \Psi_n)}}{2} \right]^{2\nu}
\]

\[
= \frac{1}{4^n} \sum_{\nu=0}^{2\nu} \left[ e^{i(\Psi - \Psi_n)} \right]^{2\nu} \left[ e^{-i(\Psi - \Psi_n)} \right]^{2\nu}
\]

\[
= \frac{1}{4^n} \sum_{\nu=0}^{2\nu} e^{i(2\nu - 2\nu)\Psi - i(2\nu - 2\nu)\Psi_n}
\]

Therefore

\[
\Theta = \frac{1}{(2\pi)^2 4^n} \int \int \left[ \sum_{\nu=0}^{2\nu} e^{-i(\lambda - \lambda' - 2n + 2\nu)\Psi} e^{-i(\lambda' - \lambda + 2n - 2\nu)\Psi_n} \right] d\Psi d\Psi_n
\]

\[
= \frac{1}{4^n} \left\{ \delta_{\lambda - \lambda' - 2n} \delta_{\lambda' - 2n + 2} + \delta_{\lambda - \lambda' - 2n + 2} \delta_{\lambda' - 2n - 2} + \cdots \right\}
\]

Hence, from the angular part, the selection rules for the non-vanishing matrix elements are the following:

\[
\Delta \lambda = 2n ; \quad \Delta \epsilon = -2n \quad \text{simultaneously}
\]

or \[\Delta \lambda = 2n - 2 ; \quad \Delta \epsilon = -2n + 2\]

or \[\Delta \lambda = 2n - 4 ; \quad \Delta \epsilon = -2n + 4\]
or $\Delta \lambda = -2n + 2$; $\Delta \ell = 2n + 2$ simultaneously

or $\Delta \lambda = -2n$; $\Delta \ell = 2n$.

As a particular case, for $n=\frac{1}{2}$, that is, dipole displacement of the nuclei,

\[\begin{cases} \Delta \lambda = -\Delta \ell = 1 \text{ simultaneously} \\ \Delta \lambda = -\Delta \ell = -1 \end{cases}\]

But for the lowest degenerate electronic state, that is $\ell = 1$, and for the lowest degenerate nuclear state, that is $\lambda = 1$, in order to have non-vanishing off-diagonal elements, $\Delta \lambda = \pm 2$ and $\Delta \ell = \pm 2$. (This is shown in Chapter VI, where the matrix is written in full.) Thus to first order, dipole displacements do not contribute to the Renner splitting. It would be natural to go on to second order correction to the dipole term but if it is assumed that the difference between the electronic energy levels is much greater than that between the vibrational levels, then the second order contribution is negligible.

For $n=1$, that is, for quadrupole displacements,

\[\begin{cases} \Delta \lambda = -\Delta \ell = 2 \text{ simultaneously} \\ \Delta \lambda = -\Delta \ell = 0 \end{cases}\]

\[\begin{cases} \Delta \lambda = -\Delta \ell = -2 \end{cases}\]

and hence these elements will contribute to the Renner splitting.

In general, by whatever amount the electronic angular momentum changes, the nuclear angular momentum also changes by that amount, but in the opposite
direction. This means that the projection of the angular momentum along the axis is always conserved even after the interaction is turned on. That is, whatever angular momentum the electrons lose, the nuclei gain, and vice-versa, so that it is always meaningful to talk of $\Sigma$, $\Pi$, $\Delta$ ... states.
b) Radial matrix elements.

The non-vanishing radial matrix elements (V-3),
\[ \langle \sigma \ell | \rho^n | \sigma' \ell' \rangle = \frac{1}{\mathcal{N}_{\sigma \ell} \mathcal{N}_{\sigma' \ell'}} \int_{0}^{\infty} e^{-\rho} \rho^{\frac{1}{2} (\ell + \ell')} \rho^n L_{\ell}^{\ell} (\rho) L_{\ell'}^{\ell'} (\rho) \frac{d\rho}{\ell!} \]
can be found from the generating function of the Laguerre polynomials given in the appendix; that is
\[
\frac{1}{\mathcal{N}_{\sigma \ell} \mathcal{N}_{\sigma' \ell'}} \sum_{\sigma = \sigma} \sum_{\ell = \ell'} \frac{\int e^{-\rho} \rho^{\frac{1}{2} (\ell + \ell')} \rho^n L_{\ell}^{\ell} (\rho) L_{\ell'}^{\ell'} (\rho) \frac{d\rho}{\ell!}}{\mathcal{N}_{\sigma \ell} \mathcal{N}_{\sigma' \ell'}}
\]

The procedure is to integrate over \( \rho \) in the right hand side, expand the remaining form in \( (\mathbf{u}, \mathbf{u}') \) and compare coefficients with the left hand side.

The right hand side
\[
\frac{1}{\ell!} \frac{(-1)^{\ell + \ell'} u^{\ell} u'^{\ell'}}{(1-u)^{\ell+1} (1-u')^{\ell'+1}} \int_{0}^{\infty} e^{-\rho} \left\{ \rho \left[ \frac{u}{1-u} + \frac{u'}{1-u'} + 1 \right] - \rho^n \right\} \rho^{\frac{1}{2} (\ell + \ell')} \frac{d\rho}{\ell!}
\]
Using the definition of the \( \Gamma \) function,
\[
\Gamma (n) = \int_{0}^{\infty} x^{n-1} e^{-x} \, dx,
\]
the right hand side
\[
\frac{1}{\ell!} \frac{(-1)^{\ell + \ell'} u^{\ell} u'^{\ell'}}{(1-u)^{\ell+1} (1-u')^{\ell'+1}} \frac{\Gamma \left( n + \frac{\ell}{2} + \frac{\ell'}{2} + 1 \right)}{\left[ \frac{u}{1-u} + \frac{u'}{1-u'} + 1 \right]^{n + \frac{\ell}{2} + \frac{\ell'}{2} + 1}}
\]
\[
\frac{1}{\ell!} \frac{(-1)^{\ell + \ell'} u^{\ell} u'^{\ell'}}{(1-u)^{\ell+1} (1-u')^{\ell'+1}} \frac{\Gamma \left( n + \frac{\ell}{2} + \frac{\ell'}{2} + 1 \right)}{(1-uu')^{n + \frac{\ell}{2} + \frac{\ell'}{2} + 1}}
\]
Using the expansion

\[(1 - \lambda)^{-\beta} = \sum_{k=0}^{\infty} \frac{\Gamma(\beta + k)}{\Gamma(\beta) \Gamma(k + 1)} \lambda^{k}\]

which is valid for all \(q\), the right hand side

\[
\sum_{k=0}^{\infty} \sum_{\nu=0}^{\infty} \sum_{\nu' = 0}^{\infty} \frac{(-1)^{k+\nu}}{2} \lambda \left( \frac{\nu + \nu'}{2} + \frac{\lambda}{2} \right) \Gamma(\frac{\nu + \nu' + \lambda}{2}) \Gamma(\frac{\nu + \nu' - \lambda}{2}) \Gamma(\nu + \nu' + 1) \Gamma(\nu + \nu' - 1) \Gamma(\nu + 1) \Gamma(\nu' + 1)
\]

where

\[
f(\lambda, \nu, \nu')
\]

Putting \(\lambda + \lambda' = \sigma\), \(\lambda' + \lambda = \sigma'\), the right hand side

\[
\sum_{k=0}^{\infty} \sum_{\nu=0}^{\infty} \sum_{\nu' = 0}^{\infty} f(\lambda, \sigma - \lambda - \lambda, \sigma' - \lambda' - \lambda) \lambda^{\nu} \lambda^{\nu'}
\]

But

\[
\sum_{k=0}^{\infty} \sum_{\nu=0}^{\infty} \sum_{\nu' = 0}^{\infty} \sigma - \lambda - \lambda\]

Thus the right hand side

\[
\sum_{\sigma = \lambda}^{\infty} \left\{ \sum_{k=0}^{\sigma - \lambda} \sigma' - \lambda' + k \right\} f(\lambda, \sigma - \lambda - \lambda, \sigma' - \lambda' - \lambda) \lambda^{\sigma} \lambda^{\sigma'}
\]
A similar relation holds for \((\sigma - \ell)\) and \((\sigma' - \ell')\) interchanged, depending on which is smaller. Therefore the right hand side

\[
\sum_{\sigma = \ell} \sum_{\sigma' = \ell'} \sum_{k=0}^{\min(\sigma, \sigma')} \delta(k, \sigma - \ell - k, \sigma' - \ell' - k) u^\sigma u'^{\sigma'}
\]

Comparing polynomials with the left hand side,

\[(\mathbf{V}-\mathbf{6}) \quad <\ell \in \mathcal{P} \mid \mathcal{P} \sigma' \ell'>
\]

\[
= N_{\sigma \ell} N_{\sigma' \ell'} \Gamma(\sigma+1) \Gamma(\sigma'+1) \sum_{k=0}^{\min(\sigma, \sigma')} \delta(k, \sigma - \ell - k, \sigma' - \ell' - k)
\]

\[
= N_{\sigma \ell} N_{\sigma' \ell'} \frac{\Gamma(\sigma+1) \Gamma(\sigma'+1)}{\Gamma(\frac{\sigma - \ell - \eta}{2} - \frac{\ell'}{2} - \eta)} \times \sum_{k=0}^{\min(\sigma, \sigma')} \frac{\Gamma(\sigma - \ell - k + \frac{\ell'}{2} + k + 1) \Gamma(\sigma - \ell - k - \frac{\ell'}{2} - \eta) \Gamma(\sigma' - \ell' - k + \frac{\ell'}{2} + k + 1) \Gamma(\sigma' - \ell' - k - \frac{\ell'}{2} - \eta)}{\Gamma(\sigma - \ell - k + 1) \Gamma(\sigma - \ell - k + 1) \Gamma(\sigma' - \ell' - k + 1) \Gamma(\sigma' - \ell' - k + 1)}
\]

In order to see which matrix elements vanish, only those \(\Gamma\) functions whose argument may be negative have to be considered, that is

\[
\sum_{k=0}^{\min(\sigma, \sigma')} \frac{\Gamma(\sigma - \ell - k - \eta - \frac{\ell'}{2} - \eta)}{\Gamma(\frac{\sigma - \ell - \eta}{2} - \frac{\ell'}{2} - \eta)} \frac{\Gamma(\sigma' - \ell' - k + \frac{\ell'}{2} + k + 1)}{\Gamma(-\eta + \frac{\ell'}{2} - \frac{\ell'}{2})}
\]

Since \(\sigma - \ell - k > 0\) and \(\sigma' - \ell' - k > 0\), then

for \(-\eta + \ell' - \frac{\ell'}{2} > 0\) and

\(-\eta - \frac{\ell'}{2} + \frac{\ell'}{2} > 0\)

there are no non-vanishing elements. However, if either of the last two mentioned terms are zero or negative, the arguments of the \(\Gamma\) function appearing in the denominator are zero or negative, and the arguments of the \(\Gamma\) function appearing in the numerator are greater than zero, then there
are vanishing elements. That is, in order to have no non-vanishing elements,

if \( \sigma' - \ell < \sigma - \ell' \), then \( \sigma' - \ell' - \sigma - \ell - n - \frac{\ell}{2} - \frac{\ell'}{2} \leq 0 \)

or \( \sigma' - \sigma - \frac{\ell}{2} + \frac{\ell}{2} \leq n \);

if \( \sigma' - \ell' < \sigma - \ell \), then \( \sigma - \sigma' - \frac{\ell}{2} + \frac{\ell'}{2} \leq n \)

or \( -(\sigma' - \sigma - \frac{\ell}{2} + \frac{\ell}{2}) \leq n \).

That is

\[
\left\{ \begin{array}{c}
\text{if } \sigma' - \ell < \sigma - \ell', \quad \text{then } \\
\frac{n}{2} > |\sigma - \sigma' - \frac{\ell}{2} + \frac{\ell'}{2}|
\end{array} \right.
\]

(V-7)

\[
\text{and } -n + \frac{\ell}{2} - \frac{\ell'}{2}, -n - \frac{\ell}{2} + \frac{\ell'}{2} \text{ are zero or negative integers.}
\]

Since the selection rules for \( \Delta \ell \) are known from the treatment of the angular dependence, the selection rules for \( \Delta \sigma \) can be found from (V-7).

For example, for \( n = \frac{1}{2} \), \( \Delta \ell = \pm 1 \)

For \( \ell' - \ell = \Delta \ell = +1 \),

\[
\frac{1}{2} > |\sigma - \sigma' + \frac{1}{2}|
\]

Therefore \( \sigma = \sigma' \) or \( \sigma' = \sigma + 1 \)

In terms of the \( V_\sigma \)'s,

\[
\Delta \sigma = 0 \quad \text{gives } \quad \Delta V_2 = -1
\]

\[
\Delta \sigma = +1 \quad \text{gives } \quad \Delta V_2 = +1
\]

For \( \ell' - \ell = \Delta \ell = -1 \),

\[
\frac{1}{2} > |\sigma - \sigma' - \frac{1}{2}|
\]

Therefore \( \sigma' = \sigma \) or \( \sigma' = \sigma - 1 \)

or \( \Delta V_2 = +1 \); \( \Delta V_2 = -1 \)
For $n=1$, the selection rules on $\ell$ are
$$\Delta \ell = 0, \pm 2.$$

For $\ell' = \ell$,
$$| \ell | > | \sigma - \sigma' |$$

Therefore $\sigma' = \sigma - 1$ which gives $\Delta \nu_2 = -2$
or $\sigma' = \sigma$ which gives $\Delta \nu_2 = 0$
or $\sigma' = \sigma + 1$ which gives $\Delta \nu_2 = +2$

For $\ell' = \ell + 2$,
$$| \ell + 2 | > | \sigma - \sigma' + 1 |$$

Therefore $\sigma' = \sigma$ which gives $\Delta \nu_2 = -2$
or $\sigma' = \sigma + 1$ which gives $\Delta \nu_2 = 0$
or $\sigma' = \sigma + 2$ which gives $\Delta \nu_2 = +2$

For $\ell' = \ell - 2$,
$$| \ell - 2 | > | \sigma - \sigma' - 1 |$$

Again $\sigma' = \sigma$ which gives $\Delta \nu_2 = +2$
or $\sigma' = \sigma - 1$ which gives $\Delta \nu_2 = 0$
or $\sigma' = \sigma - 2$ which gives $\Delta \nu_2 = -2$

In summary, the selection rules for the non-vanishing matrix elements of the dipole and quadrupole displacement of the nuclei are given in Table I. The non-vanishing matrix elements of $(V-3)$ have been given in the literature; although the selection rules given in Table 1 were not stated, the matrix elements that were calculated do conform with the selection rules given in Table 1.
<table>
<thead>
<tr>
<th>selection rules for</th>
<th>( \Delta V_2 = +1 ), ( \Delta \ell = +1 ), ( \Delta \Lambda = -1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = \frac{1}{2} ), or for dipole displacements of the nuclei</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = -1 ), ( \Delta \ell = +1 ), ( \Delta \Lambda = -1 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = +1 ), ( \Delta \ell = -1 ), ( \Delta \Lambda = +1 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = -1 ), ( \Delta \ell = -1 ), ( \Delta \Lambda = +1 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = 0 ), ( \Delta \ell = 0 ), ( \Delta \Lambda = 0 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = 2 ), ( \Delta \ell = 0 ), ( \Delta \Lambda = 0 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = -2 ), ( \Delta \ell = 0 ), ( \Delta \Lambda = 0 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = 0 ), ( \Delta \ell = +2 ), ( \Delta \Lambda = -2 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = 2 ), ( \Delta \ell = +2 ), ( \Delta \Lambda = -2 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = -2 ), ( \Delta \ell = +2 ), ( \Delta \Lambda = -2 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = 0 ), ( \Delta \ell = -2 ), ( \Delta \Lambda = +2 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = 2 ), ( \Delta \ell = -2 ), ( \Delta \Lambda = +2 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta V_2 = -2 ), ( \Delta \ell = -2 ), ( \Delta \Lambda = +2 )</td>
<td></td>
</tr>
</tbody>
</table>

**Table I**
c) Evaluation of radial matrix elements.

The actual values of the non-vanishing matrix elements (V-6) can be worked out by direct substitution. A few cases, to show how this calculation goes, will be worked out shortly, and all other cases pertaining to \( n=\frac{3}{2}, 1 \) will be tabulated in Tables II, III. These matrix elements were calculated by Schaffer, however, he did not state at all the general selection rule (V-7), nor did he give the general formula (V-6) for any radial matrix element.

From (V-6),

\[
\langle \sigma \ell | \rho^{m} | \sigma' \ell' \rangle = N_{\sigma \ell} N_{\sigma' \ell'} \cdot \frac{(-1)^{\ell+\ell'}}{2} \frac{\Gamma(\sigma+1) \Gamma(\sigma'+1)}{\Gamma(-\frac{\Delta \ell}{2} - \nu) \Gamma(\frac{\Delta \ell}{2} - \nu)} \sum_{k} \frac{\Gamma(n+\frac{3}{2}+\frac{\Delta \ell}{2}+k+1) \Gamma(\sigma-\ell-k-n-\frac{\Delta \ell}{2}) \Gamma(\sigma'-\ell'-k-n+\frac{\Delta \ell}{2})}{\Gamma(\sigma-\ell-k+1) \Gamma(\sigma'-\ell'-k+1)}
\]

Example 1.

\( n = \frac{1}{2} \); \( \sigma' = \sigma - 1 \), \( \ell' = \ell - 1 \)

Therefore \( \sigma' - \ell' = \sigma - \ell \)

\[
\langle \sigma \ell | \rho^{m} | \sigma' \ell' \rangle = N_{\sigma \ell} N_{\sigma' \ell'} \cdot \frac{(-1)^{\ell+\ell'}}{2} \frac{\Gamma(\sigma+1) \Gamma(\sigma)}{\Gamma(3) \Gamma(-1)} \sum_{k} \frac{\Gamma(\sigma-\ell-k) \Gamma(\sigma-\ell-k+1) \Gamma(\sigma-\ell-k-1)}{\Gamma(\sigma-\ell-k+1) \Gamma(\sigma-\ell-k+1) \Gamma(\sigma-\ell-k+1)}
\]

\( \Delta \ell = -1 \), \( \sigma' = \sigma - 1 \), \( \ell' = \ell - 1 \)

Example 2.

\( \nu = \frac{1}{2} \); \( \sigma' = \sigma \); \( \ell' = \ell - 1 \)

Therefore \( \Delta \ell = -1 \), \( \sigma' - \ell' = \sigma - \ell + 1 \)

\[
\langle \sigma \ell | \rho^{m} | \sigma' \ell' \rangle = N_{\sigma \ell} N_{\sigma' \ell'} \cdot \frac{(-1)^{\ell+\ell'}}{2} \frac{\Gamma(\sigma+1) \Gamma(\sigma+1) \Gamma(\sigma+1) \Gamma(\sigma+1) \Gamma(\sigma+1)}{\Gamma(3) \Gamma(1) \Gamma(1)} \sum_{k=0}^{\sigma-\ell} \frac{\Gamma(\sigma-\ell-k) \Gamma(\sigma-\ell-k+1) \Gamma(\sigma-\ell-k+1) \Gamma(\sigma-\ell-k+1)}{\Gamma(\sigma-\ell-k+1) \Gamma(\sigma-\ell-k+1) \Gamma(\sigma-\ell-k+1) \Gamma(\sigma-\ell-k+1)}
\]
Again $k$ can only be $\sigma - \ell$.

$$
\langle \sigma \ell | p^T | \sigma' \ell' \rangle = 2 \left[ \frac{1}{(\sigma!)^2} \right] \left[ \frac{1}{(\sigma'!)^2} \right] \frac{(-1)^{2\ell-1}}{2} \left( \frac{1}{\Gamma(\ell)\Gamma(2)} \right) \frac{\sigma!}{(\sigma - \ell)!} \frac{\sigma'!}{(\sigma' - \ell')!}
$$

$$
= \left[ \frac{(\sigma - \ell)! (\sigma - \ell + 1)!}{(\sigma - \ell)!} \right]^\frac{1}{2}
$$

$$
= (\sigma - \ell + 1)^\frac{1}{2}
$$

The non-vanishing radial elements for $n=\frac{1}{2}$, $n=1$ are given in Tables II and III respectively. The values given in the tables agree with those given by Schäffer (reference 8).
| $\sigma'$ | $\ell'$ | $\langle \sigma e | \rho^{\frac{1}{2}} | \sigma' \ell' \rangle = \langle V_2 e | \pi | V_2' \ell' \rangle$ | $V_2'$ | $\ell'$ |
|---|---|---|---|---|
| $\sigma$ | $\ell - 1$ | $(\sigma - \ell + 1)^{\frac{1}{2}} = \left[ \frac{V_2 - \ell}{\frac{1}{2}} + 1 \right]^{\frac{1}{2}}$ | $V_2 + 1$ | $\ell - 1$ |
| $\sigma + 1$ | $\ell + 1$ | $-(\sigma + 1)^{\frac{1}{2}} = -\left[ \frac{V_2 + \ell}{\frac{1}{2}} + 1 \right]^{\frac{1}{2}}$ | $V_2 + 1$ | $\ell + 1$ |
| $\sigma - 1$ | $\ell - 1$ | $-\sigma^{\frac{1}{2}} = -\left[ \frac{V_2 + \ell}{\frac{1}{2}} \right]^{\frac{1}{2}}$ | $V_2 - 1$ | $\ell - 1$ |
| $\sigma$ | $\ell + 1$ | $(\sigma - \ell)^{\frac{1}{2}} = \left[ \frac{V_2 - \ell}{\frac{1}{2}} \right]^{\frac{1}{2}}$ | $V_2 - 1$ | $\ell + 1$ |

*Table II*

| $\sigma'$ | $\ell'$ | $\langle \sigma e | \sigma \sigma e \rangle = \langle V_2 e | \pi^2 | V_2' \ell' \rangle$ | $V_2'$ | $\ell'$ |
|---|---|---|---|---|
| $\sigma$ | $\ell$ | $(2\sigma - \ell + 1) = V_2 + 1$ | $V_2$ | $\ell$ |
| $\sigma + 1$ | $\ell$ | $\left\lfloor \frac{(\sigma + \frac{1}{2} + \frac{1}{2})(\sigma - \ell + \frac{1}{2} + \frac{1}{2})}{2} \right\rfloor^{\frac{1}{2}} = \left[ \frac{V_2 + \ell + 1}{\frac{1}{2}} \left( \frac{V_2 - \ell + 1}{\frac{1}{2}} + 1 \right) \right]^{\frac{1}{2}}$ | $V_2 \pm 2$ | $\ell$ |
| $\sigma + 2$ | $\ell \pm 2$ | $\left\lfloor \frac{(\sigma + 1)(\sigma + 1 \pm 1)}{2} \right\rfloor^{\frac{1}{2}} = \left[ \frac{V_2 + \ell + 1}{\frac{1}{2}} \left( \frac{V_2 + \ell + 2 \pm 1}{\frac{1}{2}} + 1 \right) \right]^{\frac{1}{2}}$ | $V_2 \pm 2$ | $\ell + 2$ |
| $\sigma + 1$ | $\ell \pm 2$ | $-2\left[ (\sigma + \frac{1}{2} + \frac{1}{2})(\sigma - \ell + \frac{1}{2} + \frac{1}{2}) \right]^{\frac{1}{2}} = -2\left[ \frac{V_2 + \ell + 1}{\frac{1}{2}} \left( \frac{V_2 - \ell + 1}{\frac{1}{2}} + 1 \right) \right]^{\frac{1}{2}}$ | $V_2$ | $\ell \pm 2$ |
| $\sigma$ | $\ell \pm 2$ | $\left\lfloor \frac{(\sigma - \ell + 1)(\sigma - \ell + 1 \pm 1)}{2} \right\rfloor^{\frac{1}{2}} = \left[ \frac{V_2 - \ell + 1}{\frac{1}{2}} \left( \frac{V_2 - \ell + 1 \pm 1}{\frac{1}{2}} + 1 \right) \right]^{\frac{1}{2}}$ | $V_2 \pm 2$ | $\ell \pm 2$ |

*Table III*
CHAPTER VI

Discussion of the Secular Equation

Having found the selection rules for the non-vanishing matrix elements, and their values, it is now possible to write out the entire matrix corresponding to the determinant (IV-4), and to diagonalize it. Since only two terms in the expansion of \( U_{\text{ne}} \) were retained, the \( \Pi \) and \( \Delta \) electronic states will be considered; \( \ell \) will be given the values of 0 and 1.

The notation used in this chapter is the following:

\[
\begin{align*}
\langle \chi_{\Lambda} | - \lambda_2^{(0)} \chi_{\Lambda'} \rangle &= D_{\Lambda\Lambda'} \\
\langle \chi_{\Lambda} | - \lambda_2^{(1)} \chi_{\Lambda'} \rangle &= Q_{\Lambda\Lambda'}^d \\
\langle \chi_{\Lambda} | - \lambda_2^{(2)} \chi_{\Lambda'} \rangle &= Q_{\Lambda\Lambda'}^q
\end{align*}
\]

The \( \chi_{\Lambda} \) were introduced in equation (III-2).

The full matrix, showing the non-vanishing matrix elements, is given on page 38. The label of each row or column is \((\Lambda, \ell)\); the symbol \(d\) indicates a non-vanishing dipole element and the \(q\) a quadrupole element. The diagonal non-vanishing quadrupole element. The diagonal non-vanishing quadrupole elements have been left out.

The same matrix is given again on page 39, with the rows and columns rearranged. In both matrices

\[ E_{ij} = E_{ei} + E_{nj} \]

Some obvious facts can be immediately seen from the latter form of the matrix. They are the following:

1) the entire matrix can be grouped into submatrices, each sub-matrix being characterized by the value of \( |k| = |\Lambda + \ell| \).
The full matrix
The matrix with rows and columns rearranged.
That is, it can be broken up as follows:

Moreover, the submatrix for $K = +1$ is identical to that for $K = -1$, and that for $K = 2$ is identical to that for $K = -2$, etc. That this subdivision is possible is a result of the general selection rules given in table 1 of Chapter V, and it will always occur, no matter what the approximation is.

2) If higher order terms in the Hamiltonian were considered, then it would be more obvious that each of the above submatrices could be re-arranged in the following manner:

The terms in the upper left corner matrix represent mixing due to quadrupole interaction between $\Sigma$ and $\Delta$ electronic states, and these would be very much negligible compared to the dipole terms. But, the lower right submatrix gives the Renner splitting of the degenerate states.
The other submatrices take on similar shape, and the meaning of each term can be similarly read from it. Of course, this is obvious only when higher approximations are considered.
a) $K = 0$

In the approximation made, the Renner splitting for the electronic state can be obtained and this is found from the submatrix in which $K = 0$, which is

$$
\begin{pmatrix}
E_{e0} + k\nu_2 + Q_{e0}^d & -\frac{1}{2}D_{01} \\
-\frac{1}{2}D_{10} & E_{e1} + 2k\nu_2 + 2Q_{11}^d \\
-\frac{1}{2}D_{10} & \frac{1}{2}Q_{11}^d & E_{e1} + 2k\nu_2 + 2Q_{11}^d
\end{pmatrix}
$$

Performing a unitary transformation by the matrix

$$
U = \begin{pmatrix}
1 & 0 & 0 \\
0 & \frac{1}{\sqrt{\lambda}} & \frac{1}{\sqrt{\lambda}} \\
0 & -\frac{1}{\sqrt{\lambda}} & \frac{1}{\sqrt{\lambda}}
\end{pmatrix}
$$

the matrix for $K=0$ becomes

$$
\begin{pmatrix}
E_{e0} + k\nu_2 + Q_{e0}^d & 0 & -\frac{D_{01}}{\sqrt{\lambda}} \\
0 & E_{e1} + 2k\nu_2 + Q_{11}^d + \frac{1}{2}Q_{11}^d & 0 \\
-\frac{D_{10}}{\sqrt{\lambda}} & 0 & E_{e1} + 2k\nu_2 + Q_{11}^d - \frac{1}{2}Q_{11}^d
\end{pmatrix}
$$

Thus the Renner splitting of the vibronic state characterized by $\Lambda = 1$, $\ell = 1 = \sqrt{\lambda}$ is

$$Q_{11}^d$$
Moreover the energy values of the states

\[ \Lambda = \ell = 0 \quad \text{and} \quad \Lambda = \ell = 1 \]

are

\[
\begin{align*}
E_1 &= \frac{1}{\alpha} \left\{ [E_{e1} + E_{e1} + 3 \hbar \nu_a + Q_{00} - \frac{1}{2} Q_{11}^{nd}] + \right. \\
&\quad \left. \left[ (E_{e0} - E_{e1} - \hbar \nu_a + Q_{11}^{d} - Q_{11}^{d} + \frac{1}{2} Q_{11}^{nd})^2 + 2 \left| D_{01} \right|^2 \right] \right\}^{\frac{1}{2}} \\
E_2 &= E_{e1} + 2 \hbar \nu_a + Q_{11}^{d} + \frac{1}{2} Q_{11}^{nd} \\
E_3 &= \frac{1}{\alpha} \left\{ [E_{e0} + E_{e1} + 3 \hbar \nu_a + Q_{00} - \frac{1}{2} Q_{11}^{nd}] - \right. \\
&\quad \left. \left[ (E_{e0} - E_{e1} - \hbar \nu_a + Q_{00} - Q_{11}^{d} + \frac{1}{2} Q_{11}^{nd})^2 + 2 \left| D_{01} \right|^2 \right] \right\}^{\frac{1}{2}}
\end{align*}
\]
b) \( K = 1 \)

The matrix for \( K = 1 \) is

\[
\begin{pmatrix}
E_{ee} + 2\mu_2 + 2Q_{x0} & \frac{1}{2\sqrt{2}} D_{01} & \frac{1}{2} Q_{20}^d \\
\frac{1}{2\sqrt{2}} D_{01} & E_{e1} + \mu_2 + Q_{11}^d & -\frac{1}{2} D_{21} \\
\frac{1}{2} Q_{20}^d & -\frac{1}{2} D_{12} & E_{e2} + 2\mu_2 + 2Q_{22}^d
\end{pmatrix}
\]

This matrix will give the corrected energy values to the vibronic states for which

\[
\lambda = 0, \quad \ell = 1 ;
\]

\[
\lambda = 1, \quad \ell = 0 ;
\]

\[
\lambda = 2, \quad \ell = 1 .
\]

The dipole term \( D_{01} \) mixes the electronic \( \Sigma \) and \( \Pi \) states and \( D_{21} \) mixes the electronic \( \Pi \) and \( \Delta \) states, whereas the quadrupole term \( Q_{20}^d \) mixes the \( \Sigma \) and \( \Delta \) states; hence \( Q_{20}^d \) can be neglected compared to the dipole terms, and this is even more obvious from the expressions \( \lambda_{21}^{(1)} \) and \( \lambda_{22}^{(2)} \) given in Chapter II. \( \lambda_{21}^{(1)} \) occurs in the expression for \( D_{\Sigma\Sigma} \) and it contains terms of the order of \( \frac{1}{R_{ie}^2} \), whereas \( \lambda_{22}^{(2)} \) occurring in \( Q_{\Pi\Pi}^d \) contains terms of the order of \( \frac{1}{R_{ie}^3} \).

The matrix for \( K = 1 \) becomes

\[
\begin{pmatrix}
E_{ee} + 2\mu_2 + 2Q_{x0} & \frac{1}{2\sqrt{2}} D_{01} & 0 \\
\frac{1}{2\sqrt{2}} D_{01} & E_{e1} + \mu_2 + Q_{11}^d & -\frac{1}{2} D_{21} \\
0 & -\frac{1}{2} D_{12} & E_{e2} + 2\mu_2 + 2Q_{22}^d
\end{pmatrix}
\]

The eigenvalues of this matrix are the roots of a cubic equation which will be called \( E_4 \), \( E_5 \) and \( E_6 \).
c) $K = 2$

The matrix for $K = 2$ is

\[
\begin{pmatrix}
E_e + 2\hbar \nu_2 + 2Q_{11}^d & -\frac{1}{2} D_{12} \\
-\frac{1}{2} D_{21} & E_e + 2\hbar \nu_2 + 2Q_{22}^d
\end{pmatrix}
\]

which will give the corrected energy values of the vibronic states

$\Lambda = 1, \ell = 1$; $\Lambda = 2, \ell = 0$

given by

\[
\begin{align*}
E_7 &= \frac{1}{2} \left\{ (E_e + E_{e2} + 2\hbar \nu_2 + 2Q_{11}^d + Q_{22}^d) + \\
& \quad \left[ (E_e - E_{e2} + \hbar \nu_2 + 2Q_{11}^d - Q_{22}^d)^2 + |D_{12}|^2 \right]^{1/2} \right\} \\
E_8 &= \frac{1}{2} \left\{ (E_e + E_{e2} + 2\hbar \nu_2 + 2Q_{11}^d + Q_{22}^d) - \\
& \quad \left[ (E_e - E_{e2} + \hbar \nu_2 + 2Q_{11}^d - Q_{22}^d)^2 + |D_{12}|^2 \right]^{1/2} \right\}
\end{align*}
\]
d) $K = 3$

For this case, the matrix element is just $E_{e2} + 2 \delta \mu_2 + 2 Q^d$, which is just the energy value of the vibronic state $\Lambda = 2, \ell = 1$ with a slight correction to it. In the approximation made, the splitting of this state could not be obtained.
Summary:

The result of all the calculations can best be seen in an energy diagram. Diagram 1 on the following page gives the unperturbed energy levels and Diagram 2 the corrected levels. The arrows indicate allowed transitions. Neither diagrams are drawn to scale because the energy values are not known.

The measurable quantities are

1) the Renner splitting of the $\Pi$ state, that is $E_2 - E_3$

2) the relative intensities of the five transition lines given. (These can be obtained in terms of the six parameters $Q_{00}^d$, $Q_{11}^d$, $Q_{11}^a$, $Q_{22}^d$, $D_{01}$, and $D_{12}$ since the eigenvalues of the matrices for $K = 0, 1, 2$ are given; from these eigenvalues it is possible to construct the unitary matrices that will diagonalize the matrices for $K = 0, 1, 2$.)

Thus it has been possible to obtain for the linear $XY_2$ molecule such as CO$_2$ and CS$_2$ an explicit expression of the Renner splitting of the electronic $\Pi$ state and the relative intensities of the spectral lines between the $\Sigma$, $\Pi$, and $\Delta$ electronic states in terms of six parameters.
APPENDIX

Associated Laguerre Polynomials

The wave equation for $\Psi_n (g_{2a}, g_{2b})$ is, from Chapter III, Part (b),

$$(A-1) \left[ -\left( \frac{1}{2} \frac{d^2}{d\varphi^2} (g_{2a} g_{2b}^2) + \frac{1}{2} \frac{d}{d\varphi} (g_{2a}^2 + g_{2b}^2 - \varepsilon) \right) \Psi_n \right] = 0$$

In polar co-ordinates $(q_r, \varphi_n)$ defined by

$$q_{2b} = q_r \cos \varphi_n$$
$$q_{2a} = q_r \sin \varphi_n$$

equation (A-1) becomes

$$\left[ \frac{1}{4} \frac{d^2}{d\varphi^2} (q_r^2 \varphi_n^2) + \frac{1}{8} \frac{d}{d\varphi} (\varepsilon - q_r^2) \right] \Psi = 0$$

(The subscripts $n$ on $\Psi_n$ and 2 on $q_r$ will be omitted in this appendix.)

$\Psi$ is separable into

$$R(q) \Phi(\varphi)$$

and

$$\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{\pm i\varphi}$$

with $l = 0, 1, 2 \ldots$, a positive integer. The radial function $R$ satisfies

$$\left( \frac{d^2}{d\varphi^2} + \frac{1}{8} \frac{d}{d\varphi} + \varepsilon - q_r^2 - \frac{\varepsilon^2}{q_r^2} \right) R = 0$$

Putting

$$R(q) = e^{-q_r^2} F(q)$$

$F(q)$ satisfies

$$\left[ \frac{d^2}{d\varphi^2} + (\frac{1}{8} - 2q_r) \frac{d}{d\varphi} + (\varepsilon - 2 - \frac{\varepsilon^2}{q_r^2}) \right] F = 0$$

In trying to find a power series solution, it is convenient to put

$$F(q) = q^{\frac{\varepsilon}{2}} f(q)$$

and

$$\left[ \frac{d^2}{d\varphi^2} + \left[ (2l + 1) \frac{1}{8} - 2q_r \right] \frac{d}{d\varphi} + (\varepsilon - 2 \varepsilon - 2) \right] f = 0$$
In terms of the variable \( \rho = q^2 \),
\[
\ell(q) = g(\rho)
\]
and
\[
\left[ \rho \frac{d^2}{d\rho^2} + (\ell+1-\rho) \frac{d}{d\rho} + \frac{1}{4} (\ell - 2\ell - 2) \right] g = 0
\]
A power series solution gives
\[
\ell = 2 \left( V_\lambda + 1 \right)
\]
with \( V_\lambda = 0, 1, 2, \ldots \)
\[
\ell = V_\lambda, V_\lambda - 2, V_\lambda - 4, \ldots, 1 \text{ or } 0.
\]
Thus
\[
E_\lambda = \frac{\ell \nu_\lambda}{2}
\]
or (A-2)
\[
E_\lambda = \ell \nu_\lambda \left( V_\lambda + 1 \right)
\]
The equation for \( g \) can be written as
\[
\left[ \rho \frac{d^2}{d\rho^2} + (\ell+1-\rho) \frac{d}{d\rho} + (\sigma - \ell) \right] g = 0
\]
with \( \sigma - \ell = \frac{V_\lambda - \ell}{2} \)
or \( \sigma = \frac{V_\lambda + \ell}{2} \)
which is the equation of the associated Laguerre polynomials \( L^\ell_\sigma (\rho) \);
\[
g(\rho) = L^\ell_\sigma (\rho)
\]
Thus
\[
(A-3) \left\{ \begin{array}{l}
R_{V_\lambda} e(q) = R_{\sigma \ell} (\rho) \\
= N_{\sigma \ell} e^{-\rho/2} \rho^{\ell/2} L^\ell_\sigma (\rho)
\end{array} \right.
\]
The generating function of the Laguerre polynomials is given by
\[
U(\rho, u) = \sum_{\sigma = \ell}^\infty L^\ell_\sigma (\rho) \frac{u^\sigma}{\sigma!}
\]
\[
= (-u)^\ell \left[ \exp \left( -\frac{\rho u}{1-u} \right) \right] \frac{1}{(1-u)^{\ell+1}}
\]
The normalizing factor $N_{\sigma\epsilon}$ is found to be

$$N_{\sigma\epsilon} = \sqrt{2} \left[ \frac{(\sigma - \epsilon)!}{(\sigma!)^{\frac{3}{2}}} \right]^{\frac{1}{2}}$$
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