A STUDY OF THE RENNER EFFECT

IN THE LINEAR XY_2 MOLECULE

by

COSMO CARLONE

B.Sc.(Hon.), University of Windsor, 1963

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

PHYSICS

We accept this thesis as conforming to the

required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1965

In presenting this thesis in partial fulfilment of

the requirements for an advanced degree at the University of

British Columbia, I agree that the Library shall make it freely

available for reference and study. I further agree that per-

mission for extensive copying of this thesis for scholarly

purposes may be granted by the Head of my Department or by

his representatives. It is understood that copying or publi-

cation of this thesis for financial gain shall not be allowed

without my written permission.

Department of ___Physics___

The University of British Columbia,
Vancouver 8, Canada

Date ___April 21, 1965___

ABSTRACT

A variational principle is applied to the Schroedinger 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 Π state is obtained.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

INTRODUCTION

In linear molecules, to the zeroeth 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 Λ $\hbar$. For

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

the states are called

$$\Sigma, \Pi, \Delta, \cdots$$

respectively; states higher than Δ are not usually encountered. The Σ
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 $\pm$ Λ $\hbar$.

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.[1]

The method customarily used to obtain expressions for the Renner
splitting has been the Born-Oppenheimer approximation.[2] However, this
method leads to a pair of second order coupled equations;[3,4] 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 Schroedinger 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 N is the total number of electrons and
N′ 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,[5]
that is, if S_α is the α th normal co-ordinate of a molecule, then the
kinetic energy is

$$T = \frac{1}{2} \sum_\alpha m_\alpha \dot{S}_\alpha^2 ,$$

where m_α is a reduced mass associated with S_α (see Chapter I); similarly,
the potential energy contains the sum of quadratic terms in S_α [5]
if harmonic oscillations are considered.

The set of displacements, or modes of vibration S_α , 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 $\ell\hbar$ be the nuclear angular momentum, with ℓ = 0, ±1, ±2, ... then

$$K = |\Lambda + \ell| = 0, 1, 2, \cdots$$

characterizes states comprising the nuclear vibrations and electronic motion, that is, the vibronic states. Likewise, vibronic states are called

$$\Sigma, \Pi, \Delta, \cdots$$

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 acetyline 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 XY_2 Linear Molecule

The XY_2 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 $+S_{2a}$ ($+S_{2b}$) is the displacement of the X atom in the $y(x)$ direction, then again by conservation of linear momentum, each Y atom must move $-\dfrac{M_2}{2M_1} S_{2a} (S_{2b})$.

Mode 3:

If $+S_3$ is the displacement of atom X in the Z direction, then each Y atom must move $-S_3 \dfrac{M_2}{2M_1}$ in the Z direction.

5
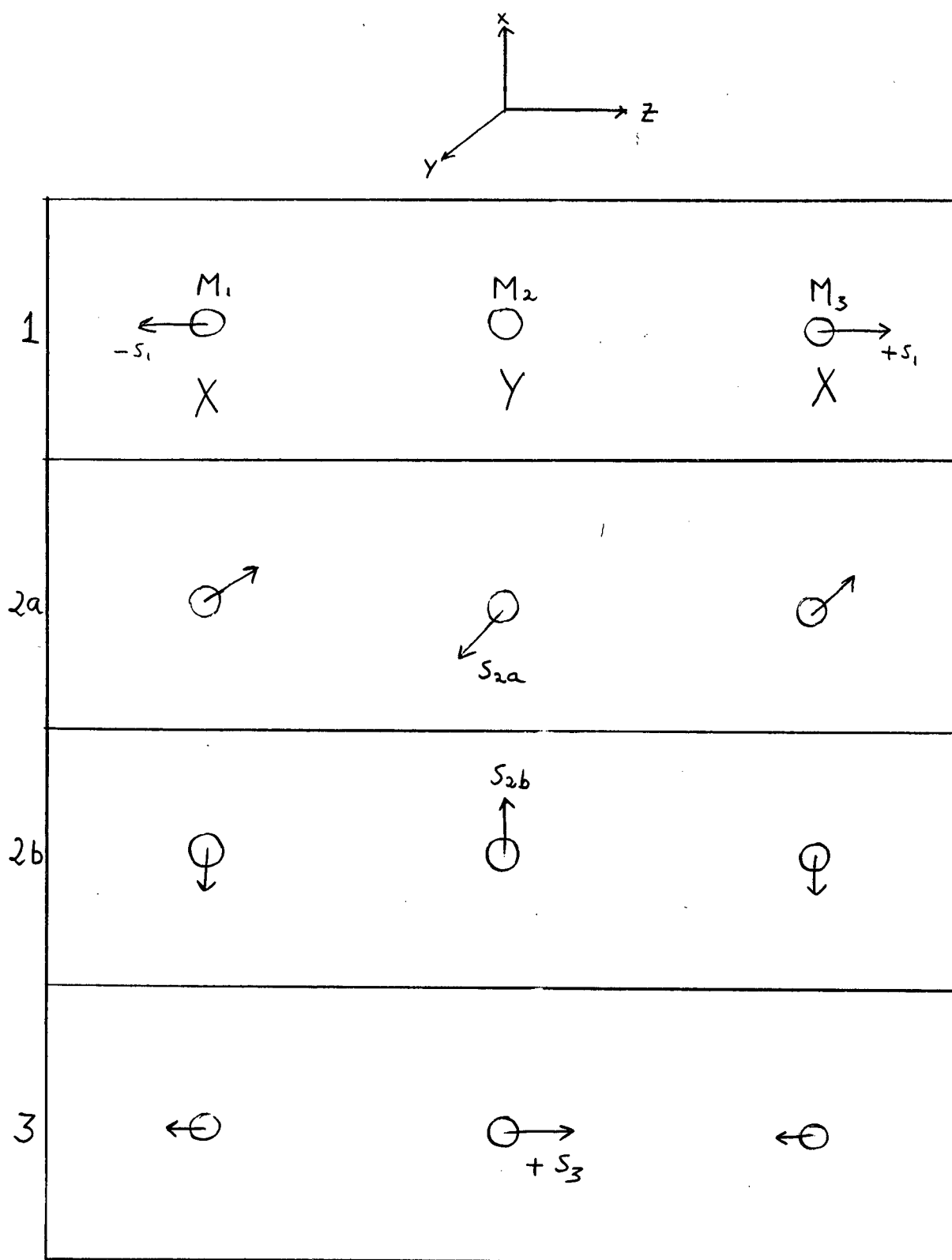
Figure 1

The four normal modes of the linear XY_2 molecule.

·Let

$$u = \frac{M_2}{2M_1} ,$$

then the total displacement of the XY_2 linear molecule can be summarized as

in·Chart I.

The nuclear kinetic energy is given by

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

$$= \frac{1}{2}\left\{ \left[(u\,\dot{S}_{2b})^2 + (u\,\dot{S}_{2a})^2 + (u\,\dot{S}_3 + \dot{S}_1)^2\right]M_1 \right.$$

$$+ M_2\left[\dot{S}_{2b}^2 + \dot{S}_{2a}^2 + \dot{S}_3^2\right]$$

$$\left. + M_1\left[(u\,\dot{S}_{2b})^2 + (u\,\dot{S}_{2a})^2 + (\dot{S}_1 - u\,\dot{S}_3)^2\right]\right\}$$

$$T_n = \frac{1}{2}m_1\dot{S}_1^2 + \frac{1}{2}m_2(\dot{S}_{2a}^2 + \dot{S}_{2b}^2) + \frac{1}{2}m_3\dot{S}_3^2 \qquad (I-1)$$

where

$$m_1 = 2M_1$$

$$m_2 = m_3 = M_2(1+u)$$

Similarly·the potential energy is bilinear in the Cartesian co-ordinates,

but by definition of the normal co-ordinates,[5] it becomes

$$V = \frac{1}{2}\lambda_1 S_1^2 + \frac{1}{2}\lambda_2 (S_{2a}^2 + S_{2b}^2) + \frac{1}{2}\lambda_3 S_3^2 \qquad (I-2)$$

It is hereby assumed that the molecule executes simple harmonic oscillations

only.

$x_1 = - u S_{2b}$	$y_1 = - u S_{2a}$	$z_1 = - S_1 - u S_3 - \ell$
$x_2 = S_{2b}$	$y_2 = + u S_{2a}$	$z_2 = + S_3$
$x_3 = - u S_{2b}$	$y_3 = - u S_{2a}$	$z_3 = + S_1 - u S_3 + \ell$

Chart 1

The displacements of the Linear XY_2 molecule
in terms of its normal co-ordinates

Note: 2ℓ is the equilibrium distance
between the Y 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

$$\mathcal{H} = T_e + U_{ee} + T_n + U_{nn} + U_{ne} \tag{II-1}$$

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[6] 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 6 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 $\underline{Q}$. (Vector quantities will be denoted by a bar under the quantity.) Let

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

In the static approximation, one solves for

$$H_e(\underline{Q}_0)|\alpha_i(\underline{Q}_0)\rangle = [T_e + U_{ee} + V(\underline{Q}_0)]|\alpha_i(\underline{Q}_0)\rangle$$
$$= E_{ei}(\underline{Q}_0)|\alpha_i(\underline{Q}_0)\rangle \qquad \Big\} (II-2)$$

where $\{\underline{Q}_0\}$, the equilibrium position of the nuclei is determined by solving

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

and putting

$$\frac{\partial E_{ei}(\underline{Q})}{\partial \underline{Q}}\bigg|_{\underline{Q}=\underline{Q}_0} \equiv \frac{\partial E_{ei}}{\partial \underline{Q}_0} = 0$$

The $|\alpha_i(\underline{Q}_0)\rangle$ are the degenerate electronic states and the $\underline{Q}_0$ dependence will be omitted henceforth. Since the $\{\underline{Q}_0\}$ are assumed to be independent of the electronic states, which is a very good approximation for the CO_2, CS_2 molecules, the $|\alpha_i\rangle$ form a complete set.

The nuclear Hamiltonian is

$$H_n = T_n + \frac{1}{2}\frac{\partial^2 E_{ei}}{\partial \underline{Q}_0 \partial \underline{Q}_0} : \delta\underline{q}\,\delta\underline{q} \qquad (II-3)$$

where

$$\underline{Q} = \underline{Q}_0 + \delta\underline{q}$$

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

$$H_{en} = V(\underline{Q}) - V(\underline{Q}_0) - \frac{1}{2} \frac{\partial^2 E_{el}}{\partial Q_0 \partial Q_0} \delta q \, \delta q$$

Since the nuclear displacements δq are much smaller than the equilibrium nuclear separations and the distance from any electron to any nucleus, $V(\underline{Q})$ can be expanded about $\underline{Q}_0$ and

$$H_{en} = \frac{\partial V}{\partial Q_0} \delta q + \frac{1}{2} \frac{\partial^2 V}{\partial Q_0 \partial Q_0} \delta q \, \delta q + \cdots - \frac{1}{2} \frac{\partial^2 E_{el}}{\partial Q_0 \partial Q_0} \delta q \, \delta q . \qquad (\text{II-4})$$

Explicit expressions for $\frac{\partial V}{\partial Q_0}$ and $\frac{\partial^2 V}{\partial Q_0 \partial Q_0}$ will now be obtained for linear molecules such as CO_2, CS_2.

a) Expansion of U_{ne}

The explicit expression for U_{ne} is

$$U_{ne} = -e^2 \sum_{i=1}^{N} \sum_{i'=1}^{N'} \frac{z_{i'}}{r_{ii'}}$$

where

$z_{i'}$ is the charge number on the i'th nucleus,

$r_{ii'}$ is the distance between the i'th nucleus and the ith electron.
Since the vibration of each nucleus is small, $r_{ii'}$ 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

$$\underline{r}_1 = -\ell \,\hat{k} , \qquad \underline{r}_2 = 0 , \qquad \underline{r}_3 = \ell \,\hat{k} .$$
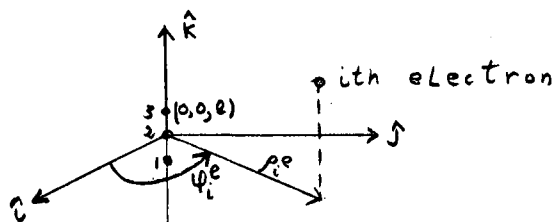
Figure I

Let $R'_{ii'}$ be the position vector of the ith electron from the equilibrium position of the i'th nucleus. Put

$$a\, R'_{ii'} = R_{ii'} = (z_i + z_{i'})\hat{k} + \underline{\rho}_i^{\,e}$$

where

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

$\qquad\qquad$ (a has been introduced to have all co-ordinates

$\qquad\qquad\qquad$ dimensionless)

$\qquad\qquad \underline{\rho}_i^{\,e}$ is the radial vector from the Z axis to the ith

$\qquad\qquad\qquad$ electron.

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

$$a\, \underline{Q}'_1 = \underline{Q}_1 = -\mu\, \underline{q}_2 - (q_1 + \mu\, q_3)\hat{k}$$

$$a\, \underline{Q}'_2 = \underline{Q}_2 = \underline{q}_2 + q_3\,\hat{k}$$

$$a\, \underline{Q}'_3 = \underline{Q}_3 = -\mu\, \underline{q}_2 + (q_1 - \mu\, q_3)\hat{k}$$

where the q's are dimensionless normal co-ordinates analogous to the S's with

$$\underline{q}_2 = q_{2b}\,\hat{\imath} + q_{2a}\,\hat{\jmath} = a\left(S_{2b}\,\hat{\imath} + S_{2a}\,\hat{\jmath}\right)$$

The interaction potential is

$$U_{me} = -e^2 \sum_i \sum_{i'} \frac{z_{i'}}{a^{-1}|R_{ii'} - Q_{i'}|}$$

$$= -e^2 a \sum_i \sum_{i'} \frac{z_{i'}}{R_{ii'}} \left[1 - 2\frac{R_{ii'}\cdot Q_{i'}}{R_{ii'}^2} + \left(\frac{Q_{i'}}{R_{ii'}}\right)^2\right]^{-\frac{1}{2}}$$

$$= -e^2 a \sum_i \sum_{i'} \frac{z_{i'}}{R_{ii'}} \left[1 - 2\frac{Q'_{i'}}{R_{ii'}}\cos(\underline{Q}_{i'}\cdot \underline{R}_{ii'}) + \left(\frac{Q'_{i'}}{R_{ii'}}\right)^2\right]^{-\frac{1}{2}}$$

But $\left(1 - 2hz + z^2\right)^{-\frac{1}{2}}$ is the generating function of the Legendre polynomials $P_\omega(z)$ if

$$|2hz - z^2| < 1 \quad \text{and} \quad \left[|2hz| + |z^2|\right] < 1 \qquad \cdots \, 7$$

i.e. $\left(1 - 2hz + z^2\right)^{-\frac{1}{2}} = \sum_{\omega=0}^{\infty} P_\omega(z)\, h^\omega$

Since the displacement of the nuclei is much smaller than the distance from the equilibrium position of the nuclei to the electrons,

$$Q_i \ll R_{ii'}$$

and

$$U_{me} = -e^2 a \sum_i \sum_{i'} \frac{z_{i'}}{R_{ii'}} \sum_{\omega=0}^{\infty} P_\omega\left(\cos(\underline{Q}_i \cdot \underline{R}_{ii'})\right)\left(\frac{Q_i}{R_{ii'}}\right)^\omega .$$

Let

$$U_{me}^{(\omega)} = -e^2 a \sum_i \sum_{i'} \frac{z_{i'}}{R_{ii'}} P_\omega\left(\cos(\underline{Q}_i \cdot \underline{R}_{ii'})\right)\left(\frac{Q_i}{R_{ii'}}\right)^\omega .$$

The first few Legendre polynomials $P_\omega(z)$ are

$$P_0(z) = 1$$
$$P_1(z) = z$$
$$P_2(z) = \frac{1}{2}\left(3z^2 - 1\right) .$$

Thus,

$$U_{me}^{(0)} = -e^2 a \sum_i \sum_{i'} \frac{z_{ii'}}{R_{ii'}}$$

$$U_{me}^{(1)} = -e^2 a \sum_i \left\{ \left[(\ell - z_i)\frac{z_1}{R_{i1}^3} + (\ell + z_i)\frac{z_3}{R_{i3}^3} \right] q_1 \right.$$

$$+ \left[u(\ell - z_i)\frac{z_1}{R_{i1}^3} + \frac{z_1}{R_{i2}^3} z_i - u(\ell + z_i)\frac{z_3}{R_{i3}^3} \right] q_3$$

$$\left. + \left[\frac{z_2}{R_{i2}^3} - u\left(\frac{z_1}{R_{i1}^3} + \frac{z_3}{R_{i3}^3}\right) \right] \rho_i^e \, q_2 \cos(\varphi_i^e - \varphi_\eta) \right\}$$

where ψ_n is the azimuthal angle of q_2 .

Let

$$e^2 a \sum_i \left[\mu(\ell - z_i) \frac{\mathfrak{z}_1}{R_{i1}^3} + (\ell + z_i) \frac{\mathfrak{z}_3}{R_{i3}^3} \right] = \lambda_1^{(1)}$$

$$e^2 a \sum_i \left[\mu(\ell - z_i) \frac{\mathfrak{z}_1}{R_{i1}^3} + \frac{\mathfrak{z}_2}{R_{i2}^3} z_i - \mu(\ell + z_i) \frac{\mathfrak{z}_3}{R_{i3}^3} \right] = \lambda_3^{(1)}$$

$$\left\{ \left(\sum_i a_i \cos \psi_i^e \right)^2 + \left(\sum_i a_i \sin \psi_i^e \right)^2 \right\}^{\frac{1}{2}} = \lambda_2^{(1)}$$

$$\tan \psi_e = \frac{\sum_i a_i \sin \psi_i^e}{\sum_i a_i \cos \psi_i^e}$$

with

$$a_i = e^2 a \left[\frac{\mathfrak{z}_2}{R_{i2}^3} - \mu \left(\frac{\mathfrak{z}_1}{R_{i1}^3} + \frac{\mathfrak{z}_3}{R_{i3}^3} \right) \right] \rho_i^e .$$

Then

$$U_{me}^{(1)} = -\left[\lambda_1^{(1)} q_1 + \lambda_2^{(1)} \cos(\psi_e - \psi_n) q_2 + \lambda_3^{(1)} q_3 \right] .$$

$$U_{me}^{(2)} = -e^2 a \sum_i \left(\left\{ \frac{3}{4} \left[\mathfrak{z}_1 \mu^2 \left(\frac{1}{R_{i1}^5} + \frac{1}{R_{i3}^5} \right) + \frac{\mathfrak{z}_2}{R_{i2}^5} \right] \rho_i^{e\,2} \cos 2(\psi_i^e - \psi_n) \right\} q_2^2 \right.$$

$$+ \frac{3}{2} \left\{ 2\mu^2 \mathfrak{z}_1 \left(\frac{z_i - \ell}{R_{i1}^5} - \frac{z_i + \ell}{R_{i3}^5} \right) q_1 + \left[\frac{2 \mathfrak{z}_2 z_i}{R_{i2}^5} + 2\mu^2 \mathfrak{z}_1 \left(\frac{z_i - \ell}{R_{i1}^5} + \frac{z_i + \ell}{R_{i3}^5} \right) \right] \times \right.$$

$$\left. q_3 \right\} \rho_i^e \cos(\psi_i^e - \psi_n) q_2$$

$$+ \frac{3}{4} \left\{ \left[\mathfrak{z}_1 \mu^2 \left(\frac{1}{R_{i1}^5} + \frac{1}{R_{i3}^5} \right) + \frac{\mathfrak{z}_2}{R_{i2}^5} \right] \rho_i^{e\,2} - \frac{1}{2} \left[\mathfrak{z}_1 \mu^2 \left(\frac{1}{R_{i1}^3} + \frac{1}{R_{i3}^3} \right) + \frac{\mathfrak{z}_2}{R_{i2}^3} \right] \right\} q_2^2$$

$$+ \frac{1}{2} \mathfrak{z}_1 \left[3 \left(\frac{(z_i - \ell)^2}{R_{i1}^5} + \frac{(z_i + \ell)^2}{R_{i3}^5} \right) - \left(\frac{1}{R_{i1}^3} + \frac{1}{R_{i3}^3} \right) \right] q_1^2$$

$$+ \frac{1}{2} \left[3\mu^2 \mathfrak{z}_1 \left(\frac{(z_i - \ell)^2}{R_{i1}^5} + \frac{(z_i + \ell)^2}{R_{i3}^5} \right) + \left(\frac{3 z_i^2}{R_{i2}^5} - \frac{1}{R_{i2}^3} \right) \mathfrak{z}_2 - \mathfrak{z}_1 \mu^2 \left(\frac{1}{R_{i1}^3} + \frac{1}{R_{i3}^3} \right) \right] q_3^2$$

$$+ \mu \left[3 \mathfrak{z}_1 \left(\frac{(z_i - \ell)^2}{R_{i1}^5} - \frac{(z_i + \ell)^2}{R_{i3}^5} \right) - \mathfrak{z}_1 \left(\frac{1}{R_{i1}^3} - \frac{1}{R_{i3}^3} \right) \right] q_1 q_3 \right)$$

Alternatively, $U_{ne}^{(2)}$ can be written as

$$U_{ne}^{(2)} = -\left[\frac{1}{2}\lambda_1^{(2)}q_1^2 + \frac{1}{2}\lambda_2^{(2)}q_2^2 + \frac{1}{2}\lambda_3^{(2)}q_3^2 + \lambda_{22}^{(2)}q_2^2\cos 2(\psi_e' - \psi_n) + \right.$$

$$\left. + \lambda_{12}^{(2)}q_1 q_2 \cos(\psi_e'' - \psi_n) + \lambda_{13}^{(2)}q_1 q_3 \cos(\psi_e''' - \psi_n) + \lambda_{23}^{(2)}\cos(\psi_e'''' - \psi_n)q_2 q_3\right]$$

where

$$\tan 2\psi_e' = \frac{\sum_i\left\{\frac{3}{4}\left[3\mu^2\left(\frac{1}{R_{i1}^5} + \frac{1}{R_{i3}^5}\right) + \frac{32}{R_{i2}^5}\right]\rho_i^{e^2}\sin 2\psi_i^e\right\}}{\sum_i\left\{\frac{3}{4}\,3\mu^2\left(\frac{1}{R_{i1}^5} + \frac{1}{R_{i3}^5}\right) + \frac{32}{R_{i2}^5}\right]\rho_i^{e^2}\cos 2\psi_i^e\right\}}$$

$$\lambda_{22}^{(2)} = e^2 a\left[\left\{\sum_i \frac{3}{4}\left[3\mu^2\left(\frac{1}{R_{i1}^5} + \frac{1}{R_{i3}^5}\right) + \frac{32}{R_{i2}^5}\right]\rho_i^{e^2}\sin 2\psi_i^e\right\}^2\right.$$

$$\left. + \left\{\sum_i \frac{3}{4}\left[3\mu^2\left(\frac{1}{R_{i1}^5} + \frac{1}{R_{i3}^5}\right) + \frac{32}{R_{i2}^5}\right]\rho_i^{e^2}\cos 2\psi_i^e\right\}^2\right]^{\frac{1}{2}}$$

and similarly for

$$\tan\psi_e'',\ \tan\psi_e''',\ \tan\psi_e'''',\ \lambda_{13}^{(2)},\ \lambda_{23}^{(2)},\ \lambda_1^{(2)},\ \lambda_2^{(2)},\ \lambda_3^{(2)}.$$

$U_{ne}^{(0)}$ represents the interaction between the electrons and the nuclei fixed at their equilibrium position; $U_{ne}^{(0)} + U_{nn}^{(0)} \equiv V(\underline{Q}_0)$. Thus, the electronic eigenstates $|\alpha_i(\underline{Q}_0)\rangle$ 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 q_1 and q_3 do not remove the cylindrical symmetry and they will be omitted; similarly the terms involving $q_1 q_2$ and $q_2 q_3$ in $U_{ne}^{(2)}$ will be omitted because these represent a coupling between the q_1 (q_3) and q_2 vibration with the electronic motion and will be considered a second order effect. Thus

$$U_{ne}^{(1)} = - \lambda_2^{(1)} q_2 \cos(\varphi_e - \varphi_n)$$

$$U_{ne}^{(2)} = - \frac{1}{2} \left[\lambda_2^{(2)} q_2^2 + \lambda_{22}^{(2)} q_2^2 \cos 2(\varphi_e' - \varphi_n) \right].$$

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

$$U_{nn}^{(0)} = \frac{e^2 a}{\ell} \left(\frac{3_1 3_3}{2} + 3_2 3_3 + 3_1 3_2 \right)$$

$$U_{nn}^{(1)} = \frac{e^2 a}{2 \ell^2} \left\{ - \left(\frac{3_1 3_3}{2} + 3_2 3_3 + 3_1 3_2 \right) q_1 + (1 + u)(3_2 3_3 - 3_1 3_2) q_3 \right\}$$

$$U_{nn}^{(2)} = \frac{e^2 a}{2 \ell^3} \left\{ 3_1 3_3 q_1^2 - 2(1 + u)^2 3_2 3_3 q_2^2 \right\}$$

Omitting the terms in q_1 and q_3 ,

$$U_{nn}^{(1)} = 0$$

$$U_{nn}^{(2)} = - \frac{e^2 a}{\ell^3} (1 + u)^2 3_2 3_3 q_2^2$$

c) Explicit expression for H_{en}

Incorporating into $\lambda_2^{(2)}$ the coefficient of q_2^2 from $U_{nn}^{(2)}$ and also

$$\frac{\partial^2 E_{ei}}{\partial q_2 \partial q_2} ,$$

$$H_{en} = - \lambda_2^{(1)} q_2 \cos(\varphi_e - \varphi_n) - \frac{1}{2} \left[\lambda_2^{(2)} q_2^2 + \lambda_{22}^{(2)} q_2^2 \cos 2(\varphi_e' - \varphi_n) \right]$$

$$(\text{II} - 5)$$

CHAPTER III

Unperturbed Eigenstates

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

$$(III-1) \qquad \mathcal{H} = H_e + H_n + H_{en}$$

where

$$H_e = T_e + U_{ee} + U_{ne}^{(0)} + U_{nn}^{(0)}$$

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

$$H_n = T_n + \frac{1}{2} \frac{\partial^2 E_{ei}}{\partial \underline{a}_0 \partial \underline{a}_0} \, \delta q \, \delta q$$

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 g_2 only; since the energy of the nuclear states does not depend on the electronic states for linear XY_2 molecules such as CO_2, CS_2, from (I-1) and (I-2),

$$(III-2) \qquad H_n = \frac{1}{2} m_2 \left(S_{2a}^{\cdot \, 2} + S_{2b}^{\cdot \, 2} \right) + \frac{1}{2} \lambda_2 \left(S_{2a}^{2} + S_{2b}^{2} \right)$$

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

a) Eigenstates of H_e

Due to the culindrical symmetry of the nuclear field, the wave function of the electrons can be written as $\chi_\Lambda \, e^{\pm i \Lambda \varphi}$, and the states shall be represented simply as $|\Lambda^{\pm}\rangle$. Here it is assumed that when the electrons are rotated through an angle φ , the symmetric $\left(\chi_\Lambda e^{+i \Lambda \varphi} \right)$ and antisymmetric $\left(\chi_\Lambda e^{-i \Lambda \varphi} \right)$ wave functions of the degenerate

electronic state transform like $e^{i\Lambda\varphi}$ and $e^{-i\Lambda\varphi}$ respectively.

Λ 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) $\qquad H_e \lvert \Lambda^{\pm} \rangle = E_{e\Lambda} \lvert \Lambda^{\pm} \rangle$

b) Eigenstates of H_n

The nuclear Hamiltonian is

$$H_n = \frac{1}{2} m_2 \left(\dot{S}_{2a}^2 + \dot{S}_{2b}^2 \right) + \frac{1}{2} \lambda_2 \left(S_{2a}^2 + S_{2b}^2 \right)$$

where $\qquad \lambda_2 = 4\pi^2 m_2 \nu_2^2$

and ν_2 is the observed classical frequency of oscillation.

$$H_n = \frac{P_{2a}^2}{2m_2} + \frac{P_{2b}^2}{2m_2} + 2\pi^2 m_2 \nu_2^2 \left(S_{2a}^2 + S_{2b}^2 \right)$$

where P_ν is the momentum conjugate to S_ν. In terms of the dimensionless co-ordinates q_{2a}, q_{2b},

$$H_n = a^2 \frac{P_{2a}^2 + P_{2b}^2}{2m_2} + \frac{2\pi^2}{a^2} m_2 \nu_2^2 \left(q_{2a}^2 + q_{2b}^2 \right)$$

By putting $\quad P_i = -i\hbar \frac{\partial}{\partial q_i}$ and $\mathcal{E} = \frac{2 E_n}{\hbar \nu_2}$,

$$H_n \Psi_n = E_n \Psi_n$$

becomes

$$\left[-\left(\frac{\partial^2}{\partial q_{2a}^2} + \frac{\partial^2}{\partial q_{2b}^2} \right) + q_{2a}^2 + q_{2b}^2 \right] \Psi_n = \mathcal{E}_n \Psi_n$$

where Ψ_n is the nuclear wave function. From the appendix where the solution to this equation is discussed,

$$\Psi_n(q_{2a}, q_{2b}) \equiv \Psi_n(q_2, \varphi_n) \equiv \Psi(\rho, \varphi_n)$$

and

(III-4) $\qquad \Psi(\rho, \varphi_n) = \dfrac{N_{\sigma \ell}}{\sqrt{2\pi}} \exp\left(-\dfrac{\rho}{2}\right) \rho^{\ell/2} L_\sigma^\ell(\rho) e^{\pm i \ell \varphi_n}$

where

$$\rho = q_2^2$$
$$\sigma - \ell = \dfrac{V_2 - \ell}{2}$$
$$E_n = \hbar \mu_2 (V_2 + 1), \qquad V_2 = 0, 1, 2, \ldots$$
$$\ell = V_2, V_2 - 2, \ldots, 1 \text{ or } 0.$$

$N_{\sigma \ell}$ is a normalizing constant

L_σ^ℓ is the associated Laguerre polynomial.

Once again, the nuclear states will be denoted by $|V_2, \ell^{\pm}\rangle$ (or $|\sigma, \ell^{\pm}\rangle$) and

(III-5) $\qquad H_n |V_2, \ell^{\pm}\rangle = E_{nV_2} |V_2, \ell^{\pm}\rangle.$

CHAPTER IV

Application of the Variational Principle

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

$$(\text{IV}-1) \qquad\qquad \mathcal{H}\,|\,\Psi) = E\,|\,\Psi)$$

where

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

The Hamiltonian $\mathcal{H}$ operates in the Hilbert space of both the electrons and the nuclei, and to denote this, the round ket, 1), has been used. The usual ket $1\rangle$ denotes a state in the Hilbert space of either the electrons, or the nuclei, that is,

$$H_e\,|\Lambda^{\pm}\rangle = E_{e\Lambda}\,|\Lambda^{\pm}\rangle$$

$$H_n\,|V_2,\ell^{\pm}\rangle = E_{nV_2}\,|V_2,\ell^{\pm}\rangle$$

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 Λ. The one-to-one correspondence between α_i and $\Lambda^{(s)}$ may be made in the following manner:

$$|\alpha_0\rangle = |0\rangle, \quad ;$$

$$|\alpha_1\rangle = |1^+\rangle \quad ; \quad |\alpha_2\rangle = |1^-\rangle$$

$$|\alpha_3\rangle = |2^+\rangle \quad ; \quad |\alpha_4\rangle = |2^-\rangle$$

etc.

Thus (III-3) becomes

(IV-2) $\quad H_e|\alpha_i\rangle = E_{ei}|\alpha_i\rangle \quad , i = 0, 1, 2, \cdots$

and $\quad E_{ei} = E_{e(i+1)} \quad$ 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:

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

etc.

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

Thus (III-5) becomes

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

and

$$E_{n1} = E_{n2}$$
$$E_{n3} = E_{n4} = E_{n5}$$
$$E_{n6} = E_{n7} = E_{n8} = E_{n9} , etc.$$

The $|\alpha_i\rangle, |\beta_j\rangle$ each form a complete orthonormal set in the Hilbert space of the electrons and nuclei respectively, since for linear molecules such as CO_2, CS_2 the equilibrium intermuclear 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

$$\delta[(\Psi|\mathcal{H}|\Psi) - E(\Psi|\Psi)] = 0 \quad ; \quad \delta E = 0$$

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

$$|\Psi) = \sum_i \sum_j a_{ij} |\alpha_i\rangle \times |\beta_j\rangle,$$

$$|\Psi) = \sum_i \sum_j a_{ij} |\alpha_i \beta_j)$$

that is, $|\Psi)$ 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,

$$(\Psi|\mathcal{H}|\Psi)$$

$$= \sum_{i,j} \sum_{i',j'} a_{ij}^* a_{i'j'} (\alpha_i \beta_j | H_e + H_n + H_{en} | \alpha_{i'} \beta_{j'})$$

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

$$\text{where} \quad H_{jj'}^{ii'} = (\alpha_i \beta_j | H_{en} | \alpha_{i'} \beta_{j'}).$$

$$(\Psi|\Psi) = \sum_{i,j} \sum_{i',j'} a_{ij}^* a_{i'j'} \delta_{ii'} \delta_{jj'}$$

Therefore

$$(\Psi|\mathcal{H}|\Psi) - E(\Psi|\Psi)$$

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

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

$$\text{where} \quad \Delta E_{ij} = E - E_{ei} - E_{nj}.$$

Applying a variation with respect to a_{ij}^{*} ,

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

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

(IV-4) $\left| H_{jj'}^{ii'} - \Delta \bar{E} \delta_{ii'} \delta_{jj'} \right| = 0$

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

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

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

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

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 $H_{jj'}^{ii'}$ are non-vanishing, and before analyzing the determinant (IV-4) the values of the non-vanishing matrix elements $H_{jj'}^{ii'}$ will have to be found.

CHAPTER V

Non-vanishing Matrix Elements

From (II-5), the interaction Hamiltonian is

$$H_{en} = - \lambda_2^{(1)} q_2 \cos(\varphi_e - \varphi_n) - \frac{1}{2}\left[\lambda_2^{(2)} q_2^2 + \lambda_{22}^{(2)} q_2^2 \cos 2(\varphi_e' - \varphi_n)\right]$$

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

$$\varphi = \varphi_e + \varphi'$$

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

$$\int e^{-i\Lambda\varphi_e} e^{-i\ell\varphi_n} \cos(\varphi_e - \varphi_n) e^{i\Lambda'\varphi} e^{i\ell'\varphi_n} d\varphi_e \, d\varphi_n .$$

The subscript e in φ_e will be omitted from now on and φ_e' will also be put equal to φ .

Substituting $q_2^2 = \rho$, equation (II-5) becomes

(V-1) $\quad H_{en} = - \lambda_2^{(1)} \rho^{\frac{1}{2}} \cos(\varphi - \varphi_n) - \frac{1}{2}\left[\lambda_2^{(2)} \rho + \lambda_{22}^{(2)} \rho \cos 2(\varphi - \varphi_n)\right]$

The angular part of the matrix elements $H_{jj'}^{ii'}$ can be obtained from the following integral:

(V-2) $\quad \Theta = \frac{1}{(2\pi)^2} \iint\limits_{0 \ 0}^{2\pi \ 2\pi} e^{-i\Lambda\varphi} e^{-i\ell\varphi_n}\left[\cos(\varphi - \varphi_n)\right]^{2n} e^{i\Lambda'\varphi} e^{i\ell'\varphi_n} d\varphi \, d\varphi_n$

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:

(V-3) $\quad \langle \sigma\ell | \rho^n | \sigma'\ell' \rangle = \int\limits_0^\infty e^{-\rho} \rho^{\frac{1}{2}(\ell+\ell')} \rho^n \, L_\sigma^\ell(\rho) \, L_{\sigma'}^{\ell'}(\rho) \, \frac{d\rho}{2} .$

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 ω in $U_{ne}^{(\omega)}$. No matter what ω is, $H_{jj'}^{ii'}$ always contains products of (V-2) and (V-3) $\times \delta_{\Lambda-\Lambda'}$, where

$$\delta_{\Lambda-\Lambda'} = \begin{cases} 1 & \text{if } \Lambda = \Lambda' \\ 0 & \text{if } \Lambda \neq \Lambda' \end{cases}$$

Thus, the evaluation of (V-2), (V-3) allows one to go to any order to approximation in $U_{ne}^{(\omega)}$ 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.

$$\Theta = \frac{1}{(2\pi)^2} \int_0^{2\pi} \int_0^{2\pi} e^{-i(\Lambda - \Lambda')\varphi} \, e^{-i(\ell - \ell')\varphi_n} \cos^{2n}(\varphi - \varphi_n) \, d\varphi \, d\varphi_n$$

But

$$\cos^{2n}(\varphi - \varphi_n) = \left[\frac{e^{i(\varphi - \varphi_n)} + e^{-i(\varphi - \varphi_n)}}{2} \right]^{2n}$$

$$= \frac{1}{4^n} \sum_{\nu=0}^{\infty} \left[e^{i(\varphi - \varphi_n)} \right]^{2n - \nu} \left[e^{-i(\varphi - \varphi_n)} \right]^{\nu}$$

$$= \frac{1}{4^n} \sum_{\nu=0}^{2n} e^{i(2n - 2\nu)\varphi} \, e^{-i(2n - 2\nu)\varphi_n}$$

Therefore

$$\Theta = \frac{1}{(2\pi)^2 4^n} \int\int \sum_{\nu=0}^{2n} e^{-i(\Lambda - \Lambda' - 2n + 2\nu)\varphi} \, e^{-i(\ell - \ell' + 2n - 2\nu)\varphi_n} \, d\varphi \, d\varphi_n$$

$$= \frac{1}{4^n} \left\{ \delta_{\Lambda - \Lambda' - 2n} \, \delta_{\ell - \ell' + 2n} + \delta_{\Lambda - \Lambda' - 2n + 2} \, \delta_{\ell - \ell' + 2n - 2} + \cdots \right.$$

$$\left. \cdots + \delta_{\Lambda - \Lambda' + 2n} \, \delta_{\ell - \ell' - 2n} \right\}$$

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

$$\Delta \Lambda = 2n \quad ; \quad \Delta \ell = -2n \qquad \text{simultaneously}$$

or $$\Delta \Lambda = 2n - 2 \quad ; \quad \Delta \ell = -2n + 2 \qquad \text{"}$$

or $$\Delta \Lambda = 2n - 4 \quad ; \quad \Delta \ell = -2n + 4 \qquad \text{"}$$

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,

(V-4)
$$\left\{ \begin{array}{l} \Delta\Lambda = -\Delta\ell = 1 \quad\text{simultaneously} \\ \Delta\Lambda = -\Delta\ell = -1 \quad\text{"} \end{array} \right.$$
or

But for the lowest degenerate electronic state, that is $=1$, and for the lowest degenerate nuclear state, that is $\ell = 1$, 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,

(V-5)
$$\left\{ \begin{array}{l} \Delta\Lambda = -\Delta\ell = 2 \quad\text{simultaneously} \\ \text{or} \quad \Delta\Lambda = -\Delta\ell = 0 \quad\text{"} \\ \text{or} \quad \Delta\Lambda = -\Delta\ell = -2 \quad\text{"} \end{array} \right.$$

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 Σ , Π , Δ ... states.

b) Radial matrix elements.

The non-vanishing radial matrix elements (V-3),

$$\langle \sigma \ell | \rho^n | \sigma' \ell' \rangle = \int_0^\infty e^{-\rho} \rho^{\frac{1}{2}(\ell+\ell')} \rho^n \, L_\sigma^\ell(\rho) \, L_{\sigma'}^{\ell'}(\rho) \, \frac{d\rho}{2}$$

can be found from the generating function of the Laguerre polynomials given in the appendix; that is

$$\sum_{\sigma=\ell}^\infty \sum_{\sigma'=\ell'}^\infty \frac{u^\sigma u'^{\sigma'}}{\sigma! \, \sigma'!} \frac{1}{N_{\sigma\ell}} \frac{1}{N_{\sigma'\ell'}} \langle \sigma \ell | \rho^n | \sigma' \ell' \rangle$$

$$= \int_0^\infty \frac{(-u)^\ell}{(1-u)^{\ell+1}} \left[\exp\left(\frac{-\rho u}{1-u}\right) \right] \frac{(-u')^{\ell'}}{(1-u')^{\ell'+1}} \left[\exp\left(\frac{-\rho u'}{1-u'}\right) \right] e^{-\rho} \rho^n \rho^{\frac{1}{2}(\ell+\ell')} \frac{d\rho}{2}$$

The procedure is to integrate over ρ in the right hand side, expand the remaining form in (uu') and compare coefficients with the left hand side. The right hand side

$$= \frac{1}{2} \frac{(-1)^{\ell+\ell'} u^\ell u'^{\ell'}}{(1-u)^{\ell+1}(1-u')^{\ell'+1}} \int_0^\infty \exp\left\{ -\rho \left[\frac{u}{1-u} + \frac{u'}{1-u'} + 1 \right] \right\} \rho^n \rho^{\frac{1}{2}(\ell+\ell')} \frac{d\rho}{2}$$

Using the definition of the Γ function,

$$\Gamma(n) = \int_0^\infty X^{n-1} e^{-X} \, dX,$$

the right hand side

$$= \frac{1}{2} \frac{(-1)^{\ell+\ell'} u^\ell u'^{\ell'}}{(1-u)^{\ell+1}(1-u')^{\ell'+1}} \frac{\Gamma\left(n + \frac{\ell}{2} + \frac{\ell'}{2} + 1\right)}{\left[\frac{u}{1-u} + \frac{u'}{1-u'} + 1\right]^{n+\frac{\ell}{2}+\frac{\ell'}{2}+1}}$$

$$= \frac{(-1)^{\ell+\ell'} u^\ell u'^{\ell'}}{2(1-u)^{(\frac{\ell}{2}-\frac{\ell'}{2}-n)}(1-u')^{(\frac{\ell'}{2}-\frac{\ell}{2}-n)}} \frac{1}{(1-uu')^{n+\frac{\ell}{2}+\frac{\ell'}{2}+1}} \Gamma\left(n+\frac{\ell}{2}+\frac{\ell'}{2}+1\right)$$

Using the expansion

$$(1-X)^{-q} = \sum_{k=0}^{\infty} \frac{\Gamma(k+q)}{\Gamma(q)\Gamma(k+1)} X^q$$

which is valid for all q, the right hand side

$$= \sum_{k=0}^{\infty} \sum_{\nu=0}^{\infty} \sum_{\nu'=0}^{\infty} \frac{(-1)^{\ell+\ell'} u^\ell u'^{\ell'}}{2} \Gamma\left(n+\frac{\ell}{2}+\frac{\ell'}{2}+1\right) \frac{\Gamma\left(n+\frac{\ell}{2}+\frac{\ell'}{2}+k+1\right)}{\Gamma\left(n+\frac{\ell}{2}+\frac{\ell'}{2}+1\right)\Gamma(k+1)} (uu')^k$$

$$\times \frac{\Gamma\left(\frac{\ell}{2}-\frac{\ell'}{2}-n+\nu\right)}{\Gamma\left(\frac{\ell}{2}-\frac{\ell'}{2}-n\right)\Gamma(\nu+1)} u^\nu \frac{\Gamma\left(\frac{\ell'}{2}-\frac{\ell}{2}-n+\nu'\right)}{\Gamma\left(\frac{\ell'}{2}-\frac{\ell}{2}-n\right)\Gamma(\nu'+1)} u'^{\nu'}$$

$$= \sum_{k=0}^{\infty} \sum_{\nu=0}^{\infty} \sum_{\nu'=0}^{\infty} f(k,\nu,\nu') \, u^{\ell+k+\nu} u'^{\ell'+k+\nu'}$$

where $f(k,\nu,\nu')$

$$= \frac{(-1)^{\ell+\ell'}}{2} \frac{\Gamma\left(n+\frac{\ell}{2}+\frac{\ell'}{2}+k+1\right)}{\Gamma(k+1)} \frac{\Gamma\left(\frac{\ell}{2}-\frac{\ell'}{2}-n+\nu\right)}{\Gamma\left(\frac{\ell}{2}-\frac{\ell'}{2}-n\right)\Gamma(\nu+1)} \frac{\Gamma\left(\frac{\ell'}{2}-\frac{\ell}{2}-n+\nu'\right)}{\Gamma\left(\frac{\ell'}{2}-\frac{\ell}{2}-n\right)\Gamma(\nu'+1)}$$

Putting $\ell+k+\nu = \sigma$, $\ell'+k+\nu' = \sigma'$,
the right hand side

$$= \sum_{k=0}^{\infty} \sum_{\sigma=\ell+k}^{\infty} \sum_{\sigma'=\ell'+k}^{\infty} f(k, \sigma-\ell-k, \sigma'-\ell'-k) \, u^\sigma u'^{\sigma'}$$

But

$$\sum_{k=0}^{\infty} \sum_{\sigma=\ell+k}^{\infty} = \sum_{\sigma=\ell}^{\infty} \sum_{k=0}^{\sigma-\ell}$$

Thus the right hand side

$$= \sum_{\sigma=\ell}^{\infty} \sum_{k=0}^{\sigma-\ell} \sum_{\sigma'=\ell'+k}^{\infty} f(k, \sigma-\ell-k, \sigma'-\ell'-k) \, u^\sigma u'^{\sigma'}$$

$$= \sum_{\sigma=\ell}^{\infty} \left\{ \sum_{\sigma'=\ell'}^{\sigma-\ell'} \sum_{k=0}^{\sigma'-\ell'} + \sum_{\sigma'=\sigma-\ell+1}^{\infty} \sum_{k=\sigma'-\ell'+1}^{\sigma-\ell} \right\} f \, u^\sigma u'^{\sigma'}$$

A similar relation holds for $(\sigma - \ell)$ and $(\sigma' - \ell')$ interchanged, depending on which is smaller. Therefore the right hand side

$$= \sum_{\sigma=\ell}^{\infty} \sum_{\sigma'=\ell'}^{\infty} \sum_{k=0}^{\min\binom{\sigma-\ell}{\sigma'-\ell'}} f(k, \sigma-\ell-k, \sigma'-\ell'-k) \, u^{\sigma} u'^{\sigma'}$$

Comparing polynomials with the left hand side,

$$(\text{V-6}) \qquad \langle \sigma \ell \mid \rho^n \mid \sigma' \ell' \rangle$$

$$= N_{\sigma \ell} N_{\sigma' \ell'} \, \Gamma(\sigma+1) \, \Gamma(\sigma'+1) \sum_{k=0}^{\min\binom{\sigma-\ell}{\sigma'-\ell'}} f(k, \sigma-\ell-k, \sigma'-\ell'-k)$$

$$= N_{\sigma \ell} N_{\sigma' \ell'} \frac{(-1)^{\ell+\ell'}}{2} \frac{\Gamma(\sigma+1) \, \Gamma(\sigma'+1)}{\Gamma(\frac{\ell}{2} - \frac{\ell'}{2} - n) \Gamma(\frac{\ell'}{2} - \frac{\ell}{2} - n)} \times$$

$$\sum_{k=0}^{\min\binom{\sigma-\ell}{\sigma'-\ell'}} \frac{\Gamma(n + \frac{\ell}{2} + \frac{\ell'}{2} + k + 1) \, \Gamma(\sigma - k - n - \frac{\ell}{2} - \frac{\ell'}{2}) \, \Gamma(\sigma' - k - n - \frac{\ell}{2} - \frac{\ell'}{2})}{\Gamma(k+1) \, \Gamma(\sigma - \ell - k + 1) \, \Gamma(\sigma' - \ell' - k + 1)}$$

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

$$\sum_{k=0}^{\min\binom{\sigma-\ell}{\sigma'-\ell'}} \frac{\Gamma(\sigma - k - n - \frac{\ell}{2} - \frac{\ell'}{2}) \, \Gamma(\sigma' - k - n - \frac{\ell}{2} - \frac{\ell'}{2})}{\Gamma(\frac{\ell}{2} - \frac{\ell'}{2} - n) \, \Gamma(\frac{\ell'}{2} - \frac{\ell}{2} - n)}$$

$$= \sum_{k=0}^{\min\binom{\sigma-\ell}{\sigma'-\ell'}} \frac{\Gamma(\sigma - \ell - k - n + \frac{\ell}{2} - \frac{\ell'}{2})}{\Gamma(-n + \frac{\ell}{2} - \frac{\ell'}{2})} \cdot \frac{\Gamma(\sigma' - \ell' - k - n - \frac{\ell}{2} + \frac{\ell'}{2})}{\Gamma(-n - \frac{\ell}{2} + \frac{\ell'}{2})}$$

Since $\sigma - \ell - k \geqslant 0$ and $\sigma' - \ell' - k \geqslant 0$, then

for $-n + \frac{\ell}{2} - \frac{\ell'}{2} > 0$ and

$-n - \frac{\ell}{2} + \frac{\ell'}{2} > 0$

there are no non-vanishing elements. However, if either of the last two mentioned terms are zero or negative, the arguments of the Γ function appearing in the denominator are zero or negative, and the arguments of the Γ 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 $-\left(\sigma' - \sigma - \frac{\ell'}{2} + \frac{\ell}{2} \right) \leq n$.

That is

(V-7)
$$\begin{cases} n \geqslant \left| \sigma - \sigma' - \frac{\ell}{2} + \frac{\ell'}{2} \right| \\[2ex] \text{and } -n + \frac{\ell}{2} - \frac{\ell'}{2}, \ -n - \frac{\ell}{2} + \frac{\ell'}{2} \text{ are zero or negative integers.} \end{cases}$$

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 $\ell' - \ell = \Delta\ell = +1,$

$$\frac{1}{2} \geqslant \left| \sigma - \sigma' + \frac{1}{2} \right|$$

Therefore $\sigma = \sigma'$ or $\sigma' = \sigma + 1$

In terms of the V_2's,

$$\Delta\sigma = 0 \quad \text{gives} \quad \Delta V_2 = -1$$
$$\Delta\sigma = +1 \quad \text{gives} \quad \Delta V_2 = +1$$

For $\ell' - \ell = \Delta\ell = -1,$

$$\frac{1}{2} \geqslant \left| \sigma - \sigma' - \frac{1}{2} \right|$$

Therefore $\sigma' = \sigma$ or $\sigma' = \sigma - 1$

or $\Delta V_2 = +1$, $\Delta V_2 = -1$

For n=1, the selection rules on ℓ are

$$\Delta \ell = 0, \pm 2.$$

For $\ell' = \ell$,　　　$1 \geqslant |\sigma - \sigma'|$

Therefore　$\sigma' = \sigma - 1$　which gives　$\Delta V_2 = -2$

or　　　$\sigma' = \sigma$　which gives　$\Delta V_2 = 0$

or　　　$\sigma' = \sigma + 1$　which gives　$\Delta V_2 = +2$

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

Therefore　$\sigma' = \sigma$　which gives　$\Delta V_2 = -2$

or　　　$\sigma' = \sigma + 1$　which gives　$\Delta V_2 = 0$

or　　　$\sigma' = \sigma + 2$　which gives　$\Delta V_2 = +2$

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

Again　　$\sigma' = \sigma$　which gives　$\Delta V_2 = +2$

or　　　$\sigma' = \sigma - 1$　which gives　$\Delta V_2 = 0$

or　　　$\sigma' = \sigma - 2$　which gives　$\Delta V_2 = -2$

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[8]; 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.

selection rules for $n = \frac{1}{2}$, or for dipole displacements of the nuclei	$\Delta V_2 = +1$, $\Delta \ell = +1$, $\Delta \Lambda = -1$
	$\Delta V_2 = -1$, $\Delta \ell = +1$, $\Delta \Lambda = -1$
	$\Delta V_2 = +1$, $\Delta \ell = -1$, $\Delta \Lambda = +1$
	$\Delta V_2 = -1$, $\Delta \ell = -1$, $\Delta \Lambda = +1$
selection rules for $n = 1$ or, for quadrupole displacements of the nuclei	$\Delta V_2 = 0$, $\Delta \ell = 0$, $\Delta \Lambda = 0$ $\Delta V_2 = 2$, $\Delta \ell = 0$, $\Delta \Lambda = 0$ $\Delta V_2 = -2$, $\Delta \ell = 0$, $\Delta \Lambda = 0$
	$\Delta V_2 = 0$, $\Delta \ell = +2$, $\Delta \Lambda = -2$ $\Delta V_2 = 2$, $\Delta \ell = +2$, $\Delta \Lambda = -2$ $\Delta V_2 = -2$, $\Delta \ell = +2$, $\Delta \Lambda = -2$
	$\Delta V_2 = 0$, $\Delta \ell = -2$ $\Delta \Lambda = +2$ $\Delta V_2 = 2$, $\Delta \ell = -2$ $\Delta \Lambda = +2$ $\Delta V_2 = -2$, $\Delta \ell = -2$ $\Delta \Lambda = +2$

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 $n=\frac{1}{2}$, 1 will be tabulated in Tables II, III. These matrix elements were calculated by Schaffer [8], 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),

$$\langle \sigma\ell|\rho^n|\sigma'\ell'\rangle = N_{\sigma\ell}\, N_{\sigma'\ell'} \cdot \frac{(-1)^{\ell+\ell'}}{2}\; \frac{\Gamma(\sigma+1)\,\Gamma(\sigma'+1)}{\Gamma\!\left(-\frac{\Delta\ell}{2}-n\right)\Gamma\!\left(\frac{\Delta\ell}{2}-n\right)} \times$$

$$\sum_{k} \frac{\Gamma\!\left(n+\frac{\ell}{2}+\frac{\ell'}{2}+k+1\right)\Gamma\!\left(\sigma-\ell-k-n-\frac{\Delta\ell}{2}\right)\Gamma\!\left(\sigma'-\ell'-k-n+\frac{\Delta\ell}{2}\right)}{\Gamma(\sigma-\ell-k+1)\,\Gamma(\sigma'-\ell'-k+1)}$$

Example 1. $n=\frac{1}{2}$; $\sigma'=\sigma-1$, $\ell'=\ell-1$

Therefore $\sigma'-\ell' = \sigma-\ell$

$$\langle \sigma\ell|\rho^{\frac{1}{2}}|\sigma'\ell'\rangle = N_{\sigma\ell}\, N_{\sigma'\ell'}\frac{(-1)^{\ell+\ell'}}{2}\;\frac{\Gamma(\sigma+1)\Gamma(\sigma)}{\Gamma(0)\Gamma(-1)} \sum_{k} \frac{\Gamma(k+1+\ell)\,\Gamma(\sigma-\ell-k)\,\Gamma(\sigma-\ell-k-1)}{\Gamma(k+1)\,\Gamma(\sigma-\ell-k+1)\,\Gamma(\sigma-\ell-k+1)}$$

k can take the value of $\sigma-\ell$ only.

$$\langle \sigma\ell|\rho^{\frac{1}{2}}|\sigma'\ell'\rangle = N_{\sigma\ell}\, N_{\sigma'\ell'} \cdot \frac{(-1)^{\ell+\ell'}}{2}\;\frac{\Gamma(\sigma+1)\Gamma(\sigma)}{\Gamma(0)\Gamma(-1)}\;\frac{\Gamma(\sigma+1)\,\Gamma(0)\,\Gamma(-1)}{\Gamma(\sigma-\ell+1)\Gamma(1)\Gamma(1)}$$

$$= 2\left[\frac{(\sigma-\ell)!}{(\sigma!)^3}\right]^{\frac{1}{2}}\left[\frac{(\sigma-\ell)!}{[(\sigma-1)!]^3}\right]^{\frac{1}{2}}\frac{(-1)^{2\ell-1}}{2}\;\frac{(\sigma!)^2\,(\sigma-1)!}{(\sigma-\ell)!}$$

$$= -\sigma^{\frac{1}{2}}$$

Example 2: $n=\frac{1}{2}$; $\sigma'=\sigma$; $\ell'=\ell-1$

Therefore $\Delta\ell=-1$, $\sigma'-\ell'=\sigma-\ell+1$

$$\langle \sigma\ell|\rho^{\frac{1}{2}}|\sigma'\ell'\rangle = N_{\sigma\ell}\, N_{\sigma'\ell'}\frac{(-1)^{2\ell-1}}{2}\;\frac{\Gamma(\sigma+1)\,\Gamma(\sigma+1)}{\Gamma(0)\,\Gamma(-1)}\sum_{k=0}^{\sigma-\ell}\frac{\Gamma(\sigma-\ell-k)\,\Gamma(\sigma-\ell-k)\,\Gamma(\ell+k+1)}{\Gamma(\sigma-\ell-k+1)\,\Gamma(\sigma-\ell-k+2)\,\Gamma(k+1)}$$

8

σ'	ℓ'	$\langle \sigma e \lvert \rho^{\frac{1}{2}} \rvert \sigma'\ell' \rangle \quad = \langle V_2 \ell \lvert r \rvert V_2'\ell' \rangle$		V_2'	ℓ'
σ	$\ell-1$	$(\sigma-\ell+1)^{\frac{1}{2}}$	$= \left[\dfrac{V_2-\ell}{2} + 1 \right]^{\frac{1}{2}}$	V_2+1	$\ell-1$
$\sigma+1$	$\ell+1$	$-(\sigma+1)^{\frac{1}{2}}$	$= -\left[\dfrac{V_2+\ell}{2} + 1 \right]^{\frac{1}{2}}$	V_2+1	$\ell+1$
$\sigma-1$	$\ell-1$	$-\sigma^{\frac{1}{2}}$	$= -\left[\dfrac{V_2+\ell}{2} \right]^{\frac{1}{2}}$	V_2-1	$\ell-1$
σ	$\ell+1$	$(\sigma-\ell)^{\frac{1}{2}}$	$= \left[\dfrac{V_2-\ell}{2} \right]^{\frac{1}{2}}$	V_2-1	$\ell+1$

Table II

σ'	ℓ'	$\langle \sigma e \lvert \rho \rvert \sigma e \rangle \qquad = \langle V_2 \ell \lvert r^2 \rvert V_2'\ell' \rangle$		V_2'	ℓ'
σ	ℓ	$(2\sigma-\ell+1)$	$= \qquad V_2+1$	V_2	ℓ
$\sigma\pm1$	ℓ	$-\left[\left(\sigma+\tfrac{1}{2}\pm\tfrac{1}{2}\right)\left(\sigma-\ell+\tfrac{1}{2}\pm\tfrac{1}{2}\right)\right]^{\frac{1}{2}}$	$= -\left[\left(\dfrac{V_2+\ell+1}{2}\pm\tfrac{1}{2}\right)\left(\dfrac{V_2-\ell+1}{2}\pm\tfrac{1}{2}\right)\right]^{\frac{1}{2}}$	$V_2\pm2$	ℓ
$\sigma\pm2$	$\ell\pm2$	$\left[(\sigma\pm1)(\sigma+1\pm1)\right]^{\frac{1}{2}}$	$= \left[\left(\dfrac{V_2+\ell}{2}\pm1\right)\left(\dfrac{V_2+\ell+2}{2}\pm1\right)\right]^{\frac{1}{2}}$	$V_2\pm2$	$\ell\pm2$
$\sigma\pm1$	$\ell\pm2$	$-2\left[\left(\sigma+\tfrac{1}{2}\pm\tfrac{1}{2}\right)\left(\sigma-\ell+\tfrac{1}{2}\mp\tfrac{1}{2}\right)\right]^{\frac{1}{2}}$	$= 2\left[\left(\dfrac{V_2+\ell+1}{2}\pm\tfrac{1}{2}\right)\left(\dfrac{V_2-\ell+1}{2}\mp\tfrac{1}{2}\right)\right]^{\frac{1}{2}}$	V_2	$\ell\pm2$
σ	$\ell\pm2$	$\left[(\sigma-\ell\mp1)(\sigma-\ell+1\mp1)\right]^{\frac{1}{2}}$	$= \left[\left(\dfrac{V_2-\ell}{2}\mp1\right)\left(\dfrac{V_2-\ell}{2}+1\mp1\right)\right]^{\frac{1}{2}}$	$V_2\mp2$	$\ell\pm2$

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_{ne} were retained, the Π and Δ electronic
states will be considered; ℓ will be given the values of 0 and 1.

The notation used in this chapter is the following:

$$\langle \chi_\Lambda | - \lambda_2^{(1)} | \chi_{\Lambda'} \rangle = D_{\Lambda\Lambda'}$$

$$\langle \chi_\Lambda | - \frac{\lambda_2^{(2)}}{2} | \chi_{\Lambda'} \rangle = Q_{\Lambda\Lambda'}^{d}$$

$$\langle \chi_\Lambda | - \frac{\lambda_{22}^{(2)}}{2} | \chi_{\Lambda'} \rangle = Q_{\Lambda\Lambda'}^{nd}$$

The χ_Λ 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 (Λ, ℓ); 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 $|K| = |\Lambda + \ell|$.

	00	01	0-1	10	11	1-1	-10	-11	-1-1	20	21	2-1	-20	-21	-2-1	·	·	·
00	E_{00}					d		d										
01		E_{01}		d								q						
0-1			E_{01}					d						q				
10		d		E_{10}								d						
11					E_{11}				d									
1-1	d					E_{11}		q										
-10			d				E_{10}							d				
-11	d				q			E_{11}										
-1-1									E_{11}			d						
20					d					E_{20}								
21											E_{21}							
2-1		q		d								E_{21}						
-20									d				E_{20}					
-21		q			d									E_{21}				
-2-1															E_{21}			
·																·		
·																	·	
·																		·

The full matrix

	00	1-1	-11	01	10	2-1	0-1	-10	-21	11	20	-1-1	-20	21	-2-1
00	E_{00}	d	d												
1-1	d	E_{11}	q												
-11	d	q	E_{11}												
01				E_{01}	d	q									
10				d	E_{10}	d									
2-1				q	d	E_{21}									
0-1							E_{01}	d	q						
-10							d	E_{10}	d						
-21							q	d	E_{21}						
11										E_{11}	d				
20										d	E_{20}				
-1-1												E_{11}	d		
-20												d	E_{20}		
21														E_{21}	
-2-1															E_{21}

The matrix with rows and columns rearranged.

39

That is, it can be broken up as follows:

$$
\begin{pmatrix}
\boxed{K=0} & & & & \\
& \boxed{K=1} & & & \\
& & \boxed{K=-1} & & \\
& & & \boxed{K=2} & \\
& & & & \boxed{K=-2} \\
& & & & & \ddots
\end{pmatrix}
$$
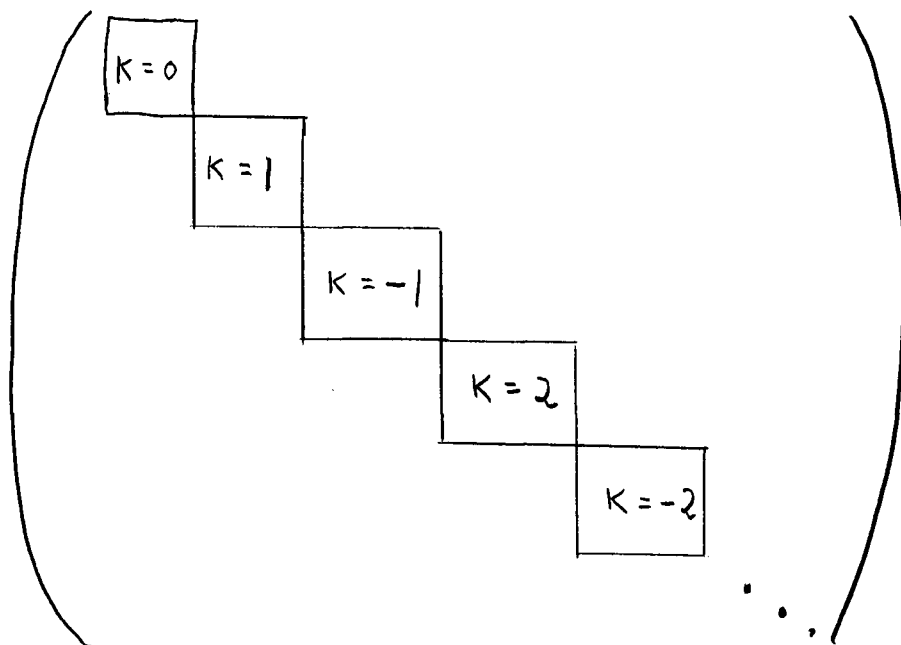
Moreover, the submatrix for $K = +1$ is identical to that for $K = -1$, and that

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:

$$
K = 0 \qquad
\begin{array}{cc}
\Lambda = 0,2 & \Lambda = 1 \\
\end{array}
$$

$$
K = 0 \qquad
\left(
\begin{array}{c|c}
\text{Quadrupole terms} & \text{dipole terms} \\
\hline
\text{dipole terms} & \text{quadrupole terms}
\end{array}
\right)
$$

The terms in the upper left corner matrix represent mixing due to quadrupole

interaction between Σ and Δ 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 Π state can be obtained and this is found from the submatrix in which K = 0, which is

$$
\begin{pmatrix}
E_{eo} + h\nu_2 + Q_{oo}^d & -\tfrac{1}{2} D_{o1} & \\
-\tfrac{1}{2} D_{1o} & E_{e1} + 2h\nu_2 + 2 Q_{11}^d & \\
-\tfrac{1}{2} D_{1o} & \tfrac{1}{2} Q_{11}^{nd} & E_{e1} + 2h\nu_2 + 2 Q_{11}^d
\end{pmatrix}
$$

Performing a unitary transformation by the matrix

$$
U = \begin{pmatrix}
1 & 0 & 0 \\
0 & \tfrac{1}{\sqrt{2}} & \tfrac{1}{\sqrt{2}} \\
0 & -\tfrac{1}{\sqrt{2}} & \tfrac{1}{\sqrt{2}}
\end{pmatrix}
$$

the matrix for K=0 becomes

$$
\begin{pmatrix}
E_{eo} + h\nu_2 + Q_{oo}^d & 0 & -\dfrac{D_{o1}}{\sqrt{2}} \\
0 & E_{e1} + 2h\nu_2 + Q_{11}^d + \tfrac{1}{2} Q_{11}^{nd} & 0 \\
-\dfrac{D_{1o}}{\sqrt{2}} & 0 & E_{e1} + 2h\nu_2 + Q_{11}^d - \tfrac{1}{2} Q_{11}^{nd}
\end{pmatrix}
$$

Thus the Renner splitting of the vibronic state characterized by $\Lambda = 1$, $\ell = 1 = \nu_2$ is

$$
Q_{11}^{nd}
$$

Moreover the energy values of the states

$$\Lambda = \ell = 0 \qquad \text{and}$$

$$\Lambda = \ell = 1 \qquad \text{are}$$

$$(\text{VI-1}) \begin{cases} E_1 = \frac{1}{2}\left\{\left[E_{e0} + E_{e1} + 3\hbar\nu_2 + Q_{00}^d - \frac{1}{2}Q_{11}^{nd}\right] + \right. \\ \qquad \left. \left[(E_{e0} - E_{e1} - \hbar\nu_2 + Q_{00}^d - Q_{11}^d + \frac{1}{2}Q_{11}^{nd})^2 + 2|D_{01}|^2\right]^{\frac{1}{2}}\right\} \\ E_2 = E_{e1} + 2\hbar\nu_2 + Q_{11}^d + \frac{1}{2}Q_{11}^{nd} \\ E_3 = \frac{1}{2}\left\{\left[E_{e0} + E_{e1} + 3\hbar\nu_2 + Q_{00}^d - \frac{1}{2}Q_{11}^{nd}\right] - \right. \\ \qquad \left. \left[(E_{e0} - E_{e1} - \hbar\nu_2 + Q_{00}^d - Q_{11}^d + \frac{1}{2}Q_{11}^{nd})^2 + 2|D_{01}|^2\right]^{\frac{1}{2}}\right\} \end{cases}$$

b) $K = 1$

The matrix for $K = 1$ is

$$\begin{pmatrix} E_{\varrho 0} + 2k\nu_2 + 2Q_{00}^d & \frac{1}{2\sqrt{2}} D_{01} & \frac{1}{2} Q_{20}^{nd} \\[3mm] \frac{1}{2\sqrt{2}} D_{10} & E_{e1} + k\nu_2 + Q_{11}^d & -\frac{1}{2} D_{21} \\[3mm] \frac{1}{2} Q_{20}^{nd} & -\frac{1}{2} D_{12} & E_{e2} + 2k\nu_2 + 2Q_{22}^d \end{pmatrix}$$

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 Σ and Π states and D_{21} mixes the electronic Π and Δ states, whereas the quadrupole term Q_{20}^{nd} mixes the Σ and Δ states; hence Q_{20}^{nd} can be neglected compared to the dipole terms, and this is even more obvious from the expressions $\lambda_2^{(1)}$ and $\lambda_{22}^{(2)}$ given in Chapter II. $\lambda_2^{(1)}$ occurs in the expression for $D_{\Lambda\Lambda'}$ and it contains terms of the order of $\frac{1}{R_{ii'}^2}$, whereas $\lambda_{22}^{(2)}$ occurring in $Q_{\Lambda\Lambda'}^{nd}$ contains terms of the order of $\frac{1}{R_{ii'}^3}$.

The matrix for $K = 1$ becomes

$$\begin{pmatrix} E_{\varrho 0} + 2k\nu_2 + 2Q_{00}^d & \frac{1}{2\sqrt{2}} D_{01} & 0 \\[3mm] \frac{1}{2\sqrt{2}} D_{01} & E_{e1} + k\nu_2 + Q_{11}^d & -\frac{1}{2} D_{21} \\[3mm] 0 & -\frac{1}{2} D_{21} & E_{e2} + 2k\nu_2 + 2Q_{22}^d \end{pmatrix}$$

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

$$
\begin{pmatrix}
E_{e_1} + 2k\nu_2 + 2Q_{11}^d & -\tfrac{1}{2} D_{12} \\[2mm]
-\tfrac{1}{2} D_{21} & E_{e_2} + k\nu_2 + Q_{22}^d
\end{pmatrix}
$$

which will give the corrected energy values of the vibronic states

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

given by

$$(\underline{VI}\text{-}2)
\begin{cases}
E_7 = \tfrac{1}{2}\left\{\left(E_{e_1} + E_{e_2} + 2k\nu_2 + 2Q_{11}^d + Q_{22}^d\right) + \right. \\[2mm]
\qquad\qquad \left.\left[\left(E_{e_1} - E_{e_2} + k\nu_2 + 2Q_{11}^d - Q_{22}^d\right)^2 + |D_{12}|^2\right]^{\tfrac{1}{2}}\right\} \\[4mm]
E_8 = \tfrac{1}{2}\left\{\left(E_{e_1} + E_{e_2} + 2k\nu_2 + 2Q_{11}^d + Q_{22}^d\right) - \right. \\[2mm]
\qquad\qquad \left.\left[\left(E_{e_1} - E_{e_2} + k\nu_2 + 2Q_{11}^d - Q_{22}^d\right)^2 + |D_{12}|^2\right]^{\tfrac{1}{2}}\right\}
\end{cases}
$$

d) K = 3

For this case, the matrix element is just $E_{e_2} + 2\ell\nu_2 + 2 Q_{22}^d$,
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 Π 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}^{α} , Q_{11}^{α} , $Q_{11}^{\pi\alpha}$, Q_{22}^{α} , 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 Π state and the relative intensities of the spectral lines between the Σ , Π , and Δ electronic states in terms of six parameters.
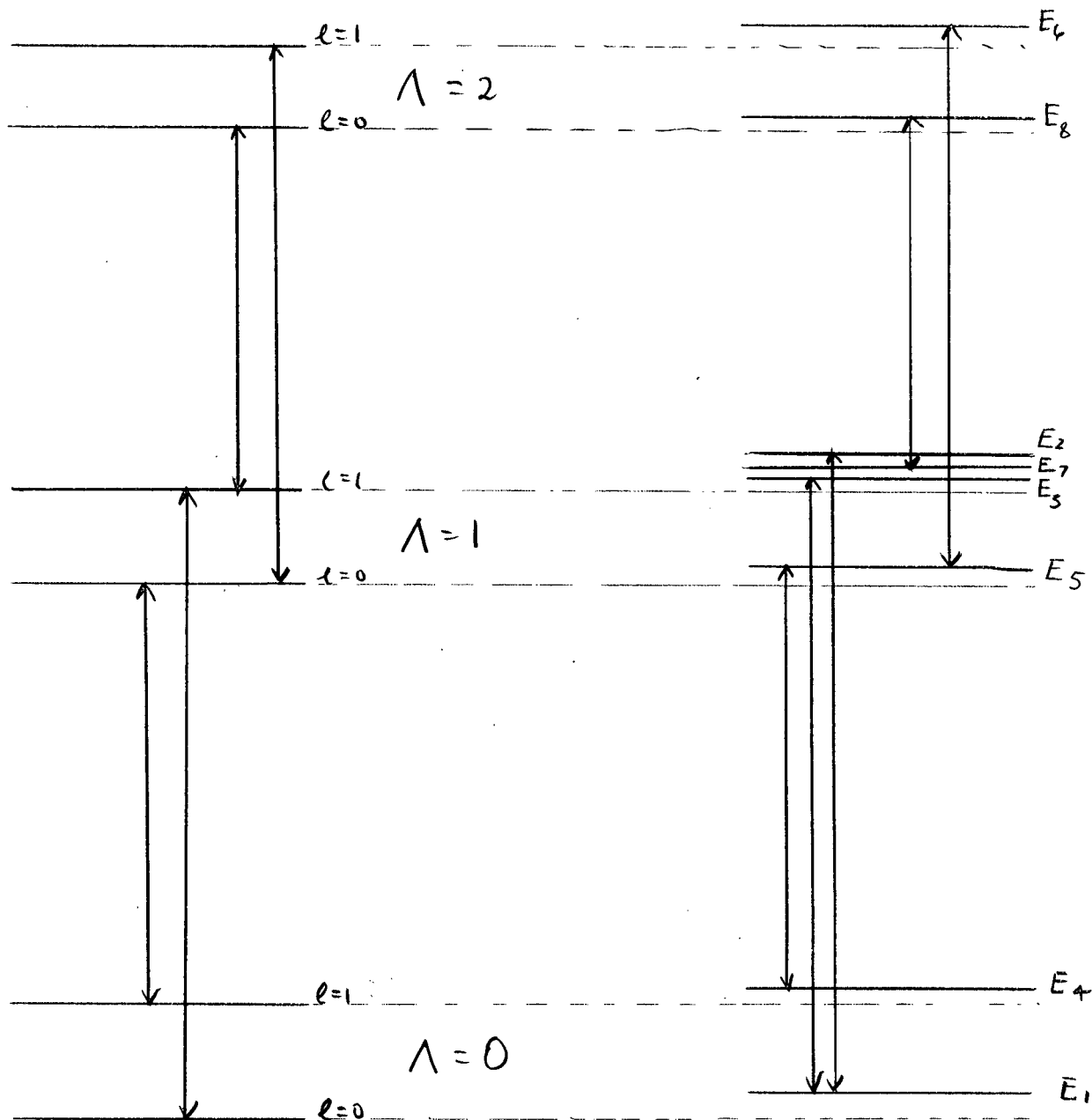
Diagram 1   Diagram 2

APPENDIX

Associated Laguerre Polynomials[8]

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

(A-1) $\quad \left[-\left(\frac{\partial^2}{\partial q_{2a}^2} + \frac{\partial^2}{\partial q_{2b}^2}\right) + q_{2a}^2 + q_{2b}^2 - \mathcal{E}\right] \Psi_n = 0$

In polar co-ordinates $\left(q_2, \varphi_n\right)$ defined by

$$q_{2b} = q_2 \cos \varphi_n$$
$$q_{2a} = q_2 \sin \varphi_n$$

equation (A-1) becomes

$$\left[\frac{1}{q}\frac{\partial}{\partial q}\left(q\frac{\partial}{\partial q}\right) + \frac{1}{q^2}\frac{\partial^2}{\partial \varphi^2} + \left(\mathcal{E} - q^2\right)\right]\Psi = 0$$

(The subscripts n on Ψ_n and 2 on q_2 will be omitted in this appendix.)

Ψ is separable into

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

and

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

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

$$\left(\frac{d^2}{dq^2} + \frac{1}{q}\frac{d}{dq} + \mathcal{E} - q^2 - \frac{\ell^2}{q^2}\right)R = 0$$

Putting $\quad R(q) = e^{-q^2/2}\,F(q)$

F(q) satisfies

$$\left[\frac{d^2}{dq^2} + \left(\frac{1}{q} - 2q\right)\frac{d}{dq} + \left(\mathcal{E} - 2 - \frac{\ell^2}{q^2}\right)\right]F = 0$$

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

$$F(q) = q^\ell f(q)$$

and

$$\left[\frac{d^2}{dq^2} + \left[(2\ell+1)\frac{1}{q} - 2q\right]\frac{d}{dq} + \left(\mathcal{E} - 2\ell - 2\right)\right]f = 0$$

In terms of the variable $\rho = q^2$,

$$f(q) \equiv g(\rho)$$

and

$$\left[\rho \frac{d^2}{d\rho^2} + (\ell + 1 - \rho) + \frac{1}{4}(\varepsilon - 2\ell - 2) \right] g = 0$$

A power series solution gives

$$\varepsilon = 2(V_2 + 1)$$

with $V_2 = 0, 1, 2, \ldots$

$$\ell = V_2, V_2 - 2, V_2 - 4, \cdots, 1 \text{ or } 0.$$

Thus

$$E_2 = \frac{\hbar \nu_2}{2} \varepsilon$$

or $(A-2)$

$$E_2 = \hbar \nu_2 (V_2 + 1)$$

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

$$\sigma - \ell = \frac{V_2 - \ell}{2}$$

or

$$\sigma = \frac{V_2 + \ell}{2}$$

which is the equation of the associated Laguerre polynomials $L_\sigma^\ell(\rho)$;

$$g(\rho) = L_\sigma^\ell(\rho)$$

Thus

$(A-3)$
$$\begin{cases} R_{V_2 \ell}(q) = R_{\sigma\ell}(\rho) \\ \qquad = N_{\sigma\ell} \, e^{-\rho/2} \rho^{\ell/2} L_\sigma^\ell(\rho) \end{cases}$$

The generating function of the Laguerre polynomials is given by

$$U(\rho, u) = \sum_{\sigma = \ell}^{\infty} L_\sigma^\ell(\rho) \frac{u^\sigma}{\sigma!}$$

$$= (-u)^\ell \left[\exp\left(\frac{-\rho u}{1-u} \right) \right] \frac{1}{(1-u)^{\ell+1}}$$

The normalizing factor $N_{\sigma\ell}$ is found to be

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

References:

1. R. Renner,
        Zeits. f. Physik $\underline{92}$, 172 (1934).

2. M. Born and R. Oppenheimer,
        Ann. d. Physik $\underline{84}$, 457 (1927).

3. H. Sponer and E. Teller,
        Rev. of Mod. Phys. $\underline{13}$, 75 (1941).

4. H.C. Longuet-Higgins,
        Advances in Molecular Spectroscopy, Vol II, Edited by
        H.W. Thompson, Interscience Publishers Inc., New York.

5. G. Herzberg,
        Molecular Spectra and Molecular Structure II.   Infra-red and
        Raman Spectra of Polyatomic molecules. ....
        D. Van Nostrand Co., Inc., Toronto, p.72.

6. J.J. Markham,
        Phys. Rev. $\underline{103}$, 588 (1956).

7. E.T. Wittaker and G.N. Watson,
        A course of Modern Analysis, fourth edition, Cambridge
        University Press, 1963, p.302.

8. W.H. Shaffer,
        Rev. of Mod. Phys. $\underline{16}$, 245 (1944).