VIBRONIC INTERACTION
IN
LINEAR POLYATOMIC MOLECULES

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LINEAR POLYATOMIC MOLECULES

By

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SCOPE AND CONTENTS:

This thesis deals with the weak interaction between the electronic and degenerate vibrational motions in linear polyatomic molecules. Second-order vibronic energy expressions are obtained for triatomic and tetratomic molecules in degenerate electronic states.

PREFACE

In certain molecular systems, the motion of the electrons are strongly influenced by the vibrational motion of the nuclei. In particular, when this coupling between the electronic and nuclear motions occurs in a linear molecule, the vibronic interaction is termed the Renner effect.

In this thesis, we investigate the consequence of the Renner effect on the properties of linear polyatomic molecules. This problem has been previously considered in detail only for a triatomic system. The complication encountered in extending the study to polyatomic systems lies in the increase in the number of nuclear vibrational motions which can couple with the motion of the electron.

Knowledge begins with the observation of nature and theoretical predictions based upon a consideration of these observations must then be turned again to nature and tested against further observation. My regret is that the final step in this process is not at the moment possible for the prediction contained in this thesis because of lack of experimental data.

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$\vec{r}_i$	the position vector of the "single" electron; $\vec{r}_i = (\rho,\theta,z)$.
$\vec{r}_\alpha$	the position vector of the atom α; $\vec{r}_\alpha = (\rho_\alpha,\theta_\alpha,z_\alpha)$ or $(x_\alpha,y_\alpha,z_\alpha)$; $(\alpha = A,B,\ldots\ldots,N)$.
Q	stands for: (a) a collective set of vibrational coordinates; (b) a configuration for the molecule.
Q^o	the "equilibrium" or linear configuration ($Q^o = 0$).
$\underline{q}_k$	the k^{th} doubly degenerate (bending) normal coordinate; $\underline{q}_k = (q_{ka},q_{kb})$; a,b = +,- or x,y; $(k = 1,2,\ldots\ldots,t)$.
r_k,ϕ_k	the radial amplitude and the azimuthal angle of the k^{th} bending mode.
q_λ^+,q_λ^-	$\equiv e^{\pm i\lambda\theta}$
Q_λ^+,Q_λ^-	e.g., $Q_\pi^\pm = \sum_{k=1}^{t} r_k^2 e^{\pm 2i\phi_k}$ for symmetrical linear tetratomic molecules.
ℓ_k^α	coordinate transformation matrix elements.
m_e	mass of electron.
e_i,e	electronic charge.
$\hbar$	$1/2\pi$ Planck constant.
m_α	mass of the α-atom.
$\mathcal{Z}_\alpha$	the effective charge of the α-atom.
μ_k	the reduced mass of the k^{th} oscillator.
ω_k	angular frequency for the k^{th} vibrational mode.
$\mathcal{k}$	the force constant for the k^{th} mode vibration, $\mathcal{k} = \mu_k\omega_k^2$.
a_k	$= \hbar/\mu_k\omega_k$.
ε_k	the Renner parameters (second-order).
η_k	the 4^{th} order vibronic parameters.

U, $U(Q)$	vibrational potential: $U(Q) = U^o(r_k^2) + U'(Q)$.
H'_λ	representative vibronic perturbation in the λ-electronic level.
H'	representative total perturbation: $H' = U'(Q) + H'_\lambda$.
$H^{(2)}$, $H^{(4)}$	quadratic and quartic perturbation functions: $H^{(2)}(r_k^2,\theta-\phi_k)$, $H^{(4)}(r_k^4,\theta-\phi_k)$.
$H_e(\lambda)$	representative electronic Hamiltonian in the λ-electronic level: $H_e(\lambda) = H_e^o + U + H'_\lambda$.
H	representative vibronic Hamiltonian: $H = H_e(\lambda) + T_N$.
$W_{ea}(Q)$, $W_\lambda(Q)$	electronic energy at nuclear configuration Q; a Born-Oppenheimer potential; a potential (vibrational) surface.
$W_e^o(Q^o)$, W_λ^o	electronic energy at $Q^o = 0$, a constant.
$\mathcal{E}^o_{\nu_k}$, $\mathcal{E}^o_{\nu_1,\nu_2}$	the zeroth-order vibrational energy.
$\mathcal{E}_j^{(1)}(K;\nu_1,\nu_2)$	the first-order vibronic energy correction for the j^{th} component in the vibronic level $[\nu_1,\nu_2]^K$.
$\mathcal{E}_j^{(2)}(K;\nu_1,\nu_2)$	the second-order vibronic energy correction.
$E_j(K;\nu_1,\nu_2)$	vibronic energy; $E_j(K;\nu_1,\nu_2) = \mathcal{E}^o_{\nu_1,\nu_2} + \mathcal{E}_j^{(1)}(K;\nu_1,\nu_2) + \mathcal{E}_j^{(2)}(K;\nu_1,\nu_2)$.

$\rangle$	state, state kets, or state function.
$\|\Lambda\rangle$, $\|\psi_\Lambda^o\rangle$	the Λ-electronic state.
$\psi_{ea}(\vec{r}_i;Q)$	Q-dependent electronic wave functions; Born-Oppenheimer electronic wave functions; adiabatic electronic wave functions.
$\psi_e^o(\vec{r}_i,Q^o)$	Q-independent electronic wave function.
$\psi_\Lambda^o(\vec{r}_i;0)$	the zeroth-order electronic wave function, $\psi_\Lambda^o(r_i,0) = u_\lambda(z,\rho)e^{i\Lambda\theta}$.
$\Phi^{ea}(Q)$, $\Phi^e(Q)$, $\Phi_r(Q)$, $\chi_r(Q)$	vibrational functions; variational nuclear functions.
$\phi_r^o(K;\nu_1,\nu_2)$	$= \|\Lambda^{(r)};\nu_1,\ell_1^{(r)};\nu_2,\ell_2^{(r)}\rangle$, with $K = \Lambda^{(r)} + \ell_1^{(r)} + \ell_2^{(r)}$.
$\phi_r^{(1)}$, $\phi_r^{(2)}$	the first- and second-order corrections to the Van Vleck basis functions, ψ_r^o.

ψ_r^o, $\psi_r^o(K;v_1,v_2)$	the r^{th} Van Vleck basis function in the $[v_1,v_2]^K$-level: $\psi_r^o = \phi_r^o + \phi_r^{(1)} + \phi_r^{(2)}$.
$\Psi_j^o(K;v_1,v_2)$	the correct zeroth-order vibronic wave function.
$\Psi_j^{(1)}(K;v_1,v_2)$	the first-order correction for the vibronic state function.
$\Psi_j(K;v_1,v_2)$	the j^{th} vibronic state function in the vibronic level $[v_1,v_2]^K$.
$\Phi_j^{\pm}(K;v_1,v_2)$	the vibrational wave functions associated with the (+) and (-) electronic state; $\Psi_j(K;v_1,v_2) = \psi_+^o(\vec{r}_i,0)\cdot\Phi_j^+(K;v_1,v_2) + \psi_-^o(\vec{r}_i;0)\cdot\Phi_j^-(K;v_1,v_2)$.
$\mathbb{S}(K;v_1,v_2)$	orthogonal transformation matrices for the vibronic level $[v_1,v_2]^K$.
a_r, $a_r(K;v_1,v_2)$	by-diagonal elements in the Van Vleck degenerate matrices.
z_r, $z_r(K;v_1,v_2)$	diagonal elements in the Van Vleck degenerate matrices.
$\mathbb{Z}(K;v_1,v_2)$	$= \text{diag.}\ (z_1,z_2,\ldots\ldots,z_n)$.
$\mathbb{P}_z$	vibronic angular momentum matrix (operator).
$\mathbb{G}_z$	vibrational angular momentum matrix (operator).
$\mathbb{H}_v$	vibrational Hamiltonian matrix (operator).
Σ_σ	Pauli spin matrices, $\sigma = 1,2,3$.
$C_{\Lambda\ V_1\ell_1 v_2\ell_2}^{\Lambda' V_1'\ell_1' v_2'\ell_2'}$	interaction coefficients.
$\langle\psi_e\|\hat{O}\|\psi_{e'}\rangle_{el.}$	electronic integrals.
$\langle\Phi_v\|\hat{O}\|\chi_v\rangle_Q$	vibrational integrals.
$q(v_k+a,\ell_k+b)$, $A(v_k+a,\ell_k+b)$, $B(v_k+a,\ell_k+b)$	vibrational radial integrals: $(R_{v\|\ell\|}(r)\|r^m\|R_{v'\|\ell'\|}(r))$, m = 1, 2 and 4.
$\vec{M}$	dipole moment vector: $\vec{M} = (M_+,M_o,M_-)$; M_σ $(\sigma = +, o, -)$.
f_σ^{mn}	oscillator strength for σ-component in the transition from state n to state m.
M_σ^{mn}	transition moment integral for the transition $m \leftarrow n$.

CHAPTER 1

INTRODUCTION

1-1 Interactions Within a Molecule

"Interaction", in most cases, is just another name for "approximation". There are, for example, rotational-vibrational (vibrorotatory) interactions, rotational-electronic (rotonic) interactions, vibrational-electronic (vibronic) interactions, configuration interactions, rotational-vibrational-electronic (rovibronic) interactions, etc. (see Table 1-1). In solving molecular Schröedinger equations we are forced to deal with various kinds of interactions via approximate methods because no exact solutions are possible except for the simplest systems.

To date, the universally-accepted scheme to solve the molecular Schröedinger equations is that of Born and Oppenheimer(1,2). The Hamiltonian of the translationless molecule is partitioned into terms of increasing power of κ which is the fourth root of the ratio of the electronic mass (m) to the nuclear mass (M), i.e., $\kappa = (m/M)^{1/4}$. In so doing, we have(3)

$$H_{mol}(\beta,\vec{r}_i,\underline{q}_k,\chi_R) = H_e(\beta,\vec{r}_i;\vec{r}^{\,o}_\alpha) + \kappa H'_{evR}(\vec{r}_i,\underline{q}_k,\chi_R) + \kappa^2 H_v(\underline{q}_k;\vec{r}^{\,o}_\alpha)$$

$$+ \kappa^3 H'_{vR}(\underline{q}_k,\chi_R) + \kappa^4 H_R(\chi_R;\vec{r}^{\,o}_\alpha) \qquad (1.1.1)$$

where the functions H'_{evR}, H_v, H'_{vR}, H_R, etc. can be written as

$$\kappa H'_{evR}(\vec{r}_i,\underline{q}_k,\chi_R) = \kappa \sum_k \left(\frac{\partial H_{mol}}{\partial \underline{q}_k}\right)_{Q^o} \cdot \underline{q}_k + \kappa^2 \sum_k \sum_{k'} \frac{1}{2} \left(\frac{\partial^2 H_{mol}}{\partial \underline{q}_k \partial \underline{q}_{k'}}\right)_{Q^o} \cdot \underline{q}_k \underline{q}_{k'} + \dots$$

$$\kappa^2 H_v(\underline{q}_k;\vec{r}^{\,o}_\alpha) = \kappa^2 H^o_v(\frac{\partial^2}{\partial\underline{q}_k\partial\underline{q}_{k'}};\ \vec{r}^{\,o}_\alpha) + \kappa^3 \sum_k (\frac{\partial H_v}{\partial\underline{q}_k})_{Q^o}\cdot\underline{q}_k + \ldots$$

$$\kappa^3 H'_{vR}(\underline{q}_k,\chi_R) = \kappa^3 H^o_{vR}(\chi_R,\ \frac{\partial}{\partial\underline{q}_k},\ \frac{\partial}{\partial\chi_R};Q^o) + \kappa^4 \sum_k (\frac{\partial H_{vR}}{\partial\underline{q}_k})_{Q^o}\cdot\underline{q}_k + \ldots$$

$$\kappa^4 H_v(\chi_R;Q^o) = \kappa^4 H^o_R(\chi_R,\ \frac{\partial^2}{\partial\chi_R\partial\chi_{R'}};Q^o) + \kappa^5 \sum_k (\frac{\partial H_R}{\partial\underline{q}_k})_{Q^o}\cdot\underline{q}_k + \ldots$$

where β, $\vec{r}_i$, $\underline{q}_k$ and χ_R are spin, electronic, vibrational and rotational coordinates respectively. $\vec{r}^{\,o}_\alpha$ are the cartesian coordinates of nuclear position vectors at equilibrium or of a chosen nuclear configuration Q^o.

In general, none of the terms in Equation (1.1.1) is completely solvable. Thus we have to speak of spin-orbit coupling, and configuration interactions in the function $H_e(\beta,\vec{r}_i;\vec{r}^{\,o}_\alpha)$; anharmonic vibrations in $H_v(\underline{q}_k;\vec{r}^{\,o}_\alpha)$ and asymmetric top rotations in $H_R(\chi_R;\vec{r}^{\,o}_\alpha)$. When other terms are momentarily ignored, these three Hamiltonian functions will give the following equation

$$\{H_e(\beta,\vec{r}_i;\vec{r}^{\,o}_\alpha) + \kappa^2 H_v(\underline{q}_k;\vec{r}^{\,o}_\alpha) + \kappa^4 H_R(\chi_R;\vec{r}^{\,o}_\alpha) - E\}\Psi(\beta,\vec{r}_i,\underline{q}_k,\chi_R;\vec{r}^{\,o}_\alpha) = 0 \qquad (1.1.2)$$

whose solutions will be in a product form$^{(4)}$:

$$\Psi(\beta,\vec{r}_i,\underline{q}_k,\chi_R;\vec{r}^{\,o}_\alpha) = \psi_e(\beta,\vec{r}_i;\vec{r}^{\,o}_\alpha)\cdot\psi_v(\underline{q}_k;\vec{r}^{\,o}_\alpha)\cdot\psi_R(\chi_R;\vec{r}^{\,o}_\alpha) \qquad (1.1.3)$$

When H'_{evR} and H'_{vR} are taken into account, the product solution (1.1.3) will be no longer valid. H'_{vR}, which contains inseparable vibrational and rotational coordinates, will "couple" the vibrational motion with the rotational motion and thus affect the last two factors of Equation (1.1.3). The term H'_{evR}, which contains terms involving inseparable electronic-vibrational, electronic-rotational as well as electronic-vibrational-

TABLE 1-1

Examples of Interactions in Molecular Systems

Angular momentum coupling and coordinate coupling can be represented by the "cosine rule", $H' = \alpha\beta\cdot\gamma$ where the coefficient α is a constant of proportionality. In angular momentum coupling both β and γ are angular momentum operators. In coordinate coupling, they are functions of coordinate vectors. For symbols, see the "list of symbols and notations".[†]

Effects	Systems	Perturbations $H' = \alpha\beta\cdot\gamma$	References
Spin-orbit interaction	Linear molecules	$H' = \zeta L_z S_z$	E. Hill and J. H. Van Vleck, Phys. Rev. 32, 250 (1928).
Nuclear Zeeman effect	Atoms	$H' = \gamma \mathbf{I}\cdot S$	Condon and Shortley, "The Theory of Atomic Spectra" p. 421-7.
Nuclear spin-spin coupling	Nuclear spin states N.M.R.	$H' = \sum_{ij} J_{ij} I_i \cdot I_j$	N. F. Ramsey, Phys. Rev. 91, 303, (1953).
ρ-type doubling (spin doubling)	Diatomic molecules Hund's case (b)	$H' = \gamma J\cdot S$	R. S. Mulliken, Rev. Mod. Phys. 2, 60 (1930).
Λ-type doubling	Diatomic molecule linear molecule	$H' = -2B[J^+L^- + J^-L^+]$	J. H. Van Vleck, Rev. Mod. Phys. 23, 213 (1951).
Ω-type doubling	Diatomic, Hund's case (c)	$H' = -2BJ\cdot(L + S)$	G. Herzberg, "Spectra of Diatomic Molecule" p. 229, D. Van Nostrand, Inc.
K-type doubling	Linear molecules in degenerate vibronic state, i.e., $\lvert K\rvert > 0$	$H' = -B(J^+P^- + J^-P^+)$	J. W. C. Johns, J. Mol. Spect. 15, 473 (1965).
j-type doubling	Jahn-Teller molecules	$H' = \frac{1}{4}\mu_\perp[(J^+-L^+)(J^--L^-) + (J^--L^-)(J^+-L^+)]$	M. S. Child, Mol. Phys. 5, 391 (1962).

TABLE 1-1 (continued)

Effects	Systems	Perturbations $H' = \alpha\beta\cdot\gamma$	References
ℓ-type doubling	Axially symmetric molecules in degenerate vib. state	$H' = -\sum_{i=x,y,z} \frac{J_i G_i}{I^e_{ii}}$	H. H. Nielsen, Phys. Rev. 75, 1961 (1949).
P-type doubling	Linear molecules $^2\Sigma$ vibronic levels, Hund's case (c)	$H' = \tilde{A}(L_x S_x + L_y S_y)$ $- 2\tilde{B}\, W\cdot J$	J. T. Hougen, J. Chem. Phys. 36, 519, (1962).
Coulomb interactions	Atoms molecules	$H' = \sum_{i,j} \frac{1}{r_{ij}}$	
Vibrational ℓ-type doubling	Axially symmetric molecules in degenerate vibrational states	H' = anharmonic terms $H' = k_{stt'}(q_t + q'_-$ $+ q_- q'_+)\cdot q_{s/2}$	T. Oka, J. Chem. Phys. 47, 5410 (1967).
Jahn-Teller splitting	Symmetrical non-linear molecules in electronic degenerate states	$H' = f(q_+^2 + q_-^2)q_1$ $+ ig(q_+^2 - q_-^2)q_2$	J. T. Hougen, J. Mol. Spect. 13, 149 (1960).
Renner splitting	Linear molecule in (π) electronic degenerate states; linear molecules in λ-electronic state	$H' = \frac{1}{2}f(q_+^2 q_{2-}^2 + q_-^2 q_{2+}^2)$ $H' = q_\lambda^+ Q_\lambda^- + q_\lambda^- Q_\lambda^+$	J. A. Pople, Mol. Phys. 3, 16 (1960). Thesis, Chapter 3.

[†] S: spin angular momentum (electron); I: nuclear spin angular momentum;

J: total angular momentum; W = L + S + G. $W_2 \rightarrow P\not{K}$; $(P = \Lambda + \Sigma + \ell)$

rotational coordinates will couple all three motions together.

1.2 Vibrational-Electronic (Vibronic) Interactions

The present investigation is concerned only with vibrational and electronic motions within a molecule. We can prohibit the molecule from rotating by setting the rotational angular momentum equal to zero, and the right-hand side of Equation (1.1.1) will be reduced to

$$H_e(\beta,\vec{r}_i;Q^o) + \kappa H'_{ev}(\vec{r}_i,\underline{q}_k) + \kappa^2 H_v(\underline{q}_k;Q^o)$$

which with some rearrangement of terms and the neglect of the spins gives the spinless-, rotationless- and translationless-Hamiltonian, or vibronic Hamiltonian:

$$H_{ev}(\vec{r}_i,Q) = T_e(\nabla_i^2) + V(\vec{r}_i,Q) + T_N(\nabla_k^2) \tag{1.2.1}$$

where Q stands for a collective set of nuclear displacement or normal coordinates. T_e and T_N are kinetic energy operators for electrons and nuclei respectively, and $V(\vec{r}_i,Q)$ is the electrostatic potential within the molecule. The solution $\Psi_{ev}(\vec{r}_i,Q)$ which satisfy the eigen-value equation

$$\{H_{ev}(\vec{r}_i,Q) - E_{ev}\}\Psi_{ev}(\vec{r}_i,Q) = 0 \tag{1.2.2}$$

is called the "vibronic wavefunction", a combined function which describes the vibrational and electronic motions of the molecule.

In the Born-Oppenheimer approximation$^{(1,2)}$, the solution of Equation (1.2.2) is written as

$$\Psi_{ev}(\vec{r}_i,Q) = \psi_e(\vec{r}_i;Q)\cdot\Phi_v^e(Q) \tag{1.2.3}$$

where $\psi_e(\vec{r}_i;Q)$ is the "electronic wavefunction" which contains the nuclear coordinates parametrically, that is, it satisfies the electronic Schröedinger equation for fixed values of Q:

$$\{T_e(\nabla_i^2) + V(\vec{r}_i;Q) - W_e(Q)\}\psi_e(\vec{r}_i;Q) = 0 \qquad (1.2.4)$$

where the eigenvalue $W_e(Q)$ is called a "Born-Oppenheimer Potential" which is a function of nuclear coordinates; this will describe the potential surface in the electronic state $|\psi_e>$. $\Phi_v^e(Q)$, which is a function of nuclear coordinates only, describes the nuclear motion under the influence of the potential $W_e(Q)$. Thus the combined motion described by Equation (1.2.3) is simply a superposition of the vibrational motion on the electronic motion.

Equation (1.2.3) rests on the premise that the spacings in electronic energies $[W_{e'}(Q) - W_e(Q)]$ are much greater than the vibrational ones. In a lower-order of approximation, the electronic wavefunction $\psi_e(\vec{r}_i;Q)$ may be replaced by $\psi_e^o(\vec{r}_i;Q^o)$ which satisfies, instead of Equation (1.2.4), the following equation

$$\{T_e(\nabla_i^2) + V^o(\vec{r}_i,Q^o) - W_e^o(Q^o)\}\psi_e^o(\vec{r}_i;Q^o) = 0 \qquad (1.2.5)$$

where $V^o(\vec{r}_i,Q^o) = \lim_{Q \to Q^o} V(\vec{r}_i,Q)$, with Q^o referring to an arbitrary nuclear configuration, say the "equilibrium" configuration.

In a higher-order of approximation, or when the electronic level $W_e(Q)$ is degenerate or nearly degenerate, the product function (1.2.3) no longer provides a satisfactory description of the system. If we want to preserve even partly the idea of "electronic plus vibrational" motions, Ψ_{ev} must be given in a "Born development"(5,6,7)

$$\Psi_{ev}(\vec{r}_i,Q) = \sum_{e'} \psi_{e'}(\vec{r}_i;Q)\Phi_v^{e'}(Q) \qquad (1.2.6)$$

Equation (1.2.6) presupposes that the electronic wavefunctions $\psi_e(\vec{r}_i,Q)$ are intimately associated with a unique "potential energy surface" $W_e(Q)$, and that the nuclear function $\Phi_v^e(Q)$ describes the nuclear movements upon this surface. The summation implies a rapid induced distortion of both the electronic and nuclear wavefunctions.

Herzberg$^{(8)}$ has distinguished two types of vibronic interaction.

(a) Type (a) vibronic interaction: refers to the dependence of the electronic wavefunction upon the nuclear coordinates Q, i.e., $\psi_e = \psi_e(\vec{r}_i,Q) \neq \psi_e^o(\vec{r}_i,Q^o)$.

(b) Type (b) vibronic interaction: refers to the case where the molecular wavefunction $\Psi_{ev}(\vec{r}_i,Q)$ can not be given as a simple product function for degenerate or nearly degenerate electronic levels.

In discussing the type (a) interaction and obtaining the Born-Oppenheimer potential $W_e(Q)$, one has the so-called "Static Problem", for the nuclei are "clamped" at a fixed configuration Q. In discussing the type (b) interaction and obtaining the total (vibronic) energy spectrum E_{ev}, one has then the "Dynamical Problem" because the nuclear kinetic energy operators are included.

1.3 Kinetic Effect and Potential Effect

The dynamical problem of interaction can be treated in two ways.

(i) The dependence of the electronic wavefunction ψ_e on nuclear coordinates Q is achieved by writing, into Equation (1.2.4),

$$V(\vec{r}_i,Q) = V^o(\vec{r}_i,Q^o) + V'(\vec{r}_i,Q) \qquad (1.3.1)$$

The "unperturbed" Equation (1.2.5) is first solved, and then $\psi_e(\vec{r}_i;Q)$ of

Equation (1.2.4) is developed in terms of $\psi_e^o(\vec{r}_i;Q^o)$:

$$\psi_e(\vec{r}_i;Q) = \sum_{e'} \psi_{e'}^o(\vec{r}_i;Q^o)C_{e'e}(Q) \tag{1.3.2}$$

where the summation ($\sum_{e'}$) is over the closely-spaced "unperturbed" states $|\psi_{e'}^o>$. Thus the $\psi_e(\vec{r}_i;Q)$ will exhibit the symmetry properties of the vibrating molecule.

However, as the nuclei are displaced from the "equilibrium" Q^o, the electronic charge density, represented by $|\psi_e(\vec{r}_i;Q)|^2$, relaxes in such a way so to exert forces $-(\partial W_e(Q))/\partial Q$ on the nuclei and thus modified the nuclear kinetic energy(9). Conversely, the movement of the nuclei forces the electron to move back and forth rapidly among the degenerate or nearly degenerate electronic states $|\psi_e(\vec{r}_i;Q)>$. Hence it is a good approximation to write the vibronic solution $\Psi_{ev}(\vec{r}_i,Q)$ for Equation (1.2.2) as

$$\Psi_{ev}(\vec{r}_i,Q) = \sum_{e}^{\text{"degenerate" level}} \psi_e(\vec{r}_i;Q)\Phi_v^e(Q) \tag{1.3.3}$$

where $\Phi^e(Q)$ will be determined by perturbation method(5,6) or variational method(7).

(ii) The second treatment of the dynamical problem is as follows: one obtains the Q-independent electronic wavefunctions $\psi_e^o(\vec{r}_i;Q^o)$ from Equation (1.2.5), but does not proceed to obtain $\psi_e(\vec{r}_i;Q)$ by Equation (1.3.2) and Equation (1.2.4) as in the first treatment. Thus one does not have to consider the (a)-type vibronic interaction. Instead the vibronic wavefunctions are given directly by

$$\Psi_{ev}(\vec{r}_i,Q) = \sum_{e'}^{\text{"degenerate"level}} \psi^o_{e'}(\vec{r}_i;Q^o)\cdot\Phi^{e'}_{v'}(Q) \qquad (1.3.4)^\dagger$$

The perturbation potential $V'(\vec{r}_i,Q)$ of Equation (1.3.1) is combined with the nuclear kinetic energy operator T_N in determining the (b)-type vibronic interaction, i.e., the variational functions $\Phi^{e'}(Q)$ of Equation (1.3.4), and the vibronic energies, E_{ev}. Since $\psi^o_e(\vec{r}_i;Q^o)$ does not vary as Q, the nuclear kinetic energy operator T_N, will not give any coupling effect between different electronic states $|\psi^o_e>$, namely $T_N|\psi^o_e> = 0$. Only the perturbed potential $V'(\vec{r}_i,Q)$ couple the $\psi^o_e(\vec{r}_i,Q^o)$ in the type (b) vibronic interaction.

These two treatments have been unified by Hobey and McLachlan(10,11) and discussed by many authors(7,12). We shall slightly modify Hobey and McLachlan's theory in Chapter 2, and call the first treatment the "Adiabatic Formulation" and the second treatment, the "Harmonic Formulation".†† They are so termed because in the "Adiabatic Formulation", one uses the electronic wavefunctions for the "deformed" molecules as if an adiabatic separation of nuclear and electronic motions were feasible. In the "Harmonic Formulation" the use of a Q-independent electronic wavefunction implies that the electron disregards the instantaneous positions of the nuclei and instead sees the nuclear charges only at the averaged positions of the nuclear harmonic motion in the vicinity of Q^o.

1.4 Angular Momentum Coupling and Coordinate Coupling

As seen from Table 1-1, whenever kinetic operators (differentiations) are involved we have angular momenta coupling(13,14), and whenever potential

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† Equations (1.3.3) and (1.3.4) are formally the same as far as $\psi_e(\vec{r}_i,Q)$ of Equation (1.3.3) are expressible in terms of Equation (1.3.2). However, (theoretically), $\psi_e(\vec{r}_i,Q)$ may be obtained, say, by direct solution of Eq. (1.2.4)

†† A. D. Liehr(12) has used the names "extremal" and "cuspidal" expansions respectively.

functions are involved we have coordinate coupling. Therefore we expect that there are both angular momentum coupling and coordinate coupling in the Adiabatic Formulation while there is only coordinate coupling in the Harmonic Formulation. However, since only the total energy of the system is conserved, the kinetic energy and the potential energy must relate intimately with each other. This relationship may be implied in the commutator $[x,p] = i\hbar$, and any coordinate coupling may be transformed into angular momentum coupling. (For example, the operator equivalent method in Ligand Field Theory(15).) Moffitt and Thorson(17) constructed an angular momentum operator for the vibronic systems by making the operator commute with both the perturbed potential $V'(\vec{r}_i,Q)$ and the unperturbed vibronic Hamiltonian $H^o_{ev}(\vec{r}_i,Q^o)$. Thus one can speak of the coupling of the vibrational angular momentum with the electronic (orbital) angular momentum, and the resultant vibronic wavefunctions can be classified by their total (vibronic) angular momentum quantum number, which, for linear molecule, is defined by(18)

$$K \equiv \Lambda + \ell$$

where Λ is the z-component of the electronic (orbital) angular momentum and ℓ is the z-component of the vibrational angular momentum. In the absence of vibronic interaction, both Λ and ℓ are good quantum numbers, but in the presence of vibronic interaction, only their sum remains as a good quantum number. For axially symmetrical molecules, the total (vibronic) angular momentum is denoted by 2j with(19)

$$j = \ell + \tfrac{1}{2} \quad \text{or} \quad \ell - \tfrac{1}{2}$$

1.5 Jahn-Teller-Renner Effect

The Jahn-Teller Effect and the Renner Effect are two aspects of the vibronic interaction problem, the former referring to non-linear molecules, the latter to linear molecules.

As we have previously noted, the vibronic interactions originate in the changes in the potential field resulting from the molecular vibrations and the nuclei are displaced from the more symmetrical positions. The difference between the instantaneous electrical potential and the potential of the "hyperthetically" symmetrical configuration Q^o will act as the perturbation. This perturbation couples strongly two or more electronic states (with reference to the symmetrical configuration) if they are close in (electronic) energy. Usually, the term "Jahn-Teller-Renner Effect" is applied to the vibronic interactions in a degenerate electronic level. For the vibronic interactions of nearly degenerate electronic states, we use the term "pseudo Jahn-Teller-Renner Effect".

The vibronic perturbation, in most cases, is obtained by Taylor's series expansion in increasing power of nuclear displacement coordinates (or normal coordinates) with the assumption of infinitesimal vibrations(20,21) i.e.,

$$V'(\vec{r}_i,Q) = \left(\frac{\partial V}{\partial Q}\right)_{Q^o}\cdot Q + \frac{1}{2!}\left(\frac{\partial^2 V}{\partial Q^2}\right)_{Q^o}\cdot Q^2 + \frac{1}{3!}\left(\frac{\partial^3 V}{\partial Q^3}\right)_{Q^o}\cdot Q^3 + \dots \qquad (1.5.1)$$

where the derivatives $\left(\frac{\partial^n V}{\partial Q^n}\right)_{Q^o}$ are evaluated at $Q = Q^o$ and thus are independent of nuclear coordinates Q, but they are functions of electronic coordinates. When the problem of the geometrical stability(21,22,23) of the molecule is investigated, a Taylor's series expansion may be applied to the electronic matrix elements, i.e.,

$$<\psi^{o}_{e'}(\vec{r}_i,Q^{o})|T + V(\vec{r}_i,Q)|\psi^{o}_{e}(\vec{r}_i,Q^{o})>_{el}$$

$$= (W^{o} + T_N)\delta_{ee'} + V^{Q}_{e'e}\cdot Q + \frac{1}{2} V^{QQ}_{e'e}\cdot Q^2 + \ldots\ldots \qquad (1.5.2)$$

where $V^{Q}_{e'e}\cdot Q = \sum_k V^{k}_{e'e}\cdot \underline{q}_k$ and $\psi^{o}_{e'}$ and ψ^{o}_{e} are the component states of a degenerate electronic level with reference of symmetrical configuration Q^{o}.

The well-known Jahn-Teller theorem$^{(20)}$ was proved by group theory taking only the terms $V^{Q}_{e'e}\cdot Q$ into consideration. It states that "if a symmetrical non-linear molecule has a spatially degenerate electronic level than in this level it will tend to distort in such a way as to remove the electronic degeneracy". Mathematically, in the hyperthetical (symmetrical) molecule concerned, there exists at least one nontotally symmetrically normal vibration, say $\underline{q}_k$, so that the electronic integral

$$V^{k}_{e'e} \equiv \int \psi^{o}_{e'}\ (\vec{r}_i,Q^{o})\ \frac{\partial V}{\partial \underline{q}_k}\ \psi^{o}_{e}(\vec{r}_i,Q^{o})d\tau_i \qquad (1.5.3)$$

is different from zero.

In order to obtian the finer structure of the electronic potential surfaces$^{(24)}$ or to treat the dynamical problem of Jahn-Teller effect in a higher order of approximation$^{(25)}$, higher power terms of Equation (1.5.2) should be included. When only linear terms of Equations (1.5.1) or (1.5.2) are considered, we have the <u>linear Jahn-Teller Effect</u>$^{(17)}$ or the first-order Jahn-Teller Effect, whereas the name, the <u>quadratic Jahn-Teller Effect</u> or the second-order Jahn-Teller Effect is designated to the quadratic terms.

For linear molecules, it can be shown (Chapter 3) that no terms in $\underline{q}_k$ of odd degree can enter into Equation (1.5.2). Renner$^{(5)}$ pointed out that the splitting of the electronic potential surface is proportional to $Q^{2\lambda}$ in the λ-electronic level, where $\lambda = |\Lambda| = 0, 1, 2, 3, \ldots$ etc. are corresponding to Σ, Π, Δ, Φ..... etc. electronic levels respectively.

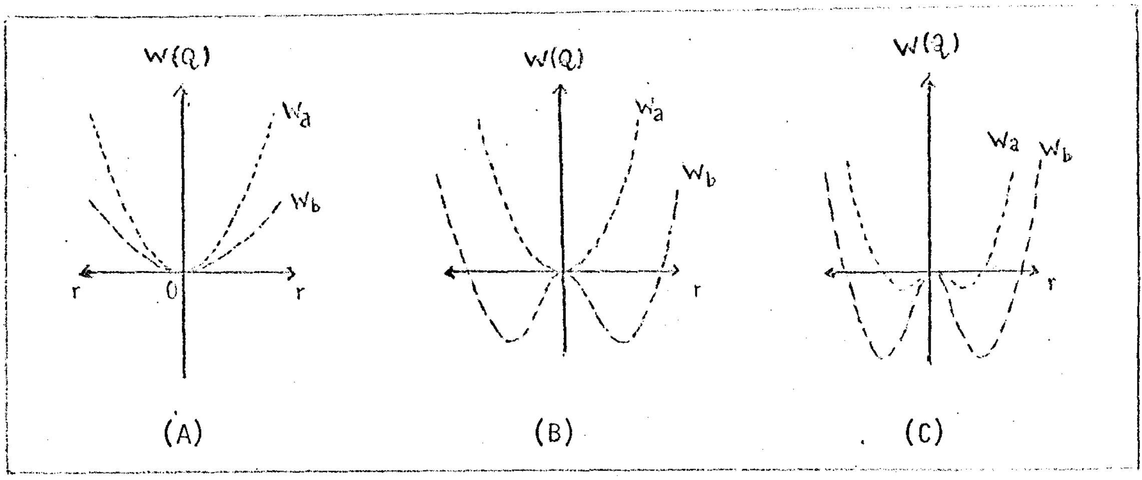
It is clear then that the Jahn-Teller and Renner effects are actually one and the same, depending on whether the first-degree or second-degree terms is predominate in Equation (1.5.2)$^{(26)}$.

1.6 Renner Effect in Linear Molecules

The Renner Effect in linear triatomic molecules has been discussed in detail for only a few cases (Table 1.2). The Born-Oppenheimer potentials which are denoted by $W_{ea}(Q)$, $W_{eb}(Q)$, are the eigen values of the electronic Hamiltonian matrix. The potentials are functions of a single bending coordinate and they may exhibit any one of the three possible structures shown in Fig. 1.3 (4.1) (Chapter 4 and Reference 18).

Fig. 1.3 Born-Oppenheimer Potentials of Linear Triatomic Molecules in a π-electronic level

r is the radial coordinate of the bending mode. $W_a(Q)$ is referred to the upper potential while $W_b(Q)$ the lower one.



The separation between the upper and the lower potential surfaces is proportional to r^2, r^4,..... etc. in π, Δ,..... etc. electronic levels

TABLE 1-2

Renner Effect in Linear Molecules

1.2A Weak Renner interactions in linear triatomic molecules; ω_2 = angular frequency of the bending vibration; ε = Renner parameter.

Systems, molecules	Electronic states	ω_2	$\varepsilon\omega_2$	ε	Observed Electronic Transitions	References
"CO_2" "NH_2"	Π $^2\Pi$	—			—	R. Renner, Z. Phys. <u>92</u>, 172 (1930). J. A. Pople (28)
NCO	$\tilde{X}^2\Pi$	539 cm^{-1}	-86 cm^{-1}	-0.181	Infrared	R. N. Dixon, Phil. Trans. <u>A252</u>, 165 (1960).
C_3	$\tilde{A}^1\Pi$	307.9 cm^{-1}	165.3 cm^{-1}	0.537	$\tilde{A}\leftrightarrow\tilde{X}^1\Sigma_g^+$ 4100-3400 Å	Gausset et al, Disc. Faraday Soc. (1960) 1963.
BO_2	$\tilde{X}\,^2\Pi_g$	464 cm^{-1}	-92.2 cm^{-1}	0.199	Infrared	J. W. C. Johns, Can. J. Phys. <u>39</u>, 1738 (1961).
	$\tilde{A}^2\Pi_u$	502 cm^{-1}	-13.1 cm^{-1}	0.026	$\tilde{A}\leftrightarrow\tilde{X}$ 6450-3965 Å	
CO^+_2	$\tilde{X}^2\Pi_g$		-93 cm^{-1}		Infrared	J. W. C. Johns, Can. J. Phys. <u>42</u>, 1004 (1964).
NCN	$\tilde{A}^3\Pi$	~460 cm^{-1}	-85.7 cm^{-1}	0.185	$\tilde{A}\leftarrow\tilde{X}\,^3\Sigma_g^-$ 3285-3260 Å	G. Herzberg, D. N. Travis, Can. J. Phys. <u>42</u>, 1658 (1964).
N_3	$\tilde{X}^2\Pi_g$	~500 cm^{-1}	-94.38 cm^{-1}~	-0.19	Infrared	A. E. Douglas and W. J. Jones, Can. J. Phys. <u>43</u>, 2216 (1965).

TABLE 1-2 (continued)

Systems, molecules	Electronic states	ω_2	$\varepsilon\omega_2$	ε	Observed electronic transitions	References
CCN	$\tilde{X}^2\Pi$	~325 cm^{-1}	144.1	~0.44	Infrared	A. J. Merer and D. N. Travis, Can. J. Phys. 43, 1795 (1965).
CNC	$\tilde{X}^2\Pi_g$	321 cm^{-1}	176.20	0.549	Infrared	A. J. Merer and D. N. Travis, Can. J. Phys. 44, 353 (1966).
CCN	$\tilde{A}^2\Delta_u$	~475 cm^{-1}	$\eta^2/\omega_2 = 0.14\ cm^{-1}$		$\tilde{A} \leftarrow \tilde{X}$ 4710-3770 Å	Can. J. Phys. 43, 1795 (1965).
CNC	$\tilde{A}^2\Delta_u$	440 cm^{-1}	$\eta^2/\omega_2 = 0.12\ cm^{-1}$		$\tilde{A} \leftarrow \tilde{X}$ 3320-3250 Å	Can. J. Phys. 44, 353 (1966).

1.2B Large Renner Interactions

Systems, molecules	Electronic states	Type of Potential Surfaces	Observed Transitions	References
"NH_2"	$^2\Pi$	(B); (Type B potential of Fig. 1.3)		J. A. Pople and H. C. Longuet-Higgins, Mol. Phys. 1, 372 (19).
BH_2	$^2\Pi_u \left[\begin{array}{l}\tilde{A}^2B_1(\pi)\\ \tilde{X}^2A_1\end{array}\right.$	(B)	$\tilde{A} \leftarrow \tilde{X}$ 8650-6400 Å	Polyatomic Molecules, G. Herzberg, Vol. III, p. 490.
$A\ell H_2$	$^2\Pi_u \left[\begin{array}{l}\tilde{A}^2B_1(\pi)\\ \tilde{X}^2A_1\end{array}\right.$	(B)		Electronic Spectra, G. Herzberg, Vol. III, p. 490.
CH_2	$^1\Delta_g \left[\begin{array}{l}\tilde{b}^1B_1\\ \tilde{a}^1A_1\end{array}\right.$	(C)	$\tilde{b} \leftarrow \tilde{a}$ 9000-5000 Å	G. Herzberg and J. W. C. Johns, Proc. Roy. Soc. (London) A295, 107 (1966).

TABLE 1-2 (continued)

Systems, molecules	Electronic states	Types of Potential surfaces	Observed Transitions	References
NH_2	$^2\Pi_u$ $\tilde{A}^2A_1(\pi)$ $\tilde{X}^2B_1$	(C)	$\tilde{A}\leftrightarrow\tilde{X}$ 9000-4300 Å	K. Drossler and D. A. Ramsay, Phil. Trans. A251, 553 (1959); R. N. Dixon, Mol. Phys. 9, 357 (1965).

1.2C Some Linear Four-, Five-, and Six-Atomic Molecules

Molecules	Electronic States	Bending Vibrations	Bond Systems	References
C_2H_2	$\tilde{G}^1\Pi_u$	$\nu_4(\pi_u);\nu_5(\pi_g)$	$\tilde{G}\leftarrow\tilde{X}^1\Sigma_g^+$ 1250-1160 Å	G. Herzberg, Disc. Faraday Soc. 35, 7 (1963).
HCCN	$\tilde{C}(^1\Pi_u)$	$\nu_4(\pi);\nu_5(\pi)$	$\tilde{C}\leftarrow\tilde{X}$ 1519-1403 Å	P. G. Wilkinson, J. Mol. Spect. 2, 387 (1958).
C_2N_2	$\tilde{A}(^1\Delta_u)$	$\nu_4(\pi_u);\nu_5(\pi_g)$	$\tilde{A}(^1\Delta_u)\leftarrow\tilde{X}^1\Sigma_g^+$ 2260-1820 Å	G. Herzberg, Vol. III, Appendix XI.
HCCCN	$A(^1\Delta)$	$\nu_5(\pi);\nu_6(\pi);\nu_7(\pi)$	$\tilde{A}(\Sigma^-$ or $\Delta)\leftarrow\tilde{X}(\Sigma^+)$ 2300 Å	V.A. Job and G. W. King, J. Mol. Spectry 19, 178 (1966).
$C_4H_2^+$	$^2\Pi_u$		$\tilde{A}^2\Pi_u\leftarrow\tilde{X}^2\Pi_g$ 5900-5000 Å	J. H. Callaman, Can. J. Phys. 34, 1046 (1956).
C_4N_2	$\tilde{B}(^1\Delta_u)$		$\tilde{B}(^1\Delta_u)\leftarrow\tilde{X}^1\Sigma_g$ 2720-2250 Å	F. A. Miller and R. B. Hannan, Spectrochem. Acta 12, 321 (1958).
C_4H_2				

respectively. Thus the Renner effect will be most significant in the π-electronic level since in this case, the perturbation possesses the same Q-dependence (viz proportional to r^2) as does the harmonic potential itself, for the harmonic potential for the bending vibration is given by $\frac{1}{2}\mu_2\omega_2^2 r^2$.

Any linear triatomic molecule which exhibits the electronic potentials of case (A) in Fig. 1.3 is called a Renner Molecule. The vibronic perturbation for such molecule in π-electronic level is represented by

$$H'_{\pi} = fr^2\cos 2(\theta-\phi); \qquad f = \varepsilon\mu\omega^2 \qquad (1.6.1)$$

where ε is defined as "Renner parameter", θ is the electronic azimuthal angle and ϕ the azimuthal angle of the bending vibration, both are measured from a fixed plane in space.

Renner's study on "CO_2"(5) is important because it is the first quantitative treatment of a vibronic problem which showed that the Born development (Equation 1.2.6) must be used in case the electronic level is degenerate. The success of Pople and Longuet-Higgins' treatment of "NH_2"(18) which exhibits the case (B) potential surface may be taken as the confirmation of the existence of Renner Effect. Inclusion of spin-orbit coupling in the $^2\Pi$ state of the NH_2 radical has been studied by Pople(27). Dixon found that a more satisfactory description of the NH_2 system is to attribute its electronic potential surfaces to case (C).

For electronic levels with $|\Lambda| > 1$, Δ, Φ,..... etc. states, the leading terms of the vibronic perturbation are proportional to r^4, r^6,..... etc. respectively. They are small in comparison with the quadratic dependent

Harmonic oscillator potential and thus will not show any significant effect but modify the anharmonicity constants(28,29).

Although Liehr has given the electronic Hamiltonian matrix elements in terms of the bending coordinates for π-electronic levels of acetylene C_2H_2(24), no one has attempted the dynamical problem for linear molecules having more than one bending vibration. The aim of the thesis is to investigate this dynamical problem.

CHAPTER 2

GENERAL THEORY FOR VIBRONIC PROBLEM

2.1 Breakdown of Born-Oppenheimer Approximation

The vibronic Schröedinger equation is represented by

$$\{H_{ev}(\vec{r}_i,Q) - E_{ev}\}\Psi_{ev}(\vec{r}_i,Q)$$

$$= \{T_e + V(\vec{r}_i,Q) + T_N - E_{ev}\}\Psi_{ev}(\vec{r}_i,Q) = 0 \qquad (2.1.1)$$

where $V(\vec{r}_i,Q)$ is the electrostatic potential within the molecule, T_e and T_N are the kinetic energy operators for electrons and nuclei respectively. If there is only one electron, T_e is given by

$$T_e = -\frac{\hbar^2}{2m}\nabla_i^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

The nuclear kinetic energy operator will be denoted by

$$T_N = -\frac{\hbar^2}{2}\frac{d^2}{dQ^2} \doteq -\sum_k \frac{\hbar^2}{2\mu_k}\frac{\partial^2}{\partial \underline{q}_k^2}$$

where μ_k is the reduced mass for k^{th} oscillator. Since T_N is of order κ^{2}(1,2,3), it can be regarded "a priori" as a perturbation to $T_e + V(\vec{r}_i,Q)$ in solving Equation (2.1.1).

When we remove T_N from Equation (2.1.1), we have the electronic Schröedinger equation for a fixed configuration Q:

$$\{T_e + V(\vec{r}_i,Q) - W_{ea}(Q)\}\psi_{ea}(\vec{r}_i;Q) = 0 \qquad (2.1.2)$$

When the "perturbation" T_N is added, the solution of Equation (2.1.1) can be written by

$$\Psi_{ev}(\vec{r}_i,Q) = \sum_e \sum_a \psi_{ea}(\vec{r}_i;Q)\Phi^{ea}(Q) \qquad (2.1.3)$$

where $\Phi^{ea}(Q)$ are the variational functions to be determined. The subscripts (e,a) are proposed in the spirit that the functions $\psi_{ea}(\vec{r}_i;Q)$ $\{a = 1,2,\ldots,De\}$ constitute a set of degenerate or nearly degenerate states which are "well separated" from other sets of states $|\psi_{e'a'}>$. The "well separated" condition is that the (electronic) energy difference between members of the same set is much smaller than the energy difference between members of two different sets, i.e.,

$$\frac{|W_{ea}(Q) - W_{ea''}(Q)|}{|W_{e'a}(Q) - W_{ea''}(Q)|} << 1 \qquad (2.1.4)$$

[The sufficient condition should be

$$\frac{|<\psi_{ea}|\frac{\partial V}{\partial Q}|\psi_{e'a'}>|}{|W_{e'a'}(Q)-W_{ea}(Q)|} << \frac{|<\psi_{ea}|\frac{\partial V}{\partial Q}|\psi_{ea''}>|}{|W_{ea}(Q)-W_{ea''}(Q)|}$$

(see Equations 9-11).]

The solutions $\psi_{ea}(\vec{r}_i,Q)$ of Equation (2.1.2), in general, have to be evaluated by perturbation theory, because only for the configuration of high symmetry (Q^o) is the electronic equation "solvable". In fact, what we mean by "solvable" is to achieve the symmetry representations for the electronic wavefunctions. Hence, we assume that we have solved the following "unperturbed" electronic wavefunction:

$$\{T_e + V^o(\vec{r}_i;Q^o) - W^o_{eb}(Q^o)\}\psi^o_{eb}(\vec{r}_i;Q^o) = 0 \qquad (2.1.5)$$

We then expand $\psi_{ea}(\vec{r}_i;Q)$ in terms of $\psi^{o}_{eb}(\vec{r}_i;Q^{o})$

$$\psi_{ea}(\vec{r}_i;Q) = \sum_{b=1}^{De} \psi^{o}_{eb}(\vec{r}_i;Q^{o})C_{b,a}(Q) \qquad (2.1.6)$$

Euqation (2.1.6) implies also that the unperturbed states, $|\psi^{o}_{eb}>$, $\{b = 1,2,.....De\}$, are "well separated" from others.

We note, therfore, that the double-perturbation (Equations (2.1.6) and (2.1.3)) is characteristic for the vibronic problems.

Putting Equation (2.1.6) into Equation (2.1.1), we have

$$0 = \sum_{e,a}\sum(\{W_{ea}(Q) - E\}\psi_{ea}(\vec{r}_i;Q)\Phi^{ea}(Q) - \frac{\hbar^2}{2}[\{\frac{\partial^2}{\partial Q^2}\psi_{ea}(\vec{r}_i;Q)\}\cdot\Phi^{ea}(Q)$$

$$+ 2\{\frac{\partial}{\partial Q}\psi_{ea}(\vec{r}_i;Q)\}\cdot\{\frac{\partial}{\partial Q}\Phi^{ea}(Q)\} + \psi_{ea}(\vec{r}_i;Q)\frac{\partial^2}{\partial Q^2}\Phi^{ea}(Q)]) \qquad (2.1.7)$$

Multiplying Equation (2.1.7) from the left by $\psi_{ea}^{*}(\vec{r}_i;Q)$, then integrating over the electronic space, and making use of the orthonormal conditions:

$$<\psi_{ea}(\vec{r}_i;Q)|\psi_{e'a'}(\vec{r}_i;Q)> = \int_{el}\psi_{ea}^{*}(\vec{r}_i;Q)\psi_{e'a'}(\vec{r}_i;Q)d\tau_i$$

$$= \delta_{ee'}\delta_{aa'} \qquad (2.1.8)$$

we obtain

$$0 = \{W_{ea}(Q) - E\}\Phi^{ea}(Q) - \frac{\hbar^2}{2}\sum_{e'}^{\infty}\sum_{a'}^{D_e'}[<\psi_{ea}|\frac{\partial^2}{\partial Q^2}|\psi_{e'a'}>\cdot\Phi^{ea}(Q)$$

$$+ 2<\psi_{ea}|\frac{\partial}{\partial Q}|\psi_{e'a'}>\cdot\frac{\partial}{\partial Q}\Phi^{ea}(Q) + \frac{\partial^2}{\partial Q^2}\Phi^{ea}] \qquad (2.1.9)$$

where the notation $<\psi_{ea}|\frac{\partial}{\partial Q}|\psi_{e'a'}>\cdot\frac{\partial}{\partial Q}$ stands for

$$<\psi_{ea}|\frac{\partial}{\partial Q}|\psi_{e'a'}>\cdot\frac{\partial}{\partial Q} = \sum_k \frac{1}{\mu_k}<\psi_{ea}|\frac{\partial}{\partial \underline{q_k}}|\psi_{e'a'}>\cdot\frac{\partial}{\partial \underline{q_k}}$$

By Schröedinger Equation (2.1.2) it can be shown that$^{(10)}$

$$<\psi_{ea}(\vec{r}_i;Q)|\frac{\partial}{\partial Q}|\psi_{e'a'}(\vec{r}_i;Q)> = \begin{cases} 0 & \text{if } e' = e,\ a' = a \\ \dfrac{<\psi_{ea}|\frac{\partial V}{\partial Q}|\psi_{e'a'}>}{W_{e'a'}(Q)-W_{ea}(Q)} & \text{if } e' \neq e \text{ or if } e' = e \text{ but } a' \neq a \end{cases} \tag{2.1.10a}$$

and that

$$<\psi_{ea}(\vec{r}_i;Q)|\frac{\partial^2}{\partial Q^2}|\psi_{e'a'}(\vec{r}_i;Q)>$$

$$= \sum_{e'',a''} <\psi_{ea}|\frac{\partial}{\partial Q}|\psi_{e''a''}>\cdot<\psi_{e''a''}|\frac{\partial}{\partial Q}|\psi_{e'a'}> + \frac{\partial}{\partial Q}\cdot<\psi_{ea}|\frac{\partial}{\partial Q}|\psi_{e'a'}> \tag{2.1.10b}$$

Since the terms of (2.1.10) are inversely proportional to the energy differences in Equation (2.1.9), the terms involving two components of the same set are so large that the terms connecting two different sets are suppressed and can be neglected. By dropping off the summation over e' in Equation (2.1.9), we obtain

$$0 = \{-\frac{\hbar^2}{2}\frac{d^2}{dQ^2} + W_{ea}(Q) - \frac{\hbar^2}{2}<\psi_{ea}|\frac{\partial^2}{\partial Q^2}|\psi_{ea}> - E\}\Phi^{ea}(Q)$$

$$+ \sum_{a'\neq a}^{De} \mathcal{V}_{a,a'}(Q,\frac{\partial}{\partial Q})\Phi^{ea'}(Q), \qquad (a = 1,2,\ldots\ldots,De) \tag{2.1.11}$$

where

$$\mathcal{V}_{a,a'}(Q,\frac{\partial}{\partial Q}) = -\frac{\hbar^2}{2}[<\psi_{ea}|\frac{\partial^2}{\partial Q^2}|\psi_{ea'}> + 2<\psi_{ea}|\frac{\partial}{\partial Q}|\psi_{ea'}>\cdot\frac{\partial}{\partial Q}\cdot] \tag{2.1.12}$$

Only if all the $\mathcal{V}_{a,a'}$'s are negligibly small is the Born-Oppenheimer approximation a good one. The summation over a' in Equation (2.1.11) is an indication of the breakdown of this approximation. The $\Phi^{ea}(Q)$ functions (De of them) are determined by De equations like that of Equation (2.1.11). Then the vibronic solution $\Psi_{ev}(\vec{r}_i,Q)$ of Equation (2.1.3) is represented by a limited number of terms:

$$\Psi_{ev}(\vec{r}_i,Q) = \sum_{a=1}^{De} \psi_{ea}(\vec{r}_i;Q)\Phi^{ea}(Q) \tag{2.1.13}$$

2.2 Coupling Terms and Different Formulations

The use of perturbation method to solve the coupled Equations (2.1.11) requires that the first part of the Equation (2.1.1):

$$\{-\frac{\hbar^2}{2}\frac{d^2}{dQ^2} + W_{ea}(Q) - \frac{\hbar^2}{2}<\psi_{ea}|\frac{\partial^2}{\partial Q^2}|\psi_{ea}>\}\Phi^{ea}(Q) \tag{2.2.1}$$

should be "heavier" than the sum

$$\sum_{a'\neq a}^{De} \mathcal{V}_{a,a'}(Q,\frac{\partial}{\partial Q})\cdot\Phi^{ea'}(Q) \tag{2.2.2}$$

However, as seen from Equations (2.1.10) and (2.1.12), the coupling terms $\mathcal{V}_{a,a'}$ may be very large so that the sum (2.2.2) becomes larger than (2.2.1). To avoid this difficulty, we try to make the coupling terms as small as possible by choosing special variable linear combinations of $\psi_{ea}(\vec{r}_i;Q)$, {a = 1,2,.....De}, as a basis set, i.e., let

$$\chi_{ec}(\vec{r}_i,Q) = \sum_{a=1}^{De} \psi_{ea}(\vec{r}_i;Q)\alpha_{a,c}(Q), \qquad (c = 1,2,.....De) \tag{2.2.3}$$

with normalization conditions

$$\langle \chi_{ec} | \chi_{ec'} \rangle = \delta_{cc'} = \sum_{a=1}^{De} \alpha_{ac}(Q)^{*} \alpha_{ac'}(Q) \tag{2.2.4}$$

We see that $\chi_{ec}(\vec{r}_i;Q)$ will no longer be the eigen function of the operator $T + V(\vec{r}_i,Q)$; instead

$$\langle \chi_{ec} | T_e + V(\vec{r}_i,Q) | \chi_{ec'} \rangle = \sum_{a} \alpha_{ac}{}^{*} \alpha_{ac'} W_{ea}(Q) \equiv \xi_{c,c'}(Q) \tag{2.2.5}$$

since the $W_{ea}(Q)$ are not necessarily all equal.

Writing the trial function $\Psi_{ev}(\vec{r}_i,Q)$ in terms of this new basis set we have:

$$\Psi_{ev}(\vec{r}_i,Q) = \sum_{c=1}^{De} \chi_{ec}(\vec{r}_i;Q)\Phi^{c}(Q) \tag{2.2.6}$$

Substituting Equation (2.2.6) into Equation (2.1.1), we obtain

$$\{-\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q^2} + W_{ec}(Q) + \mathcal{V}_{c,c}(Q,\frac{\partial}{\partial Q}) - E\}\Phi^{c}(Q)$$

$$+ \sum_{c' \neq c} P_{c,c'}(Q,\frac{\partial}{\partial Q})\Phi^{ec'}(Q) = 0, \qquad \{c = 1,2,\ldots\ldots De\} \tag{2.2.7}$$

where $W_{ec}(Q) = \xi_{c,c}(Q) = \sum_{a} |\alpha_{a,c}|^2 W_{ea}(Q)$

$$\mathcal{V}_{c,c'}(Q,\frac{\partial}{\partial Q}) = -\frac{\hbar^2}{2}\left[\langle \chi_{ec} | \frac{\partial^2}{\partial Q^2} | \chi_{ec'} \rangle + 2\langle \chi_{ec} | \frac{\partial}{\partial Q} | \chi_{ec'} \rangle \cdot \frac{\partial}{\partial Q}\right]$$

$$P_{c,c'}(Q,\frac{\partial}{\partial Q}) = \xi_{c,c'}(Q) + \mathcal{V}_{c,c'}(Q,\frac{\partial}{\partial Q})$$

In Equation (2.2.7), the coupling terms are $P_{c,c'}(Q,\frac{\partial}{\partial Q})$. The variational functions $\alpha_{a,c}(Q)$ of Equation (2.2.3) are determined by minimizing $P_{c,c'}$ terms. They are dealt with differently in the following formulations:

(A) Adiabatic Formulation

In this Formulation, if $c' \neq c$

$$\xi_{c,c'}(Q) = \langle \chi_{ec} | T_e + V(\vec{r}_i, Q) | \chi_{ec'} \rangle = 0$$

so that $P_{c,c'} = \mathcal{V}_{c,c'}$. Under this condition, the $\chi_{ec}(\vec{r}_i;Q)$'s reduce to the $\psi_{ea}(\vec{r}_i;Q)$'s which are eigen functions of the electronic Hamiltonian $H_e = T_e + V(\vec{r}_i, Q)$. Then we may have the difficulty previously mentioned.

(B) Harmonic Formulation

In this Formulation, one uses Q-independent electronic wavefunctions

$$\chi_{ec}(\vec{r}_i;Q) \equiv \chi_{ec}(\vec{r}_i;Q^o) = \sum_{b=1}^{De} \psi^o_{eb}(\vec{r}_i;Q^o)\beta_{b,c} \qquad (2.2.8)$$

where $\beta_{b,c}$ are constants. Hence

$$\mathcal{V}_{c,c'}(Q, \frac{\partial}{\partial Q}) = 0$$

But now $\xi_{c,c'}(Q)$ can vanish only at one configuration Q^o, and may otherwise be large.

(C) Intermediate Formulation

In this Formulation, the two parts of $P_{c,c'}$ ($\xi_{cc'}$ and $\mathcal{V}_{cc'}$) are suppressed simultaneously. To make $\xi_{c,c'}(Q)$ as small as possible, we separate the nearly degenerate set of functions $\psi_{ea}(\vec{r}_i;Q)$ $\{a = 1,2,\ldots\ldots De\}$ into two sets: the set $\psi_{ea'}$ $\{a' = 1,2,\ldots\ldots de\}$ (with $de < De$) which becomes truly degenerate as $Q \to Q^o$ and is of interest to us; and the other set $\psi_{ea''}$ $\{de < a'' \leq De\}$ which does not. Then we let $\chi_{ec}(\vec{r}_i;Q)$ be linear combination of the degenerate set $\{a'\}$, and $\chi_{ec''}$, the linear combination of set $\{a''\}$, i.e.,

$$\chi_{ec'}(\vec{r}_i;Q) = \sum_{a'=1}^{de} \psi_{ea'}(\vec{r}_i;Q)\alpha_{a',c'}(Q), \ \{c' = 1,2,\ldots\ldots de\} \quad (2.2.9a)$$

$$\chi_{ec''}(\vec{r}_i;Q) = \sum_{a''>de}^{De} \psi_{ea''}(\vec{r}_i;Q)\alpha_{a'',c''}(Q), \ \{de < c'' \leq De\} \quad (2.2.9b)$$

Thus

$$\xi_{c'c''} = \langle\chi_{ec'}|T_e + V(\vec{r}_i,Q)|\chi_{ec''}\rangle$$

$$= \langle \sum_{a'=1}^{de} \alpha_{a'c'}\psi_{ea'}|T_e + V(\vec{r}_i,Q)| \sum_{a''>de}^{De} \alpha_{a'',c''}\psi_{ea''}\rangle$$

$$= \sum_{a=1}^{de} \sum_{a''>de}^{De} \alpha^*_{a'c'}\alpha_{a''c''}\langle\psi_{ea'}|T_e + V(\vec{r}_i,Q)|\psi_{ea''}\rangle$$

$$= \sum_{a'=1}^{de} \sum_{a''>de}^{De} \alpha^*_{a'c'}\alpha_{a''c''} \ \delta_{a'a''}\cdot W_{ea'}(Q)$$

$$= 0 \quad (2.2.10)$$

and

$$\xi_{c',c} = \langle\chi_{ec'}|T_e + V(\vec{r}_i,Q)|\chi_{ec}\rangle$$

$$= W_e^o(Q^o)\delta_{c'c} + k_{c'c}\cdot Q + f_{c'c}Q^2 + \ldots\ldots$$

$$(c,c' = 1,2,\ldots\ldots de) \quad (2.2.11)$$

where $W_e^o(Q^o) = \lim_{Q\to Q^o} W_{ea'}(Q)$. Thus, for infinitesimal vibrations, the $\xi_{c'c}(Q)$ are small. They are at most linear in Q. If $k_{c'c}$ is different from zero, we have Jahn-Teller effect; if $k_{c'c}$ is zero but $f_{c'c}$ is different from zero, we have Renner effect.

To make $\mathcal{V}_{c,c'}(Q)$ as small as possible, we choose $\alpha_{a,c}(Q)$ of Equation (2.2.9a) so that $<\psi_{ea'}|\frac{\partial}{\partial Q}|\chi_{ec'}>$ are <u>approximately</u> equal to zero, i.e.,

$$<\psi_{ea'}|\frac{\partial}{\partial Q}|\chi_{ec'}> \simeq 0 \quad \text{(for all } a',c' = 1,2,\ldots\ldots de \text{ and } Q) \qquad (2.2.12)$$

Substituting Equation (2.2.9a) into (2.2.12), we find that the $\alpha_{a,c}(Q)$ satisfy the following simultaneous differential equations

$$\frac{\partial\alpha_{a,c}(Q)}{\partial Q} + \sum_{a'=1}^{de} <\chi_{ea}(\vec{r}_i,Q)|\frac{\partial}{\partial Q}|\psi_{ea}(\vec{r}_i,Q)>\cdot\alpha_{a',c}(Q) \simeq 0 \qquad (2.2.13)$$

With this choice, $<\chi_{ec}|\frac{\partial^2}{\partial Q^2}|\chi_{ec'}>$ will also be small, and so will $\mathcal{V}_{c,c'}(Q,\frac{\partial}{\partial Q})$ and $P_{c,c'}(Q,\frac{\partial}{\partial Q})$. Then Equation (2.2.7) becomes

$$\begin{aligned}&\{-\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q^2} + W_{ec}(Q) + \mathcal{V}_{c,c}(Q,\frac{\partial}{\partial Q}) - E\}\Phi^{ec}(Q)\\ &\quad + \sum_{c'\neq c}^{de} P_{c,c'}(Q,\frac{\partial}{\partial Q})\Phi^{ec'}(Q) + \sum_{c''>de}^{De} \mathcal{V}_{c,c''}(Q,\frac{\partial}{\partial Q})\Phi^{c''}(Q)\\ &\quad = 0 \qquad \text{(for } c = 1,2,\ldots\ldots de)\end{aligned} \qquad (2.2.14a)$$

$$\begin{aligned}&\{-\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q^2} + W_{ec}(Q) + \mathcal{V}_{c,c}(Q,\frac{\partial}{\partial Q}) - E\}\Phi^{ec}(Q)\\ &\quad + \sum_{c''>de}^{De} P_{c,c''}(Q,\frac{\partial}{\partial Q})\Phi^{ec''}(Q) + \sum_{c'=1}^{de} \mathcal{V}_{c,c'}(Q,\frac{\partial}{\partial Q})\Phi^{e'}(Q)\\ &\quad = 0 \qquad \text{(for } de < c \leq De)\end{aligned} \qquad (2.2.14b)$$

Equations (2.2.14) in matrix form are shown as follows:

$$\left[\begin{array}{cc:c}
H_{11}-E & P_{1,2}\cdots\cdots P_{1,d} & \mathcal{V}_{1,d+1}\cdots\cdots\mathcal{V}_{1,D} \\
P_{2,1} & H_{22}-E\cdots P_{2,d} & \mathcal{V}_{2,d+1}\cdots\cdots\mathcal{V}_{2,D} \\
P_{3,1} & P_{3,2}\cdots\cdots P_{3,d} & \mathcal{V}_{3,d+1}\cdots\cdots\mathcal{V}_{3,D} \\
\vdots & \vdots & \vdots \qquad \vdots \\
P_{d,1} & P_{d,2}\cdots\cdots H_{dd}-E & \mathcal{V}_{d,d+1}\cdots\cdots\mathcal{V}_{d,D} \\
\hdashline
\mathcal{V}_{d+1,1} & \mathcal{V}_{d+1,2}\cdots\mathcal{V}_{d+1,d} & H_{d+1,d+1}-E\cdots P_{d+1,D} \\
\vdots & \vdots & \vdots \qquad \vdots \\
\mathcal{V}_{D,1} & \mathcal{V}_{D,2}\cdots\cdots\mathcal{V}_{D,d} & P_{D,d+1}\cdots\cdots H_{D,d}-E
\end{array}\right]
\left[\begin{array}{c}
\Phi^{1} \\ \Phi^{2} \\ \Phi^{3} \\ \vdots \\ \Phi^{d} \\ \hdashline \Phi^{d+1} \\ \vdots \\ \Phi^{D}
\end{array}\right] = 0 \qquad (2.2.14')$$

where $d = de$, $D = De$ and $H_{cc} = H_{cc}(Q,\frac{\partial}{\partial Q}) = -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q^2} + W_{ec}(Q)$

$$+ \mathcal{V}_{c,c}(Q,\frac{\partial}{\partial Q}).$$

Although Equation (2.2.14$'$) is general for any molecule in a degenerate or nearly degenerate electronic level, the rather loose conditions imposed by Equation (2.2.13) require rather complicated mathematical devices$^{(11)}$ for the solution of these equations.

The Adiabatic Formulation was used by Renner$^{(5)}$ and the Harmonic Formulation by Moffit and Liehr$^{(6)}$, and by Pople and Longuet-Higgins$^{(18)}$. Although the results of the two methods for triatomic molecules are equivalent, we shall see in Chapter 5 of this thesis that for linear molecules having more than one Renner active degenerate vibrations, only the Harmonic Formulation is practicable.

2.3 Doubly-Degenerate Electronic Level

In the case where the electronic level is doubly-degenerate and is well-separated from other levels, the coupled equations in the various formulations are summarized as follows:

(A) Adiabatic Formulation

The vibronic function is given by

$$\Psi_{ev}(\vec{r}_i,Q) = \psi_a(\vec{r}_i;Q)\Phi^a(Q) + \psi_b(\vec{r}_i;Q)\Phi^b(Q)$$

where ψ_a and ψ_b satisfy

$$\{T_e + V(\vec{r}_i,Q) - W_a(Q)\}\psi_a(\vec{r}_i;Q) = 0$$

The vibrational equations are given by

$$\begin{bmatrix} -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q^2} + W_a(Q) + \mathcal{V}_{aa}(Q,\frac{\partial}{\partial Q}) - E & \mathcal{V}_{a,b}(Q,\frac{\partial}{\partial Q}) \\ \mathcal{V}_{b,a}(Q,\frac{\partial}{\partial Q}) & -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q^2} + W_b(Q) + \mathcal{V}_{bb}(Q,\frac{\partial}{\partial Q}) - E \end{bmatrix} \begin{bmatrix} \Phi^a(Q) \\ \Phi^b(Q) \end{bmatrix} = 0 \qquad (2.3.1)$$

(B) Harmonic Formulation

The vibronic wavefunction is given by

$$\Psi_{ev}(\vec{r}_i,Q) = \psi_+^o(\vec{r}_i;Q^o)\Phi^+(Q) + \psi_-^o(\vec{r}_i;Q^o)\Phi^-(Q)$$

where $\psi_\pm^o$ satisfy

$$\{T_e + V^o(\vec{r}_i,Q^o) - W^o\}\psi_\pm^o(\vec{r}_i;Q^o) = 0$$

The vibrational equations are given by

$$\begin{bmatrix} -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q^2} + \xi_{++}(Q) - E & \xi_{+-}(Q) \\ \xi_{-+}(Q) & -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q^2} + \xi_{--}(Q) - E \end{bmatrix} \begin{bmatrix} \Phi^+(Q) \\ \Phi^-(Q) \end{bmatrix} = 0 \qquad (2.3.2)$$

where $$\xi_{+-}(Q) = \langle\psi_+^o(\vec{r}_i;Q^o)|T_e + V(\vec{r}_i,Q)|\psi_-^o(\vec{r}_i;Q^o)\rangle, \text{ etc.}$$

(C) Intermediate Formulation

The vibronic function is represented by

$$\Psi(r_i,Q) = \chi_1(\vec{r}_i;Q)\Phi^1(Q) + \chi_2(\vec{r}_i;Q)\Phi^2(Q)$$

where χ_1 and χ_2 are linear combinations of $\psi_a(\vec{r}_i,Q)$ and $\psi_b(\vec{r}_i,Q)$.

The vibrational equations are given by

$$\begin{bmatrix} -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q^2} + W_1(Q) + \mathcal{V}_{11}(Q,\frac{\partial}{\partial Q}) - E & \xi_{12}(Q) + \mathcal{V}_{12}(Q,\frac{\partial}{\partial Q}) \\ \xi_{21}(Q) + \mathcal{V}_{21}(Q,\frac{\partial}{\partial Q}) & -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q^2} + W_2(Q) + \mathcal{V}_{22}(Q,\frac{\partial}{\partial Q}) - E \end{bmatrix} \begin{bmatrix} \Phi^1(Q) \\ \Phi^2(Q) \end{bmatrix} = 0 \quad (2.3.3)$$

The relations between $\{\psi_a,\psi_b\}$, $\{\psi_+^o,\psi_-^o\}$ and $\{\chi_1,\chi_2\}$ can be obtained only to the first-order of approximation. They are given by

$$\begin{bmatrix} \psi_a(\vec{r}_i;Q) \\ \psi_b(\vec{r}_i;Q) \end{bmatrix} = \begin{bmatrix} C_{+a}(Q) & C_{-a}(Q) \\ C_{+b}(Q) & C_{-b}(Q) \end{bmatrix} \begin{bmatrix} \psi_+^o(\vec{r}_i;Q^o) \\ \psi_-^o(\vec{r}_i;Q^o) \end{bmatrix} = \begin{bmatrix} \alpha_{a1}^*(Q) & \alpha_{a2}^*(Q) \\ \alpha_{b1}^*(Q) & \alpha_{b2}^*(Q) \end{bmatrix} \begin{bmatrix} \chi_1(\vec{r}_i;Q) \\ \chi_2(\vec{r}_i;Q) \end{bmatrix} \quad (2.3.4)$$

$$\begin{bmatrix} \chi_1(\vec{r}_i;Q) \\ \chi_2(\vec{r}_i;Q) \end{bmatrix} = \begin{bmatrix} \alpha_{a1}(Q) & \alpha_{b1}(Q) \\ \alpha_{a2}(Q) & \alpha_{b2}(Q) \end{bmatrix} \begin{bmatrix} \psi_a(\vec{r}_i;Q) \\ \psi_b(\vec{r}_i;Q) \end{bmatrix} = \begin{bmatrix} \beta_{+1}(Q) & \beta_{-1}(Q) \\ \beta_{+2}(Q) & \beta_{-2}(Q) \end{bmatrix} \begin{bmatrix} \psi_+^o(\vec{r}_i;Q^o) \\ \psi_-^o(\vec{r}_i;Q^o) \end{bmatrix} \quad (2.3.5)$$

where $$\beta_{\pm 1}(Q) = \alpha_{a1}(Q)\, C_{\pm a}(Q) + \alpha_{b1}(Q)\, C_{\pm b}(Q)$$
$$\beta_{\pm 2}(Q) = \alpha_{a2}(Q)\, C_{\pm a}(Q) + \alpha_{b2}(Q)\, C_{\pm b}(Q)$$

and

$$\begin{bmatrix} \psi_+^o(\vec{r}_i;Q^o) \\ \\ \psi_-^o(\vec{r}_i;Q^o) \end{bmatrix} = \begin{bmatrix} C_{+a}^*(Q) & C_{+b}^*(Q) \\ \\ C_{-a}^*(Q) & C_{-b}^*(Q) \end{bmatrix} \begin{bmatrix} \psi_a(\vec{r}_i;Q) \\ \\ \psi_b(\vec{r}_i;Q) \end{bmatrix} = \begin{bmatrix} \beta_{+1}^*(Q) & \beta_{-1}^*(Q) \\ \\ \beta_{+2}^*(Q) & \beta_{-2}^*(Q) \end{bmatrix} \begin{bmatrix} \chi_1(\vec{r}_i;Q) \\ \\ \chi_2(\vec{r}_i;Q) \end{bmatrix} \tag{2.3.6}$$

2.4 Classification of Electronic States for Molecules of Linear Conformation

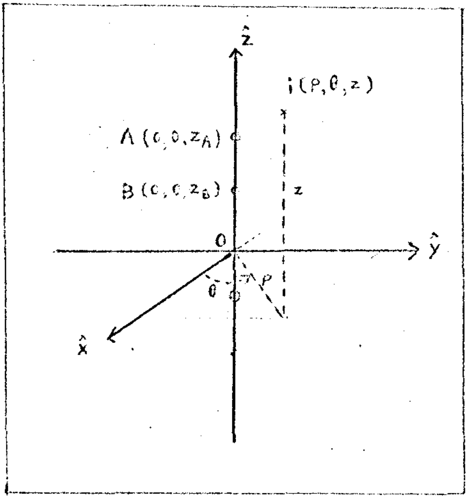
The following two sections concern only the electronic wavefunctions for molecules of linear conformation.

A linear molecule is most conveniently described by the cylindrical coordinate system. Suppose there is only one electron $i(\rho,\theta,z)$, and the "effective charges" of atoms $A(0,0,z_A)$, $B(0,0,z_B)$,.....etc. are Z_A, Z_B,...etc. respectively (Fig. 2.1), then the electrical potential within the molecule is given by

$$V^o(\vec{r}_i,0) = \sum_{\alpha=A,B\ldots} \frac{Z_\alpha e}{[(z-z_\alpha)^2 + \rho^2]^{1/2}} + \sum_{\alpha<\alpha'}\sum \frac{Z_\alpha Z_{\alpha'}}{|z_\alpha - z_{\alpha'}|} \tag{2.4.1}$$

Fig. 2.1 Coordinate system for linear molecules.

The centre of mass is assumed to be the origin. The nuclear positions are $\alpha(0,0,z_\alpha)$.



The electronic kinetic energy operator is:

$$T_e = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\theta^2} + \frac{\partial^2}{\partial z^2}\right) \qquad (2.4.2)$$

And the electronic Schröedinger equation is given by

$$\{H_e^o(\vec{r}_i,0) - W_e^o\}\psi_e^o(\vec{r}_i;0)$$

$$= \{T_e + V^o(\vec{r}_i,0) - W_e^o\}\psi_e^o(\vec{r}_i;0) = 0 \qquad (2.4.3)$$

Since $V^o(\vec{r}_i,0)$ does not contain the electronic azimuthal angle θ, it commutes with the operator $\frac{\partial}{\partial\theta}$, and $\frac{\partial}{\partial\theta}$ always commutes with the electronic kinetic energy operator T_e, therefore,

$$[H_e^o,\frac{\hbar}{i}\frac{\partial}{\partial\theta}] = [T_e + V^o,\frac{\hbar}{i}\frac{\partial}{\partial\theta}] = 0$$

Thus the eigenfunctions $\psi_e^o(\vec{r}_i,0)$ of Equation (2.4.3) are also eigenfunctions of the z-component angular momentum operator $\frac{\hbar}{i}\frac{\partial}{\partial\theta}$. Let the eigenvalue of $\psi_e^o(\vec{r}_i)$ be $\Lambda\hbar$, and we have

$$\frac{\hbar}{i}\frac{\partial}{\partial\theta}\psi_e^o = \Lambda\hbar\psi_e^o \qquad (2.4.4)$$

Supposing that $\psi_e^o(\vec{r}_i,0)$ can be written as

$$\psi_e^o(\vec{r}_i;0) = u(z,\rho)\Theta_\Lambda(\theta) \qquad (2.4.5)$$

then we have, from Equation (2.4.4),

$$\frac{\partial}{\partial\theta}\Theta_\Lambda(\theta) = i\Lambda\Theta_\Lambda(\theta)$$

and thus

$$\Theta_\Lambda(\theta) \sim e^{i\Lambda\theta}$$

Since we must have single-valued space function, therefore

$$\Theta_\Lambda(\theta + 2\pi) = \Theta_\Lambda(\theta)$$

Hence Λ must be an integer; i.e., $\Lambda = \pm\lambda$, with $\lambda = 0, 1, 2, \ldots$ etc.

Substituting Equation (2.4.6) into Equation (2.4.3), we find that $u(z,\rho)$ have to satisfy the following equation:

$$\Big\{-\frac{\hbar^2}{2m}\Big(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} - \frac{\Lambda^2}{\rho^2} + \frac{\partial^2}{\partial z^2}\Big) + \sum_\alpha \frac{Z_\alpha e}{[(z-z_\alpha)^2+\rho^2]^{\frac{1}{2}}}$$

$$+ \sum_{\alpha<\alpha'} \frac{Z_\alpha Z_{\alpha'}}{|z_\alpha - z_{\alpha'}|} - W_e^o\Big\} u(z,\rho) = 0 \qquad (2.4.6)$$

Thus the eigenvalue, W_e^o, and the radial function, $u(z,\rho)$, do not depend on Λ but on Λ^2 $(= \lambda^2)$. We may label the radial function by λ: $u_\lambda(z,\rho)$ and the corresponding eigenvalue by W_λ^o. Therefore when $\lambda > 0$, W_λ^o denotes a doubly-degenerate electronic level, and its two component states are represented by $\{\psi_{+\lambda}^o, \psi_{-\lambda}^o\}$:

$$\psi_\Lambda^o = \left\{\begin{aligned} \psi_{+\lambda}^o &= u_\lambda(z,\rho)e^{i\lambda\theta} \\ \psi_{-\lambda}^o &= u_\lambda(z,\rho)e^{-i\lambda\theta} \end{aligned}\right\} = u_\lambda(z,\rho)e^{i\Lambda\theta} \qquad (2.4.7)$$

or by their linear combinations, for example:

$$\begin{aligned} \psi_{\lambda 1}^o &= \frac{1}{\sqrt{2}}\{\psi_{+\lambda}^o + \psi_{-\lambda}^o\} = \sqrt{2}\, u_\lambda(z,\rho)\cos\lambda\theta \\ \psi_{\lambda 2}^o &= \frac{1}{\sqrt{2}}\{\psi_{+\lambda}^o - \psi_{-\lambda}^o\} = \sqrt{2}\, u_\lambda(z,\rho)\sin\lambda\theta \end{aligned} \qquad (2.4.8)$$

To classify the symmetry representation of the λ-electronic level, we denote the level $(\lambda > 0)$ by a two-component column vector,

$$\psi_\lambda^o = \begin{bmatrix} \psi_{+\lambda}^o \\ \\ \psi_{-\lambda}^o \end{bmatrix} = u_\lambda(z,\rho) \begin{bmatrix} e^{i\lambda\theta} \\ \\ e^{-i\lambda\theta} \end{bmatrix} \tag{2.4.9}$$

Since the rotational operation $C_\infty(\Phi)$ on the electronic coordinates has the effect that

$$\theta \to \theta - \Phi;\ z \to z;\ \rho \to \rho$$

therefore

$$C_\infty(\Phi)\cdot\psi_\lambda^o(\vec{r}_i) = \psi_\lambda^o(C_\infty(-\Phi)\vec{r}_i) = u_\lambda(z,\rho) \begin{bmatrix} e^{i\lambda(\theta + \Phi)} \\ \\ e^{-i\lambda(\theta + \Phi)} \end{bmatrix} = \begin{bmatrix} e^{i\lambda\Phi} & 0 \\ \\ 0 & e^{-i\lambda\Phi} \end{bmatrix} \psi_\lambda^o$$

The character of this operation is

$$\chi[C_\infty] = e^{+i\lambda\Phi} + e^{-i\lambda\Phi} = 2\cos\lambda\Phi \tag{2.4.10}$$

Hence for $\lambda = 0, 1, 2, \ldots$..etc. we have representations $\Sigma, \Pi, \Delta, \ldots$..etc. respectively [Appendix A].

If the linear molecule has a centre of symmetry ($D_{\infty h}$ group), the electronic states must also be classified by their g or u symmetry. The application of the inversion operator E^{-1} on the electron coordinates causes

$$\theta \to \theta - \pi,\ z \to -z,\ \rho \to \rho$$

Therefore we have

$$E^{-1}\psi_\lambda^o = u_\lambda(-z,\rho) \begin{bmatrix} e^{i\lambda(\theta + \pi)} \\ \\ e^{-i\lambda(\theta + \pi)} \end{bmatrix} = u_\lambda(-z,\rho) \begin{bmatrix} -1 & 0 \\ \\ 0 & -1 \end{bmatrix} \begin{bmatrix} e^{i\lambda\theta} \\ \\ e^{-i\lambda\theta} \end{bmatrix}$$

If ψ_λ belongs to g representation, i.e.,

$$E^{-1}\psi_{\lambda,g}^o = +\psi_{\lambda,g}^o$$

then $$u_{\lambda,g}(-z,\rho) = -u_{\lambda,g}(z,\rho) \qquad (2.4.11a)$$

If ψ_λ, on the other hand, belongs to u respresentation, we have

$$u_{\lambda,u}(-z,\rho) = +u_{\lambda,u}(z,\rho) \qquad (2.4.11b)$$

2.5 Electronic Wavefunctions for Pseudo-Linear Triatomic Molecules

When the nuclei are displaced infinitesimally from the linear configuration, the electrical potential will be given by

$$V(\vec{r}_i,Q) = \sum_{\alpha=1}^{3} \frac{Z_\alpha e}{[(z-z_\alpha)^2 + \rho^2 + \rho_\alpha^2 - 2\rho\rho_\alpha \cos(\theta-\phi)]^{\frac{1}{2}}} + \frac{1}{2}\sum^{3}\sum^{3}_{\alpha\neq\alpha'} \frac{Z_\alpha Z_{\alpha'}}{[(z_\alpha - z_{\alpha'})^2 + (\rho_\alpha - \rho_{\alpha'})^2]^{\frac{1}{2}}} \qquad (2.5.1)$$

where ϕ is the angle between a fixed plane, say xz-plane, and the plane which contains all three nuclei. Because of the $(\theta-\phi)$ dependence in the potential, the electronic wavefunction ψ_e will lose its rotational symmetry and will also be $(\theta-\phi)$ dependent, i.e.,

$$\frac{\partial\psi_e}{\partial\theta} = -\frac{\partial\psi_e}{\partial\phi}$$

However, we can measure the electronic azimuthal angle with respect to the bending plane by defining

$$\theta' \equiv \theta - \phi \qquad (2.5.2)$$

The electronic kinetic energy operator becomes

$$T_e = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\theta'^2} + \frac{\partial^2}{\partial z^2}\right) \qquad (2.5.3)$$

i.e., $\frac{\partial^2}{\partial\theta^2}$ in Equation (2.4.2) is replaced by $\frac{\partial^2}{\partial\theta'^2}$.

Since a reflection with respect to the ϕ-plane causes

$$\theta' \to -\theta', \ \rho \to \rho, \ z \to z$$

therefore $V(\vec{r}_i,Q)$ is invariant to this reflection. Hence the electronic wavefunctions of the bent triatomic molecule can be classified under the point group C_{2v} (if the molecule is symmetrical, e.g., CO_2) or point group C_s (if unsymmetrical, e.g., CCN). The representations for $\psi_e(\vec{r}_i,Q)$ are then [Appendix A-5]

A' and A''	(C_s point group)
B_1 and B_2 or A_1 and A_2	(C_{2v} point group)

The angular functions which transform like $A'(B_1)$ symmetry are

$$\cos\theta', \cos2\theta', \cos3\theta', \ldots\ldots \text{etc.}$$

and the angular functions which transform like $A''(B_2)$ are

$$\sin\theta', \sin2\theta', \sin3\theta', \ldots\ldots \text{etc.}$$

The large dependence of $\psi_e(\vec{r}_i,Q)$ on ϕ is obvious, since ϕ is involved in the differential operator T_e. However the variation of ψ_e on the radial coordinates z_α and ρ_α will be small, since both z_α and ρ_α are involved only in the potential $V(\vec{r}_i,Q)$. For infinitesimal (bending) displacement, $z_\alpha \simeq z^o_\alpha$ and $\rho_\alpha \simeq 0$, Equation (2.5.1) can be approximated by

$$V(\vec{r}_i,Q) = \sum_{\alpha=1}^{3} \frac{Z_\alpha e}{[(z-z_\alpha)^2 + \rho^2 - 2\rho\rho_\alpha \cos\theta']^{\frac{1}{2}}} + \frac{1}{2}\sum^{3}\sum^{3}_{\alpha\neq\alpha'} \frac{Z_\alpha Z_{\alpha'}}{|z_\alpha - z^o_{\alpha'}|}$$

$$= V^o(\vec{r}_i, 0) + \sum_{\alpha=1}^{3} \frac{Z_\alpha e}{[(z-z_\alpha^o)^2 + \rho^2]^{3/2}} \cdot \rho_\alpha \rho \cos\theta' + \ldots\ldots \qquad (2.5.4)$$

Thus the electronic Schröedinger equation for the pseudo-linear triatomic molecule is:

$$\{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\theta'^2} + \frac{\partial^2}{\partial z^2}\right) + V^o(\vec{r}_i, 0)$$

$$+ \sum_{\alpha=1}^{3} \frac{Z_\alpha e \cdot \rho_\alpha \rho \cos\theta'}{[(z-z_\alpha)^2 + \rho^2]^{3/2}} + \ldots\ldots - W(Q)\}\psi_e = 0 \qquad (2.5.5)$$

Taking $[\sum_{\alpha=1}^{3} \frac{Z_\alpha e \cdot \rho_\alpha \rho \cos\theta'}{[(z-z_\alpha)^2 + \rho^2]^{3/2}} + \ldots\ldots]$ as perturbation, and caring for the C_s (or C_{2v}) symmetry, the solutions of Equation (2.5.5) will be of the form:

$$\psi_e = \begin{Bmatrix} \sqrt{2}\, u_\lambda(z,\rho;z_\alpha^o)\cos\lambda\theta' + \text{higher order terms} \\ \sqrt{2}\, u_\lambda(z,\rho;z_\alpha^o)\sin\lambda\theta' + \text{higher order terms} \end{Bmatrix} \qquad (2.5.6)$$

CHAPTER 3

VIBRONIC PERTURBATION FOR LINEAR POLYATOMIC MOLECULES

3.1 The Coulomb Potential in the Molecule

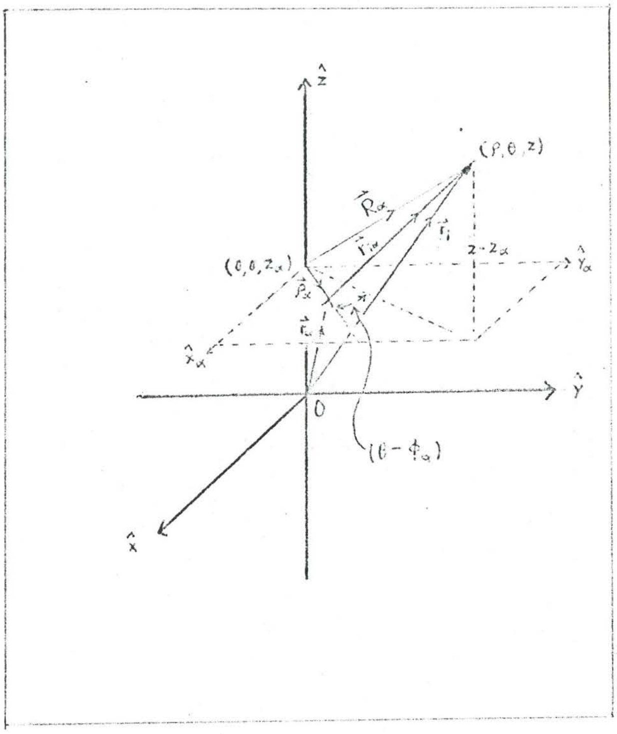
In discussing vibronic problems, one has to obtain some potential energy function to couple the electronic states of interest. This is usually done by using a Taylor series expansion and noting that the Hamiltonian must be real and reflect the total symmetry of the system. In this thesis, we shall derive the vibronic perturbation using a different method, namely the multipole expansion(30). We shall see that this method provides us with an interpretation of the vibrational force constants and the anharmonicities. Besides, this method is in line with Renner's dipole model and enables us to have some idea of the structure of the Renner parameters. The parametric integrals may be evaluated if reliable electronic wavefunctions are provided.

We assume that the instantaneous configuration of the molecule is never far from linear. Therefore, it is convenient to use a cylindrical coordinate system to describe the positions of the electrons and nuclei (Fig. 4.1). Suppose that we have a "single" electron i at the position $\vec{r}_i(\rho,\theta,z)$ and atomic charges $Z_A, Z_B, \ldots$..etc. at positions $\vec{r}_A(\rho_A,\phi_A,z_A)$, $\vec{r}_B(\rho_B,\phi_B,z_B)$.....etc. respectively, then the coulombic potential of the molecule is

$$V(\vec{r}_i,Q) = V_{eN}(\vec{r}_i,Q) + V_{NN}(Q) \qquad (3.1.1)$$

where the electronic-nuclear potential V_{eN} and nuclear-nuclear potential V_{NN} are given by

Figure 3.1 The Coordinate System for vibrating molecules.



$$V_{eN} = V_{eN}(\vec{r}_i, Q) = \sum_{\alpha=A,\ldots}^{N} \frac{Z_\alpha e}{|\vec{r}_i - \vec{r}_\alpha|} \tag{3.1.2}$$

$$V_{NN} = V_{NN}(Q) = \sum_{\alpha<\alpha'}^{N}\sum^{N} \frac{Z_\alpha Z_{\alpha'}}{|\vec{r}_{\alpha'} - \vec{r}_\alpha|} \tag{3.1.3}$$

We define the unperturbed electronic-nuclear, nuclear-nuclear and vibronic potentials respectively by

$$V^o_{eN} = V^o_{eN}(\vec{r}_i, Q^o) \equiv \lim_{Q\to 0} V_{eN}(\vec{r}_i, Q) = \sum_{\alpha=A}^{N} \frac{Z_\alpha e}{R_\alpha} \tag{3.1.4}$$

$$V^o_{NN} = V^o_{NN}(Q^o) \equiv \lim_{Q\to 0} V_{NN}(Q) = \sum_{\alpha<\alpha'}^{N}\sum^{N} \frac{Z_\alpha Z_{\alpha'}}{|z_{\alpha'} - z_\alpha|} \tag{3.1.5}$$

and $$V^o = V^o(\vec{r}_i, Q^o) \equiv \lim_{Q\to 0} V(\vec{r}_i, Q) = V^o_{eN} + V^o_{NN} \tag{3.1.6}$$

We also define the electronic-nuclear, nuclear-nuclear and vibronic perturbations respectively by:

$$V'_{eN} = V'_{eN}(\vec{r}_i,Q) \equiv V_{eN} - V^o_{eN} \tag{3.1.7}$$

$$V'_{NN} = V'_{NN}(Q) \equiv V_{NN} - V^o_{NN} \tag{3.1.8}$$

and $V' = V'(\vec{r}_i,Q) \equiv V - V^o$

$$= V'_{eN} + V'_{NN} \tag{3.1.9}$$

In Equation (3.1.9) it is the function V'_{eN} involving both the electronic and nuclear coordinates which is responsible for the "vibronic coupling". Thus if $|\psi^o_{+\lambda}>$ and $|\psi^o_{-\lambda}>$ are the electronic states under the potential $V^o(\vec{r}_i,Q^o)$, then the addition of the perturbation V'_{eN} will couple the two states.

3.2 The Vibronic Perturbation: $V'(\vec{r}_i,Q)$

(A) The electronic-nuclear perturbation: $V'_{eN}(\vec{r}_i,Q)$

The instantaneous distance between the electron i and the atom α is given by (Fig. 3.1)

$$r_{i\alpha} = |\vec{r}_i - \vec{r}_\alpha| = [R^2_\alpha - 2\rho\rho_\alpha\cos\theta_\alpha + \rho^2_\alpha]^{1/2} \tag{3.2.1}$$

where $R_\alpha \equiv [(z - z_\alpha)^2 + \rho^2]^{1/2}$ (3.2.2)

$$\theta_\alpha \equiv \theta - \phi_\alpha \tag{3.2.3}$$

Thus the electronic-nuclear potential can be written as

$$V_{eN}(\vec{r}_i,Q) = \sum_{\alpha=A}^{N} \frac{Z_\alpha e}{R_\alpha[1 - 2\frac{\rho_\alpha}{R_\alpha}\cdot\frac{\rho}{R_\alpha}\cos\theta_\alpha + (\frac{\rho_\alpha}{R_\alpha})^2]^{1/2}} \tag{3.2.4}$$

Since $(1 - 2yx + y^2)^{-\frac{1}{2}} \equiv \sum_{\ell=0}^{\infty} y^{\ell} P_{\ell}(x)$, if $y < 1$

where $P_{\ell}(x)$ are the Legendre Polynomials which can be written as

$$P_{\ell}(x) = \sum_{i=0}^{\ell/2 \text{ or } \ell-1/2} b_{\ell}^{(i)} x^{\ell-2i}$$

$$\text{with } b_{\ell}^{(i)} = (-1) b_{\ell}^{(i-1)} \frac{(\ell - 2i + 1)(\ell - 2i + 2)}{2i(2\ell - 2i + 1)} \; ; \; b_{\ell}^{(0)} \equiv \frac{(2\ell)!}{2^{\ell}(\ell!)^2} \tag{3.2.6}$$

On identifying ρ_{α}/R_{α} with y, $(\rho/R_{\alpha})\cos\theta_{\alpha}$ with x, Equation (3.2.4) becomes

$$V_{eN}(\vec{r}_i, Q) = \sum_{\ell=0} \sum_{\alpha=A}^{N} \frac{Q_{\ell}^{(\alpha)}}{R_{\alpha}^{\ell+1}} \tag{3.2.7}$$

This is the result of the multipole expansion of the potential. $Q_{\ell}^{(\alpha)}$ is called the 2^{ℓ}-multipole generated by the α^{th} electric charge. It is given by

$$Q_{\ell}^{(\alpha)} = Z_{\alpha} e \, \rho_{\alpha}^{\ell} \, P_{\ell}\left(\frac{\rho}{R_{\alpha}} \cos\theta_{\alpha}\right) \tag{3.2.8}$$

The monopole strength is $Q_0^{(\alpha)} = Z_{\alpha} e$, the dipole strength is $Q_1^{(\alpha)} = Z_{\alpha} \rho_{\alpha} \frac{\rho}{R_{\alpha}} \cos\theta_{\alpha}$, the quadrupole strength is $Q_2^{(\alpha)} = Z_{\alpha} e \rho_{\alpha}^2 \cdot P_2\left(\frac{\rho}{R_{\alpha}} \cos\theta_{\alpha}\right)$, etc. and so on. Since

$$2^m (\cos\theta_{\alpha})^m = \begin{cases} \displaystyle\sum_{n=1,3,5\ldots}^{m} 2 \binom{m}{\frac{m-n}{2}} \cos n\theta_{\alpha}, & \text{if } m = \text{odd} \\[2ex] \displaystyle\sum_{n=2,4,6\ldots}^{m} 2 \binom{m}{\frac{m-n}{2}} \cos n\theta_{\alpha} + \binom{m}{\frac{m}{2}}, & \text{if } m = \text{even} \end{cases} \tag{3.2.9}$$

Therefore Equations (3.2.6) to (3.2.9) give

$$V_{eN}(\vec{r}_i, Q) = \sum_{\alpha=A}^{N} G_0^{(\alpha)} + \sum_{n\geq 1} \sum_{\alpha=A}^{N} 2G_n^{(\alpha)} \cos n(\theta - \phi_{\alpha}) \tag{3.2.10}$$

where

$$G_n^{(\alpha)} = G_n^{(\alpha)}(\rho,R_\alpha;\rho_\alpha) = \sum_{\ell\geq 0}^{\infty} F_{n\ell}^{(\alpha)}(\rho,R_\alpha)\cdot\rho_\alpha^{2\ell+n}$$

$$G_o^{(\alpha)} = \frac{Z_\alpha e}{R_\alpha} + \sum_{\ell\geq 1}^{\infty} F_{o,\ell}^{(\alpha)}(\rho,R_\alpha)\cdot\rho_\alpha^{2\ell} \qquad (3.2.11)$$

$$F_{n,\ell}^{(\alpha)} = F_{n,\ell}^{(\alpha)}(\rho,R_\alpha) = \sum_{j=0}^{\ell/2 \overset{\text{or}}{,} (\ell-1)/2} a_{n\ell j}\,\frac{Z_\alpha e}{R_\alpha}\,\frac{\rho^{2j+n}}{R_\alpha^{2(n+\ell+j)}}$$

and (3.2.12)

$$a_{n\ell j} = 2^{-(n+2j)}\cdot\binom{n+2j}{j}\cdot b_{n+2\ell}^{(\ell-j)}$$

By equations (3.1.4), (3.1.7), (3.2.10) and (3.2.11), we obtain for the electronic-nuclear perturbation V'_{eN}:

$$V'_{eN} = V'_o + \sum_{n\geq 1} V'_n \qquad (3.2.13)$$

where $$V'_o = V'_o(\rho,R_\alpha;\rho_\alpha) = \sum_{\alpha=A}^{N}\sum_{\ell\geq 1}^{\infty} F_{o,\ell}^{(\alpha)}(\rho,R_\alpha)\cdot\rho_\alpha^{2\ell} \qquad (3.2.14)$$

and $$V'_n = V'_n(\rho,R_\alpha\theta_\alpha;\rho_\alpha) = \sum_{\alpha=A}^{N} 2G_n^{(\alpha)}\cos n(\theta-\phi_\alpha) \qquad (3.2.15)$$

(B) The Nuclear-Nuclear Perturbation: $V'_{NN}(Q)$

As we have assumed for small vibrations: $|\rho_\alpha| \sim 0$, we can use binormial expansion for the nuclear-nuclear potential $V_{NN}(Q)$:

$$V_{NN}(Q) = \sum_{\alpha<\alpha'}^{N}\sum^{N} \frac{Z_\alpha Z_{\alpha'}}{|z_\alpha - z_\alpha|\left[1 + \frac{|\vec{\rho}_{\alpha'} - \vec{\rho}_\alpha|^2}{|z_{\alpha'} - z_\alpha|^2}\right]^{1/2}}$$

$$= \sum_{\alpha<\alpha'}^{N}\sum^{N} \frac{Z_\alpha Z_{\alpha'}}{|z_{\alpha'} - z_\alpha|}\left\{1 - \frac{1}{2}\cdot\frac{|\vec{\rho}_\alpha - \vec{\rho}_{\alpha'}|^2}{(z_\alpha - z_\alpha)^2} + \frac{3}{4}\,\frac{|\vec{\rho}_{\alpha'} - \vec{\rho}_\alpha|^4}{(z_{\alpha'} - z_\alpha)^4} - \ldots.\right\}$$

Hence, the nuclear-nuclear perturbation is given by

$$V'_{NN} = -\frac{1}{2}\sum_{\alpha<\alpha'}\sum \frac{Z_\alpha Z_\alpha}{|z_{\alpha'} - z_\alpha|^3}\{|\vec{\rho}_{\alpha'} - \vec{\rho}_\alpha|^2$$

$$- \frac{3}{2(z_{\alpha'} - z_\alpha)^2}|\vec{\rho}_{\alpha'} - \vec{\rho}_\alpha|^4 + \ldots\} \qquad (3.2.16)$$

(C) The Vibronic Perturbation: $V'(r_i,Q)$

Addition of Equation (3.2.16) to Equation (3.2.13) will give the total perturbation

$$V' = \{V'_{NN}(\rho_\alpha,\phi_\alpha) + V'_o(\rho,R_\alpha;\rho_\alpha)\} + \sum_{n\geq 1} V'_n(\rho,R_\alpha,\theta_\alpha;\rho_\alpha) \qquad (3.2.17)$$

For a given nuclear configuration, the schematic representations of the perturbation terms of Equation (3.2.17) in the basis $\{\psi^o_{+\lambda},\psi^o_{-\lambda}\}$ are shown in Fig. 3.2.

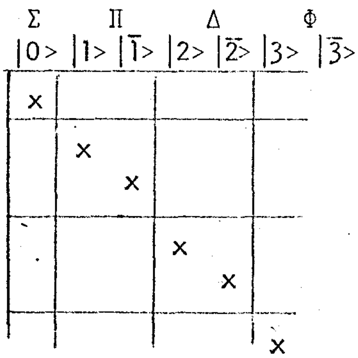
We can see from Fig. 3.2 that, the first two terms of Equation (3.2.17), i.e., V'_{NN} and V'_o, do not couple different electronic states. V'_1, V'_3,...V'_{2m+1},... do not contribute first-order energy corrections to any electronic level λ. V'_2 gives first-order energy correction to π electronic level ($\lambda = 1$), and V'_4 gives first-order (electronic) energy correction to Δ level ($\lambda = 2$). Hence $V'_{2\lambda}$ gives first-order energy correction to the λ-level.

3.3 Effective Vibronic Perturbation in Terms of Nuclear Displacements.

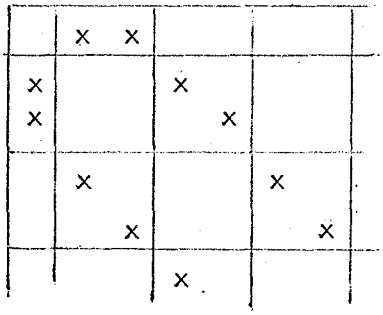
The infinite series $\sum_{n\geq} V'_n$ is responsible for the vibronic interaction. However most terms are negligibly small since $\frac{\rho}{R_\alpha} < 1$ and $\frac{\rho_\alpha}{R_\alpha} << 1$. By Equations (3.2.11) and (3.2.12), we see that

Fig. 3.2 Representation matrices of perturbation terms: (a) $V'_{NN} + V'_{o}$; (b) V'_1; (c) V'_2; (d) V'_3 and (e) V'_4. A cross (x) denotes a non-vanishing element (not necessarily equal), otherwise zero.

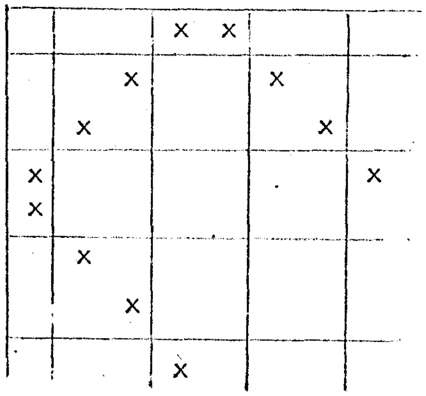
(a) $[V'_{NN}+V'_{o}]$



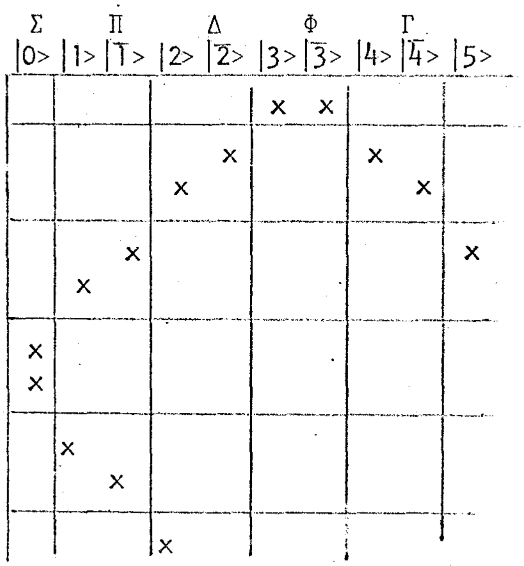
(b) $[V'_1]$



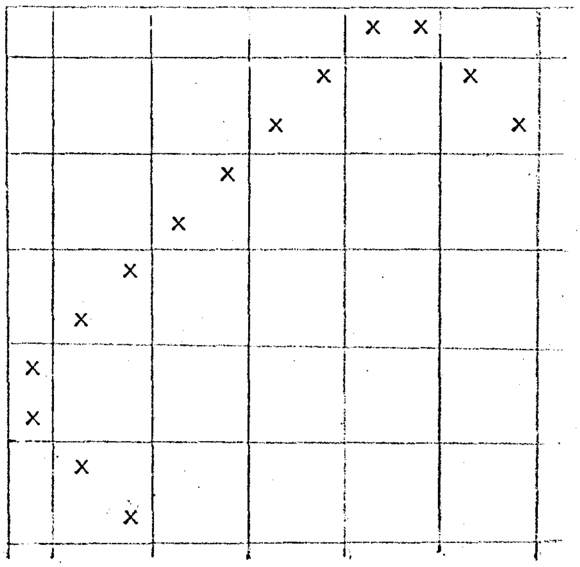
(c) $[V'_2]$



(d) $[V'_3]$



(e) $[V'_4]$



$$\lim_{\rho_\alpha \to 0} G_n^{(\alpha)} = a_{n,o,o} \frac{Z_\alpha e}{R_\alpha} \left(\frac{\rho}{R_\alpha}\right)^n \left(\frac{\rho_\alpha}{R_\alpha}\right)^n$$

therefore $$\frac{V'_{n+1}}{V'_n} \propto - \frac{G_{n+1}^{(\alpha)}}{G_n^{(\alpha)}} = \frac{1}{2} \left(\frac{\rho\rho_\alpha}{R_\alpha^{\ 2}}\right) << 1$$

The series V'_1, $V'_2, \ldots\ldots V'_n, V'_{n+1}, \ldots\ldots$ decreases so rapidly that it is necessary to retain only the first few members of the series, say, V'_1, $V'_2 \ldots\ldots V'_{n*}$. Furthermore, if we are interested in the λ-electronic level, <u>and</u> if all other electronic levels are "well separated" from this level, then we shall retain only the terms which give the first-order energies for $\psi^o_{+\lambda}$ and $\psi^o_{-\lambda}$, i.e., the terms which couple the two components of the λ-level.† It is easily verified that

$$<\psi^o_{+\lambda}|V'_n|\psi^o_{-\lambda}> = 0 \qquad \text{unless } n = 2\lambda$$

---

† For second-order approximation, the only term in the truncated series $V'_1, V'_2, \ldots\ldots V'_{n*}$, that can give the first-order electronic energy to $\psi^o_{+\lambda}$ and $\psi^o_{-\lambda}$ is $V'_{2\lambda}$. The first-order energy correction due to $V'_{2\lambda}$ is

$$W'_1 = |<\pm\lambda|V'_{2\lambda}|\mp\lambda>|$$

$$= |<\pm\lambda|\sum_\alpha \sum_\ell F^{(\alpha)}_{2\lambda,\ell}(\rho_\alpha \rho)\cdot\rho_\alpha^{\ 2\ell}\cdot\rho_\alpha e^{\pm i2\lambda(\theta-\phi_\alpha)}|\mp\lambda>|$$

$$= |\sum_{\alpha=A} \sum_{\ell>0}^{\infty} <F^{(\alpha)}_{2\lambda,\ell}>\rho_\alpha^{\ 2\ell}(\rho_\alpha e^{i\phi_\alpha})^{2\lambda}|$$

$$\simeq |\sum_{\alpha=A}^{N} <F^{(\alpha)}_{2\lambda,0}>(\rho_\alpha e^{i\phi_\alpha})^{2\lambda}|$$

$$W'_1 \propto <F^{(\alpha)}_{2\lambda,0}>\rho_\alpha^{\ 2\lambda} \qquad (1)$$

Suppose a term V'_n, other than $V'_{2\lambda}$ in the series V'_1, $V'_2, \ldots\ldots, V'_{n*}$ gives a significant second-order energy corrections to $\psi^{o}_{+\lambda}$ and $\psi^{o}_{-\lambda}$. Then from wellknown perturbation theory, the second-order energy correction is

$$
\begin{aligned}
W_2' &= \frac{|\langle s\lambda | V_n' | s'\lambda' \rangle|^2}{W^{o}_{\lambda'} - W^{o}_{\lambda}} \\
&= \frac{|\langle s\lambda | \sum_{\alpha}^{N} \sum_{\ell \geq 0} F^{(\alpha)}_{n,\ell}(\rho, R_\alpha)\, \rho_\alpha^{2\ell+n}\, e^{\pm in(\theta-\phi_\alpha)} | s'\lambda' \rangle|^2}{W^{o}_{\lambda'} - W^{o}_{\lambda}} \\
&\doteq \frac{|\sum_{\alpha} \langle s\lambda | F^{(\alpha)}_{n,0}(\rho, R_\alpha)\, e^{\pm in\theta} | s'\lambda' \rangle\, \rho_\alpha^{n}\, e^{\mp in\phi_\alpha}|^2}{W^{o}_{\lambda'} - W^{o}_{\lambda}} ,
\end{aligned}
\qquad (2)
$$

If $\langle s\lambda | F^{(\alpha)}_{n,0}(\rho, R_\alpha) e^{\pm in\theta} | s'\lambda' \rangle \neq 0$, $(s, s' = \pm)$

it requires that $\lambda' = n \pm \lambda \equiv \lambda^*$ (3)

Therefore

$$W_2' \propto \frac{[I^{(\alpha)}_{n,o}(\lambda, \lambda^*)]^2\, \rho_\alpha^{2n}}{W^{o}_{\lambda'} - W^{o}_{\lambda}} \qquad (2')$$

where $I^{(\alpha)}_{n,o}(\lambda, \lambda^*) = \iint u_\lambda(z, \rho)\, F^{(\alpha)}_{n,o}(\rho, R_\alpha)\, u_{\lambda^*}(z, \rho)\, \rho\, d\rho\, dz$.

Considering the nuclear coordinate dependence first, we see that if the magnitude of W_2' is to be comparable with that of W_1' then n must be smaller than λ. Secondly, since W_2' is inversely proportional to $(W^{o}_{\lambda'} - W^{o}_{\lambda})$, λ' should be a low-lying level. The following table lists what terms should be retained in the series $\sum_{n \geq 1} V_n'$ under different given conditions:

The unperturbed electronic level λ	$\lambda = 1$ Π-level	$\lambda = 2$ Δ-level		$\lambda = 3$ Φ-level		
Term giving first-order energy correction = V_2'	V_2'	V_4'		V_6'		
Low-lying electronic levels λ^* <u>if</u> exist	Σ, or Δ	Π, or Φ	Σ or Γ	Δ or Γ	Π or H	Σ or I

The unperturbed electronic level λ	$\lambda = 1$ Π-level	$\lambda = 2$ Δ-level		$\lambda = 3$ Φ-level		
Term giving significant second-order energy correction V'_n	$n = 1$ $V'_n = V'_1$	$n = 1$ $V'_n = V'_1$	$n = 2$ $V'_n = V'_2$	$n = 1$ $V'_n = V'_1$	$n = 2$ $V'_n = V'_2$	$n = 3$ $V'_n = V'_3$
The effective vibronic perturbation is $V'(\lambda)$	$V'(\Pi)$ $= (V'_{NN}+V'_o)$ $+ (V'_2+V'_1)$	$V'(\Delta)$ $=(V'_{NN}+V'_o)$ $+(V'_4+V'_1)$	$V'(\Delta)$ $=(V'_{NN}+V'_o)$ $+(V'_4+V'_2)$	$V'(\Phi)$ $=(V'_{NN}+V'_o)$ $+(V'_6+V'_1)$	$V'(\Phi)$ $=(V'_{NN}+V'_o)$ $+(V'_6+V'_2)$	$V'(\Phi)$ $=(V'_{NN}+V'_o)$ $+(V'_6+V'_3)$

†

Therefore the effective vibronic perturbation in the λ-electronic level (denoted by $V'(\lambda)$) is

$$V'(\lambda) = V'_{NN}(Q) + V'_o(\vec{r}_i,Q) + V'_{2\lambda}(\vec{r}_i,Q) \tag{3.3.1}$$

In terms of nuclear displacements ρ_α, $V'(\lambda)$ yields

$$\begin{aligned} V'(\lambda) = & -\frac{1}{2}\sum_{\alpha<\alpha'}\sum \frac{Z_\alpha Z_{\alpha'}}{|z_{\alpha'}-z_\alpha|^3}\left\{ |\vec{\rho}_{\alpha'}-\vec{\rho}_\alpha|^2 - \frac{3}{2}\frac{|\vec{\rho}_{\alpha'}-\vec{\rho}_\alpha|^4}{(z_{\alpha'}-z_\alpha)^2} + \cdots\cdots \right\} \\ & + \sum_{\ell\geq 1}\sum_{\alpha=1}^{N} F^{(\alpha)}_{0,\ell}\,\rho_\alpha^{2\ell} \\ & + \sum_{\ell\geq 0}\sum_{\alpha=1}^{N} F^{(\alpha)}_{2\lambda,\ell}\,\rho_\alpha^{2\ell+2\lambda}\left\{ e^{+i2\lambda(\theta-\phi_\alpha)} + e^{-i2\lambda(\theta-\phi_\alpha)} \right\} \end{aligned} \tag{3.3.1'}$$

The effective electronic Hamiltonian in λ-electronic level is given by

$$H_e(\lambda) = H_e^o(\vec{r}_i,Q^o) + V'(\lambda) \tag{3.3.2}$$

whose representation matrix is:

$$[H_e(\lambda)] = \begin{bmatrix} \langle\psi^o_{+\lambda}|H_e(\lambda)|\psi^o_{+\lambda}\rangle & \langle\psi^o_{+\lambda}|H_e(\lambda)|\psi^o_{-\lambda}\rangle \\ \langle\psi^o_{-\lambda}|H_e(\lambda)|\psi^o_{+\lambda}\rangle & \langle\psi^o_{-\lambda}|H_e(\lambda)|\psi^o_{-\lambda}\rangle \end{bmatrix}$$

$$= \begin{bmatrix} W^o_\lambda + V'_{NN} + \langle\psi^o_{+\lambda}|V'_o|\psi^o_{+\lambda}\rangle & \langle\psi^o_{+\lambda}|V'_{2\lambda}|\psi^o_{-\lambda}\rangle \\ \langle\psi^o_{-\lambda}|V'_{2\lambda}|\psi^o_{+\lambda}\rangle & W^o_\lambda + V'_{NN} + \langle\psi^o_{+\lambda}|V'_o|\psi^o_{+\lambda}\rangle \end{bmatrix} \tag{3.3.3}$$

where the matrix elements are:

$$\langle \psi^o_{s\lambda} | V'_o | \psi^o_{s\lambda} \rangle = \sum_{\ell \geq 1} \sum_{\alpha = A}^{N} \langle F^{(\alpha)}_{o,\ell} \rangle \rho_\alpha^{2\ell} \tag{3.3.4}$$

$$\langle \psi^o_{\mp\lambda} | V'_{2\lambda} | \psi^o_{\pm\lambda} \rangle = \sum_{\ell \geq 0} \sum_{\alpha = A}^{N} \langle F^{(\alpha)}_{2\lambda,\ell} \rangle \rho_\alpha^{2\ell} \left(\rho_\alpha e^{\pm i \phi_\alpha} \right)^{2\lambda} \tag{3.3.5}$$

with
$$\langle F^{(\alpha)}_{n,\ell} \rangle = \int_{z=-\infty}^{\infty} \int_{\rho=0}^{\infty} u_\lambda(z,\rho)^2 \sum_{j=0}^{\ell_1 = \frac{\ell-1}{2}} a_{n,\ell,j} \frac{Z_\alpha e}{R_\alpha} \left(\frac{\rho}{R_\alpha} \right)^{n+2j} \left(\frac{1}{R_\alpha} \right)^{n+2\ell} \rho \, d\rho \, dz \tag{3.3.6}$$

The summation over N atoms and the integrals (4.3-6) will account for specific molecules.

3.4 Effective Perturbation in Terms of Bending Mode Coordinates and Force Constants for Bending Vibrations.

In this section we shall give a short note on the bending normal coordinates and express Equations (3.3.1') and (3.3.5) in terms of these coordinates.

As a normal coordinate belongs to the same symmetry properties as the molecule, it can be constructed from a linear combination of the symmetry coordinates of the same symmetry species. Hence, if $S_j(\Gamma)$ is the jth symmetry coordinate of Γ-symmetry and L_{kj} are the transformation coefficients, then the coordinates of the kth normal mode $\underline{q}_k = (q_{kx}, q_{ky})$ of Γ-symmetry can be written as

$$q_{kx}(\Gamma) = \sum_{j}^{\Gamma\text{-species}} L_{kj} S_{jx}(\Gamma) \tag{3.4.1}$$

The symmetry coordinates are normally not difficult to write in terms of a linear combination of nuclear displacements using Eckart's conditions$^{(31)}$ and symmetry properties.

$$S_{jx}(\Gamma) = \sum_{\alpha=A}^{N} D_{j\alpha} x_{\alpha} \tag{3.4.2}$$

where x_α is the x-displacement of the α-atom, and $D_{j\alpha}$ are the appropriate coefficients. Substituting Equation (3.4.2) into (3.4.1), we have

$$q_{kx}(\Gamma) = \sum_{\alpha=A}^{N} \ell_{k\alpha} x_{\alpha} \tag{3.4.3}$$

where $\ell_{k\alpha} = \sum_j L_{kj} D_{j\alpha}$. The reverse transformation of Equation (3.4.3) will give

$$\rho_\alpha \cos\phi_\alpha \equiv x_\alpha = \sum_{k=1}^{t} \ell_k^\alpha q_{kx} \tag{3.4.4a}$$

where t is the total number of bending modes, and the coefficients ℓ_k^α can be shown to be $(\ell^\intercal)_{\alpha k}$ where $(\ell^\intercal)$ is the transpose of the matrix $\ell = ||\ell_{k\alpha}||$.

Similarly, we have

$$\rho_\alpha \sin\phi_\alpha \equiv y_\alpha = \sum_{k=1}^{t} \ell_k^\alpha q_{ky} \tag{3.4.4b}$$

where y_α is the y-displacement of the α-atom. If we define r_k and ϕ_k by

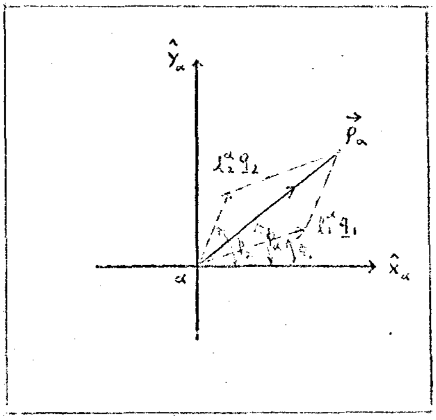
$$\begin{aligned} q_{kx} &\equiv r_k \cos\phi_k \\ q_{ky} &\equiv r_k \sin\phi_k \end{aligned} \tag{3.4.5}$$

then, Equation (3.4.4) becomes

$$\begin{aligned} \rho_\alpha \cos\phi_\alpha &= \sum_{k=1}^{t} \ell_k^\alpha r_k \cos\phi_k \\ \rho_\alpha \sin\phi_\alpha &= \sum_{k=1}^{t} \ell_k^\alpha r_k \sin\phi_k \end{aligned} \tag{3.4.6}$$

Thus the displacement vector of the α-atom ($\vec{\rho}_\alpha$) can be regarded as a superposition of bending coordinate vectors $\underline{q}_k$ (Fig. 3.3).

Fig. 3.3 Superposition of two bending vibrational vectors associated with the α-atom.



The ℓ_k^α's are the proportionalities which can be positive or negative depending on the phase we choose for the kth mode. However, the relative phases and magnitudes of ℓ_k^α's are fixed for a given kth mode.

In this thesis, we shall not evaluate the ℓ_k^α's. We mention only that the ratios $\ell_k^\alpha : \ell_k^{\alpha'} : \ell_k^{\alpha''} : \ldots\ldots$ can not be determined unless we know the Born-Oppenheimer potential for each vibrational mode$^{(32,33)}$. We shall use Equation (3.4.6) as it stands and substitute it into the potential to obtain expressions which are functions of r_k and ϕ_k. It can be shown from Equations (3.4.5) and (3.4.6) that

$$\begin{aligned}
\rho_\alpha e^{\pm i \phi_\alpha} &= \sum_{k=1}^{t} \ell_k^\alpha r_k e^{\pm i \phi_k} \\
\rho_\alpha \rho_{\alpha'} \cos(\phi_\alpha - \phi_{\alpha'}) &= \sum_{k=1}^{t} \sum_{k'}^{t} \ell_k^\alpha \ell_{k'}^{\alpha'} r_k r_{k'} \cos(\phi_k - \phi_{k'}) \\
\rho_\alpha^2 &= \sum_{k} \sum_{k'} \ell_k^\alpha \ell_{k'}^\alpha r_k r_{k'} \cos(\phi_k - \phi_{k'}) \qquad (3.4.7) \\
\left|\vec{\rho}_{\alpha'} - \vec{\rho}_\alpha\right|^2 &= \sum_{k} \sum_{k'} (\ell_k^\alpha - \ell_k^{\alpha'})(\ell_{k'}^\alpha - \ell_{k'}^{\alpha'}) r_k r_{k'} \cos(\phi_k - \phi_{k'})
\end{aligned}$$

Therefore, Equations (3.3.1), (3.3.4), and (3.3.5) become:

$$\begin{aligned} V'(\lambda) = {} & -\frac{1}{2} \sum_{\alpha<\alpha'} \sum \frac{Z_\alpha Z_{\alpha'}}{|z_{\alpha'}-z_\alpha|^3} \Big\{ \sum_k \sum_{k'} (l_k^\alpha - l_k^{\alpha'})(l_{k'}^\alpha - l_{k'}^{\alpha'}) r_k r_{k'} \cos(\phi_k - \phi_{k'}) \\ & - \frac{3}{2(z_{\alpha'}-z_\alpha)^2} \Big[\sum \sum (l_k^\alpha - l_k^{\alpha'})(l_{k'}^\alpha - l_{k'}^{\alpha'}) r_k r_{k'} \cos(\phi_k - \phi_{k'}) \\ & + \cdots \Big\} + \sum_{l\geq 1} \sum_\alpha F_{0,l}^{(\alpha)} \Big[\sum_k \sum_{k'} l_k^\alpha l_{k'}^\alpha r_k r_{k'} \cos(\phi_k - \phi_{k'}) \Big]^l \\ & + \sum_{l\geq 0} \sum_\alpha F_{2\lambda,l}^{(\alpha)} \Big[e^{i2\lambda\theta} \Big(\sum_k l_k^\alpha r_k e^{i\phi_k} \Big)^\lambda + \\ & e^{-i2\lambda\theta} \Big(\sum_k l_k^\alpha r_k e^{i\phi_k} \Big)^\lambda \Big] \cdot \Big[\sum_k \sum_{k'} l_k^\alpha l_{k'}^\alpha r_k r_{k'} \cos(\phi_k - \phi_{k'}) \Big]^l . \end{aligned} \tag{3.4.8}$$

$$\begin{aligned} \langle \psi_{-\lambda}^0 | V'(\lambda) | \psi_{+\lambda}^0 \rangle = {} & \sum_{\alpha=1}^{N} \Big[\langle F_{2\lambda,0}^{(\alpha)} \rangle + \langle F_{2\lambda,1}^{(\alpha)} \rangle \sum_k \sum_{k'} \\ & l_k^\alpha l_{k'}^\alpha r_k r_{k'} \cos(\phi_k - \phi_{k'}) + \cdots \Big] \cdot \\ & \Big[\sum_k^t l_k^\alpha r_k e^{i\phi_k} \Big]^{2\lambda} \end{aligned} \tag{3.4.9}$$

$$\begin{aligned} \langle \psi_{s\lambda}^0 | V'(\lambda) | \psi_{s\lambda}^0 \rangle = {} & \frac{1}{2} \sum_k \Big[\sum_\alpha 2 \langle F_{0,1}^{(\alpha)} \rangle (l_k^\alpha)^2 - \sum_{\alpha<\alpha'} \sum \frac{Z_\alpha Z_{\alpha'}}{|z_\alpha - z_{\alpha'}|^3} (l_k^\alpha - l_k^{\alpha'})^2 \Big] r_k^2 \\ & + \sum_k \sum_{k'} \Big[\sum_\alpha 2 \langle F_{0,1}^{(\alpha)} \rangle l_k^\alpha l_{k'}^\alpha - \sum_{\alpha<\alpha'} \sum \frac{Z_\alpha Z_{\alpha'}}{|z_\alpha - z_{\alpha'}|^3} (l_k^\alpha - l_k^{\alpha'}) \cdot (l_{k'}^\alpha - l_{k'}^{\alpha'}) \Big] \cdot \\ & r_k r_{k'} \cos(\phi_k - \phi_{k'}) + \sum_k \sum_{k'} \sum_{k''} \sum_{k'''} \Big[\sum_{\alpha=1}^{N} \langle F_{0,2}^{(\alpha)} \rangle l_k^\alpha l_{k'}^\alpha l_{k''}^\alpha l_{k'''}^\alpha \\ & + \sum_{\alpha<\alpha'} \sum \frac{3 Z_\alpha Z_{\alpha'}}{4|z_\alpha - z_{\alpha'}|^5} (l_k^\alpha - l_k^{\alpha'})(l_{k'}^\alpha - l_{k'}^{\alpha'})(l_{k''}^\alpha - l_{k'}^{\alpha'})(l_{k'''}^\alpha - l_{k'''}^{\alpha'}) \cdot \\ & \cdot r_k r_{k'} r_{k''} r_{k'''} \cos(\phi_{k'} - \phi_k) \cdot \cos(\phi_{k'''} - \phi_{k''}) \end{aligned} \tag{3.4.10}$$

+ terms higher than 4th power.

If the off-diagonal matrix elements of Equation (3.3.3), i.e., terms of the type given in Equation (3.4.9), vanish, then Equation (3.4.10) will give the Born-Oppenheimer energies for the λ-electronic level. These energies yield the potential for the vibrational motion of the molecule in this λ-level. The coefficients in front of r_k^2 will have the significance as the force constants $k_k = \mu_k\omega_k^2$: i.e.,

$$k_k = \mu_k \omega_k^2 = \sum_{\alpha=A}^{N} 2 \langle F_{0,1}^{(\alpha)} \rangle (\ell_k^\alpha)^2 - \sum_{\alpha<\alpha'}\sum \frac{Z_\alpha Z_{\alpha'}}{|z_\alpha - z_{\alpha'}|^3} (\ell_k^\alpha - \ell_k^{\alpha'})^2 \tag{3.4.11a}$$

Since we demand that the normal coordinates are such that the vibrational potentials in terms of them does not contain cross-terms in second-order, then whenever $k' \neq k$, the coefficients in front of $r_k r_{k'} \cos(\phi_k - \phi_{k'})$ have to be zero, i.e.,

$$0 = \sum_{\alpha=A}^{N} 2 \langle F_{0,1}^{(\alpha)} \rangle \ell_k^\alpha \cdot \ell_{k'}^\alpha - \sum\sum \frac{Z_\alpha Z_{\alpha'}}{|z_\alpha - z_{\alpha'}|^3} (\ell_k^\alpha - \ell_k^{\alpha'})(\ell_{k'}^\alpha - \ell_{k'}^{\alpha'}) \tag{3.4.11b}$$

Equation (3.4.11), together with the symmetry properties, Eckart's conditions and the orthonormal properties of normal coordinates, may be used to determine the coefficients ℓ_k^α and the force constants $k_k = \mu_k\omega_k^2 (k = 1,2,\ldots\ldots t)^\dagger$. With these understandings, Equation (3.4.10) is reduced to

$$\langle \psi_{s\lambda}^0 | V'(\alpha) | \psi_{s\lambda}^0 \rangle \doteq \sum_k \frac{1}{2} k_k r_k^2 + \sum\sum\sum\sum g_{kk'k''k'''} r_k r_{k'} r_{k''} r_{k'''} \cos(\phi_k - \phi_{k'}) \cdot \cos(\phi_{k''} - \phi_{k'''})$$

$$+ \text{ terms of higher order} \tag{3.4.12}$$

where $g_{kk'k''k'''}$ are the anharmonic constants, given by

$$g_{kk'k''k'''} = \sum_{\alpha=A}^{N} \langle F_{0,2}^{(\alpha)} \rangle \ell_k^\alpha \cdot \ell_{k'}^\alpha \cdot \ell_{k''}^\alpha \cdot \ell_{k'''}^\alpha +$$

$$\sum_{\alpha<\alpha'}\sum \frac{3 Z_\alpha Z_{\alpha'}}{4 |z_\alpha - z_{\alpha'}|^3} (\ell_k^\alpha - \ell_k^{\alpha'})(\ell_{k'}^\alpha - \ell_{k'}^{\alpha'})(\ell_{k''}^\alpha - \ell_{k''}^{\alpha'}) \cdot (\ell_{k'''}^\alpha - \ell_{k'''}^{\alpha'}) , \tag{3.4.13}$$

[†] This statement can be verified as follows: For a linear N-atomic molecule, the number of bending modes is t = N - 2 (Appendix A). Thus the number of force constants is t = N - 2, and the number of coefficients ℓ_k^α is Nt = N(N - 2).

The total number of unknown quantities is $t + Nt = (N + 1)(N - 2)$.

We must have sufficient number of equations to determine these unknowns. In fact we have (a) normalization conditions (one for each mode); $t = (N - 2)$ of them; (b) orthogonal conditions, $\binom{t}{2} = \frac{(N-2)(N-3)}{2}$; (c) Eckart's conditions (two for each bending mode, i.e., rotationless and translationless): $2t = 2(N - 2)$; (d) potential equations (3.4.11): $t + \binom{t}{2} = (N - 2) + \frac{1}{2}(N - 2)(N - 3)$. Hence the total number of equations is $(N + 1)(N - 2)$ (Q.E.D.). †

3.5 The Renner Parameters

We shall expand Equation (3.4.9), the off-diagonal matrix elements of Equation (3.3.3), for various linear molecules, and give the Renner parameters in terms of integrals for each case.

(a) Linear Triatomic Molecules (ABC)

There is only one bending mode, $\underline{q}_k = (r,\phi)$; therefore

$$\rho_\alpha e^{\pm i\phi_\alpha} = \ell^\alpha_k \, r e^{\pm i\phi}$$

and Equation (3.4.9) becomes

$$<\psi^o_{\mp\lambda}|V'(\lambda)|\psi^o_{\mp\lambda}> = \sum_{\alpha=A,B,C} [<F^{(\alpha)}_{2\lambda,o}>+<F^{(\alpha)}_{2\lambda,1}>(\ell^\alpha_k)^2 r^2+\dots]$$

$$\cdot(\ell^\alpha_k \, re^{\pm i\phi})^{2\lambda} \tag{3.5.1}$$

If we denote $\sigma_0, \sigma_2, \dots$ etc. for a general λ-level, by

$$\sigma_0 = \sum_{\alpha=A,B,C} <F^{(\alpha)}_{2\lambda,o}>(\ell^\alpha_k)^{2\lambda}$$

$$\sigma_2 = \sum_{\alpha=A,B,C} <F^{(\alpha)}_{2\lambda,1}>(\ell^\alpha_k)^{2\lambda+2}$$

then Equation (3.5.1) can be written as

$$\langle\psi^{o}_{\mp\lambda}|V'(\lambda)|\psi^{o}_{\pm\lambda}\rangle = (\sigma_0 + \sigma_2 r^2 + \ldots\ldots) r^{2\lambda} e^{\pm 2i\lambda\phi} \tag{3.5.2}$$

For π-electronic level, i.e., $\lambda = 1$, we adopt in place of σ_0, σ_2,..... etc. the following notation

$$\tfrac{1}{2}f = \sigma_0(\lambda = 1)$$

$$\tfrac{1}{2}h = \sigma_2(\lambda = 1)$$

Thus we have

$$\langle\psi^{o}_{\mp 1}|V'(\pi)|\psi^{o}_{\pm 1}\rangle = \tfrac{1}{2}(f + hr^2 + \ldots\ldots) r^2 e^{\pm i2\phi} \tag{3.5.3}$$

The Renner parameter for a linear triatomic molecule in π-electronic level is defined by$^{(27)}$

$$\epsilon = \frac{f}{k} = \frac{3}{4\mu\omega^2}\sum_{\alpha}(\ell^{\alpha}_{k})^2 \iint |u_\pi(z,\rho)|^2 \frac{Z_\alpha e}{R_\alpha}\frac{\rho^2}{R_\alpha^4}\,\rho\,d\rho\,dz \tag{3.5.4}$$

where $\mu\omega^2$ is the force constant k for the bending vibration, and $a = \dfrac{\hbar}{\mu\omega}$.

For Δ-electronic level, i.e., $\lambda = 2$, we write $\tfrac{1}{2}h$ for σ_0 in Equation (3.5.2). Thus

$$\langle\psi^{o}_{\mp\Delta}|V'(\Delta)|\psi^{o}_{\pm\Delta}\rangle = \tfrac{1}{2}(h + \cdots) r^4 e^{\pm i4\phi} \tag{3.5.5}$$

We may define a numerical constant η by

$$\eta = \frac{ha^2}{\hbar\omega} = \frac{35}{64\,\omega}\sum_{\alpha}(\ell^{\alpha}_{k})^4 \iint |u_\Delta(z,\rho)|^2 \frac{Z_\alpha e}{R_\alpha}\frac{\rho^4}{R_\alpha^8}\,\rho\,d\rho\,dz \tag{3.5.6}$$

(b) Unsymmetrical Linear Tetratomic Molecules (ABCD)

There are two bending modes (t = 2; k = 1 and 2). Therefore,

$$\rho_\alpha e^{\pm i\phi_\alpha} = \ell^{\alpha}_{1} r_1 e^{\pm i\phi_1} + \ell^{\alpha}_{2} r_2 e^{\pm i\phi_2} \tag{3.5.7}$$

For π-electronic level, i.e., λ = 1, Equation (3.4.9) can be written as

$$\begin{aligned}\langle \psi^{0}_{\mp\pi} | V'(\pi) | \psi_{\pm\pi} \rangle = {} & \frac{1}{2} \left(f_1 + h_{4,0}\, r_1^2 + 3\, h_{2,2}\, r_2^2 \right) r_1^2\, e^{\pm 2i\phi_1} \\ & + \frac{1}{2} \left(f_2 + h_{0,4}\, r_2^2 + 3\, h_{22}\, r_1^2 \right) r_2^2\, e^{\pm 2i\phi_2} \\ & + \frac{1}{2} \left(2 f_{12} + 3\, h_{31}\, r_1^2 + 3\, h_{13}\, r_2^2 \right) r_1 r_2\, e^{\pm i(\phi_1 + \phi_2)} \\ & + \frac{1}{2} \left(h_{31}\, r_1^3 r_2\, e^{\pm i(3\phi_1 - \phi_2)} + h_{13}\, r_1 r_2^3\, e^{\pm i(3\phi_2 - \phi_1)} \right) \\ & + \text{terms higher than } 4^{\text{th}} \text{ order} \end{aligned} \tag{3.5.8}$$

where

$$\begin{aligned} f_k &= 2 \sum_{\alpha = A,B,C,D} \langle F^{(\alpha)}_{2,0} \rangle \left(\ell^{\alpha}_k \right)^2 \\ f_{12} &= 2 \sum_{\alpha = A,B,C,D} \langle F^{(\alpha)}_{2,0} \rangle\, \ell^{\alpha}_1 \cdot \ell^{\alpha}_2 \\ h_{ab} &= 2 \sum_{\alpha = A,B,C,D} \langle F^{(\alpha)}_{2,1} \rangle \left(\ell^{\alpha}_1 \right)^a \cdot \left(\ell^{\alpha}_2 \right)^b \end{aligned} \tag{3.5.9}$$

For Δ-electronic level, i.e., λ = 2, we obtain

$$\begin{aligned}\langle \psi^{0}_{\mp\Delta} | V'(\Delta) | \psi^{0}_{\pm\Delta} \rangle = {} & \frac{1}{2}\, h_{40}\, r_1^4\, e^{\pm i 4\phi_1} + \frac{1}{2}\, h_{04}\, r_2^4\, e^{\pm i 4\phi_2} \\ & + 2\, h_{31}\, r_1^3 r_2\, e^{\pm i(3\phi_1 + \phi_2)} + 2\, h_{13}\, r_1 r_2^3\, e^{\pm i(\phi_1 + 3\phi_2)} \\ & + 3\, h_{22}\, r_1^2 r_2^2\, e^{\pm i 2(\phi_1 + \phi_2)} \\ & + \text{terms higher than } 4^{\text{th}} \text{ order} \end{aligned} \tag{3.5.10}$$

(c) Symmetrical Linear Tetratomic Molecules (ABBA)

The Equations (3.5.9) and (3.5.10) can be greatly simplified because of the presence of inversion symmetry. Let the linear configuration be defined by $\alpha(0,0,z_\alpha)$ and $\overline{\alpha}(0,0,-z_\alpha)$ (see Fig. 5-1a, Chapter 5):

$A(0,0,a)$, $B(0,0,b)$, $\overline{B}(0,0,-b)$ and $\overline{A}(0,0,-a)$.

The atomic charges, Z, are: Z_A, Z_B, $Z_{\overline{B}} = Z_B$, $Z_{\overline{A}} = Z_A$. We also designate the normal modes by

$$\underline{q}_k = \begin{cases} \underline{q}_k\ (\pi_u) & \text{if } k = \text{odd} \\ \underline{q}_k\ (\pi_g) & \text{if } k = \text{even} \end{cases} \tag{3.5.11}$$

so that $$E^{-1}\underline{q}_k = (-1)^k\ \underline{q}_k,\quad (E^{-1} = \text{inversion operation}) \tag{3.5.12}$$

Since the integrals $<F_{n\ell}^{(\alpha)}>$, defined by Equation (3.3.6), are constants they are invariant under the symmetry operations. And since the inversion operation effects:

$$z \rightarrow -z,\ \rho \rightarrow \rho$$

therefore

$$\begin{aligned} \langle F_{n\ell}^{(\alpha)} \rangle &= E^{-1} \cdot \langle F_{n\ell}^{(\alpha)} \rangle \\ &= E^{-1} \sum_{j=0}^{\frac{\ell}{2}\text{ or }\frac{\ell-1}{2}} a_{n\ell j} \iint |u_\lambda(z,\rho)|^2 \frac{Z_\alpha e\ \rho^{n+2j}}{[(z-z_\alpha)^2+\rho^2]^{n+\ell+j+\frac{1}{2}}} \rho\, d\rho\, dz \\ &= \sum_{j=0}^{\frac{\ell}{2}, \frac{\ell-1}{2}} a_{n\ell j} \iint |u_\lambda(-z,\rho)|^2 \frac{Z_\alpha e\ \rho^{n+2j}}{[(-z-z_\alpha)^2+\rho^2]^{n+\ell+j+\frac{1}{2}}} \rho\, d\rho\, dz \\ &= \sum_{j=0}^{\frac{\ell}{2}, \frac{\ell-1}{2}} a_{n\ell j} \iint |u_\lambda(z,\rho)|^2 \frac{Z_{\bar{\alpha}} e\ \rho^{n+2j}}{[(z+z_\alpha)^2+\rho^2]^{n+\ell+j+\frac{1}{2}}} \rho\, d\rho\, dz \\ &= \langle F_{n,\ell}^{(\bar{\alpha})} \rangle \end{aligned} \tag{3.5.13}$$

We have used the relation (Chapter 2)

$$u_\lambda(-z,\rho) = \pm u_\lambda(z,\rho)$$

in obtaining the fourth line.

The x-displacement of α-atom is given by

$$x_\alpha = \sum_{k=1}^{t} \ell_k^\alpha\ q_{kx} \tag{3.5.14}$$

The inversion operation has the effect of shifting the displacement originally associated with α-atom to $\bar{\alpha}$-atom, and the direction of the displacement vector is reversed, i.e.,

$$E^{-1} x_{\alpha} = -x_{\bar{\alpha}} \tag{3.5.15}$$

Equations (3.5.12), (3.5.14) and (3.5.15) give

$$\ell_k^{\bar{\alpha}} = (-1)^{k+1} \ell_k^{\alpha} \tag{3.5.16}$$

The properties (3.5.16) for the symmetrical linear tetratomic molecules are shown in Table 3.4$^{(35)}$.

Table 3.4

ℓ_k^{α} coefficients for symmetrical A-B-B-A molecules.
m_A = mass of atom A and $\bar{A}$; m_B = mass of atom B and $\bar{B}$;
$\mu_1 = 2m_A m_B/(m_A+m_B)$; $\mu_2 = m_A m_B (a+b)^2/2(m_A a^2 + m_B b^2)$.

ℓ_k^{α}	ℓ_k^{A}	ℓ_k^{B}	$\ell_k^{\bar{B}}$	$\ell_k^{\bar{A}}$
k=1	$\frac{\mu_1^{1/2}}{2m_A}$	$-\frac{\mu_1^{1/2}}{2m_B}$	$-\frac{\mu_1^{1/2}}{2m_B}$	$\frac{\mu_1^{1/2}}{2m_A}$
k=2	$\frac{\mu_2^{1/2}}{2m_A}\ \frac{2b}{(a+b)}$	$-\frac{\mu_2^{1/2}}{2m_B}\ \frac{2a}{(a+b)}$	$\frac{\mu_2^{1/2}}{2m_B}\ \frac{2a}{(a+b)}$	$-\frac{\mu_2^{1/2}}{2m_A}\ \frac{2b}{(a+b)}$

Using Equations (3.5.13) and (3.5.16), we obtain for Equation (3.5.9)

$$\frac{1}{2} h_{a,b} = \sum_{\alpha=A,B} \langle F_{n\ell}^{(\alpha)} \rangle (\ell_1^{\alpha})^a (\ell_2^{\alpha})^b + \sum_{\bar{\alpha}=\bar{A},\bar{B}} \langle F_{n\ell}^{(\bar{\alpha})} \rangle (\ell_1^{\bar{\alpha}})^a (\ell_2^{\bar{\alpha}})^b$$

$$= \sum_{\alpha=A,B} \langle F_{n\ell}^{(\alpha)} \rangle (\ell_1^{\alpha})^a (\ell_2^{\alpha})^b \left[1 + (-1)^b \right]$$

$$= \begin{cases} 0 & \text{if } b = \text{odd} . \\ \sum\limits_{\alpha=A,B} 2 \langle F_{n,j}^{(\alpha)} \rangle (\ell_1^{\alpha})^{a} (\ell_2^{\alpha})^{b} , & \text{if } b = \text{even} \end{cases} \tag{3.5.17}$$

and $\frac{1}{2} f_{11} = 0$

Thus Equations (3.5.9) and (3.5.10) become:

(for $\lambda = 1$)

$$\langle \psi_{\mp\pi}^{0} | V'(\pi) | \psi_{\pm\pi}^{0} \rangle = \frac{1}{2} (f_1 + h_{40} r_1^2 + 3 h_{22} r_2^2) r_1^2 e^{\pm i 2 \phi_1}$$

$$+ \frac{1}{2} (f_2 + h_{04} r_2^2 + 3 h_{22} r_1^2) r_2^2 e^{i 2 \phi_2}$$

$$+ \text{ terms higher than } 4^{\text{th}} \text{ order} \tag{3.5.18}$$

(for $\lambda = 2$)

$$\langle \psi_{\mp\Delta}^{0} | V'(\Delta) | \psi_{\pm\Delta}^{0} \rangle = \frac{1}{2} h_{40} r_1^4 e^{\pm 4 i \phi_1}$$

$$+ \frac{1}{2} h_{04} r_2^4 e^{\pm i 4 \phi_2} + 3 h_{22} r_1^2 r_2^2 e^{\pm i 2 (\phi_1 + \phi_2)}$$

$$+ \text{ terms higher than } 4^{\text{th}} \text{ order} \tag{3.5.19}$$

Formulae analogous to Equation (3.5.18) have been obtained by A. D. Liehr$^{(24)}$ who used the Taylor series expansion first and then applied (implicitly) symmetry arguments to the normal coordinates r_1, r_2, not on the constants as we have done.

3.6 Anharmonic Constants for Symmetrical Linear Molecules

The anharmonicities are given by [Equation (3.4.13)]:

$$g_{kk'k''k'''} = g^{I}_{kk'k''k'''} + g^{II}_{kk'k''k'''} \tag{3.6.1}$$

where

$$g^{I}_{kk'k''k'''} = \sum_{\alpha=A}^{N} \langle F_{0,4}^{(\alpha)} \rangle \ell_k^{\alpha} \ell_{k'}^{\alpha} \ell_{k''}^{\alpha} \ell_{k'''}^{\alpha} . \tag{3.6.2a}$$

and

$$g^{II}_{kk'k''k'''} = \sum_{\alpha < \alpha'} \sum \frac{3 Z_{\alpha} Z_{\alpha'}}{4 |z_{\alpha} - z_{\alpha'}|^5} (\ell_k^{\alpha} - \ell_k^{\alpha'}) (\ell_{k'}^{\alpha} - \ell_{k'}^{\alpha'}) (\ell_{k''}^{\alpha} - \ell_{k''}^{\alpha'}) (\ell_{k'''}^{\alpha} - \ell_{k'''}^{\alpha'}) \tag{3.6.2b}$$

Using Equations (3.5.13) and (3.5.16) we can show that

$$g^{I}_{kk'k''k'''} = \begin{cases} 0 & \text{if } k+k'+k''+k''' = \text{odd} \\ 2\sum_{\alpha=A,B} \langle F^{(\alpha)}_{0,z} \rangle \ell^{\alpha}_{k} \ell^{\alpha}_{k'} \ell^{\alpha}_{k''} \ell^{\alpha}_{k'''}, & \text{if } k+k'+k''+k''' = \text{even} \end{cases}$$

and that

$$g^{II}_{kk'k''k'''} = \begin{cases} 0 & \text{if } k+k'+k''+k''' = \text{odd} \\ \neq 0 & \text{otherwise} \end{cases}$$

therefore

$$g_{kk'k''k'''} = \begin{cases} 0 & \text{if } k+k'+k''+k''' = \text{odd} \\ \neq 0 & \text{otherwise} \end{cases} \tag{3.6.3}$$

Also from Equations (3.6.1) and (3.6.2) for any linear molecule, we have

$$g_{1122} = g_{1212} = g_{1221} = g_{2112} = g_{2121} = g_{2211}$$

and for any permulation of {k,k',k'',k'''}:

$$g_{kk'k''k'''} = g_{\{kk'k''k'''\}}. \tag{3.6.4}$$

3.7 Representative Hamiltonian

We have mentioned that we know very little about the electronic wavefunctions aside from its angular dependence. Furthermore, when we give the vibronic perturbation, Equation (3:2.17), we assume acknowledgement of the effective charges of the atoms and the transformation of the atomic displacement coordinates to normal coordinates, quantities which are actually not known. However, we can put all unknown quantities into a few parametric constants. To this end, we shall use the "representative vibronic perturbation", H'_λ instead of Equation (3.3.1'). The "representative electronic Hamiltonian" will be given by

$$H_e(\lambda) = H_e^o + U^o(r_k^2) + U'(Q) + H'_\lambda \tag{3.7.1}$$

This is defined so that Equation (3.7.1) will give the same matrix elements in the basis $\{\psi^o_{+\lambda}, \psi^o_{-\lambda}\}$ as does Equation (3.3.2). $U^o(r^2)$ is the Harmonic potential while $U'(Q)$ denotes the anharmonic part of the vibrational potential:

$$U^o(r_k^2) = \sum_{k=1}^{t} \frac{1}{2} \mu_k \omega_k^2 r_k^2 \tag{3.7.2}$$

$$U'(Q) = \sum_k \sum_{k'} \sum_{k''} \sum_{k'''} g_{kk'k''k'''} r_k r_{k'} r_{k''} r_{k'''} \cos(\phi_k - \phi_{k'}) \cdot \cos(\phi_{k''} - \phi_{k'''}) \tag{3.7.3}$$

The representative electronic Hamiltonians for various molecules in π- or Δ-electronic level are listed in Table 3.5. We see that H'_λ can be written as

$$H'_\lambda = q^+_\lambda Q^-_\lambda + q^-_\lambda Q^+_\lambda \tag{3.7.4}$$

where $\quad q^\pm_\lambda = e^{\pm i\lambda\theta}$

and $Q^\pm_\lambda$ are functions of vibrational coordinates. For example, for symmetrical linear tetratomic molecules in a π-electronic level and neglecting terms higher than 4th order, we have

$$Q^\pm_\pi = \sigma_1(r_1, r_2)\, e^{\pm i 2\phi_1} + \sigma_2(r_1, r_2)\, e^{\pm i 2\phi_2} \tag{3.7.5}$$

where

$$\sigma_1(r_1, r_2) = \frac{1}{2}\left(f_1 r_1^2 + h_{40} r_1^4 + 3 h_{22} r_1^2 r_2^2 \right)$$

$$\sigma_2(r_1, r_2) = \frac{1}{2}\left(f_2 r_2^2 + h_{04} r_2^4 + 3 h_{22} r_1^2 r_2^2 \right)$$

Table 3.5

Representative vibronic perturbations and Hamiltonians for linear triatomic, tetratomic and pentatomic molecules in π- or Δ-electronic levels (λ = 1 or 2).

$$H_e(\lambda) = H_e^o + U(Q) + H'_\lambda$$

$$U(Q) = U^o(r_k^2) + U'(Q) = \text{vibrational potential.}$$

(a) Linear triatomic molecules (λ = 1,2)

$$U(Q) = \tfrac{1}{2}\mu_k\omega_k^2 r^2 + g_k r^4 + 0(r^6)$$

$$H'_\lambda = 2(\sigma_0 + \sigma_2 r^2 + \ldots\ldots)r^{2\lambda}\cos 2\lambda(\theta-\phi)$$

(b) Unsymmetrical linear tetratomic molecules

$$\begin{aligned} U(Q) = {} & (\tfrac{1}{2}\mu_1\omega_1^2 r_1^2 + \tfrac{1}{2}\mu_2\omega_2^2 r_2^2) + (g_{1111}r_1^4 + 2g_{1122}r_1^2 r_2^2 + g_{2222}r_2^4 \\ & + 4[r_1^2 + r_2^2 + r_1 r_2\cos(\phi_1-\phi_2)]r_1 r_2\cos(\phi_1-\phi_2)) + 0(r_k^6) \end{aligned}$$

$$\begin{aligned} (\lambda=1) \quad H'_\pi = {} & (f_1 + h_{40}r_1^2 + 3h_{22}r_2^2)r_1^2\cos 2(\theta-\phi_1) \\ & + (f_2 + h_{04}r_2^2 + 3h_{22}r_2^2)r_2^2\cos 2(\theta-\phi_2) \\ & + (2f_{12} + 3h_{31}r_1^2 + 3h_{13}r_2^2)r_1 r_2\cos(2\theta-\phi_1-\phi_2) \\ & + h_{31}r_1^3 r_2\cos(2\theta-3\phi_1+\phi_2) + h_{13}r_1 r_2^3\cos(2\theta-3\phi_1-\phi_2) \\ & + 0(r_k^6) \end{aligned}$$

$$\begin{aligned} (\lambda=2) \quad H'_\Delta = {} & h_{40}r_1^4\cos 4(\theta-\phi_1) + h_{04}r_2^4\cos 4(\theta-\phi_2) \\ & + 4h_{31}r_1^3 r_2\cos(4\theta-3\phi_1-\phi_2) + 4h_{13}r_1 r_2^3\cos(4\theta-3\phi_2-\phi_1) \\ & + 6h_{22}r_1^2 r_2^2\cos(4\theta-2\phi_1-2\phi_2) \\ & + 0(r_k^6) \end{aligned}$$

(c) Symmetrical linear tetratomic molecules

$$\begin{aligned} U(Q) = {} & (\tfrac{1}{2}\mu_1\omega_1^2 r_1^2 + \tfrac{1}{2}\mu_2\omega_2^2 r_2^2) + (g_{1111}r_1^4 + 4g_{1122}r_1^2 r_2^2 + g_{2222}r_2^4 \\ & + 2g_{1122}r_1^2 r_2^2\cos 2(\phi_1-\phi_2)) + 0(r_k^6) \end{aligned}$$

$$\begin{aligned} (\lambda=1) \quad H'_\pi = {} & (f_1 + h_{40}r_1^2 + 3h_{22}r_2^2)r_1^2\cos 2(\theta-\phi_1) \\ & + (f_2 + h_{04}r_2^2 + 3h_{22}r_2^2)r_2^2\cos 2(\theta-\phi_2) \\ & + 0(r_k^6) \end{aligned}$$

$$
\begin{aligned}
(\lambda=2) \quad H'_{\Delta} &= h_{40} r_1^4 \cos 4(\theta-\phi_1) + h_{04} r_2^4 \cos 4(\theta-\phi_2) \\
&+ 6h_{22} r_1^2 r_2^2 \cos(4\theta-2\phi_1-2\phi_2) \\
&+ 0(r_k^6)
\end{aligned}
$$

(d) Unsymmetrical linear pentatomic molecules

$$
\begin{aligned}
U(Q) &= \sum_{k=1}^{3} \tfrac{1}{2}\mu_k \omega_k^2 r_k^2 + \sum_k \sum_{k'} \sum_{k''} \sum_{k'''} g_{kk'k''k'''} r_k r_{k'} r_{k''} r_{k'''} \\
&\cdot \cos(\phi_k-\phi_{k'}) \cos(\phi_{k''}-\phi_{k'''})
\end{aligned}
$$

$$
\begin{aligned}
(\lambda=1) \quad H'_{\pi} &= (f_1 + h_{400} r_1^2 + 3h_{220} r_2^2 + 3h_{202} r_3^2) r_1^2 \cos 2(\theta-\phi_1) \\
&+ (f_2 + h_{040} r_2^2 + 3h_{220} r_1^2 + 3h_{022} r_3^2) r_2^2 \cos 2(\theta-\phi_2) \\
&+ (f_3 + h_{004} r_3^2 + 3h_{202} r_1^2 + 3h_{022} r_2^2) r_3^2 \cos 2(\theta-\phi_3) \\
&+ (2f_{12} + 3h_{310} r_1^2 + 3h_{130} r_2^2 + 6h_{112} r_3^2) r_1 r_2 \cos(2\theta-\phi_1-\phi_2) \\
&+ (2f_{13} + 3h_{301} r_1^2 + 3h_{103} r_3^2 + 6h_{121} r_2^2) r_1 r_3 \cos(2\theta-\phi_1-\phi_3) \\
&+ (2f_{23} + 3h_{031} r_2^2 + 3h_{103} r_3^2 + 6h_{211} r_1^2) r_2 r_3 \cos(2\theta-\phi_2-\phi_3) \\
&+ h_{310} r_1^3 r_2 \cos(2\theta-3\phi_1+\phi_2) + h_{130} r_1 r_2^3 \cos(2\theta-3\phi_2-\phi_1) \\
&+ h_{301} r_1^3 r_3 \cos(2\theta-3\phi_1+\phi_3) + h_{103} r_1 r_3^3 \cos(2\theta-3\phi_3-\phi_1) \\
&+ h_{031} r_2^3 r_3 \cos(2\theta-3\phi_2+\phi_3) + h_{013} r_2 r_3^2 \cos(2\theta-3\phi_3+\phi_2) \\
&+ 3h_{211} r_1^2 r_2 r_3 [\cos(2\theta-2\phi_1+\phi_2-\phi_3) + \cos(2\theta-2\phi_1-\phi_2+\phi_3)] \\
&+ 3h_{121} r_1 r_2^2 r_3 [\cos(2\theta-2\phi_2+\phi_3-\phi_1) + \cos(2\theta-2\phi_2-\phi_3+\phi_1)] \\
&+ 3h_{112} r_1 r_2 r_3^2 [\cos(2\theta-2\phi_3+\phi_1-\phi_2) + \cos(2\theta-2\phi_3-\phi_1+\phi_2)] \\
&+ 0(r_k^6)
\end{aligned}
$$

$$
\begin{aligned}
(\lambda=2) \quad H'_{\Delta} &= h_{400} r_1^4 \cos 4(\theta-\phi_1) + h_{040} r_2^4 \cos 4(\theta-\phi_2) + h_{004} r_3^4 \cos 4(\theta-\phi_3) \\
&+ 4h_{310} r_1^3 r_2 \cos(4\theta-3\phi_1-\phi_2) + 4h_{130} r_1 r_2^3 \cos(4\theta-3\phi_2-\phi_1) \\
&+ 4h_{301} r_1^3 r_3 \cos(4\theta-3\phi_1-\phi_3) + 4h_{103} r_1 r_3^3 \cos(4\theta-3\phi_3-\phi_1) \\
&+ 4h_{031} r_2^3 r_3 \cos(4\theta-3\phi_2+\phi_3) + 4h_{013} r_2 r_3^2 \cos(4\theta-3\phi_3-\phi_2) \\
&+ 6h_{220} r_1^2 r_2^2 \cos(4\theta-2\phi_1-2\phi_2) + 6h_{202} r_1^2 r_3^2 \cos(4\theta-2\phi_1-2\phi_3) \\
&+ 6h_{022} r_2^2 r_3^2 \cos(4\theta -2\phi_2-2\phi_3) + 12h_{121} r_1 r_2^2 r_3 \cos(4\theta-\phi_1-2\phi_2-\phi_3) \\
&+ 12h_{211} r_1^2 r_2 r_3 \cos(4\theta-2\phi_1-\phi_2-\phi_3) + 12h_{112} r_1 r_2 r_3^2 \cos(4\theta-\phi_1-\phi_2-2\phi_3) \\
&+ 0(r_k^6)
\end{aligned}
$$

(e) Symmetrical linear pentatomic molecules

$$U(Q) = \sum_{k=1}^{3} \tfrac{1}{2}\mu_k\omega_k r_k^2 + \{ \sum_{k=1}^{3} g_k r_k^4 + 4g_{1122}r_1^2r_2^2 + 4g_{2233}r_2^2r_3^2$$

$$+ 4g_{1133}r_1^2r_3^2 + 2g_{1122}r_1^2r_2^2\cos2(\phi_1-\phi_2) + 2g_{2233}r_2^2r_3^2\cos2(\phi_2-\phi_3)$$

$$+ 2g_{1133}r_1^2r_3^2\cos2(\phi_1-\phi_3) + 4(g_{1113}r_1^3r_3 + g_{1333}r_1r_3^3)\cos(\phi_1-\phi_3)$$

$$+ 8g_{1223}r_1r_2^2r_3\cos(\phi_1-\phi_3) + 4g_{1223}r_1r_2^2r_3\cos(\phi_1+\phi_3-2\phi_2)\}$$

(λ=1)

$$H'_\pi = (f_1 + h_{400}r_1^2 + 3h_{220}r_2^2 + 3h_{202}r_3^2)r_1^2\cos2(\theta-\phi_1)$$

$$+ (f_2 + h_{040}r_2^2 + 3h_{220}r_1^2 + 3h_{022}r_3^2)r_2^2\cos2(\theta-\phi_2)$$

$$+ (f_3 + h_{004}r_3^2 + 3h_{202}r_1^2 + 3h_{022}r_2^2)r_3^2\cos2(\theta-\phi_3)$$

$$+ (2f_{13} + 3h_{301}r_1^2 + 6h_{121}r_2^2 + 3h_{103}r_3^2)r_1r_3\cos(2\theta-\phi_1-\phi_3)$$

$$+ h_{301}r_1^3r_3\cos(2\theta-3\phi_1+\phi_3) + h_{103}r_1r_3^3\cos(2\theta-3\phi_3+\phi_2)$$

$$+ 3h_{121}r_1r_2^2r_3[\cos(2\theta-2\phi_2-\phi_1+\phi_3)\cos(2\theta-2\phi_2+\phi_1-\phi_3)]$$

$$+ 0(r_k^6)$$

(λ=2)

$$H'_\Delta = h_{400}r_1^4\cos4(\theta-\phi_1) + h_{040}r_2^4\cos4(\theta-\phi_2) + h_{004}r_3^4\cos4(\theta-\phi_3)$$

$$+ 4[h_{301}r_1^3r_3\cos(4\theta-3\phi_1-\phi_3) + h_{103}r_1r_3^3\cos(4\theta-3\phi_3-\phi_1)]$$

$$+ 6h_{220}r_1^2r_2^2\cos(4\theta-2\phi_1-2\phi_2) + 6h_{202}r_1^2r_3^2\cos(4\theta-2\phi_1-2\phi_3)$$

$$+ 6h_{022}r_2^2r_3^2\cos(4\theta-2\phi_2-2\phi_3) + 12h_{121}r_1r_2^2r_3\cos(4\theta-\phi_1-\phi_3-2\phi_2)$$

$$+ 0(r_k^6)$$

CHAPTER 4

Renner Effect in Linear Triatomic Molecules

4.1 Static Problem--Electronic Wavefunctions and Energies

For linear triatomic molecules, there are two stretching modes and one bending mode of vibration denoted by $q_1(\sigma+)$, $q_3(\sigma+)$ and $\underline{q}_2(\pi)$ respectively. Since the electronic wavefunction is less sensitive to the stretching coordinates q_1 and q_3 than it is to the bending coordinates we can ignore the q_1- and q_3-dependence from the molecular potential V. The vibronic Schröedinger equation is then given by

$$\{T_e + V(\vec{r}_i,\underline{q}_2) + T_N(\frac{\partial^2}{\partial \underline{q}_2^2}) - E\}\Psi(\vec{r}_i,\underline{q}_2) = 0 \qquad (4.1.1)$$

where

$\underline{q}_2 = \underline{q}_2(r,\phi)$ and

$$T_N = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial \underline{q}_2^2} = -\frac{\hbar^2}{2\mu}(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}) \qquad (4.1.2)$$

When the nuclei are held fixed at $\underline{q}_2$, the electronic motion is obtained by solving the following electronic Schröedinger equation:

$$\{T_e + V(\vec{r}_i;\underline{q}_2) - W_e(\underline{q}_2)\}\psi_e(\vec{r}_i;\underline{q}_2) = 0 \qquad (4.1.3)$$

Particularly when $\underline{q}_2 = 0$, we have

$$\{T_e + V^o(\vec{r}_i;0) - W_e^o\}\psi_e^o(\vec{r}_i;0) = 0 \qquad (4.1.4)$$

The solutions of Equation (4.1.4) have been discussed in Chapter 2. They are

$$\psi_\Lambda^o(\vec{r}_i;0) = u_\lambda(z,\rho)e^{i\Lambda\theta}$$

with energies W_λ^o.

When $\underline{q}_2 \neq 0$ but is small, the potential $V(\vec{r}_i, \underline{q}_2)$ can be expressed in terms of the multipole expansion. If the $\lambda > 0$ electronic level is of interest we have (Section 3.7):

$$\begin{aligned} V(\vec{r}_i, \underline{q}_2) &= U(\underline{q}_2) + H'_\lambda \\ &= \left(\tfrac{1}{2}\mu\omega^2 r^2 + g_k r^4 + \cdots\right) + 2(\sigma_0 + \sigma_2 r^2 + \cdots) r^{2\lambda} \cos 2\lambda(\theta - \phi) \end{aligned} \tag{4.1.5}$$

And the electronic wavefunction ψ_e of Equation (4.1.3) can be expressed in terms of $\psi^o_{+\lambda}$ and $\psi^o_{-\lambda}$, i.e.,

$$\psi_e(\vec{r}_i; \underline{q}_2) = \psi^o_{+\lambda} C_+(\underline{q}_2) + \psi^o_{-\lambda} C_-(\underline{q}_2) \tag{4.1.6}$$

Substituting Equations (4.1.5) and (4.1.6) into Equation (4.1.3), we obtain the coupled equations for $C_+(\underline{q}_2)$ and $C_-(\underline{q}_2)$: ($\underline{q}_2$ fixed)

$$\begin{bmatrix} W^o_\lambda + U(\underline{q}_2) - W(q_2) & \sigma(r) e^{-i2\lambda\phi} \\ \sigma(r) e^{+i2\lambda\phi} & W^o_\lambda + U(\underline{q}_2) - W(q_2) \end{bmatrix} \begin{bmatrix} C_+(q_2) \\ C_-(q_2) \end{bmatrix} = 0 \tag{4.1.7}$$

where $\sigma(r) = (\sigma_0 + \sigma_2 r^2 + \ldots\ldots) r^{2\lambda}$. The first-order electronic energies and the correct zeroth-order electronic wavefunctions are obtained with reference to Appendix B. The correct zeroth-order electronic wavefunctions are

$$\psi_{\lambda a}(\vec{r}_i; \underline{q}_2) = \sqrt{2}\, u_\lambda(z, \rho) \cos\lambda(\theta - \phi) \tag{4.1.8a}$$

$$\psi_{\lambda b}(\vec{r}_i; \underline{q}_2) = \sqrt{2}\, u_\lambda(z, \rho) \sin\lambda(\theta - \phi) \tag{4.1.8b}$$

which are independent of the bending radial coordinate r.

The corresponding energies are independent of the bending azimuthal angle ϕ:

$$W_{\lambda a} = W^o_\lambda + U(\underline{q}_2) + \sigma(r)$$

$$W_{\lambda b} = W^o_\lambda + U(\underline{q}_2) - \sigma(r)$$

As we do not consider the mixing between different electronic levels, we may put W_λ^o equal to zero, i.e., we measure energies with respect to this value, thus

$$W_a = U(\underline{q}_2) + \sigma(r) \qquad (4.1.9a)$$

$$W_b = U(\underline{q}_2) - \sigma(r) \qquad (4.1.9b)$$

A plot of the function

$$W_{\substack{a\\b}} = \tfrac{1}{2}kr^2 + gr^4 \pm (\sigma_0 + \sigma_2 r^2 + \ldots\ldots)r^{2\lambda} \qquad (4.1.9')$$

has been shown in Fig. 1.3 (Chapter 1). If $\lambda = 1$ (π-electronic level) we write for Equation (4.1.9'):

$$W_{\substack{a\\b}} = \tfrac{1}{2}kr^2 + gr^4 \pm (\tfrac{1}{2}fr^2 + \tfrac{1}{2}hr^4) \qquad (4.1.10)$$

Figure 1.3A is obtained if $k = \mu\omega^2 > |f|$; Fig. 1.3B will be obtained if $0 < k < |f|$. However Fig. 1.3C is possible only if $k < 0$, i.e., the force constant is negative! In the last two cases, to make the curves concave upward, $g - \tfrac{1}{2}|h|$ should be greater than zero. The radial extremes and the height of the potential hump of Fig. 1.3B (or Fig. 1.3C) are obtained by derivative of W_b (assuming that $W_a > W_b$ for any value of r) with respect to r. They are

$$r_{min} = \frac{1}{2}\left(\frac{f-k}{g-\frac{1}{2}h}\right)^{1/2} \qquad (f > k > 0 \text{ and } g - \frac{h}{2} > 0)$$

and

$$W_b(r_{min}) = -\frac{(f-k)^2}{16(g-\frac{1}{2}h)}$$

The electronic wavefunction $\psi_{\lambda a}$ of Equation (4.1.8a) is symmetrical with respect to the molecular plane defined by $\phi = \phi'$ which contains the three atoms. The function $\psi_{\lambda b}$ is antisymmetrical with respect to the same plane. If the molecule is symmetrical, these wavefunctions can be classified under the C_{2v} point group by the representations B_1 and B_2 (or A_1 and A_2) respectively (Appendix A-5). Equations (4.1.8) also show that, in the first-order of approximation used, $\psi_{\lambda a}$ and $\psi_{\lambda b}$ have no r-dependence but large ϕ-dependence. This ϕ-dependence is as large as the θ-dependence, i.e.,

$$\frac{\partial}{\partial\phi}\psi_{\lambda a} = -\frac{\partial}{\partial\theta}\psi_{\lambda a} = \lambda\psi_{\lambda b}$$

$$\frac{\partial}{\partial\phi}\psi_{\lambda b} = -\frac{\partial}{\partial\theta}\psi_{\lambda b} = -\lambda\psi_{\lambda a}$$

and $$\frac{\partial^2}{\partial\phi^2}\psi_{\lambda a} = -\lambda^2\psi_{\lambda a}\,, \quad \frac{\partial^2}{\partial\phi^2}\psi_{\lambda b} = -\lambda^2\psi_{\lambda b} \qquad (4.1.11)$$

$$\frac{\partial}{\partial r}\psi_{\lambda a} = \frac{\partial}{\partial r}\psi_{\lambda b} = 0$$

4.2 Dynamical Problem: Zeroth-order Vibronic Solutions

In solving the vibronic equation (4.1.1), Renner has shown that one can not write the solution $\Psi(\vec{r}_i,\underline{q}_2)$ as a simple product function. The reason being that if we assume Ψ to be either

$$\Psi' = \psi_{\lambda a}(r_i,q_2)\,\Phi^a(q_2) \quad \text{or}$$

$$\Psi'' = \psi_{\lambda b}(r_i\,q_2)\,\Phi^b(q_2) \qquad (4.2.1)$$

The nuclear operator $T_N(\frac{\partial^2}{\partial \underline{q}_2^2})$ acting on these functions will cause a mixing of them. By Equation (4.1.11), we see that

$$T_N\left\{\psi_{\lambda a}\cdot\Phi^a\right\} = -\frac{\hbar}{2\mu r^2}\left[-\lambda^2\psi_{\lambda a}\Phi^a + 2\lambda\psi_{\lambda b}\frac{\partial}{\partial\phi}\Phi^a\right] + \psi_{\lambda a}T_N\Phi^a$$

$$T_N\left\{\psi_{\lambda b}\cdot\Phi^b\right\} = -\frac{\hbar}{2\mu r^2}\left[-\lambda^2\psi_{\lambda b}\Phi^b - 2\lambda\psi_{\lambda b}\frac{\partial}{\partial\phi}\Phi^b\right] + \psi_{\lambda b}T_N\Phi^b$$

thus we should write $\Psi(\vec{r}_i,\underline{q}_2)$ as a linear combination of Ψ' and Ψ'', i.e.,

$$\Psi(\vec{r}_i,\underline{q}_2) = \psi_{\lambda a}(\vec{r}_i,\underline{q}_2)\cdot\Phi^a(\underline{q}_2) + \psi_{\lambda b}(\vec{r}_i,\underline{q}_2)\cdot\Phi^b(\underline{q}_2) \qquad (4.2.2)$$

This equation together with Equations (4.2.1) and (2.3.1a) of Adiabatic Formulation given in Chapter 2, give the following coupled differential equations for the variational functions Φ^a and Φ^b:

$$\begin{bmatrix} -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right)+U(r)+\sigma(r)+\frac{\lambda^2\hbar}{2\mu r^2}-E & \frac{2\lambda\hbar}{2\mu r^2}\frac{\partial}{\partial\phi} \\ -\frac{2\lambda\hbar}{2\mu r^2}\frac{\partial}{\partial\phi} & -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right)+U(r)-\sigma(r)+\frac{\lambda^2\hbar^2}{2\mu r^2}-E \end{bmatrix}\begin{bmatrix}\Phi^a(q_2)\\ \Phi^b(q_2)\end{bmatrix}=0 \qquad (4.2.3)$$

Equation (4.2.3) for $\lambda = 1$ has been solved by Renner$^{(5)}$. His method for $\lambda \geq 1$ electronic levels has been generalized by E. Teller$^{(36)}$. In order to deduce the <u>vibronic angular momentum</u> in a more natural way, we shall use a different mathematical approach.

We define a number of matrices as follows:

$$\mathbb{I}=\begin{bmatrix}1&0\\0&1\end{bmatrix},\quad \Sigma_1=\begin{bmatrix}0&1\\1&0\end{bmatrix},\quad \Sigma_2=\begin{bmatrix}0&i\\i&0\end{bmatrix}\quad \Sigma_3=\begin{bmatrix}1&0\\0&-1\end{bmatrix} \qquad (4.2.4)$$

$$\mathbb{P}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\cdot\mathbb{I} = \begin{bmatrix}\frac{\hbar}{i}\frac{\partial}{\partial\phi} & 0\\ 0 & \frac{\hbar}{i}\frac{\partial}{\partial\phi}\end{bmatrix} \qquad (4.2.5)$$

$$\mathbb{G}_z = \mathbb{P}_z - \lambda\hbar\,\Sigma_2 = \begin{bmatrix}\frac{\hbar}{i}\frac{\partial}{\partial\phi} & i\lambda\hbar\\ -i\lambda\hbar & \frac{\hbar}{i}\frac{\partial}{\partial\phi}\end{bmatrix} \qquad (4.2.6)$$

($\Sigma_1,\Sigma_2,\Sigma_3$, are Pauli spin matrices$^{(17)}$. The physical significances of $\mathbb{P}_z$ and $\mathbb{G}_z$ will be observed later.)

and the vector

$$\Phi = \begin{bmatrix} \Phi^a(q_2) \\ \Phi^b(q_2) \end{bmatrix} \tag{4.2.7}$$

Hence Equation (4.2.3) becomes

$$\left\{ -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right)\mathbb{I} - \frac{1}{2\mu r^2}\mathbb{G}_z^2 + U(r)\,\mathbb{I} + \sigma(r)\sum_3 - E \right\}\Phi$$

$$= \left\{ \mathbb{H}_v - E \right\}\Phi = 0 \tag{4.2.8}$$

where $\mathbb{H}_v = \mathbb{H}_v^0 + U'(r)\,\mathbb{I} + \sigma(r)\sum_3$ (4.2.9)

with $\mathbb{H}_v^0 = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right)\cdot\mathbb{I} + \frac{1}{2\mu r^2}\mathbb{G}_z^2 + U^0(r)\cdot\mathbb{I}$ (4.2.10)

$U'(r) = U(r) - U^0(r) = gr^4 +$ higher order terms (4.2.11)

$U^0(r) = \frac{1}{2}\mu\omega^2 r^2$ (4.2.12)

For zeroth-order, we set

$U'(r) = 0$ i.e., $U(r) = U^0(r) = \frac{1}{2}\mu\omega^2 r^2$

and $\sigma(r) = 0$

so that

$$\left\{ \mathbb{H}_v^0 - E \right\}\Phi^0$$

$$= \left\{ -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2\mu r^2}\mathbb{G}_z^2 + \frac{1}{2}\mu\omega^2 r^2 - E \right\}\Phi^0$$

$$= 0 \tag{4.2.13}$$

This equation is similar in form to the ordinary two-dimensional oscillator equation (Appendix D-5a), therefore $\mathbb{G}_z$ can be regarded as the <u>vibrational angular momentum operator</u>. Since $\mathbb{G}_z$ and $\mathbb{P}_z$ commute with $\mathbb{H}_v^0$, thus Φ^0 can be chosen to be a simultaneous eigenfunction of the three operators. Supposing that $\Phi^0_{v\ell;K}$ are eigenfunctions of $\mathbb{G}_z$ and $\mathbb{P}_z$ with eigenvalues $\ell\hbar$ and $K\hbar$ respectively, then

$$\mathbb{G}_z \Phi^0_{v\ell;K} = \ell\hbar\,\Phi^0_{v\ell;K} \tag{4.2.14}$$

$$\mathbb{P}_z\, \bar{\Phi}^{0}_{v\ell;K} = K\hbar\, \bar{\Phi}^{0}_{v\ell;K} \tag{4.2.15}$$

The quantum number v will be determined by Equation (4.2.13).

By separation of variables, we assume that $\Phi^{0}_{v\ell;K}$ can be written as

$$\bar{\Phi}^{0}_{v\ell;K} = \begin{bmatrix} B^{a}(r)\cdot A^{a}(\phi) \\ B^{b}(r)\cdot A^{b}(\phi) \end{bmatrix} \tag{4.2.16}$$

which, in matrix product form, is

$$\bar{\Phi}^{0}_{v\ell;K} = \begin{bmatrix} B^{a}(r) & 0 \\ 0 & B^{b}(r) \end{bmatrix} \begin{bmatrix} A^{a}(\phi) \\ A^{b}(\phi) \end{bmatrix} \tag{4.2.16'}$$

By Equations (4.2.14) and (4.2.16'), we have

$$\mathbb{G}_z \begin{bmatrix} A^{a}(\phi) \\ A^{b}(\phi) \end{bmatrix} = \ell\hbar \begin{bmatrix} A^{a}(\phi) \\ A^{b}(\phi) \end{bmatrix} \tag{4.2.17}$$

Using the definition of $\mathbb{G}_z$, Equation (4.2.6), we obtain the coupled equations :

$$\left(\frac{\partial}{\partial\phi} - i\ell\right) A^{a}(\phi) - \lambda A^{b}(\phi) = 0 \tag{4.2.18a}$$

$$\left(\frac{\partial}{\partial\phi} - i\ell\right) A^{b}(\phi) + \lambda A^{a}(\phi) = 0 \tag{4.2.18b}$$

These can be solved by writing

$$A^{a}(\phi) - is\, A^{b}(\phi) \equiv \mathcal{G}_{s}(\phi) \tag{4.2.19}$$

where s is a number to be so chosen that we can obtain simple solutions for A^a and A^b. Multiplication of Equation (4.2.18b) by is, followed by addition to Equation (4.2.18a), yields

$$\left[\frac{\partial}{\partial\phi} - i(\ell + s\lambda)\right] g_s(\phi) - \lambda(1-s^2)\, A^b(\phi) = 0$$

Choosing $s^2 \equiv 1$, i.e., $s = \pm 1$, we obtain

$$\left[\frac{\partial}{\partial\phi} - i(\ell + s\lambda)\right] g_s(\phi) = 0\,, \qquad (s = \pm 1) \tag{4.2.20}$$

The solutions are readily seen to be

$$g_s(\phi) \sim e^{i(\ell + s\lambda)\phi} \tag{4.2.21}$$

By Equations (4.2.18a), (4.2.19) and (4.2.21), we obtain

$$A^a_s = \frac{1}{2}\, g_s(\phi) = \frac{1}{2}\, e^{i(\ell+s\lambda)\phi}$$

$$A^b_s = \frac{is}{2}\, g_s(\phi) = \frac{is}{2}\, e^{i(\ell+s\lambda)\phi}$$

Hence the normalized angular column matrix is

$$N_\phi \begin{bmatrix} A^a_s \\ A^b_s \end{bmatrix} = \frac{1}{\sqrt{4\pi}} \begin{bmatrix} 1 \\ is \end{bmatrix} e^{i(\ell+s\lambda)\phi}\,, \qquad (s = \pm 1) \tag{4.2.22}$$

By Equations (4.2.15) and (4.2.22), we have

$$K\hbar\, \Phi^0_{v\ell;K} = \mathbb{P}_z\, \Phi^0_{v\ell;K} = (\ell + s\lambda)\hbar\, \Phi^0_{v\ell;K}$$

therefore $K = \ell + s\lambda = \ell + \Lambda$, $(\Lambda = s\lambda)$ (4.2.23)

which is a sum of vibrational angular momentum quantum number and the electronic angular momentum quantum number. Thus K can be defined as the vibronic angular momentum quantum number, and the matrix $\mathbb{P}_z$ will then be a vibronic angular momentum operator.

To complete the solution of $\Phi^0_{v\ell;K}$, we substitute Equation (4.2.16') into Equation (4.2.13); we obtain

$$\left\{-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{\ell^2}{r^2}\right) + \frac{1}{2}\mu\omega^2 r^2 - E^0\right\} \begin{bmatrix} B^a(r) \\ B^b(r) \end{bmatrix} = 0 \tag{4.2.24}$$

The solutions are earily seen to be (Appendix D-6b):

$$B^a(r) = B^b(r) = R_{\upsilon|\ell|}(r)$$

and $$\tag{4.2.25}$$

$$E^0 = \mathcal{E}^0_\upsilon = (\upsilon+1)\hbar\omega$$

Thus

$$\bar{\Phi}^0_{v\ell;K} = R_{v|\ell|}(r)\frac{1}{\sqrt{4\pi}}\begin{bmatrix} 1 \\ is \end{bmatrix} e^{iK\phi} \equiv \bar{\Phi}^0_{v\ell;\Lambda K}, \quad \left(s = \frac{K-\ell}{\lambda} = \frac{\Lambda}{\lambda} = \pm\right) \tag{4.2.26}$$

and

$$\langle \bar{\Phi}^0_{v'\ell'\Lambda'K'} | \bar{\Phi}^0_{v\ell\Lambda K} \rangle = \delta_{v'v} \cdot \delta_{\ell'\ell} \cdot \delta_{\Lambda'\Lambda} \cdot \delta_{K'K} \tag{4.2.27}$$

4.3 Second-Order Vibronic Energy Expressions

As $\sigma(r)\Sigma_3 \neq 0$, we shall use the Van Vleck degenerate perturbation theory[(38,39,40)] to obtain the energy expressions correct to second-order for Equation (4.2.8). The basis functions will be $\Phi^0_{v\ell\Lambda K}$ of Equation (4.2.26) and the perturbation is $U'(r) + \sigma(r)\Sigma_3 = H'$.

Since G_z does not commute with $\mathbb{H}_V$, but $\mathbb{P}_z$ does, thus the eigenfunctions Φ of Equation (4.2.8) can still be characterized by the vibronic quantum number K. Hence we expect that there is no nonvanishing matrix element between states of different K. In fact

$$\begin{aligned}
&\langle \bar{\Phi}^0_{v\ell\Lambda K} | \sigma(r)\Sigma_3 | \bar{\Phi}_{v'\ell'\Lambda'K'} \rangle \\
&= \int_{r=0}^{\infty}\int_{\phi=0}^{2\pi} R_{v|\ell|}(r)\cdot[1 \quad is]^* \cdot \frac{e^{iK\phi}}{\sqrt{4\pi}}^* \sigma(r)\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} R_{v'|\ell'|}(r)\begin{bmatrix} 1 \\ is' \end{bmatrix}\frac{e^{iK'\phi}}{\sqrt{4\pi}} \, r\,dr\,d\phi \\
&= [1 \quad -is]\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 1 \\ is' \end{bmatrix}\cdot\frac{1}{2}\int_{r=0}^{\infty} R_{v|\ell|}(r)\,\sigma(r)\,R_{v'|\ell'|}(r)\,r\,dr \int_{\phi=0}^{2\pi}\frac{1}{2\pi}e^{-iK\phi}e^{iK'\phi}\,d\phi \\
&= \frac{1}{2}(1-ss')\cdot\left(R_{v|\ell|}(r)\,|\,\sigma(r)\,|\,R_{v'|\ell'|}(r)\right)\cdot\delta_{KK'} \\
&= \begin{cases} \left(R_{v|K-\Lambda|}\,|\,\sigma(r)\,|\,R_{v'|K+\Lambda|}\right) & \text{if } K'=K, \text{ and } s'=-s \text{ (i,e, } \Lambda'=-\Lambda) \\ 0 & \text{otherwise} \end{cases}
\end{aligned} \tag{4.3.1}$$

We shall designate the vibronic level of given υ and K by $[\upsilon]^K$. For this level, Van Vleck's basis functions are (Appendix C):

$$\bar{\Phi}_{K(\Lambda,\ell);v} = \bar{\Phi}^{0}_{v\ell;\Lambda K} + \phi^{(1)}_{v\ell;\Lambda K} + \phi^{(2)}_{v\ell;\Lambda K} , \qquad (\Lambda+\ell=K) \tag{4.3.2}$$

where

$$\phi^{(1)}_{v\ell;\Lambda K} = \sum_{v'\neq v} \sum_{\ell'} \bar{\Phi}^{0}_{v'\ell'\Lambda' K} \, C^{\Lambda' v' \ell'}_{\Lambda v \ell} \tag{4.3.3}$$

with

$$C^{\Lambda' v' \ell'}_{\Lambda v \ell} = - \frac{\langle \bar{\Phi}^{0}_{v'\ell'\Lambda' K} | \mathbb{H}' | \bar{\Phi}^{0}_{v\ell\Lambda K} \rangle}{(v'-v)\hbar\omega} \tag{4.3.4}$$

which can be called interaction coefficients.

The $\phi^{(2)}_{\upsilon\ell;\Lambda K}$ are added mainly for maintaining orthogonality between different functions of the form of Equation (4.3.2). If we are not interested in the energy higher than third-order, we can drop this term from the expression.

The representation of the Hamiltonian $\mathbb{H}_V$ in the level $[\upsilon]^K$, which is doubly degenerate $K < (\upsilon+\lambda)$ is given by:

$$\begin{bmatrix} \langle \bar{\Phi}_{K(+,\ell);v} | \mathbb{H}_v | \bar{\Phi}_{K(+,\ell)v} \rangle & \langle \bar{\Phi}_{K(+\ell),v} | \mathbb{H}_v | \bar{\Phi}_{K(-\ell''),v} \rangle \\ \langle \bar{\Phi}_{K(-,\ell'');v} | \mathbb{H}_v | \bar{\Phi}_{K(+,\ell)v} \rangle & \langle \bar{\Phi}_{K(-\ell),v} | \mathbb{H}_v | \bar{\Phi}_{K(-\ell''),v} \rangle \end{bmatrix} \tag{4.3.5}$$

The diagonal matrix elements will be denoted by:

$$\langle \bar{\Phi}_{K(+,\ell)v} | \mathbb{H}_v | \bar{\Phi}_{K(+,\ell)v} \rangle = \mathcal{E}^{0}_{v} + d_1 + z_1 \tag{4.3.6a}$$

$$\langle \bar{\Phi}_{K(-,\ell'')v} | \mathbb{H}_v | \bar{\Phi}_{K(-\ell'')v} \rangle = \mathcal{E}^{0}_{v} + d_2 + z_2 \tag{4.3.6b}$$

where

$$d_r = \langle \bar{\Phi}^{0}_{v\ell\Lambda K} | U'(r) | \bar{\Phi}^{0}_{v\ell\Lambda K} \rangle , \qquad (r = {}^{1}_{2} , \text{ for } \Lambda = \pm\lambda) \tag{4.3.7a}$$

$$z_r = \sum_{v'\neq v} \sum_{\ell'} (\mathcal{E}^{0}_{v} - \mathcal{E}^{0}_{v'}) \left| C^{\Lambda' v' \ell'}_{\Lambda v \ell} \right|^2 ; \qquad (r = {}^{1}_{2} , \ell = K \mp \lambda) \tag{4.3.7b}$$

The off-diagonal matrix element will be denoted by:

$$\langle \bar{\Phi}_{K(+l)v} | H_v | \bar{\Phi}_{K(-l'')v} \rangle = a_r + y_r \tag{4.3.8}$$

where

$$a_r = \langle \bar{\Phi}^0_{vl\Lambda K} | \sigma(r)\, \bar{\Sigma}_3 | \bar{\Phi}^0_{vl''\bar{\Lambda}K} \rangle = (R_{v|K-\lambda|} | \sigma(r) | R_{v|K+\lambda|}) \tag{4.3.9a}$$

$$y_r = \sum_{v' \neq v} \sum_{l'} (\mathcal{E}^0_v - \mathcal{E}^0_{v'}) \cdot C^{\Lambda' v' l'}_{\Lambda v l} \cdot C^{\Lambda' v' l'}_{\Lambda v l''} , \tag{4.3.9b}$$

The energies which are correct through second-order are obtained by diagonalization of the matrix (4.3.5). This gives (Appendix B-20):

$$E_j(K;v) = \mathcal{E}^0_v + \tfrac{1}{2}(d_1 + d_2 + z_1 + z_2) \pm \left\{ \left(\frac{d_1 - d_2 + z_1 - z_2}{2} \right)^2 + (a+y)^2 \right\}^{1/2} ; \quad (j=1,2) \tag{4.3.10}$$

4.4 Linear Triatomic Molecules in π- or Δ-Electronic Level: Vibronic Energies

We assume that the perturbation H' is truncated at the fourth power term (r^4), i.e., in the perturbation

$$H' = U'(r) + \sigma(r)\Sigma_3 .$$

We assume $U'(r)$ and $\sigma(r)$ to be

$$U'(r) = gr^4$$

$$\sigma(r) = \begin{cases} \tfrac{1}{2}hr^4 & \text{for } \lambda = 2\ (\Delta) \text{ electronic level} \\ \tfrac{1}{2}fr^2 + \tfrac{1}{2}hr^4 & \text{for } \lambda = 1\ (\pi) \text{ electronic level} \end{cases} \tag{4.4.1}$$

Consider the vibronic level $[v]^K$ which consists of two states:

$$|\Phi^0_{vl\Lambda K}\rangle : \quad |v, l; +K\rangle \text{ and } |v, l''; -K\rangle \qquad (K < v+\lambda)$$

with $\ell = K-\lambda$, and $\ell'' = K+\lambda$ and <u>interaction diagram</u> (Fig. 4.1) demonstrates with what states these two components will interact. Evaluation of the interaction coefficients matrix elements for Π- and Δ-electronic levels are listed in Tables (4.2) and (4.3) respectively. In the tables, we define the parameters ε, η and γ by:

$$\begin{aligned} \varepsilon &\equiv \frac{f}{k} = \frac{f}{\mu\omega^2}, \quad \text{or } fa = \varepsilon\hbar\omega \\ \eta &\equiv h\,\frac{a^2}{\hbar\omega} \quad \text{or } ha^2 = \eta\hbar\omega \quad ; \quad (a = \frac{\hbar}{\mu\omega}) \\ \gamma &\equiv g\,\frac{a^2}{\hbar\omega} \quad \text{or } ga^2 = \gamma\hbar\omega \end{aligned} \tag{4.4.2}$$

The use of Equations (4.3.7), (4.3.9) and (4.3.10) produce the following results:

(i) <u>$\lambda = 1$: Π-electronic level:</u>

Assuming that $\varepsilon >> \eta \sim \gamma$, we have

$$z_1 = -\frac{\varepsilon^2}{8}(\upsilon+1)(K+1)\hbar\omega$$

$$z_2 = +\frac{\varepsilon^2}{8}(\upsilon+1)(K-1)\hbar\omega$$

$$\tfrac{1}{2}(z_1 + z_2) = -\frac{\varepsilon^2}{8}(\upsilon+1)\hbar\omega$$

$$\tfrac{1}{2}(z_1 - z_2) = -\frac{\varepsilon^2}{8}(\upsilon+1)K\hbar\omega$$

For $K = \upsilon+1$ or $\upsilon = K-1$, there is only one state:

$$E(K;\upsilon) = (\upsilon+1)\left[1 - \left(\frac{\varepsilon^2}{8} - \gamma\right)(\upsilon+2)\right]\hbar\omega \tag{4.4.3}$$

For $K < (\upsilon+1)$,

$$\begin{aligned} E_{1,2}(K;\upsilon)/\hbar\omega = {} & (\upsilon+1) \pm \frac{\varepsilon}{2}\left\{\left[1 + \frac{3\eta}{2\varepsilon}(\upsilon+1)\right]^2\left[(\upsilon+1)^2 - K^2\right] \right. \\ & \left. + \frac{\varepsilon^2 K^2}{16}\left(\upsilon+1 - \frac{8\gamma}{\varepsilon^2}\right)^2\right\}^{1/2} \\ & - \frac{\varepsilon^2}{8}(\upsilon+1) + \frac{\gamma}{2}\left[3(\upsilon+1)^2 - K^2\right] \end{aligned} \tag{4.4.4}$$

For $K = 0$, (Σ-vibronic levels):

$$E_{\frac{1}{2}}(0;v)/\hbar\omega = (v+1)\left[1 \pm \frac{\varepsilon}{2} - \frac{\varepsilon^2}{8}\right] + \frac{3}{4}\left[2\gamma \pm \eta\right](v+1)^2 \tag{4.4.5}$$

We can compare our results with that obtained by Renner by putting $\eta = \gamma = 0$ into Equation (4.4.4). We have:

$$E_{\frac{1}{2}}(K;v)/\hbar\omega = (v+1) \pm \left\{(v+1)^2 - K^2 + \frac{\varepsilon^2}{16} K^2 (v+1)\right\}^{1/2} - \frac{\varepsilon^2}{8}(v+1)^2 \tag{4.4.4'}$$

We notice that this expression is different from that given by Renner(5). We have an additional term $\varepsilon^2 K^2 (v+1)^2/16$ in the square root. The difference is the consequence of the different perturbation methods used, and that the two diagonal matrix elements of the Van Vleck perturbation matrix (4.3.5) are in general not equal. We shall see in the next chapter that if we use a modified Van Vleck's method in the diagonalizing process of Hamiltonian matrices, we obtain results that the ordinary second-order perturbation theory (Schröedinger degenerate perturbation theory) will give.

(ii) λ=2, Δ-electronic level:

Assuming that $\eta/2 > \gamma$, we obtain (for $K \neq v+2$, $K \neq v$):

$$z_1 = \frac{\eta^2}{32}(v+1)\left[17\,v(v+1) - 3K(5K+12)\right](K-2) \quad \hbar\omega$$

$$z_2 = -\frac{\eta^2}{32}(v+1)\left[17\,v(v+1) - 3K(5K-12)\right](K+2) \quad \hbar\omega$$

or

$$\frac{1}{2}(z_1+z_2) = -\frac{\eta^2}{16}(\upsilon+1)\left[17\upsilon(\upsilon+2)+3K^2\right]\ \hbar\omega$$

$$\frac{1}{2}(z_1-z_2) = \frac{\eta^2}{32}(\upsilon+1)\left[17\upsilon(\upsilon+2)-15K^2+72\right]K\ \hbar\omega$$

(4.4.6)

Similar, but not identical expressions had been given by Merer and Travis(34). Our γ-parameter corresponds to their g_{22}. Both are constants which account for anharmonicity. But instead of $g_{22}\ell^2 = g_{22}(K\pm2)$, in our case, the correction term is

$$d_r = \frac{\gamma}{2}[3(\upsilon+1)^2 + 1 - \ell^2]$$

which are functions of υ as well as ℓ. This arises because we treat the anharmonic potential $U'(r)$ as a vibronic operator.†

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†The resemblance of the anharmonic and vibronic perturbations has been discussed by Liehr(24) and by T. Oka(29). That anharmonic perturbation is also a vibronic perturbation is implied in Longuet-Higgins and Pople's theory for NH_2(18).

Fig. 4.1 Interaction diagram for the vibronic level $[v]^K$ under the perturbation (4.4.1). The dashed lines (—·—·—) represent the interactions through the term U'(r); the broken lines (-----) represent the interactions through the term $\sigma(r)\Sigma_3$.

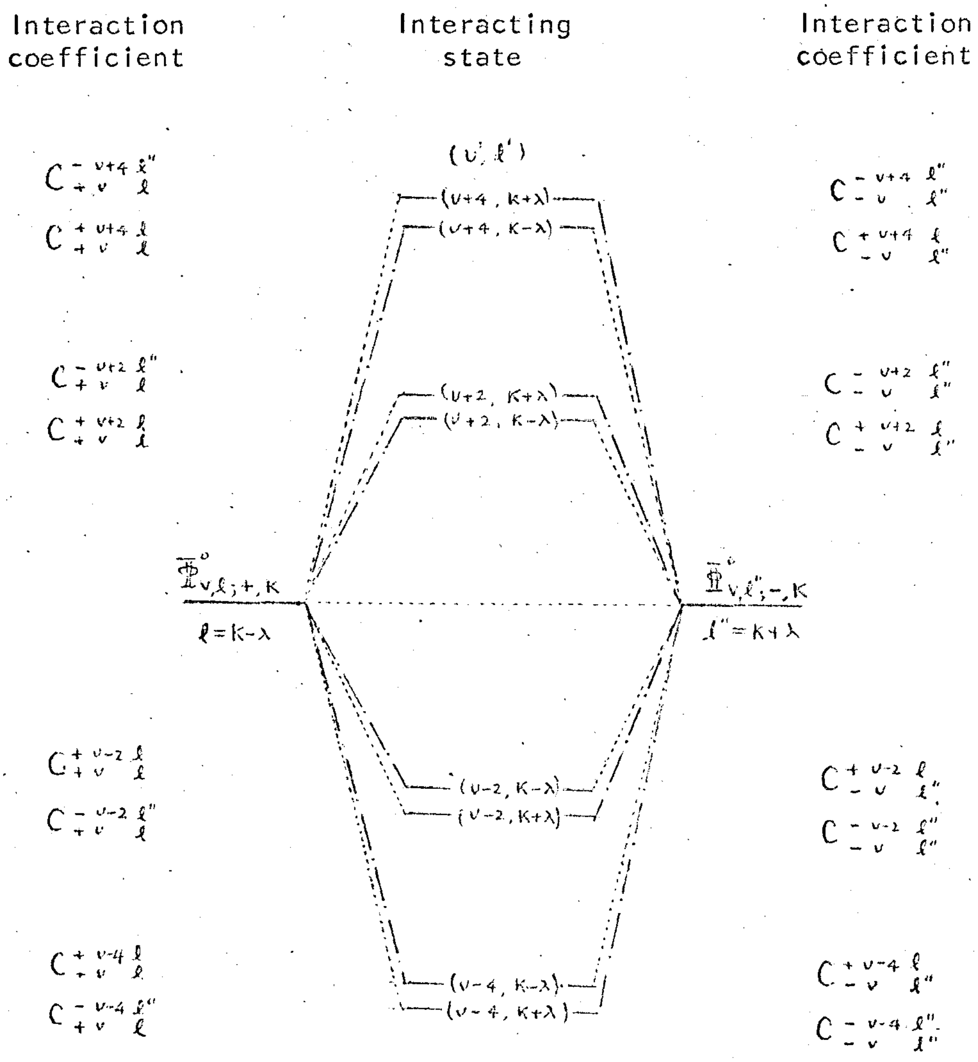


Table 4.2 Interaction coefficients and matrix elements for linear triatomic molecules in π-electronic level (λ = 1)

$$C^{\Lambda'V'\ell'}_{\Lambda\ V\ \ell} = -\frac{\langle \Phi^{o}_{\upsilon'\ell'\Lambda'\ K}|gr^4 + \frac{1}{2}(fr^2 + hr^4)\Sigma_3|\Phi^{o}_{\upsilon\ell\Lambda K}\rangle}{\mathcal{E}^{o}_{V'} - \mathcal{E}^{o}_{V}}$$

υ'	ℓ'	$C^{\Lambda'V'\ell'}_{\Lambda\ V,K-\Lambda}$	
		$C^{\Lambda'V'\ell'}_{\Lambda\ V\ K-\Lambda}$	$C^{\Lambda'V'\ell'}_{\Lambda\ V\ K-\Lambda}$
$\upsilon+4$,	K+1	$-\eta\ \frac{1}{32}(\upsilon-K+3)^{\frac{1}{2}}(\upsilon+K+1)^{\frac{1}{2}}(\upsilon+K+3)^{\frac{1}{2}}(\upsilon+K+5)^{\frac{1}{2}}$	$-\gamma\ \frac{1}{16}(\upsilon+K+3)^{\frac{1}{2}}(\upsilon-K+1)^{\frac{1}{2}}(\upsilon-K+3)^{\frac{1}{2}}(\upsilon+K+5)^{\frac{1}{2}}$
	K-1	$-\gamma\ \frac{1}{16}(\upsilon-K+3)^{\frac{1}{2}}(\upsilon+K+1)^{\frac{1}{2}}(\upsilon+K+3)^{\frac{1}{2}}(\upsilon-K+5)^{\frac{1}{2}}$	$-\eta\ \frac{1}{32}(\upsilon+K+3)^{\frac{1}{2}}(\upsilon-K+1)^{\frac{1}{2}}(\upsilon-K+3)^{\frac{1}{2}}(\upsilon-K+5)^{\frac{1}{2}}$
$\upsilon+2$,	K+1	$-\varepsilon\ \frac{1}{8}(\upsilon+K+1)^{\frac{1}{2}}(\upsilon+K+3)^{\frac{1}{2}}$ $-\eta\ \frac{1}{8}(\upsilon+K+1)^{\frac{1}{2}}(\upsilon+K+3)^{\frac{1}{2}}(2\upsilon-K+4)$	$-\gamma\ \frac{1}{2}(\upsilon-K+1)^{\frac{1}{2}}(\upsilon+K+3)^{\frac{1}{2}}(\upsilon+2)$
	K-1	$-\gamma\ \frac{1}{2}(\upsilon+K+1)^{\frac{1}{2}}(\upsilon-K+3)^{\frac{1}{2}}(\upsilon+2)$	$-\varepsilon\ \frac{1}{8}(\upsilon-K+1)^{\frac{1}{2}}(\upsilon-K+3)^{\frac{1}{2}}$ $-\eta\ \frac{1}{8}(\upsilon-K+1)^{\frac{1}{2}}(\upsilon-K+3)^{\frac{1}{2}}(2\upsilon+K+4)$
$\upsilon-2$,	K+1	$+\varepsilon\ \frac{1}{8}(\upsilon-K-1)^{\frac{1}{2}}(\upsilon-K+1)^{\frac{1}{2}}$ $+\eta\ \frac{1}{8}(\upsilon-K-1)^{\frac{1}{2}}(\upsilon-K+1)^{\frac{1}{2}}(2\upsilon+K)$	$\gamma\frac{1}{2}(\upsilon-K-1)^{\frac{1}{2}}(\upsilon+K+1)^{\frac{1}{2}}\upsilon$
	K-1	$\gamma\frac{1}{2}(\upsilon-K+1)^{\frac{1}{2}}(\upsilon+K-1)^{\frac{1}{2}}$	$\varepsilon\ \frac{1}{8}(\upsilon+K-1)^{\frac{1}{2}}(\upsilon+K+1)^{\frac{1}{2}}$ $+\eta\ \frac{1}{8}(\upsilon+K-1)^{\frac{1}{2}}(\upsilon+K+1)^{\frac{1}{2}}(2\upsilon-K)$
$\upsilon-4$,	K+1	$\eta\ \frac{1}{32}(\upsilon+K-1)^{\frac{1}{2}}(\upsilon-K+1)^{\frac{1}{2}}(\upsilon-K-1)^{\frac{1}{2}}(\upsilon-K-3)^{\frac{1}{2}}$	$\gamma\ \frac{1}{16}(\upsilon+K-1)^{\frac{1}{2}}(\upsilon+K+1)^{\frac{1}{2}}(\upsilon-K-1)^{\frac{1}{2}}(\upsilon-K-3)^{\frac{1}{2}}$
	K-1	$\gamma\ \frac{1}{16}(\upsilon+K-1)^{\frac{1}{2}}(\upsilon-K+1)^{\frac{1}{2}}(\upsilon-K-1)^{\frac{1}{2}}(\upsilon+K-3)^{\frac{1}{2}}$	$\eta\ \frac{1}{32}(\upsilon+K-1)^{\frac{1}{2}}(\upsilon+K+1)^{\frac{1}{2}}(\upsilon-K-1)^{\frac{1}{2}}(\upsilon+K-3)^{\frac{1}{2}}$

$$d_1 = (R_{V,K-1}|gr^4|R_{V,K-1}) = \gamma\hbar\omega\cdot\frac{1}{2}[3(\upsilon+1)^2 + 1 - (K-1)^2]$$

$$d_2 = (R_{v,K+1}|gr^4|R_{v,K+1}) = \gamma\hbar\omega\cdot\tfrac{1}{2}[3(v+1)^2 + 1 - (K+1)^2]$$

$$\begin{aligned} a_r &= (R_{v,K-1}|\tfrac{1}{2}fr^2 + \tfrac{1}{2}hr^4|R_{v,K+1}) \\ &= \tfrac{1}{2}[\varepsilon + \frac{3}{2}\,\eta(v+1)]\hbar\omega[(v+1)^2 - K^2]^{\frac{1}{2}} \end{aligned}$$

$$\tfrac{1}{2}(d_1 + d_2) = \gamma\hbar\omega\tfrac{1}{2}[3(v+1)^2 - K^2]$$

$$\tfrac{1}{2}(d_1 - d_2) = \gamma\hbar\omega\cdot K$$

$$y_r = -\frac{3}{2}\varepsilon\gamma\cdot\hbar\omega(v+1)[(v+1)^2 - K^2]^{\frac{1}{2}} - \frac{1}{8}\eta\gamma\hbar\omega[(v+1)^2 - K^2]^{\frac{1}{2}}\{34(v+1)^2 + 5(4-K^2)\}$$

Table 4.3 Interaction coefficients and matrix elements for linear triatomic molecules in Δ-electronic level ($\lambda = 2$)

$$C^{\Lambda' V' \ell'}_{\Lambda\ V\ \ell} = - \frac{\langle \Phi^{o}_{v'\ell'\Lambda' K} | gr^4 + \tfrac{1}{2}hr^4\Sigma_3 | \Phi^{o}_{v\ell\Lambda K}\rangle}{\mathcal{E}^{o}_{V'} - \mathcal{E}^{o}_{V}}$$

v'	ℓ'	$C^{\Lambda' V' \ell'}_{\Lambda\ V, K-\Lambda}$ ($\Lambda = \pm 2$)	
		$C^{\Lambda' V' \ell'}_{\Lambda\ V.\ K-\Lambda}$	$C^{\Lambda' V' \ell'}_{\Lambda\ V\ K-\Lambda}$
$v+4$,	K+2	$-\eta\ \frac{1}{32}(v+K)^{\frac{1}{2}}(v+K+2)^{\frac{1}{2}}(v+K+4)^{\frac{1}{2}}(v+K+6)^{\frac{1}{2}}$	$-\gamma\ \frac{1}{16}(v-K)^{\frac{1}{2}}(v-K+2)^{\frac{1}{2}}(v+K+4)^{\frac{1}{2}}(v+K+6)^{\frac{1}{2}}$
	K-2	$-\gamma\ \frac{1}{16}(v+K)^{\frac{1}{2}}(v+K+2)^{\frac{1}{2}}(v-K+4)^{\frac{1}{2}}(v-K+6)^{\frac{1}{2}}$	$-\eta\ \frac{1}{32}(v-K)^{\frac{1}{2}}(v-K+2)^{\frac{1}{2}}(v-K+4)^{\frac{1}{2}}(v-K+6)^{\frac{1}{2}}$
$v+2$,	K+2	$-\eta\ \frac{1}{4}(v+K)^{\frac{1}{2}}(v+K+2)^{\frac{1}{2}}(v-K+2)^{\frac{1}{2}}(v+K+4)^{\frac{1}{2}}$	$-\gamma\ \frac{1}{2}(v-K)^{\frac{1}{2}}(v+K+4)^{\frac{1}{2}}(v+2)$
	K-2	$-\gamma\ \frac{1}{2}(v+K)^{\frac{1}{2}}(v-K+4)^{\frac{1}{2}}(v+2)$	$-\eta\ \frac{1}{4}(v-K)^{\frac{1}{2}}(v-K+4)^{\frac{1}{2}}(v-K+2)^{\frac{1}{2}}(v+K+2)^{\frac{1}{2}}$
$v-2$,	K+2	$\eta\ \frac{1}{4}(v+K)^{\frac{1}{2}}(v-K)^{\frac{1}{2}}(v-K+2)^{\frac{1}{2}}(v-K-2)^{\frac{1}{2}}$	$\gamma\ \frac{1}{2}(v+K+2)^{\frac{1}{2}}(v-K-2)^{\frac{1}{2}}v$
	K-2	$\gamma\ \frac{1}{2}(v-K+2)^{\frac{1}{2}}(v+K-2)^{\frac{1}{2}}v$	$\eta\ \frac{1}{4}(v+K)^{\frac{1}{2}}(v+K+2)^{\frac{1}{2}}(v+K-2)^{\frac{1}{2}}(v-K)^{\frac{1}{2}}$

υ'	ℓ'	$C^{\Lambda'V'\ell'}_{\Lambda\ V,K-\Lambda}$	
		$C^{\Lambda'V'\ell'}_{\Lambda\ V,K-\Lambda}$	$C^{\Lambda'V'\ell'}_{\Lambda\ V,K-\Lambda}$
$\upsilon-4,$	$K+2$	$\eta\ \frac{1}{32}(\upsilon-K-4)^{\frac{1}{2}}(\upsilon-K)^{\frac{1}{2}}(\upsilon-K+2)^{\frac{1}{2}}(\upsilon-K-2)^{\frac{1}{2}}$	$\gamma\ \frac{1}{16}(\upsilon+K)^{\frac{1}{2}}(\upsilon+K+2)^{\frac{1}{2}}(\upsilon-K-2)^{\frac{1}{2}}(\upsilon-K-4)^{\frac{1}{2}}$
	$K-2$	$\gamma\ \frac{1}{16}(\upsilon+K-4)^{\frac{1}{2}}(\upsilon-K)^{\frac{1}{2}}(\upsilon-K+2)^{\frac{1}{2}}(\upsilon+K-2)^{\frac{1}{2}}$	$\eta\ \frac{1}{32}(\upsilon+K)^{\frac{1}{2}}(\upsilon+K+2)^{\frac{1}{2}}(\upsilon+K-2)^{\frac{1}{2}}(\upsilon+K-4)^{\frac{1}{2}}$

$$d_1 = (R_{v,K-2}|gr^4|R_{v,K-2}) = \gamma\hbar\omega\cdot\frac{1}{2}[3(\upsilon+1)^2 + 1 - (K-2)^2]$$

$$d_2 = (R_{v,K+2}|gr^4|R_{v,K+2}) = \gamma\hbar\omega\cdot\frac{1}{2}[3(\upsilon+1)^2 + 1 - (K+2)^2]$$

$$a_r = (R_{v,K-2}|\tfrac{1}{2}hr^4|R_{v,K+2}) = \eta\hbar\omega\cdot\frac{3}{4}(\upsilon+K)(\upsilon-K)(\upsilon+K+2)(\upsilon-K+2)$$

$$\tfrac{1}{2}(d_1 + d_2) = \gamma\hbar\omega\cdot\tfrac{1}{2}[3\upsilon(\upsilon+2) - K^2]$$

$$\tfrac{1}{2}(d_1 - d_2) = \gamma\hbar\omega\cdot 4K$$

CHAPTER 5

Renner Effect in Linear Tetratomic Molecules

5.1 Static Problem for Symmetrical Linear Tetratomic Molecules in the Π-Electronic Level

The representative vibronic perturbation for linear tetratomic molecules A-B-B-A has been obtained in Chapter 3. In a Π-electronic level, it is given by

$$H' = U'(Q) + H'_{\pi}(r_k, \theta-\phi_k) \tag{5.1.1}$$

where

$$U'(Q) = g_1 r_1^4 + g_2 r_2^4 + 2g_{12} r_1^2 r_2^2 [2 + \cos 2(\phi_1-\phi_2)] + O(r_k^6)$$

$$H'_{\pi}(r_k, \theta-\phi_k) = \sum_{k=1,2} 2\sigma_k(r_1, r_2) \cos 2(\theta-\phi_k) \tag{5.1.2}$$

with

$$2\sigma_1(r_1, r_2) = f_1 r_1^2 + h_{40} r_1^4 + 3h_{22} r_1^2 r_2^2 + O(r_k^6)$$

$$2\sigma_2(r_1, r_2) = f_2 r_2^2 + h_{04} r_2^4 + 3h_{22} r_1^2 r_2^2 + O(r_k^6)$$

The representative vibronic and electronic Hamiltonians are given by

$$H = H_e(\pi) + T_N \tag{5.1.3}$$

$$H_e(\pi) = H_e^o + H' = H_e^o + U^o(r_k) + U'(Q) + H'_{\pi} \tag{5.1.4}$$

respectively in which

$$T_N = -\sum_{k=1,2} \frac{\hbar^2}{2\mu_k} \left(\frac{\partial^2}{\partial r_k^2} + \frac{1}{r_k}\frac{\partial}{\partial r_k} + \frac{1}{r_k^2}\frac{\partial^2}{\partial \phi_k^2}\right) \tag{5.1.5}$$

and

$$U^o(r_k) = \tfrac{1}{2}\mu_1 \omega_1^2 r_1^2 + \tfrac{1}{2}\mu_2 \omega_2^2 r_2^2 \tag{5.1.6}$$

Thus the representation of the electronic Hamiltonian in the basis $\{\psi^{o}_{+\pi}(\vec{r}_i;0),\psi^{o}_{-\pi}(\vec{r}_i;0)\}$ is shown to be:

$$[H_e(\pi)] = \begin{array}{cc} \psi^{o}_{+\pi} & \psi^{o}_{-\pi} \\ \left[\begin{matrix} W^{o}_{\pi} + U^{o}(r_k) + U'(Q) & R(r_1,r_2;\phi_1-\phi_2)e^{-2i\chi} \\ R(r_1,r_2;\phi_1-\phi_2)e^{+2i\chi} & W^{o}_{\pi} + U^{o}(r_k) + U'(Q) \end{matrix}\right] & \end{array} \tag{5.1.7}$$

where R and χ are defined by:

$$R(r_1,r_2,\phi_1-\phi_2)e^{\pm 2i\chi} = \sum_{k=1,2} \sigma_k(r_1,r_2)e^{\pm 2i\phi_k} \tag{5.1.8}$$

$$\begin{aligned} \therefore \quad R(r_1,r_2,\phi_1-\phi_2) &= \sum_{k=1,2} \sigma_k(r_1,r_2)\cos 2(\chi-\phi_k) \\ 0 &= \sum_{k=1,2} \sigma_k(r_1,r_2)\sin 2(\chi-\phi_k) \end{aligned} \tag{5.1.9}$$

The Born-Oppenheimer potentials (electronic energies correct to first-order) are obtained by diagonalization of the matrix (5.1.7). They are

$$\begin{aligned} W_a &= W^{o}_{\pi} + U^{o}(r_k) + U'(Q) + R(r_1,r_2,\phi_1-\phi_2) \\ W_b &= W^{o}_{\pi} + U^{o}(r_k) + U'(Q) - R(r_1,r_2,\phi_1-\phi_2) \end{aligned} \tag{5.1.10}$$

The corresponding "correct zeroth-order" electronic wave functions are given by

$$\begin{aligned} \psi_a(\vec{r}_i;Q) &= \sqrt{2}\, u_{\pi}(z,\rho)\cos(\theta-\chi) \\ \psi_b(\vec{r}_i;Q) &= \sqrt{2}\, u_{\pi}(z,\rho)\sin(\theta-\chi) \end{aligned} \tag{5.1.11}$$

These electronic wave functions can be regarded as functions symmetrical and antisymmetrical to the "χ-plane" of the molecule. The "χ-plane" is, for molecules having more than 3 atoms, only a mathematical plane. Only if r_1 or $r_2 = 0$ (cf triatomic molecules: Equation (4.1.8)) can be a geometrical plane defined by the bending azimuthal angle ϕ_2 or

ϕ_1 respectively and the molecule will have a C_{2v} or C_{2h} symmetry (Fig. 5.1).

The plotting of W_a and W_b gives the electronic potential surfaces shown in Fig. 5.2. In the figures, we have neglected the r_k^4 terms. When these terms in the perturbation are considered, the Equation (5.1.10) may have minima at values of $r_k \neq 0$. If the molecule is trapped in one of the potential minima, the molecular symmetry will be effectively reduced from $D_{\infty h}$ to C_{2v} ($r_1 = 0$, $r_2 \neq 0$) or C_{2h} ($r_1 \neq 0$, $r_2 = 0$) or C_1 ($r_1 \neq 0$, $r_2 \neq 0$). However, there will be a finite probability of tunnelling from one potential well to another, and if this is taken into account one may still be able to classify the vibronic levels according to $D_{\infty h}$ space group$^{(19)}$.

5.2 Failure of Adiabatic Formulation for Dynamical Problem in Linear Tetratomic Molecules.

The vibronic Schröedinger wave equation is denoted by

$$\{H_e^o + U^o(r_k) + U'(Q) + H_\lambda' + T_N - E\}\Psi(\vec{r}_i,Q) = 0 \tag{5.2.1}$$

In the adiabatic formulation, the trial solution $\Psi(\vec{r}_i,Q)$ is expanded in terms of Equations (5.1.11), i.e.,

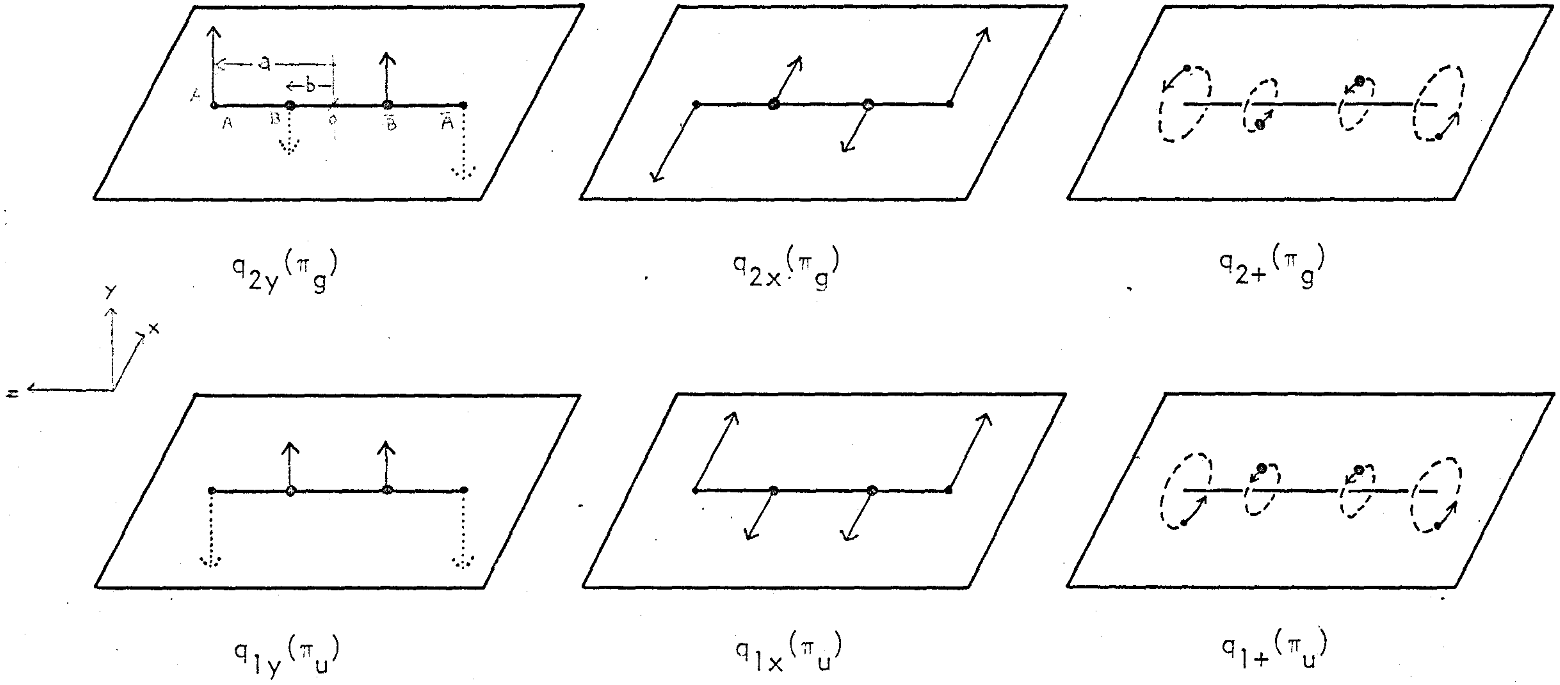
$$\Psi(\vec{r}_i,Q) = \psi_a(\vec{r}_i;Q)\Phi^a(Q) + \psi_b(\vec{r}_i;Q)\Phi^b(Q) \tag{5.2.2}$$

By Equation (5.1.11), we have

$$\frac{\partial\psi_a}{\partial r_k} = \psi_b \frac{\partial\chi}{\partial r_k}, \quad \frac{\partial\psi_b}{\partial r_k} = -\psi_a \frac{\partial\chi}{\partial r_k}$$

$$\frac{\partial\psi_a}{\partial\phi_k} = \psi_b \frac{\partial\chi}{\partial\phi_k}, \quad \frac{\partial\psi_b}{\partial\phi_k} = -\psi_a \frac{\partial\chi}{\partial\phi_k}$$

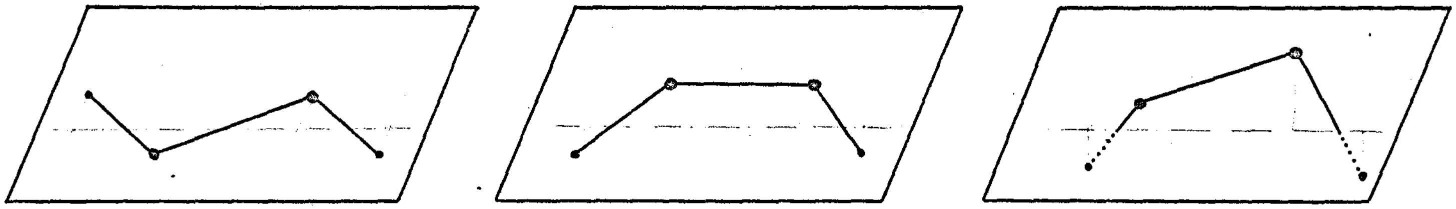
$$\frac{\partial^2\psi_a}{\partial {r_k}^2} = -\psi_a \left(\frac{\partial\chi}{\partial r_k}\right)^2 + \psi_b \frac{\partial^2\chi}{\partial {r_k}^2}$$



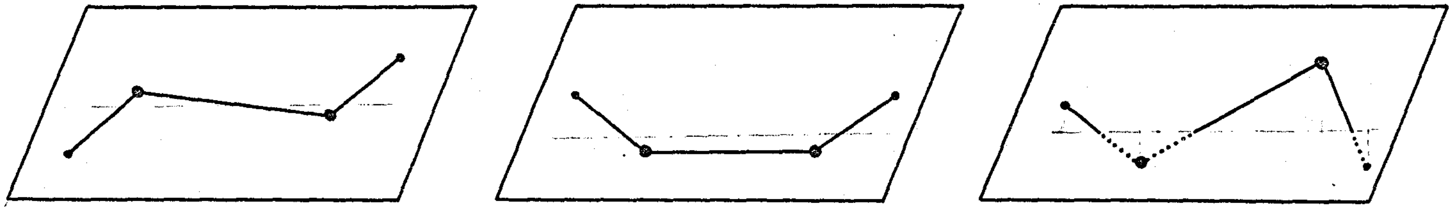
$q_{2y}(\pi_g)$ $q_{2x}(\pi_g)$ $q_{2+}(\pi_g)$

$q_{1y}(\pi_u)$ $q_{1x}(\pi_u)$ $q_{1+}(\pi_u)$

Fig. 5.1a The bending coordinates of linear "acetylene". The designations $q_{1+}(\pi_u)$ and $q_{2+}(\pi_g)$ represent the complex displacements $q_{1x} + iq_{1y}$ and $q_{2x} + iq_{2y}$ each.

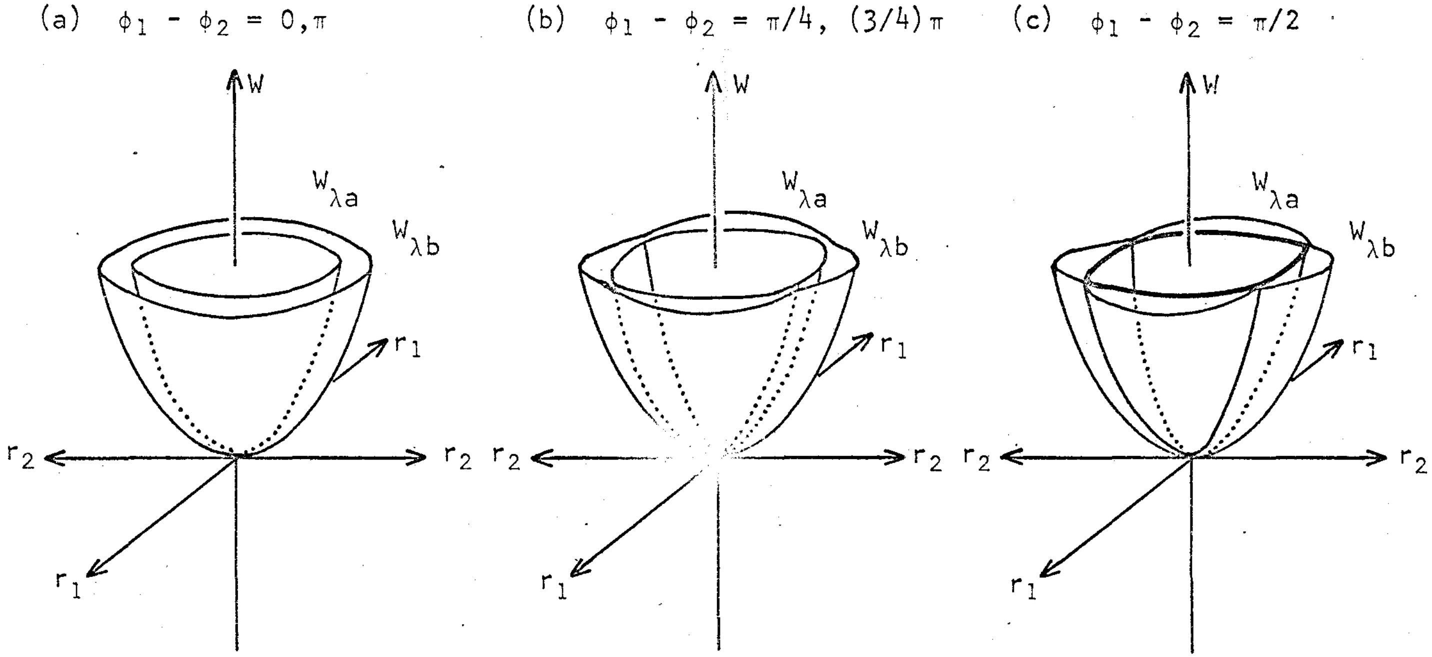


Case 1 $\phi_2 = 0$ Case 3 $\phi_1 = 0$ Case 5 $\phi_2 = 0, \phi_1 = \pi/2$



Case 2 $\phi_2 = \pi$ Case 4 $\phi_1 = \pi$ Case 5 $\phi_1 = 0, \phi_2 = \pi/2$

Fig. 5.1b Distorted geometries possible for a linear "acetylene" molecule in a degenerate electronic state.(24) Cases 1 and 2 apply to an extremum for which $\underline{q}_1$ equals to zero; cases 3 and 4 for $\underline{q}_2$ zero; and cases 5 and 6 to an extremum for which neither is zero. In all cases vibrational angular momentum has been partially (or completely) quenched and replaced by over-all rotational angular momentum of the distorted non-linear molecule.



(a) $\phi_1 - \phi_2 = 0, \pi$

(b) $\phi_1 - \phi_2 = \pi/4,\ (3/4)\pi$

(c) $\phi_1 - \phi_2 = \pi/2$

Fig. 5.2 The electronic potential energy surfaces of linear "acetylene" in Π-electronic level, assuming that

$$W_{\lambda\substack{a\\b}} = \tfrac{1}{2}\mu_1\omega_1^2 r_1^2 + \tfrac{1}{2}\mu_2\omega_2^2 r_2^2 \pm \left[(f_{20}r_1^2)^2 + (f_{02}r_2^2)^2 + 2f_{20}f_{02}r_1^2r_2^2\cos 2(\phi_1-\phi_2)\right]^{\frac{1}{2}}$$

$$\frac{\partial^2\psi_b}{\partial r_k{}^2} = -\psi_b\left(\frac{\partial\chi}{\partial r_k}\right)^2 - \psi_a \frac{\partial^2\chi}{\partial r_k{}^2}$$

$$\frac{\partial^2\psi a}{\partial\phi_k{}^2} = -\psi_a\left(\frac{\partial\chi}{\partial\phi_k}\right)^2 + \psi_b \frac{\partial^2\chi}{\partial\phi_k{}^2}$$

$$\frac{\partial^2\psi_b}{\partial\phi_k{}^2} = -\psi_b\left(\frac{\partial\chi}{\partial\phi_k}\right)^2 - \psi_a \frac{\partial^2\chi}{\partial\phi_k{}^2}$$

Putting Equation (5.2.2) into (5.2.1), we obtain

$$\begin{aligned}\{H_e(\lambda) - E\}\{\psi_a\cdot\Phi^a + \psi_b\cdot\Phi^b\} - \sum_{s=a,b}\ \sum_{k=1,2} \frac{\hbar^2}{2\mu_k}\{\psi_s \frac{\partial^2}{\partial r_k{}^2}\Phi^s + 2\,\frac{\partial\psi_s}{\partial r_k}\cdot\frac{\partial\Phi^s}{\partial r_k} \\ + \frac{\partial^2\psi_s}{\partial r_k{}^2}\cdot\Phi^s + \frac{1}{r_k}\left(\psi_s\cdot\frac{\partial}{\partial r_k}\Phi^s + \frac{\partial\psi_s}{\partial r_k}\cdot\Phi^s\right) \\ + \frac{1}{r_k{}^2}\left(\psi_s \frac{\partial^2\Phi^s}{\partial\phi_k{}^2} + 2\,\frac{\partial\psi_s}{\partial\phi_k}\cdot\frac{\partial\Phi^s}{\partial\phi_k} + \frac{\partial^2\psi_s}{\partial\phi_k{}^2}\cdot\Phi^s\right)\} \\ = 0 \qquad (5.2.4)\end{aligned}$$

Multiplying Equation (5.2.4) by $\psi_a{}^*$ from the left and then integrating over electronic space, noting that

$$\int_{Q\text{ fixed}} \psi_a{}^*(\vec{r}_i;Q)\,\psi_b(\vec{r}_i;Q)\,d\tau_i = \delta_{ab}$$

and that

$$\int_{Q\text{ fixed}} \psi_a{}^*(\vec{r}_i;Q)\,H_e(\vec{r}_i,Q)\,\psi_b(\vec{r}_i;Q)\,d\tau_i = W_a(Q)\cdot\delta_{ab}$$

together with Equation (5.2.3), we obtain

$$\Big[\sum_{k=1,2}\Big\{-\frac{\hbar^2}{2\mu_k}\left(\frac{\partial^2}{\partial r_k{}^2} + \frac{1}{r_k}\frac{\partial}{\partial r_k} + \frac{1}{r_k{}^2}\frac{\partial^2}{\partial\phi_k{}^2}\right)$$

$$+ \tfrac{1}{2}\mu_k\omega_k^2 r_k^2 + \frac{\hbar^2}{2\mu_k}\left[\left(\frac{\partial\chi}{\partial r_k}\right)^2 + \frac{1}{r_k^{\,2}}\left(\frac{\partial\chi}{\partial\phi_k}\right)^2\right]\}$$

$$+ U'(Q) + R(r_k,\chi-\phi_k) - (E - W_\pi^o)]\Phi^a(Q)$$

$$+ [\sum_{k=1,2} \frac{\hbar^2}{2\mu_k}\{\frac{\partial^2\chi}{\partial r_k^{\,2}} + \frac{1}{r_k}\frac{\partial\chi}{\partial r_k} + \frac{1}{r_k^{\,2}}\frac{\partial^2\chi}{\partial\phi_k^{\,2}}$$

$$+ 2\left(\frac{\partial\chi}{\partial r_k}\cdot\frac{\partial}{\partial r_k} + \frac{1}{r_k^{\,2}}\frac{\partial\chi}{\partial\phi_k}\cdot\frac{\partial}{\partial\phi_k}\right)\}]\Phi^b(Q) = 0 \qquad (5.2.5a)$$

Similarly, multiplying Equation (5.2.4) by ψ_b^*, followed by integrating over electronic space, we obtain

$$[\sum_{k=1,2}\{-\frac{\hbar^2}{2\mu_k}\left(\frac{\partial^2}{\partial r_k^{\,2}} + \frac{1}{r_k}\frac{\partial}{\partial r_k} + \frac{1}{r_k^{\,2}}\frac{\partial^2}{\partial\phi_k^{\,2}}\right)$$

$$+ \tfrac{1}{2}\mu_k\omega_k^2 r_k^2 + \frac{\hbar^2}{2\mu_k}\left[\left(\frac{\partial\chi}{\partial r_k}\right)^2 + \frac{1}{r_k^{\,2}}\left(\frac{\partial\chi}{\partial\phi_k^{\,2}}\right)^2\right]\}$$

$$+ U'(Q) - R(r_k,\chi-\phi_k) - (E - W_\pi^o)]\Phi^b(Q)$$

$$- [\sum_{k=1,2} \frac{\hbar^2}{2\mu_k}\{\frac{\partial^2\chi}{\partial r_k^{\,2}} + \frac{1}{r_k}\frac{\partial\chi}{\partial r_k} + \frac{1}{r_k^{\,2}}\frac{\partial^2\chi}{\partial\phi_k^{\,2}}$$

$$+ 2\left(\frac{\partial\chi}{\partial r_k}\cdot\frac{\partial}{\partial r_k} + \frac{1}{r_k^{\,2}}\frac{\partial\chi}{\partial\phi_k}\cdot\frac{\partial}{\partial\phi_k}\right)\}]\Phi^a(Q) = 0 \qquad (5.2.5b)$$

If we take the simplest $\sigma_k(r_1,r_2)$ functions to be

$$\begin{aligned}\sigma_1(r_1,r_2) &= \sigma_1(r_1) = \tfrac{1}{2}f_1r_1^2\\ \sigma_2(r_1,r_2) &= \sigma_2(r_2) = \tfrac{1}{2}f_2r_2^2\end{aligned} \qquad (5.2.6)$$

and assume that $U'(Q) = 0$

then by Equation (5.1.9), we can show that

$$R = \tfrac{1}{2}[(f_1 r_1^2)^2 + (f_2 r_2^2)^2 + 2f_1 r_1^2 f_2 r_2^2 \cos 2(\phi_1 - \phi_2)]^{\frac{1}{2}}$$

$$\tfrac{1}{2} r_k \frac{\partial R}{\partial r_k} = R \frac{\partial \chi}{\partial \phi_k} = \tfrac{1}{2} f_k r_k^2 \cos 2(\chi - \phi_k)$$

$$-\tfrac{1}{2} \frac{\partial R}{r_k \partial \phi_k} = R \frac{\partial \chi}{\partial r_k} = -\tfrac{1}{2} f_k r_k \sin 2(\chi - \phi_k)$$

$$R \frac{\partial^2 \chi}{\partial {\phi_k}^2} = f_k r_k^2 \sin 2(\chi - \phi_k) - 2 \frac{\partial R}{\partial \phi_k} \cdot \frac{\partial \chi}{\partial \phi_k}$$

$$R \frac{\partial^2 \chi}{\partial {r_k}^2} = -\tfrac{1}{2} f_k \sin 2(\chi - \phi_k) - 2 \frac{\partial R}{\partial r_k} \cdot \frac{\partial \chi}{\partial r_k}$$

and that

$$R\left(\frac{\partial^2 \chi}{\partial {r_k}^2} + \frac{1}{r_k}\frac{\partial \chi}{\partial r_k} + \frac{1}{{r_k}^2}\frac{\partial^2 \chi}{\partial {\phi_k}^2}\right) = -2\left(\frac{\partial R}{\partial r_k} \cdot \frac{\partial \chi}{\partial r_k} + \frac{\partial R}{\partial \phi_k} \cdot \frac{\partial \chi}{\partial \phi_k}\right) = 0 \qquad (5.2.7)$$

Hence Equation (5.2.5) becomes:

$$\Big\{\sum_{k=1,2}\Big[-\frac{\hbar^2}{2\mu_k}\left(\frac{\partial^2}{\partial {r_k}^2} + \frac{1}{r_k}\frac{\partial}{\partial r_k} + \frac{1}{{r_k}^2}\frac{\partial^2}{\partial {\phi_k}^2}\right)$$

$$+ \tfrac{1}{2}\mu_k \omega_k^2 r_k^2 + \frac{\hbar^2}{2\mu_k}\frac{\cdot {f_k}^2}{4R^2(r_k, \chi - \phi_k)} r_k^2 + R(r_k, \chi - \phi_k)R - E'\Big\}\Phi^a$$

$$+ \sum_{k=1,2} \frac{\hbar^2}{2\mu_k}\frac{f_k}{R(r_k, \chi - \phi_k)}\left[\cos 2(\chi - \phi_k)\frac{\partial}{\partial \phi_k} - r_k \sin 2(\chi - \phi_k)\frac{\partial}{\partial r_k}\right] \cdot \Phi^b$$

$$= 0 \qquad (5.2.8a)$$

$$\Big\{\sum_{k=1,2}\Big[-\frac{\hbar^2}{2\mu_k}\left(\frac{\partial^2}{\partial {r_k}^2} + \frac{1}{r_k}\frac{\partial}{\partial r_k} + \frac{1}{{r_k}^2}\frac{\partial^2}{\partial {\phi_k}^2}\right)$$

$$+ \tfrac{1}{2}\mu_k \omega_k^2 r_k^2 + \frac{\hbar^2}{2\mu_k}\frac{{f_k}^2}{4R^2(r_k, \chi - \phi_k)} \cdot r_k^2 - R(r_k, \chi - \phi_k) - E'\Big\}\Phi^b$$

$$- \sum_{k=1,2} \frac{\hbar^2}{2\mu_k} \frac{f_k}{R(r_k,\chi-\phi_k)} [\cos 2(\chi-\phi_k)\frac{\partial}{\partial\phi_k} - r_k \sin 2(\chi-\phi_k)\frac{\partial}{\partial r_k}]\cdot\Phi^a$$

$$= 0 \qquad (5.2.8b)$$

where $E' = E - W_\pi^o$.

The complexities of the Equation system (5.2.8) occur because the two degenerate vibrations which individually interact with the electronic motion couple with each other indirectly. No solution for this equation system is possible if both f_1 and f_2 are different from zero. When one of the f_k's is zero, the system reduces to Renner's case in which only one degenerate vibration is excited. Only then is the adiabatic formulation[†] applicable.

5.3 Harmonical Formulation for the Dynamical Problem

In the Harmonic Formulation, we expand $\Psi(\vec{r}_i,Q)$ by

$$\Psi(\vec{r}_i,Q) = \psi^o_{+\pi}(\vec{r}_i;0)\Phi^+(Q) + \psi^o_{-\pi}(\vec{r}_i;0)\cdot\Phi^-(Q) \qquad (5.3.1)$$

If we let $\Phi^\pm(Q)$ be linear combination of the vibrational product functions, i.e.,

$$\Phi^\pm(Q) = \sum_{\nu_1\ell_1\nu_2\ell_2} C^\pm_{\nu_1\ell_1\nu_2\ell_2} \Phi_{\nu_1\ell_1}(r_1,\phi_1)\cdot\Phi_{\nu_2\ell_2}(r_i,\phi_2) \qquad (5.3.2)$$

where $\Phi_{\nu_k\ell_k}(r_k,\phi_k)$ are harmonic oscillator functions, then Equation (5.3.1) becomes

$$\Psi(\vec{r}_i,Q) = \sum_{\Lambda=+,-} \sum_{\nu_1\ell_1\nu_2\ell_2} |\Lambda;\nu_1,\ell_1;\nu_2\ell_2\rangle C^\Lambda_{\nu_1\ell_1,\nu_2\ell_2} \qquad (5.3.3)$$

where vibronic state $|\Lambda;\nu_1\ell_1;\nu_2\ell_2\rangle$ represents the zeroth-order vibronic wave function:

$$\langle\vec{r}_i,Q|\Lambda;\nu_1\ell_1;\nu_2\ell_2\rangle = \psi^o_\Lambda(\vec{r}_i;0)\cdot\Phi_{\nu_1\ell_1}(r_1,\phi_1)\cdot\Phi_{\nu_2\ell_2}(r_2,\phi_2)$$

[†] Discussions on the application of Adiabatic and Harmonic formulations have been given by Liehr$^{(24,27)}$ who used the terms "extremal development" and "cuspidal expansion" instead.

and that

$$(H_e^o + T_N + U^o(r_k))\,|\Lambda;\upsilon_1\ell_1;\upsilon_2\ell_2> = \mathcal{E}^o_{\upsilon_1,\upsilon_2}|\Lambda;\upsilon_1\ell_1;\upsilon_2\ell_2>$$

with

$$\mathcal{E}^o_{\upsilon_1,\upsilon_2} = (\upsilon_1+1)\hbar\omega_1 + (\upsilon_2+1)\hbar\omega_2 \tag{5.3.4}$$

Since the perturbation is

$$H' = U'(Q) + H'_\pi(r_k,\theta-\phi_k)$$

the state $|\Lambda';\upsilon_1'\ell_1';\upsilon_2'\ell_2'>$ will give nonvanishing interaction with the state $|\Lambda;\upsilon_1\ell_1;\upsilon_2\ell_2>$ only if

$$P^{\Lambda'\upsilon_1'\ell_1'\upsilon_2'\ell_2'}_{\Lambda\ \upsilon_1\ell_1\upsilon_2\ell_2} \equiv <\Lambda';\upsilon_1'\ell_1';\upsilon_2'\ell_2'|U'(Q) + H'_\pi(r_k,\theta-\phi_k)|\Lambda;\upsilon_1\ell_1\upsilon_2\ell_2> \neq 0$$

We find that

$$P^{\Lambda'\upsilon_1'\ell_1'\upsilon_2'\ell_2'}_{\Lambda\ \upsilon\ \ell_1\upsilon_2\ell_2} = \begin{cases} (\upsilon_1'\ell_1';\upsilon_2'\ell_2'|U'(Q)|\upsilon_1\ell_1;\upsilon_2\ell_2), & \text{if } \Lambda'=\Lambda,\ \ell_1'+\ell_2' = \ell_1+\ell_2 \\ (\upsilon_1'\ell_1';\upsilon_2'\ell_2'|\sigma_1(r_1,r_2)|\upsilon_1\ell_1;\upsilon_2\ell_2), & \text{if } \Lambda'=-\Lambda, \ell_1'=\ell_1+2\Lambda, \ell_2'=\ell_2 \\ (\upsilon_1'\ell_1;\upsilon_2'\ell_2'|\sigma_2(r_1,r_2)|\upsilon_1\ell_1;\upsilon_2\ell_2), & \text{if } \Lambda'=-\Lambda, \ell_2'=\ell_2+2\Lambda, \ell_1'=\ell_1 \\ 0 & \text{otherwise} \end{cases} \tag{5.3.5}$$

Thus for nonvanishing matrix elements $P^{\Lambda'\upsilon_1'\ell_1'\upsilon_2'\ell_2'}_{\Lambda\ \upsilon_1\ell_1\upsilon_2\ell_2}$, we must have

$$\Lambda' + \ell_1' + \ell_2' = \Lambda + \ell_1 + \ell_2 = \kappa \tag{5.3.6}$$

and thus states with different "vibronic angular momentum quantum number" κ will never mix. As seen from Equation (5.1.1) and (5.1.2), $U'(Q)$ and $\sigma_k(r_1,r_2)$ are even functions of r_k, hence

$$|\upsilon_k' - \upsilon_k| = \text{even integer}$$

Therefore the vibronic wave functions can be classified by a quantum number κ and the even and odd characters of the vibrational quantum numbers v_1 and v_2. This is done in Fig. 5.3. In Fig. 5.3 only states in the same column can interact with each other. If κ is even, then either v_1 or v_2 must be even. If κ is odd, then v_1 and v_2 must be both odd or both even.

For <u>strong</u> vibronic interaction, the coefficients $C^{\Lambda}_{v_1\ell_1;v_2\ell_2}$ and the vibronic energies are determined by diagonalization of a very large matrix for each κ:

$$\left| P^{\Lambda' v_1'\ell_1' v_2'\ell_2'}_{\Lambda\ v_1\ell_1 v_2\ell_2} - E\delta_{\Lambda'\Lambda}\cdot\delta_{v_1'v_1}\,\delta_{\ell_1'\ell_1}\,\delta_{v_2'v_2}\cdot\delta_{\ell_2'\ell_2} \right| = 0 \qquad (5.3.7)$$

If we know the values for f_k's, g's, h's as well as the force constants $(\mu_k\omega_k^2)$, then the secular Equation (5.3.7) may be solved by use of an electronic computer. Since this is in general not the case, we shall assume that the coupling between states are <u>weak</u>, and ask only for the vibronic energies correct to second-order, i.e., within the level of the same v_1, v_2, and κ.

5.4 Interaction Diagrams

We shall use the Van Vleck degenerate perturbation method to obtain the energies correct to second-order of approximation and we introduce <u>interaction diagrams</u> as an aid in following the results of this method.

We have two types of interaction diagrams: the <u>first-order</u> and the <u>second-order</u>.

In the first-order interaction diagram (Fig. 5.4), we consider the interactions between all states with the same κ, v_1 and v_2 values. The number of these states is designated by $n_\kappa(v_1,v_2)$. It can be verified by

Figure 5.3. Classification and energy scheme of vibronic kets $|\Lambda;\nu_1,\ell_1\nu_2\ell_2>$ in π-electronic level with $K = \Lambda+\ell_1+\ell_2 \geq 0$. (Negative K states are obtained by changing all the signs of Λ, ℓ_1 and ℓ_2). We designate $|\Lambda;\nu_1\ell_1\nu_2\ell_2>$ by $[\nu_1,\nu_2](\Lambda,\ell_1,\ell_2)$. $\bar{\Lambda} = -\Lambda$.

$[v_1, v_2]$	v_1 = odd v_2 = even (oe)	v_1 = even v_2 = odd (eo)	v_1 = odd v_2 = odd (oo)	v_1 = even v_2 = even (ee)	v_1 = odd v_2 = even (oe)	v_1 = even v_2 = odd (eo)	v_1 = odd v_2 = odd (oo)	v_1 = even v_2 = even (ee)	v_1 = odd v_2 = even (oe)	v_1 = even v_2 = odd (eo)
[0,3]		(-01) $(+0\bar{1})$				(-03) $(+01)$				$(+03)$
[1,2]	$(-\bar{1}2)$ $(+1\bar{2})$ (-10) $(+\bar{1}0)$				$(+10)$ (-12) $(+\bar{1}2)$				$(+12)$	
[2,1]		$(-2\bar{1})$ $(+\bar{2}1)$ (-01) $(+0\bar{1})$				$(+01)$ (-21) $(+2\bar{1})$				$(+21)$
[3,0]	(-10), $(+\bar{1}0)$				$(+10)$ (-30)				$(+30)$	
[0,2]				(-02) $(+0,0)$				$(+02)$		
[1,1]			$(+1,\bar{1})$ $(-1,1)$ $(+\bar{1},1)$				$(+11)$			
[2,0]				$(-2,0)$ $(+0,0)$				$(+20)$		
[0,1]		(-01) $(+0\bar{1})$				$(+01)$				
[1,0]	(-10), $(+\bar{1}0)$				$(+10)$					
[0,0]										
	K = 0		K = 1		K = 2		K = 3		K = 4	

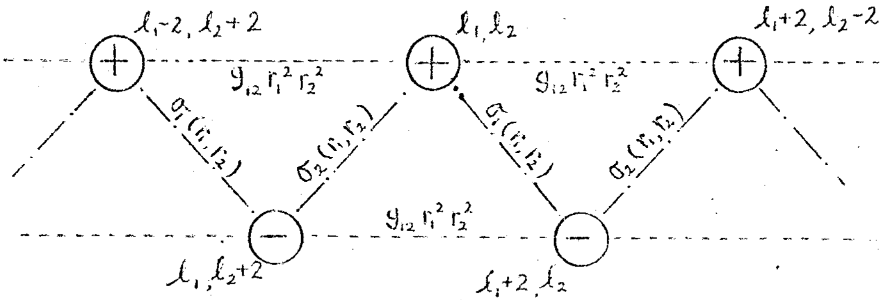
Fig. 5.3 that

$$n_\kappa(\upsilon_1,\upsilon_2) = \begin{cases} \upsilon_1 + \upsilon_2 + 2 - \kappa\ , & \text{if } |\upsilon_2-\upsilon_1| < \kappa \quad (\kappa > 0) \\ 2(\tilde{\upsilon} + 1)\ , & \text{if } 0 < \kappa < |\upsilon_2-\upsilon_1|\ , \end{cases}$$

$$\tilde{\upsilon} \text{ is the smaller of } \upsilon_1 \text{ and } \upsilon_2. \tag{5.4.1}$$

These $n_\kappa(\upsilon_1,\upsilon_2)$ states consist of a degenerate <u>vibronic level</u> $[\upsilon_1,\upsilon_2]^\kappa$ which will be split in first-order by the perturbation H'.

Fig. 5.4 First-order interaction diagrams within the vibronic level $[\upsilon_1,\upsilon_2]^K$. The perturbation H' is given by Equation (5.1.1).



In Figure 5.4, the $\textcircled{\Lambda}^{(r)}\ \ell_1^{(r)}\ell_2^{(r)}$ stands for the r^th^ state of zeroth-order set.

$$\phi_r^o(\kappa;\upsilon_1,\upsilon_2) = |\Lambda^{(r)};\upsilon_1,\ell_1^{(r)};\upsilon_2,\ell_2^{(r)}> \tag{5.4.2}$$

The dashed lines refer to the interactions through the perturbation function H'; the broken lines refer to the interactions through U'(Q). The vibrational terms, e.g., $\sigma_k(r_1,r_2)$ written between the states $\textcircled{\Lambda}^{\ell_1,\ell_2}$ and $\textcircled{\Lambda'}^{\ell_1',\ell_2'}$ will give the matrix element:

$$<v_1\ell_1;v_2\ell_2|\sigma_k(r_1,r_2)|v_1\ell_1';v_2\ell_2'>$$

which is different from zero.

In the "second-order interaction diagrams", we show what states will interact with a given state in presence of specific perturbations. For the symmetrical linear tetratomic molecules in π-electronic level, the second-order interaction diagrams for the state $|\Lambda v_1\ell_1 v_2\ell_2>$ under the perturbation H' of Equation (5.1.1) are shown in Fig. 5.5A and B.

The interaction coefficients are defined by:

$$C^{\Lambda' v_1'\ell_1' v_2'\ell_2'}_{\Lambda\ v_1\ell_1 v_2\ell_2} \equiv - \frac{<\Lambda' v_1'\ell_1' v_2'\ell_2'|H'|\Lambda v_1\ell_1 v_2\ell_2>}{\mathcal{E}^{o}_{v_1'v_2'} - \mathcal{E}^{o}_{v_1 v_1}} \qquad (5.4.3)$$

which can be expressed in terms of the "vibrational radial integrals":

$$\begin{aligned} A(v_k+a,\ell_k+b) &\equiv (v_k+a,\ell_k+b|r^2|v_k,\ell_k) \\ B(v_k+a,\ell_k+b) &\equiv (v_k+a,\ell_k+b|r^4|v_k,\ell_k) \end{aligned} \qquad (5.4.4)$$

Evaluation of these integrals are listed in Appendix D.

Since the r^{th} Van Vleck-basis function in the level $[v_1,v_2]^{\kappa}$ is given by:

$$\begin{aligned} \psi_r^c(\kappa;v_1,v_2) &= \{\kappa(\Lambda^{(r)},\ell_1^{(r)},\ell_2^{(r)});v_1 v_2\} = \phi_r^c(\kappa;v_1v_2)+\phi_r^{(1)}(\kappa;v_1v_2)+\phi_r^{(2)}(\kappa;v_1v_2) \\ &= |\Lambda^{(r)};v_1\ell_1^{(r)};v_2\ell_2^{(r)}> + \sum_{\substack{v_1',v_2' \\ \ell_1'+\ell_2'=\kappa-\Lambda'}}' |\Lambda';v_1'\ell_1';v_2'\ell_2'> C^{\Lambda' v_1'\ell_1' v_2'\ell_2'}_{\Lambda^{(r)} v_1\ell_1^{(r)} v_2\ell_2^{(r)}} + \phi_r^{(2)} \end{aligned}$$

with

$$\phi_r^{(1)}(\kappa;v_1,v_2) = \sum_{\substack{v_1',v_2' \\ \ell_1'+\ell_2'=\kappa-\Lambda'}}' |\Lambda';v_1'\ell_1';v_2'\ell_2'> \cdot C^{\Lambda' v_1'\ell_1' v_2'\ell_2'}_{\Lambda^{(r)} v_1\ell_1^{(r)} v_2\ell_2^{(r)}} \qquad (5.4.5)$$

Therefore, the first-order correction $(\phi_r^{(1)})$ to the basis function (ψ_r^o) is a sum of the products of the two columns given in Fig. 5.5, i.e.,

$$\phi_r^{(1)}(\kappa;v_1v_2) = \Sigma|\text{interacting states}\rangle\cdot\text{interaction coefficients}$$

Fig. 5.5A The second-order interaction diagram for the perturbation

$$U'(Q) = g_1 r_1^4 + g_2 r_2^4 + 2g_{12} r_1^2 r_2^2 [2 + \cos 2(\phi_1 - \phi_2)].$$

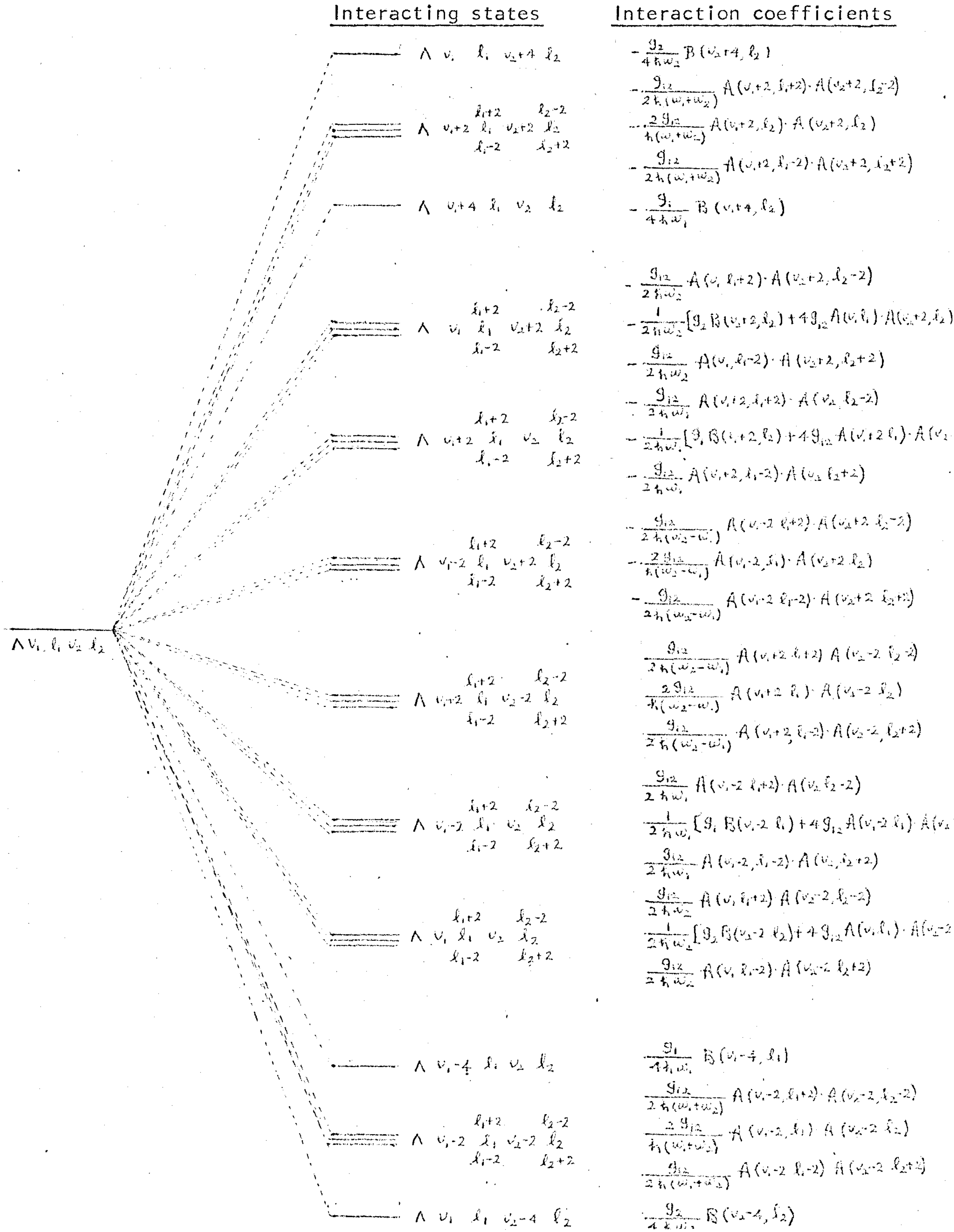
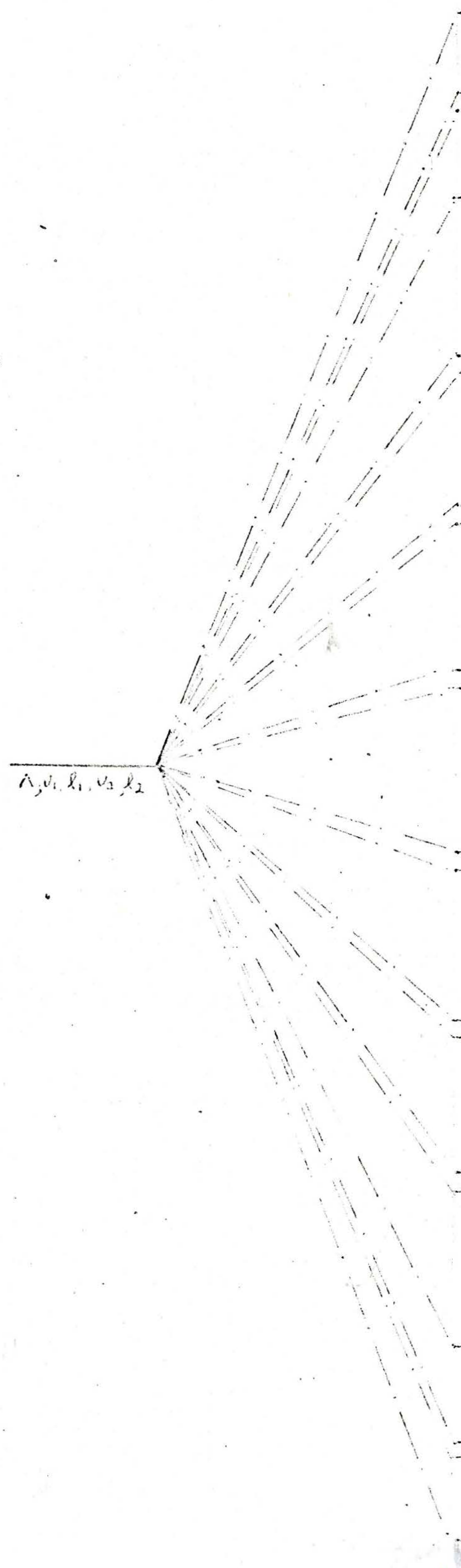


Fig. 5.5B The second-order interaction diagram for the perturbation

$$H'_{\pi} = (f_1 r_1^2 + h_1 r_1^4 + 3h_{12} r_1^2 r_2^2)\cos 2(\theta-\phi_1)$$
$$+ (f_2 r_2^2 + h_2 r_2^4 + 3h_{12} r_1^2 r_2^2)\cos 2(\theta-\phi_2).$$



Interacting states	Interaction coefficients
$\overline{\Lambda}\ v_1\ l_1\ v_2+4\ l_2+2\Lambda$	$-\frac{h_2}{8\hbar\omega_2} B(v_2+4, l_2+2\Lambda)$
$\overline{\Lambda}\ v_1+2\ \begin{smallmatrix} l_1+2\Lambda \\ l_1 \end{smallmatrix}\ v_2+2\ \begin{smallmatrix} l_2 \\ l_2+2\Lambda \end{smallmatrix}$	$-\frac{3h_{12}}{4\hbar(\omega_1+\omega_2)} A(v_1+2, l_1+2\Lambda)\cdot A(v_2+2, l_2)$ $-\frac{3h_{12}}{4\hbar(\omega_1+\omega_2)} A(v_1+2, l_1)\cdot A(v_2+2, l_2+2\Lambda)$
$\overline{\Lambda}\ v_1+4\ l_1+2\Lambda\ v_2\ l_2$	$-\frac{h_1}{8\hbar\omega_1} B(v_1+4, l_1+2\Lambda)$
$\overline{\Lambda}\ v_1\ \begin{smallmatrix} l_1+2\Lambda \\ l_1 \end{smallmatrix}\ v_2+2\ \begin{smallmatrix} l_2 \\ l_2+2\Lambda \end{smallmatrix}$	$-\frac{3h_{12}}{4\hbar\omega_2} A(v_1, l_1+2\Lambda)\cdot A(v_2+2, l_2)$ $-\frac{1}{4\hbar\omega_2}\left[f_2 A(v_2+2, l_2+2\Lambda) + h_2 B(v_2+2, l_2+2\Lambda) + 3h_{12} A(v_1, l_1)\cdot A(v_2+2, l_2+2\Lambda)\right]$
$\overline{\Lambda}\ v_1+2\ \begin{smallmatrix} l_1+2\Lambda \\ l_1 \end{smallmatrix}\ v_2\ \begin{smallmatrix} l_2 \\ l_2+2\Lambda \end{smallmatrix}$	$-\frac{1}{4\hbar\omega_1}\left[f_1 A(v_1+2, l_1+2\Lambda) + h_1 B(v_1+2, l_1+2\Lambda) + 3h_{12} A(v_1+2, l_1+2\Lambda)\ A(v_2, l_2)\right]$ $-\frac{3h_{12}}{4\hbar\omega_1} A(v_1+2, l_1)\cdot A(v_2, l_2+2\Lambda)$
$\overline{\Lambda}\ v_1-2\ \begin{smallmatrix} l_1+2\Lambda \\ l_1 \end{smallmatrix}\ v_2+2\ \begin{smallmatrix} l_2 \\ l_2+2\Lambda \end{smallmatrix}$	$-\frac{3h_{12}}{4\hbar(\omega_2-\omega_1)} A(v_1-2, l_1+2\Lambda)\cdot A(v_2+2, l_2)$ $-\frac{3h_{12}}{4\hbar(\omega_2-\omega_1)} A(v_1-2, l_1)\cdot A(v_2+2, l_2+2\Lambda)$
$\overline{\Lambda}\ v_1+2\ \begin{smallmatrix} l_1+2\Lambda \\ l_1 \end{smallmatrix}\ v_2-2\ \begin{smallmatrix} l_2 \\ l_2+2\Lambda \end{smallmatrix}$	$\frac{3h_{12}}{4\hbar(\omega_2-\omega_1)} A(v_1+2, l_1+2\Lambda)\cdot A(v_2-2, l_2)$ $\frac{3h_{12}}{4\hbar(\omega_2-\omega_1)} A(v_1+2, l_1)\cdot A(v_2-2, l_2)$
$\overline{\Lambda}\ v_1-2\ \begin{smallmatrix} l_1+2\Lambda \\ l_1 \end{smallmatrix}\ v_2\ \begin{smallmatrix} l_2 \\ l_2+2\Lambda \end{smallmatrix}$	$\frac{1}{4\hbar\omega_1}\left[f_1 A(v_1-2, l_1+2\Lambda) + h_1 B(v_1-2, l_1+2\Lambda) + 3h_{12} A(v_1-2\ l_1+2\Lambda)\cdot A(v_2\ l_2)\right]$ $\frac{3h_{12}}{4\hbar\omega_1} A(v_1-2\ l_1)\cdot A(v_2\ l_2+2\Lambda)$
$\overline{\Lambda}\ v_1\ \begin{smallmatrix} l_1+2\Lambda \\ l_1 \end{smallmatrix}\ v_2-2\ \begin{smallmatrix} l_2 \\ l_2+2\Lambda \end{smallmatrix}$	$\frac{3h_{12}}{4\hbar\omega_2} A(v_1\ l_1+2\Lambda)\cdot A(v_2-2\ l_2)$ $\frac{1}{4\hbar\omega_2}\left[f_2 A(v_2-2\ l_2+2\Lambda) + h_2 B(v_2-2, l_2+2\Lambda) + 3h_{12} A(v_1 l_1)\ A(v_2-2, l_2+2\Lambda)\right]$
$\overline{\Lambda}\ v_1-4\ l_1+2\Lambda\ v_2\ l_2$	$\frac{h_1}{8\hbar\omega_1} B(v_1-4, l_1+2\Lambda)$
$\overline{\Lambda}\ v_1-2\ \begin{smallmatrix} l_1+2\Lambda \\ l_1 \end{smallmatrix}\ v_2-2\ \begin{smallmatrix} l_2 \\ l_2+2\Lambda \end{smallmatrix}$	$\frac{3h_{12}}{4\hbar(\omega_1+\omega_2)} A(v_1-2, l_1+2\Lambda)\ A(v_2-2\ l_2)$ $\frac{3h_{12}}{4\hbar(\omega_1+\omega_2)} A(v_1-2\ l_1)\ A(v_2-2\ l_2+2\Lambda)$
$\overline{\Lambda}\ v_1\ l_1\ v_2-4\ l_2+2\Lambda$	$\frac{h_2}{8\hbar\omega_2} B(v_2-4, l_2+2\Lambda)$

5.5 A Modified Form of Van Vleck's Degenerate Perturbation Method

We partition the perturbation H' into two parts:

$$H' = H^{(2)} + H^{(4)} \tag{5.5.1}$$

The first part is second-order in vibrational radial coordinates:

$$H^{(2)} = f_1 r_1^2 \cos 2(\theta-\phi_1) + f_2 r_2^2 \cos 2(\theta-\phi_2) \tag{5.5.2}$$

The second part is fourth-order in vibrational radial coordinates:

$$\begin{aligned} H^{(4)} &= U'(Q) + (H'_\pi - H^{(2)}) \\ &= g_1 r_1^4 + g_2 r_2^4 + 2g_{12} r_1^2 r_2^2 (2 + \cos 2(\phi_1-\phi_2) \\ &\quad + (h_1 r_1^4 + 3h_{12} r_1^2 r_2^2) \cos 2(\theta-\phi_1) \\ &\quad + (h_2 r_2^4 + 3h_{12} r_1^2 r_2^2) \cos 2(\theta-\phi_2) \end{aligned} \tag{5.5.3}$$

where we have changed the parameters g_{1111}, g_{2222}, g_{1122}, h_{40}, h_{22} and h_{04} into g_1, g_2, g_{12}, h_1, h_{12} and h_2 respectively.

To a good approximation, one would be satisfied with the first- and second-order energy contributions from $H^{(2)}$ and the first-order energy contribution from $H^{(4)}$. To achieve this and to avoid the difficulties in diagonalization of the Van Vleck degenerate perturbation matrices (see below, (B)), we shall modify Van Vleck's method as follows:

(A) Consider the system H^o to be perturbed only by $H^{(2)}$. The Van Vleck degenerate perturbation method gives the basis functions in the level $[v_1,v_2]^K$ as:

$$\psi_r^0(K;v_1,v_2) = \{K(\Lambda^{(r)},\ell_1^{(r)},\ell_2^{(r)}),v_1,v_2\} = \phi_r^0(K;v_1,v_2) + \phi_r^{(1)}(K;v_1,v_2) + \phi_r^{(2)} \tag{5.5.4}$$

where $\phi_r^0(K;v_1,v_2) = |\Lambda^{(r)}; v_1, \ell_1^{(r)}; v_2, \ell_2^{(r)}\rangle$

$$\phi_r^{(1)}(K;v_1,v_2) = \sum_{\substack{(v_1',v_2') \\ \ell_1'+\ell_2' \cdot K+\Lambda^{(r)}}}{}' \, |\overline{\Lambda^{(r)}}; v_1' \ell_1' \; v_2' \ell_2'\rangle \cdot C^{\overline{\Lambda^{(r)}}\; v_1' \ell_1' \; v_2' \ell_2'}_{\Lambda^{(r)}\; v_1 \ell_1^{(r)} \; v_2 \ell_2^{(r)}} \tag{5.5.5}$$

with $$C^{\Lambda^{(r)} v_1' \ell_1' v_2' \ell_2'}_{\Lambda^{(r)} v_1 \ell_1^{(r)} v_2 \ell_2^{(r)}} = -\frac{\langle \overline{\Lambda^{(r)}}; v_1' \ell_1' v_2' \ell_2' \,|\, H^{(2)} \,|\, \Lambda^{(r)}; v_1, \ell_1^{(r)}; v_2\, \ell_2^{(r)} \rangle}{\mathcal{E}^{o}_{v_1', v_2'} - \mathcal{E}^{o}_{v_1, v_2}} \tag{5.5.6}$$

The $\phi_r^{(2)}(\kappa; v_1, v_2)$ is added for orthonormality of ψ_r^o (Appendix D).

Equations (5.5.2) and (5.5.4) to (5.5.6) give (dropping off $\phi_r^{(2)}$)

$$\begin{aligned}\psi_r^o(K; v_1, v_2) = {} & |\Lambda^{(r)}; v_1, \ell_1^{(r)}; v_2, \ell_2^{(r)}\rangle \\ & + \sum_{\substack{k=1,\\(k'\neq k)}}^{2} -\frac{\varepsilon_k}{8}\Big[(v_k + \Lambda^{(r)}\ell_k^{(r)} + 2)^{1/2}(v_k + \Lambda^{(r)}\ell_k^{(r)} + 4)^{1/2}\,|\overline{\Lambda^{(r)}}; v_k + 2, \ell_k^{(r)} + 2\Lambda^{(r)}; v_{k'}, \ell_{k'}^{(r)}\rangle \\ & \quad - (v_k - \Lambda^{(r)}\ell_k^{(r)} - 2)^{1/2}(v_k - \Lambda^{(r)}\ell_k^{(r)})^{1/2}\,|\overline{\Lambda^{(r)}}; v_k - 2, \ell_k^{(r)} + 2\Lambda^{(r)}; v_{k'}, \ell_{k'}^{(r)}\rangle\Big]\end{aligned}$$

where $$\varepsilon_k = \frac{f_k}{\mu_k \omega_k^2} = \frac{f_k a_k}{\hbar \omega_k} \tag{5.5.4'}$$

The representation of $H^o + H^{(2)}$ in the basis (5.5.4') will have the following form:

$$[H^o + H^{(2)}] = \mathcal{E}^o_{v_1 v_2} + \begin{array}{c} \begin{array}{ccccccccc} \psi_1^o & \psi_2^o & \psi_3^o & \cdots & \psi_r^o & \psi_{r+1}^o & \cdots & \psi_{n-1}^o & \psi_n^o \end{array} \\ \left[\begin{array}{ccccccccc} z_1 & a_1 & 0 & \cdots & 0 & 0 & \cdots & 0 & 0 \\ a_1 & z_2 & a_2 & \cdots & 0 & 0 & \cdots & 0 & 0 \\ & a_2 & z_3 & \cdots & 0 & 0 & \cdots & 0 & 0 \\ & \vdots & \vdots & & \vdots & \vdots & & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & z_r & a_r & \cdots & 0 & 0 \\ & & & & a_r & z_{r+1} & \cdots & \vdots & \\ & & & & & \vdots & & & \\ & & & & & & \cdots & z_{n-1} & a_{n-1} \\ & & & & & & & a_{n-1} & z_n \end{array}\right] \end{array}$$

where the diagonal matrix elements z_r are given by

$$\begin{aligned} z_r = z_r(K; v_1, v_2) & = \{K(\Lambda^{(r)}, \ell_1^{(r)}, \ell_2^{(r)}), v_1, v_2 \;\; H^{(2)} \;\; K(\Lambda^{(r)}, \ell_1^{(r)}, \ell_2^{(r)}), v_1, v_2\} \\ & = \sum_{\substack{v_1', v_2' \\ \ell_1' + \ell_2' = K + \Lambda^{(r)}}} (\mathcal{E}^o_{v_1' v_2'} - \mathcal{E}^o_{v_1, v_2}) \left| C^{\overline{\Lambda^{(r)}} v_1' \ell_1' v_2' \ell_2'}_{\Lambda^{(r)} v_1 \ell_1^{(r)} v_2 \ell_2^{(r)}} \right|^2 \\ & = -\frac{\hbar}{8}\left[\varepsilon_1^2 \omega_1 (v_1 + 1)(2 + \Lambda^{(r)}\ell_1^{(r)}) + \varepsilon_2^2 \omega_2 (v_2 + 1)(2 + \Lambda^{(r)}\ell_2^{(r)})\right] \end{aligned} \tag{5.5.8}$$

The off-diagonal matrix elements a_r are given by:

$$
\begin{aligned}
a_r = a_r(\kappa;\nu_1\nu_2) &\equiv \{\psi_r^o(\kappa;\nu_1,\nu_2)|H^{(2)}|\psi_{r+1}^o(\kappa;\nu_1\nu_2)\} \\
&= \begin{cases} <\bar{\Lambda}^{(r)};\nu_1,\ell_1^{(r)} + 2\Lambda^{(r)};\nu_2,\ell_2^{(r)}|H^{(2)}|\Lambda^{(r)};\nu_1,\ell_1^{(r)};\nu_2,\ell_2^{(r)}>, \text{ or} \\ <\bar{\Lambda}^{(r)};\nu_1,\ell_1^{(r)};\nu_2,\ell_2^{(r)} + 2\Lambda^{(r)}|H^{(2)}|\Lambda^{(r)};\nu_1,\ell_1^{(r)};\nu_2,\ell_2^{(r)}> \end{cases} \\
&= \begin{cases} \frac{\hbar}{2}\,\varepsilon_1\omega_1(\nu_1-\Lambda^{(r)}\ell_1^{(r)})^{\frac{1}{2}}(\nu_1+\Lambda^{(r)}\ell_1^{(r)}+2)^{\frac{1}{2}} \text{ or} \\ \frac{\hbar}{2}\,\varepsilon_2\omega_2(\nu_2-\Lambda^{(r)}\ell_2^{(r)})^{\frac{1}{2}}(\nu_2+\Lambda^{(r)}\ell_2^{(r)}+2)^{\frac{1}{2}} \end{cases}
\end{aligned}
\tag{5.5.9}
$$

(B) To obtain the energies correct to second-order, one has to diagonalize the matrix (5.5.7). As $z_1 \neq z_2 \neq \ldots\ldots$, the exact diagonalization is possible only for $n_\kappa(\nu_1,\nu_2) \leq 3$, because we can not solve algebraically a general polynormial equation higher than cubic order.

However, if $\varepsilon_k < 1$, then as seen from Equation (5.5.8) that the z_r are proportional to ε_k^2 which are small in comparison with a_r which are linearly proportional to ε_k. Hence we shall adopt the following approximate method:

We let

$$
\mathbb{A}_n(\kappa;\nu_1,\nu_2) = \begin{bmatrix} 0 & a_1 & 0 & & & \\ a_1 & 0 & a_2 & & 0 & \\ 0 & a_2 & 0 & & & \\ & & & \ddots & & \\ & 0 & & & 0 & a_{n-1} \\ & & & & a_{n-1} & 0 \end{bmatrix}
\tag{5.5.10}
$$

We obtain a transformation matrix $\mathbb{S}(\kappa;\nu_1,\nu_2)$ such that (Appendix E):

$$
\mathbb{S}^{-1}(\kappa;\nu_1,\nu_2)\cdot\mathbb{A}_n(\kappa;\nu_1\nu_2)\cdot\mathbb{S}(\kappa;\nu_1\nu_2) = \begin{bmatrix} \mathcal{E}_1^{(1)} & & 0 \\ & \mathcal{E}_2^{(1)} & \\ & & \ddots & \\ 0 & & & \mathcal{E}_n^{(1)} \end{bmatrix}
\tag{5.5.11}
$$

The $\mathcal{E}_j^{(1)}$ obtained will be the first-order energy corrections for the j^{th} state in the level $[\upsilon_1,\upsilon_2]^\kappa$.

(C) The wave function for the j^{th} state correct to first-order is given by

$$\Psi_j(\kappa;\upsilon_1,\upsilon_2) = \sum_{r=1}^{n_\kappa(\upsilon_1,\upsilon_2)} \tilde{S}_{jr}\,\Psi_r^0(\kappa;\upsilon_1,\upsilon_2) = \sum_{r=1}^{n} \Psi_r^0(\kappa;\upsilon_1,\upsilon_2)\,S_{rj}$$
$$= \Psi_j^0(\kappa;\upsilon_1,\upsilon_2) + \Psi_j^{(1)}(\kappa;\upsilon_1,\upsilon_2) \qquad (5.5.12)$$

where $\tilde{S} = [\tilde{S}_{jr}]$ = the transpose of the matrix $S = [S_{rj}]$. Ψ_j^o is the j^{th} "correct zeroth-order" vibronic wave function which is given by

$$\Psi_j^0(\kappa;\upsilon_1,\upsilon_2) = \sum_{r=1}^{n} \phi_r^0(\kappa;\upsilon_1,\upsilon_2)\,S_{rj} = \sum_{r=1}^{n} |\Lambda^{(r)};\upsilon_1\ell_1^{(r)};\upsilon_2\ell_2^{(r)}\rangle\,S_{rj} \qquad (5.5.13)$$

The $\Psi_j^{(1)}(\kappa;\upsilon_1,\upsilon_2)$ is the first-order correction to the wave function of the j^{th} vibronic state in the level $[\upsilon_1,\upsilon_2]^\kappa$:

$$\Psi_j^{(1)}(\kappa;\upsilon_1,\upsilon_2) = \sum_{r=1}^{n} \phi_r^{(1)}(\kappa;\upsilon_1,\upsilon_2)\,S_{rj}$$
$$= \sum_{r=1}^{n} \sum_{\substack{\upsilon_1'\upsilon_2' \\ \ell_1'+\ell_2'=\kappa+\overline{\Lambda}^{(r)}}} |\overline{\Lambda}^{(r)};\upsilon_1'\ell_1';\upsilon_2'\ell_2'\rangle\, C_{\Lambda^{(r)}\,\upsilon_1\ell_1^{(r)}\,\upsilon_2\ell_2^{(r)}}^{\overline{\Lambda}^{(r)}\,\upsilon_1'\ell_1'\,\upsilon_2'\ell_2'} \cdot S_{rj} \qquad (5.5.14)$$

(D) Let us denote the diagonal matrices $\mathbb{Z}(\kappa;\upsilon_1\upsilon_2)$ by

$$\mathbb{Z}(\kappa;\upsilon_1,\upsilon_2) \equiv [Z_{ir}] \equiv \begin{bmatrix} z_1 & & & \\ & z_2 & & \\ & & \ddots & \\ & & & z_n \end{bmatrix} \qquad (5.515)$$

Performing the following transformation:

$$S^{-1}(\kappa;\upsilon_1,\upsilon_2)\cdot\mathbb{Z}(\kappa;\upsilon_1\upsilon_2)\cdot S(\kappa;\upsilon_1\upsilon_2) \qquad (5.5.16)$$

We obtain the second-order energy contributions from $H^{(2)}$ which are defined by the diagonal matrix elements of $\mathcal{S}^{-1}\cdot\mathcal{Z}\cdot\mathcal{S}$, i.e.,

$$\begin{aligned}\mathcal{E}_j^{(2)}(K;v_1,v_2) &= \sum_i^n \sum_r^n \tilde{S}_{ji} Z_{ir} S_{rj} = \sum_{r=1}^n \tilde{S}_{jr} z_r S_{rj} \\ &= \sum_{r=1}^n z_r S_{rj}^2 \end{aligned} \tag{5.5.17}$$

The first-order and second-order energy corrections [Equations (5.5.11), (5.5.17)] are just the results one would obtain in using ordinary Schröedinger perturbation theory [Appendix F]†. This is the justification for us to treat the problem through Equations (5.5.7) to (5.5.17).

(E) The first-order contributions from $H^{(4)}$ may be computed by using Equation (5.5.12) which are given by

$$\begin{aligned}&\langle \Psi_j(K;v_1,v_2) | H^{(4)} | \Psi_j(K;v_1,v_2)\rangle \\ &= \sum_{r=1}^n \sum_{r'=1}^n \langle \Psi_r^\circ(K;v_1,v_2) | H^{(4)} | \Psi_{r'}^\circ(K;v_1,v_2)\rangle S_{rj}^* S_{r'j} \\ &= \sum_{r=1} \sum_{r'=1} \langle \Phi_r^\circ(K;v_1,v_2) | H^{(4)} | \Phi_{r'}^\circ(K;v_1,v_2)\rangle S_{rj}^* S_{r'j} + \text{higher order}\end{aligned} \tag{5.5.18}$$

Hence the vibronic energies correct to second-order are given by

$$E_j(K,v_1,v_2) = \mathcal{E}_{v_1,v_2}^\circ + \mathcal{E}_j^{(1)}(K;v_1,v_2) + \mathcal{E}_j^{(2)}(K;v_1,v_2) + \langle \Psi_j^\circ | H^{(4)} | \Psi_j^\circ \rangle \tag{5.5.19}$$

5.6 The Second-Order Vibronic Energies for Symmetrical Linear Tetratomic Molecules in Π-Electronic Level

Since the above-mentioned method involves the diagonalization of the matrices (5.5.11), general energy-expressions are only possible for a group of levels $[v_1,v_2]^K$ whose first-order perturbation matrices are of the same

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†We may show that Equation (5.5.17) is equal to Equation (F-22).

dimensions, i.e., these levels have the same $n = n_K(v_1,v_2)$ values. Furthermore, our method can not be used for the cases in which $n_K(v_1,v_2)$ is greater than 7 [Appendix F].

In this section, we shall list results only for the cases for which the $n_K(v_1,v_2)$ are equal to 1, 2, 3 and 4, and for which $K \geqslant 0$. The same equations will be obtained if $K \leqslant 0$, thus for $|K| > 0$, each state $\Psi_j(|K|;v_1,v_2)$ is at least doubly degenerate![†]

Table 5.6 The second-order energy-expressions for vibronic states of symmetrical linear tetratomic molecules in π-electronic level. (setting $\hbar = 1$).

Case A: $n_K(v_1,v_2) = 1$[♯]

$$\psi_r^\circ(K;v_1,v_2) = |+;v_1,v_2;v_2,v_2\rangle + \frac{\varepsilon_1}{4}(v_1+1)^{1/2}(v_1+2)^{1/2}|-;v_1+2,v_1+2;v_2,v_2\rangle + \frac{\varepsilon_2}{4}(v_2+1)^{1/2}(v_2+2)^{1/2}|-;v_1,v_1;v_2+2,v_2+2\rangle$$

$$a_r(K;v_1,v_2) = 0$$

$$z_r(K;v_1,v_2) = -\frac{1}{8}\left[\varepsilon_1^2\omega_1(v_1+1)(v_1+2) + \varepsilon_2^2\omega_2(v_2+1)(v_2+2)\right]$$

$$\$(K;v_1,v_2) = 1$$

$$\Psi_j(K;v_1,v_2) = \psi_r^\circ(K;v_1,v_2)$$

$$\mathcal{E}^\circ_{v_1 v_2} = (v_1+1)\omega_1 + (v_2+1)\omega_2$$

$$\mathcal{E}_j^{(1)}(K;v_1,v_2) = 0$$

$$\mathcal{E}_j^{(2)}(K;v_1,v_2) = z_r(K;v_1,v_2)$$

$$\langle\Psi_j|H^{(4)}|\Psi_j\rangle = g_1 B(v_1,v_1) + g_2 B(v_2,v_2) + 4 g_{12} A(v_1,v_1)\cdot A(v_2,v_2)$$

[♯] The $[v_1,v_2]^K$ levels are those with $v_1+v_2+1 = K$: $[0,0]^1$, $[0,1]^2$, $[1,0]^2$; $[0,2]^3$, $[1,1]^3$, $[2,0]^3$; $[0,3]^4$, $[1,2]^4$, $[2,1]^4$, $[3,0]^4$; $[0,4]^5$, $[1,3]^5$, $[2,2]^5$, $[3,1]^5$, $[4,0]^5$; $[0,5]^6$, $[1,4]^6$, $[2,3]^6$, $[3,2]^6$, $[4,1]^6$, $[5,0]^6$; etc.

[†] Rotational-vibrational interaction may remove this degeneracy. It is called K-type doubling. (J. W. C. Johns, J. Mol. Spect. 15, 473, (1960)).

Case B: $n_K(v_1, v_2) = 2$[#]

$$\psi_r^{\circ}(K;v_1,v_2) = \begin{cases} \psi_1^{\circ} = |+;v_k,K-1;0,0\rangle + \Big\{ \frac{\varepsilon_k}{8}\Big[(v_k+K+1)^{1/2}(v_k+K+3)^{1/2}|-;v_k+2,K+1;0,0\rangle - (v_k-K+1)^{1/2}(v_k-K-1)^{1/2}|-;v_k-2,K+1;0,0\rangle\Big] \\ \qquad + \frac{\varepsilon_{k'}}{4}\sqrt{2}\,|-;v_k,K-1;2,2\rangle \Big\} \\ \psi_2^{\circ} = |-;v_k,K+1;0,0\rangle + \Big\{ \frac{\varepsilon_k}{8}\Big[(v_k-K+1)^{1/2}(v_k-K+3)^{1/2}|+;v_k+2,K-1;0,0\rangle - (v_k+K+1)^{1/2}(v_k+K-1)^{1/2}|+;v_k-2,K-1;0,0\rangle\Big] \\ \qquad + \frac{\varepsilon_{k'}}{4}\sqrt{2}\,|+;v_k,K+1;2,-2\rangle \Big\} \end{cases}$$

$$a_r(K;v_1v_2) = a = \frac{1}{2}\varepsilon_k\omega_k\left[(v_k+1)^2 - K^2\right]^{1/2}$$

$$z_r(K;v_1v_2) = z_{\substack{1\\2}} = -\frac{1}{8}\left[\varepsilon_k^2\omega_k(v_k+1)(1\mp K) + 2\varepsilon_{k'}^2\omega_{k'}\right]$$

$$\mathcal{S}(K;v_1,v_2) = \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}$$

$$\Phi_j^{\circ}(K;v_1v_2) = \Phi_{\substack{1\\2}}^{\circ} = \frac{1}{\sqrt{2}}\left[\pm|+;v_k,K-1;0,0\rangle + |-;v_k,K+1;0,0\rangle\right]$$

$$\Phi_j^{(1)}(K;v_1v_2) = \Phi_{\substack{1\\2}}^{(1)} = \frac{1}{8\sqrt{2}}\varepsilon_k\Big[\pm(v_k+K+1)^{1/2}(v_k+K+3)^{1/2}|-;v_k+2,K+1;0,0\rangle + (v_k-K+1)^{1/2}(v_k-K+3)^{1/2}|+;v_k+2,K-1;0,0\rangle$$
$$\mp(v_k-K+1)^{1/2}(v_k-K-1)^{1/2}|-;v_k-2,K+1;0,0\rangle - (v_k+K+1)^{1/2}(v_k+K-1)^{1/2}|+;v_k-2,K-1;0,0\rangle\Big]$$
$$+\frac{1}{4}\varepsilon_{k'}\left[\pm|-;v_k,K-1;2,2\rangle + |+;v_k,K+1;2,-2\rangle\right]$$

$$\mathcal{E}^{\circ}_{v_1,v_2} = (v_k+1)\omega_k + \omega_{k'}$$

$$\mathcal{E}_j^{(1)}(K;v_1,v_2) = \mathcal{E}^{(1)}_{\substack{1\\2}} = \pm\frac{1}{2}\varepsilon_k\omega_k\left[(v_k+1)^2 - K^2\right]^{1/2}$$

$$\mathcal{E}_j^{(2)}(K;v_1,v_2) = \mathcal{E}^{(2)}_{\substack{1\\2}} = -\frac{1}{8}\left[\varepsilon_k^2\omega_k(v_k+1) + 2\varepsilon_{k'}^2\omega_{k'}\right],$$ [□], [□□]

$$\langle\Phi_j^{\circ}|H^{(4)}|\Phi_j^{\circ}\rangle = \frac{1}{2}g_k\left[B(v_k,l_k=K-1) + B(v_k,l_k=K+1)\right] + g_{k'}B(v_{k'}=0,l_{k'}=0)$$
$$+2g_{12}A(v_{k'}=0,l_{k'}=0)\left[A(v_k,l_k=K-1) + A(v_k,l_k=K+1)\right]$$
$$\pm\frac{1}{4}\Big\{h_k\left[B(v_k,(K+1)-2) + B(v_k,(K-1)+2)\right] + 3h_{12}A(v_{k'}=0,l_{k'}=0)\left[A(v_k,(K+1)-2) + A(v_k,(K-1)+2)\right]\Big\}.$$

[#] Levels are $[v_k,0]^K$, with $v_k \geq K+1$ and $v_{k'} = 0$: $[0,1]^0$, $[0,3]^0$, $[0,5]^0$..... $[0,2]^1$, $[0,4]^1$, $[0,6]^1$.....$[0,2]^2$, $[0,5]^2$, $[0,7]^2$.....$[1,0]^0$, $[3,0]^0$, $[5,0]^0$.....$[2,0]^1$, $[4,0]^1$, $[6,0]^1$.....$[3,0]^2$, $[5.0]^2$, $[7,0]^2$.....etc.

[□] If $\varepsilon_{k'}=0$, we obtain Renner's expressions for triatomic molecules!

[□□] Complete diagonalization of the 2 x 2 Van Vleck perturbation matrix gives

$$\mathcal{E}_j^{(1)} + \mathcal{E}_j^{(2)} = \frac{z_1+z_2}{2} \pm \sqrt{\left(\frac{z_1-z_2}{2}\right)^2 + a}$$
$$= -\frac{1}{8}\left[\varepsilon_k^2\omega_k(v_k+1) + 2\varepsilon_{k'}^2\omega_{k'}\right] \pm \frac{\varepsilon_k\omega_k}{2}\left\{(v_k+1)^2 - K^2\left[1 - \frac{\varepsilon_k^2}{16}(v_k+1)^2\right]\right\}^{1/2}.$$

Case C: $n_K(\upsilon_1,\upsilon_2) = 3$[‡]

$$\psi_r^c(K;\upsilon_1,\upsilon_2) = \begin{cases} \psi_1^c & |+;\upsilon_1,\upsilon_1;\upsilon_2,\upsilon_2-2\rangle + \frac{1}{4}\Big\{ \varepsilon_1(\upsilon_1+1)^{1/2}(\upsilon_1+2)^{1/2}\,|-;\upsilon_1+2,\upsilon_1+2;\upsilon_2,\upsilon_2-2\rangle \\ & \quad + \varepsilon_2\,\upsilon_2^{1/2}(\upsilon_2+1)^{1/2}\,|-;\upsilon_1,\upsilon_1;\upsilon_2+2,\upsilon_2\rangle \Big\} \\ \psi_2^c & |-;\upsilon_1,\upsilon_1;\upsilon_2,\upsilon_2\rangle + \frac{1}{4}\Big\{ \varepsilon_1\big[\sqrt{2}\,|+;\upsilon_1+2,\upsilon_1-2;\upsilon_2,\upsilon_2\rangle - \upsilon_1^{1/2}(\upsilon_1-1)^{1/2}\,|+;\upsilon_1-2,\upsilon_1-2;\upsilon_2,\upsilon_2\rangle\big] \\ & \quad + \varepsilon_2\big[\sqrt{2}\,|+;\upsilon_1,\upsilon_1;\upsilon_2+2,\upsilon_2-2\rangle - \upsilon_2^{1/2}(\upsilon_2-1)^{1/2}\,|+;\upsilon_1,\upsilon_1;\upsilon_2-2,\upsilon_2-2\rangle\big] \\ \psi_3^c & |+;\upsilon_1,\upsilon_1-2;\upsilon_2,\upsilon_2\rangle + \frac{1}{4}\Big\{ \varepsilon_1(\upsilon_1)^{1/2}(\upsilon_1+1)^{1/2}\,|-;\upsilon_1+2,\upsilon_1;\upsilon_2,\upsilon_2\rangle \\ & \quad + \varepsilon_2(\upsilon_2+1)^{1/2}(\upsilon_2+2)^{1/2}\,|-;\upsilon_1,\upsilon_1-2;\upsilon_2+2,\upsilon_2+2\rangle \Big\} \end{cases}$$

$$a_r(K;\upsilon_1,\upsilon_2) = \begin{cases} a_1 = \upsilon_2^{1/2}\,\varepsilon_2\omega_2 \\ a_2 = \upsilon_1^{1/2}\,\varepsilon_1\omega_1 \end{cases}$$

$$z_r(K;\upsilon_1,\upsilon_2) = \begin{cases} z_1 = -\frac{1}{8}\left[\varepsilon_1^2\omega_1(\upsilon_1+1)(2+\upsilon_1) + \varepsilon_2^2\omega_2(\upsilon_2+1)\upsilon_2\right] \\ z_2 = -\frac{1}{8}\left[\varepsilon_1^2\omega_1(\upsilon_1+1)(2-\upsilon_1) + \varepsilon_2^2\omega_2(\upsilon_2+1)(2-\upsilon_2)\right] \\ z_3 = -\frac{1}{8}\left[\varepsilon_1^2\omega_1(\upsilon_1+1)\upsilon_1 + \varepsilon_2^2\omega_2(\upsilon_2+1)(2+\upsilon_2)\right] \end{cases}$$

$$\mathcal{S}(K;\upsilon_1,\upsilon_2) = \begin{bmatrix} \frac{a_1}{\sqrt{2}N} & \frac{a_2}{N} & \frac{a_1}{\sqrt{2}N} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ \frac{a_2}{\sqrt{2}N} & -\frac{a_1}{N} & \frac{a_2}{\sqrt{2}N} \end{bmatrix}, \qquad N = (a_1^2 + a_2^2)^{1/2} = (\upsilon_1 + \upsilon_2 p^2)^{1/2}\varepsilon_1\omega_1 ; \quad p = \frac{\varepsilon_2\omega_2}{\varepsilon_1\omega_1}$$

$$\mathcal{E}^c_{\upsilon_1,\upsilon_2} = (\upsilon_1+1)\omega_1 + (\upsilon_2+1)\omega_2$$

$$\mathcal{E}_j^{(1)}(K;\upsilon_1,\upsilon_2) = \begin{cases} \mathcal{E}_1^{(1)} = +(\upsilon_1+\upsilon_2 p^2)^{1/2}\varepsilon_1\omega_1 , \quad p \;\; \frac{\varepsilon_2\omega_2}{\varepsilon_1\omega_1} \\ \mathcal{E}_2^{(1)} = 0 \\ \mathcal{E}_3^{(1)} = -(\upsilon_1+\upsilon_2 p^2)^{1/2}\varepsilon_1\omega_1 \end{cases}$$

$$\mathcal{E}_j^{(2)}(K;\upsilon_1,\upsilon_2) = \begin{cases} \mathcal{E}_{1,3}^{(2)} = -\frac{1}{8}\left[\left(\upsilon_1 + \frac{\upsilon_2 p^2}{\upsilon_1+\upsilon_2 p^2}\right)(\upsilon_1+1)\varepsilon_1^2\omega_1 + \left(\upsilon_2 + \frac{\upsilon_1}{\upsilon_1+\upsilon_2 p^2}\right)(\upsilon_2+1)\varepsilon_2^2\omega_2\right] \\ \mathcal{E}_2^{(2)} = -\frac{1}{8}\left[\left(\upsilon_1 + \frac{2\upsilon_1}{\upsilon_1+\upsilon_2 p^2}\right)(\upsilon_1+1)\varepsilon_1^2\omega_1 + \left(\upsilon_2 + \frac{2\upsilon_2 p^2}{\upsilon_1+\upsilon_2 p^2}\right)(\upsilon_2+1)\varepsilon_2^2\omega_2\right] \end{cases}$$

[‡] Levels are with $\upsilon_1+\upsilon_2-1 = K$: $[1,1]^1$; $[1,2]^2$, $[2,1]^2$; $[1,3]^3$, $[2,2]^3$, $[3,1]^3$; $[2,2]^3$, $[3,1]^3$; $[1,4]^4$, $[2,3]^4$, $[3,2]^4$, $[4,1]^4$;....., etc.

Case 4: $n_K(v_1, v_2) = 4^*$

$$\psi_r^{\circ}(K; v_1, v_2) = \begin{cases} \psi_1^{\circ} = |+; v_k, K-2; 1,1\rangle + \frac{\varepsilon_k}{8}\left\{(v_k+K)^{1/2}(v_k+K+2)^{1/2}|-; v_k+2, K; 1,1\rangle - (v_k-K+2)^{1/2}(v_k-K)^{1/2}|-; v_k-2, K; 1,1\rangle\right\} \\ \qquad + \frac{\varepsilon_{k'}}{4}\sqrt{6}\,|-; v_k, K-2; 3,3\rangle \\ \psi_2^{\circ} = |-; v_k, K; 1,1\rangle + \frac{\varepsilon_k}{8}\left\{(v_k-K+2)^{1/2}(v_k-K+4)^{1/2}|+; v_k+2, K-2; 1,1\rangle - (v_k+K)^{1/2}(v_k+K-2)^{1/2}|+; v_k-2, K-2; 1,1\rangle\right\} \\ \qquad + \frac{\varepsilon_{k'}}{4}\sqrt{2}\,|+; v_k, K; 3,\bar{1}\rangle \\ \psi_3^{\circ} = |+; v_k, K; 1,\bar{1}\rangle + \frac{\varepsilon_k}{8}\left\{(v_k+K+2)^{1/2}(v_k+K+4)^{1/2}|-; v_k+2, K+2; 1,\bar{1}\rangle - (v_k-K)^{1/2}(v_k-K-2)^{1/2}|-; v_k-2, K+2; 1,\bar{1}\rangle\right\} \\ \qquad + \frac{\varepsilon_{k'}}{4}\sqrt{2}\,|-; v_k, K; 3,1\rangle \\ \psi_4^{\circ} = |-; v_k, K+2; 1,\bar{1}\rangle + \frac{\varepsilon_k}{8}\left\{(v_k-K)^{1/2}(v_k-K+2)^{1/2}|+; v_k+2, K; 1,\bar{1}\rangle - (v_k+K+2)^{1/2}(v_k+K)^{1/2}|+; v_k-2, K; 1,\bar{1}\rangle\right\} \\ \qquad + \frac{\varepsilon_{k'}}{4}\sqrt{6}\,|+; v_k, K+2; 3,\bar{3}\rangle \end{cases}$$

$$a_r(K; v_1, v_2) = \begin{cases} a_{1,3} = \frac{1}{2}(v_k \pm K)^{1/2}(v_k \mp K+2)^{1/2}\varepsilon_k\omega_k \\ a_2 = \varepsilon_{k'}\omega_{k'} \end{cases}$$

$$z_r(K; v_1, v_2) = \begin{cases} z_{1,4} = -\frac{1}{8}\left[\pm \varepsilon_k^2\omega_k(v_k+1)K + 6\varepsilon_{k'}^2\omega_{k'}\right] \\ z_{2,3} = -\frac{1}{8}\left[\varepsilon_k^2\omega_k(v_k+1)(2\mp K) + 2\varepsilon_{k'}^2\omega_{k'}\right] \end{cases}$$

$$S(K; v_1, v_2) = \left[S_{rj}\right]; \quad S_{1j} = \frac{a_1}{N_j}, \quad S_{2j} = \frac{\lambda_j}{N_j}, \quad S_{3j} = \frac{\lambda_j^2 - a_1^2}{a_2 N_j}, \quad S_{4j} = \frac{a_3}{\lambda_j}S_{3j};$$

$$\lambda_j = \pm\frac{1}{\sqrt{2}}\left[(a_1^2+a_2^2+a_3^2) \pm \sqrt{(a_1^2+a_2^2+a_3^2)^2 - 4a_1^2a_3^2}\,\right]^{1/2}$$

$$N_j^2 = a_1^2 + \lambda_j^2 + \left(\frac{\lambda_j^2 - a_1^2}{a_2}\right)^2\left(1 + \frac{a_3^2}{\lambda_j^2}\right)$$

$$\varepsilon^{\circ}_{v_1, v_2} \doteq (v_k+1)\omega_k + 2\omega_{k'}$$

$$\varepsilon_j^{(1)}(K; v_1, v_2) = \begin{cases} \varepsilon_{1,4}^{(1)} = \pm\frac{1}{\sqrt{2}}\left[(a_1^2+a_2^2+a_3^2) + \sqrt{(a_1^2+a_2^2+a_3^2)^2 - 4a_1^2a_3^2}\,\right]^{1/2} \\ \varepsilon_{2,3}^{(1)} = \pm\frac{1}{\sqrt{2}}\left[(a_1^2+a_2^2+a_3^2) - \sqrt{(a_1^2+a_2^2+a_3^2)^2 - 4a_1^2a_3^2}\,\right]^{1/2} \end{cases}$$

$$\varepsilon_j^{(2)}(K; v_1, v_2) = -\frac{1}{4}\left\{\left[(v_k+1)\varepsilon_k^2\omega_k - 2\varepsilon_{k'}^2\omega_{k'}\right](S_{2j}^2 + S_{3j}^2) + 3\varepsilon_{k'}^2\omega_{k'}\right\}.^{\square}$$

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*Levels are $[v_k, 1]^K$, with $v_k - 2 > K$; $v_{k'} = 1$: $[1,2]^0$, $[1,4]^0$, $[1,6]^0$.... $[2,1]^0$, $[4,1]^0$, $[6,1]^0$.....$[1,3]^1$, $[1,5]^1$, $[1,7]^1$.....$[3,1]^1$, $[5,1]^1$, $[7,1]^1$.....$[1,4]^2$, $[1,6]^2$, $[1,8]^2$.....$[4,1]^2$, $[6,1]^2$, $[8,1]^2$.....etc.

□ For $K = 0$

$$\varepsilon_j^{(1)}(0; v_1, v_2) \quad \pm\frac{1}{2}\left\{\left[v_k(v_k+2)\varepsilon_k^2\omega_k^2 + \varepsilon_{k'}^2\omega_{k'}^2\right]^{1/2} \pm \varepsilon_{k'}\omega_{k'}\right\}$$

$$\varepsilon_j^{(2)}(0; v_1, v_2) \quad -\frac{1}{8}\left\{\varepsilon_k^2\omega_k(v_k+1)\left[1 \pm \frac{\varepsilon_{k'}\omega_{k'}}{\left[v_k(v_k+2)\varepsilon_k^2\omega_k^2 + \varepsilon_{k'}^2\omega_{k'}^2\right]^{1/2}}\right] + \varepsilon_{k'}^2\omega_{k'}\left[4 \mp \frac{2\varepsilon_{k'}\omega_{k'}}{\left[v_k(v_k+2)\varepsilon_k^2\omega_k^2 + \varepsilon_{k'}^2\omega_{k'}^2\right]^{1/2}}\right]\right\}.$$

Using Table 5.6, the first-order vibronic wave functions $\Psi_j(K;\upsilon_1,\upsilon_2)$ for the lowest vibronic levels may be evaluated (Table 5.7) and the second-order vibronic energies as functions of the Renner parameters ε_k are shown in Figure 5.8.

Table 5.7. First-order vibronic wave functions $\Psi_j(K;\upsilon_1,\upsilon_2)$ for $(\upsilon_1+\upsilon_2) < 3$. The first-order vibronic wave function of j^{th} state in the level $[\upsilon_1,\upsilon_2]^K$ is written as $\Psi_j(K;\upsilon_1,\upsilon_2) = \psi_+^o\,\Phi_j^+(K;\upsilon_1,\upsilon_2) + \psi_-^o\,\Phi_j^-(K;\upsilon_1,\upsilon_2)$ where $\psi_\pm^o \sim |\pm\lambda\rangle$ and $\Phi_j^\pm$ will be linear combination of $|\upsilon_1'\ell_1';\upsilon_2'\ell_2'\rangle$, the Harmonic oscillator wave functions (Equation (5.3.2)).

$$\Psi_j(1;00)\quad \begin{cases} \Phi^+(1;0,0) = |0,0;0,0\rangle \\ \Phi^-(1;00) = \frac{\sqrt{2}}{4}\{\varepsilon_1|2,2;0,0\rangle + \varepsilon_2|0,0;2,2\rangle\} \end{cases}$$

$$\Psi_1(0;10):\quad \begin{cases} \Phi_1^+(0;10) = \frac{1}{\sqrt{2}}|1,\bar{1};0,0\rangle + \frac{1}{4}\{\varepsilon_1|3,\bar{1};0,0\rangle + \varepsilon_2|1,1;2,\bar{2}\rangle\} \\ \Phi_1^-(0;10) = \frac{1}{\sqrt{2}}|1,1;0,0\rangle + \frac{1}{4}\{\varepsilon_1|3,1;0,0\rangle + \varepsilon_2|1,\bar{1};2,2\rangle\} \end{cases}$$

$$\Psi_2(0;1,0):\quad \begin{cases} \Phi_2^+(0;10) = -\frac{1}{\sqrt{2}}|1,\bar{1};0,0\rangle + \frac{1}{4}\{\varepsilon_1|3,\bar{1};0,0\rangle + \varepsilon_2|1,1;2\bar{2}\rangle\} \\ \Phi_2^-(0;10) = \frac{1}{\sqrt{2}}|1,1;0,0\rangle - \frac{1}{4}\{\varepsilon_1|3,1;0,0\rangle + \varepsilon_2|1,\bar{1};2,2\rangle\} \end{cases}$$

$$\Psi(2;10):\quad \begin{cases} \Phi^+(2;10) = |1,1;0,0\rangle \\ \Phi^-(2;10) = \frac{1}{4}\{\sqrt{6}\,\varepsilon_1|3,3;0,0\rangle + \sqrt{2}\,\varepsilon_2|1,1;2,2\rangle\} \end{cases}$$

$$\Psi_1(1;20)\quad \begin{cases} \Phi_1^+(1;2,0) = \frac{1}{\sqrt{2}}|2,0;0,0\rangle + \frac{1}{4}\{\varepsilon_1|4,0;0,0\rangle - \varepsilon_1|0,0;0,0\rangle + \varepsilon_2|2,2;2,\bar{2}\rangle\} \\ \Phi_1^-(1;2,0) = \frac{1}{\sqrt{2}}|2,2;0,0\rangle + \frac{1}{4}\{\sqrt{3}\,\varepsilon_1|4,2;0,0\rangle \qquad + \varepsilon_2|2,0;2,2\rangle\} \end{cases}$$

$$\Psi_2(1;20):\quad \begin{cases} \Phi_2^+(1;20) = -\frac{1}{\sqrt{2}}|2,0;0,0\rangle + \frac{1}{4}\{\varepsilon_1|4,0;0,0\rangle - \varepsilon_1|0,0;0,0\rangle + \varepsilon_2|2,2;2,\bar{2}\rangle\} \\ \Phi_2^-(1;2,0) = \frac{1}{\sqrt{2}}|2,2;0,0\rangle - \frac{1}{4}\{\sqrt{3}\,\varepsilon_1|4,2;0,0\rangle \qquad + \varepsilon_2|2,0;2,2\rangle\} \end{cases}$$

$$\Psi(3;20):\quad \begin{cases} \Phi^+(3;2,0) = |2,2;0,0\rangle \\ \Phi^-(3;20) = \frac{1}{4}\{\sqrt{2}\,\varepsilon_1|2,2;2,2\rangle + 2\sqrt{3}\,\varepsilon_2|4,4;0,0\rangle\} \end{cases}$$

$$\Psi_1(1;1,1):\quad \begin{cases} \Phi_1^+(1;1,1) = \frac{1}{\sqrt{2}(1+p^2)^{1/2}}[p|1,1;1,\bar{1}\rangle + |1,\bar{1};1,1\rangle] + \frac{1}{4}\{\varepsilon_1|3,\bar{1};1,1\rangle + \varepsilon_2|1,1;3,\bar{1}\rangle\} \\ \Phi_1^-(1;1,1) = \frac{1}{\sqrt{2}}|1,1;1,1\rangle + \frac{1}{4(1+p^2)^{1/2}}\{\sqrt{3}\,p\,\varepsilon_1|3,3;1,\bar{1}\rangle + p\,\varepsilon_2|1,1;3,1\rangle + \varepsilon_1|3,1;1,1\rangle + \sqrt{3}\,\varepsilon_2|1,\bar{1};3,3\rangle\} \end{cases}$$

$$\Psi_2(1;1,1):\quad \begin{cases} \Phi_2^+(1;1,1) = \frac{1}{(1+p^2)^{1/2}}[-p|1,\bar{1};1,1\rangle + |1,1;1,\bar{1}\rangle] \\ \Phi_2^-(1;1,1) = \frac{1}{2\sqrt{2}(1+p^2)^{1/2}}\{2\varepsilon_1|3,3;1,\bar{1}\rangle + \varepsilon_2|1,1;3,1\rangle - \varepsilon_1|3,1;1,1\rangle - \sqrt{3}\,\varepsilon_2|1,\bar{1};3,3\rangle\} \end{cases}$$

$$\Psi_3(1;1,1):\quad \begin{cases} \Phi_3^+(1;1,1) = \frac{1}{\sqrt{2}(1+p^2)^{1/2}}[p|1,1;1,\bar{1}\rangle + |1,\bar{1};1,1\rangle] - \frac{1}{4}\{\varepsilon_1|3,\bar{1};1,1\rangle + \varepsilon_2|1,1;3,\bar{1}\rangle\} \\ \Phi_3^-(1;1,1) = -\frac{1}{\sqrt{2}}|1,1;1,1\rangle + \frac{1}{4(1+p^2)^{1/2}}\{\sqrt{3}\,p\,\varepsilon_1|3,3;1,\bar{1}\rangle + p\,\varepsilon_2|1,1;3,1\rangle + \varepsilon_1|3,1;1,1\rangle + \sqrt{3}\,\varepsilon_2|1,\bar{1};3,3\rangle\} \end{cases}$$

Table 5.7 (Cont'd.)

$$\Phi(3;1,1):\begin{cases}\Phi^{+}(3;1,1) = |1,1;1,1\rangle \\ \Phi^{-}(3;1,1) = \frac{\sqrt{6}}{4}\left\{\varepsilon_1|3,3;1,1\rangle + \varepsilon_2|1,1;3\,3\rangle\right\}\end{cases}$$

$$\Phi_1(2;3,0):\begin{cases}\Phi_1^{+}(2;3,0) = \frac{1}{\sqrt{2}}|3,1;0,0\rangle + \frac{1}{4}\left\{\varepsilon_1|5,1;0,0\rangle - \sqrt{3}\,\varepsilon_1|1,1;0,0\rangle + \sqrt{2}\,\varepsilon_2|3,3;2,\bar{2}\rangle\right\} \\ \Phi_1^{-}(2;3,0) = \frac{1}{\sqrt{2}}|3,3;0,0\rangle + \frac{1}{4}\left\{\sqrt{6}\,\varepsilon_1|5,3;0,0\rangle + \varepsilon_2|3,1;2,2\rangle\right\}\end{cases}$$

$$\Phi_2(2;3,0):\begin{cases}\Phi_2^{+}(2;3,0) = -\frac{1}{\sqrt{2}}|3,1;0,0\rangle + \frac{1}{4}\left\{\varepsilon_1|5,1;0,0\rangle - \sqrt{3}\,\varepsilon_1|1,1;0,0\rangle + \sqrt{2}\,\varepsilon_2|3,3;2,\bar{2}\rangle\right\} \\ \Phi_2^{-}(2;3,0) = \frac{1}{\sqrt{2}}|3,3;0,0\rangle - \frac{1}{4}\left\{\sqrt{6}\,\varepsilon_1|5,3;0,0\rangle + \varepsilon_2|3,1;2,2\rangle\right\}\end{cases}$$

$$\Phi(4;3\,0):\begin{cases}\Phi^{+}(4;3,0) = |3,3;0,0\rangle \\ \Phi^{-}(4;3,0) = \frac{1}{4}\left\{2\sqrt{5}\,\varepsilon_2|5,5;0,0\rangle + \sqrt{2}\,\varepsilon_2|3,3;2,2\rangle\right\}\end{cases}$$

$$\Phi_1(2;1,2):\begin{cases}\Phi_1^{+}(2;1,2) = \frac{1}{\sqrt{2}(1+2p^2)^{1/2}}\left[\sqrt{2}\,p|1,1;2,0\rangle + |1,\bar{1};2,2\rangle\right] + \frac{1}{4}\left\{\varepsilon_1|3,\bar{1};2,2\rangle + \varepsilon_2|1,1;4,0\rangle - \varepsilon_2|1,1;0,0\rangle\right\} \\ \Phi_1^{-}(2;1,2) = \frac{1}{\sqrt{2}}|1,1;2,2\rangle + \frac{1}{4(1+2p^2)^{1/2}}\left\{\sqrt{6}\,p\,\varepsilon_1|3,3;2,0\rangle + \sqrt{6}\,p\,\varepsilon_2|1\,1\,4\,0\rangle + \varepsilon_1|3\,1\,2\,2\rangle + \sqrt{6}\,\varepsilon_2|1,\bar{1};4\,4\rangle\right\}\end{cases}$$

$$\Phi_2(2;1,2):\begin{cases}\Phi_2^{+}(2;1,2) = \frac{1}{(1+2p^2)^{1/2}}\left[p|1,1;2,0\rangle - \sqrt{2}\,|1,\bar{1};2,2\rangle\right] \\ \Phi_2^{-}(2;1,2) = \frac{1}{4(1+2p^2)^{1/2}}\left\{\sqrt{6}\,\varepsilon_1|3\,3\,2\,0\rangle + \sqrt{6}\,\varepsilon_2|1\,1\,4\,0\rangle - 2\varepsilon_1|3\,1\,2\,2\rangle - 2\sqrt{6}\,\varepsilon_2|1,\bar{1};4,4\rangle\right\}\end{cases}$$

$$\Phi_3(2;1,2):\begin{cases}\Phi_3^{+}(2;1,2) = \frac{1}{\sqrt{2}(1+2p^2)^{1/2}}\left[\sqrt{2}\,p|1,1;2,2\rangle + |1,\bar{1};2,2\rangle\right] - \frac{1}{4}\left\{\varepsilon_1|3,\bar{1};2,2\rangle + \varepsilon_2|1\,1\,4\,0\rangle - \varepsilon_2|1\,1\,0\,0\rangle\right\} \\ \Phi_3^{-}(2;1,2) = -\frac{1}{\sqrt{2}}|1,1;2,2\rangle + \frac{1}{4(1+2p^2)^{1/2}}\left\{\sqrt{6}\,p\,\varepsilon_1|3,3;2,0\rangle + \sqrt{6}\,p\,\varepsilon_2|1,1;4,0\rangle + \varepsilon_1|3\,1\,2\,2\rangle + \sqrt{6}\,\varepsilon_2|1\,\bar{1}\,4\,4\rangle\right\}\end{cases}$$

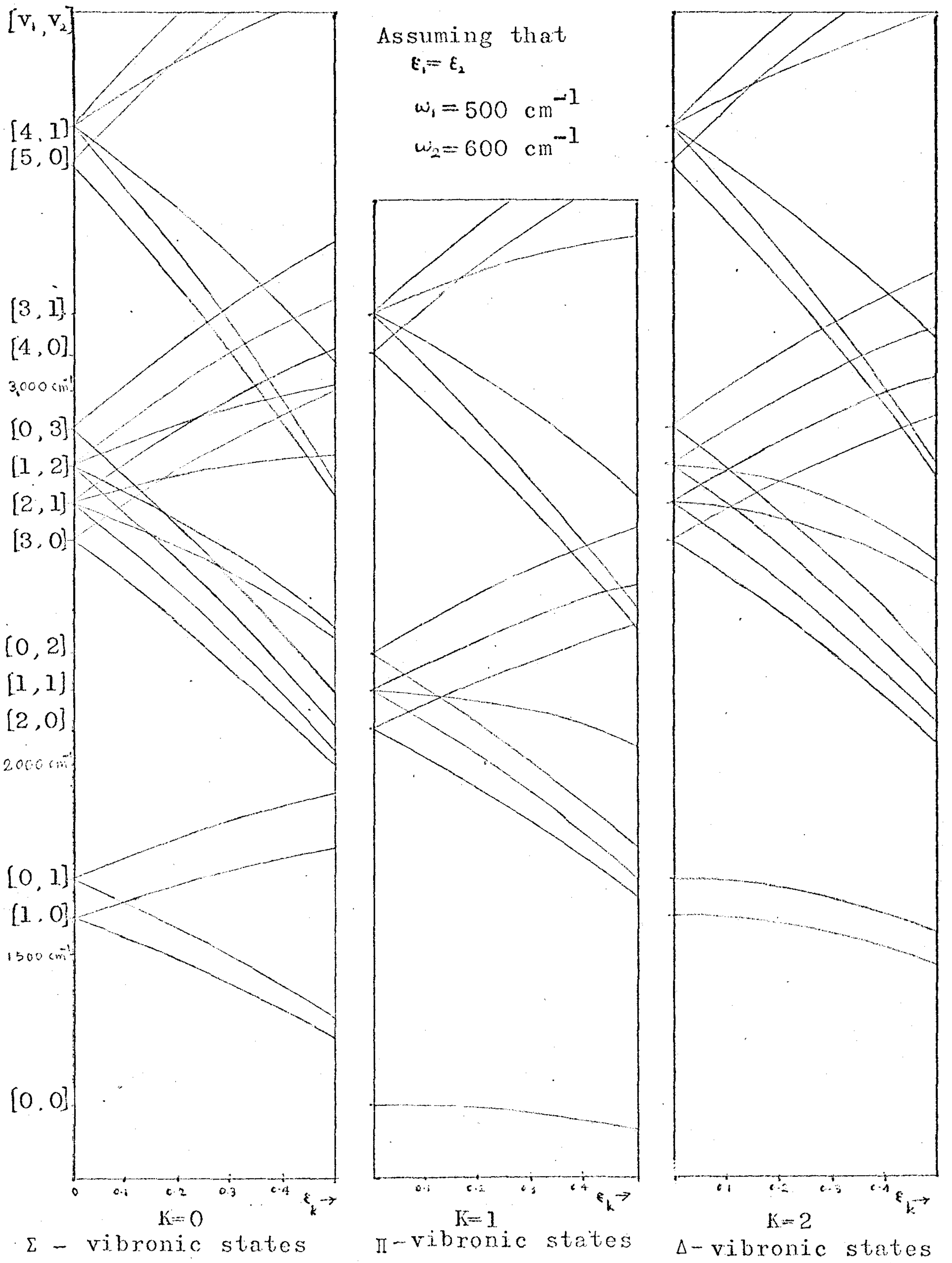
$$\Phi_1(0;1,2):\begin{cases}\Phi_1^{+}(0;1\,2) = \frac{1}{N_1}\left[\sqrt{2}\,p|1,1;2,\bar{2}\rangle + \frac{(1+8p^2)^{1/2}+1}{2}|1,\bar{1};2,0\rangle\right] \\ \qquad + \frac{1}{2N_1}\left\{\frac{(1+8p^2)^{1/2}+1}{4}\left[\sqrt{2}\,\varepsilon_1|3\,\bar{1}\,2\,0\rangle + \sqrt{6}\,\varepsilon_2|1\,1\,4\,\bar{2}\rangle\right] + p\left[\sqrt{3}\,\varepsilon_1|3\,\bar{3}\,2\,2\rangle + \varepsilon_2|1\,\bar{1}\,4\,0\rangle - \varepsilon_2|1\,\bar{1}\,0\,0\rangle\right]\right\} \\ \Phi_1^{-}(0;1\,2) = \frac{1}{N_1}\left[\frac{(1+8p^2)^{1/2}+1}{2}|1\,1\,2\,0\rangle + \sqrt{2}\,p|1,\bar{1};2,2\rangle\right] \\ \qquad + \frac{1}{2N_1}\left\{\frac{(1+8p^2)^{1/2}+1}{4}\left[\sqrt{2}\,\varepsilon_1|3\,1\,2\,0\rangle + \sqrt{6}\,\varepsilon_2|1,\bar{1};4\,2\rangle\right] + p\left[\sqrt{3}\,\varepsilon_1|3\,3\,2\,\bar{2}\rangle + \varepsilon_2|1\,1\,4\,0\rangle - \varepsilon_2|1\,1\,0\,0\rangle\right]\right\}\end{cases}$$

$$\Phi_2(0;1\,2):\begin{cases}\Phi_2^{+}(0;1\,2) = \frac{1}{N_2}\left[\sqrt{2}\,p|1\,1\,2\,\bar{2}\rangle - \frac{(1+8p^2)^{1/2}-1}{2}|1\,\bar{1};2\,0\rangle\right] \\ \qquad + \frac{1}{2N_2}\left\{\frac{(1+8p^2)^{1/2}-1}{4}\left[\sqrt{2}\,\varepsilon_1|3\,\bar{1}\,2\,0\rangle + \sqrt{6}\,\varepsilon_2|1\,1\,4\,\bar{2}\rangle\right] - p\left[\sqrt{3}\,\varepsilon_1|3\,\bar{3}\,2\,2\rangle + \varepsilon_2|1\,\bar{1}\,4\,0\rangle - \varepsilon_2|1\,\bar{1}\,0\,0\rangle\right]\right\} \\ \Phi_2^{-}(0;1,2) = \frac{1}{N_2}\left[\frac{(1+8p^2)^{1/2}-1}{2}|1,1;2\,0\rangle - \sqrt{2}\,p|1,\bar{1};2,2\rangle\right] \\ \qquad + \frac{1}{2N_2}\left\{p\left[\sqrt{3}\,\varepsilon_1|3\,3\,2\,\bar{2}\rangle + \varepsilon_2|1\,1\,4\,0\rangle - \varepsilon_2|1\,1\,0\,0\rangle\right] - \frac{(1+8p^2)^{1/2}-1}{4}\left[\sqrt{2}\,\varepsilon_1|3\,1\,2\,0\rangle + \sqrt{6}\,\varepsilon_2|1\,\bar{1}\,4\,2\rangle\right]\right\}\end{cases}$$

$$\Phi_3(0;1,2):\begin{cases}\Phi_3^{+}(0;1\,2) = \frac{1}{N_2}\left[\sqrt{2}\,p|1,1;2,\bar{2}\rangle - \frac{(1+8p^2)^{1/2}-1}{2}|1,\bar{1};2,0\rangle\right] \\ \qquad + \frac{1}{2N_2}\left\{p\left[\sqrt{3}\,\varepsilon_1|3\,\bar{3}\,2\,2\rangle + \varepsilon_2|1\,\bar{1}\,4\,0\rangle - \varepsilon_2|1\,\bar{1}\,0\,0\rangle\right] - \frac{(1+8p^2)^{1/2}-1}{4}\left[\sqrt{2}\,\varepsilon_1|3\,\bar{1}\,2\,0\rangle + \sqrt{6}\,\varepsilon_2|1\,1\,4\,\bar{2}\rangle\right]\right\} \\ \Phi_3^{-}(0;1,2) = \frac{1}{N_2}\left[-\frac{(1+8p^2)^{1/2}-1}{2}|1\,1\,2\,0\rangle + \sqrt{2}\,p|1\,\bar{1}\,2\,2\rangle\right] \\ \qquad + \frac{1}{2N_2}\left\{p\left[\sqrt{3}\,\varepsilon_1|3\,3\,2\,\bar{2}\rangle + \varepsilon_2|1\,1\,4\,0\rangle - \varepsilon_2|1\,1\,0\,0\rangle\right] - \frac{(1+8p^2)^{1/2}-1}{4}\left[\sqrt{2}\,\varepsilon_1|3\,1\,2\,0\rangle + \sqrt{6}\,\varepsilon_2|1\,\bar{1}\,4\,2\rangle\right]\right\}\end{cases}$$

$$\Phi_4(0;1,2):\begin{cases}\Phi_4^{+}(0;1,2) = \frac{1}{N_1}\left[\sqrt{2}\,p|1,1;2\,\bar{2}\rangle + \frac{(1+8p^2)^{1/2}+1}{2}|1,\bar{1};2\,0\rangle\right] \\ \qquad - \frac{1}{2N_1}\left\{p\left[\sqrt{3}\,\varepsilon_1|3\,\bar{3}\,2\,2\rangle + \varepsilon_2|1\,\bar{1}\,4\,0\rangle - \varepsilon_2|1\,\bar{1}\,0\,0\rangle\right] + \frac{(1+8p^2)^{1/2}+1}{4}\left[\sqrt{2}\,\varepsilon_1|3\,\bar{1}\,2\,0\rangle + \sqrt{6}\,\varepsilon_2|1\,1\,4\,\bar{2}\rangle\right]\right\} \\ \Phi_4^{-}(0;1\,2) = -\frac{1}{N_1}\left[\frac{(1+8p^2)^{1/2}+1}{2}|1\,1;2\,0\rangle + \sqrt{2}\,p|1\,\bar{1}\,2\,2\rangle\right] \\ \qquad + \frac{1}{2N_1}\left\{p\left[\sqrt{3}\,\varepsilon_1|3\,3\,2\,\bar{2}\rangle + \varepsilon_2|1\,1\,4\,0\rangle - \varepsilon_2|1\,1\,0\,0\rangle\right] + \frac{(1+8p^2)^{1/2}+1}{4}\left[\sqrt{2}\,\varepsilon_1|3\,1\,2\,0\rangle + \sqrt{6}\,\varepsilon_2|1\,\bar{1}\,4\,2\rangle\right]\right\}\end{cases}$$

Figure 5-8 Vibronic structure in π-electronic level as function of the Renner parameters (correct to second order).



5.7 Unsymmetrical Linear Tetratomic Molecules in π-Electronic Level

We assume that terms higher than the second-order (in vibrational r_k coordinates) are neglected. We have

$$H' = H^{(2)} = f_1 r_1^2 \cos 2(\theta-\phi_1) + f_2 r_2^2 \cos 2(\theta-\phi_2) + 2f_{12} r_1 r_2 \cos(2\theta-\phi_1-\phi_2) \tag{5.7.1}$$

The second-order interaction diagrams are shown by Fig. 5.9. The non-zero off-diagonal elements of the Van Vleck degenerate perturbation matrices are given by the same equation as Equation (5.5.9) of symmetrical molecules. The diagonal matrix elements are given by

$$\begin{aligned} z_r' &= \{\psi_r^o | H' | \psi_r^o\} \\ &= z_r - \frac{f_{12}^2 a_1 a_2}{2\hbar} (\upsilon_1+1)(1+\Lambda\ell_2)\left[\frac{1}{\omega_1+\omega_2} + \frac{1}{\omega_2+\omega_1}\right] \\ &\quad - \frac{f_{11}^2 a_1 a_2}{2\hbar} (\upsilon_2+1)(1+\Lambda\ell_1)\left[\frac{1}{\omega_1+\omega_2} - \frac{1}{\omega_2-\omega_1}\right] \end{aligned}$$

If we define ε_{12} by

$$\varepsilon_{12}^2 = \frac{f_{12} a_1 a_2}{\hbar |\omega_2^2 - \omega_1^2|} . \tag{5.7.2}$$

then

$$z_r' = z_r - \varepsilon_{12}^2 [\omega_2(\upsilon_1+1)(1+\Lambda\ell_2) - (\upsilon_2+1)(1+\Lambda\ell_1)\omega_1] \tag{5.7.3}$$

where z_r are given by Equation (5.5.8).

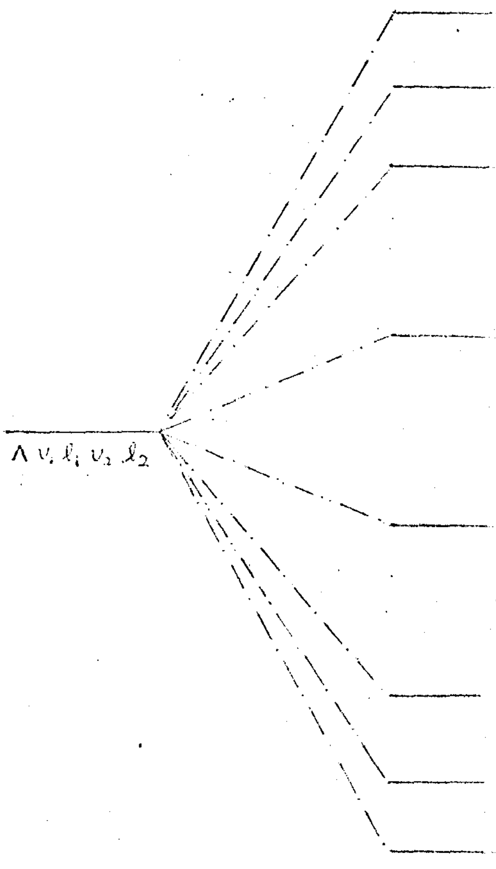
Hence if we replace z_r by z_r' into Section 5.6, the second-order vibronic energies for unsymmetrical linear tetratomic molecules may be obtained.

5.8 Symmetrical Linear Tetratomic Molecules in the Δ-Electronic Level

We shall complete the tetratomic case by showing the first-order

Fig. 5.9 The second-order interaction diagram for

$$H' = f_1 r_1^2 \cos 2(\theta-\phi_1) + f_2 r_2^2 \cos 2(\theta-\phi_2) + 2f_{12} r_1 r_2 \cos(2\theta-\phi_1-\phi_2)$$



Interacting states	Interaction coefficients
$\bar{\Lambda}\ v_1\ l_1\ v_2+2\ l_2+2\Lambda$	$-\frac{f_2}{4\hbar\omega_2} A(v_2+2, l_2+2\Lambda)$
$\bar{\Lambda}\ v_1+1\ l_1+\Lambda\ v_2+1\ l_2+\Lambda$	$-\frac{f_{12}}{\hbar(\omega_1+\omega_2)} q(v_1+1, l_1+\Lambda)\cdot q(v_2+1, l_2+\Lambda)$
$\bar{\Lambda}\ v_1+2\ l_1+2\Lambda\ v_2\ l_2$	$-\frac{f_1}{4\hbar\omega_1} A(v_1+2, l_1+2\Lambda)$
$\bar{\Lambda}\ v_1-1\ l_1+\Lambda\ v_2+1\ l_2+\Lambda$	$-\frac{f_{12}}{\hbar(\omega_2-\omega_1)} q(v_1-1, l_1+\Lambda)\cdot q(v_2+1, l_2+\Lambda)$
$\bar{\Lambda}\ v_1+1\ l_1+\Lambda\ v_2-1\ l_2+\Lambda$	$\frac{f_{12}}{\hbar(\omega_2-\omega_1)} q(v_1+1, l_1+\Lambda)\cdot q(v_2-1, l_2+\Lambda)$
$\bar{\Lambda}\ v_1-2\ l_1+2\Lambda\ v_2\ l_2$	$\frac{f_1}{4\hbar\omega_1} A(v_1-2, l_1+2\Lambda)$
$\bar{\Lambda}\ v_1-1\ l_1+\Lambda\ v_2-1\ l_2+\Lambda$	$\frac{f_{12}}{\hbar(\omega_1+\omega_2)} q(v_1-1, l_1+\Lambda)\cdot q(v_2-1, l_2+\Lambda)$
$\bar{\Lambda}\ v_1\ l_1\ v_2-2\ l_2+2\Lambda$	$\frac{f_2}{4\hbar\omega_2} A(v_2-2, l_2+2\Lambda)$

interaction diagrams for the symmetrical molecules in the Δ-electronic level. However, we shall not evaluate the energy expressions.

The vibronic perturbation for symmetrical linear tetratomic molecules in the Δ-electronic level is

$$H' = U'(Q) + H'_{\Delta} \tag{5.8.1}$$

where $U'(Q)$ is given by Equation (5.1.1) and H'_{Δ} is given by

$$H'_{\Delta} = h_1 r_1^4 \cos 4(\theta-\phi_1) + h_2 r_2^4 \cos 4(\theta-\phi_2) + 3h_{12} r_1^2 r_2^2 \cos(4\theta-2\phi_1-2\phi_2) \\ + \text{higher terms} \tag{5.8.2}$$

To symplify the dynamical problem, we shall neglect the anharmonic potential function $U'(Q)$ from Equation (5.8.1). Then the matrix elements

$$\langle\Lambda' v_1' \ell_1' v_2' \ell_2'|H'|\Lambda v_1 \ell_1 v_2 \ell_2\rangle = \langle\Lambda' v_1' \ell_1' v_2' \ell_2'|H'_{\Delta}|\Lambda v_1 \ell_1 v_2 \ell_2\rangle$$

are equal to zero unless

$$\Lambda' = -\Lambda \text{ and } \Lambda'+\ell_1'+\ell_2' = \Lambda+\ell+\ell_2 \equiv K; \; (\Lambda = \pm 2) \tag{5.8.3}$$

The classification of the vibronic state kets is shown in Fig. (5.10). The number of states with the same v_1, v_2 and K is $n_K(v_1,v_2)$. This denotes the size of the perturbation matrix. We list the $n_K(v_1,v_2)$ values in Table 5.11 . The second-order interaction diagram for a given state is shown by Fig. 5.12. The Van Vleck's basis function will be given by:

$$\psi_r^0(K; v_1 v_2) = |\Lambda^{(r)}; v_1, \ell_1^{(r)}; v_2, \ell_2^{(r)}\rangle - \frac{h_1}{8\hbar\omega_1}\Big\{ B(v_1+4, \ell_1+2\Lambda)|\bar{\Lambda}, v_1+4, \ell_1^{(r)}+2\Lambda^{(r)}; v_2\, \ell_2^{(r)}\rangle \\ - B(v_1-4, \ell_2+2\Lambda)|\bar{\Lambda}, v_1-4, \ell_1^{(r)}+2\Lambda^{(r)}, v_2, \ell_2^{(r)}\rangle + 2B(v_1+2, \ell_1+2\Lambda)|\bar{\Lambda}; v_1+2, \ell_1^{(r)}+2\Lambda^{(r)}; v_2, \ell_2^{(r)}\rangle \\ - 2B(v_1-2, \ell_1+2\Lambda)|\bar{\Lambda}, v_1-2, \ell_1^{(r)}+2\Lambda^{(r)}; v_2, \ell_2^{(r)}\rangle \Big\} -$$

Figure 5.10 Classification of vibronic kets $|\Lambda;v_1\ell_1v_2\ell_2\rangle = [v_1v_2](\Lambda;\ell_1\ell_2)$ in Δ-electronic level.

$[v_1,v_2]$	ee	oo	eo	oe	ee	oo	eo	oe	ee	oo	eo	oe	ee	oo
[05]			$(2,0\bar{1})(\bar{2},03)$				$(2,01)(\bar{2},05)$				$(2,03)$			
[14]				$(2\bar{1}0)(2,\bar{1}4)$ $(2,1\bar{2})(\bar{2},12)$				$(\bar{2},14)$ $(2,10)(2,\bar{1}2)$				$(2,12)(2,\bar{1}4)$		
[23]			$(\bar{2},21)(\bar{2},03)$ $(2,2\bar{3})(2,0\bar{1})(2,\bar{2}1)$				$(\bar{2},23)(2,\bar{2}3)$ $(2,2\bar{1})(2,01)$				$(2,03)(2,21)$			
[32]				$(\bar{2},30)(\bar{2},12)$ $(2,1\bar{2})(2\bar{1}0)(2,\bar{3}2)$				$(\bar{2},32)(2,3\bar{2})$ $(2,10)(2\bar{1}2)$				$(2,30)(2,12)$		
[41]			$(\bar{2},4\bar{1})(\bar{2};21)$ $(2,0\bar{1})(2,\bar{2}1)$				$(\bar{2},41)$ $(2,2\bar{1})(2,01)$				$(2,4\bar{1})(2,21)$			
[50]				$(\bar{2},30)(2,\bar{1}0)$				$(\bar{2},50)(2,10)$				$(2,30)$		
[04]	$(20\bar{2})(\bar{2}02)$				$(2,00)(\bar{2},04)$				$(2,02)$				$(2,04)$	
[13]		$(\bar{2},\bar{1}3)(\bar{2},11)$ $(2,\bar{1}3)(2,\bar{1}\bar{1})$				$(\bar{2},13)$ $(21\bar{1})(2,\bar{1}1)$				$(2,11)(2,\bar{1}3)$				$(2,13)$
[22]	$(\bar{2},02)(2,\bar{2}0)$ $(\bar{2},20)(2,0\bar{2})$				$(\bar{2},22)(2,\bar{2}2)$ $(2,2\bar{2})(2,00)$				$(2,20)(2,02)$				$(2,22)$	
[31]		$(\bar{2},3\bar{1})(\bar{2},11)$ $(2,\bar{3}1)(2,\bar{1}\bar{1})$				$(\bar{2},31)$ $(2,1\bar{1})(2,\bar{1}1)$				$(2,3\bar{1})(2,11)$				$(2,31)$
[40]	$(\bar{2},20)(2,\bar{2}0)$				$(2,00)(\bar{2},40)$				$(2,20)$				$(2,40)$	
[03]			$(2,0\bar{1})(\bar{2},03)$				(201)				(203)			
[12]				$(\bar{2},12)$ $(2,1\bar{2})(2,\bar{1}0)$				$(2,10)(2,\bar{1}2)$				(212)		
[21]			$(2,\bar{2}1)$ $(\bar{2};21)(2;0\bar{1})$				$(2;2,\bar{1})(2,01)$				(221)			
[30]				$(\bar{2};30)(2,\bar{1}0)$				$(2,10)$				(230)		
[02]	$(2;0,\bar{2})(\bar{2},02)$				$(2;00)$				$(2;02)$					
[11]		$(\bar{2};1,1)(2,\bar{1},\bar{1})$				$(2;1,\bar{1})(2;\bar{1},1)$				$(2;11)$				
[20]	$(2;\bar{2}0)(\bar{2};20)$				$(2;00)$				$(2;20)$					
[0,1]			$(2;01)$				$(2;01)$							
[1,0]				$(2;\bar{1},0)$				$(2;10)$						
[0,0]					$(2;0,0)$									
	K = 0		K = 1		K = 2		K = 3		K = 4		K = 5		K = 6	

Table 5.11 Number of states in $[\nu_1\nu_2]^K$ level within Δ-electronic level.

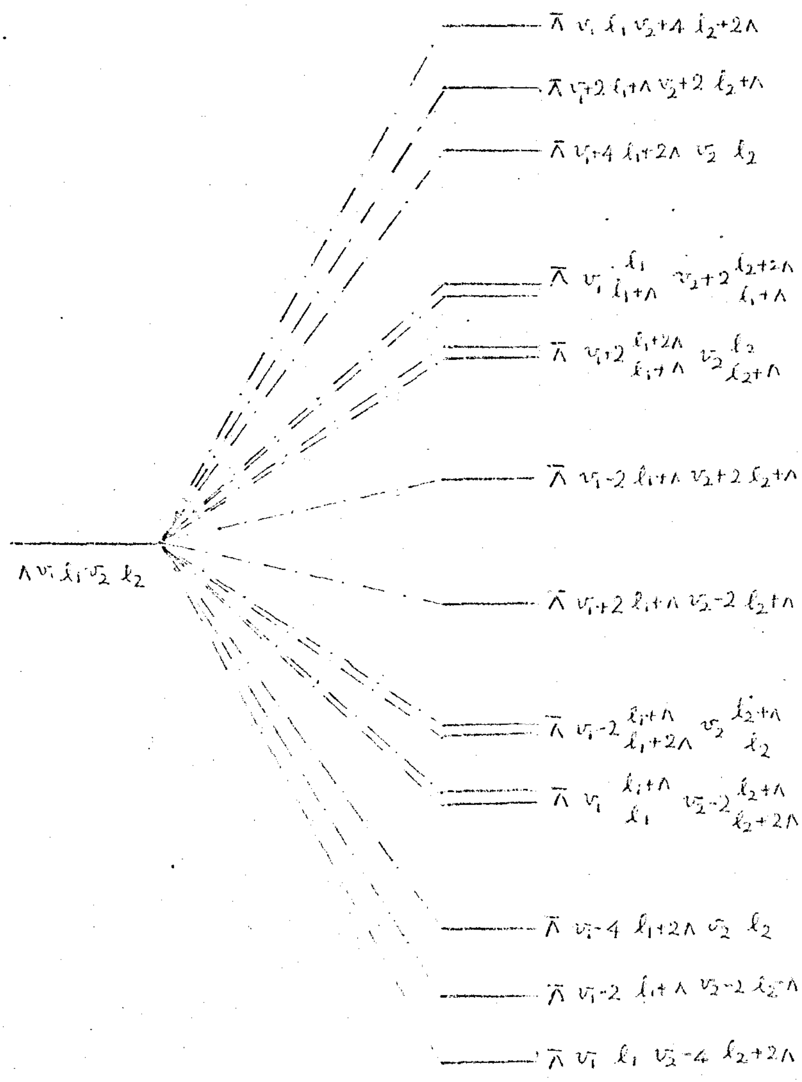
K $n_K(\nu_1\nu_2)$	0	2	4	6	8		
$n_K(0,0)$	0	1					
$n_K(0,2)$	2	1	1				
$n_K(0,4)$	2	2	1	1			
$n_K(0,6)$	2	2	2	1	1		
$n_K(0,8)$	2	2	2	2	1	1	
⋮							
$n_K(2,0)$	2	1	1				
$n_K(2,2)$	4	4	2	1			
$n_K(2,4)$	6	5	4	2	1		
$n_K(2,6)$	6	6	5	4	2	1	
$n_K(2,8)$	6	6	6	5	4	2	1
⋮							
$n_K(4,0)$	2	2	1	1	1		
$n_K(4,2)$	6	5	4	2	1		
$n_K(4,4)$	8	8	6	4	2	1	
$n_K(4,6)$	10	9	8	6	4	2	1
⋮							
$n_K(1,1)$	1	2	1				
$n_K(1,3)$	4	3	2	1			
$n_K(1,5)$	4	4	3	2	1		
$n_K(1,7)$	4	4	4	3	2	1	
⋮							
$n_K(3,1)$	4	3	2	1			
$n_K(3,3)$	6	6	4	2	1		
$n_K(3,5)$	8	7	6	4	2	1	
$n_K(3,7)$	8	8	7	6	4	2	1
⋮							
$n_K(5,1)$	4	4	3	2	1		
$n_K(5,3)$	8	7	6	4	2	1	
$n_K(5,5)$	10	10	8	6	4	2	1
⋮							

K $n_K(\nu_1\nu_2)$	1	3	5	7	9	
$n_K(0,1)$	1	1				
$n_K(0,3)$	2	1	1			
$n_K(0,5)$	2	2	1	1		
$n_K(0,7)$	2	2	2	1	1	
⋮						
$n_K(2,1)$	3	2	1			
$n_K(2,3)$	5	4	2	1		
$n_K(2,5)$	6	5	4	2	1	
$n_K(2,7)$	6	6	5	4	2	1
⋮						
$n_K(4.1)$	4	3	2	1		
$n_K(4,3)$	7	6	4	2	1	
$n_K(4,5)$	9	8	6	4	2	1
⋮						
$n_K(1,0)$	1	1				
$n_K(1,2)$	3	2	1			
$n_K(1,4)$	4	3	2	1		
$n_K(1,6)$	4	4	3	2	1	
⋮						
$n_K(3,0)$	2	1	1			
$n_K(3,2)$	5	4	2	1		
$n_K(3,4)$	7	6	4	2	1	
$n_K(3,6)$	8	7	6	4	2	1
⋮						
$n_K(5,0)$	2	2	1	1		
$n_K(5,2)$	6	5	4	2	1	
$n_K(5,4)$	9	8	6	4	2	1
⋮						

Fig. 5.12 The second-order interaction diagrams for the perturbation:

$$H'_\Delta = h_1 r_1^4 \cos 4(\theta-\phi_1) + h_2 r_2^4 \cos 4(\theta-\phi_2) + 3h_{12} r_1^2 r_2^2 \cos(4\theta-2\phi_1-2\phi_2)$$

in Δ-electronic level ($\Lambda = \pm 2$).



Interacting states $\vert\Lambda'; v_1'\ell_1'; v_2'\ell_2'\rangle$	Interaction coefficients $C^{\Lambda' v_1' \ell_1' v_2' \ell_2'}_{\Lambda\ v_1\ \ell_1\ v_2\ \ell_2}$
$\bar\Lambda\ v_1\ \ell_1\ v_2+4\ \ell_2+2\Lambda$	$-\frac{h_2}{8\hbar\omega_2} B(v_2+4, \ell_2+2\Lambda)$
$\bar\Lambda\ v_1+2\ \ell_1+\Lambda\ v_2+2\ \ell_2+\Lambda$	$-\frac{3h_{12}}{4\hbar(\omega_1+\omega_2)} A(v_1+2, \ell_1+\Lambda)\cdot A(v_2+2, \ell_2+\Lambda)$
$\bar\Lambda\ v_1+4\ \ell_1+2\Lambda\ v_2\ \ell_2$	$-\frac{h_1}{8\hbar\omega_1} B(v_1+4, \ell_1+2\Lambda)$
$\bar\Lambda\ v_1\ \ell_1\ v_2+2\ \ell_2+2\Lambda$ $\bar\Lambda\ v_1\ \ell_1+\Lambda\ v_2+2\ \ell_1+\Lambda$	$-\frac{h_2}{4\hbar\omega_2} B(v_2+2, \ell_2+2\Lambda)$ $-\frac{3h_{12}}{4\hbar\omega_2} A(v_1, \ell_1+\Lambda)\cdot A(v_2+2, \ell_2+\Lambda)$
$\bar\Lambda\ v_1+2\ \ell_1+2\Lambda\ v_2\ \ell_2$ $\bar\Lambda\ v_1+2\ \ell_1+\Lambda\ v_2\ \ell_2+\Lambda$	$-\frac{h_1}{4\hbar\omega_1} B(v_1+2, \ell_1+2\Lambda)$ $-\frac{3h_{12}}{4\hbar\omega_1} A(v_1+2, \ell_1+\Lambda)\cdot A(v_2, \ell_2+\Lambda)$
$\bar\Lambda\ v_1-2\ \ell_1+\Lambda\ v_2+2\ \ell_2+\Lambda$	$-\frac{3h_{12}}{4\hbar(\omega_2-\omega_1)} A(v_1-2, \ell_1+\Lambda)\cdot A(v_2+2, \ell_2+\Lambda)$
$\bar\Lambda\ v_1+2\ \ell_1+\Lambda\ v_2-2\ \ell_2+\Lambda$	$\frac{3h_{12}}{4\hbar(\omega_2-\omega_1)} A(v_1+2, \ell_1+\Lambda)\cdot A(v_2-2, \ell_2+\Lambda)$
$\bar\Lambda\ v_1-2\ \ell_1+\Lambda\ v_2\ \ell_2+\Lambda$ $\bar\Lambda\ v_1-2\ \ell_1+2\Lambda\ v_2\ \ell_2$	$\frac{3h_{12}}{4\hbar\omega_1} A(v_1-2, \ell_1+\Lambda)\cdot A(v_2, \ell_2+\Lambda)$ $\frac{h_1}{4\hbar\omega_1} B(v_1-2, \ell_1+2\Lambda)$
$\bar\Lambda\ v_1\ \ell_1+\Lambda\ v_2-2\ \ell_2+\Lambda$ $\bar\Lambda\ v_1\ \ell_1\ v_2-2\ \ell_2+2\Lambda$	$\frac{3h_{12}}{4\hbar\omega_2} A(v_1, \ell_1+\Lambda)\cdot A(v_2-2, \ell_2+\Lambda)$ $\frac{h_2}{4\hbar\omega_2} B(v_2-2, \ell_2+2\Lambda)$
$\bar\Lambda\ v_1-4\ \ell_1+2\Lambda\ v_2\ \ell_2$	$\frac{h_1}{8\hbar\omega_1} B(v_1-4, \ell_1+2\Lambda)$
$\bar\Lambda\ v_1-2\ \ell_1+\Lambda\ v_2-2\ \ell_2+\Lambda$	$\frac{3h_{12}}{4\hbar(\omega_1+\omega_2)} A(v_1-2, \ell_1+\Lambda)\cdot A(v_2-2, \ell_2+\Lambda)$
$\bar\Lambda\ v_1\ \ell_1\ v_2-4\ \ell_2+2\Lambda$	$\frac{h_2}{8\hbar\omega_2} B(v_2-4, \ell_2+2\Lambda)$

$$- \frac{h_2}{8\hbar\omega_2} \Big\{ B(v_2+4, \ell_2+2\Lambda)\, |\bar{\Lambda}^{(r)}; v_1, \ell_1^{(r)}; v_2+4, \ell_2^{(r)}+2\Lambda^{(r)}\rangle - B(v_2-4, \ell_2+2\Lambda) \cdot$$

$$|\bar{\Lambda}^{(r)}; v_1, \ell_1^{(r)}; v_2-4, \ell_2^{(r)}+2\Lambda^{(r)}\rangle + 2B(v_2+2, \ell_2+2\Lambda)\, |\bar{\Lambda}^{(r)}; v_1, \ell_1^{(r)}; v_2+2, \ell_2^{(r)}+2\Lambda^{(r)}\rangle$$

$$- 2B(v_2-2, \ell_2+2\Lambda)\, |\bar{\Lambda}^{(r)}; v_1, \ell_1^{(r)}; v_2-2, \ell_2^{(r)}+2\Lambda^{(r)}\rangle \Big\}$$

$$- \frac{3h_{12}}{4(\omega_1+\omega_2)} \Big\{ A(v_1+2, \ell_1+\Lambda) \cdot A(v_2+2, \ell_2+\Lambda)\, |\bar{\Lambda}^{(r)}; v_1+2, \ell_1^{(r)}+\Lambda^{(r)}; v_2+2, \ell_2^{(r)}+\Lambda\rangle - A(v_1-2, \ell_1+\Lambda) \cdot A(v_2-2, \ell_2+\Lambda)\, |\bar{\Lambda}; v_1-2, \ell_1^{(r)}+\Lambda^{(r)}, v_2-2,$$

$$- \frac{3h_{12}}{4(\omega_2-\omega_1)} \Big\{ A(v_1-2, \ell_1+\Lambda) A(v_2+2, \ell_2+\Lambda)\, |\bar{\Lambda}^{(r)}; v_1-2, \ell_1+\Lambda; v_2+2, \ell_2+\Lambda\rangle - A(v_1+2, \ell_1+\Lambda) A(v_2-2, \ell_2+\Lambda)\, |\bar{\Lambda}; v_1-2, \ell_1+\Lambda; v_2-2,$$

$$- \frac{3h_{12}}{4\hbar\omega_1} \Big\{ A(v_1+2, \ell_1+\Lambda) \cdot A(v_2, \ell_2+\Lambda)\, |\bar{\Lambda}^{(r)}; v_1+2, \ell_1+\Lambda; v_2, \ell_2+\Lambda\rangle - A(v_1-2, \ell_1+\Lambda) \cdot A(v_2, \ell_2+\Lambda)\, |\bar{\Lambda}^{(r)}; v_1-2, \ell_1+\Lambda; v_2, \ell_2$$

$$- \frac{3h_{12}}{4\hbar\omega_2} \Big\{ A(v_1, \ell_1+\Lambda) \cdot A(v_2+2, \ell_2+\Lambda)\, |\bar{\Lambda}^{(r)}; v_1, \ell_1+\Lambda; v_2+2, \ell_2+\Lambda\rangle - A(v_1, \ell_1+\Lambda) A(v_2-2, \ell_2+\Lambda)\, |\bar{\Lambda}^{(r)}; v_1, \ell_1+\Lambda; v_2+2, \ell_2$$

In this basis, the diagonal matrix elements of the Van Vleck degenerate perturbation matrix are given by:

$$z_r(K; v_1, v_2) = \sum_{v_1' v_2'} \left(\mathcal{E}^0_{v_1' v_2'} - \mathcal{E}^0_{v_1 v_2} \right) \left| C^{\bar{\Lambda}\, v_1' \ell_1' v_2' \ell_2'}_{\Lambda\, v_1 \ell_1 v_2 \ell_2} \right|^2$$

$$= \frac{h_2^2}{16\hbar\omega_2} \Big\{ B(v_2+4, \ell_2+2\Lambda)^2 - B(v_2-4, \ell_2+2\Lambda)^2 + 2B(v_2+2, \ell_2+2\Lambda)^2 - 2B(v_2-2, \ell_2+2\Lambda)^2 \Big\}$$

$$+ \frac{h_1^2}{16\hbar\omega_1} \Big\{ B(v_1+4, \ell_1+2\Lambda)^2 - B(v_1-4, \ell_1+2\Lambda)^2 + 2B(v_1+2, \ell_1+2\Lambda)^2 - 2B(v_1-2, \ell_1+2\Lambda)^2 \Big\}$$

$$+ \frac{9h_{12}^2}{8\hbar(\omega_1+\omega_2)} \Big\{ A(v_1+2, \ell_1+\Lambda)^2 \cdot A(v_2+2, \ell_2+\Lambda)^2 - A(v_1-2, \ell_1+\Lambda)^2 \cdot A(v_2-2, \ell_2+\Lambda)^2 \Big\}$$

$$+ \frac{9h_{12}^2}{8\hbar(\omega_2-\omega_1)} \Big\{ A(v_1-2, \ell_1+\Lambda)^2\, A(v_2+2, \ell_2+\Lambda)^2 - A(v_1+2, \ell_1+\Lambda)^2 \cdot A(v_2-2, \ell_2+\Lambda)^2 \Big\}.$$

$$+ \frac{9h_{12}^2}{8\hbar\omega_1} A(v_2, \ell_2+\Lambda)^2 \Big\{ A(v_1+2, \ell_1+\Lambda)^2 - A(v_1-2, \ell_1+\Lambda)^2 \Big\}$$

$$+ \frac{9h_{12}^2}{8\hbar\omega_2} A(v_1, \ell_1+\Lambda)^2 \Big\{ A(v_2+2, \ell_2+\Lambda)^2 - A(v_2-2, \ell_2+\Lambda)^2 \Big\}.$$

The non-zero, off-diagonal elements will be:

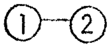
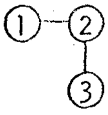
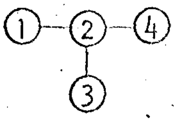
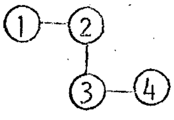
$$a_r(K; v_1, v_2) = \{ \psi_r^0(K; v_1, v_2) \,|\, H'_\Delta \,|\, \psi_{r+1}^0(K; v_1, v_2) \}$$

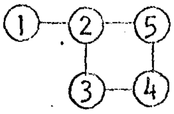
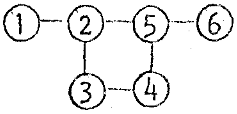
$$= \begin{cases} \langle \bar{\Lambda}^{(r)}; v_1, \ell_1^{(r)}+2\Lambda^{(r)}; v_2, \ell_2^{(r)} \,|\, H'_\Delta \,|\, \Lambda^{(r)}; v_1, \ell_1^{(r)}; v_2, \ell_2^{(r)} \rangle, & \text{or} \\ \langle \bar{\Lambda}^{(r)}; v_1, \ell_1^{(r)}; v_2, \ell_2^{(r)}+2\Lambda^{(r)} \,|\, H'_\Delta \,|\, \Lambda^{(r)}; v_1, \ell_1^{(r)}; v_2, \ell_2^{(r)} \rangle, & \text{or} \\ \langle \bar{\Lambda}^{(r)}; v_1, \ell_1^{(r)}+\Lambda; v_2, \ell_2^{(r)}+\Lambda^{(r)} \,|\, H'_\Delta \,|\, \Lambda^{(r)}; v_1, \ell_1^{(r)} v_2, \ell_2^{(r)} \rangle \end{cases}$$

$$= \begin{cases} \frac{h_1}{2} B(v_1, \ell_1^{(r)}+2\Lambda^{(r)}) , & \text{or} \\ \frac{h_2}{2} B(v_2, \ell_2^{(r)}+2\Lambda^{(r)}) ; & \text{or} \\ \frac{3h_{12}}{2} A(v_1, \ell_1^{(r)}+\Lambda^{(r)}) \cdot A(v_2; \ell_2^{(r)}+\Lambda^{(r)}) \end{cases}$$

If we ignore the diagonal matrix elements from the Van Vleck perturbation matrices, we obtain the ordinary first-order perturbation matrices. In the first-order interaction diagrams, the circle ⓡ stands for the rth state of the $[\nu_1, \nu_2]^K$ level, i.e., the state $|\psi_r^0(K; \nu_1, \nu_2)\rangle$. The $n_K(\nu_1, \nu_2)$ states can be so arranged (so numbered) that the first-order perturbation matrices will have the symmetrical appearance as shown in Fig. 5.13.

Fig. 5.13 The first-order interaction diagrams and their first-order perturbation matrices.

$n_K(v_1,v_2)$	Corresponding first-order perturbation matrices	First-order interaction diagrams	Vibronic levels $[v_1,v_2]^K$
$n_K(v_1,v_2) = 1$	$\begin{array}{c} \psi^o \\ \boxed{} \end{array}$		$[0,0]^2,[1,0]^1,[1,0]^3;$ $[2,0]^2,[2,0]^4;[1,1]^4,$ $[3,0]^3,[3,0]^5;[2,1]^5,$ $[4,0]^4,[4,0]^6,[3,1]^6,$ etc.
$n_K(v_1,v_2) = 2$	$\begin{array}{cc} \psi_1^o & \psi_2^o \\ & \\ & \end{array}$		$[1,1]^2,[2,1]^3,[3,1]^4,$ $[2,2]^4,[4,1]^5,[3,2]^5,$ etc.
$n_K(v_1,v_2) = 2$	$\begin{pmatrix} & a \\ a & \end{pmatrix}$		$[2,0]^0,[1,1]^0,[3,0]^1,$ $[4,0]^0,[4,0]^2,[5,0]^1,$ $[5,0]^3$, etc.
$n_K(v_1,v_2) = 3$	$\begin{array}{ccc} \psi_1^o & \psi_2^o & \psi_3^o \\ & a_1 & \\ a_1 & & a_2 \\ & a_2 & \end{array}$		$[2,1]^1,[3,1]^2,[4,1]^3,$ etc.
$n_K(v_1,v_2) = 4$	$\begin{array}{cccc} \psi_1^o & \psi_2^o & \psi_3^o & \psi_4^o \\ & a_1 & & \\ a_1 & & a_2 & a_2' \\ & a_2 & & \\ & a_2' & & \end{array}$		$[2,2]^2,[3,2]^3$, etc.
$n_K(v_1,v_2) = 4$	$\begin{array}{cccc} & a_1 & & \\ a_1 & & a_2 & \\ & a_2 & & a_3 \\ & & a_3 & \end{array}$		$[3,1]^0,[2,2]^0,[4,1]^1,$ etc.

$n_K(\nu_1,\nu_2)$	Corresponding first-order perturbation matrices	First-order interaction diagrams	Vibronic Levels $[\nu_1,\nu_2]^K$
$n_K(\nu_1,\nu_2) = 5$	$\begin{array}{cccccc} \psi_1^o & \psi_2^o & \psi_3^o & \psi_4^o & \psi_5^o & \psi_6^o \\ & a_1 & & & & \\ a_1 & & a_2 & & a_2' & \\ & a_2 & & a_3 & & \\ & & a_3 & & a_4 & \\ & a_2' & & a_4 & & a_5 \\ & & & & a_5 & \end{array}$		[3,2] ,[4,2] ,[5,2] , etc.
$n_K(\nu_1,\nu_2) = 6$			[4,2] , etc.

CHAPTER 6

First-Order Vibronic Interactions For General Linear Polyatomic Molecules in Π-Electronic Level

6-1. Linear Pentatomic Molecules

The vibronic Schröedinger Equation for a linear pentatomic molecule can be represented by:

$$\{H_e^o + U^o(Q) + H' + T_N - E\}\Psi = 0$$

where the perturbation H' in second-order of vibrational coordinates is given by:

$$\begin{aligned} H' = {} & f_1 r_1^2 \cos 2(\theta-\phi_1) + f_2 r_2^2 \cos 2(\theta-\phi_2) + f_3 r_3^2 \cos 2(\theta-\phi_3) \\ & + 2f_{12} r_1 r_2 \cos(2\theta-\phi_1-\phi_2) + 2f_{13} r_1 r_3 \cos(2\theta-\phi_1-\phi_3) \\ & + 2f_{23} r_2 r_3 \cos(2\theta-\phi_2-\phi_3) \end{aligned} \tag{6.1.1}$$

(If the molecule is symmetrical, $f_{12} = f_{23} = 0$.)

Thus a given "unperturbed" state $|\Lambda;v_1,\ell_1;v_2\ell_2;v_3\ell_3>$ can interact at most with twenty-one other states (Fig. 6.1); three of them have the same v_1, v_2 and v_3 values.

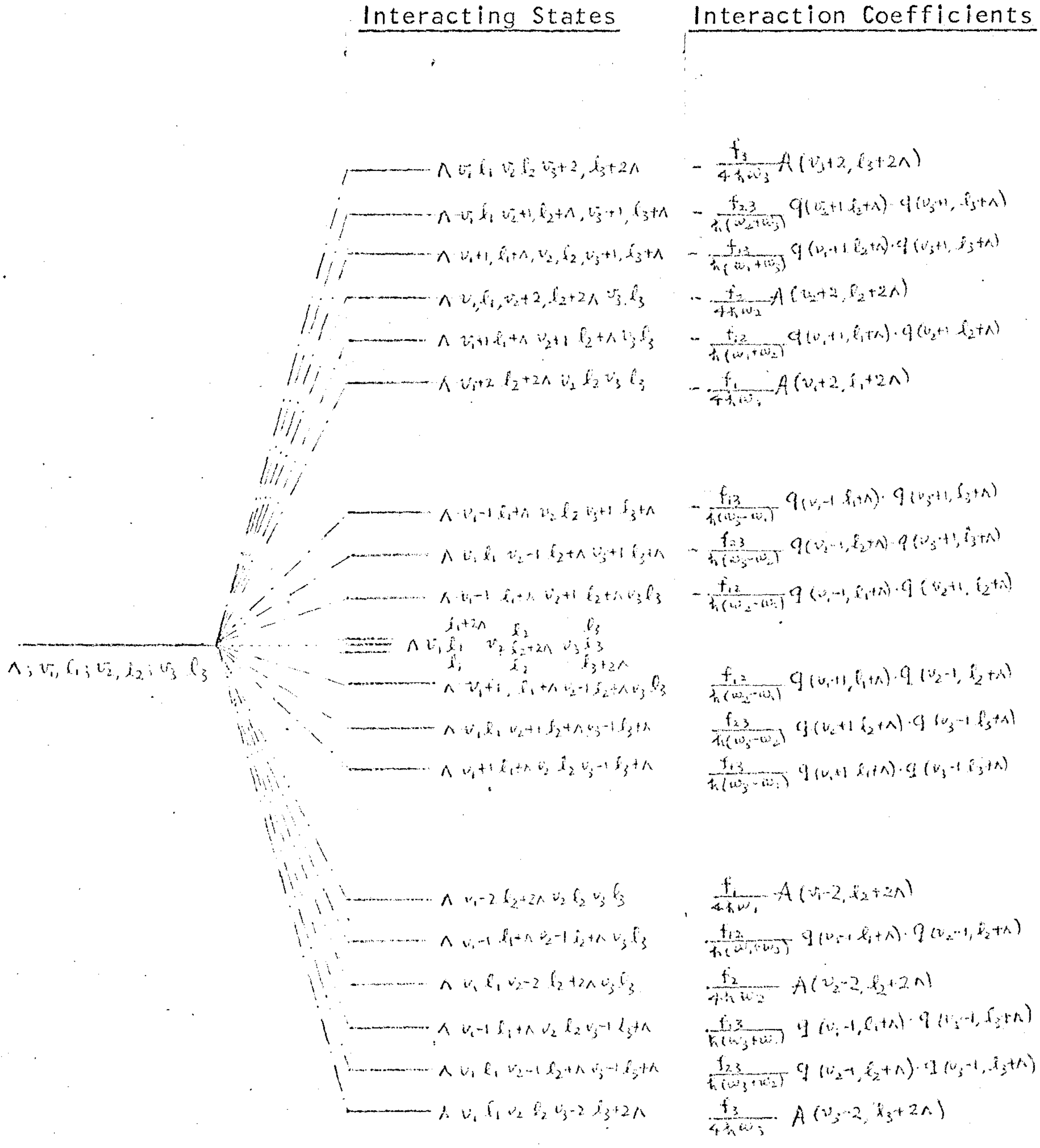
A vibronic level with vibronic quantum number K and vibrational quantum numbers v_1, v_2 and v_3 will be designated by $[v_1,v_2,v_3]^K$. The number of components of such level is denoted by $n_K(v_1,v_2,v_3)$. If $n_K(v_1,v_2,v_3) > 1$, then the level will be split in first-order by the perturbation (6.1.1).

The Van Vleck basis functions are: $(\Lambda^{(r)} = \pm 1)$

$$\psi_r^o(K;v_1,v_2,v_3) = |\Lambda^{(r)};v_1,\ell_1^{(r)};v_2,\ell_2^{(r)};v_3,\ell_3^{(r)}> + \phi_r^{(1)}(K;v_1,v_2,v_3)$$

Fig. 6.1 Second-order interaction diagrams for H'_π:

$$H'_\pi = \sum_k f_k r_k^2 \cos 2(\theta-\phi_k) + \sum_{k'<k}\sum 2f_{k'k} r_{k'} r_k \cos(2\theta-\phi_{k'}-\phi_k)$$



where
$$\phi_r^{(1)}(K;v_1,v_2,v_3) = -\sum_{k=1}^{3} \frac{f_k}{4\hbar\omega_k} \Big\{ A(v_k+2, \ell_k^{(r)}+2\Lambda^{(r)}) \,|\bar{\Lambda}^{(r)}; \cdots v_k+2, \ell_k^{(r)}+2\Lambda^{(r)}; \cdots \rangle$$
$$- A(v_k-2, \ell_k^{(r)}+2\Lambda^{(r)}) \cdot |\bar{\Lambda}^{(r)}; \; v_k-2, \ell_k+2\Lambda \rangle \Big\} - \sum_{k<k'}^{3}\sum \frac{f_{kk'}}{\hbar(\omega_k+\omega_{k'})} \Big\{ q(v_k+1, \ell_k^{(r)}+\Lambda^{(r)}) \cdot$$
$$\cdot q(v_{k'}+1, \ell_{k'}^{(r)}+\Lambda^{(r)}) \,|\bar{\Lambda}^{(r)}; v_k+1, \ell_k^{(r)}+\Lambda^{(r)}; v_{k'}+1, \ell_{k'}^{(r)}+\Lambda^{(r)}; v_{k''}, \ell_{k''}^{(r)} \rangle - q(v_k-1, \ell_k^{(r)}+\Lambda^{(r)}) \cdot$$
$$\cdot q(v_{k'}-1, \ell_{k'}^{(r)}+\Lambda^{(r)}) \,|\bar{\Lambda}^{(r)}; v_k-1, \ell_k^{(r)}+\Lambda^{(r)}, v_{k'}-1, \ell_{k'}^{(r)}+\Lambda^{(r)}; v_{k''}, \ell_{k''}^{(r)} \rangle \Big\} - \sum_{k<k'}\sum \frac{f_{kk'}}{(\omega_k-\omega_{k'})\hbar} \Big\{$$
$$\cdot q(v_k+1, \ell_k^{(r)}+\Lambda^{(r)}) \cdot q(v_{k'}-1, \ell_{k'}^{(r)}+\Lambda^{(r)}) \,|\bar{\Lambda}^{(r)}; v_k+1, \ell_k^{(r)}+\Lambda^{(r)}; v_{k'}-1, \ell_{k'}^{(r)}+\Lambda^{(r)}; v_{k''}, \ell_{k''}^{(r)} \rangle$$
$$- q(v_k-1, \ell_k^{(r)}+\Lambda^{(r)}) \, q(v_{k'}+1, \ell_{k'}^{(r)}+\Lambda^{(r)}) \,|\bar{\Lambda}^{(r)}; v_k-1, \ell_k^{(r)}+\Lambda^{(r)}; v_{k'}+1, \ell_{k'}^{(r)}+\Lambda^{(r)}; v_{k''}, \ell_{k''}^{(r)} \rangle \Big\}.$$

Hence the diagonal elements of the Van Vleck perturbation matrix are given by: (setting $\hbar = 1$)

$$z_r(K;\nu_1,\nu_2,\nu_3) = -\frac{1}{8} \sum_{k=1}^{3} \varepsilon_k^2 \omega_k (\nu_k+1)(2+\Lambda^{(r)}\ell_k^{(r)})$$
$$- 8\varepsilon_{12}^2[\omega_2(\nu_2+1)(1 + \Lambda^{(r)}\ell^{(r)}) - \omega_1(\nu_1+1)(1 + \Lambda^{(r)}\ell_2^{(r)})]$$
$$- 8\varepsilon_{23}^2[\omega_3(\nu_3+1)(1 + \Lambda^{(r)}\ell_2^{(r)}) - \omega_2(\nu_2+1)(1 + \Lambda^{(r)}\ell_3^{(r)})]$$
$$- 8\varepsilon_{13}^2[\omega_3(\nu_3+1)(1 + \Lambda^{(r)}\ell_1^{(r)}) - \omega_1(\nu_1+1)(1 + \Lambda^{(r)}\ell_3^{(r)})]$$
$$= -\frac{1}{8} \sum_{k=1}^{3} \{(\nu_k+1)(2 + \Lambda^{(r)}\ell_k^{(r)})\varepsilon_k^2 + \sum_{k'\neq k} 8\, s_{kk'}(\nu_k+1)$$
$$(1 + \Lambda^{(r)}\ell_{k'}^{(r)})\varepsilon_{kk'}^2\}\omega_k \qquad (6.1.2)$$

where we have defined that

$$\varepsilon_k = \frac{f_k a_k}{\hbar\omega_k}$$

$$\varepsilon_{kk'}^2 = \frac{f_{kk'}^2 a_k a_{k'}}{\hbar^2|\omega_k^2 - \omega_{k'}^2|}; \qquad (k' \neq k) \qquad (6.1.3)$$

and
$$s_{kk'} = \frac{|\omega_k^2 - \omega_{k'}^2|}{\omega_k^2 - \omega_{k'}^2} = \begin{cases} +1, & \text{if } \omega_k > \omega_{k'} \\ -1, & \text{if } \omega_k < \omega_{k'} \end{cases}$$

The nonvanishing off-diagonal matrix elements are:

$$\begin{aligned} a_r(K;\upsilon_1,\upsilon_2,\upsilon_3) &= \tfrac{1}{2}f_k\langle\upsilon_k,\ell_k^{(r)} + 2\Lambda|q^2_{k\Lambda}|\ \upsilon_k,\ell_k^{(r)}\rangle \\ &= \tfrac{1}{2}f_k A(\upsilon_k+0,\ell_k^{(r)}+2\Lambda) \\ &= \tfrac{1}{2}\varepsilon_k\hbar\omega_k(\upsilon_k - \Lambda^{(r)}\ell_k^{(r)})^{\frac{1}{2}}(\upsilon_k+\Lambda^{(r)}\ell_k^{(r)}+2)^{\frac{1}{2}}; \\ &(k = 1,\ 2,\ 3) \qquad (6.1.4) \end{aligned}$$

We see that the $f_{kk'}r_kr_{k'}\cos(2\theta-\phi_k-\phi_{k'})$ terms enter only in second-order, since the $f_{kk'}$ appear in the elements z_r, but not in the elements a_r.

The dynamical solutions can be classified into three cases:

Case (A): $[\upsilon_k,0,0]^K$

When two of the $[\upsilon_1,\upsilon_2,\upsilon_3]$ are equal to zero, or only one f_k is different from zero, the problem is analogous to that in triatomic molecules. Chapter 4 can be applied.

Case (B): $[\upsilon_k,\upsilon_{k'},0]^K$

When one of the $[\upsilon_1,\upsilon_2,\upsilon_3]$ is equal to zero, or one of the f_k's is zero, we have the problem analogous to that in tetratomic molecules and thus Chapter 5 is useful.

Case (C): $[\upsilon_1,\upsilon_2,\upsilon_3]^K$

Neither υ_k nor f_k is equal to zero. The first-order perturbation matrices are usually of large dimension. The forms of these perturbation matrices and their corresponding first-order interaction diagrams with the basis component states properly ordered are shown in Fig. 6-2. We notice that there is no matrix of $n_K(\upsilon_1\upsilon_2\upsilon_3) = 2, 3, 5, 15$, etc. Only matrices of $n_K(\upsilon_1\upsilon_2\upsilon_3) \lesssim 6$ can be solved algebraically.

Fig. 6-2. The first-order interaction diagrams and their corresponding perturbation matrices for linear pentatomic molecules.
—ⓡ— refer to the r^{th} component of the level $[v_1,v_2,v_3]^K$.

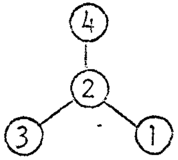
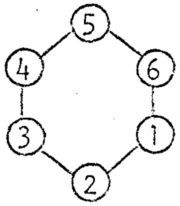
Degeneracy of the level $[v_1,v_2,v_3]^K$: $n_K(v_1,v_2,v_3)$	The first-order interaction diagrams	The first-order perturbation matrices	Vibronic levels $[v_1,v_2,v_3]^K$
$n_K(v_1,v_2,v_3) = 1$		$\begin{array}{c} \psi_1^0 \\ \hline \multicolumn{1}{\|c\|}{\quad} \\ \hline \end{array}$	$K = v_1+v_2+v_3+1$ e.g., $[1,1,1]^4$, $[1,2,2]^6$,......
$n_K(v_1,v_2,v_3) = 4$		$\begin{array}{cccc} \psi_1^0 & \psi_2^0 & \psi_3^0 & \psi_4^0 \\ \hline & a_1 & & \\ a_1 & & a_2 & b \\ & a_2 & & \\ & b & & \\ \hline \end{array}$	$K = v_1+v_2+v_3-1$ e.g., $[1,1,1]^2$, $[1,1,3]^4$, $[1,2,4]^6$ ......
$n_K(v_1,v_2,v_3) = 6$		$\begin{array}{cccccc} \psi_1^0 & \psi_2^0 & \psi_3^0 & \psi_4^0 & \psi_5^0 & \psi_6^0 \\ \hline & a_1 & & & & b_{1,6} \\ a_1 & & a_2 & & & \\ & a_2 & & a_3 & & \\ & & a_3 & & a_4 & \\ & & & a_4 & & a_5 \\ b_{1,6} & & & & a_5 & \\ \hline \end{array}$	$[1,1,1]^0$

Fig. 6-2 cont'd.

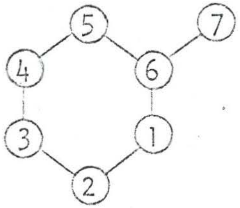
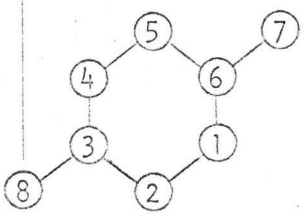
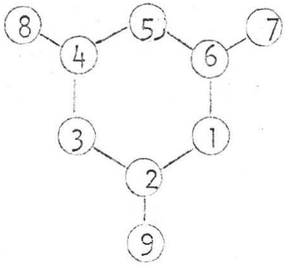
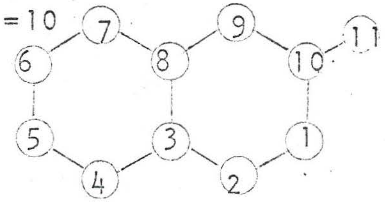
Degeneracy of the level $[\nu_1,\nu_2,\nu_3]^K$: $n_K(\nu_1,\nu_2,\nu_3)$	The first-order interaction diagrams	The first-order perturbation matrices	Vibronic levels $[\nu_1,\nu_2,\nu_3]^K$
$n_K(\nu_1,\nu_2,\nu_3) = 7$		$\begin{array}{ccccccc} \psi_1^0 & \psi_2^0 & \psi_3^0 & \psi_4^0 & \psi_5^0 & \psi_6^0 & \psi_7^0 \\ & a_1 & & & & b_{1,6} & \\ a_1 & & a_2 & & & & \\ & a_2 & & a_3 & & & \\ & & a_3 & & a_4 & & \\ & & & a_4 & & a_5 & \\ b_{1,6} & & & & a_5 & & a_6 \\ & & & & & a_6 & \end{array}$	$[1,1,2]^{1}$, $[1,1,3]^{2}$, $[1,1,4]^{3}$, $[1,1,5]^{4}$
$n_K(\nu_1,\nu_2,\nu_3) = 8$		$\begin{array}{cccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ & a_1 & & & & b_{1,6} & & \\ a_1 & & a_2 & & & & & \\ & a_2 & & a_3 & & & & b_{3,8} \\ & & a_3 & & a_4 & & & \\ & & & a_4 & & a_5 & & \\ b_{1,6} & & & & a_5 & & a_6 & \\ & & & & & a_6 & & \\ & & b_{3,8} & & & & & \end{array}$	$[1,1,3]^{0}$, $[1,1,4]^{1}$, $[1,1,5]^{0}$, $[1,1,5]^{2}$, $[1,2,2]^{2}$, $[1,3,3]^{4}$

Fig. 6-2 cont'd.

Degeneracy of the level $[\nu_1,\nu_2,\nu_3]^K$ $n_K(\nu_1,\nu_2,\nu_3)$	The first-order interaction diagrams	The first-order perturbation matrices	Vibronic levels $[\nu_1,\nu_2,\nu_3]^K$
$n_K(\nu_1,\nu_2,\nu_3)=8$		$\begin{array}{ccccccccc} 1&2&3&4&5&6&7&8&9 \\ \hline &a_1&&&&b_{1,6}&&& \\ a_1&&a_2&&&&&&b_{2,9} \\ &a_2&&a_3&&&&& \\ &&a_3&&a_4&&&b_{4,8}& \\ &&&a_4&&a_5&&& \\ b_{1,6}&&&&a_5&&a_6&& \\ &&&&&a_6&&& \\ &&&b_{4,8}&&&&& \\ &b_{2,9}&&&&&&& \end{array}$	$[1,2,2]^2$ $[1,2,3]^3$ $[1,2,4]^4$
$n_K(\nu_1,\nu_2,\nu_3)=9$			$[2,2,2]^3$ $[2,2,3]^4$
$n_K(\nu_1,\nu_2,\nu_3)=10$		$\begin{array}{ccccccccccc} 1&2&3&4&5&6&7&8&9&10&11 \\ \hline &a_1&&&&&&&&b_{1,10}& \\ a_1&&a_2&&&&&&&& \\ &a_2&&a_3&&&&b&&& \\ &&a_3&&a_4&&&&&& \\ &&&a_4&&a_5&&&&& \\ &&&&a_5&&a_6&&&& \\ &&&&&a_6&&a_7&&& \\ &&b_{3,8}&&&&a_7&&a_8&& \\ &&&&&&&a_8&&a_9& \\ b_{1,10}&&&&&&&&a_9&&a_{10} \\ &&&&&&&&&a_{11}& \end{array}$	$[1,2,2]^0$
$n_K(\nu_1,\nu_2,\nu_3)=11$			$[1,2,3]^1$ $[1,2,4]^2$

6-2 First-order Vibronic Interaction for General Linear Polyatomic Molecules in Π-Electronic Level.

In the Π-electronic level, the vibronic perturbation to second-order in the vibrational coordinates can be written as

$$H' = \sum_{k=1}^{t} f_k r_k^2 \cos 2(\theta-\phi_k) + \sum_{k<k'}^{t} \sum^{t} 2 f_{kk'} r_k r_{k'} \cos(2\theta-\phi_k-\phi_{k'})$$

where t=number of bending vibrations. Only the first portion of the function H' is responsible for the first-order effect. We may define H' by

$$H_1' \equiv \sum_{k=1}^{t} f_k r_k^2 \cos 2(\theta-\phi_k) \qquad (6\text{-}2\text{-}2)$$

If we donate $q_{\Pi}^{(+)}$, $q_{\Pi}^{(-)}$, $Q_{\Pi}^{(+)}$ and $Q_{\Pi}^{(-)}$ respectively by:

$$q_{\Pi}^{(+)} = e^{\pm 2i} = q_{\pm}^2$$

$$Q_{\Pi}^{(\pm)} = \sum_{k=1}^{t} \frac{1}{2} f_k r_k^2 e^{\pm 2i\phi k} = \frac{1}{2} \sum_{k=1} f_k q_{k\pm}^2 \qquad (6\text{-}2\text{-}3)$$

then

$$H_1' = q_{\Pi}^{(+)} Q_{\Pi}^{(-)} + q_{\Pi}^{(-)} Q_{\Pi}^{(+)} \qquad (6\text{-}2\text{-}2')$$

We may use H_1' to evaluate the first-order perturbation matrices and the first-order vibronic energies. However, we have shown in Ch. 5 and §6-1 that, even in those cases where the first-order perturbation theory is sufficent, we still have mathematical difficulties, namely the algebraic solution of the general quartic and higher order equations. For example (App. D)

$$C_o\lambda^n + C_1\lambda^{n-1} + C_2\lambda^{n-2} + \ldots + C_{n-1}\lambda + C_n = 0 \qquad (6\text{-}2\text{-}4)$$

$$(n \geq 4)$$

Numerical solutions of equations of the type (6-2-4) are possible only if all C_n are know, which means that in order to obtain the splittings of the vibronic levels, we have to know the values of the f_k and ω_k; because the C_n are functions of these quantities. One could try to obtain these quantities from electronic spectroscopy. Unfortunately, in the presence of a 'multiple' Reuner effect, the spectra of linear molecules are very complicated(43), the assignments for the spectral lines needs the guidance of theory, and only after that can one calculate the values of f_k and ω_k. Such interdependence between theory and experiment is not unusual. In the cases where the theory is applicable, one may evaluate the vibronic energy levels using the different sets of values for f_k and ω_k. By using these results one can predict the appearance of the spectrum (Ch. 7). The coincidence of the theoretical spectrum and the experimental one will be a proof of the existence of multiple Renner effect. Or if some preliminary assignments of a few experimental lines is possible these few lines can be used to evaluate the Renner parameters and then the other spectral lines can be calculated from theory.

To obtain the first-order vibronic energies, one has to set up the first-order perturbation matrices. We have seen in the previous chapter and sections that a given first-order interaction diagram will give one particular form of the perturbation matrix. Each form of matrix requires one specific diagonalization method. In the following we shall only summarize the first-order vibronic interaction diagrams for linear molecules (having t bending modes) in Π-electronic level. No mathematical solutions are attempted.

We denote that

$$|\Lambda; \underset{\sim}{v}, \underset{\sim}{\ell}\rangle = |\Lambda; v_1, \ell_1; v_2, \ell_2; v_3, \ell_3 \cdots\rangle = |\Lambda\rangle \prod_{k=1}^{t} |v_k, \ell_k\rangle \qquad (6\text{-}2\text{-}4)$$

Within the vibronic level $[v_1, v_2, \ldots]^K$, the nonvanishing matrix elements are:

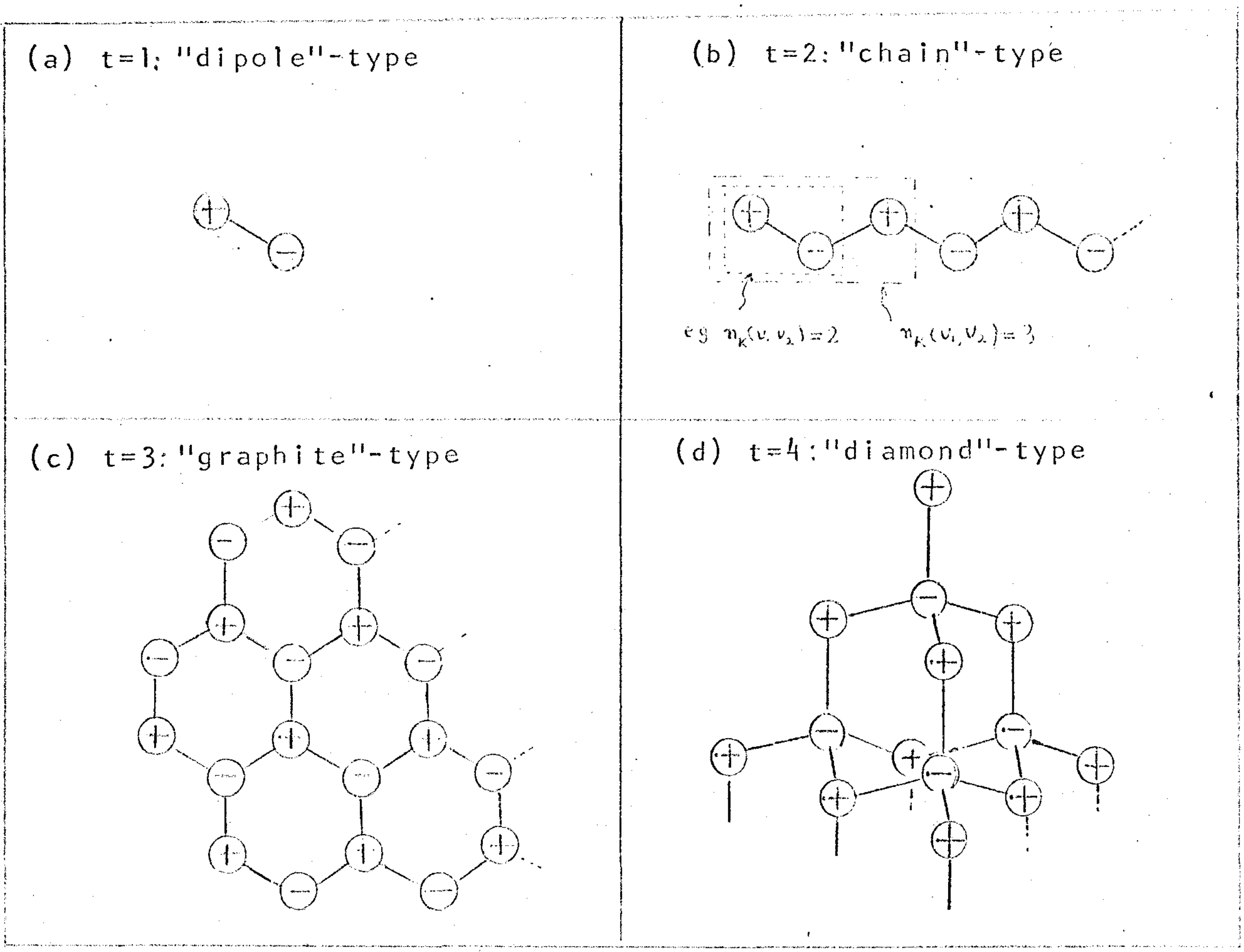
$$\langle \bar{\Lambda}^{(r)}; \underset{\sim}{v}, \underset{\sim}{\ell}' | H_1' | \Lambda^{(r)}, \underset{\sim}{v}, \underset{\sim}{\ell}^{(r)}\rangle = \langle \bar{\Lambda}^{(r)} | q_\Pi^{\bar{\Lambda}} | \Lambda^{(r)}\rangle \langle \underset{\sim}{v}, \underset{\sim}{\ell}' | Q_\Pi^{\Lambda^{(r)}} | \underset{\sim}{v}, \underset{\sim}{\ell}^{(r)}\rangle, \qquad \Lambda^{(r)} = \pm 1,$$

Since $\langle \bar{\Lambda}^{(r)} | q_\Pi^{\bar{\Lambda}} | \Lambda^{(r)}\rangle = 1$,

$$\langle \bar{\Lambda}^{(r)}; \underset{\sim}{v}, \underset{\sim}{\ell}' | H_1' | \Lambda^{(r)}; \underset{\sim}{v}, \underset{\sim}{\ell}^{(r)}\rangle = \sum_{k=1}^{t} \tfrac{1}{2} f_k \langle v_k, \ell_k' | q_{k\Lambda}^2 | v_k, \ell_k\rangle \prod_{k' \neq k}^{t} \delta_{\ell_{k'}', \ell_{k'}} = \tfrac{1}{2} f_k \mathcal{A}(v_k, \ell_k + 2\Lambda); \quad (k = 1, 2, \cdots t) \qquad (6\text{-}2\text{-}5)$$

Equation (6-2-5) says that the number of nonvanishing (off-diagonal) matrix element in one row (or column) can be as large as the number of bending modes (t). As number of bending modes (t) increases, the forms of the first-order perturbation matrices and the types of the general first-order interaction diagrams become more complicated (Fig. 6-3).

Fig. 6-3. The general first-order vibronic interaction diagrams for molecules having t bending vibrations. For a given t, any first-order interaction diagram is a part of the general diagram. Figures (a), (b), (c), and (d) are for t=1,2,3, and 4 respectively. The + and - signs in the circles refer to $\Lambda^{(r)} = +1$ or -1,



(a) t=1; "dipole"-type

(b) t=2: "chain"-type

(c) t=3: "graphite"-type

(d) t=4: "diamond"-type

CHAPTER 7

Vibronic Transitions

7-1 Electric dipole transitions

A transition between two states Ψ_m and Ψ_m resulting in the emission or absorption of radiation is possible only if the transition moment integral

$$\vec{M}^{mn} = \int \Psi_m{}^* \vec{M} \Psi_n d\tau \qquad (7\text{-}1\text{-}1)$$

is different from zero. The 'dipole' moment vector $\vec{M}$ is given by

$$\vec{M} = \vec{M}^e + \vec{M}^N \qquad (7\text{-}1\text{-}2)$$

with $$\vec{M}^e = \sum_i^{\text{electrons}} e\vec{r}_i$$

and $$\vec{M}^N = \sum_\alpha^{N\ \text{atoms}} Z_\alpha \vec{r}_\alpha$$

where e is the electronic charge and Z_α the nuclear charge of the αth atom. The three components of $\vec{M}$ (M_x, M_y, M_z) will transform as the translational operators T_x, T_y and T_z respectively in any point group. If we define M_σ $(\sigma = +, 0, -)$ by

$$M_\sigma = \begin{cases} M_0 = M_z \\ M_{\pm} = \frac{1}{\sqrt{2}}(M_x \pm iM_y) \end{cases} \qquad (7\text{-}1\text{-}3)$$

then in the $D_{\infty h}$ point group, M_0 belongs to Σ_u^+ representation, M_+ and M_- belong to $\Pi_u^{(+)}$ and $\Pi_u^{(-)}$ representations. Under the rotational operation $C_\infty(\Phi)$:

$$\left.\begin{aligned} C_\infty(\Phi) M_\sigma &= M_\sigma \\ C_\infty(\Phi) M_{\pm} &= e^{\pm i\Phi} M_{\pm} \end{aligned}\right\} \quad \text{or } C_\infty(\Phi) M_\sigma = e^{i\sigma\Phi} M_\sigma \qquad (7\text{-}1\text{-}4a)$$

Because of the u-symmetry, the inversion operation gives

$$E^{-1}M_\sigma = -M_\sigma \qquad (7\text{-}1\text{-}4b)$$

For each component M_σ, we have from Eq. (7-1-1),

$$M_\sigma^{mn} = \int \Psi_m{}^* M_\sigma \Psi_n \, d\tau \qquad (7\text{-}1\text{-}1)$$

If M_σ^{mn} is different from zero, we have parallel transition. This requires that the symmetry product

$\Gamma(\Psi_m)$ X $\Gamma(\Psi_n)$ must contain Σ_u^+ representation. (7-1-5a)

If M_+^{mn} and /or M_-^{mn} are/is different from zero, we have perpendicular transition. This requires that

$\Gamma(\Psi_m)$ X $\Gamma(\Psi_n)$ must contain Π_u representation. (7-1-5b)

Formal selection rules give no information about how strong a band will be if it is 'allowed'. However the selection rules say that under certain circumstances a band is 'forbidden' and must have zero intensity. The quantity relating the transition moment integral to the relative intensities of the bands is the so-called 'oscillater strength' (f) which is given by (for absorption):

$$\begin{aligned} f_\sigma^{mn} &= \frac{\Pi m_e c}{3he^2} |M_\sigma^{mn}|^2 \Delta\mathcal{E}_{mn} \\ &= 1.085 \times 10^{11} \frac{|M_\sigma^{mn}|^2}{e^2} \Delta\mathcal{E}_{mn} (\mathrm{cm}^{-1}) \qquad (7\text{-}1\text{-}6) \end{aligned}$$

where m_e and e are mass and charge of the electron, and $\Delta\mathcal{E}_{mn}$ is the energy difference between the states m and n. As the quantity 1.085 X 10^{11} is in units of cm^{-1}, and $|M_{\sigma}^{mn}|^2/e^2$ in units of $(\mathring{A})^2=10^{-16}\mathrm{cm}^2$, the oscillator strength f_{σ}^{mn} is a number which may be of the order one for a strong electronic transition.

Often a band will be forbidden for an idealized system, such as a harmonic oscillator or a molecule without vibronic interaction, but will be allowed when various kinds of interactions occur. For convenience such bands are generally referred to as 'forbidden' bands and the relatively small intensities for these bands which are actually observed provide information about the true nature of the molecule.(42)

7-2 Electronic Transitions and Vibronic Perturbations

We shall discuss the electronic transitions in increasing order of vibronic interactions. In the following, we assume that the excited and ground states are of Π_u and Σ_g^+ symmetry respectively.

(A) Zeroth-order approximation.

If both (a) and (b) type vibronic interaction (1.2) are negligibly small, the vibronic wave functions may be given by:

$$\Psi^m = \psi_{\Lambda'}^{o}(r_i;o)\Phi_v(Q) \qquad (7\text{-}2\text{-}1a)$$

and

$$\Psi^n == \psi_{\Lambda}^{o}(r_i;o)\chi_v(Q) \qquad (7\text{-}2\text{-}1b)$$

where the $\psi_{\Lambda'}^{o}$ and ψ_{Λ}^{o} are the zeroth-order electronic wave functions which are independent of nuclear coordinates and that

$$\langle\psi_{\Lambda'}^{o}|\psi_{\Lambda}^{o}\rangle_{el}=\int\psi_{\Lambda'}^{o}(r_i;o)^*\psi_{\Lambda}^{o}(r_i;o)\,d\tau_e=\delta_{\Lambda'\Lambda}$$

The $\Phi_{v'}(Q)$ and $\chi_v(Q)$ are the nuclear functions associated with the Λ' and Λ-electronic states respectively.

Thus the transition moment integrals become

$$\begin{aligned} M_\sigma^{\Lambda'v';\Lambda v} &= \int \Phi_{v'}(Q)^* \, \psi_{\Lambda'}^{o}(\vec{r}_i;o)^*(M_\sigma^e+M_\sigma^N)\psi_\Lambda^o(\vec{r}_i;o)\chi_v(Q)\,d\tau_{el}\,d\tau_Q \\ &= \langle\psi_{\Lambda'}^o(\vec{r}_i,o)|M_\sigma^e|\psi_\Lambda^o\rangle_{el} \int \Phi_{v'}^*(Q)\cdot\chi_v(Q)\,d\tau_Q \\ &+\langle\psi_{\Lambda'}^{o}(\vec{r}_i;o)|\psi_\Lambda^o(\vec{r}_i;o)\rangle_{el} \int \Phi_{v'}^*(Q)M_\sigma^N\,\chi_v(Q)\,d\tau_Q \end{aligned}$$

By definition of 'Electronic Transitions', Λ' is different from Λ then

$$M_\sigma^{\Lambda'v'\Lambda v} = M_\sigma^{\Lambda'\Lambda}(Q^\circ)\langle\Phi_{v'}^*(Q)|\chi_v(Q)\rangle_Q \tag{7-2-2}$$

where $$M_\sigma^{\Lambda'\Lambda}(Q^\circ) = \langle\psi_{\Lambda'}^o(\vec{r}_i;o)|M_\sigma^e|\psi_\Lambda^o(\vec{r}_i;o)\rangle_{el} \tag{7-2-3}$$

Thus in the zeroth order approximation, $M_\sigma^{\Lambda'v'\Lambda v}$ is proportional to the electronic transition moment integral $(M_\sigma^{\Lambda'\Lambda})$ and the vibrational overlap integral. If $M_\sigma^{\Lambda'\Lambda}$ is different from zero, the transition is called 'electronically allowed', otherwise, 'electronically forbidden'.

The selection rules for electronically allowed transitions in linear molecules are (4):

(a) for parallel transition, i.e. $\langle\psi_{\Lambda'}^o(\vec{r}_i;0)|M_o|\psi_\Lambda^o(\vec{r}_i;o)\rangle\neq 0$,

$$\Delta\Lambda = \Lambda' - \Lambda = 0 \text{ , e.g. } \Sigma-\Sigma,\ \Pi-\Pi,\ \Delta-\Delta \text{ etc.} \tag{7-2-4a}$$

(b) for perpendicular transitions, i.e. $\langle\psi_{\Lambda'}^o(\vec{r}_i;o)|M_{\pm}|\psi_\Lambda^o(\vec{r}_i;0)\rangle\neq 0$

$$\Delta\Lambda = \Lambda' - \Lambda = \pm 1, \text{ e.g. } \Sigma-\Pi,\ \Pi-\Delta, \text{ etc.} \tag{7-2-4b}$$

(c) for symmetrical linear molecules, since the $M_o, M_\pm$ belong to u symmetry, the selection rule on parity of the states are

$$g \leftrightarrow u, \quad g \not\leftrightarrow g, \quad u \not\leftrightarrow u \qquad (7\text{-}2\text{-}4c)$$

Thus the electronic transition $\Pi_u \leftarrow \Sigma_g^+$ is a perpendicular one. The vibrational transitions will be proportional to the vibraitonal overlap integral. The transitions form three sequences; $\Delta v_k = +2, 0$, and -2, of which the one with $\Delta v_k = 0$ is the strongest. (Ref 8, p158). This is shown in Fig. 7-1a.

(B) First-order electronic transitions.

When the (b) type vibronic interaction is negligibly small (or when the electronic are nondegenerate), the vibronic wave funciton can be given in Born-Oppenheimer approximation:

$$\Psi^m = \psi_{\Lambda'}(\vec{r}_i;Q)\cdot\Phi_{v'}(Q) \qquad (7\text{-}2\text{-}5a)$$

and

$$\Psi^n = \psi_{\Lambda}(r_i;Q)\cdot\ {}_{v}(Q) \qquad (7\text{-}2\text{-}5b)$$

Thus the transition moment integral is given by

$$M_\sigma^{\Lambda'v';\Lambda v} = \int \Phi_v(Q)^* \langle\psi_{\Lambda'}(\vec{r}_i;Q)|M_\sigma^e|\psi_\Lambda(\vec{r}_i;Q)\rangle_{el}\cdot\chi_v(Q)\,d\tau_Q$$

$$+ \langle\psi_{\Lambda'}(\vec{r}_i;Q)|\psi_\Lambda(\vec{r}_i;Q)\rangle_{el}\cdot\int \Phi_v(Q)^* M_\sigma^N\,\chi_v(Q)\,d\tau_Q$$

For different electronic states, the Born-Oppenheimer electronic wave functions are orthogonal, therefore

$$M_\sigma^{\Lambda'v';\Lambda v} = \langle\Phi_v(Q)|M_\sigma^{\Lambda'\Lambda}(Q)|\chi_v(Q)\rangle_Q \qquad (7\text{-}2\text{-}6)$$

where the electronic dipole moments integral $M_\sigma^{\Lambda'\Lambda}(Q)$ is a function of normal coordinates:

$$M_\sigma^{\Lambda'\Lambda}(Q) \equiv \langle\psi_{\Lambda'}(\vec{r}_i;Q)\,|M_\sigma^e|\psi_\Lambda(\vec{r}_i;Q)\rangle_{el} \qquad (7\text{-}2\text{-}7)$$

which may be expanded in the power series as

$$M_\sigma^{\Lambda'\Lambda}(Q) = M_\sigma^{\Lambda'\Lambda}(Q^\circ) + \sum_{\underline{q}_k} \underline{q}_k \cdot \left(\frac{\partial M_\sigma^{\Lambda'\Lambda}(Q)}{\partial \underline{q}_k}\right)_{Q=Q^\circ} + \ldots \qquad (7\text{-}2\text{-}8)$$

If the functions $\psi_\Lambda(\vec{r}_i,Q)$, could be given by

$$\psi_\Lambda(\vec{r}_i,Q) = \psi_{\Lambda'}^{0}(\vec{r}_i;Q^\circ) + \psi_{\Lambda'}^{(1)}(\vec{r}_i;Q)$$

then $M_\sigma^{\Lambda'\Lambda}(\overset{\circ}{Q})$ of Eq. (7-2-7) will just be given by Eq. (7-2-3) and Eq. (7-2-6) becomes

$$M_\sigma^{\Lambda'v;\Lambda v} = M_\sigma^{\Lambda'\Lambda}(Q^\circ)\cdot\langle\Phi_{v'}(Q)|\chi_v(Q)\rangle_Q + \sum_{\underline{q}_k}\left(\frac{\partial M_\sigma^{\Lambda'\Lambda}(Q)}{\partial \underline{q}_k}\right)_{Q^\circ}$$
$$\cdot\langle\Phi_{v'}(Q)|\underline{q}_k|\chi_v(Q)\rangle + \ldots \qquad (7\text{-}2\text{-}9)$$

Thus $M_\sigma^{\Lambda'v;\Lambda v}$ is not necessarily equal to zero as $M_\sigma^{\Lambda'\Lambda}(Q^\circ)$ is zero (while in case (a), it is). If $M_\sigma^{\Lambda'\Lambda}(Q^\circ)$ is zero but $M_\sigma^{\Lambda'\Lambda}(Q)$ is different from zero, the transitions are defined as 'electronically forbidden' but 'vibroncially allowed'. In this case, Eq. (7-2-9) becomes

$$M_\sigma^{\Lambda'v;\Lambda v} = \sum_{\underline{q}_k}\left(\frac{\partial M_\sigma^{\Lambda'\Lambda}(Q)}{\partial q_k}\right)_{Q^\circ}\cdot\langle\Phi_{v'}(Q)|\underline{q}_k|\chi_v(Q)\rangle$$
$$(7\text{-}2\text{-}10)$$

Since the nonvanishing terms are arised from the first-order and higher terms of the Taylor series expansion, they are presumably very small. Hence the (relative) intensities, which is proportional to $|M_{\sigma}^{\Lambda' v' \Lambda v}|^2$, in this case will be very weak in comparison with the 'electronically allowed' transitions.

Consider the absorption transition from the Σ_g^+ ground electronic state to the Π_u excited state for an acetylene-like molecule without the (b) type vibronic interaction. We may write, for the excited states (Section 5-1):

$$\begin{aligned} \psi_{\Pi a}(\vec{r}_i, Q)\ \Phi^a(Q) &= \sqrt{2} u_{\Pi}(z,p)\cos(\theta-\chi)\cdot\Phi_{v'}(Q), \text{ or} \\ &\sqrt{2} u_{\Pi}(z,p)\sin(\theta-\chi)\cdot\Phi\ (Q) \end{aligned}$$

and for the ground state:

$$\psi_{\Sigma}(\vec{r}_i;Q)\chi_v(Q)$$

When the (a)-type vibronic interaction is not negligible, the ground state function $\psi_{\Sigma}(\vec{r}_i;Q)$ correct to the first-order will be given by

$$\psi_{\Sigma}(\vec{r}_i,Q) = \psi_{\Sigma}^{0}(\vec{r}_i,Q) + \psi_{\Sigma}^{(1)}(\vec{r}_i;Q)$$

Since there exists a perturbation term in the multipole expansion (Ch. 3)

$$\begin{aligned} V_1' &= \sum_{\alpha=A}^{N} 2\ G_1^{(\alpha)}\cos(\theta-\phi\alpha) \\ &= \sum_k\left(\sum_\alpha \ell_k^\alpha F_{10}^{(\alpha)}(z,p)e^{i\theta}\right)r_k e^{-i\phi_k} \\ &+ \sum_k\left(\sum_\alpha \ell_k^\alpha F_{10}^{(\alpha)}(z,p)e^{-i\theta}\right)r_k e^{+i\phi_k} \\ &+ 0(r_k^2) \end{aligned}$$

Thus the first-order correction to ψ_{Σ} is given by

$$\psi_{\Sigma}^{(1)} = \psi_{+\Pi}^{0} \sum_{k} \beta_k q_{k-} + \psi_{-n}^{0} \sum_{k} \beta_k q_{k+}$$

with

$$\beta_k = (W_{\Pi}^{\circ} - W_{\Sigma}^{\circ})^{-1} <\pm\Pi | \sum_{\alpha} \ell_k^{\alpha} F_{1,0}^{(\alpha)}(z,p) e^{\pm i\theta} | \Sigma>$$

The M_o^e component of Eq. (7-2-1) will give the following electric dipole integral:

$$\begin{aligned} M_o^{\Pi\leftarrow\Sigma}(Q) &= <\psi_{\Pi a}(\vec{r}_i, Q) | M_o^e | \psi_{\Sigma}^{\circ} + \psi_{\Sigma}^{(1)}>_{el} \\ &= <\psi_{\Pi a}(\vec{r}_i, Q) | M_o^e | \psi_{\Pi}^{(1)}> \\ &= <+\Pi | M_o^e | +\Pi>_{el} \sum_{k} \frac{1}{\sqrt{2}} \beta_k r_k e^{-i(\phi_k - \chi)} \\ &\pm <-\Pi | M_o^e | -\Pi>_{el} \sum_{k} \frac{1}{\sqrt{2}} \beta_k r_k e^{+i(\phi_k - \chi)} \qquad (7\text{-}2\text{-}11) \end{aligned}$$

which will be different from zero if the molecule is unsymmetrical (if the molecule is symmetrical and if there is only one Π state, $<\pm\Pi | M_{\sigma}^e | \pm\Pi> = 0$) and thus the 'forbidden' parallel electronic transition become allowed. However, it is expected to be weak for the β_k factors are inversely proportional to the energy difference, $(W_{\Pi}^{\circ} - W_{\Sigma}^{\circ})$, and will be small.

(C) John-Teller-Renner Effect

When the (b)-type vibronic interaction becomes significant, the wave functions of the $[v_1, v_2]^K$ vibronic level for 'acetylene' molecules in Π- electronic state are given by [Eq (5-5-12)]:

$$\Psi_j(K;v_1,v_2) = \sum_{r=1}^{n_K(v_1,v_2)} \psi_r^0(K;v_1,v_2)S_{rj}(K;v_1,v_2)$$

These states are characterized by the vibronic angular momentum quantum number K and the even and odd values of v_1 and v_2. The oddness and evenness of v_1 and v_2 together with g or u symmetry of the electronic state determine the parity of the vibronic state. The quantum number K determines the rotational symmetry ie.

$$C_\infty(\phi)|\Psi_j(K;v_1,v_2)>= e^{iK\phi}|\Psi_j(K;v_1,v_2)> \qquad (7\text{-}2\text{-}12)$$

Of course, the vibronic states of any electronic level of linear molecule may be characterized by a quantum number K and the parities of v_1 and v_2 : $\Psi_i(K;v_1,v_2)$. The transition from the i-state of the ground state to the j-state of the excited state is possible only if the transition moment integrals

$$M_\sigma^{ji} = < \Psi_j(K;v_1,v_2)|M_\sigma| \Psi(K';v_1',v_2')>$$

are different from zero. Thus the direct product $\Gamma(\Psi_j)X\Gamma(\Psi_i)X\Gamma(M_\sigma)$, must contain the totally symmetric representation. Using Eq's (7-2-12) and (7-1-4a), we obtain the selection rules in K:

$$\Delta K = K' - K = 0, \pm 1$$

The selection rules for the total angular momentum are $\Delta K=0$, in the case of a Π-Π electronic transition, and $|\Delta K| = 1$ when the electronic transition is between a Π- and a Σ or a Π and Δ-state.

For small values of the Renner parameters ε_k, and particularly when there is no significant mutual influence of electronic levels, then the selection ruel is: $\Delta v_k = 0, 2, 4$ where $\Delta v_k = 0$ sequences is the strongest (Ref 8, p158). For strong interactions, the second-order perturbation theory will fail, and the significance of the $[v_1, v_2]$ designation of the vibronic level is lost.

The most important consequence of vibronic interaction is the Renner-Teller splitting of the spectral lines (Fig. 7-1b). The splitting introduces a lot of complications and difficulties in analyzing the spectrum. However, the existence of this splitting may be used to recognize the degeneracy of a given electronic state of a linear molecule even if the rotational structure is not resolved$^{(43)}$. For a given vibrational level $[v_1, v_2]$ in Π-electronic level, the total number of splittings $\mathcal{N}_{v_1, v_2}$ due to Renner-Teller Effect is given by:

$$\mathcal{N}_{v_1 v_2} = \begin{cases} (v_1+1)(v_2+1), & \text{if } (v_1+v_2) \text{ is even} \\ \sum\limits_{k=o,2}^{v_1+v_2+1} n_k(v_1, v_2), & \text{if } (v_1+v_2) \text{ is odd} \end{cases} \qquad (7\text{-}2\text{-}13)$$

where $n_K(v_1,v_2)$ is given by Eq. (5-5-1).

The band system at 1250 Å of C_2H_2 has been found to be a $^1\Pi_u - ^1\Sigma_g^+$ transition. The hot bands accompanying the main bands show evidence of Renner-Teller splitting.(43) Energy expressions for the lowest vibronic states in the Π-electronic level can be obtained from §5-6. In Table 7-2, we list some preliminary results for the $\tilde{G}(\Pi_u) \leftarrow \tilde{X}(\Sigma_g)$ system of C_2H_2 and C_2D_2 using the data provided by Dr. G. Herzberg.(44) The data given is insufficient to determine all necessary parameters, ie., two vibrational frequencies and two Renner parameters. However, we have been able to estimate the following values

for C_2D_2 : $\omega_2(\pi_g) \simeq 604.45$ cm^{-1}, $\varepsilon_2 \simeq 0.1022$

and for C_2H_2 : $\omega_2(\pi_g) \sim 732.1$ cm^{-1}, $\varepsilon_2 \sim 0.1023$

We can not verify these values, and we have no idea about the magnitude of ε_1 and $\omega_1(\pi_u)$. If we assume that $\varepsilon_2 = \varepsilon_1$, then for C_2D_2, $\omega_1 = 253.2$ cm^{-1} and for C_2H_2, $\omega_1 = 406.8$ cm^{-1}. Fig. 7-1 c,d are constructed with the above mentioned values.

7-3 Infrared Spectroscopy*

We shall consider the vibrational transitions in linear tetratomic molecules with doubly degenerate electronic

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*Formulation of this section borrows a lot from M. G. Child et al(19) thus it can be regarded as one of the many comparisons between Jahn-Teller and Renner effects.

Table 7-2

Vibronic energies in the $\tilde{G}(\Pi_u)$ electronic state of C_2D_2 and C_2H_2 molecules

vibronic states	Energies in cm^{-1} C_2D_2	C_2H_2	Second order vibronic energy expressions**
$[0,1]^0\Sigma_u^{-}$***	80815.4*	80916.7	$E_o+\omega_1+2\omega_2+\varepsilon_2\omega_2-\frac{1}{4}(\varepsilon_1^2\omega_1+\varepsilon_2^2\omega_2)$
$[0,1]^2\Delta_u$	80744.0		$E_o+\omega_1+2\omega_2-\frac{1}{4}(\varepsilon_1^2\omega_1+3\varepsilon_2^2\omega_2)$
$[0,1]^0\Sigma_u^+$	80691.9	80766.9	$E_o+\omega_1+2\omega_2-\varepsilon_2\omega_2-\frac{1}{4}(\varepsilon_1^2\omega_1+\varepsilon_2^2\omega_2)$
$[1,0]^2\Delta_g$	80401.1	80514.35	$E_o+2\omega_1+\omega_2-\frac{1}{4}(3\varepsilon_1^2\omega_1+\varepsilon_2^2\omega_2)$
$[0,0]^1\Pi_u$	80149.2	80109.7	$E_o+\omega_1+\omega_2-\frac{1}{4}(\varepsilon_1^2\omega_1+\varepsilon_2^2\omega_2)$

---

* energies are measured from the Q heads to the vibrationless state of the ground electronic state.

** ω_1 and ω_2 correspond to $\nu_5(\pi_u)$ and $\nu_4(\pi_g)$ respectively. E_o is the energy of the unperturbed [0,0] vibrational level of the ${}^1\pi_u$ state

*** We have interchanged the Σ_u^- and Δ_u designations given by Dr. G. Henzberg because from the energy expressions, Δ_u $[0,1]^2$state, should be between the two $\Sigma_u[0,1]^0$ states.

Figure 7-1. Schematic vibronic transitions for "acetylene" molecule: (a) without Renner-Teller splitting; (b) with Renner-Teller splitting; (c) spectra for hyperthetic C_2H_2; (d) spectra for hyperthetic C_2D_2.

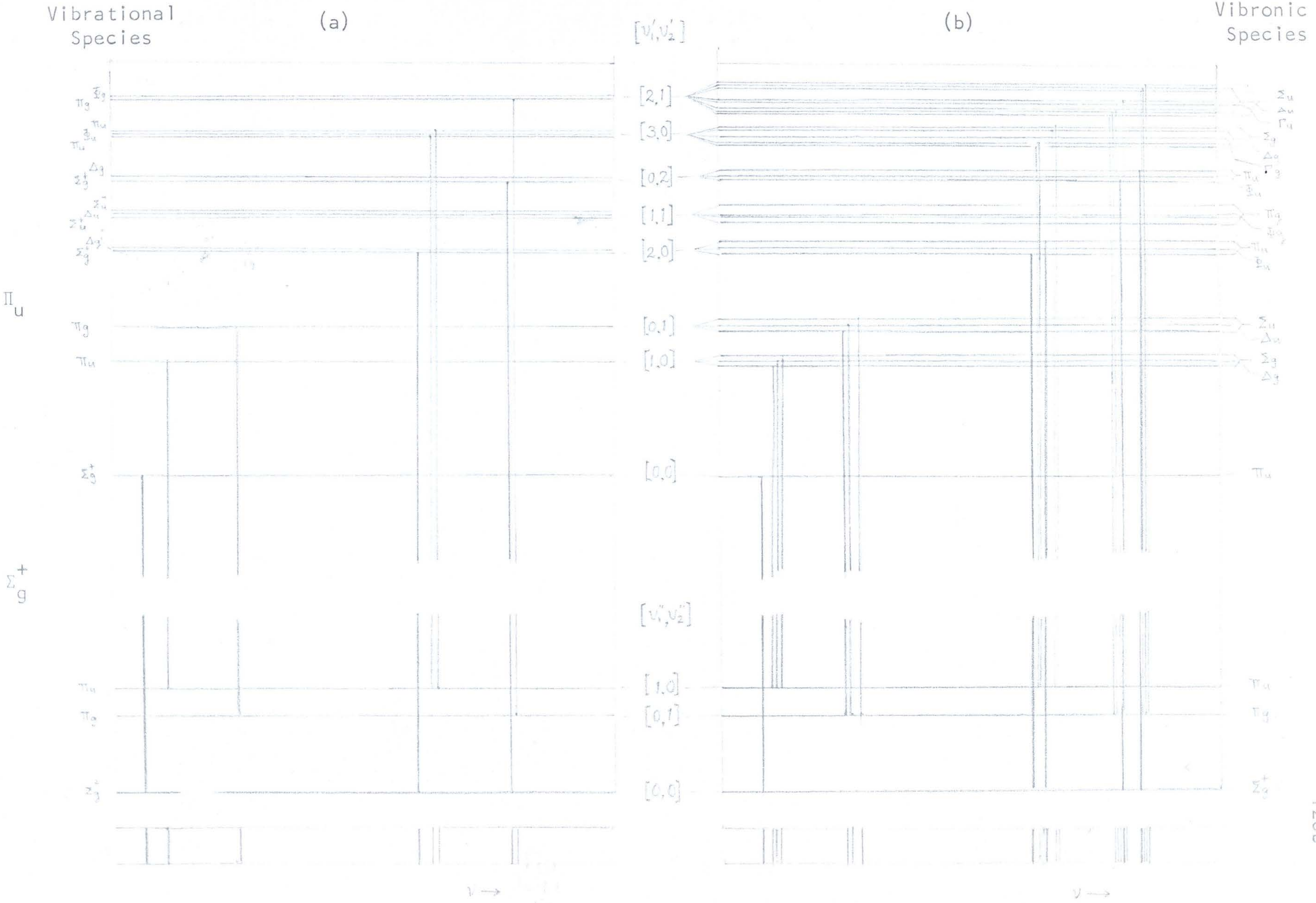
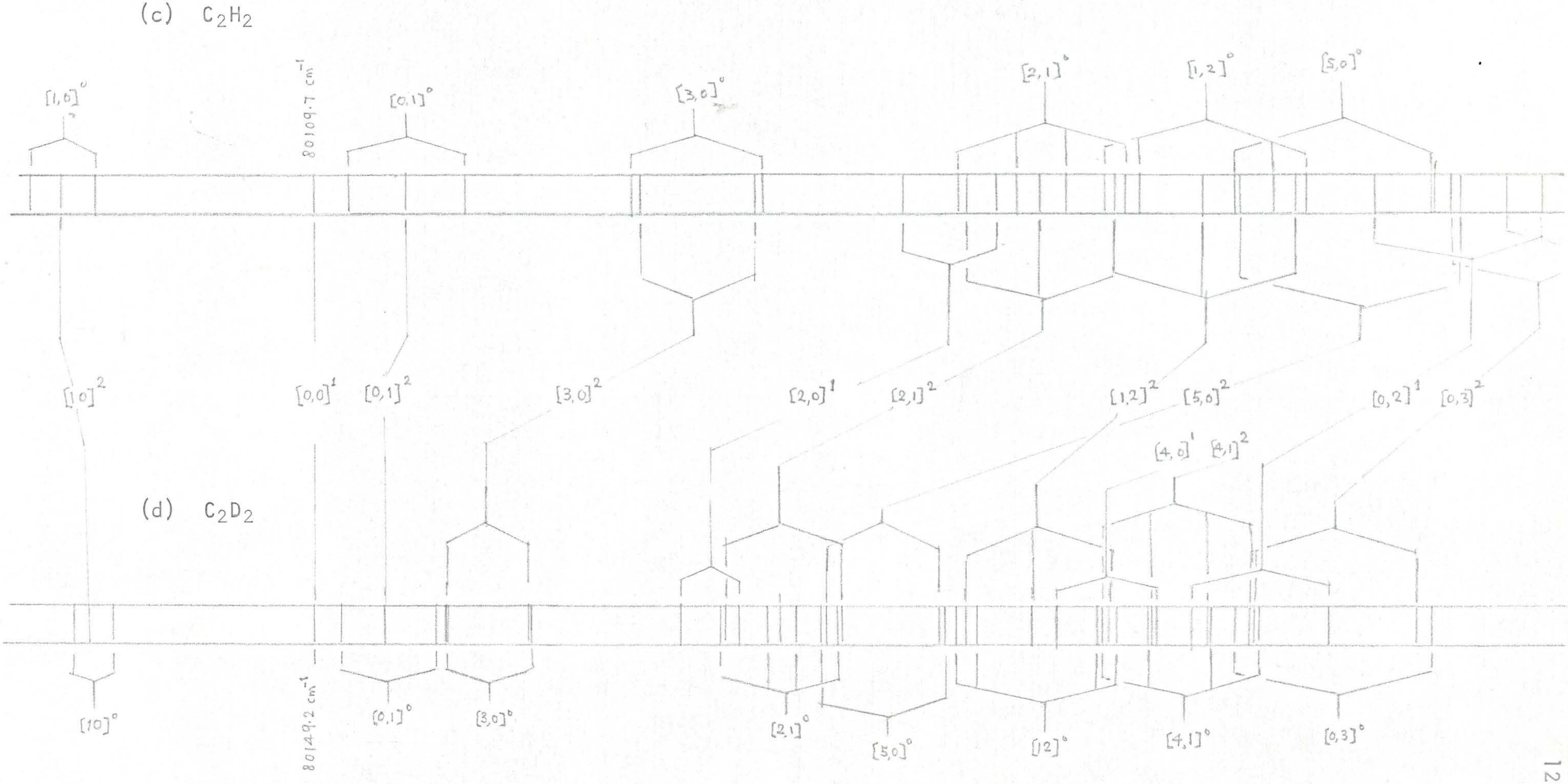


Figure 7-1 (Cont'd.) (c) Spectrum for hyperthetic C_2H_2 with $\omega_1(\pi_u) = 406.8\ \mathrm{cm}^{-1}$, $\omega_2(\pi_g) = 732.1\ \mathrm{cm}^{-1}$, $\varepsilon_1 = \varepsilon_2 = 0.1022$;

(d) Spectrum for hyperthetic C_2D_2 with $\omega_1(\pi_u) = 253.2\ \mathrm{cm}^{-1}$, $\omega_2(\pi_g) = 604.45\ \mathrm{cm}^{-1}$, $\varepsilon_1 = \varepsilon_2 = 0.1022$.

The upper states that the lines arised from are denoted by $[\upsilon_1,\upsilon_2]^K$.


(c) C_2H_2

(d) C_2D_2

state (e.g. $C_2H_2^+$; where ground state is $^2\Pi$; Ref 8, p518) We may write the vibronic wave functions as (Table 5-7):

$$\Psi_j(K;v_1,v_2) = |+\rangle\Phi_j^{(+)}(K;v_1,v_2) + |-\rangle\Phi_j^{(-)}(K;v_1,v_2) \tag{7-3-1}$$

where $|+\rangle$ and $|-\rangle$ are the electronic wave functions $\psi_{\pm}^{o}(\vec{r}_i,0)$

The transition moments between the states $\Psi_{j'}(K';v_1',v_2') \leftarrow \Psi_j(K;v_1,v_2)$ are given by

$$M_\sigma^{j'j} = \langle\Psi_{j'}(K',v_1',v_2')|\ M_\sigma\ |\Psi_j(K;v_1,v_2)\rangle \tag{7-3-2}$$

which may be written as

$$M_\sigma^{j'j} = \begin{bmatrix}\Phi_{j'}^{(+)} & \Phi_j^{(-)}\end{bmatrix} \begin{bmatrix}\langle+|M_\sigma|+\rangle & \langle+|M_\sigma|-\rangle \\ \langle-|M_\sigma|+\rangle & \langle-|M_\sigma|-\rangle\end{bmatrix} \begin{bmatrix}\Phi_j^{(+)} \\ \Phi_j^{(-)}\end{bmatrix} \tag{7-3-3'}$$

where $\langle\Lambda'|M_\sigma|\Lambda\rangle$ are electronic integrals and are functions of vibrational coordinates. Expanding $\langle\Lambda'|M_\sigma|\Lambda\rangle$ in power series of $\underline{q_k}$, we have

$$\langle\Lambda'|M_\sigma|\Lambda'\rangle = \langle\Lambda'|M_\sigma|\Lambda'\rangle_{Q=Q^\circ} + \sum_k \sum_{a=\pm}{}' q_{ka}\frac{\partial}{\partial q_{ka}}\langle\Lambda'|M_\sigma|\Lambda'\rangle_{Q^\circ} + \ldots \tag{7-3-4}$$

The symmetry properties of both sides must be identical. Hence to the first-order in the vibraitonal coordinates, the electronic matrices in Eq. (7-3-3') for any linear tetratanic molecules are found to be:

$$[M_o^{\Lambda'\Lambda}] = \begin{bmatrix} \mathfrak{m}^o & \\ & \mathfrak{m}^o \end{bmatrix} \quad ; \; \mathfrak{m}^o = <+|M_o|+> = <-|M_o|->$$

$$[M_+^{\Lambda'\Lambda}] = \begin{bmatrix} \mathfrak{m}_1^{(1)} q_{1-} + \mathfrak{m}_1^{(2)} q_{2-} & \mathfrak{m}_2^{(1)} q_{1+} + \mathfrak{m}_2^{(2)} q_{2+} \\ 0 & \mathfrak{m}_1^{(1)} q_{1-} + \mathfrak{m}_1^{(2)} q_{2-} \end{bmatrix} \qquad (7\text{-}3\text{-}5)$$

and
$$[M_-^{\Lambda'\Lambda}] = \begin{bmatrix} \mathfrak{m}_1^{(1)} q_{1+} + \mathfrak{m}_1^{(2)} q_2 & 0 \\ \mathfrak{m}_2^{(1)} q_{1-} + \mathfrak{m}_2^{(2)} q_{2-} & \mathfrak{m}_1^{(1)} q_{1+} + \mathfrak{m}_1^{(2)} q_{2+} \end{bmatrix}$$

where $\mathfrak{m}_{1,2}^{(k)}$ are dipole moment derivatives:

$$\mathfrak{m}_1^{(k)} \equiv \frac{\partial}{\partial q_{k\mp}} < \Lambda|M_{\pm}|\Lambda> \Big|_{Q=Q^\circ} \qquad (7\text{-}3\text{-}6)$$

$$\mathfrak{m}_2^{(k)} \equiv \frac{\partial}{\partial q_{k\pm}} < \Lambda|M_{\pm}|\Lambda> \Big|_{Q=Q^\circ}$$

In $D_{\infty h}$ symmetry group, the reducible representations of dipole moment operator $\vec{M}$ belong to Σ_u^+ and Π_u. The u symmetry of the operator M does not permit $\underline{q_2}$ (Π_g) vibrational coordinates to occur linearly in Eq. (7-3-4).

i.e. $\mathfrak{m}_{1,2}^{(2)}=0$

Putting Eq's. (7-3-5) into (7-3-3'), the matrix elements to be evaluated are of the following types

$$s_k(j',j) = \begin{bmatrix} \Phi_j^{(+)} & \Phi_j^{(-)} \end{bmatrix} \begin{bmatrix} q_{k+} & 0 \\ 0 & q_{k+} \end{bmatrix} \begin{bmatrix} \Phi_j^{(+)} \\ \Phi_j^{(-)} \end{bmatrix}$$

$$= < \Phi_{j'}^{(+)}(k';v_1',v_2')|q_{k+}|\Phi_j^{(+)}(K;v_1,v_2)>$$

$$+ < \Phi_{j'}^{(-)}(K';v_1',v_2')|q_{k+}|\Phi_j^{(-)}(K;v_1,v_2)>$$

(7-3-7a)

$$t_k(j',j) = \begin{bmatrix} \Phi_{j'}^{(+)}, \Phi_{j'}^{(-)} \end{bmatrix} \begin{bmatrix} 0 & q_{k-} \\ 0 & 0 \end{bmatrix} \begin{bmatrix} \Phi_j^{(+)} \\ \Phi_j^{(-)} \end{bmatrix}$$

$$= \langle \Phi_j^{(+)}(K';v_1',v_2',) | q_{k-} | \Phi_j^{(-)}(K;v_1,v_2) \rangle \qquad (7\text{-}3\text{-}7b)$$

$$s_k^*(j'j) = \begin{bmatrix} \Phi_{j'}^{(+)}, \Phi_{j'}^{(-)} \end{bmatrix} \begin{bmatrix} q_{k-} & 0 \\ 0 & q_{k-} \end{bmatrix} \begin{bmatrix} \Phi_j^{(+)} \\ \Phi_j^{(-)} \end{bmatrix}$$

$$= \langle \Phi_{j'}^{(+)}(K';v_1',v_2') | q_{k-} | \Phi_j^{(+)}(K;v_1,v_2) \rangle$$

$$+ \langle \Phi_{j'}^{(-)}(K';v_1',v_2') | q_{k-} | \Phi_j^{(-)}(K;v_1,v_2) \rangle \qquad (7\text{-}3\text{-}7c)$$

and

$$t_k^*(j'j) = \begin{bmatrix} \Phi_{j'}^{(+)} \Phi_{j'}^{(-)} \end{bmatrix} \begin{bmatrix} 0 & 0 \\ q_{k+} & 0 \end{bmatrix} \begin{bmatrix} \Phi_j^{(+)} \\ \Phi_j^{(-)} \end{bmatrix} \qquad (7\text{-}3\text{-}7d)$$

$$= \langle \Phi_{j'}^{(-)}(K';v_1',v_2') | q_{k+} | \Phi_j^{(+)}(K;v_1,v_2) \rangle$$

Since $C_\infty(\phi)\ \Phi_j^{(\pm)}(K;v_1,v_2) = e^{i(K\mp 1)\phi}\Phi_j^{(\pm)}(K;v_1,v_2,)$ and

$$C_\infty(\phi) q_{k\pm} = e^{\mp i\phi} q_{k\pm} \qquad (7\text{-}3\text{-}8)$$

the selection rules for K in the integrals s_k, t_k, s_k^*, and t_k^*, are: $(\Delta K = K' - K)$

$$s_k(j'j),\ t_k(j'j):\quad \Delta K = +1$$

$$s_k^*(j'j),\ t_k^*(j'j):\quad \Delta K = -1 \qquad (7\text{-}3\text{-}9)$$

Thus we have

$$M_o^{j'j} = \mathfrak{m}_o\, \delta_{j'j} \qquad (D_{\infty h}\ \&\ C_{\infty v}\ \text{molecules})$$

$$M_{+}^{j'j} = \begin{cases} \mathfrak{m}_1^{(k)}\, s_k(j'j) + \mathfrak{m}_2^{(k)}\, t_k(j'j), \quad (k=1) & (D_{\infty h} \text{ molecules}) \\ \sum_{k=1,2} \left[\mathfrak{m}_1^{(k)}\, s_k(j'j) + \mathfrak{m}_2^{(k)}\, t_k(j'j) \right], & (C_{\infty v} \text{ molecules}) \end{cases}$$

$$M_{-}^{j'j} = \begin{cases} \mathfrak{m}_1^{(k)}\, s_k^*(j'j) + \mathfrak{m}_2^{(k)}\, t_k^*(j'j), \quad (k=1) & (D_{\infty h} \text{ molecules}) \\ \sum_{k=1,2} \left[\mathfrak{m}_1^{(k)}\, s_k^*(j'j) + \mathfrak{m}_2^{(k)}\, t_k^*(j'j) \right], & (C_{\infty v} \text{ molecules}) \end{cases} \tag{7-3-10}$$

From Eq. (7-3-10a), we see that, M_o will not produce a vibronic infrared spectrum in the bending vibrations, because the final j'-vibronic state can not be different from the initial j-state. (However, there are vibrational transitions in the stretching modes $\nu_1(\sigma^+)$, $\nu_2(\sigma^+)$ and $\nu_3(\sigma^+)$ for $C_{\infty v}$ molecules; or $\nu_3(\sigma_u^+)$ for $D_{\infty h}$ molecules which are of no interest to us).

We are mainly concerned with perpendicular transitions in symmetrical linear tetratanic molecules. The ground vibronic state is either

$K=+1 \quad \Psi(1;00)=|+;00;00\rangle+\frac{\sqrt{2}}{4}\left\{\varepsilon_1|-;22;00\rangle+\varepsilon_2|-;00;22\rangle\right\}$. or

$K=-1 \quad \Psi(-1;00)=|-;00;00\rangle+\frac{\sqrt{2}}{4}\left\{\varepsilon_1|+;2\bar{2};00\rangle+\varepsilon_2|+;00;2\bar{2}\rangle\right\}$

(They may be split by the rotation-vibrational interaction(45); K type doubling). It will be sufficient to study transitions from only one of the two components, $\Psi(1;00)$ for instance:

for every transition from $\Psi(1;00)$, there corresponds one of equal energy and intensity from $\Psi(-1;00)$. Figs. 7-3 present some synthetic infrared spectra for 'acetylene' type molecules (at low temperature) for various values of Renner parameters ε_1 and ε_2. In each diagram the excitation energy is given in cm^{-1}, the vertical scale is the calculated order of the oscillator strength: log $f_\sigma^{j\leftarrow 0}$ where $f_\sigma^{j\leftarrow 0}$ is given by Eq. (7-1-6). The appearance of such spectra will clearly depend on the choice of the relevant molecular constants. We have used the following values:

$$\omega_1 = 500.0 \text{ cm}^{-1}, \qquad \omega_2 = 600.0 \text{ cm}^{-1}$$

$$\frac{\mathfrak{m}_1^{(k)} a_k^{1/2}}{e} = \frac{\mathfrak{m}_2^{(k)} a_k^{1/2}}{e} = 10^{-8} \text{cm}, \qquad \left(a_k = \frac{\hbar}{\mu_k \omega_k}\right)$$

For polyatomic molecules, the harmonic oscillater selection rules restrict the transitions to those in which one quantum of vibrational energy is invloved. Thus, when the initial state belongs to $v_1=0$, $v_2=0$ level (denoted by $[0,0]$), the only level it can reach is that $v_1=1$ and $v_2=0$, i.e. $[1,0]$. Therefore the harmonically unallowed transitions $[1,2]\leftarrow[0,0]$ and $[3,0]\leftarrow[0,0]$ in Fig. 7-3 are induced by vibronic interaction. Such interactions are of second order and thus these transitions are rather weak in comparison with the fundamental band $[1,0]\leftarrow[0,0]$. As many transitions induced by vibronic interaction can also be induced by anharmonicities, one may distinguish a weak vibronic interaction from the anharmonic interactions by the 'Renner-Teller splitting' which is a first-order effect. In absence of vibronic interaction, i.e. when the Renner parameters are negligibly small, the transition $[1,0] \leftarrow [0,0]$ should consist of only one band. When the vibronic interaction is in effect, it is expected that the line will split into three corresponding to the three Renner-Teller components: Σ^+, Σ^-, and Δ. However, it is interesting to note that if the Σ^+ component (which is assumed to be the lower in energy of the two component) is very much weaker in intensity then Σ^- (which is the higher energy one). As the value of the Renner parameters increases, the splittings between components of the same $[v_1 v_2]$ level increase and more and more lines will show up.

Summary

In this work, we are concerned with the dynamical problem of vibrational electronic interaction in linear molecules.

We have reviewed the theoretical background and the relation between various formulations in solving the dynamical problem. We have proposed a multipole expansion method for the derivation of the necessary perturbation terms. The bending force constants, anharmonicities and Renner parameters are shown to arise from the same vibronic phenomenon and appear in a single representative Hamiltonian function. We have followed Renner's Adiabatic Formulation in the calculation of the second-order vibronic energies for linear triatomic molecules, but have used a different mathematical technique which gives rather naturally the definition of the vibronic angular momentum. We point out the difficulty in using the Adiabatic Formulation when the problem involves two or more bending vibrations. The Harmonic Formulation is consulted and vibronic energies correct to second-order are obtained for linear tetratomic molecules. The perturbation theory used is called the 'modified Van Vleck degenerate perturbation method' and we introduced the first-and second-order 'interaction diagram's as an aid to understand this theory. The method produces the

same results as does the commonly used Schroedinger perturbation theory. As the number of interacting bending vibrations increases, the Van Vleck perturbation matrices become sizable and complicated. The size and form of the matrices can be represented by the first-order interaction diagram. The topological aspect of the diagrams may be of interest to mathematicians. Finally we present some predicted spectra for acetylene-like molecules. Hopefully, these predictions will aid the experimentalists in unravelling the observed spectral lines of linear tetratomic molecules which exhibit a Renner effect.

APPENDIX A

Linear Point Group

A-1 Character Table for $D_{\infty h}$ Symmetry Group, (for $C_{\infty v}$ no g and u designations).

$\Gamma_{(\lambda)}$	E	$2C_\infty^\Phi$	$\infty\sigma_v$	E^{-1}	$2S_\infty^\Phi$	∞C_2	R	$2C_\infty^\Phi R$		
Σ_g^+	1	1	1	1	1	1	1	1		x^2+y^2, z^2
Σ_g^-	1	1	-1	1	1	-1	1	1	R_z	
Π_g	2	$2\cos\Phi$	0	2	$-2\cos\Phi$	0	2	$2\cos\Phi$	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\Phi$	0	2	$2\cos 2\Phi$	0	2	$2\cos 2\Phi$		(x^2-y^2, xy)
Φ_g	2	$2\cos 3\Phi$	0	2	$-2\cos 3\Phi$	0	2	$2\cos 3\Phi$		
Γ_g	2	$2\cos 4\Phi$	0	2	$2\cos 4\Phi$	0	2	$2\cos 4\Phi$		
H_g	2	$2\cos 5\Phi$	0	2	$-2\cos 5\Phi$	0	2	$2\cos 5\Phi$		
I_g	2	$2\cos 6\Phi$	0	2	$2\cos 6\Phi$	0	2	$2\cos 6\Phi$		
J_g	2	$2\cos 7\Phi$	0	2	$-2\cos 7\Phi$	0	2	$2\cos 7\Phi$		
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮		
Σ_u^+	1	1	1	-1	-1	-1	1	1	T_z	
Σ_u^-	1	1	-1	-1	-1	1	1	1		
Π_u	2	$2\cos\Phi$	0	-2	$2\cos\Phi$	0	2	$2\cos\Phi$	(T_x, T_y)	
Δ_u	2	$2\cos 2\Phi$	0	-2	$-2\cos 2\Phi$	0	2	$2\cos 2\Phi$		
Φ_u	2	$2\cos 3\Phi$	0	-2	$2\cos 3\Phi$	0	2	$2\cos 3\Phi$		
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮		

A-2 Power of π-representation: $[\Gamma(1)]^p$

$$(\pi)^p = [\Gamma(1)]^p = \sum_{n=0}^{p/2 \text{ or } (p-1)/2} \binom{p}{n} \Gamma(p-2n)$$

where $\binom{p}{n}$ = Binormial coefficients = $\frac{p!}{n!(p-n)!}$; and $\Gamma(0) = \frac{1}{2}(\Sigma^+ + \Sigma^-)$.

For example: $\pi^4 = \Gamma + 4\Delta + 3(\Sigma^+ + \Sigma^-)$

A-3 Multiplication Table for $D_{\infty h}$, $C_{\infty v}$, D_{∞}

	$\Gamma(\lambda)$	Σ^+	Σ^-	Π	Δ	Φ	Γ	H
$\Gamma(0)$	Σ^+	Σ^+						
	Σ^-	Σ^-	Σ^+					
$\Gamma(1)$	Π	Π	Π	$\Sigma^+,[\Sigma^-],\Delta$				
$\Gamma(2)$	Δ	Δ	Δ	Π,Φ	$\Sigma^+,[\Sigma^-],\Gamma$			
$\Gamma(3)$	Φ	Φ	Φ	Δ,Γ	Π,H	$\Sigma^+,[\Sigma^-],I$		
$\Gamma(4)$	Γ	Γ	Γ	Φ,H	Δ,I	Π,J	$\Sigma^+,[\Sigma^-],K$	
$\Gamma(5)$	H	H	H	Γ,I	Φ,J	Δ,K	Π,L	$\Sigma^+,[\Sigma^-],M$

N.B. [ ] antisymmetric product

g x g = g, u x u = g, u x g = u.

A-4 Table: Number of Vibrations in Linear Polyatomic Molecules

Point Group	Species of vibrations	Number of Vibrations (t)			
		Triatomic (N=3)	Tetratomic (N=4)	Pentatomic (N=5)	Hexatomic (N=6)
$D_{\infty h}$	Σ_g^+	1	2	2	3
	Σ_u^+	1	1	2	2
	Π_u	1	1	2	2
	Π_g		1	1	2
$C_{\infty v}$	Σ^+	2	3	4	5
	Π	t=1	t=2	t=3	t=4

A-5 Lowering of Symmetry: Correlations of Symmetry Representations

	$z \to z$	$z \to z$
$D_{\infty h}$	C_{2v}	C_{2h}
$\Pi_{u,g}$	B_1+B_2	$2B_{u,g}$
$\Delta_{u,g}$	A_1+A_2	$2A_{u,g}$
$\Phi_{u,g}$	B_1+B_2	$2B_{u,g}$

	$\sigma_v \to \sigma$
$C_{\infty v}$	C_s
Π	$A'+A''$
Δ	$A'+A''$
Φ	$A'+A''$

APPENDIX B

Transformation Matrices for Doubly-Degenerate Perturbation Matrices

Suppose $|\psi_1^o>$ and $|\psi_2^o>$ are two degenerate states of the "unperturbed" Hamiltonian H^o. The representation of the perturbation H' in the basis $\{\psi_1^o, \psi_2^o\}$ is given by

$$H' \rightarrow [H'_{ij}] = \begin{bmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{bmatrix} \qquad \text{(B-1)}$$

where $H'_{ij} = <\psi_i^o|H'|\psi_j^o>$. The perturbation equation can then be written in a matrix form:

$$H' \begin{bmatrix} \psi_1^o \\ \psi_2^o \end{bmatrix} = \begin{bmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{bmatrix} \begin{bmatrix} \psi_1^o \\ \psi_2^o \end{bmatrix} \qquad \text{(B-2)}$$

On the left-hand side H' acts as operator. If we can find a transform matrix S, such that

$$S^{-1} \begin{bmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{bmatrix} S = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} \qquad \text{(B-3)}$$

then we can construct new basis $\{\psi_1, \psi_2\}$ by

$$\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = S' \begin{bmatrix} \psi_1^o \\ \psi_2^o \end{bmatrix} \text{, } (S' = \text{transpose of } S) \qquad \text{(B-4)}$$

so that the operator H' acting on ψ_1 and ψ_2 gives eigen-equations denoted by

$$H' \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} \qquad \text{(B-5)}$$

Equation (B-3) will determine λ_1, λ_2 and the $\mathfrak{S}$-matrix.

Case (a)

$$H'_{11} = H'_{22};\ H'^{*}_{12} = H'_{21}\text{(complex)}$$

In this case, it implies that $\psi^{o*}_1 = \psi^o_2$. By hermiticity of the Hamiltonian (the perturbation), it can be proved that $H'_{11} = H'_{22}$ = real quantity.

We can define $\mathcal{R}$ and η by

$$H'_{12} = |H_{12}|e^{-2i\eta} = \mathcal{R}e^{-2i\eta} \tag{B-6}$$

Thus the representation of H' in the basis $\{\psi^o_1, \psi^o_2\}$ will be denoted by

$$[H'_{ij}] = \begin{bmatrix} H'_{11} & \mathcal{R}e^{-2i\eta} \\ \mathcal{R}e^{+2i\eta} & H'_{11} \end{bmatrix} \tag{B-7}$$

The matrix $[H'_{ij}]$ is hermitian. It can be diagonalized by a unitary transformation:

$$U^{+}[H'_{ij}]U = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} \tag{B-8}$$

The most general 2x2 unitary matrix is given by

$$U = \frac{1}{\sqrt{2}} \begin{bmatrix} de^{-ia} & -ce^{ib} \\ ce^{-ib} & de^{-ia} \end{bmatrix} \tag{B-9}$$

where a, b, c and d are real. The U matrix will satisfy the following unitary properties:

$$U^{-1} \equiv U^{+} = U'^{*} = \frac{1}{\sqrt{2}} \begin{bmatrix} de^{-ia} & ce^{-ib} \\ -ce^{-ib} & de^{ia} \end{bmatrix} \tag{B-10a}$$

$$\sum_j U^*_{ij}\, U_{j\ell} = \delta_{i\ell} \tag{B-10b}$$

$$\det U = \det U^+ = \det U^{-1} = +1 \tag{B-10c}$$

By Equations (B-10b) or (B-10c), we have

$$d^2 + c^2 = 2 \tag{B-11}$$

Then by Equations (B-8), (B-7), (B-9) and (B-10a), we obtain

$$\frac{1}{2}\begin{bmatrix} de^{-ia} & ce^{ib} \\ -ce^{-ib} & de^{ia} \end{bmatrix}\begin{bmatrix} H'_{11} & \mathcal{R}e^{-2i\eta} \\ \mathcal{R}e^{+2i\eta} & H'_{11} \end{bmatrix}\begin{bmatrix} de^{ia} & -ce^{ib} \\ ce^{-ib} & de^{-ia} \end{bmatrix} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$$

Equating the corresponding matrix elements on both sides, we have

$$0 = \mathcal{R}[d^2e^{-i(2\eta+2a)} - c^2e^{i(2\eta+2b)}] \tag{B-12a}$$

$$0 = \mathcal{R}[d^2e^{+2i(\eta+a)} - c^2e^{-2i(\eta+b)}] \tag{B-12b}$$

$$\lambda_1 = H'_{11} + cd\mathcal{R}\cos(2\eta+a+b) \tag{B-12c}$$

$$\lambda_2 = H'_{11} - cd\mathcal{R}\cos(2\eta+a+b) \tag{B-12d}$$

Equations (B-12a) and (B-12b) will be satisfied if we put

$$a = b = -\eta \tag{B-13a}$$

$$d^2 = c^2 = 1 \tag{B-13b}$$

Equation (B-13b) and Equation (B-11) give c,d = +1 or -1 :

$$cd = +1 \quad \text{or} \quad cd = -1 \tag{B-13c}$$

It is free to choose cd = +1 so that c = d = ±1. Then Equations (B-12c) and (B-12d) give

$$\begin{aligned} \lambda_1 &= H'_{11} + \mathcal{R} \\ \lambda_2 &= H'_{11} - \mathcal{R} \end{aligned} \tag{B-14}$$

Substituting Equation (B-13) into Equation (B-9), we obtain

$$U = \frac{c}{\sqrt{2}} \begin{bmatrix} e^{-i\eta} & -e^{-i\eta} \\ e^{i\eta} & e^{i\eta} \end{bmatrix}$$

The phase factor c (= ±1) does not have any physical significance. Thus we can set c = +1. The transpose of U is

$$U' = \frac{1}{\sqrt{2}} \begin{bmatrix} e^{-i\eta} & e^{i\eta} \\ -e^{in} & e^{in} \end{bmatrix} \tag{B-15}$$

Thus the new basis functions are given by

$$\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = U' \begin{bmatrix} \psi_1^o \\ \psi_2^o \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} e^{-i\eta}\psi_1^o + e^{i\eta}\psi_2^o \\ -e^{-i\eta}\psi_1^o + e^{i\eta}\psi_2^o \end{bmatrix} \tag{B-16}$$

When $\psi_{1,2}^o = u_\lambda e^{\pm i\lambda\theta}$, then

$$\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \begin{bmatrix} \sqrt{2}\, u_\lambda \cos\lambda(\theta - \eta/\lambda) \\ i\sqrt{2}\, u_\lambda \sin\lambda(\theta - \eta/\lambda) \end{bmatrix} \tag{B-17}$$

Case (b)

$$H'_{11} \neq H'_{22},\ H'_{12} = H'_{21} \text{ (real)}$$

The matrix $[H'_{ij}]$ is real and symmetric; thus it can be diagonalized by an orthogonal transformation. The "proper" orthogonal matrix S is:

$$S = \begin{bmatrix} \sin\alpha & -\cos\alpha \\ \cos\alpha & \sin\alpha \end{bmatrix} \tag{B-18a}$$

whose determinant is +1. The transpose of S is:

$$S' = S^{-1} = \begin{bmatrix} \sin\alpha & \cos\alpha \\ -\cos\alpha & \sin\alpha \end{bmatrix} \qquad \text{(B-18b)}$$

To satisfy Equation (B-3), it is found that

$$\tan 2\alpha = \frac{2H'_{12}}{H'_{22} - H'_{11}} \qquad \text{(B-19a)}$$

or

$$\cos\alpha = \frac{1}{\sqrt{2}}\{1 + \frac{H'_{22} - H'_{11}}{\sqrt{(H'_{22} - H'_{11})^2 + 4H'^2_{12}}}\}^{\frac{1}{2}} \qquad \text{(B-19b)}$$

$$\sin\alpha = \frac{1}{\sqrt{2}}\{1 - \frac{H'_{22} - H'_{11}}{\sqrt{(H'_{22} - H'_{11})^2 + 4H'^2_{12}}}\}^{\frac{1}{2}} \qquad \text{(B-19c)}$$

and

$$\lambda_1 = H'_{11} + H'_{12}\cos\alpha = \frac{H'_{11} + H'_{22}}{2} + H'_{12}\cos 2\alpha$$

$$= \frac{H'_{22} + H'_{11}}{2} + [(\frac{H'_{22} - H'_{11}}{2})^2 + H'^2_{12}]^{\frac{1}{2}} \qquad \text{(B-20a)}$$

$$\lambda_2 = H'_{22} - H'_{12}\cos\alpha = \frac{H'_{22} + H'_{11}}{2} - H'_{12}\cos 2\alpha$$

$$= \frac{H'_{22} + H'_{11}}{2} - [(\frac{H'_{22} - H'_{11}}{2})^2 + H'^2_{12}]^{\frac{1}{2}} \qquad \text{(B-20b)}$$

Case (c)

$$H'_{11} = H'_{22},\ H'_{12} = H'_{21} \text{ (real)}$$

The results are:

$$S' = S^{-1} = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} \qquad \text{(B-21)}$$

$$S^{-1}[H'_{ij}]S = \begin{bmatrix} H'_{11} + H_{12} & 0 \\ 0 & H'_{11} - H_{12} \end{bmatrix} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} \tag{B-22}$$

and

$$\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = S' \begin{bmatrix} \psi_1^o \\ \psi_2^o \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} \psi_1^o + \psi_2^o \\ -\psi_1^o + \psi_2^o \end{bmatrix} \tag{B-23}$$

APPENDIX C

Van Vleck's Degenerate Perturbation Method(38,39,40)

Suppose the unperturbed Schröedinger Equation is represented by

$$H^o\psi^o_{nr} = E^o_{nr}\psi^o_{nr} \qquad (r = 1, 2, \ldots\ldots d_n) \tag{C-1}$$

and the perturbed system is given by

$$(H^o + V')\psi = E\psi \tag{C-2}$$

The basic features in the Van Vleck's treatment are:(40)

(a) it depends on the degenerate block, say n, in which we are interested;

(b) it eliminates the first-order coupling between n and n', n'', etc., blocks due to the perturbation V';

(c) it preserves orthonormality through third-order;

(d) the identity of the initial states is preserved until the final diagonalization; and

(e) the energies obtained are correct through third-order.

In ordinary first-order perturbation theory, one uses ψ^o_{nr} as basis functions, but in Van Vleck's theory, one uses the Van Vleck's <u>basis functions</u> denoted by

$$\psi_{nr} = \psi^o_{nr} + \psi^{(1)}_{nr} + \psi^{(2)}_{nr} \tag{C-3}$$

The first-order correction $\psi^{(1)}_{nr}$ is determined by the condition (b), that

$$\langle\psi_{n'g'}|H^o + V'|\psi_{nr}\rangle$$

vanish in first-order for all $|\psi_{n'r'}\rangle$ states which are outside the n-block and are orthogonal to ψ_{nr}. Thus

$$\psi_{n'j'} = \phi^{o}_{n'j'} - \sum_{r=1}^{d_n} |\psi^{o}_{nr}><\psi^{(1)}_{nr}|\psi^{o}_{n'j'}> \text{ + higher order} \qquad \text{(C-4)}$$

and thus

$$<\psi_{n'j'}|\{(H^{o} - E^{o}_{nr})|\phi^{(1)}_{nr}> + V'|\phi^{o}_{nr}>\} = 0 \qquad \text{(C-5)}$$

$$\text{Let } \phi^{(1)}_{nr} = \sum_{n'r'} \phi^{o}_{n'j'} C_{n'j';nr} \qquad \text{(C-6a)}$$

then Equation (C-5) gives the interaction coefficients:

$$C_{n'j',nr} = - \frac{<\phi^{o}_{n'j'}|V'|\phi^{o}_{nr}>}{E^{o}_{n'j'} - E^{o}_{nr}} \qquad \text{(C-6b)}$$

The $C_{nr',nr}$ ($n' = n$) are left undetermined but can be set equal to zero. $\phi^{(2)}_{nr}$ is added to satisfy the orthonormality condition (c) for the n-block, i.e.,

$$<\psi_{nr}|\psi_{nr'}> = \delta_{rr'} \quad \text{(within the n-block)} \qquad \text{(C-7)}$$

If we let

$$\phi^{(2)}_{nr} = \sum_{r'=1}^{d_n} \phi^{o}_{nr'} \cdot a_{r',r} \qquad \text{(C-8a)}$$

then Equations (C-3), (C-6) and (C-7) give

$$a_{r'r} = - \tfrac{1}{2}<\phi^{(1)}_{nr'}|\phi^{(1)}_{nr}> \qquad \text{(C-8b)}$$

The energies which are correct through third-order will be obtained by the following secular equation:

$$|<\psi_{nr}|H^{o} + V'|\psi_{nr'}> - E\delta_{rr'}| = 0 \qquad \text{(C-9)}$$

Using Equations (C-1), (C-6) and (C-8), the matrix elements are given by

$$
\begin{aligned}
&<\psi_{nr}|H^0 + V'|\psi_{nr'}> \\
&\quad = <\phi^0_{nr} + \phi^{(1)}_{nr} + \phi^{(2)}_{nr}|H^0 + V'|\phi^0_{nr'} + \phi^{(1)}_{nr'} + \phi^{(2)}_{nr'}> \\
&\quad = E^0_{nr}\delta_{rr'} + <\psi^0_{nr}|V'|\psi^0_{nr'}> \\
&\quad - \sum_{n'j'}{}' \, [E^0_{n'j'} - \tfrac{1}{2}(E^0_{nr} + E^0_{nr'})] \frac{<\phi^0_{nr}|V'|\psi^0_{n'j'}><\psi^0_{n'j'}|V'|\psi^0_{nr'}>}{(E^0_{n'j'} - E^0_{nr})(E^0_{n'j'} - E^0_{nr'})} \\
&\quad + \{ \sum_{n'j'} \sum_{n''j''} \frac{<\phi^0_{nr}|V'|\psi^0_{n'j'}><\psi^0_{n'j'}|V'|\psi^0_{n''j''}><\psi^0_{n''j''}|V'|\psi^0_{nr'}>}{(E^0_{n'j'} - E^0_{nr})(E^0_{n''j''} - E^0_{nr'})} \\
&\quad - \tfrac{1}{2} \sum_{r''} [<\psi^0_{nr}|V'|\psi^0_{nr''}> \sum_{n'j'}{}' \frac{<\psi^0_{nr''}|V'|\psi^0_{n'j'}><\psi^0_{n'j'}|V'|\psi^0_{nr'}>}{(E^0_{n'j'} - E^0_{nr''})(E^0_{n'j'} - E^0_{nr'})} \\
&\quad + <\psi^0_{nr''}|V'|\psi^0_{nr'}> \sum_{n'j'}{}' \frac{<\psi^0_{nr}|V'|\psi^0_{n'j'}><\psi^0_{n'j'}|V'|\psi^0_{nr''}>}{(E^0_{n'j'} - E^0_{nr})(E^0_{n'j'} - E^0_{nr''})}] \qquad \text{(C-10)}
\end{aligned}
$$

If $E^0_{nr} = E^0_{nr'} = E^0_{nr''} \equiv E^0_n$, then Equation (C-10) becomes:

$$
\begin{aligned}
&<\psi_{nr}|H^0 + V'|\psi_{nr'}> \\
&\quad = E^0_n\delta_{rr'} + <\phi^0_{nr}|V'|\psi^0_{nr'}> \\
&\quad - \sum_{n'j'}{}' \frac{<\phi^0_{nr}|V'|\psi^0_{n'j'}><\psi^0_{n'j'}|V'|\psi^0_{nr'}>}{(E^0_{n'} - E^0_n)} \\
&\quad + \Bigg\{ \sum_{n'j'}{}' \sum_{n''j''}{}' \frac{<\phi^0_{nr}|V'|\psi^0_{n'j'}><\psi^0_{n'j'}|V'|\phi^0_{n''j''}><\psi^0_{n''j''}|V'|\psi^0_{nr'}>}{(E^0_{n'} - E^0_n)(E^0_{n''} - E^0_n)} \\
&\quad - \tfrac{1}{2} \sum_{r''} [<\psi^0_{nr}|V'|\psi^0_{nr''}> \sum_{n'j'}{}' \frac{<\psi^0_{nr''}|V'|\psi^0_{n'j'}><\psi^0_{n'j'}|V'|\psi^0_{nr'}>}{(E^0_{n'} - E^0_n)^2} \\
&\quad + <\psi^0_{nr''}|V'|\psi^0_{nr'}> \sum_{n'j'}{}' \frac{<\psi^0_{nr}|V'|\psi^0_{n'j'}><\psi^0_{n'j'}|V'|\phi^0_{nr''}>}{(E^0_{n'} - E^0_n)^2}] \Bigg\} \qquad \text{(C-11)}
\end{aligned}
$$

APPENDIX D

Matrix Elements in Doubly-Degenerate (Normal) Vibration Representation

D-1 Definition of Doubly-Degenerate Normal Vibration

(i) In number-space (N-representation), states are denoted by $|n_+,n_->$ which are eigenstates of two "observables", N and L, such that

$$\begin{aligned} N|n_+,n_-> &\equiv (n_+ + n_-)|n_+,n_-> \\ L|n_+,n_-> &\equiv (n_+ - n_-)|n_+,n_-> \end{aligned} \qquad \text{(D-1)}$$

and that

$$<n'_+,n'_-|n_+n_-> = \delta_{n'_+n_+} \cdot \delta_{n'_-n_-}$$

Annihilation and creation operators are defined by:

for "positive" particles:

$$A_+|n_+,n_-> = n_+^{1/2}|n_+-1,n_->$$

$$A_+^+|n_+,n_-> = (n_++1)^{1/2}|n_++1,n_->$$

for "negative" particles: (D-2)

$$A_-|n_+,n_-> = n_-^{1/2}|n_+,n_--1>$$

$$A_-^+|n_+,n_-> = (n_-+1)^{1/2}|n_+,n_-+1>$$

If $A_+|0,0> = A_-|0,0> \equiv 0$ (D-3)

then

$$|n_+,n_-> = (n_+!n_-!)^{1/2}(A_+^+)^{n_+}(A_-^+)^{n_-}|0,0> \qquad \text{(D-4)}$$

By defining

$$N_+ \equiv A_+^+A_+, \text{ and } N_- \equiv A_-^+A_-$$

we have

$$N = N_++N_-, \text{ and } L = N_+-N_-$$

(ii) In normal coordinate space, the state functions $\phi^{o}_{\nu\ell}$ satisfy the following definitive equations;

$$H^{o}_{\nu}\phi^{o}_{\nu\ell} \equiv [\frac{1}{2\mu}(p_x^2 + p_y^2) + \tfrac{1}{2}\mu\omega^2(q_x^2 + q_y^2)]\phi^{o}_{\nu\ell} = \mathcal{E}^{o}_{\nu}\phi^{o}_{\nu\ell} \equiv (\nu+1)\hbar\omega\phi^{o}_{\nu\ell}$$

$$G_z\phi^{o}_{\nu\ell} \equiv (q_x p_y - q_y p_x)\phi^{o}_{\nu\ell} = \ell\hbar\phi^{o}_{\nu\ell}; \quad (\ell = \nu,\ \nu=2, \ldots\ldots -\nu+2, -\nu) \tag{D-5}$$

where q_x, q_y are the two orthogonal normal coordinates and p_x, p_y are their conjugate momenta: $p_i = \frac{\hbar}{i}\frac{\partial}{\partial q_i}$. μ is the reduce mass of the two-dimensional oscillator and ω is the angular frequency of the harmonic vibration. The force constant is given by $k = \mu\omega^2$.

As we define r and ϕ by

$$re^{\pm i\phi} \equiv q_x \pm iq_y = q_{k\pm} \tag{D-6}$$

then Equation (D-5) becomes

$$H^{o}_{\nu}\phi^{o}_{\nu\ell}(r,\phi) \equiv [-\frac{\hbar^2}{2\mu}(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}) + \frac{1}{2\mu r^2}G_z^2 + \tfrac{1}{2}\mu\omega^2 r^2]\phi^{o}_{\nu\ell}(r,\phi)$$

$$= \mathcal{E}^{o}_{\nu}\phi^{o}_{\nu\ell}(r,\phi) \equiv (\nu+1)\hbar\omega\phi^{o}_{\nu\ell}(r,\phi) \tag{D-7a}$$

$$G_z\phi^{o}_{\nu\ell}(r,\phi) \equiv \frac{\hbar}{i}\frac{\partial}{\partial\phi}\phi^{o}_{\nu\ell}(r,\phi) = \ell\hbar\phi^{o}_{\nu\ell}(r,\phi) \tag{D-7b}$$

The analytical solutions for $\phi^{o}_{\nu\ell}(r,\phi)$ are$^{(37)}$

$$\phi^{o}_{\nu\ell}(r,\phi) = R_{\nu|\ell|}(r)\frac{1}{\sqrt{2n}}e^{i\ell\phi} \tag{D-8a}$$

where the radial functions $R_{\nu|\ell|}(r)$ satisfy:

$$[-\frac{\hbar^2}{2\mu}(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{\ell^2}{r^2}) + \tfrac{1}{2}\mu\omega^2 r^2 - \mathcal{E}^{o}_{\nu}]R_{\nu|\ell|}(r) = 0 \tag{D-8b}$$

D-2 Matrix Elements in Doubly-Degenerate Vibration Representation

The matrix elements for a function of operators p_i and q_k, $f(p_i, q_k)$:

$$\langle\nu'\ell'|f(p_i,q_k)|\nu,\ell\rangle = \int_{r=0}^{\infty}\int_{\phi=0}^{2\pi} \phi^{o*}_{\nu'\ell'} f(p_i,q_k)\phi^{o}_{\nu\ell} r dr d\phi \qquad \text{(D-9)}$$

are readily obtained by using Equations (D-1), (D-2) and (D-6) if we make the following correspondences:

$$\begin{aligned} q_x \pm iq_y &\equiv q_{k\pm} \longleftrightarrow a^{\frac{1}{2}}(A^{+}_{\pm} + A_{\mp});\ (a \equiv \frac{\hbar}{\mu\omega}) \\ p_x \pm ip_y &\equiv p_{\pm} \longleftrightarrow ia^{-\frac{1}{2}}(A^{+}_{\pm} - A_{\mp}), \\ H^{o}_{\nu} &\longleftrightarrow (N+1)\hbar\omega \\ G_z &\longleftrightarrow L\hbar \end{aligned} \qquad \text{(D-10)}$$

and

$$\phi^{o}_{\nu\ell}(r,\phi) = e^{i\alpha(\nu,\ell)}\langle r,\phi|n_+,n_-\rangle;\ (\nu = n_+ + n_-;\ \ell = n_+ - n_-) \qquad \text{(D-11)}$$

Therefore

$$\langle\nu'\ell'|q_{k\pm}|\nu,\ell\rangle = e^{-i\alpha'}\cdot e^{i\alpha}\langle n'_+ n'_-|a^{\frac{1}{2}}(A^{+}_{\pm} + A_{\mp})|n_+ n_-\rangle$$

With different choices of the phase $e^{i\alpha}$, matrix elements of the same operator will differ by a phase factor. For instance, the matrix elements of $q_{k\pm}$ evaluated by various authors are shown in the following table:

Table D-1 Matrix elements of $q_{k\pm} = re^{\pm i\phi}$

	$e^{i\alpha}=1$; Longuet-Higgins, Ref. 25	$e^{i\alpha}=e^{i\nu\frac{\pi}{2}}$; Moffitt and Liehr, Ref. 6	$e^{i\alpha}=e^{i(\nu+\ell)\frac{\pi}{2}}$; Shaffer, Ref. 37
$\langle\nu+1,\ell+1|q_{k+}|\nu,\ell\rangle$	$\frac{1}{\sqrt{2}}(\nu+\ell+2)^{\frac{1}{2}}a^{\frac{1}{2}}$	$-i\ \frac{1}{\sqrt{2}}(\nu+\ell+2)^{\frac{1}{2}}a^{\frac{1}{2}}$	$-\ \frac{1}{\sqrt{2}}(\nu+\ell+1)^{\frac{1}{2}}a^{\frac{1}{2}}$
$\langle\nu-1,\ell+1|q_{k+}|\nu,\ell\rangle$	$\frac{1}{\sqrt{2}}(\nu-\ell)^{\frac{1}{2}}a^{\frac{1}{2}}$	$i\ \frac{1}{\sqrt{2}}(\nu-\ell)^{\frac{1}{2}}a^{\frac{1}{2}}$	$\frac{1}{\sqrt{2}}(\nu-\ell)^{\frac{1}{2}}a^{\frac{1}{2}}$
$\langle\nu+1,\ell-1|q_{k-}|\nu,\ell\rangle$	$\frac{1}{\sqrt{2}}(\nu-\ell+2)^{\frac{1}{2}}a^{\frac{1}{2}}$	$-i\ \frac{1}{\sqrt{2}}(\nu-\ell+2)^{\frac{1}{2}}a^{\frac{1}{2}}$	$\frac{1}{\sqrt{2}}(\nu-\ell+2)^{\frac{1}{2}}a^{\frac{1}{2}}$
$\langle\nu-1,\ell-1|q_{k-}|\nu,\ell\rangle$	$\frac{1}{\sqrt{2}}(\nu+\ell)^{\frac{1}{2}}a^{\frac{1}{2}}$	$i\ \frac{1}{\sqrt{2}}(\nu+\ell)^{\frac{1}{2}}a^{\frac{1}{2}}$	$-\ \frac{1}{\sqrt{2}}(\nu+\ell)^{\frac{1}{2}}a^{\frac{1}{2}}$

We shall adopt the phase $e^{i\alpha}$ to be unity, and define the radial integrals by

$$(\nu'\ell'|r^m|\nu,\ell) = \int_{r=0}^{\infty} R_{\nu'|\ell'|}(r)\, r^m R_{\nu|\ell|}(r)\, r\,dr \qquad \text{(D-12)}$$

Also, we denote the radial integrals of r, r^2 and r^4 respectively by:

$$\begin{aligned} q(\nu+a,\ell+b) &= (\nu+a,\ell+b|r|\nu,\ell) \\ A(\nu+a,\ell+b) &= (\nu+a,\ell+b|r^2|\nu,\ell) \\ B(\nu+a,\ell+b) &= (\nu+a,\ell+b|r^4|\nu,\ell) \end{aligned} \qquad \text{(D-13)}$$

Thus

$$q(\nu+1,\ell+\Lambda) = (\nu+1,\ell+\Lambda|r|\nu,\ell) = <\nu+1,\ell+\Lambda|q_{k\Lambda}|\nu,\ell>= \frac{1}{\sqrt{2}}(\nu+\Lambda\ell+2)^{\frac{1}{2}}a^{\frac{1}{2}}, \quad (\Lambda=\pm 1)$$

$$q(\nu-1,\ell+\Lambda) = (\nu-1,\ell+\Lambda|r|\nu,\ell) = <\nu-1,\ell+\Lambda|q_{k\Lambda}|\nu,\ell>= \frac{1}{\sqrt{2}}(\nu-\Lambda\ell)^{\frac{1}{2}}a^{\frac{1}{2}} \qquad \text{(D-14)}$$

The integrals $A(\nu+a,\ell+b)$ and $B(\nu+a,\ell+b)$ are listed in Tables D-2 to D-5.

Table D-2 Matrix elements of $q^2_{k\pm} = r^2e^{\pm 2i\phi}$ or $q^2_{k\Lambda} = r^2e^{2i\Lambda\phi}$ ($\Lambda = \pm 1$).

$$<\nu+2,\ell+2\Lambda|q^2_{\Lambda}|\nu,\ell>= \tfrac{1}{2}(\nu+\Lambda\ell+2)^{\frac{1}{2}}(\nu+\Lambda\ell+4)^{\frac{1}{2}}a = (\nu+2,\ell+2\Lambda|r^2|\nu,\ell) = A(\nu-2,\ell+2\Lambda)$$

$$<\nu,\ell+2\Lambda|q^2_{\Lambda}|\nu,\ell>= (\nu+\Lambda\ell+2)^{\frac{1}{2}}(\nu-\Lambda\ell)^{\frac{1}{2}}a = (\nu,\ell+2\Lambda|r^2|\nu,\ell) = A(\nu,\ell+2\Lambda)$$

$$<\nu-2,\ell+2\Lambda|q^2_{\Lambda}|\nu,\ell = \tfrac{1}{2}(\nu-\Lambda\ell-2)^{\frac{1}{2}}(\nu-\Lambda\ell)^{\frac{1}{2}}a = (\nu-2,\ell+2\Lambda|r^2|\nu,\ell) = A(\nu-2,\ell+2\Lambda)$$

Table D-3 Matrix elements of $q^4_{k\Lambda} = r^4e^{4i\Lambda\phi}$ ($\Lambda = \pm 1$).

$$\begin{aligned} <\nu+4,\ell+4\Lambda|q^4_{k\Lambda}|\nu,\ell> &= \frac{1}{4}(\nu+\Lambda\ell+2)^{\frac{1}{2}}(\nu+\Lambda\ell+4)^{\frac{1}{2}}(\nu+\Lambda\ell+6)^{\frac{1}{2}}(\nu+\Lambda\ell+8)^{\frac{1}{2}}a^2 \\ &= B(\nu+4,\ell+4\Lambda) \end{aligned}$$

$$\begin{aligned} <\nu+2,\ell+4\Lambda|q^4_{k\Lambda}|\nu,\ell> &= (\nu+\Lambda\ell+2)^{\frac{1}{2}}(\nu+\Lambda\ell+4)^{\frac{1}{2}}(\nu+\Lambda\ell+6)^{\frac{1}{2}}(\nu-\Lambda\ell)^{\frac{1}{2}}a^2 \\ &= B(\nu+2,\ell+4\Lambda) \end{aligned}$$

$$\begin{aligned} <\nu,\ell+4\Lambda|q^4_{k\Lambda}|\nu,\ell> &= \frac{3}{2}(\nu+\Lambda\ell+2)^{\frac{1}{2}}(\nu+\Lambda\ell+4)^{\frac{1}{2}}(\nu-\Lambda\ell-2)^{\frac{1}{2}}(\nu-\Lambda\ell)^{\frac{1}{2}}a^2 \\ &= B(\nu+0,\ell+4\Lambda) \end{aligned}$$

$$\begin{aligned} <\nu-2,\ell+4\Lambda|q^4_{k\Lambda}|\nu,\ell> &= (\nu+\Lambda\ell+2)^{\frac{1}{2}}(\nu-\Lambda\ell-4)^{\frac{1}{2}}(\nu-\Lambda\ell-2)^{\frac{1}{2}}(\nu-\Lambda\ell)^{\frac{1}{2}}a^2 \\ &= B(\nu-2,\ell+4\Lambda) \end{aligned}$$

$$<\nu-4,\ell+4\Lambda|q^4_{k\Lambda}|\nu,\ell> = \frac{1}{4}(\nu-\Lambda\ell-6)^{\frac{1}{2}}(\nu-\Lambda\ell-4)^{\frac{1}{2}}(\nu-\Lambda\ell-2)^{\frac{1}{2}}(\nu-\Lambda\ell)^{\frac{1}{2}}a^2$$

$$= \mathcal{B}(\nu-4,\ell+4\Lambda)$$

Table D-4 Matrix elements of r^4.

$$<\nu+4,\ell|r^4|\nu,\ell> = \frac{1}{4}(\nu+\ell+2)^{\frac{1}{2}}(\nu-\ell+2)^{\frac{1}{2}}(\nu+\ell+4)^{\frac{1}{2}}(\nu-\ell+4)^{\frac{1}{2}}a^2 = \mathcal{B}(\nu+4,\ell+0)$$

$$<\nu+2,\ell|r^4|\nu,\ell> = (\nu+\ell+2)^{\frac{1}{2}}(\nu-\ell+2)^{\frac{1}{2}}(\nu+2)a^2 = \mathcal{B}(\nu+2,\ell+0)$$

$$<\nu,\ell|r^4|\nu,\ell> = \frac{1}{2}[3(\nu+1)^2 + 1 - \ell^2]a^2 = \mathcal{B}(\nu+0,\ell+0)$$

$$<\nu-2,\ell|r^4|\nu,\ell> = (\nu+\ell)^{\frac{1}{2}}(\nu-\ell)^{\frac{1}{2}}\nu a^2 = \mathcal{B}(\nu-2,\ell+0)$$

$$<\nu-4,\ell|r^4|\nu,\ell> = \frac{1}{4}(\nu+\ell)^{\frac{1}{2}}(\nu-\ell)^{\frac{1}{2}}(\nu+\ell-2)^{\frac{1}{2}}(\nu-\ell-2)^{\frac{1}{2}}a^2 = \mathcal{B}(\nu-4,\ell+0)$$

Table D-5 Matrix elements of $r^2q^2_{k\Lambda} = r^4e^{2i\Lambda\phi}$.

$$<\nu+4,\ell+2\Lambda|r^2q^2_{k\Lambda}|\nu,\ell> = \frac{1}{4}(\nu+\ell+2)^{\frac{1}{2}}(\nu+\Lambda\ell+4)^{\frac{1}{2}}(\nu+\Lambda\ell+6)^{\frac{1}{2}}(\nu-\ell+2)^{\frac{1}{2}}a^2$$

$$= \mathcal{B}(\nu+4,\ell+2\Lambda)$$

$$<\nu+2,\ell+2\Lambda|r^2q^2_{k\Lambda}|\nu,\ell> = \frac{1}{2}(\nu+\Lambda\ell+2)^{\frac{1}{2}}(\nu+\Lambda\ell+4)^{\frac{1}{2}}[2(\nu+1) - (\Lambda\ell-1)]a^2$$

$$= \mathcal{B}(\nu+2,\ell+2\Lambda)$$

$$<\nu,\ell+2\Lambda|r^2q^2_{k\Lambda}|\nu,\ell> = \frac{3}{2}(\nu+\Lambda\ell+2)^{\frac{1}{2}}(\nu-\Lambda\ell)^{\frac{1}{2}}(\nu+1)a^2 = \mathcal{B}(\nu,\ell+2\Lambda)$$

$$<\nu-2,\ell+2\Lambda|r^2q^2_{k\Lambda}|\nu,\ell> = \frac{1}{2}(\nu-\Lambda\ell)^{\frac{1}{2}}(\nu-\Lambda\ell-2)^{\frac{1}{2}}[2(\nu+1) + (\Lambda\ell-1)a^2$$

$$= \mathcal{B}(\nu-2,\ell+2\Lambda)$$

$$<\nu-4,\ell+2\Lambda|r^2q^2_{k\Lambda}|\nu,\ell> = \frac{1}{4}(\nu-\ell)^{\frac{1}{2}}(\nu-\Lambda\ell-2)^{\frac{1}{2}}(\nu-\Lambda\ell-4)^{\frac{1}{2}}(\nu+\ell)^{\frac{1}{2}}a^2$$

$$= \mathcal{B}(\nu-4,\ell+2\Lambda)$$

Appendix E

Transformation Matrices $\mathbb{S}(n)$

We define that

$$\mathbb{A}(n) \equiv \begin{bmatrix} 0 & a_1 & 0 & \cdots & \cdots & 0 & 0 \\ a_1 & 0 & a_2 & & & 0 & 0 \\ 0 & a_2 & 0 & \cdots & \cdots & 0 & 0 \\ \cdot & & & & & \cdot & \\ \cdot & & & & & \cdot & \\ 0 & 0 & 0 & & & 0 & a_{n-1} \\ 0 & 0 & 0 & \cdots & \cdots & a_{n-1} & 0 \end{bmatrix} \qquad (\text{E-1})$$

The orthogonal transformation matrices $\mathbb{S}(n)$ are determined by the following matrix equation:

$$\mathbb{S}(n)^{-1} \cdot \mathbb{A}(n) \cdot \mathbb{S}(n) = \mathrm{diag}(\lambda_1, \lambda_2, \ldots \lambda_n) \equiv \Lambda(n) . \qquad (\text{E-2})$$

In the diagonal matrix $\mathrm{diag}(\lambda_1, \lambda_2, \ldots \lambda_n)$, we shall arrange the λ's in the order that

$$\lambda_1 \geqq \lambda_2 \geqq \lambda_3 \quad \cdots \geqq \lambda_n . \qquad (\text{E-3})$$

The results aregiven in Table E-1.

Table E-1 Diagonalization of A-matrices
$\mathbb{S}^{-1} \cdot \mathbb{A} \cdot \mathbb{S} = \Lambda$

n	$\mathbb{A}(n)$	$\mathbb{S}(n)$	$\Lambda(n)$
1	$\mathbb{A}(1) = 0$	$\mathbb{S}(1) = 1$	$\Lambda(1) = 0$
2	$\mathbb{A}(2) = \begin{bmatrix} a_1 & a_1 \\ a_1 & a \end{bmatrix}$	$\mathbb{S}(2) = \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}$	$\Lambda(2) = \begin{bmatrix} a_1 & 0 \\ 0 & -a_1 \end{bmatrix}$.
3	$\begin{bmatrix} 0 & a_1 & 0 \\ a_1 & 0 & a_2 \\ 0 & a_2 & 0 \end{bmatrix}$	$\mathbb{S}(3) = \begin{bmatrix} \frac{1}{\sqrt{2}}\frac{a_1}{N} & \frac{a_2}{N} & \frac{1}{\sqrt{2}}\frac{a_1}{N} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}}\frac{a_2}{N} & -\frac{a_1}{N} & \frac{1}{\sqrt{2}}\frac{a_2}{N} \end{bmatrix}$ $N = (a_1^2 + a_2^2)^{1/2}$	$\Lambda(3) = \begin{bmatrix} (a_1^2+a_2^2)^{1/2} & & \\ & 0 & \\ & & -(a_1^2+a_2^2)^{1/2} \end{bmatrix}$.

n	$\mathbb{A}(n)$	$\mathbb{S}(n)$	$\mathbb{\Lambda}(n)$
4	$\begin{bmatrix} 0 & a_1 & 0 & 0 \\ a_1 & 0 & a_2 & 0 \\ 0 & a_2 & 0 & a_3 \\ 0 & 0 & a_3 & 0 \end{bmatrix}$	$\mathbb{S}(4)=[\vec{s}_1\ \vec{s}_2\ \vec{s}_3\ \vec{s}_4]$ $\vec{s}_j=\frac{1}{N_j}\begin{bmatrix} a_1 \\ \lambda_j \\ (\lambda_j^2-a_1^2)/a_2 \\ (\lambda_j^2-a_1^2)a_3/a_2\lambda_j \end{bmatrix}$ $N_j^2=a_1^2+\lambda_j^2+\left(\frac{\lambda_j^2-a_1^2}{a_2}\right)^2\cdot\left(\frac{\lambda_j^2+a_3^2}{\lambda_j^2}\right)$	$\mathbb{\Lambda}(4)=\mathrm{diag}(\lambda_1\ \lambda_2\ \lambda_3\ \lambda_4)$ $\lambda_j=\pm\left[\frac{1}{2}(a_1^2+a_2^2+a_3^2)\pm\frac{1}{2}\{(a_1^2+a_2^2+a_3^2)^2-4a_1^2a_3^2\}^{1/2}\right]^{1/2}$ $\lambda_4=-\lambda_1$. $\lambda_3=-\lambda_2$.
5	$\begin{bmatrix} 0 & a_1 & 0 & 0 & 0 \\ a_1 & 0 & a_2 & 0 & 0 \\ 0 & a_2 & 0 & a_3 & 0 \\ 0 & 0 & a_3 & 0 & a_4 \\ 0 & 0 & 0 & a_4 & 0 \end{bmatrix}$	$\mathbb{S}(5)=[\vec{s}_1\ \vec{s}_2\ \vec{s}_3\ \vec{s}_4\ \vec{s}_5]$ $\vec{s}_j=\frac{1}{N_j}\begin{bmatrix} a_1 \\ \lambda_j \\ (\lambda_j^2-a_1^2)/a_2 \\ \{\lambda_j^3-\lambda_j(a_1^2+a_2^2)\}/a_2a_3 \\ (\lambda_j^2-a_1^2-a_2^2)a_4/a_2a_3\lambda_j \end{bmatrix}$ $N_j^2=a_1^2+\lambda_j^2+\left(\frac{\lambda_j^2-a_1^2}{a_2}\right)^2+\frac{\lambda_j^2+a_4^2}{a_2^2a_3^2}(\lambda_j^2-a_1^2-a_2^2)^2$	$\mathbb{\Lambda}(5)=\mathrm{diag}(\lambda_1\ \lambda_2\ \lambda_3\ \lambda_4\ \lambda_5)$ $\lambda_j=\pm\left[\frac{1}{2}(a_1^2+a_2^2+a_3^2+a_4^2)\pm\frac{1}{2}\{(a_1^2+a_2^2+a_3^2+a_4^2)^2-4(a_1^2a_3^2+a_1^2a_4^2+a_2^2a_4^2)\}^{1/2}\right]^{1/2}$ $(j=1,2,4,5)$. $\lambda_3=0$
6	$\begin{bmatrix} 0 & a_1 & 0 & 0 & 0 & 0 \\ a_1 & 0 & a_2 & 0 & 0 & 0 \\ 0 & a_2 & 0 & a_3 & 0 & 0 \\ 0 & 0 & a_3 & 0 & a_4 & 0 \\ 0 & 0 & 0 & a_4 & 0 & a_5 \\ 0 & 0 & 0 & 0 & a_5 & 0 \end{bmatrix}$	$\mathbb{S}(6)=[\vec{s}_1\ \vec{s}_2\ \vec{s}_3\ \vec{s}_4\ \vec{s}_5\ \vec{s}_6]$ $\vec{s}_j=[S_{1j},S_{2j},S_{3j},S_{4j}\ S_{5j}\ S_{6j}]^T$ $S_{1j}=a_1/N_j$; $S_{2j}=\lambda_j/N_j$; $S_{3j}=(\lambda_j^2-a_1^2)/a_2N_j$; $S_{4j}=(\lambda_j^2-a_1^2-a_2^2)\lambda_j/a_2a_3N_j$ $S_{5j}=\frac{\lambda_j^4-\lambda_j^2(a_1^2+a_2^2+a_3^2)+a_1^2a_3^2}{a_2a_3a_4N_j}$ $S_{6j}=[\lambda_j^5-\lambda_j^3(a_1^2+a_2^2+a_3^2+a_4^2)+\lambda_j(a_1^2a_3^2+a_1^2a_4^2+a_4^2a_2^2)]/a_2a_3a_4a_5N_j$ $\sum_{r=1}^{6}S_{rj}^2=1$.	$\mathbb{\Lambda}(6)=\mathrm{diag}(\lambda_1\lambda_2\lambda_3\lambda_4\lambda_5\lambda_6)$ $\lambda_j=\pm\left\{\frac{1}{3}\left(\sum_{r=1}^{5}a_r^2\right)+\frac{2}{3}\left[\left(\sum_r^5 a_r^2\right)^2-3(a_1^2a_3^2+a_1^2a_4^2+a_1^2a_5^2+a_2^2a_4^2+a_2^2a_5^2+a_3^2a_5^2)\right]^{1/2}\cos\frac{\phi+2n\pi}{3}\right\}^{1/2}$, $(n=0,1,2)$. $\cos\phi=\left\{\sum a_i^2\left[2\left(\sum a_i^2\right)^2-9\sum_{i=1}^{3}\sum_{j=i+2}^{5}a_i^2a_j^2\right]+27a_1^2a_3^2a_5^2\right\}\cdot\left\{2\left[\left(\sum a_i^2\right)^2-3\sum_i^3\sum_{j=i+2}^{5}a_i^2a_j^2\right]\right\}^{-1}$.

n	$\mathbb{A}(n)$	$\mathbb{S}(n)$	$\Lambda(n)$
7	$\begin{bmatrix} 0 & a_1 & 0 & 0 & 0 & 0 & 0 \\ a_1 & 0 & a_2 & 0 & 0 & 0 & 0 \\ 0 & a_2 & 0 & a_3 & 0 & 0 & 0 \\ 0 & 0 & a_3 & 0 & a_4 & 0 & 0 \\ 0 & 0 & 0 & a_4 & 0 & a_5 & 0 \\ 0 & 0 & 0 & 0 & a_5 & 0 & a_6 \\ 0 & 0 & 0 & 0 & 0 & a_6 & 0 \end{bmatrix}$	$\mathbb{S}(7) = \left[S_{rj} \right]$. $S_{rj} = \frac{a_i}{N_j \prod_{n=1}^{i-1} a_n} \cdot \Big\{ (\lambda_j)^{i-1} - (\lambda_j)^{i-3} \cdot \sum_{n=1}^{i-2} a_n^2 + (\lambda_j)^{i-5} \sum_{n=1}^{i-4} \sum_{m=n+2}^{i-2} a_n^2 a_m^2 - (\lambda_j)^{i-7} \sum_{n=1}^{i-6} \sum_{m=n+2}^{i-4} \sum_{l=m+2}^{i-2} a_n^2 a_m^2 a_l^2 + \cdots \Big\}$.	$\Lambda(7) = \mathrm{diag}(\lambda_1\ \lambda_2 \cdots \lambda_7)$ $\lambda_4 = 0$ $\lambda_j = \pm \Big\{ \frac{1}{3} \sum_{i=1}^{6} a_i^2 + \frac{2}{3} \Big[\Big(\sum_i^6 a_i^2 \Big)^2 - 3 \sum_{i=1}^{4} \sum_{j=i+2}^{6} a_i^2 a_j^2 \Big]^{1/2} \cdot \cos \frac{\phi + 2\pi n}{3} \Big\}^{1/2}$. $\cos\phi = \Big\{ \sum_i^6 a_i^2 \Big[2 \Big(\sum_i a_i^2 \Big)^2 - 9 \sum_{i=1}^{4} \sum_{j=i+2}^{6} a_i^2 a_m^2 + 27 \sum_{i=1}^{2} \sum_{j=i+2}^{4} \sum_{l=j+2}^{6} a_i^2 a_j^2 a_l^2 \Big\} \frac{1}{2} \Big[\Big(\sum_i a_i^2 \Big)^2 - 3 \sum_i^4 \sum_{j=i+2}^{6} a_i^2 a_j^2 \Big]^{-3/2}$.
8	$\begin{bmatrix} & a_1 & & & & & & \\ a_1 & & a_2 & & & & & \\ & a_2 & & a_3 & & & & \\ & & a_3 & & a_4 & & & \\ & & & a_4 & & a_5 & & \\ & & & & a_5 & & a_6 & \\ & & & & & a_6 & & a_7 \\ & & & & & & a_7 & \end{bmatrix}$	The λ's are obtained by setting $\det \lvert \mathbb{A}(8) - \lambda \rvert = 0$ Thus $(\lambda^2)^4 - \sum_{i=1}^{7} a_i^2 (\lambda^2)^3 + \sum_{i=1}^{5} \sum_{j=i+2}^{7} a_i^2 a_j^2 (\lambda^2)^2 - \sum_{i=1}^{3} \sum_{j=i+2}^{5} \sum_{l=j+2}^{7} a_i^2 a_j^2 a_l^2 \lambda^2 + a_1^2 a_3^2 a_5^2 a_7^2 = 0$	

APPENDIX F

Schröedinger Degenerate Perturbation Theory

We denote the column matrices $\Phi^{o}(K;\upsilon_1,\upsilon_2)$, Φ_K, $\mathbb{P}_K(\upsilon_1',\upsilon_2';\upsilon_1,\upsilon_2)$, $\mathbb{H}(K;\upsilon_1,\upsilon_2)$ and $[H_K]$ by:

(a) $$\Phi^{o}(K;\upsilon_1,\upsilon_2) = \|\phi_1^{o},\phi_2^{o},\ldots\ldots,\phi_r^{o},\ldots\ldots,\phi_n^{o}\|^{T} \qquad \text{(F-1)}$$

where T designates the transpose of the matrix, and ϕ_r^{o} are the eigen functions of the unperturbed Hamiltonian H^{o}:

$$\phi_r^{o} = \phi_r^{o}(K;\upsilon_1,\upsilon_2) = |\Lambda^{(r)};\upsilon_1,\ell_1^{(r)};\upsilon_2,\ell_2^{(r)}>$$

(b) $$\bar{\Phi}_K = \left\| \cdots\ \bar{\Phi}^{o}(K,\upsilon_1,\upsilon_2)^{T},\ \bar{\Phi}^{o}(K;\upsilon_1,\upsilon_2+2)^{T},\ \cdots\ \bar{\Phi}^{o}(K;\upsilon_1+2,\upsilon_2)^{T},\ \bar{\Phi}^{o}(K;\upsilon_1+2,\upsilon_2+2)^{T},\ \cdots \right\|^{T} \qquad \text{(F-2)}$$

which is a canonical column matrix having infinitive number of elements.

(c) The finite matrices $\mathbb{P}_K(\upsilon_1',\upsilon_2';\upsilon_1,\upsilon_2)$ collect all interaction integrals $<\phi_{r'}^{o}(K;\upsilon_1',\upsilon_2')|H'|\phi_r^{o}(K;\upsilon_1,\upsilon_2)>$ with given K, υ_1', υ_2' and υ_1,υ_2:

$$\mathbb{P}_K(\upsilon_1',\upsilon_2';\upsilon_1,\upsilon_2) = \left\| \langle \phi_{r'}^{o}(K;\upsilon_1',\upsilon_2')|H'|\phi_r^{o}(K;\upsilon_1,\upsilon_2)\rangle;\ \begin{matrix} r'\downarrow = 1,2,\cdots,n_K'(\upsilon_1',\upsilon_2') \\ r\rightarrow = 1,2,\cdots,n_K(\upsilon_1,\upsilon_2) \end{matrix} \right\|$$

(F-3)

(d) The finite matrices $\mathbb{H}(K;\upsilon_1,\upsilon_2)$ are the representation of the Hamiltonian, $(H^{o} + H')$ in the basis $\{\phi_1^{o},\phi_2^{o},\ldots,\phi_n^{o}(K;\upsilon_1\upsilon_2)\}$ within the level $[\upsilon_1,\upsilon_2]^{K}$; i.e.,

$$\mathbb{H}(K;\upsilon_1,\upsilon_2) = \left\| \langle \phi_{r'}^{o}(K;\upsilon_1,\upsilon_2)|H^{o}+H'|\phi_r^{o}(K;\upsilon_1,\upsilon_2)\rangle,\ \begin{matrix} r'\downarrow = 1,2,\cdots n_K(\upsilon_1,\upsilon_2) \\ r\rightarrow = 1,2,\cdots n_K(\upsilon_1,\upsilon_2) \end{matrix} \right\|,$$

(F-4)

(e) The representation of $H^{o} + H'$ in the basis of (F-2) is denoted by the following canonical perturbation matrix:

$$[H_K] = \begin{bmatrix} \ddots & & & & \\ & \mathbb{H}(K;\upsilon_1,\upsilon_2) & \mathbb{P}_K(\upsilon_1,\upsilon_2;\upsilon_1,\upsilon_2+2)\ldots\ldots & \mathbb{P}_K(\upsilon_1,\upsilon_2;\upsilon_1+2,\upsilon_2) & \mathbb{P}_K(\upsilon_1,\upsilon_2;\upsilon_1+2,\upsilon_2+2)\ldots\ldots \\ & \mathbb{P}_K(\upsilon_1,\upsilon_2+2;\upsilon_1,\upsilon_2) & \mathbb{H}(K;\upsilon_1,\upsilon_2+2)\ldots\ldots & \mathbb{P}_K(\upsilon_1,\upsilon_2+2;\upsilon_1+2,\upsilon_2) & \mathbb{P}_K(\upsilon_1,\upsilon_2+2,\upsilon_1+2,\upsilon_2+2)\ldots \\ & \vdots & \ddots & & \\ & \mathbb{P}_K(\upsilon_1+2,\upsilon_2;\upsilon_1,\upsilon_2) & \mathbb{P}_K(\upsilon_1+2,\upsilon_2;\upsilon_1,\upsilon_2+2)\ldots\ldots & \mathbb{H}(K;\upsilon_1+2,\upsilon_2) & \mathbb{P}_K(\upsilon_1+2,\upsilon_2;\upsilon_1+2,\upsilon_2+2)\ldots \\ & \mathbb{P}_K(\upsilon_1+2,\upsilon_2+2;\upsilon_1,\upsilon_2) & \mathbb{P}_K(\upsilon_1+2,\upsilon_2+2;\upsilon_1,\upsilon_2+2)\ldots\ldots & \mathbb{P}_K(\upsilon_1+2,\upsilon_2+2;\upsilon_1+2,\upsilon_2) & \mathbb{H}(K;\upsilon_1+2,\upsilon_2+2)\ldots\ldots \\ & \vdots & \vdots & \vdots & \vdots \end{bmatrix}$$

When the perturbation H' is

$$H' = fr_1^2\cos 2(\theta-\phi_1) + f_2r_2^2\cos 2(\theta-\phi_2) \tag{F-6}$$

the submatrices of $[H_K]$, i.e., $\mathbb{H}(K;\upsilon_1,\upsilon_2)$ and $\mathbb{P}_K(\upsilon_1'\upsilon_2';\upsilon_1\upsilon_2)$ have the following forms (e.g., Fig. F-1):

$$\begin{array}{cc} \phi_r^o(K;\upsilon_1,\upsilon_2): & \begin{array}{cccccc} \phi_1^o & \phi_2^o & \phi_3^o & \cdots\cdots & \phi_{n-1}^o & \phi_n^o \end{array} \\ \mathbb{H}(K;\upsilon_1,\upsilon_2) = & \begin{bmatrix} \mathcal{E}^o_{\upsilon_1,\upsilon_2} & a_1 & 0 & & & \\ a_1 & \mathcal{E}^o_{\upsilon_1,\upsilon_2} & a_2 & & & \\ 0 & a_2 & \mathcal{E}^o_{\upsilon_1,\upsilon_2} & & & \\ & & & & & \\ & & & & \mathcal{E}^o_{\upsilon_1,\upsilon_2} & a_{n-1} \\ & & & & a_{n-1} & \mathcal{E}^o_{\upsilon_1,\upsilon_2} \end{bmatrix} \end{array} \tag{F-4'}$$

$$\text{where } a_r = a_r(K;\upsilon_1,\upsilon_2) = \langle\phi_r^o(K;\upsilon_1,\upsilon_2)|H'|\phi_{r+1}^o(K;\upsilon_1,\upsilon_2)\rangle. \tag{F-7}$$

The off-diagonal submatrices $\mathbb{P}_K(\upsilon_1'\upsilon_2';\upsilon_1\upsilon_2)$ are

(a) when $\upsilon_1' = \upsilon_1$, $\upsilon_2' = \upsilon_2-2$, we have

Fig. F-1. (K = 2, ν_1 = even, ν_2 = odd.) Canonical Perturbation Matrix.

$$
[H_{K=2}] = \begin{array}{ccccccccccccccccccccc}
[\nu_1,\nu_2] & [0.1] & [0.3] & & [0.5] & & & [2.1] & & & [2.3] & & & & & [2.5] & & & & & \\
(\Lambda\ell_1\ell_2) & (+01) & (+01) & (-03) & (+01) & (-03) & \cdots & (+2\overline{1}) & (-21) & (+01) & (+2\overline{1}) & (-21) & (+01) & (-03) & (+\overline{2}3) & (+2\overline{1}) & (-21) & (+01) & (-03) & (+\overline{2}3) & (-\overline{2}5) \\
 & & & x_1 & & & & 0 & x_1 & 0 & & & & & & & & & & & \\
 & & & a & & x_1 & & & & & 0 & x_1 & 0 & & & & & & & & \\
 & x_1 & a & & x_2 & & & & & & & & & 0 & x_2 & & & & & & \\
 & & & x_2 & & a & & & & & & & & & & 0 & x_1 & 0 & & & \\
 & & x_1 & & a & & & & & & & & & & & & & & 0 & x_2 & 0 \\
 & & & & & & \ddots & & & & & & & & & & & & & & \\
 & 0 & & & & & & & a_1 & & 0 & x_1 & & & & & & & & & \\
 & x_1 & & & & & & a_1 & & a_2 & x_2 & 0 & & & & & & & & & \\
 & 0 & & & & & & & a_2 & & & & 0 & x_3 & & & & & & & \\
 & & 0 & & & & & 0 & x_2 & & & a_1 & & & & 0 & x_1 & & & & \\
 & & x_1 & & & & & x_1 & 0 & & a_1 & & a_2 & & & x_2 & 0 & & & & \\
 & & 0 & & & & & & & 0 & & a_2 & & a_3 & & & & 0 & x_3 & & \\
 & & & 0 & & & & & & x_3 & & & a_3 & & a_4 & & & x_4 & 0 & & \\
 & & & x_2 & & & & & & & & & & a_4 & & & & & 0 & x_5 &
\end{array}
$$

$$\mathbb{P}_K(\upsilon_1,\upsilon_2-2;\upsilon_1,\upsilon_2) = \begin{bmatrix} 0 & x_1 & & & \\ x_2 & 0 & & & \\ & & 0 & x_3 & \\ & & x_4 & 0 & \\ & & & & \ddots \end{bmatrix} \qquad \text{(F-3a)}$$

where $x_\ell = x_\ell(\upsilon_1'\upsilon_2';\upsilon_1,\upsilon_2)$ is the only non-zero element in the ℓ^{th} row of the $\mathbb{P}_K(\upsilon_1'\upsilon_2';\upsilon_1,\upsilon_2)$ matrix.

(b) When $\upsilon_1' = \upsilon_1-2$, $\upsilon_2' = \upsilon_2$, we have

$$\mathbb{P}_K(\upsilon_1-2,\upsilon_2;\upsilon_1,\upsilon_2) = \begin{bmatrix} 0 & x_1 & & & \\ & & 0 & x_2 & \\ & & x_3 & 0 & \\ & & & & \ddots \end{bmatrix} \qquad \text{(F-3b)}$$

(c) $\mathbb{P}_K(\upsilon_1',\upsilon_2';\upsilon_1,\upsilon_2) = 0$ unless (i) $\upsilon_1' = \upsilon_1$; <u>and</u> $\upsilon_2' = \upsilon_2 \pm 2$ (F-3c)

or (ii) $\upsilon_1' = \upsilon_1 \pm 2$, <u>and</u> $\upsilon_2' = \upsilon_2$

We notice that

$$\mathbb{P}_K(\upsilon_1',\upsilon_2';\upsilon_1,\upsilon_2) = [\mathbb{P}_K(\upsilon_1,\upsilon_2;\upsilon_1',\upsilon_2')]^T \qquad \text{(F-8)}$$

thus

$$\mathbb{P}_K(\upsilon_1',\upsilon_2';\upsilon_1,\upsilon_2)^T\cdot\mathbb{P}_K(\upsilon_1',\upsilon_2';\upsilon_1,\upsilon_2) = \begin{bmatrix} x_1^2 & & & \\ & x_2^2 & & \\ & & \ddots & \\ & & & x_m^2 \end{bmatrix} \qquad \text{(F-9)}$$

where m is the smaller value of $n_K(\upsilon_1,\upsilon_2)$ and $n_K'(\upsilon_1',\upsilon_2')$.

The energies correct to first-order are obtained by diagonalization of the <u>first-order perturbation</u> matrices $\mathbb{H}(K;\upsilon_1\upsilon_2)^{(16)}$, i.e.,

$$\mathbb{S}(K;\upsilon_1,\upsilon_2)^{-1}\cdot\mathbb{H}(K;\upsilon_1,\upsilon_2)\cdot\mathbb{S}(K;\upsilon_1,\upsilon_2) = \mathbb{E}^{o}_{\upsilon_1\upsilon_2} + \mathbb{E}^{(1)}(K;\upsilon_1,\upsilon_2) \qquad \text{(F-10)}$$

The orthogonal transformation matrices $\mathbb{S}(K;\upsilon_1,\upsilon_2)$ and the first-order correction matrices $\mathfrak{C}^{(1)}(K;\nu_1,\nu_2)$ have been tabulated in Appendix E in terms of $\mathcal{S}(n)$ and $\lambda(n)$.

The "correct zeroth-order" wave functions are obtained by

$$\Psi^{o}(K;\nu_1,\nu_2) = \mathcal{S}(K;\nu_1,\nu_2)^{T}\cdot\Phi^{o}(K;\nu_1,\nu_2) \tag{F-11}$$

or more explicitly, by

$$\begin{bmatrix} \psi_1^o(K;\nu_1,\nu_2) \\ \psi_2^o(K;\nu_1,\nu_2) \\ \vdots \\ \psi_j^o(K;\nu_1,\nu_2) \\ \vdots \\ \psi_n^o(K;\nu_1,\nu_2) \end{bmatrix} = \begin{bmatrix} \tilde{S}_{11} & \tilde{S}_{21} \cdots\cdots & \tilde{S}_{n1} \\ \tilde{S}_{12} & \tilde{S}_{22} \cdots\cdots & \tilde{S}_{n2} \\ \vdots & & \\ \vdots & & \\ \tilde{S}_{1n} & \tilde{S}_{2n} \cdots\cdots & \tilde{S}_{nn} \end{bmatrix} \begin{bmatrix} \phi_1^o(K;\nu_1,\nu_2) \\ \phi_2^o(K;\nu_1,\nu_2) \\ \vdots \\ \phi_r^o(K;\nu_1,\nu_2) \\ \vdots \\ \phi_n^o(K;\nu_1,\nu_2) \end{bmatrix} \tag{F-12}$$

where $\tilde{S}_{j\ell} = [\mathcal{S}(K;\nu_1,\nu_2)]_{\ell j}$ is the ℓ^{th}-row-and-j^{th}-column element of the transformation matrix $\mathcal{S}(K;\nu_1,\nu_2)$.

To obtain the second-order energy corrections, one constructs the following canonical transformation matrices$^{(5)}$:

$$[S_K] = \begin{bmatrix} \ddots & & & & & \\ & \mathcal{S}(K;\nu_1,\nu_2) & 0 & & & \\ & 0 & \mathcal{S}(K;\nu_1,\nu_2+2) & & & \\ & & & \ddots & & \\ & & & & \mathcal{S}(K;\nu_1+2,\nu_2) & 0 \\ & & & & 0 & \mathcal{S}(K;\nu_1+2,\nu_2+2) \\ & & & & & & \ddots \end{bmatrix} \tag{F-13}$$

Then the correct zeroth-order wave functions are contained in the column matrix Ψ_K^o, obtained by

$$\Psi_K^o = [S_K]^T \cdot \phi_K^o \tag{F-14}$$

In the basis of (F 14), the Hamiltonian $H = H^o + H'$ will be represented by $[H_K]'$ (e.g., Fig. F-2):

$$[H_K]' = [S_K]^T \cdot [H_K] \cdot [S_K]$$

$$= \begin{bmatrix} \mathcal{E}^o_{\nu_1\nu_2} + \mathcal{E}^{(1)}(K;\nu_1,\nu_2) & \mathbb{P}_K'(\nu_1\nu_2;\nu_1,\nu_2+2) & 0 \\ \mathbb{P}_K'(\nu_1,\nu_2+2;\nu_1,\nu_2) & \mathcal{E}^o_{\nu_1,\nu_2+2} + \mathcal{E}^{(1)}(K;\nu_1,\nu_2+2) & \mathbb{P}_K'(\nu_1,\nu_2+2,\nu_1,\nu_2+4)\ldots \\ 0 & \mathbb{P}_K'(\nu_1,\nu_2+4;\nu_1,\nu_2+2) & \mathcal{E}^o_{\nu_1,\nu_2+4} + \mathcal{E}^{(1)}(K;\nu_1,\nu_2+4)\ldots \\ & & \ddots \end{bmatrix} \tag{F-15}$$

where $\mathbb{P}_K'(\nu_1'\nu_2';\nu_1\nu_2) = S(K;\nu_1,\nu_2)^{-1} \cdot P_K(\nu_1',\nu_2';\nu_1,\nu_2) \cdot S(K;\nu_1,\nu_2)$. (F-16)

Thus the energies correct to first-order are given by the diagonal matrices:

$$\mathcal{E}^o_{\nu_1\nu_2} + \mathcal{E}^{(1)}(K;\nu_1,\nu_2).$$

The second energy corrections are determined by the off-diagonal matrices $\mathbb{P}_K'$. Suppose the correct zeroth-order state to be perturbed is $|\phi_j(K;\nu_1,\nu_2)>$, then the second-order energy correct is given by$^{(16)}$:

$$\mathcal{E}_j^{(2)}(K;\nu_1,\nu_2) = -\sum_{1',2'}\sum_{j} \frac{|<\Psi^o_{j'}(K;\nu_1',\nu_2')|H'|\Psi^o_j(K;\nu_1,\nu_2)>|^2}{\mathcal{E}^o_{\nu_1'\nu_2'} - \mathcal{E}^o_{\nu_1\nu_2}} \tag{F-17}$$

If we define that

$$W_{j'j}(\nu_1'\nu_2';\nu_1,\nu_2) \equiv \sum_{j'} |<\Psi^o_{j'}(K;\nu_1'\nu_2')|H'|\Psi^o_j(K;\nu_1,\nu_2)>|^2$$

$$= \sum_{j'} <\Psi^o_j(K;\nu_1\nu_2)|H'|\Psi^o_{j'}(K;\nu_1'\nu_2')><\Psi^o_{j'}(K;\nu_1'\nu_2')|H'|\Psi^o_j(K;\nu_1,\nu_2)> \tag{F-18}$$

We observe that W_{jj} is the j^th diagonal matrix element of the matrix defined by

$$\mathbb{W}_K(\nu_1'\nu_2';\nu_1,\nu_2) \equiv [\mathbb{P}_K'(\nu_1'\nu_2';\nu_1\nu_2)]^T\cdot\mathbb{P}_K'(\nu_1'\nu_2';\nu_1\nu_2) \qquad \text{(F-19)}$$

(This can be proved by multiplication of matrices.) Substituting Equation (F-16) into (F-19), we have

$$\begin{aligned}\mathbb{W}_K(\nu_1'\nu_2';\nu_1\nu_2) &= [\mathbb{S}(K;\nu_1'\nu_2')^{-1}\cdot\mathbb{P}_K(\nu_1'\nu_2';\nu_1\nu_2)\cdot\mathbb{S}(K;\nu_1'\nu_2')^{-1}\cdot\mathbb{P}_K(\nu_1'\nu_2';\nu_1\nu_2)\cdot\mathbb{S}(K;\nu_1\nu_2)]\\ &= [\mathbb{S}(K;\nu_1\nu_2)^{-1}\cdot\mathbb{P}_K(\nu_1'\nu_2';\nu_1\nu_2)^T\cdot\underbrace{\mathbb{S}(K;\nu_1'\nu_2')]\cdot[\mathbb{S}(K;\nu_1'\nu_2')^{-1}}_{\mathbb{1}}\cdot\mathbb{P}_K(\nu_1'\nu_2'\nu_1\nu_2)\cdot\mathbb{S}(K;\nu_1\nu_2)]\\ &= \mathbb{S}(K;\nu_1,\nu_2)^{-1}\cdot\underbrace{\mathbb{P}_K(\nu_1'\nu_2';\nu_1,\nu_2)^T\cdot\mathbb{P}_K(\nu_1'\nu_2';\nu_1\nu_2)}_{[x_\ell^2\delta_{\ell\ell'}]}\cdot\mathbb{S}(K;\nu_1,\nu_2)\\ &= \left|\left|\sum_\ell x_\ell^2(\nu_1'\nu_2';\nu_1\nu_2)S_{\ell i}S_{\ell j}\right|\right| \end{aligned} \qquad \text{(F-20)}$$

Therefore

$$W_{jj} = \sum_\ell x_\ell^2(\nu_1'\nu_2';\nu_1\nu_2)S_{\ell j}^2 \qquad \text{(F-21)}$$

and hence Equation (F-17) becomes

$$\mathcal{E}_j^{(2)}(K;\nu_1,\nu_2) = -\sum_{\nu_1'\nu_2'}{}' \frac{W_{jj}(\nu_1'\nu_2';\nu_1\nu_2)}{\mathcal{E}^o_{\nu_1'\nu_2'} - \mathcal{E}^o_{\nu_1\nu_2}} = -\sum_\ell \sum_{\nu_1'\nu_2'}{}' \frac{x_\ell^2(\nu_1'\nu_2';\nu_1\nu_2)}{\mathcal{E}^o_{\nu_1'\nu_2'} - \mathcal{E}^o_{\nu_1\nu_2}}\cdot S_{\ell j}^2(K;\nu_1\nu_2) \qquad \text{(F-22)}$$

The first-order wave functions for the j^th state in $[\nu_1,\nu_2]^K$ level is given by:

$$\Psi_j(K;\nu_1,\nu_2) = \Psi_j^o(K;\nu_1,\nu_2) - \sum_{\nu'\nu'}{}' \sum_{j'} \frac{\langle\Psi_j^o(K;\nu_1\nu_2)|H'|\Psi_{j'}^o(K;\nu_1'\nu_2')\rangle}{\mathcal{E}^o_{\nu_1'\nu_2'} - \mathcal{E}^o_{\nu_1\nu_2}}\cdot\Psi_j^o(K;\nu_1'\nu_2') \qquad \text{(F-23)}$$

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