CHAPTER IV

Synopsis

The class of methods discussed in this chapter may be described as non-variational non-perturbative methods. They differ from those presented in earlier chapters in that they are based on equation of motion and furnish transition energy directly, not as differences. The methods have been presented in many body diagrammatic language. Spin coupling, wherever necessary, has also been carried out using spin algebra with attendant diagrams.

Of the two methods, we have attempted, the first one, Random Phase Approximation or RPA, sets up an eigenvalue type equation, solution of which gives transition energy directly. Results of singlet transition are expected to be good and calculations have been kept confined to singlet transitions only. We have also calculated same transition energies by TDA. From the eigenvectors of the RPA matrix, which are effectively transition amplitudes, correlation energies for the ground states are obtained by application of a suitable condition, known as 'killer' condition.

The second category of methods, is a comparatively recent development. With the help of the exponential formalism and applying contraction and linked cluster factorization principle an 'effective' Hamiltonian is constructed. This 'effective' Hamiltonian is then used for setting up simultaneous equations - solution of which ultimately leads to evaluation of correlation energies of the
ground state. Depending on the nature of the simultaneous equations, whether they are linear or quadratic, linear or non-linear correlation is achieved. Extending the same process a set of eigenvalue equations is built up for the calculation of transition energies. The beauty of the method lies in the fact that by suitable manipulation all types of correlations and polarizations are brought in and as such the results obtained are expected to be of high order accuracy.

The calculation of triplet transition energy is somewhat intricate, involved and interesting. These arise mainly due to vector character of the triplet excitation operator (particularly in case of double excitation). We have tried to solve the problem of spin tangle in a simple manner.

**Key Words**

EOM - RPA - EXP(T) and EXP(S) - Linear and non-linear correlation - Singlet and Triplet Transition.
In addition to the perturbative and variational techniques attempts are being made to develop non-variational non-perturbative methods for the calculation of correlation as well as transition energies. The advantages of these methods in the first place are that i) they can totally do away with the determinantal scheme and the accompanying computational hazard; ii) these methods furnish transition energies directly and not as difference of ground and excited state energies, separately improved. The first advantage is due to the ease and convenience with which the methods can be translated into many body language and as such the actual calculation involves molecular orbitals directly. That the methods can be cast into many body scheme leads to the advantage that the requisite spin integration can be diagrammatically performed.

Here attention has been focussed on two non-perturbative schemes one is the equation of motion (EOM) method cast in the form of Random Phase Approximation (RPA) which has been in practice for quite sometime\(^{[4.1]}\) and another which strictly speaking is being just developed and studied, is a response function approach to the direct determination of transition energies in a multi-cluster expansion formalism\(^{[4.2]}\). The advantages of the second methods are a) it stays within the confines of a closed shell cluster expansion formalism b) it uses time independent diagrammatic techniques right from the beginning c) it allows one to compute the associated response function of the system besides the calculations of transition energies.
The Random Phase Approximation (RPA)

Usually in the derivation of EOM, variational procedures are applied\[^{[4.3]}\]. Here we have applied a different technique. The approximations of RPA model concern:

1) The form of the exciting operator. The exciting operator taken as a linear combination of hole \((\phi)\) particle \((n)\) excitation and de-excitation operators

\[
S^+ = \sum_{\lambda \mu} X_{\lambda\mu} a_{\lambda}^+ a_{\mu}^\dagger - \sum_{\lambda \mu} Y_{\lambda\mu} a_{\lambda}^\dagger a_{\mu}^{
}
\]

This implicitly assumes that the low lying excited states are under consideration and that they are reached both by hole particle excitation (presumably from the HF component of the ground state) and by de-exciting an electron from a particle to a hole orbital (from the doubly excited component of the ground state).

ii) The nature of the ground state.

If the ground state be well approximated by the HF and contributions of doubly excited states are comparatively small it may be assumed that the \(X_{\lambda\mu}\) amplitudes in the \(S^+\) operator are far more important than and dominant over the \(Y_{\lambda\mu}\) parts \[^{[4.1]}\]. In that case they may be assumed to be independent of each other; this means that the 'phases' of excitation and de-excitation are random. Fortunately it has been found that for most of the stable molecular systems this criterion is satisfied.
We now proceed to derive the RPA equations in diagram-based many body language using considerations somewhat different from the usual derivation as has been indicated before. We feel that the derivation has some pedagogic values too for it turns out to be very brief.

The operator $S^+$ generates an exact excited state $|\psi_{ex}\rangle$ of the system by acting on the exact ground state

$$|\psi_{ex}\rangle = S^+ |\psi_0\rangle$$

Using Schrödinger equation for the ground and excited states we have,

$$H|\psi_{ex}\rangle = HS^+ |\psi_{ex}\rangle = (E_{ex} + \Delta E) S^+ |\psi_0\rangle$$

$$HS^+ |\psi_{ex}\rangle = S^+ E_{ex} |\psi_{ex}\rangle + \Delta E S^+ |\psi_0\rangle$$

$$HS^+ |\psi_{ex}\rangle = S^+ H |\psi_{ex}\rangle + \Delta E S^+ |\psi_0\rangle$$

$$[H S^+ - S^+ H] |\psi_{ex}\rangle = \Delta E S^+ |\psi_0\rangle$$

where $\Delta E$ is the excitation energy.

Now by Wick's theorem

$$[H S^+ - S^+ H] = N [H S^+] + [H S^+] H - N [S^+ H] - [S^+ H]$$

$$= \frac{1}{2} (H S^+ - S^+ H)$$

$$[H S^+ - S^+ H] |\psi_0\rangle = \Delta E S^+ |\psi_0\rangle$$
Projecting onto singly excited configurations we get a set of equations

\[ \left\langle \phi^m_{\alpha} \mid H S^+ - S^+_H \mid \chi^r_{\beta} \right\rangle = \Delta E \left\langle \phi^m_{\alpha} \mid s^+ \mid \chi^r_{\beta} \right\rangle \]  
(4.8)

With HF as vacuum the Hamiltonian takes the form (see eqn. 3.3 to 3.5)

\[ H = E_{HF} + F + V \]  
(4.9)

\[ F = \text{One electron part} \]
\[ V = \text{Two electron part} \]

We depict the vertices corresponding to \( X_{\mu \alpha} a^+_\mu a^\alpha \) and \( Y_{\mu \alpha} a^+_\mu a^\alpha \) as in Figures (4.1a) and (4.1b). With these we shall now evaluate

\[ \left\langle \phi^m_{\alpha} \mid H S^+ - S^+_H \mid \chi^r_{\beta} \right\rangle \]  
(4.10)

We must remember that only those terms in \( H S^+ - S^+_H \) that can generate \( \phi^m_{\alpha} \) by acting on \( \chi^r_{\beta} \) will have non-vanishing values for the matrix elements. Thus the shape of all the attendant diagrams will be of the types shown in Figures (4.3b) and (4.4b) i.e. of the same forms as the hole particle excitation or de-excitation as shown in figures (4.1a) and (4.1b). Henceforth we would designate the collection of all diagrams having same shape as constituting blocks. In Figures (4.3) and (4.4) we show all the diagrams that constitute the blocks representing excitation and de-excitation respectively in Hugenholtz convention of depicting \( V \) vertices. We now consider the hole particle excitation and
**Fig 4.1.**

**Fig 4.2.**

**Fig 4.3.**

**Fig 4.4.**

**Figures and Legends:**

- **BLOCK-STRUCTURE OF ABOVE EQUATIONS**

- (b)
de-excitation amplitudes to be random and thus independent, so that we may decouple the excitation and de-excitation amplitudes and equate similar quantities on both sides. The corresponding equations thus generated would be of the form,

Contribution from block for excitation \( \alpha \rightarrow m = \Delta E X_{m \alpha} \)

Contribution from block for de-excitation \( m \rightarrow \alpha = -\Delta E Y_{m \alpha} \)

**Diagrammatic**

With HF as vacuum the one and two electron parts are

\[
\hat{F} = \sum_{AB} \langle A | f | B \rangle a_A^+ a_B
\]

and

\[
\hat{V} = \frac{1}{2} \sum_{ABCD} \langle AB | v | CD \rangle a_A^+ a_B^+ a_D a_C
\]

The total Hamiltonian is given by

\[
H = E_{HF} + \hat{F} + \hat{V}
\]

The diagrammatic representation of \( \hat{F} \) and \( \hat{V} \) are given in Figure (4.2). The hole and particle lines are indicated by Greek and English alphabets. \( \hat{F} \) has two lines and \( \hat{V} \) has four lines. Hole and particle orbitals being eigenfunctions of \( \hat{F} \), the lines attached to \( \hat{F} \) must have the same hole or particle labels. \( \hat{V} \) has four lines which can be rotated and particles can be converted into holes and vice versa. The vertex of the exciting part of \( S^\dagger \), 

\( S_{ex} \) is \( X^S \), \( S \) being spin associated with \( X \). Of the lines drawn to the left of the vertex, the entering lines represent holes
and those emerging out are particles. These emerging and incoming lines cannot be rotated because by such a change the excitation part \( S_{eX} \) of \( S^+ \) will be converted into the de-excitation part \( S_{dX} \). In case of X vertex since \( S_{eX} \) has no line to the right it can contract with \( \hat{F} \) and \( \hat{V} \) from right only. Reverse is the case, with Y vertex, here the vertex is \( \gamma^S \) and the line from right is particle and the line to the right is a hole. This \( S_{dX} \) part can thus can contract only from left with \( \hat{F} \) and \( \hat{V} \).

As has been already described the excitation and de-excitation operators are denoted by \( S_{max} a_{m}^{\dagger}a_{\lambda}^{\dagger} \) and \( S_{max} a_{\lambda}^{\dagger}a_{m} \) respectively where \( S \) is the spin associated with X and Y i.e. for singlet transition \( S = 0 \) and for triplet \( S = 1 \). If the hole and particle spins are properly coupled\([4.5]\) and with them is added the spin of the operator the pictorial form represented by the diagram corresponds to that of \( 6j \) symbol. Shibuya\([4,6]\) et al have shown a method of achieving the spin integration. We have used a comparatively simpler technique. A typical coupling has been shown in the diagram (4.6).

The contractions \( (F + V) S^+ \) etc. have been diagrammatically evaluated in accordance with the Figures (4.3) and (4.4) using Hugenholtz convention i.e. the values are obtained in terms of Hugenholtz antisymmetrised reduced matrix elements. With the incorporation of spin integration values the overall equations obtained as depicted diagrammatically (Fig. 4.5 and 4.6) are
**Some Useful Rules for Diagrammatic Coupling of Angular Momenta**

**Clebsch-Gordon Coefficient**  \[ \left\langle j_1, j_2 \mid j_3 \right\rangle \rightarrow \left[ j_3 \right] (-1)^{j_1-j_3+m_3} \left( j_1 \ j_2 \ j_3 \right) \left( m_1 \ m_2 \ m_3 \right) \]

where \[ \left[ j_3 \right] = (2j_3+1)^{\frac{1}{2}} \]

\[
\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_2-m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}
\]

**Diagrammatic Representation of**

\[
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\downarrow \quad j_1 \\
\downarrow \quad j_2 \\
\downarrow \quad j_3 \\
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\]

\[
\begin{array}{c}
\begin{array}{c}
\downarrow \quad j_1 \\
\downarrow \quad j_2 \\
\downarrow \quad j_3 \\
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\]

To change the order of coupling

\[
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\downarrow \quad j_2 \\
\downarrow \quad j_3 \\
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\]

\[
\begin{array}{c}
\begin{array}{c}
\downarrow \quad j_1 \\
\downarrow \quad j_2 \\
\downarrow \quad j_3 \\
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\]

To reverse the arrow direction

\[
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\downarrow \quad j_1 \\
\downarrow \quad j_2 \\
\downarrow \quad j_3 \\
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\]

\[
\begin{array}{c}
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\downarrow \quad j_1 \\
\downarrow \quad j_2 \\
\downarrow \quad j_3 \\
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\]

A list of standard 3ry figures relevant to our calculations:

\[ n=1 \]

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\end{array} \]

\[ = 1 \quad \left( j_1 + j_2 \right) > j_3 \geq \left| j_1 - j_2 \right| \]

\[ = 0 \quad \text{otherwise} \]

\[ n=2 \]

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\[ \begin{array}{c}
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\end{array} \]
\[ \langle m | g | x \rangle \]

**Corresponding Spin Coupling Part**

\[
\sum_{\delta_1, \delta_2} \left\langle \frac{1}{2} | s \right| \left| \delta_1 \right\rangle \left\langle \left| \frac{1}{2} \right| \frac{1}{2} \left| s \right\rangle \left( -1 \right)^{\delta_2 - \delta_1} \left| \delta_1 \right\rangle \left| \frac{1}{2} \right\rangle \right\rangle
\]

**Converted to Wigner's 3j Symbols**

\[
\begin{pmatrix} -1 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \delta_1 & \delta_2 \\ \frac{1}{2} & \frac{1}{2} & s \end{pmatrix}
\]

**Converted to Standard Form**

\[ \left[ s \right] \left[ \frac{1}{2} \right] \left[ \frac{1}{2} \right] \]

**The Matrix Element After Spin Coupling**

\[ \left[ s \right] \left[ \frac{1}{2} \right] \left( m | g | \alpha \right) \]

**Fig 4.5**
\[ \langle m| \beta | x \gamma \rangle \langle n| x | \beta \rangle \]

\[ \sum_{s_1} \sum_{s_1} \left( \begin{array}{l} \frac{1}{2} \\ \frac{1}{2} \end{array} \right| \left( \begin{array}{c} s_1 \\ 0 \end{array} \right) \left( \begin{array}{c} s_1 \\ \frac{1}{2} \end{array} \right| M_1 \right) \left( \begin{array}{c} s_1 \\ \frac{1}{2} \end{array} \right| M_1 \right) \]

\[ (-1)^{s_1} \left[ \frac{s^2}{2} \right] \left[ s \right] \left[ \frac{1}{2} \right] \]

\[ \text{Corresponding Figure} \]

\[ \left( \begin{array}{cc} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{array} \right) \]

\[ \left( \begin{array}{cc} s_1 & s_2 \\ s_1 & s_2 \end{array} \right) \]

\[ \left( \begin{array}{cc} s_1 & s_1 \\ s_1 & s_1 \end{array} \right) \]

\[ \left( \begin{array}{cc} \frac{1}{2} \frac{1}{2} \\ \frac{1}{2} \frac{1}{2} \end{array} \right) \left( \begin{array}{c} m \delta \gamma \rangle \langle n| x | \beta \rangle \langle s_1 \rangle \right) \left( \begin{array}{c} s_1 \rangle \langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \end{array} \right) \left( \begin{array}{c} \frac{1}{2} \frac{1}{2} \frac{1}{2} \end{array} \right) \left( \begin{array}{c} \frac{1}{2} \frac{1}{2} \frac{1}{2} \end{array} \right) \]

\[ \sum_{s_1} (-1)^{s_1} \left[ \frac{s_1^2}{2} \right] \left[ s \right] \left[ \frac{1}{2} \right] \]

\[ \text{N-matrix Element After Spin Coupling} \]

\[ \text{Fig 4.6} \]
\[(101)\]

\[
(\varepsilon_n - \varepsilon_\alpha) X_{n\alpha} + \sum_{n\beta} \sum_{S_i} (2S_i + 1) (-1)^{S_i+1} \{ \frac{1}{2} \frac{1}{2} S \} \{ \eta_{\beta} | v | \alpha_{n} \}_{S_i}^S \chi_{n\beta}^S
\]

\[
+ \sum_{n\beta} \sum_{S_i} (2S_i + 1) (-1)^{S_i+1} \{ \alpha_{\beta} | v | \alpha_{n} \}_{S_i}^S \chi_{n\beta}^S = \Delta E \chi_{n\alpha}^S
\]

\[
(4.11)
\]

\[
(\varepsilon_n - \varepsilon_\alpha) \gamma_{n\alpha} + \sum_{n\beta} \sum_{S_i} (2S_i + 1) (-1)^{S_i+1} \{ \frac{1}{2} \frac{1}{2} S \} \{ \alpha_{\beta} | v | \alpha_{n} \}_{S_i}^S \gamma_{n\beta}^S
\]

\[
+ \sum_{n\beta} \sum_{S_i} (2S_i + 1) (-1)^{S_i+1} \{ \alpha_{\beta} | v | \alpha_{n} \}_{S_i}^S \gamma_{n\beta}^S = -\Delta E \gamma_{n\alpha}^S
\]

\[
(4.12)
\]

where \[\{ \frac{1}{t} \frac{1}{t} \frac{1}{t} \frac{1}{t} S \}_{S_i} \] is the 6j symbol.

On substitution of the values of proper 6j in equations (4.11) and (4.12) the equations ultimately take the forms

\[
(\varepsilon_n - \varepsilon_\alpha) X_{n\alpha} + \sum_{n\beta} \left[ (1 + (-1)^S) \langle \alpha_{\beta} | v | \alpha_n \rangle - \langle \eta_{\beta} | v | \alpha_n \rangle \right] X_{n\beta}
\]

\[
+ \sum_{n\beta} \left[ (1 + (-1)^S) \langle \alpha_n | v | \epsilon_{\beta} \rangle - \langle \alpha_n | v | \beta_n \rangle \right] \gamma_{n\beta}
\]

\[
= \Delta E \chi_{n\alpha}
\]

\[
(4.13)
\]

\[
(\varepsilon_n - \varepsilon_\alpha) \gamma_{n\alpha} + \sum_{n\beta} \left[ (1 + (-1)^S) \langle \alpha_n | v | \alpha_{n\beta} \rangle - \langle \alpha_n | v | \beta_{n\beta} \rangle \right] \gamma_{n\beta}
\]

\[
+ \sum_{n\beta} \left[ (1 + (-1)^S) \langle \alpha_{n\beta} | v | \alpha_n \rangle - \langle \epsilon_{n\beta} | v | \beta_n \rangle \right] X_{n\beta}
\]

\[
= -\Delta E \gamma_{n\alpha}
\]

\[
(4.14)
\]

\(S\) is the spin value i.e. \(S = 0\) for singlet and \(S = 1\) for triplet excitations. The equations (4.11) to (4.14) are the RPA equations.
For more clear display of the RPA equations the following matrices are introduced

\[ A_{\alpha \beta} = (\epsilon_m - \epsilon_n) \delta_{\alpha \beta} + [1 + (-1)^s] \langle \phi \mid \nu \mid \kappa \rangle - \langle \phi \mid \nu \mid \phi \rangle \]

(4.15)

and

\[ B_{\alpha \beta} = \left[ 1 + (-1)^s \right] \langle m \mid \nu \mid \beta \rangle - \langle m \mid \nu \mid \alpha \rangle \]

(4.16)

The equations (4.13) and (4.14) may be written as eigenvalue equations

\[ \begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \Delta E \begin{pmatrix} X \\ Y \end{pmatrix} \]

(4.17)

Since the orbitals we are concerned with are all real the RPA equations take the form

\[ \begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \Delta E \begin{pmatrix} X \\ Y \end{pmatrix} \]

(4.18)

Solution of the above eigenvalues directly provides the transition energies from ground to singly excited states. Solution requires diagonalisation of the matrix \( \begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \) where \( A \) and \( B \) are blocks of real symmetric matrices. So the matrix itself is an unsymmetric one.

We have kept our calculation confined to singlet and have omitted those for triplet. We have done this since Thouless's theorem\[4.7\] predicts that triplet transition energies will not be real. If the \( Y \) part of \( S^+ \) is omitted and only the \( X \) part retained then transition energies between HF as ground and singly
excited states formed by superposition of singly excited states only are obtained. These are known as TDA and are in effect equivalent to a CI comprising of singly excited states only.

Calculation of Ground State Correlation Energy

For the calculation of correlation energy in the ground state, we assume that there is no 'excitation' in the ground state. This implies that the adjoint $S$ of the operator $S^+$ should annihilate the ground state - this condition is often referred to as "Killer condition".

The above condition leads to the equation

$$S |\psi_{gr}\rangle = 0$$

(4.19)

If the ground state is represented by

$$|\psi_{gr}\rangle = \left[1 + \frac{i}{(2\!\!1)^2} \sum_{\alpha,\beta} \langle m\!\!m | c | \kappa\beta \rangle a_\alpha^+ a_\alpha^+ a_\beta a_\alpha \right] |\phi_{\text{HF}}\rangle$$

We arrive with the help of equation (4.19) to an equation

$$\sum_{\alpha,\beta} \left[2 \langle m\!\!m | c | \kappa\beta \rangle - \langle m\!\!m | c | \beta\alpha \rangle \right] X_{m\alpha} = Y_{m\beta}$$

(4.20)

: In matrix notation

$$XC = Y$$

(4.21)

where the matrix element $C_{m\alpha,\eta\beta}$ is defined as

$$C_{m\alpha,\eta\beta} = 2 \langle m\!\!m | c | \kappa\beta \rangle - \langle m\!\!m | c | \beta\alpha \rangle$$

(4.22)
From the relation (4.21) we have
\[ \tilde{\gamma} = x^{-1} \gamma \]  \hspace{1cm} (4.23)

Now,
\[ H | \tilde{\psi}_{qr} \rangle = E | \tilde{\psi}_{qr} \rangle \]  \hspace{1cm} (4.24)

or
\[ \langle \phi_{HF} | H | \tilde{\psi}_{qr} \rangle = E \tilde{\psi}_{qr} \]  \hspace{1cm} (4.25)

If the Hamiltonian is written in normal order/in (4.9) then
\[ \langle \phi_{HF} | (\hat{\mathcal{F}} + \check{\mathcal{V}}) \tilde{\gamma} | \phi_{HF} \rangle = \Delta E_{\text{corr}} \]  \hspace{1cm} (4.26)

The left hand side thus reduces to vacuum expectation of the operator. The non-vanishing terms must be completely contracted ones (Fig. 4.7). So that
\[ \Delta E_{\text{corr}} = \sum \left[ 2 \langle m\nu | \mathcal{E} | \alpha_\beta \rangle - \langle m\nu | e | \beta\alpha \rangle \right] \langle m\nu | \nu \rangle | \langle \beta \rangle \rangle \]
\[ = \sum \tilde{C}_{m\alpha, n\beta} V_{m\nu, n\alpha} \]  \hspace{1cm} (4.27)

We have given the transition energies both from RPA and TDA in Table (4.1) and correlation in Table (4.2).
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Transitions</th>
<th>SCF</th>
<th>RPA</th>
<th>TDA</th>
<th>Extensive CI</th>
<th>Full CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>Gr - B</td>
<td>6.91</td>
<td>6.21</td>
<td>6.27</td>
<td>5.47</td>
<td>5.07</td>
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<tr>
<td></td>
<td>Gr - A</td>
<td>8.03</td>
<td>7.56</td>
<td>7.64</td>
<td>8.10</td>
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<td>Gr - B</td>
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<td>Gr - A</td>
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<td>Pyrimidine</td>
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Transition Energies by RPA and TDA in ev

'Gr' refers to Ground State

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Ground State Correlation Energies by RPA in ev.

Table 4.2
The method to be discussed was first developed in the late sixties. We have formulated a somewhat novel scheme for the calculation of transition energies. The discussion on the method is to be presented into two parts.

I. Calculation of Ground State Correlation Energies

II. The scheme put forward for calculating transition energies directly.

The methods are based on many-body formalism and as such creation and annihilation operators and attendant Feynmann type diagrams are used extensively.

I. Calculation of Ground State Correlation Energy

The exact ground state wavefunction is given by

\[ |\psi\rangle = |\phi_{HF}\rangle + \sum \mathfrak{C}_\alpha |\phi_\alpha\rangle + \frac{1}{2!} \sum \mathfrak{C}_{\alpha_1,\alpha_2} |\phi_{\alpha_1,\alpha_2}\rangle + \cdots \]

(4.28)

which in terms of creation-annihilation operator with HF as vacuum takes the form

\[ |\psi\rangle = \left[ 1 + \sum \langle \phi | \xi \rangle a_\alpha^+ a_\xi + \frac{1}{2!} \sum \langle \phi_{bq} | c_\xi \rangle a_\alpha^+ a_\beta^+ a_\beta a_\alpha + \cdots \right] \]

(4.29)
This form representing exact ground state is structurally similar to the wavefunction written as

$$|\psi\rangle = \exp(T)|0\rangle$$

(4.30)

where $T$ contains various types of excitation operators like

$$T = \sum_{\alpha'} \langle \beta| t_{\alpha'} \alpha \rangle a_{\alpha'}^+ a_{\alpha} + \frac{1}{2!} \sum_{\beta_1 \beta_2} \langle \beta_1 | t_{\beta_2} | \beta_2 \rangle a_{\beta_1}^+ a_{\beta_2}^+ a_{\beta_2} a_{\beta_1} + \ldots$$

(4.31)

For exact eigenfunction

$$H |\psi\rangle = E |\psi\rangle$$

so that

$$H \exp(T)|0\rangle = E \exp(T)|0\rangle$$

(4.32)

With the definition of $H$ given in (4.9). From equation (4.32) we get

$$\langle E_{HF} + F + V \rangle \exp(T)|0\rangle = E \exp(T)|0\rangle$$

(4.33)

Therefore the correlation energy $E_{corr}$ is given by

$$\langle F + V \rangle \exp(T)|0\rangle = E_{corr} \exp(T)|0\rangle$$

(4.34)

The operators in the left hand side of the equation (4.34) can be expanded to give

$$\langle F + V \rangle \exp(T) = \sum_n (F + V) \frac{1}{n!} T^n$$

(4.35)
Application of Wick's theorem gives
\[ \sum_{n=0}^{\infty} \frac{i^n}{n!} (\hat{F} + \hat{V}) T^n = \sum_{n=0}^{\infty} \frac{i^n}{n!} \sum_{m=0}^{\infty} (\hat{F} + \hat{V}) T^n \frac{L^n}{L^m L^{(n-m)}} T^{n-m} \]  
(4.36)

since there can be \( n^m \) ways of selecting \( m \) operators out of \( n \) such operators, the equation reduces to
\[ \sum_{n=0}^{\infty} \frac{i^n}{n!} (\hat{F} + \hat{V}) T^n = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \left[ \hat{F} + \hat{V} \right] T^n \frac{T^m}{L^m} \frac{T^{n-m}}{L^{(n-m)}} \]  
(4.37)

If \( m \) is made to have values greater than \( n \), \( (n-m) \) with tend to \( \infty \) and as such will not contribute to the above sum.

Keeping this in mind we can write the sum as
\[ \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{i^n}{n!} \left[ \hat{F} + \hat{V} \right] T^n \frac{T^m}{L^m} \frac{T^{n-m}}{L^{(n-m)}} \]

Redefining \( n \) & \( m \), we get
\[ \sum_{n_1=0}^{\infty} \frac{T^{n_1}}{L^{n_1}} \sum_{n_2=0}^{\infty} \left[ \hat{F} + \hat{V} \right] T^{n_2} \frac{T^{n_1}}{L^{n_1}} \frac{T^{n_2}}{L^{n_2}} = \exp(T) \bar{H} \]

where
\[ \bar{H} = \sum_{n=0}^{\infty} \left[ \hat{F} + \hat{V} \right] T^n \frac{L^n}{L} \]

(4.38)

i.e. \( \bar{H} \) corresponds to all possible contractions of \( \left[ \hat{F} + \hat{V} \right] \) and \( \exp(T) \). The above proof is somewhat similar to Linked Cluster Theorem of Goldstone in MBPT.
From the equation (4.34) we now have

\[(\hat{F} + \hat{V}) \exp(\tau) |\sigma\rangle = \exp(\tau) \hat{H} |\sigma\rangle = E_{\text{corr}} \exp(\tau) |\sigma\rangle\]

so that

\[\hat{H} |\sigma\rangle = E_{\text{corr}} |\sigma\rangle\]  

(4.39)

If \(|\phi_{ex}\rangle\) be any excited state in IPM approximation

\[\langle\phi_{ex}|\hat{H}|\sigma\rangle = E_{\text{corr}} \langle\phi_{ex}|\sigma\rangle = 0\]  

(4.40)

The set of equations which is nontrivially equal to zero actually is a set of simultaneous equations in \(T\)'s, as variables. Their solutions furnish the values of various \(T\)'s. These \(T\)'s can then be utilized for the calculation of ground state correlation energy according to the equation (4.39)

\[E'_{\text{corr}} = \langle\sigma|\hat{H}|\sigma\rangle\]  

(4.41)

Equations and Diagrams

Diagrams with \((\hat{F} + \hat{V})\) contracted to various \(T\)'s are drawn. For the ground state, pair correlation being the most important contributor, we are mainly interested in \(T_2\)'s. Of the diagrams drawn in Goldstone formalism only those with block structures of two hole lines entering and two particle lines emanating (Fig. 4.8) represent \(T_2\) effectively. So these are to be equal to zero for the values of \(T_2\)'s. The equations that are obtained are of the form
FIG 4.7

\[ \langle \rho \Gamma t_2 | \kappa \Phi \rangle \]

FIG 4.8
and the total equation is
\[ G(\alpha', \beta') + G(\beta', \alpha') = 0 \]  
(4.42)

Various \( T_2 \)'s are defined by particular hole and particle orbitals involved. If the coefficients of \( T \), which are various \( V \) terms and orbital energies, are denoted by \( A \) and the constant quantities by \( B \) the equations in matrix formulation takes the form

\[ \sum_{IN} A(IN, NEQN) T_2(IN) = B(NEQN) \]

\[ A T_2 = B \]  
(4.43)

As indicated above, \( IN \) is obtained from the holes and particles the particular \( T_2 \) generates and the equation number \( NEQN \) is obtained by the ultimate incoming hole lines and outgoing particle lines.
Programme

In actual programming a number matrix is generated to locate uniquely the $T_2's$ in a serial order. This number matrix is to find out the equation number $NEQN$ as well as $IN$. The equation number is defined in a loop defining ultimate excitation after contraction. Similarly the hole and particles involved in internal summation define $IN$ in another loop. The equations thus generated are then solved by standard simultaneous equation solution technique.

Non-Linear Correlation

In the above discussion we kept our attention confined to pair correlation brought in by unit power of $T_2$ or more precisely only to linear correlation. An interesting outcome of this theory is that it is possible to estimate higher order correlation viz. pair-pair type correlation by simulation of higher excitation such as quadrupole excitation by retaining the quadratic terms of $T_2's$. The quadruply excited states constructed by $\alpha\beta \rightarrow \gamma\delta$ and $\gamma\delta \rightarrow \eta\zeta$ are induced and only direct $\alpha\beta \eta\zeta \rightarrow \gamma\delta \eta\zeta$ are left out. The measure of correlation that is obtained is thus a sum of pair and pair-pair correlation energy. As the quadratic $T_2's$ are involved the correlation is defined as non-linear correlation. Here again $\sqrt{\frac{T_2}{c}}$ contractions are evaluated by means of appropriate diagrams (Fig. 4.9) and quadratic equations in $T_2's$ are constructed [$S$ cannot contract with $T_2^2$]. The actual equations are obtained by adding to the left hand side of the linear equation the following terms quadratic in $T_2$ as furnished by the diagrams.
The equation will then have the form
\[ AT_2 + CT_2^2 = B, \quad AT_2 = B - CT_2 \] (4.44)

The non-linear equations (4.44) are solved in an iterative manner. First 'guess' \( T_2 \)'s or the trial \( T_2 \)'s are obtained by solution of linear equations
\[ AT_2 = B \]

These values of \( T_2 \)'s are then introduced in the right hand side of the equation to get an equation of the form \( AT_2 = B' \) where
\[ B' = B - CT_2 \]

The process is carried out iteratively till a reasonable convergence is attained (\( \sim 10^{-3} \) ev).

The actual correlation energy is given by completely closed diagrams shown in (Fig. 4.10) and amount to
\[ E_{\text{conv}} = \sum_{\alpha \beta \gamma} \{ 2 \langle 2 \phi | v | 2 \phi \rangle - \langle 2 \phi | v | 2 \phi \rangle \} t_2 (\alpha \beta | \gamma | \alpha \beta) \] (4.45)

The results have been given in Table 4.3.
We have applied the method, proposed by Mukherjee et al., to actual calculation of singlet and triplet transition energies with necessary spin integration. We have been able to find out a novel recipe for solving the special problem encountered in case of triplet transition due to the vector character of two body excitation operator and obtained the equation in Goldstone formulation.

II. Calculation of Transition Energies

The system Hamiltonian may be written in occupation number representation as

$$H_M = \sum_{\rho_\theta} \langle \rho | H | 0 \rangle a^\dagger_\rho a_\theta + \frac{1}{2} \sum_{\rho_\theta} \langle \rho | V | \rho \rangle a^\dagger_\rho a^\dagger_\theta a_\theta a_\rho$$

(4.46)

The system is now supposed to be immersed in a photon field which ultimately plays the role of external perturbation of frequency with a Hamiltonian

$$H_{ph} = \hbar \omega c^\dagger c$$

(4.47)

when $c$ and $c^\dagger$ are the destruction and creation operators for the photon field.

The Schrödinger equation for the system and the photon field in the absence of mutual interaction may be written as

$$(H_M + H_{ph}) \psi_o \gamma_{ph} = E_o \psi_o \gamma_{ph}$$

(4.48)

where $\psi_o$ is the electronic ground state eigenfunction of $H_M$ and $\gamma_{ph}$ is the photon field eigenstate of $H_{ph}$. $\gamma_{ph}$ is given by

$$\gamma_{ph} = \frac{1}{\sqrt{m}} (c^\dagger)^n | 0 \rangle$$

(4.49)

As before we construct the exact ground state from $\psi_o$ by mixing with it configurations involving various excitations affected by an $\varepsilon^T$ type operator

$$\psi_o = \varepsilon^T \phi_o$$

(4.50)

$\phi_o$ is the HF and $\psi_o$ is the exact ground state.
For the ground state we have from (4.38)

\[ \bar{H}_M \epsilon^T \phi_0 = \epsilon^T \bar{H}_M \phi_0 \]  

(4.51)  

the energy of the system in the ground state is ground state energy plus that of the photon field

\[ E_0 = \langle \phi_0 \chi_{ph} | \bar{H}_M + H_{ph} | \phi_0 \chi_{ph} \rangle = \omega_0 + n \hbar \omega \]  

(4.52)  

Naturally \( \omega_0 \) refers to total ground state energy of the molecular system as obtained by summing up all the completely closed diagrams of \( \bar{H}_M \). \( n \hbar \omega \) corresponds to the photon energy of the photon state \( \chi_{ph} \).

Now we are to focus our attention to the interaction of the molecular system with the surrounding photon field resulting in the excitation of the systems.

In the electric/magnetic dipole interaction, the interaction Hamiltonian may be given as [4.10]

\[ H_{int} = -i \sum_{\beta \gamma} \langle \beta | d \cdot \eta | \gamma \rangle \sqrt{\frac{\hbar \omega}{2}} [c - c^+] a^\dagger_\beta a_\gamma \]  

(4.53)  

where \( d \) is the electric or magnetic dipole operator under consideration and \( \eta \) is a kind of polarisation vector. \( \eta \) is just the same as the unit vector \( \epsilon \) along the direction of the electric field for the electric dipole case; it is equal to \( \hat{n}_k \times \epsilon \) where \( \hat{n}_k \) is unit vector along the wave vector of the associated photon field. Under the action of the perturbation the ground state will absorb photons and in the case under consideration where the response
function is linear with respect to external perturbation, the number of photons absorbed or emitted should be only one.

In the presence of the interaction the unperturbed (system + photon) state: \( \psi_0 \chi_{\phi_h} \) would be thrown into a perturbed state \( \psi' \) which would cease to have definite number of photons and the nature of correlation will always undergo some modification. A major component in the perturbed electronic wavefunction would be singly excited determinants taking care of the orbital polarisation effect and there would be an added contribution to pair correlation energy due to orbital polarisation. Triply excited states are also to be taken into account as these are obtained through mixing of singly excited determinants. The ultimate aim is to compute the transition energies. This can be achieved if we succeed in locating the poles of the response function as a function of photon frequency \( \omega \).

Since the ground state is correlated by contribution from doubly (linear) and still higher excited states (for non-linear) the excited states may be obtained as an improved admixture of singly, doubly and triply and still higher excited determinants by proper manipulation. A way to construct the perturbed state \( \psi' \) is

\[
\psi' = e^{T_2} e^S \phi_0 \chi_{\phi_h}
\]

We are here interested in one photon absorption/emission process so that we choose an operator \( S \) which consists of one and two body terms with respect to electronic operator and which at the same time induces absorption and emission of a single photon. The triple excitations are thus simulated by product of \( T_2 \) and the one body part of \( S \). \( S \) is given by
\[ S = S^+ + S^- \]  

**Equation 4.54**

\[ S^+ = \text{photon emission} \quad S^- = \text{photon absorption} \]

\[ S^- = \left[ \sum_{k \in \phi_0}^{} \beta_1 \langle \phi | \lambda_1 \eta | A \rangle a^+_b a_a + \sum_{k \in \phi_0}^{} \langle \lambda_2 \eta | AB \rangle a^+_b a^+_a a_a \right] (i \sqrt{\frac{\hbar}{2}} e) \]

**Equation 4.55**

A similar expression may be written for \( S^+ \) which would involve \( C^+ \) and a factor containing \( -i \).

Let us now look at the Schrödinger equation
\[ (H_M + H_{ph} + H_{int}) e^T e^S \phi_0 \chi_{ph} = E e^T e^S \phi_0 \chi_{ph} \]

**Equation 4.56**

using LCT involving \( e^T \) (equation 4.51) we have
\[ (H_M + H_{ph} + H_{int}) e^S \phi_0 \chi_{ph} = E e^S \phi_0 \chi_{ph} \]

**Equation 4.57**

since \( H_{ph} \) has no interaction with \( e^T \) and
\[ H_{int} e^T = e^T H_{int} \]

**Equation 4.58**

Total energy \( E \) in fact consists of two parts:

1) The correlated ground state energy + photon field energy i.e. the sum of the closed parts of \( \langle \phi_0 | H_M | \phi_0 \rangle \) which refers to molecular correlated ground state energy and \( \langle \chi_{ph} | H_{ph} | \chi_{ph} \rangle \)
ii) A shift $\Delta E$ which corresponds to the open part i.e. the rest.

Unperturbed energy of the system $E_0$ is thus

$$E_0 = \langle \phi_0 | \tilde{H}_M | \phi_0 \rangle + \langle x_{ph} | H_{ph} | x_{ph} \rangle$$  \hspace{1cm} (4.59)

Combining equation (4.59) with equation (4.57) we get

$$[ \tilde{H}_M^0 + H_{ph}^0 + \tilde{H}_{int} ] e^S \phi_0 x_{ph} = \Delta E e^S \phi_0 x_{ph}$$  \hspace{1cm} (4.60)

where $\tilde{H}_M^0$ and $H_{ph}^0$ refer to the open part of $H_M$ and $H_{ph}$.

Using a linked cluster theorem involving $e^S$ through the relations

$$\tilde{H}_M^0 e^S = e^S \tilde{H}_M$$

$$H_{ph}^0 e^S = e^S H_{ph}$$

$$\tilde{H}_{int} e^S = e^S \tilde{H}_{int}$$  \hspace{1cm} (4.61)

We have

$$[ \tilde{H}_M + \tilde{H}_{ph} + \tilde{H}_{int} ] \phi_0 x_{ph} = \Delta E \phi_0 x_{ph}$$  \hspace{1cm} (4.62)

$\tilde{H}_M$, $\tilde{H}_{ph}$ and $\tilde{H}_{int}$ may be interpreted as effective operator for the perturbed system including the correlation and are all dependent on $S$. For linear response theory we have to write the explicit cluster expansion from each of these operators and should keep terms which are linear in $C$ i.e. those involving creation and destruction of one photon only.

We then have

$$[ \tilde{H}_M^{(1)} + \tilde{H}_{ph}^{(1)} + \tilde{H}_{int}^{(1)} ] \phi_0 x_{ph} = \Delta E \phi_0 x_{ph}$$  \hspace{1cm} (4.63)
In equation (4.63) as involves creation and destruction of one photon we have to retain only this as the zeroth order term from \( \overline{H}_{\text{int}} \).

Projected into excited states \( \langle \phi_{\ell} | \chi_{ph}^\pm \rangle \) where \( \phi_{\ell} \) are the singly and doubly excited states induced by \( S \). \( \chi_{ph}^\pm \) are photon states with one photon created and destroyed from \( \chi_{ph} \), we have

\[
\langle \phi_{\ell} | \chi_{ph}^\pm \rangle \left( \overline{H}_{\text{M}}^{(\ell)} + \overline{H}_{ph}^{(\ell)} + \overline{H}_{\text{int}} \right) | \phi_{\ell} \chi_{ph} \rangle = 0
\]

(4.64)

These are coupled simultaneous equations involving the matrix elements of \( S \), solutions of which will furnish the appropriate values.

The operator \( S \) is given as a sum of the photon creation operator \( S^+ \) and photon destruction operator \( S^- \). If the equations (4.64) are now written in terms of \( S^+ \) and \( S^- \) the non-trivial set of equations may be obtained by projecting with \( |\phi_{\ell} \chi_{ph}^+\rangle \) and \( |\phi_{\ell} \chi_{ph}^-\rangle \) respectively.

We have thus, for \( S^+ \)

\[
\langle \phi_{\ell} \chi_{ph}^+ \mid \overline{H}_{\text{M}}^{(\ell)} + \overline{H}_{ph}^{(\ell)} + \overline{H}_{\text{int}} \mid \phi_{\ell} \chi_{ph} \rangle = 0
\]

and for \( S^- \)

\[
\langle \phi_{\ell} \chi_{ph}^- \mid \overline{H}_{\text{M}}^{(\ell)} + \overline{H}_{ph}^{(\ell)} + \overline{H}_{\text{int}} \mid \phi_{\ell} \chi_{ph} \rangle = 0
\]

(4.65)

The forms of the equations (4.65) will be quite apparent when we shall discuss the diagrammatics. The equations get decoupled automatically and this has a definite advantage over RPA and HRPA.
We now calculate the energy which depends on the first order function \( S(\phi | x_{ph}) \) but is second order in \(*d*\) in total. This finally comes out to be equivalent to calculation of the expectation value

\[
\Delta E^{(2)} = \langle \phi | x_{ph} | H_{int} S | \phi | x_{ph} \rangle
\]

(4.66)

The interaction part of the Hamiltonian can be expressed in short as

\[
H_{int} = V_{el} (c + c^+) \quad (4.67)
\]

Since as far as our discussion is concerned the explicit form and of \( V_{el} \) is quite unimportant it is possible to present the equations (4.66) in the form

\[
\Delta E^{(2)}(\omega) = n \ G(V_{el}, \omega) + \sum_{m \neq 0} \frac{| \langle \psi_m | V_{el} | \psi_0 \rangle |^2}{E Mc - E Mc - \hbar \omega} \quad (4.68)
\]

where \( \psi_m \) refer to excited electronic eigenstates of \( H_M \) to the photon number.

The quantity \( n \ G(V_{el}, \omega) \) can be looked upon as a linear response function due to its linear dependence on the photon number.

Actually this \( \Delta E^{(2)} \) corresponds to dynamic polarisability either electronic or magnetic depending on the nature of the interaction Hamiltonian. When the external frequency matches the energy difference of various states of the molecular systems the expression should blow up as is apparent from the equation (4.68).
Diagrammatics

In the Hamiltonian of combined system (molecule and radiation) we have three terms $H_M, H_{ph}, H_{int}$. The term $H_M$ is expressed in normal order with HF state as vacuum.

To bring in a distinction between the hole particle convention and the photon creation and destruction, the latter have been depicted by wiggles. Creation is diagrammatically represented as arrow coming out of a vertex and destruction by one entering a vertex. The interaction part of the Hamiltonian $H_{int}$ which contains C and $C^+$ is a composite operator. It is represented by vertices involving creation and destruction of electron labels together with destruction or creation of a photon as has been shown in the diagram (Fig. 4.11).

As has been shown before, linked cluster factorisation first leads to a set of equations involving $\bar{H}_M$ which includes the correlation effect in the ground state. For the second LCF (linked clustered factorisation) we are to retain only open part of $\bar{H}_M$ viz. $\bar{H}_M^0$, i.e. one and two body parts represented by $\bar{F}$ and $\bar{V}$ respectively and are to discard the completely closed part or zero body part of $\bar{H}_M$ as that cannot undergo further contraction with $S_1$ and $S_2$. Same is also applicable to $\bar{H}_{int}$. In this connection it should be explicitly mentioned that though $H_{int}$ may be of one body form $\bar{H}_{int}$ may have two open lines achieved through coupling with two body operator $T_2$.

As pointed out before the operator $S$ consists of $S^+$ and $S^-$. The $S_1^-$ and $S_2^-$ of $S^-$ have been depicted in Figure 4.12. They
comprise of one hole one particle, two holes two particles excitations as well as photon destruction. The matrix elements associated with the vertices are shown below the respective figures.

For appropriate diagrammatic translation of the set of equations for the matrix elements $S_\pm^t$ we are to remember that the shape of diagrams inducing the transition from $\Phi^t \chi_{ph}^t$ to $\Phi^t \chi_{ph}^+\pm$ would look like those for $\nu_S^{\pm}$. Thus we need draw all the linked diagrams of the shape of $S^{\pm}_t$ and which should involve a) one $H_\nu^0$ vertex and one $S^{\pm}_t$ or $S^{\pm}_s$ vertex. b) One $H_{ph}$ vertex and one $S^{\pm}_t$ or $S^{\pm}_s$ vertex; c) One $H_{int}$ vertex. We are to draw all the linked diagrams by putting $S^{\pm}_t$ and $S^{\pm}_s$ operators on the left and on the right of $H_\nu^0$ and $H_{ph}$.

Particular advantage of this method is that the matrix element decides which of $S^+$ and $S^-$ should contribute. For example in the case of the matrix element $\langle \Phi^t \chi_{ph} \mid H_\nu^0 + H_{ph} + H_{int} \mid \Phi^t \chi_{ph} \rangle$

only diagrams involving $S^-$ and $d$ contribute. The equations for $S^+$ and $S^-$ thus get decoupled automatically. For example, for $S^-$ we have only $S^-_2$ 1h-1p excitations and 2h-2p excitations $S^-_2$ - this is definitely an advantage over HRPA methods.

In the RPA methods we are to double the space in order to accommodate the de-excitation.

For the creation and destruction operators for the photon $C^+$ and $c^+$ we have to take care of the fact that

\[
C^+ \mid \chi_{ph} \rangle = \sqrt{n_{+1}} \mid \chi_{ph}^+ \rangle
\]

and

\[
c^+ \mid \chi_{ph} \rangle = \sqrt{n} \mid \chi_{ph}^- \rangle
\]

(4.69)
where $|\chi_{ph}\rangle$ corresponds to n-photon state.

With these in mind we can now sum up the diagram rules.

(1) The internal lines must be summed over appropriate (hole or particles) labels.

(2) The overall sign of a diagram is given by $(-1)^{l+l+\mathcal{L}+\mathcal{L}'}$ where $\mathcal{L}$ is the number of hole lines, $l$ the number of loops, $\mathcal{L}'$ the number of $S'$ vertices joined to $\bar{H}_M$ and $\bar{H}_p$ from left and $\mathcal{L}''$ the total number of $d$ vertices.

(3) For each possible labels on $S_1^\pm$ and $S_2^\pm$ operator, one would draw the appropriate diagrams using the considerations (1) and (2). The labelling should be done in such a manner that exactly same hole-particle excitation is indicated by the overall diagram as that by the $S_1^\pm$ operator. All the diagrams entering into the calculation of the matrix elements $\langle \phi_{\tilde{\alpha}} | \chi_{ph} \rangle | \bar{H}_M^{(i)} + \bar{H}_p^{(i)} + \bar{H}_{int}^{(i)} | \phi_{\tilde{\alpha}} \rangle$ which are the variables for the equations of $S_1^\pm$ have been drawn. Same has been done for the two body part $S_2^\pm$. All these diagrams have been shown in the figures (Fig. 4.13 and Fig. 4.14).

In the compact form the set of equations can be represented as

$$(A \quad B) \begin{pmatrix} \alpha_1^+ \\ \alpha_2^+ \end{pmatrix} = \mp \hbar \omega \begin{pmatrix} \alpha_1^- \\ \alpha_2^- \end{pmatrix} + \left( \begin{pmatrix} A_1^- \\ A_2^- \end{pmatrix} \right)$$

(4.70)

where $\alpha_1^+$ and $\alpha_2^+$ stand for matrix elements of the forms $\langle \beta | \alpha \rangle_{\tilde{\alpha}}$ and $\langle \beta | \alpha \rangle_{\tilde{\alpha}}$ respectively.
The expressions for $A, B, C, D$ the set of coefficients appearing in the above shown simultaneous equations (4.70) are given below in terms of anti-symmetrised matrix elements

\[
A_{\alpha\beta,\gamma\delta} = \langle m | f | n \rangle_{\delta\gamma} - \langle \beta | f | \alpha \rangle_{\delta\gamma} + \langle m | p | n \rangle_{\delta\gamma}
\]

\[
B_{\alpha\beta, \gamma\delta} = -\langle \gamma | \delta | \alpha \beta \rangle_{\delta\gamma} + \langle m | p | \alpha \beta \rangle_{\delta\gamma}
\]

\[
C_{\alpha\beta, \gamma\delta} = -\langle \gamma | \delta | \alpha \beta \rangle_{\delta\gamma} - \langle m | p | \alpha \beta \rangle_{\delta\gamma} + \langle m | \nu | \beta \alpha \rangle_{\delta\gamma} + \langle m | \nu | \beta \alpha \rangle_{\delta\gamma}
\]

\[
D_{\alpha\beta, \gamma\delta} = \delta_{\alpha\gamma} \delta_{\beta\delta} \left[ \langle m | f | p \rangle_{\delta\gamma} + \langle m | f | p \rangle_{\delta\gamma} \right]_{\delta\gamma} - \left[ \langle \gamma | \delta | \alpha \beta \rangle_{\delta\gamma} + \langle \delta | \beta \alpha \rangle_{\delta\gamma} \right]_{\delta\gamma} + \langle m | \nu | \beta \alpha \rangle_{\delta\gamma} + \langle m | \nu | \beta \alpha \rangle_{\delta\gamma} - \langle \gamma | \delta | \alpha \beta \rangle_{\delta\gamma} - \langle \delta | \beta \alpha \rangle_{\delta\gamma} + \langle m | \nu | \beta \alpha \rangle_{\delta\gamma} + \langle m | \nu | \beta \alpha \rangle_{\delta\gamma}
\]

Representing the grand matrix of (4.70) by $R$ we can write the equations in still shorter form as

\[
R \beta^\pm = \pm \kappa \omega \beta^\pm + d
\]

\[
(R \pm \kappa \omega) \beta^\pm = \bar{d}
\]
so that

\[ \beta^\pm = (R \pm \hbar \omega)^{-1} \tilde{A} \]

In order to have the transition energy we exploit the fact as has been mentioned earlier in our discussion that \( \beta^\pm \) should blow up at the transition frequency. Putting in a slightly different fashion it may be argued that at these values the matrix \( (R \pm \hbar \omega) \) should become singular. Mathematically this is equivalent to the solution of an eigenvalue equation of the form

\[ R \beta^\pm = \mp \hbar \omega \beta^\pm \]

(4.71)

or specially

\[ R \beta^- = \hbar \omega \beta^- \]

or

\[ \begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{C} & \mathcal{D} \end{pmatrix} \begin{pmatrix} \beta_1^- \\ \beta_2^- \end{pmatrix} = \hbar \omega \begin{pmatrix} \beta_1^- \\ \beta_2^- \end{pmatrix} \]

(4.72)

till now we have not considered the spin integration. But proper evaluation of the matrix elements necessitates explicit spin integration.

In case of singlet excitation the spin operator is a spin zero or scalar operator. The spin integration thus becomes same as that encountered in the discussion of RPA.

In case of triplet excitation, the integration becomes a lot involved. In this case i.e., transition from ground to triplet excited state spin flipping is necessary and the excitation operator instead of being a scalar one, should contain spin.
In order to carry out the spin integration we have adopted
the graphical method of angular momentum algebra \([4, 5]\). The
representatives of each type of spin integration are shown in the
figures (Figs. 4.5, 4.6, 4.15 to 4.18).

The equations after spin integration can be written in terms
of 'reduced' matrix elements as shown below

\[
\begin{align*}
\langle m | G | S, i \rangle^\otimes &= \sum_{\nu} \langle m | G^\otimes | \nu \rangle \langle \nu | G | S, i \rangle^\otimes - \sum_{\nu} \langle \nu | G^\otimes | m \rangle \langle m | G | S, i \rangle^\otimes \\
&+ \frac{1}{2} \sum_{S_1, S_2} (-1)^{S_1+S_2} (S_2+1) \sqrt{\frac{(2S_1+1)}{2}} \langle \nu | \rho^\otimes | S, i \rangle^\otimes \sum_{S_1} \langle \nu | \rho^\otimes | S_1, i \rangle^\otimes \\
&+ \frac{1}{2} \sum_{S, i} (-1)^{S_1+S_2} (2S_1+1) \sqrt{\frac{(2S_1+1)}{2}} \langle \nu | \rho^\otimes | S, i \rangle^\otimes \sum_{S_1} \langle \nu | \rho^\otimes | S_1, i \rangle^\otimes \\
&\sum_{\nu} \langle m | G^\otimes | \nu \rangle \langle \nu | G | S, i \rangle^\otimes \langle \nu | G^\otimes | m \rangle \langle m | G | S, i \rangle^\otimes = 0
\end{align*}
\]

and

\[
\begin{align*}
\langle m, n | G^\otimes | (\nu, \rho) \rangle^\otimes &= \sum_{\nu} \langle m | G^\otimes | \nu \rangle \langle \nu | G^\otimes | n, \rho \rangle^\otimes - \sum_{\nu} \langle \nu | G^\otimes | m \rangle \langle m | G^\otimes | n, \rho \rangle^\otimes \\
&+ \frac{1}{2} \sum_{S, i} (-1)^{S_1+S_2} (S_2+1) \sqrt{\frac{(2S_1+1)}{2}} \langle \nu | \rho^\otimes | S, i \rangle^\otimes \sum_{S_1} \langle \nu | \rho^\otimes | S_1, i \rangle^\otimes \\
&+ \frac{1}{2} \sum_{S, i} (-1)^{S_1+S_2} (2S_1+1) \sqrt{\frac{(2S_1+1)}{2}} \langle \nu | \rho^\otimes | S, i \rangle^\otimes \sum_{S_1} \langle \nu | \rho^\otimes | S_1, i \rangle^\otimes \\
&\sum_{\nu} \langle m, n | G^\otimes | \nu \rangle \langle \nu | G^\otimes | m, \rho \rangle^\otimes \langle \nu | G^\otimes | n, \rho \rangle^\otimes = 0
\end{align*}
\]
\[ \langle m_f | \nu | s_f \rangle \langle s_f | s_e | \nu \rangle. \]

\[
\begin{align*}
\langle \frac{1}{2} \frac{1}{2} | S_2 \rangle &\langle \frac{1}{2} \frac{1}{2} | S_2 \rangle \langle \frac{1}{2} \frac{1}{2} | S_2 \rangle \langle \frac{1}{2} \frac{1}{2} | S_2 \rangle \\
\langle \frac{1}{2} \frac{1}{2} | S_i \rangle &\langle \frac{1}{2} \frac{1}{2} | S_i \rangle \langle \frac{1}{2} \frac{1}{2} | S_i \rangle \langle \frac{1}{2} \frac{1}{2} | S_i \rangle \\
\langle \frac{1}{2} \frac{1}{2} | M_1 \rangle &\langle \frac{1}{2} \frac{1}{2} | M_1 \rangle \langle \frac{1}{2} \frac{1}{2} | M_1 \rangle \langle \frac{1}{2} \frac{1}{2} | M_1 \rangle \\
\langle \frac{1}{2} \frac{1}{2} | N \rangle &\langle \frac{1}{2} \frac{1}{2} | N \rangle \langle \frac{1}{2} \frac{1}{2} | N \rangle \langle \frac{1}{2} \frac{1}{2} | N \rangle
\end{align*}
\]

\( \text{BY CLEBSCH-GORDON ORTHOGONALITY} \)

\( \text{CONVERTING TO WIGNER'S} \ 3j \ \text{SYMBOL} \)

\[
\begin{pmatrix}
S_2 \rangle [S_i] [s] \\
M_2 \rangle [M_1] [S_2] [S_i] \rangle [S_1] [S] \rangle [S]
\end{pmatrix}
\]

\( \langle S_2 | S_1 | S \rangle \langle \frac{1}{2} \frac{1}{2} | M_2 | \frac{1}{2} M_1 | \frac{1}{2} S_1 | N \rangle \)

\( \text{CONVERTED TO STANDARD FORM OF} \ 3j \)

\[
\begin{pmatrix}
S_2 \rangle [S_i] [s] [S]
\end{pmatrix}
\]

\( \text{CORRESPONDING SIGNS ETC} \)

\[
\begin{pmatrix}
\begin{pmatrix}
\frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2}
\end{pmatrix}
\end{pmatrix}
\]

\( \text{MATRIX ELEMENT AFTER SPIN COUPLING} \)

\[
\begin{pmatrix}
\begin{pmatrix}
S_2 \rangle [S_i] [S] \langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2}
\end{pmatrix}
\end{pmatrix}
\]

\[
\begin{pmatrix}
\begin{pmatrix}
S_2 \rangle \langle \frac{1}{2} \frac{1}{2}
\end{pmatrix}
\end{pmatrix}
\]

\( \text{FIG 415} \)
\[ \langle m_1 | G | \chi \beta \rangle \]

**CORRESPONDING SPIN COUPLING PART**

\[ \begin{align*}
\langle \frac{1}{2} \; \frac{1}{2} | s_1, s_2 \rangle & \quad \langle \frac{1}{2} \; \frac{1}{2} | s_3, s_4 \rangle \\
\langle \frac{1}{2} \; \frac{1}{2} | s_3, s_4 \rangle & \quad \langle s_1, s_2 | s_3, s_4 \rangle \\
\langle s_2, s_1 | s \rangle & \quad \text{CLEBSCH GORDON ORTHOGONALITY} \\
\langle s_1, s_2 | s \rangle & \quad \langle s_3, s_4 | s \rangle (\text{rotation}) \\
\langle s_2, s_1 | s \rangle & \quad [s_2 | [s] (m \rho)^{s_2} G^s (\chi \beta)^{s_1}] \\
\end{align*} \]

**FIG 4.16**
\[ \langle m | 3 \rangle | p \rangle \] \[ \langle \tau | 4 | \theta \rangle \]

**Corresponding Spin Coupling Part**

\[
\sum_{\sigma_f, \sigma_i} \langle \frac{1}{2} \frac{1}{2} \sigma_f | \sigma_i \rangle \langle \frac{1}{2} \frac{1}{2} \sigma_i | \frac{1}{2} \sigma_f \rangle
\]

**Figure**

\[ (-1)^{\frac{1}{2}} [S_2] [S] [S_f] \quad [1/2] \]

**Corresponding to Wigner's 3j Symbol**

\[ (-1)^{S_2 + S_1 + 1} \]

**Matrix Element After Spin Coupling**

\[ (-1)^{S_2 + S_1} \left[ S_2 \right] \left[ S \right] \left[ S_f \right] \quad [1/2] \]

\[ \left\{ s_2 + S_1 \right\} \left\{ n_m \right\} \left\{ n_0 \right\} \left\{ \tau \mid 4 \mid \theta \right\}_{S_2} \]

**Fig-4.17**
\[ \langle m_f | \delta(k) | \delta(f') \rangle \]

**Corresponding Spin Coupling Part**

\[
\sum \langle \mathbf{S}_1 | \frac{1}{2} \mathbf{S}_2 | \mathbf{S}_3 \rangle \langle \mathbf{S}_2 | \frac{1}{2} \mathbf{S}_3 | \mathbf{S}_1 \rangle \\
S_1, S_2 \in \Gamma \]

**Corresponding Figure**

**Converted to Wigner's 3j Symbols**

\[
\begin{bmatrix}
S_1^2 & S_2^2 & S_3^2 \\
S_1 & S_2 & S_3 \\
M_1 & M_2 & M_3
\end{bmatrix}
\]

\[
\begin{pmatrix}
\frac{1}{2} & \frac{1}{2} & M_1 \\
0 & 0 & S_1 \\
M_1 & M_3 & S_3
\end{pmatrix}
\]

**Converted to Standard Figure of 124**

**Corresponding Expression with Sign**

\[
(-1)^{S_z + S_2 + S_1} \\
\begin{bmatrix}
S_1^2 & S_2^2 & S_3^2 \\
S_1 & S_2 & S_3 \\
S_1 & S_2 & S_3
\end{bmatrix}
\]

FIG 418
In order to reduce complications and involvement in computational scheme and make it simple we have expressed the equations in terms of spatial basis functions only. To achieve this we have to adopt different techniques for singlet and triplet transitions and so we have discussed them under separate headings.

a) Singlet Transition

In constructing the equations for singlet transitions, it is to be noted that for 2h-2p excitations we have two types of matrix elements
\[
\langle \psi_q | \gamma_2 | \phi_2 \rangle^6 = \frac{1}{4} \left( \langle \psi_q | \gamma_2 | \phi_2 \rangle + \langle \psi_q | \gamma_2 | \phi_2 \rangle \right)
\]
and
\[
\langle \psi_q | \gamma_2 | \phi_2 \rangle^4 = \frac{1}{4} \left( \langle \psi_q | \gamma_2 | \phi_2 \rangle - \langle \psi_q | \gamma_2 | \phi_2 \rangle \right).
\]

Matrix elements of the right hand side are expressed in spatial form only.

Similarly, for the block structure \( \mathcal{S} \) involving 2h-2p excitation
\[
\langle \psi_q | \mathcal{S}_2 | \phi_2 \rangle^6 \quad \mathcal{S}_1 = \mathcal{S}_2
\]
and \( \mathcal{S}_1 \) and \( \mathcal{S}_2 \) can have values 0, 1.

We can rearrange the two types of 2h-2p equations
The plus combination gives

\[ \langle \phi_1 | G | \alpha \beta \rangle + \langle \phi \beta \mid G \mid \beta \alpha \rangle = 0 \]  

(4.79)

In the other equation the hole labels are merely interchanged.

The equation for singlet transition then becomes

1) For block structure with $1h$-$1p$ excitation

\[ G^{(m,\alpha)} = \sum_{n} \langle m \mid \overline{\beta} \mid n \rangle \langle n \mid \beta_{1} \mid \alpha \rangle - \sum_{\beta} \langle \beta_{1} \mid \overline{\alpha} \mid \beta \rangle \langle m \mid \beta \mid \alpha \rangle + \sum_{\beta n} \left[ 2 \langle m \beta \mid \overline{\alpha} \mid n \beta \rangle - \langle m \beta \mid \overline{\alpha} \mid n \beta \rangle \right] \langle n \beta_{1} \mid \alpha \rangle \\
+ \sum_{\beta n} \left[ 2 \langle m \beta_{1} \mid \overline{\alpha} \mid n \beta \rangle - \langle m \beta_{1} \mid \overline{\alpha} \mid n \beta \rangle \right] \langle n \beta_{1} \mid \alpha \rangle - \hbar \omega \langle m \mid \beta_{1} \mid \alpha \rangle = 0 \]  

(4.80)
(130)

ii) The equation for 2h-2p excitation

\[ G(m_\alpha, n_\beta) = \sum_p \langle m_\alpha | f_p \rangle \langle h_m | \beta_2 \rangle - \sum_q \langle m_\alpha | q_\beta \rangle \langle h_n | \beta_2 \rangle \\
+ \sum_p \langle m_\alpha | \overline{\nu}_p \rangle \langle h_p | \beta_2 \rangle - \sum_q \langle m_\alpha | \overline{\nu}_q \rangle \langle h_q | \beta_2 \rangle \\
+ \sum_p \left[ 2 \langle m_\alpha | \overline{\nu}_p \rangle \langle h_p | \beta_2 \rangle - \langle m_\alpha | \overline{\nu}_p \rangle \langle h_p | \beta_2 \rangle \right] \langle m_\alpha | \beta_2 \rangle \langle \alpha \beta \rangle \\
- \sum_p \left[ \langle m_\alpha | \overline{\nu}_p \rangle \langle h_p | \beta_2 \rangle - \langle m_\alpha | \overline{\nu}_p \rangle \langle h_p | \beta_2 \rangle \right] \langle m_\alpha | \beta_2 \rangle \langle \alpha \beta \rangle \\
+ \frac{1}{2} \sum_{pq} \langle m_\alpha | \overline{\nu}_p \rangle \langle h_p | \beta_2 \rangle \langle n_q | \beta_2 \rangle + \frac{1}{2} \sum_{pq} \langle m_\alpha | \overline{\nu}_p \rangle \langle h_p | \beta_2 \rangle \langle n_q | \beta_2 \rangle \\
- \hbar \omega \langle m_\alpha | \beta_2 \rangle \langle \alpha \beta \rangle = 0 \]

\[ (4.81) \]

The relevant matrix elements of \( f \) and \( \overline{\nu} \) are given in appendix E.3.

For the block \( G(m_\alpha) \) we have generated a serial number which is the equation number for the particular hole-particle excitation. These numbers are stored in matrix. In order to locate 2h-2p excitation, we have generated a symmetric number matrix for all possible \( \alpha \rightarrow \beta \) and \( \beta \rightarrow \gamma \) excitations so that location number for \( \beta_2 (\alpha \beta, \beta \gamma) \) is the same as \( \beta_2 (\beta \gamma, \alpha \beta) \). The same number matrix is used to locate the \( t_2 \) matrix elements. For the block with 2h-2p excitation structure, we have generated labels \( \beta, \gamma, \alpha, \beta \) in four different loops and used the same symmetry in equation numbers i.e. the equation number associated with \( G(\alpha \beta, \beta \gamma) \) is the same as that with \( G(\beta \gamma, \alpha \beta) \). So the condition that

\[ G(\alpha \beta, \beta \gamma) + G(\beta \gamma, \alpha \beta) = 0 \]
is automatically satisfied.

To find out the transition energies these equations are to be transformed to eigenvalue equations.

The matrix to be diagonalised is a non-hermitian one. So we are to first transform it to Hessenberg form\(^{[4.11]}\) and this is to be followed by seeking of roots and inverse iteration\(^{[4.12]}\).

b) **Triplet Transition**

For the triplet a somewhat complicated situation arises. The 2h-2p excitations are of three types when the hole particle labels are all different.

The excitations are

i) **Spin paired hole labels** → Spin parallel particle pair
   (they may have same label)

ii) **Spin parallel hole pair** → Spin paired particles
   (they may have same labels)

iii) **Spin parallel holes** → Spin parallel particles.

The corresponding reduced matrix elements are

i) \[
\langle \beta \gamma \rangle^1 | \lambda^2 \rangle \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 \langle \gamma \phi \rangle^0 \langle \phi \beta \rangle^0 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\phi \beta \rangle^0 \langle \gamma \phi \rangle}
Our objective is now to express these as matrix elements involving space part only. At this point it is to be noted that these reduced matrix elements are symmetric with respect to electron exchange.

Let us now examine closely the operator $\beta_2^1$. The $\beta_2$ should consist of two parts - space and spin. To allow triplet excitation it is warranted that the spin part should be triplet in nature.

The space part can always be partitioned in two parts $X_a$ antisymmetric and $X_s$ symmetric with respect to electron exchange.

For the first two of these reduced matrix elements the particle pair of parallel spin in one and the hole pair of parallel spin in the other are triplet in nature and so must be antisymmetric in space part. The other pair being spin paired are, symmetric in space part. The hole and particle pairs taken together must be antisymmetric in space part. So to preserve the overall symmetry of the reduced matrix elements the antisymmetric part $X_a$ of the space part of excitation operator $\beta_2$ will be responsible for the transition and not the symmetric counter part of the operator. Reverse is the case for the third one. Here both the particle pair and hole pair are spin parallel couple and so both are antisymmetric in space part. So the two pairs taken together the space part is restored symmetric with respect to electron exchange. Naturally to maintain the overall symmetry of the reduced matrix element only the symmetric part $X_s$ of $\beta_2$ will be operative.
The second factors in the expressions appearing on the right hand side obviously refer to reduced matrix elements associated with spin integration.

For the reduced matrix elements in (4.82a) and (4.82b) the same space part $X_\lambda$ of $\beta_2$ is associated with different reduced spin matrix elements. Our attempt is to express one of these reduced matrix elements having identical space parts in terms of the other.

This is easy provided we note that

$$\langle \sum_0^0 | \sum_0^0 | \sum_0^0 \rangle = \langle \sum_0^0 | \sum_0^0 | \sum_0^0 \rangle$$

(4.83)

where $\sum_0^0$ and $\sum_0^0$ represent $m = 0$ component of the triplet and singlet spin functions respectively.

Application of Wigner Eckart theorem to the above identity gives

$$\langle 1 | 1 | 0 \rangle \langle 0 | \frac{1}{\lambda} | \frac{1}{\lambda} \rangle = \langle 0 | 1 | 1 \rangle \langle \frac{1}{\lambda} | \frac{1}{\lambda} | 0 \rangle$$

(4.84)
The second terms of the left and right hand sides of (4.84) represent the appropriate Clebsche Gordon coefficient (C-G coefficient).

So that putting the values of the C-G coefficients we get

\[ \langle 1|1|0 \rangle = \langle 0|1|1 \rangle x - \frac{1}{\sqrt{3}} \]

or

\[ \langle 0|1|1 \rangle = -\sqrt{3} \langle 1|1|0 \rangle \]

If we now absorb \( \langle 1|1|0 \rangle \) in \( \chi_a \) the expressions in (4.82a) and (4.82b) reduce to

\[ \xi (b_q)^2 \beta_2^4 |(\kappa \beta)^0 \rangle = \langle (b_q)^2 | x_a | (\kappa \beta)^0 \rangle \]

\[ = \langle b_q | x_a | \kappa \beta \rangle + \langle b_q | x_a | \beta \kappa \rangle \]

(4.86a)

and

\[ \xi (b_q)^0 \beta_2^4 |(\kappa \beta)^4 \rangle = \langle (b_q)^0 | x_a | (\kappa \beta)^4 \rangle \]

\[ = -\sqrt{3} \langle b_q | x_a | \kappa \beta \rangle - \langle b_q | x_a | \beta \kappa \rangle \]

(4.86b)

We can similarly write the third one as

\[ \xi (b_q)^4 \beta_2^4 |(\kappa \beta)^4 \rangle = \langle (b_q)^4 | x_a | (\kappa \beta)^4 \rangle \]

\[ = \langle b_q | x_a | \kappa \beta \rangle - \langle b_q | x_a | \beta \kappa \rangle \]

(4.86c)

by absorbing the reduced matrix elements in the space part.

The same analysis can be applied to the block structure of 2h-2p excitation i.e.
So that by a slight manipulation we can rearrange the equations (4.87 and 4.88) as
\[
\begin{align*}
\left\{ (p_\alpha)^4 \left| G^4 \right| (\nu_\beta)^4 \right\} &= \left\{ (p_\alpha)^4 \left| g^a \right| (\nu_\beta)^4 \right\} \\
&= \frac{1}{2} \left[ \left\langle p_\alpha \left| g^a \right| \nu_\beta \right\rangle + \left\langle \nu_\beta \left| g^a \right| \rho_\alpha \right\rangle - \left\langle \nu_\beta \left| g^a \right| \rho_\beta \right\rangle \right] = 0
\end{align*}
\]

i.e.
\[
\left\langle p_\alpha \left| g^a \right| \nu_\beta \right\rangle - \left\langle \nu_\beta \left| g^a \right| \rho_\alpha \right\rangle = 0
\]
or
\[
G^a (p_\alpha, \nu_\beta) - G^a (\nu_\beta, p_\alpha) = 0
\]  
(4.89)

The third set of equation gives
\[
\begin{align*}
\left\{ (p_\alpha)^4 \left| G^4 \right| (\nu_\beta)^2 \right\} &= 0 \\
\text{i.e.} \quad \left\langle p_\alpha \left| g^s \right| \nu_\beta \right\rangle - \left\langle \nu_\beta \left| g^s \right| \rho_\alpha \right\rangle - \left\langle \nu_\beta \left| g^s \right| \rho_\beta \right\rangle + \left\langle \rho_\beta \left| g^s \right| \rho_\alpha \right\rangle = 0
\end{align*}
\]
or
\[
G^s (p_\alpha, \nu_\beta) - G^s (\nu_\beta, p_\alpha) - G^s (\nu_\beta, \rho_\alpha) + G^s (p_\alpha, \rho_\alpha) = 0
\]  
(4.90)
Now we are in a position to write down the expressions for the equations with different block structures.

The expressions assume much simpler form if we redefine reduced matrix elements \( \langle \psi | \lambda 2 | \alpha \rangle \) and \( \langle m | \lambda 2 | \alpha \rangle \) as

\[
\left\langle \psi \right| \lambda 2 \left| \alpha \right\rangle = \sqrt{2} m \left| x_5 \right| \langle \alpha | \beta \rangle - \langle \psi | x_5 \right| \langle \beta | \alpha \rangle
\]

and

\[
\langle m | \lambda 2 | \alpha \rangle = \sqrt{3} \langle m | \lambda 1 | \alpha \rangle
\]  

(4.91)

\[
G_{\alpha}^{\psi} (m, \alpha) = \sum_{\gamma} \langle m | \bar{f} | \gamma \rangle \langle \gamma | \lambda 1 | \alpha \rangle - \sum_{\beta} \langle \gamma | \bar{f} | \beta \rangle \langle m | \lambda 1 | \beta \rangle
- \sum_{\gamma} \langle m | \bar{1} | \gamma \rangle \langle \gamma | \lambda 2 | \alpha \rangle + \sum_{\beta} \langle \gamma | \bar{1} | \beta \rangle \langle m | \lambda 2 | \beta \rangle
+ \sum_{\gamma} \left[ \langle m | \bar{1} | \gamma \rangle \langle \gamma | \lambda 2 | \alpha \rangle - \langle m | \bar{1} | \gamma \rangle \langle \gamma | \lambda 2 | \alpha \rangle \right] 
\]

(4.92)

\[
G_{\alpha}^{m} (m, \alpha) = \sum_{\gamma} \langle m | \bar{f} | \gamma \rangle \langle \gamma | \lambda 2 | \alpha \rangle - \sum_{\beta} \langle \gamma | \bar{f} | \beta \rangle \langle m | \lambda 2 | \beta \rangle
+ \frac{1}{2} \sum_{\gamma} \langle m | \bar{1} | \gamma \rangle \langle \gamma | \lambda 2 | \alpha \rangle + \frac{1}{2} \sum_{\beta} \langle \gamma | \bar{1} | \beta \rangle \langle m | \lambda 2 | \beta \rangle
+ \sum_{\gamma} \left[ \langle m | \bar{1} | \gamma \rangle \langle \gamma | \lambda 2 | \alpha \rangle - \langle m | \bar{1} | \gamma \rangle \langle \gamma | \lambda 2 | \alpha \rangle \right] 
\]

(4.93)
As in the case with the singlet the location number for \( X_\alpha (\beta \gamma, \alpha \beta) \) is generated serially for all possible \( \alpha \rightarrow \beta \), \( \beta \rightarrow \gamma \) excitations in the form of a matrix. Here, the number matrix is made antisymmetric, the location number is obtained from the absolute value of the number and the sign is determined from the sign associated with the number matrix element. The labels \( \alpha, \beta, \gamma \) are generated in four different loops with the exception \( \alpha = \beta \) and \( \beta = \gamma \). Same location technique is used for \( G^s \). Here also the sign and the equation number, are obtained from the antisymmetric number matrix, so that the equation \( G^s (\alpha \beta, \beta \gamma) - G^s (\beta \gamma, \alpha \beta) = 0 \) is automatically generated.

In the case of symmetric part \( G^S (\alpha \beta, \beta \gamma) \) the index labels are generated with a constraint that \( \alpha < \beta \) and

Then by redefining the input the whole equation (4.90) is generated at a time. The equations are recast in form of eigenvalue equations. As usual this is then diagonalised using the same algorithm as was used for the singlet. The results are given in Table (4.3).
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Different Levels of Approximation for the Correlation Energy and Transition Energy Data (in ev.)
## Correlation Energy and Transition Energy Data (\text{int \cdot y})

\[ \langle \text{Exp}(T) \rangle = \langle \text{Exp}(S) \rangle \]

of

Five Heterocyclic Compounds

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A = excited state with same symmetry as ground state
B = excited state with different symmetry as ground state

Table 4.3
Results

The results of our calculations have been given in Table 4.3. Comparison with CI (full & extensive) is given in Table 5.1 - 5.3.

Ground State Correlation

We have already explained before that the ground state correlation energy has been calculated first by retaining only \( T_2 \) terms i.e. mixing only doubly excited states with HF and secondly by extending to \( T_2^2 \) i.e. by simulation of higher excited states. The first one we have termed, as indicated before, linear and the second non-linear correlation. The data have also been presented under the same headings. As is to be expected the important share of correlation comes from doubly excited states. Addition of quadruply excited states by simulation of the same through \( T_2^2 \) improves results by an energy of the order of \( \approx 0.03 \) ev in almost all the compounds. The obvious reason is that the gap between ground and these excited states higher than doubly excited states is too great for their contribution to be significant. However, it has been definitely shown that a greater depression is easily brought in by \( T_2^2 \) without much complications as regards computations etc. though the effect may be marginal.

Transition Energies

Transition energies have been calculated with linearly and non-linearly correlated ground state on one hand and excited states with \( S_1 \) i.e. one hole one particle and \( S_2 \) i.e. two holes two particles excitation operators on the other. When \( S_1 \)
only is used, the excited state is then in fact a superposition of singly excited states with triply excited ones (through $T_2$) but no doubly excited states are included. When both $S_1$ and $S_2$ are used all possible excitations are virtually taken into account. The linear and non-linear values given separately do not differ much, as is to be expected.

We have thus first diagonalised the portion of $A$ - matrix involving $S_1$ only i.e. a 9 x 9 matrix and then have diagonalised the whole $A$ - matrix i.e. a 54 x 54 one. The results have been given under headings $S_1$ and $S_1 + S_2$. Both singlet and triplet transition energies are given under appropriate headings.

In case of $S_1$ since only singly excited states are in effect allowed to mix and no doubly excited states are included the excited state energy is not much depressed, whereas the ground state is well correlated. So the gap in fact increases and this is apparent if we compare the data with CI or even TDA, indicating that importance of doubly excited states even in the calculation of transition energies of low lying excited states. In TDA the position gets reversed. Here the ground state is HF but the singly excited states are somewhat improved by mixing among themselves. Though the excited state is not even as improved as those obtained through $T_2S$ (since higher excitations are totally absent) the transition energy calculated compares better with CI.

The results are totally reversed when we use both $S_1$ and $S_2$ for excitation and diagonalise the whole 54 x 54 matrix. In this case both ground and excited states are equally correlated
(since new doubly excited states have been allowed to mix through $S_2$). The transition energies now calculated compare well with those obtained by CI.

Another important feature to be noted is that when the polarisation is not properly brought in (in case of $S_1$) the order of excited states may sometimes differ from that when extensive polarisation is affected through $S_1 + S_2$. To cite an example, in Tetrazine singlet transition the third and fourth excited states of $S_1$ have interchanged their positions when complete $S_1 + S_2$ have been used.
Appendix

\[ \langle \psi_1 \mid \delta \mid \psi_2 \rangle = \sum_{\gamma \delta e} \langle \psi_1 \mid \gamma \delta e \mid \psi_2 \rangle \] 
\[ + \sum_{\gamma \delta s} \langle \psi_1 \mid \gamma \delta s \mid \psi_2 \rangle \] 
\[ \langle \beta \mid \psi_1 \rangle = e_{\alpha} \delta_{\alpha \beta} + \sum_{\gamma \delta s} \langle \gamma \delta s \mid \psi_1 \rangle \langle \psi_1 \mid \gamma \delta s \rangle \] 
\[ \langle \alpha \mid \psi_1 \rangle = 0.0 \] 
\[ \langle \psi_1 \mid \psi_2 \rangle = \langle \psi_1 \mid \psi_2 \rangle + \sum_{\gamma \delta s} \langle \gamma \delta s \mid \psi_1 \rangle \langle \psi_1 \mid \gamma \delta s \rangle \] 
\[ \langle \gamma \delta s \mid \alpha \beta \rangle = \langle \gamma \delta s \mid \alpha \beta \rangle + \sum_{\gamma \delta s} \langle \gamma \delta s \mid \psi_1 \rangle \langle \psi_1 \mid \gamma \delta s \rangle \] 
\[ \langle \psi_1 \mid \psi_2 \rangle = \langle \psi_1 \mid \psi_2 \rangle + \sum_{\delta \gamma s} \langle \delta \gamma s \mid \psi_1 \rangle \langle \psi_1 \mid \delta \gamma s \rangle \] 
\[ + \sum_{\gamma \delta s} \langle \gamma \delta s \mid \psi_1 \rangle \langle \psi_1 \mid \gamma \delta s \rangle \] 
\[ \langle \psi_1 \mid \psi_2 \rangle = \langle \psi_1 \mid \psi_2 \rangle + \sum_{\gamma \delta s} \langle \gamma \delta s \mid \psi_1 \rangle \langle \psi_1 \mid \gamma \delta s \rangle \] 
\[ + \sum_{\gamma \delta s} \langle \gamma \delta s \mid \psi_1 \rangle \langle \psi_1 \mid \gamma \delta s \rangle \] 
\[ \langle \psi_1 \mid \psi_2 \rangle = \langle \psi_1 \mid \psi_2 \rangle \] 
\[ \langle \psi_1 \mid \psi_2 \rangle = 0.0 \] 

\[ \beta, \gamma, \ldots \text{ denote particle orbitals; } \alpha, \beta, \ldots \text{ denote hole orbitals.} \]

A, B, \ldots\text{ stand for hole/particle orbitals.}
References

    idem ibid (1968).


    idem ibid 22, 78 (1961).


