ELECTRIC DIPOLE TRANSITIONS IN CARBON ISOELECTRONIC SEQUENCE UNDER PURE STATES OBTAINED FROM SUPERPOSITION OF CONFIGURATION

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PREFACE

This thesis contains the new calculations made on F^{+++} Oscillator Strengths using wavefunctions which describe symmetry projected states and contain non-dynamical electronic correlations. These results are much more accurate than those obtained with simple Hartree Fock wavefunctions.

The Z dependence of oscillator strengths of different transitions in carbon isoelectronic sequence is examined by showing them graphically. This helps in predicting oscillator strengths for six electron ions with large Z. The improvement in the numerical values of oscillator strengths through the inclusion of correlation effects is strikingly shown in the graphs.

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CHAPTER I

INTRODUCTION TO THE PROBLEM

Calculations of oscillator strengths and transition probabilities have been done before, using wavefunction, which are not rigorous eigenfunctions of L^2 and S^2. These wavefunctions are obtained by using the configuration interaction method, as described by Öksüz and Sinanoğlu (1).

It is possible to have wavefunctions which are exact eigenfunctions of L^2 and S^2, if the wavefunctions are projected out using Löwdin's (2) projector operators or, if they are formed out of a closed set of determinants. This will be explained in detail later on.

It was realized that a pure[1] state was needed in order to make a computation of oscillator strengths and the electric dipole transition probability. Then a comparison may be made of these results with those obtained when the functions used are not exact eigenfunctions of L^2 and S^2.

Öksüz and Sinanoğlu (1) have made CI calculations of energy and wavefunctions using determinants describing correlations depicted by one and two particle excitations from Hartree-Fock state. The important point here is that the wavefunction, which is a linear combination of

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[1] The states obtained after Löwdin's projector operator has operated on the configuration interaction (CI) wavefunction will be referred to as pure states. The simple CI expansion will also be referred to as superposition of configuration.

determinants in which just one and two particles excitations are considered may not be sufficient to give the required symmetry of the state. One method used to get a function of required symmetry is the obtaining of a closed set of determinants. That is, one obtains an extended set of determinatns by operating with the (M_+M_-) operator (this does not change M_L and M_S value of determinants) on all the determinants obtained by one and two particles excitations from the HF state. This operation of (M_+M_-) is continued on the newly obtained set until no new set of determinant is obtained. This final set of determinants is called a "closed set". This is a closed set of determinants which has the M_L and M_S value with which we started. It also has in it terms which have more than two particles excitations. This closed set of determinants guarantees that a pure state can be obtained from a linear combination of some or all of these determinants. Öksüz and Sinanoğlu found that the energy calculated using a set of determinants with at most one and two particle excitations from Hartree-Fock sea and a closed set of determinants differed by an amount less than .005 eV.

On the other hand, if one uses an unprojected CI wavefunction and a pure state CI wavefunction obtained by using Löwdin's projector operators on that CI wavefunctions, the energy calculations would show the same result. This will become clear using a set of equations. Hamiltonian will be set up in a truncated basis. Then this approximate Hamiltonian matrix will be diagonalized. This will yield eigenvalue of approximate Hamiltonian. A wavefunction can be written as sum of HF part and correlation part, therefore let

$$\psi = \phi_{HF} + \chi \qquad [1]$$

such that

$$\langle\phi_{HF}|\phi_{HF}\rangle = 1 \qquad [2]$$

and

$$\langle\phi_{HF}|\chi\rangle = 0 \qquad [3]$$

Equation [3] implies that correlated part is orthogonal to HF part.

If [2] and [3] are satisfied, then

$$H|\phi_o + \bar{\chi}\rangle = E_{\phi_o + \bar{\chi}}|\phi_o + \bar{\chi}\rangle \text{ and } E_{\phi_o + \bar{\chi}} = \langle\phi_o|H|\phi_o\rangle + \langle\phi_o|H|\bar{\chi}\rangle$$

these are certainly true for exact χ and H but are also true for any approximate $\bar{\chi}$ and H, where H is a matrix obtained in truncated basis set (ref (1) footnote 15). For eigenvalue of approximate non-relativistic Hamiltonian, when the wavefunction is expanded in a truncated basis set, we have:

$$E_{approximate} = \langle\phi_{HF}|H|\phi_{HF} + \chi\rangle \qquad [4]$$

Next we try to write E_{app} in terms of a projected function. Projection operator has the following properties:

(A) $P = P^{\dagger}$, P is Hermitian

(B) $P^2 = P$, P is idempotent [5]

(C) $HP = PH$, P commutes with Hamiltonian

In terms of projected wavefunctions expectation value of energy becomes

$$\tilde{E}_{app} = \langle\phi_{HF}|HP|\phi_{HF} + \chi\rangle \qquad [6]$$

$$= \langle\phi_{HF}|PH|\phi_{HF} + \chi\rangle \qquad [7]$$

$$= \langle P^{\dagger}\phi_{HF}|H|\phi_{HF} + \chi\rangle \qquad [8]$$

$$= \langle P\phi_{HF}|H|\phi_{HF} + \chi\rangle \qquad [9]$$

$$= \langle\phi_{HF}|H|\phi_{HF} + \chi\rangle \qquad [10]$$

$= E_{app}$. Same as given by Eqn. [4].

Four types of electron correlation terms are included in χ in addition to HF part (1) to get a wavefunction as expressed by Eqn. [1]. These are:

1) Internal correlation,
2) Semi-internal correlation,
3) Single particle all external correlation, also called polarization effect,
4) Two or more particle all external.

First two types of correlations occur in open shell only. Single particle all external correlations occur in both, closed and open shell. However, within the first order corrections to HF orbitals in the perturbation theory, the contributions from polarization effects in the closed shell are zero. As we go to second and higher order perturbations they are formally present. The fourth type viz two or more particle all external correlations are important in both open and closed shell systems.

Correlation Energies

The total correlation energy is defined as (1)

$$E_{CORR} = (E_{TOT} - E_{REL}) - E_{HF} = E_{NON-REL} - E_{HF}$$

where E_{TOT} = total energy of atom and ion can be obtained experimentally.

and E_{REL} = relativistic energy correction including spin orbit coupling, which can be calculated using a semiempirical procedure (1). This determines E_{CORR}. If we have the exact correlation function χ then:

$$E_{NON-REL} = <\phi_{HF}|H|\phi_{HF} + \chi_{int} + \chi_F + \chi_U>$$

where χ_F includes semi-internal and polarization part of correlation. χ_U is all external correlation function.

$$E_{NON-REL} = E_{HF} + E_{int} + E_F + E_U$$

$$E_{NON-REL} - E_{HF} = (E_{int} + E_F) + E_U$$

$$E_{CORR} = (E_{int} + E_F) + E_U$$

or $E_U = E_{CORR} - (E_{int} + E_F)$ and this now gives an explicit expression for all external correlation energy. We saw through Eqn. [10] and [4] that energy does not change when using a projected wavefunction. In the 'closed set' method the difference in energy may be attributed to diagonalizing the Hamiltonian matrix in a different basis set before and after the set is closed. It is necessary in the above discussion to include the correlation effects in the wavefunction to make the wavefunction more accurate. As the formula stands, for transition probability, it is proportional to a matrix element which requires evaluation between two eigenfunctions. An eigenfunction can be obtained if we expand a wavefunction in terms of HF part and include an infinite CI expansion.

For all practical purposes, it is very hard to comprehend the term 'infinite CI expansion'. At the same time, just the HF part of the wavefunction is insufficient to compute accurate oscillator strengths for many important transition.

Therefore for the practical purposes one must decide to what extent he wants to include electronic correlations while trying to improve a wavefunction. In this work we include first three types of correlations only. Thus, the total wavefunction will consist of the sum of HF part, correlation function arising from excitation of one or two particles from the HF sea to orbitals previously unoccupied in the sea (internal correlation), correlation function arising from excitation of one particle from the sea to an orbital outside the sea and one particle from the sea to an orbital inside the sea (semi-internal part), and finally, terms coming from excitation of a single particle from the sea to an orbital outside the sea (polarization).

Two or more particle all external correlations are not included in this work. It has been previously argued (3) that in the calculations of transition probability these may not be very important. Moreover in the polarization, semi-internal and interal correlation function, only one and two particle excitations from HF state are considered in obtaining a wavefunction.

There are infinite number of orbitals outside HF sea, therefore, limiting the excitation to 4f as it is done in this thesis work one is truncating the CI expansion to a certain term and thus one is neglecting all the virtual excitation that could occur to orbitals beyond 4f. The correlation functions are expanded in terms of Slater determinants which differ from HF state in one and two particle excitations. In general, functions thus obtained are not eigenfunctions of L^2 and S^2 (are not pure states). We make them a pure state by applying projector operator technique. In the projector operator method, all one does is to feed the output of a CI wavefunction to a specially designed projector operator program. The result is a pure state.

The difference in the oscillator strengths and the dipole transition probability using pure and impure states inspired this work.

To further stress the importance of a wavefunction which is eigenfunction of L^2 and S^2 in obtaining the oscillator strengths, one should take a glance at the two expressions of multiplet absorption oscillator strengths for electric dipole transitions. First, in terms of the dipole length lperator $\underline{R} = \sum_{i=1}^{N} r_i$

$$f_{\underline{R}}(\nu LS \rightarrow \nu'L'S') = \frac{2}{3}\,\frac{E(\nu'L'S') - E(\nu LS)}{(2L+1)(2S+1)} \sum_{M_L=-L}^{L} \sum_{M_S=-S}^{S} \sum_{M_L'=-L'}^{L'} \sum_{M_S'=-S'}^{S'}$$

$$|\langle \psi_{\nu LSM_LM_S} | \underline{R} | \psi_{\nu'L'S'M_L'M_S'} \rangle|^2$$

and second, in terms of dipole velocity operator $\underline{\nabla} = \sum_{i=1}^{N} \nabla_i$

$$f_{\underline{\nabla}}(\nu LS \rightarrow \nu'L'S') = \frac{2}{3}\;\frac{\sum_{M_L=-L}^{L} \sum_{M_S=-S}^{S} \sum_{M_L'=-L'}^{L'} \sum_{M_S'=-S'}^{S'} |\langle \psi_{\nu LSM_LM_S} | \underline{\nabla} | \psi_{\nu'L'S'M_L'M_S'} \rangle|^2}{(2L+1)(2S+1)\,[E(\nu'L'S') - E(\nu LS)]}$$

this equivalently can also be written in terms of acceleration operator. These expressions give exactly the same result if the wavefunctions ψs and energies Es are eigenfunctions and eigenvalues respectively of the non-relativistic, electrostatic Hamiltonian

$$H = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} \frac{-Z}{|r_i|} + \sum_{i<j}^{N} \frac{1}{|r_i - r_j|}$$

Here atomic units have been used, therefore $\hbar = 1$, $m_e = 1$, $q_e = 1$. This will hold true for the rest of the treatment too. With approximate functions, dipole velocity and dipole position results are not necessarily equal, but one expects better agreement between the two, the "nearer" the wavefunctions are to the exact ones.

At places a quantity gotten by taking square root of products of oscillator strengths obtained using position and momentum operators will be used for certain kind of comparisons.

Oscillator strengths and transition probabilities are also compared when wavefunctions used have and do not have the electron correlation. This is essentially an extension of work done by Westhaus and Sinanoğlu (3).

During the process of these studies one could also see nature, properties and advantages of obtaining a wavefunction which has been approximated such that it includes the electron correlation in addition to Hartree-Fock part.

Finally, to make an important point here, one sees that the Z-depencence of oscillator strengths cannot be set aside. A graphical representation of oscillator strengths versus $\frac{1}{Z}$ will be given for different transitions, which will be helpful in examination and interpretation of some trends of variation in oscillator strengths.

A new series of calculations are shown for the $^1D \rightarrow {}^1D$, $^1S \rightarrow {}^1P$, and $^1D \rightarrow {}^1P$ transitions from the configurations $1s^2\ 2s^2\ 2p^2 \rightarrow 1s^2\ 2s\ 2p^3$ for F^{+++} using pure states obtained from projector operator. Also some new calculations on the triplet-state transitions will be shown.

CHAPTER II

HARTREE FOCK THEORY AND ELECTRON CORRELATION

Definition: Hartree Fock orbitals are those orbitals which satisfy the HF equations.

HF equations are obtained using variational principle on the expectation value of Hamiltonian when the trial function is restricted to a single configuration. An equation gives one electron orbital energy for a particular orbital. These orbitals are then explicitly obtained using self consistency. Then, they are eigenfunctions of one electron Hamiltonian. For a system of N electrons, a linear combination of antisymmetric product of these orbitals can be formed which will be eigenfunctions of N electrons HF Hamiltonian.

One particle bare nucleus Hamiltonian is (4);

$$\overset{o}{h}_i = -\frac{1}{2}\nabla_i^{2} - \frac{Z}{r_i} \qquad [1]$$

First term is knietic energy and second term is potential energy of ith electron. N particle HF Hamiltonian is:

$$H_o = \sum_{i=1}^{N} (\overset{o}{h}_i + V_i) = \sum_{i=1}^{N} h_i \qquad [2]$$

First term is sum of bare nucleus Hamiltonian and second term is average potential of ith electron in the field of rest of (N-1) electrons. V_i is said to be HF potential of entire N electrons medium acting on electron i.

Non relativistic, electrostatic Hamiltonian for N electron problem can be written as:

$$H = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{1\leq i<j\leq N} \frac{1}{r_{ij}} \qquad [3]$$

This Hamiltonian can be broken into two parts as follows:

$$H = \sum_{i=1}^{N} \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + V_i\right) + \left[\sum_{1\leq i<j\leq N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} V_i\right] \qquad [4]$$

Where $\sum_{i=1}^{N} V_i$ has been added to first term and subtracted from second term, with no net change in the Hamiltonian. Let us label this as

$$H = H_o + H_1 \qquad [5]$$

where H_o is defined by Equations [2] and [1], H_1 is now defined as the quantity in the second square bracket in Equation [4].

Expression for V_i, the HF potential is obtained from writing the HF equation for a HF orbital U_i as follows (5).

$$-\frac{1}{2}\nabla_1^2\, U_i(1) - \frac{Z}{r_1} U_i(1) + \left[\sum_{j\neq i}^{N} \int \frac{d\chi_2\, U_j^*(2)(1-P_{12})U_j(2)}{r_{12}}\right] U_i(1) = \varepsilon_i U_i(1) \qquad [6]$$

P_{12} = two particles permutation.

The quantity in square bracket in Equation [6] is sum of differences of two terms viz coulomb (direct) and exchange potentials acting on electron in orbital i. The integral terms can be written as:

$$\int \frac{d\chi_2}{r_{12}} U_j^*(2) \left[U_j(2)\, U_i(1) - P_{12}\, (U_j(2)\, U_i(1))\right]$$

$$= \int \frac{d\chi_2}{r_{12}} U_j^*(2)\, U_j(2)\, U_i(1) - \int \frac{d\chi_2}{r_{12}} U_j^*(2)\, P_{12}(U_j(2)\, U_i(1))$$

$$= \quad S_j(1)\, U_i(1) - R_j''(1)\, U_i(1)$$

$$= \quad [S_j(1) - R_j''(1)]U_i(1) = \bar{S}_j(1)U_i(1) \qquad [6a]$$

where S_j and R_j'' denote the direct and exchange terms respectively. Note here that for $i = j$ the direct and exchange potentials yield equal results when acting on a particular HF orbital U_i and they subtract out to zero. The summation term $i = j$ is not included in Eqn. [6]. For a HF orbital U_i we have:

$$V_i(1)\, U_i(1) = \sum_{j\neq i}^{N} \int \frac{d\chi_2\, U_j^*(2)\ (1-P_{12})U_j(2)}{r_{12}}\, U_i(1) \qquad [7]$$

For electron 1 in orbital i and electron 2 in orbital j. Summation goes over all j, except j = i. More explicitly for i = 1 and i = 2, Eqn. [7] can be written as

$$V_1(1)\, U_1(1) = \sum_{j\neq 1}^{N} \int \frac{d\chi_2\, U_j^*(2)\ (1-P_{12})U_j(2)}{r_{12}}\, U_1(1) \qquad [8]$$

$$V_2(1)\, U_2(1) = \sum_{j\neq 2}^{N} \int \frac{d\chi_2\, U_j^*(2)\ (1-P_{12})U_j(2)}{r_{12}}\, U_2(1) \qquad [9]$$

In Eqns. [8] and [9] j = 1 and j = 2 terms are excluded. However, if we include those terms, the potential terms are identical in both Equations [8] and [9]. That is including the missing terms in V_1 and V_2 yields another expression whose action on U_1 and U_2 is the same. In that case Eqns. [8] and [9] may be written as follows:

$$V_1(1)\, U_1(1) = V(1)\, U_1(1) \qquad [10]$$

$$V_2(1)\, U_2(1) = V(1)\, U_2(1) \qquad [11]$$

where V(1) is the potential expression without any restriction on the orbitals. Thus HF potential without any restriction on the orbitals can be written as

$$V(1) = \sum_{j=1}^{N} \int \frac{dX_2\, U_j^*(2)\ (1-P_{12})\ U_j(2)}{r_{12}} . \qquad [12]$$

Now HF potential may be defined in two ways viz through Eqn. [6] or Eqn. [12]. This does not affect H in Eqn. [4], however, H_o and H_1 are affected independently.

Two expressions for HF potential are:

$$V_i(1) = \sum_{j\neq i}^{N} \bar{S}_j(1) \quad \text{and} \qquad [13]$$

$$V(1) = \sum_{j=1}^{N} \bar{S}_j(1) \qquad [14]$$

where $\bar{S}_j(1)$ is difference of coulomb and exchange potentials.

$$\bar{S}_j(1) = \int \frac{dX_2\, U_j^*(2)\ (1-P_{12})\ U_j(2)}{r_{12}} \quad \text{with} \quad \bar{S}_j(1)\ U_j(1) = 0$$

From Eqn. [5], we have $H = H_o + H_1$

$$\therefore\ <\phi_o|H|\phi_o> = <\phi_o|H|\phi_o> + <\phi_o|H_1|\phi_o> \qquad [15]$$

where ϕ_o is antisymmetric product of HF orbitals

$$\therefore\ E_{HF} = E_o + E_1 \qquad [16]$$

In the following lines we try to evaluate E_o and E_1. [A] Evaluation of E_o: we know that H_o is N particle HF Hamiltonian, therefore, expectation value in HF orbital basis should yield $E_o = \sum_{i=1}^{N} \varepsilon_i$ that is total sum of one electron orbital energy, summed over N electrons. This will be proved below.

We have

$$<\phi_o|H_o|\phi_o> = <A(U_1(1)U_2(2)----U_N(N))|\sum_i h_i|A(U_1(1)U_2(2)----U_N(N))> \qquad [17]$$

A is N particle antisymmetrizer, is Hermitian and has the following property:

$$A = \frac{1}{\sqrt{N!}} \sum_P (-1)^{\sigma_P} P \qquad [18]$$

$$A^\dagger = A \qquad [19]$$

$$A^\dagger A = A^2 = \sqrt{N!}\ A \qquad [20]$$

$$\therefore\ <\phi_o|H_o|\phi_o> = <U_1(1)U_2(2)---U_N(N)|A^\dagger\sum_i h_i|A(U_1(1)U_2(2)---U_N(N))>$$

But $A^\dagger\sum_i h_i = \sum_i h_i A^\dagger = \sum_i h_i A$

$$\therefore\ <\phi_o|H_o|\phi_o> = <U_1(1)U_2(2)---U_N(N)|\sum_i h_i A|A(U_1(1)U_2(2)---U_N(N))>$$

But $AA = A^2 = \sqrt{N!}\ A$

$$\therefore\ <\phi_o|H_o|\phi_o> = <U_1(1)U_2(2)---U_N(N)|\sum_i h_i\ \sqrt{N!}|A(U_1(1)---U_N(N))>$$

$$= \sqrt{N!}\ <U_1(1)U_2(2)---U_N(N)|A(h(1) + h(2) + --- h(N))|U_1(1)U_2(2)---U_N(N)>$$

$$= \sqrt{N!}\ <U_1(1)U_2(2)---U_N(N)|\frac{1}{\sqrt{N!}}\sum_P (-1)^{\sigma_P} P\ h(1) + h(2)---h(N)|U_1(1)---U_N(N)>$$

$$= \frac{\sqrt{N!}}{\sqrt{N!}} < U_1(1)U_2(2)---U_N(N)|\Sigma(-1)^{\sigma_P} P\ (\varepsilon_1+\varepsilon_2 + -- \varepsilon_N)|U_1(1)U_2(2)---U_N(N)>$$

$$= \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \text{---}\ \varepsilon_N \ < U_1(1)U_2(2)\text{---}U_N(N) \,|\, \Sigma(-1)^{\sigma_P} P \,|\, U_1(1)U_2(2)\text{---}U_N(N)>$$

$$= \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \text{---}\ \varepsilon_N = \sum_{i=1}^{N} \varepsilon_i = E_o \qquad [21]$$

[B] Evaluation of E_1:

We have

$$E_1 = <\phi_o|H_1|\phi_o>$$

$$= <A(U_1(1)U_2(2)\text{----}U_N(N)\,|\,\sum_{i<j} \frac{1}{r_{ij}} - \sum_j V(j)\,|\,A(U_1(1)\text{---}U_N(N))> \qquad [22]$$

Now proceed on the same lines as [17] through [21]. Note that in [22] Eqn. [14] has been used.

$$E_1 = \sqrt{N!}\ <U_1(1)U_2(2)\text{----}U_N(N)\,|\,\sum_{i<j} \frac{1}{r_{ij}} - \sum_j V(j)\,|\,A(U_1(1)U_2(2)\text{---}U_N(N))> \qquad [23]$$

$$= \frac{\sqrt{N!}}{\sqrt{N!}} <U_1(1)U_2(2)\text{---}U_N(N)\,|\,\sum_{i<j} \frac{1}{r_{ij}}\,|\,\sum_P (-1)^{\sigma_P}\, P\ U_1(1)U_2(2)\text{----}U_N(N)>$$

$$- \frac{\sqrt{N!}}{\sqrt{N!}} <U_1(1)U_2(2)\text{---}U_N(N)\,|\,\sum_j V(j)\,|\,\sum_P (-1)^{\sigma_P}\, P\ U_1(1)U_2(2)\text{----}U_N(N)> \qquad [24]$$

The first term has two electron operator between two N electron functions and the second term has one electron operator. Because of orthogonality of orbitals we know that all the matrix elements with more than two particle permutations will be zero in the first term and all the matrix elements with more than one particle permutation will be zero in the second term. This simplifies evaluation of [24] as the first term reduces to sum of one and two particle matrix elements and second term to sum of one particle matrix elements. Rewriting [24] as follows:

$$\therefore\ E_1 = \langle U_1(1)---U_N(N)|\sum_{i<j}\frac{1}{r_{ij}} - \sum_j V(j)|\sum_p(-1)^{\sigma_p} P(U_1(1)---U_N(N))\rangle \quad [25]$$

$$= \sum_{i<j}[\langle U_i(1)U_j(2)|\ \frac{1}{r_{ij}}\ |\sum_{p_j}(-1)^{\sigma_p} P_{12}\ U_i(1)U_j(2)\rangle]$$

$$- \sum_{i=1}^{N} \langle U_i(1)|V(1)|U_i(1)\rangle \quad [26]$$

The first term in expansion [26] is:

$$\sum_{i<j}[\langle U_i(1)U_j(2)|\frac{1}{r_{ij}}|U_i(1)U_j(2)\rangle - \langle U_i(1)U_j(2)|\frac{1}{r_{ij}}|U_i(2)U_j(1)\rangle]$$

These are simply differecnes of coulomb (direct) and exchange integrals. Denoting them by $(J_{ij} - K_{ij})$ we get first term of Equation [26] as $\sum_{i<j}[J_{ij} - K_{ij}]$. Now look at second term in Eqn. [26]. It can be expanded as follows:

$$\sum_{i=1}^{N} \int dX_1\ U_i^*(1)\ V(1)\ U_i(1).$$

$$= \sum_{i=1}^{N} \int dX_1\ U_i^*(1)\ [\sum_{j=1}^{N} \int \frac{dX_2\ U_j^*(2)\ \ (1 - P_{12})U_j(2)}{r_{12}}]U_i(1)$$

$$= \sum_{i=1}^{N}\sum_{j=1}^{N} \int dX_1 \int \frac{dX_2\ U_i^*(1)\ U_j^*(2)\ \ (1-P_{12})}{r_{12}}\ U_j(2)U_i(1)$$

$$= \sum_{i<j} \int dX_1 \int dX_2\ \frac{U_i^*(1)U_j^*(2)(1-P_{12})}{r_{12}}\ U_i(1)U_j(2) + \sum_{j<i} \int dX_1 \int dX_2$$

$$\frac{U_i^*(1)U_j^*(2)(1-P_{12})U_i(1)U_j(2)}{r_{12}}\ .$$ Any term with i=j is zero.

$$= \sum_{i<j}[\langle U_i(1)U_j(2)|\frac{1-P_{12}}{r_{12}}|U_i(1)U_j(2)\rangle + \langle U_j(2)U_i(1)|\frac{1-P_{12}}{r_{12}}|U_j(2)U_i(1)\rangle$$

$$= 2\sum_{i<j}[\langle U_i(1)U_j(2)|\frac{1-P_{12}}{r_{12}}|U_i(1)U_j(2)\rangle]$$

$$= 2\sum_{i<j}[\langle U_i(1)U_j(2)|\frac{1}{r_{12}}|U_i(1)U_j(2)\rangle - \langle U_i(1)U_j(2)|\frac{1}{r_{12}}|U_i(2)U_j(1)\rangle]$$

$$= 2\sum_{i<j}[J_{ij} - K_{ij}].$$

Putting all the terms together of Eqn. [26] we get

$$E_1 = \sum_{i<j}[(J_{ij}-K_{ij}) - \{(J_{ij}-K_{ij}) + (J_{ij}-K_{ij})\}]$$

$$E_1 = \sum_{i<j} - (J_{ij}-K_{ij}) \qquad [27]$$

Equations [5] and [16] combined together give

$$H - E_{HF} = (H_o + H_1) - (E_o + E_1)$$

$$= (H_o-E_o) + (H_1-E_1) \qquad [28]$$

$$= [\sum_{i=1}^{N} (h_i-\varepsilon_i)] + [\sum_{i<j}(\frac{1}{r_{ij}} + J_{ij} - K_{ij}) - \sum_{i=1}^{N} V_i] \qquad [29]$$

$$= \sum_{i=1}^{N} e_i + \sum_{i<j} m_{ij} \qquad [29A]$$

It is the second term in Eqn. [29A] that is responsible for correlation effects and is known as fluctuation potential (4). This can be expressed in two ways depending upon how V is chosen. For V given by [14], fluctuation potential will be defined by:

$$\sum_{i<j} m_{ij} = \sum_{i<j} (\frac{1}{r_{ij}} + J_{ij} - K_{ij}) - \sum_{i=1}^{N} \sum_{j=1}^{N} \bar{S}_j(i)$$

$$= \sum_{i<j} (\frac{1}{r_{ij}} + J_{ij} - K_{ij}) - \sum_{i=1}^{N} \sum_{j=1}^{N} (S_j(i) - R''_j(i))$$

$$= \sum_{i<j} (\frac{1}{r_{ij}} + J_{ij} - K_{ij}) - \sum_{i<j} (S_j(i)-R''_j(i)) - \sum_{j<i}(S_j(i) -$$

$$R''_j(i)) - \sum_{i=1}^{N}(S_i(i) - R''_i(i)) \qquad [30]$$

Collecting the terms Equation [30] can be written as:

$$\sum_{i<j} m_{ij} = \sum_{i<j}[(\frac{1}{r_{ij}} + J_{ij} - K_{ij}) - (S_j(i) - R''_j(i) - (S_i(j) - R''_i(j))$$

$$- \frac{1}{(N-1)} \{(S_i(i) - R''_i(i)) + (S_j(j) - R''_j(j))\}] \qquad [31]$$

This is the expression (9) for fluctuation potential that is responsible for electron correlation.

CHAPTER III

CONTIGURATION INTERACTION IN MULTIELECTRON ATOMS

The aim of this chapter may be summarized in brief, as that of finding eigenfunctions of a Hamiltonian of N electrons system. The Hamiltonian may be written as

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\frac{Ze^2}{r_i} + \sum_{1\leq i<j\leq N}\frac{e^2}{r_{ij}} \qquad [1]$$

where Z is nuclear charge and Hartree's atomic units have been used. There exist certain Hermitian operators which commute with one another and with the Hamiltonian described in [1]. These are L^2, S^2, L_z, S_z, Parity, etc. More explicitly

$$L^2 = L_x^{\ 2} + L_y^{\ 2} + L_z^{\ 2}$$

$$S^2 = S_x^{\ 2} + S_y^{\ 2} + S_z^{\ 2}$$

L_z and S_z are components of L and S operators on the Z-axis respectively. For a complex atom consisting of N electrons, $L_x = \sum_{i=1}^{N} L_{xi}$ and similarly L_y, L_z. Also $S_x = \sum_{i=1}^{N} S_{xi}$ and similarly S_y, S_z. These operators satisfy the following algebra:

$$[L_x, L^2] = [L_y, L^2] = [L_z, L^2] = 0 \qquad [2]$$

$$[H, S^2] = [H, L^2] = [H, L_z] = [H, S_z] = 0 \qquad [3]$$

$$[S_x, S^2] = [S_y, S^2] = [S_z, S^2] = 0 \qquad [4]$$

$$[L_x, L_y] = i\hbar L_z \ , \quad [L_y, L_z] = i\hbar L_x \ , \quad [L_z, L_x] = i\hbar L_y \qquad [5]$$

$$[S_x, S_y] = i\hbar S_z \ , \quad [S_y, S_z] = i\hbar S_x \ , \quad [S_z, S_x] = i\hbar S_y \qquad [5a]$$

Equation [2] through [4] are examples of operators which are said to commute. Eqn. [5] and [6] are example of operators which do not commute. The components of the total angular momentum L of any number of particles satisfy the same commutation relations as those of the angular momentum of a single particle (6).

Two commuting operators have many simultaneous eigenfunctions (6), in fact as many as, that they form a complete set. A 'complete set' will be defined little later. This means corresponding to Equation [3] we can find ψ_1, ψ_2, ψ_3 such that

$$H\psi_1 = E_1\psi_1 \ , \quad L^2\psi_1 = L_1(L_1+1)\psi_1 \ , \quad L_z\psi_1 = M_{L_1}\psi_1 \ , \quad S^2\psi_1 = S_1(S_1+1)\psi_1 \ , \quad S_z\psi_1 = M_{S_1}\psi_1$$

$$H\psi_2 = E_2\psi_2 \ , \quad L^2\psi_2 = L_2(L_2+1)\psi_2 \ , \quad L_z\psi_2 = M_{L_2}\psi_2 \ , \quad S^2\psi_2 = S_2(S_2+1)\psi_2 \ , \quad S_z\psi_2 = M_{S_2}\psi_2$$

$$H\psi_3 = E_3\psi_3 \ , \quad L^2\psi_3 = L_3(L_3+1)\psi_3 \ , \quad L_z\psi_3 = M_{L_3}\psi_3 \ , \quad S^2\psi_3 = S_3(S_3+1)\psi_3 \ , \quad S_z\psi_3 = M_{S_3}\psi_3$$

where all operators are N electron operators, ψ_1, ψ_2, ψ_3 are eigenfunctions of corresponding operators.

The operators L^2, L_z, S^2, S_z are known as symmetry operators.

They all commute with the Hamiltonian given by Eqn. [1] and they commute among themselves. Eigenfunctions of such a Hamiltonian are also eigenfunctions of the above mentioned symmetry operators.

As we know it is hard to calculate exact eigenfunctions of Hamiltonian, we must calculate approximate eigenfunctions of Hamiltonian, however, we will demand that these approximate eigenfunctions of Hamiltonian be exact eigenfunctions of the symmetry operators.

The problem here is to find a basis vectors or basis set of functions for the expansion of eigenfunctions of Hamiltonian. At this point we may define the basis vectors.

Definition: In an n dimensional subspace of Hilbert space any n vectors $\vec{U}_1$, $\vec{U}_2 \ldots \vec{U}_n$ are said to form a set of 'basis vector' or a complete set in that subspace if any vector $\vec{x}$ in that subspace is expressible as a linear combination of the vectors $\vec{U}_i$. Formation of basis vectors is not unique however any number of bases for this finite dimensional subspace have the same number of basis vectors viz n. For more detail a book in Linear Algebra (7) may be consulted. A more generalized form of the above treatment applies to entire Hilbert spaces. To expand an eigenfunction of one electron Hamiltonian one could choose complete set of one electron orbitals. For a many electron system one could consider complete set of determinants made up of antisymmetric products of these one electron orbitals. One could also choose a linear combination of these determinants with specified properties. These linear combinations will be called symmetry adapted unperturbed functions and will be explained later. The symmetry adapted basis or the determintal basis will be "complete" for N electron problem provided the basis for one electron problem was chosen to be 'complete'. Completeness of the basis set is necessary for the expansion of eigenfunction of Hamiltonian. The HF one electron spin orbitals are eigenfunctions of one electron Hamiltonian. They form a complete basis set for the expansion of any one electron-functions in one particle Hilbert space. For a multielectron system we have to choose a basis set in a different vector space viz N particle space for N particles problem. We can construct a set of functions spanning the N-particle space by taking all possible antisymmetrized products of one particle orbitals. One choice of basis functions in this N-particle space would be determinants made up of antisymmetric product of one electron HF spin orbitals. If we make an approximation that we have K basis functions in one particle space, we can form $\binom{K}{N} = \frac{K!}{N!(K-N)!}$ antisymmetric products of one particle orbitals to give $\binom{K}{N}$ determinants having N number of orbitals in each one of them. These determinants span a $\binom{K}{N}$ dimensional subspace of the entire N particle Hilbert Space. Therefore, we can now expand approximate eigenfunction of Hamiltonian in the set: $\{\Delta_i\}$ $i = 1,2,\ldots\ldots\ldots\binom{K}{N}$.

These determinants can always be made eigenfunctions of L_z and S_z i.e., they will have a fixed value of M_L and M_S.

The second choice of basis functions spanning the truncated N particle space is that formed by taking linear combinations of the above mentioned determinants such that linear combinations are eigenfunctions of symmetry operators L^2, S^2, L_z, S_z. In forming this basis, known as symmetry adapted, we shall take linear combination of determinants, all of which in any one linear combination belong to the same configuration, and have the same M_L and M_S value. This gives a basis in which the functions are symmetry adapted.

$\therefore$ $\phi_i = \sum_j b_{ij} \Delta_j$ where all the Δ's belong to same configuration and have a fixed M_L, M_S value in a particular linear combination. Therefore, a new basis set is: $\{\phi_i\} = i = 1,2,\ldots\binom{K}{N}$ provided the set Δ's was closed in the sense of description of Chapter I. The basis sets $\{\phi_i\}$ and $\{\Delta_i\}$ span the same $\binom{K}{N}$ dimensional space. Thus the choice of the basis function depends on the type of the problem one is dealing with. Changing the basis function from determinantal form to certain linear combinations of determinants is equivalent to rotation of a coordinate system in $\binom{K}{N}$ dimensional space.

One electron spin orbitals we will use are simple products of a spin function and an orbital function. They are assumed to be orthogonal to each other (orbital part and spin part, both). General form of a single particle orbital may look like as:

$$\Phi_{n\ell m_\ell m_s}(\bar{r},\sigma) = R_{n\ell}(r)\, Y_\ell^{m_\ell}(\theta,\varphi)\, \chi_{s,m_s}(\sigma) \qquad [6]$$

where n, ℓ, m_ℓ, m_s are the usual quantum numbers with

$n = 1, 2, \ldots$ an integer

$\ell = o, 1, 2, \ldots < n$

$m_\ell = \ell \ldots, -\ell$

$S = 1/2$

$m_s = \pm 1/2$

σ is spin variable of spin function space. $Y_\ell^{m_\ell}$ are usual normalized spherical harmonics. χ is the spin function of the spin orbital. The radial part $R_{n\ell}(r)$ is expanded in terms of Slater type orbitals as follows:

$$R_{n\ell}(r) = \sum_i A_{n\ell}(i)\, r^{I_{n\ell}(i)}\, e^{-\xi_{n\ell}(i)\, r} \qquad [7]$$

$A_{n\ell}$ are the expansion coefficients. $I_{n\ell}$ are integers indicating which STOs were considered in the basis when expanding. $\xi_{n\ell}$ are optimizing parameters chosen such as to give minimum energy of the state under consideration. The detail of method of obtaining the radial part is described in tables of atomic function (8). As an example consider Table 01-03 which describes on the top line 2p state of Boron from configuration $1s^2 2s^2 2p$. The radial part of 1s HF orbital in terms of STO is:

$$R_{10} = .92109\ r^o\ e^{-4.4661r} + .07847\ r^o\ e^{-7.85r} - .00036r\ e^{-.832r}$$

$$+ .00085r\ e^{-1.1565r} + .00002r\ e^{-1.91197r} + .01146r\ e^{-3.5213r}$$

where as the radial part of 2p HF orbital in terms of STO is

$$R_{21} = .54005r\ e^{-.8783r} + .38245r\ e^{-1.3543r} + .13208r\ e^{-2.2296}$$

$$+ .00957r\ e^{-5.37} \text{ and so on.}$$

Thus $A_{n\ell}$, $I_{n\ell}$, $\xi_{n\ell}$ are listed in the table for the expansion with STO's as the basis functions. Consider a two electron system.Hamiltonian for a two electron system can be written down as

$$H(1,2) = \frac{-\hbar^2}{2m}\sum_{i=1}^{2}\nabla_i^2 - \sum_{i=1}^{2}\frac{Ze^2}{r_i} + \frac{1}{r_{12}}$$

(Z = nuclear charge, Hartree's atomic units have been used). Suppose we want an exact eigenfunction of this Hamiltonian, with the help of configuration interaction for the configuration $1s^2$. The simplest possible configurations one can think of for a two electrons system are

$$1s^2,\ 1s2s,\ 2s^2,\ 2s2p,\ 2p^2,\ 1s2p$$

Using the rules of vector coupling model and Hund's rule for equivalent electrons one can find the different possible states that come out of these configurations

Configuration	Possible States
$1s^2$	^1S
$1s2s$	^1S, ^3S
$2s^2$	^1S

2s2p	${}^1P$, ${}^3P$,
$2p^2$	${}^1S$, ${}^3P$, ${}^1D$
1s2p	${}^1P$, ${}^3P$

In order to construct a wavefunction of a given symmetry (for example ${}^1S$) one has to consider the contribution from all configuration to the wavefunctions which give ${}^1S$ symmetry. Then an approximate wavefunction of a particular symmetry will be a linear combination of the symmetry adapted wavefunctions which have that symmetry present.

$$\therefore\ \Psi_{1s^2}^{{}^1S} = C_1\Phi_{1s^2}^{{}^1S} + C_2\Phi_{1s2s}^{{}^1S} + C_3\Phi_{2s^2}^{{}^1S} + C_4\Phi_{2p^2}^{{}^1S} \qquad [8]$$

(For given M_L and M_S, both are zero here)

This is an approximate eigenfunction because the expansion is in terms of a basis set which is finite in dimension. In other words it is a truncated basis expansion of an eigenfunction. There are as many approximate wavefunctions as are the number of basis set functions. Number of symmetry adapted basis function of a given symmetry coming from different configurations may be labeled as follows

$$\phi_i^{{}^1S} \quad i = 1,2,3, \ldots\ n_{{}^1S}$$

$$\phi_i^{{}^1P} \quad i = 1,2,3, \ldots\ n_{{}^1P}$$

and so on. i denotes the configurations. Thus in the above notation Eqn. [8] can be written as

$$\Psi_{1s^2}^{{}^1S} = \sum_{i=1}^{n_{{}^1S}} C_i\Phi_i^{{}^1S} \qquad [9]$$

The coefficient C_1 will have highest value in comparison to C_2, C_3, ... etc. This method of obtaining a wavefunction in terms of linear combination of another basis set of functions is called the method of configuration interaction. The method of obtaining the expansion coefficients whether a function is being expanded in terms of $\{\Delta_i\}$ or $\{\phi_i\}$ is exactly the same viz that of diagonalizing the Hamiltonian matrix. An example of obtaining symmetry adapted function from determinantal functions may be described here. Determinanal functions for p^2 configuration are given by Slater (5) as

$$\Delta_1 = (2P_+\beta \;\; 2P_-\alpha) \qquad \Delta_2 = (2P_+\alpha \;\; 2P_-\beta) \qquad \Delta_3 = (2P_0\beta \;\; 2P_0\alpha)$$

with $M_L = 0$ and $M_S = 0$. Symmetry adapted wavefunctions of symmetry ^3P, ^1D, ^1S can be formed using a linear combinations of the following determinants with $M_L = 0$ and $M_S = 0$

$$\phi^{^3P} = \frac{1}{\sqrt{2}}(\Delta_1 + \Delta_2)$$

$$\phi^{^1D} = \frac{1}{\sqrt{6}}(\Delta_1 - \Delta_2 + 2\Delta_3)$$

$$\phi^{^1S} = \frac{1}{\sqrt{3}}(\Delta_1 - \Delta_2 - \Delta_3)$$

These functions are in no way eigenfunctions of two particle Hamiltonian but are exact eigenfunctions of symmetry operators. Determinants as such have no symmetry property, but a linear combination can give a function which has a given symmetry. The coefficeints in front of the linear combinations are obtainable from group theory and symmetry properties or by using a projector operator to get a symmetric state. Expansion of eigenfunction in terms of $\{\phi_i\}$ and the advantage, will be discussed now. To begin with, we write the Hamiltonian matrix of the problem in ϕ basis. H_{ij} is a matrix element of the Hamiltonian matrix between symmetry adapted states ϕ_i and ϕ_j. The Hamiltonian matrix will now look like

$$\underset{\sim}{H} = \begin{bmatrix} \langle \phi_1 | H | \phi_1 \rangle & \langle \phi_1 | H | \phi_2 \rangle & \langle \phi_1 | H | \phi_3 \rangle & \cdots & \cdots & \langle \phi_1 | H | \phi_K \rangle \\ \langle \phi_2 | H | \phi_1 \rangle & \langle \phi_2 | H | \phi_2 \rangle & \langle \phi_2 | H | \phi_3 \rangle & \cdots & \cdots & \langle \phi_2 | H | \phi_K \rangle \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \langle \phi_K | H | \phi_1 \rangle & \cdots & \cdots & \cdots & \cdots & \langle \phi_K | H | \phi_K \rangle \end{bmatrix}$$

The Hamiltonian consists of one and two particles operators and ϕs are symmetry adapted functions; therefore, an element H_{ij} of the Hamiltonian matrix vanishes if any of the symmetry indicating quantum numbers (L, S, M_L, M_S) differ in ϕ_i and ϕ_j .

e.g

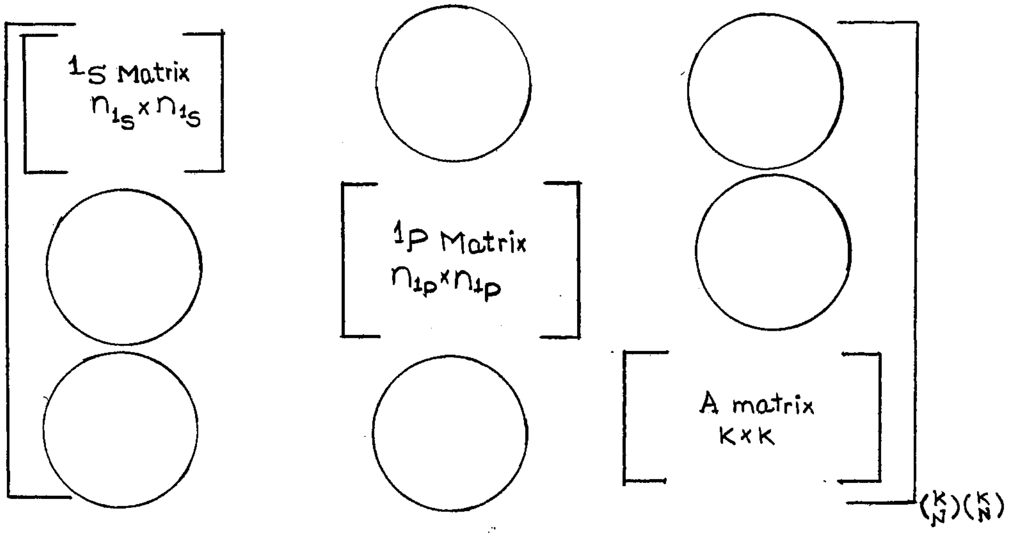
$$\langle \phi_i^{1S} | H | \phi_j^{3S} \rangle = 0 \quad , \quad i = 1 \text{-----} n_{1S} \; ; \; j = 1 \text{-----} n_{3S}$$

$$\langle \phi_i^{3S} | H | \phi_j^{3P} \rangle = 0 \quad , \quad i = 1 \text{-----} n_{3S} \; ; \; j = 1 \text{-----} n_{3P}$$

But,

$$\langle \phi_i^{1S} | H | \phi_j^{1S} \rangle \neq 0 \quad , \quad i, j = 1 \text{----------} n_{1S}$$

This means formation of Hamiltonian matrix in a symmetry adapted basis gives a number of off diagonal terms as zero to begin with. That is to say Hamiltonian matrix is obtained in a block diagonal form. It is much easier to diagonalize a matrix which is in block diagonal form than one which has all the off diagonal elements non zero. In the symmetry adapted basis it will look like



That is a number of off diagonal elements will be zero to begin with. Therefore, obviously it is advantageous to work in symmetry adapted unperturbed functions as basis functions. Once agreed on this, let us see how to obtain the CI coefficients in the expansion of ψ in terms of Φ. We had $\psi = \sum_{i=1}^{\binom{K}{N}} C_i \Phi_i$ in $\binom{K}{N}$ dimensional space. Expectation value of energy can be written down as

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$= \frac{\langle \sum_i c_i \phi_i | H | \sum_j c_j \phi_j \rangle}{\langle \sum_i c_i \phi_i | \sum_j c_j \phi_j \rangle}$$

$$= \frac{\sum_i \sum_j c_i^* c_j \langle \phi_i | H | \phi_j \rangle}{\sum_i \sum_j c_i^* c_j \langle \phi_i | \phi_j \rangle}$$

Φs form an orthonormal basis function.

$$\therefore E = \frac{\sum_{ij} c_i^* c_j \langle \phi_i | H | \phi_j \rangle}{\sum_{ij} c_i^* c_j \, \delta_{ij}}$$

$$\therefore\quad E\sum_{ij} C_i^* C_j \delta_{ij} = \sum_{ij} C_i^* C_j H_{ij}$$

or transfering the terms on one side we get

$$\sum_{ij} C_i^* C_j (\delta_{ij} E - H_{ij}) = 0$$

or

$$\sum_j \sum_i C_i^* (\delta_{ij} E - H_{ij}) C_j = 0$$

note here that C_i^* are arbitrary coefficients. For a fixed value of i we get

$$\sum_j C_i^* (\delta_{ij} E - H_{ij}) C_j = 0 \qquad i = 1, 2, \text{------} \binom{K}{N}$$

This gives a set of Eqns in which C_i^* or C_j could be used as a variational parameter to minimize energy. Considering C_i^* as the variational parameter differentiate each Eqn of the set by corresponding C_i^* we get

$$\sum_j (\delta_{ij} E - H_{ij}) C_j = 0$$

This is a set of $\binom{K}{N}$ homogeneous equations. The $\binom{K}{N}$ sets of C_j's and E's are to be determined simultaneously. Written out explicitly they have the form

$$\begin{array}{lllr}
(E-H_{11})C_1 + & H_{12}C_2 + H_{13}C_3 + & \text{----------} + H_{1\binom{K}{N}} C_{\binom{K}{N}} & = 0 \\
H_{21} C_1 + & (E-H_{22})C_2 + & \text{------------} + H_{2\binom{K}{N}} C_{\binom{K}{N}} & = 0 \\
| & | & & = 0 \\
| & | & & = 0 \\
| & | & & = 0 \\
H_{\binom{K}{N}1}C_1 + & H_{\binom{K}{N}2}C_2 + & \text{----------} + (E - H_{\binom{K}{N}\binom{K}{N}})C_{\binom{K}{N}} & = 0
\end{array}$$

This set of Eqn. has a solution $C_j = 0$, $j = 1, \text{--} \binom{K}{N}$ which is trivial. Neglecting that, these also have a solution when determinant of coefficients of Cs equals zero. In other words when $\det\left|\sum_{j} \delta_{ij} E - H_{ij}\right| = 0$ $i = 1,2 \ldots$ More explicitly,

$$\begin{vmatrix} (E-H_{11}) & H_{12} & H_{13} & — & — & — & H_{1\binom{K}{N}} \\ H_{21} & (E-H_{22}) & H_{23} & — & — & — & H_{2\binom{K}{N}} \\ — & — & — & — & — & — & — \\ — & — & — & — & — & — & — \\ H_{\binom{K}{N}1} & H_{\binom{K}{N}2} & H_{\binom{K}{N}3} & - & - & - & (E-H_{\binom{K}{N}\binom{K}{N}}) \end{vmatrix} = 0 \qquad [10]$$

In this determinant everything is known except E. Solving the equation (known as secular equation) we come out with $\binom{K}{N}$ solutions as the determinant on expansion, will give a polynomial of the $\binom{K}{N}^{th}$ degree in E therefore has $\binom{K}{N}$ roots. Label them as E_o, E_1, E_2, ... $E_{\binom{K}{N}-1}$ in ascending order of magnitude. The lowest energy E_o is an upperbound to lowest energy obtained from an infinite CI expansion for the wavefunction which would have been an exact wavefunction. Substitute the lowest energy viz E_o in the $\binom{K}{N}$ set of Equations [10], we are left with $\binom{K}{N}$ equations and $\binom{K}{N}$ unknowns. Solve these equations simultaneously to get C_js the CI expansioncoefficients. Associate them with the corresponding ϕ to get ψ. This was the method of expansion of approximate eigenfunction of Hamiltonian in the $\{\phi_i\}$ basis. One could also set up the Hamiltonian matrix on exactly the same lines as described above, in the determinantal basis.

Use of determinantal basis for expansion of approximate eigenfunction of Hamiltonian of appropriate symmetry requires that the set $\{\Delta_i\}$ be closed in the sense of description of Chapter I. If we do not have a closed set of determinants then we first form an approximate eigenfunction of Hamiltonian and project out the appropriate symmetry using a projection operator. This is the approach used in this work.

MET calculations ((1); note 26) gives determinants which have one and two particle excitation from HF sea. These determinants do not necessarily form a closed set. Therefore, an approximate eigenfunction is obtained from this non closed set of determinants and then a projection operator is operated on this function to get a symmetric, approximate eigenfunction of Hamiltonian or a pure eigenstate.

CHAPTER IV

CORRELATION EFFECTS IN CLOSED AND OPEN SHELLS

Closed Shell System

A subshell will be said to be closed if all of the available orbitals in it are occupied by electrons. That is to say if M orbitals are available in a subshell and if it is a P particle problem, then the subshell will be closed if P = M.

A closed shell system is comparatively easy as far as description of correlation function is concerned. This is mainly because, according to many electron theory (MET) descriptions (1), only external correlations occur in a closed shell. Generally speaking one and more particles can be virtually excited from HF Sea to orbitals outside the HF Sea. However, dominant contributions come from pair excitations and unlinked clusters of pair excitations.

This and other details will be explained in the chapter as we proceed. Therefore, external correlations predominatly consist of virtual excitations of even number of electrons outside HF Sea. The external correlations in closed shells are said to be dynamical, as they depend upon fluctuation potential.

In the last chapter the method of finding an approximate eigen function of Hamiltonian using a configuration interaction method was discussed. In this chapter we will show that such a wavefunction can also be written in terms of electron correlation functions. The coefficients in the expansion of the correlation functions may be determined by comparing the wavefunction with that obtained from CI, or by comparing the wavefunction with the expansion of the wavefunction in terms of perturbation theory.

A word regarding HF Sea is in order. It is the minimal set of symmetry orbitals that are necessary to construct a set of N particle basis functions for one or more irreducible representations of the symmetry group of the Hamiltonian. Minimal set refers to the set of minimum orbitals that must be included to close the irreducible representation arising from a particular configuration. For Be with configuration $1s^2\ 2s^2$ the minimum orbitals needed to construct HF Sea are four viz ($1s\alpha$ $1s\beta$ $2s\alpha$ $2s\beta$). One could include other orbitals in this, but they are not needed.

Consider another example; that of a carbon atom in the ground state configuration $1s^2 2s^2 2p^2$. One needs a complete set of 6 particle, basis functions constructed from the set of orbitals[1] ($1s\alpha$, $1s\beta$, $2s\alpha$, $2s\beta$, $2p_-\alpha$, $2p_-\beta$, $2p_o\alpha$, $2p_o\beta$, $2p_+\alpha$, $2p_+\beta$).

Therefore, a set of the 10 orbitals given above forms HF sea for C atom. Consider the ground state of the Be atom for a closed shell.

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[1] In the above and the discussion to follow we put the orbital labels in one to one correspondence with integers.

1 - $1s\alpha$
2 - $1s\beta$
3 - $2s\alpha$
4 - $2s\beta$
5 - $2p_-\alpha$
6 - $2p_-\beta$
7 - $2p_o\alpha$
8 - $2p_o\beta$
9 - $2p_+\alpha$
10 - $2p_+\beta$

Ground state configuration can be written as $1s^2 2s^2$ with the term symbol ^1S. The HF determinant is

$$\Phi_0 = (1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta) = \Delta_0 = \Delta_{1234}$$

An exact wavefunction of ^1S symmetry for the ground state of Be atom in terms of CI would be

$$\psi^{^1S} = \Phi_0 + \tilde{C}_1 \Phi_1 + \tilde{C}_2 \Phi_2 + ---------- \qquad [1]$$

Φ_0 is the HF function and Φ_1, Φ_2, Φ_3, Φ_4, etc., are the symmetry adapted functions which have ^1S symmetry but arise from different configurations of four electrons. The different configurations come from one, two, three, etc., particles' excitations from HF sea to orbitals outside the sea. Symmetry adapted functions from all such configurations will have to be considered in expansion [1]. The Φ's in Equation [1] are linear combinations of Slater determinants. We can collect all the determinants in the expansion [1] which come from one particle excitation, two particle excitation, three particle excitation, etc., and correspondingly label the coefficients. Then, the CI expansion [1] can be written as sum over infinite virtual orbitals, i.e.,

$$\psi^{^1S} = \Delta_0 + C_1 \Delta_1 + C_2 \Delta_2 + ----------$$

or

$$\psi^{^1S} = \Delta_0 + \sum_{i=5}^{\infty} C_{i234} A_4 (\varphi_i(1)\varphi_2(2)\varphi_3(3)\varphi_4(4)) + ----\binom{4}{1}$$

Other terms of this kind $$+ \sum_{5\leqslant i<j}^{\infty} C_{ij34} A_4 (\varphi_i(1)\varphi_j(2)\varphi_3(3)\varphi_4(4)) + ----\binom{4}{2}$$

Other terms of this kind $$+ \sum_{5\leqslant i<j<k}^{\infty} C_{ijk4} A_4 (\varphi_i(1)\varphi_j(2)\varphi_k(3)\varphi_4(4)) + -\binom{4}{3}$$

Other terms of this kind $$+ \sum_{5\leqslant i<j}^{\infty} C_{ijkl} A_4 (\varphi_i(1)\varphi_j(2)\varphi_k(3)\varphi_l(4)) \qquad [2]$$

There are 4 infinite sums of the kind of the second term, $\binom{4}{2}$ infinite sums of the kind of the third term. $\binom{4}{3}$ of that of the fourth term and so on in the expansion [2]. Here $N_{c_n} = \binom{N}{n} = \frac{N!}{n!\cdot(N-n)!}\cdot A_4$ antisymmetrizes the product of four orbitals in the paranthesis. Henceforth, A_4 will be called simply an antisymmetrizer. In terms of correlation corrections, the approximate wavefunction can be written as (4)(1):

$$\Psi = \Phi_0 + \chi \quad \text{with} \quad \langle \Phi_0 | \chi \rangle = 0 \quad , \quad \langle \Phi_0 | \Phi_0 \rangle = 1 \qquad [3]$$

For a four particle system χ will be given by:

$$\chi = \sum_{i=1}^{4} \{\hat{f}_i\} + \sum_{1\leq i<j\leq 4} \{\hat{U}'_{ij}\} + \sum_{1\leq i<j<k\leq 4} \{\hat{U}'_{ijk}\} + \{\hat{U}'_{1234}\} \qquad [4]$$

Where $\{\hat{f}_i\}$, $\{\hat{U}'_{ij}\}$, $\{\hat{U}'_{ijk}\}$ are one, two, three electron correlation parts and $\{\hat{U}'_{1234}\}$ is the correlation part in which all of the four particles are virtually excited. More explicitly, the correlation functions appear as follows:

$$\{\hat{f}_i\} = A_4 \left\{ (\varphi_1 \varphi_2 \varphi_3 \varphi_4) \frac{f_i(x_i)}{i} \right\} \qquad [5]$$

This is a symbolic notation indicating that the ith orbital $(i = 1,2,3,4)$ is virtually excited to orbitals outside the HF sea and is replaced by $f_i(x_i)$, a one particle function. As an example, look at $\{\hat{f}_1\}$ and $\{\hat{f}_2\}$

$$\{\hat{f}_1\} = \frac{A_4}{\sqrt{1!}} \left\{ \left(\varphi_{1s\beta}^{(2)} \varphi_{2s\alpha}^{(3)} \varphi_{2s\beta}^{(4)} \right) f_{1s\alpha}^{(x_1)} \right\} = \{\hat{f}_{1s\alpha}\} \qquad [6]$$

$$\{\hat{f}_2\} = \frac{A_4}{\sqrt{1!}} \left\{ \left(\varphi_{1s\alpha}^{(1)} \varphi_{2s\alpha}^{(3)} \varphi_{2s\beta}^{(4)} \right) f_{1s\beta}^{(x_2)} \right\} = \{\hat{f}_{1s\beta}\} \qquad [7]$$

and so on. Thus, $\{\hat{f}_i\}$ are four particle functions, where as f_i are one particle functions. The two particle correlation function looks like:

$$\{\hat{U}'_{ij}\} = \frac{A_4}{\sqrt{2!}} \left[(\varphi_1 \varphi_2 \varphi_3 \varphi_4) \; \frac{U_{ij}(x_i x_j)}{ij} \right] \qquad [8]$$

This is again in terms of a very symbolic notation, meaning that two orbitals, i and j, are missing. Symbolically denoted by division by ij and U_{ij}, a two particle function, replaces them, so that the quantity inside the large rectangular bracket is again a function of 4 particles.

As an example look at $\{\hat{U}'_{12}\}$:

$$\{\hat{U}'_{12}\} = \{\hat{U}'_{1s\alpha\,1s\beta}\} = \frac{A_4}{\sqrt{2!}} \; \{\varphi^{(3)}_{2s\alpha}\, \varphi^{(4)}_{2s\beta}\, U^{(x_1,x_2)}_{1s\alpha\,1s\beta}\} \qquad [9]$$

Thus, electron correlation discussion is one way of interpreting the CI terms. The correlation functions can be related to the coefficients in CI expansion as follows. Let us, for example, express a one particle correlation function in terms of CI. Comparing [6] to the second term of expansion [2] we get

$$\{\hat{f}_1\} = \sum_{i=5}^{\infty} C_{i234}\, A_4 \left(\varphi_i(1)\varphi_2(2)\varphi_3(3)\varphi_4(4)\right) \qquad [10]$$

$$= A_4 \left[\left(\sum_{i=5}^{\infty} C_{i234}\, \varphi_i(1)\right) \varphi_2(2)\varphi_3(3)\varphi_4(4) \right] \qquad [11]$$

The quantity $\sum_{i=5}^{\infty} C_{i234}\varphi_i(1)$ is expression for one particle function f_1. To express two electron correlation functions in terms of CI, equate the third term of [2] to [8] so that

$$\{\hat{U}'_{12}\} = \sum_{5\leq i<j}^{\infty} C_{ij34}\, A_4 \left[\varphi_i(1)\varphi_j(2)\varphi_3(3)\varphi_4(4)\right]$$

$$= A_4 \left[\left(\sum_{5\leq i<j}^{\infty} C_{ij34}\,\varphi_i(1)\varphi_j(2)\right)\varphi_3(3)\varphi_4(4)\right] \qquad [12]$$

Let us expand the two particle function U_{12} appearing in [9] in terms of virtual orbitals:

$$U_{12}(x_1,x_2) = A_2\left[\sum_{5\leq i<j}^{\infty} d_{ij34}\,\varphi_i(1)\varphi_j(2)\right] \qquad [13]$$

and substitute this in Eqn. [9]

$$\therefore\ \{\hat{U}'_{12}\} = \frac{A_4}{\sqrt{2!}}\left[A_2\left(\sum_{5\leq i<j} d_{ij34}\,\varphi_i(1)\varphi_j(2)\right)\varphi_3(3)\varphi_4(4)\right] \qquad [14]$$

where

$$A_4 = \frac{1}{\sqrt{4!}}\sum_{P}(-1)^{\sigma_P} P \qquad [15]$$

$$A_2 = \frac{1}{\sqrt{2!}}\sum_{P}(-1)^{\sigma_P} P \qquad [16]$$

σ_p = number of permutation

$$A_4 A_2 = \frac{1}{\sqrt{4!\,2!}}\sum_{P}(-1)^{\sigma_P} P\,(1-P_{12}) \qquad [17]$$

P are all possible four particle permutations and P_{12} is particle 1 and 2 permutation. $\sum_p(-1)^{\sigma_p} P$ is the sum of the identity plus 2, 3 and 4 particle permutation. The group of elements A_2 are contained in the group of elements A_4. When multiplied, we get the elements of group A_4. In general,

$$A_N A_n = \sqrt{n!}\, A_N \qquad n \leq N \tag{18}$$

$$\therefore \quad A_4 A_2 = \sqrt{2!}\, A_4$$

$$\therefore \quad \{\hat{U}'_{12}\} = \sqrt{2!}\, \frac{A_4}{\sqrt{2!}} \left[\left(\sum_{5 \leq i < j}^{\infty} d_{ij34}\, \varphi_i(1) \varphi_j(2) \right) \varphi_3(3) \varphi_4(4) \right] \tag{19}$$

Comparing [12] and [19] we get

$$c_{ij34} = d_{ij34} \tag{20}$$

Therefore, writing a wavefunction in terms of MET functions is equivalent to summing CI expansion, and the coefficients of expansion of MET functions are CI expansion coefficients. A similar case can be discussed when three or more excitations are considered.

The importance of the pair correlation becomes clear when one tries to obtain the expansion coefficients in terms of first order perturbation theory. From the first order non-degenerate perturbation theory we know (10) that:

$$\psi = \Phi_0 + \sum_k{}' \frac{V_{km}}{\epsilon_k - \epsilon_m} |\Delta_k\rangle \tag{21}$$

where V is perturbation part of the four particle Hamiltonian and m = 0 for ground state. The prime denotes that k = m term is to be omitted in the series expansion of ψ in terms of the linear combination of unperturbed wavefunction. Thus, now one to one correspondence can be made between first order CI coefficients and the first order perturbation theory coefficients. A general expansion coefficient in [21] may look like:

$$C^{(1)}_{j_1 j_2 j_3 j_4} = \frac{\langle \Delta_{j_1 j_2 j_3 j_4} | V | \Delta_{1234} \rangle}{(\epsilon_{j_1} + \epsilon_{j_2} + \epsilon_{j_5} + \epsilon_{j_4}) - (\epsilon_1 + \epsilon_2 + \epsilon_3 + \epsilon_4)} \tag{22}$$

where ε's are eigenvalues of one electron Hamiltonian $h_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + V_i$. Therefore, ε's are the orbital energies. Superscript 1 on $C^{(1)}_{j1j2j3j4}$ indicates that it is a first order perturbation theory coefficient, as [21] is expansion of wavefunction in accordance with first order perturbation theory. In fact, if one wants to be rigorous at this stage, he will note that a coefficient in CI expansion can be expended as:

$$C_{j_1j_2j_3j_4} = C^{(1)}_{j_1j_2j_3j_4} + C^{(2)}_{j_1j_2j_3j_4} + C^{(3)}_{j_1j_2j_3j_4} + \text{--------} \qquad [23]$$

where subscripts 1, 2, 3, etc. on C indicate that they are first, second, etc., order perturbation theory contributions to C. Similarly, the correlation functions will have sums coming from different order corrections, that is to say

$$\chi = \chi^{(1)} + \chi^{(2)} + \chi^{(3)} + \text{---------} \qquad [24]$$

where $$\chi^{(1)} = \sum_{i=1}^{4} \{f_i\}^{(1)} + \sum_{1\leq i<j\leq 4} \{U_{ij}\}^{(1)} + \text{------}$$

and similarly $\chi^{(2)}$, $\chi^{(3)}$ ... etc.

Let us look at the general matrix element [22] when one particle excitations take place from HF sea. In the first order perturbation theory, for one particle excitation the CI coefficient, for example is

$$C^{(1)}_{j_1 1s\beta 2s\alpha 2s\beta} = \frac{\langle \Delta_{j_1 1s\beta 2s\alpha 2s\beta} | V | \Delta_{1234} \rangle}{(\epsilon_{j_1} - \epsilon_1)} \qquad [25]$$

where Φ_{1234} is the function denoting the HF determinant for Be viz $A_4(1s\alpha \;\; 1s\beta \;\; 2s\alpha \;\; 2s\beta)$. j_1 denotes the orbital to which an electron has been virtually excited outside the HF sea from 1sα. The matrix elements on the R·H·S of [25] have determinants which differ from each other in one orbital. One particle excitation orbitals try to correct the occupied orbitals, but according to Brillouin's theorem if we have HF orbitals (which is the case here) these matrix elements vanish.

Next, look at the general matrix element [22] when three or more particle excitations take place from HF sea. In this case the matrix elements [22] have determinants which differ from each other in three or more orbitals. Note here that V is made up of one and two particle operators and the orbitals we are working with are orthonormal. Orthonormality of the orbitals implies that a matrix element in which two determinants differ by three or more orbitals on the two sides of V, vanishes. Thus in the first order perturbation theory for the electron correlation corrections, we are left with pair correlation terms only.

$$\therefore\ \chi^{(1)} = \sum_{5\leq j_1<j_2} \frac{\langle \Delta_{j_1 j_2 3 4}|V|\Delta_{1234}\rangle}{[(\epsilon_{j_1}+\epsilon_{j_2})-(\epsilon_1+\epsilon_2)]}|\Delta_{j_1 j_2 3 4}\rangle + \text{-------} \qquad [26]$$

totally there will be $\binom{4}{2}$ such terms in first order $\chi^{(1)}$ series.

In this method of series expansion, second and higher order perturbation theory corrections are not included. As we go to higher order perturbation theory one and three particle correlation corrections are small. Sinanoğlu (4) has shown that main contribution to four particle correlation correction comes from unlinked products of two particle correlation. At this point unlinked clusters may be described briefly.

Unlinked Clusters

After the above treatment a natural question arises is that do we necessarily have to consider more than two particles virtually excited in the original determinant? The answer to this is yes and so one describes many particle collision in terms of Unlinked Clusters (4). A four particle correlation function may be looked upon as four particle collision. This includes all four particles colliding at the same time, two binary collision, three at a time, etc. That is to say actual many electron collisions are linked clusters and products of independent but simultaneous collisions. These in terms, can be looked upon predominantly as Unlinked Clusters of pair collisions. Pair collisions are the most important ones in correlation theory, as the fluctuation potential is a two particle function which causes electron correlation.

Two, three, four particle collisions can be represented as sum of one, two, three and four particle collisions taking place at a time.

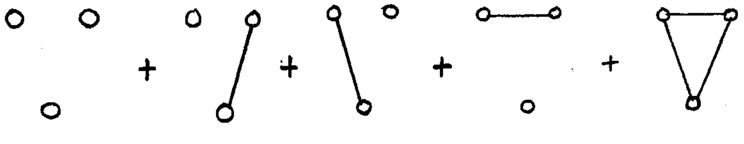
In Sinanoğlu's (4) notations let small circles with no lines attached to them, represent $\hat{f}_i$'s, the one electron function. The linked clusters will be denoted by $\hat{U}$'s by straight lines drawn between the linked particles.

$\hat{U}'_{ij}$ = two electron correlation function

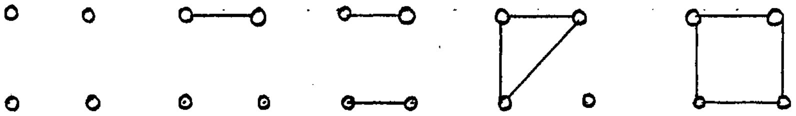
$$= A_2(\hat{f}_i\,\hat{f}_j) + \hat{U}_{ij}$$

$\hat{U}'_{ijk}$ = 3 particle correlation function

$$= A_3\left[\hat{f}_i\hat{f}_j\hat{f}_k + \hat{f}_i\frac{U_{jk}}{\sqrt{2!}} + \frac{\hat{U}_{ik}}{\sqrt{2!}}\hat{f}_j + \frac{U_{ij}}{\sqrt{2!}}\hat{f}_k\right] + \hat{U}_{ijk}$$



and similarly $\hat{U}'_{ijkl}$ will have the following diagram:



This is the simplest possible treatment of many particle excitation and will not be dealt with in any further detail. The most important point is that many particle excitation can be broken down into products of unlinked clusters of two particle excitation terms and the treatment can be given on the basis of closed shell theory.

Open Shell System

Open shell has more correlations coming because of presence of electrons outside the closed shell. The correlations that arise in open shell may be classified as

1) Internal Correlation
2) Semi-internal Correlation → Non dynamical = χ_F
3) One particle all external correlations
4) All external (two and more particles) → dynamical = χ_U

The non-dynamical correlations are characteristic of open shells only while dynamical occur in both open and closed shells (1)(3). The non-dynamical correlation corrections can be expanded in terms of a finite CI expansion.

These are described by (a) wavefunctions which have two orbitals[1] excited to previously unoccupied orbitals in the HF sea. Let a circle denote a HF sea. The shaded half-circle denote the orbitals occupied

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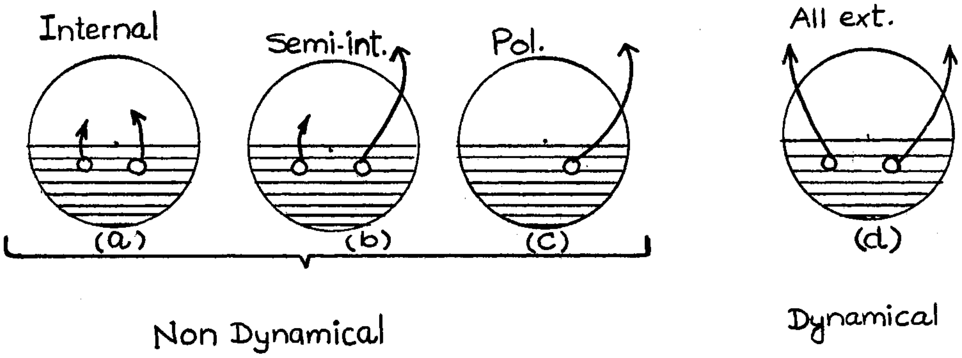
[1] Two particle excitation are the most important.

in the sea.



Picture (a) denotes virtual excitation of two orbitals within the sea. Such terms give rise to internal correlation. (b) Excitations involving one particle being expelled outside the sea and another being virtually excited to an orbital previously unoccupied in the sea gives rise to semi-internal correlation. This is shown in picture (b). (c) When one particle is excited to orbitals outside HF sea, this gives terms which give rise to polarization effect, as shown in picture (c) and finally (d) Two particle excitation of orbitals to orbitals outside HF sea gives terms which cause all external correlations. A wavefunction for an open shell can be written as

$$\psi = \Phi_o + \tilde{\chi} \qquad [28]$$

where $\tilde{\chi} = \tilde{\chi}_{\text{internal}} + \tilde{\chi}_{\text{semi-internal}} + \tilde{\chi}_{\text{polarization}} + \tilde{\chi}_{\text{all external}}$ [29]

How different correlation terms arise from scrambling of orbitals is described below. For this discussion consider carbon atom with its ground state configuration $1s^2$, $2s^2$, $2p^2$. There are 6 electrons in the atom and 10 orbitals available for them. The HF sea consists of the orbitals [$1s\alpha$, $1s\beta$, $2s\alpha$, $2s\beta$, $2p_-\alpha$, $2p_-\beta$, $2p_o\alpha$, $2p_o\beta$, $2p_+\alpha$, $2p_+\beta$]. Exact wavefunction for carbon of a given symmetry can be written as

$$\Psi = C_0 \Phi_0 + C_1 \Phi_1 + C_2 \Phi_2 + ------ \qquad [30]$$

Where Φs are symmetry adapted unperturbed wavefunctions. Φ_0 is HF part of the entire wavefunction. Equation [30] can be written in terms of a model operator (11)

$$\Psi = \Omega \Phi_0 \qquad [31]$$

with

$$\phi_0 = \sum_{k=1}^{\alpha} C_k \Delta_k \qquad [32]$$

where α is the number of determinants needed from the set of $\binom{10}{6}$ determinants to form RHF state. The sum is over (α) determinats for carbon atom.

$$\therefore \ \Psi = \Omega \sum_{K=1}^{\alpha} C_K \Delta_K = \sum_{K=1}^{\alpha} C_K (\Omega \Delta_K) \qquad [33]$$

The model operator operates on linear combination of determinants to give another series of determinants. The problem is that Ω is not uniquely defined by Equation [31], there could be several other operator which would give ψ from ϕ_s. Consider one such operator on a particular determinant

$$\Omega \Delta_k = \sum_{l_1<l_2<N} d_{l_1 l_2 \ldots l_N} \Delta_{l_1 l_2 \ldots l_N} \qquad [34]$$

the result is a linear combination of determinants with scrambled orbitals. In the resulting determinants some orbitals will be in the sea which were unoccupied in Δ_k and some will not be in the sea. This is where the classification of correlation terms comes in.

Suppose Ω operates on one of the carbon determinants to give the following linear combination

$$\Omega\, \Delta\, (1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ 2p_0\alpha\ 2p_0\beta) = a(1s\alpha\ 1s\beta\ 2p_-\beta\ 2p_0\alpha\ 2p_0\beta\ 3p_+\alpha)$$

$$+\, b(1s\alpha\ 1s\beta\ 2p_0\alpha\ 2p_0\beta\ 4s\alpha\ 5s\beta) + c(1s\alpha\ 1s\beta\ 2s\beta\ 2p_0\alpha\ 2p_0\beta\ 3s\alpha)$$

$$+\, d(1s\alpha\ 1s\beta\ 2p_0\alpha\ 2p_0\beta\ 2p_+\alpha\ 2p_-\beta) + e(- - - - - -) +$$

$$f(- - - - - -) + - - - - - - \qquad [35]$$

In Equation [35] the determinant with coefficient a is an example of semi-internal correlation. $2s\alpha$ and $2s\beta$ in the original determinant are excited to orbitals $2p_-\beta$ and $3p_+\alpha$. $2p_-\beta$ is in the HF sea but $3p_+\alpha$ is outside the sea. Therefore it is a semi-internal correlation term. The determinant with coefficient b is an example of all external correlation terms. Here $2s\alpha$, $2s\beta$ in the original determinant go to $4s\alpha$, $5s\beta$ both are outside the sea. The determinant with coefficient c is an example of one particle all external correlation term. $2s\alpha$ from the original determinant goes to $3s\alpha$, an orbital outside sea. Electrons in other orbitals are not altered. Finally in the determinant with coefficient d two particles are in the orbitals $2p_+\alpha$, and $2p_+\beta$ one in each. These come from $2s\alpha$, $2s\beta$ being excited in the original determinants to orbitals inside the HF sea. This is an example of internal correlations. Present work neglects the dynamical correlations. The non-dynamical correlations can be expressed in terms of a finite CI, this is precisely done here. Inclusion of non-dynamical terms is important in calculation of transition probabilities.

CHAPTER V

PROJECTOR OPERATOR TECHNIQUE

Any operator P with the following properties

$$\text{i)}\quad P = P^{\dagger} \text{ (Hermitian Conjugate)} \qquad [1a]$$

$$\text{ii)}\quad P^2 = P \text{ (Idempotent)} \qquad [1b]$$

is a projector operator (12).

This means if p is eigenvalue of P with $|u>$ as its eigenvector, then

$$\begin{aligned}(P^2 - P)|u> &= (p^2 - p)|u> \qquad [2]\\ &= 0 \quad \text{from [1b]}\end{aligned}$$

Since $|u> \neq 0$, $p^2 - p = 0$

or

$$\begin{aligned}p(p - 1) &= 0\\ p = 0 \text{ or } p &= 1 \qquad [3]\end{aligned}$$

Therefore P has eigenvalues 0 or 1. Eigenvalue 0 corresponds to an eigenvector which is completely annihilated when operated on by P and eigenvalue 1 corresponds to an eigenvector which is left as it was originally when operated on by P. The vector resulting from the action of projector operator on a given vector lies in a subspace of Hibert Space. This subspace is characterized by the projection operator. Geometrically speaking this is orthogonal projection of an arbitrary vector onto a subspace.

A projection operator on a particular symmetric subspace, when it operates on a function of no symmetry, gives out that part of the function which has definite symmetry or annihilates the function completely if it did not have the symmetry we are looking for. By using projector operator technique, we can now obtain pure state functions which are useful in calculating transition probabilities.

Construction of projection operator is based on a simple idea that only that part of the function be projected out which has the required symmetry and the rest of it be annihilated. For example, angular-momentum projection operator onto the subspace of eigenvectors of $\hat{L}^2$ with the eigenvalue L(L + 1) may be constructed as follows: Consider a wavefunction ψ which is an eigenfunction of $\hat{L}^2$ so that

$$\hat{L}^2\psi_L = L(L+1)\psi_L \tag{4}$$

$$\therefore \ [\hat{L}^2 - L(L+1)]\ \psi_L = 0 \tag{5}$$

The operator in the square bracket annihilates a wavefunction with orbital angular momentum quantum number L. When a wavefunction is a linear combination of several terms of various symmetries, we have to consider several factors of the form [5] so that all terms with different L values except one with the required L can be annihilated one after another as the factors in the operator, operate on different parts of functions.

In other words, if

$$\prod_j [\hat{L}^2 - L_j\ (L_j + 1)]\ \psi = 0$$

and we desire to produce a wavefunction with quantum number L_i we have to operate on the wavefunction with an operator

$$\prod_{j\neq i} \frac{[\hat{L}^2 - L_j(L_j + 1)]}{[L_i(L_i + 1) - L_j(L_j + 1)]}$$

i.e., product of factors containing all L_js except $L_j = L_i$. The factor in the denominator makes the operator idempotent. The result of the operation gives either zero or an eigenfunction of $\hat{L}^2$ with eigenvalue $L_i(L_i + 1)$.

On the same lines, a projector operator for $\hat{L}_z$ with an eigenvalue M_{L_i} would be

$$\prod_{j\neq i} \frac{[\hat{L}_z - M_{L_j}]}{(M_{L_i} - M_{L_j})} \qquad [6]$$

which is again a product of factors.

Löwdin has defined the projector operators for $\hat{L}^2$ and $\hat{L}_z$ as follows (2).

$$O_K(\hat{L}^2) = \prod_{\ell\neq K} \frac{[\hat{L}^2 - \ell(\ell + 1)]}{K(K + 1) - \ell(\ell + 1)} \qquad [7]$$

$$O_{M_L}(\hat{L}_z) = \prod_{\mu\neq M_L} \frac{[\hat{L}_z - \mu]}{M_L - \mu} \qquad [8]$$

Equation [7] can also be written as

$$O_K(\hat{L}^2) = \prod_{\ell\neq K} [1 - \frac{\hat{L}^2 - K(K + 1)}{(\ell - K)(\ell + K + 1)}] \qquad [9]$$

The values of ℓ are determined by using the addition theorem of angular momentum. Thus ℓ goes from $\ell = M_L$ to $\ell = K_{max}$ (determined from addition theorem). Let $K_{max} - M_L = n$ and in Eqn. [7] replace ℓ by $\ell + M_L$, then

$$O_K(\hat{L}^2) = \prod_{\ell=o,n}^{\ell\neq K-M_L} \frac{\hat{L}^2 - (\ell + M_L)(\ell + M_L + 1)}{K(K+1) - (\ell + M_L)(\ell + M_L + 1)} \qquad [10]$$

As suggested by Löwdin Eqn. [10] is most convenient form of angular momentum projection operator for practical purposes and a computer program has been written for the same. On exactly the same lines, one could treat $\hat{S}^2$ and $\hat{S}_z$ operators. This is mainly because, as we know, angular momentum and spin momentum operators have similar properties. The same computer program can project out wavefunctions which are eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ as well as $\hat{S}^2$ and $\hat{S}_z$.

A brief description of program written for Löwdin's projector operator is in order. The program consists of four subroutines apart from main program. A given wavefunction is fed in as a linear combination of determinants with their proper coefficients.

In writing the algorithm for the computer code we have introduced two new definitions of "subshells". In the orbital angular momentum projection, spin orbitals having the same n, ℓ and m_s are classified in the same "subshell". While in the spin projection, spin orbitals having the same n, ℓ and m_ℓ are classified in the same "subshell". Clearly what we term a "subshell" and the "occupation of a subshell" depends on which projection, spin or orbital angular momentum we are considering. With the unorthodox definition of subshell we also introduce a new designation of the word "configuration" based on our redefinition of subshells. For example, consider a set of orbitals $1s\alpha$ $1s\beta$ $2s\alpha$ $2s\beta$ $2p_o\alpha$ $2p_o\beta$ $2p_-\alpha$ $2p_-\beta$ $2p_+\alpha$ $2p_+\beta$. Form the following three determinants from these orbitals.

1: $(1s\alpha\ 2s\beta\ 2p_-\alpha\ 2p_o\beta\ 2p_+\alpha)$

2: $(1s\alpha\ 2s\beta\ 2p_-\alpha\ 2p_o\beta\ 2p_o\alpha)$

3: $(1s\alpha\ 2s\alpha\ 2p_-\beta\ 2p_o\alpha\ 2p_+\alpha)$

The usual term configuration as available in literature is specified by the occupation of subshells i denoted by the quantum numbers n_i, ℓ_i; that is to say determinant NO 1, NO 2 and NO 3 belong to same configuration viz 1s 2s $2p^3$. The work undertaken separates the subshells with respect to m_ℓ and m_s. In classifying these determinants for spin projection we have

a: $((1s_o)^1(2s_o)^1(2p_-)^1(2p_o)^1(2p_+)^1)$

b: $((1s_o)^1(2s_o)^1(2p_-)^1(2p_o)^2)$

c: $((1s_o)^1(2s_o)^1(2p_-)^1(2p_o)^1(2p_+)^1)$

The determinants a and c belong to the same configuration.

On the other hand, in classifying these determinants for orbital angular momentum projection, we have

x: $((1s\alpha)^1(2s\beta)^1(2p\alpha)^2(2p\beta)^1)$

y: $((1s\alpha)^1(2s\beta)^1(2p\alpha)^2(2p\beta)^1)$

z: $((1s\alpha)^1(2s\alpha)^1(2p\alpha)^2(2p\beta)^1)$

whereby classifying these determinants for orbital angular momentum projection we find determinant NO x and NO y belong to the same configuration. In a given wavefunction, determinants belong to different configurations. A subroutine in the projector operator program checks the configurations these determinants belong to. That is to say configuration of each determinant is tested and a configuration number is assigned to them.

First thing that projection operator does is to reorder the orbitals in a determinant, and separate the open subshells to the left hand side and closed subshell to the right hand side. A proper phasefactor is put in front of each determinant depending upon how the reshuffling of orbitals takes place. The projection operator then operates on each of the determinants of a given configuration in order. Several other determinants are produced during this process and all the determinants which are alike have their coefficients added up. Determinants which have coefficients zero or whose coefficients add to zero are eliminated during the process of projection. The final projected determinants and their respective coefficients are then printed out in the main program, next to each other. Successive configurations are treated one after another. The linear combination then gives a symmetry adapted wavefunction which has L and M_L values, S and M_s values as were specified or required.

This is projection operator method of obtaining a pure state or a symmetrized wavefunction.

CHAPTER VI

ELECTRIC DIPOLE TRANSITIONS PROBABILITY AND MULTIPLET OSCILLATOR STRENGTHS

A formula for electric dipole transition probability can be derived based on the semi-classical treatment of interaction of radiation with mattar. Several approximations will be used in the process of derivation of formula. It may be said here that this formula can be satisfactorily used for finding effect of radiation field on the particles, i.e., so called absorption and induced emission, but cannot be used for spontaneous processes.

Hamiltonian for a system particles of mass m and charge e in an electromagnetic field described by vector and scalar potentials is given by Schiff (13) as

$$\begin{aligned} H &= \sum_{i=1}^{N} \frac{-\hbar^2}{2m} \nabla_i^2 + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{i} \frac{-Ze^2}{r_i} \\ &+ \sum_{i=1}^{N} \frac{e}{2m} \left(i\hbar \bar{\nabla}_i \cdot \bar{A}(r_i,t) + i\hbar \bar{A}(\bar{r}_i,t) \cdot \bar{\nabla}_i \right) \\ &+ \sum_{i=1}^{N} \frac{e^2}{2m} \left(\bar{A}(\bar{r}_i,t) \cdot \bar{A}(r_i,t) \right) + \sum_{i=1}^{N} e\phi(r_i,t) \end{aligned} \qquad [1]$$

where $\vec{A}(\vec{r}_i,t)$ is vector potential of electromagnetic field evaluated at $\vec{r}_i$ at time t. $\phi(r_i,t)$ is scalar potential at the position of ith particle at time t. Hamiltonian as expressed by Eqn. [1] is sum of two parts and can be written as

$$H = H_o + H'$$

where

$$H_o = \sum_{i=1}^{N} \frac{-\hbar^2}{2m} \nabla_i^2 + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{i} \frac{Ze^2}{r_i} \qquad [2]$$

and H' is sum of rest of the terms in Eqn. [1]. A close look at H_o and H' will show that H_o is time-in dependent Electrostatic Hamiltonian of the isolated atom, and H' is interaction of particles with time dependent Electromagnetic field. Therefore the entire problem can be expressed in terms of time dependent Schrödinger Equation

$$i\hbar \frac{\partial\psi}{\partial t} = H\psi \qquad [3]$$

and then to calculate transitions probabilities between atomic states (bound) of the particle. Therefore Hamiltonian describes a system completely at different times, that is to say it unfolds the system with respect to time. Here we may also speak of the time development of the state in Schrödinger and interaction pictures. Interaction picture is defined as follows (13):

$$|\alpha_I(t)\rangle \equiv e^{iH_{os}\frac{t}{\hbar}} |\alpha_s(t)\rangle$$

$$\Omega_I(t) \equiv e^{iH_{os}\frac{t}{\hbar}} \Omega_s \, e^{-iH_{os}\frac{t}{\hbar}} \qquad [4]$$

where Hamiltonian in two pictures is written as

$$H_S = H_{oS} + H_S'$$

$$H_I = H_{oI} + H_I' \qquad [5]$$

The two pictures are equivalent if there is no perturbation part in the Hamiltonian. Assume a Unitary operator $U_I(t,t_o)$ such that it takes a state of system described in the interaction picture at time $t = t_o$ to a state at time $t = t$.

$$|\Psi_I(t)\rangle = U_I(t,t_0)\,|\Psi_I(t_0)\rangle \qquad [6]$$

To obtain an explicit expression for $U_I(t,t_o)$, the Unitary operator consider first the equation of motion of $|\alpha_I(t)\rangle$ of [4]. We have

$$-\frac{\hbar}{i}\frac{d}{dt}|\alpha_I(t)\rangle = -\frac{\hbar}{i}\frac{d}{dt}\left[e^{\frac{i}{\hbar}H_{o_s}t}\,|\alpha_s(t)\rangle\right] \qquad [7]$$

$$= -\frac{\hbar}{i}\left[\frac{i}{\hbar}H_{o_s}e^{\frac{i}{\hbar}H_{o_s}t}|\alpha_s(t)\rangle + e^{\frac{i}{\hbar}H_{o_s}t}\frac{d}{dt}|\alpha_s(t)\rangle\right]$$

$$= -H_{o_s}e^{\frac{i}{\hbar}H_{o_s}t}|\alpha_s(t)\rangle - \frac{\hbar}{i}e^{\frac{i}{\hbar}H_{o_s}t}\frac{d}{dt}|\alpha_s(t)\rangle$$

$$= -H_{o_s}e^{\frac{i}{\hbar}H_{o_s}t}|\alpha_s(t)\rangle + e^{\frac{i}{\hbar}H_{o_s}t}H_s|\alpha_s(t)\rangle$$

$$= -H_{o_s}e^{\frac{i}{\hbar}H_{o_s}t}|\alpha_s(t)\rangle + e^{\frac{i}{\hbar}H_{o_s}t}(H_{o_s}+H'_s)|\alpha_s(t)\rangle$$

$$= -H_{o_s}e^{\frac{i}{\hbar}H_{o_s}t}|\alpha_s(t)\rangle + e^{\frac{i}{\hbar}H_{o_s}t}H_{o_s}|\alpha_s(t)\rangle + e^{\frac{i}{\hbar}H_{o_s}t}H'_s|\alpha_s(t)\rangle$$

Note here that $e^{i/h\, H_{o_s} t}$ and H_{o_s} commute and therefore

$$-\frac{\hbar}{i}\frac{d|\alpha_I(t)\rangle}{dt} = -H_{o_s}e^{\frac{i}{\hbar}H_{o_s}t}|\alpha_s(t)\rangle + H_{o_s}e^{\frac{i}{\hbar}H_{o_s}t}|\alpha_s(t)\rangle + e^{\frac{i}{\hbar}H_{o_s}t}H'_s|\alpha_s(t)\rangle$$

The first two terms cancel out and thus

$$-\frac{\hbar}{i}\frac{d|\alpha_I(t)\rangle}{dt} = e^{\frac{i}{\hbar}H_{o_s}t}H'_s|\alpha_s(t)\rangle$$

$$= e^{\frac{i}{\hbar}H_{o_s}t}H'_s\,e^{-\frac{i}{\hbar}H_{o_s}t}\,e^{\frac{i}{\hbar}H_{o_s}t}|\alpha_s(t)\rangle$$

$$= H'_I\,|\alpha_I(t)\rangle$$

Equation of motion for $|\alpha_I(t)>$ is

$$-\frac{\hbar}{i}\frac{d|\alpha_I(t)>}{dt} = H_I' |\alpha_I(t)> \qquad [8]$$

This is the equation of motion for any state function $|\psi_I(t)>$ given by Equation [6]. In interaction picture this will give

$$-\frac{\hbar}{i}\frac{d}{dt}\left[U_I(t,t_0)|\psi_I(t_0)>\right] = H_I' \, U_I(t,t_0)|\psi_I(t_0)> \qquad [9]$$

or

$$-\frac{\hbar}{i}\left[\frac{d\,U_I(t,t_0)}{dt}\right]|\psi_I(t_0)> = H_I' \, U_I(t,t_0)|\psi_I(t_0)> \qquad [10]$$

This must be true for all $|\psi_I(t_o)>$. In general, as an operator equation this can be written as

$$-\frac{\hbar}{i}\frac{d\,U_I(t,t_0)}{dt} = H_I' \, U_I(t,t_0) \qquad [11]$$

this can be solved formally to give

$$U_I(t,t_0) = e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' \, H_I'(t')} \qquad [12]$$

with $U_I(t_o,t_o) = 1$

This describes U_I in the interaction picture for Equation [6]. U_I given by Equation [12] is a series expansion of exponential operator viz

$$e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' \, H_I'(t')} = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt' \, H_I'(t') + \text{Higher order terms} \qquad [13]$$

Therefore the state $|\psi_I(t)>$ is now completely specified for all times.

$$|\psi(t)> = U(t,t_0)\,|\psi(t_0)> = \sum_k C_k(t)\,|k> \qquad [14]$$

and $|\psi_I(t)\rangle$ can be expanded in terms of complete set of states. Interpretation of coefficients in the expansion: $|C_L(t)|^2$ is the probability that at time t a state vector will be found in a basis state L. The basis set is assumed to be complete and orthonormal. Equation [14] gives $C_L(t) = \langle L|\psi(t)\rangle$ which is a complex number and is amplitude,

or
$$C_L(t) = \langle L|\, U_I(t,t_o)\, \Psi(t_o)\rangle \qquad [15]$$

$|C_L(t)|^2 = |\langle L\,|U_I(t,t_o)\psi(t_o)\rangle|^2$ is the probability of a state function being found in state L at time t when initially, it was in state $\psi(t_o)$ at time t_o. Note that $\sum_L |C_L(t)|^2 = 1$ if initial state was normalized. ie

$$\begin{aligned}\langle\Psi(t)|\Psi(t)\rangle &= \langle\Psi(t_o)\, U^\dagger(t,t_o)|U(t,t_o)\,\Psi(t_o)\rangle\\ &= \langle\Psi(t_o)|\Psi(t_o)\rangle\\ &= 1 \qquad\qquad \because U^\dagger U = I\end{aligned}$$

also and $\langle\Psi_L|\Psi_K\rangle = \delta_{LK}$

$$\begin{aligned}\langle\Psi|\Psi\rangle &= \langle \textstyle\sum_L C_L(t)\,\Psi_L \,|\, \sum_K C_K(t)\,\Psi_K\rangle\\ &= \sum_{LK} C_L^* C_K \,\langle\Psi_L|\Psi_K\rangle\\ &= \sum_{LK} C_L^* C_K\, \delta_{LK}\\ &= \sum_L |C_L(t)|^2\\ &= 1\end{aligned}$$

All this means is that the system has got to be in some state at all the times.

Consider two atomic states a and b which are eigen states of H_o such that $H_o|a\rangle = E_a|a\rangle$ $H_o|b\rangle = E_b|b\rangle$. Let us calculate the transition probability of going from atomic state a at time $t = t_o$ to an atomic state b at time t = t. That is to calculate $|C_{b\to a}(t,t_o)|^2$.

Look at the coefficient $C_{b\to a}^{(t,t_o)} = \langle a|U_I(t,t_o)|b\rangle$ in the limit as [16] $t \to \infty$ and $t_o \to -\infty$. This is done in accordance with Heisenberg's uncertainty relation that energy transferred during the transition and the time of transition cannot be determined precisely simultaneously. Therefore one has to look in the time duration of $-\infty$ to ∞, assuming energy of transitions are precisely known. To the first order we retain only first two terms in the expansion of

$$U_I(t,t_o) = e^{-\frac{i}{\hbar}\int_{t_o}^{t} dt' H_I'(t')}$$

$$\doteqdot 1 - \frac{i}{\hbar}\int_{t_o}^{t} dt' H_I'(t')$$

$$\therefore \; C_{b\to a}^{(t,t_o)} = \langle a|1 - \frac{i}{\hbar}\int_{t_o}^{t} dt' H_I'(t')|b\rangle$$

$$= \langle a|1|b\rangle - \frac{i}{\hbar}\int_{t_o}^{t} dt' \langle a|H_I'(t')|b\rangle \qquad [17]$$

The first term is δ_{ab}. The integrand in second term is $\langle a|H_I'(t')|b\rangle$ where $H_I'(t') = e^{\frac{i}{\hbar}H_{os}t'} H_s' \; e^{-\frac{i}{\hbar}H_{os}t'}$; therefore writing it in interaction picture in terms of Schrödinger operator gives

$$\langle a|H_I'(t')|b\rangle = \langle a|e^{\frac{i}{\hbar}H_{os}t'} H_s'(t') \; e^{-\frac{i}{\hbar}H_{os}t'}|b\rangle \qquad [18]$$

$|a\rangle$ and $|b\rangle$ are atomic states of the unperturbed part of the Hamiltonian and therefore;

$$\langle a|H_I(t')|b\rangle = \langle a|e^{\frac{i}{\hbar}E_a t'} H_s'(t') \; e^{-\frac{i}{\hbar}E_b t'}|b\rangle$$

ie $$\langle a|H_I(t')|b\rangle = e^{\frac{i}{\hbar}(E_a-E_b)t'}\langle a|H_s'(t')|b\rangle \qquad [19]$$

Next, we have to plug in H' from Equation [1] with proper approximations. We have

$$H'\psi = \sum_{i=1}^{N}\frac{e}{2m}i\hbar\left[\bar{\nabla}_i\cdot(\bar{A}\psi) + \bar{A}\cdot\bar{\nabla}_i\psi\right] + \sum_{i=1}^{N}\frac{e^2}{2m}A^2\psi + \sum_{i=1}^{N}e\phi\psi$$

$$= \sum_{i=1}^{N}\frac{e}{2m}i\hbar\left[(\bar{\nabla}_i\cdot\bar{A})\psi + \bar{A}\cdot\bar{\nabla}_i\psi + \bar{A}\cdot\bar{\nabla}_i\psi\right] + \sum_{i=1}^{N}\frac{e^2}{2m}A^2\psi + \sum_{i=1}^{N}e\phi\psi \qquad [20]$$

The vector and scalar potential $A(\vec{r},t)$ and $\phi(\vec{r},t)$ can be gauge transformed so that the new potentials satisfy the Lorentz condition. In completely empty space (charge and current densities equal to zero) it is possible to choose the gauge transformation (13) such that $\bar{\nabla}\cdot\vec{A} = 0$ and $\phi = 0$. Under these conditions Equation [20] becomes

$$H'\psi = \sum_{i=1}^{N}\frac{e}{m}i\hbar\,(\bar{A}\cdot\nabla_i\psi) + \sum_{i=1}^{N}\frac{e^2}{2m}A^2\psi \qquad [21]$$

The term $(\frac{e^2}{2m})A^2$ leads to physical processes in which two protons are emitted or absorbed during transitions. This term can be omitted in the first order corrections (15), when we are considering only one photon emission and absorbtion between the states a and b such that

$$E_b - E_a = \hbar\omega \qquad [22]$$

Thus [21] gives

$$H'\psi = \sum_{i=1}^{N}i\hbar\frac{e}{m}(\bar{A}\cdot\bar{\nabla}_i\psi) \qquad [23]$$

This should hold good for any state function and therefore

$$H' = \sum_{i=1}^{N} i\hbar \frac{e}{m} (\bar{A}\cdot\bar{\nabla}_i) \qquad [24]$$

Let us take a monochromatic, linearly polarized plane wave for the vector potential, i.e., $\vec{A} = A\hat{e}\{e^{i(\omega t-\vec{k}\cdot\vec{r})} + e^{-i(\omega t-\vec{k}\cdot\vec{r})}\}$ where $\hat{e}$ is polarization vector, usually the direction in which electric field is aligned and $\vec{k}$ is propogation vector such that $\hat{e}\cdot\vec{k} = 0$ i.e., they are mutually orthogonal. This then completely specifies the perturbed part of the Hamiltonian. Equation [19] now becomes:

$$\langle a|H_1'(t')|b\rangle = e^{\frac{i}{\hbar}(E_b-E_a)t'} \langle a| i\hbar\frac{e}{m}\sum_{i=1}^{N}\left(e^{i(\omega t'-\vec{k}\cdot\vec{r}_i)} + e^{-i(\omega t'-\vec{k}\cdot\vec{r}_i)}\right)\hat{e}\cdot\bar{\nabla}_i|b\rangle \qquad [25]$$

$$= i\hbar\frac{e}{m}A\Big[e^{\frac{i}{\hbar}(E_a-E_b+\hbar\omega)t'}\langle a|\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}\,\hat{e}\cdot\nabla_i|b\rangle + e^{\frac{i}{\hbar}(E_a-E_b-\hbar\omega)t'}\langle a|\sum_{i=1}^{N} e^{i\vec{k}\cdot\vec{r}_i}\,\hat{e}\cdot\bar{\nabla}_i|b\rangle\Big] \qquad [26]$$

Substituting this back in Equation [17] we get a quantity whose absolute square is proportional to transition probability. In Equation [17] consider that state a is different from state b. Then

$$C_{b\to a}(t,t_0) = -\frac{i}{\hbar}\int_{t_0}^{t} dt'\, i\hbar\frac{e}{m}A\Big[e^{\frac{i}{\hbar}(E_a-E_b+\hbar\omega)t'}\langle a|\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}\,\hat{e}\cdot\bar{\nabla}_i|b\rangle + e^{\frac{i}{\hbar}(E_a-E_b-\hbar\omega)t'}\langle a|\sum_{i=1}^{N} e^{i\vec{k}\cdot\vec{r}_i}\,\hat{e}\cdot\vec{\nabla}_i|b\rangle\Big] \qquad [27]$$

Arranging the constant factors proberly and taking limit of this quantity as $t_0 \to -\infty$ and $t \to \infty$ we get the following

$$C_{b\to a}(\infty,-\infty) = \frac{e}{m}A\int_{-\infty}^{\infty} dt'\Big[e^{\frac{i}{\hbar}(E_a-E_b+\hbar\omega)t'}\langle a|\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}\,\hat{e}\cdot\bar{\nabla}_i|b\rangle + e^{\frac{i}{\hbar}(E_a-E_b-\hbar\omega)t'}\langle a|\sum_{i=1}^{N} e^{i\vec{k}\cdot\vec{r}_i}\,\hat{e}\cdot\bar{\nabla}_i|b\rangle\Big] \qquad [28]$$

On the time dependent part of integration use the property that

$$\delta(\alpha-\beta) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\; e^{i(\alpha-\beta)t}$$

Thus [28] gives

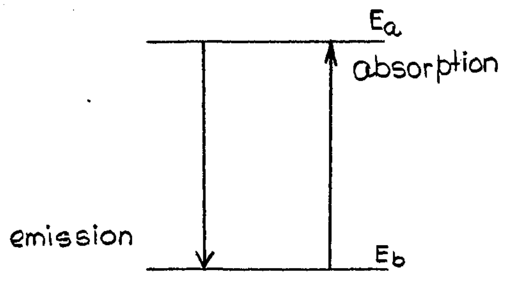
$$C_{b\to a}^{(\infty,-\infty)} = 2\pi\frac{e}{m}A\Bigg[\delta\left(\frac{E_a-E_b-\hbar\omega}{\hbar}\right)\langle a|\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}\hat{e}\cdot\vec{\nabla}_i|b\rangle + \delta\left(\frac{E_a-E_b+\hbar\omega}{\hbar}\right)\langle a|\sum_{i=1}^{N} e^{i\vec{k}\cdot\vec{r}_i}\hat{e}\cdot\vec{\nabla}_i|b\rangle \qquad [29]$$

The δ function determines a condition under which transition probability is non-vanishing. In Equation [29] either the first δ equals zero or the second. They cannot be non-zero simultaneously. In other words we have either induced emission or absorption. The transition probability of emission equals zero unless

$$\frac{(E_a-E_b)-(\hbar\omega)}{\hbar} = 0 \quad \text{ie} \quad (E_a-E_b) = \hbar\omega$$

and the transition probability of absorption equals zero unless

$$\frac{(E_a-E_b)-(-\hbar\omega)}{\hbar} = 0 \quad \text{ie} \quad E_b-E_a = \hbar\omega$$



These two conditions show that energy is conserved i.e., the difference in energy between initial and final states equals that due to emission or absorption of one photon. Note here that of the two terms in the summation in Equation [29] one term need be considered at a time. For the further discussion we will consider the process of emission in the dipole approximation and the discussion for absorption will be very similar to that.

Now consider the quantity $\langle a|\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}(\hat{e}\cdot\bar{\nabla}_i)|b\rangle$ in Equation [29]. Here $|a\rangle$ and $|b\rangle$ are the kets for atomic states a and b. $\langle a|x_1x_2\ldots x_n\rangle$, $\langle x_1 \ldots x_n|b\rangle$ therefore are functions of coordinates. When any of the electrons is far away from nucleus, the magnitude of that function is very small and contributions to the matrix element from these regions of configuration space are insignificant. The major contribution to the matrix element comes from those regions of configuration space where wavefunction is large. That is a region of atomic space in which all N electrons are within the "radius" r of the atom. In this region of space $\vec{r}_i \leq r << \lambda$ where λ = wavelength of radiation ≈ 1000 Å in UV region and r = "radius" of the atom $\approx 10^{-8}$ cm. Thus for large enough wavelengths only first term is to be retained in the series expansion of $e^{-i\vec{k}\cdot\vec{r}} = 1 - i\vec{k}\cdot\vec{r} + \ldots$. which corresponds to electric dipole term. Therefore electric dipole transition probability is proportional to $|\langle a|\sum_{i=1}^{N} \hat{e}\cdot\nabla_i|b\rangle|^2$.

$$\therefore C_{b\to a}^{(\infty,-\infty)} = 2\pi\frac{e}{m}A\left[\delta\left(\frac{E_a-E_b-\hbar\omega}{\hbar}\right)\langle a|\sum_{i=1}^{N}\hat{e}\cdot\bar{\nabla}_i|b\rangle + \delta\left(\frac{E_a-E_b+\hbar\omega}{\hbar}\right)\langle a|\sum_{i=1}^{N}\hat{e}\cdot\nabla_i|b\rangle\right] \qquad [30]$$

where

$$\hat{e}\cdot\bar{\nabla}_i = \left(e_x\frac{\partial}{\partial x_i} + e_y\frac{\partial}{\partial y_i} + e_z\frac{\partial}{\partial z_i}\right) \qquad [31]$$

While obtaining the transition probability expression, omit the δ function which determines the conditions under which transition probability is non-vanishing. Thus the atomic transition probability will now be given by:

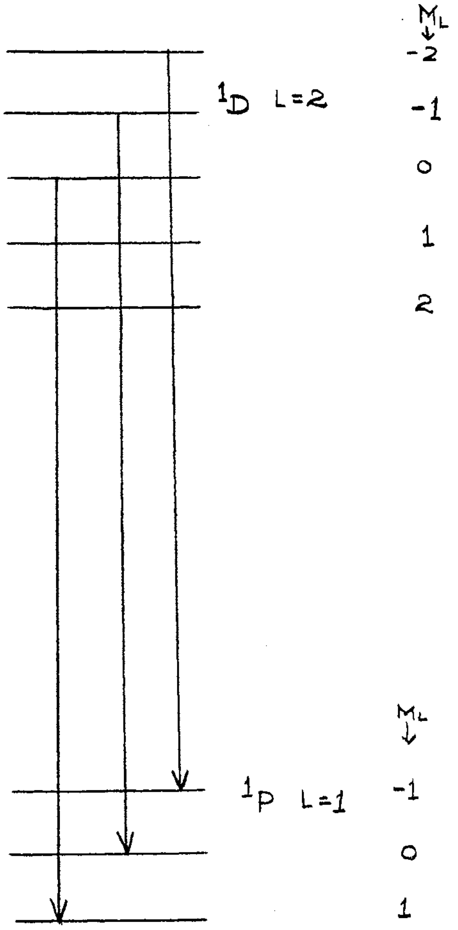
$$\left|C_{b\to a}^{(\infty,-\infty)}\right|^2 = 4\pi^2A^2\frac{e^2}{m^2}\left|\sum_{i=1}^{N}\langle a|\hat{e}_x\frac{\partial}{\partial x_i} + \hat{e}_y\frac{\partial}{\partial y_i} + \hat{e}_z\frac{\partial}{\partial z_i}|b\rangle\right|^2$$

$$\left|C^{(\infty,-\infty)}_{b\to a}\right|^2 = 4\pi^2 A^2 \frac{e^2}{m^2} \langle a|\hat{e}\cdot\sum_{i=1}^{N}\bar{\nabla}_i|b\rangle \langle a|\hat{e}\cdot\sum_{i=1}^{N}\nabla_i|b\rangle^*$$

$$= 4\pi^2 A^2 \frac{e^2}{m^2}\left[\hat{e}\cdot\langle a|\sum_{i=1}^{N}\bar{\nabla}_i|b\rangle\right]\left[\hat{e}\cdot\langle a|\sum_{i=1}^{N}\bar{\nabla}_i|b\rangle\right]^*$$

$$= 4\pi^2 \frac{e^2}{m^2} A^2 \left|\hat{e}\cdot\langle a|\sum_{i=1}^{N}\bar{\nabla}_i|b\rangle\right|^2 \qquad [32]$$

The transition probability is directly proportional to A^2, i.e., intensity and square of modulus of the matrix element of velocity ($\bar{\nabla}_i$) operator. Other operators that can replace $\bar{\nabla}_i$ are position and acceleration operator and one can get alternate forms of the transition probability formula (14). A dimensionless quantity proportional to transition probability formula is also sometimes defined as oscillator strength. It is well known that each atomic term has a degeneracy of (2L + 1)(2S + 1). $^1D \rightarrow {}^1P$ transition is shown in the diagram. Multiplet splitting is also shown here. When we consider a transition from one term to another we have to



Sum up all the transitions from each multiplet and weighted average taken over the degeneracy. The weighted average of oscillator strengths is called multiplet oscillator strength and explained in Chapter VII. Note here that non-vanishing of the matrix elements in the expression for transition probability defines the selection rules for electric dipole allowed transitions.

$\Delta L = \pm 1$

$\Delta S = 0$

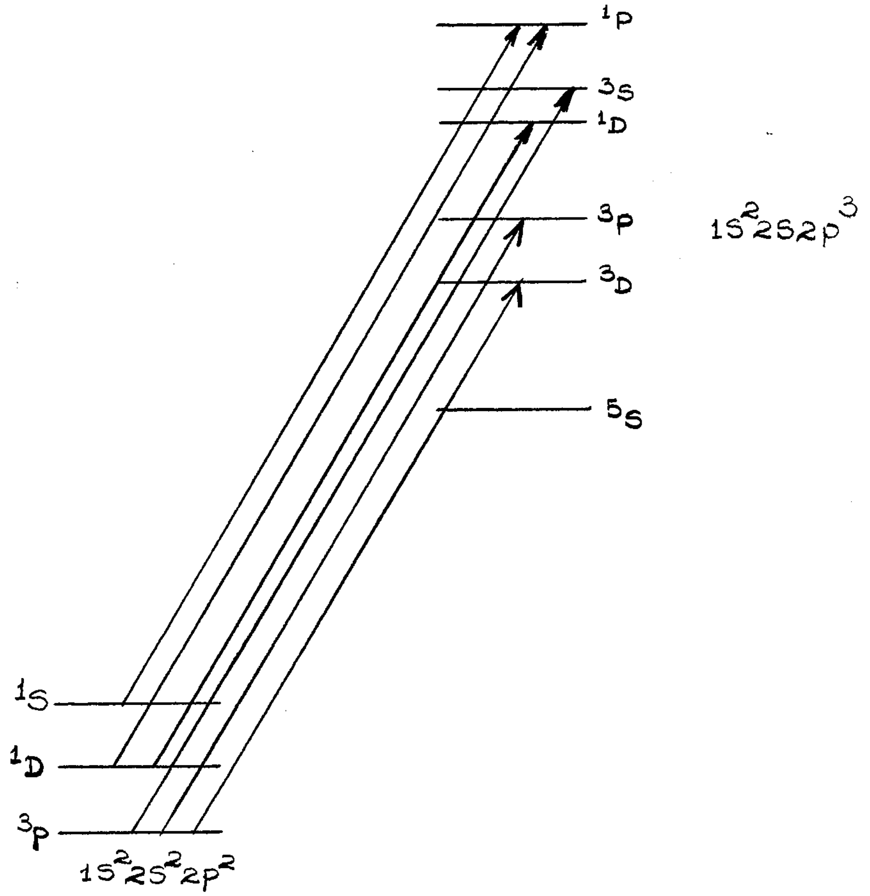
$\Delta M_L = 0, \pm 1$, For $\Delta M_L = 0$, $M_L = 0$ is forbidden

$\Delta M_S = 0, \pm 1$, For $\Delta M_S = 0$, $M_S = 0$ is forbidden

CHAPTER VII

RESULTS AND CONCLUSIONS

F^{+++} energy level diagram with allowed absorption transitions from lower states of $2s^2 2p^2$ to upper states of $2s2p^3$ are presented in the following diagram.



The wavelengths of the transitions are listed in Table I. In the energy level diagram each level consists of (2L + 1)(2S + 1) degenerate states. When we speak of transitions from one level to another we take into account the degeneracy of each level. In this respect we define

TABLE I

DATA ANALYSIS OF ELECTRIC DIPOLE TRANSITIONS IN THE ARRAY $1s^2 2s^2 2p^2 \rightarrow 1s^2 2s 2p^3$ FOR F^{+++}

$1s^2 2s^2 2p^2 - 1s^2 2s 2p^3$	$\lambda_{experimental}$ in Å	$\longleftarrow$	$\lambda_{theoretical}$	$\longrightarrow$
		$_{RHF}^{RHF}$	$_{HF}^{HF+INT}$	$_{MET}^{MET}$
$^3P - {}^3D$	678.18	693.404	664.616	664.978
$^3P - {}^3P$	572.00	582.05	561.63	549.55
$^3P - {}^3S$	420.38	409.33	399.124	411.527
$^1D - {}^1D$	491.00	474.67	461.035	482.39
$^1D - {}^1P$	430.76	421.0	410.24	414.49
$^1S - {}^1P$	490.57	507.2	453.07	479.63

$\lambda_{experimental}$ are the experimentally observed wavelengths of transitions and were obtained from: Atomic Transition probabilities - Hydrogen through Neon • Wiese, Smith, Glennon. NSRDS - NBS4, Vol. I.

$\lambda_{theoretical}$ are the wavelengths of transition calculated by Westhaus and Sinanoğlu's (3) program. For example ΔE_{HF}^{HF+INT} = $<\phi_{HF}|H|\phi_{HF+INT}> - <\phi_{HF}|H|\phi_{HF}>$ and this can be converted into λ_{HF}^{HF+INT} through constant terms and so on. The details of this was described in Chapter I.

multiplet oscillator strengths. Recalling the expression (14) for oscillator strength in terms of dipole length operator $\vec{R}$ for a transition denoted by $\alpha L\, SM_L\, M_S \rightarrow \alpha' L' S' M_L' M_S'$ we have

$$f_{\alpha LSM_LM_S;\alpha'L'S'M_L'M_S'} = \frac{2}{3}\; E(\alpha'L'S') - E(\alpha LS) \left| \langle \psi_{\alpha LSM_LM_S} | \bar{R} | \psi_{\alpha'L'S'M_L'M_S'} \rangle \right|^2 \qquad [1]$$

or in terms of dipole velocity operator as

$$f_{\alpha LSM_LM_S;\alpha'L'S'M_L'M_S'} = \frac{2}{3} \frac{1}{E(\alpha'L'S') - E(\alpha LS)} \left| \langle \psi_{\alpha LSM_LM_S} | \bar{\nabla} | \psi_{\alpha'L'S'M_L'M_S'} \rangle \right|^2$$

where

$$\bar{R} = \sum_{i=1}^{N} r_i \qquad \text{and} \quad \bar{\nabla} = \sum_{i=1}^{N} \nabla_i$$

The multiplet oscillator strength will now be defined as

$$f_{\alpha LS;\alpha'L'S'} = \frac{1}{(2L+1)(2S+1)} \sum_{M_LM_L'} \sum_{M_SM_S'} f_{\alpha LSM_LM_S;\alpha'L'S'M_L'M_S'} \qquad [2]$$

(2L + 1) (2S + 1) is degeneracy of lower state. $f\,\alpha L s;\alpha' L' S'$ is a dimensionless quantity. All the tables in this chapter describing f's are multiplet oscillator strengths defined by Equation [2]. Multiplet oscillator strengths are calculated using the electric dipole transition program of Westhaus and Sinanoğlu (3). One needs to feed the wavefunction and energy of each state involved in a transition corresponding to one non-vanishing term of Equation [2]. The remaining terms in the summation are obtained from this given term by group theory. Wavefunction and energy of each state are first computed using Öksüz and Sinanoğlu's (1) program, projected out using our projector operator program and then fed to Westhaus's transition probability program. The transition probability program converst the energy difference between two states to wavelength of transitions, and will be called the theoretical wavelengths for the transitions. This program can also use directly the wavelength of transitions found out experimentally. f values[1] have also been calculated using this experimental wavelength of transition denoted by λ experimental in the Tables II and III.

The approximate wavefuntions for two different states under consideration are used by the transition probability program. In general, as predicted by MET each state can be approximated by four types of wavefunctions which contain various parts of non-dynamical correlations. Four types of wavefunctions are restricted Hartree Fock, HF + CI part, HF + SEMI INTERNAL part and HF + INTERNAL part and each approximate wavefunction has corresponding energy. However, in the states coming from $1s^2\ 2s\ 2p^3$ there are no internal correlations considered. The program computes f values using each type of approximate wavefunctions for two states in terms of dipole length, velocity and acceleration operators. The output of the program also gives a quantity denoted by $f_{\sqrt{\ }}$, this is square root of product of f values calculated in terms of length and velocity operators. The square root results are kind of averaging of oscillator strengths and do not depend explicitly upon the energy difference of the two states (14). It may be noted here that the oscillator strength formulas given in Chapter I in terms of dipole velocity operator is as fundamental as it is in terms of dipole length operator. In fact they are derivable from each other (14). The length, velocity and acceleration formula would give the same result for f value if we are working with a pure eigenfunction of electrostatic Hamiltonian.

f values for different transitions in F^{+++} in the array $1s^2 2s^2 2p^2 \rightarrow$

---

[1] f values, oscillator strengths and transition probability are being used interchangeably throughout the text of this chapter, as several other authors have done so.

TABLE II

			$^3P \to {}^3D$ (a)	$\lambda_{Experimental} = 678.18$Å		
Type	RHF f^{RHF}	HF+INT f^{HF}	MET f^{MET}	HF f^{HF}	HF+INT f^{HF}	MET f^{MET}
Length	.1695	.1308	.0931	.1734	.1282	.0913
Velocity	.1798	.2172	.0959	.1758	.2216	.0978
Square root	.1746	.1686	.0945	.1746	.1686	.0945
			$^3P \to {}^3P$ (b)	$\lambda_{Experimental} = 572$Å		
Length	.1212	.1583	.1161	.1233	.1554	.1116
Velocity	.0905	.0646	.1284	.089	.0658	.1337
Square root	.1048	.1011	.1221	.1048	.1011	.1221
			$^3P \to {}^3S$ (c)	$\lambda_{Experimental} = 420.38$		
Length	.2298	.1743	.1578	.2237	.1655	.1545
Velocity	.0849	.1043	.1621	.0872	.1099	.1656
Square root	.1397	.1349	.1599	.1397	.1349	.1599

TABLE III

			$^1D - {}^1D$ (a)	$\lambda_{Experimental}$ = 491Å		
Type	RHF f^{RHF}	HF+INT f^{HF}	MET f^{MET}	RHF f^{RHF}	HF+INT f^{HF}	MET f^{MET}
Length	.4506	.3429	.2699	.4356	.3220	.2652
Velocity	.2336	.2861	.2874	.2417	.3046	.2925
Square root	.3244	.3132	.2875	.3245	.3132	.2785
			$^1D - {}^1P$ (b)	$\lambda_{Experimental}$ = 430.76Å		
Length	.1693	.2191	.1884	.1655	.2086	.1813
Velocity	.0691	.0498	.1751	.0707	.0522	.1820
Square root	.1081	.1044	.1817	.1081	.1044	.1817
			$^1S - {}^1P$ (c)	$\lambda_{Experimental}$ = 490.57		
Length	.5613	.3283	.2622	.5803	.3032	.2564
Velocity	.3340	.4458	.3046	.3231	.4827	.2689
Square root	.4330	.3825	.2826	.4330	.3825	.2826

$1s^2 2s2p^3$ are listed in Tables II and III for triplet and Singlet transitions respectively. In these tables f^{A}_{B} will mean that the f value was computed in terms of dipole length or velocity operator when the function for lower state was A and that for the upper state was B. Each of the Tables II and III is divided into two parts showing oscillator strength results for theoretical and experimental wavelengths of corresponding transitions. The first column in these tables is the type of operator which is considered to evaluate the oscillator strength. These are length and velocity operator and the third item is square root value. The second column is f value evaluated with lower state consisting of HF + INTERNAL correlation and upper state consisting of HF part only. (Recall that the upper state does not have internal correlation.) In the third column are listed f values when both upper and lower states are made up of MET wavefunctions[2]. The other half of these tables gives the similar information when experimentally obtained wavelengths of transitions are used.

Numerical values of oscillator strengths show a tremendous consistency calculated in dipole length and velocity operators, when non-dynamical correlations are included in the wavefunctions and the wavefunctions are pure states. For example consider the transition ^3P-^3S. In this case f^{RHF}_{RHF} under length and velocity formula differs by about 63% where as f^{MET}_{MET} differ by about 2.71%. This is just an example. The degree of variation differs from state to state. The above percentages

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[2] Large CI wavefunction containing non-dynamical correlation, which has been called as MET wavefunction is also termed as charge density function by Nicholaides, Sinanoğlu, Westhaus (Phys. Rev., to be published).

are calculated as follows:

$$\% \text{ difference} = \frac{|f_{\text{length}} - f_{\text{velocity}}|}{f_{\text{length}}} \times 100$$

In certain cases e.g., in ^3P - ^3D transitions we have calculations in F^{+++} that the oscillator strengths calculated using the dipole length and dipole velocity operators agree with one another surprisingly well when we use the HF wavefunctions for both the lower and upper states. Indeed one might be tempted to conclude from such consistency that the HF calculations represent accurate oscillator strengths. However, when all the non-dynamical correlation effects are included in both the lower and upper states, the MET results for the dipole length and dipole velocity operators again agree among themselves but are substantially different from the HF results (in the example under consideration by almost a factor of two). Hence the temptation to conclude that consistency be-
RHF RHF
f^{RHF}_{vel} and f^{RHF}_{len} is a guarantee of accuracy must be avoided, on the other
MET
hand f^{MET} calculated in terms of length and velocity operator are consistent throughout the Tables IIa,b,c through IIIa,b,c. f values in MET basis may not be anywhere close to those in RHF basis but their consistency throughout the calculations of different types of transition may be taken for implying their absolute numerical accuracy.

This will become more clear when this F^{+++} data will be plotted with some of the already existing calculation of the members of carbon isoelectronic science. This will be done in graphs for Tables V through X.

In Table IV are compared the f values computed by Bolotin et al.

TABLE IV

COMPARISON OF DOUBLE CONFIGURATION DATA AND $f_{\mathrm{HF}}^{\mathrm{HF+INT}}$ FOR F_{IV} IN DIFFERENT TRANSITION STATES IN THE ARRAY $1s^2 2s^2 2p^2 - 1s^2 2s 2p^3$

Transitions $1s^2 2s^2 2p^2 - 1s^2 2s 2p^3$	Double Configuration Data*	$f_{\mathrm{HF}}^{\mathrm{HF+INT}}$
$^3P - {}^3D$	.13	.1308
$^3P - {}^3P$	.16	.1583
$^3P - {}^3S$	.16	.1743
$^1D - {}^1D$	.31	.3492
$^1D - {}^1P$	.21	.2191
$^1S - {}^1P$	.30	.3283

*This is Bolotin, Levinson and Levin's data as listed in NBS tables.

(18) in the double configurational approximation with our $f^{\substack{HF + INT \\ HF}}$ value. In the double configurational approximation they have mixing of $1s^2 2s^2 2p^2 - 1s^2 2p^4$. This is very similar to our mixing of HF - INTERNAL CORRELATION. This is mainly because states arising from the configuration $1s^2 2s^2 2p^2$ do not mix with those arising from the configuration $1s^2 2s 2p^3$ as they have different parities. Therefore, in the internal correlation part we are left with only $1s^2 2s^2 2p^2 - 1s^2 2p^4$ mixing which is exactly Bolotin's double configuration approximation. Their orbitals for each state are linear combinations of Slater type probitals, each orbital containing four parameters all of which were obtained by minimizing the energy in the single configuration approximation.

In our calculations the orbitals data for ^3S, ^3P, ^3D from the $1s^2 2s 2p^3$ configuration is approximated by the HF orbitals data for ^3P from $1s^2 2s^2 2p^2$ configuration and the orbitals data for ^1P, ^1D in the $1s^2 2s 2p^3$ configuration is approximated by that for ^1D in the $1s^2 2s^2 2p^2$ configuration. HF orbital data for lower states was taken from Clementi's tables of atomic functions (8).

To see the consistency in the $f^{\substack{MET \\ MET}}$ values for length and velocity operator, we will plot the results of F^{+++} with those of large CI calculations (16) for C_I and MET calculations (3) for N_{II} and O_{III} obtained from other sources. The extrapolation of these graphs will help in the prediction of f values of highly ionized atoms. For this purpose we need to investigate the systematic dependence of oscillator strengths on nuclear charge Z. Consider Hamiltonian for an atomic system of N electrons

$$H = \sum_{i=1}^{N} \left(\frac{1}{2} \nabla_i^2 + \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}} \qquad [3]$$

$$H = H_o + H_1 \qquad [4]$$

where we now treat $H_1 = \sum_{i<j}^{N} \frac{1}{r_{ij}}$ as the perturbing part of the Hamiltonian. Here we define a quantity $\rho_i = Zr_i$ in order to obtain Z dependence in the perturbed part of the Hamiltonian. Rewrite H as follows (19):

$$H = Z^2 \left(\sum_{i=1}^{N} -\frac{1}{2} \nabla^2_{\rho_i} + \frac{1}{\rho_i} \right) + \sum_{i<j} \frac{Z}{\rho_{ij}} \qquad [5]$$

Now divide Equation [3] throughout by Z^2 we get

$$HZ^{-2} = \left(\sum_{i=1}^{N} -\frac{1}{2} \nabla^2_{\rho_i} + \frac{1}{\rho_i} \right) + \frac{1}{Z} \sum_{i<j} \frac{1}{\rho_{ij}} \qquad [6]$$

Let $H' = H_{Z^{-2}}$ then the problem reduces to finding eigenfunctions and eigenvalues of H'. The eigenvalues of H are then obtained by multiplying a constant (Z^2) to the eigenvalues of H'.

$$H' = H_o' + \frac{1}{Z} H_1' \qquad [7]$$

The Schrödinger equation for N electron system becomes $(H_o' + \frac{1}{Z} H_1')\psi = \epsilon \psi$ where by ϵ and ψ may be expanded in power series of $\frac{1}{Z}$.

$$\psi = \varphi_o + \varphi_1 \frac{1}{Z} + \varphi_2 + \frac{1}{Z^2} + \text{-----} \qquad [8]$$

$$\epsilon = \epsilon_o + \epsilon_1 \frac{1}{Z} + \epsilon_2 \frac{1}{Z^2} + \text{-----} \qquad [9]$$

where ψ and ϵ are eigenfunction and eigenvalues of H'. Eigenvalues of H are given by

$$E = \epsilon_o Z^2 + \epsilon_1 Z + \epsilon_2 + \text{------} \qquad [10]$$

Recalling that f value for a transition from lower state i to upper state k is given by

$$f_{ik} = \frac{2}{3}\left(E_k - E_i\right)\left|\langle i|\sum_{p}\vec{r}_p|k\rangle\right|^2$$

Making use of Equations [8] [9] [10] it can be shown that oscillator strength f can be expanded in power of $\frac{1}{Z}$ as follows

$$f = a_0 + a_1\frac{1}{Z} + a_2\frac{1}{Z^2} + \cdots\cdots \qquad [11]$$

Note that as $Z \rightarrow \infty$, the second term in Equation [4] → 0 and we are left with sum of hydrogenic Hamiltonians on the R·H·S of Equation [6]. In Equation [9], then $\varepsilon = \varepsilon_0$ are the sum of eigenvalues of hydrogenic Hamiltonian. From elementary quantum mechanics we know that hydrogen atom has energies which are degenerate in ℓ for a given n, i.e., 2s,2p have some energy. Therefore, when we consider transitions in the array $1s^2 2s^2 2p^2 - 1s^2 2s 2p^3$ in the limit $Z \rightarrow \infty$ we have that the states coming from two configurations have same energy and $(E_k - E_i) = 0$. Therefore, $f_{ik} \rightarrow 0$ as $\frac{1}{Z} \rightarrow 0$ and that gives an additional point on the plot of oscillator strength versus $\frac{1}{Z}$. Graphs for Tables V through X are the plots of oscillator strengths versus $\frac{1}{Z}$ for C_I, N_{II}, O_{III}, F_{IV}. F_{IV} data is entirely ours, where as the data for other species was obtained from other sources. With the help of these data points, graphs have been extrapolated to origin (0,0) of axes. (0,0) is a point to be considered as explained before. The extrapolated region of the graphs helps in predicting f values in highly ionized atoms. To avoid too many curves on the graphs the lines drawn are for $f^{RHF}_{\surd}$, $f^{MET}_{\surd}$, as they are averaging values of f obtained in terms of length and velocity operators. NBS data is also shown on the graphs for comparison purpose. As seen numerically, through the tables that MET data is by far the best becomes more clear through these graphs. Some of the $f_{\sqrt{\;}}^{MET}$, f_{length}^{MET} and and f_{vel}^{MET} points lie over each other whereas the same points for HF basis are scattered far away from each other.

TABLE V

$^3P - {}^3D$

Species	Z	$\frac{1}{Z}$	Type	HF	NBS	MET
C_I	6	.167	Length	.286(16)	(.091)[#]	.102[§]
			Velocity	.332(16)		.117[§]
			Square root	.308		.109
N_{II} ⊗	7	.143	Length	.236	(.17)	.100
			Velocity	.268		.105
			Square root	.251		.102
O_{III} ⊗	8	.125	Length	.2	(.15)	.100
			Velocity	.225		.104
			Square root	.212		.102
F_{IV}	9	.111	Length	.1695	(.13)[†]	.093
			Velocity	.1798		.096
			Square root	.1746		.095

[§] Actually they are not MET results but large C_I calculations made by A. W. Weiss, Phys. Rev. 162, 71-80 (1967).

[†] Bolotin, A. B., Levinson, I. B., and Levin, L. I., Soviet Phys. JETP 2, 391-395 (1956). Their method of calculation is essentially analogous to our method in which we have (HF + INT) correlation.

[#] Experimentally obtained value [Boldt, G., Z. Naturforsch. 18a, 1107-1116 (1963)].

⊗ Data for N^+ and O^{++} is obtained from (3).

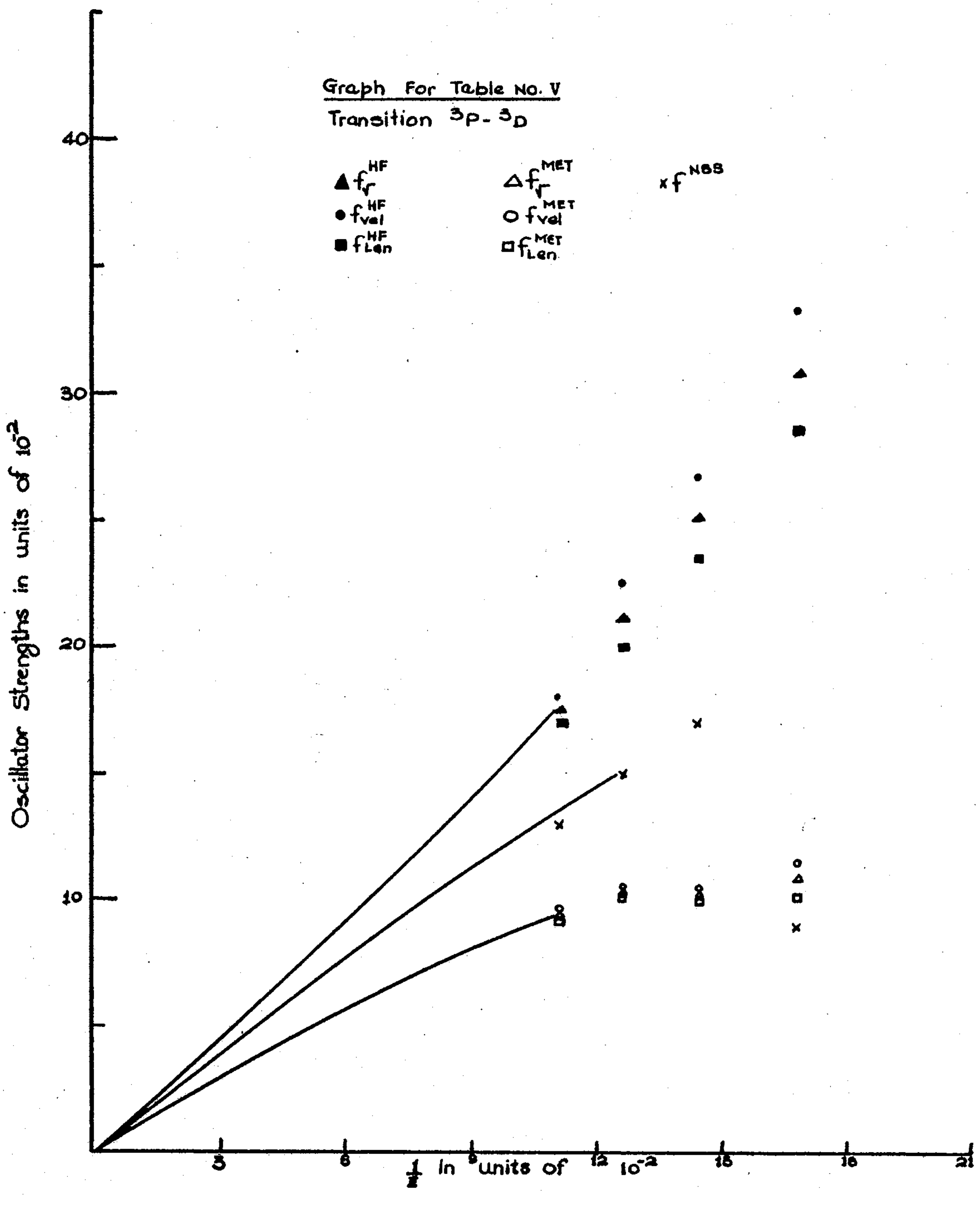

Graph For Table No. V
Transition ³P - ³D
▲ f_r^{HF}
△ f_r^{MET}
× f^{NBS}
● f_{vel}^{HF}
○ f_{vel}^{MET}
■ f_{Len}^{HF}
□ f_{Len}^{MET}
Oscillator Strengths in units of 10^{-2}
10
20
30
40
3
6
9
12
15
18
21
$\frac{1}{Z}$ in units of 10^{-2}

TABLE VI

$^3P - {}^3P$

Species	Z	$\frac{1}{Z}$	Type	HF	NBS	MET
C_I	6	.167	Length	.202(16)	(.038)#	.097§
			Velocity	.171(16)		.105§
			Square root	.186		.100
N_{II} ⊗	7	.143	Length	.170	(.22)	.137
			Velocity	.138		.155
			Square root	.153		.146
O_{III} ⊗	8	.125	Length	.143	(.18)	.127
			Velocity	.117		.135
			Square root	.129		.131
F_{IV}	9	.111	Length	.121	(.16)†	.116
			Velocity	.090		.128
			Square root	.105		.122

For symbols, see Table V.

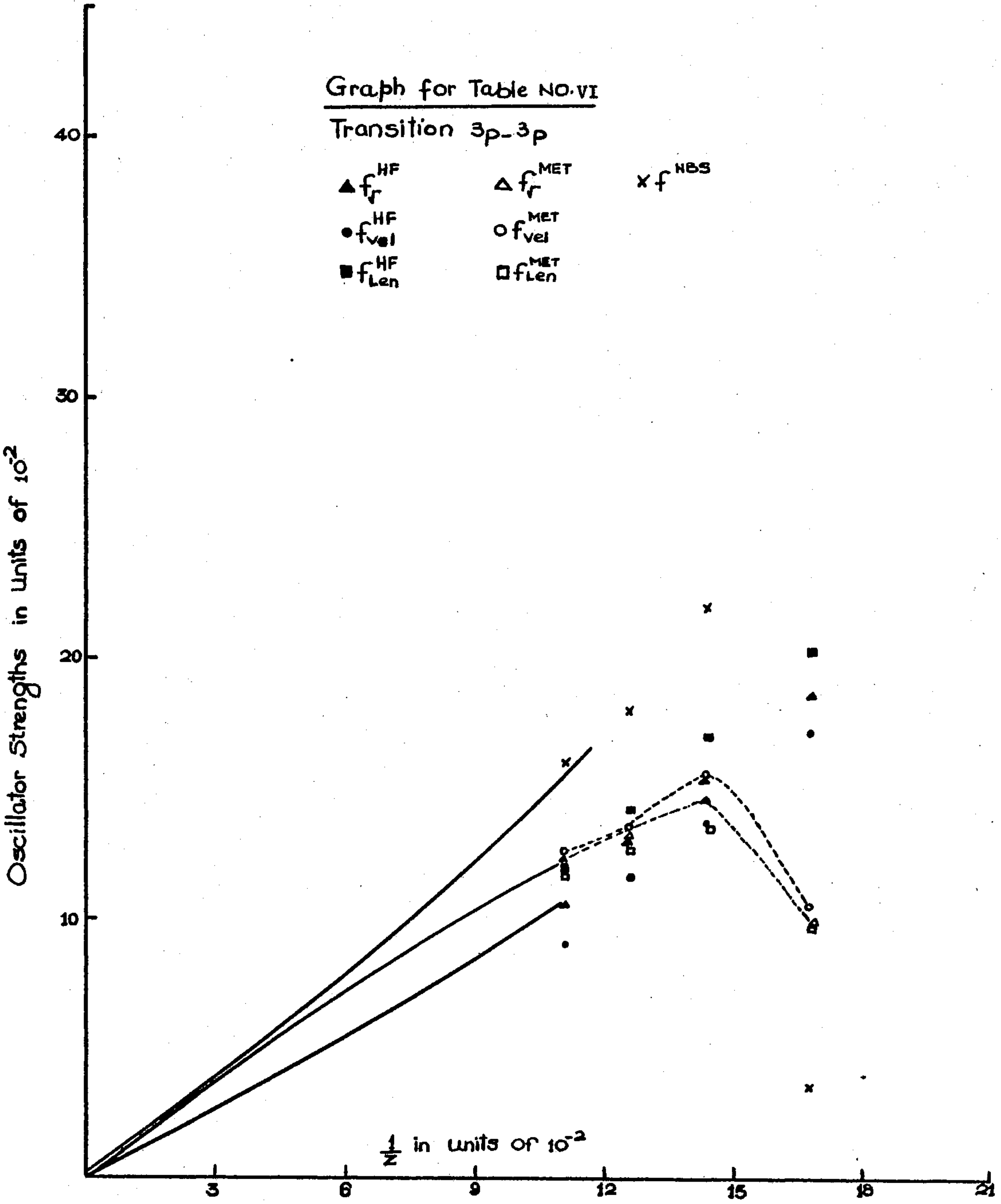

Graph for Table NO. VI
Transition 3P-3P
▲ f_r^{HF}
△ f_r^{MET}
× f^{HBS}
● f_{vel}^{HF}
○ f_{vel}^{MET}
■ f_{Len}^{HF}
□ f_{Len}^{MET}
Oscillator Strengths in Units of 10^{-2}
40
30
20
10
$\frac{1}{Z}$ in units of 10^{-2}
3
6
9
12
15
18
21

TABLE VII

$^3P \rightarrow {}^3S$

Species	Z	$\frac{1}{Z}$	Type	HF	NBS	MET
C_{I}	6	.167	Length			
			Velocity		(.27)[#]	
			Square root			
$N_{II}^{\otimes}$	7	.143	Length	.334		.218
			Velocity	.110	(.23)	.203
			Square root	.192		.210
$O_{III}^{\otimes}$	8	.125	Length	.272		.183
			Velocity	.092	(.19)	.173
			Square root	.158		.178
F^{+++}	9	.111	Length	.229		.1578
			Velocity	.085	(.16)[†]	.1621
			Square root	.139		.1599

For symbols, see Table V.

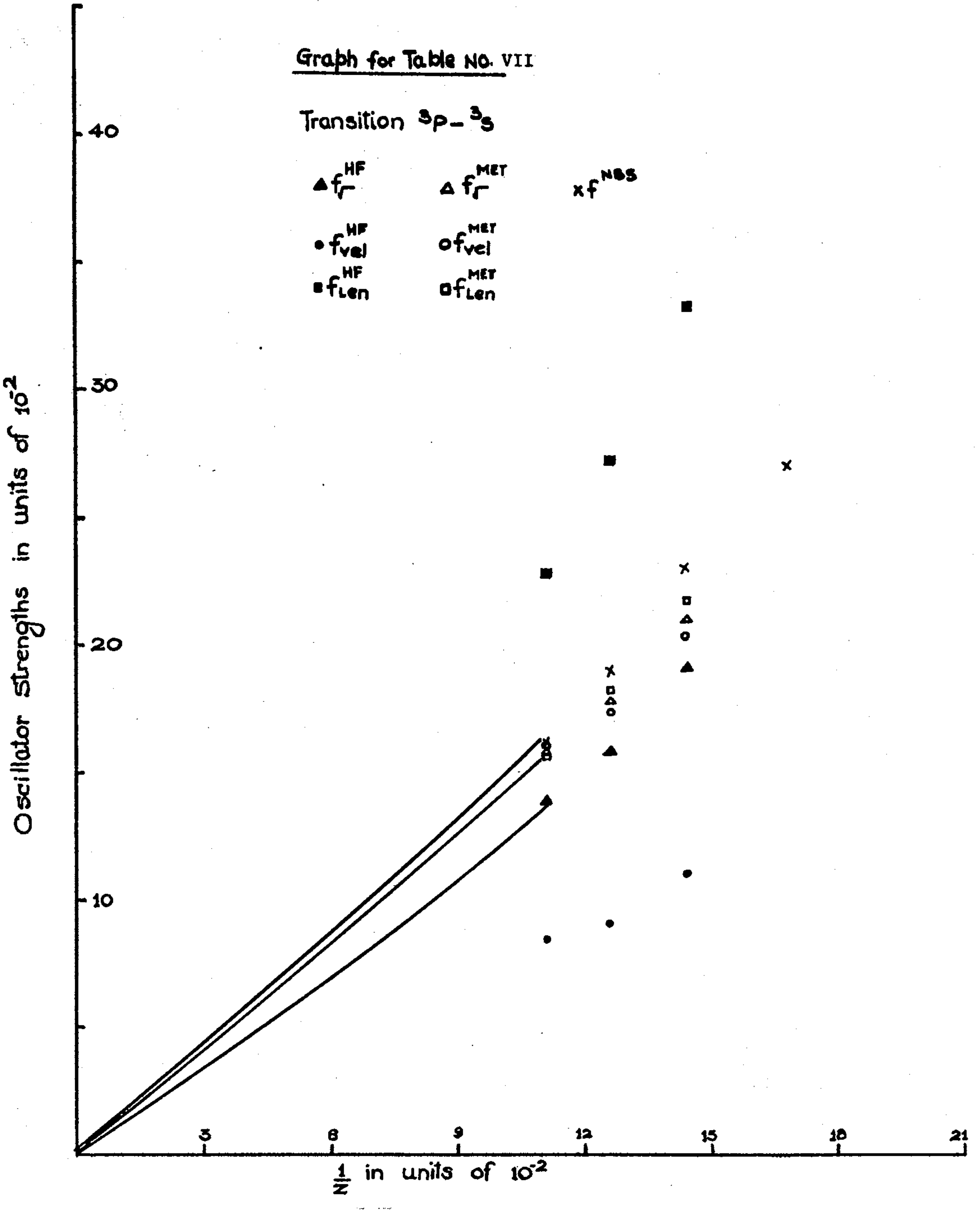

Graph for Table No. VII
Transition ³P – ³S
▲ f_r^HF
△ f_r^MET
× f^NBS
• f_vel^HF
○ f_vel^MET
■ f_Len^HF
□ f_Len^MET
Oscillator strengths in units of 10⁻²
40
30
20
10
3
6
9
12
15
18
21
1/Z in units of 10⁻²

TABLE VIII

$^1D \rightarrow {}^1D$

Species	Z	$\frac{1}{4}$	Type	HF	NBS	MET
C_I	6	.167	Length			
			Velocity			
			Square root			
$N_{II}^{\otimes}$	7	.143	Length	.651	(.45)	.314
			Velocity	.310		.327
			Square root	.449		.320
$O_{III}^{\otimes}$	8	.125	Length	.534	(.37)	.297
			Velocity	.263		.303
			Square root	.375		.300
F_{IV}	9	.111	Length	.450	(.31)†	.269
			Velocity	.234		.287
			Square root	.324		.278

For symbols, see Table V.

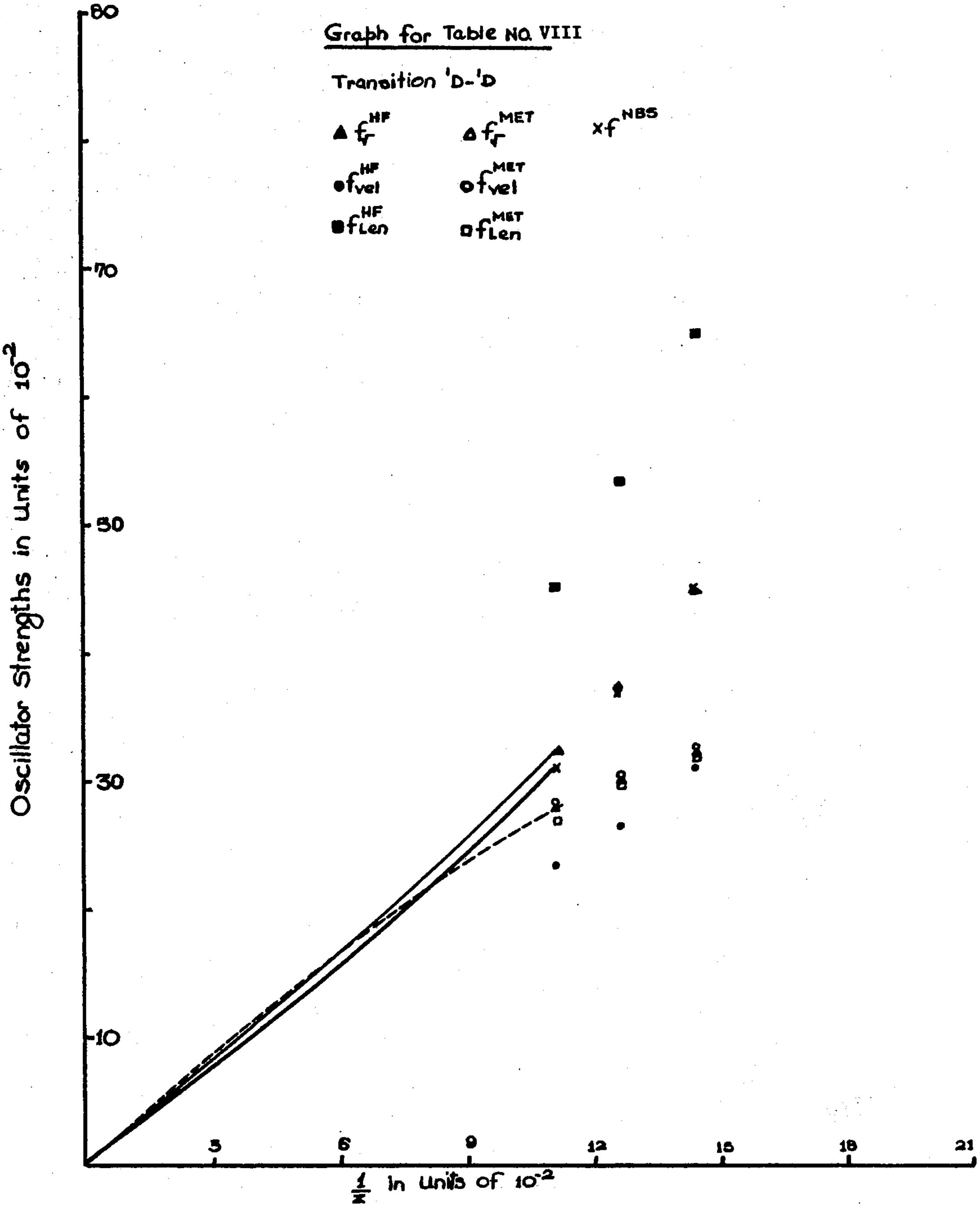

Graph for Table NO. VIII
Transition ¹D-¹D
▲ f_r^{HF}
△ f_r^{MET}
× f^{NBS}
● f_{vel}^{HF}
○ f_{vel}^{MET}
■ f_{Len}^{HF}
□ f_{Len}^{MET}
Oscillator Strengths in Units of 10^{-2}
80
70
50
30
10
3
6
9
12
15
18
21
$\frac{1}{x}$ in Units of 10^{-2}

TABLE IX

$^1D \rightarrow {}^1P$

Species	Z	$\frac{1}{Z}$	Type	HF	NBS	MET
C_I	6	.167	Length			
			Velocity			
			Square root			
N_{II}⊗	7	.143	Length	.245	(.30)	.298
			Velocity	.094		.261
			Square root	.152		.279
O_{III}⊗	8	.125	Length	.202	(.25)	.219
			Velocity	.080		.193
			Square root	.127		.206
F_{IV}	9	.111	Length	.169	(.21)†	.188
			Velocity	.069		.175
			Square root	.108		.182

For symbols, see Table V.

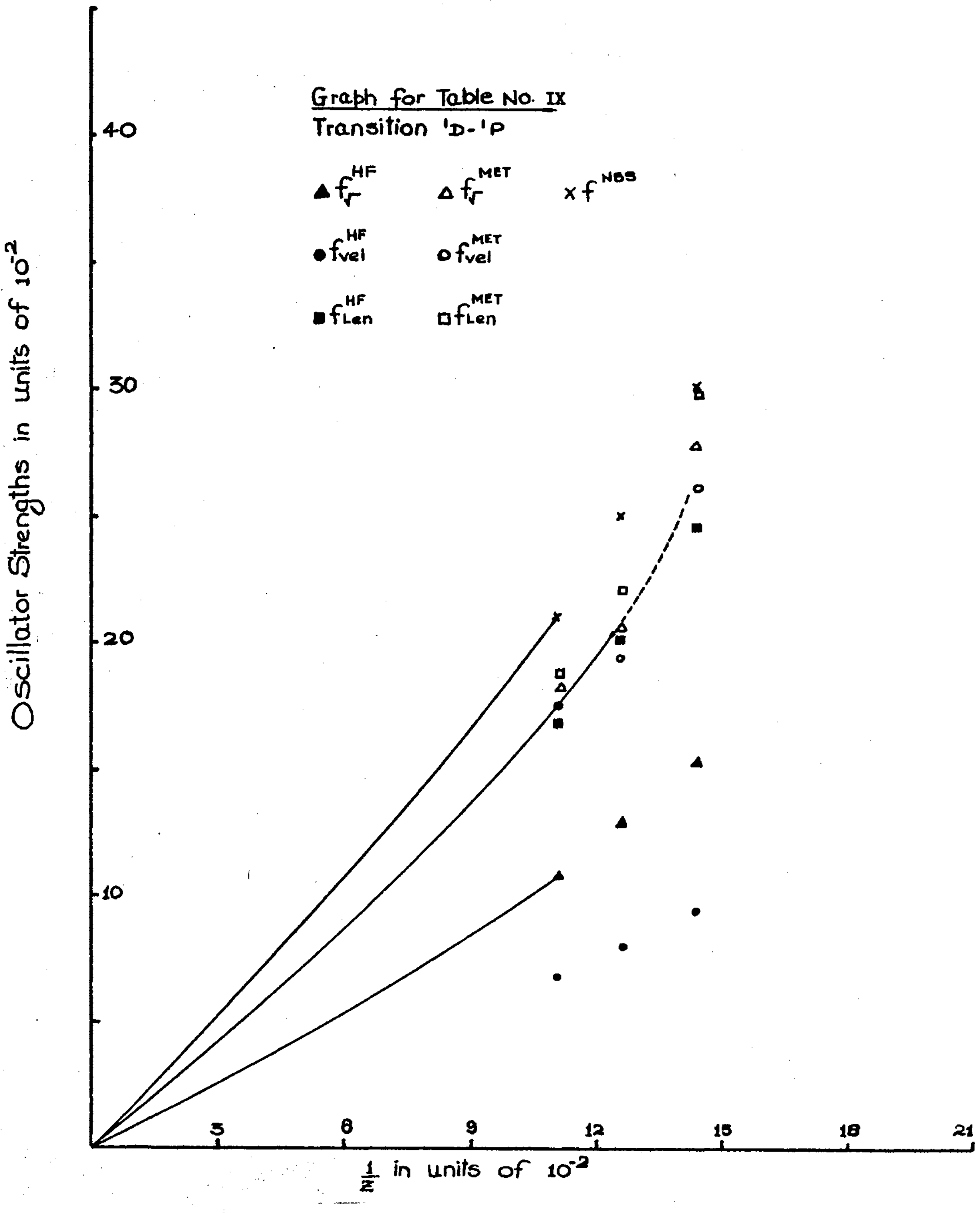
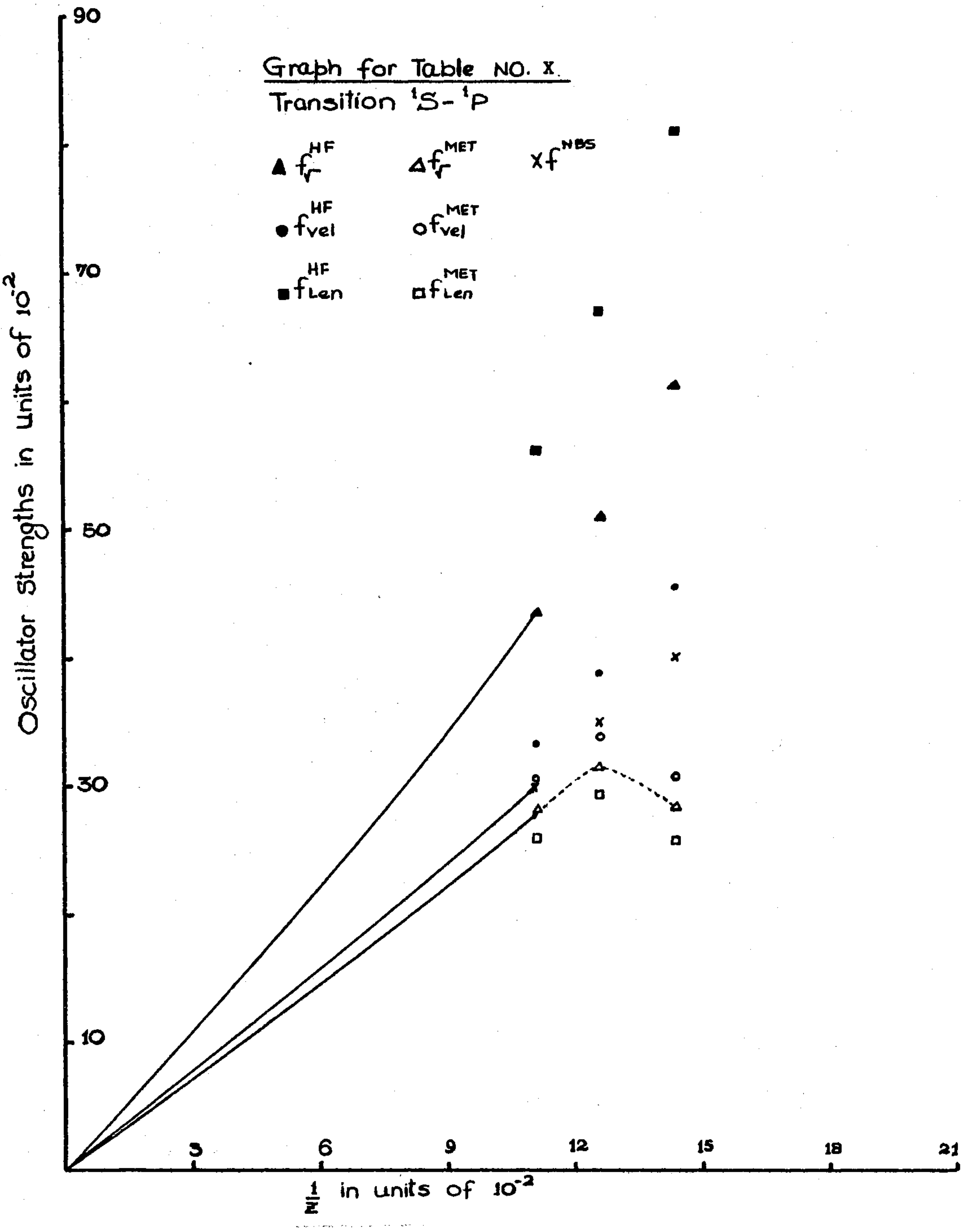

Graph for Table No. IX
Transition ¹D-¹P
▲ f_r^{HF}
△ f_r^{MET}
× f^{NBS}
● f_{vel}^{HF}
○ f_{vel}^{MET}
■ f_{Len}^{HF}
□ f_{Len}^{MET}
40
30
20
10
3
6
9
12
15
18
21
Oscillator Strengths in units of 10^{-2}
$\frac{1}{Z}$ in units of 10^{-2}

TABLE X

$^1S \rightarrow {}^1P$

Species	Z	$\frac{1}{Z}$	Type	HF	NBS	MET
C_{I}	6	.167	Length			
			Velocity			
			Square root			
N_{II} ⊗	7	.143	Length	.817	(.40)	.259
			Velocity	.457		.309
			Square root	.611		.283
O_{III} ⊗	8	.125	Length	.669	(.35)	.294
			Velocity	.388		.337
			Square root	.509		.315
F_{IV}	9	.111	Length	.569	(.30)†	.262
			Velocity	.334		.305
			Square root	.433		.283

For symbols, see Table V.


Graph for Table NO. X.
Transition ¹S-¹P
▲ f_r^HF
△ f_r^MET
× f^NBS
● f_vel^HF
○ f_vel^MET
■ f_Len^HF
□ f_Len^MET
90
70
50
30
10
Oscillator Strengths in units of 10⁻²
3
6
9
12
15
18
21
1/Z in units of 10⁻²

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APPENDIX

PROGRAM FOR THE PROJECTION OPERATOR

This includes subroutines ORDER, CONTES, COMPAR and RALO apart from main program.

This program is based on Löwdin's projector operator method. Ref: Rev. Mod. Phys. 36, 966 (1964). Let us take these subroutines one by one and see how they work.

ORDER: This subroutine separates the orbitals in every determinant into closed-open subshells and reorders the orbitlas in each subshell in ascending order. Precise manner of separation depends upon whether spin or angular momentum projection is being considered. It is convenient to separate closed subshell orbitals from open subshell orbitals and allow the projection operator to operate only on the open subshell orbitals.

CONTES: Subroutine CONTES tests and classifies the configurations of the determinants in a way described in the chapter on "Projector Operator Technique". Each configuration is numbered. Once a particular configuration number has been assigned to a determinant it does not change in a projected determinant because the projected determinant remains within the irreducible representation, that is to say the parent and daughter determinant belong to some configuration. The projection operation treats all the determinants in a particular configuration at a time.

RALO: Each factor in the projection operator as expressed in Eqn.

[23] and [24] of reference (2), is essentially in terms of the identity operator and the products of step up (M_+) and step down (M_-) operators. This subroutine brings about these operation in a desired order. The determinants resulting from applying the RAising and LOwering operators to a given determinant are computed in this routine. The corresponding coefficients of the resulting determinants are also calculated here.

COMPAR: The determinants computed in RALO along with that resulting from the identity operator are compared step by step in subroutine COMPAR. The coefficients of two identical determinants are combined together. Determinants whose coefficients add to zero are eliminated. Each successive factor in the projection operator is applied to the result of the preceeding operations.

Finally the coefficients and the determinants are written next to each other with assigned configuration numbers in the output.

PROGRAM FOR PROJECTOR OPERATOR

```
      IMPLICIT REAL*8(A-H,C-Z)
      DIMENSION COE(99),
     CJSLDET   (2,25,10),COFF(2,25),SLAG(2),SMLAG(2),DOE(25),CDET(25,25)
     C,COPP(25),ITAM(20),ISLDET(99,10),NRO(42),LORB(42),MORB(42),
     CIREP(2,42),NREP(2,21),LREP(14),NCOM(25),KSLDET(25),NPR(21),IP(21),
     CIQ(21),LSLDET(25,10),NELCS(25),NELOS(25),IJSLD(25,25,10),NDCF(25),
     CKMAX(25),NPAR(25,21),NPROD(25)
      COMMON    COE,PHASE,XMULT,COFF,CDET,SLAG,SMLAG,DOE,ISLDET,NRO,
     CLORB,MORB,IREP,NREP,LREP,INDET,ICFT,IJSLD,NPART,JSLDET,LSLDET,
     CNELCS,NELOS,NDCF,KMAX,LMAX,NPAR,LORS,K1,K2,NPROD,KREP,NTOTA
      READ(5,20) (IREP(1,I), I=1,42)
      READ(5,20) (IREP(2,I), I=1,42)
      READ(5,20) (NREP(1,I), I=1,14)
      READ(5,20) (NREP(2,I), I=1,21)
      READ(5,20) (LREP(I),I=1,14)
   20 FORMAT(16I5)
      READ (5,12) (NRO(I),LORB(I),MORB(I),I=1,42)
   12 FORMAT(3I5)
C     ***************************************************************************
C     ***************** SHORT EXPLANATION **********************
C     NTRYAL= # OF STATES TC BE PROJECTED OUT
C     NPART= # OF PARTICLES IN THE PROBLEM
C     NFUNC = #OF TYPES OF FUNCTIONS.NFUNC=1 IS HF,NFUNC=2 IS TOTAL CI
C     NFUNC=3 IS SEMI-INT PART,NFUNC=4 IS INTERNAL PART
C     SLAG(1)= TOTAL  L VALUE OF THE STATE DESIRED
C     SMLAG(1)= TOTAL ML VALUE OF THE STATE DESIRED
C     SLAG(2)= TOTAL  S VALUE OF THE STATE DESIRED
C     SMLAG(2)= TOTAL MS VALUE OF THE STATE DESIRED
C     LORS=1 IS L PROJECTICN ONLY
C     LORS=2 IS S PROJECTICN ONLY
C     FIRST ITAM READS STATE& CONFIGURATION(E.G THIS IS 1P STATE OF N+ FROM
C     1S2 2S 2P3 ETC)
C     SECOND ITAM READS KIND OF FUNCTION(E.G. *** TOTAL C.I*** ETC)
C     EMFD,INDET READ THE ENERGYCONTRIBUTION FROMTHAT KIND OF FUNCTION&NUMBER
C     OF DETTS IN THAT KIND OF FUNCTION******THEN COE&ISLDET ARE READ
C     ***************************************************************************
C     ***************************************************************************
      READ(5,9) NTRYAL
      DO 11570 ITRY=1,NTRYAL
      READ(5,9) NPART,NFUNC
      READ(5,21)(SLAG(LORS),SMLAG(LORS),LORS=1,2)
   21 FORMAT(4F5.2)
      READ(5,52) (ITAM(I),I=1,20)
      WRITE(6,52) (ITAM(I),I=1,20)
   52 FORMAT(20A4)
      WRITE(7,52) (ITAM(I),I=1,20)
      DO 11570 JTRYAL=1,NFUNC
      READ(5,22) (ITAM(I),I=1,20)
   22 FORMAT(20A4)
      WRITE(6,24) (ITAM(I),I=1,20)
      WRITE(7,22) (ITAM(I),I=1,20)
   24  FORMAT('1',20A4)
      READ(5,801) EMFD,INDET
  801 FORMAT(F13.9,I2)
      DO 3 I=1,INDET
      READ(5,903) COE(I),(ISLDET(I,J),J=1,NPART)
    3 CONTINUE
    9 FORMAT(4I5)
```

```
   11 FORMAT(06I5)
  911 FORMAT(10F11.9)
      NTP=INDET
      DO 4000 LORS=1,2
      IF (LORS-1) 700,710,720
  700  WRITE(6,701)
  701  FORMAT(' LORS IS LESS THAN 1 IN MAIN PROGRAM')
      STOP
  710 WRITE(6,905) SLAG(1),SMLAG(1)
  905 FORMAT(' FOLLOWING ARE WRITTEN AFTER L PROJECTION WITH L=',F5.2,
     C'AND ML=',F5.2)
      GO TO 725
  720     WRITE(6,906) SLAG(2),SMLAG(2)
  906 FORMAT(' FOLLOWING WRITTEN AFTER L-S PROJECTION WITH S=',F5.2,
     C'AND MS=',F5.2)
  725  CONTINUE
      SLANG=SLAG(LORS)
      SMLANG=SMLAG(LORS)
      NTOTA=NTP
      CALL ORDER
C     ICFT = TOTAL # OF "CONFIGURATIONS"INTO WHICH THE SET OF DETTS MAY
C     BE DIVIDED.
      IPR=0
      NTP=0
      IF (ICFT.EQ.0) GO TO 5000
      DO 3000 ICF=1,ICFT
      NTOP= NDCF(ICF)
      NPARTP= NELOS(ICF)
      NPART= NELOS(ICF)+NELCS(ICF)
      X=2.0D+0*SLANG
      IX=X
      DO 823 I = 1, NTOP
      DO 822 K = 1, NPARTP
  822 JSLDET(1,I,K) = IJSLD(ICF,I,K)
  823 COFF(1,I) = CDET(ICF,I)
      KLAST = 1
      LZ = NTOP
C     THE FOLLOWING STATEMENT IS A SPECIAL CASE OF ALL CLOSED "SUBSHELL"
      IF((KMAX(ICF)-IX).LT.0) GO TO 600
      IF(KMAX(ICF).EQ.0.AND.SLANG.EQ.0.0D+0) GO TO 601
      Y=2.0D+0*SMLANG
      IY=Y
   50 LMAX=(KMAX(ICF)-IY)/2+1
C     **************************************************************************
C     *IN THE 500 DO LOOP WE APPLY  LOWDIN'S PROJECTOR OPERATOR IN PRODUCT
C     * FORM, EACH VALUE OF DO LOOP PARAMETER INDEXES AFACTOR IN THE PRODUCT
C     * REFERENCE FOR THIS PROGRAM IS : PER-OLOV LOWDIN,REV.MOD.PHYS. 36
C     * 966,976 (1964)
C     **************************************************************************
      DO 500 LL=1,LMAX
      SLA=DFLOAT(LL-1)
      K1 = (3+(-1)**LL)/2
      K2 = (3+(-1)**(LL+1))/2
      NDET=LZ
C     IN THE PRODUCT,THE FACTOR, CORROSPONDING TO THE VALUE OF DESIRED L-ML
C     OR S-MS IS UNITY AND STATEMENT 80 THROUGH 400 ARE OMITTED.
      IF(SLA.EQ.(SLANG-SMLANG)) GO TO 400
   80 XMULT=1.0D+0/((SLANG-SMLANG-SLA)*     (SLANG+SMLANG+SLA+1.0D+0))
```

```
      LZ=0
C     IN THE DO LOOP 100 A GIVEN FACTOR IN THE PROJECTION OPERATOR IS APPLIED
C     TO ALL THE DETTS IN A GIVEN CONFIGURATION WHICH HAVE ARISEN IN APPLYING
C     PREVIOUS FACTORS IN THE PROJECTICN OPERATOR.
      DO 100 I=1,NDET
      LY=LZ
      FMULT=-(SLA+SMLANG)*(SLA+SMLANG+1.0D+0)+SMLANG*(SMLANG-1.0D+0)
      IF (FMULT.EQ.0.0D+0)GO TO 30
      LY=LZ+1
      DO 25KK=1,NPARTP
   25 JSLDET(K2,LY,KK) = JSLDET(K1,I,KK)
      COFF(K2,LY ) = FMULT*XMULT*COFF(K1,I)
   30 CALL RALO (LY,LZ,I,NPARTP)
  100 CONTINUE
      ISIM=1
      IF(LZ) 550,600,500
  550 WRITE(6,555)
  555 FORMAT( 'LZ IS NEGATIVE')
      STOP
  400 DO 450 I=1,NDET
      DO 440 J=1,NPARTP
  440 JSLDET(K2,I,J) = JSLDET(K1,I,J)
  450 COFF(K2,I) = COFF(K1,I)
  500 CONTINUE
      KLAST = K2
      IF (LZ.GT.0) GO TO 606
  600 WRITE(6,605) ICF
  605 FORMAT(' IN THE CONFIG SYMMETRY ABSENT IS ',I4)
      NPROD(ICF)=0
      GO TO 3000
  601 LZ=NDCF(ICF)
      COFF(KLAST, 1) = CDET(ICF,1)
      NDO=1
      IF(LZ.EQ.1) GO TO 606
      WRITE(6,602) LZ
  602 FORMAT(' STOPPED AT 602 MAIN PROG., LZ=',I5)
  606 NPROD(ICF)=LZ
      WRITE(6,990) ICF,NPRCD(ICF)
  990 FORMAT(' IN CONFIGURATION ',I2,' THERE ARE ',I3,' PROJECTED DETTS'
     C)
      DO 1000 I=1,LZ
      IPR=IPR+1
C     THE PROJECTED DETTS ARE NOW FORMED AND ARE STORED IN ISLDET.FOR EACH
C     DETT DO LOOP 950 ENTERS THE OPEN SUB-SHELL ORBITALS AND DO LOOP 975
C     ENTERS CLOSED SUB-SHELL ORBITALS
      IF(NPARTP.EQ.0) GO TO 970
      DO 950 K=1,NPARTP
  950 ISLDET(IPR,K) = JSLDET(KLAST,I,K)
      NDO=NPARTP+1
      IF(NDO.GT.NPART) GO TO 980
  970 DO 975 K=NDO,NPART
  975 ISLDET(IPR,K)= IJSLD(ICF,1,K)
  980 CONTINUE
      COE(IPR) = COFF(KLAST,I)
      PHASE=1.0D+0
      DO 982 K=1,NPART
      IF(K.EQ.NPART) GO TO 983
      KP=K+1
```

```
C     DO LOOP 982 RECORDS THE DETTS WITH THE PROPER PHASE SO THAT  THE ORBITALS
C     OCCUR IN ASCENDING ORDER.
      DO 982 KK=KP,NPART
      IF(ISLDET(IPR,K)-ISLDET(IPR,KK)) 982,981,985
  981 WRITE(6,951)
  951 FORMAT(' TWO ORBITALS SAME IN PROJECTED DETTSTOPPED BEFORE 982
     CIN MAIN PROGRAM')
      STOP
  985 MP=ISLDET(IPR,K)
      ISLDET(IPR,K)=ISLDET (IPR,KK)
      ISLDET(IPR,KK)=MP
      PHASE=(-1.0)*PHASE
  982 CONTINUE
  983 CONTINUE
      COE(IPR)=PHASE*COE(IPR)
      WRITE(6,903) COE(IPR),(ISLDET(IPR,K),K=1,NPART)
      WRITE(7,903) COE(IPR),(ISLDET(IPR,K),K=1,NPART)
  903 FORMAT(F13.9,10I3)
 1000 CONTINUE
      NTP=NTP+LZ
 3000 CONTINUE
      IF(NTP.EQ.0) GO TO 5000
 4000 CONTINUE
      WRITE(6,551) EMFD,NTP
      WRITE(7,551) EMFD,NTP
  551 FORMAT(F13.9,I2)
      GO TO 11570
 5000 WRITE(6,70)
   70 FORMAT( ' NO COMPONENT OF THIS SYMMETRY')
11570 CONTINUE
      STOP
      END
```

```
      SUBROUTINE RALO(LY,LZ,I,NPARTP)
      IMPLICIT REAL*8(A-H,C-Z)
      DIMENSION COE(99),
     CJSLDET    (2,25,10),COFF(2,25),SLAG(2),SMLAG(2),DOE(25),CDET(25,25)
     C,COPP(25),ITAM(20),ISLDET(99,10),NRO(42),LORB(42),MORB(42),
     CIREP(2,42),NREP(2,21),LREP(14),NCOM(25),KSLDET(25),NPR(21),IP(21),
     CIQ(21),LSLDET(25,10),NELCS(25),NELOS(25),IJSLD(25,25,10),NDCF(25),
     CKMAX(25),NPAR(25,21),NPROD(25)
      COMMON     COE,PHASE,XMULT,COFF,CDET,SLAG,SMLAG,DOE,ISLDET,NRO,
     CLORB,MORB,IREP,NREP,LREP,INDET,ICFT,IJSLD,NPART,JSLDET,LSLDET,
     CNELCS,NELOS,NDCF,KMAX,LMAX,NPAR,LORS,K1,K2,NPROD,KREP,NTOTA
C     *************************************************************************
C     *************************************************************************
C     * STANDARD RAISING AND LOWRING OPERATORS .OPERATIONS ARE BROUGHT UP IN
C     * DESIRED ORDER.
C     * THIS PROGRAM OPERATES ON A DETT MSLDET WITH THE OPERATOR M+M-.THE
C     * RESULTING DETTS ARE PUT IN JSLDET AND THE RESULTING COEFFICIENTS TIMES
C     * A NORMALISING DENOMINATOR ARE PUT IN COFF.
C     *************************************************************************
C     *************************************************************************
C     THE FOLLOWING BRINGS ABOUT M- OPERATION
      LY1=0
      DO 138 K=1,NPARTP
      LY1=LY1+1
      DO 135 KK=1,NPARTP
  135 LSLDET(LY1,KK) = JSLDET(K1,I,KK)
      L=LSLDET(LY1,K)
      IF(LORS.EQ.2) GO TO 125
      MM=MORB(L)
      LL=LORB(L)
      MMN=MM-1
      LSLDET(LY1,K)= L-2
      IF (MMN.LT.(-LL)) GO TO 137
      IF(K.EQ.1      ) GO TO 136
      KP=K-1
      IF(LSLDET(LY1,K).EQ.LSLDET(LY1,KP)) GO TO 137
  136 L1=(LL+MM)
      L2=(LL-MM+1)
      GO TO 139
  125 IF((2*(L/2)-L).EQ.0) GO TO 137
      LSLDET(LY1,K)=L+1
      L1=1
      L2=1
  139 COPP(LY1) =DSQRT(DFLOAT(L1*L2))*COFF(K1,I)
      GO TO 138
  137 LSLDET(LY1,K)=L
      LY1=LY1-1
  138 CONTINUE
      IF (LY1.EQ.0) RETURN
C     THE FOLLOWING BRINGS ABOUT M+ OPERATION ON THE OUT PUT DETTS     OF M-.
      DO 150 LLL=1,LY1
      DO 38K=1,NPARTP
      LY=LY+1
      DO 35 KK=1,NPARTP
   35 KSLDET(KK) = LSLDET(LLL,KK)
      L = KSLDET(K)
      IF(LORS.EQ.2) GO TO 25
      MM=MORB(L)
```

```
      LL=LORB(L)
      MMN=MM+1
      KSLDET(K) = L + 2
      IF (MMN.GT.LL) GO TO 37
      IF(K.EQ.NPARTP) GO TO  36
      KP=K+1
      IF(KSLDET(K).EQ. KSLDET(KP)) GO TO 37
   36 L1=(LL-MM)
      L2=(LL+MM+1)
      GO TO 39
   25 IF((2*(L/2)-L).NE.0) GO TO  37
      KSLDET(K)=L-1
      L1=1
      L2=1
   39 COFF(K2,LY) = DSQRT(DFLOAT(L1*L2))*XMULT*COPP(LLL)
      DO 30 KK = 1,NPARTP
   30 JSLDET(K2,LY,KK) = KSLDET(KK)
      GO TO  38
   37 LY = LY - 1
   38 CONTINUE
      IF(LY.EQ.0) GO TO 1399
      CALL        COMPAR (LY,LZ,NPARTP)
 1399 LZ=LY
  150 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE COMPAR (LY,LZ,NPARTP)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION COE(99),
     CJSLDET   (2,25,10),COFF(2,25),SLAG(2),SMLAG(2),DOE(25),CDET(25,25)
     C,COPP(25),ITAM(20),ISLDET(99,10),NRO(42),LORB(42),MORB(42),
     CIREP(2,42),NREP(2,21),LREP(14),NCOM(25),KSLDET(25),NPR(21),IP(21),
     CIQ(21),LSLDET(25,10),NELCS(25),NELOS(25),IJSLD(25,25,10),NDCF(25),
     CKMAX(25),NPAR(25,21),NPROD(25)
      COMMON    COE,PHASE,XMULT,COFF,CDET,SLAG,SMLAG,DOE,ISLDET,NRO,
     CLORB,MORB,IREP,NREP,LREP,INDET,ICFT,IJSLD,NPART,JSLDET,LSLDET,
     CNELCS,NELOS,NDCF,KMAX,LMAX,NPAR,LORS,K1,K2,NPROD,KREP,NTOTA
C     ****************************************************************************
C     * THIS ROUTINE COMPARES DETTS TO SEE IF SOME ARE IDENTICAL. IF IT IS SO
C     * THEIR COEFFICIENTS ARE ADDED AND IF THE RESULTING COEFFICIENTS TURN OUT
C     * TO BE ZERO, THEN THOSE DETTS ARE THROWN AWAY
C     ****************************************************************************
      SMALL=0.00000001D+0
      NQ=0
      KM=LZ
  600 KM=KM+1
      IF(KM-LY) 601,601,799
  601 CONTINUE
      JM=0
  700 JM=JM+1
      IF(JM-KM) 702,600,600
  702 K=0
  701 K=K+1
      IF(K-NPARTP)705,705,706
  705 IF(JSLDET(K2,KM,K)-JSLDET(K2,JM,K)) 700, 701, 700
  706 COFF(K2,JM) = COFF(K2,JM) + COFF(K2,KM)
      NQ=NQ+1
      NCOM(NQ)=KM
      GO TO 600
  799 CONTINUE
      NQMAX=NQ
      IK=0
      MQ=0
      DO 901 J = 1,LY
      NQ=MQ+1
      IF(NQ.GT.NQMAX) GO TO 906
      IF(NCOM(NQ)-J) 906,905,906
  906 IF(DABS(COFF(K2,J)).LT.SMALL) GO TO 920
  915 IF (MQ.EQ.0.AND.IK.EQ.0) GO TO 907
  916 LQ= J-MQ-IK
      COFF(K2,LQ) = COFF(K2,J)
      DO 904 K=1,NPARTP
  904 JSLDET(K2,LQ,K) = JSLDET(K2,J,K)
      GO TO 900
  920 IK=IK+1
      COFF(K2,J) = 0.0D+0
      GO TO 900
  905 MQ=MQ+1
  907 CONTINUE
  900 CONTINUE
  901 CONTINUE
 1000 CONTINUE
      LY = LY - MQ - IK
      RETURN
```

```
      SUBROUTINE CONTES (III,ICF)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSICN COE(99),
     CJSLDET    (2,25,10),CCFF(2,25),SLAG(2),SMLAG(2),DOE(25),CDET(25,25)
     C,COPP(25),ITAM(20),ISLDET(99,10),NRO(42),LORB(42),MORB(42),
     CIREP(2,42),NREP(2,21),LREP(14),NCOM(25),KSLDET(25),NPR(21),IP(21),
     CIQ(21),LSLDET(25,10),NELCS(25),NELOS(25),IJSLD(25,25,10),NDCF(25),
     CKMAX(25),NPAR(25,21),NPROD(25)
      COMMON    COE,PHASE,XMULT,COFF,CDET,SLAG,SMLAG,DOE,ISLDET,NRO,
     CLORB,MORB,IREP,NREP,LREP,INDET,ICFT,IJSLD,NPART,JSLDET,LSLDET,
     CNELCS,NELOS,NDCF,KMAX,LMAX,NPAR,LORS,K1,K2,NPROD,KREP,NTOTA
C     **********************************************************************
C     * THIS SUBROUTINE TESTS TO SEE IF PRESENTLY CONSIDERED DETT WITH PROPERLY
C     * ORDERED ORBITALS BELCNGS TO THE SAME "CONFIGURATION" AS ONE OF THE
C     * PREVIOUS DETT. ICF LABELS "CONFIGRATION" AND NDCF(ICF) WILL BE # OF DETT
C     * -S IN CONFIGURATION ICF.
C     **********************************************************************
      ICF1=ICF-1
      IF (ICF1.EQ.0) GO TO 13
      DO 8 I= 1,ICF1
      JJ=0
    4 JJ=JJ+1
      IF(JJ.GT.KREP) GO TO 10
      IF(NPAR(ICF,JJ)-NPAR(I,JJ))8,4,8
    8 CONTINUE
      GO TO 13
   10 NDCF(I)= NDCF(I)+1
      N=NDCF(I)
C     *IJSLD(I,N,KK)= IJSLD(CONFIGURATION # ICF,DETT # N IN THE CONFI., ORBITAL
C     * INDEX.)
      DO 11 KK=1,NPART
   11 IJSLD(I,N,KK)= ISLDET(III,KK)
      CDET(I,N)= PHASE*COE(III)
      DO 12 J=1,KREP
   12 NPAR(ICF,J)=0
      NELOS(ICF)=0
      NELCS(ICF)=0
      ICF=ICF-1
      GO TO 15
   13 NDCF(ICF)=1
      N= NDCF(ICF)
      DO 14 KK=1, NPART
   14 IJSLD(ICF,N,KK)= ISLDET(III,KK)
      CDET(ICF,N)= PHASE* COE(III)
   15 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE ORDER
      IMPLICIT REAL*8(A-H,C-Z)
      DIMENSION COE(99),
     CJSLDET    (2,25,10),COFF(2,25),SLAG(2),SMLAG(2),DOE(25),CDET(25,25)
     C,COPP(25),ITAM(20),ISLDET(99,10),NRO(42),LORB(42),MORB(42),
     CIREP(2,42),NREP(2,21),LREP(14),NCOM(25),KSLDET(25),NPR(21),IP(21),
     CIQ(21),LSLDET(25,10),NELCS(25),NELOS(25),IJSLD(25,25,10),NDCF(25),
     CKMAX(25),NPAR(25,21),NPROD(25)
      COMMON     COE,PHASE,XMULT,COFF,CDET,SLAG,SMLAG,DOE,ISLDET,NRO,
     CLORB,MORB,IREP,NREP,LREP,INDET,ICFT,IJSLD,NPART,JSLDET,LSLDET,
     CNELCS,NELOS,NDCF,KMAX,LMAX,NPAR,LORS,K1,K2,NPROD,KREP,NTOTA
C     WE WANT COMPUTATION TO BE DONE ONLY ON THE NON CLOSED SHELL
C     THEREFORE KEEP THE CLCSED SHELL AWAAYIN THE BIGINING AND ADD IT
C     LATER
C     THE FOLLOWING CHECKS  IF WE HAVE A CLOSED SHELL
      KREP=7*LORS+7
      ICF=0
      III=0
      IF( NTOTA.EQ.0) RETURN
      DO 300 JJJ=1, NTOTA
      DO 5K=1,KREP
      IP(K)=0
      IQ(K)=0
      MS=0
      ML=0
    5 NPR(K)=0
      PHASE=1.0D+0
      IF(LORS.EQ.2) GO TO 101
C     NOW WE ARE BRANCHING OFF TO EITHER L OR S ORDERING
      II=0
C     FOLLOWING SEPARATES THE ORBITALS IN A GIVEN DETT, FIRST ODD ONES(ALPHA),
C     THEN EVEN ONES (BETA).
      DO 120L=1,2
      DO 10 I=1,NPART
      KK=2*(ISLDET(JJJ,I)/2)-ISLDET(JJJ,I)
      IF(KK.EQ.0.AND.L.EQ.1.OR.   KK.EQ.-1.AND.L.EQ.2) GO TO 10
      II=II+1
        KSLDET(II)= ISLDET(JJJ,I)
      J=KSLDET(II)
      ML=ML+MORB(J)
      MS=MS+(-1)**(J+1)
      IF(L.EQ.2) GO TO 10
   14 PHASE=((-1.0)**(II-I))*PHASE
   10 CONTINUE
      IF(L.EQ.2) GO TO 120
      NALPHA=II
  120 CONTINUE
      IF(DFLOAT(ML).NE.SMLA G(1).OR.DFLOAT(MS)/2..NE.SMLA G(2)) GO TO
     C450
C     NOW TO ARRANGE THESE ORBITALS IN ASCENDING ORDER, ODD AMONG ODD AND EVEN
C     AMONG EVEN.
C     UPTO 92 ORDES FOR L PROJECTION.
      IF (NALPHA.EQ.0) GO TO 90
      DO 80 J=1,NALPHA
      IF (J.EQ.NALPHA) GO TO 90
      JP=J+1
      DO80 JJ=JP,NALPHA
      IF (KSLDET(J)-KSLDET(JJ))80,81,85
```

```
   81 WRITE(6,50)
   50 FORMAT(83H TWO ORBITALS ARE SAME IN THE INPUT DETT AND COMPUTATION
     CSTOPPED BEFORE STATEMENT 81)
      STOP
   85 MP=KSLDET(J)
      KSLDET(J)=KSLDET(JJ)
      KSLDET(JJ)=MP
      PHASE= (-1.0)*PHASE
   80 CONTINUE
   90 NBETA=NPART-NALPHA
      IF(NBETA.EQ.0) GO TO 92
      NDBET=NALPHA+1
      DO 82 J= NDBET,NPART
      IF(J.EQ.NPART) GO TO 92
      JP=J+1
      DO 82 JJ=JP,NPART
      IF(KSLDET(J)-KSLDET(JJ))82,83,87
   83 WRITE(6,51)
   51 FORMAT('TWO ORBITALS SAME,STOPPED BEFORE STATEMENT 83')
      STOP
   87 MP=KSLDET(J)
      KSLDET(J)=KSLDET(JJ)
      KSLDET(JJ)=MP
      PHASE= (-1.0)*PHASE
   82 CONTINUE
   92 CONTINUE
      IF (LORS.EQ.1) GO TO 94
C     UP TO STATEMENT 102 ORDERS FOR S PROJECTION.
  101 DO 6 J=1,NPART
    6 KSLDET(J)= ISLDET(JJJ,J)
      DO 180 J= 1, NPART
      IF(J.EQ.NPART) GO TO 102
      JP=J+1
      DO 180 JJ= JP,NPART
      IF(KSLDET(J)-KSLDET(JJ)) 180,181,185
  181 WRITE(6,151)
  151 FORMAT( ' TWO ORBITALS ARE SAME IN THE DETT STOPPED BEFORE
     CSTATEMENT 181 IN ORDER')
      STOP
  185 MP=KSLDET(J)
      KSLDET(J)=KSLDET(JJ)
      KSLDET(JJ)=MP
      PHASE=(-1.0)*PHASE
  180 CONTINUE
  102 CONTINUE
   94 CONTINUE
C     ¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬
C     BEGINING OF CLASSIFICATION OF ORBITALS INTO "SUB- SHELLS" AND DETERMINING
C     WHICH SUB-SHELLS ARE FILLEC(CLOSED SUBSHELL) AND WHICH ARE PARTIALLY
C     FILLED(OPEN SUBSHELL).ICF WILL LABEL A CONFIGURATION. A CONFIGURATION IS
C     GIVEN BY BY LISTING THE OCCUPANCY OF THE "SUB SHELLS". THIS OCCUPANCY IS
C     STORED IN NPAR(ICF,J)
C     ***********************************************************************
      III=III+1
      ICF=ICF+1
      DO 100I=1,NPART
      L=KSLDET(I)
      J=IREP(LORS,L)
```

```
      NPR(J)=NPR(J)+1
  100 CONTINUE
C     NPR= # OF ORBITALS IN A PARTICULAR "SUBSHELL".
C     NPARTP= TOTAL # OF PARTICLES IN OPEN SUBSHELL.
      NPARTP=0
      NC=0
      KMAX(ICF)=0
      DO 175 J=1,KREP
      NPAR(ICF,J)=NPR(J)
      IF(LORS.EQ.2) GO TO 401
      KMAX(ICF)= KMAX(ICF)+NPR(J)*(2*LREP(J)+1-NPR(J))
      IF(LORS.EQ.1) GO TO 400
  401 KMAX(ICF)=KMAX(ICF)+NPR(J)*(2-NPR(J))
  400 IF (NPR(J))130,175,125
  130 WRITE(6,135)
  135 FORMAT(1X'STOPPED BEFORE STATEMENT 130')
      STOP
C     IN THE FOLLOWING ,GOING TO STATEMENT 175 MEANS WE HAVE A CLOSED SUBSHELL
C     AND GOING TO  STATEMENT 150 MEANS WE HAVE AN OPEN SUB-SHELL,THAT IS THE TY
C     PE WE WANT TO PROJECT.
  125 IF(NPR(J)-NREP(LORS,J)) 150,175,160
  160 WRITE(6,165)
  165 FORMAT(' STOPPED BEFORE STATEMENT 160 IN ORDER')
      STOP
  150 NC=NC+1
      NPARTP=NPARTP+NPR(J)
      IP(NC)=J
C     THE ABOVE GIVES ORBITALS NOT IN CLOSED SHELL
  175 CONTINUE
C     IF THERE ARE NO OPEN SUB-SHELLS WE WANT TO GO AT THE END OF THE PROGRAM
C     WE NOW SEPARATE OPEN AND CLOSED SUB-SHELL.
      IF(NC.EQ.0) GO TO 952
      IF(LORS.EQ.2) GO TO 402
      II=0
      DO 136 L=1,2
      DO 15 I=1,NC
      KK=2*(IP(I )/2)-IP(I)
      IF(KK.EQ.0.AND.L.EQ.1.OR.KK.EQ.-1.AND.L.EQ.2) GO TO 15
      II=II+1
      IQ(II)=IP(I)
   15 CONTINUE
      IF(L.EQ.2) GO TO 136
      MAX=II
  136 CONTINUE
C     THE FOLLOWING SEPARATES OPEN SUB-SHELLS & PLACES THEM TO L.H.S AND CLOSED
C     SUB-SHELL TO THE R.H.S.
  402 JO=0
      JC=NPARTP
      KKK=0
      K=1
      I=1
    1 IF(I.GT.NPART) GOTO 95
      L=KSLOET(I)
      J=IREP(LORS,L)
      IF (LORS.EQ.2) GO TO 403
      IF(J.NE.IQ(K)) GO TO 55
      IF(LORS.EQ.1) GO TO 404
  403 IF(J.NE.IP(K)) GO TO 55
```

```
404 KUP=NPR(J)
    JUP=KUP+I-1
    DO 40 LL=I,JUP
    JO=JO+1
    PHASE=PHASE*(-1.0)**KKK
 40 ISLDET(III,JO)=KSLDET(LL)
    K=K+1
    GO TO 88
 55 CONTINUE
    KUP=NPR(J)
    JUP=KUP+I-1
    DO 60 LL=I,JUP
    JC=JC+1
    ISLDET(III,JC)=KSLDET(LL)
 60 CONTINUE
    KKK=KKK+NREP(LORS,J)
 88 I=I+KUP
    GO TO 1
 95 CONTINUE
    GO TO 97
952 DO 953 JC=1,NPART
953 ISLDET(III,JC)=KSLDET(JC)
 97 CONTINUE
    NELOS(ICF)=NPARTP
    NELCS(ICF)=NPART-NPARTP
 98 CONTINUE
    CALL CONTES(III,ICF)
    GO TO 300
450 WRITE(6,420) JJJ
420 FORMAT(' DETT',I3,'HAS BEEN THROWN AWAY')
300 CONTINUE
    ICFT=ICF
    RETURN
    END
```

SAMPLE OUTPUT

```
                *********** TOTAL CI***********
FOLLOWING ARE WRITTEN AFTER L PROJECTION WITH L= 0.0 AND ML= 0.0
IN CONFIGURATION  1 THERE ARE   3 PROJECTED DETTS
 0.408248300  1  2  3  5  8 10
 0.408248300  1  2  3  6  7 10
 0.408248300  1  2  3  6  8  9
IN CONFIGURATION  2 THERE ARE   3 PROJECTED DETTS
-0.408248300  1  2  4  5  8  9
-0.408248300  1  2  4  5  7 10
-0.408248300  1  2  4  6  7  9
IN CONFIGURATION  3 THERE ARE   6 PROJECTED DETTS
 0.000854982  1  2  4  5 10 15
-0.000854982  1  2  4  7 10 13
-0.000854982  1  2  4  5  8 17
-0.000854982  1  2  4  8  9 13
-0.000854982  1  2  4  6  7 17
 0.000854982  1  2  4  6  9 15
IN CONFIGURATION  4 THERE ARE   3 PROJECTED DETTS
 0.012418971  1  2  5  8  9 12
 0.012418971  1  2  5  7 10 12
 0.012418971  1  2  6  7  9 12
IN CONFIGURATION  5 THERE ARE   9 PROJECTED DETTS
 0.034923114  1  2  5  8  9 24
-0.017461557  1  2  5  7 10 24
 0.030244304  1  2  5  7  8 26
-0.017461556  1  2  6  7  9 24
-0.030244303  1  2  5  6  9 26
-0.030244303  1  2  7  8  9 22
 0.030244304  1  2  5  9 10 22
 0.042771904  1  2  5  6  7 28
-0.042771904  1  2  7  9 10 20
IN CONFIGURATION  6 THERE ARE   9 PROJECTED DETTS
-0.030244304  1  2  7  8 10 21
 0.017461557  1  2  5  8 10 23
-0.042771904  1  2  8  9 10 19
 0.030244303  1  2  6  9 10 21
-0.034923113  1  2  6  7 10 23
-0.030244304  1  2  5  6 10 25
 0.017461556  1  2  6  8  9 23
 0.030244303  1  2  6  7  8 25
 0.042771904  1  2  5  6  8 27
IN THE CONFIG SYMMETRY ABSENT IS     7
IN CONFIGURATION  8 THERE ARE   6 PROJECTED DETTS
 0.000854982  1  2  3  5  8 18
 0.000854982  1  2  3  6  7 18
-0.000854982  1  2  3  5 10 16
-0.000854982  1  2  3  6  9 16
 0.000854982  1  2  3  7 10 14
 0.000854982  1  2  3  8  9 14
IN THE CONFIG SYMMETRY ABSENT IS     9
IN CONFIGURATION 10 THERE ARE   3 PROJECTED DETTS
-0.002974576  1  2  3  6 10 15
 0.002974576  1  2  3  8 10 13
 0.002974576  1  2  3  6  8 17
IN THE CONFIG SYMMETRY ABSENT IS    11
IN THE CONFIG SYMMETRY ABSENT IS    12
IN THE CONFIG SYMMETRY ABSENT IS    13
IN CONFIGURATION 14 THERE ARE   3 PROJECTED DETTS
-0.012418971  1  2  5  8 10 11
-0.012418971  1  2  6  7 10 11
-0.012418971  1  2  6  8  9 11
IN THE CONFIG SYMMETRY ABSENT IS    15
IN CONFIGURATION 16 THERE ARE   3 PROJECTED DETTS
-0.002974576  1  2  4  5  7 18
```

VITA

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Candidate for the Degree of

Master of Science

Thesis: ELECTRIC DIPOLE TRANSITIONS IN CARBON ISOELECTRONIC SEQUENCE UNDER PURE STATES OBTAINED FROM SUPERPOSITION OF CONFIGURATION

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