CHAPTER - I

Theoretical approach for atomic Structure
Calculations

One electron systems (like H- atom) are two body problems whose exact solutions involving even the relativistic quantum mechanics have been worked out satisfactorily. For more than one electron system (many body problem), many electron configurations, the theoretical treatment becomes so complex that it becomes almost impossible to obtain an exact solution. The theoretical treatment is generally based on the assumption that the electron may be regarded to the first approximation as moving independently in a Central field which arises as a net result of the positive charge of the nucleus and the average distribution of the negative charges of the electrons. This is so called Central Field Approximation. The state of the atom is then characterized by assigning definite \( n \) and \( \ell \) value to each electron. Even though the quantum mechanical validity of this description is limited, but it at least gives a starting point to the description. In this approximation the energy depends on the charge distribution in the different electronic shells and on the quantum numbers \( n \) and \( \ell \) but is independent of the mutual orientation of electron orbits and spin. Latter on these effects can be introduced as perturbation which splits the state into a number of terms corresponding to different combinations of \( m_\ell \) and \( m_s \) of valence electrons.

The generalized Schrödinger’s equation for \( n \)- electrons describing electrostatic interactions is
\[
\sum_i \left\{ -\frac{\hbar^2}{2m} V_i + \sum_{i>j} \left( \frac{e^2}{r_{ij}} \right) \right\} \psi = E \psi \quad (1)
\]

Where \( \sum_{i>j} \left( \frac{e^2}{r_{ij}} \right) \) represents electrostatic repulsion between two electrons separated by a distance \( r_{ij} \).

There are no spin dependent terms in equation (1). The presence of this two electron operator prevents an immediate separation of the wave function into one electron functions. This repulsion is also a bit too large to be treated as a perturbation. The procedure is to regroup the Hamiltonian in equation (1). The strong effect of the attractive potential term \( \sum_i -Z_e^2/r_i \) is considerably reduced

the central part in the repulsive term \( \sum_{i>j} e^2/r_{ij} \). This partial cancellation is

manifested as a screening, from other electrons of the central charge by the inner electrons.

Let central part of \( \sum_{i>j} e^2/r_{ij} \) be \( \sum_i S (r_i) \)

Therefore total central potential = \( \sum_i -Z_e^2/r_i + S (r_i) = \sum_i u (r_i) \)

Thus we write (1) as

\[ H = H_0 + H_1 \]

Where \[ H_0 = \sum_i \frac{-\hbar^2}{2m} V_i + u (r_i) \]

and \[ H_1 = \sum_{i>j} \left( e^2/r_{ij} \right) - \left( \sum_i Z_e^2/r_i + u (r_i) \right) \]
We can also introduce spin orbit interaction

$$H_2 = \sum_i \xi (r_i) \vec{l}_i \cdot \vec{s}_i$$

The standard perturbation theory calculations can be carried out the angular part of the solutions give rise to angular coefficients which are functions of $\mathcal{U}$ and $m_l$ and can be calculated and tabulated once and for all. What is left in the diagonal matrix element of $e^2/r_{12}$ is a set of radial integrals (called Slater Integrals): $F^k$, which are direct integrals and $G^k$, which are exchange integrals. These are of the form:

$$F^k = e^2 \int \int_0^\infty \frac{r_<}{r_>} \left[ P_{n1} f_1(r_1) P_{n2} f_2(r_2) \right]^2 dr_1 dr_2$$

$$G^k = e^2 \int \int_0^\infty \frac{r_<}{r_>} \left[ P_{n1} f_1(r_1) P_{n2} f_2(r_1) P_{n1} f_1(r_2) P_{n2} f_2(r_2) \right] dr_1 dr_2$$

Where, $r<$ is lesser of $r_1$ and $r_2$, and $r>$ is the greater.

$P_{n\ell}(r)$ are Legendre Polynomials.

$k = $ Extends over a small integral. It should satisfy two conditions

$$|\ell_1 - \ell_2| \leq k \leq |\ell_1 + \ell_2|$$
where $I$'s are orbital angular momentum. $k$ must also obey that $I_1+I_2+k = \text{even integer}$ [these conditions are imposed so that the coefficient in the matrix elements of $e^2$ should not vanish].

For $F^k$'s the sets are $(k, I_1, I_1), (k, I_2, I_2)$ whereas for $G^k$ the sets are $(k, I_1, I_2)$. Higher is $k$, lower are the value of $F^k$ and $G^k$.

$F^k$ and $G^k$ have to be worked out with a knowledge of radial wave functions. Since these wave functions are not known or not expressible in a simple way, these integrals are usually not evaluated but are treated as adjustable parameters in application to observed spectra.

The integrals appearing in the formula express the energy arising from the mutual interactions of two electrons.

**$F^k$ Integrals**: represent that part of the electrostatic energy which depends on the $\mathbf{I}$ vectors and is responsible for the separation of terms with different $L$-values in the LS-Coupling. e.g. in p.p configuration separation of $^3F$, $^3D$ and $^3P$.

**$G^k$ Integrals**: give energies due to the exchange forces which depend on the spin orientations. They cause the splitting of terms with same $L$ but different $S$ (multiplicity) viz. $^1F$ and $^3F$.

After they have been evaluated, spin orbit interaction acting as perturbation gives fine structure splitting i.e. $^3F_4$, $^3F_3$, $^3F_2$ etc with spin orbit interaction parameter $\zeta$. 


In case of two electrons, one of which is in an s orbit and the other is in an arbitrary orbit \( n_l \), the terms are given by the expressions: [1]

\[
\begin{align*}
ns \ n_l & : \\
1S & = F^0 + G^L \\
3L & = F^0 - G^L \\
\end{align*}
\]

\( F^k \) and \( G^k \) are positive quantities therefore singlets are higher than the triplets, this generally agrees well with experimental observations except for a few cases where interaction is too large and that causes mixing of the levels.

For np np configurations the relationship is as:

\[
\begin{align*}
np \ np & : \\
1S, 3S & = F^0 + 10 F^2 \pm (G^0 + 10G^2) \\
1P, 3P & = F^0 - 5 F^2 \mp (G^0 - 5G^2) \\
1D, 3D & = F^0 + F^2 \pm (G^0 + G^2) \\
\end{align*}
\]

Since \( G^k \) decrease rapidly with \( k \), the quantities in parenthesis could be treated as positive. Note that even though \( 1S \) and \( 1D \) are higher than \( 3S \) and \( 3D \); \( 1P \) is lower than \( 3P \). The \( 3S \), is also lower than \( 3P \). Thus Hund’s empirical rule is only an approximate rule. The expression for equivalent electrons can be derived from those of the non equivalent electrons by omitting \( G \)’s, for instance.
The formula for any \( k \) in \( p^k \) is

\[
\begin{align*}
\hbar^2 \quad &\begin{cases}
1S = F^0 + 10F^2 \\
1D = F^0 + F^2 \\
3P = F^0 - 5F^2
\end{cases} \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ Quad
From (i) \[
\frac{E^{(1S)} - E^{(1D)}}{E^{(1D)} - E^{(3P)}} = \frac{9F^2}{6F^2} = 1.5
\]

Experimentally observed value is = 1.48

Theoretical picture of sp configuration based on the relationship given below can be seen in fig (1.2)

\[
\begin{align*}
{^1L} &= F^0 + G^L \\
{^3L} &= F^0 - G^L
\end{align*}
\]

Cowan’s Approach and Ab Initio Calculations:

As described in the preceding section, the structure for two electrons system can be worked out in principle but when you deal with complex system like three electron or even four electron system this becomes almost impossible to calculate the entire structure or to estimate the transition probabilities for different transitions. Therefore, Hartree - Fock calculations are performed with relativistic correction and correlation effects. Various computer codes have been developed for such kind of calculations like those of R.D. Cowan [2 - 4], C.F. Fisher [5], MCDF [6,7] etc. The availability of fast computers with huge memory
capacity made it possible to calculate the structure to the extent of rare earth elements. In doing so various approximations are used.

The Central Field Approximation is good enough to give good qualitative and quantitative agreement with experiment. The basic assumption in the Central-Field Approximation is that “Each electron moves in a central, or spherically symmetrical force field produced by the nucleus and other electrons” (Slater [8]). It explains the spectrum of a neutral alkali atom in fair detail. However for the complex system the torque exerted by one electron on the other was neglected in the Central Field Model, makes things more complicated. This model includes the electron spin and Pauli’s exclusion principle, and finally the Hartree’s proposal of the Self-Consistant Field method. The more successful approach by the Hartree-Fock [8] (HFS Scheme) is described very briefly as follows:

The time independent Schrodinger’s wave equation can be written as

\[(H - E) U (r_1, \theta_1, \phi_1) = 0\]  

Where \(E\) is the energy, \(H\) is the Hamiltonian and \(U\) the wave function. The one electron hydrogenic wave function as given by Slater [8] as

\[U_{n\ell m}(r, \theta, \phi) = (-1)^{m+\frac{\ell}{2}} \frac{(\frac{\ell}{2}+\frac{\ell}{2})!}{(\frac{\ell}{2}+\frac{\ell}{2})!} R_{\ell m}(r) P^{\ell m}(\cos \theta) e^{-\frac{r}{a_0}}\]
Where \( R_{nl}(r) = P_{nl}(r)/r \)

and \( R_{nl} \) or \( P_{nl} \) is normalized so that

\[
\int_{0}^{\infty} \left[ P_{nl}(r) \right]^2 dr = 1
\]

Therefore, the wave function for an atom/ion with \( N \) electrons can be constructed by taking the product of wave function of all its electron as

\[
\Psi_N(r_1, \theta_1, \varphi_1, r_2, \theta_2, \varphi_2, \ldots, r_N, \theta_N, \varphi_N) = U_{n_1l_1m_1} U_{n_2l_2m_2} \cdots U_{n_Nl_Nm_N} (r_1, \theta_1, \varphi_1) \cdots (r_N, \theta_N, \varphi_N)
\]

A more complete form of Hamiltonian for an atom can be written in general as:

\[
H = -\frac{\hbar^2}{2m} \sum_{j=1}^{N} \nabla_j^2 + \frac{1}{2M_k} \nabla_k^2 - e^2 \sum_{k} Z_k / r_{kj} + e^2 \sum_{k,l} \frac{Z_k Z_l}{r_{KL}} + e^2 \sum_{j<i} 1/r_{ij} + H_{SS} + H_{SO} + H_{hfs} + H_{etc}
\]

Where the first term represent the K.E of the electron involved, second that of nucleus, third the interaction between electrons and protons, fourth that between protons and fifth between electrons. \( H_{SS} \) represents spin-spin interaction and \( H_{SO} \) spin-orbit interaction. \( H_{hfs} \) is the hyperfine structure hamiltonian and \( H_{etc} \) stands for all additional effects left out so far.
Schrodinger’s wave equation can not be solved for such a complicated Hamiltonian. Therefore, the Central Field Approximation which was lacking electron spin part was modified by Hartree as Self- Consistant Field Method [8] where the presence of extra nuclear charge was also considered. Hartree started with the wave function of the type (B) and Hamiltonian (C) simplified to the extent of retaining only the first, third and fifth terms and rendered the solution of Schrodinger’s wave equation Self- Consistant through iteration. Though Hartree’s wave function was symmetric, his method did not include Pauli’s exclusion principle. This short-coming was removed by Fock by taking anti symmetrical wave function in what is called “Hartree- Fock (HF) method (Slater [8]). The simplest wave function which satisfies the conditions of anti- symmetrization is a determinental function of the type

\[
\Psi = (N!)^{-1/2} \begin{vmatrix}
U_1(1) & U_1(2) & \cdots & U_1(N) \\
U_2(1) & U_2(2) & \cdots & U_2(N) \\
\vdots & \vdots & \ddots & \vdots \\
U_N(1) & U_N(2) & \cdots & U_N(N)
\end{vmatrix}
\]

The linear combination of determinental function will also satisfy the condition.

Now solving these complicated equation was not an easy task. Scientists therefore, tried to make it practically feasible. Slater [8], Condon and Shortley...
Froese Fischer [5] and R.D Cowan’s [2 - 4] contribution made it possible to calculate the structure of atoms or ions. The atomic energy structure is expressed in Hartree- Fock Slater theory in the form of complicated integro- differential equation. These have been simplified so as to divide the whole complex into smaller manageable integrals, called “Slater Parameters” written in the form of $F^k, G^k, R^k$ and $\zeta_{n\mathfrak{l}}$ as explained earlier in the beginning, these integrals can be evaluated on rigorous theoretical basis [2,3,4,8,9] or treated simply as adjustable parameters in application to observed spectra.

The integral $F^k (n\mathfrak{l}, n\mathfrak{l}')$ represents that part of the electrostatic energy which depends on the orientation of the $\mathbf{L}$ vectors and is responsible for the separation of terms with different $L$-values in LS coupling notation those denoted by $G^k (n\mathfrak{l}, n\mathfrak{l}')$ are the exchange integrals that give energies due to the exchange forces which depend on the spin orientations; they cause the splitting of terms with equal $L$ but different total spin $S$, for instance the separation of singlet term from the triplet etc. In case of equivalent electrons like $p^2, p^3, d^2$ the $G^k$ parameters vanish. $\zeta_{n\mathfrak{l}}$ is the magnetic spin orbit interaction responsible for fine structure splitting.

Since R.D Cowan’s Code has been used extensively to compute the structure of the ions for the present work, its brief sketch will be presented in the following lines:

The Cowan’s Code is a set of 4 programs working in a sequence. The output from one provides the input to the other. The sequence they follow is:
The Program **RCN** calculates single-configuration radial wave functions $P_{n\ell}(r)$ for a spherically symmetrized atom. The primary input information is always to RCN. A typical example of RCN input file for Sb V is given in table 1.1. In addition to the radial wave functions, also calculated for each configuration are various radial integrals $R^k$, $F^k$, $G^k$, $\zeta$ and total energy of the atom $E_{av}$ including approximate relativistic and correlation energy corrections.

The **RCN2** accepts radial wavefunctions for one or more different configurations of one or more atoms or ions from RCN and calculates various multiple-configuration radial integrals, overlap integrals, $< P|P' >$. Configuration interaction coulomb integrals $R^k$ and spin orbit interaction integrals $\zeta_{n\ell}$ and radial electric- dipole and electric- quadrupole integrals. In its most commonly used option, it automatically computes all quantities required for calculating energy levels and spectra of an atom.

The third part of the programs **RCG** computes the angular factor of various matrix elements in the theory of Atomic Spectra [4]. The program employs Racah-algebra techniques and input containing coefficients of fractional parentage (cfp) for each subshell $\ell$ involved in the electron configurations.
The angular factors are:

(i) Coefficients of unit matrix $E_{av}$, the centre of gravity of each configuration.

(ii) The coefficients $f_k$, $g_k$, and $d$ of the single configuration direct and exchange Coulomb interaction ($F^k$ and $G^k$) and spin orbit interaction $\zeta$ radial integrals and the coefficient $r^d_k$ and $r^e_k$ of the direct and exchange configuration interaction coulomb radial integrals $R^k$ which are involved in the calculation of the Hamiltonian (energy level) matrix elements.

(iii) The magnetic- dipole matrix elements and the angular coefficients of the electric- dipole and electric- quadrupole reduced matrix elements;

$$P_{l1} = \langle \ell | r^1 | \ell \rangle$$

also possible are angular coefficients of certain effective- coulomb interaction operator $\alpha$, $\beta$, $\gamma$, $T$, $T_1$ and $T_2$ and “illegal - k” operators $F^k$ and $G^k$ used in representing weak configuration- interaction effects. If numerical values of the radial integrals $E_{av}$, $F^k$, $G^k$, $\zeta$, $R^k$ are provided, energy levels and intermediate-coupling eigenvectors are computed. If numerical values of the electric dipole integrals are supplied, then the energy levels and eigenvectors are used to compute the spectrum line, wavelengths, the associated oscillator strengths and
radiative transition probabilities. Usually all these inputs are automatically provided by the program RCN2.

RCG can also calculate the photo ionization cross sections, autoionization transition probabilities and plane wave Born electron impact collision strength [8].

RCE is the least squares fitting programs. When sufficient numbers of energy levels are established then these experimental levels are used to adjust the Slater Parameters according to the experimental levels. The unknown levels are then predicted more precisely and becomes easier to establish.

The fitting process is carried out by an automatic iterative procedure until the parameter values no longer change from one iteration cycle to the next by more than 0.03 cm$^{-1}$ or for a specified maximum number of cycles. The iteration can be carried out in any one of the seven angular-momentum coupling schemes available in program RCG. Final eigen vectors are printed in the desired representation. Finally when all or most of the levels are experimentally known, the fitted parameters are used back in RCG to recalculate the transition probability or radiative life time, energy eigen values etc. It has been noticed that the observed intensities are fairly in good agreement when least squares fitted parameters are used for calculations.
Table: 1.1

Input file for the program RCN to calculate the structure of Sb V

<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>Configuration</th>
<th>Electronic Distribution</th>
<th>Orbital</th>
<th>Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d105s</td>
<td>4D10</td>
<td>5s1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d106s</td>
<td>4D10</td>
<td>6s1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d107s</td>
<td>4D10</td>
<td>7s1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d108s</td>
<td>4D10</td>
<td>8s1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d105d</td>
<td>4D10</td>
<td>5d1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d106d</td>
<td>4D10</td>
<td>6d1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d107d</td>
<td>4D10</td>
<td>7d1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d105g</td>
<td>4D10</td>
<td>5g1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d106g</td>
<td>4D10</td>
<td>6g1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d95s5d</td>
<td>4D9</td>
<td>5s1 5d1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d95s6s</td>
<td>4D9</td>
<td>5s1 6s1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d105p</td>
<td>4D10</td>
<td>5p1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d106p</td>
<td>4D10</td>
<td>6p1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d107p</td>
<td>4D10</td>
<td>7p1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d108p</td>
<td>4D10</td>
<td>8p1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d104f</td>
<td>4D10</td>
<td>4f1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d105f</td>
<td>4D10</td>
<td>5f1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d106f</td>
<td>4D10</td>
<td>6f1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d94f5s</td>
<td>4D9</td>
<td>4f1 5s1</td>
</tr>
<tr>
<td>51</td>
<td>5sb4+</td>
<td>4d95s5p</td>
<td>4D9</td>
<td>5s1 5p1</td>
</tr>
</tbody>
</table>

Where 51 in the first column stands for atomic number of Sb, the next number 5 indicates the fifth spectrum of antimony, the third column represents the configuration identification while the last column represents the electronic distribution in different orbitals.
Ground Configuration of Si I
Theoretical Picture of sp configuration

Fig 1.2
References: