8. Complexes of Transition Metal Ions, Viewed from the Point of View of Molecular Orbital Theory

8.1 In the introductory section of this thesis, we briefly reviewed how the inadequacy of pure point charge model, led to the realistic models based on the molecular orbital theory. In this section we briefly describe how the key parameters, the cubic field constant (Dq), spin-orbit interaction constant (g), electrostatic interaction constants (B, C) are interpreted in the molecular orbital theory. We also see how the orbital reduction factor can account for the covalency. Finally we give one variant of molecular orbital theory which is increasingly used to calculate the energy levels of a molecular complex containing transition metal ion.

8.2 There has been a considerable progress in our understanding of the nature of chemical bonds in the complexes of transition metal ions. The general methods which treat the bonding between atoms can be classified into two broad categories: the valence bond method and the molecular orbital method. If no approximations are made, both approaches lead to the same results. However, one always needs to make some approximation at one stage or the other. If the atoms in a complex are not much removed from their equilibrium positions, the molecular orbital method leads to correct physical properties of the complex, especially if configuration interaction is taken into account (CF49). For this reason we use the
molecular orbital theory to study molecules containing transition metal ions.

The first step consists of choosing suitable molecular orbitals. These are written as a linear combination of atomic orbitals

$$\Psi_{M,0} = \sum_i C_i \chi_i$$

where $C_i$ are coefficients to be determined and $\chi_i$ are atomic orbitals centred at the atoms constituting the molecule. The number of atomic orbitals and the type of atomic orbital to be included in Eq. 8.1 depends upon the nature of the molecule and problem. These will be given later for the case of an octahedral complex. In order to make full use of the symmetry of the molecule and anticipating that we will be interested in a complex containing a metal ion and ligands, the orbital given by the Eq. 8.1, can be written

$$\Psi^\Gamma_{\gamma} = \alpha \phi^\Gamma_{\gamma} + \beta \chi^\Gamma_{\gamma}$$

The molecular orbital $\Psi^\Gamma_{\gamma}$, metal orbital $\phi^\Gamma_{\gamma}$, and a linear combination of ligand atomic orbitals $\chi^\Gamma_{\gamma}$, all transform as $\Gamma^\text{th}$ irreducible representation and $\gamma^\text{th}$ row. $\alpha$ and $\beta$ are coefficients to be determined. The coefficients of the linear combination $\chi^\Gamma_{\gamma}$ are given solely by the geometry of the molecule and its symmetry type under the transformations of the group ($\Gamma$). Unlike $\alpha$ and $\beta$, these are not subject to variation.
Fig. 8.4 Coordinate system for an octahedral complex
<table>
<thead>
<tr>
<th>Representation</th>
<th>Metal Orbital</th>
<th>Ligand Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>$s$</td>
<td>$\frac{1}{\sqrt{3}} (z_1 + z_2 + z_3)$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>$e$</td>
<td>$\frac{1}{\sqrt{3}} (z_1 - z_2 - z_3)$</td>
</tr>
<tr>
<td>$\Gamma_{1u}$</td>
<td>$p_x$</td>
<td>$\frac{1}{\sqrt{2}} (z_1 - z_3)$</td>
</tr>
<tr>
<td></td>
<td>$p_y$</td>
<td>$\frac{1}{\sqrt{2}} (z_2 - z_4)$</td>
</tr>
<tr>
<td></td>
<td>$p_z$</td>
<td>$\frac{1}{\sqrt{2}} (z_5 - z_6)$</td>
</tr>
<tr>
<td>$\Gamma_{3g}$</td>
<td>$\gamma$</td>
<td>$\frac{1}{\sqrt{2}} (y_1 + y_3)$</td>
</tr>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\frac{1}{\sqrt{2}} (x_2 + y_5 + y_4)$</td>
</tr>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\frac{1}{\sqrt{2}} (x_4 + y_6)$</td>
</tr>
<tr>
<td>$\Gamma_{1g}$</td>
<td>$\gamma$</td>
<td>$\frac{1}{\sqrt{2}} (y_1 - x_5)$</td>
</tr>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\frac{1}{\sqrt{2}} (x_2 - y_5 + y_4 - x_6)$</td>
</tr>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\frac{1}{\sqrt{2}} (x_4 - y_6)$</td>
</tr>
<tr>
<td>$\Gamma_{2u}$</td>
<td>$\gamma$</td>
<td>$\frac{1}{\sqrt{2}} (y_1 - x_5)$</td>
</tr>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\frac{1}{\sqrt{2}} (x_2 - y_5 + y_4) - x_6$</td>
</tr>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\frac{1}{\sqrt{2}} (x_4 - y_6)$</td>
</tr>
</tbody>
</table>
8.3. There are two methods by which the coefficients $\alpha$ and $\beta$ in Eq. 8.2 can be obtained. One is by extending Hartree-Fock self-consistent-field calculation to molecular clusters. This was first formulated by Rotheaan (R60) for molecules and later applied to clusters of transition metal ions by a number of authors (RSVP71, SS64, ST65, SS63, WF64). Also one can use a semi-empirical method (BG65). In the SCF methods the coefficients in the linear combination Eq. 8.2 can be interpreted in terms of 'covalency'. These can be separately calculated for both $\sigma$ and $\pi$ bonding and (hopefully) compared with experimental results. On the other hand, the semi-empirical method gives $\alpha$'s but usually the results are interpreted in terms of charge densities. From the computational viewpoint, this method is comparatively simple and energy levels of the complex can be easily determined.

8.4 First we briefly outline the SCF method. If we denote by $\Psi_i$, an orbital of the type given by Eq. 8.2, a given state (normally we are interested in the ground and a few excited states) of $n$ electrons can be represented by a linear combination of Slater determinants constructed out of orbitals $\Psi_i$ and spin functions $\alpha$ or $\beta$. We denote this state by $\Psi$. The coefficients of the linear combination are found by the requirement $\Psi$ be an eigenfunction of the operator $S^2$, ($S$ being total spin) and transform according to an irreducible representation of the symmetry group of the Hamiltonian ($\Gamma \Psi$). The latter
requirement corresponds to the demand in atomic spectroscopy that total wavefunction should be an eigenfunction of the operator $L^2$ ($\mathbf{L}$ = total angular momentum).

By using the condition for the stationary states,

$$\delta \langle \Psi | H | \Psi \rangle = 0 \quad 8.3$$

with the subsidiary condition,

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad 8.4$$

One gets a set of simultaneous integro-differential equations for the orbitals. The Hamiltonian in Eq. 8.3, can be written as a sum of one particle and two particle operators:

$$H = \sum_{i=1}^{n} f_i + \sum_{i<j}^{n} g_{ij} \quad 8.5$$

Thus Eqs. 8.3 and 8.4 lead to the set of equations,

$$h_i \psi_i = \xi_i \psi_i + \lambda_{ij} \psi_j \quad 8.6$$

$h_i$ is a single electron Hamiltonian and can be written in terms of matrix elements of operators $f$ and $g$.

First, for the sake of simplicity let us assume, that there is a single metal orbital $\phi$ and a single ligand orbital $\chi$. This leads to two molecular orbitals, one of which predominantly contains the metal orbital $\phi$ and the other $\chi$.

$$\psi_i = \frac{1}{\sqrt{N_1}} (\phi - \lambda \chi) \quad 8.7$$
\[ \Psi_2 = \frac{1}{\sqrt{N_2}} (\chi + \gamma \phi) \tag{8.8} \]

\(N_1\) and \(N_2\) are normalization constants. \(\lambda\) and \(\gamma\) are related to each other by the orthogonality condition (Eq. 8.4)

\[ \lambda = \frac{\gamma + S}{1 + \gamma S}, \]

\[ N_1 = 1 - 2S \lambda + \lambda^2, \]

\[ N_2 = 1 + 2S \gamma + \gamma^2. \tag{8.9} \]

\(S\) is the overlap integral \(\langle x|\phi\rangle\) is traditionally termed as covalency parameter, since this gives charge delocalisation from the metal ion to the ligand. The orbital given by the Eq. 8.7 is known as antibonding orbital and the other (Eq. 8.8) is known as bonding orbital. The ligand 2p or 2s orbitals have lower energy than the metal d, s, p orbitals. Hence the bonding orbitals are stabilised whereas the antibonding are destabilised.

In the case of molecular clusters of transition metal ions, the molecular orbitals corresponding to the metal \(t_2\) and \(e\) orbitals are

\[ \Psi^{t_2}_{t_e} = \frac{1}{\sqrt{N_{t_e}}} (\chi_{\pi} + \gamma_{\pi} \phi_{t_e}) \]

\[ \Psi^{e_o}_{e_{o\sigma}} = \frac{1}{\sqrt{N_{e_{o\sigma}}}} (\chi_{\sigma} + \gamma_{\sigma} \phi_{e_o} + \gamma_{e_o} \chi_{\sigma}) \tag{8.10} \]

\[ \Psi^{e_s}_{e_{s\sigma}} = \frac{1}{\sqrt{N_{e_{s\sigma}}}} (\chi_{\sigma} + \gamma_{\sigma} \phi_{e_s} + \gamma_{e_{s\sigma}} \chi_{\sigma}) \]
If \( = (4 - \alpha_x \chi_x - \lambda \chi_\sigma) \),

\[
\psi_e^a = \frac{1}{\sqrt{2N_0}} (\phi_e - \lambda \chi_\sigma - \lambda_0 \chi_\sigma),
\]

\[
\psi_t^a = \frac{1}{\sqrt{2N_t^2}} (\phi_t - \lambda \chi_\pi).
\]

The metal orbital \( \psi \) can form bonds both with the s orbitals and \( \sigma \) orbitals (of p orbitals) of the ligands. These are distinguished by the suffix s and \( \sigma \). The superscripts a and b refer to antibonding and bonding orbitals respectively. \( N, \alpha, \lambda \) satisfy relations analogous to Eqs. 8.9.

8.5 Consequences of Molecular Orbital Theory

We discuss some of the consequences of using the orbitals given by Eqs. 8.11 instead of pure d-orbitals, without going into the derivations (STK70).

Crystalline Field Splitting Parameter (10 Dq)

Since the crystalline field splits a d-level into \( t_2 \) and e levels, the promotional energy of an electron from the \( t_2 \) orbital to the e orbital can be defined as crystalline field splitting = 10 Dq. In a similar way, in the molecular orbital picture, the energy difference between the anti-bonding \( t_2 \) and e orbitals is defined as 10 Dq i.e.
8.12

\[ 10 \Delta q = \langle e^a | \hat{h} | e^a \rangle - \langle t_2^a | \hat{h} | t_2^a \rangle \]

where \( \hat{h} \) is a single electron Hamiltonian, analogous to the one defined in Eqs. 8.6. Its exact form depends upon the particular case. Some authors instead of using single orbitals in Eq. 8.12, define 10 \( \Delta q \) as the difference in energy between many electron states. With the explicit form of \( \hat{h} \), it is possible to identify various contributions to 10 \( \Delta q \), such as, point charge, correction due to spread of ligand wavefunctions, etc. Generally it is found that the point charge contribution is only a part of the total splitting. The magnitudes of other contributions, some of which cancel each other, depend upon the approximation made in the calculations. Even in the best studied example of \( \text{KNiF}_3 \) the agreement is not good (WF64, ST65).

**Orbital Reduction Factors**

Consider the matrix elements of the angular momentum operator \( \hat{l}_2 \). Using ionic wavefunctions it can be shown.

\[ \langle t_2^\xi | \hat{l}_2 | t_2^\eta \rangle = i \]

and \[ \langle t_2^\xi | \hat{l}_2 | e^c \rangle = 2i \]

However, when the molecular orbitals (Eqs. 8.11) are used in place of pure \( | t_2^\xi \rangle \) etc. in the above expressions, it can be shown that
where $A = R_0 \langle \Phi_x | \frac{\partial}{\partial x} | \Phi_e \rangle$ ($R_0$ - metal ligand distance).

The factor $A$ appears in the evaluation of $\langle \chi_{5e} | l_z | \chi_{5e} \rangle$.

We can rewrite the Eqs. 8.14 as

$$\langle t_2 \bar{S} | l_z | t_2 \eta \rangle = \frac{k}{\sqrt{N_t^a N_e^a}} \left( 1 - \lambda_\pi S_\pi - \lambda_\sigma S_\sigma - \lambda_\pi S_\pi - \lambda_\sigma (\lambda_\pi + A \lambda_\sigma) / 2 \right)$$

8.14

it being understood that the right hand side matrix elements are evaluated using pure ionic wavefunctions. Neglecting quantities of the order $\lambda^3$ and above, it can be shown

$$k \approx 1 - \frac{1}{2} \lambda_\pi^2$$

$$k' \approx 1 - \frac{1}{2} \left( \lambda_\sigma^2 + \lambda_\sigma^2 + \lambda_\pi^2 \right) - \frac{1}{2} \lambda_\pi (\lambda_\sigma + A \lambda_\sigma).$$

8.16

This justifies the procedure of replacing the operator $L$ by $k L$, to take into account covalency in a phenomenological way.

Spin-Orbit Interaction Constant

In the discussion on the spin-orbit interaction, we showed that two spin-orbit interaction constants describe the
behaviour of a single electron in a cubic field (cf. Eq. 5.12). These are defined by the reduced matrix elements
\[
\langle t_2 | l.s | t_2 \rangle = 3i \xi \\
\langle t_2 | l.s | e \rangle = -3\sqrt{2}i \xi'.
\]

In the case of pure d-orbitals \( \xi = \xi' \). In a polycentric system the spin orbit interaction operator can be shown to be (Eq. 5.14)
\[
H_{SO} = \xi_0 (n) \hat{L} \cdot \hat{s} + \sum_{k} \xi_k (r_k) \hat{l}_k \cdot \hat{s}_k
\]
\( 0 \) denotes the metal ion and \( k \) the ligands.

If we use this expression for the spin-orbit interaction and the molecular orbitals given by Eqs. 8.11, the reduced matrix elements, after some lengthy manipulations reduce to
\[
\langle t_2 | l.s | t_2 \rangle = 3i (\xi_d + \frac{1}{2} \lambda_\pi \xi_{LP})/N^\alpha_t \\
\langle t_2 | l.s | e \rangle = -3\sqrt{2}i (\xi_d - \frac{1}{2} \lambda_\sigma \lambda_\pi \xi_{LP})/\sqrt{N^\alpha_t N^\alpha_e}
\]

In this expression \( \xi_d \) is spin-orbit interaction constant for the d-electron and \( \xi_{LP} \) of the ligand \( \pi \) electron. Using the expressions for \( N^\alpha_s \) and retaining terms up to second order alone, and comparing with Eqs. 8.17 we get
\[
\xi \approx \left[1 + (s^2_\pi - s^2_\sigma)\right] \xi_d + \frac{1}{2} \lambda_\sigma^2 \xi_{LP} \\
\xi' \approx \left[1 + \frac{1}{2} (s^2_\pi - s^2_\sigma) + \frac{1}{2} (s^2_\sigma - s^2_\pi) + \frac{1}{2} (s^2_\sigma - s^2_\pi)\right] \xi_d - \frac{1}{2} \lambda_\sigma \lambda_\pi \xi_{LP}
\]
This justifies the use of spin-orbit interaction constants differing from the free ion values to account for the covalency.

**Racah Parameters**

We normally use Racah parameters to represent Coulomb interaction between the electrons. These parameters are related to the Slater integrals $F_2$ and $F_4$. When molecular orbitals are used $F_2$ and $F_4$ become multicentre integral which are difficult to evaluate. Therefore, to see the changes in these integrals brought by the use of molecular orbitals, we retain only the ionic function and the normalization constant in the molecular orbital. Since the Slater integrals contain product of four molecular orbitals, we can write

\[
B' = k B_{\text{free ion}}
\]

\[
C' = k C_{\text{free ion}}
\]

with

\[
k = \frac{1}{(N_e^N)^{1/2}} \cdot \frac{1}{(N_t^{N-e})^{1/2}}
\]

where $N_e$ is number of $e$ electrons in the integrals. Calculation of $k$ involves calculation of overlap integrals and covalency parameters. Whether $k$ exceeds 1 or not depends upon these values. Since reduced values of $B_{\text{free ion}}$, $C_{\text{free ion}}$ fit experimental spectra, this reduction is generally attributed to covalency.
Apart from the SCF method outlined above a semi-empirical method is often used. This was first applied to the case of tetrahedral complexes of transition metal ions by Wolfsberg and Helmholz (WH52). This method has been later refined by Ballhausen and Gray and their coworkers (BG65).

Let $\mathcal{H}$ be Hamiltonian for a single electron in the molecular skeleton. The molecular orbitals can be written in the fashion of Eq. 8.2:

$$\Psi_{i}^{\alpha} = \alpha_{i} \Phi_{\alpha} + \sum_{k} \beta_{i}^{\alpha} \chi_{k}^{\alpha}.$$

The suffix $i$ is for the case of molecular orbitals of the same symmetry. The summation over $k$ is necessary when more than one linear combination of ligand functions transform as $|\Gamma \psi\rangle$. Then the energy is given by

$$W = \langle \Psi_{i}^{\alpha} | \mathcal{H} | \Psi_{i}^{\alpha} \rangle.$$

Now, the variational principle is applied to this energy with the subsidiary condition that $\Psi_{i}^{\alpha}$ are normalized. $\alpha$s and $\beta$s are variational parameter. This amounts to solving eigenvalues and eigenvectors of the matrix

$$|\mathcal{H}_{ij} - \tilde{G}_{ij} W| = 0,$$

where for simplicity we have condensed the three indices $\Gamma \psi$, $i$ into one $i$. $\tilde{G}_{ij}$ are group overlap integrals (Note that
are linear combination of ligand atomic orbitals).

Since the Hamiltonian is invariant under the symmetry group of the Hamiltonian, the matrix 8.24 is in block form. In the case of degenerate level, as the degenerate partners span the same irreducible representation, it is sufficient to set up the matrix for one component of irreducible representation and diagonalise it. This reduction to block form reduces labour considerably. The diagonal elements of the matrix, $H_{ii}$, can be interpreted as energy of $i^{th}$ electron in the molecular skeleton. This approximation consists of using the valence state ionisation potential (VSIE), of the $i^{th}$ orbital for the integral $H_{ii}$. The next approximation is to do with $H_{ij}$. Wolfsberg and Helmholtz, in their original calculation approximated

$$H_{ij} = F G_{ij} \frac{(H_{ii} + H_{jj})}{2} \tag{8.25}$$

where $F$ is a numerical factor between 1 and 2. Ballhausen and Gray have suggested (BG.65)

$$H_{ij} = -2 G_{ij} \sqrt{H_{ii} \cdot H_{jj}} \tag{8.26}$$

Then knowing the geometry of the molecule, the overlap integrals can be evaluated and hence the eigenvalues of the matrix 8.24 can be determined. The refinement in the method consists of doing a self-consistent calculation for the electronic charge distribution among the orbitals. Suppose initially there is a net charge $\varphi$ on the ion and $d, s, p$
response to static magnetic fields: diamagnetic, paramagnetic and ferromagnetic. There is another class of compounds, outside this naive picture, wherein the arrangement of magnetic ions in the lattice determines the magnetic properties. There are ferrimagnetism, antiferromagnetism in compounds and helical, spiral and other structures in metals and alloys.

9.3 Paramagnetic Susceptibility

If we confine ourselves to dilute systems and static applied magnetic field, the most important property is paramagnetic susceptibility. If \( M \) is induced magnetic moment per molar volume, then the susceptibility is defined as

\[
\chi = \frac{M}{H}
\]

where \( H \) is magnitude of the applied field. We wish to connect the observed susceptibility with the properties of the ion. The Hamiltonian for the interaction between the ion and applied field can be written

\[
\mathcal{H} = \beta (\mathbf{k} \cdot \mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H}
\]

where \( \beta = \frac{e_k}{2mc} \) (Bohr magneton), and \( k \) is orbital reduction factor to take into account of covalency (see Sec. 8). If \( E \) is total energy of the system, then Eq. 9.1 can be written

\[
\chi = -\frac{1}{H} \left\langle \frac{\partial E}{\partial H} \right\rangle
\]
we obtain Van Vleck's formula for paramagnetic susceptibility

\[ \chi = N \frac{\sum \left\{ \left( \frac{E_i}{kT} \right)^2 - 2 \frac{E_i^2}{k^2T^2} \right\} e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \] \hspace{1cm} (9.7)

An alternative derivation of this expression is given by Griffith (G61).

9.4 Discussion of Expression (9.7)

In the expression (9.7), the factor \( \frac{E_i^2}{k^2T^2} \) gives rise to temperature independent paramagnetism. This is also known as high frequency term and is associated with the name of Van Vleck who first showed that this term is due to polarization of the ground state.

Often experimentalists and theoreticians discuss magnetic properties in terms of an effective moment \( \mu_{\text{eff}} \), which is defined by the equation: (using the analogy of Curie law for susceptibility)

\[ \chi = N\beta^2 \frac{\mu_{\text{eff}}^2}{3kT} \] \hspace{1cm} (9.8)

\[ \mu_{\text{eff}} = \sqrt{\frac{3k}{N\beta^2T}} \chi = 2.83\sqrt{\chi T} \] \hspace{1cm} (9.9)
term we get Curie law for susceptibility. If the ground state is orbitally non-degenerate, expression (9.7) reduces to spin only formula for susceptibility:

\[ \chi = N\beta^2 \frac{4s(s+1)}{3kT} \]

9.12

When the symmetry surrounding the ion is no longer spherical and \( \mu_{\text{eff}} \) becomes predominantly temperature dependent via the exponential factors. Also the susceptibility becomes anisotropic. When the field was symmetry lower than that of cubic, the axis of quantization (\( \mathbf{z} \)) is taken along the tetragonal or trigonal axis.

Then we evaluate the expression (9.6) using \( \zeta = \chi, \gamma, Z \) \( \gamma \) being quantized along \( \mathbf{z} \) axis. And then substitute in (9.7) to get anisotropic susceptibilities. In section 11, we have calculated susceptibilities of Mo\(^{5+} \) compounds this way.

9.5 Simple Applications

Kotani (K49) first showed that temperature variation of \( \mu_{\text{eff}} \) of iron group ions can be explained if we take into account of the spin orbit splitting of ground terms. His formula for effective magnetic moment \( \mu_{\text{eff}} \) are known as Kotani formula. As there have been rederived by a number of authors and well tabulated (See e.g. GR61), we illustrate the method for the \( d^1 \) ion in the octahedral field. In an octahedral field \( ^2T_{2g} \) is ground term and \( ^2E_g \) is separated
by 10 Dq. This term can be neglected since normally we encounter ions with 10 Dq > 10000 cm⁻¹.

Due to spin orbit interaction this splits into a quartet with energy \( -\frac{1}{2} \xi \) and a doublet with energy \( \xi \). The levels transform like \( \Gamma_8 \) and \( \Gamma_7 \) representation respectively. We use the bases functions given by equations (5.8) i.e.

\[
\begin{align*}
\Psi_1 &= |\Gamma_8(t_2)^{3/2}\rangle \\
\Psi_2 &= |\Gamma_8(t_2)^{1/2}\rangle \\
\Psi_3 &= |\Gamma_8(t_2)^{-1/2}\rangle \\
\Psi_4 &= |\Gamma_8(t_2)^{-3/2}\rangle \\
\Psi_5 &= |\Gamma_7(t_2)^{1/2}\rangle \\
\Psi_6 &= |\Gamma_7(t_2)^{-1/2}\rangle
\end{align*}
\]

Using these wavefunctions \( E_2^0 \) are

\[
\begin{align*}
E_1^0 &= E_2^0 = E_3^0 = E_4^0 = -4 Dq - \frac{\xi}{2} \\
E_5^0 &= E_6^0 = -4 Dq + \xi
\end{align*}
\]

The first order and second order Zeeman energies are

\[
\begin{align*}
E_1^1 &= E_2^1 = E_3^1 = E_4^1 = 0 \\
E_5^1 &= E_6^1 = \beta \\
E_1^2 &= E_4^2 = 0 \\
E_2^2 &= E_3^2 = -\frac{4}{35} \beta^2 \\
E_5^2 &= E_6^2 = \frac{4}{35} \beta^2
\end{align*}
\]

\[9.13\]

\[9.14\]

\[9.15\]
Substituting (9.15), (9.14) in (9.7) we obtain

\[
\chi = \frac{N\beta^2}{3kT} \left[ \frac{8 + (3x - 8)e^{-3x/2}}{\chi(2 + e^{-3x/2})} \right]
\]

Thus

\[
\mu_{\text{eff}} = \sqrt{\frac{8 + (3x - 8)e^{-3x/2}}{\chi(2 + e^{-3x/2})}}
\]

where \( \chi = \frac{kT}{S} \)

When lower symmetric fields are present, expression for \( \mu_{\text{eff}} \) or \( \chi \) is pretty complicated. Alternatively if the matrices of \( (k_L + 2S) \) are known, the expression (9.7) can be programmed and evaluated using a digital computer (See Appendix III ).