The overall wave function has the following form,

\[ \psi_{n,\ell,m}(r, \theta, \phi) = R_{n,\ell}(r)Y_{\ell,m}(\theta, \phi) \]

where the radial, \( R_{n,\ell}(r) \), and angular wave functions have previously been defined. Both \( R_{n,\ell}(r) \) and \( Y_{\ell,m}(\theta, \phi) \) are orthonormal wave functions. The functional form of the spherical harmonic wave functions for solutions of \( \ell \) and \( m \) are:

*Spherical Harmonics for \( \ell = 0, 1, 2, 3, 4 \)*
Table removed due to copyright considerations.
The complex part of the wave function is removed by taking the following linear combinations,

\[
\begin{align*}
    d_{2z} &= \psi_{n,2,0} \\
    d_{x^2-y^2} &= \frac{1}{\sqrt{2}} (\psi_{n,2,2} + \psi_{n,2,-2}) \\
    d_{xy} &= \frac{1}{i\sqrt{2}} (\psi_{n,2,2} - \psi_{n,2,-2}) \\
    d_{xz} &= \frac{1}{\sqrt{2}} (\psi_{n,2,1} - \psi_{n,2,-1}) \\
    d_{yz} &= \frac{1}{i\sqrt{2}} (\psi_{n,2,1} - \psi_{n,2,-1})
\end{align*}
\]

Because \(\psi_{n,\ell,m}\) and \(\psi_{n,\ell,-m}\) are eigenfunctions of the same eigenvalue \(E_{n,\ell}\), then linear combinations must be eigenfunctions of \(E_{n,\ell}\) too. The real orthonormal wavefunctions are:

\[
\begin{align*}
    d_{2z} &= \psi_{n,2,0} \\
    d_{x^2-y^2} &= \frac{1}{\sqrt{2}} (\psi_{n,2,2} + \psi_{n,2,-2}) \\
    d_{xy} &= \frac{1}{i\sqrt{2}} (\psi_{n,2,2} - \psi_{n,2,-2}) \\
    d_{xz} &= \frac{1}{\sqrt{2}} (\psi_{n,2,1} - \psi_{n,2,-1}) \\
    d_{yz} &= \frac{1}{i\sqrt{2}} (\psi_{n,2,1} - \psi_{n,2,-1})
\end{align*}
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    d_{xz} &= \frac{1}{\sqrt{2}} (\psi_{n,2,1} - \psi_{n,2,-1}) \\
    d_{yz} &= \frac{1}{i\sqrt{2}} (\psi_{n,2,1} - \psi_{n,2,-1})
\end{align*}
\]

Real orthonormalized linear combinations of the spherical harmonics

\[
Y_{\ell,m} (\theta, \phi) \] for \(\ell = 0, 1, 2\)

Table removed due to copyright considerations.
Ligand field theory assumes that the electrons move in a potential field of the central ion and in the electrostatic potential of all the ligands. To a first approximation (pure crystal field) quantum mechanical exchange among electrons of the central ion and the electrons of the ligand are neglected... i.e., the problem is described by an intra-complex Stark effect resulting from the charge distribution of the ligands operating on the electrons of the central ion.

The Hamiltonian for the motion of 

\[
\sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z'^2}{r_i} \right) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} eV(r_i)
\]

The above Hamiltonian differs from the central field Schrödinger problem because of the additional potential energy or ‘crystal field’ term \( \sum_{i=1}^{N} V(r_i) \). This problem can again be analyzed by perturbation methods where

\[
H_0 = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z'^2}{r_i} \right)
\]
\[
H' = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} eV(r_i)
\]

In a central field, all \( \Phi \) functions of the same electron configuration (e.g. \((\text{nd})^N\)) are degenerate and describe states of energy \( E_0 \)

\[
H_0 \Phi = E_0 \Phi \quad \text{where } E_0 = N \cdot e_{n,d}
\]

The eigenvalues of the perturbation operator are determined from the secular determinant

\[
\left\| \left( \Phi_r | H | \Phi_s \right) - \Delta \delta_{r,s} \right\| = 0 \quad r, s = 1, 2, \ldots , \eta
\]
The perturbation is ordered according to

weak crystal field: \[ \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{e^2}{r_{ij}} \geq \sum_{i=1}^{N} eV(r_i) \quad \ldots \text{high-spin case} \]

strong crystal field: \[ \sum_{i=1}^{N} eV(r_i) \geq \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{e^2}{r_{ij}} \quad \ldots \text{low-spin case} \]

The ligand field potential, \( eV(r_i) \), is defined as follows: assume all ligands of a given complex ion have spatial distributions with density \( \rho(\vec{R}) = \rho(R, \Theta, \Phi) \) where \( \vec{R} \) is the vector from the nucleus of the central ion to a point having spherical coordinates \( R, \Theta, \Phi \)

The potential at \( \vec{r} = \{r, \theta, \phi\} \) is defined as

\[
V(\vec{r}) = \frac{1}{|\vec{R} - \vec{r}|} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell + 1} \frac{r_{\ell m}^{\ell}}{r_{\ell m}^{\ell}} \int \rho(\vec{R}) Y_{\ell m}^*(\Theta, \Phi) Y_{\ell m}(\Theta, \Phi) d\tau_R
\]

The \( \frac{1}{|\vec{R} - \vec{r}|} \) coordinate is convenient because it can be replaced by a well-known expression in spherical harmonics (Eyring, Walter, Kimball)

Substitution yields the crystal field potential expanded in spherical harmonics,

\[
V(\vec{r}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell + 1} Y_{\ell m}^*(\Theta, \Phi) \int \rho(\vec{R}) \frac{r_{\ell m}^{\ell}}{r_{\ell m}^{\ell}} Y_{\ell m}(\Theta, \Phi) d\tau_R
\]

\[ \text{a constant dependent on} \quad \text{ligand charge distribution} \]
where \( r_< = \) shorter radial distance to origin and \( r_> = \) longer radial distance to origin. In the region of interest, i.e. the interbond region... \( r = r_< \) and \( R=r_> \). In the expansion of \( V(r) \), we have an infinite number of terms for the general problem. However we are evaluating these integrals for d-orbitals, leading to the following constraints:

- the crystal field integral must be symmetric to inversion... since d orbitals are even functions, the perturbation Hamiltonian (i.e. crystal field operator) also must be even

\[
\int \psi_{3d} H' \psi_{3d} g \times g \times g \;
\]

\( \therefore \ell \) must be even \((0, 2, 4, 6, \ldots)\) if integral is to be \( \neq 0 \)

- the subintegrals \( \left\langle \Phi_i \sum_{i=1}^{N} V(r_i) \Phi_i \right\rangle \) may always be reduced to integrals of one-electron functions because \( V(r_i) \) terms are one-electron operators...

\[
\left\langle \psi_{n_3,m_3} \middle| A_{r_{12},m_2} r_{12} Y_{12} \middle| \psi_{n_3,m_3} \right\rangle = [A_{r_{12},m_2} \left\langle R_{n_3} \right| r_{12} \left| R_{n_3} \right\rangle \left\langle \psi_{n_3,m_3} \psi_{r_{12},m_2} \psi_{n_3,m_3} \right]\]

A property of spherical harmonics,

\[
\int_0^\pi \int_0^{2\pi} Y_{1}^{m_1} Y_{1}^{m_2} Y_{1}^{m_2} \sin \theta \, d\theta d\phi \neq 0 \quad \text{if} \quad \ell_1 + \ell_3 \geq \ell_2
\]

for d orbitals \( \ell_1 = \ell_3 = 2 \therefore \ell_2 \leq 4 \) and therefore expansion is over \( \sum_{\ell=0,2,4} \)

Thus for a d electron system,

\[
V(\vec{r}) = A_{0,0} r^{0} Y_{0,0} + \sum_{m=-2}^{+2} A_{2,m} r^{2} Y_{2,m} + \sum_{m=-4}^{+4} A_{4,m} r^{4} Y_{4,m}
\]

Note... this is a generalized crystal field for d-electrons in the absence of symmetry considerations. The potential field may be further simplified with consideration of the symmetry of the ligand field.
The potential energy, \( V(r_i) \), must remain invariant under all symmetry operations. Under the \( O_h \) point group, this condition is met for
\[-i m \pi = 2 \pi n \quad (n = 0, \pm 1, \pm 2 \ldots), A_{2,0} = 0 \text{ and } A_{i,m} = A_{-i,-m}, \text{ thus yielding}
\]
\[
V_{O_h}(r_i) = A_{0,0} r^0 Y_{0,0} + A_{4,0} r^4 \left[ Y_{4,0} + \frac{\sqrt{3}}{\sqrt{10}} (Y_{4,1} + Y_{4,-1}) \right]
\]

We now have the octahedral crystal field in terms of the appropriate spherical harmonics, solving for the \( A_{i,m} \) coefficients

\[
A_{i,m} = \left[ b_i \sum_k Y^*_{i,m} (\Theta_k, \Phi_k) \right] \quad \text{where}
\]

In the \( O_h \) crystal field,

\[
\text{ligand coordinates } \Rightarrow \quad \Theta_1 = 0, \quad \Theta_2 = \pi, \quad \Theta_3 = \frac{\pi}{2}, \quad \Phi_3 = \frac{\pi}{2}, \quad \Theta_4 = \frac{\pi}{2}, \quad \Phi_4 = 0, \quad \Theta_5 = \frac{\pi}{2}, \quad \Phi_5 = \frac{3\pi}{2}, \quad \Theta_6 = \frac{\pi}{2}, \quad \Phi_6 = \pi
\]

Solving for the spherical harmonics of the ligand set

\[
A^{(L)}_{0,0} = b_0 \left[ Y^*_{0,0} (\Theta_1, \Phi_1) + Y^*_{0,0} (\Theta_2, \Phi_2) + Y^*_{0,0} (\Theta_3, \Phi_3) + Y^*_{0,0} (\Theta_4, \Phi_4) + Y^*_{0,0} (\Theta_5, \Phi_5) + Y^*_{0,0} (\Theta_6, \Phi_6) \right]
\]

but \( Y_{0,0} \) is a constant \( \frac{1}{\sqrt{4\pi}} \) \( \therefore A^{(L)}_{0,0} = a_0^{(L)} \cdot 6 \cdot \frac{1}{\sqrt{4\pi}} = \frac{3}{\sqrt{\pi}} a_0^{(L)} \)

\[
A^{(L)}_{4,0} = a_4 \sum_{k=1}^{6} Y^*_{4,0} (\Theta_k, \Phi_k) \quad \text{where } Y_{4,0} = \frac{3}{16\sqrt{\pi}} (35\cos^4 \theta - 30\cos^2 \theta + 3)
\]

\[
\therefore A^{(L)}_{4,0} = a_4 \left[ \left( 4 \cdot \frac{3}{16\sqrt{\pi}} \cdot 3 \right) + \left( 2 \cdot \frac{3}{16\sqrt{\pi}} \cdot (35 - 30 + 3) \right) \right] = \frac{21}{4\sqrt{\pi}} a_4^{(L)}
\]
The complete octahedral (O\textsubscript{h}) crystal field is therefore,

\[
V_{\text{Oh}}^{(L)} = \frac{3}{\sqrt{\pi}} a_0^{(L)} r^0 Y_{0,0} + \frac{21}{4\sqrt{\pi}} a_4^{(L)} r^4 \left[ Y_{4,0} + \frac{5}{14} (Y_{4,+4} + Y_{4,-4}) \right]
\]

For a tetrahedral (T\textsubscript{d}) crystal field,

\[
V_{\text{Td}}^{(L)} = \frac{2}{\sqrt{\pi}} a_0^{(L)} r^0 Y_{0,0} - \frac{7}{3\sqrt{\pi}} a_4^{(L)} r^4 \left[ Y_{4,0} + \frac{5}{14} (Y_{4,+4} + Y_{4,-4}) \right]
\]

The first term is constant... \(Y_{0,0}\) is independent of \(\bar{r}\) – the reference point from which potential is measured... For a point charge, the term describes a spherical shell on which the charges of the ligands are equally distributed. The second term has the same \(\bar{r}\) dependence for all cubic fields (i.e. spherical harmonic dependance), only the pre-factor differs

\[
\begin{array}{c|cc}
V(r_i) & A_{0,0} & A_{4,0} \\
\hline
V_{\text{Oh}} & \frac{3}{\sqrt{\pi}} a_0^{(L)} & \frac{21}{4\sqrt{\pi}} a_4^{(L)} \\
V_{\text{Td}} & \frac{2}{\sqrt{\pi}} a_0^{(L)} & -\frac{7}{3\sqrt{\pi}} a_4^{(L)} \\
\end{array}
\]

constant angular dimension

\[
\frac{A_{0,0}^{(Td)}}{2 a_0^{(L)}} = \frac{A_{0,0}^{(Oh)}}{3 a_0^{(L)}} \quad \frac{A_{4,0}^{(Td)}}{-7 a_4^{(L)}} = \frac{21 a_4^{(L)}}{4\sqrt{\pi}}
\]

\[
A_{0,0}^{(Td)} = \frac{2}{3} A_{0,0}^{(Oh)} \quad A_{4,0}^{(Td)} = \frac{4}{9} A_{4,0}^{(Oh)}
\]

since this is the only angular dependence retained in the energy description of the crystal field,

\[
V_{\text{Td}} = -\frac{4}{9} V_{\text{Oh}}
\]