METHODS of APPROXIMATION

Why use approximation methods?

- Can't solve Schrödinger equation exactly, too difficult, too many variables
- Actually can get more physical insight into the problem by approximation methods
- Can systematically increase the accuracy by going to higher and higher order.

SIMPLE MODEL SYSTEM:

Only 2 energy levels

Hamiltonian	Eigenfunctions	Eigenvalues
H	Ψ unknown	E unknown
$H^{(0)}$	ϕ_1 ϕ_2 known	E_1, E_2 known

Need to solve $H\Psi = E\Psi$. How? Use matrix form of this equation: Find the matrix representation of H in the complete orthonormal set $\{\phi_1, \phi_2\}$

$$\mathbb{H} = \begin{vmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{vmatrix} \qquad \Psi = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

$H\Psi = E\Psi$ in matrix form is:

$$H_{11}c_1 + H_{12}c_2 = Ec_1$$
$$H_{21}c_1 + H_{22}c_2 = Ec_2$$

$$\det \begin{vmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{22}-E \end{vmatrix} = 0$$

$$(H_{11}-E)(H_{22}-E) - H_{21}H_{12} = 0$$

$$E_{\pm} = \frac{1}{2}(H_{11}+H_{22}) \pm \frac{1}{2}\left\{(H_{11}-H_{22})^2 + 4H_{12}H_{21}\right\}^{1/2}$$

Suppose H is only slightly different from $H^{(0)}$

$$H = H^{(0)} + h$$ — a small "perturbation"

Then: $\det\begin{vmatrix} (E_1+h_{11}-E) & h_{12} \\ h_{21} & (E_2+h_{22}-E) \end{vmatrix} = 0$ gives the roots

$$E_{\pm} = \frac{1}{2}(E_1+h_{11}+E_2+h_{22}) \pm \frac{1}{2}\left\{(E_1+h_{11}-E_2-h_{22})^2 + 4h_{12}h_{21}\right\}^{1/2}$$

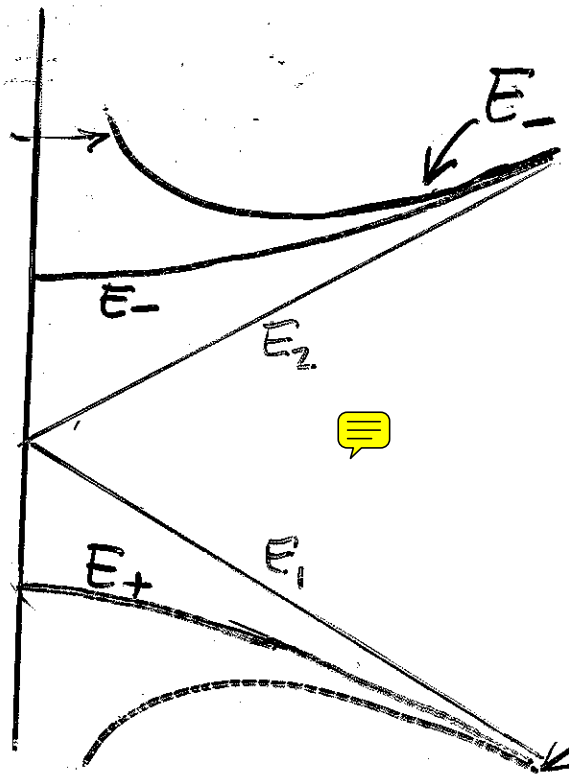
For the SPECIAL CASE where $h_{11}=h_{22}=0$, then

$$E_{\pm} = \frac{1}{2}(E_1+E_2) \pm \frac{1}{2}\left\{(E_1-E_2)^2 + 4h_{12}^2\right\}^{1/2}$$

$$= \frac{1}{2}(E_1+E_2) \pm \frac{1}{2}\left\{1 + \frac{4h_{12}^2}{(E_1-E_2)^2}\right\}^{1/2}(E_1-E_2)$$

Expand the square root: $\sqrt{1+x} \approx 1+\frac{1}{2}x+\cdots$

$$E_{\pm} = \frac{1}{2}(E_1+E_2) \pm \frac{1}{2}(E_1-E_2)\left\{1 + 2\left(\frac{h_{12}}{E_1-E_2}\right)^2 + \cdots\right\}$$



$$E_- \approx E_2 - \frac{h_{12}^2}{(E_1-E_2)}$$

The change in energy in going from $H^{(0)}$ to $H = H^{(0)}+h$ depends on the integral of h between ϕ_1 and ϕ_2 and on the energy difference $\Delta E = E_1 - E_2$

$$E_+ \approx E_1 + \frac{h_{12}^2}{(E_1-E_2)}$$

What about the functions? Find c_1 and c_2 by substituting E_+ into

$$E_1 c_1 + h_{12} c_2 = E_+ c_1$$

and using $c_1^2 + c_2^2 = 1$ (normalization)

$$\cos^2\beta + \sin^2\beta \equiv 1$$

$$\Psi_+ = \phi_1 \cos\beta + \phi_2 \sin\beta$$
$$\Psi_- = -\phi_1 \sin\beta + \phi_2 \cos\beta$$

} use of sin and cos GUARANTEES that $\Psi_\pm$ are NORMALIZED and ORTHOGONAL

where $\tan\beta = \frac{-h_{12}}{\Delta E}$

Two cases: (1) When $\frac{h_{12}^2}{\Delta E} << 1$ then $\sin\beta \approx \tan\beta = \frac{-h_{12}}{\Delta E}$, $\cos\beta \approx 1$

In which case

$$\Psi_+ \approx \phi_1 - \frac{h_{12}}{\Delta E}\phi_2$$
$$\Psi_- \approx \frac{h_{12}}{\Delta E}\phi_1 + \phi_2$$

} each state is like one state of $H^{(0)}$ slightly contaminated with the other state.

(2) When $E_1 = E_2$ then $\det \begin{vmatrix} E_1 - E & h_{12} \\ h_{12} & E_1 - E \end{vmatrix} = 0$

$E = E_1 \pm h_{12}$ which when substituted back into the equation lead to

$E = E_1 + h_{12} \Rightarrow -h_{12}c_1 + h_{12}c_2 = 0$

$$\Psi_+ = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \longleftarrow c_1 = c_2$$

or for $E = E_1 - h_{12} \Rightarrow h_{12}c_1 + h_{12}c_2 = 0$

$$\Psi_- = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \longleftarrow c_1 = -c_2$$

END of SIMPLE MODEL SYSTEM (2-LEVEL SYSTEM)

Now let us generalize to more levels:

A. NON-DEGENERATE TIME-INDEPENDENT PERTURBATION THEORY

Given: $H = \underbrace{H^{(0)}}_{\text{large part}} + \underbrace{\lambda h}_{\text{a small part}}$ λ keeps track of orders of magnitude of smallness

To solve: $H\Psi = E\Psi$ E unknown, Ψ unknown

Let us use $H^{(0)}\phi_i = \epsilon_i \phi_i$ ϵ_i all known, ϕ_i all known

[One way is to set up the MATRIX $[H]$ for operator H in the complete orthonormal set $\{\phi_1\ \phi_2\ \phi_3 \cdots\}$ and diagonalize it and find the eigenvalues E_i and eigenvectors $\begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix}$ which provide $\Psi_i = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \cdots$]

- Use perturbation theory as an ALTERNATE way:
  Express both the unknown E and the unknown Ψ in a power series expansion:

$$\left.\begin{aligned} E &= E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots \\ \Psi &= \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \cdots \end{aligned}\right\} \text{for each answer}$$

Substitute these into $H\Psi_i = E_i\Psi_i$ and collect terms in powers of λ

λ^0 terms: $H^{(0)}\phi_i = \epsilon_i\phi_i$

λ^1 terms: $\{H^{(0)} - \epsilon_i\}\Psi_i^{(1)} = \{E_i^{(1)} - h\}\phi_i$

λ^2 terms: etc...

From the λ^1 equation we get by $\int \phi_i^* d\tau$ on both sides:

$$0 = \int \phi_i^* (E_i^{(1)} - h)\phi_i \, d\tau$$

$$\text{or } E_i^{(1)} = \int \phi_i^* h \phi_i \, d\tau$$

[or $\lambda E_i^{(1)} = \int \phi_i^* \lambda h \phi_i \, d\tau$ so you see we can just leave off the λ]

Let $\Psi = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \ldots$

$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots$

Substitute these expansions into $\mathcal{H}\Psi = E\Psi$

$\{\mathcal{H}^{(0)} + \lambda h\}\{\Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \ldots\} =$

$\{E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots\}\{\Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \ldots\}$

collecting all the terms in λ^0 we get

$$\mathcal{H}^{(0)}\,\Psi^{(0)} = E^{(0)}\,\Psi^{(0}$$

collecting all the terms in λ^1 we get

$$\mathcal{H}^{(0)}\,\Psi^{(1)} + h\Psi^{(0)} = E^{(0)}\,\Psi^{(1)} + E^{(1)}\,\Psi^{(0)}$$

collecting all the terms in λ^2 we get

$$\mathcal{H}^{(0)}\,\Psi^{(2)} + h\Psi^{(1)} = E^{(0)}\,\Psi^{(2)} + E^{(1)}\,\Psi^{(1)} + E^{(2)}\,\Psi^{(0)}$$

and so on.

Let us now examine $\mathcal{H}^{(0)}\,\Psi^{(0)} = E^{(0)}\,\Psi^{(0}$

This states that $\Psi^{(0)}$ are the eigenfunctions of $\mathcal{H}^{(0)}$ with eigenvalues $E^{(0)}$.

If $\mathcal{H}^{(0)}$ is a ***non-degenerate*** system,

then there is only one $\Psi_i^{(0)}$ for each $E_i^{(0)}$.

Since we already know that $\mathcal{H}^{(0)}\,\phi_i = \varepsilon_i\,\phi_i$

Thus,

$$\lim_{\lambda h \to 0} \{\Psi_i^{(0)} = \phi_i \;;\; E_i^{(0)} = \varepsilon_i\}$$

Let us now examine

$\mathcal{H}^{(0)}\Psi^{(1)} + \boldsymbol{h}\Psi^{(0)} = E^{(0)}\Psi^{(1)} + E^{(1)}\Psi^{(0)}$

make use of what we have found about $^{(0)}$,

$\mathcal{H}^{(0)}\Psi_i^{(1)} + \boldsymbol{h}\phi_i = \varepsilon_i\Psi_i^{(1)} + E_i^{(1)}\phi_i$

rearrange to

$(\mathcal{H}^{(0)} - \varepsilon_i)\Psi_i^{(1)} = (E_i^{(1)} - \boldsymbol{h})\phi_i$

Here, unknowns are $E_i^{(1)}$ and $\Psi_i^{(1)}$.

Let us solve for $E_i^{(1)}$

Operating with $\int\phi_i^* d\tau$ on both sides,

$\int\phi_i^* (\mathcal{H}^{(0)} - \varepsilon_i)\Psi_i^{(1)}\, d\tau = \int\phi_i^* (E_i^{(1)} - \boldsymbol{h})\phi_i\, d\tau$

using Hermitian property of $\mathcal{H}^{(0)}$:

LHS: $\int(\mathcal{H}^{(0)} - \varepsilon_i)^*\phi_i^*\Psi_i^{(1)}d\tau = (\varepsilon_i - \varepsilon_i)\bullet\int\phi_i^*\Psi_i^{(1)}d\tau$

$= 0$ don't need $\Psi_i^{(1)}$!

RHS: $E_i^{(1)} - \int\phi_i^*\boldsymbol{h}\,\phi_i\, d\tau$

Thus, $E_i^{(1)} = \int\phi_i^*\boldsymbol{h}\,\phi_i\, d\tau$, call it $\boldsymbol{h}_{ii}$

Note that if we had been carrying around the λ we have $\lambda E_i^{(1)} = \int\phi_i^*\lambda\boldsymbol{h}\,\phi_i\, d\tau$;

It is not necessary to include λ explicitly except as a means of keeping track of orders of magnitude.

What about the function?

Let us expand the unknown function $\Psi_i^{(1)}$ in terms of the complete orthonormal set:

$$\Psi_i^{(1)} = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \cdots$$

Putting this back into the λ' equation,

$$\{H^{(0)} - \epsilon_i\}(c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \cdots) = \{E_i^{(1)} - h\}\phi_i$$

Now operate on both sides by $\int \phi_n^* d\tau$:

$$(\epsilon_n - \epsilon_i)c_n = -\int \phi_n^* h \phi_i \, d\tau$$

$$\text{or } c_n = \frac{-h_{ni}}{\epsilon_n - \epsilon_i} \quad \text{for } n \neq i$$

Therefore,

$$\Psi_i^{(1)} = -\left[\frac{h_{1i}}{\epsilon_1 - \epsilon_i}\phi_1 + \frac{h_{2i}}{\epsilon_2 - \epsilon_i}\phi_2 + \frac{h_{3i}}{\epsilon_3 - \epsilon_i}\phi_3 + \cdots\right]$$

Furthermore, we can use this to calculate $E_i^{(2)}$, the second order correction, giving

$$E_i^{(2)} = -\left[\frac{|h_{1i}|^2}{\epsilon_1 - \epsilon_i} + \frac{|h_{2i}|^2}{\epsilon_2 - \epsilon_i} + \frac{|h_{3i}|^2}{\epsilon_3 - \epsilon_i} + \cdots\right]$$

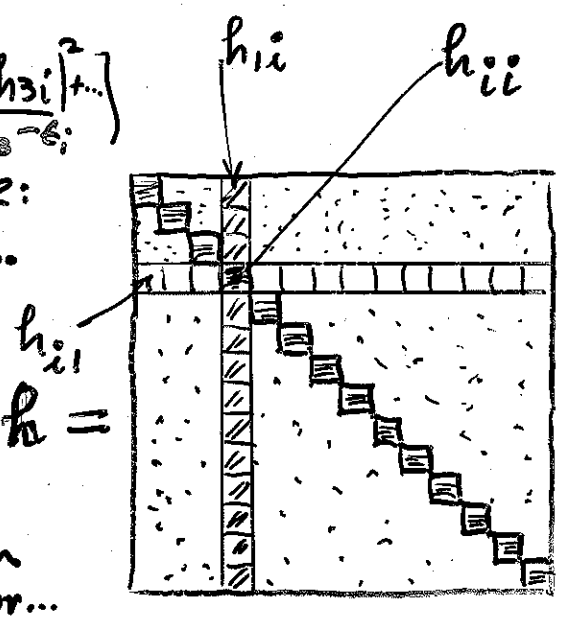
SUMMARY:

Energy correct to 2nd ORDER:

$$E_i = \epsilon_i + h_{ii} - \left[\frac{|h_{1i}|^2}{\epsilon_1 - \epsilon_i} + \frac{|h_{2i}|^2}{\epsilon_2 - \epsilon_i} + \frac{|h_{3i}|^2}{\epsilon_3 - \epsilon_i} + \cdots\right]$$

Wavefunction correct to 1ST ORDER:

$$\Psi_i = \phi_i - \frac{h_{1i}}{\epsilon_1 - \epsilon_i}\phi_1 - \frac{h_{2i}}{\epsilon_2 - \epsilon_i}\phi_2 - \cdots$$



MATRIX h is MOSTLY ZEROES since SYMMETRY DICTATES where ZEROES are:

$\Gamma_n \otimes \Gamma_i \otimes \Gamma_h$ must contain A_{1g}, or A_1, or A_g or...

To find the second order correction to the energy, $E_i^{(2)}$:

When we collected all the terms in λ^2, we got

$$\mathcal{H}^{(0)}\Psi_i^{(2)}+\boldsymbol{h}\Psi_i^{(1)} = E_i^{(0)}\Psi_i^{(2)}+ E_i^{(1)}\Psi_i^{(1)}+ E^{(2)}\Psi_i^{(0)}$$

Let us now make use of what we have found about $^{(0)}$ and $E^{(1)}$:

$$\mathcal{H}^{(0)}\,\Psi_i^{(2)} +\boldsymbol{h}\Psi_i^{(1)} = \varepsilon_i\Psi_i^{(2)} + \boldsymbol{h}_{i\,i}\Psi_i^{(1)} + E_i^{(2)}\phi_i$$

Let us solve for $E_i^{(2)}$ by operating on both sides with $\int\phi_i^*d\tau$:

$$\int\phi_i^*\mathcal{H}^{(0)}\Psi_i^{(2)}d\tau + \int\phi_i^*\boldsymbol{h}\Psi_i^{(1)}d\tau = \varepsilon_i\int\phi_i^*\Psi_i^{(2)}d\tau + \boldsymbol{h}_{i\,i}\int\phi_i^*\Psi_i^{(1)}d\tau + E_i^{(2)}\int\phi_i^*\phi_i\,d\tau$$

$$E_i^{(2)} =\int\phi_i^*\mathcal{H}^{(0)}\Psi_i^{(2)}d\tau + \int\phi_i^*\boldsymbol{h}\Psi_i^{(1)}d\tau -\varepsilon_i\int\phi_i^*\Psi_i^{(2)}d\tau - \boldsymbol{h}_{i\,i}\int\phi_i^*\Psi_i^{(1)}d\tau$$

Since $\mathcal{H}^{(0)}$ is Hermitian,

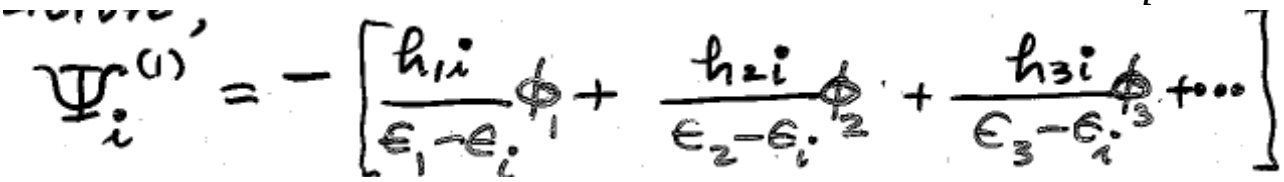
$$\int\phi_i^*\mathcal{H}^{(0)}\Psi_i^{(2)}d\tau = \{\int\Psi_i^{(2)*}\mathcal{H}^{(0)}\phi_i\,d\tau\}^* = \{\int\Psi_i^{(2)*}\varepsilon_i\,\phi_i d\tau\}^* = \varepsilon_i\int\phi_i^*\,\Psi_i^{(2)}d\tau$$

Collecting terms:

$$E_i^{(2)} = (\varepsilon_i -\varepsilon_i)\int\phi_i^*\,\Psi_i^{(2)}d\tau + \int\phi_i^*\boldsymbol{h}\Psi_i^{(1)}d\tau - \boldsymbol{h}_{i\,i}\int\phi_i^*\Psi_i^{(1)}d\tau$$

$$E_i^{(2)} = \int\phi_i^*\boldsymbol{h}\Psi_i^{(1)}d\tau - \boldsymbol{h}_{i\,i}\int\phi_i^*\Psi_i^{(1)}d\tau$$

Let us now make use of our found $\Psi_i^{(1)}$:



This sum does not include ϕ_i therefore,
$\int \phi_i^* \Psi_i^{(1)} d\tau = 0$. Therefore,
$E_i^{(2)} = \int \phi_i^* \boldsymbol{h} \Psi_i^{(1)} d\tau$
We now substitute the above $\Psi_i^{(1)}$ to get $E_i^{(2)}$:

$$E_i^{(2)} = -\left[\frac{(h_{1i})(h_{i1})}{(\varepsilon_1 - \varepsilon_i)} + \frac{(h_{2i})(h_{i2})}{(\varepsilon_2 - \varepsilon_i)} + \frac{(h_{3i})(h_{i3})}{(\varepsilon_3 - \varepsilon_i)} + \ldots \right]$$

EXAMPLE:

Ground state of a He-like atom (2 electrons):

$$H = \frac{-\hbar^2}{2\mu}(\nabla_1^2 + \nabla_2^2) - \left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2}\right) + \underbrace{\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}}_{\frac{e^2}{r_{12}}}$$

Let $H = H^{(0)} + h$

$$H^{(0)} = \frac{-\hbar^2}{2\mu}\nabla_1^2 - \frac{Ze^2}{r_1} \quad \frac{-\hbar^2}{2\mu}\nabla_2^2 - \frac{Ze^2}{r_2}$$

$$h = e^2/r_{12}$$

1. The known solutions are:

$$H^{(0)}\phi_0(\vec{r}_1, \vec{r}_2) = \epsilon_0 \phi_0(\vec{r}_1, \vec{r}_2)$$

$$\phi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1) \cdot \psi_{100}(\vec{r}_2)$$

ground state $n=1\ l=0\ m=0$ for each electron

is the solution to

$$\left(\frac{-\hbar^2}{2\mu}\nabla_1^2 - \frac{Ze^2}{r_1}\right)\psi_{100}(\vec{r}_1) = -\frac{Z^2}{1^2}\left(\frac{e^2}{2a_0}\right)\psi_{100}(\vec{r}_1)$$

a hydrogen-like atom

$$\epsilon_0 = -\frac{Z^2}{1^2}\frac{e^2}{2a_0} + \frac{-Z^2}{1^2}\frac{e^2}{2a_0} = -2\frac{Z^2}{1^2}\frac{e^2}{2a_0}$$

$$\phi_0(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr_1}{a_0}} \cdot \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr_2}{a_0}}$$

2. The first order correction to energy is

$$E_0^{(1)} = \int \phi_0^* \frac{e^2}{r_{12}} \phi_0 \, d\tau = \frac{5}{4} Z \frac{e^2}{2a_0}$$

Energy correct to first order

$$E_0 = \epsilon_0 + E_0^{(1)} = \left(-2Z^2 + \frac{5}{4}Z\right)\frac{e^2}{2a_0}$$

The second order correction has also been calculated

$$E_0^{(2)} = -0.31532\ e^2/2a_0$$

3. Now make h as small as possible:

Let $H^{(0)} = -\frac{\hbar^2}{2\mu}(\nabla_1^2+\nabla_2^2) - Z'\frac{e^2}{r_1} - \frac{Z'e^2}{r_2}$

and $h = \frac{e^2}{r_{12}} - (Z-Z')\left(\frac{e^2}{r_1}+\frac{e^2}{r_2}\right)$

Then $\phi_0(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{3/2} e^{-\frac{Z'r_1}{a_0}} \cdot \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{3/2} e^{-\frac{Z'r_2}{a_0}}$

$$\epsilon_0 = -\frac{(Z')^2}{1^2}\frac{e^2}{2a_0} - \frac{(Z')^2}{1^2}\frac{e^2}{2a_0}$$

THE SAME AS BEFORE, only Z' now instead of Z

The first order correction to energy is

$$E_0^{(1)} = \int \phi_0^* \left\{\frac{e^2}{r_{12}} - (Z-Z')\left(\frac{e^2}{r_1}+\frac{e^2}{r_2}\right)\right\}\phi_0 \, d\tau$$

$$= \frac{5}{4}Z'\frac{e^2}{2a_0} - (Z-Z')\cdot 4Z'\frac{e^2}{2a_0}$$

The energy good to first order:

$$E_0 = \epsilon_0 + E_0^{(1)} = \left\{-2(Z')^2 + \frac{5}{4}Z' - (Z-Z')4Z'\right\}\frac{e^2}{2a_0}$$

Now choose Z' such as to make $E_0^{(1)}$ vanish (i.e. make h as small as possible:

$$E_0^{(1)} = 0 = \left[\frac{5}{4}Z' - (Z-Z')4Z'\right]\frac{e^2}{2a_0}$$

$$\frac{5}{4} = 4(Z-Z') \quad \text{or} \quad Z' = \left(Z - \frac{5}{16}\right)$$

then $E_0 = \epsilon_0 + 0 = -2(Z')^2\frac{e^2}{2a_0} = -2\left(Z-\frac{5}{16}\right)^2\frac{e^2}{2a_0}$

Comparisons with EXPERIMENT (in units of $e^2/2a_0$):

	EXPT	to FIRST ORDER	to 1st ORDER (*)	to 2nd order	ϵ_0
He $Z=2$	−2.904	−2.750	−2.848	−2.908	−4
Li^+ $Z=3$	−7.280	−7.125	−7.223	−7.283	−9

ϵ_0 using $Z' = Z - \frac{5}{16}$

B. DEGENERATE TIME-INDEPENDENT PERTURBATION THEORY

If some of the states of $H^{(0)}$ are DEGENERATE, that is if several ϕ_i have the SAME ENERGY ϵ_i (PARTNER FUNCTIONS) then ① The functions ϕ_i are not unique for an energy ϵ_i since ANY LINEAR COMBINATION of the degenerate set can satisfy the Schrödinger eqn.

② We can not afford to have ZEROes in the $(\epsilon_n - \epsilon_i)$ in the denominator!!

Therefore, we must **FIRST FIND THE APPROPRIATE LINEAR COMBINATIONS of the DEGENERATE PARTNER FUNCTIONS**. How to do it? $\psi_i^{(0)} = a_1\phi_1 + a_2\phi_2 + a_3\phi_3 + \cdots$

For the degenerate partner functions we must do this: (Suppose there are 4 of them)

$$\det \begin{vmatrix} h_{11} - E_i^{(1)} & h_{12} & h_{13} & h_{14} \\ h_{21} & h_{22} - E_i^{(1)} & h_{23} & h_{24} \\ h_{31} & h_{32} & h_{33} - E_i^{(1)} & h_{34} \\ h_{41} & h_{42} & h_{43} & h_{44} - E_i^{(1)} \end{vmatrix} = 0$$

The roots obtained from solving the above give $E_i^{(1)}$ (4 roots in this case) and the desired coefficients can be found.

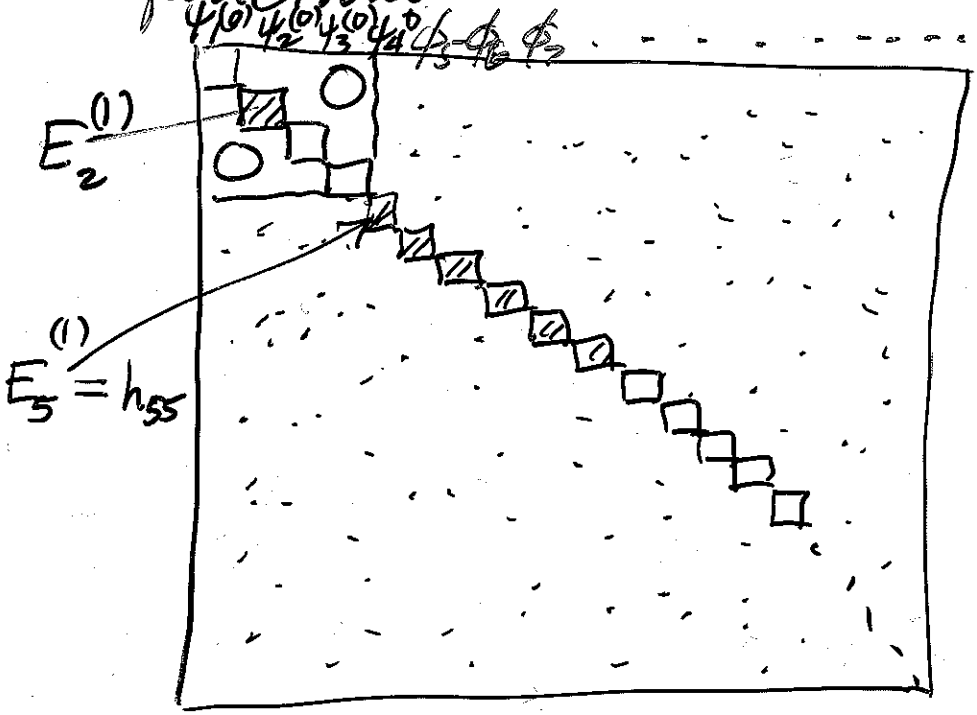
$$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} \quad \begin{bmatrix} \ \\ \ \\ \ \\ \ \end{bmatrix} \quad \begin{bmatrix} \ \\ \ \\ \ \\ \ \end{bmatrix} \quad \begin{bmatrix} \ \\ \ \\ \ \\ \ \end{bmatrix}$$

one set of coeff. for each $E_i^{(1)}$

$$\psi_1^{(0)} = a_1\phi_1 + a_2\phi_2 + a_3\phi_3 + a_4\phi_4$$

In other words, first we find the linear combinations of $\phi_1, \phi_2, \phi_3, \phi_4$ that DIAGONALIZES that block of the h matrix.

Now set up the h matrix in terms of these functions



And now proceed as before

$$\Psi_i^{\text{(corrected to 1st order)}} = \psi_i^{(0)} - \frac{\langle \phi_5 | h | \psi_i^{(0)} \rangle}{\epsilon_5 - \epsilon_i} \phi_5 - \frac{\langle \phi_6 | h | \psi_i^{(0)} \rangle}{\epsilon_6 - \epsilon_i} \phi_6 - \cdots$$

where $\psi_i^{(0)} = a_1 \phi_1 + a_2 \phi_2 + a_3 \phi_3 + a_4 \phi_4$

** Note that the now zero off-diagonal elements in the formerly DEGENERATE block ensure that no term in $\frac{h_{ij}}{\epsilon_j - \epsilon_i}$ ever arise from the functions in that block. That is why we DIAGONALIZED first before evaluating $\Psi_i^{(1)}$.

Need to do this for every degenerate block. After that the h matrix can be used as in the NON-DEGENERATE case.

EXAMPLE:

Consider a single electron in DEGENERATE states described by the functions (5 of them)

$\phi_i = R_{nl}(r)\, Y_{lm}(\theta,\phi)$ where $l=2$, $m=0,\pm1,\pm2$

[This is the approximate description for an ion with a single electron in a d orbital and closed inner shells.]

Place this electron in an **ELECTROSTATIC CRYSTALLINE FIELD OF POINT CHARGES** (V_{CF}) $-q_i e$ at positions $\vec{r}_i$

To find the new states we let

$$H = H^{(0)} + h$$

and

$$h = V_{CF} = \sum_i \frac{(-e)(-q_i e)}{|\vec{r}_i - \vec{r}|}$$

First let us examine how we may express h such as to make it easier to solve this problem.

$\frac{1}{|\vec{r}_i - \vec{r}|}$ can be expressed as an expansion in terms of the angular coordinates θ and ϕ of the electron and the FIXED coordinates θ_i and ϕ_i of the ith POINT CHARGE

$$\frac{1}{|\vec{r}_i - \vec{r}|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{r_<^{\,l}}{r_>^{\,l+1}} Y_{lm}^*(\theta_i,\phi_i)\, Y_{lm}(\theta,\phi)$$

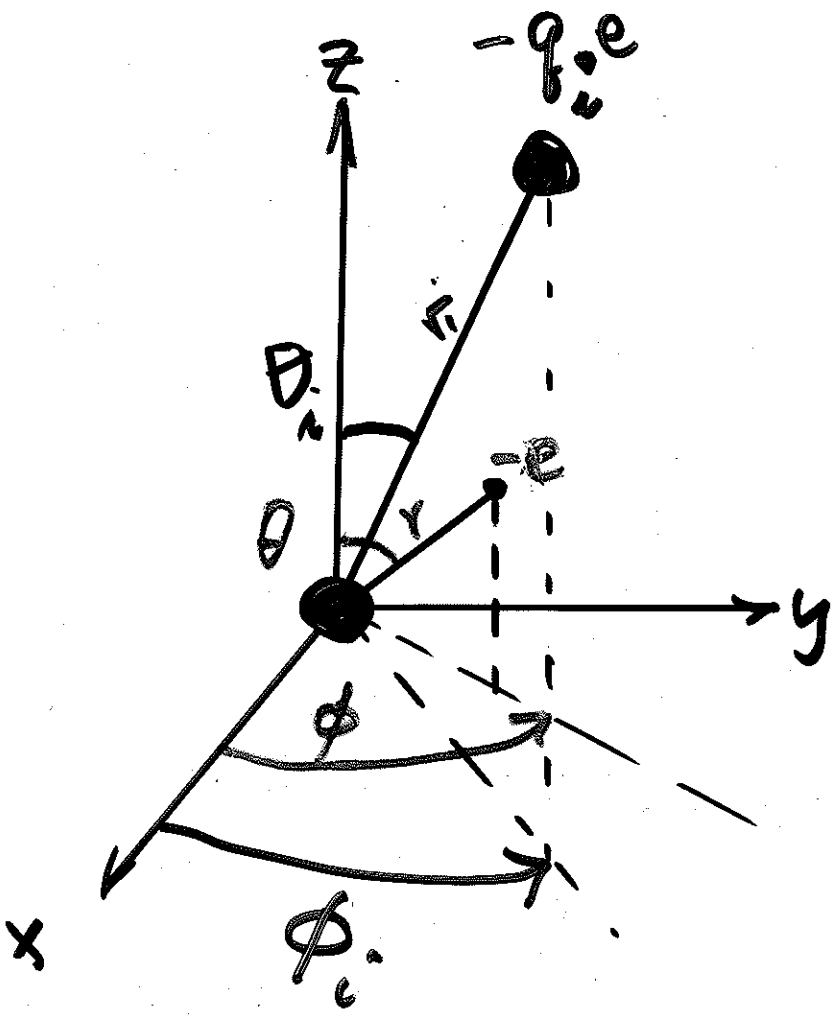
same lm for electron and for i^{th} LIGAND ION

where $r_<$ is the LESSER of $|\vec{r}_i|$ and $|\vec{r}|$

$r_>$ is the GREATER one of the two

electron is at r, θ, ϕ i^{th} LIGAND ION is at r_i, θ_i, ϕ_i

We need to set up the h matrix and diagonalize it to find the correct SALCs and $E^{(1)}$ values.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ϕ
x
ϕ_i

The matrix elements of h are: (for row m column m')

$$h_{mm'} = \int R_{nl}(r)^* Y_{2m'}^*(\theta,\phi)\, V_{CF}\, R_{nl}(r)\, Y_{2m}(\theta,\phi)\, d\tau$$

Each term in the matrix element will be of the form

$$\sum_{l=0}^{\infty} \sum_{m''=-l}^{+l} \frac{4\pi}{2l+1} Y_{lm''}(\theta_i,\phi_i) \int_{r=0}^{\infty} |R_{nl}(r)|^2 \frac{(r_<)^l}{(r_>)^{l+1}} r^2 dr \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} Y_{2m'}^* Y_{lm''} Y_{2m} \sin\theta\, d\theta\, d\phi$$

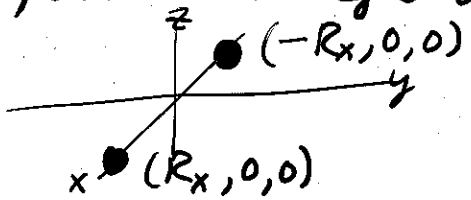
Since $Y_{lm}(\theta,\phi)$ functions are ORTHONORMAL, only certain of the integrals $\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} Y_{2m'}^* Y_{lm''} Y_{2m} \sin\theta\, d\theta\, d\phi$ will NOT VANISH.

Because the product $Y_{2m'}^* Y_{2m}$ will give a LINEAR COMBINATION of Y_{lm} functions with l no greater than 2+2 or 4 in this case of a d orbital, then the l in $Y_{lm''}$ can only be $l = 4$ (max), 2, or 0. Odd l values will give rise to ZERO integrals.

Now let us place the point charges:

Consider 2 point charges on the x axis:

$x_i = \pm R_x$
$y_i = 0$
$z_i = 0$



Substitute these values into

$$Y_{20}(\theta_i,\phi_i) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\left(\frac{3z^2-r^2}{r^2}\right) \text{ etc}$$

to get

$$Y_{00}(\theta_i,\phi_i) = \frac{1}{2\sqrt{\pi}} \quad Y_{20}(\theta_i,\phi_i) = -\frac{1}{4}\sqrt{\frac{5}{\pi}}$$

$$Y_{2\pm1}(\theta_i,\phi_i) = 0 \quad Y_{2\pm2}(\theta_i,\phi_i) = \frac{1}{4}\sqrt{\frac{5}{2\pi}}$$

$$Y_{40} = \frac{9}{16\sqrt{\pi}} \quad Y_{4\pm1} = 0 \quad Y_{4\pm2} = -\frac{3}{8}\sqrt{\frac{5}{2\pi}}$$

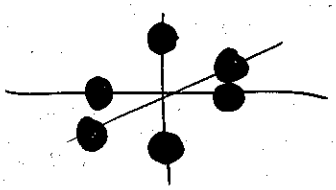
$$Y_{4\pm3} = 0 \quad Y_{4\pm4} = \frac{3}{16}\sqrt{\frac{35}{2\pi}}$$

Therefore, for 2 negative ions (charge $= -qe$) positioned on the x axis,

$$V_{CF} = 2q\left\{ \frac{1}{r_>} + \frac{4\pi}{5}\left(-\frac{1}{4}\sqrt{\frac{5}{\pi}}\right)\frac{r_<^2}{r_>^3} Y_{20}(\theta,\phi) \right.$$
$$+ \frac{4\pi}{5}\left(\frac{1}{4}\sqrt{\frac{15}{2\pi}}\right)\frac{r_<^2}{r_>^3}\left(Y_{22}(\theta,\phi) + Y_{2-2}(\theta,\phi)\right)$$
$$+\frac{4\pi}{9}\left(\frac{9}{16\sqrt{\pi}}\right)\frac{r_<^4}{r_>^5} Y_{40}(\theta,\phi)$$
$$+\frac{4\pi}{9}\left(-\frac{3}{8}\sqrt{\frac{5}{2\pi}}\right)\frac{r_<^4}{r_>^5}\left(Y_{42}(\theta,\phi) + Y_{4-2}(\theta,\phi)\right)$$
$$\left. + \frac{4\pi}{9}\left(\frac{3}{16}\sqrt{\frac{35}{2\pi}}\right)\frac{r_<^4}{r_>^3}\left(Y_{44}(\theta,\phi) + Y_{4-4}(\theta,\phi)\right)\right\}$$

These are the coordinates of the electron

We can do the same for 2 point charges (LIGAND IONS) on the y axis and 2 on the z axis. If OCTAHEDRAL O_h CRYSTAL FIELD, then sum up over all 3 sets and make $R_x = R_y = R_z = R$



(the terms in $\frac{r_<^2}{r_>^3}$ cancelled out)

$$V_{CF} = \frac{2q}{R}\left\{ 3 + \left(\frac{r}{R}\right)^4\left[\frac{7}{6}\sqrt{\pi}\, Y_{40}(\theta,\phi) + \frac{1}{6}\sqrt{\frac{35\pi}{2}}\left(Y_{44}(\theta,\phi) + Y_{4-4}(\theta,\phi)\right)\right]\right\}$$

for $R > r$

So that the matrix elements of h

$$h_{m'm} = \int R(r)^* Y_{2m'}^*(\theta,\phi)\, V_{CF}\, R(r)\, Y_{2m}(\theta,\phi)\, d\tau$$

can be calculated.

If we let $x \equiv \frac{1}{6} q \frac{\langle r^4 \rangle}{R^5}$ where $\langle r^4 \rangle \equiv \int_0^\infty |R_{nl}(r)|^2 r^4 r^2 dr$

and $\int Y_{2m'} Y_{40} Y_{2m} \sin\theta d\theta d\phi$ can be looked up in tables

$= \frac{1}{21}$ for $m' = m = 2$ and $m' = m = -2$ for example

We find the entire h matrix:

$h =$

$\phi_i =$	Y_{22}	Y_{21}	Y_{20}	Y_{2-1}	Y_{2-2}
2	$\frac{69}{R} + X$	0	0	0	$5X$
1	0	$\frac{69}{R} - 4X$	0	0	0
0	0	0	$\frac{69}{R} + 6X$	0	0
−1	0	0	0	$\frac{69}{R} - 4X$	0
−2	$5X$	0	0	0	$\frac{69}{R} + X$

Which we can rearrange, of course, to give

$\phi_i =$	Y_{21}	Y_{20}	Y_{2-1}	Y_{22}	Y_{2-2}
1	$\frac{69}{R} - 4X$	0	0	0	0
0	0	$\frac{69}{R} + 6X$	0	0	0
−1	0	0	$\frac{69}{R} - 4X$	0	0
2	0	0	0	$\frac{69}{R} + X$	$5X$
−2	0	0	0	$5X$	$\frac{69}{R} + X$

DIAGONALIZE it and get 5 roots: $\psi_i^{(0)}$

$E_1^{(1)} = \frac{69}{R} - 4X \quad Y_{21}$

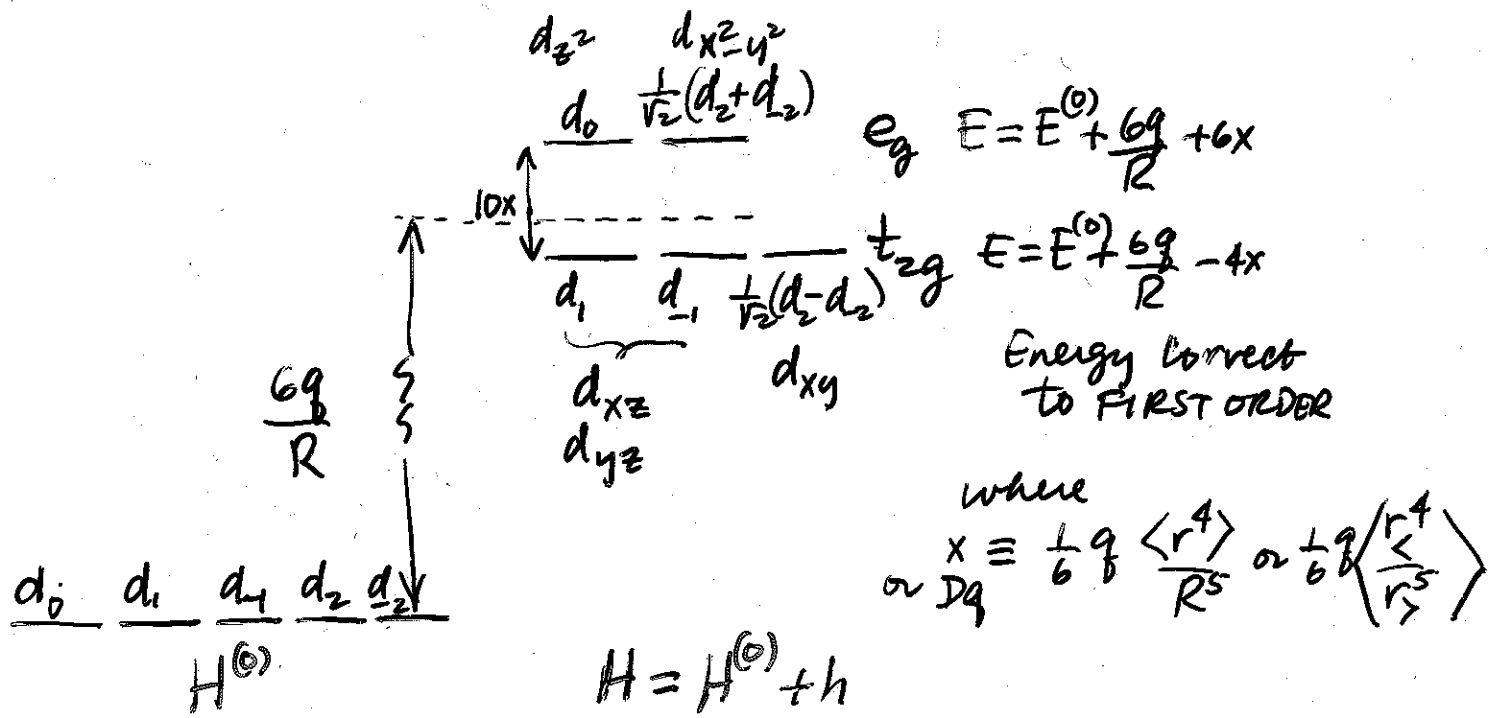
$E_0^{(1)} = \frac{69}{R} + 6X \quad Y_{20}$

$E_{-1}^{(1)} = \frac{69}{R} - 4X \quad Y_{2-1}$

directly and from the 2×2 we get

$E_+^{(1)} = \frac{69}{R} + 6X \quad \frac{1}{\sqrt{2}}(Y_{22} + Y_{2-2})$

$E_-^{(1)} = \frac{69}{R} - 4X \quad \frac{1}{\sqrt{2}}(Y_{22} - Y_{2-2})$



where

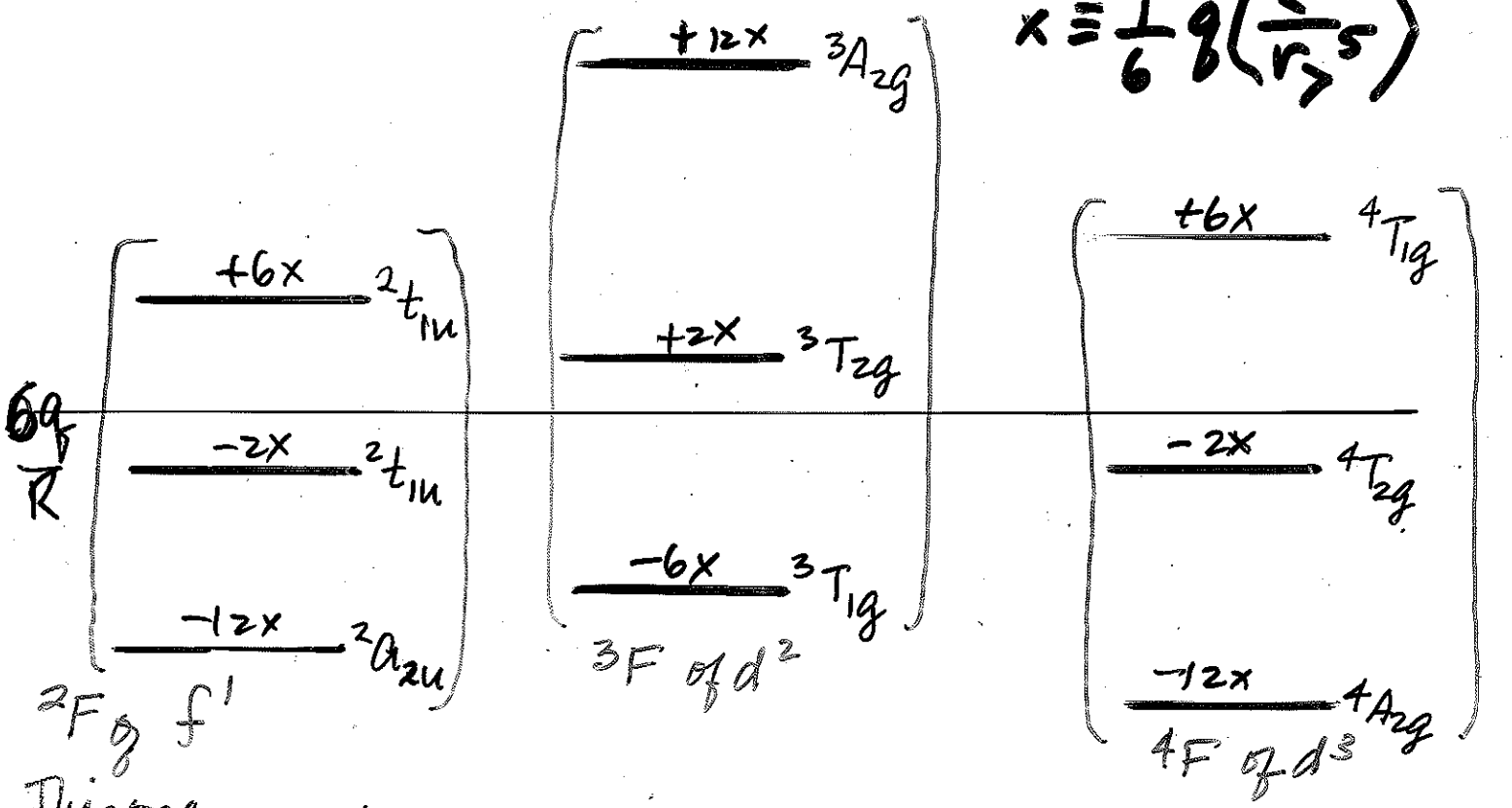
$x \equiv \frac{1}{6} q \langle r^4 \rangle / R^5$ or $\frac{1}{6} q \left\langle \frac{r_<^4}{r_>^5} \right\rangle$ or Dq

THIS is the basis for CRYSTAL FIELD THEORY.
It is merely a simple application of degenerate perturbation theory. Can do it for ANY arrangement of the IONS (tetrahedral, square planar, etc.)

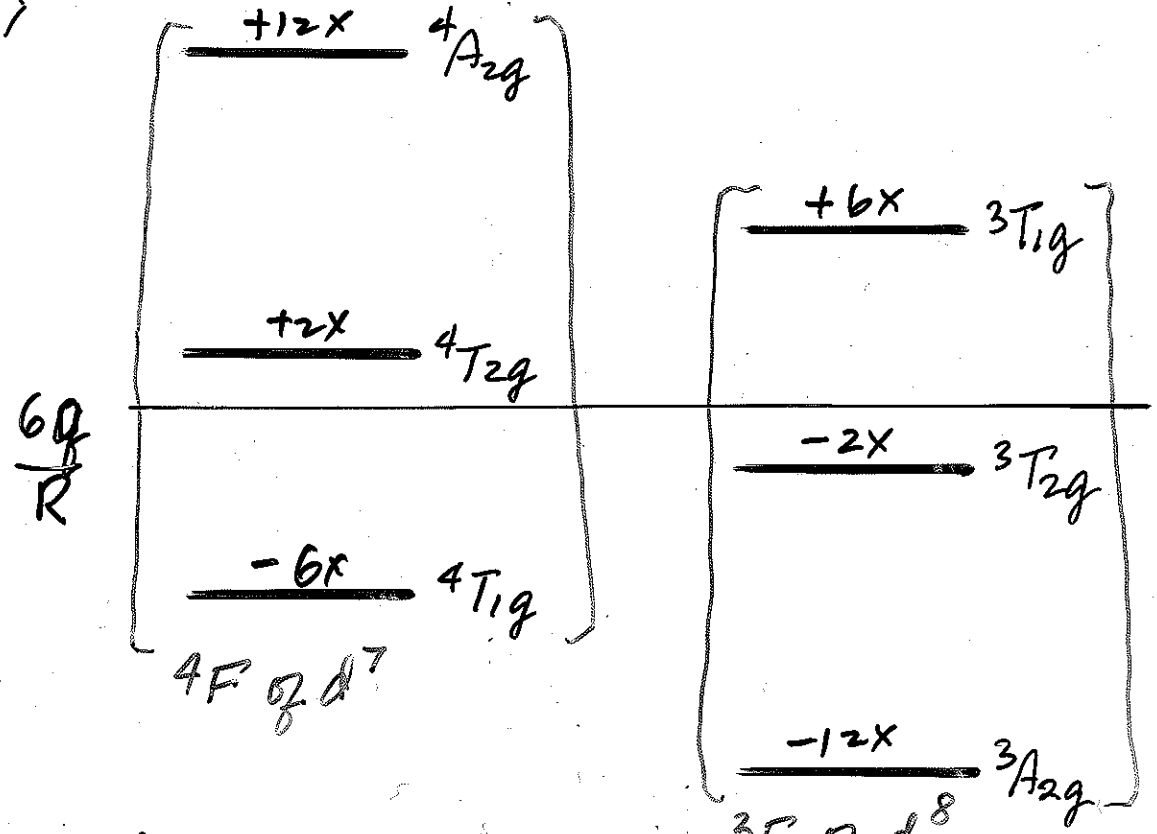
SPLITTING of ONE-ELECTRON LEVELS in various symmetries

(2l+1) partner functions	l	SYMMETRY of ENVIRONMENT O_h	T_d	D_{4h}
1	s	a_{1g}	a_1	a_{1g}
3	p	t_{1u}	t_2	$a_{2u}+e_u$
5	d	e_g+t_{2g}	$e+t_2$	$a_{1g}+b_{1g}+b_{2g}+e_g$
7	f	$a_{2u}+t_{1u}+t_{2u}$	$a_2+t_1+t_2$	$a_{2u}+b_{1u}+b_{2u}+2e_u$
9	g	$a_{1g}+e_g+t_{1g}+t_{2g}$	$a_1+e+t_1+t_2$	$2a_{1g}+a_{2g}+b_{1g}+b_{2g}+2e_g$
11	h	$e_u+2t_{1u}+t_{2u}$	$e+2t_1+t_2$	$a_{1u}+2a_{2u}+b_{1u}+b_{2u}+3e_u$
13	i	$a_{1g}+a_{2g}+e_g+t_{1g}+2t_{2g}$	$a_1+a_2+e+t_1+2t_2$	$2a_{1g}+a_{2g}+2b_{1g}+2b_{2g}+3e_g$

$x \equiv \frac{1}{6} g \left(\frac{r_<^4}{r_>^5} \right)$



This one
$x \equiv \frac{21}{33} \frac{1}{6} g \left(\frac{r_<^4}{r_>^5} \right)$



Note:
u for f^1
g for any number of d electrons
$d^n \simeq d^{(10-n)}$
d^2 and f^1 are related by factor $\frac{-21}{33}$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$f^{(j)}$
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1	
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1	
E_g	2	−1	0	0	2	2	0	−1	2	0	$3z^2-r^2, x^2-y^2$
E_u	2	−1	0	0	2	−2	0	1	−2	0	
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	R_x, R_y, R_z
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1	xy, xz, zy
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	x, y, z
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1	

D_{4h}	E	$2C_4^{(z)}$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	$f^{(j)}$
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	$x^2+y^2; z^2$
A_{1u}	+1	+1	+1	+1	+1	−1	−1	−1	−1	−1	
A_{2g}	+1	+1	+1	−1	−1	+1	+1	+1	−1	−1	R_z
A_{2u}	+1	+1	+1	−1	−1	−1	−1	−1	+1	+1	z
B_{1g}	+1	−1	+1	+1	−1	+1	−1	+1	+1	−1	x^2-y^2
B_{1u}	+1	−1	+1	+1	−1	−1	+1	−1	−1	+1	
B_{2g}	+1	−1	+1	−1	+1	+1	−1	+1	−1	+1	xy
B_{2u}	+1	−1	+1	−1	+1	−1	+1	−1	+1	−1	
E_g	+2	0	−2	0	0	+2	0	−2	0	0	$R_x, R_y; xz, yz$
E_u	+2	0	−2	0	0	−2	0	+2	0	0	x, y

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	$f^{(j)}$
A_1	1	1	1	1	1	$x^2+y^2+z^2$
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	$3z^2-r^2, x^2-y^2$
T_1	3	0	−1	1	−1	R_x, R_y, R_z
T_2	3	0	−1	−1	1	$x, y, z; xy, xz, yz$

VARIATIONAL METHOD

Take an arbitrary well-behaved function Ψ_{trial}.
Expand it in terms of the eigenfunctions of H
$\{\phi_0\ \phi_1\ \phi_2 \cdots\}$ so that $H\phi_n = E_n\phi_n$

$$\Psi_{trial} = c_0\phi_0 + c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \cdots$$

Form the quantity: ($\mathcal{E}$)

$$\mathcal{E} = \frac{\int \Psi_{trial}^* H \Psi_{trial}\, d\tau}{\int \Psi_{trial}^* \Psi_{trial}\, d\tau} = \frac{(c_0^2E_0 + c_1^2E_1 + c_2^2E_2 + \cdots)}{(c_0^2 + c_1^2 + c_2^2 + \cdots)}$$

Factor out E_0 (the ground state energy)

$$\mathcal{E} = \frac{E_0\left(c_0^2 + c_1^2\frac{E_1}{E_0} + c_2^2\frac{E_2}{E_0} + \cdots\right)}{(c_0^2 + c_1^2 + c_2^2 + \cdots)}$$

$\mathcal{E}$: calculated with arbitrary Ψ_{trial}

$\geq E_0$ ← true ground state energy

This inequality allows us to obtain an **UPPER BOUND** to E_0 when we don't know what it is, by choosing Ψ_{trial} to be dependent on any number of VARIABLE PARAMETERS $a_1, a_2, \ldots$ To find the BEST VALUES of the parameters, minimize $\mathcal{E}$, that is,

$$\frac{\partial \mathcal{E}}{\partial a_1} = 0, \quad \frac{\partial \mathcal{E}}{\partial a_2} = 0, \quad \ldots$$

The minimum value of $\mathcal{E}$ for these values of the parameters gives an upper bound to the unknown E_0.

EXAMPLE: 2-electron atom

$$\mathcal{H} = \frac{-\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2}\right) + \frac{e^2}{r_{12}}$$

Let $\Psi_{trial} = N e^{-\frac{Z'(r_1+r_2)}{a_0}}$ normalized by N

$$\mathcal{E} = \frac{\int \Psi_{trial}^* \mathcal{H} \Psi_{trial} d\tau}{1} =$$ (same integrals we have seen before in doing perturbation theory on same atom)

$\frac{\partial \mathcal{E}}{\partial Z'} = 0$ gives $Z' = Z - \frac{5}{16}$

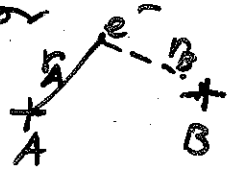
$\Psi_{trial} = N e^{-\frac{(Z-5/16)(r_1+r_2)}{a_0}}$, can then find N.

EXAMPLE:

A very common choice of Ψ_{trial} is a linear combination:

$$\Psi_{trial} = c_1\phi_1 + c_2\phi_2$$

where ϕ_1 and ϕ_2 are two known functions, not necessarily orthogonal to each other. For example $\phi_1 = \psi_{100}(\vec{r}_A)$ $\phi_2 = \psi_{100}(\vec{r}_B)$ in



$$\mathcal{E} = \frac{c_1^2 H_{11} + 2c_1c_2H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1c_2S_{12} + c_2^2 S_{22}}$$

where $H_{12} \equiv \int \phi_1^* H \phi_2 d\tau$, etc...

$$S_{12} \equiv \int \phi_1^* \phi_2 d\tau, \text{ etc.}$$

$\frac{\partial \mathcal{E}}{\partial c_1} = 0$ is of the form $d\left(\frac{u}{v}\right) = \frac{v\,du - u\,dv}{v^2} = \frac{1}{v}\int du - \left(\frac{u}{v}\right) dv$ ($\mathcal{E}$)

$$\frac{\partial \mathcal{E}}{\partial c_1} = 0 = \frac{(2c_1H_{11} + 2c_2H_{12}) - \mathcal{E}(2c_1S_{11} + 2c_2S_{12})}{c_1^2S_{11} + 2c_1c_2S_{12} + c_2^2S_{22}}$$

This reduces to

$$c_1(H_{11}-\mathcal{E}S_{11}) + c_2(H_{12}-\mathcal{E}S_{12}) = 0$$
$$c_1(H_{12}-\mathcal{E}S_{12}) + c_2(H_{22}-\mathcal{E}S_{22}) = 0$$

Solutions occur if

$$\det \begin{vmatrix} H_{11}-\mathcal{E}S_{11} & H_{12}-\mathcal{E}S_{12} \\ H_{12}-\mathcal{E}S_{12} & H_{22}-\mathcal{E}S_{22} \end{vmatrix} = 0$$

Two roots in this case. Choose that root for $\mathcal{E}$ less than the lower one of $\frac{H_{11}}{S_{11}}$ or $\frac{H_{22}}{S_{22}}$.

In general, need to solve

$$\det \begin{vmatrix} H_{11}-\mathcal{E}S_{11} & H_{12}-\mathcal{E}S_{12} & H_{13}-\mathcal{E}S_{13} & \cdots \\ H_{12}-\mathcal{E}S_{12} & H_{22}-\mathcal{E}S_{22} & H_{23}-\mathcal{E}S_{23} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} = 0$$

Choose the lowest $\mathcal{E}$ as the approximation to the true E_0. This substituted back into the equations provides the best approximate Ψ as

$$\Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \cdots$$

the set obtained with the lowest $\mathcal{E}$.