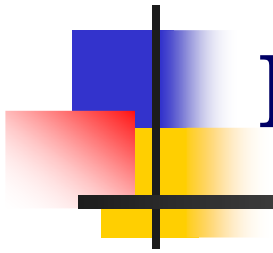


Lecture #13

Self-consistent fields

Hartree-Fock equations: He-like systems

Chapter 3, pages 61-77, Lectures on Atomic Physics

He-like systems

Z=2: He

Z=3: Li^+

Z=4: Be^{++}

...

$$H(\mathbf{r}_1,\mathbf{r}_2) = h_0(\mathbf{r}_1) + h_0(\mathbf{r}_2) + \frac{1}{r_{12}}$$

Coulomb repulsion between two electrons

$$h_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

$$h_0\psi_a(\mathbf{r}) = \varepsilon_a\psi_a(\mathbf{r})$$

Solutions: Coulomb (H-like) wave functions

$$\psi_{nlm}(\mathbf{r}) = \frac{1}{r}P_{nl}(r)Y_{lm}(\theta,\phi)$$

One-electron wave functions

$$H(\mathbf{r}_1,\mathbf{r}_2)\Psi(\mathbf{r}_1,\mathbf{r}_2) = E\,\Psi(\mathbf{r}_1,\mathbf{r}_2)$$

$$P_{1s}(r) = 2Z^{3/2}re^{-Zr}$$

$$\Psi_{1s,1s}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{4\pi}\frac{1}{r_1}P_{1s}(r_1)\frac{1}{r_2}P_{1s}(r_2)\frac{1}{\sqrt{2}}\left\{\left|\tfrac{1}{2}\,\tfrac{1}{2},\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle - \left|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}\,\tfrac{1}{2}\right\rangle\right\}$$

Two-electron ground state wave function

Derivation of Hartree-Fock equation for 1s orbital

$$E_{1s1s} = \left\langle \Psi_{1s1s} \left| h_0(\mathbf{r}_1) + h_0(\mathbf{r}_2) + \frac{1}{r_{12}} \right| \Psi_{1s1s} \right\rangle$$

$$\left\langle \Psi_{1s1s} \left| h_0(\mathbf{r}_1) \right| \Psi_{1s1s} \right\rangle = \frac{1}{(4\pi)^2} 4\pi \underbrace{\int_0^\infty r_2^2 dr_2 \frac{1}{r_2^2} P_{1s}^2(r_2)}_{\int_0^\infty dr_2 P_{1s}^2(r_2) = 1} \int_0^\infty 4\pi r_1^2 dr_1 \frac{1}{r_1} P_{1s}(r_1) \left[-\frac{\nabla^2}{2} - \frac{Z}{r_1} \right] \frac{1}{r_1} P_{1s}(r_1)$$

← Normalization condition

$$= \int_0^\infty dr \left[-\frac{1}{2} P_{1s}(r) \frac{d^2 P_{1s}(r)}{dr^2} - \frac{Z}{r} P_{1s}^2(r) \right] = \int_0^\infty dr \left[\frac{1}{2} \left(\frac{dP_{1s}(r)}{dr} \right)^2 - \frac{Z}{r} P_{1s}^2(r) \right]$$

(integrating by parts)

$$\left\langle \Psi_{1s1s} \left| h_0(\mathbf{r}_1) + h_0(\mathbf{r}_2) \right| \Psi_{1s1s} \right\rangle = 2 \int_0^\infty dr \left[\frac{1}{2} \left(\frac{dP_{1s}(r)}{dr} \right)^2 - \frac{Z}{r} P_{1s}^2(r) \right]$$

Derivation of Hartree-Fock equation for 1s orbital

$$\left\langle \Psi_{1s1s} \left| \frac{1}{r_{12}} \right| \Psi_{1s1s} \right\rangle$$

$r_<$ and $r_>$ are lesser and greater of r_1, r_2

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{k} Y_{kq}^*(\theta_1,\phi_1) Y_{kq}(\theta_2,\phi_2)$$

The spherical harmonics are orthonormal on the unit sphere:

$$\int d\Omega\, Y_{k'q'}^*(\theta,\phi) Y_{kq}(\theta,\phi) = \delta_{kk'}\delta_{qq'}$$

Therefore: $\int d\Omega_1 Y_{kq}^*(\theta_1,\phi_1) Y_{00} = \delta_{k0}\delta_{q0}$ and only one term $k=0$ $q=0$ contributes from the sums over k and q for 1s1s integral.

$$\left\langle \Psi_{1s1s} \left| \frac{1}{r_{12}} \right| \Psi_{1s1s} \right\rangle = \int_0^{\infty} dr_1\; P_{1s}^2(r_1) \int_0^{\infty} dr_2\; P_{1s}^2(r_2) \frac{1}{r_>}$$

Derivation of Hartree-Fock equation for 1s orbital

$$\left\langle \Psi_{1s1s} \left| \frac{1}{r_{12}} \right| \Psi_{1s1s} \right\rangle = \int_0^\infty dr_1 \; P_{1s}^2(r_1) \underbrace{\int_0^\infty dr_2 \; P_{1s}^2(r_2) \frac{1}{r_>}}$$

$r_>$ is the greater of r_1, r_2

$$\upsilon_0(1s, r_1) = \int_0^\infty dr_2 \; P_{1s}^2(r_2) \frac{1}{r_>}$$

← New designation

This is a potential at r_1 of a spherically symmetric charge distribution with radial density $P_{1s}^2(r)$.

$$\left\langle \Psi_{1s1s} \left| \frac{1}{r_{12}} \right| \Psi_{1s1s} \right\rangle = \int_0^\infty dr_1 \; P_{1s}^2(r_1) \, \upsilon_0(1s, r_1)$$

Put it all together

$$E_{1s1s} = \left\langle \Psi_{1s1s} \middle| h_0(\mathbf{r}_1) + h_0(\mathbf{r}_2) + \frac{1}{r_{12}} \middle| \Psi_{1s1s} \right\rangle$$

$$= \int_0^\infty dr \left[\left(\frac{dP_{1s}(r)}{dr} \right)^2 - \frac{2Z}{r} P_{1s}^2(r) + \upsilon_0(1s, r) P_{1s}^2(r) \right]$$

$$\left\langle \Psi_{1s1s} \middle| \Psi_{1s1s} \right\rangle = 1 \quad \rightarrow \quad N_{1s} = \int_0^\infty dr P_{1s}^2(r) = 1 \longleftarrow$$

Normalization condition

Variational principle: we require that energy be stationary with respect to variation of the radial function subject to normalization constant.

$$\delta\left(E_{1s1s} - \lambda N_{1s} \right) = 0$$

Lagrange multiplier

HF equation

$$\delta P_{1s}(0) = \delta P_{1s}(\infty) = 0$$

$$\delta \frac{dP_{1s}}{dr} = \frac{d}{dr}\delta P_{1s}$$

$$\delta\left(E_{1s1s} - \lambda N_{1s}\right) = \int_0^\infty dr\left[\delta\left(\frac{dP_{1s}(r)}{dr}\right)^2 - \frac{2Z}{r}\delta[P_{1s}^2(r)] + \upsilon_0(1s,r)\delta[P_{1s}^2(r)] - \lambda\delta[P_{1s}^2(r)]\right]$$

$$= 2\int_0^\infty dr\left[\frac{dP_{1s}(r)}{dr}\delta\left(\frac{dP_{1s}(r)}{dr}\right) - \frac{2Z}{r}P_{1s}(r)\delta P_{1s}(r) + \upsilon_0(1s,r)P_{1s}(r)\delta P_{1s}(r) - \lambda\delta P_{1s}(r)\delta P_{1s}(r)\right]$$

$$= 2\int_0^\infty dr\left[-\frac{d^2P_{1s}(r)}{dr^2} - \frac{2Z}{r}P_{1s}(r) + 2\upsilon_0(1s,r)P_{1s}(r) - \lambda P_{1s}(r)\right]\delta P_{1s}(r)$$

(integrating by parts)

HF equation

$$\delta\left(E_{1s1s}-\lambda N_{1s}\right)=2\int_0^\infty dr\left[-\frac{d^2P_{1s}(r)}{dr^2}-\frac{2Z}{r}P_{1s}(r)+2\upsilon_0(1s,r)P_{1s}(r)-\lambda P_{1s}(r)\right]\delta P_{1s}(r)$$

$$-\frac{1}{2}\frac{d^2P_{1s}(r)}{dr^2}-\frac{Z}{r}P_{1s}(r)+\upsilon_0(1s,r)P_{1s}(r)=\varepsilon_{1s}P_{1s}(r)$$

HF equation for 1s orbital

Just the radial Schrödinger equation for a particle with l=0 moving in a potential

$$V(r)=-\frac{Z}{r}+\upsilon_0(1s,r)$$

HF equation: solution procedure

$$-\frac{1}{2}\frac{d^2P_{1s}(r)}{dr^2}-\frac{Z}{r}P_{1s}(r)+\upsilon_0(1s,r)P_{1s}(r)=\varepsilon_{1s}P_{1s}(r)$$

1. Pick a function $P_{1s}(r)$ which is our best known approximation to 1s wave function (screened Coulomb wave function with effective charge β)

$$P_{1s}(r)=2\beta^{3/2}re^{-\beta r},\quad \beta=Z-\frac{5}{16}$$

2. Use it to calculate the potential $\upsilon_0(1s,r)$: $\upsilon_0(1s,r_1)=\int_0^\infty dr_2\ P_{1s}^2(r_2)\frac{1}{r_>}$

3. Substitute this potential to HF equation and solve it for P_{1s} and ε_{1s}.

4. Now use our new wave function to evaluate to potential $\upsilon_0(1s,r)$ again.

5. Repeat until ε_{1s} converges (equation is solved iteratively).

Convergence parameter $\longrightarrow$ $\delta=\frac{\varepsilon^{(n)}-\varepsilon^{(n-1)}}{\varepsilon^{(n-1)}}$ $\varepsilon^{(n)}$ energy after iteration n

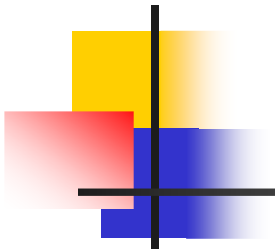
Back to the calculation of total energy

Iteration of ε_{1s}: energy converges to 10 digits after 18 iterations ε_{1s}=-0.9179 a.u.

$$E_{1s1s} = \left\langle \Psi_{1s1s} \left| h_0(\mathbf{r}_1) + h_0(\mathbf{r}_2) + \frac{1}{r_{12}} \right| \Psi_{1s1s} \right\rangle = \left\langle 1s \left| 2h_0 + v_0(1s, r) \right| 1s \right\rangle$$

$$= 2\varepsilon_{1s} - \left\langle 1s \left| v_0(1s, r) \right| 1s \right\rangle \approx -2.861 \text{ a.u.} = -77.8 \text{ eV}$$

The improvement is small for He but it is the best which can be obtained within the framework of *Independent-particle approximation.*



HF equations for closed shell systems

Why do we need approximation methods?

$$H(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N} h_0(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

$$H(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = E \, \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

Why do we need approximate methods?

Lets take an iron atom. It has 26 electrons: wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ depends on 3×26 =78 variables.

Using a grid of only 10 points we need 10^{78} numbers to tabulate iron wave function!

This is larger than the estimated number of particles in the Solar system!

This is why approximations to “exact” solutions and the methods of improving accuracy of these solutions are of such interest.

Independent-particle approximation

$$H(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\sum_{i=1}^{N}h_0(\mathbf{r}_i)+\frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}=H_0+V$$

$$H_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\sum_{i=1}^{N}h_0(\mathbf{r}_i)+\sum_{i=1}^{N}U(\mathbf{r}_i)$$

$$=\sum_{i=1}^{N}h(\mathbf{r}_i)$$

$$V(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}-\sum_{i=1}^{N}U(\mathbf{r}_i)$$

add and subtract

Why? To have better lowest order and smaller V.

Note: we redefined our lowest order and our lowest order wave functions are solutions of $h\psi_a(\mathbf{r})=\varepsilon_a\psi_a(\mathbf{r})$.

What are our indices a ? ⟶ Full set of quantum numbers which defines orbital a. For example:

$$a=(n_a,l_a,m_a,\mu_a)$$

Lowest order energy

$$E^{(0)}_{ab\ldots n}=\varepsilon_a+\varepsilon_b+\ldots+\varepsilon_n$$

Matrix elements

How to evaluate matrix elements of H_0 and V?

$$H_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\sum_{i=1}^{N}h_0(\mathbf{r}_i)+\sum_{i=1}^{N}U(\mathbf{r}_i) \qquad V(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}-\sum_{i=1}^{N}U(\mathbf{r}_i)$$

one-body matrix elements

two-body matrix element

Need to evaluate:

$$\left\langle\Psi_{ab\ldots n}\left|\sum_{i=1}^{N}h_0(\mathbf{r}_i)\right|\Psi_{ab\ldots n}\right\rangle \qquad \left\langle\Psi_{ab\ldots n}\left|\sum_{i=1}^{N}U(\mathbf{r}_i)\right|\Psi_{ab\ldots n}\right\rangle$$

$$\left\langle\underbrace{\Psi_{ab\ldots n}}\left|\frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}\right|\underbrace{\Psi_{ab\ldots n}}\right\rangle$$

same sets of indices

System of N particles: many-particle operators

$$F = \sum_{i=1}^{N} f(\mathbf{r}_i)$$

One-particle operators

Example: $H = \sum_{i=1}^{N} h_i$

Lets designate our Slater determinate functions $\Psi_{ab\ldots n}$

How to evaluate the corresponding matrix elements?

$$\left\langle \Psi_{a'b'\ldots n'} \middle| F \middle| \Psi_{ab\ldots n} \right\rangle = \sum_{i=a}^{N} f_{ii}$$

If the sets of indices $\{a'b'\ldots n'\}$ and $\{ab\ldots n\}$ are the same.

$$f_{ab} = \langle a | f | b \rangle = \int d^3 r \, \psi_a^{\dagger}(\mathbf{r}) f(\mathbf{r}) \psi_b(\mathbf{r})$$

System of N particles: many-particle operators

$$G = \frac{1}{2}\sum_{i \neq j} g(r_{ij})$$

Two-particle operators

Example: $\frac{1}{2}\sum_{i \neq j} \frac{1}{r_{ij}}$

$$\left\langle \Psi_{a'b'\ldots n'} \middle| G \middle| \Psi_{ab\ldots n} \right\rangle = \frac{1}{2}\sum_{i,j}\left(g_{ijij} - g_{ijji} \right)$$

If the sets of indices $\{a'b'\ldots n'\}$ and $\{ab\ldots n\}$ are the same.

$$g_{abcd} = \langle ab | g | cd \rangle = \int d^3 r_1 \int d^3 r_2 \, \psi_a^\dagger(\mathbf{r}_1)\psi_b^\dagger(\mathbf{r}_2)\, g(r_{12})\, \psi_c(\mathbf{r}_1)\psi_d(\mathbf{r}_2)$$

Matrix elements

How to evaluate matrix elements of H_0 and V?

$$F = \sum_{i=1}^{N} f(\mathbf{r}_i) \qquad \left\langle \Psi_{ab\ldots n} \middle| F \middle| \Psi_{ab\ldots n} \right\rangle = \sum_{i=a}^{N} f_{ii}$$

$$G = \frac{1}{2} \sum_{i \neq j} g(r_{ij}) \qquad \left\langle \Psi_{ab\ldots n} \middle| G \middle| \Psi_{ab\ldots n} \right\rangle = \frac{1}{2} \sum_{i,j} \left(g_{ijij} - g_{ijji} \right)$$

$$\left\langle \Psi_{ab\ldots n} \middle| \sum_{i=1}^{N} h_0(\mathbf{r}_i) \middle| \Psi_{ab\ldots n} \right\rangle = \sum_{i=1}^{N} (h_0)_{ii}$$

$$\left\langle \Psi_{ab\ldots n} \middle| \sum_{i=1}^{N} U(\mathbf{r}_i) \middle| \Psi_{ab\ldots n} \right\rangle = \sum_{i=1}^{N} U_{ii}$$

$$\left\langle \Psi_{ab\ldots n} \middle| \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \middle| \Psi_{ab\ldots n} \right\rangle = \frac{1}{2} \sum_{i,j} \left(g_{ijij} - g_{ijji} \right)$$

↑

Coulomb matrix elements

Closed-shell systems: He, Be, Ne, ...

Helium	$\mathrm{He}: \; 1s^2$
Beryllium	$\mathrm{Be}: \; 1s^2 2s^2$
Neon	$\mathrm{Ne}: \; 1s^2 2s^2 2p^6$
Magnesium	$\mathrm{Mg}: \; 1s^2 2s^2 2p^6 3s^2$
Argon	$\mathrm{Ag}: \; 1s^2 2s^2 2p^6 3s^2 3p^6$
Calcium	$\mathrm{Ca}: \; 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

...

Closed-shell systems: He, Be, Ne, …

Lets use the following designations again: sum over core (closed-shell orbitals) is designated by the indices from the beginning of the alphabet: a,b,c,d …

$$\left\langle \Psi_{ab\ldots n} \left| \sum_{i=1}^{N} h_0(\mathbf{r}_i) \right| \Psi_{ab\ldots n} \right\rangle = \sum_{i=1}^{N} (h_0)_{ii} = \sum_{a} (h_0)_{aa}$$

$$\left\langle \Psi_{ab\ldots n} \left| \sum_{i=1}^{N} U(\mathbf{r}_i) \right| \Psi_{ab\ldots n} \right\rangle = \sum_{i=1}^{N} U_{ii} = \sum_{a} U_{aa}$$

$$\left\langle \Psi_{ab\ldots n} \left| \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \right| \Psi_{ab\ldots n} \right\rangle = \frac{1}{2} \sum_{i,j} \left(g_{ijij} - g_{ijji} \right) = \frac{1}{2} \sum_{ab} \left(g_{abab} - g_{abba} \right)$$

Sum over a means sum over the entire set of quantum numbers of all the core electrons

For example, Be: $n_a l_a : (1s, 2s)$

$$\sum_{a} = \sum_{n_a\, l_a\, m_a\, \mu_a}$$

Closed-shell systems: He, Be, Ne, ...

$$E^{(0)}_{ab\ldots n} = \left\langle \Psi_{ab\ldots n} \middle| H_0 \middle| \Psi_{ab\ldots n} \right\rangle = \sum_a (h_0)_{aa} + \sum_a U_{aa}$$

$$E^{(1)}_{ab\ldots n} = \left\langle \Psi_{ab\ldots n} \middle| V \middle| \Psi_{ab\ldots n} \right\rangle = \frac{1}{2}\sum_{ab} \left(g_{abab} - g_{abba} \right) - \sum_a U_{aa}$$

$$E_{ab\ldots n} = \sum_a (h_0)_{aa} + \frac{1}{2}\sum_{ab} \left(g_{abab} - g_{abba} \right)$$

Note: our lowest-order eigenvalues ε_a and eigenfunctions are solutions of

$$h\,\psi_a(\mathbf{r}) = \varepsilon_a \psi_a(\mathbf{r}) \qquad h = h_0 + U(r)$$

and not of the $h_0 \psi_a(\mathbf{r}) = \varepsilon_a \psi_a(\mathbf{r})$.

$$\psi_a(\mathbf{r}_i) = \frac{1}{r_i} P_{n_a l_a}(r_i)\, Y_{l_a m_a}(\theta_i, \phi_i)\, \chi_{\mu_a}(i)$$

What do we need to calculate to derive HF equations?

We already have the expression for the energy:

$$E_{ab\ldots n} = \sum_a (h_0)_{aa} + \frac{1}{2}\sum_{ab}\left(g_{abab} - g_{abba}\right)$$

Normalization condition:
(radial functions with the same value of l are orthonormal)

$$N_{n_a l_a, n_b l_a} = \int_0^\infty dr P_{n_a l_a} P_{n_b l_a} = \delta_{n_a n_b}$$

Variational principal
(We introduce Lagrange multipliers λ to accommodate normalization constrains).

$$\delta\left(E_{ab\ldots n} - \sum_{n_a n_b l_a} \lambda_{n_a l_a, n_b l_a} N_{n_a l_a, n_b l_a}\right) = 0$$

1. Need to calculate: $\sum_a (h_0)_{aa}$, $\sum_{ab} g_{abab}$, $\sum_{ab} g_{abba}$.

2. Apply the variational principal.

1. Evaluation of $\sum_a (h_0)_{aa}$

$$(h_0)_{aa} = \int_0^\infty dr P_{n_a l_a} \left(-\frac{1}{2}\frac{d^2 P_{n_a l_a}}{dr^2} + \frac{l_a(l_a+1)}{2r^2} P_{n_a l_a} - \frac{Z}{r} P_{n_a l_a} \right)$$

(Remember radial Schrödinger equation for a particle with angular momentum *l*)

$$= \int_0^\infty dr \left(\frac{1}{2}\left(\frac{dP_{n_a l_a}}{dr} \right)^2 + \frac{l_a(l_a+1)}{2r^2} P_{n_a l_a}^2 - \frac{Z}{r} P_{n_a l_a}^2 \right) \equiv I(n_a l_a)$$

(integrating by parts)

2. Evaluation of $\sum_{ab} g_{abab}$ and $\sum_{ab} g_{abba}$.

Lets obtain the general expression for the Coulomb matrix elements g_{abcd} and then calculate $\sum_{ab} g_{abab}$ and $\sum_{ab} g_{abba}$.

Note: we derived it in the previous lectures.

$$g_{abcd} = \int d^3 r_1 \int d^3 r_2 \, \psi_a^{\dagger}(\mathbf{r}_1)\psi_b^{\dagger}(\mathbf{r}_2)\frac{1}{\mathrm{r}_{12}}\psi_c(\mathbf{r}_1)\psi_d(\mathbf{r}_2)$$

The functions ψ are given by $\psi_{nlm}(\mathbf{r}) = \frac{1}{r} P_{nl}(r) Y_{lm}(\theta,\phi)$

Coulomb matrix element

The $1/r_{12}$ can be expanded as

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{k} Y_{kq}^*(\theta_1,\phi_1) Y_{kq}(\theta_2,\phi_2)$$

This expression may be re-written using C-tensors defined by

$$C_q^k(\hat{r}) = \sqrt{\frac{4\pi}{(2k+1)}} Y_{kq}(\theta,\phi)$$

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{k} (-1)^q \, C_q^k(\hat{r}_1) \, C_{-q}^k(\hat{r}_2)$$

Coulomb matrix element

We now substitute the expressions for ψ and $1/r_{12}$ back into our matrix element and separate dr and dΩ integrals

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{k} (-1)^q \, C_q^k(\hat{r}_1)\, C_{-q}^k(\hat{r}_2)$$

$$\psi_{nlm}(\mathbf{r}) = \frac{1}{r} P_{nl}(r) Y_{lm}(\theta,\phi)$$

$$g_{abcd} = \int d^3 r_1 \int d^3 r_2 \, \psi_a^\dagger(\mathbf{r}_1)\psi_b^\dagger(\mathbf{r}_2) \frac{1}{\mathrm{r}_{12}} \psi_c(\mathbf{r}_1)\psi_d(\mathbf{r}_2)$$

$$= \sum_{k=0}^{\infty} \int_0^\infty dr_1 \int_0^\infty dr_2 \, P_{n_a l_a}(r_1) P_{n_b l_b}(r_2) \frac{r_<^k}{r_>^{k+1}} P_{n_c l_c}(r_1) P_{n_d l_d}(r_2)$$

$R_k(abcd)$

radial integral

$$\times \sum_{q=-k}^{k} (-1)^q \int d\Omega_1 Y_{l_a m_a}(\theta_1,\phi_1)\, C^k{}_q(\theta_1,\phi_1) Y_{l_c m_c}(\theta_1,\phi_1) \rightarrow \left\langle l_a m_a \left| C_q^k \right| l_c m_c \right\rangle$$

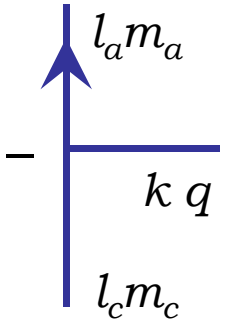
$$\int d\Omega_2 Y_{l_b m_b}(\theta_2,\phi_2)\, C^k{}_{-q}(\theta_2,\phi_2) Y_{l_d m_d}(\theta_2,\phi_2) \rightarrow \left\langle l_b m_b \left| C_{-q}^k \right| l_d m_d \right\rangle$$

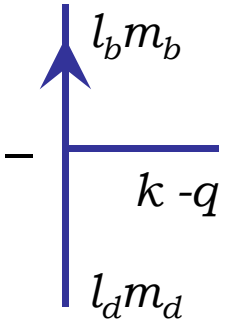
Coulomb matrix element

$$g_{abcd} = \sum_{k=0}^{\infty} R_k(abcd) \sum_{q=-k}^{k} (-1)^q \left\langle l_a m_a \left| C^k_q \right| l_c m_c \right\rangle \left\langle l_b m_b \left| C^k_{-q} \right| l_d m_d \right\rangle$$

Next, we use Wigner-Eckart theorem for both of the matrix elements:

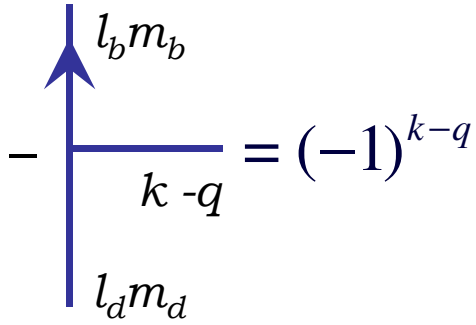
$$g_{abcd} = \sum_{k=0}^{\infty} R_k(abcd) \sum_{q=-k}^{k} (-1)^q$$



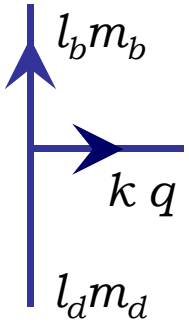


$$\left\langle l_a \left\| C^k \right\| l_c \right\rangle \left\langle l_b \left\| C^k \right\| l_d \right\rangle$$

We use



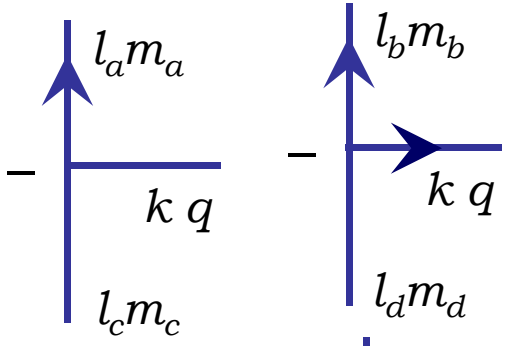
$= (-1)^{k-q}$



Note: k and q are integers

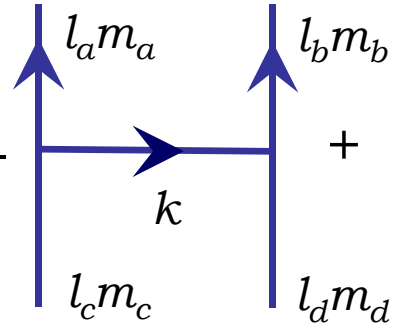
Coulomb matrix element

$$g_{abcd} = \sum_{k=0}^{\infty} R_k(abcd) \sum_{q=-k}^{k} (-1)^k$$



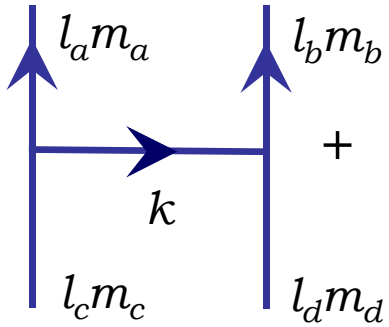
$$\langle l_a \| C^k \| l_c \rangle \langle l_b \| C^k \| l_d \rangle$$

$$= \sum_{k=0}^{\infty} (-1)^k R_k(abcd) \langle l_a \| C^k \| l_c \rangle \langle l_b \| C^k \| l_d \rangle$$



$$+$$

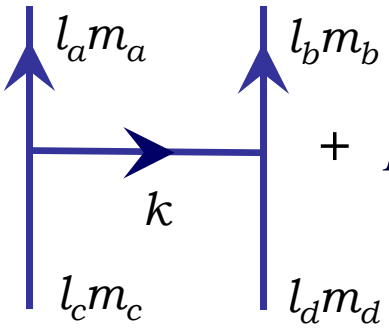
$$g_{abcd} = \sum_{k=0}^{\infty} (-1)^k$$



$$+ \quad R_k(abcd) \langle l_a \| C^k \| l_c \rangle \langle l_b \| C^k \| l_d \rangle$$

Summary: Coulomb matrix element (non-relativistic case)

$$g_{abcd} = \sum_{k=0}^{\infty} (-1)^k$$



$$+ \; R_k(abcd) \left\langle l_a \left\| C^k \right\| l_c \right\rangle \left\langle l_b \left\| C^k \right\| l_d \right\rangle$$

$$R_k(abcd) = \int_0^\infty dr_1 \int_0^\infty dr_2 \; P_{n_a l_a}(r_1) P_{n_b l_b}(r_2) \frac{r_<^k}{r_>^{k+1}} P_{n_c l_c}(r_1) P_{n_d l_d}(r_2)$$

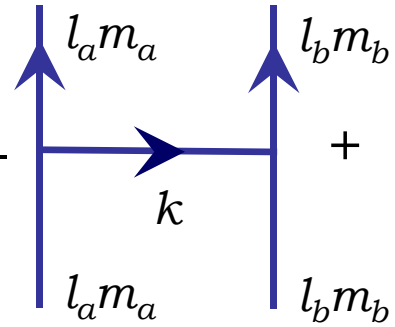
$$\left\langle l_1 \left\| C^k \right\| l_2 \right\rangle = (-1)^{l_1} \sqrt{(2l_1+1)(2l_2+1)} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\left\langle l_2 \left\| C^k \right\| l_1 \right\rangle = (-1)^k \left\langle l_1 \left\| C^k \right\| l_2 \right\rangle$$

Note: $l_1 + k + l_2$ is an even integer

2a. Evaluation of $\sum_{ab} g_{abab}$.

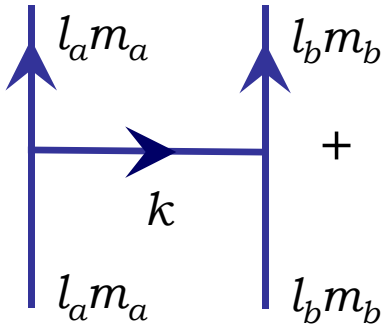
$$g_{abab} = \sum_{k=0}^{\infty} (-1)^k$$



$$+ \; R_k(abab) \langle l_a \| C^k \| l_a \rangle \langle l_b \| C^k \| l_b \rangle$$

Lets sum over m_b and μ_b:

$$g_{abab} = \sum_{m_b \mu_b} \sum_{k=0}^{\infty} (-1)^k$$

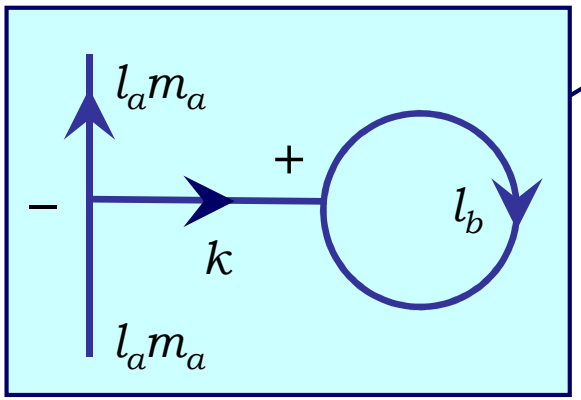


$$+ \; R_k(abab) \langle l_a \| C^k \| l_a \rangle \langle l_b \| C^k \| l_b \rangle$$

Sum over μ_b gives a factor of 2.

$$= \sqrt{\frac{2l_b+1}{2l_a+1}}\,\delta_{k0}$$

$$= \sum_{k=0}^{\infty} (-1)^k$$



$$R_k(abab) \langle l_a \| C^k \| l_a \rangle \langle l_b \| C^k \| l_b \rangle$$

2a. Evaluation of $\sum_{ab} g_{abab}$.

$$\left\langle l \left\| C^0 \right\| l \right\rangle = \sqrt{2l+1}$$

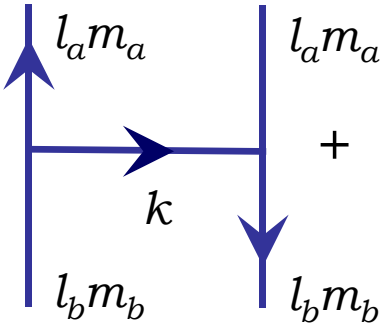
$$\sum_{m_b \mu_b} g_{abab} = 2\sqrt{\frac{2l_b+1}{2l_a+1}}\, R_0(abab) \left\langle l_a \left\| C^0 \right\| l_a \right\rangle \left\langle l_b \left\| C^0 \right\| l_b \right\rangle$$

$$= 2\sqrt{\frac{2l_b+1}{2l_a+1}}\, \sqrt{2l_a+1}\, \sqrt{2l_b+1}\, R_0(abab) = 2(2l_b+1) R_0(abab)$$

$$R_0(abab) = \int_0^\infty dr_1 \int_0^\infty dr_2\; P_{n_a l_a}(r_1) P_{n_b l_b}(r_2) \frac{1}{r_>} P_{n_a l_a}(r_1) P_{n_b l_b}(r_2)$$

2b. Evaluation of $\sum_{ab} g_{abba}$.

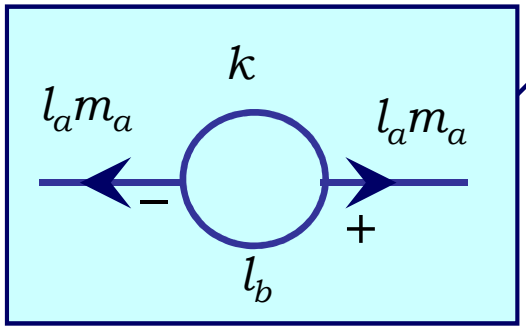
$$\sum_{m_b\mu_b} g_{abba} = \sum_{m_b\mu_b} \sum_{k=0}^{\infty} (-1)^{k+l_a+l_b+k} -$$



$$+ \quad R_k(abba)\langle l_a \| C^k \| l_b \rangle \langle l_b \| C^k \| l_a \rangle$$

$$\langle l_a \| C^k \| l_b \rangle = (-1)^k \langle l_b \| C^k \| l_a \rangle \quad \textit{Note}: \; l_a + k + l_b \text{ is an even integer}$$

$$= \sum_{k=0}^{\infty} \delta_{\mu_a\mu_b} \underbrace{(-1)^{k+l_a+l_b}}_{1}$$



$$= \frac{1}{2l_a+1} R_k(abba)\langle l_b \| C^k \| l_a \rangle^2$$

$$\sum_{m_b\mu_b} g_{abba} = \sum_{k=0}^{\infty} \frac{\langle l_b \| C^k \| l_a \rangle^2}{2l_a+1} R_k(abba)$$

Summary

$$(h_0)_{aa} \equiv I(n_a l_a) = \int_0^\infty dr \left(\frac{1}{2}\left(\frac{dP_{n_a l_a}}{dr} \right)^2 + \frac{l_a(l_a+1)}{2r^2} P^2_{n_a l_a} - \frac{Z}{r} P^2_{n_a l_a} \right)$$

$$\sum_{m_b \mu_b} g_{abab} = 2(2l_b+1) R_0(abab)$$

$$\sum_{m_b \mu_b} g_{abba} = \sum_{k=0}^{\infty} \frac{\left\langle l_b \left\| C^k \right\| l_a \right\rangle^2}{2l_a+1} R_k(abba)$$

$$E_{ab\ldots n} = \sum_a (h_0)_{aa} + \frac{1}{2} \sum_{ab} \left(g_{abab} - g_{abba} \right)$$

Putting it all together

$$E_{ab\ldots n} = \sum_a (h_0)_{aa} + \frac{1}{2}\sum_{ab}\left(g_{abab} - g_{abba}\right)$$

$$= \sum_{n_a l_a}\sum_{m_a \mu_a}(h_0)_{aa} + \frac{1}{2}\sum_{n_a l_a}\sum_{m_a \mu_a}\sum_{n_b l_b}\sum_{m_b \mu_b}\left(g_{abab} - g_{abba}\right)$$

$$= \sum_{n_a l_a}\sum_{m_a \mu_a}\left\{ I(n_a l_a) + \sum_{n_b l_b}(2l_b+1)\left(R_0(abab) - \sum_{k=0}^{\infty} \frac{\langle l_b \| C^k \| l_a \rangle^2}{2(2l_a+1)(2l_b+1)} R_k(abba) \right)\right\}$$

$\Lambda_{l_a\, k\, l_b}$

Does not depend on m_a, μ_a so we can sum over these indices by multiplying by $2(2l_a+1)$

$$E_{ab\ldots n} = \sum_{n_a l_a} 2(2l_a+1)\left\{ I(n_a l_a) + \sum_{n_b l_b}(2l_b+1)\left(R_0(abab) - \sum_{k=0}^{\infty} \Lambda_{l_a\, k\, l_b} R_k(abba) \right)\right\}$$

Summary

$$E_{ab\ldots n} = \sum_{n_a l_a} 2(2l_a+1)\left\{ I(n_a l_a) + (2l_b+1)\sum_{n_b l_b}\left(R_0(abab) - \sum_{k=0}^{\infty} \Lambda_{l_a k l_b} R_k(abba) \right)\right\}$$

$$\Lambda_{l_a k l_b} = \frac{\left\langle l_b \left\| C^k \right\| l_a \right\rangle^2}{2(2l_a+1)(2l_b+1)} = \frac{1}{2}\begin{pmatrix} l_a & k & l_b \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$I(n_a l_a) = \int_0^{\infty} dr \left(\frac{1}{2}\left(\frac{dP_{n_a l_a}}{dr} \right)^2 + \frac{l_a(l_a+1)}{2r^2} P_{n_a l_a}^2 - \frac{Z}{r} P_{n_a l_a}^2 \right)$$

$$N_{n_a l_a, n_b l_a} = \int_0^{\infty} dr P_{n_a l_a} P_{n_b l_a} = \delta_{n_a n_b}$$

$$\delta\left(E_{ab\ldots n} - \sum_{n_a n_b l_a} \lambda_{n_a l_a, n_b l_a} N_{n_a l_a, n_b l_a} \right) = 0$$

This expression must be stationary with respect to variations $\delta P_{n_a l_a}(r)$.

Some designations

$$E_{ab\ldots n} = \sum_{n_a l_a} 2(2l_a+1)\left\{ I(n_a l_a) + \sum_{n_b l_b} (2l_b+1)\left(R_0(abab) - \sum_{k=0}^{\infty} \Lambda_{l_a k l_b} R_k(abba) \right) \right\}$$

$$R_0(abab) = \int_0^{\infty} dr_1 P_a^2(r_1) \underbrace{\int_0^{\infty} dr_2 P_b^2(r_2) \frac{1}{r_>}}_{\upsilon_0(b,r_1)} = \int_0^{\infty} dr P_a^2(r)\, \upsilon_0(b,r)$$

Note designations for indices a and b: index a labels an orbital with $n=n_a$ and $l=l_a$, $b=\{n_b,l_b\}$ now. For example 1s, 2s, 2p, …

$$R_k(abba) = \int_0^{\infty} dr_1\, P_a(r_1) P_b(r_1) \underbrace{\int_0^{\infty} dr_2\, P_b(r_2) P_a(r_2) \frac{r_<^k}{r_>^{k+1}}}_{\upsilon_k(b,a,r_1)} \qquad P_a(r) \equiv P_{n_a l_a}(r)$$

$$= \int_0^{\infty} dr\, P_a(r) P_b(r)\, \upsilon_k(b,a,r) \qquad NOTE: \upsilon_k(a,a,r) \equiv \upsilon_k(a,r)$$

Our formula with new designations

$$E_{ab\ldots n} = \sum_{n_a l_a} 2(2l_a+1)\left\{ I(n_a l_a) + \sum_{n_b l_b} (2l_b+1)\left(R_0(abab) - \sum_{k=0}^{\infty} \Lambda_{l_a k l_b} R_k(abba) \right) \right\}$$

$$= \sum_a 2(2l_a+1)\int_0^{\infty} dr \left(\frac{1}{2}\left(\frac{dP_a}{dr}\right)^2 + \frac{l_a(l_a+1)}{2r^2} P_a^2 - \frac{Z}{r} P_a^2 \right.$$

$$\left. + (2l_b+1)\sum_b \left(P_a^2(r)\, v_0(b,r) - \sum_{k=0}^{\infty} \Lambda_{l_a k l_b} P_a(r) P_b(r)\, v_k(b,a,r) \right) \right)$$

HF equations for closed-shell systems

$$\delta\left(E_{ab\ldots n} - \sum_{n_a n_b l_a} \lambda_{n_a l_a, n_b l_a} N_{n_a l_a, n_b l_a} \right) = 0$$

$$\varepsilon_{n_a l_a, n_b l_a} = \lambda_{n_a l_a, n_b l_a} / (4l_a + 2)$$

$$\varepsilon_a = \varepsilon_{n_a l_a, n_a l_a} = \lambda_{n_a l_a, n_a l_a} / (4l_a + 2)$$

$$-\frac{1}{2}\frac{d^2 P_a(r)}{dr^2} + \frac{l_a(l_a+1)}{2r^2} P_a(r) - \frac{Z}{r} P_a(r) +$$

$$+\sum_b (4l_b + 2)\left(\upsilon_0(b,r) P_a(r) - \sum_k \Lambda_{l_a k l_b} \upsilon_k(b,a,r) P_b(r) \right)$$

$$= \varepsilon_a P_a(r) + \sum_{n_a \neq n_b} \varepsilon_{n_a l_a, n_b l_a} P_{n_b l_a}(r)$$

HF equations for closed-shell systems
Example: He atom: $1s^2$

$$a = 1s, \quad b = 1s, \quad \Lambda_{l_a k l_b} = \Lambda_{0k0} = \begin{cases} 1/2 \ for \ k = 0 \\ 0 \quad for \ \ k \neq 0 \end{cases}$$

$$Line\ 2: \ \sum_b (4l_b + 2)\left(\upsilon_0(b,r) P_a(r) - \sum_k \Lambda_{l_a k l_b} \upsilon_k(b,a,r) P_b(r) \right)$$

$$= 2\left(\upsilon_0(1s,r) P_{1s}(r) - \Lambda_{l_a\, 0 l_b} \upsilon_0(1s,1s,r) P_{1s}(r) \right) = 2\left(\upsilon_0(1s,r) P_{1s}(r) - \frac{1}{2} \upsilon_0(1s,r) P_{1s}(r) \right)$$

$$= \upsilon_0(1s,r) P_{1s}(r)$$

$$-\frac{1}{2}\frac{d^2 P_{1s}(r)}{dr^2} - \frac{Z}{r} P_{1s}(r) + \upsilon_0(1s,r) P_{1s}(r) = \varepsilon_{1s} P_{1s}(r)$$

(Just as we obtained earlier).

HF equations for closed-shell systems
Example: Be atom: $1s^2\,2s^2$

$$a = 1s, 2s \quad b = 1s, 2s \quad \Lambda_{l_a k l_b} = \Lambda_{0k0} = \begin{cases} 1/2 \ \ for\ k = 0 \\ 0 \quad for \ \ k \neq 0 \end{cases}$$

HF *equation for* $1s$ *orbital* $(a = 1s,\ b = 1s, 2s)$

$$Line\ 2: \ \sum_b (4l_b + 2)\left(\upsilon_0(b,r) P_a(r) - \sum_k \Lambda_{l_a k l_b} \upsilon_k(b,a,r) P_b(r) \right)$$

$$= 2\left(\upsilon_0(1s,r) P_{1s}(r) + \upsilon_0(2s,r) P_{1s}(r) - \frac{1}{2}\upsilon_0(1s,1s,r) P_{1s}(r) - \frac{1}{2}\upsilon_0(2s,1s,r) P_{2s}(r) \right)$$

$$= \upsilon_0(1s,r) P_{1s}(r) + 2\upsilon_0(2s,r) P_{1s}(r) - \upsilon_0(2s,1s,r) P_{2s}(r)$$

$$-\frac{1}{2}\frac{d^2 P_{1s}(r)}{dr^2} + \left\{ -\frac{Z}{r} + \upsilon_0(1s,r) + 2\upsilon_0(2s,r) \right\} P_{1s}(r) - \upsilon_0(2s,1s,r) P_{2s}(r)$$

$$= \varepsilon_{1s} P_{1s}(r) + \varepsilon_{1s,2s} P_{2s}(r)$$

HF equations for closed-shell systems
Example: Be atom: $1s^2\,2s^2$

HF *equation for* $2s$ *orbital* $(a = 2s,\ b = 1s, 2s)$

$$\textit{Line 2}: \sum_b (4l_b + 2)\left(\upsilon_0(b,r)P_a(r) - \sum_k \Lambda_{l_a k l_b} \upsilon_k(b,a,r)P_b(r) \right)$$

$$= 2\left(\upsilon_0(1s,r)P_{2s}(r) + \upsilon_0(2s,r)P_{2s}(r) - \frac{1}{2}\upsilon_0(1s,2s,r)P_{1s}(r) - \frac{1}{2}\upsilon_0(2s,2s,r)P_{2s}(r) \right)$$

$$= 2\upsilon_0(1s,r)P_{2s}(r) + \upsilon_0(2s,r)P_{2s}(r) - \upsilon_0(1s,2s,r)P_{1s}(r)$$

$$-\frac{1}{2}\frac{d^2P_{2s}(r)}{dr^2} + \left\{ -\frac{Z}{r} + 2\upsilon_0(1s,r) + \upsilon_0(2s,r) \right\} P_{2s}(r) - \upsilon_0(1s,2s,r)P_{1s}(r)$$

$$= \varepsilon_{2s}P_{2s}(r) + \varepsilon_{2s,1s}P_{1s}(r)$$

Note: we can chose off-diagonal Lagrange multipliers to be zero for closed-shell systems, i.e. $\varepsilon_{1s,2s}=\varepsilon_{2s,1s}=0$.

HF potential V_{HF}

HF potential is defined by specifying its action on an arbitrary orbital $P_*(r)$

$$V_{\mathrm{HF}} P_*(r) = V_{\mathrm{dir}} P_*(r) + V_{\mathrm{exc}} P_*(r)$$

$$V_{\mathrm{dir}} P_*(r) = \sum_b (4l_b + 2)\, \upsilon_0(b, r) P_*(r) \qquad \text{Direct potential}$$

$$V_{\mathrm{exc}} P_*(r) = -\sum_b (4l_b + 2) \sum_k \Lambda_{l_b k l_*} \upsilon_k(b, *, r) P_b(r) \qquad \text{Exchange potential}$$

$$(V_{\mathrm{HF}})_{aa} = \sum_b (g_{abab} - g_{abba}) \qquad [\textit{Follows from the derivation}]$$

Using this designation we can re-write our HF equation for orbital a of the closed-shell system

$$-\frac{1}{2}\frac{d^2 P_a(r)}{dr^2} + \left(V_{\mathrm{HF}} - \frac{Z}{r} + \frac{l_a(l_a+1)}{2r^2} \right) P_a(r) = \varepsilon_a P_a(r)$$

$$(V_{\mathrm{HF}})_{aa} = \sum_b (g_{abab} - g_{abba})$$

Calculation of energy

$$E_{ab\ldots n} = \sum_a (h_0)_{aa} + \sum_a U_{aa} + \frac{1}{2}\sum_{ab}(g_{abab} - g_{abba}) - \sum_a U_{aa} \qquad U = V_{HF}$$

$$= \sum_a h_{aa} + \frac{1}{2}\sum_{ab}(g_{abab} - g_{abba}) - \sum_a (V_{\mathrm{HF}})_{aa} \qquad \textit{Here,} \sum_a = \sum_{n_a l_a m_a \mu_a}$$

$$= \sum_a \varepsilon_a + \frac{1}{2}\sum_{ab}(g_{abab} - g_{abba}) - \sum_{ab}(g_{abab} - g_{abba})$$

$$= \sum_a \varepsilon_a - \frac{1}{2}\sum_{ab}(g_{abab} - g_{abba})$$

$$= \sum_{n_a l_a} 2(2l_a+1)\left\{\varepsilon_a - \sum_{n_b l_b}(2l_b+1)\left(R_0(abab) - \sum_{k=0}^{\infty}\Lambda_{l_a k l_b} R_k(abba)\right)\right\}$$

ε_a is obtained from the iterative solution of the HF equation