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The Hartree-Fock Approximation and Beyond

The Hartree-Fock approximation underlies the most common method for calculating electron wave functions of atoms and molecules. It is the best approximation to the true wave function where each electron is occupying an orbital, the picture that most chemists use to rationalize chemistry. The Hartree-Fock approximation is, furthermore, the usual starting point for more accurate calculations.

The full Hamiltonian for a system of N electrons in the presence of M nuclei with charge Z_A is:

$$H^{exact} = \sum_i^N h(i) + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

where

$$h(i) \equiv -\frac{1}{2} \nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}}.$$

The units here are *atomic units* (Szabo, page 41):

Unit of length is the Bohr radius a_0.
Unit of mass is the electron mass m_e.
Unit of charge is the electron charge e.
Unit of energy is the Hartree = 27.211 eV = 2 E_I.

Solving the Schrödinger equation with this Hamiltonian is very difficult because the term $1/r_{ij}$ correlates the motion of all the electrons. As is frequently done with such many body problems, we will seek a *mean field* approximation, where each electron is treated independently but the effect of all the other electrons is included in an average way. The approximation we obtain to the wavefunction can be regarded as the true solution to a different problem, where the Hamiltonian is only an approximation to the true Hamiltonian

$$H^{app} = \sum_i^N \left(h(i) + v_i^{HF}(i) \right) = H_1 + H_2 + \ldots H_N$$

where $v_i^{HF}(i)$ is the average potential experienced by the $i-th$ electron due to the presence of the other electrons. The problem now is to find the best effective interaction $v_i^{HF}(i)$ as well as the wavefunction. Since the Hamiltonian H^{app} separates, the wave function can be written as a Slater determinant formed from spin-orbitals:

$$|\psi_0 >= |\chi_1 \chi_2 \ldots \chi_N > .$$

To find the optimal spin-orbitals and interaction v_i^{HF} we use the variational principle taking all single determinant wavefunctions, $|\psi_0>$, formed from N orthonormal spin-orbitals as the family of trial functions: That is, we minimize

$$E_0 \ = < H > = < \psi_0 | H^{exact} | \psi_0 >$$

with respect to the determinantal wave function $|\psi_0>$ and in the process we obtain the optimal single determinant wave function and the optimal effective potential $v_i^{HF}(i)$. We have previously found that the expectation value of the Hamiltonian can be written as

$$E_0 = \sum_{a}^{N} [a|h|a] + \frac{1}{2} \sum_{a}^{N} \sum_{b}^{N} [aa|bb] - [ab|ba]$$

where the summation indices a and b range over all occupied spin-orbitals. In searching for the optimal wavefunction, we must impose the constraint that all the spin-orbitals remain orthonormal, i.e.

$$[a|b] - \delta_{ab} = 0$$

for $a = 1, 2, \ldots, N$ and $b = 1, 2, \ldots, N$, a total of N^2 constraints.

The standard method for finding an extremum (minimum or maximum) subject to a constraint is Lagrange's method of undetermined multipliers: The constraint equations are each multiplied by some constant and added to the expression to be optimized. Thus, we define a new quantity L:

$$L \equiv E_0 - \sum_{a}^{N} \sum_{b}^{N} \epsilon_{ba} \Big([a|b] - \delta_{ab} \Big).$$

When the constraints are satisfied, this new quantity equals the expectation value of the Hamiltonian, E_0. The unknown constants ϵ_{ba} are the Lagrange multipliers. The quantity L (as well as E_0) is a functional of the spin-orbitals $\chi_a, \chi_b, \ldots, \chi_N$ and the problem is to find stationary points of L. That is, given infinitesimal change in the spin-orbitals, $\chi_a \rightarrow \chi_a + \delta\chi_a$, the change in L, $(L \rightarrow L + \delta L)$, should be zero, i.e.:

$$0 \ = \ \delta L = \delta E_0 - \sum_{a=1}^{N} \sum_{b=1}^{N} \epsilon_{ba} \ \delta[a|b] \ .$$

We now evaluate the terms on the right hand side of this expression. Inserting the new spin-orbitals $\chi_a + \delta\chi_a$, etc. into the expression for E_0, and using the fact that the integration indicated by [ ] is a linear operation, the change in E_0 is to first order:

$$\begin{aligned} \delta E_0 = &\sum_{a=1}^{N} \left([\delta\chi_a|h|\chi_a] + [\chi_a|h|\delta\chi_a] \right) \\ &+ \frac{1}{2} \sum_{a=1}^{N} \sum_{b=1}^{N} \Big\{ [\delta\chi_a\chi_a|\chi_b\chi_b] + [\chi_a\delta\chi_a|\chi_b\chi_b] + [\chi_a\chi_a|\delta\chi_b\chi_b] + [\chi_a\chi_a|\chi_b\delta\chi_b] \\ &\qquad - [\delta\chi_a\chi_b|\chi_b\chi_a] - [\chi_a\delta\chi_b|\chi_b\chi_a] - [\chi_a\chi_b|\delta\chi_b\chi_a] - [\chi_a\chi_b|\chi_b\delta\chi_a] \Big\} \ . \end{aligned}$$

From the definition of the integrals it is clear that $[\delta\chi_a|h|\chi_a]^* = [\chi_a|h|\delta\chi_a]$ and $[\delta\chi_a\chi_a|\chi_b\chi_b]^* = [\chi_a\delta\chi_a|\chi_b\chi_b]$, *etc.* Furthermore, $[\delta\chi_a\chi_a|\chi_b\chi_b] = [\chi_b\chi_b|\delta\chi_a\chi_a]$ as can be seen by relabeling the integration variables representing the electron coordinates. The change in E_0 can therefore be rewritten as:

$$\delta E_0 = \sum_{a=1}^{N} [\delta\chi_a|h|\chi_a] + \sum_{a=1}^{N}\sum_{b=1}^{N} [\delta\chi_a\chi_a|\chi_b\chi_b] - [\delta\chi_a\chi_b|\chi_b\chi_a] + \text{ c.c.}$$

The notation *c.c.* stands for complex conjugate.

Using the factor rule of differentiation on the second term in the expression for δL

$$\delta[a|b] = \delta[\chi_a|\chi_b] = [\delta\chi_a|\chi_b] + [\chi_a|\delta\chi_b]$$

gives

$$\sum_{ab} \epsilon_{ba}\delta[\chi_a|\chi_b] = \sum_{ab} \epsilon_{ba}[\delta\chi_a|\chi_b] + \sum_{ab} \epsilon_{ba}[\chi_a|\delta\chi_b] \ .$$

Interchanging the summation indices a and b in the second sum on the right hand side gives:

$$\sum_{ab} \epsilon_{ba}\delta[\chi_a|\chi_b] = \sum_{ab} \epsilon_{ba}[\delta\chi_a|\chi_b] + \sum_{ab} \epsilon_{ab}[\chi_b|\delta\chi_a] \ .$$

L is a real quantity and by taking the complex conjugate of the expression defining L, it can be shown that $\epsilon_{ba} = \epsilon^*_{ab}$, that is the Lagrange multipliers are elements of a Hermitian matrix. This means the second sum is just the complex conjugate of the first, and we have

$$\sum_{ab} \epsilon_{ba}\delta[\chi_a|\chi_b] = \sum_{ab} \epsilon_{ba}[\delta\chi_a|\chi_b] + \text{ c.c.}.$$

Finally, the expression for δL becomes:

$$\delta L = \sum_{a=1}^{N} [\delta\chi_a|h|\chi_a] + \sum_{a=1}^{N}\sum_{b=1}^{N} \Big\{[\delta\chi_a\chi_a|\chi_b\chi_b] - [\delta\chi_a\chi_b|\chi_b\chi_a] - \epsilon_{ba}[\delta\chi_a|\chi_b]\Big\} + \text{ c.c.}$$

In this expression we have $[\delta\chi_a$ appearing on the left hand side of each term. We can symbolically rewrite

$$\delta L = \sum_{a=1}^{N} [\delta\chi_a \left(|h|\chi_a] + \sum_{b=1}^{N}\{\chi_a|\chi_b\chi_b] - \chi_b|\chi_b\chi_a] - \epsilon_{ba}|\chi_b]\} \right) + c.c.$$

More explicitly, the expresssion for δL is

$$\delta L = \sum_{a=1}^{N} \int d\vec{x}_1 \delta\chi_a^* \left(h(1)\chi_a(1) + \sum_{b=1}^{N}\{\big(J_b(1) - K_b(1)\big)\chi_a(1) - \epsilon_{ba}\chi_b(1)\} \right) + c.c.$$

where we have defined two new operators, J and K. The *Coulomb operator*, J_b, is defined as

$$J_b(1) \equiv \int d\vec{x}_2 \; |\chi_b(2)|^2 \frac{1}{r_{12}}$$

such that

$$J_b(1)\chi_a(1) = \left[\int d\vec{x}_2 \chi_b^*(2) \frac{1}{r_{12}} \chi_b(2)\right] \chi_a(1)$$

and, in particular we have

$$\int d\vec{x}_1 \; \chi_a^*(1) J_b(1) \chi_a(1) = [aa|bb] \; .$$

The *exchange operator*, $K_b(1)$, is defined such that

$$K_b(1)\chi_a(1) \equiv \left[\int d\vec{x}_2 \chi_b^*(2) \; \frac{1}{r_{12}} \; \chi_a(2)\right] \chi_b(1) \; .$$

Note how the labels a and b on spin-orbitals for electron 1 get interchanged. In particular, we have

$$\int d\vec{x}_1 \; \chi_a^*(1) K_b(1) \chi_a(1) = [ab|ba] \; .$$

Note that the exchange operator is a *non-local* operator in that there does not exist a simple potential function giving the action of the operator at a point $\vec{x}_1$. The result of operating with $K_b(1)$ on $\chi_a(1)$ depends on χ_a throughout all space (not just at $\vec{x}_1$).

Now set $\delta L = 0$ to obtain the optimal spin-orbitals. Since $\delta\chi_a^*$ is arbitrary, we must have

$$\left[h(1) + \sum_{b=1}^{N} \{J_b(1) - K_b(1)\}\right] \chi_a(1) = \sum_{b=1}^{N} \epsilon_{ba}\chi_b(1)$$

for each spin-orbital χ_a with $a = 1, 2, \ldots, N$. Defining the *Fock operator* as

$$f(1) \equiv h(1) + \sum_{b}^{N} \{J_b(1) - K_b(1)\} \; ,$$

the solution to the optimization problem, i.e. the optimal spin-orbitals, satisfy

$$f \; \chi_a \;\; = \;\; \sum_{b=1}^{N} \; \epsilon_{ba} \; \chi_b \; .$$

This equation can be diagonalized, i.e., we can find a unitary transformation of the spin-orbitals that diagonalizes the matrix ϵ which has matrix elements ϵ_{ba}. The Fock operator is invariant under a unitary transformation (see Szabo, page 121). That is, we can define a new set of spin-orbitals

$$\chi_a' = \sum_b \chi_b U_{ba}$$

where $U^\dagger = U^{-1}$ such that $\tilde{\epsilon}' = U^\dagger \tilde{\epsilon}\, U$ is diagonal. Then

$$f\ \chi'_a \ = \ \epsilon'_{ba}\ \chi'_a\ .$$

This is the *Hartree-Fock equation*, a one electron equation for the optimal spin-orbitals. It is non-linear, since the Fock operator, f, itself depends on the spin-orbitals χ_a.

Occupied and Virtual Orbitals:

From the Hartree-Fock equation we get a set of spin-orbitals (dropping the primes now):

$$f\chi_j = \epsilon_j \chi_j \qquad\qquad j = 1, 2, \ldots, \infty.$$

Solving this equation we can generate an infinit number of spin-orbitals. The Fock operator, f, depends on the N spin-orbitals that have electrons, the *occupied orbitals.* Those will be labeled with $a, b, c, ...$. Once the occupied orbitals have been found, the Hartree-Fock equation becomes an ordinary, linear eigenvalue equation and an infinit number of spin-orbitals with higher energies can be generated. Those are called *virtual orbitals* and will be labeled with $r, s, ...$.

The orbital energies

What is the significance of the orbital energies ϵ_i? Left multiplying the Hartree-Fock equation with $< \chi_i|$ gives

$$< \chi_i|f|\chi_j >= \epsilon_i < \chi_i|\chi_j >= \epsilon_j \delta_{ij}\ .$$

Therefore

$$\begin{aligned}
\epsilon_i &=< \chi_i|f|\chi_i > \\
&=< \chi_i|h + \sum_b^N (J_b - K_b)|\chi_i > \\
&=< i|h|i > + \sum_b < ib|ib > - < ib|bi > \\
&=< i|h|i > + \sum_b < ib||ib >\ .
\end{aligned}$$

where the summation index, b, runs over all occupied spin-orbitals.

The first term $< i|h|i >$ is a one body energy, the electron kinetic energy and the attractive interaction with the fixed nuclei. The second term, the sum over all occupied spin-orbitals, is a sum of two body interactions, the Coulomb and exchange interaction between electron i and the electrons in all occupied spin-orbitals. The total energy of the system is not just the sum of ϵ_i for all occupied orbitals, because then the pairwise terms would be double counted. Recall the expression for E_0:

$$E_0 = \sum_a^N\ < a|h|a > + \frac{1}{2}\ \sum_a^N \sum_b^N\ < ab||ab > \neq\ \sum_a \epsilon_a\ .$$

The factor 1/2 prevents double counting the two electron integrals.

The significance of the ϵ_i becomes apparent when we add or subtract an electron to the N electron system. If we assume the spin-orbitals do not change when we, for example, remove an electron from spin-orbital χ_c, then the determinant describing the $N-1$ electron system is

$$|^{N-1}\psi_c >= |\chi_1\chi_2 \ldots \chi_{c-1}\chi_{c+1} \ldots \chi_N >$$

with energy

$$\begin{aligned} {}^{N-1}E_c &=<^{N-1} \psi_c|H|\psi_c^{N-1} > \\ &= \sum_{a \neq c} < a|h|a > + \frac{1}{2} \sum_{a \neq c} \sum_{b \neq c} < ab||ab > . \end{aligned}$$

The energy required to remove the electron, which is called the *ionization potential*, is:

$$\begin{aligned} IP &=^{N-1} E_c - E_0 \\ &= - < c|h|c > - \frac{1}{2} \Big(\sum_b^N < cb||cb > + \sum_a^N < ac||ac > \Big) . \end{aligned}$$

We do not need to restrict the summation to exclude c since $< cc||cc >= 0$. Using the fact that $< ac||ac >=< ca||ca >$ this can be rewritten as

$$\begin{aligned} IP &= - < c|h|c > - \sum_b^N < cb||cb > \\ &= -\epsilon_c . \end{aligned}$$

So, the orbital energy is simply the ionization energy.

Similarly, after adding an electron to the N-electron system into a virtual orbital χ_r, the state is

$$|^{N+1}\psi_r >= |\chi_1\chi_2 \ldots \chi_N\chi_r >$$

and the energy is

$${}^{N+1}E_r = <^{N+1} \psi_r|H|\psi_r^{N+1} > .$$

The energy difference is called the *electron affinity*, EA. Assuming the spin-orbitals stay the same, we have

$$EA = E_0 - {}^{N+1}E_r = - \epsilon_r .$$

Koopman's Rule:

The orbital energy ϵ_i is the ionization potential for removing an electron from an occupied orbital χ_i or the electron affinity for adding an electron into virtual orbital χ_i, in either case assuming the spin-orbitals do not change when the number of electrons is changed. This is a remarkably good approximation due apparently to cancellations of corrections due to adjustments in the orbitals.

Restricted Hartree-Fock:

For computational purposes, we would like to integrate out the spin functions α and β. This is particularly simple when we have spatial orbitals that are independent of spin, in the sense that a given spatial orbital can be used twice, once for spin up and once for spin down. For example, from a spatial orbital ψ_a we can generate two orthogonal spin-orbitals χ_1 and χ_2:

$$\chi_1(\vec{x}) = \psi_a(\vec{r})\alpha(\omega)$$

$$\chi_1(\vec{x}) = \psi_a(\vec{r})\beta(\omega) \ .$$

Determinants constructed from such spin-orbitals are called *restricted determinants.*

Transition from Spin Orbitals to Spatial Orbitals: (Szabo, page 81)

The restricted determinant can be written as

$$\begin{aligned} |\psi > &= |\chi_1\chi_2\chi_3 \cdots \chi_{N-1}\chi_N > \\ &= |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2 \ldots \psi_{N/2}\bar{\psi}_{N/2} > \end{aligned}$$

where the ψ_i denote spatial orbitals occupied by a spin-up electron and $\bar{\psi}_i$ denote the same spatial orbitals occupied by a spin-down electron.

The energy of a determinantal wave function is

$$E =< \psi|H|\psi >= \sum_a^N [a|h|a] + \frac{1}{2}\sum_a^N\sum_b^N [aa|bb] - [ab|ba].$$

We will, furthermore, assume here that all the electrons are paired (closed shell). The wave function then contains $N/2$ spin orbitals with spin up and $N/2$ spin orbitals with spin down, and we can write:

$$\sum_a^N \chi_a = \sum_a^{N/2} (\psi_a + \bar{\psi}_a \ ).$$

Any one electron integral involving spin-orbitals with opposite spin vanishes because of the orthogonality of the spin functions, $\int \alpha^*\beta \ d\omega = 0$. For example,

$$[\psi_i|h|\bar{\psi}_j] = [\bar{\psi}_i|h|\psi_j] = 0 \ .$$

Since the spin functions are normalized, $\int |\alpha|^2 dw = 1$, the integration over spin does not affect the value of non-vanishing matrix elements. We therefore define yet another notation for matrix elements

$$(\psi_i|h|\psi_j) \equiv [\psi_i|h|\psi_j] = [\bar{\psi}_i|h|\bar{\psi}_j].$$

The round brackets indicate *spatial* integration only. Spin has already been integrated out.

Similarly, for two electron integrals:

$$\begin{aligned}[\psi_i\psi_j|\psi_k\psi_\ell] &= [\psi_i\psi_j|\bar{\psi}_k\bar{\psi}_\ell] \\ &= [\bar{\psi}_i\bar{\psi}_j|\psi_k\psi_\ell] \\ &= [\bar{\psi}_i\bar{\psi}_j|\bar{\psi}_k\bar{\psi}_\ell] \\ &\equiv (\psi_i\psi_j|\psi_k\psi_\ell).\end{aligned}$$

Any two electron integral with only one bar on either side vanishes, for example:

$$[\psi_i\bar{\psi}_j|\psi_k\psi_l] = [\psi\bar{\psi}_j|\psi_k\bar{\psi}_l] = 0.$$

The energy for a single determinant wave function becomes:

$$\begin{aligned}E &= 2\sum_a^{N/2} (\psi_a|h|\psi_a) \\ &+ \sum_a^{N/2}\sum_b^{N/2} 2(\psi_a\psi_a|\psi_b\psi_b) - (\psi_a\psi_b|\psi_b\psi_a) \\ &= 2\sum_a (a|h|a) + \sum_{ab} 2(aa|bb) - (ab|ba)\end{aligned}$$

with the summation being over the spatial orbitals only. The first type of two electron integrals, $J_{ij} \equiv (ii|jj)$, is called the *Coulomb integral* since it represents the classical Coulomb repulsion between the charge clouds $|\psi_i(\vec{r})|^2$ and $|\psi_j(\vec{r})|^2$. The second type, $K_{ij} \equiv (ij|ji)$, is called *exchange integral* and does not have a classical interpretation but arises from the antisymmetrization of the wave function. It results from the exchange correlation. The energy of two electrons in orbitals ψ_1 and ψ_2 is

$$E(\uparrow\downarrow) = h_{11} + h_{22} + J_{12}$$

if their spin is antiparallel, but

$$E(\uparrow\uparrow) = h_{11} + h_{22} + J_{12} - K_{12}$$

if their spin is parallel. The energy is lower when the spin is parallel ($K_{12} > 0$) because the antisymmetrization prevents the electrons from being at the same location.

In summary: Given a determinantal wave function, the energy can be obtained in the following way:
(1) each electron in spatial orbital ψ_i contributes h_{ii} to the energy,
(2) each unique pair of electrons contributes J_{ij} (irrespective of spin),
(3) each pair of electons with parallel spin contributes $-K_{ij}$.

Restricted Hartree-Fock equation

Using the above expression for the energy, the Hartree-Fock equation becomes:

$$f(1)\psi_j(1) = \epsilon_j \psi_j(1)$$

where the Fock operator can now be expressed as:

$$f(1) = h(1) + \sum_a^{N/2} 2J_a(1) - K_a(1)$$

and the restricted Coulomb and exchange operators are:

$$J_a(1) = \int d\vec{r}_2 \psi_a^*(\vec{r}_2) \, \frac{1}{r_{12}} \, \psi_a(\vec{r}_2)$$

and

$$K_a(1)\psi_i(1) = \Big(\int d\vec{r}_2 \psi_a^*(\vec{r}_2) \, \frac{1}{r_{12}} \, \psi_i(\vec{r}_2) \Big) \psi_a(\vec{r}_1) \ .$$

The total energy of the system can be written as:

$$\begin{aligned} E &= 2\sum_a^{N/2} (a|h|a) + \sum_a^{N/2} \sum_b^{N/2} 2(aa|bb) - (ab|ba) \\ &= 2\sum_a^{N/2} h_{aa} + \sum_a \sum_b 2J_{ab} - K_{ab} \end{aligned}$$

and the orbital energies are:

$$\epsilon_i = (i|h|i) + \sum_b^{N/2} 2(ii|bb) - (ib|bi) = h_{ii} + \sum_b^{N/2} 2J_{ib} - K_{ib}$$

All these expresssions are in terms of the spatial orbitals only, there is no explicit reference to spin.

The Roothaan Equations:

The spatial Hartree-Fock equation:

$$f(\vec{r}_1)\psi_i(\vec{r}_1) = \epsilon_i \ \psi_i(\vec{r}_1)$$

can be solved numerically for atoms. The results of such calculations have been tabulated by Hermann and Skilman. However, for molecules there is no practical procedure known for solving the equation directly (recall f depends on the orbitals) and the orbitals ψ_i are instead expanded in some known basis functions ϕ_μ:

$$\psi_i = \sum_\mu^K C_{\mu i} \ \phi_\mu \qquad i = 1, 2, \ldots, K.$$

If the number of basis functions is K, we can generate K different orbitals. If the set $\{\phi_\mu\}$ is complete the results would be the same as a direct numerical solution to the Hartree-Fock equation. But, for practical reasons the set $\{\phi_\mu\}$ is always finite and therefore not complete and some error is introduced by expanding ψ_i. This is called the *basis set error*.

The problem now is reduced to determining the expansion coefficients $C_{\mu i}$. Inserting the expansion into the Hartree-Fock equation gives

$$f(1)\sum_\gamma C_{\gamma i}\phi_\gamma(1) = \epsilon_i \sum_\gamma C_{\gamma i}\phi_\gamma(1).$$

Left multiplying with $\phi^*_\mu(1)$ and integrating gives:

$$\sum_\gamma C_{\gamma i} \underbrace{\int d\vec{r}_1 \phi^*_\mu(1) f(1) \phi_\gamma(1)}_{\substack{\equiv F_{\mu\gamma} \\ \text{the Fock matrix}}} = \epsilon_i \sum_\gamma C_{\gamma i} \underbrace{\int d\vec{r}_1 \phi^*_\mu(1) \phi_\gamma(1)}_{\substack{\equiv S_{\mu\gamma} \\ \text{the overlap matrix}}}$$

$$\sum_\gamma F_{\mu\gamma}C_{\gamma i} = \epsilon_i \sum_\gamma S_{\mu\gamma}C_{\gamma i}$$

$$\tilde{F}\tilde{C} = \tilde{S}\tilde{C}\bar{\epsilon}.$$

This is a matrix representation of the Hartree-Fock equation and is called the *Roothaan equations*. The matrices $\tilde{F}, \tilde{S}$ and $\tilde{C}$ are $K \times K$ matrices and $\bar{\epsilon}$ is a vector of length K. The problem is therefore reduced to solving algebraic equations using matrix techniques. Only if $K \to \infty$ are the Roothan equations equivalent to the Hartree-Fock equation.

The Roothaan equations are non-linear:

$$\tilde{F}_{(\tilde{C})}\tilde{C} = \tilde{S}\tilde{C}\bar{\epsilon}.$$

Since $\tilde{F}$ depends on $\tilde{C}$ and therefore they need to be solved in an iterative fashion. Given an estimate for $\tilde{C}_n$ we can find an estimate for $\tilde{F}_{(\tilde{C}_n)}$ and then solve the equation

$$\tilde{F}_{(\tilde{C}_n)}\tilde{C}_{n+1} = \tilde{S}\tilde{C}_{n+1}\bar{\epsilon}$$

to obtain a new estimate for the $\tilde{C}$ matrix. If $\tilde{C}_{n+1} = \tilde{C}_n$ to within reasonable tolerance then self consistency has been achieved and $\tilde{C}_n$ is the solution. Most workers refer to such a solution as self-consistent-field (SCF) solution for any finite basis set $\{\phi_i\}$ and reserve the term Hartree-Fock limit to the infinite basis solution. The equation is solved at each step by diagonalizing the overlap matrix $\tilde{S}$, i.e., by finding a unitary transformation $\tilde{X}$ such that

$$X^\dagger S X = 1.$$

The transformed basis function are

$$\phi'_\mu = \sum_\gamma X_{\gamma\mu}\phi_\gamma \qquad \mu = 1, 2, \ldots, K$$

and form an orthonormal set, i.e.,

$$\int d\vec{r}\phi'^*_\mu \phi'_\gamma = \delta_{\mu\gamma}.$$

Then the equation becomes an ordinary eigenvalue equation:

$$F'C' = C'\epsilon \qquad \text{where } F' \equiv X^\dagger F X \qquad \text{and } C' \equiv X^{-1}C.$$

The main computational effort in doing a large SCF calculation lies in the evaluation of the two-electron integrals. If there are K basis functions then there will be on the order of $K^4/8$ unique two-electron integrals. This can be on the order of millions even for small basis sets and moderately large molecules. The accuracy and efficiency of the calculation depends very much on the choice of basis functions, just as any variational calculation depends strongly on the choice of trial functions.

Basis Set Functions: (see Szabo, page 153)

Two types of basis functions are frequently used:

(1) Slater type functions, which for a 1S orbital centered at $\vec{R}_A$ has the form

$$\phi^{SF}_{1S}(\zeta, \vec{r} - \vec{R}_A) = \sqrt{\zeta/\pi}\; e^{-\zeta|\vec{r}-\vec{R}_A|}$$

with ζ a free parameter and

(2) Gaussian type function

$$\phi^{GF}_{1S}(\alpha, \vec{r} - \vec{R}_A) = \left(\frac{2\alpha}{\pi}\right)^{3/2} \; e^{-\alpha|\vec{r}-\vec{R}_A|^2}$$

with α a free parameter.

The Slater type functions have a shape which matches better the shape of typical orbital functions.In fact, the wave function for the hydrogen atom is a Slater type function with $\zeta = 1$. More generally, it can be shown that molecular orbitals decay as $\psi_i \sim e^{-ar}$ just like Slater type functions and at the position of nuclei $|\vec{r} - \vec{R}_A| \to 0$ there is a cusp because the potential $-e/|r - R_A|$ goes to $-\infty$.

Gaussian type functions have zero slope at $|\vec{r} - \vec{R}_A| = 0$ (i.e., no cusp) and decay much more rapidly than Slater functions. Since Slater type functions more correctly describe qualitative features of molecular orbitals than Gaussian functions, fewer Slater type functions are needed to get comparable results. However, the time it takes to evaluate the integrals over Slater function is much longer than for Gaussian functions. The two electron integrals can involve four different centers $\vec{R}_A, \vec{R}_B, \vec{R}_C$ and $\vec{R}_D$ which makes the evaluation of integrals over Slater functions very time consuming. The product of two Gaussians, on the other hand, is again a Gaussian

$$\phi^{GF}_{1S}(\alpha, \vec{r} - \vec{R}_A)\; \phi^{GF}_{1S}(\beta, \vec{r} - \vec{R}_B) = K_{AB}\; \phi^{GF}_{1S}(p, \vec{r} - \vec{R}_p)$$

where the new Gaussian is centered at

$$\vec{R}_p = \frac{\alpha \vec{R}_A + \beta \vec{R}_B}{\alpha + \beta}.$$

A common practice is to choose basis functions ϕ_μ that are constructed from a few Gaussians

$$\phi_\mu^{CGF}(\gamma, \vec{r} - \vec{R}_A) = \sum_{p=1}^{L} dp\mu \; \phi_p^{GF}(\alpha_{p\mu}, \vec{r} - \vec{R}_A)$$

in such a way as to mimic (in a least squares sense) a Slater function. Those are called *contracted Gaussian functions* and a standard notation for such basis functions is $STO - NG$, meaning Slater Type Orbital constructed from N Gaussians. A typical value for N is 3, i.e. three gaussians are used in each orbital.

In a more flexible basis set called **6-31G**, the core electrons are represented by a single Slater type orbital which is described by six Gaussians (contracted) while valence electrons are represented by two Slater type orbitals, one described by three Gaussians (contracted) and the other described by a single Gaussian. When an atom is placed in an external field, the electron cloud is distorted (polarized). To describe this, it is necessary to include also excited atomic orbitals, i.e. orbitals which are not occupied in the ground state. In the **6-31G**** basis set, excited atomic orbitals are included for all atoms (for example d-orbital functions for O atoms), while in the **6-31G*** basis set, the excited atomic orbitals are included for all elements but H atoms. It turns out that H atoms are hard to polarize so it is often a good approximation to only include polarization of the heavier atoms.

The main computational effort in doing a large SCF calculation lies in the evaluation of two-electron integrals. If there are K basis functions then there will be on the order of K^4 two-electron integrals. This can be on the order of millions even for small basis sets and moderately large molecules. The accuracy and efficiency of the calculation depends very much on the choice of basis functions, just as any variational calculation depends strongly on the choice of trial functions.

The results of an $STO-3G$ calculation for H_2 using restricted Hartree- Fock is shown in the figure below (Szabo, Fig. 3.5). The limit of large r is not reproduced correctly because H_2 does not dissociate into two closed shell fragments. In restricted Hartree-Fock the dissociation products incorrectly include H^- and H^+.

The Charge Density: In a system with paired electrons, the electron density, i.e., the probability of finding an electron in a volume element $d\vec{r}$ around a point $\vec{r}$ is

$$\rho(\vec{r})d\vec{r} = 2\sum_a^{N/2} |\psi_a(\vec{r})|^2 d\vec{r}.$$

Because the orbitals are orthogonal, the total charge density is just a sum of charge densities for each of the accupied orbitals. The integral is

$$\int d\vec{r}\rho(\vec{r}) = 2\sum_a^{N/2} \int dr|\psi_a(\vec{r}_1)|^2 = 2\sum_a^{N/2} 1 = N$$

the total number of electrons.

Configuration Interaction: (see Szabo, page 58)

Recall that the Hartree-Fock solution does not include any correlation in the motion of electrons with opposite spins because of the approximate treatment of the $1/r_{12}$ interaction. However, the 'exact' solution, i.e., the solution to the Hamiltonian H^{exact} can be obtained from the orbitals generated in the Hartree-Fock procedure because they from a complete set. Note that this 'exact' solution is still approximate because it involves the non-relativistic approximation and the Born-Oppenheimer approximation. When K spatial basis functions are used, $2K$ spin orbitals are generated in the Hartree-Fock calculation. The best estimate of the Hartree-Fock ground state is a single Slater determinant generated from the N spin orbitals with the lowest energy:

$$|\psi_0 >= |\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N > .$$

A *singly excited* determinant is one with an electron in a virtual orbital, for example χ_r rather than χ_a:

$$|\psi_a^r>=|\chi_1\chi_2\cdots\chi_r\chi_b\cdots\chi_N>$$

and a *doubly excited* determinant is, similarly:

$$|\psi_{ab}^{rs}>=|\chi_1\chi_2\cdots\chi_r\chi_s\cdots\chi_N>.$$

A total of

$$\binom{2K}{N}=\frac{(2K)!}{N!(2K-N)!}$$

determinants can be formed. We can consider these determinants as a set of N electron basis functions which we use to expand the 'exact' wave function

$$|\Phi>=C_0|\psi_0>+\sum_r\sum_a C_a^r|\psi_a^r>+\sum_a\sum_{b>a}\sum_r\sum_{s>r} C_{ab}^{rs}|\psi_{ab}^{rs}>+\ldots.$$

The first term is the Hartree-Fock approximation. Since each term can be thought of as a specific configuration the procedure is called *configuration interaction (CI).* In the limit of infinit basis functions, $K\to\infty$, the first term $|\psi_0>$ reaches the Hartree-Fock limit with energy E_0 and the set of determinants becomes a complete set so $|\Phi>$ becomes the 'exact' wave function with energy ϵ_0 (we still have non-relativistic and Born-Oppenheimer approximation). The *correlation energy* is defined to be

$$E_{corr}\equiv\epsilon_0-E_0.$$

fig.

For any finite K, we get *'full CI'* when all $\binom{2K}{N}$ determinants are used to find $|\Phi>$.