Ib. The Hartree-Fock Approximation:

The Hartree-Fock approximation underlies the most commonly used method in chemistry 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 that can, in principle, become exact.

It is most convenient to use 'atomic units' in calculations of electronic wave functions for atoms and molecules. The unit chosen for

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

where E_I is the energy of the ground state of the hydrogen atom with respect to separated electron and proton. In these units, $\hbar$ becomes unity.

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

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

where

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

and r_{iA} is the distance between nucleus A and electron i.

Solving the Schrödinger equation with this Hamiltonian is very difficult because the $1/r_{ij}$ terms correlate the distribution 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 separately and the effect of all the other electrons is included in an average way. The way this is done is to carry out a variational calculation where the trial function is of the form of a single Slater determinant

$$|\psi_0> = \ |\psi_0(1,2,\ldots,n)> = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_a(1) & \chi_b(1) & \ldots & \chi_0(1) \\ \chi_a(2) & \chi_b(2) & \ldots & \chi_0(2) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_a(n) & \chi_b(n) & \ldots & \chi_0(n) \end{vmatrix} \equiv |\chi_1\chi_2\cdots\chi_N>$$

The one-electron wave functions, χ, are called *orbitals* and they in general depend both on the spatial coordinates, r, of the electron, and the spin. The name 'spin-orbital' emphasizes that spin is inlcuded. The spin is specified by the projection onto the z-axis and is either 'up' denoted by α, or 'down', denoted by β. The Slater determinant is the simplest form for a wave function of many electrons, but is only exact for independent electrons, i.e. a Hamiltonian that separates into terms, each involving just coordinates of one electron

$$H^{app} \ = \ H_1 \ + \ H_2 \ \ldots \ H_N$$

In the Hartree-Fock calculation, the expectation value of the true Hamiltonian using a Slater determinant trial function

$$< H > = < \psi_0 | H | \psi_0 >$$

is minimized with respect to the orbitals in order to get an approximation to the ground state energy, E_0. In the process an optimal single determinant approximation to the stationary state wave function is obtained. Such a form of the function can, however, never give an exact wave function for the full Hamiltonian because it contains terms of the form $1/\mathrm{r}_{ij}$, which necessarily involves coordinates of two electrons at a time. But, the Hartree-Fock approximation can be a useful first approximation and underlies how chemists typically think about electronic structure of atoms and molecules. Various corrections, so-called post-Hartree-Fock methods, can then be applied to get better estimates of the wave function.

One can better understand the approximation being made here by thinking of the resulting eigen function as an exact solution to a different problem, one where the Hamiltonian is an approximation to the true Hamiltonian

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

Here, $v_i^{HF}(i)$ is an effective potential experienced by the $i-th$ electron due to the presence of the other electrons, but it cannot depend on the coordinates of the other electrons and thus represents a spatially averaged interaction. During the variational optimization of the spin-orbitals an optimal effective interaction $v_i^{HF}(i)$ is obtained as well as the stationary state wave functions. Since the approximate Hamiltonian H^{app} separates, its eigenfunctions can indeed be written as a Slater determinant formed from spin-orbitals

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

The variational minimization of the energy with respect to arbitrary variations of the spin-orbitals leads to equations for the spin-orbitals and the optimal, effective potential. The derivation of these equations, called the Hartree-Fock equations is given below. The expectation value of the Hamiltonian for a Slater determinant wave function can be shown to be

$$< H >= \sum_a^N [\chi_a | h | \chi_a] + \frac{1}{2} \sum_a^N \sum_b^N [\chi_a \chi_a | \chi_b \chi_b] - [\chi_a \chi_b | \chi_b \chi_a]$$

where

$$[\chi_i | h | \chi_j] \equiv \int dx_1 \chi_i^*(1) h(\vec{r}_1) \chi_j(1)$$

and

$$[\chi_i \chi_j | \chi_k \chi_\ell] \equiv \int dx_1 \int dx_2 \; \chi_i^*(1) \chi_j(1) \frac{1}{r_{12}} \chi_k^*(2) \chi_\ell(2)$$

The integration variable x_i denotes both the spatial and spin coordinates of electron i (note, we assume the Hamiltonian does not depend on spin and therefore denote the variable there as $\vec{r}_1$) and the summation indices a and b range over all occupied spin-orbitals. In searching for the optimal wave function, we must impose the constraint that all the spin-orbitals remain orthonormal, i.e.

$$[\chi_a|\chi_b] - \delta_{ab} = 0$$

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 functional L:

$$L \equiv < H > - \sum_a^N \sum_b^N \epsilon_{ba} \Big([\chi_a|\chi_b] - \delta_{ab} \Big).$$

When the constraints are satisfied, this new quantity equals the expectation value of the Hamiltonian, $< H >$. The unknown constants ϵ_{ba} are the Lagrange multipliers. The quantity L (as well as $< H >$) 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, $\chi_a \to \chi_a + \delta\chi_a$, the change in L, $(L \to L + \delta L)$, should be zero, i.e.:

$$0 \ = \ \delta L = \delta < H > - \sum_{a=1}^N \sum_{b=1}^N \epsilon_{ba} \ \delta[\chi_a|\chi_b] \ .$$

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

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

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 $< H >$ can therefore be rewritten as:

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

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

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

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

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

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

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

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

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

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

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, that is a transformation where a new set of spin-orbitals is defined by taking linear combinations of orbitals in the original orbitals. The new set of spin-orbitals is defined as

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

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

$$f \; \chi_a' \;\; = \;\; \epsilon_a' \; \chi_a' \; .$$

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):

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

By 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 $a, b, c, \ldots.$ 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 $r, s, \ldots.$

The orbital energy

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

$$\begin{aligned} \epsilon_i &= [\chi_i|f|\chi_i] \\ &= [\chi_i|h + \sum_b^N (J_b - K_b)|\chi_i] \\ &= [\chi_i|h|\chi_i] + \sum_b [\chi_i\chi_i|\chi_b\chi_b] - [\chi_i\chi_b|\chi_b\chi_i] \end{aligned}$$

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 $< H >$:

$$< H >= \sum_a^N [\chi_a|h|\chi_a] + \frac{1}{2} \sum_a^N \sum_b^N [\chi_a\chi_a|\chi_b\chi_b] - [\chi_a\chi_b|\chi_b\chi_a] \ \neq \sum_a \epsilon_a \ .$$

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. Let E_0 now denote the energy obtained for the ground state, $E_0 =< H >$. 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

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

with energy

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

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

$$\begin{aligned} IP &=^{N-1}E_c-E_0 \\ &=-[\chi_c|h|\chi_c]-\frac{1}{2}\left(\sum_b^N[\chi_c\chi_c|\chi_b\chi_b]-[\chi_c\chi_b|\chi_b\chi_c]+\sum_a^N[\chi_a\chi_a|\chi_c\chi_c]-[\chi_a\chi_c|\chi_c\chi_a]\right)\ . \end{aligned}$$

We do not need to restrict the summation to exclude c since the $[cc|cc]$ term cancels out. Using the fact that $[ac|ac]=[ca|ca]$ this can be rewritten as

$$\begin{aligned} IP &=-[\chi_c|h|\chi_c]-\sum_b^N[\chi_c\chi_c|\chi_b\chi_b]-[\chi_c\chi_b|\chi_b\chi_c] \\ &=-\epsilon_c\ . \end{aligned}$$

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

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

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 energy corresponding to 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 the assumption is that the spin-orbitals do not change when the number of electrons is changed. This turns out to be a remarkably good approximation due to cancellations of corrections due to adjustments in the orbitals and the errors inherent in Hartree-Fock (the missing correlation energy).

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:

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

$$\chi_2(\vec{x}) = \psi_a(\vec{r})\beta(\omega) \ .$$

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

Integration over spin to get purely spatial orbitals:

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 determinant wave function is

$$E =< \psi|H|\psi >= \sum_a^N [\chi_a|h|\chi_a] + \frac{1}{2}\sum_a^N\sum_b^N [\chi_a\chi_a|\chi_b\chi_b] - [\chi_a\chi_b|\chi_b\chi_a].$$

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 were all the electrons are paired becomes

$$< H >= 2\sum_a^{N/2} (\psi_a|h|\psi_a) + \sum_a^{N/2}\sum_b^{N/2} 2(\psi_a\psi_a|\psi_b\psi_b) - (\psi_a\psi_b|\psi_b\psi_a)$$

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

$$< H > (\uparrow\downarrow) = h_{11} + h_{22} + J_{12}$$

if their spin is antiparallel, but

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

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 determinant 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:

$$\begin{aligned} E &= 2\sum_{a}^{N/2} (\psi_a|h|\psi_a) + \sum_{a}^{N/2} \sum_{b}^{N/2} 2(\psi_a\psi_a|\psi_b\psi_b) - (\psi_a\psi_b|\psi_b\psi_a) \\ &= 2\sum_{a}^{N/2} h_{aa} + \sum_{a} \sum_{b} 2J_{ab} - K_{ab} \end{aligned}$$

and the orbital energies are:

$$\epsilon_i = (\psi_i|h|\psi_i) + \sum_{b}^{N/2} 2(\psi_i\psi_i|\psi_b\psi_b) - (\psi_i\psi_b|\psi_b\psi_i) = h_{ii} + \sum_{b}^{N/2} 2J_{ib} - K_{ib}$$

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