Derivation of the Hartree-Fock Equation

In this article, the Hartree-Fock equation is derived with the help of Lagrange multiplier. It should be mentioned that derivations without Lagrange multiplier also exist. Afterwards, we obtain the Roothaan-Hall equation for a closed-shell system by introducing a basis set.

1 Hartree-Fock method

Because of the variational principle, the expectation value of energy of a approximated wave function will be always higher than that of the true wave function. Since a Slater determinant is an approximation of the true many-electron wave function in an interacting system, minimising its energy expectation value with respect to the one-electron wave functions would give us the best approximation in the framework of Slater determinants. This is exactly what Hartree-Fock method does.

Since we want to keep the one-electron wave functions orthonormal while minimising the energy, it is a optimisation with equality constrains. This type of problems can be solved the the method of Lagrange multipliers. However, since the energy E_Ψ depends on functions φ_i, it is a functional and methods of functional analysis should be applied. The methods in this case, however, are very similar to those in "regular" analysis.

The trick is to add an zero to the function(al) we want to minimise. We start by writing down the constrain $\langle \varphi_i | \varphi_j \rangle - \delta_{ij} = 0$. Since a constant times zero is still zero, this constrain can be extended to $\epsilon_{ij} \cdot (\langle \varphi_i | \varphi_j \rangle - \delta_{ij}) = 0$, where ϵ_{ij} is called the Lagrange multiplier. Since orthonormality holds for all possible pairs of i and j, summing them up would give us the most general (zero-valued) constrain function

$$g[\Psi] = \sum_{i,j} \epsilon_{ij} \cdot (\langle \varphi_i | \varphi_j \rangle - \delta_{ij}). \tag{1.1}$$

Then we just subtract the constrain functional from the energy functional to obtain the Lagrangian

$$\begin{aligned}
\mathcal{L}[\Psi, \epsilon] &= E[\Psi] - g[\Psi] \\
&= \sum_{i=1}^{N} \langle \varphi_i | h_i | \varphi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N} \left(\langle \varphi_i \varphi_j | V_{ij} | \varphi_i \varphi_j \rangle - \langle \varphi_i \varphi_j | V_{ij} | \varphi_j \varphi_i \rangle \right) - \sum_{i,j} \epsilon_{ij} \cdot (\langle \varphi_i | \varphi_j \rangle - \delta_{ij}).
\end{aligned} \tag{1.2}$$

Making the Lagrangian stationary by letting its derivative with respect to one-particle wave functions vanish is a necessary condition for minimisation. We choose to differentiate $\mathcal{L}$ with respect to $\varphi_k^*(x)$, which will lead to a nicer-looking equation in the end. Also, we will write the integrals explicitly in order to see exactly what is happening. Thus, we arrive this set of

equations

$$\frac{\delta\mathcal{L}}{\delta\varphi_k^*(x)} \overset{!}{=} 0$$

$$= \frac{\delta}{\delta\varphi_k^*(x)} \sum_i \int \mathrm{d}x_1 \varphi_i^*(x_1) h_i \varphi_i(x_1) \tag{1.3a}$$

$$+ \frac{1}{2}\frac{\delta}{\delta\varphi_k^*(x)} \sum_{i,j} \int \mathrm{d}x_1 \int \mathrm{d}x_2 \varphi_i^*(x_1)\varphi_j^*(x_2) V_{ij}\varphi_i(x_1)\varphi_j(x_2) \tag{1.3b}$$

$$- \frac{1}{2}\frac{\delta}{\delta\varphi_k^*(x)} \sum_{i,j} \int \mathrm{d}x_1 \int \mathrm{d}x_2 \varphi_i^*(x_1)\varphi_j^*(x_2) V_{ij}\varphi_i(x_2)\varphi_j(x_1) \tag{1.3c}$$

$$- \frac{\delta}{\delta\varphi_k^*(x)} \sum_{i,j} \epsilon_{ij} \cdot \left(\int \mathrm{d}x_1 \varphi_i^*(x_1)\varphi_j(x_1) - \delta_{ij} \right). \tag{1.3d}$$

But what the hack does it mean to differentiate with respect to a function?! Well, we shall first take a look at how a functional works. While a function takes in a number and spits out a number, a functional takes in a function and also spits out a number. The derivative of a function (at a certain position) shows how the output value varies with the input number, thus the derivative of a functional should show how the output value varies with the input function. It might sound complicated, but figure 1 should illustrate this idea better. The dashed line shows the original function $\varphi(x)$. Now just wiggle $\varphi(x)$ a bit at the position $x = x_0$. One gets a

Figure 1: A illustration of functional variation.

new function which is the sum of the original function $\varphi(x)$ and its variation $\delta\varphi(x)$. Expressing the variation in the most simplistic term of variation, the Dirac delta function multiplied by a constant ϵ, $\delta\varphi(x)$ can be written as $\delta\varphi(x) = \epsilon \cdot \delta(x - x_0)$. Imagine a functional G which takes $\varphi(x)$ as its input. The difference between its values before and after wiggling the function $\varphi(x)$ by the amount of ϵ, divided by ϵ is, when ϵ approaches zero, the definition of the functional derivative:

$$\frac{\delta G[\varphi]}{\delta\varphi(x_0)} = \lim_{\epsilon\to 0} \frac{G[\varphi + \epsilon \cdot \delta(x - x_0)] - G[\varphi]}{\epsilon}. \tag{1.4}$$

Note the similarities between the functional derivative and "ordinary" derivatives of functions.

Now we can calculate the derivative of a special functional using equation (1.4). Since a functional is just something that takes a function and spits out a number, "evaluating the value of φ_i^* at x_1", i.e. $\varphi_1^*(x_1)$ is also be a functional. The derivative of this functional with respect to $\varphi_k^*(x)$ is, using the definition in equation (1.4), we obtain

$$\frac{\delta\varphi_i^*(x_1)}{\delta\varphi_k^*(x)} = \delta_{ik} \lim_{\epsilon\to 0} \frac{\varphi_i^*(x_1) + \epsilon \cdot \delta(x_1 - x) - \varphi_i^*(x_1)}{\epsilon}$$

$$= \delta_{ik} \lim_{\epsilon\to 0} \frac{\epsilon \cdot \delta(x_1 - x)}{\epsilon}$$

$$= \delta_{ik}\delta(x_1 - x). \tag{1.5}$$

The Kronecker-delta δ_{ik} arises since our special functional evaluates the value of φ_i^*. A different function would just behave like a constant and vanish during differentiation. With equation
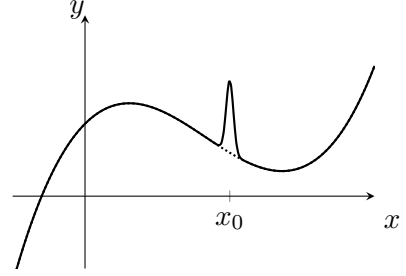
(1.5) in hand, we can now tackle the terms in equation (1.3), one by one.

Starting with (1.3a) by applying the derivative on φ_i^*. The resulting Kronecker delta δ_{ik} kills the sum and the Dirac delta function $\delta(x_1 - x)$ kills the integral:

$$\frac{\delta}{\delta\varphi_k^*(x)} \sum_i \int \mathrm{d}x_1 \varphi_i^*(x_1) h_i \varphi_i(x_1)$$

$$= \sum_i \int \mathrm{d}x_1 \frac{\delta\varphi_i^*(x_1)}{\delta\varphi_k^*(x)} h_i \varphi_i(x_1)$$

$$= \sum_i \int \mathrm{d}x_1 \delta_{ik}\delta(x_1 - x) h_i \varphi_i(x_1)$$

$$= h_k \varphi_k(x).$$

For the two electron part (1.3b) we use the product rule and obtain

$$\frac{1}{2}\frac{\delta}{\delta\varphi_k^*(x)} \sum_{i,j} \int \mathrm{d}x_1 \int \mathrm{d}x_2 \varphi_i^*(x_1)\varphi_j^*(x_2) V_{ij} \varphi_i(x_1)\varphi_j(x_2)$$

$$= \frac{1}{2} \sum_{i,j} \int \mathrm{d}x_1 \int \mathrm{d}x_2 \frac{\delta\varphi_i^*(x_1)}{\delta\varphi_k^*(x)} \varphi_j^*(x_2) V_{ij} \varphi_i(x_1)\varphi_j(x_2)$$

$$+ \frac{1}{2} \sum_{i,j} \int \mathrm{d}x_1 \int \mathrm{d}x_2 \varphi_i^*(x_1) \frac{\delta\varphi_j^*(x_2)}{\delta\varphi_k^*(x)} V_{ij} \varphi_i(x_1)\varphi_j(x_2)$$

$$= \frac{1}{2}\left(\sum_j \int \mathrm{d}x_2 \varphi_j^*(x_2) V_{kj} \varphi_k(x)\varphi_j(x_2) + \sum_i \int \mathrm{d}x_1 \varphi_i^*(x_1) V_{ik} \varphi_i(x_1)\varphi_k(x) \right)$$

$$= \sum_i \int \mathrm{d}x_1 \varphi_i^*(x_1) V_{ik} \varphi_i(x_1)\varphi_k(x).$$

Note that in the last step, we renamed $j \to i$ and $x_2 \to x_1$ since the summation index j and the integration variable x_2 can be named whatever we want. Using the fact that $V_{ki} = V_{ik}$, these two terms become identical. By defining

$$\int \mathrm{d}x_1 \varphi_i^*(x_1) V_{ik} \varphi_i(x_1) = J_k, \tag{1.6}$$

which we call Coulomb operator, equation (1.3b) becomes

$$\sum_i J_i \varphi_k(x).$$

Treating (1.3c) analogously, we arrive at

$$-\sum_i \int \mathrm{d}x_1 \varphi_i^*(x_1) V_{ik} \varphi_k(x_1)\varphi_i(x).$$

If we try to define an operator like J_i for equation (1.3b), we will run into a problem, since the orbital, where the operator should act on, is inside the integral. Nevertheless, we can define the effect of such an operator on the orbital $\varphi_k(x)$ as

$$K_i \varphi_k(x) = \int \mathrm{d}x_1 \varphi_i^*(x_1) V_{ik} \varphi_k(x_1)\varphi_i(x). \tag{1.7}$$

Since the "naked" operator K_i would somehow exchange the coordinates of $\varphi_i(x_1)$ and $\psi_k(x)$, we call it the exchange operator.

This leaves us with the fourth and the last term, (1.3d). Since δ_{ij} is just a number which vanishes upon differentiating, this term behaves exactly the same as 1.3a and we get

$$-\frac{\delta}{\delta\varphi_k^*(x)}\sum_{i,j}\epsilon_{ij}\cdot\left(\int \mathrm{d}x_1\varphi_i^*(x_1)\varphi_j(x_1)-\delta_{ij}\right) = -\sum_j \epsilon_{kj}\varphi_j(x).$$

Wrapping up all four terms, we obtain

$$\left(h_k + \sum_i (J_i - K_i)\right)\varphi_k(x) = \sum_j \epsilon_{kj}\varphi_j(x), \tag{1.8}$$

which is known as the general Hartree-Fock (HF) equation. Defining the Fock operator $\hat{f} = (h_k + \sum_i(J_i - K_i))$, we realise that equation (1.8) is not quite a eigenvalue equation. This however can easily be fixed by diagonalising ϵ with a unitary transformation $\mathbf{U}$: $\epsilon_{kj} = \sum_{m,n} U_{km}D_{mn}U_{nj}^\dagger$, where $\mathbf{D}$ is a diagonal matrix. By using the transformation matrix $\mathbf{U}^\dagger$, we can define another set of orthonormal orbitals ϕ_m, which is related to the original basis by $\varphi_k = \sum_m U_{km}^\dagger\phi_m$. Inserting this relation into (1.8), we obtain

$$\hat{f}\sum_m U_{km}^\dagger\phi_m = \sum_j\sum_m \epsilon_{kj}U_{jm}^\dagger\phi_m.$$

Multiplying $\mathbf{U}$ from left on both sides leads to

$$\hat{f}\sum_{m,n} U_{kn}U_{nm}^\dagger\phi_m = \sum_j\sum_{m,n} U_{kn}\epsilon_{mj}U_{jm}^\dagger\phi_m,$$

which is, after using the unitarity of $\mathbf{U}$ and the equation of diagonalisation for ϵ

$$\hat{f}\sum_m \delta_{km}\phi_m = \sum_m D_{km}\phi_m$$
$$\hat{f}\phi_k = D_k\phi_k,$$

where D_k's are the diagonal elements of D_{km}. This *is* an eigenvalue equation! Using more familiar symbols, i.e. renaming D to ϵ and ϕ to φ, we arrive at the so called canonical Hartree-Fock equation:

$$\hat{f}\varphi_k(x) = \left(h_k + \sum_i (J_i - K_i)\right)\varphi_k(x) = \epsilon_k\varphi_k(x). \tag{1.9}$$

The Lagrange multipliers ϵ_k can thus be interpreted as the energy of the one-electron wave function (orbital) φ_k.

2 Closed-shell Roothaan-Hall equation

Although I mentioned that the canonical Hartree-Fock equation (1.9) is an eigenvalue equation and its form also suggest it, it is only a delusion. Inspecting the definition of Coulomb and exchange operators, we can realise that they contain φ_i, which are the eigenfunctions we want to solve for: We must know the solution to build the equation for solving it. Does it mean that

the HF equation is useless? Well, if we somehow "guess" an approximated form of φ_i's and plug them into the equation, we can get another set of φ_i's which can be plugged in again. Doing this long enough would, in most cases, give us φ_i's which do not change after inserting them into HF equation. These wave functions are called to be self-consistent and are solutions of the HF equation. This iterative process is thus called the self-consistent field (SCF) method.

Being an integro-differential equation however, HF equation is everything but easy to solve. The only way of solving is doing it numerically, if we are not dealing with the easiest problems. Performing the integrations and differentiations on a grid in 3D space would take a *very* long time and is mostly only feasible for atomic systems. Therefore, instead of expanding the wave functions into the spatial grid, we shall use another set of basis, which converges much faster. The linear combination of atomic orbitals (LCAO) was put through and became the standard basis for almost all quantum chemical calculations today. Using this basis, we can rewrite the HF equation into a matrix equation, which is called the Roothaan-Hall equation. Since most chemical systems consist of a equal number of electrons with α and β spin, we shall take this into account and simplify the HF equation (1.9) into the so called restricted Hartree-Fock (RHF) equation.

The spin-orbital $\varphi_k(x)$ can be written as a product of a spatial orbital and a spin wave function: $\varphi_k(x) = \varphi_k(r) \cdot \Omega(\omega)$. Using the fock operator on the spin-orbital and project the result on to a spin wave function, e.g. $\alpha(\omega)$, we can eliminate the spin from the equation. Assuming that there is a equal number of electrons with α-spin and β-spin, we can obtain a compact equation. Let us now consider all three parts in the Fock-operator one by one, assuming that φ_k has α-spin.

The projection for h-operator is straight forward. Since h only operates on spatial coordinates, the bra and ket of α just combines and give a 1 due to orthonormality.

$$\langle\alpha|h\varphi_k(x)\rangle = \langle\alpha|h\varphi_k(r)\alpha\rangle = \langle\alpha|\alpha\rangle\, h\varphi_k(r) = h\varphi_k(r). \tag{2.1}$$

The resulting expression looks very similar to the starting expression, just without the spin coordinate.

Now we deal with J. Since there are N electrons in N spin-orbitals and there is a equal amount of α and β orbitals, we split the sum in two parts, each from 1 to $N/2$.

$$
\begin{aligned}
\langle\alpha(\omega)|\sum_{i=1}^{N} J_i\varphi_k(x)\rangle &= \langle\alpha|\,\langle\varphi_i(x')|\frac{1}{r_{12}}|\varphi_i(x')\rangle\,|\varphi_k(x)\rangle \\
&= \sum_{i=1}^{N/2} \langle\alpha(\omega)|\,\langle\varphi_i(r')\alpha(\omega')|\frac{1}{r_{12}}|\varphi_i(r')\alpha(\omega')\rangle\,|\varphi_k(r)\alpha(\omega)\rangle \\
&+ \sum_{i=1}^{N/2} \langle\alpha(\omega)|\,\langle\varphi_i(r')\beta(\omega')|\frac{1}{r_{12}}|\varphi_i(r')\beta(\omega')\rangle\,|\varphi_k(r)\alpha(\omega)\rangle \\
&= \sum_{i=1}^{N/2} \Bigg[\langle\alpha(\omega)|\alpha(\omega)\rangle\,\langle\alpha(\omega')|\alpha(\omega')\rangle\,\langle\varphi_i(r')|\frac{1}{r_{12}}|\varphi_i(r')\rangle\,\varphi_k(r) \\
&\qquad + \langle\alpha(\omega)|\alpha(\omega)\rangle\,\langle\beta(\omega')|\beta(\omega')\rangle\,\langle\varphi_i(r')|\frac{1}{r_{12}}|\varphi_i(r')\rangle\,\varphi_k(r) \Bigg]
\end{aligned}
$$

$$= 2 \sum_{i=1}^{N/2} \langle \varphi_i(r') | \frac{1}{r_{12}} | \varphi_i(r') \rangle \, \varphi_k(r)$$

$$\langle \alpha | \sum_{i=1}^{N} J_i \varphi_k(x) \rangle = 2 \sum_{i=1}^{N/2} J_i \varphi_k(r). \tag{2.2}$$

Again, since J does not operate on spin coordinates, we can combine the spin wave functions and get a bunch of 1's which does not change anything. The expression we got is also very familiar this time: We just sum over all Coulomb-operators for spatial orbitals and multiply the quantity by 2 to account for double the amount of spin orbitals.

At last, we shall deal with the exchange operator. Like we have experienced before, only little changes should occur, right? Well, projecting analogously to J, we obtain

$$\langle \alpha(\omega) | \sum_{i=1}^{N} K_i \varphi_k(x) \rangle = \langle \alpha | \, \langle \varphi_i(x') | \frac{1}{r_{12}} | \varphi_k(x') \rangle \, | \varphi_i(x) \rangle$$

$$= \sum_{i=1}^{N/2} \langle \alpha(\omega) | \, \langle \varphi_i(r')\alpha(\omega') | \frac{1}{r_{12}} | \varphi_k(r')\alpha(\omega') \rangle \, | \varphi_i(r)\alpha(\omega) \rangle$$

$$+ \sum_{i=1}^{N/2} \langle \alpha(\omega) | \, \langle \varphi_i(r')\beta(\omega') | \frac{1}{r_{12}} | \varphi_k(r')\alpha(\omega') \rangle \, | \varphi_i(r)\beta(\omega) \rangle \, .$$

$$= \sum_{i=1}^{N/2} \Bigg[\langle \alpha(\omega)|\alpha(\omega) \rangle \, \langle \alpha(\omega')|\alpha(\omega') \rangle \, \langle \varphi_i(r') | \frac{1}{r_{12}} | \varphi_i(r') \rangle \, \varphi_k(r)$$

$$+ \langle \alpha(\omega)|\beta(\omega) \rangle \, \langle \beta(\omega')|\alpha(\omega') \rangle \, \langle \varphi_i(r') | \frac{1}{r_{12}} | \varphi_i(r') \rangle \, \varphi_k(r) \Bigg]$$

Just like for J, we could isolate the brakets for spin coordinates this will give us, again due to orthonormality, a bunch of 1's... Wait a minute, the second term becomes zero since different spins appear in the same braket! This happens because K exchanges the spin coordinate of φ_k, which is always α with the coordinate of φ_i, which is β half the time. Therefore, only a half of the integrals survive and we are left with

$$\langle \alpha | \sum_{i=1}^{N} K_i \varphi_k(x) \rangle = \sum_{i=1}^{N/2} \langle \varphi_i(r') | \frac{1}{r_{12}} | \varphi_k(r') \rangle \, \varphi_i(r)$$

$$= \sum_{i=1}^{N/2} K_i \varphi_k(r). \tag{2.3}$$

Now, we can project the entire HF-equation (1.9) onto $\langle \alpha |$ by using the results from equations (2.1), (2.2) and (2.3) for the left hand side. The right hand side is trivially done since no operator is involved. We obtain the so called closed-shell Hartree-Fock equation, or restricted

Hartree-Fock (RHF) equation:

$$\hat{f}\varphi_a(r) = \left(h + \sum_{b=1}^{N/2} (2J_b - K_b) \right) \varphi_a(r) = \epsilon_a \varphi_a(r). \qquad (2.4)$$

Since we are dealing with spatial orbitals, the MO index k is changed to a and the summation index i changed to b to eliminate confusion, in the case that the upper bound of $N/2$ is not clear enough.

We can then proceed to expand the molecular orbitals into atomic orbitals by using

$$\varphi_a = \sum_{\nu=1}^{\#AO} c_{\nu a}\phi_\nu, \qquad (2.5)$$

where ϕ_ν are atomic orbitals and $c_{\nu a}$ are expansion coefficients, also known as MO coefficients. Since it is tedious to write the summation bound #AO, we will drop it from now on. Inserting this expansion into (2.4), we get

$$\hat{f}\sum_\nu c_{\nu a}\phi_\nu = \epsilon_a \sum_\nu c_{\nu a}\varphi_\nu.$$

Projecting the equation onto $\langle\phi_\mu|$ and using the shorthand $\langle\mu|$, the equation simplifies to

$$\sum_\nu c_{\nu a} \langle\mu|\hat{f}|\nu\rangle = \epsilon_a \sum_\nu c_{\nu a} \langle\mu|\nu\rangle$$

$$\sum_\nu c_{\nu a} F_{\mu\nu} = \epsilon_a \sum_\nu c_{\nu a} S_{\mu\nu},$$

where we defined the matrix elements $F_{\mu\nu} = \langle\mu|\hat{f}|\nu\rangle$ and $S_{\mu\nu} = \langle\mu|\nu\rangle$. One should mention that since the atomic orbitals are not necessarily centred on the same core for molecular systems, the braket $\langle\mu|\nu\rangle$ does not have to reduce to the Kronecker-delta $\delta_{\mu\nu}$. Shifting around the elements in the equation above, we can obtain

$$\sum_\nu F_{\mu\nu} c_{\nu a} = \sum_\nu S_{\mu\nu} c_{\nu a} \epsilon_a,$$

which can be written as an equation involving matrices and vectors

$$\mathbf{F}\vec{c}_a = \mathbf{S}\vec{c}_a \epsilon_a$$

for the molecular orbital a. This equation can be expanded for all molecular orbitals by promoting the column vector $\vec{c}_a$ to matrix $\mathbf{C}$ and the number ϵ_a as the diagonal matrix $\boldsymbol{\epsilon}$. This will reproduce the set of coupled equations for all coefficients $\vec{c}_a$. We then get an matrix equation

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}, \qquad (2.6)$$

which is known as the Roothaan-Hall equation.

With the introduction of a (finite, or at most countable infinite) basis, we thus transform the integro-differential equation into a matrix equation, which does not have to be solved on a spatial grid. But in hindsight, these two methods are actually equivalent. Defining a molecular orbital on a spatial grid breaks down to setting the functional value for every grid point, which

results in lots of numbers which can be arranged to a vector, just like the coefficient vector $\vec{c}_a$. The differential operator in h and potential energies in J and K can also be written as matrices on a grid. The expansion in AO basis is thus conceptually not different from the spatial grid: It just uses a abstract grid in the AO vector space, while the spatial grid uses the euclidean space. It is however more convenient to use the AO basis in most cases, since the molecular orbitals do have similar shapes as linear combination of atomic orbitals and therefore less basis functions are needed for convergence.

We shall now take a closer look at matrix elements $F_{\mu\nu}$, for which we split the fock operator into one- and two-electron parts. The one-electron part shall be called $F_{\mu\nu}^{core}$ and

$$F_{\mu\nu}^{core} = \langle\mu|h|\nu\rangle = \langle\mu| -\frac{1}{2}\nabla^2 - \sum_{I=1}^{\#core} \frac{Z_I}{|R_I - r|}|\nu\rangle\,.$$

The two-electron part is often called $G_{\mu\nu}$ and

$$G_{\mu\nu} = \sum_{b=1}^{N/2} \langle\mu|(2J_b - K_b)|\nu\rangle$$

$$= \sum_{b=1}^{N/2} \left[2\,\overset{1}{\langle\mu|}\,\overset{2}{\langle\varphi_b|}r_{12}^{-1}\overset{2}{|\varphi_b\rangle}\,\overset{1}{|\nu\rangle} - \overset{1}{\langle\mu|}\,\overset{2}{\langle\varphi_b|}r_{12}^{-1}\overset{1}{|\nu\rangle}\,\overset{2}{|\varphi_b\rangle} \right]\,.$$

The numbers over brakets show the corresponding electron coordinates. By again expanding MOs into AOs, we obtain

$$G_{\mu\nu} = \sum_{b=1}^{N/2}\sum_{\lambda\sigma} c_{\lambda b}c_{\sigma b}\left[2\,\langle\mu\lambda|\nu\sigma\rangle - \langle\mu\lambda|\sigma\nu\rangle\right]$$

$$= \sum_{\lambda\sigma} 2\sum_{b=1}^{N/2} c_{\lambda b}c_{\sigma b}\left(\langle\mu\lambda|\nu\sigma\rangle - \frac{1}{2}\langle\mu\lambda|\sigma\nu\rangle\right)$$

$$= \sum_{\lambda\sigma} P_{\lambda\sigma}\left(\langle\mu\lambda|\nu\sigma\rangle - \frac{1}{2}\langle\mu\lambda|\sigma\nu\rangle\right)\,,$$

where we defined the density matrix $P_{\lambda\sigma} = 2\sum_{b=1}^{N/2} c_{\lambda b}c_{\sigma b}$.

Thus, using the one- and two-eletron integrals in AO basis, we can compute $F_{\mu\nu}^{core}$ and $G_{\mu\nu}$ by doing some algebra, and then build the Fock-matrix $\mathbf{F}$. Again, we see that the MO coefficients are needed to build the density matrix $\mathbf{P}$ and therefore a iterative procedure must be applied. The elements of the overlap matrix $S_{\mu\nu}$ are just the overlap of AOs: $S_{/mu\nu} = \langle\mu|\nu\rangle$. Now, we have everything we need in Roothaan-Hall equation (2.6) and the only thing left is to solve it.

Starting from an initial guess of the density matrix and compute $\mathbf{F}$, simply diagonalising it will give us its eigenvalues and eigenvectors, which we recognise to be the energies and coefficients of... Wait a minute! We do *not* have an eigenvalue equation here! Since our basis, the AOs are not orthonormal, we introduced the non-unity overlap matrix and get a generalised eigenvalue equation, which cannot be solved by a simple diagonalisation. We have to do better. Inspecting equation (2.6), we may get the idea to multiply both sides by $\mathbf{S}^{-1}$. This gets rid of the overlap on the right hand side and with the substitution $\widetilde{\mathbf{F}} = \mathbf{S}^{-1}\mathbf{F}$, the original equation can be converted to a eigenvalue equation $\widetilde{\mathbf{F}}\mathbf{C} = \mathbf{C}\epsilon$. This quick method, however, comes with a caveat: $\widetilde{\mathbf{F}}$ is

no longer hermitian and could therefore cause some problems. It would be beneficial to obtain an eigenvalue problem with a hermitian matrix. What if we somehow split the transformation matrix $\mathbf{S}^{-1}$? Since $\mathbf{S}$ is hermitian, all of its eigenvalues are real. Furthermore, one can show that it is positive definite, as long as the AO basis are linear independent. Since this also applies to its inverse $\mathbf{S}^{-1}$, we can uniquely determine their matrix square root $\mathbf{S}^{1/2}$ and $\mathbf{S}^{-1/2}$. Using the new transformation matrix, one can insert $\mathbb{1}$ into both sides and obtain

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}$$
$$\mathbf{F}\underbrace{\mathbf{S}^{-1/2}\mathbf{S}^{1/2}}_{\mathbb{1}}\mathbf{C} = \mathbf{S}\underbrace{\mathbf{S}^{-1/2}\mathbf{S}^{1/2}}_{\mathbb{1}}\mathbf{C}\boldsymbol{\epsilon}.$$

Defining $\mathbf{C}' = \mathbf{S}^{1/2}\mathbf{C}$

$$\mathbf{FS}^{-1/2}\mathbf{C}' = \mathbf{SS}^{-1/2}\mathbf{C}'\boldsymbol{\epsilon}$$

and multiply $\mathbf{S}^{-1/2}$ from left

$$\mathbf{S}^{-1/2}\mathbf{FS}^{-1/2}\mathbf{C}' = \mathbf{S}^{-1/2}\mathbf{SS}^{-1/2}\mathbf{C}'\boldsymbol{\epsilon},$$

we can finally eliminate the overlap and obtain an eigenvalue problem

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\boldsymbol{\epsilon},$$

where $\mathbf{F}' = \mathbf{S}^{-1/2}\mathbf{FS}^{-1/2}$. What we did was basically orthogonalising our basis which converts the overlap matrix to unity. This somewhat symmetrical procedure is called Löwdin orthogonalisation. But how do we know that the new matrix $\mathbf{F}'$ is still hermitian? We can just try to compute $(\mathbf{F}')^{\dagger}$

$$\left(\mathbf{F}'\right)^{\dagger} = \left(\mathbf{S}^{-1/2}\mathbf{FS}^{-1/2}\right)^{\dagger} = \left(\mathbf{S}^{-1/2}\right)^{\dagger}\mathbf{F}^{\dagger}\left(\mathbf{S}^{-1/2}\right)^{\dagger}. \tag{2.7}$$

Now assume a unitary matrix $\mathbf{U}$ diagonalises $\mathbf{S}$, i.e. $\mathbf{S} = \mathbf{U}^{\dagger}\mathbf{DU}$, then

$$\left(\mathbf{F}'\right)^{\dagger} = \left(\mathbf{U}^{\dagger}\mathbf{D}^{-1/2}\mathbf{U}\right)^{\dagger}\mathbf{F}\left(\mathbf{U}^{\dagger}\mathbf{D}^{-1/2}\mathbf{U}\right)^{\dagger} \tag{2.8}$$
$$= \left(\mathbf{U}^{\dagger}\left(\mathbf{D}^{-1/2}\right)^{\dagger}\mathbf{U}^{\dagger\dagger}\right)\mathbf{F}\left(\mathbf{U}^{\dagger}\left(\mathbf{D}^{-1/2}\right)^{\dagger}\mathbf{U}^{\dagger\dagger}\right). \tag{2.9}$$

Since a diagonal matrix is always hermitian,

$$\left(\mathbf{F}'\right)^{\dagger} = \left(\mathbf{U}^{\dagger}\mathbf{D}^{-1/2}\mathbf{U}\right)\mathbf{F}\left(\mathbf{U}^{\dagger}\mathbf{D}^{-1/2}\mathbf{U}\right) \tag{2.10}$$
$$= \mathbf{S}^{-1/2}\mathbf{FS}^{-1/2} = \mathbf{F}'. \tag{2.11}$$

We indeed got a hermitian eigenvalue problem, which can be efficiently solved numerically.