Exercise | We derive the Hartree-Fock equations.

The Hartree-Fock equations are a version of the Schrödinger equation describing N fermions interacting with an arbitrary two particle potential. To start, we compute the expectation value of the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} = \sum_i T(x_i) + \sum_{i<j} V(x_i, x_j),$$

when the wavefunction is a totally antisymmetric combination of N single-particle wavefunctions (known as a Slater determinant).

$$\Psi(x_1, \dots, x_n) = \frac{1}{\sqrt{N!}} \sum_{i_1, \dots, i_N = 1}^{N} \varepsilon_{i_1 \cdots i_N} \phi_{i_1}(x_1) \cdots \phi_{i_N}(x_N)$$

It can be shown that Ψ vanishes unless the ϕ_i's are linearly independent, so by Gram-Schmidt, we can guarantee that

$$\langle \phi_i | \phi_j \rangle = \int dx\, \phi_i^*(x)\, \phi_j(x) = \delta_{ij}.$$

Furthermore, we remark that x may include position, spin, and isospin (i.e. proton vs. neutron) information, and the integrals over these quantities should be understood accordingly.

First, we compute $\langle \hat{T} \rangle$:

$$\langle \hat{T} \rangle = \langle \Psi | \hat{T} | \Psi \rangle = \int \prod_{k=1}^{N} dx_k\, \Psi^*(x_1, \dots, x_N)\, \hat{T}\, \Psi(x_1, \dots, x_N)$$

$$= \sum_i \int \prod_{k=1}^{N} dx_k \, \Psi^*(x_1, \dots, x_N)\, T(x_i)\, \Psi(x_1, \dots, x_n).$$

We remark that under the interchange $x_i \longleftrightarrow x_j$, this expression remains invariant, so we can replace the outer sum with N copies of one term. We choose the $T(x_1)$ term without loss of generality. Substituting the definition of the Slater determinant, we have

$$N \int \prod_{k=1}^{N} dx_k \left(\frac{1}{\sqrt{N!}} \sum_{j_1, \dots, j_N} \varepsilon_{j_1 \cdots j_N} \phi^*_{j_k}(x_k) \right) \cdot T(x_1) \cdot$$

$$\left(\frac{1}{\sqrt{N!}} \sum_{i_1 \cdots i_N} \varepsilon_{i_1 \cdots i_N} \phi_{i_k}(x_k) \right) =$$

$$\frac{1}{(N-1)!} \sum_{\substack{i_1 \cdots i_N \\ j_1 \cdots j_N}} \varepsilon_{i_1 \cdots i_N} \varepsilon_{j_1 \cdots j_N} \int \prod_{k=1}^{N} \phi^*_{j_k}(x_k)\, T(x_1)\, \phi_{i_k}(x_k) =$$

$$\frac{1}{(N-1)!} \sum_{\substack{i_1 \cdots i_N \\ j_1 \cdots j_N}} \varepsilon_{i_1 \cdots i_N} \varepsilon_{j_1 \cdots j_N} \left(\int \phi^*_{j_1}(x_1) T(x_1) \phi_{i_1}(x_1)\, dx_1 \right) \cdot$$

$$\left(\prod_{k=2}^{N} \int dx_k \, \phi^*_{j_k}(x_k)\, \phi_{i_k}(x_k) \right) =$$

$$\frac{1}{(N-1)!} \sum_{\substack{i_1 \cdots i_N \\ j_1 \cdots j_N}} \varepsilon_{i_1 \cdots i_N} \varepsilon_{j_1 \cdots j_N} \left(\int \phi^*_{j_1}(x_1) T(x_1) \phi_{i_1}(x_1)\, dx_1 \right) \cdot$$

$$\prod_{k=2}^{N} \delta_{j_k i_k} = \frac{1}{(N-1)!} \sum_{\substack{i_1 \cdots i_N \\ j_1}} \varepsilon_{i_1 \cdots i_N} \varepsilon_{j_1 i_2 \cdots i_N} \int \phi^*_{j_1}(x) T(x) \phi_{i_1}(x) dx .$$

Suppose we fix $i_2, \ldots, i_N$. Then i_1 will only have one possible value if $\varepsilon_{i_1 \cdots i_N}$ is not to vanish. This implies that j_1 can also only have one possible value of $\varepsilon_{j_1 i_2 \cdots i_N}$ is not to vanish: $j_1 = i_1$. Thus, our expression further simplifies to

$$\frac{1}{(N-1)!} \sum_{i_1 \cdots i_N} \left(\varepsilon_{i_1 \cdots i_N}\right)^2 \int \phi^*_{i_1}(x) T(x) \phi_{i_1}(x) dx .$$

The integral only depends on index i_1 and not on any of the remaining indices. For each value of i_1, there will be $(N-1)!$ copies of the same integral in the sum. Thus, we have

$$\langle \hat{T} \rangle = \sum_{i_1=1}^{N} \int \phi^*_{i_1}(x) T(x) \phi_{i_1}(x) dx =$$

$$-\frac{\hbar^2}{2m} \sum_{i_1=1}^{N} \int \phi^*_{i_1}(x) \nabla^2 \phi_{i_1}(x) dx =$$

$$\frac{\hbar^2}{2m} \int \sum_{i=1}^{N} \nabla \phi^*_i(x) \cdot \nabla \phi_i(x) dx .$$

Next, we compute $\langle \hat{V} \rangle$.

$$\langle \hat{V} \rangle = \langle \Psi | \hat{V} | \Psi \rangle = \sum_{i<j} \int \prod_{k=1}^{N} \Psi(x_1, \ldots, x_N)\, V(x_i, x_j)\, \Psi(x_1, \ldots, x_N)\, dx_k .$$

We observe that $x_i \longleftrightarrow x_\ell$, $x_j \longleftrightarrow x_m$ leaves the integral invariant, so we can simply replace the sum by $N(N-1)/2$ copies of a single integral. Without loss of generality, we choose the integral of $V(x_1, x_2)$. Making this substitution, our expression becomes

$$\frac{N(N-1)}{2} \int \prod_{k=1}^{N} dx_k \left(\frac{1}{\sqrt{N!}} \sum_{j_1 \cdots j_N} \varepsilon_{j_1 \cdots j_N}\, \phi^*_{j_k}(x_k) \right) \cdot V(x_1, x_2) \cdot \left(\frac{1}{\sqrt{N!}} \sum_{i_1 \cdots i_N} \varepsilon_{i_1 \cdots i_N}\, \phi_{i_k}(x_k) \right) =$$

$$\frac{1}{2(N-2)!} \sum_{\substack{i_1 \cdots i_N \\ j_1 \cdots j_N}} \varepsilon_{i_1 \cdots i_N}\, \varepsilon_{j_1 \cdots j_N} \int \prod_{k=1}^{N} dx_k\, \phi^*_{j_k}(x_k)\, V(x_1, x_2)\, \phi_{i_k}(x_k) =$$

$$\frac{1}{2(N-2)!} \sum_{\substack{i_1 \cdots i_N \\ j_1 \cdots j_N}} \varepsilon_{i_1 \cdots i_N}\, \varepsilon_{j_1 \cdots j_N} \left(\int dx_1 dx_2\, \phi^*_{j_1}(x_1)\, \phi^*_{j_2}(x_2)\, V(x_1, x_2)\, \phi_{i_1}(x_1)\, \phi_{i_2}(x_2) \right) \cdot \left(\prod_{k=3}^{N} \int dx_k\, \phi^*_{j_k}(x_k)\, \phi_{i_k}(x_k) \right) =$$

$$\frac{1}{2(N-2)!} \sum_{\substack{i_1 \cdots i_N \\ j_1 \cdots j_N}} \varepsilon_{i_1 \cdots i_N}\, \varepsilon_{j_1 \cdots j_N} \left(\int dx_1 dx_2\, \phi^*_{j_1}(x_1)\, \phi^*_{j_2}(x_2)\, V(x_1, x_2)\, \phi_{i_1}(x_1)\, \phi_{i_2}(x_2) \right) \cdot \left(\prod_{k=3}^{N} \delta_{j_k i_k} \right) =$$

$$\frac{1}{2(N-2)!}\sum_{\substack{i_1\cdots i_N\\ j_1 j_2}} \varepsilon_{i_1\cdots i_N}\varepsilon_{j_1 j_2 i_3\cdots i_N}\left(\int dx_1 dx_2\, \phi^*_{j_1}(x_1)\phi^*_{j_2}(x_2)V(x_1,x_2)\phi_{i_1}(x_1)\phi_{i_2}(x_2)\right).$$

Now suppose we fix $i_3,\dots,i_N$. There are only two cases that the Levi-Civita symbols will not vanish: $i_1=j_1$ or $i_1=j_2$. The latter will be subtracted from the former due to the antisymmetry of the Levi-Civita symbols upon the interchange of two indices. We also remark that the indices $i_3,\dots,i_N$ otherwise do not contribute to the sum and instead provide $(N-2)!$ copies of the summand. Combining these two results, our expectation value simplifies to

$$\langle \hat{V}\rangle = \frac{1}{2}\sum_{i_1\neq i_2}\int dx_1 dx_2\, V(x_1,x_2)\Big[\phi^*_{i_1}(x_1)\phi_{i_1}(x_1)\phi^*_{i_2}(x_2)\phi_{i_2}(x_2)$$

$$-\phi^*_{i_2}(x_1)\phi^*_{i_1}(x_2)\phi_{i_1}(x_1)\phi_{i_2}(x_2)\Big] =$$

$$\frac{1}{2}\int dx\,dy\, V(x,y)\sum_{i,j=1}^{N}\Big[\phi_i^*(x)\phi_i(x)\phi_j^*(y)\phi_j(y) -$$

$$\phi_j^*(x)\phi_i^*(y)\phi_i(x)\phi_j(y)\Big].$$

It follows that the expectation value of the Hamiltonian is given by

$$\langle \hat{H}\rangle = \frac{\hbar^2}{2m}\int\sum_{i=1}^{N}\nabla\phi_i^*(x)\cdot\nabla\phi_i(x)\,dx\ +$$

$$\frac{1}{2}\int dx\,dy\, V(x,y) \sum_{i,j=1}^{N} \Big[\phi_i^*(x)\,\phi_i(x)\,\phi_j^*(y)\,\phi_j(y) - \phi_j^*(x)\,\phi_i^*(y)\,\phi_i(x)\,\phi_j(y) \Big].$$

Having computed the expectation value, we now find the single-particle wavefunctions ϕ_k which minimize the expectation, subject to the condition that $\langle \phi_i | \phi_j \rangle = \delta_{ij}$.

In the language of functional differentiation, this can be phrased as

$$\frac{\delta}{\delta \phi_k^*(z)} \Big(\langle H \rangle - \sum_{i,j} \lambda_{ij} \langle \phi_i | \phi_j \rangle \Big) =$$

$$\frac{\delta}{\delta \phi_k^*(z)} \Big(\langle H \rangle - \sum_{i,j} \lambda_{ij} \int \phi_i^*(x)\,\phi_j(x)\,dx \Big) = 0.$$

Using the definition of the functional derivative

$$\frac{\delta I[f]}{\delta f(z)} = \lim_{\varepsilon \to 0} \frac{1}{\varepsilon} \Big(I[f(x) + \varepsilon\,\delta(x-z)] - I[f(x)] \Big),$$

it is possible to derive the following identities:

- $$\frac{\delta}{\delta f(z)} \int \nabla f(x)\, g(x)\, dx = -\nabla \left(\frac{\partial}{\partial(\nabla f)} (\nabla f \cdot g) \right) = -\nabla g(z)$$

- $$\frac{\delta}{\delta f(z)} \int f(x) f(y) h(x,y)\, dx\, dy = \int dx\, f(x) \frac{\delta}{\delta f(z)} \int f(y) h(x,y)\, dy \; +$$

$$\int dy\, f(y) \frac{\delta}{\delta f(z)} \int f(x) h(x,y)\, dx \qquad \text{(product rule)}$$

We now compute the functional derivatives:

$$\frac{\delta \langle \hat{T} \rangle}{\delta \phi_k^*(z)} = -\frac{\hbar^2}{2m} \nabla^2 \phi_k(z).$$

$$\frac{\delta \langle \hat{V} \rangle}{\delta \phi_k^*(z)} = \frac{1}{2} \int dy\, V(z,y) \sum_j \phi_k(z) \phi_j^*(y) \phi_j(y)$$

$$+ \frac{1}{2} \int dx\, V(x,z) \sum_i \phi_i^*(x) \phi_i(x) \phi_k(z)$$

$$- \frac{1}{2} \int dy\, V(z,y) \sum_i \phi_i^*(y) \phi_i(z) \phi_k(y)$$

$$- \frac{1}{2} \int dx\, V(x,z) \sum_j \phi_j^*(x) \phi_k(x) \phi_j(z) =$$

$$\int dx \cdot \frac{1}{2}\left(V(x,z)+V(z,x)\right)\sum_i \Big[|\phi_i(x)|^2\phi_k(z) -$$
$$\phi_i^*(x)\phi_i(z)\phi_k(x)\Big] =$$

$$\int dx\, V(x,z)\sum_i \left[|\phi_i(x)|^2\phi_k(z) - \phi_i^*(x)\phi_i(z)\phi_k(x)\right],$$

where we used in the last line that $V(x,z) = V(z,x)$. Now, let us define

$$U(z) \equiv \int V(z,x)\sum_i |\phi_i(x)|^2\, dx, \quad \text{and}$$

$$U(z,x) \equiv V(z,x)\sum_i \phi_i^*(x)\,\phi_i(z)$$

Then, we have

$$\frac{\delta\langle\hat{V}\rangle}{\delta\phi_k^*(z)} = U(z)\phi_k(z) + \int U(z,x)\phi_k(x)\,dx.$$

Finally, we differentiate

$$\frac{\delta}{\delta\phi_k^*(x)}\int\sum_{i,j}\lambda_{ij}\phi_i^*(x)\phi_j(x)\;dx = \sum_j \lambda_{kj}\,\phi_j(z)$$

Thus, combining our results, we get

$$-\frac{\hbar^2}{2m}\nabla^2\phi_k(z)+U(z)\phi_k(z)+\int U(z,x)\phi_k(x)dx=\sum_j\lambda_{kj}\phi_j(z).$$

Finally, we recognize that

$$\left(\lambda_{ij}\langle\phi_i|\phi_j\rangle\right)^*=\lambda_{ij}^*\langle\phi_i|\phi_j\rangle^*=\lambda_{ij}^*\langle\phi_j|\phi_i\rangle$$

$$=\lambda_{ji}\langle\phi_j|\phi_i\rangle\implies\lambda_{ij}=\lambda_{ji}^*.$$

(I'm sorry that I don't understand this last part as well as I should.)

That is, λ is Hermitian, so it can be diagonalized by a unitary matrix:

$$\lambda=U\varepsilon U^+\implies\hat{H}\phi_k=(\lambda\phi)_k=(U\varepsilon U^+\phi)_k\implies$$

$$U^+H\phi_k=(\varepsilon U^+\phi)_k\implies\hat{H}U^+\phi_k=(\varepsilon U^+\phi)_k=\varepsilon_k(U^+\phi)_k.$$

So if we define $\Psi_k\equiv U^+\phi_k$, then we arrive at the Hartree-Fock equation:

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\Psi_k(z)+U(z)\Psi_k(z)+\int U(z,x)\Psi_k(x)dx=\varepsilon_k\Psi_k(z)}$$

This looks like the Schrödinger equation, except it has an additional "exchange" term. Solving it would yield the optimal single-particle wavefunctions, but it is an extremely complicated equation!