

9. Hartree-Fock: Pass 2

a. Recap of the general Hartree-Fock (HF) discussion

For now we restrict the discussion to local, two-body potentials \widehat{V} , which means $V(\mathbf{x}, \mathbf{y})$ in first quantization (see Fig. 1 for local versus non-local). We will usually assume a translationally invariant potential, which means $V(\mathbf{x}, \mathbf{y}) = V(\mathbf{x} - \mathbf{y})$ (in an overloaded notation; that is, the meaning is dictated by the number of arguments). But we could also imagine having an external trap potential seen by all the fermions, which would not be translationally invariant.

HF is a limited variational calculation: the trial wave function is the best Slater determinant from all possible A single-particle wave functions $\{\phi_i(\mathbf{x})\}$, $i = 1, \dots, A$, where i stands for a complete set of quantum numbers to define the basis state. This could be $\{n, l, m_l, s = 1/2, m_s, t = 1/2, m_t\}$ in a finite system, or we could couple them differently (e.g., coupling l and s to j), or we could have plane waves in a uniform system. The notation \mathbf{x} will in general include not only the spatial coordinate (in an appropriate coordinate system) but also the coordinates for the spin and isospin. If we make the other coordinates explicit, then \mathbf{x} will just mean the usual spatial coordinate vector. This is a limited variational wave function because a *sum* of Slater determinants would be more complete, and therefore give a better variational estimate.

So our trial wave function is (det means to form a determinant)

$$|\Psi_{HF}\rangle = \det\{\phi_i(\mathbf{x}), i = 1, \dots, A\}, \quad (1)$$

which is an anti-symmetric product wave function. [What if we just used a product of the A wave functions without anti-symmetrizing? Is this a variational calculation? We seem to violate the principle of Fermi symmetry; does this make it unphysical?] The first quantized Hamiltonian is

$$\widehat{H} = \sum_{i=1}^A \widehat{T}(\mathbf{x}_i) + \frac{1}{2} \sum_{i,j=1}^A \widehat{V}(\mathbf{x}_i, \mathbf{x}_j), \quad (2)$$

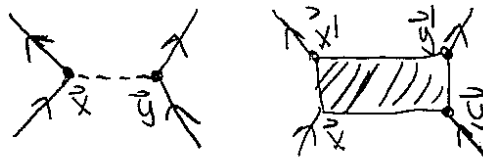
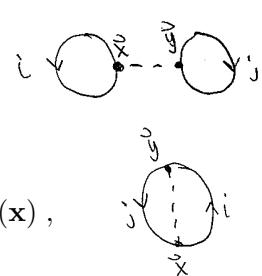


Figure 1: Left: a local potential $V(\mathbf{x}, \mathbf{y})$, which can be represented in a Feynman diagram as a single line with coordinates at the ends. $V(\mathbf{x} - \mathbf{y})$ means it is translationally invariant. In momentum representation this potential line would be labeled by a single momentum, which is the momentum transfer between the fermions. (If the potential is not translationally invariant, then the Fourier transform is not a function of a single momentum.) Right: a non-local potential, which is represented as a box with coordinates at the corners. Translational invariance here means that V is a function of $\mathbf{x} - \mathbf{y}$ and $\mathbf{x}' - \mathbf{y}'$. If it is separable, then one can imagine the top and bottom halves of the box being pulled apart, representing a product of functions of $\mathbf{x} - \mathbf{y}$ and $\mathbf{x}' - \mathbf{y}'$.

where the spin-isospin indices are implicit. Then, as in Section 8, we have:

$$\begin{aligned}
 \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle &= \sum_{i=1}^A \frac{1}{2m} \int d\mathbf{x} \nabla \phi_i^\dagger \cdot \nabla \phi_i \\
 H : \quad &+ \frac{1}{2} \int d\mathbf{x} \int d\mathbf{y} \sum_{i=1}^A |\phi_i(\mathbf{x})|^2 V(\mathbf{x}, \mathbf{y}) \sum_{j=1}^A |\phi_j(\mathbf{y})|^2 \\
 F : \quad &- \frac{1}{2} \int d\mathbf{x} \int d\mathbf{y} \sum_{i=1}^A \phi_i^\dagger(\mathbf{x}) \phi_i(\mathbf{y}) V(\mathbf{x}, \mathbf{y}) \sum_{j=1}^A \phi_j^\dagger(\mathbf{y}) \phi_j(\mathbf{x}),
 \end{aligned}$$


where the Hartree (H) and Fock (F) terms are indicated. In the Fock term, the density matrix

$$\rho(\mathbf{x}, \mathbf{y}) \equiv \sum_{i=1}^A \phi_i^\dagger(\mathbf{x}) \phi_i(\mathbf{y}) \tag{4}$$

can be identified. We can associate these general forms with diagrams as shown in Eq. (3).

What would these look like in detail if $V(\mathbf{x}, \mathbf{y}) \rightarrow V(\mathbf{r}_x, \mathbf{r}_y) \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2$? Then

$$H : \quad \int d^3 r_x \int d^3 r_y \phi_i^*(\mathbf{r}_x)_\alpha (\boldsymbol{\sigma}^a)_{\alpha\beta} \phi_i(\mathbf{r}_x)_\beta V(\mathbf{r}_x, \mathbf{r}_y) \phi_j^*(\mathbf{r}_y)_\gamma (\boldsymbol{\sigma}^a)_{\gamma\delta} \phi_j(\mathbf{r}_y)_\delta, \tag{5}$$

$$F : \quad \int d^3 r_x \int d^3 r_y \phi_i^*(\mathbf{r}_x)_\alpha (\boldsymbol{\sigma}^a)_{\alpha\delta} \phi_j(\mathbf{r}_x)_\delta V(\mathbf{r}_x, \mathbf{r}_y) \phi_j^*(\mathbf{r}_y)_\gamma (\boldsymbol{\sigma}^a)_{\gamma\beta} \phi_i(\mathbf{r}_y)_\beta, \tag{6}$$

with implied sums over $\alpha, \beta, \gamma,$ and δ . Everything is a component here, so the ordering is just for clarity. These terms are associated with the fully labeled Feynman diagrams in Fig. 2. Note that the Pauli spin matrices live at the vertices, with the associated spin indices.

The HF equations follow as before from minimizing the HF energy subject to the constraints that all of the single-particle wave functions are normalized:

$$\frac{\partial}{\partial \phi_i^\dagger(\mathbf{x})} \left(\langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle - \sum_{j=1}^A \varepsilon_j \int d\mathbf{y} |\phi_j(\mathbf{y})|^2 \right), \tag{7}$$

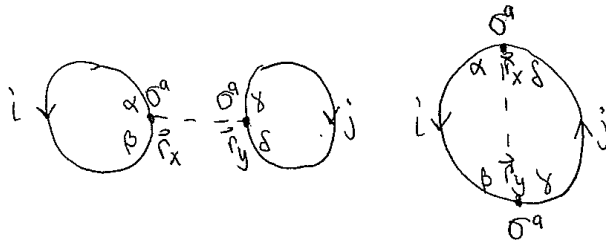


Figure 2: Feynman diagrams for Hartree and Fock contributions corresponding to Eqs. (5) and (6).

which yields the equations (you fill in the details!):

$$\left[-\frac{\nabla^2}{2m} + \Gamma_H(\mathbf{x}) \right] \phi_i(\mathbf{x}) + \int d\mathbf{y} \Gamma_F(\mathbf{x}, \mathbf{y}) \phi_i(\mathbf{y}) = \varepsilon_i \phi_i(\mathbf{x}) , \quad (8)$$

where

$$\Gamma_H(\mathbf{x}) = \int d^3y V(\mathbf{x}, \mathbf{y}) \sum_{j=1}^A |\phi_j(\mathbf{y})|^2 = \int d^3y V(\mathbf{x}, \mathbf{y}) \rho(\mathbf{y}, \mathbf{y}) , \quad (9)$$

$$\Gamma_F(\mathbf{x}, \mathbf{y}) = -V(\mathbf{x}, \mathbf{y}) \sum_{j=1}^A \phi_j^\dagger(\mathbf{y}) \phi_j(\mathbf{x}) = -V(\mathbf{x}, \mathbf{y}) \rho(\mathbf{y}, \mathbf{x}) . \quad (10)$$

As discussed before, in the HF Schrödinger equation, Γ_H acts like an external local potential while Γ_F acts like an external non-local potential. Some additional comments:

- In $|\Psi_{HF}\rangle$, each of the A particles occupies a definite single-particle state (up to anti-symmetry from identical particles).
- Thus, each particle moves in a single-particle potential that comes from its *average* interaction with all other particles, accounting for identical particles.
- The equations (8)–(10) must be solved *self-consistently* for the A single-particle wave functions and energies (next section!).
- Note that while we only use the A lowest solutions to Eq. (8) for Eqs. (9) and (10), a complete set of solutions can be found.
- Solutions to the HF equations have to be found numerically in a finite system.

b. Self-Consistency Procedure

Here is a summary of the procedure to solve the Hartree-Fock equations. We assume A fermions.

1. Start the cycle with initial guesses for the A single-particle wave functions $\phi_i(\mathbf{x})$, where i is a complete set of quantum numbers and \mathbf{x} is a complete set of coordinates. An example for a finite nucleus would be a set of harmonic oscillator wave functions. They should correspond to the lowest filled states. [An alternative to starting with the ϕ_i 's would be to start with guesses for Γ_H and Γ_F .]
2. Calculate $\Gamma_H(\mathbf{x})$ and $\Gamma_F(\mathbf{x}, \mathbf{y})$ by substituting the ϕ_i 's' and carrying out the sums and integral.
3. Solve the integro-differential equation for the A lowest ε_i 's and the corresponding $\phi_i(\mathbf{x})$'s. Note that it is possible that the set of i 's in one iteration is changed in another.
4. Check how much the ε_i 's have changed. If the change is within a specified stopping tolerance, go to 5. If not, go to 2.
5. With the self-consistent set of ϕ_i 's and ε_i 's, calculate the energy and any other quantity of interest (e.g., densities).

Some questions:

- Does this procedure always converge?
- How can we accelerate convergence?
- What can we do for the “open shell” case?
- What if the occupancy is not either 0 or 1 for each state i in a particular iteration? (This will happen with pairing.)
- How would you generalize the procedure to account for finite temperature and a chemical potential?

c. Uniform System

Let’s apply the Hartree-Fock procedure from the last section to the uniform system with a translationally invariant V and the particular case of the contact interaction $V(\mathbf{x}, \mathbf{y}) = C_0 \delta^3(\mathbf{x} - \mathbf{y})$.

For step 1, let’s guess

$$\phi_i(\mathbf{x}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}_i \cdot \mathbf{x}} \eta_\alpha, \quad (11)$$

where the \mathbf{k}_i are the discrete momentum levels and α is the spin coordinate. To be clear on the latter:

$$\eta = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \implies \eta_1 = 1, \eta_2 = 0; \quad \eta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \implies \eta_1 = 0, \eta_2 = 1. \quad (12)$$

We need to take the lowest A values of k_i^2 (accounting for spin/isospin). However, we will convert from the discrete sums to continuous integrals whenever needed.

For step 2 we get (for spin-independent, translationally invariant V)

$$\Gamma_H(\mathbf{x}) = \int d^3y V(\mathbf{x} - \mathbf{y}) \sum_{j=1}^A |\phi_j(\mathbf{y})|^2 = \int d^3y V(\mathbf{x} - \mathbf{y}) \rho, \quad (13)$$

where ρ is the *constant* density $\rho = A/\Omega$ (i.e., independent of \mathbf{x}). Whenever we come across an integral like this, the first thought should be whether a change of variables can simplify it; in this case $\mathbf{y}' = \mathbf{x} - \mathbf{y}$, under which the integration volume is invariant (the minus signs from the variable change are countered by the flip of the integration limits). Further, any volume integral can be thought of as a Fourier transform with zero argument. The result is:

$$\int d^3y V(\mathbf{x} - \mathbf{y}) = \int d^3y' V(\mathbf{y}') = \int d^3y' V(\mathbf{y}') e^{-i\mathbf{k}' \cdot \mathbf{y}'} \Big|_{\mathbf{k}'=0} = \tilde{V}(0), \quad (14)$$

where we indicate the Fourier transform with a tilde. Thus

$$\Gamma_H(\mathbf{x})_{\alpha\beta} = \delta_{\alpha\beta} \rho \tilde{V}(0) \longrightarrow \delta_{\alpha\beta} \rho C_0, \quad (15)$$

where we’ve indicated the result for the pionless LO interaction. In the Schrödinger equation this is a spatial constant times $\phi_i(\mathbf{x})$.

The result for Γ_F is immediate:

$$\Gamma_F(\mathbf{x}, \mathbf{y})_{\alpha\beta} = -\delta_{\alpha\beta} V(\mathbf{x} - \mathbf{y}) \frac{1}{\Omega} \frac{\mathcal{N}}{(2\pi)^3} \int^{k_F} d^3 k' e^{i\mathbf{k}' \cdot (\mathbf{x} - \mathbf{y})}, \quad (16)$$

where the $\delta_{\alpha\beta}$ follows from assuming a spin-independent interaction and we've converted the sum to an integral up to the Fermi momentum. Note how the volume dependence cancels, which serves as a check. In the Schrödinger equation for ϕ_i , we can do the spatial integral after shifting $\mathbf{y}' = \mathbf{x} - \mathbf{y}$:

$$\begin{aligned} \int d^3 y \Gamma_F(\mathbf{x}, \mathbf{y})_{\alpha\beta} \phi_i(\mathbf{y})_{\alpha} &= - \int^{k_F} \frac{d^3 k'}{(2\pi)^3} \int d^3 y V(\mathbf{x} - \mathbf{y}) e^{i\mathbf{k}' \cdot (\mathbf{x} - \mathbf{y})} \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k} \cdot \mathbf{y}} \delta_{\alpha\beta} \eta_{\beta} \\ &= - \int^{k_F} \frac{d^3 k'}{(2\pi)^3} \left[\int d^3 y' V(\mathbf{y}') e^{-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{y}'} \right] \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k} \cdot \mathbf{x}} \eta_{\alpha} \\ &= - \int^{k_F} \frac{d^3 k'}{(2\pi)^3} \tilde{V}(\mathbf{k} - \mathbf{k}') \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k} \cdot \mathbf{x}} \eta_{\alpha}. \end{aligned} \quad (17)$$

So if we start with a plane wave as $\phi_i(\mathbf{x})$, this also returns a constant times the same plane wave, as we found for the Hartree term.

Combining these two results, we find that $\phi_i(\mathbf{x}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}_i \cdot \mathbf{x}} \eta_{\alpha}$ is a self-consistent solution with

$$\varepsilon_{\mathbf{k}} = \frac{k^2}{2m} + \rho \tilde{V}(0) - \int \frac{d^3 k'}{(2\pi)^3} \tilde{V}(\mathbf{k} - \mathbf{k}'). \quad (18)$$

For the contact potential, this is

$$\varepsilon_{\mathbf{k}} = \frac{k^2}{2m} + \rho \left(1 - \frac{1}{\nu}\right) C_0. \quad (19)$$

Thus the self-consistency loop is closed with our first guess for single-particle wave functions, even though the single-particle *spectrum* is changed from the non-interacting result of $k^2/2m$.

Let's now calculate the energy density $\langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle / \Omega$ using the self-consistent result for the contact term. First the kinetic energy density:

$$\begin{aligned} \sum_{i=1}^A \frac{1}{2m\Omega} \int d\mathbf{x} \nabla \phi_i^{\dagger} \cdot \nabla \phi_i &= \frac{\nu}{\Omega} \sum_{\mathbf{k}}^{k_F} \frac{1}{2m} \int d^3 x \frac{1}{\Omega} (-i\mathbf{k} \cdot i\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{x}} e^{i\mathbf{k} \cdot \mathbf{x}} \eta_{\alpha}^{\dagger} \eta_{\alpha} \\ &= \frac{\nu}{\Omega} \int^{k_F} \frac{d^3 k}{(2\pi)^3} \frac{k^2}{2m} \int d^3 x \frac{1}{\Omega} \\ &= \frac{3}{5} \frac{k_F^2}{2m} \rho, \quad \checkmark \end{aligned} \quad (20)$$

then the direct term (note how the factors of Ω work out):

$$\begin{aligned} \frac{1}{2\Omega} \int d^3 x \int d^3 y \sum_{i=1}^A |\phi_i(\mathbf{x})|^2 \frac{1}{\Omega} V(\mathbf{x}, \mathbf{y}) \sum_{j=1}^A |\phi_j(\mathbf{y})|^2 \frac{1}{\Omega} &= \frac{C_0}{2} \left(\frac{\nu}{\Omega} \sum_{\mathbf{k}}^{k_F} 1 \right)^2 \int d^3 x \frac{1}{\Omega} \\ &= \frac{C_0}{2} \rho^2, \quad \checkmark \end{aligned} \quad (21)$$

then finally the exchange term:

$$\begin{aligned}
 -\frac{1}{2\Omega} \int d^3x \int d^3y \sum_{i=1}^A \phi_i^\dagger(\mathbf{x}) \phi_i(\mathbf{y}) V(\mathbf{x}, \mathbf{y}) \sum_{j=1}^A \phi_j^\dagger(\mathbf{y}) \phi_j(\mathbf{x}) &= -\frac{C_0}{2} \frac{1}{\nu} \left(\frac{\nu}{\Omega} \sum_{\mathbf{k}}^{k_F} 1 \right)^2 \\
 &= -\frac{C_0}{2} \frac{1}{\nu} \rho^2. \quad \checkmark
 \end{aligned} \tag{22}$$

(We've left the intermediate steps in the exchange term for the reader; be careful of the spin index contractions.) We might have naively thought that the energy would be given by the sum of the eigenvalues from Eq. (19). It looks close, but

$$\frac{1}{\Omega} \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = \frac{3}{5} \frac{k_F^2}{2m} \rho + \frac{C_0}{2} \left(1 - \frac{1}{\nu}\right) \rho^2 \neq \frac{\nu}{\Omega} \sum_{\mathbf{k}}^{k_F} \varepsilon_{\mathbf{k}}, \tag{23}$$

which has a factor of 1/2 in the term proportional to C_0 . The reason is that $\varepsilon_{\mathbf{k}}$ includes the effect on one fermion of the pairwise potential of all the other fermions. So these pairwise potentials double count the energy contribution, which means we need a 1/2 factor. In contrast, the kinetic energy is a single-particle term, which means it is counted correctly by just summing the eigenvalue.

Finally, note that the integrals here were all finite at the Hartree-Fock level for the uniform system (i.e., no sensitivity to short-distance physics). Is this also true in a finite system, such as fermions in a harmonic trap?