

Sheet 3

October 27, 2025

Please hand in a zip-archive, containing a pdf for exercise 1, 2 and the plots for exercise 2, which is named `<firstname>-<lastname>-sheet-<number>`.

The deadline is Monday, Nov. 3rd, 12:00 (noon). Please hand in your solution via moodle.

1 Antisymmetry Adventures

One important property of electrons, which the Hartree-Fock method takes into account, is that they are fermions, and therefore their wavefunctions are antisymmetric. This means that for a **pairwise permutation** of two arguments of the wave function, it will change its sign, e.g.

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = -\Psi(\vec{r}_2, \vec{r}_1, \dots, \vec{r}_N). \quad (1)$$

In the following we will prove and derive several important properties of Slater determinants and the exchange operator which found application in the lecture.

1. The exchange operator is defined as the operator which switches the i th and j th arguments of a product of single-particle wave functions:

$$\hat{P}_{ij}[\phi_a(\vec{r}_1) \dots \phi_b(\vec{r}_i) \dots \phi_c(\vec{r}_j) \dots \phi_z(\vec{r}_N)] = \phi_a(\vec{r}_1) \dots \phi_b(\vec{r}_j) \dots \phi_c(\vec{r}_i) \dots \phi_z(\vec{r}_N). \quad (2)$$

Show the following properties of the exchange operator \hat{P}_{ij} :

- a) The exchange operator is involutive, i.e. it is its own inverse $\hat{P}_{ij}^{-1} = \hat{P}_{ij}$
- b) The exchange operator is a unitary operator $\hat{P}_{ij}^{-1} = \hat{P}_{ij}^\dagger$
- c) The exchange operator has eigenvalues of ± 1 .
- d) The exchange operator commutes with the interacting many-electron Hamiltonian for N electrons

$$\hat{H} = \sum_{i=1}^N \left(-\frac{\hbar^2 \nabla_i^2}{2m} + V_{ext}(\vec{r}_i) \right) + \sum_{i=1}^N \sum_{j=i+1}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|}. \quad (3)$$

2 points

2. We now introduce the antisymmetrizer operator, which when applied to a regular product of single-particle wave functions will turn it into a Slater determinant.

$$\hat{A}[\phi_a(\vec{r}_1)\phi_b(\vec{r}_2)\dots\phi_z(\vec{r}_N)] = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(\vec{r}_1) & \phi_b(\vec{r}_1) & \cdots & \phi_z(\vec{r}_1) \\ \phi_a(\vec{r}_2) & \phi_b(\vec{r}_2) & \cdots & \phi_z(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_a(\vec{r}_N) & \phi_b(\vec{r}_N) & \cdots & \phi_z(\vec{r}_N) \end{vmatrix}$$

We use the notation of S_N for the group of all possible permutations in a N-particle wave function and $p \in S_N$ are elements of that group.

\hat{P}^p is the exchange operator which corresponds to the permutation p . Any permutation p can be written as the successive application of pairwise permutations between two elements i, j , so every \hat{P}^p can be written as the successive application of operators \hat{P}_{ij} (Note that the \hat{P}_{ij} do NOT commute!)

$$\hat{P}^p = \prod_{(i,j)} \hat{P}_{ij}. \quad (4)$$

We define the parity $(-1)^p$ of a permutation p as being +1 if it can be written as an even number of successive pairwise permutations, and -1 if the number is odd. Then the antisymmetrizer operator is defined as

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_{p \in S_N} (-1)^p \hat{P}^p \quad (5)$$

- a) Show that \hat{A} commutes with the Hamiltonian from eq. 3
- b) Show that a Slater determinant is antisymmetric.
- c) Show that two Slater determinants containing at least one differing single-particle state are orthogonal.

3 points

2 Hartree Fock for homogeneous electron gas

The homogeneous electron gas (also known under the name *Jellium*) is a popular toy model for treating electron-electron interactions. We imagine an infinite space filled with a positive background-charge n_B , with the electrons also creating a homogeneous charge density $-n_B$. This system is described by the Hamiltonian

$$\hat{H} = \hat{T}_e + \hat{V}_{EX} = -\frac{\nabla^2}{2} - \sum_{\nu=\uparrow,\downarrow} \sum_{j=1}^N \int d^3r' \frac{1}{|\vec{r} - \vec{r}'|} \left(\frac{\phi_{j,\nu}^*(\vec{r}') \phi_{i,\sigma}(\vec{r}') \phi_{j,\nu}(\vec{r})}{\phi_{i,\sigma}(\vec{r})} \right). \quad (6)$$

For those who are interested in how to derive eq. 6 based on the formalism shown in the lecture, please see the section 3 at the end of the sheet.

Since the entire problem is translation invariant, a natural Ansatz are plane waves. Because we assume the space to be infinite, our basis are the plane waves $e^{i\vec{k}\cdot\vec{r}}$, with $\vec{k} \in \mathbb{R}^3$. The momentum eigenstates are occupied up to the Fermi energy E_F , corresponding to the Fermi-level k_F . Usually, we would sum over all occupied states $\phi_{j,\nu}$, but the momenta are a continuous variable, so we need to replace the sum with an integral over the momenta in the volume $\Omega_{k_F} = \{\vec{k} \in \mathbb{R} \text{ with } |\vec{k}| \leq k_F\}$: $\sum_j \rightarrow \frac{1}{(2\pi)^3} \int_{\Omega_{k_F}} d^3k$.

1. Show that the plane waves $e^{i\vec{k}\vec{r}}$ are the eigenstates of the Hamiltonian in eq. 6, and calculate the total energy.

a) First replace the sum over the states ϕ_j with an integral, and apply the Hamiltonian to any plane wave $e^{i\vec{k}\vec{r}}$.

b) Execute both integrals. You may use the identity $\frac{1}{(2\pi)^3} \int_{\Omega_{k_F}} d^3k \frac{4\pi}{|\vec{k}_i - \vec{k}|^2} = \frac{k_F}{\pi} \left(1 + \frac{1}{2} \left(\frac{k_F}{k_i} - \frac{k_i}{k_F}\right) \ln\left(\frac{k_F + k_i}{k_F - k_i}\right)\right)$.

2 points

2. **Programming Exercise:** By integrating over all occupied states, we see that the total energy of the system is given by eq. 7.

$$E[\zeta, n_B] = \sum_{\nu=\uparrow, \downarrow} \int_{\Omega_{k_F(\nu)}} d^3k \left(\frac{k^2}{2} - \frac{k_F(\nu)}{\pi} \left(1 + \frac{1}{2} \left(\frac{k_F(\nu)}{k} - \frac{k}{k_F(\nu)} \right) \ln \left(\frac{k_F(\nu) + k}{k_F(\nu) - k} \right) \right) \right) \quad (7)$$

Note that, if there are different numbers of spin-up and spin-down electrons, each spin component will have its own Fermi-level $k_F(\uparrow)$ or $k_F(\downarrow)$. We define the degree of spin polarization ζ as the ratio of the totals densities for each component

$$\zeta = \frac{n(\uparrow) - n(\downarrow)}{n(\uparrow) + n(\downarrow)} = \frac{k_F^3(\uparrow) - k_F^3(\downarrow)}{k_F^3(\uparrow) + k_F^3(\downarrow)}. \quad (8)$$

Here we used that density of the electrons and the background is the same, and can be calculated as $n_B = \sum_{\sigma} \frac{1}{(2\pi)^3} \int_{\Omega_{k_F}} d^3k = n(\uparrow) + n(\downarrow)$.

Calculate the total energy numerically (e.g. using python) for different values of n_B and ζ . For which values of n_B is the total energy minimised for a spin-zero configuration, and for which values is it minimised for a spin-polarised configuration?

- a) First explicitly calculate $k_F(\nu)$ as a function of n_B and ζ .
- b) Then calculate the total energy for a range of n_B and ζ (note that $\zeta \in [0, 1]$).
- c) Identify the ζ with the lowest energy for each n_B , and create a plot of ζ vs n_B

2 points

3. What is the physical explanation for the transition? What interpretation does this result in for the exchange energy? Back up your idea with the plots from exercise 2, and by analysing the scaling of the two terms of the total energy with respect to n_B and ζ .

1 point

3 Appendix

For those who are interested in how to derive the Hamiltonian of the homogeneous electron gas, here's a quick overview: Ignoring the self-interaction of the background with itself, which only adds an infinite constant to the energy, we start with the time-independent Schrödinger equation

$$\left(\hat{V}_{e-B}(\vec{r}) + \hat{V}_{e-e}^{i,\sigma}(\vec{r}) + \hat{T}_e \right) \phi_{i,\sigma}(\vec{r}) = E \phi_{i,\sigma}(\vec{r}). \quad (9)$$

The first term is the interaction of the electrons with the background

$$V_{e-B}(\vec{r}) = \int d^3R \frac{n_B}{|\vec{r} - \vec{R}|}. \quad (10)$$

The second is the interaction of the electrons with each other, which we approximate with the Hartree-Fock potential from the lecture (Note that the index $i = 1, \dots, N$ identifies the occupied orbitals, and $\sigma = \uparrow, \downarrow$ identifies the spin)

$$V_{e-e}^{i,\sigma}(\vec{r}) = \sum_{\nu=\uparrow,\downarrow} \sum_{j=1}^N \int d^3r' \frac{1}{|\vec{r} - \vec{r}'|} \left(|\phi_{j,\nu}(\vec{r}')|^2 - \frac{\phi_{j,\nu}^*(\vec{r}') \phi_{i,\sigma}(\vec{r}') \phi_{j,\nu}(\vec{r})}{\phi_{i,\sigma}(\vec{r})} \right). \quad (11)$$

The third and final is the kinetic energy of the electrons, given by

$$\hat{T}_e = -\frac{\nabla^2}{2}. \quad (12)$$

The fact that the electron gas is homogeneous means we have a constant overall charge density $\sum_{\nu=\uparrow,\downarrow} \sum_{j=1}^N |\phi_{j,\nu}(\vec{r}')|^2 = -n_B$. Therefore, the interaction with the background cancels the Hartree-term in the electron-electron interaction, leaving only the exchange energy. The remaining Hamiltonian is

$$\hat{H} = \hat{T}_e + \hat{V}_{EX} = -\frac{\nabla^2}{2} - \sum_{\nu=\uparrow,\downarrow} \sum_{j=1}^N \int d^3r' \frac{1}{|\vec{r} - \vec{r}'|} \left(\frac{\phi_{j,\nu}^*(\vec{r}') \phi_{i,\sigma}(\vec{r}') \phi_{j,\nu}(\vec{r})}{\phi_{i,\sigma}(\vec{r})} \right) \quad (13)$$