

Week 42: Hartree-Fock theory and density functional theory

Morten Hjorth-Jensen¹

Department of Physics and Center for Computing in Science Education,
University of Oslo, Norway¹

October 13-17, 2025

© 1999-2025, Morten Hjorth-Jensen. Released under CC Attribution-NonCommercial 4.0 license

Week 42, October 13-17, 2025

Topics to be covered

Thursday:

1. The first lecture aims at finalizing the calculation of the ground state energy of the homogeneous electron gas in three dimensions
2. Start discussion of density functional theory
3. Video of lecture at https://youtu.be/Ry_5h842TrA
4. Whiteboard notes at <https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/HandwrittenNotes/2025/FYS4480October16.pdf>

Friday:

1. Density functional theory
2. Discussions of first midterm
3. Lecture Material: These slides and handwritten notes
4. First midterm set at <https://github.com/ManyBodyPhysics/FYS4480/blob/>

Hartree-Fock ground state energy for the electron gas in three dimensions

We consider a system of electrons in infinite matter, the so-called electron gas. This is a homogeneous system and the one-particle states are given by plane wave function normalized to a volume V for a box with length L (the limit $L \rightarrow \infty$ is to be taken after we have computed various expectation values)

$$\psi_{\mathbf{k}\sigma}(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp(i\mathbf{k}\mathbf{r})\xi_{\sigma}$$

where \mathbf{k} is the wave number and ξ_{σ} is a spin function for either spin up or down

$$\xi_{\sigma=+1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \xi_{\sigma=-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Periodic boundary conditions

We assume that we have periodic boundary conditions which limit the allowed wave numbers to

$$k_i = \frac{2\pi n_i}{L} \quad i = x, y, z \quad n_i = 0, \pm 1, \pm 2, \dots$$

We assume first that the particles interact via a central, symmetric and translationally invariant interaction $V(r_{12})$ with $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The interaction is spin independent.

Total Hamiltonian

The total Hamiltonian consists then of kinetic and potential energy

$$\hat{H} = \hat{T} + \hat{V}.$$

The operator for the kinetic energy is given by

$$\hat{T} = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma}.$$

Find the expression for the interaction \hat{V} expressed with creation and annihilation operators.

The expression for the interaction has to be written in k space, even though V depends only on the relative distance. It means that you need to set up the Fourier transform $\langle k_i k_j | V | k_m k_n \rangle$.

A general two-body interaction element is given by (not using anti-symmetrized matrix elements)

$$\hat{V} = \frac{1}{2} \sum_{pqrs} \langle pq\hat{v}|rs \rangle a_p^\dagger a_q^\dagger a_s a_r,$$

where \hat{v} is assumed to depend only on the relative distance between two interacting particles, that is $\hat{v} = v(\vec{r}_1, \vec{r}_2) = v(|\vec{r}_1 - \vec{r}_2|) = v(r)$, with $r = |\vec{r}_1 - \vec{r}_2|$.

With spin degrees of freedom

In our case we have, writing out explicitly the spin degrees of freedom as well

$$\hat{V} = \frac{1}{2} \sum_{\substack{\sigma_p \sigma_q \\ \sigma_r \sigma_s}} \sum_{\substack{k_p k_q \\ k_r k_s}} \langle k_p \sigma_p, k_q \sigma_q | v | k_r \sigma_r, k_s \sigma_s \rangle a_{k_p \sigma_p}^\dagger a_{k_q \sigma_q}^\dagger a_{k_s \sigma_s} a_{k_r \sigma_r}. \quad (1)$$

Plane waves

Inserting plane waves as eigenstates we can rewrite the matrix element as

$$\langle k_p \sigma_p, k_q \sigma_q | \hat{v} | k_r \sigma_r, k_s \sigma_s \rangle = \frac{1}{V^2} \delta_{\sigma_p \sigma_r} \delta_{\sigma_q \sigma_s} \int \int \exp -i(k_p \cdot r_p) \exp -i(k_q \cdot$$

where we have used the orthogonality properties of the spin functions. We change now the variables of integration by defining $r = r_p - r_q$, which gives $r_p = r + r_q$ and $d^3r = d^3r_p$.

Integration limits

The limits are not changed since they are from $-\infty$ to ∞ for all integrals. This results in

$$\begin{aligned}\langle k_p \sigma_p, k_q \sigma_q | \hat{v} | k_r \sigma_r, k_s \sigma_s \rangle &= \frac{1}{V^2} \delta_{\sigma_p \sigma_r} \delta_{\sigma_q \sigma_s} \int \exp i(k_s - k_q) \cdot r_q \int v(r) \exp \\ &= \frac{1}{V^2} \delta_{\sigma_p \sigma_r} \delta_{\sigma_q \sigma_s} \int v(r) \exp i[(k_r - k_p) \cdot r] \int \exp\end{aligned}$$

Recognizing integral

We recognize the integral over r_q as a δ -function, resulting in

$$\langle k_p \sigma_p, k_q \sigma_q | \hat{v} | k_r \sigma_r, k_s \sigma_s \rangle = \frac{1}{V} \delta_{\sigma_p \sigma_r} \delta_{\sigma_q \sigma_s} \delta_{(k_p + k_q), (k_r + k_s)} \int v(r) \exp i [(k_r -$$

For this equation to be different from zero, we must have conservation of momenta, we need to satisfy $k_p + k_q = k_r + k_s$.

Conservation of momentum

We can use the conservation of momenta to remove one of the summation variables resulting in

$$\hat{V} = \frac{1}{2V} \sum_{\sigma\sigma'} \sum_{k_p k_q k_r} \left[\int v(r) \exp i [(k_r - k_p) \cdot r] d^3 r \right] a_{k_p \sigma}^\dagger a_{k_q \sigma'}^\dagger a_{k_p + k_q - k_r, \sigma'} a_{k_r \sigma}$$

which can be rewritten as

$$\hat{V} = \frac{1}{2V} \sum_{\sigma\sigma'} \sum_{k p q} \left[\int v(r) \exp -i(q \cdot r) dr \right] a_{k+q, \sigma}^\dagger a_{p-q, \sigma'}^\dagger a_{p \sigma'} a_{k \sigma}, \quad (2)$$

Some definitions

In the last equation we defined the quantities $p = k_p + k_q - k_r$,
 $k = k_r$ og $q = k_p - k_r$.

Reference energy

Let us now compute the expectation value of the reference energy using the expressions for the kinetic energy operator and the interaction. We need to compute

$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \langle \Phi_0 | \hat{T} | \Phi_0 \rangle + \langle \Phi_0 | \hat{V} | \Phi_0 \rangle$, where $|\Phi_0\rangle$ is our reference Slater determinant, constructed from filling all single-particle states up to the Fermi level. Let us start with the kinetic energy first

$$\langle \Phi_0 | \hat{T} | \Phi_0 \rangle = \langle \Phi_0 | \left(\sum_{\mathbf{p}\sigma} \frac{\hbar^2 p^2}{2m} a_{\mathbf{p}\sigma}^\dagger a_{\mathbf{p}\sigma} \right) | \Phi_0 \rangle = \sum_{\mathbf{p}\sigma} \frac{\hbar^2 p^2}{2m} \langle \Phi_0 | a_{\mathbf{p}\sigma}^\dagger a_{\mathbf{p}\sigma} | \Phi_0 \rangle.$$

Kinetic energy

From the possible contractions using Wick's theorem, it is straightforward to convince oneself that the expression for the kinetic energy becomes

$$\langle \Phi_0 | \hat{T} | \Phi_0 \rangle = \sum_{i \leq F} \frac{\hbar^2 k_i^2}{m} = \frac{V}{(2\pi)^3} \frac{\hbar^2}{m} \int_0^{k_F} k^2 dk.$$

The sum of the spin degrees of freedom results in a factor of two only if we deal with identical spin 1/2 fermions. Changing to spherical coordinates, the integral over the momenta k results in the final expression

$$\langle \Phi_0 | \hat{T} | \Phi_0 \rangle = \frac{V}{(2\pi)^3} \left(4\pi \int_0^{k_F} k^4 dk \right) = \frac{4\pi V}{(2\pi)^3} \frac{1}{5} k_F^5 = \frac{4\pi V}{5(2\pi)^3} k_F^5 = \frac{\hbar^2 V}{10\pi^2 m}$$

Density of states

The density of states in momentum space is given by $2V/(2\pi)^3$, where we have included the degeneracy due to the spin degrees of freedom. The volume is given by $4\pi k_F^3/3$, and the number of particles becomes

$$N = \frac{2V}{(2\pi)^3} \frac{4}{3}\pi k_F^3 = \frac{V}{3\pi^2} k_F^3 \quad \Rightarrow \quad k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}.$$

This gives us

$$\langle \Phi_0 | \hat{T} | \Phi_0 \rangle = \frac{\hbar^2 V}{10\pi^2 m} \left(\frac{3\pi^2 N}{V} \right)^{5/3} = \frac{\hbar^2 (3\pi^2)^{5/3} N}{10\pi^2 m} \rho^{2/3}, \quad (3)$$

Potential energy

We are now ready to calculate the expectation value of the potential energy

$$\begin{aligned}\langle \Phi_0 | \hat{V} | \Phi_0 \rangle &= \langle \Phi_0 | \left(\frac{1}{2V} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} \left[\int v(r) \exp -i(\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \right] a_{\mathbf{k}+\mathbf{q},\sigma}^\dagger a_{\mathbf{p}-\mathbf{q},\sigma'}^\dagger a_{\mathbf{p}\sigma'} a_{\mathbf{k}\sigma} \right) | \Phi_0 \rangle \\ &= \frac{1}{2V} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} \left[\int v(r) \exp -i(\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \right] \langle \Phi_0 | a_{\mathbf{k}+\mathbf{q},\sigma}^\dagger a_{\mathbf{p}-\mathbf{q},\sigma'}^\dagger a_{\mathbf{p}\sigma'} a_{\mathbf{k}\sigma} | \Phi_0 \rangle\end{aligned}$$

Non-zero term

The only contractions which result in non-zero results are those that involve states below the Fermi level, that is $k \leq k_F$, $p \leq k_F$, $|p - q| < k_F$ and $|k + q| \leq k_F$. Due to momentum conservation we must also have $k + q = p$, $p - q = k$ and $\sigma = \sigma'$ or $k + q = k$ and $p - q = p$. Summarizing, we must have

$$k + q = p \quad \text{and} \quad \sigma = \sigma', \quad \text{or} \quad q = 0.$$

Direct and exchange terms

We obtain then

$$\langle \Phi_0 | \hat{V} | \Phi_0 \rangle = \frac{1}{2V} \left(\sum_{\sigma\sigma'} \sum_{\mathbf{q}\mathbf{p} \leq F} \left[\int v(r) dr \right] - \sum_{\sigma} \sum_{\mathbf{q}\mathbf{p} \leq F} \left[\int v(r) \exp -i(\mathbf{q} \cdot \mathbf{r}) \right] \right)$$

The first term is the so-called direct term while the second term is the exchange term.

Potential energy

We can rewrite this equation as (and this applies to any potential which depends only on the relative distance between particles)

$$\langle \Phi_0 | \hat{V} | \Phi_0 \rangle = \frac{1}{2V} \left(N^2 \left[\int v(r) dr \right] - N \sum_{\mathbf{q}} \left[\int v(r) \exp -i(\mathbf{q} \cdot \mathbf{r}) dr \right] \right), \quad (4)$$

where we have used the fact that a sum like $\sum_{\sigma} \sum_{\mathbf{k}}$ equals the number of particles. Using the fact that the density is given by $\rho = N/V$, with V being our volume, we can rewrite the last equation as

$$\langle \Phi_0 | \hat{V} | \Phi_0 \rangle = \frac{1}{2} \left(\rho N \left[\int v(r) dr \right] - \rho \sum_{\mathbf{q}} \left[\int v(r) \exp -i(\mathbf{q} \cdot \mathbf{r}) dr \right] \right).$$

Interaction part

For the electron gas the interaction part of the Hamiltonian operator is given by

$$\hat{H}_I = \hat{H}_{el} + \hat{H}_b + \hat{H}_{el-b},$$

with the electronic part

$$\hat{H}_{el} = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{e^2}{2} \sum_{i \neq j} \frac{e^{-\mu|r_i-r_j|}}{|r_i-r_j|},$$

where we have introduced an explicit convergence factor (the limit $\mu \rightarrow 0$ is performed after having calculated the various integrals).

Positive background

Correspondingly, we have

$$\hat{H}_b = \frac{e^2}{2} \int \int dr dr' \frac{n(r)n(r')e^{-\mu|r-r'|}}{|r-r'|},$$

which is the energy contribution from the positive background charge with density $n(r) = N/V$. Finally,

$$\hat{H}_{el-b} = -\frac{e^2}{2} \sum_{i=1}^N \int dr \frac{n(r)e^{-\mu|r-x_i|}}{|r-x_i|},$$

is the interaction between the electrons and the positive background.

Positive charge contribution

We can show that

$$\hat{H}_b = \frac{e^2}{2} \frac{N^2}{V} \frac{4\pi}{\mu^2},$$

and

$$\hat{H}_{el-b} = -e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}.$$

Thermodynamic limit

For the electron gas and a Coulomb interaction, these two terms are cancelled (in the thermodynamic limit) by the contribution from the direct term arising from the repulsive electron-electron interaction. What remains then when computing the reference energy is only the kinetic energy contribution and the contribution from the exchange term. For other interactions, like nuclear forces with a short range part and no infinite range, we need to compute both the direct term and the exchange term.

We can show that the final Hamiltonian can be written as

$$H = H_0 + H_I,$$

with

$$H_0 = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma},$$

and

$$H_I = \frac{e^2}{2V} \sum_{\sigma_1 \sigma_2} \sum_{\mathbf{q} \neq 0, \mathbf{k}, \mathbf{p}} \frac{4\pi}{q^2} a_{\mathbf{k}+\mathbf{q}, \sigma_1}^\dagger a_{\mathbf{p}-\mathbf{q}, \sigma_2}^\dagger a_{\mathbf{p}\sigma_2} a_{\mathbf{k}\sigma_1}.$$

Ground state energy

Calculate $E_0/N = \langle \Phi_0 | H | \Phi_0 \rangle / N$ for this system to first order in the interaction. Show that, by using

$$\rho = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_0^3},$$

with $\rho = N/V$, r_0 being the radius of a sphere representing the volume an electron occupies and the Bohr radius $a_0 = \hbar^2/e^2m$, that the energy per electron can be written as

$$E_0/N = \frac{e^2}{2a_0} \left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} \right].$$

Here we have defined $r_s = r_0/a_0$ to be a dimensionless quantity.

Plot the energy as function of r_s . Why is this system stable?
Calculate thermodynamical quantities like the pressure, given by

$$P = - \left(\frac{\partial E}{\partial V} \right)_N,$$

and the bulk modulus

$$B = -V \left(\frac{\partial P}{\partial V} \right)_N,$$

and comment your results.

Density functional theory

Hohenberg and Kohn proved that the total energy of a system including that of the many-body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy.

Functional of density

The electronic energy E is said to be a functional of the electronic density, $E[\rho]$, in the sense that for a given function $\rho(r)$, there is a single corresponding energy. The Hohenberg-Kohn theorems (two) confirms that such a functional exists, but does not tell us the form of the functional.

Density functional theory has turned out to be a resounding success. A large majority of crystalline materials, many molecules and molecular structures have been explained using DFT. Walter Kohn, involved in both the Hohenberg-Kohn theory and development of the Kohn-Sham equations, received the Nobel Prize in Chemistry for DFT and computational chemistry in 1998. DFT is used in a broad spectrum of disciplines, including quantum chemistry, materials science, condensed matter physics and low-energy nuclear physics

The many-particle equation

Any material on earth, whether in crystals, amorphous solids, molecules or yourself, consists of nothing else than a bunch of atoms, ions and electrons bound together by electric forces. All these possible forms of matter can be explained by virtue of one simple equation: the many-particle Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \Phi(\mathbf{r}; t) = \left(- \sum_i^N \frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial \mathbf{r}_i^2} + \sum_{i < j}^N \frac{e^2 Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Phi(\mathbf{r}; t). \quad (5)$$

Here $\Phi(\mathbf{r}; t)$ is the many-body wavefunction for N particles, where each particle has its own mass m_i , charge Z_i and position \mathbf{r}_i . The only interaction is the Coulomb interaction e^2/r .

Born-Oppenheimer approximation

In atomic and molecular physics, materials science and quantum chemistry, the Born-Oppenheimer approximation arises from the physical problem we want to study: the ground state of a collection of interacting ions and electrons. Because even the lightest ion is more than a thousand times heavier than an electron, we approximate our Hamiltonian to not include the dynamics of the ions all-together. This is known as the **Born-Oppenheimer** approximation.

Time-independent equation

We then write the time-independent Schrödinger equation for a collection of N electrons subject to the electric potential created by the fixed ions, labeled $v_{\text{ext}}(\mathbf{r})$,

$$\left(\sum_i^N \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + v_{\text{ext}}(\mathbf{r}_i) \right) + \sum_{i < j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}) = E_0 \Psi(\mathbf{r}),$$

where \mathbf{r}_i are the positions of the electrons.

We can replace the explicit Coulomb repulsion with a generic two-body interaction

$$\sum_i^N \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + v_{\text{ext}}(\mathbf{r}_i) \right) + \sum_{i < j}^N v(r_{ij}) (= E_0 \Psi(\mathbf{r})),$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

Potential term

The potential $v_{\text{ext}}(\mathbf{r}_i)$ is created by the charged ions,

$$v_{\text{ext}}(\mathbf{r}_i) = - \sum_j \frac{e^2 Z_j}{|\mathbf{r}_i - \mathbf{R}_j|}$$

where \mathbf{R} is the (static) positions of the ions and Z_j their charge.

The one-body density

The one-body reduced density matrix of a many-body system at zero temperature gives direct access to many observables, such as the charge density, kinetic energy and occupation numbers. In a coordinate representation it is defined as the expectation value of the number operator

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i),$$

resulting in

$$n(\mathbf{r}) = \frac{\langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$

Here Ψ can be any state. In the equations that follow we assume it has been normalized properly.

One-body density

The one-body or just electronic density here, is thus obtained by integrating out all electron degrees of freedom except one, that is (setting $\mathbf{r} = \mathbf{r}_1$)

$$n(\mathbf{r}) = n(\mathbf{r}_1) = \int d^3\mathbf{r}_2 \cdots d^3\mathbf{r}_N |\Psi(\mathbf{r}_1 \cdots \mathbf{r}_N)|^2.$$

If Ψ is a single reference Slater determinant defined in terms of the single-particle functions ψ_i , then we have

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2.$$

More general definitions

In an N -particle quantum system with wavefunction $\Psi(x_1, \dots, x_N)$, the one-body reduced density matrix $\rho^{(1)}$ is obtained by tracing out (integrating over) $N - 1$ particles. It is defined as

$$\rho^{(1)}(x'; x) = N \int dx_2, dx_3 \cdots dx_N, \Psi^*(x_2, \dots, x_N, x'), \Psi(x_2, \dots, x_N, x).$$

Here x denotes the combined spatial and spin coordinates of a single particle.

What does the one-body density represents

Intuitively, $\rho^{(1)}(x', x)$ gives the amplitude for a particle at x to be found at x' . Its diagonal

$$n(x) = \rho^{(1)}(x, x)$$

is the one-body density (the probability density of finding a particle at x). The one-body density matrix is hermitian, and for fermions it is often normalized such that

$$\int n(x) dx = N.$$

Two-body density matrix in many-fermion systems

Two-body density matrix:

$$\rho^{(2)}(x_1, x_2, y_1, y_2) = \frac{N(N-1)}{2} \int dx_3 \cdots dx_N, \Psi^*(x_3, \dots, x_N, y_1, y_2), \Psi(x_3, \dots, x_N, x_1, x_2)$$

This two-body reduced density matrix is a function of two coordinate pairs (x_1, x_2) and (y_1, y_2) . Its diagonal part

$$\rho^{(2)}(x_1, x_2) \equiv \rho^{(2)}(x_1, x_2, x_1, x_2)$$

gives the joint probability density of finding one particle at x_1 and another at x_2 .

The factor $N(N-1)/2$ ensures proper normalization (since there are $N(N-1)/2$ distinct pairs).

In other words

In words, $\rho^{(2)}(x_1, x_2)$ is essentially the two-particle distribution function. It encodes two-body correlations and contains all information needed to compute expectation values of any two-particle operators. (For example, the expectation of an interaction $\sum_{i < j} V(x_i, x_j)$ can be obtained from $\rho^{(2)}$.)

Antisymmetry and the Pauli principle in fermionic systems

Fermions (like electrons) have wavefunctions that are antisymmetric under exchange of any two particles. Mathematically,

$$\Psi(\dots, x_i, \dots, x_j, \dots) = -\Psi(\dots, x_j, \dots, x_i, \dots),$$

for $i \neq j$.

This antisymmetry has important consequences for the density matrices: it enforces the Pauli exclusion principle, which forbids two identical fermions from occupying the same quantum state. In particular, if x_1 and x_2 represent the same single-particle state (including spin), then $\Psi(\dots, x_1, x_2, \dots) = 0$, implying that the two-body density $\rho^{(2)}(x_1, x_2)$ vanishes when $x_1 = x_2$ (no probability for two fermions to be at the same point with the same spin).

More on the antisymmetry

More generally, the antisymmetry imposes that the two-body density matrix changes sign upon exchanging the two particles' coordinates:

$$\rho^{(2)}(x_1, x_2; y_1, y_2) = -\rho^{(2)}(x_2, x_1; y_1, y_2),$$

(and similarly for exchanging $y_1 \leftrightarrow y_2$ in the bra indices).

This property leads to exchange effects in any fermionic two-body quantity. For example, the one-body density matrix of a fermionic system cannot have an eigenvalue larger than 1, reflecting the fact that each single-particle state can be occupied by at most one fermion (for spin- $\frac{1}{2}$ particles, one per spin state). In fact, for a single Slater determinant state, $\rho^{(1)}$ is a projector onto the subspace of occupied orbitals, with eigenvalues 1 or 0 only.

Identical fermions

Antisymmetry also means that identical fermions avoid each other in phase space beyond just classical repulsion – even non-interacting fermions exhibit an effective repulsion due to the Pauli principle. This is evident in the pair distribution: for two fermions with the same spin, the probability of finding them at the same location (or very close) is suppressed, whereas for opposite-spin fermions the Pauli exclusion does not act (they can occupy the same spatial position since their spin state is different) . In a single-determinant state, electrons of opposite spin are uncorrelated in the absence of interactions, while same-spin electrons show a reduced two-body density at short distances due to antisymmetry . These effects must be reflected in the two-body density matrix.

Factorization in the non-interacting (Slater determinant) case

A Slater determinant is a many-fermion wavefunction that is a single antisymmetrized product of one-particle orbitals. It represents a system of N non-interacting (or mean-field) fermions occupying N orthonormal spin-orbitals. For such a state, the N -body wavefunction factorizes in terms of single-particle orbitals except for the overall antisymmetrization. Importantly, for a Slater determinant, the two-body reduced density matrix is completely determined by the one-body density matrix. In other words, there are no two-particle correlations beyond the statistical (exchange) effects, so $\rho^{(2)}$ can be expressed in terms of $\rho^{(1)}$ alone. The explicit form is obtained by applying the Slater determinant expansion or using Wick's theorem for fermion creation/annihilation operators. The result is

$$\rho^{(2)}(x_1, x_2; y_1, y_2) = \rho^{(1)}(x_1; y_1) \rho^{(1)}(x_2; y_2) - \rho^{(1)}(x_1; y_2) \rho^{(1)}(x_2; y_1).$$

Factorization of two-body density matrices

This is the factorization of the two-body density matrix in a single-determinant (Hartree–Fock) state, often written symbolically as $\rho^{(2)} = \rho^{(1)} \otimes \rho^{(1)} - \rho^{(1)} \wedge \rho^{(1)}$ (the second term representing the exchange antisymmetrization). The above expression (sometimes called the Hartree–Fock approximation for $\rho^{(2)}$) is in fact exact for any Slater determinant state. Each term has a clear meaning:

$$\rho^{(1)}(x_1; y_1)\rho^{(1)}(x_2; y_2)$$

is the naive product of one-body densities (as if the particles were independent), while

$$\rho^{(1)}(x_1; y_2)\rho^{(1)}(x_2; y_1)$$

is the exchange term that subtracts out the contribution from exchanging two identical fermions. This exchange term is essential to satisfy the antisymmetry of the wavefunction.

The diagonal term

Taking the diagonal $y_1 = x_1$ and $y_2 = x_2$ in the above formula yields the factorization for the two-body density (pair density) in a Slater determinant:

$$\rho^{(2)}(x_1, x_2) = \rho^{(1)}(x_1; x_1) \rho^{(1)}(x_2; x_2) - |\rho^{(1)}(x_1; x_2)|^2.$$

In this form, $\rho^{(1)}(x; x) = n(x)$ is the ordinary one-body density at x , so the first term is $n(x_1)n(x_2)$ (the product of densities), and the second term subtracts the overlap probability $|\rho^{(1)}(x_1; x_2)|^2$. For a Slater determinant, $\rho^{(1)}(x_1; x_2) = \sum_{i \in \text{occ}} \phi_i^*(x_2) \phi_i(x_1)$ is the projector onto the occupied orbitals, so $|\rho^{(1)}(x_1; x_2)|^2$ acts as an exchange correction ensuring, for example, that if $x_1 = x_2$ (same position and spin), then

$\rho^{(2)}(x_1, x_2) = n(x_1)n(x_1) - |\rho^{(1)}(x_1; x_1)|^2 = n(x_1)^2 - n(x_1)^2 = 0$, consistent with Pauli exclusion. Thus, in a non-interacting fermion system (Hartree–Fock state), the two-body density almost factorizes as a product of one-body densities, except for the crucial antisymmetric exchange term.

Exchange terms and correlation corrections

The exchange term

$$-\rho^{(1)}(x_1; y_2)\rho^{(1)}(x_2; y_1),$$

in the Slater determinant formula is a direct consequence of Fermi–Dirac statistics. It does not appear for distinguishable particles or bosons in a product state (where $\rho^{(2)}$ would simply factorize as $\rho^{(1)}\rho^{(1)}$). In a fermionic system, this term ensures that $\rho^{(2)}$ obeys the required antisymmetry and exclusion principle. One immediate effect is the reduction of $\rho^{(2)}(x_1, x_2)$ below the uncorrelated product $n(x_1)n(x_2)$ when x_1 and x_2 are **close** or identical – this reduction for same-spin fermions is the exchange hole mentioned earlier. In the case of a single Slater determinant (the non-interacting or mean-field case), exchange is the only source of two-particle correlation, and it is fully accounted for by the one-body density matrix. Indeed, for a Slater determinant, the equation for the two-body density is exact and no additional terms are needed.

Summarizing densities

In summary, the two-body density matrix can be written as a product of one-body density matrices only under very restricted conditions: essentially when the system's wavefunction is a single Slater determinant (or an uncorrelated product state). In the idealized Hartree product (fully factorized wavefunction) one would have $\rho^{(2)}(x_1, x_2) = n(x_1)n(x_2)$, but a Hartree product is not antisymmetric and thus not a valid fermionic state. The physically allowed closest scenario is a single Slater determinant, in which $\rho^{(2)}$ takes the Hartree–Fock form above – a quasi-factorization that includes the $-\rho^{(1)}(x_1; y_2)\rho^{(1)}(x_2; y_1)$ exchange correction enforcing antisymmetry. Beyond that, for real interacting fermion systems, two-body density matrices generally cannot be exactly factorized into one-body pieces; additional two-particle exchange and correlation terms must be included to accurately describe the physics. Such terms ensure that both the Pauli principle and interaction-induced correlations are respected in $\rho^{(2)}$.

Hohenberg-Kohn theory

Assume we found a solution for our Hamiltonian of interest with ground state energy E_0 and a certain electronic density $n(\mathbf{r})$. The strength of the Coulomb interaction and the mass of an electron are constants of nature, so the only input that can possibly influence the electronic density $n(\mathbf{r})$ and the energy E_0 of our ground state is our choice of potential $v_{\text{ext}}(\mathbf{r})$. In other words, the ground state energy is a *functional* of the input potential,

$$E_0[v_{\text{ext}}(\mathbf{r})] = \mathcal{F}_E[v_{\text{ext}}(\mathbf{r})].$$

We have dropped the spin degrees of freedom here.

Energy functional

A functional is nothing else than a function whose input is another function; in this case the functional \mathcal{F} takes as input the electric potential generated by the ions and outputs the ground state energy based on the Born-Oppenheimer approximation.

At first this result seems counterintuitive. After all, the ground state energy clearly contains the kinetic energy T , the interaction energy U and the potential energy. Only the latter term explicitly depends on the potential. We can thus write the ground state energy in terms of a separate functional for the kinetic and interaction energy, and the potential energy

How to find the functional

Knowing this functional, for any given potential $V(\mathbf{r})$ we minimize the right hand side by checking all possible electronic density distributions.

There are only two minor problems. We don't know what this functional looks like. And even if we did, we don't know how to find the right electronic density.

Approximating the functional

The unknown functional $\mathcal{F}[n(\mathbf{r})]$ should describe the kinetic and interaction energy of a system described by for example the Born-Oppenheimer approximation. Even though we cannot find its exact shape, we can look at its shape in some limiting cases that we can solve.

We know that a free homogeneous electron gas (HEG) with density n has a ground state energy of

$$E_0 = \frac{3\hbar^2 (3\pi^2)^{2/3}}{10m} n_0^{5/3}.$$

Using the results from the HEG

For a slowly varying electronic density, we can approximate the kinetic energy contribution to the full functional $\mathcal{F}[n(\mathbf{r})]$ as the energy evaluated at each point separately,

$$\mathcal{T}_0[n(\mathbf{r})] = \frac{3\hbar^2 (3\pi^2)^{2/3}}{10m} \int d^3\mathbf{r} (n(\mathbf{r}))^{5/3}.$$

Hartree term to the energy

We have also earlier derived that the simplest energy contribution from Coulomb interactions is given by the Hartree term

$$\mathcal{U}_{\text{H}}[n(\mathbf{r})] = \frac{e^2}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

Final functional

It is natural to write out the full functional as containing the homogeneous electron gas term and the Hartree term. The remaining terms, though still unknown, should be small. This unknown part is conventionally called the *exchange-correlation potential* $E_{xc}[n(\mathbf{r})]$. The full Hohenberg-Kohn functional, including the potential energy, is thus

$$\mathcal{E}_{\text{HK}}[n(\mathbf{r})] = \mathcal{T}_0[n(\mathbf{r})] + \int d^3\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + \mathcal{U}_{\text{H}}[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})].$$

Many-Electron Problem and Hohenberg–Kohn Theorems: Theorem I

For any many-electron system in an external potential

$$V_{\text{ext}}(\mathbf{r}),$$

the potential is uniquely determined (up to an additive constant) by the ground-state electron density

$$n(\mathbf{r}).$$

Equivalently, the mapping

$$V_{\text{ext}}(\mathbf{r}) \mapsto n(\mathbf{r}),$$

is one-to-one (for non-degenerate ground states) . This means no two different external potentials can yield the same ground-state density. As a corollary, the ground-state density $n(\mathbf{r})$ uniquely determines the full Hamiltonian (up to constant shift in energy) and thus all properties of the system .

Many-Electron Problem and Hohenberg–Kohn Theorems:

Theorem II

There exists a universal functional $F[n]$ such that for any N -electron density $n(\mathbf{r})$, the energy can be written as

$$E[n] = F[n] + \int d^3r V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}),$$

and the true ground-state density minimizes this energy functional. In other words,

$$F[n] = T[n] + V_{\text{int}}[n],$$

is a universal functional (the same for all systems, independent of V_{ext}), and for the correct ground-state density $n_0(\mathbf{r})$, $E[n_0]$ is the global minimum of $E[n]$. The minimum value equals the ground-state energy E_0 .

Many-Electron Problem and Hohenberg–Kohn Theorems: corollary

The functional $E[n]$ is sufficient to obtain the exact ground-state energy and density . Excited states, however, are not obtained from this ground-state functional and must be accessed by other means (e.g. time-dependent DFT or other methods).

Discussion: Consequences of HK Theorems

DFT exists in principle: the first theorem establishes that the ground-state density is as fundamental as the wavefunction – it encapsulates all the information needed to determine the system's Hamiltonian and thus all ground-state observables. This is a remarkable reduction: instead of a complicated wavefunction Ψ , we can work with $n(r)$.

Discussion: Consequences of HK Theorems

Energy as a functional of density: the second theorem guarantees an energy functional $E[n]$ exists. However, the theorems themselves do not provide an explicit form for

$$F[n] = T[n] + V_{\text{int}}[n].$$

They are existence theorems. The challenge of DFT (and much the what we do in many-body physics) is how to approximate $F[n]$ in practice, especially the many-body terms hidden in it.

Variational principle

Given the second theorem, one can variationally obtain the ground state: if we had the exact $E[n]$ functional, minimizing $E[n]$ with respect to $n(r)$ (subject to $\int n(r)d^3r = N$) yields the true ground-state density and energy. In formal terms,

$$\delta E[n] - \mu(\int n - N)/\delta n(r) = 0,$$

leads to a condition

$$\frac{\delta E[n]}{\delta n(r)} \Big|_{n=n_0} = \mu,$$

with a constant Fermi level μ for the ground state.

Proof of the first theorem, I

It is instructive to see why two different potentials cannot give the same density. Suppose

$$V_{\text{ext}}^{(1)}(r),$$

and

$$V_{\text{ext}}^{(2)}(r),$$

yield the same ground-state density $n(r)$ but different ground-state wavefunctions $\psi^{(1)}$ and $\psi^{(2)}$.

Proof of the first theorem, II

Let $E^{(1)}$ and $E^{(2)}$ be their ground-state energies. Without loss of generality, assume $E^{(1)} < E^{(2)}$.

Then, using $\Psi^{(2)}$ in Hamiltonian 1 gives

$$E^{(1)} < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle + \int [V_{\text{ext}}^{(1)}(r) - V_{\text{ext}}^{(2)}(r)] n(r) d^3r$$

Similarly, exchanging 1 with 2 leads to

$$E^{(2)} < E^{(1)} + \int [V_{\text{ext}}^{(2)} - V_{\text{ext}}^{(1)}] n(r) d^3r.$$

Proof of the first theorem, III

Adding these two inequalities yields

$$E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)},$$

a contradiction. Thus $V_{\text{ext}}^{(1)}$ and $V_{\text{ext}}^{(2)}$ cannot produce the same $n(r)$. This proves the uniqueness.

Not every arbitrary $n(r)$ is a valid ground-state density of some physical V_{ext} (this is the issue of v -representability). The theorems assume $n(r)$ comes from some ground state of a Hamiltonian.

Modern proofs (Levy–Lieb constrained search) circumvent some v -representability issues by considering minimization over all wavefunctions yielding a density n .

Proof of the first theorem, implications

The ground-state energy can be obtained in principle by minimizing $E[n]$. However, without an expression for $F[n]$, one cannot perform this minimization in practice. Enter the Kohn–Sham approach (to be discussed later) which provides a clever way to approximate $F[n]$ using orbitals.

Kohn-Sham equation

We replaced an intractable problem with the task of minimizing an unknown functional $\mathcal{F}[n(\mathbf{r})]$ over infinitely many possible electronic densities $n(\mathbf{r})$. In the previous section we already gave some first suggestions for the functional. But once we found it, how to find the right electronic density $n(\mathbf{r})$?

Because the correct density minimizes the functional, we can find the functional by setting it's derivative to zero,

$$\frac{\delta \mathcal{F}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = 0.$$

Kohn-Sham equations

Using the functional Eq(insert), we write out

$$\frac{\delta \mathcal{T}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' + \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = 0.$$

The equations

The idea of Kohn and Sham was to treat this as if it is a single-particle problem. The first term represents the kinetic energy, and the remaining terms form the Kohn-Sham potential

$$V_{\text{KS}}(\mathbf{r}) = V(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}.$$

The Kohn-Sham equation is the single-particle Schrödinger equation with the potential given by the last equation,

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V_{\text{KS}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}).$$

Numerical solution

The Kohn-Sham equations have to be solved numerically. As with our discussions of Hartree-Fock theory, this is tractable because the equations are just given by a set of coupled differential equation. The electronic density is obtained by occupying the N solutions $\psi_i(\mathbf{r})$ with the lowest energy,

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2.$$

Now the electronic density obtained this way can be used to calculate a new Kohn-Sham potential. We continue this iterative procedure until we reach convergence.