Week 42: Hartree-Fock theory and density functional theory

Morten Hjorth-Jensen[1]

Department of Physics and Center for Computing in Science Education, University of Oslo, Norway[1]

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Topics to be covered

1. Thursday:
   - The first lecture is about the finalization of the calculation of the ground state energy of the homogeneous electron gas in three dimensions
   - Start discussion of density functional theory
   - Discussions of first midterm
   - Video of lecture at https://youtu.be/VbLlyZYRnYg
   - Whiteboard notes at https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/HandwrittenNotes/2024/NotesOctober17.pdf
2. Friday:
   - Density functional theory
   - Discussions of first midterm
3. Lecture Material: These slides and handwritten notes
4. First midterm set at https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/Exercises/2024/FirstMidterm2024.pdf

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 $L \to \infty$ is to be taken after we have computed various expectation values)

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

where 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

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

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

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

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 $\langle \mathrm{k}_i \mathrm{k}_j | V | \mathrm{k}_m \mathrm{k}_n \rangle$.
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 explicitely the spin degrees of freedom as well

$$\hat{V} = \frac{1}{2} \sum_{\substack{\sigma_p\sigma_q \\ \sigma_r\sigma_s}} \sum_{\substack{\mathsf{k}_p\mathsf{k}_q \\ \mathsf{k}_r\mathsf{k}_s}} \langle \mathsf{k}_p\sigma_p, \mathsf{k}_q\sigma_2 | v | \mathsf{k}_r\sigma_3, \mathsf{k}_s\sigma_s \rangle a^\dagger_{\mathsf{k}_p\sigma_p} a^\dagger_{\mathsf{k}_q\sigma_q} a_{\mathsf{k}_s\sigma_s} a_{\mathsf{k}_r\sigma_r}. \quad (1)$$

Plane waves

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

$$\langle \mathrm{k}_p\sigma_p, \mathrm{k}_q\sigma_q|\hat{v}|\mathrm{k}_r\sigma_r, \mathrm{k}_s\sigma_s\rangle = \frac{1}{V^2}\delta_{\sigma_p\sigma_r}\delta_{\sigma_q\sigma_s}\int\int \exp -i(\mathrm{k}_p\cdot\mathrm{r}_p)\exp -i(\mathrm{k}_q\cdot$$

where we have used the orthogonality properties of the spin functions. We change now the variables of integration by defining $\mathrm{r} = \mathrm{r}_p - \mathrm{r}_q$, which gives $\mathrm{r}_p = \mathrm{r} + \mathrm{r}_q$ and $d^3\mathrm{r} = d^3\mathrm{r}_p$.

Integration limits

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

$$\begin{aligned}\langle \mathrm{k}_p\sigma_p, \mathrm{k}_q\sigma_q|\hat{v}|\mathrm{k}_r\sigma_r, \mathrm{k}_s\sigma_s\rangle &= \frac{1}{V^2}\delta_{\sigma_p\sigma_r}\delta_{\sigma_q\sigma_s}\int \exp i(\mathrm{k}_s-\mathrm{k}_q)\cdot \mathrm{r}_q \int v(r)\exp \\ &= \frac{1}{V^2}\delta_{\sigma_p\sigma_r}\delta_{\sigma_q\sigma_s}\int v(r)\exp i\left[(\mathrm{k}_r-\mathrm{k}_p)\cdot \mathrm{r}\right]\int \exp\end{aligned}$$

Recognizing integral

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

$$\langle \mathrm{k}_p\sigma_p, \mathrm{k}_q\sigma_q|\hat{v}|\mathrm{k}_r\sigma_r, \mathrm{k}_s\sigma_s\rangle = \frac{1}{V}\delta_{\sigma_p\sigma_r}\delta_{\sigma_q\sigma_s}\delta_{(\mathrm{k}_p+\mathrm{k}_q),(\mathrm{k}_r+\mathrm{k}_s)}\int v(r)\exp i\left[(\mathrm{k}_r -\right.$$

For this equation to be different from zero, we must have conservation of momenta, we need to satisfy $\mathrm{k}_p + \mathrm{k}_q = \mathrm{k}_r + \mathrm{k}_s$.

Conservation of momentum

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

$$\hat{V} = \frac{1}{2V} \sum_{\sigma\sigma'} \sum_{\mathrm{k}_p \mathrm{k}_q \mathrm{k}_r} \left[\int v(r) \exp i \left[(\mathrm{k}_r - \mathrm{k}_p) \cdot \mathrm{r} \right] d^3 r \right] a^{\dagger}_{\mathrm{k}_p \sigma} a^{\dagger}_{\mathrm{k}_q \sigma'} a_{\mathrm{k}_p + \mathrm{k}_q - \mathrm{k}_r, \sigma'} a_{\mathrm{k}}$$

which can be rewritten as

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

Some definitions

In the last equation we defined the quantities $\mathrm{p} = \mathrm{k}_p + \mathrm{k}_q - \mathrm{k}_r$, $\mathrm{k} = \mathrm{k}_r$ og $\mathrm{q} = \mathrm{k}_p - \mathrm{k}_r$.

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

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

Kinetic energy

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

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

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

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

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

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

Potential energy

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

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

$$= \frac{1}{2V} \sum_{\sigma\sigma'} \sum_{\mathrm{kpq}} \left[\int v(r) \exp -i(\mathrm{q} \cdot \mathrm{r}) d\mathrm{r} \right] \langle \Phi_0 | a^{\dagger}_{\mathrm{k+q},\sigma} a^{\dagger}_{\mathrm{p-q},\sigma'} a_{\mathrm{p}\sigma'} a_{\mathrm{p}}$$

Non-zero term

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

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

Direct and exchange terms

We obtain then

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

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)

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

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

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

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

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

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

Positive background

Correspondingly, we have

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

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

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

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

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

and

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

Ground state energy

Calculate $E_0/N = \langle \Phi_0 | H | \Phi_0 \rangle / N$ for 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 $a_0 = \hbar^2/e^2 m$, 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.

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,

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

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

Despite its apparent simplicity, the above equation is notoriously difficult to solve. This is where density functional theory (DFT) comes in. Using a set of reasonable physical approximations we can simplify the many-particle Schrödinger equation to something that we can actually solve numerically.

Born-Oppenheimer approximation

The first 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 will forget about 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,

$$\left(\sum_{i}^{N} \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \boldsymbol{r}_i^2} + V(\boldsymbol{r}_i) \right) + \sum_{i<j}^{N} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \right) \Psi(\boldsymbol{r}) = E_0 \Psi(\boldsymbol{r})$$

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

Potential term

The potential $V(\boldsymbol{r}_i)$ is created by the charged ions,

$$V(\boldsymbol{r}_i) = -\sum_j \frac{e^2 Z_j}{|\boldsymbol{r}_i - \boldsymbol{R}_j|}$$

where $\boldsymbol{R}$ is the (static) positions of the ions and Z_j their charge. Note that the above Hamiltonian, the left hand side of the last equation, contains three terms: the kinetic energy (T), the potential energy (V) and the interaction energy (U).

Electronic density

The electronic density is obtained by integrating out all electron degrees of freedom except one,

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

The total potential energy V is just given by the integral over the potential $V(\boldsymbol{r})$ times the density,

$$V = \int d^3\boldsymbol{r}\, V(\boldsymbol{r}) n(\boldsymbol{r}).$$

Hohenberg-Kohn theory

Assume we found a solution for the Hamiltonian from the Born-Oppenheimer approximation, with ground state energy E_0 and a certain electronic density $n(\boldsymbol{r})$. 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 $n(\boldsymbol{r})$ and the energy E_0 of our ground state is our choice of potential $V(\boldsymbol{r})$. In other words, the ground state energy is a *functional* of the input potential,

$$E_0[V(\boldsymbol{r})] = \mathcal{F}_E[V(\boldsymbol{r})]$$

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 thr Born-Oppenheimer approximation.
At first this results 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

$$E[n(\boldsymbol{r})] = \mathcal{F}'_E[V(\boldsymbol{r})] + \int d^3\boldsymbol{r}\, V(\boldsymbol{r}) n(\boldsymbol{r})$$

Conjugate varibales

Hohenberg and Kohn came to the elegant insight that the *potential* $V(\boldsymbol{r})$ *and electronic density* $n(\boldsymbol{r})$ *are conjugate variables*. Other conjugate variables you may know are for example pressure and volume in thermodynamics or momentum and position in classical physics. The fact that the potential $V(\boldsymbol{r})$ and the density $n(\boldsymbol{r})$ are conjugate means you can equally well describe any solution of the Hamiltonian problem using the potential or the density.

Legendre transform

Formally known as a Legendre transform (in the same way you go from the Hamiltonian to the Lagrangian formulation of classical mechanics), we can change the functional of the last equation to depend on the density $n(\boldsymbol{r})$ rather than the potential $V(\boldsymbol{r})$. This is the *Hohenberg-Kohn theorem*: there exists a **universal** functional of electronic density, $\mathcal{F}[n(\boldsymbol{r})]$, such that for the correct density $n(\boldsymbol{r})$ it provides the ground state energy of the Hamiltonian under study

$$E[n(\boldsymbol{r})] = \mathcal{F}[n(\boldsymbol{r})] + \int d^3\boldsymbol{r}\, V(\boldsymbol{r}) n(\boldsymbol{r}).$$

How to find the functional

Knowing this functional, for any given potential $V(\boldsymbol{r})$ 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 $\mathcal{F}[n(\boldsymbol{r})]$ 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

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

Using the results from the HEG

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

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

Hartree term to the energy

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

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

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* $E_{xc}[n(\boldsymbol{r})]$. The full Hohenberg-Kohn functional, including the potential energy, is thus

$$\mathcal{E}_{\mathrm{HK}}[n(\boldsymbol{r})] = \mathcal{T}_0[n(\boldsymbol{r})] + \int d^3\boldsymbol{r}\, V(r) n(\boldsymbol{r}) + \mathcal{U}_{\mathrm{H}}[n(\boldsymbol{r})] + E_{xc}[n(\boldsymbol{r})].$$

Kohn-Sham equation

We replaced an intractable problem with the task of minimizing an unknown functional $\mathcal{F}[n(\boldsymbol{r})]$ over infinitely many possible electronic densities $n(\boldsymbol{r})$. 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 $n(\boldsymbol{r})$?
Because the correct density minimizes the functional, we can find the functional by setting it's derivative to zero,

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

Kohn-Sham equations

Using the functional Eq(insert), we write out

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

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

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

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

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

Numerical solution

We solve these equations numerically, which is tractable because it is just a linear differential equation. The electronic density is obtained by occupying the N solutions $\psi_i(\boldsymbol{r})$ with the lowest energy,

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

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.

A final comment is in order: in the above derivation we completely ignored the spin of electrons. Of course, real electrons have spin so that you need that degree of freedom as well. This does not change anything fundamental about how to use the Kohn-Sham equation.

We have reached the end-goal: using the Born-Oppenheimer approximation, with an appropriate choice of functional, we use the Kohn-Sham equations to find the ground state energy and electronic density of a system of interacting electrons and ions.

This combination of approximations and techniques is called *density*