Sheet 4

November 6, 2025

Please hand in a pdf for exercise 1, 2, 3, including the plots for exercise 1, which is named *<firstname>_<lastname>_sheet_<number>*.

The deadline is Monday, Nov. 10th, 12:00 (noon). Please hand in your solution via moodle.

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1 Thomas-Fermi Theory

One noteworthy, if crude, predecessor to DFT is known as the Thomas-Fermi model. The assumption shared with DFT is that the electron density is the central variable upon which the formalism rests. However, where DFT is formally exact, and strives to treat both exchange and correlation effects, which arise from the discrete nature of the electrons, Thomas-Fermi theory assumes that the electrons are an infinitely divisible liquid.

Due to this, it ignores e.g. the exchange energy completely, and makes a simple approximation for the kinetic energy. On the last sheet we derived that the kinetic energy scales with density as $E_{kin} \propto n^{5/3}$. Thomas Fermi-Theory essentially assumes that the variation of the potential energy over a small volume is negligible, and therefore the kinetic energy can be approximated as that of the homogeneous electron gas locally

$$E_{kin}(\vec{r}) = \frac{3h^2}{10m_e}\left(\frac{3}{8\pi}\right)^{2/3} n^{5/3}(\vec{r}) = C_{kin} n^{5/3}(\vec{r}). \tag{1}$$

The potential energy is given by the Coulomb repulsion of the electrons and their attraction to the nuclei

$$V(\vec{r}) = n(\vec{r})\left(eV_{ext}(\vec{r}) + \frac{e^2}{2}\int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}\right). \tag{2}$$

The solution to this model is found by minimising the total energy $E_{tot} = \int d^3 E_{kin}(\vec{r}) + V(\vec{r})$, while keeping the total number of electrons constant. For a rotationally symmetric external potential $V(r) \propto \frac{1}{r}$, after changing units to remove all dependencies on physical constants, this results in the universal form of the Thomas-Fermi equation for $n(r) \propto \frac{\chi^{3/2}(r)}{r^{3/2}}$

$$\frac{d^2\chi(r)}{dr} = \frac{1}{\sqrt{r}}\chi^{3/2}(r). \tag{3}$$

1. Solve the Thomas-Fermi equation numerically. The first boundary condition is set as $\chi(0) = 1$, but the second has three options:

   a) $\chi(\infty) \longrightarrow 0$

   b) $\chi(x_0) = 0$ for finite x_0

   c) $\chi(\infty) > 0$.

   For the first case, you may choose a range of [0,5] to calculate the function on, and assume that $5 \approx \infty$, so $\chi(5) = 0$. Choose x_0 for the second case such that the qualitative difference to case 1 is visible. Choose a large finite value at $x = 5$ for third case, and explain why it should fulfil condition c). Note that, since χ is proportional to the charge density, negative values are not allowed.

   Create plots of $\chi(x)$ and $n(r) \propto \frac{\chi^{3/2}(r)}{r^{3/2}}$ (up to a prefactor) on the range $x \in [0, 5]$.

   2 points

2. The three options correspond to different possible ratios of the number of electrons N vs the total charge of the nucleus Z. Assign the three options below to the three options above, and justify your ideas using the plots generated previously.

   a) $\frac{N}{Z} < 1$

   b) $\frac{N}{Z} = 1$

   c) $\frac{N}{Z} > 1$

   1 point

3. Equation 3 is true for any number of electrons N, and the boundary conditions only affect the ratio $\frac{N}{Z}$. This means the total charge density will always have the same shape, regardless of number of electrons N. Explain why this is not a correct representation of the charge density in an atom.

   0.5 points

4. How do Hartree-Fock theory and DFT improve on the Thomas-Fermi model? Name at least one change for each, and the qualitative improvement in the description of real electrons they imply.

   0.5 points

2 Self-Interaction Error

As seen in the lecture, the Hartree term describes the interactions of one electron with the charge density that is due to all electrons. Since all electrons contribute to the density each electron „interacts with itself“ via the electron density, which is called self interaction. Some theories, e.g. DFT have a net interaction with the charge density even when only a single electron is present, but Hartree-Fock theory avoids this error.

Show that Hartree-Fock theory is free of self-interaction error. This is true if, in the case of a single electron, the Hartree-Fock equations simplify to the Schrödinger equation of a single electron.

3 points

3 Hohenberg-Kohn Theorem

In the lecture you showed the Hohenberg-Kohn Theorem. One important detail is that, for a system of non-interacting electrons which obey the Schrödinger equation eq. 4, two different external potentials will result in two different ground-state wave functions. Why is this the case?

$$\left(\frac{\nabla^2}{2} + V_{ext}(\vec{r})\right)\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{4}$$

3 points