Problem Set 2 "Foundations of DFT"

Problem 3 (Thomas-Fermi model)

For non-interacting electrons moving in the external potential $v(\mathbf{r}) = 0$ the single-particle orbitals are given by the plane waves

$$\varphi_{\mathbf{k}\sigma}(\mathbf{r}) = \frac{1}{\sqrt{\mathcal{V}}} \exp(i\mathbf{k}\cdot\mathbf{r}) \tag{1}$$

where $\mathcal{V}$ is the volume of the system ($\mathcal{V} \to \infty$).

a) Calculate the density of a Slater determinant where all plane waves with $|\mathbf{k}| \leq k_F$ are occupied with a spin-up and a spin-down electron.

b) Calculate the non-interacting kinetic energy per unit volume $t_s(n)$ as function of the density.

c) For a system of electrons moving in an external potential $v_0(\mathbf{r})$ calculate the variational equation for the density which minimizes the approximate energy functional

$$E^{TF}[n] = T_s^{TF}[n] + \int \mathrm{d}^3r\; v_0(\mathbf{r})n(\mathbf{r}) + \frac{1}{2}\int \mathrm{d}^3r \int \mathrm{d}^3r'\; \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{2}$$

under the constraint that the density integrates to N electrons. Here

$$T_s^{TF}[n] = \int \mathrm{d}^3r\; t_s(n)\Big|_{n=n(\mathbf{r})} \tag{3}$$

is the Thomas-Fermi approximation for the non-interacting kinetic energy.

Problem 4 (Hartree-Fock equations)

Consider a system of N electrons described by the Hamiltonian

$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2} + v(\mathbf{r}_i)\right) + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{4}$$

The expectation value of this Hamiltonian with respect to a Slater determinant is the Hartree-Fock energy expression

$$\begin{aligned} E^{HF}[\{\varphi_{k\sigma}(\mathbf{r})\}] \;=\; & \sum_{\sigma=\uparrow,\downarrow}\sum_{k=1}^{N_\sigma} \int \mathrm{d}^3r\; \varphi_{k\sigma}^*(\mathbf{r})\left(-\frac{\nabla^2}{2}\right)\varphi_{k\sigma}(\mathbf{r}) + \int \mathrm{d}^3r\; v(\mathbf{r})n(\mathbf{r}) \\ & + \frac{1}{2}\int \mathrm{d}^3r \int \mathrm{d}^3r'\; \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{1}{2}\sum_{\sigma}\int \mathrm{d}^3r \int \mathrm{d}^3r'\; \frac{|\rho_\sigma(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \end{aligned} \tag{5}$$

with the single-particle density matrix

$$\rho_\sigma(\mathbf{r},\mathbf{r}') = \sum_{k=1}^{N_\sigma} \varphi^*_{k\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}') \tag{6}$$

and the density $n(\mathbf{r}) = \sum_\sigma \rho_\sigma(\mathbf{r},\mathbf{r})$.

Derive the Hartree-Fock equations for the orbitals minimizing E^{HF} by calculating

$$\frac{\delta}{\delta\varphi^*_{j\sigma}(\mathbf{r})}\left[E^{HF}[\{\varphi_{k\sigma'}(\mathbf{r})\}] - \sum_{\sigma'}\sum_{k=1}^{N_{\sigma'}} \varepsilon_{k\sigma'}\left(\int \mathrm{d}^3r'\ |\varphi_{k\sigma'}(\mathbf{r}')|^2 - 1\right)\right] = 0 \tag{7}$$

where the last term incorporates the constraint in the minimization that the single-particle orbitals should be normalized.

Hint: When calculating the functional derivative you can take $\varphi^*_{j\sigma}(\mathbf{r})$ and $\varphi_{j\sigma}(\mathbf{r})$ as independent variables.