Introduction to Density Functional Theory (SS 2008)

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Problem set No. 3

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1. The homogeneous electron gas.

A "homogeneous electron gas" (HEG) is a system of electrons with homogeneous density, $\rho(\vec{r}) = \rho$. It extends over all space, containing an infinite number of electrons. In order to make calculations, however, one considers a HEG with N electrons contained in a cubic box of side L: $0 \leq x, y, z \leq L$. The calculations provide the exact results in the limit $L \to \infty$.

For symmetry reasons, the external potential v must be a constant, which we can arbitrarily set to zero. If we assume non-interacting electrons, we can find the single orbitals by solving Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\varphi(\vec{r}) = \varepsilon\varphi(\vec{r})\,. \tag{1}$$

(a) Prove that, if we assume periodic boundary conditions, the solutions are plane waves:

$$\varphi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}}e^{i\vec{k}\vec{r}}\,, \tag{2}$$

$$\vec{k} = \frac{2\pi}{L}(n_x\hat{x} + n_y\hat{y} + n_z\hat{z})\,, \tag{3}$$

$$\varepsilon_k = \frac{\hbar^2}{2m}k^2 \tag{4}$$

where $\Omega = L^3$ is the volume of the box, and n_x, n_y, n_z are integer numbers (1 point).

(b) In order to obtain the ground state of the system, we must fill the $N/2$ lowest energy orbitals (two electrons on each of them, one for each spin value). The last orbital to get filled will have the maximum energy, the so-called "Fermi energy": $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$. Prove that the density $\rho = \frac{N}{\Omega}$ and k_F are related by:

$$\rho = \frac{k_F^3}{3\pi^2}\,. \tag{5}$$

(1 point)
Hint: You must find all $\vec{k}$ vectors such that $k < k_F$, and assign two electrons to each. This can be written as:

$$N = 2 \sum_{\substack{\vec{k} \\ |\vec{k}|<k_F}} 1 \,. \tag{6}$$

In order to make sums of the type $\sum_{|\vec{k}|} a(\vec{k})$, it is useful to approximate them by an integral (which corresponds to taking the limit $L \to \infty$ mentioned above), in the following way:

$$\sum_{\substack{\vec{k} \\ |\vec{k}|<k_F}} a(\vec{k}) = \frac{\Omega}{(2\pi)^3} \int_{|\vec{k}|<k_F} d^3k \; a(\vec{k}) \,. \tag{7}$$

2. Kinetic energy of the homogeneous electron gas

Prove that the kinetic energy density (density per volume unit) of the homogeneous electron gas,

$$T = \frac{2}{\Omega} \sum_{\substack{\vec{k} \\ |\vec{k}|<k_F}} \int_\Omega \mathrm{d}^3r \varphi^*_{\vec{k}}(\vec{r})(-\frac{1}{2}\nabla^2)\varphi_{\vec{k}}(\vec{r}) \,. \tag{8}$$

is given by:

$$T[\rho] = \frac{\hbar^2}{m}\frac{1}{10\pi^2}(3\pi^2)^{(5/3)}\rho^{(5/3)} \,. \tag{9}$$

(3 points).

3. Exchange energy of the homogeneous electron gas

The exchange energy of a spin-compensated system (2 electrons per orbital) system of N electrons distributed in a set of orbitals $\{\varphi_a\}_a$ is given by:

$$E_x = -\frac{1}{2}\sum_a \sum_{a'} \int \mathrm{d}^3r \int \mathrm{d}^3r' \frac{\varphi^*_a(\vec{r})\varphi^*_{a'}(\vec{r}')\varphi_a(\vec{r}')\varphi_{a'}(\vec{r})}{|\vec{r}-\vec{r}'|} \tag{10}$$

(a) Prove that

$$E_x = -\frac{1}{2}\int \mathrm{d}^3r \int \mathrm{d}^3u \frac{|\rho^{(1)}(\vec{r},\vec{r}+\vec{u})|^2}{|\vec{u}|} \,, \tag{11}$$

where the "one-body density matrix" is defined as:

$$\rho^{(1)}(\vec{r}', \vec{r}) = \sum_a \varphi_a^*(\vec{r})\varphi_a(\vec{r}') \,. \tag{12}$$

(1 point)

(b) Using the previous expression for the exchange energy in terms of the density matrix, prove that the exchange energy density of the HEG is given by:

$$E_x[\rho] = -\frac{3}{4\pi}(3\pi^2)^{(1/3)}\rho^{(4/3)} \tag{13}$$

(4 points)

Hint:

$$\int_0^\infty \mathrm{d}\theta \frac{(\sin(\theta) - \theta\cos(\theta))^2}{\theta^5} = \frac{1}{4} \,. \tag{14}$$