Uniform Electron Gas

Exchange and Correlation

Hamiltonian for interacting electrons in a solid can be written in second quantized for as

$$\hat{H}_e = \sum_{\nu,\lambda} \langle \nu | \hat{H}_1 | \lambda \rangle a_\nu^\dagger a_\lambda + \frac{1}{2} \sum_{\nu\lambda\alpha\beta} \langle \nu\ \lambda | \frac{e^2}{r_1 - r_2} | \alpha\ \beta \rangle\ a_\nu^\dagger a_\lambda^\dagger a_\beta a_\alpha \tag{1}$$

The electrons are free particles, which mutually interact by Coulomb's law e^2/r. There are N_e electron in a large volume v, with an average density $n_0 = N_e/v$. A positive charge of density n_0 is spread uniformly through the volume v. THe positive background maintains the overall charge neutrality of the system. The homogeneous electron gas is also called the *jellium model* of a solid.

One of the important quantity is the ground state energy per particle E_g, which can depend only on the particle density $E_g(n_0)$. The total energy of the N_e particle system is just $N_e E_g = E_T$, since surface effects are ignored.

The parameter r_s is universally used to describe the density of an electron gas,

$$\frac{4\pi n_0 a_0^3}{3} r_s^3 = 1 \tag{2}$$

where a_0 is the Bohr radius. In an electron gas with uniform density n_0, r_s is the radius in atomic units of the sphere which encloses one unit of electron charge. Thus r_s is small for a high-density electron gas and it is large for a low-density gas. Other properties of an electron gas bay be expressed in terms of this parameter. The density may be related to Fermi wave vector,

$$n_0 = 2 \int \frac{d^3p}{(2\pi)^3} n_p = \frac{1}{\pi^2} \int_0^{k_F} p^2 dp = \frac{k_F^3}{3\pi^2} \tag{3}$$

so that the Fermi wave vector and energy are related to r_s,

$$k_F a_0 = \left(3\pi^2 n_0\right)^{1/3} a_0 = \left(\frac{9\pi}{4}\right)^{1/3} \left(\frac{4\pi n_0 a_0^3}{3}\right)^{1/3} = \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} = \frac{1.9192}{r_s} \tag{4}$$

$$E_F = \frac{\hbar^2 k_F^2}{2m} = (k_F a_0)^2 \left(\frac{\hbar^2}{2ma_0^2}\right) = \frac{3.6832}{r_s^2} E_{ry}$$

where $E_{ry} = 13.60eV$ will be the standard unit of energy. Similarly, the plasma frequency is

$$\hbar\omega_p = \hbar \left(\frac{4\pi e^2 n_0}{m}\right)^{1/2} = \left(\frac{12}{r_s^3}\right)^{1/2} E_{ry} = \frac{3.4641}{r_s^{3/2}} E_{ry} \tag{5}$$

In the homogeneous electron gas, the average kinetic energy of the electrons is going to be proportional to $E_F \approx \langle K.E. \rangle \sim k_F^2$, which, by dimensional analysis, is inversely proportional to the square of the characteristic length of the system, whihc is r_s. Therefore $\langle K.E. \rangle \propto 1/r_s^2$. Similarly, dimensional analysis suggests that the average Coulomb energy per particle will be e^2 divided by the characteristic length, or $\langle P.E. \rangle \propto 1/r_s$. When the electron gas has sufficiently high density, which is small r_s, the kinetic energy term will be larger than the potential energy term. In this case, the electrons will behave as free particles, since the potential energy is a perturbation on the dominant kinetic energy. In the high-density limit, the free-particle picture is expected to be valid.

The potential energy terms cannot be found exactly, but the result can be expressed as a power series, - with logarithm terms - in parameter r_s. This series should be accurate at small values of r_s. A term-by-term derivation of this series is derived below.

Kinetic Energy The first energy term is the kinetic energy. For a single particle it is $\varepsilon_k = k^2/2m$. The contribution to the ground state energy is obtained by summing over all the particles in the ground state:

$$E_{T,KE} = \sum_{p\sigma} \varepsilon_p n_p = 2v \int \frac{d^3p}{(2\pi)^3} \frac{p^2}{2m} n_p = \left(\frac{N_e}{n_0}\right) \frac{1}{2\pi^2 m} \int_0^{k_F} p^4 dp$$

$$E_{T,KE} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} N_e = \frac{3}{5} E_F N_e \tag{6}$$

$$\frac{3}{5} E_F = \frac{2.2099}{r_s^2} E_{ry} \tag{7}$$

The average kinetic energy is $\frac{3}{5}E_F$, which is given in terms of r_s.

Hartree All the remaining terms in the energy come from the Coulomb interaction between the particles. This contribution has not been evaluated exactly. Instead, approximate expressions are obtained by a variety of means. The first term which occurs is the Coulomb interaction between the electrons and the uniform positive background, which is called the *Hartree interaction*. In the model of the homogeneous electron gas, the time-averaged electron density is uniform throughout the system, as is the positive background. These equal and opposite charge densities exactly cancel, so that the net system is charge neutral. The Hartree energy is zero. That is, this energy is given by the equation

$$N_e E_0 = \frac{e^2}{2} \int \frac{d^3r_1 d^3r_2}{|r_1 - r_2|} \left[\rho_e(r_1) - \rho_i(r_1)\right] \left[\rho_e(r_2) - \rho_i(r_2)\right] \tag{8}$$

but the ion and electron particle densities are $\rho_e = \rho_i = n_0$, and the contribution is zero.