

## Uniform Electron Gas

This chapter illustrates the idea that all properties of the homogeneous electron gas (HEG) can be calculated from electron density.

### Intuitive Representation of Density

Electron density  $n$  is a very physically meaningful quantity, but just to make it more intuitive (and even measurable!), let's define

$$r_s \equiv \left(\frac{3}{4\pi n}\right)^{1/3} \quad (1)$$

such that

$$\frac{4}{3}\pi r_s^3 = \frac{1}{n} = \frac{\Omega}{N_e} \quad (2)$$

Since  $n$  is uniform in HEG,  $r_s$  is a valid alternative representation of density.

### Electron Hamiltonian

Recall the electron Hamiltonian (first line of (3.1) on p52)

$$\mathcal{H}_e = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_i \sum_{j \neq i} k \frac{e^2}{r_{ij}} - \sum_{i,I} k \frac{Z_I e^2}{r_{iI}} \quad (3)$$

in atomic units

$$\mathcal{H}_e = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}} - \sum_{i,I} \frac{Z_I}{r_{iI}} \quad (4)$$

when both the electrons and the background ions are uniformly distributed, the last term (electron-ion interaction) can be approximated by density interaction

$$\mathcal{H}_e = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}} - \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n^2}{|\vec{r} - \vec{r}'|} \quad (5)$$

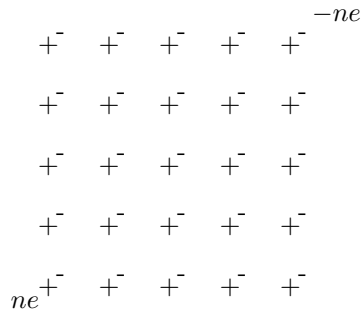


Figure 1: Uniform electrons and ions

now, if we use  $r_s$  as the length unit instead of Bohr  $a_o$

$$\begin{aligned}
\mathcal{H}_e &= -\frac{1}{2} \sum_i \left(\frac{a_o}{r_s}\right)^2 \tilde{\nabla}_i^2 + \frac{1}{2} \sum_i \sum_{j \neq i} \left(\frac{a_o}{r_s}\right) \frac{1}{\tilde{r}_{ij}} - \frac{1}{2} \left(\frac{a_o}{r_s}\right) \int d\vec{r} d\vec{r}' \frac{n^2}{|\vec{r} - \vec{r}'|} \\
&= \left(\frac{a_o}{r_s}\right)^2 \left[ -\frac{1}{2} \sum_i \tilde{\nabla}_i^2 + \frac{1}{2} \frac{r_s}{a_o} \left( \sum_i \sum_{j \neq i} \frac{1}{\tilde{r}_{ij}} - \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n^2}{|\vec{r} - \vec{r}'|} \right) \right] \\
&= \left(\frac{a_o}{r_s}\right)^2 \sum_i \left[ -\frac{1}{2} \tilde{\nabla}_i^2 + \frac{1}{2} \frac{r_s}{a_o} \left( \sum_{j \neq i} \frac{1}{\tilde{r}_{ij}} - \frac{1}{2} \frac{3}{2\pi} \int d\vec{r} \frac{n^2}{\tilde{r}} \right) \right] \quad (6)
\end{aligned}$$

We see that as we increase density (decrease  $r_s$ ), the total energy of HEG goes up (duh), but its behavior also changes due to a rescaling of the relative strengths of the kinetic and interaction terms.

### Non-interacting Limit

Without interaction, since the system is homogeneous each electron feels a background potential  $V_o$  and the Hamiltonian is simple

$$\mathcal{H}_e^{NI} = \hat{T} = -\frac{1}{2} \sum_i \nabla_i^2 + V_o \quad (7)$$

the eigenfunctions are plane waves

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k} \cdot \vec{r}} \quad (8)$$

and the eigenvalues are

$$\epsilon_k = \frac{1}{2} k^2 \quad (9)$$

For all  $N_e^\sigma$  electrons with the same spin  $\sigma$ , we can calculate the Fermi vector due to Pauli exclusion as

$$\begin{aligned}
\frac{4\pi}{3} k_F^\sigma{}^3 &= \frac{(2\pi)^3}{\Omega} N_e^\sigma = (2\pi)^3 n^\sigma \Rightarrow \\
k_F^\sigma &= (6\pi^2)^{1/3} n^{\sigma 1/3} \quad (10)
\end{aligned}$$

since each  $k$  state has size  $\frac{(2\pi)^3}{\Omega}$  in reciprocal space. The Fermi energy per electron  $E_{F_o}^\sigma = E_F^\sigma / N_e^\sigma$  is given by

$$E_{F_o}^\sigma = \frac{1}{2} k_F^\sigma{}^2 \quad (11)$$

and kinetic energy per electron

$$\begin{aligned}
T_o^\sigma &= \frac{1}{N_e^\sigma} \sum_k \epsilon_k \sim \left( \int_{\vec{0}}^{\vec{k}_F^\sigma} \frac{d\vec{k}}{(2\pi)^3/\Omega} \right)^{-1} \int_{\vec{0}}^{\vec{k}_F^\sigma} \frac{d\vec{k}}{(2\pi)^3/\Omega} \frac{1}{2} k^2 \\
&= \left( \frac{4\pi}{3} k_F^\sigma{}^3 \right)^{-1} \cdot \frac{4\pi}{5} \left( \frac{1}{2} k_F^\sigma{}^5 \right) = \frac{3}{5} E_{F_o}^\sigma \quad (12)
\end{aligned}$$

## Hartree-Fock Approximation

With the inclusion of coulomb and exchange interactions, the Hamiltonian

$$\mathcal{H}_e^{HF} = \hat{T} + \hat{V}_{ext} + \hat{V}_x \quad (13)$$

the eigenfunctions are still plane waves

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}} \quad (14)$$

but the eigenvalues are modified by matrix elements of the exchange operator

$$\epsilon_k = \frac{1}{2}k^2 + \frac{k_F}{\pi} f(x) \quad (15)$$

where  $x = k/k_F$  and Luttinger guarantees that  $k_F$  is still (10), further

$$f(x) = -\left(1 + \frac{1-x^2}{2x} \ln \left| \frac{1+x}{1-x} \right| \right) \quad (16)$$

Notice  $\lim_{x \rightarrow 0} f(x) = -2$  and  $\lim_{x \rightarrow 1} f(x) = -1$ , thus as  $k$  is varied from 0 to  $k_F$ ,  $\epsilon_k$ 's lowest reach is extended by  $2k_F/\pi$ , whereas its highest reach is reduced by  $k_F/\pi$ , resulting in a net broadening of allowed energy band width  $\Delta W = k_F/\pi$ . If we normalize (15) with the Fermi energy  $\epsilon_F = \frac{1}{2}k_F^2$ , we get

$$\eta(x) = \epsilon_k/\epsilon_F = x^2 + \frac{2}{\pi k_F} f(x) \quad (17)$$

If we further measure energy from the Fermi surface ( $\tilde{\eta}(1) = 0$ ), we need

$$\tilde{\eta}(x) = (x^2 - 1) + \frac{2}{\pi k_F} (f(x) + 1) \quad (18)$$

This "Normalized energy" is plotted in the book (Figure 5.2 Right).

## Exchange Energy

Recall the  $\frac{k_F}{\pi} f(x)$  contribution to energy comes from the exchange operator, therefore the exchange energy per electron

$$\epsilon_x^\sigma = \frac{1}{2} \left\langle \frac{k_F^\sigma}{\pi} f(x) \right\rangle = -\frac{3}{4\pi} k_F^\sigma = -\frac{3}{4} \left( \frac{6}{\pi} n^\sigma \right)^{1/3} \quad (19)$$

notice the factor 1/2 is to eliminate over-count and the average value of  $f(x)$  throughout the Fermi sphere

$$\langle f(x) \rangle = \left( \frac{4}{3} \pi k_F^3 \right)^{-1} \int_{\vec{0}}^{\vec{k}_F} d\vec{k} f(k) = -\frac{3}{2} \quad (20)$$

The average exchange energy per electron for both  $\uparrow$  and  $\downarrow$  electrons is

$$\begin{aligned} \epsilon_x = E_x/N &= \frac{N^\uparrow \epsilon_x^\uparrow + N^\downarrow \epsilon_x^\downarrow}{N} = \frac{n^\uparrow \epsilon_x^\uparrow + n^\downarrow \epsilon_x^\downarrow}{n} \\ &= -\frac{3}{4} \left( \frac{6}{\pi} \right)^{1/3} \cdot \frac{n^{\uparrow 4/3} + n^{\downarrow 4/3}}{n} \end{aligned} \quad (21)$$

If we define the degree of polarization to be  $\zeta = \frac{n^\uparrow - n^\downarrow}{n}$ , we can rewrite (21) as

$$\begin{aligned}\epsilon_x &= -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}\frac{1}{2^{4/3}}[(1+\zeta)^{4/3}+(1-\zeta)^{4/3}]n^{1/3} \\ &= An^{1/3}\cdot\frac{1}{2}[(1+\zeta)^{4/3}+(1-\zeta)^{4/3}]\end{aligned}\quad (22)$$

at the un-polarized and fully-polarized extremes

$$\begin{cases}\epsilon_x(n, 0) = An^{1/3} \\ \epsilon_x(n, 1) = An^{1/3}\cdot 2^{1/3}\end{cases}\quad (23)$$

for some inexplicable reason, we want to rewrite (22) as an interpolation

$$\epsilon_x(n, \zeta) = \epsilon_x(n, 0) + [\epsilon_x(n, 1) - \epsilon_x(n, 0)] \cdot \left\{ \frac{1}{2} \frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{1/3} - 1} \right\} \quad (24)$$

### Exchange Hole

The Fermi exchange hole can be calculated as (see (3.56) on p66)

$$\begin{aligned}g(\vec{x}; \vec{x}') &= 1 - \frac{|\rho_\sigma(\vec{x}, \vec{x}')|^2}{n(\vec{x})n(\vec{x}')} \Rightarrow \\ g_x^{\sigma, \sigma}(y) &= 1 - \left(\frac{\rho(y)}{n}\right)^2\end{aligned}\quad (25)$$

where  $y = k_F^\sigma r$  with  $r = |\vec{r} - \vec{r}'|$  being the separation between electrons and  $\rho(y)$  is the first order reduced density matrix for independent Fermions given by

$$\begin{aligned}\rho(r = |\vec{r} - \vec{r}'|) &= \int d\vec{k} \langle \vec{r} | \vec{k} \rangle f(\epsilon(k)) \langle \vec{k} | \vec{r}' \rangle \\ &= \frac{1}{(2\pi)^3} \int d\vec{k} f(\epsilon(k)) e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} \\ &= \frac{\beta}{(2\pi)^2} \frac{1}{r} \frac{d}{dr} \frac{1}{r} \frac{d}{dr} \int_{-\infty}^{\infty} dk \cos(kr) f'(\beta(\frac{1}{2}k^2 - \mu))\end{aligned}\quad (26)$$

where  $f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}$  is the Fermi-Dirac distribution and  $\langle \vec{r} | \vec{k} \rangle = \frac{1}{\sqrt{(2\pi)^3}} e^{i\vec{k}\cdot\vec{r}}$  are just plane waves. The last line was obtained using partial integration and this final form is REALLY revealing!

$$\rho(y) = \frac{k_F}{3\pi^2} \left[ 3 \frac{\sin(y) - y \cos(y)}{y^3} \right] = n^2 \left[ 3 \frac{\sin(y) - y \cos(y)}{y^3} \right] \quad (27)$$

Finally, plugging (27) into (25) we have

$$g_x^{\sigma, \sigma}(y) = 1 - \left[ 3 \frac{\sin(y) - y \cos(y)}{y^3} \right]^2 \quad (28)$$

### Correlation Energy

In general, it is impossible to determine the correlation energy analytically. Exact solutions are only available in certain limits. For un-polarized gas  $\zeta = 0$ , results are available for the high density ( $r_s \rightarrow 0$ ) and low density case ( $r_s \gg 1$ )

$$\epsilon_c(r_s, 0) \rightarrow \begin{cases} 0.311 \ln(r_s) - 0.048 + r_s(A \ln(r_s) + C) + \dots & r_s \rightarrow 0 \\ \frac{a_1}{r_s} + \frac{a_2}{r_s^{3/2}} + \frac{a_3}{r_s^2} + \dots & r_s \gg 1 \end{cases} \quad (29)$$

Some data are also available for fully polarized gas  $\epsilon_c(n, 1)$ . Thus Perdew-Zunger(PZ) boldly (and quite correctly) guessed that  $\epsilon_c$  interpolates in the same way that  $\epsilon_x$  does. They proposed

$$\epsilon_c(n, \zeta) = \epsilon_c(n, 0) + [\epsilon_c(n, 1) - \epsilon_c(n, 0)]f_x(\zeta) \quad (30)$$

where  $f_x(\zeta)$  is the same interpolation function at the end of (24).

### Correlation Hole

The total contribution from exchange and correlation can be expressed as an integral of exchange-correlation hole

$$\epsilon_{xc}(r_s) = \frac{1}{2n} e^2 \int d\vec{r} \frac{n_{xc}^{av}(r)}{r} \quad (31)$$

where  $n_{xc}^{av}(r)$  is the coupling-constant-averaged hole

$$n_{xc}^{av}(r) = \int_0^1 d\lambda n_{xc}^\lambda(r) \quad (32)$$

### Bonding in Metals

The alkali metals are remarkably well represented by energy of HEG plus attractive interaction with the positive cores. With this model, the total energy per electron

$$\epsilon_{tot} = \frac{E_{total}}{N} = \frac{1.105}{r_s^2} - \frac{0.458}{r_s} + \epsilon_c - \frac{1}{2} \frac{\alpha}{r_s} + \epsilon_R \quad (33)$$

where  $\epsilon_c$  is the correlation energy per electron,  $\alpha$  is the Madelung constant for point charges and  $\epsilon_R$  is due to core repulsion owing to the finite sizes of ions, which amounts to removing attraction in regions with core radius  $R_C$  around the ions

$$\epsilon_R = n2\pi \int_0^{R_C} dr r^2 \frac{e^2}{r} = \frac{3}{2} \frac{R_C^2}{r_s^3} \quad (34)$$

We can now predict the density of these metals by finding the minimum of (33), taking  $\alpha = 1.80$  and  $R_C = 2$ , we get  $r_s = 4$  which is not bad. Further, the predicted bulk modulus

$$B = \Omega \frac{d^2 E}{d\Omega^2} = \frac{51.7}{r_s^5} \text{Mbar} \quad (35)$$

is often quite good for sp-bonded metals to strongly bonded covalent solids.

## Excitation

Here we're mainly interested in collective excitations that don't change the number of electrons. Examples are charge density fluctuations (plasma oscillation) described by dielectric function and spin fluctuations described by spin response functions. In a homogeneous system, the dielectric function is simply a response to an internal field. In Fourier space

$$\vec{D}(q, \omega) = \vec{E}(q, \omega) + 4\pi\vec{P}(q, \omega) = \epsilon(q, \omega)\vec{E}(q, \omega) \quad (36)$$

In terms of potentials

$$\epsilon(q, \omega) = \frac{\delta V_{ext}(\vec{q}, \omega)}{\delta V_{test}(\vec{q}, \omega)} = 1 - \frac{4\pi e^2}{q^2} \chi_n^*(\vec{q}, \omega) \quad (37)$$