Chapter 3.2: Electron Gas / Liquid.
Jellium Model.
Wigner Crystal.

Ref: G. Giuliani & G. Vignale.

P. Phillips.

The H.F. procedure, we derived in the previous chapter, produces a set of equations to be computed self-consistently for $u_\alpha(\vec{r})$ and ε_α. In fact the first computer used in physics in 1950-60, was used to solve the H.F. equations. Solving it analytically is not easy, except perhaps, if the solution $u_\alpha(\vec{r})$ is known, say, by symmetry. Note that $u_\alpha(\vec{r})$ are solutions involving both v_{ion} and v_{ee}, and v_{ie} breaks the continuous translational symmetry. So, the solutions can be expressed in terms of Bloch wave $u_\alpha(r) \to u_k(r)\, e^{i\vec{k}\cdot\vec{r}}$ and one needs to then solve for the $u_k(\vec{r})$ part numerically.

For an analytical solution, one makes a simplest, but not necessarily correct, approximation for v_{ie}, i.e., we assume v_{ie} is completely uniform in the system : $v_{ie}(\vec{r}-\vec{R}) = v_{ion}(0)$. In another way of saying is that the nucleons are distributed uniformly to give a positive background charge $n_{ion}(\vec{r})$ which is uniform $n_{ion}(\vec{r}) = n_{ion}(0)$. This is called the **Jellium Model.**

This is an ok approximation for the very long-wavelength, or small wave vector electronic states, but then one needs to perform intergration in k all the way to infinity and encounter unrealistic results. This, in real space, means the electrons are comming to close to each other, which causes divergence in the Coulomb repulsion. There is another divergence in the Coulomb potential in the momentum space that occurs as $k \to 0$. These two divergences are very well known in the field theory or continuum / low-energy theory.

called the ulltra-violate (UV) or high-energy divergence for $k \to \infty$ case and infra red (IR) or low-energy dirergence for $k \to 0$ one. In the Jellium model, these two diversinces are removed by the condition on charge-neutrality at all positions and the effect of screening of the electronic charge density.

But the great advantage of the Jelium model is the translational symmetry of the Hamiltonian, which dictates that the solutions of the interacting Hamiltonian must be plane-wave states, i.e

$$u_\alpha(\vec{r}) \to u_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}.\vec{r}} \quad \text{--(1)}$$ where V = volume.

(Plane waves are the eigenstates of momentum, and hence that of the K.E term. Any local potential gives wave packet. A plane wave H.F. wavefunction means the final H.F. Hamiltonian will be roughly a K.E term, with renormalized mass.).

- Then the H.F. wavefunction in the Jelium model is

$$|G\rangle = \prod_{k \leq k_F} c_k^+ |0\rangle \quad \text{--(2).}$$

where k_F is the Fermi-momentum.

H.W. (i) Write a H.F. wavefunction by including electron's spin $\sigma = \uparrow, \downarrow$.

(ii) Assume a ferromagnetic case with magnetization $m = \mu_B(N_\uparrow - N_\downarrow) \neq 0$, μ_B = Bohr magneton. Write the H.W. wavefunction for this case in the Jellium model.

(iii) Include orbital / sublattice index in a_k^+ and rewrite eq (2) for a multi-orbital / multiband model.

- Now we compute various terms in the H. F. equation.

$$h_{\alpha\alpha} = \langle\alpha| -\frac{\hbar^2}{2m}\nabla^2 + V_{ie}(\vec{r})|\alpha\rangle \;, \text{ for } |\alpha\rangle = |k\rangle \text{ state.}$$

$$= \frac{\hbar^2 k^2}{2m} + \underset{\uparrow \text{ constant.}}{V_{ie}(0)} = h_{kk} = \varepsilon_k = \text{"K.E." of electrons.}$$

$$\text{So,}\quad H_1 = \sum_{k,\sigma} \frac{\hbar^2 k^2}{2m} C^+_{k,\sigma} C_{k,\sigma} . \text{ in the 2nd quantized form.} \quad ---(3)$$

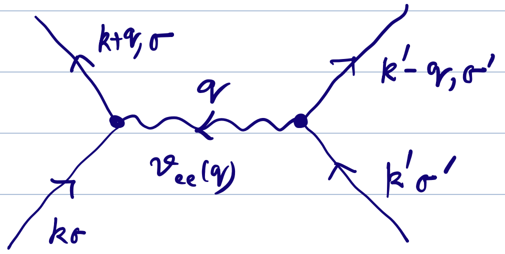
- The electron-electron interaction. The electron-electron interaction in the 2nd quantized form for this H.F. plane-wave case is the same as that was obtained in the momentum space by Fourier transforming to the k-space in the previous chapter. This is because the Fourier transformation coefficients are nothing but the plane-wave solutions. So, we have

$$H_2 = \frac{1}{2V}\sum_{k,k',q} V_{ee}(q)\, C^+_{k+q,\sigma} C^+_{k'-q,\sigma'} C_{k'\sigma'} C_{k\sigma} \quad ---(4)$$

where $V_{ee}(q)$ is the Fourier component of the electron-electron interaction. For the case of long-range Coulomb interaction $V_{ee}(r) = e^2/r$, its Fourier transformation is (solved in H.W. 1)

$$V_{ee}(q) = \int d^3r\, e^{i\vec{q}\cdot\vec{r}}\, V_{ee}(r) = \frac{4\pi e^2}{q^2} \quad --(5).$$

In eq (4), we have assumed continuous translational invariance, which translates into the incoming momentum and outgoing momentum must be the same. In the Feynmann diagram, this momentum conservation ensures that the total momentum at each vertex is conserved as shown in the picture:



Since the Coulomb interaction does not allow spin-flip, so the spin is also conserved at each vertex/contact.

- The next step is, of course, to obtain the expectation values of H_1, H_2 w.r.to the plane wave states.

for spin.

$$\langle G|H_1|G\rangle = \sum_{k,\sigma} \varepsilon_k n_{k,\sigma} = 2\sum_{k<k_F} \varepsilon_k = 2\sum_{k<k_F} \frac{\hbar^2 k^2}{2m} + V_{Ie} \quad -(6a)$$

$$\left[\begin{aligned} &= 2V\frac{\hbar^2}{2m}\int_0^{k_F} \frac{4\pi k^2 dk}{(2\pi)^3}\cdot k^2 + V_{ie} \\ &= 2V\frac{\hbar^2}{(2\pi)^3}\pi k_F^5 + V_{ie} \quad \cdots (6b) \end{aligned} \right].$$

$$\langle G|H_2|G\rangle = \frac{1}{2V}\sum_{k,k',q} V_{ee}(q) \langle G| c^\dagger_{k+q,\sigma} c^\dagger_{k'-q,\sigma'} c_{k'\sigma'} c_{k\sigma} |G\rangle .$$

We use Wick's theorem, which breaks this quartic term into the product of expectation values of all possible bilinear terms. In the present case we have direct and exchange terms:

$$= \frac{1}{2V}\sum_{\substack{k,k',q\\ \sigma,\sigma'}} V_{ee}(q) \Big[\langle G| c^\dagger_{k+q,\sigma} \big[\underbrace{\delta_{k'-q,k'}}_{q=0} \delta_{\sigma\sigma'} - c_{k'\sigma'} c^\dagger_{k'-q\sigma'} \big] c_{k\sigma} |G\rangle$$

$$= \frac{1}{2V}\sum_{\substack{kk'q\\ \sigma,\sigma'}} V_{ee}(q) \Big[\langle G| c^\dagger_{k,\sigma} c_{k\sigma} |G\rangle - \langle G| c^\dagger_{k+q,\sigma} c_{k'\sigma} |G\rangle \langle G| c^\dagger_{k'-q,\sigma'} c_{k\sigma} |G\rangle \Big]$$

$$---(7)$$

Direct Term: The first term is the Direct term

$$H_2^{(H)} = \frac{1}{V}\sum_q v_{ee}(q)\,\underbrace{\sum_k \langle G|c^\dagger_{k\sigma}c_{k\sigma}|G\rangle}_{n_{q=0}\,=\,\text{total number of electrons.}}$$

$$= \frac{1}{V}\sum_q \frac{4\pi e^2}{q^2}\,n_{q=0}. \qquad ---(8a)$$

Now, we see that at $q=0$, the Coulomb interaction diverges. This is where the uniform positive potential comes to rescue. Let us look back at the ionic potential term:

$$v_{ie} = -e^2\int d^3r\,d^3R\,\frac{n_{ion}(\vec{R})\,n(\vec{r})}{|\vec{r}-\vec{R}|}.$$

$$= -e^2 N_{ion}\int d^3r\,\frac{n(\vec{r})}{|\vec{r}|}, \quad \text{since } n_{ion}(\vec{R}) = n_{ion}(0), \text{ so we set } \vec{R}=0.$$

$$= -\frac{N_{ion}}{V}\sum_q \frac{4\pi e^2}{q^2}\,n_{q=0}. \qquad --(8b)$$

We are looking at a single electron's case, which is in the outermost shell and it experiences an average positive charge of +1. Because, its the nucleons charge - the core electron's charge. Therefore, $N_{ion}=1$. Hence eq(8a) and (8b) exactly cancel each other at all values of q. Therefore, in the Jellium model of uniform positive charge background, the direct or Hartree term drops out - eliminating one of the divergence/singularity of the problem. This is an important achievement of the Jellium model.

Exchange term: The only contributing term of the interaction is the exchange term, with a negative sign (so it lower the energy).

$$H_2^{(F)} = -\frac{1}{2V}\sum_{\substack{k,k',q\\ \sigma,\sigma'}} V_{ee}(q)\, \langle G|\, c^\dagger_{k+q,\sigma}\, c_{k'\sigma'}\,|G\rangle \times \langle G|\, c^\dagger_{k'-q\,\sigma'}\, c_{k\sigma}\,|G\rangle.$$

For the same reason that the ground state is a Fermi sea, the momentum & spin conservation in each term restricts $\sigma'=\sigma$, and $k+q=k'$. This same spins on different state is clearly due to the quantum effect:

$$= -\frac{1}{2V}\sum_{\substack{k\neq k'\\ \sigma,\sigma'}} V_{ee}(|\vec{k}-\vec{k}'|)\; n_{k\sigma}\, n_{k'\sigma}.$$

$$= -\frac{1}{2V}\sum_{\substack{k<k_F,\,k'<k_F\\ \sigma,\sigma'}} \frac{e^2}{|k-k'|^2}$$, since $n_{k\sigma}=1$ for $k<k_F$.

$$= -\sum_{k<k_F,\,\sigma} \epsilon_{ex}(k)$$

[We have sumed over σ', which gives a factor of 2].

where $$\epsilon_{ex}(k) = -\frac{4\pi e^2}{V}\sum_{k'<k_F}\frac{1}{|\vec{k}-\vec{k}'|^2}$$

$$= -\frac{4\pi e^2}{V}\cdot V\int\frac{d^3k'}{(2\pi)^3}\,\frac{1}{|\vec{k}-\vec{k}'|^2},$$ $\left[\because \sum_k \to \frac{V}{(2\pi)^3}\int d^3k\right.$

$$= -\frac{4\pi e^2}{(2\pi)^3}\int_{k'=0}^{k_F}\int_{-1}^{1}\frac{2\pi k'\, dk'\, d(\cos\theta)}{\left(k^2+k'^2-2kk'\cos\theta\right)}$$

$$= -\frac{e^2}{\pi}\int_0^{k_F}\frac{k'\,dk'}{k}\left[\ln(k-k') - \ln|k+k'|\right]$$

$$= -\frac{e^2}{\pi}\frac{1}{k}\left[\frac{(k'^2-k^2)}{2}\ln\left|\frac{k-k'}{k+k'}\right| + \frac{1}{4}(k+k')^2 + \frac{(k-k')^2}{4}\right]_0^{k_F}$$

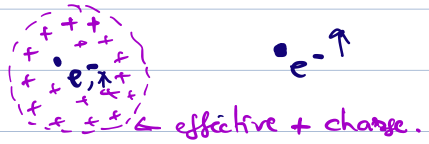
$$\left[\because \int x\ln(x+a)\,dx = \frac{x^2-a^2}{2}\ln(x+a) - \frac{1}{4}(x-a)^2\right].$$

$$= -\frac{e^2}{\pi}k_F\left[1+\frac{1-x^2}{2x}\ln\frac{1+x}{1-x}\right], \quad \boxed{x = k/k_F}$$

$$= k_F F(x)$$

(This is the famous F(x) we will keep seeing it again & again) - - - . (9)

- Because $x \lesssim 1$ as $k \lesssim k_F$ at zero temperature, so, the exchange term remains negative. Recall that the exchange term comes from two electrons of same spin σ, trying to occupy two different momentum states. Note that we started with coulomb repulsion with a positive sign, but obtain an effective interaction with negative sign - like an attraction between two electrons. This is because, the actual "classical" coulomb repulsion term is cancelled by the background charge, and what is left is a the correlation term due to Pauli exclusion principle of the quantum statistics. Its a correlation between two electrons of the same spin are correlated since they know that they can not occupy the same state. As a result, each electron is surrounded by an "exchange hole" - a region around the electron in which the density of same-spin electron is depleted than average, such that the positive background charge does not exactly cancel this negative charge in this region. Hence the "exchange hole" region effectively acts as positive charge and "attract" the other electron of same spin.



One may wonder that the other electron is also screened to be an "exchange hole" and hence one could have a repulsion between "exchange-hole". But this way of thinking is not correct since the "exchange hole" is a quantum state seen by the electronic part of the other electron with same spin. From the electronic part of the first electron, the second one looks as an "exchange hole".

- We also notice that the exchange term only contributes for the same spin. And the exchange energy is negative. Both these properties suggests that the system prefers to have all states occupied by the same spin as that lowers the energy of the ground state. Therefore, the exchange energy favors ferromagnetic order, and sometimes ferromagnetism is called the ferromagnetic exchange energy.

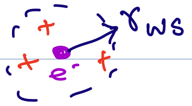
- **Pair Correlation Function:** This quantum correlation between electrons can be quantified by defining something called the pair correlation function $g(\vec{r},\vec{r}')$. This is analogous to joint probability density: normalized probability of finding an electron at $\vec{r}$, given that at the same time, there is another electron of same spin at $\vec{r}'$.

$$g_{\sigma\sigma'}(\vec{r},\vec{r}') = \frac{1}{n(\vec{r})\,n(\vec{r}')}\left\langle \sum_{i\neq j} \underbrace{\delta^{(3)}(\vec{r}-\vec{r}_{i,\sigma})}_{\psi^{\dagger}_{\sigma}(\vec{r})\,\psi_{\sigma}(\vec{r})}\,\underbrace{\delta^{(3)}(\vec{r}\,'-\vec{r}_{j,\sigma'})}_{\psi^{\dagger}_{\sigma'}(\vec{r}')\,\psi_{\sigma'}(\vec{r}')}\right\rangle$$

where the expectation value is taken over the H. F. ground state. By going to the momentum space and using Wick's theorem we can evaluate it. Needless to say, its the e-e interaction that contributes to the pair correlation function.

See Vignale's book.

- ## Dimensionless Length Scale r_s.



Exchange hole is not completely local, rather a cloud of positive background charge that cancels the negative charge. This is like the exclusion volume in the Van der Waal theory of weakly interacting gas molecules, such that above this lengthscale the particles act like classical one. This means, the total volume of electrons with charge neutral volume should make up the whole volume of the system, V. This gives:

$$\frac{4\pi r_{WS}^3}{3} N = V \quad \text{--- (10a)}$$

Now, $N = 2\sum_{k<k_F} n_k = 2V\int_0^{k_F} \frac{d\vec{k}}{(2\pi)^3} = V\left(\frac{k_F^3}{3\pi^2}\right)$, where $n_k = 1$ --- (11a)

or, the density of electrons $n_e = N/V = k_F^3/3\pi^2$. - (11b)

So, we get $\boxed{r_{WS} = \left(\frac{9\pi^2}{4}\right)^{1/3} k_F^{-1}}$ — (10b)

r_{WS} is called the Wigner-Seitz radium.

- In typical material, the lattice constant ~ Å. So, for $r_e \sim 1$ Å, we get the Fermi velocity $v_F \sim \hbar k_F/m \sim 10^8$ cm/s $\sim c/300$.
- A more appropriate lengthscale to compare r_{WS} is the Bohr radius $a_0 = \hbar^2/me^2$. It is conventional to work with a dimensionless lengthscale r_s, defined by $r_s = r_{WS}/a_0$.

$r_s \ll 1$: called the dense limit

$r_s \gg 1$: called the dilute limit.

$2 \leq r_s \leq 6$ in typical metals.

- In the dilute limit, one can roughly say that the "electrons" are far from each other, hence its K.E. is quenched. Because only the potential energy is present, so, the wavefunction must be localized in real space.
  In fact, the electrons get localized in a periodic crystal (not the one from the periodic arrangement of the nucleons, because here we don't even have a lattice). This electronic crystal is called the Wigner Crystal.

- In the dense limit ($r_s \ll 1$), the electron's hopping is enhanced, and we have good metals.

- In between the two limits, $r_s \sim 1$, both K.E. and the correlation effects become compareable. Here interesting phase transitions, symmetry breaking phenomena (such as Ferromagnetism) happen.

$r_s \ll 1$	r_s	$r_s \gg 1$
K.E dominates.	K.E and P.E are comparable.	P. E. dominates
Electron gas, meltalic behavior.	Symmetry breaking phases, such as FM, spin, charge density wave	Electrons are localized. Wigner Crystal
Extended states – Wave properties of electron	Wave - Particle duality	Particle - like properties
Plane-wave ansatz for H.F wave function	Try a wave packet ansatz for the single particle state and construct a slater determinant.	δ- function states for H.F. W.f.

⊛ So adding eqs (6) & (9), we now have the total energy of the Jellium model as.

$$E_{\text{Jellium}} = \langle G | H_1 + H_2 | G \rangle$$

$$= 2 \sum_{k<k_F} \left[\frac{\hbar^2 k^2}{2m} + \frac{1}{2} \varepsilon_{ex}(k) \right]$$

$$= 2V \int_0^{k_F} \frac{4\pi k^2 dk}{(2\pi)^3} \Big[\underbrace{\frac{\hbar^2 k^2}{2m}}_{\frac{\hbar^2}{m(2\pi)^2} \frac{k_F^5}{5}} + \underbrace{\frac{1}{2} \varepsilon_{ex}(k)}_{-\frac{2e^2}{(2\pi)^3} k_F^4} \Big] . \quad \text{(Check).}$$

$$\cdots (12a)$$

→ We want to massage this expression to write each term in terms of dimensionless length: $r_s = \left(\frac{9\pi^2}{4}\right)^{1/3} k_F^{-1}$, which gives :

$$\boxed{\begin{aligned} \frac{E_{\text{Jellium}}}{N} &= \text{total energy per electron} \\ &= \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} + \cdots \right) R_y, \quad \cdots (12b) \end{aligned}}$$

where R_y is the Rydberg constant $= e^2/2a_0 = 13.6$ ev.

- Its now obvious that as $r_s \ll 1$, i.e. in the dense limit, the first term, i.e., the K.E. term dominates. In the other limit $r_s \gg 1$, the exchange term dominates over the kinetic energy. Since its a negative energy, we essentially have bound electrons. Ignoring the other corrections denoted by $\cdots$, this transition happens at $r_s \sim 2.41$. For metals $2 < r_s < 6$, which means most of the metals would become Wigner crystal. This does not happen, due to other corrections, as well as due to electron-phonon coupling.

- Since the K.E term $E_{K.E} \sim 1/r_s^2$ and $E_{Coulomb} \sim 1/r_s$, one can also treat $r_s = E_{Coulomb}/E_{K.E}$, as the ratio between the long-range Coulomb repulsion and the K.E. energy. As r_s increases, the coulomb interaction becomes more and more important.

- So, it looks like r_s is a nice expansion parameter and we obtain so far a power series in terms of $r_s \sim r_e/a_0 \sim k_F^{-1}$. One can try to obtain higher order terms in r_s. Gell-Mann and Brueckner obtained higher order terms by treating H_2 as perturbations. Then the exchange term we obtain above is the first order perturbation term. They obtain 2nd and third order terms which goes as

$$E_{Jallium}/N = \left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.062 \ln r_s - 0.096\right] Ry$$

So, we again encounter another log-singularity in the 2nd order term. This log singularity term implies that a system with charge neutrality cannot be stable/analytic at all length scales. In fact, most of the metals have $r_s > 1$, and hence the above series is not convergent in the series expansion of r_s. One needs to either consider all orders in r_s, in which some of these singularities are removed, or consider a full lattice of positive charge where bandwidth of electrons are finite, or use advanced numerical methods such as QMC.

⊛ Excitation spectrum, Singularity, introduction to Screening:

Returning back to the dispersion relation, it is now modified to

$$\mathcal{E}(k) = \frac{\hbar^2 k^2}{2m} - \underbrace{\frac{1}{2}\,\varepsilon_{ex}(k)}_{\Sigma(k)\,=\,\text{Self-energy.}}$$

$$= \varepsilon_F\left[x^2 - 0{\cdot}663\, r_s\, F(x)\right], \quad \text{---}\,(12)$$

$$x = k/k_F$$

where ε_F = Fermi energy $= \hbar^2 k_F^2/2m$ and

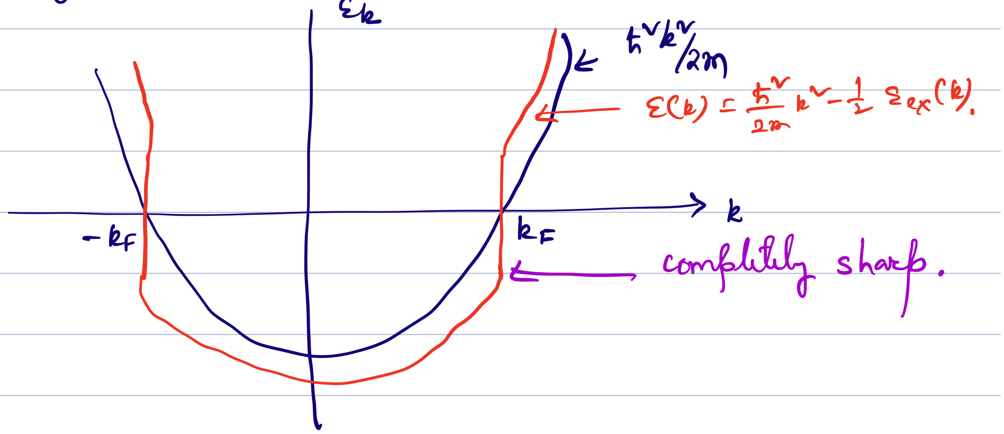
$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x}\ln\frac{1+x}{1-x}.$$

- We often call the correction to single particle energy as Self-energy.
- We notice that for $x \ll 1$, ie, for states away from the fermi-level, the leading term remains the K.E. term, and one obtains a quadratic dispersion $\mathcal{E}_k \approx \frac{\hbar^2 k^2}{2m^*}$, but with an effective mass $\frac{1}{2m^*} = \frac{1}{m} - 0{\cdot}33\, r_s\, \varepsilon_F$. These are called "quasiparticle" excitations.

- The problem arises at $x = k/k_F = 1$. Here the $\log(1-x)$ term in the exchange energy diverges. But there is $(1-x^2)$ term in the numerator. So, we need to check the limits. It turns out that the effective mass goes to zero as $k \to k_F$, ie, the Fermi-velocity $v_F \to \infty$ at $k \to k_F$. The dispersione becomes completely sharp at $k = k_F$ (see the picture below). This can be seen as follows: $v_F = \frac{\partial \mathcal{E}_k}{\hbar\,\partial k}\Big|_{k_F}$ and $\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 \mathcal{E}_k}{\partial k^2}\Big|_{k_F} \approx \frac{1}{\hbar^2 k_F}\frac{\partial \mathcal{E}_k}{\partial k}\Big|_{k_F}$

or $v_F = k_F/m^*$.

Now, $\frac{\partial \Sigma_{ex}}{\partial k} \sim \ln(k-k_F) \to \infty$ as $k \to k_F$. As $\varepsilon_k \approx v_F(k-k_F)+\cdots$ and $v_F \to \infty$, so, the energy dispersion has a logarithmic singularity in the slope at $k \to k_F$.



The density of states at the fermi level DOS $\sim 1/v_F \to 0$, ie, there is a complete suppression of density of states around the Fermi level – this is called the Coulomb gap. For metallic systems, this singularity is unphysical and not observed experimentally. The origin of this artifact can be traced back to the long-range Coulomb interaction $\sim 1/q^2$, which causes divergences in the interaction strength at small momentum transfer q. (Note that the direct term only removes $q=0$ term, but not all small q terms). In real material, the long-range coulomb interaction becomes screened by other electrons. This changes the coulomb interaction to be short-ranged as $e^{-kr}/r \sim 1/q^2+k^2$, where k^{-1} is the Thomas-Fermi screening length. This screening removes this divergence, and one has finite fermi velocity and mass – which are different from bare electron's velocity & mass – at the Fermi level.

* Exchange term in 3D, 2D, 1D :

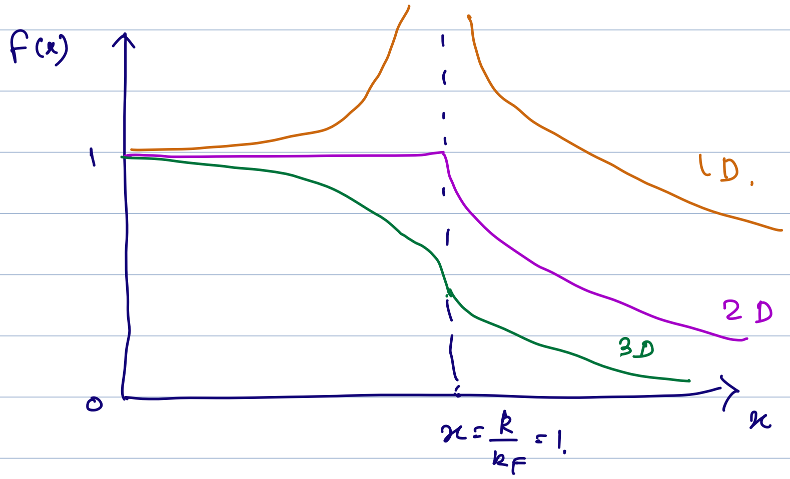
It turns out the above discussion of divergences in v_F at k_F for 3D is even more severe in 2D & 1D. The exchange energy, i.e., the $F(x)$ function has the form as

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \frac{1+x}{1-x} . \qquad \text{in } 3D$$

$$= 1 - \theta(x-1) \frac{\sqrt{x^2-1}}{x} \qquad \text{in } 2D$$

$$= \frac{1}{x} \ln\left(\frac{x+1}{x-1}\right) \qquad \text{in } 1D.$$

The function behaves as



In 3D, $F(x)$ is continuous, but its derivative (i.e., v_F) has discontinuous jump. In 2D, $F(x)$ is discontinuous, while in 1D, $F(x)$ has log-divergence. Therefore, the exchange energy in the Jellium model is singular in all dimensions.

3.3 Wigner Crystal :

Now let us turn to the low density (i.e. $r_s >> 1$) limit. In this case the separation between electrons are large enough that the electrons K.E. term is irrelevant and the only term that is important is the exchange term. Since it's a potential energy term, the corresponding wavefunction is localized in space (since the energy eigenstates would be the eigenstate of the position operator). Now, all electrons cannot localize at a given position, they must maintain some optimum distance between them to avoid correlation. It does not really make sense that the electrons would just position themselves randomly - because a disorder arrangement of electrons have finite entropy and we are really at some very low temperature. Therefore, the most logical situation here would be to have the electrons arranged in a periodic crystal. Indeed, this happens in the limit of $r_s \to \infty$. Such a crystal is called the Wigner crystal.

Wigner consider a δ- function for each particles wavefunctions $\delta(\vec{r}-\vec{R}_i)$ in some lattice defined by $\vec{R}_i$, and wrote a Slater determinant for the many-body state. It turns out to be an exact wavefunction for the exchange energy. It is not obvious what sort of Bravais lattice one gets and it depends on many factors including Z. It is generally seen that in 2D, one obtains hexagonal or triangular lattice, while in 3D, bcc has lower energy than fcc and than simple cubic structure.

The criterion we would impose, of course, that the charge remain neutral within an unit cell, because otherwise the whole system will not maintain charge neutrality. This determines the volume of the unit cell, say Ω_{WS} as $\Omega_{WS}\, n = Z$, where n is the density of electrons and Z is the number of electrons per unit cell. (For a Bravais lattice $Z=1$).

Estimates of energy of a Wigner Crystal :

Since the kinetic energy is quenched, we only focus on the potential energy :

$$U = \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i-\vec{r}_j|} - \sum_i \underset{\text{(unit cell)}}{\int} d^3\vec{r}\, \frac{(n_b e)e}{|\vec{r}-\vec{r}_i|} + \frac{1}{2}\int d^3\vec{r}\, d^3\vec{r}\,' \frac{(n_b e)^2}{|\vec{r}-\vec{r}\,'|}, \longrightarrow (13)$$

where $\vec{r}_i$ are the positions of electrons, and $n_b e$ is the constant positive background charge density.

We can try to minimize the energy by taking a Slater determinant of delta function or some broadened function (Wannier function). But because of the divergence of the long-range interaction, it's hard to obtain converged solutions. But, as we saw above, the divergent terms cancel each other so that one expects a finite solution, meaning Wigner crystal occurs.

⊛ Our rough estimate of the total energy within the Jellium model already predicts that the exchange energy dominates over the Kinetic energy in the limit of $r_s >> 1$. Therefore, the kinetic energy is suppressed and the potential energy dominates and hence electrons are indeed in a bound state within the radius of r_{WS}. The only issue here is that we started with plane-wave solution as ansatz and obtain bound state, and hence they are not self-consistent. We have to start from a localized state (like delta-function) as the wavefunction ansatz and obtain the expectation value of the K.E, Electron-ion, Direct and exchange energies. Then we want to show that indeed such bound state (negative total energy) exists for $r_s >> 1$. This was rigorously done by Wigner.

We will here make some semi-classical estimate of the same.

- We can however make some quick estimates (semi-classical).

→ Treat the crystal as a collection of electrically neutral unit-cell – say each unit cell has one electron and +1 positive background charge.

→ There is no dipole moment in an unit cell, i.e., the charge centers of electrons coincide with that of the background.

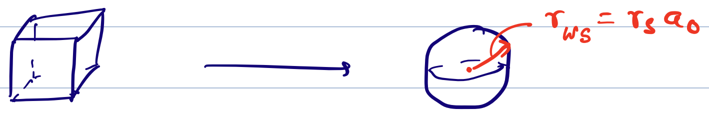
→ Each electron interacts with finite number of nearest neighbors – something like a short range interaction with a cut off beyond a given nearest neighbor. So, this interaction does not depend on the total number of unit cells in a crystal. This is why the total energy scales as N, not N^2 even for two particle interactions:

$$U = \sum_i V_{cell}(r_i) = N\, V_{cell}(r_0).$$

where $V_{cell}(r_0)$ is the energy per unit cell, in which the electron in that unit cell only interact with a few nearest neighbors.

→ We map the actual unit cell volume/area (in 3D/2D) to that of a sphere or disk (Wigner-Seitz cells), with the volume/area being preserved.

e.g

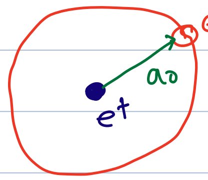


The radius of this cell is the Wigner-Seitz cell $r_e = r_s a_0$.
where a_0 = Bohr radius and r_s is as introduced earlier.

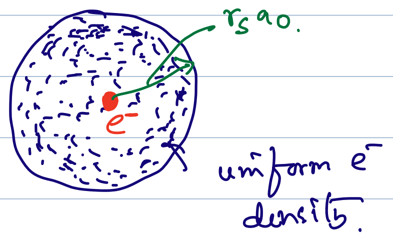
→ These neutral spheres do not interact with each other. Therefore, there is no kinetic energy for the electrons, as that would mean electrons are hopping from one sphere to another. But that is discarded in this approximation.

→ We evaluate the "onsite" potential energy of an electron inside a WS spherical unit cell interacting with the positive uniform potential.

Atom



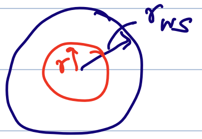
W.S. Cell



→ The difference of the electron in the W.S. cell with an electron in an hydrogen atom is that in the W.S. the positive ionic potential is uniform, whereas in an atom, the positive potential is concentrated at the center of it. In an atom, the bound state energy is $-e^2/2a_0 = -13.6$ eV and the wave function is $\sim e^{-r/a_0}$ for the s-orbital. Here the electron has kinetic energy & Coulomb interaction and using the virial theorem for Coulomb potential $-\langle \frac{e^2}{r} \rangle$ we have $-\frac{e^2}{2a_0}$.

– we have a slightly different situation here. The electrons are completely localized and hence there is no Kinetic energy. The potential energy profile is also different.

The potential due to the positive background potential at r is given by the charge contained inside the sphere of radius r - According to the Gauss law. The total charge in the volume of radius r_{ws} is e. The uniform positive charge density is $n_{ion} = \frac{e}{\frac{4\pi r_{WS}^3}{3}} = \frac{3e}{4\pi r_{WS}^3}$.



Then the potential at any distance r from the center is

$$\phi(r) = \int_{r'=r_{WS}}^{r} \frac{n_{ion}}{|r-r'|} d^3r'$$

$$= \frac{3e}{4\pi r_{WS}^3} \int_{r'=r_{WS}}^{r} \frac{1}{|r-\bar{r}'|} = \frac{3e}{2r_{WS}}\left[1-\frac{r^2}{2r_{WS}^2}\right].$$

- This is the potential felt by a charge particle sitting at r. Then the potential energy felt by the electron sitting at the center r=0 is

$$U_{ie} = \langle V_{ie}(r)\rangle = -e\,\phi(0) = -\frac{3e^2}{2r_{WS}}.$$

The potential energy due to ion-ion interaction is

$$\bullet \quad U_{ii} = \int_{r=r_{WS}}^{0} d^3r \int_{r'=r_{WS}}^{0} d^3r' \frac{n_{ion}\, n_{im}}{|r-r'|} = \left(\frac{3e}{4\pi r_{WS}^3}\right)^2 \int_{r}\int_{r'} \frac{d^3r\, d^3r'}{|r-r'|}$$

$$= \frac{(3e)^2}{4\pi r_{WS}^4} \int_{r=r_{WS}}^{0} \left(1-\frac{r^2}{2r_{WS}^2}\right) d^3r = \frac{6}{5}\,\frac{e^2}{2r_{WS}}$$

- Since there is single electron in the W-S cell, there is no electron-electron interaction, $U_{ee} = 0$. And kinetic energy is also zero.

- Therefore, the total energy per W.S. is

$$U_{cell} = U_{ii} + U_{ie} + U_{ee} + K.E.$$
$$= -\frac{9}{5}\frac{e^2}{2 r_{WS}} = -\frac{1.8}{r_s} \; R_y.$$

We notice that this energy is slightly lower than the atomic energy for $r_s \to 1$, and for $2 < r_s < 6$ for metal already we have higher energy than atomic energy. Of course with H.F. calculation and with corrections, the result improves and one indeed have Wigner crystal.

⊛ What about the exchange term?

Recall that the exchange term arises from the overlap between the wavefunctions. In the above semi-classical estimate, we have delta-function wavefunction. Hence no overlap and no exchange term. But in reality, the wavefunctions are broadened due to many-body interaction and one has the exchange energy, which is negative and thus lowers the energy further. The exchange energy was evaluated earlier to be for plane waves.

$$U^{(ex)}_{cell} \simeq -\frac{0.916}{r_s} \, Ry.$$

⊛ Correlation Energy: The defination of a "quantum" correlation energy is the energy difference between fully quantum minus semi-classical energy:

$$U^{(corr)}_{cell} = U^{ex}_{cell} - U^{WS}_{cell}$$

$$\simeq -\frac{0.884}{r_s} \, Ry, \quad \text{for } r_s \to \infty.$$

⊛ Concluding Remarks :

In this chapter, we studied the many-body Hamiltonian of electrons with long-range coulomb interaction through the Hartree-Fock wavefunction ansatz. The H.F. wave function is a simple product state of single particle states, with a Slater determinant form to take into account the fermionic statistics of electrons. The single particle states are the variational functions - so that in the variational many body ground state these single particles are not really the non-interacting electrons that we started with, but some sort of "quasi particles" which are the solutions of a non-linear Schrödinger like equations - called H.F equations.

In the H.F. equation, we have the quasiparticle wave function, with the typical K.E., and an mean-field, local Hartree / Direct potential energy (classical), and a non-local Fock / Exchange potential energy. The exchange term is the most interesting term - arising due to quantum statistics of the wavefunction.

Next, we solved this H.F. equation, with a uniform positive potential background (Jellium model), using two different wavefunction ansatz. First, we considered an plane-wave solution - for electron gas / liquid - which works in the cases where K.E. dominate. This works for metals. The second example, we considered was for fully localized (δ-function) wave function - which works when the potential energy (Coulomb) interaction dominates. Here we obtained Wigner Crystal. These two limits are achived for dense ($r_s \ll 1$) and dilute ($r_s \gg 1$) electron density limits.

The solutions in between when $r_s \sim 1$, i.e. when K.E. & Coulomb interactions are comparable, is not known analytically. Here we propose that lot of interesting effects such as symmetry breaking phases will arise. Solving them for long-range interaction is extremely difficult, as one obtains all sorts of divergences / singularities. In reality, also, the Coulomb interaction in many-electron system do not remain long-range - they become short-ranged due to screening. We will study the screening effect first and obtain expressions for screened Coulomb interaction and also simplify it to onsite Coulomb interaction (Hubbard model) before attempting to solve the intermediate coupling region.