Beyond the independent electron approximation

Schrodinger eq. for electrons in metals

Independent electron approximation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2+U_{ion}(\vec{r})\right]\psi(\vec{r})=\varepsilon\psi(\vec{r}),$$

$$U_{ion}(\vec{r}_i)=-Z\sum_{\vec{R}}\frac{e^2}{|\vec{r}-\vec{R}|}\ \text{(bare ion core potential from all ions)}$$

→ get band structure using either NFE (chap 9) or TB (chap 10) or more complicated techniques (chap 11), Fermi surface… etc

In general, there are e-e interactions,

$$H=\sum_{i=1}^{N}\frac{p_i^2}{2m}+\sum_{i=1}^{N}U_{ion}(\vec{r}_i)+\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}U_{e-e}(\vec{r}_i-\vec{r}_j),$$

$$U_{e-e}(\vec{r}_i-\vec{r}_j)=\frac{e^2}{|\vec{r}_i-\vec{r}_j|},$$

$$H\Psi(\vec{r}_1,\vec{r}_2,\cdots)=E\Psi(\vec{r}_1,\vec{r}_2,\cdots),\ \text{(electron spin ignored)}$$

This is a differential eq. with N=10^{23} degrees of freedom. No one is able to solve it exactly. So we need

Hartree approximation:

Each electron still retains its own identity. It moves in the potential from all the other electrons,

$$\text{assume}\quad \Psi(\vec{r}_1,\vec{r}_2,\cdots)=\psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\cdots\psi_N(\vec{r}_N)$$

$$\overset{\text{Prob.1}}{\Rightarrow}\quad \left[-\frac{\hbar^2}{2m}\nabla^2+U_{ion}(\vec{r})\right]\psi_i(\vec{r})+\underbrace{\left[e^2\int d^3\vec{r}\,'\frac{\sum_j|\psi_j(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}\right]}_{U_{e-e}^{H}(r),\ \text{Hartree (or direct) potential}}\psi_i(\vec{r})=\varepsilon_i\psi_i(\vec{r})$$

- Need to be solved self-consistently (by iteration)!
- Self-consistency doesn't mean the result is correct.

What’s wrong with the HA?

1. The manybody wave function violates the Pauli principle
2. The calculated total energy is positive (means the electron gas is unstable)

So we need Hartree-Fock approximation:

$$\text{assume }\ \Psi(\vec r_1, s_1, \vec r_2, s_2 \cdots) = \begin{vmatrix} \psi_1(\vec r_1, s_1) & \psi_1(\vec r_2, s_2) & \cdots & \psi_1(\vec r_N, s_N) \\ \psi_2(\vec r_1, s_1) & \psi_2(\vec r_2, s_2) & \cdots & \psi_2(\vec r_N, s_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\vec r_1, s_1) & \psi_N(\vec r_2, s_2) & \cdots & \psi_N(\vec r_N, s_N) \end{vmatrix}$$

With the help of the variational principle (or the method of 2nd quantization, which is easier), we’ll be able to get (Prob. 2)

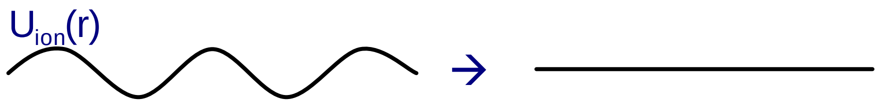
$$-\frac{\hbar^2}{2m}\nabla^2 + U_{ion} + U_{e-e}^{H}\ \psi_i(\vec r) - e^2 \delta_{s_i, s_j} \int d\vec r' \underbrace{\frac{\sum_j \psi_j{}^*(\vec r')\psi_j(\vec r)}{|\vec r - \vec r'|}}_{} \psi_i(\vec r') = \varepsilon_i \psi_i(\vec r)$$

$u_{e-e}^F(r,r')$ Fock (or exchange) potential

- Notice that the exchange potential exists only between electrons with parallel spins.
- The exchange potential is non-local! This makes the HFA much harder to calculate!
- Still need self-consistency.
- Still no guarantee on the correctness (even qualitatively) of the self-consistent result!

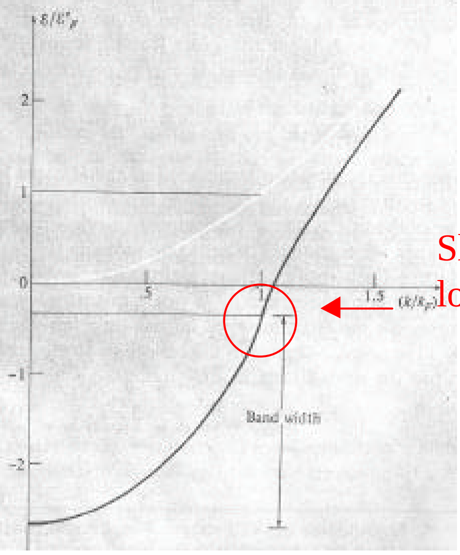
In the following, we will use HFA to calculate the ground state energy of an electron gas. Before doing that, we need

The jellium approximation



HF energy per electron $\varepsilon_i(k)$

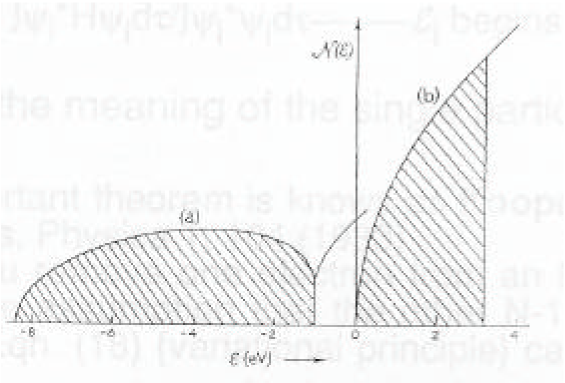
$$e(\vec{k}) = \frac{\hbar^2 k^2}{2m} - e^2 \int_{k<k_F} \frac{d^3\vec{k}'}{(2p)^3} \frac{4p}{|\vec{k}-\vec{k}'|^2} = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{p} k_F \left[\frac{1}{2} + \frac{1-x^2}{4x} \ln\left|\frac{1+x}{1-x}\right| \right], \quad x = \frac{k}{k_F}$$



Slope at ε_F has logarithmic divergence

- If, when you remove one electron from an N-electron system, the other N-1 wave functions do not change, then $|\varepsilon_i(k)|$ is the ionization energy from the i-th level (Koopman’s theo. 1933).
- In reality, the other N-1 electrons would relax to screen the hole created by ionization. (“final state effect”, could be very large!)

DOS for an electron gas in HA and HFA



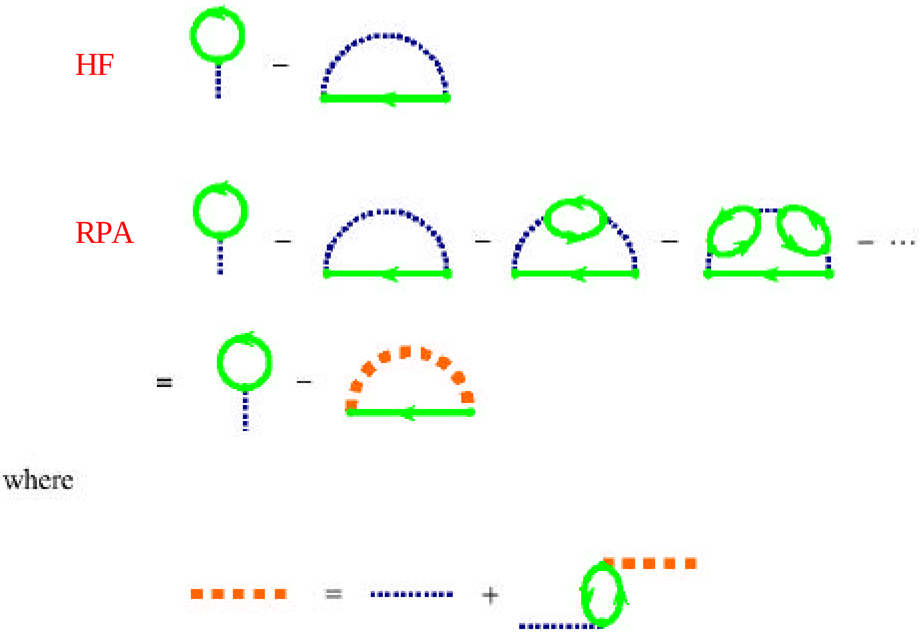
What’s wrong with HFA?

- In the HFA, the DOS goes to zero at the Fermi energy!
  HFA gets the specific heat and the conductivity seriously wrong!
- The band width is 2.4 times too wide (compared to free e)

The manybody wave f’n is not necessarily a Slater determinant!

Beyond HFA:

- Configuration interaction (superimpose many Slater determinants formed from excited states)
- Density functional theory (beyond jellium model! Kohn and Sham, 1956; Nobel Chem. Prize 1998)
- Green function method (systematic perturbation expansion)
  Eg, Hartree-Fock vs Random Phase Approx.



$$E_{HF} = N \left(\frac{3}{5} e_F - \frac{3}{4} \frac{e^2 k_F}{p} \right)$$

The energy correction beyond HFA is called the correlation energy.

$$E_C \equiv E_{HF} - E_{EXACT}$$

Gell-Mann+Bruckner's result (for high density electron gas, 1957)

$E/N = 2.21/r_S^2 + 0 - 0.916/r_S + 0.0622 \ln(r_S) - 0.096 + O(r_S)$

$= \quad E_K \quad + E_H \quad - E_F \quad + E_C$ (E in Ry, r_S in a_0)

- This is still under the jellium approximation!
- Good for $r_S<1$, less accurate for electrons with low density
  Usual metals have $2 < r_S < 5$!
- E. Wigner predicted that very low-density electron gas ($r_S >$ 20 !?) would spontaneously form a non-uniform phase (Wigner crystal)

Exchange-correlation hole

Pair “correlation” function g(r,r’)

≡ the probability to find one electron at a r and another at r’

$$=\Psi^*(\vec r,\vec r\,')\Psi(\vec r,\vec r\,')$$

Electrons with parallel spins in HF theory

Average over all electrons in the Fermi sea

$$\Psi(\vec r,\vec r\,')=\frac{1}{\sqrt{2V}}\left(e^{i\vec k_1\cdot\vec r+i\vec k_2\cdot\vec r\,'}-e^{i\vec k_1\cdot\vec r\,'+i\vec k_2\cdot\vec r}\right)$$

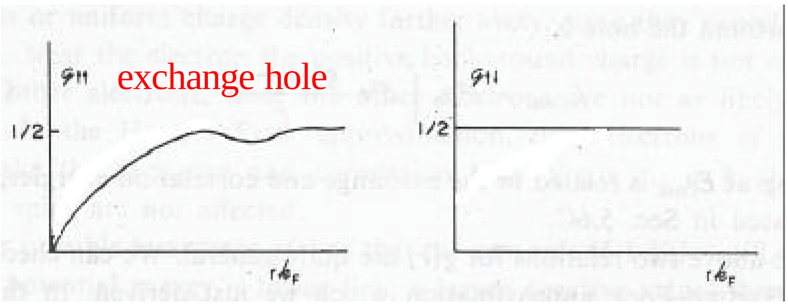
$$\Rightarrow\qquad g(\vec r,\vec r\,')=\frac{1}{V}\left[1-\cos(\vec k_1-\vec k_2)\cdot(\vec r-\vec r\,')\right]$$

$$<g(\vec r)>=\frac{1}{N^2}\sum_{\vec k_1,\vec k_2}\left[1-e^{i(\vec k_1-\vec k_2)\cdot\vec r}\right],\quad N=\#\text{ of k-states}$$

$$=1-f^2(k_F r)$$

$$\text{where } f(k_F r)=\frac{V}{N(2\pi)^3}\int_{k<k_F}d^3\vec k e^{i\vec k\cdot\vec r}=3\left(\frac{\sin k_F r-k_F r\cos k_F r}{k_F^3 r^3}\right)=\frac{3}{k_F r}j_1(k_F r)$$

Exchange effect keeps electrons with the same spin separated

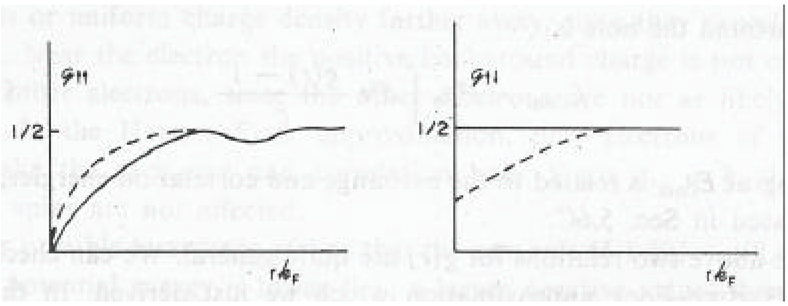


$$E_{X\,hole}=e^2\left(\frac{N}{V}\right)\int d^3\vec r\,\frac{g(r)-1}{r}=-\frac{3}{4}\frac{e^2k_F}{\pi}!\quad(g=g_{\uparrow\uparrow}+g_{\uparrow\downarrow})$$

Beyond HFA

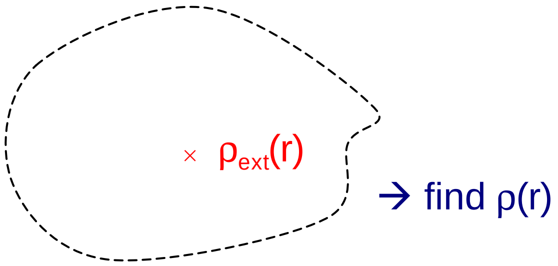
Now there is a hole even if the electrons have different spins!

exchange-correlation (xc) hole (named by Wigner)



Electronic screening

Screening is closely related to the dielectric function, which characterizes the charge response to an external charge



$\rho(r) = \rho_{ext}(r) + \rho_{ind}(r)$; $\nabla^2\phi_{ext}(r) = -4\pi\rho_{ext}(r)$
$\phi(r) = \phi_{ext}(r) + \phi_{ind}(r)$; $\nabla^2\phi(r) = -4\pi\rho(r)$

Instead of considering charge and potential distributions in r-space, we should consider these distributions in k-space.

$$\rho(\vec{r}) = \int \frac{d^3\vec{q}}{(2\pi)^3} e^{i\vec{q}\cdot\vec{r}} \rho(\vec{q}), \text{ plane wave decomposition}$$

$$\phi(\vec{r}) = \int \frac{d^3\vec{q}}{(2\pi)^3} e^{i\vec{q}\cdot\vec{r}} \phi(\vec{q}).$$

then, $q^2\phi(\vec{q}) = 4\pi\rho(\vec{q})$ similarly for ρ_{ext} and ρ_{ind}

Dieletric function and electric susceptibility

define $\boxed{\phi(q) = [1/\varepsilon(q)]\, \phi_{ext}(q)}$

where $\varepsilon(q)$ is the q-dependent dielectric function

Note: in real space, it becomes the non-local form

$$\phi_{ext}(\vec{r}) = \int d^3\vec{r}'\, \varepsilon(\vec{r}-\vec{r}')\phi(\vec{r}')$$

also, define $\boxed{\rho_{ind}(q) = \chi(q)\, \phi(q)}$

where $\chi(q)$ is the q-dependent electric susceptibility

Then $\boxed{\varepsilon(\vec{q}) = 1 - \frac{4\pi}{q^2}\chi(\vec{q})}$ Note that it differs from the usual definition $\varepsilon = 1 + 4\pi\chi$!

Thomas-Fermi theory of screening (1927)

The goal is to find the connection $\rho_{ind} \leftrightarrow \phi$ and obtain χ

In order to know charge response, we need Schrodinger eq.

$$\rho(\vec{r}) = -\frac{2e}{V}\sum_{\vec{k}} f_{\vec{k}} |\psi_{\vec{k}}(\vec{r})|^2$$

Using the Hartree approximation

$$-\frac{\hbar^2}{2m}\nabla^2 - e\phi_{ion} - e\phi_{el} \quad \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}),$$

$$\text{where } \phi_{el}(\vec{r}) = \phi^H_{e-e} + \phi_{ext}(\vec{r}) + \phi_{ind}(\vec{r})$$

$\phi_{ion}+\phi_{e\text{-}e}^H=0$ in the jellium approximation.

ϕ_{ind} is of course unknown. Instead solving it self-consistently, we use the following approx. when $\phi(r)$ is much smoother than λ_F:

$$\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m} - e\phi(\vec{r})$$

The shifted levels will change the Fermi-Dirac distribution of the electrons, and give rise to induced charges

$$\text{before:} \quad \boxed{n_0 = \int \frac{d^3\vec{k}}{4\pi^3} \frac{1}{e^{[\hbar^2k^2/2m-\mu]/kT}+1}}$$

$$\text{after:} \quad n(\vec{r}) = \int \frac{d^3\vec{k}}{4\pi^3} \frac{1}{e^{[\hbar^2k^2/2m-e\phi(\vec{r})-\mu]/kT}+1} = n_0(\mu + e\phi(\vec{r}))$$

$$\Rightarrow \quad \rho_{ind}(\vec{r}) = -e[n_0(\mu+e\phi(\vec{r})) - n_0(\mu)]$$

$$\approx \underset{\chi}{\boxed{-e^2\frac{\partial n_0}{\partial \mu}}}\phi(\vec{r}) \quad \text{if } \phi \text{ is weak}$$

Dielectric function

$$e(\vec{q}) = 1 - \frac{4p^2}{q^2} c = 1 + \frac{4pe^2}{q^2}\frac{\partial n_0}{\partial m} = 1 + \frac{k_0^2}{q^2}$$

$$\text{where } k_0^2 \equiv 4pe^2 \frac{\partial n_0}{\partial m}$$

$$= 4pe^2 \int deg(e)\frac{\partial f(e-m)}{\partial m}$$

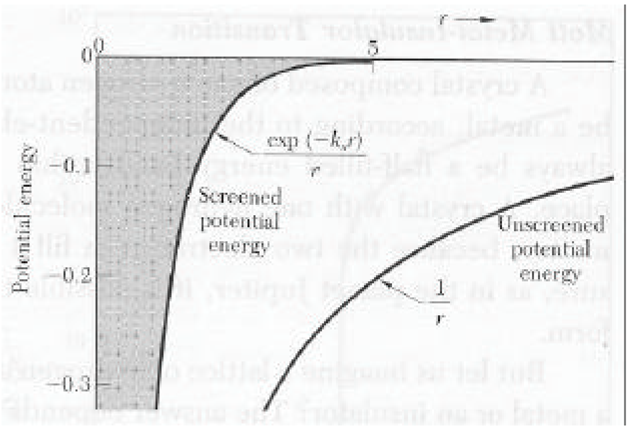
$$= 4pe^2 g(e_F) \ \text{ at T} = 0$$

It can be shown that

$$\text{For } f_{ext}(\vec{r}) = Q/r \quad \Leftrightarrow \quad f_{ext}(\vec{q}) = 4pQ/q^2$$

$$f(\vec{q}) = \frac{f_{ext}(\vec{q})}{e(\vec{q})} = 4p\frac{Q}{q^2 + k_0^2}$$

$$\Rightarrow \quad f(\vec{r}) = \int \frac{d^3\vec{q}}{(2p)^3} f(\vec{q}) e^{i\vec{q}\cdot\vec{r}} = \boxed{\frac{Q}{r}e^{-k_0 r}}$$



For free electron gas, $g(\varepsilon_F) = mk_F/\hbar^2\pi^2$,

→ $(k_0/k_F)^2 = (4/\pi)(1/k_F a_0) \approx O(1)$

Lindhard theory of screening (1954)

When the external potential is weak, we can use perturbation theory to calculate the charge density response to low orders

Still under Hartree approx.

$$-\frac{\hbar^2}{2m}\nabla^2 - e f_{ion} - e f_{el} \quad y_i(\vec{r}) = e_i y_i(\vec{r}),$$

where $f_{el}(\vec{r}) = f^{H}_{e-e} + \boxed{f_{ext}(\vec{r})} + f_{ind}(\vec{r}),$

f^{H}_{e-e} cancels with f_{ion} and f_{ind} is of 2nd order (neglected)

Wave function correction to first order,

$$y_k = y^0_k - e\sum_{k'}\frac{y^0_{k'}\left\langle y^0_{k'}\middle| f_{ext} \middle| y^0_k\right\rangle}{e_k - e_{k'}}, \text{ combining with}$$

$$r(\vec{r}) = -\frac{2e}{V}\sum_{\vec{k}} f_{\vec{k}} |y_{\vec{k}}(\vec{r})|^2 = r_0 + r_{ind}(\vec{r}),$$

$$\overset{\text{Prob.5}}{\Rightarrow} \quad r_{ind}(\vec{q}) = \boxed{-\frac{2e^2}{V}\sum_{\vec{k}}\frac{f_{\vec{k}-\vec{q}/2} - f_{\vec{k}+\vec{q}/2}}{e_{\vec{k}+\vec{q}/2} - e_{\vec{k}-\vec{q}/2}}} f(\vec{q})$$

Nozieres and Pine, RPA, 1958

Ehrenreich and Cohen, SCF, 1959

In the long wave length limit,

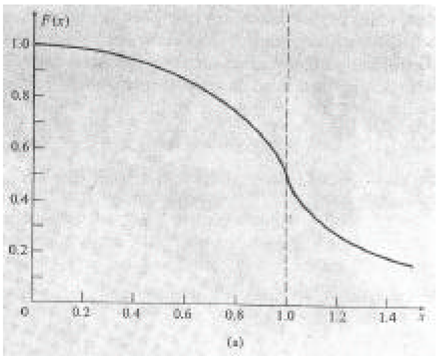
$$c(\vec{q}) \approx -\frac{2e^2}{V}\sum_{\vec{k}}\frac{(\hbar^2/m)\vec{q}\cdot\vec{k}(-\partial f_{\vec{k}}/\partial e)}{(\hbar^2/m)\vec{q}\cdot\vec{k}}$$

$$= -\frac{2e^2}{V}\sum_{\vec{k}} -\frac{\partial f_{\vec{k}}}{\partial e} = e^2\frac{\partial n_0}{\partial e}(= c_{TF})$$

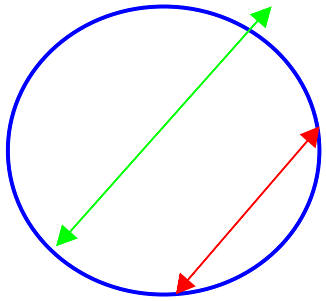
Lindhard's result remains valid for non-smooth perturbation.

For general wave length, we have

$$c(\vec{q}) = -e^2 g(e_F) \quad \frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right| \quad = c_{TF}F(x), \quad x = q/2k_F$$



Why the response vanishes for $q>>2k_F$?



Fermi sphere

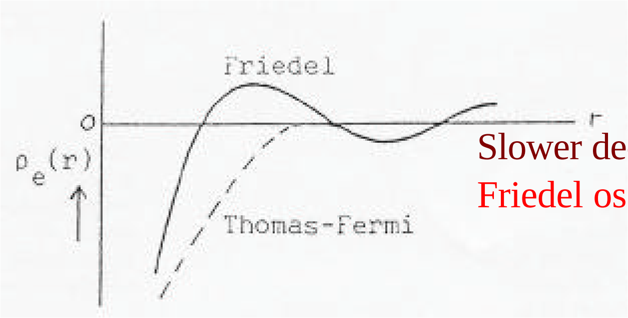
$q > 2k_F$

$q < 2k_F$

When $q >> 2k_F$ (or $\lambda<<\lambda_F$), the scale of potential variation << the size of electron and is unable to screen the charge (Mathematically, when $q < 2k_F$, the denominator of χ can be small and makes larger contribution.)

It can be shown (not easy) that for $k_F r>>1$

$$f_{ind}(\vec{r}) = \int \frac{d^3\vec{q}}{(2p)^3}\left[\frac{f_{ext}(\vec{q})}{e(\vec{q})} - f_{ext}(\vec{q})\right]e^{i\vec{q}\cdot\vec{r}} \approx \frac{c}{r^3}\cos 2k_F r$$



Slower decay with Friedel oscillation

- The NN distance R in fcc metal = $a/\sqrt{2}$, charge density $n = 4Z/a^3$

  $$2k_F R = 2(3\pi^2 n)^{1/3} a/\sqrt{2} \approx 7Z^{1/3}$$

  Thus, the screening charge around a charge impurity oscillates more rapidly in Al (Z=3) than in Cu (Z=1)
- According to Blandin and Deplante, two NN Zn impurities in Cu would repel, while in Al they would attract each other!
  May explain why Zn in Cu tend to order at low T, while Zn in Al precipitates
- Similar oscillation is observed in magnetic system (with magnetic impurities), and is called RKKY oscillation. (1954+)

Frequency-dependent Lindhard screening

Related to plasma oscillation, Cooper pair formation (chap26)… etc

$$\chi(\vec{q},\omega) = -\frac{2e^2}{V}\sum_{\vec{k}} \frac{f_{\vec{k}-\vec{q}/2} - f_{\vec{k}+\vec{q}/2}}{\varepsilon_{\vec{k}+\vec{q}/2} - \varepsilon_{\vec{k}-\vec{q}/2} \boxed{+\hbar\omega}}$$

Again consider long wave length limit (with finite ω)

$$\chi(\vec{q}) \approx -\frac{2e^2}{V}\sum_{\vec{k}} \frac{(\hbar^2/m)\vec{q}\cdot\vec{k}\,(-\partial f_{\vec{k}}/\partial\varepsilon)}{(\hbar^2/m)\vec{q}\cdot\vec{k} + \hbar\omega}$$

$$\approx e^2\left(\frac{\hbar}{m\omega}\right)^2 \int \frac{d^3\vec{k}}{4\pi^2}\left(\vec{k}\cdot\vec{q}\right)^2\left(-\frac{\partial f}{\partial\varepsilon}\right)$$

$$= \frac{2e^2}{m\omega^2}\frac{k_F^3 q^2}{3\pi^2}$$

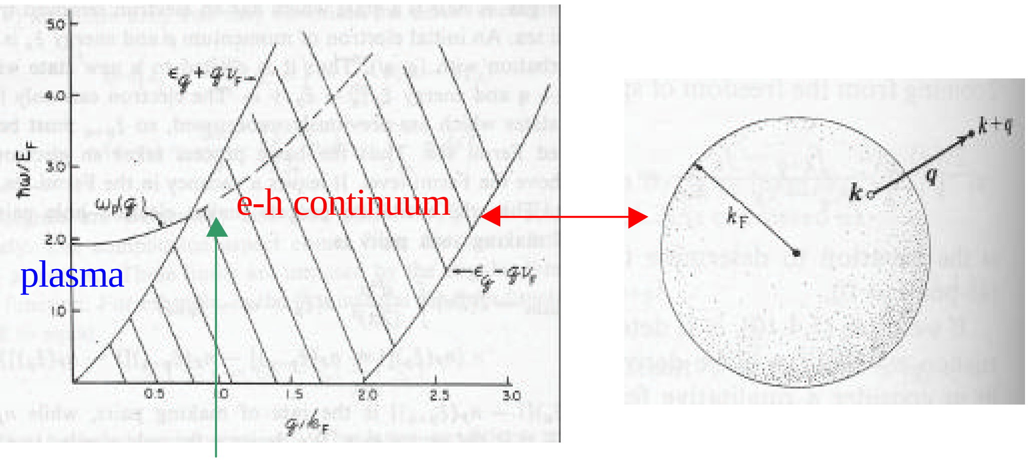
$$\Rightarrow \varepsilon(\vec{q},\omega) = 1 - \frac{4\pi n e^2/m}{\omega^2} = 1 - \frac{\omega_p^2}{\omega^2}.$$

This is the same as the classical result derived in Eq.(1.37)! (q→0)

Next order correction from finite q gives the energy dispersion for plasma wave (let ε=0)

$$\omega(\vec{q}) = \omega_p \quad 1 + \frac{3}{10}\frac{q^2 v_F^2}{\omega_p^2} + \cdots$$

Collective excitation vs quasiparticle (e-h pair) excitation in metal



plasma excitation decays into pair excitations

Low dimensional electron gas (2D and 1D)

Two-dimensional electron gas (2DEG)

According to F. Stern (PRL, 1967)

$$c(\vec{q}) = \begin{cases} -\dfrac{2me^2}{h} & if\ q \le 2k_F \\ -\dfrac{2me^2}{h}\ 1-\sqrt{1-\ 2k_F/q\ ^2} & if\ q > 2k_F \end{cases}$$

$$e(\vec{q}) = \begin{cases} 1+\dfrac{k_0}{q} & if\ q \le 2k_F \\ 1+\dfrac{k_0}{q}\ 1-\sqrt{1-\ 2k_F/q\ ^2} & if\ q > 2k_F \end{cases}$$

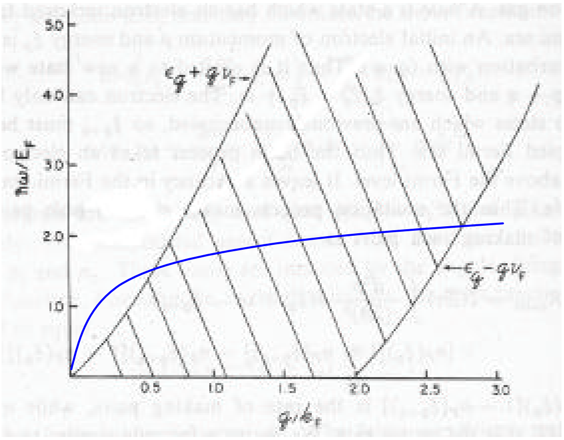
$$\Rightarrow \quad f(\vec{r}) = \int \frac{d^2\vec{q}}{(2p)^2}\frac{f_{ext}(\vec{q})}{e(\vec{q})}e^{i\vec{q}\cdot\vec{r}}$$

$$\approx \frac{Zek_0}{1+k_0/2k_F\ ^2}\frac{\sin(2k_Fr)}{(2k_Fr)^2} \quad \text{for } k_Fr >> 1$$

Similar Friedel oscillation with slightly different r-dependence

Again we can use time-dependent formalism to get the plasma dispersion. The result for long wavelength is

$$w_p^2 = \frac{2pne^2}{m}q + \frac{3}{4}q^2v_F^2 + O(q^3)$$

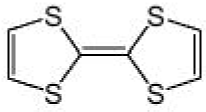


There is NO plasma gap!

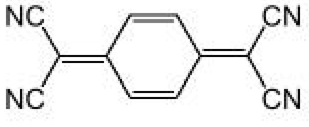
One-dimensional electron gas (according to A.J. Dekker's note)

Examples of 1D conductors: KDP, TTF-TCNQ… etc

TTF-TCNQ is an ionic salt that contains only C, H, S, N, which at about 60K has a conductivity close to copper's at room temperature. (discovered by A. Heeger in 1973)



Tetrathiofulvalene (TTF)
DONOR

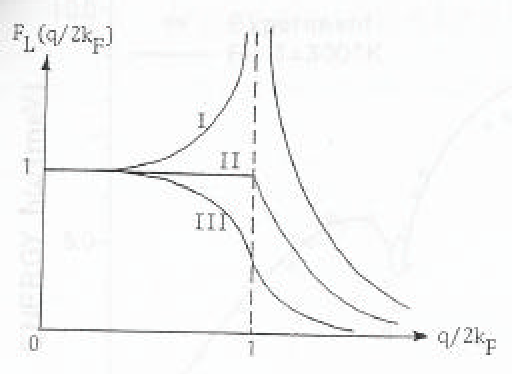


Tetracyanoquinodimethane (TCNQ)
ACCEPTOR

It can be shown that

$$c(q) = -\frac{e^2}{pq} \ln \frac{q+2k_F}{q-2k_F}$$ diverges at $q=2k_F$!

Dimensionality and susceptibility



It will be shown later (chap 26) that the electrons will respond to screen the charge variations due to ionic vibration (phonons)

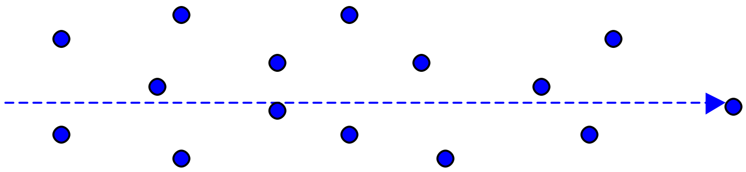
$$\text{phonon freq.} \quad \Omega^2(q) = \frac{\Omega_{pi}^2}{e(q)}$$

Therefore, such a divergence "softens" the phonon frequency at $q=2k_F$, and the lattice will spontaneously distort at this length scale. It is called Peierl's instability. For example, when the Bloch band is half filled ($k_F=\pi/2a$), the period of distortion is 2a. It explains the "dimerization" in conjugated polymers.

Pauli principle and e-e interaction near Fermi energy

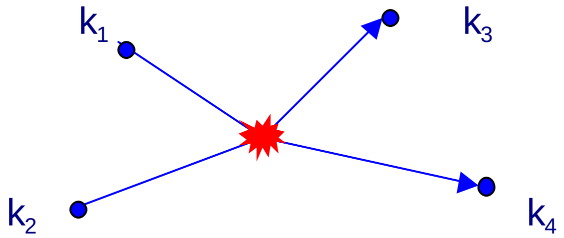
→ Average e-e separation in a metal is about 2 A

← Experiments find e mean free path about 10000 A (at 300K)



At 1 K, it can move 10 cm without being scattered! Why?

A scattering event:



calculate the e-e scattering rate using Fermi’s golden rule

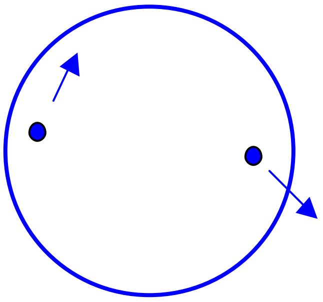
$$\frac{1}{t} = \frac{2p}{\hbar} \sum_{i,f} \left| \langle f | V_{e-e} | i \rangle \right|^2 d(E_i - E_f)$$

The scattering amplitude $\left| \langle f | V_{e-e} | i \rangle \right|^2 = \left| \langle k_3, k_4 | V_{e-e} | k_1, k_2 \rangle \right|^2$

The summation is over all possible initial and final states that obey energy and momentum conservation.

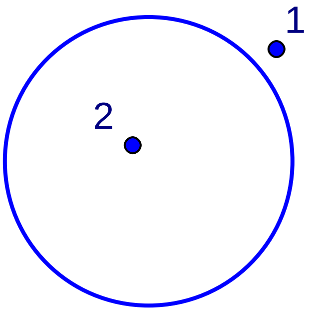
Pauli principle reduces available states for the following reasons:

- 2 e’s inside the FS cannot scatter with each other (energy conservation + Pauli principle)



one of them must be outside of the FS

- One e is “shallow” outside, the other is “deep” inside also cannot scatter with each other, since the 2nd e has nowhere to go



- If $|E_2| < E_1$, then $E_3+E_4 > 2E_F$

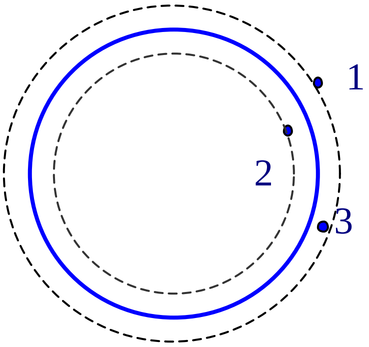
  But since $E_1+E_2 = E_3+E_4$, 3 and 4 cannot be very far from the FS when 1 is close to it.

  Let’s fix energy E_1, and study possible initial and final states

  Initial states $\propto$ the volume of the allowed E_2 shell

  Final states $\propto$ the volume of the E_3 shell

  (E_4 is uniquely determined)



phase space available $\propto k_F^2|k_1-k_F| \times k_F^2|k_3-k_F|$

$|k_1-k_F| \equiv \delta k_1$, then $\delta E_1 \propto k_F \delta k_1$

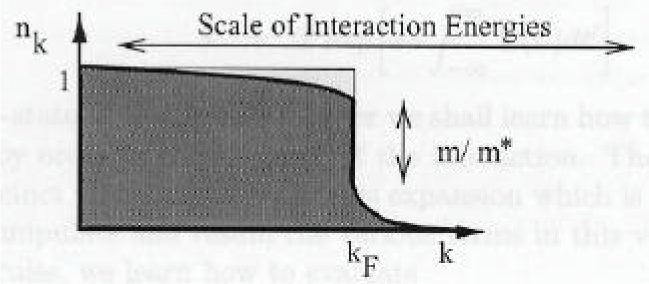
$\therefore$ available phase space $\propto E_F(\delta E_1)^2$

Total volume of FS $\propto (k_F^3)^2 \propto E_F^3$

Therefore, only $(\delta E_1/E_F)^2$ of all electrons participate e-e scatterings.

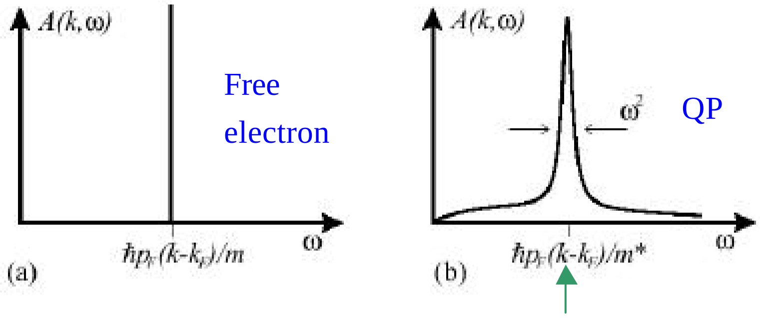
- At finite temperature T, E_1 electron is out there by thermal excitation. ∴ $\delta E_1 \approx KT$ = 1/40 eV at room temperature
  If E_F = 2.5 eV, then only 10^{-4} electrons participate scatterings
- It follows that the e-e scattering rate $\tau^{-1} \propto (\delta E_1)^2 \propto T^2$
  Usually need very low T (a few K) and very pure sample to eliminate thermal and impurity scatterings before the effect of e-e scattering can be observed.

Modification of the Fermi sea due to e-e interaction (T=0!)



- Even though the interaction energy is of the order of E_F, the Fermi surface is stabilized because of the Pauli principle.
- There is still a sharp jump (which defines the FS).
  Its magnitude Z (<1) is related to the effective mass of a QP.
  It is also related to the wave function overlap between a free electron and a QP at the FS.

- A QP can be viewed as an electron "dressed" by other electrons.
  A strongly interacting electron gas = a weakly interacting gas of QPs! (first suggested by Landau, 1957)
- It is a quasi-particle because, it has a finite life-time (collision time). Therefore, its spectral function has a finite width:



This peak sharpens as we get closer to the FS.