Density functional theory

Electron density contains all the inform of a many – electron wavefunction

$$n(r) = \langle \Psi | \sum_{\ell=1}^{N} \delta(r - R_\ell) | \Psi \rangle$$

$$= N \int dr_1 \ldots dr_N \, \delta(r_1 - r) \, \Psi^*(r_1 \ldots r_N) \Psi(r_1 \ldots r_N)$$

From $n(r)$ one can deduce $U(r)$ which uniq. determines $\Psi(r_1 \ldots r_N)$

Suppose $\exists$ two $U_1(r)$ and $U_2(r)$ that result in the same density (but dif wvfnc)

Ψ_1 is the ground state for U_1 and Ψ_2 is the g.s for U_2

$$\mathcal{E}_1 = \langle \Psi_1 | \mathcal{H}_1 | \Psi_1 \rangle < \langle \Psi_2 | \mathcal{H}_1 | \Psi_2 \rangle$$

$$\mathcal{E}_1 < \langle \Psi_2 | \mathcal{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \mathcal{H}_1 - \mathcal{H}_2 | \Psi_2 \rangle$$

$$\mathcal{E}_1 < \mathcal{E}_2 + \int dr \, n(r) \cdot [U_1(r) - U_2(r)]$$

$$\mathcal{E}_2 < \mathcal{E}_1 + \int dr \, n(r) \, [U_2(r) - U_1(r)]$$

$$\mathcal{E}_1 + \mathcal{E}_2 < \mathcal{E}_1 + \mathcal{E}_2 \quad \text{— contradiction}$$

Hence $\mathcal{E}[n] = E_{kin}[n] + U[n] + U_{ee}[n]$

$$F_{HK}[n] = T[n] + U_{ee}[n]$$

is a universal functional! It depends only on $n(r)$.

Thomas-Fermi-Dirac theory

Kinetic: $E_{kin} = n \cdot \frac{3}{5} E_F = V \frac{\hbar^2}{2m} \frac{3}{5} (3\pi^2)^{2/3} n^{5/3}$

Exchange: $- V n \frac{3}{4} \frac{e^2}{\pi} k_F = - V \cdot \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} e^2 n^{4/3}$

Direct: $\frac{1}{2} \int dr_2 \, dr_1 \frac{e^2 n(r_1) n(r_2)}{|r_1 - r_2|}$

$$\boxed{\begin{aligned} \mathcal{E}[n] = {} & \frac{\hbar^2}{2m} \frac{3}{5} (3\pi^2)^{2/3} \int dr \, n^{5/3} + \int dr \, n(r) \, U(r) \\ & - \int dr \, \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} e^2 n^{4/3}(r) \\ & + \frac{1}{2} \int dr_2 \, dr_1 \frac{e^2 n(r_1) n(r_2)}{|r_1 - r_2|} \end{aligned}}$$

Kohn–Sham equations

TFD neglects the role of high gradients in kinetic energy → use $E_{kin}[n]$ from the noninteracting electrons

KS eqs

$$-\frac{\hbar^2}{2m}\nabla^2\psi_e(r) + \left[U(r) + \int dr' \frac{e^2 n(r')}{|r-r'|} + \frac{\partial \mathcal{E}_{xc}}{\partial n}\right]\times$$

$$\times\,\psi_e(r) = \varepsilon_e \psi_e(\vec{r})$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_e(r) + \left[U(r) + \int dr' \frac{e^2 n(r')}{|r-r'|} - e^2\left(\frac{3}{\pi}n\right)^{1/3}\right]\times$$

$$\times\,\psi_e(r) = \varepsilon_e \psi_e(r)$$

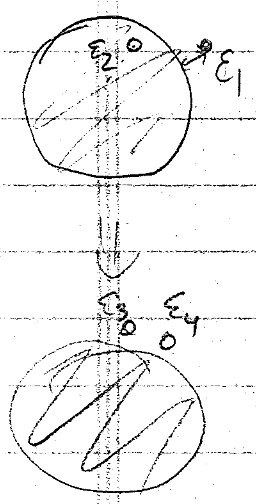
Landau hypothesis

the energy spetrum of an interacting Fermi liquid is very similar to the spectrum of an ideal Fermi gas The classification Of the energy levels remains uchanged when the interactions is gradually switched on. The role of gas particles is taken by elementary quasiparticles, whose # is eq to the el. # and that have Fermi statistics.

Landau FL theory

① The energies of one electron levels are modified (like in HF)

② There is a qp scattering but it is small close to the FS



$\varepsilon_1 > \varepsilon_F$

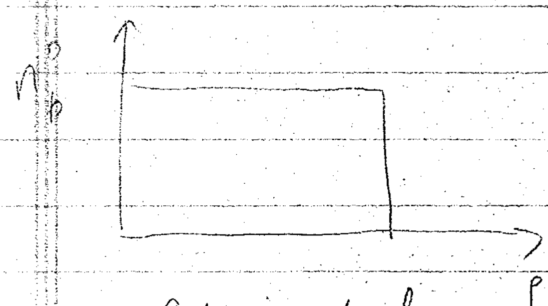
$\varepsilon_2 < \varepsilon_F$

$\varepsilon_3 > \varepsilon_F$

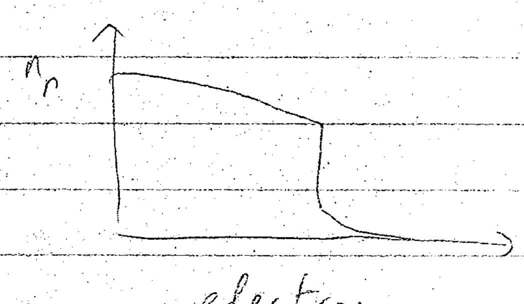
$\varepsilon_4 > \varepsilon_F$

When $\varepsilon_1 \to \varepsilon_F$ there is no phase space for scattering

$$\frac{1}{\tau} \simeq a \cdot (\varepsilon_1 - \varepsilon_F)^2 + b \cdot (k_B T)^2$$



quasiparticles



electrons

$$\boxed{F = F_0 + \sum_p (\varepsilon_p - \mu)\,\delta n_p + \frac{1}{2V} \sum_{pp'\sigma\sigma'} f_{p\sigma p'\sigma'}\,\delta n_{p\sigma}\,\delta n_{p'\sigma'}}$$