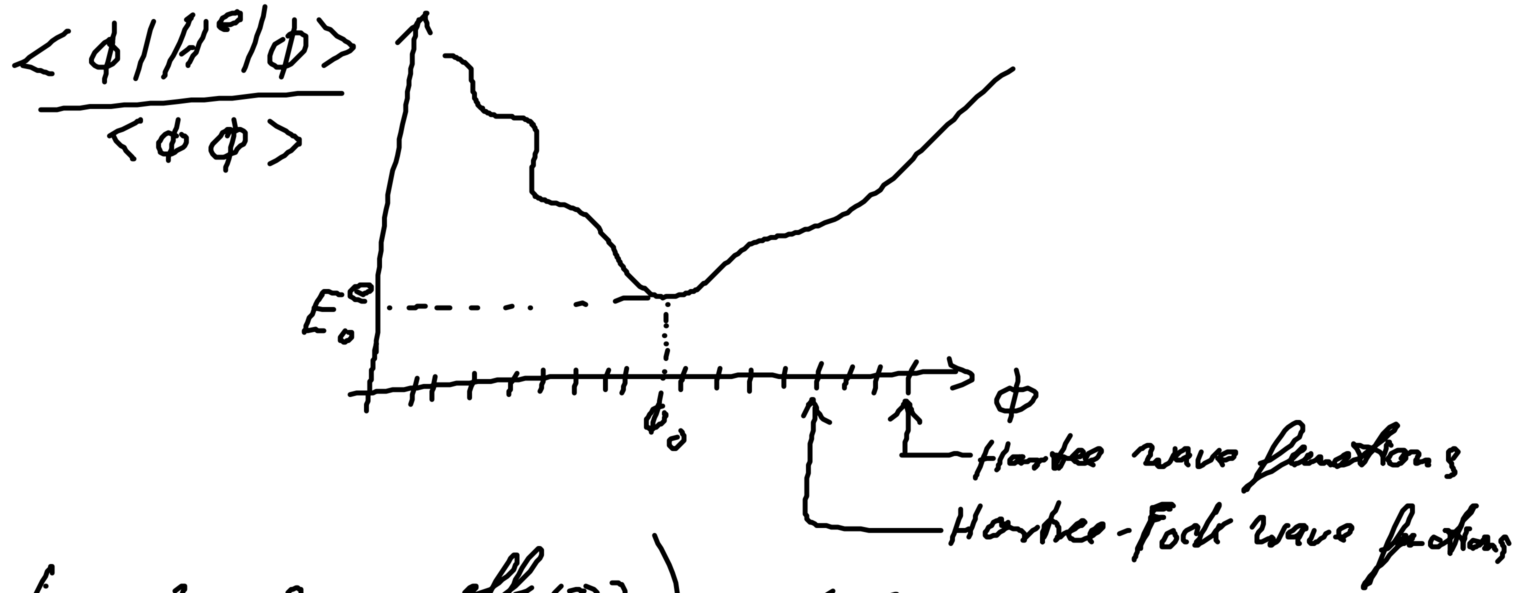
Reminder



$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_k^{eff}(\vec{r}) \right) \varphi_{0_k}(\vec{r}) = \epsilon_{0_k} \varphi_{0_k}(\vec{r})$$

ϕ^{HF} = single Slater Determinant built from $\varphi_{0_k}(\vec{r}) \chi_{s_k}$

3.4 Exchange Interaction

~~What~~ is it? and what is missing.

$$H = \frac{-\hbar^2}{2m}\nabla^2 + v(\vec r) + v^{Hartree}(\vec r)$$

$$+ \begin{cases} \dfrac{-e^2}{4\pi\varepsilon_0}\displaystyle\int \dfrac{n_k^H(\vec r\,')}{|\vec r - \vec r\,'|} d^3\vec r\,' = v^{SIC} \equiv \text{Hartree theory} \\ \dfrac{-e^2}{4\pi\varepsilon_0}\displaystyle\int \dfrac{n_k^{HF}(\vec r, \vec r\,')}{|\vec r - \vec r\,'|} d^3\vec r\,' \equiv v_k^x(\vec r) \equiv \text{Hartree Fock theory} \end{cases}$$

with $n_k^H(\vec r) = |\varphi_{0k}(\vec r)|^2$

$$n_k^{HF}(\vec r, \vec r\,') = \sum_{i=1}^{N} \delta_{s_i s_k} \frac{\varphi^*_{0_i s_i}(\vec r\,')\,\varphi_{0_k s_k}(\vec r\,')\,\varphi_{0_i s_i}(\vec r)}{\varphi_{0_k s_k}(\vec r)}$$

We have "sum rules"

$$\int n_k^H(\vec r\,')\, d^3\vec r\,' = 1$$

$$\int n_k^{HF}(\vec r, \vec r\,')\, d^3\vec r\,' = 1$$

Both densities represent one electron. In both cases the SI is corrected.

n_k^{HF} contains more

$\Uparrow$ we look jellium

$v(\vec r) = \text{const.}$

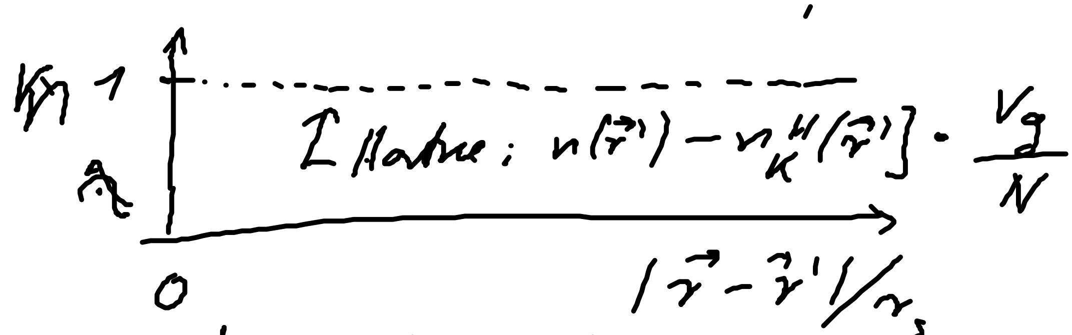
solutions of HF theory = plane waves

$$\varphi_{0_i}(\vec r) = \frac{1}{\sqrt{V_g}} e^{i\vec k_i \cdot \vec r}$$

$$v^H = \frac{e^2}{4\pi\varepsilon_0}\int \frac{n(\vec r\,')}{|\vec r - \vec r\,'|} d^3 r'$$

$$n_k^H(\vec r) = \frac{1}{V_g} = \text{const.}$$

if particle k is at position $\vec r$, where are the other "electrons"? $n(\vec r\,') - n_k^H(\vec r\,') = \frac{N}{V_g} - \frac{1}{V_g}$



Distribution of the $N-1$ other electrons.

r_s = density parameter $= \frac{4}{3}\pi r_s^3 = \frac{V_g}{N} = \frac{1}{n}$

Now Hartree - Fock

$$n(\vec{r}') - n_k^{HF}(\vec{r}, \vec{r}')$$

$$n_k^{HF}(\vec{r}, \vec{r}') = \sum_{i=1}^{N} \delta_{s_i s_k} \frac{\varphi^*_{0_i s_i}(\vec{r}')\,\varphi_{0_k s_k}(\vec{r}')\,\varphi_{0_i s_i}(\vec{r})}{\varphi_{0_k s_k}(\vec{r})}$$

$$= \sum_{\vec{k}_i}^{N/2} \frac{1}{V_g}\, e^{i(\vec{k}_i - \vec{k}_k)(\vec{r} - \vec{r}')}$$

* non-magnetic = every $\vec{k}_i$ state is occupied with 2 electrons.

* average over all states.

$$\bar{n}^{HF}(\vec{r}, \vec{r}') = \sum_{k=1}^{N} \frac{\langle \varphi_k | n_k^{HF} | \varphi_k \rangle}{n(\vec{r})}$$

$$= \frac{V_g}{N} \frac{1}{V_g} \frac{1}{V_g}\, 2 \sum_{\vec{k}_k}^{N/2} e^{-i\vec{k}_k(\vec{r} - \vec{r}')}$$

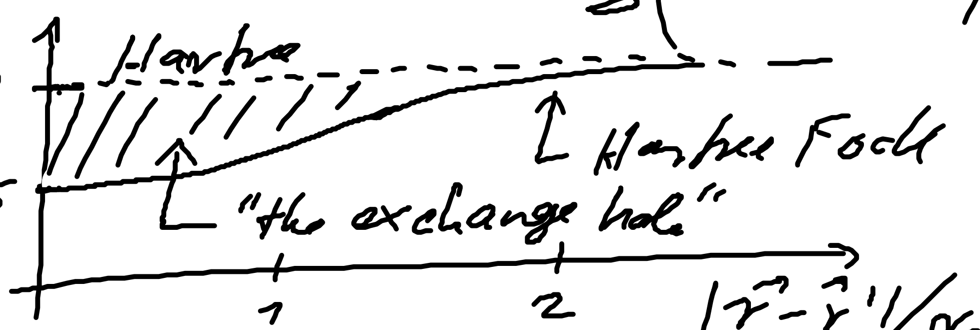
$$\times \sum^{N/2} e^{i\vec{k}_i(\vec{r} - \vec{r}')}$$

$$\sum_{k_i}^{N/2} \longrightarrow \int_0^{k_F} \frac{V_g}{(2\pi)^3}\, d^3\vec{k}_i \quad \text{// integral table}$$

$$\frac{V_g}{(2\pi)^3} \int_0^{k_F} e^{i\vec{k}(\vec{r}-\vec{r}\,')}\, d^3\vec{k} = \quad \text{//} \ \hat{r} = \vec{r}-\vec{r}\,'$$

$$= \frac{3}{2} N \frac{(k_F \hat{r})\cos(k_F\hat{r}) - \sin(k_F\hat{r})}{(k_F\hat{r})^3}$$

$$\Rightarrow \bar{n}^{HF}(\vec{r},\vec{r}\,') = \frac{9}{2}\frac{N}{V_g}\left(\frac{k_F\hat{r}\cos - \sin}{k_F\hat{r}}\right)^2$$



Distribution of all other electrons if the considered electron is at position $\vec{r}$.

$\Rightarrow$ at position $\vec{r}$: 50% of the electrons are repelled. $\equiv$ Pauli principle

$\equiv$ result of "dynamical Pauli correlation"

$\equiv$ like a person in a crowd

what is missing in HF?

$\Rightarrow$ coulomb correlation.

<u>now</u> inspect $v_k^x(\vec{r}) =$

$$= \frac{-e^2}{4\pi\varepsilon_0} \int \frac{n_k^{HF}(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|} d^3\vec{r}'$$

$$= \frac{-e^2}{4\pi\varepsilon_0} \frac{1}{(2\pi)^3} \int_0^{k_F} \int \frac{e^{i(\vec{k}'-\vec{k})\hat{r}}}{\hat{r}} d^3k\, d^3\vec{r}$$

$$\frac{1}{|\vec{r}-\vec{r}'|} = 4\pi \frac{1}{(2\pi)^3} \int \frac{e^{i\vec{q}(\vec{r}-\vec{r}')}}{q^2} d\vec{q}$$

$$\Rightarrow \boxed{v_k^x = \frac{-e^2}{4\pi\varepsilon} \frac{4\pi}{(2\pi)^3} \int \frac{1}{|\vec{k}-\vec{k}'|^2} d^3\vec{k}}$$

<u>we used</u>

$$\int e^{i(\vec{q}-\vec{k}+\vec{k}')\hat{r}} d^3\hat{r} \overset{\circ}{=} (2\pi)^3 \delta(\vec{q}+\vec{k}-\vec{k}')$$

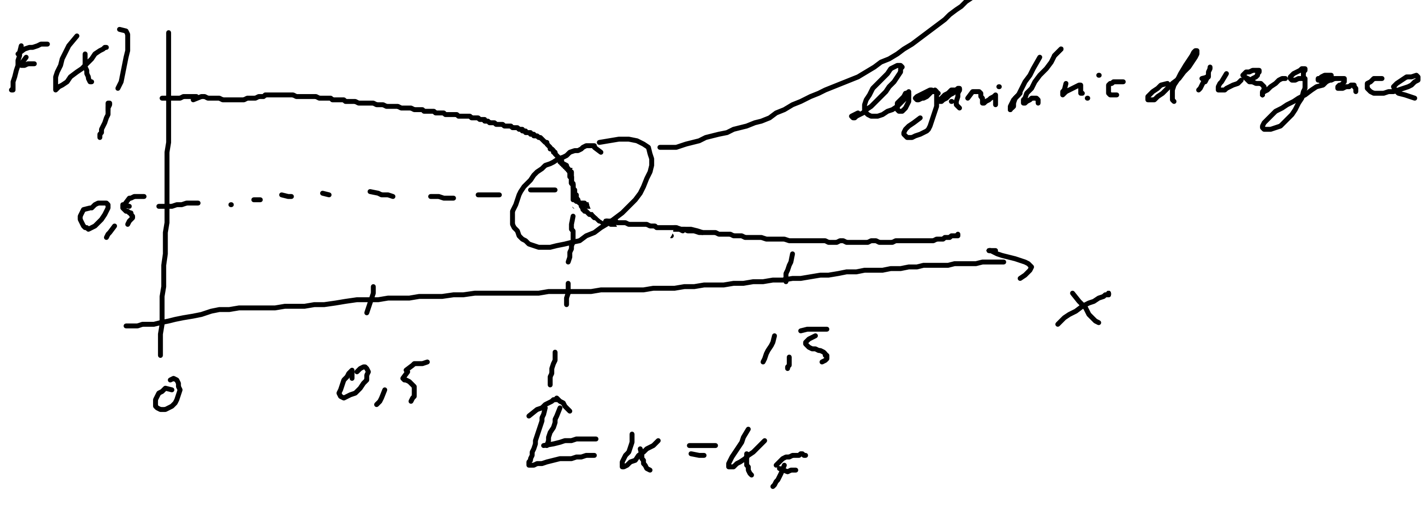
doing this last $\vec{k}$ integration

→ inspect the integral table

$$\Rightarrow v_k^x(\vec{r}) = \frac{-e^2}{4\pi\varepsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right)$$

with

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



the HF eigenvalues:

$$\langle \varphi_k | h | \varphi_k \rangle = \epsilon(\vec{k})$$ for jellium

$$= \frac{\hbar^2}{2m} k^2 + \langle \varphi_k | v^x_k | \varphi_k \rangle$$

again setting the energy zero such that

$$v(\vec{r}) + v^{Hartree}(\vec{r}) \overset{!}{=} \text{zero}$$

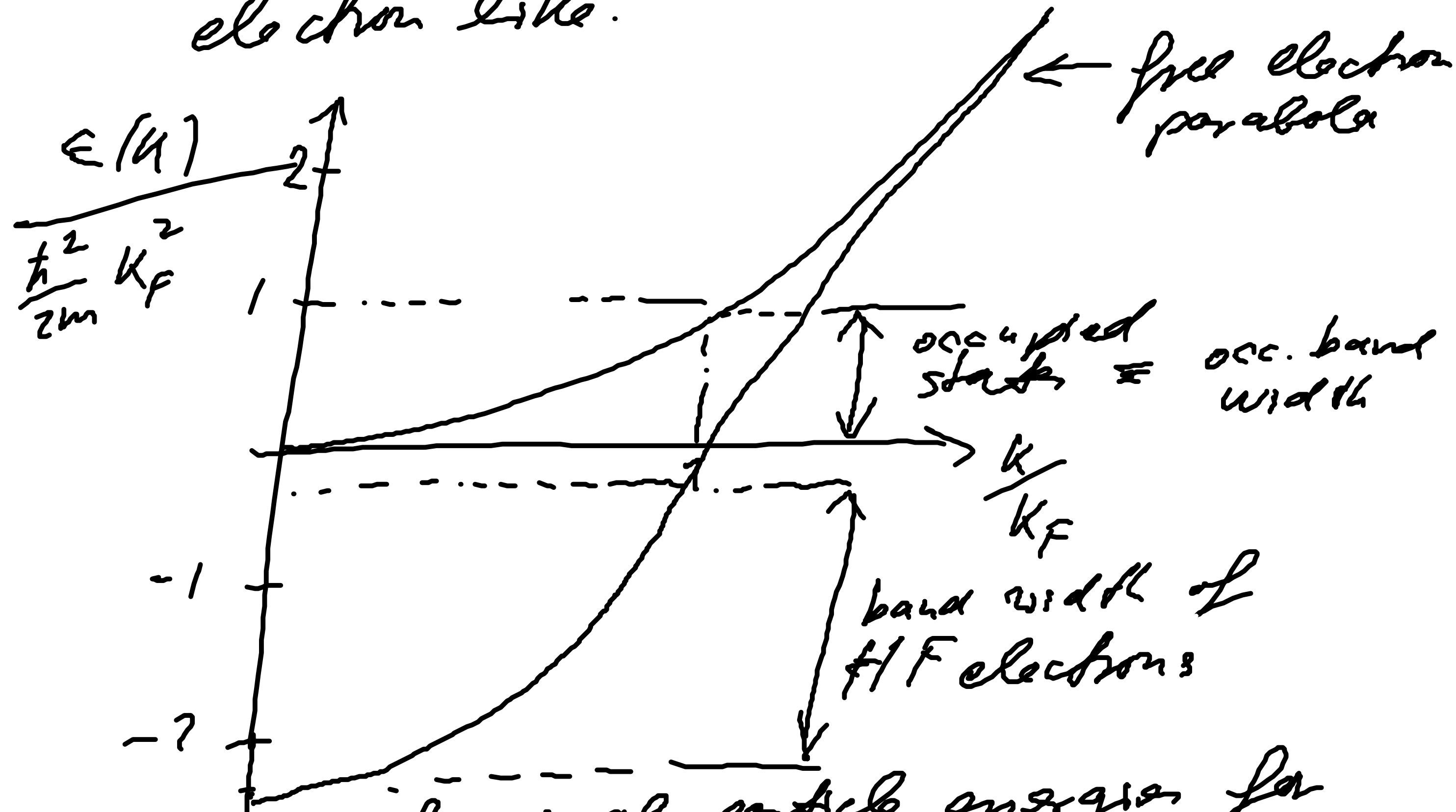
$$\langle \varphi_k | v^x_k | \varphi_k \rangle = v^x_k \langle \varphi_k | \varphi_k \rangle =$$

$$\epsilon(k) = \underbrace{\frac{\hbar^2}{2m} k^2}_{\text{free electron}} + \underbrace{\frac{-e^2}{4\pi\varepsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right)}_{\text{modification}}$$

→ plane waves diagonalize the HF single particle hamilton

→ $\epsilon(\vec{k})$ is no longer free

electron like.



Dispersion of single particle energies for jellium, with $r_s = 4$ bohr

Conclusion:

1) $\vec{k} \to 0$

$$\epsilon^{HF}(\vec{k}) = \frac{\hbar^2}{2m^*} k^2 + C$$

$$\frac{m^*}{m} = \frac{1}{1 + 0{,}22\left(r_s/a_B\right)} \quad \| \; m^* \text{ is smaller than } m$$

2) bandwith of occupied states is very different;

3) $k \to k_F$: $\frac{d\epsilon}{dk} \to \infty$

Problems for analyzing conductivity and specific heat.

Origin of this failure: $\frac{1}{|\vec{r} - \vec{r}'|}$ Singularity for screened Coulomb potential

$$\frac{e^{-\lambda|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}$$

the problem would not occur

4) size of v_k^x : $5 - 15\,eV$

typically what counts is $\approx 0{,}1 - 0{,}5\,eV$

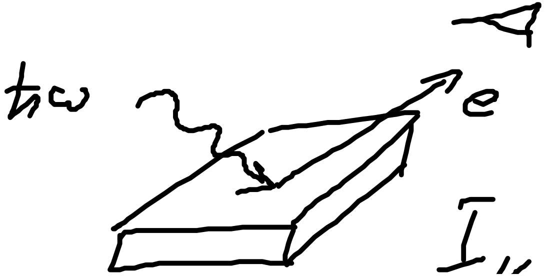
3.5 Koopmans' theorem

physical meaning of $\epsilon(k)$ in HF theory

dimension of $\epsilon(k)$ = energy

meaning : Lagrange multiplier

I_k = ionization energy = energy to remove the k-th electron



$$I_k = E^{N-1} - E^N$$

$$\langle \phi^{N-1} | H^{e,N-1} | \phi^{N-1} \rangle - \langle \phi^{N} | H^{e,N} | \phi^{N} \rangle$$

HF-theory $\equiv$ ϕ $\equiv$ single Slater det.

assume the $\varphi_{o_k s_k}$ that build ϕ^{N-1} are the same as those for ϕ^{N}.

Difference between ϕ^{N-1} & ϕ^{N} $\equiv$ in ϕ^{N-1} one row and one column is missing — φ_{o_k}

... exercise

$$\Rightarrow \boxed{I_k = - \epsilon_{o_k s_k}} \Leftarrow$$ Result with assumption

Koopmans' theorem