Electron - Electron Interaction

Recall:

$$H^e \Phi_\nu(\{\underline{r}_i \sigma_i\}) = E_\nu \Phi_\nu(\{\underline{r}_i \sigma_i\})$$

$$H^e = -\frac{\hbar^2}{2m}\sum_{k=1}^{N} \nabla_{\underline{r}_k}^2 + \sum_{k=1}^{N} v(\underline{r}_k) + \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0} \underbrace{\sum_{\substack{k,k' \\ k\neq k'}}^{N\,N} \frac{1}{|\underline{r}_k - \underline{r}_{k'}|}}_{\text{this makes life complicated}}$$

Hartree: Try simple product wave function anyway

$$\rightarrow \left(-\frac{\hbar^2}{2m}\underline{\nabla}^2 + v(\underline{r}) + \frac{e^2}{4\pi\varepsilon_0}\int d^3r' \frac{n(\underline{r}')}{|\underline{r}-\underline{r}'|} - \frac{e^2}{4\pi\varepsilon_0}\int d^3r' \frac{|\varphi_{0i}(\underline{r}')|^2}{|\underline{r}-\underline{r}'|}\right)\varphi_{0i}(\underline{r})$$

$$= \varepsilon_{0i}\,\varphi_{0i}(\underline{r})$$

much simpler – but not enough!

How can we do better?

Hartree-Fock theory

Fermions: No two electrons may occupy the <u>same</u> spatial and spin states.

Fulfill by antisymmetric wave fn.:

$$\Phi_\nu(\underline{r}_1\sigma_1, \ldots, \underline{r}_i\sigma_i, \ldots, \underline{r}_j\sigma_j, \ldots, \underline{r}_N\sigma_N) =$$

$$= -\Phi(\underline{r}_1\sigma_1, \dots, \underline{r}_j\sigma_j, \dots, \underline{r}_i\sigma_i, \dots, \underline{r}_N\sigma_N)$$

Simplest (?) separable form for this: Slater Determinant

$$\Phi^{HF}(\{\underline{r}_i\sigma_i\}) = \frac{1}{\sqrt{N!}} \cdot \begin{vmatrix} \varphi_{o_1 s_1}(\underline{r}_1\sigma_1) & \cdots & \varphi_{o_N s_N}(\underline{r}_1\sigma_1) \\ \vdots & & \vdots \\ \varphi_{o_1 s_1}(\underline{r}_N\sigma_N) & \cdots & \varphi_{o_N s_N}(\underline{r}_N\sigma_N) \end{vmatrix}$$

Notes: - For N electrons, need at least N different <u>functions</u>

labelled by
- quantum number o_N (e.g. (k_1, k_2, k_3) from Jellium)
- spin state ($\uparrow$ or $\downarrow$)

Two-electron system:

$$\Phi^{HF} = \frac{1}{\sqrt{2}} \left(\varphi_1(\underline{r}_1\sigma_1)\varphi_2(\underline{r}_2\sigma_2) - \varphi_1(\underline{r}_2\sigma_2)\varphi_2(\underline{r}_1\sigma_1) \right)$$

Orthonormality of $\langle \varphi_{o_i s_i} | \varphi_{o_j s_j} \rangle = \delta_{o_i o_j} \cdot \delta_{s_i s_j}$

$\longrightarrow$ This ensures $\langle \Phi^{HF} | \Phi^{HF} \rangle = 1$!

Why 1, not N ?

$\int d^3r \, n(\underline{r}) = N$, but $n(\underline{r}) = \sum_{k=1}^{N} \langle \Phi | \delta(\underline{r} - \underline{r}_k) | \Phi \rangle$

One more: Cannot skip over spin this time

Product $\varphi_{o_i s_i}(\underline{r}\sigma) \rightarrow \varphi_{o_i s_i}(\underline{r}) \chi_{s_i}(\sigma_i)$

Spin functions ensure $\sum_\sigma \chi^*_{s_i}(\sigma)\chi_{s_j}(\sigma) = \delta_{s_i,s_j}$

Once again: Set up functional $E^{HF}[\Phi^{HF}]$ and apply variational principle.

$$E^{HF}[\Phi^{HF}] = \langle \Phi^{HF} | H^e | \Phi^{HF} \rangle$$

$$= \sum_{i=1}^{N} \sum_\sigma \int d^3r \; \varphi^*_{o_i s_i}(\underline{r}\sigma) \left\{ -\frac{\hbar^2}{2m}\nabla^2 + v(\underline{r}) \right\} \varphi_{o_i s_i}(\underline{r}\sigma)$$

$$+ \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0} \sum_{\substack{i,j \\ i\neq j}}^{N\,N} \sum_{\sigma\sigma'} \int d^3r\, d^3r' \; \frac{\varphi^*_{o_i s_i}(\underline{r}'\sigma')\varphi^*_{o_j s_j}(\underline{r}\sigma)\varphi_{o_i s_i}(\underline{r}'\sigma')\varphi_{o_j s_j}(\underline{r}\sigma)}{|\underline{r}-\underline{r}'|},$$

$$- \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0} \sum_{\substack{i,j \\ i\neq j}}^{N\,N} \sum_{\sigma\sigma'} \int d^3r\, d^3r' \; \frac{\varphi^*_{o_i s_i}(\underline{r}\sigma)\varphi^*_{o_j s_j}(\underline{r}'\sigma')\varphi_{o_i s_i}(\underline{r}'\sigma')\varphi_{o_j s_j}(\underline{r}\sigma)}{|\underline{r}-\underline{r}'|}$$

Note: $\varphi^*_{o_i s_i}(\underline{r}\sigma)\,\varphi_{o_i s_i}(\underline{r}'\sigma')$ does not break down to a simple density any more

Spin: What happens?

1. line: $\sum_\sigma \chi^*_{s_i}(\sigma)\chi_{s_i}(\sigma) = 1$

2. line: $\sum_{\sigma\sigma'} \chi^*_{s_i}(\sigma')\chi_{s_i}(\sigma')\chi^*_{s_j}(\sigma)\chi_{s_j}(\sigma)$

$= 1 \cdot 1 = 1$

3. line: $\sum_{\sigma\sigma'} \chi^*_{s_i}(\sigma)\chi_{s_i}(\sigma')\chi^*_{s_j}(\sigma')\chi_{s_j}(\sigma)$

$$= \delta_{s_i, s_j}$$

Last line becomes:

$$\tilde{E}^x[\{\varphi^*_{0_i s_i}, \varphi_{0_i s_i}\}] =$$

$$-\frac{1}{4\pi\epsilon_0}\frac{e^2}{2}\sum_{\substack{i,j \\ i \neq j}}^{NN'} \delta_{s_i s_j} \int d^3r\, d^3r' \frac{\varphi^*_{0_i s_i}(\underline{r})\varphi^*_{0_j s_j}(\underline{r}')\varphi_{0_i s_i}(\underline{r}')\varphi_{0_j s_j}(\underline{r})}{|\underline{r}-\underline{r}'|}$$

"exchange term"

$E^{HF}[\bar{\Phi}^{HF}]$ is a sum of

$$T_s[\{\varphi^*_{0_i s_i}, \varphi_{0_i s_i}\}] = \sum_{i=1}^{N} \int d^3r\, \varphi^*_{0_i s_i}(\underline{r})\left(-\frac{\hbar^2}{2m}\underline{\nabla}^2\right)\varphi_{0_i s_i}(\underline{r})$$

$$E^{e-ion}[\ldots] = \int d^3r\, n(\underline{r}) \cdot v(\underline{r})$$

$$E^{Hartree}[\ldots] = \frac{1}{2}\frac{e^2}{4\pi\epsilon_0}\int d^3r \frac{n(\underline{r})\,n(\underline{r}')}{|\underline{r}-\underline{r}'|}$$

$$E^x[\ldots] = -\frac{1}{2}\frac{e^2}{4\pi\epsilon_0}\sum_{i,j}^{NN'} \delta_{s_i s_j}\int d^3r\, d^3r' \cdot$$

$$\cdot \frac{\varphi^*_{0i}(\underline{r})\varphi^*_{0j}(\underline{r}')\varphi_{0i}(\underline{r}')\varphi_{0j}(\underline{r})}{|\underline{r}-\underline{r}'|}$$

Now let's do physics:

variational principle

- with constraint $\langle \varphi_{o_i s_i} | \varphi_{o_j s_j} \rangle = \delta_{o_i s_i, o_j s_j}$

- and throw in a unitary transformation to get:

$$\Rightarrow \left\{ -\frac{\hbar^2}{2m} \underline{\nabla}^2 + V(\underline{r}) + V^{\text{Hartree}}(\underline{r}) + V_k^{x}(\underline{r}) \right\} \tilde{\varphi}_{o_k s_k}(\underline{r}) = \epsilon_{o_k s_k} \tilde{\varphi}_{o_k s_k}(\underline{r})$$

Like Hartree, this contains a term with an <u>explicit</u> k dependence

$$V_k^{x}(\underline{r}) \tilde{\varphi}_{o_k}(\underline{r}) = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N} \delta_{s_i s_k} \int d^3r' \left(\frac{\tilde{\varphi}^*_{o_i s_i}(\underline{r}') \varphi_{o_k s_k}(\underline{r}') \varphi_{o_i s_i}(\underline{r})}{|\underline{r} - \underline{r}'|} \right)$$

Why did I write <u>this</u> then?

Because we can <u>define</u>

$$V_k^x(\underline{r}) = -\frac{e^2}{4\pi\epsilon_0}\int d^3r' \, \frac{n^{HF}(\underline{r},\underline{r}')}{|\underline{r}-\underline{r}'|}$$

with
$$n^{HF}(\underline{r},\underline{r}') := \sum_{i=1}^{N} \delta_{s_i s_k} \frac{\tilde{\varphi}^*_{0is_i}(\underline{r}')\,\tilde{\varphi}_{0ks_k}(\underline{r}')\,\varphi_{0is_i}(\underline{r})}{\tilde{\varphi}_{0ks_k}(\underline{r})}$$

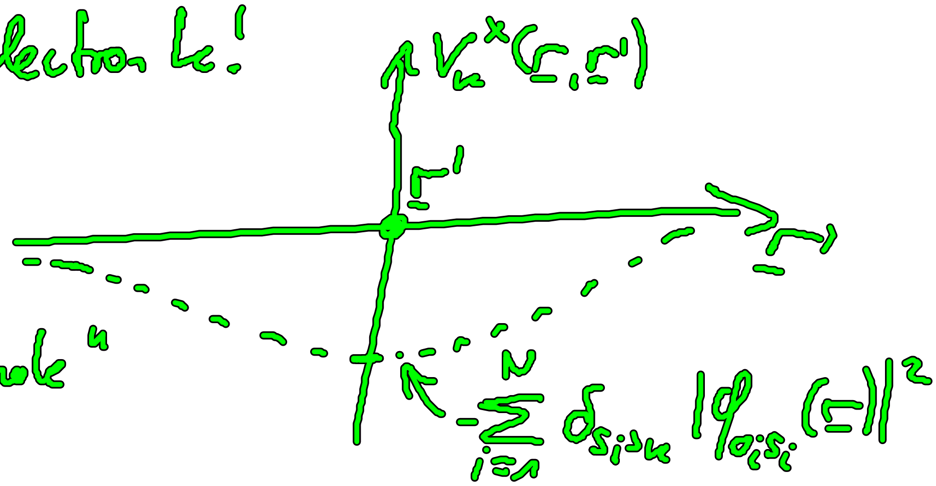
Now this (a) is a cheap trick?

(b) is maybe deeper than it looks??

(b): $n_k^{HF}(\underline{r},\underline{r}')$ <u>acts</u> like a charge density!

But depends on at <u>which</u> place $\underline{r}$ we look at electron k!

Schematic



"exchange hole"

Let's go investigate:

<u>The exchange interaction</u>

Recall : Single-particle Hamiltonian

$$h_k = -\frac{\hbar^2}{2m}\underline{\nabla}^2 + v(\underline{r}) + v^{\text{Hartree}}(\underline{r})$$

$$+ \begin{cases} -\dfrac{e^2}{4\pi\epsilon_0}\displaystyle\int d^3r' \, \dfrac{n_k^H(\underline{r}')}{|\underline{r}-\underline{r}'|} & \text{Hartree} \\[2ex] -\dfrac{e^2}{4\pi\epsilon_0}\displaystyle\int d^3r' \, \dfrac{n_k^{HF}(\underline{r},\underline{r}')}{|\underline{r}-\underline{r}'|} & \text{HF} \end{cases}$$

$$n_k^H(r') = |\varphi_{0k}(\underline{r}')|^2 \quad \text{from } V^{SIC}$$

easy to show

$$\int d^3r \, n_k^H(\underline{r}) = 1$$

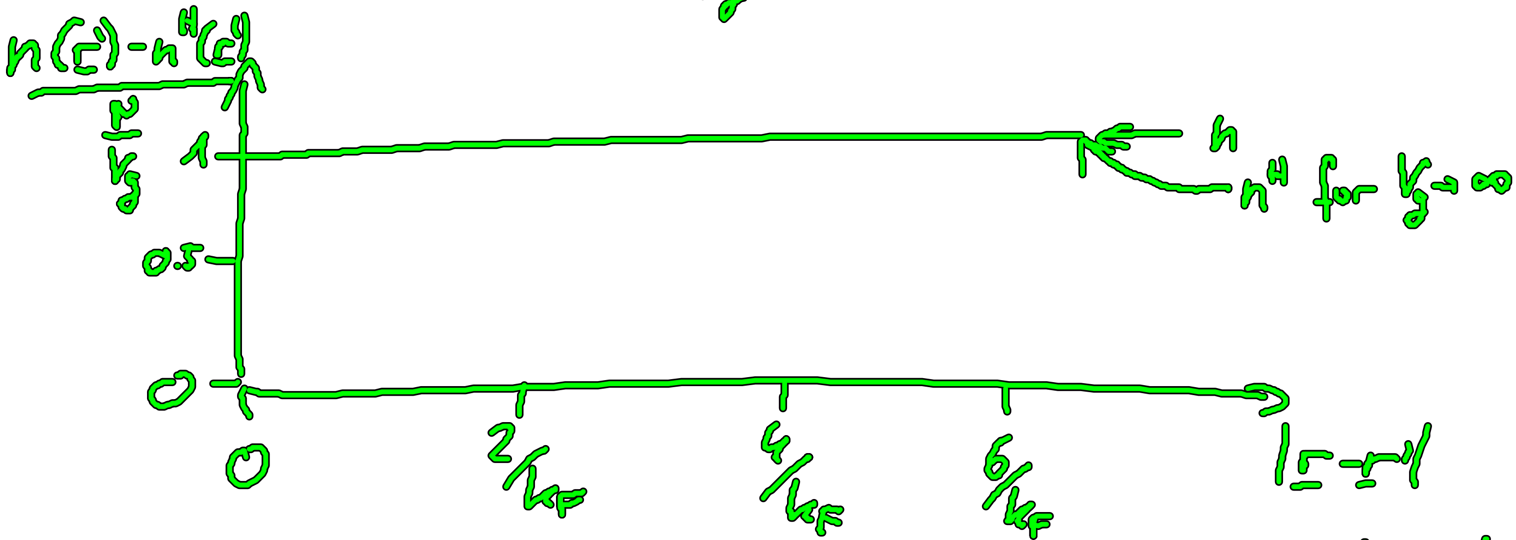
$$\int d^3r' \, n_k^{HF}(\underline{r},\underline{r}') = 1$$

one electron each!
no self-interaction.

Exchange-hole for Jellium

Set $v(\underline{r}) = \underline{\text{const.}}$; $\varphi_{0_i s_i} = \frac{1}{\sqrt{V_g}} e^{i\underline{k}_i\underline{r}_i}$

Hartree: $n_k^H(\underline{r}') = \frac{1}{V_g} = \text{const.}$



V^{sic} is negligible in extended systems!

Hartree-Fock:

Can we calculate $n_k^{HF}(\underline{r},\underline{r}')$?

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

$$= \sum_{i=1}^{\frac{N}{2}} \frac{1}{V_g} e^{-i\underline{k}_i\underline{r}'} e^{i\underline{k}_k\underline{r}'} e^{i\underline{k}_i\underline{r}} e^{-i\underline{k}_k\underline{r}}$$

non spin-polarized

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

This expression is:

- an average over all electrons i for <u>each</u> e^- k
- times a phase factor $e^{-i\underline{k}_k(\underline{r}-\underline{r}')}$

(Spherical) average: $\sum_i^{N/2} \longrightarrow \int_0^{k_F} \frac{V_g}{(2\pi)^3} d^3k$

$$\frac{V_g}{(2\pi)^3} \int_0^{k_F} d^3k \; e^{i\underline{k}(\underline{r}-\underline{r}')}$$

- spherical coords
- $(\underline{r}-\underline{r}')$ along z
- some substitutions
- $\int dx \, (x \cdot \sin x)$

<u>and</u> $k_F^3 = 3\pi \frac{N}{V_g}$

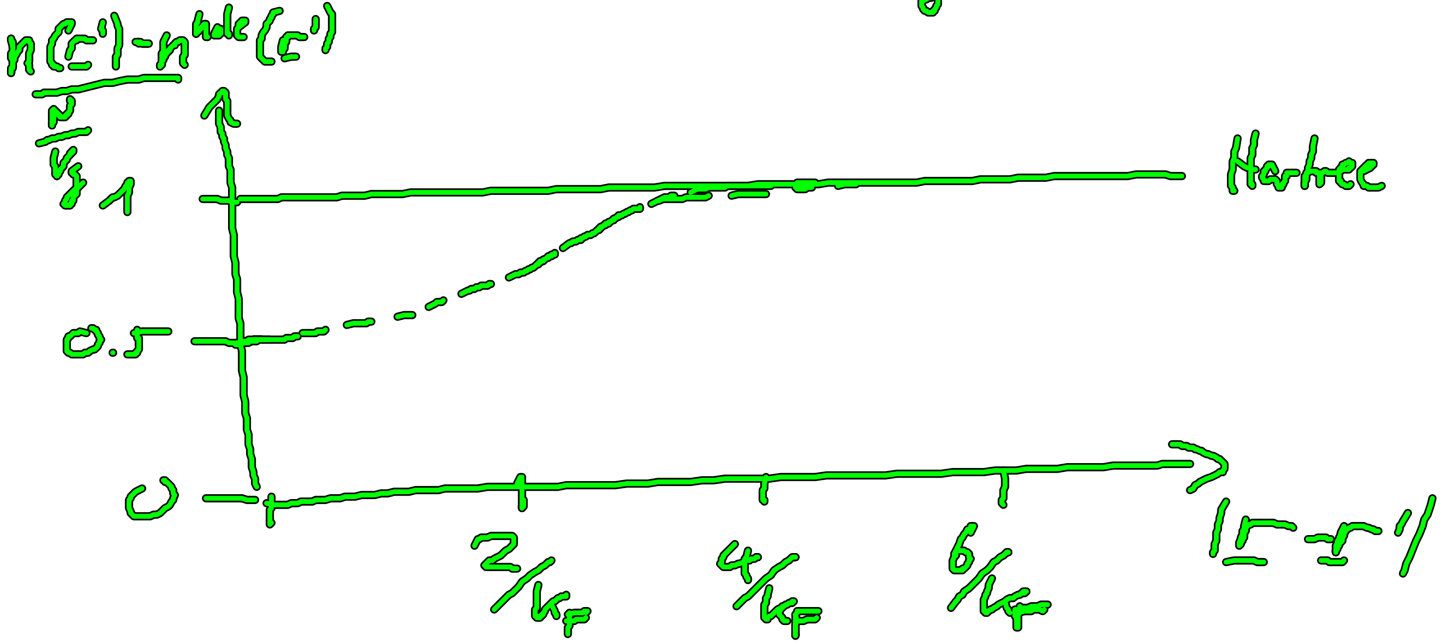
$$n_k^{HF}(\underline{r},\underline{r}') = \frac{1}{V_g} \cdot e^{-\underline{k}_k(\underline{r}-\underline{r}')} \cdot \frac{3}{2} N \cdot \frac{x\cos x - \sin x}{x^3}$$

$$x := k_F \cdot |\underline{r}-\underline{r}'|$$

Look at spherical average of

n_k^{HF} over all k

$$=: \overline{n_k^{HF}}(|\underline{r}-\underline{r}'|) = \frac{9}{2}\frac{N}{V_g}\left(\frac{\overbrace{x}^{k_F|\underline{r}-\underline{r}'|}\cos x - \sin x}{x^3}\right)^2$$



What about the exchange potential

$$V_k^x(\underline{r}) = -\frac{e^2}{4\pi\epsilon_0}\int d^3r' \, \frac{n_k^{HF}(|\underline{r}-\underline{r}'|)}{|\underline{r}-\underline{r}'|}$$

$$= -\frac{e^2}{4\pi\epsilon_0}\frac{1}{(2\pi)^3}\int^{k_F} d^3k' \int d^3(\underline{r}-\underline{r}')\,\frac{e^{i(\underline{k}'-\underline{k})(\underline{r}-\underline{r}')}}{|\underline{r}-\underline{r}'|}$$

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

note $\int d^3(\underline{r}-\underline{r}') \, e^{i(q-\underline{k}+\underline{k}')(\underline{r}-\underline{r}')}$

$$= (2\pi)^3 \, \delta(q \overset{?}{\pm} \underline{k}' \overset{?}{\mp} \underline{k})$$

$\rightarrow$ No more $\underline{r}-\underline{r}'$ in

$$V_{\underline{k}}^{x} = -\frac{1}{4\pi\varepsilon_0} \frac{4\pi}{(2\pi)^3} \underbrace{\int_0^{k_F} d^3k' \frac{1}{|\underline{k}-\underline{k}'|^2}}$$

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

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

Drawing: see script

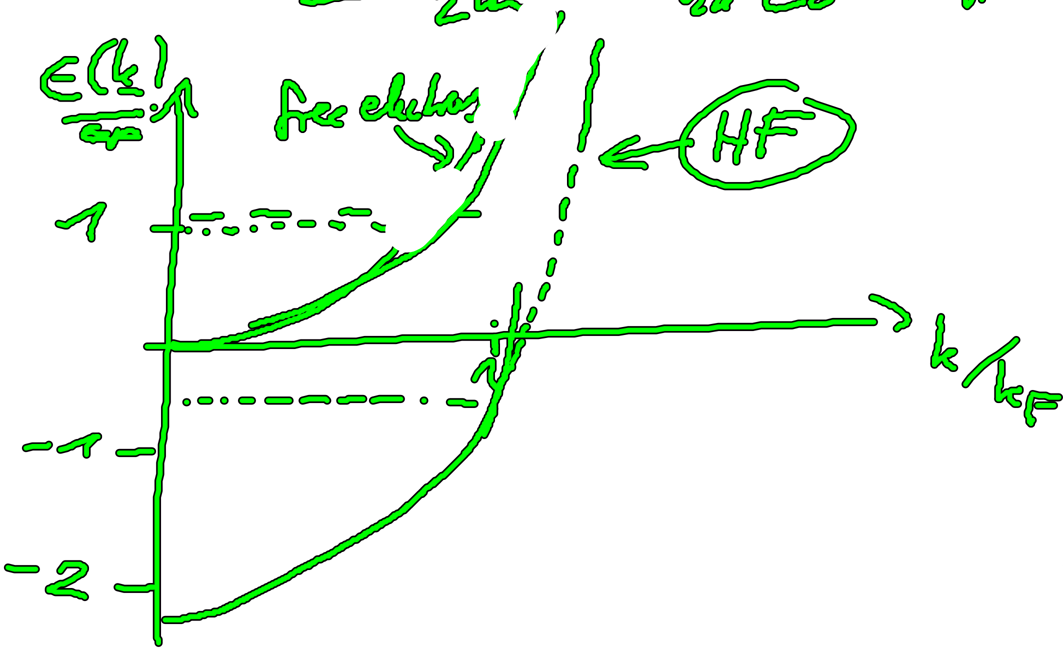
Now: The icing on the cake
(Why Hartree-Fock and metals do not get along)

HF eigenvalues:

$$\epsilon(\underline{k}) = \langle \varphi_{\underline{k}} | h^{el} | \varphi_{\underline{k}} \rangle$$

$$= \frac{\hbar^2 k^2}{2m} + \langle \varphi_{\underline{k}} | v_{\underline{k}}^{x} | \varphi_{\underline{k}} \rangle + \text{const.}$$

$$= \frac{\hbar^2 k^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right)$$



$$\left.\frac{\partial \epsilon^{HF}}{\partial k}\right|_{k=k_F} = \infty$$