

Hartree-Fock equations:

Approximation: assumed Slater-determinant form of wave function.

Result: spin-dependent non-local exchange potential, tends to align spins.

$$\varepsilon_i \varphi_i(r_1) = \frac{\hbar^2 \nabla^2}{2m} \varphi_i(r_1) + U_{ion}(r_1) \varphi_i(r_1) + \left[\sum_{j \neq i} \int d^3 r_2 \varphi_j^*(r_2) \varphi_j(r_2) \frac{e^2}{|r_2 - r_1|} \right] \varphi_i(r_1) - \sum_{j \neq i} \int d^3 r_2 \varphi_j^*(r_2) \varphi_i(r_2) \frac{e^2}{|r_2 - r_1|} \varphi_j(r_1) \delta_{s_1 s_2}$$

Hartree approx.

Exchange term

Counter-example:

“LCAO H₂ molecule”

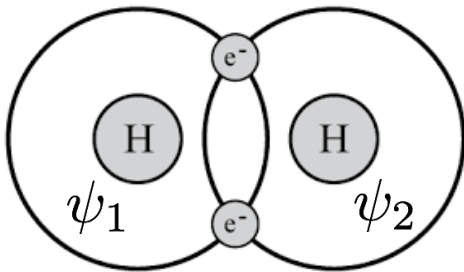
$$\psi_s = \psi_1 + \psi_2$$



With singlet spin state, has required anti-symmetry

$$\psi_s(r_1)\psi_s(r_2)(|+\rangle_1|-\rangle_2 - |-\rangle_1|+\rangle_2)$$

Slater; large probability both electrons coincide.



$$\left[\psi_1(r_1)\psi_2(r_2) + \psi_1(r_2)\psi_2(r_1) \right] (|+\rangle_1|-\rangle_2 - |-\rangle_1|+\rangle_2)$$

Non-Slater; “correlated” state, may be lower energy.

- General result for solids: Insulators often antiferromagnetic, spins anti-aligned
- Effect due to correlations; e.g. cobalt oxide (CoO) non-metallic but odd # electrons per cell, band picture breaks down.

Hartree-Fock equations:

Approximation: assumed Slater-determinant form of wave function.

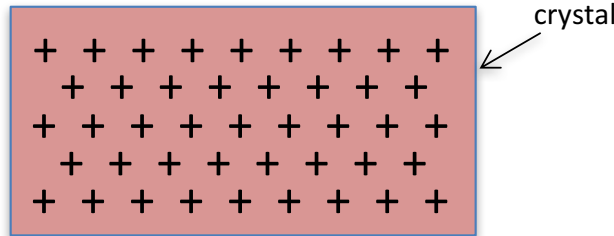
Result: spin-dependent non-local exchange potential

$$\varepsilon_i \varphi_i(r_1) = \frac{\hbar^2 \nabla^2}{2m} \varphi_i(r_1) + U_{ion}(r_1) \varphi_i(r_1) + \left[\sum_{j \neq i} \int d^3 r_2 \varphi_j^*(r_2) \varphi_j(r_2) \frac{e^2}{|r_2 - r_1|} \right] \varphi_i(r_1) - \sum_{j \neq i} \int d^3 r_2 \varphi_j^*(r_2) \varphi_i(r_2) \frac{e^2}{|r_2 - r_1|} \varphi_j(r_1) \delta_{s_1 s_2}$$

Hartree approx.

Exchange term

Simple plane wave solutions in 3D:

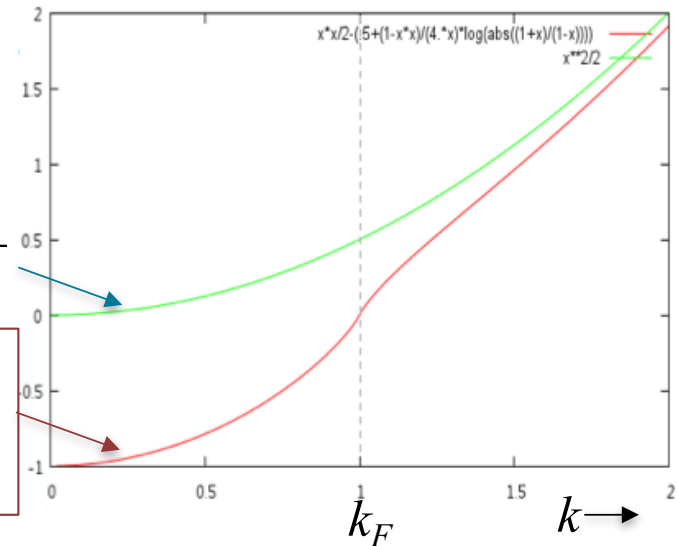


“Jellium” uniform positive background:

- Hartree Coulomb interaction terms cancel.
- Usual free-electron KE
- States fill spherical Fermi surface in k space.
- Total energy is sum of the single-state energies.

$$\varepsilon_o(k) \equiv \frac{\hbar^2 k^2}{2m}$$

with exchange energy



Hartree-Fock free-electron:

$$\begin{aligned}
 - \sum_{j \neq i} \int d^3 r_2 \varphi_j^*(r_2) \varphi_i(r_2) \frac{e^2}{|r_2 - r_1|} \varphi_j(r_1) \delta_{s_1 s_2} &= - \frac{e^2}{V} \int d^3 r' \frac{\sum_{k's'} e^{i\vec{k}' \cdot (\vec{r} - \vec{r}')} \delta_{s, s'}}{|\vec{r} - \vec{r}'|} \frac{e^{i\vec{k} \cdot \vec{r}'}}{\sqrt{V}} \\
 \text{Exchange term} &= - \frac{4\pi e^2}{V} \sum_{k'} \frac{1}{|\vec{k} - \vec{k}'|^2} \psi_k(\vec{r}, s)
 \end{aligned}$$

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

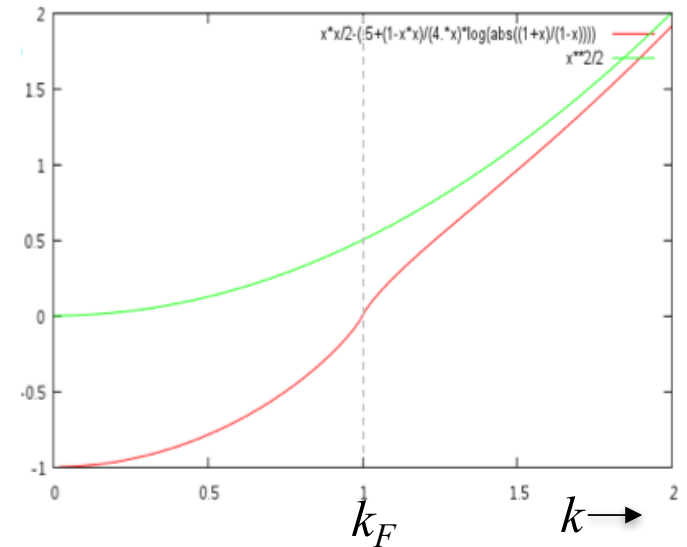
Lindhard function:

- singular at k_F (screening may fix this; see ch. 17)

Total energy:

$$E/N = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} - \frac{3}{4} \frac{e^2 k_F}{\pi}$$

$$\Delta E/N = -\frac{3}{4} (3/\pi)^{1/3} e^2 n^{1/3}$$



Simple local density approximation (LDA) exchange/correlation energy [Kohn-Sham, Dirac]