

# Hohenberg-Kohn Theorem

"Density is the basic variable"; this is equivalent to:

DFT

there is a one-to-one correspondence between the density and the EXTERNAL POTENTIAL.

## PROOF

The ground-state energy for a system of interacting electrons is defined as:

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle, \quad \hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{ee}$$

This is a symbolic writing for minimization over all possible wfs. We can split this minimization in 2 parts:

- 1) First minimize over all  $\Psi$  which correspond to a given  $n$ :  $\Psi \rightarrow n$
- 2) Minimize over all possible  $n$ 's.

$$1) \quad \min_{\Psi \rightarrow n} \langle \Psi | \hat{H} | \Psi \rangle = \min_{\Psi \rightarrow n} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \langle \Psi | \hat{V}_{ext} | \Psi \rangle \right\} =$$

$$= \min_{\Psi \rightarrow n} \left[ \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \right] + \int d^3 r v(\underline{r}) n(\underline{r}) = E_{\hat{v}}[n]$$

The ground state energy is a functional of  $n(\underline{r})$  which depends on  $v(\underline{r})$ .

$$E_v[n] = \underbrace{\langle \Psi_{min}^{(n)} | \hat{T} + \hat{V}_{ee} | \Psi_{min}^{(n)} \rangle}_{F[n]} + \int d^3 r v(\underline{r}) n(\underline{r})$$



$$E^{(0)} = \min_n E_V[n] = \min_n \left\{ F[n] + \int d^3r v(r) n(r) \right\}$$



Number of particles is fixed

$$\delta \left\{ F[n] + \int d^3r v(r) n(r) - \mu \int d^3r n(r) \right\} = 0$$

$$\frac{\delta F[n]}{\delta n(r)} + v(r) = \mu$$

← The external potential is uniquely determined by the ground state density. (c.v.d.)

Kohn-Sham auxiliary system

Now, let us derive the self-consistent equations for the K-S auxiliary system.

The K-S auxiliary system is defined as a fictitious non-interacting system which has the same density as the original, interacting system.

KOHN-SHAM

If the system is non-interacting,  $\hat{V}_{ee} = 0$ .

$$\langle \phi_{min} | \hat{T} + \hat{V}_{ee} | \phi_{min} \rangle = \langle \phi_{min}^{(n)} | \hat{T} | \phi_{min}^{(n)} \rangle = T_S[n] = F_S[n]$$



The "external potential" ( $v_s$ ) and density have to satisfy the equations:

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$$\frac{\delta F_s[n]}{\delta n(\underline{r})} + v_s(\underline{r}) = \mu \quad \Leftrightarrow \quad \frac{\delta T_s[n]}{\delta n(\underline{r})} + v_s(\underline{r}) = \mu$$

For the interacting system, we define an  $Exc[n(\underline{r})]$  so that:  $F[n] \stackrel{DEF}{=} T_s[n] + Exc[n] + U[n]$

$$\frac{\delta T_s[n]}{\delta n(\underline{r})} + \frac{\delta U[n]}{\delta n(\underline{r})} + \frac{\delta Exc[n]}{\delta n(\underline{r})} + v_{ext}(\underline{r}) = \mu$$

$$\Leftrightarrow v_s[n(\underline{r})] = v_{ext}(\underline{r}) + \frac{\delta U[n]}{\delta n(\underline{r})} + \frac{\delta Exc[n]}{\delta n(\underline{r})}$$

and this leads to the usual formulations of the  $n$ - $s$  equations.

The total energy is given by:

$$E = \sum_{\alpha\sigma} \theta(\mu - \epsilon_{\alpha\sigma}) \epsilon_{\alpha\sigma} - \underbrace{U[n] - \int d^3r (n(\underline{r})) v_{xc}(n(\underline{r}); \underline{r})}_{\text{double-counting correction}} + Exc[n]$$

$\approx$  double-counting correction.



## Exchange and Correlation Energy:

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$$E_{xc}[n] = E_x[n] + E_c[n]$$

$$\rightarrow E_x[n] = \langle \phi_n^{\text{min}} | \hat{V}_{ee} | \phi_n^{\text{min}} \rangle - U[n]$$

This is the definition of the Hartree-Fock exchange energy for a Slater determinant of non-interacting K-S orbitals.

$$\rightarrow E_c[n] = \langle \Psi_n^{\text{min}} | \hat{V}_{ee} | \Psi_n^{\text{min}} \rangle - \langle \phi_n^{\text{min}} | \hat{V}_{ee} | \phi_n^{\text{min}} \rangle$$

$|\Psi_n^{\text{min}}\rangle =$  Wavefunction of the interacting system (many-body)

$|\phi_n^{\text{min}}\rangle =$  Wavefunction of the K-S system (non-interacting)

Just a small reminder about Hartree-Fock's theory:

Hartree-Fock's equations are obtained minimizing  $\langle \Psi | H | \Psi \rangle$ , with the constraint that  $|\Psi\rangle$  is a determinant of single-particle wavefunctions  $\psi_i(\underline{z})$ .



This single-particle wavefunctions have to obey the equations:

$$\left[ -\frac{\nabla^2}{2} + V_{ext}(\underline{r}) + V_H(\underline{r}) \right] \varphi_i(\underline{r}) - \sum_j \int d^3r' \frac{e^2}{|\underline{r} - \underline{r}'|} \varphi_j^*(\underline{r}') \varphi_i(\underline{r}') \varphi_i(\underline{r}) \delta_{si} \delta_{sj} = \epsilon_i \varphi_i(\underline{r})$$

$$V_H(\underline{r}) = \sum_i \int d^3r' \frac{|\varphi_i(\underline{r}')|^2}{|\underline{r} - \underline{r}'|} \quad \leftarrow \text{Hartree potential}$$

Exchange potential

For an homogeneous  $e^-$  gas (uniform distribution of  $e^-$  + uniform distribution of ions)  $\langle V_{ext} \rangle + \langle V_H \rangle = 0$ ;  
 the Exchange term survives and gives:

$$\Rightarrow E(\underline{n}) = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi} k_F F\left(\frac{k}{k_F}\right),$$

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

The total energy is:

$$\frac{E}{N} = \underbrace{\left[ \frac{2.21}{(r_s/a_0)^2} \right]}_{\text{Free electron (kinetic energy)}} - \underbrace{\left[ \frac{0.961}{(r_s/a_0)} \right]}_{\text{Exchange energy}} \text{ Ry}$$

$r_s/a_0 = 2 \div 6$  in metals;

$r_s$  is defined as the radius of a sphere whose volume is equal to the volume of (conduction) electron.

$$\frac{1}{n} = \frac{4\pi r_s^3}{3} \Rightarrow r_s = \left( \frac{3}{4\pi} \right)^{1/3} \cdot \frac{1}{n^{1/3}}$$

[The correlation energy contains higher-order terms in  $\frac{r_s}{a_0}$ :  $E_c = -0.0622 \ln\left(\frac{r_s}{a_0}\right) - 0.076 \left(\frac{r_s}{a_0}\right)$



From the definition of the exchange energy for a free electron gas,

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Slater derived a simple approximation to include the effect of Exchange also in cases

where the density is non-uniform:  $n(\underline{r}) \neq n$

$$\tilde{E}_x[n(\underline{r})] = -2.95 \left( a_0^3 \cdot n(\underline{r}) \right)^{1/3} \quad [\text{Ryd}] \quad (1953)$$

These simplified self-consistent equations bear a strong resemblance to DFT (H-S) equations

but there is no formal justification to why they should work:

SLATER

$$\left\{ \begin{array}{l} \left( -\frac{\nabla^2}{2} + v_{\text{ext}}(\underline{r}) + v_H[n(\underline{r})] + \tilde{E}_x[n(\underline{r})] \right) \psi_i(\underline{r}) = \epsilon_i \psi_i(\underline{r}) \\ n(\underline{r}) = \sum_{i \text{ occ}} |\psi_i(\underline{r})|^2 \end{array} \right.$$

[And correlation energy is disregarded].



The CORRELATION ENERGY of the uniform electron gas <sup>is</sup> known DFT 7  
 at the limits  $r_s \rightarrow 0$ ,  $r_s \rightarrow \infty$ , and the intermediate points are known  
 from accurate QMC calculations at finite  $r_s$ .

The two limits are:

$r_s \rightarrow 0$

$$e_c(n) = c_0 \ln r_s = c_1 + c_2 r_s \ln r_s - c_3 r_s + \dots$$

$r_s \rightarrow +\infty$

$$e_c(n) \rightarrow -\frac{d_0}{r_s} + \frac{d_1}{r_s^{3/2}} + \dots$$

An interpolating formula is:

$$e_c(n) = -2c_0(1 + d_1 r_s) \ln \left[ 1 + \frac{1}{2c_0(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)} \right]$$

This is the essence of the local density approximation. It can be extended to the spin-polarized case (local spin density approximation).  
 By construction, the local (spin) density approximation is exact for a uniform density, and is thus a good approximation for a DENSITY that varies slowly over space. However, due to error cancellation, it works surprisingly well in most solids.