

## Hohenberg-Kohn Theorems

### One H-K 1

An electron density  $\rho(r)$  uniquely determines its external potential  $V(r)$  (up to an additive constant).

- Proof by contradiction.

Suppose there are two potentials  $V_1$  and  $V_2$  that give rise to same density  $\rho(r)$

We have then two different Hamiltonians,

$$\hat{H}_1 = \hat{T} + \hat{V}_{ee} + \hat{V}_1 \quad \text{and} \quad \hat{H}_2 = \hat{T} + \hat{V}_{ee} + \hat{V}_2$$

s.t.  $H_1 \Psi_1 = E_1^\circ \Psi_1$   
 $H_2 \Psi_2 = E_2^\circ \Psi_2$

Apply variational principle, valid for ground state, non-degenerate WF:

$$E_1^\circ < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | H_2 | \Psi_2 \rangle + \langle \Psi_2 | H_1 - H_2 | \Psi_2 \rangle \\ = E_2^\circ + \int \rho(r) (V_1 - V_2) dr \quad \text{--- (1)}$$

$$\text{Similarly, } E_2^\circ < \langle \Psi_1 | H_2 | \Psi_1 \rangle = \langle \Psi_1 | H_1 | \Psi_1 \rangle + \langle \Psi_1 | H_2 - H_1 | \Psi_1 \rangle \\ = E_1^\circ + \int \rho(r) (V_2 - V_1) dr \quad \text{--- (2)}$$

$$\text{Add (1) + (2), } \Rightarrow E_1^\circ + E_2^\circ < E_1^\circ + E_2^\circ \quad \text{a contradiction}$$

✗ (thus, there cannot exist two diff. ~~not~~ external potentials for same e-density)

thus, the same e-density  $\rho(r)$  cannot give rise to 2 different potentials  
 ie,  $\rho(r)$  uniquely determines  $V(r)$ .

- Bright-Wilson Proof

If we know the electron density,  $\rho(\underline{r})$ , then we have

$$(i) \quad \int \rho(\underline{r}) d\underline{r} = N \text{ total no. of } e^- \text{ in the system.}$$

(ii) positions of nuclei,  $\underline{R}_A$ , which occur at cusps of  $e^-$ -density  $\rho$

(iii) nuclear charges of nuclei,  $z_A$ , at cusps since the cusps condition gives

$$\frac{\partial}{\partial \underline{r}_A} \bar{\rho}(\underline{r}_A) \Big|_{\underline{r}_A=0} = -2z_A \bar{\rho}(0)$$

i.e.,  $|\nabla \rho|$  at nuclear cusps gives  $z_A$

From  $\{N, z_A, \underline{R}_A\}$  we have uniquely determined Hamiltonian

$$\begin{aligned} \hat{H} &= -\frac{1}{2} \sum_i^N \nabla_i^2 + V_{ee} + V_{Ne} \\ &= -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_{i>j}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \sum_{A=1}^M \frac{z_A}{|\underline{r}_i - \underline{R}_A|} \end{aligned}$$

∴ can find properties (eg. energy) of the system.

• Proof using Levy Constrained Search

$$E_0 = \min_{\Psi} \langle \Psi | H | \Psi \rangle$$

$$= \min_{\Psi} \langle \Psi | T + V_{ee} + V_{Ne} | \Psi \rangle$$

At energy minimum, we know that we get g.s. density,  $\rho$ .

$\therefore$  we search over all antisymmetrized WF that upon quadrature give the <sup>g.s.</sup> density  $\rho$ .

We then lift the constraint and search over all  $\rho$  that integrates to total no. of electrons  $N$ .

$$E = \min_{\rho \rightarrow N} \left( \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} + V_{Ne} | \Psi \rangle \right)$$

$$= \min_{\rho \rightarrow N} \left( \min_{\Psi \rightarrow \rho} \left( \langle \Psi | V_{Ne} | \Psi \rangle + \langle \Psi | T + V_{ee} | \Psi \rangle \right) \right)$$

$$= \min_{\rho \rightarrow N} \left( \min_{\Psi \rightarrow \rho} \left( \int \rho(r) V_{Ne}(r) dr + \langle \Psi | T + V_{ee} | \Psi \rangle \right) \right)$$

$$= \min_{\rho \rightarrow N} \left( \int \rho(r) V_{Ne}(r) dr + \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} | \Psi \rangle \right)$$

$$= \min_{\rho \rightarrow N} \left( \int \rho(r) V_{Ne}(r) dr + F[\rho] \right) = \min_{\rho} E[\rho]$$

$$E_0[\rho] = \min_{\rho} E[\rho]$$

$\therefore$  g.s. density can give minimum energy

$\Leftrightarrow$  1-1 mapping  
of density & potential!

For a trial electron density  $\tilde{\rho}(r)$  s.t.  $\int \tilde{\rho}(r) dr = N$  and  $\tilde{\rho}(r) \geq 0$   
 $\tilde{\rho}(r) \rightarrow 0$  as  $r \rightarrow \infty$ , we have

$$E[\tilde{\rho}(r)] \geq E[\rho_0(r)]$$

where  $\rho_0(r)$  is the ground state density.

Proof.

By Hohenberg - Kohn theorem one, we know that

$\tilde{\rho}(r)$  uniquely determines external potential  $\tilde{V}(r)$ , thus, Hamiltonian  
 and ~~the~~ its wavefunction  $\tilde{\Psi}$ .

We use  $\tilde{\Psi}$  as our trial WF:

$$\begin{aligned} \tilde{E} &= \langle \tilde{\Psi} | H | \tilde{\Psi} \rangle = \langle \tilde{\Psi} | T + V_{ee} + \tilde{V} | \tilde{\Psi} \rangle \\ &= \int \tilde{\rho}(r) \tilde{V}(r) dr + \langle \tilde{\Psi} | T + V_{ee} | \tilde{\Psi} \rangle \\ &= E[\tilde{\rho}] \geq E_0 = \langle \Psi_0 | H | \Psi_0 \rangle \\ &= \langle \Psi_0 | T + V_{ee} + V | \Psi_0 \rangle \\ &= \int \rho_0(r) V(r) dr + \langle \Psi_0 | T + V_{ee} | \Psi_0 \rangle \\ &= E[\rho_0] \\ \Rightarrow E[\tilde{\rho}] &\geq E[\rho_0] \end{aligned}$$

## Finding Chemical Potentials given functionals

$$E[\rho] = \int \rho(r) v(r) dr + T[\rho] + V_{ee}[\rho]$$

Apply variational principle to minimize  $E[\rho]$  subject to constraint  $\int \rho(r) dr = N$ , we get,

$$\min \quad \left( E[\rho] - \mu \left( \int \rho(r) dr - N \right) \right)$$

$$\Rightarrow \mu = \frac{\delta E[\rho]}{\delta \rho} = v(r) + \frac{\delta T[\rho]}{\delta \rho} + \frac{\delta V_{ee}[\rho]}{\delta \rho}$$

## Thomas-Fermi Theory

Energy functional:  $E[\rho] = T[\rho] + V_{ee}[\rho] + V_{Ne}[\rho]$

Using Uniform Electron Gas Model, we have:

$$T[\rho] = -\frac{1}{2} \cancel{\sum}$$

$$= c_F \int \rho^{5/3}(\underline{r}) d\underline{r} \quad c_F = \frac{3}{10} (3\pi^2)^{\frac{2}{3}}$$

$$V_{ee}[\rho] = J[\rho] = \frac{1}{2} \iint \frac{\rho(\underline{r})\rho(\underline{r}')}{|\underline{r}-\underline{r}'|} d\underline{r} d\underline{r}'$$

So,  $E[\rho] = c_F \int \rho^{5/3}(\underline{r}) d\underline{r} + \frac{1}{2} \iint \frac{\rho(\underline{r})\rho(\underline{r}')}{|\underline{r}-\underline{r}'|} d\underline{r} d\underline{r}' + \int \rho(\underline{r}) v(\underline{r}) d\underline{r}$

Minimization of  $E[\rho]$  subject to constraint  $\int \rho(\underline{r}) d\underline{r} = N$ , we have

$$\min [E[\rho] - \mu (\int \rho(\underline{r}) d\underline{r} - N)]$$

$$\Rightarrow c_F \frac{5}{3} \cancel{\rho^{5/3}(\underline{r})} + \int \frac{\rho(\underline{r})}{|\underline{r}-\underline{r}'|} d\underline{r}' + v(\underline{r}) = \mu$$

- Devastating drawback

$$E[\underline{R}] = E^{TF}[\rho; \underline{R}] + \sum_{A>B} \frac{z_A z_B}{|\underline{R}_A - \underline{R}_B|} \quad \text{decreases as } |\underline{R}_A - \underline{R}_B| \rightarrow \infty$$

~~Teller~~ Teller's non-binding theorem

## Kohn-Sham Theory

Introduce a non-interacting reference system having same electron density as the real, interacting system and having WF that is a single determinant of  $N$  Kohn-Sham orbitals  $\phi_i$ .

Then,

$$T_s[\rho] = \sum_i^N \langle \phi_i | T | \phi_i \rangle = -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle$$

$$\rho(\underline{r}) = \sum_i^N |\phi_i(\underline{r})|^2$$

The orbitals satisfy K-S equation:  $\hat{H}^{ks} \phi_i = [-\frac{1}{2} \nabla^2 + v_s(\underline{r})] \phi_i = \varepsilon_i \phi_i$

Need to determine  $v_s(\underline{r})$ ; first write energy functional as

$$E^{ks}[\rho] = T_s[\rho] + J[\rho] + V_{ne}[\rho] + E_{xc}[\rho]$$

$$\text{where } E_{xc}[\rho] = (J[\rho] - T_s[\rho]) + (V_{xc}[\rho] - J[\rho])$$

Minimization of  $E^{ks}[\rho]$  subject to constraint  $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ , we have,

$$\min [E^{ks}[\rho] - \varepsilon_i (\langle \phi_i | \phi_i \rangle - \delta_{ij})]$$

$$\Rightarrow (-\frac{1}{2} \nabla^2 + v_J(\underline{r}) + V_{ne}(\underline{r}) + V_{xc}[\underline{r}]) \phi_i = \varepsilon_i \phi_i$$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\underline{r}) \rho(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' \Rightarrow v_J(\underline{r}) = \frac{\delta J}{\delta \rho} = \int \frac{\rho(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' \text{ (product rule)}$$

$$V_{ne}(\underline{r}) = \sum_A \frac{-Z_A}{|\underline{r} - \underline{R}_A|} \quad \text{and} \quad V_{xc}[\underline{r}] = \frac{S E_{xc}[\rho]}{\delta \rho}$$

Comparing we have  $v_s(\underline{r}) = v_J(\underline{r}) + V_{ne}(\underline{r}) + V_{xc}(\underline{r})$

## Coordinate Scaling

Consider  $\int \rho(\underline{r}) d\underline{r} = N$

Scaling  $\underline{r} \rightarrow \lambda \underline{r}$   $\therefore d\underline{r} \rightarrow \lambda^3 d\underline{r}$

$$\rho(\underline{r}) \rightarrow \rho(\lambda \underline{r})$$

$\therefore \int \rho(\underline{r}) d\underline{r} = N$  becomes

$$\int \rho_\lambda(\underline{r}) d\underline{r}$$

$$\int \rho(\lambda \underline{r}) \lambda^3 d\underline{r} = N$$

$$\int \rho(\lambda \underline{r}) \lambda^3 d\underline{r} = N$$

Introduce **scaled density**  $\rho_\lambda(\underline{r}) = \lambda^3 \rho(\lambda \underline{r})$  to get  $\phi_{i\lambda}(\underline{r}) = \lambda^{3/2} \phi_i(\lambda \underline{r})$

$$\int \rho_\lambda(\underline{r}) d\underline{r} = N$$

• Scaling of **exact exchange energy**

$$E_x = \frac{1}{2} \langle ij | ij \rangle$$

$$\begin{aligned}
 E_x[\phi_{i\lambda}(\underline{r})] &= \frac{1}{2} \iint \frac{\phi_{i\lambda}^*(\underline{r}_1) \phi_{j\lambda}^*(\underline{r}_1) \phi_{i\lambda}(\underline{r}_2) \phi_{j\lambda}(\underline{r}_2)}{|\underline{r}_1 - \underline{r}_2|} d\underline{r}_1 d\underline{r}_2 \\
 &= \frac{1}{2} \iint \frac{\lambda^{3/2} \phi_i^*(\lambda \underline{r}_1) \lambda^{3/2} \phi_j^*(\lambda \underline{r}_1) \lambda^{3/2} \phi_i(\lambda \underline{r}_2) \lambda^{3/2} \phi_j(\lambda \underline{r}_2)}{|\underline{r}_1 - \underline{r}_2|} d\underline{r}_1 d\underline{r}_2 \\
 &= \frac{\lambda^6}{2} \iint \frac{\phi_i^*(\lambda \underline{r}_1) \phi_j^*(\lambda \underline{r}_1) \phi_i(\lambda \underline{r}_2) \phi_j(\lambda \underline{r}_2)}{|\underline{r}_1 - \underline{r}_2|} d\underline{r}_1 d\underline{r}_2
 \end{aligned}$$

$$= \frac{\lambda^6}{2\pi^6} \iint \frac{\phi_i(\lambda r_1) \phi_i(\lambda r_2) \phi_j(\lambda r_1) \phi_j(\lambda r_2)}{|r_1 - r_2|} (\lambda^3 dr_1) (\lambda^3 dr_2)$$

$d(\lambda r_1) d(\lambda r_2)$

$$= \frac{1}{2} \lambda \iint \frac{\phi_i(\lambda r_1) \phi_i(\lambda r_2) \phi_j(\lambda r_1) \phi_j(\lambda r_2)}{|\lambda r_1 - \lambda r_2|} d(\lambda r_1) d(\lambda r_2)$$

$$= \lambda \frac{1}{2} \iint \frac{\phi_i(r_1) \phi_i(r_2) \phi_j(r_1) \phi_j(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

) replace  
 $\lambda r$  by  $r$

$$= \lambda \operatorname{Ex} [\phi_i(r)]$$

\* Scaling of kinetic energy.

$$\begin{aligned} T_s[\rho_\lambda(r)] &= -\frac{1}{2} \sum_i \langle \phi_{i\lambda}(r) | \nabla^2 | \phi_{i\lambda}(r) \rangle \\ &= -\frac{1}{2} \sum_i \langle \lambda^{3/2} \phi_i(\lambda r) | \nabla^2 | \lambda^{3/2} \phi_i(\lambda r) \rangle \\ &= -\frac{1}{2} \lambda^3 \sum_i \iiint \phi_i(\lambda r) \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \phi_i(\lambda r) dx dy dz \\ &= -\frac{1}{2} \lambda^3 \sum_i \iiint \phi_i(\lambda r) \lambda^2 \left[ \frac{\partial^2}{\partial (\lambda x)^2} + \frac{\partial^2}{\partial (\lambda y)^2} + \frac{\partial^2}{\partial (\lambda z)^2} \right] \phi_i(\lambda r) \frac{d(\lambda x)}{\lambda} \frac{d(\lambda y)}{\lambda} \frac{d(\lambda z)}{\lambda} \\ &= -\frac{1}{2} \frac{\lambda^3}{\lambda^3} \lambda^2 \sum_i \iiint \phi_i(\lambda r) \left[ \frac{\partial^2}{\partial (\lambda x)^2} + \frac{\partial^2}{\partial (\lambda y)^2} + \frac{\partial^2}{\partial (\lambda z)^2} \right] \phi_i(\lambda r) d\lambda x \\ &= \lambda^2 \left[ -\frac{1}{2} \sum_i \iiint \phi_i(r) \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \phi_i(r) dx dy dz \right] \quad \text{replace } \lambda r \text{ by } r \\ &= \lambda^2 T_s[\rho(r)] \end{aligned}$$

Use of coordinate scaling in determining form of  $E_x^{local}[\rho]$  and  $T_s^{local}[\rho]$  of HEG

coordinate scaling  $\underline{r} \rightarrow \lambda \underline{r}$

$$d\underline{r} \rightarrow \lambda^3 d\underline{r}$$

$$\rho_\lambda(\underline{r}) = \lambda^3 \rho(\lambda \underline{r}) \quad \text{scaled density}$$

$$\phi_{i\lambda}(\underline{r}) = \cancel{\lambda^{3/2}} \phi_i(\lambda \underline{r}) \quad \text{scaled orbitals}$$

$$\bullet E_x^{local} [\rho(\underline{r})] = c \int \rho^k(\underline{r}) d\underline{r}$$

To find  $k$ , apply coordinate scaling, so that the scaled quantity is now,

$$E_x^{local} [\rho_\lambda(\underline{r})] = c \int \rho_\lambda^k(\underline{r}) d\underline{r} \quad \Rightarrow \text{sub scaled density}$$

$$= c \int [\lambda^3 \rho(\lambda \underline{r})]^k d\underline{r}$$

$$= c \lambda^{3k} \int \rho(\lambda \underline{r})^k d\underline{r}$$

$$= c \lambda^{3k} \cdot \int \rho(\lambda \underline{r})^k \frac{d(\lambda \underline{r})}{\lambda^3}$$

$$= c \lambda^{3k-3} \int \rho(\lambda \underline{r})^k d(\lambda \underline{r}) \quad \begin{matrix} \downarrow & \text{replace dummy variable} \\ \lambda \underline{r} & \text{by } \underline{r} \end{matrix}$$

$$= \lambda^{3k-3} c \int \rho(\underline{r})^k d\underline{r} = \lambda^{3k-3} E_x^{local} [\rho(\underline{r})]$$

but we know that  $E_x^{local} [\rho_\lambda(\underline{r})] = \lambda E_x^{local} [\rho(\underline{r})]$  scaling relation,

thus,  ~~$3k-3$~~   $3k-3=1 \Rightarrow k=\frac{4}{3}$

$$\therefore E_x^{local} [\rho(\underline{r})] = c \int \rho^{4/3}(\underline{r}) d\underline{r}$$

$$T_s^{\text{local}} [\rho(\underline{r})] = c \int \rho^k(\underline{r}) d\underline{r}$$

Under same scaling, we have,

$$\begin{aligned}
T_s^{\text{local}} [\rho_\lambda(\underline{r})] &= c \int [\rho_\lambda(\underline{r})]^k d\underline{r} \\
&= c \int [\lambda^3 \rho(\lambda \underline{r})]^k d\underline{r} \\
&= c \lambda^{3k} \int \rho^k(\lambda \underline{r}) d\underline{r} \\
&= c \frac{\lambda^{3k}}{\lambda^3} \int \rho^k(\lambda \underline{r}) \frac{d\lambda^3 \underline{r}}{\lambda^3} \\
&= c \frac{\lambda^{3k}}{\lambda^3} \int \rho^k(\lambda \underline{r}) d(\lambda \underline{r}) \\
&= c \lambda^{3k-3} \int \rho^k(\underline{r}) d\underline{r} \\
&= \lambda^{3k-3} T_s^{\text{local}} [\rho(\underline{r})]
\end{aligned}$$

→ replace dummy variable  $\lambda \underline{r}$  by  $\underline{r}$

but we know the scaling relation for  $T_s$

$$T_s[\rho_\lambda(\underline{r})] = \lambda^2 T_s[\rho(\underline{r})]$$

thus, we get

$$3k-3 = 2$$

$$k = \frac{5}{3}$$

$$\Rightarrow T_s^{\text{local}} [\rho(\underline{r})] = c \int \rho^{\frac{5}{3}}(\underline{r}) d\underline{r}$$

## Adiabatic Connection

Scaling of ee repulsion s.t. the density is kept constant  $\forall \lambda$ .

$$\hat{H}_\lambda = T + \lambda V_{ee} + \sum_i v^\lambda(r_i) \quad \left\{ \begin{array}{l} \lambda=1 \Rightarrow \text{full interacting system} \\ \lambda=0 \Rightarrow \text{Kohn-Sham system} \end{array} \right.$$

$$H_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda \quad \text{where } \Psi_\lambda \text{ is minimising WF, i.e., } \frac{\partial \Psi_\lambda}{\partial \lambda} = 0$$

We consider,

$$\frac{d}{d\lambda} \langle \Psi_\lambda | T + \lambda V_{ee} | \Psi_\lambda \rangle$$

$$= \underbrace{\frac{d}{d\lambda} \Psi_\lambda |}_{\circlearrowleft} | T + \lambda V_{ee} | \Psi_\lambda \rangle + \langle \Psi_\lambda | \frac{d}{d\lambda} (T + \lambda V_{ee}) | \Psi_\lambda \rangle + \langle \Psi_\lambda | T + \lambda V_{ee} | \cancel{\frac{d\Psi_\lambda}{d\lambda}} \rangle$$

$$= \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle$$

$$\therefore \int_0^1 \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle d\lambda' = \langle \Psi_\lambda | T + \lambda V_{ee} | \Psi_\lambda \rangle$$

$$\int_0^1 \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle d\lambda = \int_0^1 \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | T + \lambda V_{ee} | \Psi_\lambda \rangle d\lambda$$

$$\langle \Psi_1 | T + V_{ee} | \Psi_1 \rangle - \langle \Psi_0 | T | \Psi_0 \rangle = \int_0^1 \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle d\lambda$$

$$\langle \Psi_1 | T | \Psi_1 \rangle + \langle \Psi_1 | V_{ee} | \Psi_1 \rangle - \langle \Psi_0 | T | \Psi_0 \rangle = \int_0^1 \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle d\lambda$$

$$T[\rho] + V_{ee}[\rho] - T_s[\rho] = \int_0^1 \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle d\lambda$$

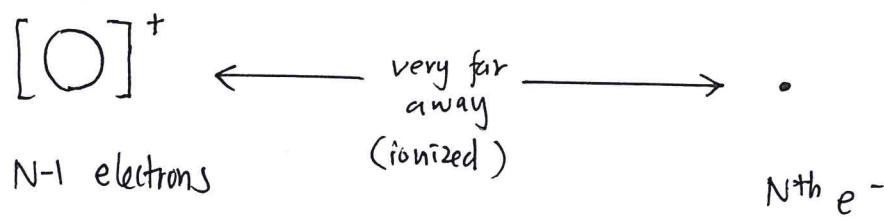
$$(T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]) = \int_0^1 \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle d\lambda - J[\rho]$$

$$Exc[\rho] = \int_0^1 w_\lambda d\lambda$$

$$\text{... i.e. } h/s = \langle \Psi_1 | V_{ee} | \Psi_1 \rangle - T[\rho] - J[\rho]$$

## Asymptotic behavior of density

Consider the system



$$\underline{H}_N = \underline{H}_{N-1} \phi_N \quad \text{with} \quad \hat{H}_N = \hat{H}_{N-1} + \hat{h}_N$$

The Schrödinger equation for the system becomes

$$H_N \Psi_N = E_N \Psi_N$$

$$(H_{N-1} + h_N) (\Psi_{N-1} \phi_N) = E_N (\Psi_{N-1} \phi_N)$$

$$\left( \hat{H}_{N-1} \Psi_{N-1} \right) \phi_N + \Psi_{N-1} \hat{h}_N \phi_N = E_N \Psi_{N-1} \phi_N$$

$$E_{N-1} \cancel{\psi_{N-1}} \phi_N + \cancel{h_{N-1}} \hat{h}_N \phi_N = E_N \cancel{\psi_{N-1}} \phi_N$$

$$\hat{h}_N \phi_N = (E_N - E_{N-1}) \phi_N = -I \phi_N$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)\phi_N = -I\phi_N$$

To solve this system, guess a trial function  $\phi_N = e^{-\alpha r}$ .

Upon substitution:  $-\frac{1}{2} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} e^{-\alpha r} \right) - \frac{1}{r} e^{-\alpha r} = -I e^{-\alpha r}$

$$-\frac{1}{2} \frac{1}{r^2} \frac{\partial}{\partial r} (-dr^2 e^{-\alpha r}) - \frac{1}{r} e^{-\alpha r} = -I e^{-\alpha r}$$

$$-\frac{1}{2r^2} - (\alpha^2 r^2 - 2\alpha r) e^{-\alpha r} - \frac{1}{r} e^{-\alpha r} = -I e^{-\alpha r}$$

$$-\frac{\alpha^2}{2} + \frac{\alpha}{r} - \frac{1}{r} = -I$$

$$-\frac{\alpha^2}{2} + \frac{\alpha-1}{r} = -I$$

$$\text{as } r \rightarrow \infty \quad \frac{\alpha-1}{r} \rightarrow 0$$

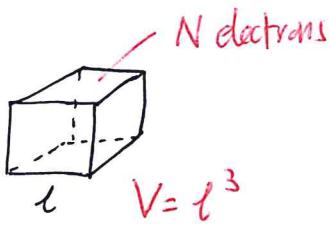
$$\therefore \alpha^2 = 2I$$

$$\alpha = \sqrt{2I}$$

$$\therefore \phi_N \sim e^{-\alpha r} = e^{-\sqrt{2I} r}$$

$$\rho(r) \sim e^{-2\sqrt{2I} r}$$

# LDA Uniform Electron Gas



$$\rho = \frac{N}{V} \text{ remains finite as } N \rightarrow \infty \text{ and } V \rightarrow 0$$

KS eqn satisfied by plane waves  $\phi_{\underline{k}}(\underline{r}) = \frac{1}{\sqrt{V}} e^{i \underline{k} \cdot \underline{r}}$

where periodic b.c. gives  $\underline{k} = \frac{2\pi}{l} \underline{n}$  so that

$$d^3 \underline{k} = \left( \frac{2\pi}{l} \right)^3 d^3 \underline{n}$$

From one particle density matrix, we have,

$$\begin{aligned} \rho_1(\underline{r}_1, \underline{r}_2) &= \cancel{\sum}_{\underline{k}} \underbrace{2 \sum_{\substack{\text{occ.} \\ \underline{k}}} \phi_{\underline{k}}^*(\underline{r}_2) \phi_{\underline{k}}(\underline{r}_1)}_{\text{closed shell}} \\ &= \frac{2}{V} \sum_{\substack{\text{occ.} \\ \underline{k}}} \frac{1}{\sqrt{V}} e^{i \underline{k} \cdot (-\underline{r}_2)} \frac{1}{\sqrt{V}} e^{i \underline{k} \cdot \underline{r}_1} \\ &= \frac{2}{V} \sum_{\substack{\text{occ.} \\ \underline{k}}} e^{i \underline{k} \cdot (\underline{r}_1 - \underline{r}_2)} \end{aligned}$$

replace  $\sum$  by integral  $\equiv \int d\underline{n}$  and using  $d\underline{n} = \frac{l^3}{(2\pi)^3} d\underline{k} = \frac{V}{(2\pi)^3} d\underline{k}$ , we have,

$$\begin{aligned} \rho_1(\underline{r}_1, \underline{r}_2) &= \frac{2}{V} \int \frac{V}{8\pi^3} e^{i \underline{k} \cdot (\underline{r}_1 - \underline{r}_2)} d\underline{k} \\ &= \frac{1}{4\pi^3} \int e^{i \underline{k} \cdot \underline{r}_{12}} d\underline{k} \end{aligned}$$

Electron density  $\rho(\underline{r}) = \rho_1(\underline{r}_1, \underline{r}_1) = \frac{1}{4\pi^3} \int e^{i\underline{k} \cdot (\underline{r}_1 - \underline{r}_1)} d\underline{k}$  (\*)

$$= \frac{1}{4\pi^3} \int d\underline{k}$$

$$= \frac{1}{4\pi^3} \int_{k=0}^{k_F} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} k^2 \sin\theta dk d\theta d\phi$$

$$= \frac{1}{4\pi^3} \left[ \int_{k=0}^{k_F} k^2 dk \right] \left[ \int_{\theta=0}^{\pi} \sin\theta d\theta \right] \left[ \int_{\phi=0}^{2\pi} d\phi \right]$$

$$= \frac{1}{4\pi^3} \left[ \frac{k^3}{3} \right]_0^{k_F} [\cos\theta]_0^{\pi} (2\pi)$$

$$= \frac{1}{4\pi^3} \frac{1}{3} (k_F)^3 (2)(2\pi)$$

$$= \frac{1}{3\pi^2} k_F^3$$

$$\Rightarrow \text{Fermi level}, \quad k_F = [3\pi^2 \rho(\underline{r})]^{\frac{1}{3}}$$

kinetic energy is

$$T_s[\rho] = -\frac{1}{2} \int \left[ \nabla_{\underline{r}}^2 \rho(\underline{r}', \underline{r}) \Big|_{\underline{r}'=\underline{r}} \right] d\underline{r}$$

) sub (\*)

$$= -\frac{1}{2} \int \left[ \frac{1}{4\pi^3} \int (ik)^2 d\underline{k} \right] d\underline{r}$$

$$= \frac{1}{8\pi^3} \int \left[ \iiint k^2 k^2 \sin\theta dk d\theta d\phi \Big|_{\underline{r}} \right]$$

$$= \frac{1}{8\pi^3} \int \left[ \int_{k=0}^{k_F} k^4 dk \right] \left[ \int_{\theta=0}^{\pi} \sin\theta d\theta \right] \left[ \int_{\phi=0}^{2\pi} d\phi \right] d\underline{r}$$

$$= \frac{1}{8\pi^3} \int \left[ \frac{1}{5} k^5 \right]_0^{k_F} (2)(2\pi) d\underline{r}$$

$$= \frac{1}{10\pi^2} \int k_F^5(\underline{r}) d\underline{r} = \frac{1}{10\pi^2} \int [3\pi^2 \rho(\underline{r})]^{5/3} d\underline{r} = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \int \rho(\underline{r})^{5/3} d\underline{r}$$

Ground state ~~total energy~~ of UEG is

$$E[\rho] = T_S[\rho] + J[\rho] + \int \rho(\underline{r}) V(\underline{r}) d\underline{r} + E_{xc}[\rho] + E_b[\rho]$$

$E_b$  is electrostatic energy of ~~the~~ +ve background

Since +ve ~~electron~~ density ~~is~~  $n(\underline{r}) = -\rho(\underline{r})$ , we have,

$$E_b[\rho] = \frac{1}{2} \iint \frac{n(\underline{r}) n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' = \frac{1}{2} \iint \frac{\rho(\underline{r}) \rho(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' = J[\rho]$$

External potential due to +ve background is:

$$V(\underline{r}) = \int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}'$$

s.t.  $\int \rho(\underline{r}) V(\underline{r}) d\underline{r} = \iint \frac{\rho(\underline{r}) n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' = - \iint \frac{\rho(\underline{r}) \rho(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}'$

so that  $E_{Ne} + J + E_b = 0$

$$\begin{aligned} \therefore E[\rho] &= T_S[\rho] + E_{xc}[\rho] \\ &= T_S[\rho] + E_x[\rho] + E_c[\rho] \end{aligned}$$

Numerical simulations of UEG using quantum monte-Carlo can give  $E[\rho]$  subtract  $T_S[\rho]$  and  $E_x^{DA}[\rho]$  (Dirac exchange energy) to get  $E_c[\rho]$

## Generalised Gradient Approximation

includes  $\nabla \rho$ ; use reduced density  $x = \frac{|\nabla \rho|}{\rho^{4/3}}$  dimensionless  
density far from slowly varying;  $x$  diverges at molecular tails

$E_x^{\text{B88}}$  → make sure energy does not diverge as  $x \rightarrow \infty$ .

$E_x^{\text{B88}}$  → most widely used; correct asymptotic behavior of exchange energy density

$E_x^{\text{PBE}}$

~~BLYP~~

## Correlation functionals

$E_c^{\text{PBE}}$

$E_c^{\text{LYP}}$  → fitted to He atom; correlated WF for  $2e^-$  system; contains  $\nabla \rho$

## Hybrid Functionals

mix in  $E_x^{\text{HF}} = W_0$        $W_1 = E_{xc}^{\text{WA}} = W_1^{\text{LOA}}$

## Fitted exchange-correlation functionals