

# Elementary Concepts: density matrices

(Electron) density  $\rho(\mathbf{x})$ ,  $\mathbf{x} = \overset{\text{space coord.}}{\mathbf{r}}, s$   
 1-el. density matrix  $\gamma(\mathbf{x}, \mathbf{x}')$   $\swarrow$  spin coord.

2-el. density matrix  $\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2)$

$|\Psi(\overset{\text{elec. 1}}{\mathbf{P}}, \overset{\text{elec. 2}}{\mathbf{Q}}, \dots, \overset{\text{elec. } N}{\mathbf{Z}})|^2$

probability to find el. 1 at  $\mathbf{P} = \mathbf{r}_p, s_p$   
 and „ „ el. 2 at  $\mathbf{Q} = \mathbf{r}_q, s_q$

and „ „ el.  $N$  at  $\mathbf{Z} = \mathbf{r}_z, s_z$

In  $\Psi$ : at first position variables of el. 1  $\rightarrow$   
 at 2<sup>nd</sup> position variables of el. 2  
 etc.

$$|\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2$$

probab. for el. 1 at  $\mathbf{x}_1$ ,  
 el. 2 at  $\mathbf{x}_2$   
 etc.

Probability to be at  $\mathbf{R} = \mathbf{r}, s$ ,  
*regardless of* where the other electrons are:

for el. 1:  $\int |\Psi(\mathbf{R}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_2 \dots d\mathbf{x}_N$

for el. 2:  $\int |\Psi(\mathbf{x}_1, \mathbf{R}, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 d\mathbf{x}_3 \dots d\mathbf{x}_N$

for el. 3:  $\int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{R}, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 d\mathbf{x}_3 \dots d\mathbf{x}_N$

⋮

for el.  $N$ :  $\int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{N-1}, \mathbf{R})|^2 d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_{N-1}$

are all equal (electrons are identical and indistinguishable)

*↳ due to (anti)symm. of wavefunction under permutation.*

Probability to find *an* el. (*any* el.) at  $\mathbf{R}$ , which is the electron density  $\rho(\mathbf{R})$ , is sum of probabilities to find el. 1, el. 2, ..., el.  $N$ ,  
 =  $N$  times the probab. to find el. 1:

$$\rho(\mathbf{R}) = N \int |\Psi(\mathbf{R}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_2 \dots d\mathbf{x}_N$$

$$\int \rho(\mathbf{R}) d\mathbf{R} = N \int |\Psi(\mathbf{R}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{R} d\mathbf{x}_2 \dots d\mathbf{x}_N = N (\Psi \text{ is normal.})$$

E.J. Baerends

Dec. 2000

# One-particle density matrix

diag. element

$$\gamma(\mathbf{x}, \mathbf{x}') = \mathcal{N} \int \Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}', \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \quad \rho(\mathbf{x}) = \gamma(\mathbf{x}, \mathbf{x})$$

Expect. value of one-el. property like kin. en.  $\hat{T} = \sum_{i=1}^N \hat{t}(i) = \sum_{i=1}^N -\frac{1}{2} \nabla^2(i)$ :

$$\langle \hat{t}(1) \rangle = \langle \hat{t}(2) \rangle = \dots \langle \hat{t}(N) \rangle \text{ (all equal!)}$$

$$\text{So } T = \langle \hat{T} \rangle = N \langle \hat{t}(1) \rangle$$

$$= N \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \left( -\frac{1}{2} \nabla^2(1) \right) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N$$

*only operates on  $\vec{x}_1$  (not  $\vec{x}_i$  !!)*

$$= N \int_{\mathbf{x}_1 \rightarrow \mathbf{x}_1'} -\frac{1}{2} \nabla^2(1) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1', \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N$$

$$= \int_{\mathbf{x}_1 \rightarrow \mathbf{x}_1'} -\frac{1}{2} \nabla^2(1) \gamma(\mathbf{x}_1, \mathbf{x}_1') d\mathbf{x}_1$$

*$\nabla^2$  does not operate on  $x_1'$*

*off-diag. elements!*

**A general one-particle property like  $T$  requires knowledge of  $\gamma$ , not the complete  $\Psi$  (general is: not multiplicative, with derivatives)**

*⇒ 1-elc. properties require full density matrix (not just diag. elements)*

For 2-particle operators like  $1/r_{12}$ , we need 2-part. density matrix

$$\hat{W} = \sum_{i < j} \frac{1}{r_{ij}} = \sum_{i < j} \hat{w}(i, j)$$

$$W = \langle \hat{W} \rangle = \langle \Psi | \sum_{i < j} \hat{w}(i, j) | \Psi \rangle = \underbrace{\frac{1}{2} \mathcal{N}(\mathcal{N}-1)}_{\text{nr. of pairs}} \underbrace{\langle \Psi | \hat{w}(1, 2) | \Psi \rangle}_{\text{expect. value one pair}}$$

$$= \frac{1}{2} \mathcal{N}(\mathcal{N}-1) \int \frac{1}{r_{12}} \Psi^*(1, 2, \dots, \mathcal{N}) \Psi(1, 2, \dots, \mathcal{N}) d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N$$

$$= \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{1}{r_{12}} \underbrace{\mathcal{N}(\mathcal{N}-1) \int \Psi(1, 2, \dots, \mathcal{N}) \Psi^*(1, 2, \dots, \mathcal{N}) d\mathbf{x}_3 \dots d\mathbf{x}_N}_{\Gamma(1, 2; 1, 2) = \Gamma(1, 2)}$$

$$= \frac{1}{2} \int \frac{1}{r_{12}} \Gamma(1, 2) d\mathbf{x}_1 d\mathbf{x}_2$$

*↑  
2-particle density matrix (diag. elements)*

# Definition of two-particle density matrix

Probability to be at "positions"  $\mathbf{x}_1 = \mathbf{r}_1, s_1$  and  $\mathbf{x}_2 = \mathbf{r}_2, s_2$

for el. 1 at  $\mathbf{x}_1$  and el. 2 at  $\mathbf{x}_2$ :  $\int |\Psi(\mathbf{x}_1, \mathbf{x}_2, 3, \dots, N)|^2 d\mathcal{B} \dots dN$

for el. 3 at  $\mathbf{x}_1$  and el. 4 at  $\mathbf{x}_2$ :  $\int |\Psi(1, 2, \mathbf{x}_1, \mathbf{x}_2, 5, \dots, N)|^2 d1 d2 d5 \dots dN$

:

for el. 1 at  $\mathbf{x}_2$  and el. 2 at  $\mathbf{x}_1$ :  $\int |\Psi(\mathbf{x}_2, \mathbf{x}_1, 3, \dots, N)|^2 d\mathcal{B} \dots dN$

etc. are all equal!

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2) = \mathcal{N} \binom{N-1}{\uparrow} \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, 3, \dots, N)|^2 d\mathcal{B} \dots dN$$

nr. of pairs

is probability to find two electrons (any two electrons) at positions  $\mathbf{x}_1$  and  $\mathbf{x}_2$

El.-el. interaction energy:  $(1/2) \int \Gamma(\mathbf{x}_1, \mathbf{x}_2) / r_{12} d\mathbf{x}_1 d\mathbf{x}_2$

## Definition of conditional probability of finding an (other) el. at $\mathbf{x}_2$ when an el. is found at $\mathbf{x}_1$

Carry out measurements in volumes  $d\mathbf{x}_1$  at  $\mathbf{x}_1$  and  $d\mathbf{x}_2$  at  $\mathbf{x}_2$  simultaneously

Measurement	$d\mathbf{x}_1$	$d\mathbf{x}_2$
1	yes	no
2	no	no
3	yes	no
:		
$n$	no	yes

*pair prob.*

Say  $n_2$  times yes + yes.  $\rightarrow \Gamma(\mathbf{x}_1, \mathbf{x}_2) = n_2/n$

Say  $n_1$  times yes + (no or yes)  $\rightarrow \rho(\mathbf{x}_1) = n_1/n$

*elec. at  $\mathbf{x}_1$ , regardless of  $\mathbf{x}_2$  (regardless of other electrons)*

So out of the  $n_1$  times there was an el. at  $\mathbf{x}_1$ , only  $n_2$  times there was also an el. at  $\mathbf{x}_2$ .

So conditional probability is  $n_2/n_1 = \Gamma(\mathbf{x}_1, \mathbf{x}_2) / \rho(\mathbf{x}_1) \equiv \rho^{cond}(\mathbf{x}_2 | \mathbf{x}_1)$



Physics of correlation:

$$E = \langle \hat{T} \rangle + \langle \hat{V} \rangle + \frac{1}{2} \int \frac{1}{r_{12}} \Gamma(1,2) d1 d2$$

$\Gamma(1,2)$ : probability to find an electron at 1

and an electron at 2

$$\Gamma(1,2) \equiv \underbrace{\rho(1)\rho(2)}_{\text{independent particles}} + \underbrace{\Gamma_{XC}(1,2)}_{\text{exch.-correl.}}$$

$\frac{\Gamma(1,2)}{\rho(1)}$ : conditional probability to find el.

at 2 if one is at 1

$$= \rho^{cond.}(2|1) = \underbrace{\rho(2)}_{\text{uncond. probability "electr. dens."}} + \underbrace{\frac{\Gamma_{XC}(1,2)}{\rho(1)}}_{\text{exch.-correl. hole}} \rho_{xc}^{hole}(2|1)$$

4  $\rho^{cond.}(2|1)$  integrates (over  $\vec{x}_2$ ) to  $N-1$  (there are  $N-1$  other electrons)

for all reference positions  $\vec{x}_1$

(i.e. electron cannot see itself, hence  $N-1$ )

So  $\rho_{xc}^{hole}(2|1)$  integrates to  $-1$ :

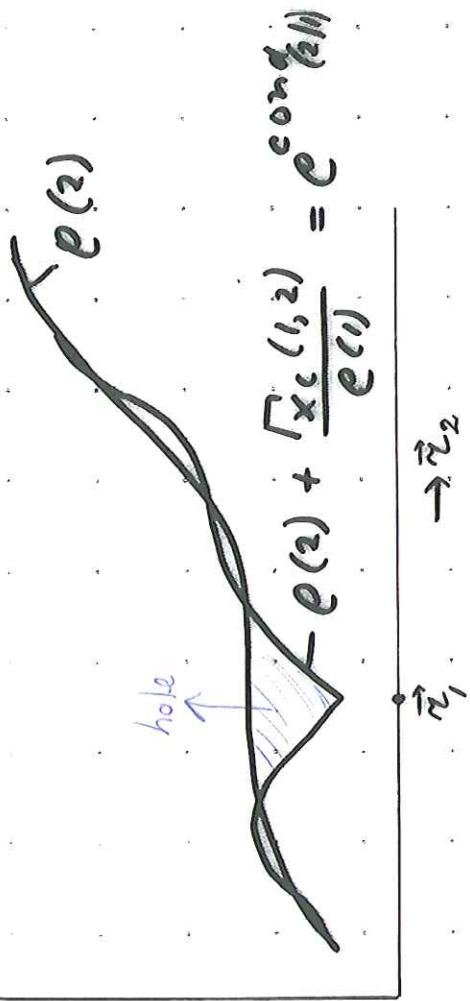
$$\int \rho^{cond.}(2|1) d2 = N-1$$

$$= \int \rho(2) d2 + \int \rho_{xc}^{hole}(2|1) d2$$

$N$   $\downarrow$   $-1$

# THE HK THEOREMS

Hohenberg  
Kohn



1) for:

- non-degenerate ground states  $\Psi_0$
- local external potential  $v(r)$

$\Rightarrow$  one-to-one mapping:

$$\boxed{\rho(r) \leftrightarrow v(r) \leftrightarrow \Psi_0}$$

so  $\Psi_0 = \Psi_0[v] = \Psi_0[\rho]$

and  $\hat{\Omega}[\rho] = \langle \Psi_0 | \rho | \hat{\Omega} | \Psi_0 \rangle$

any property

**all properties are functionals of  $\rho$**

e.g.  $T[\rho]$

$E[\rho]$

$\Rightarrow$  only 1 and 2-elec. density matrices needed to calculate anything.

$$\begin{aligned} \frac{1}{2} \int \frac{\Gamma(r_1, r_2)}{r_{12}} d_1 d_2 &= \frac{1}{2} \int \frac{e^{(1)} e^{(2)}}{r_{12}} d_1 d_2 + \frac{1}{2} \int \frac{\Gamma_{xc}(r_1, r_2)}{r_{12}} d_1 d_2 \\ &= \frac{1}{2} \int e^{(1)} \cdot \underbrace{\int \frac{e^{(2)}}{r_{12}} d_2}_{V_{Coul}^{(1)}} d_1 + \frac{1}{2} \int e^{(1)} \underbrace{\int \frac{\Gamma_{xc}(r_1, r_2)}{e^{(1)} r_{12}} d_2}_{w_{xc}^{hole}} d_1 \end{aligned}$$

$$W = W_{Coul} + W_{xc}$$





# KS orbitals:

Kohn-Sham (KS) orbitals

- are similar to HF orbitals
- have somewhat (sometimes much) better shape:
  - build exact density, not the too diffuse HF density
  - have better  $T_s$  (closer to exact  $T$  than  $T^{HF}$ )
  - have perfect el.-nuclear energy:
 
$$\int \rho_s(\mathbf{r}) v_{nuc}(\mathbf{r}) d\mathbf{r} = \int \rho^{exact}(\mathbf{r}) v_{nuc}(\mathbf{r}) d\mathbf{r} = V^{exact}$$
- have rather accurate one-el. energies  $\{\epsilon_i\}$  for occupied orbitals (very close to  $-IP_i$ , at least for upper valence MOs)
- have virtual orbital energies  $\{\epsilon_a\}$  such that  $\epsilon_a - \epsilon_i$  are good zero order approximations to excitation energies

**Why? Because  $v_s$  has correlation effects built into it!**

*Kohn claims that KS orbitals have hardly any physical meaning, but EJB disagrees.*

## Elementary Concepts

*$T[\rho]$  and  $E[\rho]$  have not been found yet.*

### Ansatz of Kohn-Sham:

for any system of interacting ( $= \sum_{i < j} 1/r_{ij}$ ) electrons moving in local potential  $v(\mathbf{r})$  there exists a noninteracting electron system in a local potential  $v_s(\mathbf{r})$ ,

$$(-1/2)\nabla^2 + v_s(\mathbf{r}) \psi_i^s = \epsilon_i \psi_i^s$$

with properties:

*!!  $\rho_s(r)$  consisting of non-interacting elec's is equal to exact  $\rho$  !!*

- $\rho_s(\mathbf{r}) = \sum_i^N |\psi_i^s(\mathbf{r})|^2 = \rho^{exact}(\mathbf{r})$

- $v_s(\mathbf{r})$  is unique (apply HK to system with  $= 0$ )

- $v_s(\mathbf{r})$  yields exact  $\rho$  (cf. Hartree-Fock)

And it can be shown:

- if:  $v_s(\mathbf{r}) \rightarrow 0$ :  $\epsilon_{HOMO} = -IP^{exact}$   
 $(r \rightarrow \infty) \quad \epsilon_i \approx -IP_i (i < HOMO)$

- virtual-occupied orbital energy differences  $\epsilon_a - \epsilon_i$  are zero-order approx. to excitation energy

- features of  $v_s$  are related to the physics of electron correlation







# Coulomb hole

(Correlation hole)

either:

$$\rho_{\text{cond}}(2|1) - \rho_{\text{cond, HF}}(2|1)$$

$$= \rho(2) + \frac{\Gamma_{XC}(1,2)}{\rho(1)} - \rho^{\text{HF}}(2) - \frac{\Gamma_X^{\text{HF}}(1,2)}{\rho^{\text{HF}}(1)}$$

exact density # exact

$$= \Delta \rho(2) + \left( \frac{\Gamma_{XC}(1,2)}{\rho(1)} - \frac{\Gamma_X^{\text{HF}}(1,2)}{\rho^{\text{HF}}(1)} \right)$$

↑ disadvantage

OZ:  $\rho_{\text{cond}}(2|1) - \rho_{\text{cond, KS}}(2,1)$

$$= \rho(2) + \frac{\Gamma_{XC}(1,2)}{\rho(1)} - \rho(2) - \frac{\Gamma_X^{\text{KS}}(1,2)}{\rho(1)}$$

both exact ⇒ cancel

$$= \frac{\Gamma_{XC}(1,2) - \Gamma_X^{\text{KS}}(1,2)}{\rho(1)} = \rho_C^{\text{hole}}(2|1)$$

$$V_C^{\text{hole}}(1) = V_{XC}^{\text{hole}}(1) - V_X^{\text{hole}}(1)$$

★ correlation hole potential

⇒ correlation

not exact I think because defined in terms of det.

→ We want to know exact E. Two ways:

① Traditional:

$$E = T + \int \rho v dr + \frac{1}{2} \int \rho v \text{Coul} dr + W_{xc}$$

② Kohn-Sham:

$$E = T_s + \int \rho v dr + \frac{1}{2} \int \rho v \text{Coul} dr + E_{xc}$$

correlation correction  
↓ to kin. energy

$$\Rightarrow E_{xc} = T - T_s + W_{xc}$$

exact exchange-corr. (elec.-elec.)

$$E^{\text{KS}} \equiv \langle \Psi_s | \hat{H} | \Psi_s \rangle \quad (\text{cf. } E^{\text{HF}})$$

$$E^{\text{KS}} = T_s + \int \rho v dr + \frac{1}{2} \int \rho v \text{Coul} dr + W_x$$

$$\Rightarrow E_C = E - E^{\text{KS}} = E_{xc} - W_x = T_c + W_c \quad \uparrow$$

$$W_{xc} = \frac{1}{2} \int \int \frac{\rho(x) \rho(y)}{|x-y|} dx dy$$

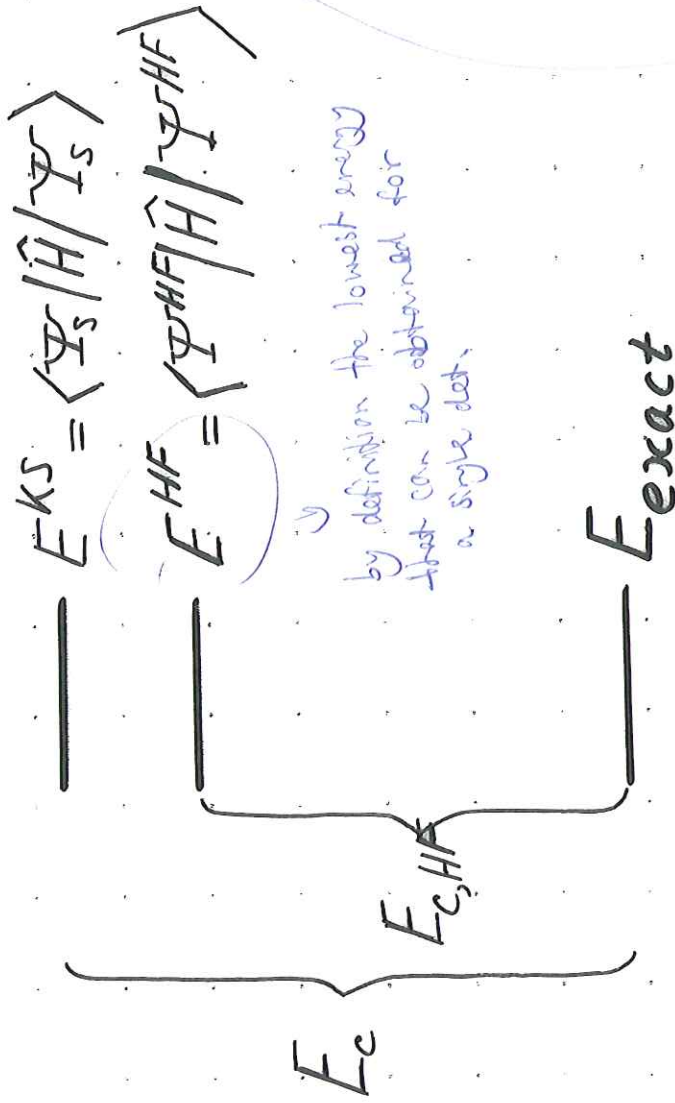
$$E_{xc} = W_x + E_c$$

$$E - E^{\text{KS}} = \frac{E - E^{\text{KS}}}{T} + W_c = W_c - W_x$$

$$W_c = W_{xc} - W_x$$

in KS theory, correlation energy is defined as  $E_{\text{exact}} - E^{\text{KS}}$

$E^{\text{HF}}$  is by definition lower than  $E^{\text{KS}}$ , so correlation in HF is always smaller than correlation in KS theory.



$$E_C^{\text{HF}} = E - E^{\text{HF}}$$

$$= T - T^{\text{HF}} \rightsquigarrow T_C^{\text{HF}}$$

$$+ \int \Delta e v d\vec{z} \rightsquigarrow V_C^{\text{HF}}$$

$$\left\{ \begin{aligned} &+ \int \frac{\Delta e(1) e^{\text{HF}}(2)}{r_{12}} d\vec{z}_1 d\vec{z}_2 \\ &+ \frac{1}{2} \int \frac{\Delta e(1) \Delta e(2)}{r_{12}} d\vec{z}_1 d\vec{z}_2 \end{aligned} \right\} \rightsquigarrow W_{H,c}^{\text{HF}}$$

$$+ W_{Xc} - W_X^{\text{HF}} \rightsquigarrow W_C^{\text{HF}}$$

Note:

$$W_C^{\text{HF}} = W_{Xc} - W_X^{\text{HF}} = W_X + W_c - W_X^{\text{HF}} = \Delta W_X^{\text{s, HF}} + W_c$$

$$\Delta \rho = \rho - \rho^{\text{HF}}!$$

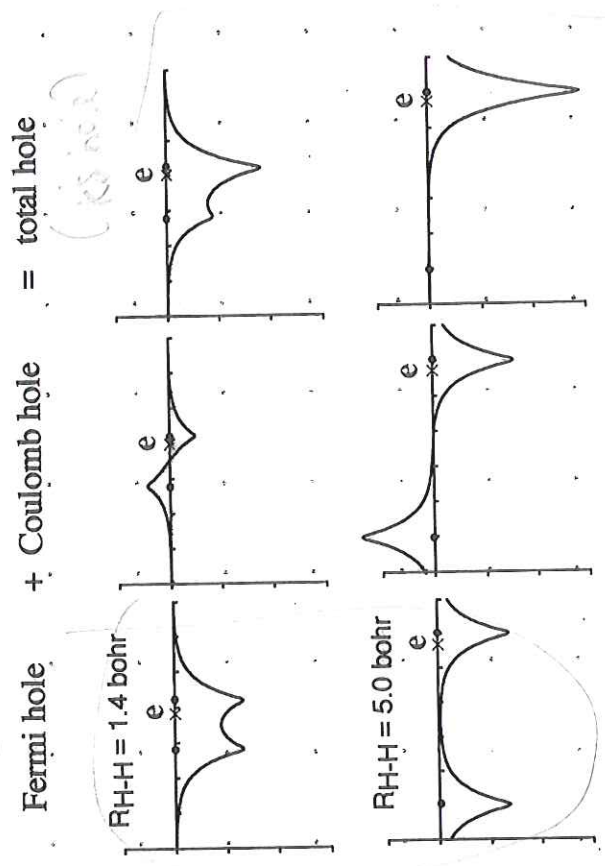
$$\left( \begin{aligned} &(\rho^{\text{HF}} + \Delta \rho) (\rho^{\text{HF}} + \Delta \rho) \\ &\frac{1}{2} \int \frac{\rho(1)\rho(2)}{r_{12}} d\vec{z}_1 d\vec{z}_2 - \frac{1}{2} \int \frac{\rho^{\text{HF}}(1)\rho^{\text{HF}}(2)}{r_{12}} d\vec{z}_1 d\vec{z}_2 \end{aligned} \right)$$

*cancel*

$\Rightarrow$  cross terms  $\Delta \rho \rho^{\text{HF}}$  &  $\rho^{\text{HF}} \Delta \rho$  left, and  $\Delta \rho \Delta \rho$ .



H<sub>2</sub> molecule



Fermi hole, Coulomb hole and total hole in the hydrogen molecule at various values of the internuclear distance. In all plots the reference electron is placed 0.3 bohr at the left of the right H-atom.

Buijse, Baerends, Mol. Phys. 100 (2002) 4  
 Buijse, thesis, 1991

Hartree-Fock only has exchange hole

in H<sub>2</sub>, overlap between s functions is ~0.8 !!  
 very large !! → H<sub>2</sub> is more like He than like a molecule!

Hartree-Fock densities are often poor

	$E^{corr}$	$E_{KIN}^{corr}$	$E_{eN}^{corr}$	$E_{ee}^{corr}$
H <sub>2</sub> (R = R <sub>e</sub> ) (equil. distance for H <sub>2</sub> relatively small)	-1.1 eV	+1.3	-0.5	-1.9
H <sub>2</sub> (R = 5.0 a.u.)	-3.9	+8.9	-8.5	-4.4
H <sub>2</sub> (R = 10.0 a.u.)	-6.3	+7.9	-8.6	-5.6

↑  
 $W_{e,c}^{HF} + W_{H,c}^{HF}$

One-el. energies T and  $V = E_{eN}$  have large errors!

Conclusion:  $\rho^{HF}$  is (way) too diffuse.

Why?

(13)	$E^{\text{core}}$	$E^{\text{KIN}}$	$E_{\text{en}}$	$E_{\text{ee}}$
He	-1.1 eV	+1.1	-0.1	-2.1
H <sub>2</sub> O	-7.0	+6.5	+1.0	-14.5
Ne	-8.9	+8.3	+1.4	-18.5
N <sub>2</sub>	-11.0	+13.7	-13.8	-11.0
MnO <sub>4</sub> <sup>-</sup>	-14.4	+35.7	-115.5	+65.4
Ni(CO) <sub>4</sub>	-3.4	-35.0	+147.8	-116.3
C <sub>2</sub> (CO) <sub>6</sub>	-4.5	-4.5	+30.8	-30.

In H<sub>2</sub> Fermi hole  $\rho_X^{\text{hole}}(\mathbf{r}_2|\mathbf{r}_1)$  for el. at  $\mathbf{r}_1$  is only self-interaction correction term  $-|\sigma_g(\mathbf{r}_2)|^2$

So independent of  $\mathbf{r}_1$ !

When  $R(\text{H-H})$  is large and  $\mathbf{r}_1$  is close to nucleus b, hole is,

with  $\sigma_g(\mathbf{r}_2) \approx (1/\sqrt{2}) [1s_a(\mathbf{r}_2) + 1s_b(\mathbf{r}_2)]$ ,

$$-|\sigma_g(\mathbf{r}_2)|^2 \approx -(1/2) [|1s_a(\mathbf{r}_2)|^2 + |1s_b(\mathbf{r}_2)|^2 + 2 \cdot 1s_a(\mathbf{r}_2) \cdot 1s_b(\mathbf{r}_2)] \approx 0$$

Since total  $\rho$  is  $|1s_a(\mathbf{r}_2)|^2 + |1s_b(\mathbf{r}_2)|^2$ , the field that the HF electron at  $\mathbf{r}_1$  feels is due to  $\rho(\mathbf{r}_2) + \rho_X^{\text{hole}}(\mathbf{r}_2|\mathbf{r}_1) = (1/2) [|1s_a(\mathbf{r}_2)|^2 + |1s_b(\mathbf{r}_2)|^2]$

Wrong! The other el. should be around nucleus a!

The erroneous charge of  $(1/2)|1s_b(\mathbf{r}_2)|^2$  that el. around b feels screens nucleus b: the HF orbital becomes too diffuse.

→ HF is v. size-inconsistent, and bad model for chemical bonding.

# The crucial difference: $v_{xc}$ versus $-\hat{K}$ 146

Write formally:  $E_{xc}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}(\mathbf{r}) d\mathbf{r}$  to obtain  $v_{xc}(\mathbf{x}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{x})}$

↑  
definition of the xc energy density at r

exchange operator in HF

$\varepsilon_{xc}(\mathbf{r})$  is a functional of  $\rho$  since  $E_{xc}$  is.

Can an exact  $\varepsilon_{xc}(\mathbf{r})$  be written?

Energy densities can be written for many properties; they are not unique (any  $f(\mathbf{r})$  with  $\int \rho(\mathbf{r}) f(\mathbf{r}) d\mathbf{r} = 0$  can be added).

Example:  $T^{HF} = \langle \Psi^{HF} | \hat{T} | \Psi^{HF} \rangle = \sum_{i=1}^N \int \psi_i^*(\mathbf{x}_1) \left(-\frac{1}{2} \nabla^2\right) \psi_i(\mathbf{x}_1) d\mathbf{x}_1$

$$= \int \rho(\mathbf{x}_1) \frac{\sum_{i=1}^N \psi_i^*(\mathbf{x}_1) \left(-\frac{1}{2} \nabla^2\right) \psi_i(\mathbf{x}_1)}{\rho(\mathbf{x}_1)} d\mathbf{x}_1$$

$$T = \sum \frac{1}{2} |\nabla \psi_i(\mathbf{x}_1)|^2 d\mathbf{x}_1 = \int \rho(\mathbf{x}_1) \frac{\sum \frac{1}{2} |\nabla \psi_i|^2}{\rho(\mathbf{x}_1)} d\mathbf{x}_1$$

14a

## The one-particle model of DFT: Kohn-Sham

Minimization of

$$E = \sum_{i=1}^N \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int \rho v_{nuc} d\mathbf{r} + \frac{1}{2} \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}$$

$$= T_s + V + W_{Coul} + E_{xc}$$

leads to one-el. equations for optimal (KS) orbitals:

$$\left( -\frac{1}{2} \nabla^2 + v_{nuc}(\mathbf{r}_1) + v_{Coul}(\mathbf{r}_1) + v_{xc}(\mathbf{r}_1) \right) \psi_i(\mathbf{x}_1) = \varepsilon_i \psi_i(\mathbf{x}_1)$$

$\uparrow$   $\int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2$        $\uparrow$   $\frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r}_1)}$

What about potentials, orbitals and density in the KS model?

Common statements: "KS orbitals have no physical meaning"

"The only use for the KS orbitals is to build the density"

We will prove these statements to be totally wrong!



$$E_{xc} = \int \rho(\mathbf{x}) \epsilon_{xc}(\mathbf{x}) d\mathbf{x}$$

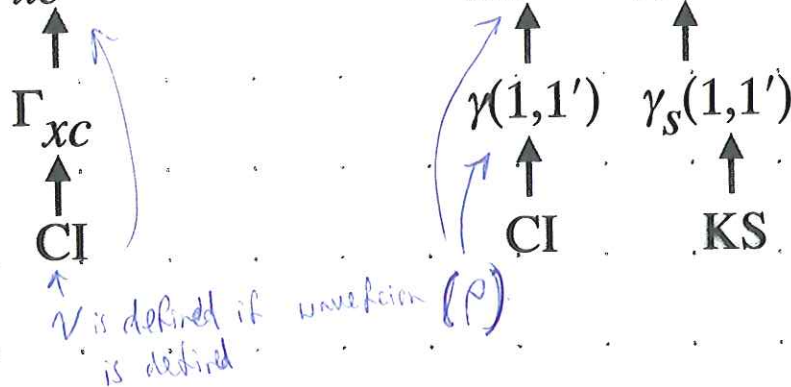
Approximations: LDA, GEA, GGA,.....:

$$\epsilon_{xc}(\mathbf{x}) \approx f(\rho(\mathbf{x}), \rho'(\mathbf{x}), \rho''(\mathbf{x}), \dots)$$

Exact  $\epsilon_{xc}(\mathbf{x})$  from

$$E_{xc} = W_{xc} + T - T_s$$

$$= (1/2) \int \rho(\mathbf{x}) v_{xc}^{hole}(\mathbf{x}) d\mathbf{x} + \int \rho(\mathbf{x}) (v_{kin}(\mathbf{x}) - v_{s,kin}(\mathbf{x})) d\mathbf{x}$$



## Energy density for $T_c$

Write exact  $T$  as 
$$T = \int_{1 \rightarrow 1'} \left(-\frac{1}{2} \nabla^2\right) \gamma(1,1') d\mathbf{x}_1 = T_W + \int \rho(\mathbf{x}) v_{kin}(\mathbf{x}) d\mathbf{x}$$

where 
$$T_w = N \int \sqrt{\frac{\rho(\mathbf{x})}{N}} \left(-\frac{1}{2} \nabla^2\right) \sqrt{\frac{\rho(\mathbf{x})}{N}} d\mathbf{x}$$

$T_W$  is called the Weiszäcker kinetic energy,  $N$  times the kinetic energy of the "density orbital"  $\sqrt{\rho/N}$  → normalized to 1 (density for 1 elec.)

Similarly write  $T_s$  as 
$$T_s = T_W + \int \rho(\mathbf{x}) v_{s,kin}(\mathbf{x}) d\mathbf{x}$$

Explicit kinetic energy densities  $v_{kin}(\mathbf{x})$  and  $v_{s,kin}(\mathbf{x})$ , see later.

$$T_c = T - T_s = \int \rho(\mathbf{x}) [v_{kin}(\mathbf{x}) - v_{s,kin}(\mathbf{x})] d\mathbf{x}$$

$$\epsilon_{xc}(\mathbf{r}) = \frac{1}{2} v_{xc}^{hole}(\mathbf{r}) + v_{kin}(\mathbf{r}) - v_{s,kin}(\mathbf{r})$$

$v_{c,kin}(\mathbf{r})$

Relation between  $\epsilon_{xc}$  and  $v_{xc}$  ?

Define pair correlation factor  $g(1,2)$ :

$$\Gamma(1,2) = \underbrace{\rho(1)\rho(2)}_{\text{unconditional densities}} + \Gamma_{xc}(1,2)$$

$$\rho^{cond}(2|1) = \frac{\Gamma(1,2)}{\rho(1)}$$

$$= \rho(2) + \frac{\Gamma_{xc}(1,2)}{\rho(1)}$$

$$= \rho(2) + \rho^{hole}(2|1)$$

$$= g(1,2)\rho(2)$$

$$\rho^{hole}(2|1) = \frac{\Gamma_{xc}(1,2)}{\rho(1)} = (g(1,2) - 1)\rho(2)$$

$$\rho^{hole}(2|1) = \frac{\Gamma_{xc}(1,2)}{\rho(1)} = (g(1,2) - 1)\rho(2)$$

$$W_{xc} = \frac{1}{2} \int \frac{\Gamma_{xc}(1,2)}{v_{12}} d^2d1$$

$$= \frac{1}{2} \int \rho(1) \int \underbrace{\frac{\rho^{hole}(2|1)}{v_{12}}}_{v_{xc}^{hole}(1)} d^2d1 = \frac{1}{2} \int \rho(1) v_{xc}^{hole}(1) d1$$

$$= \frac{1}{2} \int \frac{\rho(1)(g(1,2) - 1)\rho(2)}{v_{12}} d^2d1$$

in QM, there is a finite probability that 2 elec.'s are at the same position. ( $\rightarrow \infty$  large negative)

in HF (KS), this probability is assumed zero

$$E_{xc} = T_c + W_{xc}$$

$$= \int \rho(1) v_{c,kin}(1) d1 + \frac{1}{2} \int \frac{\rho(1)(g(1,2) - 1) \rho(2)}{r_{12}} d1 d2$$

$$v_{xc}(3) = \frac{\delta E_{xc}}{\delta \rho(3)} = \frac{\delta T_c}{\delta \rho(3)} + \frac{\delta W_{xc}}{\delta \rho(3)}$$

$$\frac{\delta T_c}{\delta \rho(3)} = \int \frac{\delta \rho(1)}{\delta \rho(3)} v_{c,kin}(1) d1 + \int \rho(1) \frac{\delta v_{c,kin}(1)}{\delta \rho(3)} d1$$

$\delta(1-3)$  - delta function

response of kinetic energy

$$+ v_{c,kin}(3)$$

kinetic energy

$$\frac{\delta W_{xc}}{\delta \rho(3)} = \frac{1}{2} \int \frac{\delta \rho(1)}{\delta \rho(3)} \frac{(g(1,2) - 1) \rho(2)}{r_{12}} d1 d2 + \frac{1}{2} \int \frac{\rho(1)(g(1,2) - 1) \delta \rho(2)}{\delta \rho(3)} \frac{d1 d2}{r_{12}}$$

integrating over  $\delta$ -functions  $\delta(1-3)$  and  $\delta(2-3)$

$$= \int \frac{(g(3,2) - 1) \rho(2)}{r_{32}} d2$$

$v_{xc}^{hole}(3)$

$$+ \frac{1}{2} \int \frac{\rho(1) \rho(2)}{r_{12}} \frac{\delta g(1,2)}{\delta \rho(3)} d1 d2 \Rightarrow v_{xc}^{resp}(3)$$

$$E_{xc}(\mathbf{r}) = \frac{1}{2} v_{xc}^{hole}(\mathbf{r}) + v_{c,kin}(\mathbf{r}) - v_{s,kin}(\mathbf{r})$$

$v_{c,kin}(\mathbf{r})$

$$v_{xc}(\mathbf{r}) = v_{xc}^{hole}(\mathbf{r}) + v_{c,kin}(\mathbf{r}) + v_{resp}(\mathbf{r})$$

The important quantities in DFT!!!

$v_{xc}^{hole} = v_x^{hole} + v_c^{hole}$ , primarily important for shape

of KS orbitals.

Cf. H<sub>2</sub> at long distance:

HF: only  $v_x^{hole}$

KS: correl. hole localizes hole properly around refer. el.,

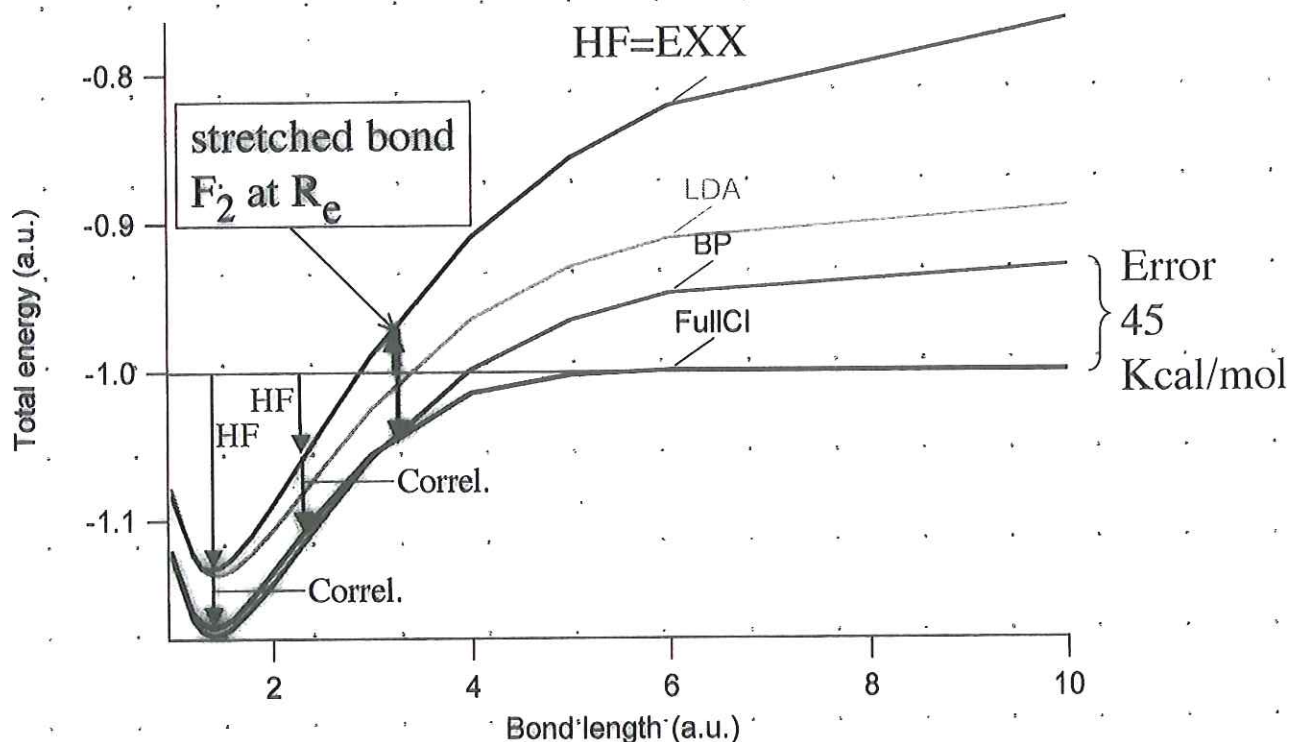
$v_x^{hole} + v_c^{hole}$  cancels  $v_{Coul}$  of el. density at same site

-> electron sees nuclear charge unscreened and obtains perfect 1s shape



# $E$ versus $R$ curves (restricted HF/KS) for dissociating $H_2$

186

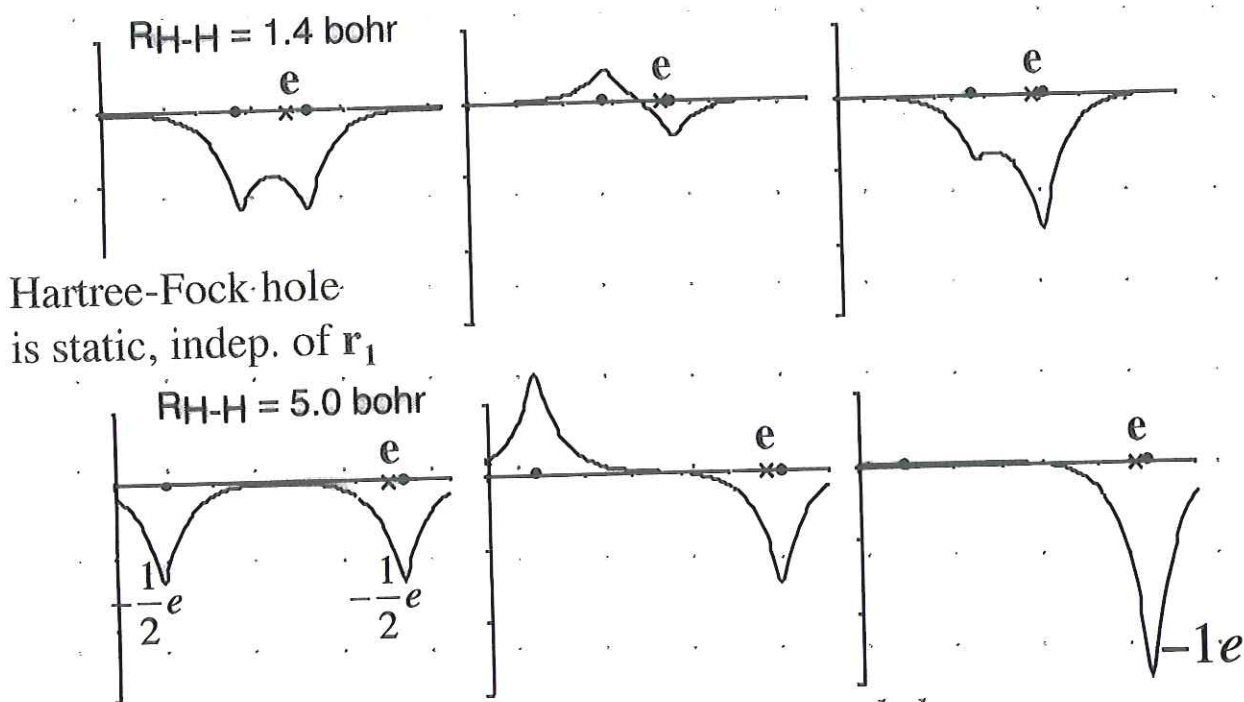


Grüning, Gritsenko, Baerends, JCP 118 (2003) 7183

## Holes in $H_2$

18a

Fermi = Hartree-Fock hole + Coulomb hole = total hole  
 $= -|\sigma_g(r_2)|^2$

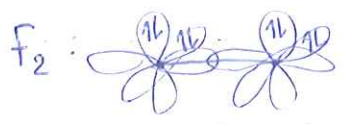


NB: Kohn-Sham  $v_{xc} = v_{c,kin} + v_{xc}^{hole} + v^{resp}$

KS  $\rightarrow$  correlation built into 1-elec. density !! (in contrast with HF)

# Hartree-Fock errors for bond energies (kcal/mol)

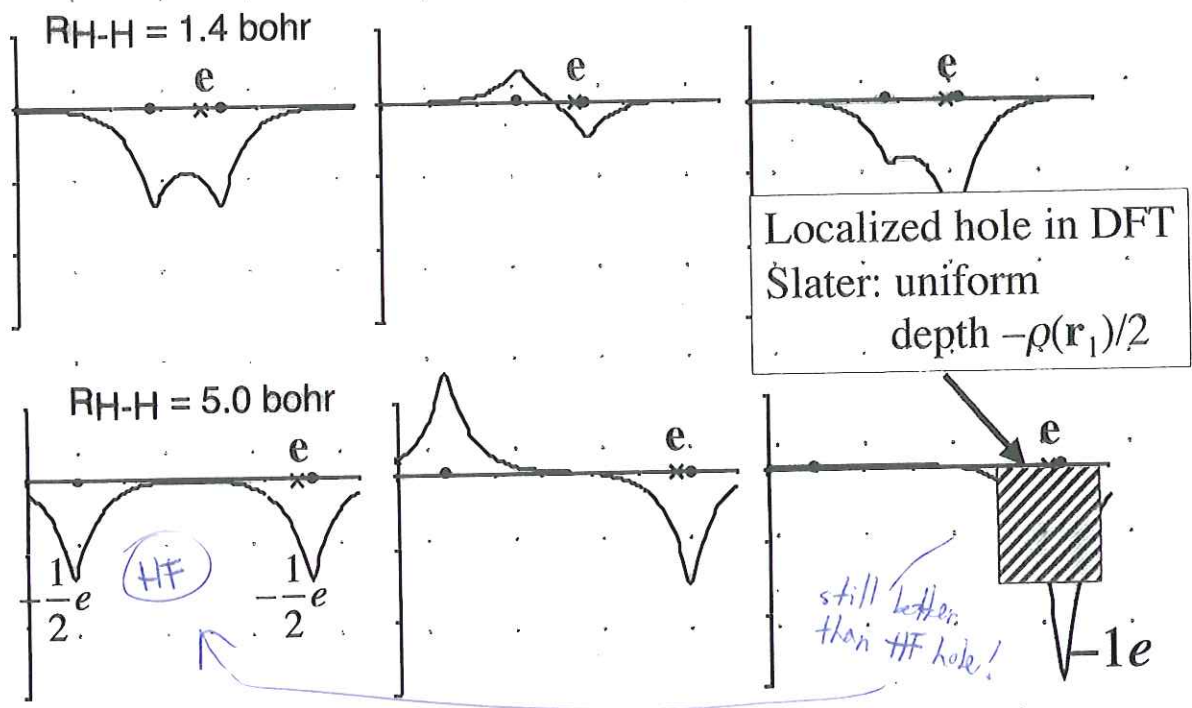
	HF	Obs.	Error (% of Obs.)
N <sub>2</sub>	-115.2	-228.6	49.6%
F <sub>2</sub>	+37.1	-38.5	196.4%
H <sub>2</sub> O	-155.5	-232.2	33.0%
O <sub>2</sub>	-33.1	-120.5	72.5%



lone pairs repel each other → v. large bond distance.  
 → HF predicts even positive (repulsive) bond energy!  
 (but HF is bad for bonding)

## Holes in H<sub>2</sub>

Fermi hole + Coulomb hole = total hole



NB. KS  $v_s = v_{nuc} + v_{Coul} + v_{xc}$       $v_{xc} = v_{c,kin} + v_{xc}^{hole} + v^{resp}$

# Produce EXACT KS orbitals

20

Hohenberg-Kohn: change  $v$  to  $v' = v + \Delta v$   
 then  $\rho \rightarrow \rho' = \rho + \Delta\rho, \Delta\rho \neq 0$

$$\langle \Psi | H' | \Psi \rangle > \langle \Psi' | H' | \Psi' \rangle \Rightarrow T + W + \int v' \rho d\mathbf{r} > T' + W' + \int v' \rho' d\mathbf{r}$$

plus  $\langle \Psi' | H | \Psi' \rangle > \langle \Psi | H | \Psi \rangle \Rightarrow T' + W' + \int v \rho' d\mathbf{r} > T + W + \int v \rho d\mathbf{r}$

yields  $\int v' \rho d\mathbf{r} + \int v \rho' d\mathbf{r} > \int v' \rho' d\mathbf{r} + \int v \rho d\mathbf{r}$  or  $\int \Delta v \Delta \rho d\mathbf{r} < 0$

So to get from trial  $v$  with density  $\rho$  to target  $\rho' = \rho + \Delta\rho$ ,  
 use update  $\Delta v(\mathbf{r}) (\cdot) - \Delta\rho(\mathbf{r})$  and iterate

*if  $\Delta v$  changes somewhere then  $\Delta\rho$  must also change, and with opposite sign, such that  $\int \Delta v \Delta \rho d\mathbf{r} < 0$  !!*

(R. van Leeuwen, E. J. Baerends, *Phys. Rev. A* **49** (1994) 2421)

KS and HF energies of  $N_2$   $D_e = 0.37$  a.u.

R (bohr)	2.074 ( $R_e$ )	3.0	3.5
$T_s$	109.070	108.095	108.223
$T - T_s = T_{kin}^{corr}$ (KS)	0.329	0.328	0.313
$T - T^{HF} = T_{kin}^{corr}$ (HF)	0.625	1.020	1.216
$T_s - T^{HF} =$	0.296	0.692	0.903
$V_{el-nuc}$ (exact=KS)	-303.628	-288.260	-283.780
$V_{el-nuc}^{corr}$ (HF)	-0.558	-1.330	-1.759
$W_{Coul}$ (exact=KS)	75.068	67.858	65.666
$W_{Coul}^{corr}$ (HF)	0.274	0.716	0.980



KS and HF energies of N<sub>2</sub>     D<sub>e</sub> = 0.37 a.u.

R (bohr)	2.074	3.0	3.5
W <sub>X</sub> (KS orbitals)	-13.114	-12.621	-12.490
W <sub>X</sub> - W <sub>X</sub> <sup>HF</sup> =	0.006	-0.040	-0.067
W <sub>c</sub> = W <sub>XC</sub> - W <sub>X</sub>	-0.804	-0.969	-1.063
W <sub>c</sub> (HF) = W <sub>XC</sub> - W <sub>X</sub> <sup>HF</sup>	-0.810	-1.009	-1.124
E <sub>c</sub>	-0.475	-0.641	-0.750
E <sub>c</sub> (HF)	-0.469	-0.603	-0.687
E <sub>c</sub> - E <sub>c</sub> (HF)	-0.006	-0.038	-0.063

HF & KS equally poor, because they're both based on single det.

KS nearly as good as HF

Gritsenko, Schipper, Baerends, *J. Chem. Phys.* **107** (1997) 5007

(considering that HF is by definition the lowest energy for a single det.)

energy relative to exact energy

N<sub>2</sub> at R<sub>e</sub>

$$\begin{aligned}
 \text{KS: } E_c &= T_c + W_c \\
 &= 0.329 - 0.804 \\
 \text{HF: } E_c^{HF} &= T_c^{HF} + V_c^{HF} + W_{H,c}^{HF} + W_c^{HF} \\
 &= 0.625 - 0.558 + 0.274 - 0.814 \\
 &= 0.341
 \end{aligned}$$

# Conclusion

- P-HF better total energy (marginally)  
 $E_C \lesssim E_{HF}$

-  $T_S$  better for:

no correlation error  
 $V_{el}$  (Kohn-Sham determinant)  
 $W_H$ : elec-elec. Coulomb (Hartree)  
 $T_S$ : (much) smaller correlation error

HF "distorts" density (more diffuse) if gain by lowering  $T_{HF}$  is larger (even if barely) than loss by less stable  $V$

Buijse, Baerends; J.C.P. 93 (1990) 4129 (MnO<sub>2</sub>)  
 Buijse, Baerends, T.C.A. 79 (1991) 389 (MnO<sup>+</sup>)

Energy components for CO at  $R_e = 2.132$  bohr ( $D_e \approx 4$  a.u.)

	LDA	BLYP	EXX	HF	KS	CI
$T/T^s$	111.951	113.181	112.395	112.641	112.881	113.185
$\Delta CI^s$	+1.234	+0.004	+0.790	+0.544	+0.304	
$V_{en}$	-310.170	-311.520	-310.651	-310.879	-311.256	-311.256
$\Delta CI^{en}$	-1.086	+0.264	-0.605	-0.377	0.00	
$W^H$	76.204	76.391	76.251	76.262	76.399	76.399
$\Delta CI^H$	+0.195	+0.008	+0.148	+0.137	0.00	
$W^X$	-12.064	-13.475	-13.296	-13.331	-13.319	-14.089
$\Delta KS^X$	-1.255	+0.156	-0.023	+0.012		
$E_{el}$	-134.079	-135.423	-135.301	-135.307	-135.295	
$E_c^c$	-1.682	-0.338	-0.460	-0.454	-0.466	
$E_c^e$	-0.950	-0.486				
$E_{tot}$	-135.029	-135.909				-135.761
$\Delta CI^{tot}$	-0.732	+0.148				