

# DFT – Wavefunction relationships

E. J. Baerends  
Dec. 2008

DFT is a theory in the field of many-electron physics.

All information for a many-electron system is in the wavefunction.

Therefore the quantities of DFT must follow from  $\Psi$ !

Let us make those relations explicit.

Summary so far: Kohn-Sham eq.  $\left(-\frac{1}{2}\nabla^2(i) + v_S(i)\right) \psi_i^S(i) = \epsilon_i \psi_i^S(i)$

$$\rho_S(i) = \sum_i |\psi_i^S(i)|^2 = \rho_{\text{exact}}$$

$$v_S(i) = v_{\text{nuc}}(i) + v_{\text{coul}}(i) + v_{xc}(i)$$

$$v_{xc}(i) = v_{xc}^{\text{hole}} + v_{xc}^{\text{kin}} + v^{\text{response}} \frac{\delta E_{xc}}{\delta \rho(i)}$$

# DFT – Wavefunction relationships

The components of  $\epsilon_{xc}$  and  $v_{xc}$  can be obtained from the wavefunction, i.e. from the conditional amplitude

$$\Phi(2, 3, \dots, N | 1) = \frac{\Psi(1, 2, \dots, N)}{\sqrt{\rho(1) / N}}$$

$$|\Phi(2, 3, \dots, N | 1)|^2 = \frac{|\Psi(1, 2, \dots, N)|^2}{\rho(1) / N}$$

is probability distribution of electrons 2...N when electron 1 is at  $\mathbf{r}_1, s_1$

$\Phi$  incorporates effects of correlation  
 $\Phi$  describes XC hole !  
(and total el. density)

can be seen as trial wavefunction

One-el. density associated with wavefunction  $\Phi$  is  $\rho^{cond}(2|1)$ , the density of the *other* electrons at  $\mathbf{x}_2 = \mathbf{r}_2, s_2$  when el. 1 is known to be at  $\mathbf{x}_1$

$$(N-1) \int \Phi^*(2, 3, \dots, N | 1) \Phi(2, 3, \dots, N | 1) d3 \dots dN$$

$$= (N-1) \int \frac{\Psi^*(1, 2, 3, \dots, N)}{\sqrt{\rho(1)/N}} \frac{\Psi(1, 2, 3, \dots, N)}{\sqrt{\rho(1)/N}} d3 \dots dN$$

$$= \frac{N(N-1)}{\rho(1)} \int \Psi^*(1, 2, 3, \dots, N) \Psi(1, 2, 3, \dots, N) d3 \dots dN$$

$$= \frac{\Gamma(1, 2)}{\rho(1)} \equiv \rho^{cond}(2|1) = \rho(2) + \rho_{xc}^{hole}(2|1)$$

A)  $v_{xc}^{hole}$  follows from  $\Phi$

Potential of all other electrons at pos.  $\mathbf{r}_1$  of ref. el.

$$\int \Phi^*(2,3,\dots,N | 1) \Phi(2,3,\dots,N | 1) \left( \sum_{p=2}^N \frac{1}{r_{1p}} \right) d\mathbf{x}_2 d\mathbf{x}_3 \dots d\mathbf{x}_N$$

$$= (N-1) \int d\mathbf{x}_2 \frac{1}{r_{12}} \int \frac{\Psi^*(1\dots N)}{\sqrt{\rho(1)/N}} \frac{\Psi(1\dots N)}{\sqrt{\rho(1)/N}} d\mathbf{x}_3 \dots d\mathbf{x}_N$$

$$= \frac{N(N-1)}{\rho(1)} \int \frac{\Gamma(\mathbf{x}_1, \mathbf{x}_2)}{\rho(\mathbf{x}_1)} \frac{1}{r_{12}} d\mathbf{x}_2 = v_{Coul}(\mathbf{x}_1) + v_{xc}^{hole}(\mathbf{x}_1)$$

$$\downarrow$$

$$\rho^{cond}(\mathbf{x}_2 | \mathbf{x}_1)$$

$$= \rho(\mathbf{x}_2) + \rho_{xc}^{hole}(\mathbf{x}_2 | \mathbf{x}_1)$$

Pot. at 1 due to elec. 2:

$$\int \int |\phi(\vec{y}, 3, \dots, N | \vec{x})|^2 d\mathbf{z} \dots dN \frac{1}{|\vec{x} - \vec{y}|} d\vec{y}$$

$\downarrow$                        $\downarrow$                        $\uparrow$   
 el. 2                      el. 1                       $\frac{1}{r_{12}}$

$$\begin{aligned}
v_{kin}(1) &= \int \Phi^*(2 \dots N | 1) \left( -\frac{1}{2} \nabla^2(1) \right) \Phi(2 \dots N | 1) d\mathbf{x}_2 \dots d\mathbf{x}_N \\
&= +\frac{1}{2} \int |\nabla_1 \Phi(2 \dots N | 1)|^2 d\mathbf{x}_2 \dots d\mathbf{x}_N \\
&\text{(proof is not by partial integration)}
\end{aligned}$$

Similarly

$$\begin{aligned}
v_{s,kin}(1) &= \int \Phi_s^*(2 \dots N | 1) \left( -\frac{1}{2} \nabla^2(1) \right) \Phi_s(2 \dots N | 1) d\mathbf{x}_2 \dots d\mathbf{x}_N \\
&= +\frac{1}{2} \int |\nabla_1 \Phi_s(2 \dots N | 1)|^2 d\mathbf{x}_2 \dots d\mathbf{x}_N
\end{aligned}$$

$$T = T_W + \int \rho v_{kin} d\mathbf{x} \qquad T_s = T_W + \int \rho v_{s,kin} d\mathbf{x}$$

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

In two-el, system the KS det. wavef., like the HF det., has static ~~(exchange hole)~~  $\rightarrow v_{s,kin} = 0!!$

$$v_{c,kin} = v_{kin}$$

$$V_{e,kin} \equiv V_{corr,kin} = \underbrace{V_{kin}}_{\text{complete kin. energy of system}} - \underbrace{V_{s,kin}}_{\text{kin. energy of KS}}$$

## B) Definition of $v_{kin}$

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

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

$$= N \int \left[ \sqrt{\frac{\rho(1)}{N}} \left( -\frac{1}{2} \nabla^2(1) \right) \sqrt{\frac{\rho(1)}{N}} \right] \underbrace{\int \Phi^*(2 \dots N | 1) \Phi(2 \dots N | 1) d\mathbf{x}_2 \dots d\mathbf{x}_N d\mathbf{x}_1}_{=1}$$

kin. energy of density orbitals

→  $T_W$   
if  
"Wigner"

$$+ \underbrace{\int \rho(1) \int \Phi^*(2 \dots N | 1) \left( -\frac{1}{2} \nabla^2(1) \right) \Phi(2 \dots N | 1) d\mathbf{x}_2 \dots d\mathbf{x}_N d\mathbf{x}_1}_{v_{kin}(1)}$$

$$+ N \int \sqrt{\frac{\rho(1)}{N}} \Phi^*(2 \dots N | 1) \left( -\nabla(1) \sqrt{\frac{\rho(1)}{N}} \right) (\nabla(1) \Phi(2 \dots N | 1)) d\mathbf{x}_2 \dots d\mathbf{x}_N d\mathbf{x}_1$$

$$= N \int \left[ \sqrt{\frac{\rho(1)}{N}} \left( -\frac{1}{2} \nabla^2(1) \right) \sqrt{\frac{\rho(1)}{N}} \right] d\mathbf{x}_1 + \int \rho(1) v_{kin}(1) d\mathbf{x}_1 = T_W + \int \rho(1) v_{kin}(1) d\mathbf{x}_1$$

Third term is zero because of normalization of  $\Phi$  at all positions  $\mathbf{x}_1$ :

$$\nabla_1 \int \Phi^*(2, 3, \dots, N | 1) \Phi(2, 3, \dots, N | 1) d2 \dots dN = 0$$

$T_W$  is  $N$  times kinetic energy of "density orbital"  $\sqrt{\frac{\rho(1)}{N}}$

$$v_{kin}(1) = + \frac{1}{2} \int |\nabla_1 \Phi(2 \dots N | 1)|^2 d\mathbf{x}_2 \dots d\mathbf{x}_N$$

*definite positive!*

Interpretation:

$v_{xc}^{hole}$  reflects shape of hole around position 1

$v_{kin}$  reflects rate of change of hole w.r.t. change of reference electron "position"  $1 = r_1, s_1$

"how strongly motion of reference electron is correlated with motion of other electrons"

## Special cases for $v_{kin}$ :

A)  $1 \rightarrow \infty$  (elec. 1 is out of the system)

$$\lim_{1 \rightarrow \infty} \Phi(2 \cdots N | 1) = \Psi_0^{N-1}(2 \cdots N)$$

Katriel+Davidson, *PNAS* 77 (1980) 4403

$$\nabla_1 \Phi |_{1 \rightarrow \infty} \rightarrow 0 \quad \Rightarrow \quad v_{kin}(\infty) = 0$$

B)  $1 \rightarrow R_\alpha$  (position of nucleus  $\alpha$ )

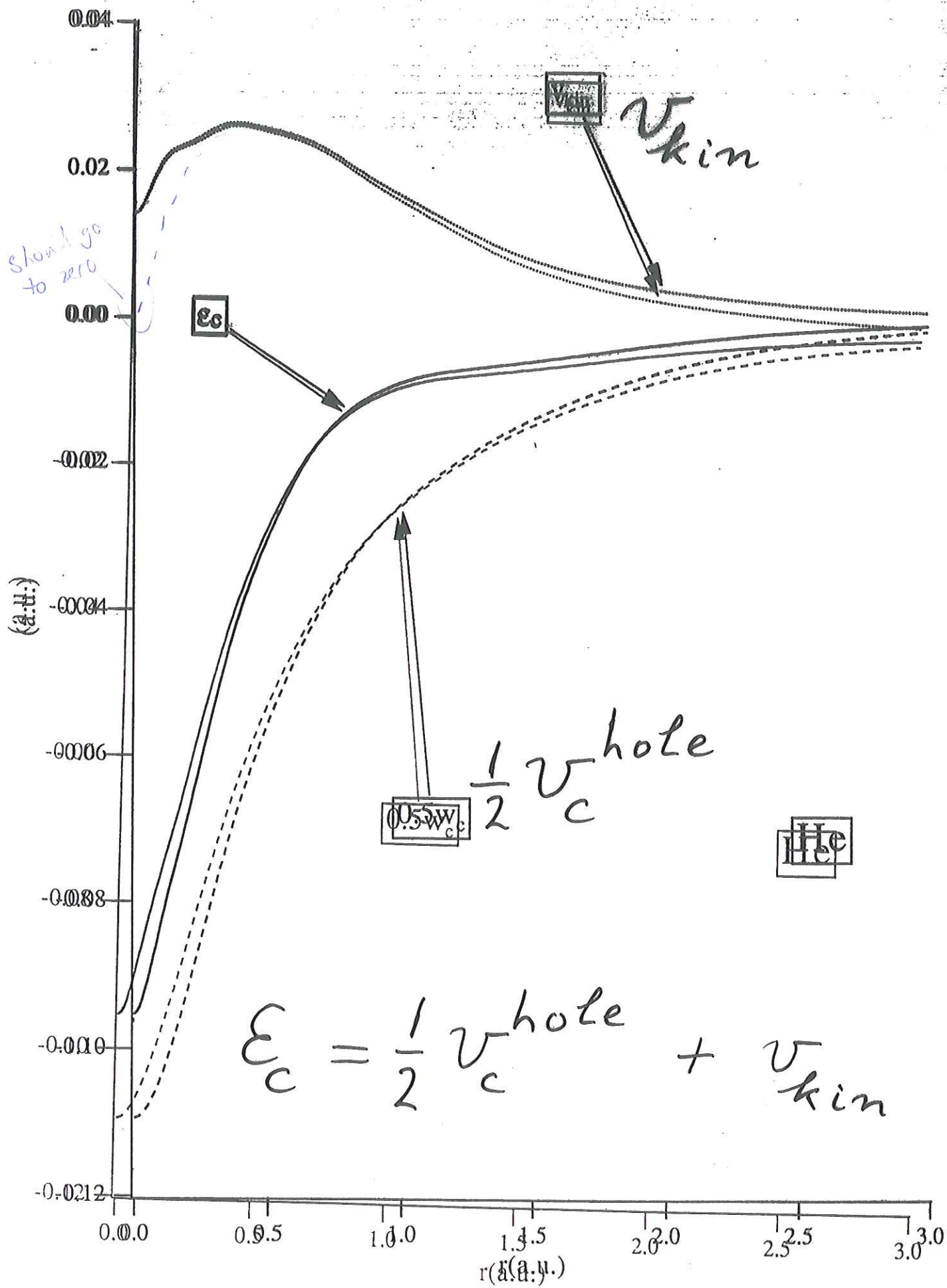
$$\nabla_1 \Phi |_{1 \rightarrow R_\alpha} \text{ small } (=0 \text{ for s-atoms He, Be ?})$$

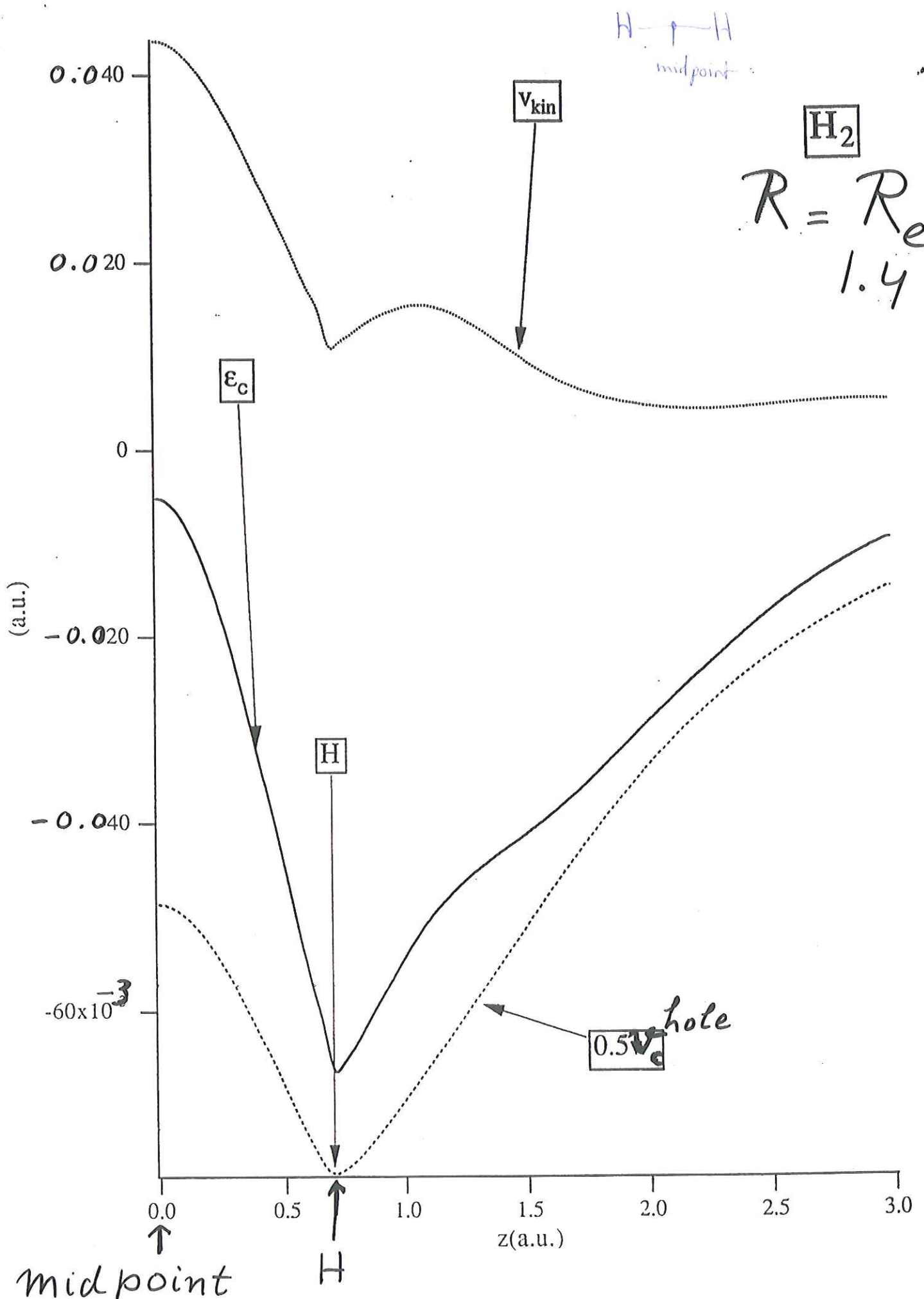
(near nucleus the hole is  $-1s$  orbital, so it doesn't change)

C)  $\nabla_1 \Phi$  large when

- Fermi hole changes rapidly
- Coulomb hole changes rapidly





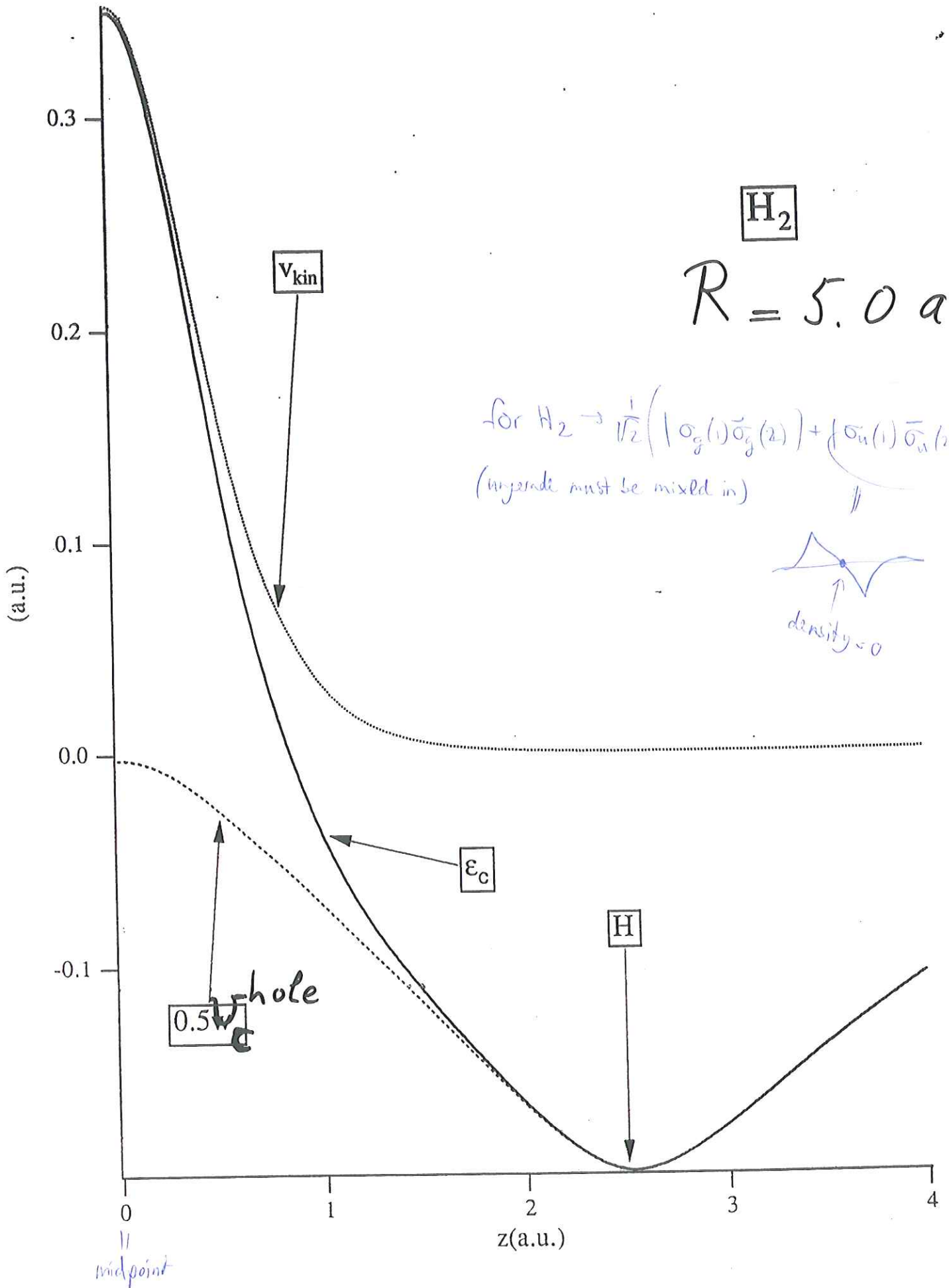
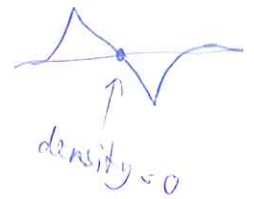


Süle, Gritsenko, Nagy, Baerends, J.C.P. 103 (1995) 10 085

$\boxed{H_2}$

$R = 5.0 \text{ a.u.}$

for  $H_2 \rightarrow \frac{1}{\sqrt{2}} \left( |\sigma_g(1)\bar{\sigma}_g(2)\rangle + |\sigma_u(1)\bar{\sigma}_u(2)\rangle \right)$   
(ungerade must be mixed in)



## C) The potential $v^{response}$

We have derived:

$$\begin{aligned} v^{resp}(\mathbf{x}_1) &= v_{c,kin}^{resp}(\mathbf{x}_1) + v_{hole}^{resp}(\mathbf{x}_1) \\ &= \int \rho(\mathbf{x}_2) \frac{\delta v_{c,kin}(\mathbf{x}_2)}{\delta \rho(\mathbf{x}_1)} d\mathbf{x}_2 \quad \Rightarrow \quad v_{c,kin}^{resp}(\mathbf{x}_1) \\ &\quad + \frac{1}{2} \int \frac{\rho(\mathbf{x}_2)\rho(\mathbf{x}_3)}{r_{23}} \frac{\delta g(\mathbf{x}_2, \mathbf{x}_3)}{\delta \rho(\mathbf{x}_1)} d\mathbf{x}_2 d\mathbf{x}_3 \quad \Rightarrow \quad v_{hole}^{resp}(\mathbf{x}_1) \end{aligned}$$

Difficult to develop further.

Use instead:

$$v^{resp}(\mathbf{x}_1) \text{ is also equal to: } v^{N-1}(\mathbf{x}_1) - v_s^{N-1}(\mathbf{x}_1)$$

*Buise, Baerends, Snijders, Phys. Rev. A* **40** (1989) 4190

What is shape/role of  $v^{resp} = v^{N-1} - v_s^{N-1}$  ?

1) Step structure  $v_s^{N-1}$ ,  $v^{N-1}$

2) Step structure  $v^{resp}$  in atoms  
(exchange effect)

3) Step structure in molecules  
(correlation effect)

*NOTE:* Correct (or sufficiently accurate)  $v^{resp}$  necessary for:

1) correct covalency, charge distribution, dipole moments, .....  
(in particular in weak bonding cases)

2) correct  $\epsilon_i^{KS}$  (occ. and virt.)

$\Rightarrow$  response properties

$$v^{resp} = v^{N-1} - v_s^{N-1} = v^{resp}$$

$$v^{N-1}(\mathbf{x}_1) = \int \Phi^*(2,3,\dots,N | 1) \hat{H}^{N-1} \Phi(2,3,\dots,N | 1) d2 \dots dN - E_0^{N-1}$$

$$= E^{N-1}(\mathbf{x}_1) - E_0^{N-1} > 0$$

↓  
ground state of ion

$$E^{N-1}(\mathbf{x}_1):$$

The energy of an  $(N-1)$ -el. system with wavefunction  $\Phi$ , i.e. the "state" of the system of electrons  $2\dots N$  when el. 1 would be at  $\mathbf{x}_1$ .

This is not the ground state of the  $(N-1)$ -el. ion!

El.  $2\dots N$  move in pot  $v_{nuc}$  and have  $1/r_{ij}$  interactions; no interaction with el. 1 in energy  $E^{N-1}(\mathbf{x}_1)$

$\Phi(2,..N)$  differs from  $(N-1)$ -el. gr. state  $\Psi_0^{N-1}$   
which has energy  $E_0^{N-1}$

->  $\nu^{N-1}(1) = E^{N-1}(\mathbf{x}_1) - E_0^{N-1} \geq 0$  (variation theorem)

$\nu^{N-1}(\infty) \rightarrow 0$  since  $\Phi(2\dots N | 1) \xrightarrow{1 \rightarrow \infty} \Psi_0^{N-1}$

### Interpretation:

$\nu^{N-1}(\mathbf{x}_1)$  is "relaxation energy" from  $\Phi$  to  $\Psi_0^{N-1}$

which depends on the reference position  $\mathbf{x}_1$  in  $\Phi$

For the KS system of noninteracting electrons the analogous definition holds:

$$v_s^{N-1} = \int \Phi_s^*(\mathbf{x}_2 \dots \mathbf{x}_N | \mathbf{x}_1) \hat{H}_s^{N-1} \Phi_s(\mathbf{x}_2 \dots \mathbf{x}_N | \mathbf{x}_1) d\mathbf{x}_2 \dots d\mathbf{x}_N - E_0^{N-1}$$

$\hat{H}_s^{N-1}$  is the KS Hamiltonian for  $N-1$  el., moving in the original field  $v_s$  for the  $N$ -el. system:

$$\hat{H}_s^{N-1} = \sum_{i=2}^N \hat{h}_s(i) = \sum_{i=2}^N \left( -\frac{1}{2} \nabla^2(i) + v_s(\mathbf{r}_i) \right)$$

Since electrons are noninteracting in the KS system, it is elementary to work out the matrixelement (à la Slater-Condon method for matrix elements of determinant wavefunctions):

Write  $\Phi_s(\mathbf{x}_2 \dots \mathbf{x}_N | \mathbf{x}_1) = \Psi_s(\mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N) / \sqrt{\rho(\mathbf{x}_1) / N}$   
 where  $\Psi_s$  is KS determ. wavefunction,

$$v_s^{N-1} = \frac{N}{\rho(1)} \int \Psi_s^*(1 \dots N) \hat{H}_s^{N-1} \Psi_s(1 \dots N) d\mathbf{x}_2 \dots d\mathbf{x}_N$$



Expand determinant  $\Psi_s$  with respect to first column containing elements  $\psi_j(\mathbf{x}_1)$  and its (unnorm.) cofactors

$$\begin{aligned}\Psi_s &= \frac{1}{\sqrt{N!}} \det\{\psi_1(\mathbf{x}_1) \ \psi_2(\mathbf{x}_2) \dots \psi_N(\mathbf{x}_N)\} \\ &= \frac{1}{\sqrt{N!}} \sum_{j=1}^N \psi_j(\mathbf{x}_1) (-1)^{j+1} \Psi_s^{(j1)}(\mathbf{x}_2 \dots \mathbf{x}_N)\end{aligned}$$

and use orthogonality of the cofactors:

$$\int \Psi_s^{(j1)*}(\mathbf{x}_2 \dots \mathbf{x}_N) \Psi_s^{(i1)}(\mathbf{x}_2 \dots \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N = (N-1)! \delta_{ji}$$

to obtain

$$\begin{aligned}v_s^{N-1} &= \frac{N}{\rho(1)} \int \Psi_s^*(1 \dots N) \hat{H}_s^{N-1} \Psi_s(1 \dots N) d\mathbf{x}_2 \dots d\mathbf{x}_N \\ &= \frac{1}{\rho(1)} \sum_j |\psi_j^s(1)|^2 \sum_{k \neq j} \langle \psi_k^s | \hat{h} | \psi_k^s \rangle \\ &= \frac{1}{\rho(1)} \sum_j |\psi_j^s(1)|^2 \sum_{k \neq j} \epsilon_k^s \\ &= \frac{1}{\rho(1)} \sum_j |\psi_j^s(1)|^2 E_{s,j}^{N-1}\end{aligned}$$

$\epsilon_k^s$

$E_{s,j}^{N-1}$  is energy of KS ion with el. ionized from  $\psi_j^s$   
 (which is sum of orbital energies with  $\epsilon_j$  omitted)

This shows that  $v_s^{N-1}$  has step behavior:

$$v_s^{N-1}(1) = \frac{N}{\rho(1)} \int \Psi_s^* \hat{H}_s^{N-1} \Psi_s d\mathbf{x}_2 \dots d\mathbf{x}_N - E_{s,0}^{N-1}$$

$$= \frac{1}{\rho(1)} \sum_j^N |\psi_j^s(1)|^2 E_{s,j}^{N-1} - E_{s,0}^{N-1}$$

(use  $\sum_j^N |\psi_j^s(1)|^2 / \rho(1) = 1$ )

$$= \sum_j^N \frac{|\psi_j^s(1)|^2}{\rho(1)} E_{s,j}^{N-1} - \sum_j^N \frac{|\psi_j^s(1)|^2}{\rho(1)} E_{s,0}^{N-1}$$

$$= \sum_j^N \frac{|\psi_j^s(1)|^2}{\rho(1)} \left( E_{s,j}^{N-1} - E_{s,0}^{N-1} \right)$$

$$v_s^{N-1}(1) = \sum_j^N \frac{|\psi_j^s(1)|}{\rho(1)} \left( E_{s,j}^{N-1} - E_{s,0}^{N-1} \right)$$

In a region (core, lone pair, atomic shell) where one particular  $|\psi_j^{N-1}(1)|^2$  dominates, i.e.  $|\psi_j^{N-1}(1)|^2 \approx \rho(1)$ , the potential has step height

$$\left( E_{s,j}^{N-1} - E_{s,0}^{N-1} \right)$$

In the region of the HOMO,  $j=\text{HOMO}$ , the potential is zero since  $E_{s,j=\text{HOMO}}^{N-1} = E_{s,0}^{N-1}$

$\left( E_{s,j}^{N-1} - E_{s,0}^{N-1} \right)$  is difference of energy of ionization to ion state  $\Psi_{s,j}^{N-1}$  by ionizing from orbital  $\psi_j^s$  (which is  $-\varepsilon_j$ ) and the first ionization,  $I_0 = -\varepsilon_{\text{HOMO}}$ :

$$v_s^{N-1} = \sum_j^N \frac{|\psi_j^s(1)|^2}{\rho(1)} \left( -\varepsilon_j - I_0 \right)$$

$\psi^{N-1}$  has similar structure as  $\psi_s^{N-1}$

Use Dyson expansion:

$$\Psi_0^N = \sum_i \frac{d_i(1)}{\sqrt{N}} \Psi_i^{N-1}(2\dots N)$$

$\Psi_i^{N-1}$  are all states of the ion

$d_i$  are Dyson orbitals (one - el. wavefunctions),  
one for each ion state :

$$d_j(1) = \sqrt{N} \int \Psi_j^{N-1*}(2\dots N) \Psi_0^N(1,2\dots N) d\mathbf{x}_2 \dots d\mathbf{x}_N$$

Note that set  $\{d_i\}$  is overcomplete, nonorthogonal and not normalized, and

$$\begin{aligned} \rho(1) &= N \int \Psi_0^{N*}(1,2\dots N) \Psi_0^N(1,2\dots N) d\mathbf{x}_2 \dots d\mathbf{x}_N \\ &= N \sum_{i,j} \frac{d_i^*(1)}{\sqrt{N}} \frac{d_j(1)}{\sqrt{N}} \int \Psi_i^{N-1*}(2\dots N) \Psi_j^{N-1}(2\dots N) d\mathbf{x}_2 \dots d\mathbf{x}_N \\ &= \sum_{i,j} d_i^*(1) d_j(1) \delta_{ij} = \sum_i |d_i^*(1)|^2 \end{aligned}$$

$$v^{N-1}(1) = \int \Phi^*(2\dots N) |1\rangle \hat{H}^{N-1} \Phi(2\dots N) |1\rangle dx_2 \dots dx_N - E_0^{N-1}$$

$$[\text{use } \Psi = \sqrt{\frac{\rho(1)}{N}} \Phi(x_2 \dots x_N | x_1)]$$

$$= \int \sqrt{\frac{N}{\rho(1)}} \Psi^*(1\dots N) \hat{H}^{N-1} \sqrt{\frac{N}{\rho(1)}} \Psi(1\dots N) dx_2 \dots dx_N - E_0^{N-1}$$

$$= \frac{N}{\rho(1)} \sum_{i,j} \frac{d_i^*(1)}{\sqrt{N}} \frac{d_j(1)}{\sqrt{N}} \int \Psi_i^{N-1*}(2\dots N) \hat{H}^{N-1} \Psi_j^{N-1}(2\dots N) dx_2 \dots dx_N$$

$$= \frac{1}{\rho(1)} \sum_j |d_j(1)|^2 E_j^{N-1} - E_0^{N-1}$$

So

$$v^{N-1} = \sum_j \frac{|d_j(1)|^2}{\rho(1)} E_j^{N-1} - E_0^{N-1} = \sum_j \frac{|d_j(1)|^2}{\rho(1)} (E_j^{N-1} - E_0^{N-1})$$

$$= \sum_j \frac{|d_j(1)|^2}{\rho(1)} (I_j - I_0)$$

## B) Steps $v^{\text{resp}}$ in atoms.

Exchange-only optim. pot. meth. (OPM)

- det. wavef.  $\Psi = |\varphi_1(1) \varphi_2(2) \dots \varphi_N(N)|$

- orbitals solns. of local pot.

$$\left\{ -\frac{1}{2} \nabla^2(1) + v(1) \right\} \varphi_i(1) = \varepsilon_i \varphi_i(1)$$

$\Rightarrow$  What is optimal  $v$ ?

X-only OPM  $\rightarrow v_X^{\text{OPM}}$

N.B.  $v_X^{\text{OPM}}$  close to but not identical

to true  $v_X = \frac{\delta W_X}{\delta \rho} \leftarrow$  KS orbitals

Very good approximation by Krieger, Li and Iafrate:

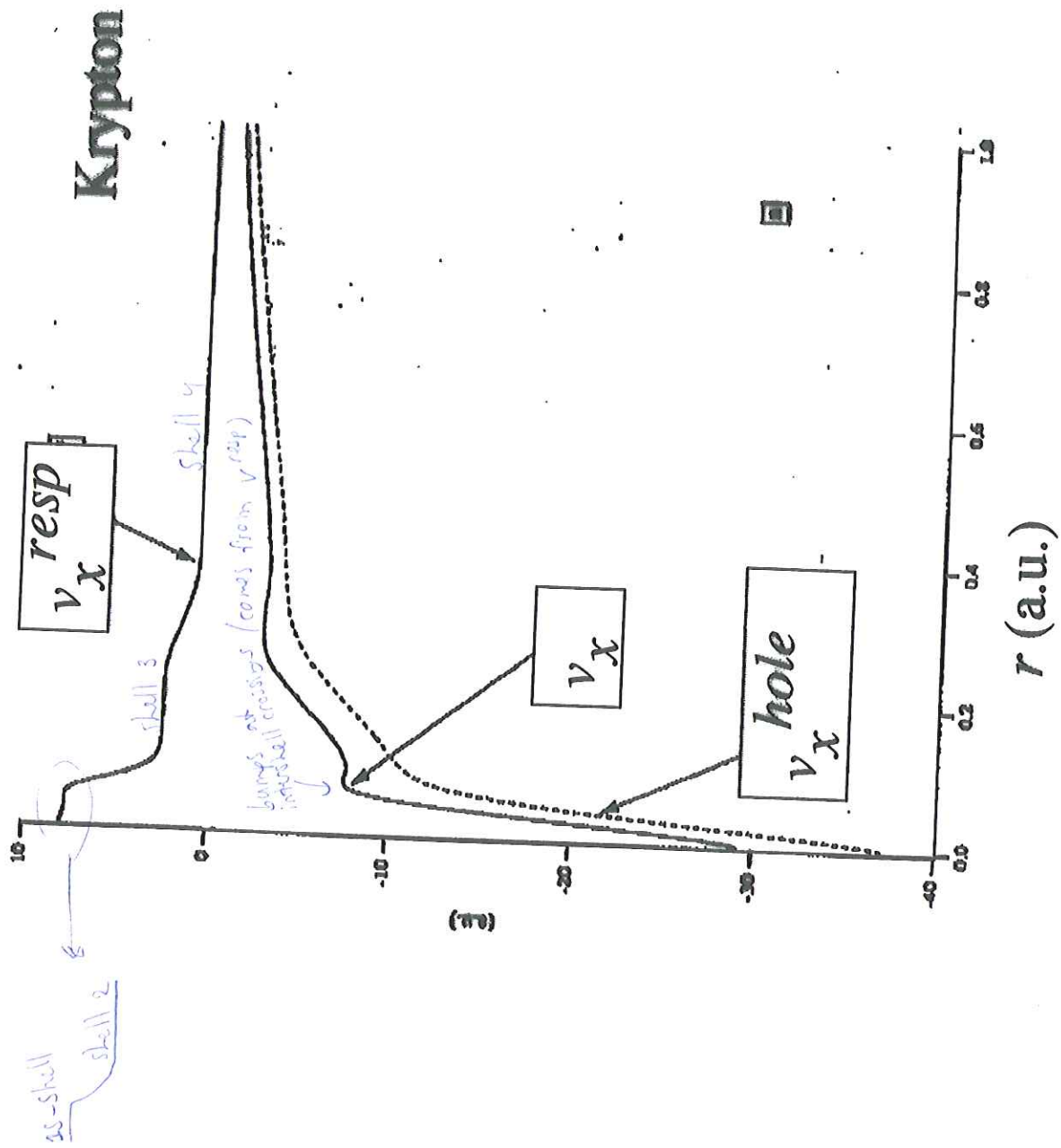
$$v_X^{\text{KLI}}(\vec{r}) = v_{S(\text{later})}(\vec{r}) + \sum_{i=1}^{N-1} w_i \frac{|\varphi_i(\vec{r})|^2}{\rho(\vec{r})}$$

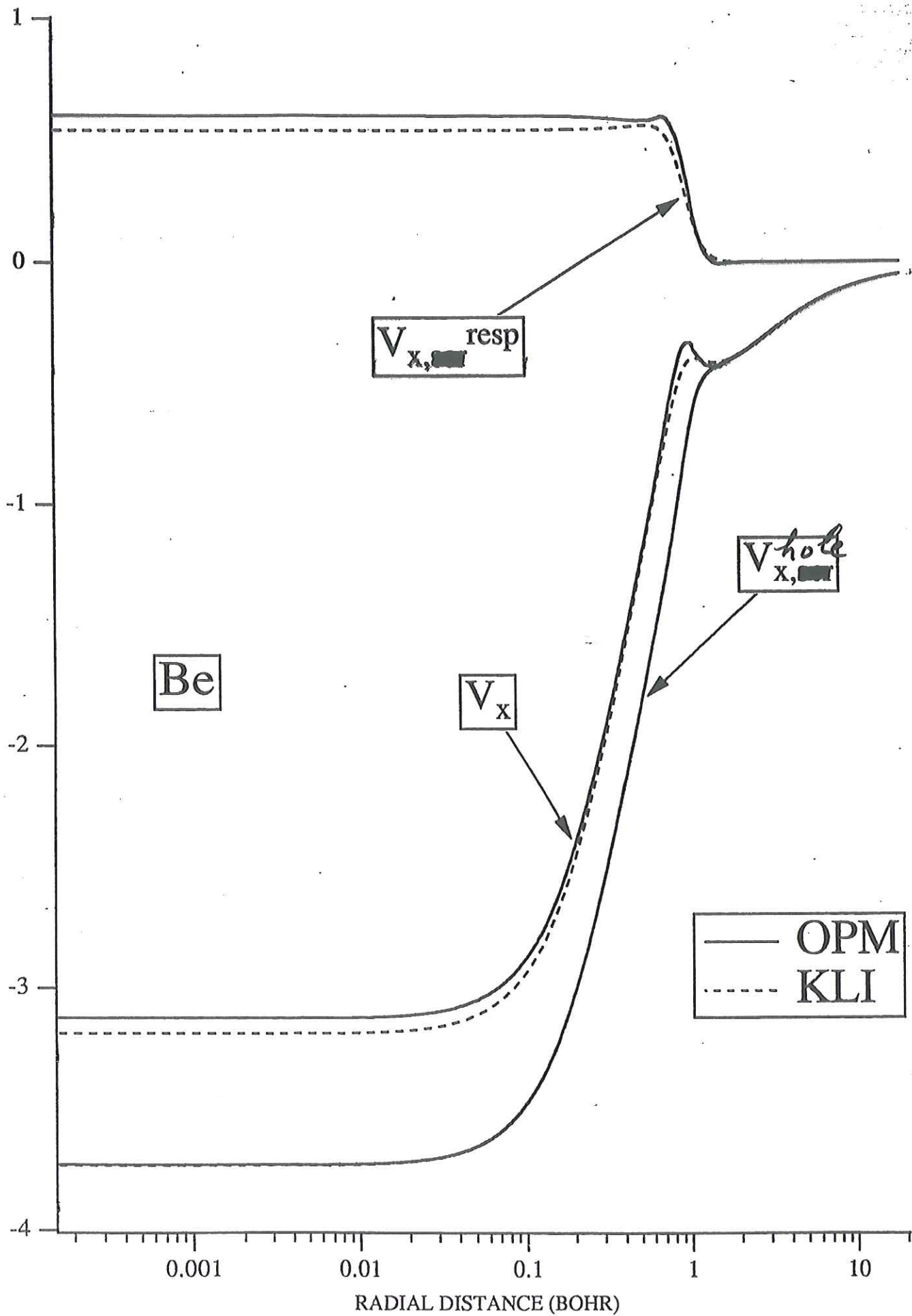
$\uparrow$   
 $v_X^{\text{hole}}$

$\uparrow$   
 $v_X^{\text{resp}}$

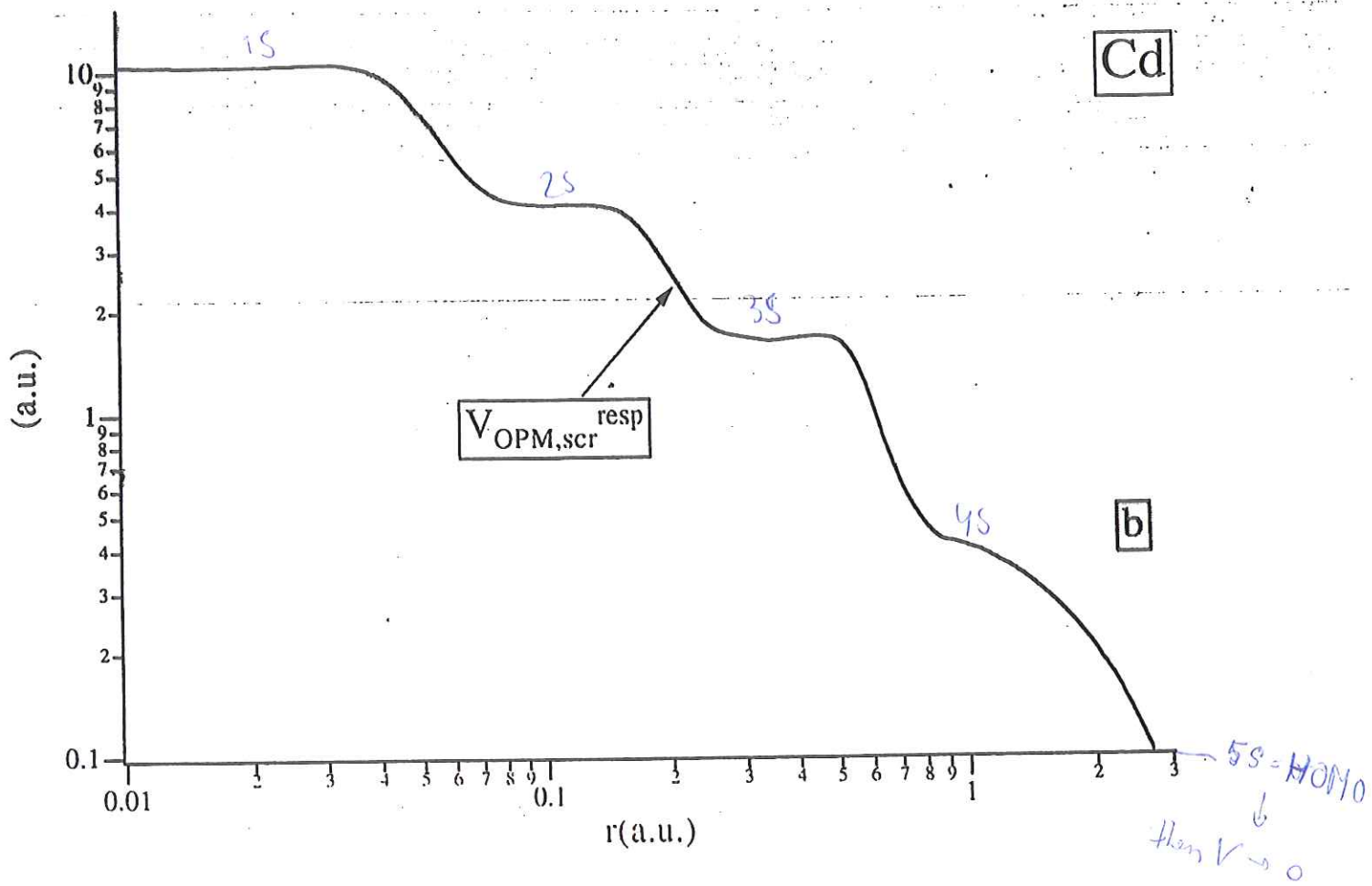
steps!

Steps in the (exchange) pot. of Krypton come from response part of pot.

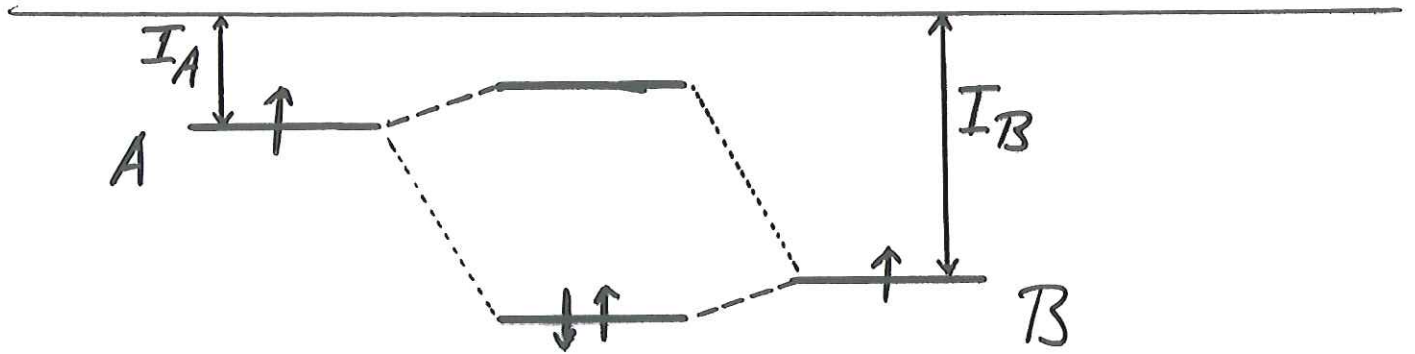








# C) Steps in (dissociating) heteronuclear diatomic



KS calcul. with  $v_S(\vec{r}, \in \Omega_A) = v_S(\text{isolated A})$   
 $v_S(\vec{r}, \in \Omega_B) = v_S(\text{isolated B})$

fails: charge transfer A  $\rightarrow$  B!  
(should dissociate into neutral A & B, but fails because it dissociates into  $A^+B^-$ )

Perdew }  $v_S(\vec{r}, \in \Omega_B) \rightarrow v_S(\text{isolated B})$   
 von Barth }  $+ (I_B - I_A)$   
 $\uparrow$  Step

This step is feature of  $v^{resp}$ .

Consider  $\vec{r}_i$  in HOMO region (outer region of either A or B)

so  $v_S^{N-1}(\vec{r}_i) \approx 0$

and  $v^{resp}(\vec{r}_i) = v^{N-1}(\vec{r}_i) = E^{N-1}(\vec{r}_i) - E_0^{N-1}$

$E_0^{N-1}$  corresponds to ionized A:

$$E_0^{N-1} = E_0(A) + I_A + E_0^B + E_{int}(A^+ - B)$$

Suppose first  $\vec{z}_1 \in \Omega_B$

then  $\Phi(2 \dots N | \vec{z}_1 \in \Omega_B)$  describes:

- ground state A
- ion  $B^+$ , not quite ion gr. st., "polarized"

$$E_0^{N-1}(\vec{z}_1 \in \Omega_B) = E_0^A + E_0^B + I_B + E_{int}(A - B^+) + \Delta E_{pol}(B^+)$$

$$V^{resp}(\vec{z}_1 \in \Omega_B) = I_B - I_A + E_{int}(A - B^+) - E_{int}(A^+ - B) + \Delta E_{pol}(B^+)$$

Suppose next  $\vec{z}_1 \in \Omega_A$

then  $\Phi(2 \dots N | \vec{z}_1 \in \Omega_A)$  describes:

- ground state B
- ion  $A^+$ , somewhat "polarized"

$$E_0^{N-1}(\vec{z}_1 \in \Omega_A) = E_0^A + I_A + E_0^B + E_{int}(A^+ - B) + \Delta E_{pol}(A^+)$$

$$V^{resp}(\vec{z}_1 \in \Omega_A) = \Delta E_{pol}(A^+)$$

$$v^{resp}(\vec{r}, \in \Omega_B) = I_B - I_A + E_{int}(A-B^+) - E_{int}(A^+-B) + \Delta E_{pol}(B^+)$$

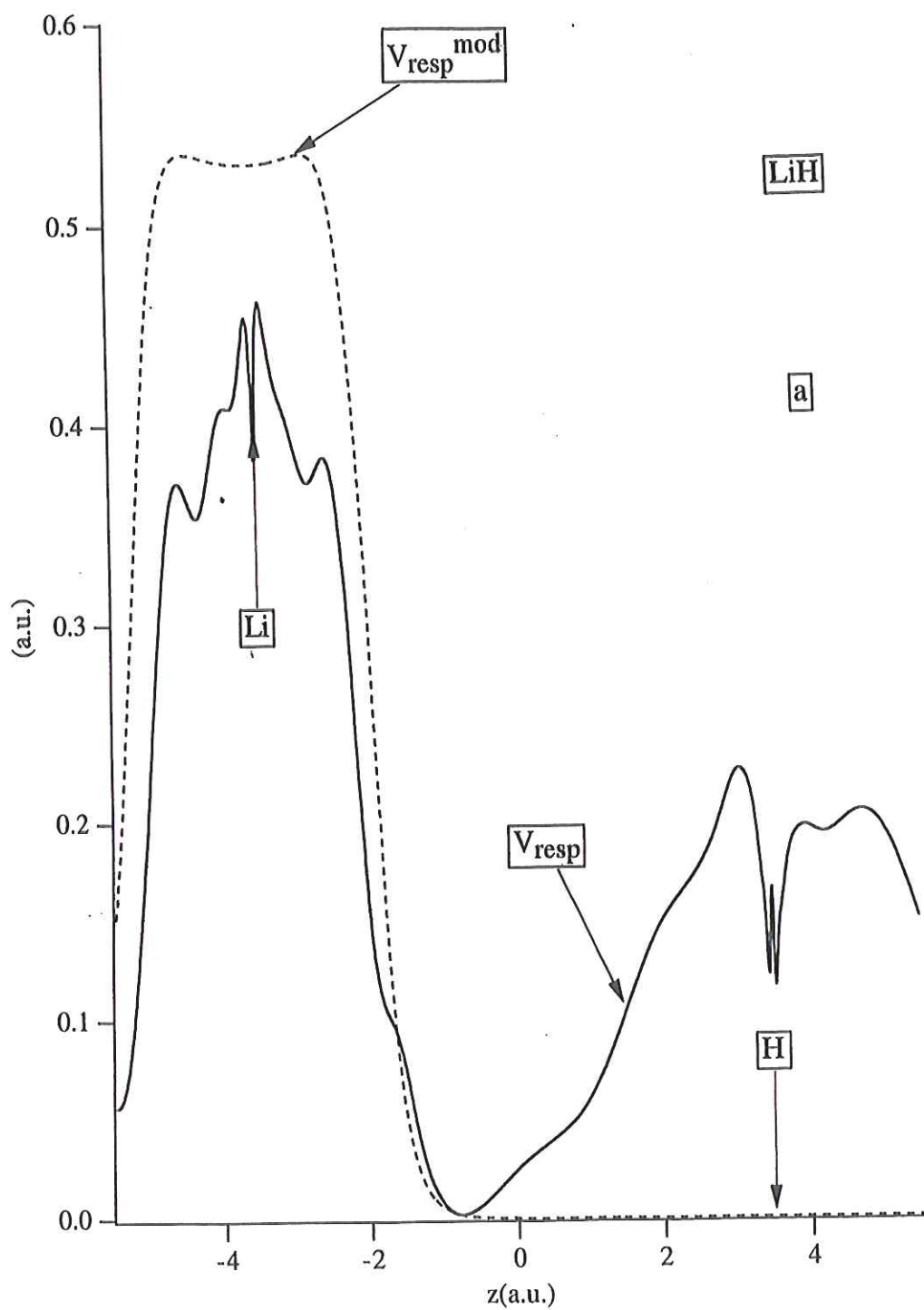
$$v^{resp}(\vec{r}, \in \Omega_A) = \Delta E_{pol}(A^+)$$

$$\Delta v^{resp} = v^{resp}(\vec{r}, \in \Omega_B) - v^{resp}(\vec{r}, \in \Omega_A)$$

$$= I_B - I_A$$

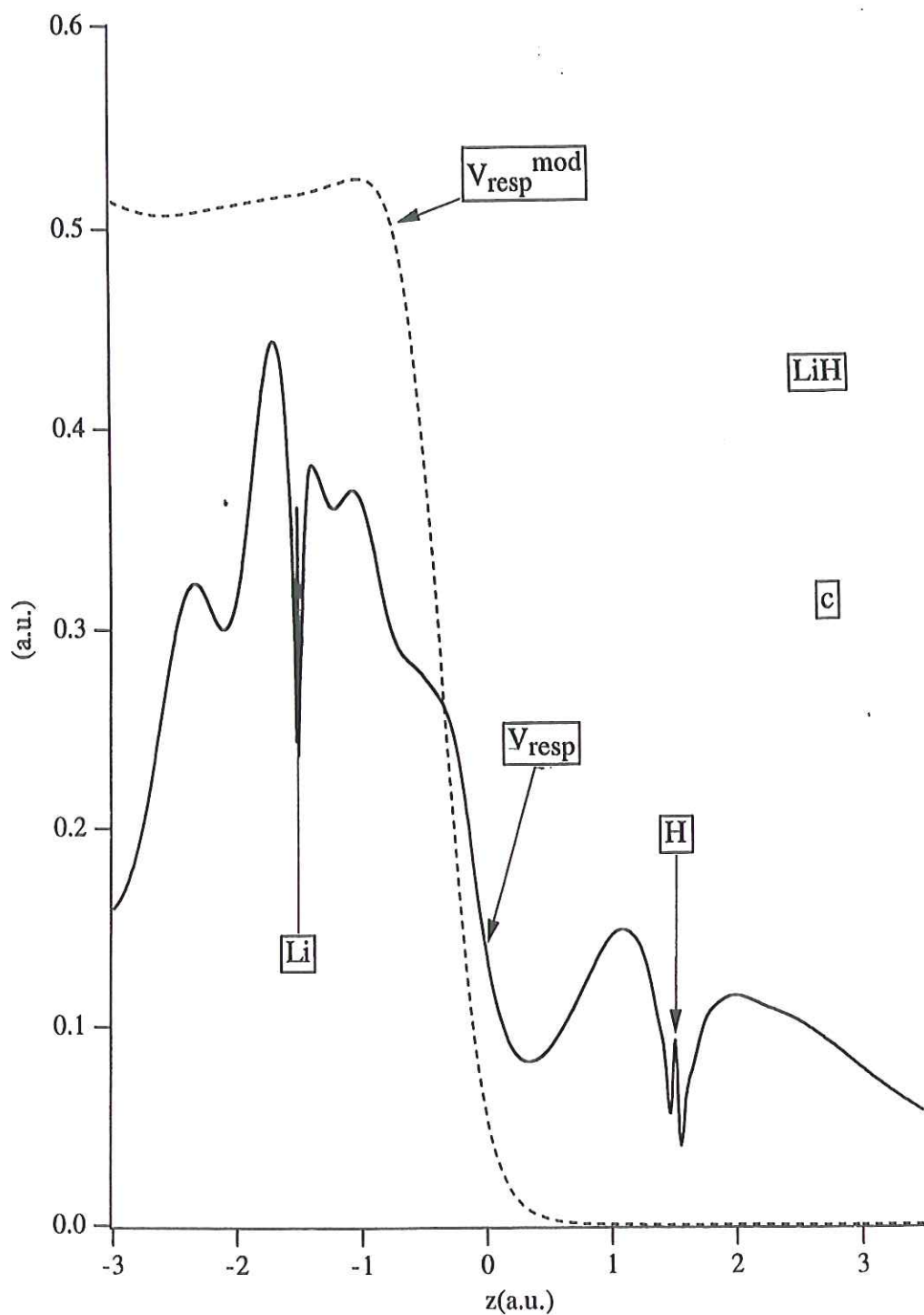
$$+ E_{int}(A-B^+) - E_{int}(A^+-B)$$

$$+ \Delta E_{pol}(B^+; \vec{r}, \in \Omega_B) - \Delta E_{pol}(A^+; \vec{r}, \in \Omega_A)$$



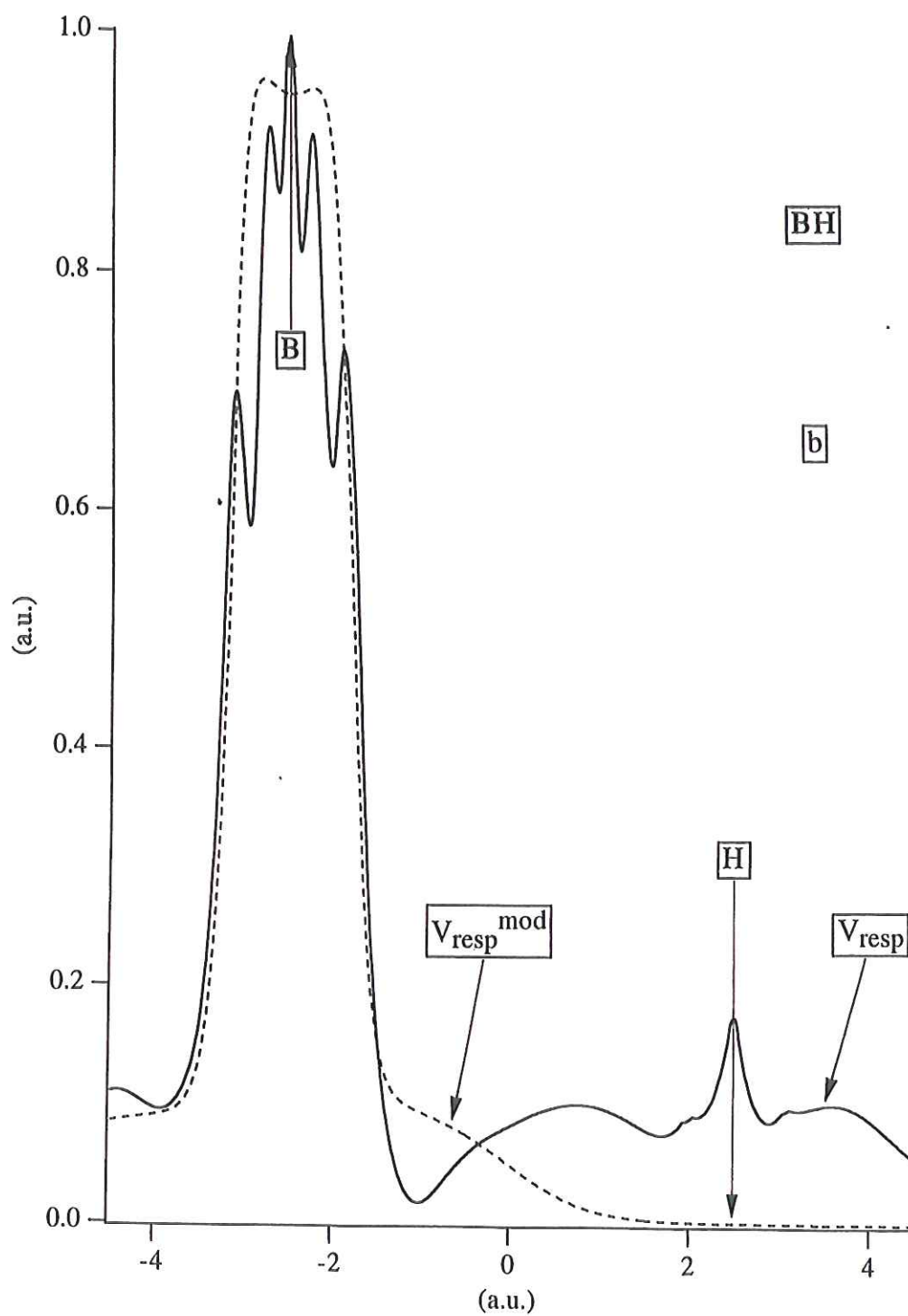
$\text{LiH}$  at  $R = 7.0$  a.u. ( $R_e = 3.015$  a.u.)

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LiH at  $R_e = 3.015$  a.u.

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BH at  $R = 5.0$  a.u. ( $R_e = 2.33$  a.u.)

# CO : KS, GGA-BP and HF orbital energies and VIPs

CO	MO	HF	GGA-BP	KS	Expt.
		$-\epsilon_i$	$-\epsilon_i$	$-\epsilon_i$	$I_i$
	$5\sigma$	15.12	9.18 (4.83)	14.01	14.01
	$1\pi$	17.42	11.95 (16.78)	16.80	16.91
	$4\sigma$	21.94	14.27 (19.10)	19.37	19.72
AAD		1.28	5.08 (0.25)	0.15	
(val)					
	$3\sigma$	41.47	29.47 (34.29)	34.70	38.3
	$2\sigma$	309.17	272.50 (277.33)	279.27	296.21
	$1\sigma$	562.36	513.53 (518.37)	519.92	542.55
AAD		11.98	20.52 (15.69)	14.39	
(inner)					