Orbitals and Orbital Energies in DFT and (TD)DFT

Evert Jan Baerends

SCM and Theoretical Chemistry
Vrije Universiteit, Amsterdam, Netherlands

Common misunderstandings

1) The KS orbitals have no physical meaning, they serve only to build the density.

No: the orbitals have a better shape and energy than the HF orbitals. They are better suited for qualitative and quantitative MO theory.

2) HF is the best one-electron model (lowest one-det. energy)

HF orbitals are the best orbitals / the “real” orbitals

No: HF orbitals and density are too diffuse;

T (kin. en.) and V (el.-nucl. en.) are poor, more in error than W

Comment: In HF the one-el. properties are OK, the error is in W (el.-el. energy) due to neglect of correlation
No: errors in one-el. terms T and V are larger!

3) There is no Koopmans' theorem in DFT. The occupied orbital energies (except HOMO: $\varepsilon_H = - I_0$) are meaningless.

No: there is a better-than-Koopmans relation in DFT between (*exact Kohn-Sham*) orbital energies and IPs:

deviation for valence of ca. 0.1 eV, against HF ca. 1.1 eV.

And theoretically justified!

NB: LDA/GGA orbital energies are very wrong: 4 – 6 eV up

4) The KS HOMO-LUMO gap (in molecules) and the KS band gap (in solids) is wrong (much too small).

No: the KS virtual orbitals have different physical meaning and different orbital energies than HF virtuals.

The KS gap (HOMO-LUMO orbital energy difference) is in molecules an excellent approximation for the first excitation energy.

In solids the fundamental gap (I–A) and optical gap (usually close to fundamental gap) are different from the KS band gap **for a reason.**

(The **reason** is not the derivative discontinuity.)

5) Charge-transfer transitions (excitation out of the HOMO of one molecule to the LUMO of another molecule) are not OK in TDDFT "because of" the derivative discontinuity

No: they are more problematic than local excitations because of the physical nature of the KS unoccupied orbitals

6) Computational cost of KS is same as Hartree, much lower than HF.

No: *higher cost* than HF

(unless tricks: density fitting to scale Coulomb part down to N^3 scaling)

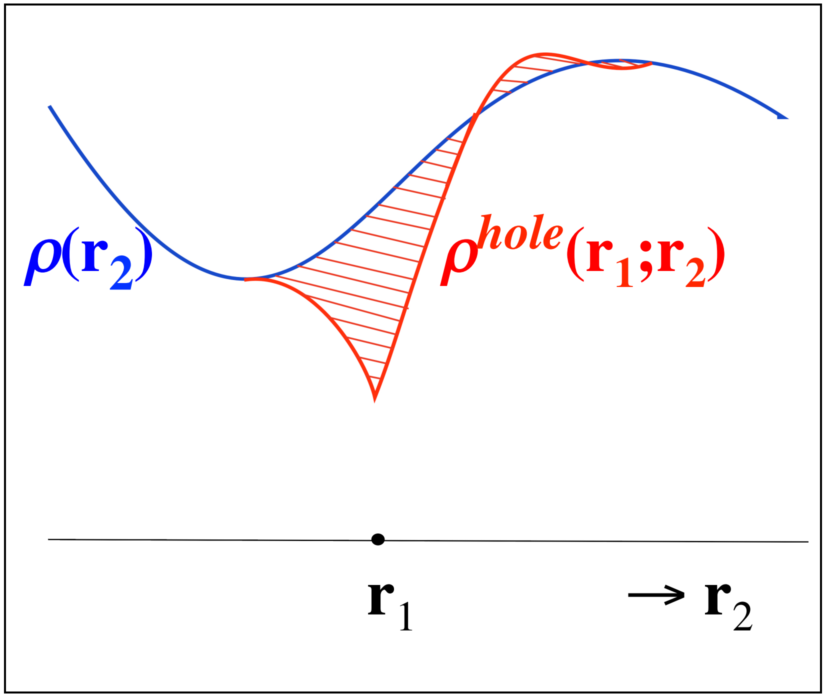
Exchange-correlation energy W_{xc}

$$E = \langle \Psi | H | \Psi \rangle = T + \int \rho(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} + \frac{1}{2} \int \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 + W_{xc}$$

$$W_{XC} = \frac{1}{2} \int d\boldsymbol{r}_1 \rho(\boldsymbol{r}_1) \underbrace{\int \frac{\rho_{XC}^{hole}(\boldsymbol{r}_2 | \boldsymbol{r}_1)}{r_{12}} d\boldsymbol{r}_2}_{v_{xc}^{hole}(\boldsymbol{r}_1)}$$

$$\Gamma(\boldsymbol{r}_1, \boldsymbol{r}_2) = \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) + \Gamma_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2) \Rightarrow$$

$$\frac{\Gamma(\boldsymbol{r}_1, \boldsymbol{r}_2)}{\rho(\boldsymbol{r}_1)} = \rho(\boldsymbol{r}_2) + \underbrace{\Gamma_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2) / \rho(\boldsymbol{r}_1)}_{\rho_{XC}^{hole}(\boldsymbol{r}_2 | \boldsymbol{r}_1)}$$



W_{xc} and Kohn-Sham E_{xc}

The Kohn-Sham Molecular Orbital model:

There is a unique local potential $v_s(\mathbf{r})$ (the KS pot.) such that

$$\hat{h}_s \psi_i^s(\mathbf{r}) = \left\{ -\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_s(\mathbf{r}) \right\} \psi_i^s(\mathbf{r}) = \varepsilon_i^s \psi_i^s(\mathbf{r})$$

gives KS orbitals such that $\sum_{i=1}^{H} |\psi_i^s(\mathbf{r})|^2 = \rho^{exact}(\mathbf{r})$

$$E = T + \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_1\, d\mathbf{r}_2 + W_{xc}$$

$$E = T_s + \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_1\, d\mathbf{r}_2 + E_{xc}$$

$\Rightarrow E_{xc} = \underbrace{T - T_s}_{T_c} + W_{xc}$ $\quad$ $E_{xc}[\rho]$: fcntl of ρ since $E[\rho]$ is.

$$v_s = v_{nuc} + v_{Coul} + v_{xc}$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}$$

Not very transparent! Therefore use:

$$E_{xc} = T - T_s + W_{xc} = \int \rho(\mathbf{r}) v_{c,kin}(\mathbf{r})\, d\mathbf{r} + \frac{1}{2}\int \rho(\mathbf{r}) v_{xc}^{hole}(\mathbf{r})\, d\mathbf{r}$$

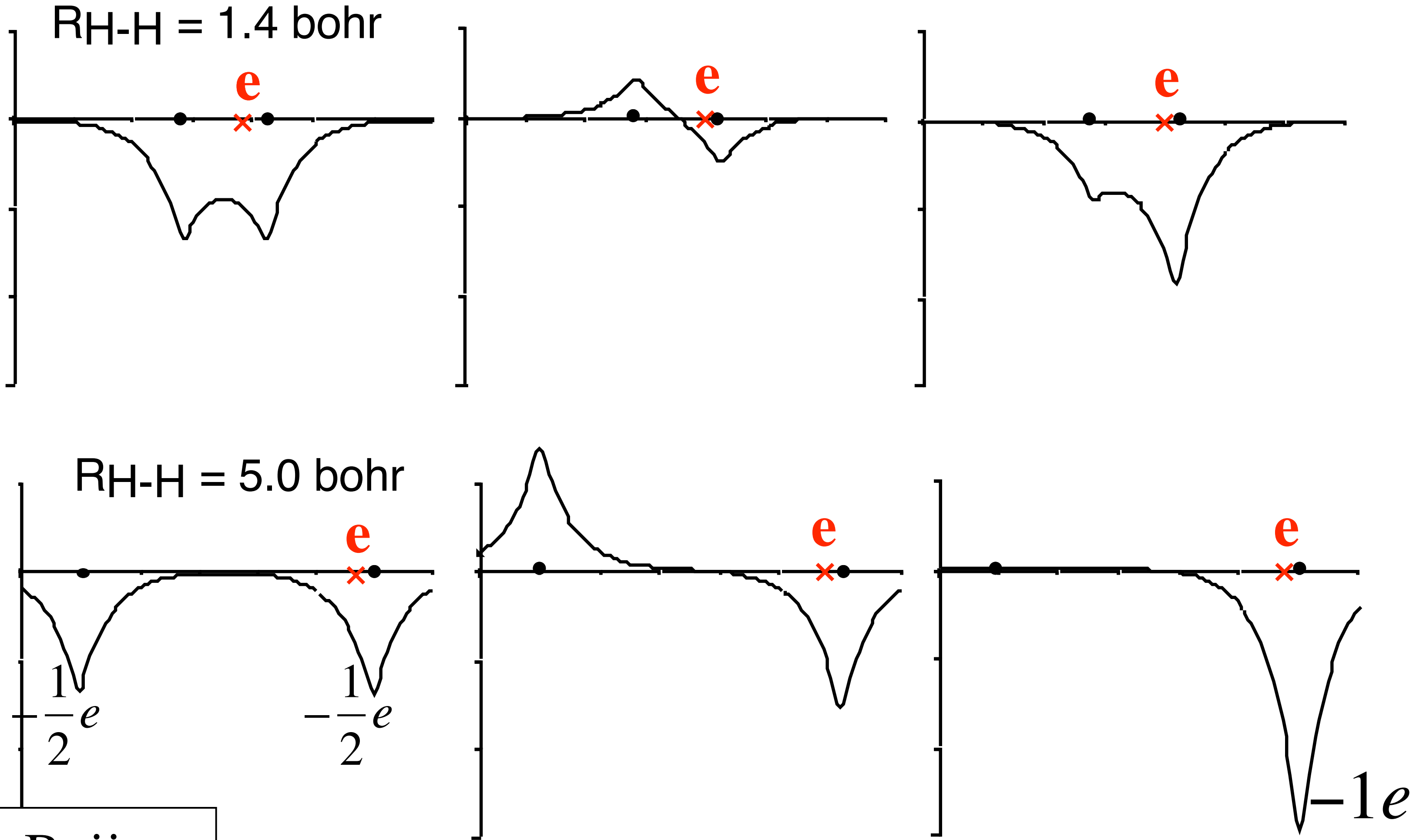
$$\frac{\delta E_{xc}}{\delta\rho(\mathbf{r})} = \frac{1}{2}\int \underbrace{\frac{\delta\rho(\mathbf{r}')}{\delta\rho(\mathbf{r})}}_{\delta(\mathbf{r}-\mathbf{r}')} v_{xc}^{hole}(\mathbf{r}')\, d\mathbf{r}' \quad \rightarrow v_{xc}^{hole}(\mathbf{r})$$

$$+\int \frac{\delta\rho(\mathbf{r}')}{\delta\rho(\mathbf{r})} v_{c,kin}(\mathbf{r}')\, d\mathbf{r}' \quad \rightarrow v_{c,kin}(\mathbf{r})$$

$$+\int \rho(\mathbf{r}') \frac{\delta}{\delta\rho(\mathbf{r})}\left[\frac{1}{2} v_{xc}^{hole}(\mathbf{r}') + v_{c,kin}(\mathbf{r}')\right] d\mathbf{r}' \rightarrow v^{resp}(\mathbf{r})$$

Holes in H_2

Fermi hole + Coulomb hole = total hole



M. A. Buijse,
Thesis 1991

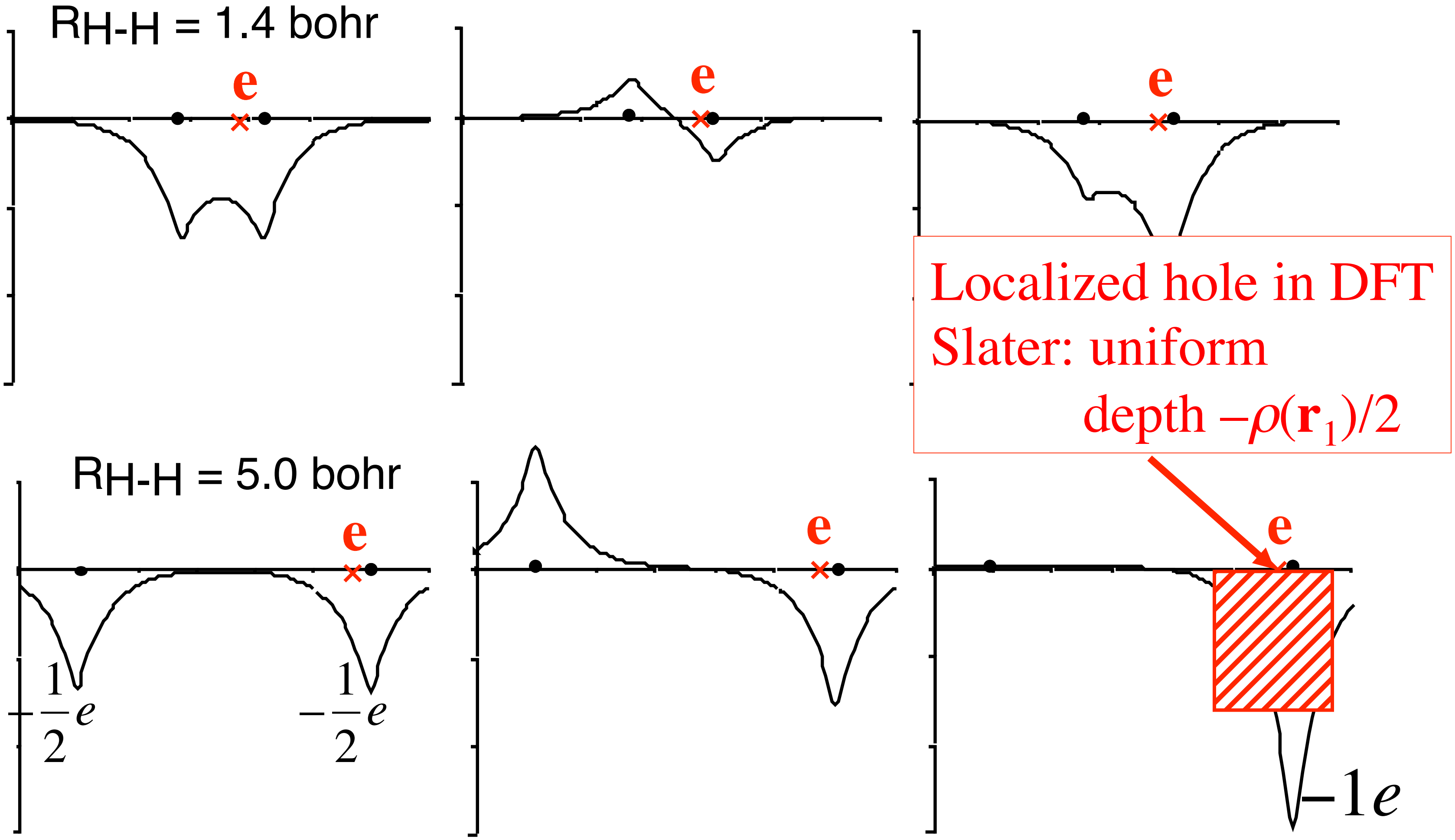
NB. $v_{xc} = v_{c,kin} + \boldsymbol{v}_{\boldsymbol{xc}}^{\boldsymbol{hole}} + v^{resp}$

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

	HF	Obs.	Error (% of Obs.)
N_2	115.2	228.6	– 49.6%
F_2	–37.1	38.5	– 196.4%
H_2O	155.5	232.2	– 33.0%
O_2	33.1	120.5	– 72.5%

Holes in H_2

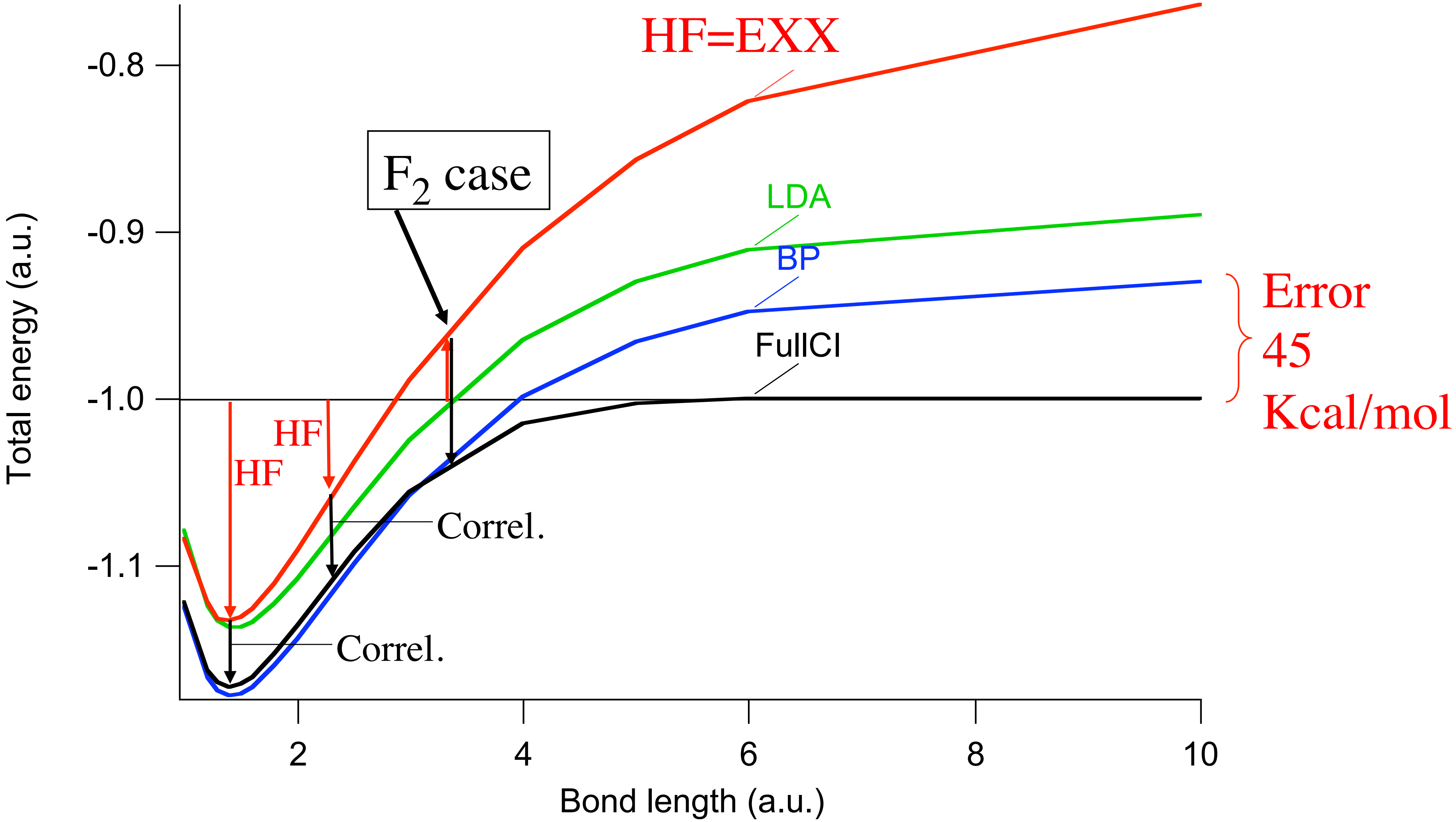
Fermi hole + Coulomb hole = total hole



Localized hole in DFT
Slater: uniform
depth $-\rho(\mathbf{r}_1)/2$

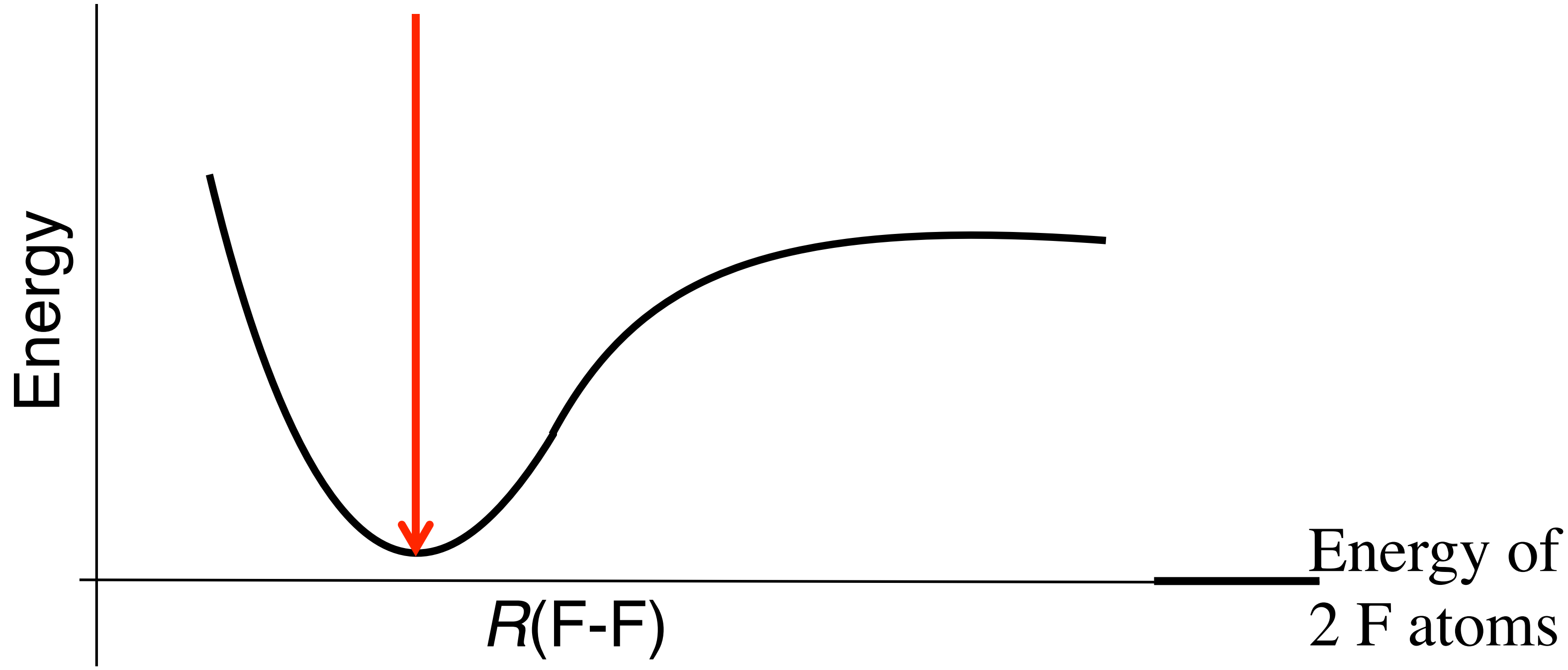
NB. $v_{xc} = v_{c,kin} + \boldsymbol{v}_{\boldsymbol{xc}}^{\boldsymbol{hole}} + v^{resp}$

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



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

The anomalous F_2 case: RHF energy above two F atoms! Why? Because of long distance RHF error.



Exchange-only (i.e. Hartree-Fock model) yields 98-99% of total energy, so good zero-order model.
("Unfortunately bond energies are of the order of 1-2% so correlation is essential for quantum chemistry")

A WRONG PERSPECTIVE!

Hartree-Fock (and EXX) relatively OK
for some systems: electron gas, atoms -> molecules total energy

Hartree-Fock (and EXX) are lousy zero-order approximation for electron-pair bonding (= chemistry).

LDA and GGA work with localized holes,
that is why they easily do better than HF; but not accurate and not along complete dissociation coordinate!

Hartree-Fock densities are often poor due to bad HF potential: H_2

	E_{total}^{corr}	T_{kin}^{corr}	V_{el-nuc}^{corr}	W_{el-el}^{corr}
H_2 (R=R_e)	–1.1 eV	+1.3	–0.5	–1.9
H_2 (R=5.0 bohr)	–3.9	+8.9	–8.5	–4.4
H_2 (R=10.0 bohr)	–6.3	+7.9	–8.6	–5.6

Hartree-Fock densities are often poor due to bad potential: He, H_2O, Ne, N_2

	E_{total}^{corr}	T_{kin}^{corr}	V_{el-nuc}^{corr}	W_{el-el}^{corr}
He	–1.1 eV	+1.1	–0.1	–2.1
H_2O	–7.0	+6.5	+1.0	–14.5
Ne	–8.9	+8.3	+1.4	–18.5
N_2	–11.0	+13.7	–13.8	–11.0

Exact Kohn-Sham orbitals and energies

There is only one KS potential that generates the exact densities (HK):
KS orbitals and orbital energies are uniquely defined!
Given exact $\rho(\mathbf{r})$, how to find v_s?

$$\left\langle \Psi_2 \middle| \hat{H}_1 \middle| \Psi_2 \right\rangle > \left\langle \Psi_1 \middle| \hat{H}_1 \middle| \Psi_1 \right\rangle = E_1$$

$$T_2 + W_2 + \int \rho_2 v_1 \, d\mathbf{r} > T_1 + W_1 + \int \rho_1 v_1 \, d\mathbf{r}$$

and

$$\left\langle \Psi_1 \middle| \hat{H}_2 \middle| \Psi_1 \right\rangle > \left\langle \Psi_2 \middle| \hat{H}_2 \middle| \Psi_2 \right\rangle = E_2$$

$$T_1 + W_1 + \int \rho_1 v_2 \, d\mathbf{r} > T_2 + W_2 + \int \rho_2 v_2 \, d\mathbf{r}$$

sum up

$$\int \rho_2 v_1 \, d\mathbf{r} + \int \rho_1 v_2 \, d\mathbf{r} > \int \rho_1 v_1 \, d\mathbf{r} + \int \rho_2 v_2 \, d\mathbf{r}$$

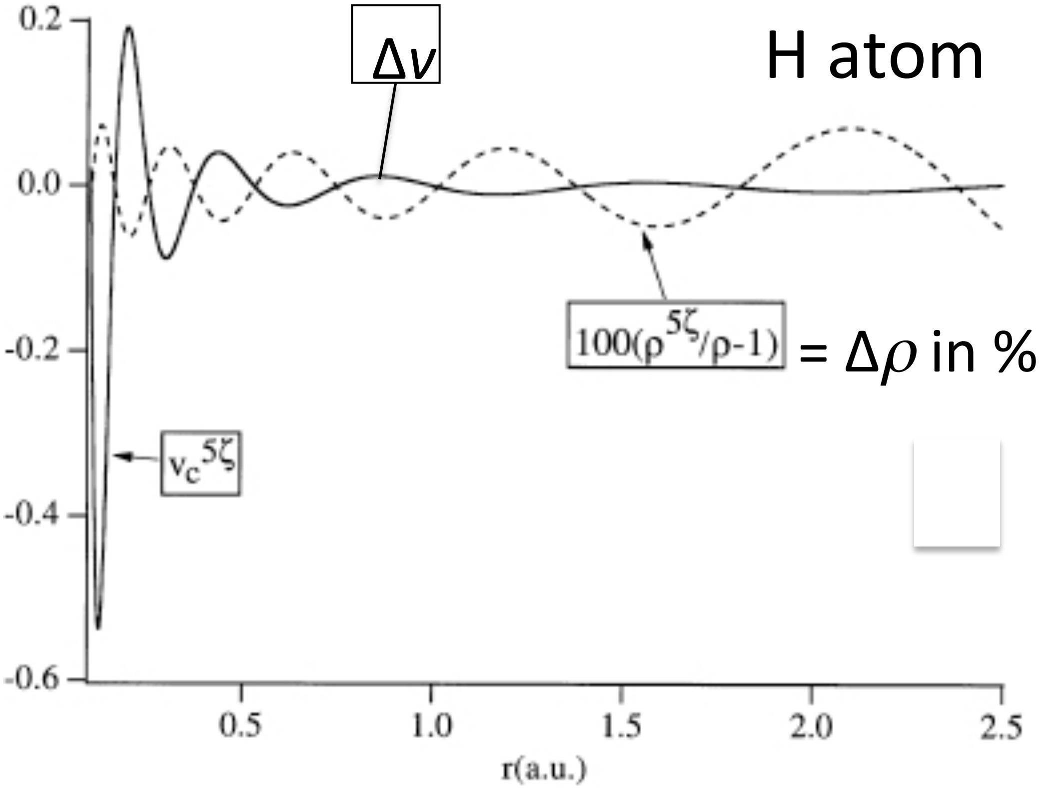
or

$$\int (\rho_2 - \rho_1)(v_2 - v_1) \, d\mathbf{r} < 0, \text{ i.e. } \int \Delta\rho \, \Delta v \, d\mathbf{r} < 0$$

$$\int(\rho_2-\rho_1)(v_2-v_1)\,d\mathbf{r}<0,\ \text{i.e.}\ \int\Delta\rho\,\Delta v\,d\mathbf{r}<0$$

If in a small region the potential is decreased, Δ*v* < 0,
then ρ must change (cf. HK!),
and $\Delta\rho$ must be positive over that region, and *v.v.* (van Leeuwen-Baerends, PRA 1994)

Apply to the KS potential v_s: by locally adjusting v_s the density can be made to approach the exact (correlated) density from e.g. CI arbitrarily closely → generates the *exact* KS potential



Calculate H atom in Gaussian basis: small deviations from exact density.

Generate potential that produces exactly that Gaussian density: small deviations from $-1/r$,
when $\Delta\rho$ positive Δ*v* negative,
and *vice versa.*

Schipper, Gritsenko, Baerends,
Theor. Chem. Acc. **98** (1997) 16

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

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

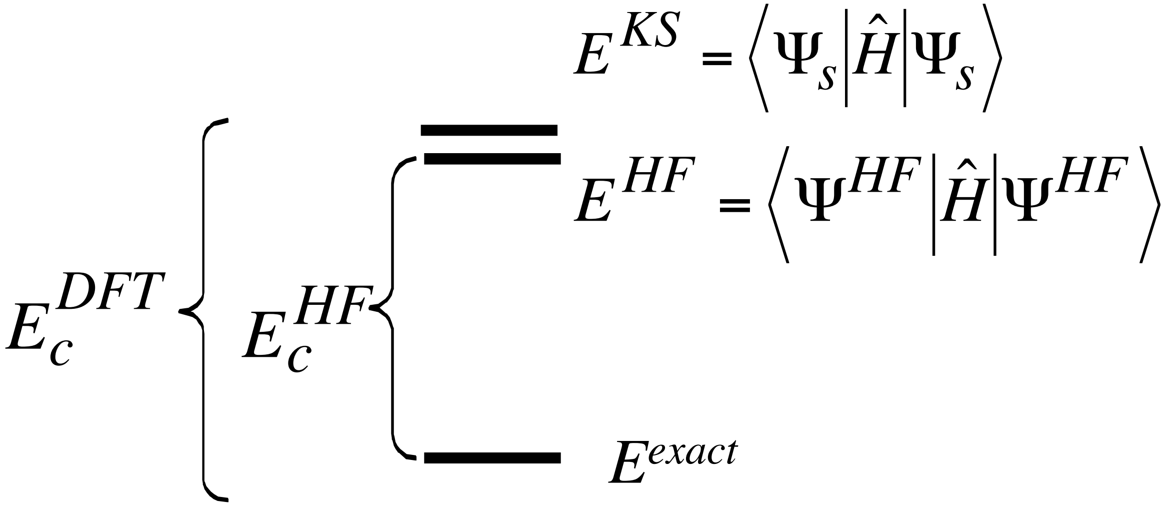
Gritsenko, Schipper, Baerends, *J. Chem. Phys.* **107** (1997) 5007

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

R (bohr)	2.074	3.0	3.5
W_X (*KS orbitals*)	–13.114	–12.621	–12.490
$W_X - W_X^{HF} =$	0.006	–0.040	–0.067
$W_c = W_{XC} - W_X$	–0.804	–0.969	–1.063
$W_c(HF) = W_{XC} - W_X^{HF}$	–0.810	–1.009	–1.124
E_c(KS)	–0.475	–0.641	–0.750
E_c(HF)	–0.469	–0.603	–0.687
E_c(KS) – E_c(HF)	–0.006	–0.0038	–0.063

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

Definition of correlation energy



$$E^{KS} = \left\langle \Psi_s \middle| \hat{H} \middle| \Psi_s \right\rangle$$

$$E^{HF} = \left\langle \Psi^{HF} \middle| \hat{H} \middle| \Psi^{HF} \right\rangle$$

E_c^{DFT}

E_c^{HF}

E^{exact}

Conclusion HF versus KS det.

$-\Psi^{\mathrm{HF}}$ better total energy (marginally)

$$E_c \leq E_c^{HF}$$

Ψ_{s} better for:

$$\left.\begin{array}{l} V_{el\text{-}nuc} \\ W_{Coul} \end{array}\right\} \text{ no correlation error}$$

T_s : (much) smaller correl. error

HF "distorts" density (more diffuse) if:

gain by lowering T^{HF} is larger

(even if barely) than

loss by less stable V

Hartree-Fock: good for atoms,
not for molecules (bonds)

In an electron pair bond:

a) HF orbitals will be too diffuse (density too diffuse)

→ kinetic energy too low

→ electron-nuclear energy too high (not negative enough)

b) this is worse in case of multiple bonds

c) common statement

“one-particle properties (also the electron density!) are good in the Hartree-Fock model, it is the el.-el. interaction that is wrong, because of lack of electron correlation (electrons do not avoid each other sufficiently, cf. the presence of ionic configurations in the H_2 wavefunction)”

IS WRONG

What is the meaning of KS orbital energies?

Prevailing view, see e.g.

R.G. Parr, W. Yang,
DFT of Atoms and Molecules, 1989:

"..one should expect no simple physical meaning for the KS orbital energies. *There is none*."

KS and HF orbital energies and VIPs for H_2O

H_2O	MO	HF $-\varepsilon_k$	KS $-\varepsilon_k$	Expt. I_k	$I_k+\varepsilon_k$	$\sqrt{\varepsilon_N-\varepsilon_k}$
	$1b_1$	13.76	12.63	12.62	–0.01	
	$3a_1$	15.77	14.78	14.74	–0.04	
	$1b_2$	19.29	18.46	18.55	0.09	
Average Dev.		0.97	0.05			
	$2a_1$	36.48	30.89	32.2	1.31	4.27
	$1a_1$	559.37	516.96	539.90	22.94	22.46
Average Dev.		11.88	12.13			

Chong, Braïda,Gritsenko,
Baerends, JCP 2002-2004

HCl: KS, BP and HF orbital energies and VIPs

HCl	MO	HF $-\varepsilon_i$	GGA-BP $-\varepsilon_i$	KS $-\varepsilon_i$	Expt. I_i
	2π	12.97	8.13 (+4.64=12.77)	12.77	12.77
	5σ	17.04	11.90 (16.53)	16.53	16.6
	4σ	30.41	21.22 (25.86)	25.82	25.8
AAD(val)		1.75	4.68 (0.04)	0.03	
	1π	218.77	190.98 (195.62)	199.59	
	3σ	218.84	191.27 (195.91)	199.79	
	2σ	287.75	250.44 (255.08)	259.80	

v_{xc}^{hole} in KS pot.: consequences

1) Good shape of occupied orbitals and density, good orbital energies

2) Good shapes and energies of virtual orbitals.
Consequences for excitation energies etc. (TDDFT):
excitations from occupied orbitals φ_i ($i,j,k,$.. for occ. orbitals) to
unoccupied orbitals to φ_a (a,b,c,d.. for unocc. (virtual) orbitals)

What are virtuals like in DFT? And in Hartree-Fock?

Big difference between HF and KS virtuals:
necessary to understand the difference to understand

- why TDDFT works so well (in general for molecules);
- why there is a problem with charge-transfer transitions
- the “bandgap problem” in solids

HF, DFA and exact KS HOMO orbital energies

	HF	**LDA**	**BLYP**	**KS = –I**
H_2	–16.18	–10.26	–10.39	–16.44
H_2O	–13.88	–7.40	–7.21	–12.62
HF	–17.69	–9.82	–9.64	–16.19
N_2	–16.71	–11.89	–11.49	–16.68
CO	–15.1	–9.11	–9.00	–14.01
HCN	–13.50	–9.23	–8.87	–13.61
FCN	–13.65	–8.97	–8.62	–13.67
HCl	–12.98	–8.15	–7.91	–12.77

KS HOMO is equal to – I;
HF HOMO is appr. equal to – I (frozen orbital approx.)
LDA, GGA orbital energies are upshifted by ca. 4.5 eV
(uniformly: occup. and unoccup *valence* orbitals)

HF, DFA and exact KS LUMO orbital energies

	HF	**LDA**	**BLYP**	**KS**
H_2	+1.42	+0.31	+0.12	–3.93
H_2O	+0.80	–0.92	–1.06	–5.11
HF	+0.81	–0.93	–1.13	–5.71
N_2	+3.91	–2.21	–1.91	–6.77
CO	+1.88	–2.24	–1.94	–6.56
HCN	+1.93	–1.33	–1.07	–5.53
FCN	+1.16	–1.66	–1.59	–6.01
HCl	+0.79	–1.11	–1.15	–5.36

KS LUMO is at negative energy: a bound one-electron state in the KS potential.
HF LUMO is most of the time *unbound* (positive orbital energy)
LDA,GGA LUMO: still negative -> therefore bound state

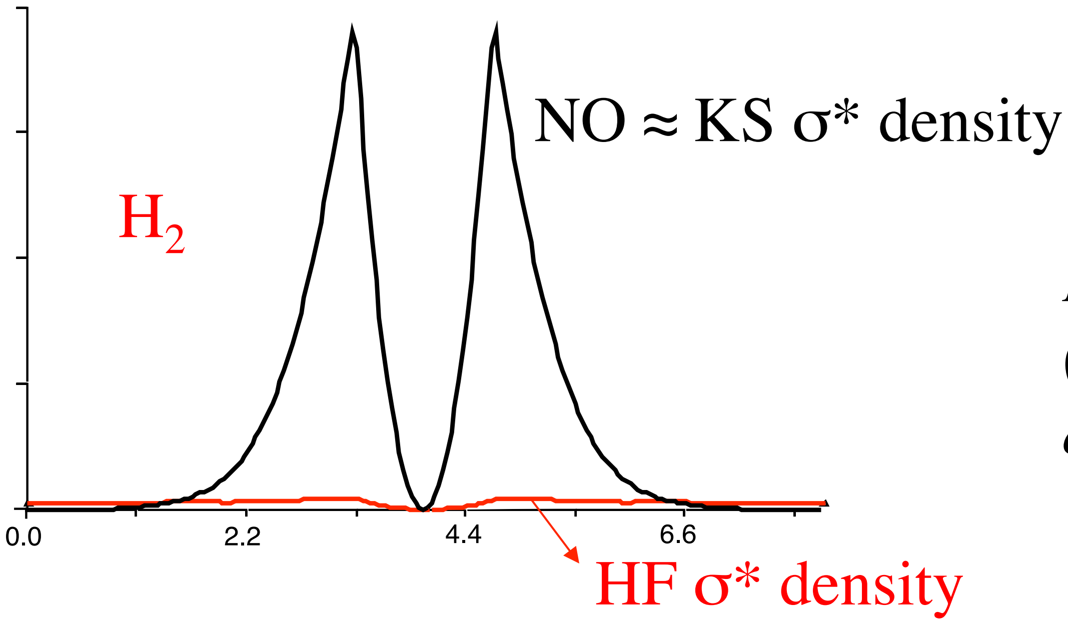
Meaning of unoccupied orbital energies ε_a, ε_b, ….

HF: unocc. orbital represents *added* electron

→ ε_a^{HF} is *affinity* level; $\varepsilon_a^{HF} - \varepsilon_i^{HF}$ is NOT excitation energy

KS: unocc. orbital represents *excited* electron

→ $\varepsilon_a^{KS} - \varepsilon_i^{KS}$ IS good appr. to excitation energy



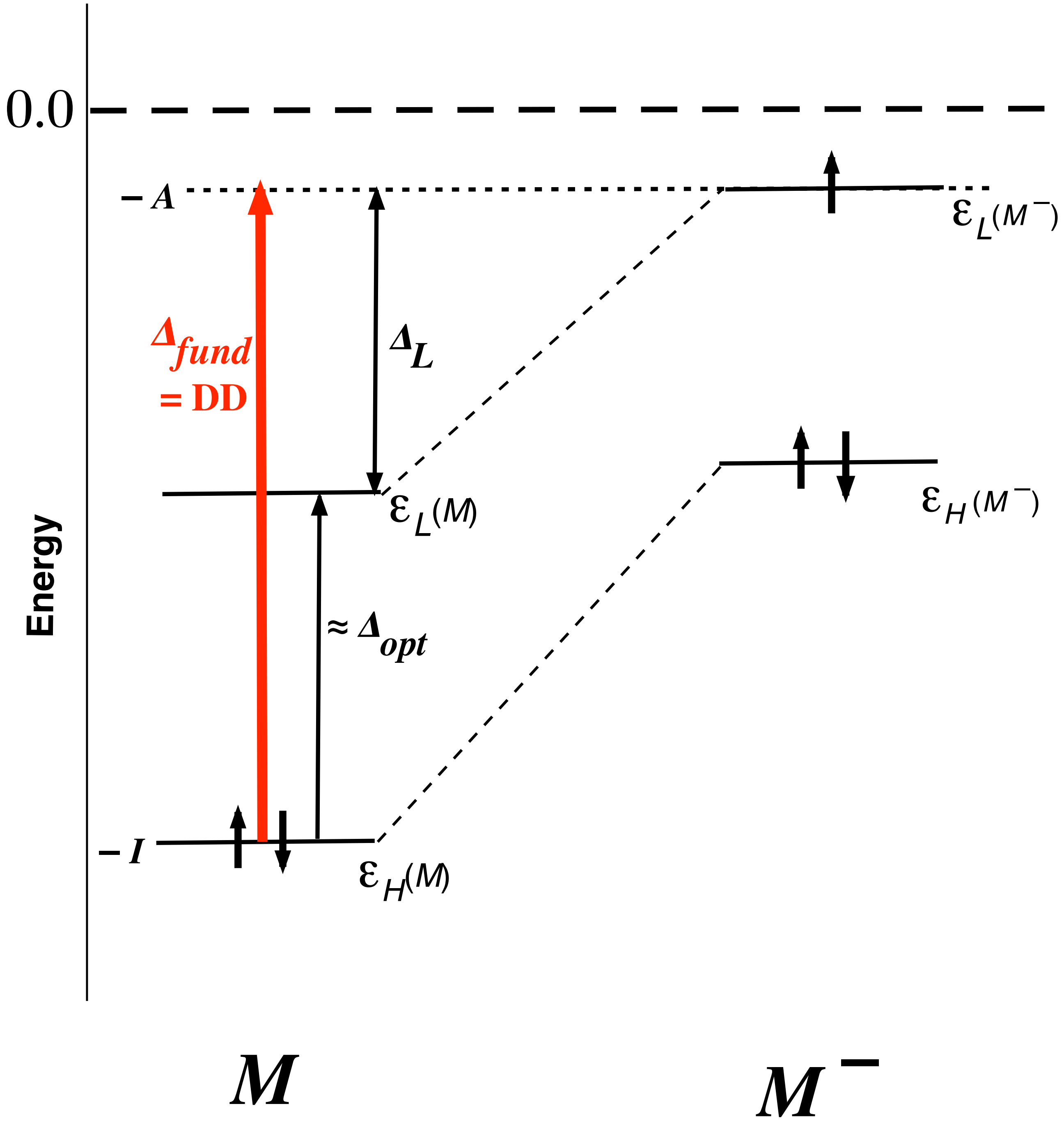
HF virtual orbitals are at
(much) higher energy
and (way) more diffuse
than KS virtual orbitals

KS HOMO-LUMO gaps Δ are excellent approx. to excitation energies

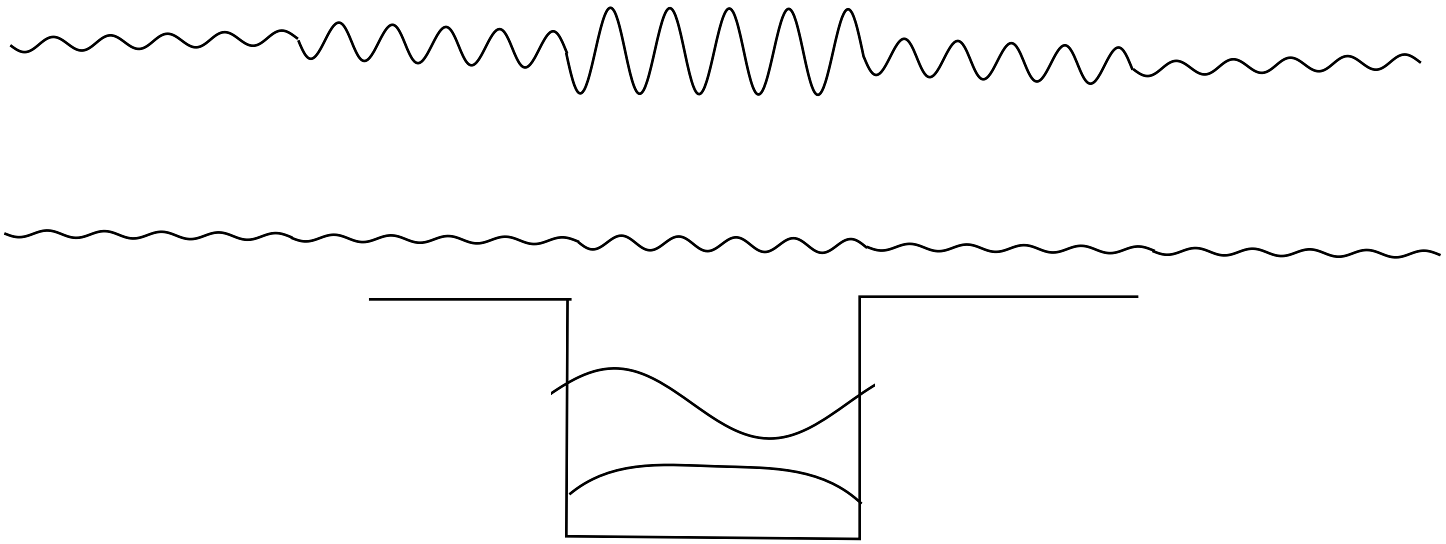
	Δ^{HF}	Δ^{LDA}	Δ^{BLYP}	Δ^{KS}	**Expt. excit. energy**	
					singlet	**triplet**
H_2	17.6	10.6	10.5	12.5	**12.7**	**11.7**
H_2O	14.7	6.5	6.2	7.5	**7.65**	**7.5**
HF	18.5	8.9	8.5	10.5	**10.3**	**9.9**
N_2	19.9	9.7	9.6	9.9	**9.3-10.3**	**7.8-8.9**
CO	17.0	6.9	7.1	7.5	**8.5**	**6.3**
HCN	15.4	7.9	7.8	8.0	**8.8**	**6.2**
FCN	14.8	7.3	7.0	7.6	**8.4**	**7.8**
HCl	13.8	7.0	6.8	7.4	**7.8**	**7.4**

1) The LDA, GGA gaps are similar (slightly smaller) than KS gaps
-> the upshift is similar for HOMO and (a bit smaller for) LUMO
2) HF gaps are much larger: they are Koopmans' approx. IP – EA

Orbital
energies in
exact KS



What is the meaning of a LUMO with positive orbital energy?



resonances
at specific E

What is the meaning of HF LUMO with positive energy?

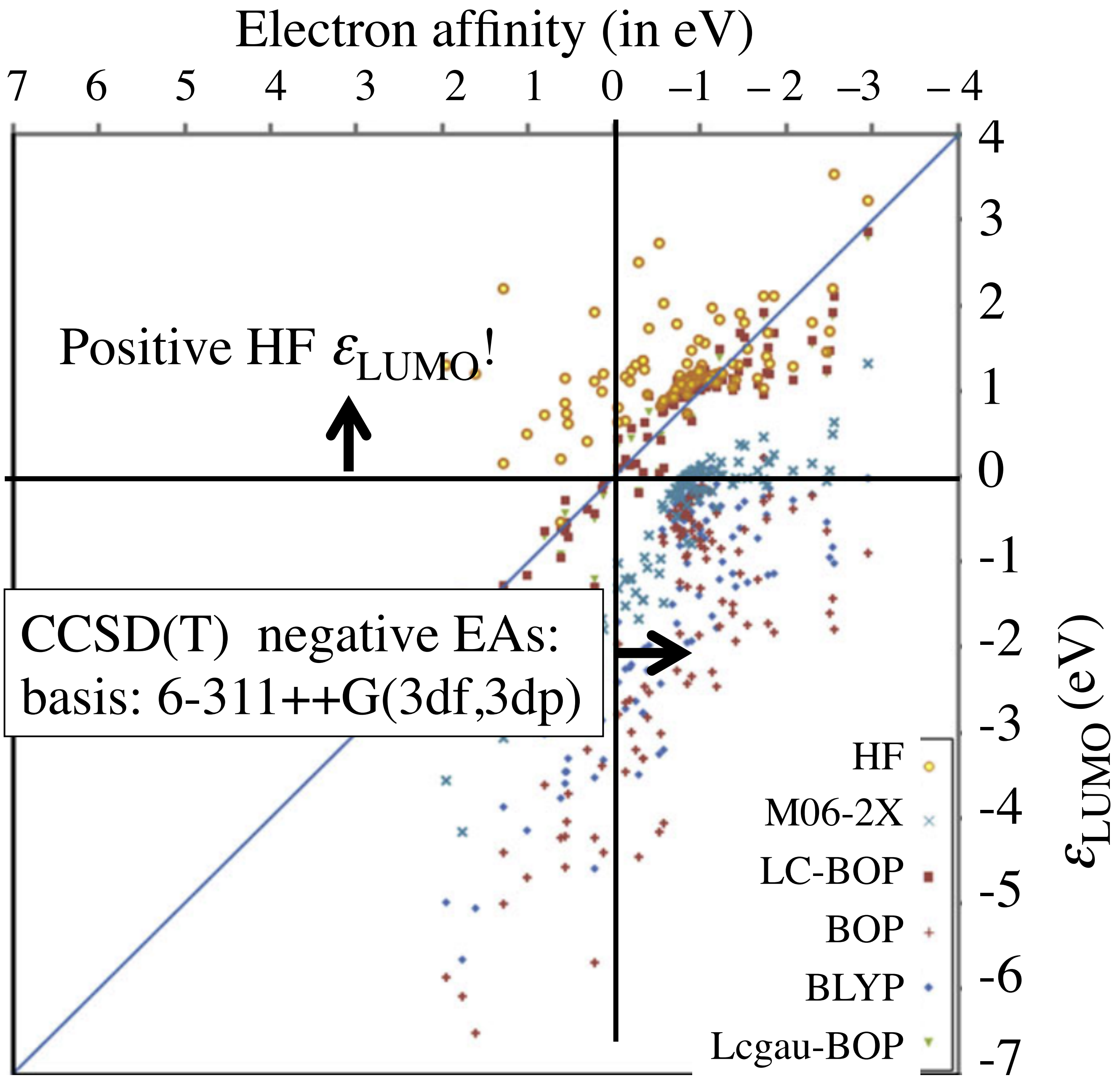
Note: positive one-electron states in a potential (zero at infinity):

- there is a continuum of positive states;
- most have plane-wave behavior with only a few orthogonality wiggles over the molecular region;
- at specific energy (small energy ranges) the one-electron states have large amplitude in the molecular region (small plane-wave like outside)

-> "scattering resonances" with resonance energies corresponding to potential electron capture to form a temporary negative ion, which will decay after some time to molecule + free electron.

Since energy at scattering resonance is *positive*,
i.e. *higher* than free molecule and electron: *negative electron affinity*!

If there are no negative energy unoccupied orbitals (bound states) for the HF operator (frequently!), what is the meaning of the pos. energy orbitals?



Positive HF $\varepsilon_{\mathrm{LUMO}}$!

CCSD(T) negative EAs:
basis: 6-311++G(3df,3dp)

Calculated LUMO energies vs EA for 113 molecules.
EA from CCSD(T), basis:
6-311++G(3df,3dp)

(Kar, Song, Hirao, JCC 2013)

Almost all HF $\varepsilon_{\mathrm{LUMO}}$ positive!

Orbital energies (eV) of the positive energy HF LUMO of H_2 as function of the basis (STOs)

	SZ	**DZ**	**DZP**	**TZP**	**TZ2P**	**QZ4P**	**ETQZ3P 2D**
$1\sigma_u$	18.12	5.52	5.11	3.39	3.45	2.67	1.18
$1\sigma_g$	–15.88	–16.26	–16.20	–16.21	–16.20	–16.18	–16.18
gap	34.00	21.77	21.31	19.59	19.66	18.85	17.36

Orbital energies (eV) of the positive energy HF LUMO of H_2 as function of the basis (Gaussians)

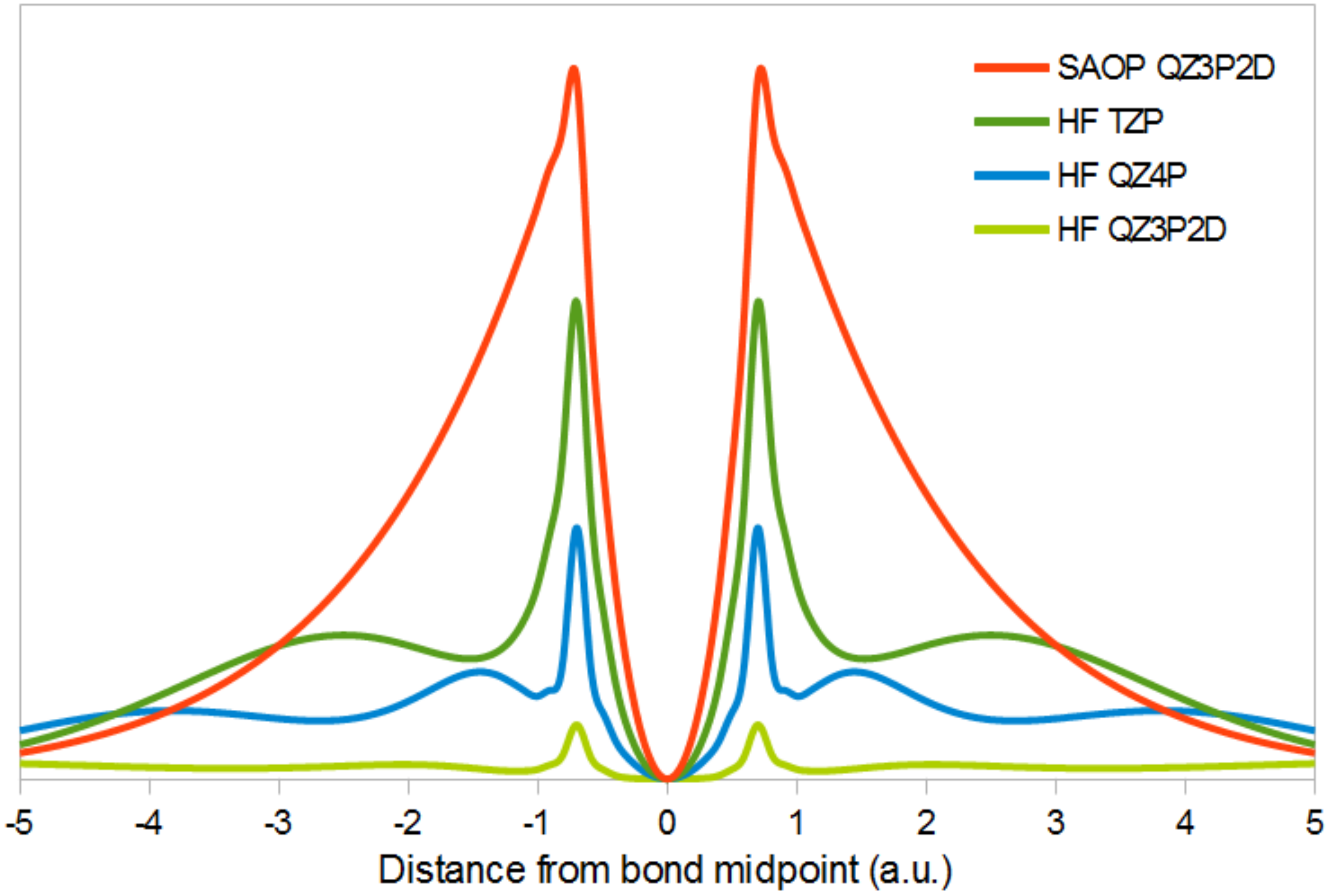
	cc-pVDZ	**cc-pVQZ**	**cc-pV5Z**	**aug-cc-pVDZ**	**aug-cc-pVTZ**	**aug-cc-pVQZ**	**aug-cc-pV5Z**
$1\sigma_u$	5.372	3.91	3.14	1.67	1.42	1.28	1.14
$1\sigma_g$	–16.11	–16.18	–16.18	–16.12	–16.18	–16.18	–16.18
gap	21.48	20.66	19.33	17.80	17.60	17.46	17.32

Orbital energies of LUMO are arbitrary; completely determined by the basis set.

Go to zero for complete basis.

What about shape? Should go to infinitely extended.

Shape of the $1\sigma_u$ LUMO density of H_2 as a function of basis set:



Practical ways to get scattering resonances (negative EAs) with basis set calculations

Stabilization method (H. S. Taylor et al.), also called SKT (stabilization Koopmans' method):
Systematically scan through the spectrum of positive energies by scaling the coefficients of all diffuse basis functions to very low value (diffuse).
Then orbital energies go down in energy as function of scaling parameter α.
Detect resonance energies by inspecting the orbitals; when getting high amplitude in molecular region, you are at resonance energy.

Or by looking at curves of orbital energy as function of α: resonance energies show up as "avoided crossing".

See K. Jordan et al. (JPC-A **104** (2000) 9605) and Cheng et al. (JPC-A **116** (2012) 12364)

Orbital energies and excitation energy calculations (TDDFT)

TDDFT: $\left(\mathcal{E}^2 + 2\sqrt{\mathcal{E}}K\sqrt{\mathcal{E}}\right)\mathbf{F}_q = \omega_q^2\mathbf{F}_q$

$\left(\mathcal{E}^2\right)_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i)^2$

K is "coupling matrix", see later

Suppose $i \to a$ does not couple to other $j \to b$

(single pole approximation, SPA), $q \cong i \to a$

$$\left[(\varepsilon_a - \varepsilon_i)^2 + 2(\varepsilon_a - \varepsilon_i)\int \varphi_i(\mathbf{r})\varphi_a(\mathbf{r}) f_{xc}(\mathbf{r},\mathbf{r}')\varphi_i(\mathbf{r}')\varphi_a(\mathbf{r}')d\mathbf{r}d\mathbf{r}'\right]\mathbf{F}_q = \omega^2\mathbf{F}_q$$

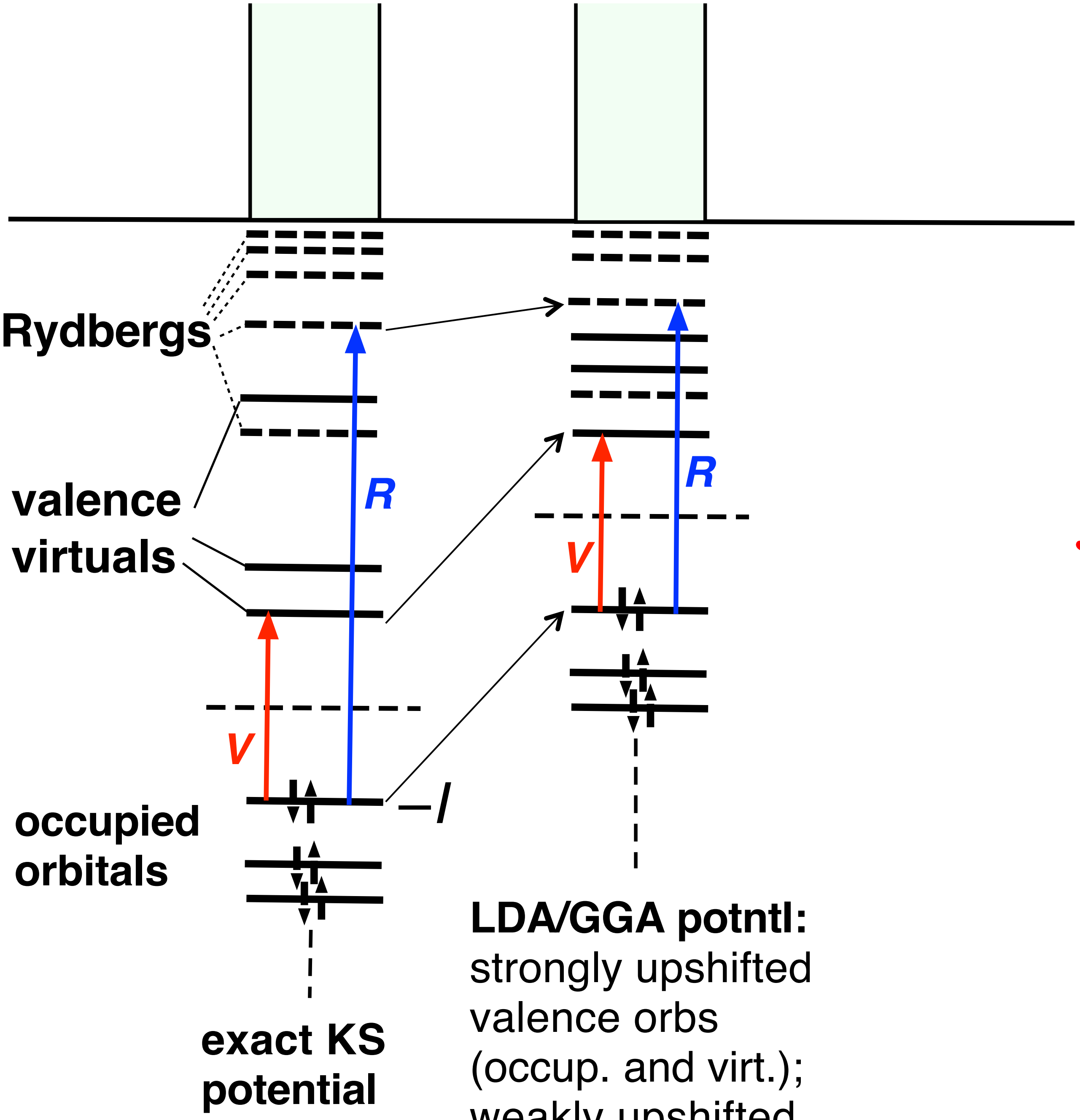
$$\Rightarrow \omega \approx (\varepsilon_a - \varepsilon_i) + \underbrace{\left\langle \varphi_i\varphi_a \middle| f_{xc} \middle| \varphi_i\varphi_a \right\rangle}_{small}$$

$(\varepsilon_a - \varepsilon_i) \approx$ excitation energy (in molecules!)

KS HOMO-LUMO gaps Δ are excellent approx. to excitation energies

	Δ^{HF}	Δ^{LDA}	Δ^{BLYP}	Δ^{KS}	**Expt. excit. energy**	
					singlet	**triplet**
H_2	17.6	10.6	10.5	12.5	**12.7**	**11.7**
H_2O	14.7	6.5	6.2	7.5	**7.65**	**7.5**
HF	18.5	8.9	8.5	10.5	**10.3**	**9.9**
N_2	19.9	9.7	9.6	9.9	**9.3-10.3**	**7.8-8.9**
CO	17.0	6.9	7.1	7.5	**8.5**	**6.3**
HCN	15.4	7.9	7.8	8.0	**8.8**	**6.2**
FCN	14.8	7.3	7.0	7.6	**8.4**	**7.8**
HCl	13.8	7.0	6.8	7.4	**7.8**	**7.4**

1) The LDA, GGA gaps are similar (slightly smaller) than KS gaps
-> the upshift is similar for HOMO and (a bit smaller for) LUMO
2) HF gaps are much larger: they are Koopmans' approx. IP – EA



Rydbergs

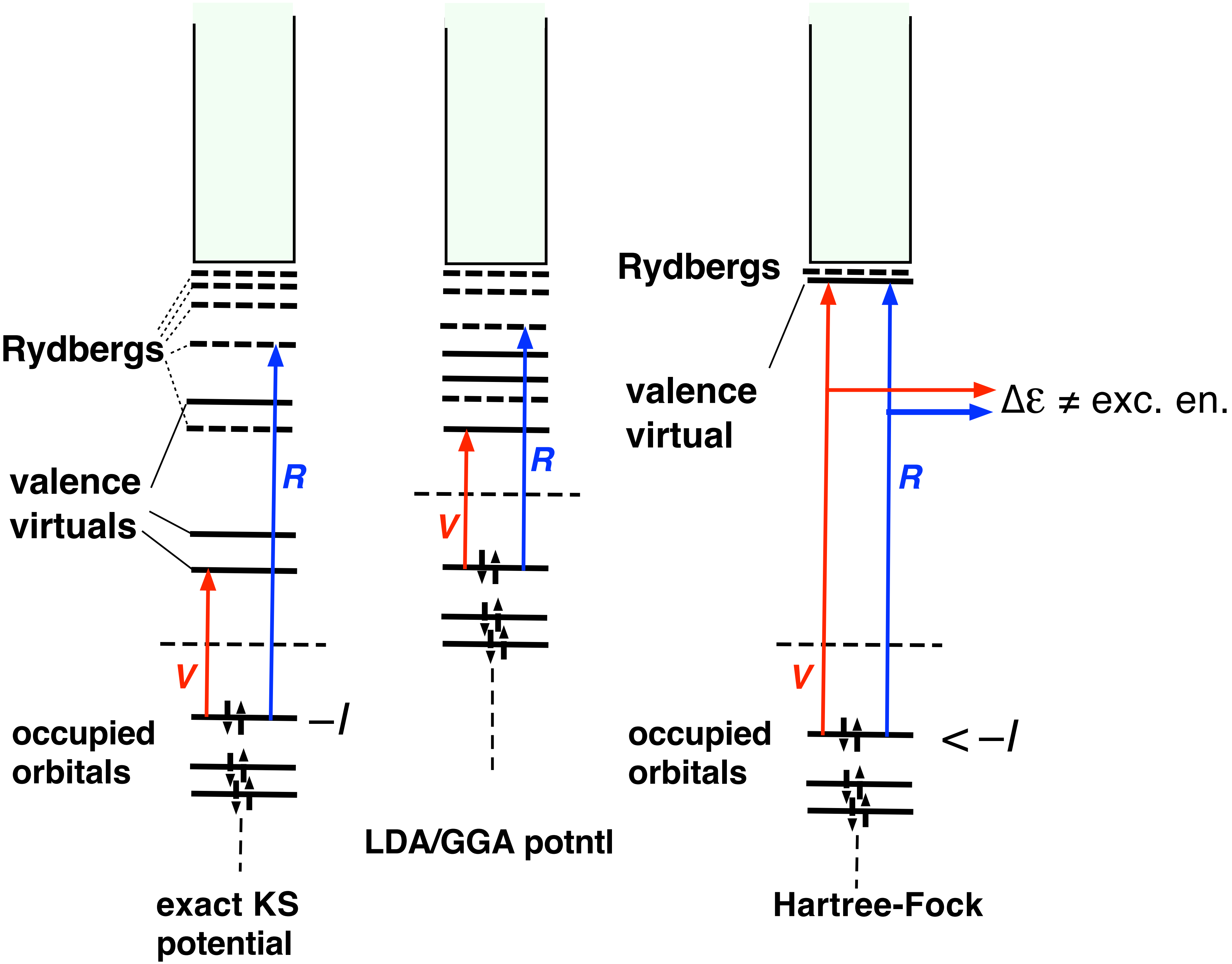
valence virtuals

occupied orbitals

exact KS potential

LDA/GGA potntl:
strongly upshifted valence orbs (occup. and virt.); weakly upshifted fewer Rydbergs

proper KS pot. important for virtual orbital spectrum!



exact KS potential

LDA/GGA potntl

Hartree-Fock

Acetone: orbital energy differences and excitation energies (eV)

Funct.	**State**	**Weight**	ε_i	ε_a	$\Delta\varepsilon_{ia}$	ω	$\omega - \Delta\varepsilon_{ia}$	$\omega - E_{exp}$
SAOP	$1A_2$	1.00	–10.25	–5.92	4.33	4.59	0.26	0.16
(“exact”	$1B_2$	1.00	–10.25	–4.18	6.07	6.09	0.02	-0.27
KS)	$2A_2$	0.84	–10.25	–2.72	7.53	7.52	0.00	0.16
	$2A_1$	0.97	–10.25	–3.09	7.16	7.21	0.05	-0.20
	$2B_2$	0.97	–10.25	–2.63	7.62	7.64	0.02	0.15
	$3A_1$	0.97	–10.25	–2.04	8.21	8.20	0.00	0.40
	$3B_2$	0.97	–10.25	–2.51	7.74	7.74	0.00	-0.35
	$1B_1$	0.95	–10.25	–1.83	8.42	8.43	0.01	0.26
BP86	$1A_2$	1.00	–5.71	–1.70	4.01	4.27	0.26	-0.16
	$1B_2$	1.00	–5.71	–0.61	5.10	5.10	0.00	-1.26
	$2A_2$	1.00	–5.71	–0.11	5.60	5.59	0.00	-1.77
	$2A_1$	1.00	–5.71	–0.13	5.58	5.58	0.00	-1.83
JCTC **10**	$2B_2$	1.00	–5.71	–0.07	5.64	5.64	- 0.01	-1.85
4432	$3A_1$	0.98	–5.71	+0.36	6.07	6.06	- 0.01	-1.74
(2014)	$3B_2$	1.00	–5.71	+0.05	5.76	5.75	0.00	-2.34
	$1B_1$	1.00	–5.71	+0.31	6.02	6.01	-0.01	-2.16

Acetone: orbital energy differences and excitation energies (eV)

Funct.	**State**	**Weight**	ε_i	ε_a	$\Delta\varepsilon_{ia}$	ω	$\omega - \Delta\varepsilon_{ia}$	$\omega - E_{exp}$
HF	$1A_2$	0.47	–11.23	+3.96	15.18	5.03	-10.15	0.60
	$1B_2$	0.36	–11.23	+0.62	11.85	8.24	-3.61	1.88
	$2A_2$	0.43	–11.23	+1.02	12.25	9.02	-3.23	1.66
	$2A_1$	0.20	–11.23	+0.96	12.19	9.07	-3.12	1.66
	$2B_2$	0.31	–11.23	+1.20	12.43	9.13	-3.30	1.64
	$3A_1$	0.21	–13.20	+3.96	17.15	9.41	-7.74	1.61
	$3B_2$	0.23	–11.23	+1.74	12.96	9.59	-3.37	1.50
	$1B_1$	0.29	–15.23	+3.96	19.18	9.66	-9.52	1.49
M06-2X	$1A_2$	0.52	–8.85	+0.78	9.63	4.03	-5.60	-0.40
	$1B_2$	0.73	–8.85	–0.34	8.51	6.54	-1.97	0.18
	$2A_2$	0.62	–8.85	+0.04	8.88	7.33	-1.55	-0.03
	$2A_1$	0.62	–8.85	+0.03	8.87	7.38	-1.49	-0.03
	$2B_2$	0.45	–8.85	+0.15	9.00	7.40	- 1.60	-0.09
	$3A_1$	0.79	–8.85	+0.74	9.58	8.03	- 1.55	0.23
	$3B_2$	0.42	–8.85	+0.64	9.49	7.80	-1.69	-0.29
	$1B_1$	0.92	–8.85	+0.73	9.58	8.12	-1.45	-0.05

JCTC **10**
4432
(2014)

occupied orbital energies

LDA/GGA: typically 4 – 6 eV too high

(HF typically 1 eV too low)

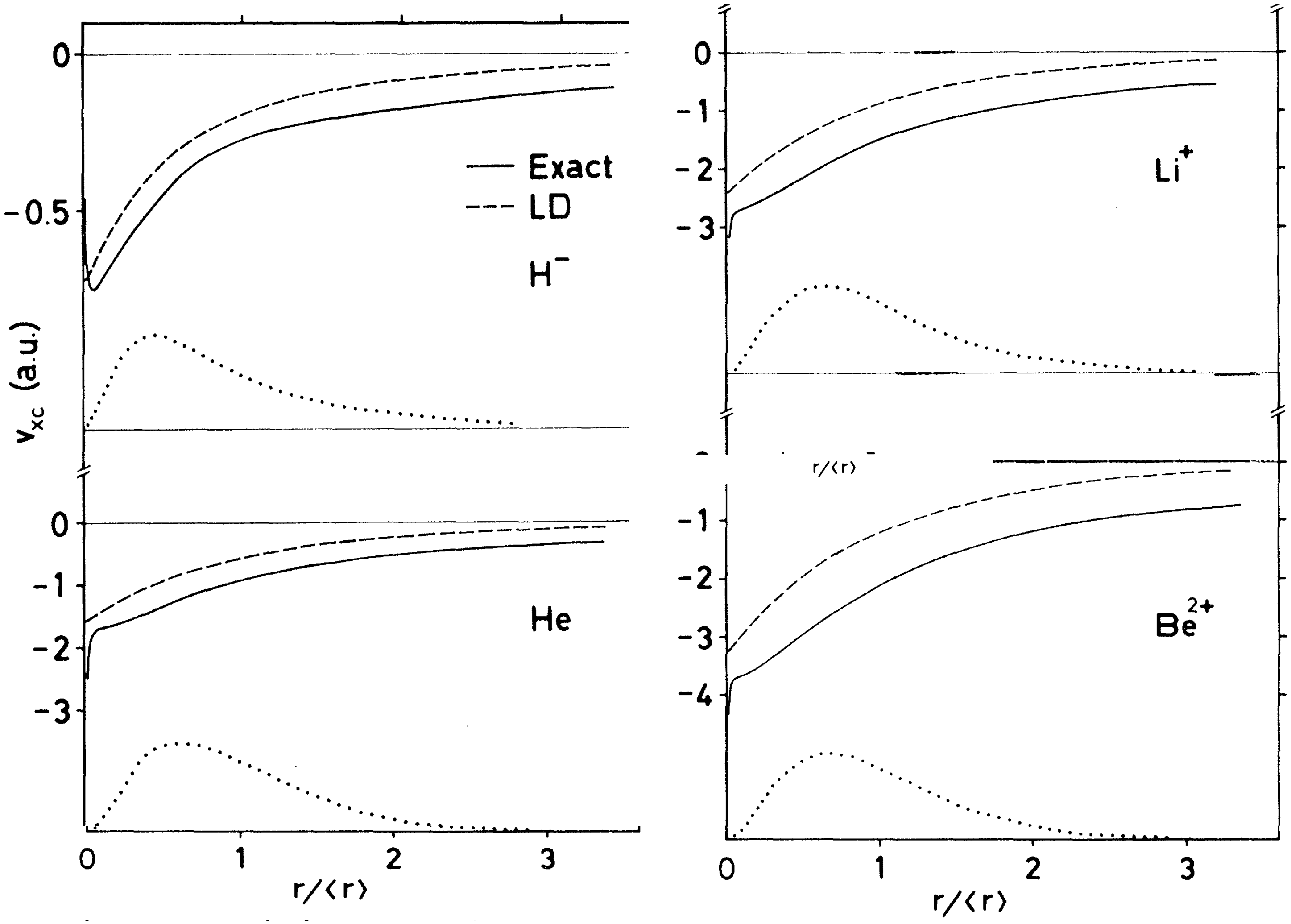
(an error of 100 – 140 kcal/mol, totally unacceptable in the total energy!)

Why?

- Not because of wrong asymptotics of potentials
- Not because of self-interaction error

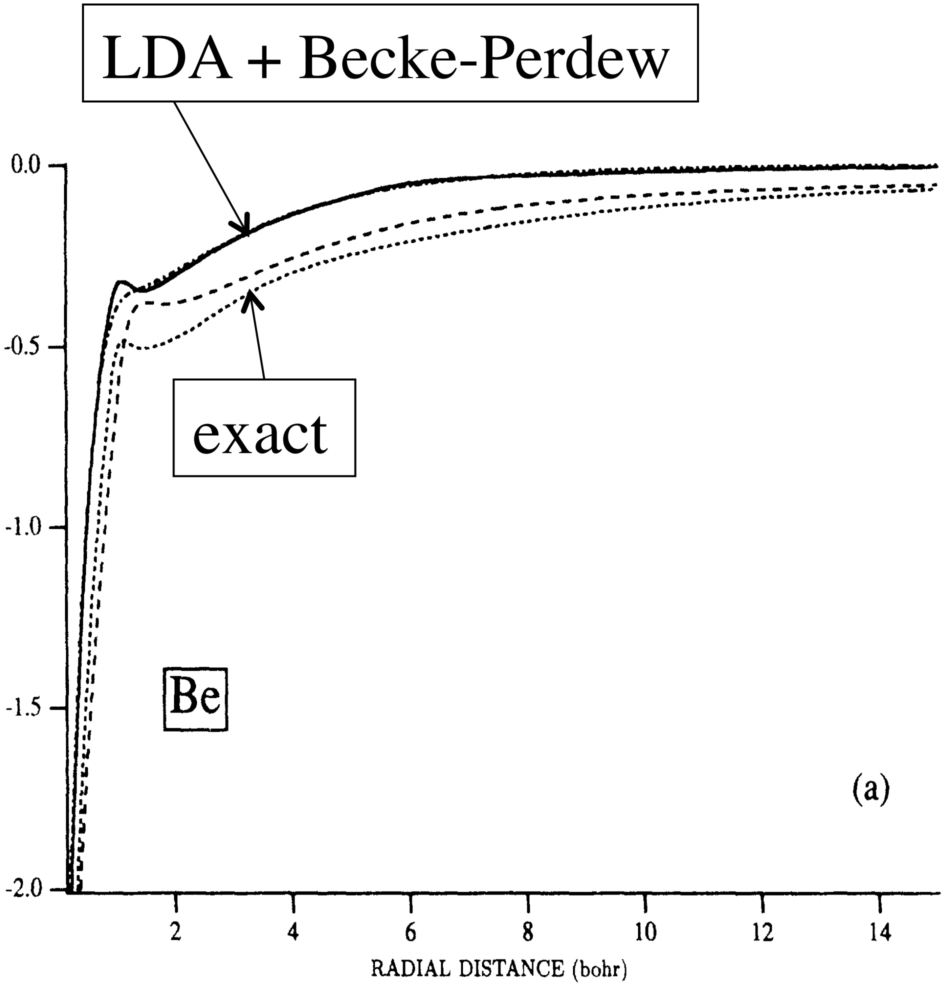
But because LDA/GGA potentials are strongly upshifted in the bulk molecular region

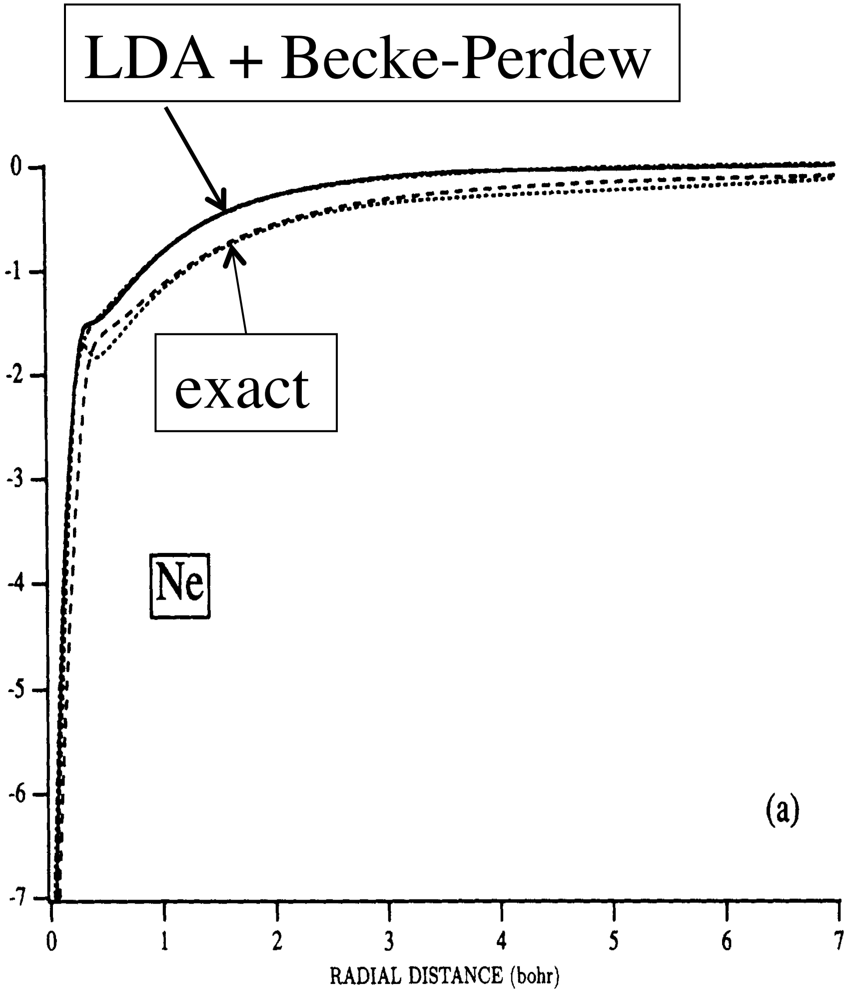
Exact and LDA KS potentials



Almbladh and Pedroza, PRB 1985

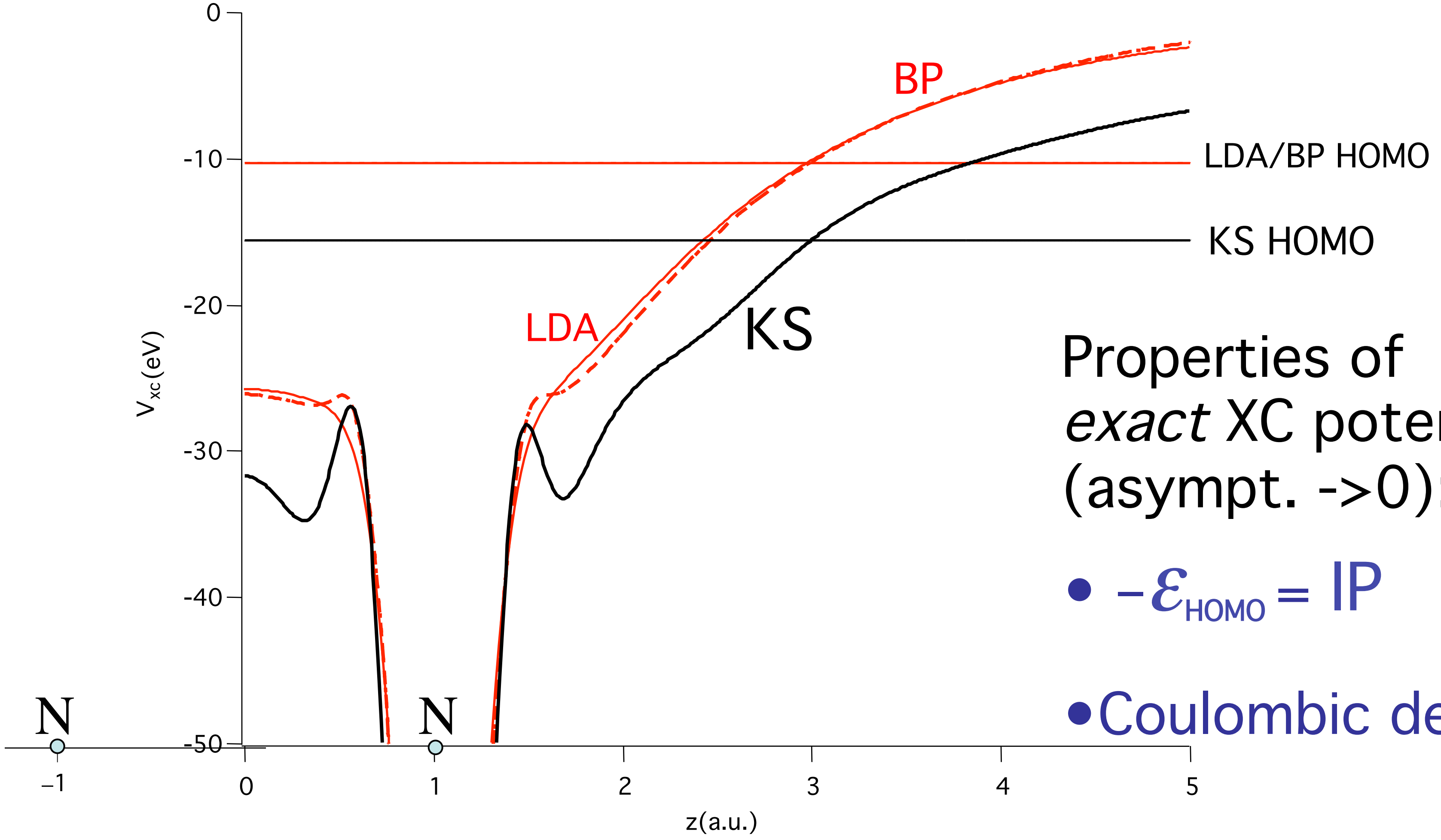
Exact and LDA KS potentials





van Leeuwen and Baerends, PRA 1994

N_2: XC potentials along bond axis



Properties of *exact* XC potential (asympt. ->0):

- $-\varepsilon_{\text{HOMO}} = \text{IP}$
- Coulombic decay

Grüning, Gritsenko, Baerends, JCP 2002

Electron Gas (EG) exchange energy

$$E_X^{LDA} \equiv \int \rho(\mathbf{r})\varepsilon_X^{LDA}(\mathbf{r})d\mathbf{r} = \frac{1}{2}\int \rho(\mathbf{r})v_{Xhole}^{EG}(\mathbf{r})d\mathbf{r}$$

$$v_{Xhole}^{EG}(\mathbf{r}) = -3\left(\frac{3}{8\pi}\right)^{\frac{1}{3}}\rho(\mathbf{r})^{\frac{1}{3}}$$

Slater: square hole around position **r** of electron with depth –(1/2)$\rho(\mathbf{r})$, integrating to – 1, gives practically same potential $C\rho(\mathbf{r})^{1/3}$

Slater (band structure theorists) applied this in one-electron equations as exchange potential

Gaspar-Kohn-Sham (DFT):

Proper variational derivation of one-el. equations for the optimal orbitals yields:

$$v_X^{LDA}(\mathbf{r}) = \frac{2}{3} v_{Xhole}^{EG}(\mathbf{r})$$

→Slater's Xα method: use potential $\alpha . v_{Xhole}^{EG}(\mathbf{r})$

α has been determined in various ways in atoms (e.g. K. Schwarz, 1972):

- exact exchange energy optimized;
- Virial Theorem obeyed
- energy equal to Hartree-Fock energy

→ α in range 0.78 (lightest elements) – 0.71 (beyond first row)

or in molecules (E. J. Baerends, 1973) (α = 0.70)

→Slater's Xα method: use potential αv_{Xhole}^{EG}

Actually, Slater resisted initially:
- orbital energies are "better" with full Slater (EG) exchange pot.!

J.C. Slater, *Quantum Theory of Molecules and Solids*,
Vol. 3 (1967): *Insulators, semiconductors and metals*
p. 243: Some writers have felt that on account of the importance of the variation principle for the toal energy, it was more important to use ... an exchange correction determined by variation of the total energy ...

The author does not agree with this point of view, feeling that the one-electron energies are more important in energy-band calculations.

The slightly different wavefunctions which we find by use of [the full $v_{Xhole}^{EG}(\mathbf{r})$] rather than $(2/3)v_{Xhole}^{EG}(\mathbf{r})$ will only make a second order change in the total energy.

Orbital energies from Slater (EG), LDA, GGA compared to exact KS

N_2	$3\sigma_g$	$1\pi_u$	$2\sigma_u$
$-I_i$	– 15.58	– 16.83	– 18.75
ε_i (KS)	– 15.58	– 16.84	– 18.89
ε_i (Slater)	– 15.39	– 16.66	– 18. 62
ε_i(BLYP)	– 10.28	– 11.49	– 13.39

Orbital energies from Slater (EG), LDA, GGA compared to exact KS

H_2CO	$2b_2$	$1b_1$	$5a_1$	$1b_2$	$4a_1$
$-I_i$	– 10.9	– 14.5	– 16.1	– 17.0	– 21.4
ε_i (KS)	– 10.90	– 14.26	– 15.51	– 16.46	– 20.04
ε_i (Slater)	– 10.99	– 14.56	– 15.91	– 16.82	– 20.57
ε_i(BLYP)	– 6.22	– 9.94	– 10.93	– 12.08	– 15.59

The LDA X-response pot. is (way) too repulsive

$$E_X^{LDA} \equiv \int \rho(\mathbf{r})\varepsilon_X^{LDA}(\mathbf{r})d\mathbf{r} = \frac{1}{2}\int \rho(\mathbf{r})v_{Xhole}^{EG}(\mathbf{r})d\mathbf{r}$$

$$v_X^{LDA}(\mathbf{r}) = \frac{\delta E_X^{LDA}}{\delta\rho(\mathbf{r})} = v_{Xhole}^{EG}(\mathbf{r}) + v_{Xresp}^{LDA}(\mathbf{r})$$

$$v_X^{LDA}(\mathbf{r}) = -2\left(\frac{3}{8\pi}\right)^{\frac{1}{3}}\rho(\mathbf{r})^{\frac{1}{3}} = -3\left(\frac{3}{8\pi}\right)^{\frac{1}{3}}\rho(\mathbf{r})^{\frac{1}{3}} + \left(\frac{3}{8\pi}\right)^{\frac{1}{3}}\rho(\mathbf{r})^{\frac{1}{3}}$$

$$v_{Xhole}^{EG}(\mathbf{r}) \qquad +v_{Xresp}^{LDA}(\mathbf{r})$$

(1/3) of hole pot.!

(1/2) of total X pot.!

What is the right response potential?

$$v_s = v_{nuc} + v_{Coul} + v_{xc}(\mathbf{r})$$

$$v_{xc}(\mathbf{r}) = \underset{\text{energy density for } W_{xc}}{\underset{\downarrow}{v_{xc}^{hole}}}(\mathbf{r}) + \underset{\text{for } T_c}{\underset{\downarrow}{v_{c,kin}}}(\mathbf{r}) + v^{resp}(\mathbf{r})$$

What is the right response potential?

$$v_s = v_{nuc} + v_{Coul} + v_{xc}(\mathbf{r})$$

$$v_{xc}(\mathbf{r}) = \underset{\substack{\downarrow \\ \text{energy density for } W_{xc}}}{v_{xc}^{hole}(\mathbf{r})} + \underset{\substack{\downarrow \\ \text{for } T_c}}{v_{c,kin}(\mathbf{r})} + v^{resp}(\mathbf{r})$$

$$v^{resp}(\mathbf{r}) = \int \rho(\mathbf{r}') \frac{\delta v_{c,kin}(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r}' + \frac{1}{2} \int \rho(\mathbf{r}') \rho(\mathbf{r}'') \frac{\delta g(\mathbf{r}', \mathbf{r}'')}{\delta \rho(\mathbf{r})} d\mathbf{r}' d\mathbf{r}''$$

exact expression for v^{resp}: $v^{N-1} - v_s^{N-1}$

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

Dyson orbitals:
very similar to KS orbitals
and HF orbitals for
primary ion states

exact ionization energies

The response potential consists of contributions that have step like behavior when going from one shell to the next in an atom or molecule

What is the right response potential?

Krieger-Li-Iafrate (1994) derived a good approximation to the OEP potential in the exact-exchange only case:

$$v_X^{KLI}(\mathbf{r}) \approx v_{Xav}^{HF} + \sum_{i=1}^{H} w_i \frac{|\psi_i(\mathbf{r})|^2}{\rho(\mathbf{r})}$$

$$v_{Xav}^{HF}(\mathbf{r}) = \sum_i^{H} \frac{|\psi_i(\mathbf{r})|^2 \, v_{Xi}^{HF}(\mathbf{r})}{\rho(\mathbf{r})} \quad \text{a.k.a. } v_X^{Slater}(\mathbf{r})$$

Note $E_X^{HF} = \frac{1}{2}\int \rho(\mathbf{r}) v_{Xav}^{HF}(\mathbf{r}) d\mathbf{r}$

Approximation (GLLB) of v_{Xresp}

Step behavior introduced with $w_i = f(\varepsilon_F - \varepsilon_i)$

scaling density $\rho_\lambda(\mathbf{r}) = \lambda^3\rho(\lambda\mathbf{r})$ yields $v_x[\rho_\lambda](\mathbf{r}) = \lambda v_x[\rho](\lambda\mathbf{r})$

dictates, with $\varepsilon_i[\rho_\lambda] = \lambda^2\varepsilon_i[\rho]$,

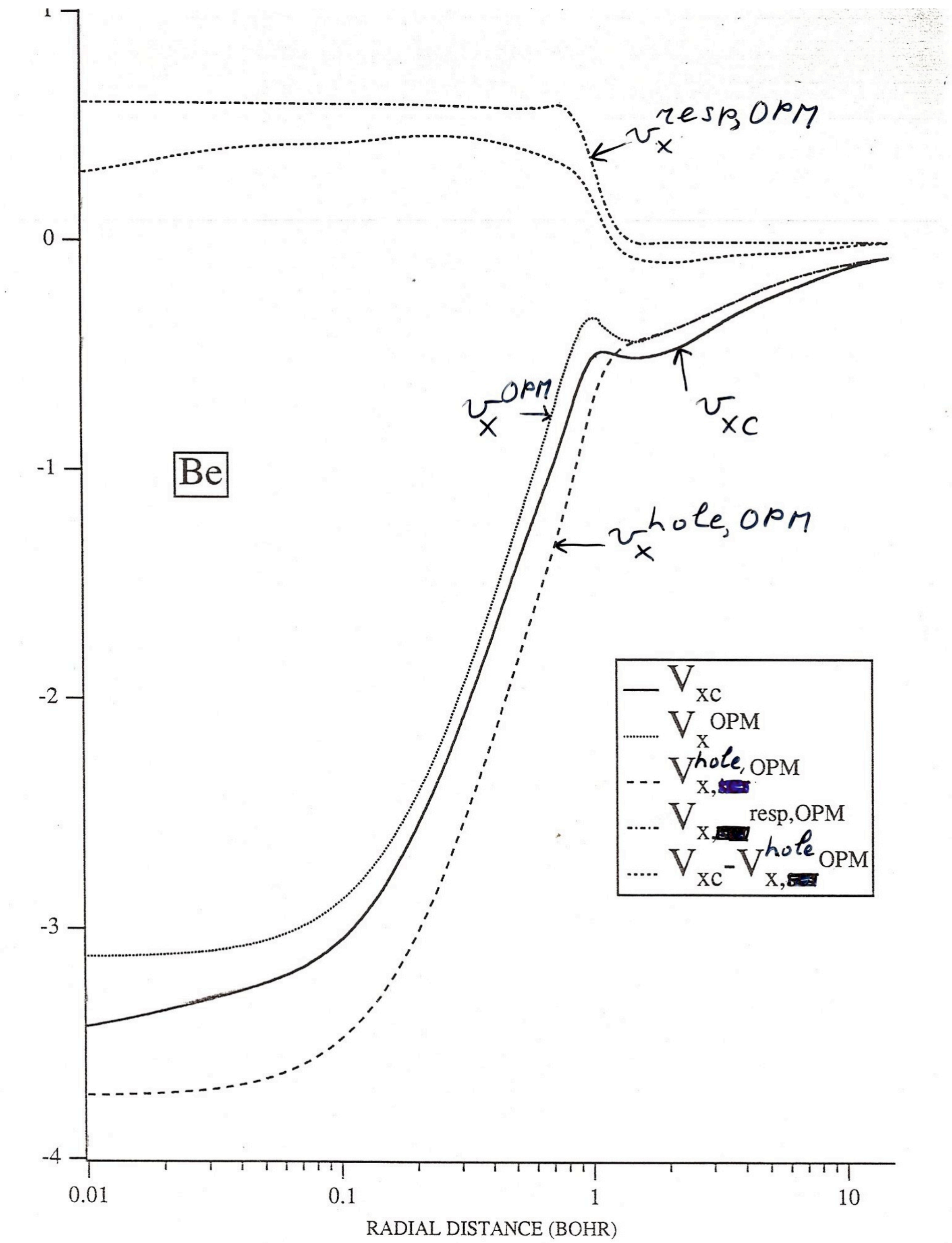
$f(\lambda^2(\varepsilon_F - \varepsilon_i)) = \lambda f(\varepsilon_F - \varepsilon_i)$ so f must be prop. to square root:

$$f \to K\sqrt{\varepsilon_F - \varepsilon_i}$$

$$v_{Xresp}^{\text{model}}(\mathbf{r}) = K[\rho]\sum_{i=1}^{H}\sqrt{\varepsilon_F - \varepsilon_i}\,\frac{|\psi_i(\mathbf{r})|^2}{\rho(\mathbf{r})}$$

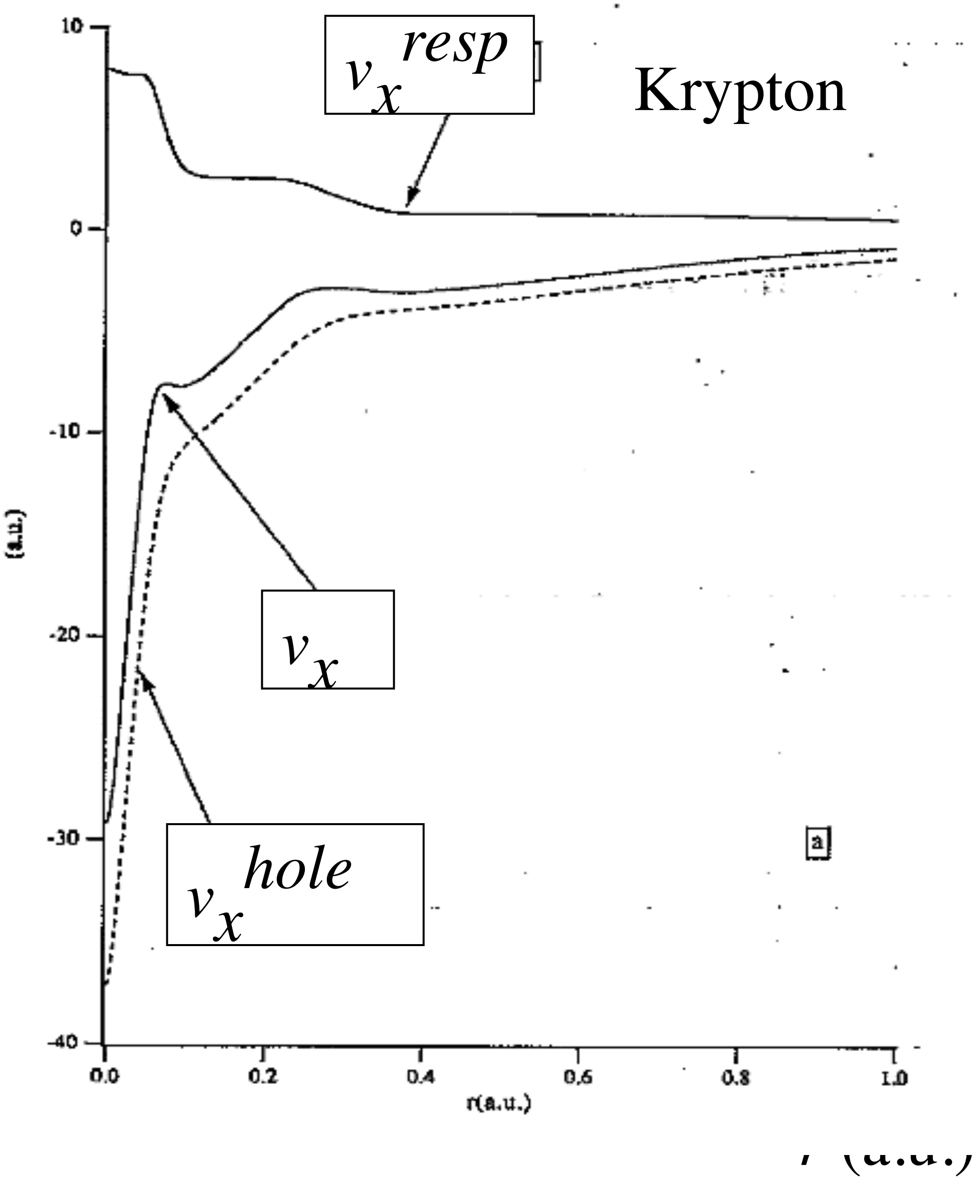
Exact in EG with $K = 0.382$

Response potential in Be



R. van Leeuwen, O. Gritsenko, E. J. Baerends, Z. Phys. D **33** (1995) 229

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



O. Gritsenko, R. van Leeuwen,
E. J. Baerends
J. Chem. Phys. **101** (1994) 8955

N_2 orbital energies

N_2 (K=0.382)	**$2\sigma_g$**	**$2\sigma_u$**	**$2\pi_u$**	**$3\sigma_g$ (HOMO)**
$v_{xhole,ii}$ (LDA)	– 29.47	– 24.72	– 23.51	– 24.89
$v_{xhole,ii}$ (B)	– 1.83	– 2.52	– 2.48	– 2.54
$v_{xresp,ii}$ (GLLB)	+ 6.05	+ 3.97	+ 5.10	+ 4.56
$v_{c,ii}$ (VWN)	– 1.91	– 1.76	– 1.75	– 1.76
$v_{xctot,ii}$	**– 27.16**	**– 25.03**	**– 22.63**	**– 24.63**
$h_{ii} + v_{H,ii}$	– 6.17	+ 5.73	+ 6.16	+ 8.89
ε_i	– 33.33	– 19.30	– 16.47	– 15.74
ε_i (KS)	– 33.67	– 18.89	– 16.84	– 15.58
$\Delta\varepsilon_i$	0.34	– 0.41	0.37	– 0.16

N_2 orbital energies

N_2 (K=0.382)	$2\sigma_g$	$2\sigma_u$	$2\pi_u$	$3\sigma_g$(HOMO)
$v_{xhole,ii}$ (LDA)	– 29.47	– 24.72	– 23.51	– 24.89
$v_{xhole,ii}$ (B)	– 1.83	– 2.52	– 2.48	– 2.54
$v_{xresp,ii}$ (GLLB)	+ 6.05	+ 3.97	+ 5.10	+ 4.56
$v_{c,ii}$ (VWN)	– 1.91	– 1.76	– 1.75	– 1.76
$\boldsymbol{v_{xctot,ii}}$	**– 27.16**	**– 25.03**	**– 22.63**	**– 24.63**
$h_{ii} + v_{H,ii}$	– 6.17	+ 5.73	+ 6.16	+ 8.89
ε_i	– 33.33	– 19.30	– 16.47	– 15.74
ε_i (KS)	– 33.67	– 18.89	– 16.84	– 15.58
$\Delta\varepsilon_i$	0.34	– 0.41	0.37	– 0.16
$\Delta\varepsilon_i$ (BVWN-KS)	5.00	4.99	4.91	4.82

HCOOH orbital energies (K=0.34)

	10a′	**2a″**	**9a′**	**1a″**	**8a′**	**7a′**
$v_{xhole,ii}$ (LDA)	–27.33	– 27.95	– 27.16	– 25.03	– 28.02	– 24.38
$v_{xhole,ii}$ (B)	– 2.63	– 2.63	– 2.57	– 2.55	– 2.61	– 2.32
$v_{xresp,ii}$ (GLLB)	+ 4.86	+ 5.64	+ 5.74	+ 5.86	+ 5.69	+ 5.64
$v_{c,ii}$ (VWN)	– 1.83	– 1.85	– 1.83	– 1.78	–1.87	– 1.78
$\boldsymbol{v_{xctot,ii}}$	**– 26.94**	**– 26.81**	**– 25.82**	**– 23.50**	**– 26.79**	**– 22.83**
$h_{ii} + v_{H,ii}$	+15.33	+14.20	+11.59	+ 8.06	+10.20	+5.68
ε_i	–11.61	– 12.61	– 14.23	– 15.44	– 16.59	– 17.15
ε_i (KS)	– 11.51	– 12.38	– 14.48	– 15.43	– 16.64	– 17.27
$\Delta\varepsilon_i$	– 0.10	– 0.23	0.25	– 0.01	0.05	0.12
$\Delta\varepsilon_i$ (BVWN-KS)	4.23	3.82	4.07	3.78	4.17	3.82

HCOOH orbital energies (K=0.34)

	7a′	**6a′**	**5a′**	**4a′**
$v_{xhole,ii}$ (LDA)	– 24.38	– 24.95	– 31.36	– 29.60
$v_{xhole,ii}$ (B)	– 2.32	– 2.24	– 2.08	– 2.05
$v_{xresp,ii}$ (GLLB)	+ 5.64	+ 5.99	+ 5.91	+ 6.12
$v_{c,ii}$ (VWN)	– 1.78	– 1.79	– 1.95	– 1.90
$\boldsymbol{v_{xctot,ii}}$	**– 22.83**	**– 23.01**	**– 29.48**	**– 27.44**
$h_{ii} + v_{H,ii}$	+ 5.68	+ 2.17	– 1.11	– 5.41
$\boldsymbol{\varepsilon_i}$	– 17.15	– 20.84	– 30.95	– 32.85
ε_i (KS)	– 17.27	– 21.17	– 30.43	– 32.94
$\Delta\varepsilon_i$	0.12	– 0.33	– 0.16	0.09
$\Delta\varepsilon_i$ (BVWN-KS)	3.82	3.88	4.14	4.14

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On the errors of LDA and GGA approximations to the KS potential
and orbital energies, to be publ.