

Excitation energy calculations  
with (nearly) exact  
Kohn-Sham potentials

Evert Jan Baerends

Vrije Universiteit, Amsterdam, The Netherlands

# 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

# HF, DFA and exact KS HOMO orbital energies

	<b>HF</b>	<b>LDA</b>	<b>BLYP</b>	<b>-IP = <math>\epsilon^{\text{KS}}</math></b>
H <sub>2</sub>	-16.18	-10.26	-10.39	-16.44
H <sub>2</sub> O	-13.88	-7.40	-7.21	-12.62
HF	-17.69	-9.82	-9.64	-16.19
N <sub>2</sub>	-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 - 6 eV  
(uniformly: occup. and unoccup *valence* orbitals)

# occupied orbital energies

- LDA/GGA: typically 4 – 6 eV too high  
(HF typically 1 eV too low)

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 for a different reason

orbital energy determined by bulk molecular region

$$\varepsilon_i = \langle \psi_i(\mathbf{r}) | -\frac{1}{2} \nabla^2 + V_{nuc}(\mathbf{r}) + V_{Coul}(\mathbf{r}) + V_{XC}(\mathbf{r}) | \psi_i(\mathbf{r}) \rangle$$

Determined by molecular region where  $\psi_i(\mathbf{r})$  has largest amplitude and where potentials

$V_{nuc}(\mathbf{r})$ ,  $V_{Coul}(\mathbf{r})$ ,  $V_{XC}(\mathbf{r})$  are large.

*Asymptotic regions contribute little!*

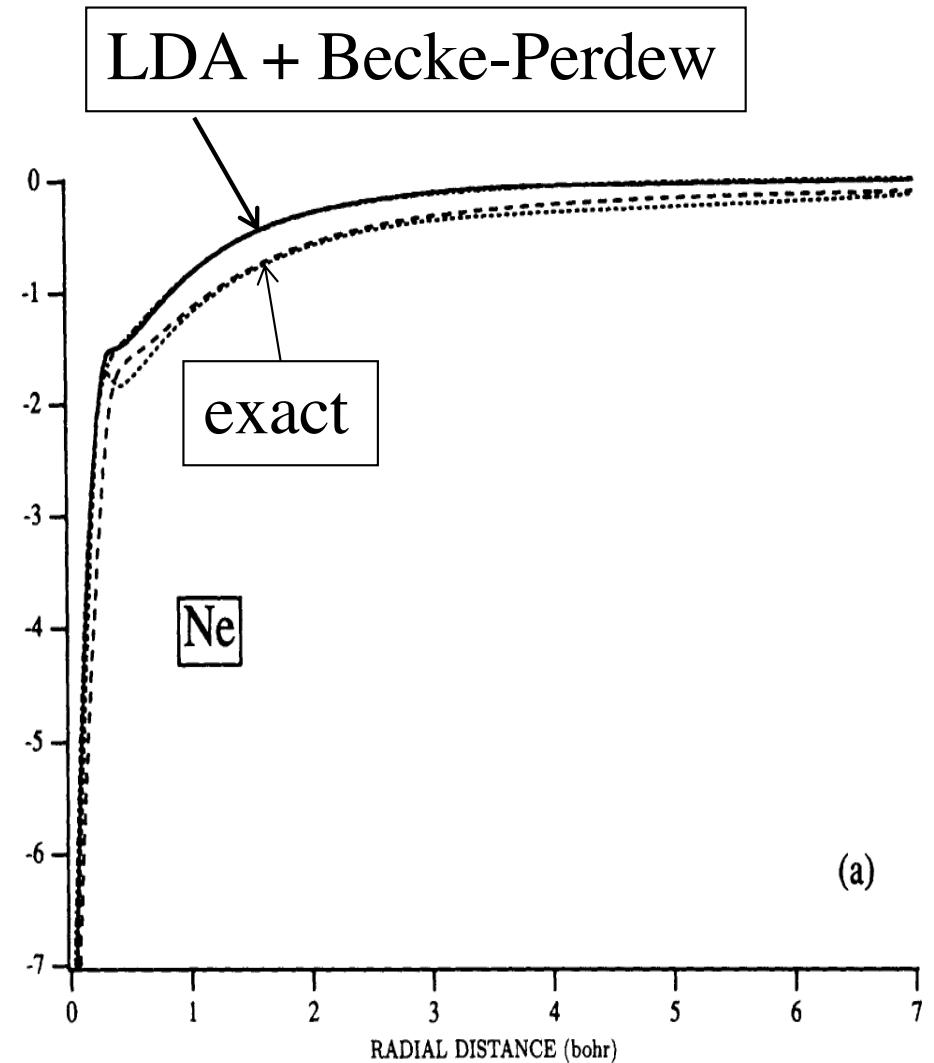
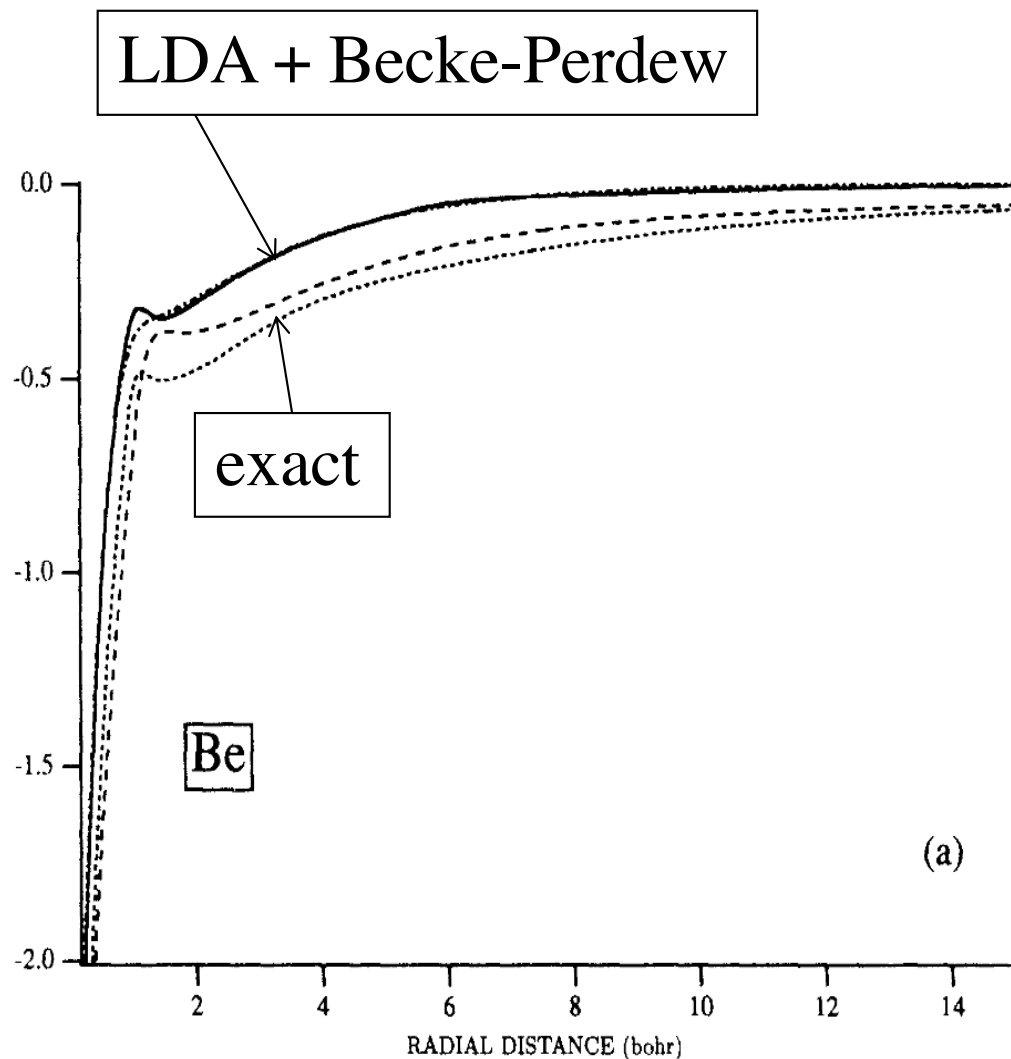
*(Except for Rydberg orbitals.)*

*Too high orbital energies:*

*LDA/GGA potentials are strongly upshifted*

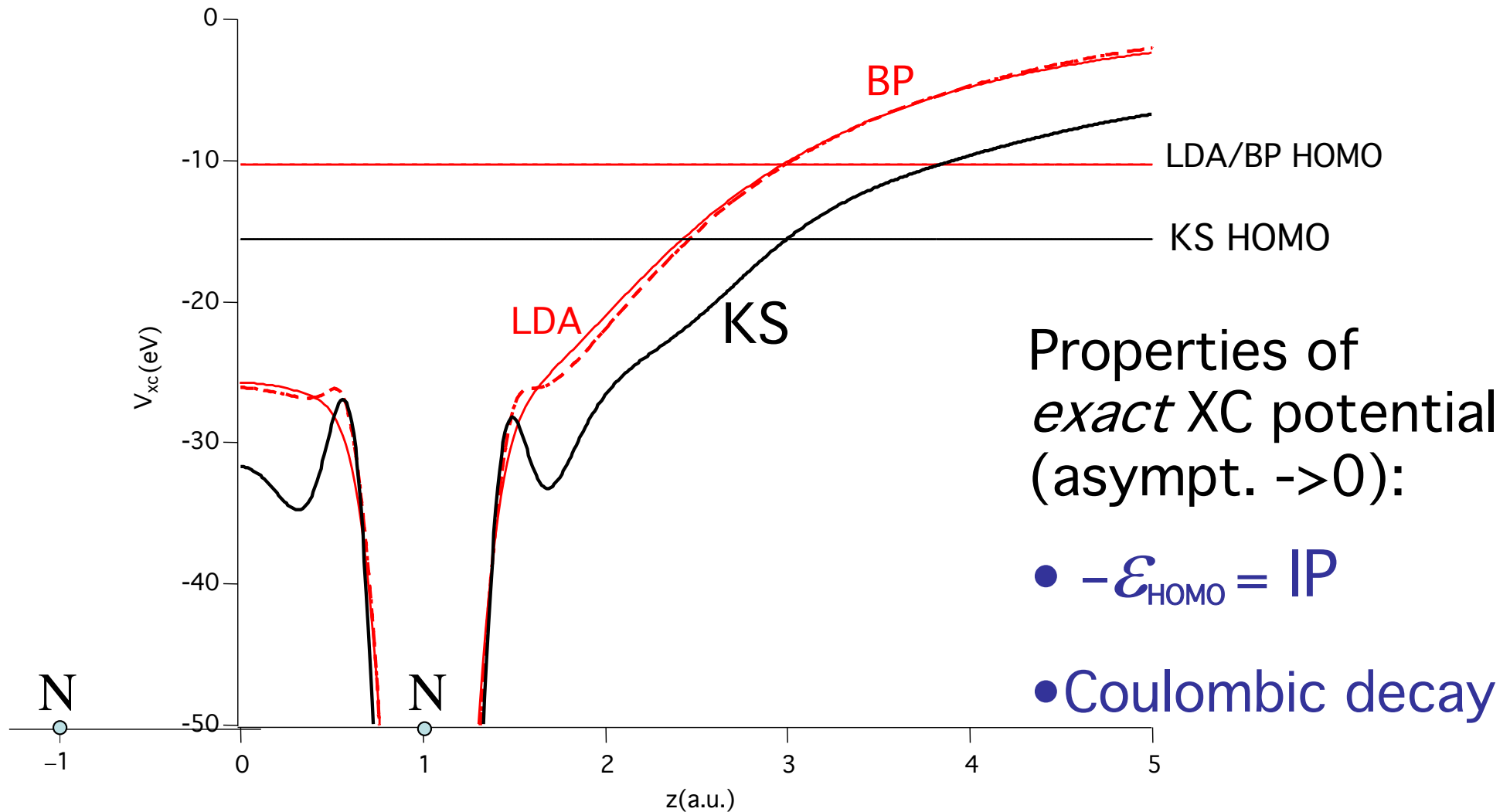
*in the bulk molecular region*

# Exact and LDA KS potentials



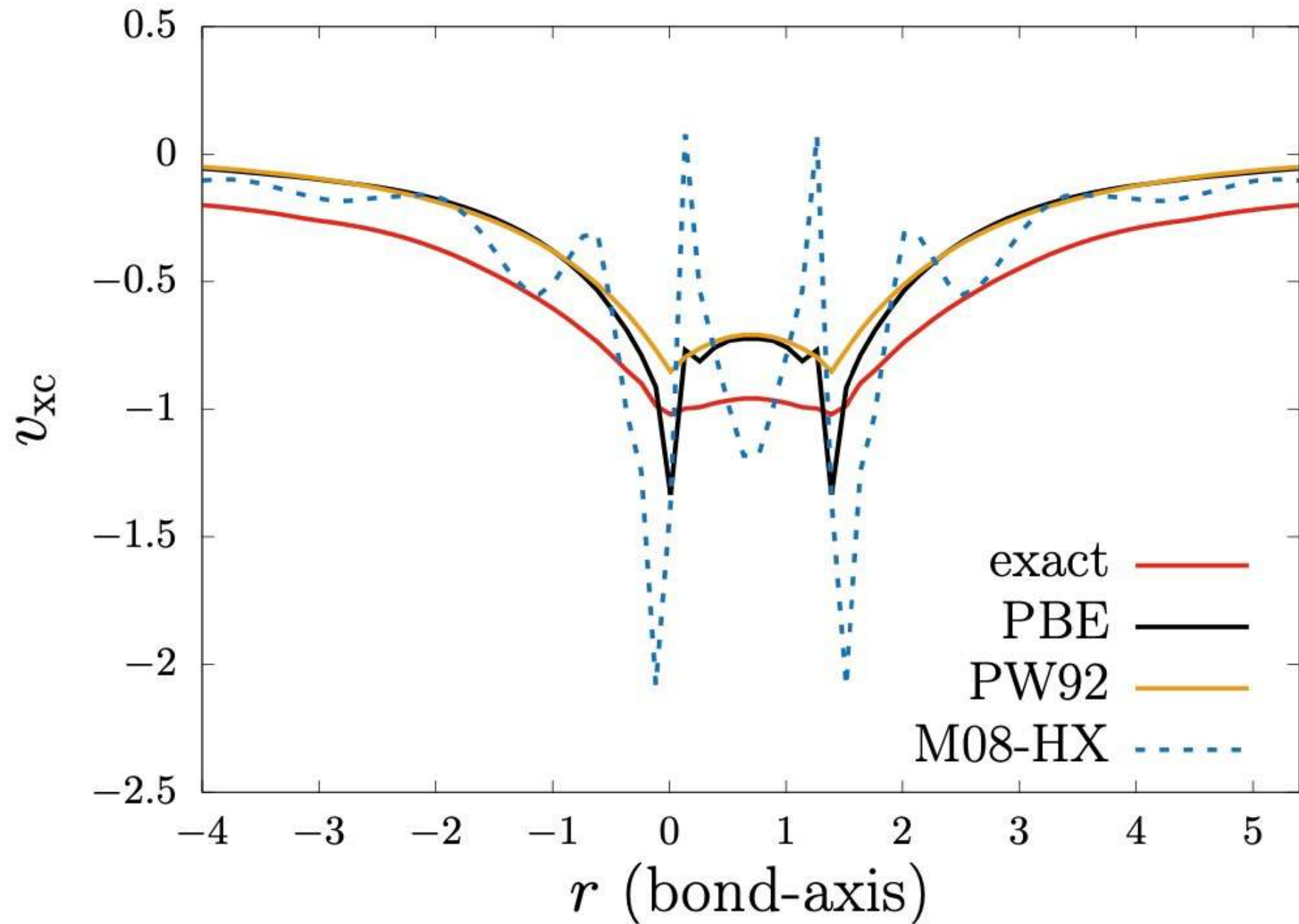
van Leeuwen and Baerends, PRA 1994

# N<sub>2</sub>: XC potentials along bond axis



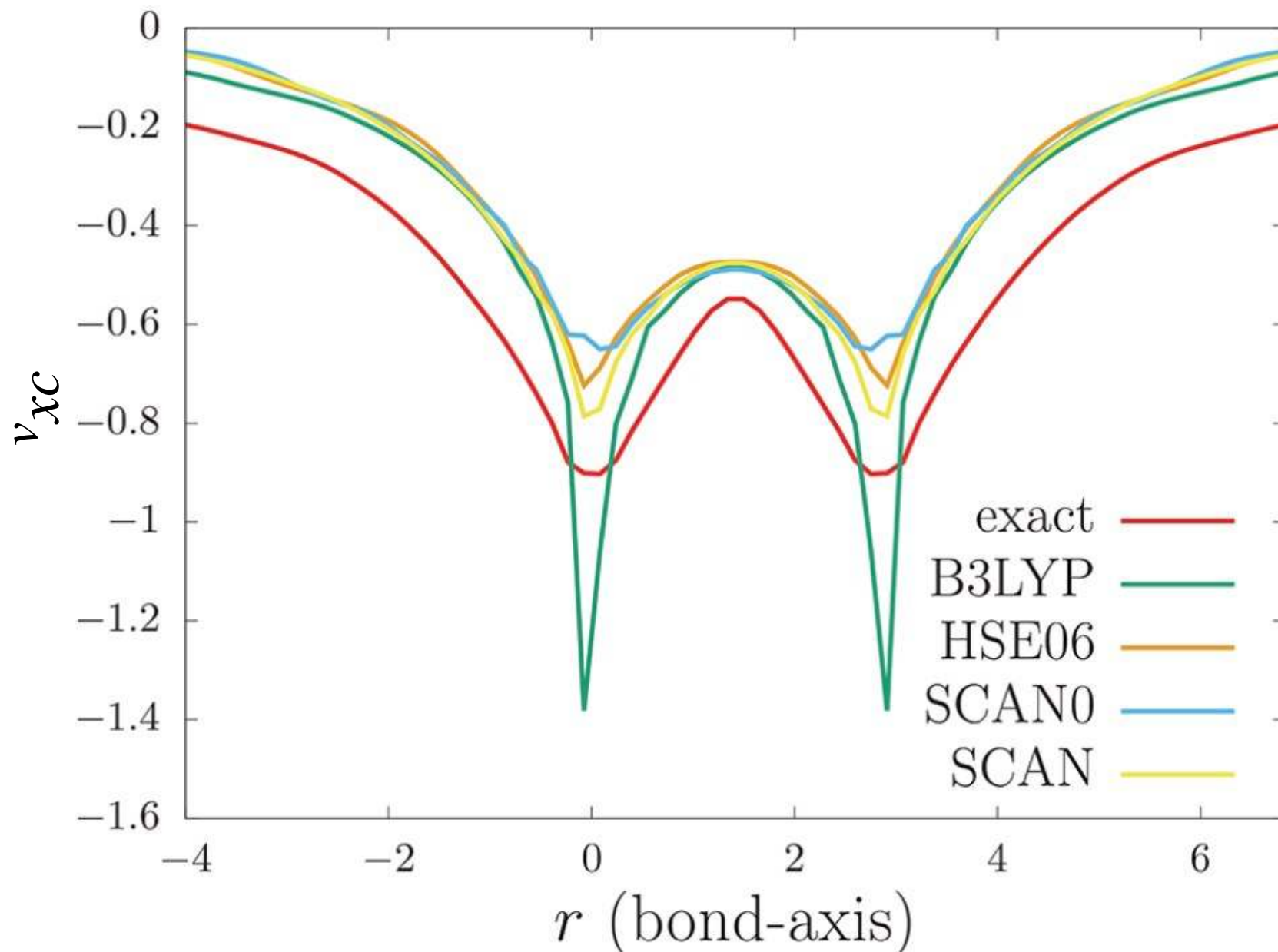
Grüning, Gritsenko, Baerends, JCP 2002

# Gavini et al. JPCL 12(2021): H<sub>2</sub> at $R_e$





# Gavini et al. JPCL 12(2021): H<sub>2</sub> at 2R<sub>e</sub>

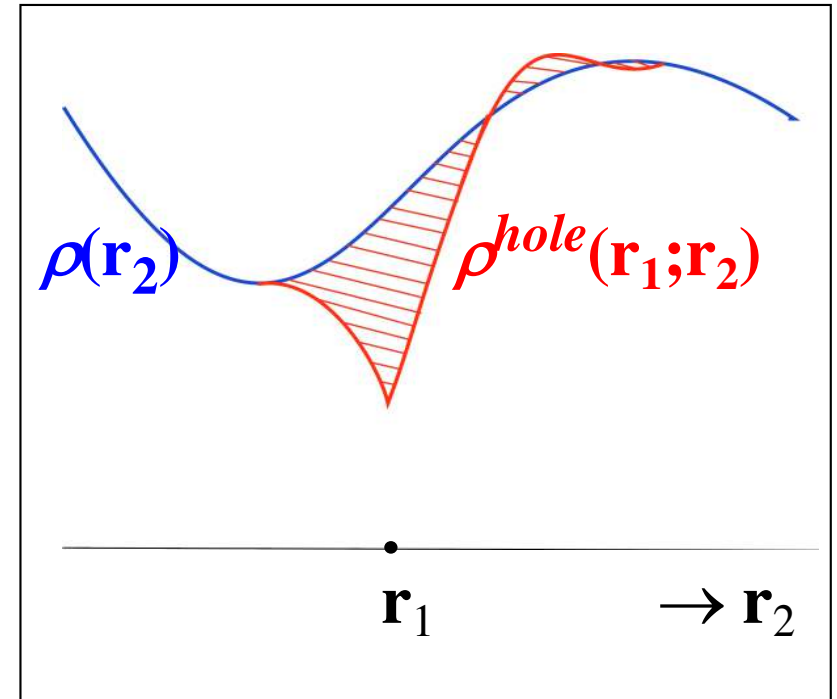


Why is LDA/GGA potential so upshifted?  
 Because response part of potential is wrong!

$$E_{XC} \equiv \int \rho(\mathbf{r}) \varepsilon_{XC}(\mathbf{r}) d\mathbf{r}$$

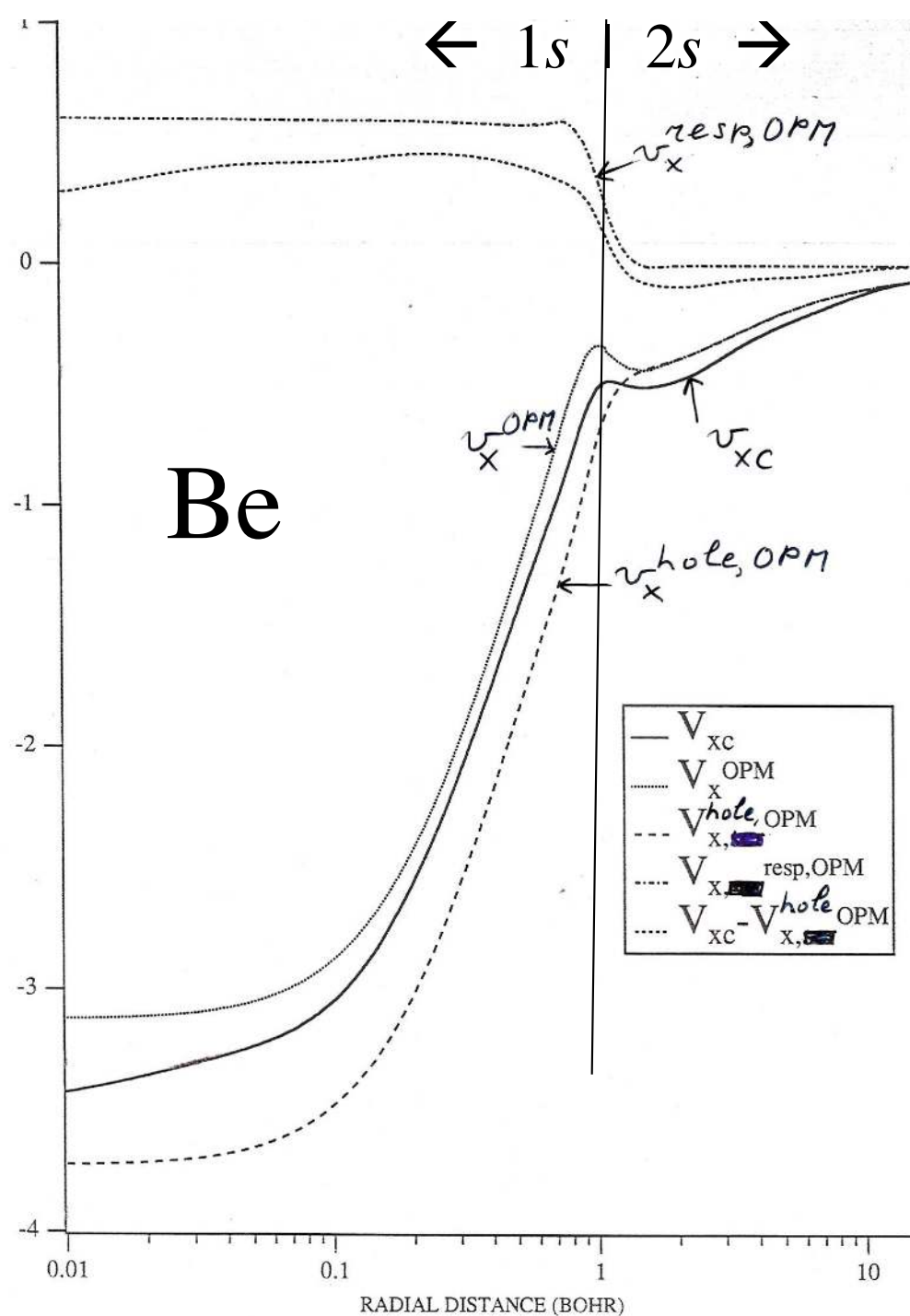
$$= \frac{1}{2} \int \rho(\mathbf{r}) \bar{v}_{XC}^{hole}(\mathbf{r}) d\mathbf{r}$$

$$\Rightarrow \varepsilon_{XC}(\mathbf{r}) = \frac{1}{2} \bar{v}_{XC}^{hole}(\mathbf{r}_1)$$



$$v_{XC}(\mathbf{r}) = \frac{\delta E_{XC}}{\delta \rho(\mathbf{r})} = \varepsilon_{XC}(\mathbf{r}) + \int \rho(\mathbf{r}_1) \frac{\delta \varepsilon_{XC}(\mathbf{r}_1)}{\delta \rho(\mathbf{r})} d\mathbf{r}_1$$

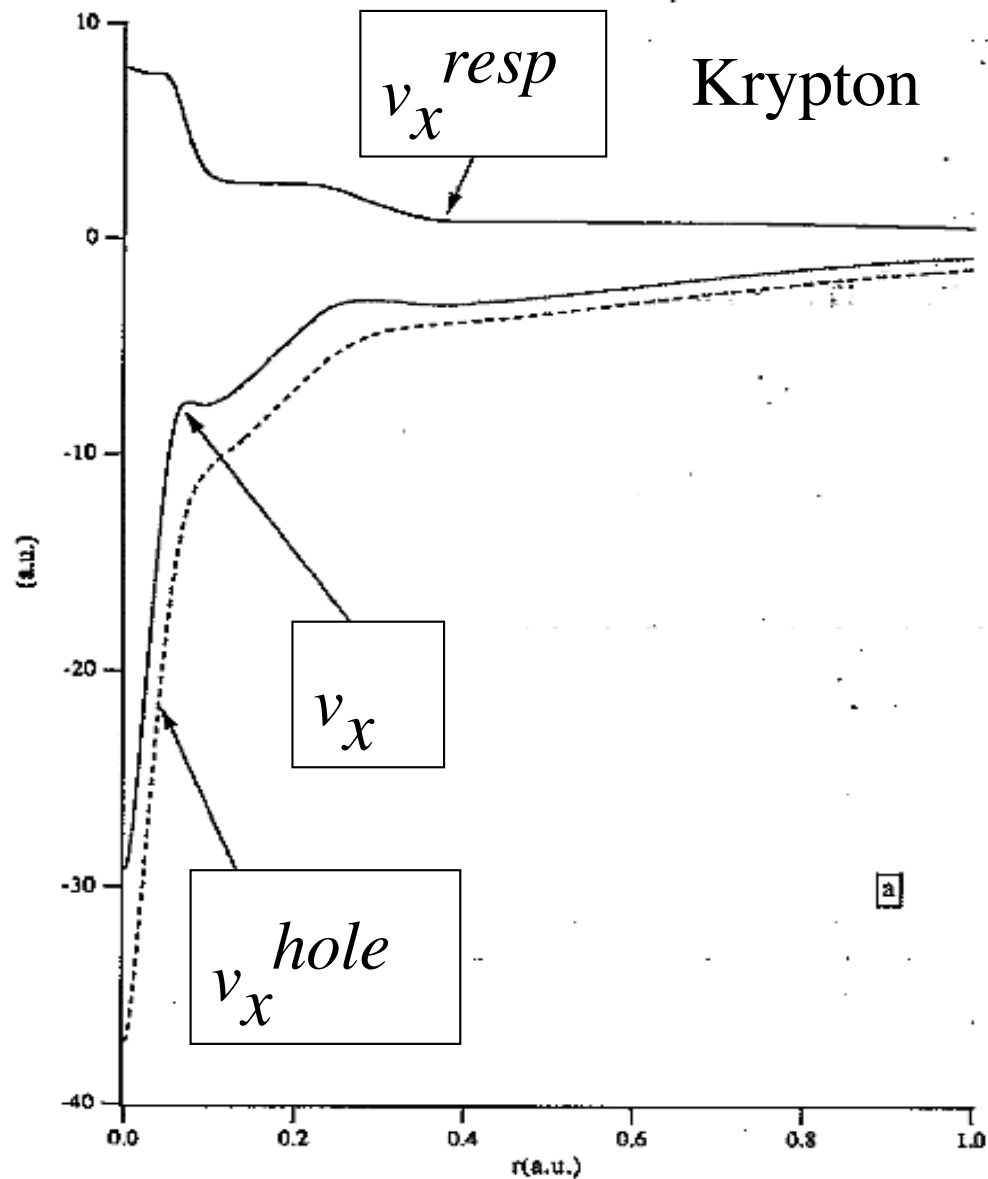
$$\begin{array}{ccc} \downarrow & & \downarrow \\ \frac{1}{2} \bar{v}_{XC}^{hole}(\mathbf{r}) & + & \frac{1}{2} \bar{v}_{XC}^{hole}(\mathbf{r}) + v_{XC}^{resp}(\mathbf{r}) \end{array}$$



How does reponse potential look?

It has steps;  
zero in HOMO  
region

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

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

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

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*

# LDA/GGA response pot.: no steps!

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

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

Long before LDA:

Slater: square hole around position  $\mathbf{r}$  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  $X\alpha$  method: use potential  $\alpha \cdot v_{Xhole}^{EG}(\mathbf{r})$

$\alpha$  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

→  $\alpha$  in range 0.78 (lightest elements) – 0.71 (beyond first row)

or in molecules (E. J. Baerends, 1973) ( $\alpha = 0.70$ )

→Slater's  $X\alpha$  method: use potential  $\alpha v_{Xhole}^{EG}$

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 total 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

$\text{N}_2$	$3\sigma_g$	$1\pi_u$	$2\sigma_u$
$-I_i$	-15.58	-16.83	-18.75
$\epsilon_i$ (KS)	-15.58	-16.84	-18.89
$\epsilon_i$ (Slater)	-15.39	-16.66	-18.62
$\epsilon_i$ (BLYP)	-10.28	-11.49	-13.39

Gritsenko, Mentel, Baerends, JCP 144 (2016) 204114

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

<b>H<sub>2</sub>CO</b>	<b>2b<sub>2</sub></b>	<b>1b<sub>1</sub></b>	<b>5a<sub>1</sub></b>	<b>1b<sub>2</sub></b>	<b>4a<sub>1</sub></b>
$-I_i$	- 10.9	- 14.5	- 16.1	- 17.0	- 21.4
$\mathcal{E}_i$ (KS)	- 10.90	- 14.26	- 15.51	- 16.46	- 20.04
$\mathcal{E}_i$ (Slater)	- 10.99	- 14.56	- 15.91	- 16.82	- 20.57
$\mathcal{E}_i$ (BLYP)	- 6.22	- 9.94	- 10.93	- 12.08	- 15.59

Gritsenko, Mentel, Baerends, JCP 144 (2016) 204114

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

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

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

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

(1 / 3) of hole pot.!

(1 / 2) of total X pot.!

*Wrong response potential causes  
uniform upshift of orbital energies!*

# How to model the response potential?

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

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

KLI exch.-response pot.: steps of height  $w_i$

# 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:

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

$$v_{Xresp}^{GLLB}(\mathbf{r}) = K[\rho] \sum_{i=1}^H \sqrt{\varepsilon_F - \varepsilon_i} \frac{|\psi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \quad \text{Exact in EG with } K = 0.382$$

Gritsenko, van Leeuwen, van Lenthe, Baerends, PRA 1995

# Build up correct potential:

1)  $v_X^{hole}(\mathbf{r})$  from  $2\varepsilon_X^{GGA}[\rho(\mathbf{r})](\mathbf{r}) = 2\varepsilon_X^{LDA}(\mathbf{r}) + 2\varepsilon_X^{B88}(\mathbf{r})$

-  $2\varepsilon_X^{LDA}(\mathbf{r}) = v_{Xhole}^{LDA}(\mathbf{r})$  no factor 2/3!

- note: B88 correction makes energy density go like  $-1/2r$

so  $v_{Xhole}^{B88}(\mathbf{r})$  has proper  $-1/r$  asymptotics

2)  $v_X^{resp}(\mathbf{r})$  taken as  $v_{Xresp}^{GLLB}(\mathbf{r})$

3) correlation potential (hole + resp.) from LDA:  $v_{corr}^{VWN}(\mathbf{r})$

----> B-GLLB-VWN

# N<sub>2</sub> orbital energies

N <sub>2</sub> (K=0.382)	3σ <sub>g</sub> (HOMO)	2π <sub>u</sub>	2σ <sub>u</sub>	2σ <sub>g</sub>
$v_{xhole,ii}$ (LDA)	- 24.89	- 23.51	- 24.72	- 29.47
$v_{xhole,ii}$ (B)	- 2.54	- 2.48	- 2.52	- 1.83
$v_{xresp,ii}$ (GLLB)	+ 4.56	+ 5.10	+ 3.97	+ 6.05
$v_{c,ii}$ (VWN)	- 1.76	- 1.75	- 1.76	- 1.91
$v_{xctot,ii}$	<b>- 24.63</b>	<b>- 22.63</b>	<b>- 25.03</b>	<b>- 27.16</b>
$h_{ii} + v_{H,ii}$	+ 8.89	+ 6.16	+ 5.73	- 6.17
$\mathcal{E}_i$ (BGLLBVWN)	<b>- 15.74</b>	<b>- 16.47</b>	<b>- 19.30</b>	<b>- 33.33</b>
$\mathcal{E}_i$ (KS)	- 15.58	- 16.84	- 18.89	- 33.67
$\Delta\mathcal{E}_i$	- 0.16	0.37	- 0.41	0.34

# N<sub>2</sub> orbital energies

N <sub>2</sub> (K=0.382)	3σ <sub>g</sub> (HOMO)	2π <sub>u</sub>	2σ <sub>u</sub>	2σ <sub>g</sub>
$v_{xhole,ii}$ (LDA)	- 24.89	- 23.51	- 24.72	- 29.47
$v_{xhole,ii}$ (B)	- 2.54	- 2.48	- 2.52	- 1.83
$v_{xresp,ii}$ (GLLB)	+ 4.56	+ 5.10	+ 3.97	+ 6.05
$v_{c,ii}$ (VWN)	- 1.76	- 1.75	- 1.76	- 1.91
$v_{xctot,ii}$	<b>- 24.63</b>	<b>- 22.63</b>	<b>- 25.03</b>	<b>- 27.16</b>
$h_{ii} + v_{H,ii}$	+ 8.89	+ 6.16	+ 5.73	- 6.17
$\mathcal{E}_i$ (BGLLBVWN)	<b>- 15.74</b>	<b>- 16.47</b>	<b>- 19.30</b>	<b>- 33.33</b>
$\mathcal{E}_i$ (KS)	- 15.58	- 16.84	- 18.89	- 33.67
$\Delta\mathcal{E}_i$	- 0.16	0.37	- 0.41	0.34
$\Delta\mathcal{E}_i$ (LDA+B-KS)	4.82	4.91	4.99	5.00



# HCOOH orbital energies (K=0.34)

	<b>10a'</b> HOMO	<b>2a''</b>	<b>9a'</b>	<b>1a''</b>	<b>8a'</b>	<b>7a'</b>
$v_{xhole,ii}$ (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
$v_{xctot,ii}$	<b>-26.94</b>	<b>-26.81</b>	<b>-25.82</b>	<b>-23.50</b>	<b>-26.79</b>	<b>-22.83</b>
$h_{ii} + v_{H,ii}$	+15.33	+14.20	+11.59	+8.06	+10.20	+5.68
$\epsilon_i$ (BGLLBVWN)	<b>-11.61</b>	<b>-12.61</b>	<b>-14.23</b>	<b>-15.44</b>	<b>-16.59</b>	<b>-17.15</b>
$\epsilon_i$ (KS)	-11.51	-12.38	-14.48	-15.43	-16.64	-17.27
$\Delta\epsilon_i$	-0.10	-0.23	0.25	-0.01	0.05	0.12
$\Delta\epsilon_i$ (LDA+B)	4.23	3.82	4.07	3.78	4.17	3.82

# HCOOH lower orbital energies (K=0.34)

	<b>7a'</b>	<b>6a'</b>	<b>5a'</b>	<b>4a'</b>
$v_{xhole,ii}$ (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
$v_{xctot,ii}$	<b>- 22.83</b>	<b>- 23.01</b>	<b>- 29.48</b>	<b>- 27.44</b>
$h_{ii} + v_{H,ii}$	+ 5.68	+ 2.17	- 1.11	- 5.41
$\mathcal{E}_i$ (BGLLBVWN)	<b>- 17.15</b>	<b>- 20.84</b>	<b>- 30.95</b>	<b>- 32.85</b>
$\mathcal{E}_i$ (KS)	- 17.27	- 21.17	- 30.43	- 32.94
$\Delta\mathcal{E}_i$	0.12	- 0.33	- 0.16	0.09
$\Delta\mathcal{E}_i$ (LDA+B-KS)	3.82	3.88	4.14	4.14

# Good orbital energies (not upshifted) very important in anions

LB94: HOMO  $F^- = 3.48 \text{ eV}$  ; IP = 3.40 eV

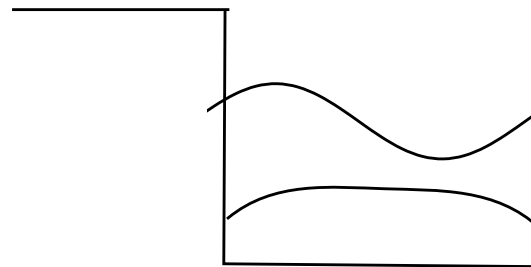
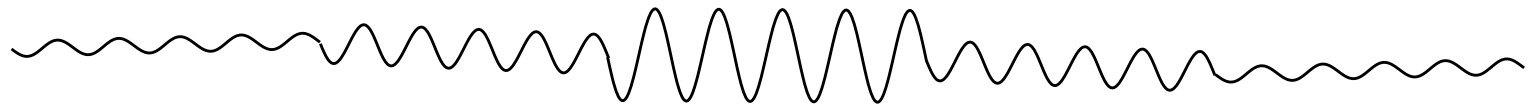
B-GLLB-VWN, see Amati, Baerends JCTC 16 (2020) 443:

Many closed shell anions: MAE + 0.14 eV

Many open shell anions: MAE + 0.48 eV

# What is the meaning of an orbital with positive orbital energy?

resonances  
at specific E



bound states below  
zero energy

# What is the meaning of KS orbital energies?

Prevailing view on **occupied** orbital energies:  
”..one should expect no simple physical  
meaning for the KS orbital energies. *There is  
none.*”

**WRONG!**

Prevailing view on **virtual** KS orbital energies:  
The HOMO-LUMO gap is too low  
(the “band gap” problem of KS DFT)

**WRONG!**

KS HOMO-LUMO gaps  $\Delta$  are excellent  
approx. to **excitation energies**

	$\Delta^{\text{HF}}$	$\Delta^{\text{LDA}}$	$\Delta^{\text{BLYP}}$	$\Delta^{\text{KS}}$	Expt. excit. energy singlet	triplet
H <sub>2</sub>	17.6	10.6	10.5	12.5	<b>12.7</b>	<b>11.7</b>
H <sub>2</sub> O	14.7	6.5	6.2	7.5	<b>7.65</b>	<b>7.5</b>
HF	18.5	8.9	8.5	10.5	<b>10.3</b>	<b>9.9</b>
N <sub>2</sub>	19.9	9.7	9.6	9.9	<b>9.3-10.3</b>	<b>7.8-8.9</b>
CO	17.0	6.9	7.1	7.5	<b>8.5</b>	<b>6.3</b>
HCN	15.4	7.9	7.8	8.0	<b>8.8</b>	<b>6.2</b>
FCN	14.8	7.3	7.0	7.6	<b>8.4</b>	<b>7.8</b>
HCl	13.8	7.0	6.8	7.4	<b>7.8</b>	<b>7.4</b>

1) The LDA, GGA gaps (aug-cc-pVTZ basis) 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: Koopmans' approx. to IP – EA if  $\epsilon_{\text{LUMO}}$  neg.  
**Many HF LUMOs at positive orbital energy!**

# HF, DFA and exact KS LUMO orbital energies

	HF	LDA	BLYP	KS
H <sub>2</sub>	+1.42	+0.31	+0.12	-3.93
H <sub>2</sub> O	+0.80	-0.92	-1.06	-5.11
HF	+0.81	-0.93	-1.13	-5.71
N <sub>2</sub>	+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)

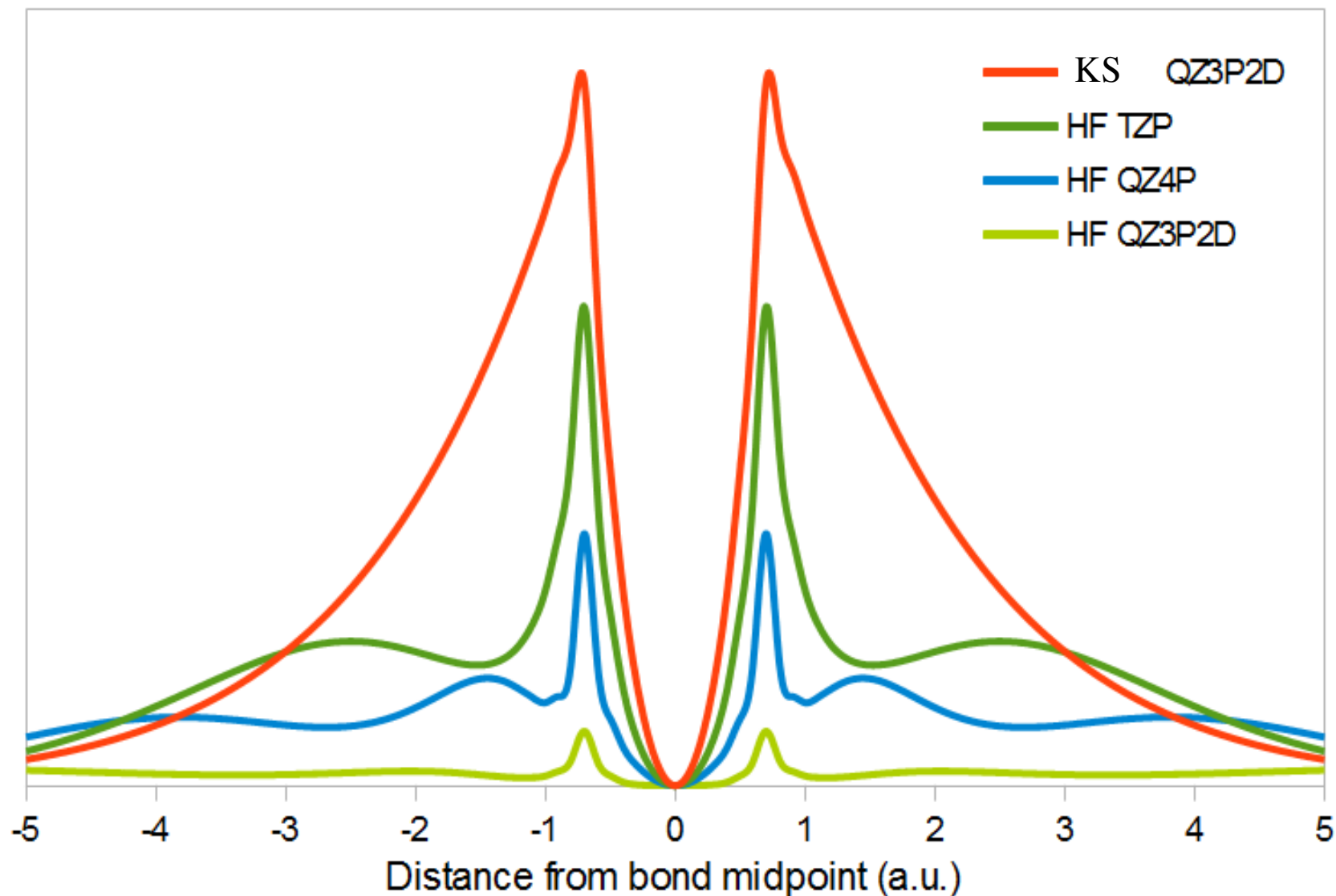
LDA, GGA LUMO: still negative -> therefore bound state

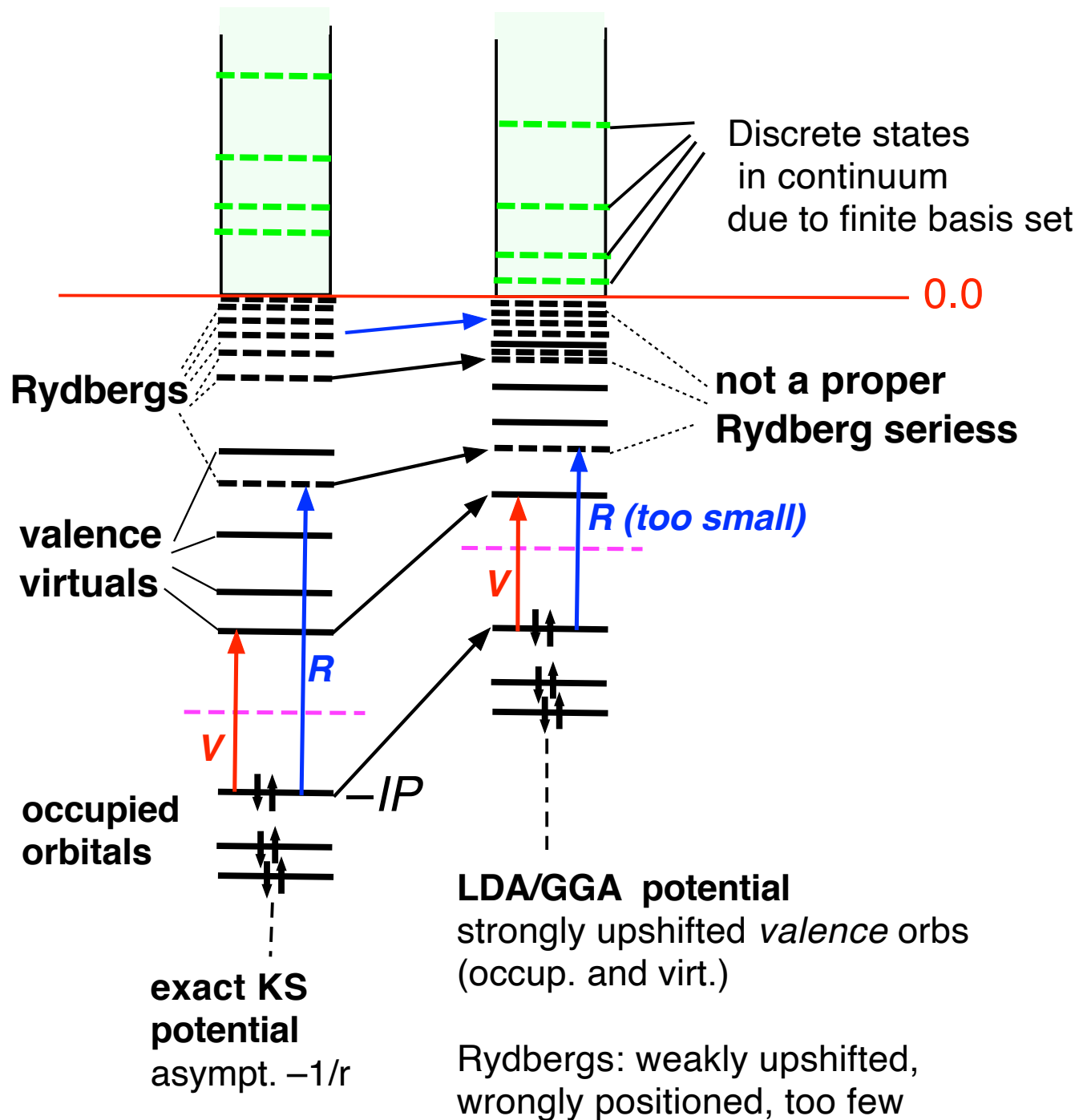
# Orbital energies (eV) of the positive energy HF LUMO of H<sub>2</sub> as function of the basis (STOs)

	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

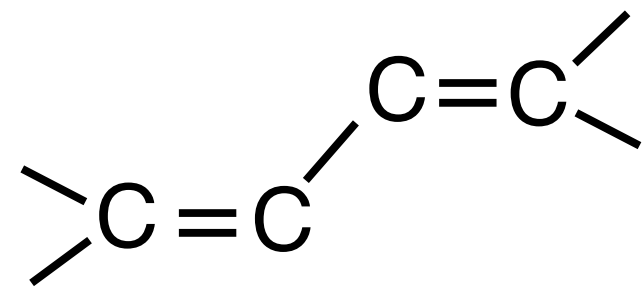
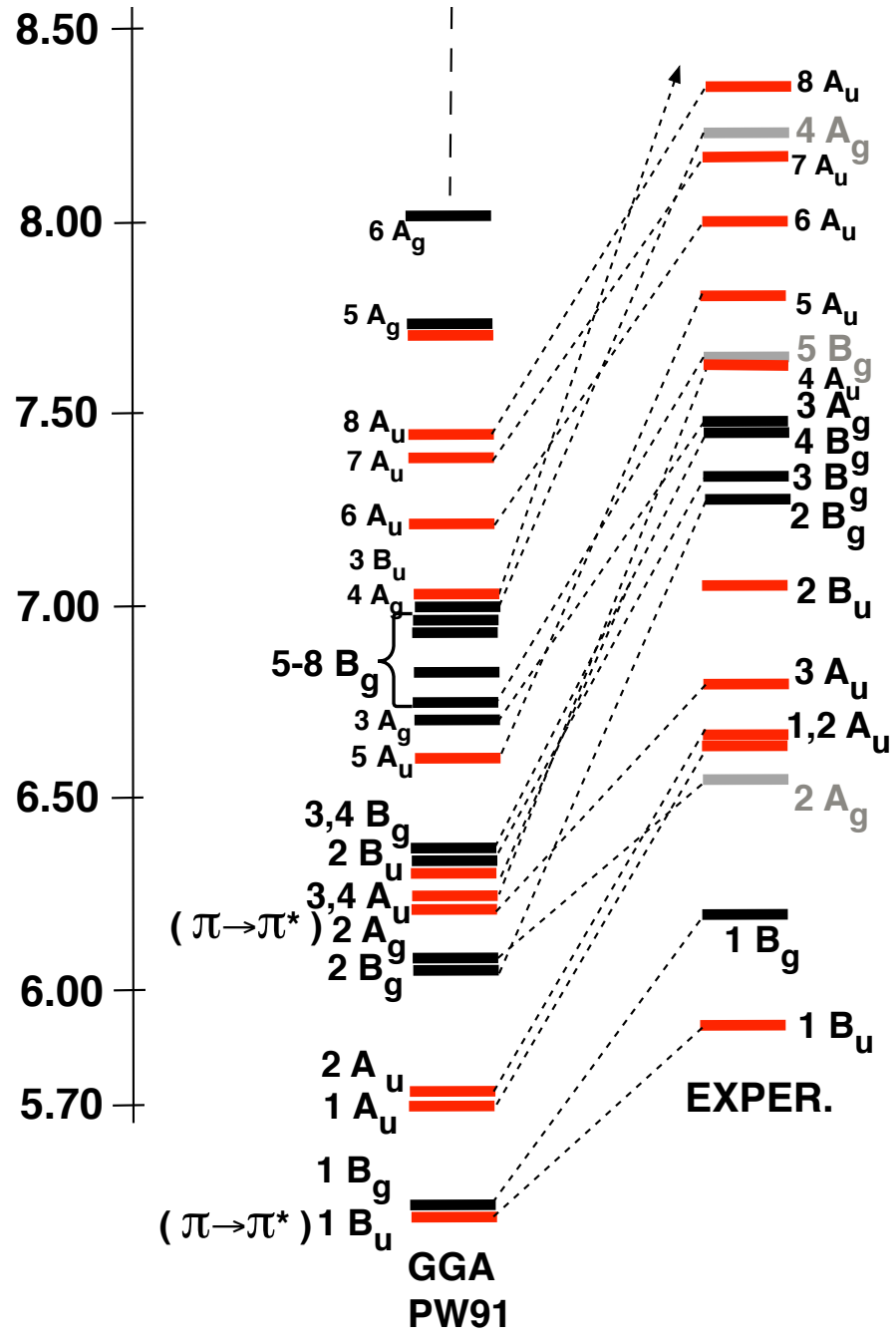


# Shape of the $1\sigma_u$ LUMO density of $H_2$ as a function of basis set:





proper  
KS pot.  
important  
for *virtual*  
orbital  
spectrum!



transbutadiene

GGA (PW91)  
excitation energies

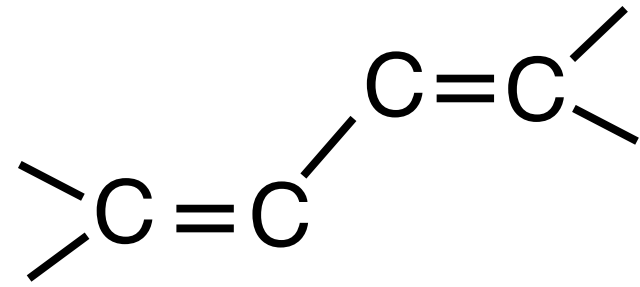
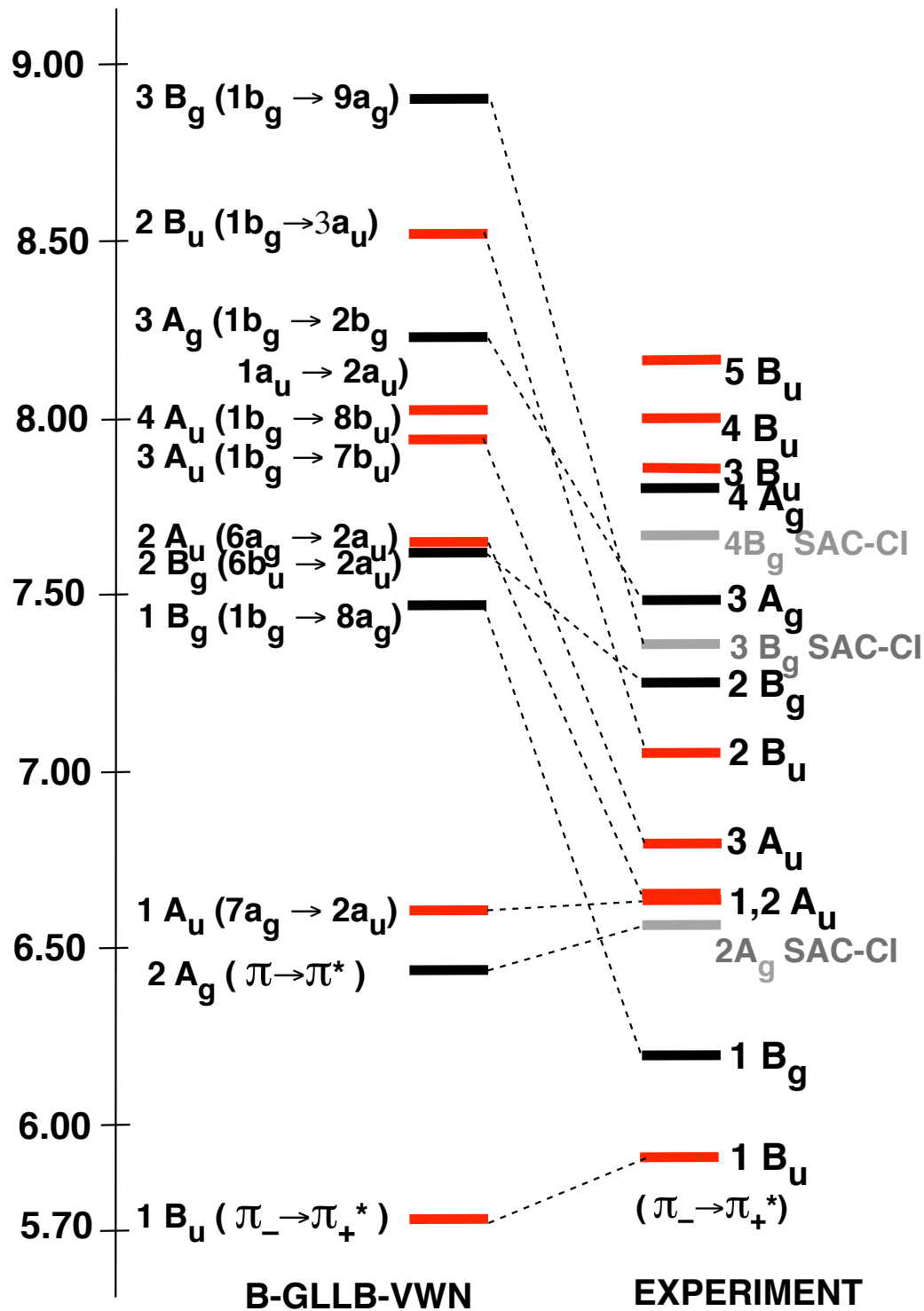
For TDDFT it is essential to have  
orbitals and orbital energies  
from good approx. to exact KS potential

→ B-GLLB-VWN!

- good occupied and virtual orbital energies

- from B88 correction to LDA proper  $-1/r$   
asymptotics of potential expected

→ Rydbergs OK?



Vertical excitations  
 1,3-transbutadiene  
 TDDFT with  
 B-GLLB-VWN approx. to  
 exact KS potential  
 + ALDA kernel

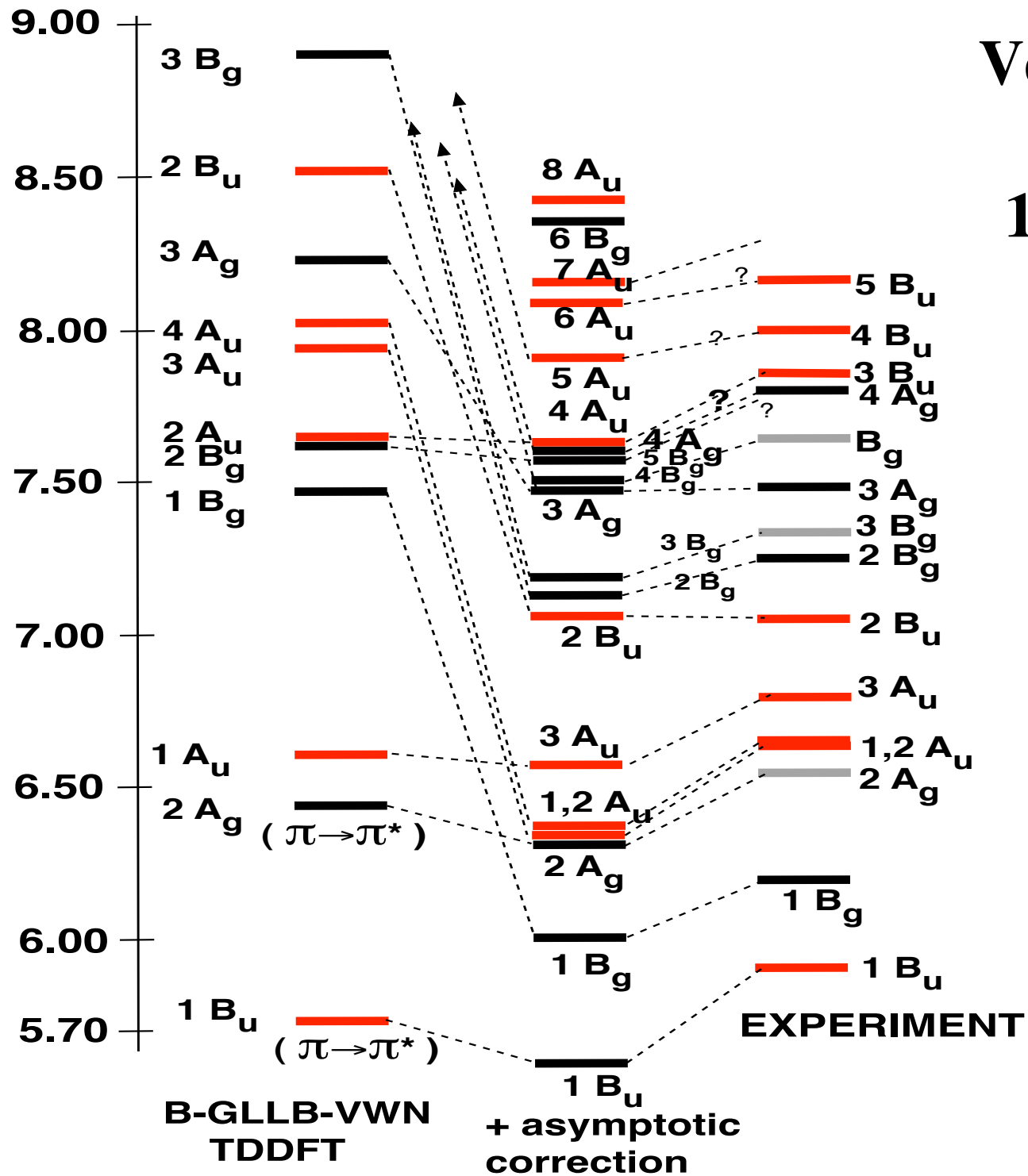
**poor!**  
 Rydbergs too much  
 upshifted  
 -> asymptotics of  
 potential not right?

# Why such poor TDDFT results with B-GLLB-VWN potential?

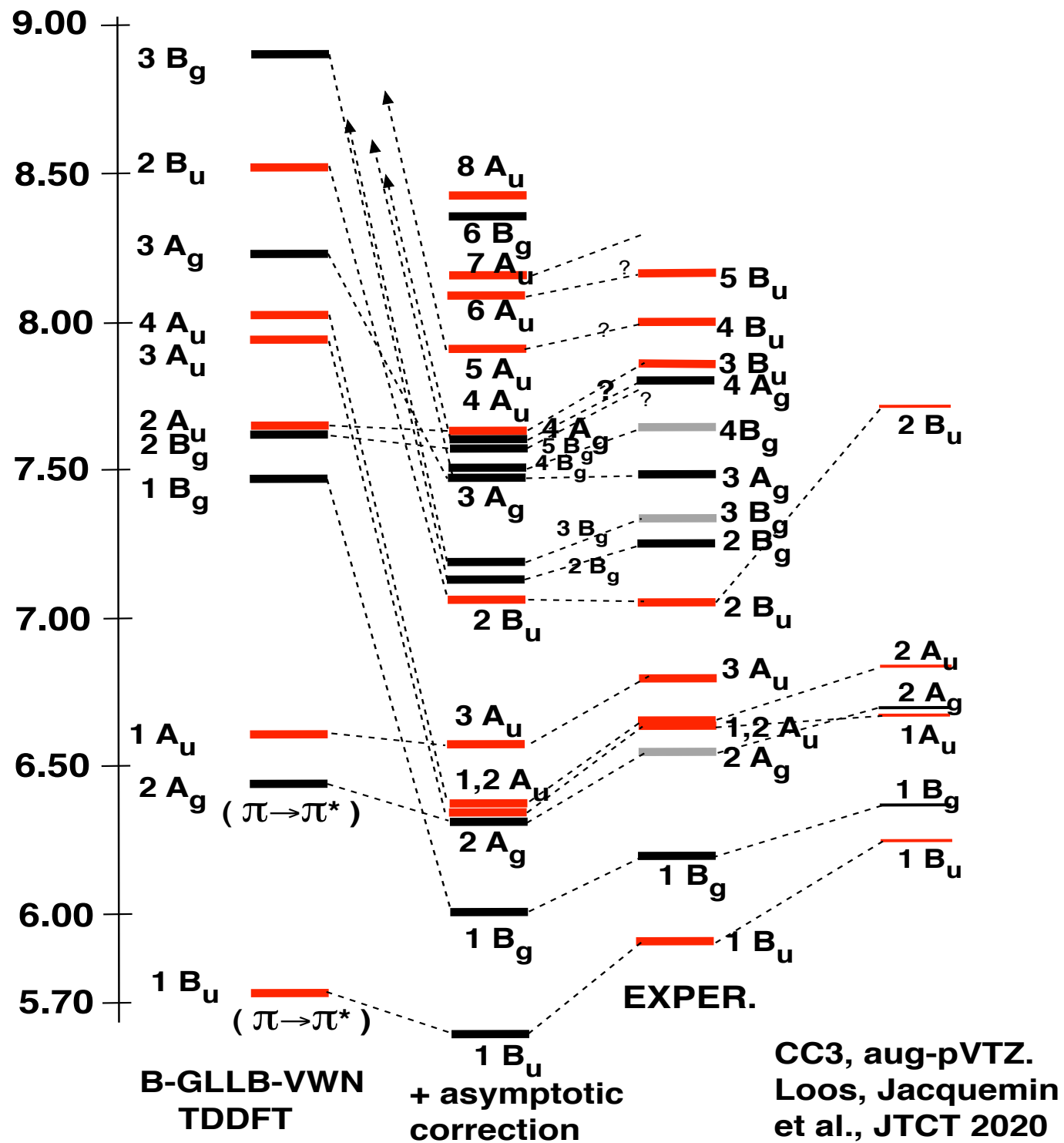
Possibly due to deficient long range / asymptotic behavior of potential, in spite of  $-1/r$  asymptotics coming from B88 energy density ?

Test: add asymptotic behavior of LB94 KS potential (R. van Leeuwen, E. J. Baerends, PRA 1994)

Vertical excitation  
energies (eV)  
1,3-transbutadiene  
with  
proper  
asymptotics



# Compare to CC

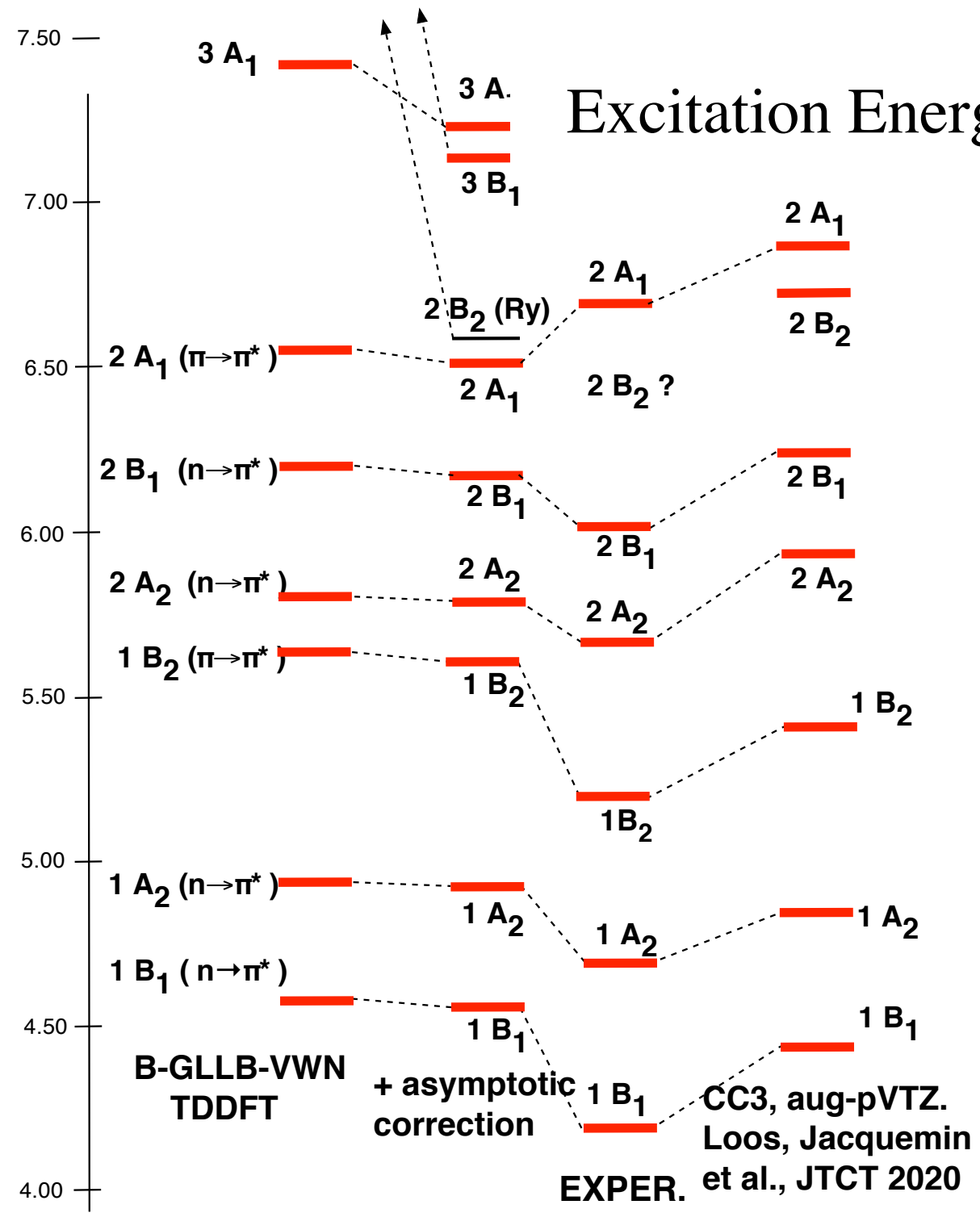




# Excitations 1,3-transbutadiene, best theoretical results

	6-31G(d) CC3	aug-cc-pVTZ			th.	th.	EXP.
	CC3	CC3	CCSDT	NEV- PT2	SAC-CI	MR- AQCC	
<b>B<sub>u</sub></b>	<b>6.41</b>	<b>6.22</b>	<b>6.24</b>	<b>6.68</b>	<b>6.33</b>	<b>6.36</b>	<b>5.92</b>
<b>B<sub>g</sub></b>	<b>6.53</b>	<b>6.33</b>	<b>6.34</b>	<b>6.44</b>	<b>6.18</b>	<b>6.32</b>	<b>6.21</b>
<b>A<sub>u</sub></b>	<b>6.87</b>	<b>6.64</b>	<b>6.66</b>	<b>6.84</b>	<b>6.45</b>	<b>6.56</b>	<b>6.64</b>
<b>A<sub>g</sub></b>	<b>6.73</b>	<b>6.67</b>	<b>6.60</b>	<b>6.70</b>	<b>6.56</b>	<b>6.50</b>	
<b>A<sub>u</sub></b>	<b>6.93</b>	<b>6.80</b>	<b>6.81</b>	<b>7.01</b>	<b>6.65</b>	<b>6.74</b>	<b>6.80</b>
<b>B<sub>u</sub></b>	<b>7.98</b>	<b>7.68</b>	-	<b>7.45</b>	<b>7.08</b>	<b>7.02</b>	<b>7.07</b>

# Excitation Energies Pyrimidine



# Acetone: orbital en. differences and excit. energies (eV)

Funct.	State	Weight	$\varepsilon_i$	$\varepsilon_a$	$\Delta\varepsilon_{ia}$	$\omega_{TD-DFT}$	$\omega - \Delta\varepsilon_{ia}$	$\omega - E_{exp}$
	1A <sub>2</sub>	1.00	-10.25	-5.92	4.33	4.59	0.26	0.16
“exact” KS pot. (SAOP)	1B <sub>2</sub>	1.00	-10.25	-4.18	6.07	6.09	0.02	-0.27
	2A <sub>2</sub>	0.84	-10.25	-2.72	7.53	7.52	0.00	0.16
	2A <sub>1</sub>	0.97	-10.25	-3.09	7.16	7.21	0.05	-0.20
	2B <sub>2</sub>	0.97	-10.25	-2.63	7.62	7.64	0.02	0.15
	3A <sub>1</sub>	0.97	-10.25	-2.04	8.21	8.20	0.00	0.40
	3B <sub>2</sub>	0.97	-10.25	-2.51	7.74	7.74	0.00	-0.35
	1B <sub>1</sub>	0.95	-10.25	-5.92	7.92	8.17	0.24	0.00

# Acetone: orbital en. differences and excit. energies (eV)

Funct.	State	Weight	$\epsilon_i$	$\epsilon_a$	$\Delta\epsilon_{ia}$	$\omega_{TD-DFT}$	$\omega - \Delta\epsilon_{ia}$	$\omega - E_{exp}$
BP86	1A <sub>2</sub>	1.00	-5.71	-1.70	4.01	4.27	0.26	-0.16
	1B <sub>2</sub>	1.00	-5.71	-0.61	5.10	5.10	0.00	-1.26
	2A <sub>2</sub>	1.00	-5.71	-0.11	5.60	5.59	0.00	-1.77
	2A <sub>1</sub>	1.00	-5.71	-0.13	5.58	5.58	0.00	-1.83
	2B <sub>2</sub>	1.00	-5.71	-0.07	5.64	5.64	-0.01	-1.85
	3A <sub>1</sub>	0.98	-5.71	+0.36	6.07	6.06	-0.01	-1.74
	3B <sub>2</sub>	1.00	-5.71	+0.05	5.76	5.75	0.00	-2.34
	1B <sub>1</sub>	1.00	-5.71	+0.31	6.02	6.01	-0.01	-2.16

# Acetone: orbital en. differences and excit. energies (eV)

Funct.	State	Max. Weight	$\varepsilon_i$	$\varepsilon_a$	$\Delta\varepsilon_{ia}$	$\omega_{TD-DFT}$	$\omega - \Delta\varepsilon_{ia}$	$\omega - E_{exp}$
TDHF	1A <sub>2</sub>	0.47	-11.23	+3.96	15.18	5.03	-10.15	0.60
	1B <sub>2</sub>	0.36	-11.23	+0.62	11.85	8.24	-3.61	1.88
	2A <sub>2</sub>	0.43	-11.23	+1.02	12.25	9.02	-3.23	1.66
	2A <sub>1</sub>	0.20	-11.23	+0.96	12.19	9.07	-3.12	1.66
	2B <sub>2</sub>	0.31	-11.23	+1.20	12.43	9.13	-3.30	1.64
	3A <sub>1</sub>	0.21	-11.23	+3.96	17.15	9.41	-7.74	1.61
	3B <sub>2</sub>	0.23	-11.23	+1.74	12.96	9.59	-3.37	1.50
	1B <sub>1</sub>	0.84	-11.23	+1.12	12.35	9.89	-2.46	1.72

# Acetone: orbital energy differences and excitation energies (eV)

<b>Funct.</b>	<b>State</b>	<b>Max. Weight</b>	$\epsilon_i$	$\epsilon_a$	$\Delta\epsilon_{ia}$	$\omega_{TD-DFT}$	$\omega - \Delta\epsilon_{ia}$	$\omega - E_{exp}$
<b>M06-2X</b>	<b>1A<sub>2</sub></b>	<b>0.52</b>	<b>-8.85</b>	<b>+0.78</b>	<b>9.63</b>	<b>4.03</b>	<b>-5.60</b>	<b>-0.40</b>
	<b>1B<sub>2</sub></b>	<b>0.73</b>	<b>-8.85</b>	<b>-0.34</b>	<b>8.51</b>	<b>6.54</b>	<b>-1.97</b>	<b>0.18</b>
	<b>2A<sub>2</sub></b>	<b>0.62</b>	<b>-8.85</b>	<b>+0.04</b>	<b>8.88</b>	<b>7.33</b>	<b>-1.55</b>	<b>-0.03</b>
	<b>2A<sub>1</sub></b>	<b>0.62</b>	<b>-8.85</b>	<b>+0.03</b>	<b>8.87</b>	<b>7.38</b>	<b>-1.49</b>	<b>-0.03</b>
	<b>2B<sub>2</sub></b>	<b>0.45</b>	<b>-8.85</b>	<b>+0.15</b>	<b>9.00</b>	<b>7.40</b>	<b>-1.60</b>	<b>-0.09</b>
	<b>3A<sub>1</sub></b>	<b>0.79</b>	<b>-8.85</b>	<b>+0.74</b>	<b>9.58</b>	<b>8.03</b>	<b>-1.55</b>	<b>0.23</b>
	<b>3B<sub>2</sub></b>	<b>0.42</b>	<b>-8.85</b>	<b>+0.64</b>	<b>9.49</b>	<b>7.80</b>	<b>-1.69</b>	<b>-0.29</b>
	<b>1B<sub>1</sub></b>	<b>0.92</b>	<b>-8.85</b>	<b>+0.73</b>	<b>9.58</b>	<b>8.12</b>	<b>-1.45</b>	<b>-0.05</b>

# References:

M. Amati, E. J. Baerends

*TDDFT excitation energies with accurate KS potentials: the B-GLLB-VWN approximation to the exact KS potential*

to be subm.

O. Gritsenko, R. van Leeuwen, E. Van Lenthe, E. J. Baerends

*Self-consistent approximation to the Kohn-Sham potential*

Phys. Rev. A 51 (1995) 1944

O. Gritsenko, L. Mentel, E. J. Baerends,

*On the errors of LDA and GGA approximations to the KS potential and orbital energies: B-GLLB-VWN*

J. Chem. Phys. 144 (2016) 204114

E. J. Baerends, O. V. Gritsenko, R. Van Meer

*The Kohn-Sham gap, the fundamental gap and the optical gap: the physical meaning of occupied and virtual Kohn-Sham orbital energies*

PCCP (Perspective) **15** (2013) 16408

R. van Meer, O. V. Gritsenko, E. J. Baerends

*Physical meaning of virtual Kohn-Sham orbitals and orbital energies: an ideal basis for the description of molecular excitations*

J. Chem. Theor. Comp. **10** (2014) 4432