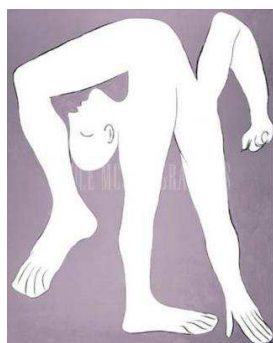


# Advanced TDDFT III

Molecular Dissociation and Long-Range Charge-Transfer Excitations:  
*Effect of Ground-State Static Correlation on fxc*



*Neepa T. Maitra*

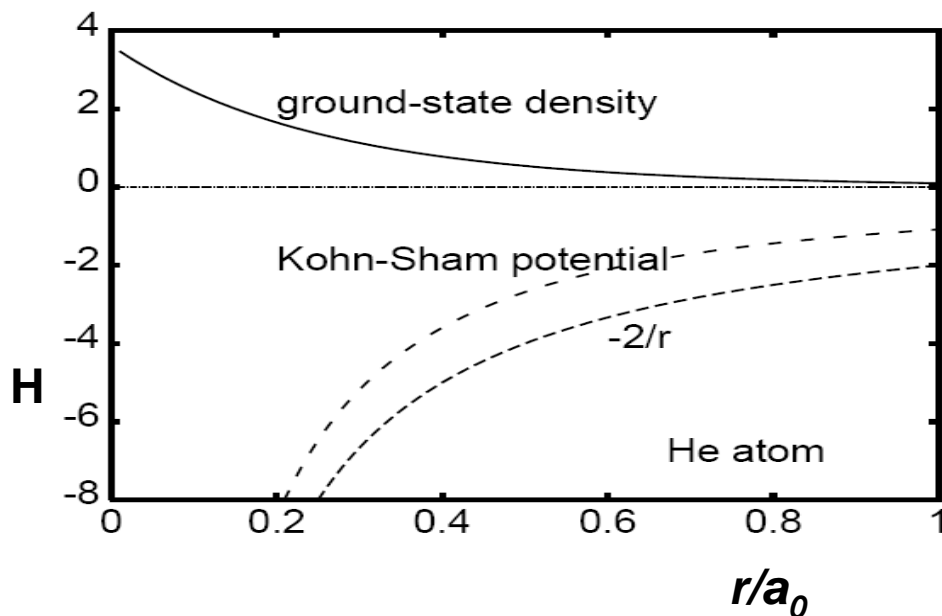
*Hunter College and the Graduate Center of the  
City University of New York*



# Exact ground-state KS potentials...

For 2-e systems, easy to find if know the exact density, since  $\phi(r) = \sqrt{n(r)}/2$

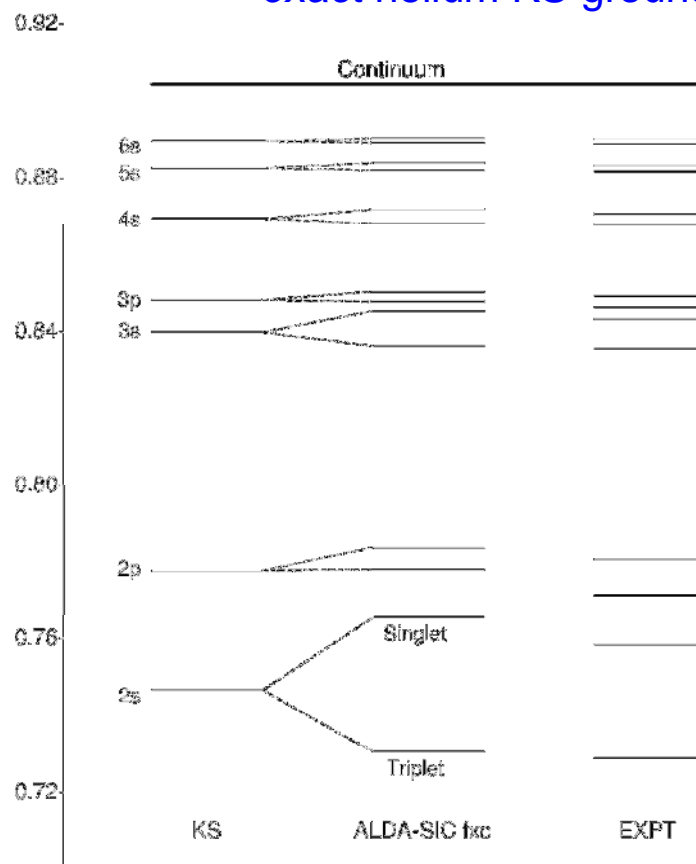
*Eg. the Helium atom:*



Already the KS excitations are pretty good: most fxc approxs give similar corrections

*Burke, Petersilka & Gross (2000)*

TDDFT linear response from exact helium KS ground state:



# How about a Simple Model of a Diatomic Molecule?

Model a hetero-atomic diatomic molecule composed of open-shell fragments (eg. LiH) with two “one-electron atoms” in 1-d:

$$H = -\frac{1}{2} \frac{d^2}{dx_1^2} - \frac{1}{2} \frac{d^2}{dx_2^2} + v_{\text{ext}}(x_1) + v_{\text{ext}}(x_2) + v_{\text{ee}}(x_1 - x_2)$$

$$v_{\text{ext}}(x) = -\frac{1}{\sqrt{a + (x - R/2)^2}} - \frac{1}{\sqrt{b + (x + R/2)^2}}$$

$$v_{\text{ee}}(x_1, x_2) = \frac{1}{\sqrt{c + (x_1 - x_2)^2}}$$

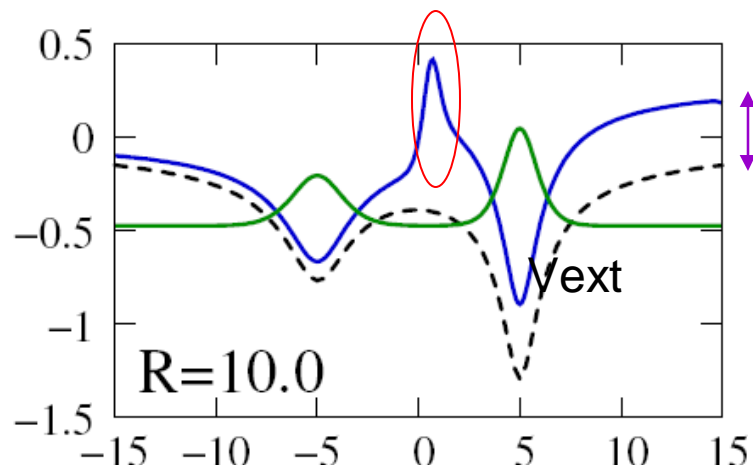
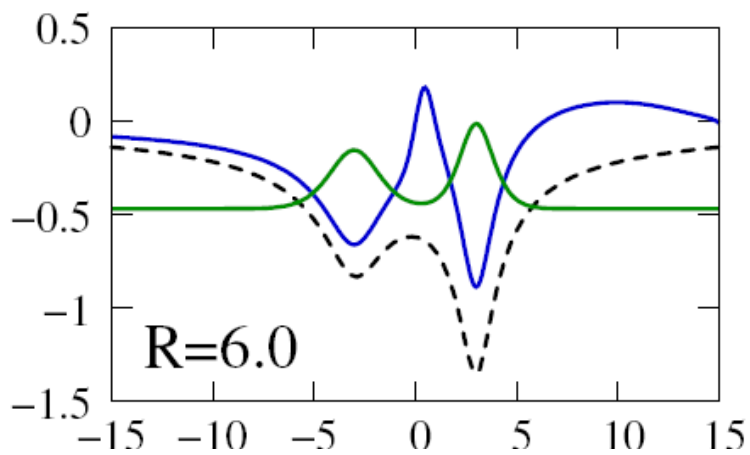
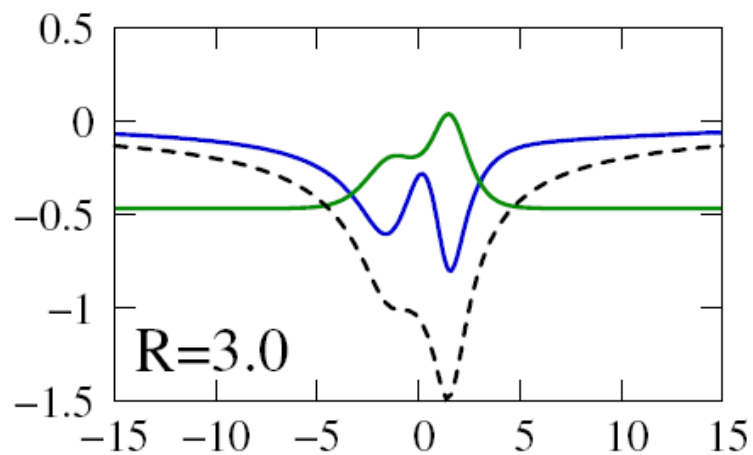
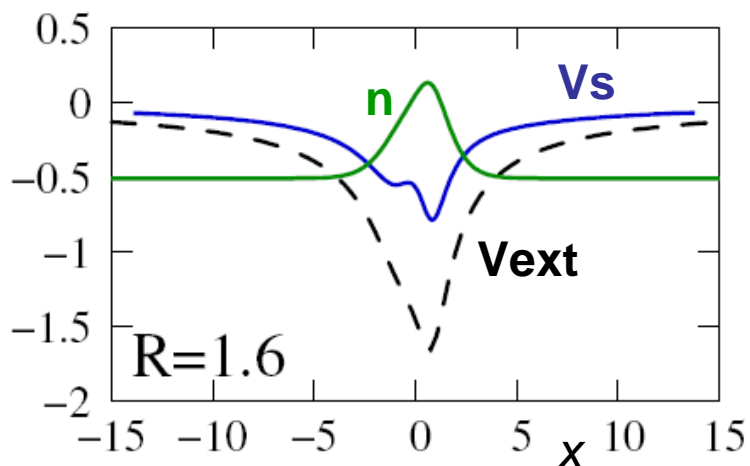
“softening parameters”

(choose to reproduce eg. IP's of different real atoms...)

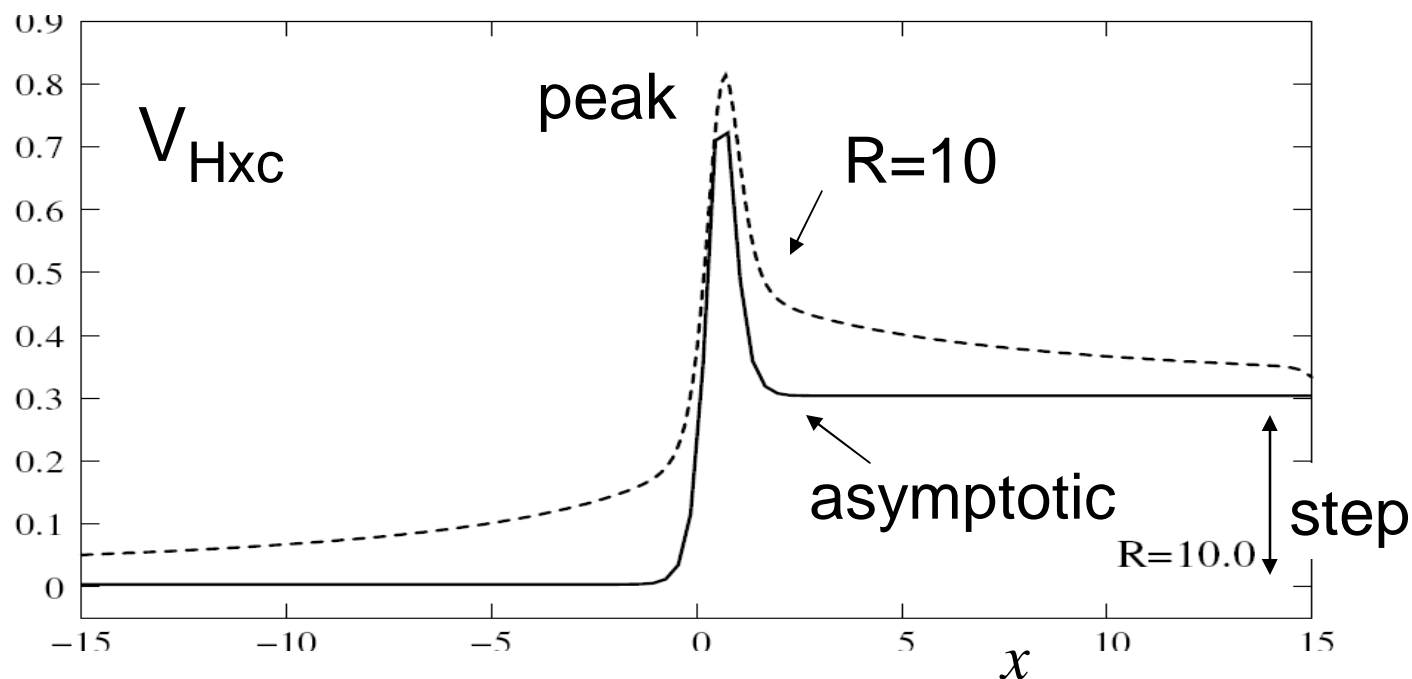
Can simply solve exactly numerically  $\Psi(r_1, r_2) \rightarrow$  extract  $\rho(r) \rightarrow \phi_0(\mathbf{r}) = \sqrt{\frac{\rho(\mathbf{r})}{2}}$

$$\rightarrow \text{exact } v_{\text{S}}[\rho](\mathbf{r}) = \frac{\nabla^2 \sqrt{\rho(\mathbf{r})}}{2\sqrt{\rho(\mathbf{r})}} - I$$

# Exact ground-state KS potentials... Molecular Dissociation (1d "LiH")



“Peak” and  
“Step”  
structures



*J.P. Perdew, in Density Functional Methods in Physics, ed. R.M. Dreizler and J. da Providencia (Plenum, NY, 1985), p. 265.*

*C-O Almbladh and U. von Barth, PRB. **31**, 3231, (1985)*

*O. V. Gritsenko & E.J. Baerends, PRA **54**, 1957 (1996)*

*O.V.Gritsenko & E.J. Baerends, Theor.Chem. Acc. **96** 44 (1997).*

*D. G. Tempel, T. J. Martinez, N.T. Maitra, J. Chem. Th. Comp. **5**, 770 (2009)  
& citations within.*

*N. Helbig, I. Tokatly, A. Rubio, JCP **131**, 224105 (2009).*

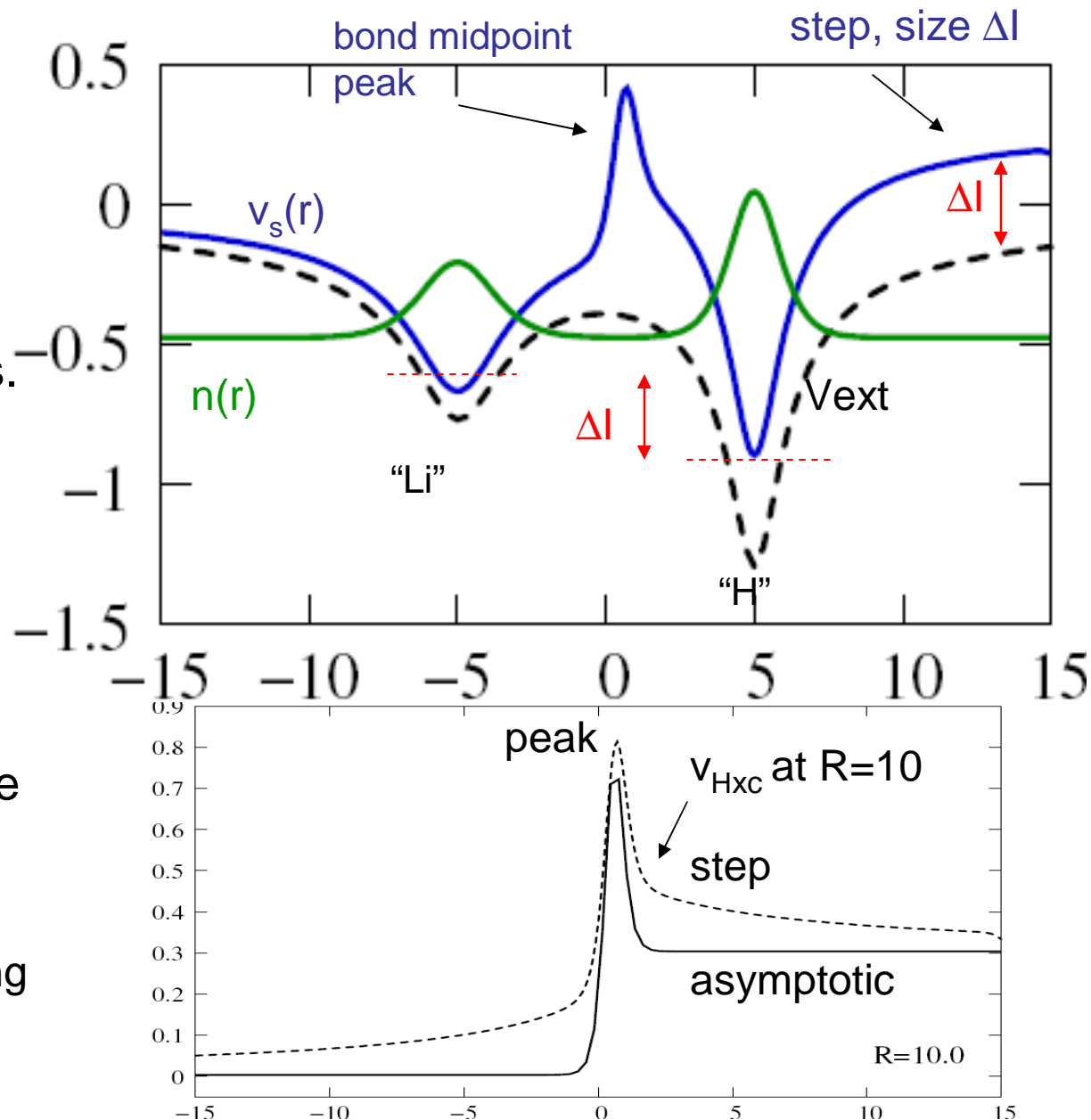
## The Step

- Step has size  $\Delta I$  and aligns the atomic HOMOs
- Prevents dissociation to unphysical fractional charges.

LDA/GGA - wrong!

- At which separation is the step onset?

Step marks location and sharpness of avoided crossing b/n gs and lowest CT state..



Tempel, Martinez, Maitra, *J. Chem. Theory Comp.* **5**, 770 (2009).

## An Exercise!

Another way to deduce the step in the potential in the bonding region between two open-shell fragments at large separation:

Take a model molecule consisting of two different “one-electron atoms”. The KS ground-state is the doubly-occupied bonding orbital:

$$\Phi_0 = \phi_0(\mathbf{r}_1)\phi_0(\mathbf{r}_2)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$$



where  $\phi_0(r) = \sqrt{n(r)/2}$  and  $n(r) = \phi_1^2(r) + \phi_2^2(r)$  is the sum of the atomic densities.

Insert  $\phi_0$  into the KS equation, solving for  $V_S$ , showing it must have a step of size  $I_2 - I_1$  between the atoms.

# The Peak

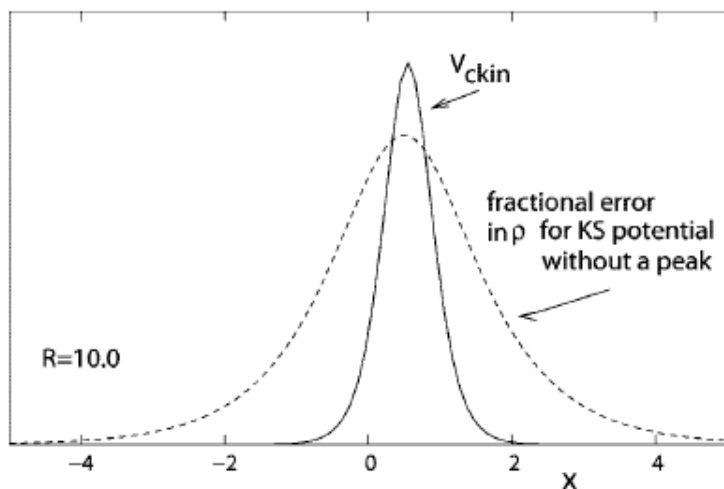
- A “kinetic correlation” effect (*Gritsenko, van Leeuwen, Baerends JCP 1996*). Also occurs in stretched H<sub>2</sub>
- *Another interpretation*: peak pushes away density from the bonding region:

Asymptotically, with  $\phi = \sqrt{(\rho_H + \rho_{Li})/2}$  → peak in  $v_s$

but with the LCAO  $\phi_{\text{bond}} = (\sqrt{\rho_H/2} + \sqrt{\rho_{Li}/2})$  → no peak in  $v_s$

$$\rho_{\text{bond}} = 2|\phi_{\text{bond}}|^2 = \rho_H + \rho_{Li} + 2\sqrt{\rho_H\rho_{Li}}$$

Error – most significant in bonding region



→ peak in  $v_c$  acts as a barrier to push back to the atomic regions this extraneous density.

*Tempel, Martinez, Maitra, JCTC 5, 770 (2009)*

*Helbig, Tokatly, & Rubio, JCP 131, 224105 (2009).*



# Capturing the Step and Peak in Approximations: Hard! Need non-local $n$ -dependence

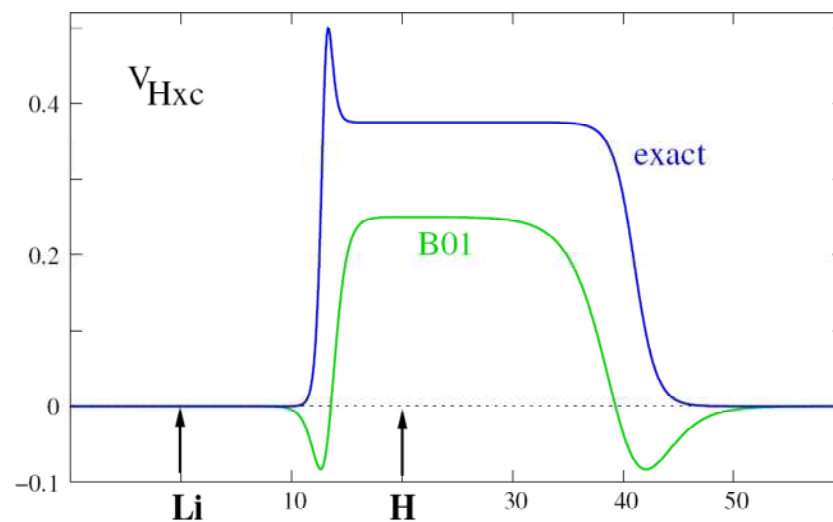
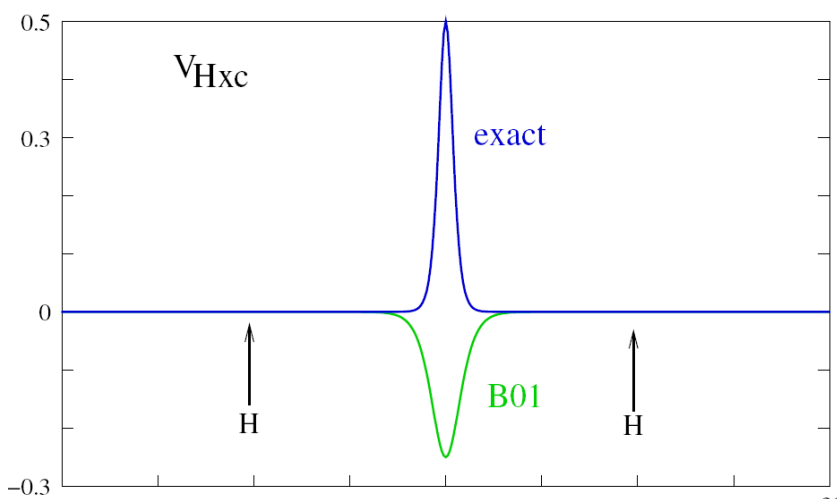
**Baerends functional B01** of occupied and selected virtual orbitals  
(*Baerends PRL 87 133004 (2001)*)

Inspired by density-matrix functional theory.

**Does the B01 potential have the step and peak?**

Step  $\sim$  difference in electron affinities,  $\Delta A < \Delta I$

What about the peak? It's actually a dip!!



## So far:

- Discussed step and peak structures in the ground-state potential of a dissociating molecule
- Fundamentally, these stark structures arise due to the SSD description of KS – the true wavefunction, even qualitatively, requires 2 determinants

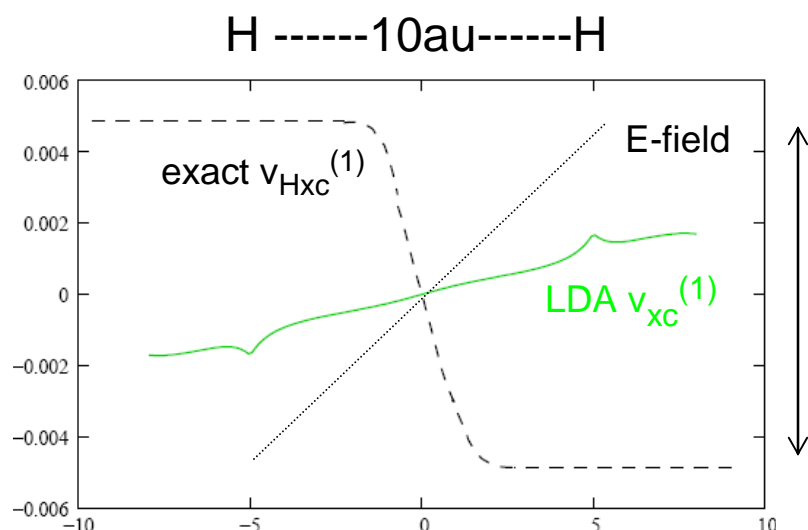
*Next: What are the consequences of the peak and step beyond the ground state?*

*Response and Excitations*

## Implications for Response

- **Step:** Similar step structure seen with homo-atomics in electric fields

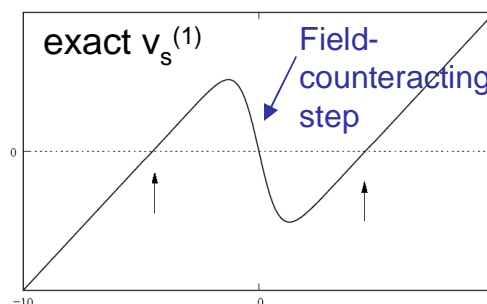
Eg: Stretched- $H_2$  in E-field,  $\epsilon = 0.001$  au



Step-size  $\epsilon R$

exactly compensates the field in exact KS potential.

✓ two locally polarized H atoms



- But usual functional approximations completely miss this step, and therefore yield fractional charges (global charge transfer)
- Related problem: usual functionals overestimates polarizabilities of long-chains. (see Carsten's talk, Matteo's talk)
- Need *non-local* spatial dependence

**Peaks:** appear in zero-field potential (not shown), act as barriers to transport – neglected in present-day transport calculations

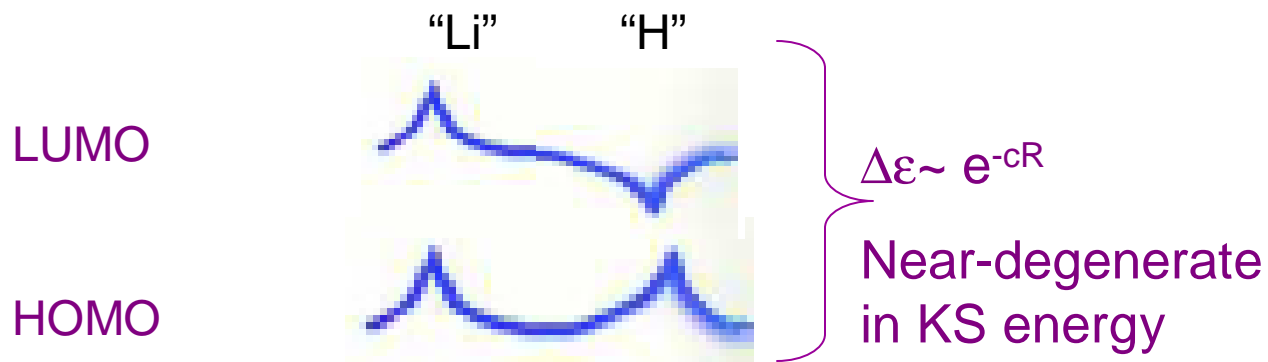
## What about excitations of the dissociating molecule?

Use TDDFT !

Recall the KS excitations are the starting point; these then get corrected via  $f_{xc}$  to the true ones.

Step  $\rightarrow$  KS  
molecular HOMO  
and LUMO  
delocalized and  
near-degenerate

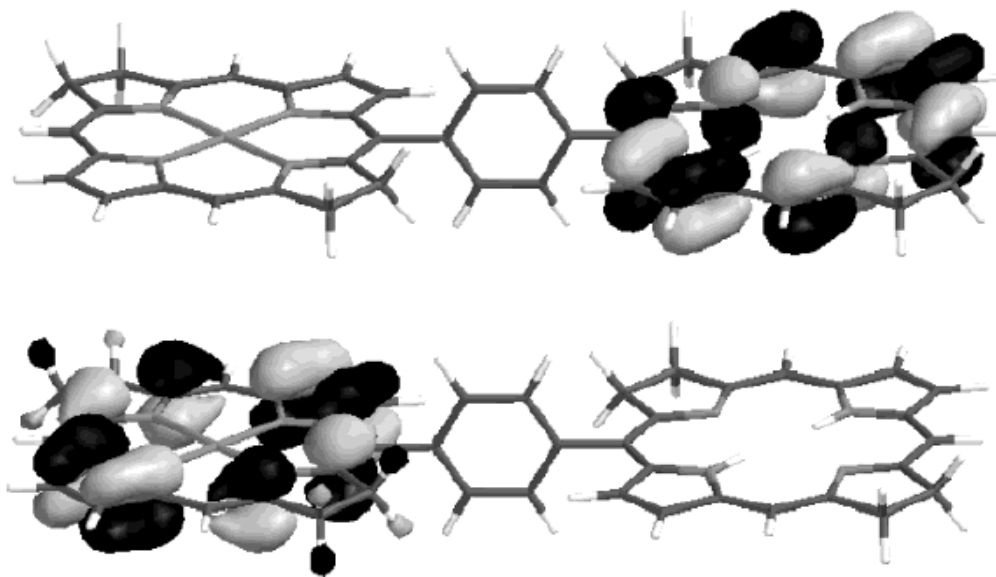
*But the true  
excitations are not!*



Find: *The step induces dramatic structure in the exact TDDFT kernel ! Implications for **long-range charge-transfer**.*

# TDDFT typically severely underestimates Long-Range CT energies

Eg. Zincbacteriochlorin-Bacteriochlorin complex (light-harvesting in plants and purple bacteria)



TDDFT predicts CT states energetically well below local fluorescing states.  
Predicts CT quenching of the fluorescence.

**! Not observed !**

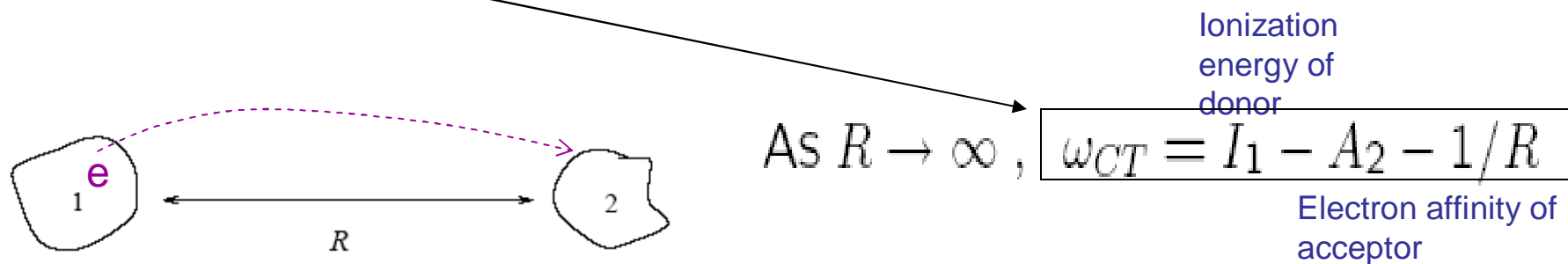
TDDFT error ~ 1.4eV

*Dreuw & Head-Gordon, JACS 126 4007, (2004).*

But also note Dmitriy Rappoport's comment in his talk: excited state properties (eg vib freqs) might be quite ok even if absolute energies are off, eg DMABN.

# Why usual TDDFT approx's fail for long-range CT:

First, we know what the *exact* energy for charge transfer at long range should be:



As  $R \rightarrow \infty$ ,  $\omega_{CT} = I_1 - A_2 - 1/R$

$\omega = \omega_q + 2[q|f_{HXC}(\omega_q)|q]$

Now to analyse TDDFT, use single-pole approximation (SPA):

$$\omega = \underbrace{\epsilon_2^L - \epsilon_1^H}_{\substack{-A_{s,2} \quad -I_1}} + \underbrace{\int \int dr dr' \phi_1^H(\mathbf{r}) \phi_2^L(\mathbf{r}) f_{HXC}(\mathbf{r}, \mathbf{r}' \omega) \phi_1^H(\mathbf{r}') \phi_2^L(\mathbf{r}')}_{\sim 0 \text{ overlap}}$$

$$\approx I_1 - A_{s,2}$$

- i.e. get just the bare KS orbital energy difference: missing xc contribution to acceptor's electron affinity,  $A_{xc,2}$ , and  $-1/R$
- Also, usual g.s. approxs underestimate  $I$

Dreuw, J. Weisman, and M. Head-Gordon, *JCP* **119**, 2943 (2003)

Tozer, *JCP* **119**, 12697 (2003)

## Wait!!

!! We just saw that for dissociating LiH-type molecules, the HOMO and LUMO are delocalized over both Li and H → **fxc contribution will not be zero!**

- Important difference between (closed-shell) molecules composed of
  - (i) open-shell fragments, and ← HOMO delocalized over both fragments
  - (ii) those composed of closed-shell fragments. ← HOMO localized on one or other

➤ Revisit the previous analysis of CT problem for open-shell fragments:

Eg. apply SMA (or SPA)  
to **HOMO→LUMO**  
transition

$$\omega^2 = \omega_q^2 + 4\omega_q [q | f_{\text{HXC}}(\omega_q) | q]$$

But this is  
now zero !

$q =$  **bonding** → **antibonding**

Now no longer zero –  
substantial overlap on both  
atoms. But still wrong.

# How to get accurate CT from TDDFT?

Many attempts in the recent literature.

Most are motivated by the fact that CIS (and TDHF) get the correct  $1/R$  asymptote, but, having no correlation, absolute energies are off by  $\sim 1\text{eV}$ . So what about a hybrid?

**Pure TDDFT:**  $\tilde{\Omega}(\omega)_{qq'} = \delta_{qq'} \omega_q^2 + 4 \sqrt{\omega_q \omega_{q'}} [q|f_{\text{HXC}}(\omega)|q']$

$$[q|f_{\text{HXC}}(\omega)|q'] = \int d\mathbf{r} d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_a(\mathbf{r}) f_{\text{HXC}}(\mathbf{r}, \mathbf{r}', \omega) \phi_{i'}(\mathbf{r}') \phi_{a'}^*(\mathbf{r}')$$

donor-acceptor  
overlap 0

**Hybrids with HF:**  $[q|f_{\text{HXC}}(\omega)|q'] \longrightarrow (1 - c_{\text{HF}}) [q|f_{\text{HXC}}(\omega)|q']$

$$- \delta_{\sigma\tau} c_{\text{HF}} (i_{\sigma} j_{\sigma} | a_{\tau} b_{\tau})$$

Non-zero correction to bare  
KS energies

But, this asymptotically gives  $-c_{\text{HF}}/R$ , not  $-1/R$

**So, look to other schemes...**



## Attempts to fix TDDFT for CT:

**Eg.** *Dreuw, Weisman, & Head-Gordon, JCP (2003)* – use CIS curve but shifted vertically to match  $\Delta$ SCF-DFT to account for correlation

**Eg.** *Tawada, Tsuneda, S. Yanagisawa, T. Yanai, & K. Hirao, J. Chem. Phys. (2004)*: “Range-separated” interaction in TDDFT matrix, with parameter  $\mu$

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}$$

Short-ranged, use GGA                      Long-ranged, use HF, gives -1/R

**Eg.** *Vydrov, Heyd, Krukau, & Scuseria (2006)*, 3 parameter range-separated, SR/LR decomposition...

**Eg.** *Zhao & Truhlar (2006)* M06-HF – empirical functional with 35 parameters!!! Ensures -1/R.

**Eg.** *Stein, Kronik, and Baer, JACS 131, 2818 (2009)* – range-separated hybrid, but with non-empirically determined  $\mu$

**Eg.** *Heßelmann, Ipatov, Görling, PRA 80, 012507 (2009)* – exact-exchange kernel

**Eg.** Staying in pure TDDFT

*Gritsenko & Baerends JCP 121, 655, (2004)*

*Neugebauer, Gritsenko & Baerends, JCP 124, 214102 (2006).*

$$f_{xc}^{asympt}(\mathbf{r}_1, \mathbf{r}_2)$$

$$= \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \frac{\exp(-K_{da,da}^{Coul}/K)}{K_{da,da}^{Coul}} \left[ \Delta^A - K_{da,aa}^{Coul} + \frac{(\Delta^A - K_{dd,aa}^{Coul})^2}{2(\epsilon_a - \epsilon_d)} \right]$$

$\sim \exp(-const * R)$

$K \ll 1$  empirical parameter, “switches on” for vanishing  $\phi_D \phi_A$  overlap

$$\sim \frac{\exp(const * R)}{|r1 - r2|} \dots$$

**Note:** Near CT frequency, kernel blows up exponentially with the fragment separation, R

Interpolation with usual GGA/LDA

Apply only to the CT excitations. Asymptotic correction to ALDA switches on when the orbital density overlap becomes small enough, as controlled by  $K$

$$K_{ia,jb} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_i(\mathbf{r}_1) \phi_a(\mathbf{r}_1) \left[ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega) \right] \phi_j(\mathbf{r}_2) \phi_b(\mathbf{r}_2)$$

Eg. He--Be

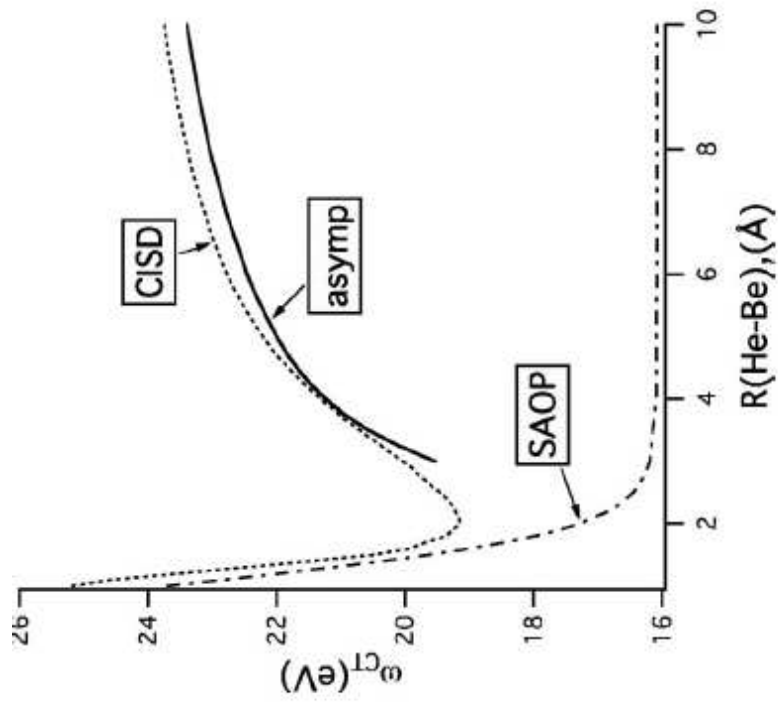


Fig. 2. The CT excitation energy  $\omega_{CT}$  as a function of  $R(\text{He-Be})$  computed with SDCI, SAOP-ALDA, and with  $f_{xc}^{\text{asypm}}$ .

Neugebauer, Gritsenko & Baerends, JCP 2006.

*? Can we find a simple model to explicitly solve exactly for the EXACT xc kernel and understand the origin of eg. the  $\exp(cR)$  behavior better?*

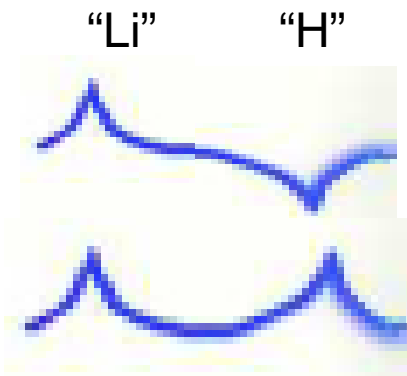
Try two-electron system – two “1-e atoms “ at large separation.

This is two **open-shells** – recall:

Step → KS  
molecular HOMO  
and LUMO  
delocalized and  
near-degenerate

LUMO

HOMO



$\Delta\epsilon \sim e^{-cR}$

Near-degenerate  
in KS energy

*But the true  
excitations are not!*

Static correlation induced by the step that fxc  
must undo !

# Undoing KS static correlation...



- These three KS states are nearly degenerate:

$$\left\{ \begin{array}{l} \Phi_0 = \phi_0(\mathbf{r}_1)\phi_0(\mathbf{r}_2) \\ \Phi_q = (\phi_0(\mathbf{r}_1)\bar{\phi}_0(\mathbf{r}_2) + \bar{\phi}_0(\mathbf{r}_1)\phi_0(\mathbf{r}_2)) / \sqrt{2} \\ \Phi_D = \bar{\phi}_0(\mathbf{r}_1)\bar{\phi}_0(\mathbf{r}_2) \end{array} \right.$$

- The electron-electron interaction splits the degeneracy: Diagonalize true H in this basis to get:

$$\left\{ \begin{array}{l} \text{Heitler-London gs} \quad \Psi_0 = (\phi_1(\mathbf{r})\phi_2(\mathbf{r}') + \phi_2(\mathbf{r})\phi_1(\mathbf{r}')) / \sqrt{2} \\ \text{CT states} \quad \begin{array}{l} \rightarrow \Psi_{2 \rightarrow 1} \equiv \phi_1(\mathbf{r})\phi_1(\mathbf{r}') \quad \omega = I_2 - A_1 - 1/R \\ \rightarrow \Psi_{1 \rightarrow 2} \equiv \phi_2(\mathbf{r})\phi_2(\mathbf{r}') \quad \omega = I_1 - A_2 - 1/R \end{array} \end{array} \right.$$

atomic orbital on atom2 or 1

where  $A = A_s + A_{XC}^{\text{approx}}$ , with

$$A_{XC}^{\text{approx}} = - \int d^3r \int d^3r' \phi_H(\mathbf{r})^2 \phi_H(\mathbf{r}')^2 V_{ee}(\mathbf{r} - \mathbf{r}')$$

# What does the exact fxc looks like?

Diagonalization is (thankfully) NOT TDDFT! Rather, mixing of excitations is done via the fxc kernel...recall double excitations lecture...

## KS density-density response function:

$$\chi_s(\mathbf{r}, \mathbf{r}', \omega) = \sum_q \frac{F_q(\mathbf{r})F_q(\mathbf{r}')}{\omega - \omega_q + i0^+} + c.c.(\omega \rightarrow -\omega) \quad \text{with } F_q = \phi_i\phi_a,$$

only single excitations contribute to this sum

$$\approx \frac{2\bar{\omega}}{\omega^2 - (\bar{\omega})^2} X_s(\mathbf{r}, \mathbf{r}', (\omega))$$

Vanishes with separation as  $e^{-R}$

Finite overlap between occ. (bonding) and unocc. (antibonding)

## Interacting response function:

$$\chi(\mathbf{r}, \mathbf{r}', \omega) \approx \frac{2\omega_1}{\omega^2 - \omega_1^2} X_1(\mathbf{r}, \mathbf{r}', (\omega)) + \frac{2\omega_2}{\omega^2 - \omega_2^2} X_2(\mathbf{r}, \mathbf{r}', (\omega))$$

Vanishing overlap between interacting wavefn on donor and acceptor

Finite CT frequencies

Extract the xc kernel from:

$$f_{\text{HXC}}(\omega) = \chi_s^{-1}(\omega) - \chi^{-1}(\omega)$$

# Exact $f_{XC}$ matrix elt for CT between open-shells

Within the dressed SMA  $\omega^2 = \omega_q^2 + 4\omega_q [q|f_{HXC}(\omega_q)|q]$

the exact fxc is:...

...  
...  
...

$\bar{\phi}_0\phi_0$  - nonzero overlap

Interacting CT transition from 2 to 1, (eg in the approx found earlier)

$$\bar{\omega} [q|f_{HXC}(\omega)|q] = \delta^2 + \frac{\omega_1\omega_2 - \bar{\omega}^2}{4} + \frac{\omega_1\omega_2\delta^2}{\omega^2 - \omega_1\omega_2}$$

KS antibonding transition freq, goes like  $e^{-cR}$

$$\delta = (\omega_1 - \omega_2)/2$$

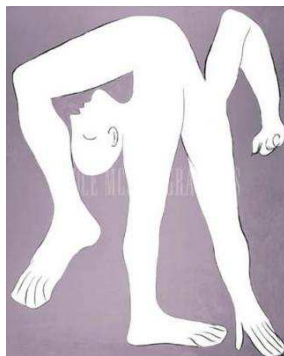
Note: **strong non-adiabaticity!**

(i) Also for closed-shell CT, and for homoatomics

**Upshot:** (i)  $f_{xc}$  blows up exponentially with R,  $f_{xc} \sim \exp(cR)$   
(ii)  $f_{xc}$  strongly frequency-dependent

## How about higher excitations of the stretched molecule?

- Since antibonding KS state is near-degenerate with ground, any single excitation  $\phi_0 \rightarrow \phi_a$  is near-degenerate with double excitation ( $\phi_0 \rightarrow \phi_a, \phi_0 \rightarrow \phi_a$ )
- Ubiquitous doubles – ubiquitous poles in  $fxc(\omega)$
- Complicated form for kernel for accurate excited molecular dissociation curves
- Even for *local* excitations, need strong frequency-dependence.



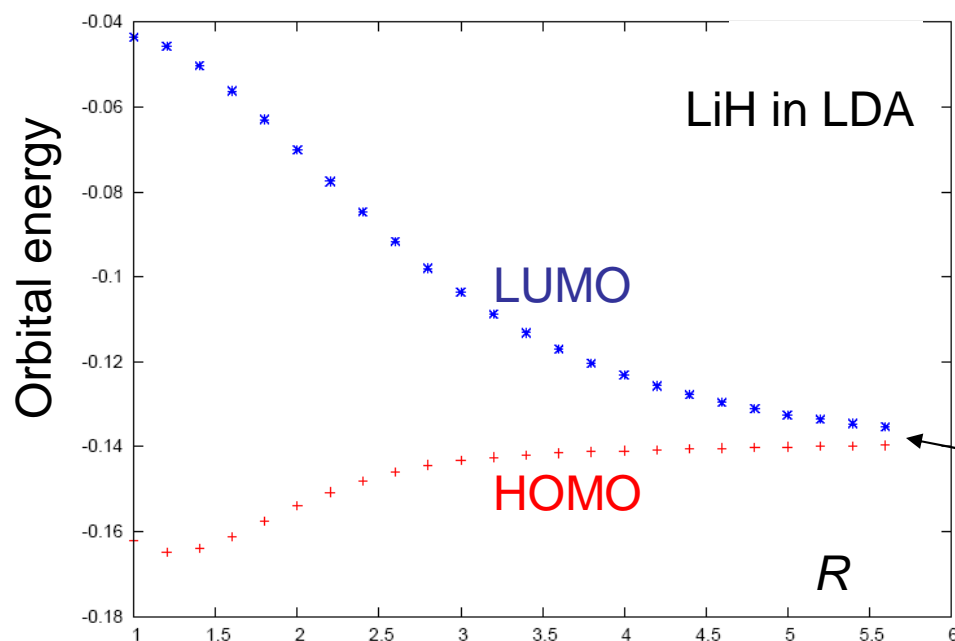
*N. T. Maitra and D. G. Tempel, J. Chem. Phys. 125 184111 (2006).*



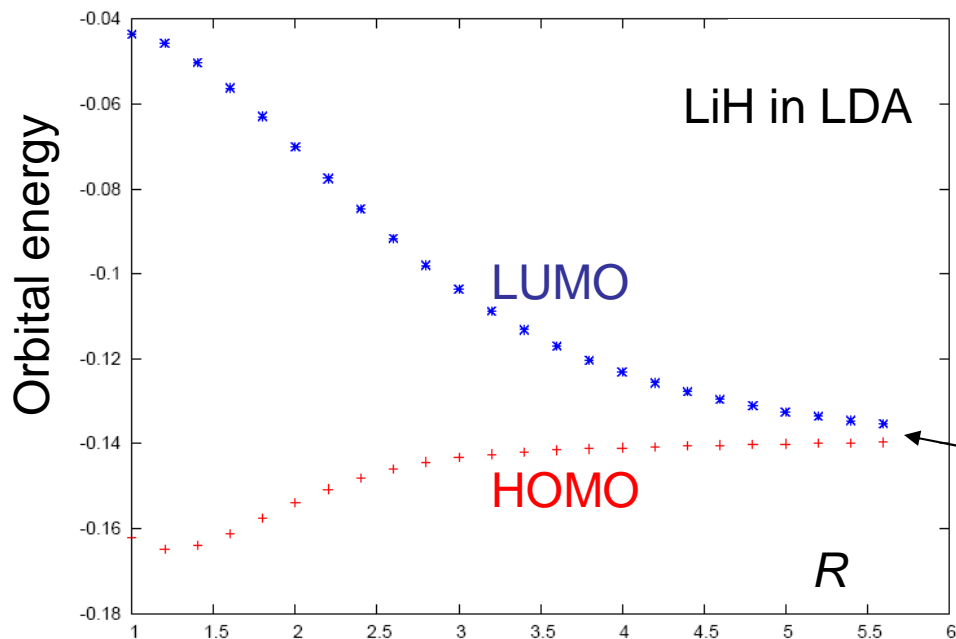
But almost no approximate  $v_s$  has the step, so is static correlation and  $\omega$ -dep. relevant practically ??

Yes !

- Static correlation is an important feature of LDA and GGA's too:



HOMO and LUMO become degenerate as the molecule dissociates



HOMO and LUMO become degenerate as the molecule dissociates

- As the molecule dissociates into fractional charged species ( $\text{Li}^{+0.25} \text{H}^{-0.25}$ ), the atomic potentials distort so as to align the highest levels of Li and H. The LiH molecular HOMO and LUMO are both **delocalized** over both atoms.
  - So, again, *any* single excitation  $\phi_{\text{H}} \rightarrow \phi_{\text{a}}$  is near-degenerate with the double  $(\phi_{\text{H}}, \phi_{\text{H}}) \rightarrow (\phi_{\text{a}}, \phi_{\text{L}})$
  - requiring again strongly frequency-dependent  $f_{xc}$  for both local and CT excitations.

# Summary

- Long-range charge-transfer excitations are particularly challenging for TDDFT approximations to model, due to vanishing overlap between the occupied and unoccupied states.
- Require exponential dependence of the kernel on fragment separation for frequencies near the CT ones.
- Strong frequency-dependence in the exact xc kernel is needed to accurately capture long-range charge-transfer excitations in a molecule composed of open-shell species
- Origin of complicated  $\omega$ -structure of kernel is the step in the ground-state potential – making the bare KS description a poor one. **Static correlation.**
- Static correlation problems also in conical intersections.
- Note also : general problem with non-overlapping occupied-unoccupied transitions, even when no CT, discussed in *Heiringer & Görling Chem. Phys. Lett.* **419**, 517 (2006)