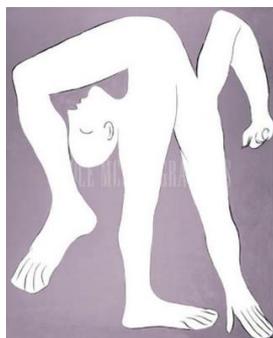


Advanced TDDFT III

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



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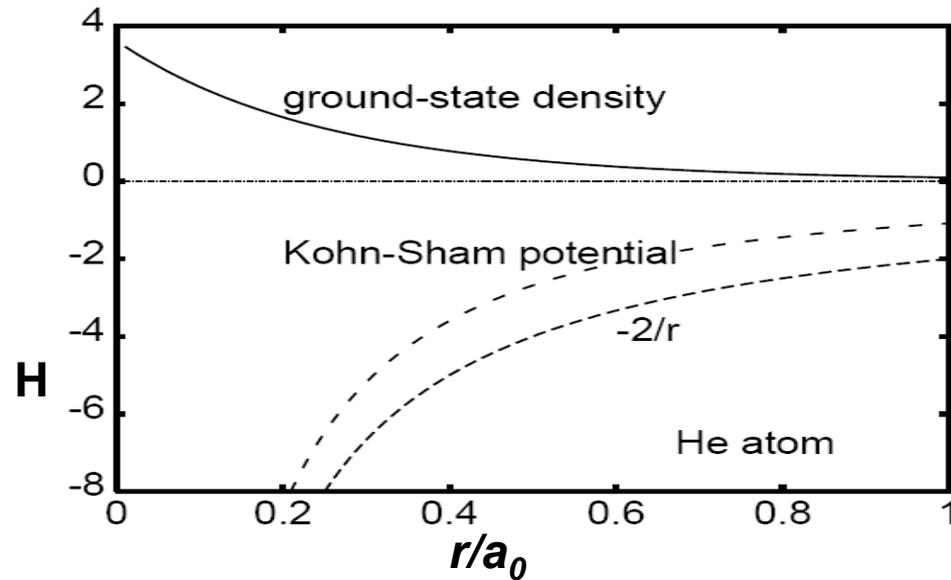
Plan

- Exact KS potential in molecular dissociation
- Long-range charge-transfer excitations
- Simplest model of CT to exactly solve to get an idea about $f_{xc}(\omega)$

Exact ground-state KS potentials...

For 2-e systems, easy to find if know the exact density, since
 $\phi(r) = \sqrt{\rho(r)/2}$ and so $v_S[\rho](\mathbf{r}) = \frac{\nabla^2 \sqrt{\rho(\mathbf{r})}}{2\sqrt{\rho(\mathbf{r})}} - I$

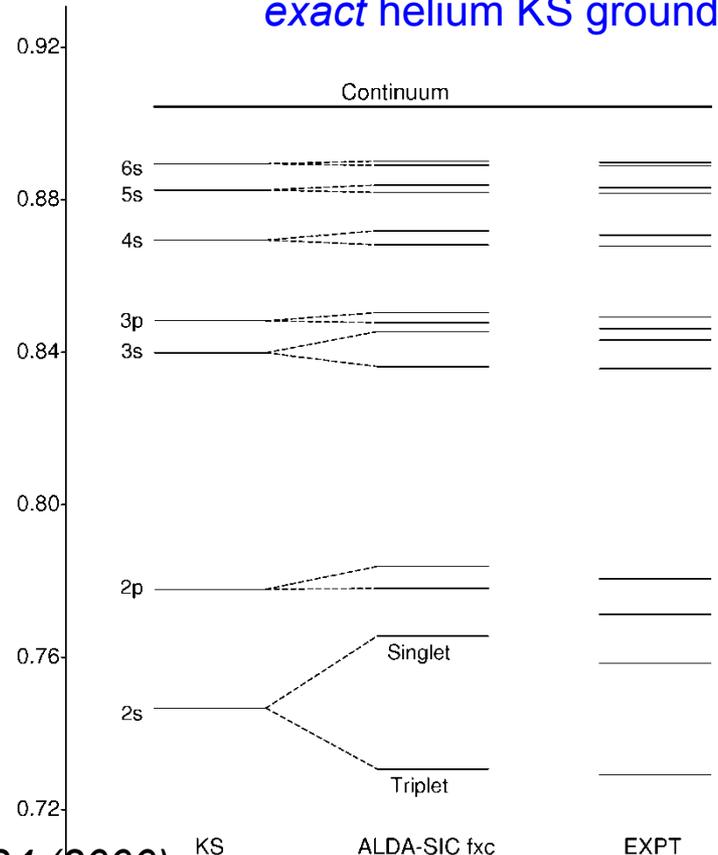
Eg. the Helium atom:



Already the KS excitations are pretty good, and most *fxc* approxs give similar corrections

Petersilka, Burke, & Gross *IJQC* **80**, 534 (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”

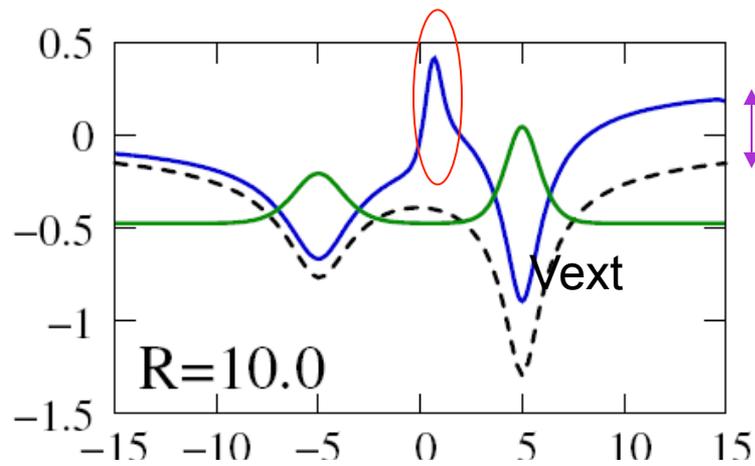
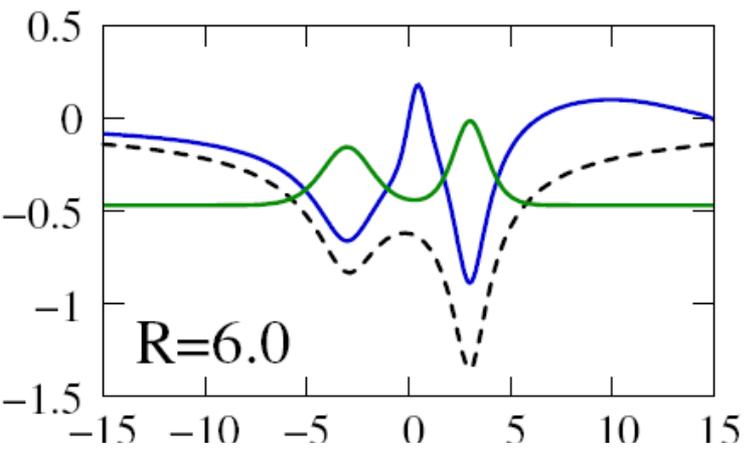
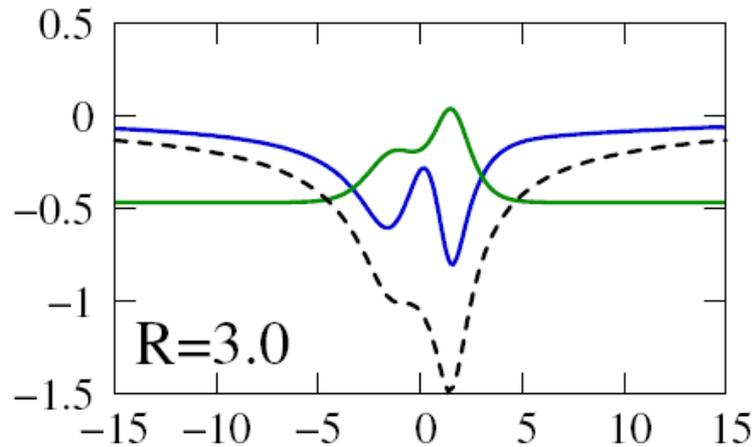
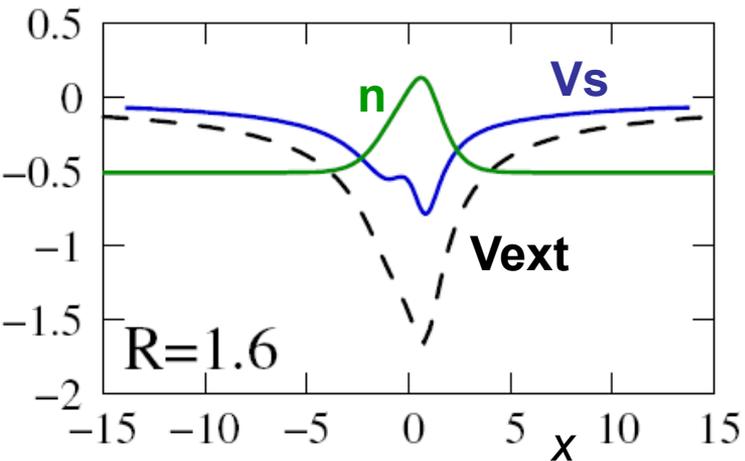
(choose to reproduce eg. IP's of different real atoms...)

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

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

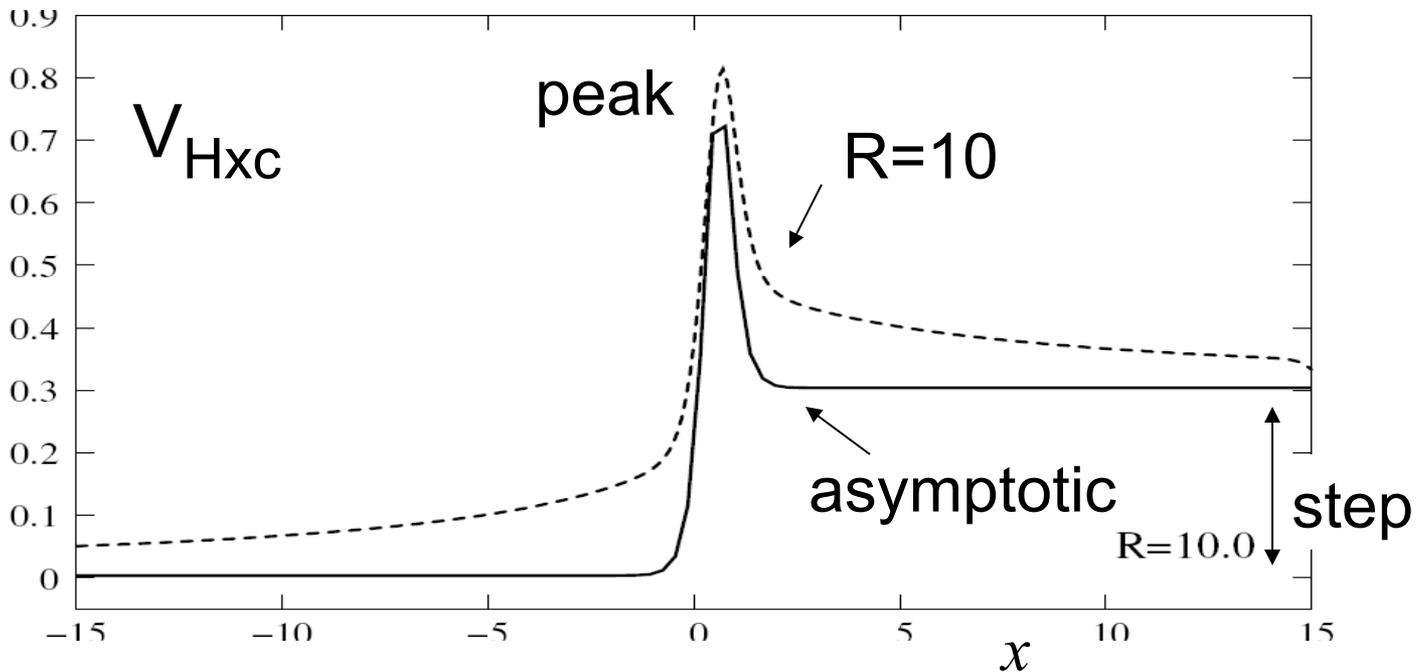
Exact ground-state KS potentials...

Molecular Dissociation (1d "LiH")



“Peak” and
“Step”
structures.

(step goes
back down at
large R)



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).*

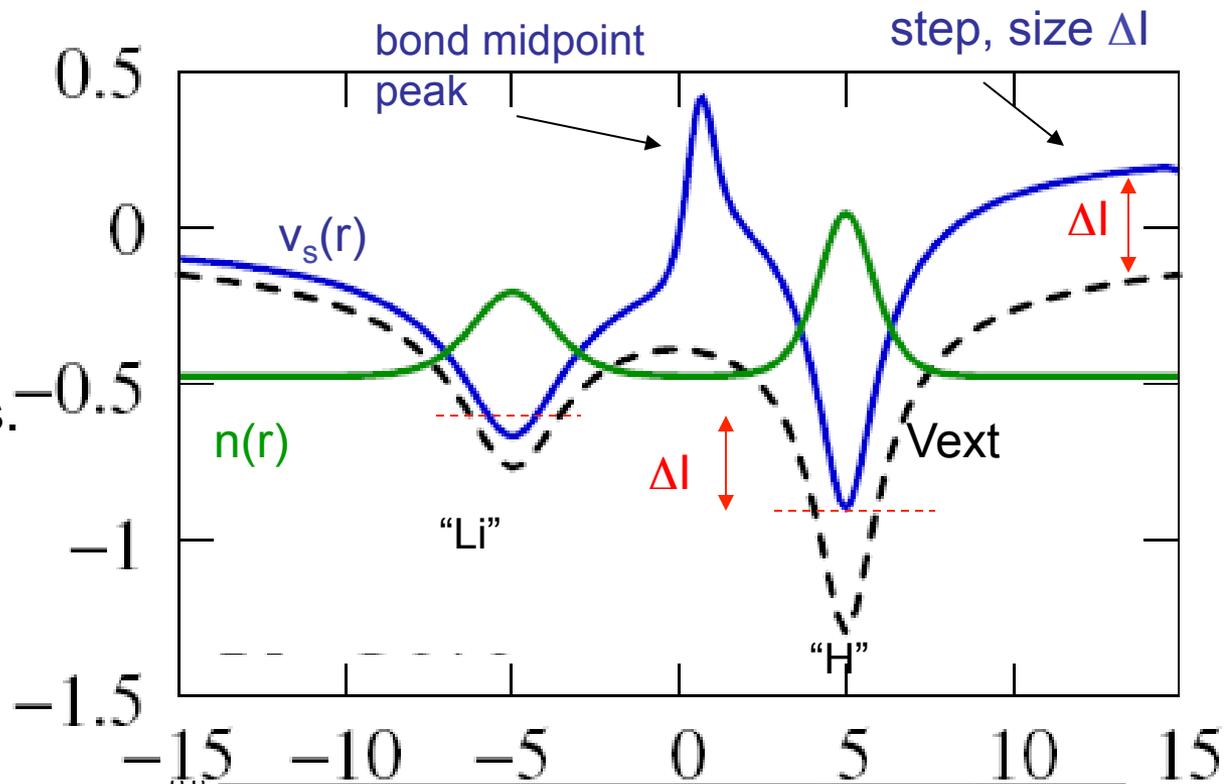
*D. G. Tempel, T. J. Martinez, N.T. Maitra, J. Chem. Th. Comp. **5**, 770 (2009)
& citations within.*

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

The Step

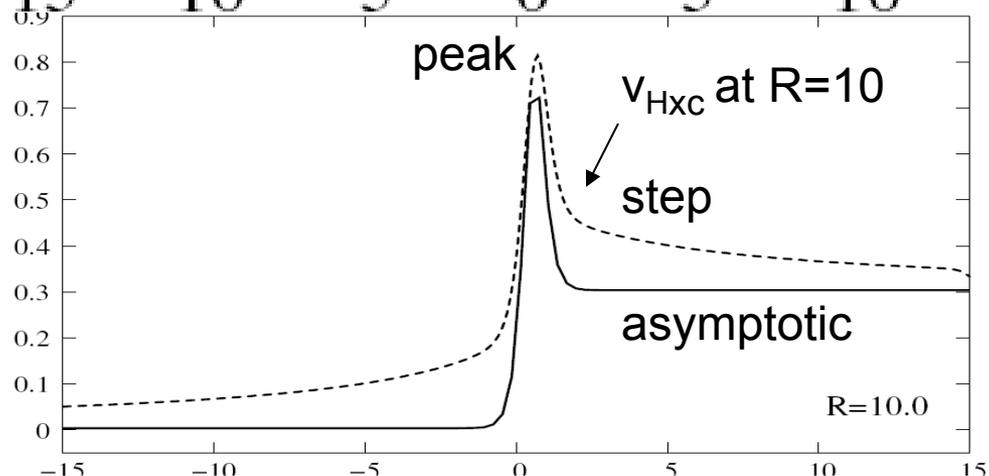
- Step has size ΔI and aligns the atomic HOMOs
- Prevents dissociation to unphysical fractional charges.

LDA/GGA – wrong, because no step!



- At which separation is the step onset?

Step marks location and sharpness of avoided crossing between ground and lowest CT state..



A Useful Exercise!

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” (1 and 2) at large separation. 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. The KS eigenvalue ϵ_0 must = $\epsilon_1 = -I_1$ where I_1 is the smaller ionization potential of the two atoms.

Consider now the KS equation $-\nabla^2 \phi_0/2 + v_s \phi_0 = \epsilon_0 \phi_0$ for r near atom 1, where $\phi_0 \approx \phi_1$ and again for r near atom 2, where $\phi_0 \approx \phi_2$,

Noting that the KS equation must reduce to the respective atomic KS equations in these regions, show that V_s must have a step of size $\epsilon_1 - \epsilon_2 = I_2 - I_1$ between the atoms.

The Peak

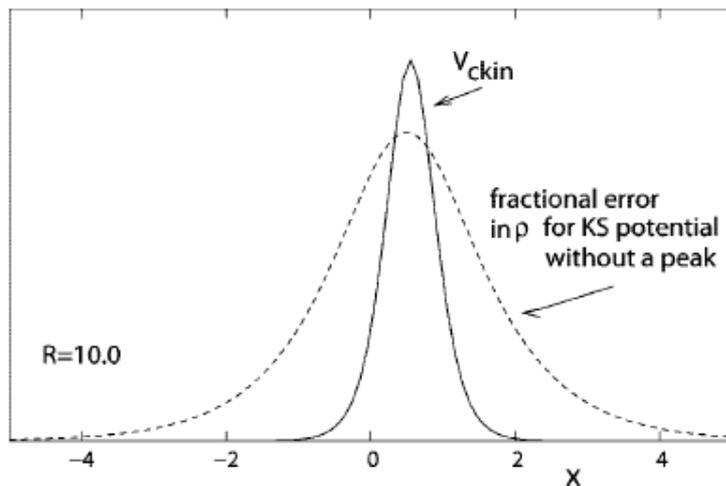
- A “kinetic correlation” effect (*Gritsenko, van Leeuwen, Baerends JCP 1996*). Also occurs in stretched H_2
- *Another interpretation*: peak pushes away density from the bonding region:

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

but with the LCAO $\phi_{\text{bond}} = (\sqrt{\rho_H/2} + \sqrt{\rho_{Li}/2})$ \rightarrow 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



\rightarrow 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

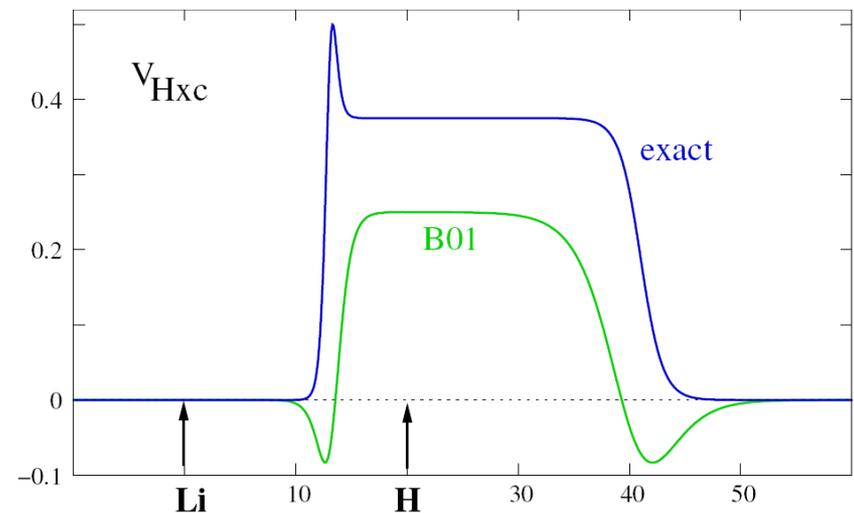
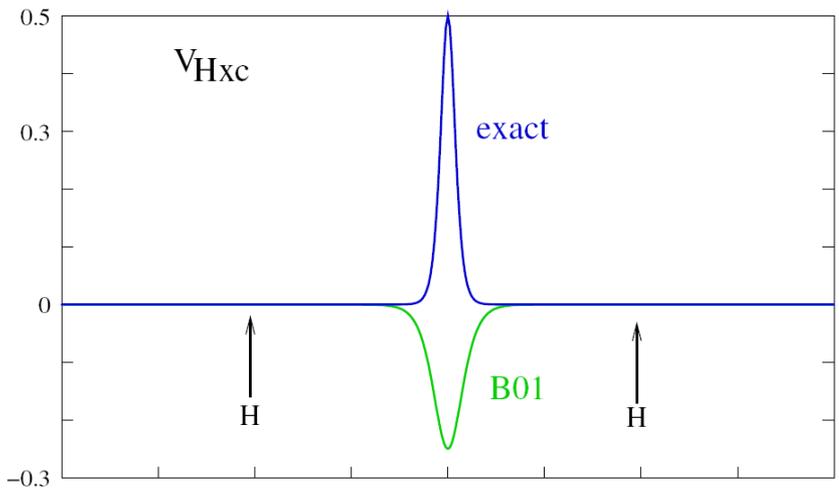
- Self-interaction-corrected LDA appears to have step- and peak-like features *Vieira, Capelle, Ullrich, PCCP 11, 4647 (2009) – quantum well studies*
- Baerends functional B01: functional of occupied and selected virtual orbitals (*Baerends PRL 87 133004 (2001)*)

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 single-Slater-determinant description of KS (one doubly-occupied orbital) – the *true* wavefunction, requires minimally 2 determinants (Heitler-London form)

$$\Psi_0 = (\phi_1(\mathbf{r})\phi_2(\mathbf{r}') + \phi_2(\mathbf{r})\phi_1(\mathbf{r}')) \sqrt{2}$$

- In practise, could treat ground-state by spin-symmetry breaking → good ground-state energies but wrong spin-densities

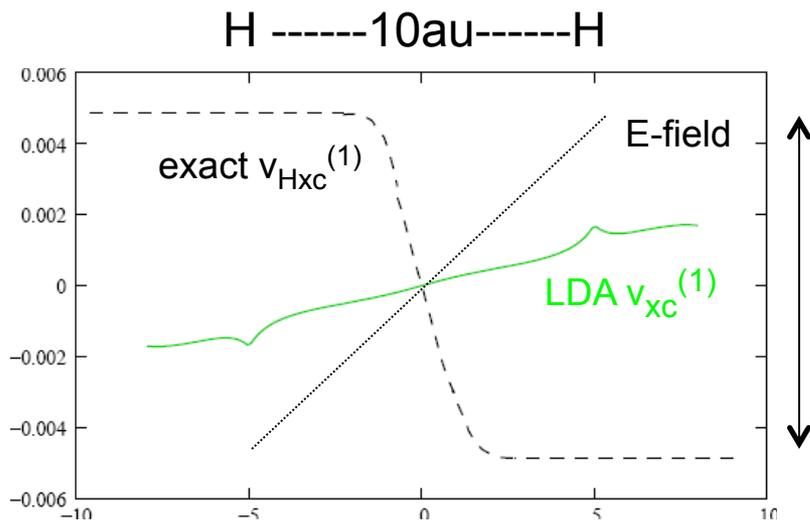
Next: What are the consequences of the peak and step beyond the ground state?

Response and Excitations

Implications for Static Response

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

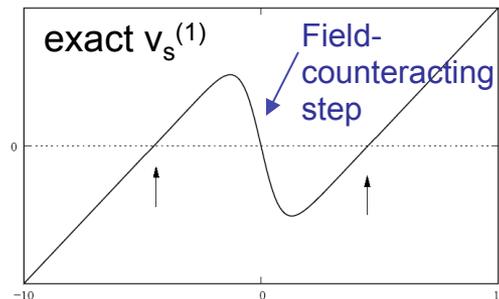
Eg: Stretched-H₂ in E-field, $\epsilon = 0.001$ au



Step-size ϵR

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 overestimate polarizabilities of long-chains.
-- Need *non-local* spatial dependence

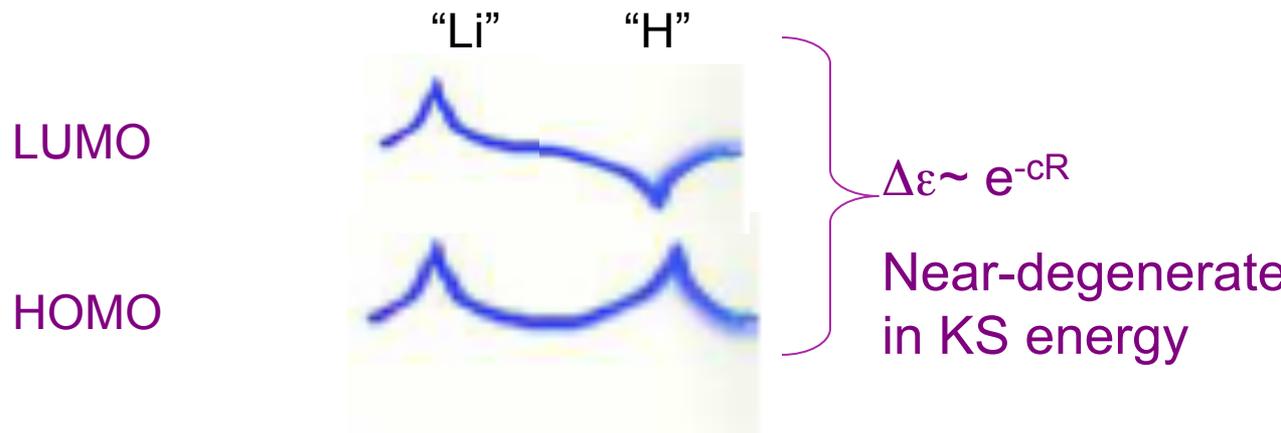
Peaks: appear in zero-field potential (not shown), act as barriers to transport – neglected in present-day transport calculations

What about TDDFT excitations of the dissociating molecule?

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!*



Static correlation induced by the step!

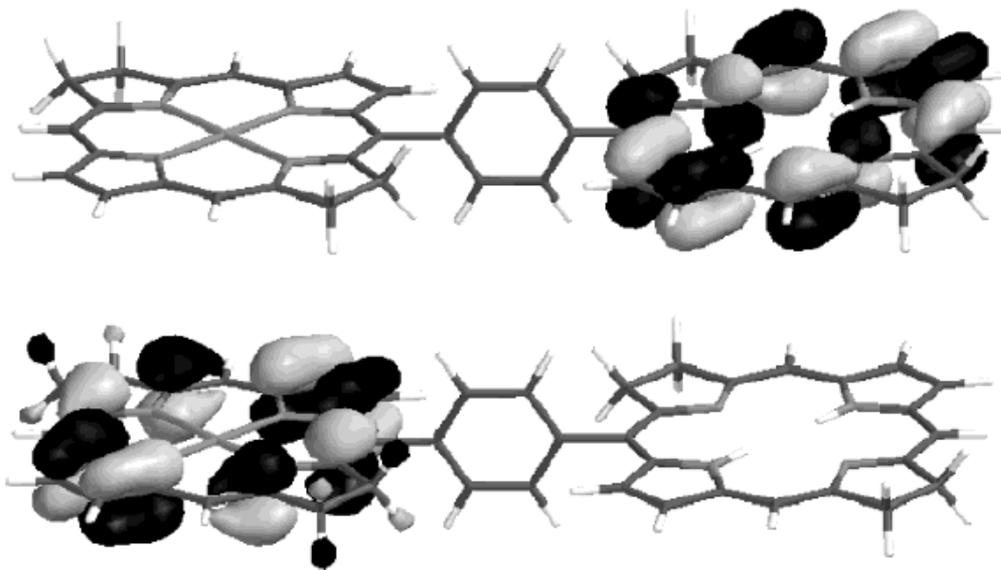
Find: *The step induces dramatic structure in the exact TDDFT kernel ! Implications for long-range charge-transfer.*

Plan

- Exact KS potential in molecular dissociation
- Long-range charge-transfer excitations
- Simplest model of CT to exactly solve to get an idea about $f_{xc}(\omega)$

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 !

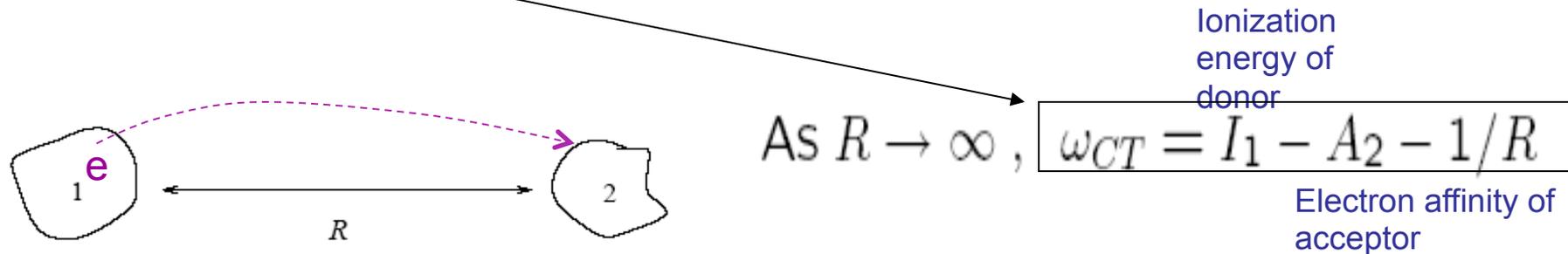
TDDFT error $\sim 1.4\text{eV}$

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

But also note: excited state properties (eg vibrational freqs) might be quite ok even if absolute energies are off (eg DMABN, Rappoport and Furche, JACS 2005)

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:



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

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

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

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

- 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 ground-state approximations 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 $\rightarrow f_{xc}$ contribution will *not* be zero!

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

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

Eg. apply SMA (or SPA)
to HOMO \rightarrow LUMO
transition

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

But this is
now zero !

$q =$ bonding \rightarrow 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.

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

$$[q|f_{\text{HXC}}(\omega)|q'] = \int d\mathbf{r} d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_a(\mathbf{r}) f_{\text{HXC}}(\mathbf{r}, \mathbf{r}', \omega) \underbrace{\phi_{i'}(\mathbf{r}') \phi_{a'}^*(\mathbf{r}')}_{\text{donor-acceptor overlap} \rightarrow 0}$$

donor-acceptor
overlap $\rightarrow 0$

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

$$- c_{\text{HF}} \int \phi_i(r) \phi_{i'}(r) \frac{1}{|r - r'|} \phi_a(r') \phi_{a'}(r') dr dr'$$

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...

E.g. *Dreuw, Weisman, & Head-Gordon, JCP (2003)* – use CIS curve but shifted vertically to match Δ SCF-DFT to account for correlation

E.g. *Tawada, Tsuneda, S. Yanagisawa, T. Yanai, & K. Hirao, J. Chem. Phys. (2004)*: “Range-separated hybrid” with empirical parameter μ

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

Short-ranged, use GGA

Long-ranged, use Hartree-Fock, gives $-1/R$

E.g. *Stein, Kronik, and Baer, JACS 131, 2818 (2009); Baer, Livshitz, Salzner, Annu. Rev. Phys. Chem. 61, 85 (2010)* – range-separated hybrid, with non-empirical “optimally tuned” μ :

Choose μ to give the closest fit of donor’s HOMO to it’s ionization energy, and acceptor anion’s HOMO to it’s ionization energy. → [Leeor Kronik talk next week!](#)

Note: idea of range-separated hybrids in ground-state came from *Leininger, Stoll, Werner, Savin, Chem. Phys. Lett. (1997)*

Note also: hybrids *do* fall under rigorous “generalized Kohn-Sham theory”, see *Görling and Levy, JCP (1997)*

...attempts to fix TDDFT for CT:

E.g. *Heßelmann, Ipatov, Görling, PRA 80, 012507 (2009)* – exact-exchange (EXX) kernel (non-empirical)

E.g. *Gritsenko & Baerends JCP 121, 655, (2004)* – model kernel to get CT excitations correct in the asymptotic limit, switches on when donor-acceptor overlap becomes smaller than a chosen parameter $f_{xc} \sim \frac{\exp(const * R)}{|r_1 - r_2|}$

E.g. *Hellgren & Gross, arXiv: 1108.3100v1 (2011)* – shows discontinuity in f_{xc} as a function of # electrons; demonstrates relation to a diverging spatial step in f_x (using EXX) that grows exponentially with separation → [Maria Hellgren talk next week!!](#)

E.g. *Fuks, Rubio, & Maitra, PRA 83, 042501 (2011)* – explores use of symmetry-breaking for the case of open-shell fragments, to avoid the static correlation problem.

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

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

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

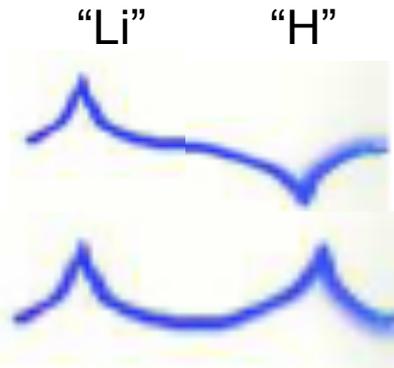
Try two-electron system – two “1-e atoms “ at large separation.

This is two **open-shells** – recall:

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

LUMO

HOMO



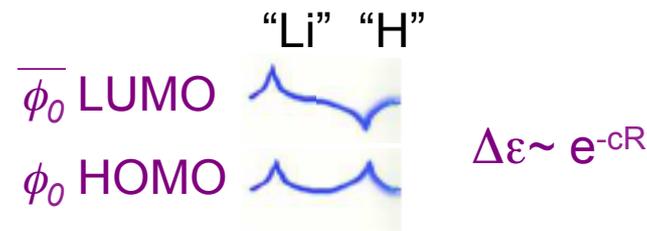
$$\Delta\varepsilon \sim e^{-cR}$$

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 f_{xc} 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 f_{XC} is:...

...
...

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

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

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

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

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

Note: **strong non-adiabaticity!**

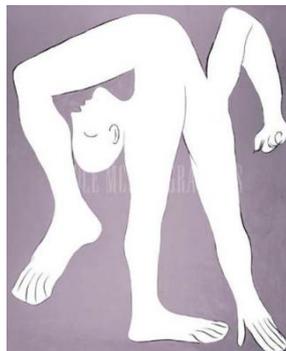
Upshot: (i) f_{XC} blows up exponentially with R, $f_{XC} \sim \exp(cR)$
(ii) f_{XC} strongly frequency-dependent

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

(Gritsenko and Baerends (JCP 2004))

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 $f_{xc}(\omega)$
- Complicated form for kernel for accurate excited molecular dissociation curves
- Even for *local* excitations, need strong frequency-dependence.

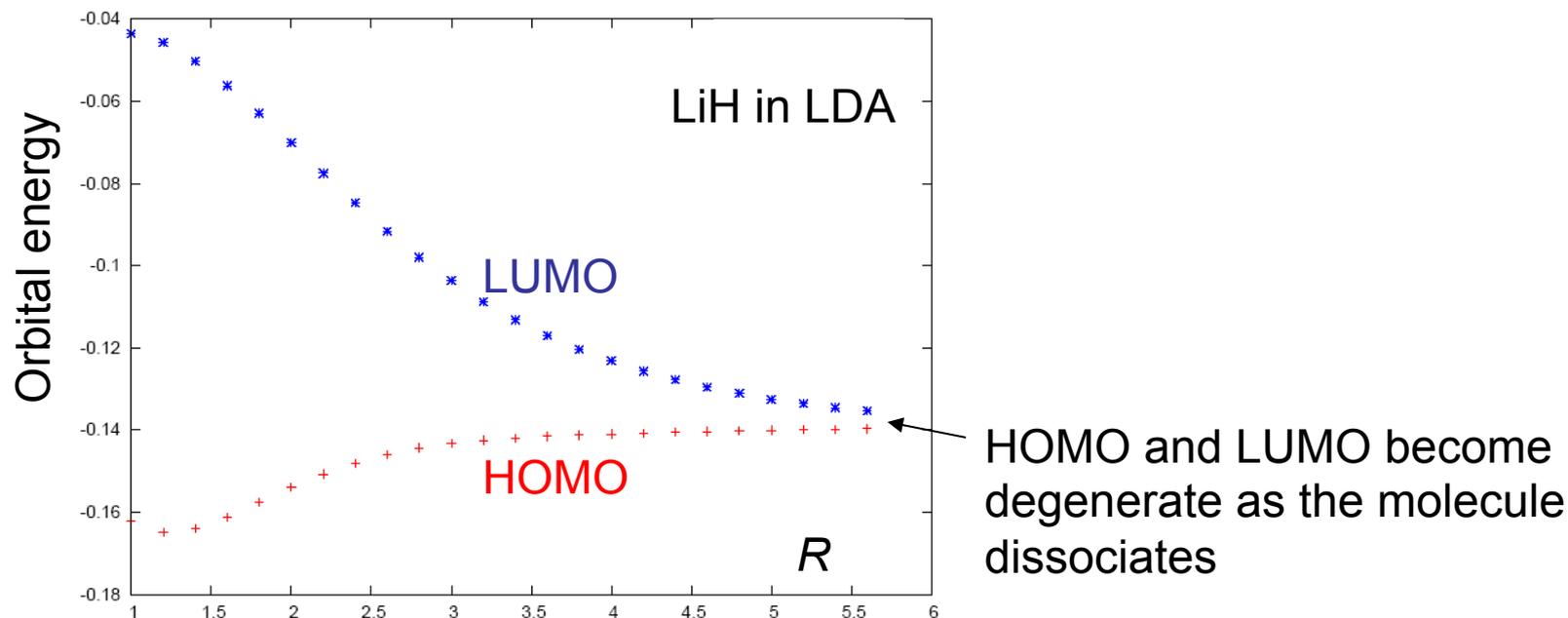


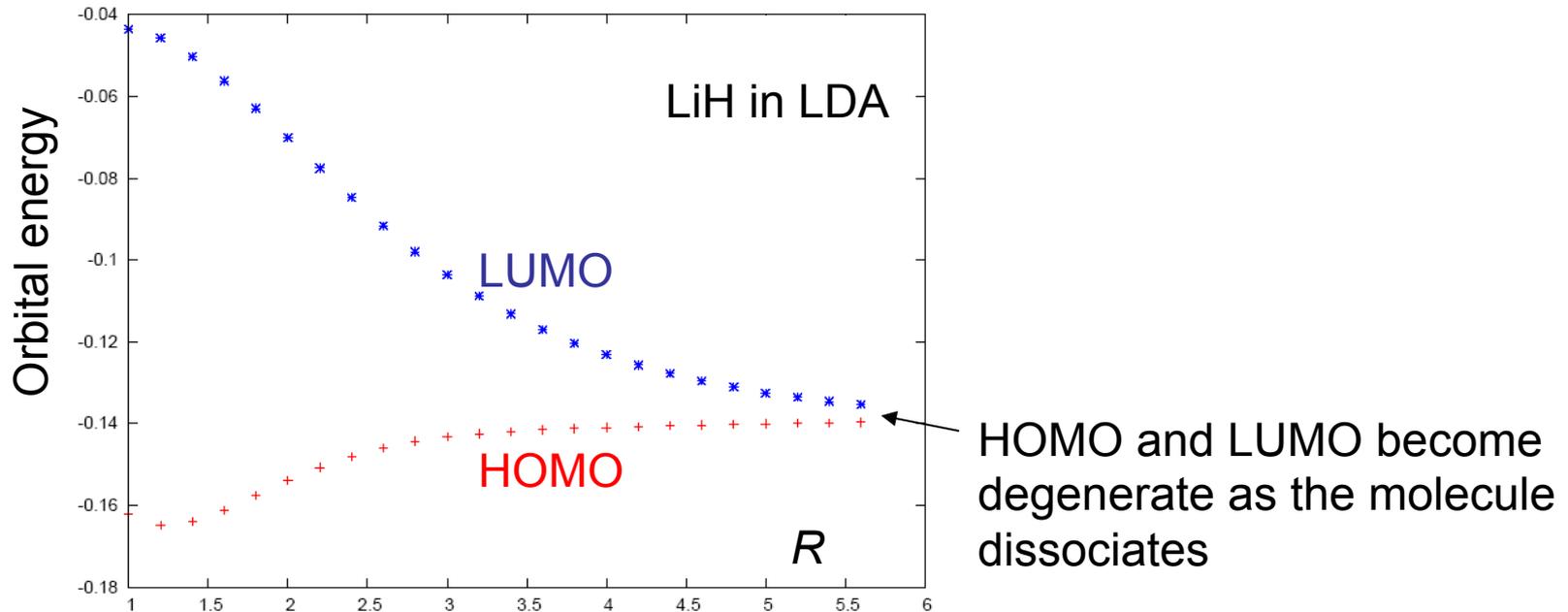
N. T. Maitra and D. G. Tempel, J. Chem. Phys. 125 184111 (2006).

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

Yes !

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





- 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 $\phi_H \rightarrow \phi_a$ is near-degenerate with the double $(\phi_H, \phi_H) \rightarrow (\phi_a, \phi_L)$

- 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 ω -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 *Hieringer & Görling Chem. Phys. Lett.* **419**, 517 (2006)