Orbitals and orbital energies in DFT and TDDFT

E. J. Baerends

Vrije Universiteit, Amsterdam

Common misunderstandings

1) The best orbitals are the HF orbitals

or

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

No: HF orbitals and density are too diffuse!

1a) In HF the one-el. properties are OK (el. density, kinetic energy),

the error is in W (el.-el. energy) due to neglect of correlation

No: errors in one-el. terms T and V are larger!

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

 No: the orbitals have a better shape and energy (see 3) than the HF orbitals. They are better suited for qualitative and quantitative MO theory.

3) There is no Koopmans' theorem in DFT. The occupied orbital energies (except the first) are meaningless.

No: there is a better-than-Koopmans relation in DFT between orbital energies and IPs: deviation for valence of ca. 0.1 eV, against HF deviation of ca. 1.1 eV.

And theoretically justified!

4) the KS band gap (orbital energy gap between HOMO and LUMO in a molecule) is wrong (much too small)

No: In <u>molecules</u> the KS gap (HOMO-LUMO orbital energy difference) is much smaller than $I{-}A$ (called the fundamental gap) but it is physically expected to be

(and numerically found to be)

an excellent approximation for the first excitation energy (optical gap).

In <u>solids</u> the fundamental gap ($I{-}A$) *and* optical gap (usually close to fundamental gap) are very different from the KS band gap **for a reason** (not **because of** 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)

The Hohenberg-Kohn Theorems
for non-degenerate ground states

HK theorems are a consequence of the variation theorem.

Var. theorem: $E[\Psi] = \dfrac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0$

$E[\Psi]$: E is <u>functional</u> of Ψ: assigns to each Ψ (out of the domain on which $E[\Psi]$ is defined) a real number E.

Function $f(x)$ maps real (or complex) variable x on real (or complex) f.

Functional $F[f]$ maps function $f(x)$ on real (or complex) F.

Inequality!

Var. Theorem:

in particular for a non-degen. ground state Ψ_0 :

if $\Psi \neq \Psi_0$:, and Ψ is normalized, then

$$\langle \Psi | \hat{H} | \Psi \rangle > E_0$$

Equality only if $\Psi = \Psi_0$!

Formulation of HK theorems-1

HK-1: for non-degenerate ground states Ψ_0 and local external potentials $v(\boldsymbol{r})$ (usually el.-nucl. pot. $v_{nuc}(\boldsymbol{r})$):

$$\Rightarrow \quad \text{one-to-one mapping}$$

$$\rho_0(\mathbf{r}) \leftrightarrow v(\mathbf{r}) \leftrightarrow \Psi_0$$

Only ground states Ψ_0 and ground state densities ρ_0!

$\rightarrow$ if you change v, then Ψ_0 and ρ_0 must change!

- two different v's cannot have the same ρ_0 (or Ψ_0)

- different: $v_2 - v_1 \neq C$ (over a finite domain)

$\rightarrow$ map $\Psi_0 \rightarrow \rho_0$ is invertible: $\Psi_0 \leftrightarrow \rho_0$

Formulation of HK theorems-2

Conseq.: all gr. state properties are functionals of ρ_0:

$$A[\rho_0] = \left\langle \Psi_0[\rho_0] \middle| \hat{A} \middle| \Psi_0[\rho_0] \right\rangle$$

e.g. $T[\rho_0]$ kinetic energy (not full 1RDM needed)

$E[\rho_0]$ total energy (not full 2RDM needed)

Note: in $E[\rho_0]$ the operator $\hat{H}$ depends on ρ_0: ρ_0 determines v, and therefore $\hat{H} = \hat{T} + \hat{V} + \hat{W}$

$$\hat{T} = \sum_{i=1}^{N} -\frac{1}{2}\nabla^2(i) \qquad \hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i) \qquad \hat{W} = \sum_{i<j} \frac{1}{r_{ij}}$$

Formulation of HK theorems-3

$$E[\rho_0] = \left\langle \Psi_0[\rho_0] \middle| \hat{T} + \hat{V}[\rho_0] + \hat{W} \middle| \Psi_0[\rho_0] \right\rangle$$

This energy has no obvious lower bound:

We can always look for a ρ_0 belonging to a system with a lower energy i.e. with a more attractive $v(\mathbf{r})$.

HK-2: a functional with lower bound exists:

For a *fixed* potential v, the functional

$$E_v[\rho_0] = \left\langle \Psi_0[\rho_0] \middle| \hat{T} + \hat{V} + \hat{W} \middle| \Psi_0[\rho_0] \right\rangle$$

keep $v(\mathbf{r})$ fixed

assumes a minimum for the ρ_0 that corresponds to $v(\mathbf{r})$

Corollary of HK: take v_2 different from v_1

$$\langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle > \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle = E_1 \qquad \text{because } \Psi_2 \neq \Psi_1$$

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

and

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

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

sum up

$$\int \rho_2 v_1 \, d\mathbf{r} + \int \rho_1 v_2 \, d\mathbf{r} > \int \rho_1 v_1 \, d\mathbf{r} + \int \rho_2 v_2 \, d\mathbf{r} \qquad \text{(HK: } \rho_2 = \rho_1 \text{ leads to contrdiction)}$$

or

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

There is an iterative way to find the unique $v(\mathbf{r})$ belonging to a given ρ_0: change $v(\mathbf{r})$ locally to increase or decrease ρ.

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

If in a small region the potential is decreased, $\Delta v < 0$,

then ρ must change (cf. HK!),

and $\Delta\rho$ must be positive over that region, and *vice versa*.

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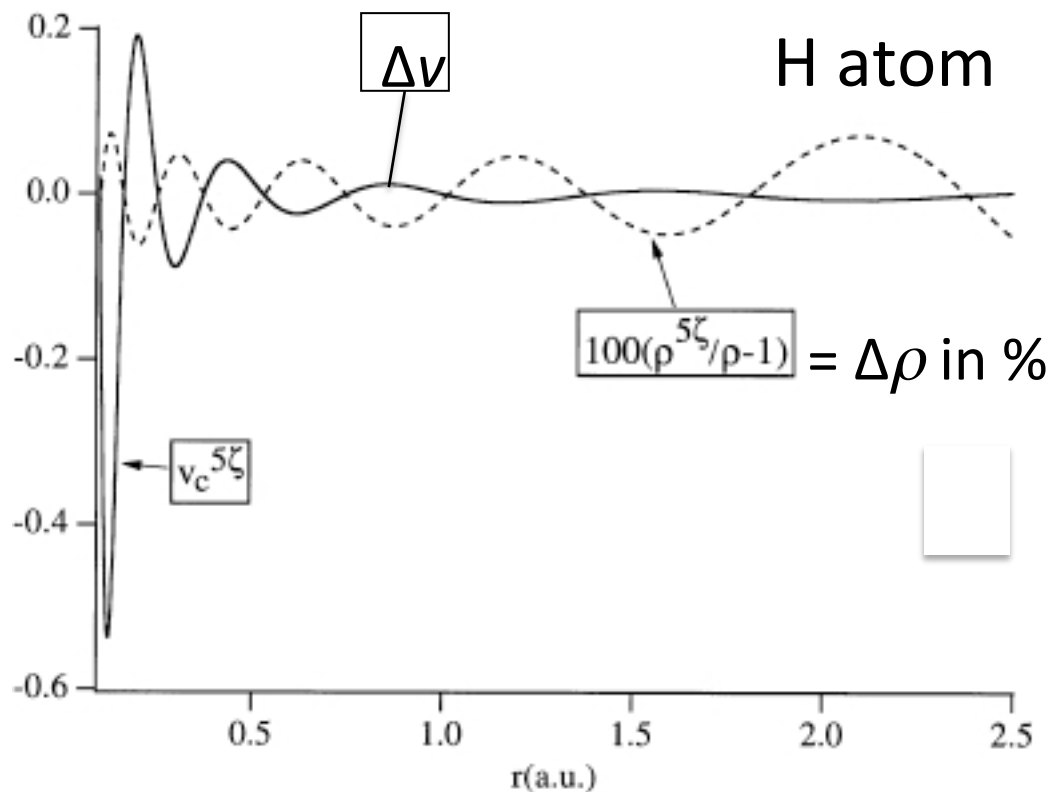
Example:
Calculate H atom in Gaussian basis: small deviations from exact density.

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

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

Criticisms of HK

1) What about degenerate ground states? There are many!

2) Only ground states! What about excitations?

3) Can (good approximations to) $E_v[\rho]$ or $F_{HK}[\rho]$ ever be found?

Degenerate Ground States

Suppose set of acceptable potentials V contains potentials $v(\mathbf{r})$ that have a degenerate ground state:

$H\Psi_i = E_0\,\Psi_i,\; i = 1, ..\, q$ (nondegenerate case for $q = 1$)

v defines a space $\{\Psi_v\}$ of ground state wave functions:

$$\{\Psi_v\} = \left\{ \Psi \;\middle|\; \Psi = \sum_{i=1}^{q} c_i \Psi_i,\;\; \sum_{i=1}^{q} |c_i|^2 = 1 \right\}$$
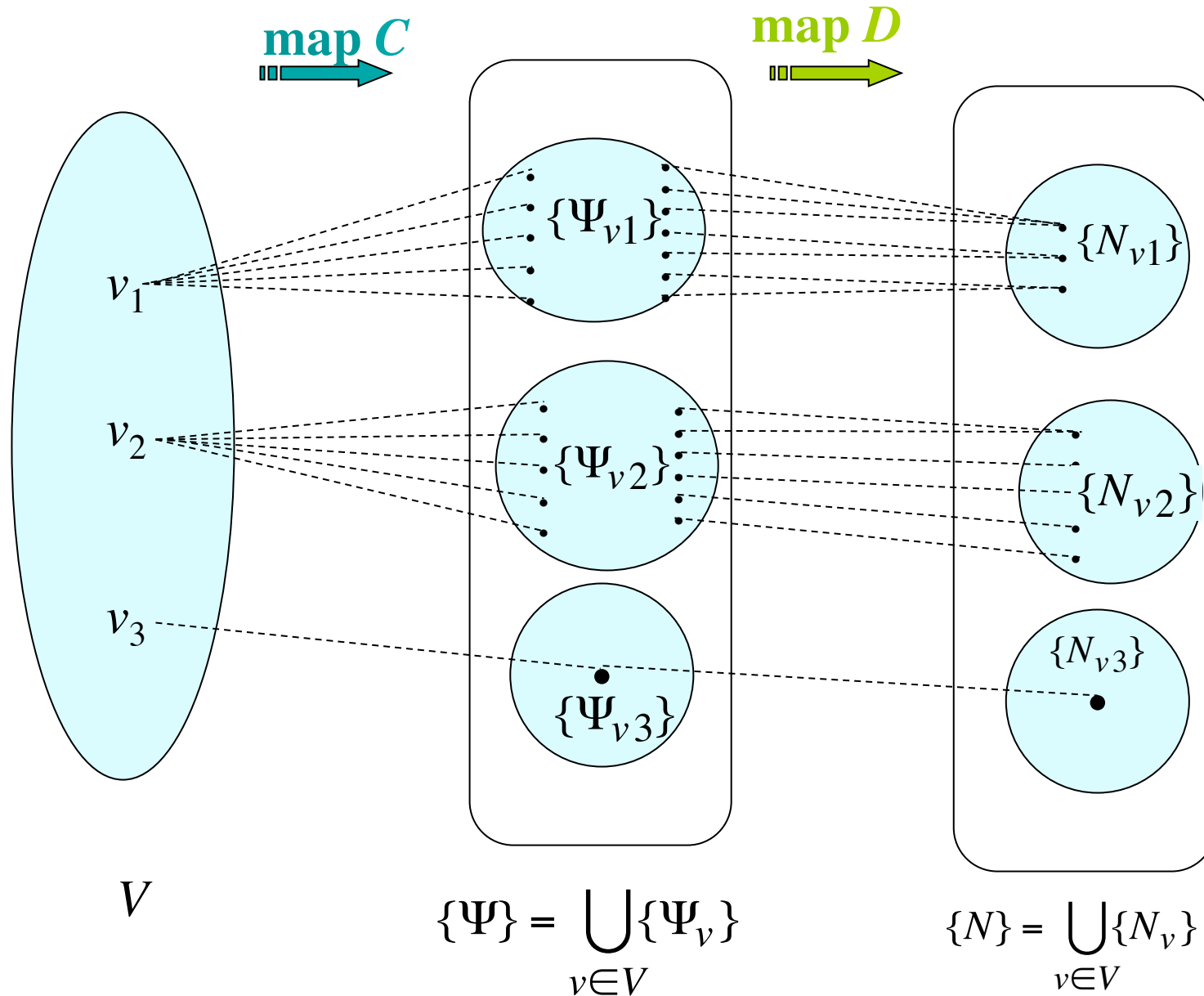
Group together ground state densities corresponding to $v(\mathbf{r})$ in set N_v :

$$\{N_v\} = \left\{ \rho(\mathbf{r}) \;\middle|\; \rho(\mathbf{r}) = \int |\Psi(\mathbf{r}\sigma, \mathbf{x}_2 \ldots \mathbf{x}_N)|^2 \, d\sigma d\mathbf{x}_2 \ldots d\mathbf{x}_N,\;\; \Psi \in \{\Psi_v\} \right\}$$

Total sets of wavefunctions and of densities by union :

$$\{\Psi\} = \bigcup_{v \in V} \{\Psi_v\} \qquad\qquad \{N\} = \bigcup_{v \in V} \{N_v\}$$

Mapping of potentials on wavefunctions on densities

map C

map D

v_1

v_2

v_3

$\{\Psi_{v1}\}$

$\{\Psi_{v2}\}$

$\{\Psi_{v3}\}$

$\{N_{v1}\}$

$\{N_{v2}\}$

$\{N_{v3}\}$

V

$\{\Psi\} = \bigcup_{v \in V} \{\Psi_v\}$

$\{N\} = \bigcup_{v \in V} \{N_v\}$

properties of maps:

C is no longer a proper map: one potential v is associated with more Ψ's. If $v_2 \neq v_1 +$ constant, then each element of $\{\Psi_{v1}\}$ differs from each element of $\{\Psi_{v2}\}$ (same argument as before).

C^{-1}:$\{\Psi_{v1}\} \rightarrow v_1$ is a proper map (sets $\{\Psi_{v1}\}$ and $\{\Psi_{v2}\}$ etc. are disjoint)

map D: two ground states Ψ_1 and Ψ_2 coming from different potentials $v_2 \neq v_1 +$constant lead to different densities $\rho_2(\mathbf{r}) \neq \rho_1(\mathbf{r})$ (same argument as before) $\rightarrow$ sets N_{v1} and N_{v2} are disjoint.

However, Ψ' and Ψ coming from the same v may yield the *same* density: D^{-1} is not a proper map, $\Psi[\rho]$ is not a unique functional.

Example: $v(\mathbf{r}) = -Z/r$, set p states, $p_+ = (1/\sqrt{2})(p_x + ip_y)$ etc.

$$|p_+(\mathbf{r})|^2 = |p_-(\mathbf{r})|^2 = (1/2)\left(|p_x(\mathbf{r})|^2 + |p_y(\mathbf{r})|^2\right) \neq |p_0(\mathbf{r})|^2 = |p_z(\mathbf{r})|^2$$

Summary for degenerate states:

1) Ground state expectation values of an arbitrary operator A
is not a unique functional of ρ, since $\langle \Psi | A | \Psi \rangle$ may differ from $\langle \Psi' | A | \Psi' \rangle$

2) But energy is still unique functional of ρ, since Ψ and Ψ' that give the same ρ must belong to same v, characterized by the degenerate ground state energy.
Therefore $F_{HK}[\rho]$ may be defined as $F_{HK}[\rho] = \langle \Psi_i[\rho] | T + W | \Psi_i[\rho] \rangle$
with $\Psi_i[\rho] \in \{\Psi_v\}, \; v = v[\rho]$

$E_v[\rho]$ is now defined for all densities $\rho(\mathbf{r})$ corresponding to a ground state (degenerate or not). It is variational:

$E_v[\rho] = E_0$ **(the ground state energy of v) if $\rho \in N_v$**

$E_v[\rho] > E_0$ **if $\rho \notin N_v$**

Is minimization of $E_v[\rho]$ with constraint $\int\rho(\mathbf{r})d\mathbf{r}=N$ viable? (orbital-free DFT)

$E_v[\rho] = \left\langle \Psi_0[\rho] \middle| \hat{T} + \hat{V} + \hat{W} \middle| \Psi_0[\rho] \right\rangle$ is minimum at ρ_0 of v

$$\frac{\delta}{\delta\rho(\mathbf{r})}\left[E_v[\rho] - \mu\left(\int \rho\, d\mathbf{r} - N\right)\right] = 0$$

$$\frac{\delta E_v}{\delta\rho(\mathbf{r})} - \mu = 0 \quad \longrightarrow \quad \frac{\delta\{T[\rho] + W[\rho]\}}{\delta\rho(\mathbf{r})}\Bigg|_{\rho_0 \text{ of } v} = -v(\mathbf{r}) + \mu$$

But the HK theorems offer no presciption for obtaining $T[\rho]$ or $W[\rho]$. Until now no success in finding sufficiently accurate T functional.

Therefore: this route has not been successful!

The Kohn-Sham molecular orbital model of DFT

Kohn-Sham Ansatz: there is an independent particle system of non-interacting electrons, all moving in the same local potential $v_s(\mathbf{r})$ such that the density is equal to the exact one (of the interacting electron system in given external potential $v_{ext}(\mathbf{r})$:

Kohn-Sham orbitals from: $\left(-\frac{1}{2} \nabla^2(1) + v_s(\mathbf{r}_1) \right) \varphi_i(\mathbf{r}_1) = \varepsilon_i(\mathbf{r}_1)$

$$\text{with} \quad \rho_s(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2 = \rho^{exact}(\mathbf{r})$$

The HK theorems also hold for non-interacting electrons ($W=0$) since proofs do not use form of W.

So $v_s(\mathbf{r})$ is in one-one correspondence with gr. st. $\rho_s(\mathbf{r})$ (and $\rho^{exact}(\mathbf{r})$).

If $v_s(\mathbf{r})$ exists (no proof by KS; non-int. v-represent. problem) then it is unique: no other system, with different v and ρ_0, has same v_s.
It determines KS orbitals and energies: these are system properties.

Kohn-Sham model -1

How to obtain approximations to $v_s(\mathbf{r})$? Later.

Suppose we have $v_s(\mathbf{r})$, obtain the true KS orbitals and $\rho_s = \rho^{exact} = \rho$. Write *exact* total energy:

$$E = T_s + \int \rho v_{ext}\, d\mathbf{r} + (1/2)\int \rho V_{Coul}\, d\mathbf{r} + E_{xc}$$

$$= \sum_{i=1}^{N} \left\langle \varphi_i \left| -\frac{1}{2}\nabla^2 \right| \varphi_i \right\rangle \quad \text{everything we don't know if } \{\varphi_i\} \text{ are known}$$

E_{xc}: called exchange-correlation energy of DFT;
  is defined by above equation: that part of exact E we do not yet know when $\{\varphi_i\}$ and ρ have been obtained.

E_{xc} is functional of ρ since other terms are:
$E_{xc}[\rho] = E[\rho] - T_s[\rho] - \int \rho v_{ext}\, d\mathbf{r} - (1/2)\int \rho V_{Coul}\, d\mathbf{r}$

Kohn-Sham model -2

How does E_{xc} compare to exchange energy of HF, E_x^{HF}, and the correlation energy of HF, E_c^{HF}?

E_x^{HF} is exchange energy of det. wavef.: $-(1/2)\sum_{ij} K_{ij}$

$E_c^{HF} = E - E^{HF}$

What is the exchange energy and what is the correlation energy in DFT?

Write exact energy in the traditional way:

$$E = T + \int \rho v_{ext}\, d\mathbf{r} + (1/2)\int \rho V_{Coul}\, d\mathbf{r} + W_{xc}$$

exact kinetic energy   exchange-correlation part of el.-el. interaction

$$W_{xc} = W - (1/2)\int \rho V_{Coul}\, d\mathbf{r} = (1/2)\int \rho(\mathbf{r}_1)\, v_{xc}^{hole}(\mathbf{r}_1)\, d\mathbf{r}$$

$$\left\langle \Psi_0 \left| \sum_{i<j} \frac{1}{r_{ij}} \right| \Psi_0 \right\rangle$$

Kohn-Sham model -3

$v_{xc}{}^{hole}(\mathbf{r}_1)$ is the potential of the exact hole $\rho_{xc}{}^{hole}(\mathbf{r}_1; \mathbf{r}_2)$ surrounding an electron at position $\mathbf{r}_1$:

if a given electron is at $\mathbf{r}_1$, the probability to find any one of the other electrons at a point $\mathbf{r}_2$ is not the total density $\rho(\mathbf{r}_2)$ (which gives the Coulomb potential),

but is diminished in the neighborhood of $\mathbf{r}_1$ due to the Coulomb repulsion between electrons

$\rho^{hole}(\mathbf{r_2};\mathbf{r_1})$

$\rho(\mathbf{r_2})$

$\rho^{cond}(\mathbf{r_2};\mathbf{r_1})$
$= \rho + \rho^{hole}$

$\mathbf{r_1} \qquad \rightarrow \mathbf{r_2}$
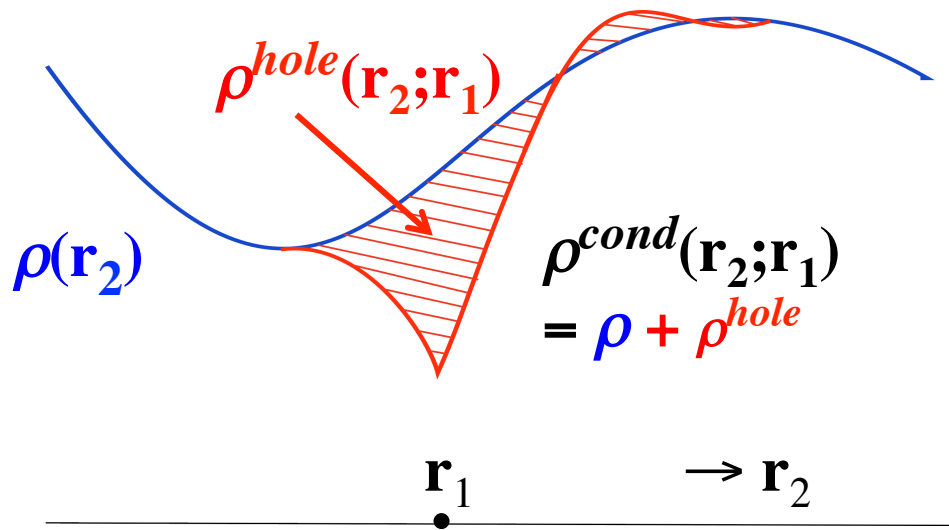
An electron traveling through a molecule

does not see $\rho(\mathbf{r_2})$ with

potential $v_{Coul} = \int \rho(\mathbf{r_2})/r_{12}d\mathbf{r_2}$

but $\rho(\mathbf{r_2}) + \rho^{hole}(\mathbf{r_2}; \mathbf{r_1})$

$$W = \left\langle \hat{W} \right\rangle = \frac{1}{2}\int \frac{1}{r_{12}}\Gamma(1,2)d1d2$$

$$= \frac{1}{2}\int \frac{\rho(1)\rho(2)}{r_{12}}d1d2 + \frac{1}{2}\int \frac{\Gamma_{xc}(1,2)}{r_{12}}d1d2$$

$$= \frac{1}{2}\int \rho(1) \underbrace{\int \frac{\rho(2)}{r_{12}}d2}_{V_{Coul}(1)} d1 + \frac{1}{2}\int \rho(1) \underbrace{\int \frac{\Gamma_{xc}(1,2)}{\rho(1)r_{12}}d2}_{v_{xc}^{hole}} \; d1$$

$$W = \qquad W_{Coul} \qquad + \qquad\qquad W_{xc}$$
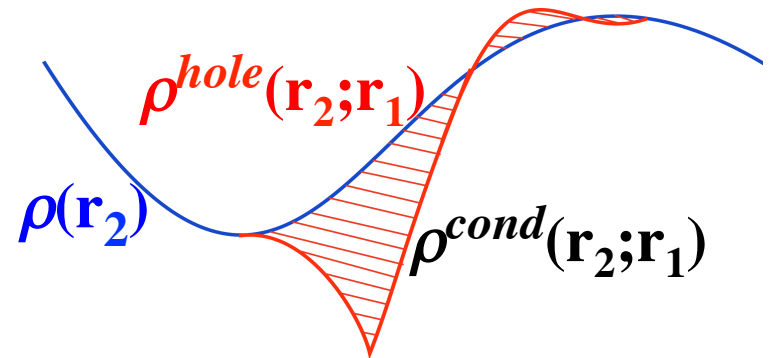
statistical physics definition

Exchange-correlation energy W_{xc}

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

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

$\rho^{hole}(\mathbf{r}_2; \mathbf{r}_1)$

$\rho(\mathbf{r}_2)$

$\rho^{cond}(\mathbf{r}_2; \mathbf{r}_1)$

$\mathbf{r}_1 \qquad \rightarrow \mathbf{r}_2$

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

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

Definition of E_x, E_c, E_{xc}

$$E = \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle = T + \int \rho v \, d\mathbf{r} + \frac{1}{2} \int \rho v_{Coul} \, d\mathbf{r} + W_{xc} \qquad E \text{ in traditional way}$$

$$E = T_s + \int \rho v \, d\mathbf{r} + \frac{1}{2} \int \rho v_{Coul} \, d\mathbf{r} + E_{xc} \qquad E \text{ in Kohn-Sham way}$$

$$\Rightarrow E_{xc} = \underbrace{T - T_s}_{T_c} + W_{xc} \equiv E_c + W_x \Rightarrow E_c = E_{xc} - W_x$$

Use KS orbitals to write exchange energy as $W_x = -\dfrac{1}{2}\sum_{ij}^{N} K_{ij}$

$W_{xc} - W_x \equiv W_c$ the correlation part of W_{xc}

$E_c = T_c + W_c$ the correlation energy of DFT

Compare E_c to E_c^{HF}

$$E_c^{HF} = E - E^{HF}$$

$$= T - T^{HF} \qquad \rightarrow T_c^{HF}$$

$$+ \int \rho v \, d\mathbf{r} - \int \rho^{HF} v \, d\mathbf{r} = \int \Delta \rho v \, d\mathbf{r} \quad \rightarrow V_c^{HF}$$

$$+ W_{Coul} - W_{Coul}^{HF} \qquad \rightarrow W_{Coul,c}^{HF}$$

$$+ W_{xc} - W_x^{HF} \qquad \rightarrow W_c^{HF}$$

$$E_c^{HF} = T_c^{HF} + V_c^{HF} + W_{Coul,c}^{HF} + W_c^{HF}$$

$E_c = T_c + W_c$ is much simpler!

Compare to HF

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

$$\Rightarrow E - E^{HF} \equiv E_c^{HF}$$

And DFT? Put KS orbitals in determinant:

$$E^{KS} = \left\langle \Psi_s \middle| \hat{H} \middle| \Psi_s \right\rangle = T_s + \int \rho v \, d\mathbf{r} + \frac{1}{2} \int \rho v_{Coul} \, d\mathbf{r} + W_x$$

Compare to exact E

$$E = T_s + \int \rho v \, d\mathbf{r} + \frac{1}{2} \int \rho v_{Coul} \, d\mathbf{r} + E_{xc}$$

$$\Rightarrow E - E^{KS} = E_{xc} - W_x \equiv E_c$$

Correl. energy of DFT is also energy of det. w.r.t. exact energy

Definition of correlation energy

Ψ_s is determinant of KS orbitals

Ψ^{HF} is Hartree-Fock determinant

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

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

E_c^{DFT} E_c^{HF}

E^{exact}

$$\left| E_c^{DFT} \right| > \left| E_c^{HF} \right|$$

but by how much?

The one-particle model of DFT: Kohn-Sham

Minimization of

$$E = \sum_{i=1}^{N} \langle \psi_i | -\frac{1}{2}\nabla^2 | \psi_i \rangle + \int \rho v_{nuc} d\mathbf{r} + \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}$$

$$= T_s + V + W_{Coul} + E_{xc}$$

leads to one-el. equations for optimal (KS) orbitals:

$$\left(-\frac{1}{2}\nabla^2(1) + v_{nuc}(\mathbf{r}_1) + v_{Coul}(\mathbf{r}_1) + v_{xc}(\mathbf{r}_1) \right)\psi_i(\mathbf{x}_1) = \varepsilon_i \psi_i(\mathbf{x}_1)$$

$$\int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \qquad \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r}_1)}$$

What about potentials, orbitals and density in the KS model?

Common statements: "KS orbitals have no physical meaning"

"The only use for the KS orbitals is to build the density"

We will prove these statements to be totally wrong!

Energy density for E_{xc}

$E_{xc} = \int \rho(\mathbf{x}) \varepsilon_{xc}(\mathbf{x}) d\mathbf{x}$

Approximations: LDA, GEA, GGA,.....:

$\varepsilon_{xc}(\mathbf{x}) \approx f(\rho(\mathbf{x}), \rho'(\mathbf{x}), \rho''(\mathbf{x}),....)$

Exact $\varepsilon_{xc}(\mathbf{x})$ from

$E_{xc} = W_{xc} + T - T_s$

$= (1/2) \int \rho(\mathbf{x}) v_{xc}^{hole}(\mathbf{x}) d\mathbf{x} + \int \rho(\mathbf{x})(v_{kin}(\mathbf{x}) - v_{s,kin}(\mathbf{x})) d\mathbf{x}$

Γ_{xc} $\gamma(1,1')$ $\gamma_s(1,1')$

CI   CI   KS

El. correlation is described by $\Phi(2\ldots N|1)$

so no wonder that v_s can be derived from $\Phi(2\ldots N|1)$:

$$v_s = v_{ext} + \underbrace{v_{Coul} + v_{xc}^{hole}}_{v^{cond}} + \underbrace{(v_{kin} - v_{s,kin})}_{v_{c,kin}} + \underbrace{v^{resp}}_{\text{from } \Phi}$$

from Φ $\qquad$ γ and γ_s

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

No information from this expression:
Shape?
Physics?
Even $E_{xc}[\rho]$ is unknown

Composition of v_{xc}

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}$$ Not very transparent! Therefore use:

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

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

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

$$+\int \rho(\mathbf{r}') \frac{\delta}{\delta \rho(\mathbf{r})}\left[\frac{1}{2} v_{xc}^{hole}(\mathbf{r}') + v_{c,kin}(\mathbf{r}')\right] d\mathbf{r}' \longrightarrow v^{resp}(\mathbf{r})$$
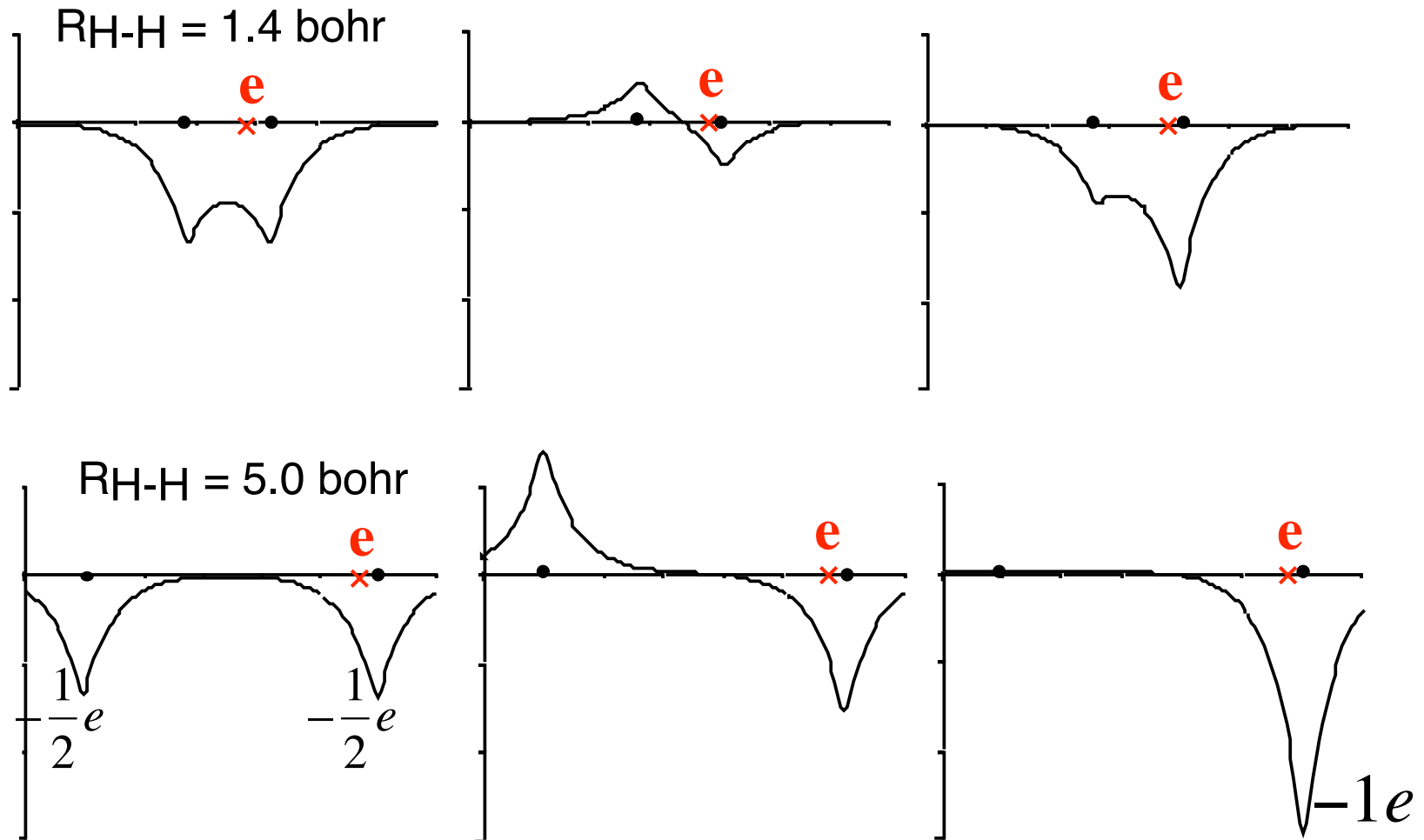
Holes in H$_2$

Fermi hole   + Coulomb hole   =   total hole

R$_{H-H}$ = 1.4 bohr

R$_{H-H}$ = 5.0 bohr

$\frac{1}{2}e$ $-\frac{1}{2}e$

$-1e$

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

In H_2 Fermi hole $\rho_X^{hole}(\mathbf{r}_2|\mathbf{r}_1)$ for el. at $\mathbf{r}_1$ is only self-interaction correction term $-|\sigma_g(\mathbf{r}_2)|^2$

So independent of $\mathbf{r}_1$!

When R(H-H) is large and $\mathbf{r}_1$ is close to nucleus b, hole is,

with $\sigma_g(\mathbf{r}_2) \approx (1/\sqrt{2})\,[1s_a(\mathbf{r}_2) + 1s_b(\mathbf{r}_2)]$,

$-|\sigma_g(\mathbf{r}_2)|^2 \approx -(1/2)\,[|1s_a(\mathbf{r}_2)|^2 + |1s_b(\mathbf{r}_2)|^2 + 2.1s_a(\mathbf{r}_2).1s_b(\mathbf{r}_2)]$

$$\approx 0$$

Since total ρ is $|1s_a(\mathbf{r}_2)|^2 + |1s_b(\mathbf{r}_2)|^2$, the field that the HF electron at $\mathbf{r}_1$ feels is due to $\rho(\mathbf{r}_2)+\rho_X^{hole}(\mathbf{r}_2|\mathbf{r}_1) = (1/2)\,[|1s_a(\mathbf{r}_2)|^2 + |1s_b(\mathbf{r}_2)|^2]$

Wrong! The other el. should be around nucleus a!
The erroneous charge of $(1/2)|1s_b(\mathbf{r}_2)|^2$ that el. around b feels screens nucleus b: the HF orbital becomes too diffuse.

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	+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

Hartree-Fock densities are often poor due to bad potential: TM complexes

	E_{total}^{corr}	T_{kin}^{corr}	V_{el-nuc}^{corr}	W_{el-el}^{corr}
MnO_4^-	–14.4	+35.7	–115.5	+65.4
$Ni(CO)_4$	–3.4	–35.0	+147.8	+116.3
$Cr(CO)_6$	–4.5	–4.5	+30.8	–18.5

Hartree-Fock errors for bond energies (kcal/mol), because of lack of left-right correl. in bond orbitals

	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%
H_2	83.8	109.5	–23.4 %

Holes in H₂

Fermi hole + Coulomb hole = total hole

$R_{H-H} = 1.4$ bohr

$R_{H-H} = 5.0$ bohr

$\frac{1}{2}e$ $-\frac{1}{2}e$

$-1e$

Localized hole in DFT
Slater: uniform
depth $-\rho(\mathbf{r}_1)/2$
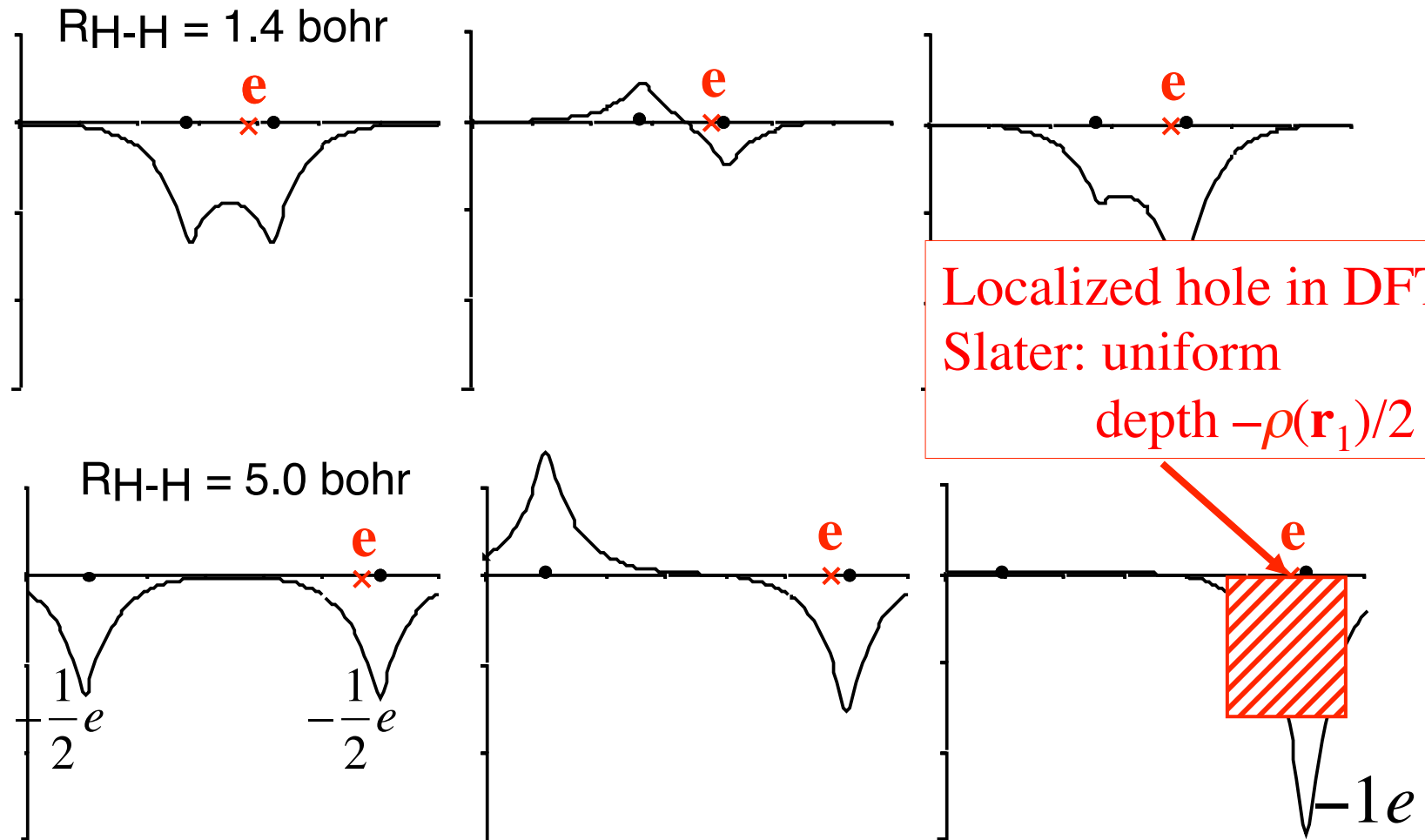
NB. $v_{xc} = v_{c,kin} + \boldsymbol{v_{xc}^{hole}} + v^{resp}$

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

Grüning, Gritsenko, Baerends, JCP 118 (2003) 7183
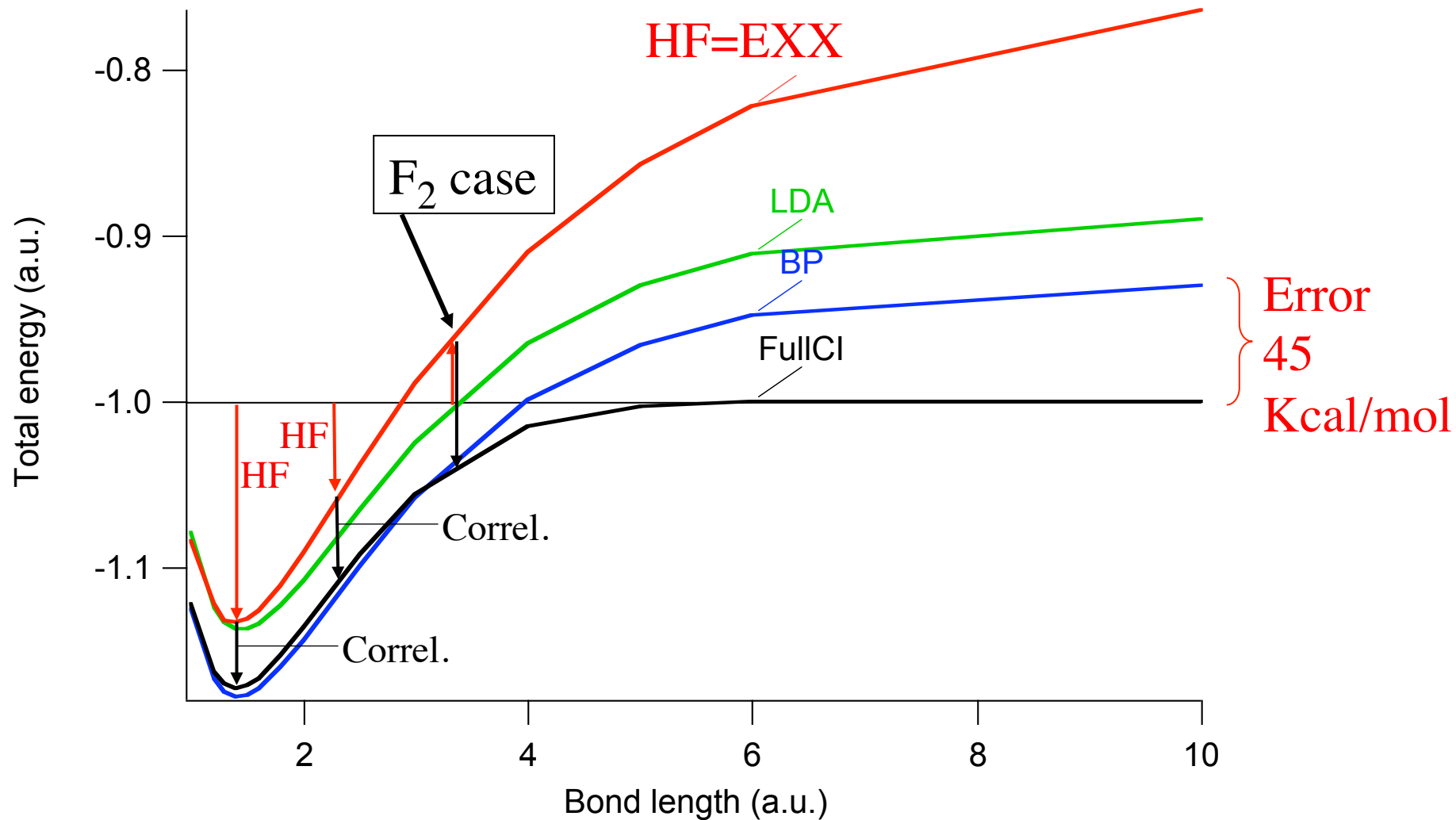
The anomalous F_2 case: RHF energy above two F atoms!

Energy

R(F-F)

Energy of
2 F atoms
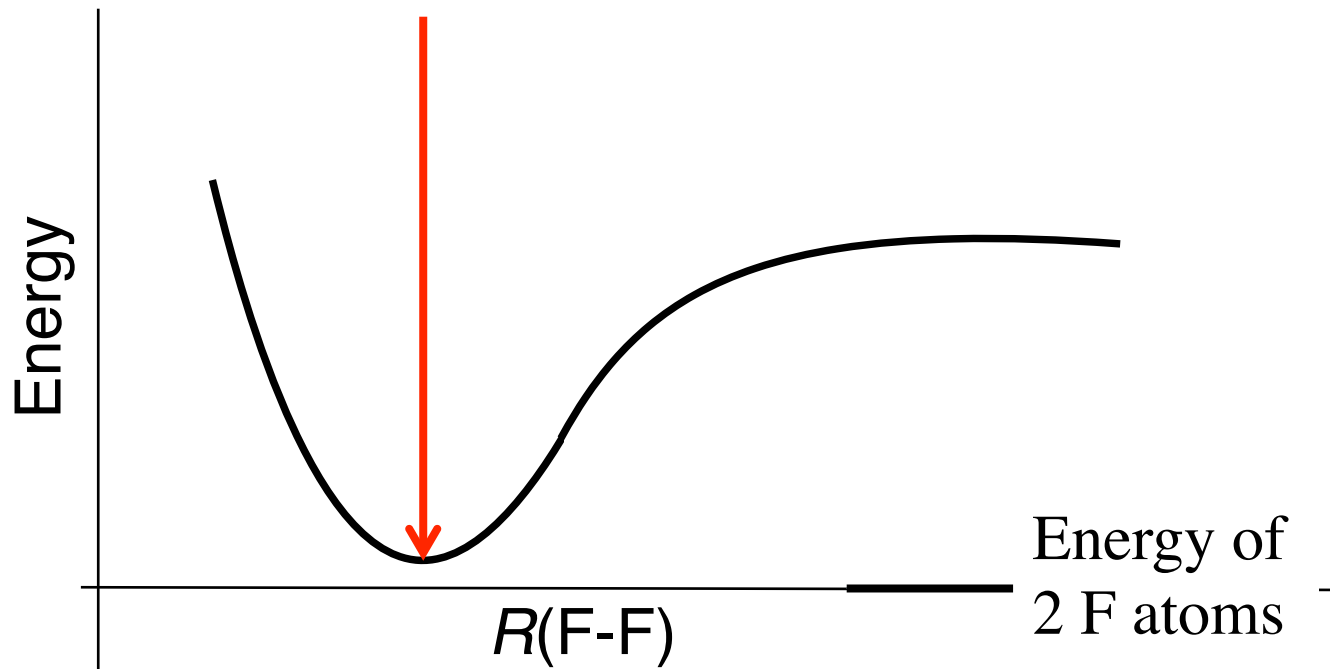
The functional Cloud

Courtesy of Peter Elliott, Hunter College, New York

"exact" 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
$W_{Coul}^{corr}(HF)$	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	−0.475	−0.641	−0.750
$E_c(HF)$	−0.469	−0.603	−0.687
$E_c - E_c(HF)$	−0.006	−0.0038	−0.063

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

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

In an electron pair bond:

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

$\rightarrow$ kinetic energy too low

$\rightarrow$ 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

Conclusion HF versus KS det.

– Ψ^{HF} better total energy (marginally)

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

Ψ_s better for:

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

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

Energy components for CO at R_e=2.132 bohr

	LDA	BLYP	EXX	HF	KS	CI
T_s Δ^{KS}	111.951 +0.930	113.181 −0.300	112.395 +0.790	112.641 +0.544	112.881 +0.304	113.185 (T)
V_{en} Δ^{KS}	−310.170 −1.086	−311.520 +0.264	−310.651 −0.605	−310.879 −0.377	−311.256 0.00	−311.256
W_H Δ^{KS}	76.204 +0.195	76.391 +0.008	76.251 +0.148	76.262 +0.137	76.399 0.00	76.399
W_X^{fn} Δ^{KS}	**−12.064** −1.255	**−13.475** +0.156	−13.296 −0.023	−13.331 +0.012	−13.319	−14.089 (W_{XC})
Sum Δ^{CI}	−134.079	−135.423	−135.301 **−0.460**	−135.307 **−0.454**	−135.295 **−0.466**	−135.761
E_c^{fn}	**−0.950**	**−0.486**	(−0.460)	(−0.454)	(−0.466)	
E_{tot} Δ^{CI}	**−135.029** −0.732	**−135.909** +0.148		**Baerends, Gritsenko JCP 123 (2005) 062202**		−135.761

Energy components for CO at $R=2.8$ bohr

	LDA	BLYP	EXX	HF	KS	CI
T_s Δ^{KS}	111.023 + 0.950	112.257 − 0.280	111.437 +0.833	111.662 +0.608	111.977 +0.293	112.270
V_{en} Δ^{KS}	−298.862 − 0.915	−300.239 +0.462	−299.216 − 0.561	−299.430 − 0.347	−299.777 0.00	−299.777
W_H Δ^{KS}	71.038 + 0.035	71.241 −0.168	71.071 + 0.002	71.045 + 0.028	71.073 0.00	71.073
$\mathbf{W_X^{fn}}$ Δ^{KS}	**−11.752** −1.228	**−13.168** +0.188	−12.973 − 0.007	−13.027 +0.047	−12.980	−13.822 (W_{XC})
Sum Δ^{CI}	−128.553	−129.909	−129.738 **− 0.518**	−129.750 **− 0.506**	−129.707 **− 0.549**	−130.256
$\mathbf{E_c^{fn}}$	**−0.935**	**−0.472**	**(− 0.518)**	**(− 0.506)**	**(− 0.549)**	
E_{tot} Δ^{CI}	**−129.489** **− 0.767**	**−130.381** **+ 0.125**		**Baerends, Gritsenko JCP 123 (2005) 062202**		−130.256

Time-dependent DFT

Runge-Gross: HK theorem holds for time-dependent case

$$v(\mathbf{r},t) \Leftrightarrow \rho(\mathbf{r},t) \Leftrightarrow \Psi_0(t)$$

Kohn-Sham (orbital model) in time-dependent case :

$$\left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r},t)\right)\psi_i^s(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\psi_i^s(\mathbf{r},t)$$

$$\rho_s(\mathbf{r},t) = \sum_{i=1}^{N}\left|\psi_i^s(\mathbf{r},t)\right|^2 = \rho^{exact}(\mathbf{r},t)$$

LINEAR RESPONSE (1st order Pert. Theory)

$$\delta\rho(\mathbf{r},\omega) = \int \chi(\mathbf{r},\mathbf{r}',\omega)\delta v(\mathbf{r}',\omega)d\mathbf{r}'$$

$\chi(\mathbf{r},\mathbf{r}',\omega)$: first order response function; difficult

(requires sum over all excited states)

Kohn - Sham : $\delta\rho(\mathbf{r},\omega) = \delta\rho_S(\mathbf{r},\omega)$

$$= \int \chi_S(\mathbf{r},\mathbf{r}',\omega)\delta v_S(\mathbf{r}',\omega)d\mathbf{r}'$$

$\uparrow$

response function of

noninteracting system : simple!

$\delta v_S(\mathbf{r}',\omega)$: how related to $\delta v(\mathbf{r}',\omega)$?   (difficult?)

Linear response: δv_s

$$\delta v_s(\mathbf{r}',\omega) = \delta v(\mathbf{r}',\omega) + \delta v_{\text{coul}}(\mathbf{r}',\omega) + \delta v_{\text{xc}}(\mathbf{r}',\omega) \equiv \delta v(\mathbf{r}',\omega) + \delta v_{\text{induced}}(\mathbf{r}',\omega)$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$\int \frac{\delta\rho(\mathbf{r}'',\omega)}{|\mathbf{r}'-\mathbf{r}''|}d\mathbf{r}'' \qquad \int \underbrace{\frac{\delta v_{xc}(\mathbf{r}',\omega)}{\delta\rho(\mathbf{r}'',\omega)}}_{f_{xc}(\mathbf{r}',\mathbf{r}'',\omega)}\delta\rho(\mathbf{r}'',\omega)d\mathbf{r}''$$

the xc kernel

$$v_{xc}(\mathbf{r},\omega) = \frac{\delta E_{xc}}{\delta\rho(\mathbf{r},\omega)} \qquad f_{xc}(\mathbf{r},\mathbf{r}',\omega) = \frac{\delta E_{xc}}{\delta\rho(\mathbf{r},\omega)\delta\rho(\mathbf{r}',\omega)}$$

$$\text{LDA - Xonly}: E_{xc} = K\int\rho^{4/3}d\mathbf{r}; \ \ v_{xc}(\mathbf{r},\omega) = \frac{4K}{3}\rho^{1/3}(\mathbf{r},\omega);$$

$$f_{xc}(\mathbf{r},\mathbf{r}',\omega) \text{ in local, adiabatic appr. (ALDA)} = \frac{4K}{9}\rho^{-2/3}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$$

$\boxed{\chi_S(\mathbf{r},\mathbf{r}') \text{ from first order perturbation theory:}}$

Perturbation $\delta v_S(\mathbf{r})$ induces changes in the orbitals:

$$\delta\varphi_i(\mathbf{r}) = \sum_{p \neq i} \frac{-\langle \varphi_i | \delta v_s | \varphi_p \rangle}{\varepsilon_p - \varepsilon_i} \varphi_p(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{i=1}^{H} n_i \varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r})$$

$$\delta\rho(\mathbf{r}) = \sum_{i=1}^{H} n_i \left(\varphi_i(\mathbf{r}) \delta\varphi_i^*(\mathbf{r}) + \delta\varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r}) \right)$$

$$= \sum_{i=1}^{H} \sum_{p \neq i} \left[\frac{-\varphi_i(\mathbf{r}) \langle \varphi_i | \delta v_s | \varphi_p \rangle^* \varphi_p^*(\mathbf{r})}{\varepsilon_p - \varepsilon_i} + \frac{-\langle \varphi_i | \delta v_s | \varphi_p \rangle \varphi_p(\mathbf{r}) \varphi_i^*(\mathbf{r})}{\varepsilon_p - \varepsilon_i} \right]$$

convention for summation indices:

$i, j, k, l,$ .... indices for occupied orbitals, $\leq N$

$a, b, c, d,$ ....indices for unoccupied orbitals, $> N$

$p, q, r, s,$ .... general indices

occ.- occ. pairs drop out

$$\delta\rho(\mathbf{r}) = \sum_{i=1}^{H} \sum_{p \neq i} \left[\frac{-\varphi_i(\mathbf{r}) \left\langle \varphi_i \middle| \delta v_s \middle| \varphi_p \right\rangle^* \varphi_p^*(\mathbf{r})}{\varepsilon_p - \varepsilon_i} + \frac{-\left\langle \varphi_i \middle| \delta v_s \middle| \varphi_p \right\rangle \varphi_p(\mathbf{r}) \varphi_i^*(\mathbf{r})}{\varepsilon_p - \varepsilon_i} \right]$$

if i and p are both occupied orbitals, e.g. k and l, then:

for $i = k, p = l$: $\dfrac{-\varphi_k \varphi_l^* V_{s,lk}}{\varepsilon_l - \varepsilon_k} + \dfrac{-V_{s,kl} \varphi_l \varphi_k^*}{\varepsilon_l - \varepsilon_k}$

for $i = l, p = k$: $\dfrac{-\varphi_l \varphi_k^* V_{s,kl}}{\varepsilon_k - \varepsilon_l} + \dfrac{-V_{s,lk} \varphi_k \varphi_l^*}{\varepsilon_k - \varepsilon_l}$

CANCEL!

Only p-values with p unocc. survive

Definition of χ_S

$$\delta\rho(\mathbf{r}) = \sum_{i=1}^{H} \sum_{a>H} \left[\frac{-\varphi_i(\mathbf{r})\langle\varphi_i|\delta v_s|\varphi_a\rangle^* \varphi_a^*(\mathbf{r})}{\varepsilon_a - \varepsilon_i} + \frac{-\langle\varphi_i|\delta v_s|\varphi_a\rangle \varphi_a(\mathbf{r})\varphi_i^*(\mathbf{r})}{\varepsilon_a - \varepsilon_i} \right]$$

$$= \int d\mathbf{r}' \sum_{i\in occ} \sum_{a\in unocc} \left[\frac{-\varphi_i(\mathbf{r})\varphi_i(\mathbf{r}')\varphi_a^*(\mathbf{r}')\varphi_a^*(\mathbf{r})}{\varepsilon_a - \varepsilon_i} + \frac{-\varphi_i^*(\mathbf{r}')\varphi_a(\mathbf{r}')\varphi_a(\mathbf{r})\varphi_i^*(\mathbf{r})}{\varepsilon_a - \varepsilon_i} \right] \delta v_s(\mathbf{r}')$$

$$\equiv \chi_S(\mathbf{r},\mathbf{r}')$$

χ_S comes straightforwardly from 1st order pert. theory;
only KS orbitals and orbital energies needed

Time-dependent case (linear response =1st order Pert. Th.)

$$\delta\rho(\mathbf{r},t) = \sum_i n_i \Big(\psi_i(\mathbf{r},t)\delta\psi_i^*(\mathbf{r},t) + \psi_i^*(\mathbf{r},t)\delta\psi_i(\mathbf{r},t) \Big)$$

Suppose perturbation $\delta v_{ext}(\mathbf{r},t)$ with single frequency ω:

$$\delta\rho(\mathbf{r},\omega) = \sum_i^{occ} \sum_a^{virt} n_i \psi_i(\mathbf{r})\psi_a(\mathbf{r}) \Big(X_{ia}^{\omega} + X_{ia}^{-\omega*} \Big) e^{-i\omega t} + c.c.$$

$$X_{ia}^{\omega} = \frac{\langle \psi_i(\mathbf{r}) | \delta v_s(\mathbf{r},\omega) | \psi_a(\mathbf{r}) \rangle}{\varepsilon_i - \varepsilon_a + \omega} \equiv X_{ia} \qquad X_{ia}^{-\omega*} \equiv Y_{ia}$$

$$\delta v_s(\mathbf{r},\omega) = \delta v_{ext}(\mathbf{r},\omega) + \underbrace{\int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|} + \delta v_{xc}[\delta\rho](\mathbf{r},\omega)}_{v_{induced}}$$

$$\delta v_s(\mathbf{r},\omega) = \delta v_{ext}(\mathbf{r},\omega) + \underbrace{\int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|} + \delta v_{xc}[\delta\rho](\mathbf{r},\omega)}_{\color{red}v_{induced}(\mathbf{r},\omega)}$$

"uncoupled": $v_{ind} = 0$

"coupled":   Coulomb part: $\delta v_{Coul}(\mathbf{r},\omega) = \int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|}$

XC part: $\delta v_{xc}(\mathbf{r},\omega) = \int d\mathbf{r}' \underbrace{\frac{\delta v_{xc}(\mathbf{r},\omega)}{\delta\rho(\mathbf{r}',\omega)}}_{\uparrow} \delta\rho(\mathbf{r}',\omega)$

$$f_{xc}(\mathbf{r},\mathbf{r}',\omega)$$

usually adiabatic LDA (no ω dependence)

for XC kernel $f_{xc}(\mathbf{r},\mathbf{r}',\omega)$

Shortcut to matrix equations for excitation energies

Put in matrix form with basis sets:

$$\delta\rho(\mathbf{r},\omega) \rightarrow \delta P_{ia}(\omega) \rightarrow \delta\mathbf{P}(\omega) \; \textit{density perturb.} \quad \text{occ.unocc supervector}$$

$$\Pi(\omega)_{ia,jb} \rightarrow \textit{response + coupling} \; \text{occ.unocc} \times \text{occ.unocc supermatrix}$$

$$\delta v_{ia}(\omega) \rightarrow \textit{external perturb. potential} \quad \text{occ.unocc supervector}$$

$$\delta\mathbf{P}(\omega) = \Pi(\omega)\delta\mathbf{V}(\omega) \; \textit{density response due to external perturb. field}$$

$$\Pi(\omega)^{-1}\delta\mathbf{P}(\omega) = \delta\mathbf{V}(\omega)$$

$\Pi(\omega)^{-1}$ often has structure $(\mathbf{K} - \omega\mathbf{1})$

Then $(\mathbf{K} - \omega\mathbf{1})\delta\mathbf{P}(\omega) = \delta\mathbf{V}(\omega)$ is solvable for $\delta\mathbf{V}(\omega) = 0$ (no perturb.)

when $\det\{\mathbf{K} - \omega\mathbf{1}\} = 0$, or at eigenvalues of $\mathbf{K}$: $\mathbf{K}\delta\mathbf{P}_i = \omega_i\delta\mathbf{P}_i$:

Excitation energies!

A system can have free oscillations $\delta\mathbf{P}_i$ ("response") without perturbation at its eigenfrequencies $\{\omega_i\}$

Leads to TDKS (cf. TDHF) equations, dimension $n_{occ}n_{virt} \times n_{occ}n_{virt}$:

$$\left(\mathcal{E}^2 + 2\mathcal{E}^{\frac{1}{2}}\mathbf{K}\mathcal{E}^{\frac{1}{2}} - \omega^2\right)\underbrace{\mathcal{E}^{-\frac{1}{2}}(\mathbf{X}+\mathbf{Y})}_{\mathbf{F}} = \delta\mathbf{V}^{ext}(\omega)$$

Cf. χ^{-1} . $\delta\rho$ $=$ δv

$$\delta\mathbf{V}_{ia}^{ext} = \left\langle \psi_i(\mathbf{r}) \left| v_{ext}(\mathbf{r},\omega) \right| \psi_a(\mathbf{r}) \right\rangle$$

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

$$\sum_{jb} \mathbf{K}_{ia,jb}(\mathbf{X}+\mathbf{Y})_{jb} = \left\langle \psi_i(\mathbf{r}) \left| v_{ind} \right| \psi_a(\mathbf{r}) \right\rangle$$

Inhomogeneous equation ($\delta\mathbf{V}^{ext}(\omega) \neq 0$):

at each ω: $\mathbf{F}(\omega) \rightarrow \delta\rho(\mathbf{r},\omega) \rightarrow$ polarizability $\alpha(\omega)$ etc.

Excitation energies: $\delta V^{ext} = 0$

$$\left(\mathcal{E}^2 + 2\mathcal{E}^{\frac{1}{2}} \mathbf{K} \mathcal{E}^{\frac{1}{2}} - \omega^2 \right) \mathbf{F} = \delta \mathbf{V}^{ext}(\omega) = 0$$

Homogeneous linear equations ($\delta \mathbf{V}^{ext} = 0$):
eigenfrequencies of system (excitation energies) are solutions of

$$\left(\mathcal{E}^2 + 2\mathcal{E}^{\frac{1}{2}} \mathbf{K} \mathcal{E}^{\frac{1}{2}} - \omega^2 \right) \mathbf{F} = 0 \ \text{or} \ \left(\mathcal{E}^2 + 2\mathcal{E}^{\frac{1}{2}} \mathbf{K} \mathcal{E}^{\frac{1}{2}} \right) \mathbf{F} = \omega^2 \mathbf{F}$$

⇑

Excitation energies!

Ingredients: orbital energies ε_i, ε_a
orbital shapes ψ_i, ψ_a
xc kernel f_{xc}

So we need good orbital shapes and good orbital energies.
But: 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*"

Orbital energies of occupied orbitals:

Exact Kohn-Sham:

- HOMO orbital energy exactly $-I_0$ (ionization en. to ion ground st.)
  because of asymptotic density behavior
- upper valence orbitals: very close to ionization energies (~ 0.1 eV)
- core orbitals: still good, too high lying by $10 - 20$ eV

LDA, GGA:

- all orbital energies are shifted up by a molecule-dependent constant
of ca. $4 - 6$ eV

Gritsenko, Baerends: *JCP* **116** (2002) 1760 (with Chong);
        JCP 117 (2003) 9154; JCP 119 (2003) 1937 (with Braïda);
        JCP 120 (2004) 8364; JCP

v_{xc}^{hole} and the interpretation of orbital energies

1°. Long range (asymptotic, $r \to \infty$) behavior

$$-\frac{1}{2}\nabla^2 = -\frac{1}{2}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}(\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \varphi^2}\right]$$

$$= -\frac{1}{2}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right] + \frac{1}{r^2}D_\theta + \frac{1}{r^2}D_\varphi$$

Consider limit $r \to \infty$ of KS equation $\left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right)\psi_i = \varepsilon_i\psi_i$

$$-\frac{1}{2}\left[\frac{\partial^2\psi_i}{\partial r^2} + \frac{2}{r}\frac{\partial\psi_i}{\partial r}\right] + \frac{1}{r^2}D_\theta\psi_i + \frac{1}{r^2}D_\varphi\psi_i + v_s(\mathbf{r})\psi_i = \varepsilon_i\psi_i$$

At each point $\mathbf{r}$ this must be an identity.

At $|\mathbf{r}| \to \infty$ all terms are negligible compared to:

$$-\frac{1}{2}\frac{\partial^2\psi_i}{\partial r^2} + v_s(\infty)\psi_i = \varepsilon_i\psi_i$$

So asymptotic solution is $\psi_i \sim e^{-\sqrt{-2(\varepsilon_i - v_s(\infty))}\ r}$

All potentials in v_s go to 0: $\psi_i \sim e^{-\sqrt{-2\varepsilon_i}\ r}$

Long range behavior

So asymptotic solution is $\psi_i \sim e^{-\sqrt{-2\left(\varepsilon_i - v_s(\infty)\right)}\ r}$

All potentials in v_s go to 0: $v_s(\infty) = 0, \quad \psi_i \sim e^{-\sqrt{-2\varepsilon_i}\ r}$

Each orbital has its own exponential decay, so density decays as

slowest orbital density decay, i.e. HOMO: $\rho(\mathbf{r}) \sim e^{-2\sqrt{-2\varepsilon_H}\ r}$

Katriel-Davidson (1980): density decays like $e^{-2\sqrt{2I}\ r}$

Conclusion: $\varepsilon_H = -I$

Now take anion: LUMO now occup., slowest decay

$$\varepsilon_L(M^-) = -I(M^-) = -A(M)$$

$$I(M) = E_0^{N-1} - E_0^N \qquad A(M) = E_0^N - E_0^{N+1}$$

$$I(M^-) = E_0^N - E_0^{N+1} = A(M)$$

KS and HF orbital energies and VIPs for H $_2$O

H$_2$O	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, Gritsenko, Baerends, *JCP* **116** (2002) 1760		

CO : KS and HF orbital energies and VIPs

CO	MO	HF $-\varepsilon_k$	KS $-\varepsilon_k$	Expt. I_k	$I_k - (-\varepsilon_k)$	$\sqrt{\varepsilon_N - \varepsilon_k}$
	5σ	15.10	14.01	14.01	0.00	
	1π	17.43	16.77	16.91	0.14	
	4σ	21.90	19.33	19.72	0.39	
Average Dev.		1.26	0.18			
	3σ	41.41	34.69	38.3	3.61	4.54
	2σ	309.13	278.83	296.21	17.38	16.27
	1σ	562.32	519.71	542.55	22.84	22.49
Average Dev.		11.93	14.61			

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

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

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
	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	

SiO: HF, GGA-BP and KS orbital energies, expt. Ips

BP: HOMO 4.02 eV higher than $-IP$; second column: all $\varepsilon_i^{BB} - 4.02$

SiO	MO	HF $-\varepsilon_i$	GGA-BP $-\varepsilon_i$		KS $-\varepsilon_i$	Expt. I_i
	7σ	11.93	7.59	(4.02)	11.61	11.61
	2π	12.90	8.22	(12.24)	12.29	12.19
	6σ	16.63	10.83	(14.84)	14.80	14.80
AAD (val)		0.95	4.05	(0.03)	0.03	
	5σ	34.41	23.59	(27.61)	28.01	
	1π	116.22	95.82	(99.84)	101.62	
	4σ	116.20	95.61	(99.63)	101.96	
	3σ	167.88	138.95	(142.97)	145.51	
	2σ	558.69	510.48	(514.50)	518.75	
	1σ	1872.70	1783.13	(1787.15)	1802.16	

N$_2$: KS, BP and HF orbital energies and VIPs

N$_2$	MO	HF $-\varepsilon_k$	KS $-\varepsilon_k$	Expt. I_k	$I_k + \varepsilon_k$
	$3\sigma_g$	17.27	15.57	15.58	0.01
	$1\pi_u$	16.72	16.68	16.93	0.25
	$2\sigma_u$	21.21	18.77	18.75	–0.02
Average dev.		1.45	0.09		
	$2\sigma_g$	40.04	33.69	37.3	3.61
	$1\sigma_u$	426.67	389.72	409.98	20.26
	$1\sigma_g$	426.76	389.76	409.98	20.22
Average dev.		12.07	14.70		

Virtual orbital energies

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

Difference between KS and HF virtuals are consequence of
v_{xc}^{hole} in KS potential, and absence in HF exchange operator

v_{xc}^{hole} leads to good shapes and energy of KS virtuals
        (as it did for KS occupied orbitals)
-

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

NO ≈ KS σ* density

H$_2$
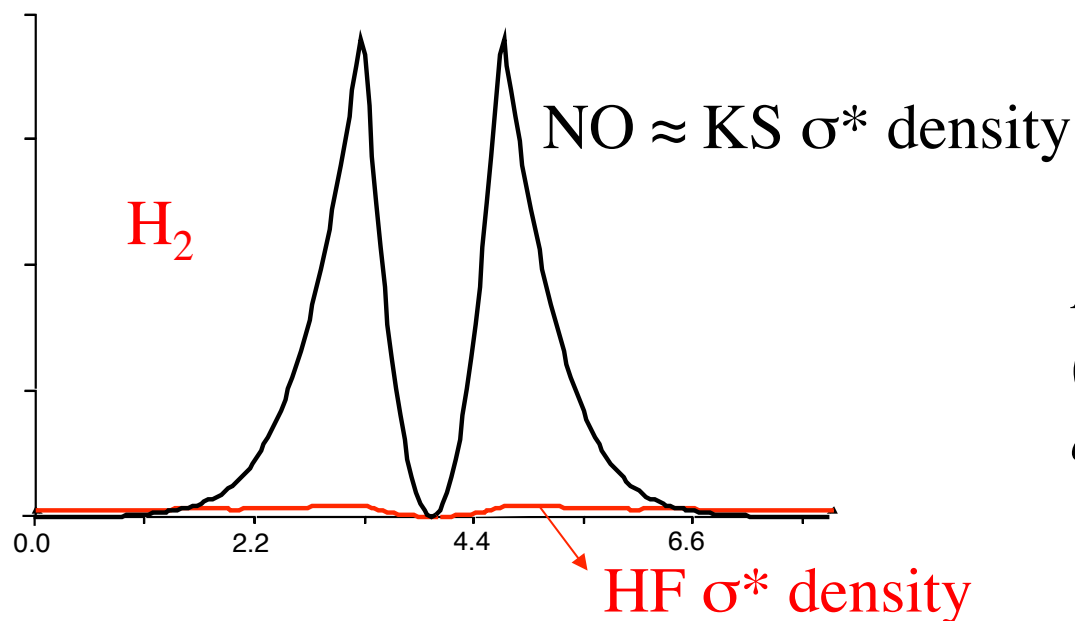
HF virtual orbitals are at (much) higher energy and (way) more diffuse than KS virtual orbitals

HF σ* density

0.0 2.2 4.4 6.6

HF, DFA and exact KS HOMO orbital energies

	HF	LDA	BLYP	KS = $-I_0$
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 $-I_0$;
HF HOMO is appr. equal to $-I_0$ (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

# 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
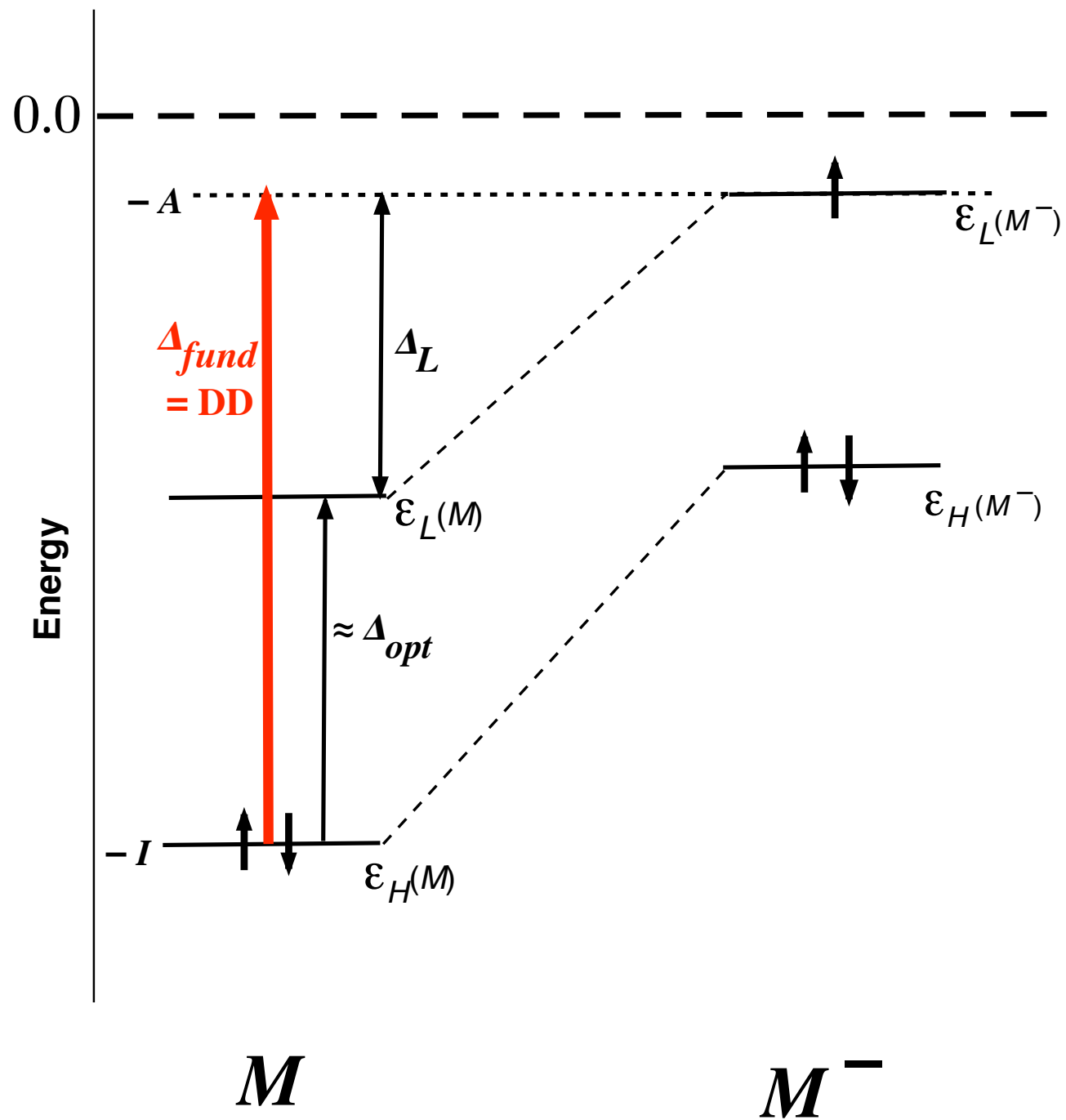
What is the meaning of a (HF) LUMO with positive orbital energy?

resonances
at specific E
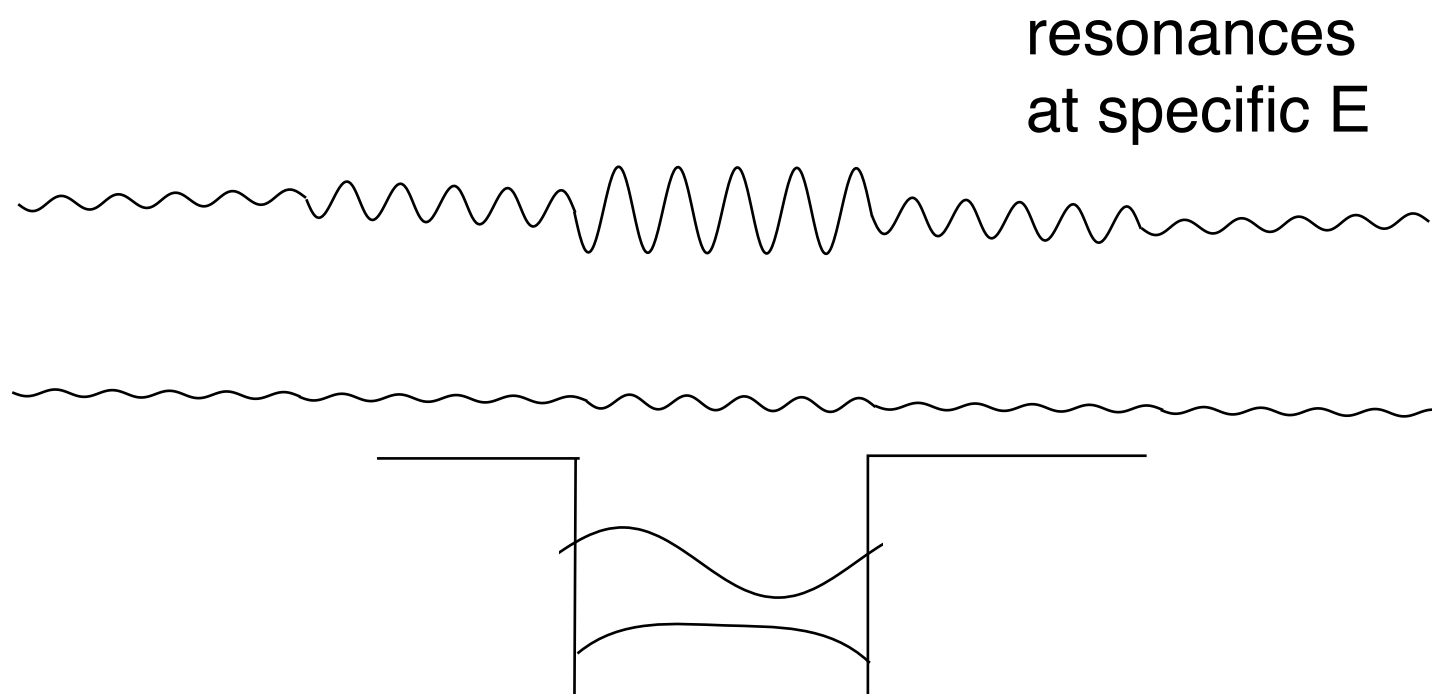
What is the meaning of HF LUMO with positive energy?

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?

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

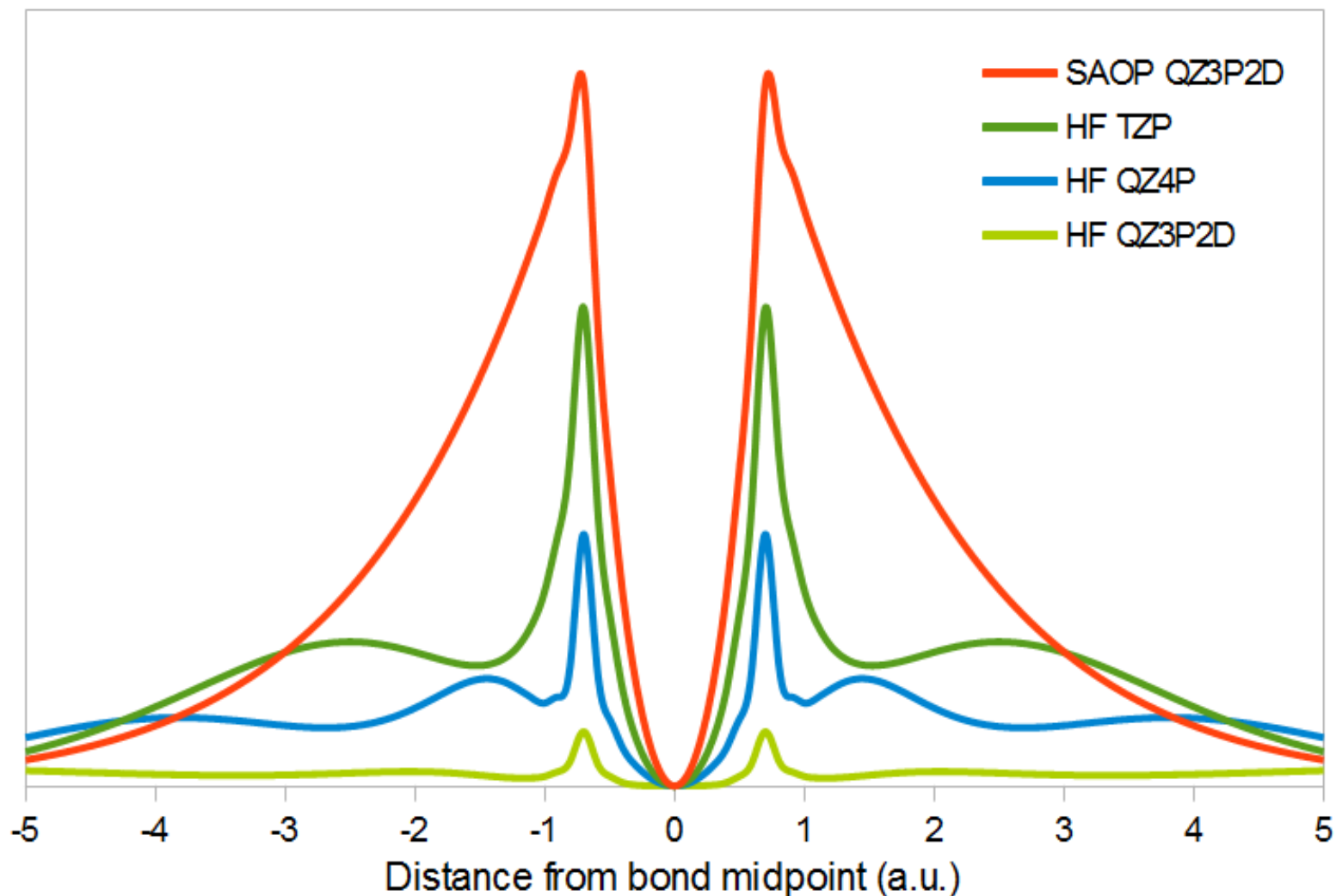Orbital energies of LUMO are arbitrary; completely determined by the basis set.
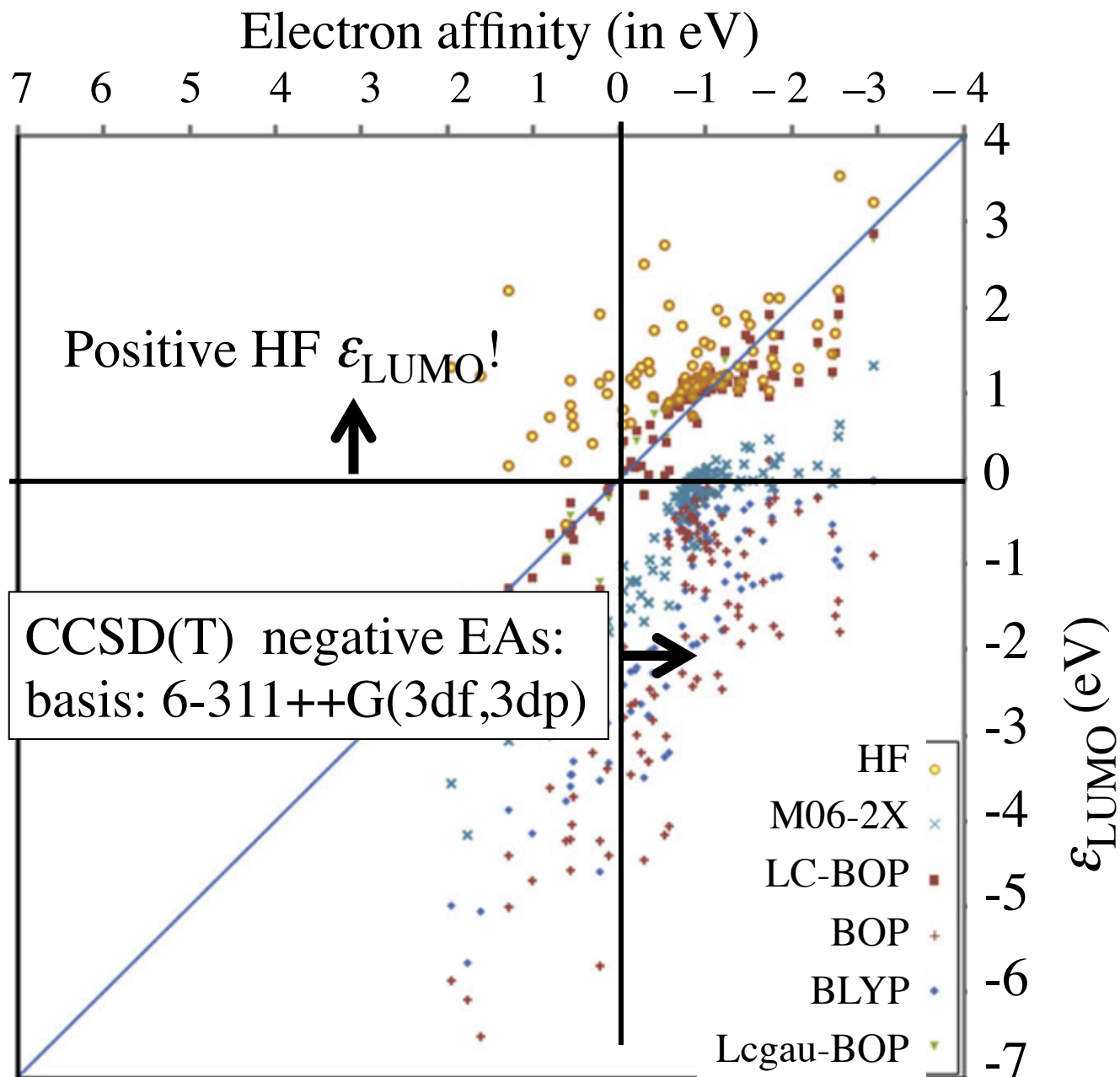
Go to zero for complete basis.

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:

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 ε_{LUMO} positive!

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

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

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

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

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

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
($\approx$ KS)	$1B_2$	1.00	–10.25	–4.18	6.07	6.09	0.02	-0.27
	$2A_2$	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	–5.92	7.92	8.17	0.24	0.00
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
	$2B_2$	1.00	–5.71	–0.07	5.64	5.64	- 0.01	-1.85
	$3A_1$	0.98	–5.71	+0.36	6.07	6.06	- 0.01	-1.74
	$3B_2$	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

Orbital energies
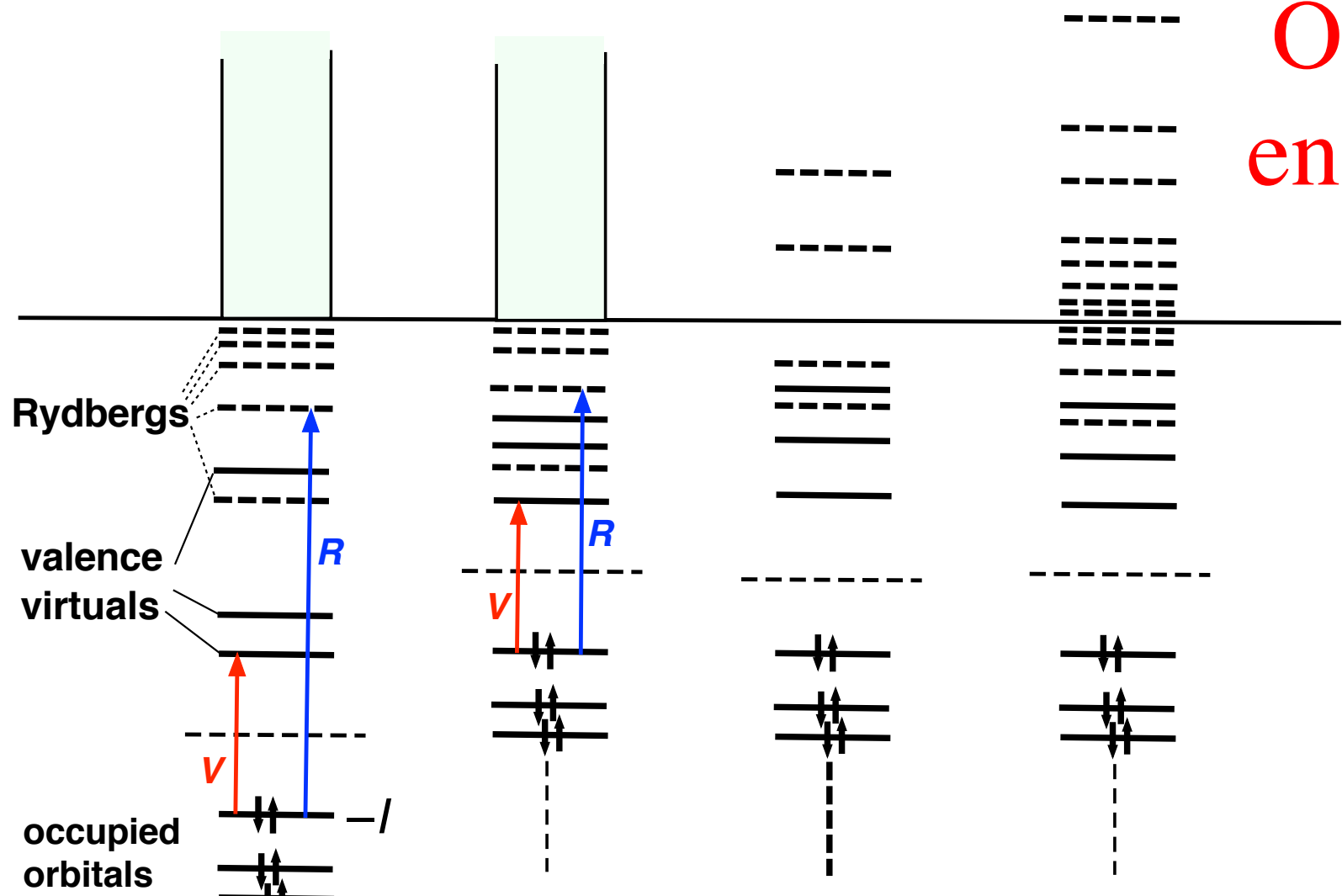
Rydbergs

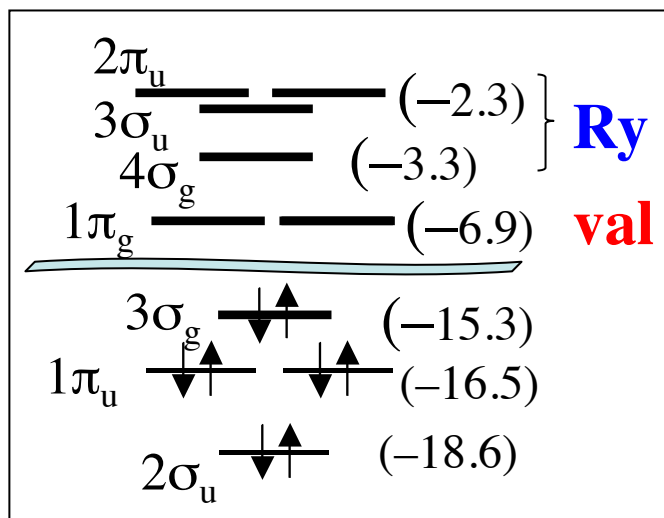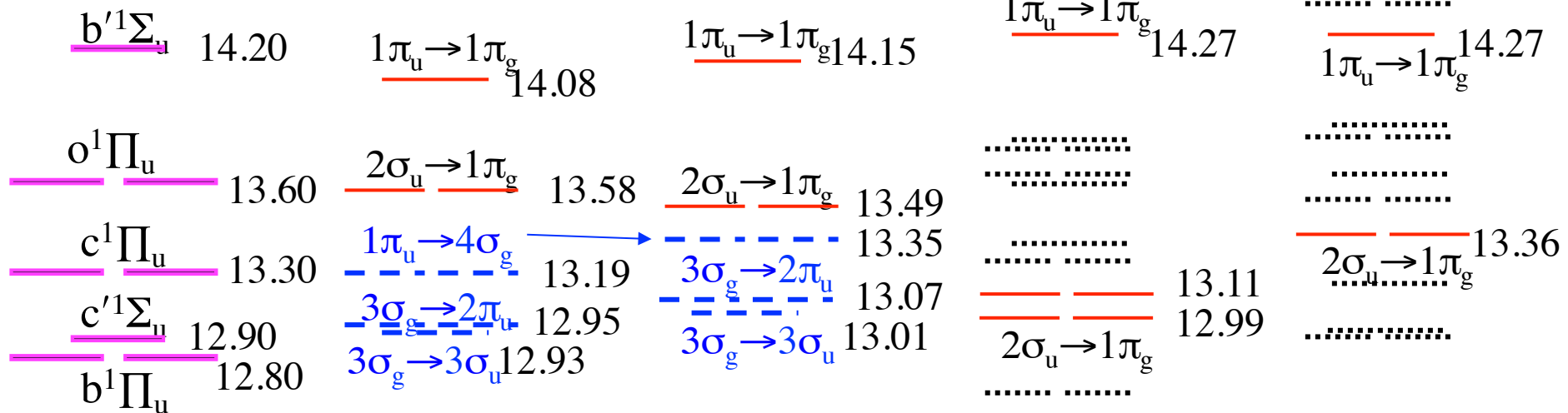valence virtuals

R

R

V

V

occupied orbitals

V

−*I*

exact KS potential

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

LDA/GGA small basis

LDA/GGA large basis

Level diagram of excited states in N$_2$

$b'^1\Sigma_u$ 14.20

$1\pi_u \rightarrow 1\pi_g$ 14.08

$1\pi_u \rightarrow 1\pi_g$ 14.15

$1\pi_u \rightarrow 1\pi_g$ 14.27

$1\pi_u \rightarrow 1\pi_g$ 14.27

$o^1\Pi_u$ 13.60

$2\sigma_u \rightarrow 1\pi_g$ 13.58

$2\sigma_u \rightarrow 1\pi_g$ 13.49

$c^1\Pi_u$ 13.30

$1\pi_u \rightarrow 4\sigma_g$ 13.19

13.35

$3\sigma_g \rightarrow 2\pi_u$ 13.07

$2\sigma_u \rightarrow 1\pi_g$ 13.36

$c'^1\Sigma_u$ 12.90

$3\sigma_g \rightarrow 2\pi_u$ 12.95

$3\sigma_g \rightarrow 3\sigma_u$ 13.01

13.11

12.99

$b^1\Pi_u$ 12.80

$3\sigma_g \rightarrow 3\sigma_u$ 12.93

$2\sigma_u \rightarrow 1\pi_g$

$2\pi_u$
$3\sigma_u$ (−2.3)
$4\sigma_g$ (−3.3)   **Ry**

$1\pi_g$ (−6.9)   **val**

$1\pi_u \rightarrow 4\sigma_g$ 11.75

$1\pi_u \rightarrow 4\sigma_g$ 11.49

$3\sigma_g$ (−15.3)

$1\pi_u$ (−16.5)

$2\sigma_u$ (−18.6)

$3\sigma_g \rightarrow 2\pi_u$ 10.51

$3\sigma_g \rightarrow 3\sigma_u$ 10.46

$3\sigma_g \rightarrow 2\pi_u$ 10.36

$3\sigma_g \rightarrow 3\sigma_u$ 10.35

EXP   SAOP   BP-GRAC   LDA   BP

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	−11.23	+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
	$1B_1$	0.84	−11.23	+1.12	12.35	9.89	-2.46	1.72
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

Pyrimidine: valence excitations (eV)

Funct.	State	Weight	ε_i	ε_a	$\Delta\varepsilon_{ia}$	ω	$\omega - \Delta\varepsilon_{ia}$	$\omega - E_{exp}$
SAOP	$1B_1$	1.00	−10.30	−6.52	3.78	3.97	0.19	0.12
($\approx$ KS)	$1A_2$	0.98	−10.30	−6.12	4.19	4.27	0.09	−0.35
	$1B_2$	0.74	−11.45	−6.52	4.93	5.57	0.64	0.45
	$2A_2$	0.98	−11.54	−6.52	5.02	5.27	0.24	−0.25
	$2B_1$	0.99	−11.54	−6.12	5.43	5.57	0.15	−0.33
	$1A_1$	0.76	−11.45	−6.12	5.33	6.44	1.12	−0.26
BP86	$1B_1$	0.99	−6.03	−2.42	3.61	3.80	0.19	−0.05
	$1A_2$	0.99	−6.03	−2.07	3.96	4.04	0.08	−0.58
	$1B_2$	0.72	−7.41	−2.42	4.98	5.58	0.60	0.46
	$2A_2$	0.98	−7.28	−2.42	4.86	5.11	0.26	−0.41
	$2B_1$	0.99	−7.28	−2.07	5.21	5.35	0.15	−0.55
	$1A_1$	0.71	−7.41	−2.07	5.33	6.44	1.11	−0.26

Pyrimidine: valence excitations (eV)

Funct.	State	Weight	ε_i	ε_a	$\Delta\varepsilon_{ia}$	ω	$\omega - \Delta\varepsilon_{ia}$	$\omega - E_{exp}$
TDHF	$1B_1$	0.73	–11.31	2.20	13.51	5.70	–7.81	1.85
	$1A_2$	0.29	–11.31	2.61	13.92	6.38	–7.54	1.76
	$1B_2$	0.69	–10.21	2.20	12.41	6.12	–6.29	1.00
	$2A_2$	0.63	–12.87	2.20	15.07	7.30	–7.77	1.78
	$2B_1$	0.49	–10.21	0.68	10.89	7.32	–3.57	1.42
	$1A_1$	0.52	–10.21	0.63	10.84	8.19	–2.65	1.49
M06-2X	$1B_1$	0.95	–8.92	–0.49	8.42	4.26	–4.17	0.41
	$1A_2$	0.93	–8.92	–0.15	8.77	4.75	–4.01	0.13
	$1B_2$	0.76	–9.43	–0.49	8.94	5.72	–3.22	0.60
	$2A_2$	0.91	–10.31	–0.49	9.82	5.73	–4.09	0.21
	$2B_1$	0.94	–10.31	–0.15	10.16	6.21	–3.96	0.31
	$1A_1$	0.69	–9.43	–0.15	9.28	6.37	–2.91	–0.33

Difference orbital energies in Hartree-Fock and DFT (1)

Molecular excitation

el. wavef.

hole

xc
hole
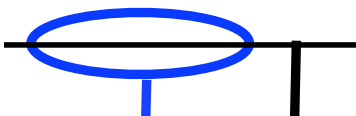
wavef.

Why is KS virtual-occup. orbital energy difference a good approx. to excitation energy?
The xc hole plays a crucial role here: it is a local hole, exerting a strong attraction at each position **r**. This attraction mimicks the attraction that in reality would occur by the "depletion hole" in orbital i where the electron came from.

The virtual orbital in KS theory is a one-electron state for an electron that feels a hole potential, i.e. is like the electron in the electron-hole pair that is created in an excitation.

Difference orbital energies in Hartree-Fock and DFT (2)

Molecular excitation

el. wavef.

ε_a

no hole attraction in HF virtual orb. energy

hole

ε_i

wavef.

Hartree-Fock det. $\Phi_0 = \left| \psi_1 \psi_2 \ldots \psi_N \right|$

Koopmans' appr. to excitation (frozen orb.):

$i \to a \quad \Phi_i^a = \left| \psi_1 \psi_2 \ldots \psi_i \psi_a \ldots \psi_N \right|$

$$E[\Phi_i^a] - E[\Phi_0] = \varepsilon_a^{HF} - \varepsilon_i^{HF} - \underbrace{J_{ia}}_{} + \underbrace{K_{ia}}_{}$$

$\underbrace{\phantom{J_{ia}}}_{\text{electron-hole attraction}}$ $\quad$ $small$

$J_{ia} = \left\langle i(1)a(2) \middle| i(1)a(2) \right\rangle$

High HF ε_a^{HF} (due to lack in Fock operator for virtual ψ_a) is "pulled down" by depletion hole (J_{ia}).

ε_a^{KS} need not be pulled down, it is already low lying due to pull by xc hole.

NB. shape of ψ_a^{HF} and ψ_a^{KS} is very different!

ψ_a^{HF} not realistic!

Compare to how TD-DFT works in EXX variant
(see Gonze-Scheffler, PRL 1999

EXX: local potential $v_x(\mathbf{r})$ appr. to KS pot. with only W_x^{KS} as xc functional (also called OPM). $v_x(\mathbf{r})$ has X hole, ψ_a is "pulled down".

TD-EXX gives kernel correction to $(\varepsilon_a - \varepsilon_i)$ for excitation energy:

$$\omega = (\varepsilon_a - \varepsilon_i) + \left\langle \varphi_i \varphi_a \left| f_{xc}^{EXX} \right| \varphi_i \varphi_a \right\rangle$$

$$= (\varepsilon_a - \varepsilon_i) + \left\langle \varphi_a \left| \hat{K}^{HF} - v_x \right| \varphi_a \right\rangle - \left\langle \varphi_i \left| \hat{K}^{HF} - v_x \right| \varphi_i \right\rangle - J_{ia} + K_{ia}$$

- 2^{d} term shifts ε_a up from (appr.) KS level ε_a^{KS} to (appr.) HF level ε_a^{HF} (because ψ_a is unoccupied!)
- 3^{d} term has little correction on ε_i ($\varepsilon_i^{KS} \approx \varepsilon_i^{HF} \approx -\mathrm{IP}_i$) anyway
- 4th term ($-J_{ia}$) provides electron-hole attraction to correct ε_a after upshift from 2d term back to $\approx \varepsilon_a^{KS}$.

- 5th term small.

TD-EXX benefits from good shape of $\psi_a^{KS\text{-}EXX}$ compared to ψ_a^{HF} !

Charge transfer excitations between two remote molecules are much too low in TDDFT. Why?
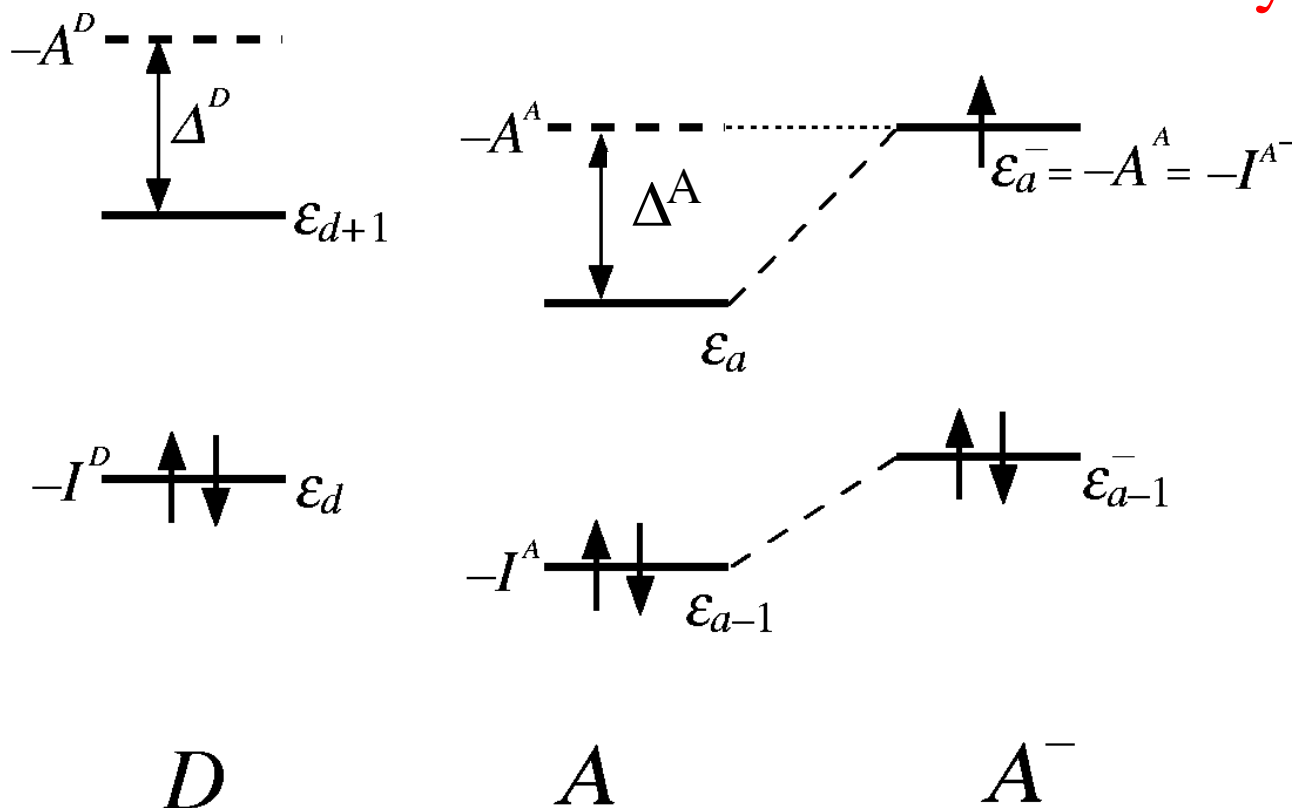
CT transition should be: $I^D - A^A - J_{da} (\approx -1/R)$

Exact KS: $\varepsilon_d = -I^D, \quad \varepsilon_a = -A^A - \Delta^A$

TDDFT gives appr. $(\varepsilon_a - \varepsilon_d) + \langle \psi_a \psi_d | f_{xc} | \psi_a \psi_d \rangle$

$I^D - A^A - \Delta^A$ ≈ 0 over all space if R large

wrong by Δ^A! $\rightarrow$ zero contrib. from kernel term

Charge transfer excitations between two remote molecules

TDDFT gives appr. $(\varepsilon_a - \varepsilon_d) + \langle \psi_a \psi_d | f_{xc} | \psi_a \psi_d \rangle \approx I^D - A^A - \Delta^A$

Now KS orbital energy difference is NOT good! Why?
Because xc hole and actual depletion hole are too different.

$v_{xc}{}^{hole}$: potential due to hole of -1 electron (is $+1$ charge) around each reference point $\rightarrow$ strongly attractive

depletion hole $-|\psi_d|^2$ is far from points **r** on A where potential is evaluated, so little stabilization should be experienced by electron from far away hole;
electron is like an *added* electron to A.
Now HF $\varepsilon_a{}^{HF} \approx -A^A$ (Koopmans) would be better:

$$\varepsilon_a^{HF} = \left\langle \psi_a \left| -\frac{1}{2}\nabla^2 + v_{nuc} + v_{Coul} + \hat{K}^{HF} \right| \psi_a \right\rangle \ (\hat{K}^{HF} \text{no hole for virtual orb.!})$$

Charge transfer excitations between two remote molecules are much too low in TDDFT. Why?

Molecular excitation
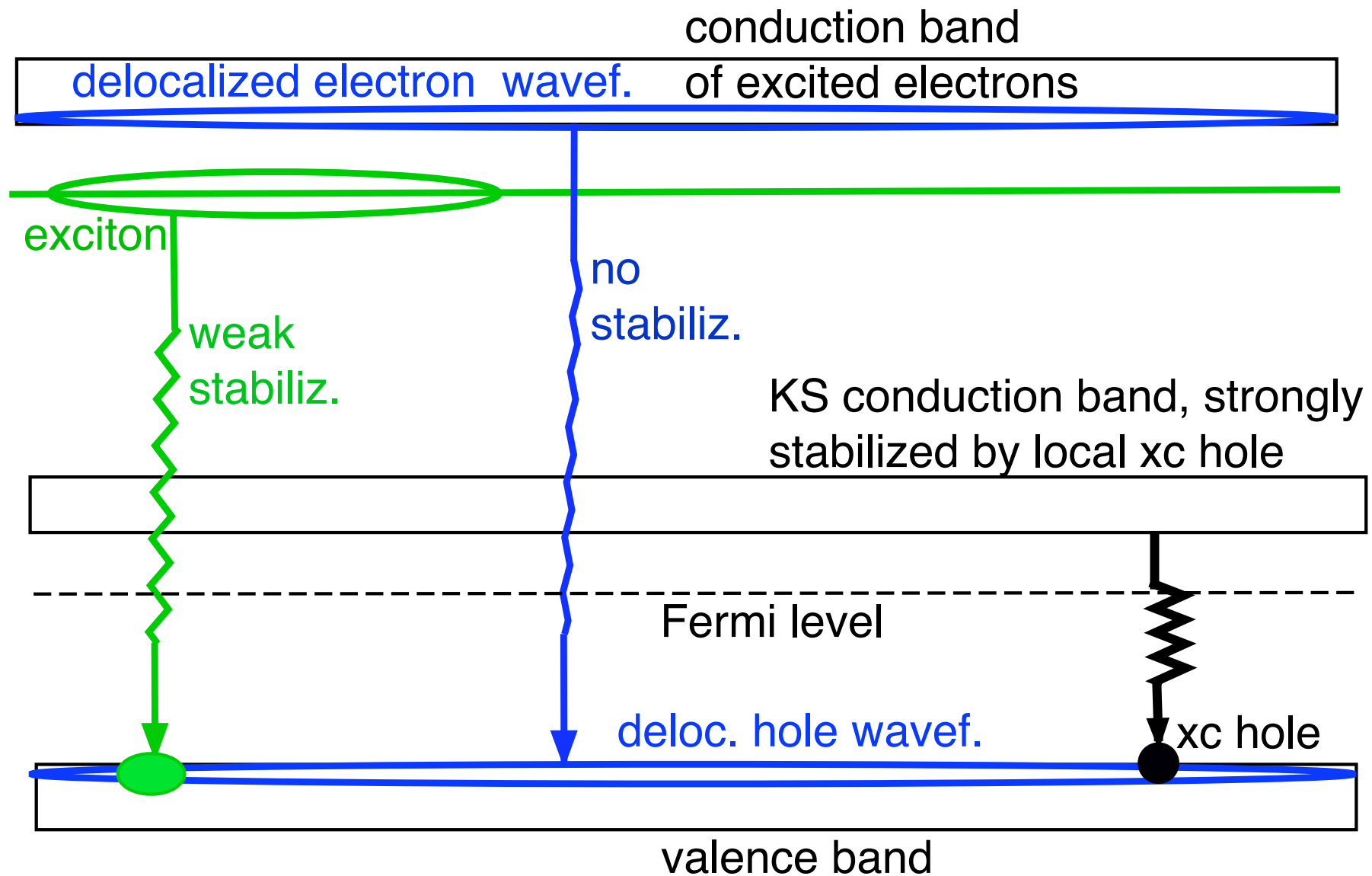
el. wavef.

hole wavef.

$\approx$

xc hole

Charge transfer excitation

transferred el. wavef.

KS LUMO stabilized

hole wavef.

$\neq$

by xc hole

Donor   Acceptor

Comment on bandgap in solids (1)

conduction band

delocalized electron wavef.   of excited electrons

exciton

no
stabiliz.

weak
stabiliz.

KS conduction band, strongly
stabilized by local xc hole

Fermi level

deloc. hole wavef.   xc hole

valence band
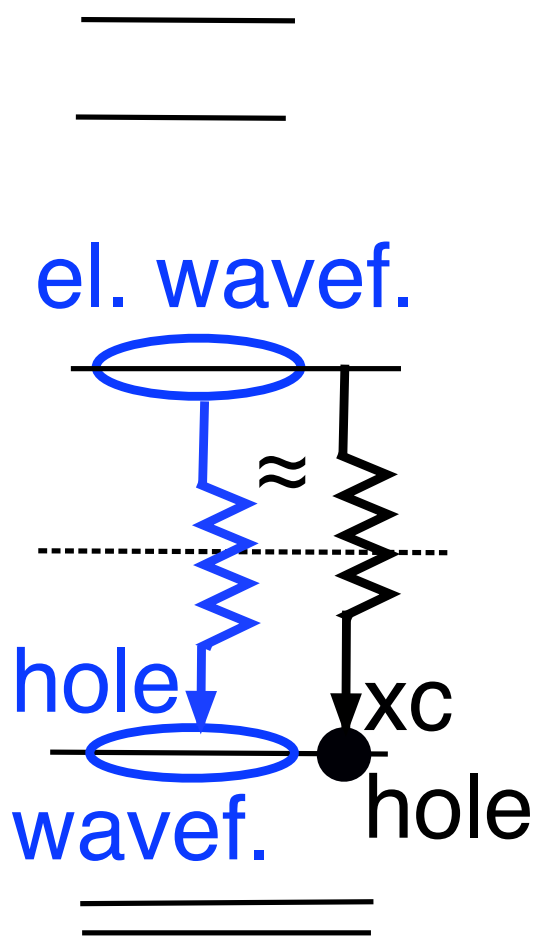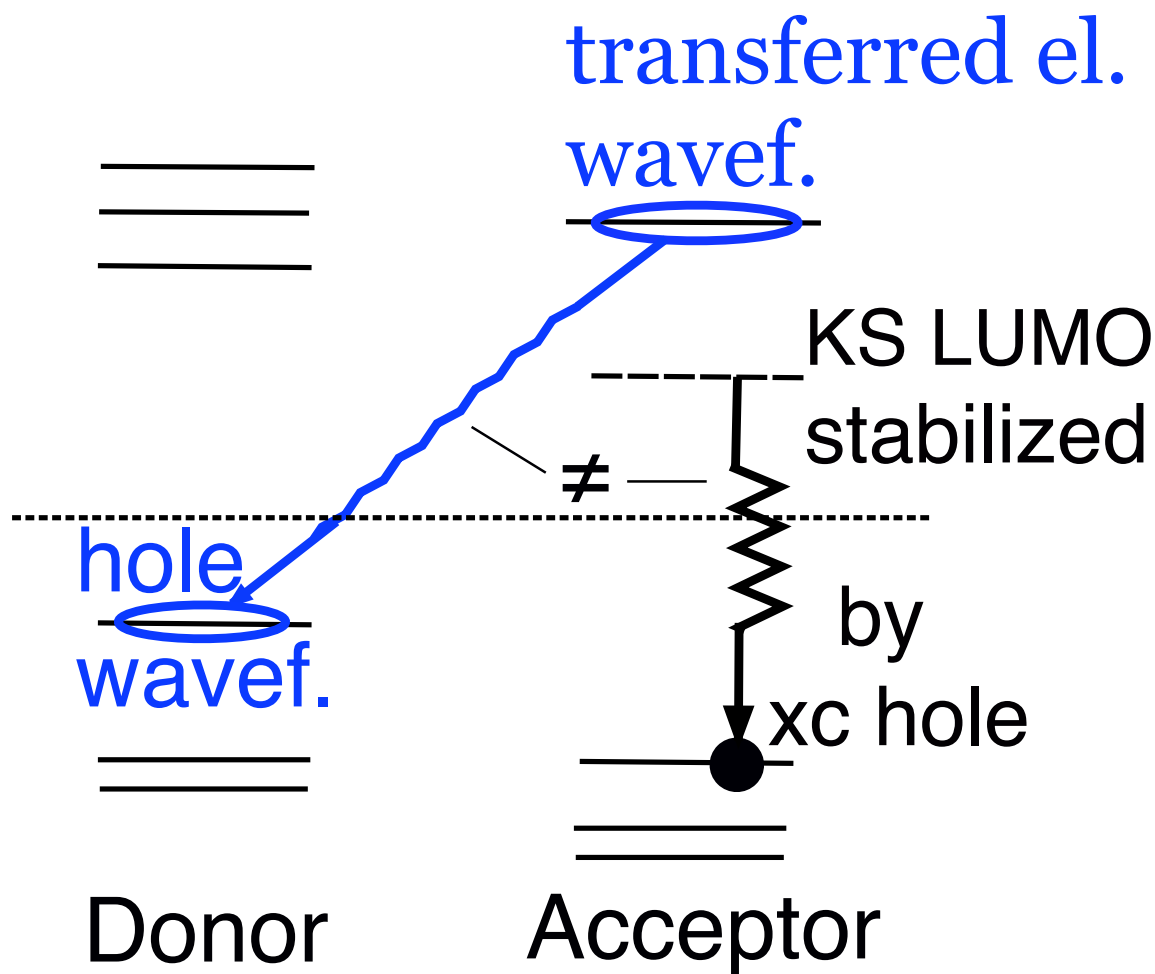
Do not expect bottom of conduction band states in DFT to be *affinity level*

Comment on bandgap in solids (2)

LDA/GGA bandgap often only 30 – 50% of the fundamental gap ($I - A$)
Surprise?
Maybe *true* KS gap will be close to ($I - A$)?
No: Godby, Schlüter, Sham 1986; Grüning, Marini, Rubio (2006):
LDA/GGA gap ≈ KS gap (as we saw for molecules!)

To be expected:
Actual hole-electron interaction is different from electron - KS xc hole
interaction:
- KS xc hole is small (~ atomic size, one unit cell in Si) -> strong pull
- fully delocalized electron and hole states: no pull
- excitons: Wannier-Mott: still diffuse electron wavefunction,
e.g. Si: Bohr radius of exciton ca. 4.3 nm ≈ 100 bohr
→ very little electron-hole stabilization
[Frenkel excitons in e.g. molecular solid may be more like molecules]

NB. explanation for solids very much like for the CT problem

References:

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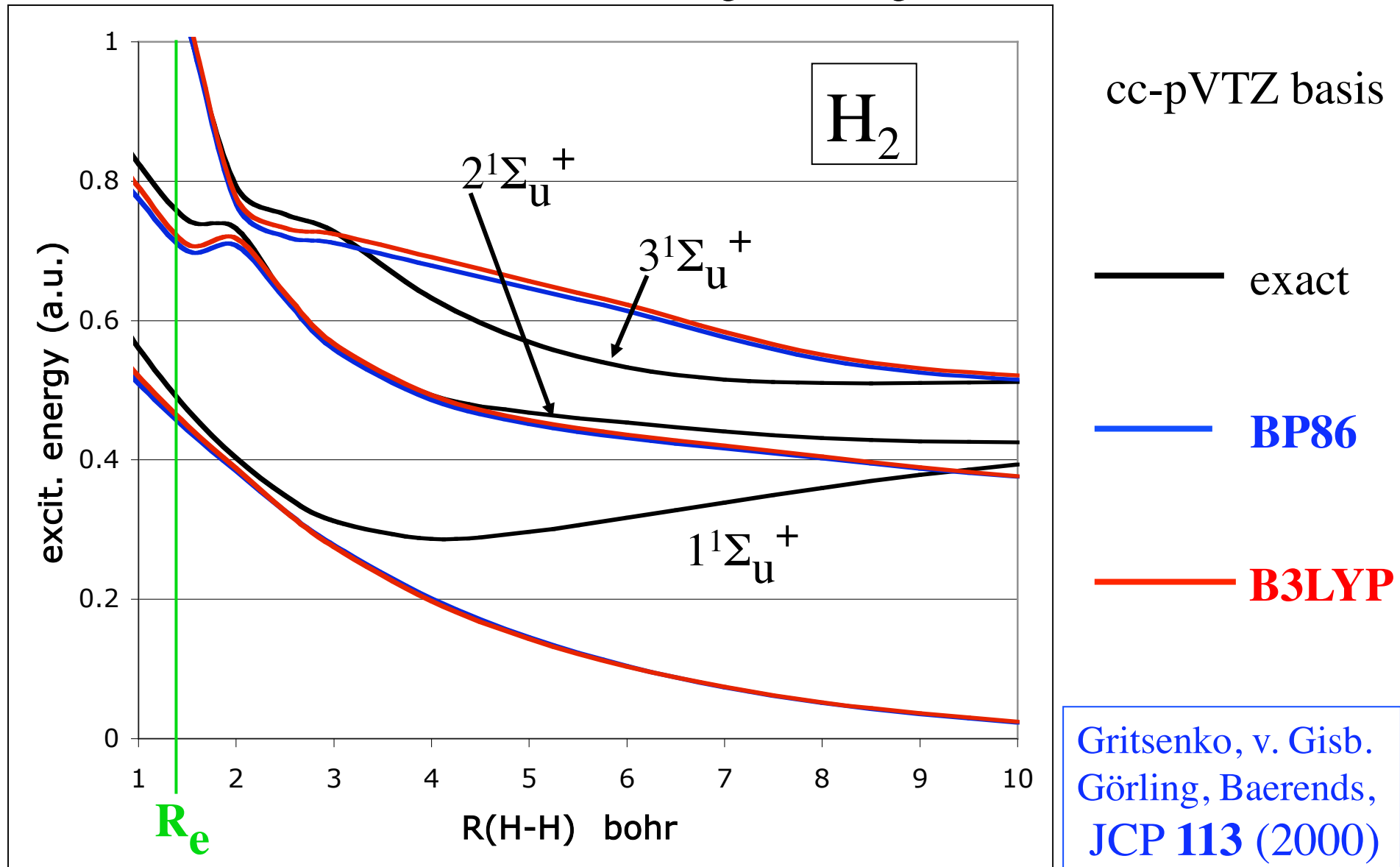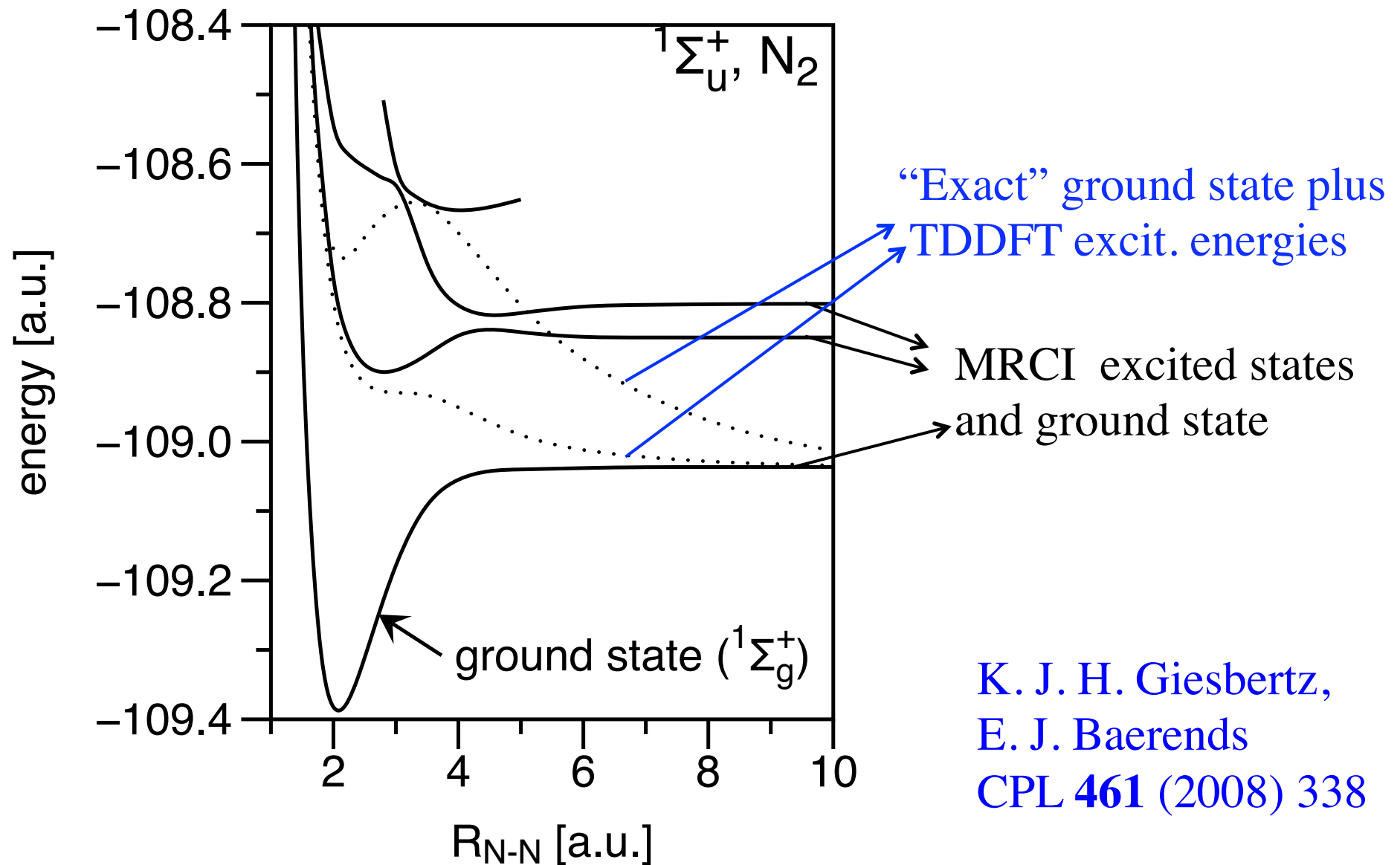J. Chem. Theor. Comp. **10** (2014) 4432

Failures of time-dependent DFT

a) Wrong Potential Energy Surface (PES) for
     bonding → antibond. excitation

b) Failure to treat doubly excited configurations

c) Too low charge transfer excitation energy

a) and c) are cases where leading term $(\varepsilon_a - \varepsilon_i)$ is
   wrong and usual kernel (ALDA) fails to correct

a) Bonding-antibond. excitation problem in TDDFT

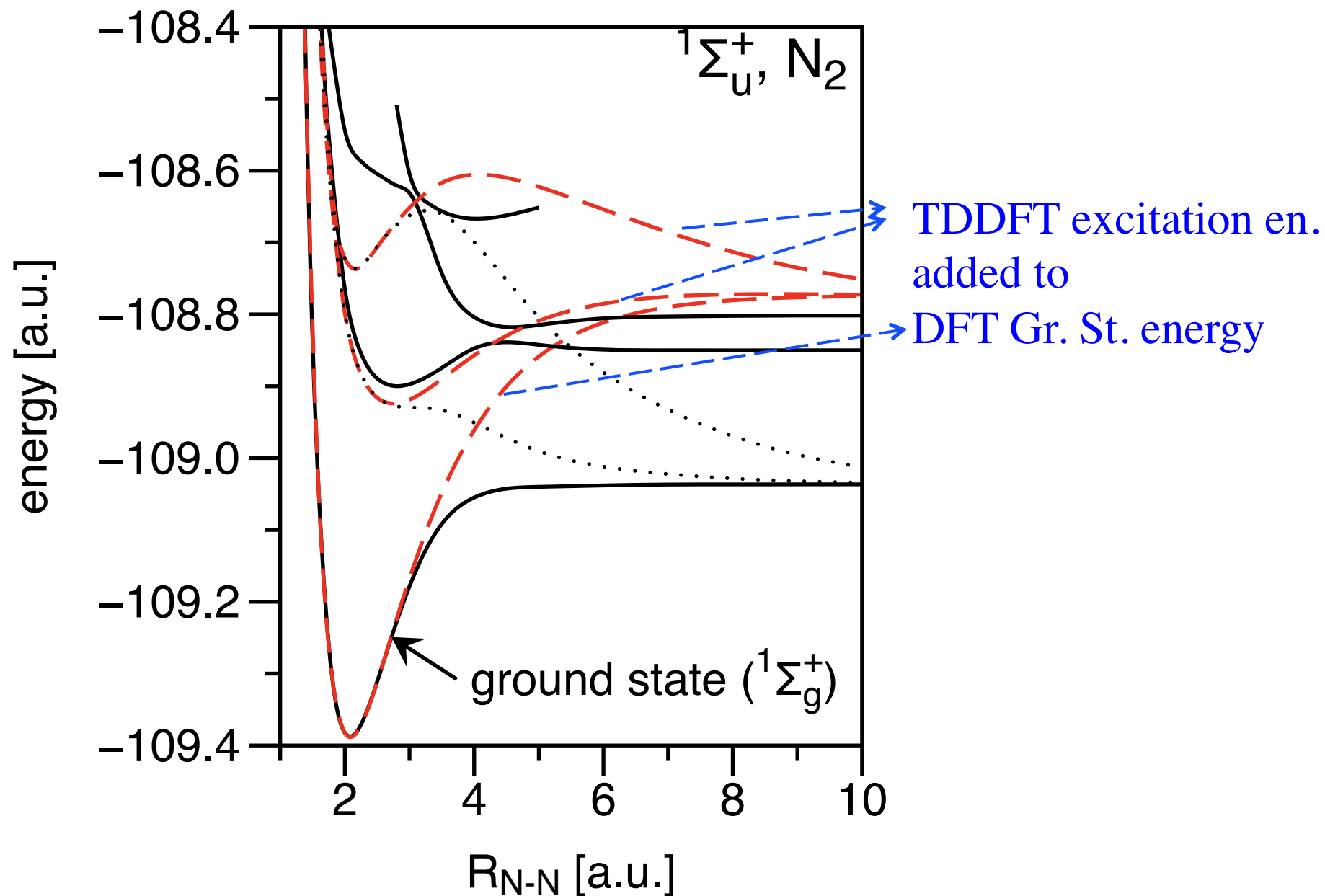$^1\Sigma_u^+$ states in H_2: lowest is $(\sigma_g)^2 \rightarrow (\sigma_g)^1(\sigma_u)^1$

cc-pVTZ basis

— exact

— BP86

— B3LYP

Gritsenko, v. Gisb. Görling, Baerends, JCP **113** (2000)

N$_2$ $^1\Sigma_u^+$ PECs: exact Gr. St. + TDDFT

$^1\Sigma_u^+$, N$_2$

"Exact" ground state plus TDDFT excit. energies

MRCI excited states and ground state

ground state ($^1\Sigma_g^+$)

K. J. H. Giesbertz, E. J. Baerends CPL **461** (2008) 338
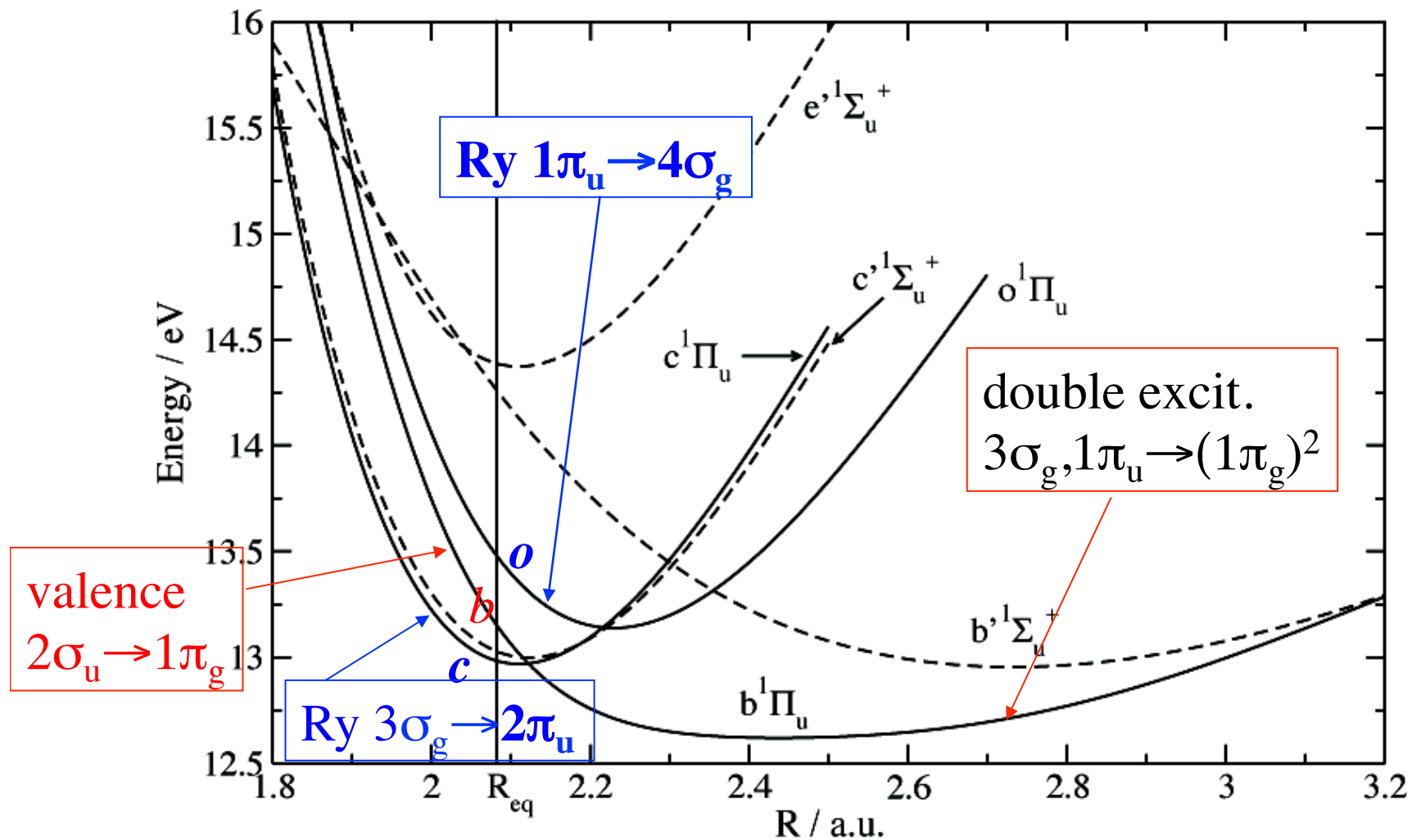
N_2 $^1\Sigma_u^+$ PECs: DFT Gr. St. + TDDFT

$^1\Sigma_u^+$, N_2

TDDFT excitation en. added to

DFT Gr. St. energy

ground state ($^1\Sigma_g^+$)

energy [a.u.]

R_{N-N} [a.u.]

b) Double excitation problem in TDDFT: $^1\Sigma_g^+$ states of H_2
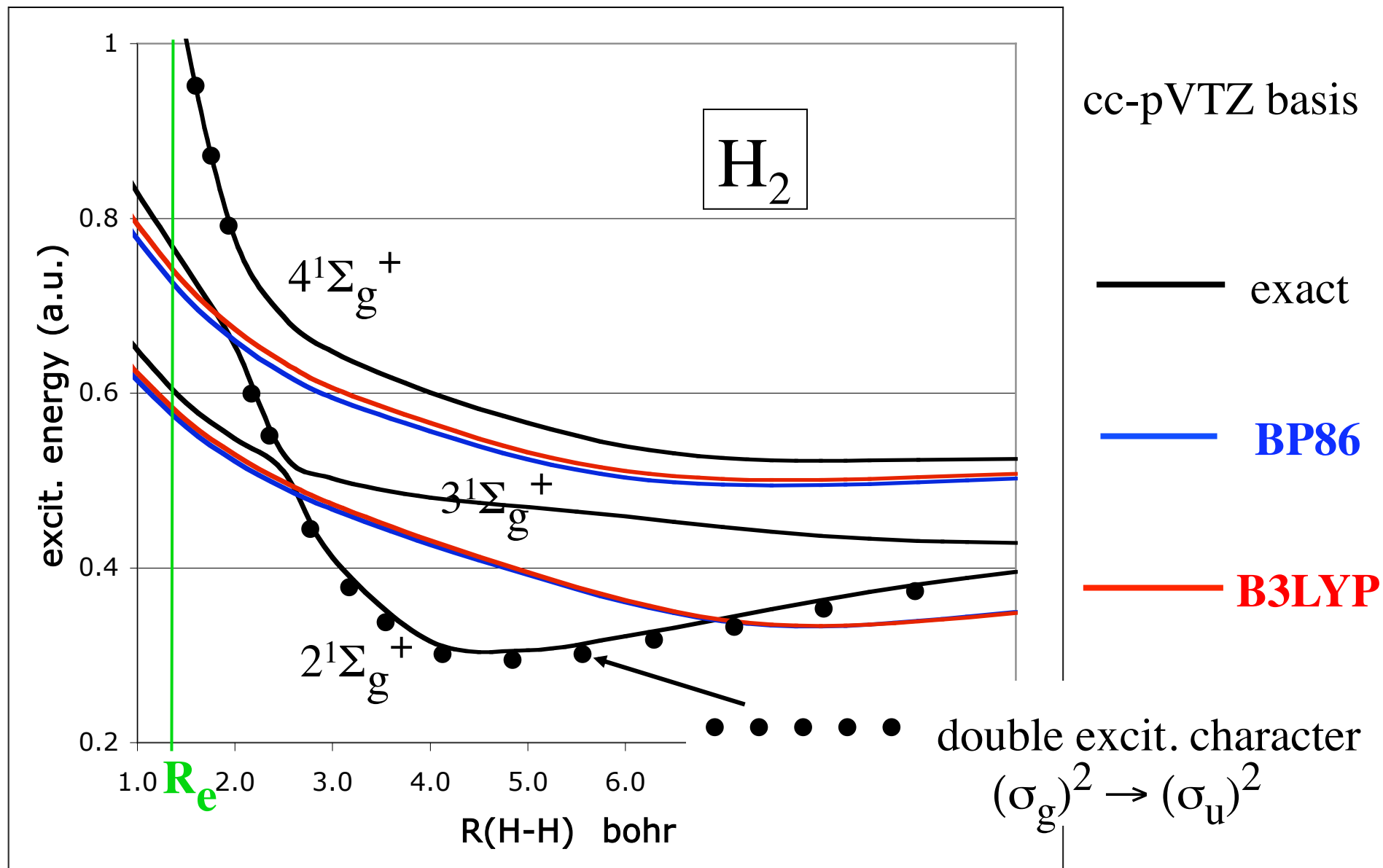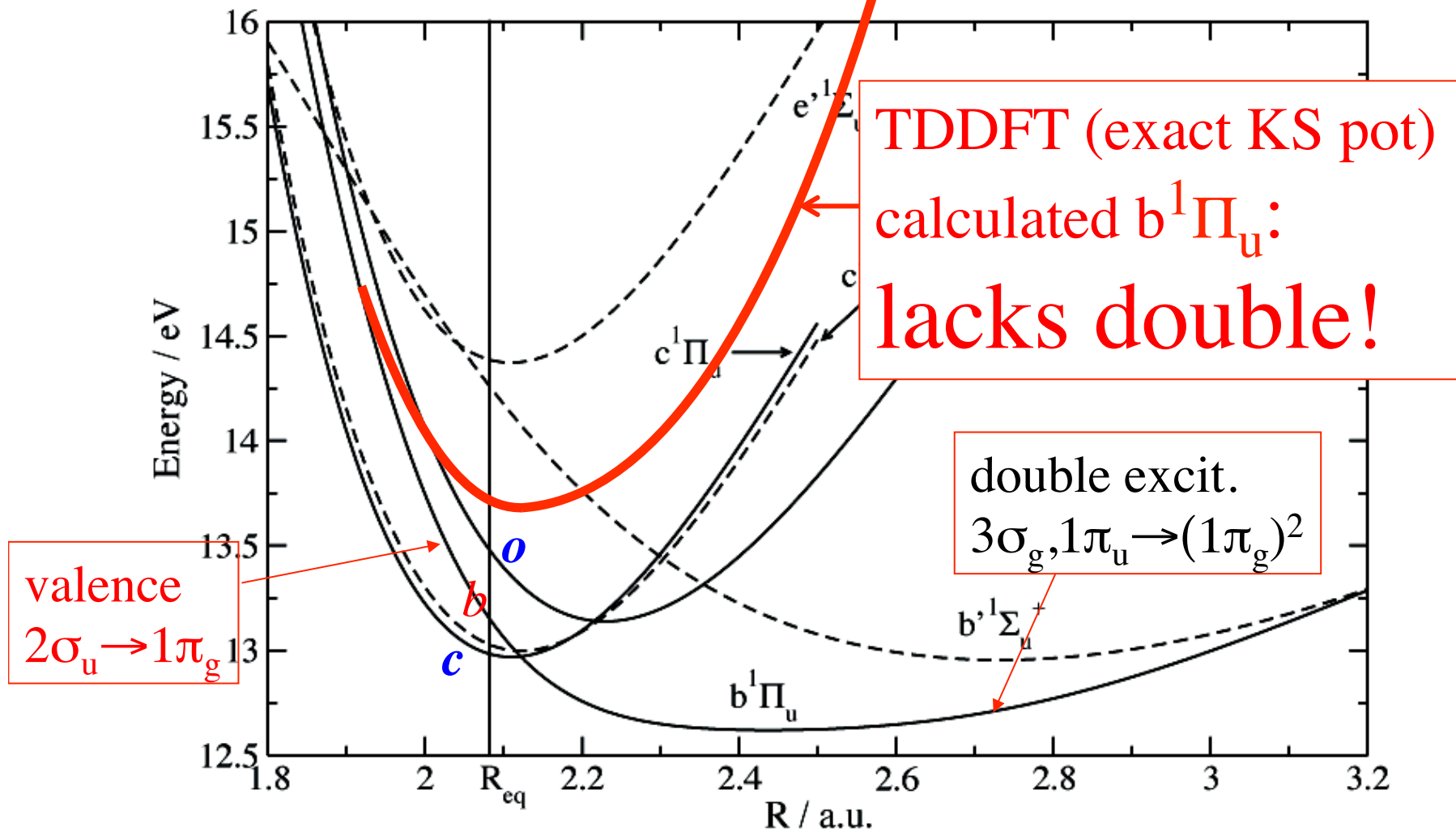
Benchmark diabatic potential energy curves from MRCI and fit to expt. (Spelsberg&Meyer, 2001)
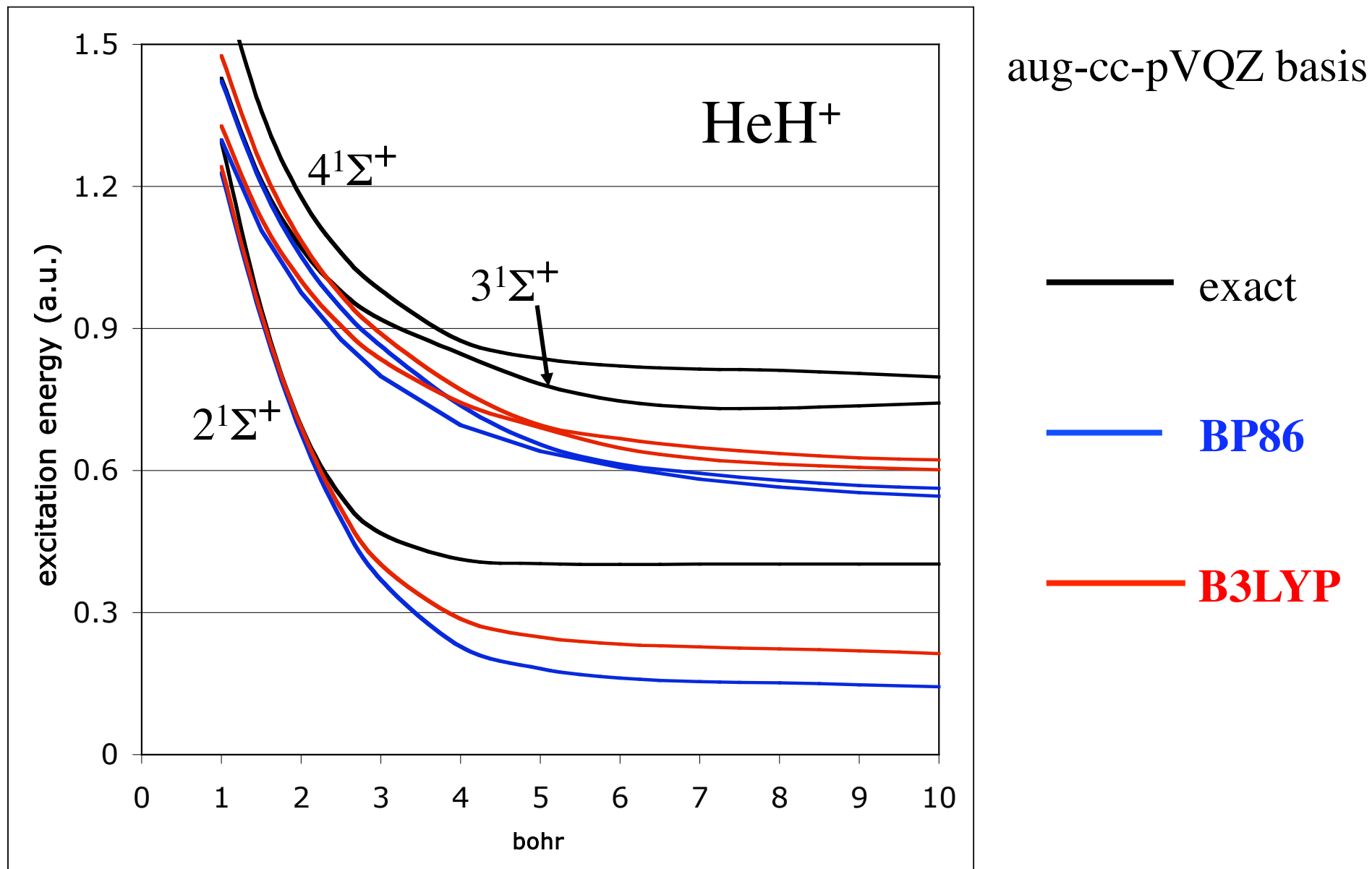
Benchmark diabatic potential energy curves from MRCI and fit to expt. (Spelsberg&Meyer, 2001)

TDDFT (exact KS pot) calculated $b^1\Pi_u$:

lacks double!

valence $2\sigma_u \to 1\pi_g$

double excit. $3\sigma_g, 1\pi_u \to (1\pi_g)^2$

TDDFT $b^1\Pi_u$ (valence $2\sigma_u \to 1\pi_g$) *above* the Rydb states because of lack of doubles: always a problem at long distance!

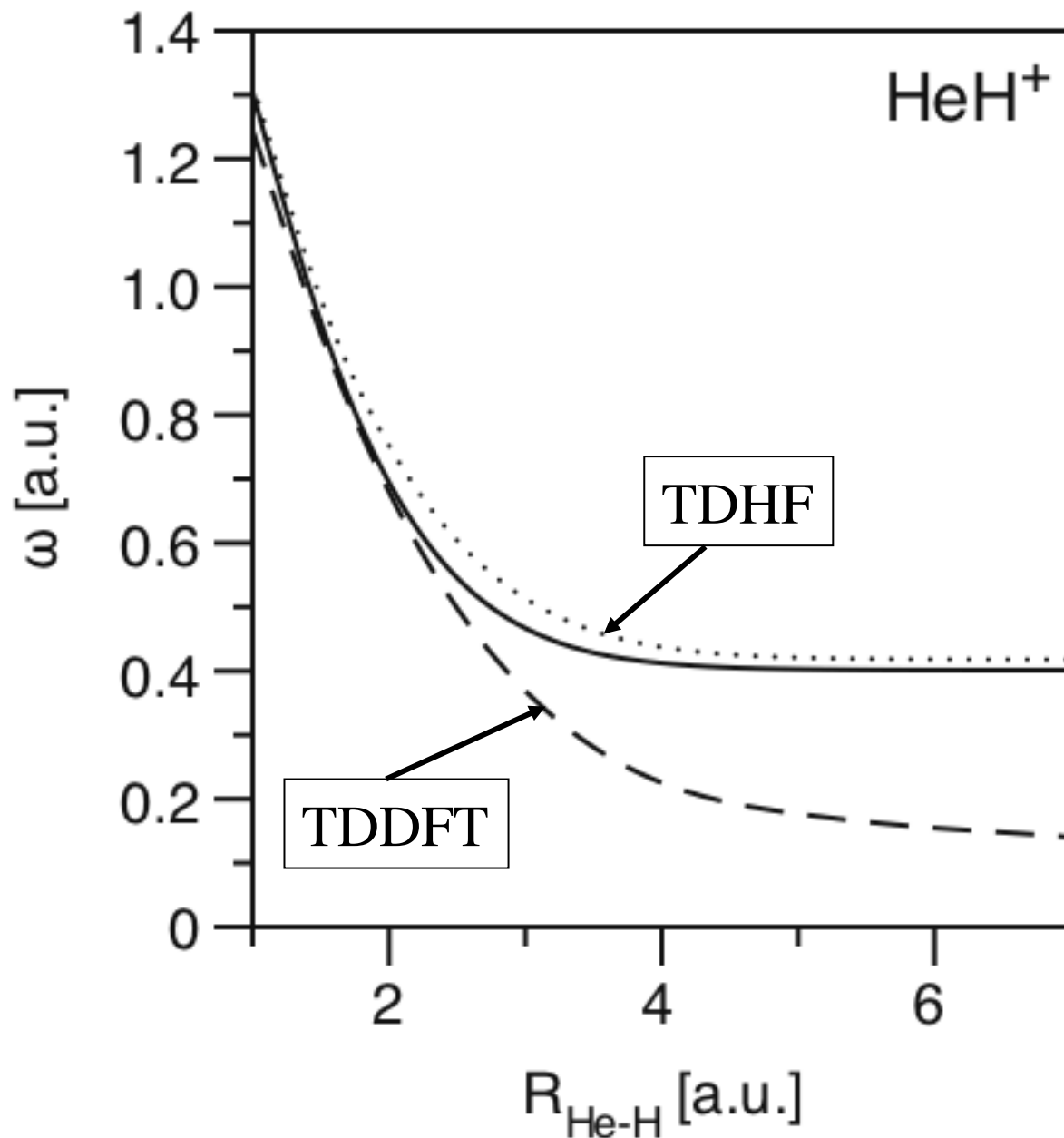# c) Charge transfer problem of TDDFT: $^1\Sigma^+$ excited st. in HeH$^+$

TDHF solves CT problem, see

Dreuw + Head-Gordon

Cf. hybrid methods

TDHF does not solve $(\sigma_g)^2 \rightarrow (\sigma_g)^1(\sigma_u)^1$ problem