Orbitals and orbital energies in DFT and TDDFT

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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 molecules 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 solids 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.

\[ E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0 \]

\( E[\Psi] \): \( E \) is \underline{functional} of \( \Psi \): assigns to each \( \Psi \) (out of the domain on which \( E[\Psi] \) is defined) a real number \( E \).

\( f(x) \): \( f(x) \) maps real (or complex) variable \( x \) on real (or complex) \( f \).

\( F[f] \): \( F[f] \) maps function \( f(x) \) on real (or complex) \( F \).
Inequality!

Var. Theorem: in particular for a non-degen. ground state $\Psi_0$:

if $\Psi \neq \Psi_0$, and $\Psi$ 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 $\Psi_0$ and local external potentials $\nu(r)$ (usually el.-nucl. pot. $\nu_{nuc}(r)$):

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

$$\rho_0(r) \leftrightarrow \nu(r) \leftrightarrow \Psi_0$$

Only ground states $\Psi_0$ and ground state densities $\rho_0$!

$\rightarrow$ if you change $\nu$, then $\Psi_0$ and $\rho_0$ must change!

- two different $\nu$’s cannot have the same $\rho_0$ (or $\Psi_0$)

- different: $\nu_2 - \nu_1 \neq C$ (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 $\rho_0$:

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

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 $\rho_0$: $\rho_0$
determines $\nu$, and therefore $\hat{H} = \hat{T} + \hat{V} + \hat{W}$

$$\hat{T} = \sum_{i=1}^{N} -\frac{1}{2} \nabla^2(i) \quad \hat{V} = \sum_{i=1}^{N} \nu(\mathbf{r}_i) \quad \hat{W} = \sum_{i<j} \frac{1}{r_{ij}}$$
Formulation of HK theorems-3

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

This energy has no obvious lower bound:
We can always look for a \( \rho_0 \) belonging to a system with a lower energy i.e. with a more attractive \( v(r) \).

HK-2: a functional with lower bound exists:
For a fixed potential \( v \), the functional
\[ E_v[\rho_0] = \langle \Psi_0[\rho_0] | \hat{T} + \hat{V} + \hat{W} | \Psi_0[\rho_0] \rangle \]
\( \text{keep } v(r) \text{ fixed} \)
assumes a minimum for the \( \rho_0 \) that corresponds to \( v(r) \).
Corollary of HK: take \( v_2 \) different from \( v_1 \)

\[
\langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle > \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle = E_1 \quad \text{because } \Psi_2 \neq \Psi_1
\]

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

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

\[
\int \rho_2 v_1 \, d\mathbf{r} + \int \rho_1 v_2 \, d\mathbf{r} > \int \rho_1 v_1 \, d\mathbf{r} + \int \rho_2 v_2 \, d\mathbf{r} \quad \text{ (HK: } \rho_2 = \rho_1 \text{ leads to contradiction)}
\]

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 \( \rho_0 \): change \( v(\mathbf{r}) \) locally to increase or decrease \( \rho \).
If in a small region the potential is decreased, \( \Delta v < 0 \), then \( \rho \) 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

\[
\int (\rho_2 - \rho_1)(v_2 - v_1) \, dr < 0, \text{ i.e. } \int \Delta \rho \Delta v \, dr < 0
\]

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 \( \Delta v \) negative, and vice versa.

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 $v(r)$ that have a degenerate ground state:

$$H \Psi_i = E_0 \Psi_i, \ i = 1, \ldots, q$$  \hspace{5pt} \text{(nondegenerate case for } q = 1)$$

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

$$\{\Psi_v\} = \left\{ \Psi \mid \Psi = \sum_{i=1}^{q} c_i \Psi_i, \ \sum_{i=1}^{q} |c_i|^2 = 1 \right\}$$

Group together ground state densities corresponding to $v(r)$ in set $N_v$:

$$\{N_v\} = \left\{ \rho(r) \mid \rho(r) = \int \left| \Psi(r, \sigma, x_2 \ldots x_N) \right|^2 \, d\sigma dx_2 \ldots dx_N, \ \Psi \in \{\Psi_v\} \right\}$$

Total sets of wavefunctions and of densities by union:

$$\{\Psi\} = \bigcup_{v \in V} \{\Psi_v\} \hspace{5pt} \text{and} \hspace{5pt} \{N\} = \bigcup_{v \in V} \{N_v\}$$
Mapping of potentials on wavefunctions on densities

\[ \{ \Psi \} = \bigcup_{v \in V} \{ \Psi_v \} \]

\[ \{ N \} = \bigcup_{v \in V} \{ N_v \} \]
properties of maps:

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

\[
C^{-1}: \{ \Psi_{v_1} \} \rightarrow v_1 \text{ is a proper map (sets } \{ \Psi_{v_1} \} \text{ and } \{ \Psi_{v_2} \} \text{ etc. are disjoint)}
\]

map \( D \): two ground states \( \Psi_1 \) and \( \Psi_2 \) coming from different potentials \( v_2 \neq v_1 + \text{constant} \) lead to different densities \( \rho_2(\mathbf{r}) \neq \rho_1(\mathbf{r}) \) (same argument as before) \( \rightarrow \) sets \( N_{v_1} \) and \( N_{v_2} \) are disjoint.

However, \( \Psi' \) and \( \Psi \) 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.

\[
|p_+(\mathbf{r})|^2 = |p_-(\mathbf{r})|^2 = (1/2)(|p_x(\mathbf{r})|^2 + |p_y(\mathbf{r})|^2) \neq |p_0(\mathbf{r})|^2 = |p_z(\mathbf{r})|^2
\]
Summary for degenerate states:

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

2) But energy is still unique functional of $\rho$, since $\Psi$ and $\Psi'$ that give the same $\rho$ 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:

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

$$E_v[\rho] > E_0 \text{ if } \rho \notin N_v$$
Is minimization of $E_v[\rho]$ with constraint
\[ \int \rho(\mathbf{r}) d\mathbf{r} = N \] viable? (orbital-free DFT)

\[ E_v[\rho] = \langle \Psi_0[\rho] | \hat{T} + \hat{V} + \hat{W} | \Psi_0[\rho] \rangle \] is minimum at $\rho_0$ of $\nu$

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

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

But the HK theorems offer no prescription 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 $v_s(r)$ such that the density is equal to the exact one (of the interacting electron system in given external potential $v_{ext}(r)$):

Kohn-Sham orbitals from:

$$\left( -\frac{1}{2} \nabla^2 + v_s(r_1) \right) \psi_i(r_1) = \epsilon_i(r_1)$$

with

$$\rho_s(r) = \sum_{i=1}^{N} |\psi_i(r)|^2 = \rho^{exact}(r)$$

The HK theorems also hold for non-interacting electrons ($W=0$) since proofs do not use form of $W$.
So $v_s(r)$ is in one-one correspondence with gr. st. $\rho_s(r)$ (and $\rho^{exact}(r)$).

If $v_s(r)$ exists (no proof by KS; non-int. $v$-represent. problem) then it is unique: no other system, with different $v$ and $\rho_0$, has same $v_s$.
It determines KS orbitals and energies: these are system properties.
How to obtain approximations to $v_s(r)$? Later.

Suppose we have $v_s(r)$, obtain the true KS orbitals and $\rho_s = \rho^{\text{exact}} = \rho$.

Write exact total energy:

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

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

$E_{\text{xc}}$: called exchange-correlation energy of DFT;

is defined by above equation: that part of exact $E$ we do not yet know when $\{\psi_i\}$ and $\rho$ have been obtained.

$E_{\text{xc}}$ is functional of $\rho$ since other terms are:

$$E_{\text{xc}}[\rho] = E[\rho] - T_s[\rho] - \int \rho v_{\text{ext}} \, dr - (1/2) \int \rho V_{\text{Coul}} \, dr$$
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:

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

$W_{xc} = W - (1/2)\int \rho V_{Coul} \, dr = (1/2)\int \rho(r_1) v_{xc}^{\text{hole}}(r_1) \, dr$

$$\langle \Psi_0 | \sum_{i<j} \frac{1}{r_{ij}} | \Psi_0 \rangle$$
$v_{xc}^{\text{hole}}(\mathbf{r}_1)$ is the potential of the exact hole $\rho_{xc}^{\text{hole}}(\mathbf{r}_1; \mathbf{r}_2)$ 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
An electron traveling through a molecule does not see $\rho(\mathbf{r}_2)$ with potential $v_{\text{Coul}} = \int \rho(\mathbf{r}_2)/r_{12} d\mathbf{r}_2$ but $\rho(\mathbf{r}_2) + \rho^{\text{hole}}(\mathbf{r}_2; \mathbf{r}_1)$

\[
W = \langle \hat{W} \rangle = \frac{1}{2} \int \frac{1}{r_{12}} \Gamma(1,2) d1d2
\]

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

\[
= \frac{1}{2} \int \rho(1) \int \frac{\rho(2)}{r_{12}} d2d1 + \frac{1}{2} \int \rho(1) \int \frac{\Gamma_{xc}(1,2)}{\rho(1)r_{12}} d2d1
\]

\[
W = W_{\text{Coul}} + W_{\text{xc}}
\]
Exchange-correlation energy $W_{xc}$

$$E = \langle \Psi | H | \Psi \rangle = T + \int \rho(r) v(r) \, dr + \frac{1}{2} \int \frac{\rho(r_1) \rho(r_2)}{r_{12}} \, dr_1 \, dr_2 + W_{xc}$$

$$W_{xc} = \frac{1}{2} \int dr_1 \rho(r_1) \int \frac{\rho_{xc}^{\text{hole}}(r_2 | r_1)}{r_{12}} \, dr_2$$

$$\Gamma(r_1, r_2) = \rho(r_1) \rho(r_2) + \Gamma_{xc}(r_1, r_2) \Rightarrow$$

$$\rho_{\text{cond}}(r_2; r_1) = \frac{\Gamma(r_1, r_2)}{\rho(r_1)} = \rho(r_2) + \frac{\Gamma_{xc}(r_1, r_2)}{\rho(r_1)}$$
Definition of $E_x$, $E_c$, $E_{xc}$

$$E = \langle \Psi | \hat{H} | \Psi \rangle = T + \int \rho v \, dr + \frac{1}{2} \int \rho v_{\text{Coul}} \, dr + W_{xc} \quad E \text{ in traditional way}$$

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

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

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

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

$E_c = T_c + W_c$ the correlation energy of DFT
Compare $E_c$ to $E_c^{HF}$

\[
E_c^{HF} = E - E^{HF} = T - T^{HF} \rightarrow T_c^{HF}
\]

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

\[
+ W_{Coul} - W_{Coul}^{HF} \rightarrow W_{Coul,c}^{HF}
\]

\[
+ W_{xc} - W_x^{HF} \rightarrow W_c^{HF}
\]

\[
E_c^{HF} = T_c^{HF} + V_c^{HF} + W_{Coul,c}^{HF} + W_c^{HF}
\]

\[
E_c = T_c + W_c \text{ is much simpler!}
\]
Compare to HF

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

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

And DFT? Put KS orbitals in determinant:

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

Compare to exact $E$

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

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

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

\( \Psi_s \) is determinant of KS orbitals

\( \Psi^{HF} \) is Hartree-Fock determinant

\[
E_{c}^{DFT} = |E_{c}^{KS}| = \langle \Psi_s | \hat{H} | \Psi_s \rangle
\]

\[
E_{c}^{HF} = |E_{c}^{HF}| = \langle \Psi^{HF} | \hat{H} | \Psi^{HF} \rangle
\]

\[ |E_{c}^{DFT}| > |E_{c}^{HF}| \]

but by how much?
The one-particle model of DFT: Kohn-Sham

Minimization of

\[ E = \sum_{i=1}^{N} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int \rho v_{\text{nuc}} dr + \frac{1}{2} \int \frac{\rho(r_1) \rho(r_2)}{r_{12}} dr_1 dr_2 + E_{xc} \]

\[ = T_s + V + W_{\text{Coul}} + E_{xc} \]

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

\[
\left( -\frac{1}{2} \nabla^2 (1) + v_{\text{nuc}}(r_1) + v_{\text{Coul}}(r_1) + v_{xc}(r_1) \right) \psi_i(x_1) = \varepsilon_i \psi_i(x_1)
\]

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 $E_{xc}$

$$E_{xc} = \int \rho(x) \epsilon_{xc}(x) dx$$

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

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

Exact $\epsilon_{xc}(x)$ from

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

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

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

CI CI KS
El. correlation is described by $\Phi(2\ldots N|1)$
so no wonder that $v_s$ can be derived from $\Phi(2\ldots N|1)$:

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

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$
No information from this expression:
Shape?
Physics?
Even $E_{xc}[\rho]$ is unknown
Composition of $\nu_{xc}$

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

Not very transparent! Therefore use:

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

$$\frac{\delta E_{xc}}{\delta \rho(r)} = \frac{1}{2} \int \frac{\delta \rho(r')}{\delta \rho(r)} \nu_{xc}^{hole}(r')\,dr'$$

$$+ \int \frac{\delta \rho(r')}{\delta \rho(r)} \nu_{c,kin}(r')\,dr'$$

$$+ \int \rho(r') \frac{\delta}{\delta \rho(r)} \left[ \frac{1}{2} \nu_{xc}^{hole}(r') + \nu_{c,kin}(r') \right] \,dr'$$
Holes in $\text{H}_2$

Fermi hole $+ \text{Coulomb hole} = \text{total hole}$

$RH-H = 1.4 \text{ bohr}$

$RH-H = 5.0 \text{ bohr}$

NB. $v_{xc} = v_{c,\text{kin}} + v_{xc}^{\text{hole}} + v^\text{resp}$
In H$_2$ Fermi hole $\rho^\text{hole}_X(r_2|r_1)$ for el. at $r_1$ is only self-interaction correction term $-|\sigma_g(r_2)|^2$

So independent of $r_1$!

When $R$(H-H) is large and $r_1$ is close to nucleus b, hole is, with $\sigma_g(r_2) \approx (1/\sqrt{2}) [1s_a(r_2) + 1s_b(r_2)]$,

$-|\sigma_g(r_2)|^2 \approx -(1/2) [ |1s_a(r_2)|^2 + |1s_b(r_2)|^2 + 2.1s_a(r_2).1s_b(r_2)] 
\approx 0$

Since total $\rho$ is $|1s_a(r_2)|^2 + |1s_b(r_2)|^2$, the field that the HF electron at $r_1$ feels is due to $\rho(r_2) + \rho^\text{hole}_X(r_2|r_1) = (1/2) [ |1s_a(r_2)|^2 + |1s_b(r_2)|^2 ]$

Wrong! The other el. should be around nucleus $a$!

The erroneous charge of $(1/2)|1s_b(r_2)|^2$ 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: $H_2$

<table>
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<tr>
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<th>$E_{total}^{corr}$</th>
<th>$T_{kin}^{corr}$</th>
<th>$V_{el-nuc}^{corr}$</th>
<th>$W_{el-el}^{corr}$</th>
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<tr>
<td>$H_2 (R=R_e)$</td>
<td>$-1.1 \text{ eV}$</td>
<td>$+1.3$</td>
<td>$-0.5$</td>
<td>$-1.9$</td>
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<td>$H_2 (R=5.0 \text{ bohr})$</td>
<td>$-3.9$</td>
<td>$+8.9$</td>
<td>$-8.5$</td>
<td>$-4.4$</td>
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<td>$H_2 (R=10.0 \text{ bohr})$</td>
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<td>$+7.9$</td>
<td>$-8.6$</td>
<td>$-5.6$</td>
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Hartree-Fock densities are often poor due to bad potential: He, H$_2$O, Ne, N$_2$

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<td>H$_2$O</td>
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</tr>
<tr>
<td>Ne</td>
<td>-8.9</td>
<td>+8.3</td>
<td>+1.4</td>
<td>-18.5</td>
</tr>
<tr>
<td>N$_2$</td>
<td>-11.0</td>
<td>+13.7</td>
<td>-13.8</td>
<td>-11.0</td>
</tr>
</tbody>
</table>
Hartree-Fock densities are often poor due to bad potential: TM complexes

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{total}}^{\text{corr}}$</th>
<th>$T_{\text{kin}}^{\text{corr}}$</th>
<th>$V_{\text{el-nuc}}^{\text{corr}}$</th>
<th>$W_{\text{el-el}}^{\text{corr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO$_4^-$</td>
<td>$-14.4$</td>
<td>$+35.7$</td>
<td>$-115.5$</td>
<td>$+65.4$</td>
</tr>
<tr>
<td>Ni(CO)$_4$</td>
<td>$-3.4$</td>
<td>$-35.0$</td>
<td>$+147.8$</td>
<td>$+116.3$</td>
</tr>
<tr>
<td>Cr(CO)$_6$</td>
<td>$-4.5$</td>
<td>$-4.5$</td>
<td>$+30.8$</td>
<td>$-18.5$</td>
</tr>
</tbody>
</table>
Hartree-Fock errors for bond energies (kcal/mol), because of lack of left-right correl. in bond orbitals

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>Obs.</th>
<th>Error (% of Obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>115.2</td>
<td>228.6</td>
<td>–49.6%</td>
</tr>
<tr>
<td>( \text{F}_2 )</td>
<td>–37.1</td>
<td>38.5</td>
<td>–196.4%</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>155.5</td>
<td>232.2</td>
<td>–33.0%</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>33.1</td>
<td>120.5</td>
<td>–72.5%</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>83.8</td>
<td>109.5</td>
<td>–23.4%</td>
</tr>
</tbody>
</table>
Holes in $\text{H}_2$

Fermi hole $+ \text{Coulomb hole} = \text{total hole}$

$R_{\text{H-H}} = 1.4 \text{ bohr}$

$R_{\text{H-H}} = 5.0 \text{ bohr}$

Localized hole in DFT
Slater: uniform depth $-\rho(r_1)/2$

NB. $\nu_{xc} = \nu_{c,\text{kin}} + \nu_{xc}^{\text{hole}} + \nu^{\text{resp}}$
$E$ versus $R$ curves (restricted HF/KS) for dissociating $\text{H}_2$

\[ \text{Total energy (a.u.)} \]
\[ \text{Bond length (a.u.)} \]

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

Courtesy of Peter Elliott, Hunter College, New York
"exact" KS and HF energies of N$_2$ \hspace{1cm} $D_e$=0.37 a.u.

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

<table>
<thead>
<tr>
<th>$R$ (bohr)</th>
<th>2.074</th>
<th>3.0</th>
<th>3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_X - W_X^{HF}$</td>
<td>0.006</td>
<td>−0.040</td>
<td>−0.067</td>
</tr>
<tr>
<td>$W_c = W_{XC} - W_X$</td>
<td>−0.804</td>
<td>−0.969</td>
<td>−1.063</td>
</tr>
<tr>
<td>$W_c^{(HF)} = W_{XC} - W_X^{HF}$</td>
<td>−0.810</td>
<td>−1.009</td>
<td>−1.124</td>
</tr>
<tr>
<td>$E_c$</td>
<td>−0.475</td>
<td>−0.641</td>
<td>−0.750</td>
</tr>
<tr>
<td>$E_c^{(HF)}$</td>
<td>−0.469</td>
<td>−0.603</td>
<td>−0.687</td>
</tr>
<tr>
<td>$E_c - E_c^{(HF)}$</td>
<td>−0.006</td>
<td>−0.0038</td>
<td>−0.063</td>
</tr>
</tbody>
</table>

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

In an electron pair bond:

a) HF orbitals will be too diffuse (density too diffuse)
   → kinetic energy too low
   → electron-nuclear energy too high (not negative enough)

b) this is worse in case of multiple bonds

c) common statement
   “one-particle properties (also the electron density!) are good in the
   Hartree-Fock model, it is the el.-el. interaction that is wrong,
   because of lack of electron correlation
   (electrons do not avoid each other sufficiently, cf. the presence of ionic
   configurations in the H$_2$ wavefunction)”

IS WRONG
Conclusion HF versus KS det.

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

$E_c \leq E_c^{HF}$

$\Psi_s$ better for:

\[
\begin{align*}
V_{el-nuc} \ \ W_{Coul} \\
T_s : (\text{much}) \text{ smaller correl. error}
\end{align*}
\]

HF "distorts" density (more diffuse) if:

gain by lowering $T^{HF}$ is larger

even if barely) than

loss by less stable $V$
<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>BLYP</th>
<th>EXX</th>
<th>HF</th>
<th>KS</th>
<th>CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_s$ $\Delta_{KS}$</td>
<td>111.951</td>
<td>113.181</td>
<td>112.395</td>
<td>112.641</td>
<td>112.881</td>
<td>113.185</td>
</tr>
<tr>
<td></td>
<td>+0.930</td>
<td>−0.300</td>
<td>+0.790</td>
<td>+0.544</td>
<td>+0.304</td>
<td>(T)</td>
</tr>
<tr>
<td>$V_{en}$ $\Delta_{KS}$</td>
<td>−310.170</td>
<td>−311.520</td>
<td>−310.651</td>
<td>−310.879</td>
<td>−311.256</td>
<td>−311.256</td>
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<tr>
<td></td>
<td>−1.086</td>
<td>+0.264</td>
<td>−0.605</td>
<td>−0.377</td>
<td>0.00</td>
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<tr>
<td>$W_H$ $\Delta_{KS}$</td>
<td>76.204</td>
<td>76.391</td>
<td>76.251</td>
<td>76.262</td>
<td>76.399</td>
<td>76.399</td>
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<tr>
<td></td>
<td>+0.195</td>
<td>+0.008</td>
<td>+0.148</td>
<td>+0.137</td>
<td>0.00</td>
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<tr>
<td></td>
<td>−1.255</td>
<td>+0.156</td>
<td>−0.023</td>
<td>+0.012</td>
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<td>(W_{XC})</td>
</tr>
<tr>
<td>Sum $\Delta_{CI}$</td>
<td>−134.079</td>
<td>−135.423</td>
<td>−135.301</td>
<td>−135.307</td>
<td>−135.295</td>
<td>−135.761</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>−0.460</td>
<td>−0.454</td>
<td>−0.466</td>
<td></td>
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<tr>
<td>$E_{c}$ $\Delta_{CI}$</td>
<td>−0.950</td>
<td>−0.486</td>
<td>(−0.460)</td>
<td>(−0.454)</td>
<td>(−0.466)</td>
<td></td>
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<tr>
<td>$E_{tot}$ $\Delta_{CI}$</td>
<td>−135.029</td>
<td>−135.909</td>
<td>−135.029</td>
<td>−135.029</td>
<td>−135.295</td>
<td>−135.761</td>
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</tbody>
</table>

Baerends, Gritsenko
JCP 123 (2005) 062202
### Energy components for CO at $R=2.8$ bohr

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>BLYP</th>
<th>EXX</th>
<th>HF</th>
<th>KS</th>
<th>CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_s$</td>
<td>111.023</td>
<td>112.257</td>
<td>111.437</td>
<td>111.662</td>
<td>111.977</td>
<td>112.270</td>
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<tr>
<td>$\Delta_{KS}$</td>
<td>+0.950</td>
<td>−0.280</td>
<td>+0.833</td>
<td>+0.608</td>
<td>+0.293</td>
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<tr>
<td>$V_{en}$</td>
<td>−298.862</td>
<td>−300.239</td>
<td>−299.216</td>
<td>−299.430</td>
<td>−299.777</td>
<td>−299.777</td>
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<tr>
<td>$\Delta_{KS}$</td>
<td>−0.915</td>
<td>+0.462</td>
<td>−0.561</td>
<td>−0.347</td>
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<tr>
<td>$W_H$</td>
<td>71.038</td>
<td>71.241</td>
<td>71.071</td>
<td>71.045</td>
<td>71.073</td>
<td>71.073</td>
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<tr>
<td>$\Delta_{KS}$</td>
<td>+0.035</td>
<td>−0.168</td>
<td>+0.002</td>
<td>+0.028</td>
<td>0.00</td>
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<tr>
<td>$\Delta_{KS}$</td>
<td>−1.228</td>
<td>+0.188</td>
<td>−0.007</td>
<td>+0.047</td>
<td></td>
<td>(W_{XC})</td>
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<tr>
<td>Sum</td>
<td>−128.553</td>
<td>−129.909</td>
<td>−129.738</td>
<td>−129.750</td>
<td>−129.707</td>
<td>−130.256</td>
</tr>
<tr>
<td>$\Delta_{CI}$</td>
<td></td>
<td></td>
<td>−0.518</td>
<td>−0.506</td>
<td>−0.549</td>
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<tr>
<td>$E_c^{fn}$</td>
<td>−0.935</td>
<td>−0.472</td>
<td>(−0.518)</td>
<td>(−0.506)</td>
<td>(−0.549)</td>
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</tr>
<tr>
<td>$E_{tot}$</td>
<td>−129.489</td>
<td>−130.381</td>
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<td>−130.256</td>
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<tr>
<td>$\Delta_{CI}$</td>
<td>−0.767</td>
<td>+0.125</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

---

Baerends, Gritsenko JCP 123 (2005) 062202
Time-dependent DFT

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

\[ v(r,t) \Leftrightarrow \rho(r,t) \Leftrightarrow \Psi_0(t) \]

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

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

\[
\rho_s(r,t) = \sum_{i=1}^{N} \left| \psi_i^s(r,t) \right|^2 = \rho^{\text{exact}}(r,t)
\]
LINEAR RESPONSE (1st order Pert. Theory)

\[ \delta \rho(r, \omega) = \int \chi(r, r', \omega) \delta v(r', \omega) \, dr' \]

\( \chi(r, r', \omega) \): first order response function; difficult
(requires sum over all excited states)

Kohn - Sham: \( \delta \rho(r, \omega) = \delta \rho_s(r, \omega) \)

\[ = \int \chi_s(r, r', \omega) \delta v_s(r', \omega) \, dr' \]

↑
response function of
noninteracting system: simple!

\( \delta v_s(r', \omega) \): how related to \( \delta v(r', \omega) \)? (difficult?)
Linear response: $\delta v_s$

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

$$\downarrow \quad \downarrow$$

$$\int \frac{\delta \rho(r'',\omega)}{|r' - r''|} dr'' \quad \int \frac{\delta v_{\text{xc}}(r',\omega)}{\delta \rho(r'',\omega)} \delta \rho(r'',\omega) dr''$$

the xc kernel

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

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

$$f_{\text{xc}}(r,r',\omega) \text{ in local, adiabatic appr. (ALDA)} = \frac{4K}{9} \rho^{-2/3}(r) \delta(r - r')$$
\( \chi_s(r,r') \) from first order perturbation theory:

Perturbation \( \delta v_s(r) \) induces changes in the orbitals:

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

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

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

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

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

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

$p, q, r, s, \ldots$ general indices
occ.- occ. pairs drop out

\[
\delta \rho (r) = \sum_{i=1}^{H} \sum_{p \neq i} \left[ \frac{-\varphi_i(r) \left( \varphi_i \right| \delta v_s \left| \varphi_p \rightangle^{\ast} \varphi_p^{\ast}(r)}{\epsilon_p - \epsilon_i} + \frac{-\left( \varphi_i \right| \delta v_s \left| \varphi_p \rightangle \varphi_p(r) \varphi_i^{\ast}(r)}{\epsilon_p - \epsilon_i} \right]
\]

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

\[
\begin{align*}
\text{for } i = k, p = l : & \quad \frac{-\varphi_k \varphi_l^{\ast} V_{s,kl}}{\epsilon_l - \epsilon_k} + \frac{-V_{s,kl} \varphi_l \varphi_k^{\ast}}{\epsilon_l - \epsilon_k} \\
& \quad \text{CANCEL!}
\end{align*}
\]

\[
\begin{align*}
\text{for } i = l, p = k : & \quad \frac{-\varphi_l \varphi_k^{\ast} V_{s,kl}}{\epsilon_k - \epsilon_l} + \frac{-V_{s,kl} \varphi_k \varphi_l^{\ast}}{\epsilon_k - \epsilon_l} \\
\end{align*}
\]

Only \( p \)-values with \( p \) unocc. survive
Definition of $\chi_s$

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

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

\[ \equiv \chi_s(r,r') \]

$\chi_s$ comes straightforwardly from 1st order pert. theory;
only KS orbitals and orbital energies needed
**Time-dependent case (linear response = 1\textsuperscript{st} order Pert. Th.)**

\[
\delta \rho(r,t) = \sum_i n_i \left( \psi_i(r,t) \delta \psi_i^*(r,t) + \psi_i^*(r,t) \delta \psi_i(r,t) \right)
\]

Suppose perturbation \( \delta v_{\text{ext}}(r,t) \) with single frequency \( \omega \):

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

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

\[
\delta v_s(r,\omega) = \delta v_{\text{ext}}(r,\omega) + \int dr' \frac{\delta \rho(r',\omega)}{|r - r'|} + \delta v_{xc}[\delta \rho](r,\omega)
\]

\( \nabla_{\text{induced}} \)
\[ \delta v_s(r, \omega) = \delta v_{ext}(r, \omega) + \int dr' \frac{\delta \rho(r', \omega)}{|r - r'|} + \delta v_{xc}[\delta \rho](r, \omega) \]

\[ v_{induced}(r, \omega) \]

"uncoupled": \( v_{ind} = 0 \)

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

XC part: \( \delta v_{xc}(r, \omega) = \int dr' \frac{\delta v_{xc}(r, \omega)}{\delta \rho(r', \omega)} \delta \rho(r', \omega) \uparrow f_{xc}(r, r', \omega) \)

usually adiabatic LDA (no \( \omega \) dependence)

for XC kernel \( f_{xc}(r, r', \omega) \)
Shortcut to matrix equations for excitation energies

Put in matrix form with basis sets:

\[ \delta \rho(\mathbf{r}, \omega) \rightarrow \delta P_{ia}(\omega) \rightarrow \delta \mathbf{P}(\omega) \text{ density perturb. } \text{occ.unocc supervector} \]

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

\[ \delta v_{ia}(\omega) \rightarrow \text{ external perturb. potential } \text{occ.unocc supervector} \]

\[ \delta \mathbf{P}(\omega) = \Pi(\omega) \delta \mathbf{V}(\omega) \text{ density response due to external perturb. field} \]

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

\[ \Pi(\omega)^{-1} \text{ often has structure } (\mathbf{K} - \omega \mathbf{1}) \]

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 $n_{occ} n_{virt} \times n_{occ} n_{virt}$:

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

Cf. \( \chi^{-1} \). \( \delta \rho = \delta V \)

$$\delta V_{ia}^{ext} = \langle \psi_i(r) | v_{ext}(r,\omega) | \psi_a(r) \rangle$$

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

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

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

at each $\omega$: $F(\omega) \rightarrow \delta \rho(r,\omega) \rightarrow$ polarizability $\alpha(\omega)$ etc.
Excitation energies: $\delta V^{ext} = 0$

$$\left( \epsilon^2 + 2\epsilon^2 K \epsilon^2 - \omega^2 \right) F = \delta V^{ext}(\omega) = 0$$

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

$$\left( \epsilon^2 + 2\epsilon^2 K \epsilon^2 - \omega^2 \right) F = 0 \text{ or } \left( \epsilon^2 + 2\epsilon^2 K \epsilon^2 \right) F = \omega^2 F$$

↑

Excitation energies!

Ingredients: orbital energies $\epsilon_i, \epsilon_a$
orbital shapes $\psi_i, \psi_a$
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
$v_{xc}^{\text{hole}}$ and the interpretation of orbital energies

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

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

\[-\frac{1}{2} \nabla^2 = -\frac{1}{2} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] + \frac{1}{r^2} D \theta + \frac{1}{r^2} D \phi \]

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

\[-\frac{1}{2} \left[ \frac{\partial^2 \psi_i}{\partial r^2} + \frac{2}{r} \frac{\partial \psi_i}{\partial r} \right] + \frac{1}{r^2} D \theta \psi_i + \frac{1}{r^2} D \phi \psi_i + v_s(r) \psi_i = \varepsilon_i \psi_i \]

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 \( \psi_i \sim e^{-\sqrt{-2(\varepsilon_i - \nu_s(\infty))} r} \)

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

Each orbital has its own exponential decay, so density decays as slowest orbital density decay, i.e. HOMO: \( \rho(r) \sim e^{-2\sqrt{-2\varepsilon_H} r} \)

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

Conclusion: \( \varepsilon_H = -I \)

Now take anion: LUMO now occup., slowest decay

\[
\varepsilon_L(M^-) = -I(M^-) = -A(M) \\
I(M) = E_0^{N-1} - E_0^N \quad A(M) = E_0^N - E_0^{N+1} \\
I(M^-) = E_0^N - E_0^{N+1} = A(M)
\]
### KS and HF orbital energies and VIPs for H$_2$O

<table>
<thead>
<tr>
<th>H$_2$O</th>
<th>MO</th>
<th>HF $-\varepsilon_k$</th>
<th>KS $-\varepsilon_k$</th>
<th>Expt. $I_k$</th>
<th>$I_k + \varepsilon_k$</th>
<th>$\sqrt{\varepsilon_N - \varepsilon_k}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$b_1$</td>
<td>13.76</td>
<td>12.63</td>
<td>12.62</td>
<td>–0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3$a_1$</td>
<td>15.77</td>
<td>14.78</td>
<td>14.74</td>
<td>–0.04</td>
<td></td>
<td></td>
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<tr>
<td>1$b_2$</td>
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<td>2$a_1$</td>
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<td>30.89</td>
<td>32.2</td>
<td>1.31</td>
<td>4.27</td>
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<tr>
<td>1$a_1$</td>
<td>559.37</td>
<td>516.96</td>
<td>539.90</td>
<td>22.94</td>
<td>22.46</td>
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## CO : KS and HF orbital energies and VIPs

<table>
<thead>
<tr>
<th>CO</th>
<th>MO</th>
<th>HF $-\varepsilon_k$</th>
<th>KS $-\varepsilon_k$</th>
<th>Expt. $I_k$</th>
<th>$I_k - (-\varepsilon_k)$</th>
<th>$\sqrt{\varepsilon_N - \varepsilon_k}$</th>
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<tbody>
<tr>
<td>5σ</td>
<td>15.10</td>
<td>14.01</td>
<td>14.01</td>
<td>0.00</td>
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<td></td>
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<td>1π</td>
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<td>16.91</td>
<td>0.14</td>
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<td></td>
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<tr>
<td>4σ</td>
<td>21.90</td>
<td>19.33</td>
<td>19.72</td>
<td>0.39</td>
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<tr>
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<tr>
<td>3σ</td>
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<td>34.69</td>
<td>38.3</td>
<td>3.61</td>
<td>4.54</td>
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<tr>
<td>2σ</td>
<td>309.13</td>
<td>278.83</td>
<td>296.21</td>
<td>17.38</td>
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</tr>
<tr>
<td>1σ</td>
<td>562.32</td>
<td>519.71</td>
<td>542.55</td>
<td>22.84</td>
<td>22.49</td>
<td></td>
</tr>
<tr>
<td>Average Dev.</td>
<td>11.93</td>
<td>14.61</td>
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### CO: KS, GGA-BP and HF orbital energies and VIPs

<table>
<thead>
<tr>
<th>MO</th>
<th>HF $-\varepsilon_i$</th>
<th>GGA-BP $-\varepsilon_i$</th>
<th>KS $-\varepsilon_i$</th>
<th>Expt. $I_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5\sigma$</td>
<td>15.12</td>
<td>9.18 (4.83)</td>
<td>14.01</td>
<td>14.01</td>
</tr>
<tr>
<td>$1\pi$</td>
<td>17.42</td>
<td>11.95 (16.78)</td>
<td>16.80</td>
<td>16.91</td>
</tr>
<tr>
<td>$4\sigma$</td>
<td>21.94</td>
<td>14.27 (19.10)</td>
<td>19.37</td>
<td>19.72</td>
</tr>
<tr>
<td>AAD (val)</td>
<td>1.28</td>
<td>5.08 (0.25)</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>$3\sigma$</td>
<td>41.47</td>
<td>29.47 (34.29)</td>
<td>34.70</td>
<td>38.3</td>
</tr>
<tr>
<td>$2\sigma$</td>
<td>309.17</td>
<td>272.50 (277.33)</td>
<td>279.27</td>
<td>296.21</td>
</tr>
<tr>
<td>$1\sigma$</td>
<td>562.36</td>
<td>513.53 (518.37)</td>
<td>519.92</td>
<td>542.55</td>
</tr>
<tr>
<td>AAD (inner)</td>
<td>11.98</td>
<td>20.52 (15.69)</td>
<td>14.39</td>
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</tr>
</tbody>
</table>
# HCl: KS, BP and HF orbital energies and VIPs

<table>
<thead>
<tr>
<th>HCl</th>
<th>MO</th>
<th>HF $-\epsilon_i$</th>
<th>GGA-BP $-\epsilon_i$</th>
<th>KS $-\epsilon_i$</th>
<th>Expt. $I_i$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$2\pi$</td>
<td>12.97</td>
<td>8.13</td>
<td>(4.64)</td>
<td>12.77</td>
</tr>
<tr>
<td></td>
<td>$5\sigma$</td>
<td>17.04</td>
<td>11.90</td>
<td>(16.53)</td>
<td>16.53</td>
</tr>
<tr>
<td></td>
<td>$4\sigma$</td>
<td>30.41</td>
<td>21.22</td>
<td>(25.86)</td>
<td>25.82</td>
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<tr>
<td>AAD(val)</td>
<td>1.75</td>
<td>4.68</td>
<td>(0.04)</td>
<td>0.03</td>
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<tr>
<td></td>
<td>$1\pi$</td>
<td>218.77</td>
<td>190.98</td>
<td>(195.62)</td>
<td>199.59</td>
</tr>
<tr>
<td></td>
<td>$3\sigma$</td>
<td>218.84</td>
<td>191.27</td>
<td>(195.91)</td>
<td>199.79</td>
</tr>
<tr>
<td></td>
<td>$2\sigma$</td>
<td>287.75</td>
<td>250.44</td>
<td>(255.08)</td>
<td>259.80</td>
</tr>
</tbody>
</table>
SiO: HF, GGA-BP and KS orbital energies, expt. Ips
BP: HOMO 4.02 eV higher than $-I_P$; second column: all $\varepsilon_i^{BB} - 4.02$

<table>
<thead>
<tr>
<th>SiO</th>
<th>MO</th>
<th>HF $-\varepsilon_i$</th>
<th>GGA-BP $-\varepsilon_i$</th>
<th>KS $-\varepsilon_i$</th>
<th>Expt. $I_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7 $\sigma$</td>
<td>11.93</td>
<td>7.59 (4.02)</td>
<td>11.61</td>
<td>11.61</td>
</tr>
<tr>
<td></td>
<td>2 $\pi$</td>
<td>12.90</td>
<td>8.22 (12.24)</td>
<td>12.29</td>
<td>12.19</td>
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<tr>
<td></td>
<td>6 $\sigma$</td>
<td>16.63</td>
<td>10.83 (14.84)</td>
<td>14.80</td>
<td>14.80</td>
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<tr>
<td>AAD (val)</td>
<td></td>
<td>0.95</td>
<td>4.05 (0.03)</td>
<td>0.03</td>
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</tr>
<tr>
<td></td>
<td>5 $\sigma$</td>
<td>34.41</td>
<td>23.59 (27.61)</td>
<td>28.01</td>
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</tr>
<tr>
<td></td>
<td>1 $\pi$</td>
<td>116.22</td>
<td>95.82 (99.84)</td>
<td>101.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 $\sigma$</td>
<td>116.20</td>
<td>95.61 (99.63)</td>
<td>101.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 $\sigma$</td>
<td>167.88</td>
<td>138.95 (142.97)</td>
<td>145.51</td>
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</tr>
<tr>
<td></td>
<td>2 $\sigma$</td>
<td>558.69</td>
<td>510.48 (514.50)</td>
<td>518.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 $\sigma$</td>
<td>1872.70</td>
<td>1783.13 (1787.15)</td>
<td>1802.16</td>
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</table>
### $\text{N}_2$: KS, BP and HF orbital energies and VIPs

<table>
<thead>
<tr>
<th>MO</th>
<th>HF $-\varepsilon_k$</th>
<th>KS $-\varepsilon_k$</th>
<th>Expt. $I_k$</th>
<th>$I_k + \varepsilon_k$</th>
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</thead>
<tbody>
<tr>
<td>$3\sigma_g$</td>
<td>17.27</td>
<td>15.57</td>
<td>15.58</td>
<td>0.01</td>
</tr>
<tr>
<td>$1\pi_u$</td>
<td>16.72</td>
<td>16.68</td>
<td>16.93</td>
<td>0.25</td>
</tr>
<tr>
<td>$2\sigma_u$</td>
<td>21.21</td>
<td>18.77</td>
<td>18.75</td>
<td>–0.02</td>
</tr>
<tr>
<td><strong>Average dev.</strong></td>
<td>1.45</td>
<td>0.09</td>
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<tr>
<td>$2\sigma_g$</td>
<td>40.04</td>
<td>33.69</td>
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<td>3.61</td>
</tr>
<tr>
<td>$1\sigma_u$</td>
<td>426.67</td>
<td>389.72</td>
<td>409.98</td>
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<tr>
<td>$1\sigma_g$</td>
<td>426.76</td>
<td>389.76</td>
<td>409.98</td>
<td>20.22</td>
</tr>
<tr>
<td><strong>Average dev.</strong></td>
<td>12.07</td>
<td>14.70</td>
<td></td>
<td></td>
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</tbody>
</table>
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 $v_{xc}^{\text{hole}}$ in KS potential, and absence in HF exchange operator

$v_{xc}^{\text{hole}}$ leads to good shapes and energy of KS virtuals
(as it did for KS occupied orbitals)
Meaning of unoccupied orbital energies $\varepsilon_a, \varepsilon_b, \ldots$

*HF*: unocc. orbital represents *added* electron

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

*KS*: unocc. orbital represents *excited* electron

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

*HF virtual orbitals are at (much) higher energy and (way) more diffuse than KS virtual orbitals*
## HF, DFA and exact KS HOMO orbital energies

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>LDA</th>
<th>BLYP</th>
<th>KS = –I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>−16.18</td>
<td>−10.26</td>
<td>−10.39</td>
<td>−16.44</td>
</tr>
<tr>
<td>H₂O</td>
<td>−13.88</td>
<td>−7.40</td>
<td>−7.21</td>
<td>−12.62</td>
</tr>
<tr>
<td>HF</td>
<td>−17.69</td>
<td>−9.82</td>
<td>−9.64</td>
<td>−16.19</td>
</tr>
<tr>
<td>N₂</td>
<td>−16.71</td>
<td>−11.89</td>
<td>−11.49</td>
<td>−16.68</td>
</tr>
<tr>
<td>CO</td>
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<td>−9.11</td>
<td>−9.00</td>
<td>−14.01</td>
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<td>−9.23</td>
<td>−8.87</td>
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</tr>
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<td>−13.65</td>
<td>−8.97</td>
<td>−8.62</td>
<td>−13.67</td>
</tr>
<tr>
<td>HCl</td>
<td>−12.98</td>
<td>−8.15</td>
<td>−7.91</td>
<td>−12.77</td>
</tr>
</tbody>
</table>

**KS HOMO** is equal to – I₀;

HF HOMO is appr. equal to – I₀ (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**

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>LDA</th>
<th>BLYP</th>
<th>KS</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
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<td>+0.31</td>
<td>+0.12</td>
<td>−3.93</td>
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<td>H₂O</td>
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<td>−0.92</td>
<td>−1.06</td>
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<td>−1.13</td>
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<td>N₂</td>
<td>+3.91</td>
<td>−2.21</td>
<td>−1.91</td>
<td>−6.77</td>
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<tr>
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<td>+1.88</td>
<td>−2.24</td>
<td>−1.94</td>
<td>−6.56</td>
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<td>−1.33</td>
<td>−1.07</td>
<td>−5.53</td>
</tr>
<tr>
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<td>−1.66</td>
<td>−1.59</td>
<td>−6.01</td>
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<tr>
<td>HCl</td>
<td>+0.79</td>
<td>−1.11</td>
<td>−1.15</td>
<td>−5.36</td>
</tr>
</tbody>
</table>

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 $\Delta$ are excellent approx. to excitation energies

<table>
<thead>
<tr>
<th></th>
<th>$\Delta_{HF}$</th>
<th>$\Delta_{LDA}$</th>
<th>$\Delta_{BLYP}$</th>
<th>$\Delta_{KS}$</th>
<th>Expt. excit. energy</th>
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<td>$H_2O$</td>
<td>14.7</td>
<td>6.5</td>
<td>6.2</td>
<td>7.5</td>
<td>7.65</td>
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<tr>
<td>HF</td>
<td>18.5</td>
<td>8.9</td>
<td>8.5</td>
<td>10.5</td>
<td>10.3</td>
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<td>$N_2$</td>
<td>19.9</td>
<td>9.7</td>
<td>9.6</td>
<td>9.9</td>
<td>9.3-10.3</td>
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<td>7.4</td>
<td>7.8</td>
</tr>
</tbody>
</table>

1) The LDA, GGA gaps are similar (slightly smaller) than KS gaps
   $\rightarrow$ 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

\[ E_{\text{opt}} - I = \Delta L = \Delta_{\text{fund}} = \Delta \]

\[ \Delta L \approx \Delta_{\text{opt}} \]

Orbital energies in exact KS
What is the meaning of a (HF) LUMO with positive orbital energy?
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)

<table>
<thead>
<tr>
<th></th>
<th>SZ</th>
<th>DZ</th>
<th>DZP</th>
<th>TZP</th>
<th>TZ2P</th>
<th>QZ4P</th>
<th>ETQZ3P 2D</th>
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<tr>
<td>(1\sigma_u)</td>
<td>18.12</td>
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<td>3.39</td>
<td>3.45</td>
<td>2.67</td>
<td>1.18</td>
</tr>
<tr>
<td>(1\sigma_g)</td>
<td>–15.88</td>
<td>–16.26</td>
<td>–16.20</td>
<td>–16.21</td>
<td>–16.20</td>
<td>–16.18</td>
<td>–16.18</td>
</tr>
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<td>34.00</td>
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<td>21.31</td>
<td>19.59</td>
<td>19.66</td>
<td>18.85</td>
<td>17.36</td>
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Orbital energies (eV) of the positive energy HF LUMO of H$_2$ as function of the basis (Gaussians)

<table>
<thead>
<tr>
<th></th>
<th>cc-pVDZ</th>
<th>cc-pVQZ</th>
<th>cc-pV5Z</th>
<th>aug-cc-pVDZ</th>
<th>aug-cc-pVTZ</th>
<th>aug-cc-pVQZ</th>
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<td>1.67</td>
<td>1.42</td>
<td>1.28</td>
<td>1.14</td>
</tr>
<tr>
<td>1σ$_g$</td>
<td>–16.11</td>
<td>–16.18</td>
<td>–16.18</td>
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<tr>
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<td>17.80</td>
<td>17.60</td>
<td>17.46</td>
<td>17.32</td>
</tr>
</tbody>
</table>

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:
Electron affinity (in eV)

-7 -6 -5 -4 -3 -2 -1 0 1 2 3 4

Calculated LUMO energies vs EA for 113 molecules. EA from CCSD(T), basis: 6-311++G(3df,3dp) (Kar, Song, Hirao, JCC 2013)

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

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

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

\[
\text{TDDFT: } \left( \mathcal{E}^2 + 2\sqrt{\mathcal{E} K \mathcal{E}} \right) F_q = \omega_q^2 F_q
\]

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

\(K\) is "coupling matrix", see later

Suppose \(i \rightarrow a\) does not couple to other \(j \rightarrow b\)

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

\[
\left[ (\varepsilon_a - \varepsilon_i)^2 + 2(\varepsilon_a - \varepsilon_i) \int \varphi_i(r) \varphi_a(r) f_{xc}(r,r') \varphi_i(r) \varphi_a(r') dr dr' \right] F_q = \omega^2 F_q
\]

\(\Rightarrow \omega = (\varepsilon_a - \varepsilon_i) + \left\langle \varphi_i \varphi_a \vert f_{xc} \vert \varphi_i \varphi_a \right\rangle_{\text{small}} \)

\((\varepsilon_a - \varepsilon_i) \approx \text{excitation energy (in molecules!)}\)
Acetone: orbital energy differences and excitation energies (eV)

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<tr>
<th>Funct.</th>
<th>State</th>
<th>Weight</th>
<th>$\varepsilon_i$</th>
<th>$\varepsilon_a$</th>
<th>$\Delta\varepsilon_{ia}$</th>
<th>$\omega$</th>
<th>$\omega - \Delta\varepsilon_{ia}$</th>
<th>$\omega - E_{\text{exp}}$</th>
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<tr>
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<td>6.07</td>
<td>6.09</td>
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<td>7.52</td>
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<td>6.02</td>
<td>6.01</td>
<td>-0.01</td>
<td>-2.16</td>
</tr>
</tbody>
</table>
Valence virtuals

Rydbergs

Occupied orbitals

Exact KS potential

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

LDA/GGA small basis

LDA/GGA large basis

Orbital energies
Level diagram of excited states in N₂

### Ry

\[
\begin{align*}
2\pi_u & \quad (-2.3) \\
3\sigma_u & \quad (-3.3) \\
4\sigma_g & \\
1\pi_g & \quad (-6.9) \\
3\sigma_g & \quad (-15.3) \\
1\pi_u & \quad (-16.5) \\
2\sigma_u & \quad (-18.6)
\end{align*}
\]

### val

\[
\begin{align*}
2\pi_u \\
3\sigma_u \\
4\sigma_g \\
1\pi_g \\
3\sigma_g \\
1\pi_u \\
2\sigma_u
\end{align*}
\]

### EXP

\[
\begin{align*}
b'1\Sigma_u & \quad 14.20 \\
o1\Pi_u & \quad 13.60 \\
c1\Pi_u & \quad 13.30 \\
c'1\Sigma_u & \quad 12.90 \\
b1\Pi_u & \quad 12.80
\end{align*}
\]

### 1\pi_u \rightarrow 1\pi_g

\[
\begin{align*}
1\pi_u & \rightarrow 1\pi_g & 14.08 \\
2\sigma_u & \rightarrow 1\pi_g & 13.58 \\
1\pi_u & \rightarrow 1\pi_g & 13.19 \\
3\sigma_g & \rightarrow 2\pi_u & 12.95 \\
3\sigma_g & \rightarrow 3\sigma_u & 12.93 \\
3\sigma_g & \rightarrow 3\sigma_u & 13.01 \\
2\sigma_u & \rightarrow 1\pi_g & 12.99
\end{align*}
\]

### EXP, SAOP, BP-GRAC, LDA, BP

\[
\begin{align*}
1\pi_u & \rightarrow 1\pi_g & 14.27 \\
3\sigma_g & \rightarrow 2\pi_u & 10.51 \\
3\sigma_g & \rightarrow 3\sigma_u & 10.46 \\
3\sigma_g & \rightarrow 3\sigma_u & 10.36
\end{align*}
\]
## Acetone: orbital energy differences and excitation energies (eV)

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<td>$\epsilon_a$</td>
<td>$\Delta\epsilon_{ia}$</td>
<td>$\omega$</td>
<td>$\omega - \Delta\epsilon_{ia}$</td>
</tr>
<tr>
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### Pyrimidine: valence excitations (eV)

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<th>State</th>
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<th>$\varepsilon_i$</th>
<th>$\varepsilon_a$</th>
<th>$\Delta\varepsilon_{ia}$</th>
<th>$\omega$</th>
<th>$\omega - \Delta\varepsilon_{ia}$</th>
<th>$\omega - E_{exp}$</th>
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<tbody>
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<tr>
<td>(≈ KS)</td>
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<td>( \varepsilon_a )</td>
<td>( \Delta\varepsilon_{ia} )</td>
<td>( \omega )</td>
<td>( \omega - \Delta\varepsilon_{ia} )</td>
<td>( \omega - E_{exp} )</td>
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<td>1B(_1)</td>
<td>0.73</td>
<td>−11.31</td>
<td>2.20</td>
<td>13.51</td>
<td>5.70</td>
<td>−7.81</td>
<td>1.85</td>
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<td>−11.31</td>
<td>2.61</td>
<td>13.92</td>
<td>6.38</td>
<td>−7.54</td>
<td>1.76</td>
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<td>−10.21</td>
<td>2.20</td>
<td>12.41</td>
<td>6.12</td>
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<td>−10.21</td>
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<td>10.84</td>
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<tr>
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<td>1B(_1)</td>
<td>0.95</td>
<td>−8.92</td>
<td>−0.49</td>
<td>8.42</td>
<td>4.26</td>
<td>−4.17</td>
<td>0.41</td>
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<td>8.77</td>
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<td>8.94</td>
<td>5.72</td>
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<td>−0.49</td>
<td>9.82</td>
<td>5.73</td>
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<td>0.94</td>
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<td>−0.15</td>
<td>10.16</td>
<td>6.21</td>
<td>−3.96</td>
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<tr>
<td></td>
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<td>0.69</td>
<td>−9.43</td>
<td>−0.15</td>
<td>9.28</td>
<td>6.37</td>
<td>−2.91</td>
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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 \( \mathbf{r} \). 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

Hartree-Fock det. \( \Phi_0 = |\psi_1\psi_2 \ldots \psi_N | \)

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

\[ i \rightarrow a \quad \Phi_i^a = |\psi_1\psi_2 \ldots \psi_i\psi_a \ldots \psi_N | \]

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

no hole attraction in HF virtual orb.
energy

No. shape of \( \psi_a^{HF} \) and \( \psi_a^{KS} \) is very different!
\( \psi_a^{HF} \) not realistic!

High HF \( \varepsilon_a^{HF} \) (due to lack in Fock operator for virtual \( \psi_a \)) is “pulled down” by
deposition hole \( (J_{ia}) \).

\( \varepsilon_a^{KS} \) need not be pulled down, it is already low
lying due to pull by xc hole.
Compare to how TD-DFT works in EXX variant (see Gonze-Scheffler, PRL 1999)

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

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

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

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

- $2^\text{d}$ term shifts $\varepsilon_a$ up from (appr.) KS level $\varepsilon_a^{KS}$ to (appr.) HF level $\varepsilon_a^{HF}$ (because $\psi_a$ is unoccupied!)
- $3^\text{d}$ term has little correction on $\varepsilon_i$ ($\varepsilon_i^{KS} \approx \varepsilon_i^{HF} \approx -\text{IP}_i$) anyway
- $4^\text{th}$ term ($-J_{ia}$) provides electron-hole attraction to correct $\varepsilon_a$ after upshift from 2d term back to $\approx \varepsilon_a^{KS}$.
- $5^\text{th}$ term small.

TD-EXX benefits from good shape of $\psi_a^{KS-EXX}$ compared to $\psi_a^{HF}$!
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. \((\varepsilon_a - \varepsilon_d) + \langle \psi_a \psi_d | f_{xc} | \psi_a \psi_d \rangle\)

\( I^D - A^A - \Delta^A \approx 0 \) over all space if \( R \) large

wrong by \( \Delta^A \)!

→ zero contrib. from kernel term
Charge transfer excitations between two remote molecules

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

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:

\[ \varepsilon_a^{HF} = \left< \psi_a \left| -\frac{1}{2}\nabla^2 + v_{\text{nuc}} + v_{\text{Coul}} + \hat{K}^{HF} \right| \psi_a \right> (\hat{K}^{HF}\text{ no hole for virtual orb.}) \]
Charge transfer excitations between two remote molecules are much too low in TDDFT. Why?

Molecular excitation

\[ \approx \]

\[ \approx \]

charged el. wavef.

\[ \approx \]

hole wavef.

\[ \approx \]

hole

\[ \approx \]

xc

\[ \approx \]

Donor

Charge transfer excitation

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

transferred el. wavef.

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

\[ \approx \]

KS LUMO stabilized

\[ \approx \]

by

\[ \approx \]

xc hole

\[ \approx \]

Acceptor
Comment on bandgap in solids (1)

**Conduction Band**
- **Delocalized electron wavef.** of excited electrons

**Valence Band**
- **Deloc. hole wavef.**

**Exciton**
- Weak stabiliz.

**KS Conduction Band**
- Strongly stabilized by local xc hole

**Fermi Level**

**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 \(\approx\) 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) \(\rightarrow\) 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 \(\approx\) 100 bohr
\(\rightarrow\) 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
Failures of time-dependent DFT

a) Wrong Potential Energy Surface (PES) for bonding $\rightarrow$ 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 $(\sigma_g)^2 \rightarrow (\sigma_g)^1(\sigma_u)^1$

$N_2 \: ^1\Sigma_u^+ \: \text{PECs: exact Gr. St. + TDDFT}$

$\Sigma^+_u + N_2$ ground state ($^1\Sigma^+_u + g$) energy [a.u.]

-109.4
-109.2
-109.0
-108.8
-108.6
-108.4

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

2
4
6
8
10

Ground state ($^1\Sigma^+_g$)

"Exact" ground state plus TDDFT excit. energies

MRCl excited states and ground state

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

-108.4
-108.6
-108.8
-109.0
-109.2
-109.4

energy [a.u.]

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

$^1\Sigma_u^+$, $N_2$

TDDFT excitation en. added to DFT Gr. St. energy

ground state ($^1\Sigma_g^+$)
b) Double excitation problem in TDDFT: $1\Sigma_g^+$ states of $H_2$

\begin{itemize}
  \item $4\Sigma_g^+$
  \item $3\Sigma_g^+$
  \item $2\Sigma_g^+$
\end{itemize}

cc-pVTZ basis

- **exact**
- **BP86**
- **B3LYP**

\[
\begin{align*}
(\sigma_g)^2 & \rightarrow (\sigma_u)^2
\end{align*}
\]
Benchmark diabatic potential energy curves from MRCI and fit to expt. (Spelsberg&Meyer, 2001)

1. Ry 1\pi_u \rightarrow 4\sigma_g
2. valence 2\sigma_u \rightarrow 1\pi_g
3. Ry 3\sigma_g \rightarrow 2\pi_u
4. 3\sigma_g, 1\pi_u \rightarrow (1\pi_g)^2
5. double excit.
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!

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

TDDFT $b^1\Pi_u$ (valence $2\sigma_u \rightarrow 1\pi_g$) 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$^+$

![Graph showing excitation energy vs. bohr for HeH$^+$ with different basis sets: BP86 and B3LYP.](image-url)
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