Investigating rigorous combinations of wave function and density-functional theories

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Outline

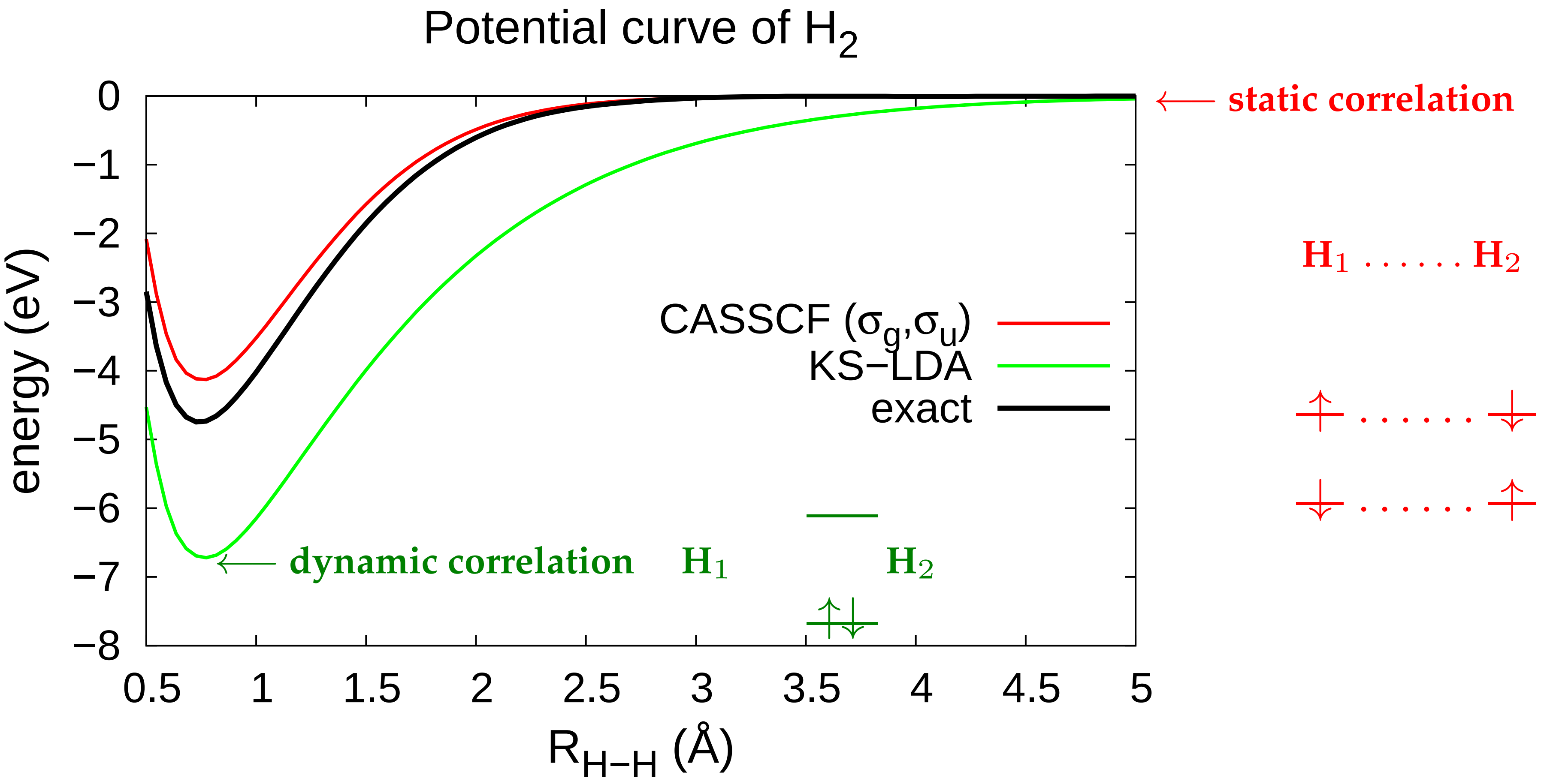
- Merging wave function (**WFT**) and density-functional (**DFT**) theories: why ?
- **Hohenberg-Kohn** (HK) theorems
- HK theorems at work:

  Kohn-Sham (pure functionals: LDA, PBE, ...)

  hybrid HF-DFT (hybrid functionals: PBE0, B3LYP, CAMB3LYP, ...)

  post-HF-DFT (double hybrids, range-separated schemes, ...)

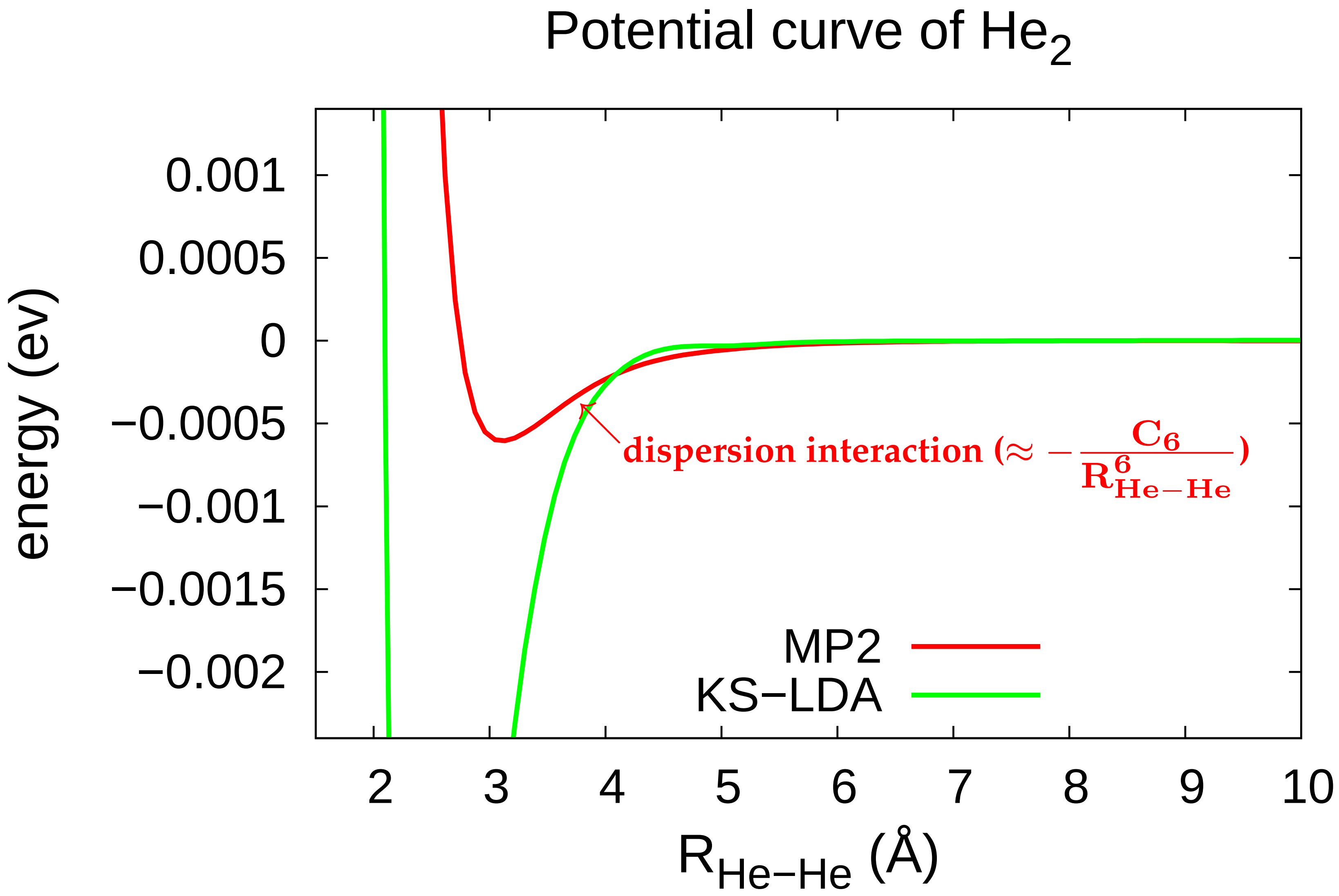
Merging WFT and DFT: why ?



← **static correlation**

← **dynamic correlation**

Merging WFT and DFT: why ?



Notations

- N-electron Hamiltonian within the Born-Oppenheimer approximation:

$$\hat{H} = \hat{T} + \hat{W}_{\rm ee} + \hat{V}_{\rm ne}$$

$$\hat{T} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2$$ → kinetic energy

$$\hat{W}_{\rm ee} = \frac{1}{2}\sum_{i\neq j}^{N} \hat{w}_{\rm ee}(r_{ij}) \qquad \text{with } w_{\rm ee}(r_{12}) = \frac{1}{r_{12}}$$ → full electron-electron repulsion

$$\hat{V}_{\rm ne} = \sum_{i=1}^{N} \hat{v}_{\rm ne}(\mathbf{r_i}) \qquad \text{with } v_{\rm ne}(\mathbf{r}) = -\sum_{A}^{\rm nuclei} \frac{Z_A}{|\mathbf{r}-\mathbf{r}_A|}$$ → electron-nuclei attraction

- electron density $n(\mathbf{r})$ fulfills $\int d\mathbf{r}\; n(\mathbf{r}) = N$

Notations

- Density operator in the 1-electron case: $\hat{n}(\mathbf{r}) = |\mathbf{r}\rangle\langle\mathbf{r}|$

$$n_{\psi}(\mathbf{r}) = \psi^*(\mathbf{r})\,\psi(\mathbf{r}) = \langle\psi|\mathbf{r}\rangle\langle\mathbf{r}|\psi\rangle = \langle\psi|\hat{n}(\mathbf{r})|\psi\rangle$$

- local nuclear potential operator: $\hat{v}_{\rm ne}(\mathbf{r}) = \int d\mathbf{r}\; v_{\rm ne}(\mathbf{r})\,|\mathbf{r}\rangle\langle\mathbf{r}| = \int d\mathbf{r}\; v_{\rm ne}(\mathbf{r})\,\hat{n}(\mathbf{r})$
- Generalization to the N-electron case (second quantization):

$$n_{\Psi}(\mathbf{r}) = \langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle \quad \text{where } \Psi \text{ is an N-electron wave function}$$

$$\hat{V}_{\rm ne} = \sum_{i=1}^{N} \hat{v}_{\rm ne}(\mathbf{r_i}) = \int d\mathbf{r}\; v_{\rm ne}(\mathbf{r})\,\hat{n}(\mathbf{r})$$

$$\langle\Psi|\hat{V}_{\rm ne}|\Psi\rangle = \int d\mathbf{r}\; v_{\rm ne}(\mathbf{r})\,\langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle = \int d\mathbf{r}\; v_{\rm ne}(\mathbf{r})\,n_{\Psi}(\mathbf{r})$$

Hohenberg and Kohn theorems

HK1: There is a one to one correspondence between the local potential $v(\mathbf{r})$, up to a constant, and the non-degenerate ground-state density $n(\mathbf{r})$ of the electronic Hamiltonian

$$\hat{H}[v] = \hat{T} + \hat{W}_{\rm ee} + \int d\mathbf{r}\; v(\mathbf{r})\hat{n}(\mathbf{r})$$

Proof:

- $v(\mathbf{r}) \quad \rightarrow \quad \Psi[v]$ ground state of $\hat{H}[v] \quad \rightarrow \quad n_{\Psi[v]}(\mathbf{r}) = \langle \Psi[v] | \hat{n}(\mathbf{r}) | \Psi[v] \rangle$
- $n(\mathbf{r}) \quad \rightarrow$ unique $v(\mathbf{r})$ (up to a constant) so that the density of $\Psi[v]$ equals $n(\mathbf{r})$?

  Let us assume that we can find two local potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$ that differ from more than a constant and lead to the same ground-state density:

$$n_{\Psi[v]}(\mathbf{r}) = n_{\Psi[v']}(\mathbf{r}) = n(\mathbf{r})$$

Hohenberg and Kohn theorems

- $\Psi[v]$ cannot be equal to $\Psi[v']$ otherwise

$$\hat{H}[v]|\Psi[v]\rangle = E[v]|\Psi[v]\rangle \quad \text{and} \quad \hat{H}[v']|\Psi[v']\rangle = E[v']|\Psi[v']\rangle$$

leads to $\hat{H}[v]|\Psi[v]\rangle - \hat{H}[v']|\Psi[v']\rangle$

$$= \left(\hat{H}[v] - \hat{H}[v']\right)|\Psi[v]\rangle = \int d\mathbf{r}\ \underbrace{\left(v(\mathbf{r}) - v'(\mathbf{r})\right)}_{\neq \text{ constant}} \hat{n}(\mathbf{r})|\Psi[v]\rangle = \left(E[v] - E[v']\right)|\Psi[v]\rangle \quad (!)$$

Comment: the eigenvectors of a local potential operator correspond to electrons fixed at given positions in space

Hohenberg and Kohn theorems

- Non-degeneracy implies

$$\langle\Psi[v']|\hat{H}[v]|\Psi[v']\rangle > E[v] \quad \text{and} \quad \langle\Psi[v]|\hat{H}[v']|\Psi[v]\rangle > E[v']$$

$$\langle\Psi[v']|\hat{T}+\hat{W}_{\text{ee}}|\Psi[v']\rangle - \langle\Psi[v]|\hat{T}+\hat{W}_{\text{ee}}|\Psi[v]\rangle > \int d\mathbf{r}\ v(\mathbf{r})\ \big(n_{\Psi[v]}(\mathbf{r}) - n_{\Psi[v']}(\mathbf{r})\big) = 0$$

$$\langle\Psi[v']|\hat{T}+\hat{W}_{\text{ee}}|\Psi[v']\rangle - \langle\Psi[v]|\hat{T}+\hat{W}_{\text{ee}}|\Psi[v]\rangle < \int d\mathbf{r}\ v'(\mathbf{r})\ \big(n_{\Psi[v]}(\mathbf{r}) - n_{\Psi[v']}(\mathbf{r})\big) = 0 \ \ (!)$$

- Conclusion: $n_{\Psi[v]}(\mathbf{r}) \ \rightarrow \ v(\mathbf{r}) \ \rightarrow \ \Psi[v] \ \rightarrow \ E[v]$

the ground-state energy $E[v]$ is a functional of the ground-state density $n_{\Psi[v]}(\mathbf{r})$

$$E[v] = E[n_{\Psi[v]}]$$

Hohenberg and Kohn theorems

HK2: The ground-state density $n_0(\mathbf{r})$ of the electronic Hamiltonian

$$\hat{H}[v_{\mathrm{ne}}] = \hat{T} + \hat{W}_{\mathrm{ee}} + \int d\mathbf{r}\; v_{\mathrm{ne}}(\mathbf{r})\hat{n}(\mathbf{r})$$

minimizes the energy density-functional $E[n] = F[n] + \int d\mathbf{r}\; v_{\mathrm{ne}}(\mathbf{r})n(\mathbf{r})$,

where the Hohenberg and Kohn universal functional $F[n]$ is defined as

$$F[n] = \langle \Psi[n]|\hat{T} + \hat{W}_{\mathrm{ee}}|\Psi[n]\rangle,$$

and the minimum equals the exact ground-state energy E_0:

$$\boxed{\min_n E[n] = E[n_0] = E_0}$$

Comment: we know from **HK1** that $n(\mathbf{r}) \;\rightarrow\; v[n](\mathbf{r}) \;\rightarrow\; \Psi[v[n]] = \Psi[n]$

Hohenberg and Kohn theorems

Proof:

- for any density $n(\mathbf{r})$, $\Psi[n]$ is well defined according to **HK1** and

$$\langle\Psi[n]|\hat{H}[v_{\rm ne}]|\Psi[n]\rangle \geq E_0$$

$$\underbrace{\langle\Psi[n]|\hat{T}+\hat{W}_{\rm ee}|\Psi[n]\rangle}_{F[n]} + \int d\mathbf{r}\ v_{\rm ne}(\mathbf{r})\,\underbrace{n_{\Psi[n]}(\mathbf{r})}_{n(\mathbf{r})} \geq E_0$$

leading to $\boxed{E[n] \geq E_0}$

- When $n(\mathbf{r})$ equals the exact ground-state density $n_0(\mathbf{r})$:

$$n_0(\mathbf{r}) \;\rightarrow\; v_{\rm ne}(\mathbf{r}) \;\rightarrow\; \Psi[n_0] = \Psi[v_{\rm ne}] = \Psi_0$$

$$E[n_0] = \langle\Psi_0|\hat{T}+\hat{W}_{\rm ee}|\Psi_0\rangle + \int d\mathbf{r}\ v_{\rm ne}(\mathbf{r})n_0(\mathbf{r}) = \langle\Psi_0|\hat{T}+\hat{W}_{\rm ee}+\hat{V}_{\rm ne}|\Psi_0\rangle = E_0$$

Kohn-Sham DFT (KS-DFT)

- the energy density-functional

$$E[n] = F[n] + \int d\mathbf{r}\; v_{\text{ne}}(\mathbf{r})n(\mathbf{r})$$

is fully known from the HK functional $F[n]$, for which the explicit expression is unknown (!)

$$\boxed{unknown = known + (unknown - known)}$$

- **HK1** was formulated for "fully-interacting" electrons described by the Hamiltonian

$$\hat{T} + \hat{W}_{\text{ee}} + \int d\mathbf{r}\; v(\mathbf{r})\hat{n}(\mathbf{r}) \quad : \quad n(\mathbf{r}) \quad \rightarrow \quad \Psi[n] \quad \rightarrow \quad F[n] = \langle\Psi[n]|\hat{T} + \hat{W}_{\text{ee}}|\Psi[n]\rangle$$

- **HK1** is actually also valid for fictitious "non-interacting" electrons described by the Hamiltonian

$$\hat{T} + \int d\mathbf{r}\; v(\mathbf{r})\hat{n}(\mathbf{r}) \qquad\qquad : \quad n(\mathbf{r}) \quad \rightarrow \quad \Phi^{\text{KS}}[n] \quad \rightarrow \quad T_S[n] = \langle\Phi^{\text{KS}}[n]|\hat{T}|\Phi^{\text{KS}}[n]\rangle$$

Kohn-Sham DFT (KS-DFT)

- The Hamiltonian of "non-interacting" electrons is a one-electron operator:

$$H^{\mathrm{KS}} = \hat{T} + \int d\mathbf{r}\ v(\mathbf{r})\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 + \hat{v}(\mathbf{r_i})$$

- Its exact ground state $\Phi^{\mathrm{KS}}[n]$ is therefore a single Slater determinant:

$$\Phi^{\mathrm{KS}}[n] = |\varphi_1^2\varphi_2^2\ldots\varphi_{\frac{N}{2}}^2|$$

  where the Kohn-Sham orbitals φ_i fulfill

$$-\frac{1}{2}\nabla_i^2\varphi_i + v(\mathbf{r_i})\varphi_i = \varepsilon_i\varphi_i$$

- The "non-interacting" kinetic energy is then easy to calculate:

$$T_S[n] = \langle\Phi^{\mathrm{KS}}[n]|\hat{T}|\Phi^{\mathrm{KS}}[n]\rangle = -2 \times \frac{1}{2}\sum_{i=1}^{\frac{N}{2}} \int d\mathbf{r}\ \varphi_i(\mathbf{r})\nabla^2\varphi_i(\mathbf{r})$$

Kohn-Sham DFT (KS-DFT)

- The kinetic energy of non-interacting electrons being "known":

$$F[n] = T_S[n] + \Big(\underbrace{F[n] - T_S[n]}_{E_{\mathrm{Hxc}}[n]}\Big)$$

- Hartree, exchange and correlation energy functional: $E_{\mathrm{Hxc}}[n] = \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}d\mathbf{r}' + E_{\mathrm{xc}}[n]$

- Energy expression in KS-DFT deduced from **HK2**

$$E_0 = \min_n \left\{ T_S[n] + E_{\mathrm{Hxc}}[n] + \int d\mathbf{r}\ v_{\mathrm{ne}}(\mathbf{r})n(\mathbf{r}) \right\}$$

- The exact explicit expression of $T_S[n]$ is unknown (!)

Kohn-Sham DFT (KS-DFT)

- Let us consider an arbitrary wave function Ψ of density $n_{\Psi}(\mathbf{r}) \quad \rightarrow \quad \Phi^{\mathrm{KS}}[n_{\Psi}]$ which is the ground state of a "non-interacting" Hamiltonian

$$\hat{H}^{\mathrm{KS}} = \hat{T} + \int d\mathbf{r}\; v(\mathbf{r})\hat{n}(\mathbf{r})$$

$$\langle \Psi|\hat{H}^{\mathrm{KS}}|\Psi\rangle \geq \langle \Phi^{\mathrm{KS}}[n_{\Psi}]|\hat{H}^{\mathrm{KS}}|\Phi^{\mathrm{KS}}[n_{\Psi}]\rangle$$

$$\langle \Psi|\hat{T}|\Psi\rangle - \langle \Phi^{\mathrm{KS}}[n_{\Psi}]|\hat{T}|\Phi^{\mathrm{KS}}[n_{\Psi}]\rangle \geq \int d\mathbf{r}\; v(\mathbf{r}) \Big(n_{\Phi^{\mathrm{KS}}[n_{\Psi}]}(\mathbf{r}) - n_{\Psi}(\mathbf{r})\Big) = 0$$

leading to $\boxed{\langle \Psi|\hat{T}|\Psi\rangle \geq T_S[n_{\Psi}]}$

<u>Conclusion</u>: the kinetic energy of a "fully interacting" electronic system is larger than the kinetic energy of the "non-interacting" electronic system which has the same electron density

Kohn-Sham DFT (KS-DFT)

- Consequence: minimization over densities $n(\mathbf{r}) \quad \leftrightarrow \quad$ minimization over wave functions Ψ:

for any Ψ,
$$\langle\Psi|\hat{T}+\hat{V}_{\rm ne}|\Psi\rangle \geq T_S[n_\Psi] + \int d\mathbf{r}\; v_{\rm ne}(\mathbf{r}) n_\Psi(\mathbf{r})$$

$$\langle\Psi|\hat{T}+\hat{V}_{\rm ne}|\Psi\rangle + E_{\rm Hxc}[n_\Psi] \geq \underbrace{T_S[n_\Psi] + E_{\rm Hxc}[n_\Psi] + \int d\mathbf{r}\; v_{\rm ne}(\mathbf{r}) n_\Psi(\mathbf{r})}_{E[n_\Psi]\,\geq\, E_0}$$

- When Ψ equals the non-interacting ground state $\Phi^{\rm KS}[n_0]$ associated to the exact density $n_0(\mathbf{r})$

$$\langle\Phi^{\rm KS}[n_0]|\hat{T}+\hat{V}_{\rm ne}|\Phi^{\rm KS}[n_0]\rangle + E_{\rm Hxc}[n_{\Phi^{\rm KS}[n_0]}] = E[n_0] = E_0$$

$$\boxed{E_0 = \min_\Psi \left\{\langle\Psi|\hat{T}+\hat{V}_{\rm ne}|\Psi\rangle + E_{\rm Hxc}[n_\Psi]\right\}}$$

Comparing WFT and KS-DFT

- $E_0 = \min\limits_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\rm ne} + \hat{W}_{\rm ee} | \Psi \rangle \right\} = \min\limits_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\rm ne} | \Phi \rangle + E_{\rm Hxc}[n_\Phi] \right\}$

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

$$\underbrace{\Psi = \Phi^{\rm HF} + \sum_k C_k \det{}_k}_{\text{multideterminantal wave function}} \qquad\qquad \underbrace{\Phi = |\varphi_1^2 \varphi_2^2 \dots \varphi_{\frac{N}{2}}^2|}_{\text{single determinant}}$$

- approximations to $E_{\rm xc}[n]$: LDA, PBE, ... known as pure functionals since they depend explicitly on the density $n(\mathbf{r})$, its gradient $|\boldsymbol{\nabla} n(\mathbf{r})|$, etc ... → problems with self-interaction error, charge transfers, ...

Merging Hartree-Fock (HF) and DFT

HK3: There is a one to one correspondence between the local potential $v(\mathbf{r})$, up to a constant, and the non-degenerate Hartree-Fock ground-state density $n^{\mathrm{HF}}(\mathbf{r})$ of the electronic Hamiltonian

$$\hat{H}[v] = \hat{T} + \hat{W}_{\mathrm{ee}} + \int d\mathbf{r}\ v(\mathbf{r})\hat{n}(\mathbf{r})$$

- $v(\mathbf{r}) \quad \rightarrow \quad \Phi^{\mathrm{HF}}[v]$ HF approximation for $\hat{H}[v] \quad \rightarrow \quad n_{\Phi^{\mathrm{HF}}[v]}(\mathbf{r}) = \langle\Phi^{\mathrm{HF}}[v]|\hat{n}(\mathbf{r})|\Phi^{\mathrm{HF}}[v]\rangle$
- $n(\mathbf{r}) \quad \rightarrow$ unique $v(\mathbf{r})$ (up to a constant) so that the density of $\Phi^{\mathrm{HF}}[v]$ equals $n(\mathbf{r})$?

  Assuming that we can find two local potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$ that differ from more than a constant and lead to the same HF ground-state density is absurd !

- **HK1** was formulated for "fully-interacting" electrons described by the Hamiltonian
  $\hat{T} + \hat{W}_{\rm ee} + \int d\mathbf{r}\ v(\mathbf{r})\hat{n}(\mathbf{r}) \quad : \quad n(\mathbf{r}) \quad \rightarrow \quad \Psi[n] \quad \rightarrow \quad F[n] = \langle \Psi[n]|\hat{T} + \hat{W}_{\rm ee}|\Psi[n]\rangle$

- **HK3** is formulated at the HF level of approximation for electrons described by the Hamiltonian
  $\hat{T} + \hat{W}_{\rm ee} + \int d\mathbf{r}\ v(\mathbf{r})\hat{n}(\mathbf{r}) \quad : \quad n(\mathbf{r}) \ \rightarrow \ \Phi^{\rm HF}[n] \ \rightarrow \ F^{\rm HF}[n] = \langle \Phi^{\rm HF}[n]|\hat{T} + \hat{W}_{\rm ee}|\Phi^{\rm HF}[n]\rangle$

- The Hartree-Fock energy of "fully-interacting" electrons being "known":

$$F[n] = F^{\rm HF}[n] + \left(\underbrace{F[n] - F^{\rm HF}[n]}_{E_c[n]}\right)$$

- Energy expression in the "hybrid functionals" scheme deduced from **HK2**

$$E_0 = \min_n \left\{ \langle \Phi^{\rm HF}[n]|\hat{T} + \hat{W}_{\rm ee}|\Phi^{\rm HF}[n]\rangle + E_{\rm c}[n] + \int d\mathbf{r}\ v_{\rm ne}(\mathbf{r})n(\mathbf{r}) \right\}$$

Comparing WFT and the "hybrid functionals" scheme

- $E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}} | \Psi \rangle \right\} = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}} | \Phi \rangle + E_c[n_\Phi] \right\}$

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

$$\underbrace{\Psi = \Phi^{\mathrm{HF}} + \sum_k C_k \mathrm{det}_k} \qquad\qquad \Phi = \underbrace{|\varphi_1^2 \varphi_2^2 \dots \varphi_{\frac{N}{2}}^2|}$$

multideterminantal wave function

single determinant

- approximations to $E_{\mathrm{c}}[n]$: LDA, PBE, ...
- A modified electron-electron interaction is used in practice: $\boxed{\hat{W}_{\mathrm{ee}} \rightarrow \hat{W}_{\mathrm{ee}}^m}$

$\hat{W}_{\mathrm{ee}}^m = a_x \hat{W}_{\mathrm{ee}}$ a_x=25% for PBE0 and a_x=20% for B3LYP

$\hat{W}_{\mathrm{ee}}^m = \hat{W}_{\mathrm{ee}}^{\mathrm{lr}}$ long range part of the electron-electron repulsion → CAMB3LYP, ...

Merging *post*-HF methods with DFT

- A proper description of multireference systems requires more than a single determinant
  → a complete active space (CAS) must be defined

H. . .H CAS = $|\sigma_g^2|, |\sigma_u^2|$

Be CAS = $|1s^2 2s^2|, |1s^2 2p_x^2|, |1s^2 2p_y^2|, |1s^2 2p_z^2|$

- Natural multireference extension of the hybrid functional scheme:

$$E_0 = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{W}_{\rm ee} + \hat{V}_{\rm ne} | \Phi \rangle + E_c[n_\Phi] \right\} \;\rightarrow\; \min_{\Psi \in \mathrm{CAS}} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\rm ne} + \hat{W}_{\rm ee} | \Psi \rangle + \underbrace{E_c^{\rm CAS}[n_\Psi]} \right\}$$

leads to a "double counting problem" not universal !

Merging *post*-HF methods with DFT

$$\hat{W}_{\mathrm{ee}} = \hat{W}^{m}_{\mathrm{ee}} + \left(\underbrace{\hat{W}_{\mathrm{ee}} - \hat{W}^{m}_{\mathrm{ee}}} \right)$$

$$\swarrow \qquad\qquad\qquad\qquad \searrow$$

post-HF methods

$\hat{W}^{cm}_{\mathrm{ee}}$ complement of $\hat{W}^{m}_{\mathrm{ee}}$ $\rightarrow$ $E^{cm}_{\mathrm{Hxc}}[n]$

- **HK1** was formulated for "fully-interacting" electrons described by the Hamiltonian
  $\hat{T} + \hat{W}_{\mathrm{ee}} + \int d\mathbf{r}\ v(\mathbf{r})\hat{n}(\mathbf{r}) \quad : \quad n(\mathbf{r}) \quad \rightarrow \quad \Psi[n] \quad \rightarrow \quad F[n] = \langle \Psi[n]|\hat{T} + \hat{W}_{\mathrm{ee}}|\Psi[n]\rangle$

- **HK1** is also valid for fictitious electrons with modified interactions as described by the Hamiltonian
  $\hat{T} + \hat{W}^{m}_{\mathrm{ee}} + \int d\mathbf{r}\ v(\mathbf{r})\hat{n}(\mathbf{r}) \quad : \quad n(\mathbf{r}) \quad \rightarrow \quad \Psi^{m}[n] \quad \rightarrow \quad F^{m}[n] = \langle \Psi^{m}[n]|\hat{T} + \hat{W}^{m}_{\mathrm{ee}}|\Psi^{m}[n]\rangle$

- Assuming that it is possible to compute accurately correlation for $\hat{W}^{m}_{\mathrm{ee}}$:

$$F[n] = F^{m}[n] + \left(\underbrace{F[n] - F^{m}[n]}_{E^{cm}_{\mathrm{Hxc}}[n]}\right)$$

- Hybrid *post*-HF-DFT energy expression deduced from **HK2**

$$E_0 = \min_{n} \left\{ \langle \Psi^{m}[n]|\hat{T} + \hat{W}^{m}_{\mathrm{ee}}|\Psi^{m}[n]\rangle + E^{cm}_{\mathrm{Hxc}}[n] + \int d\mathbf{r}\ v_{\mathrm{ne}}(\mathbf{r})n(\mathbf{r}) \right\}$$

Comparing WFT and combined *post*-HF-DFT

- $E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi \rangle \right\} = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{W}^{m}_{\text{ee}} + \hat{V}_{\text{ne}} | \Psi \rangle + E^{cm}_{\text{Hxc}}[n_\Psi] \right\}$

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

$$\underbrace{\Psi = \Phi_{\text{HF}} + \sum_k C_k \det_k}_{\text{multideterminantal wave function}} \qquad\qquad \underbrace{\Psi = \Phi^{m}_{\text{HF}} + \sum_k C^{m}_k \det^{m}_k}_{\text{multideterminantal character induced by } \hat{W}^{m}_{\text{ee}}}$$

- approximations to $E^{cm}_{\text{Hxc}}[n]$: LDA-type, PBE-type, ...
- $\hat{W}^{m}_{\text{ee}}$ can in principle be described with any *post*-HF method (MP2, CC, CI, CASSCF, CASPT2, ...)
- MP2 with $\hat{W}^{m}_{\text{ee}} = a_x \hat{W}_{\text{ee}}$ → double hybrid functionals of S. Grimme (J. Toulouse *et al.*)
- CASSCF with $\hat{W}^{m}_{\text{ee}} = \hat{W}^{\text{lr}}_{\text{ee}}$ → multireference range-separated DFT schemes (see lecture 2)