On the combination of density-functional and wave function theories for the description of both ground and excited states

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Outline

- Long-range / short-range separation of electron correlation in molecular systems: why and how?
- Long-range wave function theory (WFT) / short-range density-functional theory (DFT)
- Excited states in range-separated DFT: linear response and ensemble DFT
- Conclusions and outlook
On the combination of density-functional and wave function theories for the description of both ground and excited states

Range separation of electron correlation: why and how?

regular electron-electron interaction $w_{ee}(r_{12})=1/r_{12}$

short range DFT

long-range WFT
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Range separation of electron correlation: why and how?

Potential curve of $H_2$

- Static correlation
- Dynamic correlation

CASSCF ($\sigma_g, \sigma_u$)

KS–LDA

exact
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Range separation of electron correlation: why and how?

Potential curve of \( \text{He}_2 \)

\[
\text{dispersion interaction } (\approx -\frac{C_6}{R_{\text{He-He}}^6})
\]
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\[
\frac{1}{r_{12}} = \frac{\text{erf}(\mu r_{12})}{r_{12}} + \frac{1 - \text{erf}(\mu r_{12})}{r_{12}}
\]

where

\[
\text{erf}(\mu r_{12}) = \frac{2}{\sqrt{\pi}} \int_{0}^{\mu r_{12}} e^{-t^2} dt
\]

\[
\mu = 0.5
\]

\[
\frac{1}{\mu} : \text{reference distance in a.u.}
\]
long-range WFT / short-range DFT (srDFT)

- Ground state energy:

\[
E_0 = \min_{\Psi} \{ \langle \Psi | \hat{T} + \hat{W}_{ee}^{lr,\mu} + \hat{V}_{\text{ne}} | \Psi \rangle + E_{\text{sr},\mu}^{\text{Hx}}[n_{\Psi}] + E_{\text{sr},\mu}^{c}[n_{\Psi}] \}
\]

\[
\Rightarrow (\hat{T} + \hat{W}_{ee}^{lr,\mu} + \hat{V}_{\text{ne}} + \hat{V}_{\text{Hx}}^{\text{sr},\mu}[n_{\Psi \mu}] + \hat{V}_{c}^{\text{sr},\mu}[n_{\Psi \mu}]) | \Psi^{\mu} \rangle = E^{\mu} | \Psi^{\mu} \rangle
\]

long-range interaction: MCSCF, ...
short-range interaction: srLDA, srPBE ...

- Excitation energies: linear response theory

\[
\left( \hat{T} + \hat{W}_{ee}^{lr,\nu} + \hat{V}_{\text{ne}} + \hat{V}(t) + \hat{V}^{\nu}(t) - i\partial_t \right) | \tilde{\nu}(t) \rangle = Q^{\nu}(t) | \tilde{\nu}(t) \rangle
\]

\[
\forall \nu \quad n^{\nu}(r, t) = n(r, t)
\]
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\[ \mu = 0 \text{ limit: Kohn-Sham DFT} \]

\[ \mu = 0.05 \]

\[ E_0 = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{Hxc}}[n_\Phi] \right\} = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{W}_{\text{lr}, \mu} + \hat{V}_{\text{ne}} | \Psi \rangle + E_{\text{Hxc}}^{\text{sr}, \mu}[n_\Psi] \right\} \]
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\[ \mu \to \infty \text{ limit: WFT} \]

\[ \mu = 10.0 \]

\[ E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{W}_{ee} | \Psi \rangle \right\} = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{W}_{ee}^{lr,\mu} + \hat{V}_{ne} | \Psi \rangle + E_{\text{Hxc}}^{sr,\mu} [n_{\Psi}] \right\} \]
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Multi-state srDFT: why?

![Graph showing energy vs. nuclear displacement with curves for $S_0$ and $S_1$ states.](image-url)
Rayleigh-Ritz variational principle

We consider the particular case where the two lowest eigenfunctions $\Psi_1$ and $\Psi_2$ of the Hamiltonian
\[ \hat{H} = \hat{T} + \hat{W}_{ee} + \int dr \, v(r)\hat{n}(r) \] are non-degenerate ($E_1 < E_2$)

For any orthonormal set $\{\Psi'_1, \Psi'_2\}$ and $0 \leq w < \frac{1}{2}$:

\[ (1 - w) \langle \Psi'_1 | \hat{H} | \Psi'_1 \rangle + w \langle \Psi'_2 | \hat{H} | \Psi'_2 \rangle \geq (1 - w) E_1 + w E_2. \]

The equality is fulfilled if and only if $\Psi'_1 = \Psi_1$ and $\Psi'_2 = \Psi_2$

Hohenberg and Kohn theorem for non-degenerate two-state ensembles

If the local potentials $v(r)$ and $v'(r)$ differ from more than a constant, then the ensemble densities

$$n_w[v](r) = (1 - w)n_{\Psi_1}(r) + wn_{\Psi_2}(r) \quad \text{and} \quad n_w[v'](r) = (1 - w)n_{\Psi'_1}(r) + wn_{\Psi'_2}(r)$$

built from the two lowest states of

$$\hat{H} = \hat{T} + \hat{W}_{ee} + \int dr \, v(r)\hat{n}(r) \quad \text{and} \quad \hat{H}' = \hat{T} + \hat{W}_{ee} + \int dr \, v'(r)\hat{n}(r)$$

respectively,

with $0 \leq w < \frac{1}{2}$,

are not equal.

The ensemble energy $E_w = (1 - w) E_1 + w E_2$ associated to the molecular Hamiltonian

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

is a functional of the ensemble density $n_w(\mathbf{r}) = (1 - w)n_\Psi(\mathbf{r}) + wn_\Psi(\mathbf{r})$.

$$E[w, n_w] = E_w$$
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- Range separation of the ensemble energy:

\[
E_w = E[w, n_w] = (1 - w)E_1 + wE_2 - \int dr \, v_{Hxc}^{sr, \mu}[w, n_w](r)n_w(r) + E_{Hxc}^{sr, \mu}[w, n_w]
\]

where

\[
(\hat{T} + \hat{W}_{ee}^{lr, \mu} + \hat{V}_{ne} + \hat{V}_{Hxc}^{sr, \mu}[w, n_w] |\Psi_1^\mu\rangle = \mathcal{E}_1^\mu |\Psi_1^\mu\rangle
\]

\[
(\hat{T} + \hat{W}_{ee}^{lr, \mu} + \hat{V}_{ne} + \hat{V}_{Hxc}^{sr, \mu}[w, n_w] |\Psi_2^\mu\rangle = \mathcal{E}_2^\mu |\Psi_2^\mu\rangle
\]

- \[
\frac{dE_w}{dw} = \frac{d}{dw} ((1 - w) E_1 + w E_2) = E_2 - E_1
\]

\[
E_2 - E_1 = \mathcal{E}_2^\mu - \mathcal{E}_1^\mu + \frac{\partial E_{Hxc}^{sr, \mu}[w, n]}{\partial w} \bigg|_{n=n_w}
\]

\[
\longrightarrow_{\mu=0} \frac{E_2 - E_1}{\mu} = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} + \frac{\partial E_{Hxc}[w, n]}{\partial w} \bigg|_{n=n_w}
\]
Conclusions and outlook

- WFT and DFT can be merged rigorously using a range separation of the electron-electron repulsion

- Current srDFT schemes describe ground state only (implemented in DALTON and MOLPRO)

- Implementation of TD-srDFT (linear response) in progress

- A two-state ensemble srDFT has been derived (investigate approximations for the ensemble short-range functional)