

An introduction to ensemble density-functional theory for excited states

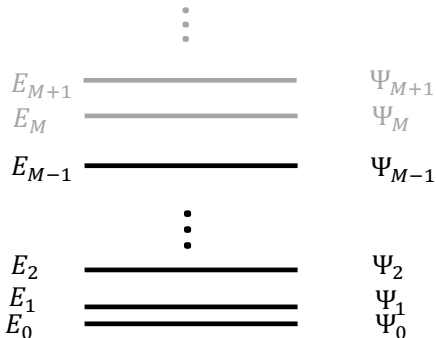
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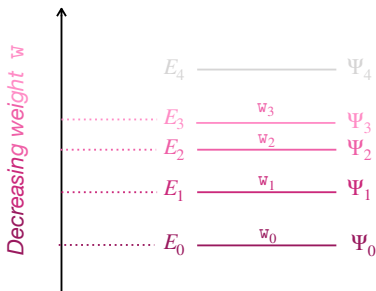
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(Time-independent) DFT for canonical ensembles

$$\hat{H}\Psi_I = E_I\Psi_I$$



DFT for (canonical) ensembles



Gross-Oliveira-Kohn (GOK) DFT:

The *ensemble energy* $E^w := \sum_{l \geq 0} w_l E_l$ is a functional of the *ensemble density* $n^w(\mathbf{r}) := \sum_{l \geq 0} w_l n_{\Psi_l}(\mathbf{r})$.

A. K. Theophilou, *J. Phys. C: Solid State Phys.* **12**, 5419 (1979).

E. K. U. Gross, L. N. Oliveira, and W. Kohn, *Phys. Rev. A* **37**, 2805 (1988).

E. K. U. Gross, L. N. Oliveira, and W. Kohn, *Phys. Rev. A* **37**, 2809 (1988).

L. N. Oliveira, E. K. U. Gross, and W. Kohn, *Phys. Rev. A* **37**, 2821 (1988).

- We would like to *describe many states* within a *single* DFT-like calculation.
- This can be achieved by extending DFT to an *ensemble of ground and excited states*.¹
- The ensemble energy is a *weighted sum* of ground- and excited-state energies:

$$E^{\mathbf{w}} = \sum_{i=0}^{M-1} w_i E_i, \quad w_i \geq w_{i+1} \geq 0, \quad \sum_{i=0}^{M-1} w_i = 1,$$

where the excited-state *weights* $\mathbf{w} \equiv (w_1, w_2, \dots, w_{M-1})$ are *fixed* and *ordered*.

- The ensemble energy $E^{\mathbf{w}} \equiv E^{\mathbf{w}}[n^{\mathbf{w}}]$ is a functional of the *ensemble density*¹

$$n^{\mathbf{w}}(\mathbf{r}) = \sum_{i=0}^{M-1} w_i n_{\Psi_i}(\mathbf{r}) \quad \text{where} \quad \hat{H}\Psi_i = E_i\Psi_i.$$

- *Each ensemble* has *its own* universal xc functional:^{2,3}

$$E_{\text{xc}}[n] = E_{\text{xc}}^{\mathbf{w}=0}[n] \quad \longrightarrow \quad E_{\text{xc}}^{\mathbf{w}}[n] = E_{\text{xc}}^{\{w_1, w_2, \dots, w_{M-1}\}}[n]$$

¹E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2809 (1988).

²K. Deur and E. Fromager, J. Chem. Phys. **150**, 094106 (2019).

³E. Fromager, Phys. Rev. Lett. **124**, 243001 (2020).

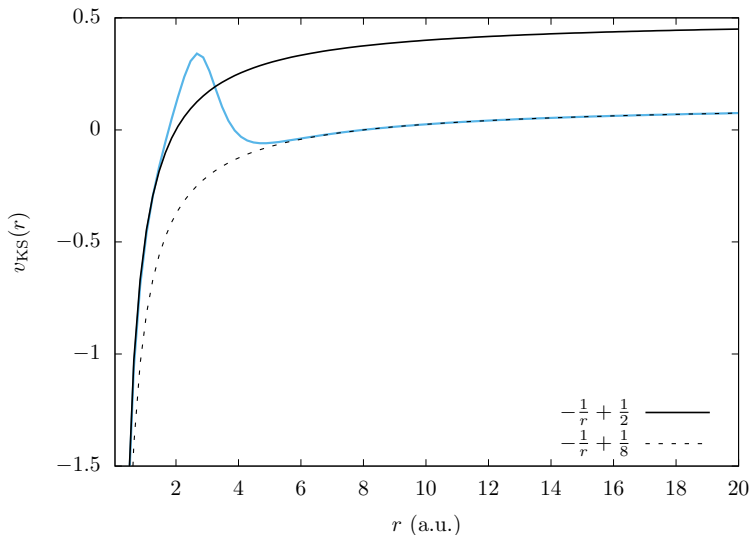
Why is the ensemble xc density functional *weight-dependent*?

Because a GOK ensemble cannot be identified solely from its density!

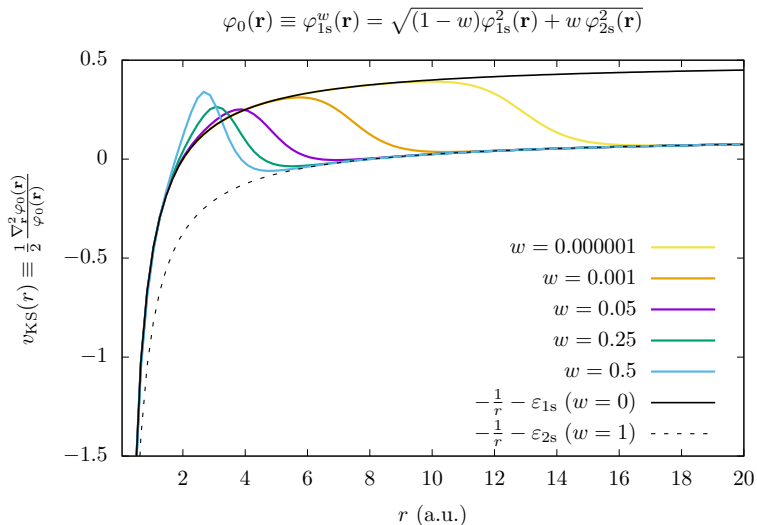
For example, an ensemble density might also be a pure ground-state density.

In this case, you need to know if you have to evaluate a regular (ground-state) xc energy or an ensemble one...

Quiz time: ground-state or ensemble density?



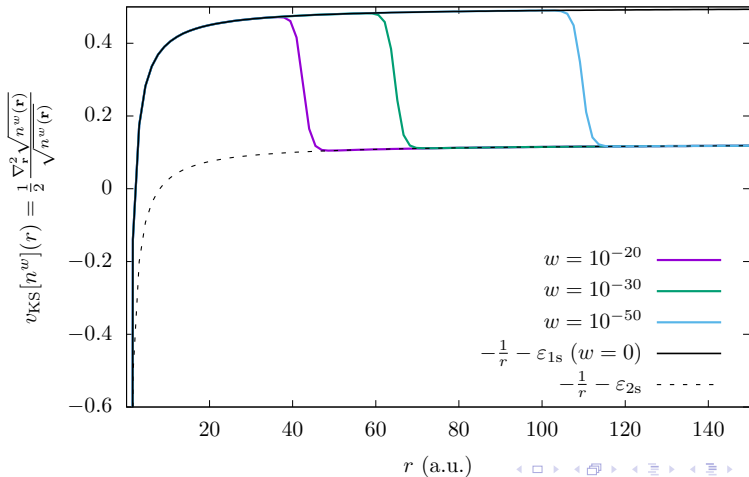
Hydrogen atom: ground-state or ensemble density? both!



Hydrogen atom: ground-state or ensemble density? both!

$$n^w(\mathbf{r}) = (1 - w)n_{1s}(\mathbf{r}) + w n_{2s}(\mathbf{r})$$

$$v_{\text{KS}}[n^{w=0}](r \rightarrow +\infty) - v_{\text{KS}}[n^{w \rightarrow 0^+}](r \rightarrow +\infty) = \varepsilon_{2s} - \varepsilon_{1s}$$



Ensemble DFT for excited states

- DFT for ensembles relies on the Gross–Oliveira–Kohn **variational principle***

$$\sum_{i=0}^{M-1} w_i \langle \tilde{\Psi}_i | \hat{H} | \tilde{\Psi}_i \rangle \geq E^{\mathbf{w}},$$

where $\hat{H} = \hat{T} + \hat{W}_{\text{ee}} + \sum_{i=1}^N v_{\text{ne}}(\mathbf{r}_i)$ is the electronic Hamiltonian

and $\{\tilde{\Psi}_i\}_{i=0,1,\dots,M-1}$ is a **trial orthonormal set** of many-body wavefunctions.

- The latter principle rationalizes the **state-averaging** procedure used in wavefunction theory.
- In **Kohn–Sham** (KS) DFT for ensembles, the exact ensemble energy reads

$$E^{\mathbf{w}} = \sum_{i=0}^{M-1} w_i \langle \Phi_i^{\mathbf{w}} | \hat{T} | \Phi_i^{\mathbf{w}} \rangle + \int d\mathbf{r} v_{\text{ne}}(\mathbf{r}) n^{\mathbf{w}}(\mathbf{r}) + E_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}].$$

*E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2805 (1988).

- *Ensemble KS equations:*

$$\left(\hat{T} + \sum_{i=1}^N v_{\text{KS}}^{\mathbf{w}}(\mathbf{r}_i) \times \right) \Phi_I^{\mathbf{w}} = \mathcal{E}_I^{\mathbf{w}} \Phi_I^{\mathbf{w}},$$

where $v_{\text{KS}}^{\mathbf{w}}(\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + \frac{\delta E_{\text{H}}[n^{\mathbf{w}}]}{\delta n(\mathbf{r})} + \frac{\delta E_{\text{xc}}^{\mathbf{w}}[n^{\mathbf{w}}]}{\delta n(\mathbf{r})}$ and $\mathcal{E}_I^{\mathbf{w}} = \sum_{p \in I} \varepsilon_p^{\mathbf{w}}$.

- Extraction of *excitation energies:*

$$E_I - E_0 \stackrel{I \geq 0}{=} \frac{dE^{\mathbf{w}}}{dw_I} = \mathcal{E}_I^{\mathbf{w}} - \mathcal{E}_0^{\mathbf{w}} + \left. \frac{\partial E_{\text{xc}}^{\mathbf{w}}[n]}{\partial w_I} \right|_{n=n^{\mathbf{w}}}.$$

- *Connection with DFT* and linear response *TDDFT*: Just consider the $\mathbf{w} = 0$ limit!
- For a *single electron* $i \rightarrow a$ *excitation*, for example, it comes:

$$E_{i \rightarrow a} - E_0 = \varepsilon_a - \varepsilon_i + \left. \frac{\partial E_{\text{xc}}^{\mathbf{w}}[n_0]}{\partial w_{i \rightarrow a}} \right|_{\mathbf{w}=0}.$$

E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2805 (1988).

K. Deur and E. Fromager, J. Chem. Phys. **150**, 094106 (2019).

Bi-ensemble DFT

- The *bi-ensemble* energy reads $E^w = (1 - w)E_0 + wE_1$ where $w \equiv w_1$.
- Note that the ensemble energy is **linear** in w so that the exact first excitation energy $\omega = E_1 - E_0$ can be expressed as

$$\omega = \frac{dE^w}{dw} = \varepsilon_L^w - \varepsilon_H^w + \left. \frac{\partial E_{xc}^w[n]}{\partial w} \right|_{n=n^w} \quad \text{or} \quad \omega = 2(E^{w=1/2} - E^{w=0}).$$

- *KS equations* for the biensemble:

$$\left(-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{ne}(\mathbf{r}) + \int d\mathbf{r}' \frac{n^w(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}^w[n^w]}{\delta n(\mathbf{r})} \right) \varphi_p^w(\mathbf{r}) = \varepsilon_p^w \varphi_p^w(\mathbf{r}),$$

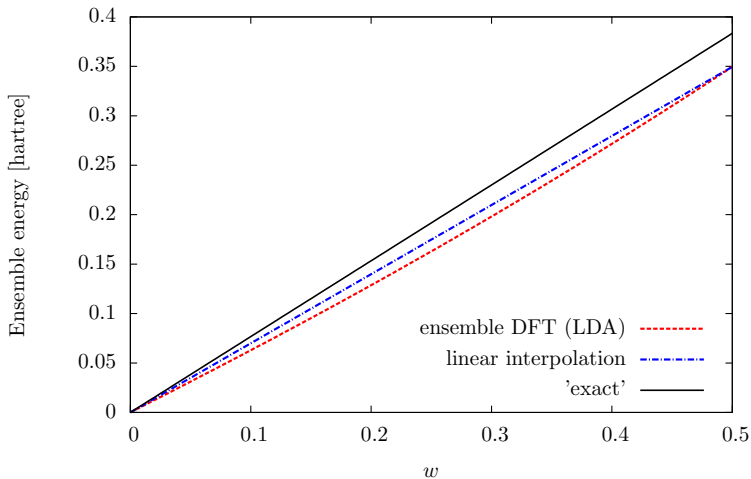
where

$$n^w(\mathbf{r}) = 2 \left(\sum_{p=1}^{H-1} |\varphi_p^w(\mathbf{r})|^2 \right) + (2 - w)|\varphi_H^w(\mathbf{r})|^2 + w|\varphi_L^w(\mathbf{r})|^2,$$

if the first excitation is a **single-electron** one from the HOMO (H) to the LUMO (L).

$$E_{xc}^w[n] \approx E_{xc}[n] \Rightarrow \frac{\partial E_{xc}^w[n]}{\partial w} \approx 0$$

He $\{1^1S, 2^1S\}$

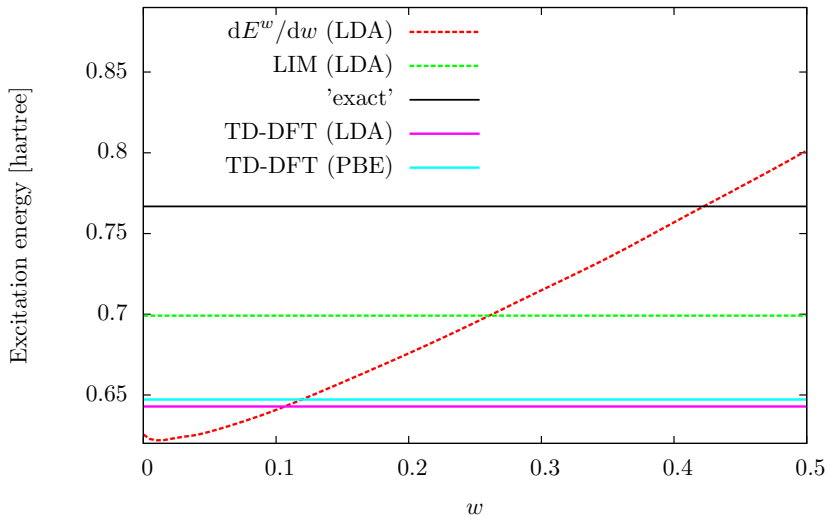


B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, *Phys. Rev. A* **92**, 012518 (2015).

Md. M. Alam, S. Knecht, and E. Fromager, *Phys. Rev. A* **94**, 012511 (2016).

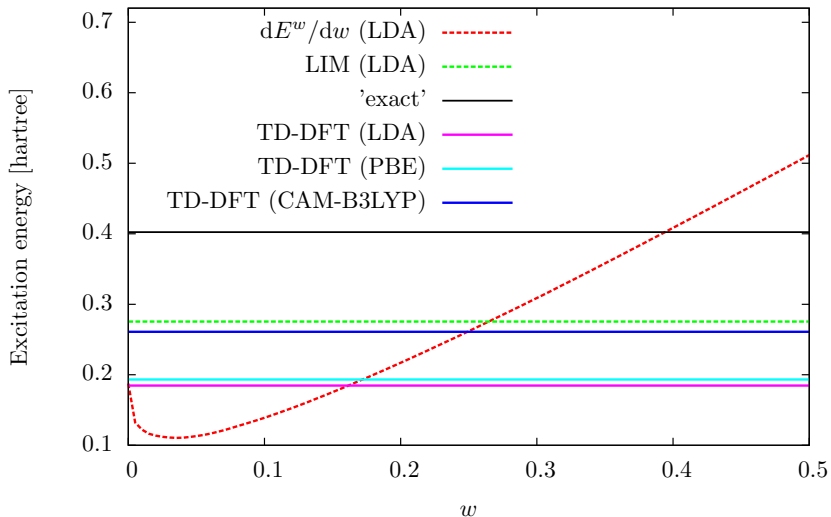
Md. M. Alam, K. Deur, S. Knecht, and E. Fromager, *J. Chem. Phys.* **147**, 204105 (2017).

He $\{1^1S, 2^1S\}$



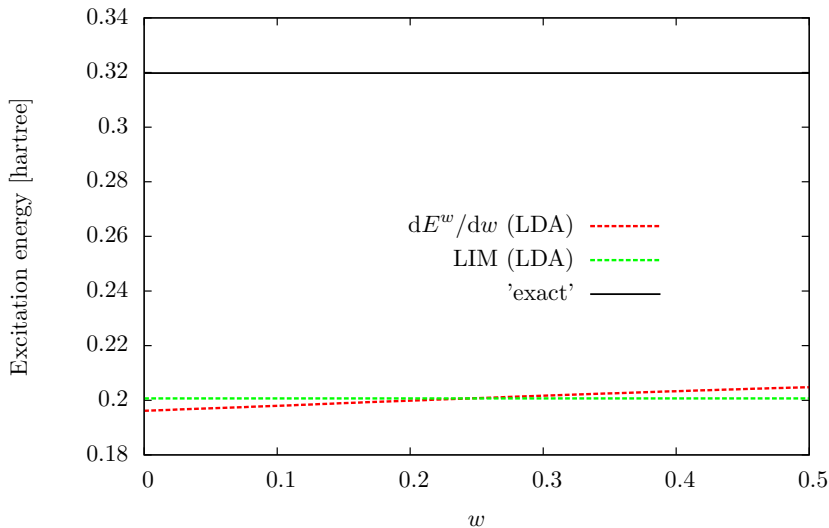
B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, *Phys. Rev. A* **92**, 012518 (2015).

HeH⁺ {1¹Σ⁺, 2¹Σ⁺, R = 8.0a₀}



B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, *Phys. Rev. A* **92**, 012518 (2015).

$\text{H}_2 \{1^1\Sigma_g^+, 2^1\Sigma_g^+, R = 3.7a_0\}$



B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, *Phys. Rev. A* **92**, 012518 (2015).