Density-functional theory for excited states: An ensemble perspective

Emmanuel Fromager

Laboratoire de Chimie Quantique, Institut de Chimie de Strasbourg,
Université de Strasbourg, Strasbourg, France.

Department of Chemistry and Pharmaceutical Sciences,
Vrije Universiteit Amsterdam, The Netherlands.

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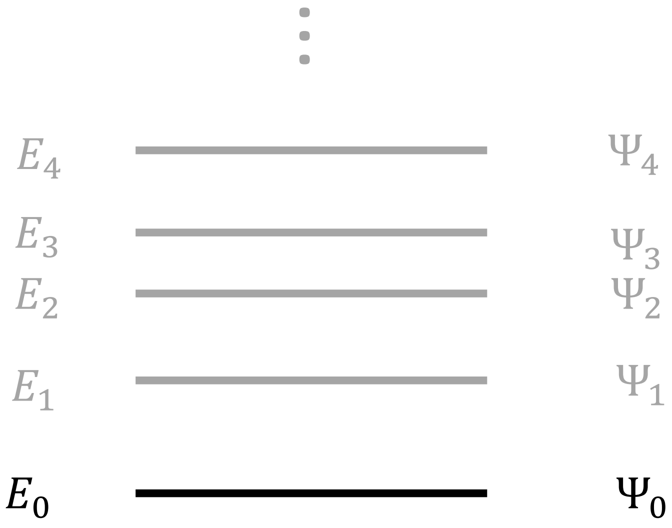
Outline

- (Time-independent) DFT for excited states: why and how?
- Connecting Kohn-Sham orbital energies to real (ground- and excited-state) energies.
- Individual exchange-correlation functionals for excited states (within an ensemble).

DFT and excited states

$$\boxed{\hat{H}\Psi_0 = E_0\Psi_0}$$



Hohenberg-Kohn theorem:

Ground- *and* *excited-state* energies are in principle functionals of the ground-state density n_{Ψ_0}.

P. Hohenberg and W. Kohn, Phys. Rev. ***136****, B864 (1964).*

(Linear response) time-dependent DFT

$$E_I - E_0 = \varepsilon_a^{\mathrm{KS}} - \varepsilon_i^{\mathrm{KS}} + \dots \longrightarrow \frac{\delta^2 \mathscr{A}_{\mathrm{Hxc}}[n_{\Psi_0}]}{\delta n(\mathbf{r}', t')\delta n(\mathbf{r}, t)}$$

True excitation energy

Kohn-Sham excitation energy

Hartree-exchange-correlation kernel

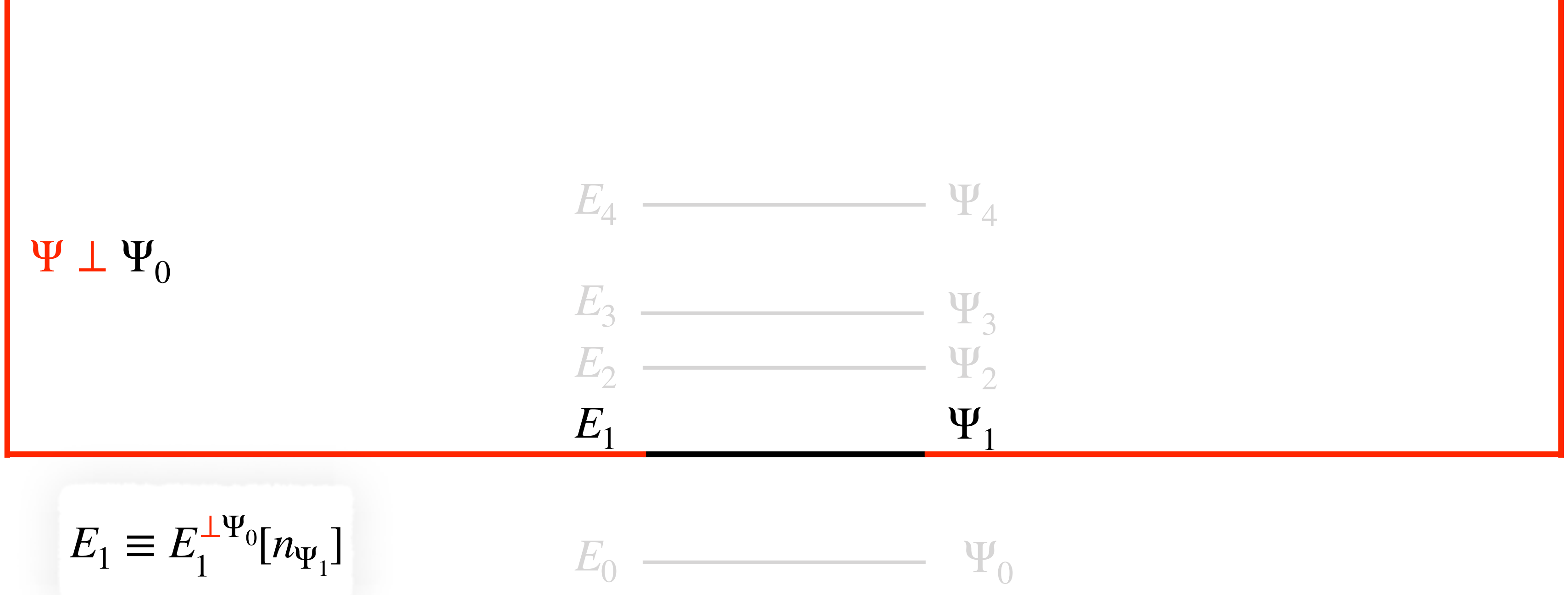
$$E_I \equiv E_I[n_{\Psi_0}]$$

Practical limitations:

- *Single-reference* perturbation theory (not adequate for *nearly-degenerate* situations).
- Memory effects are absent from standard functionals (*adiabatic approximation*).
- *Multiple-electron excitations* are absent from the adiabatic TD-DFT spectrum.

E. Runge and E. K. U. Gross, Phys. Rev. Lett. ***52****, 997 (1984).*
M. Casida and M. Huix-Rotllant, Annu. Rev. Phys. Chem. ***63****, 287 (2012).*
G. Vignale, Phys. Rev. A ***77****, 062511 (2008).*

(Excited) state-specific DFT



$$E_1 \equiv E_1^{\perp\Psi_0}[n_{\Psi_1}]$$

*M. Levy and A. Nagy, Phys. Rev. Lett. **83**, 4361 (1999).*

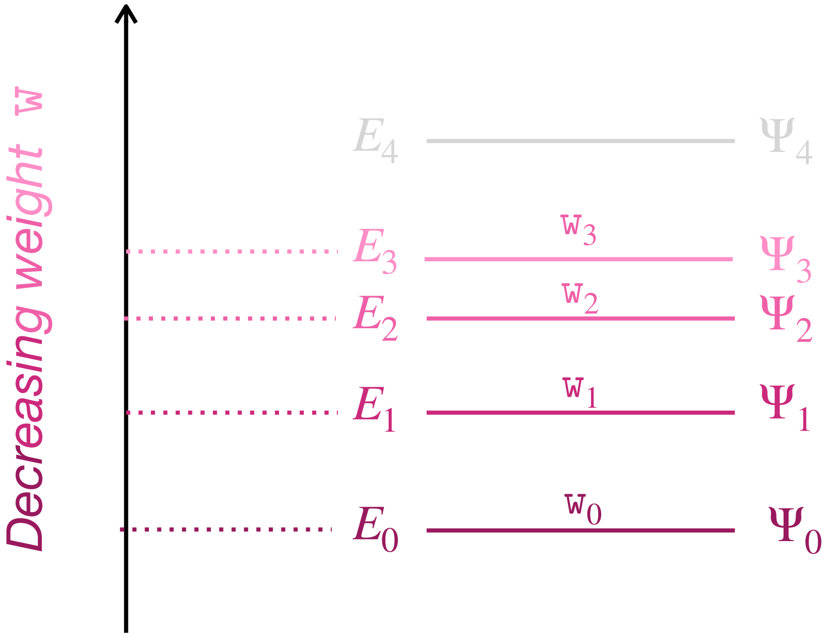
In *Coulomb systems*, individual densities are sufficient, i.e.

$$E_I \equiv E^{Coul}[n_{\Psi_I}]$$

$$v(\mathbf{r}) = -\sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}$$

*P. W. Ayers, M. Levy, and A. Nagy, Phys. Rev. A **85**, 042518 (2012).*
*P. W. Ayers, M. Levy, and A. Nagy, J. Chem. Phys. **143**, 191101 (2015).*
*P. W. Ayers, M. Levy, and A. Nagy, Theor. Chem. Acc. **137**, 152 (2018).*

DFT for (canonical) ensembles



Gross-Oliveira-Kohn (GOK) DFT:

The *ensemble energy* $E^{\mathbf{w}} := \sum_{I\geq 0} \mathtt{w}_I E_I$ is a functional of the *ensemble density* $n^{\mathbf{w}}(\mathbf{r}) := \sum_{I\geq 0} \mathtt{w}_I n_{\Psi_I}(\mathbf{r})$.

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).*

From DFT to GOK-DFT

Ensemble Hxc functional:

I am here to say that n is an ensemble density!

$$E_{\rm Hxc}[n] \longrightarrow E^{\bf w}_{\rm Hxc}[n]$$

Example: $\varphi^{\mathtt{w}}_{1s}(\mathbf{r}) = \sqrt{(1-\mathtt{w})\varphi^2_{1s}(\mathbf{r})+\mathtt{w}\varphi^2_{2s}(\mathbf{r})}$

Ensemble Kohn-Sham equations:

$$n^{\bf w}(\mathbf{r}) = \sum_{I\geq 0} \mathtt{w}_I \sum_{i\in I} |\varphi_i(\mathbf{r})|^2$$

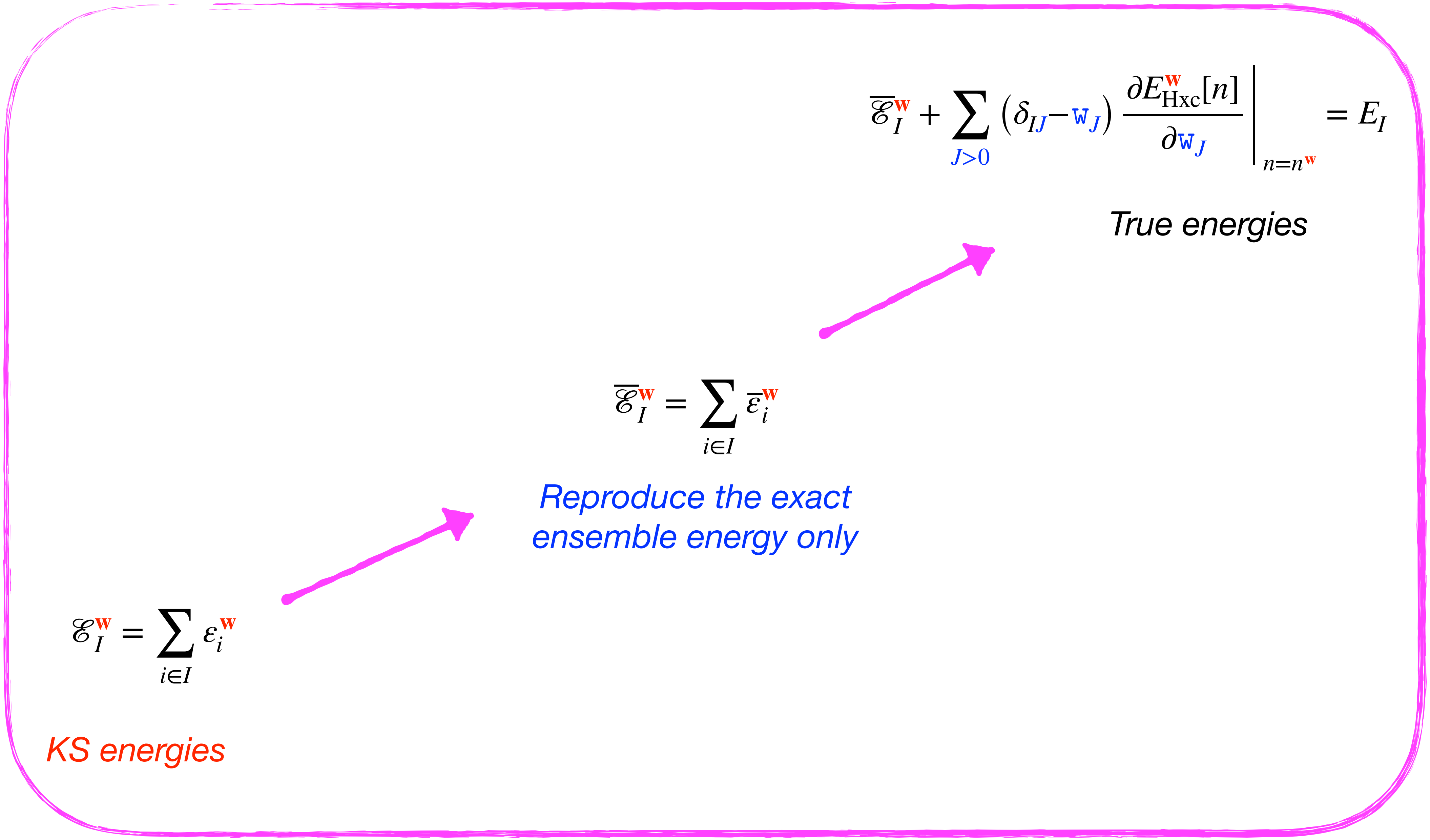
$$\left[-\frac{\nabla^2}{2} + v_{\rm ext}(\mathbf{r}) + \left.\frac{\delta E^{\bf w}_{\rm Hxc}[n]}{\delta n(\mathbf{r})}\right|_{n=n^{\bf w}}\right]\varphi_i(\mathbf{r}) = \varepsilon_i^{\bf w}\varphi_i(\mathbf{r})$$

Levy-Zahariev *shift:**

$$\varepsilon_i^{\bf w} \rightarrow \overline{\varepsilon}_i^{\bf w} = \varepsilon_i^{\bf w} + \left.\frac{E^{\bf w}_{\rm Hxc}[n] - \int d\mathbf{r}\frac{\delta E^{\bf w}_{\rm Hxc}[n]}{\delta n(\mathbf{r})}n(\mathbf{r})}{\int d\mathbf{r}\; n(\mathbf{r})}\right|_{n=n^{\bf w}}$$

*M. Levy and F. Zahariev, Phys. Rev. Lett. **113**, 113002 (2014).

Extracting individual energies



$$\overline{\mathcal{E}}_I^{\mathbf{w}} + \sum_{J>0} \left(\delta_{IJ} - \mathtt{w}_J\right) \left.\frac{\partial E_{\mathrm{Hxc}}^{\mathbf{w}}[n]}{\partial \mathtt{w}_J}\right|_{n=n^{\mathbf{w}}} = E_I$$

True energies

$$\overline{\mathcal{E}}_I^{\mathbf{w}} = \sum_{i\in I} \overline{\varepsilon}_i^{\mathbf{w}}$$

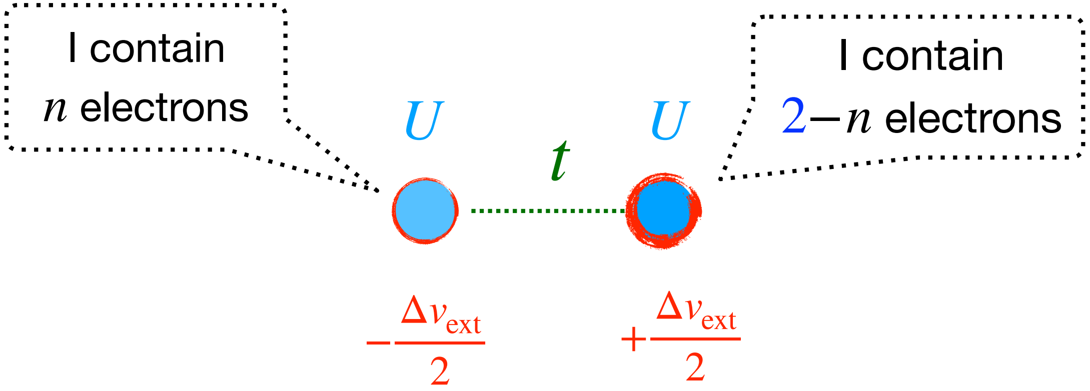
Reproduce the exact ensemble energy only

$$\mathcal{E}_I^{\mathbf{w}} = \sum_{i\in I} \varepsilon_i^{\mathbf{w}}$$

KS energies

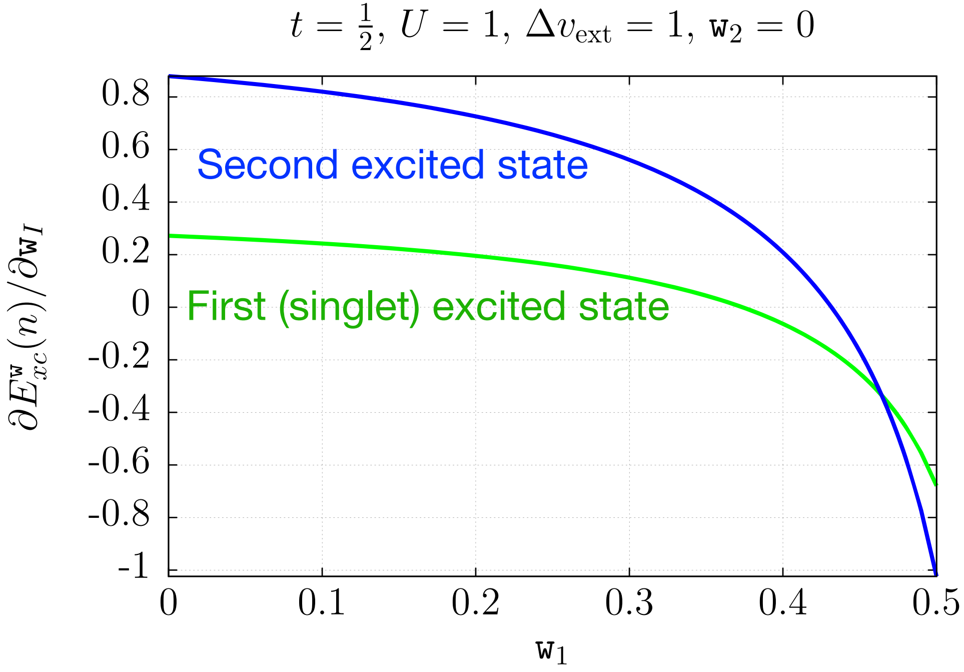
K. Deur and E. Fromager, J. Chem. Phys. ***150****, 094106 (2019).*

(Two-electron) Hubbard dimer model

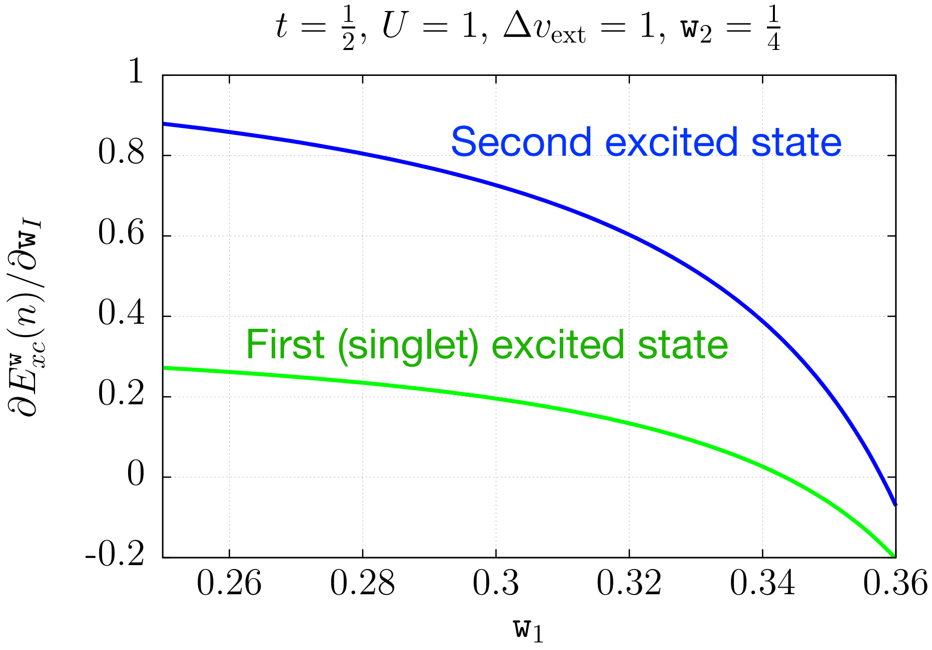


I contain n electrons

I contain $2-n$ electrons



$t=\frac{1}{2},\ U=1,\ \Delta v_{\text{ext}}=1,\ \mathtt{w}_2=0$



$t=\frac{1}{2},\ U=1,\ \Delta v_{\text{ext}}=1,\ \mathtt{w}_2=\frac{1}{4}$

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

Modeling density-functional correlations in ensembles: Where to start?

Individual correlations:

$$E_{\mathrm{c}}^{\mathbf{w}}[n^{\mathbf{w}}] = \sum_{I\geq 0} \mathtt{w}_I \langle \Psi_I | \hat{H} | \Psi_I \rangle - \sum_{I\geq 0} \mathtt{w}_I \langle \Phi_I^{\mathbf{w}} | \hat{H} | \Phi_I^{\mathbf{w}} \rangle$$

$$\boxed{\sum_{I\geq 0} \mathtt{w}_I \, n_{\Psi_I}(\mathbf{r}) = \sum_{I\geq 0} \mathtt{w}_I \, n_{\Phi_I^{\mathbf{w}}}(\mathbf{r})}$$

$$\sum_{I\geq 0} \mathtt{w}_I \, E_{\mathrm{c},I}^{\mathbf{w}} \equiv \sum_{I\geq 0} \mathtt{w}_I \left(\langle \Psi_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi_I \rangle - \langle \Phi_I^{\mathbf{w}} | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi_I^{\mathbf{w}} \rangle \right)$$

$$\boxed{n_{\Psi_I}(\mathbf{r}) \neq n_{\Phi_I^{\mathbf{w}}}(\mathbf{r})}$$

I am the correlation energy of state I
within the ensemble

$$E_{\mathrm{c},I}^{\mathbf{w}} \neq \langle \Psi_I | \hat{H} | \Psi_I \rangle - \langle \Phi_I^{\mathbf{w}} | \hat{H} | \Phi_I^{\mathbf{w}} \rangle$$

T. Gould and S. Pittalis, Phys. Rev. Lett. ***123****, 016401 (2019).*

State- and density-driven correlations in ensembles

$$E^{\mathbf{w}}_{\mathrm{c},I} = \langle \Psi_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi_I \rangle - \langle \Phi^{\mathbf{w}}_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi^{\mathbf{w}}_I \rangle$$

$$= \langle \Psi_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi_I \rangle - \langle \overline{\Phi}_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \overline{\Phi}_I \rangle$$

State-specific KS determinant

$$n_{\Psi_I}(\mathbf{r}) = n_{\overline{\Phi}_I}(\mathbf{r})$$

I am the *state-driven* correlation energy

$$= \langle \Psi_I | \hat{H} | \Psi_I \rangle - \langle \overline{\Phi}_I | \hat{H} | \overline{\Phi}_I \rangle$$

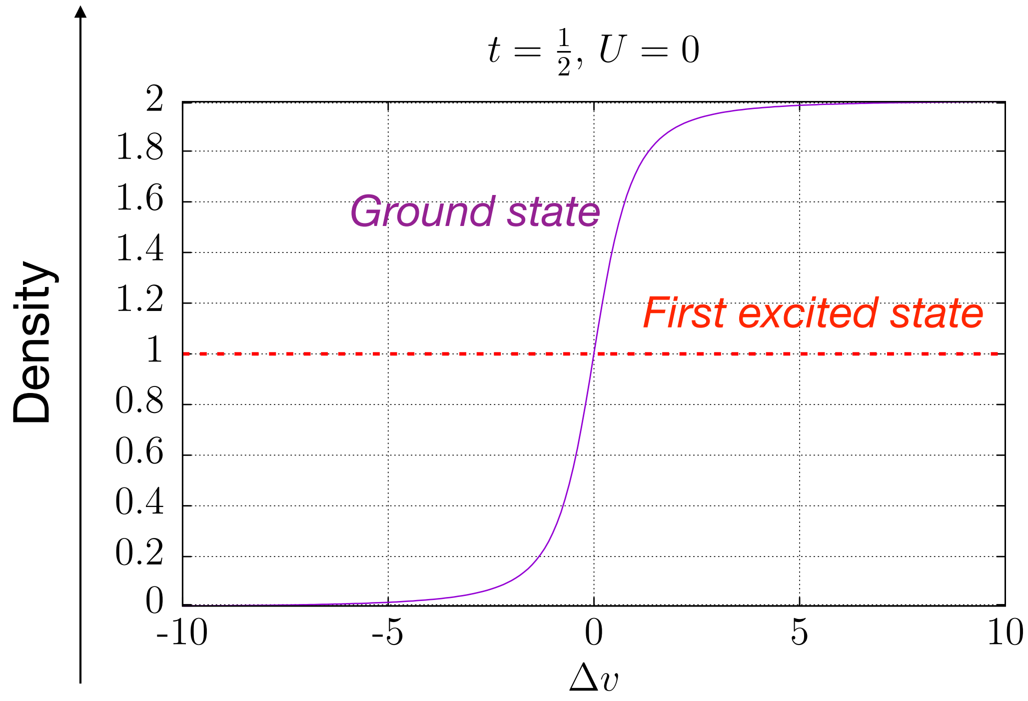
$$+ \langle \overline{\Phi}_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \overline{\Phi}_I \rangle - \langle \Phi^{\mathbf{w}}_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi^{\mathbf{w}}_I \rangle$$

I am the *density-driven* correlation energy

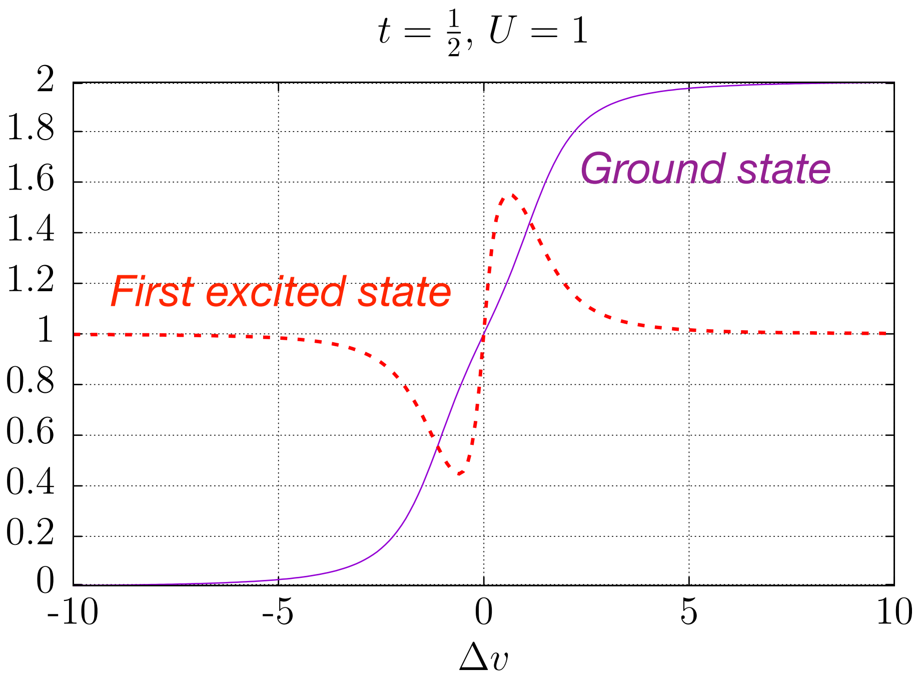
T. Gould and S. Pittalis, Phys. Rev. Lett. ***123****, 016401 (2019).*

Non-uniqueness or -existence of state-driven KS states

Non-interacting Hubbard dimer



Interacting Hubbard dimer



*K. Deur, L. Mazouin, and E. Fromager, Phys. Rev. B **95**, 035120 (2017).*

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Title:Individual correlations in ensemble density-functional theory: State-driven/density-driven decomposition without additional Kohn-Sham systems

Authors:Emmanuel Fromager
(Submitted on 23 Jan 2020 (v1), last revised 28 Jan 2020 (this version, v2))

Abstract: Gould and Pittalis [Phys. Rev. Lett. 123, 016401 (2019)] recently revealed a density-driven correlation energy in many-electron ensembles that must be accounted for by approximations. We show that referring to auxiliary state-driven Kohn-Sham (KS) systems, which was inherent to its evaluation, is in fact not needed. Instead, individual-state densities can be extracted directly from the KS ensemble. On that basis, a simpler and more general expression is derived and tested. The importance of density-driven effects is thus confirmed, and a direct route to approximations is introduced.

State-/density-driven decomposition without additional KS systems

- There is *no need* to introduce additional KS wave functions:

$$n_{\Psi_I}(\mathbf{r}) = n^{\mathbf{w}}(\mathbf{r}) + \sum_{J>0} \left(\delta_{IJ} - \mathtt{w}_J\right) \frac{\partial n^{\mathbf{w}}(\mathbf{r})}{\partial \mathtt{w}_J}$$

→ obtained from a *static* ensemble *coupled perturbed* equation.

- *Exact expressions* for **state-driven** (SD) and **density-driven** (DD) correlation energies:

$$E_{\mathrm{c},I}^{\mathrm{SD}} := E_{\mathrm{c}}^{\mathbf{w}}[n^{\mathbf{w}}] + \sum_{J>0} \left(\delta_{IJ} - \mathtt{w}_J\right) \frac{dE_{\mathrm{c}}^{\mathbf{w}}[n^{\mathbf{w}}]}{d\mathtt{w}_J}$$

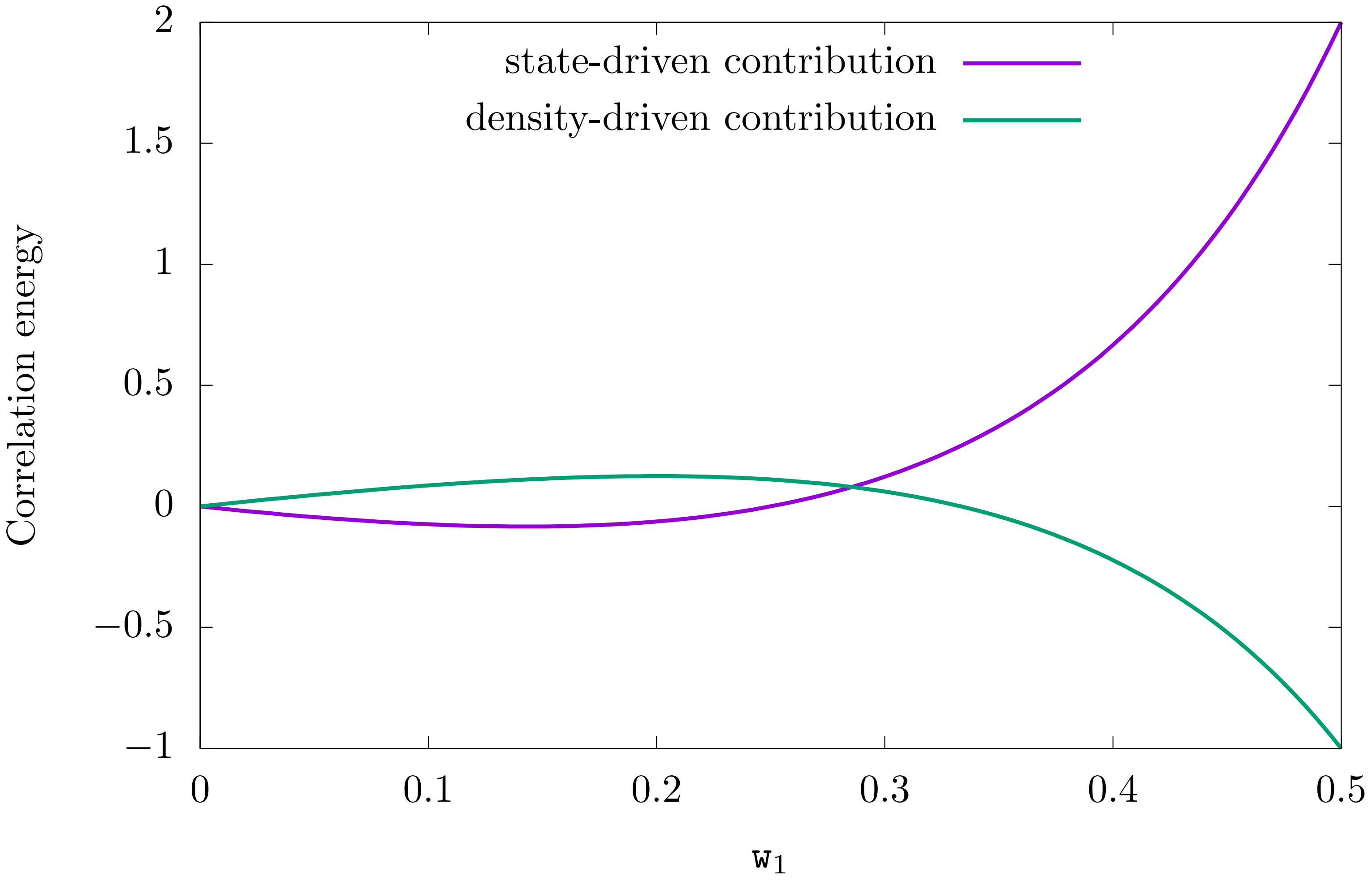
$$E_{\mathrm{c},I}^{\mathrm{DD}} := \int d\mathbf{r} \frac{\delta E_{\mathrm{c}}^{\mathbf{w}}[n^{\mathbf{w}}]}{\delta n(\mathbf{r})} \left(n_{\Phi_I^{\mathbf{w}}}(\mathbf{r}) - n_{\Psi_I}(\mathbf{r})\right)$$

E. Fromager, **arXiv:2001.08605** (2020).

Application to the Hubbard dimer: the bi-ensemble case

$$\boxed{\frac{\Delta v_{\text{ext}}}{t} << \frac{t}{U} << 1}$$

First (singlet) excited-state correlation energy per unit of $U(U\Delta v_{\text{ext}})^2/(4t^4)$



E. Fromager, ***arXiv:2001.08605*** *(2020).*

Conclusions and perspectives

- *Individual* energies and densities can be extracted *exactly* from GOK-DFT[1,2].

- A general and exact *SD/DD decomposition* has been derived[2].

- The approach is applicable to *grand canonical* ensembles[3,4] (fundamental *gaps*, quantum *embedding*,…).

- Local SD correlation functionals can be extracted from *finite* uniform electron gases[5]: *collaboration with Pierre-François Loos (Toulouse).*

- Connections with *imaginary TD-DFT* $[t \rightarrow -\mathrm{i}\tau]$ under investigation.

- Extraction of *(non-adiabatic) couplings* from GOK-DFT under investigation.

---

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

[2] *E. Fromager,* ***arXiv:2001.08605*** *(2020).*

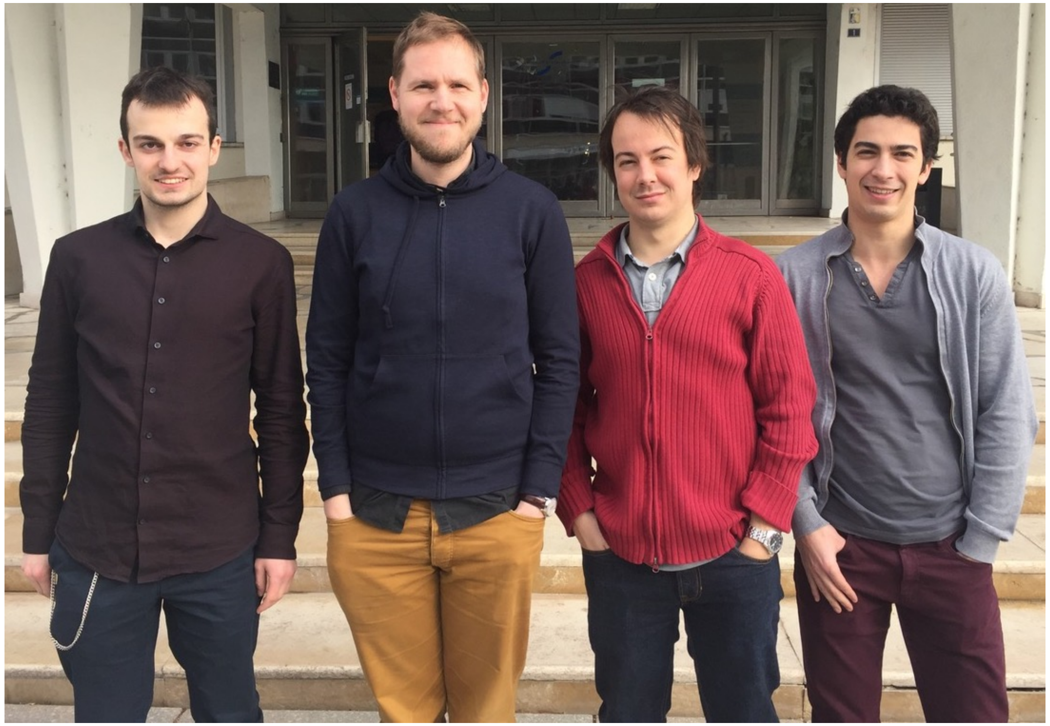
[3] *B. Senjean and E. Fromager, Phys. Rev. A* ***98****, 022513 (2018).*

[4] *B. Senjean and E. Fromager, Int. J. Quantum Chem. (2020),* ***DOI: 10.1002/qua.26190***

[5] *P. F. Loos and E. Fromager, to be submitted.*

Funding and acknowledgements

LABEX, University of Strasbourg



Laurent Mazouin, E.F., Killian Deur, and *Bruno Senjean (now in Leiden and Amsterdam)*

N-centered grand canonical ensembles

density:

$$n^{\mathcal{N}}(\mathbf{r}) = (1-\alpha)n^{N}(\mathbf{r})+\alpha\, n^{N-1}(\mathbf{r})$$

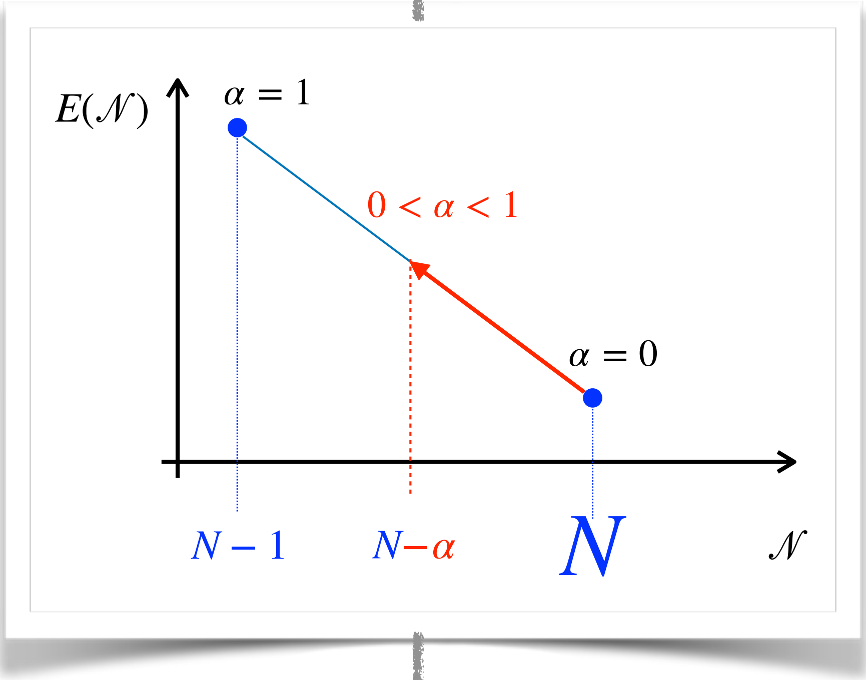
Look at me!

electron ***number***:

$$\mathcal{N} = N-\alpha$$

energy:

$$E\left(\mathcal{N}\right) = (1-\alpha)E^{N}+\alpha E^{N-1}$$



density:

$$n^{\{N,\alpha\}}(\mathbf{r}) = (1-\alpha)n^{N}(\mathbf{r}) + \frac{N\alpha}{N-1}\, n^{N-1}(\mathbf{r})$$

Look at me!

electron ***number***:

$$N$$

energy:

$$\mathcal{E}^{\{N,\alpha\}} = (1-\alpha)E^{N} + \frac{N\alpha}{N-1}E^{N-1}$$

$$\left[\left(1-\frac{\alpha}{N}\right) - \frac{\alpha(1-\alpha)}{N}\frac{\partial}{\partial\alpha}\right]$$

Conventional *picture* ← *N-centered picture*

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. (2020), ***DOI: 10.1002/qua.26190***