Université de Strasbourg

Institut de Chimie de Strasbourg
UMR 7177

Ensemble density-functional approach to electronic excitations: Exact theory and open practical questions

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[d]ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
[e]Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, Toulouse, France

Online Discussion-Seminars organised by N. Gidopoulos, Durham University **24/03/2022**

Part 1: Exact theory

- *Unified description of charged and neutral electronic excitations within ensemble DFT*

- *Equivalence between xc ensemble weight derivatives and xc derivative discontinuities*

Part 2: Weight-dependent density-functional approximations (DFAs)

- *The exact Hartree-exchange dilemma in ensemble DFT*

- *Recycling ground-state correlation DFAs: What about state- and density-driven correlations?*

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REVIEW

Ensemble Density Functional Theory of Neutral and Charged Excitations

Exact Formulations, Standard Approximations, and Open Questions

Filip Cernatic[1] · **Bruno Senjean**[2] · **Vincent Robert**[1] · **Emmanuel Fromager**[1]

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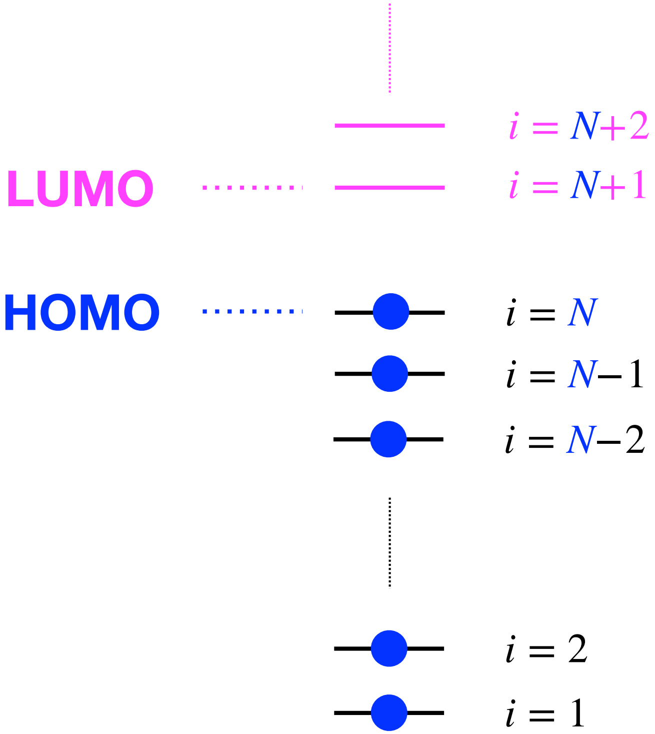
Abstract
Recent progress in the field of (time-independent) ensemble density-functional theory (DFT) for excited states are reviewed. Both Gross–Oliveira–Kohn (GOK) and N-centered ensemble formalisms, which are mathematically very similar and allow for an in-principle-exact description of neutral and charged electronic excitations, respectively, are discussed. Key exact results, for example, the equivalence between the infamous derivative discontinuity problem and the description of weight dependencies in the ensemble exchange-correlation density functional, are highlighted. The variational evaluation of orbital-dependent ensemble Hartree-exchange (Hx) energies is discussed in detail. We show in passing that state-averaging individual exact Hx energies can lead to severe (although solvable) v-representability issues. Finally, we explore the possibility of using the concept of density-driven correlation, which has been introduced recently and does not exist in regular ground-state DFT, for improving state-of-the-art correlation density-functional approximations for ensembles. The present review reflects the efforts of a growing community to turn ensemble DFT into a rigorous and reliable low-cost computational method for excited states. We hope that, in the near future, this contribution will stimulate new formal and practical developments in the field.

Keywords Density-functional theory · Excited states · Many-body ensembles

DFT for N-electron ground states

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{Hxc}}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$$



$i = N+2$

LUMO $i = N+1$

HOMO $i = N$

$i = N-1$

$i = N-2$

$i = 2$

$i = 1$

DFT for N-electron ground states

$$\left[-\frac{\nabla^2_{\mathbf{r}}}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{Hxc}}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$$

$$\boxed{n_0^N(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2}$$

exact ground-state
density

DFT for N-electron ground states

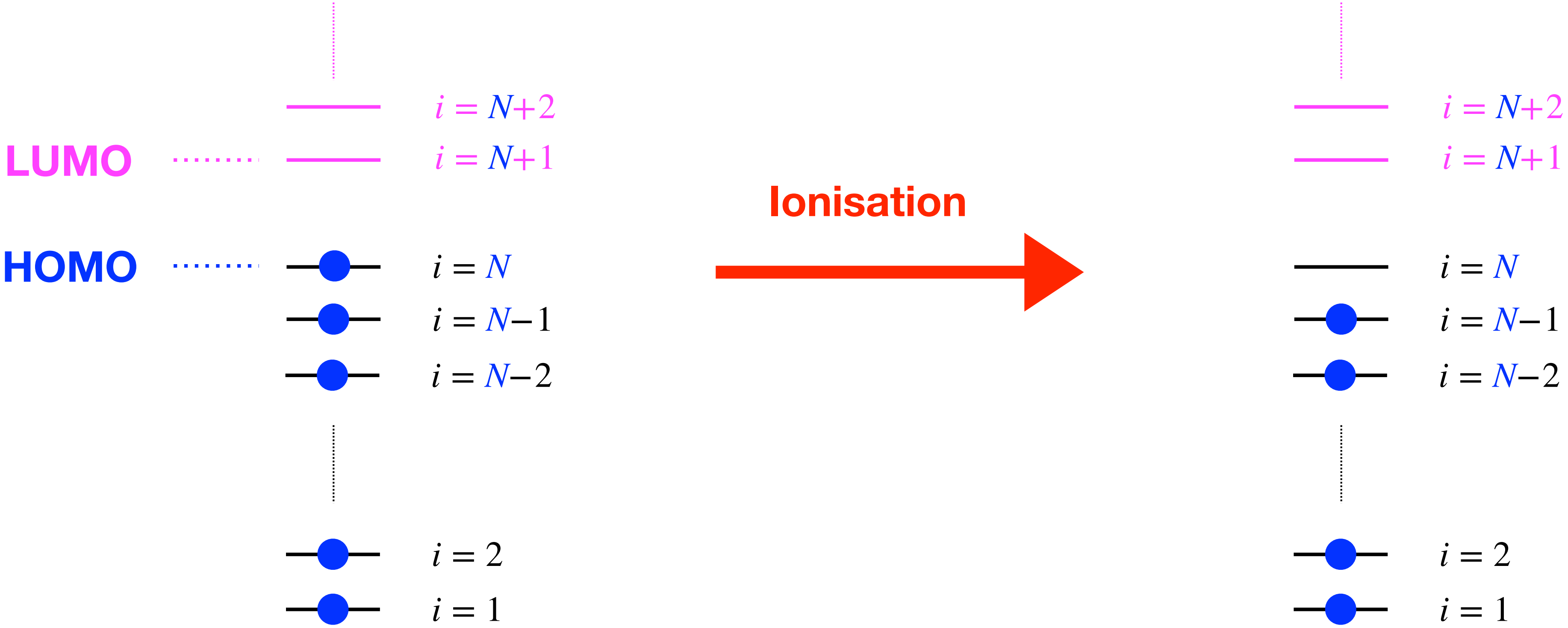
$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2}+v_{\rm ext}(\mathbf{r})+v_{\rm Hxc}(\mathbf{r})\right]\varphi_i(\mathbf{r})=\varepsilon_i\varphi_i(\mathbf{r})$$

$$\uparrow$$

$$v_{\rm Hxc}(\mathbf{r})=\left.\frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})}\right|_{n=n_0^N}$$

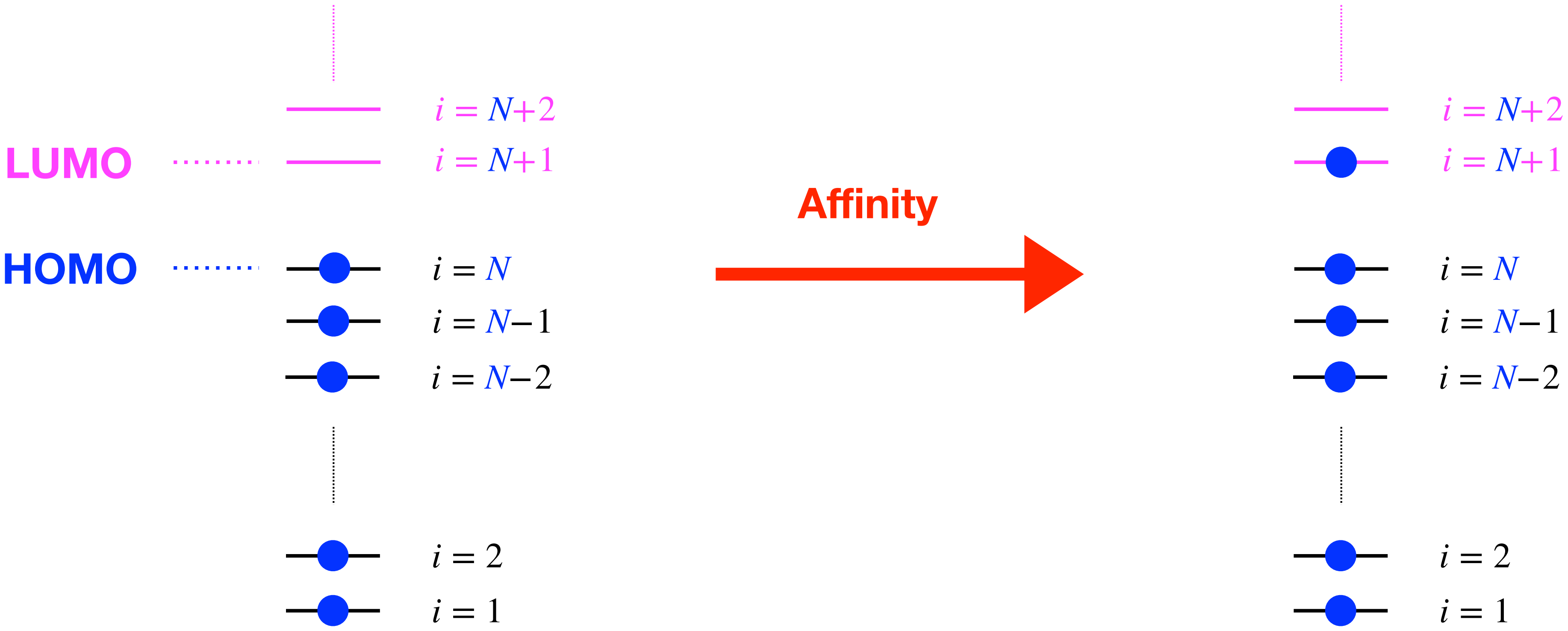
Hartree-exchange-correlation ***potential***

From the N-electron ground state to the excited states



Reference N-electron Kohn-Sham system

From the N-electron ground state to the excited states



LUMO

HOMO

$i = N+2$

$i = N+1$

$i = N$

$i = N-1$

$i = N-2$

$i = 2$

$i = 1$

Affinity

$i = N+2$

$i = N+1$

$i = N$

$i = N-1$

$i = N-2$

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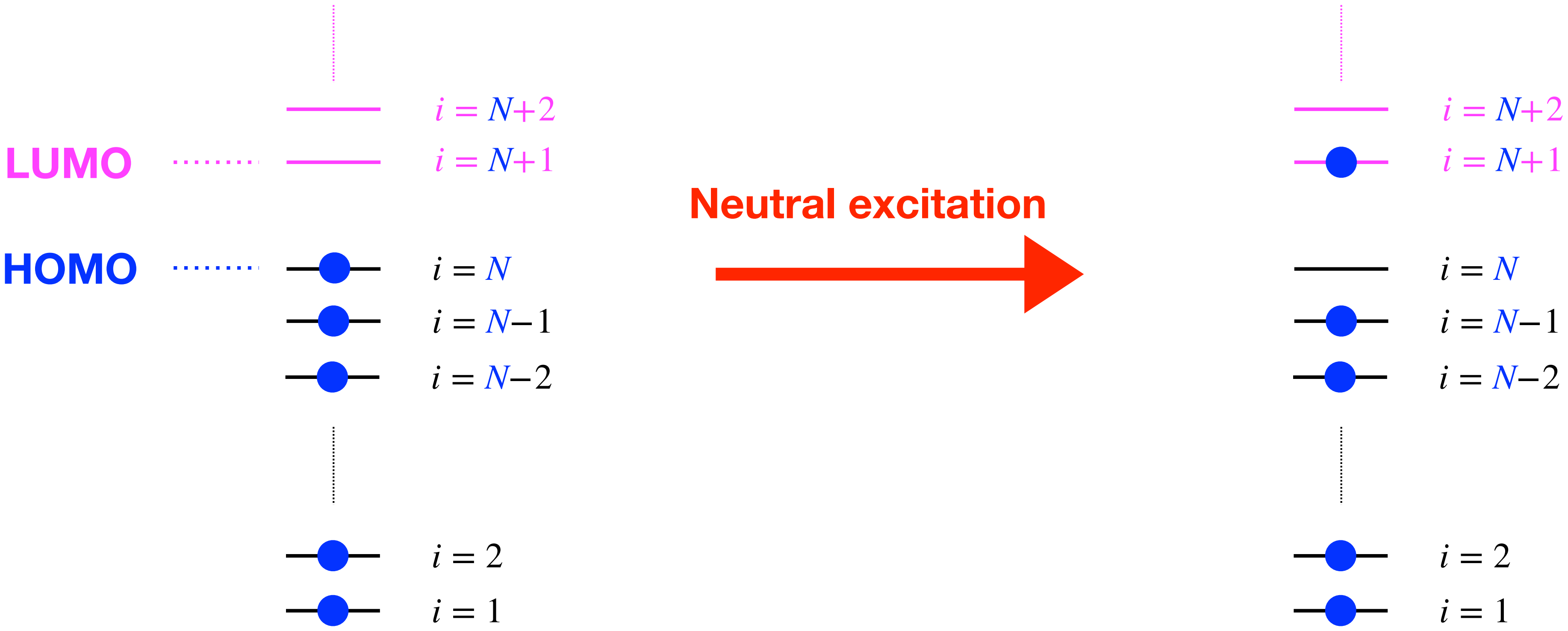
$i = 1$

Reference N-electron Kohn-Sham system

From the N-electron ground state to the excited states



LUMO

HOMO

$i = N+2$

$i = N+1$

$i = N$

$i = N-1$

$i = N-2$

$i = 2$

$i = 1$

Neutral excitation

$i = N+2$

$i = N+1$

$i = N$

$i = N-1$

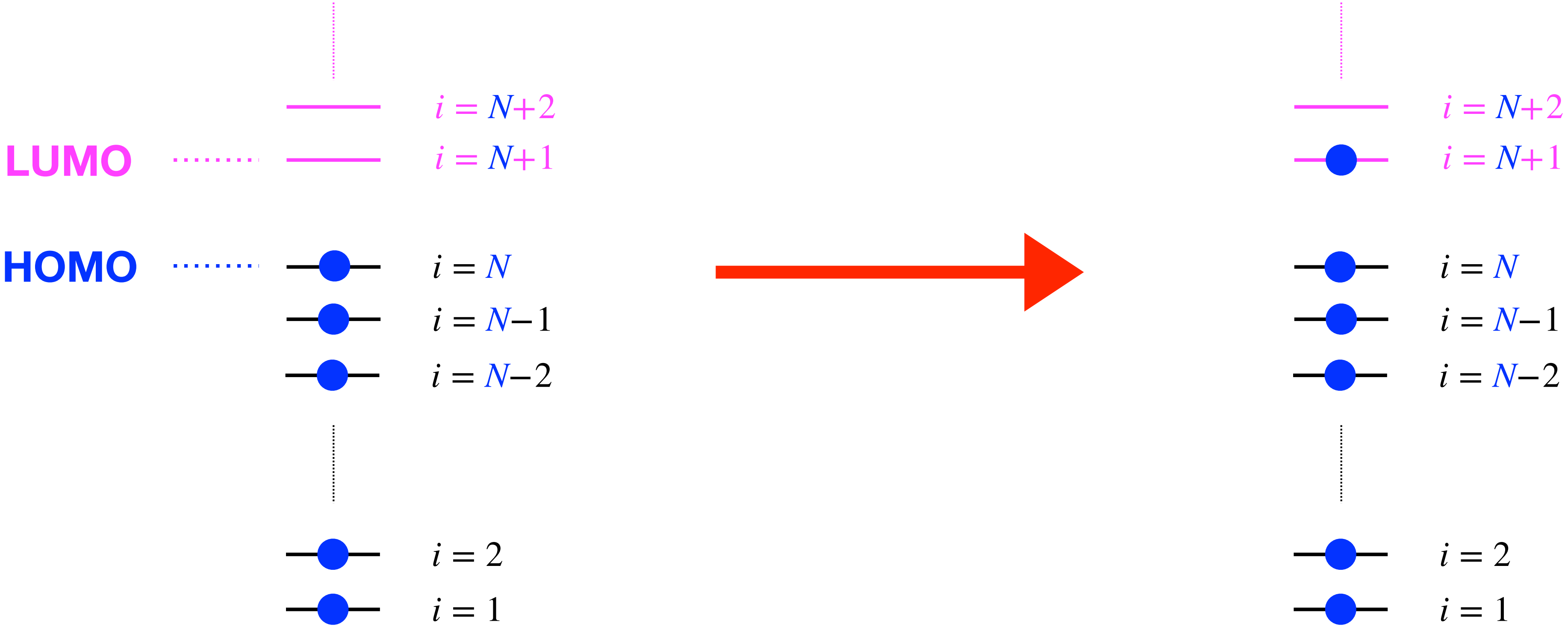
$i = N-2$

$i = 2$

$i = 1$

Reference N-electron Kohn-Sham system

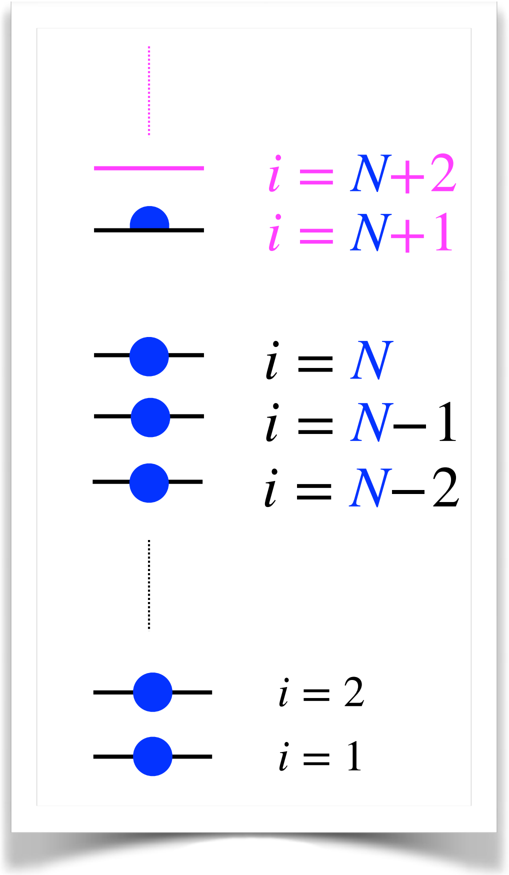
From the N-electron ground state to the excited states



Simple connection to the
real (interacting) ***excited*** *states?*

DFT for fractional electron numbers

Continuous affinity process



J.P. Perdew, R.G. Parr, M. Levy, J.L. Balduz Jr, Phys. Rev. Lett. ***49****, 1691 (1982).*

DFT for fractional electron numbers

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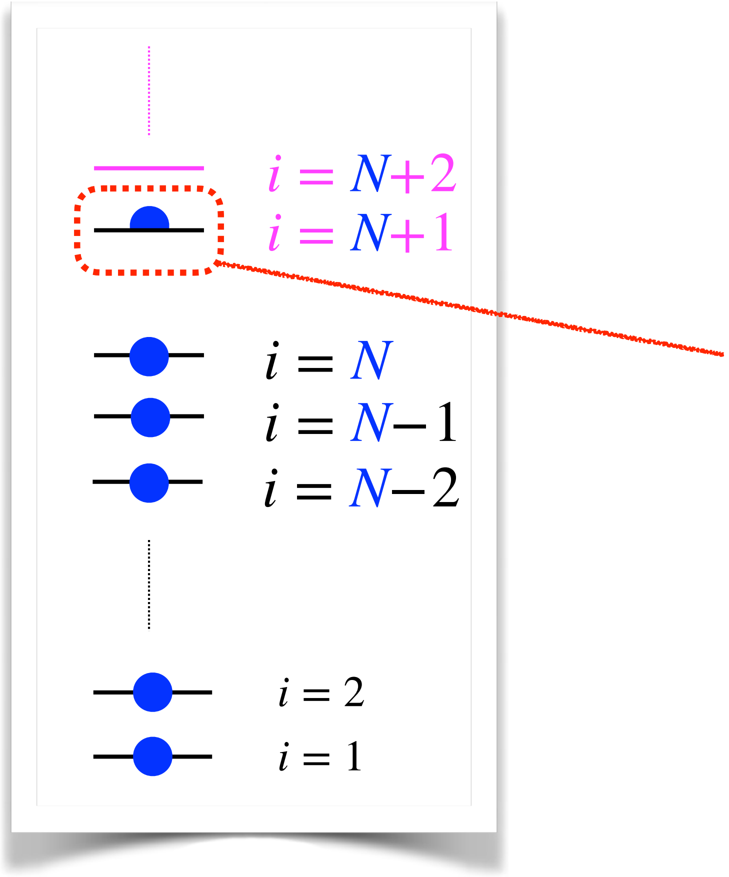
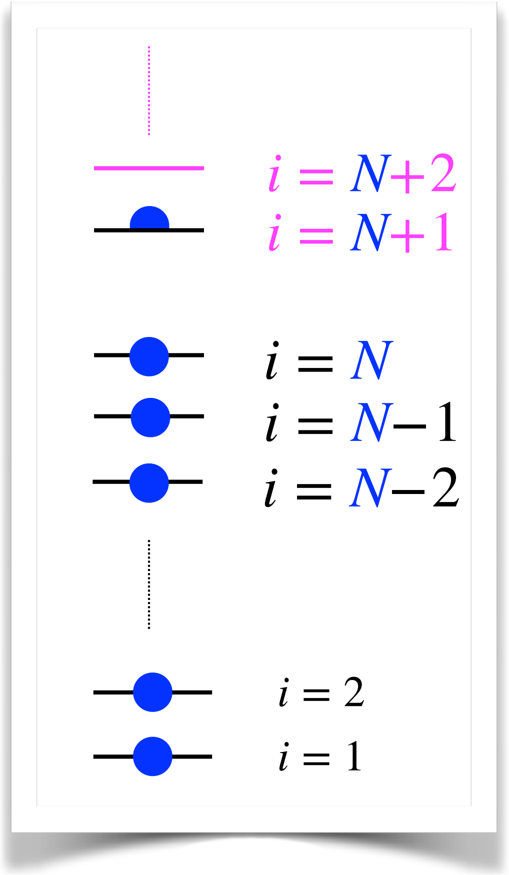


Fractional occupation

J.P. Perdew, R.G. Parr, M. Levy, J.L. Balduz Jr, Phys. Rev. Lett. ***49****, 1691 (1982).*
J. P. Perdew and M. Levy, Phys. Rev. Lett. ***51****, 1884 (1983).*

DFT for fractional electron numbers

Continuous affinity process



$$n(\mathbf{r}) \equiv (1-\alpha)n_0^{N}(\mathbf{r})+\alpha n_0^{N+1}(\mathbf{r})$$

$$0 < \alpha \leq 1$$

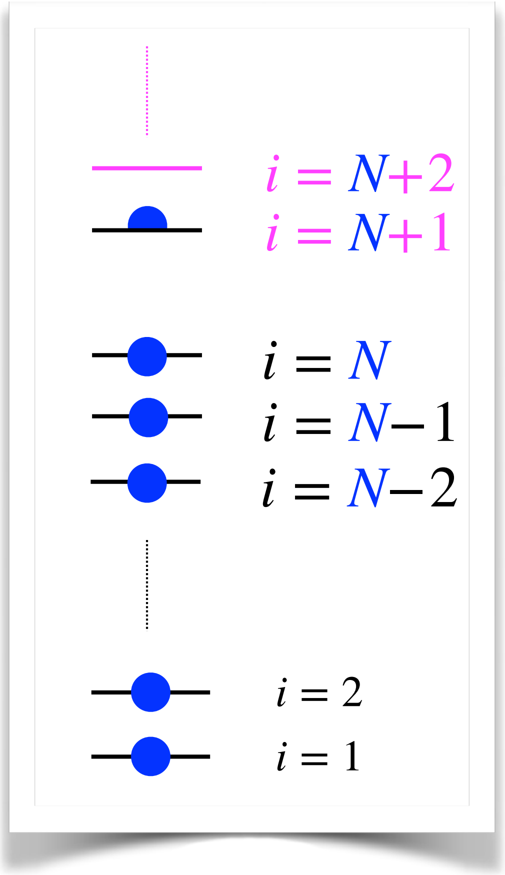
↓

“Grand canonical” ***ensemble weight***

E. Kraisler, L. Kronik, Phys. Rev. Lett. ***110****, 126403 (2013).*

DFT for fractional electron numbers

Continuous affinity process



$$n(\mathbf{r}) \equiv (1-\alpha)n_0^N(\mathbf{r})+\alpha n_0^{N+1}(\mathbf{r})$$

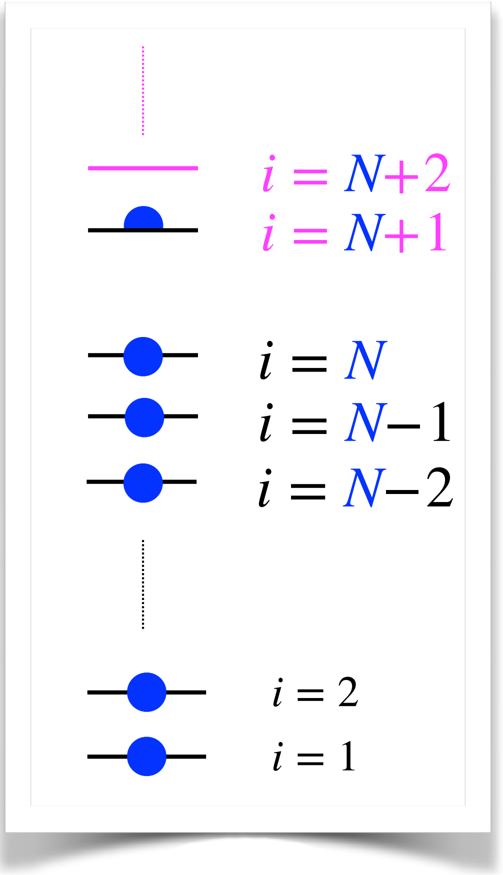
$$0 < \alpha \leq 1$$

*We "just" need to **extend** $E_{\mathrm{xc}}[n]$ to densities n integrating to **fractional** electron numbers*

E. Kraisler, L. Kronik, Phys. Rev. Lett. ***110****, 126403 (2013).*

DFT for fractional electron numbers

Continuous affinity process



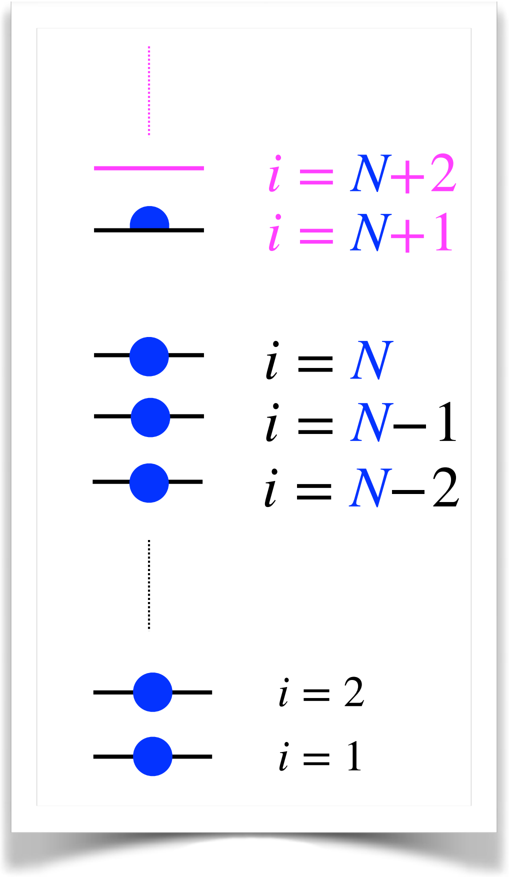
$$\boxed{I_0^{N+1} = -\,\varepsilon_{N+1}}$$

Janak's theorem

*J. F. Janak, Phys. Rev. B **18**, 7165 (1978).*

DFT for fractional electron numbers

Continuous affinity process



$$\boxed{I_0^{N+1} = -\,\varepsilon_{N+1}}$$

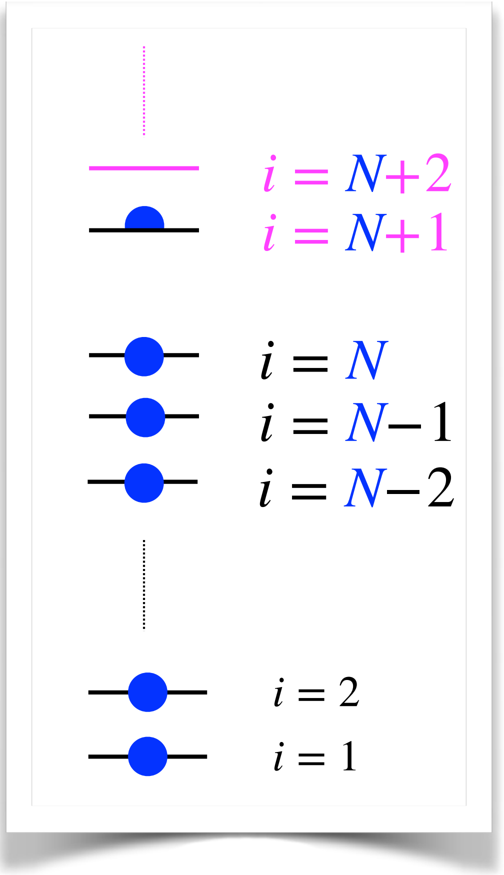
$$v_{\mathrm{Hxc}}[n](\mathbf{r}) = \frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})}$$

exhibits ***discontinuities*** when crossing an integer electron number

J. P. Perdew and M. Levy, Phys. Rev. Lett. ***51****, 1884 (1983).*

DFT for fractional electron numbers

Continuous affinity process



$$\boxed{I_0^{N+1} = -\varepsilon_{N+1}}$$

$$\Big\downarrow$$

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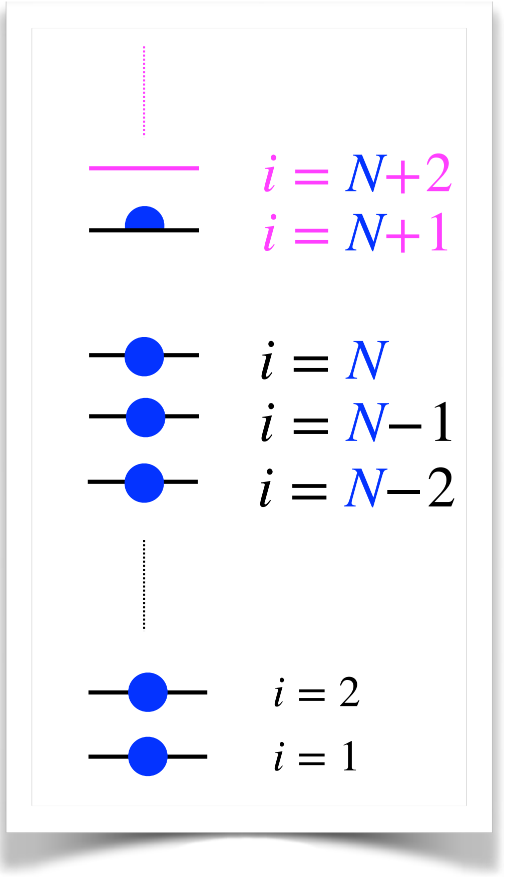
Continuous affinity process



$$n(\mathbf{r}) \equiv (1-\alpha)n_0^{N}(\mathbf{r})+\alpha n_0^{N+1}(\mathbf{r})$$

↓

$$\int d\mathbf{r}\, n(\mathbf{r}) = N + \alpha$$

E. Kraisler, L. Kronik, Phys. Rev. Lett. ***110****, 126403 (2013).*
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

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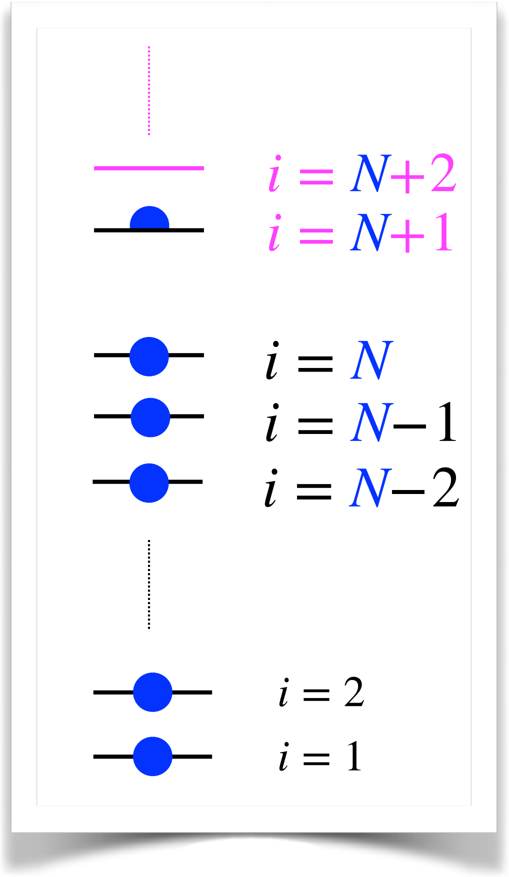

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↓

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↓

$$\alpha \equiv \alpha[n]$$

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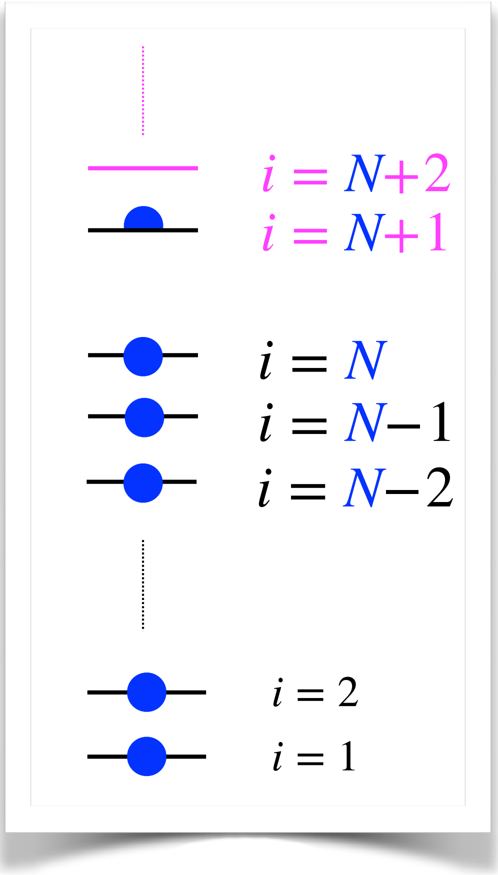

$$n(\mathbf{r}) \equiv (1-\alpha)n_0^{N}(\mathbf{r})+\alpha n_0^{N+1}(\mathbf{r})$$

The **ensemble weight** and the **density** are *not* independent variables

E. Kraisler, L. Kronik, Phys. Rev. Lett. ***110****, 126403 (2013).*
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

N-centered ensemble density

$$n(\mathbf{r}) \equiv (1-\alpha)n_0^{N}(\mathbf{r})+\alpha n_0^{N+1}(\mathbf{r})$$

Traditional approach

$$n(\mathbf{r}) \equiv \left(1-\frac{N+1}{N}\xi_{+}\right)n_0^{N}(\mathbf{r})+\xi_{+}n_0^{N+1}(\mathbf{r})$$

N-centered approach

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190

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N-centered approach

$$\Big\downarrow$$

$$\int d\mathbf{r}\, n(\mathbf{r}) = N$$

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N-centered approach

$$\Big\downarrow$$

$$\int d\mathbf{r}\, n(\mathbf{r}) = N$$

$$\Big\downarrow$$

The **ensemble weight** ξ_+ and the **density** n are now *independent* variables

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190

N*-centered ensemble DFT*

The xc functional has become *ensemble weight-dependent*

$$E_{\mathrm{xc}}^{\xi_+}[n]$$

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190

General N-centered ensemble formalism

$$n(\mathbf{r}) \equiv \left(1 - \sum_{\nu>0}^{\textit{excited states}} \frac{N_\nu}{N}\xi_\nu\right) n_0(\mathbf{r}) + \sum_{\nu>0}^{\textit{excited states}} \xi_\nu n_\nu(\mathbf{r})$$

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190

General N-centered ensemble formalism

Charged or **neutral!**

$$n(\mathbf{r}) \equiv \left(1 - \sum_{\nu>0}^{\text{excited states}} \frac{N_\nu}{N} \xi_\nu \right) n_0(\mathbf{r}) + \sum_{\nu>0}^{\text{excited states}} \xi_\nu n_\nu(\mathbf{r})$$

A. K. Theophilou, J. Phys. C: Solid State Phys. ***12****, 5419 (1979).*
A. K. Theophilou, in The Single Particle Density in Physics and Chemistry, edited by N. H. March and B. M. Deb (Academic Press, 1987), pp. 210–212.
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).*
C. Marut, F. Cernatic, B. Senjean, P.-F. Loos, and E. Fromager, in preparation (2022).

General N-centered ensemble formalism

$$n(\mathbf{r}) \equiv \left(1 - \sum_{\nu>0}^{\text{excited states}} \frac{N_\nu}{N}\xi_\nu\right) \boxed{n_0(\mathbf{r})} + \sum_{\nu>0}^{\text{excited states}} \xi_\nu n_\nu(\mathbf{r})$$

Reference N-electron
ground-state density

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
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General N-centered ensemble formalism

$$n(\mathbf{r}) \equiv \left(1 - \overset{\text{excited states}}{\sum_{\nu>0}} \boxed{\frac{N_\nu}{N}}\,\xi_\nu\right) n_0(\mathbf{r}) + \overset{\text{excited states}}{\sum_{\nu>0}} \xi_\nu n_\nu(\mathbf{r})$$

$$\Big\downarrow$$

$$\boxed{\int d\mathbf{r}\, n(\mathbf{r}) = N}$$

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190

N-centered ensemble energy

$$E^{\{\xi_\nu\}} = \left(1 - \sum_{\nu>0} \frac{N_\nu}{N}\xi_\nu\right)\boxed{E_0} + \sum_{\nu>0} \xi_\nu E_\nu$$

Reference N-electron
ground-state ***energy***

B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).
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N-centered ensemble DFT

$$E^{\{\xi_\nu\}} = \left(1 - \sum_{\nu>0} \frac{N_\nu}{N}\xi_\nu\right) E_0 + \sum_{\nu>0} \xi_\nu E_\nu$$

Functional of the N-centered ensemble ***density***

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
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N-centered ensemble Kohn-Sham DFT

$$E^{\{\xi_\nu\}} = \left(1 - \sum_{\nu>0} \frac{N_\nu}{N} \xi_\nu \right) E_0 + \sum_{\nu>0} \xi_\nu E_\nu$$

↓

Functional of the N-centered ensemble ***density***

$$n(\mathbf{r}) \equiv \sum_i \boxed{\left(\sum_{\nu \geq 0} n_{i,\nu} \xi_\nu \right)} \left| \varphi_i^{\{\xi_\nu\}}(\mathbf{r}) \right|^2$$

***Fractionally** occupied KS orbitals*

*B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190

N-centered ensemble Kohn-Sham DFT

$$E^{\{\xi_\nu\}} = \left(1-\sum_{\nu>0}\frac{N_\nu}{N}\xi_\nu\right)E_0+\sum_{\nu>0}\xi_\nu E_\nu$$

↓

Functional of the N-centered ensemble ***density***

$$n(\mathbf{r}) \equiv \sum_i\left(\sum_{\nu\geq 0} n_{i,\nu}\xi_\nu\right)\left|\varphi_i^{\{\xi_\nu\}}(\mathbf{r})\right|^2$$

$$E_{\rm Hxc}^{\{\xi_\nu\}}[n] = E_{\rm H}[n] + \boxed{E_{\rm xc}^{\{\xi_\nu\}}[n]}$$

key ingredient

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190

N-centered ensemble energy

$$E^{\{\xi_\nu\}} = \left(1 - \sum_{\nu>0} \frac{N_\nu}{N} \xi_\nu\right) E_0 + \sum_{\nu>0} \xi_\nu E_\nu$$

Auxiliary quantity *(not an observable) …*

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
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N-centered ensemble energy

$$E^{\{\xi_\nu\}} = \left(1 - \sum_{\nu>0} \frac{N_\nu}{N} \xi_\nu \right) E_0 + \sum_{\nu>0} \xi_\nu E_\nu$$

Auxiliary quantity *(not observable) …*

*… that **varies linearly** with the ensemble **weights!***

*B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).*
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N-centered ensemble energy

$$E^{\{\xi_\nu\}} = \left(1 - \sum_{\nu>0} \frac{N_\nu}{N}\xi_\nu\right) E_0 + \sum_{\nu>0} \xi_\nu E_\nu$$

$$\Big\downarrow$$

Extraction procedure

$$\boxed{E_\mu - E_0 = \frac{\left(N_\mu - N\right)}{N} E_0 + \left.\frac{\partial E^{\{\xi_\nu\}}}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0}}$$

Excitation energy

*B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).*
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N-centered ensemble energy

$$E^{\{\xi_\nu\}} = \left(1 - \sum_{\nu>0} \frac{N_\nu}{N}\xi_\nu\right)E_0 + \sum_{\nu>0}\xi_\nu E_\nu$$

$$\downarrow$$

Infinitesimal occupation

of the targeted excited state μ,

i.e., $\xi_\mu \rightarrow 0^+$

$$\boxed{E_\mu - E_0 = \frac{\left(N_\mu - N\right)}{N}E_0 + \boxed{\left.\frac{\partial E^{\{\xi_\nu\}}}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0}}}$$

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Physical meaning of the KS orbital energies

$$E_{\mu} - E_{0} = \boxed{\mathscr{E}^{\mathrm{KS}}_{\mu} - \mathscr{E}^{\mathrm{KS}}_{0}}$$

KS excitation energy

$$+ \left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_{\nu}\}}[n_0]}{\partial \xi_{\mu}}\right|_{\{\xi_{\nu}\}=0} + \frac{\left(N - N_{\mu}\right)}{N}\left(\int d\mathbf{r}\, v_{\mathrm{Hxc}}^{\xi_{\mu}\to 0^{+}}(\mathbf{r})n_0(\mathbf{r}) - E_{\mathrm{Hxc}}[n_0]\right)$$

*M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).*
*F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) **380**, 4 (2022).*

Physical meaning of the KS orbital energies

$$E_{\mu} - E_{0} = \mathscr{E}_{\mu}^{\mathrm{KS}} - \mathscr{E}_{0}^{\mathrm{KS}}$$

$$+ \underbrace{\boxed{\left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_{\nu}\}}[n_0]}{\partial \xi_{\mu}}\right|_{\{\xi_{\nu}\}=0}}}_{\text{xc ensemble weight derivative}} + \frac{\left(N - N_{\mu}\right)}{N}\left(\int d\mathbf{r}\, v_{\mathrm{Hxc}}^{\xi_{\mu}\to 0^{+}}(\mathbf{r})n_0(\mathbf{r}) - E_{\mathrm{Hxc}}[n_0]\right)$$

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Physical meaning of the KS orbital energies

$$E_\mu - E_0 = \mathcal{E}_\mu^{\rm KS} - \mathcal{E}_0^{\rm KS}$$

$$+\boxed{\left.\frac{\partial E_{\rm xc}^{\{\xi_\nu\}}[n_0]}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0}} + \frac{\left(N-N_\mu\right)}{N}\left(\int d\mathbf{r}\, v_{\rm Hxc}^{\xi_\mu\to 0^+}(\mathbf{r})n_0(\mathbf{r}) - E_{\rm Hxc}[n_0]\right)$$

*does **not** exist in regular DFT*

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Physical meaning of the KS orbital energies

$$E_{\mu} - E_0 = \mathscr{E}_{\mu}^{\mathrm{KS}} - \mathscr{E}_{0}^{\mathrm{KS}} + \left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n_0]}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0} + \frac{\left(N - N_\mu\right)}{N}\left(\int d\mathbf{r}\, \boxed{v_{\mathrm{Hxc}}^{\xi_\mu \to 0^+}(\mathbf{r})} n_0(\mathbf{r}) - E_{\mathrm{Hxc}}[n_0]\right)$$

N-centered ensemble **Hxc potential**

*M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).*
*F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) **380**, 4 (2022).*

Physical meaning of the KS orbital energies

$$E_{\mu}-E_{0}=\boxed{\mathscr{E}_{\mu}^{\mathrm{KS}}-\mathscr{E}_{0}^{\mathrm{KS}}}+\left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_{\nu}\}}[n_{0}]}{\partial \xi_{\mu}}\right|_{\{\xi_{\nu}\}=0}+\frac{\left(N-N_{\mu}\right)}{N}\left(\int d\mathbf{r}\,\boxed{v_{\mathrm{Hxc}}^{\xi_{\mu}\rightarrow 0^{+}}(\mathbf{r})}\,n_{0}(\mathbf{r})-E_{\mathrm{Hxc}}[n_{0}]\right)$$

N-centered ensemble Hxc potential
*unique **up to a constant***

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$$E_{\mu} - E_{0} = \boxed{\mathscr{E}^{\mathrm{KS}}_{\mu} - \mathscr{E}^{\mathrm{KS}}_{0}} + \left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_{\nu}\}}[n_{0}]}{\partial \xi_{\mu}}\right|_{\{\xi_{\nu}\}=0} + \frac{\left(N - N_{\mu}\right)}{N}\left(\int d\mathbf{r}\, \boxed{v_{\mathrm{Hxc}}^{\xi_{\mu}\to 0^{+}}}(\mathbf{r})\, n_{0}(\mathbf{r}) - E_{\mathrm{Hxc}}[n_{0}]\right)$$

N-centered ensemble Hxc potential

unique ***up to a constant***

Even for charged excitations!

M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A ***103****, 012806 (2021).*
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

Let's make the charged KS excitation energies match the true ones!

$$\boxed{E_\mu - E_0 = \mathscr{E}_\mu^{\mathrm{KS}} - \mathscr{E}_0^{\mathrm{KS}}} \Leftrightarrow$$

Janak's theorem

$$\boxed{+\left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n_0]}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0} + \frac{\left(N - N_\mu\right)}{N}\left(\int d\mathbf{r}\, v_{\mathrm{Hxc}}^{\xi_\mu \to 0^+}(\mathbf{r}) n_0(\mathbf{r}) - E_{\mathrm{Hxc}}[n_0]\right)}$$

$$= 0$$

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$$\left.\frac{\partial E_{\rm xc}^{\{\xi_\nu\}}[n_0]}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0} + \frac{\left(N-N_\mu\right)}{N}\left(\int d\mathbf{r}\, v_{\rm Hxc}^{\xi_\mu\rightarrow 0^+}(\mathbf{r})n_0(\mathbf{r}) - E_{\rm Hxc}[n_0]\right) = 0$$

N-centered excitation energy ***matching constraint***

for the (charged) excited state μ

M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A ***103****, 012806 (2021).*
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***Uniquely** defined!*

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$$\Updownarrow$$

$$v_{\rm Hxc}^{\xi_\mu\to 0^+}(\mathbf{r}) \xrightarrow[|\mathbf{r}|\to+\infty]{} 0$$

for a ***molecule***

M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A ***103****, 012806 (2021).*
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

Let’s make the charged KS excitation energies match the true ones!

$$\left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n_0]}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0} + \frac{\left(N - N_\mu\right)}{N}\left(\int d\mathbf{r}\, v_{\mathrm{Hxc}}^{\xi_\mu \to 0^+}(\mathbf{r}) n_0(\mathbf{r}) - E_{\mathrm{Hxc}}[n_0]\right) = 0$$

Holds also, in principle, for an ***extended system*** *or a* ***lattice model!***

C. Marut, F. Cernatic, B. Senjean, P.-F. Loos, and E. Fromager, in preparation (2022).

Let's make the charged KS excitation energies match the true ones!

$$\left.\frac{\partial E_{\rm xc}^{\{\xi_\nu\}}[n_0]}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0} + \frac{\left(N-N_\mu\right)}{N}\left(\int d\mathbf{r}\, v_{\rm Hxc}^{\xi_\mu\rightarrow 0^+}(\mathbf{r})n_0(\mathbf{r}) - E_{\rm Hxc}[n_0]\right) = 0$$

$\xi_\mu \equiv \xi_+$ $\quad N_\mu \equiv N+1$ **Affinity**

$\xi_\mu \equiv \xi_-$ $\quad N_\mu \equiv N-1$ **Ionization**

M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A ***103****, 012806 (2021).*
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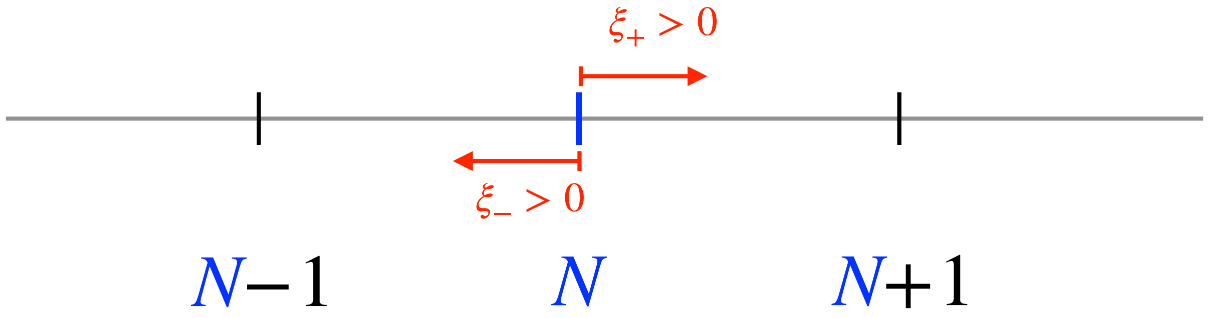
Let’s make the charged KS excitation energies match the true ones!

$$\int \frac{d\mathbf{r}}{N}\underbrace{\left(v_{\rm xc}^{\xi_+\to 0^+}(\mathbf{r}) - v_{\rm xc}^{\xi_-\to 0^+}(\mathbf{r})\right)}\, n_0(\mathbf{r}) = \left.\frac{\partial E_{\rm xc}^{\xi_+}[n_0]}{\partial \xi_+}\right|_{\xi_+=0} + \left.\frac{\partial E_{\rm xc}^{\xi_-}[n_0]}{\partial \xi_-}\right|_{\xi_-=0}$$



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Let’s make the charged KS excitation energies match the true ones!

$$\int \frac{d\mathbf{r}}{N}\underbrace{\left(v_{\mathrm{xc}}^{\xi_+\to 0^+}(\mathbf{r}) - v_{\mathrm{xc}}^{\xi_-\to 0^+}(\mathbf{r})\right)}_{\equiv\,\Delta_{\mathrm{xc}}} n_0(\mathbf{r}) = \underbrace{\left.\frac{\partial E_{\mathrm{xc}}^{\xi_+}[n_0]}{\partial \xi_+}\right|_{\xi_+=0} + \left.\frac{\partial E_{\mathrm{xc}}^{\xi_-}[n_0]}{\partial \xi_-}\right|_{\xi_-=0}}_{\equiv\,\Delta_{\mathrm{xc}}}$$

Derivative discontinuity

Exact fundamental gap

$$\boxed{E_{\mathrm{g}} = \varepsilon_{N+1} - \varepsilon_{N} + \Delta_{\mathrm{xc}}}$$

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Let's make the charged KS excitation energies match the true ones!

Now obtained from the xc weight derivatives!

$$\left.\frac{\partial E_{\mathrm{xc}}^{\xi_+}[n_0]}{\partial \xi_+}\right|_{\xi_+=0} + \left.\frac{\partial E_{\mathrm{xc}}^{\xi_-}[n_0]}{\partial \xi_-}\right|_{\xi_-=0}$$

Exact fundamental gap

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Suppression of the derivative discontinuity

$$\int \frac{d\mathbf{r}}{N}\left(v_{\mathrm{xc}}^{\xi_+\to 0^+}(\mathbf{r}) - v_{\mathrm{xc}}^{\xi_-\to 0^+}(\mathbf{r})\right) n_0(\mathbf{r}) = \Delta_{\mathrm{xc}}$$

$$\Updownarrow$$

$$\int \frac{d\mathbf{r}}{N}\left[\underbrace{\left(v_{\mathrm{xc}}^{\xi_+\to 0^+}(\mathbf{r})-\Delta_{\mathrm{xc}}\right)}_{\substack{\textbf{Shifted } N\text{-centered} \\ \text{ensemble xc potential}}} - v_{\mathrm{xc}}^{\xi_-\to 0^+}(\mathbf{r})\right] n_0(\mathbf{r}) = 0$$

*M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).*
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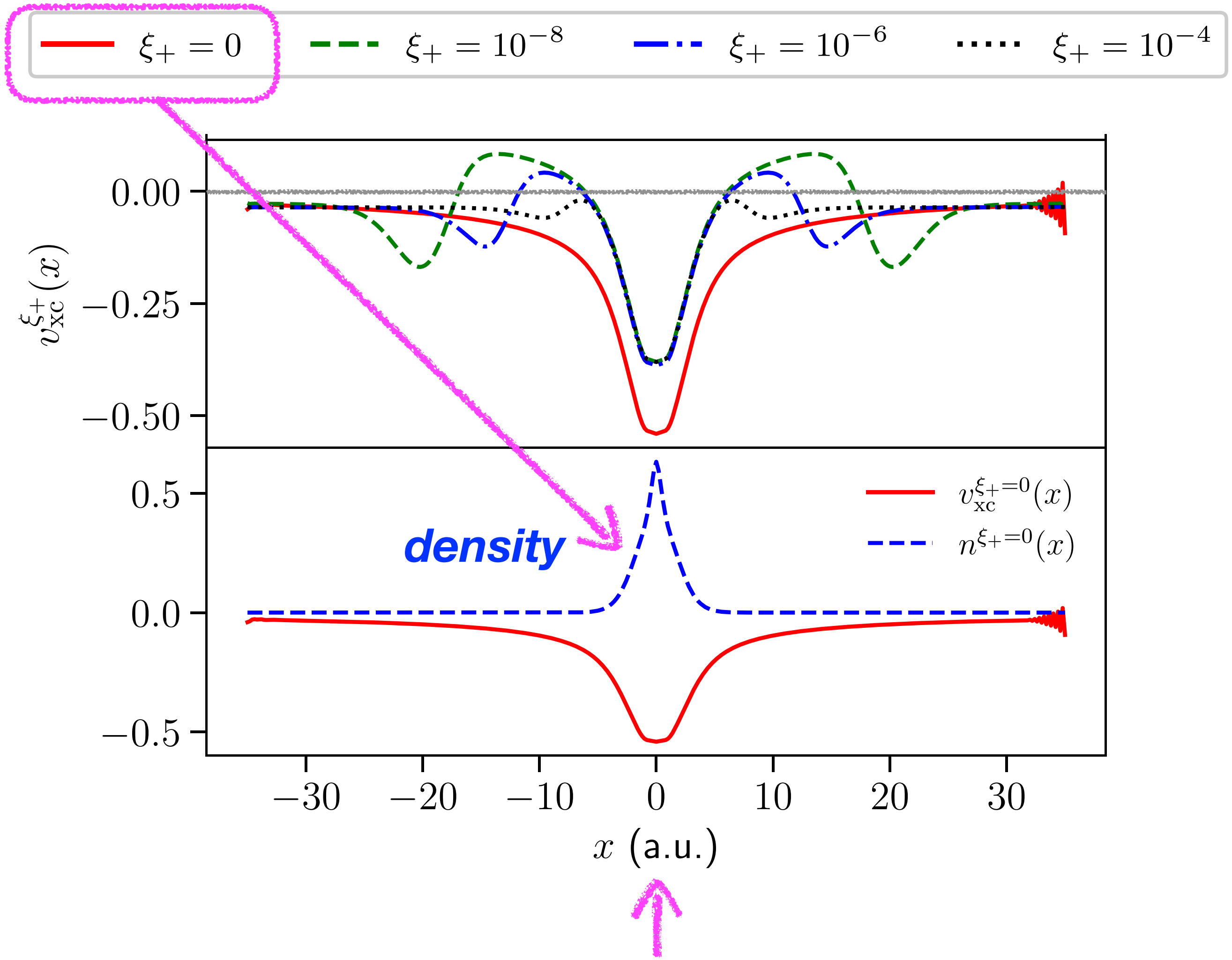
Application: Two-electron spin-polarised 1D atom

$$\hat{H} \equiv -\frac{1}{2}\sum_{i=1}^{N=2}\frac{d^2}{dx_i^2} + \left(-\sum_{i=1}^{N=2}\frac{3}{1+|x_i|} + \sum_{i<j}^{N=2}\frac{1}{1+|x_i-x_j|}\right)\times$$



density

Nucleus

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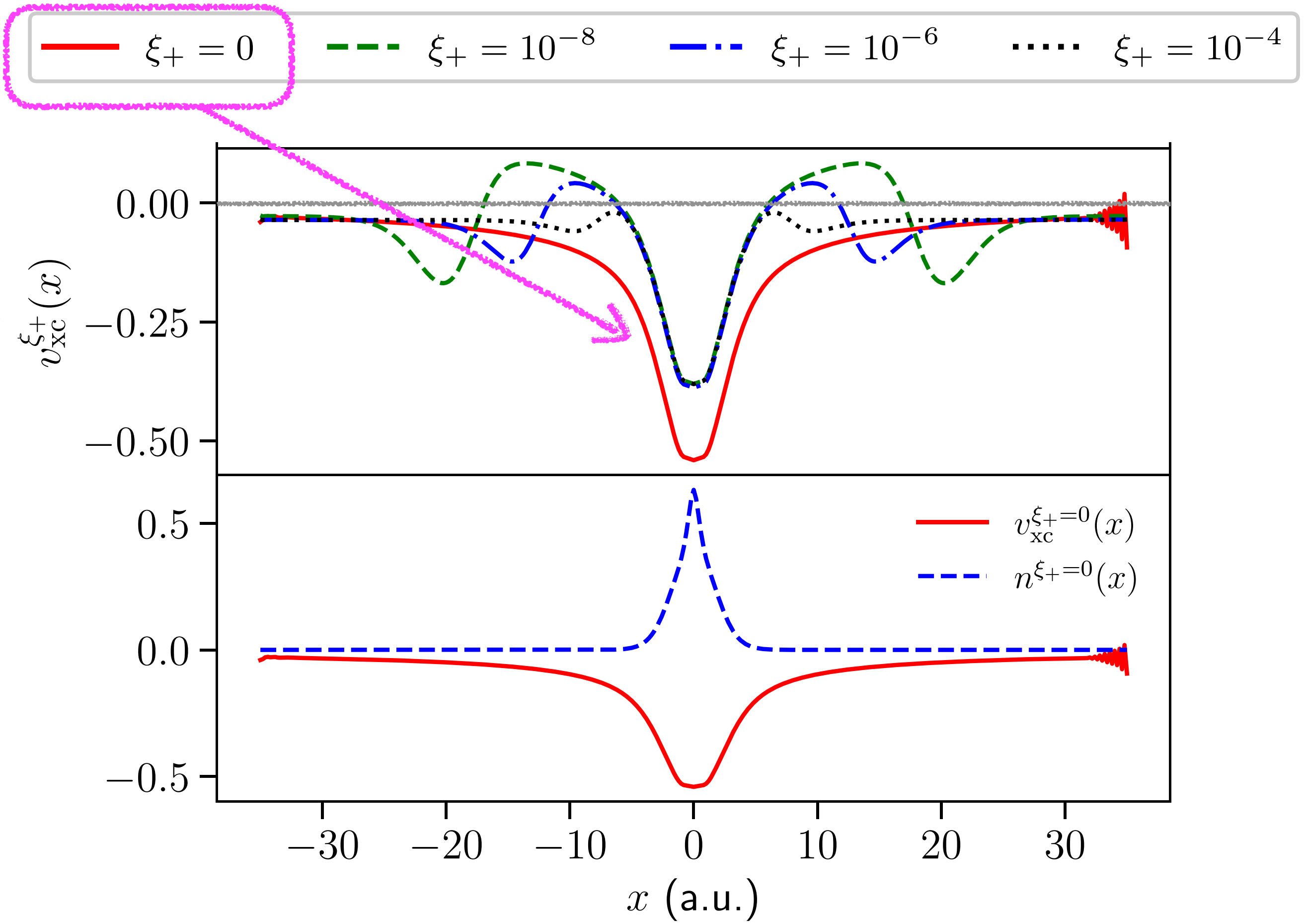

xc potential

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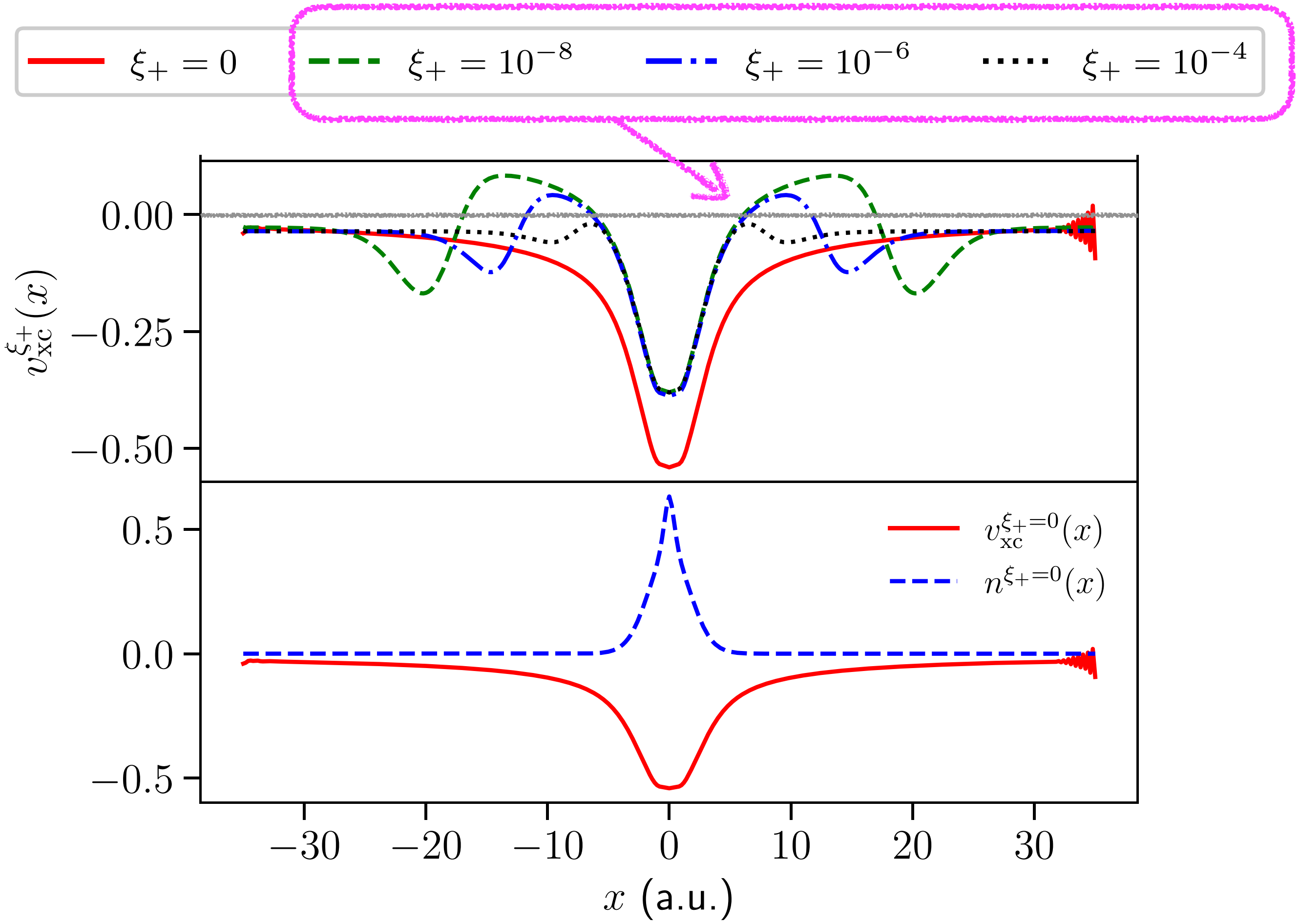

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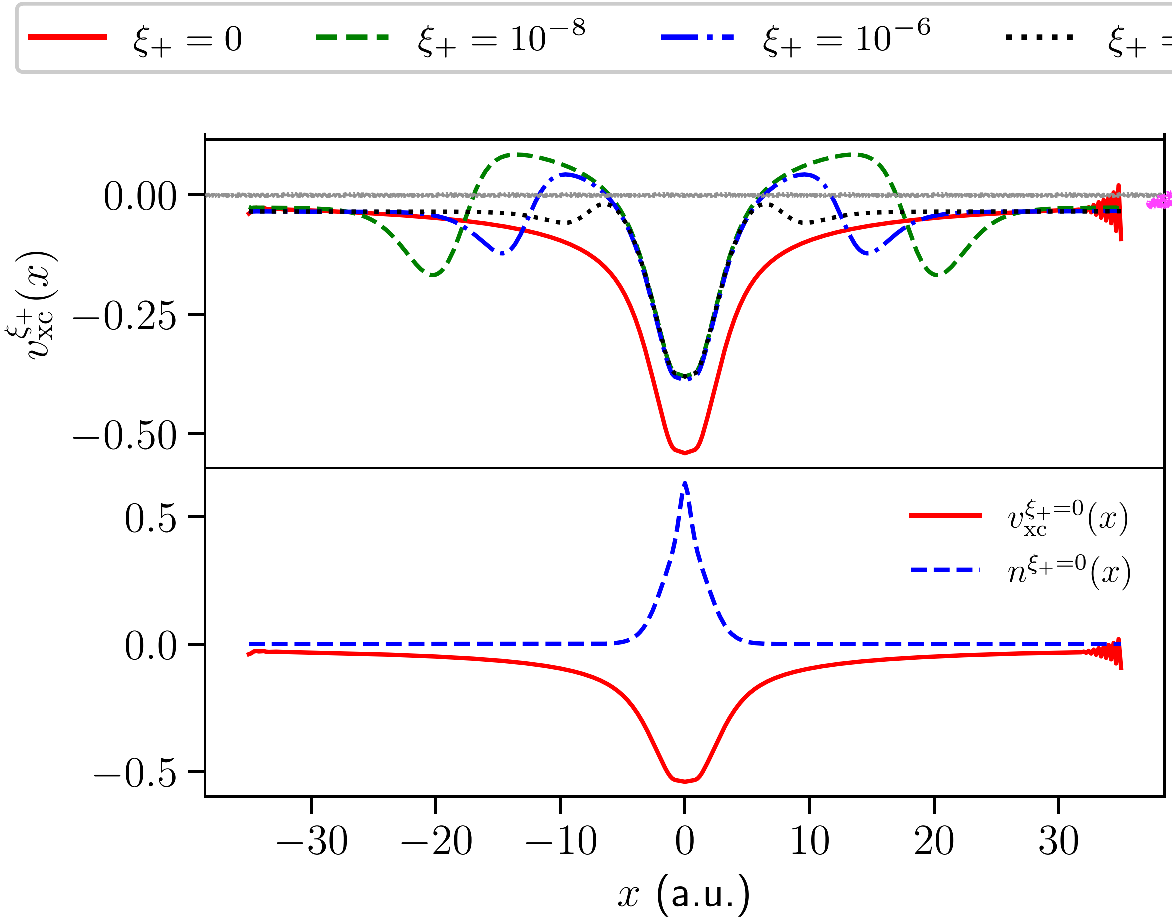

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xc potential

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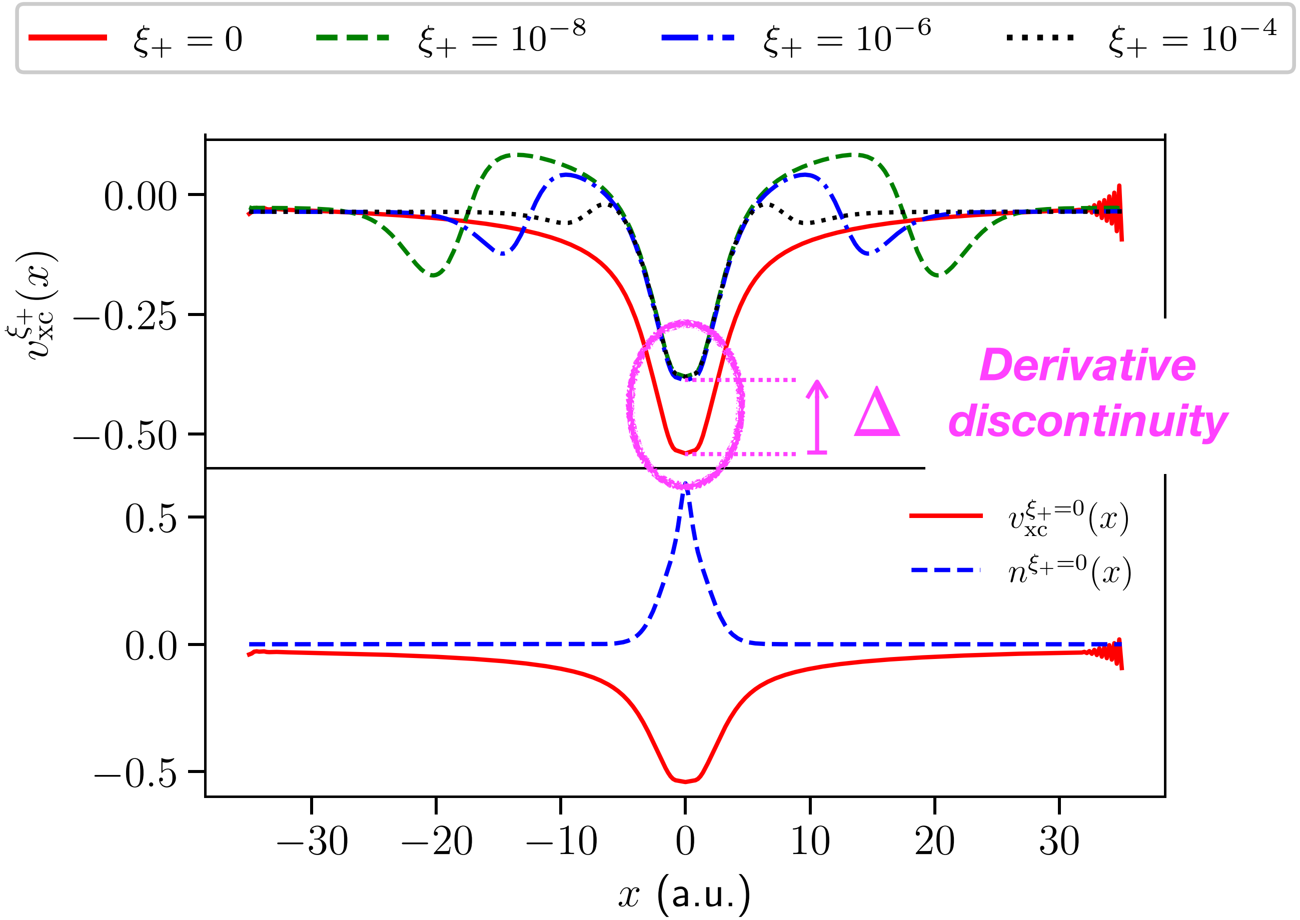


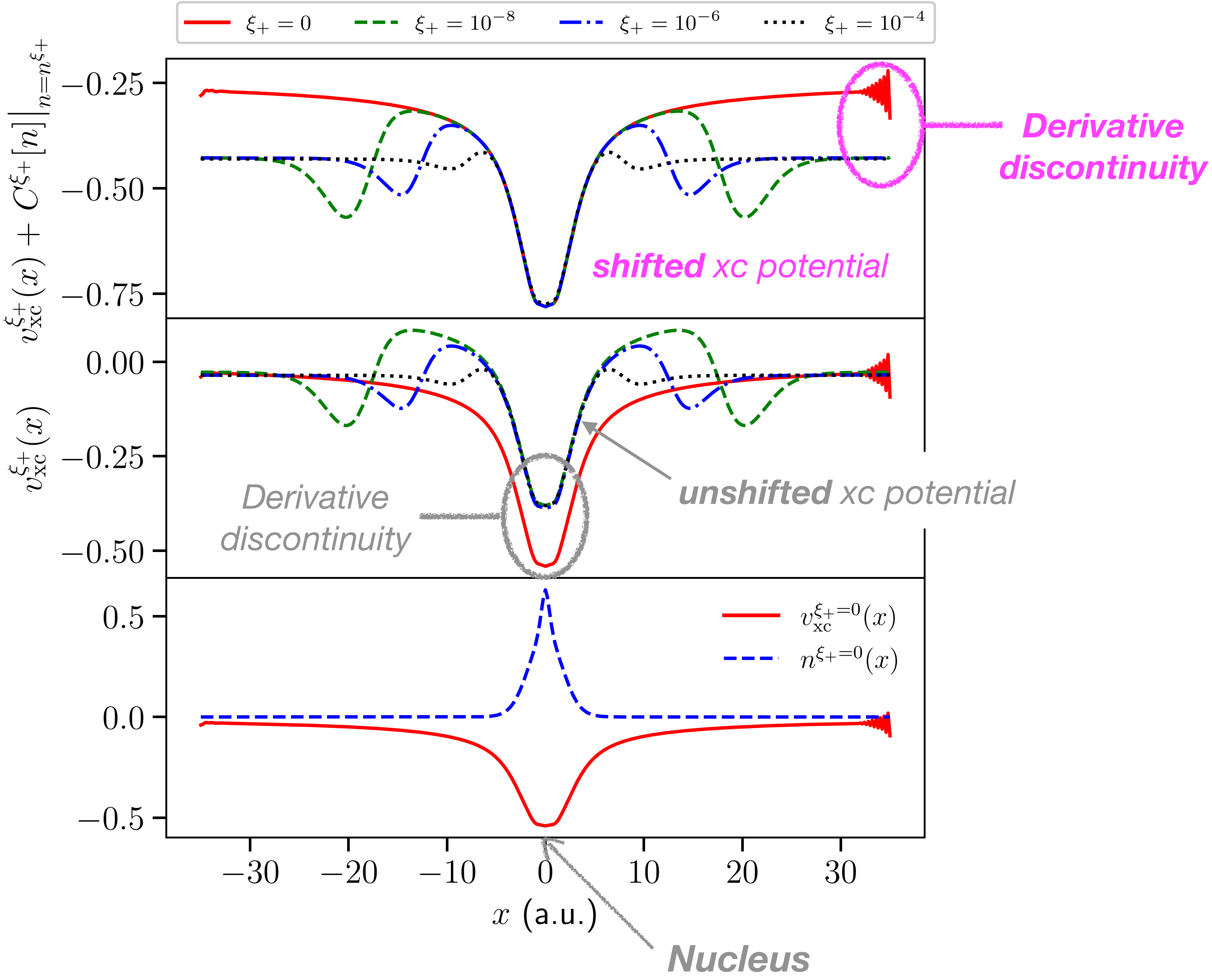
xc potential

Derivative discontinuity

Nucleus

M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).

Moving the discontinuity away from the system



*M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).*

Summary of part 1

If we can describe the weight dependence of ensemble density-functional xc energies,

there is no need for modelling derivative discontinuities.

F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

Part 2 of the presentation

*Designing **weight-dependent** ensemble density-functional **approximations**:*

How to?

Part 2 of the presentation

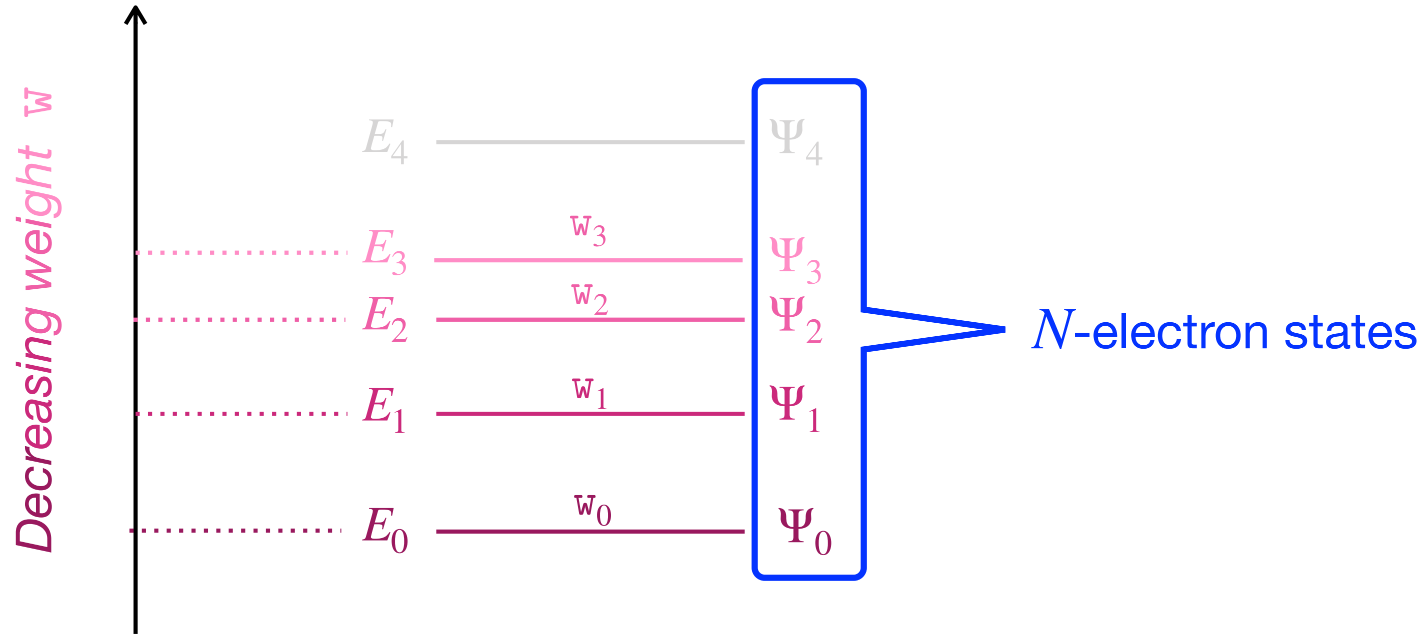
Designing ***weight-dependent*** *ensemble density-functional* ***approximations****:*

How to?

We will focus on the computation of ensemble Hartree-exchange energies.

Context

We will consider canonical (sometimes called GOK) ensembles in the following:



A. K. Theophilou, J. Phys. C: Solid State Phys. ***12****, 5419 (1979).*
A. K. Theophilou, in The Single Particle Density in Physics and Chemistry, edited by N. H. March and B. M. Deb (Academic Press, 1987), pp. 210–212.
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).*

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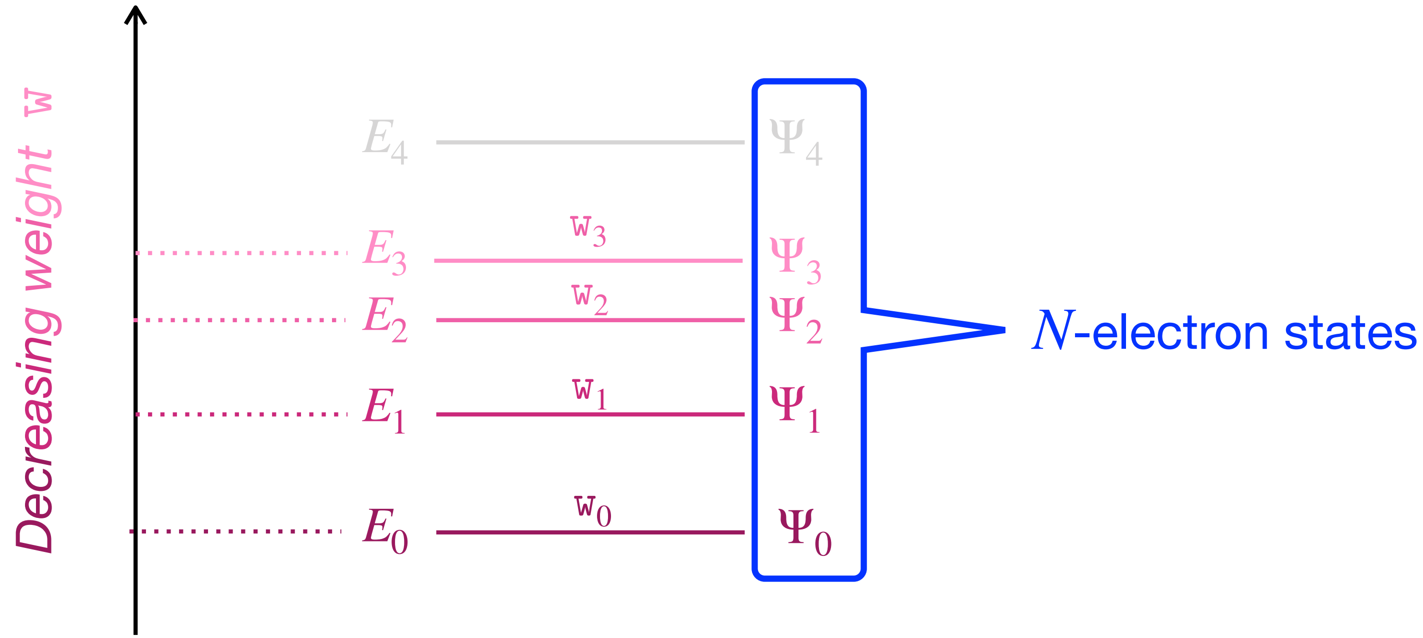

The *ensemble energy* $E^{\mathbf{w}} := \sum_{I\geq 0} \mathtt{w}_I E_I$ is a functional of the *ensemble density* $n^{\mathbf{w}}(\mathbf{r}) := \sum_{I\geq 0} \mathtt{w}_I n_{\Psi_I}(\mathbf{r})$.

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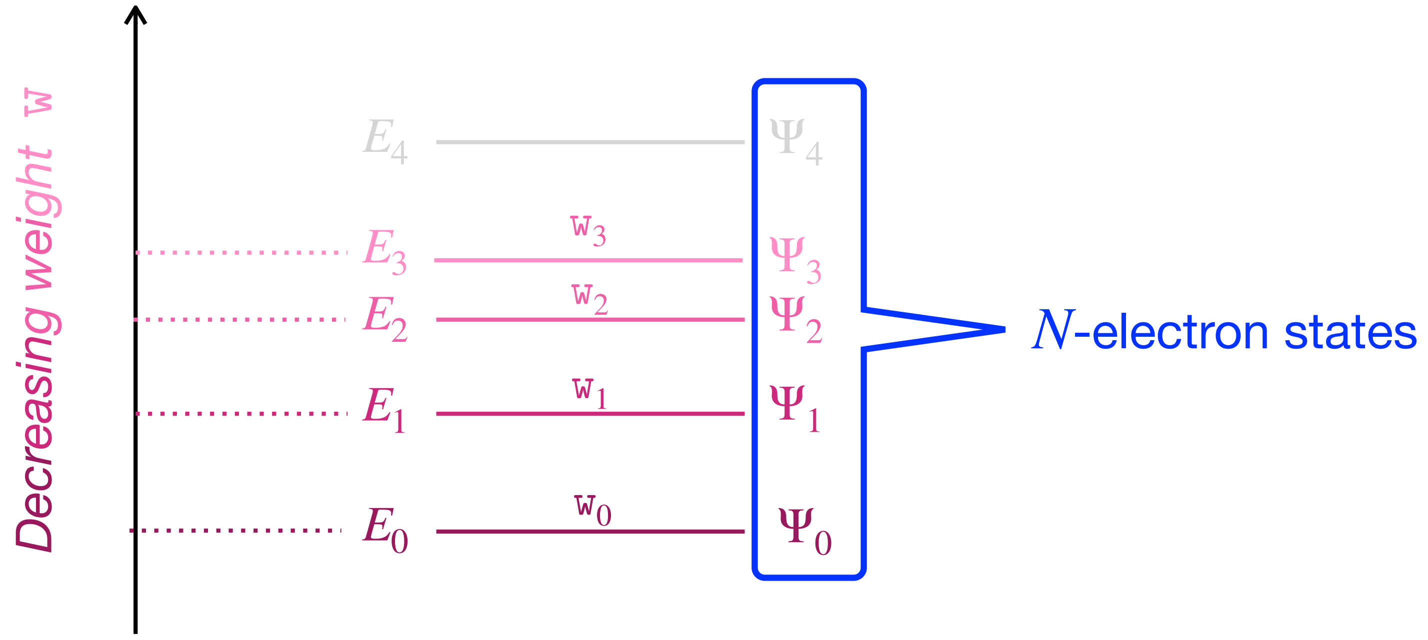

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$$\mathbf{w} \equiv (\mathtt{w}_1, \mathtt{w}_2, \ldots)$$

***Independent** excited-state ensemble weights*

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

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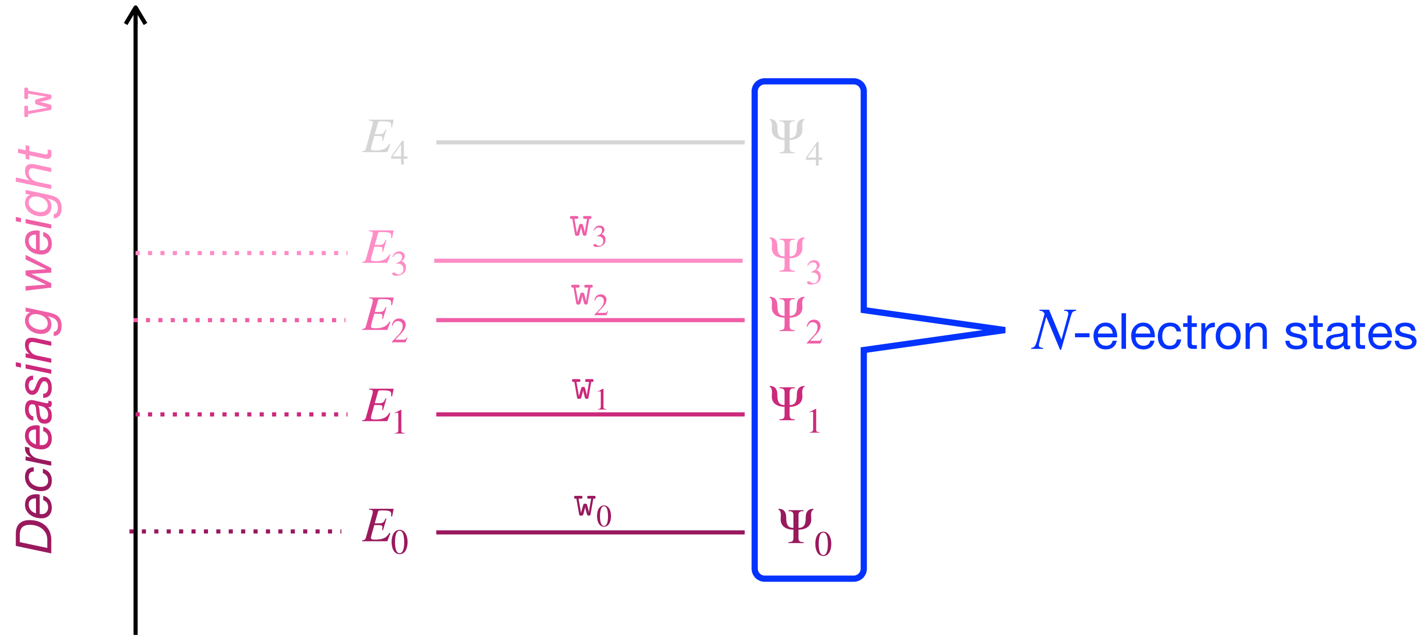

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$$\longrightarrow \mathbf{w} \equiv (\mathtt{w}_1, \mathtt{w}_2, \ldots) \longrightarrow \boxed{\mathtt{w}_0 = 1 - \sum_{I\geq 1} \mathtt{w}_I}$$

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

Original decomposition of the ensemble Hxc energy

$$E_{\mathrm{Hxc}}^{\mathbf{w}}[n] = E_{\mathrm{H}}[n] + E_{\mathrm{x}}^{\mathbf{w}}[n] + E_{\mathrm{c}}^{\mathbf{w}}[n]$$

E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A ***37****, 2809 (1988).*
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Regular ***weight-independent***
ground-state Hartree functional

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).

Original decomposition of the ensemble Hxc energy

$$E^{\mathbf{w}}_{\mathrm{Hxc}}[n] = E_{\mathrm{H}}[n] + E^{\mathbf{w}}_{\mathrm{x}}[n] + E^{\mathbf{w}}_{\mathrm{c}}[n]$$

$$\big\downarrow$$

Ground-state density-functional approximation

$$E^{\mathbf{w}}_{\mathrm{Hxc}}[n] \approx E_{\mathrm{H}}[n] + E_{\mathrm{x}}[n] + E_{\mathrm{c}}[n]$$

Original decomposition of the ensemble Hxc energy

$$E^{\mathbf{w}}_{\mathrm{Hxc}}[n] = E_{\mathrm{H}}[n] + E^{\mathbf{w}}_{\mathrm{x}}[n] + E^{\mathbf{w}}_{\mathrm{c}}[n]$$

Ground-state density-functional approximation

$$E^{\mathbf{w}}_{\mathrm{Hxc}}[n] \approx E_{\mathrm{H}}[n] + E_{\mathrm{x}}[n] + E_{\mathrm{c}}[n]$$

$$\boxed{\frac{\partial E^{\mathbf{w}}_{\mathrm{Hxc}}[n]}{\partial \mathtt{w}_I} \approx 0}$$

Excitation energies are evaluated from the bare *(although weight-dependent) KS orbital energies.*

Original decomposition of the ensemble Hxc energy

$$E_{\mathrm{Hxc}}^{\mathbf{w}}[n] = E_{\mathrm{H}}[n] + E_{\mathrm{x}}^{\mathbf{w}}[n] + E_{\mathrm{c}}^{\mathbf{w}}[n]$$

$$\downarrow \boxed{n = n^{\mathbf{w}}}$$

$$E_{\mathrm{H}}[n^{\mathbf{w}}] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n^{\mathbf{w}}(\mathbf{r})n^{\mathbf{w}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Original decomposition of the ensemble Hxc energy

$$E^{\mathbf{w}}_{\rm Hxc}[n] = E_{\rm H}[n] + E^{\mathbf{w}}_{\rm x}[n] + E^{\mathbf{w}}_{\rm c}[n]$$

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$$E_{\rm H}[n^{\mathbf{w}}] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n^{\mathbf{w}}(\mathbf{r})n^{\mathbf{w}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Curvature[1]

Ghost interaction*

$$= \sum_{I\geq 0} \mathtt{w}_I^2\, E_{\rm H}[n_{\Phi_I}] + \sum_{I<J} \mathtt{w}_I \mathtt{w}_J \int d\mathbf{r}\int d\mathbf{r}'\frac{n_{\Phi_I}(\mathbf{r})n_{\Phi_J}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Ith KS wave function

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

[*] *N. I. Gidopoulos, P. G. Papaconstantinou, and E. K. U. Gross, Phys. Rev. Lett.* ***88****, 033003 (2002).*

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

Original decomposition of the ensemble Hxc energy

$$E_{\mathrm{Hxc}}^{\mathbf{w}}[n] = E_{\mathrm{H}}[n] + E_{\mathrm{x}}^{\mathbf{w}}[n] + E_{\mathrm{c}}^{\mathbf{w}}[n]$$

is in charge of removing all those errors…

The exact Hartree-exchange dilemma in ensemble DFT

Until now we have used the regular non-interacting Kohn-Sham (KS) ensemble formalism:

The exact Hartree-exchange dilemma in ensemble DFT

Until now we have used the regular non-interacting Kohn-Sham (KS) ensemble formalism:

$$E^{\mathbf{w}}_{KS}[v] = \min_{\{\Phi_I\}} \left\{ \sum_{I\geq 0} \mathtt{w}_I \left(\langle \Phi_I | \hat{T} | \Phi_I \rangle + \int d\mathbf{r}\; v(\mathbf{r}) n_{\Phi_I}(\mathbf{r}) \right) \right\}$$

$$\boxed{v \overset{\mathbf{w}}{\longleftrightarrow} n}$$

Non-interacting ***potential-ensemble-density map***

The exact Hartree-exchange dilemma in ensemble DFT

*We could map the density onto an **ensemble** one-electron reduced **density matrix** evaluated at the **Hartree-Fock** level **(eDMHF)** instead:*

$$E^{\mathbf{w}}_{eDMHF}[v] = \min_{\{\Phi_I\}} \left\{ \sum_{I\geq 0} \mathtt{w}_I \left(\langle \Phi_I | \hat{T} | \Phi_I \rangle + \int d\mathbf{r}\; v(\mathbf{r}) n_{\Phi_I}(\mathbf{r}) \right) + W_{HF}\left[\sum_{I\geq 0} \mathtt{w}_I \gamma^{\Phi_I} \right] \right\}$$

$$v \overset{\mathbf{w}}{\longleftrightarrow} n$$

Gould T, Kronik L (2021) J Chem Phys 154(9):094125.
*F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) **380**, 4 (2022).*

The exact Hartree-exchange dilemma in ensemble DFT

We could map the density onto an ensemble one-electron reduced density matrix evaluated at the Hartree-Fock level (eDMHF) instead:

$$E^{\mathbf{w}}_{eDMHF}[v] = \min_{\{\Phi_I\}} \left\{ \sum_{I\geq 0} \mathtt{w}_I \left(\langle \Phi_I | \hat{T} | \Phi_I \rangle + \int d\mathbf{r}\; v(\mathbf{r}) n_{\Phi_I}(\mathbf{r}) \right) + \boxed{W_{HF}\left[\sum_{I\geq 0} \mathtt{w}_I \gamma^{\Phi_I} \right]} \right\}$$

$$W_{HF}[\gamma] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\gamma(\mathbf{r},\mathbf{r})\gamma(\mathbf{r}',\mathbf{r}') - \frac{1}{2}\gamma^2(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Regular HF density-matrix-functional interaction energy

Gould T, Kronik L (2021) J Chem Phys 154(9):094125.
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

The exact Hartree-exchange dilemma in ensemble DFT

We could map the density onto an ensemble one-electron reduced density matrix evaluated at the Hartree-Fock level (eDMHF) instead:

$$E^{\mathbf{w}}_{eDMHF}[v] = \min_{\{\Phi_I\}} \left\{ \sum_{I\geq0} \mathtt{w}_I \left(\langle\Phi_I|\hat{T}|\Phi_I\rangle + \int d\mathbf{r}\; v(\mathbf{r}) n_{\Phi_I}(\mathbf{r}) \right) + W_{HF}\left[\boxed{\sum_{I\geq0} \mathtt{w}_I \gamma^{\Phi_I}} \right] \right\}$$

Ensemble density matrix

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$$W_{HF}[\gamma] = \frac{1}{2}\int d\mathbf{r} \int d\mathbf{r}' \frac{\gamma(\mathbf{r},\mathbf{r})\gamma(\mathbf{r}',\mathbf{r}') \boxed{- \frac{1}{2}\gamma^2(\mathbf{r},\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|}$$

Does not remove ghost interaction errors

❌

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Single to-be-diagonalized ensemble Fock operator
(simple to implement) ← *Ensemble density matrix*

✓

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✓

Standard approach

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F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

The exact Hartree-exchange dilemma in ensemble DFT

Alternatively, we could extract the density from a ***State-Averaged Hartree-Fock (SAHF)*** *calculation:*

$$E^{\mathbf{w}}_{SAHF}[v] = \min_{\{\Phi_I\}} \left\{ \sum_{I\geq 0} \mathtt{w}_I \left(\langle\Phi_I|\hat{T}|\Phi_I\rangle + \boxed{\langle\Phi_I|\hat{W}_{\rm ee}|\Phi_I\rangle} + \int d\mathbf{r}\; v(\mathbf{r})n_{\Phi_I}(\mathbf{r}) \right)\right\}$$

$$\downarrow$$

$$v \overset{\mathbf{w}}{\longleftrightarrow} n$$

M. Filatov, WIREs Comput. Mol. Sci. ***5****, 146 (2015).*

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$$\big\downarrow$$

$$E_{\rm H}[n_{\Phi_I}] + E_{\rm x}[\Phi_I]$$

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$$\downarrow$$

$$E_{\rm H}[n_{\Phi_I}] + E_{\rm x}[\Phi_I]$$

$$\downarrow$$

Ghost-interaction-free ✓

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$$\downarrow$$

$$E_{\rm H}[n_{\Phi_I}] + E_{\rm x}[\Phi_I]$$

$$\downarrow$$

Each orbital has its own Fock operator
(computational implementation more involved) ✖

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$$\Big\downarrow$$

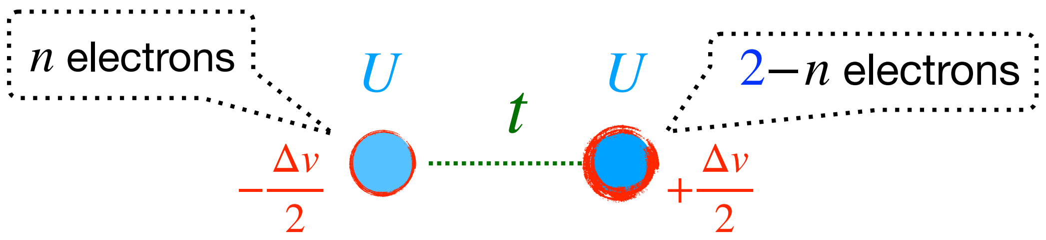
$$E_{\rm H}[n_{\Phi_I}] + E_{\rm x}[\Phi_I]$$

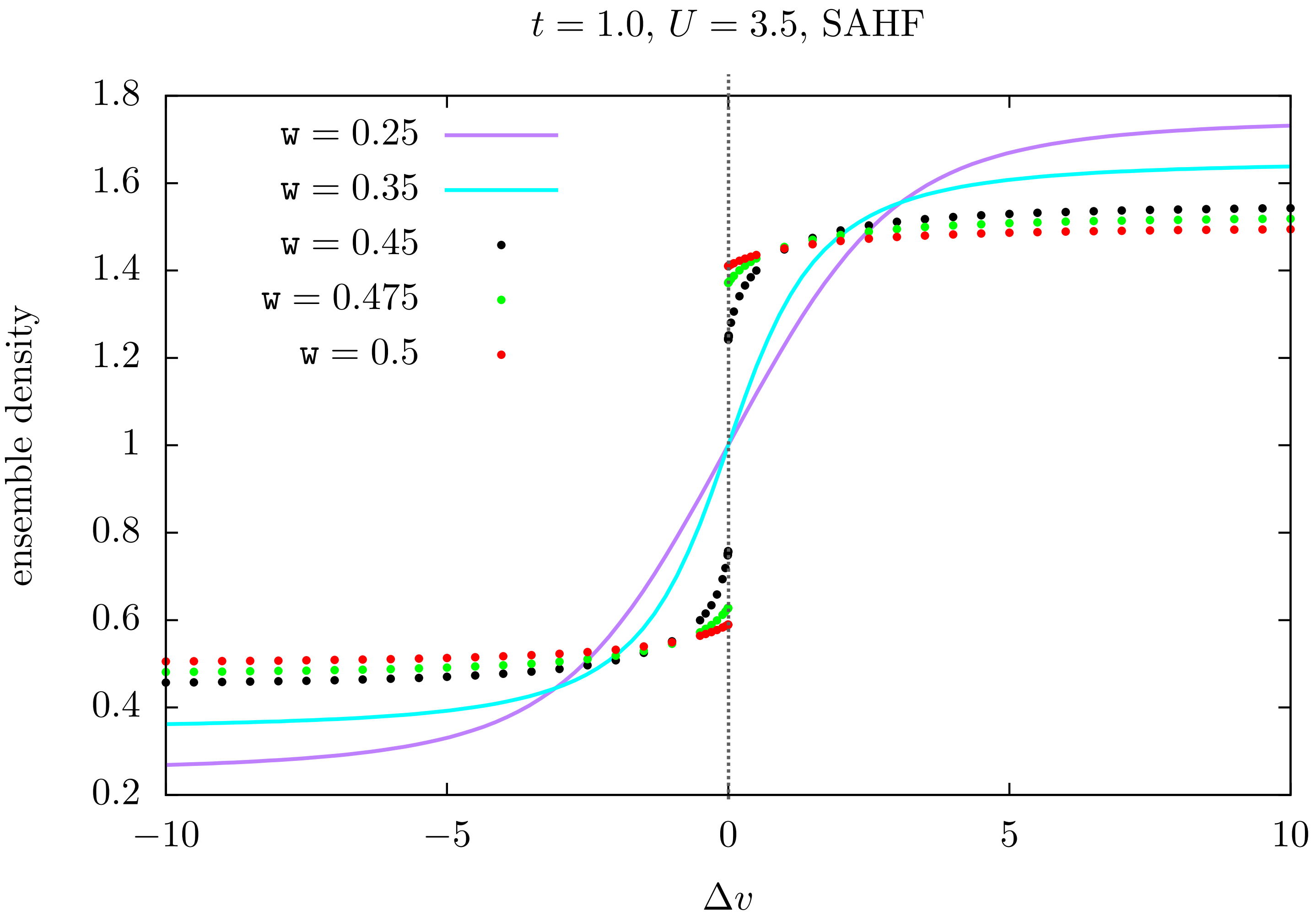
$$\Big\downarrow$$

*(Maybe less known) v-**representability issues*** ✖

*F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) **380**, 4 (2022).*

Application to the Hubbard dimer: The singlet bi-ensemble case




$t = 1.0$, $U = 3.5$, SAHF

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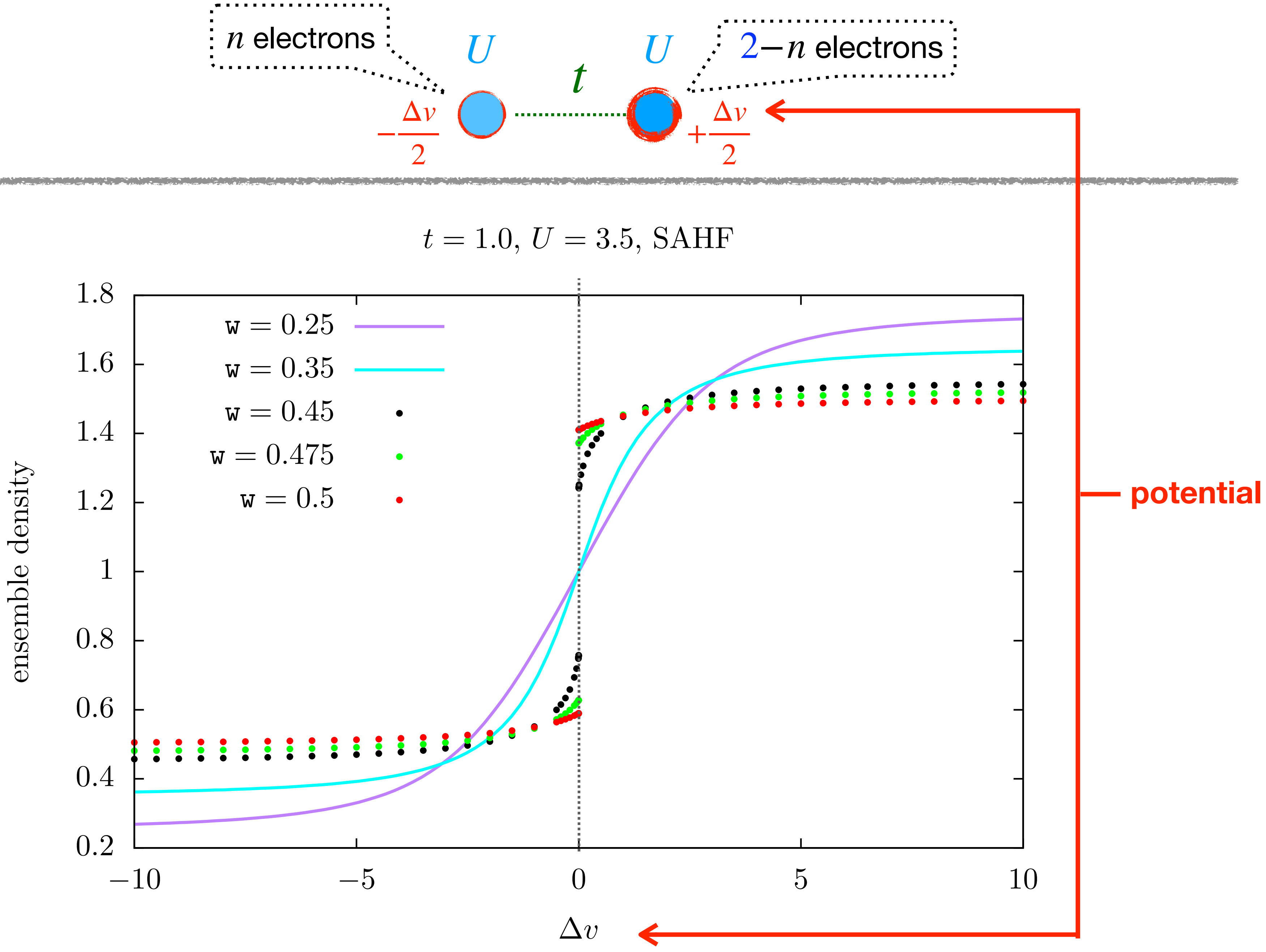

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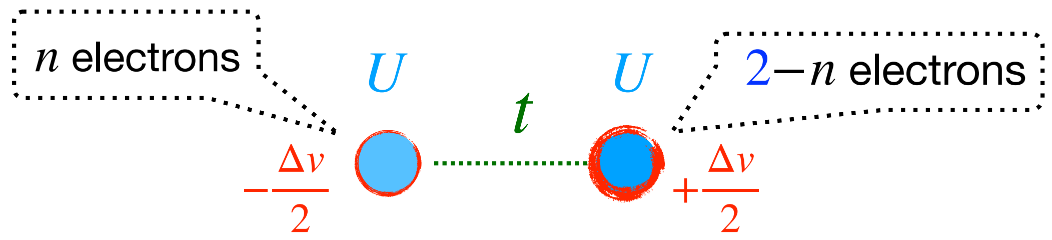

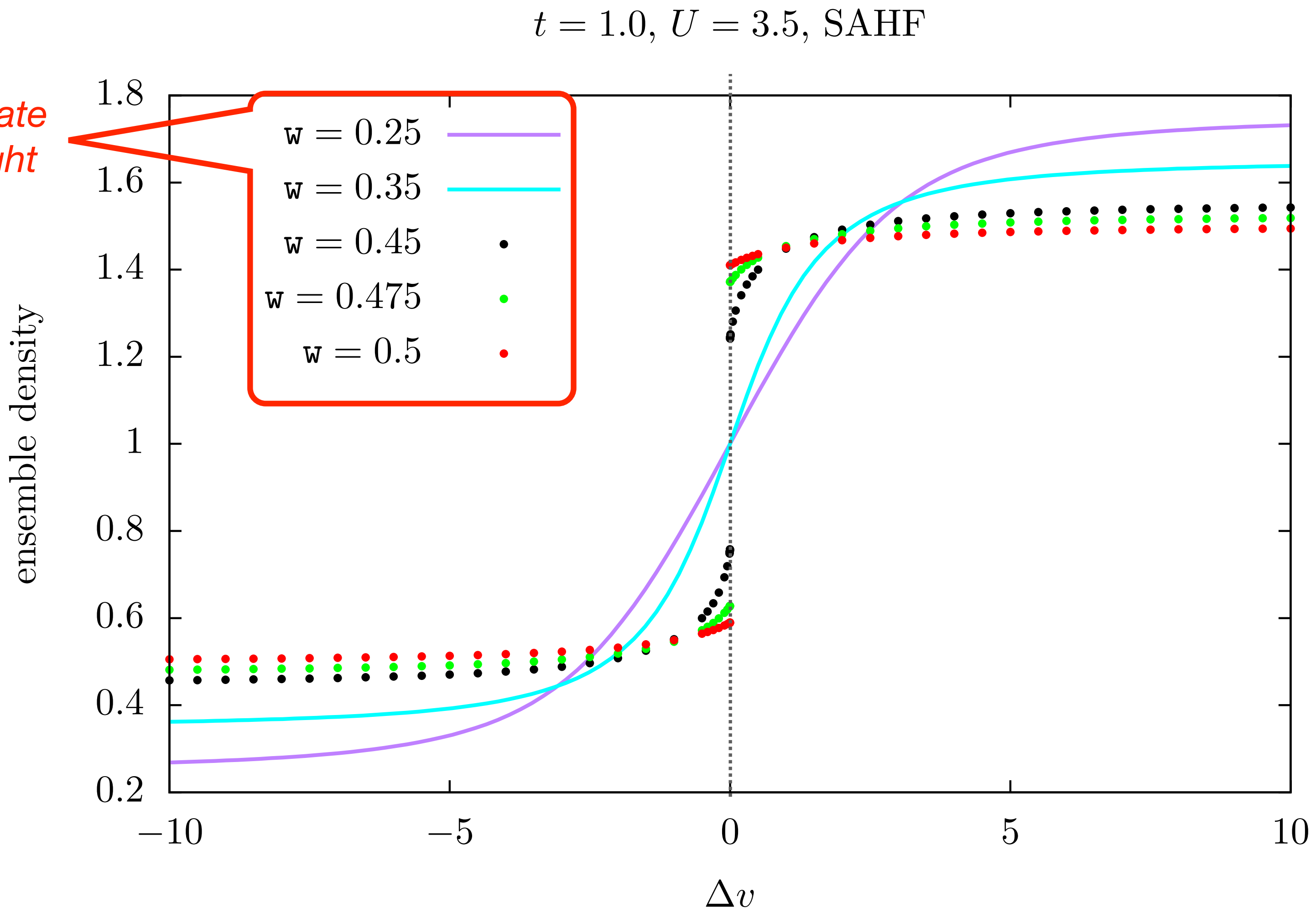

First-excited-state ensemble weight values

F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

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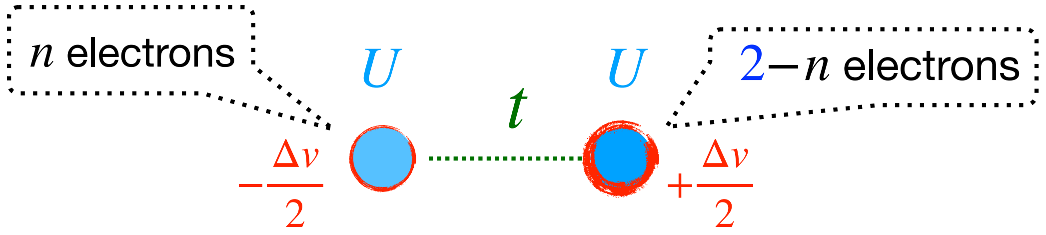

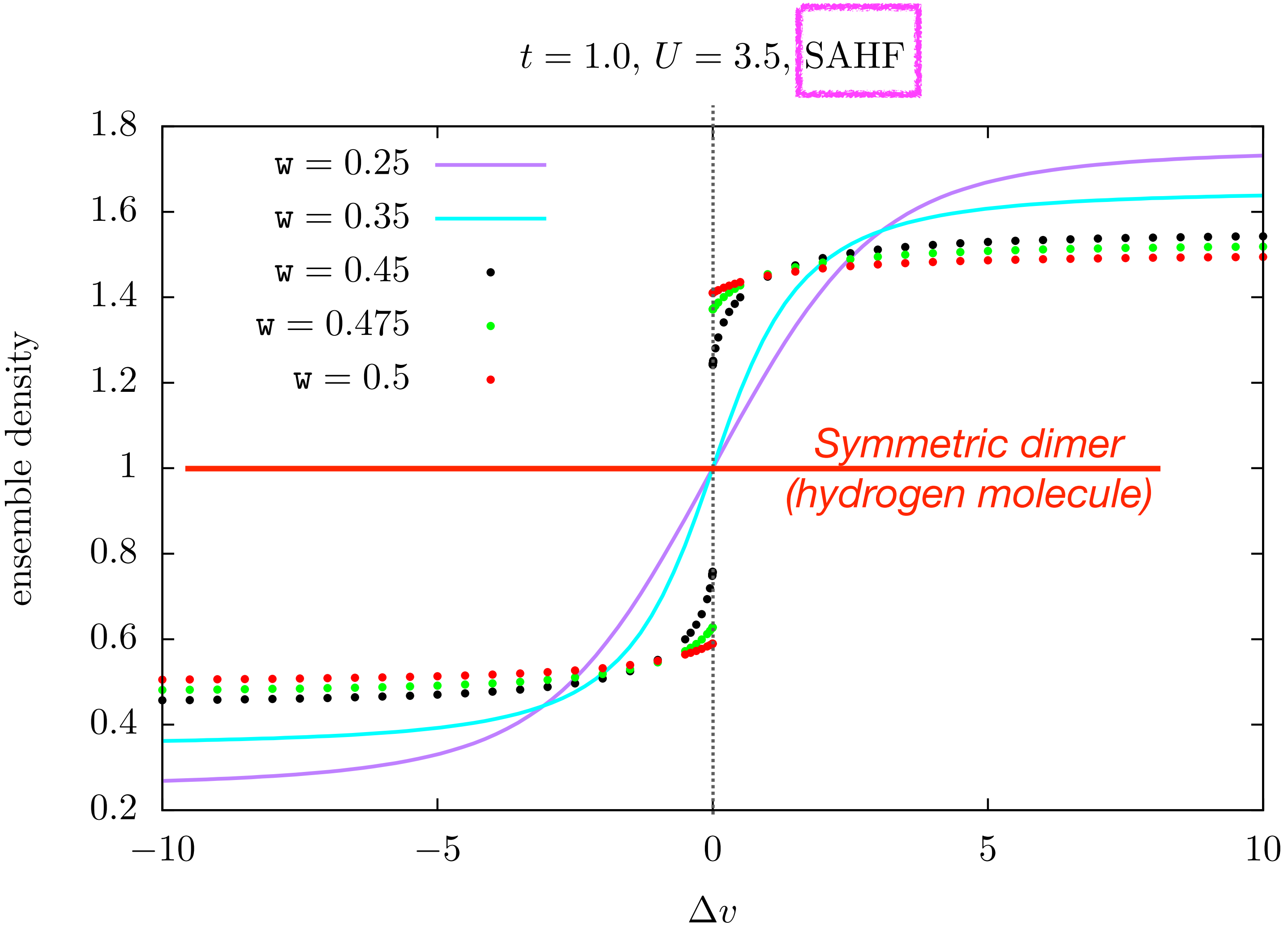

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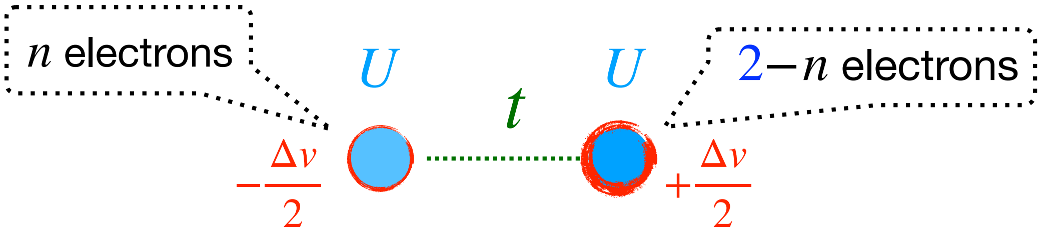

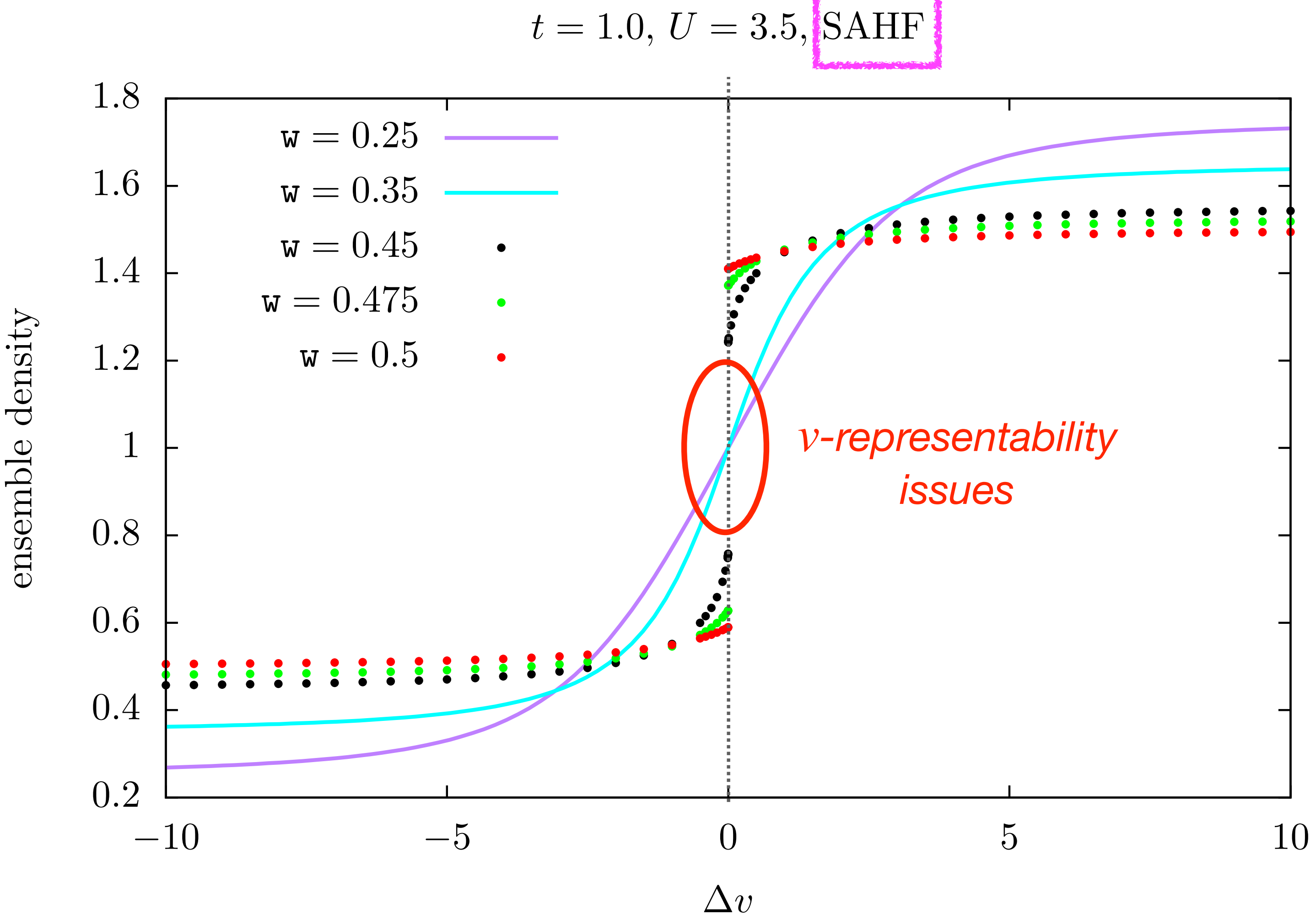

v-representability issues

F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) **380**, 4 (2022).

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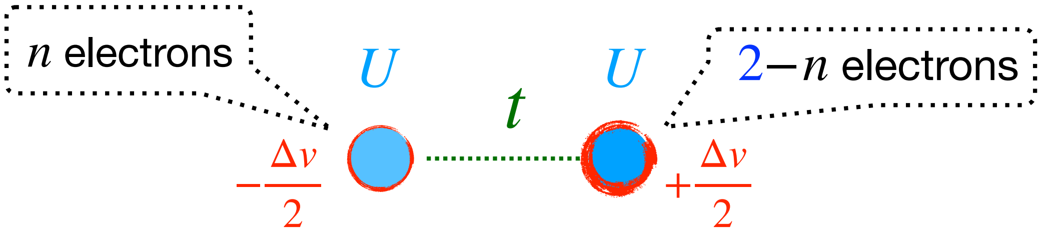

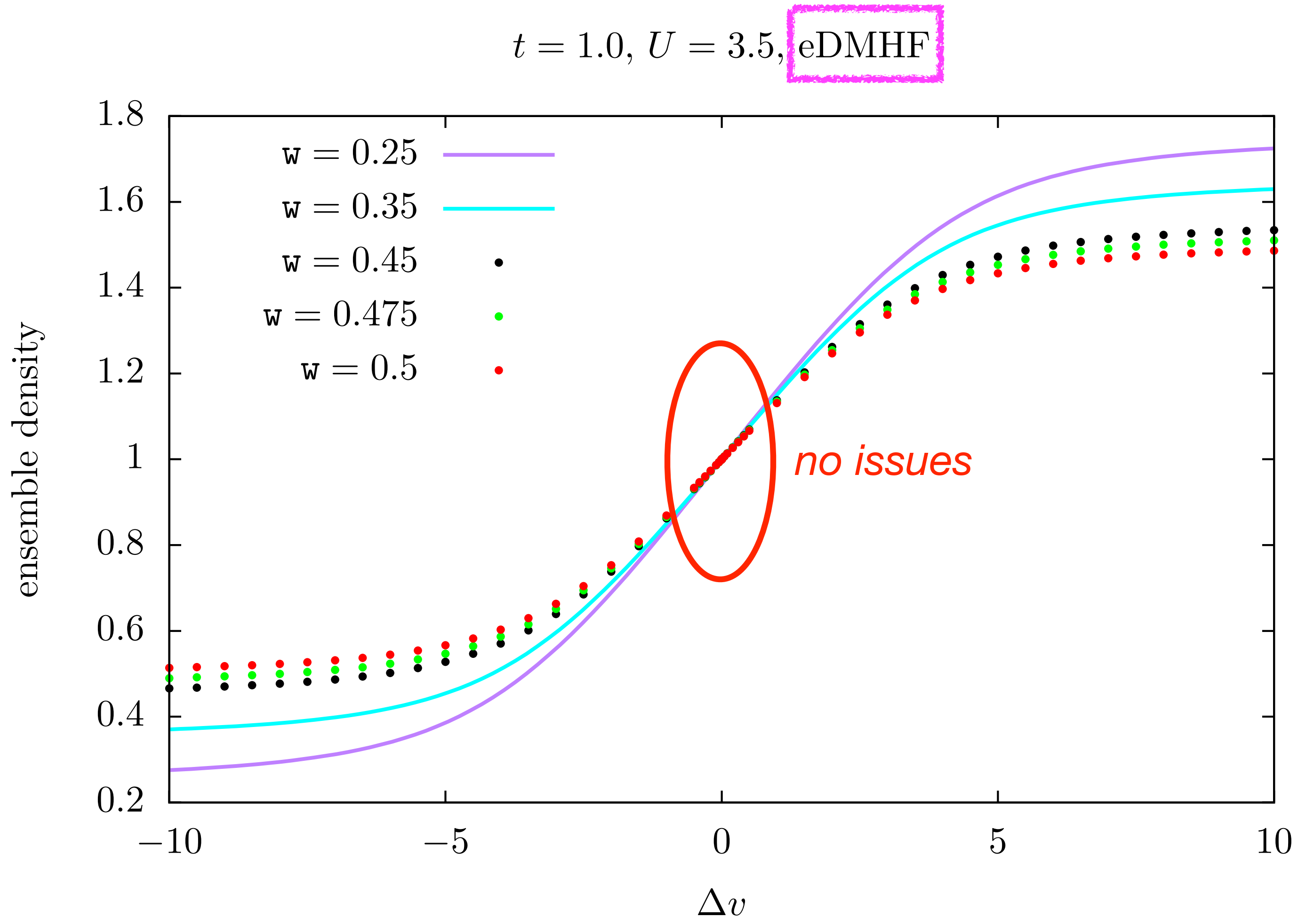

no issues

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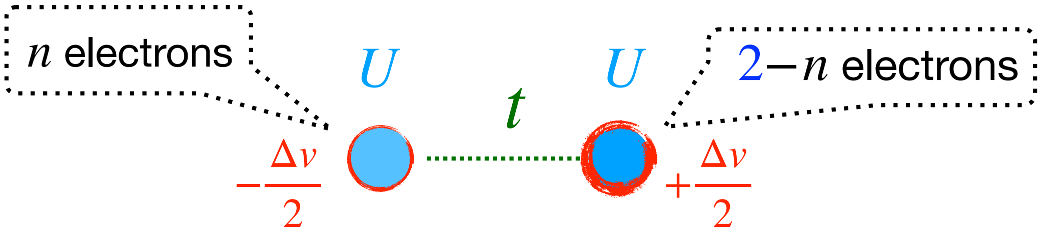

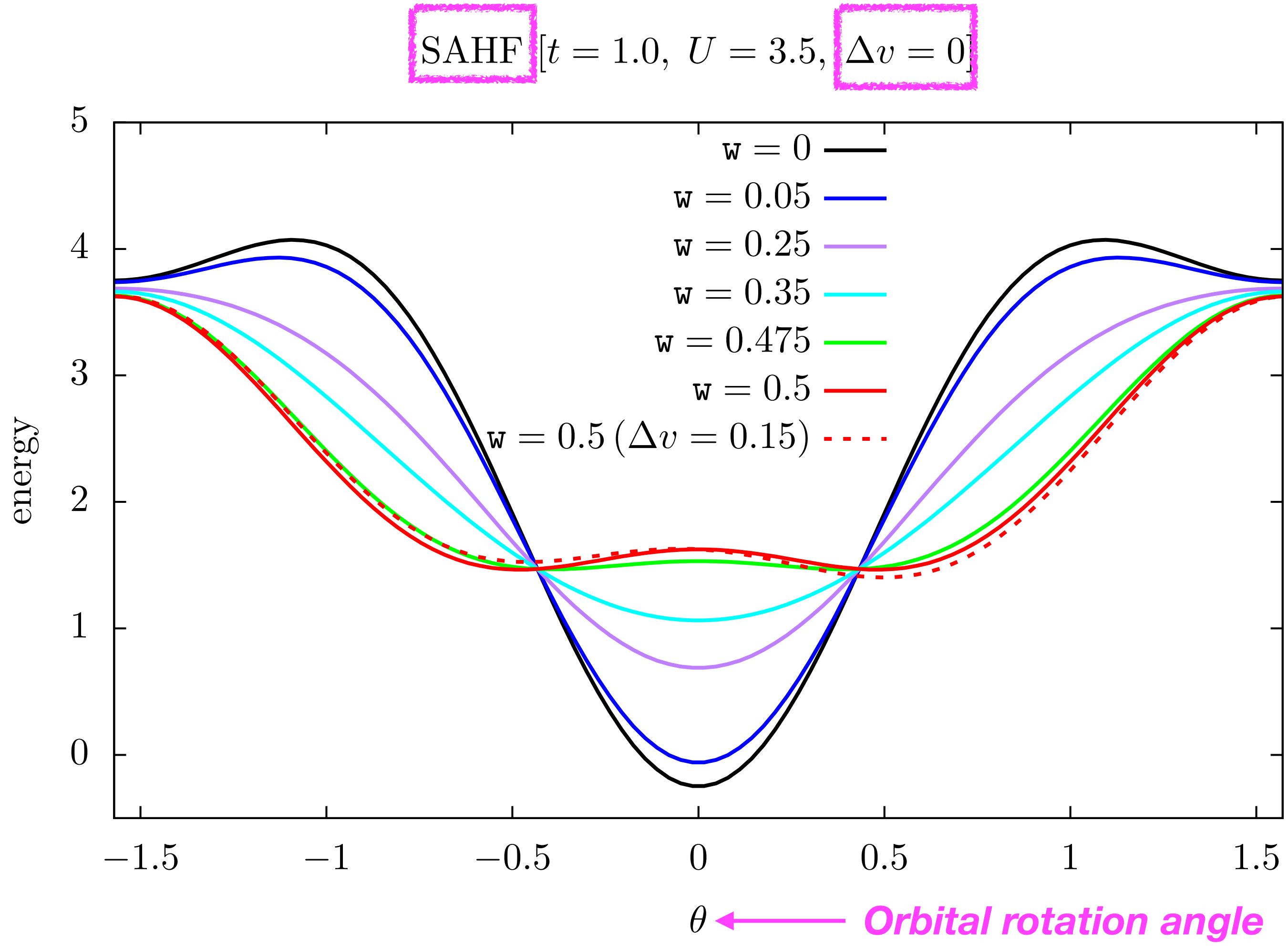

Orbital rotation angle

F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

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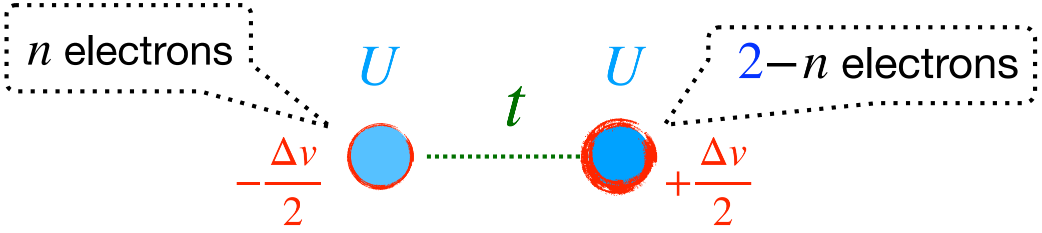

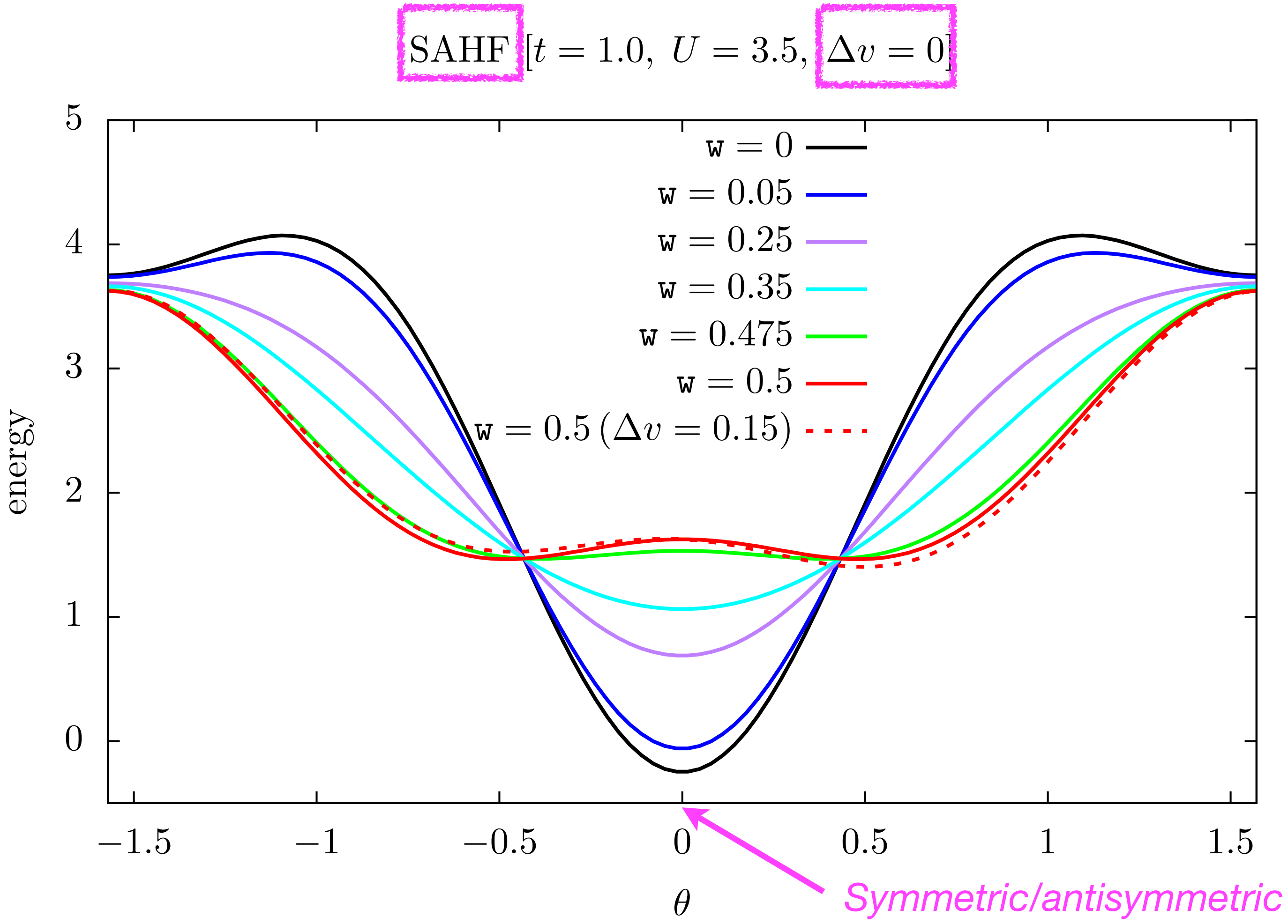

Symmetric/antisymmetric orbitals

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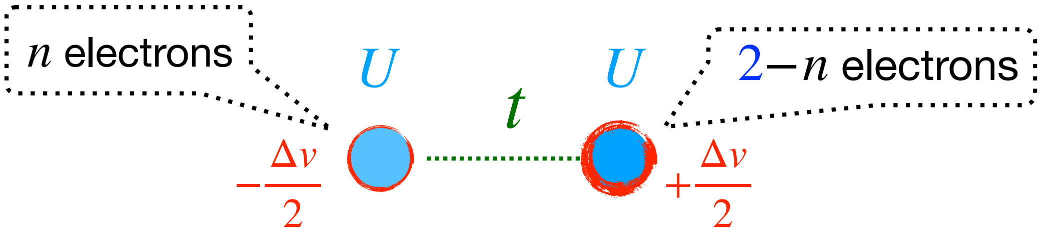
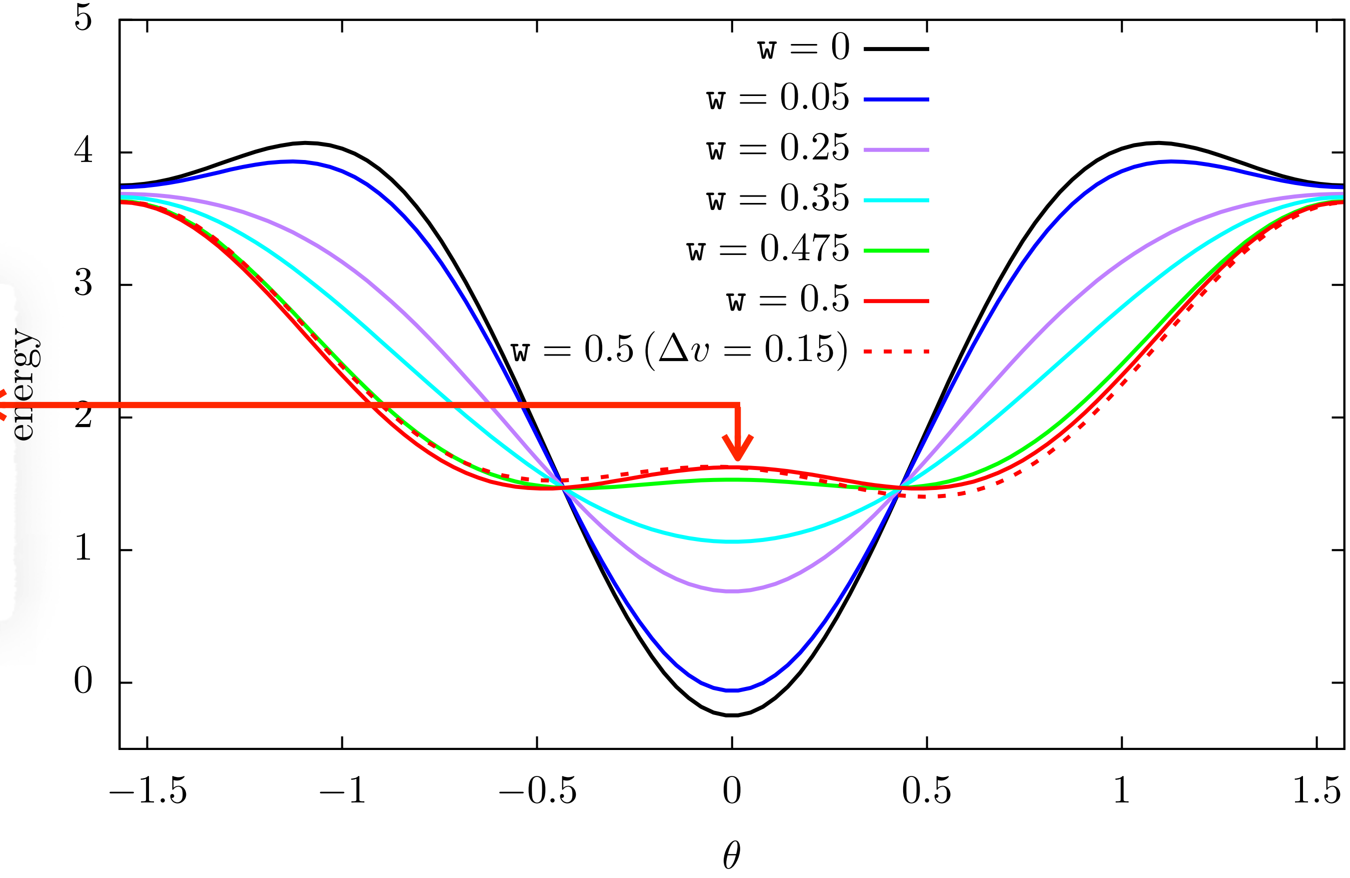


$\boxed{\text{SAHF}}\ [t = 1.0,\ U = 3.5,\ \boxed{\Delta v = 0}]$



$\mathtt{w} > 1/3$

and

$$\frac{U}{t} > \frac{2(1-\mathtt{w})}{3\mathtt{w}-1}$$

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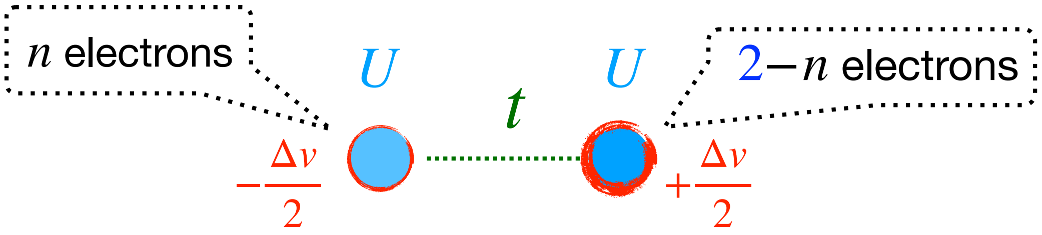

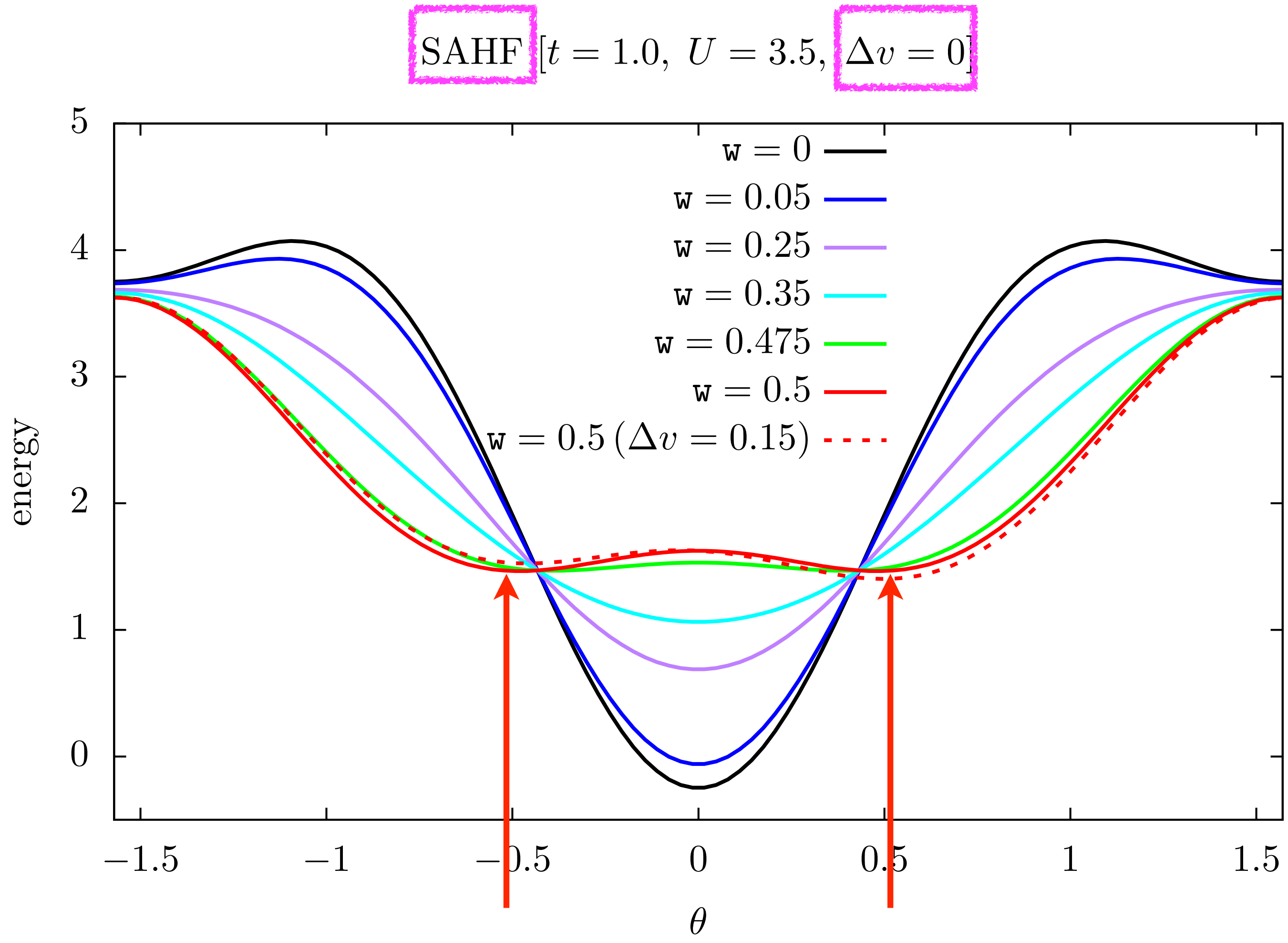

Degenerate minimising bi-ensembles

F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

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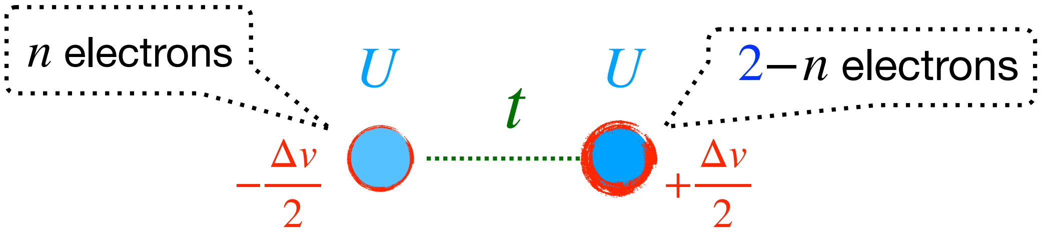

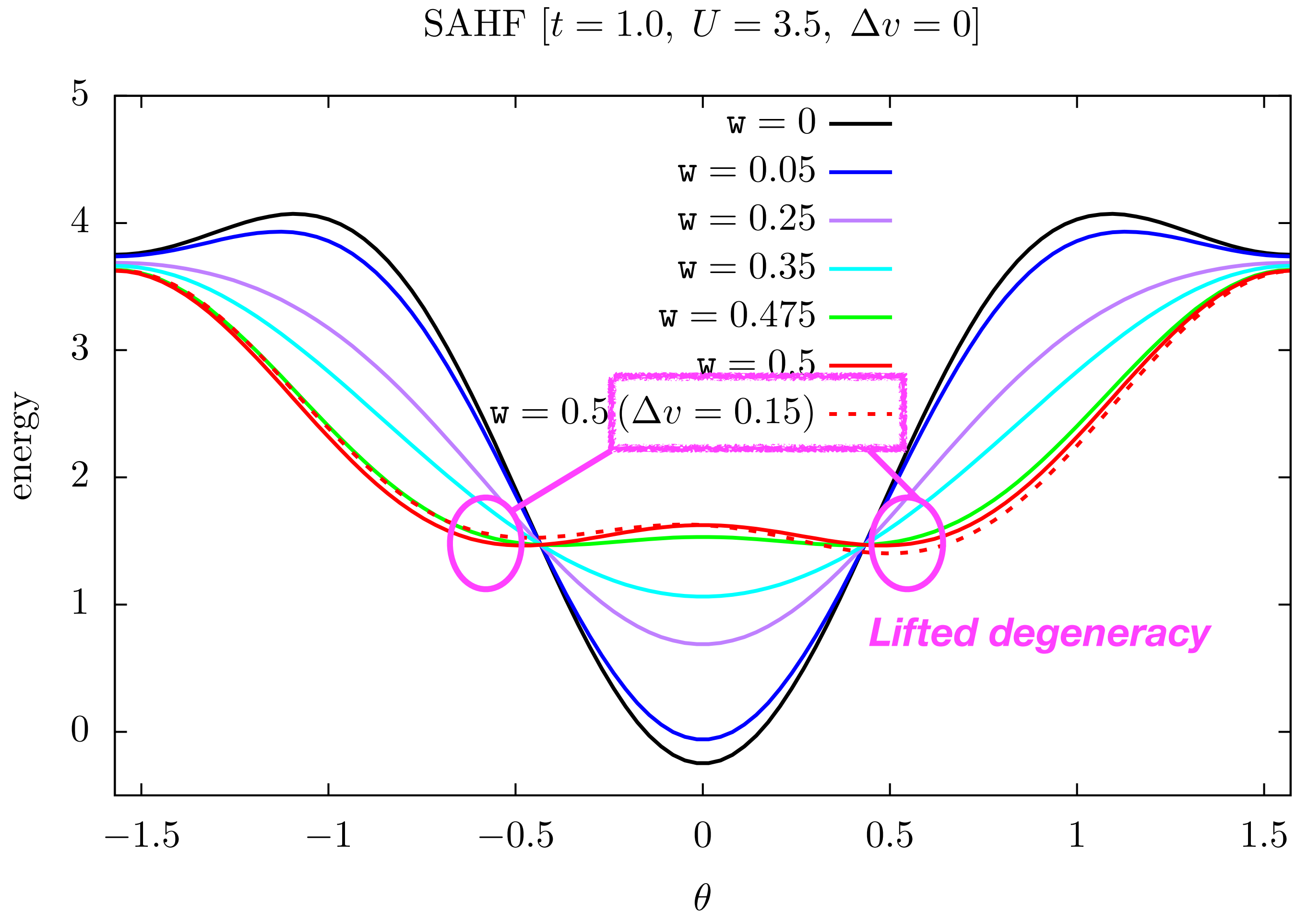

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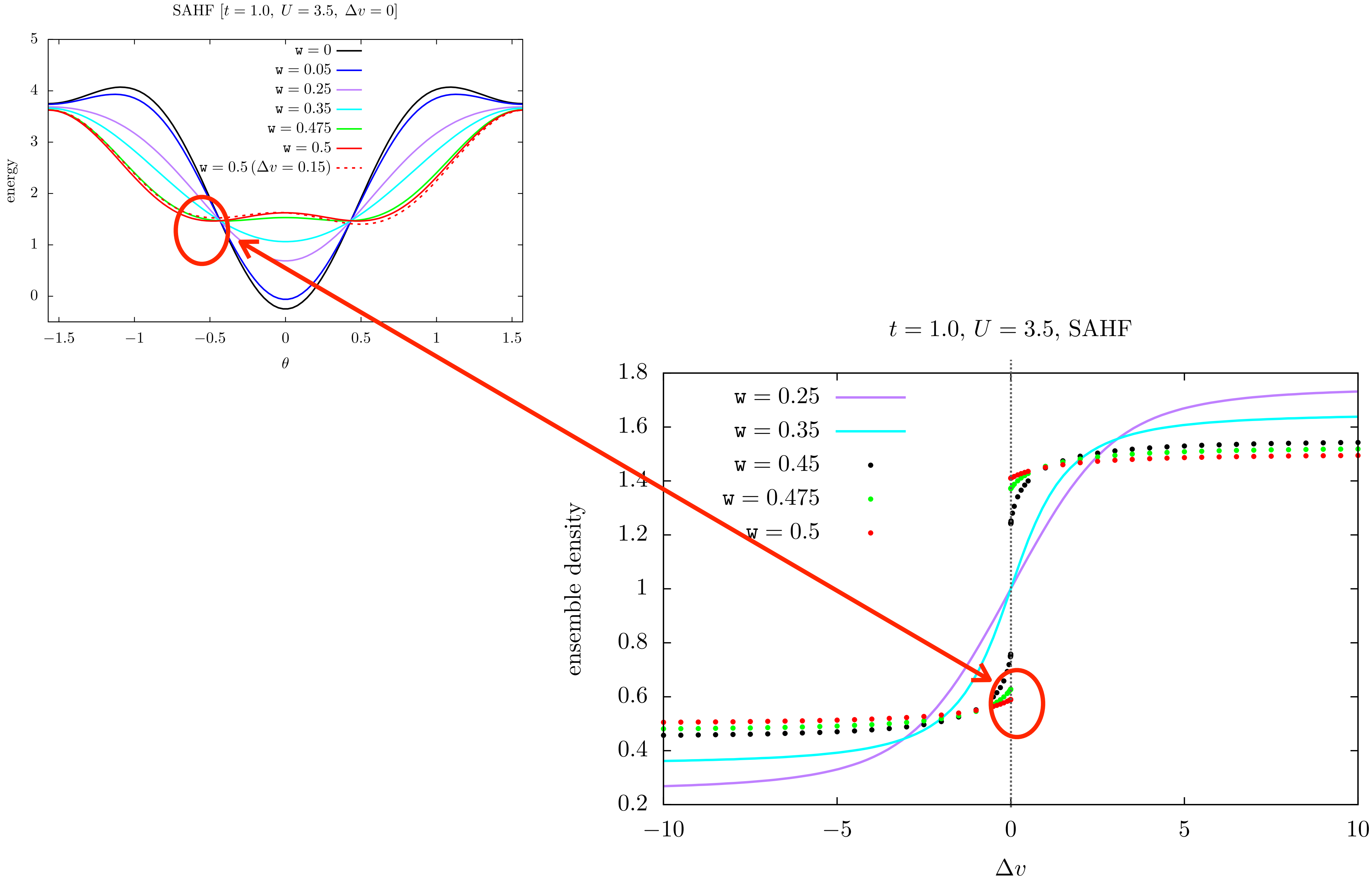

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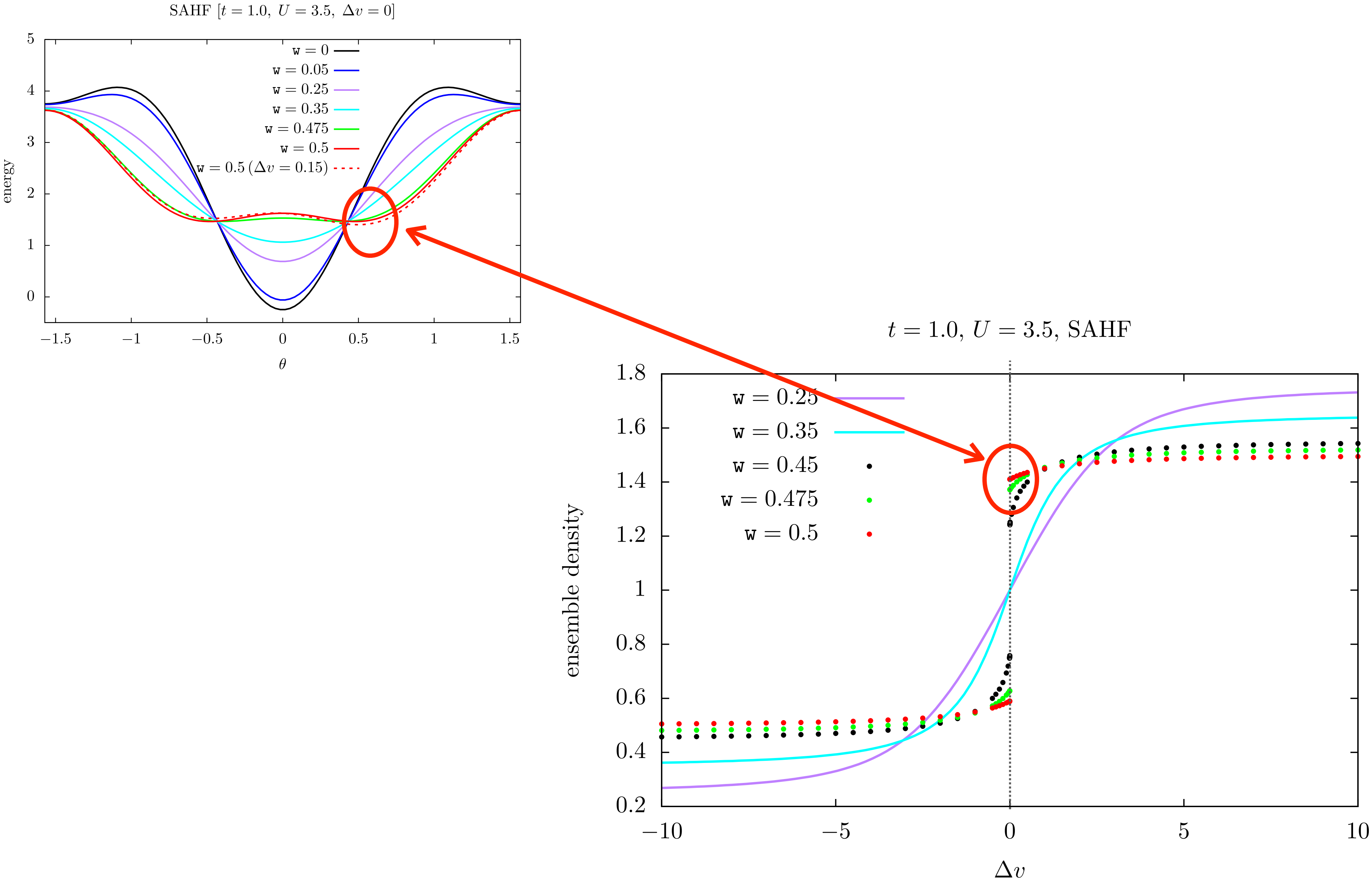

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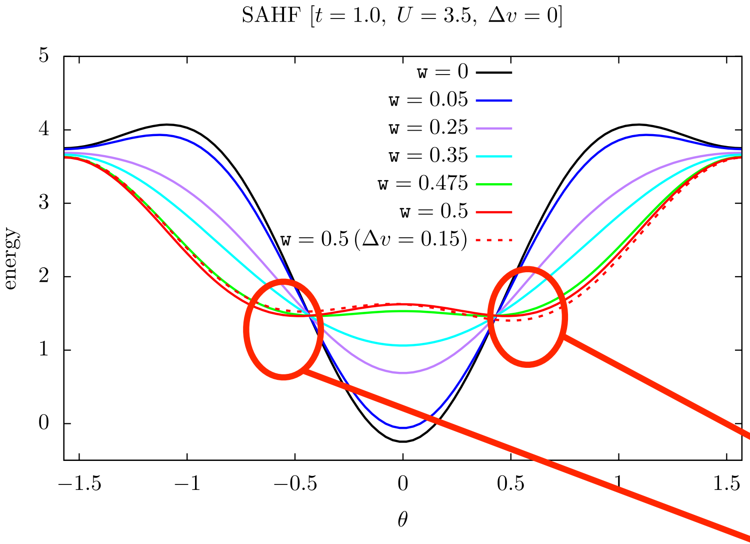
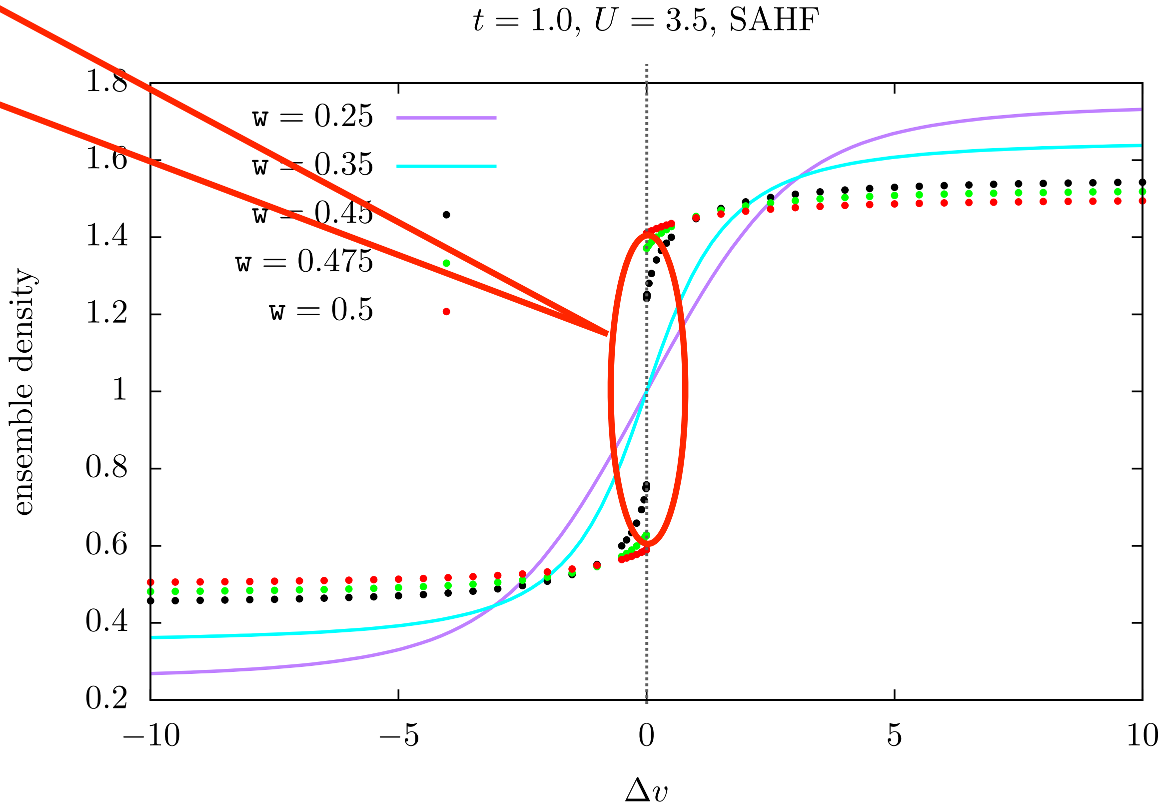


Solution *to the v-representability problem:*

Combine the two degenerate bi-ensembles!



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Part 1: Exact theory

- *Unified description of charged and neutral electronic excitations within ensemble DFT*
- *Equivalence between xc ensemble weight derivatives and xc derivative discontinuities*

Part 2: Weight-dependent density-functional approximations (DFAs)

- *The exact Hartree-exchange dilemma in ensemble DFT*
- *Recycling ground-state correlation DFAs: What about state- and density-driven correlations?*

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$$E_{\mathrm{c}}^{\mathbf{w}}[n] \approx \sum_{I \geq 0} \mathtt{w}_I \boxed{E_{\mathrm{c}}[n_{\Phi_I}]}$$

*This is a **ground-state correlation energy**, not an excited-state one*

T. Gould and S. Pittalis, Phys. Rev. Lett. ***123****, 016401 (2019).*
E. Fromager, Phys. Rev. Lett. ***124****, 243001 (2020).*
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

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State-driven correlation energies are missing

T. Gould and S. Pittalis, Phys. Rev. Lett. ***123****, 016401 (2019).*
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$$E_{\mathrm{c}}^{\mathtt{w}}[n] \approx \sum_{I\geq 0} \mathtt{w}_I \, E_{\mathrm{c}}[n_{\Phi_I}]$$

***Individual KS densities** and exact densities*
are not supposed to match
(only the ensemble densities do)

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

MDPI

Article

Local Potential Functional Embedding Theory: A Self-Consistent Flavor of Density Functional Theory for Lattices without Density Functionals

Sajanthan Sekaran [1,*], Matthieu Saubanère [2] and Emmanuel Fromager [1]

[1] Laboratoire de Chimie Quantique, Institut de Chimie, CNRS/Université de Strasbourg, 4 Rue Blaise Pascal, 67000 Strasbourg, France; fromagere@unistra.fr
[2] ICGM, Université de Montpellier, CNRS, ENSCM, 34000 Montpellier, France; matthieu.saubanere@umontpellier.fr
* Correspondence: s.sekaran@unistra.fr

Abstract: Quantum embedding is a divide and conquer strategy that aims at solving the electronic Schrödinger equation of sizeable molecules or extended systems. We establish in the present work a clearer and in-principle-exact connection between density matrix embedding theory (DMET) and density-functional theory (DFT) within the simple but nontrivial one-dimensional Hubbard model. For that purpose, we use our recent reformulation of single-impurity DMET as a Householder transformed density-matrix functional embedding theory (Ht-DMFET). On the basis of well-identified density-functional approximations, a self-consistent local potential functional embedding theory (LPFET) is formulated and implemented. Combining both LPFET and DMET numerical results with our formally exact density-functional embedding theory reveals that a single statically embedded impurity can in principle describe the density-driven Mott–Hubbard transition, provided that a complementary density-functional correlation potential (which is neglected in both DMET and LPFET) exhibits a derivative discontinuity (DD) at half filling. The extension of LPFET to multiple impurities (which would enable to circumvent the modeling of DDs) and its generalization to quantum chemical Hamiltonians are left for future work.

Keywords: density matrix functional embedding; density-functional theory; householder transformation

Citation: Sekaran, S.; Saubanère, M.; Fromager, E. Local Potential Functional Embedding Theory: A Self-Consistent Flavor of Density Functional Theory for Lattices without Density Functionals. *Computation* **2022**, *10*, 45. https://doi.org/10.3390/computation10030045

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CHEMISTRY
of COMPLEX
SYSTEMS

« Initiative d’Excellence » (IdEx) grant
University of Strasbourg

Université
de Strasbourg

CoLab ANR project

ANR

N-centered ensemble DFT

$$E^{\{\xi_\nu\}} = \left(1 - \sum_{\nu>0} \frac{N_\nu}{N}\xi_\nu\right) E_0 + \sum_{\nu>0} \xi_\nu E_\nu$$

$$\frac{\partial E^{\{\xi_\nu\}}}{\partial \xi_\mu} \underset{\mu>0}{=} E_\mu - \frac{N_\mu}{N} E_0 \qquad\qquad E_0 = E^{\{\xi_\nu\}} - \sum_{\lambda>0} \frac{\partial E^{\{\xi_\nu\}}}{\partial \xi_\lambda}\xi_\lambda$$

$$\boxed{E_\mu \underset{\mu\geq 0}{=} \frac{N_\mu}{N} E^{\{\xi_\nu\}} + \sum_{\lambda>0}\left(\delta_{\lambda\mu} - \frac{N_\mu}{N}\xi_\lambda\right)\frac{\partial E^{\{\xi_\nu\}}}{\partial \xi_\lambda}}$$

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190
M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A ***103****, 012806 (2021).*
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

N-centered ensemble DFT (with arbitrary weights)

$$E_\mu \underset{\mu\geq 0}{=} \frac{N_\mu}{N} E^{\{\xi_\nu\}} + \sum_{\lambda>0}\left(\delta_{\lambda\mu} - \frac{N_\mu}{N}\xi_\lambda\right)\frac{\partial E^{\{\xi_\nu\}}}{\partial \xi_\lambda}$$

$$\boxed{\begin{aligned} E_\mu \underset{\mu\geq 0}{=} {} & \mathcal{E}_\mu^{\{\xi_\nu\}} + \frac{N_\mu}{N}\left(E_{\mathrm{Hxc}}^{\{\xi_\nu\}}\left[n^{\{\xi_\nu\}}\right] - \int d\mathbf{r}\, v_{\mathrm{Hxc}}^{\{\xi_\nu\}}(\mathbf{r})\, n^{\{\xi_\nu\}}(\mathbf{r})\right) \\ & + \sum_{\lambda>0}\left(\delta_{\lambda\mu} - \frac{N_\mu}{N}\xi_\lambda\right)\left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n]}{\partial \xi_\lambda}\right|_{n=n^{\{\xi_\nu\}}} \end{aligned}}$$

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