Exchange-correlation density-functional derivative discontinuities revisited: An N-centered ensemble perspective

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[b]LSI, École Polytechnique and the European Theoretical Spectroscopy Facility, CNRS, Palaiseau, France
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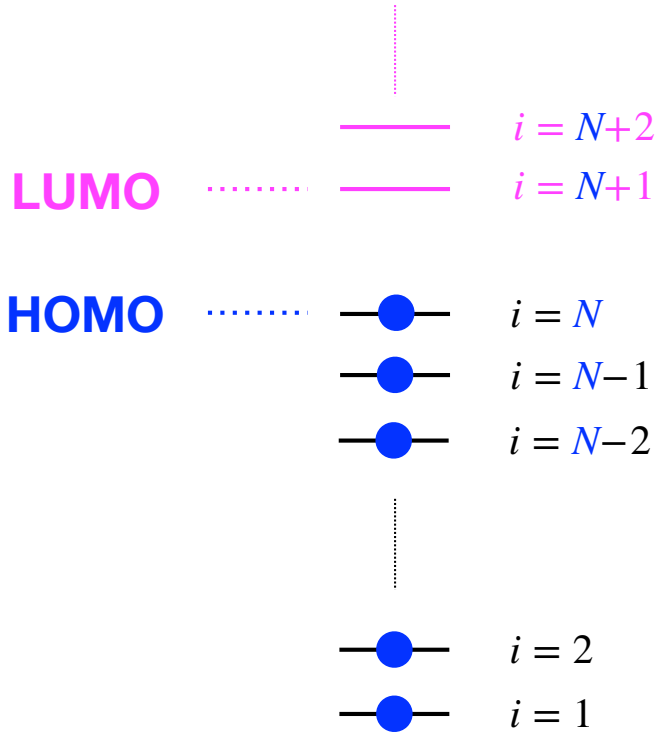
[d]ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
[e]Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, Toulouse, France

DFT for N-electron ground states

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



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

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

exact ground-state ***density***

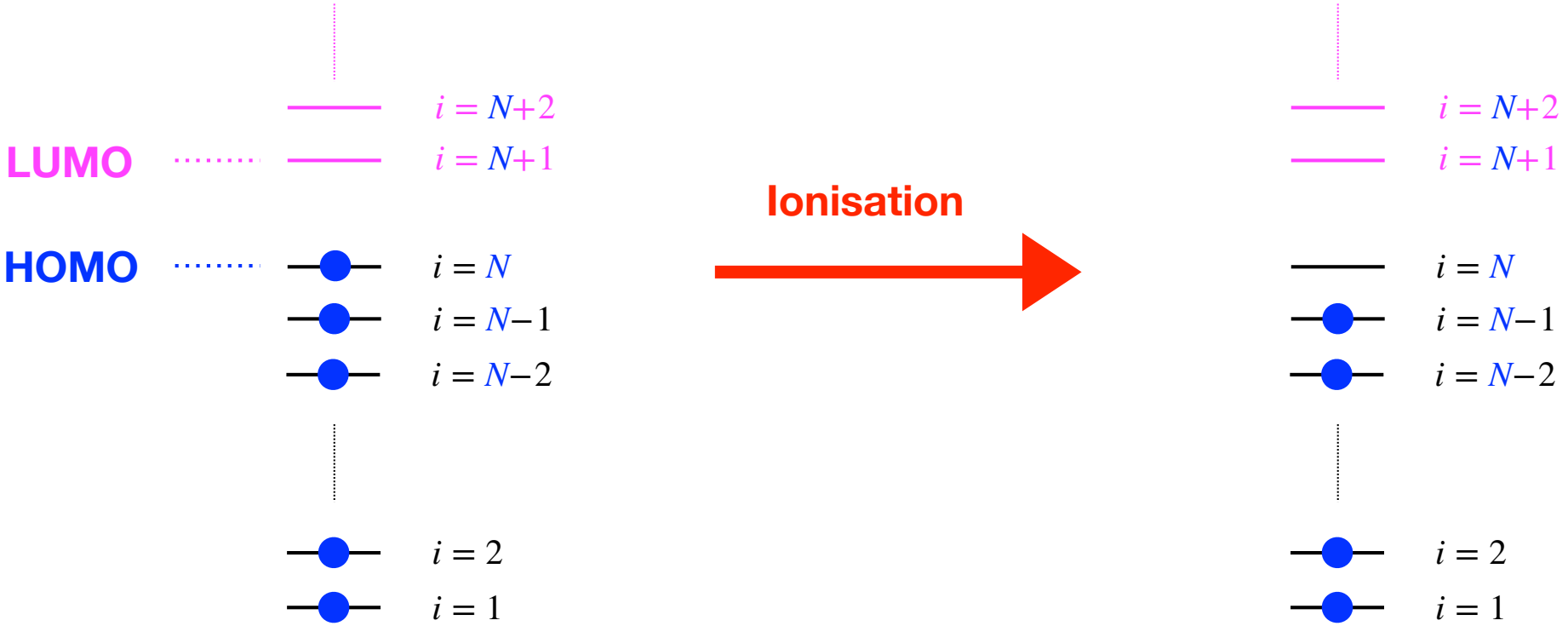
DFT for N-electron ground states

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

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

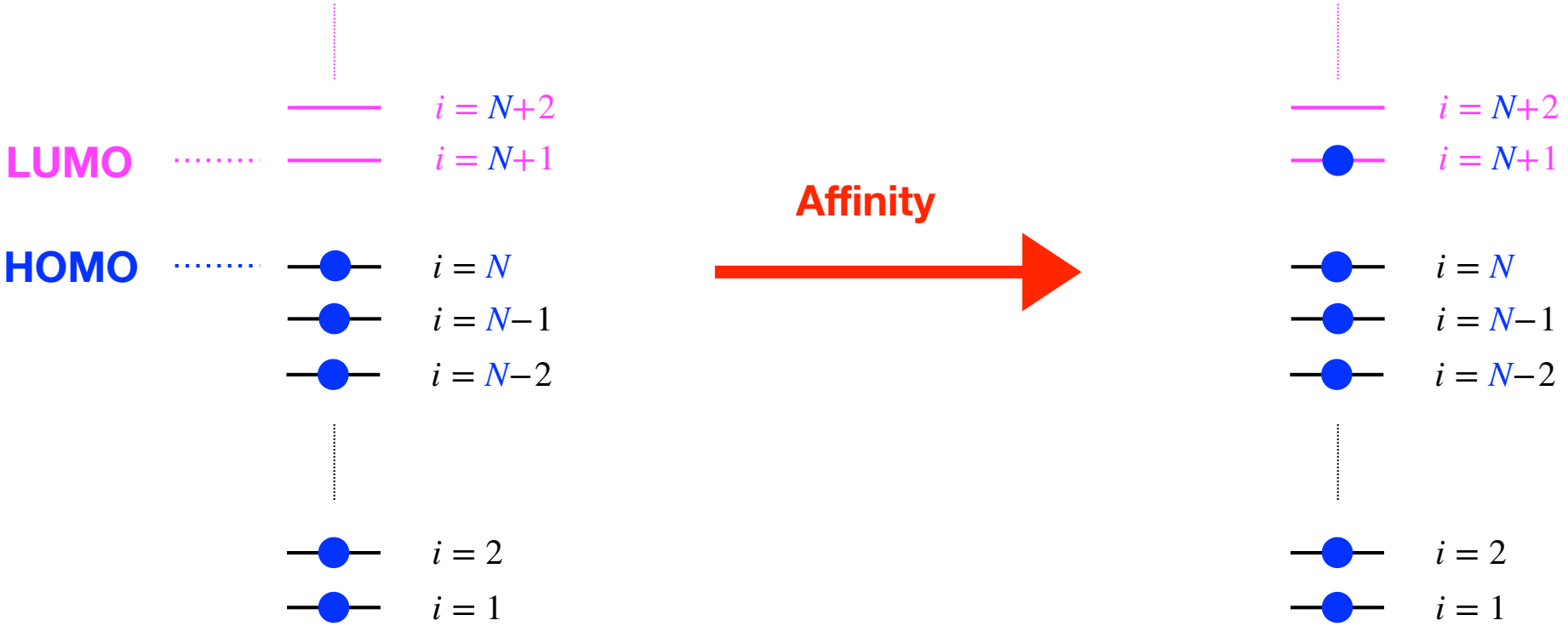
Hartree-exchange-correlation ***potential***

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



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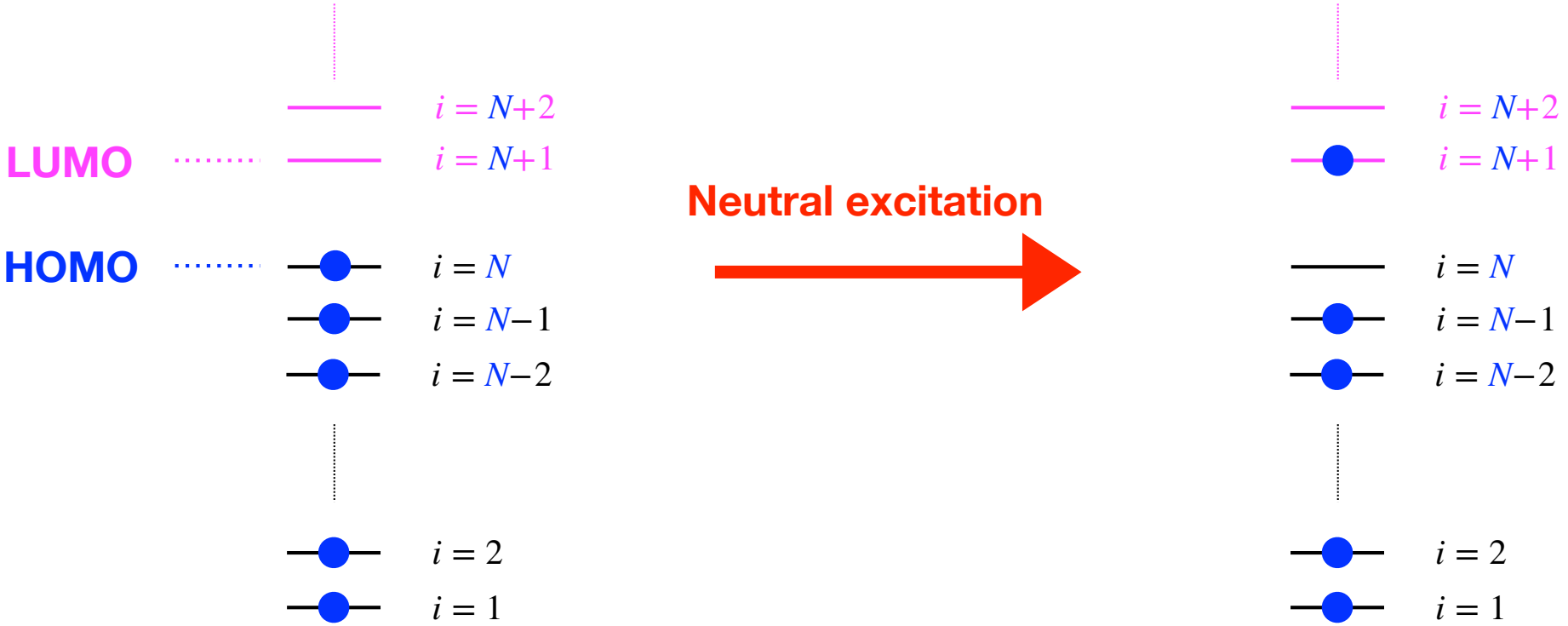

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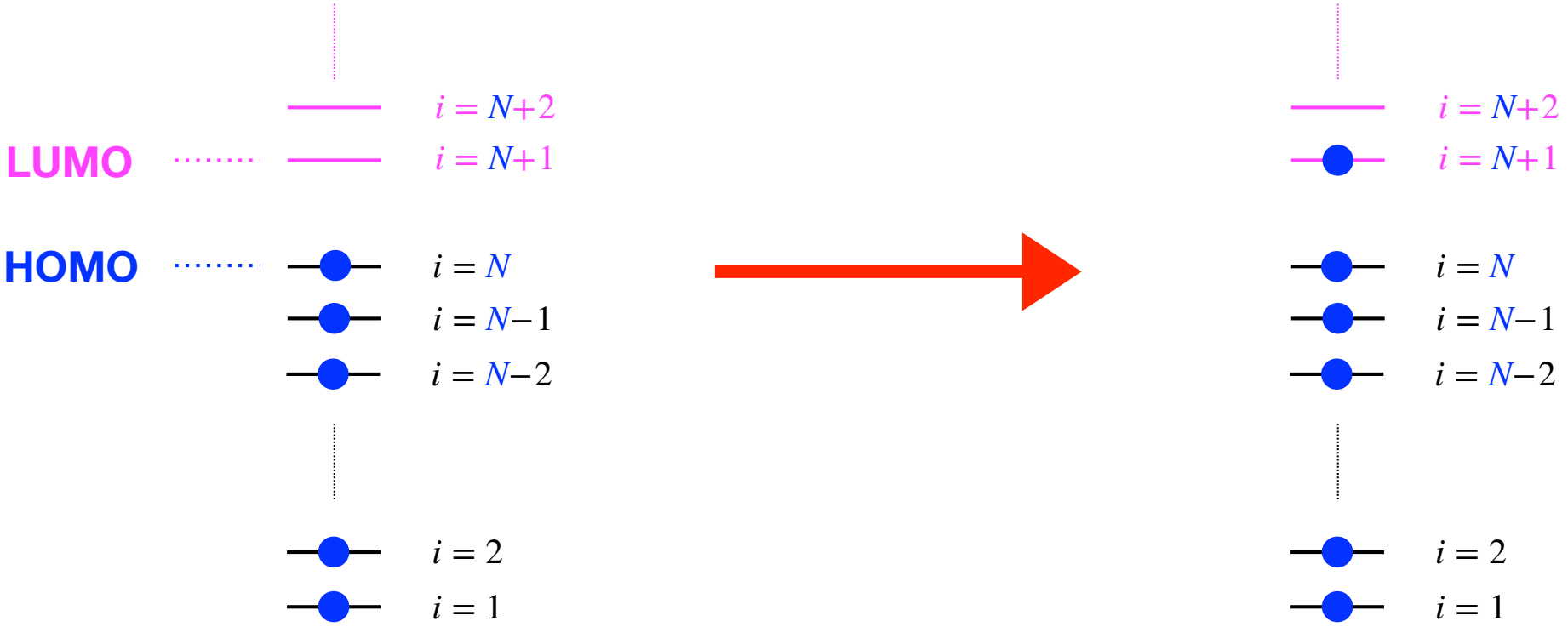
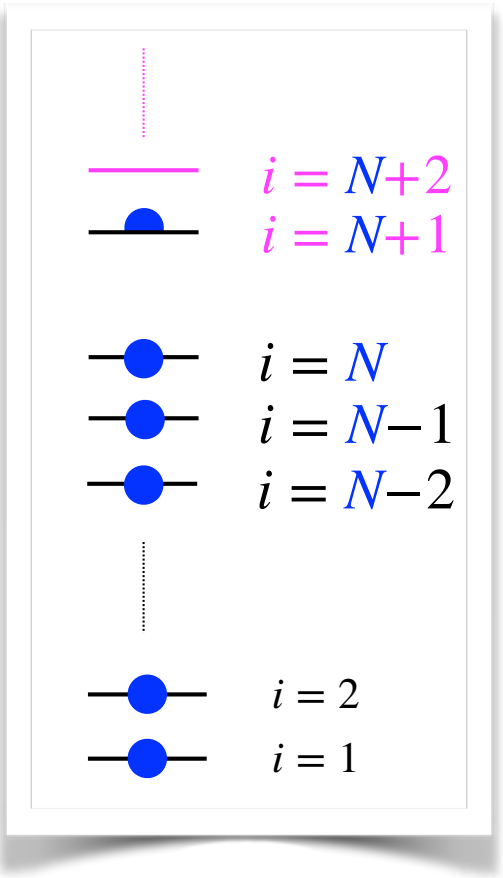


Simple connection to the
*real (interacting) **excited** states?*

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).*

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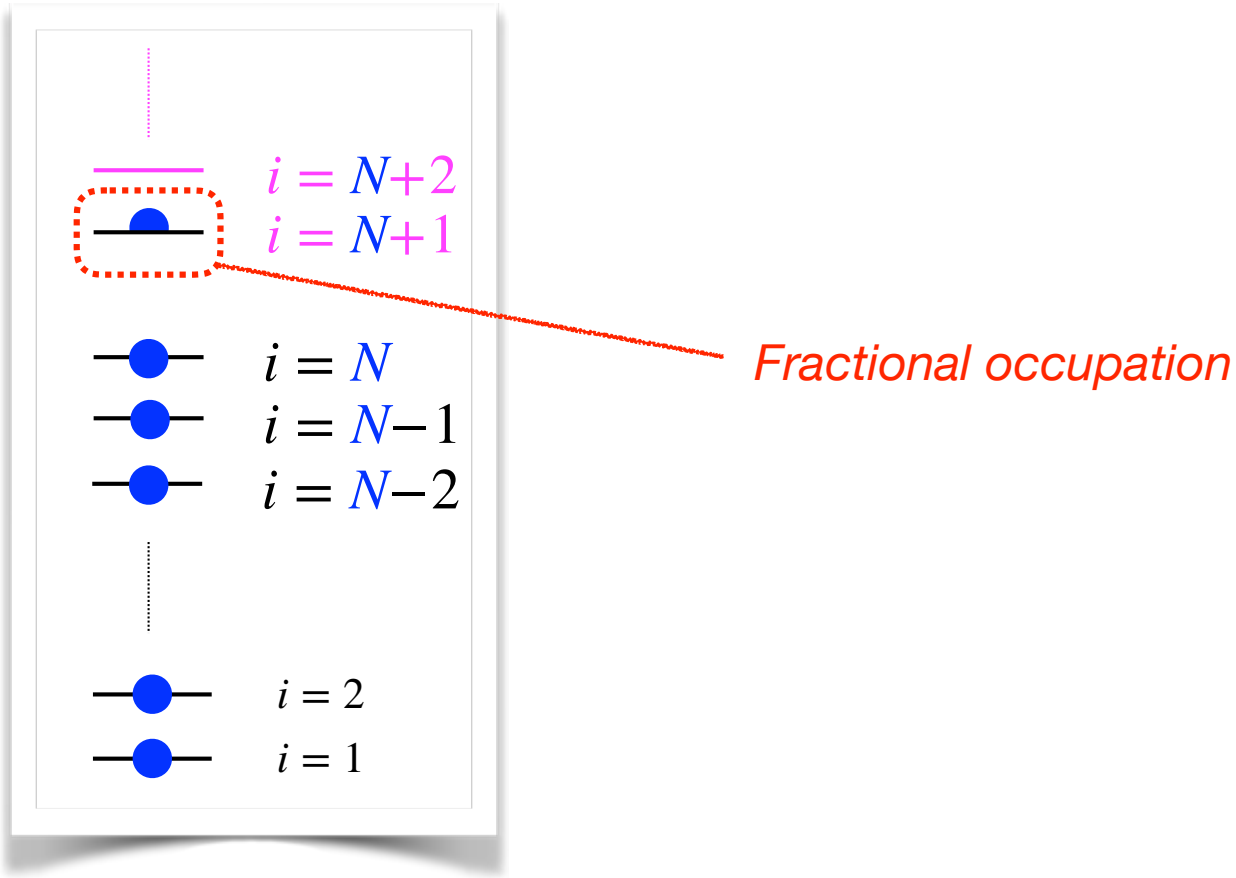

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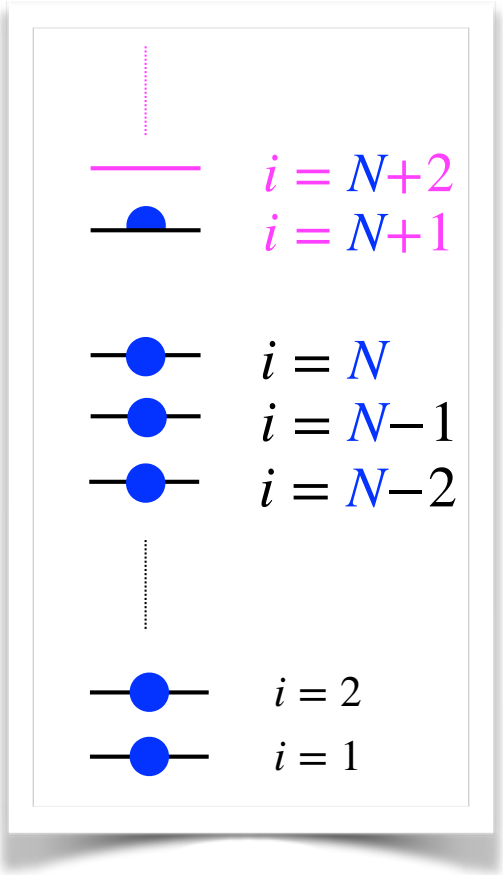


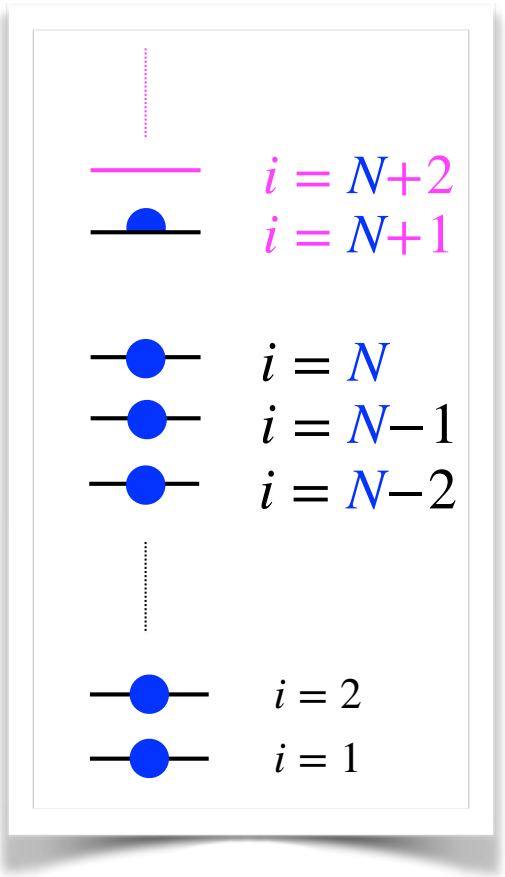
$$n(\mathbf{r}) \equiv (1-\alpha)n_0^N(\mathbf{r}) + \alpha n_0^{N+1}(\mathbf{r})$$

$$0 < \alpha \leq 1$$

"Grand canonical" ***ensemble weight***

DFT for fractional electron numbers

Continuous Affinity process



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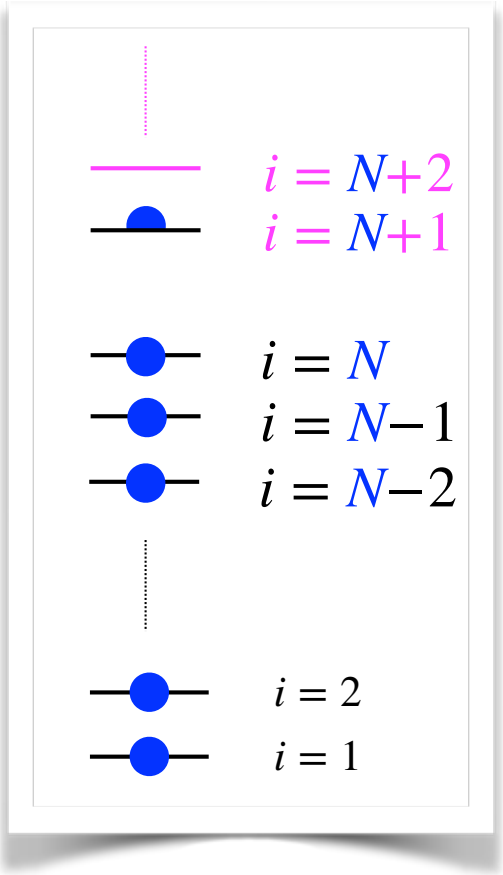
*We "just" need to **extend** $E_{\mathrm{xc}}[n]$*
to densities n integrating to
fractional *electron numbers*

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

DFT for fractional electron numbers

Continuous Affinity process



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

Janak's theorem

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

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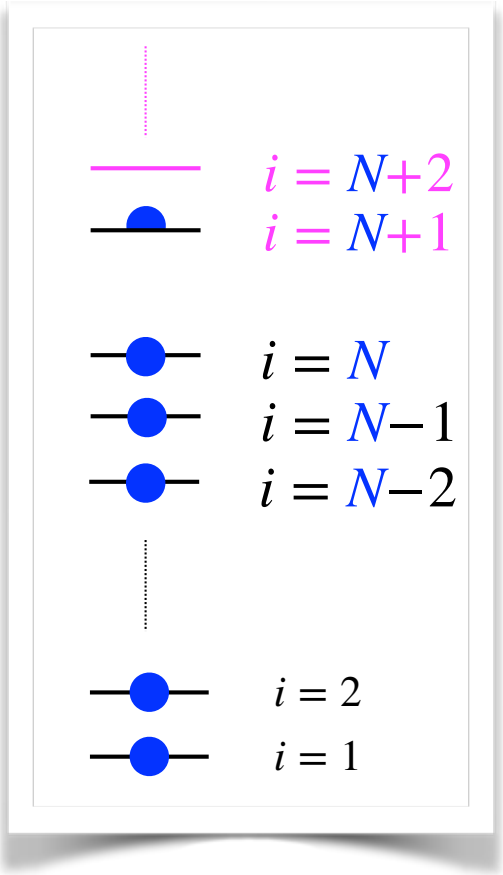

$$I_0^{N+1} = -\,\varepsilon_{N+1}$$

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

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

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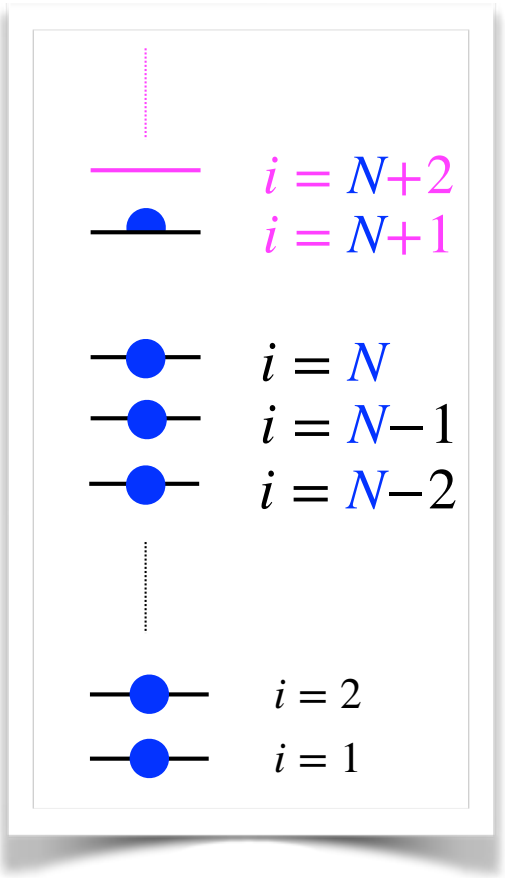

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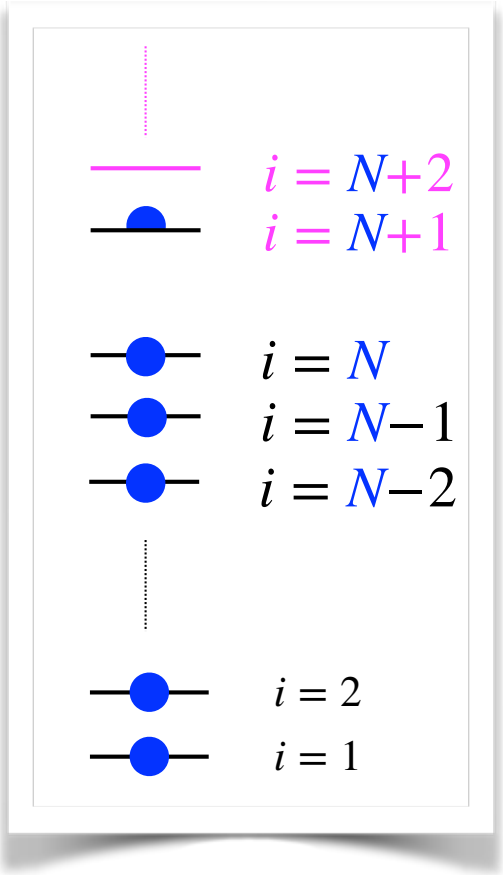

$$n(\mathbf{r}) \equiv (1-\alpha)n_0^N(\mathbf{r}) + \alpha n_0^{N+1}(\mathbf{r})$$

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

E. Kraisler, L. Kronik, Phys. Rev. Lett. ***110****, 126403 (2013).*
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, to appear in Topics in Current Chemistry (2021), Preprint: ***arXiv:2109.04943***

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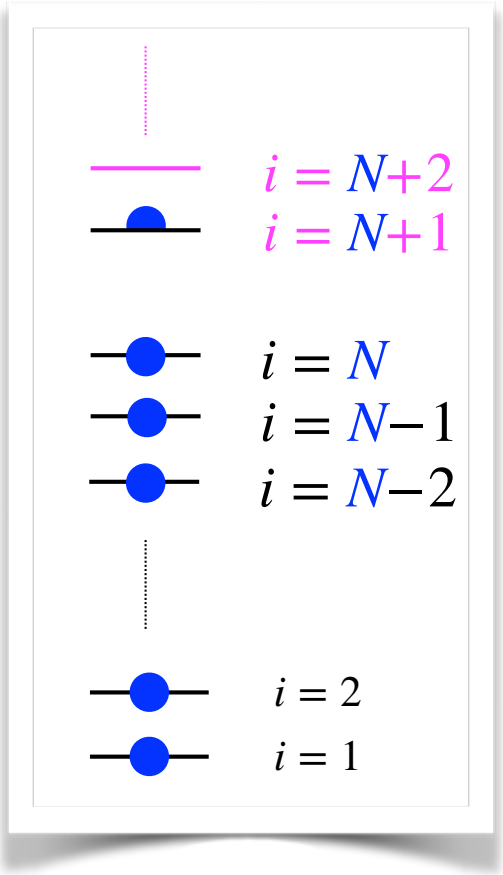

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$$\alpha \equiv \alpha[n]$$

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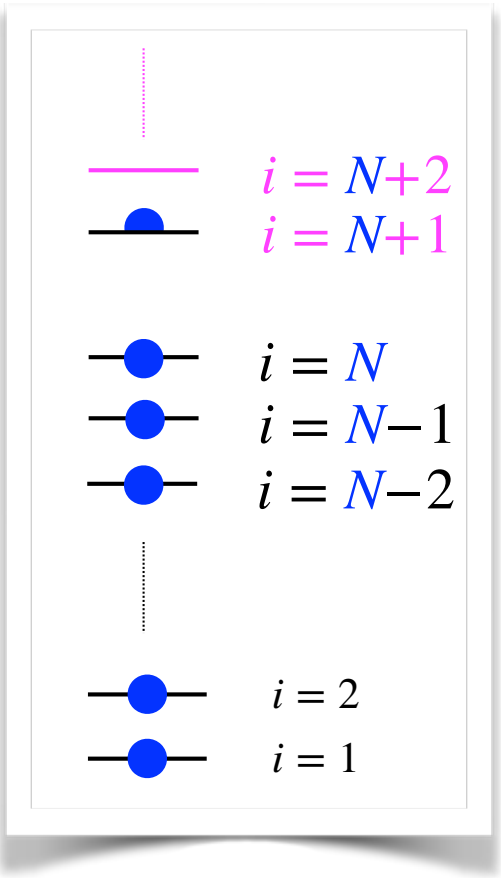

$$n(\mathbf{r}) \equiv (1-\alpha)n_0^N(\mathbf{r}) + \alpha n_0^{N+1}(\mathbf{r})$$

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

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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

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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).*
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General N-centered ensemble formalism

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

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General N-centered ensemble formalism

Charged or neutral!

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Reference N-electron ground-state density

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N-centered ensemble energy

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

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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

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

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

Fractionally *occupied KS orbitals*

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
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$$E_{\text{Hxc}}^{\{\xi_\nu\}}[n] = E_{\text{H}}[n] + E_{\text{xc}}^{\{\xi_\nu\}}[n]$$

key ingredient

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Auxiliary quantity *(not an observable) …*

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Auxiliary quantity *(not observable) …*

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

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"Theory meets experiment"

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

Excitation energy

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Infinitesimal occupation

of the targeted excited state μ,

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

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

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Physical meaning of the KS orbital energies

$$E_\mu - E_0 = \boxed{\mathscr{E}_\mu^{\mathrm{KS}} - \mathscr{E}_0^{\mathrm{KS}}} + \left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n_0]}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0} + \frac{\left(N - N_\mu\right)}{N}\left(\int d\mathbf{r}\, v_{\mathrm{Hxc}}^{\xi_\mu \to 0^+}(\mathbf{r}) n_0(\mathbf{r}) - E_{\mathrm{Hxc}}[n_0]\right)$$

KS excitation energy

M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A ***103****, 012806 (2021).*
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, to appear in Topics in Current Chemistry (2021), Preprint: ***arXiv:2109.04943***

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xc ensemble weight derivative

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

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N-centered ensemble **Hxc potential**

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*unique **up to a constant***

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N-centered ensemble Hxc potential
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Even for charged excitations!

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

$$E_\mu - E_0 = \mathscr{E}_\mu^{\mathrm{KS}} - \mathscr{E}_0^{\mathrm{KS}} \quad \Leftrightarrow \quad \textit{Janak's theorem}$$

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

$$= 0$$

M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A ***103****, 012806 (2021).*
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, to appear in Topics in Current Chemistry (2021), Preprint: ***arXiv:2109.04943***

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

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

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!*

*M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).*
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$$\left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n_0]}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0} + \frac{\left(N - N_\mu\right)}{N}\left(\int d\mathbf{r}\, v_{\mathrm{Hxc}}^{\xi_\mu \to 0^+}(\mathbf{r}) n_0(\mathbf{r}) - E_{\mathrm{Hxc}}[n_0]\right) = 0$$

$$\Updownarrow$$

$$v_{\mathrm{Hxc}}^{\xi_\mu \to 0^+}(\mathbf{r}) \underset{|\mathbf{r}|\to+\infty}{\longrightarrow} 0 \qquad \textit{for a } \textbf{\textit{molecule}}$$

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!

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*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 (2021).

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

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

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

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

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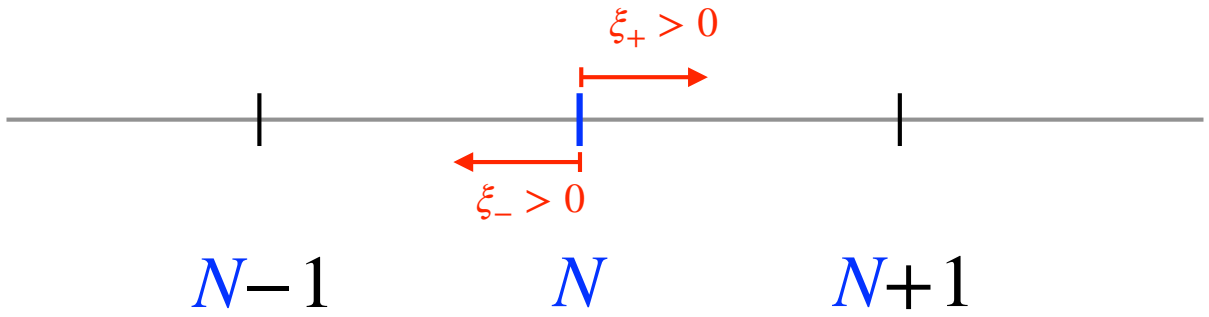
Let's make the charged KS excitation energies match the true ones!

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



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$\equiv \Delta_{\mathrm{xc}}$ **Derivative discontinuity** $\equiv \Delta_{\mathrm{xc}}$

Exact fundamental gap

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

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F. Cernatic, B. Senjean, V. Robert, and E. Fromager, to appear in Topics in Current Chemistry (2021), Preprint: ***arXiv:2109.04943***

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

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

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Suppression of the derivative discontinuity

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

$$\Updownarrow$$

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

Shifted *N-centered ensemble xc potential*

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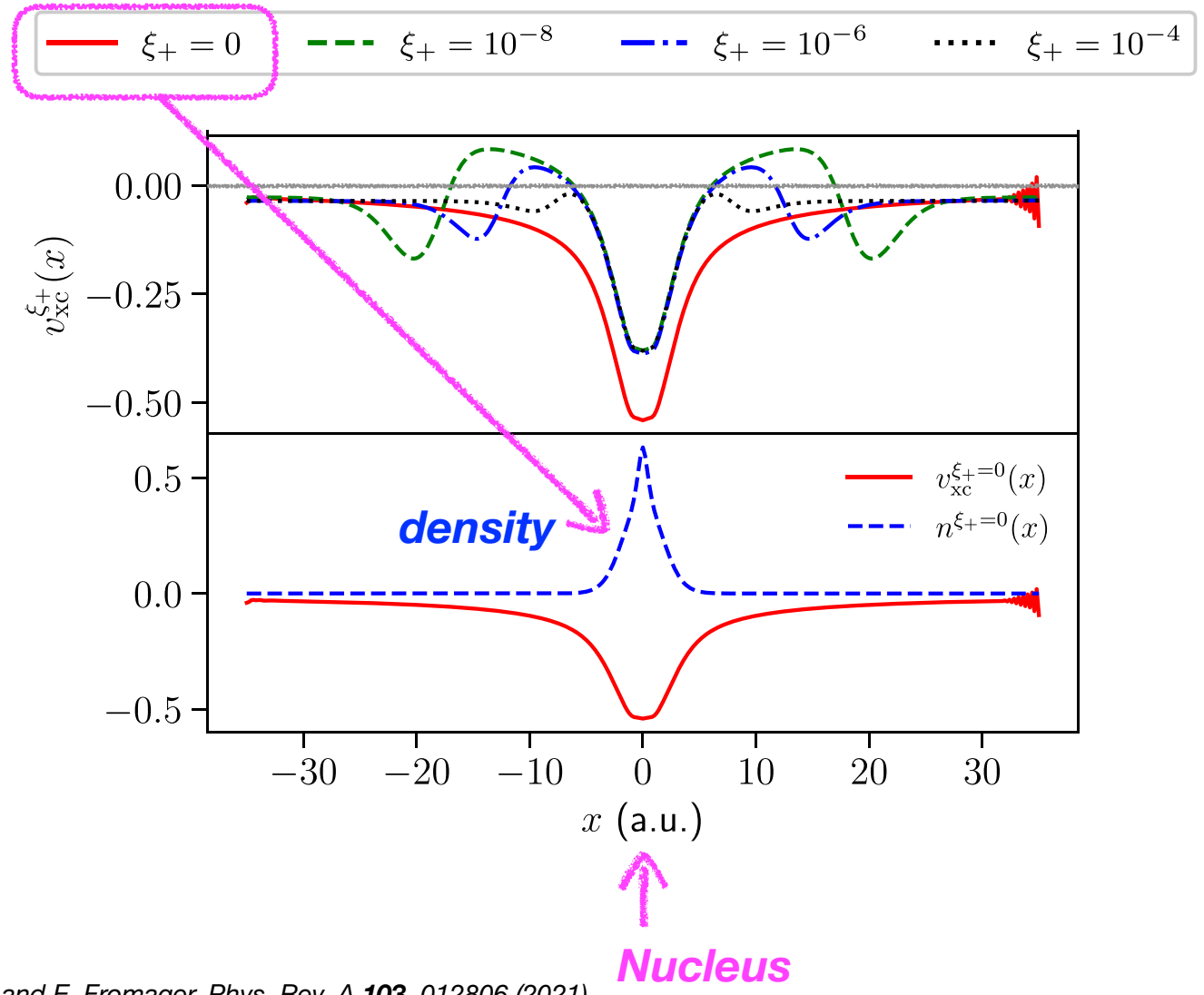
Application: Two-electron spin-polarised 1D atom

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



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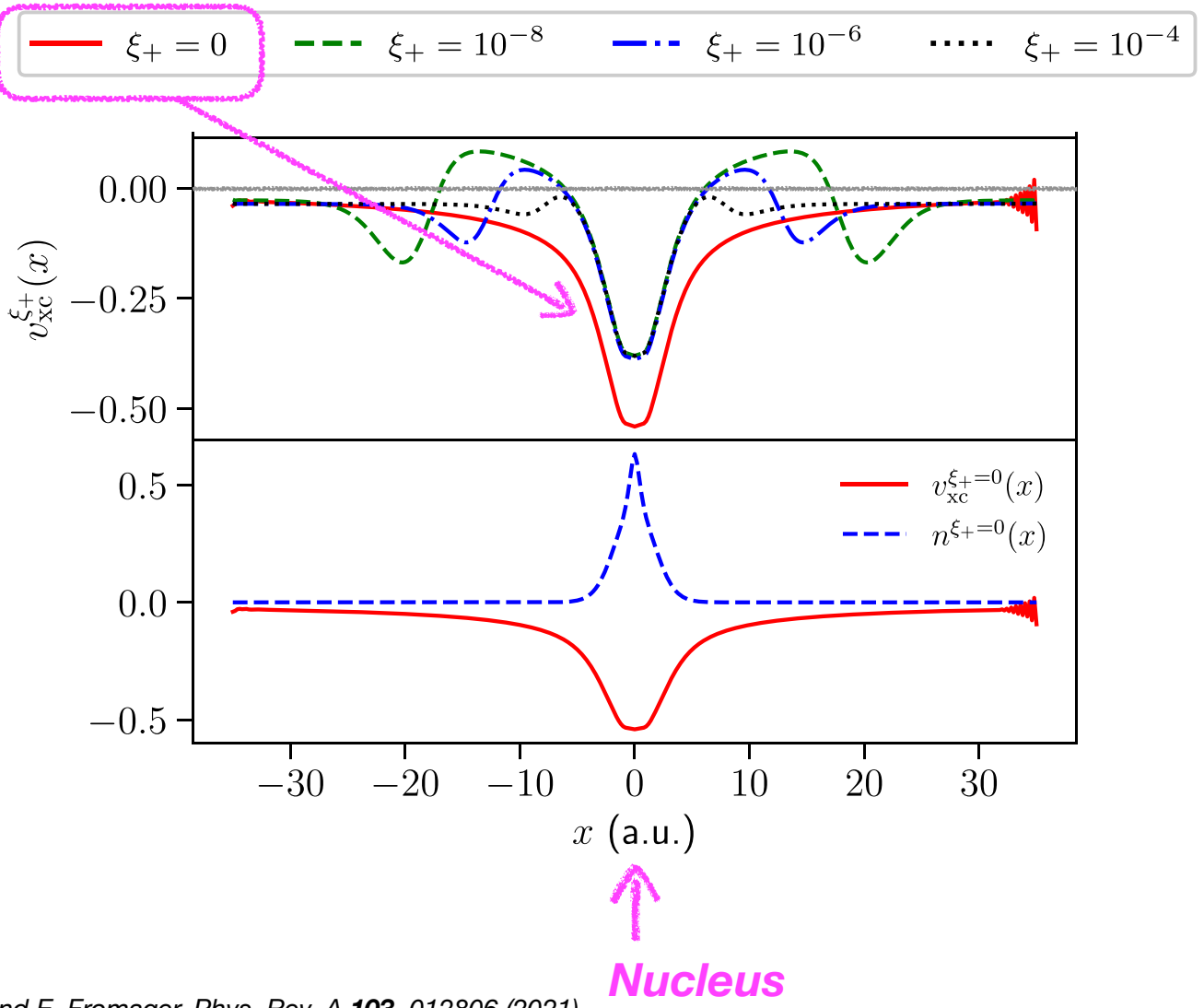

xc potential

Nucleus

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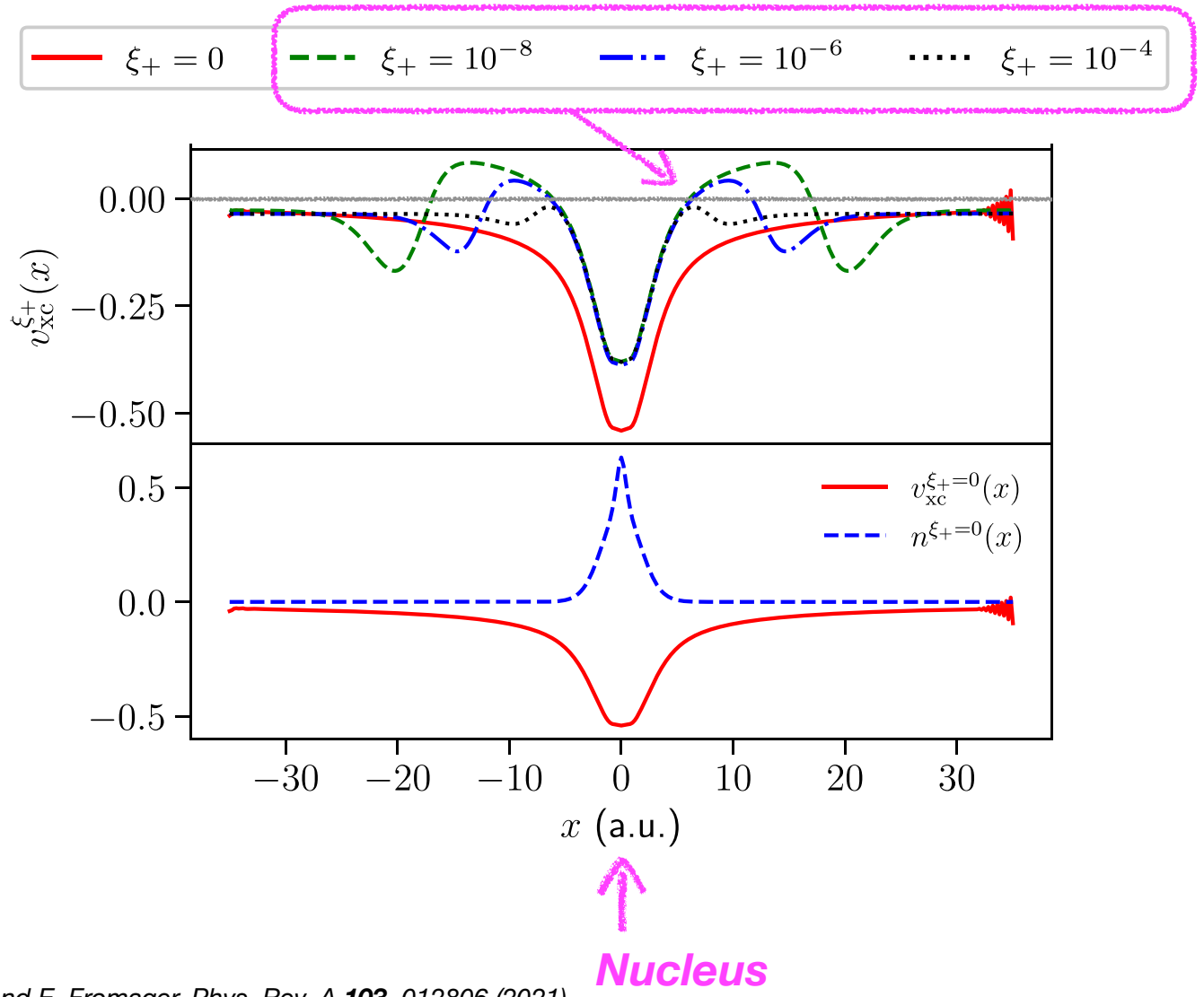

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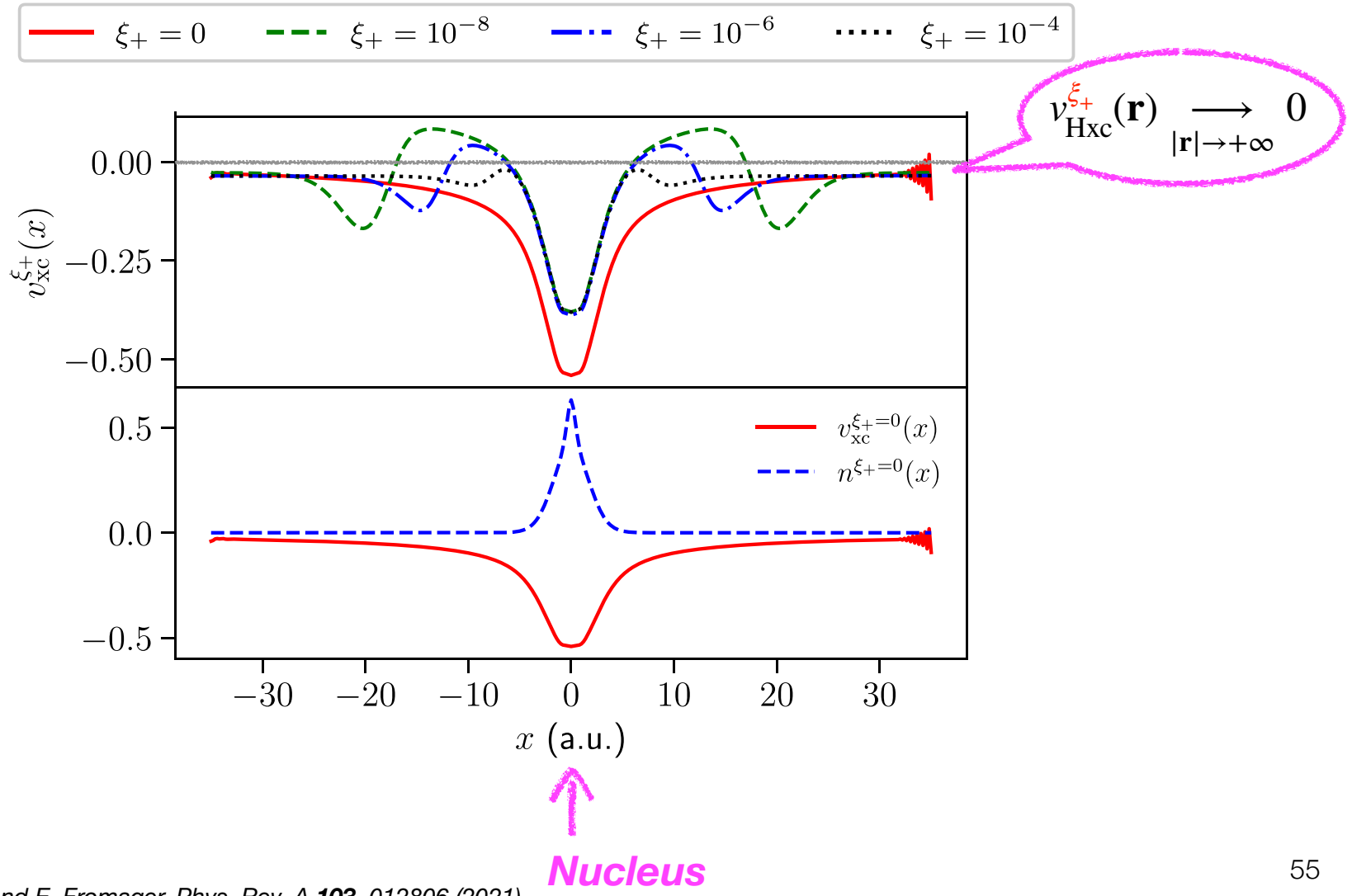

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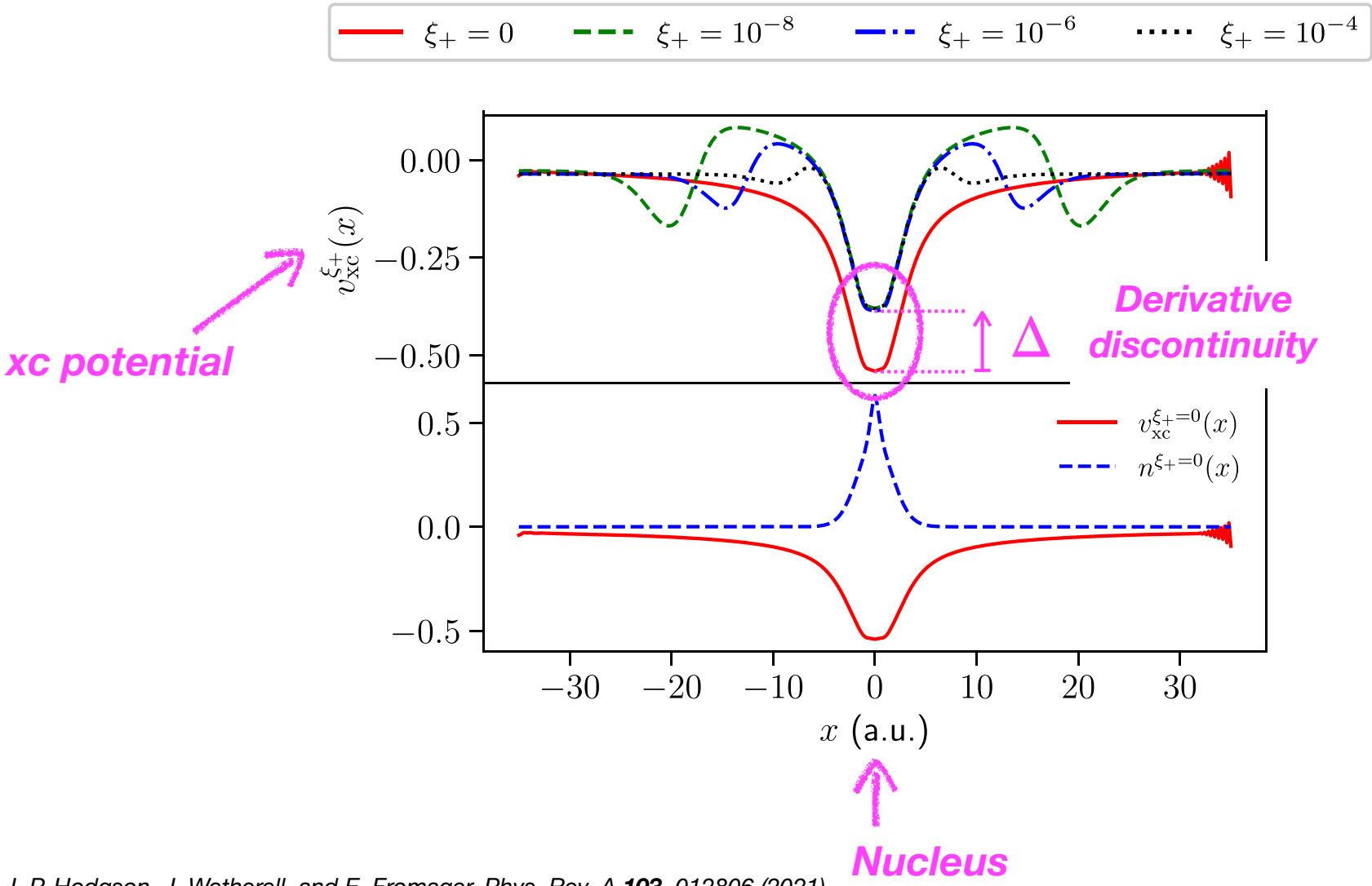
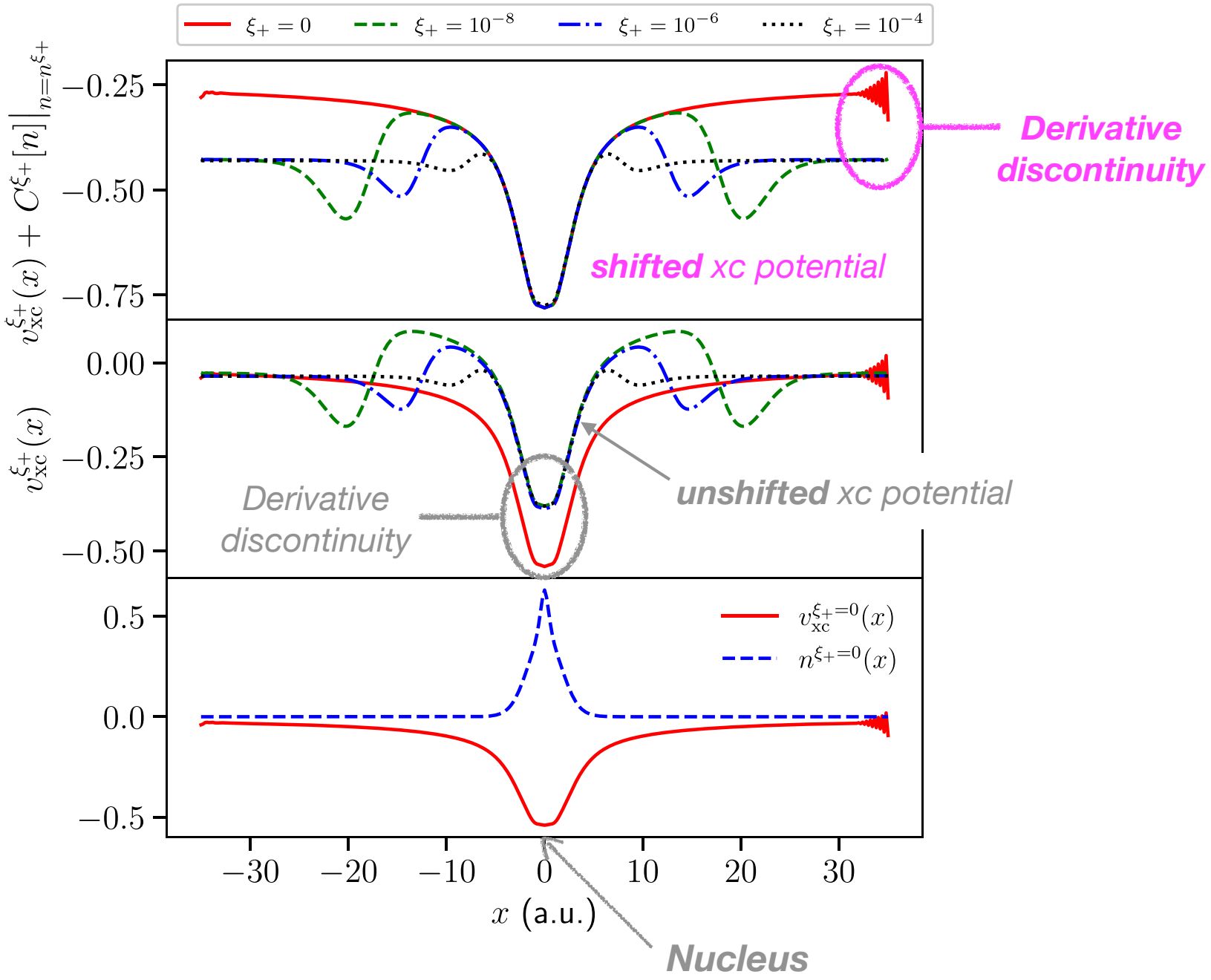


*M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).*

Moving the discontinuity away from the system



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

Outlook

Open question:

How can we incorporate weight dependencies
into
density-functional approximations?

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into
density-functional approximations?

*What about **finite** uniform electron gases?*

*P.-F. Loos and E. Fromager, J. Chem. Phys. **152**, 214101 (2020).*

*F. Cernatic, B. Senjean, V. Robert, and E. Fromager, to appear in Topics in Current Chemistry (2021), Preprint: **arXiv:2109.04943***

Outlook

*Weight dependence from **static** perturbation theory?*

*Z-h. Yang, Phys. Rev. A **104**, 052806 (2021).*

Outlook

*Weight dependence **(and more)** from static perturbation theory?*

$$\sum_i \left[-\frac{\nabla^2_{\mathbf{r}_i}}{2} + v_{\text{ext}}(\mathbf{r}_i) + v^{\xi_\mu}_{\text{Hxc}}(\mathbf{r}_i) \right] + \lambda \left[\hat{W}_{\text{ee}} - \sum_i \left(v^{\xi_\mu}_{\text{Hxc}}(\mathbf{r}_i) - \Delta v^{\xi_\mu,\lambda}_{\text{Hxc}}(\mathbf{r}_i) \right) \right]$$

Reference KS ensemble

Perturbation

Outlook

*Weight dependence (and more) from **static** perturbation theory*

$$\sum_i \left[-\frac{\nabla^2_{\mathbf{r}_i}}{2} + v_{\text{ext}}(\mathbf{r}_i) + v^{\xi_\mu}_{\text{Hxc}}(\mathbf{r}_i) \right] + \lambda \left[\hat{W}_{\text{ee}} - \sum_i \left(v^{\xi_\mu}_{\text{Hxc}}(\mathbf{r}_i) - \Delta v^{\xi_\mu,\lambda}_{\text{Hxc}}(\mathbf{r}_i) \right) \right]$$

Will hold the ensemble density
constant
(like in Görling-Levy PT)*

*A. Görling, M. Levy, Phys. Rev. A **50**(1), 196 (1994).*

Outlook

*Weight dependence (and more) from **static** perturbation theory*

$$\sum_i \left[-\frac{\nabla^2_{\mathbf{r}_i}}{2} + v_{\text{ext}}(\mathbf{r}_i) + v^{\xi_\mu}_{\text{Hxc}}(\mathbf{r}_i) \right] + \lambda \left[\hat{W}_{\text{ee}} - \sum_i \left(v^{\xi_\mu}_{\text{Hxc}}(\mathbf{r}_i) - \Delta v^{\xi_\mu,\lambda}_{\text{Hxc}}(\mathbf{r}_i) \right) \right]$$

$$E_\mu = \mathscr{E}^{\text{KS}}_\mu + \mathscr{E}^{(1)}_\mu + \mathscr{E}^{(2)}_\mu + \ldots$$

Excitation energies

$$\Psi_\mu = \Phi^{\text{KS}}_\mu + \Psi^{(1)}_\mu + \Psi^{(2)}_\mu + \ldots$$

Dyson orbitals, transition moments

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“Lab of Excellence” project:
LabEx CSC (ANR-10-LABX-0026-CSC)

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

CoLab ANR project