Exact density-functional energy gaps without derivative discontinuities

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Ionization potential (IP) theorem in DFT

Janak's theorem:

$$E_0^{N-1} - E_0^N = I^N = -\varepsilon_{i=N}^N$$

Ionisation potential
of the N-electron system

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

Ionization potential (IP) theorem in DFT

Number of electrons
in the DFT calculation

$$E_0^{N-1} - E_0^N = I^N = -\varepsilon_{i=N}^N$$

Orbital index

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

Ionization potential (IP) theorem in DFT

$$E_0^{N-1} - E_0^N = I^N = -\varepsilon_{i=N}^N$$

Kohn-Sham HOMO energy
of the N-electron system

Ionization potential (IP) theorem in DFT

$$I^N = -\varepsilon_{i=N}^N$$

$N \to N+1$

$$E_0^N - E_0^{N+1} = A^N = I^{N+1} = -\varepsilon_{i=N+1}^{N+1}$$

Electron affinity

of the N-electron system

Ionization potential (IP) theorem in DFT

$$I^N = -\varepsilon_{i=N}^N$$

$$E_0^N - E_0^{N+1} = A^N = I^{N+1} = -\varepsilon_{i=N+1}^{N+1}$$

$$E_g = I^N - A^N = \varepsilon_{i=N+1}^{N+1} - \varepsilon_{i=N}^N$$

Fundamental energy gap *of the N-electron system*

HOMO *energies*

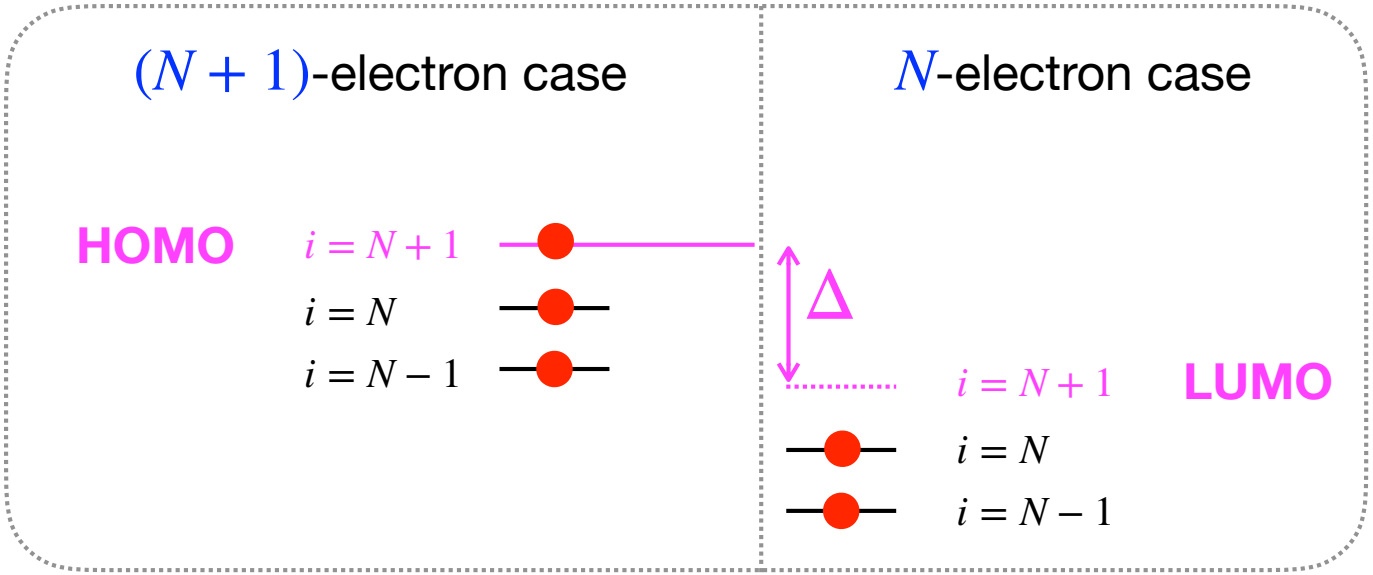
Ionization potential (IP) theorem in DFT

Extractable from the N-calculation?

$$E_g = I^N - A^N = \varepsilon_{i=N+1}^{N+1} - \varepsilon_{i=N}^{N}$$

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

Ionization potential (IP) theorem in DFT

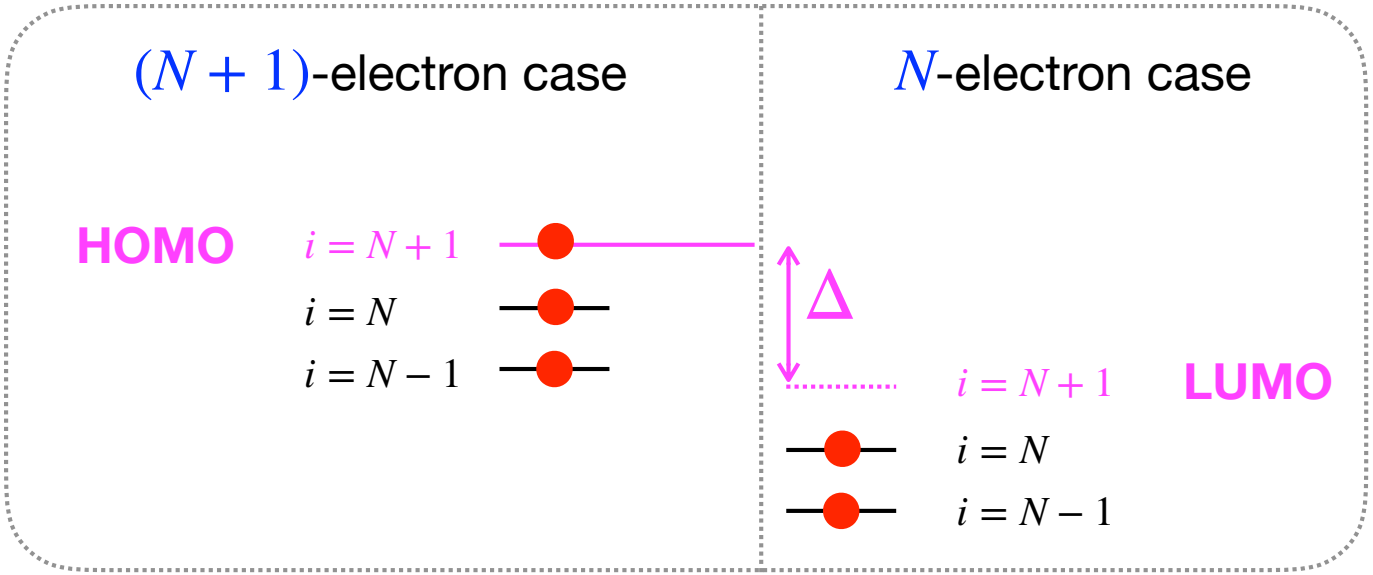


Extractable from the N-calculation?

$$E_g = I^N - A^N = \boxed{\varepsilon^{N+1}_{i=N+1}} - \varepsilon^{N}_{i=N}$$

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

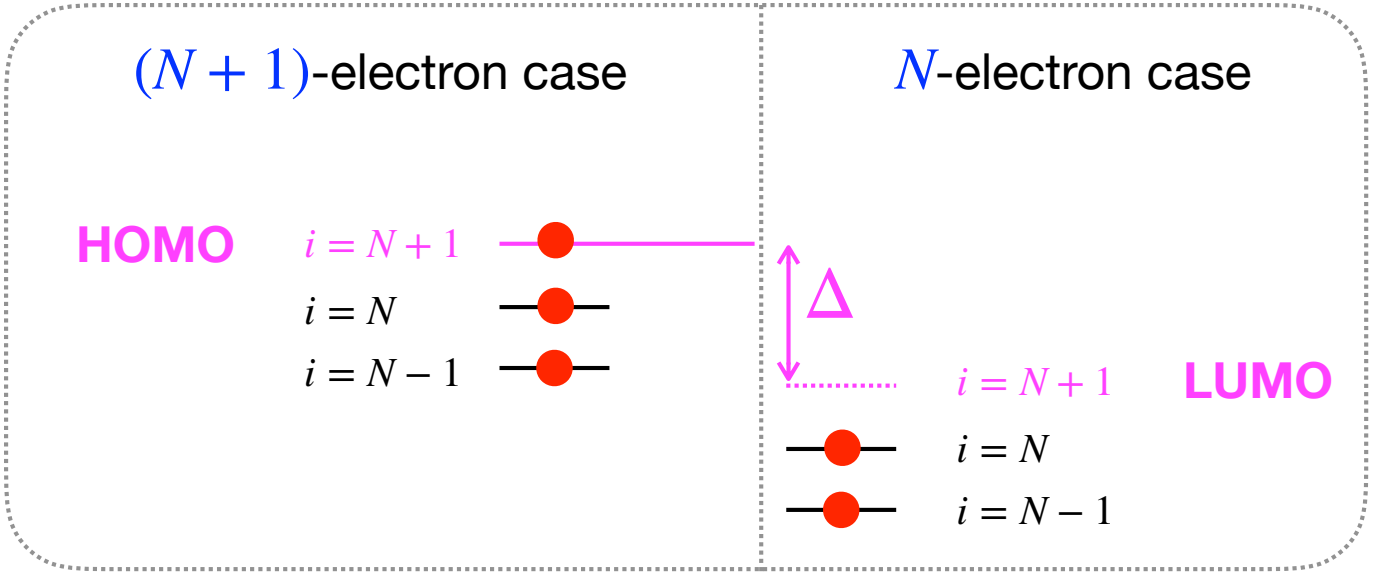
Ionization potential (IP) theorem in DFT



$$E_g = I^N - A^N = \left(\varepsilon^N_{i=N+1} + \Delta\right) - \varepsilon^N_{i=N}$$

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

Ionization potential (IP) theorem in DFT

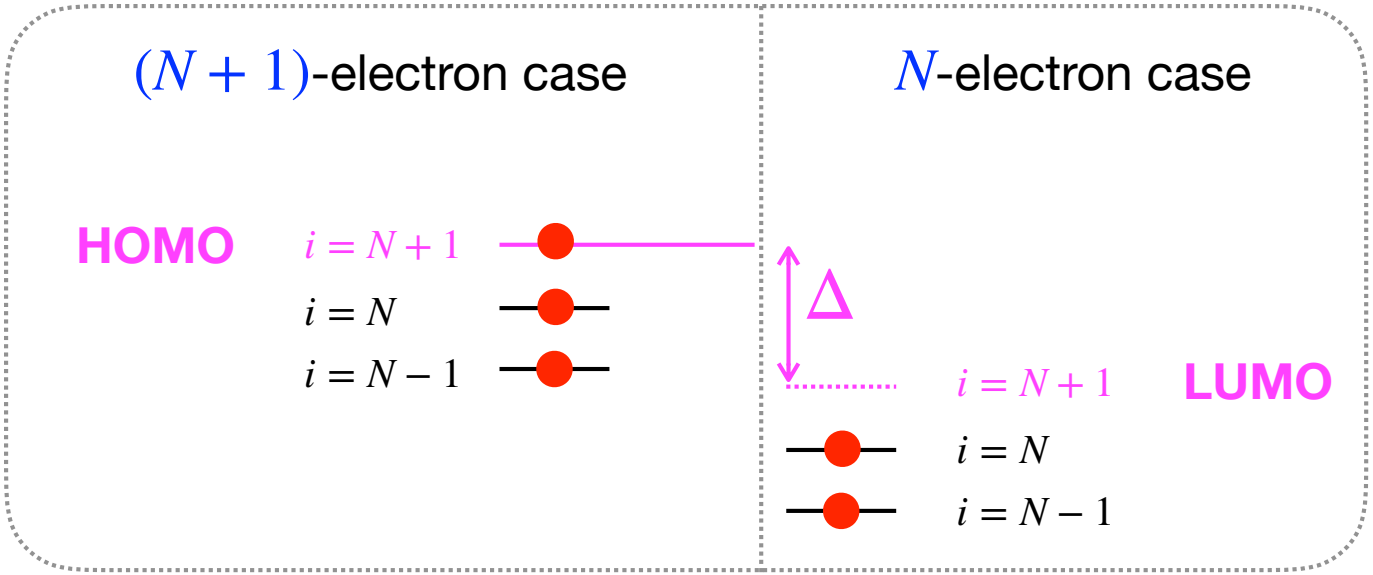


$$E_g = I^N - A^N = \varepsilon^N_{i=N+1} - \varepsilon^N_{i=N} + \Delta$$

*Kohn-Sham **HOMO-LUMO** gap of the N-electron system*

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

Ionization potential (IP) theorem in DFT



$$E_g = I^N - A^N = \varepsilon^N_{i=N+1} - \varepsilon^N_{i=N} + \Delta$$

*"derivative **discontinuity**"*

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

Alternative formulation of the IP theorem

$$I^N = -\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

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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Ensemble density

$$n_0^{\xi_-}(\mathbf{r}) = \xi_- n_0^{N-1}(\mathbf{r}) + \left[1 - \frac{\xi_-(N-1)}{N} \right] n_0^N(\mathbf{r})$$

Ionized density

Neutral density

Electron removal

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

Alternative formulation of the IP theorem

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Ensemble density

$$n_0^{\xi_-}(\mathbf{r}) = \xi_-\, n_0^{N-1}(\mathbf{r}) + \left[1 - \frac{\xi_-(N-1)}{N} \right] n_0^N(\mathbf{r})$$

Ensemble **weight**

Electron removal

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
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Alternative formulation of the IP theorem

$$I^N = -\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

Ensemble density

$$n_0^{\xi_-}(\mathbf{r}) = \xi_- n_0^{N-1}(\mathbf{r}) + \left[1 - \frac{\xi_-(N-1)}{N} \right] n_0^N(\mathbf{r})$$

$\xi_- = 0$

Neutral system

Electron removal

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

Alternative formulation of the IP theorem

$$I^N = -\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

Ensemble density

$$n_0^{\xi_-}(\mathbf{r}) = \xi_- n_0^{N-1}(\mathbf{r}) + \left[1 - \frac{\xi_-(N-1)}{N} \right] n_0^N(\mathbf{r})$$

$\xi_- > 0$

Electron removal

Partially-ionised *system*

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

Alternative formulation of the IP theorem

$$I^N = -\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

$$\int d\mathbf{r}\, n_0^{\xi_-}(\mathbf{r}) = N$$

by construction

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B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; ***120****:e26190.*

Alternative formulation of the IP theorem

$$I^N = -\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

$$\int d\mathbf{r}\, n_0^{\xi_-}(\mathbf{r}) = N$$

***N*-centered**
ensemble formalism

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Alternative formulation of the IP theorem

Exchange-correlation (xc)
energy of the ensemble

$$I^N = -\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

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Alternative formulation of the IP theorem

ensemble KS ***orbital energy*** — *ensemble xc* ***potential***

$$I^N = -\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r}) v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

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

Kohn-Sham equations
for the ensemble

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Alternative formulation of the IP theorem

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xc ensemble ***weight derivative***

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Alternative formulation of the IP theorem

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$$A^N = -\varepsilon_{i=N+1}^{\xi_+} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_+}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_+}(\mathbf{r})}{N} - \left(\frac{\xi_+}{N} - 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_+}[n]}{\partial \xi_+} \right]_{n=n_0^{\xi_+}}$$

Ensemble density

$$n_0^{\xi_+}(\mathbf{r}) = \xi_+ n_0^{N+1}(\mathbf{r}) + \left[1 - \frac{\xi_+(N+1)}{N} \right] n_0^N(\mathbf{r})$$

Anionic *density*

Electron addition

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Alternative formulation of the IP theorem

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Alternative formulation of the IP theorem

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$\xi_- = \xi_+ = 0$

Regular N-electron DFT

$$I^N - A^N = \varepsilon_{i=N+1}^N - \varepsilon_{i=N}^N + \left. \frac{\partial E_{\mathrm{xc}}^{\xi_-}\left[n_0^N\right]}{\partial \xi_-} \right|_{\xi_-=0} + \left. \frac{\partial E_{\mathrm{xc}}^{\xi_+}\left[n_0^N\right]}{\partial \xi_+} \right|_{\xi_+=0}$$

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Alternative formulation of the IP theorem

$$I^N = -\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\text{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\text{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\text{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

$$A^N = -\varepsilon_{i=N+1}^{\xi_+} - \left[\frac{E_{\text{Hxc}}^{\xi_+}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\text{Hxc}}^{\xi_+}(\mathbf{r})}{N} - \left(\frac{\xi_+}{N} - 1 \right) \frac{\partial E_{\text{xc}}^{\xi_+}[n]}{\partial \xi_+} \right]_{n=n_0^{\xi_+}}$$

$$\xi_- = \xi_+ = 0$$

Regular N-electron DFT

$$I^N - A^N = \varepsilon_{i=N+1}^N - \varepsilon_{i=N}^N + \left. \frac{\partial E_{\text{xc}}^{\xi_-}[n_0^N]}{\partial \xi_-} \right|_{\xi_-=0} + \left. \frac{\partial E_{\text{xc}}^{\xi_+}[n_0^N]}{\partial \xi_+} \right|_{\xi_+=0}$$

True gap ***KS gap*** *"derivative discontinuity"* Δ

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*B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; **120**:e26190.*

Alternative formulation of the IP theorem

*A **proper modelling** of $E_{\mathrm{xc}}^{\xi_-}[n]$ and $E_{\mathrm{xc}}^{\xi_+}[n]$ gives **access to the "derivative discontinuity".***

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

Where is the discontinuity?

$$I^N = -\,\varepsilon^{\xi_-}_{i=N} \;-\; \left[\frac{E^{\xi_-}_{\rm Hxc}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v^{\xi_-}_{\rm Hxc}(\mathbf{r})}{N} \;-\; \left(\frac{\xi_-}{N} + 1\right) \frac{\partial E^{\xi_-}_{\rm xc}[n]}{\partial \xi_-}\right]_{n=n_0^{\xi_-}}$$

$$A^N = -\,\varepsilon^{\xi_+}_{i=N+1} \;-\; \left[\frac{E^{\xi_+}_{\rm Hxc}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v^{\xi_+}_{\rm Hxc}(\mathbf{r})}{N} \;-\; \left(\frac{\xi_+}{N} - 1\right) \frac{\partial E^{\xi_+}_{\rm xc}[n]}{\partial \xi_+}\right]_{n=n_0^{\xi_+}}$$

Where is the discontinuity?

$$I^N = -\,\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1\right)\frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-}\right]_{n=n_0^{\xi_-}}$$

$$A^N = -\,\varepsilon_{i=N+1}^{\xi_+} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_+}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_+}(\mathbf{r})}{N} - \left(\frac{\xi_+}{N} - 1\right)\frac{\partial E_{\mathrm{xc}}^{\xi_+}[n]}{\partial \xi_+}\right]_{n=n_0^{\xi_+}}$$

*If, like in **regular DFT**, we impose* $v_{\mathrm{Hxc}}^{\xi_\pm}(\mathbf{r}) \underset{|\mathbf{r}|\to+\infty}{\longrightarrow} 0$

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

Where is the discontinuity?

$$I^N = -\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

$$A^N = -\varepsilon_{i=N+1}^{\xi_+} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_+}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_+}(\mathbf{r})}{N} - \left(\frac{\xi_+}{N} - 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_+}[n]}{\partial \xi_+} \right]_{n=n_0^{\xi_+}}$$

If we impose $v_{\mathrm{Hxc}}^{\xi_\pm}(\mathbf{r}) \underset{|\mathbf{r}|\to+\infty}{\longrightarrow} 0$

$$I^N \overset{\xi_- \geq 0}{=} -\varepsilon_{i=N}^{\xi_-} \quad \text{and} \quad A^N \overset{\xi_+ > 0}{=} -\varepsilon_{i=N+1}^{\xi_+}$$

Regular IP theorem

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

Where is the discontinuity?

If we impose $v_{\mathrm{Hxc}}^{\xi_\pm}(\mathbf{r}) \underset{|\mathbf{r}|\to+\infty}{\longrightarrow} 0$

$$0 = \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

$$0 = \left[\frac{E_{\mathrm{Hxc}}^{\xi_+}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_+}(\mathbf{r})}{N} - \left(\frac{\xi_+}{N} - 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_+}[n]}{\partial \xi_+} \right]_{n=n_0^{\xi_+}}$$

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Where is the discontinuity?

If we impose $v_{\mathrm{Hxc}}^{\xi_\pm}(\mathbf{r}) \underset{|\mathbf{r}|\to+\infty}{\longrightarrow} 0$

$$0 = \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

$$0 = \left[\frac{E_{\mathrm{Hxc}}^{\xi_+}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_+}(\mathbf{r})}{N} - \left(\frac{\xi_+}{N} - 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_+}[n]}{\partial \xi_+} \right]_{n=n_0^{\xi_+}}$$

Regular N-electron DFT ***limit*** $\longleftarrow$ $\xi_- = 0 \Leftrightarrow \xi_+ = 0$ *and* $\xi_+ \to 0^+$

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

Infinitesimal addition *of an electron* ***Neutral*** *system*

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

Where is the discontinuity?

If we impose $v_{\mathrm{Hxc}}^{\xi_\pm}(\mathbf{r}) \underset{|\mathbf{r}|\to+\infty}{\longrightarrow} 0$

$$0 = \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1\right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

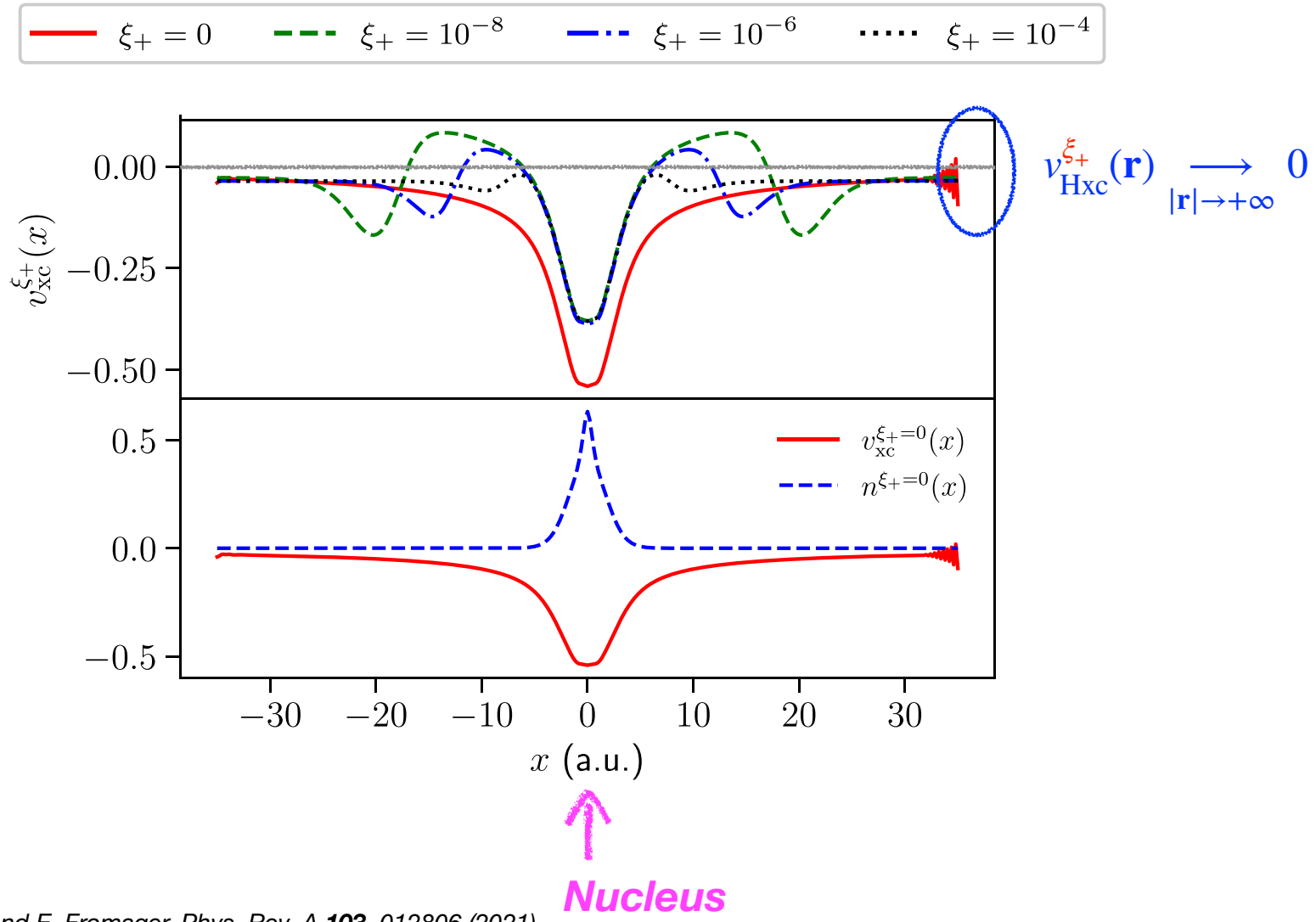
$$0 = \left[\frac{E_{\mathrm{Hxc}}^{\xi_+}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_+}(\mathbf{r})}{N} - \left(\frac{\xi_+}{N} - 1\right) \frac{\partial E_{\mathrm{xc}}^{\xi_+}[n]}{\partial \xi_+} \right]_{n=n_0^{\xi_+}}$$

$$\int d\mathbf{r}\, n_0^N(\mathbf{r}) \underbrace{\left(v_{\mathrm{xc}}^{\xi_+\to 0^+}(\mathbf{r}) - v_{\mathrm{xc}}^{\xi_+=0}(\mathbf{r}) \right)}_{\neq 0} = N\Delta$$

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

Application: Two-electron spin-polarised 1D atom

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



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

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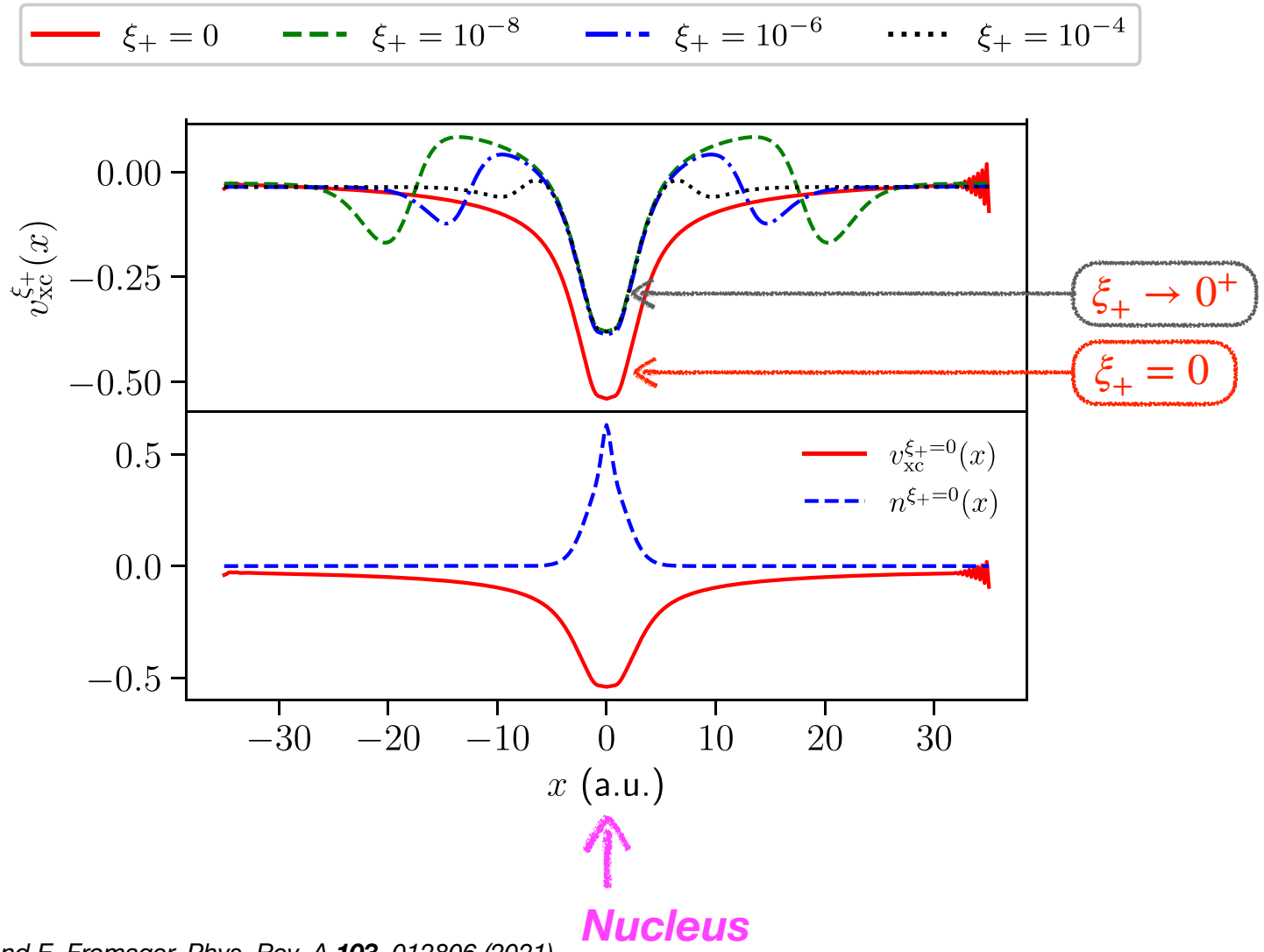

xc potential

Nucleus

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

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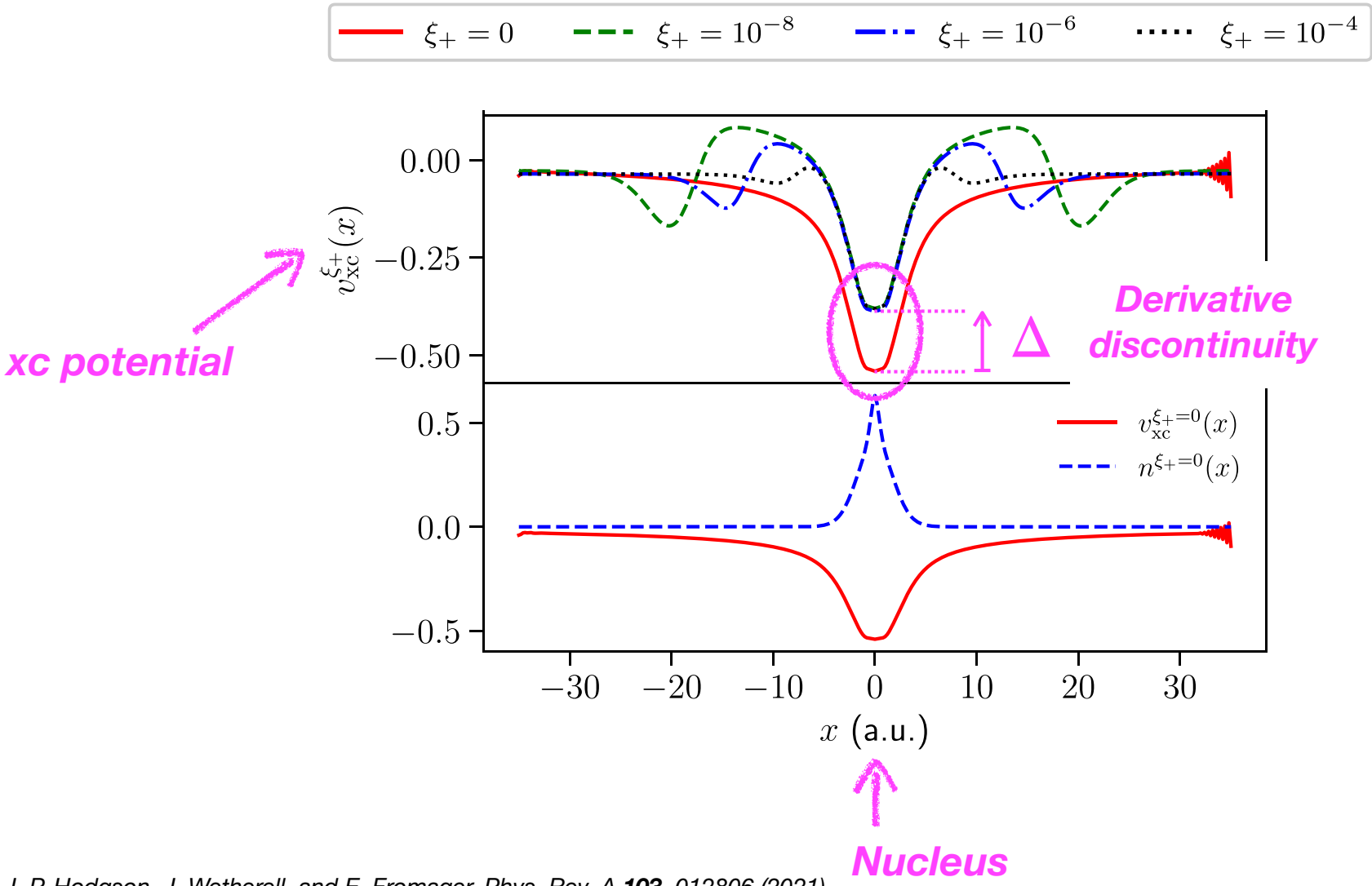

*M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).*

Moving the discontinuity away from the system

$$A^N = -\varepsilon_{i=N+1}^{\xi_+} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_+}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_+}(\mathbf{r})}{N} - \left(\frac{\xi_+}{N} - 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_+}[n]}{\partial \xi_+} \right]_{n=n_0^{\xi_+}}$$

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

Moving the discontinuity away from the system

Constant shift *applied to the xc potential*

$$A^N = -\left(\varepsilon^{\xi_+}_{i=N+1} + c\right) - \left[\frac{E^{\xi_+}_{\mathrm{Hxc}}[n] - \int d\mathbf{r}\, n(\mathbf{r})\left(v^{\xi_+}_{\mathrm{Hxc}}(\mathbf{r}) + c\right)}{N} - \left(\frac{\xi_+}{N} - 1\right)\frac{\partial E^{\xi_+}_{\mathrm{xc}}[n]}{\partial \xi_+}\right]_{n=n_0^{\xi_+}}$$

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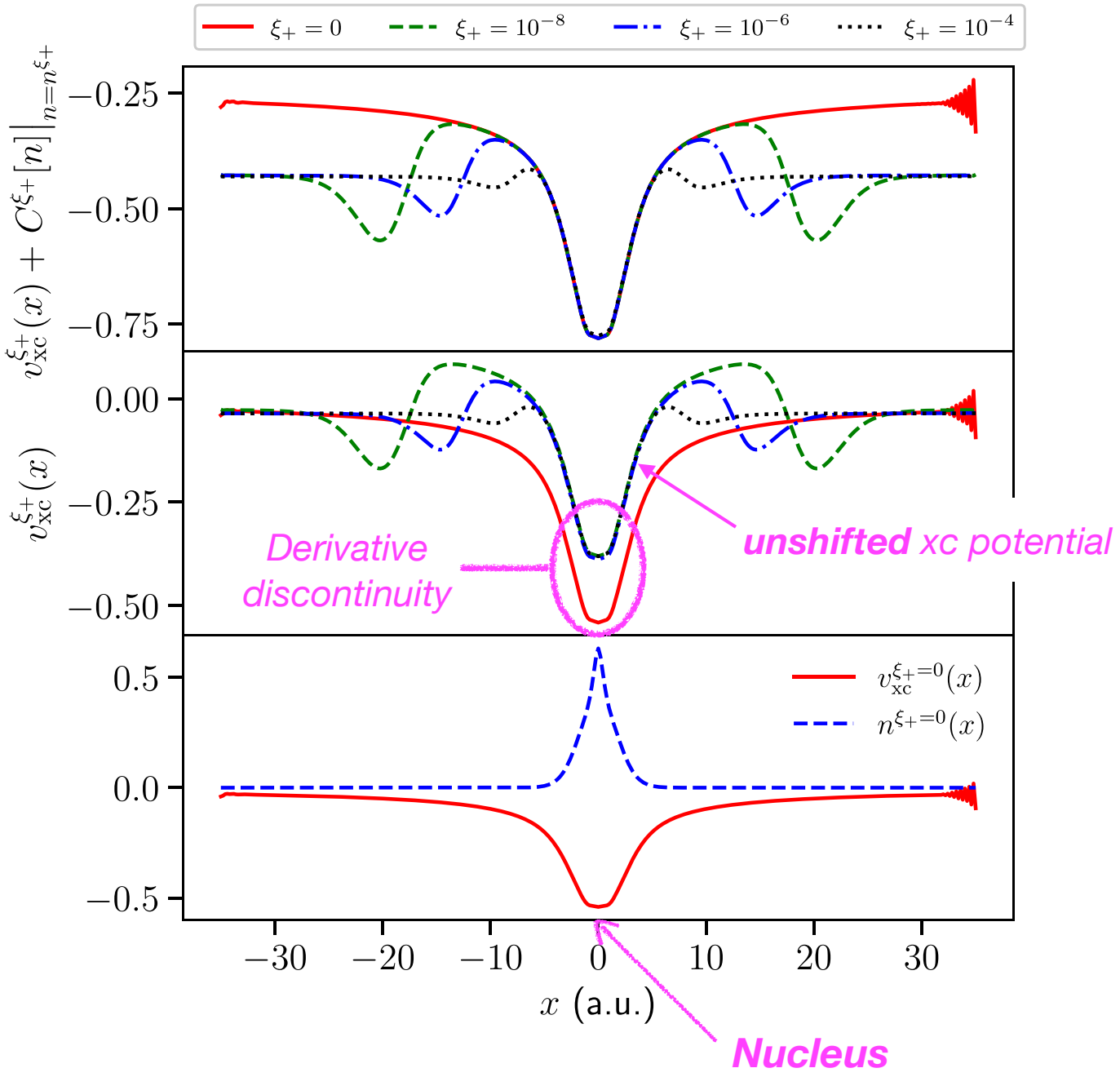

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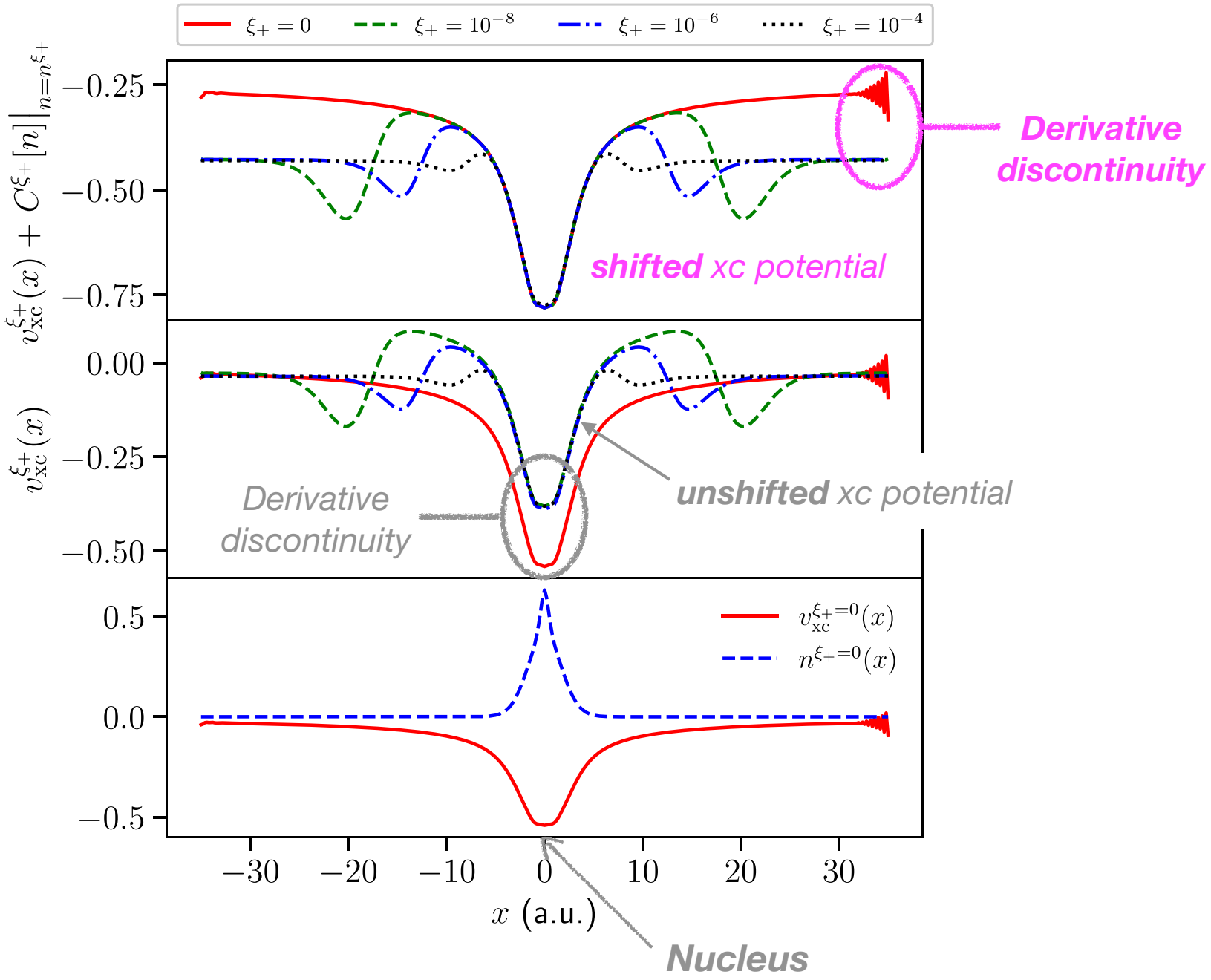

M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).

Exact gap from ensemble weight derivatives

$$I^N - A^N = \varepsilon^N_{i=N+1} - \varepsilon^N_{i=N} + \left.\frac{\partial E_{\mathrm{xc}}^{\xi_-}\left[n_0^N\right]}{\partial \xi_-}\right|_{\xi_-=0} + \left.\frac{\partial E_{\mathrm{xc}}^{\xi_+}\left[n_0^N\right]}{\partial \xi_+}\right|_{\xi_+=0}$$

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

Take-home messages

- *Fundamental gaps* can be described exactly in DFT *without derivative discontinuities*.
- Instead, N*-centered ensemble* xc density functionals must be modelled.
- Their ensemble *weight dependence* is the 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.*
M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A ***103****, 012806 (2021).*
P.-F. Loos and E. Fromager, J. Chem. Phys.* ***152**, 214101 (2020).*

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LabEx CSC (ANR-10-LABX-0026-CSC)

CoLab ANR project

Alternative formulation of the IP theorem

$$I^N = -\varepsilon_{i=N}^{\xi_-} - \left[\frac{E_{\mathrm{Hxc}}^{\xi_-}[n] - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{Hxc}}^{\xi_-}(\mathbf{r})}{N} - \left(\frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\mathrm{xc}}^{\xi_-}[n]}{\partial \xi_-} \right]_{n=n_0^{\xi_-}}$$

*Levy-Zahariev shift**

*B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).*
*B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; **120**:e26190.*
M. Levy and F. Zahariev, Phys. Rev. Lett. **113, 113002 (2014).*