Exact (ensemble) density-functional theory for energy gaps without derivative discontinuities

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Ionization potential (IP) theorem in DFT

Janak's theorem:

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

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

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

Kohn-Sham HOMO energy

of the N-electron system

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

Ionization potential (IP) theorem in DFT

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

$$\Big\downarrow$$

$$\int d\mathbf{r}\; n(\mathbf{r}) = N-\delta$$

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

Ionization potential (IP) theorem in DFT

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

*The **degree is ionisation** is given by the **density!***

$$\int d\mathbf{r}\; n(\mathbf{r}) = N - \delta$$

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

Ionization potential (IP) theorem in DFT

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

$$E_{\mathrm{xc}}[n]$$

The xc functional now applies to ***fractional electron numbers***

$$\longleftarrow \quad \int d\mathbf{r}\; n(\mathbf{r}) = N - \delta$$

Ionization potential (IP) theorem in DFT

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

$$\downarrow$$

$$v_{\mathrm{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})} \underset{|\mathbf{r}|\rightarrow +\infty}{\longrightarrow} 0$$

M. Levy, J. P. Perdew and V. Sahni, Phys. Rev. A **30**, 2745 (1984).

Electron affinity (EA)

$$I^N = -\,\varepsilon^N_{i=N}$$

$$N \rightarrow N+1$$

$$\boxed{E_0^N - E_0^{N+1} = A^N = I^{N+1}} = -\,\varepsilon^{N+1}_{i=N+1}$$

Electron affinity

of the N-electron system

Ionization potential (IP) theorem in DFT

$$I^N = -\varepsilon^N_{i=N}$$

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

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

Fundamental energy gap
of the N-electron system

***HOMO** energies*

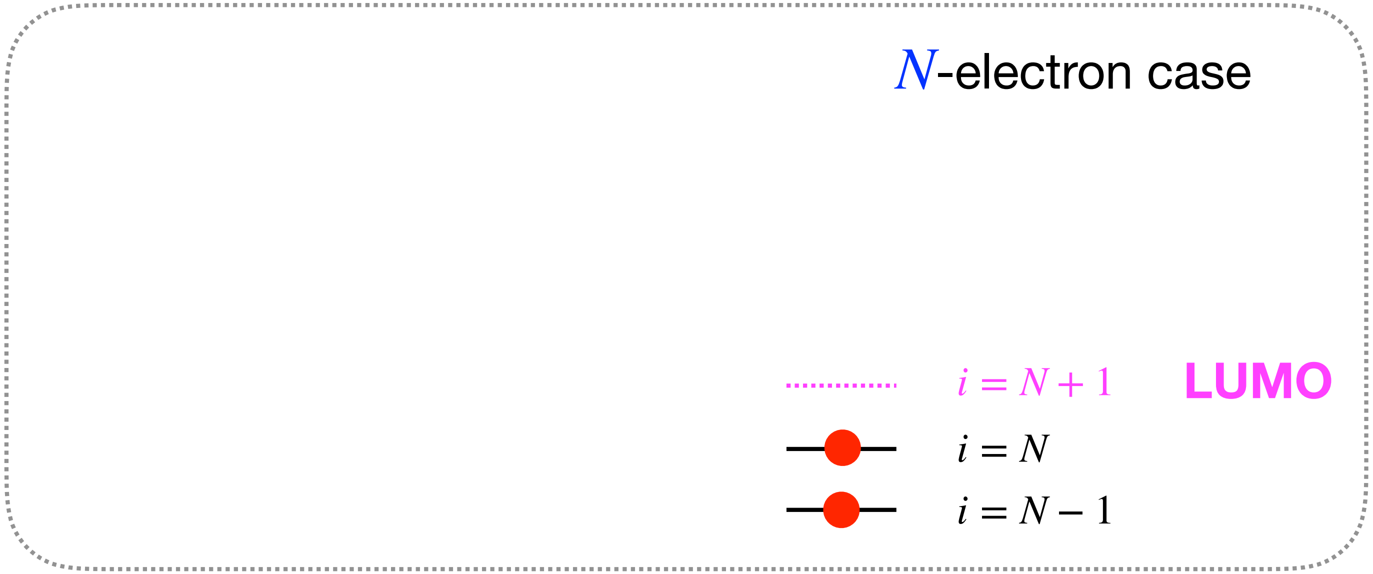
Ionization potential (IP) theorem in DFT

Extractable from the N-calculation?

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

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

Ionization potential (IP) theorem in DFT

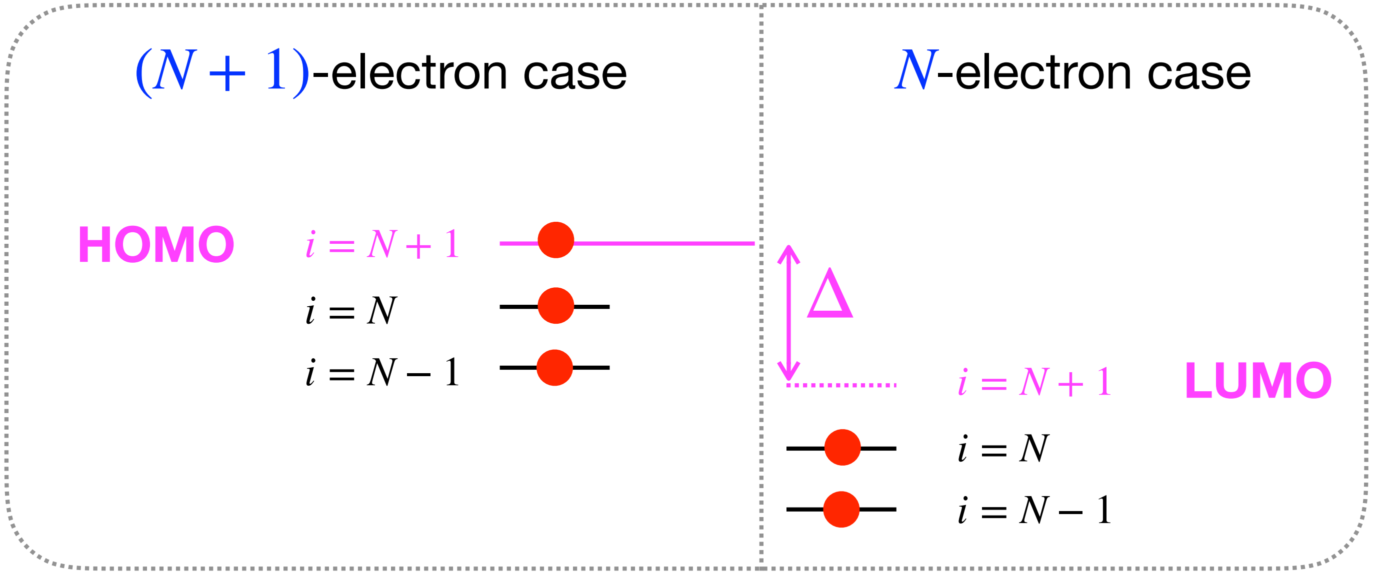


Extractable from the N-calculation?

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

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

Ionization potential (IP) theorem in DFT



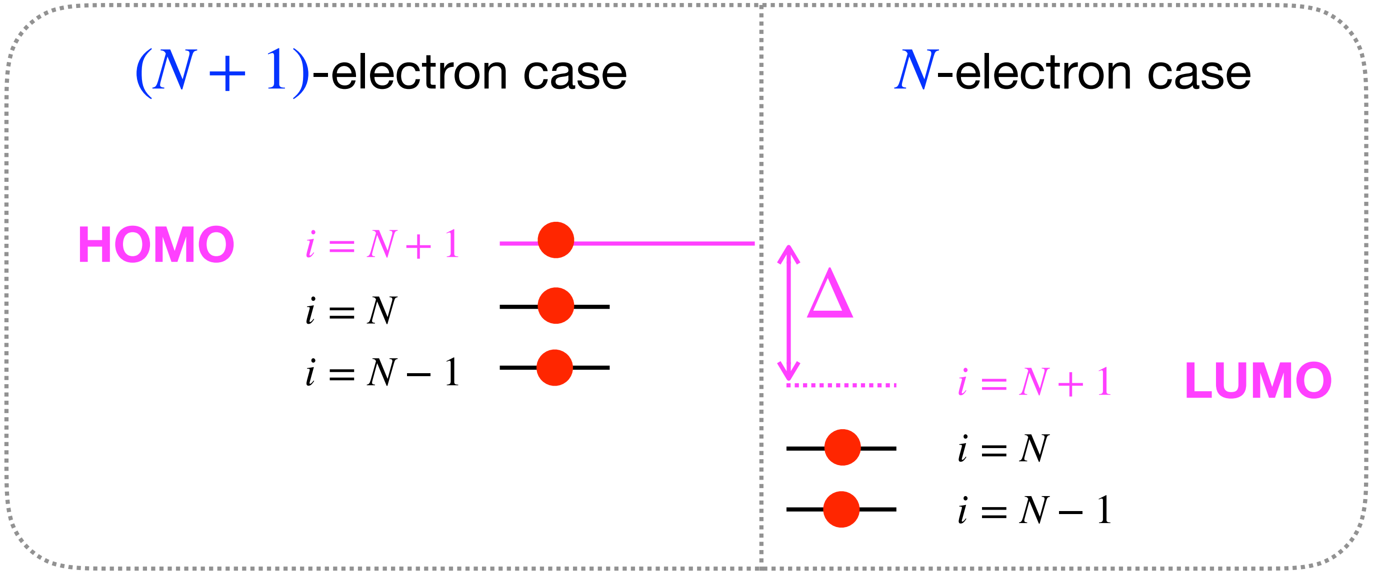
Extractable from the N-calculation?

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

$$\varepsilon^{N}_{i=N+1} + \Delta$$

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

Ionization potential (IP) theorem in DFT

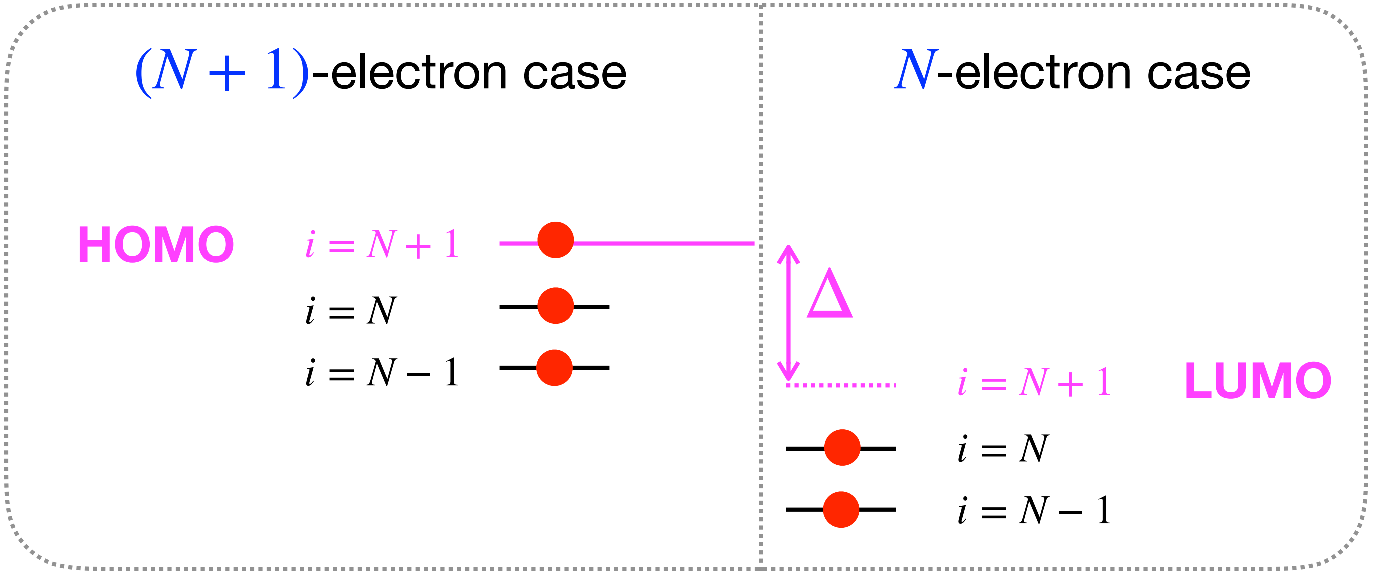


$$E_g = I^N - A^N = \boxed{\varepsilon^N_{i=N+1} - \varepsilon^N_{i=N}} + \Delta$$

*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).*

N-centered ensemble approach to charged excitations

Another exact IP theorem can be derived:

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

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

N-centered ensemble approach to charged excitations

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

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

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

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

N-centered ensemble approach to charged excitations

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

Ensemble density

$$n_0^{\xi_-}(\mathbf{r}) = \xi_- \underbrace{n_0^{N-1}(\mathbf{r})}_{\text{Ionized density}} + \left[1 - \frac{\xi_-(N-1)}{N}\right] \underbrace{n_0^{N}(\mathbf{r})}_{\text{Neutral density}}$$

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.

N-centered ensemble approach to charged excitations

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

Ensemble density

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

Ensemble ***weight***

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.

N-centered ensemble approach to charged excitations

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

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.

N-centered ensemble approach to charged excitations

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

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.

N-centered ensemble approach to charged excitations

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

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

by construction

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 approach to charged excitations

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

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

N-**centered**
ensemble formalism

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 approach to charged excitations

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

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

Degree of ionisation
not given by the density…

N-**centered**
ensemble formalism

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

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

Degree of ionisation
not given by the density…

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

… but, instead, by the ***ensemble weight*** ξ_-

N-centered
ensemble formalism

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 approach to charged excitations

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

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

Weight-dependent *xc functional*

*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 approach to charged excitations

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

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 approach to charged excitations

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

xc ensemble **weight derivative**

Electron removal

ξ_-

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

Electron affinity theorem

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

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

ξ_+

*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 approach to charged excitations

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

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

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N-centered ensemble approach to charged excitations

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

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

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

Regular N-electron DFT

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

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

N-centered ensemble approach to charged excitations

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

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

$$\downarrow \quad \xi_- = \xi_+ = 0$$

Regular N-electron DFT

$$\underbrace{I^N - A^N}_{\text{True gap}} = \underbrace{\varepsilon_{i=N+1}^N - \varepsilon_{i=N}^N}_{\text{KS gap}} + \underbrace{\left.\frac{\partial E_{\rm xc}^{\xi_-}[n_0^N]}{\partial \xi_-}\right|_{\xi_-=0} + \left.\frac{\partial E_{\rm xc}^{\xi_+}[n_0^N]}{\partial \xi_+}\right|_{\xi_+=0}}_{\text{"derivative discontinuity" } \Delta}$$

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 message

*Modelling the **weight-dependent xc energies** $E_{\rm xc}^{\xi_-}[n]$ and $E_{\rm xc}^{\xi_+}[n]$ is **sufficient** for describing the gap!*

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

Connection to regular DFT

Is there any ***"discontinuity"*** *in the N-centered ensemble picture?*

Xc potential still unique up to a constant

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

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

Xc potential still unique up to a constant

Constant shift *applied to the xc potential*

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

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

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* $v_{\mathrm{Hxc}}^{\xi_\pm}(\mathbf{r}) \underset{|\mathbf{r}|\rightarrow+\infty}{\longrightarrow} 0$

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

Where is the discontinuity?

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

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

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

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

Regular IP and EA theorems

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

Where is the discontinuity?

$$\boxed{\textit{If we impose}\quad v_{\rm Hxc}^{\xi_\pm}(\mathbf{r}) \underset{|\mathbf{r}|\rightarrow+\infty}{\longrightarrow} 0}$$

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

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

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

Where is the discontinuity?

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

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

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

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

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

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$$\downarrow$$

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

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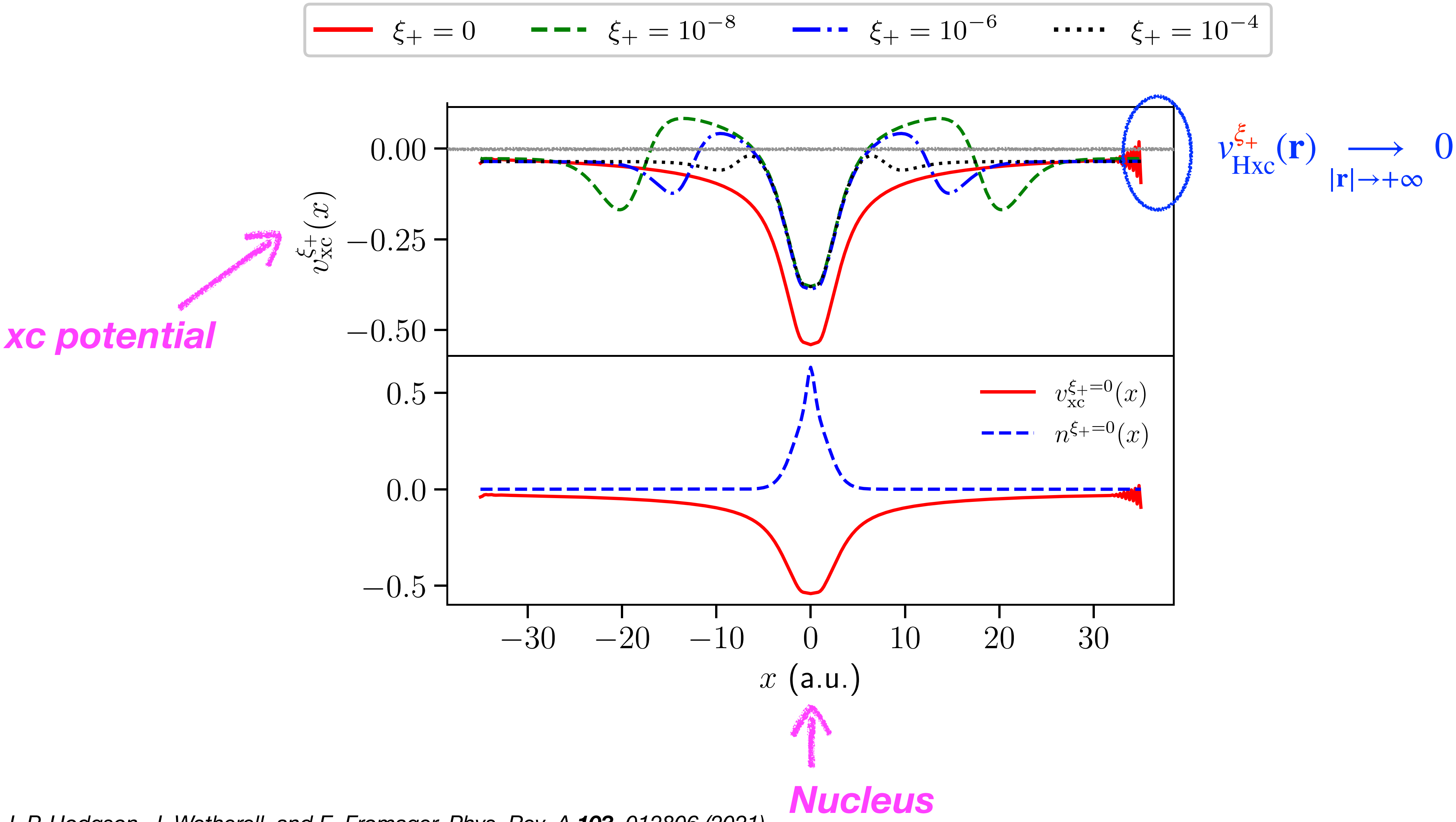
Application: Two-electron spin-polarised 1D atom

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



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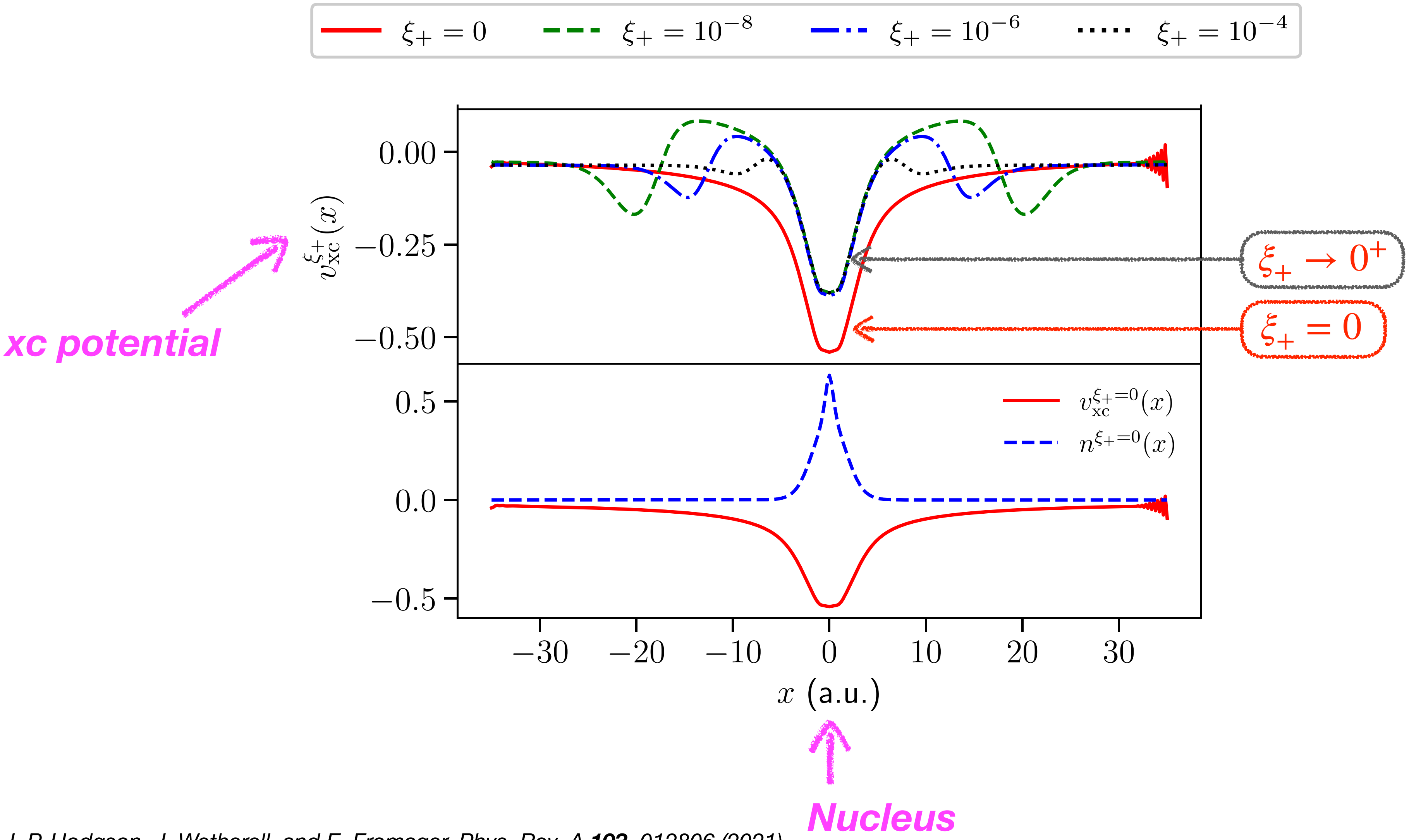

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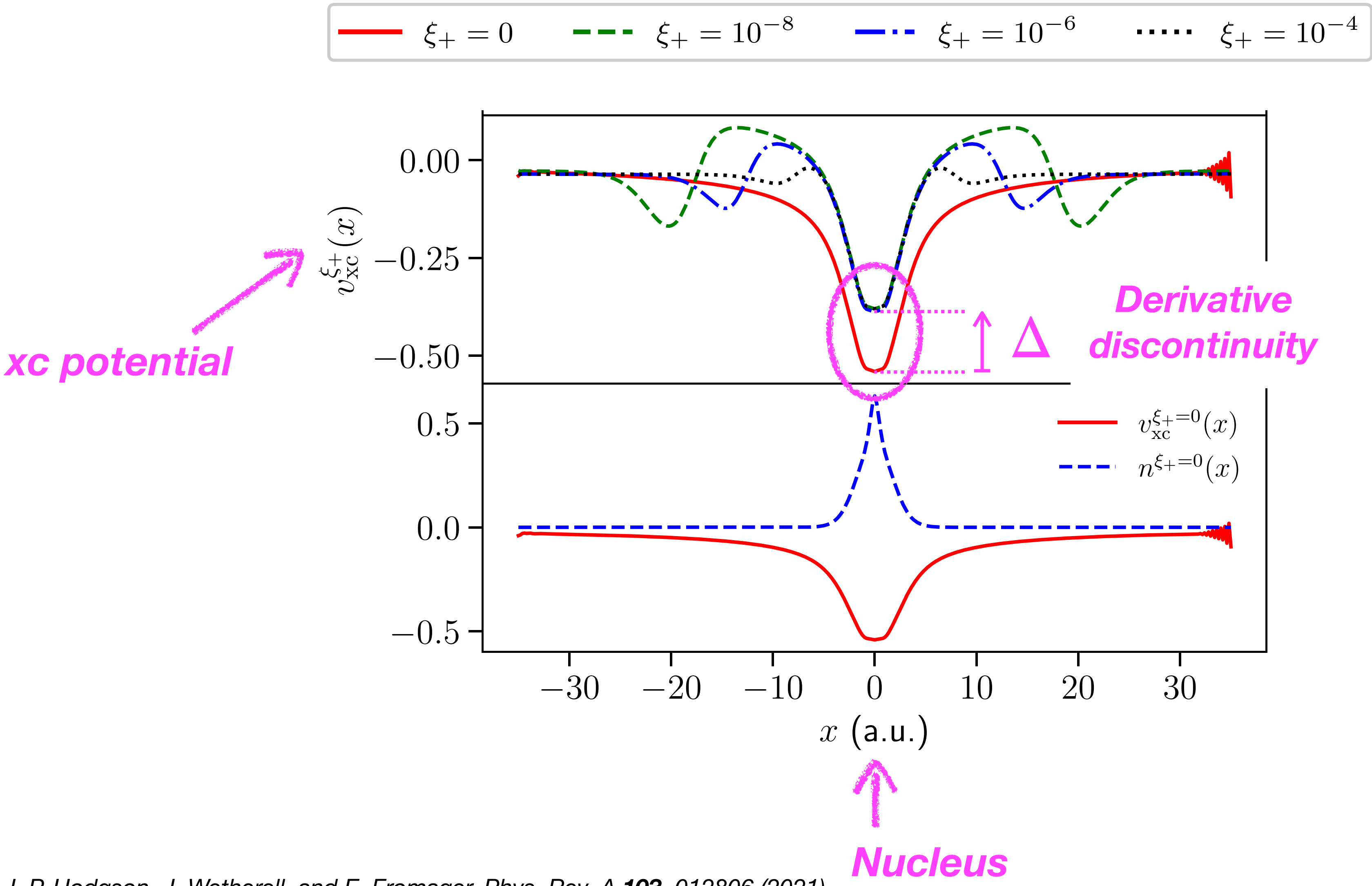

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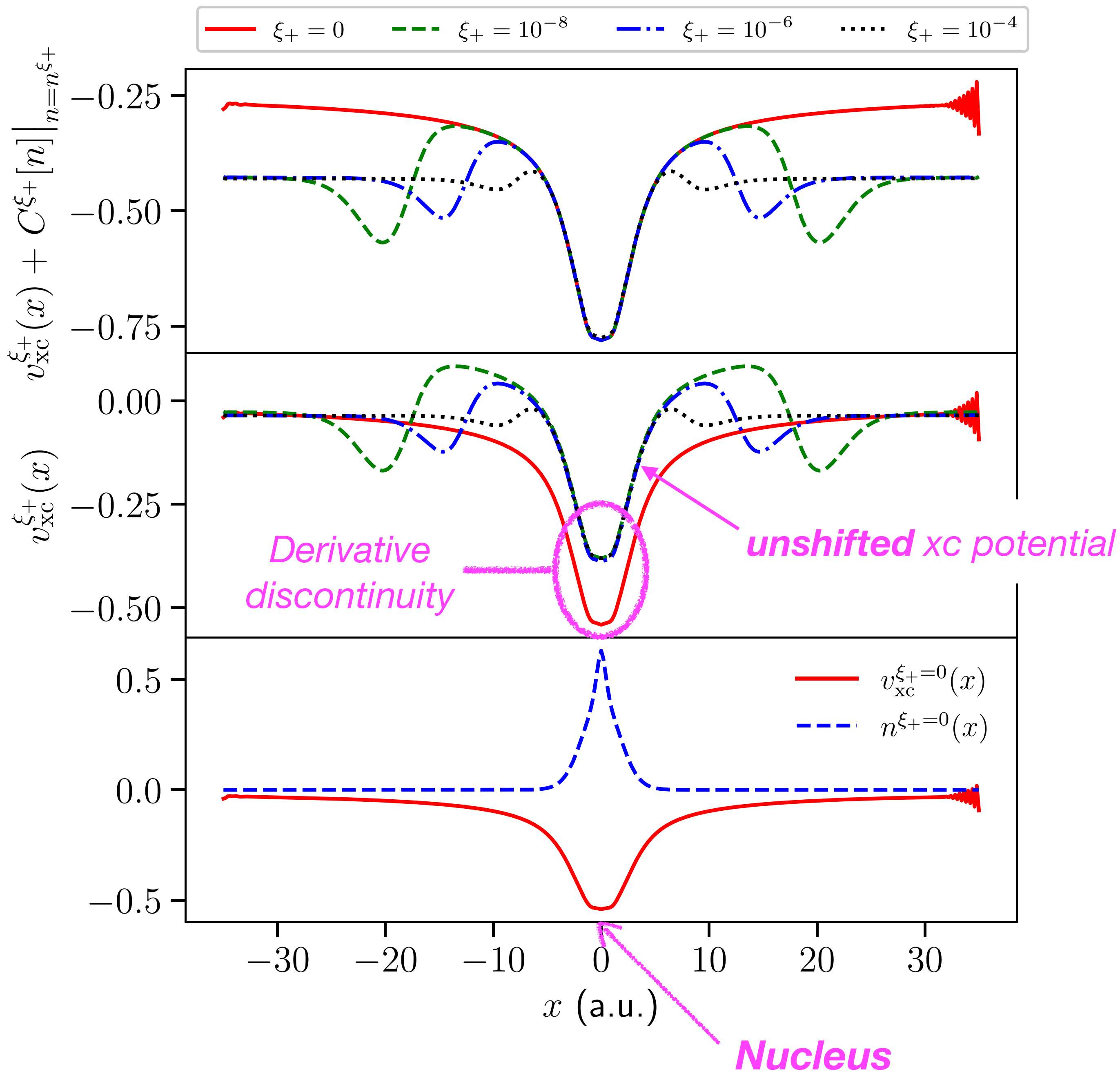
Moving the discontinuity away from the system



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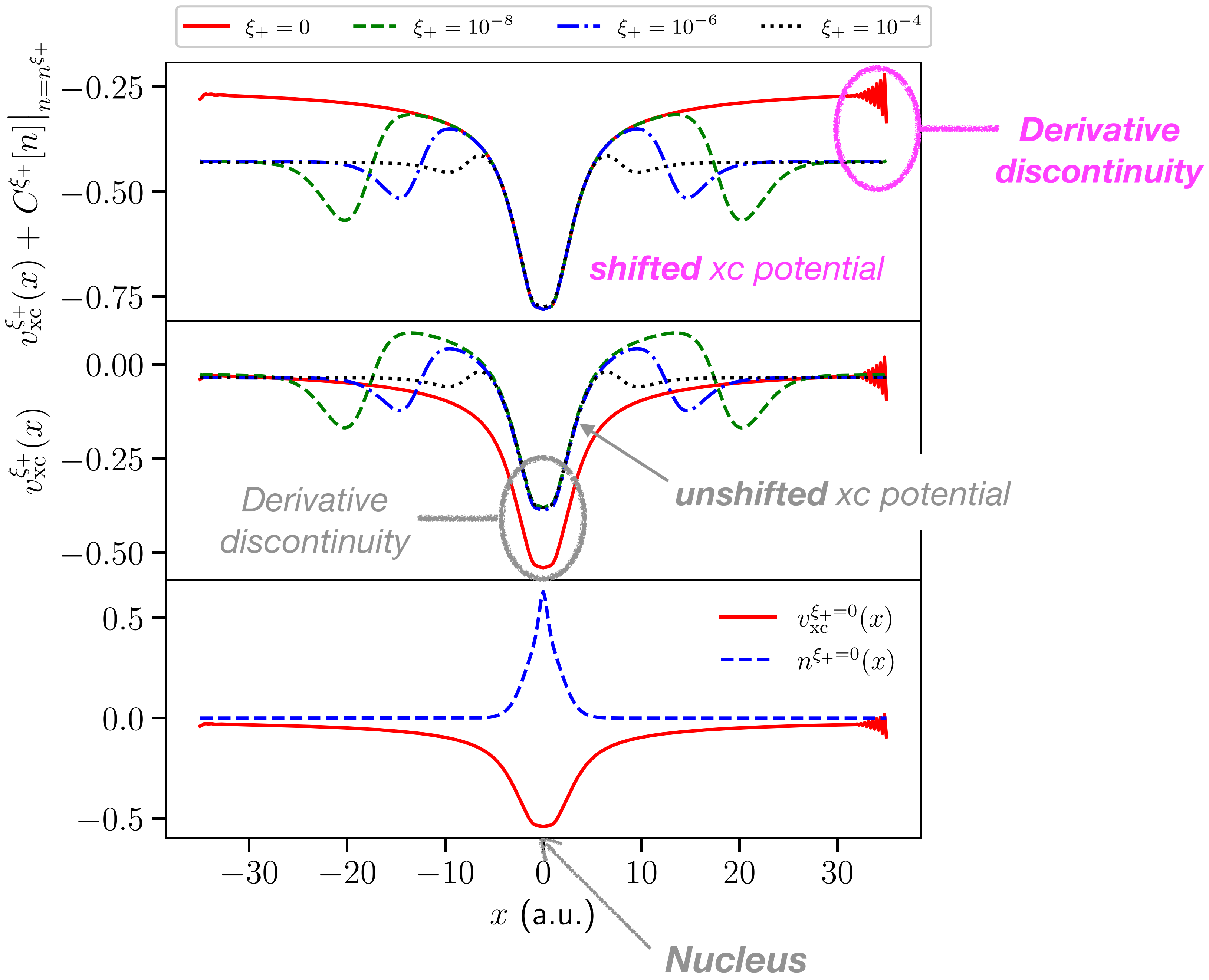

M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A ***103****, 012806 (2021).*

Conclusions and perspectives

- An alternative formulation of *DFT* for *charged excitations* has been proposed.
- The theory is referred to as N*-centered ensemble DFT*.
- In this context, the exact fundamental gap is described *without derivative discontinuities.*
- The latter can simply be *moved away from the system.*
- The *weight dependence* of the ensemble xc functional becomes the *key ingredient*.
- Ensemble LDA functionals can be constructed from *finite* uniform electron *gas* models*.
- We currently work on a many-body ensemble *density-functional perturbation theory.*

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).*
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CoLab ANR project

Exact gap from ensemble weight derivatives

$$I^N - A^N = \varepsilon^N_{i=N+1} - \varepsilon^N_{i=N} + \boxed{\left.\frac{\partial E^{\xi_-}_{\rm xc}\left[n^N_0\right]}{\partial \xi_-}\right|_{\xi_-=0} + \left.\frac{\partial E^{\xi_+}_{\rm xc}\left[n^N_0\right]}{\partial \xi_+}\right|_{\xi_+=0}}$$

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Alternative formulation of the IP theorem

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

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).