Connecting weight derivatives to derivative discontinuities in N-centered ensemble DFT

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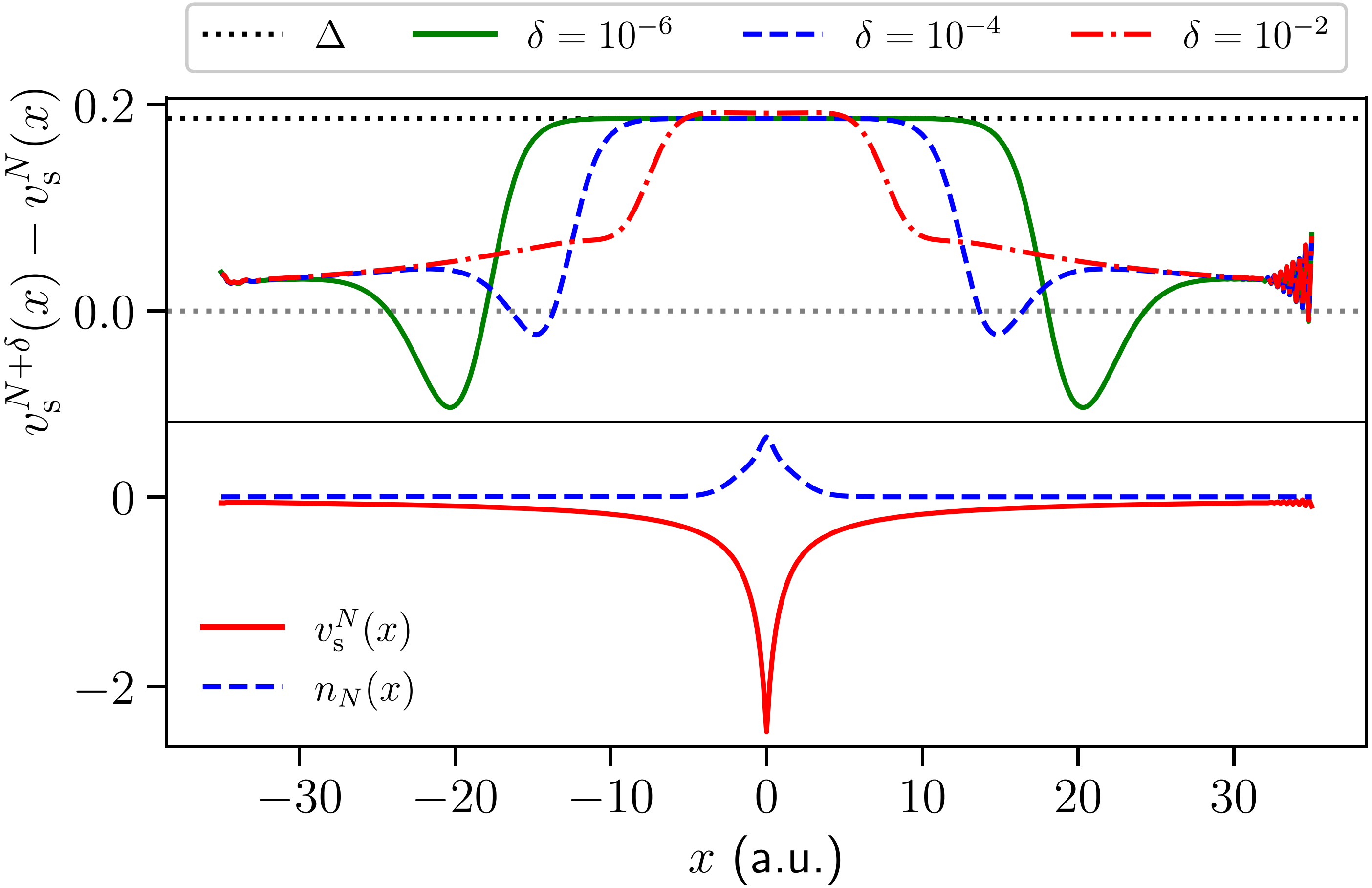
Online "Maths in DFT" meeting, Strasbourg, France **01/02/2021**

Conventional Perdew-Parr-Levy-Balduz (PPLB) approach



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

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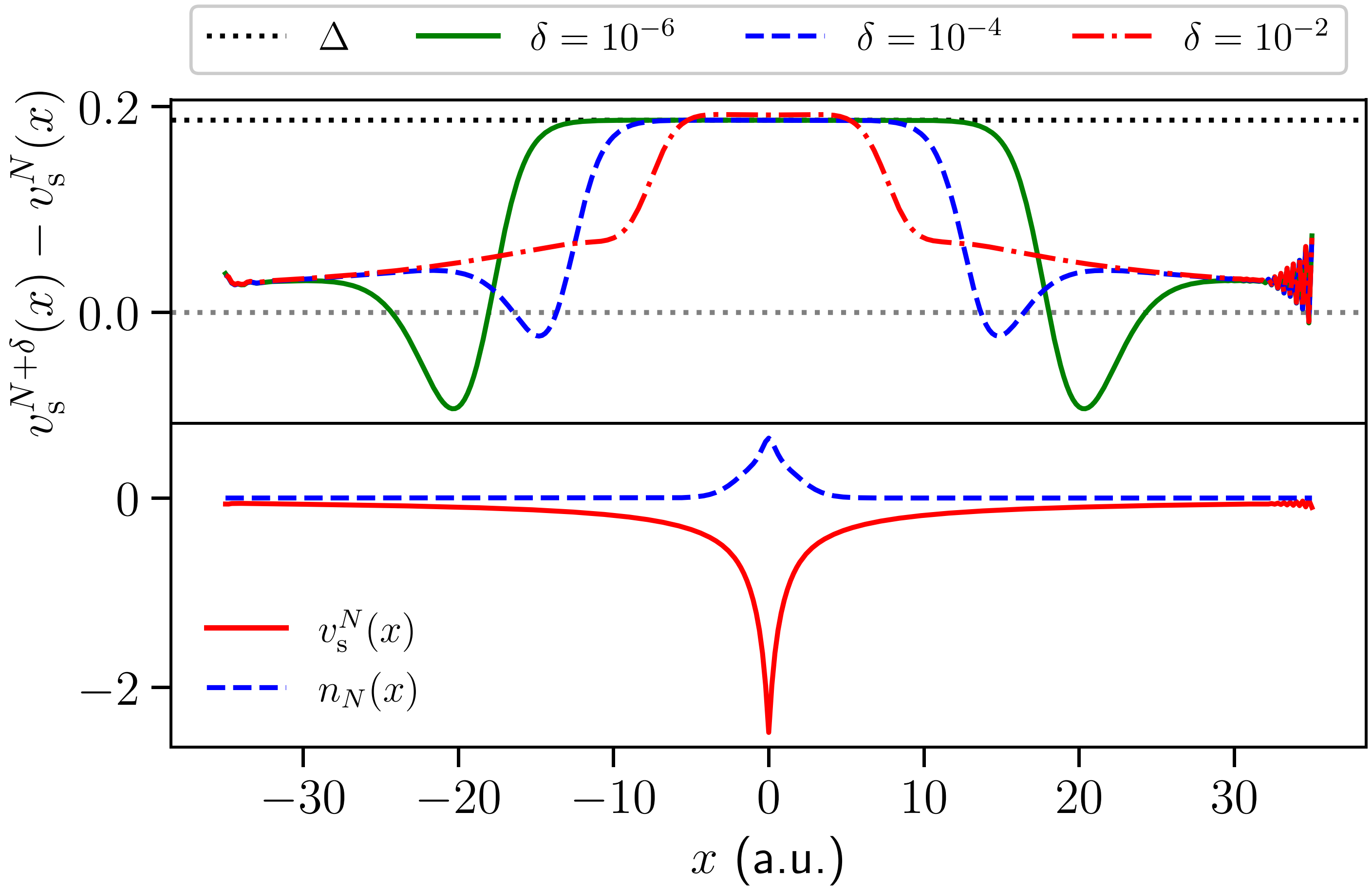

$$N = 2 \rightarrow N + \delta$$

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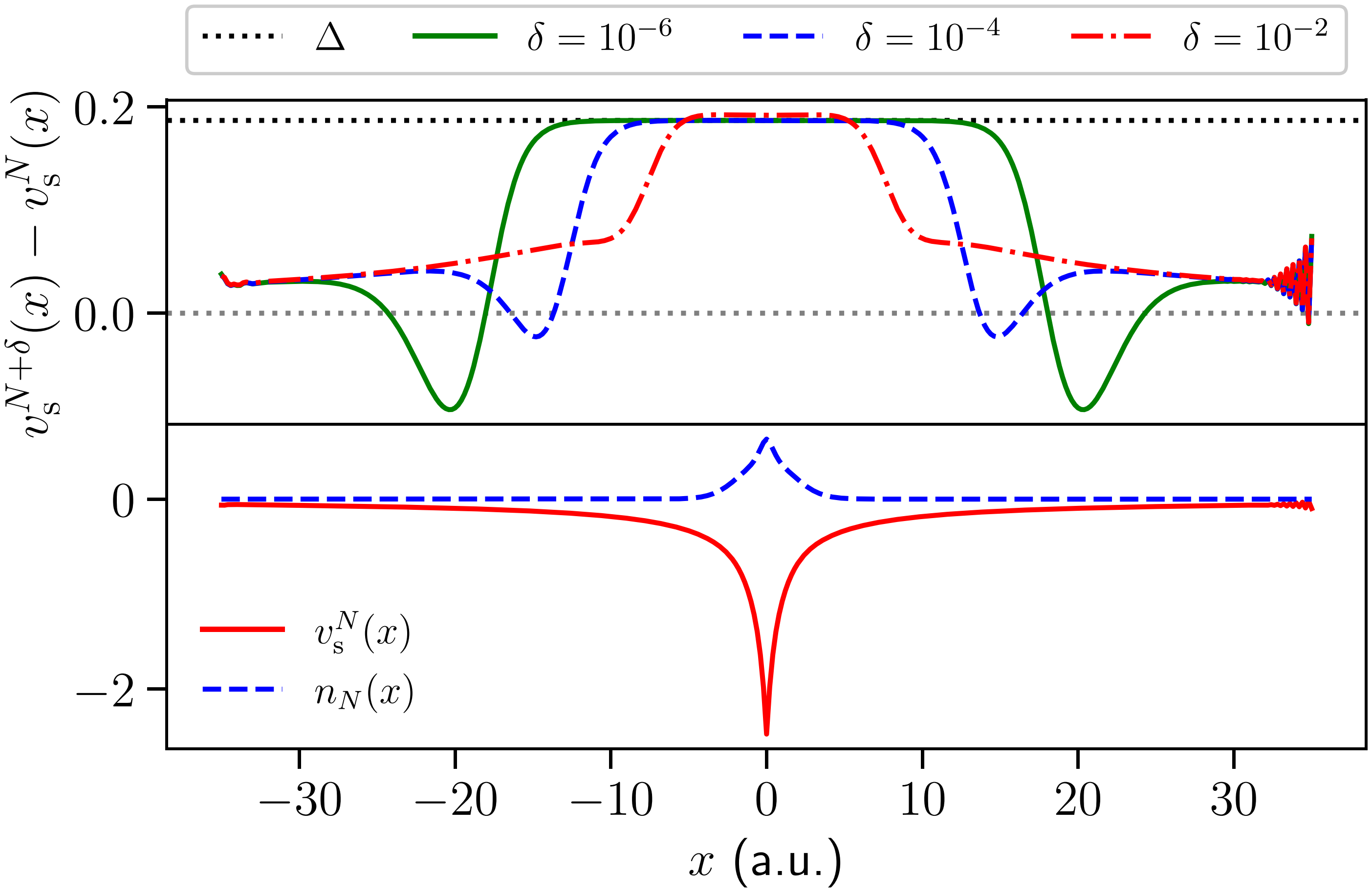

$I^N = E^{N-1} - E^N = -\varepsilon_N^N$

Ionization potential (IP)

$$\varepsilon_{N+1}^{N+1} = \varepsilon_{N+1}^{N} + \Delta$$

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

Electron affinity (EA)

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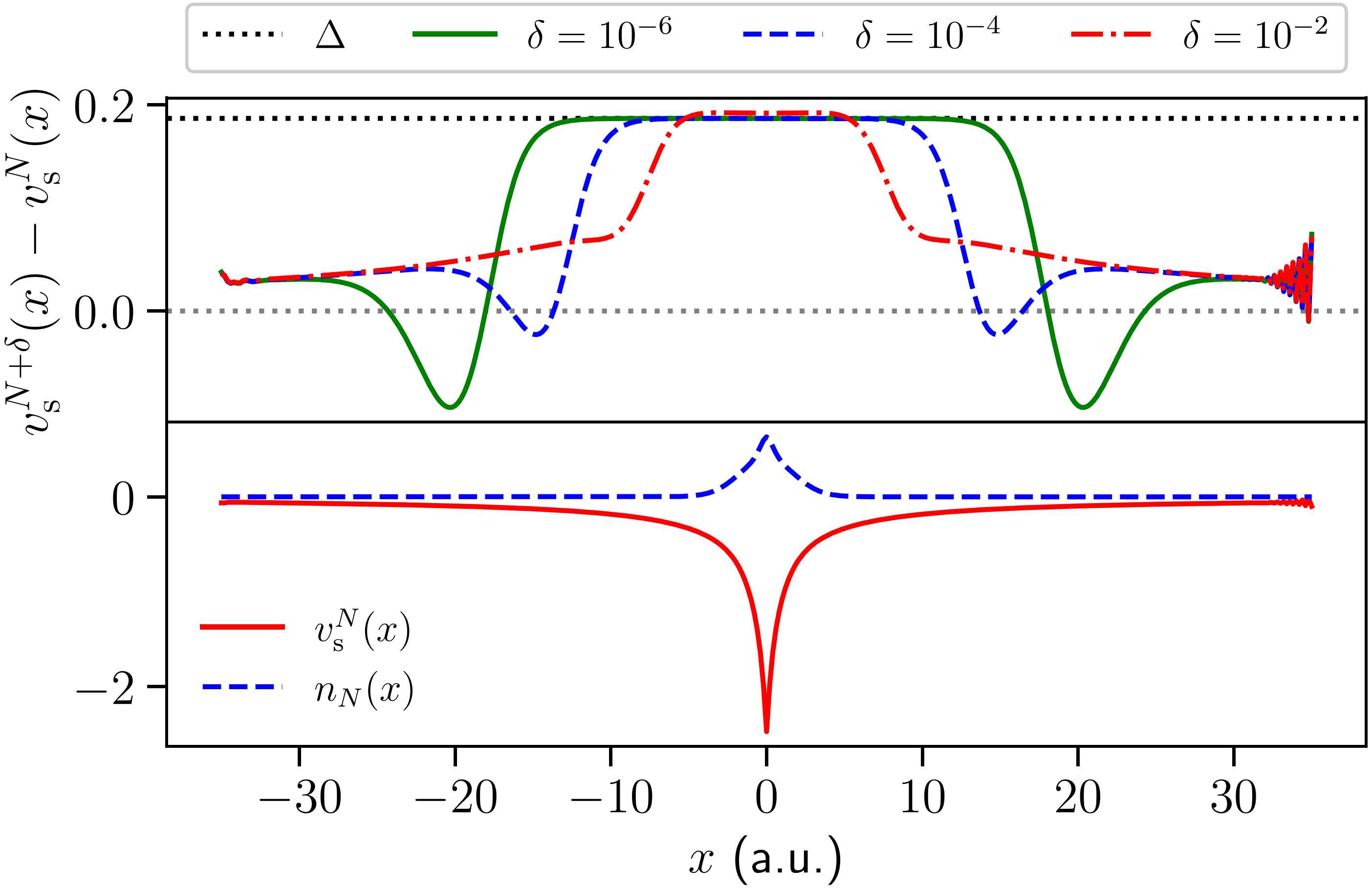

Number of electrons

$$I^N = E^{N-1} - E^N = -\varepsilon_N^N$$

$$\varepsilon_{N+1}^{N+1} = \varepsilon_{N+1}^{N} + \Delta$$

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

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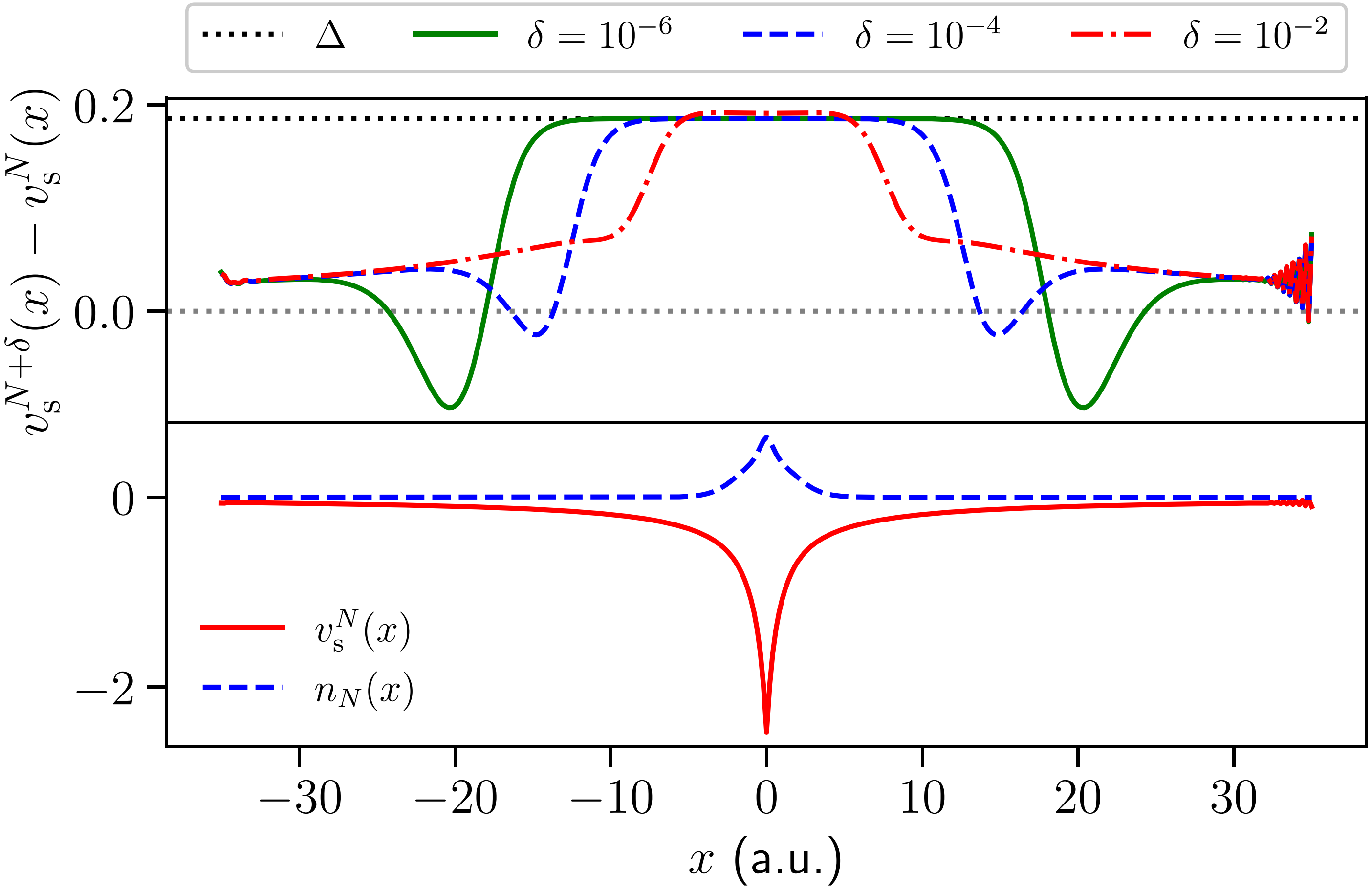

$$v_{xc}\left[n^\delta\right] \xrightarrow{|x|\to+\infty} 0 \qquad \forall \delta > 0$$

$$n^\delta(x) = (1-\delta)n_N(x) + \delta n_{N+1}(x)$$

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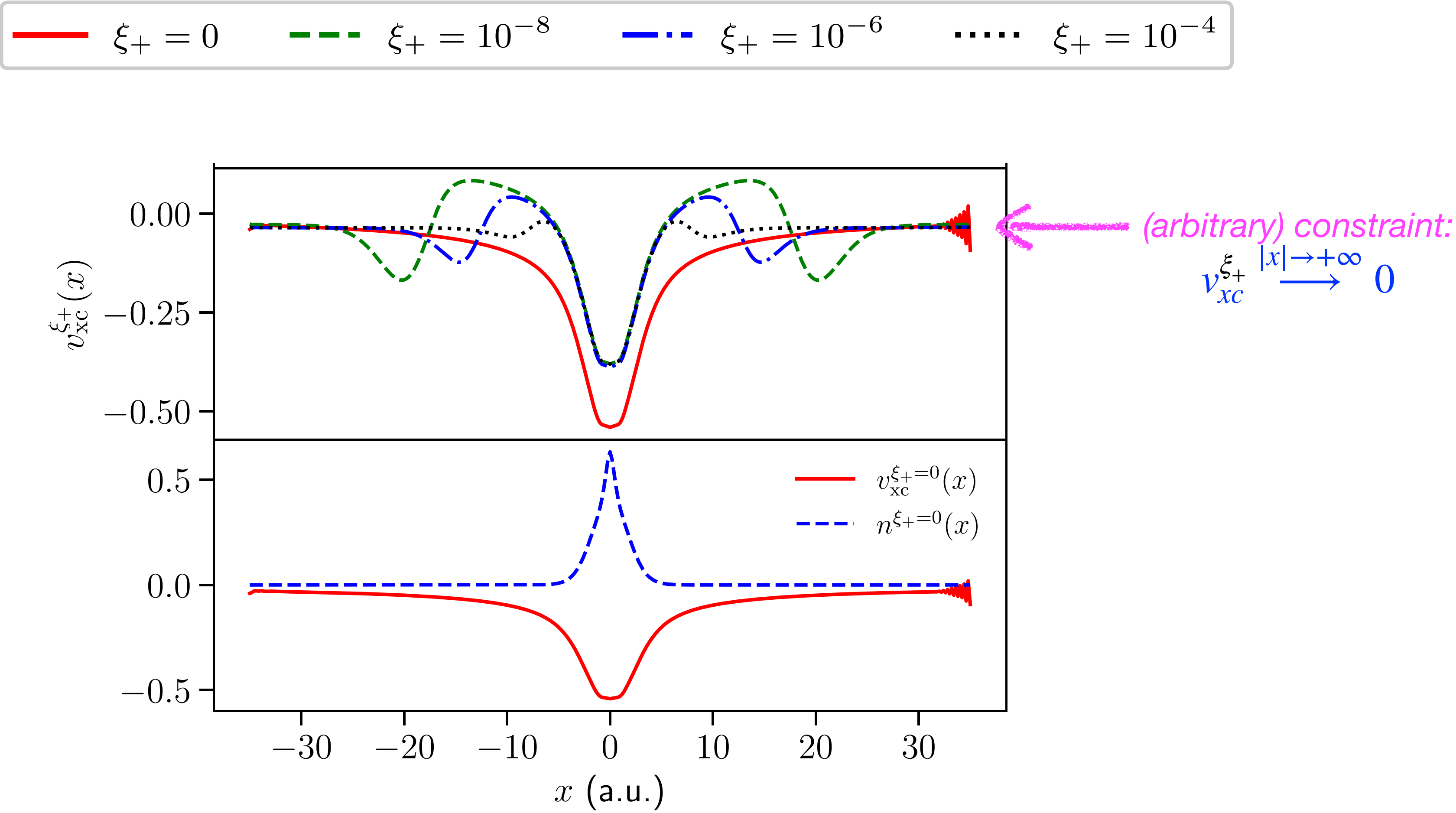
(Left) N-centered ensemble picture



$$n^{\xi_+}(x) = \left(1 - \frac{N+1}{N}\xi_+\right) n_N(x) + \xi_+ n_{N+1}(x)$$

B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).
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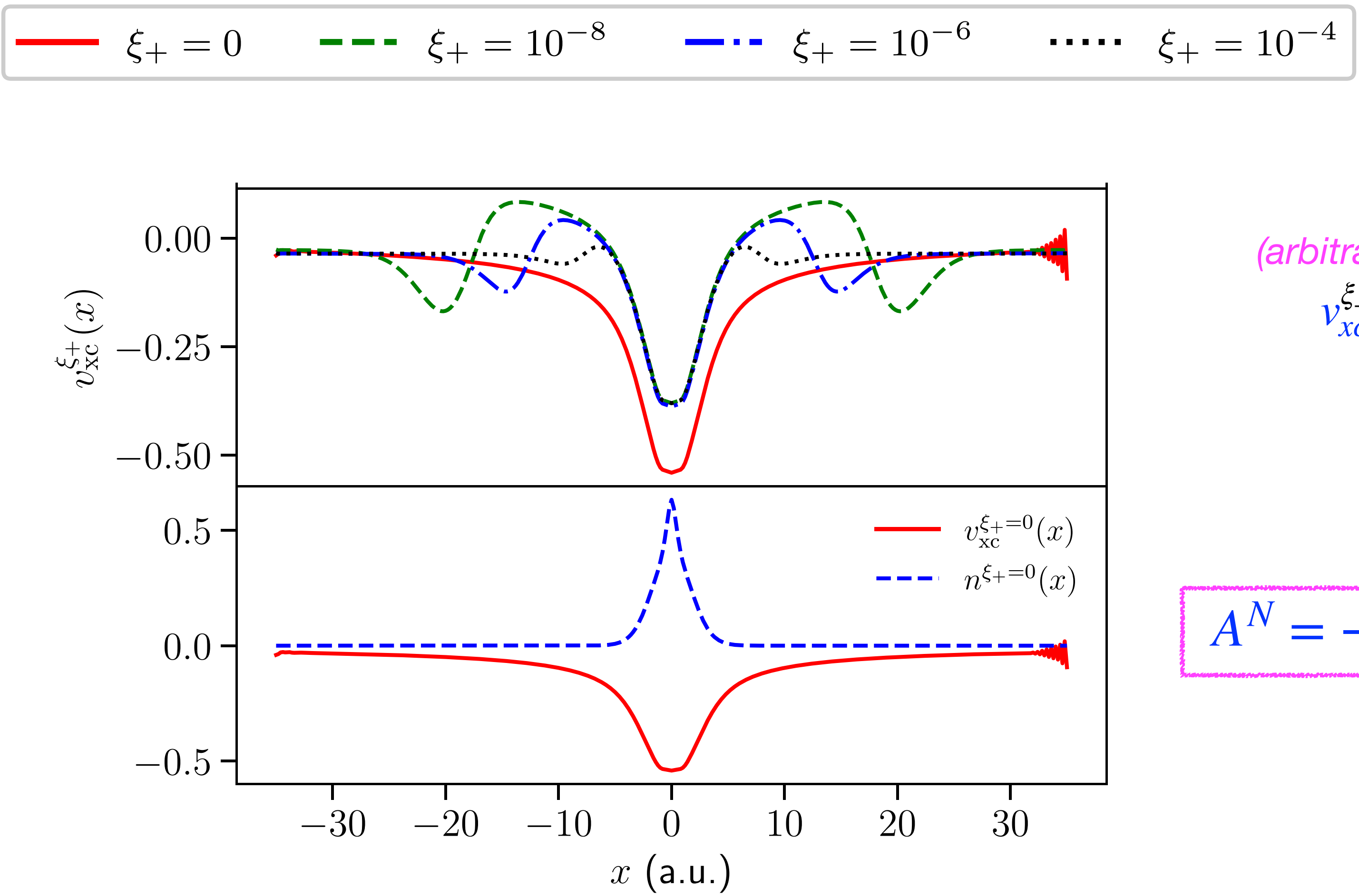
M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).

(Left) N-centered ensemble picture



(arbitrary) constraint:

$$v_{xc}^{\xi_+} \xrightarrow{|x|\rightarrow+\infty} 0$$

$$A^N = -\varepsilon_{N+1}^{\xi_+}, \ \forall \xi_+$$

$$n^{\xi_+}(x) = \left(1 - \frac{N+1}{N}\xi_+\right) n_N(x) + \xi_+ n_{N+1}(x)$$

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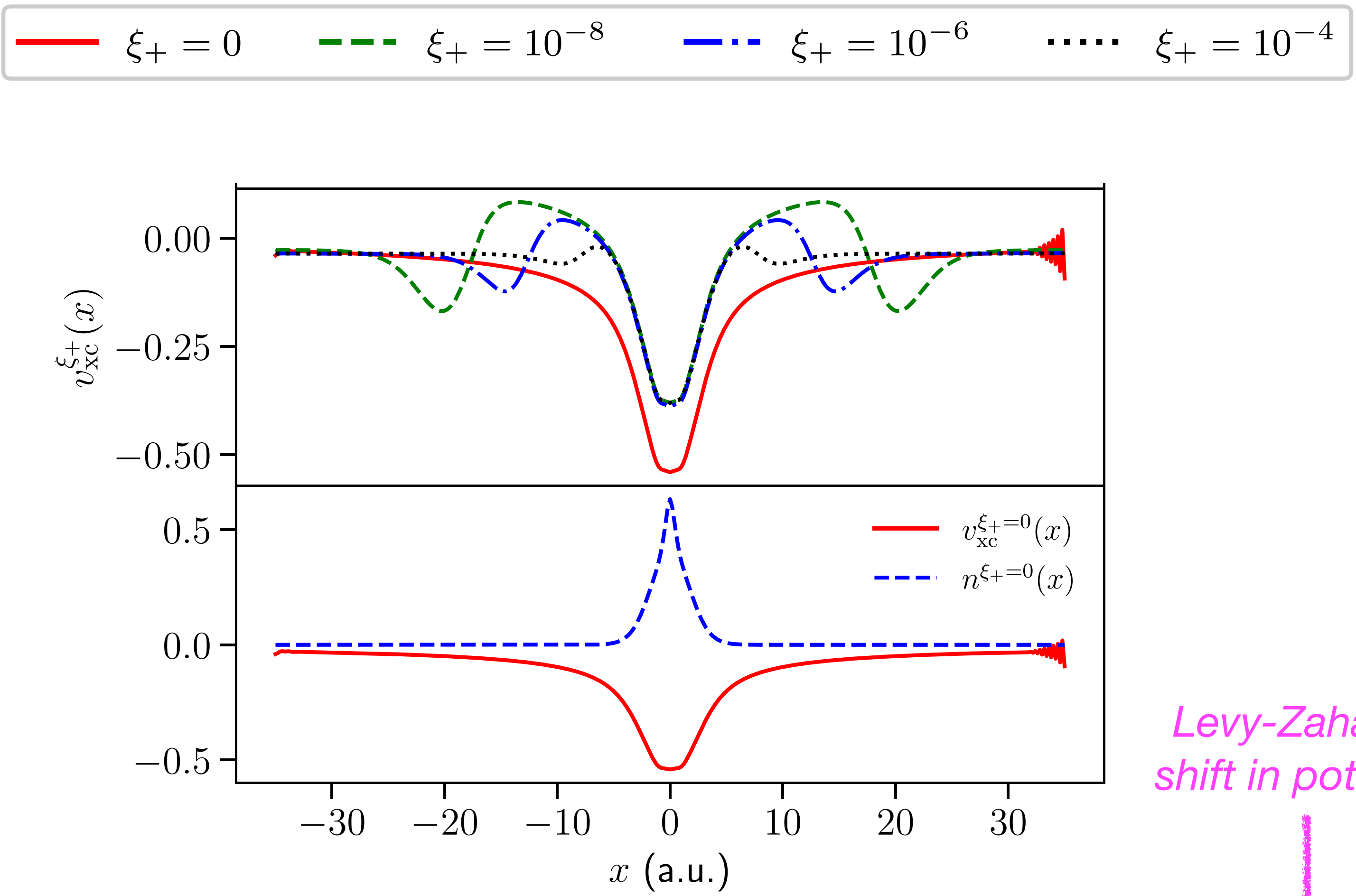
(Left) N-centered ensemble picture



Levy-Zahariev shift in potential

$$A^N = -\left[\varepsilon_{N+1}^{\xi_+} + C^{\xi_+}[n]\Big|_{n=n^{\xi_+}}\right] + \left(\frac{\xi_+}{N} - 1\right)\frac{\partial E_{\rm xc}^{\xi_+}[n]}{\partial \xi_+}\Bigg|_{n=n^{\xi_+}}$$

$$C^{\xi_+}[n] = \frac{E_{\rm Hxc}^{\xi_+}[n] - \int dx\, n(x)\, v_{\rm Hxc}^{\xi_+}[n]}{\int dx\, n(x)}$$

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N-centered ensemble picture: Summary

When $v_{xc}^{\xi_\pm} \xrightarrow{|x|\to+\infty} 0$ ....

$$C^{\xi_+}[n]\Big|_{n=n^{\xi_+}} = \left(\frac{\xi_+}{N} - 1\right) \frac{\partial E_{\rm xc}^{\xi_+}[n]}{\partial \xi_+}\Bigg|_{n=n^{\xi_+}}, \quad \xi_+ > 0 \qquad \textbf{Affinity}$$

and, similarly,

$$C^{\xi_-}[n]\Big|_{n=n^{\xi_-}} = \left(\frac{\xi_-}{N} + 1\right) \frac{\partial E_{\rm xc}^{\xi_-}[n]}{\partial \xi_-}\Bigg|_{n=n^{\xi_-}}, \quad \xi_- \geq 0 \qquad \textbf{Ionization}$$

thus leading to

Weight Derivatives $\equiv \Delta$ — Derivative Discontinuity

$$-\left(C^{\xi_+\to 0}[n] - C^{\xi_-=0}[n]\right)_{n=n_N} = \left(\frac{\partial E_{\rm xc}^{\xi_-}[n]}{\partial \xi_-}\Bigg|_{\xi_-=0} + \frac{\partial E_{\rm xc}^{\xi_+}[n]}{\partial \xi_+}\Bigg|_{\xi_+=0}\right)_{n=n_N} = \frac{1}{N}\int dx\, n_N(x)\left(v_{\rm xc}^{\xi_+\to 0}[n] - v_{\rm xc}^{\xi_+=0}[n]\right)_{n=n_N}$$

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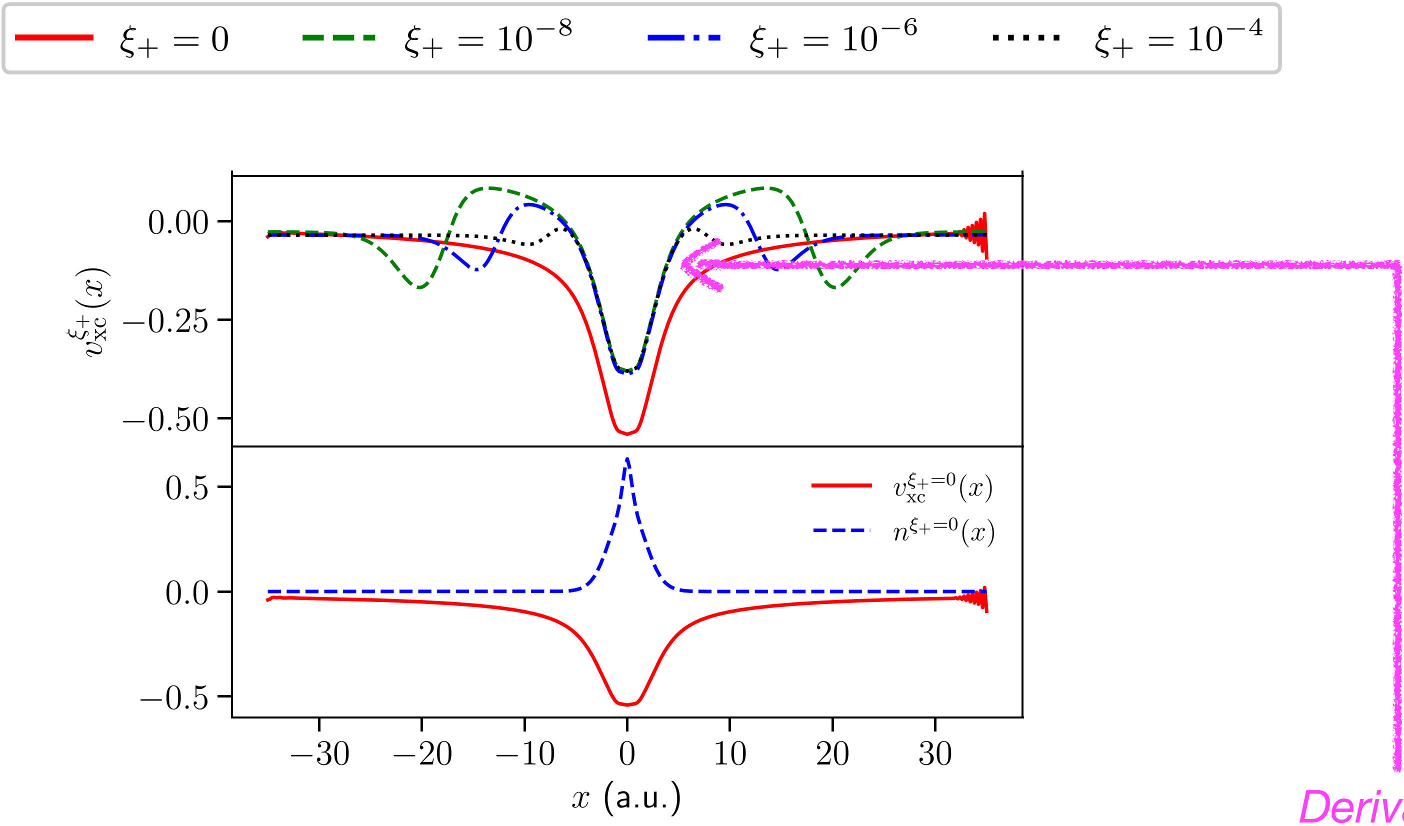
N-centered ensemble picture: Summary



Derivative Discontinuity

$$-\left(C^{\xi_+\to 0}[n] - C^{\xi_-=0}[n]\right)_{n=n_N} = \left(\left.\frac{\partial E_{\rm xc}^{\xi_-}[n]}{\partial \xi_-}\right|_{\xi_-=0} + \left.\frac{\partial E_{\rm xc}^{\xi_+}[n]}{\partial \xi_+}\right|_{\xi_+=0}\right)_{n=n_N} = \frac{1}{N}\int dx\, n_N(x)\left(v_{\rm xc}^{\xi_+\to 0}[n] - v_{\rm xc}^{\xi_+=0}[n]\right)_{n=n_N}$$

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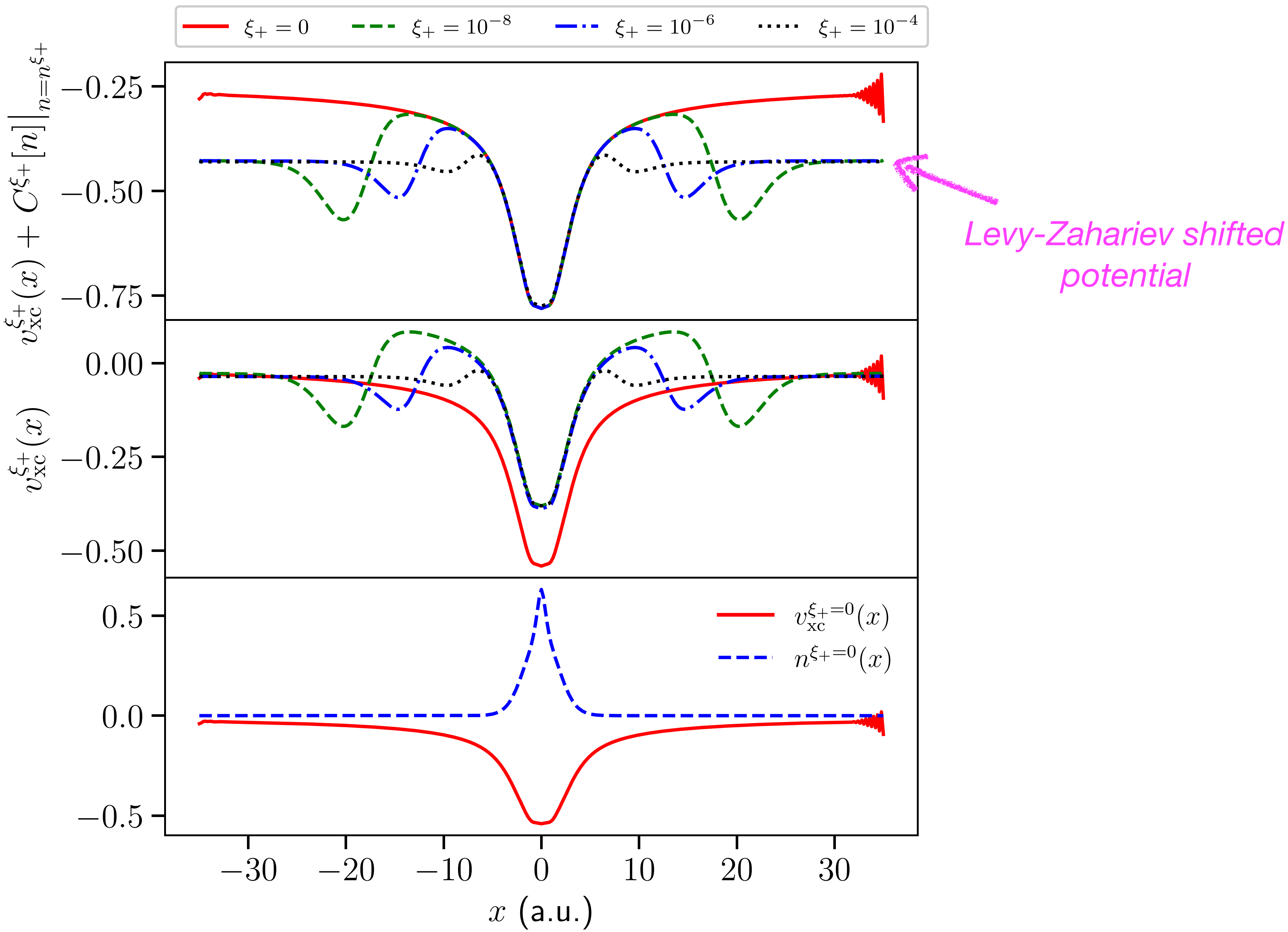
Exact gap without derivative discontinuities



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