N-centered ensemble density-functional theory for open systems

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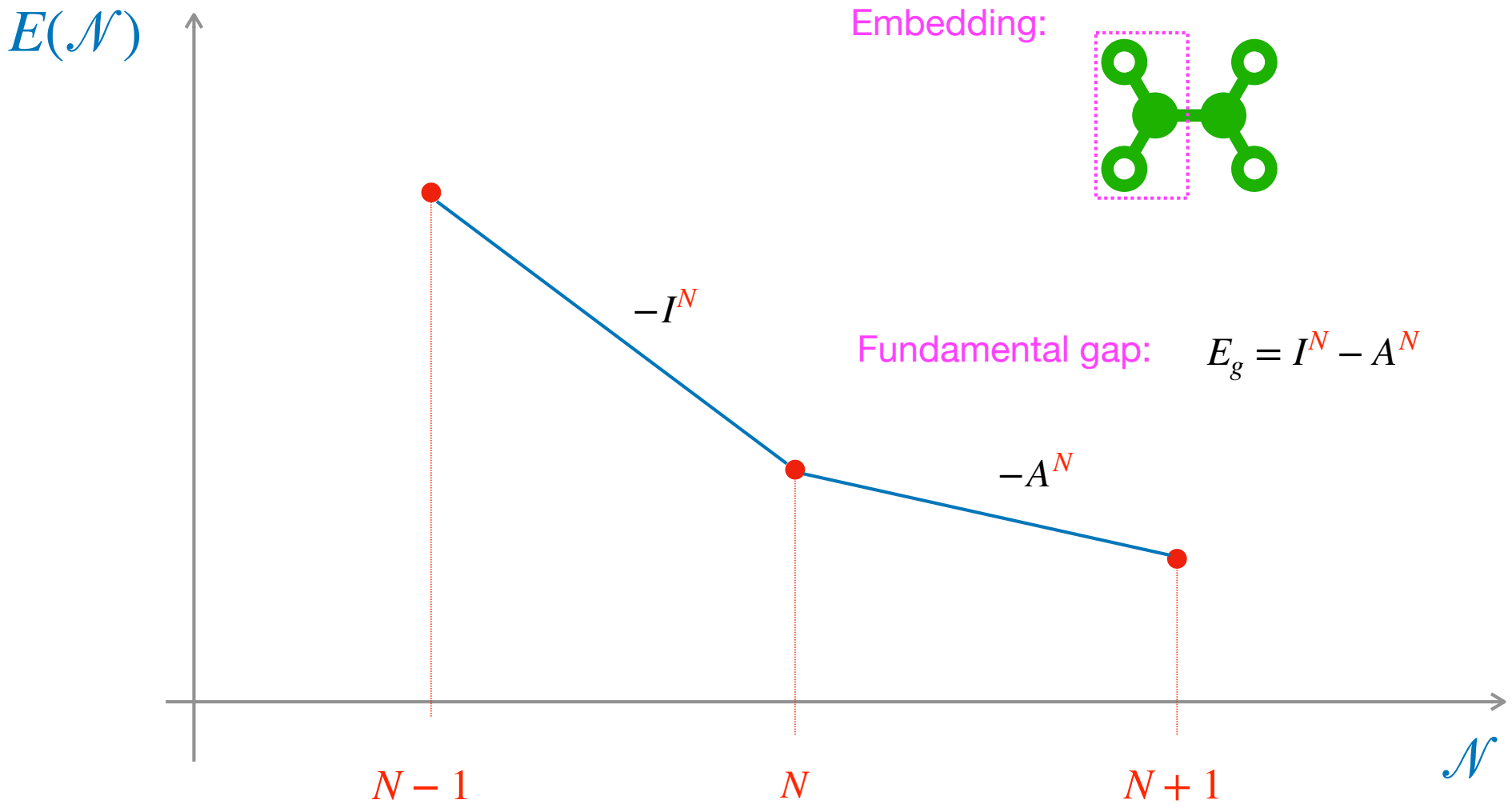
DFT for fractional electron numbers



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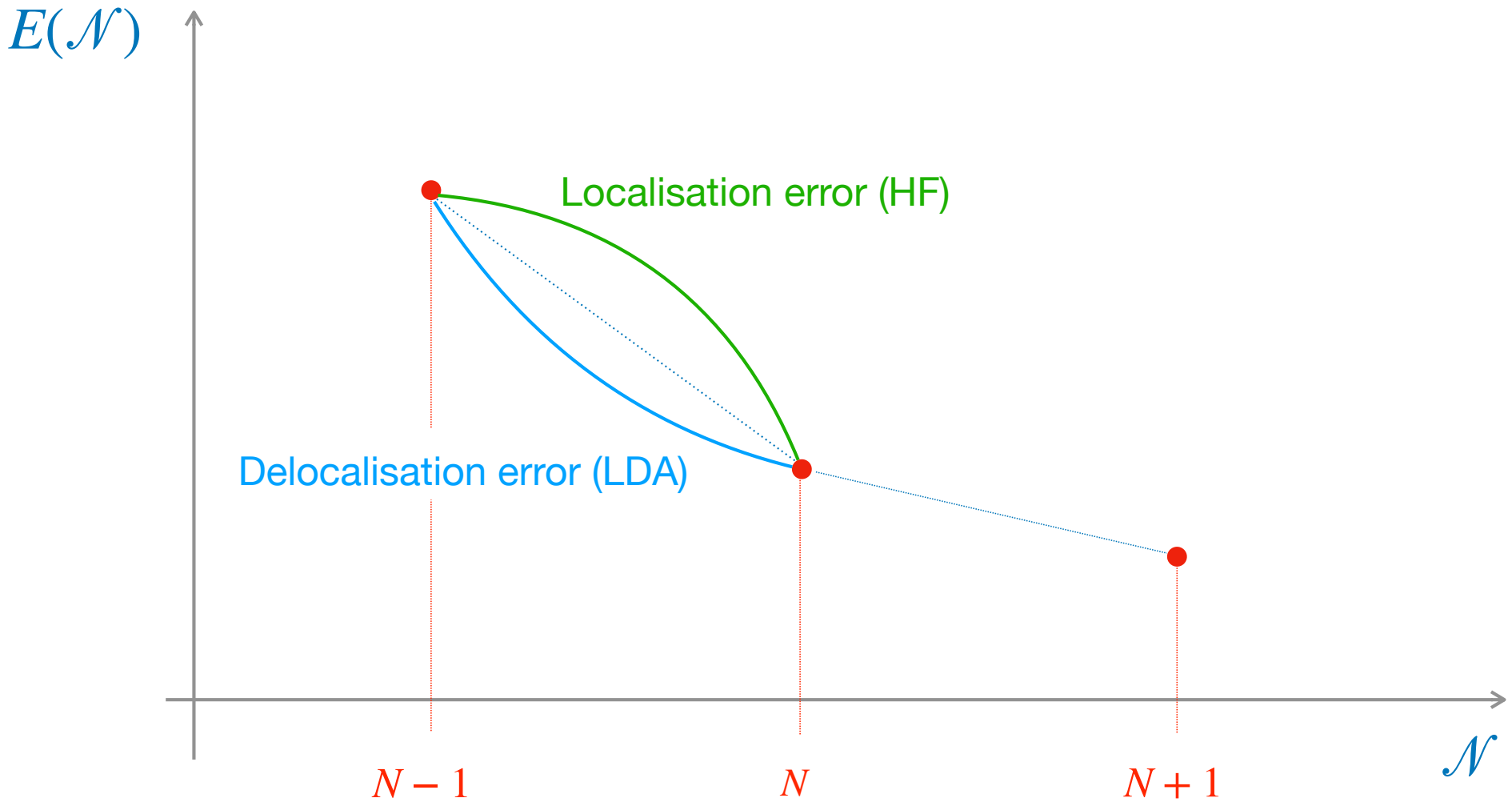
DFT for fractional electron numbers



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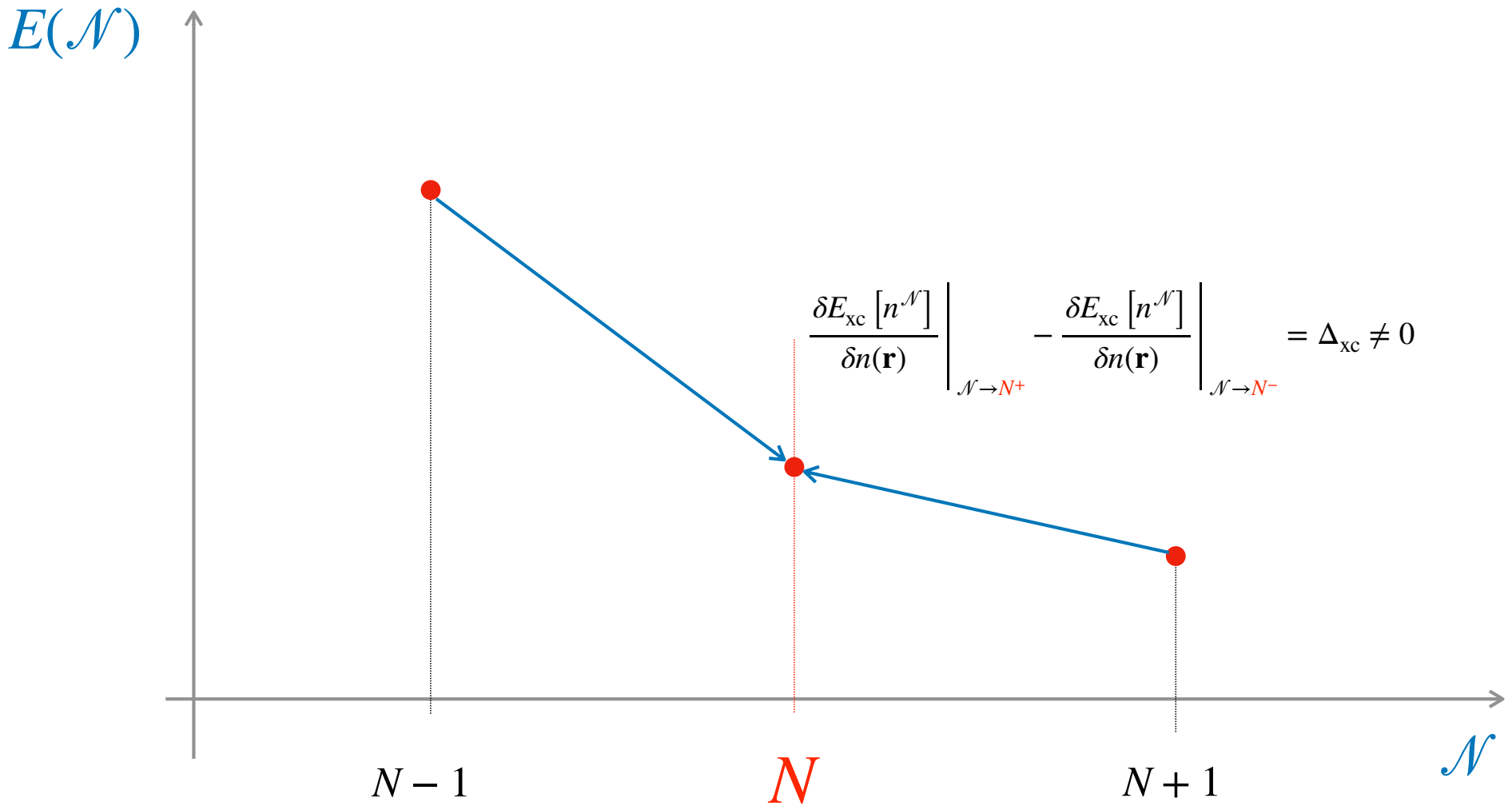
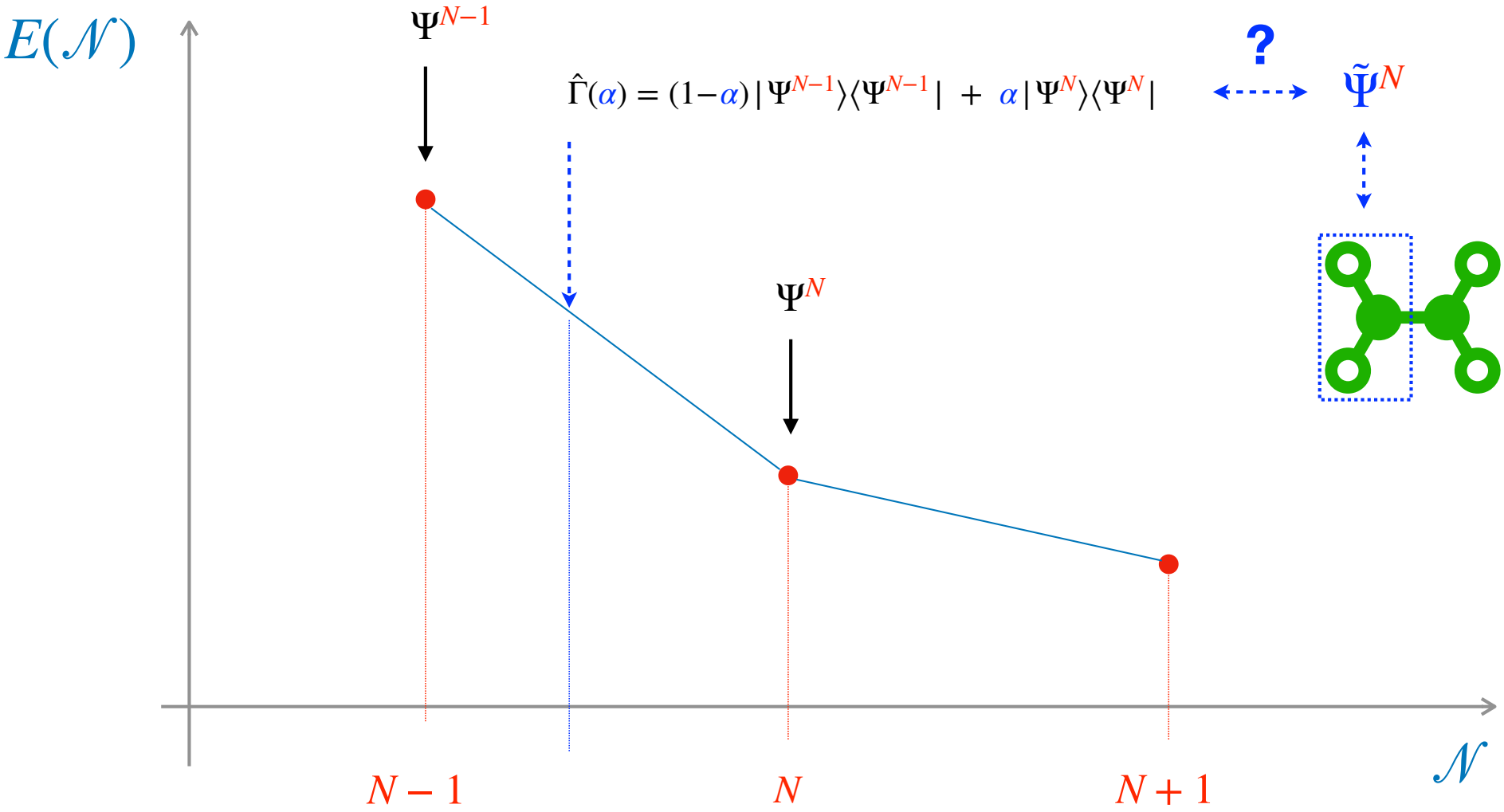
DFT for fractional electron numbers



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

Density-functional embedding



N-centered grand canonical ensembles

density:

$$n^{\mathcal{N}}(\mathbf{r}) = (1-\alpha)n^{N}(\mathbf{r}) + \alpha\, n^{N-1}(\mathbf{r})$$

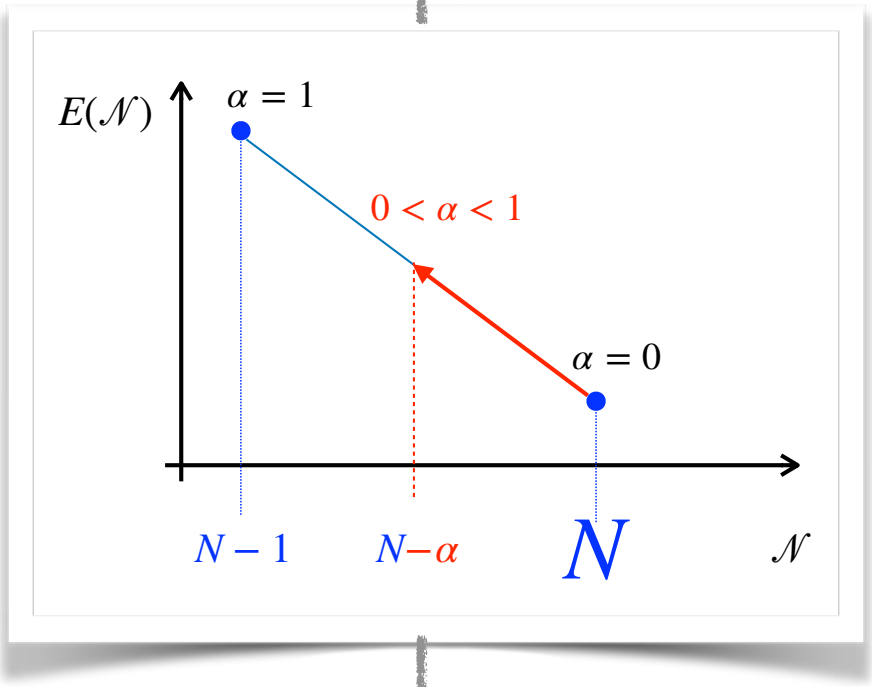
Look at me!

electron **number**:

$$\mathcal{N} = N-\alpha$$

energy:

$$E\left(\mathcal{N}\right) = (1-\alpha)E^{N} + \alpha E^{N-1}$$



density:

$$n^{\{N,\alpha\}}(\mathbf{r}) = (1-\alpha)n^{N}(\mathbf{r}) + \frac{N\alpha}{N-1}\, n^{N-1}(\mathbf{r})$$

Look at me!

electron **number**:

$$N$$

energy:

$$\mathscr{E}^{\{N,\alpha\}} = (1-\alpha)E^{N} + \frac{N\alpha}{N-1}E^{N-1}$$

$$\left[\left(1-\frac{\alpha}{N}\right) - \frac{\alpha(1-\alpha)}{N}\frac{\partial}{\partial\alpha}\right]$$

Real *picture*

(Left) *N-centered picture*

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, ***arXiv:1912.07125*** *(2019).*

DFT for N-centered ensembles

- The *N*-centered ensemble energy is a ***functional*** of the *N*-centered ***ensemble density***.

- The Hxc functional is now α-***dependent***:

Standard DFT	*N*-centered eDFT
$E_{\text{Hxc}}[n] = E_{\text{Hxc}}^{\{N,\alpha=0\}}[n]$	$E_{\text{Hxc}}^{\{N,\alpha\}}[n]$

- ***Kohn-Sham equations*** in *N*-centered ensemble DFT:

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + \frac{\delta E_{\text{Hxc}}^{\{N,\alpha\}}[n]}{\delta n(\mathbf{r})} \bigg|_{n=n^{\{N,\alpha\}}} \right] \varphi_i(\mathbf{r}) = \varepsilon_i^{\{N,\alpha\}} \varphi_i(\mathbf{r})$$

- ***Levy-Zahariev shift***:

$$\varepsilon_i^{\{N,\alpha\}} \rightarrow \overline{\varepsilon}_i^{\{N,\alpha\}} = \varepsilon_i^{\{N,\alpha\}} + \frac{E_{\text{Hxc}}^{\{N,\alpha\}}[n] - \int d\mathbf{r} \frac{\delta E_{\text{Hxc}}^{\{N,\alpha\}}[n]}{\delta n(\mathbf{r})} n(\mathbf{r})}{\int d\mathbf{r} n(\mathbf{r})} \bigg|_{n=n^{\{N,\alpha\}}}$$

*B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).*
*B. Senjean and E. Fromager, **arXiv:1912.07125** (2019).*
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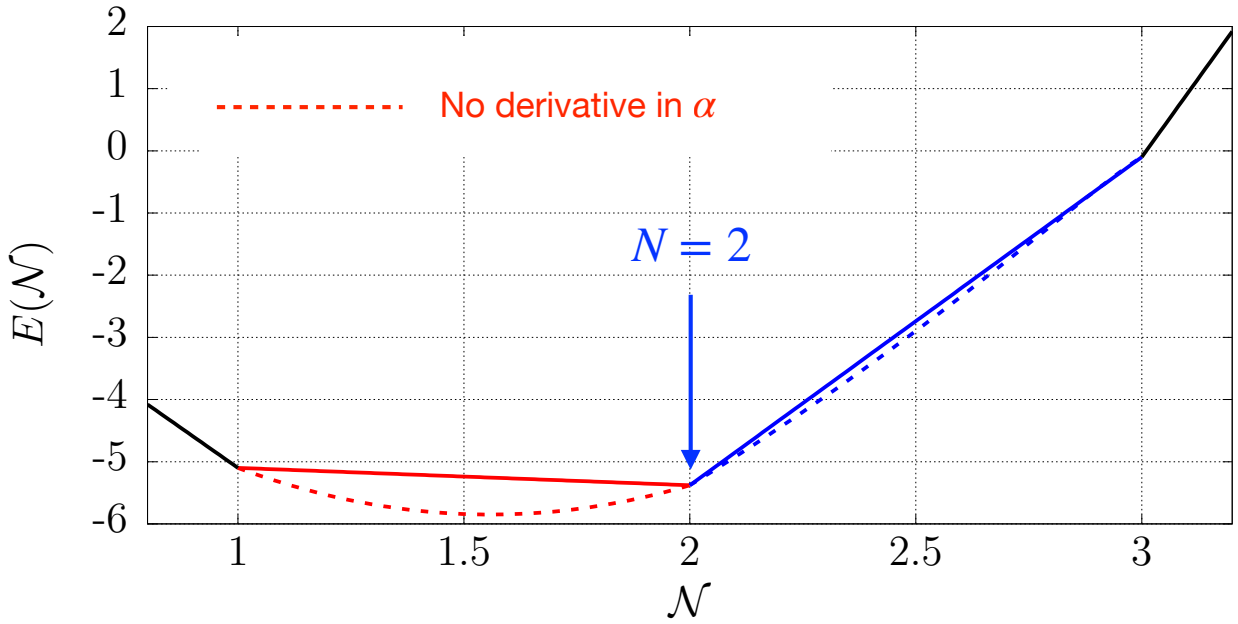
Exact energy expression in N-centered eDFT

Energy *of the true (open) system with* $\mathcal{N} = N - \alpha$ *electrons:*

$$E(\mathcal{N}) = \sum_{i=1}^{N-1} \bar{\varepsilon}_i^{\{N,\alpha\}} + (1-\alpha)\,\bar{\varepsilon}_N^{\{N,\alpha\}} \quad - \quad \frac{\alpha(1-\alpha)}{N} \frac{\partial E_{\mathrm{Hxc}}^{\{N,\alpha\}}[n]}{\partial \alpha}\bigg|_{n=n^{\{N,\alpha\}}}$$

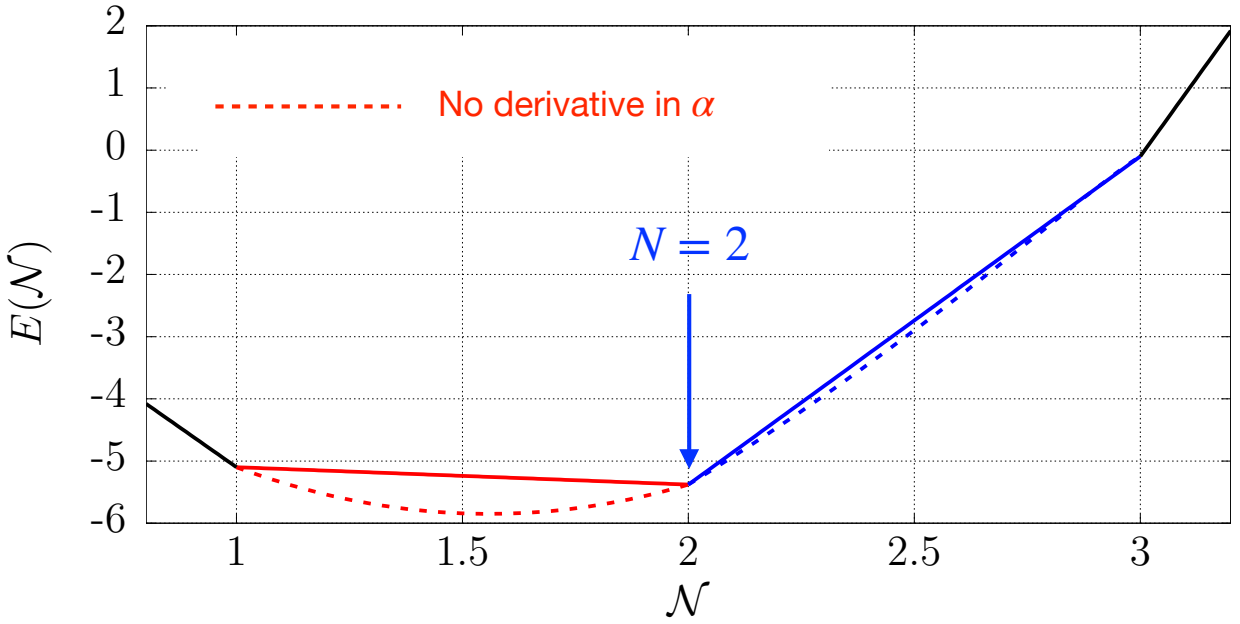


B. Senjean and E. Fromager, ***arXiv:1912.07125*** *(2019).*

Janak's theorem in N-centered eDFT

$$\frac{dE(\mathcal{N})}{d\mathcal{N}} = -I^N = \bar{\varepsilon}_N^{\{N,\alpha\}} + \frac{(1-\alpha-N)}{N} \frac{\partial E_{\mathrm{Hxc}}^{\{N,\alpha\}}[n]}{\partial \alpha}\Bigg|_{n=n^{\{N,\alpha\}}}$$

I will mimic the derivative discontinuity



B. Senjean and E. Fromager, ***arXiv:1912.07125*** *(2019).*

N-centered ensemble density-functional embedding theory

Mapping the *N*-centered ensemble density onto a pure state *N*-electron wave function:

$$\mathscr{E}^{\{N,\alpha\}} = \left[F^{\{N,\alpha\}}[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right]_{n=n^{\{N,\alpha\}}}$$

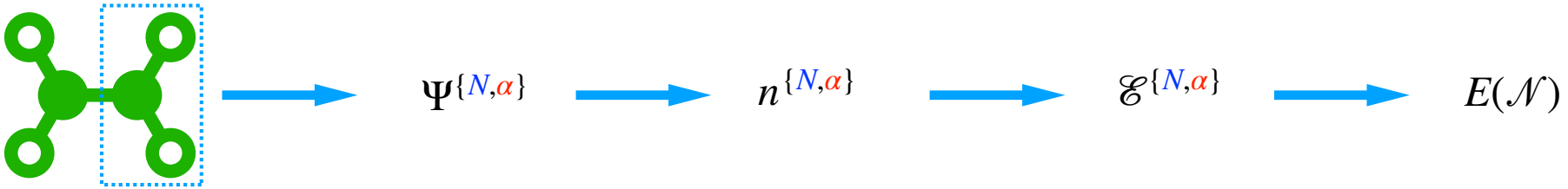
where

Regular Hohenberg-Kohn functional ($\alpha = 0$)

$$F^{\{N,\alpha\}}[n] = F[n] + \Delta F^{\{N,\alpha\}}[n]$$

and

$$F[n]\Big|_{n=n^{\{N,\alpha\}}} = \langle \Psi^{\{N,\alpha\}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\{N,\alpha\}} \rangle$$



B. Senjean and E. Fromager, ***arXiv:1912.07125*** *(2019).*
S. Sekaran, B. Senjean, and E. Fromager, work in progress.

Conclusions and perspectives

- *N*-centered ensemble DFT is an *alternative formulation of DFT* for open systems.
- The auxiliary *N*-centered ensemble density integrates to an *integral* number of electrons.
- It allows for an *exact embedding* of pure state many-body wave functions.
- The α*-dependence* in the density functionals is the *key quantity to model*.
- (Semi-) local functionals can be extracted from *finite* uniform electron gas models: *collaboration with Pierre-François Loos (a.k.a. T2).*
- α-independent v-representability domains might be obtained through *regularization*: *collaboration with Z. Belhachmi and G. Grenthe (Mulhouse/Strasbourg).*

References:
B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
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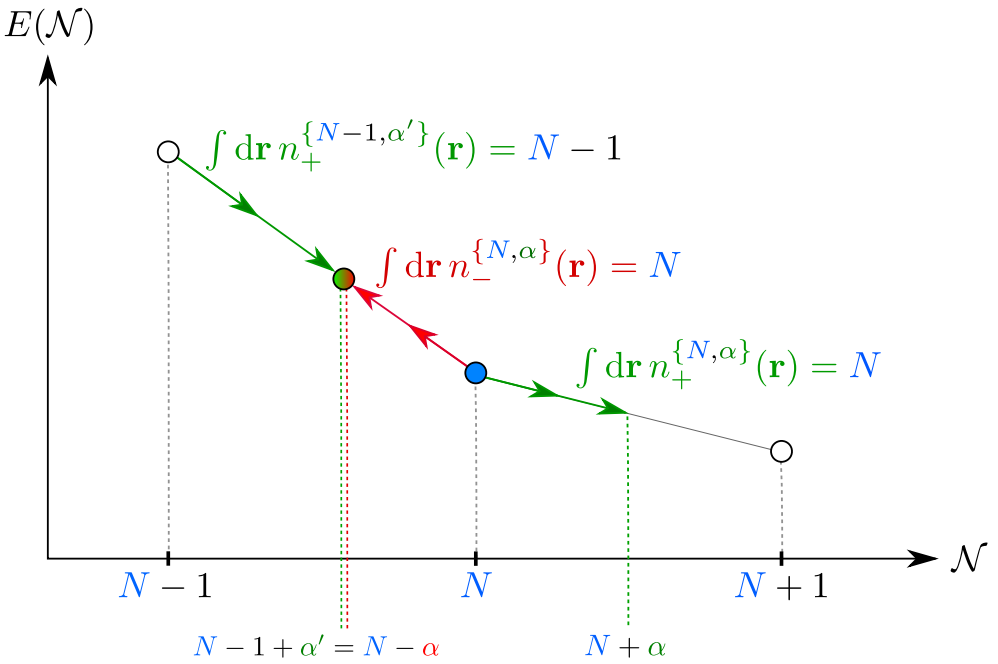
Left or right ?

***Scaling** relation:*

$$E_{\text{Hxc}-}^{\{N+1,\alpha\}}[n] = \frac{N+1}{N} E_{\text{Hxc}+}^{\{N,1-\alpha\}}\left[\frac{N}{N+1} n\right]$$

Left ensemble (-)

Right ensemble (+)



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