On the design of density-functional approximations for canonical and grand-canonical ensembles

Pierre-François Loos[a] and Emmanuel Fromager[b]

[a] Laboratoire de Chimie et Physique Quantiques, CNRS/ Université Paul Sabatier,
Toulouse, France.
[b]Laboratoire de Chimie Quantique, Université de Strasbourg, France.

fromagere@unistra.fr

Optical and fundamental gaps in DFT

- The difference in energy between the N-electron first excited and ground states is referred to as the **optical gap**. It is expressed as follows,

$$\omega^N = E_1^N - E_0^N$$

- Note that the optical gap describes a neutral excitation.
- On the other hand, the **fundamental gap** is a ground-state quantity.
- It describes the removal and addition of an electron to the system.
- It is calculated from the electron affinity [EA] A^N and the ionization potential [IP] I^N:

$$E_g^N = \underbrace{\left(E_0^{N-1} - E_0^N\right)}_{I^N} - \underbrace{\left(E_0^N - E_0^{N+1}\right)}_{A^N = I^{N+1}}$$

- Interestingly, for non-interacting electrons, the two gaps boil down to the same quantity, namely the HOMO-LUMO gap of the N-electron system:

$$\omega^N = E_g^N = \varepsilon_{\mathrm{L}}^N - \varepsilon_{\mathrm{H}}^N.$$

Limitations of the one-electron picture

Materials Horizons

FOCUS

View Article Online
View Journal | View Issue

Mind the gap!

Cite this: *Mater. Horiz.*, 2014, **1**, 17

Jean-Luc Bredas[ab]

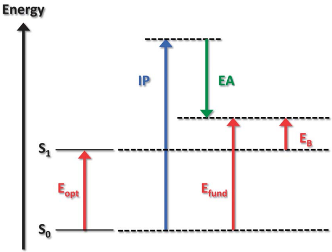
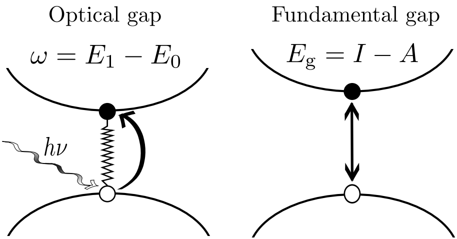


Fig. 1 Illustration of gap energies in the molecular case: S_0 denotes the (singlet) electronic ground state and S_1 the lowest (singlet) excited state (considered here to be accessible *via* one-photon absorption). The $S_1 - S_0$ energy difference then corresponds to the optical gap E_{opt}. The magnitude of the ionization potential is given by the blue vertical line and the magnitude of the electron affinity by the green vertical line; the IP − EA difference represents the fundamental gap, E_{fund}. The electron–hole pair binding energy, E_B, is given by $E_{fund} - E_{opt}$.



Optical gap

$$\omega = E_1 - E_0$$

Fundamental gap

$$E_g = I - A$$

Courtesy of B. Senjean

DFT for a fixed (integral) number N of electrons

- In quantum mechanics, the electronic repulsion energy is expressed (in atomic units) as follows,

$$W_{\mathrm{ee}} = \frac{N(N-1)}{2} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_1 \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_2 \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_3 \ldots \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_N \, \frac{\Psi^2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N)}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

  where $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N)$ is the N-electron wavefunction.

- In standard Kohn–Sham (KS) density-functional theory (DFT), the latter energy can be determined, in principle exactly, from the electron density $n(\mathbf{r})$, which is mathematically a much simpler quantity than the wavefunction.

- For that purpose, the so-called Hartree-exchange-correlation (Hxc) density functional has been introduced,

$$W_{\mathrm{ee}} \rightarrow E_{\mathrm{Hxc}}[n],$$

  where the density is determined exactly from the KS orbitals as follows,

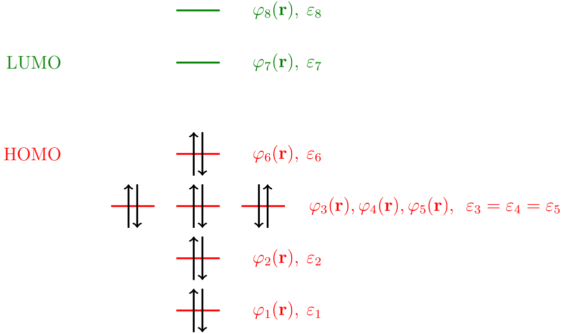
$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2 .$$

- Self-consistent equations fulfilled by the KS orbitals:

$$-\frac{1}{2}\nabla^2\varphi_i(\mathbf{r}) + \left[v_{\rm ext}(\mathbf{r}) + \frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})}\right] \times \varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}),$$

  where $v_{\rm ext}(\mathbf{r})$ is any external local (multiplicative) interaction potential energy (the nuclear-electron attraction potential for example) at position $\mathbf{r}$.

- The additional Hxc potential $\delta E_{\rm Hxc}[n]/\delta n(\mathbf{r})$ ensures that the density of the true system is recovered, in principle exactly, from the KS orbitals.



Do the KS orbital energies have any physical meaning ?

- Let us denote ε_{H} and ε_{L} the Kohn–Sham HOMO and LUMO energies, respectively.
- In the following, we will focus on the (in-principle) exact calculation of the ionization potential (IP)

  $$\boxed{I_N = E_{N-1} - E_N}$$

  and the electron affinity (EA)

  $$\boxed{A_N = E_N - E_{N+1}} = I_{N+1}$$

  of the molecule within DFT.

- The energies E_{N-1}, E_N, and E_{N+1} of the cationic, N-electron and anionic molecule, respectively, should in principle be computed with different KS orbitals and energies.
- A simple but non trivial question: can we calculate both IP and EA from the KS energies and orbitals of the N-electron molecule ?
- In other words: $\boxed{I_N \overset{?}{=} -\varepsilon_{\mathrm{H}}}$, $\boxed{A_N \overset{?}{=} -\varepsilon_{\mathrm{L}}}$, and $\boxed{I_N - A_N \overset{?}{=} \varepsilon_{\mathrm{L}} - \varepsilon_{\mathrm{H}}}$.
- This is known as the fundamental gap problem in DFT.

Chemical potential in DFT

- For a fixed (integral) number N of electrons, shifting the local potential by a constant $-\mu$ has no impact on the KS orbitals and therefore no impact on the density:

$$\begin{aligned}
-\frac{1}{2}\nabla^2\varphi_i(\mathbf{r}) + \left[v_{\rm ext}(\mathbf{r}) + \frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})} - \mu\right] \times \varphi_i(\mathbf{r}) &= \varepsilon_i\varphi_i(\mathbf{r}) - \mu\varphi_i(\mathbf{r}) \\
&= \Big(\varepsilon_i - \mu\Big)\varphi_i(\mathbf{r}),
\end{aligned}$$

- However, the total energy of the KS system is affected by such a shift:

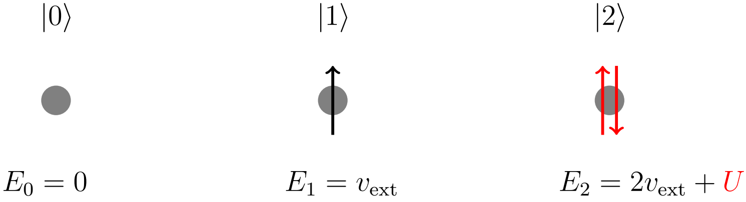
$$\sum_{i=1}^{N}\varepsilon_i \;\rightarrow\; \sum_{i=1}^{N}\Big(\varepsilon_i - \mu\Big) = \left(\sum_{i=1}^{N}\varepsilon_i\right) - \mu N.$$

- As readily seen, the impact on the energy depends on the number of electrons.

- This is the reason why the constant μ, which is nothing but the chemical potential, plays a crucial role in grand canonical ensemble DFT (where N can vary).

Fractional number of electrons in the Hubbard atom

- The Hubbard atom is a model system consisting of a single (atomic) site that can contain up to 2 electrons:



$$|0\rangle \qquad |1\rangle \qquad |2\rangle$$

$$E_0 = 0 \qquad E_1 = v_{\rm ext} \qquad E_2 = 2v_{\rm ext} + U$$

- Starting from the one-electron atom case ($N = 1$) the IP and the EA read

  $I^1 = E_0 - E_1 = -v_{\rm ext}$ and $A^1 = E_1 - E_2 = -v_{\rm ext} - U$, respectively,

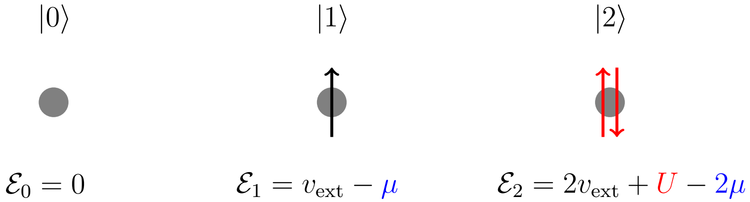
  so that the fundamental gap equals $\boxed{E_g^1 = I^1 - A^1 = U}$.

- In this simple (one-orbital atomic) model the HOMO-LUMO gap equals zero.

- Thus we conclude that, in general, the fundamental gap is *not* equal to the KS HOMO-LUMO gap.

Fractional number of electrons in the Hubbard atom

- If we now introduce the chemical potential μ, the energies are modified as follows,



$\mathcal{E}_0 = 0$ $\quad$ $\mathcal{E}_1 = v_{\rm ext} - \mu$ $\quad$ $\mathcal{E}_2 = 2v_{\rm ext} + U - 2\mu$

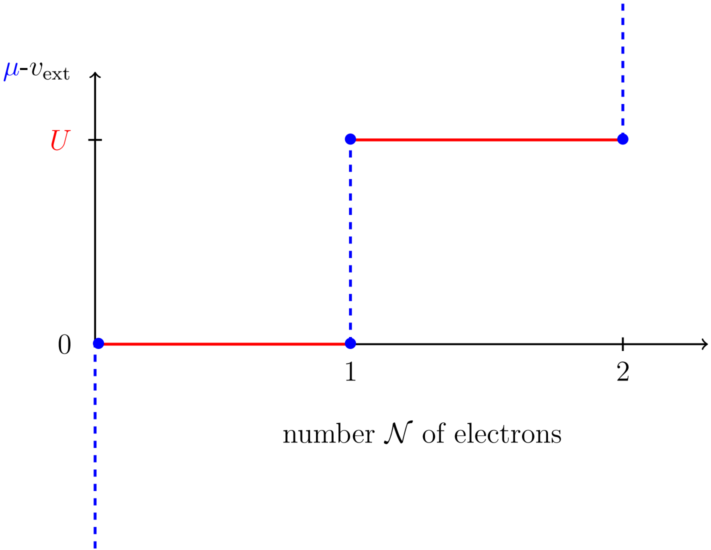
- By varying μ we will be able to change the number of electrons N continuously*.

- When $\mu < v_{\rm ext}$, the lowest energy is $\mathcal{E}_0$ thus leading to $N = 0$.
- When $v_{\rm ext} < \mu < v_{\rm ext} + U$, the lowest energy is $\mathcal{E}_1$ thus leading to $N = 1$.
- When $\mu > v_{\rm ext} + U$, the lowest energy is $\mathcal{E}_2$ thus leading to $N = 2$.

---

* *Principles of DFT*, lecture given by **Trygve Helgaker** at the GDR Correl mini-school on mathematics in electronic structure theory, Paris, January 2017.

Fractional number of electrons in the Hubbard atom



Fractional number of electrons in the Hubbard atom

- What happens when $\mu = v_{\text{ext}}$?

- In the latter case, the quantum states $|0\rangle$ and $|1\rangle$ are strictly degenerate ($\mathcal{E}_0 = \mathcal{E}_1 = 0$).

- Consequently, it is possible to mix them (and the energy will remain equal to zero) in order to obtain an $\mathcal{N}$-electron quantum state,

$$|\mathcal{N}\rangle = \sqrt{1-\mathcal{N}}\,|0\rangle + \sqrt{\mathcal{N}}\,|1\rangle$$

where $0 < \mathcal{N} < 1$.

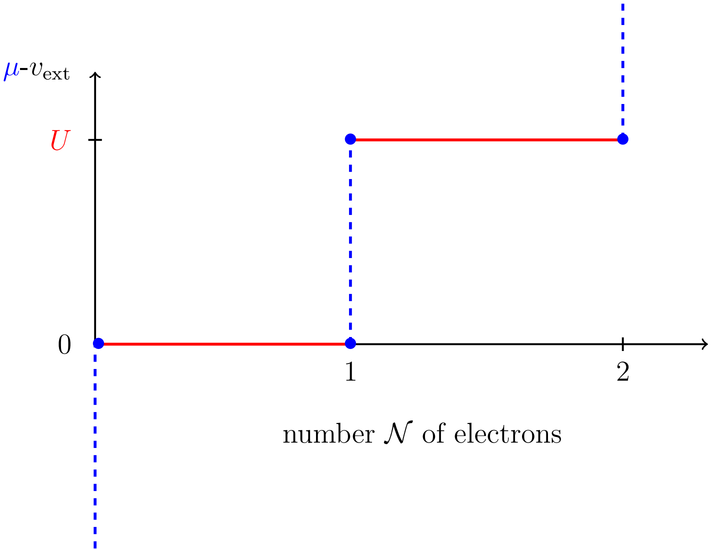
- The number of electrons $\mathcal{N}$ can vary continuously from 0 to 1 when $\mu = v_{\text{ext}}$.

- Similarly, when $\mu = v_{\text{ext}} + U$, the states $|1\rangle$ and $|2\rangle$ are strictly degenerate ($\mathcal{E}_1 = \mathcal{E}_2 = -U$).

- In the latter case, $|\mathcal{N}\rangle = \sqrt{2-\mathcal{N}}\,|1\rangle + \sqrt{\mathcal{N}-1}\,|2\rangle$ where $1 < \mathcal{N} < 2$.

- As a result, the number of electrons can vary continuously from 1 to 2 when $\mu = v_{\text{ext}} + U$.

Fractional number of electrons in the Hubbard atom



Fractional number of electrons in the Hubbard atom

- What happens to the energy (from which we remove the chemical potential contribution) when $\mu = v_{\text{ext}}$?
- For the mixed N-electron quantum state $|\mathcal{N}\rangle = \sqrt{1-\mathcal{N}}\,|0\rangle + \sqrt{\mathcal{N}}\,|1\rangle$, the expectation value for the energy reads

$$E\left(\mathcal{N}\right) = \left(\sqrt{1-\mathcal{N}}\right)^2 \times E_0 + \left(\sqrt{\mathcal{N}}\right)^2 \times E_1,$$

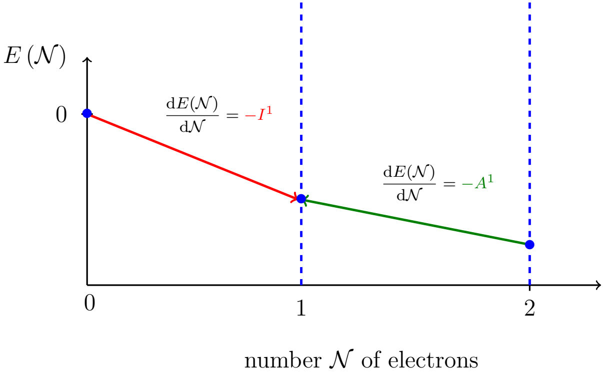
thus leading to $\boxed{E(\mathcal{N}) = (1-\mathcal{N})E_0 + \mathcal{N}E_1}$ when $0 \leq \mathcal{N} \leq 1$.

- Similarly, when $\mu = v_{\text{ext}} + U$, we have $1 \leq \mathcal{N} \leq 2$ and

$$\boxed{E(\mathcal{N}) = (2-\mathcal{N})E_1 + (\mathcal{N}-1)E_2}$$

- Important conclusion: the energy varies linearly (piecewise) with respect to the number $\mathcal{N}$ of electrons.

Fractional number of electrons in the Hubbard atom



- It is therefore possible to calculate both IP and EA from a single DFT calculation by differentiating the energy with respect to $\mathcal{N}$ around $\mathcal{N} = 1$.
- Note that $\mathcal{N} \rightarrow 1^-$ and $\mathcal{N} \rightarrow 1^+$ limits are *not* the same !
- Designing density functionals able to reproduce such a feature still remains a challenge. This is known as the derivative discontinuity problem.

IP theorem

- Let us denote ν a *fractional number* of electrons in the range $\boxed{N-1<\nu<N}$.

- In the extension of Kohn–Sham DFT to open systems, the *piecewise linear*[*] ν-electron energy $\boxed{E(\nu)=E_0^{N-1}-I^N\times(\nu-N+1)}$ is written as $E(\nu)=\min_{\{\varphi_i\}_i}\left\{E\left[\nu,\{\varphi_i\}_i\right]\right\}$ with

$$E\left[\nu,\{\varphi_i\}_i\right]=\sum_{i=1}^{N-1}\left\langle\varphi_i\middle|-\frac{\nabla^2}{2}+v_{\rm ne}(\mathbf{r})\times\middle|\varphi_i\right\rangle+\Big(\nu-N+1\Big)\left\langle\varphi_N\middle|-\frac{\nabla^2}{2}+v_{\rm ne}(\mathbf{r})\times\middle|\varphi_N\right\rangle$$

$$+E_{\rm Hxc}\left[n^\nu\right],$$

where the density $n^\nu(\mathbf{r})=\sum_{i=1}^{N-1}\left|\varphi_i(\mathbf{r})\right|^2+(\nu-N+1)\left|\varphi_N(\mathbf{r})\right|^2$ integrates to ν.

- The minimizing (ν-dependent) orbitals fulfill the KS equations:

$$\left(-\frac{\nabla^2}{2}+v_{\rm ne}(\mathbf{r})+\frac{\delta E_{\rm Hxc}\left[n^\nu\right]}{\delta n(\mathbf{r})}\right)\varphi_i^\nu(\mathbf{r})=\varepsilon_i^\nu\varphi_i^\nu(\mathbf{r}).$$

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

IP theorem

- Note that $E_{\mathrm{Hxc}}[n]$ is *"truly" universal* here as it applies to an arbitrary number of electrons (not only integral ones).

- *IP theorem:* $\boxed{\dfrac{\mathrm{d}E(\nu)}{\mathrm{d}\nu} = \varepsilon_N^{\nu}} \longrightarrow \varepsilon_N^{\nu} = -I^N \longrightarrow \boxed{I^N = -\varepsilon_{\mathrm{H}}^N}$

- Consequence of the IP theorem:

$$\boxed{E_g^N = I^N - I^{N+1} = \varepsilon_{\mathrm{H}}^{N+1} - \varepsilon_{\mathrm{H}}^N.}$$

- Note that, in principle, the LUMO of the N-electron system is *not* the HOMO of the $(N+1)$-electron one.

- Therefore, there is no reason to believe that $\varepsilon_{\mathrm{H}}^{N+1}$ is equal to $\varepsilon_{\mathrm{L}}^N$.

- Let us stress that this statement *does not give much hint* about the way the difference between the latter orbital energies can be modelled in practical calculations.

- If we simply write $\varepsilon_{\mathrm{H}}^{N+1} = \varepsilon_{\mathrm{L}}^N + \Delta_{\mathrm{xc}}^{\mathrm{fun.}}$, then we recover the standard expression

$$\boxed{E_g^N = \varepsilon_{\mathrm{L}}^N - \varepsilon_{\mathrm{H}}^N + \Delta_{\mathrm{xc}}^{\mathrm{fun.}}}$$

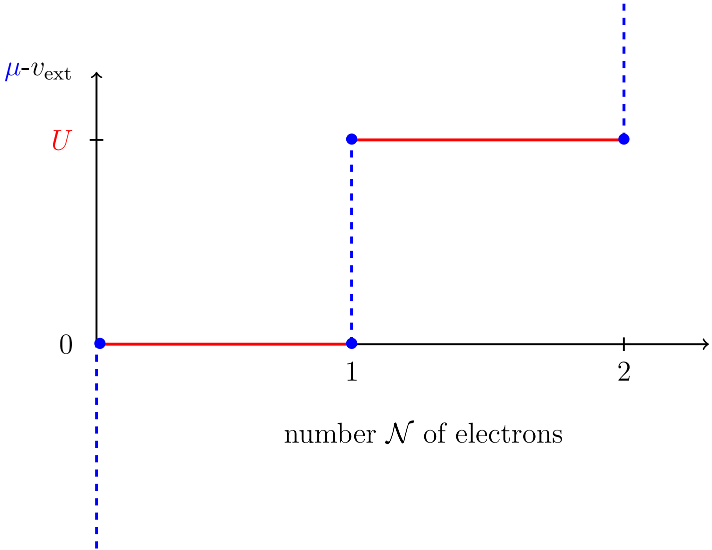
Why $\Delta_{\rm xc}^{\rm fun.}$ is referred to as *derivative discontinuity* ?

- Let us now look at what happens when the number of electrons ν crosses an integer N.
- *Three situations* should be considered in the KS equations:

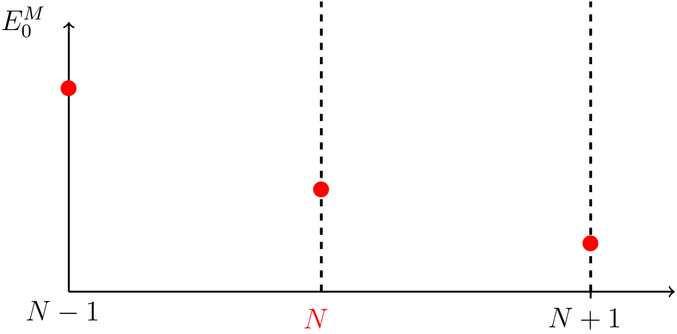
$$\left(-\frac{\nabla^2}{2}+v_{\rm ne}(\mathbf{r})+\frac{\delta E_{\rm Hxc}\left[n^{\nu}\right]}{\delta n(\mathbf{r})}\right)\varphi_i^{\nu}(\mathbf{r})=\varepsilon_i^{\nu}\varphi_i^{\nu}(\mathbf{r}).$$

- **Situation 1**: $\nu = N-\eta$ where $\eta\rightarrow 0^+$ ← KS potential unique.
- **Situation 2**: $\nu = N+\eta$ ← KS potential unique.
- **Situation 3**: $\nu = N$ ← KS potential unique **up to a constant!**
- The Hartree potential $\dfrac{\delta E_{\rm H}[n]}{\delta n(\mathbf{r})}=\displaystyle\int {\rm d}\mathbf{r}'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$ is a *continuous* functional of the density.
- Therefore $\dfrac{\delta E_{\rm xc}\left[n^{N+\eta}\right]}{\delta n(\mathbf{r})}-\dfrac{\delta E_{\rm xc}\left[n^{N-\eta}\right]}{\delta n(\mathbf{r})}=\text{constant}=\varepsilon_{\rm H}^{N+1}-\varepsilon_{\rm L}^{N}=\Delta_{\rm xc}^{\rm fun.}.$

Fractional number of electrons in the Hubbard atom



N-centered ensemble DFT



integral number M of electrons

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

Levy–Zahariev shift-in-potential procedure

- Let us consider the N-electron KS-DFT energy expression

$$
\begin{aligned}
E_0^N &= \sum_{i=1}^{N} \left\langle \varphi_i \middle| -\frac{\nabla^2}{2} + v_{\rm ne}(\mathbf{r})\times \middle| \varphi_i \right\rangle + E_{\rm Hxc}[n] \\
&= \left(\sum_{i=1}^{N} \varepsilon_i\right) + E_{\rm Hxc}[n] - \int \mathrm{d}\mathbf{r}\, \frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})} n(\mathbf{r})
\end{aligned}
$$

- Shift-in-potential approach*:

$$
\begin{aligned}
\frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})} &\rightarrow \frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})} + \frac{E_{\rm Hxc}[n] - \int \mathrm{d}\mathbf{r}\, \frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})} n(\mathbf{r})}{\int \mathrm{d}\mathbf{r}\ n(\mathbf{r})} \\
\varepsilon_i &\rightarrow \tilde{\varepsilon}_i \\
E_0^N &= \sum_{i=1}^{N} \tilde{\varepsilon}_i
\end{aligned}
$$

- Note that this procedure fixes the KS orbital energy levels. They are *not* defined anymore up to a constant.

- Levy and Zahariev have shown that $\boxed{I^N = -\tilde{\varepsilon}_{\rm H}^N + \tilde{w}[n](\mathbf{r})\big|_{r\rightarrow+\infty}}$ where $\tilde{w}[n](\mathbf{r})$ is the shifted Hxc potential.

---

* M. Levy and F. Zahariev, Phys. Rev. Lett. 113, 113002 (2014).

Two-weight N-centered ensemble DFT

- In order to extract both IP and EA separately, we consider the two-weight N-centered ensemble density,

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

where $\boldsymbol{\xi} \equiv (\xi_-, \xi_+)$ and the following convexity condition is fulfilled,

$$0 \leq (N-1)\xi_- + (N+1)\xi_+ \leq N.$$

- Note that the latter density integrates to N.

- Extension of DFT to N-centered ground-state ensembles:

$$E_{\rm xc}[n] = E_{\rm xc}^{N,\boldsymbol{\xi}=0}[n] \quad \xrightarrow[\xi_->0]{\xi_+>0} \quad E_{\rm xc}^{N,\boldsymbol{\xi}}[n] \qquad \leftarrow \textit{to be modeled !}$$

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

Two-weight N-centered ensemble DFT

- Choosing $\xi = 0$ (i.e. returning to standard N-electron DFT) leads to[1]

$$E_0^N = \sum_{i=1}^{N} \tilde{\varepsilon}_i^{N,\xi=0} \qquad \text{and} \qquad E_0^{N\pm1} = \sum_{i=1}^{N\pm1} \left[\tilde{\varepsilon}_i^{N,\xi=0} + \frac{1}{N\pm1} \left. \frac{\partial E_{\mathrm{xc}}^{N,\xi}\left[n_0^N\right]}{\partial \xi_\pm} \right|_{\xi=0} \right]$$

where $\left\{\tilde{\varepsilon}_i^{N,\xi=0}\right\}_{i=1,2,\ldots}$ are the Levy–Zahariev shifted KS orbital energies[2].

- Interestingly, we recover the Levy–Zahariev expression for the IP,

$$\boxed{I^N = E_0^{N-1} - E_0^N = -\tilde{\varepsilon}_{\mathrm{H}}^{N,\xi=0} + \left. \frac{\partial E_{\mathrm{xc}}^{N,\xi}\left[n_0^N\right]}{\partial \xi_-} \right|_{\xi=0}}$$

where the shifted Hxc potential at position $r \to \infty$ is now written explicitly as a density-functional derivative discontinuity contribution.

---

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

[2] M. Levy and F. Zahariev, Phys. Rev. Lett. 113, 113002 (2014).

How to use the N-centered paradigm in *practice* ?

- A *finite* ($N < +\infty$) and *uniform* electron gas* is the perfect toy system for modeling DDs.

- Indeed, in the latter case,

$$\begin{aligned} n^{\xi}(\mathbf{r}) &= \xi_{-}\frac{N-1}{V} + \xi_{+}\frac{N+1}{V} + \left[1 - \xi_{-}\frac{N-1}{N} - \xi_{+}\frac{N+1}{N}\right] \times \frac{N}{V} \\ &= \frac{N}{V} \\ &= n^{N}(\mathbf{r}) \qquad \leftarrow \boldsymbol{\xi}\textbf{-independent!} \end{aligned}$$

- We should be able to extract from this model *generalized LDA* functionals for ensembles*:

$$\begin{aligned} \frac{N}{V} &= n(\mathbf{r}) \\ N &\leftrightarrow \alpha(\mathbf{r}) = \frac{1}{C_{\mathrm{F}}\, n^{5/3}(\mathbf{r})}\left(\tau(\mathbf{r}) - \frac{|\boldsymbol{\nabla} n(\mathbf{r})|^2}{4n(\mathbf{r})}\right), \end{aligned}$$

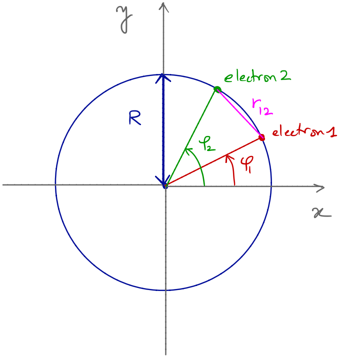
where $\tau(\mathbf{r})$ is the kinetic energy density and $C_{\mathrm{F}} = \dfrac{3}{5}(6\pi^2)^{2/3}$.

- Those *will exhibit DDs* through their $\boldsymbol{\xi}$ dependence.

---

* P.-F. Loos, J. Chem. Phys. 146, 114108 (2017).

1D finite uniform electron gas: the *ringium* model



$$r_{12}^2 = |\vec{r}_2 - \vec{r}_1|^2 = 2R^2 - 2\,\vec{r}_1\cdot\vec{r}_2$$
$$= 2R^2\left(1 - \cos\left(\varphi_2 - \varphi_1\right)\right)$$

N-electron Hamiltonian:

$$\boxed{\hat{H} = -\frac{1}{2R^2}\sum_{i=1}^{N}\frac{\partial^2}{\partial\varphi_i^2} + \sum_{i<j}^{N}\frac{1}{r_{ij}}}$$

P.-F. Loos, C. J. Ball, and P. M. W. Gill, J. Chem. Phys. 140, 18A524 (2014).

1D finite uniform electron gas: the *ringium* model

- Kohn–Sham orbitals: $\Phi_m(\varphi) = \dfrac{1}{\sqrt{2\pi R}} \exp(\mathrm{i}m\varphi)$ with $m = 0, \pm 1, \pm 2, \ldots$

- Uniform electron density: $n^N = \sum_{m=1}^{N} |\Phi_m(\varphi)|^2 = \dfrac{N}{2\pi R}$.

- Accurate Hxc energies can be computed for such a model (*generalized LDA* functional).

- Application to *non-uniform* 1D systems:

  (i) electrons in a box: *boxium* model.

  (ii) electrons in a harmonic potential: *hookium* model ← **quantum dots !**

- So far, pure ground-state energies only have been computed[*].

- The *extension* of the latter work *to N-centered ensembles* is in progress.

---

[*] P.-F. Loos, C. J. Ball, and P. M. W. Gill, J. Chem. Phys. 140, 18A524 (2014).

Individual energy levels in ensemble DFT

- For a given (non-degenerate) M-state canonical ensemble, the ensemble energy reads

$$E^{\mathbf{w}} = \left(1-\sum_{i=1}^{M-1} w_i\right) E_0^N + \sum_{i=1}^{M-1} w_i E_i^N.$$

- Similarly, the ensemble density reads

$$n^{\mathbf{w}}(\mathbf{r}) = \left(1-\sum_{i=1}^{M-1} w_i\right) n_0^N(\mathbf{r}) + \sum_{i=1}^{M-1} w_i n_i^N(\mathbf{r}).$$

- Exact energy expression for state j: $\boxed{E_j = E^{\mathbf{w}} + \sum_{i=1}^{M-1} (\delta_{ij} - w_i) \dfrac{\partial E^{\mathbf{w}}}{\partial w_i}}$, thus leading to[1]

$$E_j = \tilde{\mathcal{E}}_j^{\mathrm{KS},\mathbf{w}} + \sum_{i=1}^{M-1} (\delta_{ij} - w_i) \left.\frac{\partial E_{\mathrm{xc}}^{\mathbf{w}}[n]}{\partial w_i}\right|_{n=n^{\mathbf{w}}}.$$

- Important consequences:

  (1) excited-state molecular gradients.

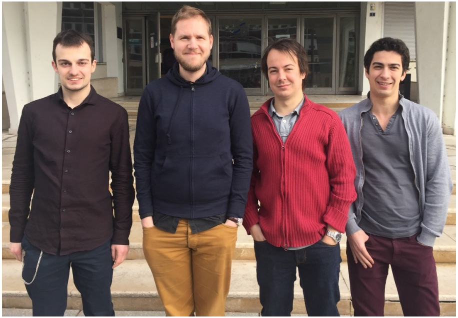
  (2) Gould-Pittalis-like[2] decomposition $E_{\mathrm{xc}}^{\mathbf{w}}[n] = \sum_{i=0}^{M-1} w_i E_{\mathrm{xc}}^{i}[n]$ of the ens. xc energy.

---

[1] K. Deur and E. Fromager, to be submitted (2018).

[2] T. Gould and S. Pittalis, **arXiv:1808.04994** (2018).

Acknowledgments



From left to right: Laurent Mazouin, E. F., Killian Deur and Bruno Senjean.

Thanks also to **P.-F. Loos** (Toulouse, France) for a nice and promising collaboration !

Funding

- ANR jeune chercheur (**MCFUNEX** project)*
- École doctorale des sciences chimiques de Strasbourg

---

*`https://quantique.u-strasbg.fr/MCFUNEX`

Conclusion

No need to

anymore ?