Ensemble density-functional theory for excited states

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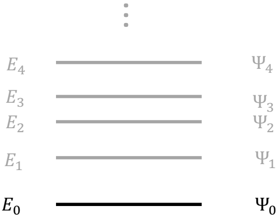
N-electron Schrödinger equation for the *ground* state

$$\boxed{\hat{H}\Psi_0 = E_0\Psi_0}$$



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where $\Psi_0 \equiv \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and $\hat{H} = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}$ with

$$\hat{T} \equiv -\frac{1}{2}\sum_{i=1}^{N} \nabla^2_{\mathbf{r}_i} = -\frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) \longrightarrow$$ *universal* kinetic energy operator

$$\hat{W}_{\text{ee}} \equiv \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\times \longrightarrow$$ *universal* two-electron repulsion operator

$$\hat{V} \equiv \sum_{i=1}^{N} v(\mathbf{r}_i)\times$$ where $$v(\mathbf{r}) = -\sum_{A}^{\text{nuclei}} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \longrightarrow$$ local *nuclear* potential operator

Kohn–Sham DFT in a nutshell

- In Kohn–Sham (KS) DFT, the many-electron problem is formally transformed into a *one-electron-like* problem.

- The "magical" one-electron wavefunctions (so-called KS orbitals) fulfill the following *self-consistent* KS equations:

$$\left(-\frac{1}{2}\nabla^2_{\mathbf{r}} + v(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})}\right)\varphi_k(\mathbf{r}) = \boxed{\varepsilon_k}\,\varphi_k(\mathbf{r})$$

where $\boxed{n(\mathbf{r}) = \sum_{k=1}^{N} \left|\varphi_k(\mathbf{r})\right|^2 = N\int d\mathbf{r}_2 \ldots \int d\mathbf{r}_N \left|\Psi_0(\mathbf{r},\mathbf{r}_2\ldots,\mathbf{r}_N)\right|^2 = n_{\Psi_0}(\mathbf{r})}.$

- When convergence is reached, the (in-principle-exact) ground-state energy reads

$$E_0 = -\frac{1}{2}\sum_{k=1}^{N}\int d\mathbf{r}\; \varphi_k^*(\mathbf{r})\nabla^2_{\mathbf{r}}\varphi_k(\mathbf{r}) + \int d\mathbf{r}\; v(\mathbf{r})n(\mathbf{r}) + \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\rm xc}[n].$$

W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).

DFT for ground-state *ensembles*

- The standard derivation of DFT holds for *pure-state* v-representable densities.
- The ground-state density is not uniquely defined in case of *degeneracy*.
- Densities of degenerate states can actually be *mixed*.
- If the ground state is g times degenerate, we have

$$E_0 = \sum_{i=0}^{g-1} w_i \left\langle \Psi_i \middle| \hat{H} \middle| \Psi_i \right\rangle, \quad \sum_{i=0}^{g-1} w_i = 1, \quad \hat{H}|\Psi_i\rangle = E_0|\Psi_i\rangle.$$

or, equivalently,

$$E_0 = \underbrace{\sum_{i=0}^{g-1} w_i \left\langle \Psi_i \middle| \hat{T} + \hat{W}_{\rm ee} \middle| \Psi_i \right\rangle}_{\equiv F[n]} + \int d\mathbf{r}\, v(\mathbf{r}) \times \underbrace{\left(\sum_{i=0}^{g-1} w_i n_{\Psi_i}(\mathbf{r})\right)}_{\equiv n(\mathbf{r})}$$

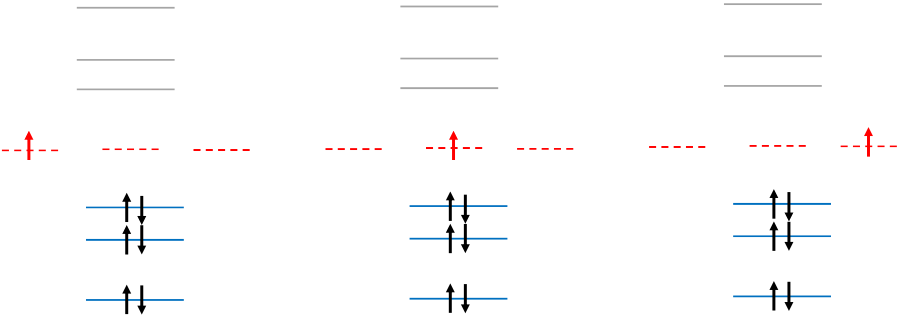
- The density n is said to be *ensemble* v-representable.

C. A. Ullrich and W. Kohn, Phys. Rev. Lett. 87, 093001 (2001).

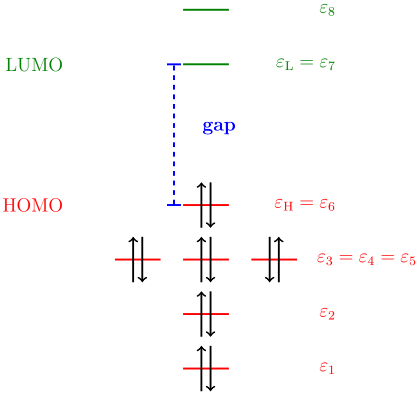
Kohn–Sham DFT for ground-state *ensembles*

- In KS-DFT, ensembles are described by *fractionally-occupied* orbitals.
- Example (with $g = 3$):

$$n(\mathbf{r}) = \sum_{i=0}^{g-1} w_i \left(\sum_{k=1}^{N-1} \left|\varphi_k(\mathbf{r})\right|^2 + \left|\varphi_{N+i}(\mathbf{r})\right|^2 \right) = \sum_{k=1}^{N-1} \left|\varphi_k(\mathbf{r})\right|^2 + \sum_{i=0}^{g-1} w_i \left|\varphi_{N+i}(\mathbf{r})\right|^2$$



Molecular orbital energy diagram and gaps



- The HOMO-LUMO gap can be interpreted in two ways.
- $\varepsilon_\mathrm{L} - \varepsilon_\mathrm{H} = \left(E_0^{N+1} - E_0^N\right) + \left(E_0^{N-1} - E_0^N\right) = E_\mathrm{g}$ ← fundamental gap [charged excit.]
- $\varepsilon_\mathrm{L} - \varepsilon_\mathrm{H} = E_1^N - E_0^N = \omega_\mathrm{g}$ ← optical gap [neutral excitation]

Limitations of the one-electron picture

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Mind the gap!

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

Jean-Luc Bredas[ab]

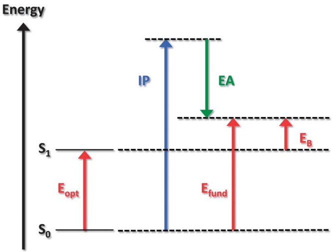
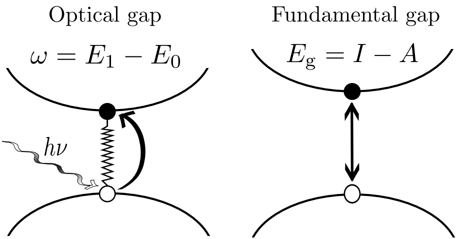


Fig. 1 Illustration of gap energies in the molecular case: S_0 denotes the (singlet) electronic ground state and S_1 the lowest (singlet) excited state (considered here to be accessible *via* one-photon absorption). The $S_1 - S_0$ energy difference then corresponds to the optical gap E_{opt}. The magnitude 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

Levy–Zahariev shift-in-potential procedure

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

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

- Shift-in-potential approach*:

$$\frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})} \rightarrow \frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})} + \frac{E_{\rm Hxc}[n] - \int d\mathbf{r}\, \frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})} n(\mathbf{r})}{\int d\mathbf{r}\; n(\mathbf{r})}$$

$$\varepsilon_k \rightarrow \tilde{\varepsilon}_k$$

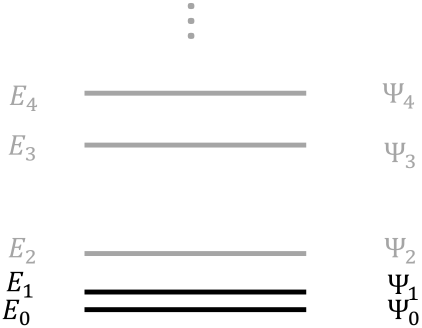
$$E_0^N = \sum_{k=1}^{N} \tilde{\varepsilon}_k$$

- Note that this procedure truly fixes (not up to a constant) the KS orbital energy levels.

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

DFT for canonical ensembles

$$\boxed{\hat{H}\Psi_I = E_I\Psi_I}$$



DFT for canonical ensembles

- An ensemble consists of a given number of states and weights assigned to these states.

- The simplest ensemble consists of the ground Ψ_0 and first excited Ψ_1 N-electron states, with weights $(1-w)$ and w, respectively.

- *Gross-Oliveira-Kohn* (GOK) variational principle:

$$(1-w)\langle\Psi|\hat{H}|\Psi\rangle + w\langle\Psi'|\hat{H}|\Psi'\rangle \geq (1-w)E_0 + wE_1 \qquad \text{with} \quad 0 \leq w \leq 1/2.$$

- The w-dependent lower bound $\boxed{E^w = (1-w)E_0 + wE_1}$ is the exact ensemble energy.

- Note that the ensemble energy is linear in w and its slope is the optical gap $\omega_{\rm g} = E_1 - E_0$.

E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2805 (1988).

DFT for canonical ensembles

- The Hohenberg–Kohn theorem can be extended to ensembles for any fixed weight w[1].
- In this context, the basic variable is the ensemble density:

$$n^w(\mathbf{r}) = (1-w)n_0^N(\mathbf{r}) + w\, n_1^N(\mathbf{r}) \qquad \text{where} \quad \int \mathrm{d}\mathbf{r}\, n^w(\mathbf{r}) = N.$$

- The xc energy of the ensemble $E_{\mathrm{xc}}^w[n]$ is a density functional which is w-dependent.

Why do we (now) need to consider w as an additional variable?

Why is the density not sufficient?

> Because a canonical ensemble density can be ground-state v-representable.[2]

> Variations in w (at fixed density) will become crucial when extracting excitation energies[3].

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[1] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2809 (1988).

[2] K. Deur, L. Mazouin, and E. Fromager, *Phys. Rev. B* **95**, 035120 (2017).

[3] K. Deur and E. Fromager, J. Chem. Phys. **150**, 094106 (2019).

The optical gap in GOK-DFT

- In GOK ensemble DFT[1], the optical gap can be expressed as follows,

$$\omega_{\rm g}=\varepsilon_{\rm L}^{N}-\varepsilon_{\rm H}^{N}+\underbrace{\left[\left.\frac{\partial E_{\rm xc}^{w}[n]}{\partial w}\right|_{n=n^{w}}\right]_{w=0}}_{\textit{derivative discontinuity}}$$

or, equivalently,[2]

$$\omega_{\rm g}=E_1^N-E_0^N \quad = \quad \tilde{\varepsilon}_{\rm L}^{N}-\tilde{\varepsilon}_{\rm H}^{N}+\left[\left.\frac{\partial E_{\rm xc}^{w}[n]}{\partial w}\right|_{n=n^{w}}\right]_{w=0}$$

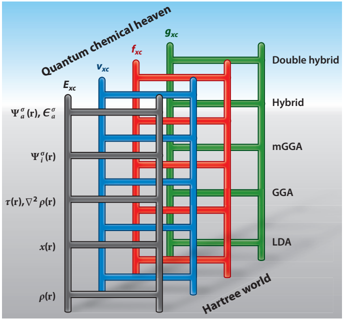
$$= \quad \underbrace{\left(\sum_{k=1}^{N-1}\tilde{\varepsilon}_k^N+\tilde{\varepsilon}_{\rm L}^{N}\right)+\left[\left.\frac{\partial E_{\rm xc}^{w}[n]}{\partial w}\right|_{n=n^{w}}\right]_{w=0}}_{E_1^N}-\underbrace{\sum_{k=1}^{N}\tilde{\varepsilon}_k^N}_{E_0^N}$$

[1] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2809 (1988).

[2] K. Deur and E. Fromager, J. Chem. Phys. **150**, 094106 (2019).

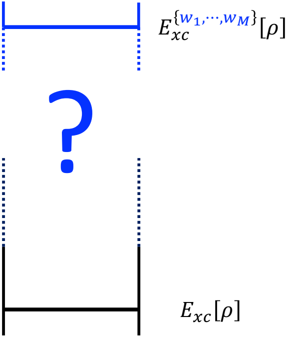
Jacob's ladder for ensembles?

DFT et TDDFT



M. Casida and M. Huix-Rotllant, Annu. Rev. Phys. Chem. 63, 287 (2012).

DFT for ensembles



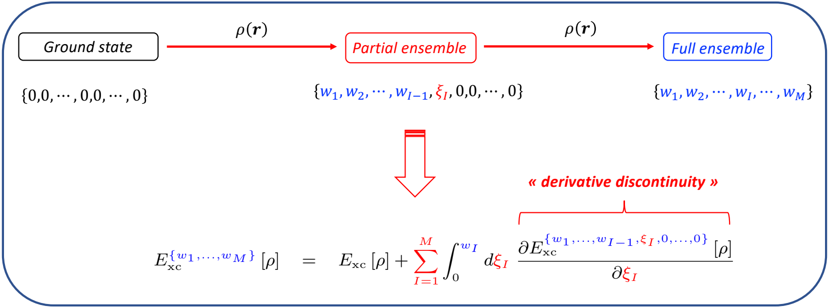
Generalized adiabatic connection for ensembles

- In ensemble DFT, the exchange-correlation functional becomes *weight-dependent*:

$$\boxed{E_{\rm xc}[n] = E_{\rm xc}^{\{w_1=0,\ldots,w_M=0\}}[n] \quad \longrightarrow \quad E_{\rm xc}^{\{w_1,\ldots,w_M\}}[n]}$$

- This weight dependence plays a crucial role in the calculation of *excited energy levels*.[1]

- Generalized adiabatic connection formalism for ensembles (GACE):[2,3]



$$\begin{tikzcd}\text{Ground state} \arrow[r, "\rho(\mathbf{r})"] & \text{Partial ensemble} \arrow[r, "\rho(\mathbf{r})"] & \text{Full ensemble}\end{tikzcd}$$

$\{0,0,\cdots,0,0,\cdots,0\}$ $\quad$ $\{w_1,w_2,\cdots,w_{I-1},\xi_I,0,0,\cdots,0\}$ $\quad$ $\{w_1,w_2,\cdots,w_I,\cdots,w_M\}$

$$E_{\rm xc}^{\{w_1,\ldots,w_M\}}[\rho] \quad = \quad E_{\rm xc}[\rho] + \sum_{I=1}^{M} \int_0^{w_I} d\xi_I \; \overbrace{\frac{\partial E_{\rm xc}^{\{w_1,\ldots,w_{I-1},\xi_I,0,\ldots,0\}}[\rho]}{\partial \xi_I}}^{\text{« derivative discontinuity »}}$$

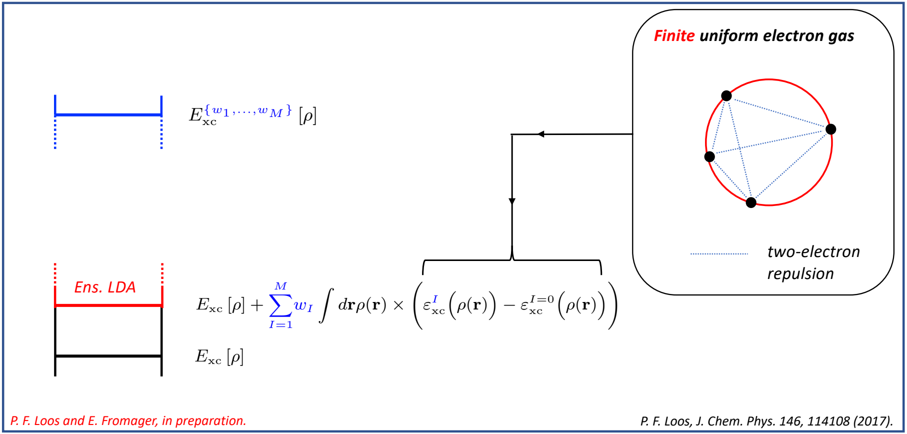
---

[1] K. Deur and E. Fromager, J. Chem. Phys. **150**, 094106 (2019).

[2] O. Franck and E. Fromager, *Mol. Phys.* **112**, 1684 (2014).

[3] K. Deur, L. Mazouin, and E. Fromager, Phys. Rev. B 95, 035120 (2017).

Jacob's ladder for ensembles? Let's try ...



$E_{\rm xc}^{\{w_1,\ldots,w_M\}}[\rho]$

Ens. LDA

$$E_{\rm xc}[\rho] + \sum_{I=1}^{M} w_I \int d\mathbf{r}\rho(\mathbf{r}) \times \overbrace{\Big(\varepsilon_{\rm xc}^{I}\big(\rho(\mathbf{r})\big) - \varepsilon_{\rm xc}^{I=0}\big(\rho(\mathbf{r})\big)\Big)}$$

$E_{\rm xc}[\rho]$

***Finite* uniform electron gas**

two-electron repulsion

P. F. Loos and E. Fromager, in preparation.

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

Ensemble DFT for charged excitations

- Can we formally express the fundamental gap as the optical one?

$$E_{\mathrm{g}} \overset{?}{=} \varepsilon_{\mathrm{L}}^{N} - \varepsilon_{\mathrm{H}}^{N} + \left[\left. \frac{\partial E_{\mathrm{xc}}^{\alpha}[n]}{\partial \alpha} \right|_{n=n^{\alpha}} \right]_{\alpha=0}$$

where $E_{\mathrm{xc}}^{\alpha}[n]$ would be the *to-be-identified* xc energy of a *grand canonical* ensemble.

Let us recall that ...

*> The problem is usually adressed by calculating the IP and the EA separately**.

> The total number $\mathcal{N}$ of electrons in a grand-canonical ensemble can be fractional.

> $\mathcal{N}$ can vary continuously between two integers.

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

Ensemble DFT for charged excitations

$$E_{\rm g} \overset{?}{=} \varepsilon_{\rm L}^{N} - \varepsilon_{\rm H}^{N} + \left[\left. \frac{\partial E_{\rm xc}^{\alpha}[n]}{\partial \alpha} \right|_{n=n^{\alpha}} \right]_{\alpha=0}$$

Let us also recall that ...

> *A grand-canonical ground-state ensemble density n is a piecewise linear function of $\mathcal{N}$[1]:*

$$n(\mathbf{r}) = \Big(N - \mathcal{N}\Big) \times n_0^{N-1}(\mathbf{r}) + \Big(\mathcal{N} - N + 1\Big) \times n_0^{N}(\mathbf{r}) \quad \text{where} \quad N - 1 \leq \mathcal{N} \leq N.$$

> *The grand-canonical ensemble weight* $\Big(\mathcal{N} - N + 1\Big)$ *is determined from the density n.*

... and therefore conclude that

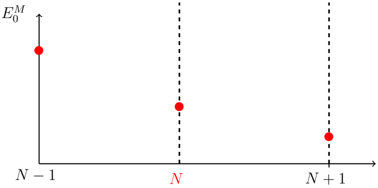
> *it makes no sense to introduce an ensemble weight α that would be independent from n.*

---

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

N-centered ensemble DFT

- It is actually *possible to push the analogy* with GOK-DFT *further*.
- We just have to choose *another* grand canonical ensemble.
- The latter will be referred to as N-centered ensemble in the following.



integral number M of electrons

- The N-centered ensemble density is defined as follows,

$$n_0^{\xi}(\mathbf{r}) = \xi n_0^{N-1}(\mathbf{r}) + \xi n_0^{N+1}(\mathbf{r}) + \Big(1-2\xi\Big) n_0^{N}(\mathbf{r}) \quad \text{where} \quad 0 \leq \xi \leq 1/2.$$

- Note that $\int d\mathbf{r}\; n_0^{\xi}(\mathbf{r}) = \xi(N-1) + \xi(N+1) + \Big(1-2\xi\Big)N = N$ $\leftarrow$ ξ-independent !

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

N-centered ensemble DFT

- Similarly, an N-centered ground-state ensemble energy can be constructed,

$$E_0^{\xi} = \xi E_0^{N-1} + \xi E_0^{N+1} + \Big(1 - 2\xi\Big) E_0^{N}.$$

- It is linear in ξ and the slope is equal to the fundamental gap.
- The latter ensemble energy is a functional of the N-centered ensemble density.
- Extension of DFT to N-centered ground-state ensembles:

$$E_{\rm xc}[n] = E_{\rm xc}^{N,\xi=0}[n] \quad \xrightarrow{\xi>0} \quad E_{\rm xc}^{N,\xi}[n]$$

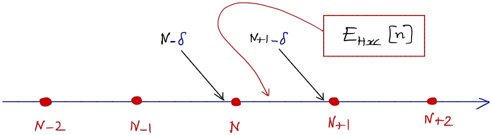
- *Exact* expression for the fundamental gap:

$$E_g^N = \frac{{\rm d}E_0^{\xi}}{{\rm d}\xi} = \varepsilon_{\rm L}^{N,\xi} - \varepsilon_{\rm H}^{N,\xi} + \left.\frac{\partial E_{\rm xc}^{N,\xi}[n]}{\partial \xi}\right|_{n=n_0^{\xi}} \qquad \leftarrow \forall \xi \in [0, 1/2]$$

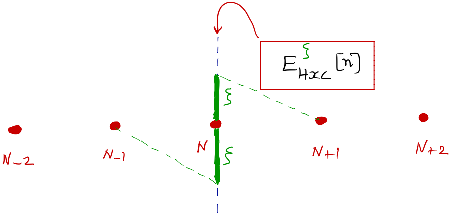
B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).

Comparing N-centered ensemble DFT with standard DFT

Standard approach (DFT for fractional electron numbers)[1]



N-centered ensemble DFT[2]



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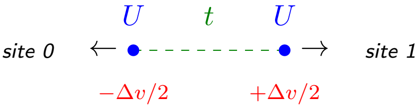
[1] J. P. Perdew and M. Levy, *Phys. Rev. Lett.* **51**, 1884 (1983).

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

Application to the Hubbard dimer



U t U

site 0 $\longleftarrow$ $\longrightarrow$ *site 1*

$-\Delta v/2$ $+\Delta v/2$

- Hamiltonian in second quantization: $\hat{\mathcal{H}} = \hat{\mathcal{T}} + \hat{U} + \dfrac{\Delta v}{2}(\hat{n}_1 - \hat{n}_0)$, where

$\hat{\mathcal{T}} = -t\sum_{\sigma=\uparrow,\downarrow}\left(\hat{a}^\dagger_{0\sigma}\hat{a}_{1\sigma} + \hat{a}^\dagger_{1\sigma}\hat{a}_{0\sigma}\right)$ $\longleftrightarrow$ kinetic energy

$\hat{U} = U\sum_{i=0}^{1}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$ $\longleftrightarrow$ two-electron repulsion

$\dfrac{\Delta v}{2}(\hat{n}_1 - \hat{n}_0)$ $\longleftrightarrow$ nuclear potential

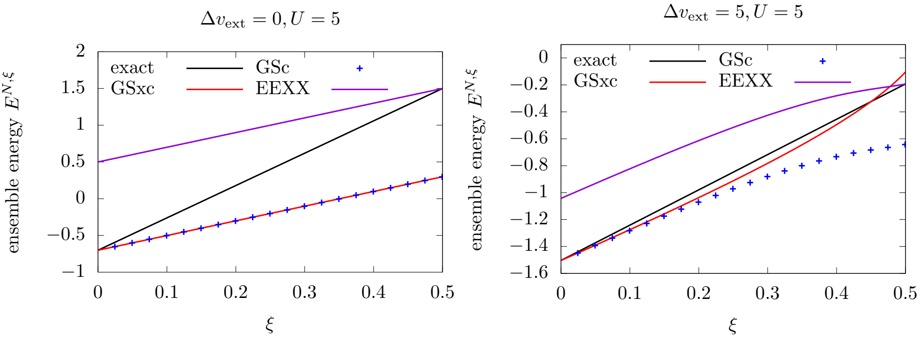
- In this context the density is a collection of two **site occupations** (n_0 and n_1).

- In the following, the number of electrons will be set to $N = 2$. Consequently, the ensemble density becomes a **single number** $\boxed{n = n_0}$ since $n_1 = 2 - n$.

D. J. Carrascal, J. Ferrer, J. C. Smith, and K. Burke, *J. Phys.: Condens. Matter* **27**, 393001 (2015).
K. Deur, L. Mazouin, and E. Fromager, *Phys. Rev. B* **95**, 035120 (2017).
K. Deur, L. Mazouin, B. Senjean, and E. Fromager, *Eur. Phys. J. B* **91**, 162 (2018) *[Hardy Gross special issue]*.

Application to the Hubbard dimer $[N = 2, t = 1]$

Ensemble energies in the symmetric (left panel) and asymmetric (right panel) cases.



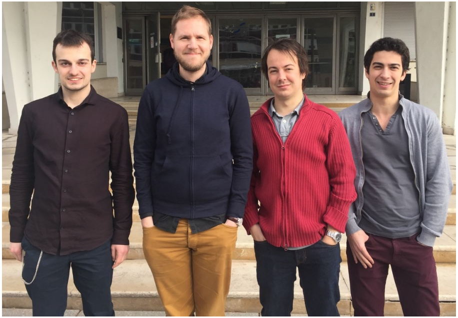
EEXX: $E_{\text{xc}}^{N,\xi}(n) \approx E_{\text{x}}^{N,\xi}(n)$

GSc: $E_{\text{xc}}^{N,\xi}(n) \approx E_{\text{x}}^{N,\xi}(n) \quad + E_{\text{c}}^{N,\xi=0}(n)$

"standard" xc functional ⟶ GSxc: $E_{\text{xc}}^{N,\xi}(n) \approx E_{\text{x}}^{N,\xi=0}(n) + E_{\text{c}}^{N,\xi=0}(n)$

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

Acknowledgments



From left to right: **Laurent Mazouin**, E. F., **Killian Deur**, **Bruno Senjean** (now in Leiden, The Netherlands),

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

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