Density-functional approximations from exact coordinate scaling constraints

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Exact exchange and correlation functionals

- Decomposition into *exchange* and *correlation* contributions:

$$E_{\mathrm{xc}}[n] = E_{\mathrm{x}}[n] + E_{\mathrm{c}}[n].$$

- *Exact* density-functional exchange energy:

$$E_{\mathrm{x}}[n] = \left\langle \Phi^{\mathrm{KS}}[n] \middle| \hat{W}_{\mathrm{ee}} \middle| \Phi^{\mathrm{KS}}[n] \right\rangle - E_{\mathrm{H}}[n].$$

- *Exact* correlation functional:

$$\begin{aligned} E_{\mathrm{c}}[n] &= F[n] - T_{\mathrm{s}}[n] - E_{\mathrm{H}}[n] - E_{\mathrm{x}}[n] \\ &= \langle \Psi[n] | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle - \left\langle \Phi^{\mathrm{KS}}[n] \middle| \hat{T} + \hat{W}_{\mathrm{ee}} \middle| \Phi^{\mathrm{KS}}[n] \right\rangle. \end{aligned}$$

Uniform coordinate scaling in wavefunctions and densities

- Let $\gamma > 0$ be a **scaling factor**.
- Applying a uniform coordinate scaling consists in multiplying each space coordinate by γ:

$$\begin{aligned} \mathbf{r} \equiv (x, y, z) \quad &\rightarrow \quad \gamma\mathbf{r} \equiv (\gamma x, \gamma y, \gamma z) \\ \mathrm{d}\mathbf{r} = \mathrm{d}x\mathrm{d}y\mathrm{d}z \quad &\rightarrow \quad \gamma^3 \mathrm{d}\mathbf{r} \end{aligned}$$

- Uniform coordinate scaling applied to the *density*:

$$n(\mathbf{r}) \quad \rightarrow \quad \boxed{n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})}$$

- Uniform coordinate scaling applied to an N-electron *wavefunction* [spin is unaffected by the scaling]:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \quad \rightarrow \quad \Psi_\gamma(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \gamma^{\frac{3N}{2}} \Psi(\gamma\mathbf{r}_1, \gamma\mathbf{r}_2, \ldots, \gamma\mathbf{r}_N)$$

Uniform coordinate scaling in wavefunctions and densities

EXERCISE

(1) Show that, if n integrates to N, then n_γ also integrates to N.

(2) Show that, if Ψ is normalized, then Ψ_γ is also normalized.

(3) Show that the density of Ψ equals n if and only if the density of Ψ_γ equals n_γ.

Exact scaling relations for $T_s[n]$ and $E_x[n]$

- We want to see how (some) universal density functionals are affected by the uniform coordinate scaling.
- We start with the simplest one, namely the Hartree functional $E_H[n]$.

EXERCISE *that we will solve together*

Show that the following scaling relation is fulfilled,

$$E_H[n_\gamma] = \gamma E_H[n].$$

- It can also be shown that the non-interacting kinetic energy and exact exchange energy functionals fulfill the following scaling relations:

$$\begin{aligned} T_s[n_\gamma] &= \gamma^2 T_s[n], \\ E_x[n_\gamma] &= \gamma E_x[n]. \end{aligned}$$

EXERCISE *(if you really want to understand where the above scaling relations come from)*

For that purpose, write the variational principle for the KS Hamiltonian $\hat{T} + \sum_{i=1}^{N} v^{KS}[n](\mathbf{r}_i)\times$, consider trial wavefunctions Ψ with density n [we denote $\Psi \rightarrow n$] and conclude that $T_s[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} | \Psi \rangle$. Deduce that $\Phi^{KS}_\gamma[n] = \Phi^{KS}[n_\gamma]$.

EXERCISE

For that purpose, write the variational principle for the KS Hamiltonian $\hat{T} + \sum_{i=1}^{N} v^{\rm KS}[n](\mathbf{r}_i)\times$, consider trial wavefunctions Ψ with density n [we denote $\Psi \rightarrow n$] and conclude that $T_{\rm s}\left[n\right] = \min\limits_{\Psi\rightarrow n} \langle\Psi|\hat{T}|\Psi\rangle$. Deduce that $\Phi^{\rm KS}_{\gamma}[n] = \Phi^{\rm KS}[n_{\gamma}]$.

Solution:

1) According to the Rayleigh–Ritz variational principle, we have for any wave function Ψ

$$\left\langle\Psi\middle|\hat{T} + \sum_{i=1}^{N} v^{\rm KS}[n](\mathbf{r}_i)\times\middle|\Psi\right\rangle = \left\langle\Psi\middle|\hat{T}\middle|\Psi\right\rangle + \left(v^{\rm KS}[n]\middle|n_{\Psi}\right)$$

$$\geq \left\langle\Phi^{\rm KS}[n]\middle|\hat{T} + \sum_{i=1}^{N} v^{\rm KS}[n](\mathbf{r}_i)\times\middle|\Phi^{\rm KS}[n]\right\rangle = T_{\rm s}[n] + \left(v^{\rm KS}[n]\middle|n\right),$$

where we used the notation $(v|n) = \int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r})$. If we now impose the density constraint $\Psi \rightarrow n$, *i.e.* $n_{\Psi} = n$, it comes $\left\langle\Psi\middle|\hat{T}\middle|\Psi\right\rangle \geq T_{\rm s}[n]$, thus leading to Levy's expression $T_{\rm s}\left[n\right] = \min\limits_{\Psi\rightarrow n} \langle\Psi|\hat{T}|\Psi\rangle$.

2) For any wave function Ψ *with density n_γ*,

$$\langle\Psi|\hat{T}|\Psi\rangle = -\frac{1}{2}\sum_{i=1}^{N}\int d\mathbf{r}_1\ldots\int d\mathbf{r}_N\;\Psi^*(\mathbf{r}_1,\ldots,\mathbf{r}_N)\nabla^2_{\mathbf{r}_i}\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N).$$

If we proceed with the change of variables $\mathbf{r}_i = \tilde{\mathbf{r}}_i/\gamma$ for all electron indices i and denote $\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \tilde{\Psi}(\gamma\mathbf{r}_1,\ldots,\gamma\mathbf{r}_N)$, then $\nabla^2_{\mathbf{r}_i}\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \gamma^2\left.\nabla^2_{\tilde{\mathbf{r}}_i}\tilde{\Psi}(\tilde{\mathbf{r}}_1,\ldots,\tilde{\mathbf{r}}_N)\right|_{\tilde{\mathbf{r}}_j\overset{\forall j}{=}\gamma\mathbf{r}_j}$, thus leading to

$$\langle\Psi|\hat{T}|\Psi\rangle = -\frac{\gamma^2}{2\times\gamma^{3N}}\sum_{i=1}^{N}\int d\tilde{\mathbf{r}}_1\ldots\int d\tilde{\mathbf{r}}_N\;\tilde{\Psi}^*(\tilde{\mathbf{r}}_1,\ldots,\tilde{\mathbf{r}}_N)\nabla^2_{\tilde{\mathbf{r}}_i}\tilde{\Psi}(\tilde{\mathbf{r}}_1,\ldots,\tilde{\mathbf{r}}_N).$$

Once we realize that $\dfrac{1}{\gamma^{\frac{3N}{2}}}\tilde{\Psi}\equiv\Psi_{\frac{1}{\gamma}}$ whose *density is $[n_\Psi]_{\frac{1}{\gamma}} = [n_\gamma]_{\frac{1}{\gamma}} = n$*, it comes

$$\langle\Psi|\hat{T}|\Psi\rangle = \gamma^2\left\langle\Psi_{\frac{1}{\gamma}}\middle|\hat{T}\middle|\Psi_{\frac{1}{\gamma}}\right\rangle \geq \gamma^2 T_{\mathrm{s}}[n].$$

We conclude that $\boxed{T_{\mathrm{s}}[n_\gamma] = \min\limits_{\Psi\rightarrow n_\gamma}\langle\Psi|\hat{T}|\Psi\rangle = \gamma^2 T_{\mathrm{s}}[n]}$. The minimum is reached when $\Psi_{\frac{1}{\gamma}} = \Phi^{\mathrm{KS}}[n]$ or, equivalently, $\Psi = \left[\Psi_{\frac{1}{\gamma}}\right]_\gamma = \Phi^{\mathrm{KS}}_\gamma[n]\equiv\Phi^{\mathrm{KS}}[n_\gamma]$.

3) We can now prove the exact coordinate scaling constraint for the exchange functional. Since

$$\begin{aligned} E_{\mathrm{x}}[n_\gamma] &= \left\langle \Phi^{\mathrm{KS}}[n_\gamma] \middle| \hat{W}_{\mathrm{ee}} \middle| \Phi^{\mathrm{KS}}[n_\gamma] \right\rangle - E_{\mathrm{H}}[n_\gamma] \\ &= \left\langle \Phi^{\mathrm{KS}}_\gamma[n] \middle| \hat{W}_{\mathrm{ee}} \middle| \Phi^{\mathrm{KS}}_\gamma[n] \right\rangle - \gamma E_{\mathrm{H}}[n], \end{aligned}$$

where

$$\begin{aligned} \left\langle \Phi^{\mathrm{KS}}_\gamma[n] \middle| \hat{W}_{\mathrm{ee}} \middle| \Phi^{\mathrm{KS}}_\gamma[n] \right\rangle &= \sum_{i<j}^{N} \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_N \, \frac{\left| \Phi^{\mathrm{KS}}_\gamma[n](\mathbf{r}_1, \ldots, \mathbf{r}_N) \right|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &= \gamma \times \gamma^{3N} \sum_{i<j}^{N} \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_N \, \frac{\left| \Phi^{\mathrm{KS}}[n](\gamma\mathbf{r}_1, \ldots, \gamma\mathbf{r}_N) \right|^2}{|\gamma\mathbf{r}_i - \gamma\mathbf{r}_j|} \\ &\overset{\mathbf{r}_j \rightarrow \tilde{\mathbf{r}}_j = \gamma \mathbf{r}_j}{=} \gamma \left\langle \Phi^{\mathrm{KS}}[n] \middle| \hat{W}_{\mathrm{ee}} \middle| \Phi^{\mathrm{KS}}[n] \right\rangle, \end{aligned}$$

it comes

$$E_{\mathrm{x}}[n_\gamma] = \gamma \left[\left\langle \Phi^{\mathrm{KS}}[n] \middle| \hat{W}_{\mathrm{ee}} \middle| \Phi^{\mathrm{KS}}[n] \right\rangle - E_{\mathrm{H}}[n] \right] = \boxed{\gamma E_{\mathrm{x}}[n] = E_{\mathrm{x}}[n_\gamma]}.$$

Local density-functional approximations

- In the *local density approximation* (LDA), any functional $S[n]$ is approached with a *function* $s\big(n(\mathbf{r})\big)$ of $n(\mathbf{r})$ as follows:

$$S[n] \approx \int \mathrm{d}\mathbf{r}\ s\big(n(\mathbf{r})\big)n(\mathbf{r})$$

- Simple LDAs to the non-interacting kinetic and exchange energies:

$$T_{\mathrm{s}}[n] \approx T_{\mathrm{s}}^{\mathrm{LDA}}[n] = A \int \mathrm{d}\mathbf{r}\ n^{\alpha}(\mathbf{r}), \qquad E_{\mathrm{x}}[n] \approx E_{\mathrm{x}}^{\mathrm{LDA}}[n] = B \int \mathrm{d}\mathbf{r}\ n^{\beta}(\mathbf{r})$$

EXERCISE *that we will solve together*

Show that, if we want these LDAs to fulfill the exact *scaling relations*, then we should have $\alpha = \frac{5}{3}$ and $\beta = \frac{4}{3}$. With $A = \frac{3}{10}(3\pi^2)^{2/3}$ and $B = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$ we recover the non-interacting kinetic (so-called Thomas–Fermi) and exchange energies of a *uniform electron gas* with density n, respectively.

A uniform electron gas (UEG) is a particular type of extended (usually infinite) electronic system where the local potential, which describes a "positive background", reads $v[n](\mathbf{r}) = -\frac{1}{2}\int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$, $n(\mathbf{r})$ *being the electronic density. Note that the full system is neutral in charge and the electronic density is uniform, i.e.* $n(\mathbf{r}) = n = \left.\frac{N}{V}\right|_{N\rightarrow+\infty, V\rightarrow+\infty}$.

EXERCISE *that we will solve together*

Explain why the ground-state energy of the UEG can be written as $E_0\big[v[n]\big] = F[n] - E_{\mathrm{H}}[n]$, where $F[n]$ and $E_{\mathrm{H}}[n]$ are the universal Hohenberg–Kohn and Hartree functionals, respectively, both evaluated for the uniform density n. $E_0\big[v[n]\big]$ is usually expressed as $E_0\big[v[n]\big] = \int d\mathbf{r}\, \varepsilon\big(n(\mathbf{r})\big)n(\mathbf{r})$, where the energy per electron $\varepsilon(n)$ can be parameterized from accurate (Quantum Monte Carlo, for example) calculations performed for different n values. Show that an *LDA correlation functional* can be constructed as $E_{\mathrm{c}}^{\mathrm{LDA}}[n] = \int d\mathbf{r}\, \varepsilon_{\mathrm{c}}\big(n(\mathbf{r})\big)n(\mathbf{r})$, where

$$\boxed{\varepsilon_{\mathrm{c}}(n) = \varepsilon(n) + \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{1/3} - \frac{3}{10}(3\pi^2)^{2/3}n^{2/3}.}$$