Uniform coordinate scaling and adiabatic connection formalism in density-functional theory

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Exact exchange and correlation functionals

- Decomposition into \textit{exchange} and \textit{correlation} contributions:

\[ E_{xc}[n] = E_x[n] + E_c[n]. \]

- \textit{Exact} density-functional exchange energy:

\[ E_x[n] = \left\langle \Phi^{KS}[n] \right| \hat{W}_{ee} \left| \Phi^{KS}[n] \right\rangle - E_H[n]. \]

- \textit{Exact} correlation functional:

= \left\langle \Psi[n] \right| \hat{T} + \hat{W}_{ee} \left| \Psi[n] \right\rangle - \left\langle \Phi^{KS}[n] \right| \hat{T} + \hat{W}_{ee} \left| \Phi^{KS}[n] \right\rangle. \]
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 $\gamma$:

$$r \equiv (x, y, z) \rightarrow \gamma r \equiv (\gamma x, \gamma y, \gamma z)$$

$$dr = dxdydz \rightarrow \gamma^3 dr$$

Uniform coordinate scaling applied to the density:

$$n(r) \rightarrow n_\gamma(r) = \gamma^3 n(\gamma r)$$

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

$$\Psi(r_1, r_2, \ldots, r_N) \rightarrow \Psi_\gamma(r_1, r_2, \ldots, r_N) = \gamma^{3N/2} \Psi(\gamma r_1, \gamma r_2, \ldots, \gamma r_N)$$
EXERCISE

(1) Show that, if \( n \) integrates to \( N \), then \( n_\gamma \) also integrates to \( N \).

(2) Show that, if \( \Psi \) is normalized, then \( \Psi_\gamma \) is also normalized.

(3) Show that the density of \( \Psi \) equals \( n \) if and only if the density of \( \Psi_\gamma \) equals \( n_\gamma \).
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**

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:

$$T_s[n_\gamma] = \gamma^2 T_s[n],$$
$$E_x[n_\gamma] = \gamma E_x[n].$$

**EXERCISE**

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 $\Psi$ 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 $\Phi^{KS}_\gamma[n] = \Phi^{KS}[n_\gamma].$
Adiabatic connection formalism

Let us consider the \textit{partially-interacting} Schrödinger equation

\[
\left( \hat{T} + \lambda \hat{W}_{ee} + \sum_{i=1}^{N} v^\lambda(r_i) \times \right) \Psi^\lambda = E^\lambda \Psi^\lambda,
\]

where \(0 \leq \lambda \leq 1\).

The potential \(v^\lambda(r)\) is adjusted such that the ground-state density constraint \(n_{\Psi^\lambda}(r) = n(r)\) is fulfilled for any value of \(\lambda\) in the range \(0 \leq \lambda \leq 1\).

Note that both Schrödinger and Kohn–Sham equations are recovered when \(\lambda = 1\) and \(\lambda = 0\), respectively.

Varying \(\lambda\) \textit{continuously} from 0 to 1 establishes a (so-called \textit{adiabatic}) connection between the real (interacting) and fictitious (non-interacting) Kohn–Sham worlds.
(1) Prove the Hellmann–Feynman theorem \( \frac{dE^\lambda}{d\lambda} = \left\langle \Psi^\lambda \left| \frac{\partial \hat{H}^\lambda}{\partial \lambda} \right| \Psi^\lambda \right\rangle \), where \( \hat{H}^\lambda = \hat{T} + \lambda \hat{W}_{ee} + \sum_{i=1}^N v^\lambda(r_i) \times \). 

(2) Deduce that

\[
E_c[n] = \int_0^1 \frac{d}{d\lambda} \left[ E^\lambda - (v^\lambda | n) \right] d\lambda - \left\langle \Psi^{\lambda=0} | \hat{W}_{ee} | \Psi^{\lambda=0} \right\rangle \\
= \int_0^1 \left[ \left\langle \Psi^\lambda | \hat{W}_{ee} | \Psi^\lambda \right\rangle - \left\langle \Psi^{\lambda=0} | \hat{W}_{ee} | \Psi^{\lambda=0} \right\rangle \right] d\lambda
\]