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

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Exact exchange and correlation functionals

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

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

- *Exact* density-functional exchange energy:

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

- *Exact* correlation functional:

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

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:

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

- 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 $T_{\rm s}[n]$ and $E_{\rm x}[n]$

- 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 $E_{\rm H}[n]$.

EXERCISE

Show that the following scaling relation is fulfilled,

$$E_{\rm H}[n_\gamma] = \gamma E_{\rm H}[n].$$

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

$$\begin{aligned} T_{\rm s}[n_\gamma] &= \gamma^2 T_{\rm s}[n], \\ E_{\rm x}[n_\gamma] &= \gamma E_{\rm x}[n]. \end{aligned}$$

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 $T_{\rm s}[n] = \min_{\Psi\rightarrow n} \langle\Psi|\hat{T}|\Psi\rangle$. Deduce that $\Phi_\gamma^{\rm KS}[n] = \Phi^{\rm KS}[n_\gamma]$.

Adiabatic connection formalism

- Let us consider the *partially-interacting* Schrödinger equation

$$\left(\hat{T} + \lambda \hat{W}_{\rm ee} + \sum_{i=1}^{N} v^{\lambda}(\mathbf{r}_i) \times \right) \Psi^{\lambda} = E^{\lambda} \Psi^{\lambda},$$

  where $0 \leq \lambda \leq 1$.

- The potential $v^{\lambda}(\mathbf{r})$ is adjusted such that the ground-state density constraint $n_{\Psi^{\lambda}}(\mathbf{r}) = n(\mathbf{r})$ is fulfilled for any value of λ 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 λ *continuously* from 0 to 1 establishes a (so-called *adiabatic*) *connection* between the real (interacting) and fictitious (non-interacting) Kohn–Sham worlds.

EXERCISE

(1) Prove the Hellmann–Feynman theorem $\dfrac{\mathrm{d}E^{\lambda}}{\mathrm{d}\lambda} = \left\langle \Psi^{\lambda} \middle| \dfrac{\partial \hat{H}^{\lambda}}{\partial \lambda} \middle| \Psi^{\lambda} \right\rangle$,

where $\hat{H}^{\lambda} = \hat{T} + \lambda \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} v^{\lambda}(\mathbf{r}_i)\times$.

(2) Deduce that

$$
\begin{aligned}
E_{\mathrm{c}}[n] &= \int_0^1 \frac{\mathrm{d}}{\mathrm{d}\lambda}\left[E^{\lambda} - (v^{\lambda}|n)\right]\mathrm{d}\lambda - \left\langle \Psi^{\lambda=0}\middle|\hat{W}_{\mathrm{ee}}\middle|\Psi^{\lambda=0}\right\rangle \\
&= \int_0^1 \left[\left\langle \Psi^{\lambda}\middle|\hat{W}_{\mathrm{ee}}\middle|\Psi^{\lambda}\right\rangle - \left\langle \Psi^{\lambda=0}\middle|\hat{W}_{\mathrm{ee}}\middle|\Psi^{\lambda=0}\right\rangle\right]\mathrm{d}\lambda
\end{aligned}
$$