

Supporting information for:

Domain Separation in Density Functional Theory

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1 Operators in first quantization form

We employed second quantization in our developments. However, the energy operators can also be expressed in first quantization, leading to the same results we derived in the main body. In terms of the position operator, the electron-electron repulsion operator for domain X can be written as:

$$\hat{W}_X = \frac{1}{2} \sum_{n \neq m} \frac{w_X(\hat{\mathbf{r}}_n) w_X(\hat{\mathbf{r}}_m)}{|\hat{\mathbf{r}}_m - \hat{\mathbf{r}}_n|} . \quad (1)$$

This interaction operator is a variation of the standard Coulomb repulsion operator:

$$\hat{W} = \frac{1}{2} \sum_{n \neq m} \frac{1}{|\hat{\mathbf{r}}_m - \hat{\mathbf{r}}_n|} . \quad (2)$$

The kinetic and electron-nuclei attraction energy operators can be expressed in the usual form:

$$\begin{aligned}\hat{T} &= -\frac{1}{2} \sum_{n=1}^N \nabla_{\hat{\mathbf{r}}_n}^2 \\ \hat{V} &= \sum_{n=1}^N v(\hat{\mathbf{r}}_n) ,\end{aligned}\tag{3}$$

where N is the total number of particles. The operator $\hat{W}_{X,Y}$ also reads:

$$\hat{W}_{X,Y} = \frac{1}{2} \sum_{n \neq m} \frac{w_X(\hat{\mathbf{r}}_n) w_Y(\hat{\mathbf{r}}_m)}{|\hat{\mathbf{r}}_n - \hat{\mathbf{r}}_m|} .\tag{4}$$

2 Note on the wave functions $\tilde{\Psi}$, $\tilde{\Phi}$, and $\tilde{\Phi}_0$

These wave functions were employed to define the partial HXC functionals. Recall the definition of the functional $G_{l,X}$:

$$G_{l,X}[\rho] = \min_{\substack{\Phi \rightarrow \rho \\ \Phi \in \mathcal{L}}} \langle \Phi | \hat{T} + \hat{W}_X | \Phi \rangle ,\tag{5}$$

for a given density ρ , and $\mathcal{L} = \mathcal{S}$. We denoted $\tilde{\Phi}$ as a wave function that minimizes the right hand side of the above equation. This can also be expressed as:

$$\tilde{\Phi}[\rho] = \operatorname{argmin}_{\Phi \rightarrow \rho, \Phi \in \mathcal{S}} \langle \Phi | \hat{T} + \hat{W}_X | \Phi \rangle ,\tag{6}$$

where argmin stands for the solution of the minimization problem shown on the right hand side of Eq. (5). Similarly, for the wave functions $\tilde{\Psi}$ and $\tilde{\Phi}_0$ we can write:

$$\begin{aligned}\tilde{\Phi}_0[\rho] &= \operatorname{argmin}_{\Phi \rightarrow \rho, \Phi \in \mathcal{S}} \langle \Phi | \hat{T} | \Phi \rangle \\ \tilde{\Psi}[\rho] &= \operatorname{argmin}_{\Psi \rightarrow \rho, \Psi \in \mathcal{H}} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle .\end{aligned}\tag{7}$$

As we mentioned in the main document, these wave functions are functionals of ρ , the reason being the density constraint shown in the above relations. With a wave function such as $\tilde{\Phi}[\rho]$ we can express, for instance, $E_{\text{Hx}}^{\text{s},X}$ as $E_{\text{Hx}}^{\text{s},X}[\rho] = \langle \tilde{\Phi}[\rho] | \hat{W}_X | \tilde{\Phi}[\rho] \rangle$.

3 Expansion based on KS-DFT for the functional $G_{\text{s},X}$

We can express the functional $G_{\text{s},X}$ as follows:

$$G_{\text{s},X}[\rho] = \langle \tilde{\Phi} | \hat{T} + \hat{W}_X | \tilde{\Phi} \rangle , \quad (8)$$

an alternative form of the above reads:

$$G_{\text{s},X}[\rho] = T_{\text{s}}[\rho] + \mathcal{E}_{\text{Hxc}}^{\text{s},X}[\rho] , \quad (9)$$

where

$$\begin{aligned} \mathcal{E}_{\text{Hx}}^{\text{s},X}[\rho] &= \langle \tilde{\Phi} | \hat{T} + \hat{W}_X | \tilde{\Phi} \rangle - \langle \tilde{\Phi}_0 | \hat{T} | \tilde{\Phi}_0 \rangle \\ &= \langle \tilde{\Phi} | \hat{W}_X | \tilde{\Phi} \rangle + (\langle \tilde{\Phi} | \hat{T} | \tilde{\Phi} \rangle - \langle \tilde{\Phi}_0 | \hat{T} | \tilde{\Phi}_0 \rangle) . \end{aligned} \quad (10)$$

The term in parenthesis resembles a kinetic correlation term. However, the interpretation is different because $\tilde{\Phi}$ is not a correlated wave function, it is the obtained when the constrained search defining $G_{\text{s},X}$ is formally carried out over the space of Slater determinants.

In the case where the wave functions $\tilde{\Phi}_0$ and $\tilde{\Phi}$ are close to each other, we can assume shown in parenthesis in Eq. (10) is negligible. Therefore

$$\mathcal{E}_{\text{Hx}}^{\text{s},X}[\rho] \approx \langle \tilde{\Phi} | \hat{W}_X | \tilde{\Phi} \rangle . \quad (11)$$

This is a functional that can be approximated in the uniform electron gas limit, and by employing standard plane wave functions.

4 Treatment of Spin

For the case of single-determinants, the starting point is the constrained search:

$$G_{s,X}[\rho_{\uparrow}, \rho_{\downarrow}] = \min_{\Phi \rightarrow \rho_{\uparrow}, \rho_{\downarrow}} \langle \Phi | \hat{T} + \hat{W}_X | \Phi \rangle . \quad (12)$$

The formal definition of the HXC functionals can be performed following the procedure shown in the main text. Here we only focus on practical aspects of the implementation.

To simplify the expression of energies, it is convenient to introduce the spin density matrix:

$$D_{X,\sigma\mu\nu} = \sum_j C_{\mu}^{j,\sigma} C_{\nu}^{j,\sigma} , \quad (13)$$

if both indices μ and ν are associated to the atom (or atoms) contained in region X , otherwise $D_{X,\sigma\mu\nu} = 0$ (we denote the spin-dependent LCAO coefficients as $\{C_{\mu}^{j,\sigma}\}$). In coordinate representation, we approximate the density matrix $\gamma_{X,\sigma}(\mathbf{r}', \mathbf{r})$ as

$$\begin{aligned} \gamma_{X,\sigma}(\mathbf{r}', \mathbf{r}) &= w_X(\mathbf{r}') w_X(\mathbf{r}) \gamma_{\sigma}(\mathbf{r}', \mathbf{r}) \\ &\approx \sum_{\mu\nu \in X} D_{X,\sigma\mu\nu} \phi_{\mu}(\mathbf{r}') \phi_{\nu}(\mathbf{r}) , \end{aligned} \quad (14)$$

where $\gamma_{\sigma}(\mathbf{r}', \mathbf{r}) = \sum_i \psi_{i\sigma}(\mathbf{r}') \psi_{i\sigma}(\mathbf{r})$, and $\{\psi_{i\sigma}\}$ are the spin orbitals, so $\psi_{i\sigma}(\mathbf{r}) = \sum_{\mu} C_{\mu}^{i,\sigma} \phi_{\mu}(\mathbf{r})$.

With the above density matrices the spin decomposed exchange matrix, $K_{X,\sigma\mu\nu}$ reads:

$$\begin{aligned} K_{X,\sigma\mu\nu} &= \int d\mu_X(\mathbf{r}) d\mu_X(\mathbf{r}') \phi_{\mu}(\mathbf{r}') \frac{\gamma_{\sigma}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_{\nu}(\mathbf{r}) \\ &\approx \int d^3\mathbf{r} d^3\mathbf{r}' \phi_{\mu}(\mathbf{r}') \frac{\gamma_{X,\sigma}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_{\nu}(\mathbf{r}) . \end{aligned} \quad (15)$$

The exchange energy for spin σ is thus expressed as:

$$K_{X,\sigma} = \sum_{\mu\nu} D_{\sigma,\mu\nu} K_{X,\sigma\mu\nu} , \quad (16)$$

with $D_{\sigma,\mu\nu}$ denoting the full spin density matrix, $D_{\sigma,\mu\nu} = \sum_j C_\mu^{j,\sigma} C_\nu^{j,\sigma}$. Following similar steps as in the spin-unpolarized case, it can be shown that the ground-state energy reads:

$$E_0 = \sum_{i\sigma} f_{i\sigma} \int d^3\mathbf{r} \psi_{i\sigma}(\mathbf{r}) \left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) \right] \psi_{i\sigma}(\mathbf{r}) + E_H[\rho_0] - K'_X + \bar{E}_{\text{xc}}^{\text{s}}[\rho_\uparrow, \rho_\downarrow] , \quad (17)$$

where

$$K'_X = \frac{1}{2} \left(K_{X,\uparrow} + K_{X,\downarrow} \right) , \quad (18)$$

and $f_{i\sigma} = 1$ for occupied orbitals. The partial XC energy is decomposed as:

$$\bar{E}_{\text{xc}}^{\text{s}}[\rho_\uparrow, \rho_\downarrow] = E_c[\rho_\uparrow, \rho_\downarrow] + \frac{1}{2} \left\{ E_{\text{x}}^{\text{s},X}[2\rho_{X,\uparrow}] + E_{\text{x}}^{\text{s},X}[2\rho_{X,\downarrow}] \right\} , \quad (19)$$

where $E_{\text{x}}^{\text{s},X}$ is the functional shown in Eq. (27) of the main text, and $\rho_{X,\sigma}(\mathbf{r}) = \gamma_{X,\sigma}(\mathbf{r}, \mathbf{r})$.

Minimization of the above functional leads to the eigenvalue equation:

$$\left\{ -\frac{1}{2}\nabla^2 + \hat{j}_\uparrow + \hat{j}_\downarrow - \hat{k}_{X,\sigma} + \bar{u}_{\text{xc},\sigma}^{\text{s}}(\mathbf{r}) + v(\mathbf{r}) \right\} \psi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma} \psi_{i\sigma}(\mathbf{r}) , \quad (20)$$

where

$$\hat{j}_\tau \psi_{i\sigma}(\mathbf{r}) = \left(\int d^3\mathbf{r}' \frac{\sum_j |\psi_{j\tau}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right) \psi_{i\sigma}(\mathbf{r}) , \quad (21)$$

with $\tau = \uparrow$ or \downarrow , and

$$\hat{k}_{X,\sigma} \psi_{i\sigma}(\mathbf{r}) = \sum_j \left[\int d\mu_X(\mathbf{r}') \frac{\psi_{i\sigma}(\mathbf{r}') \psi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right] w_X(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) . \quad (22)$$

A matrix element of the above operator is $K_{X,\sigma\mu\nu} = (\phi_\mu | \hat{k}_{X,\sigma} | \phi_\nu)$, and is approximated as shown in Eq. (15). The partial XC potential reads:

$$\bar{u}_{\text{xc},\sigma}^{\text{s}}(\mathbf{r}) = \frac{\delta E_c}{\delta \rho_\sigma(\mathbf{r})} + \frac{\delta E_{\text{x}}^{\text{s},X}}{\delta \rho_{X,\sigma}(\mathbf{r})} . \quad (23)$$

5 Hydrogen dissociation energy data

The calculations for the radicals, including the hydrogen atom, proceeded as described in the previous section. The local spin-density approximation (LSDA) was employed for the correlation energy (VWN-5 form).

Table S1: Ground-state energies calculated by several methods (with 6-31G basis) for the molecules involved in the dissociation reaction $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$. Energies expressed in atomic units, except the row below DE_H , which expressed in eV units.

Energies	LDA-nLE	CCSD(T)	LDA	HF
CH_3	-40.0267	-39.6298	-39.4038	-39.5325
H	-0.4819	-0.4760	-0.4819	-0.4760
CH_4	-40.7355	-40.2999	-40.0898	-40.1802
DE_H	0.2269	0.1941	0.2041	0.1717
DE_H (eV)	6.17	5.28	5.55	4.67
Deviation (%)	16.9	—	5.1	11.6

The deviation percentage is calculated as $100 \% \times |(E_Y - E_{\text{CCSD(T)}})/E_{\text{CCSD(T)}}|$, where E_Y is the ground-state electronic energy determined with method Y , which is LDA-nLE, LDA, or HF.

Table S2: Same as in Table 1, but for the reaction $\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3 + \text{H}$

Energies	LDA-nLE	CCSD(T)	LDA	HF
C_2H_3	-77.2761	-77.5462	-77.1206	-77.3498
H	-0.5205	-0.4760	-0.4819	-0.4760
C_2H_4	-78.0074	-78.2165	-77.8027	-78.0028
DE_H	0.2108	0.1943	0.2002	0.1769
DE_H (eV)	5.74	5.29	5.45	4.81
Deviation (%)	8.5	—	3.0	9.0