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Nonuniform coordinate scaling requirements for exchange-correlation energy

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Consider the nonuniformly scaled electron density $n_\lambda^x(x,y,z)=\lambda n(\lambda x,y,z)$, with analogous definitions for n_λ^y and n_λ^z. It is shown that it is generally true that $E_{\text{xc}}[n_\lambda^x]\neq E_{\text{xc}}[n_\lambda^y]\neq E_{\text{xc}}[n_\lambda^z]$, where E_{xc} is the exact exchange-correlation energy. A corresponding *inequality* also holds for the correlation component of E_{xc} when the correlation component is defined in one of the meaningful ways. In contrast, *equalities* always hold for the local-density approximations to these exact functionals. In other words, the local-density approximations for exchange correlation and for correlation alone do not distinguish between nonuniform scaling along different coordinates.

I. INTRODUCTION

For the purpose of improving approximate exchange-correlation density functionals it was recently shown[1] that the local-density approximation to the exchange-correlation functional does *not distinguish* between nonuniform scaling along different coordinates. That is,

$$E_{\text{xc}}^{\text{LDA}}[n_\lambda^x]=E_{\text{xc}}^{\text{LDA}}[n_\lambda^y]=E_{xc}^{\text{LDA}}[n_\lambda^z] , \tag{1}$$

where the nonuniformly scaled density is

$$n_\lambda^x(x,y,z)=\lambda n(\lambda x,y,z) . \tag{2}$$

Equation (1) follows from[1]

$$E_{\text{xc}}^{\text{LDA}}[n_\lambda^q]=\int n(\mathbf{r})\varepsilon_{\text{xc}}[\lambda n(\mathbf{r})]d^3r, \quad q=x,y,z \tag{3}$$

where $\epsilon_{\text{xc}}[n(\mathbf{r})]$ is the exchange-correlation energy per electron of a uniform electron gas of density $n(\mathbf{r})$. In contrast to Eq. (1), it was also recently conjectured[1] that the exact exchange-correlation functional E_{xc} satisfies the following inequalities for a general density without special symmetry:

$$E_{\text{xc}}[n_\lambda^x]\neq E_{\text{xc}}[n_\lambda^y]\neq E_{\text{xc}}[n_\lambda^z] . \tag{4}$$

Accordingly, it is the purpose of this article to prove Eq. (4).

II. EXCHANGE-CORRELATION ENERGY

To arrive at Eq. (4), we start with

$$F[n_\lambda^x]\leq\langle\lambda^{N/2}\Psi_n^{\min}(\lambda x_1,y_1,z_1,\ldots,\lambda x_N,y_N,z_N)|\hat{\mathrm{T}}+\hat{\mathrm{V}}_{e\text{-}e}|\lambda^{N/2}\Psi_n^{\min}(\lambda x_1,y_1,z_1,\ldots,\lambda x_N,y_N,z_N)\rangle , \tag{5}$$

which follows directly from[1,2] the constrained-search identification[3,4] of the universal Hohenberg-Kohn[5] functional $F[n]$. Here, $\Psi_n^{\min}$ is that wave function which is constrained to yield n and minimizes $\langle\hat{\mathrm{T}}+\hat{\mathrm{V}}_{e\text{-}e}\rangle$, and $F[n_\lambda^x]$ is partitioned as

$$F[n_\lambda^x]=T_s[n_\lambda^x]+U[n_\lambda^x]+E_{\text{xc}}[n_\lambda^x] , \tag{6}$$

where T_s is the Kohn-Sham[6] noninteracting kinetic energy and U is the classical electron-electron repulsion energy.

By taking into consideration that $\hat{\mathrm{T}}$ is homogeneous of degree -2 and $\hat{\mathrm{V}}_{e\text{-}e}$ is homogeneous of degree -1, Eq. (5) becomes

$$F[n_\lambda^x]-(\lambda^2T_x[n]+T_y[n]+T_z[n]+\int\Gamma_n^{\min}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)[\lambda^{-2}(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2]^{-1/2}d^3r_1d^3r_2)\leq 0 , \tag{7}$$

where $\Gamma_n^{\min}$ is the second-order matrix of $\Psi_n^{\min}$ and where

$$T_q[n]=\left\langle\Psi_n^{\min}\left|-\frac{1}{2}\frac{\partial^2}{\partial q^2}\right|\Psi_n^{\min}\right\rangle . \tag{8}$$

Next, utilize the fact that Eq. (5) exhibits its maximum at $\lambda=1$ and apply Eq. (6) to obtain

$$\left[\frac{\partial E_{\text{xc}}[n_\lambda^x]}{\partial\lambda}\right]_{\lambda=1}=2T_x[n]-2T_s^x[n]+\int\Gamma_n^{\min}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)(x_1-x_2)^2|\mathbf{r}_1-\mathbf{r}_2|^{-3}d^3r_1d^3r_2 - \int n(\mathbf{r}_1)n(\mathbf{r}_2)(x_1-x_2)^2|\mathbf{r}_1-\mathbf{r}_2|^{-3}d^3r_1d^3r_2 , \tag{9}$$

where

$$T_s^x = \left\langle \Phi_n^{\min} \left| -\frac{1}{2}\frac{\partial^2}{\partial x^2} \right| \Phi_n^{\min} \right\rangle , \tag{10}$$

and where $\Phi_n^{\min}$ is the Kohn-Sham noninteracting wave function (often a single determinant).[4,7,8] The second term in Eq. (9) arises from[1]

$$\left[\frac{\partial T_s[n_\lambda^x]}{\partial \lambda} \right]_{\lambda=1} = 2T_s^x[n] , \tag{11}$$

and the last term arises from taking $(\partial U[n_\lambda^x]/\partial\lambda)_{\lambda=1}$. Finally, it should be clear that Eq. (9) generalizes to

$$\left[\frac{\partial E_{\mathrm{xc}}[n_\lambda^q]}{\partial \lambda} \right]_{\lambda=1} = 2T_q[n] - 2T_s^q[n] + \int \Gamma_n^{\min}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)(q_1-q_2)^2|\mathbf{r}_1-\mathbf{r}_2|^{-3}d^3r_1d^3r_2 - \int n(\mathbf{r}_1)n(\mathbf{r}_2)(q_1-q_2)^2|\mathbf{r}_1-\mathbf{r}_2|^{-3}d^3r_1d^3r_2 , \tag{12}$$

for q equal to x, y, or z, so that Eq. (4) follows because, for asymmetric n, the right-hand-side of Eq. (12) clearly varies with q.

III. CORRELATION ENERGY

There are slightly different ways of defining the correlation energy in density-functional theory. The easiest definition to consider in the context of this paper is[9,10]

$$E_c[n] = \langle \Psi_n^{\min}|\hat{T}+\hat{V}_{e\text{-}e}|\Psi_n^{\min}\rangle - \langle \Phi_{n,\mathrm{HF}}^{\min}|\hat{T}+\hat{V}_{e\text{-}e}|\Phi_{n,\mathrm{HF}}^{\min}\rangle , \tag{13}$$

where $\Phi_{n,\mathrm{HF}}^{\min}$ is that single determinant which yields n and minimizes[3,11] $\langle \hat{T}+\hat{V}_{e\text{-}e}\rangle$, and where HF signifies Hartree-Fock. By following the techniques used for the whole E_{xc} above it follows that

$$\left[\frac{\partial E_c[n_\lambda^q]}{\partial \lambda} \right]_{\lambda=1} = 2T_q[n] - 2T_{\mathrm{HF}}^q[n] + \int \Gamma_n^{\min}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)(q_1-q_2)^2|\mathbf{r}_1-\mathbf{r}_2|^{-3}d^3r_1d^3r_2 - \int \Gamma_{n,\mathrm{HF}}^{\min}(\mathbf{r}_1\cdot\mathbf{r}_2|\mathbf{r}_1\cdot\mathbf{r}_2)(q_1-q_2)^2|\mathbf{r}_1-\mathbf{r}_2|^{-3}d^3r_1d^3r_2 , \tag{14}$$

where

$$T_{\mathrm{HF}}^q[n] = \langle \Phi_{n,\mathrm{HF}}^{\min}|\hat{T}|\Phi_{n,\mathrm{HF}}^{\min}\rangle , \tag{15}$$

and $\Gamma_{n,\mathrm{HF}}^{\min}$ is the 2-matrix for $\Phi_{n,\mathrm{HF}}^{\min}$.

Equation (14) reveals that $E_c[n_\lambda^q]$ depends upon q. In contrast, any local-density approximation to E_c gives a result which is independent of q:

$$E_c^{\mathrm{LDA}}[n_\lambda^q] = \int n(\mathbf{r})\epsilon_c[\lambda n(\mathbf{r})]d^3r \tag{16}$$

for all q.

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