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Exact and approximate forms of the kinetic energy functional $T_{\mathrm{s}}[\rho]$ for molecules obtained via local-scaling transformations

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Abstract. By means of a constructive procedure based on local-scaling transformations, we have obtained the following exact form for the noninteractive kinetic energy functional of general molecular systems:

$$T_{\mathrm{s}}[\rho] = T_{\mathrm{W}}[\rho] + \sum_I \int_{\Omega_I} \mathbf{d}^3\mathbf{r}_I \rho^{5/3}(\mathbf{r}_I)[1 + \mathbf{r}_I \cdot \nabla_{\mathbf{r}_I} \ln\lambda(\mathbf{r}_I)]^{-2/3} \times [3 + \mathbf{r}_I \cdot \nabla_{\mathbf{r}_I} \ln\lambda(\mathbf{r}_I)]^2 \left[\tau_N^I(\mathbf{r}_I) + \tau_N^{\mathrm{C}}(\mathbf{r}_I) + \kappa_N^I(\mathbf{r}_I) + \kappa_N^{\mathrm{C}}(\mathbf{r}_I)\right],$$

where $\lambda(\mathbf{r})$ is the local-scaling transformation function, $T_{\mathrm{W}}[\rho]$ is the von Weiszäcker term and $\tau_N^I(\mathbf{r}_I)$ and $\kappa_N^I(\mathbf{r}_I)$are the radial and angular enhancement factors, respectively, within an atomic domain Ω_I. The terms $\tau_N^{\mathrm{C}}(\mathbf{r}_I)$ and $\tau_N^{\mathrm{C}}(\mathbf{r}_I)$(where C stands for “complement of I”) contain all contributions to the radial and angular enhancement factors within Ω_I coming from the “tails” of functions centered on nuclei outside Ω_I. Also, in the context of an “atoms-in-a-molecule” approach, we discuss the construction of approximations to the kinetic energy enhancement factors appearing in the previous expression for $T_{\mathrm{s}}[\rho]$.

Keywords: Kinetic energy functional – DFT – Local-scaling transformations

Introduction

There has been a renewed interest in the development of density-dependent kinetic energy functionals because such functionals avoid the N-dependence problem inherent in the Kohn–Sham and related methods [1]. As in the Kohn–Sham approach the central idea is to solve orbital equations, the exact noninteracting kinetic energy functional is introduced in its orbital representation. However, as there are N such equations, the treatment of large systems meets with practical difficulties. For this reason, the use of orbital-free kinetic energy functionals has been advocated [2].

There is, nonetheless, a formidable obstacle barring the way to such orbital-free formulations. The fact is that since by the virial theorem the exact kinetic energy is equal in magnitude to the exact total energy, any attempt to model the kinetic energy must meet the same criterion of accuracy as is required for the total energy. This contrasts quite markedly with the case of the exchange energy, which is an order of magnitude smaller that the total energy, and even more with that of the correlation energy, which is 2 orders of magnitude smaller. Thus, while a relative error of 1/100 in the correlation energy leads to an error of 1/10,000 in the total energy the same relative error in the kinetic energy leads to an error of 1/100 in the total energy.

It is clear then, that the accuracy of any kinetic energy model functional must be at least 2 orders of magnitude greater than that of the correlation energy model functional. That this is not a trivial task is reflected by the fact that to date there are no kinetic energy functionals capable of attaining chemical accuracy [1, 3]. Moreover, even the problem of having kinetic energy functionals that lead to the correct shell structure in atoms has not been completely solved [4].

In the present work, following some earlier developments dealing with (one-dimensional) atomic radial functions [5, 6, 7, 8], we employ a constructive procedure for the purpose of generating an exact functional form for the noninteracting kinetic energy of a molecular system. The construction of this functional is possible through the use of local-scaling transformations [7, 9, 10] adapted to three-dimensional atom-centered functions. It must be mentioned that this constructive approach does not lead to the “universal functional” of the Hohenberg–Kohn version of density functional theory

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[11, 12, 13], valid for all systems, but rather to forms containing the usual $\rho^{5/3}$ term multiplied by a system-dependent enhancement factor [7].

We describe the generation of the kinetic energy functional through the application of local-scaling transformations in Sect. 2. We describe the exact decomposition of this functional into a collection of atom-centered functionals in Sect. 3. We consider a particular realization, albeit exact, of this partition based on an atoms-in-a-molecule approach in Sect. 4. We discuss an atoms-in-a-molecule approximation where all interaction terms are dropped and discuss, for the case of diatomic molecules, how a computational scheme may be devised for including these neglected terms in Sect. 5. Finally, we present some conclusions. in Sect. 6.

Constructive derivation of the kinetic energy functional for molecules

Consider a single Slater determinant:

$$\Phi([\rho];\mathbf{r}_1,s_1,\ldots\mathbf{r}_N,s_N) = \frac{\det}{\sqrt{N!}}\{\phi_1([\rho];\mathbf{r}_1)\sigma_1(s_1)\ldots\phi_N([\rho];\mathbf{r}_N)\sigma_N(s_N)\}. \tag{1}$$

The density-dependent orbitals $\{\phi_i([\rho];\mathbf{r})\}_{i=1}^N$ are obtained by applying local-scaling transformations to an arbitrary "generating" set $\{\phi_i(\mathbf{r})\}_{i=1}^N$ according to

$$\phi_i([\rho];\mathbf{r}) = \sqrt{\frac{\rho(\mathbf{r})}{\rho_{\mathrm{g}}(\mathbf{r}^T)}}\phi_i(\mathbf{r}^T), \tag{2}$$

where ρ_{g} is the density associated with the generating set:

$$\rho_{\mathrm{g}}(\mathbf{r}) = \sum_{i=1}^N \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}). \tag{3}$$

The basic problem we solve in the present work is that of obtaining from

$$T[\Phi([\rho])] = \frac{1}{2}\sum_{i=1}^N \int \mathbf{d}^3\mathbf{r}\nabla_\mathbf{r}\phi_i^*([\rho];\mathbf{r})\cdot\nabla_\mathbf{r}\phi_i([\rho];\mathbf{r}) \tag{4}$$

the corresponding kinetic energy functional expressed as a functional of the one-particle density, ρ.

In view of Eq. (2) we can rewrite Eq. (4) as follows:

$$\begin{aligned} T[\Phi([\rho])] =& T_{\mathrm{W}}[\rho] + \frac{1}{4}\int \mathbf{d}^3\mathbf{r}\rho(\mathbf{r})\frac{1}{\rho_{\mathrm{g}}^2(\mathbf{r}^{\mathrm{T}})}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \\ & \Big[\left|\phi_i^*(\mathbf{r}^{\mathrm{T}})\nabla_\mathbf{r}\phi_j(\mathbf{r}^T) - \phi_j(\mathbf{r}^{\mathrm{T}})\nabla_\mathbf{r}\phi_i^*(\mathbf{r}^{\mathrm{T}})\right|^2 \\ & + \left|\phi_i(\mathbf{r}^{\mathrm{T}})\nabla_\mathbf{r}\phi_j(\mathbf{r}^{\mathrm{T}}) - \phi_j(\mathbf{r}^{\mathrm{T}})\nabla_\mathbf{r}\phi_i(\mathbf{r}^{\mathrm{T}})\right|^2\Big], \end{aligned} \tag{5}$$

where we have used the notation $|X|^2 = XX^*$ and where $T_{\mathrm{W}}[\rho]$ is the von Weiszäcker term:

$$T_{\mathrm{W}}[\rho] = \frac{1}{8}\int \mathbf{d}^3\mathbf{r}\frac{[\nabla_\mathbf{r}\rho(\mathbf{r})]^2}{\rho(\mathbf{r})}. \tag{6}$$

Moreover, using Eq. (62) the kinetic energy becomes

$$\begin{aligned} T[\Phi([\rho])] = & T_{\mathrm{W}}[\rho] + \frac{1}{4}\int \mathbf{d}^3\mathbf{r}\rho(\mathbf{r})\lambda^2(\mathbf{r})\frac{[3+\mathbf{r}\cdot\nabla_\mathbf{r}\ln\lambda(\mathbf{r})]^2}{\rho_{\mathrm{g}}^2(\mathbf{r}^{\mathrm{T}})} \\ & \times\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\Big[\left|\phi_i^*(\mathbf{r}^{\mathrm{T}})\nabla_{\mathbf{r}^{\mathrm{T}}}\phi_j(\mathbf{r}^{\mathrm{T}}) - \phi_j(\mathbf{r}^{\mathrm{T}})\nabla_{\mathbf{r}^{\mathrm{T}}}\phi_i^*(\mathbf{r}^{\mathrm{T}})\right|^2 \\ & + \left|\phi_i(\mathbf{r}^{\mathrm{T}})\nabla_{\mathbf{r}^{\mathrm{T}}}\phi_j(\mathbf{r}^{\mathrm{T}}) - \phi_j(\mathbf{r}^{\mathrm{T}})\nabla_{\mathbf{r}^{\mathrm{T}}}\phi_i(\mathbf{r}^{\mathrm{T}})\right|^2\Big]. \end{aligned} \tag{7}$$

Now, making use of Eq. (57), we can rewrite the kinetic energy as the following implicit functional of the one-particle density:

$$T[\Phi([\rho])] = T_{\mathrm{W}}[\rho] + \frac{1}{2}\int \mathbf{d}^3\mathbf{r}\rho^{5/3}(\mathbf{r})A_N([\rho,\{\phi_i\}];\mathbf{r}), \tag{8}$$

where the kinetic energy total modulating factor is

$$A_N([\rho,\{\phi_i\}];\mathbf{r}) = L1^{-2/3}([\rho];\mathbf{r})L3^2([\rho];\mathbf{r})t_N([\rho,\{\phi_i\}];\mathbf{r}), \tag{9}$$

with (see Appendix 1)

$$L1([\rho];\mathbf{r}) = [1+\mathbf{r}\cdot\nabla_\mathbf{r}\ln\lambda(\mathbf{r})], \tag{10}$$

$$L3([\rho];\mathbf{r}) = [3+\mathbf{r}\cdot\nabla_\mathbf{r}\ln\lambda(\mathbf{r})] \tag{11}$$

and

$$\begin{aligned} t_N([\rho,\{\phi_i\}];\mathbf{r}) = & \frac{1}{2\rho_{\mathrm{g}}^{8/3}(\mathbf{r}^{\mathrm{T}})}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \\ & \times\Big[\left|\phi_i^*(\mathbf{r}^{\mathrm{T}})\nabla_{\mathbf{r}^{\mathrm{T}}}\phi_j(\mathbf{r}^{\mathrm{T}}) - \phi_j(\mathbf{r}^{\mathrm{T}})\nabla_{\mathbf{r}^{\mathrm{T}}}\phi_i^*(\mathbf{r}^{\mathrm{T}})\right|^2 \\ & + \left|\phi_i(\mathbf{r}^{\mathrm{T}})\nabla_{\mathbf{r}^{\mathrm{T}}}\phi_j(\mathbf{r}^{\mathrm{T}}) - \phi_j(\mathbf{r}^{\mathrm{T}})\nabla_{\mathbf{r}^{\mathrm{T}}}\phi_i(\mathbf{r}^{\mathrm{T}})\right|^2\Big]. \end{aligned} \tag{12}$$

This form becomes explicit when a particular choice of $\{\phi_i\}$ is made and when $\mathbf{r}^{\mathrm{T}}$ is expressed as an analytic function of the density (an approximate analytic form is given by Padé approximants).

Introducing the explicit form for $\nabla_{\mathbf{r}^{\mathrm{T}}}$ given by Eq. (63), we can decompose t_N into its radial and angular components, τ_N and κ_N , respectively:

$$t_N([\rho,\{\phi_i\}];\mathbf{r}_I) = \tau_N([\rho,\{\phi_i\}];\mathbf{r}_I) + \kappa_N([\rho,\{\phi_i\}];\mathbf{r}_I), \tag{13}$$

where

$$\tau_N([\rho,\{\phi_i\}];\mathbf{r}) = \frac{1}{2\rho_{\mathrm{g}}^{8/3}(\mathbf{r}^{\mathrm{T}})}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left[\left|f_{i^*j}(\phi)\right|^2 + \left|f_{ij}(\phi)\right|^2\right] \tag{14}$$

and

$$\begin{aligned}\kappa_N([\rho,\{\phi_i\}];\mathbf{r}) = &\frac{1}{2\rho_{\mathrm{g}}^{8/3}(\mathbf{r}^{T})}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\\ &\times\left[\frac{1}{(\mathrm{r}^{\mathrm{T}})^2}\left(\left|g_{i^*j}(\phi)\right|^2 + \left|g_{ij}(\phi)\right|^2\right)\right.\\ &\left.+\frac{1}{(\mathrm{r}^{\mathrm{T}})^2\sin^2\theta}\left(\left|h_{i^*j}(\phi)\right|^2 + \left|h_{ij}(\phi)\right|^2\right)\right].\end{aligned} \tag{15}$$

In these equations,

$$f_{i^*j}(\phi) = \phi_i^*\left(\mathbf{r}^{\mathrm{T}}\right)\frac{\partial\phi_j\left(\mathbf{r}^{\mathrm{T}}\right)}{\partial r^T} - \phi_j\left(\mathbf{r}^{\mathrm{T}}\right)\frac{\partial\phi_i\left(\mathbf{r}^{\mathrm{T}}\right)}{\partial r^{\mathrm{T}}}, \tag{16}$$

$$g_{i^*j}(\phi) = \phi_i^*\left(\mathbf{r}^{\mathrm{T}}\right)\frac{\partial\phi_j\left(\mathbf{r}^{\mathrm{T}}\right)}{\partial\theta} - \phi_j\left(\mathbf{r}^{\mathrm{T}}\right)\frac{\partial\phi_i^*\left(\mathbf{r}^{\mathrm{T}}\right)}{\partial\theta} \tag{17}$$

and

$$h_{i^*j}(\phi) = \phi_i^*\left(\mathbf{r}^{\mathrm{T}}\right)\frac{\partial\phi_j\left(\mathbf{r}^{\mathrm{T}}\right)}{\partial\varphi} - \phi_j\left(\mathbf{r}^{\mathrm{T}}\right)\frac{\partial\phi_i^*\left(\mathbf{r}^{\mathrm{T}}\right)}{\partial\varphi}, \tag{18}$$

with similar definitions $f_{ij^*}(\phi)$, $f_{ij}(\phi)$, $f_{i^*j^*}(\phi)$, etc.

Reduction of the molecular kinetic energy functional to a collection of atomic functionals

In the previous general expressions for the noninteracting kinetic functional obtained in the context of local-scaling transformations, the density-dependent transformed vector $\mathbf{r}^{\mathrm{T}}$ appears explicitly in the expansion of the modulating factor $t_N([\rho,\{\phi_i\};\mathbf{r})$. Thus, any practical implementation of the previous formulas requires the calculation of $\mathbf{r}^{\mathrm{T}}$ over the whole molecule. Now, because the molecular density is essentially made up by a collection of slightly distorted atomic densities (i.e., densities which have their maxima at the atomic nuclei), the locally scaled vector $\mathbf{r}^{\mathrm{T}}$ can be interpreted in terms of a collection of atomic vectors $\{\mathbf{r}_I^{\mathrm{T}}\}_{I=1}^{M}$, each one of them ascribed to an atomic volume $\mathbf{\Omega}_I$.

In consequence, we treat the calculation of the density-dependent radial vector $\mathbf{r}^{\mathrm{T}}([\rho];\mathbf{r})$ for a multicenter case by decomposing $\Re^3$ into a collection of atomic volumes $\mathbf{\Omega}_I$, each one centered about a nucleus I such that $\Re^3 = \bigcup_{I=1}^{K}\mathbf{\Omega}_I$.

We assume that both the generating and the transformed molecular densities $\rho_{\mathrm{g}}(\mathbf{r})$ and $\rho(\mathbf{r})$, respectively, are defined in the context of the Born–Oppenheimer approximation for the same fixed frame of neuclear coordinates. In addition, we require that these densities satisfy the normalization condition yielding the total number of electrons when integrated over the whole three-dimensional space. The details of the procedure which allows us to obtain the transformed vectors $\mathbf{r}_I^{\mathrm{T}}([\rho];\mathbf{r})$ are discussed in Appendix 2.

The integration of the kinetic energy functional given by Eq. (8) over these atomic subvolumes is given by

$$\begin{aligned}T[\Phi([\rho])] =&\sum_I\int_{\Omega_I}\mathbf{d}^3\mathbf{r}t_{\mathrm{W}}([\rho];\mathbf{r})\\ &+\frac{1}{2}\sum_I\int_{\Omega_I}\mathbf{d}^3\mathbf{r}\rho^{5/3}(\mathbf{r})A_N([\rho,\{\phi_i\}];\mathbf{r}),\end{aligned} \tag{19}$$

where $t_{\mathrm{W}}([\rho,\{\phi_i\}];\mathbf{r})$ is the von Weiszäcker kinetic energy density.

In order to treat in detail the decomposition of the modulating factor $A_N([\rho,\{\phi_i];\mathbf{r})$ over the atomic subvolumes, we refer to the usual expansion of the molecular orbital set $\{\phi_i\}_{i=1}^{N}$ in terms of atomic-centered functions:

$$\phi_i(\mathbf{r}) = \sum_{J=1}^{M}\phi^J(\mathbf{r}_J), \tag{20}$$

where $\mathbf{r}_J = \mathbf{r}-\mathbf{R}_J$. But, as the origin of the coordinate system is arbitrary, we are free to set $\mathbf{R}_I=0$ in Eq. (19) when integrating over each one of the domains $\mathbf{\Omega}_I$. When this is done, we have $\mathbf{r}=\mathbf{r}_I$.

It follows from this fact that we can rewrite the radial modulating factor as

$$\tau_N([\rho,\{\phi_i\}];\mathbf{r}_I) = \tau_N^I([\rho,\{\phi_i\}];\mathbf{r}_I) + \tau_N^{\mathrm{C}}([\rho,\{\phi_i\}];\mathbf{r}_I), \tag{21}$$

where $\tau_N^I([\rho,\{\phi_i\}];\mathbf{r}_I)$ contains all contributions coming from functions centered within $\mathbf{\Omega}_I$ and $\tau_N^{\mathrm{C}}([\rho,\{\phi_i\}];\mathbf{r}_I)$ (here C stands for "complement" of $\mathbf{\Omega}_I$) the "tails" of functions centered outside $\mathbf{\Omega}_I$.

Using Eq. (20), one can readily see that the terms appearing in Eq. (21) are given by

$$\tau_N^I([\rho,\{\phi_i\}];\mathbf{r}_I) = \frac{1}{2\rho_{\mathrm{g}}^{8/3}(\mathbf{r}^{\mathrm{T}})}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left[\left|f_{i^*j}^{II}(\phi)\right|^2 + \left|f_{ij}^{II}(\phi)\right|^2\right] \tag{22}$$

and

$$\tau_N^{\mathrm{C}}([\rho,\{\phi_i\}];\mathbf{r}_I) = \frac{1}{2\rho_{\mathrm{g}}^{8/3}(\mathbf{r}^{\mathrm{T}})}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left[\left|F_{i^*j}^{\mathrm{C}}(\phi)\right|^2 + \left|F_{ij}^{\mathrm{C}}(\phi)\right|^2\right]. \tag{23}$$

In the previous expression,

$$f^{II}_{i^*j}(\phi) = \phi^{*I}_i\left(\mathbf{r}^{\mathrm{T}}_I\right)\frac{\partial\phi^I_j\left(\mathbf{r}^{\mathrm{T}}_I\right)}{\partial r^{\mathrm{T}}_I} - \phi^I_j\left(\mathbf{r}^{\mathrm{T}}_I\right)\frac{\partial\phi^{*I}_i\left(\mathbf{r}^{\mathrm{T}}_I\right)}{\partial r^{\mathrm{T}}_I} \tag{24}$$

and

$$F^{\mathrm{C}}_{i^*j}(\phi) = \left|f_{i^*j}(\phi)\right|^2 - \left|f^{II}_{i^*j}(\phi)\right|^2, \tag{25}$$

where

$$f_{i^*j}(\phi) = \phi^*_i\left(\mathbf{r}^{\mathrm{T}}_I\right)\frac{\partial\phi_j\left(\mathbf{r}^{\mathrm{T}}_I\right)}{\partial r^{\mathrm{T}}_I} - \phi_j\left(\mathbf{r}^{\mathrm{T}}_I\right)\frac{\partial\phi_i\left(\mathbf{r}^{\mathrm{T}}_I\right)}{\partial r^{\mathrm{T}}_I}. \tag{26}$$

Similarly, we have the following decomposition for the angular modulating factor:

$$\kappa_N([\rho,\{\phi_i\}];\mathbf{r}_I) = \kappa^I_N([\rho,\{\phi_i\}];\mathbf{r}_I) + \kappa^{\mathrm{C}}_N([\rho,\{\phi_i\}];\mathbf{r}_I), \tag{27}$$

where

$$\begin{aligned}\kappa^I_N([\rho,\{\phi_i\}];\mathbf{r}_I) = & \frac{1}{2\rho^{8/3}_{\mathrm{g}}(\mathbf{r}^{\mathrm{T}})}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \\ & \times\left\{\frac{1}{\left(r^{\mathrm{T}}_I\right)^2}\left(\left|g^{II}_{i^*j}(\phi)\right|^2 + \left|g^{II}_{ij}(\phi)\right|^2\right)\right. \\ & \left.+\frac{1}{\left(r^{\mathrm{T}}_I\right)^2\sin^2\theta}\left(\left|h^{II}_{i^*j}(\phi)\right|^2 + \left|h^{II}_{ij}(\phi)\right|^2\right)\right\}\end{aligned} \tag{28}$$

and

$$\begin{aligned}\kappa^{\mathrm{C}}_N([\rho,\{\phi_i\}];\mathbf{r}_I) = & \frac{1}{2\rho^{8/3}_{\mathrm{g}}(\mathbf{r}^{\mathrm{T}})}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left[\frac{1}{\left(r^{\mathrm{T}}_I\right)^2}\left(\left|G^{\mathrm{C}}_{i^*j}(\phi)\right|^2\right.\right. \\ & \left.+\left|G^{\mathrm{C}}_{ij}(\phi)\right|^2\right) + \frac{1}{\left(r^{\mathrm{T}}_I\right)^2\sin^2\theta} \\ & \left.\times\left(\left|H^{\mathrm{C}}_{i^*j}(\phi)\right|^2 + \left|H^{\mathrm{C}}_{ij}(\phi)\right|^2\right)\right].\end{aligned} \tag{29}$$

The auxiliary terms are defined by

$$g^{II}_{i^*j}(\phi) = \phi^{*I}_i\left(\mathbf{r}^{\mathrm{T}}_I\right)\frac{\partial\phi^I_j\left(\mathbf{r}^{\mathrm{T}}_I\right)}{\partial\theta} - \phi^I_j\left(\mathbf{r}^{\mathrm{T}}_I\right)\frac{\partial\phi^{*I}_i\left(\mathbf{r}^{\mathrm{T}}_I\right)}{\partial\theta} \tag{30}$$

and

$$h^{II}_{i^*j}(\phi) = \phi^{*I}_i\left(\mathbf{r}^{\mathrm{T}}_I\right)\frac{\partial\phi^I_j\left(\mathbf{r}^{\mathrm{T}}_I\right)}{\partial\varphi} - \phi^I_j\left(\mathbf{r}^{\mathrm{T}}_I\right)\frac{\partial\phi^{*I}_i\left(\mathbf{r}^{\mathrm{T}}_I\right)}{\partial\varphi}. \tag{31}$$

In addition, we have

$$G^{\mathrm{C}}_{i^*j}(\phi) = \left|g_{i^*j}(\phi)\right|^2 - \left|g^{II}_{i^*j}(\phi)\right|^2 \tag{32}$$

and

$$H^{\mathrm{C}}_{i^*j}(\phi) = \left|h_{i^*j}(\phi)\right|^2 - \left|h^{II}_{i^*j}(\phi)\right|^2. \tag{33}$$

An atoms-in-a-molecule representation

Let us consider the 1-matrix in the representation of the atom-centered functions $\left\{\{\chi^I_i\mathbf{r}_I\}^{m_I}_{i=1}\right\}^M_{I=1}$:

$$\begin{aligned}D^1(\mathbf{r},\mathbf{r}') &= \overrightarrow{\phi}^{\dagger}(\mathbf{r})\overrightarrow{\phi}(\mathbf{r}') = \overrightarrow{\chi}^{\dagger}(\mathbf{r})\mathbf{C}^{\dagger}\mathbf{C}\overrightarrow{\chi}(\mathbf{r}') \\ &= \overrightarrow{\chi}^{\dagger}(\mathbf{r})\mathbf{N}\overrightarrow{\chi}(\mathbf{r}').\end{aligned} \tag{34}$$

In this expression, $\overrightarrow{\phi}^{\dagger}(\mathbf{r}) = \phi_1(\mathbf{r})\ldots\phi_N(\mathbf{r})$ is the row vector comprising the N occupied molecular orbitals, $\mathbf{C} = \overrightarrow{\mathbf{C}}^1\ldots\overrightarrow{\mathbf{C}}^M$ is the matrix of expansion coefficients (comprising the vectors $\overrightarrow{\mathbf{C}}^I$ over atomic functions) and $\overrightarrow{\chi}^{\dagger}(\mathbf{r}) = \overrightarrow{\chi}^{1\dagger}(\mathbf{r}_1)\ldots\overrightarrow{\chi}^{N\dagger}(\mathbf{r}_M)$, where $\overrightarrow{\chi}^{I\dagger}(\mathbf{r}_I) = \chi^{I\dagger}_1(\mathbf{r}_I)\ldots\chi^{I\dagger}_{m_I}(\mathbf{r}_I)$.

The 1-matrix $\mathbf{N}$ is

$$\mathbf{N} = \begin{pmatrix}\mathbf{N}^{11} & \cdots & \mathbf{N}^{1M} \\ \vdots & \vdots & \vdots \\ \mathbf{N}^{M1} & \cdots & \mathbf{N}^{MM}\end{pmatrix}, \tag{35}$$

where $\mathbf{N}^{IJ} = \vec{\mathbf{C}}^{I\dagger}\vec{\mathbf{C}}^J$.

At each center I we define the atoms-in-a-molecule [14, 15, 16] atomic functions as

$$\overrightarrow{\psi}^I(\mathbf{r}_I) = \mathbf{U}^I\overrightarrow{\chi}^I(\mathbf{r}_I) \tag{36}$$

such that they diagonalize the matrix $\mathbf{N}^{II}$:

$$\mathbf{n}^{II} = \mathbf{U}^I\mathbf{N}^{II}\mathbf{U}^{I\dagger}. \tag{37}$$

This allows us to separate the 1-matrix into a diagonal part, expanded in terms of the atom-in-a-molecule functions and a nondiagonal part embracing the delocalized contributions:

$$D^1(\mathbf{r},\mathbf{r}) = D^1_{\mathrm{aim}}(\mathbf{r},\mathbf{r}) + D^1_{\mathrm{deloc}}(\mathbf{r},\mathbf{r}). \tag{38}$$

In terms of the atoms-in-a-molecule atomic functions $\{\{\psi^I_{g,i}(\mathbf{r}_I)\}^{m_I}_{i=1}\}^M_{I=1}$ (where $m_I \geqslant \mathbf{N}_I$, with $\sum_{I=1}^{M}\mathbf{N}_I = \mathbf{N}$) the atom-in-a-molecule part of the 1-matrix is

$$D^1_{\mathrm{aim}}(\mathbf{r},\mathbf{r}) = \sum_{I=1}^{M}\sum_{i=1}^{m_I} n^{II}_{ii}\psi^I_{g,i}(\mathbf{r}_I)\psi^I_{g,i}(\mathbf{r}'_I). \tag{39}$$

Each atom-in-a-molecule has a charge $\mathbf{N}_I = \sum_{i=1}^{m_I}\mathbf{n}^{\mathbf{II}}_{\mathbf{ii}}$ which is, in general, noninteger. Also, since $m_I \geq N_I$, there appear ground and excited atomic orbitals with fractional occupation numbers.

Let us consider now an atom-in-a-molecule decomposition of $T[\Phi_\rho]$. Dividing the total space into atomic subvolumes Ω_I, we have

$$T[\Phi[\rho]] = T_{\mathrm{W}}[\rho] + \frac{1}{2}\sum_{I=1}^{M}\int_{\Omega_I} \mathbf{d}^3\mathbf{r}_I \rho^{5/3}(\mathbf{r}_I) A_N([\rho,\{\phi_i\}];\mathbf{r}_I), \tag{40}$$

$$\begin{aligned} &A_N([\rho,\{\phi_i\}];\mathbf{r}_I) \\ &\quad = L\big([\rho];\mathbf{r}_I^{\mathrm{T}}\big)\big(t_N^I([\rho,\{\phi_i\}];\mathbf{r}_I) + t_N^{\mathrm{C}}([\rho,\{\phi_i\}];\mathbf{r}_I)\big), \end{aligned} \tag{41}$$

$$\begin{aligned} t_N^I([\rho,\{\phi_i\}];\mathbf{r}_I) = {} & \frac{1}{4\rho_{\mathrm{g}}^{8/3}(\mathbf{r}_I^{\mathrm{T}})}\sum_{i=1}^{m_I}\sum_{j=1}^{m_I} n_{ii}^{II} n_{jj}^{II} \\ & \times \left(\left|t_{i^*,j}^{II}([\psi];\mathbf{r}_I^{\mathrm{T}})\right|^2 + \left|t_{i,j}^{II}([\psi];\mathbf{r}_I^{\mathrm{T}})\right|^2\right) \end{aligned} \tag{42}$$

and

$$t_{i^*,j}^{II}([\psi];\mathbf{r}_I^{\mathrm{T}}) = \psi_i^*(\mathbf{r}_I^{\mathrm{T}})\nabla_{\mathbf{r}_I^{\mathrm{T}}}\psi_j^*(\mathbf{r}_I^{\mathrm{T}}) - \psi_j(\mathbf{r}_I^{\mathrm{T}})\nabla_{\mathbf{r}_I^{\mathrm{T}}}\psi_i^*(\mathbf{r}_I^{\mathrm{T}}). \tag{43}$$

Clearly, t_N^{C} is the complement of t_N^I and $\mathbf{r}_I^{\mathrm{T}}$ is the locally scaled position vector within an atomic subvolume Ω_I.

Approximate expressions for the atomic modulating factors

In Eq. (19), although the whole three-dimensional space is partitioned into nonoverlaping atomic volumes, the quantities $t_{\mathrm{W}}([\rho];\mathbf{r}_I)$, $\rho^{5/3}(\mathbf{r}_I)$ and $A_N([\rho];\mathbf{r}_I)$ are those of the whole molecular system within a given volume Ω_I. However, in view of the fact that in terms of the one-particle density, the superposition of atomic densities of isolated atoms (placed at the positions they would occupy in the molecule) yields a "molecular" density not too dissimilar from the actual density of the molecular system, it is of interest to determine whether the modulating factor $A_N([\rho];\mathbf{r}_I)$ for a molecule resembles or not the corresponding atomic modulating factor $A_N^I([\rho];\mathbf{r}_I)$ within the volume Ω_I.

This question has been examined elsewhere [17]. Briefly, the results indicate that the superposition of atomic modulating factors defined within nonoverlaping volumes for a diatomic molecule compares quite well with the actual molecular modulating factors. The physical meaning of this finding is not surprising. It just points toward the expected result that the inner-shell structure is maintained when atoms combine to form molecules. Essentially it is the structure of the outer shell that varies upon bond formation. The degree of variation depends, of course, upon the physical system, but, by and large, it arises from perturbations of the atomic charge densities.

In principle, therefore, the following approximation is quite reasonable:

$$\begin{aligned} A_N([\rho];\mathbf{r}_I) \simeq A_N^I([\rho];\mathbf{r}_I) \equiv {} & \left[1 + \mathbf{r}\cdot\nabla_{\mathbf{r}}\ln\lambda^I(\mathbf{r})\right]^{-2/3} \\ & \times \left[3 + \mathbf{r}\cdot\overrightarrow{\nabla}_{\mathbf{r}}\ln\lambda^I(\mathbf{r})\right]^2 t_N^I([\rho];\mathbf{r}), \end{aligned} \tag{44}$$

where $\lambda^I(\mathbf{r})$ is the atomic local-scaling function and where $t_N^I([\rho];\mathbf{r})$ is the atomic factor

$$t_N^I([\rho];\mathbf{r}) = \tau_N^I([\rho];\mathbf{r}_I) + \kappa_N^I([\rho];\mathbf{r}_I). \tag{45}$$

Again, the numerical results obtained using this approximation are quite encouraging [17] and are more accurate than those obtained with generalized gradient approximation kinetic energy functionals, for example. But, notwithstanding the value of these approximations, we discuss in this section, a feasible way for obtaining the whole term $A_N([\rho];\mathbf{r}_I)$. We illustrate this situation for the particular case of diatomic molecules.

Let us assume that the "generating" molecular orbitals for a diatomic molecule are given as linear combinations of atom-centered functions and, furthermore, let us place the center of coordinates at the nucleus A. Thus, we have

$$\phi_i(\mathbf{r}_{\mathrm{A}}) = \phi_i^{\mathrm{A}}(\mathbf{r}_{\mathrm{A}}) + \phi_i^{\mathrm{B}}(\mathbf{r}_{\mathrm{B}}), \tag{46}$$

where

$$\phi_i^{\mathrm{A}}(\mathbf{r}_{\mathrm{A}}) = \sum_j C_j^{\mathrm{A}}\chi_j^{\mathrm{A}}(\mathbf{r}_{\mathrm{A}}), \tag{47}$$

with a similar definition for $\phi_i^{\mathrm{B}}(\mathbf{r}_{\mathrm{B}})$.

We assume that the atomic orbitals for center A are given by

$$\chi_j^{\mathrm{A}}(\mathbf{r}_{\mathrm{A}}) = S_{n_j^{\mathrm{A}},l_j^{\mathrm{A}}}(r_A)Y_{l_j^{\mathrm{A}},m_j^{\mathrm{A}}}(\theta_{\mathrm{A}},\varphi_{\mathrm{A}}), \tag{48}$$

with a similar definition for center B. Although, clearly, the choice of $S_{n_j^{\mathrm{A}},l_j^{\mathrm{A}}}(r_{\mathrm{A}})$ is arbitrary, we have shown elsewhere that the generalized Slater-type orbitals (GSTOs),

$$\mathrm{S}_{\mathrm{n},l}(r) = \mathrm{N}_{nl}\mathrm{r}^{n-1}\exp\left(-\varsigma r^{\beta}\right), \tag{49}$$

form a particularly convenient basis set for atoms. In fact, by means of these functions, we have been able to obtain explicit density functionals for the energy of spherically symmetric atoms using only one GSTO per electron.

Now, for the evaluation of $\tau_N^{\mathrm{B}}([\rho];\mathbf{r}_{\mathrm{A}})$ and $\kappa_N^{\mathrm{B}}([\rho];\mathbf{r}_{\mathrm{A}})$ (for diatomics, C or the "complement" of A is B) within the subvolume Ω_{A}, we see that we would have to calculate terms such as the following one:

$$\frac{\partial \chi_j^{\mathrm{B}}\left(\mathbf{r}_{\mathrm{B}}^{\mathrm{T}}\right)}{\partial r_{\mathrm{A}}^{\mathrm{T}}} = \left(\frac{\partial S_{n_j^{\mathrm{B}},l_j^{\mathrm{B}}}\left(r_{\mathrm{B}}^{\mathrm{T}}\right)}{\partial r_{\mathrm{B}}^{\mathrm{T}}}\right)\left(\frac{\partial r_{\mathrm{B}}^{\mathrm{T}}}{\partial r_{\mathrm{A}}^{\mathrm{T}}}\right) Y_{l_j^{\mathrm{A}},m_j^{\mathrm{A}}}(\theta_{\mathrm{B}},\varphi_{\mathrm{B}}) + S_{n_j^{\mathrm{B}},l_j^{\mathrm{B}}}\left(r_{\mathrm{B}}^{\mathrm{T}}\right)\left(\frac{\partial Y_{l_j^{\mathrm{A}},m_j^{\mathrm{A}}}(\theta_{\mathrm{B}},\varphi_{\mathrm{B}})}{\partial \theta_{\mathrm{B}}}\right)\left(\frac{\partial \theta_{\mathrm{B}}}{\partial r_{\mathrm{A}}^{\mathrm{T}}}\right). \tag{50}$$

From the fact that we can express the coordinates r_{B} and θ_{B}, as functions of the coordinates in A, namely,

$$r_{\mathrm{B}} = \sqrt{r_{\mathrm{A}}^2 + R_{\mathrm{AB}}(R_{\mathrm{AB}} - 2r_{\mathrm{A}}\cos\theta_{\mathrm{A}})}, \tag{51}$$

$$\cos\theta_{\mathrm{B}} = \frac{R_{\mathrm{AB}} - r_{\mathrm{A}}\cos\theta_{\mathrm{A}}}{\sqrt{r_{\mathrm{A}}^2 + R_{\mathrm{AB}}(R_{\mathrm{AB}} - 2r_{\mathrm{A}}\cos\theta_{\mathrm{A}})}}, \tag{52}$$

we obtain the following explicit expressions:

$$\left(\frac{\partial r_{\mathrm{B}}^{\mathrm{T}}}{\partial r_{\mathrm{A}}^{\mathrm{T}}}\right) = \frac{r_{\mathrm{A}}^{\mathrm{T}} - R_{AB}\cos\theta_{\mathrm{A}}}{\sqrt{\left(r_{\mathrm{A}}^{\mathrm{T}}\right)^2 + R_{\mathrm{AB}}\left(R_{\mathrm{AB}} - 2r_{\mathrm{A}}^{\mathrm{T}}\cos\theta_{\mathrm{A}}\right)}}, \tag{53}$$

$$\left(\frac{\partial \theta_{\mathrm{B}}}{\partial r_{\mathrm{A}}^{\mathrm{T}}}\right) = \frac{R_{\mathrm{AB}}\sin\theta_{\mathrm{A}}}{\left(r_{\mathrm{A}}^{\mathrm{T}}\right)^2 + R_{\mathrm{AB}}\left(R_{\mathrm{AB}} - 2r_{\mathrm{A}}^{\mathrm{T}}\cos\theta_{\mathrm{A}}\right)}. \tag{54}$$

Similar expressions can be obtained for the terms appearing in the angular contribution to the modulating factor.

Although we have dealt here with a diatomic molecule, the extension to polyatomic molecules is more complicated but essentially straightforward. Thus, for general multicentered systems we may also obtain, in principle, analytic expressions for the radial modulating factors $\tau_N^I([\rho];\mathbf{r}_I)$ and $\tau_N^{\mathrm{C}}([\rho];\mathbf{r}_I)$ as well as for the angular modulating factors $\kappa_N^I([\rho];\mathbf{r}_I)$ and $\kappa_N^{\mathrm{C}}([\rho];\overrightarrow{\mathbf{r}}_I)$ appearing in Eqs. (22) and (28), respectively. Moreover, because we have partitioned space into nonoverlaping subvolumes, it follows that the locally scaled coordinate r_I^{T} can be calculated within each region Ω_I (this point is further discussed in Appendix 2).

Conclusions

By means of a constructive method based on the use of local-scaling transformations we have been able to derive, in the present work, a general and exact density functional for the kinetic energy term $T_{\mathrm{s}}[\rho]$. We have shown that this exact expression contains the von Weiszäcker term plus another contribution whose main factor is $\rho^{5/3}$, (namely, the Thomas–Fermi term), multiplied by the modulating factor $A_N([\rho];\mathbf{r})$. The latter depends upon the number of particles, N, and on the set, $\{\phi_i\}$, of "generating" functions. Thus, this modulating term is system-dependent.

Actual realizations of $A_N([\rho];\mathbf{r})$ and, hence, of $T_{\mathrm{s}}[\rho]$ can be obtained through the choice of a particular form for the set $\{\phi_i\}$. We advocate the use of molecular orbitals formed by atomic GSTOs, because in the case of atoms, only one GSTO per electron is needed to attain an accuracy comparable (up to millihartrees) to that of Hartree–Fock calculations. Hence, this high accuracy is reached without having to optimize linear expansion coefficients.

In the present work we have devised a method for obtaining analytic expressions for the enhancement factor $A_N([\rho];\mathbf{r})$, regardless of the form of the atomic radial wavefunctions. This method allows us, in turn, to obtain an analytic expression for $T_{\mathrm{s}}[\rho]$. Moreover, we have decomposed this analytic form into contributions circumscribed to atomic domains. This has the added advantage that within each one of these domains the local-scaling transformation function, λ, for the molecule can be calculated by the same techniques we have previously applied to atoms. The difference is that in the present case, we must deal with nonspherical atoms, a fact that adds no essential difficulty to our task.

In the present work, we have also considered an approximate evaluation of the enhancement factor $A_N([\rho];\mathbf{r})$ by applying an atoms-in-a-molecule approach. Obviously there are several advantages associated with this type of approximation. In the first place, the evaluation of both the local-scaling transformations and the energy expressions within an arbitrary atomic domain can be performed using almost the same techniques that we used in atoms. Slight modifications come from the fact that, in general, we have to deal with nonspherical atoms (this point is discussed in Appendices 1 and 2). In the second place, the present formulation allows us to treat the atomic domains as open systems, capable of either gaining or losing atomic charge. Clearly, the charge-conservation condition is enforced for the total system, but charge transfer is allowed at the atoms-in-a-molecule level. In the third place, the present formulation allows us to treat the charge occupation numbers $\left\{n_{ii}^{II}\right\}$ appearing in Eq. (42) as variational parameters. This characteristic may become quite useful for orbital-free molecular dynamics simulations employing this type of kinetic energy functional.

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Appendix 1: Local-scaling and the transformation of the gradient operator

Local-scaling transformations are generalizations of the well-known scaling transformations. The latter carry a vector $\mathbf{r}$ into a transformed vector $\lambda\mathbf{r}$, where λ is a constant. The constancy of λ means that the vector $\mathbf{r}$ is modified uniformly in each point of the Euclidean space

$\Re^3$. On the other hand, local-scaling transformations distort the vector $\mathbf{r}$ at each point of $\Re^3$, so the transformed vector becomes $\mathbf{r}^{\mathrm{T}} = (x^{\mathrm{T}}, y^{\mathrm{T}}, z^{\mathrm{T}}) \equiv [\lambda(\mathbf{r})x, \lambda(\mathbf{r})y, \lambda(\mathbf{r})z]$. In this case $\lambda(\mathbf{r})$ is a function.

The importance of local-scaling transformations for density functional theory is that they are density-dependent transformations. In fact, they satisfy the following equation relating an initial or "generating" density, $\rho_{\mathrm{g}}(\mathbf{r})$, to a final density, $\rho(\mathbf{r})$:

$$\rho(\mathbf{r}) = J\left(\mathbf{r}^{\mathrm{T}}; \mathbf{r}\right)\rho_{\mathrm{g}}\left(\mathbf{r}^{\mathrm{T}}\right), \tag{55}$$

where $J(\mathbf{r}^{\mathrm{T}};\mathbf{r})$ is the Jacobian of the transformation and is given by

$$J[\lambda(\mathbf{r})\mathbf{r}; \mathbf{r}] = \begin{pmatrix} \frac{\partial x^{\mathrm{T}}}{\partial x} & \frac{\partial y^{\mathrm{T}}}{\partial x} & \frac{\partial z^{\mathrm{T}}}{\partial x} \\ \frac{\partial x^{\mathrm{T}}}{\partial y} & \frac{\partial y^{\mathrm{T}}}{\partial y} & \frac{\partial z^{\mathrm{T}}}{\partial y} \\ \frac{\partial x^{\mathrm{T}}}{\partial z} & \frac{\partial y^{\mathrm{T}}}{\partial z} & \frac{\partial z^{\mathrm{T}}}{\partial z} \end{pmatrix} = \lambda^3(\mathbf{r})[1 + \mathbf{r} \cdot \nabla_{\mathbf{r}} \ln \lambda(\mathbf{r})]. \tag{56}$$

From Eqs. (55) and (56) we can obtain the following first-order differential equation for the transformation function $\lambda(\mathbf{r})$:

$$\lambda(\mathbf{r}) = \left[\frac{\rho(\mathbf{r})}{\rho_{\mathrm{g}}(\mathbf{r}^{\mathrm{T}})}\right]^{1/3} [1 + \mathbf{r} \cdot \nabla_{\mathbf{r}} \ln \lambda(\mathbf{r})]^{-1/3}. \tag{57}$$

In spherical coordinates, the gradient operator is given by

$$\begin{aligned} \nabla_{\mathbf{r}} &= \hat{I}_r \frac{\partial}{\partial r} + \hat{I}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \hat{I}_\varphi \frac{1}{r \sin\theta}\frac{\partial}{\partial \varphi} \\ &= \left(\hat{I}_r \cdot \hat{I}_\theta \frac{1}{r}, \hat{I}_\varphi \frac{1}{r\sin\theta}\right) \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \varphi} \end{pmatrix}. \end{aligned} \tag{58}$$

In order to rewrite this expression in terms of the transformed coordinates, we must first evaluate

$$\begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \varphi} \end{pmatrix} = \begin{pmatrix} \frac{\partial r^{\mathrm{T}}}{\partial r} & \frac{\partial \theta^{\mathrm{T}}}{\partial r} & \frac{\partial \varphi^{\mathrm{T}}}{\partial r} \\ \frac{\partial r^{\mathrm{T}}}{\partial \theta} & \frac{\partial \theta^{\mathrm{T}}}{\partial \theta} & \frac{\partial \varphi^{\mathrm{T}}}{\partial \theta} \\ \frac{\partial r^{\mathrm{T}}}{\partial \varphi} & \frac{\partial \theta^{\mathrm{T}}}{\partial \varphi} & \frac{\partial \varphi^{\mathrm{T}}}{\partial \varphi} \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial r^{\mathrm{T}}} \\ \frac{\partial}{\partial \theta^{\mathrm{T}}} \\ \frac{\partial}{\partial \varphi^{\mathrm{T}}} \end{pmatrix}. \tag{59}$$

The transformed radial coordinate is $r^{\mathrm{T}} = \lambda(\mathbf{r})r$; however, because local-scaling transformations do not change the direction of the transformed vector $\mathbf{r}^{\mathrm{T}}$, the transformed angles are $\theta^{\mathrm{T}} = \theta$ and $\varphi^{\mathrm{T}} = \varphi$. Evaluating the transformation matrix, we obtain

$$\nabla_{\mathbf{r}} = \left(\hat{l}_r \cdot \hat{l}_\theta \frac{1}{r}, \hat{l}_\varphi \frac{1}{r\sin\theta}\right) \begin{pmatrix} \left(\frac{\partial\lambda}{\partial r} r + \lambda\right) & 0 & 0 \\ \frac{\partial\lambda}{\partial\theta} r & 1 & 0 \\ \frac{\partial\lambda}{\partial\varphi} & 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial r^{\mathrm{T}}} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \varphi} \end{pmatrix}. \tag{60}$$

Noticing that

$$\begin{pmatrix} \hat{l}_r \\ \hat{l}_\theta \frac{1}{r^{\mathrm{T}}} \\ \hat{l}_\varphi \frac{1}{r^{\mathrm{T}} \sin\theta} \end{pmatrix} \left(\hat{l}_r, \hat{l}_\theta \frac{1}{r^{\mathrm{T}}}, \hat{l}_\varphi \frac{1}{r^{\mathrm{T}}\sin\theta}\right) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{61}$$

and introducing this decomposition of the unit matrix at the right of the square matrix in Eq. (60), we obtain finally

$$\nabla_{\mathbf{r}} = \lambda(\mathbf{r})[3 + \mathbf{r} \cdot \nabla_{\mathbf{r}} \ln \lambda(\mathbf{r})]\nabla_{\mathbf{r}^{\mathrm{T}}}, \tag{62}$$

where

$$\nabla_{\mathbf{r}^{\mathrm{T}}} = \hat{l}_r \frac{\partial}{\partial r^{\mathrm{T}}} + \hat{l}_\theta \frac{1}{r^{\mathrm{T}}}\frac{\partial}{\partial\theta} + \hat{l}_\varphi \frac{1}{r^{\mathrm{T}}\sin\theta}\frac{\partial}{\partial\varphi}. \tag{63}$$

Appendix 2: Local-scaling transformations for nonspherical atoms in arbitrary volumes

We consider here the problem, treated for the case of Cartesian coordinates in Ref. [7], of a general nonisotropic density transformation for the case of spherical coordinates. Let us consider a density transformation that takes $(r,\theta,\varphi) \to (r^{\mathrm{T}},\theta^{\mathrm{T}},\varphi^{\mathrm{T}})$, where we assume that

$$r^{\mathrm{T}} = r^{\mathrm{T}}(r,\theta,\varphi), \quad \theta^{\mathrm{T}} = \theta^{\mathrm{T}}(\theta,\varphi), \quad \varphi^{\mathrm{T}} = \varphi^{\mathrm{T}}(\varphi). \tag{64}$$

Clearly, when we let $\theta^{\mathrm{T}} = \theta$ and $\varphi^{\mathrm{T}} = \varphi$, we recover the particular case of local-scaling transformations. The Jacobian of this transformation is

$$\begin{aligned} J\left(\mathbf{r}^{\mathrm{T}}, \mathbf{r}\right) &= \begin{vmatrix} \frac{\partial r^{\mathrm{T}}}{\partial r} & 0 & 0 \\ \frac{\partial r^{\mathrm{T}}}{\partial \theta} & \frac{\partial \theta^{\mathrm{T}}}{\partial \theta} & 0 \\ \frac{\partial r^{\mathrm{T}}}{\partial \varphi} & \frac{\partial \theta^{\mathrm{T}}}{\partial \varphi} & \frac{\partial \varphi^{\mathrm{T}}}{\partial \varphi} \end{vmatrix} \frac{\left(r^{\mathrm{T}}\right)^2 \sin\theta^{\mathrm{T}}}{r^2\sin\theta} \\ &= \frac{\partial r^{\mathrm{T}}}{\partial r}\frac{\partial \theta^{\mathrm{T}}}{\partial \theta}\frac{\partial \varphi^{\mathrm{T}}}{\partial \varphi}\frac{\left(r^{\mathrm{T}}\right)^2 \sin\theta^{\mathrm{T}}}{r^2\sin\theta}. \end{aligned} \tag{65}$$

Using Eq. (65), we can rewrite Eq. (55) as follows:

$$\begin{aligned} &\mathbf{d}r r^2 \mathbf{d}\theta \sin\theta \mathbf{d}\varphi \rho(r,\theta,\varphi) \\ &\quad = \mathbf{d}r^{\mathrm{T}} \left(r^{\mathrm{T}}\right)^2 \mathbf{d}\theta^{\mathrm{T}} \sin\theta^{\mathrm{T}} \mathbf{d}\varphi^{\mathrm{T}} \rho_{\mathrm{g}}\left(r^{\mathrm{T}},\theta^{\mathrm{T}},\varphi^{\mathrm{T}}\right). \end{aligned} \tag{66}$$

Assuming that this system is placed within a volume $\Omega(r,\theta,\varphi)$ surrounding the origin of the coordinates and is bounded by a surface $S(r,\theta,\varphi)$, we obtain upon integration of Eq. (66) the following equation for the determination of $\varphi^{\mathrm{T}}(\varphi)$:

$$\begin{aligned} &\int_0^{\varphi} \mathbf{d}\varphi \int_0^{\pi} \mathbf{d}\theta \sin\theta \int_0^{r_S} \mathbf{d}r r^2 \rho(r,\theta,\varphi) \\ &\quad = \int_0^{\varphi^{\mathrm{T}}} \mathbf{d}\varphi \int_0^{\pi} \mathbf{d}\theta^{\mathrm{T}} \sin\theta^{\mathrm{T}} \int_0^{r_S^{\mathrm{T}}} \mathbf{d}r^{\mathrm{T}} \left(r^{\mathrm{T}}\right)^2 \rho_{\mathrm{g}}\left(r^{\mathrm{T}},\theta^{\mathrm{T}},\varphi^{\mathrm{T}}\right), \end{aligned} \tag{67}$$

where $r^S, r_S^{\mathrm{T}} \in S(r, \theta, \varphi)$. This equation can be rewritten as $A(\varphi) = A_{\mathrm{g}}(\varphi^{\mathrm{T}})$. Solving this equation, one can obtain $\varphi^{\mathrm{T}}(\varphi)$, which in turn can be used in the following equation through which $\theta^{\mathrm{T}}(\theta,\varphi)$ is determined:

$$\begin{aligned}\int_0^{\pi} \mathbf{d}\theta \sin\theta \int_0^{rs} \mathbf{d}r r^2 \rho(r, \theta, \varphi) &= \frac{\int_0^{\pi} \mathbf{d}\theta \sin\theta \int_0^{rs} \mathbf{d}r r^2 \rho(r, \theta, \varphi)}{\int_0^{\pi} \mathbf{d}\theta^{\mathrm{T}} \sin\theta^{\mathrm{T}} \int_0^{r_S^{\mathrm{T}}} \mathbf{d}r^{\mathrm{T}} (r^{\mathrm{T}})^2 \rho_{\mathrm{g}}(r^{\mathrm{T}}, \theta^{\mathrm{T}}, \varphi^{\mathrm{T}})} \\ &\times \int_0^{\theta^{\mathrm{T}}} \mathbf{d}\theta^{\mathrm{T}} \sin\theta^{\mathrm{T}} \int_0^{r_S^{\mathrm{T}}} \mathbf{d}r^{\mathrm{T}} \left(r^{\mathrm{T}}\right)^2 \rho_{\mathrm{g}}\left(r^{\mathrm{T}}, \theta^{\mathrm{T}}, \varphi^{\mathrm{T}}\right). \qquad (68)\end{aligned}$$

Using $\varphi^{\mathrm{T}}(\varphi)$ and $\theta^{\mathrm{T}}(\theta,\varphi)$ determined by Eqs. (67) and (68), respectively, one can determine $r^{\mathrm{T}}(r,\theta,\varphi)$ for r, $r^{\mathrm{T}} \in \Omega$ by solving the following equation:

$$\begin{aligned}\int_0^{r} \mathbf{d}r r^2 \rho(r, \theta, \varphi) &= \frac{\int_0^{rs} \mathbf{d}r r^2 \rho(r, \theta, \varphi)}{\int_0^{r_S^{\mathrm{T}}} \mathbf{d}r^{\mathrm{T}} (r^{\mathrm{T}})^2 \rho_{\mathrm{g}}(r^{\mathrm{T}}, \theta^{\mathrm{T}}, \varphi^{\mathrm{T}})} \\ &\times \int_0^{r^{\mathrm{T}}} \mathbf{d}r^{\mathrm{T}} \left(r^{\mathrm{T}}\right)^2 \rho_{\mathrm{g}}\left(r^{\mathrm{T}}, \theta^{\mathrm{T}}, \varphi^{\mathrm{T}}\right). \qquad (69)\end{aligned}$$

For the case when $\theta^{\mathrm{T}} = \theta$ and $\varphi^{\mathrm{T}} = \varphi$, Eq. (69) can be solved along a fixed ray θ_0,φ_0 to obtain $r^{\mathrm{T}}(r,\theta_0,\varphi_0)$. By spanning over all rays, we obtain the full locally scaled function $r^{\mathrm{T}}(r,\theta,\varphi)$.

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