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# Calculation of the defect kinetic energy in Kohn-Sham theory by means of local-scaling transformations

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The kinetic-energy difference $\Delta T = T - T_s[\rho_0]$ is calculated for the helium isoelectronic series and for the beryllium atom. $T_s[\rho_0]$ is in this case the kinetic energy corresponding to a noninteracting $N$-particle system which, however, has the same density $\rho_0$ as the exact interacting system. These densities $\rho_0$ were assumed in the present case to be well represented by those coming from the optimal Hylleraas-type expansions for the He isoelectronic series and by the Bunge-Esquivel 650-term configuration-interaction wave function for Be. The calculations are carried out by means of a constrained variational method based on local-scaling transformations. The connection between this approach and the one based on the Kohn-Sham equations is discussed.

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## I. INTRODUCTION

As is well known, the inclusion of the kinetic-energy term $T_s[\rho(\mathbf{r})]$ of a noninteracting system is essential for the derivation of the Kohn-Sham equations [1–3]. Moreover, the introduction of $T_s[\rho(\mathbf{r})]$ in the Kohn-Sham density-functional formalism brings about several advantages: (a) the orbital model of the Hartree-Fock theory is maintained in a theory that goes far beyond the independent-particle approximation, (b) a sizable part of the exact kinetic energy $T[\rho(\mathbf{r})]$ for the interacting particles is accounted for by $T_s[\rho(\mathbf{r})]$, i.e., $\{T[\rho(\mathbf{r})] - T_s[\rho(\mathbf{r})]\}/T[\rho(\mathbf{r})]$ is small [2,3], and (c) the difference $T[\rho(\mathbf{r})] - T_s[\rho(\mathbf{r})]$ is positive and hence, as a consequence of the introduction of $T_s[\rho(\mathbf{r})]$, the Kohn-Sham exchange-correlation energy becomes smaller than the true one [2–5].

But, in addition, the presence of $T_s[\rho(\mathbf{r})]$ is also important in the reformulation of the Kohn-Sham problem as a constrained variational search [6]. The variational functional, in this reformulation, is assumed to be the expectation value of the kinetic-energy operator with respect to a single Slater determinant for an $N$-particle noninteracting system constrained to yield the exact ground-state one-particle density of the equivalent $N$-particle interacting system. In the context of this constrained variation, the Lagrange multiplier function $\lambda(\mathbf{r}) = \lambda([\rho(\mathbf{r})];\mathbf{r})$, introduced in order to guarantee that the noninteracting density be equal to the exact density at all points of variation, turns out to be the exact Kohn-Sham effective potential [2,6]: $\lambda([\rho(\mathbf{r})];\mathbf{r}) = v_{\text{eff}}^{\text{KS}}([\rho(\mathbf{r})];\mathbf{r})$. For this reason, the explicit calculation of the $T_s[\rho(\mathbf{r})]$ corresponding to the exact one-particle density must proceed in a roundabout way. Thus, it is first necessary to advance an explicit expression for $v_{\text{eff}}^{\text{KS}}([\rho(\mathbf{r})]\mathbf{r})$, which, of course, may be obtained from an explicit functional for the exchange-correlation energy. Introducing this effective potential into the Kohn-Sham equations,

$$[-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}^{\text{KS}}([\rho(\mathbf{r})];\mathbf{r})]\psi_i^{\text{KS}}(\mathbf{r}) = \mathcal{E}_i^{\text{KS}}\psi_i^{\text{KS}}(\mathbf{r}) \ , \tag{1}$$

one is then able to obtain the set of eigenfunctions $\{\psi_i^{\text{KS}}(\mathbf{r})\}$ and eigenvalues $\{\mathcal{E}_i^{\text{KS}}\}$ from which the noninteracting kinetic energy $T_s[\rho(\mathbf{r})]$ can be evaluated by either of the two routes:

$$T_s[\rho(\mathbf{r})] = -\tfrac{1}{2}\sum_{i=1}^{N}\int d^3\mathbf{r}\,\psi_i^{\text{KS}*}\nabla_{\mathbf{r}}^2\psi_i^{\text{KS}} \tag{2a}$$

or

$$T_s[\rho(\mathbf{r})] = \sum_{i=1}^{N}\mathcal{E}_i^{\text{KS}} - \int d^3\mathbf{r}\,\rho(\mathbf{r})v_{\text{eff}}^{\text{KS}}([\rho(\mathbf{r})];\mathbf{r}) \ . \tag{2b}$$

Although it is rather simple to calculate $T_s[\rho(\mathbf{r})]$ for approximate Kohn-Sham potentials [7], the determination of the *exact* $T_s[\rho(\mathbf{r})]$ via either Eq. (2a) or Eq. (2b) is a formidable problem because it implies a previous knowledge of the exact Kohn-Sham effective potential [1–3]. As this potential is not known, one way to carry out this calculation is to introduce in Eq. (1) a parameter-dependent trial potential and to vary its parameters until the exact ground-state density $\rho_0(\mathbf{r}) = \sum_{i=1}^{N}\psi_i^{\text{KS}*}(\mathbf{r})\psi_i^{\text{KS}}(\mathbf{r})$ is reconstructed from the ensuing one-particle orbitals. Such is the procedure followed, for example, in the work of Almbladh and Pedroza [8]. There are, however, other attempts to solve this problem, such as the one presented by Holas and March

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[9] based on the reduction of a fermion system to boson form, or the more recent works of Zhao and Parr [10,11] where a constrained-search variational principle, which uses as its basic term the residual charge interaction—defined by the difference between a trial and the exact densities—is advanced. For completeness, let us mention other treatments [12–16] that without placing a particular emphasis on the calculation of $T_s[\rho(\mathbf{r})]$, deal, however, with the general inverse problem of how to determine the effective potential when the exact one-particle density is known.

Still another approach to density-constrained variations is afforded by local-scaling transformations [17–20]. These transformations are mappings that carry a vector $\mathbf{r}\in\mathbb{R}^3$ into another vector $\mathbf{f}(\mathbf{r})=(\mathbf{r}/r)f(\mathbf{r})\in\mathbb{R}^3$. They may be interpreted as transformations that deform three-dimensional space so as to follow the shape of a given one-particle density.

It is the purpose of this paper to apply local-scaling transformations to the calculation of the exact Kohn-Sham noninteracting kinetic-energy functional $T_s[\rho(\mathbf{r})]$. In Sec. II, we state the density-constrained variational principle for the kinetic-energy term and discuss how local-scaling transformations can be used to compute its minimum. For completeness, we discuss also some indirect methods that rely on the previous calculation of the Kohn-Sham exchange-correlation potential. In Sec. III, we compute $T_s[\rho(\mathbf{r})]$ for the He isoelectronic series and for Be. In the latter case, the calculations are carried out by a straightforward application of local-scaling transformations as well as by a density-driven approach. In Sec. IV, we present some conclusions.

## II. CONSTRAINED VARIATION OF THE KINETIC ENERGY AND LOCAL-SCALING TRANSFORMATIONS

Consider the following constrained variation [4,6]

$$T_s[\rho_{\text{fixed}}(\mathbf{r})]\equiv \inf_{\substack{\Phi_\rho\in\mathcal{S}_N\\ \Phi_\rho\to\rho_{\text{fixed}}\in\mathcal{N}_{\text{HKL}}}}\{\langle\Phi_\rho|\hat{T}|\Phi_\rho\rangle\}\ , \tag{3}$$

where $\Phi_\rho$ is a single Slater determinant that yields the *fixed* one-particle density $\rho_{\text{fixed}}(\mathbf{r})\in\mathcal{N}_{\text{HKL}}$. In the above expression, $\hat{T}$ is the kinetic-energy operator, $\hat{T}=\sum_{i=1}^{N}-\frac{1}{2}\nabla_i^2$, $\mathcal{S}_N$ is the subset containing only single Slater determinants of the $N$-particle antisymmetric Hilbert space $\mathcal{L}_N$, and $\mathcal{N}_{\text{HKL}}$ (where HKL stands for Hohenberg-Kohn-Lieb) is the set of admissible one-particle densities:

$$\mathcal{N}_{\text{HKL}}\equiv\left\{\rho(\mathbf{r})|\rho(\mathbf{r})>0\ ,\ \int d^3\mathbf{r}\,\rho(\mathbf{r})=N\ ,\right.$$
$$\left.\int d^3\mathbf{r}(\nabla_{\mathbf{r}}[\rho(\mathbf{r})]^{1/2})^2<\infty\right\}. \tag{4}$$

It has been shown by Lieb [4] that the infimum of Eq. (3) occurs at a minimum, i.e., that there exists a wave function $\Phi_{\rho_{\text{fixed}}}\in\mathcal{S}_N$ such that $T_s[\rho_{\text{fixed}}(\mathbf{r})]\equiv\langle\Phi^{\text{min}}_{\rho_{\text{fixed}}}|\hat{T}|\Phi^{\text{min}}_{\rho_{\text{fixed}}}\rangle$. Notice, however, that $\mathcal{S}_N\subset\mathcal{L}_N$ does not fulfill the conditions that define a subspace (a linear combination of determinants is, in general, not a determinant). For this reason, if $\Phi_\rho\in\mathcal{S}_N$ and $\delta\Phi_\rho\in\mathcal{S}_N$, then it does not necessarily follow that $\Phi_\rho+\delta\Phi_\rho$ belongs to $\mathcal{S}_N$. In the variational problem described by Eq. (3), as well as in the Hartree-Fock approximation, the variation cannot be carried out in $\mathcal{S}_N$ in view of the fact that it is not a subspace [21–23]. Instead, the variation is carried out in the space $\mathcal{L}_1$ of single-particle functions $\{\phi_i(\mathbf{r})\}$ from which $N$ orbitals are selected in order to construct the Slater determinant

$$\Phi_\rho(\mathbf{r}_1,s_1,\ldots,\mathbf{r}_N,s_N)=\frac{1}{\sqrt{N!}}\det[\phi_1(\mathbf{r}_1)\sigma_1(s_1)\cdots\phi_N(\mathbf{r}_N)\sigma_N(s_N)]\ , \tag{5}$$

where $\sigma(s)$ is a spin function. The one-particle density obtained from this determinant is

$$\rho(\mathbf{r})=\sum_{i=1}^{N}\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})\ . \tag{6}$$

### A. Relationship between constrained variation and the Kohn-Sham problem

For completeness, let us briefly sketch how the variational problem given by Eq. (3) is equivalent to the variational principle leading to the Kohn-Sham equations for the case when the fixed density comes from the exact ground-state wave function [6].

In terms of the single-particle orbitals, the variational problem in Eq. (3) becomes

$$\frac{\delta}{\delta\phi_i^*(\mathbf{r})}\left[\sum_{i=1}^{N}\int d^3\mathbf{r}\,\phi_i^*(\mathbf{r})(-\tfrac{1}{2}\nabla^2)\phi_i(\mathbf{r})-\int d^3\mathbf{r}\,\lambda(\mathbf{r})\left[\sum_{i=1}^{N}\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})-\rho_{\text{fixed}}(\mathbf{r})\right]+\sum_{i=1}^{N}\sum_{j=1}^{N}\tilde{\mathcal{E}}_{ij}\left[\int d^3\mathbf{r}\,\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})-\delta_{ij}\right]\right]+\text{c.c.}=0\ , \tag{7}$$

where the Lagrange multiplier function $\lambda(\mathbf{r})$ introduces the condition that $\rho(\mathbf{r})$ of Eq. (6) be equal to $\rho_{\text{fixed}}(\mathbf{r})$ and the Lagrange multiplier matrix $\tilde{\mathcal{E}}$ accounts for the orthonormality conditions on the set $\{\phi_i(\mathbf{r})\}_{i=1}^N$. Carrying out the variation indicated in Eq. (7) and defining a new set $\{\psi_i(\mathbf{r})\}_{i=1}^N$ by the unitary transformation $\boldsymbol{\psi}=U\boldsymbol{\phi}$, which diagonalizes $\tilde{\mathcal{E}}$, i.e., $U\tilde{\mathcal{E}}U^{-1}=\mathcal{E}$ (diagonal), the following set of single-particle equations is obtained [6]:

$$(-\tfrac{1}{2}\nabla^2+\lambda(\mathbf{r}))\psi_i(\mathbf{r})=\mathcal{E}_i\psi_i(\mathbf{r})\ . \tag{8}$$

It has been shown [6] that when $\rho_{\text{fixed}}(\mathbf{r})$ is the exact one-particle density $\rho_0(\mathbf{r})$ arising from the exact ground-state wave function $\Psi_0$ of an interacting system ($\hat{H}\Psi_0=E_0\Psi_0$, with $\hat{H}=\hat{T}+\hat{V}_{ee}+\hat{V}_{\mathrm{ext}}$), then Eq. (8) is *exactly* equal to Eq. (1) and hence $\lambda([\rho_0(\mathbf{r})];\mathbf{r})=v_{\mathrm{eff}}^{\mathrm{KS}}([\rho_0(\mathbf{r})];\mathbf{r})$.

Because $v_{\mathrm{eff}}^{\mathrm{KS}}([\rho_0(\mathbf{r})];\mathbf{r})$ is, in principle, determined by the exact density, one is faced with the practical inverse problem [8–16] of how to obtain this potential from the sole knowledge of $\rho_0(\mathbf{r})$. Of course, since

$$v_{\mathrm{eff}}^{\mathrm{KS}}([\rho_0(\mathbf{r})];\mathbf{r})=v(\mathbf{r})+v_{\mathrm{Coulomb}}([\rho_0(\mathbf{r})];\mathbf{r})+v_{\mathrm{XC}}^{\mathrm{KS}}([\rho_0(\mathbf{r})];\mathbf{r})\ , \tag{9}$$

where the external potential $v(\mathbf{r})$ is known and the Coulomb potential is directly determined by $\rho_0(\mathbf{r})$ through $v_{\mathrm{Coulomb}}([\rho_0(\mathbf{r})];\mathbf{r})=\int d^3\mathbf{r}\,\rho_0(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$, the actual task in this inverse problem is that of obtaining the Kohn-Sham exchange-correlation potential $v_{\mathrm{XC}}^{\mathrm{KS}}([\rho_0(\mathbf{r})];\mathbf{r})$.

Formally, this potential is defined by

$$\begin{aligned} v_{\mathrm{XC}}^{\mathrm{KS}}&([\rho_0(\mathbf{r})];\mathbf{r})\\ &=\frac{\delta}{\delta\rho(\mathbf{r})}(\{V_{ee}[\rho(\mathbf{r})]-E_{\mathrm{Coulomb}}[\rho(\mathbf{r})]\}\\ &\qquad+\{T[\rho(\mathbf{r})]-T_s[\rho(\mathbf{r})]\})|_{\rho(\mathbf{r})=\rho_0(\mathbf{r})}\ , \end{aligned}\tag{10}$$

where

$$V_{ee}[\rho(\mathbf{r})]=\langle\Psi_\rho^{\min}|\hat{V}_{ee}|\Psi_\rho^{\min}\rangle\ ,$$

$$T[\rho(\mathbf{r})]=\langle\Psi_\rho^{\min}|\hat{T}|\Psi_\rho^{\min}\rangle\ ,$$

and

$$E_{\mathrm{Coulomb}}[\rho(\mathbf{r})]=\tfrac{1}{2}\int d^3\mathbf{r}\,\rho(\mathbf{r})v_{\mathrm{Coulomb}}([\rho_0(\mathbf{r})];\mathbf{r})\ .$$

The wave function $\Psi_\rho^{\min}$ is obtained by the constrained variation

$$\begin{aligned} &T[\rho(\mathbf{r})]+V_{ee}[\rho(\mathbf{r})]=\min_{\Psi_\rho\in\mathcal{L}_N}\{\langle\Psi_\rho|\hat{T}+\hat{V}_{ee}|\Psi_\rho\rangle\}\ ;\\ &\Psi_\rho\rightarrow\rho(\mathbf{r})\in\mathcal{N}_{\mathrm{HKL}}\ . \end{aligned}\tag{11}$$

Clearly, it is rather difficult to compute $v_{\mathrm{XC}}^{\mathrm{KS}}([\rho_0(\mathbf{r})];\mathbf{r})$ from Eq. (10), as in addition to $T[\rho(\mathbf{r})]$ and $V_{ee}[\rho(\mathbf{r})]$, the right-hand side of this equation also includes $T_s[\rho(\mathbf{r})]$, which is precisely the unknown in our present problem. For this reason, in actual practice, $v_{\mathrm{XC}}^{\mathrm{KS}}([\rho_0(\mathbf{r})];\mathbf{r})$ has been determined directly from the Kohn-Sham equation [8] or by methods based on density-constrained variations [10,11] or pseudo-orbital differential equations [14]. In the work of Almbladh and Pedroza [8], for example, the potential $v_{\mathrm{XC}}^{\mathrm{KS}}([\rho_0(\mathbf{r})];\mathbf{r})$ was parametrized and the parameters were optimized until the density resulting from solving the Kohn-Sham equations became equal to $\rho_0(\mathbf{r})$.

### B. Local-scaling transformations and constrained variation

We show in what follows how local-scaling transformations [18–20] may be used to calculate directly $T_s[\rho(\mathbf{r})]$. For completeness, we succinctly review some relevant aspects of these transformations.

Consider a trial wave function $\Psi_g\in\mathcal{L}_N$ whose corresponding density is $\rho_g(\mathbf{r})\in\mathcal{N}_\Psi\subset\mathcal{N}_{\mathrm{HKL}}$, where $\mathcal{N}_\Psi$ is the set of all densities coming from wave functions $\Psi\in\mathcal{L}_N$. Clearly, to the particular wave function $\Psi_f\in\mathcal{L}_N$ there corresponds also a density $\rho_f(\mathbf{r})\in\mathcal{N}_\Psi$. A local-scaling transformation $\hat{f}$ carries a vector $\mathbf{r}\in\mathbb{R}^3$ into another vector $\mathbf{f}(\mathbf{r})\equiv(\mathbf{r}/r)f(\mathbf{r})\in\mathbb{R}^3$ such that the following relation among one-particle densities is fulfilled:

$$\rho_f(\mathbf{r})=J(\mathbf{f}(\mathbf{r});\mathbf{r})\rho(\mathbf{f}(\mathbf{r}))\ , \tag{12}$$

where $J(\mathbf{f}(\mathbf{r});\mathbf{r})$ is the Jacobian of the transformation. It is easily seen that the more familiar scaling transformations that carry a vector $\mathbf{r}\in\mathbb{R}^3$ into $\mathbf{f}_\lambda(\mathbf{r})\equiv\mathbf{r}\lambda\in\mathbb{R}^3$ are the simplest example of these more general local-scaling transformations.

For spherically symmetric densities, Eq. (12) becomes [18]

$$\rho_f(r)=\frac{df(r)}{dr}\frac{f^2(r)}{r^2}\rho(f(r))\ . \tag{13}$$

The above implicit first-order differential equation yields a unique function $f(r)$ linking the initial or generating density $\rho_g(r)$ with the final density $\rho_f(r)$. If we let the final density span over all possible densities in $\mathcal{N}_\Psi$, we generate the set $\{\hat{f}(r)\}$ of local-scaling transformations. These transformations form a continuous group $\mathcal{F}$.

When we apply the transformations $\hat{f}\in\mathcal{F}$ to an $N$-particle wave function, we assume that all particle coordinates are equally transformed. For this purpose, we introduce the $N$-particle operator $\hat{F}=\hat{f}\cdots\hat{f}$ ($N$ times), such that an $N$-particle wave function $\Psi_g(\mathbf{r}_1,s_1,\ldots,\mathbf{r}_N,s_N)$ is transformed into $\Psi_g^f(\mathbf{r}_1,s_1,\ldots,\mathbf{r}_N,s_N)$, which is defined by

$$\begin{aligned} \Psi_g^f&(\mathbf{r}_1,s_1,\ldots,\mathbf{r}_N,s_N)\\ &=\prod_{i=1}^{N}[J(\mathbf{f}(\mathbf{r}_i);\mathbf{r}_i)]^{1/2}\Psi_g(\mathbf{f}(\mathbf{r}_1),s_1,\ldots,\mathbf{f}(\mathbf{r}_N),s_n)\ . \end{aligned}\tag{14}$$

The locally scaled transformed wave function $\Psi_g^f(\mathbf{r}_1,s_1,\ldots,\mathbf{r}_N,s_N)$ yields the one-particle density $\rho_f(\mathbf{r})$, namely, the same density that comes from the wave function $\Psi_f(\mathbf{r}_1,s_1,\ldots,\mathbf{r}_N,s_N)$. Notice, however, that although these wave functions yield the same density, they are not identical.

The $N$-particle local-scaling transformation operators $\{\hat{F}\}$ also form a group $\mathcal{F}^N$ of continuous transformations. A salient characteristic of the group $\mathcal{F}^N$ is that applications of $\hat{F}\in\mathcal{F}^N$ to wave functions $\Psi\in\mathcal{L}_N$, partition $\mathcal{L}_N$ into orbits $\mathcal{O}_{\mathcal{L}_N}^{[i]}$ such that $\mathcal{L}_N=\cup_{i=1}\mathcal{O}_{\mathcal{L}_N}^{[i]}$. Because of this, any $N$-particle wave function $\Psi_\rho^{[i]}\in\mathcal{O}_{\mathcal{L}_N}^{[i]}$ is in a one-to-one correspondence with $\rho(\mathbf{r})\in\mathcal{N}_\Psi$. This means that no two wave functions in the same orbit yield the same density [19]. This property also implies that, starting from an arbitrary wave function $\Psi_g^{[i]}\in\mathcal{O}_{\mathcal{L}_N}^{[i]}$, one can generate all $N$-particle wave functions $\{\Psi_\rho^{[i]}\}$ for all possible densities $\rho(\mathbf{r})\in\mathcal{N}_\Psi$.

Let us now apply the above properties of local-scaling transformations to the constrained variation described by Eq. (3). Consider the wave function $\Phi_p$ given by Eq. (5), where the single-particle orbitals $\{\phi_i(\mathbf{r})\}$ are assumed to depend upon the set $\{a_i, b_i, \ldots\}$ of parameters (i.e., orbital exponents, expansion coefficients, etc.). Let us define an orbit-generating wave function as the single Slater determinant given by

$$\Phi_g(\mathbf{r}_1, s_1, \ldots, \mathbf{r}_N, s_N) \equiv \frac{1}{\sqrt{N!}} \det\{\phi_1([a_1^g, b_1^g, \ldots]; \mathbf{r}_1)\sigma_1(s_1) \cdots \times \phi_N([a_N^g, b_N^g, \ldots]; \mathbf{r}_N)\sigma_N(s_N)\} \ . \tag{15}$$

The one-particle density associated with this wave function is $\rho_g(\mathbf{r})$. Let us assume, furthermore, that we know the exact density $\rho_0(\mathbf{r})$ for the $N$-particle problem at hand. This exact density may correspond to a sufficiently accurate configuration-interaction (CI) wave function, or in the case of a two-electron atom, to a Hylleraas-type wave function. Let us call $f_{g,0}(r)$ the transformation function that results from solving Eq. (13) when $\rho_f(\mathbf{r}) \equiv \rho_0(\mathbf{r})$ and $\rho(\mathbf{r}) \equiv \rho_g(\mathbf{r})$. Applying the resulting transformations to the individual orbitals $\{\phi_i([a_i^g, b_i^g, \ldots]; \mathbf{r})\}$, we obtain the locally scaled transformed set $\{\phi_i^{\mathrm{LS}}([a_i^g, b_i^g, \ldots]; \mathbf{r})\}$, where the new orbitals are given by

$$\begin{aligned} \phi_i^{\mathrm{LS}}([a_i^g, b_i^g, \ldots]; \mathbf{r}) &= [J(\mathbf{f}_{g,0}(\mathbf{r}); \mathbf{r})]^{1/2} \phi_i([a_i^g, b_i^g, \ldots]; \mathbf{f}_{g,0}(\mathbf{r})) \\ &= \left[ \frac{\rho_0(\mathbf{r})}{\rho_g([a_i^g, b_i^g, \ldots]; \mathbf{f}_{g,0}(\mathbf{r}))} \right]^{1/2} \times \phi_i([a_i^g, b_i^g, \ldots]; \mathbf{f}_{g,0}(\mathbf{r})) \ . \end{aligned} \tag{16}$$

The transformed single Slater determinant, which yields $\rho_0(\mathbf{r})$, becomes

$$\Phi_{\rho_0}(\mathbf{r}_1, s_1, \ldots, \mathbf{r}_N, s_N) \equiv \frac{1}{\sqrt{N!}} \det\{\phi_1^{\mathrm{LS}}([a_1^g, b_1^g, \ldots]; \mathbf{r}_1)\sigma_1(s_1) \ldots \times \phi_N^{\mathrm{LS}}([a_N^g, b_N^g, \ldots]; \mathbf{r}_N)\sigma_N(s_N)\} \ . \tag{17}$$

Introducing $\Phi_{\rho_0}$ into Eq. (3), we can search now for the minimum by varying the parameters of each orbital. At the extremum we find $\Phi_{\rho_0}^{\min}$, which is given by

$$\Phi_{\rho_0}^{\min}(\mathbf{r}_1, s_1, \ldots, \mathbf{r}_N, s_N) \equiv \frac{1}{\sqrt{N!}} \det\{\phi_1^{\mathrm{LS}}([a_1^{\min}, b_1^{\min}, \ldots]; \mathbf{r}_1)\sigma_1(s_1) \cdots \times \phi_N^{\mathrm{LS}}([a_N^{\min}, b_N^{\min}, \ldots]; \mathbf{r}_N)\sigma_N(s_N)\} \ . \tag{18}$$

Thus, we obtain the following inequality for the kinetic-energy functional

$$T_s[\rho_0] \le \sum_{i=1}^{N} \int d^3\mathbf{r}\, \phi_i^{*\mathrm{LS}}([a_1^{\min}, b_1^{\min}, \ldots]; \mathbf{r})(-\tfrac{1}{2}\nabla^2) \times \phi_i^{\mathrm{LS}}([a_1^{\min}, b_1^{\min}, \ldots]; \mathbf{r}) \ . \tag{19}$$

Clearly, the absolute minimum can be approached as closely as desired by increasing the flexibility of the basis functions $\{\phi_i^{\mathrm{LS}}([a_i, b_i, \ldots]; \mathbf{r})\}$. This, of course, may be attained by introducing sufficient variational parameters.

## III. CALCULATION OF $T_s$ FOR THE He ISOELECTRONIC SERIES AND FOR Be

### A. The helium isoelectronic series

For the $^1S$ state of a two-electron case, Eq. (15) becomes

$$\Phi_g(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2) \equiv \frac{1}{\sqrt{2}} \det\{\phi_1([a_1^g, b_1^g, \ldots]; \mathbf{r}_1)\alpha(s_1) \times \phi_1([a_1^g, b_1^g, \ldots]; \mathbf{r}_2)\beta(s_2)\} \ . \tag{20}$$

This equation establishes the following direct correspondence between the single orbital $\phi_1(\mathbf{r})$ and the spatial part of the one-particle density:

$$\rho_g(\mathbf{r}) = 2[\phi_1(\mathbf{r})]^2 \quad \text{or} \quad \phi_1(\mathbf{r}) = \left[ \frac{\rho_g(\mathbf{r})}{2} \right]^{1/2} , \tag{21}$$

apart from a phase factor. The locally scaled transformed function $\phi_1^{\mathrm{LS}}(\mathbf{r})$ is, in the present case, entirely determined by the final density $\rho_0(\mathbf{r})$ as Eq. (16) becomes

$$\begin{aligned} \phi_1^{\mathrm{LS}}(\mathbf{r}_1) &= \left[ \frac{\rho_0(\mathbf{r})}{\rho_g([a_1^g, b_1^g, \ldots]; \mathbf{f}_{g,0}(\mathbf{r}))} \right]^{1/2} \times \left[ \frac{\rho_g([a_1^g, b_1^g, \ldots]; \mathbf{f}_{g,0}(\mathbf{r}))}{2} \right]^{1/2} \\ &= \left[ \frac{\rho_0(\mathbf{r})}{2} \right]^{1/2} . \end{aligned} \tag{22}$$

Notice that the transformed functions do not depend upon the variational parameters. The inequality in Eq. (19) is replaced, in this case, by an equality and the kinetic energy of the transformed function is

$$T_s[\rho_0(\mathbf{r})] = \tfrac{1}{4} \int d^3\mathbf{r} \frac{[\nabla \rho_0(\mathbf{r})]^2}{\rho_0(\mathbf{r})} \ . \tag{23}$$

In Table I, we list the $T_s$ values for selected optimum Hylleraas $N$-term wave functions for two-electron systems [24] with nuclear charge $Z$. In addition, we list the values of the true kinetic energy $T$, and of the difference $T - T_s$.

### B. The beryllium atom

For this four-electron system, the locally scaled transformed orbitals do depend upon the final density as

TABLE I. Kinetic energy values $T[\rho_0]$, $T_s[\rho_0]$, and $\Delta T[\rho_0]=T[\rho_0]-T_s[\rho_0]$ in hartrees for the helium isoelectronic series computed from optimal Hylleraas $N$-term wave functions.

| $Z$ | $N$ | $T[\rho_0]$ | $T_s[\rho_0]$ | $\Delta T[\rho_0]$ |
|---|---|---|---|---|
| 1 | 1 | 0.472 656 | 0.472 656 | 0.000 000 |
|  | 4 | 0.526 927 | 0.496 500 | 0.030 427 |
|  | 7 | 0.527 617 | 0.499 480 | 0.028 137 |
|  | 10 | 0.527 680 | 0.499 750 | 0.027 930 |
| 2 | 1 | 2.847 656 | 2.847 656 | 0.000 000 |
|  | 5 | 2.903 385 | 2.866 765 | 0.036 620 |
|  | 10 | 2.903 686 | 2.867 018 | 0.036 668 |
|  | 20 | 2.903 722 | 2.867 081 | 0.036 641 |
| 3 | 1 | 7.222 656 | 7.222 656 | 0.000 000 |
|  | 4 | 7.278 505 | 7.237 761 | 0.040 744 |
|  | 7 | 7.279 666 | 7.239 566 | 0.040 100 |
|  | 10 | 7.279 856 | 7.240 159 | 0.039 697 |
| 5 | 1 | 21.972 66 | 21.972 66 | 0.000 00 |
|  | 4 | 22.029 27 | 21.984 16 | 0.045 11 |
|  | 7 | 22.030 69 | 21.987 84 | 0.042 85 |
|  | 10 | 22.030 89 | 21.988 47 | 0.042 42 |
| 10 | 1 | 93.847 66 | 93.847 62 | 0.000 04 |
|  | 4 | 93.904 87 | 93.857 81 | 0.047 06 |
|  | 7 | 93.906 48 | 93.861 47 | 0.045 01 |
|  | 10 | 93.906 69 | 93.862 09 | 0.044 60 |

TABLE II. Orbital parameters for the sets employed as generating orbitals for local-scaling transformations.

| $j$ | $n_j$ | $\alpha_j^{\text{opt}}$ | $C_{10j}$ | $C_{20j}$ |
|---|---|---|---|---|
|  |  | Set (i) | (three-term) |  |
| 1 | 1 | 3.797 248 999 | 1.000 000 00 | 0.000 000 000 |
| 2 | 1 | 1.464 109 999 | 0.000 000 00 | 0.764 497 828 |
| 3 | 2 | 1.464 109 999 | 0.000 000 00 | −1.586 133 936 |
|  |  | Set (ii) | (double-$\zeta$) |  |
| 1 | 1 | 5.279 148 000 | 0.154 466 285 | 0.000 348 290 |
| 2 | 1 | 3.422 440 999 | 0.853 358 894 | −0.232 422 954 |
| 3 | 2 | 1.011 220 000 | 0.001 845 468 | 0.932 448 921 |
| 4 | 2 | 1.143 763 000 | 0.002 420 716 | 0.098 001 764 |
|  |  | Set (iii) | (Clementi-Roetti) |  |
| 1 | 1 | 3.275 464 072 | 0.913 161 335 | −0.157 305 457 |
| 2 | 1 | 3.304 109 942 | 0.086 735 759 | −0.013 259 512 |
| 3 | 2 | 1.027 581 145 | −0.004 959 380 | 0.211 450 934 |
| 4 | 2 | 0.827 587 515 | −0.019 751 778 | 0.623 708 415 |
| 5 | 2 | 1.392 802 227 | −0.005 844 613 | 0.266 110 997 |
| 6 | 2 | 2.666 929 788 | 0.009 036 136 | −0.098 900 374 |

well as on the parameters of the orbit-generating set. Hence, in this case, the inequality given in Eq. (19) holds. How close we get to the exact $T_s[\rho]$ depends upon the choice of initial orbitals, i.e., on the number and types of variational parameters that we may optimize.

For the system at hand, the one-particle orbitals are spherically symmetric and are defined as follows:

$$\phi_1(\mathbf{r})=R_{10}(r)\frac{1}{\sqrt{4\pi}} \quad \text{and} \quad \phi_2(\mathbf{r})=R_{20}(r)\frac{1}{\sqrt{4\pi}} \; . \tag{24}$$

In general, we have expanded these orbitals in terms of Slater-type orbitals:

$$R_{nl}(r)=\sum_{j=1}^{m} C_{nlj}\chi_j(r) \; , \tag{25}$$

where

$$\begin{aligned}\chi_j(r)&=N_j r^{n_j}\exp(-\alpha_j r)\\ &=\frac{(2\alpha_j)^{n_j+1/2}}{\sqrt{(2n_j)!}}r^{n_j}\exp(-\alpha_j r) \; .\end{aligned} \tag{26}$$

In Table II, we list the values of $\{C_{nlj}\}$, $\{n_j\}$, and $\{\alpha_j^{\text{opt}}\}$ for the three orbital sets employed in these calculations, which are (i) a three-term set (a slightly improved version of a single-$\zeta$ orbital), (ii) a double-$\zeta$-type set, and (iii) a Clementi-Roetti-type set [25]. As the $\{C_{nlj}\}$ in these sets are chosen so as to guarantee orthonormality of the $R_{10}$ and $R_{20}$ orbitals, but remain quite arbitrary otherwise, we have selected them by requiring that orbitals $R_{10}$ and $R_{20}$ have a maximum overlap with their respective canonical Hartree-Fock self-consistent-field (SCF) orbitals $R_{10}^{\text{HF}}$ and $R_{20}^{\text{HF}}$, where the latter are expressed in terms of Raffenetti's 12-term basis set [26]. The final one-particle density corresponds to the Bunge-Esquivel 650-term CI wave function [27].

In addition to a direct application of local-scaling transformations in order to generate new orbitals that yield the exact density, we have also treated this problem by resorting to a "density-driven" approach [28–30]. This approach may be succinctly characterized as follows. Consider an arbitrary orthonormal primitive basis set $\{\psi_j^{(k)}(r)\}_{j=1}^{m}$ in whose terms we construct the matrices $\mathcal{T}^{(k)}$ and $\mathcal{S}^{(k)}$ and solve the eigenvalue problem

$$(\mathcal{T}^{(k)}-t\mathcal{S}^{(k)})\mathbf{C}^{(k)}=\mathbf{0} \; , \tag{27}$$

with

$$\mathcal{T}_{ij}\equiv\langle\psi_i^{(k)}(r)|-\tfrac{1}{2}\nabla^2|\psi_j^{(k)}(r)\rangle \; ,$$

$$\mathcal{S}_{ij}\equiv\langle\psi_i^{(k)}(r)|\psi_j^{(k)}(r)\rangle \; .$$

The coefficients corresponding to the first two eigenvalues $t_1$ and $t_2$ of the above variational problem are then used to construct the orbitals $R_{i0}^{(k)}(r)=\sum_{j=1}^{m}C_{i0j}^{(k)}\psi_j^{(k)}(r)$ for $i=1,2$. The one-electron density $\rho^{(k)}(r)=2\sum_{i=1}^{2}|R_{i0}^{(k)}(r)|^2$ is then expressed in terms of these orbitals. The density $\rho^{(k)}(r)$, appearing at the $k$th iteration step, is then used in this "density-driven" method in order to generate the $(k+1)$th primitive basis set

$$\psi_j^{(k+1)}(r)=\left[\frac{\rho_0(r)}{\rho^{(k)}(r)}\right]^{1/2}\psi_j^{(k)}(r) \; , \tag{28}$$

and the procedure is repeated until, at the $p$th iteration, we have $\rho^{(p)}(r)=\rho_0(r)$. In the present case, $\rho_0(r)$ is again the Bunge-Esquivel density [27] for Be. The primitive one-particle functions are $\psi_1(r)=(\alpha^3/\pi)^{1/2}\exp(-\alpha r)$ and $\psi_2(r)=B(1-\beta\lambda r)\exp(-\beta r)$, where in order to guarantee orthonormality, $B=\{\beta^3/[\pi(3\lambda^2-3\lambda+1)]\}^{1/2}$

TABLE III. Optimum parameters for the "density-driven" orbitals.

| | DD(i) | DD(ii) |
|---|---|---|
| $\alpha^{\mathrm{opt}}$ | 4.318 016 7 | 4.343 531 1 |
| $\beta^{\mathrm{opt}}$ | 2.220 811 3 | 2.249 149 3 |
| $C_{101}$ | −0.287 000 8 | −0.287 428 9 |
| $C_{102}$ | 0.515 812 3 | 0.509 968 9 |
| $C_{201}$ | 1.955 569 6 | 1.982 379 8 |
| $C_{202}$ | 0.128 456 1 | 0.127 014 9 |

and $\lambda=(\alpha+\beta)/3\alpha$. Two sets of optimal parameters $\alpha^{\mathrm{opt}}$ and $\beta^{\mathrm{opt}}$, plus their corresponding expansion coefficients $\{C_{i0j}\}$ for the "density-driven" orbitals, are given in Table III. These coefficients are those of the $p$th or final iteration, where the elements of the converged 1-matrix differ by less than $10^{-7}$ from those of the exact one.

The results of the above calculations are given in Table IV, where we have listed $\Delta T = T - T_s$ for the three orbital sets to which the local-scaling transformations were applied as well as for the two sets of transformed orbitals generated by means of the "density-driven" procedure. For completeness, we have also included the $\Delta T$ values computed by Almbladh and Pedroza [8] and by Zhao and Parr [10,11].

## IV. DISCUSSION

The reformulation of the quantum-mechanical many-body problem in terms of a variation of the kinetic-energy functional constrained to give a fixed one-particle density opens the way to important developments in density-functional theory. In particular, it provides an alternative route for dealing with the Kohn-Sham equations. Numerically, however, this reformulation demands that adequate methods for the minimization of $T_s[\rho(\mathbf{r})]$ be developed.

TABLE IV. Defect kinetic energy $\Delta T[\rho_0]=T[\rho_0]-T_s[\rho_0]$, and $T_s[\rho_0]$ in hartrees, for the beryllium atom; values in parentheses are in eV.

| | Local scaling (this work) | | |
|---|---|---|---|
| | LS(i) | LS(ii) | LS(iii) |
| $T_s[\rho_0]$ | 14.600 407 | 14.593 177 | 14.593 163 |
| $\Delta T[\rho_0]$ | 0.065 495 | 0.073 725 | 0.073 739 |
| | (1.781) | (2.006) | (2.007) |
| | Density-driven (this work) | | |
| | DD(i) | DD(ii) | |
| $T_s[\rho_0]$ | 14.593 134 | 14.593 134 | |
| $\Delta T[\rho_0]$ | 0.073 768 | 0.073 768 | |
| | (2.007) | (2.007) | |
| | Zhao and Parr | | |
| | Ref. [10] | Ref. [11], first order | Ref. [11], second order |
| $T_s[\rho_0]$ | 14.5932 | 14.5889 | 14.5914 |
| $\Delta T[\rho_0]$ | 0.0737 | 0.0780 | 0.0755 |
| | (2.005) | (2.122) | (2.054) |
| | Almbladh and Pedroza | | |
| $\Delta T[\rho_0]$ | (2.01) | | |

We have shown in the present work how local-scaling transformations may be used in order to perform a density-constrained variation of the kinetic-energy functional. The direct transformation of the one-particle orbitals by means of local-scaling transformations is compared to the density-driven approach for the beryllium atom. As seen from Table IV, both of these approaches lead to the same kinetic-energy difference $\Delta T=2.007$ eV, a value that compares well with the results of Almbladh and Pedroza [8], $\Delta T=2.01$ eV, calculated by means of an iterative procedure involving directly the Kohn-Sham equations, and those of Zhao and Parr [10], $\Delta T=2.005$ eV, computed by solving a differential equation for the phase factor.

The present calculations are strictly variational and lead to values that are upper bounds to the exact kinetic energy $T_s[\rho(\mathbf{r})]$. In Table IV, we have listed the values of the calculated $T_s[\rho(\mathbf{r})]$'s for the locally scaled and density-driven cases considered here. It is clear that the parametric flexibility of the trial orbitals is crucial for attaining accurate kinetic-energy values in the locally scaled procedure. Thus, we observe in this case that $T_s[\rho(\mathbf{r})]$ diminishes from 14.600 407 hartrees, for the set LS(i) with only two variational parameters, to 14.593 163 hartrees for the set LS(iii) with six variational parameters. In the density-driven procedure, however, as the minimization is carried out by directly solving an eigenvalue problem for the kinetic-energy matrix, orbitals with fewer variational parameters already lead to accurate results. Thus, the set DD(i) yields a $T_s[\rho(\mathbf{r})]$ value of 14.593 134 hartrees, which slightly improves the corresponding value for LS(iii). The set DD(ii) was attained by nonlinear optimization of the initial parameters $\alpha=6.31$ and $\beta=3.22$, which correspond to the optimum parameters in DD(i) increased by 2.00 and 1.00, respectively. In spite of the different starting point, the kinetic energy attains its minimum in this case at the same value of 14.593 134 hartrees.

The $T_s[\rho(\mathbf{r})]$ values calculated in the present work, which are strict upper bounds, contrast quite markedly with the values recently computed by Zhao and Parr [11], which approximate in first and second order the solution of a one-particle energy equation expanded in terms of the global Lagrange multiplier $\lambda$. These values, which approach $T_s[\rho(\mathbf{r})]$ from below, are presented in Table IV. The six-point extrapolation in Zhao and Parr's work is 14.5818 hartrees and does not correspond to the optimal $T_s[\rho(\mathbf{r})]$ that, according to our results, must be slightly lower than 14.593 134 hartrees.

The local-scaling transformation method developed here for the calculation of the kinetic energy $T_s[\rho(\mathbf{r})]$, in addition to providing upper bounds, has the advantage of allowing us to approach the exact result as closely as we wish. This fact is of importance in quantum chemistry, where effects of the order of millihartrees are sometimes relevant. Furthermore, this well-defined variational procedure requires only the computation of kinetic-energy terms for the locally scaled transformed orbitals. Thus, in this sense, it bypasses the usual computation of integrals involving two-electron operators.

The implications of the present results for the construction of the Kohn-Sham effective potentials is in itself an interesting problem that, however, lies outside the scope of the present article and will be treated in detail elsewhere [31].

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