

2011

# Wave-function functionals for the density


Marlina Slamet  
*Sacred Heart University*

Xiao-Yin Pan  
*Ningbo University*

Viraht Sahni  
*CUNY Graduate Center and CUNY Brooklyn College*

## How does access to this work benefit you? Let us know!

Follow this and additional works at: [http://academicworks.cuny.edu/gc\\_pubs](http://academicworks.cuny.edu/gc_pubs)

 Part of the [Atomic, Molecular and Optical Physics Commons](#), [Condensed Matter Physics Commons](#), and the [Quantum Physics Commons](#)

---

### Recommended Citation

M. Slamet, X.-Y. Pan, and V. Sahni, *Phys. Rev. A* **84**, 052504 (2011).

This Article is brought to you by CUNY Academic Works. It has been accepted for inclusion in Publications and Research by an authorized administrator of CUNY Academic Works. For more information, please contact [AcademicWorks@gc.cuny.edu](mailto:AcademicWorks@gc.cuny.edu).

# Wave-function functionals for the density

Marlina Slamet

*Sacred Heart University, Fairfield, Connecticut 06825, USA*

Xiao-Yin Pan\*

*Faculty of Science, Ningbo University, 315211 Ningbo, China*

Viraht Sahni†

*Brooklyn College and The Graduate School of the City University of New York, New York, New York 10016, USA*

(Received 28 August 2011; published 7 November 2011)

We extend the idea of the constrained-search variational method for the construction of wave-function functionals  $\psi[\chi]$  of functions  $\chi$ . The search is constrained to those functions  $\chi$  such that  $\psi[\chi]$  reproduces the density  $\rho(\mathbf{r})$  while simultaneously leading to an upper bound to the energy. The functionals are thereby normalized and automatically satisfy the electron-nucleus coalescence condition. The functionals  $\psi[\chi]$  are also constructed to satisfy the electron-electron coalescence condition. The method is applied to the ground state of the helium atom to construct functionals  $\psi[\chi]$  that reproduce the density as given by the Kinoshita correlated wave function. The expectation of single-particle operators  $W = \sum_i r_i^n$ ,  $n = -2, -1, 1, 2$ ,  $W = \sum_i \delta(\mathbf{r}_i)$  are exact, as must be the case. The expectations of the kinetic energy operator  $W = -\frac{1}{2} \sum_i \nabla_i^2$ , the two-particle operators  $W = \sum_n u^n$ ,  $n = -2, -1, 1, 2$ , where  $u = |\mathbf{r}_i - \mathbf{r}_j|$ , and the energy are accurate. We note that the construction of such functionals  $\psi[\chi]$  is an application of the Levy-Lieb constrained-search definition of density functional theory. It is thereby possible to rigorously determine which functional  $\psi[\chi]$  is closer to the true wave function.

DOI: [10.1103/PhysRevA.84.052504](https://doi.org/10.1103/PhysRevA.84.052504)

PACS number(s): 31.10.+z, 03.65.-w, 31.15.E-

## I. INTRODUCTION

Variational wave functions  $\psi$  that are functionals of functions  $\chi$ :  $\psi = \psi[\chi]$  expand the space of variations over those that are simply functions. A search over the functions  $\chi$  could, in principle, lead to the exact wave function. The space over which the search for the functions  $\chi$  is to be performed is large which makes the practical implementation of such a search difficult. In our work [1–4] on the construction of such variational wave-function functionals, we have therefore restricted the search for the functions  $\chi$  over a subset of the larger space. This subspace is comprised of those functions  $\chi$  such that  $\psi[\chi]$  satisfies a constraint such as normalization or that of obtaining a physical observable exactly. Thus, there can be experimental input to the construction of  $\psi[\chi]$ . The determination of the functions  $\chi$  requires the solution of an integral equation that arises from the constraint condition. There could be many solutions to the integral equation, and therefore many wave-function functionals, with some of them not necessarily physical [4]. In this manner it is possible to determine functions  $\chi$  such that  $\psi[\chi]$  is simultaneously normalized, obtains the *exact* expectation of a Hermitian single- or two-particle operator, and leads to a rigorous upper bound to the energy which is accurate as a consequence of the variational principle. The wave-function functionals  $\psi[\chi]$  are thus accurate not only in the region of space contributing principally to the energy as in standard variational calculations, but also in the region of the property of interest. What we have additionally observed is that irrespective of whether the property of interest samples the exterior of an atom such

as the diamagnetic susceptibility, or the deep interior such as the Fermi contact term, the corresponding wave-function functionals are accurate throughout space as demonstrated by the expectations of other operators. The choice of the form of the functionals  $\psi[\chi]$  is also chosen such that it satisfies the electron-nucleus and electron-electron coalescence conditions [5]. We refer to this framework as the constrained-search variational method. The methodology can also be applied to excited states, and in particular without modification to the lowest excited states of a given symmetry. The latter is the case because the variational principle for the energy is applicable to this lowest excited state provided the choice of the wave function functional is restricted to reflect this symmetry.

In our previous work, we had determined wave-function functionals  $\psi[\chi]$  for the ground state of two-electron atomic systems: the helium atom, its positive ions, and the negative ion of atomic hydrogen. The Hermitian operators for which the exact expectation values [6] are replicated were the single-particle operators  $W = \sum_i r_i^n$ ,  $n = -2, -1, 1, 2$ ,  $W = \sum_i \delta(\mathbf{r}_i)$ ,  $W = -\frac{1}{2} \sum_i \nabla_i^2$ , and the two-particle operators  $W = \sum_n u^n$ ,  $n = -2, -1, 1, 2$ , where  $u = |\mathbf{r}_i - \mathbf{r}_j|$ . Each expectation is a *single* value. Hence, the functionals  $\psi[\chi]$  were constructed so as to be normalized, reproduce the *single value* corresponding to the expectation of  $W$ , and to be a variational upper bound to the energy. We had concluded our work by indicating that we were investigating how to extend this method to reproduce exactly a *function*  $f(\mathbf{r})$  which is the expectation of a Hermitian operator while simultaneously leading to an upper bound to the energy. This paper reports the extension of the constrained-search variational method to determine functionals  $\psi[\chi]$  that reproduce the ground-state density  $\rho(\mathbf{r})$  of the helium atom while simultaneously obtaining an upper bound to the energy. The density  $\rho(\mathbf{r})$  is the

\*panxiaoyin@nbu.edu.cn

†vsahni@brooklyn.cuny.edu

expectation of the single-particle operator  $W = \sum_i \delta(\mathbf{r}_i - \mathbf{r})$ . In contrast to our previous work [4] where different  $\psi[\chi]$  were constructed for each operator  $W$ , the present functionals  $\psi[\chi]$  have the advantage that they lead to the *exact* expectation of *all* nondifferential single-particle operators simultaneously. They also have the advantage that they automatically satisfy the electron-nucleus coalescence condition. The expectations of two-particle operators though not exact are reasonably accurate as is the satisfaction of the virial theorem. The energy is accurate as a result of the variational principle.

The idea of constructing functionals  $\psi[\chi]$  that reproduce the ground-state density  $\rho(\mathbf{r})$  also falls under the umbrella of density functional theory [7] within the Levy-Lieb constrained-search framework [8]. In this constrained search, one searches over all antisymmetric functions  $\psi_\rho$  that generate the density  $\rho(\mathbf{r})$ . The true wave function is the one that minimizes the expectation of the sum of the kinetic and electron-interaction potential operators. The constrained-search definition is made possible because [7] there is a bijective (one-to-one) relationship between the ground-state density and the external potential operator, thereby proving that the density is a basic variable. There exist many schemes [9] for the construction of functions  $\psi_\rho$ . It is in this context that the present work falls within the rubric of density functional theory. The constrained-search variational method for the construction of  $\psi[\chi]$  that reproduce the density  $\rho(\mathbf{r})$  is an application of the Levy-Lieb definition of density functional theory. It is thereby possible to determine which functional  $\psi[\chi]$  is closer to the true wave function. We note, however, that the rationale and ideas underlying the construction of wave-function functionals  $\psi[\chi]$ , as described in the opening paragraph, are more general.

In Sec. II we describe the general framework for the construction of the functionals  $\psi[\chi]$  that reproduce the density  $\rho(\mathbf{r})$  of two-electron atoms and ions. In Sec. III we apply this framework to the ground state of the helium atom for the density [10] as obtained from the 38-parameter correlated wave function of Kinoshita [11] which leads to an energy that is exact [6] to six decimal places. In this application, we expand the space of variations for the functions  $\chi$  beyond those of our prior work. We end with concluding remarks in Sec. IV.

## II. GENERAL FRAMEWORK

The time-independent Schrödinger equation for the negative ion of atomic hydrogen, the helium atom, and the positive ions of its isoelectronic sequence is

$$\hat{H}\psi[\chi] = E_E\psi[\chi], \quad (1)$$

where the Hamiltonian in atomic units ( $e = \hbar = m = 1$ ) is

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (2)$$

with  $\mathbf{r}_1$  and  $\mathbf{r}_2$  the coordinates of the two electrons,  $Z$  the atomic number, and  $E_E$  the exact energy. We assume the ground-state wave-function functional  $\psi[\chi]$  to be of the form

$$\psi[\chi] = \Phi(\alpha; s)[1 - f(\chi; s, t, u)], \quad (3)$$

where  $\Phi(\alpha; s)$  is a determinantal prefactor of the hydrogenic form

$$\Phi(\alpha; s) = N_0 e^{-\alpha s}, \quad N_0 = \alpha^3/\pi, \quad (4)$$

with  $\alpha$  a parameter and  $f(\chi; s, t, u)$  a correlated correction term of the form

$$f(\chi; s, t, u) = e^{-qu}(1 + qu) \left[ 1 - \chi(q; s, t) \left( 1 + \frac{u}{2} \right) \right], \quad (5)$$

with  $s = r_1 + r_2$ ,  $t = r_1 - r_2$ ,  $u = |\mathbf{r}_1 - \mathbf{r}_2|$  the elliptical coordinates, and  $q$  a variational parameter. The functions  $\chi(q; s, t)$  are to be determined such that  $\psi[\chi]$  generate the exact density  $\rho_E(\mathbf{r})$ . We have expanded the space of variations beyond our previous work by searching for the functions  $\chi$  over  $(s, t)$  space rather than restricting the search over only  $s$  space.

The electron density is the expectation

$$\begin{aligned} \rho(\mathbf{r}) &= \int \psi^*[\chi] \left( \sum_i \delta(\mathbf{r}_i - \mathbf{r}) \right) \psi[\chi] d\tau \\ &= 2 \int \psi^*(\mathbf{r}, \mathbf{r}'; \chi) \psi(\mathbf{r}, \mathbf{r}'; \chi) d\mathbf{r}'. \end{aligned} \quad (6)$$

Since [2]

$$\int d\mathbf{r}' = 2\pi \int_0^\infty \frac{r'}{r} dr' \int_{|r-r'|}^{r+r'} u du, \quad (7)$$

the expression for the density  $\rho(\mathbf{r})$  on substituting for  $\psi[\chi]$  of Eq. (3) is

$$\begin{aligned} \rho(\mathbf{r}) &= 4\pi N_0^2 \int_0^\infty \frac{r'}{r} dr' e^{-2\alpha s} \{ A(q; s, t) \chi^2(q; s, t) \\ &\quad - 2B(q; s, t) \chi(q; s, t) + C(q; s, t) \}, \end{aligned} \quad (8)$$

where

$$A(q; s, t) = \int_{|t|}^s du u e^{-2qu}(1 + qu)^2 \left( 1 + \frac{u}{2} \right)^2, \quad (9)$$

$$\begin{aligned} B(q; s, t) &= \int_{|t|}^s du u [e^{-2qu}(1 + qu) - e^{-qu}] \\ &\quad \times \left( 1 + \frac{u}{2} \right) (1 + qu), \end{aligned} \quad (10)$$

$$C(q; s, t) = \int_{|t|}^s du u [1 + e^{-2qu}(1 + qu)^2 - 2e^{-qu}(1 + qu)]. \quad (11)$$

Notice that the coefficients  $A(q; s, t)$ ,  $B(q; s, t)$ , and  $C(q; s, t)$  are symmetric in an interchange of  $\mathbf{r}$  and  $\mathbf{r}'$ .

Next we assume that the exact density  $\rho_E(\mathbf{r})$  is known from an exact wave function  $\psi_E(s, t, u)$  which is of the Hylleraas form

$$\Psi_E(s, t, u) = N e^{-Z_{\text{eff}} s} \sum_{l, m, n} c_{l, m, n} s^l t^{2m} u^n, \quad (12)$$

where  $N$  is the normalization constant. The corresponding expression for the density is

$$\rho_E(\mathbf{r}) = 4\pi N^2 \int_0^\infty \frac{r'}{r} dr' e^{-2Z_{\text{eff}} s} g(s, t), \quad (13)$$

where

$$g(s,t) = \sum_{\substack{l_1, m_1, n_1 \\ l_2, m_2, n_2}} c_{l_1, m_1, n_1} c_{l_2, m_2, n_2} s^{l_1+l_2} t^{2(m_1+m_2)} \times \frac{s^{n_1+n_2+2} - |t|^{n_1+n_2+2}}{n_1 + n_2 + 2}. \quad (14)$$

To determine the  $\psi[\chi]$ , we next apply the constraint that the density  $\rho(\mathbf{r})$  of Eq. (8) obtained from this functional is equivalent to the exact density  $\rho_E(\mathbf{r})$  of Eq. (13):

$$\rho(\mathbf{r}) = \rho_E(\mathbf{r}). \quad (15)$$

With the choice  $\alpha = Z_{\text{eff}}$ , this equivalence reduces to the quadratic equation

$$A(q; s, t) \chi^2(q; s, t) - 2B(q; s, t) \chi(q; s, t) + C'(q; s, t) = 0, \quad (16)$$

with

$$C'(q; s, t) = C(q; s, t) - \frac{N^2}{N_0^2} g(s, t). \quad (17)$$

Thus, the constrained search in the  $(s, t)$  subspace for the functions  $\chi$  such that  $\psi[\chi]$  reproduces the exact density shows that there exist two functions  $\chi_1(q; s, t)$  and  $\chi_2(q; s, t)$  and therefore two functionals  $\psi[\chi_1]$  and  $\psi[\chi_2]$  for which this is the case. The solution to the quadratic equation for the  $\chi(q; s, t)$  and hence the expressions for the functionals  $\psi[\chi_1]$  and  $\psi[\chi_2]$  are analytical.

The procedure for obtaining the functional  $\psi[\chi]$  is the following. For each value of the parameter  $q$ , the functional  $\psi[\chi]$  is determined for a solution  $\chi(q; s, t)$  of the quadratic equation (16). The value of  $q$  is then varied till an upper bound to the energy  $E[\psi[\chi]]$  is obtained. The expression for the energy is the expectation

$$\begin{aligned} E[\psi[\chi]] &= \int \psi^*[\chi] \hat{H} \psi[\chi] d\tau / \int \psi^*[\chi] \psi[\chi] d\tau \\ &= \frac{2\pi^2}{\int \psi^* \psi d\tau} \int_0^\infty ds \int_0^s du \int_0^u dt \left\{ u(s^2 - t^2) \right. \\ &\quad \times \left[ \left( \frac{\partial \psi}{\partial s} \right)^2 + \left( \frac{\partial \psi}{\partial t} \right)^2 + \left( \frac{\partial \psi}{\partial u} \right)^2 \right] \\ &\quad + 2 \frac{\partial \psi}{\partial u} \left[ s(u^2 - t^2) \frac{\partial \psi}{\partial s} + t(s^2 - u^2) \frac{\partial \psi}{\partial t} \right] \\ &\quad \left. - [4Zsu - (s^2 - t^2)] \psi^2 \right\}. \quad (18) \end{aligned}$$

The energy thus obtained is an upper bound because although the densities are equivalent [see Eq. (15)], the  $\psi[\chi] \neq \psi_E$ .

We note that the functionals  $\psi[\chi]$  satisfy both the electron-electron coalescence [5] condition which is

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) &= \psi(\mathbf{r}_2, \mathbf{r}_2, \dots, \mathbf{r}_N) \left( 1 + \frac{u}{2} \right) \\ &\quad + (\mathbf{r}_1 - \mathbf{r}_2) \cdot \mathbf{C}(\mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N), \quad (19) \end{aligned}$$

where  $\mathbf{C}(\mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)$  is an unknown vector, and the

electron-nucleus coalescence condition [5] which is

$$\begin{aligned} \psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) &= \psi(0, \mathbf{r}_2, \dots, \mathbf{r}_N) (1 - Zr) \\ &\quad + \mathbf{r} \cdot \mathbf{a}(\mathbf{r}_2, \dots, \mathbf{r}_N), \quad (20) \end{aligned}$$

where  $\mathbf{a}(\mathbf{r}_2, \dots, \mathbf{r}_N)$  is unknown. The satisfaction of the latter condition is more readily seen when written in differential form in terms of the density as [5]

$$\lim_{r \rightarrow 0} \frac{d\rho(r)}{dr} = -2Z\rho(r=0), \quad (21)$$

where  $\rho(r)$  is the spherical average of  $\rho(\mathbf{r})$ . As the  $\psi[\chi]$  reproduce the *exact* density, its value and slope at the nucleus are also reproduced exactly.

With the wave-function functionals  $\psi[\chi]$ , the expectations of single-particle and two-particle operators can then be obtained. We refer the reader to [12] for a general expression for the expectation value of Hermitian operators  $W$  in elliptical coordinates.

Since both functionals  $\psi[\chi_1]$  and  $\psi[\chi_2]$  reproduce the density  $\rho_E(\mathbf{r})$ , the value of the external potential energy component of the total energy is the same for both functionals. [In terms of the density  $\rho_E(\mathbf{r})$ , this component term is  $\int \rho_E(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}$ , where  $v(\mathbf{r}) = -Z/r$ .] Then employing the constrained-search definition of density functional theory [8], viz., that the exact wave function is the one which minimizes the expectation of the kinetic and electron-interaction operators, it is possible to determine which of the two functionals is closer to the true wave function. This way of determining which wave-function functional  $\psi[\chi]$  is superior differs from that of the standard variational method. In the latter, it is solely the value of the energy upper bound that distinguishes between the wave functions. The Levy-Lieb constrained-search approach also employs the energy upper bound value condition, but in addition requires the wave functions to reproduce the true density.

Finally, it is evident that with the appropriate choice for the prefactor to reflect a certain symmetry, the above framework for the construction of wave-function functionals  $\psi[\chi]$  can be

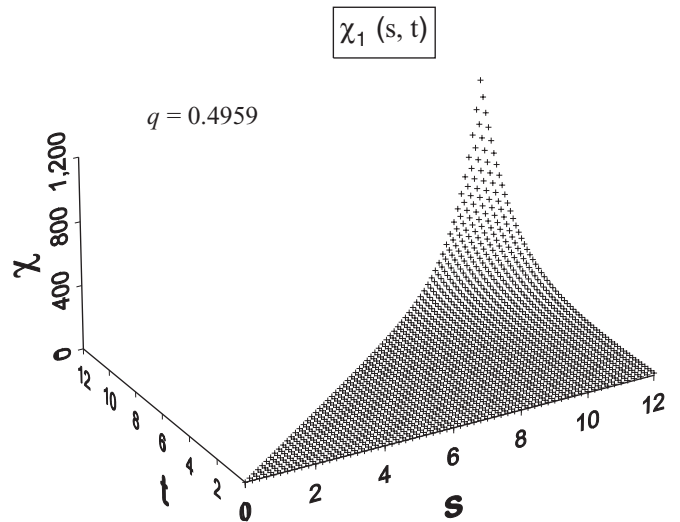


FIG. 1. Graph of the function  $\chi_1(q; s, t)$  as a function of the coordinates  $s$  and  $t$ , at the value of the parameter  $q$  that leads to the minimum of the energy.

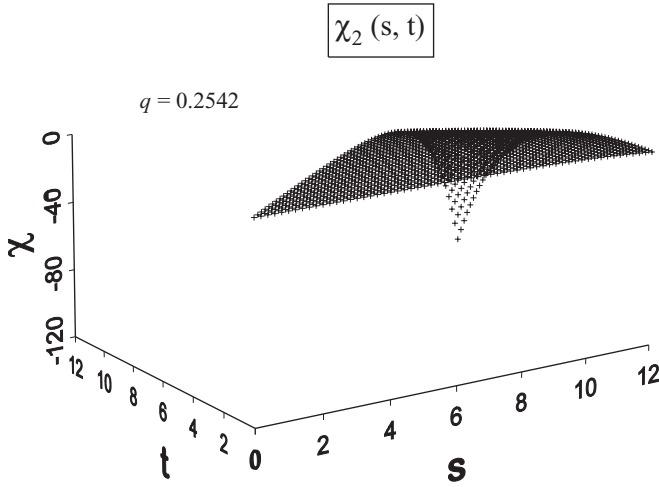


FIG. 2. Graph of the function  $\chi_2(q; s, t)$  as a function of coordinates  $s$  and  $t$ , at the value of the parameter  $q$  that leads to the minimum of the energy.

applied without modification to the lowest excited state of that symmetry.

### III. APPLICATION TO THE GROUND STATE OF HELIUM

We next apply the above framework to the ground state of the helium atom. For the exact density  $\rho_E(\mathbf{r})$  we employ that obtained from the 38-parameter correlated wave function of Kinoshita [11] which is

$$\psi_E(s, t, u) = 1.364931021e^{-1.860556s} \sum_{i=1}^{38} y_i(s, t, u). \quad (22)$$

TABLE I. Electron densities  $\rho(\mathbf{r})$  for the ground state of the helium atom as obtained from the Kinoshita wave function and the wave-function functionals  $\psi[\chi_1]$  and  $\psi[\chi_2]$ .

r (a.u.)	Electron density $\rho(\mathbf{r})$ (a.u.)		
	Kinoshita	$\psi[\chi_1]$	$\psi[\chi_2]$
0.0	3.621087819437064	3.621087819437064	3.621087819437064
0.1	2.436381500340967	2.436381500340965	2.436381500340966
0.2	1.652615187755789	1.652615187755788	1.652615187755788
0.3	1.130666655877191	1.130666655877190	1.130666655877191
0.4	0.780305411838685	0.780305411838685	0.780305411838685
0.5	0.543063013298303	0.543063013298303	0.543063013298303
0.6	0.380966113263468	0.380966113263468	0.380966113263468
0.7	0.269224394323850	0.269224394323850	0.269224394323850
0.8	0.191536789191938	0.191536789191938	0.191536789191938
0.9	0.137092890184766	0.137092890184766	0.137092890184766
1.0	0.098657244532206	0.098657244532206	0.098657244532206
2.0	0.004466660947059	0.004466660947059	0.004466660947059
3.0	0.000241398997714	0.000241398997714	0.000241398997714
4.0	0.000013928181762	0.000013928181762	0.000013928181762
5.0	0.000000824486862	0.000000824486862	0.000000824486862
6.0	0.000000049656225	0.000000049656225	0.000000049656225
7.0	0.000000003052641	0.000000003052641	0.000000003052641
8.0	0.000000000191672	0.000000000191672	0.000000000191672
9.0	0.000000000012199	0.000000000012199	0.000000000012199
10.0	0.000000000000776	0.000000000000776	0.000000000000776

A comparison with Eq. (12) shows that  $N = 1.364931021$  and  $Z_{\text{eff}} = 1.860556$ . The analytical expression for the corresponding exact density  $\rho_E(\mathbf{r})$  [together with the functions  $y_i(s, t, u)$ ] is given in [10]. The total energy due to this wave function is  $-2.903724$  a.u., and is exact to six decimal places.

On substituting this expression for  $\rho_E(\mathbf{r})$  in Eq. (15) and solving the quadratic equation Eq. (16) for the two solutions  $\chi_1(q; s, t)$  and  $\chi_2(q; s, t)$ , two wave function functionals  $\psi[\chi_1]$  and  $\psi[\chi_2]$  are obtained for each value of the parameter  $q$ . This process is repeated for different values of  $q$  till the total energy is minimized. Thus, each wave-function functional leads to an upper bound to the energy while simultaneously reproducing the exact density.

The three-dimensional plots of the functions  $\chi_1(q; s, t)$  and  $\chi_2(q; s, t)$  for the energy-minimized values of  $q$  are given in Figs. 1 and 2, respectively. Note how different these functions are as are the corresponding  $q$  values. As such the wave-function functionals  $\psi[\chi_1]$  and  $\psi[\chi_2]$  are different. Yet they both lead to the same exact density  $\rho_E(\mathbf{r})$ .

To demonstrate the accuracy of the methodology, we present in Table I the exact densities  $\rho_E(\mathbf{r})$  due to the Kinoshita wave function, and the densities obtained by the wave-function functionals  $\psi[\chi_1]$  and  $\psi[\chi_2]$ . Observe that the three are identical to 14 or 15 decimal places for any electron position. It is evident that  $\psi[\chi_1]$  and  $\psi[\chi_2]$  both satisfy the electron-nucleus coalescence condition.

In Table II we present the expectation values of single- and two-particle operators  $W$  as determined by the Kinoshita wave function and the wave-function functionals  $\psi[\chi_1]$  and  $\psi[\chi_2]$ , and the percentage difference of the latter. Notice in the first row, the  $\psi[\chi_1]$  and  $\psi[\chi_2]$  are normalized as the density is obtained exactly. For the same reason, all the single-particle expectations for both functionals are the same and exact.

TABLE II. Expectation values of operators  $W$  obtained from the Kinoshita and the wave-function functionals  $\psi[\chi_1]$  and  $\psi[\chi_2]$  that possess the same density. The percentage difference of the latter with respect to the former is also given.

Operator $W$	Expectation Values (a.u.)		%Difference
	Kinoshita	$\psi[\chi_1]$ $\psi[\chi_2]$	
1	1.000000	1.000002 1.000002	0.0002 0.0002
$\delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)$	3.621088	3.621088 3.621088	0 0
$\frac{1}{r_1} + \frac{1}{r_2}$	3.376628	3.376628 3.376628	0 0
$\frac{1}{r_1^2} + \frac{1}{r_2^2}$	12.034989	12.034989 12.034989	0 0
$r_1 + r_2$	1.858933	1.858933 1.858933	0 0
$r_1^2 + r_2^2$	2.386808	2.386808 2.386808	0 0
$-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2}$	2.903724	2.922169 2.906672	0.6352 0.1015
$ \mathbf{r}_1 - \mathbf{r}_2 ^2$	2.516337	2.526643 2.500373	0.4096 0.6344
$ \mathbf{r}_1 - \mathbf{r}_2 $	1.422062	1.430460 1.419573	0.5906 0.1750
$\frac{1}{ \mathbf{r}_1 - \mathbf{r}_2 }$	0.945821	0.931462 0.943714	1.5182 0.2228
$\frac{1}{ \mathbf{r}_1 - \mathbf{r}_2 ^2}$	1.464909	1.403079 1.449604	4.2207 1.0448
$H$	-2.903724	-2.899625 -2.902870	0.1412 0.0294
$\frac{T}{-E}$	1.000000	1.007775 1.001310	0.7775 0.1310

The expectation of the kinetic energy and two-particle operators are, of course, not expected to be exact. Nevertheless, these values are relatively accurate, with those due to  $\psi[\chi_2]$  being generally superior to those of  $\psi[\chi_1]$ . The kinetic energy for  $\psi[\chi_2]$  differs from the exact value by 0.1%. The corresponding expectation of two-particle operators differs by 1% or less. The total energies of  $\psi[\chi_1]$  and  $\psi[\chi_2]$  are within 15/100 and 3/100, respectively, of the exact value. The last row shows the satisfaction of the virial theorem. It is evident from the constrained-search definition of density functional theory that  $\psi[\chi_2]$  is closer to the exact wave function.

The results of the various expectations demonstrate, as in our previous work, that the construction of wave-function functionals leads to functions that are accurate throughout space. And that greater accuracy can be achieved with fewer parameters. The present results are obtained from an essentially one-parameter variational wave-function functional. Still

more accurate results for the energy and the two-particle expectations could be achieved with a better prefactor [3] or a superior density.

#### IV. CONCLUDING REMARKS

In this work we have extended the idea of the constrained-search variational method for the construction of wave-function functionals  $\psi[\chi]$ . In the present case, the search for the functions  $\chi$  is constrained such that  $\psi[\chi]$  reproduces the density  $\rho(\mathbf{r})$  while simultaneously leading to an upper bound to the energy. The functionals  $\psi[\chi]$  are thus automatically normalized and also satisfy the electron-nucleus coalescence condition. They are also constructed so as to satisfy the electron-electron coalescence condition. In our prior work, the search was constrained to functions  $\chi$  such that  $\psi[\chi]$  was either normalized, or  $\psi[\chi]$  was both normalized and reproduced the exact expectation of a Hermitian operator, while also simultaneously leading to a rigorous upper bound to the energy. The search for the functions  $\chi$  in each case requires the solution of an integral equation. As noted previously, some of these solutions can be unphysical. A key conclusion arrived at from these calculations is that these constrained-search variational wave-function functionals are accurate throughout space. Additionally, with fewer parameters, a high degree of accuracy is achieved for the energy as a result of the variational principle while other physical observables are obtained exactly [4]. In the present work, for example, a one-parameter wave-function functional leads to an energy correct to three decimal places while simultaneously the density and hence all single-particle operator expectations are exact. Based on our results thus far, we believe the further development of the idea of constructing wave-function functionals to be an important research path. In that vein, we are now investigating the construction of functionals that while leading to upper bounds to the energy, also reproduce the reduced single-particle density matrix. The latter is [10] the expectation of a complex sum of Hermitian operators that involve the product of the density and translation operators. Finally, we reiterate, that in addition to all the advantages of constructing wave-function functionals that reproduce the density, it is as a consequence also possible via the constrained-search definition of density functional theory to differentiate between them as to which is closer to the exact wave function.

#### ACKNOWLEDGMENTS

The work of X.-Y.P. was sponsored by the National Natural Science Foundation of China (No. 10805029), the K. C. Wong Magna Foundation in Ningbo University, and the ZheJiang NSF (No. R6090717). The work of V.S. was supported in part by a grant from the Research Foundation of The City University of New York.

- [1] X.-Y. Pan, V. Sahni, and L. Massa, *Phys. Rev. Lett.* **93**, 130401 (2004).  
 [2] X.-Y. Pan, V. Sahni, and L. Massa, *Phys. Rev. A* **72**, 032505 (2005).  
 [3] X.-Y. Pan, V. Sahni, and L. Massa, *Philos. Mag.* **86**, 2673 (2006).

- [4] X.-Y. Pan, M. Slamet, and V. Sahni, *Phys. Rev. A* **81**, 042524 (2010).  
 [5] X.-Y. Pan and V. Sahni, *J. Chem. Phys.* **119**, 7083 (2003); W. A. Bingel, *Z. Naturforsch. A* **18A**, 1249 (1963); R. T. Pack and W. Byers Brown, *J. Chem. Phys.* **45**, 556 (1966);

- W. A. Bingel, *Theor. Chim. Acta* **8**, 54 (1967); E. Steiner, *J. Chem. Phys.* **39**, 2365 (1963); T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957).
- [6] G. W. F. Drake, in *Atomic, Molecular, and Optical Physics Handbook*, edited by G. W. F. Drake (AIP, Woodbury, NY, 1996); H. Nakashima and H. Nakatsuji, *J. Chem. Phys.* **128**, 154107 (2008); V. I. Korobov, *Phys. Rev. A* **61**, 064503 (2000); G. W. F. Drake, M. M. Cassar, and R. A. Nistor, *ibid.* **65**, 054501 (2002); V. I. Korobov, *ibid.* **66**, 024501 (2002); C. L. Pekeris, *Phys. Rev.* **115**, 1216 (1959).
- [7] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- [8] M. Levy, *Proc. Natl. Acad. Sci. USA* **76**, 6062 (1979); E. Lieb, *Int. J. Quantum Chem.* **24**, 243 (1983).
- [9] T. L. Gilbert, *Phys. Rev. B* **12**, 2111 (1975); J. E. Harriman, *Phys. Rev. A* **24**, 680 (1981); J. Cioslowski, *Phys. Rev. Lett.* **60**, 2141 (1988).
- [10] V. Sahni, *Quantal Density Functional Theory II: Approximation Methods and Applications* (Springer-Verlag, Berlin, 2010), p. 404.
- [11] T. Kinoshita, *Phys. Rev.* **105**, 1490 (1957).
- [12] X.-Y. Pan, V. Sahni, L. Massa, and K. D. Sen, *Comp. Theor. Chem.* **965**, 202 (2011).