Determination of Wave Function Functionals: The
Constrained-Search—Variational Method

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(Dated: March 31, 2022)
Abstract

In a recent paper [Phys. Rev. Lett. 93, 130401 (2004)], we proposed the idea of expanding the space of variations in variational calculations of the energy by considering the approximate wave function $\psi$ to be a functional of functions $\chi : \psi = \psi[\chi]$ rather than a function. The space of variations is expanded because a search over the functions $\chi$ can in principle lead to the true wave function. As the space of such variations is large, we proposed the constrained-search—variational method whereby a constrained search is first performed over all functions $\chi$ such that the wave function functional $\psi[\chi]$ satisfies a physical constraint such as normalization or the Fermi-Coulomb hole sum rule, or leads to the known value of an observable such as the diamagnetic susceptibility, nuclear magnetic constant or Fermi contact term. A rigorous upper bound to the energy is then obtained by application of the variational principle. A key attribute of the method is that the wave function functional is accurate throughout space, in contrast to the standard variational method for which the wave function is accurate only in those regions of space contributing principally to the energy. In this paper we generalize the equations of the method to the determination of arbitrary Hermitian single-particle operators as applied to two-electron atomic and ionic systems. The description is general and applicable to both ground and excited states. A discussion on excited states in conjunction with the theorem of Theophilou is provided. Here we construct new analytical 3-parameter ground state wave function functionals for the negative ion of atomic Hydrogen and the Helium atom through the constraint of normalization. We present the results for the total energy $E$, the expectations of the Hermitian single-particle operators $W = \sum_i r_i^n, n = -2, -1, 1, 2$, $W = \sum_i \delta(r_i)$, and $W = \sum_i \delta(r_i - r)$, the structure of the nonlocal Coulomb hole charge $\rho_c(\mathbf{rr}')$ as a function of electron position $\mathbf{r}$, and the expectations of the two particle operators $u^2, u, 1/u, 1/u^2$, where $u = |\mathbf{r}_i - \mathbf{r}_j|$. The results for all the expectation values are remarkably accurate when compared with the 1078-parameter wave function of Pekeris, thereby demonstrating the accuracy of the wave function functionals throughout space. The same accuracy is exhibited for the Coulomb holes when compared with the ‘exact’ ones determined by Slamet and Sahni. The point of the improved spatial accuracy of these functionals is further made by comparisons with the results of other wave functions that are not functionals such as those due to Hartree-Fock theory and Caratzoulas-Knowles. We conclude by describing our current work on how the constrained-search—variational method in conjunction with Quantal density functional theory is being applied to many-electron atoms.
I. INTRODUCTION

In recent work \cite{1}, we proposed the idea of expanding the space of variations in standard variational calculations of the energy \cite{2}, thereby allowing for an improvement of the energy in such calculations. Equivalently, a required level of accuracy could be achieved with fewer variational parameters. In the traditional application of the variational principle, the space of variations is limited by the choice of analytical form for the approximate wave function. For example, if Gaussian or Slater-type orbitals or a linear combination of such orbitals is employed in the energy functional, the variational space is limited by this choice of functions. The proposed manner by which the space of variations can be expanded is by considering the wave function $\psi$ to be a functional of a set of functions $\chi$: $\psi = \psi[\chi]$, rather than a function. This permits a greater flexibility for the wave function $\psi[\chi]$ because the functions $\chi$ may be chosen such that $\psi[\chi]$ reproduces any well-behaved function. In principle, a search over such functions can lead to that function $\chi$ for which $\psi[\chi]$ is the true wave function.

The space over which the search for the functions $\chi$ is to be performed, however, is simply too large for practical purposes, and a subset of this space must be considered. We define the subspace over which the search for the functions $\chi$ is to be performed by the requirement that the wave function functional $\psi[\chi]$ satisfy a constraint. Typical constraints on the functional $\psi[\chi]$ are those of normalization, the satisfaction of the Fermi-Coulomb hole sum rule, the requirement that it lead to observables such as the electron density, nuclear magnetic constant, diamagnetic susceptibility, Fermi contact term, or any other physical property of interest. With the wave function functional $\psi[\chi]$ thus determined, a rigorous upper bound to the energy is obtained by application of the variational principle. In this way, not only is a particular property of interest or constraint obtained exactly, the energy is also determined accurately since the variational principle ensures it is correct to second order in the accuracy of the wave function. We refer to this method of determining an approximate wave function as the constrained-search—variational method. The method is general in that it is applicable to both ground and excited states.

An attribute of constructing a wave function functional $\psi[\chi]$ via the constrained-search—
variational method is that there is an improvement in the structure of the wave function throughout all space. Thus, both single-particle expectations representative of different parts of space as well as two-particle expectations involving two different points in space are obtained accurately.

As in standard variational calculations, the satisfaction of constraints imposed on the wave function functional, while ensuring the exactness of a specific property or properties, will nonetheless lead to a less accurate upper bound to the energy provided the space of variations remains fixed. Any such decrease in the accuracy of the upper bound can, however, be offset by an increase in the space of variations.

The concept of the wave function $\psi$ as a functional $\psi[\chi]$ is general in that the space of variations may be expanded through the functions $\chi$. The number of functions $\chi$ are also independent of the electron number $N$. This contrasts with the Hartree-Fock theory $\Phi[\phi]$ Slater determinant wave function which is also a functional but one of the $N$-electron spin-orbitals $\phi$. Furthermore, there is no variational-flexibility of these spin-orbitals once they have been determined self-consistently by solution of the Hartree-Fock equations. The space of variations cannot be expanded further, and therefore the Hartree-Fock theory wave function functional cannot be adjusted via the spin-orbitals $\phi$ to be the true wave function. Thus, this wave function functional constitutes a point in the variational space as defined for the functional $\psi[\chi]$. The determinantal functional $\Phi[\phi]$ is therefore not general in the manner of the proposed $\psi[\chi]$.

In our original work we had noted that the constrained-search—variational method could be extended to the determination of arbitrary Hermitian single-particle operators. In sect.2 we present the equations of this generalization as applied to the ground state of the negative ion of atomic Hydrogen, the Helium atom, and its isoelectronic sequence. The extension of these ideas to excited states in conjunction with the theorem of Theophilou is also described. We had also indicated various ways by which the results presented in our prior work could be improved. One such mechanism was to improve the prefactor in the correlated-determinantal wave function functional. In sect.3 we present the results of the application of the method with such an improved 3-parameter
analytical wave function functional to the ground state of the negative ion of atomic Hydrogen and the Helium atom, with normalization as the constraint. We present the results for the total energy $E$, the expectations of the Hermitian single-particle operators $W = \sum_i r_i^n, n = -2, -1, 1, 2, W = \sum_i \delta(r_i)$, and $W = \sum_i \delta(r_i - r)$, the structure of the dynamic (nonlocal) Coulomb hole charge $\rho_e(\mathbf{r}\mathbf{r}')$ as a function of electron position $\mathbf{r}$, and the expectations of the two particle operators $u^2, u, 1/u, 1/u^2$, where $u = |\mathbf{r}_i - \mathbf{r}_j|$. The results for all the expectation values are remarkably accurate when compared with the 1078-parameter wave function of Pekeris [6], thereby indicating the accuracy of the wave function functionals throughout space. The same accuracy is exhibited in a different way by the comparison of the Coulomb holes with those of the essentially exact holes determined by Slamet and Sahni [7]. The results for the energy and two particle expectations are far superior to those of Hartree-Fock theory as expected. However, the single-particle expectations are essentially equivalent since such expectations within Hartree-Fock theory are correct to second order [8]. The comparison with Hartree-Fock theory demonstrates how two square-integrable normalized antisymmetric wave functions can lead to essentially the same electron density [9], but that one can be significantly superior to the other. Our results are also superior to those of the 3-parameter variational Caratzoulas-Knowles wave function [10] that has a similar correlation term as ours but is not a functional. In the concluding section 4, we describe our current work on how the ideas of constructing wave function functionals are being applied in conjunction with Quantal density functional theory [11] to the many-electron atom.

II. CONSTRAINED-SEARCH–VARIATIONAL METHOD

In this section we present the generalization of the constrained-search—variational method for constraints whereby typical observables such as the diamagnetic susceptibility, nuclear magnetic constant, Fermi contact term, and the constraint of normalization are determined exactly. For the two-electron systems represented by the negative ion of atomic Hydrogen, the Helium atom, and its isoelectronic sequence, these properties are represented by the expectations of the single-particle operators $W = r_1^2 + r_2^2, W = 1/r_1 + 1/r_2, W = \delta(r_1) + \delta(r_2)$, and $W = 1$. For these two-electron systems, the Hamiltonian in atomic
units \((e = \hbar = m = 1)\)

\[
\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}},
\]

where \(r_1, r_2\) are the coordinates of the two electrons, \(r_{12}\) is the distance between them, and \(Z\) is the atomic number. We next choose the form of the wave function functional to be of the general form

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

with \(\Phi(s, t, u)\) a pre-factor and \(f(\chi; s, t, u)\) a correlated correction term:

\[
f(s, t, u) = e^{-qu}(1 + qu)[1 - \chi(q; s, t, u)(1 + u/2)],
\]

where \(s = r_1 + r_2, t = r_1 - r_2, u = r_{12}\), are the Hylleraas coordinates\[12]\), and \(q\) is a variational parameter. Note that any two-electron wave function in a ground or excited state may be expressed in this form. The key to the wave function functional is the determination of the functions \(\chi(q; s, t, u)\). The prefactor may be chosen to be of some analytical form with variational parameters as in the present work, or the Hartree-Fock theory wave function \[4\], or determined self-consistently within the framework of Quantal Density Functional Theory \[11]\).

For purposes of clarity, and thereby of subsequent analytical ease of solution, we assume the prefactor to depend only on the variables \(s\) and \(t\): \(\Phi = \Phi(s, t)\), and for the ground \(1^1S\) state to be of the analytical form \[13]\)

\[
\Phi[\alpha, \beta; s, t] = Ne^{-\alpha s \cosh(\beta t)} = \frac{N}{2}[e^{-Z_1 r_1}e^{-Z_2 r_2} + e^{-Z_1 r_2}e^{-Z_2 r_1}],
\]

where different orbitals are allocated to electrons with up and down spins, \(\alpha\) and \(\beta\) are variational parameters, \(Z_1 = (\alpha - \beta), Z_2 = (\alpha + \beta)\), and \(N\) is the normalization constant (See the Appendix). (Note that the normalization of the prefactor is independent of that of the wave function.) We further assume that \(\chi\) is a function only of the variable \(s\): \(\Psi = \Psi[\chi(q; s)]\). (The space of variations could be expanded further by assuming the function \(\chi\) to depend additionally upon the variable \(t\), or still further by a dependence on \(t\) and \(u\) as well.)
The wave function functional $\Psi[\chi(q; s)]$ for the ground state then satisfies the electron-electron cusp condition which in integral form is \[14\],

\[
\Psi(r_1, r_2, ... r_N) = \Psi(r_2, r_2, r_3, ..., r_N)(1 + r_{12}/2) + r_{12} \cdot C(r_2, r_3, ..., r_N),
\]

(5)

where $C(r_2, r_3, ..., r_N)$ is an unknown vector. The wave function functional also satisfies the electron-nucleus cusp condition which is \[14\],

\[
\psi(r, r_2, ... r_N) = \psi(0, r_2, ... r_N)(1 - Zr) + r \cdot a(r_2, ... r_N),
\]

(6)

for $\alpha = 2$. Here again $a(r_2, ... r_N)$ is also an unknown vector.

In terms of the Hylleraas coordinates, the Hermitian single-particle operators noted above and the normalization operator may be expressed as $W(s, t)$ where, respectively, $W(s, t) = (s^2 + t^2)/2$, $W(s, t) = \frac{4s}{s^2 - t^2}$, $W(s, t) = \frac{1}{\pi} \left[ \frac{\delta(s + t)}{(s + t)^2} + \frac{\delta(s - t)}{4(s - t)^2} \right]$, and $W(s, t) = 1$. In general, observables can be represented by single-particle operators expressed as $W(s, t)$. The expectation of the operator $W(s, t)$ which is

\[
\langle W \rangle = \frac{\int \Psi^*[\chi] W(s, t) \Psi[\chi] d\tau}{\int \Psi^*[\chi] \Psi[\chi] d\tau},
\]

(7)

can on substitution of the wave function functional $\psi[\chi]$ of Eq.(2) be written as

\[
\int |\Phi(\alpha, \beta; s, t)|^2 [W(s, t) - \langle W \rangle] [f^2(q; s, t, u) - 2f(q; s, t, u) + 1] d\tau = 0.
\]

(8)

Equivalently, Eq.(8) may be rewritten as

\[
\int_0^\infty e^{-2\alpha s} g(s) ds = 0,
\]

(9)

where

\[
g(s) = \int_0^s du \int_0^u dt \cosh^2(\beta t) W(s, t) - \langle W \rangle (s^2 - t^2) [f^2(q; s, t, u) - 2f(q; s, t, u) + 1].
\]

(10)

We now assume that the expectation $\langle W \rangle$ is known either through experiment or via some accurate calculation \[6\].

The next step is the constrained search over functions $\chi(q; s)$ for which the expectation $\langle W \rangle$ of Eq.(7) is obtained. If the parameter $\alpha$ in Eq.(9) is fixed, then there exist many
functions $g(s)$ for which the expectation $\langle W \rangle$ can be obtained. This corresponds to a large subspace of wave function functionals (See Ref. 1). On the other hand, if the parameter $\alpha$ is variable, then the only way in which Eq.(9) can be satisfied is if

$$g(s) = 0,$$ (11)

This is equivalent to the constrained search of all wave function functionals over the subspace in which Eq.(9) is satisfied.

Substitution of $f(\chi; s, t, u)$ into Eq.(11) leads to a quadratic equation for the function $\chi(q; s)$:

$$a(q, s)\chi(q; s)^2 + 2b(q, s)\chi(q; s) + c(q, s) = 0,$$ (12)

where

$$a(q, s) = \int_0^s du(1 + u/2)^2(1 + qu)^2e^{-2qu} \int_0^u dtcosh^2(\beta t)(s^2 - t^2)[W(s, t) - \langle W \rangle],$$ (13)

$$b(q, s) = -\int_0^s du(1+u/2)(1+qu)[e^{-2qu}(1+qu) - e^{-qu}] \int_0^u dtcosh^2(\beta t)(s^2 - t^2)[W(s, t) - \langle W \rangle],$$ (14)

$$c(q, s) = \int_0^s du[e^{-2qu}(1+qu)^2 - 2e^{-qu}(1+qu) + 1] \int_0^u dtcosh^2(\beta t)(s^2 - t^2)[W(s, t) - \langle W \rangle].$$ (15)

Thus, in order to ensure that the wave function functional $\psi[\chi]$ leads to the exact expectation value $\langle W(s, t) \rangle$, one has to solve a quadratic equation for the determination of the functions $\chi(q; s)$. The subspace thus corresponds to two points. The two solutions $\chi_1(q; s)$ and $\chi_2(q; s)$ lead to two normalized wave functions $\psi[\chi_1]$ and $\psi[\chi_2]$ each of which in turn give rise to the exact expectation $\langle W(s, t) \rangle$.

For the two normalized wave function functionals as determined above, the energy func-
tional in terms of Hylleraas coordinates which is

\[ I[\psi[\chi]] = \int \psi^* \hat{H} \psi d\tau \]

\[ = 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt \{ u(s^2 - t^2)[(\partial \psi / \partial s)^2 + (\partial \psi / \partial t)^2 + (\partial \psi / \partial u)^2] \}

\[ + 2(\partial \psi / \partial u)[s(u^2 - t^2)(\partial \psi / \partial s) + t(s^2 - u^2)(\partial \psi / \partial t)] \]

\[ - [4Zsu - (s^2 - t^2)]\psi^2 \}, \]

(17)
is then minimized with respect to the parameters \(\alpha, \beta\) and \(q\).

The above framework presented for the ground \(1^1S\) state of the two electron system is general and also applicable to excited states. For example, if one were to consider the excited \(2^3S\) triplet state of the Helium atom, one could employ for the prefactor in Eq.(2) for the wave function functional \(\psi[\chi]\) the expression \(\Phi(\alpha; s, t) = \sqrt{2/3}(\alpha^4/\pi)e^{-\alpha s t}\). Note that in this simplest of choices used for explanatory purposes, screening effects are ignored. With such a choice, the procedure to determine the wave function functional \(\psi[\chi]\) is the same as described above. In addition, this procedure could be employed in conjunction with the theorem of Theophilou according to which if \(\varphi_1, \varphi_2, ..., \varphi_m, ...,\) are orthonormal trial functions for the \(m\) lowest eigenstates of the Hamiltonian \(H\), having exact eigenvalues \(E_1, E_2, E_m, ...,\) then \(\sum_{i=1}^m \langle \varphi_i | H | \varphi_i \rangle \geq \sum_{i=1}^m E_i\). In this way, a rigorous upper bound to the \(\text{sum}\) of the ground and excited states is achieved. With the ground state energy known, a rigorous upper bound to the excited state energy is then determined, while simultaneously a physical constraint or sum rule is satisfied or an observable obtained exactly.

The description of the constrained-search—variational method given in this section concerns the determination of wave function functionals that obtain the expectation value of arbitrary Hermitian single-particle operators exactly. The functions \(\chi\) were assumed to depend only on the Hylleraas coordinate \(s\), and as a consequence, a quadratic equation had to be solved for their determination. If the variational space is expanded, then one would have to solve an integral equation for the function \(\chi\).

The ideas of the constrained-search—variational method may also be applied to sum rules involving two-particle properties. For example, consider the pair-correlation density
\[ g(\mathbf{rr'}) \text{ which is the conditional density at } \mathbf{r'} \text{ of all other electrons, given that one electron is at } \mathbf{r}, \text{ and which accounts for electron correlations due to the Pauli exclusion principle and Coulomb repulsion. The pair-correlation density for an N-electron system is defined as} \]

\[
g(\mathbf{rr'}) = \langle \Psi | \sum_{i \neq j} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}) | \Psi \rangle / \rho(\mathbf{r}), \tag{18} \]

and satisfies the sum rule

\[
\int g(\mathbf{rr'}) d\mathbf{r'} = N - 1, \tag{19} \]

for each electron position \( \mathbf{r} \). However, in order to determine the wave function functional \( \psi[\chi] \) that satisfies this sum rule at each electron position, one must solve an integral equation for \( \chi \). The details of the calculation of such a wave function functional are to be presented elsewhere [15].

### III. APPLICATION TO THE GROUND STATE OF THE HELIUM ATOM AND THE NEGATIVE ION OF ATOMIC HYDROGEN

In this section we apply the constrained-search—variational method as described above to the ground state of the Helium atom and the negative ion of atomic Hydrogen. The constraint employed is that of normalization, and the prefactor is that of Eq. (4). We begin with a discussion of the wave function functionals determined.

**Wave function functionals**

The 3-parameter wave function functionals are determined by solution of the quadratic equation Eq. (12). This solution for the functions \( \chi \) is analytical so that the wave function functionals \( \psi[\chi_1] \) and \( \psi[\chi_2] \) too are analytical. We do not provide here the analytical expressions for \( \chi_1(q, \alpha, \beta; s) \) and \( \chi_2(q, \alpha, \beta; s) \), but these functions are plotted in Fig.1. Observe that the two solutions for both \( He \) and \( H^- \) are distinctly different: one is positive and monotonically decreasing while the other is negative and monotonically increasing. Thus, although the two wave functions have the same structural form, and both satisfy the normalization constraint and the electron-electron cusp condition, they are very different.
The results as determined by these two wave functions for the ground state energy, and various single- and two-particle expectations are given in the subsections below. Comparisons are made with the results of the prefactor, Hartree-Fock (HF) theory, the 3-parameter Caratzoulas-Knowles (CK), and 1078-parameter Pekeris wave functions.
Ground-state energy

In Table I, we quote the values for the ground-state energy for $H^-$ and $He$. The corresponding satisfaction of the virial theorem, and percent errors when compared to the values of Pekeris for $He$ and those of the variational-perturbation results of Aashamar for $H^-$ are also given. Observe that the energies obtained by each wave function functional for $H^-$ and $He$ are an order of magnitude superior to that of the prefactor. For $He$, these results are on the average 0.06% from the Pekeris values. They are also an order of magnitude superior to both those of HF and CK. For $H^-$, both wave function functionals lead to results within 0.1% of the Aashamar values, and to positive electron affinities as must be the case since the ion is stable. (In the HF approximation, one does not obtain the negative ion of atomic Hydrogen to be stable. The exact satisfaction of the virial theorem by HF theory, however, is a consequence of self-consistency.) The results clearly demonstrate that highly accurate ground state energies can be obtained by constructing few-parameter wave functions that are functionals. These energies are far superior to those determined by similar wave functions with the same number of parameters but ones that are not functionals.

Single-particle expectations

In this subsection we present the results of the expectations of the Hermitian single-particle operators $W = \sum_i n_i^n$, $n = -2, -1, 1, 2$, $W = \sum_i \delta(r_i)$, and $W = \sum_i \delta(r_i - r)$. We begin with the determination of the electron density $\rho(r)$, which is the expectation of the operator $W = \sum_i \delta(r_i - r)$, and from which all the other single-particle expectations may be obtained. (Of course, these expectations may also be determined directly from the wave function functionals.) The density $\rho(r)$ is also required for the determination of the nonlocal Coulomb hole charge distribution $\rho_h(\mathbf{r}, \mathbf{r})$ as explained in the following subsection.

Now the wave function functionals are in terms of the Hylleraas coordinates $(s, t, u)$ which involve the position of both the electrons or both their radial distances from the nucleus. The electron density $\rho(r)$, on the other hand, depends only on the coordinates of one of the particles. Its determination from wave functions that are written in terms of the Hylleraas
TABLE I: Rigorous upper bounds to the ground state energy of $H^-$ and $He$ in atomic units as obtained from the wave function functionals determined via the constrained-search—variational method, together with the values due to Hartree-Fock (HF) theory [4], and the Caratzoulas-Knowles (CK) [10], Pekeris [6] and Aashamar [16] wave functions. The satisfaction of the virial theorem, and the percent errors compared to the values of Pekeris and Aashamar are also given.

| Ion or Atom | Wave function | Parameters | Ground state energy | % error | $-V/T$ |
|-------------|---------------|------------|---------------------|---------|--------|
| $H^-$       | $\Phi$        | $\alpha = 0.6612$, $\beta = 0.37797$ | $-0.51330$ | 2.7374 | 2.0001 |
|             | $\psi[\chi_1]$ | $q = 0.274$, $\alpha = 0.659$, $\beta = 0.308$ | $-0.52721$ | 0.1023 | 1.9979 |
|             | $\psi[\chi_2]$ | $q = 0.094$, $\alpha = 0.659$, $\beta = 0.306$ | $-0.52712$ | 0.1194 | 1.9982 |
|             | Aashamar      |            | $-0.52775$ |        | 2.0000 |
| $He$        | $\Phi$        | $\alpha = 1.68585$, $\beta = 0.49732$ | $-2.87566$ | 0.9663 | 2.0000 |
|             | $\psi[\chi_1]$ | $q = 0.957$, $\alpha = 1.662$, $\beta = 0.399$ | $-2.90158$ | 0.0736 | 1.9975 |
|             | $\psi[\chi_2]$ | $q = 0.242$, $\alpha = 1.663$, $\beta = 0.399$ | $-2.90232$ | 0.0482 | 1.9988 |
|             | HF            |            | $-2.86168$ | 1.448  | 2.0000 |
|             | CK            |            | $-2.89007$ | 0.470  | 1.9890 |
|             | Pekeris       |            | $-2.90372$ |        | 2.0000 |

coordinates is as follows. The electron density

$$
\rho(\mathbf{r}) = \int \psi^* (\sum_i \delta(\mathbf{r}_i - \mathbf{r})) \psi d\tau = 2 \int \psi^2(\mathbf{r}, \mathbf{r}') d\tau',
$$

(20)

Using the symmetry of the two electronic system, we have

$$
\int d\mathbf{r}' = 2\pi \int_0^\infty r'^2 dr' \int_{-1}^1 d\cos\theta.
$$

(21)

With $u = \sqrt{r^2 + r'^2 - 2rr'\cos\theta}$, then, for fixed $r$ and $r'$, we can rewrite Eq.(21) as

$$
\int d\mathbf{r}' = 2\pi \int_0^\infty \frac{r'}{r} dr' \int_{|r-r'|}^{r+r'} u du.
$$

(22)

On rewriting the wave function in terms of $(r, r', u)$, and substituting Eq.(22) into Eq.(20) leads to

$$
\rho(\mathbf{r}) = 2 \int_0^\infty \frac{r'}{r} dr' \int_{|r-r'|}^{r+r'} u\psi^2(r, r', u) du
$$

$$
= \rho_0(\mathbf{r}) + \Delta \rho_0(\mathbf{r}),
$$

(23)
where $\rho_0(r)$ is the density due to the prefactor (see the Appendix for the analytical expression):

$$\rho_0(r) = 2N^2 \int e^{-2\alpha_s \cosh^2(\beta t)} dr', \quad (24)$$

and

$$\Delta \rho_0(r) = 2N^2 \int e^{-2\alpha_s \cosh^2(\beta t)} (f^2(x; s, t, u) - 2f(\chi; s, t, u)) dr'. \quad (25)$$

is the density due to the correlation term, which can be evaluated numerically.

The electron density at the nucleus is

$$\rho(0) = \int \psi^* \left( \sum_i \delta(r_i) \psi \right) d\tau = \rho_0(0) + \Delta \rho_0(0), \quad (26)$$

where $\rho_0(0)$ is the prefactor contribution (see Appendix):

$$\rho_0(r) = 2N^2 \int e^{-2\alpha r} \cosh^2(\beta r) dr, \quad (27)$$

and the correlation contribution is

$$\Delta \rho_0(r) = 2N^2 \int e^{-2\alpha r'} \cosh^2(\beta r') (f^2(x; s, t, u) - 2f(\chi; s, t, u))|_{r_1=r=0, u=r_2=r'} dr'. \quad (28)$$

In Table II we quote the expectations of the operators $W = \sum_i r_i^n$, $n = -2, -1, 1, 2$, and $W = \sum_i \delta(r_i)$, for the ground state of the He atom as determined by the functionals $\psi[\chi_1]$ and $\psi[\chi_2]$ together with those of Hartree-Fock theory, and the Caratzoulas-Knowles and Pekeris wave functions. The corresponding percent errors relative to the values of Pekeris are given in Table III. As expected (see Table III), the improvement over the prefactor values is significant. The results of the two wave function functionals and those of Hartree-Fock theory are essentially equivalent, indicating thereby that the corresponding densities are also essentially the same. The expectations of single-particle operators in Hartree-Fock theory are, of course, known to be correct to second order[8]. Hence, both the
TABLE II: The expectation value of the operator \( W = \sum_{i=1}^{2} r_i^n \); \( n = -2, -1, 1, 2 \) and \( W = \sum_{i=1}^{2} \delta(r_i) \) for the He atom employing the wave function functionals determined by the constraint-search—variational method, and by the Hartree-Fock theory (HF) \([4]\), Caratzoulas-Knowles (CK) \([10]\), and Pekeris \([6]\) wave functions (WF).

| WF          | \( \langle \delta(r_1) + \delta(r_2) \rangle \) | \( \langle 1/r_1 + 1/r_2 \rangle > \) | \( \langle 1/r_1^2 + 1/r_2^2 \rangle > \) | \( \langle r_1 + r_2 \rangle \) | \( \langle r_1^2 + r_2^2 \rangle \) |
|-------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|
| \( \Phi \)  | 3.5025                                   | 3.3717                                   | 11.930                                   | 1.8758                                   | 2.4757                                   |
| \( \psi[\chi_1] \) | 3.6295                                   | 3.3750                                   | 12.033                                   | 1.8652                                   | 2.4156                                   |
| \( \psi[\chi_2] \) | 3.6450                                   | 3.3735                                   | 12.048                                   | 1.8639                                   | 2.4112                                   |
| \( HF \)    | 3.5964                                   | 3.3746                                   | 11.991                                   | 1.8545                                   | 2.3697                                   |
| \( CK \)    | 3.3245                                   | 3.3911                                   | 11.714                                   | 1.7848                                   | 2.1292                                   |
| \( Pekeris \) | 3.62086                                  | 3.3766                                   | 12.035                                   | 1.8589                                   | 2.3870                                   |

wave function functionals are accurate throughout space including the deep interior and far exterior of the atom. The comparison with the Caratzoulas-Knowles values (see Table III) is interesting for its implications. The wave function functional values are an order of magnitude superior. Of course, one does not expect the CK results to be accurate because these single-particle expectations are correct only to first order in the accuracy of the wave function. Thus, our results once again demonstrate, that wave function functionals determined by the constrained-search—variational method are superior to variationally determined wave functions that are not functionals.

Structure of Coulomb holes

We next consider the structure of the Coulomb hole charge distribution \( \rho_c(\mathbf{rr'}) \) as a function of the electron position \( \mathbf{r} \). The definition of this nonlocal or dynamic charge whose structure changes with electron position for nonuniform electron gas systems derives from that of the pair-correlation density \( g(\mathbf{rr'}) \) of Eq.(18) and from local effective potential energy theory \([11]\). The pair-density may be separated into its local and nonlocal components as

\[
g(\mathbf{rr'}) = \rho(\mathbf{r'}) + \rho_{xc}(\mathbf{rr'}), \tag{29}
\]
TABLE III: The percentage errors of the results in Table II relative to the values of Pekeris.

| WF | \(\langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle\) | \(\langle 1/r_1 + 1/r_2 \rangle\) | \(\langle 1/r_1^2 + 1/r_2^2 \rangle\) | \(\langle r_1 + r_2 \rangle\) | \(\langle r_1^2 + r_2^2 \rangle\) |
|----|-----------------|----------------|----------------|----------------|----------------|
| \(\Phi\) | 3.270 | 0.145 | 0.872 | 0.909 | 3.716 |
| \(\psi[\chi_1]\) | 0.237 | 0.047 | 0.017 | 0.339 | 1.198 |
| \(\psi[\chi_2]\) | 0.667 | 0.092 | 0.108 | 0.269 | 1.014 |
| \(HF\) | 0.676 | 0.059 | 0.366 | 0.237 | 0.725 |
| \(CK\) | 8.185 | 0.429 | 2.667 | 3.986 | 10.800 |

where \(\rho_{xc}(\mathbf{r}'\mathbf{r}')\) is the Fermi-Coulomb hole charge. This dynamic charge distribution is the change in the pair density relative to the density that occurs as a consequence of the Pauli exclusion principle and Coulomb repulsion. It follows from Eq.(19) that its total charge is \(-1\). The definition of the Coulomb hole \(\rho_{xc}(\mathbf{r}'\mathbf{r}')\) derives in turn from that of the Fermi-Coulomb \(\rho_{xc}(\mathbf{r}'\mathbf{r}')\) and Fermi \(\rho_x(\mathbf{r}'\mathbf{r}')\) holes, the latter being defined through local effective potential energy theory. In this theory, the interacting system as described by the Schrödinger equation is replaced by one of noninteracting Fermions with the same density. The corresponding wave function is a Slater determinant of single-particle spin orbitals, and one can then write down the resulting pair-correlation density \(g_s(\mathbf{r}'\mathbf{r}')\) of the model system as

\[
g_s(\mathbf{r}'\mathbf{r}') = \rho(\mathbf{r}') + \rho_x(\mathbf{r}'\mathbf{r}'),
\]

where \(\rho_x(\mathbf{r}'\mathbf{r}')\), the Fermi hole, is the nonlocal component of this pair density, and is a consequence solely of the Pauli principle. The total charge of the Fermi hole is also \(-1\). The Coulomb hole is then defined as the difference between the Fermi-Coulomb and Coulomb holes:

\[
\rho_c(\mathbf{r}'\mathbf{r}') = \rho_{xc}(\mathbf{r}'\mathbf{r}') - \rho_x(\mathbf{r}'\mathbf{r}'),
\]

and is thus representative solely of Coulomb correlations. The total charge of the Coulomb hole is 0. For two-electron systems in local effective potential theory \[11\], the Fermi hole is then \(\rho_x(\mathbf{r}'\mathbf{r}') = -\rho(\mathbf{r}')/2\) independent of electron position \(\mathbf{r}\).

In Figs. 2-4, we plot cross sections of the Coulomb hole \(\rho_c(\mathbf{r}'\mathbf{r}')\) for different electron positions \(\mathbf{r}\) as obtained via the functional \(\psi[\chi_2]\) together with the ‘exact’ Coulomb hole
FIG. 2: Cross-section through the Coulomb holes determined from the wave function functional $\psi[\chi_2]$ for electron positions at (a) $r = 0$ (a.u.), and (b) $r = 0.566$ (a.u.). The corresponding ‘exact’ Coulomb hole cross sections are also plotted for comparison. The electron position is indicated by the arrow.
FIG. 3: The figure caption is the same as in Fig.2 except that the cross sections plotted are for electron positions at (c) $r = 0.8$ (a.u.), and (d) $r = 1.0$ (a.u.).
FIG. 4: The figure caption is the same as in Fig. 2 except that the cross sections plotted are for electron positions at (c) $r = 1.5$ (a.u.), and (d) $r = 5.0$ (a.u.).
determined by Slamet and Sahni. (The electron, indicated by the arrow, is on the z axis corresponding to $\theta = 0^0$. The cross section through the Coulomb hole plotted corresponds to $\theta' = 0^0$ with respect to the electron-nucleus direction. The graph for $r' < 0$ corresponds to the structure for $\theta' = \pi$ and $r' > 0$.) The electron positions are at $r = 0, 0.566, 0.8, 1.0, 1.5$, and $5.0$ (a.u.). It is evident from these figures that the Coulomb holes as determined from the functional $\psi[\chi_2]$ closely approximate the exact results for electron positions throughout space: in the interior, within the atom, near its surface and outside the atom, and in the far asymptotic region. Note the cusp representative of the electron-electron cusp condition at the electron position which is indicated by an arrow in the figures.

Two-particle expectations

As a consequence of the accuracy of the dynamic Coulomb holes obtained, we expect the results for the expectation of two-particle operators to also be accurate. In Table IV we quote the values for the expectations of the operators $u^2, u, 1/u, 1/u^2$, where $u = |r_i - r_j|$, together with the Hartree-Fock and Pekeris values. The corresponding percent errors compared to those of Pekeris are given in Table V. Once again, the results are an order of magnitude superior to those of the prefactor, and are accurate for both functionals, although those due to $\psi[\chi_2]$ are consistently superior (see Table V). Of course, as expected, the Hartree-Fock theory results are not accurate.

If one were able to write the expectation of arbitrary operators $\hat{O}$ as functionals of the density: $\langle \hat{O} \rangle = \langle \psi[\rho] | \hat{O} | \psi[\rho] \rangle = O[\rho]$, as is possible in principle according to the Hohenberg-Kohn theorem, then it is in the expectation of two-particle operators that the small differences between the Hartree-Fock theory density and those of the two wave function functionals would be exhibited.

IV. CONCLUDING REMARKS

The idea of expanding the space of variations in variational calculations by writing the wave function as a functional of functions is appealing not only because the functionals lead
TABLE IV: The expectation value of the operators $u^2$, $u$, $1/u$, $1/u^2$, where $u = |r_i - r_j|$ as obtained by the constrained-search—variational method together with those due to Hartree-Fock theory [4] and the Pekeris [6] wave function.

| Wave function | $<u^2>$ | $<u>$ | $<1/u>$ | $<1/u^2>$ |
|---------------|---------|-------|---------|-----------|
| HF            | 2.3694  | 1.3621| 1.0258  | 1.8421    |
| $\Phi$       | 2.4757  | 1.3957| 1.0000  | 1.6998    |
| $\psi[\chi_1]$ | 2.5325  | 1.4271| 0.9388  | 1.4300    |
| $\psi[\chi_2]$ | 2.5236  | 1.4241| 0.9434  | 1.4532    |
| Pekeris       | 2.5164  | 1.4220| 0.9458  | 1.4648    |

TABLE V: The percentage errors of the results of Table IV relative to the values of Pekeris [6].

| Wave function | $\langle u^2 \rangle$ | $\langle u \rangle$ | $\langle 1/u \rangle$ | $\langle 1/u^2 \rangle$ |
|---------------|------------------------|---------------------|-----------------------|------------------------|
| HF            | 5.845                  | 4.217               | 8.458                 | 25.764                 |
| $\Phi$       | 1.618                  | 1.853               | 5.730                 | 16.045                 |
| $\psi[\chi_1]$ | 0.636                | 0.355               | 0.738                 | 2.373                  |
| $\psi[\chi_2]$ | 0.286                | 0.142               | 0.254                 | 0.791                  |

to more accurate upper bounds for the energy with fewer parameters, but also because, as demonstrated in this work, they lead to wave functions that are accurate over all space. Thus, both single- and two-particle expectations are also determined accurately. Certainly, one could claim by comparison with the results of Hartree-Fock theory, but without rigorous proof, that single-particle expectations obtained thereby are correct to second order in the accuracy of the wave function. It is also evident that the accuracy of two-particle expectations lies somewhere between first and second order. In contrast, variationally determined wave functions that are not functionals are accurate only in those regions of space contributing to the energy. Thus, for such wave functions, it is the expectation value of only those single- and two-particle operators that appear in the Hamiltonian that are reasonably accurate. All other expectations are correct only to first order.
The results of the present work could be further improved as follows: by expanding the
space of variations through the function \( \chi \); by employing other more efficacious choices
for the analytical form of the correlation factor and thus of the wave function functional;
and by improving the prefactor. In our work so far, we have employed analytical forms
for the prefactor. (The results of our prefactor for the ground state energy of both
\( H^- \) and \( He \) are superior to those of Hartree-Fock theory, see Table I.) Of course, one
could employ the Hartree-Fock theory Slater determinant as the prefactor. Or one could
employ a determinantal prefactor based on the orbitals generated within the local effective
potential framework of Quantal density functional theory (Q-DFT). In principle, these
orbitals generate the true electron density via a model system of noninteracting Fermions.
The corresponding local potential within Q-DFT depends upon the wave functions of the
interacting and noninteracting systems. Therefore, the corresponding orbitals generated
are representative of electron correlations due to the Pauli exclusion principle, Coulomb
repulsion, and the correlation contributions to the kinetic energy.

Finally, we are presently investigating the use of wave function functionals in conjunction
with Q-DFT for the many-electron case of \( N > 2 \). In these calculations, the antisymmetric
determinantal correlated wave function functional employed is of the form

\[
\psi[\chi] = \Phi\{\phi_i\} \Pi_{i>j}(1 - f(\chi; r_i, r_j)).
\] (32)

Here \( \Phi\{\phi_i\} \) is a Slater determinant that defines the state of the system and whose orbitals \( \phi_i \)
are generated via the differential equation of Q-DFT, \( f(\chi; r_i, r_j) \) is a spinless correlation func-
tional: \( f(\chi; r_i, r_j) = e^{-\beta r^2 [1 - \chi(R)(1 + r/2)]} \), where \( r = r_i - r_j \), \( R = r_i + r_j \), \( \beta = q \rho^{1/3}(R) \),
where \( \rho \) is a variational parameter, and \( \chi(R) \) is determined by the constraint of the Coulomb
hole sum rule for each electron position. This wave function functional satisfies the
electron-electron cusp condition. In this instance an integral equation is solved \[15\] to
determine the function \( \chi(R) \). Further, the products of the correlation functional are limited
to lowest order since higher order products of these factors are less significant \[18\]. The
highest occupied eigenvalue of Q-DFT differential equation corresponds in principle to
the negative of the ionization potential \[11\]. The region that contributes principally to
this eigenvalue is the asymptotic classically forbidden region of the atom. In Q-DFT,
the asymptotic structure of the effective potential is due solely to Pauli correlations, and can be determined exactly. This is because the contributions to the potential due to Coulomb correlations and Correlation-Kinetic effects decay more rapidly than $(-1/r)^{11}$, so that the potential in this region arises only from the Fermi hole charge which is defined through the Slater determinant of the orbitals. Thus, accurate ionization potentials can be obtained via the use of correlated-determinantal wave function functionals in conjunction with Q-DFT. These are variational-self—consistent calculations that lead to upper bounds for the energy while simultaneously satisfying a nonlocal physical constraint. We are also currently investigating the construction of wave function functionals of the form employed in the present work, but with the satisfaction of constraints other than that of normalization.

APPENDIX:

We give the analytical expressions for the normalization constant, the energy, and various single- and two-particle expectation values as determined by the prefactor wave function

$$\Phi = Ne^{-as\cosh(\beta t)}. \quad (A.1)$$

**Normalization**

\[
\int d\tau \Phi^2 = 2\pi^2 N^2 \int_0^\infty ds e^{-2as} \int_0^s dt \cosh^2(\beta t) \int_t^s du (s^2 - t^2) \\
= N^2 \pi^2 \left( -2\alpha^6 + 3\alpha^4\beta^2 - 3\alpha^2\beta^4 + \beta^6 \right) \left( 2\alpha^6(\beta - \alpha)^3(\alpha + \beta)^3 \right) = 1. \quad (A.2)
\]

**Ground-state energy**

\[
E_0 = \int \Phi^* \hat{H} \Phi d\tau \\
= 2\pi^2 \int_0^\infty ds \int_0^s du \int_u^s dt \left\{ u(s^2 - t^2) \left[ (\frac{\partial \Phi}{\partial s})^2 + (\frac{\partial \Phi}{\partial t})^2 + (\frac{\partial \Phi}{\partial u})^2 \right] \\
+ 2\frac{\partial \Phi}{\partial u} \left[ s(u^2 - t^2) \frac{\partial \Phi}{\partial s} + t(s^2 - u^2) \frac{\partial \Phi}{\partial t} \right] - [4Zsu - (s^2 - t^2)] \Phi^2 \right\} \\
= \alpha^2 - 2Z\alpha + \frac{\alpha(\beta^2 - \alpha^2)(10\alpha^4 - 11\alpha^2\beta^2 + 5\beta^4)}{8(-2\alpha^6 + 3\alpha^4\beta^2 - 3\alpha^2\beta^4 + \beta^6)} \\
- \frac{\beta^4(3\alpha^4 - 3\alpha^2\beta^2 + \beta^4)}{(-2\alpha^6 + 3\alpha^4\beta^2 - 3\alpha^2\beta^4 + \beta^6)}. \quad (A.3)
\]
Expectation values

\[ \rho_0(\mathbf{r}) = \langle \delta(\mathbf{r}_1 - \mathbf{r}) + \delta(\mathbf{r}_2 - \mathbf{r}) \rangle = N^2 \pi e^{-2\alpha r_1} \left[ \frac{1}{\alpha^3} + \frac{1}{2} e^{-2\beta r_1} \left( \frac{1}{(\alpha - \beta)^3} + \frac{e^{4\beta r_1}}{(\alpha + \beta)^3} \right) \right], \quad (A.4) \]

\[ \rho_0(0) = \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle = N^2 \pi \left[ \frac{1}{\alpha^3} + \frac{1}{2} \left( \frac{1}{(\alpha - \beta)^3} + \frac{1}{(\alpha + \beta)^3} \right) \right], \quad (A.5) \]

\[ \langle r_1 + r_2 \rangle = \int d\tau s \Phi^2 = 2\pi^2 N^2 \int_0^\infty ds e^{-2\alpha s} \int_0^s dt \cosh^2(\beta t) \int_t^s du (s^2 - t^2) \]
\[ = N^2 \pi^2 \left[ \frac{3(2\alpha^8 - 4\alpha^6 \beta^2 + 6\alpha^4 \beta^4 - 4\alpha^2 \beta^6 + \beta^8)}{2\alpha^7(\beta - \alpha)^3(\alpha + \beta)^3} \right]. \quad (A.6) \]

\[ \langle \frac{1}{r_1} + \frac{1}{r_2} \rangle = \int d\tau \frac{4s}{s^2 - t^2} \Phi^2 = 2\pi^2 N^2 \int_0^\infty ds e^{-2\alpha s} \int_0^s dt \cosh^2(\beta t) \int_t^s du \]
\[ = 2\alpha. \quad (A.7) \]

\[ \langle \frac{1}{r_1^2} + \frac{1}{r_2^2} \rangle = \int d\tau \frac{8(s^2 + t^2)}{(s^2 - t^2)^2} \Phi^2 = 2\pi^2 N^2 \int_0^\infty ds e^{-2\alpha s} \int_0^s dt \cosh^2(\beta t) 4(s^2 + t^2) \]
\[ = N^2 \pi^2 \left[ \frac{4\alpha^6 - 4\alpha^4 \beta^2 + 6\alpha^2 \beta^4 - 2\beta^6}{\alpha^4(\beta - \alpha)^3(\alpha + \beta)^3} \right]. \quad (A.8) \]

\[ \langle r_1^2 + r_2^2 \rangle = \int d\tau \frac{(s^2 + t^2)}{2} \Phi^2 = N^2 \pi^2 \int_0^\infty ds e^{-2\alpha s} \int_0^s dt \frac{\cosh^2(\beta t)(s^2 + t^2)(s^2 - t^2)^2}{2} \]
\[ = N^2 \pi^2 \left[ \frac{3(-2\alpha^{10} + 4\alpha^8 \beta^2 - 10\alpha^6 \beta^4 + 10\alpha^4 \beta^6 - 5\alpha^2 \beta^8 + \beta^{10})}{\alpha^8(\beta - \alpha)^5(\alpha + \beta)^5} \right]. \quad (A.9) \]

\[ \langle r_{12} \rangle = \int d\tau u \Phi^2 = 2N^2 \pi^2 \int_0^\infty ds e^{-2\alpha s} \int_0^s dt \frac{\cosh^2(\beta t)(s^2 - t^2)}{2} \int_t^s u^2 du \]
\[ = \frac{(70\alpha^8 - 126\alpha^6 \beta^2 + 209\alpha^4 \beta^4 - 140\alpha^2 \beta^6 + 35\beta^8)}{16\alpha(\beta^2 - \alpha^2)(-2\alpha^6 + 3\alpha^4 \beta^2 - 3\alpha^2 \beta^4 + \beta^6)}. \quad (A.10) \]

\[ \langle r_{12}^2 \rangle = \int d\tau u^2 \Phi^2 = 2N^2 \pi^2 \int_0^\infty ds e^{-2\alpha s} \int_0^s dt \frac{\cosh^2(\beta t)(s^2 - t^2)}{2} \int_t^s u^3 du \]
\[ = \frac{6(-2\alpha^{10} + 4\alpha^8 \beta^2 - 10\alpha^6 \beta^4 + 10\alpha^4 \beta^6 - 5\alpha^2 \beta^8 + \beta^{10})}{\alpha^2(\beta^2 - \alpha^2)^2(-2\alpha^6 + 3\alpha^4 \beta^2 - 3\alpha^2 \beta^4 + \beta^6)}. \quad (A.11) \]
\begin{align}
\langle \frac{1}{r} \rangle_{12} &= \int d\tau \frac{1}{u} \Phi^2 = 2N^2\pi^2 \int_0^{\infty} ds e^{-2\alpha s} \int_0^s dt \cosh^2(\beta t) (s^2 - t^2) \int_t^s du \\
&= \frac{\alpha(\beta^2 - \alpha^2)(10\alpha^4 - 11\alpha^2\beta^2 + 5\beta^4)}{8(-2\alpha^6 + 3\alpha^4\beta^2 - 3\alpha^2\beta^4 + \beta^6)}. \tag{A.12}
\end{align}

\begin{align}
\langle \frac{1}{r} \rangle_{12} &= \int d\tau \frac{1}{u^2} \Phi^2 = 2N^2\pi^2 \int_0^{\infty} ds e^{-2\alpha s} \int_0^s dt \cosh^2(\beta t) (s^2 - t^2) \int_t^s \frac{1}{u} du \tag{A.13}
\end{align}

Eq. (A.13) can be evaluated numerically.

ACKNOWLEDGMENTS

This work was supported by the Research Foundation of CUNY. L. M. was supported in part by NSF through CREST, and by a “Research Centers in Minority Institutions” award, RR-03037, from the National Center for Research Resources, National Institutes of Health.

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