A Nonlinear Programming Approach to Lower Bounds for the Ground-State Energy of Helium

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ABSTRACT: Lower-bound estimates for the ground-state energy of the helium atom are determined using nonlinear programming techniques. Optimized lower bounds are determined for single-particle, radially correlated, and general correlated wave functions. The local nature of the method employed makes it a very severe test of the accuracy of the wave function. © 1999 John Wiley & Sons, Inc. Int J Quant Chem 71: 455–463, 1999

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Introduction

The purpose of this work was to study lower bounds for the ground-state energy of the helium atom using different levels of approximate wave functions. A key focus of the work was an examination of the structural features of the wave function that lead to improved lower bounds. Lower bounds for the energy levels of few-electron systems have received a considerable amount of attention in the literature (see [1, 2] for a summary of literature references). Two principal approaches have been employed: These are the method of intermediate Hamiltonians [3–6] and the application of the classical lower-bound formulas (Temple [7], Weinstein [8], Stevenson [9]), of which the Temple lower bound gives the sharpest results [10]. The best lower bound for the ground-state energy of the helium atom obtained using Temple's formula is [11]

$$-2.90372437703413 \text{ au} < E_0, \qquad (1)$$

and the error is approximately one in the last quoted digit. Both of the aforementioned ap-

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proaches have associated difficulties. The classical lower-bound formulas all require the evaluation of the expectation value $\langle H^2 \rangle$, where H is the nonrelativistic Hamiltonian of the system. This leads to considerable mathematical difficulties, particularly when attempts are made to go beyond two-electron systems [1, 12]. The method of intermediate Hamiltonians has not been applied with any significant success to systems beyond the two-electron level.

In this work, the focus was on an approach which has received relatively little attention in the literature. Our principal objective was to determine the issues that underlie the approach employed, rather than to attempt to obtain a bound as sharp as the result presented in Eq. (1).

Theory

The key result utilized in this work is

$$\inf\left(\frac{H\psi}{\psi}\right) \equiv E_{LB} \leq E_0, \tag{2}$$

where E_{LB} designates the lower bound to the exact nonrelativistic ground-state energy and ψ is an approximate solution of the Schrödinger equation

$$H\Psi = E_0\Psi. \tag{3}$$

The treatment discussed in this work is restricted to the ground states of two-electron systems, and the focus of the present investigation was the ground state of the helium atom. The factor $\psi^{-1}H\psi$ which appears in Eq. (2) is often referred to as the local energy [13]. The nonrelativistic Hamiltonian employed throughout is

$$\begin{aligned} H = &-\sum_{i=1}^{2}\left\{\frac{1}{2}\frac{\partial^2}{\partial r_i^2} + \frac{1}{r_i}\frac{\partial}{\partial r_i} + \frac{Z}{r_i}\right\} - \frac{\partial^2}{\partial r_{12}^2} \\ &- \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} + \frac{1}{r_{12}} - \frac{r_1^2 - r_2^2 + r_{12}^2}{2r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} \\ &- \frac{r_2^2 - r_1^2 + r_{12}^2}{2r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}}, \end{aligned} \tag{4}$$

where Z is the nuclear charge, r_i is the electron-nuclear coordinate, and r_{12} is the electron–electron separation. Equation (4) takes advantage of the well-known reduction in variables that results from the S-state symmetry of the ground state of the helium atom. Equation (2) and some related results have been known for a long time. Barta [14] discussed the result in connection with the fundamental vibrations of a membrane. Duffin [15] generalized the result, and Barnsley [16] gave further elaboration and several applications. A concise proof was given by Thirring [17]. Additional discussion of the approach and applications to some model problems have been investigated (see [18–25]).

If the approximate wave function ψ is written in terms of the exact ground-state eigenfunction as

$$\psi = \Psi + \delta\Psi, \tag{5}$$

then

$$E_{LB} = E_0 + \inf\left\{\frac{(H - E_0)\delta\Psi}{\Psi} + O([\delta\Psi]^2)\right\}, \tag{6}$$

and the lower bound has a first-order dependence on the error in the wave function. This is in contrast to the well-known result from the variation method, where the upper bound to E_0 depends on the error $\delta\Psi$ only in second order, a fact that underlies much of the considerable success of energy-level calculations for atomic and molecular systems. Because E_{LB} has a first-order dependence on $\delta\Psi$, this quantity may be used as a useful measure of the accuracy of an approximate wave function.

We now examine the behavior of the approximate wave function as $E_{LB} \to E_0$. In what follows, it will be assumed that the wave functions are real-valued. The following result is proved:

$$\int \Psi |(H - E_0)\psi| \, d\tau_1 \, d\tau_2 \leq \varepsilon, \tag{7}$$

where

$$\varepsilon = 2(E_0 - E_{LB}) \tag{8}$$

and $d\tau_1$ denotes a spatial volume for electron 1. We can write

$$\begin{aligned} \langle \Psi \mid (E_0 - H)\psi \rangle = &\langle \Psi \mid (E_0 - H)\psi \rangle_\sigma \\ &- \langle \Psi \mid (H - E_0)\psi \rangle_{\sigma_c}, \end{aligned} \tag{9}$$

where σ is the subset of R^6 such that $(E_0 - H)\psi \geq 0$ and σ_c is its complementary set. But

$$\langle \Psi \mid (E_0 - H)\psi \rangle = \langle (E_0 - H)\Psi \mid \psi \rangle = 0, \tag{10}$$

and, hence,

$$\langle \Psi \mid (E_0 - H)\psi \rangle_\sigma = \langle \Psi \mid (H - E_0)\psi \rangle_{\sigma_c}. \tag{11}$$

Using

$$E_0 - E_{LB} = E_0 - \inf\left(\frac{H\psi}{\psi}\right), \tag{12}$$

we can write

$$E_0\psi - H\psi \leq (E_0 - E_{LB})\psi. \tag{13}$$

Substituting Eq. (13) into Eq. (11) leads to the result

$$\langle \Psi \mid (E_0\psi - H\psi)\rangle_\sigma \leq (E_0 - E_{LB})\langle \Psi \mid \psi\rangle_\sigma \leq E_0 - E_{LB}. \tag{14}$$

To obtain Eq. (14), the nonnegativity of both Ψ and ψ [26] is employed and the Schwartz inequality has been used. Both Ψ and ψ are assumed to be normalized to unity. Using Eqs. (11) and (14) leads to

$$\int \Psi|(H - E_0)\psi|\, d\tau_1\, d\tau_2 = \int_\sigma \Psi(E_0 - H)\psi\, d\tau_1\, d\tau_2 + \int_{\sigma_c} \Psi(E_0 - H)\psi\, d\tau_1\, d\tau_2 \leq \varepsilon, \tag{15}$$

with ε defined in Eq. (8). Therefore, as $E_{LB} \to E_0$, $\varepsilon \to 0$ and the integral on the left-hand side of Eq. (15) approaches zero. In the weighted mean sense of the integral given in Eq. (15), ψ approaches Ψ as $E_{LB} \to E_0$.

A Nonlinear Programming Problem

Suppose that the approximate wave function depends on the parameter set $\{\alpha_i, i = 1, N\}$, then the problem under investigation reduces to

$$\max_{\alpha_i}\{E_{LB}(\alpha_i)\} \equiv \max_{\alpha_i}\left[\inf_{r_1, r_2, r_{12}}\left\{\frac{H\psi}{\psi}\right\}\right] \tag{16}$$

subject to the constraints

$$0 \leq r_1 \qquad 0 \leq r_2 \tag{17}$$

and

$$(r_1 - r_2)^2 \leq r_{12}^2 \leq (r_1 + r_2)^2. \tag{18}$$

In addition to the conditions given in Eqs. (17) and (18), there are constraints on the parameter set $\{\alpha_i\}$ to ensure the appropriate asymptotic behavior for the wave function and to satisfy some cusp-like relationships discussed below. Equations (16)–(18) constitute a nonlinear programming problem. The objective function

$$\inf_{r_1, r_2, r_{12}}\left\{\frac{H\psi}{\psi}\right\}$$

is, in general, highly nonlinear in the variables $\{\alpha_i\}$. Equation (16) actually represents one nonlinear programming problem (over the variables $\{r_1, r_2, r_{12}\}$) imbedded inside a second nonlinear programming problem with respect to the variables $\{\alpha_i\}$. There have been relatively few applications of the nonlinear programming to study the ground state of the helium atom (see, e.g., [27–29]).

The following computational strategy was employed: A set of parameters α_i were selected, then the minimum of $\psi^{-1}H\psi$ determined with respect to the coordinates $\{r_1, r_2, r_{12}\}$. This was carried out by solving the nonlinear programming problem indicated in equations (16)–(18) by using a sizable grid of $\{r_1, r_2, r_{12}\}$ starting values. The lowest minimum located is assigned the value E_{LB} for the particular parameter set $\{\alpha_i\}$. The parameter set $\{\alpha_i\}$ is systematically modified, until no further increase in E_{LB} could be obtained. For a number of trial wave functions examined, the function $\psi^{-1}H\psi$ displays a considerable number of local (false) minima. For this reason, it is imperative to start the search for the minimum from a large array of starting values of $\{r_1, r_2, r_{12}\}$. For the final parameter sets $\{\alpha_i\}$, a very large grid of $\{r_1, r_2, r_{12}\}$ points was used to ensure that a false minimum had not been located. Employing the obvious symmetry constraint $r_1 \geq r_2$ simplifies the search. Knowledge of the appearance of the surface for $\psi^{-1}H\psi$ was also of value in pinning down the correct result for $\inf\{\psi^{-1}H\psi\}$, at least for the simpler wave functions examined.

Single-particle Model

A number of simple wave functions were examined that fall in the category of single-particle descriptions of the helium atom. In this model, the exact wave function is approximated by

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2), \tag{19}$$

where $\phi(\mathbf{r}_1)$ denotes a one-electron wave function. The simplest one-electron wave function is (with

normalization coefficient N)

$$\phi(r) = Ne^{-kr}, \tag{20}$$

which leads to the result

$$E_{LB} = \inf\left\{-k^2 + (k - Z)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}}\right\} \tag{21}$$

$$= \begin{cases} -\infty & k < Z \\ -k^2 & k \geq Z. \end{cases} \tag{22}$$

Equations (21) and (22) were given by Barnsley [16], who then commented that attempts to improve the result in Eq. (22) using more elaborate wave functions were not successful. The optimal result for the ground state of helium is -4 au, which is the same result obtained by deleting the interelectronic contribution from the Hamiltonian.

One issue that arises from this simple example is the significance of the electron–nuclear cusp condition in obtaining the best result for E_{LB}. For the choice given in Eq. (20), the optimal result for E_{LB} occurs when the electron–nuclear cusp condition,

$$\left.\frac{\partial\phi(r)}{\partial r}\right|_{r\to 0} = -Z\phi(0), \tag{23}$$

is satisfied.

The one-particle case can be simplified in the following manner: $\psi^{-1}H\psi$ can be written in terms of the one-electron function $F(r)$ as

$$\psi^{-1}H\psi = F(r_1) + F(r_2) + r_{12}^{-1}, \tag{24}$$

where

$$F(r) = \phi(r)^{-1}\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right)\phi(r). \tag{25}$$

From the inequality

$$\frac{1}{r_1 + r_2} \leq \frac{1}{r_{12}}, \tag{26}$$

it follows that

$$\inf_{r_1, r_2}\left\{F(r_1) + F(r_2) + \frac{1}{r_1 + r_2}\right\} \leq \inf_{r_1, r_2, r_{12}}\{\psi^{-1}H\psi\}. \tag{27}$$

Also, we can write

$$\inf_{r_1, r_2, \theta_{12}}\{\psi^{-1}H\psi\} \leq \inf_{\substack{r_1, r_2 \\ \text{fixed } \theta_{12}}}\{\psi^{-1}H\psi\}, \tag{28}$$

where θ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. If we select $\theta_{12} = \pi$ for the fixed value, then Eq. (28) can be written as

$$\inf_{r_1, r_2, r_{12}}\{\psi^{-1}H\psi\} \leq \inf_{r_1, r_2}\left\{F(r_1) + F(r_2) + \frac{1}{r_1 + r_2}\right\}. \tag{29}$$

Combining Eqs. (27) and (29) allows us to write

$$\inf_{r_1, r_2, r_{12}}\{\psi^{-1}H\psi\} = \inf_{r_1, r_2}\left\{F(r_1) + F(r_2) + \frac{1}{r_1 + r_2}\right\}. \tag{30}$$

Hence, the one-particle model can be reduced to a nonlinear programming problem in the two-variable configuration space $\{r_1, r_2\}$.

The results of a selection of some of the one-particle cases that were considered are presented in Table I. The first single-particle case that was investigated is

$$\phi(r) = N(1 + br)^{-1}e^{-ar}, \tag{31}$$

with a and b regarded as flexible parameters selected to optimize E_{LB}. In the following discussion, C_{en} will denote the following:

$$C_{en} = -Z - \lim_{r_i \to 0}\left\{\psi^{-1}\frac{\partial\psi}{\partial r_i}\right\}. \tag{32}$$

The definition in Eq. (32) is clearly motivated by the form of the electron–nuclear cusp condition. C_{en} will, in general, be a function of one of the configuration space coordinates. In such cases, the limit $\lim_{r_2 \to 0} C_{en}(r_2)$ will be of interest if $r_i \equiv r_1$ in Eq. (32). To ensure finite lower bounds for E_{LB}, C_{en} must satisfy the condition

$$C_{en} \geq 0 \tag{33}$$

for the parameter set that C_{en} depends on and also for *all* values of r_2. The electron–nuclear cusp condition is satisfied when the equality sign holds in Eq. (33). For the functional form given in Eq. (31),

$$C_{en} = a + b - Z. \tag{34}$$

TABLE I
Lower bounds for various trial wave functions in the single-particle approximation.

Trial wave function $\phi(r)$	Parameters	Cusp factor ($C_{en} + Z$)	Lower bound (au)
$(1 + br)^{-1}e^{-ar}$	$a = 1.370496$, $b = 0.718675$	$a + b = 2.08917$	−3.39550
$(e^{-ar} + cre^{-br})$	$a = 1.534266$, $b = 1.953600$, $c = -0.468742$	$a - c = 2.00301$	−3.38617
$(1 + dr)^{-1}e^{-cr}\ln(a + br)$	$a = 2.933024$, $b = 4.548384$, $c = 1.419981$, $d = 2.021190$	$c + d - \frac{b}{a\ln a} = 2.00000$	−3.37838
$e^{-ar - br(1+cr)^{-1}}$	$a = 0.552955$, $b = 1.457045$, $c = 0.078413$	$a + b = 2.01000$	−3.37579
$(1 + br)^{-1}e^{-ar} + c(1 + dr)^{-1}e^{-fr}$	$a = 1.398486$, $b = 0.043587$, $c = 1.629418$, $d = 0.126384$ $f = 2.220573$	$\frac{a + b + cd + cf}{1 + c} = 2.00282$	−3.36629
$(e^{-ar} + ce^{-br})$	$a = 2.330074$, $b = 1.422874$, $c = 0.571008$	$\frac{a + bc}{1 + c} = 2.00034$	−3.36479
$(1 + br + cr^2)^{-1}e^{-ar}$	$a = 1.094570$, $b = 0.905430$, $c = 0.326774$	$a + b = 2.00000$	−3.36330

The optimal set of parameters for this case (see Table I) give $C_{en} = 0.0892$. The minimum on the surface is located at $r_1 = 0.3317$ au and $r_2 = 1.545$ au. $\psi^{-1}H\psi$ displays a relatively shallow trough near the nucleus and then rises steeply as $r_i \to 0$. Using Eq. (31), $E_{LB} = -3.395497$ au, which is a significant improvement over the value of E_{LB} obtained by Barnsley using Eq. (20). A large part of the improvement is tied to the fact that the additional parameter dependence is introduced in such a way that it contributes directly to the function C_{en}. The exponential coefficient takes values below Z, while maintaining the requirement given in Eq. (33). This is not the case for other simple trial wave functions such as $(1 + br)e^{-ar}$ (for positive b), for which $C_{en} = a - b - Z$. It is noteworthy that optimal values of the parameters a and b in Eq. (31) do not lead to a wave function that exactly satisfies the electron–nuclear cusp condition ($a + b = Z$), but do come rather close. Some wave functions which lead to a different cusp behavior were examined, for example, the Gaussian-type function e^{-ar^2}, but these wave functions do not lead to finite lower bounds for the energy.

Several other one-particle cases were examined in order to resolve two questions: The first concerns the issue of the single-particle limit for E_{LB}. Since the value of E_{LB} has a very sensitive dependence on the form of $\phi(r)$, we explored several different functional forms for $\phi(r)$ in order to determine the best possible E_{LB}. A sequence of functions of the following type were investigated:

$$\phi(r) = \sum_{i=1}^{N} C_i r^{n_i} e^{-a_i r}, \tag{35}$$

with the constraint that $C_i \geq 0$ is imposed in order to ensure the positivity of $\phi(r)$. This latter constraint can be relaxed by appropriate selection of the exponent parameters. A few of the results are summarized in Table I. The results from these cases and some additional cases suggests a single particle limit of

$$E_{LB} \approx -3.363 \text{ au}. \tag{36}$$

This limit is approximately 15.7% below the exact ground-state energy, which can be contrasted with the single-particle upper-bound limit of −2.86168 au, which is just 1.45% too high. The second issue of interest was how closely the electron–nuclear cusp condition would be satisfied for a variety of one-electron wave functions. For the functional form given in Eq. (35) with $n_i = 0$, the condition

required to circumvent the electron–nuclear singularities is

$$C_{en} = \frac{\sum_{i=1}^{N} C_i a_i}{\sum_{i=1}^{N} C_i} - Z \geq 0. \qquad (37)$$

The electron–nuclear cusp condition is satisfied by the approximate wave function of Eq. (35) (for $n_i = 0$) when the equality sign in Eq. (37) applies. For two-, three- and four-term wave functions, the C_{en} values were found to be 0.00034, 0.00000, and 0.00000, respectively. These values suggest that satisfying the electron–nuclear cusp condition is an important requirement, if an optimal value of E_{LB} is to be obtained for the one-particle model, using the functional form given in Eq. (35) (with $n_i = 0$).

Radial Correlated Model

For wave functions of the type $\psi(\mathbf{r}_1, \mathbf{r}_2)$, which includes those describing radial correlation, the following result can be established:

$$\inf_{r_1, r_2, r_{12}} \{\psi^{-1} H \psi\} = \inf_{r_1, r_2} \{\psi^{-1} \tilde{H} \psi\}, \qquad (38)$$

where

$$\tilde{H} = -\sum_{i=1}^{2} \left\{ \frac{1}{2} \frac{\partial^2}{\partial r_i^2} + \frac{1}{r_i} \frac{\partial}{\partial r_i} + \frac{Z}{r_i} \right\} + \frac{1}{r_1 + r_2}. \qquad (39)$$

The proof is similar to the one given above for the single-particle case. $\tilde{H}$ is not the conventionally designated radial Hamiltonian that would be employed in a standard variational calculation, but it is the appropriate radial Hamiltonian for the lower-bound problem of this work. This is the same Hamiltonian that arises in the single-particle case discussed above in the Single-particle Model section. Equation (38), with the application of Eq. (2) to $\tilde{H}$, implies that the best lower bound to the exact ground-state energy E_0 using radially correlated wave functions is the lowest eigenvalue of $\tilde{H}$. An estimate of the radial lower-bound limit can be found from a precise variational calculation using Eq. (39). This calculation was performed and the result obtained for the ground-state energy was -3.24594 au.

The first two examples presented in Table II correspond to radially correlated wave functions. For the first example, the result for E_{LB} is observed to be no better than the simplest single-particle result given above in the Single-particle Model

TABLE II
Lower bounds for various correlated trial wave functions.

Trial wave function $\psi(r_1, r_2, r_{12})$	Parameters	E_{LB} (au)
$(1 + br_1 + br_2)^{-1} e^{-ar_1 - ar_2}$	$a = 2.0000$, $b \to 0$	-4.0
$(1 + mr_1 + lr_1^2)^{-1}(1 + mr_2 + lr_2^2)^{-1} e^{-ar_1 - ar_2}$	$a = 1.44$, $b = -0.48$, $c = 1.02$,	-3.28287
$e^{-b(1+gr_1+gr_2)^{-1}(1+cr_1+cr_2+dr_1^2+dr_2^2)}$	$d = 1.36$, $g = 1.69$, $m = 0.40$, $l = 0.21$	
$e^{-ar_1 - ar_2 + gr_{12}}$	$a = 2.000$, $g \to 0$	-4.0
$(1 + br_1)^{-1}(1 + br_2)^{-1} e^{-ar_1 - ar_2 + gr_{12}}$	$a = 1.291846$, $b = 0.875174$, $g = 0.053005$	-3.31789
$(1 + br_1)^{-1}(1 + br_2)^{-1} e^{-ar_1 - ar_2} e^{hr_{12}(1+gr_{12})^{-1}}$	$a = 1.234669$, $b = 0.995136$, $g = 1.240851$, $h = 0.5000$	-3.27097
$e^{hr_{12}(1+gr_{12})^{-1}} e^{-fr_{12}} \prod_{i=1}^{2} e^{-kr_i - c(1+ar_i)(1+br_i)^{-1}}$	$a = 0.563$, $b = 0.161$, $c = 3.354$, $f = 0.115$, $g = 0.575$, $h = 0.500$, $k = 0.750$	-3.19190
$(1 + mr_1 + lr_1^2)^{-1}(1 + mr_2 + lr_2^2)^{-1} e^{-ar_1 - ar_2 + br_{12}}$ $e^{-c(1+kr_1+kr_2+pr_{12})^{-1}(1+dr_1+dr_2+fr_{12}+gr_1^2+gr_2^2+hr_{12}^2)}$	$a = 1.551$, $b = 0.503$, $c = 1.668$, $d = 1.41$, $f = 1.543$, $g = -0.598$, $h = 0.406$, $k = 1.218$, $l = 0.243$, $m = 0.398$, $p = 1.494$	-2.97270

section. The result for C_{en} for this case is given by

$$C_{en} = a + b(1 + br_2)^{-1} - Z \tag{40}$$

and E_{LB} is the inf of the following result:

$$\begin{aligned}\psi^{-1}H\psi = &-a^2 - 2\left\{b[1 + b(r_1 + r_2)]^{-1}\right\}^2 \\ &- 2ab[1 + b(r_1 + r_2)]^{-1} \\ &+\left(a + b[1 + b(r_1 + r_2)]^{-1} - Z\right) \\ &\times(r_1^{-1} + r_2^{-1}) + r_{12}^{-1}.\end{aligned} \tag{41}$$

The flexible parameter b does not allow a to be decreased [relative to the value obtained for the functional form given in Eq. (20) with $a = k$]. As a result, the value of the parameter b approaches zero, and the functional form for this radially correlated wave function collapses to Eq. (20).

The best radially correlated wave function discovered:

$$\begin{aligned}\psi = &(1 + mr_1 + lr_1)^{-1}(1 + mr_2 + lr_2)^{-1}e^{-ar_1 - ar_2} \\ &\times e^{-b(1+gr_1+gr_2)^{-1}(1+cr_1+cr_2+dr_1^2+dr_2^2)},\end{aligned} \tag{42}$$

gave the result

$$E_{LB} \approx -3.28287 \text{ au}. \tag{43}$$

The latter value, which is close to the optimal radially correlated estimate given above, is approximately 13% below the exact ground-state energy, which can be contrasted with the radial upper-bound limit obtained via the variational technique, $E_{rad} = -2.8790$ au, which is just 0.85% too high.

r_{12} Correlated Wave Functions

The simplified analysis presented in the last two sections no longer applies when the wave function has an explicit dependence on r_{12}. For wave functions depending on r_{12}, the Hamiltonian given in Eq. (4) is the most convenient way to evaluate $\psi^{-1}H\psi$. A number of r_{12}-dependent wave functions were investigated, and some representative examples are included in Table II. For a number of these more complicated choices, refinement of the parameter sets reported in Table II may well lead to improved results for E_{LB}. The number of local minima tends to increase with the number of variable parameters. It therefore becomes necessary to solve Eq. (16) with a larger grid of starting values of $\{r_1, r_2, r_{12}\}$. To make the problem more tractable, the size of the initial search grid for the parameters $\{\alpha_i\}$ was reduced. Because of the increased step size for the grid search, the optimal set of $\{\alpha_i\}$ parameters may be missed.

For the first case in Table II where r_{12} is incorporated in the wave function, no improvement on the single-particle result given in Eq. (22) is obtained. Let us explore the reasons for this. The following coefficient is defined:

$$C_{ee} = 1 - 2\lim_{r_{12}\to 0}\left\{\psi^{-1}\frac{\partial\psi}{\partial r_{12}}\right\}. \tag{44}$$

The definition is motivated by the standard form of the electron–electron cusp condition [30]

$$\left(\frac{\partial\psi}{\partial r_{12}}\right)_{\text{ave}}\Bigg|_{r_{12}\to 0} = \frac{1}{2}\psi(r_{12} = 0). \tag{45}$$

To obtain a finite E_{LB}, C_{ee} must satisfy the condition $C_{ee} \geq 0$. For the correlated wave function

$$\psi(r_1, r_2, r_{12}) = e^{-a(r_1+r_2)+gr_{12}}, \tag{46}$$

$$\begin{aligned}\psi^{-1}H\psi = &-a^2 - g^2 \\ &+(a - Z)(r_1^{-1} + r_2^{-1}) + (1 - 2g)r_{12}^{-1} \\ &+\frac{ag(r_1 + r_2)\left(r_{12}^2 - (r_1 - r_2)^2\right)}{2r_1r_2r_{12}}.\end{aligned} \tag{47}$$

From Eq. (46),

$$C_{en} = a - Z \geq 0 \tag{48}$$

and

$$C_{ee} = 1 - 2g \geq 0. \tag{49}$$

For the approximate wave function given by Eq. (46), the electron–electron cusp condition [Eq. (45)] is satisfied when the equality sign holds in Eq. (49). This correlated wave function does not lead to an improved value of E_{LB} because the r_{12}-dependent terms do not offset the detrimental contribution $-g^2$. Examination of the limit of the right hand side of equation (47) as $r_1, r_2 \to \infty$ for the case $\theta_{12} = 0$, and ensuring that Eqs. (48) and (49) are satisfied, gives an immediate indication of the expected optimal values of the parameters for this particular wave function. The fact that the parameter g does not contribute to C_{en} should be noted.

As for the single-particle cases, the best results for E_{LB} using r_{12}-dependent wave functions are obtained when the structure of the wave function is such that the added parameters contribute to C_{en}, in a way that allows for smaller values of the key exponent parameters while maintaining the condition $C_{en} \geq 0$. The preceding comment is an empirical observation based on an examination of a large number of trial wave functions. It is entirely possible that a very different functional form for the wave function might lead to a situation where the exponent parameters are much larger than those determined in the present investigation. For example, for the second from last entry in Table II,

$$C_{en} = k + c(a - b) - Z \geq 0, \tag{50}$$

and the optimal value of k is 0.75. For the correlated cases, the picture is somewhat more complicated than just the need to satisfy the condition $C_{en} \geq 0$. It is also necessary to keep in mind that $C_{ee} \geq 0$ must be satisfied, and, in addition, the much more complicated structure of the function $\psi^{-1}H\psi$ makes the solution of the nonlinear programming problem considerably more difficult.

Not unexpectedly, the value of E_{LB} improves when additional parameter flexibility is incorporated into ψ. The best result obtained for E_{LB} is

$$E_{LB} = -2.951817 \text{ au}, \tag{51}$$

which is about 1.7% below the known value of E_0, which is given in Eq. (1). The result in Eq. (51) was obtained with a 23-parameter wave function that is an extended form of the last entry in Table II. Efforts have been undertaken to improve the result in Eq. (51) by expanding the size of the parameter set. It appears that an improved functional form will be necessary to obtain a significantly better result for E_{LB} than the one given above.

Discussion

The standard techniques for improving the quality of the wave function are driven principally by experience gained from application of the variational method. A number of simple examples shown in Tables I and II indicate that this experience does not carry over to the formula for E_{LB}. This is to be expected, since the variational method is a global measure of the quality of the wave function, and Eq. (2) provides a stringent local measure of the accuracy of the approximate wave function. Since E_{LB} depends implicitly on the quality of the wave function taken over the $\{r_1, r_2, r_{12}\}$ configuration space, Eq. (2) becomes an extremely useful measure of the accuracy of the wave function. Two highly precise compact Kinoshita-type wave functions [31] were examined using published values for the basis sets [32]. The result $E_{LB} = -\infty$ was obtained in each case. Wave functions optimized using the variation method can easily lead to a very poor result for E_{LB}.

There are two principal difficulties associated with the method of this work when applied to the ground state of the helium atom. The first is that we have no systematic approach to improving the quality of E_{LB}. We have observed this feature for a number of simple trial wave functions. For example, the single-particle orbital $(1 + br)e^{-ar}$ and the radial correlated function $e^{-a(r_1+r_2)} + ce^{-b(r_1+r_2)}$ did not improve upon the lower-bound result obtained using $\psi = e^{-a(r_1+r_2)}$ for the range of parameters explored. It does not appear, based on the many examples considered, that a sums of terms, for example, $(1 + br)^{-1}e^{-ar} + c(1 + dr)^{-1}e^{-fr}$, will lead to significantly improved lower bounds beyond what is obtained by considering the first term alone. The implication is that improved results may not be forthcoming by simply proceeding to larger expansions of basis terms of similar type. This is in sharp contrast to the standard method for finding upper bounds to E_0, the variation method, which provides the theoretical framework for systematic improvement of the wave function. However, the variation method provides only indirect guidance for basis-set selection for properties not dependent on the energy-important region of configuration space and for addressing the shape-fitting problem implicit in such calculations.

The second difficulty is the rather elaborate nature of the optimization calculation that must be carried out. Improved understanding of the structure of the surfaces for $\psi^{-1}H\psi$ in configuration space for a variety of test functions will greatly assist in this aspect of the calculation. Very careful searching in the $\{r_1, r_2, r_{12}\}$ variables is required to avoid locating false minima. Problems of this type can probably be significantly reduced once experience with a number of standard functional forms for ψ is established.

Two problems for future investigation are the following: We intend to study the Z dependence of

E_{LB} for the helium isoelectronic series. There are reasons to expect that improved lower bounds will be obtained as Z increases. A more difficult goal is to seek extensions of the present approach to atomic systems with more than two electrons.

In summary, we report some functional forms for the wave function for the ground state of the helium atom which improve the behavior of the local energy as measured by E_{LB}. Although not simple in form, these functions, or some related extensions, might prove to be useful as basis functions for variational calculations on more complex atoms. Because of the nature of these functions, such calculations would need to be carried out using Monte Carlo techniques.

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