Upper and lower stationary bounds on $\langle r_1^2 + r_2^2 \rangle / 2$ for the ground state of helium

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A number of previously derived rigorous upper and lower stationary bound formulas are tested using as an example the expectation value of the operator $(r_1^2 + r_2^2)/2$ for the ground state of helium.

In a recent paper,[1] hereafter referred to as I, methods were derived for calculating rigorous stationary upper and lower bounds on matrix elements of quantum-mechanical operators, for almost all such operators of physical interest. It is the main purpose of the present paper to present the results of tests of these and similar stationary bound formulas and to suggest that, despite the complicated appearance of these formulas, the calculation—for a given number of parameters in the trial functions—is of comparable difficulty to that involved in various nonstationary (linear) bound formulas that have been available for some time.[2] The results similarly suggest that the stationary bounds so obtained are of at least comparable quality to the corresponding linear bounds. However, a definitive comparison of the various techniques currently available is beyond the scope of this paper; we are primarily concerned with preliminary numerical explorations of some new results and, in particular, with showing that both lower *and* upper rigorous stationary bounds can readily be obtained.

We have also a secondary purpose which may be explained as follows: Stationary bounds require, in addition to a trial wave function ψ_t, the calculation of a trial auxiliary function L_t.[1,3,4] As explained in I, it is generally desirable to determine L_t from a subsidiary minimum principle derived in connection with variational principles.[5] (This subsidiary minimum principle is in the form of a functional to be minimized, and so determination of an M-parameter ψ_t and an N-parameter L_t is no more difficult than the determination of a P-parameter ψ_t alone, with $P=M+N$. In fact, in some ways it is easier: first, the round-off error will be less of a problem for the case where P is large—it is easier to invert two smaller matrices than one larger one. Second, the M-parameter ψ_t will frequently be available from previous atomic calculations, in which case the problem is essentially reduced from a P-parameter to an N-parameter one.) This secondary purpose is then to test the adequacy of L_t's derived via the subsidiary minimum principle for use in stationary bounds.

We choose, as our matrix element to be bounded, the diagonal element of the operator $W=\frac{1}{2}(r_1^2+r_2^2)$ for the ground state of helium. This matrix element has been extensively studied before; in particular, very accurate *lower* bound results of the linear type have been obtained using split-shell-type Hylleraas wave functions with 135–140 linear parameters.[6] However, no *upper* bound results of any kind have been published before for this operator, so that the upper (stationary) bound results given below in Table I are all new.[7,8]

We begin by noting that the requirement that the trial auxiliary function L_t be orthogonal to the trial wave function ψ_t, a requirement which was imposed[1] as a matter of notational convenience, does not really introduce any significant computational complication. If L_t is a function determined as in Ref. 5, then it can readily be verified that the function $L_t - (\psi_t, L_t)\psi_t$ comprises a suitable trial auxiliary function for use in I. It can also readily be verified that the result of such a procedure will be exactly the same as dropping the requirement that L_t be orthogonal to ψ_t, replacing Eq. (2.9) of I by

$$\hat{g}' = \hat{g} - a p_t/\epsilon \,, \tag{1a}$$

and Eq. (2.12) by

$$p_t \hat{g}_t' = \hat{g}_t' p_t = (1-a)\, p_t/\epsilon \,, \tag{1b}$$

where

$$a = 1 - \epsilon(\psi_t, L_t)/(\psi_t, \Phi) \,, \tag{2}$$

and carrying through the analysis as in I. (The notation in the present paper, where otherwise undefined, is identical to that given in I.) The first step in the analysis is the derivation of stationary bounds on (ψ, Φ), where Φ is known. The modified result, using Eqs. (1a), (1b), and (2), is now found to be

$$(\psi, \Phi)^{(\pm)} = N\{a(\epsilon_{1t}/\epsilon_1)[(\psi_t, \Phi) + (L_t, h\psi_t)] \pm |\Delta|^{(+)}\} \,, \tag{3}$$

where

$$|\Delta|^{(+)} = \|J\| \times \|(h-\epsilon_1)\psi_t\|/(\epsilon_2 - \epsilon_1) \tag{4}$$

with

$$\|J\|^2 = \|(h-\epsilon_1)L_t\|^2 - \frac{2(\psi_t, hL_t)}{\epsilon_t}(\psi_t, h^2L_t) + \frac{2\epsilon_1}{\epsilon_t}(\psi_t, hL_t)^2 + 2[\Phi, (h-\epsilon_1)L_t] + 2a\epsilon_1(\Phi, \psi_t)(\psi_t, L_t)$$
$$+ \frac{(\psi_t, hL_t)^2(\psi_t h^2\psi_t)}{\epsilon_{1t}^2} - \frac{2(\psi_t, hL_t)(\Phi, h\psi_t)}{\epsilon_{1t}} + \|\Phi\|^2 + a(a-2)(\Phi, \psi_t)^2 . \quad (5)$$

In order to apply Eq. (3) to the determination of upper and lower stationary bounds on $(\psi, W\psi)$, we choose

$$\Phi = W\psi_t . \quad (6)$$

An upper stationary bound on $(\psi, W\psi)$ is then given by Eq. (3.3) of I:

$$(\psi, W\psi)^{(+)} = [2S(\psi, \Phi)^{(+)} - (\psi_t, W\psi_t) + \mathfrak{D}^{(+)}(W)]/S^2 , \quad (7)$$

where $\mathfrak{D}^{(+)}(W)$ is an upper bound on the quantity

$$\mathfrak{D}(W) \equiv (Q\psi_t, WQ\psi_t) , \quad (8)$$

and where Q is the operator which projects off the ground state. Techniques for calculating $\mathfrak{D}^{(+)}(W)$ have been given previously.[1,9,10]

If $W \geq 0$, then a stationary lower bound on $(\psi, W\psi)$ is given by

$$(\psi, W\psi)^{(-)} = [(\psi, \Phi)^{(-)}]^2/(\psi_t, W\psi_t) , \quad (9)$$

provided $(\psi, \Phi)^{(-)} = (\psi, W\psi_t)^{(-)} \geq 0$.

To test the foregoing formulas, stationary bounds on $\frac{1}{2}(r_1^2 + r_2^2)$ for the ground state of helium were calculated using Hylleraas-type wave functions, and the results compared with the "true" value of this quantity, as determined by the very accurate calculation of Pekeris.[11] For each of these wave functions, a number of trial auxiliary functions were calculated[12] using a subsidiary minimum principle previously derived for use in variational principles.[13] The form of the trial auxiliary function was chosen to be the same as that of the wave functions, that is, a polynomial in Hylleraas coordinates with linear parameters, multiplied by $e^{-\gamma s}$, where γ is a (nonlinear) parameter—the number of linear parameters being progressively increased in each case in order to study convergence.

The required upper bound on $\mathfrak{D}(r_i^2)$ was obtained from the relationship[1]

$$\mathfrak{D}(r_i^2) \leq \frac{(1-S^2) + (1-S^2)^{1/2}\|r_i^2(h-\epsilon_1)\psi_t\|}{(\epsilon_2 - \epsilon_1)} . \quad (10)$$

Values of $\mathfrak{D}^{(+)}(r_i^2)$ for the 3-, 10-, and 20-parameter wave functions were found to be $0.008\,26a_0^2$, $0.001\,72a_0^2$, and $0.000\,120a_0^2$, respectively (a_0 is the Bohr radius). The stationary bounds on S for the 3- and 10-parameter wave functions were obtained in the identical manner as described in Sec. V of Ref. 3. The stationary bounds on S for the 20-parameter wave function were obtained in the same manner as for the 10-parameter wave function.

The stationary bounds obtained from Eqs. (7) and

TABLE I. Upper and lower stationary bounds on $(\psi, r_1^2\psi)$ for the ground state of helium as a function of the number of parameters in the trial functions, in units of a_0^2. The true value [a] is 1.193483.

Number of linear parameters		First way [b]		Second way [c]	
ψ_t	L_t	Upper bound	Lower bound	Upper bound	Lower bound
3 [d]	0 [e]	1.78	0.66	1.24	1.13
	3	1.91	0.59	1.26	1.13
	7	1.56	0.86	1.23	1.16
	13	1.42	0.98	1.22	1.17
	22	1.24	1.15	1.205	1.187
10 [f]	0 [e]	1.44	0.96	1.22	1.17
	13	1.30	1.09	1.21	1.18
	22	1.22	1.17	1.197	1.1914
	34	1.208	1.180	1.1963	1.1921
20 [g]	0 [e]	1.27	1.12	1.200	1.187
	22	1.198	1.189	1.193 95	1.193 14

[a] Reference 11.
[b] Using Eq. (3) in Eqs. (7) and (9).
[c] Using Eq. (11) in Eqs. (7) and (9).
[d] Reference 15.
[e] $L_t = 0$.
[f] Reference 16.
[g] Reference 17.

(9), using (3), are given in Table I. For comparison, an alternative method[3] of bounding (ψ, Φ) was also used, viz.,

$$(\psi, \Phi)^{(\pm)} = S\alpha \pm [(1-S^2)(\beta - \alpha^2)]^{1/2} , \quad (11)$$

$$\alpha = (\psi_t, \Phi) + (\psi_t, (h-\epsilon_1) L_t) , \quad (12)$$

$$\beta = \|\Phi\|^2 + 2(\Phi, (h-\epsilon_1) L_t) + \|(h-\epsilon_1) L_t\|^2 . \quad (13)$$

These alternate stationary bounds were then used in (7) and (9), and constitute the "second way" referred to in Table I. [The "first way" uses Eq. (3) in lieu of Eq. (11)].

A notable feature of the results is that the upper and lower stationary bounds are of comparable quality, a feature which considerably enhances their usefulness. It is also to be noted, however, that although the results appear to be quite good, the stationary bound on the error term, that is, on the difference between the true value and the variational estimate, is considerably larger than the error term itself, even though both are formally second-order quantities. In other words, the second-order terms in the stationary bounds must have large numerical factors associated with them. For example, when the variational estimate of $(\psi, r_i^2 \psi)$ is calculated for the case of the 20-parameter wave function and the 22-parameter L_t according to the procedure given in Ref. 5, the value

$$(\psi, r_i^2 \psi)_{\text{var}} = 1.193\,492 a_0^2$$

is obtained[12] which implies an error of about one part in 10^5. The error in the stationary bound in the best case given in Table I is 30 times as large. This is perhaps to be expected, and is the price one pays for rigorous bounds.

It is also to be noted that the "second-way" results using Eq. (11) are considerably better than the "first-way" results which use Eq. (3) to bound (ψ, Φ). The difficulty with regard to "near singularities," which may or may not be present when L_t is determined by extremizing Eq. (11) (see Appendix A of I), does not arise here since L_t is determined from an independent subsidiary minimum principle. The reason for the difference in the two methods may be understood as follows: In both cases the stationary bound on the error is proportional to two factors, one of which (in some sense) measures the accuracy of L_t, and the other that of ψ_t. In the "first way" the latter quantity is $\|(h-\epsilon_1)\psi_1\|^2$ while the comparable "second way" quantity is $1-S^2$. Since energy-optimized ψ_t's are used, and since the former involves $(\psi_t, h^2\psi_t)$ while lower stationary bounds on S involve only $(\psi_t, h\psi_t)$, it is not surprising that the former is considerably larger than the latter, even though both are formally second-order quantities.

It should be noted that the $L_t = 0$ entries represent bounds that are linear in the error of the trial wave function since the terms which cancel the linear error terms then vanish. These $L_t = 0$ bounds are therefore equivalent in many respects to earlier work in which nonstationary bound formulas were derived.[2,7,9] In particular, the lower bound "second-way" results with $L_t = 0$ correspond exactly to a linear lower bound formula obtained previously.[14] A question of importance for workers in this area is whether one is better off using an M-parameter ψ_t and an N-parameter L_t, or using a P-parameter ψ_t ($P = M+N$) and no L_t. As mentioned earlier, an attempt to answer this question is really beyond the scope of the present paper. There are indeed some *a priori* reasons for expecting advantages to accrue from the use of an L_t. Two of them have already been mentioned, viz., the round-off error considerations and the availability of atomic ψ_t's. There is also the fact that the L_t's determined are sensitive to the particular operator W, whereas the ψ_t's are generally energy-optimized and are independent of W. Thus the advantage of using an L_t may be more apparent for some operators than for others.

There is some suggestion from Table I that the advantage of using an L_t is more apparent for the more accurate calculations. Thus, the best lower bound value of Table I ($1.193\,14 a_0^2$ with a total of 42 linear parameters) would seem to compare favorably with best linear lower bound result of $1.193\,24 a_0^2$ using 135–140 parameters.[6] On the other hand, for the less accurate calculations, it is the linear bound result which has the edge. Thus, somewhat better results are obtained using a 10-parameter ψ_t and no L_t than using a three-parameter ψ_t and seven-parameter L_t. Similarly the 20-parameter ψ_t alone is somewhat superior to a 10-parameter ψ_t and a 13-parameter L_t.

We conclude that the stationary bound formulas previously derived give good results with an amount of calculational effort that is comparable to other methods. The question of the relative merits of the various available methods is one which would seem to be well deserving of further study.

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