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Lower bound to the ground-state expectation value of a positive unbounded operator using related bounded operators

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Abstract Error bars around observables of quantum mechanical systems are extremely lacking; in most cases only an upper bound to the energy is practical. We present a new lower bound to the expectation value of an operator that is most similar to the lower bound of Weinhold. While Weinhold's bound has flexibility by incorporating expectation values (some of which may not exist) of different moments of the operator to be bounded, the flexibility of our lower bound relies on the form of a similar, but bounded, operator. Like Weinhold's bound, ours is limited to non-negative operators and the ground-state of the system. Our lower bound is shown to have properties which allow it to converge to the true expectation value of the ground state, but a practical application to the Helium atom shows that Weinhold's bound is superior in this case.

Keywords Lower bound · Expectation value · Helium

1 Introduction

We assume a quantum system characterized by eigenvalues E_{n} and normalized eigenfunctions ψ_{n} determined from the time-independent Schrödinger equation $H\psi_{\mathrm{n}} = E_n\psi_{\mathrm{n}}$ where H is the Hamiltonian operator. Since Schrödinger's presentation nearly a century ago, we have seen great progress in our ability to approximate these ener-

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gies and eigenfunctions. Nevertheless, aside from the variational theorem which gives upper bounds to energies there is still a lack of systematic and practical methods to bound system properties. Even lower bounds to the energies remain elusive for most atomic and molecular systems. In this report we consider a new method to determine a lower bound to the ground-state expectation value $\langle\psi_1|A\psi_1\rangle$ of a non-negative operator A.

Given a normalized trial function ϕ designed to approximate a normalized Hamiltonian eigenfunction ψ_n, we can approximate the value of a property $\langle\psi_n|A\psi_n\rangle$ of the system by $\langle\phi|A\phi\rangle$ for operator A. As the trial function improves in quality, as measured perhaps by the variational theorem, we expect our approximation of $\langle\psi_n|A\psi_n\rangle$ to improve. However, improvement is not guaranteed, and the amount of improvement (if any) is difficult to determine. We need error bars, i.e. lower and upper bounds to $\langle\psi_n|A\psi_n\rangle$, to assess the quality of $\langle\phi|A\phi\rangle$.

Mazziotti and Parr [1] introduced inequality (1) to bound expectation values based on the variational theorem for energy. The other parameters appearing in the bounds are defined by $(H + c^+A)\psi_n^+ = E_n^+\psi_n^+$ and $(H - c^-A)\psi_n^- = E_n^-\psi_n^-$ where c^+ and c^- are optimizable positive parameters.

$$\frac{E_1^+ - E_n}{c^+} \le \langle\psi_n|A\psi_n\rangle \le \frac{E_n - E_1^-}{c^-} \tag{1}$$

For both the upper and lower bounds of inequality (1), an upper bound to E_n is needed (easily obtained from the variational theorem). On the other hand, lower bounds to E_1^- and E_1^+ are also needed. This requires generation of energy lower bounds for the Hamiltonians $H \pm c^{\pm}A$ which are likely more difficult to calculate than for the basic Hamiltonian H. If energy lower bounds can be obtained for the original Hamiltonian, H, (perhaps from the Temple formula [2] or Bazley's special choice for intermediate problems [3]) then it is likely that lower bounds to E_1^+ can also be obtained. Unfortunately, with a lessening of the energy from E_1 to E_1^-, the methods suggested for obtaining lower bounds are likely to fail for unbounded operators A. Thus the upper bound of inequality (1) is likely impractical and for most cases only the lower bound is attainable. If the Temple bound were used to acquire a lower bound to E_1^+ or E_1^- then the expectation value of the *square* of $(H \pm c^{\pm}A)$ would have to be computed, which is typically a difficult task. Mazziotti and Parr's method of calculating bounds is especially notable because it is straightforward to apply to any of the system's states; this is not the case for other methods. However, one must note that the presence of $E_1^{\pm}$, rather than $E_n^{\pm}$, suggests that the bounds will be good for only ground state properties.

Another approach was taken by Bazley and Fox [4], Jennings and Wilson Jr [5], and Weinhold [6]. The basic idea is best expressed in inequality (2a) given by Weinhold which used various moments of the non-negative operator A with a normalized trial function ϕ.

$$\langle\psi_n|A\psi_n\rangle \ge \frac{\left(s\,\langle\phi|A^v\phi\rangle - (1-s^2)^{1/2}\left[\langle\phi|A^{2v}\phi\rangle - \langle\phi|A^v\phi\rangle^2\right]^{1/2}\right)^2}{\langle\phi|A^{2v-1}\phi\rangle} \tag{2a}$$

Common choices are $v = 1$ (requiring $\langle\phi|A\phi\rangle$ and $\langle\phi|A^2\phi\rangle$) and $v = 0$ (requiring $\langle\phi|A\phi\rangle$ and $\langle\phi|A^{-1}\phi\rangle$). The term s is the overlap of trial function ϕ and true wave function ψ_n. The need to bound $|s|$ generally restricts one to a study of ψ_1 (rather than ψ_n) using the Eckart bound [7]. One problem with this approach is that some moments of the operator may not exist. For example, in the case of atoms for $A = 1/r^2$, the expectation value $\langle\phi|A^2\phi\rangle$ does not exist for realistic ground-state trial functions. Recently Marmorino and Cassella [8] proposed a new approach for lower bounds to expectation values that shares similarities with both methods given above. Practical application of all these methods to unbounded operators is essentially limited to one-sided bounds to ground-state (not excited state) expectation values of non-negative operators.

2 Strategy

In this section we derive a straightforward method to calculate lower bounds to $\langle\psi|A\psi\rangle$ where ψ is the normalized ground-state Hamiltonian eigenfunction and $A = a^2$ is real non-negative operator. For simplicity we assume that both ψ and the normalized trial function ϕ are real-valued. Because of the positive semi-definiteness of A and the real-valued nature of A, ψ, and ϕ the following expressions are equivalent: $\langle\psi|A\phi\rangle = \langle a\psi|a\phi\rangle = \langle A\psi|\phi\rangle = \langle\phi|A\psi\rangle = \langle a\phi|a\psi\rangle = \langle A\phi|\psi\rangle$. The basis of the method is the Cauchy-Schwarz inequality (3).

$$\langle\phi|A\psi\rangle^2 = \langle a\phi|a\psi\rangle^2 \leq \langle\psi|A\psi\rangle\,\langle\phi|A\phi\rangle \tag{3}$$

The wave function ψ can be written as Eq. (4) in terms of the trial function and a normalized residual, δ, with real-valued coefficients s and x. The residual is unknown.

$$\psi = s\phi + x\delta \tag{4}$$

The left hand side of inequality (3) is equal to the square of equality (5) which is derived from equating two different expressions for an expectation value of A: $\langle\psi - s\phi|\mathrm{A}(\psi - s\phi)\rangle = \langle x\delta|\mathrm{A}(x\delta)\rangle$.

$$\langle\phi|A\psi\rangle = \frac{\langle\psi|A\psi\rangle + s^2\,\langle\phi|A\phi\rangle - x^2\,\langle\delta|A\delta\rangle}{2s} \tag{5}$$

Inserting Eq. (5) into inequality (3) yields the quadratic inequality (6) where, for simplicity, we adopt the notation $A_\psi = \langle\psi|A\psi\rangle$, $\langle A\rangle = \langle\phi|A\phi\rangle$, and $A_\delta = \langle\delta|A\delta\rangle$.

$$A_\psi^2 - 2A_\psi\left(x^2A_\delta + s^2\,\langle A\rangle\right) + s^4\,\langle A\rangle^2 + x^4A_\delta^2 - 2x^2s^2A_\delta\,\langle A\rangle \leq 0 \tag{6}$$

When this inequality is treated as a quadratic equation and roots are found, the roots provide upper and lower bounds to $\langle\psi|A\psi\rangle$. These roots are given in Eq. (7).

$$A_\psi(root) = s^2\,\langle A\rangle + x^2A_\delta \pm 2|x||s|\,\langle A\rangle^{1/2}\,A_\delta^{1/2} \tag{7}$$

These bounds can be simplified in their dependence by noting that $x^2 + s^2 = 1$ so that $x^2 = 1 - s^2$ to yield Eq. (8).

$$A_\psi(root) = s^2 \langle A \rangle + (1 - s^2) A_\delta \pm 2|s|(1 - s^2)^{1/2} \langle A \rangle^{1/2} A_\delta^{1/2} \tag{8}$$

Also note that a trivial (but likely tight) upper bound to s^2 is unity and a trivial (but likely poor) lower bound to A_δ is zero. Simplified roots are presented as upper and lower bounds to A_ψ in inequality (9).

$$\begin{aligned} s^2 \langle A \rangle - 2(1 - s^2)^{1/2} \langle A \rangle^{1/2} A_\delta^{1/2} \le A_\psi \le \langle A \rangle \\ +(1 - s^2) A_\delta + 2(1 - s^2)^{1/2} \langle A \rangle^{1/2} A_\delta^{1/2} \end{aligned} \tag{9}$$

If s^2 is indeed close to unity then terms with powers of $(1 - s^2)$ will make little contribution and we can expect tight bounds—provided that A_δ can be approximated well. In each case an upper bound to A_δ and a lower bound to s^2 are needed; the latter is given by the Eckart bound, inequality (10).

$$s^2 \ge \frac{E_2 - \langle \phi | H \phi \rangle}{E_2 - E_1} \tag{10}$$

It is the Eckart bound that brings success and difficulty to our method. Without it we would have no rigorous substitute for s^2. The difficulty lies with the energies as exact values for E_2 and E_1 are generally not available. Although lower bounds to these will suffice, *precise* lower bounds are extremely difficult to achieve—and precision for E_1 is needed to get a tight lower bound to s^2. All methods to determine lower bounds to energies are difficult and usually not practical. The most common procedure is the Temple formula [2] which requires the difficult integral $\langle \phi | H^2 \phi \rangle$. Despite its drawbacks, the Eckart bound is the simplest option for s^2. It lacks a generalization to excited states that is as simple [9] and thus we are restricted to bounding properties of the ground state.

3 Bounded operators

For the case of a bounded non-negative operator A, its maximum, $A_{\max}$, can serve as an upper bound to A_δ to yield inequality (11).

$$\begin{aligned} s^2 \langle A \rangle - 2(1 - s^2)^{1/2} \langle A \rangle^{1/2} A_{\max}^{1/2} \le A_\psi \le \langle A \rangle + (1 - s^2) A_{\max} \\ +2(1 - s^2)^{1/2} \langle A \rangle^{1/2} A_{\max}^{1/2} \end{aligned} \tag{11}$$

For a multiplicative operator $A_{\max}$ is merely the supremum of the operator over the coordinates of the space. For a more complicated operator, $A_{\max}$ is defined as the supremem of $\langle \chi | A \chi \rangle$ over all normalized χ in the domain of the operator. If the operator A has a large variation in its expectation values, then either definition of $A_{\max}$ suggests that it is likely to be a poor bound to A_δ. This will result in poor bounds to A_ψ unless s^2 is remarkably close to one.

It is instructive to compare our lower bound in inequality (11) with Weinhold's lower bound. For the case of $v = 1$, inequality (2a) expands to inequality (2b) where the small positive term $(1 - s^2)(\langle A^2\rangle - \langle A\rangle^2)/\langle A\rangle$ has been dropped.

$$\langle A\rangle_\psi \geq s^2 \langle A\rangle - 2(1 - s^2)^{1/2} \frac{\sqrt{\langle A^2\rangle - \langle A\rangle^2}}{\langle A\rangle} \tag{2b}$$

Comparison of bounds (11) and (2b) shows that the main difference is whether the square of the expectation value or the maximum of the operator is involved.

4 Unbounded operators

For an unbounded non-negative operator A, we cannot bound $A_\delta = \langle\delta|A\delta\rangle$ in inequality (9) by $A_{\max}$ because $A_{\max} = \infty$. Initially this would seem to make both the upper and lower bounds of inequalities (9) or (11) impractical; however, a lower bound is still possible by considering an auxiliary **bounded** operator B such that $B \leq A$. Lower bound, L, to $\langle\psi|B\psi\rangle$ serves as a lower bound to $\langle\psi|A\psi\rangle$ in inequality (12).

$$A_\psi \geq B_\psi \geq L = s^2 \langle B\rangle - 2(1 - s^2)^{1/2} \langle B\rangle^{1/2} B_{\max}^{1/2} \tag{12}$$

Suppose $A = x^2$, where x is one of the Cartesian coordinates. Then we can choose a cutoff point b so that $B = x^2$ when $|x| < b$ and $B = b^2$ for $|x| > b$. Operator B is bounded by $B_{\max} = b^2$, and furthermore can be varied through the choice of b to provide optimal results in inequality (12). As b increases, B approaches A—which is necessary for a good bound; but also as b increases a greater amount is being subtracted in the lower bound to $\langle\psi|B\psi\rangle$ and $\langle\psi|A\psi\rangle$—this is disadvantageous. Another option for B is $x^2\exp(-b\,x^2)$ where b can be varied as before, though it carries a different meaning. In this case $B_{\max} = 1/(2b)$ and as b decreases B approaches A, but $B_{\max}$ rises.

As $\phi \to \psi$, then $L \to B_\psi$; call this condition (i). As $B \to A$, then $B_\psi \to A_\psi$; call this condition (ii). Both conditions (i) and (ii) must be satisfied in order for $L \to A_\psi$.

5 Harmonic oscillator

For a simple illustration of our method we consider the harmonic oscillator potential in one dimension. The Hamiltonian operator is given in Eq. (13) using the mass of an electron and a force constant of $k = 4$ in atomic units.

$$H = \frac{-1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}kx^2 \tag{13}$$

We consider the observable $A = x^2$ as an example. Because x^2 is an unbounded operator we can obtain only a lower bound to A_ψ. This is done by introducing using the bounded operator $B = \{x^2 \in [-b, b], b^2 \notin [-b, b]\}$ which is bounded by $B_{\max} = b^2$.

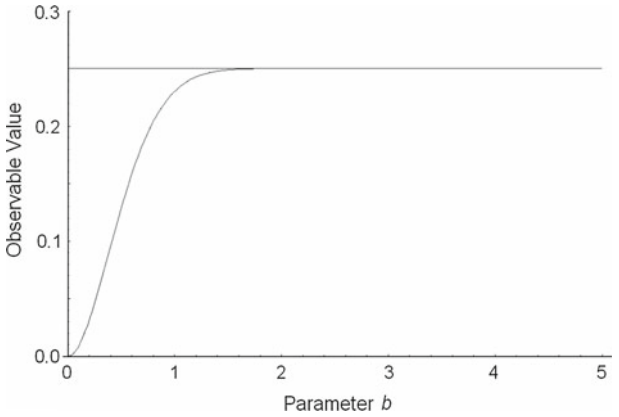

Fig. 1 Lower bounds L (*solid curve*) to A_ψ (*solid line*) are plotted against the parameter b of bounded operator B using the exact wave function (with exponential parameter $a = 1$) as the trial function

To bound s^2 in inequality (12) using the Eckart bound, the exact values of E_1 and E_2 were used (in practical application, lower bounds to both energy levels would be used instead). The normalized trial function $\phi = (2a/\pi)^{1/4}\exp(-ax^2)$ was chosen so we could illustrate just how good the bounds can be because as the exponential parameter a approaches one the trial function approaches the true ground-state wave function.

Figure 1 shows the lower bounds L (solid curve) to A_ψ (solid line) plotted against the parameter b of bounded operator B. The bounds L are given by inequality (12) using the true wave function as the trial function, thus condition (i) is satisfied. As b approaches infinity, B approaches A and condition (ii) is met as well and Fig. 1 shows the bounds L approaching A_ψ asymptotically.

Figure 2 shows the lower bounds L (solid curve) to A_ψ (solid line) plotted against the parameter b of bounded operator B for two trial functions. The bounds L are given by inequality (12). For comparison $\langle B\rangle$ (dashed curve) and $\langle A\rangle$ (dashed line) are also shown. Because the trial functions are far from the true wave function, tight bounds cannot be expected—condition (i) is not satisfied. As b rises, B becomes more like A as shown by the dashed curve rising to the dashed line. Figure 2 shows that the lower bounds initially increase because of this. However, this increase does not persist and as b increases further (B become even more like A) the lower bounds fall. Even though condition (ii) is met as b approaches infinity, the failure of ϕ to approach ψ, condition (i), prevents tight bounds. Note that unlike variational energies, observables predicted from variationally-determined trial functions can be too high (dashed line in Fig. 2a) or too low (dashed line in Fig. 2b).

6 Helium atom

We now consider the helium atom which is the simplest chemical system that is not exactly soluble in its electronic structure. In the limit of infinite nuclear mass (at the origin) and using atomic units the Hamiltonian operator is given by Eq. (14) where r_{12} is the distance between the two electrons.

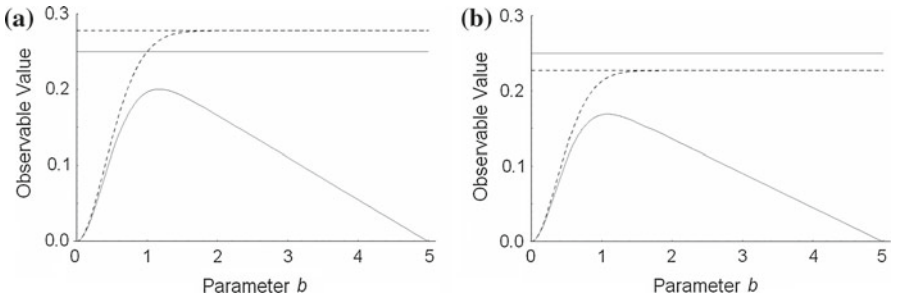

Fig. 2 Lower bounds L (*solid curve*) to A_ψ (*solid line*) and approximate observables $\langle B\rangle$ (*dashed curve*) and $\langle A\rangle$ (*dashed line*) are plotted against the parameter b of bounded operator B. **a** Exponential parameter $a = 0.9$, **b** exponential parameter $a = 1.1$

$$H = -\left(\frac{1}{2}\nabla_1^2 + \frac{2}{r_1}\right) - \left(\frac{1}{2}\nabla_2^2 + \frac{2}{r_2}\right) + \frac{1}{r_{12}} \tag{14}$$

The presence of the repulsive $1/r_{12}$ potential prevents separation of variables. Without such complication the eigenfunctions would be the products of He^+ eigenfunctions and the eigenvalues would be the sums of He^+ eigenvalues, the lowest two energies being -4 and -2.5. Because the operator $1/r_{12}$ is a positive perturbation, we can say that $E_1 \geq -4$ and $E_2 \geq -2.5$. These poor lower bounds could be used directly in the Eckart bound to s^2, but the result is poor, so instead we use more precise lower bounds. For E_2 we chose the generous lower bound $E_2 \geq -2.166$ rounded from Bazley's work [2]. For E_1 we used the Temple bound, inequality (15) with the E_2 set at -2.166 and a variational trial function. The latter was very precise, determined from a 945 dimensional matrix eigenvalue problem (see Appendix for details); this gave an upper bound of $\langle H\rangle = -2.903\,724\,377$. The Temple bound then provided $E_1 \geq -2.903\,724\,708$. Precise knowledge of E_1 is vital so that the Eckart bound (10) can approach unity as the trial function ϕ approaches the true wave function ψ. Precise knowledge of E_2 is much less important.

$$E_1 \geq \frac{E_2\langle H\rangle - \langle H^2\rangle}{E_2 - \langle H\rangle} \tag{15}$$

In the previous section we simply used a cutoff value to keep B as a bounded and lesser operator to A. Here we used a different method to construct B for powers of the radial coordinate, r (really r_1 or r_2). For $A = r$, we chose $B = r\exp(-br)$ which approaches A as $b \to 0$; $B_{\max} = (e \cdot b)^{-1}$. For $A = r^2$, we chose $B = r^2\exp(-br)$ which approaches A as $b \to 0$; $B_{\max} = 2(e \cdot b)^{-2}$. For $A = r^{-1}$, we chose $B = r^{-1}[1 - \exp(-br)]$ which approaches A as $b \to \infty$; $B_{\max} = b$.

The obvious choice $B = r^{-2}[1 - \exp(-br)]$ as a lower bound to $A = r^{-2}$ fails because B is unbounded. A simple alternative is $B = r^{-2}[1 - \exp(-br^2)]$ which has $B_{\max} = b$. However, because our computer program is based on exponentials rather than Gaussian functions we did not pursue inverse square moments. Higher positive moments are easily considered: for $A = r^n$, $n \geq 1$ we can let $B = r^n\exp(-br)$

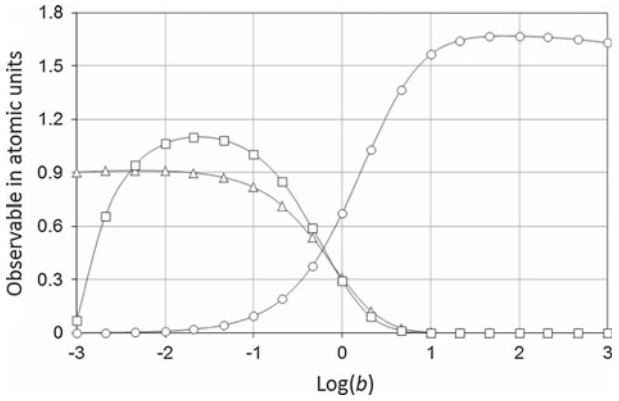

Fig. 3 Lower bounds to $\langle r\rangle_\psi$ (*triangles*), $\langle r^2\rangle_\psi$ (*squares*), and $\langle 1/r\rangle_\psi$ (*circles*) are plotted against the base-10 logarithm of the parameter b appearing in B and B_{max}. Data were obtained with a 180-term variationally-determined trial function. Data points are connected for convenience

Table 1 Truncated expectation values and best lower bounds for $\langle r\rangle_\psi$, $\langle r^2\rangle_\psi$, and $\langle 1/r\rangle_\psi$ from Fig. 2. Also shown are the Weinstein lower bounds using inequality (2a) with $v = 1$

Observable	r	r^2	$1/r$
Expectation value	0.9294	1.1934	1.6883
Weinhold lower bounds	0.9289	1.1919	1.6866
Lower bounds (this work)	0.9120	1.1005	1.6680

which approaches A as $b \to 0$; $B_{\max} = n(e \cdot b)^{-n}$. Powers of the separation between electrons, r_{12}, can be considered in a like manner.

Figure 3 plots lower bounds to the observables $\langle r\rangle_\psi$, $\langle r^2\rangle_\psi$, and $\langle r^{-1}\rangle_\psi$. These were obtained using a 180-term variationally-determined trial function in inequality (12). Like the lower bounds in Fig. 2, the optimal results did not occur as parameter b approached infinity; the optimal parameter was found through trial and error. The lower bound to each observable was achieved at a different value for the parameter b.

Table 1 records expectation values from a variational trial function and our best bounds using inequality (12) from Fig. 3. For each observable the closeness of the two is poor. For comparison, bounds using Weinhold's formula, inequality (2a), are reported for $v = 1$. Increasing the accuracy of the trial function (using a larger basis set) did not significantly improve the lower bounds. We believe the lack of improvement with basis set size is due to our limited precision of E_1 in the Eckart bound as explained in the next section.

7 Analysis

Using the harmonic oscillator as an example, Fig. 1 shows that infinitesimally tight lower bounds can result as B approaches A if the trial function happens to be the wave function. While such a situation is rare indeed, the method would be quite limited if

the lower bounds it predicted could not approach the true value in principle. The plots in Fig. 2 use trial functions that deviate from the true wave function. Even though B approaches A in these cases we find that the lower bound does not approach the true value. Furthermore we find that best lower bound is not achieved when B is closest to A. All examples with the harmonic oscillator utilized the exact ground and excited state energies to give the best estimate of s^2 using the Eckart bound.

The helium atom is a better test of our method because (1) the true wave function is not so easily approached as no solution is yet known, and (2) exact energies are not available. As predicted, and illustrated with the harmonic oscillator example, good results can be achieved only when both $\phi \approx \psi$ and $B \approx A$, i.e. both conditions (i) and (ii) are met. For the data in Fig. 3, the Eckart inequality ensured the square overlap between the trial function and wave function to be at least 0.999 999 513. By adjusting the parameter b in the bounded operator B we were able to make B as close as desired to A. Despite the appearance of meeting both of conditions (i) and (ii), the resulting observable bounds were quite poor. To better see the problems in our method we rewrite inequality (12) slightly as inequality (16).

$$A_\psi \geq B_\psi \geq L = \langle B \rangle - (1 - s^2)\,\langle B \rangle - 2(1 - s^2)^{1/2}\,\langle B \rangle^{1/2}\,B_{\max}^{1/2} \tag{16}$$

To obtain a tight bound it must be that the terms subtracted from $\langle B \rangle$ in inequality (16) are small. Of these two terms the second, T_2, is likely much larger than the first, T_1, for two reasons. The first is that the square root, rather than first power, of $(1 - s^2)$ appears. Because this is a fractional value, the square root magnifies the value. The second reason is that $B_{\max}$ is likely a poor bound to $\langle \delta | B \delta \rangle$. Data for the inverse radial coordinate with $b = 100$ support this difference with $T_1 = 8 \times 10^{-7}$ and $T_2 = 0.02$. Subtraction of T_1 is an insignificant adjustment to $\langle B \rangle = 1.686$ in inequality (16), but the subtraction of T_2 is a major adjustment.

As noted in the previous section there was little improvement for the helium atom observable bounds as the basis set size increased beyond 180 basis functions. The reason lies in the Eckart bound which estimates s^2 using a ratio of $E_{2,\mathrm{low}} - \langle H \rangle$ to $E_{2,\mathrm{low}} - E_{1,\mathrm{low}}$ where lower bounds replace the unknown E_2 and E_1 in inequality (10). Only to calculate the lower bound to E_1, using the Temple formula, did we use a very large basis set, 975 functions. To bound the observables we used a much smaller 180-term basis set. As this basis set was enlarged any improvement in the bound to s^2 was limited to $(E_{2,\mathrm{low}} - E_1)/(E_{2,\mathrm{low}} - E_{1,\mathrm{low}})$ rather than unity as $\langle H \rangle$ approaches E_1. Because $\langle H \rangle$ was already quite close to E_1, more so than was $E_{1,\mathrm{low}}$, the improvement was negligible. Thus the lower bound estimate of E_1 proved more important than the basis functions used to calculate the observables.

8 Conclusion

We have introduced a new method to bound observables for a quantum mechanical system. Like other methods there is reliance on the energy eigenvalue problem; in this case we need a lower bound to the ground-state and first excited-state energies which are used to bound the magnitude of the overlap of a trial function with the true wave

function. The main advantage of our method is that the required expectation values are kept simple; those that are required are comparable in computational difficulty to the expectation value being bounded. The method of Mazziotti and Parr [1] typically requires the use of square operators (via the Temple method) or inverse operators (via Bazley's special choice). The methods of Bazley, Fox, Jennings, Wilson, and Weinhold [4–6] require two operators, usually the one of interest and its square. In some cases, the expectation value of square operator may not exist. Like the method of Mazziotti and Parr [1], and also a relatively new approach by Marmorino and Cassella [8], the proposed method has a parameter that can be optimized. Unfortunately the optimal value cannot easily be predetermined.

Our method has the potential to perform well as illustrated by the harmonic oscillator example. However, the more practical test with the helium atom showed that it was severely limited by imprecision of the ground state energy E_1 and the likely great difference between $B_{\max}$ (approaching infinity) and the unknown value of $\langle\delta|B\delta\rangle$. Both of these issues were evident in the second subtracted term of inequality (16) and kept the lower bounds distant from the expectation values in Table 1. Using the maximum value of operator B to bound $\langle\delta|B\delta\rangle$ is very simplistic and other methods mentioned in this work use more sophisticated theory to develop their bounds.

There has long been interest in spherically-confined atoms [10] and more recently, shell-confined atoms [11]. In the former case all positive moments are bounded and in the latter case both negative and positive moments are bounded. For such systems both lower *and* upper bounds to moments could be determined using inequality (11). Furthermore for thin shell systems, the bounding of $\langle\delta|B\delta\rangle$ by $B_{\max}$ would be very reasonable and thus accurate bounds likely possible with our formalism.

Appendix

To approximate the ground-state wave function, variational calculations were performed using a non-orthonormal basis set of the following spatially symmetric functions suitable to describe singlet states.

$$\chi_{x,y,z} = e^{-a(r_1+r_2)} r_{12}^z (r_1^x r_2^y + r_1^y r_2^x) \tag{17}$$

The exponential parameter a was set at 1.875 for all calculations while integer parameters x, y, and z were allowed to vary. To determine the lower bound to E_1, x and y ranged from 0 to 13 while z ranged from 0 to 8. This created a basis set of 975 functions. Lower bounds to $\langle r\rangle_\psi$, $\langle r^2\rangle_\psi$, and $\langle r^{-1}\rangle_\psi$ were determined using a smaller basis set (180 basis functions) for the sake of time because many integrals needed to be recalculated as the exponential parameter b in the lesser observable B varied. A few observable lower bounds were calculated with more basis functions, but improvement was slight; this is thought to be due to the constant approximation of E_1 set by the 975 basis set calculation. All calculations were performed using *Mathematica* 6.0 [12].

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