New Formulas for Lower Bounds to Expectation Values

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Two new formulas are presented for rigorous lower bounds to the true quantum-mechanical expectation value of an arbitrary positive Hermitian operator. These formulas strengthen and extend previous results while requiring relatively simple additional matrix elements. Illustrative numerical applications are made at two levels of approximation to various one- and two-electron properties, powers of r_1 and r_{12}, in the normal helium atom.

I. INTRODUCTION

For a system described by the Schrödinger equation $H\psi = E_0\psi$, an approximation ϕ to the true wave function ψ provides an upper bound to the true energy level E_0 according to the familiar Ritz variational principle

$$\langle \phi | H | \phi \rangle \geq \langle \psi | H | \psi \rangle = E_0 \, .$$

It is possible further to construct lower bounds to E_0 and thereby to bracket the true energy between rigorous theoretical limits. But for properties other than the energy, the corresponding estimate $\langle \phi | F | \phi \rangle$ of the true property $\langle \psi | F | \psi \rangle$ is usually subject to errors which are much larger, and of unknown sign.[1] The estimate $\langle \phi | F | \phi \rangle$ may be found to deteriorate even as the energy estimate $\langle \phi | H | \phi \rangle$ improves.[2] It is therefore of fundamental interest and importance that rigorous upper and lower bounds be established also for properties other than the energy,[3] so that a definite theoretical statement can be made even when the exact wave function is unattainable.

Recently we have described useful methods[4,5] for giving a rigorous lower bound to the true expectation value $\langle \psi | F | \psi \rangle$ of a positive operator $F \geq 0$. We wish to show here how the previous results may again be generalized and strengthened in a natural manner which, in most instances, requires relatively little additional computational effort. Illustrative applications of the new formulas to various properties of the normal helium atom are presented in Sec. III. Lower bounds are calculated and compared with the direct estimates $\langle \phi | F | \phi \rangle$ and the true values $\langle \psi | F | \psi \rangle$ for simple one- and two-parameter variational approximations.

II. LOWER BOUNDS TO EXPECTATION VALUES

If we denote $\langle \phi | F | \phi \rangle \equiv \langle F \rangle$, the basic inequalities for our previous bounds are written as[4]

$$\langle \psi | F^{\nu} | \phi \rangle \gtrless S \langle F^{\nu} \rangle \pm \Delta F^{\nu} (1 - S^2)^{\frac{1}{2}} \, , \tag{1}$$

and[5]

$$\langle \psi | F^{\nu} | \phi \rangle \gtrless (S\alpha_{\nu} \pm \beta_{\nu}\gamma)/(\Delta H)^2 \, , \tag{2}$$

in which $S \equiv \langle \phi | \psi \rangle$ is the (positive) overlap integral of the approximation ϕ and the true wave function ψ, ΔF is the "width" of F in the state ϕ as defined by

$$(\Delta F)^2 \equiv \langle F^2 \rangle - \langle F \rangle^2 \, , \tag{3}$$

and F^{ν} denotes the νth power of the positive operator $F \geq 0$. Also in (2) we have adopted the definitions

$$\alpha \equiv \langle F \rangle (\Delta H)^2 + (\langle H \rangle - E_0)(\langle F \rangle \langle H \rangle - \langle FH \rangle) \, , \tag{4a}$$

$$\beta^2 \equiv (\Delta F)^2 (\Delta H)^2 - \langle (F - \langle F \rangle)(H - \langle H \rangle) \rangle^2 \, , \tag{4b}$$

$$\gamma^2 \equiv (1 - S^2)(\Delta H)^2 - S^2 (\langle H \rangle - E_0)^2 \, , \tag{4c}$$

where α_{ν} and β_{ν} are defined in analogous fashion by replacing F by F^{ν}.

To complete the bounds, use has been made of the Schwarz inequality in the form

$$\langle \psi | F^{\nu} | \phi \rangle \leq \langle \psi | F | \psi \rangle^{\frac{1}{2}} \langle \phi | F^{2\nu-1} | \phi \rangle^{\frac{1}{2}} \, . \tag{5}$$

This is combined with (1) to give

$$\langle \psi | F | \psi \rangle \geq \frac{[S\langle F^{\nu} \rangle - \Delta F^{\nu} (1 - S^2)^{\frac{1}{2}}]^2}{\langle F^{2\nu-1} \rangle} \tag{6}$$

and with (2) to give

$$\langle \psi | F | \psi \rangle \geq \frac{[(S\alpha_{\nu} - \beta_{\nu}\gamma)/(\Delta H)^2]^2}{\langle F^{2\nu-1} \rangle} \tag{7}$$

for all ν, so long as the required matrix elements

exist and the expressions enclosed in square brackets are non-negative.

For the present treatment we require an extension of the Schwarz inequality (5). Consider therefore the three vectors $F^{1/2}|\psi\rangle$, $F^{\nu-1/2}|\phi\rangle$, and $F^{-1/2}|\phi\rangle$, and recall that the determinant of the overlap matrix (the "Gramian") of these vectors is non-negative

$$\begin{vmatrix} \langle\psi|F|\psi\rangle & \langle\psi|F^{\nu}|\phi\rangle & S \\ \langle\psi|F^{\nu}|\phi\rangle & \langle F^{2\nu-1}\rangle & \langle F^{\nu-1}\rangle \\ S & \langle F^{\nu-1}\rangle & \langle F^{-1}\rangle \end{vmatrix} \geq 0. \tag{8}$$

In consequence of the determinantal inequality (8),

$$\langle\psi|F^{\nu}|\phi\rangle \gtrless \langle F^{-1}\rangle^{-1}\{S\langle F^{\nu-1}\rangle \pm [(\langle\psi|F|\psi\rangle\langle F^{-1}\rangle - S^2)(\langle F^{2\nu-1}\rangle\langle F^{-1}\rangle - \langle F^{\nu-1}\rangle^2)]^{\frac{1}{2}}\}, \tag{9}$$

which is the desired generalization (and strengthening) of (5).

Combining (9) with (1) leads then to the new lower bound

$$\langle\psi|F|\psi\rangle \geq S^2/\langle F^{-1}\rangle + [S(\langle F^{\nu}\rangle\langle F^{-1}\rangle - \langle F^{\nu-1}\rangle) - \langle F^{-1}\rangle\Delta F^{\nu}(1-S^2)^{\frac{1}{2}}]^2 \times\{\langle F^{-1}\rangle(\langle F^{2\nu-1}\rangle\langle F^{-1}\rangle - \langle F^{\nu-1}\rangle^2)\}^{-1}, \tag{10}$$

which is derived under the assumption that the expression in square brackets is non-negative. Combining (9) with (2) leads similarly to the bound

$$\langle\psi|F|\psi\rangle \geq S^2/\langle F^{-1}\rangle + \frac{[\langle F^{-1}\rangle(S\alpha_{\nu} - \beta_{\nu}\gamma)/(\Delta H)^2 - S\langle F^{\nu-1}\rangle]^2}{\langle F^{-1}\rangle(\langle F^{2\nu-1}\rangle\langle F^{-1}\rangle - \langle F^{\nu-1}\rangle^2)}$$

with a similar assumption on the positivity of the expression in brackets.

The new formulas (10) and (11) require only the integrals $\langle F^{-1}\rangle$ and $\langle F^{\nu-1}\rangle$ in addition to those previously required for the corresponding results (6), (7). For any fixed value of ν, (11) is certainly always the strongest and (6) the weakest of these bounds, but either (7) or (10) may be stronger in specific cases. For $\nu=1$ all four of these formulas finally coincide to an *exact* lower bound in the limit $S\to 1$. Attention may therefore be increasingly fastened on this particular value of ν as the trial function is improved. As before, a principal advantage of the variable ν is that it permits calculation of lower bounds to operators F for which matrix elements of F^2 diverge.

The functional dependence of the bounds (10), (11) on the variable ν differs in several respects from that found previously[6] for (6) and (7). Whereas both (6) and (7) tend asymptotically in the limit $\nu\to 0$ to the common value

$$\langle\psi|F|\psi\rangle \geq S^2/\langle F^{-1}\rangle,$$

formula (10), for example, approaches the limit

$$\langle\psi|F|\psi\rangle \geq \frac{S^2}{\langle F^{-1}\rangle} \times\left(1+\frac{\left[\left\langle\frac{1}{F}\right\rangle\langle\ln F\rangle - \left\langle\frac{\ln F}{F}\right\rangle - \left\langle\frac{1}{F}\right\rangle\Delta\ln F\left(\frac{1-S^2}{S^2}\right)^{\frac{1}{2}}\right]^2}{\left\langle\frac{1}{F}\right\rangle\left\langle\frac{\ln^2 F}{F}\right\rangle - \left\langle\frac{\ln F}{F}\right\rangle^2}\right)$$

and formula (11) leads to a corresponding, more complicated form. In addition, the previous bounds were found to reach a maximum which becomes more peaked and increases toward $\nu=1$ as the trial function ϕ is improved. Although similar behavior is seen for (10) and (11), the dependence on ν appears much less pronounced, at least for the trial functions to be discussed, and the maximum falls closer toward $\nu=0$. This corresponds to the fact that (8) becomes an equality for $\nu\to 0$, and the error in (10), (11) is accordingly reduced in this limit.

Finally, we remark briefly on the overlap S, which affects the lower-bound formulas in a pronounced fashion. For formulas (10) and (11), as for (6) and (7) previously, the sense of the inequalities is maintained if the overlap $S=\langle\phi|\psi\rangle$ is replaced by any lower bound to its true value. For this purpose the familiar "Eckart criterion"[7] is available

$$S^2 \geq (E_1 - \langle H\rangle)/(E_1 - E_0) \tag{12}$$

in which E_0 and E_1 are the two lowest *true*[8] energy levels of the same symmetry.[9] Weinberger[10] has shown how this inequality may be generalized and strengthened if additional excited states $E_2, E_3, \ldots$ are known, and if ϕ corresponds to one root of a secular determinant. Alternatively, Gordon[11] has given a sequence of increasingly accurate upper and lower bounds to S involving matrix elements $\langle H^n\rangle$, which, however, may appear to diverge for many cases of interest. Still another procedure utilizes some better approximation χ for which $S_1=\langle\chi|\psi\rangle$ (or a lower bound) and $S_{12}=\langle\phi|\chi\rangle$ are known; in this case[12]

$$S \geq S_1 S_{12} - [(1 - S_1^2)(1 - S_{12}^2)]^{1/2} \qquad (13)$$

which may be of use when the function χ is too complex to be handled directly in the lower-bound formulas.

III. NUMERICAL APPLICATIONS TO HELIUM ATOM

In order to characterize the lower-bound formulas numerically, we have applied (10) and (11) to the calculation of lower bounds to various powers of the nuclear-electronic and interelectronic distances r_1, r_{12}, in the normal helium atom. These applications are principally illustrative and exploratory in nature, and are intended to show the dependence of the lower-bound formulas on such factors as the operator F, the approximation ϕ, the overlap S, and the formula parameter ν.

(a) Screened-hydrogenic wave function

To obtain a direct comparison with previous results, we consider first for ϕ the simple "screened-hydrogenic" approximation[13]

$$\phi = (c^3/\pi)\exp(-cr_1 - cr_2)\,. \qquad (14)$$

For each of the operators $F = r_1^n$, r_{12}^n, $n = \pm 1$, ± 2, lower bounds have been calculated from (10) and (11) as a function both of the fraction ν and the variable scale parameter c of ϕ. We have considered both the simple Eckart estimate (12) and the improved estimate[14] (13) for the overlap S.

Table I comprehensively compares the four lower-bound formulas (6), (7), (10), (11) for the screened-hydrogenic approximation, giving the fully optimized[15] limit of accuracy available for each value of the overlap S. The direct estimate $\langle \phi | F | \phi \rangle$ (using the best-energy ϕ) is included for comparison, with all numbers expressed as a percentage of the *true*[16] value $\langle \psi | F | \psi \rangle$. Table II lists the corresponding c and ν which maximize the lower bounds.

The quality of the bounds varies widely with the specific operator under consideration, and in this connection we wish to point out the importance of the width ΔF. For r_1^n, r_{12}^n, the width increases rapidly with increasing $|n|$, and strongly affects the accuracy of both the direct estimates and the rigorous lower bounds.[17]

Table I shows that the rigorous lower bounds, while still crude, may be of the same order of accuracy as the direct estimates $\langle \phi | F | \phi \rangle$, particularly when the improved value of S is employed. Ordinarily the best lower bound cannot exceed the direct estimate,[18] but for the operators r_{12}^{-1} and r_{12}^{-2}, which are overestimated in the screening approximation, it is seen that the rigorous lower bounds may fall closer to the true value than does the direct estimate $\langle \phi | F | \phi \rangle$.

As we have previously remarked,[5] more accurate lower bounds can be obtained for $\langle \psi | r_1^{-1} | \psi \rangle$, the basic operator of the nuclear diamagnetic shielding, by combining lower bounds for $\langle \psi | r_{12}^{-1} | \psi \rangle$ with the quantum-mechanical virial theorem

$$\langle \psi | r_1^{-1} | \psi \rangle = \frac{N-1}{2Z} \langle \psi | r_{12}^{-1} | \psi \rangle - \frac{2E_0}{NZ}$$

for the N-electron atom with nuclear charge Z. For example, taking the best entry for $\langle \psi | r_{12}^{-1} | \psi \rangle$ from Table I gives a lower bound

$$\langle \psi | r_1^{-1} | \psi \rangle \geq 1.681 \text{ a.u.}$$

which is fully 99.6% of the correct value.

TABLE I. Lower bounds to various properties $\langle \psi | F | \psi \rangle$ of the normal helium atom as calculated from the formulas of the text using the screened-hydrogenic approximation (14). In each case, the upper entry corresponds to the Eckart overlap, the lower to the improved overlap (13). The direct estimate $\langle \phi | F | \phi \rangle$ is included for comparison, and all numbers are expressed as a percentage of the true value (Ref. 16).

Operator F	r_1^2	r_1	r_1^{-1}	r_1^{-2}	r_{12}^2	r_{12}	r_{12}^{-1}	r_{12}^{-2}
Formula (6)	56.2	75.2	72.4	29.7	50.0	70.4	81.2	44.7
	79.4	90.3	81.9	38.2	71.3	84.2	90.3	56.2
Formula (7)	56.4	75.2	73.5	32.4	51.3	71.4	83.1	65.4
	80.6	90.5	85.2	45.1	74.1	85.9	92.9	74.1
Formula (10)	56.7	75.5	73.2	33.8	50.6	70.7	81.7	49.2
	79.7	90.5	82.6	43.3	71.7	84.5	91.0	62.2
Formula (11)	56.8	75.6	73.8	36.0	51.9	71.9	85.3	72.5
	80.7	90.6	85.2	50.6	74.5	86.2	96.7	82.1
$\langle \phi \| F \| \phi \rangle$	88.3	95.7	100.0	94.6	83.7	91.1	111.5	129.6

TABLE II. Numerical values of parameters used in calculating lower bounds of Tables I and III. In each case, the upper entry corresponds to the Eckart overlap, the lower to the improved overlap (13).

Operator F	r_1^2	r_1	r_1^{-1}	r_1^{-2}	r_{12}^2	r_{12}	r_{12}^{-1}	r_{12}^{-2}
	Screened-hydrogenic function (see Table I)							
Formula (6)								
c	1.556	1.575	1.782	1.785	1.561	1.565	1.806	1.800
	1.438	1.466	1.760	1.739	1.466	1.469	1.785	1.751
ν	0.686	0.601	0.525	0.484	0.581	0.411	0.283	0.394
	0.764	0.720	0.683	0.569	0.700	0.587	0.517	0.514
Formula (7)								
c	1.561	1.575	1.750	1.716	1.572	1.580	1.833	2.000
	1.443	1.472	1.676	1.654	1.461	1.475	1.945	2.000
ν	0.693	0.601	0.601	0.551	0.597	0.454	0.427	0.500
	0.783	0.734	0.846	0.634	0.718	0.634	0.595	0.500
Formula (10)								
c	1.552	1.572	1.783	1.787	1.555	1.562	1.800	1.795
	1.431	1.462	1.768	1.747	1.457	1.463	1.790	1.751
ν	0.631	0.385	0.150	0.337	0.495	0.071	0.003	0.151
	0.719	0.565	0.416	0.469	0.633	0.344	0.101	0.359
Formula (11)								
c	1.557	1.570	1.759	1.719	1.568	1.579	2.000	2.000
	1.438	1.468	1.678	1.646	1.452	1.468	2.000	2.000
ν	0.639	0.373	0.342	0.462	0.509	0.056	1.000	0.500
	0.746	0.606	0.812	0.595	0.649	0.350	1.000	0.500
	Split-shell function (see Table III)							
c_1	2.157	2.142	2.258	2.260	2.164	2.161	2.187	2.192
	2.061	1.985	2.412	2.358	2.094	2.074	2.200	2.187
c_2	0.962	1.021	1.259	1.247	0.922	0.945	1.364	1.339
	1.079	1.139	1.251	1.239	1.081	1.093	1.354	1.321
ν	0.690	0.576	0.397	0.455	0.526	0.184	0.006	0.301
	0.779	0.684	0.535	0.530	0.695	0.473	0.332	0.452

(b) Split-shell wave function

A principal disadvantage of the simple screening approximation (14) is that the single variational parameter c produces simultaneous and substantial changes in all properties $\langle F\rangle$, including the energy $\langle H\rangle$. It is desirable that the trial function ϕ have sufficient flexibility that a particular property may be selectively probed while the overall shape of the function is affected as little as possible.

To partially meet this need we consider next the two-parameter "split-shell" approximation of Hylleraas[19] and Eckart[7]

$$\phi = \mathfrak{N}[\exp(-c_1 r_1 - c_2 r_2) + \exp(-c_2 r_1 - c_1 r_2)] \quad (15)$$

which effectively allows the two electrons to move in slightly different nuclear charge fields, and which therefore takes some simple account of radial electron correlation. We now consider only the improved formula (10), but the overlap S is again calculated according to both the Eckart and improved methods described previously. Table III shows the direct estimates[20] $\langle\phi|F|\phi\rangle$ and the rigorous lower bounds calculated from the split-shell function (15). Table II gives corresponding optimum values of ν and of the two variational parameters c_1 and c_2.

The results of Table III are generally a significant improvement over the corresponding entries of Table I, in accord with the fact that function (15) has a lower energy and better overlap with the true wave function than does (14). Thus for the energy-optimized functions,

$$\text{Eckart } S_{\text{screened}} = 0.962,$$

TABLE III. Lower bounds to various properties $\langle\psi|F|\psi\rangle$ of the normal helium atom as calculated from formula (10) using the split-shell approximation (15). In each case, the upper entry corresponds to the Eckart overlap, the lower to the improved overlap (13). The direct estimate $\langle\phi|F|\phi\rangle$ is included for comparison, and all numbers are expressed as a percentage of the true value (Ref. 16).

Operator F	r_1^2	r_1	r_1^{-1}	r_1^{-2}	r_{12}^2	r_{12}	r_{12}^{-1}	r_{12}^{-2}
Formula (10)	78.6	87.3	79.9	40.8	72.7	84.5	84.2	53.0
	85.8	92.6	89.0	51.6	78.8	88.3	92.7	66.1
$\langle\phi\|F\|\phi\rangle$	103.7	100.9	99.9	99.1	98.4	98.1	104.9	116.0

$$\text{Improved } S_{\text{screened}} = 0.987,$$

$$\text{Eckart } S_{\text{split}} = 0.981,$$

$$\text{Improved } S_{\text{split}} = 0.993.$$

But the bounds are not always strictly ordered according to increasing overlap (see, e.g., the operators r_{12} and r_{12}^2), thereby confirming the intrinsic value of a more flexible functional form.

Furthermore, it is clearly seen from the results for r_{12}^{-1} and r_{12}^{-2} that to compute a more elaborate lower-bound formula, such as (11), for a simple function may pay off more heavily than to simply use a more elaborate trial function in a simpler formula. Indeed, the accuracy (96.7%) of the final entry for r_{12}^{-1} in Table I rivals the accuracy (98.1%) with which the energy itself is given in the screening approximation. These results suggest that with more accurate measures of the overlap S one may hope, in favorable cases, to obtain bounds of a useful quality from relatively crude approximations.

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$$\chi = \eta \exp[-1.817(r_1+r_2)] \times [1+0.294r_{12}+0.132(r_1-r_2)^2]$$

and $S_1 = \langle\chi|\psi\rangle$ was computed from the Eckart criterion.

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suggested in Ref. 4.

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Coherent Enhancement of the Natural Linewidth

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When the interparticle distance of a gas of atoms is small compared with the spontaneous radiation wave length, the photon emitted by one atom may be absorbed by other atoms and may thus be trapped in the gas. The number of photons that are emitted is therefore reduced, as compared to the incoherent radiation of a gas of widely separated atoms. This photon trapping effect on the natural linewidth of the radiation is calculated and found to be large in certain cases. Some experimental aspects of observing such an effect are also discussed.

Recently Kuhn and Vaughan[1] reported an experimental value for the oscillator strength of the 1^1S-2^1P resonance transition in helium. The corresponding radiation width of the 2^1P level was determined as 1.31 ± 0.12 m^{-1} while the computed natural width[2] is 0.95 m^{-1}. A possible explanation of this discrepancy of about 30–40% has been suggested[3] in terms of coherent enhancement. The idea of coherent enhancement was first proposed and formulated by Dicke[4] in his discussion of the super-radiant states. More recently this effect has also been discussed[5,6] for the case of two stationary atoms. These results, however, are not applicable to a many-atom gas in nonsuperradiant states. Furthermore, the latest experiment[7] also determined the same oscillator strength from a measurement of the 2^1P lifetime to be in agreement with the computed value to ~8%. Therefore it is not clear whether this particular effect of coherent enhancement is involved in these experiments.

The purpose of this paper is to investigate the conditions under which this coherence effect may be observed. We point out here that (1) according to our calculation, a large coherent enhancement of the natural linewidth does exist in certain cases, and (2) the usual linewidth experiments such as those mentioned above, in which the radiating gas is maintained in a steady state, are not suitable for observing this particular effect.

We first consider a gas which consists of n atoms in a container whose dimension is small compared with the radiation wavelength λ. Generalization of the results to the case of a gas of large extent will be discussed later. The transition which gives rise to radiation of frequency ω_0 is assumed to take place between two nondegenerate + and − states of the individual atom, with corresponding eigenvalues $\hbar\omega_0/2$ and $-\hbar\omega_0/2$. Following Dicke,[4] we assign a quantum number m as a measure of the energy of the internal states of the gas. Thus

$$m = (n_+ - n_-)/2, \tag{1}$$

where n_+ and n_- are the number of atoms in + states and − states, respectively. Such a gas can be treated in analogy with a system of spin $\frac{1}{2}$ particles. Corresponding to the total spin of the system, we now have the "cooperation number" r, whose third component is m. The assumed small size of the gas enables us to avoid the complications caused by the Doppler effect, which will be considered later. It is also assumed that collisions do not affect the internal states of the atoms, and that the interparticle distance, although small compared to λ, is still so large that the atoms do not interact, and the wave packet of one atom does not overlap with that of the others. Under these assumptions, the quantum number r has the important property that it remains constant throughout the radiation process.

Assuming $r \gg 1$, one can use the classical model

$$m = r\cos\phi(t), \tag{2}$$