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Lower bounds to expectation values

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Abstract. A formula is presented giving a rigorous lower bound to the true quantum-mechanical expectation value $\langle\psi|F|\psi\rangle$ of a positive operator $F \geqslant 0$ in terms of some approximate wave function ϕ. This bound is compared with previous results of Bazley and Fox and of Jennings and Wilson as well as with a much more general lower-bound expression which is often applicable even when matrix elements of F^2 do not exist. It is shown that the non-linearities of the lower-bound expressions can be exploited by choosing 'symmetric sum' operators to optimize the lower bound. As an illustrative application lower bounds are calculated for various powers of the nuclear–electronic and interelectronic distances r_1, r_{12} in the normal helium atom using a simple screened hydrogenic approximation.

1. Introduction

The calculation of quantum-mechanical properties is dominated by energy considerations and the search for approximate eigenvalues of the many-particle Schrödinger equation. It is possible to compute both upper and lower bounds to the true energy levels, and in particular the quality of the (variational) energy upper bound has often been used to determine approximate wave functions for the description of a system.

Because the energy criterion may neglect certain details of the wave function which are important for other properties, the fundamental importance of attaching error bounds to the calculated values of other quantum-mechanical properties has been recently stressed (e.g. Löwdin 1960, Jennings and Wilson 1967). In the present paper a formula is presented for a guaranteed *lower* bound to the true value $\langle\psi|F|\psi\rangle$ of a given positive operator F. This bound is first compared with certain previous results due to Bazley and Fox (1966) and to Jennings and Wilson (1966, 1967). A much more general lower-bound expression is then presented which is often applicable even in cases where matrix elements of F^2 do not exist, and which is especially useful for trial wave functions of marginal accuracy. The optimal form of the lower-bound expressions is discussed in terms of operator non-linearities, and finally in § 7 an illustrative application is made to various properties of the normal helium atom.

2. Lower bound to the true value of $\langle\psi|F|\psi\rangle$

Consider the three vectors $|\psi\rangle$, $|\phi\rangle$, $F|\phi\rangle$, where $|\psi\rangle$ and $|\phi\rangle$ are normalized and $F|\phi\rangle$ is normalizable. The Gramian† G of these vectors is non-negative

$$G \equiv \begin{vmatrix} 1 & \langle\phi|\psi\rangle & \langle\phi|F|\psi\rangle \\ \langle\phi|\psi\rangle & 1 & \langle\phi|F|\phi\rangle \\ \langle\phi|F|\psi\rangle & \langle\phi|F|\phi\rangle & \langle\phi|F^2|\phi\rangle \end{vmatrix} \geqslant 0$$

and essentially limits the range of values permitted to the matrix elements $\langle\psi|F|\phi\rangle$. The function G is quadratic in $\langle\psi|F|\phi\rangle$, and the minimum permissible value of this variable is the lower root of the quadratic equation $G = 0$. Thus

$$\langle\phi|F|\psi\rangle \geqslant S\langle\phi|F|\phi\rangle - (1-S^2)^{1/2}\Delta F \tag{1}$$

where S is the (positive) overlap integral of the vectors $|\phi\rangle$ and $|\psi\rangle$:

$$S = \langle\phi|\psi\rangle$$

† As indicated, the *Gramian* is the determinant of the overlap matrix of the vectors (see, e.g., Bellman 1960, p. 46). We assume for simplicity that its elements are all real.

and ΔF is the 'width' of the operator F in the state $|\phi\rangle$ as defined by

$$(\Delta F)^2 = \langle\phi|F^2|\phi\rangle - \langle\phi|F|\phi\rangle^2.$$

We shall assume that S is sufficiently near unity as to satisfy the inequality

$$\frac{S}{(1-S^2)^{1/2}} \geqslant \frac{\Delta F}{\langle\phi|F|\phi\rangle}.$$

When F is restricted to be a *positive* operator, $F \geqslant 0$, an application of the Schwarz inequality in the form

$$\langle\psi|F|\phi\rangle \leqslant \langle\psi|F|\psi\rangle^{1/2}\langle\phi|F|\phi\rangle^{1/2} \tag{2}$$

leads finally to the desired result

$$\langle\psi|F|\psi\rangle \geqslant \frac{\{S\langle\phi|F|\phi\rangle - (1-S^2)^{1/2}\Delta F\}^2}{\langle\phi|F|\phi\rangle}. \tag{3}$$

If $|\phi\rangle$ is interpreted as some approximation to the true wave function $|\psi\rangle$, then the right-hand side of (3) provides a guaranteed lower bound to the true value of $\langle\psi|F|\psi\rangle$ in terms of the overlap S, the width ΔF and the approximate $\langle\phi|F|\phi\rangle$.

It is important to notice that the sense of the inequality (3) is held intact if S is replaced by any guaranteed *lower* bound to the true value of the overlap $\langle\phi|\psi\rangle$. Thus S may be obtained from the 'Eckart criterion' (Eckart 1930, Shull and Löwdin 1958) or some related scheme (Weinberger 1960, Weinhold 1967).

3. Comparison with Bazley–Fox formula

Under similar assumptions on the non-negativity of the operator F, Bazley and Fox (1966) have given the following inequality for $\langle\psi|F|\psi\rangle$:

$$\langle\psi|F|\psi\rangle \geqslant \frac{\{\langle\phi|F|\phi\rangle - (2-2S)^{1/2}\langle\phi|F^2|\phi\rangle^{1/2}\}^2}{\langle\phi|F|\phi\rangle}. \tag{4}$$

In the region of validity of the bounds, (3) will be superior to (4) if, and only if,

$$S\langle\phi|F|\phi\rangle - (1-S^2)^{1/2}\Delta F \geqslant \langle\phi|F|\phi\rangle - (2-2S)^{1/2}\langle\phi|F^2|\phi\rangle^{1/2}$$

or, putting $\delta \equiv 1-S$, if

$$(2\delta)^{1/2}\langle\phi|F^2|\phi\rangle^{1/2} \geqslant (2\delta-\delta^2)^{1/2}\Delta F + \delta\langle\phi|F|\phi\rangle. \tag{5}$$

Since both sides of (5) are positive they may be squared without altering the sense of the inequality. Thus we must check to see if

$$\delta\langle\phi|F^2|\phi\rangle + 2(1-\delta)\langle\phi|F|\phi\rangle^2 \geqslant 2(2\delta-\delta^2)^{1/2}\Delta F\langle\phi|F|\phi\rangle \tag{6}$$

where we have removed a common factor $\delta \neq 0$. Similarly both sides of (6) may be squared, leading then to the requirement

$$(2\langle\phi|F|\phi\rangle^2 - \delta\langle\phi|F^2|\phi\rangle)^2 \geqslant 0$$

which of course is satisfied for all values of δ. Thus the formula (3) is uniformly superior to the Bazley–Fox formula (4) throughout the region of validity of the two bounds.

4. Comparison with Jennings–Wilson formula

If we define $D = \langle\phi|F|\phi\rangle - \langle\psi|F|\psi\rangle$ and set $\lambda = \{(1-S)/2\}^{1/2}$, then (3) may be put into the form

$$D \leqslant 4\lambda\Delta F\{1+\lambda\alpha-\lambda^2(5/2)-\lambda^3\alpha+\lambda^4(7/8)+\ldots\} \tag{7}$$

where α is the quantity

$$\alpha = \frac{\langle\phi|F|\phi\rangle}{\Delta F} - \frac{\Delta F}{\langle\phi|F|\phi\rangle}.$$

Jennings and Wilson (1966) have recently proposed error limits for expectation values which may be written in the form (when $D \geqslant 0$)

$$D \leqslant 4\lambda\Delta F \tag{8}$$

and which is expected to be valid for sufficiently small $\lambda \geqslant 0$. Comparison of (8) with (7) shows that the Jennings–Wilson result is identical with (3) as $\lambda \to 0$. This is actually the only valid comparison since in the derivation of (8) higher-order terms (with positive coefficients) also appear

$$D \leqslant 4\lambda\Delta F\left\{1+\lambda\frac{\langle\phi|(F-\langle\phi|F|\phi\rangle)^4|\phi\rangle^{1/2}}{(\Delta F)^2}+\ldots\right\}$$

and these higher powers of λ were finally neglected.

However, even for larger values of λ (when (8) will no longer be strictly valid) the bound (3) will actually furnish a better bound than the truncated bound (8) if, as often happens, $\langle\phi|F|\phi\rangle$ exceeds ΔF. Since, furthermore, the bound (3) involves calculation of exactly the same matrix elements as occur in the Jennings–Wilson result, it is concluded that (3) provides a more satisfactory lower bound from both the theoretical and the practical standpoint.

Of course, the Jennings–Wilson formula applies to a more general class of operators F and provides also an *upper* bound to the true expectation value, as the present treatment is unable to do. It should further be remarked that none of these bounds can treat operators such as $\delta(r)$, for which the work of Redei (1963) may be consulted.

5. Alternative lower bounds

The formula (3) is only a special case of a much more general expression for lower bounds to expectation values. Let us write (1) again as

$$\langle\psi|g|\phi\rangle \geqslant S\langle\phi|g|\phi\rangle - (1-S^2)^{1/2}\Delta g$$

but in place of (2) we now take the Schwarz inequality (for $g \geqslant 0$) in the form

$$\langle\psi|g|\phi\rangle = \langle\psi|g^{\sigma}g^{1-\sigma}|\phi\rangle \leqslant \langle\psi|g^{2\sigma}|\psi\rangle^{1/2}\langle\phi|g^{2-2\sigma}|\phi\rangle^{1/2}$$

for any value of σ. If we set $g^{2\sigma} = F$ or $g = F^{1/2\sigma}$ we then obtain the desired result†

$$\langle\psi|F|\psi\rangle \geqslant \frac{\{S\langle\phi|F^{1/2\sigma}|\phi\rangle - (1-S^2)^{1/2}\Delta F^{1/2\sigma}\}^2}{\langle\phi|F^{(1-\sigma)/\sigma}|\phi\rangle} \tag{10}$$

which is valid for any values of σ for which the quantities are all defined and for which $\{S^2/(1-S^2)\}^{1/2} \geqslant \Delta F^{1/2\sigma}/\langle\phi|F^{1/2\sigma}|\phi\rangle$.

Formula (3) is the special case $\sigma = \frac{1}{2}$ of the general relation (10), while for very large σ we obtain

$$\langle\psi|F|\psi\rangle \geqslant \frac{S^2}{\langle\phi|F^{-1}|\phi\rangle}$$

which is recognized simply as the Schwarz inequality for the matrix element $S = \langle\psi|\phi\rangle = \langle\psi|F^{1/2}F^{-1/2}|\phi\rangle$. Another interesting special case of (10) occurs at $\sigma = 1$, where the lower bound becomes

$$\langle\psi|F|\psi\rangle \geqslant \{S\langle\phi|f|\phi\rangle - (1-S^2)^{1/2}\Delta f\}^2 \tag{11}$$

† We may remark here that (10) also furnishes a set of 'experimental' lower bounds which, however, appear to be very weak. Letting $S \to 1$ gives $\langle\psi|F|\psi\rangle \geqslant \langle\psi|F^n|\psi\rangle^2/\langle\psi|F^{2n-1}|\psi\rangle$ for all (integer or non-integer) n, where the matrix elements are only in terms of ψ.

and is expressed entirely in terms of the value and width of the square-root operator $f \equiv F^{1/2}$. Relations such as (11) are especially important in cases where the integral $\langle\phi|F^2|\phi\rangle$ diverges so that the width ΔF is undefined and the lower-bound formulae (3), (4), (8) are all inapplicable.

Inspection of the formula (10) shows that only the value $\sigma = \frac{1}{2}$, formula (3), could lead to an *exact* lower bound as $S \to 1$. It would be desirable to compare (10) with (3) for arbitrary values of σ, but the appearance of fractional operators makes this difficult except in certain special cases, and the direct differentiation of (10) appears unproductive.

Let us therefore, as a special case, compare the bounds furnished by (3) and (11). Let us denote the right-hand side of (3) by $B_{(3)}$, the right-hand side of (11) by $B_{(11)}$, and expand the difference $B_{(3)} - B_{(11)}$ in powers of $\lambda = \{(1-S)/2\}^{1/2}$. This gives

$$B_{(3)} - B_{(11)} = (\Delta f)^2 - \lambda(4\beta) + \lambda^2(4\gamma) + \lambda^3(10\beta) + \ldots$$

where

$$\beta \equiv \Delta F - \langle\phi|f|\phi\rangle\Delta f; \qquad \gamma = \frac{(\Delta F)^2}{\langle\phi|F|\phi\rangle} - 2(\Delta f)^2.$$

Thus as $S \to 1$ the bound furnished by (3) will be superior to that of (11) by an amount $(\Delta f)^2$, and it would appear that we should therefore avoid (11) altogether in cases where (3) is applicable. However, if $1-S$ is not sufficiently small and if $\beta > 0$ (i.e. if Δf is very small) the bound furnished by (11) may actually be superior to that of (3). The formula (11) should therefore be kept in mind when attempting to find the best possible lower bound for a trial wave function of marginal accuracy.

Indeed, we shall generally wish to examine the formula (10) for *all* possible values of σ so that σ can be chosen to *maximize* the lower bound. This possibility will be discussed further in § 7.

6. Non-linearity of the lower bounds: optimum choice of operators

Because the lower bounds (3), (10) are distinctly non-linear in the operator F, the lower bound to a linear combination of operators will not be identical with the same linear combination of lower bounds to the individual operators. For example, it is certainly true that arbitrary one-particle operators r_1, r_2 will satisfy

$$\tfrac{1}{2}\langle\psi|r_1+r_2|\psi\rangle = \langle\psi|r_1|\psi\rangle = \langle\psi|r_2|\psi\rangle$$

but in general it is *not* true that the lower bound to $\langle\psi|r_1|\psi\rangle$ is half the lower bound to $\langle\psi|r_1+r_2|\psi\rangle$. We shall therefore wish to explore various combinations of r_1 and r_2 in order to obtain the best possible bound for $\langle\psi|r_1|\psi\rangle$.

For simplicity we consider a set of single-particle operators r_i $(i = 1, 2, \ldots, N)$ and define

$$R = \sum_i a_i r_i$$

where the scalars a_i are restricted to satisfy

$$\sum_i a_i = 1. \tag{12}$$

Then $\langle R\rangle = \langle r_1\rangle$ for every choice of the a_i, and from the formula (3) it is apparent that we wish to choose the a_i in such a way as to *minimize* $(\Delta R)^2$:

$$(\Delta R)^2 = -\langle r_1\rangle^2 + \langle r_1^2\rangle \sum_i a_i^2 + \langle r_1 r_2\rangle \sum_i a_i(1-a_i).$$

Adopting the Lagrange multiplier $-\kappa$ for the constraint (12), we require

$$\frac{\partial(\Delta R)^2}{\partial a_i} = 2a_i(\langle r_1^2\rangle - \langle r_1 r_2\rangle) + \langle r_1 r_2\rangle - \kappa = 0$$

which shows that a_i is simply a constant for all i. Thus to obtain the *optimum* lower bound to a one-particle operator r_1 one should find the lower bound to the symmetric sum

operator R defined by

$$R = N^{-1} \sum_i r_i$$

and a similar conclusion holds also for 2, 3, ...-particle operators.

Of course the same modification will also improve the quality of the Bazley–Fox and Jennings–Wilson formulae discussed previously.

7. Application to expectation values in normal helium atom

Because of the circumstances described in § 4 the bound furnished by (3) will not differ significantly from the Jennings–Wilson result (8) when wave functions of very high accuracy are used. The reader should therefore consult their papers (Jennings and Wilson 1966, 1967) for many examples of the accuracy which is available in the most favourable cases from the formulae (3), (8).

For illustrative purposes we have instead considered the calculation of expectation values for the ground-state helium atom using the simple screened hydrogenic wave function (Pauling and Wilson 1935, p. 184)

$$\phi = \frac{c^3}{\pi} \exp(-cr_1 - cr_2), \qquad c = 27/16.$$

The calculated energy $\langle\phi|H|\phi\rangle = -2{\cdot}848$ A.U. (cf. $E_{\text{exp}} = -2{\cdot}9037$ A.U.) leads by the Eckart criterion to a value $S = 0{\cdot}9623$ for the lower bound to the true overlap integral $\langle\phi|\psi\rangle$. However, following Jennings and Wilson (1967) we may use a three-term Hylleraas wave function together with the method of Weinhold (1967) to obtain an improved lower bound of $S = 0{\cdot}9870$, which latter value has also been used in the computations.

Table 1. Lower bounds to expectation values of various properties in the normal helium atom as calculated by formula (3) and the Jennings–Wilson bound, formula (8)

F[a]	ΔF	$\langle\phi\|F\|\phi\rangle$	True $\langle\psi\|F\|\psi\rangle$[b]	Lower bounds to true expectation value $\langle\psi\|F\|\psi\rangle$	
				Equation (3)	Jennings and Wilson equation (8)
r_1^2	0·912	1·054	1·1935	0·757 0·556	0·759 (0·637)[c] 0·552 (0·345)[c]
r_1	0·363	0·889	0·9295	0·755 0·644	0·772 (0·723)[c] 0·690 (0·607)[c]
r_1^{-1}	1·193	1·688	1·6883	1·287 1·000	1·303 (1·143)[c] 1·032 (0·761)[c]
r_1^{-2}	—[d]	5·695	6·0174	—[d] —[d]	—[d] —[d]
r_{12}^2	2·193	2·107	2·5164	1·416 0·972	1·400 0·903
r_{12}	0·653	1·296	1·4221	1·064 0·883	1·086 0·938
r_{12}^{-1}	0·887	1·055	0·9458	0·765 0·568	0·769 0·568
r_{12}^{-2}	—[d]	1·898	1·4648	—[d] —[d]	—[d] —[d]

For each operator the upper entry gives the result for the improved overlap $S = 0{\cdot}9870$, the lower for the Eckart overlap $S = 0{\cdot}9623$.

a, all numbers are in A.U.; b, Pekeris 1959; c, lower bound calculated directly for the one-electron operator rather than the 'symmetric sum' operator described in § 6; d, integrals of F^2 diverge.

In table 1 are exhibited the expectation values of various powers of the nuclear–electronic and interelectronic distances r_1, r_{12} in the normal helium atom, the true values being taken from the very accurate calculations of Pekeris (1959). The final two columns give respectively the lower bounds furnished by formula (3) and the Jennings–Wilson bound (8). In both of the lower bounds to powers of r_1 we have used the symmetric sum operator described in § 6, but for the Jennings–Wilson bound we have also included in parentheses the number which would be directly calculated as the lower bound to the one-electron operator.

It is observed that the bound (3) is still entirely comparable in quality with the Jennings–Wilson lower bound (8), even though the latter would perhaps be of questionable validity for the given value of S. In fact in several cases the bound (3) is actually superior with the Jennings–Wilson result, though this could not have been anticipated.

We can improve the lower bounds given in table 1 by adopting a *variational principle* for expectation values along two distinct lines (which might also be combined).

The lower bound furnished by (3), or the more general formula (10), can be optimized by suitably choosing the values for any adjustable parameters which the trial function ϕ may contain. This possibility was explored by Jennings and Wilson (1967) for their own error limit expression (8). They found that the optimum error limit function is always very close to the optimum energy function, because the error bound depends very strongly on S and thus, through the Eckart criterion, on $\langle\phi|H|\phi\rangle$. The situation is illustrated in figure 1, which shows how the lower bounds furnished by (3) and (11) for the inverse

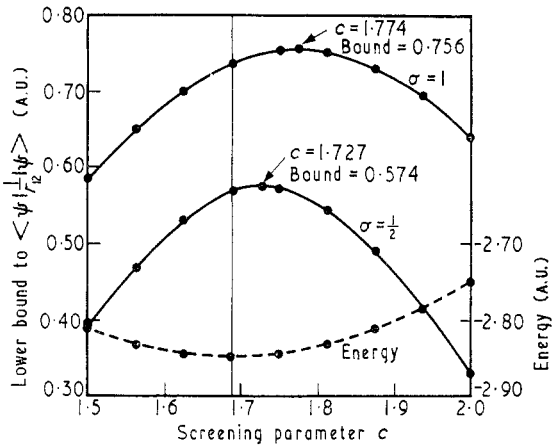

Figure 1. Variation of the lower bound to $\langle\psi|r_{12}^{-1}|\psi\rangle$ with respect to the screening parameter c in the screened hydrogenic approximation. The upper full curve is from formula (11), while the lower is from formula (3), both calculated using the Eckart criterion for overlap S. The broken line (see right scale) shows the corresponding energy expectation value, with the optimum marked at $c = 27/16$.

interelectronic distance r_{12}^{-1} vary with the screening parameter c in the screened hydrogenic approximation. It is apparent that the improvement in the lower bound is rather small for the extra computational effort involved.

But, as indicated in § 5, we can formulate an alternative 'variational principle' on the basis of the relation (10) by considering the lower bound $F_{\mathrm{LB}}(\sigma)$

$$F_{\mathrm{LB}}(\sigma) \equiv \frac{\{S\langle\phi|F^{1/2\sigma}|\phi\rangle - (1-S^2)^{1/2}\Delta F^{1/2\sigma}\}^2}{\langle\phi|F^{(1-\sigma)/\sigma}|\phi\rangle}$$

as a function of σ. This has been carried out for the screened hydrogenic ϕ at the optimum energy screening parameter $c = 27/16$. The qualitative form of the $F_{\mathrm{LB}}(\sigma)$ against σ curves

is indicated in figure 2, while figures 3 and 4 show portions of the actual curves for the operators r_1^n, r_{12}^n respectively, using both the Eckart and improved values of the overlap S. The final optimized lower bounds and corresponding optimum σ are given in table 2.

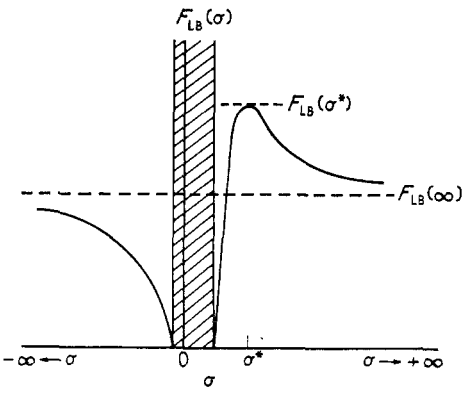

Figure 2. Qualitative plot of $F_{LB}(\sigma)$ against σ for the operators F considered in the text. The shaded region indicates a range of σ for which $F_{LB}(\sigma)$ is undefined or invalid. For (allowed) negative values of σ the lower bound rises slowly from zero to the horizontal asymptote at $F_{LB}(\infty) = S^2/\langle\phi|F^{-1}|\phi\rangle$, while for (allowed) positive values of σ the bound rises steeply from zero to some maximum at σ^* before falling back to the asymptote.

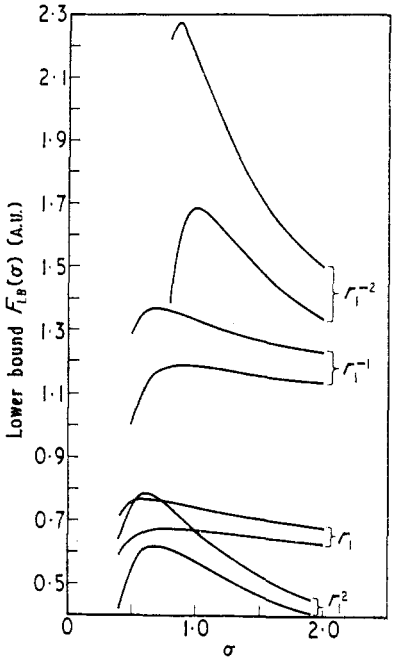

Figure 3. Lower bounds $F_{LB}(\sigma)$ from formula (10) as a function of σ for F = various powers of the nuclear–electronic distance r_1. For each operator, the upper curve corresponds to $S = 0{\cdot}9870$, the lower to $S = 0{\cdot}9623$.

The σ optimizations here improve the lower bound (3) by as much as 20–30%, which is certainly of significant value, but it is clear from figures 3 and 4 that the improvements secured by the σ optimizations are still rather small compared with the changes which result when the overlap S is improved. In general the maximum of the $F_{LB}(\sigma)$ against σ curve is observed to (*a*) become more peaked, and (*b*) shift to lower values of σ (closer to

$\sigma = \frac{1}{2}$) as the overlap S is improved, in accordance with the observation that only $\sigma = \frac{1}{2}$, formula (3), can give an exact lower bound as $S \to 1$.

Although the lower bounds are, as expected, fairly loose for the simple screened hydrogenic wave function, it is useful to recall that the Temple (1928) *energy* lower bound

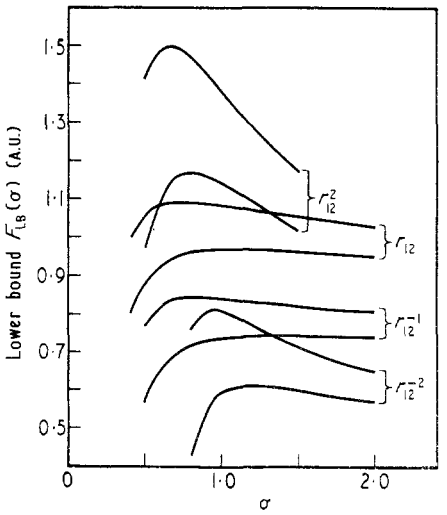

Figure 4. Lower bounds $F_{LB}(\sigma)$ from formula (10) as a function of σ for F = various powers of the interelectronic distance r_{12}. For each operator, the upper curve corresponds to $S = 0{\cdot}9870$, the lower to $S = 0{\cdot}9623$.

Table 2. Optimized lower bounds from formula (10) as a function of σ using the screened hydrogenic wave function ϕ

F	Optimum lower bound $F_{LB}(\sigma)$	Optimum σ	% improvement over formula (3)
r_1^{-2}	0·785	0·61	3·7
	0·623	0·69	12·0
r_1	0·767	0·64	1·6
	0·677	0·80	5·1
r_1^{-1}	1·370	0·69	6·4
	1·190	0·90	19·0
r_1^{-2}	2·273	0·86	—
	1·688	1·00	—
r_{12}^2	1·501	0·66	6·0
	1·171	0·80	20·6
r_{12}	1·096	0·75	3·0
	0·967	1·07	9·5
r_{12}^{-1}	0·845	0·83	10·5
	0·743	1·38	30·8
r_{12}^{-2}	0·813	0·93	—
	0·616	1·18	—

For each operator the upper entry gives the result for the improved overlap $S = 0{\cdot}9870$, the lower for the Eckart overlap $S = 0{\cdot}9623$.

of $-4{\cdot}09$ A.U. for this same screened hydrogenic function is in error by more than 40%. It is also interesting to notice that the best calculated lower bound to $\langle\psi|r_{12}^{-1}|\psi\rangle$ is actually

somewhat closer to the *true* value than is the expectation value $\langle\phi|r_{12}^{-1}|\phi\rangle$ which one would calculate directly from the trial function itself.

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