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Improved lower bounds to expectation values

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Abstract. A method recently introduced for obtaining rigorous lower bounds to the true quantum-mechanical expectation value $\langle\psi|F|\psi\rangle$ of a positive operator $F \geqslant 0$ is here extended and strengthened. The new formula always improves the previous result, but requires the more difficult integrals of FH and H^2. As a numerical illustration, lower bounds are calculated for various powers of r_1 and r_{12} in the normal helium atom. Using, particularly, the quantum-mechanical virial theorem and an improved lower bound for the overlap integral $\langle\phi|\psi\rangle$, it is shown that rigorous lower bounds accurate to 5–30% can be obtained even from the simple screened hydrogenic approximation, and the nuclear diamagnetic shielding is given correct to 1%.

1. Derivation of improved lower bounds

A method has recently been described (Weinhold 1968) for determining rigorous lower bounds to the true quantum-mechanical expectation value $\langle\psi|F|\psi\rangle$ of a positive operator $F \geqslant 0$. We wish to point out here how the previous result may be strengthened and extended if matrix elements of FH and H^2 are available (H is the Hamiltonian of the system).

Let $|\phi\rangle$ be an approximation to the true wave function $|\psi\rangle$ for a system with $H|\psi\rangle = E_0|\psi\rangle$. If we denote $\langle F\rangle = \langle\phi|F|\phi\rangle$, $S = \langle\phi|\psi\rangle$ and $(\Delta F)^2 = \langle F^2\rangle - \langle F\rangle^2$, the previous result is (Weinhold 1968)

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

which follows from the non-negativity of the Gramian determinant of the vectors $|\psi\rangle$, $|\phi\rangle$ and $F|\phi\rangle$.

Let us consider now the enlarged Gramian G of the vectors $|\psi\rangle$, $|\phi\rangle$, $F|\phi\rangle$ and $H|\phi\rangle$,

$$G = \begin{vmatrix} 1 & S & \langle\psi|F|\phi\rangle & E_0S \\ S & 1 & \langle F\rangle & \langle H\rangle \\ \langle\psi|F|\phi\rangle & \langle F\rangle & \langle F^2\rangle & \langle FH\rangle \\ E_0S & \langle H\rangle & \langle FH\rangle & \langle H^2\rangle \end{vmatrix} \geqslant 0 \tag{2}$$

where all elements are taken real and S is chosen positive. In consequence of (2)

$$\langle\psi|F|\phi\rangle \lessgtr \frac{S\alpha \pm \beta\gamma}{(\Delta H)^2} \tag{3}$$

where we have introduced the notation

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

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

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

Again F is taken to be a positive operator, and we further assume

$$S\alpha \geqslant \beta\gamma \geqslant 0 \tag{5}$$

which, however, is usually satisfied for reasonable ϕ.

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The development may now follow closely our previous treatment. Applying the Schwarz inequality in the form

$$\langle\psi|F|\phi\rangle \leqslant \langle\psi|F|\psi\rangle^{1/2}\langle\phi|F|\phi\rangle^{1/2} \tag{6}$$

we obtain the desired result

$$\langle\psi|F|\psi\rangle \geqslant \frac{\{(S\alpha-\beta\gamma)/(\Delta H)^2\}^2}{\langle F\rangle} \tag{7}$$

which always improves (1). Choosing, instead of (6), the more general form

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

we infer the more general lower bound

$$\langle\psi|F|\psi\rangle \geqslant \frac{\{(S\alpha_\omega-\beta_\omega\gamma)/(\Delta H)^2\}^2}{\langle F^{(1-\omega)/\omega}\rangle} = F_{\mathrm{LB}}(\omega) \tag{8}$$

where α_ω and β_ω are defined as in (4) by replacing F by $F^{1/2\omega}$, and where ω is arbitrary so long as restrictions analogous to (5) are satisfied and the required matrix elements exist. Only $\omega = \frac{1}{2}$ gives an exact lower bound as $S \to 1$, but other values of ω should be considered for less accurate trial functions.

Noting the restriction (5) and rewriting (4*c*) in the form

$$\gamma^2 = (\Delta H)^2 - S^2\langle(H-E_0)^2\rangle$$

it is evident that S may again be replaced by any *lower* bound to its true value without altering the sense of the inequality (8). For this purpose the 'Eckart criterion' (Eckart 1930) is available

$$S^2 \geqslant \frac{E_1-\langle H\rangle}{E_1-E_0} \tag{9}$$

where E_0 and E_1 are the two lowest energy levels (of the same symmetry) of the system. However, this estimate of S may often be improved if some *better* approximation χ is available for which $S_1 = \langle\chi|\psi\rangle$ (or a lower bound) and $S_{12} = \langle\chi|\phi\rangle$ have been obtained; in this case (Weinhold 1967)

$$S \geqslant S_1S_{12} - \{(1-S_1^2)(1-S_{12}^2)\}^{1/2}. \tag{10}$$

Other improved lower bounds for S may be given if higher energy levels are known and ϕ corresponds to one root of a secular determinant (Weinberger 1960), or if the matrix elements $\langle H^n\rangle$ exist for $n > 2$ (Gordon 1968). If these higher moments of the Hamiltonian exist it may, furthermore, be practical to include additional vectors $H^n|\phi\rangle$ in the Gramian determinant and so improve the inequality (3).

2. Numerical example and discussion

We have applied the improved lower bound formula (8) to the calculation of various powers of r_1 and r_{12} in the normal helium atom, using the simple screened hydrogenic approximation (see Pauling and Wilson 1935, p. 184):

$$\phi = \frac{c^3}{\pi}\exp(-cr_1-cr_2)$$

for which all the required matrix elements are easily computed. For each of the operators $F = r_1^n$, r_{12}^n, $n = \pm 1, \pm 2$, the lower bound $F_{\mathrm{LB}}(c, \omega)$ was computed as a function of both c and ω. Using Eckart's value (9) for the overlap S, the lower bound was obtained for the optimum c^* when $\omega = \frac{1}{2}$ (i.e. the best result of formula (7)) and the optimum ω^* when the scale parameter c is given its best-energy value $c = 27/16$. Table 1 compares these results with the value of $\langle\phi|F|\phi\rangle$, with the true value $\langle\psi|F|\psi\rangle$ (Pekeris 1959) and with the *fully* optimized lower bound $F_{\mathrm{LB}}(c^{**}, \omega^{**})$ which represents the limit of accuracy

Table 1. Lower bounds $F_{LB}(c, \omega)$ calculated from formula (8) using the Eckart estimate (9) of S. c^* optimizes the bound at $\omega = \frac{1}{2}$, ω^* optimizes the bound at $c = 27/16$, and c^{**}, ω^{**} gives the absolute optimum. The estimate $\langle\phi|F|\phi\rangle$ and the true value $\langle\psi|F|\psi\rangle$ (Pekeris 1959) are included for comparison, with all numbers given in atomic units

Operator F	r_1^2	r_1	r_1^{-1}	r_1^{-2}	r_{12}^2	r_{12}	r_{12}^{-1}	r_{12}^{-2}
$F_{LB}(27/16, \frac{1}{2})$	0·570	0·648	1·120	—	1·034	0·918	0·616	—
$F_{LB}(c^*, \frac{1}{2})$	0·592	0·661	1·123	—	1·057	0·927	0·766	—
$F_{LB}(27/16, \omega^*)$	0·631	0·678	1·226	1·944	1·225	0·991	0·749	0·652
$F_{LB}(c^{**}, \omega^{**})$	0·673	0·699	1·240	1·952	1·290	1·015	0·787	0·939
$\langle\phi\|F\|\phi\rangle$	1·054	0·889	1·688	5·695	2·107	1·296	1·055	1·898
$\langle\psi\|F\|\psi\rangle$	1·193	0·929	1·688	6·017	2·516	1·422	0·946	1·465

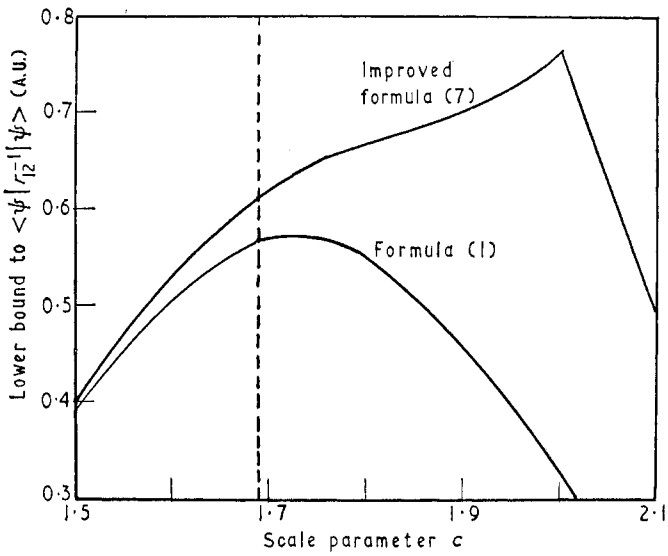

Figure 1. Comparison of the lower bound formulae (1) and (7) for r_{12}^{-1} as a function of the scale parameter c in the screened hydrogenic approximation, with the energy optimum marked at $c = 27/16$. The upper curve has a cusp at $c = 2$.

available from formula (8) with such a simple trial function ϕ and with Eckart's estimate of S. Table 2 gives numerical values of the various parameters.

Table 2. Numerical values of parameters used in calculating lower bounds of tables 1 and 3

Operator F	r_1^2	r_1	r_1^{-1}	r_1^{-2}	r_{12}^2	r_{12}	r_{12}^{-1}	r_{12}^{-2}
Using Eckart overlap								
c^*	1·611	1·611	1·683	—	1·633	1·636	2·000	—
c^{**}	1·562	1·575	1·749	1·716	1·572	1·581	1·834	1·996
ω^*	0·683	0·778	0·770	0·894	0·780	0·979	1·229	1·059
ω^{**}	0·717	0·830	0·830	0·906	0·839	1·088	1·173	1·069
Using improved overlap								
c^{**}	1·448	1·473	1·678	1·658	1·462	1·475	1·947	2·000
ω^{**}	0·628	0·679	0·591	0·789	0·695	0·791	0·826	1·000

The dependence of the improved lower bound (8) on the parameter ω is qualitatively similar to that found previously for formula (1), but the maximum becomes slightly more peaked and shifts to slightly lower values of ω (closer to $\omega = \frac{1}{2}$).

On the other hand, the dependence of (8) on the scale parameter c is significantly altered in several cases, as shown for example in figure 1. The new formula is apparently less sensitive to the strong energy dependence of the Eckart overlap (9), and may be significantly improved at values of the scale parameter which are rather far from the energy optimum $c = 1{\cdot}69$. This feature allows one to speak of a *variational principle* for expectation values in a more realistic sense, particularly with the adoption of an improved overlap estimate in which the energy dependence is still more favourably depressed.

For this reason, and because the Eckart estimate of S remains a major source of error in the lower bounds of table 1, the calculations were repeated using the improved overlap formula (10) in conjunction with a 3-term Hylleraas function (see e.g. Bethe and Salpeter 1957, p. 237)

$$\chi = \mathcal{N} \exp\{-1{\cdot}817(r_1+r_2)\}\{1+0{\cdot}294r_{12}+0{\cdot}132(r_1-r_2)^2\}$$

where $S_1 = \langle\chi|\psi\rangle$ is calculated from Eckart's criterion (9)†. The resulting, fully optimized, lower bounds are presented in table 3 and are seen to be of reasonable quality for such a

Table 3. Fully optimized lower bounds $F_{LB}(c^{**}, \omega^{**})$ calculated from formula (8) using the improved estimate (10) of S.

Operator F	r_1^2	r_1	r_1^{-1}	r_1^{-2}	r_{12}^2	r_{12}	r_{12}^{-1}	r_{12}^{-2}
Lower bound $F_{LB}(c^{**}, \omega^{**})$	0·961	0·841	1·438	2·712	1·865	1·222	0·881	1·085
Percentage of true value	80·6	90·5	85·2	45·1	74·1	85·9	93·1	74·1

simple trial function ϕ, giving usually 70–90% of the true value. In addition, two of the lower bounds are actually closer to the *true* result than is the corresponding estimate $\langle\phi|F|\phi\rangle$, which one calculates directly from the (energy optimized) trial function itself.

The tight lower bounds for r_{12}^{-1} are actually quite useful in conjunction with the quantum-mechanical *virial theorem* for estimating the important operator r_1^{-1}, which determines the diamagnetic shielding of the nucleus by the electrons. For the N-electron system (atomic or ionic) with nuclear charge Z and energy E_0 the virial theorem requires

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

and particularly for the helium atom, substituting the lower bound to $\langle\psi|r_{12}^{-1}|\psi\rangle$ from table 3 gives the rigorous lower bound

$$\langle\psi|r_1^{-1}|\psi\rangle \geqslant 1{\cdot}672$$

which, remarkably, is accurate to about 1%.

References

Bethe, H. A., and Salpeter, E. E., 1957, *Quantum Mechanics of One- and Two-Electron Systems* (Berlin: Springer-Verlag).

Eckart, C., 1930, *Phys. Rev.*, **36**, 878–92.

Gordon, R. G., 1968, *J. Chem. Phys.*, in the press.

Pauling, L., and Wilson, E. B., Jr., 1935, *Introduction to Quantum Mechanics* (New York: McGraw-Hill).

Pekeris, C. L., 1959, *Phys. Rev.*, **115**, 1216–21.

Weinberger, H. F., 1960, *J. Res. Natn. Bur. Stand.*, **64B**, 217–25.

Weinhold, F., 1967, *J. Chem. Phys.*, **46**, 2448–9.

—— 1968, *J. Phys.* A (*Proc. Phys. Soc.*), [2], **1**, 305–13.

† Thus, χ enters the lower bound calculations, aside from $\langle\chi|H|\chi\rangle$, only through the overlap integral $\langle\phi|\chi\rangle$.