New variational bounds on expectation values (in quantum mechanics)

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LETTER TO THE EDITOR

New variational bounds on expectation values

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Abstract. New variational bounds on quantum mechanical expectation values are presented. An illustrative calculation for helium gives encouraging accuracy.

In this note recent work concerning variational bounds on overlaps (Barnsley and Robinson 1975, referred to as I) is extended to yield new variational bounds on quantum mechanical expectation values. The practicality of the variational functionals is briefly discussed. An illustrative calculation for helium gives a more accurate result than comparable calculations of Weinhold (1969) and Wang (1971). As in I, the theory is first presented quite generally.

Let A be a self-adjoint operator in a Hilbert space $\mathscr{H}$ with inner product $\langle , \rangle$, and suppose that A admits a one-dimensional null space specified by an (unknown) eigenvector θ, so that

$$A\theta = 0, \qquad \langle \theta, \theta \rangle = 1. \tag{1}$$

Let L be a self-adjoint, strictly positive operator in $\mathscr{H}$, which is such that the positive quantity $\langle \theta, L\theta \rangle$ is of interest and requires bounding. Consider the following equation in $\hbar$, the subspace of $\mathscr{H}$ which is orthogonal to θ:

$$A\psi = \chi - cL\theta, \qquad \psi \in \hbar, \tag{2}$$

where

$$c = \frac{\langle \theta, \chi \rangle}{\langle \theta, L\theta \rangle} \tag{3}$$

and χ is some arbitrary known vector *not* orthogonal to θ. Since L is strictly positive it has a self-adjoint, positive inverse L^{-1}. Accordingly from (2) we have

$$AL^{-1}A\psi = AL^{-1}\chi. \tag{4}$$

The operator $AL^{-1}A$ is positive and self-adjoint, and the elementary Ritz-type variational principle associated with equation (4) is

$$-\langle \Psi, AL^{-1}A\Psi \rangle + \langle \Psi, AL^{-1}\chi \rangle + \langle AL^{-1}\chi, \Psi \rangle \leqslant \langle AL^{-1}\chi, \psi \rangle = \langle L^{-1}\chi, \chi \rangle - c\langle \chi, \theta \rangle. \tag{5}$$

This simplifies to give the result

$$\langle A\Psi - \chi, L^{-1}(A\Psi - \chi) \rangle \geqslant \frac{|\langle \chi, \theta \rangle|^2}{\langle \theta, L\theta \rangle}. \tag{6}$$

If the squared overlap $|\langle\chi, \theta\rangle|^2$ is either known, or has a known lower bound, then the variational inequality (6) provides a lower bound on $\langle\theta, L\theta\rangle$.

A variational bound complementary to that in (6) can be derived when the operator $AL^{-1}A$ is bounded below in $\mathscr{h}$ by some positive number m^2, so that

$$\langle\xi, AL^{-1}A\xi\rangle \geqslant m^2\langle\xi, \xi\rangle \qquad \text{for all } \xi \in \mathscr{h}. \tag{7}$$

This bound is given by subtracting the term

$$\frac{1}{m^2}\langle AL^{-1}A\Psi - AL^{-1}\chi, AL^{-1}A\Psi - AL^{-1}\chi\rangle \tag{8}$$

from the functional in (6) (cf Robinson 1969, Arthurs 1970), yielding

$$\frac{|\langle\chi, \theta\rangle|^2}{\langle\theta, L\theta\rangle} \geqslant \left\langle A\Psi - \chi, \left(L^{-1} - L^{-1}\frac{A^2}{m^2}L^{-1}\right)(A\Psi - \chi)\right\rangle. \tag{9}$$

(If Ψ is set equal to $\psi + \delta\psi$, it can be verified directly from (1) and (2) that the first-order term in (9) vanishes. The second-order term can be expressed as

$$\left\langle (AL^{-1}A)^{1/2}\,\delta\psi, \left(1 - \frac{AL^{-1}A}{m^2}\right)(AL^{-1}A)^{1/2}\,\delta\psi\right\rangle \tag{10}$$

and is non-positive by virtue of (7), since $(AL^{-1}A)^{1/2}\,\delta\psi \in \mathscr{h}$.)

When the operator $AL^{-1}A$ is also bounded above in $\mathscr{h}$ by some number v^2, then the variational bound

$$\left\langle A\Psi - \chi, \left(L^{-1} - L^{-1}\frac{A^2}{v^2}L^{-1}\right)(A\Psi - \chi)\right\rangle \geqslant \frac{|\langle\chi, \theta\rangle|^2}{\langle\theta, L\theta\rangle} \tag{11}$$

is available as an alternative to (6). Clearly this is a tighter bound for the same trial vector Ψ, but (6) and (11) are really equivalent for different Ψ.

In the special case $L = 1$, the variational bounds in (6), (9) and (11) reduce to the bounds on squared overlaps $|\langle\chi, \theta\rangle|^2$ which were discussed in I.

In the event that the null space of A is spanned by t orthonormal eigenvectors $\{\theta^1, \theta^2, \ldots \theta^t\}$, for which also $\langle\theta^i, L\theta^j\rangle = 0$ when $i \neq j$, then the foregoing theory supplies bounds on the quantity

$$\sum_{i=1}^{t} \frac{|\langle\theta^i, \chi\rangle|^2}{\langle\theta^i, L\theta^i\rangle}. \tag{12}$$

Most of the overlap bounds used in quantum mechanics, together with variational improvements, were derived in I from the $L = 1$ versions of the bounds given above. If a system is described by a Hamiltonian H with energy eigenvalues $\{E_i\}$ and orthonormal eigenvectors $\{\theta_i\}$, one takes θ as a particular θ_k, χ as the vector whose overlap with θ_k is of interest, and A involving a suitable factor of $(H - E_k)$. Similar substitutions can be made in the new functionals presented here in order to obtain bounds on quantum mechanical expectation values $\langle\theta_k, L\theta_k\rangle$ where L is now the operator representing some observable of interest.

Making the straightforward choice of $(H - E_k)$ for A in (6) we obtain

$$\langle (H - E_k)\Psi - \chi, L^{-1}[(H - E_k)\Psi - \chi]\rangle \geqslant \frac{|\langle\chi, \theta_k\rangle|^2}{\langle\theta_k, L\theta_k\rangle}. \tag{13}$$

Likewise (9) yields

$$\frac{|\langle\chi,\theta_k\rangle|^2}{\langle\theta_k,L\theta_k\rangle} \geqslant \left\langle (H-E_k)\Psi-\chi, \left(L^{-1}-L^{-1}\frac{(H-E_k)^2}{m^2}L^{-1}\right)[(H-E_k)\Psi-\chi]\right\rangle, \tag{14}$$

wherein if

$$\langle\xi,L^{-1}\xi\rangle \geqslant q^2\langle\xi,\xi\rangle \qquad \text{for all } \xi\in\mathscr{h} \tag{15}$$

we can take

$$m^2 = (E_j-E_k)^2q^2, \tag{16}$$

E_j being the closest eigenvalue to E_k. For the ground state θ_0, the simpler result

$$\frac{|\langle\chi,\theta_0\rangle|^2}{\langle\theta_0,L\theta_0\rangle} \geqslant \left\langle (H-E_0)\Psi-\chi, \left(L^{-1}-\frac{L^{-1}(H-E_0)L^{-1}}{(E_1-E_0)q^2}\right)[(H-E_0)\Psi-\chi]\right\rangle \tag{17}$$

is available from the choice $A = (H-E_0)^{1/2}$ together with the replacement of Ψ by $(H-E_0)^{1/2}\Psi$ in (9). If L^{-1} does not have a positive lower bound q^2 as in (15), it might be feasible to employ as m^2 some lower bound to the smallest positive (nonzero) eigenvalue of the operator $AL^{-1}A$.

We have assumed that the eigenvalue E_k is not degenerate; if it is, then certain adjustments are needed in accordance with (12).

The variational functional (13) is the simplest one to use, and provides a lower bound on the expectation value $\langle\theta_k, L\theta_k\rangle$ for any state θ_k. It is assumed that E_k is known, or has known bounds, and also that the squared overlap $|\langle\chi,\theta_k\rangle|^2$ is known, or has a known lower bound. Such assumptions are customary in deriving bounds on expectation values (Weinhold 1970, Wang 1971). Any of the variational functionals which furnish lower bounds on overlaps might be employed in conjunction with (13). For example, a combination of (13) and (17) with $L = 1$ leads to the bivariational quotient lower bound

$$\langle\theta_0,L\theta_0\rangle \geqslant \frac{1}{E_1-E_0}\,\frac{\langle(H-E_0)\Phi-\chi,(E_1-H)[(H-E_0)\Phi-\chi]\rangle}{\langle(H-E_0)\Psi-\chi,L^{-1}[(H-E_0)\Psi-\chi]\rangle}. \tag{18}$$

To illustrate the accuracy of (13), we calculated a lower bound on the expectation of $(r_{12})^{-1}$ for ground state helium. The amplitude-optimized, ground state version of (13), namely

$$\langle\chi,L^{-1}\chi\rangle - \frac{|\langle(H-E_0)\Psi,L^{-1}\chi\rangle|^2}{\langle(H-E_0)\Psi,L^{-1}(H-E_0)\Psi\rangle} \geqslant \frac{|\langle\chi,\theta_0\rangle|^2}{\langle\theta_0,L\theta_0\rangle}, \tag{19}$$

was used with $L^{-1} = r_{12}$, $E_0 = -2{\cdot}90372$ (atomic units), and as reference vector the minimum-energy hydrogenic function

$$\chi = \alpha^3/\pi\exp[-\alpha(r_1+r_2)], \qquad \alpha = 1{\cdot}6875, \tag{20}$$

for which Weinhold (1969) gives the lower bound

$$|\langle\chi,\theta_0\rangle|^2 \geqslant 0{\cdot}9870. \tag{21}$$

The hydrogenic trial function

$$\Psi = \exp[-\beta(r_1+r_2)], \qquad \beta = 2{\cdot}01 \text{ (optimal value)} \tag{22}$$

in (19) leads with (21) to the result

$$\left\langle \theta_0, \frac{1}{r_{12}} \theta_0 \right\rangle \geqslant \frac{|\langle \chi, \theta_0 \rangle|^2}{1\cdot 0629} \geqslant 0\cdot 9286. \tag{23}$$

The 'exact' value of Pekeris (1959) is 0·9458 and the lower bound in (23) is 98·2 % of that. Such accuracy from a one-parameter trial vector is remarkable. This result is superior to the more sophisticated calculation of Weinhold (1969) which gave a 96·7 % lower bound, and to Wang's (1971) best result (88·9 %). In turn, these latter improved on the method of Mazziotti and Parr (1970). One has to look to the work of Chong and Weinhold (1973) with 135-term trial vectors in order to find a tighter lower bound.

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