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Lower bounds to the overlap

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Abstract. A variational lower bound to the overlap of the ground state ψ_0 of a quantum mechanical system with an approximate wavefunction ϕ is given. The properties of this bound, which had been derived in a recent paper by the authors, are discussed. A simplified non-variational formula is deduced from this lower bound to $|\langle\phi|\psi_0\rangle|$. Both versions are illustrated with an application to the hydrogen atom and are compared with the lower bounds of Eckart and Wang. The non-variational version turns out to be a useful alternative to Eckart's bound.

1. Introduction

In order to bracket quantum mechanical properties (Weinhold 1972) the overlap $|S_k|=|\langle\phi|\psi_k\rangle|$ must often be estimated. Thereby $\langle\phi|\phi\rangle=\langle\psi_k|\psi_k\rangle=1$ and ϕ is an approximation to a solution ψ_k of the time-independent Schrödinger equation $H\psi_k=E_k\psi_k(E_k\leqslant E_{k+1};\ k=0,1,2,\ldots)$, H being self-adjoint. Furthermore $|S_k|$ is a measure of the accuracy achieved in an actual calculation. Therefore, bounds to the overlap are desirable. Such bounds have been reviewed by Weinhold (1970) and very recently a general theory of variational bounds to the overlap has been presented by Barnsley and Robinson (1975).

In a recent paper (Hoffmann-Ostenhof and Hoffmann-Ostenhof 1975) we derived variational lower bounds to $|S_k|^2$. Here we shall investigate properties of the bound to $|S_0|^2$ and derive a new non-variational bound to $|S_0|^2$. These bounds are illustrated by a numerical example and compared with the bounds of Eckart (1930) and Wang (1969).

2. Lower bounds to the overlap

In our recent paper (Hoffmann-Ostenhof and Hoffmann-Ostenhof 1975) we derived a closed expression for the overlap

$$|S_0|^2=\langle\phi|M_0^{-2}|\phi\rangle^{-1} \tag{1}$$

where

$$M_0=m(H-E_0)+|\phi\rangle\langle\phi| \tag{2}$$

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with $m>0$ and E_0 non-degenerate. Starting from (1), we deduced by means of an operator inequality the following variational bound

$$|S_0|^2 \geq q\left(1-\frac{|\langle\phi|M_0-qI|\chi\rangle|^2}{\langle\chi|M_0^3-qM_0^2|\chi\rangle}\right)^{-1}$$

from here on referred to as bound I. Thereby q is a lower bound to the lowest eigenvalue q_0 of M_0 such that $0<q\leq q_0$. χ is a variational function which should be chosen such that the occurring integrals exist. Equality is achieved in (3) for $\chi_{opt}=M_0^{-2}\phi$.

Since bound I, the main result of our previous paper, contains integrals over H^3 the application of this bound will be confined to simple systems. Therefore it is desirable to derive an inequality which is more appropriate for practical applications. Inserting ψ_0 in (3) for the variational function χ and taking into account $M_0\psi_0=S_0\phi$ we obtain a non-variational version of bound I

$$|S_0|^2 \geq \frac{1-q+m\langle\phi|H-E_0|\phi\rangle}{1-q+mq^{-1}\langle\phi|H-E_0|\phi\rangle} \tag{4}$$

where only integrals over H are encountered. However the determination of the parameters m and q poses the same problem as in bound I. In the following we shall refer to (4) as bound II.

3. Properties of the bounds

In this section various properties of bound I and bound II will be investigated.

3.1. *On the parameters m and q*

The quality of the bounds I and II depends upon the parameters m and q, q being restricted by $0<q\leq q_0$. A lower bound q to the lowest eigenvalue q_0 of M_0 might be determined, for instance, by the method of intermediate problems (Weinstein and Stenger 1972) or by Weinstein's formula (Weinstein 1934). However, M_0 contains the parameter m and therefore q and q_0 depend upon m.

We are now going to show that

$$\lim_{m\to\infty} q_0(m)=|S_0|^2. \tag{5}$$

The proof is very simple. Denoting m^{-1} by k and considering the operator $kM_0(k^{-1})$, the Hellmann–Feynman theorem leads to

$$\left.\frac{\mathrm{d}}{\mathrm{d}k}(kq_0(k^{-1}))\right|_{+0}=|S_0|^2.$$

On the other hand considering the difference quotient we arrive at

$$\left.\frac{\mathrm{d}}{\mathrm{d}k}(kq_0(k^{-1}))\right|_{+0}=\lim_{k\to+0} q_0(k^{-1}).$$

Since $q_0(m)$ is a monotonically increasing function

$$q_0(m)\leq|S_0|^2. \tag{6}$$

With similar considerations it can be shown that the highest eigenvalue of $M_0(-m)$ is always an upper bound to $|S_0|^2$ and approaches $|S_0|^2$ monotonically as m goes to infinity. For a related approach to bounds for expectation values see Maziotti (1971).

Now let us consider bound I as a function of q for fixed m and χ and denote it with $\sigma(q)$. One easily sees that $q \leq \sigma(q)$. Furthermore it can be shown (see appendix) that $\sigma(q)$ is a monotonically non-decreasing function. That is to say, the better q_0 is approximated by q the better will be the bound $\sigma(q)$. Apparently these considerations hold also for bound II.

Unfortunately the optimization of the bounds with respect to m for fixed χ is not straightforward, since q_0 varies simultaneously with m. The example in § 4 will illustrate the behaviour of the bounds with respect to m.

3.2. *The limiting behaviour of the bounds for $m \to +0$*

In the analysis of the limiting behaviour of the bounds I and II for $m \to +0$, it will be convenient to insert the eigenvalue $q_0(m)$ in (3). Applying the rule of De l'Hôpital we obtain

$$|S_0|^2 \geq \left(1 + \frac{\langle\phi|H - E_0|\phi\rangle}{(\mathrm{d}/\mathrm{d}m)q_0(+0)}\right)^{-1}. \tag{7}$$

With the aid of the Hellmann–Feynman theorem we conclude that

$$\frac{\mathrm{d}}{\mathrm{d}m} q_0(+0) = \inf_{\substack{\eta \\ \langle\eta|\phi\rangle = 0}} \frac{\langle\eta|H - E_0|\eta\rangle}{\langle\eta|\eta\rangle}. \tag{8}$$

Inequality (7) does not contain the variational function χ; hence bounds I and II approach the same value for decreasing m. This means for small m it will be sufficient to work with the simpler bound II. Obviously in (7) $(\mathrm{d}/\mathrm{d}m)q_0(+0)$ can be replaced by a lower bound.

3.3. *Behaviour for $\phi = \psi_0$*

If $\phi = \psi_0$ and $\chi \neq \psi_0$ then bound I becomes

$$1 \geq q\left(1 - \frac{(1-q)^2|\langle\psi_0|\chi\rangle|^2}{\langle\chi|M_0^2(M_0 - qI)|\chi\rangle}\right)^{-1}. \tag{9}$$

If $m \geq (E_1 - E_0)^{-1}$, $q_0 = 1$ and for $q = q_0$, (9) is an equality. For $\phi = \psi_0$ bound II becomes 1 for every possible q.

3.4. *Modification for unknown E_0*

The bounds I and II contain the ground state energy E_0 of H. However, this quantity is not usually known exactly. In the following it will be shown how we can involve an upper bound to E_0 instead of E_0 itself. For this purpose we consider the function $w(\epsilon)$, defined by $w(\epsilon) = \langle\phi|L(\epsilon)^{-2}|\phi\rangle$, whereby $L(\epsilon) = m(H - \epsilon) + |\phi\rangle\langle\phi|$, $m > 0$ and ϵ real. Note that $w(E_0) = |S_0|^{-2}$. It is easy to see that $w(\epsilon)$ is a monotonically increasing function for $\epsilon \geq E_0$, provided $L(\epsilon) > 0$. For given m and $\epsilon \geq E_0$ the positive-definiteness of L is guaranteed if $q_0(m) \geq m(\epsilon - E_0)$. If q meets the condition

$L(\epsilon)\geqslant qI>0$ and $\epsilon\geqslant E_0$ then

$$|S_0|^2\geqslant q\left(1-\frac{|\langle\phi|L(\epsilon)-qI|\chi\rangle|^2}{\langle\chi|L^3(\epsilon)-qL^2(\epsilon)|\chi\rangle}\right)^{-1}. \tag{10}$$

4. Numerical application and discussion

In the following, a numerical application of the bounds I and II to the ground state of the hydrogen atom will illustrate some of the properties investigated in the previous section. Furthermore, we compare the results with those obtained by applying Eckart's formula (1930)

$$|S_0|^2\geqslant\frac{E_1-\langle\phi|H|\phi\rangle}{E_1-E_0} \tag{11}$$

and Wang's bound (1969)

$$|S_0|^2\geqslant\frac{E_1-\langle\phi|H|\phi\rangle}{E_1-E_0}+\frac{|\langle\phi|(H-E_0)(H-E_1)|\chi\rangle^2}{(E_1-E_0)\langle\chi|(H-E_0)^2(H-E_1)|\chi\rangle} \tag{12}$$

to the same problem. These bounds require similar information as bounds II and I respectively (the same integrals are involved).

4.1. Numerical results

As trial functions we chose simple exponentials $e^{-\zeta r}$ with the exponents $\zeta=0{\cdot}6, 0{\cdot}7, 0{\cdot}8$ respectively. The corresponding expectation values of H are $\langle\phi|H|\phi\rangle=-0{\cdot}42$, $-0{\cdot}455$, $-0{\cdot}48$ au.

The variational function χ for bound I and Wang's bound was taken to be

$$\chi=[1+(\alpha-1)r]\,e^{-\alpha r} \tag{13}$$

in which the parameter α is to be varied. This function which has also been used by Weinhold (1970) ensures the existence of the integral $\langle\chi|H^3|\chi\rangle$.

For the lower bound $q(m)$ to the lowest eigenvalue of the operator $M_0(m)$ we took Weinstein's formula (1934)

$$q(m)=\langle\chi|M_0(m)|\chi\rangle-\Delta,\qquad \Delta^2=\langle\chi|M_0^2(m)|\chi\rangle-\langle\chi|M_0(m)|\chi\rangle^2 \tag{14}$$

which has been evaluated using function (13) also. Weinstein's formula is valid provided

$$\langle\chi|M_0(m)|\chi\rangle+\Delta<q_1 \tag{15}$$

holds; q_1 being the eigenvalue which is closest to q_0. To be sure that condition (15) is met we diagonalized a matrix representation of $M_0(m)$ in a basis of 17 Slater functions. We assume the first eigenvalues to be accurate, at least to four digits. In order to compute (7), $(d/dm)q_0(+0)$ was approximated in the same basis by diagonalizing a matrix representation of $(I-|\phi\rangle\langle\phi|)(H-E_0)(I-|\phi\rangle\langle\phi|)$.

The computed bounds are collected in table 1. The three columns of this table correspond to the three different trial functions used. The third and fourth row

Table 1.

ζ	0·6	0·7	0·8
$\lvert S_0\rvert^2$	0·82397461	0·90945364	0·96341833
Eckart	0·78666667	0·88000000	0·94666667
Wang	0·82395928	0·90945019	0·96341801
α	0·8225	0·8591	0·9032
Bound II	0·80846655	0·90118214	0·96058581
m_{II}	2·8	4·5	7·0
q	0·60393904	0·83344080	0·94627262
α_q	0·6984	0·7574	0·8316
Bound I	0·82330389	0·90929812	0·96339870
m_I	4·4	8·5	16·0
q	0·68667712	0·86554932	0·95093301
α_q	0·7458	0·8236	0·8905
α_I	0·7813	0·8414	0·8972
formula (7)	0·800	0·886	0·948

correspond to Wang's bound and the optimal α-value of the variational function χ. In the next row the computed values of bound II are given. The bound was optimized with respect to the parameter m. Furthermore for each value of m, q has been optimized by varying α in function (13). In the following three rows the optimal m-value m_{II}, the corresponding Weinstein bound q and the optimal α-value α_q are presented. In an analogous way the values for bound I in the next row have been determined. The values of α_I emerged from the final optimization of formula (3) with respect to χ. The last row presents an approximation to inequality (7). Since it turned out that the bounds I and II were slowly varying functions of m, we determined this parameter only to one decimal place. In all cases the parameter α in the variational function was calculated to four decimal places.

Figure 1 demonstrates the m-dependence of bound II and of q. Curve A corresponds to $q(m)$ and curve B to bound II. The third curve C represents an approximation to $q_0(m)$. The curves in figure 1 refer to the trial function, with $\zeta = 0·6$. For the other trial functions similar curves were obtained.

4.2. *Discussion of the results*

In table 1, Wang's bound exceeds bound I. The following relation explains partly the observed superiority of Wang's bound. Inserting $\chi_{\text{opt}} = M_0(m)^{-2}\phi$ into (12), equality is achieved for every $m \neq 0$. This can be verified using the identity

$$(H-E_0)\chi_{\text{opt}} = m^{-1}(S_0^{-1}\psi_0 - |S_0|^{-2}\phi).$$

However this does not imply that Wang's bound always exceeds bound I. For example with $\zeta = 0·7$, $m = 4$, $q = 0·8192$ and $\alpha_I = 1·2$ bound I gives 0·9084 compared with 0·9054 from Wang's formula with the same χ.

As demonstrated in figure 1, bound II exceeds Eckart's bound for small m. This can be an advantage since it will be difficult to obtain accurate lower bounds to $q_0(m)$ for

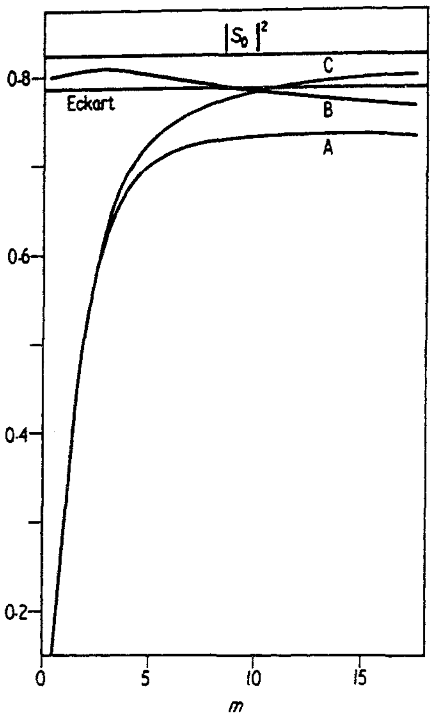

Figure 1. The m-dependence of bound II and q. A, $q(m)$; B, bound II; C, approximation to $q_0(m)$.

large m. For very small m condition (15) could not be fulfilled with our special function (13). However, formula (7) leads to bounds comparable with the corresponding Eckart values.

Let us finally compare bound I and bound II. In the example chosen, bound I always exceeds bound II, reflecting the fact that χ equals ψ_0 for $\alpha = 1$. In general this will not be the case. Hence there will be cases where the simpler bound II will supply a better approximation to $|S_0|^2$ than bound I does.

5. Concluding remarks

In bound I only the ground state energy E_0 occurs, whereas to our knowledge in other variational lower bounds to $|S_0|^2$, E_0 and E_1 must be known (eg Weinhold 1970, Barnsley and Robinson 1975). If, in Wang's bound, E_1 is not known, it must be replaced by some $\epsilon_1 \leq E_1$ and equality can no longer be achieved. In such cases it will be reasonable to apply bound I, since equality can be achieved for every q with $0<q\leq q_0$, at least in principle.

However, the most promising result of this investigation appears to be bound II because of its simplicity. Based on our results we believe that bound II will be, in many situations, a useful alternative to Eckart's bound if the evaluation of some accurate lower bound to $q_0(m)$ is not too difficult.

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Appendix

It will be shown that

$$\sigma(q)=q\left(1-\frac{|\langle\phi|M_0-qI|\chi\rangle|^2}{\langle\chi|M_0^3-qM_0^2|\chi\rangle}\right)^{-1}$$

is a monotonically non-decreasing function for $0<q\leqslant q_0$.

We shall use the abbreviations

$$a_1=\langle\chi|M_0^2|\chi\rangle,\qquad a_2=\langle\chi|M_0^3|\chi\rangle,\qquad a_3=2\,\mathrm{Re}(\langle\phi|\chi\rangle\langle\chi|M_0|\phi\rangle),$$

$$a_4=|\langle\chi|\phi\rangle|^2\quad\text{and}\quad a_5=|\langle\chi|M_0|\phi\rangle|^2.$$

The first derivative of $\sigma(q)$ exists for $0<q\leqslant q_0$ and can be written as

$$\frac{\mathrm{d}}{\mathrm{d}q}\sigma(q)=D(q)N(q)^{-2}$$

where

$$D(q)=(a_2a_4-a_1a_3+a_1^2)q^2-2a_1(a_2-a_5)q+a_2(a_2-a_5)$$

and

$$N(q)=-a_4q^2+(a_3-a_1)q+(a_2-a_5).$$

Considering the extremum (q^*, D^*) of the polynomial $D(q)$ it can be easily seen that $D^*=(a_2-a_5)bc^{-1}$, where $b=a_2^2a_4-a_1a_2a_3+a_1^2a_5$ and $c=a_2a_4-a_1a_3+a_1^2$. The replacement of a_3 by its absolute value implies $b\geqslant 0$. Since $a_2\geqslant a_5\geqslant 0$ and $a_2c\geqslant b$, $c\geqslant 0$ follows. Therefore $D(q)$ has a minimum with $D^*\geqslant 0$. Thus $(\mathrm{d}/\mathrm{d}q)\sigma(q)\geqslant 0$ for $0<q\leqslant q_0$.

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