

Upper bound to the expectation value of the squared Hamiltonian

M.G. Marmorino

Department of Chemistry, Indiana University South Bend, South Bend, IN 46634, USA
E-mail: mmarmorini@iusb.edu

Received 7 July 2003

An upper bound to the expectation value of the squared Hamiltonian $\langle H^2 \rangle$ is derived which relies on replacing products of certain operators with products of the matrix representations of said operators to reduce the computational demands of $\langle H^2 \rangle$. An example is given which shows the strength of the bound and an application with the Temple lower bound is shown.

KEY WORDS: Hamiltonian, lower bounds, moments

1. Introduction

Calculation of rigorous upper bounds using the variational method is straightforward. Rigorous lower bound calculations, however, are plagued with many difficulties, both theoretical and calculational. There exist many different lower bound methods [1] and each has their own unique problems and areas where they excel; unfortunately, there does not currently exist a method that is widely practical. One problem that is shared by many lower bound methods is the calculation of difficult integrals that make up the expectation value $\langle H^2 \rangle$, i.e., of the squared Hamiltonian. Variational calculations, on the other hand, require only the much simpler calculation of $\langle H \rangle$. Some perturbative methods [2–4] and variational methods [5] require the calculation of $\langle H^3 \rangle$ and even more difficult integrals. The ideas presented here for $\langle H^2 \rangle$ can be extended to $\langle H^3 \rangle$ and more complicated expectation values.

Because of the difficulty in the calculation of $\langle H^2 \rangle$, bounds to this value are highly desirable. A simple lower bound is $\langle H \rangle^2$, which results from the Cauchy–Schwarz inequality; however, eigenvalue lower bound methods require an upper bound to $\langle H^2 \rangle$. Two “relatively” widely-used lower bound formula are the Temple [6] and Weinstein [7] bounds. The Temple bound takes a trial function and gives a lower bound to the ground-state eigenvalue, E_1 , when a lower bound, E_2^{low} , to the first-excited state eigenvalue, E_2 , is already known:

$$E_1 \geq \frac{E_2^{\text{low}} \langle H \rangle - \langle H^2 \rangle}{E_2^{\text{low}} - \langle H \rangle}. \quad (1)$$

The Weinstein bound produces an interval in which there lies at least one eigenvalue:

$$|E_n - \langle H \rangle| \leq (\langle H^2 \rangle - \langle H \rangle^2)^{1/2}. \quad (2)$$

Both bounds require calculation of $\langle H^2 \rangle$ or an upper bound to this value. Even in the relatively simple system of the lithium atom, extensive background work [8–10] devoted to analytically solving the integrals composing $\langle H^2 \rangle$ was necessary before actual lower bounds could be calculated [11,12]. One option to analytic solution of the integrals is numerical methods, such as Monte Carlo methods, which have proved very successful in some applications [5].

2. Simple case for $\langle H^2 \rangle$

We now present an upper bound to $\langle H^2 \rangle$ which eliminates some, but not all, of the difficult integrals required in the calculation of $\langle H^2 \rangle$. We consider H to be the Hamiltonian of interest (with eigenvalues E_n and eigenfunctions ψ_n) while h is an exactly soluble base Hamiltonian that is perturbed by the perturbation p to become H :

$$H = h + p. \quad (3)$$

The base Hamiltonian h (with eigenvalues e_n and eigenfunctions f_n) is often a simple Hamiltonian; in the case of atoms, it may be the sum of the one-electron kinetic energy operators and the nuclear–electron attraction operators. The perturbation p would then be the electron–electron repulsion operators.

We first evaluate $\langle H^2 \rangle$ using the decomposition $H = h + p$ and one of the eigenfunctions f_n of h (with eigenvalue e_n):

$$\begin{aligned} \langle f_n | H^2 | f_n \rangle &= \langle f_n | (h + p)^2 | f_n \rangle \\ &= \langle f_n | h^2 + hp + ph + p^2 | f_n \rangle \\ &= e_n^2 + 2e_n \langle f_n | p | f_n \rangle + \langle f_n | p^2 | f_n \rangle. \end{aligned} \quad (4)$$

For this special case of f_n , integrals of h^2 and hp are completely avoided. Although $\langle H^2 \rangle$ can be calculated rather easily, the goal is to use $\langle H^2 \rangle$ in, say, the Temple formula to get a lower bound to E_1 . In this case f_1 is usually a poor approximation to ψ_1 unless the perturbation p is very small, and the lower bound to E_1 will be poor as well. Even more important is that the solution to a base Hamiltonian is usually not known. For atomic systems, two reasonable exactly-soluble base Hamiltonians [13,14] are known while for molecules only the unreasonable united-atom base Hamiltonian is known. To get a good lower bound to E_1 we must use a trial function that well approximates ψ_1 . This will usually be a variationally-determined function instead of the ground-state eigenfunction of a base problem. If the variational space is a subset of the base-Hamiltonian's eigenspace then the variationally-determined function will be a linear combination of base Hamiltonian eigenfunctions; although (4) gets more complicated, one still avoids the basic

integrals of h^2 and hp . Often a subset of the base Hamiltonian's eigenspace is inadequate as a variational space and a different variational space must be used. In this case a trial function that is not a linear combination of base Hamiltonian eigenfunctions results and (4) does not simplify fully and expectation values of h^2 and hp must be calculated.

3. Upper bound to $\langle H^2 \rangle$

We now use an alternate decomposition of H :

$$H = \eta + \pi, \quad \text{where } \eta = h + PpP \text{ and } \pi = p - PpP, \quad (5)$$

where the operator P is the projection onto the subspace \mathbf{S} formed from a variational basis set. We no longer require h to be exactly soluble. This alternate base Hamiltonian η , when restricted to the variational subspace \mathbf{S} to become $\eta|_{\mathbf{S}}$, is recognized to be the matrix representation of H on \mathbf{S} . Thus the eigenvalues and eigenfunctions of $\eta|_{\mathbf{S}}$ are those of the variational calculation, $\eta|_{\mathbf{S}}\phi_n = \varepsilon_n\phi_n$, although $\eta\phi_n$ produces a function that may partially exist outside of \mathbf{S} . Again we evaluate $\langle H^2 \rangle$, but this time using the decomposition $H = \eta + \pi$.

$$\begin{aligned} \langle \phi_n | H^2 | \phi_n \rangle &= \langle \phi_n | (\eta + \pi)^2 | \phi_n \rangle \\ &= \langle \phi_n | \eta^2 + \eta\pi + \pi\eta + \pi^2 | \phi_n \rangle \\ &= \langle \phi_n | \eta^2 | \phi_n \rangle + 2\langle \phi_n | \eta\pi | \phi_n \rangle + \langle \phi_n | \pi^2 | \phi_n \rangle. \end{aligned} \quad (6)$$

The first and third terms on the right-hand side expand to give:

$$\begin{aligned} \langle \phi_n | \eta^2 | \phi_n \rangle &= \langle \phi_n | (h + PpP)^2 | \phi_n \rangle \\ &= \langle \phi_n | h^2 + h(PpP) + (PpP)h + (PpP)^2 | \phi_n \rangle \\ &= \langle \phi_n | h^2 | \phi_n \rangle + 2\langle \phi_n | (PhP)(PpP) | \phi_n \rangle + \langle \phi_n | (PpP)^2 | \phi_n \rangle, \end{aligned} \quad (7)$$

$$\begin{aligned} \langle \phi_n | \pi^2 | \phi_n \rangle &= \langle \phi_n | (p - PpP)^2 | \phi_n \rangle \\ &= \langle \phi_n | p^2 - 2p(PpP) + (PpP)^2 | \phi_n \rangle \\ &= \langle \phi_n | p^2 - (PpP)^2 | \phi_n \rangle. \end{aligned} \quad (8)$$

The middle term of (6) requires a bit more work. Although $\eta|_{\mathbf{S}}\phi_n = \varepsilon_n\phi_n$, we have $\eta\phi_n = \varepsilon_n\phi_n + \phi^\perp$ where ϕ^\perp is a function orthogonal to \mathbf{S} . Thus the middle term expands to give:

$$\langle \phi_n | \eta\pi | \phi_n \rangle = \langle \eta\phi_n | \pi | \phi_n \rangle = \langle \varepsilon_n\phi_n + \phi^\perp | \pi | \phi_n \rangle = \varepsilon_n\langle \phi_n | \pi | \phi_n \rangle + \langle \phi^\perp | \pi | \phi_n \rangle. \quad (9)$$

Since $\pi = p - PpP$ and $\phi_n \in \mathbf{S}$, we have that $\langle \phi_n | \pi | \phi_n \rangle = 0$ which simplifies (9) to

$$\langle \phi_n | \eta\pi | \phi_n \rangle = \langle \phi^\perp | \pi | \phi_n \rangle. \quad (10)$$

Using the Cauchy–Schwarz inequality we can bound the term $\langle \phi^\perp | \pi | \phi_n \rangle$ as follows:

$$|\langle \phi^\perp | \pi | \phi_n \rangle| \leq \langle \phi^\perp | \phi^\perp \rangle^{1/2} \langle \phi_n | \pi^2 | \phi_n \rangle^{1/2}. \quad (11)$$

The value $\langle \phi^\perp | \phi^\perp \rangle$ can be determined from

$$\langle \phi_n | \eta^2 | \phi_n \rangle = \langle \eta \phi_n | \eta \phi_n \rangle = \langle \varepsilon_n \phi_n + \phi^\perp | \varepsilon_n \phi_n + \phi^\perp \rangle = \varepsilon_n^2 + \langle \phi^\perp | \phi^\perp \rangle \quad (12)$$

so that

$$\langle \phi^\perp | \phi^\perp \rangle = \langle \phi_n | \eta^2 | \phi_n \rangle - \varepsilon_n^2. \quad (13)$$

Inequality (11) and equation (13) are combined and used in (10) to provide an upper bound to $\langle \phi_n | \eta \pi | \phi_n \rangle$. This is then used in (6) to give an upper bound to $\langle H^2 \rangle$:

$$\langle H^2 \rangle \leq \langle \eta^2 \rangle + 2(\langle \eta^2 \rangle - \langle H \rangle^2)^{1/2} \langle \pi^2 \rangle^{1/2} + \langle \pi^2 \rangle, \quad (14)$$

$$\langle \eta^2 \rangle = \langle h^2 \rangle + 2\langle (PhP)(PpP) \rangle + \langle (PpP)^2 \rangle, \quad (7)$$

$$\langle \pi^2 \rangle = \langle p^2 \rangle - \langle (PpP)^2 \rangle, \quad (8)$$

where we have used $\langle H \rangle = \varepsilon_n$ and all expectation values are evaluated using ϕ_n . Expectation values of h^2 and p^2 are not avoided, as they occur indirectly through (7) and (8), but expectation values of hp are replaced with expectation values of $(PhP)(PpP)$ which are products of the matrix-representations of h and p on the chosen basis set. These matrices have already been constructed from the upper bound calculation (or at worst, all the integrals have been computed in the case that the matrices are not stored in memory). The operator $(PhP)(PpP)$ is just the product of two matrices. Similarly, the operator $(PpP)^2$ is just the square of the matrix PpP .

4. Numerical example

To illustrate the quality of the bound we consider the isotropic harmonic oscillator:

$$H = \frac{1}{2}(-\Delta + r^2), \quad (15)$$

where Δ is the Laplacian and atomic units are used. The simplest decomposition of the Hamiltonian is: $h = -1/2\Delta$ and $p = 1/2r^2$ which then defines η and π . The basis set for the calculations is the following set of $N + 1$ functions:

$$\phi_n = \sqrt{n!(n+2)!} e^{-r/2} \sum_{k=0}^n \frac{(-r)^k}{k!(k+2)!(n-k)!}, \quad (16)$$

where $n = 0, 1, 2, \dots, N$. This basis set is a truncated complete set; being built of exponentials it will need a large number of functions to approximate the $\exp(-r^2)$ behavior of the true eigenfunctions of H . Table 1 shows $\langle H \rangle$, $\langle H^2 \rangle$ and the upper bound to $\langle H^2 \rangle$ as a function of the size of the variational calculation, N . Also reported is the percent difference between the upper bound and exact value of $\langle H^2 \rangle$. Figure 1 plots the percent difference vs. N . Although our bound on $\langle H^2 \rangle$ is poor for most low N (there are a few exceptions in the data) this is where $\langle H^2 \rangle$ is not so difficult to calculate. As the dimension of the basis set increases then $\langle H^2 \rangle$ becomes more computationally expensive and thus a bound to $\langle H^2 \rangle$ is more important. This is where our bound is best – at large N .

Table 1
The upper bound and exact value of $\langle H^2 \rangle$ are calculated for different size calculations.
Atomic units are used.

N	$\langle H^2 \rangle$	Upper bound to $\langle H^2 \rangle$	Percent difference (%)	$\langle H \rangle$
0	90.0781	95.2524	5.7	6.12500
5	4.4314	5.59359	26	1.80415
10	5.21508	5.53359	6.1	1.52428
15	2.69785	3.00818	12	1.50629
20	2.53278	2.57952	1.8	1.50084
25	2.28865	2.31841	1.3	1.50029
30	2.28639	2.28945	0.13	1.50006

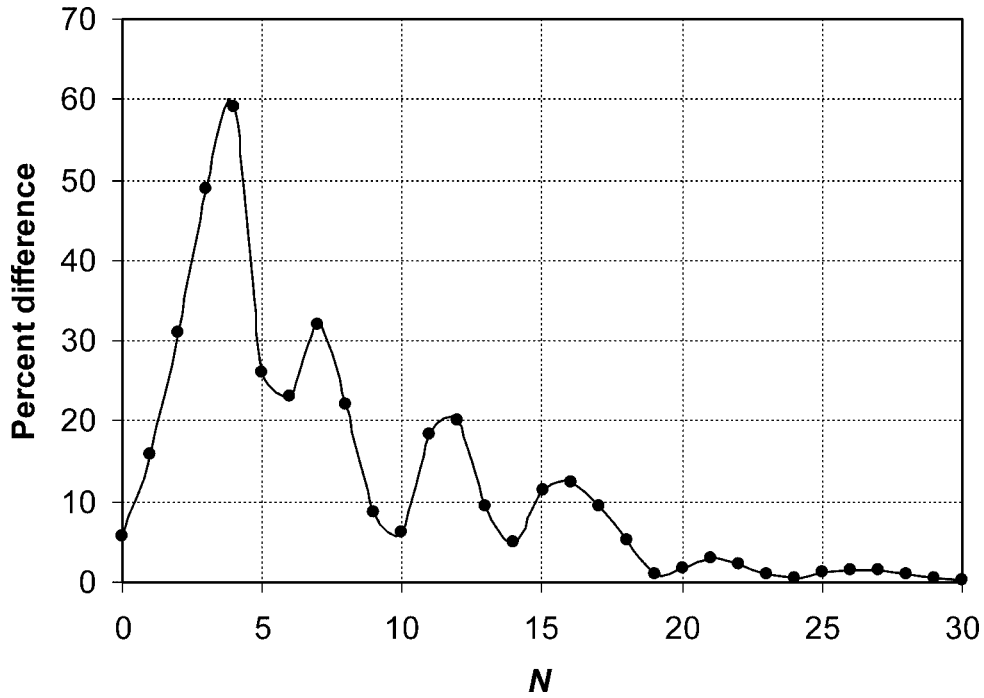


Figure 1. The percent difference between the upper bound and exact value of $\langle H^2 \rangle$ is plotted versus N .

This behavior of the bound is suggested, not only by our numerical example, but by an examination of the difference between the upper bound (14) and the true value of $\langle H^2 \rangle$, which is:

$$\langle H^2 \rangle^{\text{up}} - \langle H^2 \rangle = 2(\langle \eta^2 \rangle - \langle H \rangle^2)^{1/2} \langle \pi^2 \rangle^{1/2}. \quad (17)$$

As the variational subspace increases $\langle \eta^2 \rangle$ approaches E_1^2 while $\langle H \rangle$ approaches E_1 so that the term $\langle \eta^2 \rangle - \langle H \rangle^2$ approaches zero. Furthermore $\langle \pi^2 \rangle = \langle p^2 \rangle - \langle (PpP)^2 \rangle$ approaches zero since, as the variational subspace increases, PpP approaches p . Thus the right-hand side of (17) is the product of two terms that are approaching zero.

Table 2

The upper bound and exact value of $\langle H^2 \rangle$ are calculated for different size calculations. Atomic units are used.

N	Our lower bound	Temple lower bound	Percent difference (%)	Variational upper bound
0	NA	NA	NA	6.12500
5	0.04230	0.66077	94	1.80415
10	-0.10052	0.06069	270	1.52428
15	1.13548	1.29114	12	1.50629
20	1.33726	1.36064	1.7	1.50084
25	1.46652	1.48140	1.0	1.50029
30	1.48042	1.48196	0.10	1.50006

5. Application to Temple lower bound

In table 2 we compare the lower bound to $E_1 = 1.5$ hartree for the isotropic harmonic oscillator of section 4 calculated using the Temple lower bound (2) with the exact value of $\langle H^2 \rangle$ and with our upper bound to $\langle H^2 \rangle$. We use the exact value $E_2 = 3.5$ hartree for E_2^{low} in (2). When $N = 0$, the variational upper bound exceeds E_2 so that the Temple lower bound cannot be used: $\langle H \rangle < E_2$ is necessary. The difference between the lower bounds generally decreases as the dimension of the variational subspace increases as expected since the difference between the exact value of $\langle H^2 \rangle$ and the upper bound follows the same pattern.

6. Summary

We have proposed an upper bound to $\langle H^2 \rangle$ which lessens the computational demands of $\langle H^2 \rangle$, although is unfortunate that the quality of the bound is not *guaranteed* to improve as more computational effort is expended. The bound requires separation of H into two components. The simplest decomposition is to group all of the differential operators (i.e., the kinetic energy operator) into h and all the multiplicative operators (i.e., potential energy operator) into p as was done in section 4. This requires the need to calculate integrals like $\langle h^2 \rangle$ and $\langle p^2 \rangle$ but not $\langle hp \rangle$ which combines the differential and multiplicative operators together. Our upper bound replaces $\langle H^2 \rangle$ in an application of the Temple lower bound and the resulting bound was competitive with the Temple bound.

References

- [1] M.G. Marmorino, J. Math. Chem. 32 (2002) 19.
- [2] J. Cioslowski, Phys. Rev. Lett. 58 (1987) 83.
- [3] P.R. Surján and Á. Szabados, Int. J. Quantum Chem. 90 (2002) 20.
- [4] J.D. Mancini, Y. Zhou and P.F. Meier, Int. J. Quantum Chem. 50 (1994) 101.
- [5] H. Huang, Q. Xie, Z. Cao, Z. Li, Z. Yue and L. Ming, J. Chem. Phys. 110 (1999) 3703.
- [6] G. Temple, Proc. Roy. Soc. Ser. A 119 (1928) 276.

- [7] D.H. Weinstein, Proc. Nat. Acad. Sci. U.S. 20 (1934) 529.
- [8] F.W. King, K.J. Dykema and A.D. Lund, Phys. Rev. A 46 (1992) 5406.
- [9] F.W. King, Phys. Rev. A 44 (1991) 7108.
- [10] A. Luchow and H. Kleindienst, Int. J. Quantum Chem. 45 (1993) 445.
- [11] F.W. King, J. Chem. Phys. 102 (1995) 8053.
- [12] A. Luchow and H. Kleindienst, Int. J. Quantum Chem. 51 (1994) 211.
- [13] D.M. Russell and W.M. Greenlee, in: *Numerical Treatment of Eigenvalue Problems*, Vol. 3, International Series on Numerical Mathematics, Vol. 69 (1983) p. 89.
- [14] M.G. Marmorino, J. Math. Chem. 27 (2000) 31.