*Journal of Mathematical Chemistry Vol. 31, No. 2, February 2002 (© 2002)*

# Equivalence of two lower bound methods

M.G. Marmorino *

*Department of Chemistry, Faculty of Science, Ubon Ratchathani University, Warinchamrap, Ubon Ratchathani 34190, Thailand*
E-mail: marmorinom@berea.edu

Received 5 October 2001; revised 29 January 2002

Two lower bound methods are compared: the inverse method and a generalized variance method. As the generalized variance method is a generalization of the simple method of variance, the inverse method is shown to be a generalization of the Temple formula. We show that for the same *a priori* information and basis set, the generalized variance and inverse methods are equivalent.

**KEY WORDS:** lower bounds, Temple bound, variance minimization

## 1. Introduction

Lower bound calculation is an extremely important part of quantum mechanical eigenvalue determination to ensure that an atomic or molecular energy is accurate by complementing an upper bound calculation. Unfortunately, lower bounds receive little attention in practice because they are much more difficult to calculate than upper bounds. For references of different types of lower bound calculations see the work of Porras et al. [1]. We review two lower bound methods, the inverse method and a generalized variance method, which can be formulated to use identical information. Comparison reveals the methods yield identical lower bounds. We consider only lower bounds to the ground-state energy but the results are easily extended to excited-state bounds as well.

## 2. The inverse method and the Temple formula

The first method of interest is the inverse method used by Scrinzi [2] which is similar to the inverse method for matrices. An upper bound $\mu$ to the ground-state energy is needed which is also a lower bound to the first excited-state energy: $E_2 > \mu > E_1$. A new operator $H' = H - \mu$ is then formed by subtracting $\mu$ from the original Hamiltonian $H$. $E_1 - \mu$ is the only negative eigenvalue of $H'$. When $H'$ is inverted, creating yet another operator $H'' = (H')^{-1} = (H - \mu)^{-1}$, its lowest eigenvalue is $\gamma_1 = (E_1 - \mu)^{-1}$.

* Current address: CPO 2027, Department of Chemistry, Berea College, Berea, KY 40404, USA.

An upper bound $\gamma$ to $\gamma_1$ can be variationally determined and leads to a lower bound to $E_1$. The problem to be solved is the generalized matrix-eigenvalue problem or minimization problem:

$$\gamma = \min_{\chi \in \text{basis set}} \frac{\langle H' \rangle}{\langle (H')^2 \rangle} \geqslant \gamma_1 = (E_1 - \mu)^{-1} \tag{1}$$

which results from writing $\psi = H'\chi$ for $\chi \in$ basis set in the following Schrödinger equation [2]:

$$H''\psi = \gamma\psi. \tag{2}$$

Note that if the minimization in (1) fails to give a negative eigenvalue, then a lower bound to $E_1$ will not result. The lower bound is:

$$E_1 \geqslant \mu + \gamma^{-1}. \tag{3}$$

The inverse method can be considered a generalization of the Temple formula [3]:

$$E_1 \geqslant \frac{E_1\langle H \rangle - \langle H^2 \rangle}{E_2 - \langle H \rangle} \tag{4}$$

although the resemblance is not at all obvious. The Temple formula (4) is derived using the nonnegativity of the operator $(H - E_1)(H - E_2)$. It is straightforward to show that similar lower bound formulae can be derived using the nonnegativity of $(H-E_1)(H-\mu)$ where $E_1 < \mu < E_2$ [4]. Given a trial function $\psi$ we have:

$$E_1\big(\mu - \langle H \rangle\big) \geqslant \mu\langle H \rangle - \big\langle H^2 \big\rangle. \tag{5}$$

If the trial function is of such quality that $\langle H \rangle < \mu$, then:

$$E_1 \geqslant \frac{\langle H^2 \rangle - \mu\langle H \rangle}{\langle H \rangle - \mu}. \tag{6}$$

Algebraic manipulation shows that this is equivalent to

$$E_1 \geqslant \mu + \left[ \frac{\langle H - \mu \rangle}{\langle (H - \mu)^2 \rangle} \right]^{-1} \tag{7}$$

so that the quantity in the bracket can relate to $\gamma$ in (3) and the $\mu$ used here is the same as that in the inverse method. Because $\gamma$ in (3) results from a minimization while its counterpart in (7) is from one specific function, (3) provides a bound better than (7), or at worst, an equal bound.

## 3. The variance methods

The second method of interest is based on the variance. The variance, $\Delta H = \langle H^2 \rangle - \langle H \rangle^2$, is used in the method of variance minimization to provide an alternative to the standard variational method for calculating electronic wavefunctions by minimizing

$\Delta H$ instead of $\langle H \rangle$. The square root of the variance provides an error margin around $\langle H \rangle$ which contains at least one eigenvalue, $E_m$, of the Hamiltonian:

$$E_m \in \left[ \langle H \rangle - (\Delta H)^{1/2}, \langle H \rangle + (\Delta H)^{1/2} \right]. \tag{8}$$

If it can be established that there is only one eigenvalue in this range, then the bracket provides both upper and lower bounds to that eigenvalue. Thus *a priori* knowledge of a lower bound to $E_{m+1}$ and upper bound to $E_{m-1}$ must be available to ensure that the bound (8) contains only $E_m$. A typical application is to minimize $\langle H \rangle$ variationally until it is well below $E_2$ and then to determine the variance and a lower bound to $E_1$ using the variationally-determined wavefunction [5].

To facilitate comparison with the inverse method, we assume that we have an upper bound to $E_1$ below $E_2$, call it $\varepsilon$, which is comparable to $\mu$ in the inverse method. We do not require $\varepsilon$ to be the eigenvalue of an approximate eigenfunction since we do not use such a function to compute the variance; rather we calculate a variance-like quantity $\lambda$ by minimizing the expectation value of the operator $K = (H - \varepsilon)^2$ within the same basis set used for the inverse method. The lowest eigenvalue $\lambda_1$ of $K$ is equal to $(E_n - \varepsilon)^2$ for some eigenvalue $E_n$ of $H$. This gives the minimization problem:

$$\lambda = \min_{\chi \in \text{basis set}} \left\langle (H - \varepsilon)^2 \right\rangle \geqslant \lambda_1 = (E_n - \varepsilon)^2 \geqslant 0. \tag{9}$$

Using the quadratic formula we find that

$$E_n \in \left[ \varepsilon - \lambda^{1/2}, \varepsilon + \lambda^{1/2} \right]. \tag{10}$$

Only if $\varepsilon + \lambda^{1/2} < E_2$ will $E_n$ necessarily be $E_1$. Equation (10) looks very similar to that of the method of variance minimization (8). To compare the method of variance minimization with this generalized method, we let $\varepsilon = \langle \psi_H | H | \psi_H \rangle$ where $\psi_H$ is that function determined variationally using $H$. With this definition of $\varepsilon$ the two lower bounds are:

- Generalized variance method: $\varepsilon - \lambda^{1/2}$. (11)
- Method of variance minimization: $\varepsilon - (\langle \psi_H | H^2 | \psi_H \rangle - \varepsilon^2)^{1/2}$. (12)

The term in the square root determines which bound is superior. By the minimization in (9) it is clear that:

$$\left\langle \psi_H \middle| H^2 \middle| \psi_H \right\rangle - \varepsilon^2 = \left\langle \psi_H \middle| (H - \varepsilon)^2 \middle| \psi_H \right\rangle \geqslant \lambda \tag{13}$$

which implies that the generalized variance method is superior or, at least, not inferior.

$K$ is not the only operator that can be used in this manner. Indeed any function of the Hamiltonian, $f(H)$, is suitable provided it has a local minimum closest to the eigenstate of interest (the state of $H$ with eigenvalue $E_n$). A local minimum is sometime dangerous to work with since wide variation of the variable parameters in the trial function might force the eigenvalue out of the local well. It is safer to work with an $f(H)$

which has a global minimum closest to the eigenstate of interest. Two other possible operators which both have a global minimum at $\varepsilon$ (let $\varepsilon$ be a close estimate of $E_m$) are:

$$K^{(2)} = \frac{1}{4}H^4 - \varepsilon^3 H,$$
$$K^{(3)} = \frac{1}{4}H^4 - \varepsilon H^3 + \frac{3}{2}\varepsilon^2 H^2 - \varepsilon^3 H. \tag{14}$$

Lower bounds using operators in (14) have been tested and seem to be worse than $K$ so we discuss them no further; however, many other possibilities still exist.

## 4. Comparison

The following example illustrates the two methods. We take our Hamiltonian as the one-dimensional particle-in-a-box problem with walls at $x = 0$ and $x = \pi$ with a perturbation $x/2$. The $N$-dimensional basis set is the ($N = 10$) lowest eigenfunctions of the particle-in-a-box problem without the perturbation. Table 1 shows that as $\varepsilon$ (for the generalized variance method) and $\mu$ (for the inverse method) are varied from 1.25 to 2 hartree, the lower bound to the ground state energy ($E_1 = 1.232950148$ hartree) from the generalized variance method is superior to that from the inverse method. When $\varepsilon$ is larger than 2 hartree the generalized variance method cannot be used to generate a lower bound because the interval $\varepsilon \pm \lambda^{1/2}$ contains the first excited state ($E_2 = 2.80037459$

Table 1
The lower bound ($\mu + \gamma^{-1}$) from the inverse method is calculated from $\mu$. The bottom ($\varepsilon - \lambda^{1/2}$) and top ($\varepsilon + \lambda^{1/2}$) of the interval from the generalized variance method is calculated from $\varepsilon$. The bottom of the interval is a lower bound to $E_1$ only when the top of the interval is less than $E_2$. All units are hartree.

| $\mu$ | $\mu + \gamma^{-1}$ | $\varepsilon$ | $\varepsilon - \lambda^{1/2}$ | $\varepsilon + \lambda^{1/2}$ |
|---|---|---|---|---|
| 1.25 | 1.2328723 | 1.25 | 1.2329113 | 1.3 |
| 1.3 | 1.2329303 | 1.3 | 1.2329402 | 1.4 |
| 1.4 | 1.2329422 | 1.4 | 1.2329461 | 1.6 |
| 1.5 | 1.2329451 | 1.5 | 1.2329476 | 1.8 |
| 1.6 | 1.2329465 | 1.6 | 1.2329483 | 2.0 |
| 1.7 | 1.2329473 | 1.7 | 1.2329487 | 2.2 |
| 1.8 | 1.2329478 | 1.8 | 1.2329489 | 2.4 |
| 1.9 | 1.2329481 | 1.9 | 1.2329491 | 2.6 |
| 2.0 | 1.2329484 | 2.0 | **1.2329493** | 2.8 ($<E_2$) |
| 2.1 | 1.2329486 | 2.1 | 1.4 | 2.8 ($>E_2$) |
| 2.2 | 1.2329487 | 2.2 | 1.6 | 2.8 ($>E_2$) |
| 2.3 | 1.2329489 | 2.3 | 1.8 | 2.8 ($>E_2$) |
| 2.4 | 1.2329490 | 2.4 | 2.0 | 2.8 ($>E_2$) |
| 2.5 | 1.2329491 | 2.5 | 2.2 | 2.8 ($>E_2$) |
| 2.6 | 1.2329491 | 2.6 | 2.4 | 2.8 ($>E_2$) |
| 2.7 | 1.2329492 | 2.7 | 2.6 | 2.8 ($>E_2$) |
| 2.8 | **1.2329493** | 2.8 | 2.8 | 2.8 ($>E_2$) |

hartree). However, the inverse method can still be used and as $\mu$ increases the best lower bound by the inverse method eventually equals the best lower bound by the generalized variance method.

The parameter $\varepsilon$ in the generalized variance method, while necessary, is not key. The key point to whether a bound from the generalized variance method is applicable is whether $\varepsilon + \lambda^{1/2}$ is less than $E_2$. Thus it is reasonable compare lower bounds to $E_1$ from both methods when $\varepsilon + \lambda^{1/2}$ and $\mu$ are equal. Take the points $(\mu, \mu + \gamma^{-1})$ as an $(E_2, E_1)$-lower bound data set. Also take the calculated points $(\varepsilon + \lambda^{1/2}, \varepsilon - \lambda^{1/2})$ as an $(E_2, E_1)$-lower bound data set. When the two data sets are united and plotted, as in figure 1, the result is a single curve; it appears that the generalized variance and inverse method are the same method, but in different form.

## 5. Equivalence of the generalized variance and inverse methods

We assume that $\varepsilon + \lambda^{1/2}$ of the generalized variance method equals $\mu$ of the inverse method. Then the two methods use exactly the same information: the same lower bound to $E_2$, the same fundamental operators $H^2$ and $H$, and the same basis set. We now show that the resulting lower bounds to $E_1$ are, in fact, the same. Thus our goal is to prove:

$$\mu + \gamma^{-1} = \varepsilon - \lambda^{1/2}. \tag{15}$$

Since $\mu = \varepsilon + \lambda^{1/2}$ we can rewrite our goal as:

$$\mu + \gamma^{-1} = \mu - 2\lambda^{1/2}. \tag{16}$$

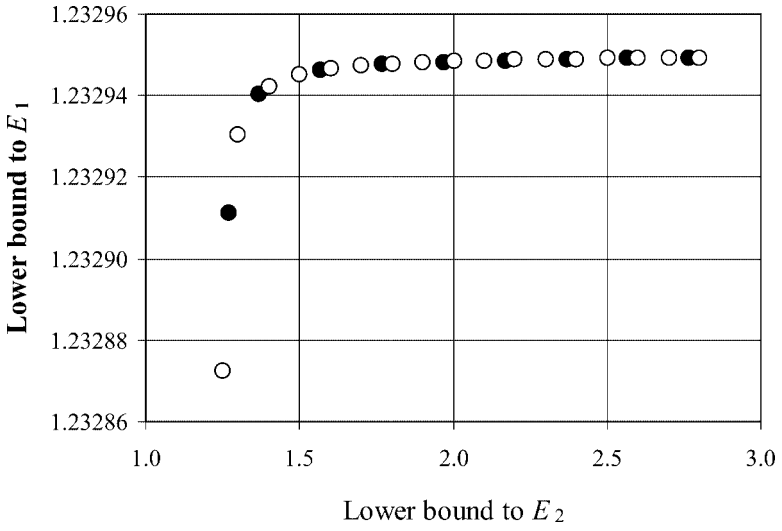


Figure 1. A plot of the combined data sets $(\mu, \mu+\gamma^{-1})$ and $(\varepsilon+\lambda^{1/2}, \varepsilon-\lambda^{1/2})$ as empty and filled circles, respectively. The two data sets form a single curve. All units are hartree.

In the following we denote expectation values using the function determined in the minimization in the generalized variance method by $\langle\,\rangle_{\rm var}$ and those from the function determined in the minimization in the inverse method by $\langle\,\rangle_{\rm inv}$. We begin by proving the first half of equality (16): $\mu+\gamma^{-1}\leqslant\mu-2\lambda^{1/2}$.

Starting only with the definition of $\lambda$ we have:

$$\left\langle(H-\mu)^2-\mu^2+\varepsilon^2+2H(\mu-\varepsilon)\right\rangle_{\rm inv}=\left\langle(H-\varepsilon)^2\right\rangle_{\rm inv}\geqslant\inf_{\chi}\left\langle(H-\varepsilon)^2\right\rangle=\lambda. \quad (17)$$

Several steps of rearrangement yield:

$$\begin{aligned}\left\langle(H-\mu)^2\right\rangle_{\rm inv}&\geqslant\left\langle\lambda+\mu^2-\varepsilon^2-2H(\mu-\varepsilon)\right\rangle_{\rm inv}\\&=\left\langle\mu^2+\varepsilon^2-2\mu\varepsilon+\mu^2-\varepsilon^2-2H\lambda^{1/2}\right\rangle_{\rm inv}\\&=\left\langle2\mu(\mu-\varepsilon)-2H\lambda^{1/2}\right\rangle_{\rm inv}\\&=-2\lambda^{1/2}\left\langle H-\mu\right\rangle_{\rm inv}.\end{aligned} \quad (18)$$

The quantity $\langle H-\mu\rangle_{\rm inv}$ is negative by assumption (otherwise the inverse method will not yield a lower bound) so that division by it reverses the inequality sign:

$$\gamma^{-1}=\frac{\langle(H-\mu)^2\rangle_{\rm inv}}{\langle H-\mu\rangle_{\rm inv}}\leqslant-2\lambda^{1/2}. \quad (19)$$

This proves the first half of equality (16). The second step is to prove the inequality in the opposite direction: $\mu+\gamma^{-1}\geqslant\mu-2\lambda^{1/2}$. We begin with the definition of $\gamma$:

$$\frac{\langle H-\mu\rangle_{\rm var}}{\langle(H-\mu)^2\rangle_{\rm var}}\geqslant\inf_{\chi}\frac{\langle H-\mu\rangle}{\langle(H-\mu)^2\rangle}=\gamma. \quad (20)$$

Again several steps of rearrangement are necessary:

$$\begin{aligned}\langle H-\mu\rangle_{\rm var}&\geqslant\left\langle(H-\mu)^2\right\rangle_{\rm var}\gamma\\&=\left\langle(H-\varepsilon)^2+2H(\varepsilon-\mu)+\mu^2-\varepsilon^2\right\rangle_{\rm var}\gamma\\&=\left\langle\lambda+2H(\varepsilon-\mu)+\mu^2-\varepsilon^2\right\rangle_{\rm var}\gamma\\&=\left\langle\mu^2+\varepsilon^2-2\varepsilon\mu-2H\lambda^{1/2}+\mu^2-\varepsilon^2\right\rangle_{\rm var}\gamma\\&=\left\langle2H\lambda^{1/2}+2\mu^2-2\varepsilon\mu\right\rangle_{\rm var}\gamma\\&=-2\lambda^{1/2}\langle H-\mu\rangle_{\rm var}\gamma.\end{aligned} \quad (21)$$

Division by the negative $\gamma$ reverses the inequality, but the inequality is again reversed by division of $\langle H-\mu\rangle_{\rm var}$. This expectation value is necessarily negative:

$$\langle H-\mu\rangle_{\rm var}=\langle H-\varepsilon\rangle_{\rm var}-\lambda^{1/2}=\langle H-\varepsilon\rangle_{\rm var}-\left\langle(H-\varepsilon)^2\right\rangle_{\rm var}^{1/2}. \quad (22)$$

Since $\langle A^2\rangle\geqslant\langle A\rangle^2$, the quantity $\langle A\rangle-\langle A^2\rangle^{1/2}\leqslant\langle A\rangle-|\langle A\rangle|\leqslant0$. Let $A=H-\varepsilon$ in (22) and the negativity of $\langle H-\mu\rangle_{\rm var}$ results. Thus $\gamma^{-1}\geqslant-2\lambda^{1/2}$ which proves the second half of the equality (16).

## 6. Conclusion

Because both the generalized variance and inverse methods yield the same bounds given the same information, neither is inherently preferred. Practical considerations point both ways. The inverse method is preferred over the generalized variance method because it more simply incorporates the lower bound to $E_2$. The generalized variance method must first introduce the parameter $\varepsilon$ and then determine whether the quantity $\varepsilon + \lambda^{1/2}$ equals or is below the lower bound to $E_2$. If below, then is it close? If not, then $\varepsilon$ should be adjusted so that a closer match results and thus a better bound to $E_1$. On the other hand, the generalized variance method is preferred over the inverse method because of its simpler solution: given an orthonormal basis set an identity matrix results on the eigenvalue side of the eigenvalue problem for the generalized variance method, $(H - \varepsilon)^2\psi = \lambda\psi$. Even with such an ideal basis set, however, the inverse method remains a generalized eigenvalue problem, $H\psi = \gamma H^2\psi$, which is more difficult to solve. The final preference of a method is determined solely by the time and effort needed to solve one generalized eigenvalue problem or possibly many standard eigenvalue problems, which is determined by the particular software available and size of the basis set.

## Acknowledgement

The author thanks the referee for a simple comment and suggestion which greatly improved the quality and presentation of this work.

## References

[1] I. Porras, D.M. Feldmann and F.W. King, Int. J. Quant. Chem. 71 (1999) 455.
[2] A. Scrinzi, Phys. Rev. A 45 (1992) 7787.
[3] G. Temple, Proc. Roy. Soc. London Ser. A 119 (1928) 276.
[4] A. Stevenson, Phys. Rev. 53 (1938) 199.
[5] F. King, J. Chem. Phys. 102 (1995) 8053.