Surpassing the Temple lower bound

M.G. Marmorino*

*Department of Chemistry, Indiana University South Bend, P.O. Box 7111,
South Bend, IN 46634, USA*
E-mail: mmarmori@iusb.edu

Pritha Gupta

*Department of Chemistry, Indiana University South Bend, P.O. Box 7111,
South Bend, IN 46634, USA*

A non-traditional derivation of the Temple lower bound formula shows how the Temple bound can be improved using expectation values of H^3. Improved upper bounds result as a byproduct as well. Since expectation values of H^2 are already quite difficult in analytical calculations we also introduce an approximate lower bound which avoids the need for H^3 but which is rigorous only in a limiting sense. Examples of the two bounds are given using the lithium and perturbed hydrogen atoms.

KEY WORDS: Temple bound, lower bound

AMS classification: 8108, 15A48, 15A18

1.   Introduction

The Temple lower bound formula [1] is one of the simplest and best ways to calculate a lower bound to the ground-state energy of a system. When a lower bound is combined with an upper bound (from application of the variational method), an error bar around the true energy results. There are, unfortunately, three drawbacks with the Temple bound. The first is that it requires the typically difficult calculation of expectation values of H^2, where H is the Hamiltonian. The second is that a lower bound to the first excited-state energy E_2 must be known. The third is that the lower bound produced is not as accurate as the upper bound which was pointed out early on [2] but is evident in any application. There are many alternatives to the Temple bound for calculating lower bounds to eigenvalues [3,4], but none is so simple and accurate as the Temple bound.

* Corresponding author.

189

We present an alternate derivation of the Temple bound which shows that it can be improved when expectation values of H^3 are used. Such expectation values are very difficult to calculate so that we introduce approximations which give lower bounds that are non-rigorous, but may be trustworthy. This situation of having a non-rigorous lower bound, i.e. a lower bound method that may not produce a lower bound, is not unusual. Even in the standard Temple method a lower bound to the first-excited state eigenvalue is needed to calculate a lower bound to the ground-state eigenvalue. Since the former is often unavailable, one must approximate it, usually with an experimental value or variational upper bound. Thus the Temple bound is often applied non-rigorously [4,5], but with estimates of the first-excited state that are such that the lower bounds from the Temple bound are trustworthy.

2.　Derivation of the Temple bound

The Temple bound is usually derived starting with the operator $A = (H - E_1)(H - E_2)$, where H is the Hamiltonian of interest and E_n is the nth energy. Given an admissible function ϕ, then $\langle \phi | A | \phi \rangle$ is guaranteed to be non-negative:

$$\langle \phi | (H - E_1)(H - E_2) | \phi \rangle \geqslant 0. \tag{1}$$

One then solves equation (1) for E_1 and obtains:

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

provided that $\langle \phi | H | \phi \rangle < E_2$. Since E_2 is usually not known, a lower bound is used and we require further that $\langle \phi | H | \phi \rangle < E_2^{\text{low}}$ which results in a poorer but more practical bound:

$$E_1 \geqslant \frac{E_2^{\text{low}} \langle \phi | H | \phi \rangle - \langle \phi | H^2 | \phi \rangle}{E_2^{\text{low}} - \langle \phi | H | \phi \rangle} \tag{3}$$

A generalization of equation (2) yields upper and lower bounds for excited states [6]. An alternate way to derive the Temple bound is to encompass $S^2 = \langle \phi | \psi_1 \rangle^2$ with upper and lower bounds, where ψ_1 is the normalized ground-state eigenfunction and ϕ (usually a variationally determined function) is a normalized approximation to ψ_1 (assume both functions are real). The upper bound to S^2 is called Rayner's inequality [7,8]:

$$S^2 \leqslant 1 - \frac{\langle \phi | H - E_1 | g \rangle^2}{\langle g | (H - E_1)^2 | g \rangle^2} \leqslant 1 \tag{4}$$

while the lower bound to S^2 is the Eckart inequality [7,9]:

$$0 \leqslant \frac{E_2^{\text{low}} - \langle \phi | H | \phi \rangle}{E_2^{\text{low}} - E_1} \leqslant S^2. \tag{5}$$

The requirement that $\langle \phi | H | \phi \rangle < E_2^{\text{low}}$ is still necessary so that a positive lower bound to S^2 results. Letting $g = \phi$ and solving for E_1 shows that E_1 lies between the Temple lower bound and the variational upper bound $\langle \phi | H | \phi \rangle$. The calculational difficulty with the Temple bound is the calculation of $\langle \phi | H^2 | \phi \rangle$. To avoid this difficulty one may let g differ from ϕ and be a very simple function to give simple integrals $\langle g | H^2 | g \rangle$; however, calculations show that the resulting inequality gives very poor lower bounds, if any.

3. Rigorous improvement

To best the Temple bound one must bound S^2 differently. Instead of the Eckart inequality (5) for the lower bound to S^2, we use Wang's inequality [7,10]:

$$\frac{E_2^{\text{low}} - \langle \phi | H | \phi \rangle}{E_2^{\text{low}} - E_1} + \frac{1}{\left(E_2^{\text{low}} - E_1\right)} \frac{\left\langle \phi | (H - E_1)(H - E_2^{\text{low}}) | f \right\rangle^2}{\left\langle f | (H - E_1)^2 (H - E_2^{\text{low}}) | f \right\rangle} \leqslant S^2. \tag{6}$$

Although Wang's inequality originally used E_2, we are able to substitute E_2^{low} instead [7]. Now the integral $\langle f | H^3 | f \rangle$, which appears in the denominator of the second term on the left-hand side of inequality (6) often diverges when $f = \phi$; even when it converges it is usually difficult to calculate. It is possible to choose f so that $\langle f | H^3 | f \rangle$ converges and is not difficult to calculate. Combining Wang's inequality (6) with Rayner's inequality (4) with $g = \phi$, we obtain

$$\begin{aligned}
G(E_1) = {} & \frac{E_2^{\text{low}} - \langle H \rangle}{E_2^{\text{low}} - E_1} \\
& + \frac{1}{\left(E_2^{\text{low}} - E_1\right)} \frac{\left\langle \phi | (H - E_1)(H - E_2^{\text{low}}) | f \right\rangle^2}{\left\langle f | (H - E_1)^2 (H - E_2^{\text{low}}) | f \right\rangle} - 1 \\
& + \frac{(\langle H \rangle - E_1)^2}{\left\langle H^2 \right\rangle - 2E_1 \langle H \rangle + E_1^2} \leqslant 0.
\end{aligned} \tag{7}$$

where $\langle H \rangle = \langle \phi | H | \phi \rangle$. An analytic solution for E_1 is not concise so it is simpler to numerically (or graphically) solve for E_1 by plotting $G(E_1)$ vs. E_1 and locating the least intercept (see figure 1). This simple approach improves upon the Temple lower bound.

As an example we take the hydrogen atom with the following Hamiltonian h in Hartree units
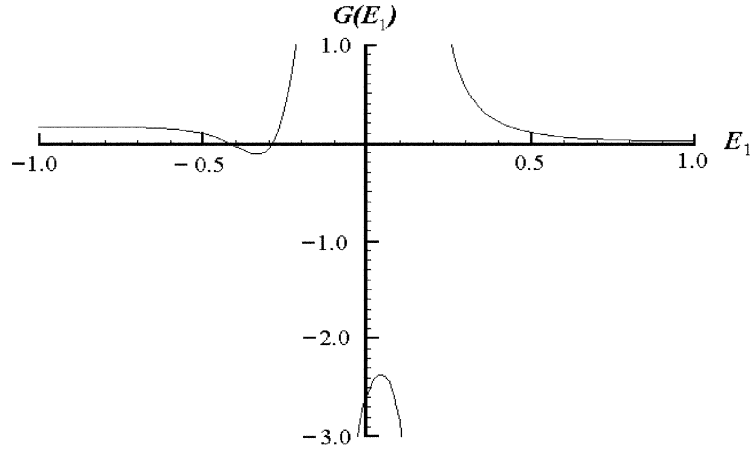
$$h = -\frac{1}{2}\Delta - r^{-1}. \tag{8}$$

Figure 1. $G(E_1)$ for $N = 1$ is plotted against E_1 to determine the upper and lower bounds to E_1.

with ground and first-excited state eigenvalues $e_1 = -0.500$ Hartree and $e_2 = -0.125$ Hartree, respectively. We perturb the system by adding the potential $0.200\, r^{-1}$ so that the perturbed Hamiltonian is

$$H = h + 0.200\, r^{-1} = -\frac{1}{2}\Delta - 0.800\, r^{-1}. \tag{9}$$

with ground and first-excited state eigenvalues $E_1 = -0.320$ Hartree and $E_2 = -0.080$ Hartree, respectively. In rigorous lower-bound problems one usually has a base Hamiltonian to work with in which the eigenfunctions and eigenvalues are known and a positive perturbation which yields the desired Hamiltonian and unknown eigenfunctions and eigenvalues. In this example the hydrogen atom is the base Hamiltonian and we will use it to bound E_1 of the perturbed Hamiltonian H. Since the perturbation is positive we can use e_2 of the base problem as a lower bound to E_2 of H.

$$E_1 < e_2 = E_2^{\text{low}} < E_2. \tag{10}$$

A particularly simple choice for f is $f = r^2 \exp(-r)$ where the r^2 term is needed to ensure that $\langle f | H^3 | f \rangle$ converges. The N-dimensional basis set used to compute the variational upper bound and approximate eigenfunction ϕ are the following orthonormal functions ϕ_n for $n = 0, 1, \ldots, N - 1$:

$$\phi_n = \left(a^3 n!(n + 2)!\right)^{1/2} \sum_{k=0}^{n} \frac{(-ar)^k e^{-ar/2}}{(k + 2)! k! (n - k)!}. \tag{11}$$

The parameter a expands or contracts the radial coordinate r.

Table 1
Bounds to S^2 and the exact value of S^2 are shown as the dimension N of the variational calculation increases.

N	Lower bound to S^2 (5)	Lower bound to S^2 (6)	Exact S^2	Upper bound to S^2 (4)
1	0.769 230 769	0.811 803 697	0.848 593 760	0.917 431 192
2	0.958 213 893	0.978 077 572	0.983 688 805	0.993 836 228
3	0.995 061 796	0.997 232 330	0.998 297 717	0.999 566 254
4	0.999 546 327	0.999 651 003	0.999 845 073	0.999 971 159
5	0.999 963 303	0.999 966 516	0.999 987 608	0.999 998 157
10	1.000 000 000	1.000 000 000	1.000 000 000	1.000 000 000

Table 2
Bounds to $E_1 = -0.320$ Hartree are shown as the dimension N of the variational calculation increases. All units are Hartree and all numbers are negative.

N	Temple lower bound (3)	Improved lower bound (7)	Improved upper bound (7)	Variational upper bound
1	0.425 000 000	0.421 348 927	0.287 947 556	0.275 000 000
2	0.369 145 068	0.367 561 034	0.316 369 100	0.311 851 709
3	0.330 049 871	0.329 825 970	0.319 492 469	0.319 037 050
4	0.321 303 728	0.321 289 754	0.319 932 651	0.319 911 533
5	0.320 135 343	0.320 134 841	0.319 993 479	0.319 992 844
10	0.320 000 000	0.320 000 000	0.320 000 000	0.320 000 000

Figure 1 demonstrates how the lower bound is obtained. $G(E_1)$ for $N = 1$ is plotted against E_1. The values of E_1 for which $G(E_1) \leqslant 0$ are possible values for the ground-state energy. The variational energy of -0.275 Hartree (see table 2) indicates that only the left-most negative region of $G(E_1)$ gives possible values for E_1. The possible values are between -0.421348927 Hartree and -0.287947556 Hartree. This gives an improvement over the Temple lower bound, as hoped, but also gives an improved upper bound, which was not expected. Table 1 demonstrates the improvement of the lower bound to S^2 using inequality (6) over inequality (5) and table 2 demonstrates the improved upper and lower bounds to the ground-state energy.

4. Non-rigorous improvement

Instead of choosing a function f that simplifies a direct calculation of $\langle f | H^3 | f \rangle$ one can choose a form of f that simplifies inequality (6) so that $\langle f | H^3 | f \rangle$ is no longer present. It is desirable to choose f so that inequality (6) contains only the terms $\langle H \rangle$, $\langle H^2 \rangle$, E_1, and E_2, i.e., we use the same information as required in the Temple bound (and yet get a better lower bound for practically no extra effort). Unfortunately we have been unable to come up with such

a function. We are, however, able to eliminate the need for $\langle H^3 \rangle$ by requiring a new integral $\langle (H - E_2^{\text{low}})^{-1} \rangle$:

To avoid integrals of $\langle f | H^3 | f \rangle$ we define f as

$$f = c(H - E_2^{\text{low}})^{-1} \phi, \tag{12}$$

where c is a normalization constant and $(H - E_2^{\text{low}})^{-1}$ exists since by assumption (10), $E_1 < E_2^{\text{low}} < E_2$. For this choice of f, Wang's inequality reads:

$$\frac{E_2^{\text{low}} - \langle \phi | H | \phi \rangle}{E_2^{\text{low}} - E_1} + \frac{1}{\left(E_2^{\text{low}} - E_1 \right)} \frac{\langle \phi | (H - E_1) | \phi \rangle^2}{\left\langle \phi \left| \frac{(H-E_1)^2}{(H-E_2^{\text{low}})} \right| \phi \right\rangle} \leqslant S^2 \tag{13}$$

Note that the normalization constant, c, need not be calculated since it cancels out. The following identity:

$$\left\langle \phi \left| \frac{(H - E_1)^2}{(H - E_2^{\text{low}})} \right| \phi \right\rangle = \langle \phi | H | \phi \rangle + E_2^{\text{low}} - 2E_1$$
$$+ (E_2^{\text{low}} - E_1)^2 \left\langle \phi | (H - E_2^{\text{low}})^{-1} | \phi \right\rangle \tag{14}$$

gives

$$\frac{E_2^{\text{low}} - \langle \phi | H | \phi \rangle}{E_2^{\text{low}} - E_1}$$
$$+ \frac{1}{\left(E_2^{\text{low}} - E_1 \right)} \frac{(\langle \phi | H | \phi \rangle - E_1)^2}{\langle \phi | H | \phi \rangle + E_2^{\text{low}} - 2E_1 + (E_2^{\text{low}} - E_1)^2 \langle \phi | (H - E_2^{\text{low}})^{-1} | \phi \rangle} \leqslant S^2. \tag{15}$$

Lacking a rigorous upper bound for $\langle \phi | (H - E)_2^{\text{low}})^{-1} | \phi \rangle$ we replace it with zero since we suppose that

$$\langle \phi | (H - E_2^{\text{low}})^{-1} | \phi \rangle \approx \frac{1}{\langle \phi | H - E_2^{\text{low}} | \phi \rangle} \leqslant 0 \tag{16}$$

and we expect more confidence in this approximate bound as ϕ approaches ψ_1; for when $\phi = \psi_1$ we have $\langle \phi | (H - E_2^{\text{low}})^{-1} | \phi \rangle = \langle \phi | H - E_2^{\text{low}} | \phi \rangle^{-1} \leqslant 0$. So at some point, as ϕ approaches ψ_1, $\langle \phi | (H - E_2^{\text{low}})^{-1} | \phi \rangle$ will become negative if it is not already so and thus zero will be a rigorous upper bound to $\langle \phi | (H - E_2^{\text{low}})^{-1} | \phi \rangle$. The problem is not so much that we lack rigor, but that we do not know what quality of ϕ is necessary to make the bound rigorous. Using zero gives the following bound on S^2:

$$\frac{E_2^{\text{low}} - \langle \phi | H | \phi \rangle}{E_2^{\text{low}} - E_1} + \frac{1}{\left(E_2^{\text{low}} - E_1 \right)} \frac{(\langle \phi | H | \phi \rangle - E_1)^2}{\langle \phi | H | \phi \rangle + E_2^{\text{low}} - 2E_1} \leqslant S^2, \tag{17}$$

Table 3
Bounds to S^2 and the exact value of S^2 are shown as the dimension N
of the variational calculation increases.

N	Lower bound to S^2 (5)	Lower bound to S^2 (16)	Exact S^2	Upper bound to S^2 (4)
1	0.769 230 769	0.812 500 000	0.848 593 760	0.917 431 192
2	0.958 213 893	0.959 889 936	0.983 688 805	0.993 836 228
3	0.995 061 796	0.995 086 062	0.998 297 717	0.999 566 254
4	0.999 546 327	0.999 543 532	0.999 845 073	0.999 971 159
5	0.999 963 303	0.999 963 304	0.999 987 608	0.999 998 157
10	1.000 000 000	1.000 000 000	1.000 000 000	1.000 000 000

which when combined with Rayner's inequality (with $g = \phi$) gives:

$$
F(E_1) = \frac{E_2^{\text{low}} - \langle H \rangle}{E_2^{\text{low}} - E_1}
$$
$$
+ \frac{1}{\left(E_2^{\text{low}} - E_1\right)} \frac{(\langle H \rangle - E_1)^2}{\langle H \rangle + E_2^{\text{low}} - 2E_1} - 1
$$
$$
+ \frac{(\langle H \rangle - E_1)^2}{\langle H^2 \rangle - 2E_1 \langle H \rangle + E_1^2} \leqslant 0.
\tag{18}
$$

$F(E_1)$ can be plotted and its intercepts with the E_1-axis give upper and lower bounds to E_1. The roots can also be determined analytically and the resulting lower bound is

$$
E_1 \geqslant \frac{E_2^{\text{low}} + \langle H \rangle - \sqrt{\left(E_2^{\text{low}} - \langle H \rangle\right)^2 + 4\left(\langle H^2 \rangle - \langle H \rangle^2\right)}}{2}
\tag{19}
$$

We cannot guarantee that this bound is better than the Temple bound in general, but in all examples here it has proved superior. The example in Section 3 is used again. Tables 3 and 4 are analogous to Tables 1 and 2. In this case, a superior upper bound does not result as before. Note that no information is required that is not used in the Temple bound: $\langle \phi | H | \phi \rangle$, $\langle \phi | H^2 | \phi \rangle$ and E_2^{low}.

As additional support we computed lower bounds for the ground-state energy of the Lithium atom using data of [3] and compare it with the Temple bound. These results are reported in table 5. The accuracy of the variational calculations is such that we are confident that our lower bounds (18) are in fact rigorous; while we cannot guarantee this, we note that they are all lower than the variational upper bounds which are very close to the exact value. The ordering in table 5 is by variance, $\langle H^2 \rangle - \langle H \rangle^2$, instead of basis set size since the former is often a better criterion for accuracy, although this notion has been challenged [11]. Note that both the Temple and our lower bounds improve as the variance lessens and not as the basis set dimension increases.

Table 4

Bounds to $E_1 = -0.320$ Hartree are shown as the dimension N of the variational calculation increases. All units are Hartree and all energies are negative.

N	Temple lower bound	Improved lower bound (18)	Variational upper bound
1	0.425 000 000	0.367 705 098	0.275 000 000
2	0.369 145 068	0.357 830 848	0.311 851 709
3	0.330 049 871	0.329 487 076	0.319 037 050
4	0.321 303 728	0.321 293 924	0.319 911 533
5	0.320 135 343	0.320 135 239	0.319 992 844
10	0.320 000 000	0.320 000 000	0.320 000 000

Table 5

Summary of results for the Lithium atom from [4] along with our lower bound for comparison calculated using $E_2^{\text{low}} = -7.386$, $\langle H \rangle$ and $\langle H^2 \rangle$ from [4]. All units are Hartree.

Variance	Basis set dimension	Variational upper bound	Temple lower bound	Improved lower bound (18)	Percent difference
2.3E−02	760	−7.478 060	−7.728 968	−7.590 830	1.8E+00
7.1E−03	50	−7.477 948	−7.555 097	−7.527 929	3.6E−01
2.7E−03	100	−7.478 020	−7.507 871	−7.501 751	8.2E−02
3.8E−04	200	−7.478 057	−7.482 223	−7.482 050	2.3E−03
2.0E−04	404	−7.478 060	−7.480 190	−7.480 143	6.3E−04
1.9E−04	300	−7.478 059	−7.480 130	−7.480 085	6.0E−04
9.2E−05	524	−7.478 060	−7.479 055	−7.479 045	1.4E−04
5.9E−05	695	−7.478 060	−7.478 702	−7.478 697	5.9E−05
2.1E−05	600	−7.478 060	−7.478 285	−7.478 284	7.3E−06

As the variance lessens, the approximate eigenfunction ϕ gets closer and closer to the true ground-state eigenfunction. This means that our lower bound formula (18) becomes more trustworthy since $\langle \phi | (H - E_2^{\text{low}})^{-1} | \phi \rangle$ gets more negative. Unfortunately, zero becomes a poorer bound for $\langle \phi | (H - E_2^{\text{low}})^{-1} | \phi \rangle$ in equation (14) since it is becoming more negative. This is easily seen as the percent difference between the Temple and our lower bound decreases.

5.   Summary

The Temple bound has been improved by introducing the need for the expectation value of H^3 using a specially chosen function f. Depending on the choice of f an improved rigorous lower bound formula or an approximate lower bound formula results. In the former case, an upper bound, superior to the variational energy, can result. On the models tested, the lithium and perturbed hydrogen atoms, both new bounds are better than the Temple bound.

The improvements in the Temple bound can be furthered by introducing more complicated versions of Rayner's inequality [7,8] and Wang's inequality [7, 10] which require higher powers of H. Due to the difficulty of calculating expectation values of high powers of H is it unlikely that further improvements in the Temple bound will be practical at this stage; however, significant progress in such calculation has taken place [12].

References

[1] G. Temple, Proc. Roy. Soc. (London) A119 (1928) 276.
[2] G.L. Caldow and C.A. Coulson, Proc. Cambridge Phil. Soc. 57 (1961) 341.
[3] For a list of references see M.G. Marmorino, J. Math Chem. 32 (2002) 19.
[4] F.W. King, J. Chem. Phys. 102 (1995) 8053.
[5] A. Lüchow and H. Kleindienst, Int. J. Quantum Chem. 51 (1994) 211.
[6] W. Kohn, Phys. Rev. 71 (1947) 902.
[7] F. Weinhold, J. Math. Phys. 11 (1970) 2127.
[8] M.E. Rayner, Equart. J. Math. (Oxford) 13 (1962) 61.
[9] C. Eckart, Phys. Rev. 36 (1930) 878.
[10] P.S.C. Wang, Int. J. Quantum Chem. 3 (1969) 57.
[11] See references (13–18) in D. Bressanini and G. Morosi, J. Chem. Phys. 116 (2002) 5345.
[12] H. Huang, J. Chem. Phys. 112 (2000) 5257.