J Math Chem (2013) 51:2062–2073
DOI 10.1007/s10910-013-0199-7

ORIGINAL PAPER

Comparison and union of the Temple and Bazley lower bounds

M. G. Marmorino

Received: 6 February 2013 / Accepted: 26 May 2013 / Published online: 8 June 2013

Abstract The Lehmann-Maehly approach and Bazley's method of special choice are matrix eigenvalue problems that allow the calculation of lower bounds to energies of atomic and molecular systems. We introduce a common derivation of their scalar versions using the overlap of a trial function with the unknown ground-state wave function. In the scalar setting, the Lehmann-Maehly approach reduces to the Temple formula. The common derivation allows us to easily unite and improve both methods in several stages within this restricted application. Finally we offer a different union that allows generalization to arbitrary dimension matrix methods. Calculations on the helium atom ground state illustrate the improvements and mergers.

Keywords Temple · Lehmann-Maehly · Bazley · Lower bound · Helium

1 Introduction

Two standard methods to calculate lower bounds to the electronic energies of atomic systems are the Lehmann-Maehly approach [1] and Bazley's method of special choice [2,3]. The Temple formula [4] is a popular simplification of the former. These methods appear dissimilar in many aspects and we compare them using the non-relativistic fixed nucleus atomic system. The Hamiltonian for such a system can be written as $H = h + R$ where h is the sum of the kinetic energy and nuclear attraction potential energy operators while R is the sum of the positive definite electron repulsion operators, $1/r_{ij}$ where r_{ij} is the distance between the i and jth electrons. The eigenvalue problem is $H\Psi_n = E_n \Psi_n$. Both methods are quite general and are formulated as variational-like

M. G. Marmorino (✉)
Indiana University South Bend, 1700 Mishawaka Ave.,
South Bend, IN 46615, USA
e-mail: mmarmori@iusb.edu

matrix methods using certain finite-dimensional basis sets to provide lower bounds to several of the lowest eigenvalues E_n of H.

The three main differences are:

(A) Bazley's method requires an exactly soluble base problem, such as $h\,\psi_n = e_n\,\psi_n$ where $h \leq H$. In its most basic form one must approximate the eigenfunctions of H using linear combinations of the incomplete base problem eigenfunctions ψ_n. The Lehmann-Maehly method allows any trial function ϕ. This difference makes the latter approach superior if one has great flexibility in ϕ so that it can be made to approach the true eigenfunction Ψ_n of H.

(B) The Lehmann-Maehly method requires the expectation value of the square Hamiltonian which, for our example, introduces the operators h^2, hR, Rh and R^2. The calculation of the expectation values for such operators is difficult and has been the subject of much work. (See [5,6] for the calculation of a lower bound to the ground-state energy of the lithium atom and for references to the necessary integrals.) Bazley's method does not use the square Hamiltonian; rather, it replaces the expectation value of each $1/r_{ij}$ appearing in R (added to h in variational calculations) with expectation values of r_{ij}. In this work we study the helium atom as an example which has only a single inter-electron distance $r_{12} = R^{-1}$.

(C) The Lehmann-Maehly approach requires knowledge of a lower bound to a certain excited state E_m. This allows calculation of lower bounds to energies $E_n < E_m$. Bazley's method requires exact knowledge of the base problem eigenvalues e_n. While a lower bound to one of E_m (for Lehmann-Maehly) and exact knowledge of several e_n (for Bazley) seem to be very different requirements, the only *ab initio* lower bound to E_m is e_m. Thus this third difference is somewhat superficial as the base problem is vital to both methods, though certainly used more in Bazley's where the eigenfunctions play a vital role.

Our goal is to merge the Bazley and Lehmann-Maehly lower bound methods. For simplicity we limit our analysis to the ground-state energy. We further limit the initial work to the scalar situation where a single trial function is studied, because it is only in this simple case that we have found a common derivation that allows a straightforward comparison and merger. Toward the end, however, we introduce a matrix method that combines aspects of both methods and allows use of arbitrarily large basis sets for lower bound calculations.

2 Bazley and Temple bounds

Bazley's lower bound to E_1 is traditionally derived by introducing the operator $H_B = h + B$ where $B = [R^{-1}]^{-1}$. $[R^{-1}]$ is the matrix representation of R^{-1} on a finite-dimensional subspace **S** and $[R^{-1}]^{-1}$ is the inverse of $[R^{-1}]$ on the subspace **S** which is then extended with null effect to the domain of the rest of Hilbert space. When subspace **S** is merely the span of ψ_1 then the eigenfunctions of H_B are the same as those of h so that $H_B\,\psi_n = e_n\,\psi_n$ for $n > 1$ and $H_B\,\psi_1 = \varepsilon\,\psi_1$ where $\varepsilon = e_1 + \langle\psi_1 \left|R^{-1}\right| \psi_1\rangle^{-1}$. If $\varepsilon < e_2$ then ε is the lowest eigenvalue of H_B and provides a lower bound to E_1 in inequality (1). Otherwise $E_1 \geq e_2$.

$$E_1 \geq \varepsilon = e_1 + \langle \psi_1 | \, R^{-1} \, | \psi_1 \rangle^{-1} \tag{1}$$

The Temple formula is the simplest version of the Lehmann-Maehly method. Given a lower bound, $E_{2,\mathrm{low}}$, to the first excited-state energy, E_2, one can compute a lower bound to the ground-state energy E_1 using inequality (2) where ϕ is a normalized trial function approximating the ground-state wave function. The Temple bound is valid only if $\langle \phi \, | H | \, \phi \rangle < E_{2,\mathrm{low}}$. Convergence to E_1 is guaranteed as ϕ approaches Ψ_1 though it is apparent from many applications that the lower bound converges more slowly than the variational upper bound [5].

$$E_1 \geq \frac{E_{2,low} \, \langle \phi | \, H \, | \phi \rangle - \langle \phi | \, H^2 \, | \phi \rangle}{E_{2,low} - \langle \phi | \, H \, | \phi \rangle} \tag{2}$$

Where does the lower bound to E_2 in the Temple formula come from? The only *ab initio* source is the base problem of the repulsionless atom. Because the electron repulsion operator is positive definite, $e_2 \leq E_2$. Thus e_2 is vital to both the Temple formula (requires $\langle \phi \, | H | \, \phi \rangle < e_2 = E_{2,\mathrm{low}}$) and the Bazley bound (requires $\varepsilon < e_2$).

3 Common derivation: Temple bound

A common derivation for the Temple and Bazley bounds is achieved by focusing on the square magnitude overlap s^2 between a normalized trial function ϕ and the unknown normalized ground-state wave function Ψ_1 of H. Trivial upper and lower bounds to s^2 are 1 and 0, respectively. A non-trivial lower bound to s^2 is provided by the Eckart bound (3) and an upper bound is given as inequality (4) [7,8]. A lower bound to E_2 may be used in place of the exact value for the Eckart bound.

$$s^2 \equiv |\langle \Psi_1 | \phi \rangle|^2 \geq \frac{E_2 - \langle \phi | \, H \, | \phi \rangle}{E_2 - E_1} \tag{3}$$

$$s^2 \leq \frac{\langle \phi | \, H^2 \, | \phi \rangle - \langle \phi | \, H \, | \phi \rangle^2}{\langle \phi | \, (H - E_1)^2 \, | \phi \rangle} \tag{4}$$

One derivation of the Temple formula begins by combining inequalities (3) and (4) to yield inequality (5) where a lower bound has been used for E_2. An inequality, quadratic in E_1, results and as long as $\langle \phi \, | H | \, \phi \rangle < E_{2,\mathrm{low}}$ the two roots are the Temple lower bound given in inequality (2) and the variational upper bound $\langle \phi \, | H | \, \phi \rangle \geq E_1$.

$$\frac{\langle \phi | \, H^2 \, | \phi \rangle - \langle \phi | \, H \, | \phi \rangle^2}{\langle \phi | \, (H - E_1)^2 \, | \phi \rangle} \geq \frac{E_{2,low} - \langle \phi | \, H \, | \phi \rangle}{E_{2,low} - E_1} \tag{5}$$

4 Common derivation: Bazley bound

If there is knowledge of a soluble base problem, and the trial function is restricted to be an eigenfunction of the base problem, $\phi = \psi_1$, then the Eckart bound can be recast as inequality (6) where we swap the roles of the base and full problems.

$$\bar{s}^2 \equiv |\langle\Psi_1|\psi_1\rangle|^2 \geq \frac{e_2 - \langle\Psi_1|\, h\,|\Psi_1\rangle}{e_2 - e_1} = \frac{e_2 - \langle\Psi_1|\, H - R\,|\Psi_1\rangle}{e_2 - e_1}$$
$$= \frac{e_2 - E_1 + \langle\Psi_1|\, R\,|\Psi_1\rangle}{e_2 - e_1} \tag{6}$$

The Cauchy-Schwarz inequality (7) allows us to bound the positive quantity $\langle\Psi_1\,|R|\,\Psi_1\rangle$ from below to yield inequality (8) as long as $R > 0$ so that $R^{1/2}$ exists.

$$\bar{s}^2 = |\langle\Psi_1|\psi_1\rangle|^2 = \left|\left\langle R^{-1/2}\Psi_1 | R^{1/2}\psi_1\right\rangle\right|^2 \leq \langle\Psi_1|\, R\,|\Psi_1\rangle\, \langle\psi_1|\, R^{-1}\,|\psi_1\rangle \tag{7}$$

$$\bar{s}^2 \geq \frac{e_2 - E_1 + \bar{s}^2\, \langle\psi_1|\, R^{-1}\,|\psi_1\rangle^{-1}}{e_2 - e_1} \tag{8}$$

We then solve for $\bar{s}^2$ and use the trivial upper bound of one to obtain inequality (9) which easily yields the Bazley bound (1) as long as $e_2 > e_1 + \langle\psi_1\left|R^{-1}\right|\psi_1\rangle^{-1}$.

$$1 \geq \bar{s}^2 \geq \frac{e_2 - E_1}{e_2 - e_1 - \langle\psi_1|\, R^{-1}\,|\psi_1\rangle^{-1}} \tag{9}$$

5 Comparison of the Temple and Bazley bounds

We now consider the helium atom which is the simplest chemical system that is not exactly soluble in its electronic structure. In the limit of infinite nuclear mass (at the origin) and using atomic units, the Hamiltonian H is given by Eq. (10) where r_{12} is the distance between the two electrons.

$$H = h + R$$
$$h = -\left(\frac{1}{2}\nabla_1^2 + \frac{2}{r_1}\right) - \left(\frac{1}{2}\nabla_2^2 + \frac{2}{r_2}\right)$$
$$R = \frac{1}{r_{12}} \tag{10}$$

The discrete eigenvalues of h are $e_n = -2(1 + 1/n^2)$ and approach the continuum $[-2, \infty)$ from below. These serve as lower bounds to the eigenvalues E_n of H due to the positive nature of the electron repulsion operator R.

Using a trial function of the form $\phi = a^3\,\pi^{-1}\,\exp[-a(r_1 + r_2)]$ where a is an adjustable parameter and r is the electron radial coordinate, the best *upper* bound to the ground-state energy is -2.84766 (with $a = 27/16$). The true energy is about -2.90372. Using the same adjustable form for the trial function in the Temple method gives a best *lower* bound of -5.29345 (with $a = 1.77158$). The Temple lower bounds are quite poor with this restricted trial function. In fact, this best lower bound is worse than the trivial lower bound provided by the base problem eigenvalue $e_1 = -4$. More flexibility in the trial function is needed to improve the Temple lower bound. Note that the trial function that gives the best upper bound does not yield the best lower bound from the Temple formula.

We now consider the Bazley bound. Because we are forced to reference the base problem we restrict the trial function to ψ_1 which corresponds to $\phi = a^3 \quad \pi^{-1} \exp[-a(r_1 + r_2)]$ with $a = 2$. This means the Bazley bound cannot be optimized. The result from inequality (1) is $E_1 \geq -3.08571$. This single value is far better than any of the lower bounds calculated using the Temple method. Despite the fact that the Temple method will outperform the Bazley lower bound as $\phi \to \Psi_1$, it seems that the Bazley bound can be very advantageous if the trial function is restricted as it has in this example.

6 Special-case Temple formula

The comparison of the Temple and Bazley bounds in the previous section may not be the best. In the special case that $\phi = \psi_1$, we have two choices for the lower bound to s^2 (now equal to $\bar{s}^2$) in the derivation of the Temple formula. Rather than use inequality (3), we can use inequality (6) and set $\langle \Psi_1 | R | \Psi_1 \rangle \geq 0$. Coupled with the standard upper bound (4) to s^2 we obtain inequality (11) instead of inequality (5).

$$\frac{\langle \psi_1 | H^2 | \psi_1 \rangle - \langle \psi_1 | H | \psi_1 \rangle^2}{\langle \psi_1 | (H - E_1)^2 | \psi_1 \rangle} \geq \bar{s}^2 \geq \frac{e_2 - E_1}{e_2 - e_1} \tag{11}$$

With this change we have lost the flexibility normally inherent in the Temple method, but we achieve a significant increase in the lower bound which rises to $E_1 \geq -3.49670$ (there are also two complex-valued solutions). This lower bound is still poorer than the Bazley bound, but at least it surpasses the trivial lower bound $e_1 = -4$.

7 Temple-Bazley bound

Instead of slightly altering the Temple formula as in the last section, we can actually merge the Temple and Bazley lower bound methods. The procedure is essentially the same as the alteration of the Temple formula that was just performed, but we don't dismiss $\langle \Psi_1 | R | \Psi_1 \rangle$. Again we combine upper and lower bounds to $\bar{s}^2$: this time inequalities (4) and (8), respectively, to yield inequality (12).

$$\frac{\langle \psi_1 | H^2 | \psi_1 \rangle - \langle \psi_1 | H | \psi_1 \rangle^2}{\langle \psi_1 | (H - E_1)^2 | \psi_1 \rangle} \geq \bar{s}^2 \geq \frac{e_2 - E_1}{e_2 - e_1 - \langle \psi_1 | R^{-1} | \psi_1 \rangle^{-1}} \tag{12}$$

This inequality can be rearranged to a cubic inequality for E_1. For the helium atom with $\phi = \psi_1$ the solutions of this inequality give a lower bound of $E_1 \geq -3.04336$ and two complex-valued solutions.

From one point of view, by incorporating a non-trivial upper bound to $\bar{s}^2$ we have added Temple-character to the Bazley bound and gained improvement of the lower bound from -3.08571. From another point of view, by incorporating Bazley's bound to $\langle \Psi_1 | R | \Psi_1 \rangle$ we have added Bazley-character to the special-case Temple formula of Sect. 6, raising the lower bound from -3.49670. Regardless of how the merger is seen, the two methods have been combined and improved.

The improvement over the Bazley bound is not great, only about +0.04 units, but the new lower bound already exceeds that provided by standard Bazley lower bound calculations when the subspace **S** is expanded from one-dimension to the span of many base problem eigenfunctions. This limit is −3.05992 [10] so that the improvement we have seen is rather remarkable.

8 An upper bound from Bazley

Note: In this section expectation values are assumed to use the base problem ground-state eigenfunction ψ_1 *unless otherwise noted, so* $\langle A \rangle = \langle \psi_1 | A | \psi_1 \rangle$ *where A is some operator.*

Continuing from the introduction, there is a fourth difference between the Temple and Bazley bounds. With the derivation in Sect. 3, the Temple method naturally gives two roots for E_1, the lower bound of inequality (2) and the variational upper bound $\langle \phi | H | \phi \rangle \geq E_1$. Bazley's method provides only a lower bound. To get more information from Bazley's approach, before merging with the Temple method, we need to get an improved bound to $\langle \Psi_1 | R | \Psi_1 \rangle$. Rather than use the Cauchy-Schwarz inequality we construct a Gram matrix from the vector $\{ R^{1/2}\Psi_1,\ R^{-1/2}\psi_1,\ R^{-1/2}H\psi_1 \}$. This yields the matrix **G** in Eq. (13).

$$\mathbf{G} = \begin{bmatrix} \langle \Psi_1 | R | \Psi_1 \rangle & \langle \Psi_1 | \psi_1 \rangle & E_1 \langle \Psi_1 | \psi_1 \rangle \\ \langle \Psi_1 | \psi_1 \rangle^* & \langle \psi_1 | R^{-1} | \psi_1 \rangle & \langle \psi_1 | R^{-1} H | \psi_1 \rangle \\ E_1 \langle \Psi_1 | \psi_1 \rangle^* & \langle \psi_1 | HR^{-1} | \psi_1 \rangle & \langle \psi_1 | HR^{-1} H | \psi_1 \rangle \end{bmatrix} \tag{13}$$

A Gram matrix has the property that its determinant is non-negative so we solve for $\langle \Psi_1 | R | \Psi_1 \rangle$ using $\mathrm{Det}[\mathbf{G}] \geq 0$. The result is inequality (14).

$$\langle \Psi_1 | R | \Psi_1 \rangle \geq \frac{\bar{s}^2 \left(\langle HR^{-1}H \rangle + E_1^2 \langle R^{-1} \rangle - \langle R^{-1}H \rangle E_1 - \langle HR^{-1} \rangle E_1 \right)}{\langle R^{-1} \rangle \langle HR^{-1}H \rangle - \langle R^{-1}H \rangle \langle HR^{-1} \rangle} \equiv \bar{s}^2 \gamma \tag{14}$$

Note that the Cauchy-Schwarz inequality (7) results from the determinant of the upper-left 2×2 submatrix of **G**. By using a larger matrix we are guaranteed a bound to $\langle \Psi_1 | R | \Psi_1 \rangle$ that is not worse. Next we use inequality (14) in inequality (6) to obtain inequality (15).

$$\bar{s}^2 \geq \frac{e_2 - E_1}{e_2 - e_1 - \gamma} \tag{15}$$

When we introduce the trivial upper bound $\bar{s}^2 \leq 1$ we seem to obtain an improved Bazley bound (16) provided that $e_2 > e_1 + \gamma$. This "bound" is misleading because γ is actually dependent on E_1.

$$E_1 \geq e_1 + \gamma \tag{16}$$

The expectation values that appear in matrix **G** and γ are not as difficult as one would assume given that the trial function is an eigenfunction of the base problem. These new expectation values are shown in Eqs. (17), (18) and reduce into combinations of e_1, $\langle R^{-1}\rangle$ and $\langle R\rangle$. The former is already in use in the Bazley lower bound while the latter is used in the variational upper bound. Thus no new information is required.

$$\left\langle HR^{-1}H\right\rangle = \langle\psi_1|\,(h+R)R^{-1}(h+R)\,|\psi_1\rangle = e_1^2\left\langle R^{-1}\right\rangle + 2e_1 + \langle R\rangle \tag{17}$$

$$\begin{aligned}\left\langle HR^{-1}\right\rangle &= \langle\psi_1|\,(h+R)R^{-1}\,|\psi_1\rangle = e_1\left\langle R^{-1}\right\rangle + 1\\ &= \langle\psi_1|\,R^{-1}(h+R)\,|\psi_1\rangle = \left\langle R^{-1}H\right\rangle\end{aligned} \tag{18}$$

Substituting Eqs. (17), (18) into γ for inequality (16) yields inequality (19) which can be rewritten as a quadratic inequality for E_1. Its two roots provide an upper and lower bound to E_1.

$$E_1 \geq e_1 + \frac{e_1^2\left\langle R^{-1}\right\rangle + 2e_1 + \langle R\rangle + E_1^2\left\langle R^{-1}\right\rangle - 2e_1\langle R\rangle E_1 - 2E_1}{\left\langle R^{-1}\right\rangle\left(e_1^2\left\langle R^{-1}\right\rangle + 2e_1 + \langle R\rangle + E_1^2\left\langle R^{-1}\right\rangle\right) - (e_1\langle R\rangle + 1)^2} \tag{19}$$

The upper bound is the variational estimate $\langle H\rangle \geq E_1$ and the lower bound is the standard Bazley bound $E_1 \geq e_1 + \langle R^{-1}\rangle^{-1}$. Thus there is no improvement to the lower bound, only the appearance of the variational upper bound has been introduced.

Actual improvement to the lower bound – and perhaps also the upper bound – could in principle be achieved by adding components such as $R^{-1/2}H^n\,\psi_1$ with $n > 1$ to the vector used to make **G**. Unfortunately this would create very difficult, or even divergent, expectation values within **G**.

9 Final improvement

Finally we combine the improved lower bound to $\bar{s}^2$, inequality (15), with inequality (4) rather than unity as the upper bound to $\bar{s}^2$. This generates inequality (20) which can be rearranged as a cubic inequality.

$$\frac{e_2 - E_1}{e_2 - e_1 - \gamma} \leq \bar{s}^2 \leq \frac{\langle\psi_1|\,H^2\,|\psi_1\rangle - \langle\psi_1|\,H\,|\psi_1\rangle^2}{\langle\psi_1|\,(H-E_1)^2\,|\psi_1\rangle} \tag{20}$$

The variational upper bound $\langle\psi_1\,|H|\,\psi_1\rangle$ is generated along with a slightly improved lower bound of -3.03848 and a useless positive root close to 1.

10 Summary

What we have done so far is to merely combine upper and lower bounds to s^2 (or $\bar{s}^2$) to achieve bounds to the ground-state energy. The variations can be summarized below in inequality (21).

$$\left\{ B_L \equiv 1,\, T_L \equiv \frac{\langle H^2\rangle - \langle H\rangle^2}{\langle (H-E_1)^2\rangle} \right\} \geq s^2 \geq \left\{ B_R \equiv \frac{e_2 - E_1 + \langle R\rangle}{e_2 - e_1},\, T_R \equiv \frac{E_2 - \langle H\rangle}{E_2 - E_1} \right\} \tag{21}$$

In Sect. 3 we derived the Temple lower bound and variational upper bound using $T_{\mathrm{L}} \geq T_{\mathrm{R}}$ while in Sect. 4 the Bazley lower bound came from $B_{\mathrm{L}} \geq B_{\mathrm{R}}$ with $\langle R\rangle \geq \tilde{s}^2\langle R^{-1}\rangle^{-1}$. In Sect. 6 we restricted the form of the trial function in the Temple method to allow use of $T_L \geq B_R$ with $\langle R\rangle = 0$. Next, in Sect. 7, we combined the Bazley and Temple methods using $T_{\mathrm{L}} \geq B_{\mathrm{R}}$ again but this time with $\langle R\rangle \geq \tilde{s}^2\langle R^{-1}\rangle^{-1}$ according to Bazley's method. A complementary upper bound was obtained in Sect. 8 from by generalizing the basic Bazley method from $B_{\mathrm{L}} \geq B_{\mathrm{R}}$ using an even better lower bound to $\langle R\rangle$. Finally the best result merger was obtained in Sect. (9) using $T_{\mathrm{L}} \geq B_{\mathrm{R}}$ with the improved bound to $\langle R\rangle$.

One combination was neglected: $B_{\mathrm{L}} \geq T_{\mathrm{R}}$ returns only the variational upper bound $\langle H\rangle \geq E_1$.

11 Removing the restriction of $\phi = \psi_1$

Note: In this section expectation values are assumed to use the general ϕ *unless otherwise noted, so* $\langle A\rangle = \langle \phi\,|A|\,\phi\rangle$ *where A is some operator.*

All of our results beyond the simple application of the Temple formula have hinged on the restriction $\phi = \psi_1$. We now introduce a simple strategy to add flexibility to the trial function. Like Bazley, we introduce an intermediate operator (call it H_{I} rather than H_{B}) with eigenvalues ε_{n} such that $h \leq H_{\mathrm{I}} \leq H$. Ordinarily this intermediate operator would be designed using a base problem as a template so that its entire spectrum can be determined exactly. Instead we proceed by using the Temple method to find a lower bound $\varepsilon_{1,\mathrm{low}}$ to the ground-state energy ε_1 of H_{I} which will in turn be a lower bound to E_1 of H. By releasing the restriction that we find the eigenvalue ε_1 of H_{I} exactly, we can remove the restriction that H_{I} must related in a special way to a sub-eigenspace of h.

We define H_{I} in Eq. (22) where $[R^{-1}]^{-1}$ takes the same meaning as before except that a general normalized trial function ϕ is used in place of base problem eigenfunction ψ_1 in forming the one-dimensional subspace $\mathbf{S}$. H_{I} thus depends on ϕ and we indicate this by $H_{\mathrm{I}}(\phi)$.

$$H \geq H_I(\phi) \equiv h + [R^{-1}]^{-1} \tag{22}$$

The advantage over the Bazley bound of using H_{I} in place of H is the flexibility provided by ϕ. The advantage over the Temple bound of using H_{I} in place of H is that the expectation values needed may be simpler. The expectation value $\langle H^2\rangle$ breaks down to the integrals $\langle h^2\rangle$, $\langle hR\rangle = \langle Rh\rangle$, and $\langle R^2\rangle$. With H_{I} replacing H, the integrals needed in $\langle H_{\mathrm{I}}^2\rangle$ are $\langle h^2\rangle$, $\left\langle h\left[R^{-1}\right]^{-1}\right\rangle = \left\langle \left[R^{-1}\right]^{-1} h\right\rangle$, and $\left\langle \left[R^{-1}\right]^{-1}\left[R^{-1}\right]^{-1}\right\rangle$. Because $[R^{-1}]^{-1}$ is a matrix restricted to the span of ϕ, the last two integrals simplify to $\langle h\rangle\left\langle \left[R^{-1}\right]^{-1}\right\rangle$ and $\left\langle \left[R^{-1}\right]^{-1}\right\rangle^2$, respectively. Thus by using H_{I} in place of H we

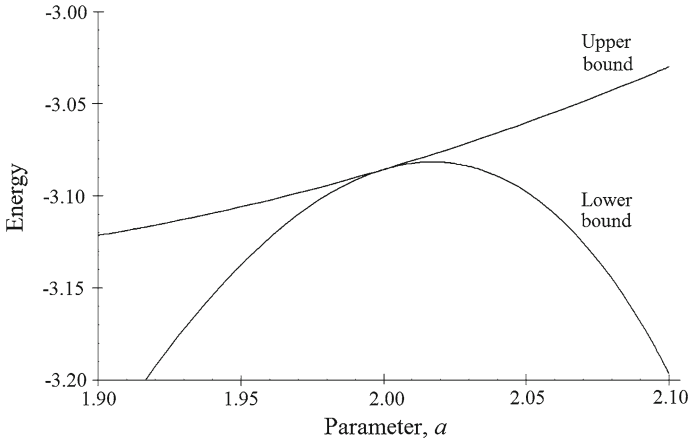

Fig. 1 The *upper* and *lower* bounds to energy ε_1 of the variable intermediate Hamiltonian $H_{\rm I}(\phi)$ are plotted against the variable parameter a in the function $\phi = a^3\,\pi^{-1}\exp[-a(r_1 + r_2)]$

replace the calculation of $\langle R\rangle$, $\langle hR\rangle$, and $\langle R^2\rangle$ with just $\left\langle \left[R^{-1}\right]^{-1}\right\rangle$. Both methods still require $\langle h^2\rangle$.

Figure (1) shows the variational upper bound and Temple lower bound for the ground-state eigenvalue of $H_{\rm I}(\phi)$ as the trial function $\phi = a^3\,\pi^{-1}\exp[-a(r_1 + r_2)]$ is varied by its exponential parameter a. The best lower bound of $E_l \geq -3.08172$ at $a = 2.01717$ is just slightly better than the traditional Bazley bound. First note that each choice of a defines a new intermediate Hamiltonian so that there is no contradiction when a smaller error bar at a' is not contained within a larger error bar at a''. Also note that for $a = 2$ the upper and lower bound to ε_1 coincide; for this choice of a, $H_{\rm I}(\phi_{a=2}) = H_{\rm B}$ so that $\phi_{a=2}$ is the exact ground-state eigenfunction.

Capturing R on only a one-dimensional subspace does not allow for $H_{\rm I}(\phi)$ to be close to H and thus even though $\varepsilon_{1,\rm low}$ is very close, or even equal, to ε_1, the calculation is not successful because ε_1 is far from E_1. This is revealed in Fig. (1) where the variational upper bounds to $H_{\rm I}(\phi)$ are well below the ground state energy $E_1 = -2.90372$ of H.

12 Convergent union

In Sect. 11 we merged the Bazley and Temple lower bound methods in such a way that a variable trial function could be used in place of a base problem eigenfunction. However, as long as $H_{\rm I}(\phi)$ incorporates the perturbation R on only a *one-dimensional* subspace it can never approach H and so the lower bounds to the ground-state of $H_{\rm I}(\phi)$ can never approach E_1 of H. In this section we generalize $H_{\rm I}(\phi)$ so that it can approach H rather than mimicking H on only a one-dimensional subspace. To do this we first review the general approach of Bazley's method.

To generate the intermediate Hamiltonian $H_{\rm B} = h + [R^{-1}]^{-1}$, Bazley chose a subspace $\mathbf{S}$ that is the span of N eigenfunctions of h. With this choice of $\mathbf{S}$ the operator

$[R^{-1}]^{-1}$ is the null extension of an $N \times N$ matrix. Outside of $\mathbf{S}$, H_{B} and h share the same eigenfunctions and eigenvalues. The spectra of H^{B} and h differ only within the subspace $\mathbf{S}$, but an $N \times N$ matrix eigenvalue problem can determine the non-matching eigenvalues and eigenfunctions. If the base problem eigenfunctions form a complete set, then as $N \rightarrow \infty$ the operator $[R^{-1}]^{-1} \rightarrow R$ so that $H_{\mathrm{B}} \rightarrow H$ and convergent lower bounds to E_{n} are obtained. Unfortunately, for atomic and molecular systems, the infinite number of *bound* states of h do not form a complete set so that the lower bounds provided by H_{B} do not converge to E_{n} of H.

As in the last section we ignore the base problem eigenfunctions and choose any subspace $\mathbf{S}$ we wish, only this time the subspace is not limited to be one-dimensional. We redefine the intermediate Hamiltonian with a dependence on a N-dimensional subspace $\mathbf{S}_{\mathrm{N}}$ in Eq. (23) indicated by $H_{\mathrm{I}}(\mathbf{S}_{\mathrm{N}})$.

$$H \geq H_I(\mathbf{S}_N) \equiv h + [R^{-1}]^{-1} \tag{23}$$

The operator $[R^{-1}]^{-1}$ takes the same meaning as in the previous section except that it is the null extension of an $N \times N$ matrix to all of Hibert space. The simplest subspace to work with is that generated by the basis set used in variational upper bound calculations. If this basis set is complete in the limit of $N \rightarrow \infty$, then $\mathbf{S}_{\mathrm{N}}$ approaches the full Hilbert space and we expect $[R^{-1}]^{-1}$ to approach R. Thus $H_{\mathrm{I}}(\mathbf{S}_{\mathrm{N}}) \rightarrow H$ as desired.

It is simplest to mimic the traditional use of the Temple formula: a variationally-determined trial functionin $\mathbf{S}_{\mathrm{N}}$ is used to determine the Temple lower bound. However, in Sect. 5 we saw that such a trial function may not yield the optimal lower bound. Thus in addition to calculating the Temple lower bound, we turn to the more general Lehmann-Maehly method and consider the matrix eigenvalue problem $[H - E_{2,\mathrm{low}}]\,\chi_{\mathrm{n}} = \Lambda_{\mathrm{n}}[(H - E_{2,\mathrm{low}})^2]\,\chi_{\mathrm{n}}$ where $[A]$ is the matrix representation of operator A on $\mathbf{S}_{\mathrm{N}}$. If $\Lambda_1 < 0$ then $E_1 \geq E_{2,\mathrm{low}} + \Lambda_1^{-1}$. We use $E_{2,\mathrm{low}} = e_2$ and naturally substitute $H_{\mathrm{I}}(\mathbf{S}_{\mathrm{N}})$ for H. This approach is described nicely in Scrinzi's application to the hydrogen anion, H^- [9].

Both bounds rely on a matrix-eigenvalue problem using a basis set composed of the functions in Eq. (24) indexed by integer parameters $0 \leq x = y \leq x_{\max}$ and $0 \leq z \leq z_{\max}$ where maximum values determine the size of the basis set. The exponential parameter a was set at 2 for all calculations.

$$\phi_{x,y,z} = e^{-a(r_1+r_2)} r_{12}^z (r_1^x r_2^y + r_1^y r_2^x) \tag{24}$$

For the Temple formula, a variational calculation was performed using the basis set and the best variational function was used to calculate the lower bound. For the Lehmann-Maehly method the eigenvalue problem $[H - E_{2,\mathrm{low}}]\,\chi_{\mathrm{n}} = \Lambda_{\mathrm{n}}[(H - E_{2,\mathrm{low}})^2]\,\chi_{\mathrm{n}}$ was solved.

Table 1 shows the convergence to $E_1 = -2.903724$ of H of the lower bounds generated by both the Temple formula and the Lehmann-Maehly method applied to $H_{\mathrm{I}}(\mathbf{S}_{\mathrm{N}})$. Also shown are the upper bounds for ε_1 of $H_{\mathrm{I}}(\mathbf{S}_{\mathrm{N}})$ which are often below E_1 because $H_{\mathrm{I}}(\mathbf{S}_{\mathrm{N}})$ is less than H. At first the basis set was constructed using similar powers for the individual electron radial positions, r_1 and r_2, and relative position r_{12} variables, but it was discovered that superior lower bounds resulted when more

Table 1 Upper and lower bounds to the ground-state energy of the intermediate Hamiltonian $H_I(\mathbf{S}_N)$ are determined for various $\mathbf{S}_N$. The lower bounds serve as lower bounds to E_1 of H for the helium atom

Basis set size = N	x_{max}	z_{max}	Upper bound	Lehmann-Maehly lower bound	Temple lower bound
1	0	0	−3.085 714 286	−3.085 714 286	−3.085 714 286
6	1	1	−2.933 974 727	−3.048 822 223	−3.138 926 160
18	2	2	−2.915 962 194	−2.947 219 805	−2.972 002 182
40	3	3	−2.909 720 909	−2.919 285 244	−2.937 062 170
75	4	4	−2.907 157 764	−2.911 208 056	−2.922 617 097
126	5	5	−2.905 911 301	−2.907 859 204	−2.915 154 402
196	6	6	−2.905 223 737	−2.906 271 725	−2.911 090 828
288	7	7	−2.904 808 897	−2.905 431 024	−2.908 748 257
405	*8*	*8*	*−2.904 541 332*	*−2.904 939 765*	*−2.907 314 266*
410	*3*	*40*	*−2.903 833 448*	*−2.903 874 639*	*−2.904 023 260*
610	3	60	−2.903 774 211	−2.903 813 435	−2.903 905 563
861	5	40	−2.903 820 073	−2.903 823 319	−2.903 900 783
1010	3	100	−2.903 742 173	−2.903 780 961	−2.903 853 075
1215	4	80	−2.903 752 053	−2.903 754 259	−2.903 766 269
1515	4	100	−2.903 742 309	−2.903 744 421	−2.903 751 243

emphasis was placed on the relative position. The two italicized rows in Table 1 illustrate the different quality of the two basis set strategies.

As the basis set size increased the difference between the upper and lower bounds to ε_1 of $H_I(\mathbf{S}_N)$ generally diminishes. The exception is the first row in table 1 for which the intermediate problem is exactly soluble so the bounds are identical. Convergence of both bounds to the true energy $E_1 = -2.903724$ of H was slower than the convergence to to ε_1 of $H_I(\mathbf{S}_N)$. Our approach using $H_I(\mathbf{S}_N)$ gave the best lower bound of -2.90374 with a basis set of 1515 functions; this matches the true energy to five digits. Identical lower bound calculations using the full form of the Hamiltonian operator show convergence to six digits with a basis set size of just 400 for both the Temple and Lehmann-Maehly methods.

13 Conclusion

Through a common derivation of the Bazley and Temple lower bound methods we have shown that significant improvements in both methods can result by merging aspects of each. Because the common derivation is valid only in the scalar setting, capitalizing on the improvements is difficult. In contrast the original Bazley method easily extends beyond the scalar form and the Temple method becomes the Lehmann-Maehly approach in matrix form.

Because of this severe limitation we introduced a new way to merge the two methods. Bazley's approach was used to define an intermediate problem with an intermediate Hamiltonian operator. However, we did not restrict the construction of the

intermediate Hamiltonian by requiring that its eigenvalue problem be exactly soluble. Rather we decided to calculate lower bounds to its eigenvalues by applying the Temple or Lehmann-Maehly method to the intermediate problem. This gives great variety in forming the intermediate Hamiltonian and it is simplest to form it in such a way that mimics a variational upper bound calculation. The results given in Sect. 12 show that convergence is possible using this final merger of two methods, though convergence may be slower than in the Temple or Lehmann-Maehly method applied to the full Hamiltonian operator.

The advantage of our method over the Bazley's approach is due entirely to the fact that we have little or no restriction for the basis set. For our example with the Helium atom, lower bounds from Bazley's method do not converge to the true energies because the basis set of the base problem is incomplete, even in the limit of infinite size. The flexibility of our method allows us to choose a potentially complete basis set and thus achieve convergence to arbitrary precision. This convergence is slower than for the Temple or Lehmann-Maehly methods. We pay this price of slow convergence for the simpler integrals required in our approach as we avoid expectation values of the full square of the Hamiltonian operator. We conclude that we have a practical lower bound method that offers some advantages over traditional methods.

References

1. C. Beattie, Electron. Trans. Num. Anal. **7**, 18–39 (1998)
2. Alexander Weinstein, William Stenger, *Methods of Intermediate Problems for Eigenvalues* (Academic Press, Inc., New York, 1972)
3. Norman W. Bazley, Phys. Rev. **120**, 144–149 (1960)
4. G. Temple, Proc. Roy. Soc. Lond. Ser. A. **119**, 276–293 (1928)
5. F.W. King, J. Chem. Phys. **102**, 8053–8058 (1995)
6. A. Luchow, H. Keindienst, Int. J. Quantum Chem. **51**, 211–224 (1994)
7. C. Eckart, Phys. Rev. **36**, 878–892 (1930)
8. F.J. Weinhold, Math. Phys. **11**(7), 2127–2138 (1970)
9. Armin Scrinzi, Phys. Rev. A **45**(11), 7787–7791 (1992)
10. M.G. Marmorino, J. Math. Chem. **49**, 1535–1543 (2011)