

# Optimization of the temple lower bound

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**Abstract** The Temple formula is perhaps the most common method used in the uncommon endeavor of calculating a lower bound to the ground-state energy of an atomic or molecular system. We generalize the Temple formula by introducing a parameter that can be varied to optimize the lower bound. This generalization does not require any information that is not already used for the traditional Temple lower bound. Examples with the helium cation and neutral atom show that improvement is greatest when the approximate wave function poorly approximates the true ground-state wave function. The examples also show that in some cases the traditional Temple lower bound may already be optimal so that our generalization gives no improvement.

**Keywords** Lower bound · Temple · Helium

## 1 Introduction

Although the application of quantum mechanics to chemistry has been very successful, there is, of course, still room for improvement. Energies and other properties predicted by calculation are generally produced with no rigorous quantification of error. For example, the variational upper bound provides the upper half of an error bar on the energy, but a lower bound is typically lacking. Furthermore, most bounds on properties other than energy rely on bounds to the latter (indirectly through the

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overlap of a trial function with the unknown exact wave function), making bounds to non-energy properties very difficult indeed [1–5]. Perhaps the best-known error bar for a system's property is the combination of the variational upper bound and the Temple lower bound to the ground-state energy,  $E_1$ . For the ground state of a system, the expectation value,  $\langle \phi | H \phi \rangle$ , of the Hamiltonian operator,  $H$ , with any allowable normalized trial function,  $\phi$ , gives an energy too high, except in the rare case that the trial function happens to be the wave function of the ground state. Inequality (1) gives the variational upper bound,  $E_{\text{var}}$ .

$$E_{\text{var}} \equiv \langle \phi | H \phi \rangle \geq E_1 \quad (1)$$

The Temple lower bound [5] is more difficult to determine than the variational upper bound. First, it requires knowledge of the first excited-state energy,  $E_2$ . This is rarely known, but a lower bound  $E_{2,\text{low}}$  can be used in place of  $E_2$  with no loss of rigor. Still, even such a lower bound is uncommon, typically requiring an exactly soluble reference (or base) problem that has energies strictly less than the problem of interest. Second, the expectation value  $\langle \phi | H^2 \phi \rangle$  must be determined and its calculation is more difficult than  $\langle \phi | H \phi \rangle$ . Furthermore, for some trial functions,  $\langle \phi | H^2 \phi \rangle$  may not exist. These three quantities are combined in inequality (2) as the Temple lower bound,  $E_{\text{Tem}}$ , valid as long as the energy estimate  $\langle \phi | H \phi \rangle$  is less than  $E_{2,\text{low}}$ .

$$E_1 \geq E_{\text{Tem}} \equiv \frac{E_{2,\text{low}} \langle \phi | H \phi \rangle - \langle \phi | H^2 \phi \rangle}{E_{2,\text{low}} - \langle \phi | H \phi \rangle} \quad (2)$$

Together, the Temple lower bound and variational upper bound give an error bar around the ground-state energy:  $E_{\text{var}} \geq E_1 \geq E_{\text{Tem}}$ . Only with an error bar can one be sure of the quality of a system property. In this report we generalize the Temple lower bound by introducing a parameter that allows optimization of the bound. This parameter is independent of the trial function and does not change any of the basic integrals that must be calculated. The only change from the traditional Temple bound is how the basic integrals comprising the expectation values  $\langle \phi | H \phi \rangle$  and  $\langle \phi | H^2 \phi \rangle$  are arithmetically combined. Thus the generalization is inherently simple. In many cases, however, the traditional Temple lower bound is already optimal.

## 2 Parameterizing the Temple bound

The Hamiltonian operator governing the system of interest is denoted by  $H$ ; its eigenvalues are denoted by  $E_n$ . In addition, we define a fictitious Hamiltonian operator  $h$  which is parameterized by  $c$ . Its eigenvalues,  $e_n$ , also depend on the parameter  $c$ . This parameter is essentially a coefficient for a part of  $H$ . For example, we initially consider the one-electron system of the helium cation,  $\text{He}^+$ , in the limit of infinite nuclear mass using atomic units. Its Hamiltonian is given in Eq. (3) in spherical coordinates. The fictitious operator,  $h$ , is given in Eq. (4) where we have chosen to parameterize the potential by  $c$ . For complicated potentials where multiplication by a scalar does not strictly increase or decrease the function, one may be able to work with just part of the potential or the kinetic energy operator.

$$H = -\frac{1}{2}\nabla^2 - \frac{2}{r} \quad (3)$$

$$h = -\frac{1}{2}\nabla^2 - \frac{c}{r} \quad (4)$$

Depending on the choice of the parameter one can construct  $h$  so that it equals  $H$  (e.g.  $c = 2$ ), is greater than  $H$  (e.g.  $c < 2$ ), or is less than  $H$  (e.g.  $c > 2$ ). We are interested in only those choices that make  $h < H$  so that the eigenvalues  $e_n$  of  $h$  are lower bounds to the eigenvalues  $E_n$  of  $H$ . Rather than calculate a lower bound to  $E_1$ , we propose to calculate a lower bound to  $e_1$ . This seems inefficient as we will calculate a lower bound ( $e_{\text{Tem}}$ ) to a lower bound ( $e_1$ ) obtaining the sequence  $E_1 > e_1 \geq e_{\text{Tem}}$ , rather than calculating a direct lower bound ( $E_{\text{Tem}}$ ) which would give  $E_1 \geq E_{\text{Tem}}$ . Nevertheless we will sometimes encounter the remarkable situation illustrated in inequality (5).

$$E_1 > e_1 \geq e_{\text{Tem}} > E_{\text{Tem}} \quad (5)$$

The Temple bound can be written differently than inequality (2) and we show this in inequality (6) for  $H$  and inequality (7) for  $h$ . For both inequalities we write  $\varepsilon_2 = E_{2,\text{low}} = e_{2,\text{low}}$  because if lower bounds to  $E_2$  and  $e_2$  are available, they are likely to be the same, as will be illustrated in the examples that follow.

$$E_1 \geq E_{\text{Tem}} = \langle \phi | H \phi \rangle - \frac{\langle \phi | H^2 \phi \rangle - \langle \phi | H \phi \rangle^2}{\varepsilon_2 - \langle \phi | H \phi \rangle} \quad (6)$$

$$E_1 > e_1 \geq e_{\text{Tem}} = \langle \phi | h \phi \rangle - \frac{\langle \phi | h^2 \phi \rangle - \langle \phi | h \phi \rangle^2}{\varepsilon_2 - \langle \phi | h \phi \rangle} \quad (7)$$

Comparing the first terms in the two lower bounds of inequalities (6) and (7) immediately shows that  $e_{\text{Tem}}$  starts as a poorer bound to  $E_1$  than  $E_{\text{Tem}}$  because  $h < H$  dictates that  $\langle \phi | h \phi \rangle < \langle \phi | H \phi \rangle$ . However, both bounds are then adjusted by the subtraction of an amount. It may be that the trial function  $\phi$  is poorly suited to  $H$  so that the energy variance  $\langle \phi | H^2 \phi \rangle - \langle \phi | H \phi \rangle^2$  is quite large and thus  $E_{\text{Tem}}$  will be much lower than  $\langle \phi | H \phi \rangle$  because of a large subtracted term in inequality (6). At the same time it may be that the trial function  $\phi$  is well suited to  $h$  so that the energy variance  $\langle \phi | h^2 \phi \rangle - \langle \phi | h \phi \rangle^2$  is very small and thus  $e_{\text{Tem}}$  will be just slightly lower than  $\langle \phi | h \phi \rangle$  because of a small subtracted term in inequality (7). In this situation, then, it could be that  $e_{\text{Tem}} > E_{\text{Tem}}$ . Furthermore, even if the variances for  $h$  and  $H$  are equal, the fact that  $h < H$  forces the denominator  $\varepsilon_2 - \langle \phi | h \phi \rangle$  to be larger than  $\varepsilon_2 - \langle \phi | H \phi \rangle$ , which would make the subtracted amount in (7) smaller than that in (6).

Despite the reasonable hope that  $e_{\text{Tem}}$  may be superior to  $E_{\text{Tem}}$  as a lower bound to  $E_1$ , we must realize the limitations. Obviously if  $h \ll H$  then it will be impossible to get a tight lower bound to  $E_1$  as we will always have that  $e_{\text{Tem}} < e_1 \ll E_1$ . While  $e_{\text{Tem}}$  may be better than  $E_{\text{Tem}}$  in such a case, the bound, though improved, will be poor. On the other hand if  $h \approx H$ , then there will be little difference in the expectation values contributing to  $e_{\text{Tem}}$  and  $E_{\text{Tem}}$  and the two bounds will be close. In this case the dominant factor in inequalities (6) and (7) may be the initial terms  $\langle \phi | H \phi \rangle$  and

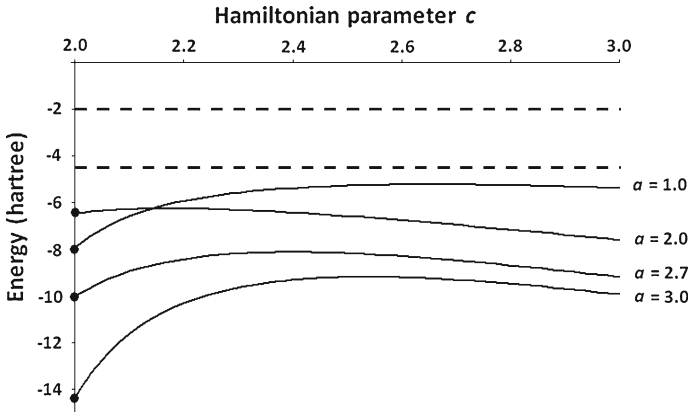
$\langle \phi | h \phi \rangle$ , respectively, so that  $E_{\text{Tem}}$  is the better bound. Our prediction then is that the parameterization of the Temple lower bound will prove most effective in increasing the lower bound when the trial function and traditional Temple lower bound are poor. For an accurate trial function we expect the traditional Temple bound to be optimal. This is upheld by the data in the following sections.

### 3 The helium cation, $\text{He}^+$

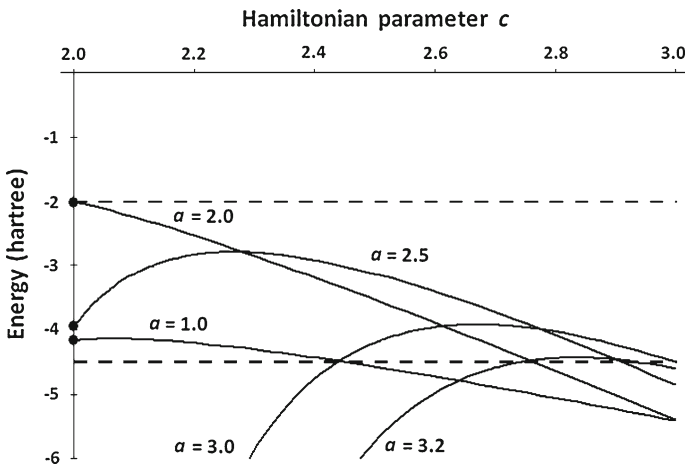
As a simple illustration of our generalized Temple lower bound we continue with the helium cation as a test system. The energy levels of all one-electron atoms ( $\text{H}$ ,  $\text{He}^+$ ,  $\text{Li}^{2+}$ , ...) are given by the formula  $E_n = -Z^2 / (2n^2)$  hartree where the atomic number  $Z$  and the quantum number  $n$  are natural numbers. We use the lithium dication,  $\text{Li}^{2+}$ , with  $Z = 3$ , as a reference (base) problem for the helium cation,  $\text{He}^+$ , with  $Z = 2$ . Because of the greater nuclear attraction of  $\text{Li}^{2+}$ , all of its energy levels lie below those of  $\text{He}^+$  to serve as poor lower bounds for the latter. In particular, the lithium dication gives the following poor lower bounds to the first two energy levels of the helium cation:  $E_1 > E_{1,\text{low}} = E_1(\text{Li}^{2+}) = -4.5$  hartree and  $E_2 > E_{2,\text{low}} = E_2(\text{Li}^{2+}) = -1.125$  hartree.

For an accurate trial function, the variational upper bound and Temple lower bound should provide a tight error bar around  $E_1 = -2$  hartree. The upper bound is merely  $\langle \phi | H \phi \rangle$ . The Temple bound is calculated using both  $H$  and  $h$ , given in Eqs. (3) and (4) for comparison. We have already noted that we must have  $c > 2$  to force  $h < H$ . It also makes sense to restrict  $c < 3$  because  $h$  becomes the Hamiltonian of the  $\text{Li}^{2+}$  system for  $c = 3$ ; for  $c \geq 3$  the Temple bound can give no better result than the ground-state energy of  $\text{Li}^{2+}$ ,  $-4.5$  hartree, which already serves as a known poor lower bound to  $E_1$ . Thus  $c$  is restricted to the range  $2 < c < 3$  for our generalization. In this range, the energies of the  $\text{Li}^{2+}$  system serve as lower bounds to the energies of both  $h$  and  $H$ , so that  $\varepsilon_2 = e_{2,\text{low}} = E_{2,\text{low}} = -1.125$  hartree (recall the shared value of  $E_{2,\text{low}}$  and  $e_{2,\text{low}}$  suggested in the previous section).

There are a wide range of simple trial functions available for the helium cation ground-state wave function besides the obvious choice of simple exponential decay,  $e^{-ar}$ , that yields the exact solution for  $a = Z$ . The following functions, shown unnormalized, were all considered before exponential decay:  $\exp(-ar^2)$ ,  $\text{sech}(ar)$ ,  $(r^2 + a^2)^{-1}$ ,  $(a + r)^{-2}$ , and  $(1 - a/r)^2$ . The last trial function is non-zero only on the range  $r \in [0, a)$ . Each trial function has a variable parameter  $a$  completely unrelated to the Hamiltonian parameter  $c$ . Data is given in Fig. 1 for only the hyperbolic secant trial function, though it is representative of all these functions. For nearly all choices of  $a$ , variation of the Hamiltonian parameter  $c$  away from its traditional value of 2 (when  $h = H$ ) allowed improvement of the lower bound. For some trial functions the improvement was enormous. Consider the case of  $a = 1.0$  in Fig. 1. The traditional Temple bound is about  $-8$  hartree (filled circle at the left) but when  $h < H$  with  $c \approx 2.7$  the Temple bound was optimized to about  $-5$  hartree. Unfortunately, even the optimized Temple bounds are worse than the poor lower bound of  $-4.5$  hartree



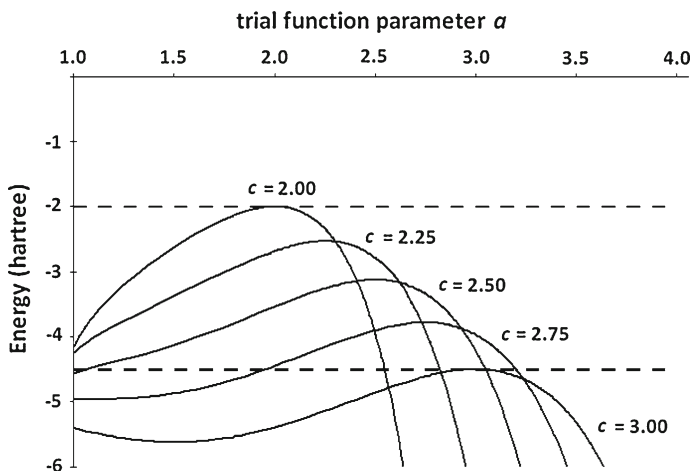
**Fig. 1** Temple lower bounds  $e_{\text{Tem}}$  from  $h$  are plotted against the Hamiltonian parameter  $c$  for the normalized trial function  $\phi = 2\pi^{-1} (3a^3)^{1/2} \text{sech}(-ar)$ . The two dashed horizontal lines are  $E_1 = -2$  hartree for the helium cation,  $\text{He}^+$ , and its poor lower bound  $E_{1,\text{low}} = -4.5$  hartree from the reference problem. Unoptimized Temple lower bounds are shown as *darkened circles*



**Fig. 2** Temple lower bounds  $e_{\text{Tem}}$  from  $h$  are plotted against the Hamiltonian parameter  $c$  for trial function  $\phi = 2a^{3/2} e^{-ar}$ . The two dashed horizontal lines are  $E_1 = -2$  hartree for the helium cation,  $\text{He}^+$ , and its poor lower bound  $E_{1,\text{low}} = -4.5$  hartree from the reference problem. Unoptimized Temple lower bounds are shown as *darkened circles*. Note that the curve for  $a = 2$  is for the true wave function

(straight line) provided by the reference problem and so are not useful. While we have succeeded in showing that the Temple lower bound can be significantly improved in some cases, we have not obtained a tight bound in this example.

To see the success of optimization over the traditional bound and the lower bound offered by the base problem we needed a superior trial function. Using normalized  $\phi = 2a^{3/2} e^{-ar}$  as the trial function, we can get arbitrarily close to the true ground-state wave function with  $a = 2$ . In Fig. 2, the Temple lower bound is plotted against Hamiltonian parameter  $c$  for various choices of  $a$ . Again optimization provides improved



**Fig. 3** Temple lower bounds  $e_{\text{Tem}}$  from  $h$  calculated using different choices of Hamiltonian parameter  $c$  are plotted against parameter  $a$  in the trial function  $\phi = 2a^{3/2}e^{-ar}$ . The two dashed horizontal lines are  $E_1 = -2$  hartree for the helium cation,  $\text{He}^+$ , and its poor lower bound  $E_{1,\text{low}} = -4.5$  hartree from the reference problem. The curve with  $c = 2.00$  is the set of traditional Temple lower bounds

lower bounds over the traditional Temple formula; the only exception is when the exact wave function ( $a = 2$ ) is used as the trial function. Furthermore, we see that as the trial function becomes more accurate ( $a \rightarrow 2$ ), the lower bounds are able to rise above the poor lower bound ( $-4.5$  hartree) of the reference problem.

To analyze the performance of optimization we plot the Temple lower bounds,  $e_{\text{Tem}}$ , against trial function parameter  $a$  for different choices of Hamiltonian parameter  $c$  in Fig. 3. For a given choice of  $c$  one finds that the lower bound is highest (best) when  $a = c$ . This is when the trial function is the true wave function for  $h$  so that the  $e_{\text{Tem}}$  is merely  $e_1 = \langle \phi | h \phi \rangle$ . The energy variance is zero so that nothing is subtracted from  $\langle \phi | h \phi \rangle$  in inequality (7) to lessen the bound. This supports our earlier suggestion that the generalization will work best when the trial function is poorly suited to the true Hamiltonian operator  $H$  and better suited to the operator  $h$ .

#### 4 The helium atom, He

We now apply our parameterization of the Temple lower bound to the simplest realistic chemical problem: the two-electron helium atom. The Hamiltonian for this system is given in Eq. (8) with  $c = 1$  using atomic units with infinite nuclear mass. The separation between the two orbiting electrons is given by  $r_{12}$ . In this system the parameter  $c$  multiplies the positive electron-repulsion potential rather than the negative nuclear-attraction potential.

$$h = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + \frac{c}{r_{12}} \quad (8)$$

The Schrödinger equation for the helium atom cannot be solved exactly. The ground-state energy is known to great precision,  $E_1 \approx -2.904$  hartree, from variational calculations supplemented with the Temple formula [6]. In this section we try to optimize the Temple lower bound as a test of our generalization. The helium atom is a positive perturbation of a hydrogenic-like atom (with no repulsion between the two electrons) for which the lowest two energies are  $-4$  hartree and  $-2.5$  hartree. These serve as poor lower bounds to  $E_1$  and  $E_2$  of the helium atom, respectively. The latter,  $E_{2,\text{low}} = -2.5$  hartree, is necessary for the Temple lower bound.

With  $c = 1$ , the variational method gives the optimal upper bound as  $E_{\text{var}} = -2.848$  hartree for the normalized trial function  $\phi = a^3 \pi^{-1} \exp[-a(r_1 + r_2)]$  with  $a = 27/16$ . Using this same trial function to calculate the Temple lower bound (again using the full Hamiltonian operator with  $c = 1$ ) gives an extremely poor value of  $-5.429$  hartree. By varying  $a$  to consider a function not optimal for the upper bound, one can slightly improve the lower bound to  $-5.293$  hartree with  $a = 1.772$ . When  $c < 1$  we have a fictitious Hamiltonian operator  $h$  with energies  $e_n$  lower than that of the helium atom. As in the previous section, lower bounds to the energies of these lesser-energy systems yield lower bounds to the true energies. Returning to  $a = 27/16$ , the optimized Temple lower bound is  $-3.980$  hartree with  $c = 0.485$ . This is well above the traditional Temple lower bound of  $-5.429$  hartree but just barely above the trivial lower bound of  $-4$  hartree from the reference problem of two electrons without electron-electron repulsion. Further improvement is achieved by varying both  $a$  (in the trial function) and  $c$  (in the operator) which gives an optimal Temple lower bound of  $-3.646$  hartree with  $a = 1.935$  and  $c = 0.472$ .

For the simple trial function with the single variable parameter  $a$ , the error bar made from the variational upper bound and the optimized Temple lower bound is  $-2.848$  hartree  $\geq E_1 \geq -3.646$  hartree. Both the upper and lower bounds are not close to the true value of  $-2.904$  hartree. A superior trial function is needed for improvement and the simplest way to proceed is with the linear variation method to first improve the upper bound. While something similar can be done for the Temple lower bound, it is simplest to use the trial function optimized in the upper bound calculation to determine expectation values of  $H$  and  $H^2$  (or  $h$  and  $h^2$ ) for use in the Temple lower bound. This is what we do now. The basis set for the variational calculation is made of the basis functions  $\chi_{x,y,z}$  expressed in Eq. (9).

$$\chi_{x,y,z} = r_{12}^z (r_1^x r_2^y + r_1^y r_2^x) e^{-a(r_1+r_2)} \quad (9)$$

The coordinates are spherical in nature, so  $x$ ,  $y$ , and  $z$  are not Cartesian coordinates, but rather integer indices denoting different  $\chi$ . The basis set is made by including all possible versions of  $\chi_{x,y,z}$  for integer  $x \in [0, x_{\text{max}}]$ ,  $y \in [0, y_{\text{max}}]$ , and  $z \in [0, z_{\text{max}}]$ . This symmetric spatial basis set is suitable for investigating the ground-state of the helium atom and excited null angular momentum singlet ( $^1S$ ) states. Once the matrix eigenvalue problem is solved to determine the best-fit trial function  $\phi$  for the ground state along with  $E_{\text{var}}$ , the former is used to determine the Temple lower bound. Rather than plot  $e_{\text{Tem}}$  against the parameter  $c$ , the optimal  $c$  was first determined symbolically in terms of the expectation values used in the traditional Temple bound.

We write the Hamiltonian in Eq. (8) as  $h = A + cB$  and substitute this in the Temple formula to give inequality (10), where we omit the trial function  $\phi$  from the expectation value symbol for simplicity. The maximum  $e_{\text{Tem}}$  is determined by the zero derivative of the right-hand side of inequality (10). Equation (11) identifies the optimal value of the parameter,  $c_{\text{opt}}$ , as one of the solutions of the resulting quadratic equation where  $X \equiv e_2 \langle A \rangle - \langle A^2 \rangle$ ,  $Y \equiv e_2 \langle B \rangle - \langle AB \rangle - \langle BA \rangle$ , and  $Z \equiv e_2 - \langle A \rangle$ . The optimal value is expressed in terms of the expectation values  $\{\langle A \rangle, \langle B \rangle\}$  used in  $\langle H \rangle$  and  $\{\langle A^2 \rangle, \langle B^2 \rangle, \langle AB \rangle, \langle BA \rangle\}$  used in  $\langle H^2 \rangle$ . Equations (10) and (11) are valid for any system as the Hamiltonian is expressed very generally as  $h = A + cB$ .

$$E_1 \geq e_{\text{Tem}} = \frac{e_2 (\langle A \rangle + c \langle B \rangle) - (\langle A^2 \rangle + c \langle AB \rangle + c \langle BA \rangle + c^2 \langle B^2 \rangle)}{e_2 - (\langle A \rangle + c \langle B \rangle)} \quad (10)$$

$$c_{\text{opt}} = \frac{Z}{\langle B \rangle} \pm \frac{1}{\langle B \rangle} \sqrt{Z^2 - \frac{ZY}{\langle B \rangle \langle B^2 \rangle} - \frac{X}{\langle B^2 \rangle}} \quad (11)$$

Note that the only effort needed beyond that of calculating a traditional Temple lower bound is a quick algebraic substitution in Eq. (11) to determine  $c_{\text{opt}}$  to use in inequality (10). All the expectation values needed have been calculated for use already in the traditional Temple lower bound. The acceptable domain of parameter  $c$  is  $c \in (0, 1]$ . If  $0 < c_{\text{opt}} < 1$  then  $e_{\text{Tem}} > E_{\text{Tem}}$  so there is improvement over the traditional Temple bound. On the other hand, if  $c_{\text{opt}} = 1$ , or if an erroneous  $c_{\text{opt}} > 1$  results, then  $E_{\text{Tem}} > e_{\text{Tem}}$  so that the traditional Temple bound is already optimal.

Table 1 reports the Temple lower bound for various basis sets denoted by the maximum values of  $x$ ,  $y$ , and  $z$ ; the exponential parameter was always  $a = 2$ . Only when the basis functions lacked dependence on  $r_{12}$  ( $z_{\text{max}} = 0$ ) did parameterization consistently improve the lower bound. In these cases improvement was significant, but because the trial function lacked flexibility to approach the true wave function the lower bound was not able to approach the true value  $E_1$ . For greater accuracy the inclusion of basis functions with powers of  $r_{12}$  ( $z_{\text{max}} > 0$ ) was needed. This greatly improved both the variational upper bound and the traditional Temple lower bound. In these cases the quality of the optimum variational trial function was such that the traditional Temple bound was not optimal in only one case ( $x_{\text{max}} = y_{\text{max}} = z_{\text{max}} = 1$ ) – otherwise  $c_{\text{opt}} > 1$  resulted. Basis sets with  $z_{\text{max}} > 1$  were tested, but the results are not shown; optimization was not successful. For a given  $z_{\text{max}}$ , the general trend was that the lower bound improved as  $x_{\text{max}}$  and  $y_{\text{max}}$  increased. There is an obvious upset to this trend for the  $x_{\text{max}} = y_{\text{max}} = 1$  data. In these cases the lower bound was worse than that for the smaller basis set calculations with  $x_{\text{max}} = y_{\text{max}} = 0$ . This is presumably caused by the optimization of the trial function for the variational upper bound, which in the cases of  $x_{\text{max}} = y_{\text{max}} = 1$  unfortunately left the trial function poorly suited for lower bound determination, optimized or not.



**Table 1** Lower bounds to the He ground-state energy

	$z_{\max} = 0$	$z_{\max} = 1$
$x_{\max} = y_{\max} = 0$	$E_{\text{Tem}} = -7.167$ $e_{\text{Tem}} = -3.675$ (0.428)	$E_{\text{Tem}} = -3.171$ $e_{\text{Tem}} = NA$ (1.067)
$x_{\max} = y_{\max} = 1$	$E_{\text{Tem}} = -5.574$ $e_{\text{Tem}} = -4.120$ (0.478)	$E_{\text{Tem}} = -3.289$ $e_{\text{Tem}} = -3.2704$ (0.932)
$x_{\max} = y_{\max} = 2$	$E_{\text{Tem}} = -4.046$ $e_{\text{Tem}} = -3.551$ (0.666)	$E_{\text{Tem}} = -2.977$ $e_{\text{Tem}} = NA$ (1.089)
$x_{\max} = y_{\max} = 3$	$E_{\text{Tem}} = -4.008$ $e_{\text{Tem}} = -3.535$ (0.672)	$E_{\text{Tem}} = -2.938$ $e_{\text{Tem}} = NA$ (1.106)
$x_{\max} = y_{\max} = 4$	$E_{\text{Tem}} = -3.967$ $e_{\text{Tem}} = -3.522$ (0.678)	$E_{\text{Tem}} = -2.936$ $e_{\text{Tem}} = NA$ (1.108)
$x_{\max} = y_{\max} = 5$	$E_{\text{Tem}} = -3.961$ $e_{\text{Tem}} = -3.515$ (0.681)	$E_{\text{Tem}} = -2.934$ $e_{\text{Tem}} = NA$ (1.110)
$x_{\max} = y_{\max} = 6$	$E_{\text{Tem}} = -3.953$ $e_{\text{Tem}} = -3.512$ (0.683)	$E_{\text{Tem}} = -2.933$ $e_{\text{Tem}} = NA$ (1.111)
$x_{\max} = y_{\max} = 7$	$E_{\text{Tem}} = -3.947$ $e_{\text{Tem}} = -3.509$ (0.684)	$E_{\text{Tem}} = -2.932$ $e_{\text{Tem}} = NA$ (1.115)

Temple lower bounds  $e_{\text{Tem}}$  and  $E_{\text{Tem}}$  are calculated for the helium atom ground-state energy  $E_1$  using variationally optimized trial functions from different basis sets distinguished by  $\{x_{\max}, y_{\max}, z_{\max}\}$  as indicated in the text. The value of  $c_{\text{opt}}$  used to calculate  $e_{\text{Tem}}$  is given in parentheses after  $e_{\text{Tem}}$ . Energies are measured in hartree units

### 5 No improvement for the variational upper bound

In light of the success in optimizing the Temple lower bound, it is reasonable to ask if the variational upper bound can be improved by an increase (rather than a decrease) in the Hamiltonian operator. That is, can we calculate an upper bound  $e_{\text{var}}$  to  $e_1$  of  $h > H$  that is superior (less) than an upper bound  $E_{\text{var}}$  to  $E_1$  of  $H$ . In this example we assign the variability to the positive-definite kinetic energy operator  $T$  and write  $H = T + V$  where  $V$  is the potential energy operator. Next we define  $h = cT + V$  where  $c > 1$ . Equation (12) shows that the variational upper bound using  $h$  can never be less than that from  $H$  for any normalized trial function  $\phi$ . Thus no improvement is possible.

$$e_{\text{var}} = \langle \phi | h \phi \rangle = c \langle \phi | T \phi \rangle + \langle \phi | V \phi \rangle > \langle \phi | T \phi \rangle + \langle \phi | V \phi \rangle = \langle \phi | H \phi \rangle = E_{\text{var}} \quad (12)$$

### 6 Conclusion

As our tests with the helium cation and helium atom show, we have successfully generalized the Temple method. By introducing a simple multiplicative parameter into part of the Hamiltonian operator of the system, the Temple lower bound itself becomes dependent on the parameter. This parameter can then be varied to optimize

the Temple lower bound. In some cases the traditional Temple bound is already optimal, but in other cases there may be significant improvement.

Our hypothesis concerning the performance of optimization was that improvement over the traditional bound would be greatest when the trial function was poor. This was confirmed with the helium atom when basis sets with few functions and functions independent of the interelectron distance were used. Confirmation is also evident in figure 1 where poor trial functions for the helium cation were used. Most often, improvement in the estimate of a system's energy is the result of improving the trial function. In some cases, this may be difficult, and a simple modification of the Hamiltonian may provide an alternative. Even in other cases, however, our generalization is worthwhile as it requires no information that is not already used in the traditional Temple bound and so is easy to implement.

## References

1. A. Mazziotti, R.G. Parr, *J. Chem. Phys.* **52**, 1605 (1970)
2. N.W. Bazley, D.W. Fox, *J. Math. Phys.* **7**, 413 (1966)
3. P. Jennings, E.B. Wilson Jr., *J. Chem. Phys.* **45**, 1847 (1966)
4. M.G. Marmorino, K. Cassella, *Int. J. Quantum Chem.* **111**, 3588 (2011)
5. G. Temple, *Proc. R. Soc. Lond. Ser. A.* **119**, 276 (1928)
6. N.W. Bazley, *Phys. Rev.* **120**, 144 (1960)