

Eigenvalue lower bounds with Bazley's special choice of an infinite-dimensional subspace

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Abstract Bazley's special choice of a finite-dimensional space to construct an intermediate operator between a base operator and the full Hamiltonian is a standard technique to calculate lower bounds to the energies of a system. We modify Bazley's method to accommodate an infinite-dimensional space that is complete in one particle of the system. An application to the helium atom shows improvement in the lower bound to the ground-state energy, indicating promise in our method. However, significant problems are revealed which include (1) poorer bounds for the excited states, (2) lack of symmetry in the intermediate operator, and (3) lack of direction for improvement.

Keywords Lower bounds · Bazley · Special choice · Helium

1 Introduction

The problem of complementing variational energies (which are upper bounds) with corresponding lower bounds has plagued computational quantum mechanics for nearly a century. Without the pair of bounds, a rigorous error bar around the true energy of a system cannot be determined so that energy estimates cannot be firmly judged as accurate. Instead one typically relies on the stabilization of upper bounds as the basis set size increases in variational calculations. The viability of this approach demands that the basis set contains functions that are able to well describe the system so that the unchanging nature of the upper bounds is due to convergence to the true energies.

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There have been many approaches to the lower bound problem and the reader is suggested to consult [1] for a brief reference to a variety of methods. All suffer from theoretical and/or computational difficulties. One approach is to construct a simpler operator that is less than the Hamiltonian of interest. Because this new operator is simpler, its eigenvalues can typically be determined either exactly or to the desired precision. Furthermore, because the new operator is less than the Hamiltonian, its eigenvalues serve as lower bounds to the system's energies.

This general idea was introduced by Weinstein and developed by Aronzajn but without a simple means to implement it [2]. Bazley [2,3] later devised a practical method for a Hamiltonian that is a positive perturbation of a simpler "base" operator with an exactly known set of eigenvalues and eigenfunctions. The essence of Bazley's approach is inequality (1) where P is a projection operator onto a subspace \mathcal{S} , R is the non-negative perturbation and $[R]$ is the representation (or restriction) of R on subspace \mathcal{S} . Bazley proved this result by considering a special type of inner product. A different proof has been given recently [4].

$$R \geq P[R^{-1}]^{-1}P \geq 0 \quad (1)$$

The application of Bazley's method has generally been limited to finite-dimensional subspaces generated from the eigenfunctions of the base operator. In this report we show that it is possible to use an infinite-dimensional space that only weakly depends on the eigenfunctions of the base operator.

2 Hamiltonian and the base operator

To illustrate our modification of Bazley's method we consider the non-relativistic helium atom with fixed nucleus using atomic units. The particles are the two electrons and the Hamiltonian operator, H , is given in Eqs. (2) and (3). Helium has the atomic number $Z = 2$, r_i is the distance from the origin (nucleus) to the i -th electron, and r_{12} is the distance between the two electrons.

$$H = h_1 + h_2 + r_{12}^{-1} \quad (2)$$

$$h_i = -\left(\frac{1}{2}\Delta_i + \frac{Z}{r_i}\right) \quad (3)$$

The presence of the electron-repulsion operator, r_{12}^{-1} , in H prevents the exact solution of the time-independent Schrödinger equation for the helium atom. The lesser base operator, F , given by Eq. (4), is merely the helium atom without the complicating electron repulsion.

$$F = h_1 + h_2 \quad (4)$$

Both F and H allow for symmetric and antisymmetric solutions, and only these are considered as physically proper because of the electron property of indistinguishability. Operator F is separable in the two particles and so are its eigenfunctions,

being symmetric or antisymmetric products of the one-electron eigenfunctions given by $h_i \psi_i^{(n)} = e^{(n)} \psi_i^{(n)}$ for natural numbers n . We use superscripts to indicate quantum numbers and subscripts (1 or 2) to indicate particle identity. The one-electron energies are $e^{(n)} = -Z^2/(2n^2)$ and the discrete eigenvalues of F are simply the sums $e^{(m)} + e^{(n)}$, which serve as poor lower bounds to the energies of the helium atom. For example, the lowest eigenvalue of F is $e^{(1)} + e^{(1)} = -4$ corresponding to the symmetric product $\psi_1^{(1)} \psi_2^{(1)}$ which is much less than the known energy of -2.9037 for the ground-state of the helium atom.

3 Bazley's intermediate operator

Because the electron-repulsion operator, r_{12}^{-1} , is non-negative we have that $F < H$. This qualifies F as a base operator to H and allows us to construct an intermediate operator G by incorporating some of the electron repulsion by inequality (1). The form of G is given in Eq. (5) yielding the relation $F \leq G \leq H$.

$$G = F + P [r_{12}]^{-1} P \quad (5)$$

Bazley's work on the helium atom [2,3] considered just the symmetric eigenfunctions with only radial dependence, the singlet S states. He constructed an N -dimensional subspace \mathcal{S} from the span of the orthogonal symmetric eigenfunctions $\psi_1^{(1)} \psi_2^{(n)} + \psi_1^{(n)} \psi_2^{(1)}$ for $n = 1$ to N of base operator F . The subspace \mathcal{S} and its orthogonal complement, \mathcal{S}^\perp , are both reducing subspaces for intermediate operator G so that the eigenvalues of G are determined by solving the eigenvalue problem on both spaces separately, and then taking the union of the two sets. On \mathcal{S}^\perp , the intermediate operator G reduces to F so the lowest eigenvalues on \mathcal{S}^\perp are $e^{(1)} + e^{(n)}$ for $n > N$. The eigenvalues on \mathcal{S} are determined by solving an $N \times N$ matrix eigenvalue problem.

For clarity, in Table 1, we report the seven lowest eigenvalues of G , which Bazley calculated many years ago, when the subspace \mathcal{S} is of dimension $N = 1, 2$ and 3. Bold eigenvalues are those determined on \mathcal{S} . Italicized eigenvalues are from F in \mathcal{S}^\perp . Also reported are data for $N = 100$.

The bound eigenfunctions $\psi_i^{(n)}$ of h_i do not form a complete set of one-particle functions so that, even in the limit of $N \rightarrow \infty$, \mathcal{S} is not able to describe a symmetric two-particle function of the form $\psi_1^{(1)} \chi_2 + \chi_1 \psi_2^{(1)}$ for arbitrary χ .

Table 1 The seven lowest eigenvalues as determined by Bazley as lower bounds to energies of the helium atom as a function of the dimension N of the projected subspace \mathcal{S} .

N	Seven lowest eigenvalues						
1	-3.086 ,	-2.500,	-2.222,	-2.125,	-2.056,	-2.041,	-2.031
2	-3.068 ,	-2.222,	-2.155 ,	-2.125,	-2.056,	-2.041,	-2.031
3	-3.064 ,	-2.166 ,	-2.125,	-2.056,	-2.041,	-2.039 ,	-2.031
100	-3.060 ,	-2.165 ,	-2.066 ,	-2.036 ,	-2.022 ,	-2.015 ,	-2.011

4 Extension to an infinite-dimensional subspace

In our variation of Bazley's method we construct the intermediate operator in the same formal sense: $G = F + P[r_{12}]^{-1}P$. The difference is that we let \mathcal{S} be an infinite-dimensional subspace which is the span of $\varphi_1^{(n)}\psi_2^{(1)}$ for $n = 1$ to ∞ where the set of $\varphi^{(n)}$ form a complete orthonormal basis set of a one-particle Hilbert space. Note that \mathcal{S} is now (1) infinite-dimensional, (2) independent of the base operator eigenfunctions for the first particle, and (3) complete in the space of the first particle. These are desirable properties. We must note, however, that the subspace is no longer symmetric, or even antisymmetric; it lacks symmetry. This property of \mathcal{S} is not desirable, but it seems necessary in order to deal with the infinite-dimensional nature.

Let us now consider the perturbation $P[r_{12}]^{-1}P$ that takes base operator F into intermediate operator G . We start by considering $[r_{12}]$ which is the matrix representation of r_{12} on \mathcal{S} . The (i, j) -th matrix element of this infinite-dimensional matrix $[r_{12}]$ is given in Eq. (6) where \mathbf{r}_i is the vector position of the i -th electron.

$$[r_{12}]_{i,j} = \int \varphi_1^{(i)*} \varphi_1^{(j)} \mathbf{dr}_1 \int |\psi_2^{(1)}|^2 r_{12} \mathbf{dr}_2 \quad (6)$$

The integral over the second particle is the same for each matrix element and yields f_1 , a function of only the first particle, as shown in Eq. (7).

$$f_1 \equiv \int |\psi_2^{(1)}|^2 r_{12} \mathbf{dr}_2 \quad (7)$$

The matrix elements $[r_{12}]_{i,j}$ thus take the form given by Eq. (8).

$$[r_{12}]_{i,j} = \int \varphi_1^{(i)*} f_1 \varphi_1^{(j)} \mathbf{dr}_1 \quad (8)$$

The matrix $[r_{12}]$ over \mathcal{S} is equivalent to the matrix $[f_1]$ over \mathcal{S} . It is well known that the inverse of an operator's representation may not equal the representation of the operator's inverse on a general subspace. The extreme case is for expectation values, $\langle A \rangle^{-1} \neq \langle A^{-1} \rangle$, where A is some operator and the subspace in question is the one-dimensional space generated by the function in the expectation value. However, if the subspace is complete in the coordinates that the operator acts upon, then there is equality between the inverse of the representation and the representation of the inverse. Because \mathcal{S} is complete in the first particle, we have $[f_1]^{-1} = [f_1^{-1}]$. Furthermore, because matrix $[r_{12}]$ is identical to $[f_1]$, it must be that $[r_{12}]^{-1} = [f_1^{-1}]$.

With the inverse of the matrix representation of r_{12} expressed essentially as a one-electron operator we rewrite the intermediate operator G as in Eq. (9).

$$G = F + P \left[f_1^{-1} \right] P \quad (9)$$

The subspace \mathcal{S} and its orthogonal complement, \mathcal{S}^\perp , are still both reducing subspaces for intermediate operator G . On \mathcal{S}^\perp , G still reduces to F allowing

immediate knowledge of these eigenvalues. However, there is a significant difference over Bazley’s method in the eigenvalues of G on \mathcal{S}^\perp . Using Bazley’s N -dimensional choice of \mathcal{S} generates an intermediate operator G that is symmetric like the base operator F and also the Hamiltonian H . It therefore allows symmetric and antisymmetric eigenfunctions and the lowest eigenvalue on \mathcal{S}^\perp is $e^{(1)} + e^{(N+1)}$. Our infinite-dimensional subspace \mathcal{S} contains $\psi_1^{(1)}\psi_2^{(1)}$ as its only symmetric function (ignoring a multiplicative constant). For $n > 1$, while $\psi_1^{(n)}\psi_2^{(1)}$ is an element of \mathcal{S} , $\psi_1^{(1)}\psi_2^{(n)}$ is not. Instead $\psi_1^{(1)}\psi_2^{(n)}$ is found in \mathcal{S}^\perp and has the eigenvalue $e^{(1)} + e^{(n)}$. These eigenvalues would be lacking in Bazley’s method and thus there will be many more (low) eigenvalues on \mathcal{S}^\perp for our method than for Bazley’s method.

Subspace \mathcal{S} contains all functions of the form $\chi_1\psi_2^{(1)}$ for arbitrary χ and the action of G on such a function is given in Eq. (10).

$$G\chi_1\psi_2^{(1)} = h_1\chi_1\psi_2^{(1)} + h_2\chi_1\psi_2^{(1)} + P[f_1^{-1}]P\chi_1\psi_2^{(1)} = (h_1 + e^{(1)} + f_1^{-1})\chi_1\psi_2^{(1)} \tag{10}$$

Separation of variables in Eq. (10), i.e. division by $\psi_2^{(1)}$, gives a one-particle eigenvalue Eq. (11) with eigenvalues $\lambda^{(n)}$ that are also eigenvalues of G on \mathcal{S} .

$$(h_1 + e^{(1)} + f_1^{-1})\chi_1^{(n)} = \lambda^{(n)}\chi_1^{(n)} \tag{11}$$

The union of these eigenvalues $\lambda^{(n)}$ of G on \mathcal{S} and those of G (or F) on \mathcal{S}^\perp , gives lower bounds to the energies of the helium atom. It remains for us to find the explicit form of f_1^{-1} .

5 Explicit form of f_1^{-1}

The one-electron operator f_1 , defined in Eq. (7), is the integral over the second electron of the product of the electron separation r_{12} and the square magnitude of the ground-state normalized hydrogenic eigenfunction $|\psi_2^{(1)}|^2 = Z^3\pi^{-1} \exp[-2Zr_2]$. Calculation of this integral requires the electron separation r_{12} to be written in terms of individual particle coordinates. This is accomplished indirectly through expansion (11) from Jen [5] where $r_> = \max[r_1, r_2]$, $r_< = \min[r_1, r_2]$, and θ is the difference in the zenith angles of the two particles $\theta_2 - \theta_1$.

$$r_{12} = r_> \sum_{k=0}^{\infty} \left(\frac{r_<^2}{r_>^2} \frac{1}{2k+3} - \frac{1}{2k-1} \right) \left(\frac{r_<}{r_>} \right)^2 P_k(\cos \theta) \tag{11}$$

The Legendre polynomial $P_k(\cos \theta)$ can be decomposed into products of associated Legendre polynomials specific to each particle as in Eq. (12).

$$P_k(\cos \theta) = \sum_{j=-k}^{+k} \frac{(k-|j|)!}{(k+|j|)!} P_k^j(\cos \theta_1) P_k^j(\cos \theta_2) e^{ij\phi_1} e^{ij\phi_2} \quad (12)$$

Combining Eq. (7, 11, and 12) yields Eq. (13).

$$\begin{aligned} f_1 &= \int_0^\infty r_2^2 dr_2 \left| \psi_2^{(1)} \right|^2 r_> \sum_{k=0}^\infty \left(\frac{r_<^2}{r_>^2} \frac{1}{2k+3} - \frac{1}{2k-1} \right) \left(\frac{r_<}{r_>} \right)^k \\ &\quad \times \sum_{j=-k}^{+k} \frac{(k-|j|)!}{(k+|j|)!} P_k^j(\cos \theta_1) e^{ij\phi_1} \\ &\quad \times \int_0^\pi \sin \theta_2 d\theta_2 P_k^j(\cos \theta_2) \int_0^{2\pi} d\phi_2 e^{ij\phi_2} \end{aligned} \quad (13)$$

The integral over the second azimuth angle is zero unless $j = 0$, in which case the integral is 2π . This means the summation over index j is but a single term and f_1 simplifies to Eq. (14). This also eliminates any functional dependence on ϕ_1 and reduces the associated Legendre polynomials to normal Legendre polynomials.

$$\begin{aligned} f_1 &= 2\pi \int_0^\infty r_2^2 dr_2 \left| \psi_2^{(1)} \right|^2 r_> \sum_{k=0}^\infty \left(\frac{r_<^2}{r_>^2} \frac{1}{2k+3} - \frac{1}{2k-1} \right) \left(\frac{r_<}{r_>} \right)^k P_k(\cos \theta_1) \\ &\quad \times \int_0^\pi \sin \theta_2 d\theta_2 P_k(\cos \theta_2) \end{aligned} \quad (14)$$

The integral over θ_2 can be rewritten by defining $z = \cos \theta_2$ resulting in Eq. (15). Because $P_0(z) = 1$ and $P_n(z)$ belong to an orthogonal set of functions over the domain $[-1, 1]$ for whole numbers n , the integral over z (i.e. θ_2) is zero unless $k = 0$, in which case it merely equals 2.

$$\int_0^\pi \sin \theta_2 d\theta_2 P_k(\cos \theta_2) = \int_{-1}^{+1} dz P_k(z) = \int_{-1}^{+1} dz P_0(z) P_k(z) \quad (15)$$

This limitation of $k = 0$ greatly simplifies f_1 to Eq. (16).

$$f_1 = 4\pi \int_0^\infty r_2^2 dr_2 \left| \psi_2^{(1)} \right|^2 \left(\frac{r_<^2}{3r_>} + r_> \right) \quad (16)$$

The final step is integrate over r_2 , first from 0 to r_1 where $r_2 = r_<$, and then from r_1 to ∞ where $r_2 = r_>$. Inversion of the result, Eq. (17), yields f_1^{-1} and we are ready to find the eigenvalues of G on \mathcal{S} .

$$\begin{aligned}
 f_1 &= 4\pi \int_0^{r_1} r_2^2 dr_2 |\psi_2^{(1)}|^2 \left(\frac{r_2^2}{3r_1} + r_1 \right) + 4\pi \int_{r_1}^{\infty} r_2^2 dr_2 |\psi_2^{(1)}|^2 \left(\frac{r_1^2}{3r_2} + r_2 \right) \\
 &= \frac{1 + Z^2 r_1^2 - e^{-2Zr_1} (1 + Zr_1/2)}{Z^2 r_1} \tag{17}
 \end{aligned}$$

6 Results

The eigenvalues of G on \mathcal{S} are determined by the one-particle eigenvalue Eq. (11) expressed below as Eq. (18) where h_1 is the hydrogenic Hamiltonian operator consisting of the kinetic energy $(-\nabla_1^2/2)$ and the nuclear attraction potential $(-Z/r_1)$. The constant value $e^{(1)} = -Z^2/2$ is the lowest energy of the He^+ atomic ion. For the helium atom, $Z = 2$.

$$\left(h_1 + e^{(1)} + \frac{Z^2 r_1}{1 + Z^2 r_1^2 - e^{-2Zr_1} (1 + Zr_1/2)} \right) \chi_1^{(n)} = \lambda^{(n)} \chi_1^{(n)} \tag{18}$$

The addition of the potential f_1^{-1} to the nuclear attraction prevents exact solution of the eigenvalue problem. Fortunately spherical coordinates allow separation of variables so that the eigenfunctions $\chi_1^{(n)}$ are products of a radial function and the spherical harmonics. Thus the eigenvalue problem is just a one-variable (radial) problem and standard variational methods allow determination of the lowest eigenvalues and eigenfunctions to essentially arbitrary precision. We therefore treat variational approximations to $\lambda^{(n)}$ of Eq. (18) from large-scale calculations as exact. The lowest eigenvalues of G on \mathcal{S} , $\lambda^{(n)}$, and those on \mathcal{S}^\perp , $\Lambda^{(n)} = e^{(1)} + e^{(n+1)}$, are reported in Table 2. For comparison we report the lowest eigenvalues for Bazley’s approach in Table 2 for $N = 100$ and accurate upper bounds [6,7].

Table 2 Lower bounds to the helium atom energies from Bazley’s method and our modification (using an infinite-dimensional subspace complete in one particle) are compared

n	Upper bound to $E^{(n)}$	Bazley’s lower bound to $E^{(n)}$	$\lambda^{(n)}$ in \mathcal{S}	$\Lambda^{(n-1)}$ in \mathcal{S}^\perp
1	-2.903 724	-3.059 921	-3.049 861	NA
2	-2.145 974	-2.164 997	-2.168 788	-2.500000
3	-2.061 272	-2.066 505	-2.067 158	-2.222222
4	-2.033 587	-2.035 693	-2.035 917	-2.125000
5	-2.021 177	-2.022 234	-2.022 328	-2.080000
6	-2.014 563	-2.015 157	-2.015 214	-2.055556

Although our infinite-dimensional variation of Bazley's special choice method has improved the lower bound to the ground-state of the helium atom energy, the improvement is slight. Furthermore there is no improvement for any of the excited states and the persistent low bounds on \mathcal{S}^\perp are undesirable.

7 Conclusion

We have taken the first step in the development of a new type of intermediate problem suitable to the calculation of lower bounds to eigenvalues based on Bazley's special choice method. By bounding the two-particle electron-repulsion operator from below by a one-particle operator on a subspace of Hilbert space we have essentially turned a single infinite-dimensional two-particle problem into two infinite-dimensional one-particle problems. Combining the solutions of a new one-particle Schrödinger equation with the solutions of the hydrogenic Schrödinger equation gives non-trivial lower bounds to some of the helium atom energies.

These bounds are not competitive with more common and intensive methods such as the Temple method [8]. Furthermore they are not yet competitive even with the standard Bazley projections onto finite-dimensional subspaces. The advantage of Bazley's approach is that it is a simple matter to increase the size of the finite-dimensional subspace to improve the lower bounds. Our approach uses an infinite-dimensional space and it is not clear how to optimally and/or simply expand the space. This is our current dilemma as expansion of the space for the projection is the most obvious way to improve the bounds. One idea is to increase the dimension of the second particle in the subspace \mathcal{S} , here expressed as $\mathcal{S} = \mathcal{H}_1 \otimes h_2$, where \mathcal{H}_1 is the complete Hilbert space of the first particle and h_2 is the incomplete space of the second particle. Currently h_2 is just the span of $\psi_2^{(1)}$. If h_2 were multidimensional, say k -dimensional, then the resulting one-particle Schrödinger equation, similar to Eq. (11), would admit a k -component vector function, rather than a scalar function, as a solution. At best, this approach would be very cumbersome.

One oddity about our method is that the wave functions of our intermediate Hamiltonian G do not have the correct symmetry. This is simply because the operator G does not have the symmetry of the full Hamiltonian, H . This lack of symmetry allows the presence of very low bounds in \mathcal{S}^\perp which interfere with the production of tight lower bounds to the excited states of the helium atom. This puts our method at a severe disadvantage and we are searching for a way to either incorporate symmetry into G or a reason to ignore these very low bounds.

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