A Lower Bound Procedure for Energy Eigenvalues*

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A lower bound procedure for energy eigenvalues based on the method of intermediate problems is given. A projection technique is used to construct a family of operators smaller than a given Hamiltonian whose eigenvalues are lower bounds to those of the given Hamiltonian. By a particular choice of subspaces associated with the projections it is possible to construct the family in such a way that certain members may have an eigenvalue coinciding with one of the real eigenvalues of a nonlinear but finite matrix eigenvalue problem. Application to the helium atom ground state indicates that the procedure may be more efficient than the procedures customarily used.

I. INTRODUCTION

IN this paper we give a lower bound procedure for energy eigenvalues based on the method of intermediate problems originated by Weinstein.[1] The procedure uses a projection technique of Aronszajn[2] for the construction of intermediate operators and is closely related to the procedures of Bazley and Fox.[3–5]

The procedure is developed in Secs. II and III. Section IV is devoted to test calculations on the ground state of the helium atom. The results of these calculations indicate that the procedure may prove to be more efficient than the procedures which have previously been used in obtaining accurate lower bounds to the helium ground state.

II. INTERMEDIATE HAMILTONIANS

We outline here the technique of Aronszajn for constructing intermediate operators. Our discussion follows that of Bazley and Fox[4] with modifications pertinent to the new procedure.

We consider a time-dependent Schrödinger equation,

$$H\psi=E\psi, \tag{2.1}$$

for which the Hamiltonian H is bounded from below and possesses a sequence of bound states lying below any continuous spectrum. We confine our attention to these states lying below the first limit point and regard them as ordered according to energy,

$$E_1\leq E_2\leq\cdots. \tag{2.2}$$

We further suppose that H can be written as the sum

$$H=H^0+V, \tag{2.3}$$

where V is positive definite, and where H^0 is bounded from below and has bound states beneath its first limit point. Although the procedure does not use the solutions to the eigenvalue equation for H^0,

$$H^0\psi^0=E^0\psi^0; \tag{2.4}$$

directly, the energies of the lowest bound states are needed. We therefore assume that the energies

$$E_1^0\leq E_2^0\leq\cdots \tag{2.5}$$

belonging to the ordered states of H^0 lying below its first limit point are known.

Since $H-H^0$ is the positive definite operator V, we have that

$$\langle H^0\rangle\leq\langle H\rangle \tag{2.6}$$

for all ψ in the domain of H, and by a theorem of Weyl,[6] this inequality is sufficient to guarantee the inequalities

$$E_i^0\leq E_i, \quad (i=1, 2, \cdots) \tag{2.7}$$

among the ordered eigenvalues of H^0 and H. The initial eigenvalues of H^0 are thus lower bounds to those of H.

To improve these bounds, we construct a sequence of intermediate Hamiltonians H^n satisfying the inequalities

$$\langle H^0\rangle\leq\langle H^n\rangle\leq\langle H^{n+1}\rangle\leq\langle H\rangle \tag{2.8}$$

so that their ordered eigenvalues satisfy

$$E_i^0\leq E_i^n\leq E_i^{n+1}\leq E_i, \quad (i=1, 2, \cdots), \tag{2.9}$$

and thus give lower bounds increasing toward the eigenvalues of H. The construction requires the introduction of projection operators in a vector space $\mathcal{U}$ characterized by the metric operator V. The inner product in $\mathcal{U}$ is therefore $\langle\varphi|V|\psi\rangle$. However, for convenience, we adopt the normalization convention

$$\langle\psi|\psi\rangle=1 \tag{2.10}$$

for elements of $\mathcal{U}$.

The projection operator O^n projecting on the linear manifold $\mathcal{U}^n$ spanned by the elements $p_1, p_2, \cdots, p_n$ of a set $\{p_i\}$ linearly independent in $\mathcal{U}$ is conveniently

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represented by

$$O^n=\sum_{i,j=1}^{n}|p_i\rangle\Lambda_{ij}{}^n\langle p_j|V, \tag{2.11}$$

where $\mathbf{\Lambda}^n$ is the inverse of the nth-order matrix with elements $\langle p_i|V|p_j\rangle$. It is readily verified that

$$\begin{aligned}&(O^n)^2=O^n,\\&O^{n\dagger}V=O^{n\dagger}VO^n=VO^n,\end{aligned} \tag{2.12}$$

so that the operator VO^n is self-adjoint. Further, from the properties of projection operators and the fact that

$$\mathfrak{V}^n\subset\mathfrak{V}^{n+1}\subset\mathfrak{V} \tag{2.13}$$

we have, with the convention (2.10),

$$0\leq\langle VO^n\rangle\leq\langle VO^{n+1}\rangle\leq\langle V\rangle. \tag{2.14}$$

This relation forms the basis for the construction of the H^n for, if they are defined by

$$H^n=H^0+VO^n, \tag{2.15}$$

the inequalities (2.8) are ensured by (2.14). Thus, provided the eigenvalue equation for the operators (2.15) can be solved, we have a means of obtaining sequences of lower bounds improving toward the eigenvalues of H. A formal solution has been given by Bazley and Fox[4] which we repeat in part here.

We consider the eigenvalue equation for the H^n,

$$H^n\psi^n=E^n\psi^n, \tag{2.16}$$

where E^n lies below the first limit point of H^0. (The H^n and H^0 have common limit points.[4]) With the aid of (2.11), (2.16) may be written as

$$\begin{aligned}(H^0-E^n)\psi^n&=-VO^n\psi^n\\&=-V\sum_{i,j=1}^{n}\Lambda_{ij}{}^n\langle p_j|V|\psi^n\rangle p_i\\&=V\sum_{i=1}^{n}C_ip_i,\end{aligned} \tag{2.17}$$

where

$$C_i=-\sum_{j=1}^{n}\Lambda_{ij}{}^n\langle p_j|V|\psi^n\rangle. \tag{2.18}$$

If E^n is not an eigenvalue of H^0, (2.15) may be multiplied by the resolvent operator $(H^0-E^n)^{-1}$ to give an expression for the eigenfunction

$$\psi^n=(H^0-E^n)^{-1}V\sum_{i=1}^{n}C_ip_i. \tag{2.19}$$

Unfortunately, (2.19) is usually not an acceptable form for the eigenfunction since the resolvent is seldom known in closed form, being generally expressible only as a spectral resolution involving infinite sums and integrals. The result is that ψ^n cannot be reduced to a linear combination of known terms, and as a consequence, the eigenvalue problem for the H^n does not reduce to a finite algebraic problem.[4]

Bazley and Fox have devised several procedures for avoiding this difficulty with the resolvent involving either special choices of the elements p_i or modification of the H^0 operator.[3–5] Our procedure eliminates the resolvent entirely from the expression (2.19) for one of the ψ^n by a different special choice of the p_i.

Prior to developing this procedure in Sec. III, we wish to comment on the convergence of the eigenvalues of the H^n to those of H. It has been shown[4] that, provided H^0 and H have completely continuous inverses, V is bounded relative to H^0, and the set $\{p_i\}$ is complete in $\mathfrak{V}$, the eigenvalues and eigenfunctions of the H^n converge to those of H. Of equal interest in applications, where only a finite number of elements p_i are used, is the rapidity of convergence. In this connection, we demonstrate that the error in a lower bound E^n is of second order in the error in the eigenfunction ψ^n and in an error arising from the error in the operator H^n. We introduce the orthogonal complement P^n to O^n defined by

$$P^n=1-O^n, \tag{2.20}$$

and having the properties

$$\begin{aligned}&(P^n)^2=P^n,\\&P^{n\dagger}V=P^{n\dagger}VP^n=VP^n,\\&O^{n\dagger}VP^n=P^{n\dagger}VO^n=0.\end{aligned} \tag{2.21}$$

We may now write H as

$$\begin{aligned}H&=H^0+V(O^n+P^n)\\&=H^n+VP^n,\end{aligned} \tag{2.22}$$

and one of its eigenfunctions as the sum

$$\psi=\psi^n+\delta, \tag{2.23}$$

where

$$\langle\psi|\psi\rangle=1,\quad\langle\psi^n|\delta\rangle=0. \tag{2.24}$$

The energy E corresponding to ψ is then[7]

$$\begin{aligned}E&=\langle\psi|H|\psi\rangle\\&=E^n\langle\psi^n|\psi^n\rangle+\langle\delta|H^n|\delta\rangle+\langle\psi|VP^n|\psi\rangle.\end{aligned} \tag{2.25}$$

If we denote $P^n\psi$ by δ', we find for the error in the lower bound

$$\begin{aligned}0\leq\Delta^-&=E-E^n\\&=\langle\delta|H^n|\delta\rangle-E^n\langle\delta|\delta\rangle+\langle\delta'|V|\delta'\rangle,\end{aligned} \tag{2.26}$$

observing that the first two terms arise from the error in ψ^n while the last arises from the error in H^n.

We give for comparison the well-known equivalent relation for the error in an upper bound obtained with the variation principle. We take φ to be a normalized trial function orthogonal to all eigenfunctions of H with

[7] We point out that $P^n\psi^n$ does not, in general, vanish.

energies less than E. We write φ as

$$\varphi=\psi+\gamma, \tag{2.27}$$

where

$$\langle\varphi|\varphi\rangle=1, \quad \langle\psi|\gamma\rangle=0. \tag{2.28}$$

If W is the upper bound obtained with φ, i.e.,

$$\begin{aligned} W&=\langle\varphi|H|\varphi\rangle \\ &=E\langle\psi|\psi\rangle+\langle\gamma|H|\gamma\rangle, \end{aligned} \tag{2.29}$$

we find for the error in the upper bound

$$\begin{aligned} 0\leq\Delta^+&=W-E \\ &=\langle\gamma|H|\gamma\rangle-E\langle\gamma|\gamma\rangle. \end{aligned} \tag{2.30}$$

Upon comparing (2.26) and (2.30), we see that the first two terms of (2.26) are of the same general form as the terms of (2.30), and if ψ^n and φ do not differ greatly, it is reasonable to suppose that these terms will be comparable in magnitude. If this is the case, we see that the error in the lower bound will be greater by approximately

$$\Delta^--\Delta^+\simeq\langle\delta'|V|\delta'\rangle. \tag{2.31}$$

III. ELEMENTS CONTAINING THE INVERSE OF THE RESOLVENT

As discussed in Sec. II, the difficulty in solving the eigenvalue equation for the intermediate Hamiltonians of (2.15) arises from the appearance of the resolvent operator $(H^0-E^n)^{-1}$ in (2.19). The procedure given in this section eliminates the resolvent from (2.19) by defining the elements p_i in terms of another set of elements f_i according to the relation[8]

$$p_i=V^{-1}(H^0-E^n)f_i, \quad (i=1, 2, \cdots). \tag{3.1}$$

In the development of the procedure, it is convenient to introduce a family of p_i which contains the p_i of (3.1) defined by

$$p_i(\epsilon)=V^{-1}(H^0-\epsilon)f_i, \quad (i=1, 2, \cdots), \tag{3.2}$$

where ϵ is regarded initially as an arbitrary scalar parameter. The f_i are restricted only in that they be linearly independent functions in the domain of H and such that the p_i are square-integrable in $\mathcal{U}$, i.e., such that $\langle p_i(\epsilon)|V|p_i(\epsilon)\rangle$ is finite.

From (2.11) we obtain for the operators $O^n(\epsilon)$ projecting on the subspace $\mathcal{U}^n(\epsilon)$ spanned by $p_1(\epsilon)$, $p_2(\epsilon)$, $\cdots$, $p_n(\epsilon)$,

$$O^n(\epsilon)=\sum_{i,j=1}^{n}|p_i(\epsilon)\rangle\Lambda_{ij}{}^n(\epsilon)\langle p_j(\epsilon)|V. \tag{3.3}$$

Using these, we construct a family of intermediate Hamiltonians parameterized by ϵ,

$$H^n(\epsilon)=H^0+VO^n(\epsilon). \tag{3.4}$$

According to (2.19), their eigenvalue equations,

$$H^n(\epsilon)\psi^n(\epsilon)=E^n\psi^n(\epsilon), \tag{3.5}$$

are satisfied, for eigenvalues different from the E_i^0 by eigenfunctions of the form

$$\psi^n(\epsilon)=(H^0-E^n)^{-1}V\sum_{i=1}^{n}C_ip_i(\epsilon), \tag{3.6}$$

with the C_i given by

$$C_i=-\sum_{j=1}^{n}\Lambda_{ij}{}^n(\epsilon)\langle p_j(\epsilon)|V|\psi^n(\epsilon)\rangle. \tag{3.7}$$

Using (3.2) in (3.6) gives an expression for the eigenfunctions in terms of the f_i,

$$\psi^n(\epsilon)=(H^0-E^n)^{-1}\sum_{i=1}^{n}C_i(H^0-\epsilon)f_i. \tag{3.8}$$

We inquire now as to whether there exist specific operators $H^n(E^n)$ of the family (3.4) having the eigenvalue E^n for, in this event, (3.8) reduces to the finite linear combination of the f_i,[9]

$$\psi^n(E^n)=\sum_{i=1}^{n}C_if_i. \tag{3.9}$$

If such operators exist, they will satisfy eigenvalue equations of the form

$$\begin{aligned} (H^0-E^n)\sum_{i=1}^{n}C_if_i&=VO^n(E^n)\sum_{i=1}^{n}C_if_i \\ &=O^{n\dagger}(E^n)V\sum_{i=1}^{n}C_if_i. \end{aligned} \tag{3.10}$$

By forming the inner product of (3.10) successively with $p_1{}^*(E^n)$, $p_2{}^*(E^n)$, $\cdots$, $p_n{}^*(E^n)$, we obtain the set of equations,

$$\begin{aligned} \sum_{i=1}^{n}[&\langle(H^0-E^n)f_j|V^{-1}|(H^0-E^n)f_i\rangle \\ &+\langle f_j|H^0-E^n|f_i\rangle]C_i=0, \\ &(j=1, 2, \cdots n). \end{aligned} \tag{3.11}$$

These constitute a nonlinear matrix eigenvalue equation of order n,

$$[\mathbf{M}^0+\mathbf{M}^1E^n+\mathbf{M}^2(E^n)^2]\mathbf{C}=0, \tag{3.12}$$

where the matrices $\mathbf{M}^0$, $\mathbf{M}^1$, and $\mathbf{M}^2$ are Hermitian and have the elements

$$\begin{aligned} M_{ij}{}^0&=\langle H^0f_i|V^{-1}|H^0f_j\rangle+\langle f_i|H^0|f_j\rangle, \\ M_{ij}{}^1&=-\langle H^0f_i|V^{-1}|f_j\rangle-\langle f_i|V^{-1}|H^0f_j\rangle-\langle f_i|f_j\rangle, \\ M_{ij}{}^2&=\langle f_i|V^{-1}|f_j\rangle. \end{aligned} \tag{3.13}$$

[8] The author is indebted to Professor P. O. Löwdin for suggesting this choice of the p_i.

[9] Since the resolvent has been eliminated in going from (3.8) to (3.9), (3.9) is not restricted to eigenvalues different from the E_i^0.

Equation (3.12) differs from the usual linear matrix eigenvalue equation involving Hermitian matrices in that it may or may not have real eigenvalues. An examination of the associated secular equation,

$$\det[\mathbf{M}^0+\mathbf{M}^1E^n+\mathbf{M}^2(E^n)^2]=0, \tag{3.14}$$

shows that it is a polynomial equation of degree $2n$ in E^n with real coefficients and may therefore have complex roots occuring in conjugate pairs. Consequently the number of real eigenvalues of (3.12) is even and may range from zero to $2n$. The existence of such real eigenvalues is the criterion for the existence of operators $H^n(E^n)$ having the eigenvalue E^n. The eigenfunction $\psi^n(E^n)$ of $H^n(E^n)$ associated with a real eigenvalue E^n of (3.12) is obtained from the corresponding eigenvector $\mathbf{C}$ whose elements are the coefficients C_i in (3.9).

We wish to emphasize that (3.12) determines only one eigenvalue for a given operator, for if (3.12) has k distinct real eigenvalues, each of these belongs to a different one of the k intermediate Hamiltonians $H^n(E_1{}^n)$, $H^n(E_2{}^n)$, $\cdots$, $H^n(E_k{}^n)$. Thus, only if an eigenvalue is multiple, is more than one state of an intermediate Hamiltonian determined. This property of supplying only one eigenvalue for a given operator is a serious disadvantage of the procedure, for, without the other eigenvalues, we cannot, in general, locate the known eigenvalue $E_j{}^n$ in the spectrum of $H^n(E_j{}^n)$, and are consequently unable to determine to which eigenvalue of H it is a lower bound.

However, if the spacing of the initial levels of H^0 is sufficiently wide we can locate $E_j{}^n$ in the spectrum of $H^n(E_j{}^n)$ in the following way. From the inequality

$$\langle H^0\rangle\leq\langle H^n(E_j{}^n)\rangle, \tag{3.15}$$

we have[10]

$$E_i{}^0\leq E_{ji}{}^n, \quad (i=1, 2, \cdots), \tag{31.6}$$

from which the theorem stated below follows.

THEOREM: If the known eigenvalue $E_j{}^n$ of $H^n(E,{}^n)$ satisfies

$$E_\alpha{}^0\leq E_j{}^n<E_{\alpha+1}{}^0, \tag{3.17}$$

and if upper bounds to $\alpha-1$ eigenvalues of H [or of $H^n(E_j{}^n)$] lie below $E_j{}^n$, then $E_j{}^n$ is a lower bound to E_α. For the ground state, the requirement reduces simply to

$$E_j{}^n<E_2{}^0. \tag{3.18}$$

In connection with the convergence of this procedure, we first consider the entire family of operators (3.4) without regard to whether they have solutions determined by (3.12). Since they are just special cases of the intermediate Hamiltonians of Sec. II, the conditions stated there are sufficient for the convergence of the operators (3.4) to H. However, the completeness of the elements (3.2) requires, in addition to the completeness of the f_i, that the transformation defined by (3.2) be nonsingular. It is easily shown that the transformation will be singular if and only if some eigenfunction $\psi_j{}^0$ of H^0 is included in the span of f_1, f_2, $\cdots$, f_n and, at the same time, $\epsilon=E_j{}^0$. Therefore, if we separate the operators (3.4) into those for which $\epsilon\neq E_i{}^0$ $(i=1, 2, \cdots)$, and those for which $\epsilon=E_i{}^0$ $(i=1, 2, \cdots)$, the former will converge to H as the f_i become complete while the latter will not. In fact, $H^n(E_j{}^0)$ will agree with H^0 on $\psi_j{}^0$, i.e.,

$$H^n(E_j{}^0)\psi_j{}^0=E_j{}^0\psi_j{}^0. \tag{3.19}$$

This follows from the easily deduced result that if f_1, f_2, $\cdots$, f^n contains $\psi_j{}^0$,

$$\langle\psi_j{}^0|\,VO^n(E_j{}^0)\,|\psi_j{}^0\rangle=0. \tag{2.20}$$

Returning now to the members of (3.4) which have an eigenvalue and eigenfunction determined by (3.12), we point out that it is entirely possible that a given equation will have no solutions at all corresponding to a situation in which (3.14) has no real roots. Further, there is no guarantee that the subspace $\mathfrak{V}^n(E_j{}^n)$ will be contained in $\mathfrak{V}^{n+1}(E_j{}^{n+1})$ since, in general, $E_j{}^n\neq E_j{}^{n+1}$. We therefore have no assurance that the sequence $E_j{}^n$, $E_j{}^{n+1}$, $\cdots$ is monotonic increasing. Because of these complicating features, we consider only a special case which, however, is the one of interest in applications. We suppose that, by a judicious choice of the f_i, we have succeeded in obtaining a set of equations (3.12) of orders q, $q+1$, $\cdots$, whose secular equations have at least one pair of real roots. In addition, we suppose that each member of the sequence $E_j{}^q$, $E_j{}^{q+1}$, $\cdots$ formed from the jth roots of the secular equations satisfies the theorem previously proved for some value of α. We then have

$$E_\alpha{}^0\leq E_j{}^n\leq E_\alpha, \quad (n=q, q+1, \cdots). \tag{3.21}$$

We now make use of the convergence properties established above to state that if n increases without limit and the f_i become complete, one or the other of the inequalities in (3.19) will hold so that the sequence will (on the average) either decrease toward $E_\alpha{}^0$ or increase toward E_α. We are, of course, interested only in lower bounds belonging to sequences exhibiting the latter behavior.

As discussed in Sec. II, the procedure is a second-order process and can be expected to be rapidly convergent provided the quantities δ and δ' of (2.26) can be made small. Since the choice of the elements f_i is essentially unrestricted in this procedure, we can, in principle, select them so as to make both quantities small. However, it is not clear how to choose the f_i so as to minimize the quantity

$$\delta'=P^n\psi=\psi-\sum_{i,j=1}^{n}\langle f_i|H^0-E^n|\psi\rangle \times\Lambda_{ij}{}^n(E^n)V^{-1}(H^0-E^n)f_j. \tag{3.22}$$

[10] The subscript i on $E_{ji}{}^n$ enumerates the ordered eigenvalues of $H^n(E_j{}^n)$.

On the other hand, it is relatively easy to select the f_i so as to make δ small. By choosing elements which are known to serve as a good basis for a variational upper-bound calculation, we may expect that the quantity $\langle\delta|H^n-E^n|\delta\rangle$ will be small, i.e., of the same order as the error $\langle\gamma|H-E|\gamma\rangle$ in the upper bound, so that the approximate relation (2.31) will hold. We can make no estimate of the relative magnitude of the remaining term $\langle\delta'|V|\delta'\rangle$ in (2.26), but it is reasonable to suppose that it will be dominant. We find confirmation in the results of the calculations on the helium ground state in the next section. The elements used in these calculations were chosen by the method just described. The lower bounds are found to have errors which are, on the average, about an order of magnitude larger than the errors in comparable upper bounds, indicating that the term in δ' is larger than the term in δ by about the same amount.

IV. LOWER BOUNDS TO THE GROUND STATE OF HELIUM

Considerable interest has been attached to the calculation of upper and lower bounds to the ground-state energy of the nonrelativistic helium Hamiltonian which confine the theoretical energy within the limits of error of the value provided by correcting the relativistic experimental energy.[11–20] While it has been possible to compute upper bounds which lie within the current experimental error,[18] equal success has not been obtained with lower-bound calculations[19] because the lower bound procedures used, those of Temple[21] and Stevenson and Crawford,[12] are substantially less efficient than the variational upper bound procedures. For example, Pekeris[18,19] has given the bounds

$$-2.903726615\ (\text{au})\leq E_1\leq -2.903724375\ (\text{au}), \quad (4.1)$$

for which Schwartz[20] estimates that the error in the lower bound, which was obtained with Temple's formula using the same 1078 term wave function which gave the upper bound, is two to three orders of magnitude greater than the error in the upper bound.

To illustrate the application of the procedure given in this paper and to compare its efficiency with that of the previously used procedures, we carry out lower bound calculations of orders through ten on the ground state of helium in this section.

In atomic units, the nonrelativistic helium Hamiltonian is

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-2/r_1-2/r_2+1/r_{12}. \quad (4.2)$$

H can be put into the form (2.3) by taking H^0 as

$$H^0=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-2/r_1-2/r_2, \quad (4.3)$$

and V as

$$V=1/r_{12}. \quad (4.4)$$

We estimate only the ground state of H which is singlet S in character. Consequently, the only knowledge of the solutions to H^0 required is the energy of its first excited singlet S state. The solutions to H^0 are well known and the ordered energies of its lowest singlet S states consist of its ground-state energy and a sequence of excited-state energies converging toward the first limit point at -2,

$$E_j^0=-2(1+1/j^2), \quad (j=1, 2, \cdots). \quad (4.5)$$

The first excited singlet S state thus has the energy $E_2^0=-2.5$. Since this is greater than the upper bound to E_1 given in (4.1), we will be able to identify lower bounds to the ground state by (3.18).

We have chosen for the f_i terms of the Hylleraas series[11] which is defined in terms of the coordinates

$$s=r_1+r_2, \quad t=r_1-r_2, \quad u=r_{12} \quad (4.6)$$

as

$$\Phi=e^{-\eta s}\sum_{\mu,\nu,\sigma=0}^{\infty} c_{\mu\nu\sigma}s^\mu t^{2\nu}u^\sigma, \quad (4.7)$$

where η is a scaling parameter. This choice of the f_i insures that the ψ^n will be automatically of singlet S character. The ten terms of (4.7) used are those found to be most effective in a tenth-order upper bound calculation.[13] They are listed below, normalized to $16\pi^2$.

$$\begin{aligned}
f_1&=[(2\eta)^3/2]e^{-\eta s},\\
f_2&=[(2\eta)^4/4(6)^{1/2}]ue^{-\eta s},\\
f_3&=[(2\eta)^5/24]t^2e^{-\eta s},\\
f_4&=[(2\eta)^4/2(42)^{1/2}]se^{-\eta s},\\
f_5&=[(2\eta)^5/24(21)^{1/2}]s^2e^{-\eta s},\\
f_6&=[(2\eta)^5/40(3)^{1/2}]u^2e^{-\eta s},\\
f_7&=[(2\eta)^5/48(3)^{1/2}]sue^{-\eta s},\\
f_8&=[(2\eta)^6/96(5)^{1/2}]t^2ue^{-\eta s},\\
f_9&=[(2\eta)^6/240(7)^{1/2}]u^3e^{-\eta s},\\
f_{10}&=[(2\eta)^7/432(30)^{1/2}]t^2u^2e^{-\eta s}.
\end{aligned} \quad (4.8)$$

The calculations require the evaluation of the matrix elements (3.13) for $i, j=1, 2, \cdots, 10$ using the functions (4.8) for the f_i and (4.3) and (4.4) for H^0 and V. The methods used to evaluate these are similar to the methods used by Wilets and Cherry[15] in evaluating integrals in their lower bound calculations on helium using Temple's formula. The elements were used to

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TABLE I. Comparison of the lower bound energies and wave functions of this paper with those of upper bounds of the same orders.

Order	Calculation[a]	Energy (au)	Error[b]	Wave function
1	upper bound	−2.8477	0.0560	$\exp(-1.69s)$
	lower bound	−3.0657	0.1620	$\exp(-1.93s)$
2	upper bound	−2.8912	0.0125	$\exp(-1.85s)[1+0.364u]$
	lower bound	−2.9437	0.0400	$\exp(-1.98s)[1+0.290u]$
3	upper bound	−2.9024	0.0013	$\exp(-1.82s)[1+0.30u+0.13t^2]$
	lower bound	−2.9208	0.0171	$\exp(-1.75s)[1+0.272u+0.093t^2]$
6	upper bound	−2.90324	0.00048	$\exp(-1.82s)[1+0.353u+0.128t^2-0.101s+0.033s^2-0.032u^2]$
	lower bound	−2.9094	0.0057	$\exp(-1.72s)[1+0.312u+0.095t^2-0.208s+0.031s^2-0.020u^2]$
10	upper bound	−2.903603	0.00012	$\exp(-1.76s)[1+0.351u+0.157t^2-0.129s+0.013s^2-0.068u^2+0.019su-0.034t^2u+0.006u^3+0.005t^2u^2]$
	lower bound	−2.9059	0.0022	$\exp(-1.76s)[1+0.327u+0.152t^2-0.134s+0.009s^2-0.066u^2+0.009su-0.010t^2u+0.001u^3+0.006t^2u^2]$

[a] The upper bounds of orders one, two, three, and six were taken from L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 224. All but that of first order are due to Hylleraas. The tenth-order upper bound was taken from Ref. 13.
[b] The errors were computed using the upper bound of (4.1) for the exact energy.

construct eigenvalue equation (3.12) of orders through ten, which were solved for their real eigenvalues and associated eigenvectors by an iterative technique of Löwdin.[22] Our results are given in Figs. 1 and 2 and in Table I.

It was stated in Sec. III that the real eigenvalues of (3.12) are even in number with an equation of order n having from zero to $2n$ real eigenvalues. In our calculations we never find more than two. This is despite the fact that, e.g., the secular equation corresponding to the eigenvalue equation of order ten is a polynomial of degree twenty in the energy. In Fig. 1 we give, as typical, the behavior of the eigenvalues of an eigenvalue equation of order two based on the elements f_1 and f_2. We see that, in the region centered around $\eta=2$, two eigenvalues are found which merge near $\eta=1.75$ and $\eta=2.20$. Outside this range no real eigenvalues are found. Both eigenvalues are lower bounds to the ground state, but we retain as useful lower bounds only those given by E_2^2. Although not displayed in the figures, it is interesting to note that as the order of the calculations increases, the lower curve E_1^n flattens out rapidly so that at $n=6$ it is quite close to the straight line $E_1^0=-4$. This supports the discussion in Sec. III regarding convergence to the E_i^0. The exact value -4 is attained at $\eta=2$ for any order, since, at this point, f_1 is identical with ψ_1^0.

In Fig. 2 we give the curves E_2^n obtained from the calculations of orders one through six and the tenth-order calculation.[23] It is gratifying to observe the monotonic increase of the lower bounds with order, since we have not proved that this must necessarily occur. At points where two curves touch as, e.g., the

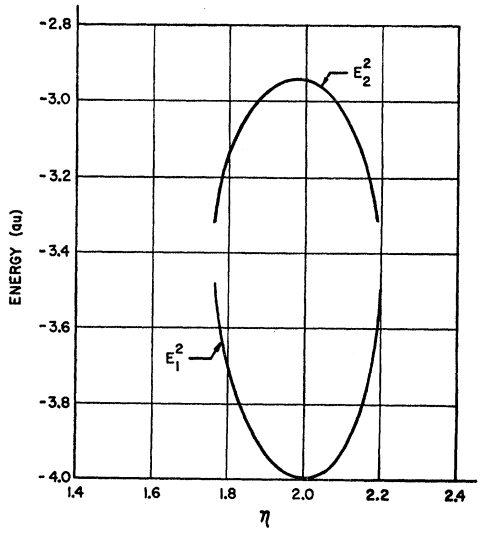

FIG. 1. Eigenvalues of an eigenvalue equation (3.12) of order two. The curves labeled E_1^2 and E_2^2 give, at any value of η, the lowest eigenvalues of the different operators $H^2(E_1^2)$ and $H^2(E_2^2)$.

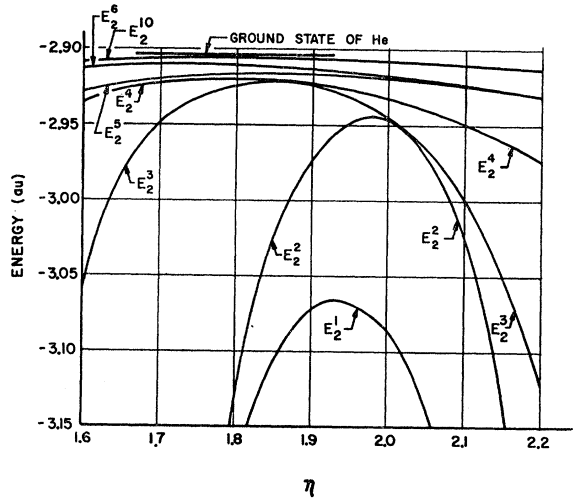

FIG. 2. Lower bounds to the ground state of helium as a function of a scaling parameter.

[22] P. O. Löwdin, J. Mol. Spectry. **10**, 12 (1963).

[23] A calculation of order n is based on the functions $f_1, f_2, \cdots, f_n$ taken in the order that they appear in (4.8).

TABLE II. Comparison of efficiencies of upper and lower bound procedures for the helium ground state. Columns (4), (6), and (8) indicate the efficiency of the procedure of this paper relative to the upper bound procedure and the other lower bound procedures.

(1) Functions used	(2) Lower bounds of this paper	(3) Upper bounds of Table I	(4) Δ^-/Δ^+ [a]	(5) Lower bounds[b,f] of Stevenson and Crawford	(6) Δ_{SC}^-/Δ^- [c]	(7) Lower bounds[d] with Temple's formula	(8) Δ_T^-/Δ^- [e]
f_1	−3.0657	−2.8477	2.9	−3.5403	3.9	−4.13	7.6
f_1—f_3	−2.9208	−2.9024	13	−2.9481	2.6	−2.965	3.6
f_1—f_6	−2.9094	−2.90324	12	−2.9215	3.1	−2.9257	3.8
f_1—f_9	−2.9068	...	...	−2.9102	2.1	...	...
f_1—f_{10}	−2.9059	−2.903603	18	...	...	−2.9136	4.5

[a] The error in the lower bounds of (2) divided by the error in the upper bounds of (3).
[b] Taken from Ref. 12.
[c] The error in the lower bounds of (5) divided by the error in the lower bounds of (2).
[d] Taken from Ref. 15.
[e] The error in the lower bounds of (7) divided by the error in the lower bounds of (2).
[f] These bounds could be improved slightly by using a less conservative value of α [see (4.11)]. Using a value of α near the optimum improved the ninth-order lower bound to −2.9089.

point near $\eta=2.02$ for E_2^2 and E_2^3 the higher order eigenfunction reduces to the lower order eigenfunction. Thus, at such points, $H^n(E_j^n)$ and $H^{n+1}(E_j^{n+1})$ have a common eigenfunction as well as a common eigenvalue.

In Table I we compare energies and wave functions of our optimized lower bounds of orders one, two, three, six, and ten with those of upper bounds of the same orders. We see that, though individual coefficients and the scaling parameter differ somewhat, corresponding wave functions have the same general form. It is evident that the lower bound procedure is much less efficient than the upper bound procedure. However, as will be shown, it appears to offer an increase in efficiency over the procedures of Temple and of Stevenson and Crawford.

The lower bounds of Temple and of Stevenson and Crawford are not connected with intermediate problems and may be derived from easily established inequalities.[24] Temple's lower bound is given in terms of a trial function ψ by

$$E_1\geq L=\langle\psi|H|\psi\rangle-\frac{\langle H\psi|H\psi\rangle-\langle\psi|H|\psi\rangle^2}{E_2-\langle\psi|H|\psi\rangle}. \quad (4.9)$$

while the more efficient[25] result of Stevenson and Crawford is given by the somewhat more involved formula

$$E_1\geq L=\alpha-[\langle H\psi|H\psi\rangle-2\alpha\langle\psi|H|\psi\rangle+\alpha^2]^{1/2}, \quad (4.10)$$

where the quantity $\langle H\psi|H\psi\rangle-2\alpha\langle\psi|H|\psi\rangle$ may be minimized by variational means, and where α must satisfy

$$\alpha\leq\tfrac{1}{2}(E_1+E_2). \quad (4.11)$$

Optimum lower bounds are obtained when there is equality in (4.11).

In Table II we compare the lower bounds of this paper with lower bounds computed with the fomulas (4.9) and (4.10). Comparison is also made with the upper bounds of Table I. The greater efficiency of the new procedure shown in Table II, while not outstanding, is significant if maintained in higher order calculations for even a small increase in efficiency can drastically reduce the amount of labor required to achieve a given accuracy in a lower bound when calculations of high order are involved. The increase in efficiency is especially significant since we judge the new procedure to be comparable in difficulty of application to the other two procedures.[26]

ACKNOWLEDGMENTS

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[24] For such a derivation of Temple's formula see Ref. 15.

[25] See Table II. The greater efficiency is maintained in higher order calculations. Kinoshita (Refs. 16 and 17), using a 39-term trail function, improved his lower bound by a factor of two in going from Temple's formula to the procedure of Stevenson and Crawford.

[26] Evaluation of integrals is one of the major difficulties encountered in these calculations. The integrals occurring in the new procedure are actually slightly less involved than those occurring in the other two procedures.