# New stationary bounds on matrix elements including positron-atom scattering lengths

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(Received 29 April 1974)

In a previous study of bound-state matrix elements of a Hermitian operator $W$, it was possible to obtain at most an upper (or lower) stationary bound. The possibility arose only for the diagonal matrix element case, and only for $W$ nonpositive (or nonnegative). In the present treatment, both upper and lower stationary bounds are obtained, for diagonal and off-diagonal matrix elements, and, though some restrictions on $W$ remain, the requirement that $W$ be of well-defined sign can be dropped. The derivation also improves upon that given previously in that the possibility of any difficulty with near singularities in the equation defining the trial auxiliary (or Lagrange) function is unambiguously avoided. As an example, the method is applied to the problem of the zero-energy scattering of positrons by atoms or ions, and an expression is derived which provides a rigorous stationary upper bound on the scattering length; the target ground-state wave function need *not* be known exactly. Crude but rigorous numerical results are obtained quite simply in the Born approximation.

## I. INTRODUCTION

Matrix elements of the form

$$W_{nm} \equiv (\psi_n, W\psi_m), \tag{1.1}$$

where $W$ is a Hermitian operator and $\psi_n$ is a normalized bound state eigenfunction of a Hamiltonian $h$, satisfying

$$(h - \epsilon_n)\psi_n = 0, \tag{1.2}$$

appear throughout physics, and it is useful to be able to calculate bounds on them. Simple numerical bounds have been obtained[1] for a wide range of operators $W$; even if crude, they can be useful as input data in the determination of the more accurate bounds to be described below. First order bounds, in which one introduces normalized trial functions $\psi_{nt}$ and $\psi_{mt}$ which contain variational parameters and for which the error is of first order in some weighted average of the errors $\delta\psi_{nt}$ in the trial functions, have also been obtained[1,2] for many operators $W$, as have quasi-stationary bounds,[3] with errors of the $\frac{3}{2}$ power of some weighted average of the $\delta\psi_{nt}$. We will be concerned here with the development of true stationary upper and lower bounds, with errors of second order in the $\delta\psi_{nt}$. One such bound was obtained for the particular case of the diagonal matrix elements of an operator of definite sign.[3] More precisely, it was shown that

$$W_{nn} \geq W_{nn}^{(-)}, \quad W \geq 0, \tag{1.3a}$$

and, as follows from an identical technique

$$W_{nn} \leq W_{nn}^{(+)}, \quad W \leq 0, \tag{1.3b}$$

where $W_{nn}^{(\pm)}$, which are given explicitly, differ in second order from $W_{nn}$. [The superscripts (+) and (−) will always denote upper and lower bounds, respectively.] We will extend the above results to the much wider class of operators for which one can readily perform the decomposition

$$W = W_+ + W_-, \tag{1.4a}$$

where

$$W_+ \geq 0, \quad W_- \leq 0. \tag{1.4b}$$

Furthermore, *both* bounds are obtained for such operators. While further generalizations may be possible we have confined the discussion (in Sec. III) to those cases, of interest in atomic physics, where $W$ can be bounded by a number, or where $W$ can be expressed as (or bounded by) a sum of terms, each term being a power of electron-electron or of electron-nucleus coordinates (or of conjugate momentum variables). The method is applicable to off-diagonal matrix elements $W_{nm}$, $n \neq m$. (The off-diagonal case is treated in Appendix B.)

The determination of bounds can often be much simplified by the use of three tactics. The first tactic is to proceed in small steps. Thus, stationary upper and lower bounds on the integral

$$(\Phi, \psi_n), \tag{1.5}$$

for $\Phi$ a known quadratically integrable function, have been obtained[3]; the problem is much simpler than that of obtaining bounds on $W_{mn}$. But $(\Phi, \psi_n)$ is equal to $W_{mn}$ for the choice $\Phi = W\psi_m$. The procedure will then be to bound $(\Phi, \psi_n)$ with $\Phi = W\psi_m$ thought of as known, and then to bound the matrix elements containing $\Phi$ in the bound on $(\Phi, \psi_n)$. The bound on $(\Phi, \psi_n)$ will contain not only $\Phi$ and $\psi_{nt}$ but the trial approximation $L_{nt}$ to the Lagrange-like function $L_n$ similar to that appearing in variational

principles,[4-9] the overlap integral

$$S_n = (\psi_n, \psi_{nt}), \tag{1.6}$$

and the exact energy $\epsilon_n$. $S_n$ and $\epsilon_n$ are relatively simple to bound, and they will often be carried through in the analysis, though of course they must ultimately be replaced by the appropriate bounds wherever they appear in the formulas.

The second tactic is not to directly bound the quantity of interest, say $W_{mn}$ or $(\Phi, \psi_n)$, but[3] to express the quantity of interest as an explicit calculable variational estimate plus a formal second order error and to obtain bounds on the second-order error term; these bounds may be simple, but they must preserve the second-order error aspect.

The third tactic is the replacement of non-positive-definite Hamiltonians by modified Hamiltonians which are positive definite. This tactic was employed earlier in the development of an upper variational bound on the scattering length $A$ for the scattering of $B$ by $C$. If $B+C$ at zero incident relative kinetic energy represents the lowest energy state of the system then with $E_{B0}$ and $E_{C0}$ the ground-state energies of the isolated system, we have $H - E_{B0} - E_{C0} > 0$ with respect to functions which decay or approach a constant at large separations of $B$ and $C$, and the problem of bounding $A$ is then very little different from the Rayleigh-Ritz variational bound on the ground state energy.[10] To obtain a bound on $A$ if $B$ and $C$ can form one or more bound states, one must extract the effects of these states without knowing the associated wave functions or energies. The extraction is possible and leads[11] to a stationary bound on $A$. The approach has been extended to a number of other problems.[12]

In Sec. II we obtain stationary upper and lower bounds on $(\Phi, \psi_n)$ slightly different from those obtained previously.[3] The advantage of these new expressions is that they make contact with some very recent work on variational principles for matrix elements; in this work, it is shown that difficulties associated with near singularities in the equation defining $L_{nt}$, near singularities which had been present in all previous papers on the subject in which generality of approach was preserved, can be avoided by use of a subsidiary minimum principle based on a modified Hamiltonian.[8]

In Sec. III, we show how the bounds obtained in Sec. II (which are often useful in their own right) can be used to obtain stationary upper and lower bounds on $W_{nn}$. More precisely, we find inequalities conjugate to those of Eq. (1.3), namely,

$$W_{nn} \leq W'^{(+)}_{nn}, \quad W \geq 0, \tag{1.7a}$$

and, as follows from an identical technique

$$W_{nn} \geq W'^{(-)}_{nn}, \quad W \leq 0, \tag{1.7b}$$

where $W'^{(\pm)}_{nn}$, which will be given explicitly, differ in second order from $W_{nn}$. Whenever the decomposition (1.4a) is possible, Eqs. (1.3) and (1.7) give the stationary upper and lower bounds on $W_{nn}$ that we are seeking.

In Sec. IV we apply these results to obtain a stationary upper bound on $A$ for the scattering of positrons by atoms or ions. The rigorous stationary upper bound on $A$ previously obtained is valid only for scattering by a target system whose wave function and energy are known precisely. (In the atomic case, we are thereby restricted to hydrogenlike systems.) Appendix B contains an extension of the results to off-diagonal matrix elements. We also obtain simple numerical results for $e^+$-He scattering in the Born approximation.

## II. STATIONARY UPPER AND LOWER BOUNDS ON $(\Phi, \psi_n)$

### A. Some notation and some known properties

It will be convenient to restrict considerations to the $(n=1)$ ground state. (The restriction can be readily removed; see Appendix B.) We will write $\psi$ rather than $\psi_1$ and $\psi_t$ rather than $\psi_{1t}$ whenever no confusion can arise. Our ground-state energy estimate is given by

$$\epsilon_{1t} \equiv (\psi_t, h\psi_t). \tag{2.1}$$

(Note that we retain the subscript 1 on the energy.) We introduce the exact and trial projection operators onto the ground state $p$ and $p_t$, and the orthogonal projection operators $q$ and $q_t$,

$$p = |\psi\rangle\langle\psi|, \quad q = 1 - p, \tag{2.2}$$

$$p_t = |\psi_t\rangle\langle\psi_t|, \quad q_t = 1 - p_t, \tag{2.3}$$

and the modified Hamiltonian

$$\hat{h} \equiv h - \frac{hp_t h}{\epsilon_{1t}}. \tag{2.4}$$

It has been shown[13] that, with respect to quadratically integrable functions,

$$\hat{h} \geq (\epsilon_1/\epsilon_{1t})\epsilon_2, \tag{2.5}$$

where $\epsilon_2$ is the energy of the first excited state if there is more than one bound state or the energy of the continuum threshold if there is only one bound state. For a good trial function $\psi_t$ the number on the right-hand side of the inequality (2.5)

will approach $\epsilon_2$. It will therefore normally be possible, using even relatively crude lower bounds on $\epsilon_1$ and $\epsilon_2$, to determine a number $\bar{\epsilon}_2$ such that

$$(\epsilon_1/\epsilon_{1t})\epsilon_2 \geq \bar{\epsilon}_2 \geq \epsilon_{1t}. \tag{2.6}$$

Under these circumstances, we have

$$\hat{h} - \bar{\epsilon}_2 \geq 0. \tag{2.7}$$

Associated with $\hat{h}$ is the resolvent operator

$$\hat{g}(\epsilon) \equiv (\epsilon - \hat{h})^{-1}. \tag{2.8}$$

It will also be convenient to introduce a modification of $\hat{g}(\epsilon)$, namely,

$$\hat{g}'(\epsilon) \equiv \hat{g}(\epsilon) - (p_t/\epsilon). \tag{2.9}$$

It is an immediate consequence of the definitions (2.1), (2.3), and (2.4) that

$$\hat{h}\psi_t = 0, \tag{2.10}$$

and, consequently, that

$$\hat{g}(\epsilon)p_t = p_t\hat{g}(\epsilon) = (p_t/\epsilon),$$

and thus that

$$p_t\hat{g}'(\epsilon) = \hat{g}'(\epsilon)p_t = 0 \tag{2.11}$$

for any $\epsilon$. Neither $\hat{g}(\epsilon)$ nor $\hat{g}'(\epsilon)$ will normally be calculable, and we introduce the trial resolvent operator $\hat{g}_t'$, chosen to satisfy

$$\hat{g}_t'(\epsilon)p_t = p_t\hat{g}_t'(\epsilon) = 0. \tag{2.12}$$

$\delta\hat{g}'$ is formally defined by

$$\delta\hat{g}'(\epsilon) \equiv \hat{g}_t'(\epsilon) - \hat{g}'(\epsilon), \tag{2.13}$$

and therefore, by Eqs. (2.11) and (2.12), satisfies

$$\delta\hat{g}'(\epsilon)q_t = q_t\delta\hat{g}'(\epsilon) = \delta\hat{g}'(\epsilon). \tag{2.14}$$

Using Eq. (1.2), we observe that

$$(\epsilon_1 - \hat{h})\psi = \left(\epsilon_1 - h + \frac{h|\psi_t\rangle\langle\psi_t|h}{\epsilon_{1t}}\right)\psi = Nh\psi_t, \tag{2.15}$$

where

$$N = (\epsilon_1/\epsilon_{1t})(\psi_t, \psi) = \epsilon_1 S^*/\epsilon_{1t}. \tag{2.16}$$

Provided only that $\epsilon_{1t} < \epsilon_2$, which we assume throughout to be the case, it follows from Eq. (2.5) that $\hat{h} > \epsilon_1$ and therefore that the inversion of $\epsilon_1 - \hat{h}$ is unique. By (2.9), and (2.15), we can then write[14]

$$\psi = N\hat{g}(\epsilon_1)h\psi_t = N[(\epsilon_{1t}/\epsilon_1)\psi_t + \hat{g}'(\epsilon_1)h\psi_t], \tag{2.17a}$$

where the normalization constant $N$ is given by Eq. (2.16). From Eq. (2.13), we have

$$\psi = N[(\epsilon_{1t}/\epsilon_1)\psi_t + \hat{g}_t'(\epsilon_1)h\psi_t] - N\delta\hat{g}'(\epsilon_1)h\psi_t. \tag{2.17b}$$

The first term of Eq. (2.17b) represents an explicit variational approximation to $\psi$, the second term being equal, by virtue of (2.14), to

$$N\delta\hat{g}'(\epsilon_1)(h - \epsilon_{1t})\psi_t,$$

a product of two first-order factors. Note that the appearance of $\epsilon_1$ as the argument of $\hat{g}_t'$ is a mere notational matter; $\hat{g}_t'(\epsilon_1)$ is to be chosen, and $\epsilon_1$ need not be known. The $\epsilon_1$'s appearing elsewhere in the expression for $\psi$, on the other hand, ultimately have to be replaced by the appropriate bound. Note too that $\hat{g}'(\epsilon_1)$ by construction, $\hat{g}_t'(\epsilon_1)$ by choice, and therefore $\delta\hat{g}'(\epsilon_1)$ are all nonsingular. We note for future reference that we can rewrite $\hat{g}'(\epsilon)$, using (2.9), (2.8), (2.10), and (2.3), as

$$\hat{g}'(\epsilon) = (\epsilon - \hat{h})^{-1}[1 - (\epsilon - \hat{h})(p_t/\epsilon)] = \hat{g}(\epsilon)q_t. \tag{2.18}$$

Since the unknown component of $\psi$ of Eq. (2.17b) is of second order and is nonsingular, the $\psi$ of (2.17b) serves as an excellent starting point for the determination of bounds on matrix elements containing $\psi$.

### B. Bounds on $(\Phi,\psi)$

Taking the inner product[15] of $\Phi$ with $\psi$ as given by Eq. (2.17b), and introducing the entity

$$L_t \equiv \hat{g}_t'(\epsilon_1)\Phi, \tag{2.19}$$

assumed to be known, we immediately obtain

$$(\Phi, \psi) \lessgtr N^{(b)}[(\epsilon_{1t}/\epsilon_1)(\Phi, \psi_t) + (L_t, h\psi_t) \pm |\Delta|^{(+)}], \tag{2.20}$$

where $|\Delta|^{(+)}$ is an upper bound on

$$|\Delta| \equiv |(\Phi, \delta\hat{g}'(\epsilon_1)(h - \epsilon_{1t})\psi_t)| \tag{2.21}$$

and $N^{(b)}$ is $N^{(+)}$ or $N^{(-)}$, as required by the sign of the quantity in square brackets. We must now obtain expressions for $|\Delta|^{(+)}$ and for $N^{(\pm)}$ which are to differ from $\Delta$ and $N$, respectively, by terms of second order.

To obtain $|\Delta|^{(+)}$, we start with Eq. (2.13), use Eq. (2.8) to replace $\hat{g}_t'$ by $-\hat{g}(\hat{h} - \epsilon_1)\hat{g}_t'$, and use Eq. (2.18) to replace $\hat{g}'$ by $\hat{g}q_t$. It then follows at once that[16,17]

$$\delta\hat{g}'(\epsilon_1) = -\hat{g}(\epsilon_1)[(\hat{h} - \epsilon_1)\hat{g}_t'(\epsilon_1) + q_t]. \tag{2.22}$$

We insert this in (2.21) and use the Schwarz inequality and (2.18) to obtain

$$|\Delta| \leq \|\hat{g}(\epsilon_1)J\| \times \|(h - \epsilon_{1t})\psi_t\|. \tag{2.23}$$

The function $J$ is defined by

$$J = q_t[(\hat{h} - \epsilon_1)\hat{g}_t' + q_t]\Phi = (\hat{h} - \epsilon_1)L_t + q_t\Phi. \tag{2.24}$$

We use the notation $\|f\|$ to represent the norm of $f$, defined by

$$\|f\| = (f, f)^{1/2}.$$

From the inequality

$$\|\hat{g}(\epsilon_1)J\| \leq (\bar{\epsilon}_2 - \epsilon_1)^{-1}\|J\|, \tag{2.25}$$

a consequence of the definition (2.8) and the inequality $\hat{h} > \bar{\epsilon}_2$ noted above, it follows that

$$|\Delta| \leq (\bar{\epsilon}_2 - \epsilon_1)^{-1} \|J\| \times \|(h - \epsilon_{1t})\psi_t\| \equiv |\Delta|^{(+)}. \quad (2.26)$$

We thus have an explicit expression for $|\Delta|^{(+)}$. The crucial point is that $|\Delta|^{(+)}$, a bound on a second order quantity, is itself of second order; thus, the norm involving $\psi_t$ is clearly of first order, as is the function $J$ since the operator $(\hat{h} - \epsilon_1)\bar{g}_t' + q_t$ which appears in Eq. (2.24) is of first order as can be seen from Eq. (2.22).

The determination of bounds on $N$ requires bounds on $S$. Choosing the arbitrary phase factor such that $S$ is positive we write

$$S^{(-)} \leq S \leq S^{(+)}$$

and note that the literature contains many expressions[18] for $S^{(\pm)}$. We record here only $S^{(+)} = 1$ and[19]

$$S^{(-)} = [(\epsilon_2 - \epsilon_{1t})/(\epsilon_2 - \epsilon_1)]^{1/2}. \quad (2.27)$$

Note that $S$ and $S^{(\pm)}$ all differ from unity, and therefore from one another, by terms of second or higher order. From (2.16) we have

$$N^{(\pm)} = (\epsilon_1/\epsilon_{1t}) S^{(\pm)}. \quad (2.28)$$

Substitution of Eqs. (2.26) for $|\Delta|^{(+)}$ and Eqs. (2.27) and (2.28) for $N^{(\pm)}$ into Eq. (2.20) gives us the desired calculable stationary upper and lower bounds on $(\Phi, \psi)$, superior to that obtained previously in that there is no possibility of near-singularity difficulties arising. The parameters in the trial Lagrangian can be obtained either directly by extremizing the bound on $(\Phi, \psi)$ or else indirectly from a subsidiary minimum principle.[8]

## III. STATIONARY UPPER AND LOWER BOUNDS ON $(\psi, W\psi)$

If $W$ is a non-negative operator, the Schwarz inequality gives the as yet formal stationary lower bound

$$(\psi, W\psi) \geq (\psi, W\psi_t)^2/(\psi_t, W\psi_t). \quad (3.1)$$

It is readily verified that the bound equation (3.1) is indeed stationary, that is, that the first-order error terms cancel. The bound is formal since $(\psi, W\psi_t)$ is not known, but with the choice $\Phi = W\psi_t$, a stationary lower bound on $(\psi, W\psi_t)$ follows from the results of Sec. II. The insertion of this result in Eq. (3.1) gives the explicit stationary lower bound on $(\psi, W\psi)$ for $W \geq 0$ referred to in the Introduction. (Note that even if $W$ is not a non-negative operator, but is bounded from below by a number $W_{\text{num}}^{(-)}$, the inequality analogous to (3.1) for the operator $W - W_{\text{num}}^{(-)}$ still leads to a stationary lower bound on $(\psi, W\psi)$. Similarly, if $W$ is not non-positive but is bounded from above by $W_{\text{num}}^{(+)}$, we can get a stationary upper bound on $(\psi, W\psi)$. These remarks may be verified by writing

$$(\psi, W\psi) = (\psi, [W - W_{\text{num}}^{(\pm)}]\psi) + W_{\text{num}}^{(\pm)}$$

and noting that $W - W^{(+)} \leq 0$ and $W - W^{(-)} \geq 0$. If $W$ is bounded from above *and* below, as for the interesting case $W = e^{ikr}$, where $W_{\text{num}}^{(\pm)} = \pm 1$, both bounds can be obtained.)

The above results are contained in Ref. 3. We will now show how stationary *upper* bounds on $(\psi, W\psi)$ can be derived for a rather wide class of operators $W$ to be defined below. This class includes operators which are not of definite sign. The stationary upper bound on $(\psi, W\psi)$ just noted provides us at the same time with a mechanism for obtaining a stationary lower bound on $(\psi, W\psi)$. Thus, if $W$ is a member of the class of operators under consideration, and if the decomposition $W = W_+ + W_-$ of (1.4a) is possible, a stationary lower bound on $(\psi, W_+\psi)$ can be obtained using the previous results and a stationary lower bound on $(\psi, W_-\psi)$ is provided by the stationary upper bound on $(\psi, [-W_-]\psi)$. The results can be extended to off-diagonal matrix elements.

### A. Identity for $\psi$ and properties of $\mathfrak{D}(W)$

Starting from the obvious identity

$$\psi_t = p\psi_t + q\psi_t$$

and using the relationship $p\psi_t = S\psi$, we have the much used identity

$$S\psi = \psi_t - q\psi_t. \quad (3.2)$$

This enables us to write

$$(\psi, W\psi) = [2S(\psi, W\psi_t) - (\psi_t, W\psi_t) + \mathfrak{D}(W)]/S^2, \quad (3.3)$$

where we have introduced the notation

$$\mathfrak{D}(B) \equiv (q\psi_t, Bq\psi_t), \quad (3.4)$$

where $B$ is an arbitrary operator. $(\psi_t, W\psi_t)$ is known and we can obtain stationary upper and lower bounds on $S$ and on $(\psi, W\psi_t)$. The determination of stationary bounds on $(\psi, W\psi)$ thereby reduces to the determination of appropriate bounds on $\mathfrak{D}(W)$. Since $q\psi_t$ is of first order ($q\psi$ being equal to zero), $\mathfrak{D}(W)$ is of second order. It follows that even a simple bound on $\mathfrak{D}(W)$ will suffice to provide a stationary bound on $(\psi, W\psi)$. More precisely, the use of $\mathfrak{D}(W) \leq \mathfrak{D}^{(+)}(W)$, where the ratio differs from 1 even in zeroth order in $\delta\psi$, so that $\mathfrak{D}^{(+)}(W)$ is of second order in $\delta\psi$, would suffice to provide a stationary upper bound on $(\psi, W\psi)$. (We could *not* allow $\mathfrak{D}^{(+)}(W)/\mathfrak{D}(W)$ to diverge as $\psi_t \to \psi$, that is, we could not allow an error of inverse order.) Correspondingly, the use of $\mathfrak{D}(W) \geq \mathfrak{D}^{(-)}(W)$, where $\mathfrak{D}^{(-)}(W)/\mathfrak{D}(W)$ differs from unity even in zeroth order, would suffice to provide a stationary lower bound on $(\psi, W\psi)$.

In particular, since $\mathfrak{D}(W)$ is linear in $W$ we have

$$\mathfrak{D}(W)<\mathfrak{D}(W^{(+)}) \text{ for } W<W^{(+)}. \tag{3.5}$$

If we can obtain a simple upper bound $\mathfrak{D}^{(+)}(W^{(+)})$ on $\mathfrak{D}(W^{(+)})$, then $\mathfrak{D}^{(+)}(W^{(+)})$ will also provide a simple upper bound on $\mathfrak{D}(W)$ and can therefore be used to obtain a stationary upper bound on $(\psi, W\psi)$. Bounds on $\mathfrak{D}(W)$ for certain simple types of operators $W$ can be obtained by methods similar to those introduced by Aranoff and Percus[20] in a somewhat different context. The possibility of bounding $\mathfrak{D}(W)$ by bounding $\mathfrak{D}(W^{+})$, to the accuracy of interest, greatly widens the range of $W$ for which the required bounds on $\mathfrak{D}(W)$ can be obtained.

As an example of the use of $\mathfrak{D}(W^{(+)})$, we note that in the determination of a stationary upper bound on $A$ for the zero energy scattering of a positron by an atom, one is faced with the need to bound $\mathfrak{D}(W)$ for a known operator $W$ which is finite for finite $r$, behaves as $\gamma r^2$ for large $r$ (with $\gamma$ known), and has a rather complicated functional dependence upon $r$ for $r$ small. It would then be difficult to bound $\mathfrak{D}(W)$ by the method of Aranoff and Percus, but their method could be used to obtain $\mathfrak{D}(W^{(+)})$, where

$$W(r)\leq W^{(+)}(r)=\alpha+\beta r+\gamma r^2,$$

with $\alpha$ and $\beta$ appropriately chosen. We shall return to this example in Sec. IV.

### B. Simple bounds on $\mathfrak{D}(W)$

The remainder of this section will be devoted to obtaining simple bounds on $\mathfrak{D}(W)$ for various simple forms of the operator $W$. The derivations given below are patterned after similar derivations in Ref. 20, and in some cases represent slight improvements over the latter. There are also some differences in definitions; the significance of some of these, and some questions of rigor, are mentioned in Appendix E of Ref. 1.

In what follows, we shall employ the language of atomic physics, and suppose that $h$ is the Hamiltonian of an atom of nuclear charge $Z$ with $Z'$ electrons. (The approach could also be applied to other types of Hamiltonians.) We will focus attention on operators which are functions of the electron-nucleus distances $r_i$ and the electron-electron distances $r_{ij}$, but it will become clear that other types of operators, particularly momentum dependent operators, can be treated as easily.

A property of $\mathfrak{D}(W)$ which will be useful in the following is recorded here: Using the indistinguishability of the electrons, it follows that for

$$W=\sum_{i=1}^{Z'} w_i, \tag{3.6}$$

where $w_i$ is a one-particle operator,

$$\mathfrak{D}(W)=Z'\mathfrak{D}(w_i). \tag{3.7}$$

It is shown in Appendix E of Ref. 1 that for Hermitian operators $B$ that have the property of becoming large at infinity, a bound on $\mathfrak{D}(B^2)$ that is often useful may be written

$$\mathfrak{D}(B^2)\leq\{([h-\epsilon_1]\psi_t, B^2[h-\epsilon_1]\psi_t)^{1/2} + \mathfrak{D}^{1/2}([\vec{B}'^{\dagger}, h]\cdot[h, \vec{B}'])\}^2/(\epsilon_2-\epsilon_1)^2, \tag{3.8}$$

where $\vec{B}'$ is a vector of odd parity satisfying

$$\vec{B}'^{\dagger}\cdot\vec{B}'=B^2. \tag{3.9}$$

Choosing $\vec{B}'=\vec{r}_i$, this becomes

$$\mathfrak{D}(r_i^2)\leq\{([h-\epsilon_1]\psi_t, r_i^2[h-\epsilon_1]\psi_t)^{1/2} + (2\hbar^2/Z'm)^{1/2}\mathfrak{D}^{1/2}(t)\}^2/(\epsilon_2-\epsilon_1)^2, \tag{3.10}$$

where $t$ is the total kinetic energy operator of the electrons, and where we have used Eq. (3.7) to give

$$\mathfrak{D}(p_i^2)=(2m/Z')\mathfrak{D}(t). \tag{3.11}$$

We note that, once having obtained a calculable bound on $\mathfrak{D}(r_i^2)$, we can calculate similar bounds for the operators $r_i$, $r_{ij}$, and $r_{ij}^2$ since

$$\mathfrak{D}(r_i)\leq(1-S^2)^{1/2}\mathfrak{D}^{1/2}(r_i^2), \tag{3.12}$$

$$\mathfrak{D}(r_{ij})\leq 2\mathfrak{D}(r_i), \tag{3.13a}$$

$$\mathfrak{D}(r_{ij}^2)\leq 4\mathfrak{D}(r_i^2). \tag{3.13b}$$

Equation (3.12) follows from

$$\mathfrak{D}^2(r_i)=(q\psi_t, r_i q\psi_t)^2\leq\|q\psi_t\|^2 \times\|r_i q\psi_t\|^2=(1-S^2)\mathfrak{D}(r_i^2). \tag{3.14}$$

Equations (3.13a) and (3.13b) are immediate consequences of $r_{ij}\leq r_i+r_j$. That these bounds lead to stationary bounds on $W_{nn}$ follows from the remarks made in conjunction with Eq. (3.5) above.

It remains, therefore, to obtain an upper bound on $\mathfrak{D}(t)$. To this end, we note that since $t=h-v$, where $v$ is the sum of the electron-nucleus and electron-electron interactions, it follows that

$$\mathfrak{D}(t)\leq|\mathfrak{D}(h)|+|\mathfrak{D}(v)|. \tag{3.15}$$

Moreover,

$$|\mathfrak{D}(v)|\leq Ze^2\sum_{i=1}^{Z'}\mathfrak{D}\left(\frac{1}{r_i}\right)+e^2\sum_{i\neq j}\mathfrak{D}\left(\frac{1}{r_{ij}}\right) =ZZ'e^2\mathfrak{D}\left(\frac{1}{r_i}\right)+\frac{Z'(Z'-1)}{2}e^2\mathfrak{D}\left(\frac{1}{r_{ij}}\right), \tag{3.16}$$

where $e$ is the electronic charge. Using (3.3) with $W=h$, one readily finds that

$$\mathfrak{D}(h)=\epsilon_{1t}-S^2\epsilon_1. \tag{3.17}$$

Comparing Eqs. (3.10), (3.15), (3.16), and (3.17), it can be seen that the last obstacles in the path of obtaining the desired bound on $\mathfrak{D}(r_i^2)$ will have been removed if we can obtain stationary bounds on $\mathfrak{D}(1/r_i)$ and $\mathfrak{D}(1/r_{ij})$. This can be most easily accomplished[20] via the commutation relationships

$$i\left(\vec{p}_i \cdot \frac{\vec{r}_i}{r_i} - \frac{\vec{r}_i}{r_i} \cdot \vec{p}_i\right) = \frac{2\hbar}{r_i}, \tag{3.18a}$$

$$i\left(\vec{p}_i \cdot \frac{\vec{r}_{ij}}{r_{ij}} - \frac{\vec{r}_{ij}}{r_{ij}} \cdot \vec{p}_i\right) = \frac{2\hbar}{r_{ij}}. \tag{3.18b}$$

It then follows from Schwarz's inequality that

$$\mathfrak{D}(1/r_i) \leq (1/\hbar)\mathfrak{D}^{1/2}(p_i^2)\mathfrak{D}^{1/2}(1) = (2m/\hbar^2 Z')^{1/2}(1-S^2)^{1/2}\mathfrak{D}^{1/2}(t) \tag{3.19a}$$

and similarly

$$\mathfrak{D}(1/r_{ij}) \leq (2m/\hbar^2 Z')^{1/2}(1-S^2)^{1/2}\mathfrak{D}^{1/2}(t). \tag{3.19b}$$

Combining Eqs. (3.17) and (3.19) with (3.15), we find

$$\mathfrak{D}(t) - (1-S^2)^{1/2} b \mathfrak{D}^{1/2}(t) - |\epsilon_{1t} - S^2\epsilon_1| \leq 0,$$

where

$$b \equiv (2m/\hbar^2 Z')^{1/2}[ZZ' + \tfrac{1}{2}Z'(Z'-1)]\, e^2. \tag{3.20}$$

It follows that

$$\mathfrak{D}^{1/2}(t) \leq \tfrac{1}{2}\{(1-S^2)^{1/2} b + [(1-S^2)b^2 + 4|\epsilon_{1t} - S^2\epsilon_1|\,]^{1/2}\}. \tag{3.21}$$

If Eq. (3.21) is not sufficiently accurate for the purposes at hand, one can use an alternative bound, though at the price of additional computational effort. The alternative bound may be derived using the virial theorem

$$(\psi, t\psi) = |\epsilon_1|. \tag{3.22}$$

We use (3.3) to express $\mathfrak{D}(t)$ in the form

$$\mathfrak{D}(t) = (\psi_t, t\psi_t) - 2S(\psi, t\psi_t) + S^2|\epsilon_1|. \tag{3.23}$$

If we replace $\epsilon_1$ and $(\psi, t\psi_t)$ by stationary lower bounds, Eq. (3.23) will give rise to the (simple) upper bound

$$\mathfrak{D}(t) \leq (\psi_t, t\psi_t) - 2S(\psi, t\psi_t)^{(-)} + S^2|\epsilon_1|. \tag{3.24}$$

The lower bound $(\psi, t\psi_t)^{(-)}$ on $(\psi, t\psi_t)$ may be obtained via Eq. (2.20) and the choice $\Phi = t\psi_t$.

The bounds we have obtained on $\mathfrak{D}^{1/2}(t)$, Eqs. (3.21) and (3.24) are each of first order, as is easily verified. Thus, when $\mathfrak{D}^{1/2}(t)$ in Eq. (3.10) is replaced by either of these expressions the resulting bound on $\mathfrak{D}(r_i^2)$ is a second-order quantity, and, in turn, the bounds on $\mathfrak{D}(r_i)$, $\mathfrak{D}(r_{ij})$, and $\mathfrak{D}(r_{ij}^2)$ calculated from Eqs. (3.12)–(3.14) using this bound will also be second order quantities.

We note that in the process of obtaining these bounds, we have obtained upper bounds on $\mathfrak{D}(1/r_i)$ and $\mathfrak{D}(1/r_{ij})$, when Eqs. (3.19) are combined with Eq. (3.21). Bounds on $\mathfrak{D}(W)$ for other powers of $r_i$ and $r_{ij}$ can be obtained by similar methods. Bounds on $\mathfrak{D}(W)$ for operators which are functions of momenta can similarly be obtained from equations such as Eq. (3.11).

Thus, when $W$ is any operator of the form of sums and products of powers of $r_i$, $r_{ij}$, $p_i$, and $p_{ij}$, rigorous, stationary upper bounds on $(\psi, W\psi)$ can be calculated directly from Eq. (3.3). Even when $W$ is not of so simple a form, we can nevertheless still compute the required stationary upper bound using (3.5) provided we can construct a sufficiently simple $W^{(+)}$.

The results of this section can be generalized to the case of off-diagonal matrix elements, as shown in Appendix B.

## IV. APPLICATION: RIGOROUS STATIONARY UPPER BOUND ON THE SCATTERING LENGTH FOR POSITRON-ATOM SCATTERING

We apply the bounds derived in Secs. I–III to obtain a stationary upper bound on the scattering length for the collisions of positrons with atoms or ions.[21] As mentioned previously, apparently no rigorous upper bound of any kind has previously been given for this quantity for atoms with more than one electron, because of the appearance of matrix elements involving the unknown target wave functions.[22]

Consider first a system consisting of a positron incident at zero energy on a neutral atom of nuclear charge $Z$. The case of Coulombic potentials requires a slightly different approach, and will be treated later on.

Let the target atom have exact energy levels $\epsilon_1, \epsilon_2, \ldots$, with corresponding exact normalized wave functions $\psi_1, \psi_2, \ldots$. Let us *temporarily* assume that $\psi_1$ and $\epsilon_1$ are known; these restrictions will be removed at the appropriate points in the derivation. If the target is initially in its spherically symmetric ground state, if no composite bound states are possible, and if pickup is not possible at zero incident energy, then a stationary bound on the $(L=0)$ scattering length is given by[10]

$$A \leq A_t + \frac{m}{2\pi\hbar^2}\int \Psi_t (H - \epsilon_1)\Psi_t \, d\vec{r}\, d\vec{\rho}. \tag{4.1}$$

Here

$$H = H(\vec{r}, \vec{\rho}) = T(\vec{\rho}) + h(\vec{r}) + V(\vec{r}, \vec{\rho}) \tag{4.2}$$

is the total Hamiltonian of the system, $\vec{\rho}$ denotes the positron coordinates and $\vec{r}$ stands for the space and spin coordinates of the target electrons, $T(\vec{\rho})$ is the positron kinetic energy operator, and

$V(\vec{r},\vec{\rho})$ is the positron-atom interaction. The exact wave function for the system $\Psi$ can be written

$$\Psi(\vec{r},\vec{\rho})=\sum_{i=1}^{\infty}\psi_i(\vec{r})u_i(\vec{\rho})=\psi_1(\vec{r})u_1(\rho)+\chi(\vec{r},\vec{\rho}), \tag{4.3}$$

where, in the zero-energy limit, $u_1(\rho)$ has the asymptotic forms

$$\begin{aligned} &u_1(\rho)\to\text{const.}, \quad \rho\to 0,\\ &u_1(\rho)\sim(A-\rho)/\rho, \quad \rho\sim\infty, \end{aligned} \tag{4.4}$$

and where $\chi(\vec{r},\vec{\rho})$, which represents the effects of all the closed channels (e.g., virtual pickup processes) falls off faster than $1/\rho$. Accordingly, without loss of generality, $\Psi_t$ can be taken to be of the form

$$\Psi_t(\vec{r},\vec{\rho})=\psi_1(\vec{r})u_{1t}(\rho)+\chi_t(\vec{r},\vec{\rho}), \tag{4.5}$$

where the asymptotic behavior of $u_{1t}$ is given by

$$\begin{aligned} &u_{1t}(\rho)\to\text{const.}, \quad \rho\to 0,\\ &u_{1t}\sim(A_t-\rho)/\rho, \quad \rho\sim\infty, \end{aligned} \tag{4.6}$$

and where $\chi_t$ is some approximation to $\chi$ which also falls off faster than $1/\rho$. In order to calculate the bound (4.1) we must therefore evaluate the integral

$$\begin{aligned} I\equiv\int\Psi_t(H-\epsilon_1)\Psi_t\,d\vec{r}\,d\vec{\rho}&=\int u_{1t}T(\vec{\rho})u_{1t}\,d\vec{\rho}\\ &+\int\psi_1(\vec{r})u_{1t}(\rho)V(\vec{r},\vec{\rho})u_{1t}(\rho)\psi_1(\vec{r})\,d\vec{r}\,d\vec{\rho}\\ &+2\int\chi_t[T(\vec{\rho})+V(\vec{r},\vec{\rho})]\psi_1(\vec{r})u_{1t}(\rho)\,d\vec{r}\,d\vec{\rho}\\ &+\int\chi_t(H-\epsilon_1)\chi_t\,d\vec{r}\,d\vec{\rho}. \end{aligned} \tag{4.7}$$

The bound (4.1) is thus far only a formal one, since $\psi_1$ and $\epsilon_1$ in (4.7) are not known exactly. However, if each term on the right-hand side of (4.7) which contains these unknown entities is replaced by a stationary upper bound, the sense of the inequality (4.1) will be preserved, as well as its stationary character, and the resulting bound on $A$ will become calculable.

To this end, let us examine each of the integrals on the right-hand side of Eq. (4.7). The first such integral can be calculated as it stands; it is furthermore finite as can be seen from Eq. (4.6), and need not be considered further. Similar considerations hold for the last integral on the right-hand side of Eq. (4.7), except that the result will contain the unknown number $\epsilon_1$. This can be then replaced by a stationary lower bound.

Consider next the third integral on the right-hand side of Eq. (4.7). After the integral over $d\vec{\rho}$ is performed, it is of the form

$$(\Phi^{(2)}(\vec{r}),\psi_1(\vec{r})), \tag{4.8a}$$

where $\Phi^{(2)}(\vec{r})$ is the known square-integrable function

$$\Phi^{(2)}(\vec{r})=\int\chi_t(T+V)u_{1t}\,d\vec{\rho}, \tag{4.8b}$$

and so may be bounded by the methods of Sec. II.

Finally, integration over $d\vec{\rho}$ in the second integral on the right-hand side of Eq. (4.7) results in the expression

$$(\psi_1(\vec{r}),W(\vec{r})\psi_1(\vec{r})), \tag{4.9}$$

where

$$W(\vec{r})\equiv\int u_{1t}(\rho)V(\vec{r},\vec{\rho})u_{1t}(\rho)\,d\vec{\rho}, \tag{4.10}$$

so that Eq. (4.9) may be bounded by the methods of Sec. III. Specifically, we note that the bound obtained using Eq. (3.3) is the one which is applicable since $W(\vec{r})\geq 0$. To see that $W(\vec{r})\geq 0$, note that Eq. (4.10) breaks up into $Z$ integrals of the form

$$\begin{aligned} w(r_i)&=4\pi e^2\int_0^{\infty}\left(\frac{1}{\rho}-\frac{1}{|\vec{r}_i-\vec{\rho}|}\right)u_{1t}^2(\rho)\rho^2\,d\rho\\ &=4\pi e^2\int_0^{r_i}\left(\frac{1}{\rho}-\frac{1}{r_i}\right)u_{1t}^2(\rho)\rho^2\,d\rho, \end{aligned} \tag{4.11}$$

which is clearly a positive quantity. It is unlikely, however, that a bound on $\mathfrak{D}(W)$ can be obtained directly. Rather, we must first construct an operator $W^{(+)}$ in accordance with the discussion of Eq. (3.5). It is not difficult to do this since it can be seen from (4.6) and (4.11) that $w(r_i)$ behaves as $4\pi e^2(\frac{1}{6}r_i^2)$ as $r_i\sim\infty$ while $w\to 0$ as $r_i\to 0$. We can therefore choose

$$W^{(+)}(\vec{r})=4\pi Ze^2(\alpha+\beta r_i+\tfrac{1}{6}r_i^2) \tag{4.12}$$

and obtain a stationary bound on $\mathfrak{D}(W^{(+)}(r))$, and hence on $\mathfrak{D}(W(r))$, with the help of Eqs. (3.10), (3.12), and (3.21). In Eq. (4.12), $\alpha$ and $\beta$ are constants which depend upon $W(r)$ and therefore upon the choice of $u_{1t}$, and thus, in general, can only be determined numerically.

We have thus accounted for all of the integrals on the right-hand side of Eq. (4.7) and shown how stationary upper bounds can be obtained for each of them, and hence how a stationary upper bound can be found for the scattering length of Eq. (4.1).

Explicitly, if the conditions listed above Eq. (4.1) hold true, and assuming real matrix elements, we have

$$\frac{2\pi\hbar^2}{m}(A-A_t) \leq \int u_{1t} T u_{1t}\, d\vec{\rho} + \int \chi_t (H-\epsilon_1)\chi_t\, d\vec{r}\, d\vec{\rho} + \frac{2\epsilon_1}{\epsilon_{1t}}\left(\frac{\epsilon_{1t}}{\epsilon_1}(\psi_t, W\psi_t) + (L_t^{(1)}, h\psi_t) + |\Delta^{(1)}|^{(+)}\right)$$
$$- \frac{1}{S^2}(\psi_t, W\psi_t) + \frac{4\pi Z e^2}{S^2}\left[\alpha(1-S^2) + \beta(1-S^2)^{1/2}[\mathfrak{D}^{(+)}(r_i^2)]^{1/2} + \tfrac{1}{6}\mathfrak{D}^{(+)}(r_i^2)\right]$$
$$+ \frac{2S\epsilon_1}{\epsilon_{1t}}\left(\frac{\epsilon_{1t}}{\epsilon_1}(\Phi^{(2)}, \psi_t) + (L_t^{(2)}, h\psi_t) + |\Delta^{(2)}|^{(+)}\right). \tag{4.13}$$

Here, $W = W(\vec{r})$ and $\Phi^{(2)} = \Phi^{(2)}(\vec{r})$ are defined by Eqs. (4.10) and (4.8b), respectively, and $L_t^{(1)}$ and $L_t^{(2)}$ are approximations to $\hat{g}\,' W\psi_t$ and $\hat{g}\,'\Phi^{(2)}$, respectively, chosen as described in Sec. II. The quantity $|\Delta^{(1)}|^{(+)}$ is given by Eq. (2.26), with $L_t^{(1)}$ as the trial auxiliary function, and $\Phi = \Phi^{(1)} \equiv W\psi_t$. Similarly, $|\Delta^{(2)}|^{(+)}$ is given by Eq. (2.26) with $L_t = L_t^{(2)}$ and $\Phi = \Phi^{(2)}$. Finally, the quantity $\mathfrak{D}^{(+)}(r_i^2)$ appearing in (4.13) is given by Eq. (3.10), and either (3.21) or (3.24).

It is also understood in (4.13) that appropriate bounds, so as to preserve the sense of the inequality, must be used to replace $\epsilon_1$, $\epsilon_2$, and $S$ wherever they appear.

Consider next the scattering of a positron by an atom of nuclear charge $Z$ with $Z'$ electrons. The case $Z = Z'$ represents scattering by a neutral atom, which we have just considered. The case $Z > Z'$ represents scattering by an ion of charge $(Z - Z')$. The foregoing procedure must in this case be modified as follows: we write, in lieu of integrals of the first type on the right-hand side of Eq. (4.7), the integrals

$$\int u_{1t}\left(T + \frac{[Z-Z']e^2}{\rho}\right)u_{1t}\, d\vec{\rho}. \tag{4.14}$$

Integrals of the type (4.14) have vanishing integrands as $\rho \to \infty$ because now $u_{1t}$ has Coulombic asymptotic behavior. The corresponding $V$ which appears in (4.10) is now of the form

$$\frac{Z'e^2}{\rho} - \sum_{i=1}^{Z'} \frac{e^2}{|\vec{r}_i - \vec{\rho}|},$$

so that Eq. (4.10) breaks up into $Z'$ integrals each of the type (4.11), which we studied previously. Thus, the foregoing procedure is readily modified to include Coulombic potentials of this type as well.

The extension to the case where the positron and the atom can form $n$ bound states is trivial. One need merely use the appropriate extension of Eq. (4.1), in which one introduces terms that effectively account for the $n$ states.[11] The additional terms involve the unknown target function in the form of an inner product with a known function and therefore may be treated by the method described in Sec. II. We exclude scattering by a negative ion because of the associated infinite number of composite bound states.

The extension to the "scattering length" $A_L$ that characterizes low-energy scattering in a state of total orbital angular momentum $L$ is also immediate. We need merely replace the $L = 0$ zero-energy asymptotic boundary conditions of Eqs. (4.4) and (4.6) by the boundary conditions appropriate to zero-energy angular momentum $L$ scattering.

The extension to electron-atom scattering is a more difficult problem. The origin of the difficulty lies in the appearance of exchange integrals. A typical such integral is of the form

$$\int u_{1t}(1)\psi_1(2,3)\left(-\frac{2}{r_2} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right) \times u_{1t}(2)\psi_1(1,3)\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3.$$

Stationary bounds on integrals of this type, which require a considerable modification of the methods given here, will be presented shortly.[23]

Finally, we note that—for computational reasons—it may not be desirable to obtain the various trial functions for use in these bounds directly from expressions such as (4.13), i.e., by varying the open parameters in the trial functions to produce a minimum. The reason is that all such parameters, whether initially introduced in a linear fashion or not, will become effectively nonlinear because of the form [Eq. (2.23)] of the bounds on $|\Delta^{(1)}|$ and $|\Delta^{(2)}|$. A simpler procedure would be to obtain these trial functions independently via some linear variational principle—for example, the trial target wave functions can be obtained from Rayleigh-Ritz (or Hylleraas-Undheim) calculations, the trial scattering function from the Kohn variational principle, and the trial auxiliary functions can be obtained from subsidiary minimum principles.[8] Of course any additional information, e.g., regarding polarizability, can be built in as desired. The trial wave functions so obtained can then be substituted into Eq. (4.13) to obtain the required rigorous stationary upper bound.

It may be useful to comment on the fact that stationary bounds on bound state matrix elements were used to obtain a stationary bound on $A$, which characterizes a continuum problem. This is possible because of the existence of the very general stationary upper bound on $A$ provided by Eq. (4.1), a stationary upper bound in which the trial scattering wave function $\Psi_t$ is chosen, subject only to

boundary conditions. Once $\Psi_t$ has been chosen, the only unknown is the target ground-state wave function, and the problem is reduced to the evaluation of bound-state matrix elements. Since stationary lower bounds on $A$ are not known, even assuming that the target ground-state wave function is known, we of course cannot use the methods of the present paper to obtain stationary lower bounds on $A$ when the target ground-state wave function is imprecisely known.

Despite its complicated appearance, (4.13) can in certain cases be used to obtain at least crude bounds with very little effort. Within the framework of the Born approximation, we have $\chi_t = 0$ and $A_t = 0$ and therefore $u_{1t} = -1$, and we further have $W = (4\pi Ze^2/6)r_i^2$, which allows the choice $\alpha = \beta = 0$; finally, we have $\Phi^{(2)} = L_t^{(2)} = \Delta^{(2)} = 0$, and (4.13) becomes

$$\frac{2\pi\hbar^2}{m} A \leq (2 - S^{-2})(4\pi Ze^2/6)(\psi_t, r_i^2\psi_t) + \frac{4\pi Ze^2}{6S^2}\mathfrak{D}^{(+)}(r_i^2) + \frac{2\epsilon_1}{\epsilon_{1t}}\{(L_t^{(1)}, h\psi_t) + |\Delta^{(1)}|^{(+)}\}. \tag{4.15}$$

[We can arrive at Eq. (4.15) more directly by noting that in the Born approximation (4.1) reduces immediately to

$$(2\pi\hbar^2/m)A \leq (4\pi Ze^2/6)(\psi, r_i^2\psi), \tag{4.16}$$

and that $(\psi, r_i^2\psi)$ can be readily bounded by using the results of Secs. II and III.]

In the particular case of helium, the exact value of $(\psi, r_i^2\psi)$ is for all practical purposes known exactly, and is given by Pekeris[24] as $1.1935a_0^2$, where $a_0$ is the Bohr radius. Since it is known that an $e^+$-He bound state does not exist,[25] and since the other requirements given above Eq. (4.1) are also fulfilled for He, we can set $Z = 2$ in (4.16) and obtain the rigorous stationary upper bound for $e^+$-He scattering:

$$A \leq 0.796a_0. \tag{4.17}$$

As anticipated, this result is quite crude, since it is rather well established[21] that $A \sim -0.5a_0$. It is nevertheless encouraging that a rigorous variational upper bound can so readily be obtained. (A rigorous lower bound[22] is $-0.7a_0$.)

## APPENDIX A: COMPARISON WITH A PREVIOUS RESULT

It will be useful to make some remarks comparing some of the present results with those contained in Ref. 3, where a stationary lower (upper) bound on $W_{nn}$ was obtained for $W \geq 0$ ($W \leq 0$).

The starting point of Ref. 3 was effectively an identity for $W_{nn}$, with $W_{nn}$ written as the sum of an explicit variational expression for $W_{nn}$ plus a (formal) second-order error term which was bounded. The starting point of the present paper is an identity for $\psi$, with $\psi$ written as the sum of an explicit variational expression for $\psi$ plus a (formal) second order error term which was bounded. Variational principles for wave functions obviously generate variational principles for matrix elements and the approaches do not differ in any significant way in this respect.

The approaches *do* differ in a significant way in that the present results are free from any possible near-singularity difficulties. We have been unable to determine whether or not the previous results are free of such difficulties. There is little doubt that the previous results represent a bound, but the interesting question arises as to what the best choice of $L_t$ is in the bound, that is, in Eq. (2.10) of Ref. 3, for the case where the energy eigenvalues are not known precisely. The suspicion arises that the best choice of $L_t$ is the solution of the differential equation (2.7) of Ref. 8, or of some other but similar differential equation, one which also possesses the near singularity difficulty discussed in detail in Ref. 8. The present paper makes it unnecessary to answer the question, because the results of the present paper have no doubts associated with them. The question should be answered nevertheless since the earlier results, if they do not in fact contain near singularities, would be somewhat simpler to use, where the earlier and present results overlap. (The present results, as noted, cover a broader range of cases.)

## APPENDIX B: OFF-DIAGONAL MATRIX ELEMENTS

We begin by describing a generalization of the result of Sec. II, in which stationary bounds on $(\Phi, \psi_n)$ were obtained, for $\psi_n$ the ground-state wave function $\psi_1$, to the case where $\psi_n$ is an excited state. We assume that a set of trial functions have been constructed, which satisfy

$$(\psi_{it}, h\psi_{jt}) = \epsilon_{it}\delta_{ij}, \qquad (\psi_i, \psi_j) = \delta_{ij} \tag{B1}$$

for $i, j = 1, 2, \ldots, n$. A variational approximation to $\psi_n$ was given previously.[14] It takes the form

$$\psi_{nv} = \psi_{nt} + \hat{g}_t' h\psi_{nt}. \tag{B2}$$

Here $\hat{g}_t'$ is an approximation to the modified resolvent operator

$$\hat{g}'(\epsilon_n) = (\epsilon_n - \hat{h})^{-1} - p_t/\epsilon_n, \tag{B3}$$

where

$$\hat{h} = h - \sum_{i=1}^{n} \frac{h|\psi_{it}\rangle\langle\psi_{it}|h}{\epsilon_{it}} \tag{B4}$$

and

$$p_t = \sum_{i=1}^{n} |\psi_{it}\rangle\langle\psi_{it}|. \tag{B5}$$

Consider now the identity

$$\psi_n = N_n[\psi_{nv} + g^{an}(\epsilon_n)(h-\epsilon_n)\psi_{nv}], \tag{B6}$$

where $N_n$ is a normalization factor and

$$g^{an}(\epsilon_n) \equiv \sum_{m\neq n} \frac{|\psi_m\rangle\langle\psi_m|}{\epsilon_n - \epsilon_m}. \tag{B7}$$

We have the inequality

$$(g^{an})^2 \leq (\epsilon_{\bar{n}} - \epsilon_n)^{-2}, \tag{B8}$$

where $\epsilon_{\bar{n}}$ is the eigenvalue closest to $\epsilon_n$. While this bound may be crude we note that $g^{an}$ appears in Eq. (B6) operating on a second-order quantity. The method of Sec. II may now be applied to provide upper and lower bounds on the overlap of $\psi_n$ either with itself (this is required to determine bounds on $N_n$) or with a given function of finite norm.

The above technique may be used, along with the appropriately generalized version of the method described in Sec. III, to provide stationary upper and lower bounds on off-diagonal matrix elements $(\psi_n, W\psi_m)$. Thus, writing Eq. (3.2) in the form

$$\psi_n = (1/S_n)[\psi_{nt} - q_n\psi_{nt}], \tag{B9}$$

where

$$q_n = 1 - |\psi_n\rangle\langle\psi_n|, \tag{B10}$$

along with a similar representation of $\psi_m$ we have, as a generalization of Eq. (3.3),

$$(\psi_n, W\psi_m) = \frac{1}{S_n}(\psi_{nt}, W\psi_m) + \frac{1}{S_m}(\psi_n, W\psi_{mt}) - \frac{1}{S_mS_n}(\psi_{nt}, W\psi_{mt}) + \frac{1}{S_nS_m}(q_n\psi_{nt}, Wq_m\psi_{mt}). \tag{B11}$$

The first two terms are overlap integrals of the type discussed above. The integrals $S_n$ and $S_m$ fall in the same category. Finally, the Schwarz inequality gives, for the last term in Eq. (B11),

$$(q_n\psi_{nt}, Wq_n\psi_{mt}) \lessgtr \pm(1-S_n^2)^{1/2}\mathfrak{D}_m^{1/2}(W^2). \tag{B12}$$

The methods described in Sec. III may be used to bound $\mathfrak{D}_m^{1/2}(W^2)$, the appropriate generalization of $\mathfrak{D}$ to the $m$th excited state.

Note that the identity (B6) does not reduce to (2.17a) for $n=1$; we have adopted a slighty different approach in our treatment of excited states. The identity for the excited-state function $\psi_n$ which reduces to (2.17a) for $n=1$ is given in Eq. (4.17) of Ref. 14. While this latter identity provides the basis for the variational approximation (B2) introduced above it is not the most convenient representation for the purpose of obtaining error bounds. The difficulty lies in the diagonalization procedure which must be carried out on the level-shift matrix, Eq. (4.18) of Ref. 14. This matrix involves a contribution of second order which is unknown and hence must be bounded. This would entail algebraic complexities (the effect of the error must be traced through the diagonalization procedure) which we avoided in the present approach based on (B6).

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*Work supported by the U. S. Army Research Office, Durham, Grant No. DA-ARO-D-31-124-72-G92 and by the Office of Naval Research Grant No. N00014-67-A-0467-0007.

†Supported in part by funds from the National Science Foundation under Grant No. GU-3186.

‡Work supported by the National Science Foundation.

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