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PHYSICAL REVIEW A VOLUME 8, NUMBER 1 JULY 1973

Upper and Lower Bounds on Quantum-Mechanical Matrix Elements*

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(Received 18 September 1972)

Upper and lower bounds were obtained previously on matrix elements of the form $W_{nm} = (\psi_n, W\psi_m)$, where W is a Hermitian operator and ψ_n and ψ_m are the wave functions of the nth and mth states of the system. The bounds are variational but nonstationary; they are expressed in terms of trial wave functions ψ_{nt} and ψ_{mt} containing variational parameters, but the error in the bound is of first order in the errors in the ψ_{nt} and ψ_{mt}. The results have been either subject to rather restrictive conditions (for example, only for certain specific choices for W and only for real wave functions) or have been very conservative. We remove most of these restrictions (W need not be positive or negative definite, the wave functions may be complex, the system may not even be invariant under time reversal) but maintain rigorous bounds of good quality. The method of using Gram-determinant inequalities, which has been employed previously, especially by Weinhold, and which we adopt, leads to variational but nonstationary bounds on W_{nm} in terms of "simple" upper bounds (which may be poor) on $W^2{}_{nn}$. Here again, only for a very few particular choices of W have such simple bounds on $W^2{}_{nn}$ been given previously (for example, n restricted to be the ground state, and W the operator z_i, the coordinate of the ith electron). The main result of this paper is to show that such simple upper bounds can be obtained for a very wide class of operators W in terms of the energy eigenvalues of the Hamiltonian. (They can be improved if given additional experimental information on oscillator strengths, for example). These simple bounds on $W^2{}_{nn}$ do not involve any trial wave functions. The method of variational but nonstationary bounds is illustrated for diagonal matrix elements of r_1 and r_1^2—we, therefore, require simple bounds on r_1^2 and r_1^4—for the states $1s^2\,{}^1S$ and $1s2s\,{}^3S$ of the helium atom, with rather good results.

I. INTRODUCTION

We will be concerned with the determination of bounds on matrix elements,

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

with a Hermitian inner product, of an arbitrary Hermitian operator W with respect to an orthonormal set of eigenfunctions defined by

$$(H - E_n)\psi_n = 0 \ .$$

These bounds can be of different classes. We will refer to the most rudimentary bounds as "simple bounds"; the bound is just a number—it does not contain any parameters to be varied. Our primary concern will ultimately be with "variational but nonstationary bounds"; the bound is a functional of trial functions ψ_{nt} and ψ_{mt} which contain parameters, and the parameters can be varied to obtain the best possible bound, but the bound is nonstationary in that the error (the difference between the bound and the true value) is of first order in the errors $\delta\psi_n$ in ψ_{nt} and $\delta\psi_m$ in $\delta\psi_{mt}$. [The error is of the form $O(\delta\psi_n) + O(\delta\psi_m)$.] In a schematic plot of the estimate *versus* one parameter c, the form of the trial function being such that for $c = c_0$ the trial function becomes the exact function, the curve is not flat at $c = c_0$ and does not even have a continuous derivative at that point; the curve does have its extremum value at $c = c_0$.

We note that for our variational but nonstationary bound the sign of the error is known but the error is of first order in $\delta\psi_n$ and in $\delta\psi_m$. On the contrary, for "variational principles," one does not know the sign of the error but the error itself is of second order. "Variational bounds" or, more accurately, variational stationary bounds combine the desired features, the error being of known sign *and* of second order. Such variational bounds on arbitrary matrix elements have not been published, but they do exist for the ground-state energy (the Rayleigh–Ritz principle) and for many of the matrix elements associated with scattering processes.[1] We will present variational bounds for arbitrary matrix elements in the following paper; for the present we merely note that they involve the evaluation of more difficult matrix elements, including matrix elements of H^2, than

need occur in variational but nonstationary bounds, so that the nonstationary results are not necessarily entirely superseded by variational bounds.

It is important to note that the variational but nonstationary bounds on W_{nn} often require bounds on $(W^2)_{nn}$; these latter bounds need not be very accurate since they appear multiplied by a quantity of second order. The simple bounds on $(W^2)_{nn}$ therefore play a useful and necessary role, even if the error is of order 100%.

Rigorous upper-bound formulas for W_{nn} have been obtained,[2-4] but no completely satisfactory general prescription has been given. The results are either very conservative[5] or applicable only to a restricted class of operators W, including the restriction that W be of a definite sign. We will obtain a number of new results, and will eliminate the definite sign restriction.

II. NOTATION AND TERMINOLOGY

E_n and ψ_n are the exact energy and the exact nth-bound-state normalized wave function, respectively, associated with the Hamiltonian $H=T+V$, where T and V are the total kinetic- and potential-energy operators.

ψ_{nt} is a normalized approximation to ψ_n.

All inner products are Hermitian inner products.

$S_n=(\psi_n, \psi_{nt})$ is an overlap integral.

$E_{\bar{n}}$ is the energy eigenvalue closest to E_n, that is, for which $|E_n-E_{\bar{n}}|$ is a minimum.

$P_n=|\psi_n\rangle\langle\psi_n|$ is the projection operator onto the nth state.

$Q_n=1-P_n$ is the orthogonal projection operator.

$G^{Q_n}=Q_n(E_n-H)^{-1}Q_n$ is a Green's-function-like operator.

A is an arbitrary operator.

$A_{nn}\equiv(\psi_n, A\psi_n)$; $A_{n,nt}\equiv(\psi_n, A\psi_{nt})$; $A_{nt,n}\equiv(\psi_{nt}, A\psi_n)$; $A_{nt,nt}\equiv(\psi_{nt}, A\psi_{nt})$.

$[H,A]$ is the commutator $HA-AH$.

$\alpha(A)=2(\psi_0, A[H,A]\psi_0)$, where ψ_0 is the ground state.

$\mathfrak{D}_n(A)\equiv[\psi_{nt}, (H-E_n)G^{Q_n}AG^{Q_n}(H-E_n)\psi_n]$.

$C^{(+)}$ and $C^{(-)}$ are upper and lower bounds, respectively, on some number C.

W is the Hermitian operator appearing in the matrix element to be bounded.

u_μ is a function for which $\sum_\mu |u_\mu|^2=1$, where the sum is over some specified set of values. The particular choice $u_{l\mu}=\mathfrak{N}_l Y_{l\mu}$, with μ ranging from $-l$ to l for any l, and $\mathfrak{N}_l=[4\pi/(2l+1)]^{1/2}$, will be used. l need not be related to the angular momentum of any particular state.

$\vec{r}_i$ is the position of the ith particle,

$$r_i=|\vec{r}_i|;\quad \vec{r}_{ij}=\vec{r}_i-\vec{r}_j;\quad r_{ij}=|\vec{r}_{ij}|;$$

z_i is a component of $\vec{r}_i$.

$\vec{p}_i$ is the momentum of the ith particle,

$$p_i=|\vec{p}_i|;\quad \vec{p}_{ij}=\vec{p}_i-\vec{p}_j;\quad p_{ij}=|\vec{p}_{ij}|\ .$$

N is the number of electrons and Z is the atomic number.

The indices i and j are particle labels, while the indices m and n are state labels. σ will denote the set of states for which specified matrix elements are experimentally known and ν will denote the complementary set.

$\|\chi\|\equiv(\chi,\chi)^{1/2}$ is the norm of χ for any function χ.

The inequalities to be used include, for any functions f_1, f_2, f_3, ..., the Schwarz inequality

$$|(f_1,f_2)|\le\|f_1\|\times\|f_2\|\ ,$$

the "triangle" inequality, based on the Schwarz inequality,

$$f_1=f_2+f_3+\cdots\rightarrow\|f_1\|\le\|f_2\|+\|f_3\|+\cdots\ ,$$

which is also true in "tensor form,"

$$\left(\sum_\mu (f_{1\mu}, f_{1\mu})\right)^{1/2}\le\left(\sum_\mu (f_{2\mu}, f_{2\mu})\right)^{1/2}+\left(\sum_\mu (f_{3\mu}, f_{3\mu})\right)^{1/2}+\cdots$$

and the Gram-determinant inequality, the nonnegative character of the $M\times M$ matrix $\vec{\vec{B}}$ with elements $B_{ij}\equiv(f_i, f_j)$.

The ijth element of the square of A will be written as either $(A^2)_{ij}$ or A^2_{ij}; the square of the ijth element of A will be written as either $(A_{ij})^2$ or $(A)^2_{ij}$.

III. BASIC INEQUALITIES

The first bounds on W_{nn} for a somewhat general Hermitian operator W were obtained by Weinhold[2] using the Gram-determinant inequality. The bound is a formal one, involving the unknown element W^2_{nn}, but multiplied by a factor which is very small for reasonable trial functions. Further, in one case, namely, $W=\sum_i z_i$, where an upper bound on W^2_{00} was previously available, Weinhold was able to obtain bounds on W_{0n}. One of our primary purposes will be to show that moderately accurate bounds on W^2_{nn}, accurate to perhaps a factor of 2, can be obtained relatively easily for a rather wide class of operators W. We will at the same time take the opportunity to rederive the basic inequalities without having to make the seemingly artificial assumption of Weinhold[2,6,7] that the matrix elements are all real.

To limit the scope of the investigation, we restrict ourselves to an approach which is based on the Gram-determinant inequality; which, further, involves only three functions; which, finally, is in a form which causes the bound to become the

exact value for the trial functions exact. The inequality becomes an equality for the three functions linearly dependent, which includes the case for which two of the functions are the same, the determinant then vanishing, and we therefore consider our three functions to be f, f_t, and g, with f_t an estimate of f. To obtain W_{nm} as one of the matrix elements, we must have ψ_n and $W\psi_m$ or $W\psi_n$ and ψ_m as two of the functions. The two cases are equivalent, and we restrict our attention to the choice ψ_n and $W\psi_m$. The third function can then be ψ_{nt} or $W\psi_{mt}$. Preliminary investigation indicates that the second choice is generally inferior, and we therefore make the choice ψ_n, ψ_{nt}, and $W\psi_m$. The matrix elements that arise are then W_{nm}, $W_{n,mt}$,

$$S_n \equiv (\psi_n, \psi_{nt}) \ ,$$

their complex conjugates, and W_{mm}^2. Thus, in addition to the desired element W_{nm}, there appear the additional elements S_n, $W_{n,mt}$, and W_{mm}^2. S_n is rather easy to bound (see Appendix A), a "simple bound" on W_{mm}^2 will be obtained, and $W_{n,mt}$ will be bounded by a second application of the Gram-determinant inequality.

To be more precise, consider a system with a Hamiltonian which satisfies $H = H^\dagger$; for the moment, we make no other assumptions, allowing systems which are not invariant under time reversal, such as a system in an external magnetic field. For three functions ψ, ψ_t, and ϕ, where $\|\psi\| = \|\psi_t\| = 1$, and $S = (\psi, \psi_t)$, the Gram-determinant inequality becomes

$$0 \geq |(\psi, \phi)|^2 - 2\,\mathrm{Re}[S(\psi_t, \phi)(\phi, \psi)] + |(\psi_t, \phi)|^2 - (1 - |S|^2)\|\phi\|^2 \ . \quad (3.1a)$$

Clearly we can rewrite this as

$$0 \geq |(\psi, \phi)|^2 - 2|S| \times |(\psi_t, \phi)| \times |(\psi, \phi)| + |(\psi_t, \phi)|^2 - (1 - |S|^2)\|\phi\|^2 \ . \quad (3.1b)$$

The allowable values of $|(\psi, \phi)|$ must lie between the roots of the equation obtained by replacing the inequality in (3.1) by an equality. We find

$$|(\psi, \phi)| \lesseqgtr |S| \times |(\psi_t, \phi)| \pm \{(1 - |S|^2)[\|\phi\|^2 - |(\psi_t, \phi)|^2]\}^{1/2} \ . \quad (3.2)$$

Choosing $\psi = \psi_n$, $\psi_t = \psi_{nt}$, and $\phi = W\psi_m$, (3.2) becomes

$$|W_{nm}| \lesseqgtr |S_n| \times |W_{nt,m}| \pm [(1 - |S_n|^2)(W_{mm}^2 - |W_{nt,m}|^2)]^{1/2} \ . \quad (3.3)$$

If, on the other hand, we choose $\psi = \psi_m$, $\psi_t = \psi_{mt}$, and $\phi = W\psi_{nt}$, (3.2) becomes

$$|W_{m,nt}| = |W_{nt,m}| \lesseqgtr |S_m| \times |W_{nt,mt}| \pm [(1 - |S_m|^2)(W_{nt,nt}^2 - |W_{nt,mt}|^2)]^{1/2} \equiv |W_{nt,m}|^{(\pm)} \ . \quad (3.4)$$

Since upper and lower bounds on $|S_m|$ can be obtained (see Appendix A), and since $W_{nt,mt}$ can be calculated once trial functions have been chosen, the upper and lower bounds $|W_{m,nt}|^{(\pm)}$ on $|W_{m,nt}|$ are calculable. Equations (3.3) and (3.4) can be combined to give

$$|W_{nm}| \lesseqgtr |S_n|\,|W_{nt,m}|^{(\pm)} \pm \{(1 - |S_n|^2)[W_{mm}^{2(+)} - (|W_{nt,m}|^{(-)})^2]\}^{1/2} \ . \quad (3.5)$$

We therefore have upper and lower bounds on $|W_{nm}|$ in terms of bounds on S_n and S_m and an upper bound on W_{mm}^2.

If we assume that all of the matrix elements that enter are real, we can repeat the above derivation, dropping Re and absolute magnitudes everywhere, and arrive at

$$W_{nm} \lesseqgtr S_n W_{nt,m}^{(\pm)} \pm \{(1 - S_n^2)[W_{mm}^{2(+)} - (W_{nt,m}^{(-)})^2]\}^{1/2} \ , \quad (3.6)$$

where

$$W_{nt,m}^{(\pm)} = S_m W_{nt,mt} \pm \{(1 - S_m^2)\,[W_{nt,nt}^2 - (W_{nt,mt})^2]\}^{1/2} \ . \quad (3.7)$$

Equations (3.6) and (3.7) represent Weinhold's result.[2]

The result contained in (3.6) is at least as good as that contained in (3.5), but the requirement that all matrix elements that enter are real can be very restrictive. There are a number of physically interesting cases in which one can improve upon (3.5), and these are discussed in Appendix B. It is shown, for example, that (3.6), together with (3.7) (with m replaced by n throughout), is applicable for bounds on W_{nn} for systems that are invariant under time reversal and under rotation.

We have throughout assumed the possibility of obtaining simple bounds on W^2, and in particular, the upper bound, $W_{mm}^{2(+)}$. In Sec. IV we turn our attention to different possibilities of doing so.

IV. SIMPLE BOUNDS

We assume that H is of the form

$$H = \sum_{i=1}^{N} T_i + V(\vec{r}_1, \vec{r}_2, \dots) \ , \quad (4.1)$$

where

$$T_i = -(\hbar^2/2m)\vec{\nabla}_i^2 \ ,$$

and we assume further that the particles are identical. (The latter restriction is a matter of convenience; the various inequalities can be obtained for nonidentical particles with little extra effort, but the formulas are much more cumbersome and the techniques are no different.) In Sec. IV A we establish formulas for simple bounds on W^2 for the ground state, which are then specialized in Sec. IV B for $W = r_i^q$. In Sec. IV C general results applicable also to excited states are established. Finally, in Sec. IV D, we present a miscellany of bounds on r_i^q, r_{ij}, p_i, and p_{ij}. In all these sections we concentrate on simple *upper* bounds because it is these that are needed in the results of Sec. III. We note, parenthetically, that simple *lower* bounds can also be obtained and may be useful as a guide to judge the quality of the upper bounds. As an example, restricting our attention to r_i^2, we have

$$(r_i^2)_{00} = \sum_m (\psi_0, \vec{r}_i\psi_m)\cdot(\psi_m, \vec{r}_i\psi_0) \geq \sum_\sigma |(\vec{r}_i)_{0m}|^2 = N^{-2}\sum_\sigma \left|\left(\sum_i \vec{r}_i\right)_{0m}\right|^2 ,$$

the matrix elements for m, a member of the set σ, being known experimentally. Another trivial result, namely, $(W^2)_{nn} \geq (W_{nn})^2$, may also be useful in getting simple bounds on W^2 when one has information on W_{nn}.

A. Ground State: *W* Arbitrary

Our first approach is a technique which represents an extension and adaptation of methods used by Rebane and Braun[8] to determine an upper bound on the total electric-dipole moment. We define a function u_μ such that $\sum_\mu |u_\mu|^2 = 1$. A convenient choice is

$$u_{l\mu} = \mathfrak{N}_l Y_{l\mu} , \tag{4.2}$$

where l is arbitrary and where

$$\mathfrak{N}_l = \left(\sum_\mu |Y_{l\mu}|^2\right)^{-1/2} = \left(\frac{4\pi}{2l+1}\right)^{1/2} , \tag{4.3}$$

μ ranging from $-l$ to l. With ψ_0 the ground state and ψ_m the complete set of states of H, we can now write

$$\begin{aligned}
&\sum_\mu (\psi_0, Wu_\mu^*[H, Wu_\mu]\psi_0) \\
&= \sum_{\mu,m} (\psi_0, Wu_\mu^*\psi_m)(\psi_m, [HWu_\mu - Wu_\mu H]\psi_0) \\
&= \sum_{\mu,m} (E_m - E_0)(\psi_0, Wu_\mu^*\psi_m)(\psi_m, Wu_\mu\psi_0) \\
&\geq (E_1 - E_0)\sum_\mu \sum_m{}' (\psi_0, Wu_\mu^*\psi_m)(\psi_m, Wu_\mu\psi_0) \\
&= (E_1 - E_0)\sum_\mu [(\psi_0, Wu_\mu^* Wu_\mu\psi_0) - |(\psi_0, Wu_\mu\psi_0)|^2] \\
&= (E_1 - E_0)\left(W_{00}^2 - \sum_\mu |(\psi_0, Wu_\mu\psi_0)|^2\right) .
\end{aligned} \tag{4.4}$$

The prime on the sum over m denotes the exclusion of the $m = 0$ term. We have assumed that W commutes with u_μ; this assumption could be relaxed if necessary, but throughout this paper we consider only W's that satisfy this condition.

Though it is not necessary to do so (and we consider in Appendix C the more general case), we will assume that

$$(\psi_0, Wu_\mu\psi_0) = 0 . \tag{4.5}$$

For $Wu_\mu = rY_{1\mu}$, for example, this is just the result that $(\psi_0, \vec{r}\psi_0) = 0$ for nondegenerate ground states. We then have

$$W_{00}^2 \leq \tfrac{1}{2}\alpha(W)(E_1 - E_0)^{-1} , \tag{4.6}$$

where

$$\begin{aligned}
\alpha(W) &\equiv 2\sum_\mu (\psi_0, Wu_\mu^*[H, Wu_\mu]\psi_0) \\
&= \sum_\mu (\psi_0, [Wu_\mu^*, [H, Wu_\mu]]\psi_0) ;
\end{aligned} \tag{4.7}$$

the last step follows trivially on writing out the commutators in detail and replacing H by E_0 whenever it is adjacent to ψ_0. The dependence of $\alpha(W)$ on u_μ has been suppressed. The bound (4.6) is useful because $\alpha(W)$ can be evaluated for a number of interesting cases, including W different powers of r_i, as we will see shortly. The particular choice $u_\mu = u_{1\mu}$ is reminiscent of a procedure used by Aranoff and Percus[5] in a different context. The formal result (4.6) is applicable in both atomic and nuclear physics. In what follows, we will mainly use the language of atomic physics. The nuclear problem differs in two ways. Not all particles are identical, and the difference between neutrons and protons is particularly important for large nuclei. On the other hand, the center-of-mass corrections [an N-nucleon nucleus has only $(N-1)$ independent coordinates, unlike an N-electron atom] are particularly significant for small nuclei.

Following a very simple technique used in bounding the dynamic polarizability of a system,[9] we can often improve the upper bound [(4.6)] by using experimental data. Assume, for example, that $W = r_i$, the radial coordinate of the ith particle, that we choose $u_\mu = u_{i1\mu}$, and that the dipole-oscillator matrix elements,

$$\left|\left(\psi_0, \sum_i \vec{r}_i\psi_m\right)\right|^2 = \sum_\mu \left|\left(\psi_0, \sum_i r_i u_{i1\mu}\psi_m\right)\right|^2 , \tag{4.8}$$

are known. The identity (4.8) follows on using

$$\sum_\mu u_{i1\mu}(\hat{r}_i)u_{i1\mu}(\hat{r}_i') = \hat{r}_i\cdot\hat{r}_i' ,$$

where

$$u_{i1\mu} = \mathfrak{N}_1 Y_{1\mu}(\theta_i, \phi_i) . \tag{4.9}$$

The energy differences $E_m - E_0$ are also assumed known for the set σ of values of m. Let the orthogonal set be denoted by ν, let m_0 be the smallest value of m contained in ν for which $(\psi_{m_0}, r_i u_{i1\mu}\psi_{m_0})$ is nonvanishing, and assume that $E_{m_0} - E_0$ also is known. Then in the expression for $\alpha(r_i)$, which is

$$\tfrac{1}{2}\alpha(r_i) = \frac{1}{2}\sum_\mu (\psi_0, [r_i u_{i1\mu}^*, [H, r_i u_{i1\mu}]]\psi_0)$$

$$= \sum_m (E_m - E_0)\left|(\psi_0, \vec{r}_i\psi_m)\right|^2 ,$$

where we have introduced a complete set of states and used (4.8), we can write

$$\tfrac{1}{2}\alpha(r_i) \geq \sum_\sigma (E_m - E_0)\left|(\psi_0, \vec{r}_i\psi_m)\right|^2 + (E_{m_0} - E_0)\sum_\nu \left|(\psi_0, \vec{r}_i\psi_m)\right|^2$$

$$= \sum_\sigma (E_m - E_{m_0})\left|(\psi_0, \vec{r}_i\psi_m)\right|^2 + (E_{m_0} - E_0)(\psi_0, r_i^2\psi_0) ,$$

where we added and subtracted

$$(E_{m_0} - E_0)\sum_\sigma \left|(\psi_0, \vec{r}_i\psi_m)\right|^2$$

and used closure over m. [Note that (4.5) is satisfied by parity considerations.] We therefore have the simple bound,

$$(\psi_0, r_i^2\psi_0) \leq (E_{m_0} - E_0)^{-1} \times \left(\tfrac{1}{2}\alpha(r_i) - \sum_\sigma (E_m - E_{m_0})\left|(\psi_0, r_i\psi_m)\right|^2\right) . \quad (4.10a)$$

With $\alpha(r_i) = 3\hbar^2/m$ from (D12) (with $l = q = 1$) and the usual definition of the atomic oscillator strength,[10]

$$f_{0m} = \frac{2m}{3\hbar^2}(E_m - E_0)\left|\left(\psi_0, \sum \vec{r}_i\psi_m\right)\right|^2 = \frac{2m}{3\hbar^2}(E_m - E_0)N^2\left|(\psi_0, \vec{r}_i\psi_m)\right|^2 ,$$

we have

$$(\psi_0, r_i^2\psi_0) \leq \frac{3\hbar^2}{2m}(E_{m_0} - E_0)^{-1} \times \left[1 - \frac{1}{N^2}\sum_\sigma\left(\frac{E_m - E_{m_0}}{E_m - E_0}\right)f_{0m}\right] . \quad (4.10b)$$

The use of experimental data to improve the bound, while illustrated for two particular examples later in Table II, can clearly be given for W arbitrary.

B. Ground State: Positive Powers of r_i

If $W = W(r_1, r_2, \ldots)$, it follows that $[H, W] = [T, W]$, where T is the kinetic-energy operator. $\alpha(W)$ is then independent of the potential V and can often be readily evaluated or bounded. Thus, for $W(r) = r_i^q$, using simple commutator analysis (see Appendix D) we have the identity, valid for $l = 1, 2, \ldots,$

$$\alpha(r_i^q) = (\hbar^2/m)[q^2 + l(l+1)](\psi_0, r_i^{2q-2}\psi_0) . \quad (4.11a)$$

[If we are to use the identity in the form (4.6), we must guarantee the validity of (4.5). This is true for all odd l, by parity, and it is true for $l > 2L$, where L is the total orbital angular momentum of the ground state, by conservation of angular momentum. (L is a good quantum number since we took V to be spin independent; it is a trivial matter to drop this restriction.)] To use (4.11a) it may be necessary to iterate, until the bound involves $(\psi_0, r_i^0\psi_0) = 1$. Thus, for the choice $l = 1$, we have

$$\alpha(r_i^q) = (\hbar^2/m)(q^2 + 2)(\psi_0, r_i^{2q-2}\psi_0) . \quad (4.11b)$$

It follows from (4.6) that

$$(\psi_0, r_i^{2q}\psi_0) \leq (\hbar^2/2m)[(q^2+2)/(E_1 - E_0)](\psi_0, r_i^{2q-2}\psi_0) . \quad (4.12a)$$

Iterating, this reduces to

$$(\psi_0, r_i^{2q}\psi_0) \leq [(\hbar^2/2m)/(E_1 - E_0)]^q(q^2+2) \times [(q-1)^2+2]\times\cdots\times(1^2+2) . \quad (4.12b)$$

In Table I we compare this simple bound with the exact values for H and He and for $q = 1$–4. For He, for $q = 1$, we also calculate the improved simple bound based on the use of experimental data[11] (Table II). In determining the bounds on r_1^{2q} for He, the energy of the lowest excited state, a $1s\,2s$ state, plays no role for $l \geq 1$; for $l = 1$, for example, the energy E_1 is taken to be that of the $1s\,2p$ state, the lowest state connected to ψ_0.

C. Ground and Excited States

Consider the nth excited state, with wave function ψ_n and energy E_n, and define $\beta(W)$ as

$$\beta(W) \equiv \sum_\mu (\psi_n, [Wu_\mu^*, H][H, Wu_\mu]\psi_n) . \quad (4.13)$$

Introducing a unit operator between the commutators in the form of the complete set of states ψ_m of the Hamiltonian H, we have

$$\beta(W) = \sum_m\sum_\mu (E_n - E_m)^2(\psi_n, Wu_\mu^*\psi_m)(\psi_m, Wu_\mu\psi_n) \geq (E_n - E_{\bar{n}})^2\left(\sum_\mu (\psi_n, W^2|u_\mu|^2\psi_n) - \sum_\mu \left|(\psi_n, Wu_\mu\psi_n)\right|^2\right) , \quad (4.14)$$

where $\bar{n}$ is the state closest to n for which $(\psi_n, Wu_\mu\psi_{\bar{n}})$ is nonvanishing. Once again, as in

TABLE I. Simple upper bounds on $(r_i)^{2q}$ with $q=1,2,3,4$, for the ground states of H and He, obtained using Eq. (4.12), with $\alpha(W)$ obtained from Eq. (4.11b). κ^2 is defined by $\kappa^2=\hbar^2/[m(E_1-E_0)]$. The true value of $(r_i^2)_{00}$ for He was taken from Ref. 12. The numerical values are in units of the appropriate power of the Bohr radius a_0 $(=\hbar^2/me^2)$.

W^2	$\alpha(W)m/\hbar^2$	Upper bound on $(W^2)_{00}$	H		He	
			Upper bound	True	Upper bound	True
r_i^2	3	$\frac{1}{2}(3\kappa^2)$	4	3	1.92	1.1935
r_i^4	$6(r_i^2)_{00}$	$\frac{1}{2}(9\kappa^4)$	32	22.5	7.40	···
r_i^6	$11(r_i^4)_{00}$	$\frac{1}{4}(99\kappa^6)$	469	315	52.2	···
r_i^8	$18(r_i^6)_{00}$	$\frac{1}{4}(891\kappa^8)$	11300	7087.5	603	···

Sec. IV A, we focus attention on the u_μ's for which $(\psi_n, Wu_\mu\psi_n)=0$, though this restriction can be relaxed (see Appendix C). Equation (4.14) then becomes

$$\beta(W)\geq(E_n-E_{\bar{n}})^2(\psi_n, W^2\psi_n)\ , \tag{4.15}$$

providing an upper bound on W_{nn}^2, n arbitrary, for a wide class of operators W for which $\beta(W)$ can be evaluated. Consider, for example,

$$W=r_i,\quad u_{i1\mu}=\mathfrak{N}_1 Y_{1\mu}(\theta_i,\phi_i)\ . \tag{4.16}$$

We then have, from Eqs. (4.13), (4.9), and (D1),

$$\beta(r_i)=(\psi_n,[\vec{r}_i,H]\cdot[H,\vec{r}_i]\psi_n)=(\hbar^2/m^2)(\psi_n,p_i^2\psi_n)$$
$$=(2\hbar^2/m)|E_n|/N\ , \tag{4.17}$$

with the second equality due to the virial theorem for an ion containing N electrons. The essential feature is the interaction through Coulomb forces. [Equation (4.17) is the first relationship restricted to the atomic case.] Thus we get a simple upper bound on $(\psi_n, r_i^2\psi_n)$,

$$(\psi_n, r_i^2\psi_n)\leq\frac{(2\hbar^2/m)|E_n|}{N(E_{\bar{n}}-E_n)^2}\ . \tag{4.18}$$

This bound can be improved upon, as in Eq. (4.10), when a set σ of the matrix elements $(\psi_n, \vec{r}_i\psi_m)$ is known, as perhaps from experimentally determined dipole-oscillator strengths. We write

$$\frac{(2\hbar^2/m)|E_n|}{N}=\sum_\sigma(E_n-E_m)^2|(\psi_m,\vec{r}_i\psi_n)|^2$$
$$+\sum_\nu(E_n-E_m)^2|(\psi_m,\vec{r}_i\psi_n)|^2$$
$$\geq\sum_\sigma(E_n-E_m)^2|(\psi_m,\vec{r}_i\psi_n)|^2$$
$$+(E_{\bar{m}_0}-E_n)^2\Big((\psi_n,r_i^2\psi_n)-\sum_\sigma|(\psi_m,\vec{r}_i\psi_n)|^2\Big)$$

or

$$(\psi_n, r_i^2\psi_n)\leq(E_{\bar{m}_0}-E_n)^{-2}\left(\frac{2\hbar^2|E_n|}{mN}-\frac{3\hbar^2}{2mN^2}\right.$$
$$\left.\times\sum_\sigma\frac{[E_m^2-E_{\bar{m}_0}^2-2E_n(E_m-E_{\bar{m}_0})]f_{nm}}{E_m-E_n}\right), \tag{4.19}$$

with f_{nm} defined as in Eq. (4.10) and $\bar{m}_0$ the value in ν closest to n for which $(\psi_{\bar{m}_0},\vec{r}_i\psi_n)$ is nonvanishing. The choice of $u_{i\mu}\propto Y_{1\mu}$ may result sometimes in small energy denominators for certain excited states. In such a case, a substantial improvement can be made by choosing $u_{i\mu}$ to be a higher spherical harmonic so that $\bar{m}_0$ lies far from n.

Note that Eq. (4.19), though applicable to the ground state, is in general inferior to Eq. (4.10b) of Sec. IV B. For example, in He, using these formulas in the simplest manner by setting $\bar{m}_0=1$ and dropping the term in $\sum_\sigma$, we have $(\psi_0, r_i^2\psi_0)\leq 4.78a_0^2$ from (4.19) to be compared with the upper bound $1.92a_0^2$ obtained from (4.10b). It may, therefore, be expected that for low-lying excited states a result superior to (4.15) will result from

TABLE II. Improvement of the simple bound on $(r_i^2)_{00}/a_0^2$ for He given in Table I by using additional experimental data; also a simple bound on the lowest triplet state of He [see Eq. (4.10b)]. Data on the oscillator strengths f_{0n} and energy levels were taken from Ref. 11, and the true values from Ref. 12. Notice in particular the considerable improvement in the ^3S value when the nearby $1s\,2p$-state contribution is accounted for. a_0 is the Bohr radius.

Number of f_{0n} used	Upper bound on $(r_i^2)_{00}/a_0^2$ [a]	
	$(1s)^2\,{}^1S$	$1s\,2s\,{}^3S$
0	1.924	35.66
1	1.779	15.89
2	1.734	13.93
3	1.715	13.25
⋮	⋮	⋮
8	1.689	12.51

[a] True values: 1.1935, 11.46.

a formula analogous to (4.6) in Sec. IV B, involving a single energy denominator instead of a square, with this denominator being bounded by $E_n - E_{\bar{n}}$, *after* all the terms involving states from 0 to n have been accounted for by experimental data (which may be feasible for small values of n).

To obtain an upper bound on $(r_i^4)_{nn}$, we choose $W = r_i^2$ and $u_{i\mu} = \mathfrak{N}_1 Y_{1\mu}(\theta_i, \phi_i)$ in (4.15). We have, following closely the derivation of (4.17),

$$\beta(r_i^2) = (\psi_n, [r_i^2 \hat{r}_i, H] \cdot [H, r_i^2 \hat{r}_i] \psi_n) \quad . \tag{4.20a}$$

But

$$[H, r_i^2 \hat{r}_i] = (-i\hbar/m)(p_{r_i} \vec{r}_i + r_i \vec{p}_i) \quad , \tag{4.20b}$$

where the Hermitian operator,

$$p_{r_i} = \frac{\hbar}{i}\left(\frac{\partial}{\partial r_i} + \frac{1}{r_i}\right) \quad ,$$

is the momentum conjugate to r_i. Use of the triangle inequality gives

$$\beta^{1/2}(r_i^2) \leq (\hbar/m)[(\psi_n, \vec{r}_i p_{r_i} \cdot p_{r_i} \vec{r}_i \psi_n)^{1/2} + (\psi_n, \vec{p}_i r_i \cdot r_i \vec{p}_i \psi_n)^{1/2}] \quad . \tag{4.21}$$

Using (D6) and (D7) we have

$$\vec{r} p_r \cdot p_r \vec{r} = p_r^2 r^2 + 2i\hbar p_r r \quad , \quad \vec{p} r \cdot r \vec{p} = p^2 r^2 + 2i\hbar \vec{p} \cdot \vec{r} \quad .$$

Use of the triangle inequality and $p_r^2 \leq p^2$ now gives

$$(\psi_n, \vec{r}_i p_{r_i} \cdot p_{r_i} \vec{r}_i \psi_n) \leq (\psi_n, r_i^4 \psi_n)^{1/2} (\psi_n, p^4 \psi_n)^{1/2} + 2\hbar (\psi_n, r_i^2 \psi_n)^{1/2} (\psi_n, p^2 \psi_n)^{1/2} \tag{4.22a}$$

and

$$(\psi_n, \vec{p}_i r_i \cdot r_i \vec{p}_i \psi_n) \leq (\psi_n, r_i^4 \psi_n)^{1/2} (\psi_n, p_i^4 \psi_n)^{1/2} + 2\hbar (\psi_n, r_i^2 \psi_n)^{1/2} (\psi_n, p_i^2 \psi_n)^{1/2} \quad . \tag{4.22b}$$

Substituting in (4.21) and using (4.15) we have

$$(\psi_n, r_i^4 \psi_n)^{1/4} \leq |E_n - E_{\bar{n}}|^{-1} \{(\hbar/m)(\psi_n, p_i^2 \psi_n)^{1/4} + [(\hbar^2/m^2)(\psi_n, p_i^4 \psi_n)^{1/2} + (2\hbar/m)(2\hbar)^{1/2} |E_{\bar{n}} - E_n| (\psi_n, r_i^2 \psi_n)^{1/4} (\psi_n, p_i^2 \psi_n)^{1/4}]^{1/2}\} \quad . \tag{4.23}$$

From the virial theorem in the form applicable to the atomic case, $(\psi_n, p_i^2 \psi_n) = 2m|E_n|/N$, and we have a bound on $(\psi_n, r_i^2 \psi_n)$ in (4.18). A bound on $(\psi_n, p_i^4 \psi_n)$ is obtained in Sec. IV D so that (4.23) gives a bound on $(\psi_n, r_i^4 \psi_n)$.

D. Miscellaneous Bounds for $W = r_i^q, r_{ij}^\gamma p_i, p_{ij}$

We here restrict our attention to atomic systems, for which the virial theorem assumes a particularly simple form. Using the commutator relationship

$$i(\vec{p} \cdot \hat{r} - \hat{r} \cdot \vec{p}) = 2\hbar/r$$

and the virial theorem, the following simple upper bound on $1/r_i$ is obtained[5]:

$$(\psi_n, (1/r_i)\psi_n) = (1/2\hbar)(\psi_n, i(\vec{p}_i \cdot \hat{r}_i - \hat{r}_i \cdot \vec{p}_i)\psi_n) \leq (\psi_n, p_i^2 \psi_n)^{1/2}/\hbar = (2m|E_n|/N\hbar^2)^{1/2} \quad ; \tag{4.24}$$

we used the Schwarz inequality and the relationship $\hat{r}_i \cdot \hat{r}_i = 1$. [Dropping the positive electron-electron interaction energy, direct use of the virial theorem for an atom or ion gives the other bound, namely, $(\psi_n, (1/r_i)\psi_n) \geq 2|E_n|/(NZe^2)$.] Similarly,

$$i(\vec{p} \cdot (\hat{r}/r) - (\hat{r}/r) \cdot \vec{p}) = \hbar/r^2$$

leads to

$$(\psi_n, (1/r_i^2)\psi_n) \leq (2/\hbar)(\psi_n, p_i^2 \psi_n)^{1/2} (\psi_n, (1/r_i^2)\psi_n)^{1/2}$$

or, squaring,

$$(\psi_n, (1/r_i^2)\psi_n) \leq (4/\hbar^2)(\psi_n, p_i^2 \psi_n) = 8m|E_n|/(\hbar^2 N) \quad . \tag{4.25}$$

To get bounds on r_{ij}, we start with

$$r_{ij} \leq r_i + r_j \quad .$$

We therefore have

$$(\psi_n, r_{ij}\psi_n) \leq 2(\psi_n, r_i \psi_n) \leq 2(\psi_n, r_i^2 \psi_n)^{1/2} \quad , \tag{4.26}$$

so that the simple bound on $(\psi_n, r_i^2 \psi_n)$ obtained previously can be used to obtain a simple bound on $(\psi_n, r_{ij}\psi_n)$.

Bounds on higher positive powers of r_{ij} may be obtained in similar fashion. For example, since

$$r_{ij}^2 \leq r_i^2 + r_j^2 + 2r_i r_j \quad ,$$

we have, by applying the Schwarz inequality to the term $(\psi_n, r_i r_j \psi_n)$,

$$(\psi_n, r_{ij}^2 \psi_n) \leq 4(\psi_n, r_i^2 \psi_n) \quad , \tag{4.27}$$

and so forth.

It is clear from the derivation of Eqs. (4.24) and (4.25) that these bounds must also hold for $1/r_{ij}$ and $1/r_{ij}^2$, respectively; i.e.,

$$(\psi_n, (1/r_{ij})\psi_n) \leq [2m|E_n|/(N\hbar^2)]^{1/2} ,$$
$$(\psi_n, (1/r_{ij}^2)\psi_n) \leq 8m|E_n|/(N\hbar^2) . \quad (4.28)$$

For the operator p_i^2, one already has an equality rather than a bound, since—for identical particles—the virial theorem tells us that

$$(\psi_n, p_i^2\psi_n) = 2m|E_n|/N .$$

To obtain a bound on p_i^4, we first note that

$$2mT = \sum_i p_i^2 .$$

We therefore have

$$(2mT)^2 = \sum_i p_i^4 + \sum_{i\neq j} (p_i p_j)^2 ,$$

so that

$$4m^2(\psi_n, T^2\psi_n) \geq N(\psi_n, p_i^4\psi_n) . \quad (4.29)$$

Next, we note that

$$T = H - V ,$$

so that the triangle inequality gives

$$(\psi_n, T^2\psi_n)^{1/2} \leq (\psi_n, H^2\psi_n)^{1/2} + (\psi_n, V^2\psi_n)^{1/2} .$$

The first term on the right-hand side is just $|E_n|$. To bound the second term suppose, for example, that V is of the form

$$V = -Ze^2 \sum_i \frac{1}{r_i} + \frac{e^2}{2} \sum_{i\neq j} \frac{1}{r_{ij}} \equiv V_- + V_+ .$$

In $V^2 = V_-^2 + V_+^2 + 2V_-V_+$, we have $V_-V_+ \leq 0$. On applying the Schwarz inequality, we have

$$V_-^2 \leq Z^2e^4N^2\langle 1/r_i^2\rangle , \quad V_+^2 \leq \tfrac{1}{4}e^4[N(N-1)]^2\langle 1/r_{ij}^2\rangle .$$

Using (4.25) and (4.28), it follows that

$$(\psi_n, V^2\psi_n) \leq e^4[Z^2N^2 + \tfrac{1}{4}N^2(N-1)^2](8m|E_n|/N\hbar^2) . \quad (4.30)$$

Substituting (4.30) in (4.29), we have

$$(\psi_n, p_i^4\psi_n) \leq (4m^2/N)\{|E_n| + e^2[Z^2N^2 + \tfrac{1}{4}N^2(N-1)^2]^{1/2} \times (8m|E_n|/N\hbar^2)^{1/2}\}^2 . \quad (4.31)$$

Finally, since

$$p_{ij} \leq p_i + p_j ,$$

bounds on powers of p_{ij} can be obtained in terms of powers of p_i just derived in the same way that bounds on powers of r_{ij} were obtained in terms of powers of r_i.

From the foregoing, it is seen that bounds on any operator which can be expressed as a polynomial in the r_i, r_{ij}, p_i, and p_{ij}'s may be obtained.

As stated above, these bounds—although they may themsleves represent a considerable overestimate—can nevertheless produce bounds of good quality when used in (3.6).

Of course it is not *necessary* to use a simple bound for W_{nn}^2; any rigorous upper bound may be used for this term where it appears in the basic inequalities of Sec. III. An alternative method for obtaining such bounds on W_{nn}^2, based on a method due to Aranoff and Percus,[5] is given in Appendix E. This method is more cumbersome to employ than the methods of this section. Since the final answer will usually be quite insensitive to the value used for W_{nn}^2, the method of simple bounds outlined above will usually turn out to be the preferred method.

V. NUMERICAL EXAMPLE: HELIUM ATOM

As an example, bounds on $(\psi_0, r_1\psi_0)$ and $(\psi_0, r_1^2\psi_0)$ were calculated for the ground state of helium. The results are shown in Table III, together with the true values.[12]

Column A shows the results using the simple bounds on r_1^2 and r_1^4 given in Table I for the term W_{nn}^2 $(= W_{00}^2)$ in Eq. (3.6), and using as trial function the normalized one-parameter function

$$\psi_t = (c^3/\pi)e^{-c(r_1+r_2)} . \quad (5.1)$$

(The unit of length is one Bohr radius.) The single parameter c was varied to give the best bound; the optimum c in each case is shown in the table. Upper and lower bounds on S[13,14] were taken from (A1) and (A2).

To obtain the results of column B, the three-parameter Hylleraas wave function was used for ψ_t, with the numerical coefficients kept fixed at the same values that lead to a minimum energy:

$$\psi_t = 1.3299[1 + 0.294r_{12} + 0.132(r_1 - r_2)^2] \times e^{-1.817(r_1+r_2)} . \quad (5.2)$$

(No variational parameters were used in this part of the calculation.)

The required upper bounds on the terms W_{00}^2 were obtained in the following manner: First, an upper bound on r_1^4 by means of (3.6) was obtained using the simple bound on r_1^8 given in Table I. This bound on r_1^4 was used for W_{00}^2 in Eq. (3.6) to obtain the bound on r_1^2 shown and this, in turn, was used to obtain the bound on r_1.

A lower bound on $S = (\psi, \psi_t)$, with ψ_t given by (5.2), was computed by means of the inequality[13,6]

$$(\psi, \psi_t) \geq (\psi, \psi_{tt})(\psi_{tt}, \psi_t) - \{[1 - |(\psi, \psi_{tt})|^2] \times [1 - |(\psi_{tt}, \psi_t)|^2]\}^{1/2} , \quad (5.3)$$

where ψ_{tt} can be a more complicated but more accurate trial function which need not appear in any other part of the analysis. We have used for ψ_{tt} the ten-parameter function of Chandrasekhar *et al.*[15] In the use of (5.3) we needed to compute only (ψ_{tt}, ψ_t), since bounds on (ψ, ψ_{tt}) are known.[13,6]

The considerable improvement obtained in column B over column A represents only a modest increase in calculational effort and illustrates the improvement that may be achieved by going to a somewhat better wave function. We emphasize that the three-parameter function was used with fixed parameters and no variation done to determine the optimum value for these parameters, whereas the results of Ref. 6, given in column C, were obtained by determining the best values of three (different) parameters.

APPENDIX A: BOUNDS ON OVERLAP INTEGRAL

Bounds on the overlap $S_n = (\psi_n, \psi_{nt})$ exist in many places in the literature.[13,14] Two of the simplest are the Eckert lower bound[16] for the ground state,

$$|S|^2 \geq \frac{E_1 - H_{0t,0t}}{E_1 - E_0} \quad , \tag{A1}$$

and the upper bound for the ground state,[13]

$$|S|^2 \leq \frac{H_{0t,0t}^2 - (H_{0t,0t})^2}{H_{0t,0t}^2 - 2E_0 H_{0t,0t} + E_0^2} \quad . \tag{A2}$$

Bounds of higher accuracy and bounds for excited states can be found in Refs. 13 and 14.

Another simple lower bound on S_n for arbitrary n that does not seem to have been recorded can be obtained from the following inequality satisfied by the Green's function $(G^{Q_n})^2$. From its definition it follows that we can write

$$G^{Q_n} = \sum_m{}' \frac{|\psi_m\rangle\langle\psi_m|}{E_n - E_m} \quad ,$$

where the prime indicates that we are to sum over all values of m other than n. We therefore have

$$(G^{Q_n})^2 = \sum_m{}' \frac{|\psi_m\rangle\langle\psi_m|}{(E_m - E_n)^2} \leq (E_{\bar{n}} - E_n)^{-2} \sum_m{}' |\psi_m\rangle\langle\psi_m| \quad ,$$

or, finally, as our Green's-function inequality,

$$(G^{Q_n})^2 \leq (E_{\bar{n}} - E_n)^{-2} Q_n \leq (E_{\bar{n}} - E_n)^{-2} \quad , \tag{A3}$$

where $E_{\bar{n}}$ is the eigenvalue closest to E_n.

Now to get a bound on $|S_n|^2$, we notice from the definition of G^{Q_n} that [see Eq. (E1) below]

$$|S_n|^2 = 1 - \|G^{Q_n}(H - E_n)\psi_{nt}\|^2 \quad . \tag{A4}$$

Therefore, from (A3), we have

$$|S_n|^2 \geq 1 - \frac{\|(H - E_n)\psi_{nt}\|^2}{(E_{\bar{n}} - E_n)^2} \quad . \tag{A5}$$

APPENDIX B: REMARKS ON BASIC INEQUALITIES

In Sec. III it was shown that the Gram-determinant inequality leads to bounds on $|W_{nm}|$ for Hermitian W and complex functions ψ_n and ψ_m with no further assumptions about the system of interest. The result (3.5) is, therefore, completely general and, in particular, independent of the choice of the phase of the functions, a choice that is left arbitrary by the defining equations for these functions, namely, $(H - E_n)\psi_n = 0$, $(\psi_n, \psi_n) = 1$. It is, however, to be expected that one can improve on (3.5) by imposing certain conditions, as can be done for a number of physically interesting systems. Assume, for example, that the system is invariant under time reversal and rotation. Then it is well known[17] that, by an appropriate choice of phases of the known orthonormal spin-orbital angular-momentum functions χ_α^{JM}, the radial functions $f_{n\alpha}^{JM}(r)$ in the expansion

$$\psi_n^{JM}(\vec{r}) = \sum_\alpha f_{n\alpha}^{JM}(r)\chi_\alpha^{JM}$$

can be chosen to be real. This serves to fix the arbitrary phase mentioned above. ψ_n^{JM} is here assumed to have well-defined values J and M of the total angular momentum and of its z component, the spin dependence of ψ_n has been suppressed, $\vec{r}$ represents the totality of coordinate vectors, and r the totality of radial coordinates. Suppressing the superscripts J and M, we write

$$\psi_n(\vec{r}) = \sum_\alpha f_{n\alpha}(r)\chi_\alpha \quad , \tag{B1a}$$

TABLE III. Variational but nonstationary upper and lower bounds on $(r_1)_{00}$ and $(r_1^2)_{00}$ for the ground state of He. All quantities are in a.u.. True values were taken from Ref. 12. The one- and three-parameter trial functions are given by Eqs. (5.1) and (5.2), respectively. The former gives a poor lower bound which is not presented. The lower bound in column C was obtained by Weinhold, using a formula which employs two trial functions and three parameters which are varied to give the best bound.

	(A) One-parameter wave function		(B) Three-parameter wave function		(C) Lower bound from	
Operator	Optimum c	Upper bound	Upper bound	Lower bound	Ref. 6	True value
r_1	1.75	1.338	0.9579	0.8937	0.864	0.9295
r_1^2	1.77	2.079	1.268	1.090	1.024	1.1935

and we take ψ_{nt} to be of the same form:

$$\psi_{nt}(\vec{r}) = \sum_{\alpha} f_{n\alpha t}(r)\chi_{\alpha} \quad , \tag{B1b}$$

with the $f_{n\alpha t}$ also real. It follows that S_n can be written as

$$S_n = (\psi_n, \psi_{nt}) = \sum_{\alpha} (f_{n\alpha}, f_{n\alpha t}) \quad ,$$

where the inner product is over the radial coordinates. It follows that S_n is real. If, further, we consider the diagonal element W_{nn}, it follows from the Hermiticity of W, without even appealing to time-reversal invariance, that W_{nn} and $(W^2)_{nn}$ are real. Even with time-reversal invariance, $W_{nt,n}$ need not be real. Choosing $\psi = \psi_n$, $\psi_t = \psi_{nt}$, and $\phi = W\psi_n$, (3.1a) therefore becomes

$$(W_{nn})^2 - 2S_n W_{nn}\,\mathrm{Re}W_{nt,n} + |W_{nt,n}|^2 - (1 - S_n^2)W_{nn}^2 \leq 0 \quad . \tag{B2}$$

The inequality (B2) is preserved if we replace $|W_{nt,n}|^2$ by $|\mathrm{Re}W_{nt,n}|^2$. We then obtain

$$W_{nn} \gtrless S_n \mathrm{Re}W_{nt,n} \pm \{(1 - S_n^2)[W_{nn}^2 - (\mathrm{Re}W_{nt,n})^2]\}^{1/2} \quad . \tag{B3}$$

Returning to (3.1a), choosing $\psi = \psi_n$, $\psi_t = \psi_{nt}$, and $\phi = W\psi_{nt}$, and again replacing $W_{nt,n}$ in the inequality by $\mathrm{Re}W_{nt,n}$, we obtain

$$\mathrm{Re}W_{nt,n} \gtrless W_{nt,n}^{(\pm)} \quad , \tag{B4}$$

where $W_{nt,n}^{(\pm)}$ is obtained from (3.4) by setting $m = n$ and dropping all absolute magnitude signs. Equations (B3) and (B4) combine to given (3.6) again.

Considering the diagonal case once again, but dropping the restriction of time-reversal invariance, we can, formally, adjust the arbitrary over-all phase γ_n of ψ_n to make S_n real. W_{nn} will of course still be real and will be independent of the choice of γ_n. Once again we can obtain (3.6). In other words, for the diagonal case, the result (3.6), originally obtained under the assumption that S and $W_{nt,n}$ are real, follows without those assumptions.

For the off-diagonal element W_{nm} and for systems that are noninvariant under time reversal, we choose ψ_{nt} and ψ_{mt} such that $W_{nt,mt}$ is real. Formally, we then choose ψ_n such that S_n is real and positive and ψ_m such that $W_{nt,m}$ is real. (We have four functions, ψ_n, ψ_{nt}, ψ_m, and ψ_{mt}, each with an arbitrary phase, but we can only arrange to have three matrix elements real since all matrix elements are invariant under the same change of phase.) It is useful to choose $W_{nt,m}$ real since it occurs in each of the two Gram-determinant inequalities used in bounding W_{nm}.

Choosing first ψ_n, ψ_{nt}, and $W\psi_m$, and then ψ_m, ψ_{mt}, and $W\psi_{nt}$, the use of (3.1) leads to

$$\mathrm{Re}W_{nm} \lessgtr S_n |W_{nt,m}|^{(\pm)} \pm \{(1 - S_n^2)[W_{mm}^{2(+)} - (|W_{nt,m}|^{(-)})^2]\}^{1/2} \quad , \tag{B5}$$

where $|W_{nt,m}|^{(\pm)}$ is given by (3.4). The fact that we do not know the phases γ_n and γ_m required to make S_n and $W_{nt,m}$ real is irrelevant; $|W_{nm}|$, is independent of γ_n and γ_m, and (B5) is therefore valid for any choice of γ_n and γ_m. The lower-bound result (B5) is slightly better than the result (3.5).

APPENDIX C: BOUNDS WHEN u IS CHOSEN SUCH THAT $(\psi_0, Wu_{\mu}\psi_0) \neq 0$

As mentioned above Eq. (4.5), it is not necessary to choose Wu_{μ} such that $(\psi_0, Wu_{\mu}\psi_0)$ vanishes in order to obtain bounds on $(\psi_0, W\psi_0)$. To illustrate the procedure to be adopted when this matrix element does not vanish, suppose we wish to obtain a bound on $(\psi_0, r_i\psi_0) = (r_i)_{00}$, and suppose we make the simplest possible choice, $u_{\mu} = 1$. We can then write

$$(\psi_0, [r_i, [H, r_i]]\psi_0) = (\hbar/m)(\psi_0, [r_i, -ip_{r_i}]\psi_0) = \hbar^2/m \quad .$$

Using (4.7), (4.4) then becomes

$$(\hbar^2/m) = 2(\psi_0, r_i[H, r_i]\psi_0) \geq 2(E_1 - E_0)[(r_i^2)_{00} - (r_i)_{00}^2]$$

or

$$(r_i^2)_{00} \leq (\hbar^2/2m)(E_1 - E_0)^{-1} + (r_i)_{00}^2 \quad . \tag{C1}$$

Next consider the Gram-determinant inequality (3.1a), with the particular choice

$$\psi = \psi_0, \quad \psi_t = \psi_{0t}, \quad \phi = W\psi_0 \quad ,$$

and, for convenience, assume that all quantities are real. The resulting inequality is seen to be

$$(r_i)_{00}^2 - 2S_0(r_i)_{0,0t}(r_i)_{00} + (r_i)_{0,0t}^2 - (1 - S_0^2)(r_i^2)_{00} \leq 0 \quad . \tag{C2}$$

The sense of the inequality (C2) is preserved if we substitute for $(r_i^2)_{00}$ the upper bound (C1). One obtains

$$S_0^2(r_i)_{00}^2 - 2S_0(r_i)_{0,0t}(r_i)_{00} + (r_i)_{0,0t}^2 - (1 - S_0^2)(\hbar^2/2m)(E_1 - E_0)^{-1} \leq 0 \quad . \tag{C3}$$

The true value of $(r_i)_{00}$ must lie between the roots of the equation obtained by replacing the inequality in (C3) by an equality. We find, upon replacing $(r_i)_{0,0t}$ by the appropriate bounds,

$$(r_i)_{00} \lessgtr (1/S_0)\{(r_i)_{0,0t}^{(\pm)} \pm [(1 - S_0^2)(\hbar^2/2m)(E_1 - E_0)^{-1}]^{1/2}\} \quad . \tag{C4}$$

If the upper and lower bounds (C4) are calculated using

the trial function (5.2), with $(r_i)^{(\pm)}_{0,0t}$ computed from (3.7), with unity taken as an upper bound on S_0, and with a lower bound on S_0 computed as described below Eq. (5.3), the following bounds on r_i are obtained:

$$0.890 \leq (\psi_0, r_i\psi_0) \leq 0.962 \text{ (a.u.)} \ .$$

These results are not quite as good as the best values published in Table III. On the other hand, less computational effort was required to get them. [We did not have to calculate the matrix elements $(r_i^4)_{0t,0t}$ and $(r_i^8)_{0t,0t}$.] It is therefore reasonable to expect that this type of procedure may sometimes represent a useful alternative to those described earlier.

APPENDIX D: COMMUTATOR RELATIONSHIPS AND $\alpha(W)$

The following are useful commutator relationships:

$$[H, \vec{r}] = -\left(\frac{i\hbar}{m}\right)\vec{p} \ , \tag{D1}$$

$$[H, r] = -\left(\frac{i\hbar}{m}\right)p_r = -\frac{\hbar^2}{m}\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \ , \tag{D2}$$

$$[H, r^2] = -\left(\frac{i\hbar}{m}\right)(\vec{p}\cdot\vec{r} + \vec{r}\cdot\vec{p}) \ , \tag{D3}$$

$$[x, p_x] = i\hbar \ , \tag{D4}$$

$$[r, p_r] = i\hbar \ , \tag{D5}$$

$$[\vec{r}, p_r] = \frac{i\hbar\vec{r}}{r} \ , \tag{D6}$$

$$[r, \vec{p}] = \frac{i\hbar\vec{r}}{r} \ . \tag{D7}$$

We next wish to evaluate $\alpha(W)$, which involves

$$\sum_\mu [Wu_\mu^*, [H, Wu_\mu]] \ , \tag{D8}$$

where

$$W = r_i^q, \quad u_\mu = \mathfrak{N}_l Y_{l\mu}(\theta_i, \phi_i) \ .$$

V commutes with Wu_μ. Therefore (D8) reduces to

$$\sum_\mu [Wu_\mu^*, [T, Wu_\mu]] = [r_i^q, [T_{r_i}, r_i^q]] + \left(\frac{r_i^{2q-2}}{2m}\right)K \ , \tag{D9}$$

where we have written

$$T = T_{r_i} + \left(\frac{1}{2mr_i^2}\right)L^2,$$

$$T_{r_i} \equiv -\left(\frac{\hbar^2}{2m}\right)\left[\frac{\partial^2}{\partial r_i^2} + \left(\frac{2}{r_i}\right)\left(\frac{\partial}{\partial r_i}\right)\right]$$

and

$$\begin{aligned} K &\equiv |\mathfrak{N}_l|^2 \sum_\mu [Y_{l\mu}^*, [L^2, Y_{l\mu}]] \\ &= |\mathfrak{N}_l|^2 \sum_\mu [Y_{l\mu}^*((L^2Y_{l\mu}) + 2(\vec{L}Y_{l\mu})\cdot\vec{L}) \\ &\qquad - ((L^2Y_{l\mu}) + 2(\vec{L}Y_{l\mu})\cdot\vec{L})Y_{l\mu}^*] \\ &= 2|\mathfrak{N}_l|^2 \sum_\mu [Y_{l\mu}^*(\vec{L}Y_{l\mu})\cdot\vec{L} - (\vec{L}Y_{l\mu})\cdot(\vec{L}Y_{l\mu}^*) \\ &\qquad - (\vec{L}Y_{l\mu})Y_{l\mu}^*\cdot\vec{L}] \\ &= -2|\mathfrak{N}_l|^2\left[\vec{L}\cdot\left(\sum_\mu Y_{l\mu}\vec{L}Y_{l\mu}^*\right) - \sum_\mu Y_{l\mu}L^2Y_{l\mu}^*\right] \\ &= 2\hbar^2 l(l+1) \ , \end{aligned} \tag{D10}$$

since it can be shown by angular-momentum algebra that

$$\vec{L}\cdot\sum_\mu (Y_{l\mu}\vec{L}Y_{l\mu}^*) = 0 \ .$$

Furthermore, using the commutation relationships given above, we find

$$\begin{aligned} [r_i^q, [T_{r_i}, r_i^q]] &= -\left(\frac{\hbar^2}{2m}\right)\left[r_i^q, q(q-1)r_i^{q-2}\right. \\ &\qquad \left. + 2qr_i^{q-1}\left(\frac{\partial}{\partial r_i}\right) + \left(\frac{2}{r_i}\right)qr_i^{q-1}\right] \\ &= -\left(\frac{\hbar^2}{2m}\right)2qr_i^{q-1}\left[r_i^q, \frac{\partial}{\partial r_i}\right] \\ &= \left(\frac{\hbar^2}{2m}\right)2q^2r_i^{2q-2} \ . \end{aligned} \tag{D11}$$

Using (D10) and (D11) in Eq. (D9) we have finally

$$\sum_\mu [Wu_\mu^*, [H, Wu_\mu]] = \frac{\hbar^2}{m}[q^2 + l(l+1)]r_i^{2q-2} \ , \tag{D12}$$

from which Eq. (4.11) for $\alpha(r_i^q)$ follows.

APPENDIX E: ALTERNATIVE METHOD FOR OBTAINING BOUNDS ON W_{nn}^2

An alternative procedure to that described in Sec. IV may be based on methods for evaluating the term $\mathfrak{D}_n(W^2)$ as given in Ref. 5.[18] This permits an alternative upper bound on W_{nn}^2 to be calculated. For convenience, we will assume real inner products. Then, starting with the identities

$$\begin{aligned} &P_n\psi_{nt} = S_n\psi_n = \psi_{nt} - Q_n\psi_{nt} = \psi_{nt} + G^{Q_n}(H - E_n)\psi_{nt} \ , \\ &G^{Q_n}(H - E) \equiv -Q_n \ , \end{aligned} \tag{E1}$$

one obtains the following identity for the matrix element $(\psi_n, W^2\psi_n)$:

$$\begin{aligned} W_{nn}^2 = S_n^{-2}[&W_{nt,nt}^2 + 2(\psi_{nt}, W^2G^{Q_n}(H - E_n)\psi_{nt}) \\ &+ (\psi_{nt}, Q_nW^2Q_n\psi_{nt})] \ . \end{aligned}$$

The last term on the right-hand side is just $\mathfrak{D}_n(W^2)$. The middle term may be bounded using the Gram-determinant inequality involving ψ_{nt}, $W^2\psi_{nt}$, and

$G^{Q_n}(H-E_n)\psi_{nt}$. The result is

$$W_{nn}^2 \leq (2-S_n^{-2})W_{nt,nt}^2 + 2S_n^{-1}\{(1-S_n^2)[W_{nt,nt}^4 - (W_{nt,nt}^2)^2]\}^{1/2} + S_n^{-2}\mathfrak{D}_n(W^2) . \quad \text{(E2)}$$

$\mathfrak{D}_n(W^2)$ may now be bounded by methods similar to those in Ref. 5. The bound in (E2) will in most instances represent a considerable overestimate, so that its primary usefulness is as an alternative upper bound on W_{nn}^2 to the simple bounds of Sec. IV for use in Eq. (3.6).

A few words are perhaps in order at this point on the evaluation of $\mathfrak{D}_n(W^2)$ for those cases in which W^2 has the property of becoming large at infinity. An alternative derivation of the bound on $\mathfrak{D}_n(W^2)$, which avoids some of the difficulties that seem to lie in the treatment of Ref. 5, is as follows: Let $\vec{W}'$ be a vector operator of odd parity satisfying

$$\vec{W}'\cdot\vec{W}' = W^2 . \quad \text{(E3)}$$

(More generally, we could employ the tensor operator Wu_μ as we did previously. For the present case, however, Wu_μ must be of odd parity; it is not sufficient in the argument below for its diagonal elements to vanish.)

An operator identity connecting the operator $\vec{W}'$ with the commutator $[H,\vec{W}']$ is readily seen to be [using (E1)]

$$Q_n\vec{W}' = -G^{Q_n}\vec{W}'(H-E_n) - G^{Q_n}[H,\vec{W}'] . \quad \text{(E4)}$$

Now assume that the parity of ψ_n is known and that ψ_{nt} is chosen to have the same parity as ψ_n. Since $Q_n+P_n=1$, we can write

$$\vec{W}'Q_n\psi_{nt} = Q_n\vec{W}'Q_n\psi_{nt} + (\psi_n, \vec{W}'Q_n\psi_{nt})\psi_n . \quad \text{(E5)}$$

Since $\vec{W}'$ is of odd parity, $\vec{W}'Q_n$ is too. The last term on the right-hand side of (E5) vanishes, and we remain with

$$\vec{W}'Q_n\psi_{nt} = Q_n\vec{W}'Q_n\psi_{nt} . \quad \text{(E6)}$$

Multiply (E4) on the right by Q_n, operate with the results on ψ_{nt}, and use (E6). We find

$$\vec{W}'Q_n\psi_{nt} = -G^{Q_n}\vec{W}'(H-E_n)\psi_{nt} - G^{Q_n}[H,\vec{W}']Q_n\psi_{nt} . \quad \text{(E7)}$$

Use of the triangle inequality, together with (A3), now yields

$$(\psi_{nt}, Q_nW^2Q_n\psi_{nt})^{1/2} = \mathfrak{D}_n^{1/2}(W^2) \leq [(\psi_{nt}, (H-E_n)W^2(H-E_n)\psi_{nt})^{1/2} + \mathfrak{D}_n^{1/2}([\vec{W}'^{+}, H]\cdot[H,\vec{W}'])] \times |E_n^- - E_n|^{-1} . \quad \text{(E8)}$$

$\mathfrak{D}_n^{1/2}([\vec{W}'^{+}, H]\cdot[H,\vec{W}'])$ may now be bounded by methods similar to those in Ref. 5.

Equation (E8) differs from a similar equation in Ref. 5 primarily in the use of the operator G^{Q_n} (making the argument rigorous) and in the use of the more convenient vector operator $\vec{W}'$.

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*Work supported by the U.S. Army Office, Durham under Grant No. DA-ARO-D-31-124-72-G92 and by the Office of Naval Research under Grant No. N000 14-67-A-0467-0007.

†Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

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