ion ($3d^5$) and the isolated neutral Mn atom ($3d^5 4s^2$), it appears that the coefficients of the $4s$ metal orbital in the A_1 or A_{1g} molecular orbitals are too small to account for the observed differences between the hyperfine constants for these two complexes. We are more inclined to attribute the observed variations to changes in the $3d$ density resulting from the crystalline or ligand field and from covalent bonding involving the $3d$ orbitals. While it is reasonable to assume that variations in hyperfine interaction with environment for a particular symmetry of ligand coordination arise from covalency effects, we feel, however, that covalency effects will not account for the somewhat larger (~20%) variations between the octahedral and tetrahedral environments. The source of ~20% reduction in the hyperfine field from octahedral to tetrahedral coordination is not exactly clear; however, it probably arises from inversion of the t_{2g} and e_g d orbitals when the symmetry of the crystalline or ligand field is changed from octahedral to tetrahedral. Further research on this point is presently in progress.

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Error Bounds for Expectation Values: Some Applications and Extensions*

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The error-bound procedure of Bazley and Fox is extended as in a previous paper and applied to the expectation values of some quantum-mechanical operators of physical interest. The quality of the bounds is discussed and it is found to be possible to improve them under certain conditions. An attempt is made to use these error-bound formulas as variational principles for expectation values. Some special cases such as Fermi contact terms and electron densities are discussed separately. Errors in Hartree–Fock expectation values are considered from the point of view of Brillouin's theorem and some qualitative predictions of their magnitudes are made. Transition probabilities are also treated and some qualitative conclusions are made concerning the accuracy of the alternative length and velocity formulas.

I. INTRODUCTION

In recent years, quantum mechanics has been applied successfully to many complex atomic and molecular systems. The aim of most calculations has been to obtain wavefunctions, upper bounds to the energy, and approximations to the physically interesting expectation values of the system. Most wavefunctions have been based on the variational principle for energy and no method has been available for translating information about the accuracy for energy into error limits for expectation values. Recently,[1] however, we have adapted an applied some results of Bazley and Fox[2] so that practical error bounds for certain expectation values can be obtained in some cases. In the present paper we give a fuller account of this work, some further applications, and some related topics.

II. BASIC METHOD

If ϕ is an approximation to the correct wavefunction ψ and B is an operator whose expectation value $\langle\psi\mid B\mid\psi\rangle$ is sought, then following Bazley and Fox,[2] we can write

$$\begin{aligned}\Delta &= \mid \langle\psi\mid B\mid\psi\rangle - \langle\phi\mid B\mid\phi\rangle \mid \\ &= \mid \langle\psi\mid B(\psi-\phi)\rangle + \langle(\psi-\phi)\mid B\mid\phi\rangle \mid \\ &\leq \epsilon(\langle\psi\mid B^2\mid\psi\rangle^{1/2} + \langle\phi\mid B^2\mid\phi\rangle^{1/2}),\end{aligned} \tag{1}$$

where Schwartz's inequality was used and

$$\epsilon^2 = \langle(\psi-\phi)\mid(\psi-\phi)\rangle = 2-2\langle\psi\mid\phi\rangle = 2-2S \tag{2}$$

is discussed below. Since even rough approximations for the error bound can be useful, we took the step of replacing

$$\langle\psi\mid B^2\mid\psi\rangle^{1/2} \quad \text{by} \quad \langle\phi\mid B^2\mid\phi\rangle^{1/2}$$

on the right, as a first approximation, yielding

$$\Delta \lesssim 2\epsilon\langle\phi\mid B^2\mid\phi\rangle^{1/2}. \tag{3}$$

To test this approximation, Eq. (1) can be applied again, replacing B by B^2. If the whole expression is expanded to second order in ϵ and now $\langle\psi\mid B^4\mid\psi\rangle$ replaced by $\langle\phi\mid B^4\mid\phi\rangle$, the result is

$$\Delta \lesssim 2\epsilon\langle\phi\mid B^2\mid\phi\rangle^{1/2} + \epsilon^2\langle\phi\mid B^4\mid\phi\rangle^{1/2}/\langle\phi\mid B^2\mid\phi\rangle^{1/2}. \tag{4}$$

For many applications the term in ϵ^2 is an order of magnitude smaller than the term in ϵ.

By subtracting a constant from B, no change in the true value of Δ occurs (ψ and ϕ are normalized) but

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* This research was supported in part by a Contract extended Harvard University by the U.S. Office of Naval Research, Nonr, 1866(14). Reproduction in whole or part is permitted for the U.S. Government, distribution is unlimited.

[1] P. Jennings and E. B. Wilson, Jr., J. Chem. Phys. 45, 1847 (1966).

[2] N. W. Bazley and D. W. Fox, Rev. Mod. Phys. 35, 712 (1963); J. Math. Phys. 7, 413 (1966); see also V. M. Buimistrov, Soviet Phys.—JETP 8, 812 (1958).

the expression on the right in Eq. (3) can be minimized to yield

$$\Delta \lesssim 2\epsilon(\langle\phi \mid B^2 \mid \phi\rangle - \langle\phi \mid B \mid \phi\rangle^2)^{1/2}, \tag{5}$$

an improvement over Eq. (3). As previously noted,[1] this treatment will not converge for all operators B; in fact, even Eq. (1) is inapplicable if $\langle\psi \mid B^2 \mid \psi\rangle$ does not exist.

The Eckart condition[3] can be used to obtain an upper bound for ϵ. For the ground state this yields

$$S^2 \geq 1-[(E_U-E_0)/(E_1-E_0)], \tag{6}$$

where $E_U=\langle\phi \mid H \mid \phi\rangle$ and E_1 is the energy of the first excited state of the same symmetry as the ground state (with energy E_0).

Thus we can write

$$\epsilon^2 \leq 2\left[1-\left(1-\frac{E_U-E_0}{E_1-E_0}\right)^{1/2}\right] \sim \frac{E_U-E_0}{E_1-E_0} \quad \text{for} \quad \epsilon^2 \ll 1. \tag{7}$$

We previously applied[1] this formula to a variety of approximate helium-atom wavefunctions with three different operators and found that it gave quite reasonable bounds when ϵ was small. For large ϵ, the bounds were much too large and this was attributed to the poor value of ϵ given by the Eckart[3] formula.

III. IMPROVED UPPER BOUNDS FOR ϵ

In certain cases it is possible to find better upper bounds for ϵ than those given by the Eckart criterion. Weinberger[4] has derived a formula that is useful when the approximate wavefunction is obtained by a configuration interaction approach. If we know a set of lower bounds E_i^L (or experimental values) for the energy levels of a system, and if the first j upper bounds E_ν^U from the secular equation satisfy

$$E_1^L \leq E_1^U < E_2^L \leq E_2^U < E_3^L \leq E_3^U \cdots E_j^U \leq E_{j+1}^L,$$

then Weinberger[4] gives as a lower bound for the overlap of the approximate wavefunction ϕ_ν with the exact ψ_ν (if $\nu \leq j$),

$$\begin{aligned} S_\nu^2 &= \mid \langle\psi_\nu \mid \phi_\nu\rangle \mid^2 \\ &\geq \left(1-\frac{E_\nu^U-E_\nu^L}{E_{j+1}^L-E_\nu^L}\right) \\ &\quad \times \prod_{\mu=1,\mu\neq\nu}^{j} \left(1-\frac{E_\nu^U-E_\nu^L}{E_\nu^U-E_\mu^U}\,\frac{E_\mu^U-E_\mu^L}{E_\nu^L-E_\mu^L}\right). \end{aligned} \tag{8}$$

By comparing with the Eckart criterion (7) we see that the first term is similar except that the denominator is larger if $j>\nu$. To illustrate this formula we apply it to Ohrn and Nordling's[5] wavefunction for the Li atom ${}^2S$ states. They solved a 3×3 secular equation for the ground-state wavefunction (see Table I) and thus gave the upper bounds listed in Table I, which also lists the values of S_1 calculated from Eq. (8) (Weinberger) with $j=3$ and from the simple Eckart formula (6).

TABLE I. Data and improved overlap integral for Li atom.

State	E (exptl.)	E^U [a]
1^2S	-7.4781	-7.4760
2^2S	-7.3541	-7.3527
3^2S	-7.3185	-7.3124
4^2S	-7.3040	

$S_1^2 \geq 0.9894$, $\epsilon_1^2 \leq 0.01206$ (Weinberger)
$S_1^2 \geq 0.98306$, $\epsilon_1^2 \leq 0.01694$ (Eckart)

[a] From Öhrn and Nordling, Ref. 5.

This is a worthwhile improvement and with a large configuration-interaction treatment the advantage of the Weinberger formula over the Eckart would be even greater. The drawback of the approach, however, is that we often do not know lower bounds to the energy levels of excited states in molecular systems.

Another procedure for obtaining a better estimate of ϵ was suggested by Weinhold.[6] Its value derives from the fact that the Eckhart upper bound to ϵ^2 may be quite good when ΔE is small but it becomes rapidly worse as ΔE increases. Weinhold showed that by using the overlap of an approximate wavefunction ϕ_2 with a better approximation ϕ_1, and using the Eckart criterion on ϕ_1, we could obtain an improved upper bound to ϵ^2 for ϕ_2. If we define the overlap integrals

$$S_1=\langle\psi \mid \phi_1\rangle,$$

$$S_{12}=\langle\phi_1 \mid \phi_2\rangle,$$

where ψ is the exact wavefunction for the state, then we can find a lower bound to

$$S_2=\langle\phi_2 \mid \psi\rangle \geq S_1S_{12}-[(1-S_1^2)(1-S_{12}^2)]^{1/2}. \tag{9}$$

In general, we can calculate S_{12} and get S_1 from the Eckart formula (6) and thus obtain a better lower bound to S_2 than we would have done using the Eckart formula alone. This may have utility where we wish to use the simpler, less-accurate wavefunction to calculate expectation values. As an example we consider the screened hydrogenic function for the helium ground state

$$\phi_2=N\exp[-1.6875(r_1+r_2)], \quad \langle\phi_2 \mid H \mid \phi_2\rangle=-2.848,$$

and find its overlap with the three-term Hylleraas function

$$\phi_1=N'\exp[-1.817(r_1+r_2)][1+0.294r_{12} +0.132(r_1-r_2)^2],$$

$$\langle\phi_1 \mid H \mid \phi_1\rangle=-2.90242.$$

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[3] C. Eckart, Phys. Rev. **36**, 878 (1930).

[4] H. F. Weinberger, J. Res. Natl. Bur. Std. **64B**, 217 (1960).

[5] Y. Öhrn and J. Nordling, Arkiv Fysik **31**, 471 (1966).

[6] F. Weinhold, J. Chem. Phys. **46**, 2448 (1967).

TABLE II. Error bounds for helium ground state using improved ϵ for hydrogenic wavefunction.

Operator	Expectation value	Δ_1 Eckart ($\epsilon_{\text{Eckart}}=0.27$)	Δ_1 Improved ($\epsilon_{\text{Improved}}=0.16$)	"True"[a] error
r_{12}	1.296	0.35	0.19	+0.126
$(r_1+r_2)/r_{12}$	1.563	0.49	0.26	−0.114
$r_1r_2\cos\theta_{12}$	0.0	0.20	0.11	−0.065

[a] Defined as (Pekeris result[8]—approximate result).

Using Weinhold's formula (9) with $S_{12}=0.99290$ and $S_1\geq 0.99913$ (from Eckart) we obtain $S_2\geq 0.9870$ or $\epsilon_2^2\leq 0.0260$, while the Eckart formula alone would have given $\epsilon^2\leq 0.0735$. Using this better estimate for ϵ we have recalculated some of the error bounds for the screened hydrogenic function. The results of Table II show that the error bounds are now quite tight and confirm our conjecture that, apart from the Eckart formula, the expression (5) gives very reasonable error bounds for a wide range of approximate wavefunctions.

These formulas (8) and (9) can be of value in Hartree–Fock calculations, as is shown in Sec. VII.

IV. FURTHER APPLICATIONS

The formula (5) can be applied to some operators of greater physical interest for some small systems in which ϵ is good enough to give worthwhile bounds. Adequate accuracy has already been attained for He, Li, and Be and also for H_2 and HeH^+. However, many of the useful physical properties have not been calculated from some of the more elaborate wavefunctions. This is an unfortunate situation because the amount of computational effort needed to calculate all the interesting expectation values is small indeed compared with the difficulty of obtaining the wavefunction itself.[7]

For the He ground state, Pekeris[8] has published a useful tabulation of expectation values calculated from his 1078-term wavefunction ($\epsilon\lesssim 5\times 10^{-5}$). The diamagnetic susceptibility of He can be written[8] as

$$\chi=-7.726\times 10^{-7}\langle r_1^2+r_2^2\rangle \text{ cm}^3/\text{mole}$$

and the nuclear magnetic shielding as[8]

$$\sigma=\tfrac{1}{3}\alpha^2\langle 1/r_1+1/r_2\rangle \text{ a.u.},$$

where α = fine structure constant Pekeris gives

$$\langle r_1^2\rangle=\langle r_2^2\rangle=1.19348 \text{ a.u.},$$

$$\langle r_1^4\rangle=\langle r_2^4\rangle=1.905 \text{ a.u.}$$

$$\langle 1/r_1\rangle=\langle 1/r_2\rangle=1.688317 \text{ a.u.},$$

$$\langle 1/r_1^2\rangle=\langle 1/r_2^2\rangle=6.01741 \text{ a.u.}$$

Applying (5) we obtain the following error bounds:

$$\langle r_1^2\rangle=\langle r_2^2\rangle=1.1935\pm 1.6\times 10^{-4},$$

$$\langle 1/r_1\rangle=\langle 1/r_2\rangle=1.6883\pm 1.5\times 10^{-4},$$

and thus

$$\chi=-(1.8913\pm 3\times 10^{-4})\times 10^{-6} \text{ cm}^3/\text{mole},$$

$$\sigma=5.9933\pm 0.0006 \text{ a.u.}$$

[The experimental value[9] of χ is $-(1.93\pm 0.01)\times 10^{-6}$ cm^3. The error ranges do not overlap and thus we must conclude that the experimental error is greater than that claimed.]

Another application is provided by the ground $(X'\Sigma_g^+)$ state of H_2, for which Wolniewicz[10] has calculated a large number of expectation values from a 54-term wavefunction[11] which is accurate in energy to less than 1 cm^{-1} (and thus $\epsilon\lesssim 3\times 10^{-3}$). The quadrupole moment of H_2 is given[7] as

$$\Theta=0.6725\times 10^{-26}(\langle R^2\rangle+\sum_{i=1}^{2}\langle 3z_i^2-r_i^2\rangle) \text{ esu}\cdot\text{cm}^2,$$

where R is the internuclear distance and the expectation values are in atomic units. The component of the diamagnetic susceptibility along the internuclear axis (chosen as the z axis) is

$$\xi_{11}=\xi_{zz}=-\frac{e^2}{4mc^2}\sum_{i=1}^{2}\langle x_i^2+y_i^2\rangle$$

$$=-1.33126\times 10^{-5}(\sum_{i=1}^{2}\langle x_i^2+y_i^2\rangle) \text{ a.u.}$$

For the ground rotational and vibrational states of $X'\Sigma_g^+$ for H_2 the following expectation values and error bounds are obtained by applying (5) to Wolniewicz's results:

$$\langle R^2\rangle=2.1271\pm 3\times 10^{-3} \text{ a.u.},$$

$$\langle 3z_1^2-r_1^2\rangle=\langle 3z_2^2-r_2^2\rangle=0.5814\pm 9\times 10^{-3} \text{ a.u.},$$

$$\langle x_1^2+y_1^2\rangle=\langle x_2^2+y_2^2\rangle=1.5498\pm 8\times 10^{-3} \text{ a.u.}$$

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[7] Some useful reviews of the most useful physical operators for atomic and molecular systems are available. The most recent include A. D. McLean and M. Yosimine, J. Chem. Phys. **45**, 3676 (1966) (linear molecules); G. Malli and S. Fraga, Theoret. Chim. Acta **6**, 278 (1966) (atoms), and earlier papers.

[8] C. L. Perkeris, Phys. Rev. **115**, 1216 (1959).

[9] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Systems* (Academic Press Inc., New York, 1957), pp. 227, 357.

[10] L. Wolniewicz, J. Chem. Phys. **45**, 515 (1966).

[11] W. Kołos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).

Thus

$$\Theta=(0.648\pm0.014)\times10^{-26}\ \text{esu}\cdot\text{cm}^2,$$

$$\xi_{11}=-(4.126\pm0.020)\times10^{-5}\ \text{a.u.}$$

The experimental values[12] are

$$\Theta=(0.637\pm0.029)\times10^{-26}\ \text{esu}\cdot\text{cm}^2,$$

$$\xi_{11}=-(4.077\pm0.040)\times10^{-5}\ \text{a.u.}$$

Here the theoretical and experimental error ranges overlap, although for ξ_{11} the actual theoretical value lies outside the experimental error ranges and vice versa.

V. VARIATIONAL PRINCIPLES FOR EXPECTATION VALUES

We attempted to use the error-bound formula as a variational principle with various helium ground-state trial functions. With a hydrogenic form the screening constant was varied to minimize the error bounds. For $\langle r_{12}\rangle$ the results are presented in Table III. We used both the Eckart and the improved form [from formula (9)] of ϵ in calculating these bounds. The results indicate that it is not just the Eckart criterion that dominates the error-bound expression, but rather the more fundamental requirement that ϵ be as small as possible. The $(\langle B^2\rangle-\langle B\rangle^2)^{1/2}$ factor does have some effect but we cannot expect it to be important except when $\langle B^2\rangle\sim\langle B\rangle^2$ or when $\langle B\rangle$ is strongly dependent on the screening constant.[13] Thus, for example, we might expect this approach to be useful in the case of an operator such as r^2 for a polyatomic system. Here the expection value is strongly dependent on the outer orbitals while the energy (and hence ϵ) is dependent to a far greater extent on the inner orbitals. In this case, if the exponent of the outer orbitals were varied to minimize the error bound, it is possible that we might get both improved error bounds and improved expectation values.

TABLE III. Error bounds for $\langle r_{12}\rangle$ for He as a function of screening constant Z'.

Z'	ϵ_{Eckart}	Δ_{Eckart}	$\epsilon_{\text{Improved}}$	Δ_{Improved}	$\langle r_{12}\rangle$
1.50	0.345	0.510	0.20	0.30	1.458
1.60	0.285	0.393	0.18	0.25	1.367
1.65	0.275	0.367	0.165	0.218	1.326
1.6875	0.270	9.351	0.161	0.211	1.296
1.70	0.272	9.352	0.165	0.223	1.287
1.75	0.280	0.353	0.19	0.24	1.250
1.80	0.302	0.370	0.21	0.27	1.215
Pekeris					1.422

The variational procedure was also tried with a more flexible function of the form $\phi=Ne^{-ks}(1+Cu)$ and this also gave minimum error bounds for a choice of constants very close to those that minimize ϵ and $\langle\phi\,|\,H\,|\,\phi\rangle$.

Bazley and Fox[2] have also derived a lower bound to the expectation value of a positive operator B,

$$\langle\psi\,|\,B\,|\,\psi\rangle\geq\frac{[\langle\phi\,|\,B\,|\,\phi\rangle-\epsilon\,|\,\langle\phi\,|\,B^2\,|\,\phi\rangle\,|^{1/2}]^2}{\langle\phi\,|\,B\,|\,\phi\rangle}\,.\quad(10)$$

If Eq. (10) is expanded to second order in ϵ, after making a suitably modified addition of a constant A, the result is

$$\langle\psi\,|\,B\,|\,\psi\rangle\geq\langle\phi\,|\,B\,|\,\phi\rangle-2\epsilon[\langle\phi\,|\,B^2\,|\,\phi\rangle-\langle\phi\,|\,B\,|\,\phi\rangle^2]^{1/2}$$
$$-\epsilon^2[2\langle\phi\,|\,B\,|\,\phi\rangle^2-\langle\phi\,|\,B^2\,|\,\phi\rangle]/\langle\phi\,|\,B\,|\,\phi\rangle,$$

which is found to be slightly better in some cases in the ϵ^2 term than Eq. (4).

Equation (10) provides an alternative variational principle if we vary ϕ to maximize the lower bound. However, for a set of screened hydrogenic functions for helium ground state we found that variation of the screening constant (relative to the energy-determined value) gave only slight improvements in the lower bounds in Eq. (10). Sometimes these improved bounds corresponded to improved expectation values but this was not always the case.

VI. SPECIAL CASES

It is apparent that the error-bound formula (5) is inapplicable to operators of the form $\delta(\mathbf{r})$, $\delta(\mathbf{r}-r_0)$ since $\langle\phi\,|\,B^2\,|\,\phi\rangle$ is infinite in this case. These operators, which are of importance in hyperfine corrections and in calculations of electron density,[8] respectively, have been treated in a different way by Redei.[14] He derives a formula of the form

$$|\,\gamma_0(r_0)-\gamma(r_0)\,|\leq[1/(1-\eta^2)]\{2C^{1/2}[\gamma(r_0)]^{1/2}$$
$$+C+\eta^2\gamma(r_0)\},$$

where $\gamma_0(r_0)$, $\gamma(r_0)$ are the true and approximate electron densities at the point r_0 [i.e., $\gamma(r_0)=\langle\phi\,|\,\delta(\mathbf{r}-\mathbf{r}_0)\,|\,\phi\rangle$], η is a perturbation parameter (see Sec. VII), $\eta^2\leq(\langle H\rangle-E_0)/(E_1-\langle H\rangle)$, C is a complicated function of $\sigma^2(=\langle H^2\rangle-\langle H\rangle^2)$ which is given explicitly in Redei's paper. It can be shown as a consequence of Brillouin's theorem that the term in $[\gamma(r_0)]^{1/2}$ drops out if ϕ is a Hartree–Fock function. However, this will be of no real value because C is too large to give reasonable bounds for such functions.

The results of applying this formula to the Fermi contact operator $\delta(\mathbf{r}_1)$ for several accurate helium ground-state wavefunctions are presented in Table IV. The first three rows represent the results obtained from the elaborate Hylleraas-type wavefunctions of Kino-

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[12] N. F. Ramsey, *Molecular Beams* (Oxford University Press, London, 1956).

[13] In principle, the error bounds can be reduced by using different ϕ for the upper and lower bounds, but little improvement was obtained in the cases tried. Note that the terms in ϵ^2 can here be important.

[14] L. B. Redei, Phys. Rev. **130**, 420 (1963).

TABLE IV. Application of Redei's formula to the Fermi contact term for helium ground state.

No. of terms	$E_{upper}=\langle H\rangle$	σ^2	$\eta_{\max}^2$	$C_{\max}$	$\gamma(0)$	Error bound
6	-2.90324	1.69×10^{-2}	4.85×10^{-4}	0.040	1.8167	0.58
18	-2.903715	9.22×10^{-4}	1.3×10^{-5}	9.06×10^{-4}	1.8102	0.082
38	-2.903722	1.15×10^{-4}	0.4×10^{-5}	2.56×10^{-4}	1.8106	0.044
Pekeris 1078	-2.903724375	1.7×10^{-6}	2×10^{-9}	2×10^{-7}	1.81042	0.0012

shita[15] and the fourth is from Pekeris'[8] 1078-term function. It is apparent that this is a comparatively inefficient method due to the multiple repetitions of Schwarz's inequality used in the derivation. However, it should also be noted that errors in expectation values of the δ function are generally relatively larger than those in the expectation values to which Formula (1) is applicable (see Ref. 7).

VII. THE HARTREE–FOCK CASE

It is well known[16,17] that the expectation values of one-electron operators calculated from Hartree–Fock wavefunctions are likely to be more accurate than those calculated with other types of wavefunctions having identical energies. We write[17] the exact wavefunction ψ as

$$\psi=(1+\eta^2)^{-(1/2)}(\phi+\eta\chi),$$

where ϕ is a Hartree–Fock approximation to ψ, η is a coefficient, and χ is the correction term. The conditions

$$\langle\psi\mid\psi\rangle=\langle\phi\mid\phi\rangle=\langle\chi\mid\chi\rangle=1, \qquad \langle\phi\mid\chi\rangle=0$$

are imposed. Then the error parameter η can be obtained from the Eckart condition since

$$\langle\phi\mid\psi\rangle=(1+\eta^2)^{-(1/2)}\langle\phi\mid\phi\rangle=(1+\eta^2)^{-(1/2)},$$

so

$$\begin{aligned}\eta^2&=(1/|\langle\phi\mid\psi\rangle|^2)-1\\ &\leq\{1-[(E_U-E_0)/(E_1-E_U)]\}^{-1}-1\\ &=(E_U-E_0)/(E_1-E_U),\end{aligned}\tag{11}$$

where $E_U=\langle\phi\mid H\mid\phi\rangle$ and E_0 and E_1 are the true first and second energy eigenvalues for the system. Now

$$\langle\psi\mid B\mid\psi\rangle=(1+\eta^2)^{-1}(\langle\phi\mid B\mid\phi\rangle+2\eta\langle\phi\mid B\mid\chi\rangle+\eta^2\langle\chi\mid B\mid\chi\rangle).$$

As a consequence of Brillouin's theorem,[18] $\langle\phi\mid B\mid\chi\rangle\sim0$ if B is a one-electron operator and ϕ is a Hartree–Fock wavefunction (since χ contains only two-electron excitations to first order and the first one-electron excitations appear only in second-order corrections). Thus

$$\langle\psi\mid B\mid\psi\rangle-\langle\phi\mid B\mid\phi\rangle\sim\eta^2(\langle\chi\mid B\mid\chi\rangle-\langle\phi\mid B\mid\phi\rangle).\tag{12}$$

In Table V we compare the errors in the expectation values of one- and two-electron operators with Hartree–Fock and screened hydrogenic wavefunctions for the He ground state. In most cases we can see that the percentage error is less than η^2 (due to the partial cancellation of $\langle\chi\mid B\mid\chi\rangle$ and $\langle\phi\mid B\mid\phi\rangle$ for one-electron expectation values from Hartree–Fock functions) while it is less than η but usually greater than η^2 for hydrogenic functions. For two-electron operators both types of wavefunctions have similar percentages of error and these all lie between η^2 and η [as Formula (5) would suggest].

Several general observations can be made concerning Hartree–Fock expectation values:

(1) If B is an operator which does not change very rapidly as we go to excited states then we can expect $\langle\chi\mid B\mid\chi\rangle$ and $\langle\phi\mid B\mid\phi\rangle$ to be similar and thus obtain small percentage errors. However, it is important to realize that as we go to larger molecular systems, the Hartree–Fock upper bound to the ground state lies above the energy of the first excited state of the same symmetry (at the same internuclear distance) even after relativistic corrections. Thus, at worst, ϕ could be a considerable mixture of the low-lying states and the expectation value will be some sort of average of the expectation values for all the low-lying states. If these expectation values change rapidly from state to state then we cannot be sure of the same high accuracy as we normally obtain from Hartree–Fock functions.

(2) The common one-electron operators most likely to be affected by a poor value of η^2 include z and $3z^2-r^2$ which are very sensitive to the charge distribution and can also take on both positive and negative values. Because of the latter property $\langle\chi\mid B\mid\chi\rangle$ and $\langle\phi\mid B\mid\phi\rangle$ could be of opposite sign and so rather than obtain cancellation in (12) we could get an augmented error. Difficulties of this kind have appeared in the dipole-

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[15] T. Kinoshita, Phys. Rev. **115**, 366 (1959).

[16] M. Cohen and A. Dalgarno, Proc. Phys. Soc. (London) **77**, 748 (1961).

[17] W. Klemperer and J. Goodisman, J. Chem. Phys. **38**, 721 (1963).

[18] See, for example, C. Møller, and M. S. Plesset, Phys. Rev. **46**, 618 (1934). Brillouin's theorem enables us to place a tighter upper bound on η^2 because, as an approximation, E_1 can be replaced in the denominator of Eq. (11) by the energy of the lowest-lying doubly excited Hartree–Fock state.

moment calculations for the ground state of CO.[19] A recent configuration interaction on CO by Moser[20] has shown that the singly excited configurations contribute strongly in the second order to give almost the correct dipole moment while producing a negligible change in the total energy. Malli[7] has also noted that Hartree–Fock functions give very poor expectation values for the Fermi contact term in atomic systems and this is due to the fact that $\langle \chi \mid B \mid \chi \rangle$ can be very large for this operator. Likewise approximate force constants, spectroscopic constants, and derivatives of the dipole moment are sensitive to the shape of the potential-energy curve and so can be expected to have rather large errors if the ground state is a mixture of several low-lying states (with appreciably differing shapes for their potential-energy curves).

(3) Although the expectation values of a given operator calculated from several good Hartree–Fock wavefunctions appear to be consistent, it has been demonstrated that they can vary widely between non-converged approximations to the Hartree–Fock. In the latter case the above error analysis does not apply and the error will be of order η and not η^2.

(4) As we showed in Sec. III, the Eckart criterion gives only an upper bound for η^2 and when η is large this may be poor. If we wish to make useful qualitative predictions of error bounds from Formula (12) we need therefore to bypass the Eckart formula. A better estimate of η^2 can be found if we know a good configuration-interaction calculation that gives a close upper bound to the true energy. Then we can follow the procedure below:

(a) Using the configuration-interaction energy along with the higher roots of the secular equation, we can apply the Weinberger result (8) and obtain a lower bound for the overlap of the CI wavefunction on the true wavefunction.

(b) Find the overlap of the Hartree–Fock function with the CI and using Weinhold's Formula (9) we get an improved lower bound for the overlap S_{HF} of the Hartree–Fock ψ with the true ψ.

(c) Now using

$$\eta_{\mathrm{HF}}^2 = (1 - S_{\mathrm{HF}}^2)/S_{\mathrm{HF}}^2$$

we get an improved estimate of η^2.

This approach could prove to be quite useful for small systems since we could calculate the expectation values of one-electron properties from both the Hartree–Fock and CI functions and obtain two different values and error ranges [which may both be of the same order of accuracy since the Hartree–Fock expectation value is correct to second order in η while for the CI, Formula (5) must be used].

TABLE V. Comparison of expectation values (in atomic units) from Hartree–Fock and screened hydrogenic wavefunctions for helium ground state.

	Hartree–Fock		Screened hydrogenic		Pekeris
$\langle H \rangle$	-2.862		-2.848		-2.90372
η	13%		16%		~0%
η^2	1.8%		2.6%		~0%
Operator	Expectation value	% Error[a]	Expectation value	% Error[a]	Expectation value
r_1^{-1}	1.69	0.1	1.688	0.05	1.6883
r_1	0.927	0.3	0.889	4.6	0.9295
r_1^2	1.18	1.0	1.053	13.3	1.193
$\delta(r_1)$	1.795	0.8	1.530	18.3	1.8104
∇_1^4	52.46	2.6	40.54	33.4	54.088
$(r_1 r_2)^{-1}$	2.85	5.1	2.848	5.1	2.709
r_{12}^{-1}	1.026	7.8	1.055	10.4	0.9458
r_{12}	1.362	4.4	1.296	9.7	1.4221
$\delta(r_{12})$	0.188	43	0.191	44	0.1064

[a] Percentage errors are expressed relative to the approximate expectation value.

VIII. OFF-DIAGONAL MATRIX ELEMENTS

The electric dipole oscillator strength is another property of considerable importance in atomic and molecular spectroscopy. It differs from the operators considered previously because it involves off-diagonal matrix elements and thus the basic formula[1] must be modified. Bazley and Fox[2] have shown that

$$\mid \langle \psi_\mu \mid B \mid \psi_\nu \rangle - \langle \phi_\mu \mid B \mid \phi_\nu \rangle \mid \leq \epsilon_\mu \mid \langle \phi_\nu \mid B^2 \mid \phi_\nu \rangle \mid^{1/2} + \epsilon_\nu \mid \langle \phi_\mu \mid B^2 \mid \phi_\mu \rangle \mid^{1/2} + \text{higher terms.}$$

Chandrasekhar[21] pointed out that there are three equivalent dipole operators which yield identical results when the exact wavefunctions are used. Thus for an electric dipole transition between the atomic states i and j the oscillator strength f is given by

(length form)

$$f_L = \tfrac{2}{3}(E_j - E_i) \mid \langle \psi_i \mid \sum_{\nu=1}^{N} \mathbf{r}_\nu \mid \psi_j \rangle \mid^2$$

(velocity form)

$$f_V = \tfrac{2}{3}(E_j - E_i)^{-1} \mid \langle \psi_i \mid \sum_{\nu=1}^{N} \boldsymbol{\nabla}_\nu \mid \psi_j \rangle \mid^2$$

(acceleration form)

$$f_A = \tfrac{2}{3} Z^2 (E_j - E_i)^{-3} \mid \langle \psi \mid \sum_{\nu=1}^{N} \frac{\mathbf{r}_\nu}{r_\nu^3} \mid \psi_j \rangle \mid^2$$

where the summation extends over the N electrons of the system. Many authors have used the relative agreement of the length and velocity forms to give an estimate of the accuracy of their results. However, no

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[19] W. Huo, J. Chem. Phys. **43**, 624 (1965).

[20] C. Moser (unpublished).

[21] S. Chandrasekhar, Astrophys. J. **102**, 223 (1945).

TABLE VI. Error bounds for helium oscillator strengths[a] (calculated from the 220-term functions of Pekeris[22]).

Transition	ϵ_i^2, $\langle z_1^2\rangle_i$, $\langle \partial^2/\partial z_1^2\rangle_i$	ϵ_j^2, $\langle z_1^2\rangle_j$, $\langle \partial^2/\partial z_1^2\rangle_j$	f_L % error	f_V % error
$1^1S\rightarrow 2^1P$	1×10^{-7}	4×10^{-7}		
	0.398	5.255	0.2761	0.2762
	0.968	0.708	1.07%	1.14%
$1^1S\rightarrow 3^1P$	1×10^{-7}	1.3×10^{-5}		
	0.398	30.5149	0.0736	0.0734
	0.968	0.686	7.4%	8.5%
$2^1S\rightarrow 2^1P$	5×10^{-5}	4×10^{-7}		
	5.363	5.255	0.3764	0.3764
	0.715	0.708	2.4%	40%
$2^1S\rightarrow 3^1P$	5×10^{-5}	1.3×10^{-5}		
	5.363	30.5149	0.1514	0.1514
	0.715	0.686	10.2%	45%

[a] The fact that in Table VI the f values computed in the two ways agree so well, suggests that our error bounds are quite conservative.

theoretical justification is given for this approach and it is conceivable that good agreement could often be accidental and the corresponding value of f might be considerably in error. We are unable to apply the error-bound formula to the acceleration form and thus we have utilized only the length and velocity formulas. This is no real drawback because the acceleration results are poor even with highly accurate wavefunctions[22] due to the weighting of the region close to the nucleus (where the singularity in the Hamiltonian is badly described by most approximate wavefunctions). For atoms we obtain two basic error-bound equations for the transition moments

$$|\langle\psi_i|z_\nu|\psi_j\rangle-\langle\phi_i|z_\nu|\phi_j\rangle|\leq\epsilon_i|\langle\phi_j|z_\nu^2|\phi_j\rangle|^{1/2}+\epsilon_j|\langle\phi_i|z_\nu^2|\phi_i\rangle|^{1/2}$$

and

$$|\langle\psi_i|\partial/\partial z_\nu|\psi_j\rangle-\langle\phi_i|\partial/\partial z_\nu|\phi_j\rangle|\leq\epsilon_i|\langle\phi_j|\partial^2/\partial z_\nu^2|\phi_j\rangle^{1/2}+\epsilon_j|\langle\phi_i|\partial^2/\partial z_\nu^2|\phi_i\rangle|^{1/2}.$$

In atoms a separate calculation of $\langle\partial^2/\partial z_\nu^2\rangle$ is not required as we know that if the approximate wavefunction satisfies the virial theorem, then

$$\langle\partial^2/\partial z_\nu^2\rangle=\tfrac{1}{3}\langle\nabla_\nu^2\rangle=(2/3N)\langle T\rangle=-(2/3N)\langle E\rangle,$$

where T is the kinetic-energy operator and $\langle E\rangle=\langle\phi|H|\phi\rangle/\langle\phi|\phi\rangle$. (Likewise if $\langle r_\nu^2\rangle$ is known we can obtain $\langle z_\nu^2\rangle=\frac{1}{3}\langle r_\nu^2\rangle$ in atomic systems.) With these simplifications we have applied the error bound method to Pekeris' 220-term helium wavefunctions[22] and obtained the bounds shown in Table VI.

It is apparent that the length formula gives the best error bounds, although the velocity results are almost as good when ΔE_{ij} is large. The velocity and acceleration results can be expected to be bad when ΔE_{ij} is small since the errors in the matrix elements are greatly magnified by the energy term (this is the major reason for the comparatively poor velocity bounds for the $2\,{}^1S\rightarrow2\,{}^1P$ and $2\,{}^1S\rightarrow3\,{}^1P$ transitions). Thus if $\Delta E_{ij}\ll1$ a.u. it is probable that the length formula will give the most accurate results from an approximate wavefunction since the errors in the matrix element will be reduced because of multiplication by a small energy factor. Conversely for values of $\Delta E_{ij}\geq1$ a.u. it seems likely that the velocity form will give the best results since it depends to a large extent on the quality of the wavefunction in the intermediate region of space.[23]

Some of these ideas are nicely illustrated by a set of calculations of oscillator strengths for transitions between low-lying states of the Li atom, in which Weiss[24] found that the length form generally gave the best results. This would be expected from the above analysis since ΔE_{ij} is very small for most of these transitions. He also found that agreement between the length and velocity results improved as the values of ΔE increased along the isoelectronic series.

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[22] C. L. Pekeris, Phys. Rev. **134**, A640 (1964).

[23] S. Ehrenson and P. E. Phillipson, J. Chem. **34**, 1224 (1961).

[24] A. W. Weiss, Astrophys. J. **138**, 1262 (1963).