Lower Bound to the Ground-State Energy and Mass Polarization in Helium-Like Atoms*

LAWRENCE WILETS AND IVAN J. CHERRY

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

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Using a method which involves finding the expectation value of the square of the Hamiltonian, lower bounds to the ground state energies of He, Li$^+$, and O^{6+} have been obtained from existing Hylleraas-type wave functions. The limit of error in the Chandrasekhar-Herzberg 18-parameter helium upper bound, -2.9037063 atomic units (a.u.), is found to be in absolute value less than 0.00179 a.u. and "probably" less than 0.00009 a.u. ($\sim$20 cm^{-1}). These results would seem to indicate that the Hylleraas series is not as rapidly convergent as previously thought.

Again using existing Hylleraas-type wave functions, values have been obtained for the mass polarization (specific mass effect) in the same helium-like atoms. The value obtained for helium is somewhat different from that given by Bethe.

I. INTRODUCTION

THE recent precision measurements by Herzberg and Zbinden[1] of the ionization potential of helium have renewed interest in the problem of calculating very accurately the ground state energies of helium-like atoms. The helium-like atoms are of special interest since they provide one of the few opportunities to test the two-body relativistic formulation of quantum mechanics.

The early nonrelativistic calculations of Hylleraas[2] have been extended by Chandrasekhar and Herzberg[3] to include (in the case of He) 18 adjustable parameters. To the nonrelativistic energies so obtained must be added the corrections for finite mass (normal and specific mass effects), relativistic effects, and Lamb shift. The last two effects will not be discussed here, but a general review of them, along with further references, will be found in the papers of Chandrasekhar and Herzberg.

At present, the experimental value of the helium ionization potential, the error in the calculated non-relativistic energy as estimated by Chandrasekhar and Herzberg, and the magnitude of the relativistic corrections are all comparable—about 2 cm^{-1}. There is hope for even further improvement in the experiments and, if necessary, more detailed nonrelativistic calculations can be made. It should also be noted that individual contributions to the relativistic corrections are of the order of 20 cm^{-1} and therefore "observable" at this time.

The purpose of the present work is to obtain an estimate of the accuracy of the calculated nonrelativistic energies. The convergence of the Hylleraas expansion to the correct energy is not a settled matter, although it does appear "plausible."[4] Even if the expansion is convergent, it is not necessarily rapidly convergent. A difficulty in estimating the speed of convergence is the non-orthogonality of the Hylleraas functions. The decrease in change of energy (as a function of the number of parameters) is not a reliable guide to convergence. The present investigation indicates that the convergence is perhaps not so rapid as estimated by Chandrasekhar and Herzberg.

Stevenson and Crawford[5] obtained lower bounds to some of the early Hylleraas wave functions by methods similar to those discussed here.

II. FORMULA FOR BOUNDS ON THE GROUND STATE ENERGY

Given any trial wave function, the expectation value of the Hamiltonian with respect to that wave function provides an upper bound to the ground state energy, according to the Ritz variational principle. Several methods[6] have been proposed for finding a lower bound to the ground state energy, all of which involve finding the expectation value of the square of the Hamiltonian. Those which give the "best" lower bound also require some knowledge of the first excited state of the same character (angular momentum and parity). The method chosen here[7] (others are roughly equivalent) bounds the ground state energy E_0 as follows:

$$\langle H \rangle \geqslant E_0 \geqslant \langle H \rangle - \frac{\langle H^2 \rangle - \langle H \rangle^2}{E_1 - \langle H \rangle}, \qquad (1)$$

where E_1 is the energy of the first excited state of the same character.

A simple derivation of (1) can be readily given. Let $\psi = \sum a_i \phi_i$, where the ϕ_i are eigenfunctions of the H

munication) expressed the belief that the Hylleraas expansion is not formally complete. He is carrying out a calculation with a more general expansion which includes negative powers of the variables. H. M. Schwartz, Bull. Am. Phys. Soc. Ser. II, **1**, 26 (1956), for similar reasons, is carrying out an expansion in fractional powers.

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[5] A. F. Stevenson and M. F. Crawford, Phys. Rev. **54**, 375 (1938).

[6] See P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, New York, 1953), Sec. 9.4, especially Eqs. (9.4 110) and (9.4 117).

[7] G. Temple, Proc. Roy. Soc. (London) **A119**, 276 (1928).

corresponding to the eigenvalues E_i; $\sum a_i{}^2 = 1$. Then

$$0 \leqslant \sum a_i{}^2(E_i - E_0)(E_i - E_1) = \langle (H - E_0)(H - E_1) \rangle$$
$$= \langle H^2 \rangle - \langle H \rangle^2 + (\langle H \rangle - E_0)(\langle H \rangle - E_1). \quad (2)$$

Equation (1) then follows directly. It can be seen that in the second comparison in Eq. (1), the equality sign holds if the trial wave function is a combination only of the ground and first excited state eigenfunctions.

III. EVALUATION OF $\langle H^2 \rangle$

For the S-state configurations the atomic wave function can be described in terms of the three coordinates

$$s = k(r_1 + r_2),$$
$$t = k(r_2 - r_1), \quad (3)$$
$$u = kr_{12},$$

where the indices 1 and 2 refer to the coordinates of the two atomic electrons. k is an arbitrary scale factor.

The Hylleraas-type wave functions are given by

$$\Psi = \mathfrak{N}e^{-\frac{1}{2}s} \sum_{lmn} C_{lmn} s^l t^m u^n, \quad (4)$$

where $\mathfrak{N}$ is a normalization factor. The ground state configuration is symmetric, so that only even powers of t are assumed. Thus the variables s, t, and u may be considered to range over positive values only, and the expectation value of an operator $\mathcal{O}$ may be written

$$\langle \mathcal{O} \rangle = (2\pi)^2 \mathfrak{N}k^{-6} \int_0^\infty ds \int_0^s u\,du \int_0^u dt(s^2 - t^2)(\Psi \mathcal{O}\Psi). \quad (5)$$

The normalization is obtained by setting $\langle 1 \rangle = 1$.

All expectation values are bilinear forms in the C_{lmn}. The coefficients in the expressions for the energy and normalization are given by Hylleraas,[2] and may also be found in the papers of Chandrasekhar and Herzberg.[3] To obtain the lowest upper bound, the parameters C_{lmn} and k are varied so as to minimize the expectation value of the energy, subject to the condition that the normalization of the wave function remain constant. Minimization with respect to the scale factor k corresponds to satisfying the virial theorem: $\langle$kinetic energy$\rangle = -\frac{1}{2}\langle$potential energy$\rangle$.

In terms of the variables s, t, u, the Hamiltonian assumes the form[5]

H (atomic units)

$$= -k^2 \left\{ \frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial t^2} + \frac{\partial^2}{\partial u^2} + \frac{2}{u}\frac{\partial}{\partial u} + \frac{2s(u^2 - t^2)}{u(s^2 - t^2)}\frac{\partial^2}{\partial s\partial u} + \frac{2t(s^2 - u^2)}{u(s^2 - t^2)}\frac{\partial^2}{\partial t\partial u} + \frac{4s}{(s^2 - t^2)}\frac{\partial}{\partial s} - \frac{4t}{(s^2 - t^2)}\frac{\partial}{\partial t} \right\} + k\left\{ -\frac{4Zs}{(s^2 - t^2)} + \frac{1}{u} \right\}. \quad (6)$$

The expression for the expectation value of the square of the Hamiltonian is then the bilinear form

$$\langle H^2 \rangle = (2\pi)^2 \mathfrak{N}k^{-6} \int_0^\infty ds \int_0^s u\,du \int_0^u dt(s^2 - t^2)(H\Psi)^2 = (2\pi)^2 \mathfrak{N}k^{-6} \sum_{\substack{lmn \\ l'm'n'}} C_{lmn} C_{l'm'n'} \begin{bmatrix} l\,m\,n \\ l'm'n' \end{bmatrix}, \quad (7)$$

where

$$\begin{bmatrix} l\,m\,n \\ l'm'n' \end{bmatrix} = \int_0^\infty s^{l+l'} e^{-s} ds \int_0^s u^{n+n'+1} du \int_0^u t^{m+m'} dt(s^2 - t^2) \left\{ -\frac{1}{4} + \frac{l}{s} + \frac{l(l-1)}{s^2} - \frac{m(m-1)}{t^2} \right.$$
$$-\frac{n(n+1)}{u^2} + \frac{1}{ku} + \frac{2}{s^2 - t^2}\left[\left\langle n\left(1 - \frac{t^2}{u^2}\right) + 2 \right\rangle \left\langle \frac{s}{2} - l \right\rangle + mn\left(1 - \frac{s^2}{u^2}\right) + 2m - \frac{2Z}{k}s \right] \right\}$$
$$\times \left\{ -\frac{1}{4} + \frac{l}{s} + \frac{l'(l'-1)}{s^2} - \frac{m'(m'-1)}{t^2} - \frac{n'(n'+1)}{u^2} + \frac{1}{ku} + \frac{2}{s^2 - t^2}\left[\left\langle n'\left(1 - \frac{t^2}{u^2}\right) + 2 \right\rangle \right. \right.$$
$$\left. \left. \times \left\langle \frac{s}{2} - l' \right\rangle + m'n'\left(1 - \frac{s^2}{u^2}\right) + 2m' - \frac{2Z}{k}s \right] \right\}. \quad (8)$$

Two types of intervals are involved. They are

$$\int_0^\infty e^{-s} ds \int_0^s du \int_0^u dt s^a t^b u^c = \frac{(a+b+c+2)!}{(b+1)(b+c+2)}, \quad (9)$$

and

$$\int_0^\infty e^{-s} ds \int_0^s du \int_0^u dt \frac{s^a t^b u^c}{s^2 - t^2}$$
$$= (a+b+c)! \left\{ -\sum_{\substack{\beta \\ \text{even}}}^b \frac{1}{(\beta-1)(\beta+c)} + F(c) \right\}. \quad (10)$$

The summation is taken as 0 for $b = 0$. In both integrals [Eqs. (9) and (10)], b only assumes even values, and $a \geqslant 0$, $b \geqslant 0$, $c \geqslant -1$. $F(c)$ is given by

$$F(c) = \frac{1}{2} \sum_{n=0}^c \binom{c}{n} \left\{ \frac{(-1)^n}{(n+1)^2} + \frac{(-1)^{c-n}}{n+1} \right.$$
$$\left. \times \left[2^{n+1} \ln 2 - \frac{2^{n+1}}{n+1} + \frac{1}{n+1} \right] \right\}, \quad c \neq -1, \quad (11)$$

$$F(-1) = \frac{1}{8}\pi^2.$$

The evaluations of the algebraic expressions for $\langle H^2 \rangle$ were carried out on the Los Alamos IBM-701 electronic

TABLE I. Summary of calculations on helium-like atoms. The reference numbers refer to footnotes in the text. Column 3 gives the upper bound in the energy $\langle H \rangle$, column 6 the absolute error in the upper bound as estimated by Eq. (1). Columns 7 and 9 compare the upper bounds with the 18-parameter lower $[\underline{E} \ (18)]$ and upper $[\bar{E} \ (18)]$ bounds, respectively. The values of E_1 are experimental; in the case of O^{6+} the first excited ^1S state is unknown, so the estimate of its energy was made from the position of the lowest ^3S state. All energies are in atomic units. The mass polarization (specific mass-effect) is obtained by dividing column 11 by the nuclear mass in units of the electron mass. The sign of this term is conventionally taken as positive if in the same sense as the normal mass effect; this is opposite to the sense of the energy shift.

1	2	3	4	5	6	7	8	9	10	11
No. of param- eters	Refer- ence	$\langle H \rangle$	$\langle H \rangle^2$	$\langle H^2 \rangle$	$\dfrac{\langle H^2 \rangle - \langle H \rangle^2}{E_1 - \langle H \rangle}$	$\langle H \rangle - \underline{E}$ (18)	(6)/(7)	$\bar{E}$ (18) $-\langle H \rangle$	(6)/(9)	$-\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$
					He ($E_1 \approx 2.146$)					
1		−2.848	8.109	9.006	1.28	0.057	20	0.056	23	0
3	2	−2.9024	8.4242	8.4715	0.0626	0.0030	21	0.0013	48	0.17764
6	2	−2.90324	8.42880	8.44589	0.0225	0.00228	10	0.00047	47	0.16437
10	3	−2.903603	8.430909	8.438489	0.0100	0.00190	5.3	0.000103	97	0.15905
14	3	−2.9037009	8.4314789	8.433529	0.00271	0.00180	1.5	0.0000054	502	0.15923
18	3	−2.9087063	8.4315103	8.4328680	0.00179	0.00179	1	⋯	⋯	0.15916
20	8	−2.9037178								
					Li$^+$ ($E_1 - E_0 \approx 0.5468$)					
10	3	−7.2797624	52.99494	53.01801	0.0420					
					O^{6+} ($E_1 - E_0 \approx 6.55$)					
10	3	−59.156422	3499.482	3499.682	0.0305					

computer. For consistency, the wave function normalizations were recalculated.

IV. RESULTS AND DISCUSSION OF LOWER-BOUND CALCULATIONS

In Table I are given the results for the 1, 5, 6, 10, 14, and 18 parameter wave functions of helium and the 10-parameter wave functions of Li$^+$ and O^{6+}.

A 20-parameter helium wave function has also been calculated by Herzberg,[8] the corresponding energy of which differs very little from the 18-parameter value; a lower bound has not been calculated for this wave function.

Comparison with the 18 parameter bounds indicates (as was found by Stevenson and Crawford) that in the other cases the upper bound is considerably closer to the true eigenvalue than is the lower bound. Thus while the absolute limit of error in the 18-parameter upper bound is 0.00179 atomic units (a.u.), it appears quite probable that the actual error is at least an order of magnitude smaller. In column 8 (or 10) of Table I is given the ratio of the error in the upper bound to that in the lower bound *assuming* the 18-parameter lower (or upper) bound gives the correct energy. It seems reasonable that this ratio *using the true energy* would generally be at least 20—perhaps greater. Thus a more *probable* limit on the 18-parameter upper bound would be 0.00009 a.u. ($\sim$20 cm^{-1}). Although this may still be an overestimate, it would seem to indicate that the convergence is not so rapid as the small change in $\langle H \rangle$ as a function of the number of parameters might imply. Further calculations with either more parameters or a

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[8] G. Herzberg (private communication).

different expansion seems required to yield accuracy comparable with the experiment.

V. MASS POLARIZATION CORRECTION

The nonrelativistic energies must be corrected for the finite mass of the nucleus. As a matter of convenience, the nuclear mass corrections are generally divided into the normal (reduced) mass and mass polarization (specific mass) effects. The separation is made as follows:

In a coordinate system where the center of mass of the atom is at rest, the atomic Hamiltonian assumes the form

$$H = (2m)^{-1} \sum_i \mathbf{p}_i^2 + V + (2M)^{-1} (\sum_i \mathbf{p}_i)^2, \quad (12)$$

where m and M are the electronic and nuclear masses, and $\mathbf{p}_i = -i\hbar \nabla_i$. It is of importance to the form of the potential energy term that the distances $\mathbf{x}_i$ are measured relative to the nucleus rather than relative to the center of mass.

The second term on the right-hand side of (12) represents a correction for the kinetic energy of the nucleus. It is convenient to separate the correction term into two parts, thusly:

$$(2M)^{-1} (\sum_i \mathbf{p}_i)^2 = (2M)^{-1} \sum_i \mathbf{p}_i^2 + (2M)^{-1} \sum_{i \neq j} \mathbf{p}_i \cdot \mathbf{p}_j. \quad (13)$$

The first term on the right-hand side of (13) has the same form as the electronic kinetic energy. It can be combined with the electronic kinetic energy term merely by replacing the electronic mass m by the reduced mass $\mu = mM/(m+M)$. The atomic energy levels [neglecting for the moment the second term on the

right-hand side of (13)] are directly proportional to the reduced mass; this gives rise to the normal, or reduced mass, correction.

The second term on the right-hand side of (13) referred to as the mass polarization or specific mass term, appears only in polyelectronic atoms. Because of the appearance of the nucleonic mass in the denominator, it is assumed to be small and can be treated by first-order perturbation theory. In most atoms, the mass polarization term can be larger than the normal mass term.

In the case of helium, the summation for the mass polarization reduces to the single term

$$H' \equiv M^{-1}\mathbf{p}_1 \cdot \mathbf{p}_2. \tag{14}$$

Written in terms of the Hylleraas variables (3), the

expectation value of the operator assumes the form[9]

$$\langle H' \rangle = -(2\pi)^2 M^{-1} \mathfrak{N} k^{-4} \int_0^\infty ds \int_0^s du \int_0^u dt$$

$$\times \{ u(s^2+t^2-2u^2)(\Psi_s{}^2-\Psi_t{}^2) - u(s^2-t^2)\Psi_u{}^2$$

$$+2s(t^2-u^2)\Psi_u\Psi_s + 2t(u^2-s^2)\Psi_u\Psi_t \}, \tag{15}$$

where the subscripts on the Ψ's indicate differentiation. For a Hylleraas-type wave function (4), the expectation value of H' assumes the bilinear form

$$\langle H' \rangle = -(2\pi)^2 \mathfrak{N} M^{-1} k^{-4} \sum_{\substack{l\,m\,n \\ l'm'n'}} C_{lmn} C_{l'm'n'} \begin{Bmatrix} l\,m\,n \\ l'm'n' \end{Bmatrix}, \tag{16}$$

where

$$\begin{Bmatrix} l\,m\,n \\ l'm'n' \end{Bmatrix} = \int_0^\infty s^{l+l'}e^{-s}ds \int_0^s u^{n+n'} \int_0^u t^{m+m'}dt \Big\{ u[s^2+t^2-2u^2] \Big[\Big(\frac{l}{s}-\frac{1}{2}\Big)\Big(\frac{l'}{s}-\frac{1}{2}\Big) - \frac{mm'}{t^2} - \frac{(s^2-t^2)}{u}nn' + \frac{s}{u}[t^2-u^2] \Big]$$

$$\times \Big[\Big(\frac{l}{s}-\frac{1}{2}\Big)n' + \Big(\frac{l'}{s}-\frac{1}{2}\Big)n + \frac{(u^2-s^2)}{u}(mn'+m'n) \Big\}. \tag{17}$$

Equation (17) may be evaluated from the integrals given in (9) to yield explicitly

$$\begin{Bmatrix} l\,m\,n \\ l'm'n' \end{Bmatrix} = \frac{4(\sigma+3)!}{(\mu+1)(\mu+\nu+3)}$$

$$\times \Big\{ \nu \Big[\frac{\frac{1}{4}(\sigma+4)(\sigma+5) - ll'}{(\mu+3)(\mu+\nu+5)} + \frac{mm'}{(\mu-1)(\mu+\nu+1)} \Big]$$

$$- \frac{nl'+n'l+nn'}{\mu+3} - \frac{nm'+n'm+nn'}{\mu+\nu+1} \Big\}, \tag{18}$$

where $\lambda=l+l'$, $\mu=m+m'$, $\nu=n+n'$ and $\sigma=\lambda+\mu+\nu$.

The algebraic expression for the mass polarization was evaluated on the Los Alamos IBM-701 electronic computer for the same wave functions as were used in calculating the lower bounds. The results are summarized in Table I.

The mass polarization term depends upon the electron correlation, and in fact vanishes unless the coordinate $r_{12}=u/k$ appears in the wave function. It is thus more critical to the accuracy of the wave function than

is the energy. Indeed, for the one-parameter wave function, the mass polarization vanishes while the energy is given to within 2%.

The value obtained from Hylleraas's 6-parameter wave function is somewhat at variance with that reported by Bethe,[9] who gives for $-\mathbf{p}_1 \cdot \mathbf{p}_2$ the value 0.173 compared with our value of 0.164. This discrepancy was noted earlier by Edmonds and Wilets and by Kinoshita (both unpublished).

VI. ACKNOWLEDGMENTS

[9] H. A. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24, Part 1, p. 375.