

Ground State of Two-Electron Atoms

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A new method is developed for solving the wave equation for two-electron atoms. The wave function is expanded into a triple orthogonal set in three *perimetric* coordinates. From the wave equation one obtains an explicit recursion relation for the coefficients in the expansion, and the vanishing of the determinant of these coefficients provides the condition for the energy eigenvalues and for the eigenvectors. The determinant was solved on WEIZAC for $Z=1$ to 10, using an iteration method. Since the elements of the determinant are integers, and only an average of about 20 per row are nonvanishing, it has been possible to go to an order of 214 before exceeding the capacity of the fast memory of WEIZAC. The nonrelativistic energy eigenvalues obtained for the ground state are lower than any previously published for all Z from 1 to 10. In the case of helium, our nonrelativistic energy value is accurate to within 0.01 cm^{-1} and is 0.40 cm^{-1} lower than the value computed by Kinoshita. From the wave functions obtained, the mass-polarization and the relativistic corrections were evaluated for $Z=1$ to 10. Using the values of the Lamb shift computed by Kabir, Salpeter, and Sucher, we obtain an ionization potential for helium of $198\,310.67 \text{ cm}^{-1}$ as against Herzberg's value of $198\,310.82 \pm 0.15 \text{ cm}^{-1}$. Comparison is also made with the available experimental data for the other values of Z . By the use of our magnetic tape storage, the accuracy of the nonrelativistic energy value for helium could be pushed to about 0.001 cm^{-1} , should future improvements in the experimental values and in the computed radiative corrections warrant it.

1. INTRODUCTION

THE nonrelativistic Schrödinger wave equation for two-electron atoms is, on neglecting the motion of the nucleus, given (in atomic units) by

$$\nabla_1^2\psi + \nabla_2^2\psi + 2\left(E + \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}}\right)\psi = 0. \quad (1)$$

Z denotes the nuclear charge, r_1 and r_2 the electron distances from the nucleus, and r_{12} their mutual distance. In the ground state, one has

$$\psi = \psi(r_1, r_2, r_{12}), \quad (2)$$

and a method of obtaining an exact solution of (1) has recently been proposed by Fock,¹ but has not yet been carried out. The exact solution starts out with the linear terms

$$\psi = 1 - Z(r_1 + r_2) + \frac{1}{2}r_{12} + \dots, \quad (3)$$

which are followed by terms of the form $R \ln R$, $R^{\frac{1}{2}} \ln R$, $R^2(\ln R)^2$ etc.,² where

$$R = r_1^2 + r_2^2. \quad (4)$$

Pending a derivation of the exact solution, the practice has been to follow the classical method of Hylleraas³ whereby (2) is substituted into (1), leading to

$$\begin{aligned} & \frac{\partial^2\psi}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial\psi}{\partial r_1} + \frac{\partial^2\psi}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial\psi}{\partial r_2} + 2 \frac{\partial^2\psi}{\partial r_{12}^2} + \frac{4}{r_{12}} \frac{\partial\psi}{\partial r_{12}} \\ & + \frac{(r_1^2 - r_2^2 + r_{12}^2)}{r_1 r_{12}} \frac{\partial^2\psi}{\partial r_1 \partial r_{12}} + \frac{(r_2^2 - r_1^2 + r_{12}^2)}{r_2 r_{12}} \frac{\partial^2\psi}{\partial r_2 \partial r_{12}} \\ & \times \frac{\partial^2\psi}{\partial r_2 \partial r_{12}} + 2\left(E + \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}}\right)\psi = 0. \quad (5) \end{aligned}$$

¹ V. A. Fock, *Izvest. Akad. Nauk. S.S.S.R. Ser. Fiz.* **18**, 161 (1954).

² V. A. Fock, reference 1; J. H. Bartlett, *Phys. Rev.* **51**, 661 (1937).

³ E. A. Hylleraas, *Z. Physik* **54**, 347 (1929).

With

$$s = r_1 + r_2, \quad t = r_2 - r_1, \quad u = r_{12}, \quad (6)$$

ψ is assumed to have the form

$$\psi = N e^{-\frac{1}{2}ks} \sum c_{lmn} k^{l+m+n} s^l t^m u^n, \quad (7)$$

and the "scale parameter" k as well as the coefficients c_{lmn} are determined from the equivalent variational form of (5). Now the asymptotic behavior of the solution of (5) for large s requires that in the exact solution k equal 2ϵ , where

$$\epsilon = \sqrt{-E}. \quad (8)$$

By allowing k to deviate from 2ϵ in the variational method, we obtain a better over-all behavior of ψ , at the sacrifice of its proper asymptotic behavior, and thus achieve higher accuracy for a given number of terms.

2. METHOD OF SOLUTION

If we attempt to develop $\psi(r_1, r_2, r_{12})$ into an orthogonal set of its three variables, we meet with the difficulty that, because of the triangular condition, these variables are not independent. This difficulty can be obviated by the use of the *perimetric* coordinates u, v, w , defined by

$$u = \epsilon(r_2 + r_{12} - r_1), \quad (9)$$

$$v = \epsilon(r_1 + r_{12} - r_2), \quad (10)$$

$$w = 2\epsilon(r_1 + r_2 - r_{12}). \quad (11)$$

These coordinates⁴ are independent, and range each from 0 to ∞ . We have

$$\begin{aligned} dx_1^3 dx_2^3 &= 8\pi^2 r_1 r_2 r_{12} dr_1 dr_2 dr_{12} \\ &= (\pi^2/32\epsilon^6) (u+v)(2u+w)(2v+w) du dv dw. \quad (12) \end{aligned}$$

Put

$$\psi = e^{-\frac{1}{2}(u+v+w)} F(u, v, w), \quad (13)$$

⁴ Perimetric coordinates were first used by H. M. James and A. S. Coolidge, *Phys. Rev.* **51**, 857 (1937).

thus assuring the proper asymptotic behavior of ψ at infinity ($k=2\epsilon$). The wave equation (5) takes on the form

$$\begin{aligned} \epsilon\{ & (4u^2v+4uv^2+4u^2w+4uvw+2uw^2)F_{uu} \\ & + (4u^2v+4uv^2+4v^2w+4uvw+2vw^2)F_{vv} \\ & + (8u^2w+8v^2w+4uw^2+4vw^2)F_{ww} \\ & - 4uw(2u+w)F_{uw}-4vw(2v+w)F_{vw} \\ & + (-4u^2+4v^2+2w^2+4uw+4vw+8uv-4uvw \\ & - 4uw^2-4u^2v)F_u+(4u^2-4v^2+2w^2 \\ & + 4uw+4vw+8uv-4uvw-4uw^2-4u^2v)F_v \\ & + (8u^2+8v^2-4w^2-2uw^2-2vw^2-4u^2w-4v^2w)F_w \\ & - 4(u+v)(u+v+w)F\} \\ & + [4Z(u+v)(u+v+w)-(2u+w)(2v+w)]F=0. \end{aligned} \tag{14}$$

The equivalent variational form of (14) is

$$\begin{aligned} I = & \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \int_0^\infty e^{-w} dw \\ & \times \{ \epsilon[(4uv^2+4u^2v+4u^2w+4uvw+2uw^2)F_u^2 \\ & + (4uv^2+4u^2v+4v^2w+4uvw+2vw^2)F_v^2 \\ & + (8u^2w+8v^2w+4uw^2+4vw^2)F_w^2 \\ & - 4uw(2u+w)F_uF_w-4vw(2v+w)F_vF_w \\ & + 4(u+v)(u+v+w)F^2] + [-4Z(u+v)(u+v+w) \\ & + (2u+w)(2v+w)]F^2\}. \end{aligned} \tag{15}$$

We now assume the expansion

$$F = \sum_{l,m,n=0}^\infty A(l,m,n)L_l(u)L_m(v)L_n(w), \tag{16}$$

where $L_n(w)$ denotes the *normalized* Laguerre polynomial⁶ of order n .

$$L_n(w) = \sum_{k=0}^n \binom{n}{k} \frac{(-w)^k}{k!}, \tag{17}$$

$$\int_0^\infty e^{-w}[L_n(w)]^2 dw = 1. \tag{18}$$

By substituting (16) into the wave equation (14), we obtain an explicit recursion relation between the coefficients $A(l,m,n)$, on using the relations⁶

$$xL_n''(x) = (x-1)L_n'(x) - nL_n(x), \tag{19}$$

$$xL_n'(x) = nL_n(x) - nL_{n-1}(x), \tag{20}$$

$$\begin{aligned} xL_n(x) = & -(n+1)L_{n+1}(x) \\ & + (2n+1)L_n(x) - nL_{n-1}(x), \end{aligned} \tag{21}$$

the primes denoting derivatives with respect to x . The recursion relation between the $A(l,m,n)$ thus obtained, containing 33 terms, is

$$\begin{aligned} & 4(l+1)(l+2)[-Z+\epsilon(1+m+n)]A(l+2,m,n)+4(m+1)(m+2)[-Z+\epsilon(1+l+n)]A(l,m+2,n) \\ & + 4(l+1)(m+1)[1-2Z+\epsilon(2+l+m)]A(l+1,m+1,n)+2(l+1)(n+1)[1-2Z+\epsilon(2+2m+n)] \\ & \times A(l+1,m,n+1)+2(m+1)(n+1)[1-2Z+\epsilon(2+2l+n)]A(l,m+1,n+1)+(n+1)(n+2)A(l,m,n+2) \\ & + (l+1)\{4Z(4l+4m+2n+7)-8m-4n-6-2\epsilon[(m+n)(4m+12l)+n^2+12l+18m+15n+14]\}A(l+1,m,n) \\ & + (m+1)\{4Z(4l+4m+2n+7)-8l-4n-6-2\epsilon[(l+n)(4l+12m)+n^2+12m+18l+15n+14]\}A(l,m+1,n) \\ & + 4(n+1)\{Z(2l+2m+2)-l-m-n-2-\epsilon[-l^2-m^2+4lm+2ln+2nm+3l+3m+2n+2]\}A(l,m,n+1) \\ & + 4\epsilon(m+1)(m+2)nA(l,m+2,n-1)+4\epsilon(l+1)(l+2)nA(l+2,m,n-1) \\ & + 2\epsilon l(n+1)(n+2)A(l-1,m,n+2)+2\epsilon m(n+1)(n+2)A(l,m-1,n+2) \\ & + \{4(2l+1)(2m+1)+4(2n+1)(l+m+1)+6n^2+6n+2-4Z[(l+m)(6l+6m+4n+12)-4lm+4n+8] \\ & + 4\epsilon[(l+m)(10lm+10mn+10ln+10l+10m+18n+4n^2+16)+lm(4-12n)+8+12n+4n^2]\}A(l,m,n) \\ & + 4l(m+1)[1-2Z+\epsilon(1+l+m)]A(l-1,m+1,n)+4(l+1)m[1-2Z+\epsilon(1+l+m)]A(l+1,m-1,n) \\ & + 2l(n+1)[1-2Z+\epsilon(2m-4l-n)]A(l-1,m,n+1)+2m(n+1)[1-2Z+\epsilon(2l-4m-n)]A(l,m-1,n+1) \\ & + 2(l+1)n[1-2Z+\epsilon(2m-4l-n-3)]A(l+1,m,n-1)+2(m+1)n[1-2Z+\epsilon(2l-4m-n-3)]A(l,m+1,n-1) \\ & + 2l\{- (4m+2n+3)+Z(8l+8m+4n+6)-\epsilon[(m+n+1)(12l+4m+2)+n+n^2]\}A(l-1,m,n) \\ & + 2m\{- (4l+2n+3)+Z(8l+8m+4n+6)-\epsilon[(l+n+1)(12m+4l+2)+n+n^2]\}A(l,m-1,n) \\ & + 4n\{- (l+m+n+1)+Z(2l+2m+2)-\epsilon[(l+m)(1+2n-l-m)+6lm+2n]\}A(l,m,n-1) \\ & + 2\epsilon n(n-1)(l+1)A(l+1,m,n-2)+2\epsilon n(n-1)(m+1)A(l,m+1,n-2)+4\epsilon l(l-1)(n+1)A(l-2,m,n+1) \\ & + 4\epsilon m(m-1)(n+1)A(l,m-2,n+1)+4l(l-1)[-Z+\epsilon(1+m+n)]A(l-2,m,n) \\ & + 4m(m-1)[-Z+\epsilon(1+l+n)]A(l,m-2,n)+n(n-1)A(l,m,n-2) \\ & + 4lm[1-2Z+\epsilon(l+m)]A(l-1,m-1,n)+2ln[1-2Z+\epsilon(2m+n+1)]A(l-1,m,n-1) \\ & + 2mn[1-2Z+\epsilon(2l+n+1)]A(l,m-1,n-1)=0. \end{aligned} \tag{22}$$

⁶ The Laguerre polynomials defined in Courant-Hilbert as well as in Morse-Feshbach are *not* normalized.

⁶ A. Erdélyi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 2, p. 188.

We note that if we write Eq. (22) in the form

$$\sum_{\alpha, \beta, \gamma=-2}^{+2} C_{\alpha, \beta, \gamma}(l, m, n) A(l+\alpha, m+\beta, n+\gamma) = 0, \quad (23)$$

then

$$C_{-\alpha, -\beta, -\gamma}(l, m, n) = C_{\alpha, \beta, \gamma}(l-\alpha, m-\beta, n-\gamma). \quad (24)$$

If ψ is symmetrical in the two electrons, then

$$A(l, m, n) = A(m, l, n), \quad \text{para}, \quad (25)$$

while in the antisymmetrical case

$$A(l, m, n) = -A(m, l, n), \quad \text{ortho}. \quad (26)$$

Equation (22) represents a set of linear equations for the determination of the coefficients $A(l, m, n)$, and the vanishing of their determinant yields the eigenvalues of the energy parameter ϵ . For this purpose, it is necessary to arrange the triple series of coefficients $A(l, m, n)$ into a one-dimensional array. We do this by first ordering the (l, m, n) in a suitable manner, and then assigning to each triplet of indices (l, m, n) an index k by the relations,

$$A(l, m, n) = B_k, \quad (27)$$

$$k(l, m, n) = (1/24)\omega(\omega+2)(2\omega+5) + \frac{1}{16}[1 - (-1)^\omega] + \frac{1}{4}(l+m)^2 + \frac{1}{8}[1 - (-1)^{l+m}] + l + 1, \quad (28)$$

where

$$\omega = l + m + n. \quad (29)$$

The scheme which we have adopted for ordering the (l, m, n) is illustrated in Table I for the symmetrical case. Substituting successively the triplets (l, m, n) into (22), we obtain the equations

$$\sum_k C_{ik} B_k = 0, \quad (30)$$

$$C_{ik} = a_{ik} + \epsilon b_{ik}. \quad (31)$$

Here the a_{ik} and b_{ik} are integers and

$$C_{ik} = C_{ki}. \quad (32)$$

A sample of the determinant for the symmetrical case is shown in Table II.

3. COMPARISON WITH THE VARIATIONAL METHOD

Had we substituted the assumed expansion (16) for F into the variational form (15), then the resulting Eulerian variational equations would also have yielded the same recursion relation (22). Our method is there-

TABLE I. Ordering of the indices l, m, n in the symmetrical case.

l	m	n	ω	k	l	m	n	ω	k
0	0	0	0	1	1	1	1	3	11
0	0	1	1	2	0	3	0	3	12
0	1	0	1	3	1	2	0	3	13
0	0	2	2	4	0	0	4	4	14
0	1	1	2	5	0	1	3	4	15
0	2	0	2	6	0	2	2	4	16
1	1	0	2	7	1	1	2	4	17
0	0	3	3	8	0	3	1	4	18
0	1	2	3	9	1	2	1	4	19
0	2	1	3	10	0	4	0	4	20

fore equivalent to the variational method. Indeed, in one respect our method is weaker than the variational method of Hylleraas because the fixed exponential form introduced in (13) deprives us of the disposable "scale parameter k " ($k=2\epsilon$). For a given number of terms B_k , Eq. (30) therefore yields an inferior value for ϵ than is possible to attain when the disposable constant k is available. Indeed, our solution is biased to assure proper behavior at infinity. However, from the point of view of economy of the electronic computer, the fixed exponential form in (13) is to be preferred because firstly it makes the elements a_{ik} and b_{ik} of the determinant in (30) integers. This allows us to maintain double-precision (18 decimals) floating accuracy in the computations, and at the same time to accommodate about four times as many elements of the determinant in the fast memory. The second advantage is that the resulting determinant is very *sparse*, having on the average only about 20 nonvanishing terms per row. In this way we have been able to reach an order of the determinant of 214, before exceeding the capacity of the fast memory of WEIZAC; while with the Hylleraas type of solution (7), where *every* element of the determinant is nonvanishing and nonintegral, only a determinant of order about 42 could be accommodated. The results obtained by our method are therefore to be compared with those of Hylleraas' method on the basis of a determinant of order 214 of the former, as against a determinant of order of about 42 of the latter.

4. SOLUTION OF THE DETERMINANT

The solution of the determinant (30) was carried out on the electronic computer (WEIZAC) of the Weizmann Institute. A program was prepared for computing the elements of the determinant a_{ik} and b_{ik} in (31), based on

TABLE II. The determinant of order 7 for the symmetrical case.

B_1	B_2	B_3	B_4	B_5	B_6	B_7
$-16Z+5+16\epsilon$						
$4Z-4-4\epsilon$	$-24Z+15+48\epsilon$					
$28Z-6-28\epsilon$	$-4Z+2-8\epsilon$	$-112Z+26+144\epsilon$				
1	$8Z-12-16\epsilon$	4ϵ	$-32Z+31+96\epsilon$			
$-4Z+2+4\epsilon$	$36Z-10-60\epsilon$	$16Z-12-16\epsilon$	$-8Z+4-20\epsilon$	$-144Z+54+336\epsilon$		
$-8Z+8\epsilon$	8ϵ	$88Z-12-104\epsilon$		$-8Z+4-32\epsilon$	$-224Z+34+320\epsilon$	
$-4Z+2+4\epsilon$		$44Z-14-72\epsilon$		$-4Z+2-4\epsilon$	$-16Z+8+24\epsilon$	$-104Z+25+208\epsilon$

TABLE III. Values of the energy parameter ϵ for various orders n of the determinant used. $E = -2e^2$ ry. The computed values are uncertain by about one unit in the last decimal figure. ω is the order of the polynomial used, n the order of the corresponding determinant. n^* denotes the highest order determinant used in which k was not consecutive after about 95; k^* and ω^* denote the highest values of k and of ω , respectively, in the determinant of order n^* .

$\omega \backslash n$	8	9	10	11					
$Z \backslash n$	95	125	101	203	n^*	Extrapolated	n^*	k^*	ω^*
1	0.726 464 050 4	0.726 464 459 0	0.726 464 630 8	0.726 464 683 0	0.726 464 709 7	0.726 464 701 2	214	517	16
2	1.704 031 510 6	1.704 031 654 2	1.704 031 722 5	1.704 031 756 8	1.704 031 781 1	1.704 031 793 6	210	438	15
3	2.698 131 255 2	2.698 131 361 3	2.698 131 411 1	2.698 131 436 0	2.698 131 453 6	2.698 131 462 0	214	437	15
4	3.695 343 695 3	3.695 343 778 0	3.695 343 816 6	3.695 343 835 7	3.695 343 849 6	3.695 343 855 6	213	444	15
5	4.693 716 047 0	4.693 716 114 4	4.693 716 145 7	4.693 716 161 2	4.693 716 172 2	4.693 716 177 2	206	444	15
6	5.692 648 357 9	5.692 648 414 7	5.692 648 441 0	5.692 648 454 0	5.692 648 463 5	5.692 648 467 4	204	444	15
7	6.691 893 891 6	6.691 893 940 6	6.691 893 963 3	6.691 893 974 5	6.691 893 982 7	6.691 893 986 0	201	444	15
8	7.691 332 382 5	7.691 332 425 6	7.691 332 445 5	7.691 332 455 4	7.691 332 462 9	7.691 332 465 4	207	444	15
9	8.690 898 172 8	8.690 898 211 2	8.690 898 229 0	8.690 898 237 8	8.690 898 244 5	8.690 898 246 7	206	437	15
10	9.690 552 367 8	9.690 552 402 5	9.690 552 418 6	9.690 552 426 4	9.690 552 432 4	9.690 552 434 5	207	437	15

the recursion relation (22) and on (28). Following the scheme of ordering indicated in Table I, *all* of the elements of the determinant were generated up to the end of a given value of ω . The determinant was then solved by an iterative procedure.⁷ If we truncate the determinant at the order n , then we may put $B_1=1$, say, and use the n equations to solve for the $(n-1)$ remaining B_k and for ϵ . In the case of the ground state, we may use the first equation to solve for ϵ , and each k th row to solve for B_k . If we start with initial values of ϵ and of the vector \mathbf{B} which are close to the exact solution for the order n , then the iteration procedure will converge rapidly. We have programmed the solution to take as initial values for the order n the final values which were obtained for the order $n-1$, and to put $B_n=0$. The iterations for a given n were programmed to stop after the value of ϵ had stabilized to within a preassigned accuracy. Thus the computations were started at $n=1$ and allowed to proceed through *all* n up to $n=125$, which constitutes the complete polynomial in the variables u , v , and w of order $\omega=9$. Next we did $n=161$ ($\omega=10$) by starting with the solution for $n=125$, and guessing initial rough values for the additional B_k . The next step was $n=203$ ($\omega=11$). Up to this stage, the computations were made in single-precision floating arithmetic. For the final refinement of the cases $n=95$, 125, 161, and 203, we changed to double-precision arithmetic, in order to avoid possible errors from round-off. At this point, the pattern of the relative magnitudes of the B_k , for a given value of Z , when proceeding to a new value of ω became clear. We then rejected certain components B_k beyond about $k=95$, which were small, and put in their place other elements (different k for different Z), up to about $k^*=450$ which were anticipated to be larger. This constitutes our solution for $n=n^*$ below.

The results for the values of the nonrelativistic energy parameter ϵ are given in Table III for $Z=1$ through 10. These values are higher than any previously pub-

lished⁸⁻¹¹ for all Z . For helium, Kinoshita⁹ obtained a value of $\epsilon=1.704\ 031\ 25$ by direct variational computation with a determinant of order 39, in which the "scale parameter k " was also varied. The latter came out 3.72, which is markedly different from 2ϵ . He also arrives at an extrapolated value of $\epsilon=1.704\ 031\ 6$.

In order to exhibit the rate of convergence of ϵ with increase in the order ω of the polynomial used, we have made an extrapolation to $\omega \rightarrow \infty$. The extrapolation is based on the fact that, except for the case $Z=1$, the ratios of the successive differences of ϵ are nearly constant. The extrapolated values in Table III were derived from the computed values of ϵ for $n=95$, 125, 161, and 203 by fitting the formula

$$\epsilon_\infty = \epsilon_{95} + \frac{(\epsilon_{125} - \epsilon_{95})}{(1-x)^a}, \quad (33)$$

where the constants x and a are determined from

$$ax = \frac{(\epsilon_{161} - \epsilon_{125})}{(\epsilon_{125} - \epsilon_{95})}, \quad \frac{(a+1)x}{2} = \frac{(\epsilon_{203} - \epsilon_{161})}{(\epsilon_{161} - \epsilon_{125})}. \quad (34)$$

If the ratio of successive differences were constant, as it nearly is, and equal to x , then a would be 1. The slight deviation of a from unity allows us to take account of the variability of this ratio.

5. MASS POLARIZATION

Our computations, so far, are based on the wave equation (5), in which the motion of the nucleus has been neglected. The nonrelativistic energy values given in Table III have first to be corrected for the motion of the nucleus. An elementary correction is to use a Rydberg constant R_M appropriate for the atom in question,

$$R_M = R_\infty \frac{M}{M+m} \sim R_\infty \left(1 - \frac{m}{M}\right). \quad (35)$$

⁸ S. Chandrasekhar and G. Herzberg, *Phys. Rev.* **98**, 1050 (1955).

⁹ T. Kinoshita, *Phys. Rev.* **105**, 1490 (1956).

¹⁰ J. F. Hart and G. Herzberg, *Phys. Rev.* **106**, 79 (1957).

¹¹ E. A. Hylleraas and J. Midtdal, *Phys. Rev.* **109**, 1013 (1958).

⁷ C. L. Pekeris, *J. Appl. Phys.* **17**, 683 (1946).

TABLE IV. Values of the mass-polarization correction $\epsilon_M = 2e^2(m/M)(A/N)R_M \text{ cm}^{-1}$.

Z	Element	R_M (cm^{-1})	$n=95$	125	$-e^2(A/N)$	161	203	ϵ_M (cm^{-1})
1	H ¹	109 677.577	0.032 884 3	0.032 881 2	0.032 880 1	0.032 879 9		-3.928
2	He ⁴	109 722.267	0.159 072	0.159 071	0.159 070	0.159 069 8		-4.785
3	Li ⁷	109 728.727	0.288 981	0.288 978	0.288 977	0.288 976		-4.960
4	Be ⁹	109 730.628	0.420 529	0.420 524	0.420 522	0.420 521		-5.619
5	B ¹¹	109 731.840	0.552 764	0.552 758	0.552 755	0.552 754		-6.046
6	C ¹²	109 732.291	0.685 349	0.685 342	0.685 338	0.685 336		-6.878
7	N ¹⁴	109 733.009	0.818 136	0.818 127	0.818 123	0.818 121		-7.036
8	O ¹⁶	109 733.544	0.951 049	0.951 039	0.951 034	0.951 032		-7.160
9	F ¹⁹	109 734.140	1.084 047	1.084 035	1.084 030	1.084 028		-6.871
10	Ne ²⁰	109 734.297	1.217 104	1.217 091	1.217 085	1.217 082		-7.331

A second correction is the so-called mass-polarization correction ϵ_M . According to Bethe,¹² this is given by

$$\epsilon_M = -\frac{m}{M} \int \left(\frac{\partial^2 \psi}{\partial x_1 \partial x_2} + \frac{\partial^2 \psi}{\partial y_1 \partial y_2} + \frac{\partial^2 \psi}{\partial z_1 \partial z_2} \right) \psi dx_1^3 dx_2^3, \quad (36)$$

provided ψ is normalized. If ψ is represented by (13), then one has

$$\epsilon_M = e^2 \frac{m A}{M N}, \quad (37)$$

where

$$A = \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \times \int_0^\infty e^{-w} dw \{ -(8u^2w + 8uvw + 4w^2)F_u^2 - (8v^2w + 8uvw + 4w^2)F_v^2 + 32uvwF_w^2 - 16(u^2v + uv^2)F_uF_v + (16u^2w + 8uw^2)F_uF_w + (16v^2w + 8vw^2)F_vF_w + (u+v)(4uw - 2vw - 2vw - w^2)F^2 \}, \quad (38)$$

$$N = \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \times \int_0^\infty e^{-w} dw (u+v)(2u+w)(2v+w)F^2. \quad (39)$$

With the coefficients $A(l, m, n)$ in the expansion (16) known, the integrals in (38) and (39) can be evaluated by using the relation

$$\int_0^\infty e^{-x} \dot{L}_n(x) \dot{L}_m(x) x dx = n \delta_{nm}, \quad (40)$$

and Eqs. (20) and (21). Table IV gives values of the mass-polarization correction ϵ_M for $Z=1$ through 10. These agree to within 0.001 cm^{-1} with the values of Hart and Herzberg.¹⁰

6. RELATIVISTIC CORRECTIONS

A. General

Since an up-to-date discussion of the relativistic corrections is available in reference 12, p. 275, it will suffice here to give a summary of the results and to show how the various terms can be evaluated from our solution of the wave equation. It is customary to express the energies in terms of the ionization potential J (see Table V),

$$J = (e^2 - \frac{1}{2}Z^2) \text{ atomic units}, \quad (41)$$

which is the quantity measured experimentally. The shift E_j in the ionization potential due to relativistic effects is given, in atomic units, by¹³

$$E_j = \alpha^2 \left[-\frac{1}{8}Z^4 + \frac{1}{4}\langle p_1^4 \rangle - \pi Z \langle \delta(\mathbf{r}_2) \rangle - \pi \langle \delta(\mathbf{r}_{12}) \rangle \right] - E_2. \quad (42)$$

Here α denotes the fine structure constant, and the various terms have the following origin: $-\frac{1}{8}\alpha^2Z^4$ is the

TABLE V. Values of the nonrelativistic ionization potential $J = (2e^2 - Z^2)R_M \text{ cm}^{-1}$. n denotes the order of the determinant used.

Z \ n	95	125	161	203	n^*	Extrapolated
1	6087.109	6087.239	6087.294	6087.311	6087.319	6087.317
2	198 317.158	198 317.265	198 317.316	198 317.342	198 317.360	198 317.370
3	610 072.469	610 072.595	610 072.654	610 072.683	610 072.704	610 072.714
4	1 241 177.40	1 241 177.54	1 241 177.60	1 241 177.63	1 241 177.65	1 241 177.66
5	2 091 701.82	2 091 701.96	2 091 702.03	2 091 702.06	2 091 702.08	2 091 702.09
6	3 161 660.61	3 161 660.75	3 161 660.82	3 161 660.85	3 161 660.87	3 161 660.88
7	4 451 087.72	4 451 087.87	4 451 087.93	4 451 087.97	4 451 087.99	4 451 088.00
8	5 959 978.57	5 959 978.71	5 959 978.78	5 959 978.81	5 959 978.84	5 959 978.85
9	7 688 349.37	7 688 349.52	7 688 349.58	7 688 349.62	7 688 349.64	7 688 349.65
10	9 636 164.80	9 636 164.95	9 636 165.02	9 636 165.05	9 636 165.08	9 636 165.09

¹² H. A. Bethe and E. E. Salpeter, *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 35, Part 1, p. 252.

¹³ Reference 12, Eq. (41.4).

shift for the ion, $\frac{1}{4}\alpha^2\langle p_1^4 \rangle$ stems from the relativistic variation of mass with velocity. The last two terms in the square brackets arise from a term characteristic in the Dirac theory, and from the interaction of the spin magnetic dipole moments of the two electrons. The last term is due to the retardation of the electromagnetic field produced by an electron.

B. $\langle p_1^4 \rangle$

We have

$$\begin{aligned} \langle p_1^4 \rangle &= \int dx_1^3 dx_2^3 (\nabla_1^2 \psi)^2 \\ &= \frac{1}{2} \int dx_1^3 dx_2^3 [(\nabla_1^2 \psi)^2 + (\nabla_2^2 \psi)^2]. \end{aligned} \quad (43)$$

Now from the wave equation (1), it follows that

$$(\nabla_1^2 \psi)^2 + (\nabla_2^2 \psi)^2 = -2\nabla_1^2 \psi \cdot \nabla_2^2 \psi + 4[E - V(r)]^2 \psi^2, \quad (44)$$

where

$$V(r) = -Z/r_1 - Z/r_2 + 1/r_{12}. \quad (45)$$

We have used the right-hand side of (44) in the integrand of (43). In terms of F defined in (13), the final result is

$$\langle p_1^4 \rangle = Q/N, \quad (46)$$

$$\begin{aligned} Q &= \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \\ &\quad \times \int_0^\infty e^{-w} dw \left[-\frac{16\epsilon^4 GH}{(u+v)} + 2BF^2 \right], \end{aligned} \quad (47)$$

where

$$\begin{aligned} G &= \{uwF_{uu} + (2uv + 2v^2 + vw)F_{vv} + 4uvwF_{vw} \\ &\quad - 4uvwF_{uv} + (uv - 2u + w)F_u \\ &\quad + (-2uv - 2v^2 - vw + 2u + 4v + w)F_v \\ &\quad + (-2uv + 4u - 2w)F_w \\ &\quad + [\frac{1}{4}(u+v)(2v+w) - 2(u+v)]F\}, \end{aligned} \quad (48)$$

$$\begin{aligned} H &= \{vwF_{vv} + (2uv + 2u^2 + uv)F_{uu} + 4vuvF_{uv} \\ &\quad - 4vuvF_{vu} + (vw - 2v + w)F_v \\ &\quad + (-2uv - 2u^2 - uv + 2v + 4u + w)F_u \\ &\quad + (-2vw + 4v - 2w)F_w \\ &\quad + [\frac{1}{4}(u+v)(2u+w) - 2(u+v)]F\}, \end{aligned} \quad (49)$$

$$\begin{aligned} B &= \left\{ \epsilon^4(u+v)(2u+w)(2v+w) \right. \\ &\quad - 16\epsilon^3 Z(u+v)(u+v+w) - 32\epsilon^2 Z(u+v+w) \\ &\quad + 4\epsilon^3(2u+w)(2v+w) + 32\epsilon^2 Z^2(u+v) \\ &\quad + \frac{16\epsilon^2 Z^2(u+v)(2u+w)}{(2v+w)} + \frac{16\epsilon^2 Z^2(u+v)(2v+w)}{(2u+w)} \\ &\quad \left. + \frac{4\epsilon^2(2u+w)(2v+w)}{(u+v)} \right\}. \end{aligned} \quad (50)$$

N is given by (39).

In order to carry out the integration in (47) we have found it expedient to prepare a program for the evaluation of the coefficients $F(a,b,c)$ in the conversion

$$\begin{aligned} F &= \sum_{l,m,n} A(l,m,n) L_l(u) L_m(v) L_n(w) \\ &= \sum_{a,b,c} F(a,b,c) u^a v^b w^c. \end{aligned} \quad (51)$$

We then use the following relations, which can be easily proved:

$$\begin{aligned} p(a,b,c) &= \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \\ &\quad \times \int_0^\infty e^{-w} dw \frac{u^a v^b w^c}{(u+v)(a+b+1)}, \end{aligned} \quad (52)$$

$$\begin{aligned} h(a,b,c) &= \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \int_0^\infty e^{-w} dw \frac{u^a v^b w^c}{(2u+w)} \\ &= b!(a+c)! \sum_{n=0}^{n=c} (-)^n \binom{c}{n} N(a+n), \end{aligned} \quad (53)$$

$$N(a) = (-)^a \left[\ln 2 - 1 + \frac{1}{2} - \frac{1}{3} + \dots + \frac{(-)^a}{a} \right]. \quad (54)$$

Values of $\langle p_1^4 \rangle$ are given in Table VI.

TABLE VI. Expectation values of $\langle p_1^4 \rangle$ in atomic units.

$Z \setminus n$	95	125	161	203	n^*	Extrapolated
1	2.462 8	2.462 5	2.462 6	2.462 6	2.462	2.462
2	54.088 8	54.088 8	54.088 7	54.088 6	54.088 7	54.088 2
3	310.548	310.549	310.549	310.548	310.546	310.548
4	1047.278	[1047.280	1047.279	1047.280	1047.29	1047.29
5	2659.729	2659.734	2659.736	2659.737	2659.72	2659.74
6	5663.354	5663.364	5663.368	5663.371	5663.35	5663.38
7	10 693.60	10 693.62	10 693.63	10 693.64	10 693.64	10 693.65
8	18 505.93	18 505.96	18 505.97	18 505.98	18 505.95	18 506.00
9	29 975.78	29 975.83	29 975.86	29 975.86	29 975.85	29 975.84
10	46 098.62	46 098.68	46 098.72	46 098.74	46 098.72	46 098.77

TABLE VII. Expectation values of $\langle \delta(\mathbf{r}_2) \rangle$ in atomic units.

$Z \setminus n$	95	125	161	203	n^*	Extrapolated
1	0.164 6	0.164 5	0.164 5	0.164 5	0.164 5	0.164 5
2	1.810 064	1.810 181	1.810 255	1.810 303	1.810 430	1.810 403
3	6.851 133	6.851 406	6.851 580	6.851 700	6.851 870	6.851 97
4	17.196 58	17.197 07	17.197 38	17.197 60	17.198 04	17.198 1
5	34.756 22	34.756 99	34.757 50	34.757 84	34.758 18	34.758 6
6	61.439 92	61.441 02	61.441 75	61.442 25	61.442 97	61.443 4
7	99.157 52	99.159 04	99.160 03	99.160 71	99.161 89	99.162 2
8	149.818 9	149.820 9	149.822 2	149.823 1	149.824 4	149.826
9	215.333 9	215.336 4	215.338 1	215.339 3	215.340 6	215.342
10	297.612 4	297.615 5	297.617 6	297.619 0	297.620 8	297.622

C. $\langle \delta(\mathbf{r}_2) \rangle$

With a normalized ψ , one has

$$\langle \delta(\mathbf{r}_2) \rangle = \int dx_1^3 \psi^2(\mathbf{r}_1, 0). \tag{55}$$

Now if $r_2=0$, we have

$$u=v=0, \quad v=2\epsilon r_1, \quad dx_1^3 = (\pi/2\epsilon^3)v^2dv, \tag{56}$$

and from (12)

$$\langle \delta(\mathbf{r}_2) \rangle = \frac{16\epsilon^3}{\pi N} \int_0^\infty e^{-v^2} F^2(0, v, 0) dv. \tag{57}$$

Let

$$F(0, v, 0) = \sum_m K_m L_m(v), \tag{58}$$

where

$$K_m = \sum_{l,n} A(l, m, n). \tag{59}$$

By applying Eq. (21) we get

$$vF(0, v, 0) = \sum_m D_m L_m(v), \tag{60}$$

with

$$D_m = -mK_{m-1} + (2m+1)K_m - (m+1)K_{m+1}. \tag{61}$$

It then follows that

$$\langle \delta(\mathbf{r}_2) \rangle = \frac{16\epsilon^3}{\pi N} \sum_m D_m^2. \tag{62}$$

Values of $\langle \delta(\mathbf{r}_2) \rangle$ are given in Table VII.

D. $\langle \delta(\mathbf{r}_{12}) \rangle$

If $r_{12}=0$, we have

$$u=v=0, \quad w=4\epsilon r_1, \quad dx_1^3 = (\pi/16\epsilon^3)w^2dw, \tag{63}$$

$$\begin{aligned} \langle \delta(\mathbf{r}_{12}) \rangle &= \int dx_1^3 \psi^2(\mathbf{r}_1, \mathbf{r}_1) \\ &= (\pi/16\epsilon^3) \int_0^\infty F^2(0, 0, w) w^2 e^{-w} dw. \end{aligned} \tag{64}$$

As before, we write

$$F(0, 0, w) = \sum_n P_n L_n(w), \tag{65}$$

$$P_n = \sum_{l,m} A(l, m, n). \tag{66}$$

Then

$$wF(0, 0, w) = \sum_n G_n L_n(w), \tag{67}$$

$$G_n = -nP_{n-1} + (2n+1)P_n - (n+1)P_{n+1}, \tag{68}$$

$$\langle \delta(\mathbf{r}_{12}) \rangle = \frac{2\epsilon^3}{\pi N} \sum_n G_n^2. \tag{69}$$

Values of $\langle \delta(\mathbf{r}_{12}) \rangle$ are given in Table VIII.

E. E_2

E_2 is the expectation value of¹⁴

$$H_2 = -\frac{e^2}{2m^2c^2r_{12}} \left[\mathbf{p}_1 \cdot \mathbf{p}_2 + \frac{\mathbf{r}_{12} \cdot (\mathbf{r}_{12} \cdot \mathbf{p}_1) \mathbf{p}_2}{r_{12}^2} \right] = -\frac{\alpha^2 S}{8r_1 r_2 r_{12}^3}, \tag{70}$$

TABLE VIII. Expectation values of $\langle \delta(\mathbf{r}_{12}) \rangle$ in atomic units.

$Z \setminus n$	95	125	161	203	n^*	Extrapolated
1	0.002 755	0.002 749	0.002 746	0.002 744	0.002 742	0.002 74
2	0.106 590	0.106 517	0.106 469	0.106 436	0.106 405	0.106 36
3	0.534 472	0.534 244	0.534 095	0.533 995	0.533 892	0.533 78
4	1.524 43	1.523 96	1.523 65	1.523 45	1.523 19	1.523 0
5	3.315 04	3.314 24	3.313 72	3.313 37	3.312 75	3.312 6
6	6.144 98	6.143 76	6.142 98	6.142 45	6.141 52	6.141 3
7	10.253 0	10.251 2	10.250 1	10.249 4	10.248 1	10.247 8
8	15.877 7	15.875 4	15.873 9	15.872 9	15.871 0	15.871
9	23.258 0	23.255 0	23.253 0	23.251 8	23.249 4	23.249
10	32.632 4	32.628 7	32.626 3	32.624 6	32.621 7	32.621

¹⁴ Reference 12, p. 267.

TABLE IX. Values of $-(2/\alpha^2)E_2$ in atomic units.

$Z \setminus n$	95	125	161	203	n^*	Extrapolated
1	0.017 78	0.017 77	0.017 76	0.017 76	0.017 75	0.017 75
2	0.278 385	0.278 310	0.278 266	0.278 240	0.278 21	0.278 20
3	0.856 434	0.856 256	0.856 155	0.856 095	0.856 04	0.856 01
4	1.758 32	1.758 01	1.757 83	1.757 73	1.757 6	1.757 6
5	2.985 20	2.984 72	2.984 45	2.984 30	2.984 1	2.984 1
6	4.537 46	4.536 78	4.536 41	4.536 19	4.535 7	4.535 9
7	6.415 26	6.414 35	6.413 85	6.413 57	6.413 2	6.413 2
8	8.618 68	8.617 52	8.616 88	8.616 51	8.615 6	8.616 0
9	11.147 8	11.146 3	11.145 5	11.145 1	11.144 7	11.144 5
10	14.002 5	14.000 8	13.999 8	13.999 3	13.998 5	13.998 5

where

$$\begin{aligned}
 S = & (-2r_1^2r_2^2 + 2r_1^2r_{12}^2 + 2r_2^2r_{12}^2 + r_1^4 + r_2^4 - 3r_{12}^4) \\
 & \times \frac{\partial^2\psi}{\partial r_1\partial r_2} - 8r_1r_2r_{12} \frac{\partial\psi}{\partial r_{12}} - 8r_1r_2r_{12}^2 \frac{\partial^2\psi}{\partial r_{12}^2} \\
 & + 4r_2r_{12}(-r_1^2 + r_2^2 - r_{12}^2) \frac{\partial^2\psi}{\partial r_1\partial r_{12}} \\
 & + 4r_1r_{12}(r_1^2 - r_2^2 - r_{12}^2) \frac{\partial^2\psi}{\partial r_2\partial r_{12}}. \quad (71)
 \end{aligned}$$

This leads to

$$E_2 = -\frac{4\alpha^2\epsilon^3}{N} \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \int_0^\infty e^{-w} dw \frac{TF}{(u+v)^2}, \quad (72)$$

with

$$\begin{aligned}
 T = & uw[(u+v)(4u+2v)+vw+2uw]F_{uu} \\
 & + vw[(u+v)(2u+4v)+uw+2vw]F_{vv} \\
 & - uvw(8u+8v-4w)F_{ww} \\
 & + uv[(u+v)(8u+8v+4w)+2w^2]F_{uv} \\
 & - uv(u+v)(8u+4v)F_{uv} - vw(u+v)(8v+4w)F_{vv} \\
 & + [4uv(u+v+w)(1-u-v)+2w(u^2+v^2)+w^2(u+v)] \\
 & \times (F_u+F_v) + [4w(u^3+v^3)-8uv(u+v+w) \\
 & + (2w^2-4w)(u^2+v^2)+2w(u+v)(6uv-w)]F_w \\
 & + [uv(u+v)(2u+2v-w) \\
 & - \frac{1}{2}w^2(u^2+v^2)-w(u^3+v^3)]F. \quad (73)
 \end{aligned}$$

In carrying out the integration in (72) we use the relation

$$\begin{aligned}
 q(a,b,c) = & \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \\
 & \times \int_0^\infty e^{-w} dw \frac{u^a v^b w^c}{(u+v)^2} = \frac{a!b!c!}{(a+b)(a+b+1)}. \quad (74)
 \end{aligned}$$

Values of $-(2/\alpha^2)E_2$ are given in Table IX, and the combination of all the above into E_j in Table X.

7. THE LAMB SHIFT

The radiative corrections to the ground-state energy of two-electron atoms have been treated by Kabir and

Salpeter¹⁵ and by Sucher.¹⁶ According to Kabir and Salpeter, the leading terms of the Lamb shift in the ionization potential of two-electron atoms ΔE_j are given by

$$\Delta E_j = E_{L,1} - E_{L,2} - E_{L,2'}. \quad (75)$$

$E_{L,1}$ represents the Lamb shift for the one-electron ion,

$$E_{L,1} = \frac{8\alpha^3 Z^4}{3\pi} \left[2 \ln \frac{1}{Z\alpha} - \ln \frac{K_0}{Z^2 \text{ ry}} + \frac{19}{30} \right] \text{ ry}, \quad (76)$$

where K_0 denotes the average excitation energy for a 1S state,¹⁷⁻¹⁹

$$K_0 = 19.77 Z^2 \text{ ry}. \quad (77)$$

$E_{L,2}$ and $E_{L,2'}$ represent radiative corrections to the ground state of two-electron atoms,

$$E_{L,2} = \frac{16}{3} \alpha^3 Z \langle \delta(r_2) \rangle \left[2 \ln \frac{1}{\alpha} - \ln \frac{k_0}{\text{ ry}} + \frac{19}{30} \right] \text{ ry}, \quad (78)$$

$$E_{L,2'} = -\frac{28}{3} \alpha^3 \langle \delta(r_{12}) \rangle \ln \left(\frac{1}{\alpha} \right) \text{ ry}. \quad (79)$$

Here k_0 denotes the average excitation energy for the ground state of two-electron atoms. In the case of helium, Kabir and Salpeter arrive at a value $k_0 = 80.5$ ry, and a more approximate calculation for lithium yields $k_0 = 191.6$ ry. These values of k_0 were used in Table XI for Z equal to 2 and 3, respectively, while for the other values of Z we have used the values of K_0 for the one-electron ion given by Eq. (77). The justification for this is, as Kabir and Salpeter point out, the fact that the values of K_0 given by (77) for Z equal to 2 and 3 are 79.08 and 177.9, respectively, which are close to their values of k_0 quoted above.

DISCUSSION OF RESULTS

The principal results of this investigation are the values of the energy parameter ϵ for the ground state of

¹⁵ P. K. Kabir and E. E. Salpeter, Phys. Rev. **108**, 1256 (1957); see also reference 12, p. 276.

¹⁶ J. Sucher, Phys. Rev. **109**, 1010 (1958).

¹⁷ H. A. Bethe, Phys. Rev. **72**, 339 (1947).

¹⁸ H. Håkansson, Arkiv Fysik **1**, 555 (1950).

¹⁹ J. M. Harriman, Phys. Rev. **101**, 594 (1956).

TABLE X. Values of the relativistic shift of the ionization potential E_j in cm^{-1} , evaluated from Eq. (42).

$Z \setminus n$	95	125	161	203	n^*	Extrapolated
1	-0.304	-0.302	-0.304	-0.303	-0.304	-0.304
2	-0.542 7	-0.549 0	-0.553 2	-0.556 0	-0.563 9	-0.562
3	19.759	19.737	19.723	19.713	19.691	19.69
4	114.655	114.603	114.565	114.544	114.505	114.52
5	373.222	373.119	373.051	373.002	372.925	372.88
6	919.583	919.407	919.287	919.202	919.015	919.00
7	1 912.93	1 912.66	1 912.46	1 912.33	1 912.08	1 911.9
8	3 547.51	3 547.09	3 546.79	3 546.58	3 546.20	3 545.9
9	6 052.64	6 052.04	6 051.66	6 051.31	6 050.92	6 050.3
10	9 692.66	9 691.83	9 691.27	9 690.86	9 690.25	9 689.5

two-electron atoms given in Table III. The highest values obtained by the direct solution of the determinant are those shown in the column labelled n^* . The extrapolation is based on the values for $n=95, 125, 161,$ and 203 and Eqs. (33) and (34). The purpose of the extrapolation was to obtain an estimate of the accuracy that one may attach to the n^* values. Judged by this criterion, the n^* values for the nonrelativistic ionization potential J given in Table V are probably within 0.01 cm^{-1} of the exact values. It is to be noted that they have been computed for the particular isotopes of the elements which are listed in Table IV. Values for the other isotopes can be obtained by using the appropriate R_M . The numerical values in Table V are of course subject to the uncertainty²⁰ in R_∞ , which amounts to $\pm 0.012 \text{ cm}^{-1}$. In the Tables VI to X, where values of the terms entering in Eq. (42) for the relativistic shift in the ionization potential E_j are given, the accuracy of the results may again be judged by comparing the n^* values with the extrapolated values.

For the completion of the calculation of the theoretical value of the ionization potential of two-electron atoms we need to apply the Lamb shift correction. Whereas we have aimed at an accuracy of 0.01 cm^{-1} in all the terms excluding the Lamb shift, the available calculations of the Lamb shift to date are subject to a larger uncertainty. Using the value of $\ln k_0=4.39$, given by Kabir

and Salpeter¹⁵ for helium, in Eq. (78) and the values of $\langle \delta(\mathbf{r}_2) \rangle$ and $\langle \delta(\mathbf{r}_{12}) \rangle$ given in Tables VII and VIII, we obtain a value of -1.267 cm^{-1} for E_j in (75), compared with the value of $-1.264 \pm 0.2 \text{ cm}^{-1}$ given by Kabir and Salpeter. Adding to this an additional α^3 correction, evaluated by Sucher,¹⁶ of -0.072 cm^{-1} , we arrive at a value of -1.339 cm^{-1} for the Lamb shift correction to the ionization potential of helium. With the value of J for n^* in Table XI, this leads to a theoretical value for the ionization potential of helium of $198\,310.67 \text{ cm}^{-1}$. The error in this value would be about 0.01 cm^{-1} if the above-mentioned Lamb shift correction is not subject to a larger uncertainty. Herzberg's experimental value²¹ of $198\,310.8_2 \pm 0.15 \text{ cm}^{-1}$ is within his stated experimental error of our theoretical value.

As for the heavier elements, the available experimental values for the ionization potential are subject to an uncertainty of the order of 100 cm^{-1} . Further refinement of the experimental values will therefore be necessary before our theoretical values can be subjected to experimental test appropriate to their accuracy.

The values for the Lamb shift correction for the ionization potential of the heavier elements may also be subject to a larger uncertainty than is indicated by the values given in Table XI. Another source of error is the uncertainty in the value of R_∞ , which enters as a factor in the J values of Table XI. When one aims at an

TABLE XI. Values of the ionization potential J of two-electron atoms, including the mass-polarization and relativistic corrections, but excluding the Lamb shift. J_{theor}^* equals J for n^* plus the Lamb shift of the ionization potential.

$Z \setminus n$	J in cm^{-1}					Lamb shift	J_{theor}^* (cm^{-1})	J_{exp}^a (cm^{-1})
	95	125	161	203	n^*			
1	6082.877	6083.009	6083.062	6083.080	6083.087	6083.085	6083.08	
2	198 311.830	198 311.931	198 311.977	198 312.001	198 312.011	198 312.023	198 310.67	198 310.8 ₂ $\pm 0.15^d$
3	610 087.268	610 087.372	610 087.417	610 087.436	610 087.435	610 087.44	610 079.61	610 079 ± 25
4	1 241 286.44	1 241 286.52	1 241 286.55	1 241 286.56	1 241 286.54	1 241 286.57	1 241 259.4	1 241 225 ± 100
5	2 092 069.00	2 092 069.04	2 092 069.03	2 092 069.01	2 092 068.96	2 092 068.93	2 092 003.3	2 091 960 ± 200
6	3 162 573.31	3 162 573.28	3 162 573.23	3 162 573.17	3 162 573.01	3 162 573.01	3 162 441	3 162 450 ± 300
7	4 452 993.62	4 452 993.49	4 452 993.36	4 452 993.26	4 452 993.04	4 452 992.9	4 452 758	4 452 800 ± 500
8	5 963 518.92	5 963 518.64	5 963 518.41	5 963 518.23	5 963 517.88	5 963 517.6	5 963 135	5 963 000 ± 600
9	7 694 395.14	7 694 394.69	7 694 394.37	7 694 394.06	7 694 393.69	7 694 393.1	7 693 810	7 693 400 ± 800
10	9 645 850.13	9 645 849.45	9 645 848.96	9 645 848.58	9 645 848.00	9 645 847.3	9 645 004	

^a Except for helium, the values for J_{exp} were taken from *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

^b See reference 15.

^c See reference 16.

^d See reference 21.

²⁰ E. R. Cohen and J. W. M. DuMond, *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 35, Part 1, p. 82.

²¹ G. Herzberg, Proc. Roy. Soc. (London) A248, 309 (1958).

accuracy of 0.01 cm^{-1} in the ionization potential, the isotopic purity of the element has also to be considered. In the case of lithium, where this is most serious, our computations are based on the isotope Li^7 . For the naturally abundant element, which contains an admixture of 7.5% of Li^6 , the ionization potential becomes uncertain by about 0.7 cm^{-1} due to the isotope effect alone.

It is clear that our method is directly applicable also to the treatment of the excited states of two-electron atoms, including the ortho states. Work is now in progress on the 2^1S , 2^3S , and $2P$ states.

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Measurements of the Interaction of 95-Mev Protons with He^4 †

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Elastic and inelastic scattering and the (p,d) "deuteron pickup" process have been studied using a proton beam of energy about 95 Mev incident on a liquid helium target. The elastic scattering shows a nuclear-Coulomb interference dip at 9° , a slight diffraction-type minimum at about 57° , and a deep minimum, approximately $10^{-29} \text{ cm}^2/\text{sterad}$ at 135° . (All angles and cross sections are in the center-of-mass system.) Inelastic scattering spectra were obtained at laboratory angles of 10° , 15° , and 30° . These spectra are characterized by broad peaks, roughly 10-Mev wide, centered around an energy about 6 Mev below the upper kinematical limit for inelastic scattering. Their interpretation is discussed qualitatively both in terms of quasi-elastic nucleon-nucleon scattering and in terms of strong interaction between parts of the dissociated α particle in virtual or continuum states. A minimum was observed in the $\text{He}^4(p,d)\text{He}^3$ differential cross section at about 29° . Analysis of the (p,d) data at 95 Mev and 32 Mev in the "transparent nucleus" Born approximation yielded inconsistent results; presumably this inconsistency is due to the failure of the model at the lower energy due to the tightly bound structure of He^4 .

I. INTRODUCTION

THE interaction of high-energy nucleons with He^4 is of particular interest because with high incident energies, one can expect to study the internal structure of the target nucleus, and the presumed complete space symmetry of the He^4 wave function should simplify the interpretation of the results. At high energies the proton- He^4 interaction can proceed through at least seven channels, from elastic scattering through complete disintegration of the alpha particle. The possible reactions, together with their respective Q values, are listed in Table I.

We hoped when this investigation was begun that by obtaining data on both the elastic differential scattering cross section and the $\text{He}^4(p,d)\text{He}^3$ "pickup" cross section at a sufficiently high energy, we could deduce an equivalent single-particle wave function for He^4 . This purpose might be accomplished as follows: (A) If the elastic scattering is analyzed on the impulse approximation,¹ the total scattering amplitude factors into the product of a nuclear form factor and a sum of nucleon-

nucleon scattering amplitudes. The latter sum involves the non-spin-flip parts of the triplet and singlet p - n and p - p scattering amplitudes. If one knew what to insert for these amplitudes, one could then obtain from the experimental data the nuclear form factor—which is equivalent to obtaining the nuclear wave function. (Inversely, of course, if the nuclear wave function were known, one could get information on the nucleon-nucleon scattering amplitudes.) (B) Analysis of the (p,d) pickup data, on the "transparent-nucleus" or

TABLE I. Possible interactions and Q values of high-energy protons with He^4 .

Reaction	Q (Mev)	Experimental observation
1. $\text{He}^4(p,p)\text{He}^4$	0	Elastic scattering
2. $\text{He}^4(p,d)\text{He}^3$	-18.32	"Pickup" deuterons
3. $\text{He}^4(p,2p)\text{H}^3$	-19.81	a (Quasi-elastic p - p type)
4. $\text{He}^4(p,pn)\text{He}^3$	-20.55	a (Quasi-elastic p - n type)
5. $\text{He}^4(p,pd)\text{H}^2$	-23.75	a, b
6. $\text{He}^4(p,2pn)\text{H}^2$	-25.97	a, b
7. $\text{He}^4(p,2p2n)\text{H}^1$	-28.2	a
8. $[\text{He}^4(p,p^1)\text{He}^{4*}]$?	Peak on the inelastic proton continuum

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¹ G. F. Chew, Phys. Rev. **80**, 196 (1950).

^a Reactions 3, 4, 5, 6, and 7 all contribute to the inelastic proton continuum, with varying "threshold" proton energies roughly equal to the difference between incident proton energy and the appropriate Q value.

^b Reactions 5 and 6 both contribute to the deuteron continuum with deuteron "threshold" energies roughly less than the peak from reaction 2 by the difference in the Q values (see Fig. 2).