Ground State of the Helium Atom. II*

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(Received February 19, 1959)

A further attempt is made to improve the theoretical prediction of the energy of the ground state of atomic helium. The nonrelativistic part is treated by the variational method of Stevenson and Crawford which is useful for improving the lower bound for the ground-state energy. Linear combinations of up to 80 terms of generalized Hylleraas type are employed in the numerical computation. The best trial function gives -2.9037237 atomic units as an upper bound and -2.9037467 atomic units as a lower bound for the ground-state energy. It is estimated from the calculated results that the exact nonrelativistic energy of He ground state will be found in the neighborhood of -2.9037247 atomic units. Rigorous formulas are derived which can be used for calculating the upper limits to the errors in the expectation values of mass polarization and relativistic corrections. Although these formulas give very broad limits of error, they are useful in estimating the order of magnitude of actual errors in a semiempirical manner. With mass polarization and relativistic corrections as well as electrodynamical corrections, the theoretical ionization potential becomes 198310.77 cm^{-1} which is in good agreement with the latest observed value $198310.8_2 \pm 0.15$ cm^{-1}.

1. INTRODUCTION

In recent years there has been renewed interest in the eigenvalue problem of two electron atomic systems,[1–3] since it offers an opportunity for a very precise test of the present atomic theory which is seldom possible except in the exactly soluble case of one electron systems. For the He atom, in particular, the latest observed value[1] for the ionization potential of the ground state is $198310.8_2 \pm 0.15$ cm^{-1}, an accuracy of better than 1 in 10^6. The best theoretical value has been 198310.6_4 cm^{-1} which is in good agreement with the measurement.[2]

However, the theoretical result has not been completely satisfactory for precise comparison with experimental results because: (1) The estimated accuracy of the nonrelativistic part of the ionization potential is about ± 0.3 cm^{-1} or possibly somewhat worse. This is based on the determination of the exact ground-state energy of the He atom by extrapolation from the calculated upper and lower bounds. The uncertainty arises since the difference between upper and lower bounds is quite large (~ 33 cm^{-1}) even for the best trial functions. (2) The magnitude of the errors in the expectation values of the relativistic and mass polarization corrections has so far been entirely unknown. It has been estimated only from apparent convergence of these expectation values as more and more accurate trial functions were used. However, this might have been only accidental. (3) The magnitude of the electrodynamical corrections[4] for the He ground state has been estimated to be 1.336 ± 0.2 cm^{-1}. Some improvement in the accuracy of this calculation would be highly desirable.[5]

In this paper, we attempt to improve the theoretical predictions on the first two points. In Sec. 2, trial functions of up to 80 terms are determined by a variational method for the lower bound which is particularly suitable for reducing the discrepancy between upper and lower bounds. A method is developed in Sec. 3 which enables us to determine rigorous limits for the errors in the expectation values of the mass polarization and relativistic corrections. Although these limits are very broad, they are useful in estimating the order of magnitude of actual errors in a semiempirical way.

2. VARIATIONAL METHOD FOR THE LOWER BOUND

In our previous paper,[2] it was found that the upper bound for the ground-state energy of the He atom calculated with a 39-term trial function agrees with the observed value within a fraction of 1 cm^{-1} when the corrections due to mass polarization and relativistic effects as well as the electrodynamical effects are taken into account. On the other hand, the corresponding lower bound is found to be about 33 cm^{-1} lower than the upper bound, indicating a very large uncertainty in the accuracy of this calculation. This is not surprising, however, since it was obtained by a straightforward variational method for $\lambda=(\psi,H\psi)$, which pays no attention to the improvement of the lower bound λ_L. Obviously, if one wants to make the difference $\lambda-\lambda_L$ as small as possible, one should rather try to maximize the lower bound of the ground-state energy,

$$\lambda_L=(\psi,H\psi)-\frac{(H\psi,H\psi)-(\psi,H\psi)^2}{E_1-(\psi,H\psi)}, \qquad (2.1)$$

* Partially supported by the joint program of the Office of Naval Research and the U. S. Atomic Energy Commission.
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[1] G. Herzberg, Proc. Roy. Soc. (London) **A248**, 309 (1958).
[2] T. Kinoshita, Phys. Rev. **105**, 1490 (1957). This paper will be quoted as I.
[3] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955); J. F. Hart and G. Herzberg, Phys. Rev. **106**, 79 (1957); E. A. Hylleraas and J. Midtdal, Phys. Rev. **109**, 1013 (1958).
[4] P. K. Kabir and E. E. Salpeter, Phys. Rev. **108**, 1256 (1957); J. Sucher, Phys. Rev. **109**, 1010 (1958).
[5] An attempt is being made at Cornell to improve the accuracy of the Lamb shift calculation of the He ground state [M. Zaidi (private communication)].

TABLE I. The constants of the 39-term ground-state wave function of the helium atom determined by the variational method for the lower bound. The trial function is of the form $\varphi=e^{-s/2}\sum C_{lmn}s^{l-m}u^{m-n}t^n$. For convenience, the expansion coefficients C_{lmn} listed are multiplied by 10^l. For other notations, see Sec. 3 of reference 2.

$\lambda=-2.9037200$ $\lambda_L=-2.9037906$		$k=3.7098126$ $\sigma=0.0000536$		$(\varphi,\varphi)=70.9359074$ $(\varphi,K\varphi)=14.9663846$ $(\varphi,V\varphi)=111.0449667$		$(K\varphi,K\varphi)=11.4604114$ $-2(K\varphi,V\varphi)=108.4707813$ $(V\varphi,V\varphi)=288.1384239$	
lmn	$10^l C_{lmn}$	lmn	$10^l C_{lmn}$	lmn	$10^l C_{lmn}$	lmn	$10^l C_{lmn}$
000	1.00000000	240	−0.17406605	322	−0.79438516	442	−0.25236459
100	−0.27028452	212	0.01212105	332	0.42137612	444	0.01468821
110	1.29386710	222	1.79502475	342	0.17609233	540	0.25502650
120	−0.10961317	232	−1.31753640	400	0.09723145	550	−0.04312723
112	0.00071339	242	0.32604973	410	0.05017234	560	0.09487272
122	0.07914980	300	−0.34830525	420	−0.34517959	522	−0.11457850
200	0.51627618	310	0.00440996	430	−0.37652043	552	0.06839501
210	−0.01965337	320	1.30616359	440	−0.04120541	660	−0.04853323
220	−1.49662980	330	−0.10499914	450	−0.12748955	662	−0.00380729
230	0.71060994	340	0.07443304	422	0.59010047		

directly, where E_1 is the exact energy of the first excited state having the same symmetry property as the ground state.[6] A variational method useful for such a purpose was developed by Stevenson and Crawford some years ago.[7] Their method is based on a somewhat different lower-bound formula,

$$\lambda_L=\zeta-[\zeta^2-2\zeta(\psi,H\psi)+(H\psi,H\psi)]^{\frac{1}{2}}, \qquad (2.2)$$

where ζ is a parameter satisfying

$$\zeta\leqslant(E_0+E_1)/2. \qquad (2.3)$$

This is equivalent to (2.1) if ζ is chosen to be its maximum value $(E_0+E_1)/2$. The alternative formula (2.2) has the advantage that the best lower bound λ_L may be determined as a solution of the variational problem

$$-2\zeta(\psi,H\psi)+(H\psi,H\psi)=\text{minimum}. \qquad (2.4)$$

This leads us to a linear eigenvalue problem which may be solved by any known method.

Since the eigenvalue of (2.4) is known approximately beforehand, we have solved our eigenvalue problem by converting it to a set of linear homogeneous equations in which an appropriate input value is assumed for the eigenvalue. Let us call this method A. It is repeated for several values of input parameters and the best result is then picked up as the solution of the eigenvalue problem (2.4). Usually the method A gives a satisfactory result for λ_L but the upper bound obtained this way would not be very useful. Because of this, we have next tried to improve the result of method A by an iteration method[8] which is designed to minimize the upper bound $(\psi,H\psi)$. Let us call this method B. It is repeated as long as the upper bound is improved without reducing the lower bound.

The numerical work was carried out on the IBM 704 computer at the Bell Telephone Laboratories. To achieve the accuracy that we want, it was necessary to perform the calculation making use of double precision subroutines in some parts.

This scheme of computation was first applied to the 39-term trial function of our previous work in order to test its efficiency. As was found in I, it is convenient to represent each trial function ψ by the corresponding two numbers $\lambda=(\psi,H\psi)$ and $\sigma=(H\psi,H\psi)-(\psi,H\psi)^2$. In this fashion, the best 39-term function of I is expressed by the point marked 39-I in Fig. 1. The new 39-term function obtained by method A of this paper is represented by the point 39-A. When method B is applied

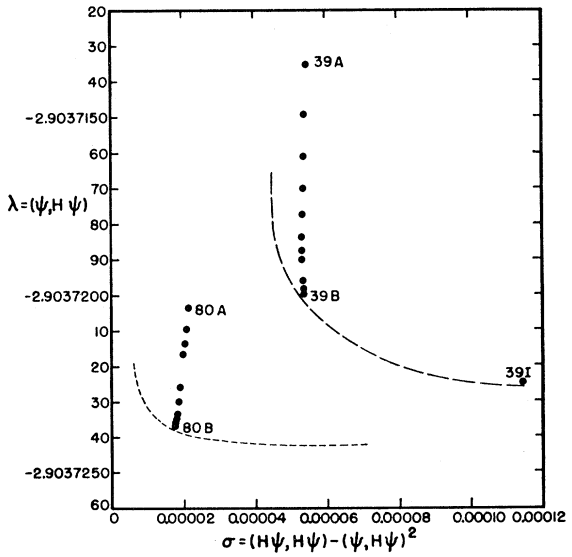

FIG. 1. The expectation value of energy $\lambda=(\psi,H\psi)$, in atomic units, *versus* $\sigma=(H\psi,H\psi)-\lambda^2$, calculated with various trial functions with 39 and 80 terms. The broken curve is drawn to indicate that no point (σ,λ) computed with the 39-term function could be found below or to the left of it. The dotted curve represents a similar boundary for the 80-term function.

[6] Strictly speaking, since the exact value of E_1 is not known, a lower bound for E_1 should be used in (2.1) to obtain a rigorous lower bound for the ground-state energy. Instead, we use the experimental value $E_1\sim-2.146$ atomic units in this paper, hoping that it will be justified in the future. Recently, N. W. Bazley [Proc. Natl. Acad. Sci. **45**, 850 (1959)] has obtained -2.165_5 as a lower bound for E_1. If we adopt this value, our values for $\lambda-\lambda_L$ must be increased by about 2.7%.

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

[8] See reference 2, footnote 15.

TABLE II. The constants of the 80-term ground-state wave function of the helium atom determined by the variational method for the lower bound. For notations, see Table I.

$\lambda=-2.9037237$ $\lambda_L=-2.9037467$		$k=3.7103976$ $\sigma=0.0000175$		$(\varphi,\varphi)=70.8093643$ $(\varphi,K\varphi)=14.9349951$ $(\varphi,V\varphi)=110.8295383$		$(K\varphi,K\varphi)=11.4370760$ $-2(K\varphi,V\varphi)=108.2456675$ $(V\varphi,V\varphi)=287.5468521$	
lmn	$10^l C_{lmn}$	*lmn*	$10^l C_{lmn}$	*lmn*	$10^l C_{lmn}$	*lmn*	$10^l C_{lmn}$
000	1.00000000	300	−1.61630470	432	−0.24814779	666	0.02362966
100	−0.32469073	310	1.31529610	442	1.10322720	710	0.03855044
110	1.36614318	320	4.92576963	444	−0.11346410	740	−0.17396807
120	−0.18630540	330	−12.79055715	466	−0.00511734	770	1.31210251
130	0.06456450	340	14.20851302	500	−1.11270472	722	0.00053868
112	0.00116929	350	−1.36376722	510	1.49911742	754	−0.00960332
122	0.08734721	360	−2.59362114	540	−7.14058346	776	0.04012495
132	−0.03251047	322	−0.69083782	550	14.15689206	800	−0.01233493
200	0.94610249	332	0.45600712	560	0.05447900	840	0.06897135
210	−0.50182428	342	−0.92555133	570	−3.72560170	880	−0.37520909
220	−2.29946461	352	0.28433621	522	−0.07921601	844	0.00090133
230	4.13843882	354	0.04526509	552	−0.68065722	888	−0.02374592
240	−4.83050787	400	1.81817487	572	−0.04133793	930	−0.00727984
250	1.86311796	410	−1.96104080	554	0.06975662	990	0.05385645
212	−0.00084518	420	−2.98831213	600	0.29940277	962	−0.00150642
222	1.87131113	430	7.32679987	610	−0.43360089	996	−0.00522167
232	−1.61026996	440	1.52473286	630	0.52570078	10,0,0	0.00044411
242	1.06628279	450	−21.12023497	660	−3.67222989	10,10,0	−0.00317963
252	−0.29065885	460	11.97252166	680	0.65235496	10,4,4	0.00052020
254	−0.00512599	422	0.50542516	662	0.19887392	10,10,10	0.00271715

to it, λ is gradually improved as is shown by several points underneath 39-*A* which represent the results obtained at various stages of iteration. The lowest point 39-*B*, which is the best result of this computation, corresponds to the following expectation values, in atomic units:

$$\begin{aligned}\lambda(39)&=-2.9037200,\\ \lambda_L(39)&=-2.9037906,\\ \sigma(39)&=\ \ 0.0000536.\end{aligned}\tag{2.5}$$

The corresponding eigenfunction is given in Table I.[9] Comparing (2.5) with the previous result

$$\begin{aligned}\lambda(39\text{-I})&=-2.9037225,\\ \lambda_L(39\text{-I})&=-2.9038737,\\ \sigma(39\text{-I})&=\ \ 0.0001146,\end{aligned}\tag{2.6}$$

it is seen that σ is improved by a factor 2.1 while the new upper bound $\lambda(39)$ is still somewhat worse than the old one.

At this stage, it was felt that it was necessary to use trial functions with more terms in order to make any substantial improvement. Thus, a function with 80 terms was chosen as the next trial function, taking the capacity of the IBM 704 into account. The point 80-*A* of Fig. 1 represents the best 80-term function obtained by method *A*. Points below it are those obtained at various stages of Method *B*. The final result of this computation, expressed by the point 80-*B*, is summarized by

$$\begin{aligned}\lambda(80)&=-2.9037237,\\ \lambda_L(80)&=-2.9037467,\\ \sigma(80)&=\ \ 0.0000175.\end{aligned}\tag{2.7}$$

The corresponding trial function is given in Table II. It is seen that the ground-state energy of the He atom is now determined with an absolute accuracy of 8×10^{-6} (corresponding to $\lambda-\lambda_L=5.0$ cm^{-1}) compared with the previous value of 5.2×10^{-5}. Although this is an appreciable improvement, there is still a long way to go if one wants to achieve an absolute precision of order 2×10^{-7} which corresponds to an accuracy of measurement ±0.15 cm^{-1}.

In general, the lower bound obtained from (2.1) or (2.2), although mathematically rigorous, lies too low for most problems and thus the actual energy eigenvalue is expected to be close to the upper bound. In I, an empirical method was proposed which helps us to guess the exact eigenvalue of the ground state. From information then available, it was inferred in I that the actual ground-state energy will be close to the value -2.9037237. Our new result (2.7) shows however that this estimate was actually too conservative. It would still be fair to say that this method, which is nothing but a linear extrapolation from available data, gave an estimate of the exact ground-state energy that is reasonably good though not accurate enough. With the somewhat better data now at hand, it would be interesting to speculate about the exact eigenvalue of the He ground state.

For this purpose, let us express the trial function ψ as

$$\psi=(1-\eta^2)^{\frac{1}{2}}\psi_0+\eta f,\tag{2.8}$$

[9] The quantities (φ,φ), $(\varphi,K\varphi)$, and $(\varphi,V\varphi)$ given in Table I are about twice as large as the corresponding quantities N,M,L of Table I of reference 2. The latter must be doubled except for the case of the 10-term trial function which needs no correction. This does not affect other parts of reference 2.

TABLE III. Relativistic and mass polarization corrections evaluated with the new 39- and 80-term trial functions. Values evaluated with the 6-term function is included here for the purpose of comparison. Figures are given in units $\alpha^2 ry$ except for the last two columns. $E_{\text{ion}}(=-4.000\,\alpha^2 ry)$ is the relativistic correction for the ground-state energy of He^{1+}. For notations, see Sec. 6 of reference 2.

Number of terms	E_1'	E_1''	$E_1'''+E_3''$	E_3'	$E_{\text{rel}}-E_{\text{ion}}$	$E_{\text{rel}}-E_{\text{ion}}$ (in cm^{-1})	E_2 (in cm^{-1})
6	−27.25	22.83	0.70	−0.29	−0.01	−0.06	4.95
39	−27.0341	22.7455	0.6682	−0.2782	0.1015	0.593	4.785
80	−27.0463	22.7516	0.6682	−0.2782	0.0953	0.557	4.786

where ψ_0 is the exact eigenfunction and f is defined by

$$(f,\psi_0)=0,\qquad (f,f)=1. \tag{2.9}$$

The parameter η is thus a measure of the deviation of ψ from ψ_0. According to (I.5.5), if two trial functions have the same value for the quantity $[(f,Hf)-E_0]/[(Hf,Hf)-2E_0(f,Hf)+E_0^2]$ and differ only in the magnitude of η, a straight line going through the points of Fig. 1 corresponding to these functions must intersect the λ-axis at $\lambda=E_0$. The difficulty of this method lies of course in the fact that it is impossible to tell whether a given pair of points satisfies this condition or not. If one blindly chooses the points 39-B and 80-B for this purpose, the linear extrapolation gives the value −2.9037254. From the limited information contained in Fig. 1, however, this value seems to be too low compared with the exact eigenvalue. This may be discussed in the following manner:

In Fig. 1, we have drawn a broken curve which runs just below the points 39-A and 39-I. This is done to indicate that no point (σ,λ) computed with the 39-term function could be found below or to the left of this curve. Although this curve is incorrect in detail, being drawn mostly by guesswork, it is probably not too far wrong as a whole. It is to be noted that the vertical part of the curve is close to the actually computed points. This is probably reasonable because (a) successive points obtained by the iteration method are found on an almost vertical line, and (b) it was found very difficult to improve the λ of the point 39-B further even though it is still not as good as that of 39-I.

Similarly, the dotted curve of Fig. 1 represents the boundary for the points (σ,λ) computed with the 80-term function. This curve unfortunately is much less reliable than the broken curve for the 39-term functions, since it is determined by only one point 80-B.[10] Here we have taken account of the fact that (a) successive points obtained by the iteration method move slowly towards the left, and (b) the value of λ at 80-B is better than that of 39-I. This seems to imply that lower bounds for some 80-term functions can be appreciably better than that of 80-B although the corresponding upper bounds may be somewhat worse. This is why the vertical part of the dotted curve is drawn far to the left of the computed points.

From these considerations it appears that the pair 39-B and 80-B are not the proper choice for the purpose of extrapolation.[11] In fact we feel that the correct ground-state energy most probably lies above the extrapolated value mentioned above. In view of the improvement of the upper bound from 39- to 80-term functions, on the other hand, it would not be too unreasonable to imagine that the upper bound might be pushed down by extensive calculation at least half of the way to the extrapolated value. We shall therefore choose

$$\lambda^*(80)=-2.9037247, \tag{2.10}$$

as our best guess for the exact nonrelativistic energy of the ground state of the He atom. If our reasoning is not too wrong, the value (2.10) will probably be accurate within the limits ± 0.0000005 (or $\pm 0.11\ \text{cm}^{-1}$).

Finally, let us estimate the accuracy of our 80-term function, which is possible since both the upper and lower bounds of its energy eigenvalue are known. Making use of the formula (I.5.11), one finds that

$$\eta_1=0.0055 \tag{2.11}$$

can be chosen as a rigorous upper limit for the accuracy η of the 80-term trial function. If one assumes that the ground-state energy E_0 is exactly given by $\lambda^*(80)$, the upper limit (2.11) may be replaced by[12]

$$\eta_2=0.0011_5 \tag{2.12}$$

according to (I.5.10). It is likely that (2.12), although this is not a rigorous limit, gives a closer estimate than (2.11) for the accuracy of the wave function.

3. ERROR ESTIMATION OF CORRECTION TERMS

In Table III are given expectation values of the mass polarization and relativistic corrections computed with the new 39- and 80-term functions. They are in good

[10] We have tried to find a different set of points by the ordinary variational method with the 80-term trial function but without much success. This is due to the unfortunate situation that the input-output instruction of our coded program of method A was written in single precision. This has been sufficiently accurate for the purpose of the lower bound variational calculation but has turned out otherwise for the upper bound variational calculation.

[11] This will also be inferred from the fact that the expectation value of the relativistic correction evaluated with the trial function 39-B is somewhat different from those evaluated with the trial function 39-I or 80-B, as is seen from Table III.

[12] The value of η_2 given by (2.12) is somewhat larger than the best η_2 in Table II of reference 2. This is partly due to the different assumption on the exact value of the ground-state energy E_0 and partly to the arithmetical error in the latter in which a multiplicative factor 1.148 was overlooked.

agreement with values calculated with the old 39-term function. It therefore seems that they are already close to the exact values corresponding to the correct eigenfunction. If one wants to determine how much the calculated values differ from the exact values, however, it turns out that there has so far been no method available for such a purpose. Here we would like to report on a search for rigorous methods that can be used to estimate the accuracy of calculated correction terms.

Our main result may be stated as follows: There is always a finite limit for the difference of expectation values evaluated with any trial function and the exact eigenfunction, *provided the trial function satisfies the boundary condition* (I.2.6). Furthermore, this limit will converge to zero as the trial function converges to the exact eigenfunction.[13] It is to be noted that, for trial functions that do not satisfy the boundary condition (I.2.6), the relativistic corrections can actually be infinitely large. But (I.2.6) is needed to prove that the Hamiltonian of the He atom is a Hermitian operator in a strict sense.[14] Thus, the same condition which guarantees the existence of eigenstates of the He atom also serves to keep the correction terms finite.

Let us first note that the inequality

$$|(1-\eta^2)(A\psi_0,B\psi_0)-(A\psi,B\psi)|\leq C, \tag{3.1}$$

with

$$C=\eta(Q[\psi,f]+Q[f,\psi])+\eta^2Q[f,f] \tag{3.2}$$

and

$$Q[g,h]\equiv|(Ag,Bh)|, \tag{3.3}$$

holds for any function ψ and operators A and B for which the inner products are finite. The parameter η and the function f are defined by (2.8). Thus our problem will be solved if it is shown that C has an upper limit when A and B represent the operators of the mass polarization and relativistic corrections. We shall now see that this is the case if one can find upper limits for $\eta(f,Kf)^{\frac{1}{2}}$ and $\eta\|Kf\|$, where K is the kinetic energy operator $-(\Delta_1+\Delta_2)/2$.

It is trivial to show this for the mass polarization term

$$E_2=-\rho(\psi,\ \nabla_1\cdot\nabla_2\psi), \tag{3.4}$$

where ρ is the mass ratio of the electron and He nucleus. Choosing $A=1$ and $B=\nabla_1\cdot\nabla_2$, one obtains

$$\begin{aligned} Q_2[f,\psi]&=\rho|(f,\ \nabla_1\cdot\nabla_2\psi)|\leqq\rho\|f\|\cdot\|\nabla_1\cdot\nabla_2\psi\|,\\ Q_2[f,f]&=\rho|(f,\ \nabla_1\cdot\nabla_2 f)|\leqq\rho(f,Kf). \end{aligned} \tag{3.5}$$

Thus

$$C_2\equiv\rho[2P\eta+\eta^2(f,Kf)], \tag{3.6}$$

with

$$P=\|\nabla_1\cdot\nabla_2\psi\| \tag{3.7}$$

may be chosen as an upper limit of error for E_2, which is finite if $\eta^2(f,Kf)$ is bounded. Note that P can be evaluated explicitly for any given ψ and is finite if the boundary condition (I.2.6) is satisfied.

To prove it for the relativistic corrections, it is convenient to express them as the expectation value of the operator

$$H_{\rm rel}=H_{\rm I}+H_{\rm II}+H_{\rm III}+H_{\rm IV}+H_{\rm V}, \tag{3.8}$$

rather than the formula (I.6.2), where

$$\begin{aligned} H_{\rm I}&=-\tfrac{1}{4}\alpha^2[\nabla_1\cdot(V_1+V_2)\nabla_1+\nabla_2\cdot(V_1+V_2)\nabla_2],\\ H_{\rm II}&=\tfrac{1}{4}\alpha^2\Delta_1\Delta_2,\\ H_{\rm III}&=-\alpha^2V_{12}\Delta_u,\\ H_{\rm IV}&=\tfrac{1}{4}\alpha^2[(\nabla_1\cdot\hat{u})V_{12}(\hat{u}\cdot\nabla_2)+(\nabla_2\cdot\hat{u})V_{12}(\hat{u}\cdot\nabla_1)],\\ H_{\rm V}&=\tfrac{1}{4}\alpha^2E_0(\Delta_1+\Delta_2), \end{aligned} \tag{3.9}$$

with $V_1=-2/r_1$, $V_2=-2/r_2$, $V_{12}=1/r_{12}$, and $\hat{u}=(\mathbf{r}_2-\mathbf{r}_1)/|\mathbf{r}_2-\mathbf{r}_1|$. This has the advantage that it does not contain δ functions explicitly.[15] Starting from (3.8), it can be shown that an upper limit for C can be chosen as

$$\begin{aligned} C_{\rm rel}=\alpha^2[&R\eta(f,Kf)^{\frac{1}{2}}+S\eta\|Kf\|\\ &+(9/2)\eta^2(f,Kf)^{\frac{1}{2}}\|Kf\|+\tfrac{1}{4}\eta^2\|Kf\|^2], \end{aligned} \tag{3.10}$$

where R and S are finite numbers defined by (B.6, 9, 16, 19). The derivation of (3.10) is given in Appendix B.

The last step is to show that $\eta(f,Kf)^{\frac{1}{2}}$ and $\eta\|Kf\|$ are in fact bounded. This is carried out in Appendix A. Our result is therefore proved.

As is seen from (A.14) and (A.19), $\eta(f,Kf)^{\frac{1}{2}}$ and $\eta\|Kf\|$ converge to zero when ψ approaches ψ_0.[13] It then follows from (3.6) and (3.10) that the expectation values E_2 and $E_{\rm rel}$ converge to exact values when ψ converges to ψ_0.[13] It is to be noted that the coefficients P of (3.6) and R, S of (3.10) have well-defined upper limits independent of individual trial functions.

Although our error estimation is rigorous, it is not likely that it gives useful and accurate estimation of errors in practice. However, it would be interesting to see what estimate can actually be obtained with these formulas. The bounds C_2 and $C_{\rm rel}$ have therefore been calculated for 1-, 3-, and 6-term functions of Hylleraas type. The results are listed in Table IV. It is assumed that the ground-state energy E_0 is given by (2.10). Table IV shows clearly that the limits of error evaluated with formulas (3.6) and (3.10) are extremely large, which is of course not unexpected.

In the last rows of Table IV, C_2 and $C_{\rm rel}$ are given for the 39- and 80-term trial functions. In this calculation, we have used quantities P, R, and S of (3.6) and (3.10) evaluated with the 6-term Hylleraas function, since they will be approximately equal to the values evaluated with better trial functions. Also, we

[13] Throughout this paper, we use the phrase "convergence of the trial function ψ to the exact eigenfunction ψ_0" to imply that $\sigma\to0$, where $\sigma=(H\psi,H\psi)-(\psi,H\psi)^2$. This definition is stronger than the usual definition $\|\psi-\psi_0\|\to0$ [or $\eta\to0$]. The condition $\sigma\to0$ is sufficient to guarantee the convergence of expectation values discussed in this section.

[14] T. Kato, Trans. Am. Math. Soc. **70**, 195, 212 (1951).

[15] It is to be noted that those arguments developed in this section as well as in the Appendixes are also useful in estimating the accuracy of expectation values of the δ functions.

have chosen (2.12) as an upper limit of η. It is seen that, even for the 80-term function, errors estimated with our formulas are still very large, being ± 0.11 cm^{-1} and ± 1.78 cm^{-1} for mass polarization and relativistic corrections, respectively.[16]

The following will be the major factors contributing to this situation: (a) In calculating expectation values of $H_{\rm rel}$, strong cancellation occurs among various terms of (3.9). In the calculation of $C_{\rm rel}$, on the other hand, no cancellation occurs since errors always accumulate. In effect, $C_{\rm rel}$ would thus represent the error in a quantity whose magnitude is much larger than $E_{\rm rel}$ itself. (b) To derive C_2 and $C_{\rm rel}$, Schwartz's inequality has been used repeatedly. Each application of this inequality would contribute to the overestimation of errors. Thus the final formulas will overestimate the C's by some orders of magnitude.

However it is possible to find semiempirically the extent to which the use of formulas (3.6) and (3.10) causes overestimation of errors, *if it is assumed that errors are overestimated more or less uniformly for all trial functions considered here.* Let us first note that the exact value of $E_{\rm rel}$, for instance, certainly lies in the range -22.81 ± 1.78 cm^{-1} as evaluated with the 80-term function. But the calculated value of $E_{\rm rel}$ is well within this range even for the 6-term function. This would imply that the true accuracy of $E_{\rm rel}$ evaluated with this function is more adequately given by the above range rather than that evaluated with rigorous formulas (3.10). If this were actually the case, the upper limit $C_{\rm rel}$ must have overestimated the error in $E_{\rm rel}$ by a factor of order $20\sim 30$. This situation would be the same for all cases listed in Table IV, if the above assumption of uniformity is valid. In particular the accuracy of $E_{\rm rel}$ evaluated with the 80-term function would be of order ± 0.09 cm^{-1} rather than the calculated value ± 1.78 cm^{-1}. Similarly, the accuracy of E_2 would be about ± 0.006 cm^{-1} rather than ± 0.11 cm^{-1}. We believe that these estimated accuracy limits are still conservative and would be surprised if the exact expectation values turn out to be outside of these limits.

TABLE IV. Rigorous limits of error for the expectation values of the mass polarization and relativistic corrections calculated with formulas (3.6) and (3.10).

References	Number of terms	C_2 (in cm^{-1})	$C_{\rm rel}$ (in cm^{-1})
a	1	52	880
a	3	4.3	78
a	6	2.5	45
a	39	0.17	2.94
	39	0.24	3.88
	80	0.11	1.78

[a] See reference 2.

[16] These values are, strictly speaking, not rigorous limits of error since they depend on the assumption that the upper bound of η is given by (2.12) which in turn depends on the assumption that the exact energy is given by (2.10). If the exact energy were -2.9037245, $C_{\rm rel}$ would be ± 1.61 cm^{-1}. If E_0 were -2.9037249, on the other hand, $C_{\rm rel}$ would be ± 1.93 cm^{-1}. Thus our error estimation is not very sensitive to the value of the exact ground-state energy.

4. DISCUSSION

As was shown in Sec. 2, the exact nonrelativistic energy of the ground state of the He atom will be found close to the value (2.10). Taking account of the finite mass of the He atom, this corresponds to the ionization potential 198317.45 cm^{-1}. When one includes corrections due to mass polarization and relativistic effects as well as electrodynamical effects, the final theoretical prediction for the ionization potential becomes

$$\text{I.P.}_{\rm theory}=198310.77\ \text{cm}^{-1}. \tag{4.1}$$

Rigorous limits for the error in (4.1) have been evaluated to be $(_{-2.3}{}^{+7.3})$ cm^{-1} which consists of $(_{-0.23}{}^{+4.83})$ cm^{-1} for the nonrelativistic energy, ± 0.11 cm^{-1} for the mass polarization effect, ± 1.78 cm^{-1} for relativistic corrections, and $(_{-0.2}{}^{+0.6})$ cm^{-1} for electrodynamical corrections.[17] These limits, however, are very likely to have been overestimated by a large factor. As we have discussed, a more reasonable measure for the accuracy of (4.1) is of order ± 0.40 cm^{-1} where ± 0.11 cm^{-1} comes from the nonrelativistic energy, ± 0.006 cm^{-1} from the mass polarization, ± 0.09 cm^{-1} from relativistic corrections, and ± 0.2 cm^{-1} from electrodynamical effects. Within this probable accuracy, the agreement of our result (4.1) with the latest experimental value,[1]

$$\text{I.P.}_{\rm experiment}=198310.8_2\pm 0.15\ \text{cm}^{-1}, \tag{4.2}$$

is quite satisfactory.

Except for the electrodynamical corrections, the largest source of error in (4.1) is still the calculation of the nonrelativistic energy. The estimated error of ± 0.11 cm^{-1} is probably less reliable than those for the mass polarization and relativistic corrections. It is therefore desirable that the accuracy of the nonrelativistic energy should be improved still further. As was indicated in Sec. 2, it would be possible to improve it to some extent even with the same 80-term function if the shape of the dotted curve of Fig. 1 is studied in more detail. It would be worth mentioning here that this could be most easily achieved if one employed an iteration method for the *lower* bound rather than that for the upper bound which was used in this work. For really significant improvement of the theoretical prediction, however, it would be necessary to work with trial functions with a larger number of terms or those of an entirely different nature from the Hylleraas-type functions.

Very recently, Pekeris[18] has developed an interesting approach to this problem which is based on an expansion of ψ into a triple orthogonal set of three perimetric

[17] The quoted error in the electrodynamical corrections is not a rigorous one, but almost certainly the actual value would lie between these limits. See Sec. 4 of the paper of Kabir and Salpeter, reference 4.

[18] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

coordinates. Making use of these trial functions with up to 210 terms, he obtained the value $\lambda=-2.9037243$ as the upper bound of the ground-state energy of the He atom in the nonrelativistic limit. This value lies just on the upper edge of the estimated accuracy of our extrapolated result and thus eliminates the possibility that the exact ground-state energy lies above the limit which was chosen somewhat arbitrarily. On the other hand, it is still possible that the exact ground-state energy lies outside our *estimated* lower limit, since no better lower bound than (2.7) is yet available. It would be very interesting to see whether this situation is greatly improved if a rigorous lower bound is calculated with Pekeris' 210-term function. Finally it is noted that the mass polarization and relativistic corrections evaluated with his 210-term function agree with the values evaluated with our 80-term function within our semiempirical limits of error.

ACKNOWLEDGMENTS

The author would like to thank Dr. C. Herring and the Bell Telephone Laboratories for the hospitality extended to him during the summer of 1958 where much of this work was carried out. He wishes to thank the members of the Computing Facility at Bell Telephone Laboratories for arranging computing time on the IBM 704 and for advice on coding. He especially wants to thank Mrs. W. L. Mammel for her continued help with the computation.

He would like to thank Professor E. E. Salpeter and Professor T. Kato for their valuable advice and for many informative discussions.

APPENDIX A. UPPER BOUNDS FOR $\eta(f,Kf)^{\frac{1}{2}}$ AND $\eta\|Kf\|$

We shall discuss the derivation of upper bounds for $\eta(f,Kf)^{\frac{1}{2}}$ and $\eta\|Kf\|$ where f is a function defined by (2.8) and thus satisfies the boundary condition (I.2.6). To begin with, we shall derive several inequalities which hold for *any* function $f(\mathbf{r}_1,\mathbf{r}_2)$ that satisfies our boundary condition. Let us first prove the inequality

$$(f,V_{12}f)\leqq(f,Kf)^{\frac{1}{2}}, \tag{A.1}$$

where K is the kinetic energy operator and $V_{12}=1/r_{12}$. To show this, note that the quantity $(f,V_{12}f)\equiv\int d\tau(1/u)f^2$ may be transformed into $-\int d\tau(\hat{u}f)\cdot(\nabla_u f)$ by partial integration. Applying Schwartz's inequality, one finds easily that

$$-\int d\tau(\hat{u}f)\cdot(\nabla_u f)\leqq\left[\int d\tau f^2\right]^{\frac{1}{2}}\left[\int d\tau(\nabla_u f)^2\right]^{\frac{1}{2}}. \tag{A.2}$$

Now formula (A.1) follows immediately since $(\nabla_u f)^2\leqq\frac{1}{2}[(\nabla_1 f)^2+(\nabla_2 f)^2]$. The same consideration applied to V_1+V_2 leads to

$$-4(f,Kf)^{\frac{1}{2}}\leqq(f,(V_1+V_2)f) \tag{A.3}$$

noting that V_1+V_2 is negative everywhere. Because $V_1+V_2\leqq V\leqq V_{12}$, one obtains the relation

$$-4(f,Kf)^{\frac{1}{2}}\leqq(f,Vf)\leqq(f,Kf)^{\frac{1}{2}}. \tag{A.4}$$

Thus, for any function f for which the expectation value of the kinetic energy K is finite, it is impossible to make the expectation value of the potential energy V arbitrarily large.

We shall consider next inequalities concerning the square of the potential energy V. Let us first show that

$$(V_{12}f,V_{12}f)\leqq4(f,Kf). \tag{A.5}$$

This follows from the relation[19,20]

$$\int d\tau\left(\frac{1}{u}-f\right)^2=-2\int\frac{1}{u}d\tau-\hat{u}f\cdot\nabla_u f$$
$$\leqq2\left[\int d\tau\left(\frac{1}{u}-f\right)^2\right]^{\frac{1}{2}}\left[\int d\tau(\nabla_u f)^2\right]^{\frac{1}{2}}, \tag{A.6}$$

which is easily proved by means of partial integration and Schwartz's inequality. Similarly

$$(V_i f,V_i f)\leqq16(f,Kf),\quad i=1,\text{ or }2. \tag{A.7}$$

To find an inequality for V as a whole, we note that

$$V^2\leqq V_1^2+V_2^2+V_1V_2+V_{12}^2 \tag{A.8}$$

holds everywhere as a consequence of $r_1+r_2\geqq u$. Thus we have only to find an inequality for V_1V_2, which may be derived as follows[19]:

$$(V_1f,V_2f)=-2\int d\tau\left[\frac{1}{r_1}-\hat{r}_2f\cdot\nabla_2f+\frac{1}{r_2}-\hat{r}_1f\cdot\nabla_1f\right]$$
$$\leqq2\left[\int d\tau\left\{\left(\frac{1}{r_1}-f\right)^2+\left(\frac{1}{r_2}-f\right)^2\right\}\right]^{\frac{1}{2}}$$
$$\times\left[\int d\tau\{(\nabla_1f)^2+(\nabla_2f)^2\}\right]^{\frac{1}{2}}$$
$$\leqq8(f,Kf), \tag{A.9}$$

where (A.7) is used in the last step. From (A.5), (A.7), and (A.9), one finally obtains

$$(Vf,Vf)\leqq44(f,Kf). \tag{A.10}$$

We are now ready to show that $\eta(f,Kf)^{\frac{1}{2}}$ and $\eta\|Kf\|$ have upper bounds if f is *defined* by (2.8). Let us first consider $\eta(f,Kf)^{\frac{1}{2}}$. For this purpose, we note that the function f defined by (2.8) satisfies

$$\eta^2(f,Hf)=(\lambda-E_0)+\eta^2E_0, \tag{A.11}$$

[19] The quantities $\hat{r}_1$, $\hat{r}_2$, and $\hat{u}$ are defined by $\mathbf{r}_1/|\mathbf{r}_1|$, $\mathbf{r}_2/|\mathbf{r}_2|$, and $(\mathbf{r}_2-\mathbf{r}_1)/|\mathbf{r}_2-\mathbf{r}_1|$, respectively.

[20] It is possible to derive a formula slightly more accurate than (A.6). The numerical results listed in Table IV are obtained using this improved formula. However, the change is only of the order of 3%.

where $\lambda=(\psi,H\psi)$. Combining this with (A.4), one obtains

$$\eta^2(f,Kf)-4\eta^2(f,Kf)^{\frac{1}{2}}\leqq(\lambda-E_0)+\eta^2E_0. \quad \text{(A.12)}$$

Solving this for $\eta(f,Kf)^{\frac{1}{2}}$, one finds immediately that

$$\eta(f,Kf)^{\frac{1}{2}}\leqq a, \quad \text{(A.13)}$$

where

$$a=2\eta+[(\lambda-E_0)+(4+E_0)\eta^2]^{\frac{1}{2}}. \quad \text{(A.14)}$$

Since λ and the bound of η are known for given ψ, a is certainly a finite number and thus $\eta(f,Kf)^{\frac{1}{2}}$ is bounded.

In order to estimate $\eta\|Kf\|$, it is sufficient to know a bound for $\eta\|Vf\|$ since the relation

$$\|Kf\|\leqq\|Hf\|+\|Vf\| \quad \text{(A.15)}$$

holds for any f, while $\eta\|Hf\|$ is given by

$$\eta\|Hf\|=[\sigma+\lambda^2-(1-\eta^2)E_0^2]^{\frac{1}{2}}, \quad \text{(A.16)}$$

where $\sigma=(H\psi,H\psi)-\lambda^2$. Now a bound for $\eta\|Vf\|$ is given by

$$\eta\|Vf\|\leqq(44)^{\frac{1}{2}}a, \quad \text{(A.17)}$$

as is seen from (A.10) and (A.13). Thus one finds

$$\eta\|Kf\|\leqq b, \quad \text{(A.18)}$$

where

$$b=(44)^{\frac{1}{2}}a+[\sigma+\lambda^2-(1-\eta^2)E_0^2]^{\frac{1}{2}}. \quad \text{(A.19)}$$

Obviously b is a finite number for given ψ and thus $\eta\|Kf\|$ is bounded.

APPENDIX B. ERROR ESTIMATION OF RELATIVISTIC CORRECTION TERMS

We shall derive formulas which give upper bounds for the errors in the expectation values of the relativistic correction terms (3.9). Let us first consider $H_{\rm I}$. To find an upper bound for the C corresponding to $H_{\rm I}$ [see (3.2)], one has to estimate the quantity

$$Q_{\rm I}[\psi,f]=\tfrac{1}{2}\alpha^2\left|\int d\tau\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\times\{(\nabla_1\psi)\cdot(\nabla_1 f)+(\nabla_2\psi)\cdot(\nabla_2 f)\}\right|. \quad \text{(B.1)}$$

This can be carried out easily if one notices that

$$Q_{\rm I}[\psi,f]\leqq\tfrac{1}{2}\alpha^2\left[\int d\tau\left(\frac{1}{r_1}+\frac{1}{r_2}\right)^2\{(\nabla_1\psi)^2+(\nabla_2\psi)^2\}\right]^{\frac{1}{2}}\times\left[\int d\tau\{(\nabla_1 f)^2+(\nabla_2 f)^2\}\right]^{\frac{1}{2}} \quad \text{(B.2)}$$

holds for any ψ and f satisfying the boundary condition (I.2.6). To evaluate $Q_{\rm I}[f,f]$, on the other hand, one may rewrite it as

$$-\tfrac{1}{2}\alpha^2\int d\tau[(\nabla_1 f)\cdot\{(\hat{r}_1\cdot\nabla_1+\hat{r}_2\cdot\nabla_2)(\nabla_1 f)\}+(\nabla_2 f)\cdot\{(\hat{r}_1\cdot\nabla_1+\hat{r}_2\cdot\nabla_2)(\nabla_2 f)\}], \quad \text{(B.3)}$$

and apply Schwartz's inequality. In this manner, one is led to

$$Q_{\rm I}[f,f]\leqq 2\alpha^2(f,Kf)^{\frac{1}{2}}\|Kf\|. \quad \text{(B.4)}$$

If one denotes by $C_{\rm I}$ an upper bound for C corresponding to $H_{\rm I}$, it is evident from (B.2) and (B.4) that $C_{\rm I}$ may be chosen as

$$C_{\rm I}=\alpha^2[aR_{\rm I}+2ab], \quad \text{(B.5)}$$

where a and b are defined by (A.14) and (A.19) and

$$R_{\rm I}=\left[2\int d\tau\left(\frac{1}{r_1}+\frac{1}{r_2}\right)^2\{(\nabla_1\psi)^2+(\nabla_2\psi)^2\}\right]^{\frac{1}{2}}. \quad \text{(B.6)}$$

The quantity $R_{\rm I}$ is finite under the boundary condition (I.2.6) and can be evaluated explicitly for any given ψ.

In the case of $H_{\rm IV}$, the integrals to be evaluated are

$$Q_{\rm IV}[\psi,f]=\tfrac{1}{4}\alpha^2\left|\int d\tau\frac{1}{u}\{(\hat{u}\cdot\nabla_1\psi)(\hat{u}\cdot\nabla_2 f)+(\hat{u}\cdot\nabla_2\psi)(\hat{u}\cdot\nabla_1 f)\}\right|, \quad \text{(B.7)}$$

and $Q_{\rm IV}[f,f]$. Using the same method as above, it is easy to show that an upper bound for C may be chosen as

$$C_{\rm IV}=\alpha^2[aR_{\rm IV}+\tfrac{1}{2}ab], \quad \text{(B.8)}$$

where

$$R_{\rm IV}=\left[\frac{1}{2}\int d\tau\frac{1}{u^2}\{(\hat{u}\cdot\nabla_1\psi)^2+(\hat{u}\cdot\nabla_2\psi)^2\}\right]^{\frac{1}{2}}. \quad \text{(B.9)}$$

It is to be noted that there are many alternative ways to derive the upper bounds. Our $C_{\rm I}$ and $C_{\rm IV}$ are selected in such a manner that their leading terms (linear in η) depend only on (f,Kf). This would give the best result since possible effects of fluctuation in the curvature of the function f are thus minimized.

For $H_{\rm II}$ or $H_{\rm III}$, however, it seems to be impossible to find an upper bound $C_{\rm II}$ or $C_{\rm III}$ whose main terms depend on (f,Kf) only. As is seen below, the main terms of $C_{\rm II}$ and $C_{\rm III}$ contain $\|Kf\|$ and thus depend on the curvature of the function f more strongly than do $C_{\rm I}$ or $C_{\rm IV}$. The integrals to be considered here are

$$Q_{\rm II}[\psi,f]=\frac{\alpha^2}{4}\left|\int d\tau\Delta_1\psi\Delta_2 f\right|, \quad \text{(B.10)}$$

and

$$Q_{\rm III}[\psi,f]=\alpha^2\left|\int d\tau\frac{1}{u}\psi\Delta_u f\right|,$$
$$Q_{\rm III}[f,\psi]=\alpha^2\left|\int d\tau\frac{1}{u}f\Delta_u\psi\right|. \quad \text{(B.11)}$$

As is seen at once from (B.11), an upper bound $C_{\rm III}$ may be chosen as

$$C_{\rm III}=\alpha^2[aR_{\rm III}+bS_{\rm III}+2ab], \quad \text{(B.12)}$$

where

$$R_{\mathrm{III}}=2\|\Delta_u\psi\|, \quad S_{\mathrm{III}}=\|V_{12}\psi\|. \tag{B.13}$$

In order to find an upper bound C_{II} corresponding to H_{II}, let us note the following inequality:

$$\left|\int d\tau\Delta_1\psi\Delta_2 f\right| \leqq \left[\int d\tau\Delta_1\psi\Delta_2\psi\right]^{\frac{1}{2}}\left[\int d\tau\Delta_1 f\Delta_2 f\right]^{\frac{1}{2}}, \tag{B.14}$$

which can be proved using Schwartz's inequality in a slightly modified manner. From this it follows that C_{II} may be chosen as

$$C_{\mathrm{II}}=\alpha^2[bS_{\mathrm{II}}+\tfrac{1}{4}b^2], \tag{B.15}$$

where

$$S_{\mathrm{II}}=\frac{1}{2}\left[\int d\tau\Delta_1\psi\Delta_2\psi\right]^{\frac{1}{2}}. \tag{B.16}$$

The last term H_{V} may be treated completely differently from the others, being proportional to the kinetic energy K. In this case, the left-hand side of (3.1) becomes

$$(1-\eta^2)(\psi_0,H_{\mathrm{V}}\psi_0)-(\psi,H_{\mathrm{V}}\psi) = -\tfrac{1}{2}\alpha^2E_0[\lambda-E_0(1-\eta^2)], \tag{B.17}$$

where it is assumed that the trial function ψ satisfies the virial theorem. Since this is the case for ψ's considered here,[21] the accuracy of $(\psi,H_{\mathrm{V}}\psi)$ is obviously just as good as that of the variational calculation of the nonrelativistic energy eigenvalue λ. We may therefore regard $(\psi_0,H_{\mathrm{V}}\psi_0)$ as exactly known and omit it from our considerations.

Collecting the results obtained, one may therefore choose

$$C_{\mathrm{rel}}=\alpha^2[aR+bS+(9/2)ab+\tfrac{1}{4}b^2], \tag{B.18}$$

with

$$\begin{aligned} R&=R_{\mathrm{I}}+R_{\mathrm{III}}+R_{\mathrm{IV}},\\ S&=S_{\mathrm{II}}+S_{\mathrm{III}}, \end{aligned} \tag{B.19}$$

as an upper bound for the error in the expectation value of the entire relativistic correction H_{rel}.

[21] This is because our trial functions are always chosen so that the upper bound λ is minimized with respect to the scale parameter k. For details, see Sec. 3 of reference 2.

PHYSICAL REVIEW VOLUME 115, NUMBER 2 JULY 15, 1959

Classical Theory of Electronic and Ionic Inelastic Collisions

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A classical theory of inelastic atomic collisions is given. It is shown that inelastic scattering, ionization, excitation, and other interactions between charged particles and atoms are due to the Coulomb interaction with atomic electrons and depend in a first approximation on their binding energy and momentum distribution. All cross sections can easily be calculated by means of differential cross sections $\sigma(\Delta E)$ and $\sigma(\Delta E,\vartheta)$ derived in the binary encounter approximation. Numerical calculations have been made for several cases and are in very good agreement with the experimental results.

I. INTRODUCTION

THE difficulty of explaining on the basis of classical mechanics some experimental facts observed in atomic collisions and the sufficiently good results obtained by wave mechanics have been viewed as proof of the nonvalidity of classical mechanics for processes involving the interaction of charged particles with the atomic shell.[1,2] Consequently the explanation of all such processes has been sought by using wave mechanics without investigating the possibilities of a classical interpretation of these phenomena. The slowing down of charged particles in a medium had also been treated in this way. In a recent paper[3] the author analyzed this process on the basis of classical mechanics and showed that the disagreement between the first classical theories[4,5] and experiment, particularly in the low-energy range, was the result of an approximation which neglected the orbital motion of the atomic electrons. It was noted that the effect of the interactions in a Coulomb field varies as the fourth power of the *relative* velocity.

The excellent agreement of the classical stopping theory given by the author with experiment automatically gave rise to the suggestion that other processes occurring in atomic collisions, which, after all, make up the stopping process, should be treated in this way. Thus, employing the results of Chandrasekhar[6] and Williamson and Chandrasekhar[7] on the collisions of gravitational masses, we shall construct in the binary

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