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Ground State of the Helium Atom*

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The energy level of the ground state of atomic helium is restudied in detail. The nonrelativistic part is treated by the conventional Ritz variation technique. However, the trial functions used are more general than the ordinary Hylleraas-type functions since they contain negative power terms in addition to the positive power terms. Linear combinations of up to 39 terms are employed in the numerical computation. The best approximation for the ground state energy of the nonrelativistic Schrödinger equation obtained so far is -2.9037225 atomic units. The precision of the variation result is estimated by the evaluation of lower bounds to the ground state energy. Our final result is about twelve times more accurate than the best published value. On the basis of these calculations, it is conjectured that the actual nonrelativistic energy will be lower than our best value by not more than 0.0000012 atomic unit. The accuracy of various approximate eigenfunctions is also estimated. It is thus found that the total contribution to our 39-parameter function from all the excited states will be of the order of 0.1%. Mass polarization and relativistic corrections are evaluated with various trial functions including our best ones. They seem to converge to certain limits with reasonable speed. We therefore believe that the mass polarization and relativistic corrections to the ionization potential of the He ground state will be very close to -4.78_6 cm^{-1} and -0.57_0 cm^{-1}, respectively. With these corrections, and also the Lamb-shift correction for the ground state of the He atom (-1.23 cm^{-1}), the theoretical ionization potential becomes 198310.38 cm^{-1} which is in a very good agreement with the best observed value 198310.5 ± 1 cm^{-1}.

1. INTRODUCTION

RECENTLY Herzberg and Zbinden[1] have greatly improved the accuracy of measurement of the ionization potential of the He atom in its ground state. This result, together with the latest experiments on some other states of the He atom, has revived theoretical interest in the study of two-electron systems. In the near future it will become possible to detect such small effects as the Lamb shift of the He atom and thus we would be able to see whether the two-electron systems can be satisfactorily explained by our present knowledge of quantum electrodynamics which has been so successful in the case of the hydrogen atom.

The necessity of improving the accuracy of theoretical prediction for the energy of the He ground state was pointed out a few years ago by Chandrasekhar, Elbert, and Herzberg.[2] They recalculated the energy of the He ground state by the Ritz variation method, making use of a trial function with ten adjustable parameters, and showed that their ground state energy, including the relativistic and mass polarization corrections, was about 21.5 cm^{-1} higher than the observed value while the error of observation was of the order of ±5 cm^{-1}. Sucher and Foley[3] have discovered some errors in previous treatments of the relativistic correction and showed that the discrepancy between theory and experiment would be even larger ($\sim$30 cm^{-1}) if all relativistic corrections of order α^2 ry are correctly taken into account. In order to identify the source of such a large discrepancy, Chandrasekhar and Herzberg[4] have extended their computation of the nonrelativistic energy up to 18 parameters and found that the theoretical ionization potential will be about 198310.4 cm^{-1}, which is only 0.1 cm^{-1} less than the latest experimental value.[1] It has thus been made clear that the large discrepancy between the observation and earlier calculations originates mostly from the poor convergence of the variation calculation.

Though the measurement and theory have reached such a high precision, it is necessary to improve the accuracy further for a serious consideration of such details as the Lamb shift and other smaller effects. It is the purpose of this paper to improve the precision of theoretical calculation so that we can determine the ionization potential with narrower limit of errors than that of the latest measurement. We shall note here a few points about the calculation of Chandrasekhar and Herzberg. (1) They have used the relativistic correction evaluated by Sucher and Foley employing a 3-parameter function of Hylleraas type.[5] It seems to be necessary, however, to evaluate it with more accurate functions since the relativistic correction is much more sensitive to the details of the wave function than the energy itself. (2) The correct value for the mass polarization correction evaluated with the 6-parameter function of Hylleraas is -4.95 cm^{-1}.[6] It is of course desirable to evaluate this with more accurate wave functions. (3) It has been pointed out by Wilets and Cherry[7] that the mathematical lower bound evaluated with the 18-parameter function of Chandrasekhar and Herzberg is about 400 cm^{-1} lower than the upper bound determined

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[1] See S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955), footnote 12.

[2] Chandrasekhar, Elbert, and Herzberg, Phys. Rev. **91**, 1172 (1953).

[3] J. Sucher and H. M. Foley, Phys. Rev. **95**, 966 (1954).

[4] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955).

[5] Those trial functions which can be written in the general form (2.7) will be said to be of Hylleraas type.

[6] This value was quoted incorrectly as -5.2 cm^{-1} by H. A. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24, Part 1, p. 375. This discrepancy was noted and corrected by A. R. Edmonds and L. Wilets (unpublished) and by T. Kinoshita (unpublished). Chandrasekhar and Herzberg (reference 4) have mistakenly quoted the value of Edmonds and Wilets as -4.1 cm^{-1}.

[7] L. Wilets and I. J. Cherry, Phys. Rev. **103**, 112 (1956).

by the ordinary variation calculation. Though it is likely that the ionization potential predicted by them by an extrapolation method is very close to the actual value, such a large limit of uncertainty is rather uncomfortable. At least, this is an indication that their trial function is not a very accurate approximation of the actual eigenfunction.

These considerations indicate that it is necessary to improve the nonrelativistic part of calculation, the wave function in particular, to a considerable extent, in order to determine the ionization potential of the He atom with the desired accuracy. Before attempting such a calculation, however, it might be useful to ask whether it is reasonable to proceed by taking more and more terms of the Hylleraas expansion, in view of the enormous number of terms already involved in the calculation of Chandrasekhar and Herzberg.

At this point, it is interesting to remark that the Hylleraas series cannot satisfy the Schrödinger equation in a formal sense, however many terms one may take.[8] It is found, as is discussed in Sec. 2 and the Appendix, that this is simply because the Hylleraas series does not contain sufficiently many terms. Fortunately, when one adds to it certain terms containing negative powers of some of the variables, the new series is shown to satisfy the Schrödinger equation formally.

Of course, the absence of formal solution may not be a serious defect of the Hylleraas series since it would be sufficient if one can approximate the actual solution arbitrarily well taking more and more of its terms into account. On the other hand, when we want to approximate it with a function of finite number of terms, it would make a large difference whether our function belongs to an expansion which satisfies the equation or not. At least, the new expansion allows us more flexible selection of terms than the Hylleraas series and thus makes it easier to approximate the actual eigenfunction even in the close neighborhood of singularities of the potential where the Hylleraas functions behave very poorly. We have therefore decided to choose the new expansion as the basis of our variation calculation of the He ground state.

Results of preliminary calculations, carried out employing few terms of negative powers, show that the accuracy is considerably better than that of the Hylleraas-type calculations involving the same number of parameters. On the other hand, it did not improve the accuracy of calculation to any large extent. We have therefore considered that it is better to use trial functions with as many terms as possible and minimize the energy with the help of an electronic computer. In this way, trial functions involving up to 39 parameters have been used. The relativistic and mass polarization corrections, as well as the mathematical lower bound for the energy of the ground state, are also evaluated with all of these trial functions.

In Sec. 2 the eigenvalue problem of the nonrelativistic Schrödinger equation for the He atom is described briefly. The properties of the Hylleraas expansion of the wave function are discussed and a new expansion is introduced which is much more general than the Hylleraas expansion and is designed to remove a difficulty of the latter. In Sec. 3, a number of terms of the new expansion are used in the variation calculation for the He ground state. The result is summarized in Table I. The lower bound of the energy of the ground state is discussed in Sec. 4. The estimated lower bounds for various trial functions are given in Table II. In Sec. 5 the actual position of the ground state eigenvalue is inferred by an extrapolation from available data. The accuracy of various approximate eigenfunctions is also discussed. In Sec. 6 the relativistic and mass corrections are evaluated with trial functions of various accuracy and the convergence of these quantities is discussed. The results of our investigation is summarized in Sec. 7. In the Appendix, some aspects of the new expansion are discussed from a more mathematical point of view. In particular, the existence of formal solutions of the He Schrödinger equation is demonstrated.

2. GENERALIZATION OF THE HYLLERAAS EXPANSION

We shall first describe the Hylleraas method briefly and show how the new expansion is introduced.

The helium atom in the nonrelativistic limit is described (in atomic units) by the following Schrödinger equation

$$\left[\tfrac{1}{2}(\Delta_1+\Delta_2)+E+\frac{2}{r_1}+\frac{2}{r_2}-\frac{1}{r_{12}}\right]\psi=0, \qquad (2.1)$$

when the motion of the nucleus is neglected. r_1 and r_2 are the distances of the two electrons from the nucleus and r_{12} is the distance between the electrons. Choosing

$$s=r_1+r_2, \quad u=r_{12}, \quad t=-r_1+r_2, \qquad (2.2)$$

as the three independent variables after separation of the Euler angles, Eq. (2.1) can be reduced to

$$\begin{aligned}u(s^2-t^2)(\psi_{ss}+\psi_{uu}+\psi_{tt})+2s(u^2-t^2)\psi_{su}+2t(s^2-u^2)\psi_{ut}\\ +4su\psi_s+2(s^2-t^2)\psi_u-4ut\psi_t\\ +8su\psi-(s^2-t^2)\psi+Eu(s^2-t^2)\psi=0, \qquad (2.3)\end{aligned}$$

for the S state. Since r_1, r_2, and r_{12} are sides of a triangle, s, u, and t satisfies the obvious relation

$$s\geqq u\geqq |t|. \qquad (2.4)$$

The singular points of the potential of (2.3) form the following three surfaces:

$$u=0, \quad s=t, \quad s=-t. \qquad (2.5)$$

Equations (2.1) and (2.3) by themselves are not sufficient to define the eigenvalue problem since they must be supplemented by a suitable boundary condi-

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[8] Bartlett, Gibbons, and Dunn, Phys. Rev. 47, 679 (1935).

tion. It has been proved by Kato[9] that, under the boundary conditions which may be written as

$$\int\int \psi^2 d^3x_1 d^3x_2 < \infty,$$
$$\int\int \left[\frac{\partial^2\psi}{\partial x_i^2}\right]^2 d^3x_1 d^3x_2 < \infty, \tag{2.6}$$

where x_i represents any one of x_1, y_1, z_1, x_2, y_2, z_2, the Hamiltonian corresponding to Eq. (2.1) becomes self-adjoint in a mathematically rigorous sense and thus it has a spectrum of eigenvalues. In particular, the lowest-lying levels are discrete. There is therefore no question about the existence of solutions of our eigenvalue problem itself.

On the other hand, the nonseparability of Eq. (2.3) makes it difficult to study the properties of its solutions in detail. We have not learned yet how to write down the solutions of Eq. (2.1) explicitly. We do not even have enough information about the analytical properties of solutions in the neighborhood of the singularities of the potential. Under such circumstances, the most powerful method developed so far is the Ritz variation method, first applied successfully to the He problem by Hylleraas.[10,11] On a basis of some qualitative arguments, Hylleraas assumed that the eigenfunction of (2.3) can be expanded into positive integral powers of s, u, and t in the form

$$\psi(s,u,t) = e^{-\frac{1}{2}s} \sum_{l,m,n}^{0,\infty} c'_{l,m,n} s^l u^m t^n. \tag{2.7}$$

The remarkable accuracy of the energy value obtained making use of the first few terms of this expansion indicates that this is in fact an appropriate expansion for our problem. On the other hand, the rather poor values for the lower bound[7] obtained with Hylleraas functions gives rise to some doubts about its adequacy in approximating the eigenfunction itself. In this connection, it was asked a long time ago by Bartlett, Gibbons, and Dunn[8] whether expansions like (2.7) could be a reasonable starting point for the mathematical investigation of the Schrödinger equation. They found the curious fact that any series of the form (2.7) cannot be a formal solution of the Schrödinger equation since the corresponding recurrence relation for the coefficients $c'_{l,m,n}$ has no solution other than the trivial one: $c'_{l,m,n}=0$ (for all l, m, and n). From this, one might be inclined to conclude that the actual eigenfunction cannot be approximated by any Hylleraas series. As was pointed out by Coolidge and James,[12] however, this does not necessarily follow from the absence of formal solutions. Coolidge and James tried further to prove that the actual solution can be approximated arbitrarily well by a Hylleraas series and the energy expectation value determined by the variation method converges to the actual eigenvalue. Their argument was not correct, however, because of an improper treatment of a double series which appears in their proof.[13] Thus, up to this moment the question whether the Hylleraas series (2.7) is a reasonable expansion or not has remained unanswered.

Even if it turns out that the Hylleraas series can be used to approximate the actual solutions as closely as we like, the absence of formal solutions might well be responsible for the slow convergence of the lower bound estimation. It would therefore be desirable to have an expansion which has no such difficulties. It must be recalled here that the expansion of form (2.7) was written down more or less arbitrarily. At first sight, (2.7) seems to be the most general expansion which remains finite everywhere, or, more precisely, satisfies the condition (2.6). It turns out, however, that the Hylleraas series is not the most general expansion satisfying the boundary condition (2.6), even if we restrict ourselves to power series expansions, because of the peculiar situation that we are treating functions of many variables whose domains are not independent of each other, as is obvious from (2.4).

We shall show this by constructing directly an expansion which is more general than (2.7) but still satisfies the same boundary conditions (2.6). For this purpose, let us introduce the new set of variables

$$s,\quad p=u/s,\quad q=t/u, \tag{2.8}$$

instead of s, u, and t, and construct a series of the form

$$e^{-\frac{1}{2}s} \sum_{l,m,n}^{0,\infty} c_{l,m,n} s^l p^m q^n \tag{2.9}$$

in analogy with the Hylleraas series. Since the domains of these variables are $(0, \infty)$, $(0, 1)$, $(-1, 1)$, respectively, they are now independent of each other. Individual terms of (2.9) are finite everywhere. Furthermore, it can be easily seen that each term is subject to the boundary condition (2.6) only if the following condition,

$$c_{l,0,n}=0 \quad \text{for} \quad n\neq 0, \tag{2.10}$$

is satisfied. If one goes back to the original variables s, u, and t, (2.9) is equivalent to the expansion

$$e^{-\frac{1}{2}s} \sum_{l,m,n}^{0,\infty} c_{l,m,n} s^{l-m} u^{m-n} t^n. \tag{2.11}$$

Obviously the Hylleraas series is a subseries of (2.11) characterized by $l \geqq m \geqq n$. Thus we have an expansion

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[9] T. Kato, Trans. Am. Math. Soc. **70**, 195, 212 (1951). The boundary condition (2.6) is not mathematically rigorous. The correct definition is given by Eq. (11) of Kato's first paper.

[10] E. A. Hylleraas, Z. Physik **54**, 347 (1929).

[11] Recently numerical methods of different kind have been developed by J. H. Bartlett [Phys. Rev. **98**, 1067 (1955)] and L. H. Thomas (private communication).

[12] A. S. Coolidge and H. M. James, Phys. Rev. **51**, 855 (1937).

[13] See footnote 21 of the second paper of reference 9.

which is much more general than the Hylleraas expansion and yet satisfies all requirements which the latter is supposed to satisfy. We can of course construct even more general expansions if we do not confine ourselves to power series or do not attempt to approximate the solution by a single expansion in the entire domain of variables.[14]

Though (2.11) is a rather simple generalization of the Hylleraas series, it is found to be general enough to contain (infinitely many) formal solutions of the Schrödinger equation (2.3) as is proved in the Appendix. Of course, the existence of formal solutions by itself is not very significant unless it can be shown that some of them converge to the actual solutions. For the purpose of numerical computation, however, the new expansion seems to have an advantage over the ordinary Hylleraas series since the former permits us much more flexible selection of terms than the latter, especially of the lowest order terms which are mainly responsible for the behavior of the wave function in the neighborhood of singularities of the potential energy. We therefore decided to carry out the variation calculation of the ground state energy of the He atom choosing trial functions of the form (2.11) rather than the more conventional form (2.7).

3. CALCULATION OF THE GROUND STATE ENERGY OF He ATOM

According to Hylleraas, we shall replace Eq. (2.3) by the following variation problem:

$$(-L+M)/N=\lambda=\text{minimum}, \tag{3.1}$$

where

$$\begin{aligned} L&=\int_0^\infty ds\int_0^s du\int_0^u dt(8su-s^2+t^2)\psi^2,\\ M&=\int_0^\infty ds\int_0^s du\int_0^u dt[u(s^2-t^2)(\psi_s{}^2+\psi_u{}^2+\psi_t{}^2)\\ &\qquad+2s(u^2-t^2)\psi_s\psi_u+2t(s^2-u^2)\psi_u\psi_t],\\ N&=\int_0^\infty ds\int_0^s du\int_0^u dtu(s^2-t^2)\psi^2. \end{aligned} \tag{3.2}$$

To accelerate the convergence of calculation, it is customary to introduce a parameter k and define a function φ by

$$\psi(s,u,t)\equiv\varphi(ks,ku,kt). \tag{3.3}$$

Then the variation problem for $\varphi(s,u,t)$ is written as

$$(-kL+k^2M)/N=\lambda=\text{minimum}, \tag{3.4}$$

where L, M, and N are now functionals of φ instead of ψ. In accordance with the argument of the last section, we shall assume that the function $\varphi(s,u,t)$ can be expressed as

$$\varphi(s,u,t)=e^{-\frac{1}{2}s}\sum_{\substack{l,m,n\\ n=\text{even}}}^{0,\infty} c_{l,m,n}s^{l-m}u^{m-n}t^n. \tag{3.5}$$

Then the integrations in (3.2) can be carried out easily and L, M, and N are expressed as bilinear forms of $c_{l,m,n}$. Assuming that only a finite number of terms of (3.5) do not vanish, the variation problem (3.4) is approximated by a finite algebraic problem. This problem may be treated in two different ways. One is to vary (3.4) with respect to the $c_{l,m,n}$'s keeping the remaining variable k unchanged and reduce it to a secular equation. Then the secular equation may be solved by any of the standard methods. The calculation may be repeated several times for various values of k until the best result is obtained. The other approach is to minimize (3.4) with respect to k first and solve the resulting problem:

$$-L^2/(4MN)=\lambda=\text{minimum}. \tag{3.6}$$

The parameter k may be determined by the relation $k=L/2M$ after λ is minimized. A variant of the relaxation method has been found useful to solve the nonlinear variation problem (3.6).[15] It has the advantage that it permits us to maintain a very high accuracy throughout the numerical work and moreover the precision is practically independent of the number of parameters involved. On the other hand, the rate of convergence of this method is extremely slow so that it will be necessary to use a reasonably good starting function selected by some other methods.

Making use of either or both of these two approaches,[16]

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[14] In particular, it has been suggested by J. H. Bartlett [Phys. Rev. **51**, 661 (1937)] that formal solutions of the He Schrödinger equation may be expanded in powers of logarithmic terms. Recently V. A. Fock [Izvest. Akad. Nauk. S.S.S.R. Ser. Fiz. **18**, 161 (1954)] has also obtained formal solutions as an expansion in a power series of logarithmic terms. It is to be noted that the logarithmic terms are not necessarily required by the structure of the Schrödinger equation itself. What is needed to construct a formal solution is a sufficient number of free parameters to manipulate, and the logarithmic expansion happens to fulfill this requirement because it contains more terms than the expansion without logarithmic terms. Whether the logarithmic terms are important in the actual numerical computation or not is, of course, a quite different matter. See the recent work of E. A. Hylleraas and J. Midtdal [Phys. Rev. **103**, 829 (1956)] in this connection.

[15] We have tried to solve the variation problem (3.6) in the following way: First take an arbitrary point $x_i{}^0$, where the parameters $c_{l,m,n}$ under consideration are regarded as components of a vector x_i. Then one can easily compute $\lambda(x_i{}^0)$, the height of the energy surface at $x_i{}^0$, and $(\partial\lambda/\partial x_i)_{x_i=x_i{}^0}$, the direction of its steepest gradient. By a suitable choice of the constants a_i, one can then determine a next point $x_i{}^1=x_i{}^0+a_i(\partial\lambda/\partial x_i{}^0)$ which gives a lower energy value than $x_i{}^0$. This procedure can be repeated as many times as one wants. The minimum of energy is attained when $\partial\lambda/\partial x_i=0$. If we choose a_i to be independent of i, we obtain the so-called method of steepest descent. To accelerate the convergence, we have found it better to use different a_i's for different i's. In the determination of our a_i's, the curvature of the energy surface is taken into account.

[16] Preliminary computation with a 10-parameter function was done by the first method by using an electronic computer at the Princeton Institute for Advanced Study. Effectiveness of the relaxation method in our problem was tested by a CPC-IBM machine at Cornell. The major part of the computation was carried out mainly by the second method using the AEC-UNIVAC at New York University.

TABLE I. The constants of various ground state wave functions of helium containing negative-power terms. The only exception is the 18-parameter case which is obtained from the function of Chandrasekhar and Herzberg by applying our relaxation method. Expansion coefficients listed are $10^l c_{l,m,n}$ and $c_{0,0,0}$ is normalized to 1.

No. of parameters	10	18	22	34	38	39
$-\bar{\lambda}$	2.9036261	2.9037150	2.9037142	2.9037223	2.9037225	2.9037225
k	3.4591498	3.8892119	3.7078208	3.7133871	3.7204746	3.7211124
L	77.5338944	70.8204634	55.4500389	55.7506367	56.2837996	56.3337661
M	11.2070737	9.1047319	7.4774433	7.5067096	7.5640619	7.5694792
N	46.1838658	47.4281727	35.4027276	35.6479843	36.0575857	36.0957835
(100)	−0.520987	0.061877	−0.221064	−0.242959	−0.234487	−0.233872
(110)	1.212836	1.066306	1.266177	1.258703	1.256856	1.256979
(120)	−0.237663		−0.201470	−0.133887	−0.132299	−0.132234
(112)	0.057465		0.024224		0.003643	0.003471
(122)	0.074288		0.117951	0.087396	0.081032	0.080887
(200)	0.227098	0.201815	0.328272	0.415123	0.417629	0.418083
(210)	−0.314547	0.586598	−0.222515	0.056239	0.057689	0.058346
(220)		−1.034044	−0.202738	−1.173334	−1.159792	−1.159635
(230)			−0.078207	0.557818	0.553048	0.553037
(240)			0.114848	−0.092967	−0.095915	−0.096000
(212)	0.118920		0.090652		0.014641	0.014958
(222)	0.548619	1.418009	0.689095	1.671338	1.636562	1.636927
(232)			−0.146695	−1.146609	−1.121680	−1.121438
(242)			−0.107252	0.286687	0.286673	0.286830
(300)		−0.042460	−0.114389	−0.225558	−0.226038	−0.226212
(310)			0.237343	0.047030	0.041420	0.041297
(320)				0.560729	0.559791	0.559480
(330)		0.818139	−0.005333	0.282002	0.282496	0.282068
(340)				−0.244042	−0.247148	−0.247617
(322)		0.531984	0.246469	−0.421915	−0.430056	−0.429969
(332)		−2.236430		0.085977	0.101488	0.101338
(342)				0.072563	0.070063	0.069747
(400)		0.026402	0.007215	0.053802	0.053455	0.053479
(410)			−0.014174	0.010048	0.013036	0.013121
(420)				−0.133344	−0.121417	−0.121398
(430)					−0.005797	−0.005826
(440)		−0.445197		−0.425197	−0.417059	−0.417101
(450)				0.302063	0.294998	0.294975
(422)		0.157459		0.309865	0.305348	0.305219
(442)		1.991624	0.077528	0.161768	0.165892	0.165445
(444)				0.028853	0.029019	0.028951
(540)					−0.019751	−0.019203
(550)		0.099651		0.170186	0.185206	0.185827
(560)				−0.134784	−0.132279	−0.131580
(522)				−0.034092	−0.028227	−0.027977
(552)		−0.896542		−0.140588	−0.149057	−0.148548
(662)		0.159351		0.037981	0.039775	0.039703
(660)						−0.000861

the energy of the He atom in the ground state has been evaluated with various trial functions. In Table I the parameters $c_{l,m,n}$, k, the energy expectation value $\bar{\lambda}$, etc., obtained in this way are given for 10-, 22-, 34-, 38-, and 39-parameter trial functions of the form (3.5). Our relaxation method is also applied to the 18-parameter function of Chandrasekhar and Herzberg. The improved result is included in column 3 of Table I. The 10- and 22-parameter calculations are carried out to estimate the effect of inclusion of negative power terms. They may be roughly compared with calculations with 10 and 18 parameters of positive powers only. Our 38-parameter function is chosen in such a way that all terms of the 22-parameter function as well as all 18 terms of Chandrasekhar and Herzberg are included. The 34-parameter function is obtained from the 38-parameter one by dropping the four least important terms. The 34-, 38-, and 39-term functions of Table I look similar to each other. This should not be regarded however as an indication that our calculation is converging. Rather this is simply because all these functions are derived from the same starting function and we have not iterated our relaxation procedure sufficiently many times to make them look different.[17] We should therefore consider that these three cases represent more or less identical physical situation.

The best energy value obtained so far is

$$\bar{\lambda} = -2.9037225 \text{ atomic units,} \tag{3.7}$$

which is better than the corresponding quantities in Table III and Eq. (17) of Chandrasekhar and Herzberg (4) by 3.55 cm^{-1} and 1.42 cm^{-1}, respectively.* Though this is a considerable improvement over previous results, the variation method itself cannot determine how close our value (3.7) is to the actual energy. In the following section, we shall therefore estimate the mathematical lower bound for the ground state energy, making use of trial functions given in Table I.

4. LOWER BOUND FOR THE GROUND STATE ENERGY

The ordinary variation method gives only an upper bound of the energy level considered. To estimate the accuracy of such a calculation, it is necessary to know some other quantities like the lower bound. For this purpose we shall use a lower bound formula first given by Temple.[18] Though this is the best formula we know of, the distance between the upper and lower bounds estimated by this formula turns out to be unrealistically large when applied to the He ground state. One might therefore say that Temple's formula is not suitable for our purpose. It seems, however, that this is a fault of our trial functions rather than that of the formula itself. In any case the lower bound estimation would be useful for the comparison of relative accuracy of various trial functions.

First we shall give a simple derivation of Temple's formula. Let H be any self-adjoint Hamiltonian whose eigenvalues and eigenvectors are E_i and ψ_i, respectively. Then the following inequality,

$$((H-E_0)\psi,\ (H-E_1)\psi) \geqq 0, \tag{4.1}$$

holds for any normalized function ψ that can be expanded as

$$\psi = \sum_i a_i\psi_i. \tag{4.2}$$

Rewriting (4.1), one easily finds an inequality

$$E_0 \geqq \bar{\lambda} - \frac{\sigma}{E_1 - \bar{\lambda}}, \tag{4.3}$$

if $E_1 - \bar{\lambda} > 0$, where

$$\bar{\lambda} = (\psi, H\psi), \tag{4.4}$$

and

$$\sigma = (H\psi, H\psi) - \bar{\lambda}^2. \tag{4.5}$$

Namely, the actual energy E_0 cannot be smaller than the right-hand side of (4.3). Equation (4.3) is Temple's formula for the lower bound. It is to be noticed that it may not be useful when the level spacing $E_1 - E_0$ is too narrow.

To evaluate the lower bound by the formula (4.3), it is necessary to know the energy E_1 of the first excited state (having the same symmetry property as the ground state). Since $E_1 - \bar{\lambda}$ will be much larger than σ here, a rough approximation for E_1 will be sufficient. We shall therefore use an experimental value $E_1 \approx 2.146$ atomic units.

The quantity σ has been evaluated by an electronic computer. In Table II are given the values of lower bounds for various trial functions. Some of the results obtained by Wilets and Cherry are also included for the convenience of comparison. As is seen immediately, the lower bounds obtained with trial functions containing negative powers (10- and 22-parameter functions of Table I) are much better than those without negative powers (10- and 18-parameter functions of Chandrasekhar and others) though their upper bounds are not much different. The distances between the upper and lower bounds, called $\Delta\lambda$, for our 34-, 38-, and 39-parameter functions are about ten times smaller than that of the 18-parameter function of Chandrasekhar and Herzberg. The best estimation of $\Delta\lambda$ is about 33 cm^{-1} which is still very large compared with the accuracy of experiment.

As was shown by Stevenson and Crawford,[19] it is possible to formulate a variation problem for σ or some similar quantity independent of the ordinary one. By this method one will be able to reduce σ considerably. Of course the accuracy of the corresponding upper bound will be somewhat sacrificed. If one uses the two variation methods alternatively, however, it would not be difficult to achieve a higher accuracy than the

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[17] In particular, the 39-parameter function is included in Table I (and also in Tables II and III) to show the effect of an additional term u^6 on the 38-parameter function after a relatively few number of iterations. It is expected that the last parameter $c_{6,6,0}$ becomes much larger in magnitude after a sufficient number of iterations and the energy value will be improved somewhat accordingly.

* *Note added in proof.*—The value of 3.55 cm^{-1} quoted above refers to the energy eigenvalue obtained by S. Chandrasekhar and G. Herzberg directly from the best of the trial wave functions which they had computed. The better value of 1.42 cm^{-1} refers to their best energy value [Eq. (17) of reference 4] derived by an interpolation method. Unfortunately, they did not obtain a wave function corresponding to this energy since the interpolation was done with the energy value only and not with the wave function. J. F. Hart and G. Herzberg (to be published) have recently extended the calculation to a trial function of 20 parameters and obtained a wave function together with a minimized energy value (−2.9037179 atomic units) which is about 1 cm^{-1} apart from our value (3.7). We would like to thank Professor Herzberg for his clarifying communications and sending us their manuscript before publication.

[18] G. Temple, Proc. Roy. Soc. (London) **A119**, 276 (1928). See also reference 20.

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

TABLE II. The upper and lower bounds for the ground state energy of helium (in atomic units) and the accuracy of various trial functions. The reference numbers refer to footnotes in the text. Data without references were obtained by using functions of Table I. η_1 and η_2 were obtained by using formulas (5.11) and (5.10), respectively.

Reference	No. of parameters	$-\bar{\lambda}$	$\sigma=(H\psi,H\psi)-\bar{\lambda}^2$	$-\lambda_L$	$\Delta\lambda=\bar{\lambda}-\lambda_L$	$\Delta\lambda$ (in cm^{-1})	η_1	η_2
a, b	6	2.90324	0.01690	2.92556	0.02232	4900	0.169	0.022
c, b	10	2.903603	0.007580	2.913608	0.010005	2200	0.114	0.011
	10	2.903626	0.004005	2.908913	0.005287	1160	0.083	0.010
d, b	14	2.9037009	0.0020500	2.9064064	0.0027055	594	0.060	0.0055
d, b	18	2.9037063	0.0013572	2.9054974	0.0017912	393	0.049	0.0042
	18	2.9037150	0.0009222	2.9049321	0.0012171	267	0.040	0.0030
	22	2.9037142	0.0007225	2.9046678	0.0009536	209	0.035	0.0031
	34	2.9037223	0.0001223	2.9038837	0.0001614	35.4	0.015	0.0012
	38	2.9037225	0.0001152	2.9038745	0.0001521	33.4	0.014	0.0011
	39	2.9037225	0.0001146	2.9038737	0.0001512	33.2	0.014	0.0011

[a] See reference 10.
[b] See reference 7.
[c] See reference 2.
[d] See reference 4.

present one in the estimation of both upper and lower bounds.

5. ESTIMATION OF THE GROUND-STATE ENERGY BY EXTRAPOLATION

Let us assume that there is a function ψ which approximates the normalized ground-state eigenfunction ψ_0. One may then write as follows:

$$\psi=(1-\eta^2)^{\frac{1}{2}}\psi_0+\eta\psi', \tag{5.1}$$

where

$$\begin{aligned}(\psi',\psi_0)&=0,\\ (\psi',\psi')&=1.\end{aligned} \tag{5.2}$$

η is a parameter to measure the deviation of ψ from ψ_0. If one computes an expectation value of H with such a ψ, one obtains

$$\begin{aligned}\bar{\lambda}&=(\psi,H\psi)=E_0+a\eta^2,\\ a&=(\psi',H\psi')-E_0.\end{aligned} \tag{5.3}$$

In the same way, one finds

$$\begin{aligned}\sigma&=(a^2+b)\eta^2-a^2\eta^4,\\ b&=(H\psi',H\psi')-(\psi',H\psi')^2.\end{aligned} \tag{5.4}$$

From (5.3) and (5.4), the following relation is obtained:

$$\bar{\lambda}-E_0=\sigma a(a^2+b)^{-1}, \tag{5.5}$$

when the η^4 term of (5.4) is negligibly small compared with the η^2 term. Since the coefficient of σ in (5.5) is a functional of a quite arbitrary function ψ', $\bar{\lambda}$ can in general assume infinitely many values for fixed values of σ and vice versa.

Since ψ' is orthogonal to the ground state, the quantity a satisfies the inequality

$$a\geqq E_1-E_0(\approx 0.758), \tag{5.6}$$

where the equality holds when and only when $\psi'=\psi_1$. The quantity b is always non-negative and it vanishes only if ψ' is one of the eigenstates ψ_i of H. Thus, one obtains

$$0<a(a^2+b)^{-1}\leqq a^{-1}\leqq(E_1-E_0)^{-1}\approx 1.320. \tag{5.7}$$

This means that the point $(\sigma,\bar{\lambda})$ corresponding to any ψ is confined to the shaded region of Fig. 1 when $\eta^2\ll 1$. If $a(a^2+b)^{-1}$ is close to the upper limit of (5.7), one may say that ψ' is a linear combination of several lowest states. On the other hand, if $a(a^2+b)^{-1}\ll 1$ or $a+ba^{-1}\gg 1$, either or both of the relations $a\gg 1$, $b\gg 1$ must hold because of (5.6). When $a\gg 1$, ψ' must have contributions from highly excited states in the positive energy continuum. When $b\gg 1$, ψ' would be a *mixture* of large number of states which must contain states of large positive energy, too.

In Fig. 1 the points $(\sigma,\bar{\lambda})$ are plotted for several trial functions listed in Table II. At each of these points, one may draw a straight line with a slope $(E_1-E_0)^{-1}\approx(E_1-\bar{\lambda})^{-1}$. The intersections of these straight lines with the $\bar{\lambda}$-axis are the corresponding lower bounds λ_L to E_0. Thus the lower bound obtained in the last section corresponds to the extreme case $\psi'=\psi_1$. The rapid improvement of the lower bounds with the increased accuracy of our trial functions indicate that our ψ' is actually a mixture of many highly excited states rather than a linear combination of the few lowest states.

It is interesting to observe that all points $(\sigma,\bar{\lambda})$ plotted in Fig. 2 lie in the neighborhood of a dashed straight line though these points could be scattered in a much wider region as is suggested by Fig. 1.[20] This leads us to a speculation that the ψ''s corresponding to our plots $(\sigma,\bar{\lambda})$ are more or less similar to each other having similar slopes $a(a^2+b)^{-1}$ at each point. If this is the case, different points $(\sigma,\bar{\lambda})$ are distinguished by different values of η only. The dashed line intersects with the $\bar{\lambda}$-axis at the point $(0,\lambda^*)$, where

$$\lambda^*=-2.9037237 \text{ atomic units.} \tag{5.8}$$

This is 0.0000012 atomic unit or 0.26 cm^{-1} lower than the value (3.7) for our 39-parameter function. If our

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[20] Actually trial functions of Hylleraas type seem to give smaller gradients than those of the form (2.11). Thus, to be more precise, we may have to draw at least two lines with slightly different slopes in Fig. 2. But the essential feature of the following argument may not be changed.

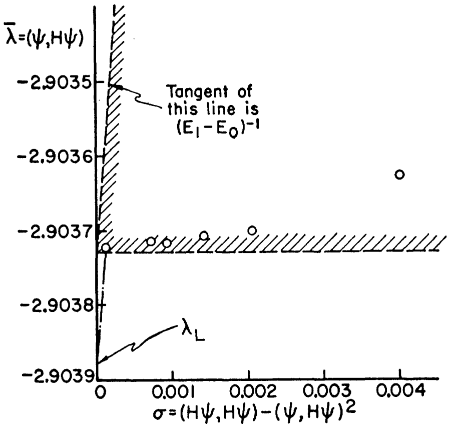

FIG. 1. The expectation value of energy $\bar{\lambda}=(\psi,H\psi)$ *versus* $\sigma=(H\psi,H\psi)-\bar{\lambda}^2$. For any ψ, the corresponding point $(\sigma,\bar{\lambda})$ will be confined to the shaded region. The boundary of this region consists of two straight lines, with gradients 0 and $(E_1-E_0)^{-1}$, respectively. Both lines must go through the point $(0,E_0)$. Note that these lines are drawn only for the sake of illustration. They are not known exactly because of uncertainty in the value of E_0. The small circles indicate the location of $(\sigma,\bar{\lambda})$ corresponding to some of the trial functions listed in Table II. At one of these points, a dashed-dotted line is drawn with a slope $(E_1-E_0)^{-1}$. The intersection of this line with the $\bar{\lambda}$ axis gives the lower bound, λ_L, of E_0.

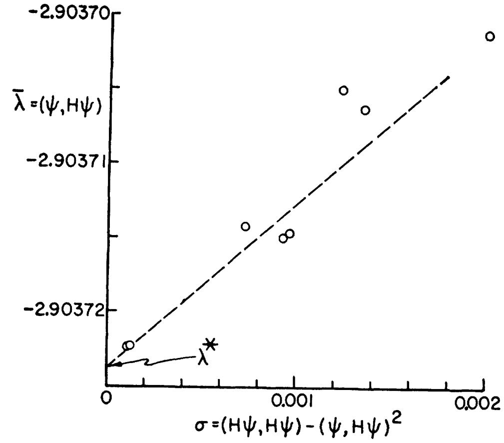

FIG. 2. A portion of Fig. 1 is magnified by a large factor (especially in the vertical direction) in order to show the details clearly. Two more points corresponding to the 18- and 22-parameter functions obtained in the intermediate stage of our iteration procedure are added. The calculated points are scattered in the neighborhood of the dashed line. The intersection of this line with the $\bar{\lambda}$ axis may be used to obtain an approximate value of the actual energy E_0.

considerations are on a right track, the value (5.8) would be a very good approximation to the actual energy E_0.

It is likely, however, that the above argument is a little oversimplified. In fact, if one studies all the available data more carefully, one finds a trend indicating that the dashed line should probably be replaced by a curve which is slightly convex downward. Thus the linearly extrapolated value (5.8) might be too low compared with the actual energy E_0. At this moment, however, we have not enough material to make a better estimation of E_0. Therefore we shall simply express our belief that the actual position of the energy E_0 will be very close to and perhaps slightly higher than the value (5.8).

It would also be interesting to estimate the accuracy of our trial functions directly.[21] For this purpose, let us first notice the obvious inequality:

$$(\psi,\,(H-E_1)\psi)+(E_1-E_0)(1-\eta^2)=\sum_{i\geqq 2}(E_i-E_1)a_i^2\geqq 0. \quad (5.9)$$

As is easily seen, this formula can be rewritten as

$$\eta^2\leqq(\bar{\lambda}-E_0)/(E_1-E_0). \quad (5.10)$$

If E_0 and E_1 are known, this formula can be used to evaluate the accuracy η of ψ. When E_0 is not known very accurately, (5.10) can be replaced by the weaker formula

$$\eta^2\leqq\frac{\sigma}{(E_1-\bar{\lambda})^2+\sigma}, \quad (5.11)$$

which follows from (5.10) and Temple's formula (4.3). In columns 8 and 9 of Table II are given the quantity η, evaluated by making use of the formula (5.11) and (5.10), respectively. In the latter case it is assumed that E_0 is given exactly by our extrapolated value (5.8). This will be a quite reasonable assumption for the relatively simple trial functions. Even for our best trial functions, it is likely that (5.10) gives a closer estimation than (5.11) of the accuracy of wave functions.

6. RELATIVISTIC AND MASS POLARIZATION CORRECTIONS

According to Sucher and Foley,[3] the expectation value of the relativistic correction in the ground state is given, correct to the order α^2, by

$$E_{\mathrm{rel}}=(E_1'+E_1''+E_1'''+E_3'+E_3'')\alpha^2\ \mathrm{ry}, \quad (6.1)$$

where

$$\begin{aligned}
E_1'&=-\frac{k^4}{4N}[(\Delta_1\varphi,\Delta_1\varphi)+(\Delta_2\varphi,\Delta_2\varphi)],\\
E_1''&=\frac{2\pi k^3}{N}[(\varphi,\delta(\mathbf{r}_1)\varphi)+(\varphi,\delta(\mathbf{r}_2)\varphi)],\\
E_1'''&=-\frac{2\pi k^3}{N}(\varphi,\delta(\mathbf{r}_{12})\varphi),\\
E_3'&=\frac{k^3}{N}\left(\varphi,\frac{1}{u}[\nabla_1\nabla_2+(n\nabla_1)(n\nabla_2)]\varphi\right),\\
E_3''&=-2E_1''',\\
N&\equiv(\varphi,\varphi)=\int_0^\infty ds\int_0^s du\int_0^u dtu(s^2-t^2)\varphi^2,
\end{aligned} \quad (6.2)$$

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[21] T. Kato, J. Phys. Soc. Japan 4, 334 (1949); Phys. Rev. 77, 413 (1950).

TABLE III. Relativistic and mass polarization corrections evaluated with various trial functions. The reference numbers refer to footnotes in the text. Data without references were obtained by using trial functions of Table I. $E_{\text{ion}}(=-4.000\alpha^2\text{ ry})$ is the relativistic correction for the ground state energy of He^{1+}. Figures are given in the units α^2 ry except for the last two columns.

Reference	No. of parameters	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})
a	1	−20.30	19.20	1.20	0	4.10	24.0	0
a	3	−26.71	22.60	0.73	−0.30	0.32	1.87	5.34
b	6	−27.25	22.83	0.70	−0.29	−0.01	−0.06	4.95
c	10	−27.209	22.74	0.69	−0.283	−0.062	−0.362	4.799
	10	−26.978	22.727	0.683	−0.281	0.151	0.882	4.591
d	18	−27.0218	22.7408	0.6735	−0.2790	0.1139	0.666	4.789
	18	−27.0367	22.7486	0.6732	−0.2788	0.1068	0.624	4.788
	22	−27.0226	22.7424	0.6725	−0.2788	0.1139	0.666	4.790
	34	−27.0507	22.7545	0.6693	−0.2784	0.0951	0.556	4.786
	38	−27.0461	22.7523	0.6694	−0.2783	0.0977	0.571	4.786
	39	−27.0459	22.7521	0.6693	−0.2783	0.0976	0.570	4.786

[a] See reference 3.
[b] See reference 10.
[c] See reference 2.
[d] See reference 4.

and φ is given by (3.5). Sucher and Foley evaluated these corrections with the Hylleraas 3-parameter function, leading to

$$E_{\text{rel}}-E_{\text{ion}}=0.32\alpha^2\text{ ry},\qquad(6.3)$$

where $E_{\text{ion}}=-4.000\alpha^2$ ry is the relativistic correction for the ground state of ionized helium.

At first sight, one might think that the relativistic correction can be evaluated with enough accuracy using a relatively simple trial function since it is small numerically. It is to be noticed, however, that E_{rel} itself is about 13.5 times larger than the difference (6.3). Moreover, the relativistic correction will be much more sensitive to the details of the wave function than the energy itself since the former contains higher derivatives of the wave function than the latter. Since the accuracy of expectation values of quantities like (6.2) will be proportional to the accuracy of the wave function itself, not to its square, it is necessary to evaluate them with a function which is accurate to the desired degree.

We have also to notice that it is not known whether the relativistic correction can be bounded from above and below. This makes it hard to find how close the computed value is to the actual value. For these reasons, we have decided to compute it with various trial functions and see whether its value will converge to a certain limit when the accuracy of the trial function is improved. In Table III are given the values of the relativistic correction evaluated with various functions up to 39 parameters. Similar calculations are carried out for the mass polarization correction

$$E_2=\frac{m}{M_{\text{He}}}\frac{k^2}{N}(\nabla_1\varphi,\nabla_2\varphi)\text{ (atomic units)},\qquad(6.4)$$

and the results are also included in the last column of Table III.

It will be seen that the expectation values fluctuate considerably for the trial functions of up to 10 parameters. For the functions with more than 18 terms, however, the fluctuation is pretty small and indicates that the expectation values are really settling down to limiting values. The accuracy of E_{rel} and E_2 may be estimated in terms of the accuracy of approximate eigenfunctions used to evaluate them. Obviously the accuracy of correction terms is proportional to η. It must be noticed, however, that nothing is known about the actual magnitude of the proportionality constant so that an absolute estimation of accuracy is impossible. From these arguments, we may conclude that the relativistic and mass polarization corrections are

$$E_{\text{rel}}-E_{\text{ion}}=0.57_0\pm0.05\text{ cm}^{-1},\qquad(6.5)$$

and

$$E_2=4.78_6\pm0.01\text{ cm}^{-1},\qquad(6.6)$$

respectively. The accuracy is derived from η_2 listed in Table II. If one uses η_1 instead of η_2, one obtains of course much broader limits. As was mentioned above, however, the limits of errors of (6.5) and (6.6) are given in a more or less arbitrary manner and therefore they by no means have an absolute significance. Nevertheless it is plausible that these limits of errors are of the correct order of magnitude.

7. DISCUSSION

When one includes the mass polarization and relativistic corrections (6.5) and (6.6), the nonrelativistic energy (3.7) obtained with our 39-parameter function leads to the ionization potential

$$198311.61\text{ cm}^{-1}\qquad(7.1)$$

for the ground state of He atom. This value does not include the Lamb shift and other smaller corrections. If one adds to this the best estimation of the Lamb shift, -1.23 ± 0.3 cm^{-1}, evaluated with the 6-parameter Hylleraas function,[22] the final theoretical prediction for

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[22] P. K. Kabir and E. E. Salpeter, Bull. Am. Phys. Soc. Ser. II, 1, 46 (1956). The quoted error of ±0.3 cm^{-1} comes largely from an estimate of the order of magnitude of some quantum electrodynamical correction terms, which have not yet been calculated.

the ionization potential (I.P.) becomes

$$\mathrm{I.P.}_{\text{theory}}=198310.38\ \mathrm{cm}^{-1}, \tag{7.2}$$

which agrees remarkably well with the present experimental value[1]

$$\mathrm{I.P.}_{\text{exp}}=198310.5\pm 1\ \mathrm{cm}^{-1}. \tag{7.3}$$

As was shown before, the mathematical limit of errors of the nonrelativistic energy is still very large. Thus the value (7.1) could be as large as 198345 cm^{-1}. But it is plausible from the argument of Sec. 5 that our value (7.1) is smaller than the correct value by only 0.3 cm^{-1} or less. If one accepts that argument, our final results (7.1) and (7.2) will have to be increased by this amount. It is therefore likely that the correct ionization potential is very close to 198310.64 cm^{-1}. Its uncertainty will be at most of the order of ± 0.5 cm^{-1}.

The accuracy of our calculation will therefore be better than that of the present experiment. It will not be sufficient, however, for the purpose of serious comparison of theory and experiment in the near future. It is therefore highly desirable to improve the accuracy of theoretical calculation still further. Though it will be possible to improve the energy value by varying our 39-parameter trial function further, since it has not minimized the energy yet, it might be necessary to add many more terms to our trial function before we can achieve a substantial improvement. At this stage, it might be more efficient to use a variation method for $(H\psi,H\psi)-(\psi,H\psi)^2$ rather than the ordinary variation method, as was mentioned in Sec. 4. More accurate evaluation of the Lamb-shift correction and higher order radiative corrections will also be required.

In this paper, we have deviated from the customary approach by introducing negative-power terms as a possible form of trial functions. Advantages of such functions have been emphasized in Sec. 2 and also in the Appendix. The real criterion for the usefulness of negative-power terms can be obtained, however, only by evaluating their effectiveness in the actual numerical calculation of energy and wave function. The result of our calculation with 10- and 22-parameter functions may be regarded as an indication that the negative terms are in fact useful for our purpose (see Table II). On the other hand, the remarkable improvement of accuracy in the cases of 34 or more terms might have been obtained simply by the large flexibility of trial functions resulting from the tremendous number of terms involved. It would be interesting to notice, however, that some of the formal requirements on $c_{l,m,n}$, such as (A.15) and (A.16), are satisfied to a better extent by trial functions containing negative-power terms than by those with positive powers only.

Finally we shall refer to other recent approaches to the eigenvalue problem of the He ground state. Schwartz[23] has used trial functions involving fractional powers of the variables and obtained a remarkably good energy value with a variation method using a 13-parameter function. Unfortunately, however, it is difficult to see whether it is physically significant or not, since the expectation value $(H\psi,H\psi)$ diverges logarithmically for his trial function at $u=0$. For the same reason the relativistic correction term E_1' becomes divergent.[24] Hylleraas and Midtdal[25] have carried out a variation calculation using a trial function with 24 terms out of which three are negative power terms and one is a logarithmic term. The energy value obtained seems to be about 1.3 cm^{-1} better than our best result (3.7). If this were true, it would upset our argument about the linear extrapolation and make our value (5.8) unreliable. On the other hand, the result of Hylleraas and Midtdal will lead to a theoretical ionization potential which is more than 1 cm^{-1} too large compared with the present experiment. In any case, it would be very profitable to investigate further trial functions of the type used by Hylleraas and Midtdal.

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APPENDIX. FORMAL SOLUTION OF THE He SCHRÖDINGER EQUATION

A. Existence of Formal Solutions

First, we shall show that we can construct infinitely many formal solutions of the He Schrödinger equation

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[23] H. M. Schwartz, Phys. Rev. **103**, 110 (1956).

[24] Closely related to these troubles is the fact that Schwartz's trial functions do not satisfy Kato's boundary conditions (2.6). Nevertheless, we have been able to convince ourselves that his energy expectation value will not become lower than the actual energy. This is quite interesting since it suggests that the expectation value of the Hamiltonian might converge to the correct limit under less stringent boundary conditions than (2.6).

[25] E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956).

(2.3) if we assume that ψ can be expanded in the generalized form (2.11). To prove this, let us introduce the expansion (2.11) into the left-hand side of (2.3) and rearrange the resulting expression into the power series of s, u, and t. Requiring that all coefficients of this series vanish, one obtains the following recurrence formula for $c_{l,m,n}$:

$$\begin{aligned} &n(n-1)c_{l,m,n}+(m-n+2)(m+n-1)c_{l,m,n-2}\\ &\quad+(l-m-n+4)(l+m-n+3)c_{l,m-2,n-2}\\ &\quad-(m-n+2)(2l-m-n+7)c_{l,m-2,n-4}\\ &\quad-(l-m+4)(l-m+3)c_{l,m-4,n-4}-c_{l-1,m-1,n-2}\\ &\quad-(l-n-5)c_{l-1,m-2,n-2}+(m-n+2)c_{l-1,m-2,n-4}\\ &\quad+c_{l-1,m-3,n-4}+(l-m+3)c_{l-1,m-4,n-4}\\ &\qquad\qquad+(E+\tfrac{1}{4})(c_{l-2,m-2,n-2}-c_{l-2,m-4,n-4})=0. \qquad \text{(A.1)}\end{aligned}$$

Altogether there are ∞^3 equations to determine ∞^3 quantities $c_{l,m,n}$.

Let us call the set of indices (l,m,n) larger than the other set (l',m',n') when

$$\begin{aligned} &l'>l,\\ \text{or}\quad &l'=l,\quad m>m',\\ \text{or}\quad &l'=l,\quad m=m',\quad n>n'. \end{aligned}\qquad \text{(A.2)}$$

Equation (A.1) has such a structure that the first term $c_{l,m,n}$ can be determined for $n\neq 0$ when the $c_{l',m',n'}$'s are known for some of the smaller indices. Therefore, if the coefficients $c_{l,m,n}$ are determined successively, starting from those of smaller indices, no inconsistency occurs in general among the equations of (A.1). For $n=0$, one obtains

$$0c_{l,m,0}=0, \qquad \text{(A.3)}$$

so that $c_{l,m,0}$ can be chosen arbitrarily for all values of l and m. Furthermore it is not difficult to show that all quantities $c_{l,m,n}(n\geqq 2)$ can be expressed uniquely as linear combinations of parameters $c_{l,m,0}$. We have thus seen that Eq. (2.3) has formal solutions of the type (2.11) with ∞^2 arbitrary parameters.

It is to be noticed that the existence proof of formal solutions given here depends on the procedure of construction of $c_{l,m,n}$ starting from quantities of smaller indices. It will, of course, be possible to construct formal solutions in different ways. However, if some of the quantities having larger indices are determined beforehand, one usually encounters some inconsistency and the whole process of construction of $c_{l,m,n}$ breaks down. In particular, it is because the restriction,

$$c_{l,m,n}=0 \quad \text{unless} \quad l\geqq m\geqq n, \qquad \text{(A.4)}$$

is imposed on the coefficients that the Hylleraas expansion cannot lead to any formal solution of Eq. (2.3).

B. Kato's Theorems

Before discussing some properties of formal solutions of Eq. (2.3), it will be useful to mention briefly Kato's theorems.[26] Kato has recently given rigorous proofs for the following two theorems about the properties of solutions of the Schrödinger equation for atomic systems. They have been assumed as obvious in many applications but have not been justified before.

1. Eigenfunctions of a Schrödinger equation are continuous everywhere (even at the singularities of the potential energy) if the potential has no stronger singularities than the Coulomb potential.

2. First derivatives of the eigenfunctions at the singularities of the potential satisfy the following relations

$$\left\langle\left(\frac{\partial\psi}{\partial r_1}\right)_{r_1=0}\right\rangle_{\text{Av}}=-2\psi(s=u=t=r_2), \qquad \text{(A.5)}$$

and

$$\left\langle\left(\frac{\partial\psi}{\partial u}\right)_{u=0}\right\rangle_{\text{Av}}=\tfrac{1}{2}\psi(s,0,0), \qquad \text{(A.6)}$$

where the left-hand side of these relations are averages of first derivatives over spheres of small radii whose centers are $r_1=0$ and $u=0$, respectively.

When the first theorem is applied to our expansion (2.11), one finds the following results:

$$c_{l,0,n}=0 \quad \text{for} \quad n\neq 0, \qquad \text{(A.7)}$$

$$c_{0,m,n}=0 \quad \text{for} \quad (m,n)\neq(0,0). \qquad \text{(A.8)}$$

This is because terms corresponding to these coefficients have finite discontinuities at $u=0$ and $s=0$, respectively, and therefore must be removed from the expansion (2.11). Equation (A.7) coincides with (2.10) which follows from the boundary conditions (2.6). This is also obtained by solving the recurrence formula (A.1) for the case $m=0$. It seems, however, that the relation (A.8) does not follow from any requirement other than continuity.[27]

Applying the second theorem to our expansion (2.11), we are led to the following relations between the coefficients:

$$\sum_{m,n}(l-m-n)c_{l,m,n}=0 \quad \text{for all } l, \qquad \text{(A.9)}$$

and

$$\sum_{n}(n+1)^{-1}c_{l,1,n}=0.5c_{l-1,0,0}. \qquad \text{(A.10)}$$

It is interesting to notice here that, for $m=1$, the recurrence relation (A.1) is simplified to

$$n(n-1)c_{l,1,n}-n(n-3)c_{l,1,n-2}-c_{l-1,0,n-2}=0. \qquad \text{(A.11)}$$

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[26] T. Kato, New York University, Research Report No. CX-25, 1956 (unpublished).

[27] As is easily seen, a discontinuity of the wave function ψ at $u=0$ is ruled out by the boundary condition (2.6). On the other hand, at $s=0$, a discontinuity (or even a logarithmic singularity) does not contradict (2.6). This is because the integration domain in the immediate neighborhood of $s=0$ is 6-dimensional while that at $u=0$ is only 3-dimensional.

Solving this set of equations, one finds

$$c_{l,1,2}=-c_{l,1,0}+0.5c_{l-1,0,0}, \tag{A.12}$$

$$c_{l,1,n}=(n-1)^{-1}c_{l,1,2} \quad \text{for} \quad n\geqq 2. \tag{A.13}$$

If one substitutes (A.13) into (A.10), the following relation is obtained:

$$0.5c_{l,1,2}+c_{l,1,0}=0.5c_{l-1,0,0}. \tag{A.14}$$

Obviously this is consistent with (A.12) only when the following relations hold:

$$c_{l,1,0}=0.5c_{l-1,0,0}, \tag{A.15}$$

$$c_{l,1,n}=0 \quad \text{for} \quad n\geqq 2. \tag{A.16}$$

(A.15) and (A.16) are valid for arbitrary values of l. In the numerical computation, where only a finite number of parameters are used and therefore the recurrence relation (A.1) cannot be satisfied exactly, the relations (A.9)-(A.16) may not have to hold strictly. We have therefore preferred to keep in our trial functions a few terms which are supposed to vanish according to (A.16) and watch their behavior when they are allowed to vary freely in the variation calculation. The result of our calculation seems to confirm the relation (A.16) since the parameters $c_{1,1,2}$ and $c_{2,1,2}$ of our 38- and 39-term functions are among the smallest terms.

C. Some Properties of Formal Solutions

Since Eq. (A.1) is very complicated, it is not easy to investigate the properties of its solutions in detail. As is seen from (A.11), however, some of the lowest order recurrence relations contain only a few nonvanishing terms and thus we can learn a little about the behavior of the solutions. In the following we shall outline some aspects of formal solutions.

(i) $l=0$. Because of the continuity condition (A.8), the only nonvanishing parameter is $c_{0,0,0}$.

(ii) $l=1$. The case $m=1$ is already included in (A.15) and (A.16). For $m=3$, one finds

$$c_{1,3,n}=\frac{3(n+2)}{2(n-1)(n-3)}c_{1,3,0}. \tag{A.17}$$

Therefore the sum

$$\sum_{n=0}^{\infty} c_{1,3,n} \tag{A.18}$$

diverges logarithmically. Similarly the sum $\sum_n c_{1,m,n}$ diverges for any fixed odd m. Since a sum like (A.18) may be regarded as the limit of a certain partial sum of our expansion (2.11), it leads to the divergence of (2.11), at the regular points of the potential $u=\pm t$. If we wish, we may avoid such trouble by assuming $c_{1,m,0}=0$ for all odd m $(\geqq 3)$.

For even m (and n), we obtain the following result:

$$c_{1,m,n}=0 \quad \text{if} \quad n\geqq m+2. \tag{A.19}$$

Thus there are at most $(m+2)/2$ nonvanishing terms for each even m. It is not known whether the series $\sum_m \sum_{n=0}^{m} c_{1,m,n}$ converges (conditionally perhaps) or not when summed over all even m.[28] If it diverges, it would lead to a singularity of the expansion (2.11) at the singular points $s=u$ of the potential energy.

(iii) In the general cases, one will have to treat various kinds of divergent partial sums. Divergences of some types may be removed consistently in the same manner as in the case of (A.18). If we try to eliminate all the divergences by removing them from our expansion, however, we might get into trouble of the same kind as that of the Hylleraas expansion. On the other hand, it is rather questionable whether one may remove *mechanically* all divergent partial sums of $c_{l,m,n}$, since our expansion (2.11) may be a conditionally convergent series, if it converges at all.

Thus it seems to be very hard to construct an actual solution starting from formal solutions. Meanwhile it would be equally useful if one could show that the actual eigenfunction can be approximated arbitrarily well when more and more terms of (2.11) are added to our trial function. To answer such a question, however, it is necessary to carry out a complicated mathematical analysis and it is not known yet whether the Hylleraas expansion (2.7) or our expansion (2.11) can lead to such a result or not.[9] For the moment, we therefore cannot tell which of the following alternatives will turn out valid: (a) Both (2.7) and (2.11) can approximate the actual eigenfunction arbitrarily closely. (b) Only (2.11) gives arbitrarily accurate approximations. (c) None of them work. In the last case, we may have to look for a totally different approach. On the basis of numerical computations, however, we are inclined to believe that the case (a) is valid. If this is true, we may have to determine why it is advantageous to introduce an expansion (2.11) when the simpler expansion (2.7) is sufficient.

D. Relation between the Hylleraas Expansion and Our Expansion

It is known[12] that the Hylleraas expansion (2.7) forms a complete set of functions in the domain of integration $0\leqq |t|\leqq u\leqq s<\infty$ with the weight function $u(s^2-t^2)$. Since our expansion (2.11) contains the Hylleraas expansion as one of its parts, it is obvious that (2.11) is also complete in the same sense. One might naturally ask whether (2.11) contains more terms than necessary.

In order to understand the situation, let us first consider a set

$$x^n;\quad n=0,1,2,\cdots, \tag{A.20}$$

defined on an interval (0,1). As is well known, (A.20) forms a complete set of functions in this interval. Now, if one removes the first few terms from (A.20) and

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[28] However, it is easily seen that a partial sum like $\sum_m c_{1,m,m}$ diverges for even m.

considers a new set

$$x^n;\quad n=n_0,\, n_0+1,\, n_0+2,\, \cdots, \tag{A.21}$$

it can be shown easily that this is also complete.[29] We have therefore two complete sets where one is a subset of the other. Such a situation may occur because the x^n's of (A.20) are not orthogonal to each other and thus the removal of some x^n's does not necessarily diminish the dimensions of the Hilbert space constructed on the set (A.20).

The orthonormal complete sets constructed from (A.20) and (A.21) may, however, look quite different. Thus a function $f(x)$ may be expanded in different ways in the different sets. Which set is more convenient will depend on the function we want to expand. It will be obvious however that the set (A.20) is more convenient than (A.21) when we expand a function which may be approximated easily by a linear combination of x^n with $n \leqq n_0$.

As is seen immediately, the relation of the Hylleraas expansion to our expansion is quite similar to that of (A.21) to (A.20). Thus the above argument suggests strongly that the actual eigenfunction of He atom will be approximated more easily and quickly by the generalized expansion (2.11) than the ordinary Hylleraas expansion (2.7), if it is possible at all.

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[29] The completeness of the set $\{x^n; n=0, 1, 2, \cdots\}$ may be expressed as follows: If $\int_0^1 f(x)x^n dx=0$ for $n=0, 1, 2, \cdots$, $f(x)$ must be identically zero. Therefore, to prove the completeness of (A.21), we have only to show that $f(x)=0$ derives from the relation $\int_0^1 f(x)x^n dx=0$ for $n=n_0, n_0+1, n_0+2, \cdots$. Now, since this relation can be rewritten as $\int_0^1 f(x)x^{n_0}x^n dx=0$ for $n=0, 1, 2, \cdots$, we obtain $f(x)x^{n_0}=0$. Thus $f(x)=0$ for $x\neq 0$. We may not have to worry about the value of $f(x)$ at $x=0$ since it does not contribute to the integral.

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Microwave Stark Effect Measurement of the Dipole Moment and Polarizability of Carbonyl Sulfide

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An improved microwave spectrograph has been developed which permits measurements of electric field intensity to one part in ten thousand. The instrument is employed to make precise Stark effect measurements. A method is also given for measuring the polarizability of polar molecules in a given rotational state. The transition $J=1\rightarrow 2$, $\Delta M=0$ for the ground vibrational state of carbonyl sulfide (OCS) was studied and the electric dipole moment was determined to be (0.7124 ± 0.0002) Debye units. In addition the polarizability anisotropy $(\alpha_{zz}-\alpha_{xx})$ was measured and found to be $(2.4\pm 3.0)\times 10^{-24}$ cm^3.

Effects caused by the fourth-order term in the perturbation expansion for the Stark Effect were observed and found to be in good agreement with theoretical predictions.

I. INTRODUCTION

THIS work was motivated by the need for improvement of the precision of Stark effect measurements in microwave molecular spectra in order to study higher order effects. The splitting of degenerate rotational energy levels through the Stark field interaction with nonvanishing electric dipole moments is in general many times greater than that caused by other Stark field interactions. Consequently, Stark displacements of rotational spectral lines are taken to be the result of dipole interactions even though other interactions are recognized and known to be present. For the most part, these weak interactions present no serious problems to the determination of electric dipole moments because of their very small effects; in addition the determination of field strengths in most microwave Stark cells is not sufficiently precise to establish their presence conclusively.

Because of its uncomplicated rotational spectrum and its lack of nuclear quadrupole coupling, carbonyl sulfide (OCS) has in recent years been the object of a number of microwave investigations.[1–3] Dakin, Good, and Coles[1] reported the first microwave Stark investigation of the molecule and later, Shulman and Townes[3] investigated its various vibrational state electric dipole moments. By using a set of carefully selected Stark

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[1] Dakin, Good, and Coles, Phys. Rev. **71**, 640 (1947).

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