his home and main duties in Leningrad. On presenting me a nice book, he told me that he would be happy to have the privilege of calling me "his old friend," and to this I consented on the condition that this be a reciprocal sort of privilege.

This was V. Fock, the second father of the famous Hartree–Fock method, whose range is far beyond the two-electron problem. The former one, Douglas R. Hartree, I shall never forget, as being one of the kindest persons I ever met, and whose premature death I sincerely regretted. The words he used of his own father, the other Hartree whose name appears in some joint publications, that he was the most wonderful artist in numerical calculations he ever know, may well be turned toward himself.

It is a sad thing to observe friends and colleagues and pioneers of the Atomic Age passing away. Among the nearly half a hundred persons I have touched upon in this review half of them are no longer alive and quite a number of them did not reach the normal length of a life. The latest, fairly normal cases, I know of are those of Niels Bohr and Charles Darwin. In this sense my review, although unintentionally, may still be called a little piece of history.

Above all we have to remember the giants of early atomic research in our century like Planck, Einstein, Rutherford, Bohr, and Sommerfeld, to mention only a few, and to these I should like to add as one of the most venerable representatives still alive from that time, Max Born of Göttingen, now, after twenty years of exile, living peacefully in the nearby Bad Pyrmont. His eightieth birthday was recently celebrated at the Physics Institute in Göttingen, on which occasion I had letters from him. Although his health is perhaps not the strongest, his mind is unusually active, and, in his memory, as I personally have learned from him, he holds a store of valuable reminiscences, particularly from early days in Berlin together with Albert Einstein.

You will forgive me that, if my lecture has turned too much towards early days in Göttingen, it has been rather to the honor of my dear friend and first teacher in theoretical atomic physics, Max Born.

REVIEWS OF MODERN PHYSICS VOLUME 35, NUMBER 3 JULY 1963

Two-Electron Atoms
II. A Perturbation Study of Some Excited States*

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I. INTRODUCTION

THE first paper of the present series,[1] hereafter referred to as I, investigated the ground state (1^1S) of the two-electron atomic species via a perturbational approach. The calculations have now been extended to include the 2^1S, 2^3S, 2^1P, and 2^3P states of the same system.

For purposes of definition, let the Hamiltonian H be written as

$$H = H_0 + \lambda H' \,.$$

When the Hamiltonian for the N-electron atom is written in appropriate units,[2] it is of this form with λ equal to the reciprocal nuclear charge Z^{-1}, and H' to the electron interaction terms. Thus, the atomic wave function for a given state is obtained as an expansion in inverse powers of the nuclear charge Z:

$$\psi = \textstyle\sum_n \psi_n Z^{-n} \,, \tag{1}$$

where summation to a particular n is called the nth-order wave function. Similarly, the energy is given by

$$E = \textstyle\sum_n \epsilon_n Z^{-n} \,, \tag{2}$$

where ϵ_n is referred to as the nth-order perturbation energy coefficient. For each state of an N-electron system, ϵ_0, ϵ_1, and ψ_0 are known exactly. The procedure used in the present series is a variational perturbation procedure due to Hylleraas.[3] It fur-

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* This work was supported by a grant from the National Aeronautics and Space Administration.

[1] R. E. Knight and C. W. Scherr, Phys. Rev. **128**, 2675 (1962).

[2] Units of length, Za_0; units of energy $2RhcZ^2$ are used unless it is explicitly indicated that atomic units are being used. These latter are units of length a_0, units of energy $2Rhc$.

[3] E. Hylleraas, Z. Physik **65**, 209 (1930); also see H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer–Verlag, Berlin, 1957), Vol. 35, Part 1, p. 208ff.

TABLE I. Perturbation energy coefficients in atomic units.

State	1^1S^a	2^1S	2^3S	2^1P	2^3P
ϵ_0	-1	$-5/8$	$-5/8$	$-5/8$	$-5/8$
ϵ_1	5/8	169/729	137/729	1705/6561	1481/6561
ϵ_2	-0.157666254	-0.11447618	-0.047409192	-0.15702123	-0.072992604
ϵ_3	0.008698679	0.00941508	-0.004871842	0.02612431	-0.016558519
Number of terms in ψ_1	70	60	60	83	83

[a] From the K wave function of I.

nishes an upper bound to the value of ϵ_2 via a variationally determined approximation to ψ_1. The calculation also gives an estimate for ϵ_3. Knight and Scherr[4,5] have extended the procedure to include approximations to the ψ_6, and thus obtain estimates of the energy coefficients through thirteenth order. The sixth-order wave function was sufficient to give an estimate of the total ground-state energy of the helium atom that is comparable in accuracy to the best previously, purely variationally, obtained results. The success of these calculations suggests an extension of the procedure to excited states. In the present paper ϵ_2, ϵ_3, and ψ_1 are calculated for the 2^1S, 2^3S, 2^1P, and 2^3P states of the two-electron atomic species.

II. METHOD

The variational equation for ϵ_2 is[3,6]

$$\epsilon_2(\psi_1') = \int d\tau\psi_1'(H_0-\epsilon_0)\psi_1' + 2\int d\tau\psi_1'(H'-\epsilon_1)\psi_0\,, \tag{3}$$

where ψ_1' is the variational trial function for ψ_1. An estimate of ϵ_3 is then obtained from

$$\epsilon_3(\psi_1') = \int d\tau\psi_1'(H'-\epsilon_1)\psi_1' - 2\epsilon_2(\psi_1')\int d\tau\psi_1'\psi_0\,. \tag{4}$$

Equations (3) and (4) are applicable to any state of the system, provided, of course, that the ϵ_0, ϵ_1, and ψ_0 appropriate to that system are used (v.i. and Appendix II).

For the 2^1S and 2^3S states, an expansion of the form

$$\psi_1 = e^{-\frac{1}{2}ks}\sum_{l,m,n\geq 0} A_{l,m,n}s^l u^n t^m \tag{5a}$$

was used, where s, t, and u are the well-known Hylleraas variables, and k is a variational parameter. The m is either even or odd as the state is either the singlet or the triplet. Initially, a form of ψ_1 was tried for the 2^3S state in which $k't$ was included in the exponent of the exponential factor. When optimization was attempted, k' became very small and seemed to make no significant difference in the results. Since considerable computational difficulties are introduced when k' is small, this factor was dropped from the expansion. For the P states, ψ_1 has the form[7]

$$\psi_1 = r_1 G\cos\theta_1 - r_2\tilde{G}\cos\theta_2\,, \tag{6a}$$

$$G(s,t,u) = \pm\tilde{G}(s,-t,u)\,, \tag{6b}$$

where the upper sign corresponds to the singlet and the lower, to the triplet. The function G was taken as an expansion of the form

$$G = e^{-\frac{1}{2}ks}\sum_{l,m,n\geq 0} B_{l,m,n}s^l u^n t^m\quad, \tag{5b}$$

where the expansion included both even and odd m. The expansions in Eq. (5) are both of the Hylleraas type, i.e., only positive powers of the metric variables are included.

The values of the ϵ_0, ϵ_1, ϵ_2, and ϵ_3 obtained for each of the states investigated as well as the previously reported 1^1S values are presented in Table I. Table I also reports the number of terms used in the expansions of Eq. (5).

Alternately, it is possible to use a variational wave function that is constructed from an expansion in Legendre polynomials. For the S states,

$$\psi_1 = \textstyle\sum_l \psi_{1l}(r_1,r_2)P_l\,(\cos\theta_{12})\;; \tag{7a}$$

and for the P states,

$$G = \textstyle\sum_l G^l\,(r_1,r_2)P_l\,(\cos\theta_{12})\,, \tag{7b}$$

where $P_l(x)$ is the lth Legendre polynomial and θ_{12} is the angle between the position vectors of the two electrons. When the summation is cut off at $l = 0, 1, 2\cdots$ the sets are referred to as the $S, P, D\cdots$ sets. The best limiting ϵ_2 that can be obtained from an infinity termed S is called an s limit (ϵ_2^0); from an

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[4] R. E. Knight and C. W. Scherr, J. Chem. Phys. **37**, 2503 (1962).

[5] C. W. Scherr and R. E. Knight, third paper of this series, Rev. Mod. Phys. **35**, 436 (1963), following paper.

[6] Throughout this paper all Ψ_n are chosen real.

[7] G. Breit, Phys. Rev. **35**, 569 (1930).

TABLE II. The *s*, *p*, and *d* limits in atomic units.

	ϵ_2^0	ϵ_2^1	ϵ_2^2	$\epsilon_2^{\text{total}}$	ϵ_2/ϵ_2^2
1^1S[a]	−0.12533198	−0.15177807	−0.15539043	−0.15766625	1.0146
2^3S	−0.045317648	−0.047219787	−0.047355088	−0.047409192	1.0011
2^1P	−0.14684854	−0.15465166	−0.15556727	−0.15702123	1.0093
2^3P	−0.070480500	−0.072670392	−0.072792279	−0.072992603	1.0028

[a] From the *S*, *P*, *D*... sets of I.

infinity termed *P*, a *p* limit (ϵ_2^1); etc. The notation is the same as that used in I. Table II displays ϵ_2^0, ϵ_2^1, and ϵ_2^2 for each of the states considered except the 2^1S.

The first-order expectation value of an operator, Ω, may be obtained from a knowledge of ψ_1 as follows [cf. I, Eq. (2)]:

$$\langle\Omega\rangle_0 + Z^{-1}\langle\Omega\rangle_1 = \int d\tau\psi_0\Omega\psi_0 + 2Z^{-1}\int d\tau\psi_0\Omega\psi_1 . \qquad (8)$$

Table III presents $\langle\Omega\rangle_1$ for a number of operators of interest.

III. DISCUSSION

In discussing the convergence of these variational perturbation calculations, it is necessary to distinguish two kinds of convergence. The first, which might appropriately be called the perturbational convergence, applies to the question of how far must the summations in Eqs. (1) and (2) be carried out in order to be assured of a desired degree of accuracy. This question is common to all perturbational approaches. The second kind of convergence, which might appropriately be called the variational convergence, is peculiar to a variational approach. It applies to the question of how well converged a particular set of ϵ_2, ϵ_3, and ψ_1 have been obtained from Eqs. (3) and (4), or, more generally, a set of ϵ_{2i}, ϵ_{2i+1}, and ψ_i from the appropriately modified form of Eqs. (3) and (4).[5]

In order to estimate the variational convergence it is desirable to have some exactly known $\langle\Omega\rangle_1$. Unfortunately, aside from a number of values of $\langle\Omega\rangle_1$ for the ground state,[8] almost nothing is available. It is shown in Appendix I that

$$\epsilon_1 = -\langle r_1^{-1} + r_2^{-1}\rangle_1 .$$

The relevant data are entered in Table IV. Since this operator is most sensitive to the form of the wave function in the same regions of space as those to which the energy is most sensitive, the accuracy of agreement shown in Table IV is most likely a good estimate of the accuracy to be claimed for ϵ_2. The ϵ_2 values reported in Tables I and II, with the exception of the 1^1S values, have been arbitrarily rounded to 8 significant figures, and the ϵ_3 values have been rounded to the same number of decimal places as their corresponding ϵ_2.

The perturbational convergence can provisionally be estimated from the data of Table V. In Table V the result of summing Eq. (2) through third order is compared with the very accurate results of Pekeris[9,10] for the total energy of a number of states of the hydrogen minus atom, helium atom, and singly ionized lithium atom. A more definitive discussion of the perturbational convergence is more appropri-

TABLE III. Some $\langle\Omega\rangle_1$ in atomic units.

Ω or ϵ_i	1^1S[a]	2^3S	2^1P	2^3P
$-\epsilon_2$	0.157666254	0.047409192	0.15702123	0.072992604
ϵ_3	0.008698679	−0.004871842	0.02612431	−0.016558519
$-\pi Z^{-2}\delta(\mathbf{r}_1)$	0.667639614[b]	0.1057962	−0.0105701	0.0436436
$-\pi Z^{-2}\delta(\mathbf{r}_{12})$	0.2429172	0.0	0.0398114	0.0
$-r_1^{-1} - r_2^{-1}$	0.625[b]	0.187928476	0.259865405	0.225724037
$Z^2(r_1 + r_2)$	1.125[b]	3.299712673	5.38797786	3.91000750
$Z^3(r_1^2 + r_2^2)$	4.78125[b]	45.4739771	64.6788400	47.0805329
$-\frac{1}{2} r_{12}^{-1}$	$-\epsilon_2$	0.047409192	0.157021230	0.072992604
$-Z \cos\theta_{12}$	0.133293412	0.047363870	0.265193693	−0.045474060
$Z^2 r_{12}$	1.02968827	3.19960728	5.59459327	3.64759916
$-Z^3\mathbf{r}_1\cdot\mathbf{r}_2$	0.378616569	0.501450559	1.63029965	0.08907800

[a] The 1^1S values are either exact or taken from the *K* wave function results of I.
[b] Exact value.

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[8] See I, and earlier references there.

[9] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959); **126**, 143, 1470 (1962).

[10] C. L. Pekeris, B. Schiff, and H. Lifson, Phys. Rev. **126**, 1057 (1962).

TABLE IV. The calculated values of $\langle r_1^{-1}+r_2^{-1}\rangle_1$ compared to the exact values.

	1^1S	2^1S	2^3S	2^1P	2^3P
$-\langle r_1^{-1}+r_2^{-1}\rangle_1$	0.624999812[a]	0.231809458	0.187928476	0.25986405	0.225724037
ϵ_1	0.625	0.2318244170	0.1879286694	0.259868922	0.2257277854

[a] Computed from the H set of I.

TABLE V. Third-order energies compared with the Pekeris[a] results in atomic units.

	1^1S[b]	2^3S	2^1P	2^3P	2^1S
$E_3(Z=1)$	−0.52396758	−0.48935237	−0.49602800	−0.48882334	−0.49823668
Pekeris	−0.527751014	−0.4993	...	...	−0.4981
$E_3(Z=2)$	−2.90331692	−2.17398777	−2.12422123	−2.12981629	−2.14611980
Pekeris	−2.90372438	−2.17522938	−2.1238429	−2.1331641	−2.14597404
$E_3(Z=3)$	−7.27976670	−5.11024713	−4.99370636	−5.02632875	−5.04086457
Pekeris	−7.27991341	−5.11072737	...	...	−5.04087673

[a] C. L. Pekeris, reference 9 (extrapolated values) and reference 10.
[b] From the K wave function of I.

ately left to a later paper in the present series where the results of calculations to higher order will be presented. In connection with Table V it is interesting to note that for the excited states the sums of the energy terms through third order are higher than Pekeris' values for the triplet states, but lower for the singlet states.[11] It may be of some use to tabulate the third-order energies. Table VI lists the third-order energies for each of the states considered for Z values from 1 to 10 inclusive. The entries in Table V are presented to an arbitrary 8 decimal places, but the entries in Table VI have been rounded to conform to the accuracy indicated by the agreement in Table IV.

The behavior of these first-order wave functions near the nucleus, interesting in itself, is also relevant in connection with the above discussions. Thus,[12] in atomic units

$$\psi(1^1S)\sim 1-1.1124Z^{-1}-(1-1.1485Z^{-1})Zs + 0.4630u+\cdots,$$

$$\psi(2^1S)\sim 1-1.7119Z^{-1}-(1-1.7718Z^{-1})Zs + 0.4042u+\cdots,$$

$$\begin{aligned}\psi(2^3S)\sim{}&(1-1.7801Z^{-1})Z^2st\\&-\tfrac{3}{4}(1-0.2540Z^{-1})Z^3s^2t\\&+\tfrac{1}{12}(1-1.4635Z^{-1})Z^3t^3+0.0326Zut\\&-0.0411Z^2u^2t+0.1914Z^2sut+\cdots,\end{aligned}$$

$$\begin{aligned}G(2^1P)\sim{}&1-2.6955Z^{-1}-\tfrac{3}{4}(1-2.7676Z^{-1})Zs\\&-\tfrac{1}{4}(1-2.4103Z^{-1})Zt+0.3946u+\cdots,\end{aligned}$$

$$\begin{aligned}G(2^3P)\sim{}&1-1.7874Z^{-1}-\tfrac{3}{4}(1-1.8269Z^{-1})Zs\\&-\tfrac{1}{4}(1-1.7426Z^{-1})Zt+0.2086u+\cdots,\end{aligned}$$

where $s=r_1+r_2$, $t=r_2-r_1$, and u is r_{12}. In the

TABLE VI. Third-order perturbation energies in atomic units.

System/state	1^1S	2^1S	2^3S	2^1P	2^3P
H^-	−0.5239676	−0.4982367	−0.4893524	−0.496028	−0.488823
He	−2.9033169	−2.1461198	−2.1739878	−2.124221	−2.129816
Li^+	−7.2797667	−5.0408646	−5.1102471	−4.993706	−5.026329
Be^{2+}	−13.6554916	−9.1848247	−9.2969125	−9.111014	−9.174221
B^{3+}	−22.0309265	−14.5784711	−14.7337402	−14.477452	−14.572665
C^{4+}	−32.4062165	−21.2219605	−21.4206492	−21.093454	−21.221386
N^{5+}	−44.7814236	−29.1153602	−29.3576045	−28.959207	−29.120264
O^{6+}	−59.1565789	−38.2587040	−38.5445888	−38.074804	−38.269240
F^{7+}	−75.5316997	−48.6520103	−48.9815925	−48.440298	−48.668282
Ne^{8+}	−93.9067964	−60.2952905	−60.6686097	−60.055720	−60.317371

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[11] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 1119ff, claim that energies through odd orders are upper bounds. These authors do not take the higher order terms into account properly, and so the theorem is not established. A similar claim by O. Sinanoglu, Phys. Rev. **122**, 493 (1961) is also in error. A correct discussion is given by P. O. Löwdin, J. Math. Phys. **3**, 979 (1962).

[12] The results previously reported in I for the 1^1S state contain a misprint in the coefficient of s.

limit of infinite Z, the coefficients of the terms not involving u approach their exact theoretical values.

The $s, p, d \cdots$ limits, of little apparent interest in themselves, are presented in Table II because expansions of this type have been discussed previously in connection with the computation of ϵ_2 values[13]; they have also been used occasionally for the construction[14] or analysis[15] of total wave functions. Usually the authors have been concerned with the ground state, and their conclusions are that the process is slowly convergent. However, a generalization may be misleading here, as the results in Table II seem to indicate that for different states the rate of convergence can vary greatly. Thus, the convergence seems to be more rapid for the triplets than for the singlets.

TABLE VII. Comparison with the results of Sharma and Coulson.

		ϵ_2	ϵ_3
2^1S	S and C[a]	-0.112990	$+0.004094$
	K and S[b]	-0.11447618	$+0.00941508$
2^3S	S and C[a]	-0.047330	-0.005040
	K and S[b]	-0.047409192	-0.004871842

[a] C. S. Sharma and C. A. Coulson, reference 16.
[b] This paper.

Sharma and Coulson[16] have previously calculated ϵ_2 and ϵ_3 for the 2^1S and 2^3S states. Their results are compared with the present results in Table VII. Since Sharma and Coulson used only 12 terms in their calculations, their results should not be so well converged as the present values. In this connection, it is well to note, as has already been pointed out by Sharma and Coulson, that the perturbation approach is not encumbered by the requirement of orthogonality between state functions. It is shown in Appendix II that Eq. (3), as it stands, is indeed a variational expression for the ϵ_2 of any atomic state if the ϵ_0, ϵ_1, and ψ_0 corresponding to that state are used. The result is general and convenient, as maintenance of orthogonality in an ordinary variational calculation frequently makes the calculation impractical.

Work is in progress on the extension of some of the above results to higher-order approximations. In addition, where practical, the calculations are being performed to a greater number of significant figures ("double precision").

ACKNOWLEDGMENTS

The computations were performed on the CDC 1604 located at the computation center of The University of Texas. The authors are very grateful to Professor A. L. Stewart (Belfast) for some critical remarks, and, in particular, for spotting our originally erroneous values for the 2^1P and 2^3P ϵ_3 values.

APPENDIX I. AN EXACT $\langle\Omega\rangle_1$

From the virial theorem,

$$E = \tfrac{1}{2}\langle V\rangle ,$$

where V is the potential energy operator. Let the perturbation be purely a potential energy term. The Hamiltonian can be written as

$$H = T_0 + V_0 + \lambda H' ,$$

where V_0 is the potential energy part of H_0 and $\lambda H'$ is the perturbation. Then to first order

$$\epsilon_0 + \lambda\epsilon_1 = \tfrac{1}{2}\langle V_0\rangle_0 + \tfrac{1}{2}\lambda\langle V_0\rangle_1 + \tfrac{1}{2}\lambda\langle H'\rangle_0 .$$

Further,

$$\epsilon_1 = \langle H'\rangle_0$$

and

$$\epsilon_0 = \tfrac{1}{2}\langle V_0\rangle_0 ,$$

so that

$$\epsilon_1 = \tfrac{1}{2}\langle V_0\rangle_1 .$$

For the special case of the N-electron atom

$$-\epsilon_1 = \sum_{i=1}^{N} < \frac{1}{r_i} >_1 . \qquad \text{(AI.1)}$$

The extent of agreement of the directly calculated sum on the right of Eq. (AI. 1) with the exactly known value of ϵ_1 constitutes both an indication of the extent to which ψ_1 satisfies the virial theorem, and also an independent check on the numerical accuracy of the calculations.

APPENDIX II. AN IMPORTANT ORTHOGONALITY THEOREM

Coulson and Sharma[16] have stated an orthogonality theorem without proof that can be put somewhat

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[13] C. Schwartz, Phys. Rev. **126**, 1015 (1962).

[14] L. C. Green, C. D. Chandler, and P. P. Rush, Phys. Rev. **104**, 1593 (1956); P. J. Luke, R. E. Meyerott, and W. W. Clendenin, Phys. Rev. **85**, 401 (1952); and H. Shull and P. O. Löwdin, J. Chem. Phys. **30**, 617 (1959).

[15] L. C. Green, M. M. Mulder, P. C. Milner, M. N. Lewis, J. W. Woll, E. K. Kolchin, and D. Mace, Phys. Rev. **96**, 319 (1954).

[16] C. S. Sharma and C. A. Coulson, Proc. Phys. Soc. (London) **80**, 81 (1962). *Note added in proof.* Quite recently, R. Perrin and A. L. Stewart, Proc. Phys. Soc. (London) **81**, 28 (1963), have published results for the same states as are considered by us, basing their calculations on an F-type wave function that uses a basis set of about 25 terms. Their results are more poorly converged than ours, of course, but are otherwise in satisfactory agreement, particularly for the s limit values.

more generally as follows: The approximate first-order wave functions obtained via Eq. (3) automatically satisfy the same orthogonality conditions as the exact first-order wave functions. In order to present a proof, define

$$(\psi,\Omega\phi) = \int d\tau\psi^*\Omega\phi \,,$$

$$(\psi,\phi) = \int d\tau\psi^*\phi \,,$$

and let the total wave function for a state p have the following perturbation expansion

$$\psi^p = \textstyle\sum_n \lambda^n \psi_n^p \,.$$

(For the particular case of an N-electron atomic system, $\lambda = Z^{-1}$, of course.) The orthogonality condition that two states, p and q, must satisfy is given by

$$(\psi_1^p,\psi_0^q) + (\psi_0^p,\psi_1^q) = 0 \,. \qquad \text{(AII.1)}$$

Let $\psi_1'^p$ be an approximation to ψ_1^p, and let

$$\psi_1'^p = \textstyle\sum_\alpha a_{1,\alpha}^p \psi_0^\alpha = a_{1,q}^p \psi_0^q + \phi_1^p \,, \qquad \text{(AII.2)}$$

so that

$$(\psi_0^q,\phi_1^p) = 0 \,,$$

and likewise

$$\psi_1'^q = \textstyle\sum_\alpha a_{1,\alpha}^q \psi_0^\alpha = a_{1,p}^q \psi_0^p + \phi_1^q$$

$$(\psi_0^p,\phi_1^q) = 0 \,. \qquad \text{(AII.3)}$$

Insertion of Eqs. (AII.2) and (AII.3) into Eq. (AII.1) yields that

$$(\psi_1'^p,\psi_0^q) + (\psi_0^p,\psi_1'^q) = a_{1,q}^p + a_{1,p}^q = 0 \qquad \text{(AII.4)}$$

must hold if the theorem is to be true. Set $\psi_1'^p$, say, into the variational equation, Eq. (3), and form the variance with respect to $a_{1,q}^p$. It follows that

$$a_{1,q}^p = (\psi_0^p,H'\psi_0^q)(\epsilon_0^p - \epsilon_0^q)^{-1} \,,$$

and likewise, by starting with ψ_1^q,

$$a_{1,p}^q = (\psi_0^q,H'\psi_0^p)(\epsilon_0^q - \epsilon_0^p)^{-1} \,.$$

A comparison of these last two equations shows that Eq. (AII.4) is valid, and hence that the theorem is established.

It is interesting to note to what extent the present 1^1S and 2^1S approximate first-order wave functions fulfill Eq. (AII.1). For the choice $p = 1^1S$, $q = 2^1S$, the computed values are

$$(\psi_0^p,\psi_1'^q) = -0.336939 \,,$$

$$(\psi_1'^p,\psi_0^q) = +0.336968 \,,$$

which sum to 2.9×10^{-5}. The exact magnitude of these integrals may be computed from elementary perturbation theory, and is $0.3369789\cdots$. Since the ϵ_2 values are regarded as converged to only six or seven decimal places, the extent of agreement obtained is satisfactory.

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Two-Electron Atoms
III. A Sixth-Order Perturbation Study of the 1^1S Ground State*

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I. INTRODUCTION

IN the two earlier papers of this series[1,2] the variational perturbation procedure of Hylleraas has been applied in first order to the ground state and to some of the lower lying excited states of the helium atom isoelectronic series. The straight (i.e., nonperturbational) variational treatment of these systems has been carried out to astonishing lengths by Pekeris[3] and others,[4] furnishing estimates of energy eigenvalues which are in some cases converged to as much as nine or more significant figures, and furnishing expectation values for other operators than the Hamiltonian with corresponding precision. With this background in mind it seems clear that for a perturbation treatment of N-electron atoms to be more than

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[1] R. E. Knight and C. W. Scherr, Phys. Rev. **128**, 2675 (1962).

[2] R. E. Knight and C. W. Scherr, Rev. Mod. Phys. **35**, 431 (1963), preceding paper.

[3] (a) C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); (b) **115**, 1216 (1959); (c) **126**, 143 (1962); (d) **126**, 1470 (1962).

[4] (a) T. Kinoshita, Phys. Rev. **105**, 1490 (1957); (b) **115**, 366 (1959).