Atomic Wave Functions for Some Excited States of Helium

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(Received January 16, 1935)

Normalized one-electron wave functions and the corresponding fields and energy parameters have been computed by the self-consistent field method for the following excited states of helium: $(1s)^2$, $(1s)(2s)$, $(1s)(2p)$, $(2s)^2$, $(2p)^2$ and $(2s)(2p)$. The results have been compared with those obtained by other methods and with experimental values.

INTRODUCTION

THE "self-consistent field" method of calculating atomic wave functions has been applied successfully to a number of atoms. So far as the authors are aware the following constitutes a reasonably complete list. O^{+3} to O, Ne, Na^+, Si^{+4}, Cl^-, K^+, Cu^+, Cs^+ have all been computed by D. R. Hartree and collaborators[1] with high accuracy. He, Li and Li^+, Be^+, Be^{+2} and Be, B, B^{+2} and B^{+3}, F^- and F, Ca^{+2}, C, N, Na and Hg have been calculated with less emphasis on extreme accuracy.[2] Rather recently Si^{+2} and Si^{+3} have been worked out approximately by H. L. Donley at Brown University (at present unpublished).

The present paper contains the results of similar calculations for certain excited states in helium. Wave functions for some excited states in helium-like atoms have already been obtained[3] by the use of variational methods. Opportunity is taken here to compare the results of the "self-consistent field" calculations both as to wave functions and energy parameters with those of other methods.

METHOD OF THE CALCULATIONS

The method of the "self-consistent field" has been described so often[4] and is now so familiar, that it is unnecessary to redescribe it in detail here. The limitations of the method have also been amply dealt with elsewhere.[5] We shall content ourselves with discussing briefly the technique used in the application of the method in the present calculations.

The states of helium investigated are: $(1s)^2$ (already worked out by Hartree, but repeated for the sake of completeness and to tabulate the wave function using smaller intervals of (r), $(1s)(2s)$, $(1s)(2p)$, $(2s)^2$, $(2p)^2$ and $(2s)(2p)$.

The only important point in which the method used in this paper differs from that recommended by Hartree is that direct integration was used throughout in preference to the so-called variation method* in obtaining the join of the inward and outward integrations of the appropriate Schrödinger equation. The extra work involved in this procedure was probably compensated for by the greater assurance of the elimination of errors. In any case the labor involved is by no means so great as might at first be thought. The successive approximations to the self-consistent field were in general made in each case by using the final field of the previous approximation. An important consideration is, of course, the assumption of the initial field, i.e., the initial Z_p (the effective nuclear charge for potential.† Several schemes have been investigated. The one generally followed may be briefly summarized as follows.

The wave function of He^+ in the $(1s)$ state was first tabulated and the corresponding field calculated. This at once provided an approximate initial Z_p for the $(2s)$ electron in the singly excited $(1s)(2s)$ state. From the distribution of

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[1] See, for example, Hartree, Proc. Roy. Soc. **A141**, 282 (1933) for a good survey of the method and some results. Hartree and Black, Proc. Roy. Soc. **A139**, 311 (1933); Hartree, Proc. Roy. Soc. **A143**, 506 (1934); J. McDougall, Proc. Roy. Soc. **A136**, 549 (1932); **A138**, 550 (1932).

[2] Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928); J. Hargreaves, Proc. Camb. Phil. Soc. **25**, 75 (1929); F. W. Brown, J. H. Bartlett and C. G. Dunn, Phys. Rev. **44**, 296 (1933); Hartree, Phys. Rev. **46**, 738 (1934); C. C. Torrance, Phys. Rev. **46**, 388 (1934); E. H. Kennard and E. Ramberg, Phys. Rev. **46**, 1034 (1934).

[3] See, for instance, C. Eckart, Phys. Rev. **36**, 878 (1930); J. P. Vinti, Phys. Rev. **37**, 448 (1931); F. G. Fender and J. P. Vinti, Phys. Rev. **46**, 77 (1934). Also E. A. Hylleraas, see reference 12.

[4] e.g., Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928).

[5] J. C. Slater, Phys. Rev. **35**, 210 (1929); V. Fock, Zeits. f. Physik **61**, 126 (1930).

* Cf. Hartree, reference 4, p. 95.

† Cf. Hartree, reference 4, p. 115.

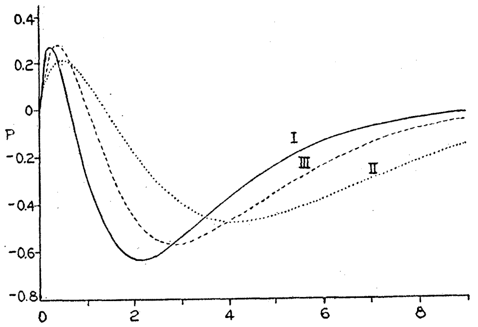

FIG. 1. Plot of the normalized wave function P.

charge of the $(2s)$ electron the initial Z_p for the $2s$ electron in the state $(2s)^2$ was computed. Similarly the distribution of charge for the $(1s)$ electron in the $(1s)(2s)$ state was used to compute an initial Z_p for the $(2p)$ electron in $(1s)(2p)$, and the $(2s)(2p)$ case was handled by starting from $(2s)^2$ and the $(2p)^2$ case from $(2s)(2p)$. The number of successive approximations required to attain self-consistency in these various cases varied from two to nine.

An alternative method of estimating the initial Z_p holding out some promise of value consisted in extrapolating the wave functions for the atoms in the second period of the natural system as calculated by Brown, Bartlett and Dunn.[2] If the reciprocals of the positions of the maxima for the $(2s)$ wave functions from boron to neon as given by them are plotted and extrapolated to beryllium, a "stretch" factor may be obtained allowing one to compute very simply the normalized $(2s)$ wave function for beryllium, which has in the normal state 2 $(1s)$ electrons and 2 $(2s)$ electrons. The latter move in the field of a nucleus of 4 positive charges and the 2 $(1s)$ electrons. Hence to a first approximation the field for large r at least may be considered to be like that for the $(2s)$ electrons in helium. This choice proves to be a rather satisfactory one as Fig. 1 shows. This presents the plot of the normalized wave function P corresponding to the assumption just indicated (curve I) compared with that obtained by using the initial Z_p from the method described in the previous paragraph (curve II) and with the final P function (curve III) for the $(2s)^2$ state. In this case the alternative method yields a rather better first approximation.[6]

RESULTS AND DISCUSSION

The principal results of the calculations are exhibited in Tables I, II, III and IV, presenting,

TABLE I. *Normalized wave functions* (P) *for helium.*

	$(1s)^2$	$(1s)(2s)$		$(2s)^2$	$(2s)(2p)$		$(2p)^2$	$(1s)(2p)$	
r	$(1s)$	$(1s)$	$(2s)$	$(2s)$	$(2s)$	$(2p)$	$(2p)$	$(1s)$	$(2p)$
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
.05	.2152	.2540	.0549	.0767	.0701	.0023	.0021	.2556	.0007
.10	.3900	.4597	.0993	.1382	.1265	.0089	.0079	.4626	.0025
.15	.5308	.6240	.1349	.1864	.1705	.0190	.0169	.6279	.0055
.20	.6428	.7530	.1628	.2228	.2038	.0322	.0286	.7576	.0093
.3	.7984	.9254	.1999	.2654	.2429	.0656	.0582	.9304	.0193
.4	.8853	1.0110	.2178	.2759	.2526	.1057	.0938	1.0157	.0317
.5	.9241	1.0358	.2213	.2620	.2403	.1497	.1329	1.0396	.0459
.6	.9296	1.0189	.2141	.2303	.2118	.1954	.1736	1.0215	.0617
.7	.9123	.9746	.1989	.1859	.1719	.2413	.2145	.9759	.0785
.8	.8798	.9134	.1778	.1330	.1242	.2859	.2545	.9134	.0962
.9	.8374	.8427	.1522	.0750	.0720	.3284	.2927	.8416	.1145
1.0	.7893	.7680	.1235	.0144	.0174	.3681	.3287	.7659	.1332
1.2	.6859	.6202	.0601	−.1065	−.0919	.4371	.3924	.6166	.1709
1.4	.5836	.4869	−.0069	−.2184	−.1940	.4913	.4440	.4826	.2081
1.6	.4891	.3746	−.0737	−.3155	−.2838	.5306	.4836	.3700	.2440
1.8	.4054	.2837	−.1377	−.3953	−.3592	.5561	.5117	.2794	.2776
2.0	.3331	.2122	−.1972	−.4576	−.4198	.5696	.5298	.2084	.3085
2.2	.2718	.1572	−.2514	−.5034	−.4664	.5728	.5390	.1539	.3364
2.4	.2205	.1155	−.2995	−.5345	−.5002	.5676	.5408	.1128	.3609
2.6	.1780	.0843	−.3413	−.5528	−.5227	.5557	.5365	.0822	.3821
2.8	.1431	.0612	−.3768	−.5603	−.5355	.5388	.5272	.0595	.4000
3.0	.1147	.0442	−.4061	−.5590	−.5400	.5180	.5140	.0429	.4145
3.2	.0916	.0318	−.4296	−.5507	−.5378	.4946	.4978	.0308	.4258
3.4	.0729	.0228	−.4476	−.5368	−.5300	.4695	.4793	.0220	.4341
3.6	.0580	.0163	−.4606	−.5187	−.5178	.4434	.4591	.0157	.4396
3.8	.0460	.0116	−.4690	−.4976	−.5021	.4168	.4379	.0112	.4425
4.0	.0364	.0082	−.4733	−.4742	−.4837	.3904	.4160	.0079	.4430
4.4	.0227	.0042	−.4713	−.4241	−.4419	.3390	.3717	.0040	.4376
4.8	.0140	.0021	−.4582	−.3729	−.3967	.2913	.3283	.0020	.4254
5.2	.0086	.0010	−.4369	−.3235	−.3511	2480	.2873	.0010	.4078
5.6	.0053	.0005	−.4102	−.2776	−.3073	.2096	.2495	.0005	.3864
6.0	.0032	$.0002_5$	−.3801	−.2361	−.2663	.1761	.2152	$.0002_5$	.3625
6.8	.0012	.0001	−.3162	−.1669	−.1953	.1223	.1573	.0001	.3110
7.6	.0004	.0000	−.2546	−.1153	−.1398	.0835	.1128	.0000	.2596
8.4	.0001		−.1999	−.0782	−.0981	.0562	.0797		.2119
9.2	.0000		−.1537	−.0523	−.0677	.0374	.0556		.1699
10.0			−.1163	−.0345	−.0462	.0246	.0384		.1342
12			−.0548	−.0117	−.0170	.0084	.0146		.0706
14			−.0243	−.0038	−.0059	.0028	.0054		.0351
16			−.0104	−.0012	−.0020	.0009	.0019		.0168
18			−.0043	−.0004	−.0007	.0003	.0007		.0078
20			−.0017	−.0001	−.0002	.0001	.0002		.0035
22			.0007	.0000	$-.0000_5$	.0000	.0001		.0016
24			.0003		−.0000		.0000		.0007
26			.0001						.0003
28			.0000						.0001
30									.0001

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[6] In this connection it may be remarked that a study was made of the use of the Fermi statistics as applied by Baker (cf. E. Fermi, Zeits. f. Physik **48**, 73 (1928); E. B. Baker, Phys. Rev. **36**, 630 (1930)) to ions of any order. This showed that for the heavier atoms the values obtained from Baker's table provide an excellent initial field for Hartree calculations. In particular in the case of Si^{+4} the former values of Z_p agree with those for the self-consistent field to within a maximum deviation of 2 percent.

TABLE Ia. *Values of P/r^{l+1} for small r.*

r	$(2s)(2p)$ $(2p)$	$(2p)^2$ $(2p)$	$(1s)(2p)$ $(2p)$
0.00	0.00000	0.00000	0.00000
.05	.04583	.04143	.01336
.10	.08721	.07884	.02547

respectively, the normalized wave functions (P values) for the various excited states, the contributions to Z (the effective nuclear charge for field intensity) of the various electrons, their contributions to Z_p,[7] and finally the values of the one-electron parameter ϵ. The figures in the first three tables are given to four decimal places, the accuracy of the computations being such that any error in P may be expected not to exceed 2 in the fourth place, and any error in Z or Z_p, 1 in the fourth place.[8] All values in the tables have actually been found by straightforward calculation: none has been interpolated. In fact the intervals used in the computation were in general half the size of those given in the tables. Table I(a) contains the values of P/r^{l+1} for small r in the case of the $2p$ electrons: these are of value in starting the outward integration. Corresponding values for the $(1s)$ and $(2s)$ states need not be tabulated since they can be computed with sufficient accuracy directly from P.

It may be noted in passing that the values of Z and Z_p for $(1s)^2$ do not agree precisely with those of Hartree (first paper in reference 2; note that the values there quoted refer to the two electrons and must be divided by 2 for comparison with those of the present paper). It should be remarked that Hartree in the case of helium limited the consistency between initial and final fields to 2 in the third decimal place which falls considerably short of the standard of accuracy set in the present paper. Incidentally as a check on the accuracy throughout the work, $\int_0^\infty dr \int_r^\infty P^2/r\,dr$ has been calculated for each electron. This gives Z_p for $r=0$ which should be unity for each electron. In the present work, it does so in every case to within 5 in the *fifth* decimal place.

The values of ϵ in Table IV are given in general to three decimals and may be assumed to be correct to that place: the extra place used in obtaining them has been discarded. Those values listed to four decimal places are expected to be in error by no more than 2 in the last place and the error for the $(1s)(2s)$ and $(1s)(2p)$ is probably considerably less. Table IV also includes $-2v_0$[*] and values of ϵ computed by other methods as mentioned in the Introduction. Comparison with experimental results is rather difficult since the latter are usually given in terms of the ionization energy of the atom in a given state[8a] while the present values are one-electron energy parameters. These can of course be used in connection with the wave functions to compute the total atomic energy values (cf. Hartree and Black[2]). For $(1s)^2$, $(2s)^2$ and $(2p)^2$ this calculation can be carried out approximately by assuming that ϵ itself is a good approximation to the ionization energy. The computed total energy for these three states then appears as 5.836, 1.4606 and 1.3861, respectively. The experimental value is known definitely only for the first and is 5.808. Some evidence with respect to the second is at hand in the recent experiments of Whiddington and Priestley[9] on energy losses in inelastic collisions in helium. Their work indicates a loss of 59.25 ± 0.12 volts in a single collision of an electron with a helium atom. Now the difference between the total energy in the $(1s)^2$ state (5.808) and that in the $(2s)^2$ state (1.4606) is 4.347, corresponding to 58.81 volts, which is very close to Whiddington and Priestley's value, making it seem likely that the transition corresponding to their indicated energy loss is really $(1s)^2-(2s)^2$. If the present calculations are at all correct it is much more likely this than $(1s)^2-(2p)^2$, although the possibility is not excluded that it may be $(1s)^2-(2s)(2p)$. Not until the total energy for the $(2s)(2p)$ is calculated can this point be decided.

In the $(1s)(2s)$ and $(1s)(2p)$ states since the ϵ value for the $(1s)$ in each case is much greater numerically than that for the 2-quantum electron, we may expect that the removal of the

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[7] Strictly speaking these are unnecessary. Their utility, however, dictates their inclusion here. Cf. Hartree, reference 1.

[8] This means of course that the maximum error to be expected in the *total* Z and Z_p (not tabulated since they are readily obtainable by summing the contributions of the individual electrons) is 2 in the fourth decimal place.

[*] Cf. Hartree, reference 4, p. 95.

[8a] e.g. Bacher and Goudsmit, *Atomic Energy States.*

[9] R. Whiddington and H. Priestley, Proc. Roy. Soc. **A145**. 462 (1934).

TABLE II. *Contributions to Z of the various electrons in helium.*

r	$(1s)^2$	$(1s)(2s)$		$(2s)^2$	$(2s)(2p)$		$(2p)^2$	$(1s)(2p)$	
	$(1s)$	$(1s)$	$(2s)$	$(2s)$	$(2s)$	$(2p)$	$(2p)$	$(1s)$	$(2p)$
0.00	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
.05	.9992	.9989	.9999	.9999	.9999	1.0000	1.0000	.9989	1.0000
.10	.9944	.9922	.9996	.9993	.9994	1.0000	1.0000	.9921	1.0000
.15	.9836	.9772	.9989	.9980	.9983	1.0000	1.0000	.9770	1.0000
.20	.9662	.9533	.9978	.9958	.9965	1.0000	1.0000	.9527	1.0000
.3	.9131	.8812	.9945	.9897	.9914	.9997	0.9998	.8798	1.0000
.4	.8414	.7862	.9900	.9823	.9851	.9990	.9992	.7838	.9999
.5	.7590	.6806	.9853	.9749	.9790	.9973	.9979	.6774	.9998
.6	.6726	.5744	.9804	.9688	.9738	.9943	.9955	.5706	.9995
.7	.5875	.4747	.9761	.9644	.9700	.9896	.9918	.4704	.9990
.8	.5071	.3854	.9725	.9618	.9679	.9826	.9863	.3810	.9982
.9	.4332	.3081	.9698	.9607	.9669	.9731	.9787	.3038	.9971
1.0	.3670	.2432	.9679	.9605	.9667	.9610	.9691	.2392	.9956
1.2	.2579	.1467	.9661	.9598	.9662	.9311	.9429	.1434	.9909
1.4	.1773	.0854	.9659	.9542	.9619	.8876	.9077	.0831	.9837
1.6	.1197	.0484	.9655	.9397	.9502	.8349	.8644	.0468	.9735
1.8	.0797	.0269	.9632	.9141	.9293	.7755	.8147	.0258	.9598
2.0	.0525	.0146	.9575	.8774	.8987	.7117	.7603	.0140	.9426
2.2	.0342	.0079	.9473	.8310	.8592	.6461	.7030	.0075	.9218
2.4	.0221	.0042	.9321	.7768	.8123	.5807	.6446	.0039	.8974
2.6	.0142	.0022	.9114	.7175	.7598	.5173	.5865	.0021	.8697
2.8	.0091	.0011	.8856	.6554	.7037	.4571	.5298	.0011	.8391
3.0	.0058	.0006	.8548	.5923	.6457	.4011	.4756	.0005	.8059
3.2	.0036	.0003	.8198	.5309	.5875	.3496	.4243	.0003	.7705
3.4	.0023	$.0002^-$	.7812	.4717	.5304	.3030	.3765	.0001	.7335
3.6	.0014	.0001	.7399	.4159	.4754	.2611	.3325	.0001	.6953
3.8	.0009	0.0000	.6966	.3642	.4234	.2240	.2922		.6564
4.0	.0006		.6522	.3170	.3747	.1913	.2558		.6163
4.4	.0002		.5625	.2361	.2888	.1379	.1937		.5393
4.8	.0001		.4758	.1725	.2184	.0981	.1447		.4647
5.2			.3955	.1240	.1624	.0690	.1068		.3951
5.6			.3236	.0878	.1191	.0480	.0780		.3320
6.0			.2611	.0615	.0862	.0331	.0564		.2758
6.8			.1638	.0292	.0437	.0154	.0288		.1848
7.6			.0985	.0134	.0214	.0069	.0143		.1193
8.4			.0573	.0060	.0102	.0031	.0069		.0752
9.2			.0323	.0026	.0047	.0013	.0033		.0460
10.0			.0178	.0011	.0021	.0006	.0015		.0276
12			.0037	.0001	.0003	0.0001	.0002		.0071
14			.0007		0.0000	0.0000			.0017
16			0.0001						.0004
18			0.0000						.0001
20									
22									

TABLE III. *Contributions to Z_p of the various electrons in helium.*

r	$(1s)^2$	$(1s)(2s)$		$(2s)$	$(2s)(2p)$		$(2p)^2$	$(1s)(2p)$	
	$(1s)$	$(1s)$	$(2s)$	$(2s)^2$	$(2s)$	$(2p)$	$(2p)$	$(1s)$	$(2p)$
0.00	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
.05	.9161	.9013	.9850	.9788	.9804	.9778	.9795	.9007	.9873
.10	.8344	.8057	.9702	.9580	.9611	.9555	.9591	.8046	.9745
.15	.7564	.7154	.9556	.9375	.9422	.9333	.9386	.7138	.9618
.20	.6832	.6314	.9413	.9176	.9237	.9110	.9182	.6295	.9491
.3	.5522	.4849	.9137	.8798	.8883	.8666	.8773	.4824	.9236
.4	.4423	.3667	.8875	.8442	.8549	.8223	.8366	.3640	.8982
.5	.3520	.2740	.8624	.8105	.8231	.7783	.7960	.2713	.8727
.6	.2787	.2027	.8383	.7783	.7924	.7348	.7559	.2002	.8473
.7	.2198	.1488	.8150	.7469	.7625	.6918	.7162	.1465	.8220
.8	.1728	.1084	.7922	.7160	.7330	.6498	.6772	.1065	.7968
.9	.1356	.0786	.7699	.6854	.7037	.6087	.6390	.0770	.7717
1.0	.1061	.0566	.7478	.6548	.6745	.5688	.6018	.0553	.7467
1.2	.0647	.0291	.7039	.5937	.6161	.4933	.5306	.0282	.6973
1.4	.0393	.0147	.6603	.5330	.5580	.4241	.4646	.0142	.6489
1.6	.0237	.0074	.6166	.4737	.5010	.3617	.4041	.0071	.6017
1.8	.0143	.0037	.5731	.4169	.4460	.3064	.3495	.0035	.5561
2.0	.0086	.0018	.5300	.3635	.3938	.2579	.3007	.0017	.5121
2.2	.0051	.0009	.4878	.3143	.3452	.2159	.2575	.0008	.4700
2.4	.0031	.0004	.4466	.2696	.3005	.1799	.2196	.0004	.4300
2.6	.0018	.0002	.4070	.2297	.2599	.1492	.1865	.0002	.3921
2.8	.0011	.0001	.3691	.1945	.2236	.1233	.1579	.0001	.3569
3.0	.0006	$.0000_5$	.3332	.1638	.1913	.1016	.1333	.0000	.3232
3.2	.0004		.2996	.1372	.1629	.0834	.1121		.2921
3.4	.0002		.2682	.1144	.1381	.0683	.0941		.2634
3.6	.0001		.2392	.0950	.1167	.0558	.0788		.2369
3.8	.0001		.2126	.0786	.0982	.0454	.0658		.2124
4.0	.0000		.1882	.0648	.0823	.0369	.0549		.1900
4.4			.1462	.0437	.0574	.0243	.0379		.1511
4.8			.1122	.0291	.0395	.0158	.0260		.1191
5.2			.0852	.0192	.0271	.0103	.0177		.0933
5.6			.0641	.0126	.0184	.0066	.0120		.0724
6.0			.0478	.0082	.0124	.0042	.0081		.0559
6.8			.0260	.0034	.0055	.0017	.0036		.0327
7.6			.0138	.0014	.0024	.0007	.0016		.0187
8.4			.0071	.0006	.0011	.0002	.0007		.0105
9.2			.0036	$.0003^-$	.0005	.0001	.0003		.0058
10.0			.0018	.0001	.0002		.0001		.0032
12			.0003		.0000		.0000		.0007
14			$.0001^-$						.0001
16									
18									
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TABLE IV. *One-electron energy parameters.*

STATE	ELECTRON	$-2v_0$	ϵ CALC.	ϵ CALC. BY OTHER METHODS
$(1s)^2$	$(1s)$	3.374	1.836	1.809[a]
$(1s)(2s)$	$(1s)$	3.972	3.469	
	$(2s)$	0.600	0.3068	
$(2s)^2$	$(2s)$	0.950	0.4606	0.49[b]
$(2s)(2p)$	$(2s)$	0.785	0.4195	
	$(2p)$	0.890	0.4443	
$(2p)^2$	$(2p)$	0.818	0.3861	
$(1s)(2p)$	$(1s)$	3.995	3.496	
	$(2p)$	0.510	0.2522	

[a] E. A. Hylleraas, Zeits. f. Physik **65**, 209 (1930).
[b] F. G. Fender and J. P. Vinti, Phys. Rev. **46**, 78 (1934).

latter electron will not materially affect the wave function of the (1s) electron and hence the ionization energy to a fair approximation will be equal to the (2*s*) or (2*p*) value of ϵ. We can then compare with the experimental values quoted by Bacher and Goudsmit (reference 8a, p. 220). They give 0.3506 for the (1*s*)(2*s*) ^3S and 0.2921 for (1*s*)(2*s*) ^1S; the latter is in fair agreement with our computed value. The experimental value for (1*s*)(2*p*) ^3P is 0.2665 and that for (1*s*)(2*p*) ^1P is 0.2478; the latter again agrees fairly well with our 0.2522. In each case the agreement appears to

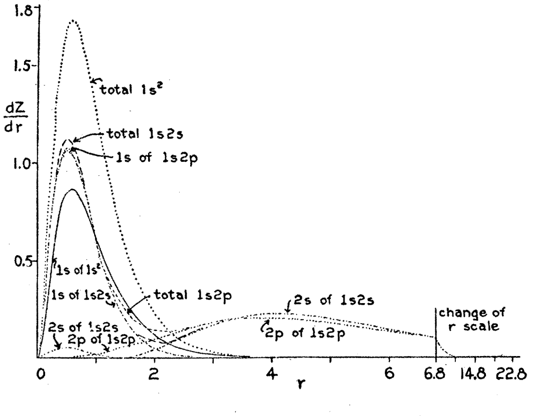

FIG. 2. Radial charge density for helium.

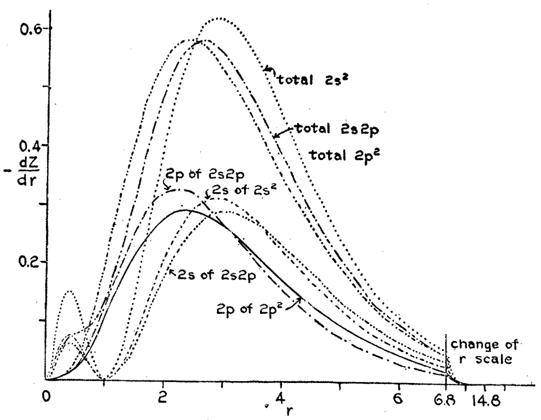

FIG. 3. Radial charge density for helium.

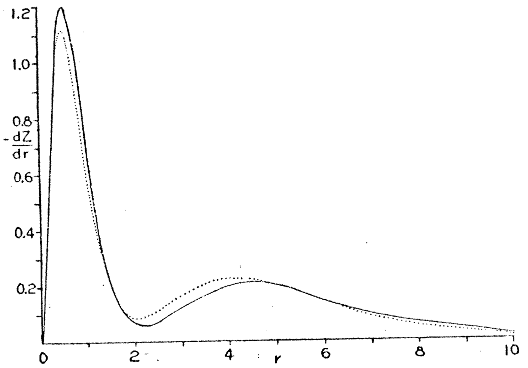

FIG. 4. Total radial charge density for He$(1s)(2s)$. Solid line, Vinti; dotted line, present paper.

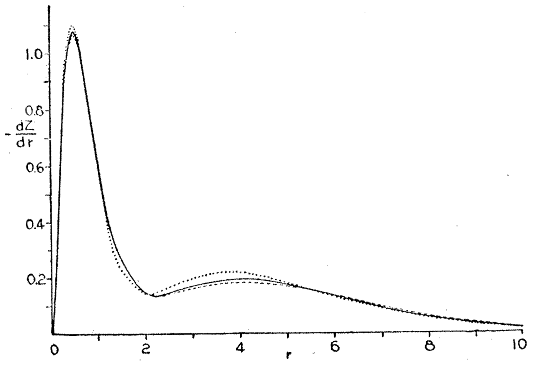

FIG. 5. Total radial charge density for He$(1s)(2p)$. Solid line, present paper; dotted line, Eckart $(1s)(2p)^3p$; dash line, Eckart $(1s)(2p)^1p$.

be better with the singlet than with the triplet state. One might indeed expect that the self-consistent field value would agree better with some average of the singlet and triplet energies. It must be emphasized again, however, that the ϵ values are one-electron energy parameters only and further discussion of this question must await the calculation of the *total* energies of the various states. These are now under way and will be published shortly. It may be remarked that Hylleraas[10] has recently computed by the general method of his previous papers many discrete energy levels for singly excited helium, such as both the singlet and triplet terms of $(1s)(2s)$ and $(1s)(2p)$. He neglects the effect of the excitation on the inner electron. The agreement of his results with experiment is in general excellent.

In line with the procedure of some other writers, curves are presented (Figs. 2 and 3) exhibiting the radial charge density $-dZ/dr$ as a function of r for the individual electrons as well as the completed group in the various states. These are self-explanatory and need no comment.

A further comparison of the results of the present calculations with those of other methods is suggested in connection with the radial charge density. Using a variational method Vinti[3] has found an analytic wave function for the $(1s)(2s)$ ^1S state. After the function has been suitably normalized to unity the radial charge density for the two electrons may be computed by multiplying the integral $2\int_0^\infty 4\pi r_2^2|\psi|^2 dr_2$ (a function of $r_1 = r$) by $4\pi r^2$. The result is plotted in Fig. 4 and compared with $-dZ/dr$ for the corresponding case of the present paper. The agreement is

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[10] E. A. Hylleraas, Zeits. f. Physik **83**, 739 (1933).

rather good considering the difference in the methods. Fig. 5 shows a similar comparison between the radial charge density for $(1s)(2p)\ ^1P$ and $(1s)(2p)\ ^3P$ as computed by Eckart[3] by the variational method and $-dZ/dr$ for this state from the self-consistent field calculations. The agreement is again seen to be very gratifying. It is interesting to note that the density for the singlet state of Eckart agrees better with the present values than does that for the triplet.

The authors wish to express their gratitude to Dr. F. E. White for his kind assistance in connection with the drawing of the curves and with some of the calculations.

MAY 1, 1935 PHYSICAL REVIEW VOLUME 47

The van der Waals Interaction of Hydrogen Atoms

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(Received March 18, 1935)

The van der Waals interaction energy of two hydrogen atoms at large internuclear distances is discussed by the use of a linear variation function. By including in the variation function, in addition to the unperturbed wave function, 26 terms for the dipole-dipole interaction, 17 for the dipole-quadrupole interaction, and 26 for the quadrupole-quadrupole interaction, the interaction energy is evaluated as

$$W''=-\frac{6.49903\ e^2}{a_0\,\rho^6}-\frac{124.399\ e^2}{a_0\,\rho^8}-\frac{1135.21\ e^2}{a_0\,\rho^{10}}-\cdots,$$

in which $\rho=R/a_0$, with R the internuclear distance. Some properties of the functions $F_{\nu\lambda\mu}(\xi,\vartheta,\varphi)$, which are orthogonal for the volume element $\xi d\xi\sin\theta d\theta d\varphi$, are discussed, and their usefulness in atomic problems is pointed out.

INTRODUCTION

An approximate second-order perturbation treatment of the inverse sixth power interaction energy of two hydrogen atoms a large distance apart (corresponding to the so-called dipole-dipole van der Waals attraction) was given in 1930 by Eisenschitz and London.[1] This treatment led to the result $W''=-e^2A/a_0\rho^6$, with $\rho=r_{AB}/a_0$ (r_{AB} being the internuclear distance for the two atoms), A being evaluated as 6.47. Applications of the variation method by Hassé[2] and by Slater and Kirkwood[3] verified this result essentially, the constant A being shown to be equal to or greater than 6.4976.

As early as 1927 this problem had been attacked by Wang,[4] using the method developed by Epstein[5] for the treatment of the Stark effect. Wang claimed to have obtained an exact solution; it was, however, pointed out by Eisenschitz and London that Wang's result is necessarily in error. It seemed to us possible that Wang's work might have contained only a numerical error, and that the method might actually be capable of giving an exact solution. Because of the usefulness which a method of exact solution of problems of this sort would have, we thought it worth while to study the problem thoroughly. We have found that the method used by Wang does not give an exact solution,[6] but that it can be extended to give as closely approximate a solution as is desired. The results of the treatment are communicated in this paper.

A rough treatment of the dipole-quadrupole and quadrupole-quadrupole interactions of two hydrogen atoms has been published by Mar-

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[1] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930).

[2] H. R. Hassé, Proc. Camb. Phil. Soc. **27**, 66 (1931).

[3] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

[4] S. C. Wang, Physik. Zeits. **28**, 663 (1927).

[5] P. S. Epstein, Phys. Rev. **28**, 695 (1926).

[6] Wang does not present the final steps in his calculation in detail, but states that he set up a sixth degree secular equation from which he obtained an accurate value for the energy. We believe that the error in his treatment occurs at this point.