Hartree Fields of Carbon

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A new method of integrating the Hartree equations for the charge distributions of the electrons in an atom is described and the wave functions for the ground state and the first excited state of carbon are tabulated.

INTRODUCTION

IN Hartree's method for determining a "self-consistent" field of an atom, a set of charge distributions is assumed for the various electrons in the atom, the potentials are computed from them, the radial parts of the wave equations are solved and the resulting charge distributions compared with those assumed. If the two sets of distributions disagree, a new distribution is assumed and the process repeated. In this paper a method is developed whereby the variation of functions (charge distributions) is reduced to the variation of two parameters for each type of electron present in the atom. By this method it is possible to calculate the requisite changes in the assumed values of the parameters so that the convergence of the successive approximations to the charge distributions is very rapid.

THEORY

The radial part of the wave equation for a stationary state of an electron in an atom can be reduced to the form[1]

$$d^2P/dr^2+\{2v(r)-\epsilon-l(l+1)/r^2\}P=0, \qquad (1)$$

where $v(r)$ is the (negative) potential of the field in which the electron is moving, ϵ is the energy of the electron in Hartree units, and l is the orbital angular momentum quantum number. The ground state of carbon has the configuration $(1s)^2$ $(2s)^2$ $(2p)^2$. Let $R(r)$, $S(r)$ and $T(r)$ be the solutions of the (radial parts) of the wave equations for these electrons; then the squares of these solutions represent the charge distributions of these electrons. It is readily seen that Eq. (1) can be put in the following forms for the $1s$, $2s$ and $2p$ electrons, respectively:

$$\frac{d^2R}{dr^2}+\left\{\frac{12}{r}+2\int_0^r\frac{1}{s^2}\int_0^s(R^2+2S^2+2T^2)dtds-E\right\}R=0, \qquad (2a)$$

$$\frac{d^2S}{dr^2}+\left\{\frac{12}{r}+2\int_0^r\frac{1}{s^2}\int_0^s(2R^2+S^2+2T^2)dtds-F\right\}S=0, \qquad (2b)$$

$$\frac{d^2T}{dr^2}+\left\{\frac{12}{r}-\frac{2}{r^2}+2\int_0^r\frac{1}{s^2}\int_0^s(2R^2+2S^2+T^2)dtds-G\right\}T=0, \qquad (2c)$$

where

$$E=2\int_0^\infty(1/r)(R^2+2S^2+2T^2)dr+\epsilon$$

and where F and G are defined in an analogous manner. The three Eqs. (2) must be solved under the following boundary conditions:

$$R(0)=S(0)=T(0)=R(\infty)=S(\infty)=T(\infty)=0, \qquad (3)$$

$$\int_0^\infty R^2dr=\int_0^\infty S^2dr=\int_0^\infty T^2dr=1. \qquad (4)$$

The numerical integration of the Eqs. (2) is simple and needs no explanation. It should be noted that the computation of the integrals (4) is merely an incidental part of the integration of the Eqs. (2) and hence involves no extra labor. The solutions of (2) are determined most con-

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[1] J. McDougall, Proc. Roy. Soc. **A138**, 552 (1932).

veniently by conditions of the form

$$R(0)=S(0)=T(0)=0,$$
$$R(0.01)=R_1,\quad S(0.01)=S_1,\quad T(0.01)=T_1, \tag{5}$$

where R_1, S_1 and T_1 may be any assigned values. Hence it is necessary only to determine the values of the six parameters E, F, G, R_1, S_1 and T_1 so that the conditions (3) and (4) are satisfied. The best method for determining these values is as follows: let $R^\circ(r)$, $S^\circ(r)$ and $T^\circ(r)$ satisfy conditions (3) and (4) and approximate the desired solutions of (2). (R°, S° and T° were obtained for carbon by interpolation from other atoms.) Assuming that R°, S° and T° constitute a solution of (2a) it is possible to tabulate with the aid of (2a) the variations of R°,

$$\int_0^r R^{\circ 2}ds, \quad \text{and} \quad \int_0^r s^{-2}\int_0^s R^{\circ 2}dtds$$

TABLE I. *Tabulated one-electron functions for carbon.*

r	Ground State $1s^2\,2s^2\,2p^2$			Excited State $1s^2\,2s\,2p^3$		
	$1s$ R	$2s$ S	$2p$ T	$1s$ R	$2s$ S	$2p$ T
0.01	0.2602	0.0575	0.0005	0.2607	0.0578	0.0005
2	.4902	.1083	.0020	.4911	.1088	.0020
3	.6928	.1529	.0043	.6941	.1536	.0044
4	.8704	.1919	.0075	.8720	.1927	.0076
5	1.0254	.2255	.0114	1.0273	.2265	.0116
6	1.1599	.2544	.0160	1.1619	.2555	.0162
7	1.2758	.2789	.0212	1.2780	.2801	.0215
8	1.3749	.2994	.0269	1.3772	.3006	.0273
9	1.4588	.3161	.0332	1.4611	.3174	.0337
.10	1.5289	.3295	.0399	1.5313	.3308	.0405
1	1.5866	.3397	.0470	1.5890	.3411	.0477
2	1.6332	.3471	.0545	1.6355	.3485	.0554
3	1.6697	.3518	.0624	1.6719	.3532	.0633
4	1.6971	.3542	.0705	1.6993	.3555	.0716
5	1.7165	.3544	.0790	1.7186	.3557	.0802
6	1.7286	.3525	.0877	1.7306	.3538	.0890
7	1.7343	.3488	.0966	1.7361	.3500	.0981
8	1.7342	.3435	.1057	1.7358	.3446	.1073
9	1.7289	.3366	.1150	1.7304	.3376	.1168
.20	1.7191	.3283	.1244	1.7204	.3292	.1264
.22	1.6879	.3080	.1437	1.6888	.3088	.1459
4	1.6443	.2834	.1634	1.6449	.2840	.1659
6	1.5913	.2554	.1833	1.5916	.2558	.1861
8	1.5316	.2247	.2034	1.5315	.2249	.2064
.30	1.4670	.1917	.2235	1.4666	.1917	.2268
2	1.3994	.1570	.2435	1.3987	.1567	.2472
4	1.3301	.1210	.2635	1.3291	.1206	.2674
6	1.2602	.0841	.2832	1.2590	.0834	.2874
8	1.1905	.0466	.3026	1.1892	.0458	.3071
.40	1.1219	+.0088	.3217	1.1204	+.0078	.3265
2	1.0549	−.0290	.3405	1.0532	−.0302	.3455
4	.9898	.0667	.3589	.9880	.0681	.3641
6	.9269	.1040	.3768	.9251	.1056	.3823
8	.8666	.1409	.3942	.8647	.1426	.4000
.50	.8090	.1771	.4111	.8070	.1790	.4172
2	.7541	.2125	.4275	.7521	.2146	.4338
4	.7020	.2471	.4434	.7000	.2493	.4499
6	.6527	.2808	.4587	,6508	.2831	.4655
8	.6061	.3135	.4735	.6043	.3160	.4805
.60	.5623	.3451	.4876	.5605	.3477	.4949
.64	.4826	.4050	.5143	.4809	.4079	.5220
.68	.4128	.4603	.5387	.4112	.4634	.5468
.72	.3520	.5109	.5608	.3506	.5142	.5693
.76	.2994	.5567	.5807	.2981	.5603	.5896
.80	.2540	.5979	.5985	.2529	.6017	.6077
.84	.2151	.6345	.6142	.2141	.6385	.6238
.88	.1818	.6668	.6280	.1809	.6709	.6378
.92	.1534	.6949	.6399	.1526	.6992	.6500
.96	.1292	.7190	.6501	.1285	.7234	.6604
1.00	.1087	.7395	.6587	.1082	.7439	.6691
1.04	.0913	.7564	.6657	.0909	.7609	.6762
1.08	767	.7701	.6713	763	.7747	.6819
1.12	643	.7808	.6756	640	.7854	.6862
1.16	538	.7887	.6787	536	.7932	.6892
1.20	451	.7941	.6806	449	.7985	.6911
1.28	315	.7980	.6815	314	.8022	.6916
1.36	221	.7941	.6788	220	.7980	.6885
1.44	155	.7839	.6732	154	.7874	.6823
1.52	108	.7686	.6652	108	.7716	.6736
1.60	76	.7494	.6552	76	.7518	.6628
1.68	53	.7270	.6435	53	.7288	.6502
1.76	37	.7023	.6306	37	.7035	.6363
1.84	26	.6760	.6167	26	.6765	.6214
1.92	18	.6486	.6020	18	.6484	.6056
2.00	13	.6205	.5866	13	.6197	.5892
2.08	9	0.5922	0.5709	9	0.5908	0.5724
2.16	6	.5640	.5548	6	.5620	.5553
2.24	4	.5360	.5386	4	.5334	.5380
2.32	3	.5085	.5223	3	.5054	.5207
2.40	2	.4816	.5060	2	.4781	.5034
2.48	2	.4555	.4898	2	.4516	.4863
2.56	1	.4303	.4738	1	.4260	.4693
2.72	1	.3825	.4422	1	.3776	.4362
2.88	0	.3387	.4117	0	.3334	.4043
3.04		.2988	.3824		.2933	.3738
3.20		.2628	.3544		.2572	.3449
3.36		.2306	.3279		.2250	.3176
3.52		.2018	.3029		.1963	.2920
3.68		.1763	.2794		.1710	.2681
3.84		.1537	.2573		.1486	.2457
4.00		.1337	.2366		.1289	.2249
4.16		.1162	.2173		.1117	.2057
4.32		.1008	.1994		.0966	.1878
4.48		.0874	.1827		835	.1713
4.64		756	.1673		720	.1562
4.80		654	.1530		621	.1422
4.96		564	.1398		535	.1294
5.12		487	.1277		460	.1176
5.28		419	.1165		395	.1068
5.44		361	.1061		339	.0969
5.60		311	.0967		291	879
5.76		267	880		250	797
5.92		229	800		214	722
6.08		197	728		183	653
6.24		169	661		157	591
6.40		145	600		134	535
6.72		107	494		98	437
7.04		79	406		72	356
7.36		58	333		53	290
7.68		42	273		39	236
8.00		31	223		28	192
8.32		23	182		21	156
8.64		17	149		15	127
8.96		12	122		11	103
9.28		9	100		8	84
9.60		7	82		6	68
9.92		5	67		4	55
10.24		4	54		3	45
10.56		3	45		2	37
10.88		2	36		2	30
11.20		1	30		1	24
11.52		1	24		1	20
11.84		1	20		1	16
12.16		1	16		1	13
12.48		0	13		0	11
12.80			11			9
13.12			9			7
13.44			7			6
13.76			6			5
14.08			5			4
14.40			4			3
14.72			3			2
15.04			3			2
15.36			2			2
15.68			2			1
16.00			1			1
16.32			1			1
16.64			1			1
16.96			1			1
17.28			1			0
17.60			0			

arising (1) from the variation ΔE° of E° (where E° is an approximate value of E obtained, for example, by interpolation from other atoms) and (2) from the variation of $R_1{}^\circ$ to $kR_1{}^\circ$ (where $R_1{}^\circ = R^\circ\ (0.01)$ and k is a constant of proportionality which is nearly unity). Similar tabulations of the variations of S°,

$$\int_0^r S^{\circ 2}ds,\quad \int_0^r s^{-2}\int_0^s S^{\circ 2}dtds,\quad T^\circ,\quad \int_0^r T^{\circ 2}ds$$

and

$$\int_0^r s^{-2}\int_0^s T^{\circ 2}dtds,$$

may be made with the aid of (2*b*) and (2*c*). Although theoretically it would be necessary to tabulate all the variations of R°, S° and T° caused by variations of each of the six parameters, experience shows that only two more tabulations are needed: the variations of S°,

$$\int_0^r S^{\circ 2}ds \quad\text{and}\quad \int_0^r s^{-2}\int_0^s S^{\circ 2}dtds,$$

caused by variation of $T_1{}^\circ$ to $kT_1{}^\circ$ and the variations of T°,

$$\int_0^r T^{\circ 2}ds \quad\text{and}\quad \int_0^r s^{-2}\int_0^s T^{\circ 2}dtds,$$

caused by variation of $S_1{}^\circ$ to $kS_1{}^\circ$.

The integration of Eqs. (2) may now be effected quickly. Values are assigned to E and R_1 and (2*a*) is integrated (by using S° and T°). By using the tabulated variations of R it is possible to calculate the requisite changes in E and R_1 so that the new solution of (2*a*) satisfies (3) and (4). Eqs. (2*b*) and (2*c*) are then integrated simultaneously, the proper parameter values are determined from the tabulated variations and the equations re-integrated. When fairly approximate solutions S and T are known it is possible to return to (2*a*) and determine R to the accuracy desired; this solution in turn permits of the final determination of S and T.

Table I gives the solutions of Eqs. (2) for the ground state of carbon and also the wave functions for the configuration $(1s)^2\ (2s)\ (2p)^3$. All figures given are correct to within a few units in the fourth decimal place; six figures were used in the computations to avoid cumulative errors. Table II gives the parameter values and the electron energies. While the ground state 2*s* electron checks with that obtained by Brown, Bartlett and Dunn,[2] the 2*p* electron differs considerably. The excitation energy works out to be 0.320 but this figure must be corrected for interactions of the electrons.

TABLE II. *Values of parameters and electron energies.*

	Ground State	
$E=40.5753$	$F=28.4866$	$G=28.2215$
$R_1=0.260205$	$S_1=0.057543$	$T_1=0.00051238$
$\epsilon=22.8377$	$\epsilon=1.2100$	$\epsilon=0.6089$
	Excited State	
$E=40.4110$	$F=28.2951$	$G=28.0153$
$R_1=0.260686$	$S_1=0.057801$	$T_1=0.00052057$
$\epsilon=22.9087$	$\epsilon=1.2454$	$\epsilon=0.6435$

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[2] Brown, Bartlett and Dunn, Phys. Rev. **44**, 298 (1933).