SELF-CONSISTENT FIELD WITH EXCHANGE FOR THE CONFIGURATIONS $1s^22s2p^3$ AND $1s^22p^4$ OF CARBON

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Solutions of Fock's equations are carried out for the configurations $1s^22s2p^3$ and $1s^22p^4$ of carbon. The energies of $(2s)$ $(2p)$ shell are calculated. The effect of superposition of configurations $1s^22s^22p^2$ and $1s^22p^4$ is evaluated.

1. Introduction

The radial wave functions for the configurations $1s^22s^22p^2$ and $1s^22s2p^3$ of carbon calculated from Hartree's are given by Torrance([1]). The wave functions for the normal configuration $1s^22s^22p^2$ calculated from Fock's equations are given by the author of this paper ([2]).

2. Solution of Fock's equations and results

The Slater method gives the following expressions for the energies of the configurations $1s^22s2p^3$ and $1s^22p^4$ in atomic units:

$$E(p^3)=2I(1s)+I(2s)+3I(2p)+F_0(1s,1s)+2F_0(1s,2s)+6F_0(1s,2p)+3F_0(2s,2p)+$$
$$+3F_0(2p,2p)-G_0(1s,2s)-G_1(1s,2p)+\alpha F_2(2p,2p)+\beta G_1(2s,2p), \quad (1)$$

$$E(p^4)=2I(1s)+4I(2p)+F_0(1s,1s)+8F_0(1s,2p)+6F_0(2p,2p)-\frac{4}{3}G_1(1s,2p)+\alpha F_2(2p,2p). \quad (2)$$

The coefficients α and β are given in Tables 2 and 3. I, F and G are integrals defined by

$$I(nl)=-\frac{1}{2}\int_0^\infty P(nl\,|\,r)\left[\frac{d^2}{dr^2}+\frac{2N}{r}-\frac{l(l+1)}{r^2}\right]P(nl\,|\,r)\,dr; \quad (3)$$

$$F_k(nl,n'l')=\int_0^\infty P^2(nl\,|\,r)\,Y_k(n'l',n'l'\,|\,r)\frac{dr}{r}=\int_0^\infty P^2(n'l'\,|\,r)\,Y_k(nl,nl\,|\,r)\frac{dr}{r}; \quad (4)$$

$$G_k(nl,n'l')=\int_0^\infty P(nl\,|\,r)\,P(n'l'\,|\,r)\,Y_k(nl,n'l'\,|\,r)\frac{dr}{r}; \quad (5)$$

$$Y_k(nl,n'l'\,|\,r)=Z_k(nl,n'l'\,|\,r)+r^{k+1}\int_r^\infty P(nl\,|\,r_1)\,P(n'l'\,|\,r_1)\frac{dr_1}{r_1^{k+1}}; \quad (6)$$

$$Z_k(nl,n'l'\,|\,r)=\frac{1}{r^k}\int_0^r P(nl\,|\,r_1)\,P(n'l'\,|\,r_1)\,r_1^k\,dr_1. \quad (7)$$

Table 1

Radial wave functions for configurations $1s^2 2s 2p^3$ and $1s^2 2p^4$ of carbon

r	1s					2s						2p								
	A	a	d	e	f	A	a	b	c	d	e	A	a	b	c	d	e	f	g	h
0.00	0.000	0	0	0	0	0.000	0	0	0	0	0	0.000	0	0	0	0	0	0	0	0
0.02	0.491	0	0	0	0	0.108	−1	−1	0	−4	0	0.002	0	0	0	0	0	0	0	0
0.04	0.872	0	−1	0	0	0.191	−3	−1	−1	−8	0	0.009	0	0	0	0	0	0	0	0
0.06	1.162	−1	−1	0	0	0.252	−3	−1	0	−10	0	0.018	0	0	0	0	0	0	0	0
0.08	1.377	−1	−1	0	+1	0.296	−4	−1	−1	−12	−1	0.031	0	0	0	0	0	0	0	0
0.10	1.531	−1	−1	0	−1	0.324	−4	−1	−1	−13	0	0.045	0	0	0	+1	+1	+1	+1	+1
0.12	1.635	−1	−1	0	−1	0.339	−4	−1	−1	−13	0	0.062	0	−1	0	+1	+1	+1	+1	0
0.14	1.699	−1	−2	0	−1	0.343	−4	−1	−1	−13	0	0.079	+1	0	+1	+2	+2	+2	+2	+1
0.16	1.730	−1	−2	0	−1	0.338	−4	−1	−1	−13	0	0.098	+1	0	+1	+2	+2	+2	+2	+1
0.18	1.735	−1	−1	0	−1	0.326	−4	−2	−1	−13	−1	0.118	+1	0	+1	+2	+3	+2	+2	+2
0.20	1.719	0	−1	+1	0	0.307	−4	−1	−1	−12	−1	0.139	+1	−1	+1	+2	+3	+2	+2	+2
0.25	1.618	0	−1	0	−1	0.238	−2	0	−1	−8	−1	0.192	+1	−1	+2	+3	+4	+3	+3	+2
0.30	1.466	0	−1	0	−1	0.150	−1	0	−1	−4	−1	0.246	+1	−2	+2	+4	+6	+4	+4	+2
0.35	1.294	0	−1	−1	−1	+0.052	+1	+1	−1	0	−1	0.299	0	−3	+2	+4	+7	+5	+4	+2
0.40	1.120	0	0	0	0	−0.050	+3	+2	0	+5	−1	0.350	0	−4	+3	+5	+9	+5	+4	+1
0.45	0.956	+1	0	0	+1	−0.151	+5	+4	+1	+10	0	0.398	0	−6	+4	+5	+11	+6	+4	+1
0.50	0.808	+1	0	−1	0	−0.247	+7	+5	+1	+15	−1	0.443	−1	−6	+4	+5	+12	+6	+4	0
0.55	0.676	+1	+2	0	+1	−0.337	+9	+6	+1	+19	−1	0.484	−2	−7	+5	+5	+14	+6	+4	0
0.60	0.562	+1	+2	0	+1	−0.420	+10	+7	+2	+23	−1	0.522	−3	−9	+4	+4	+16	+5	+3	−1
0.65	0.465	+1	+2	−1	+1	−0.494	+11	+8	+1	+26	−2	0.555	−3	−10	+6	+4	+18	+6	+4	−2
0.70	0.382	+2	+2	−1	+2	−0.561	+13	+9	+2	+30	−2	0.585	−4	−11	+6	+3	+20	+6	+3	−3
0.75	0.313	+2	+2	−1	+2	−0.619	+14	+10	+2	+33	−2	0.611	−5	−12	+6	+2	+22	+6	+3	−3
0.80	0.256	+2	+2	−1	+1	−0.669	+15	+11	+3	+35	−2	0.634	−4	−14	+7	+1	+ 3	+6	+2	−4
0.9	0.169	+2	+3	−1	+2	−0.746	+17	+12	+2	+37	−3	0.670	−8	−16	+7	−1	+25	+5	+1	−6
1.0	0.111	+2	+3	−1	+2	−0.796	+17	+12	+2	+37	−4	0.693	−8	−17	+8	−1	+27	+5	+1	−7
1.1	0.072	+3	+3	0	+2	−0.823	+16	+11	+2	+36	−5	0.707	−10	−19	+8	−3	+28	+5	0	−8
1.2	0.047	+2	+3	−1	+1	−0.832	+15	+11	+2	+33	−4	0.712	−10	−19	+8	−4	+28	+4	0	−9
1.3	0.031	+2	+2	−1	+1	−0.826	+13	+10	+1	+29	−4	0.710	−10	−19	+8	−4	+27	+4	−1	−9
1.4	0.020	+2	+2	−1	+1	−0.808	+11	+8	0	+23	−5	0.703	−10	−19	+7	−5	+24	+3	−2	−10

1.5	0.013	+2	+2	−1	+1	−0.782	+ 8	+ 6	0	+18	−4	0.690	− 9	−17	+ 7	−5	+22	+3	−2	− 9
1.6	0.008	+2	+2	0	+1	−0.750	+ 5	+ 4	0	+12	−3	0.674	− 8	−15	+ 6	−6	+20	+2	−2	− 8
1.7	0.005	+1	+2	0	+1	−0.714	+ 3	+ 2	−1	+ 6	−2	0.656	− 7	−13	+ 4	−5	+15	+1	−2	− 8
1.8	0.003_5	$+0_8$	$+0_9$	-0_3	$+0_3$	−0.675	− 1	0	−1	− 1	−2	0.635	− 6	−11	+ 4	−4	+12	+1	−2	− 7
1.9	0.002_3	$+0_5$	$+0_6$	-0_2	$+0_2$	−0.635	− 3	− 2	−1	− 6	0	0.613	− 5	− 9	+ 2	−4	+ 8	0	−2	− 6
2.0	0.001_5	$+0_4$	$+0_4$	-0_2	$+0_1$	−0.594	− 6	− 4	−2	−12	0	0.590	− 4	− 6	+ 1	−3	+ 3	−1	−2	− 5
2.1	0.001_0	$+0_2$	$+0_3$	-0_1	$+0_1$	−0.554	− 8	− 6	−2	−17	+1	0.566	− 2	− 3	0	−3	− 1	−1	−2	− 4
2.2	0.000_6	$+0_2$	$+0_3$	0	$+0_1$	−0.514	−11	− 8	−2	−23	+2	0.542	− 1	− 1	− 1	−2	− 5	−2	−2	− 2
2.3	0.000_4	$+0_1$	$+0_2$	0	$+0_1$	−0.476	−13	− 9	−2	−27	+3	0.517	+ 1	+ 2	− 1	−1	− 8	−2	−1	0
2.4	0.000_3	$+0_1$	$+0_1$	-0_1	0	−0.440	−15	−10	−2	−30	+4	0.493	+ 3	+ 5	− 2	0	−12	−2	−1	+ 1
2.6	0.000_1	$+0_1$	$+0_1$	0	0	−0.373	−17	−12	−2	−36	+6	0.446	+ 5	+ 9	− 4	+1	−18	−3	0	+ 3
2.8	0.000	$+0_1$	$+0_1$	0	0	−0.313	−19	−14	−2	−40	+6	0.402	+ 7	+13	− 6	+2	−24	−4	−1	+ 5
3.0	$b = a$					−0.261	−20	−15	−2	−42	+7	0.360	+ 9	+16	− 7	+3	−29	−4	0	+ 7
3.2	$c = 0$					−0.217	−20	−15	−2	−43	+7	0.321	+10	+19	− 8	+4	−33	−5	+1	+ 9
3.4	$h = g = f$					−0.180	−19	−14	−1	−42	+8	0.286	+11	+21	− 9	+4	−34	−5	0	+10
3.6						−0.148	−19	−14	−1	−41	+8	0.254	+11	+22	−10	+4	−36	−6	0	+10
3.8						−0.122	−17	−13	0	−38	+8	0.224	+12	+24	−10	+5	−35	−5	+1	+12
4.0						−0.099	−13	−13	−1	−37	+6	0.198	+12	+24	−10	+4	−35	−5	+1	+12
4.5						−0.060	−12	−10	0	−29	+6	0.144	+11	+23	−10	+4	−33	−5	+1	+12
5.0						−0.036	− 9	− 7	0	−22	+5	0.103	+11	+21	− 8	+4	−28	−4	+2	+11
5.5						−0.021	− 7	− 5	0	−16	+3	0.074	+ 8	+18	− 8	+3	−24	−4	+1	+10
6.0						−0.012	− 5	− 4	0	−12	+2	0.052	+ 7	+16	− 6	+3	−19	−3	+1	+ 8
6.5						−0.007	− 3	− 3	0	− 8	+1	0.037	+ 6	+12	− 5	+2	−15	−3	+1	+ 7
7 0						−0.004	− 2	− 2	0	− 6	+1	0.026	+ 4	+10	− 4	+1	−11	−2	0	+ 5
7.5						−0.002	− 2	− 2	0	− 4	0	0.018	+ 4	+ 8	− 3	+1	− 8	−2	+1	+ 4
8.0						−0.001	− 1	− 1	0	− 3	0	0 013	+ 3	+ 6	− 3	0	− 6	−2	0	+ 3
9						−0.001	0	0	0	− 1	0	0.006	+ 2	+ 4	− 1	0	− 3	−1	0	+ 2
10						0.000	0	0	0	− 1	0	0.003	+ 1	+ 2	− 1	0	− 2	−1	0	+ 1
11												0.001	+ 1	+ 2	0	+1	0	0	0	+ 1
12												0.000	+ 1	+ 1	0	+1	0	0	0	+ 1

The corresponding radial wave function is $A + x \cdot 10^{-3}$, where x is to be taken from the following table:

$1s^2\,2s\,2p^3$	^1P	^3S	^1D	^3P	^3D	^5S
	b	d	a	0	c	e
$1s^2\,2p^4$	^1S	^1D	^3P			
	h	g	f			

Here N is the nuclear charge. $P(nl\,|\,r)$ are radial wave functions, according to Hartree.

Applying the variation principle to (1) one obtains Fock's equations for the configuration $1s^2\,2s\,2p^3$:

$$\left[\frac{d^2}{dr^2}+\frac{2N-2Y_0(1s,1s\,|\,r)-2Y_0(2s,2s\,|\,r)-6Y_0(2p,2p\,|\,r)}{r}-\varepsilon_{1s,\,1s}\right]P(1s\,|\,r)+$$

$$+\left[\frac{Y_0(1s,2s\,|\,r)}{r}-\varepsilon_{1s,\,2s}\right]P(2s\,|\,r)+\frac{Y_1(1s,2p\,|\,r)}{r}P(2p\,|\,r)=0; \tag{8}$$

$$\left[\frac{d^2}{dr^2}+\frac{2N-4Y_0(1s,1s\,|\,r)-6Y_0(2p,2p\,|\,r)}{r}-\varepsilon_{2s,\,2s}\right]P(2s\,|\,r)+$$

$$+\left[\frac{2Y_0(1s,2s\,|\,r)}{r}-\varepsilon_{1s,\,2s}\right]P(1s\,|\,r)-2\beta\frac{Y_1(2s,2p\,|\,r)}{r}P(2p\,|\,r)=0; \tag{9}$$

$$\left[\frac{d^2}{dr^2}+\frac{2N-4Y_0(1s,1s\,|\,r)-2Y_0(2s,2s\,|\,r)-4Y_0(2p,2p\,|\,r)-\frac{4}{3}\alpha Y_2(2p,2p\,|\,r)}{r}-\frac{2}{r^2}-\varepsilon_{2p,\,2p}\right]P(2p\,|\,r)+$$

$$+\frac{2}{3}\frac{Y_1(1s,2p\,|\,r)}{r}P(1s\,|\,r)-\frac{2}{3}\beta\frac{Y_1(2s,2p\,|\,r)}{r}P(2s\,|\,r)=0. \tag{10}$$

Accordingly (2) gives Fock's equations for the configuration $1s^2\,2p^4$:

$$\left[\frac{d^2}{dr^2}+\frac{2N-2Y_0(1s,1s\,|\,r)-8Y_0(2p,2p\,|\,r)}{r}-\varepsilon_{1s,\,1s}\right]P(1s\,|\,r)+\frac{4}{3}\frac{Y_1(1s,2p\,|\,r)}{r}P(2p\,|\,r)=0; \tag{11}$$

$$\left[\frac{d^2}{dr^2}+\frac{2N-4Y_0(1s,1s\,|\,r)-6Y_0(2p,2p\,|\,r)-\alpha Y_2(2p,2p\,|\,r)}{r}-\frac{2}{r^2}-\varepsilon_{2p,\,2p}\right]P(2p\,|\,r)+$$

$$+\frac{2}{3}\frac{Y_1(1s,2p\,|\,r)}{r}P(1s\,|\,r)=0. \tag{12}$$

The normalized solutions of these equations are given in Table 1 and the Lagrange factors in Tables 2 and 3. The peculiarities of the wave functions are to be seen from Table 1. One point, as an example, let be noted here. The behaviour of the function $P(1s\,|\,r)$ is to be explained in the following way. It depends on the non-diagonal Lagrange factor more than on the other wave functions. For this reason in the case of configuration $1s^2 2s 2p^3$ for the terms ^1P and ^1D ($a=b$ in Table 1) the function $P(1s\,|\,r)$ within the limits of numerical errors is the same for both terms as well as for the terms ^3P and ^3D ($c=0$ in Table 1), because the difference $\Delta\varepsilon_{1s,\,2s}$ is small for those pairs of terms. In the case of configuration $1s^2 2p^4$ there is no non-diagonal Lagrange factor and $P(1s\,|\,r)$ is the same for all three terms ($h=g=f$ in Table 1).

3. Energy

The energies of $(2s)(2p)$ shell have been calculated. One obtains them by supposing [4]

$$2I(1s)+F_0(1s,1s)=0. \tag{13}$$

From equations (9), (10) and (12) we express $I(2s)$ and $I(2p)$ in terms of the integrals F and G and Lagrange factors and substitute in (1) and (2). Then taking (13) into account we obtain

$$E(p^3)=-\frac{1}{2}\varepsilon_{2s,\,2s}-\frac{3}{2}\varepsilon_{2p,\,2p}-3F_0(2p,2p)-3F_0(2s,2p)-\alpha F_2(2p,2p)-\beta G_1(2s,2p); \tag{14}$$

$$E(p^4)=-2\varepsilon_{2p,\,2p}-6F_0(2p,2p)-\alpha F_2(2p,2p). \tag{15}$$

Table 2

ε parameters, F and G integrals and the total energy of $(2s)(2p)$ shell for the configuration $1s^2 2s 2p^3$

	^1P	^3S	^1D	^3P	^3D	^5S
α	0	-0.6	-0.24	0	-0.24	-0.6
β	0	$+1/3$	0	$-2/3$	$-2/3$	-1
$\varepsilon_{1s,\,1s}$	22.887	22.832	22.841	22.761	22.721	22.579
$\varepsilon_{2s,\,2s}$	1.3340	1.0566	1.2048	1.7217	1.6992	1.8831
$\varepsilon_{2p,\,2p}$	0.6446	0.7374	0.7002	0.7445	0.8037	0.9569
$F_0\,(2s,\,2p)$	0.5378	0.5376	0.5417	0.5532	0.5573	0.5708
$F_0\,(2p,\,2p)$	0.5030	0.5207	0.5103	0.5223	0.5306	0.5511
$F_2\,(2p,\,2p)$	—	0.2316	0.2274	—	0.2385	0.2514
$G_1\,(2s,\,2p)$	—	0.3300	—	0.3398	0.3436	0,3555
E (calc.)	-9.513	-9.561	-9.624	-9.955	-10.065	-10.473
E (exp.)	-9.793*	-9.921	-9.994*	-10.199	-10.301	-10.586*

* These values are estimated according to the law of irregular doublets [C. W. Ufford, Phys. Rev., **53**, 568 (1938)].

Table 3

ε parameters, F and G integrals and the total energy of $(2s)(2p)$ shell for the configuration $1s^2 2p^4$

	Without exchange	With exchange			
		^1S	^1D	^3P	$\frac{^1S-{}^1D}{^1D-{}^3P}$
α		0	-0.36	-0.6	
$\varepsilon_{1s,\,1s}$	22.962	22.937	22.868	22.840	
$\varepsilon_{2p,\,2p}$	0.6729	0.6802	0.7376	0.7773	
$F_0\,(2p,\,2p)$	0.5034	0.5140	0.5230	0.5281	
$F_2\,(2p,\,2p)$	0.2244	—	0.2332	0.2365	
$G_1\,(1s,\,2p)$	0.0555	—	—	—	
$G_1\,(2s,\,2p)_{AB}$	—	0.3324	0.3361	0.3384	
E (a)	—	-8.889	-9.059	-9.163	1.63
E (b)	—	-8.880	-9.042	-9.150	1.50
E (c)	—	-8.768	-9.025	-9.129	2.47

Methods of calculation

a) From the radial wave functions calculated including exchange.
b) From the radial wave functions calculated without exchange.
c) Wave functions calculated with exchange, superposition of configurations $1s^2 2s^2 2p^2$ and $1s^2 2p^4$ included in energy formula.

The integrals F and G in atomic units and energies in Rydberg units are given in Tables 2 and 3. In Table 2 the observed term values are given for comparison purposes. $E(p^4)$ is calculated from the wave functions without exchange also. In this case

$$E(p^4) = -2\varepsilon_{2p,\,2p} - 6F_0(2p, 2p) - \frac{4}{3}G_1(1s, 2p) + \alpha F_2(2p, 2p). \quad (15a)$$

The effect of superposition of configurations $1s^2 2s^2 2p^2$ and $1s^2 2p^4$ is calculated according to the formula [5]

$$E - E_B = \frac{E_{AB}^2}{(E_B - E_A) + (E - E_B)}. \quad (16)$$

Here E is the energy including configuration interaction, E_A and E_B are energies of the configurations $1s^2 2s^2 2p^2$ and $1s^2 2p^4$ correspondingly without interaction of configurations. E_{AB} is defined by

$$E_{AB}^2 = c^2\gamma^2 [G_1(2s, 2p)_{AB}]^2. \quad (17)$$

$G_1(2s, 2p)_{AB}$ is the integral defined by (5), is which $P(2s|r)$ is to be taken from the configuration $1s^2 2s^2 2p^2$ and $P(2p|r)$ from that of $1s^2 2p^4$. γ is $1/3$, $1/3$ and $2/3$ for the terms ^3P, ^1D and ^1S correspondingly. c is the integral

$$\int_0^\infty P(2p|r)_A P(2p|r)_B \, dr,$$

where $P(2p|r)$ from the mentioned configurations are to be taken. It has been found that within the limits of numerical errors $c = 1$ for all three terms. E_A are taken from the previous paper of the author [2], E_B calculated here are given in the line a of Table 3. There are the integrals $G_1(2s, 2p)_{AB}$ given also.

Energies and ratios $(^1S - {^1D}) / (^1D - {^3P})$ are given in Table 3. The superposition of configurations changes that ratio from 1.63 to 2.47. Nevertheless, these results cannot be compared with experimental data, because there are no observed terms values for this configuration.

In the case of normal configuration of carbon the effect of superposition of configurations has been calculated without exact radial wave functions for the configurations $1s^2 2p^4$. Recalculation has changed the ratio of term differences from 0.69 to 0.66. This difference is small enough, so that no conclusion can be drawn from that fact.

For the more detailed study of these term differences the work on the calculation of the effect of higher configurations has been undertaken in these laboratories.

REFERENCES

1. C. C. Torrance, Phys. Rev., **46**, 388 (1934).
2. A. Jucys, Proc. Roy. Soc. (A), **173**, 59 (1939).
3. J. C. Slater, Phys. Rev., **34**, 1293 (1929).
4. D. R. Hartree a. W. Hartree, Proc. Roy. Soc. (A), **154**, 588 (1936).
5. D. R. Hartree a. B. Swirles, Proc. Cambr. Phil. Soc., **33**, 240 (1937).