SOVIET PHYSICS JETP VOLUME 2, NUMBER 3 MAY, 1956

Fock Self-Consistent Field for the Boron Atom in the Two-Configuration Approximation

I. I. GLEMBOTSKII, V. V. KIBARTAS AND A. P. IUTSIS
Physico-Technical Institute, Academy of Sciences (Lithuanian) SSR
Vilna State University

(Submitted to JETP editor July 12, 1954)
J. Exper. Theoret. Phys. USSR **29**, 617-621 (November, 1955)

Solutions are presented of the ordinary Fock equations for the ground configuration of the neutral boron atom, and of the Hartree equation, supplemented by configuration interaction terms, for the function $P(2p|r)$ of the configuration $1s^2 2p^3$, whose effect is included in the two-configuration approximation $1s^2 2s^2 2p - 1s^2 2p^3$. Values are also given for the total energy as determined in both the one-configuration and two-configuration approximations. The total potential function and the radial probability distribution are tabulated.

1. INTRODUCTION

REFERENCE 1 showed that the solution of the Fock self-consistent field equations is practically feasible in the two-configuration approximation[2]. Further study of the problem[3] led to the conclusion that if, instead of solving the exact Fock equations in the two-configuration approximation, one uses solutions of the corresponding simplified Fock equations, the result is hardly changed while the computational labor is reduced considerably. This simplification consists in solving the ordinary Fock equations for the configuration under investigation and, in addition to this, solving the Hartree equations supplemented by configuration terms for those radial wave functions of the perturbing configuration whose Fock equations contain configuration terms. In the present paper, we take advantage of this simplification in applying the Fock self-consistent field method in the two-configuration approximation to the ground configuration of the neutral boron atom.

In applying the many-configuration approximation to the ground configuration of the boron atom, the two-configuration approximation $1s^2 2s^2 2p - 1s^2 2p^3$ is of paramount importance. Therefore, in addition to solving the ordinary Fock equations for the ground configuration, one should also solve the Hartree equation, supplemented by configuration terms, for the function $P(2p|r)$ of the perturbing configuration $1s^2 2p^3$. The solutions of these equations and the corresponding values of the total energy are presented in the next section. In Section 3 we shall attempt to determine the effect of the two-configuration approximation on the total potential of the system and on the radial probability distribution of the electrons.

2. SOLUTIONS AND ENERGY VALUES

The ordinary Fock equations for the ground configuration of the boron atom have the following form:

$$\left[\frac{d^2}{dr^2}+\frac{2Z-2Y_0(1s,1s|r)-4Y_0(2s,2s|r)-2Y_0(2p,2p|r)}{r}-\varepsilon_{1s,1s}\right]P(1s|r)$$
$$+\left[\frac{2Y_0(1s,2s|r)}{r}-\varepsilon_{1s,2s}\right]P(2s|r)+\frac{1}{3}\frac{Y_1(1s,2p|r)}{r}P(2p|r)=0, \tag{2.1 a}$$

$$\left[\frac{d^2}{dr^2}+\frac{2Z-4Y_0(1s,1s|r)-2Y_0(2s,2s|r)-2Y_0(2p,2p|r)}{r}-\varepsilon_{2s,2s}\right]P(2s|r)$$
$$+\left[\frac{2Y_0(1s,2s|r)}{r}-\varepsilon_{1s,2s}\right]P(1s|r)+\frac{1}{3}\frac{Y_1(2s,2p|r)}{r}P(2p|r)=0, \tag{2.1 b}$$

$$\left[\frac{d^2}{dr^2}+\frac{2Z-4Y_0(1s,1s|r)-4Y_0(2s,2s|r)}{r}-\frac{2}{r^2}-\varepsilon_{2p,2p}\right]P(2p|r)$$
$$+\frac{2}{3}\frac{Y_1(1s,2p|r)}{r}P(1s|r)+\frac{2}{3}\frac{Y_1(2s,2p|r)}{r}P(2s|r)=0. \tag{2.1 c}$$

The Hartree equation, supplemented by configuration terms, for the function $P(2p|r)$ of the perturbing configuration $1s^2 2p^3$ of the two-configuration approximation is:

---

[1] V. V. Kibartas and A. P. Iutsis, J. Exper. Theoret. Phys. USSR **25**, 264 (1953)

[2] A. P. Iutsis, J. Exper. Theoret. Phys. USSR **23**, 129 (1952).

[3] A. P. Iutsis, V. V. Kibartas and I. I. Glembotskii, J. Exper. Theoret. Phys. USSR **27**, 425 (1954)

$$\left[\frac{d^2}{dr^2}+\frac{2Z-4Y_0(1s,\,1s\mid r)-4Y_0(2p,\,2p\mid r)}{r}-\frac{2}{r^2}-\varepsilon_{(2p,\,2p)_{22}}\right]P_2(2p\mid r)$$
$$-\frac{4\sqrt{2}}{9a_{12}}\,\frac{Y_1(2s,\,2p\mid r)_{12}}{r}\,P_1(2s\mid r)\,N(2p,\,2p)_{12}=0. \qquad (2.2)$$

TABLE I

Normalized Radial Wave Functions of the Self-consistent Fock Field for the Ground Configuration of the Neutral Boron Atom

r	$P(1s\mid r)$	$P(2s\mid r)$	$P(2p\mid r)$	$P_2(2p\mid r)$	r	$P(1s\mid r)$	$P(2s\mid r)$	$P(2p\mid r)$	$P_2(2p\mid r)$
0.00	0.0000	0.0000	0.0000	0.0000	1.20	0.1054	—0.6808	0.6068	0.6625
0.01	0.1982	0.0400	0.0003	0.0003	1.25	0.0884	—0.6958	0.6156	0.6742
0.02	0.3771	0.0 60	0.0012	0.0011	1.30	0.0741	—0.7078	0.6230	0.6839
0.03	0.5382	0.1084	0.0027	0.0024	1.35	0.0620	—0.7170	0.6290	0.6918
0.04	0.6831	0.1374	0.0048	0.0042	1.40	0.0519	—0.7236	0.6337	0.6978
0.05	0.8127	0.1631	0.0073	0.0065	1.45	0.0434	—0.7277	0.6372	0.7020
0.06	0.9283	0.1858	0.0102	0.0091	1.50	0.0363	—0.7297	0.6395	0.7046
0.07	1.0311	0.2058	0.0136	0.0120	1.55	0.0303	—0.7297	0.6407	0.7056
0.08	1.1220	0.2231	0.0173	0.0154	1.6	0.0254	—0.7279	0.6410	0.7051
0.09	1.2020	0.2379	0.0214	0.0191	1.7	0.0177	—0.7196	0.6387	0.7000
0.10	1.2720	0.2505	0.0258	0.0231	1.8	0.0124	—0.7061	0.6332	0.6901
0.11	1.3328	0.2610	0.0305	0.0273	1.9	0.0087	—0.6884	0.6251	0.6761
0.12	1.3851	0.2695	0.0355	0.0318	2.0	0.0061	—0.6676	0.6146	0.6587
0.13	1.4297	0.2762	0.0407	0.0366	2.1	0.0042	—0.6443	0.6021	0.6386
0.14	1.4672	0.2811	0.0462	0.0416	2.2	0.0030	—0.6193	0.5882	0.6164
0.15	1.4982	0.2844	0.0519	0.0468	2.3	0.0021	—0.5932	0.5730	0.5925
0.16	1.5232	0.2863	0.0578	0.0522	2.4	0.0015	—0.5664	0.5567	0.5675
0.17	1.5427	0.2868	0.0639	0.0578	2.5	0.0010	—0.5393	0.5398	0.5418
0.18	1.5572	0.2859	0.0 01	0.0636	2.6	0.0007	—0.5122	0.5223	0.5156
0.19	1.5672	0.2839	0.0765	0.0695	2.7	0.0005	—0.4854	0.5044	0.4893
0.20	1.5730	0.2808	0.0830	0.0756	2.8	0.0003	—0.4590	0.4863	0.4633
0.22	1.5738	0.2715	0.0963	0.0881	3.0	0.0002	—0.4084	0.4499	0.4124
0.24	1.5622	0.2588	0.1101	0.1011	3.2	0.0001	—0.3611	0.4140	0.3643
0.26	1.5404	0.2430	0.1242	0.1145	3.4		—0.3176	0.3792	0.3196
0.28	1.5105	0.2246	0.1385	0.1283	3.6		—0.2782	0.3460	0.2787
0.30	1.4741	0.2041	0.1530	0.1424	3.8		—0.2427	0.3146	0.2418
0.32	1.4326	0.1818	0.1676	0.1567	4.0		—0.2109	0.2850	0.2089
0.34	1.3873	0.1581	0.1822	0.1712	4.2		—0.1828	0.2575	0.1798
0.36	1.3391	0.1331	0.1969	0.1859	4.4		—0.1580	0.2321	0.1542
0.38	1.2889	0.1071	0.2116	0.2008	4.6		—0.1362	0.2087	0.1317
0.40	1.2375	0.0805	0.2262	0.2157	4.8		—0.1172	0.1872	0.1121
0.42	1.1854	0.0532	0.2408	0.2306	5.0		—0.1006	0.1676	0.0952
0.44	1.1332	0.0256	0.2552	0.2456	5.2		—0.0862	0.1499	0.0809
0.46	1.0813	—0.0022	0.2694	0.2606	5.4		—0.0738	0.1338	0.0686
0.48	1.0300	—0.0301	0.2835	0.2755	5.6		—0.0631	0.1192	0.0580
0.50	0.9796	—0.0580	0.2974	0.2904	5.8		—0.0538	0.1061	0.0489
0.52	0.9304	—0.0857	0.3111	0.3052	6.0		—0.0459	0.0942	0.0412
0.54	0.8825	—0.1132	0.3245	0.3199	6.5		—0.0307	0.0698	0.0268
0.56	0.8360	—0.1404	0.3377	0.3345	7.0		—0.0204	0.0514	0.0172
0.58	0.7911	—0.1673	0.3507	0.3490	7.5		—0.0136	0.0377	0.0111
0.60	0.7478	—0.1937	0.3634	0.3633	8.0		—0.0092	0.0275	0.0072
0.65	0.6470	—0.2574	0.3940	0.3981	8.5		—0.0061	0.0200	0.0047
0.70	0.5569	—0.3173	0.4228	0.4316	9.0		—0.0040	0.0146	0.0030
0.75	0.4771	—0.3731	0.4497	0.4635	9.5		—0.0027	0.0107	0.0019
0.80	0.4073	—0.4246	0.4746	0.4937	10		—0.0018	0.0078	0.0013
0.85	0.3467	—0.4715	0.4976	0.5220	11		—0.0008	0.0042	0.0005
0.90	0.2943	—0.5139	0.5187	0.5484	12		—0.0004	0.0023	0.0002
0.95	0.2491	—0.5519	0.5379	0.5727	13		—0.0002	0.0012	0.0001
1.00	0.2104	—0.5856	0.5552	0.5948	14		—0.0001	0.0007	
1.05	0.1774	—0.6151	0.5707	0.6149	15			0.0004	
1.10	0.1493	—0.6407	0.5844	0.6329	16			0.0002	
1.15	0.1255	—0.6625	0.5964	0.6488	17			0.0001	

In Eqs. (2.1) and (2.2), Z denotes the nuclear charge, $\epsilon_{nl,n'l}$ are Lagrange multipliers. The function $Y_k(nl, n'l \mid r)$ is defined as usual. When necessary, indices are attached to this function to indicate the number of the configuration to which the corresponding wave function refers. Since, in our approximation, the function $P(1s \mid r)$ is the same in both configurations, the function $Y_0(1s, 1s \mid r)$ in Eq. (2.2) is the same as in Eq. (2.1). In (2.2), $P(2p \mid r)$ refers to the perturbing configuration except in the case of the quantity $N(2p, 2p)_{12}$ defined in Eq. (3.1) of reference 2. Here one of the functions $P(2p \mid r)$ refers to the basic configuration (index 1), while the second refers to the perturbing configuration (index 2). The supplementary indices on the Lagrange multiplier in Eq. (2.2) indicate that it refers to configuration 2. The absolute value of the constant a_{12} gives the weight of configuration 2 relative to configuration 1.

In solving Eq. (2.1), we used as initial trial functions the corresponding solutions of the Hartree equation, given in reference 4. The solution was carried up to self-consistency index $\eta = 0.0025$ (cf. Eq. (2.8) of reference 5). To solve Eq. (2.2), the initial function $P_2(2p \mid r)$ was constructed using a hydrogen-like analytic wave function obtained with the aid of the results of references 6 and 7. For the starting value of a_{12} we took the value obtained using analytic wave functions[7], where the constants were determined in the one-configuration approximation. The solution of Eq. (2.2) was carried to a self-consistency index of 0.0050 for $P_2(2p \mid r)$ and 0.002 for a_{12}. The normalized solutions are given in Table I. We should point out that the solution of Eq. (2.1) was carried out on the assumption that $\epsilon_{1s,2s} = 0$. The orthogonality of the functions $P(2s \mid r)$ and $P(1s \mid r)$ was achieved by direct orthogonalization after each successive solution.

TABLE II

Values of the Lagrange Multipliers, Radial Integrals, and Energy, for the Ground Configuration of the Boron Atom (in Atomic Units)

$\varepsilon_{1s,\ 1s} = 15.386$	$G_0(1s,\ 2s) = 0,0385$
$\varepsilon_{2s,\ 2s} = 0.9903$	$G_1(1s,\ 2p) = 0.0430$
$\varepsilon_{2p,\ 2p} = 0.6182$	$G_1(2s,\ 2p) = 0.2728$
$\varepsilon_{(2p,\ 2p)_{22}} = 1.1452$	$F_0(2p,\ 2p)_{22} = 0.4646$
$F_0(1s,\ 1s) = 2,9325$	$F_0(1s,\ 2p)_{22} = 0.6388$
$F_0(2s,\ 2s) = 0.4602$	$G_1(1s,\ 2p)_{22} = 0.0420$
$F_0(1s,\ 2s) = 0.6485$	$G_1(2s,\ 2p)_{12} = 0.2978$
$F_0(1s,\ 2p) = 0.5994$	$N(2p,\ 2p)_{12} = 0.9894$
$F_0(2s,\ 2p) = 0.4370$	

	a	b
E_{11}	-24.562	-24.562
E_{22}	-24.045	-24.003
E_{12}	$+0.129$	$+0.139$
ΔE	-0.030	-0.033
a_{12}	-0.233	-0.238
E	-24.592	-24.595
E_{exp}	-24.658	

Footnote.- a) on the assumption that $P_2(2p \mid r) = P(2p \mid r)$; b) using $P_2(2p \mid r)$ as determined in the two-configuration approximation.

The values of the Lagrange multipliers, the

---

[4] G. K. Tsiunaitis and A. P. Iutsis, J. Exper. Theoret. Phys. USSR **28**, 452 (1955); Soviet Phys. **1**, 358 (1955).

[5] A. P. Iutsis and G. K. Tsiunaitis, J. Exper. Theoret. Phys. USSR **23**, 512 (1952).

[6] V. I. Kavetskis and A. P. Iutsis, J. Exper. Theoret. Phys. USSR **25**, 257 (1953).

[7] A. B. Bolotin and A. P. Iutsis, J. Exper. Theoret. Phys. USSR **24**, 537 (1953).

radial integrals, the constant a_{12} and the energy are given in Table II, in which the experimental energy value is also included.

3. TOTAL POTENTIAL FUNCTION AND RADIAL PROBABILITY DISTRIBUTION

In quantum-mechanical computations, the function

$$T(A_i|r) = 2\Big[Z - \sum_{nl} c_{nl} Y_0(nl, nl\,|\,r)\Big]. \tag{3.1}$$

plays an important role. Here A_i denotes the term A of the configuration i of an atom whose atomic number is Z; c_{nl} is the number of electrons in the nl shell.

The function $T(A_i|\,r)$, divided by $2r$, represents the potential of the total system. We shall call this function the total potential function.

It is not difficult to show that the total potential function for the term A of the configuration i, can be represented, in the many-configuration approximation, in the form:

$$T(A^i\,|\,r) = \frac{1}{\sum\limits_j a_{ij}^2} \sum_j a_{ij}^2\, T(A_j\,|\,r). \tag{3.2}$$

In particular, in the two-configuration approximation $1s^2 2s^2 2p - 1s^2 2p^3$, where $P(1s\,|\,r)$ is the same for both configurations, the total potential function for the configuration $1s^2 2s^2 2p$ is:

$$T(r) = 2\Big\{Z - 2Y_0(1s,\,1s\,|\,r) - \frac{1}{1 + a_{12}^2}\,[2Y_0(2s,\,2s\,|\,r)_{11} + Y_0(2p,\,2p\,|r)_{11} + 3a_{12}^2 Y_0(2p,\,2p\,|\,r)_{22}]\Big\}. \tag{3.3}$$

The subscripts on $Y_0(1s,\ 1s\,|\,r)$ have been omitted for the reason just mentioned.

In the one-configuration approximation, we have the following expression for the radial probability distribution:

$$W(A_i\,|\,r) = \sum_{nl} c_{nl} P^2(nl\,|\,r). \tag{3.4}$$

To obtain the corresponding expression in the many-configuration approximation, we must replace T by W in (3.2). We obtain the following expression for the radial distribution of the configuration

TABLE III

Total Potential Function and Radial Distribution for the Ground Configuration of the Boron Atom

r	$T(r)$	$10^3\delta T$	$W(r)$	$10^3\delta W$	r	$T(r)$	$10^3\delta T$	$W(r)$	$10^3\delta W$
0.00	10.000	0	0.000	0	1.0	2.549	—6	1.086	+4
0.02	9.547	0	0.295	—1	1.1	2.273	—7	1.209	+3
0.04	9.106	0	0.969	—2	1.2	2.019	—7	1.319	+2
0.06	8.684	0	1.789	—3	1.3	1.787	—7	1.402	+1
0.08	8.286	0	2.612	—5	1.4	1.577	—6	1.455	+1
0.10	7.914	+1	3.355	—7	1.5	1.388	—5	1.477	+1
0.12	7.569	+1	3.976	—8	1.6	1.218	—5	1.473	+1
0.14	7.249	+1	4.457	—9	1.8	0.931	—5	1.400	+2
0.16	6.955	+1	4.799	—9	2.0	0.707	—5	1.271	+2
0.18	6.685	0	5.010	—8	2.2	0.533	—5	1.114	+1
0.20	6.437	0	5.105	—8	2.4	0.400	—5	0.952	0
0.24	6.001	0	5.021	—6	2.6	0.300	—4	0.797	0
0.28	5.631	—1	4.679	—4	2.8	0.224	—4	0.657	—1
0.32	5.316	—1	4.198	—1	3.2	0.125	—2	0.430	—2
0.36	5.043	—2	3.662	+1	3.6	0.069	—2	0.272	—2
0.40	4.802	—2	3.131	+4	4.0	0.038	—1	0.168	—2
0.44	4.587	—3	2.641	+6	4.4	0.022	0	0.102	—2
0.48	4.392	—4	2.212	+8	4.8	0.013	0	0.061	—1
0.52	4.211	—4	1.852	+9	5.2	0.007	0	0.036	—1
0.56	4.041	—5	1.561	+9	5.6	0.004	0	0.022	0
0.6	3.881	—5	1.336	+10	6	0.002_5	0	0.013	0
0.7	3.509	—6	1.010	+10	7	0.000_9	0	0.003	0
0.8	3.166	—6	0.926	+8	8	0.000_4	0	0.001	0
0.9	2.847	—6	0.976	+6	9	0.000_2	0		

Footnote.- The values of T and W are given in the two-configuration approximation. Also given are the differences between the two-configuration and one-configuration values, multiplied by 1 000.

$1s^2 2s^2 2p$ in the two-configuration approximation $1s^2 2s^2 2p - 1s^2 2p^3$:

$$W(r) = 2P^2(1s\,|\,r) + \frac{1}{1+a_{12}^2}\,[2P_1^2(2s\,|\,r) + P_1^2(2p\,|\,r) + 3a_{12}^2 P_2^2(2p\,|\,r)]. \quad (3.5)$$

The values of T and W are given in Table III. In the table, the steps in r are twice the interval used in the calculations. Interpolation can easily be done if necessary. This is especially true for the total potential function, which is frequently used in computations.

4. CONCLUSIONS

From the results presented in Table II, we see that the two configuration approximation improves the theoretical energy value by 0.033 atomic units. Changing from one electron wave functions, determined in the one-configuration approximation, to functions determined in the two-configuration approximation is associated with an improvement of the result by 0.003 at.u., compared with 0.011 at.u. for the case of the neutral beryllium atom[1]. Investigation of this question shows that, for beryllium, the configuration $2s^2 2p^3$ would also give a much smaller effect than the $2s^2 2p^2$ configuration[8].

From Table III we see that the values of the total potential function T and the radial probability distribution W, as determined in the two-configuration approximation, differ from their values in the one-configuration approximation by less, in absolute value, than 0.007 and 0.010 respectively. The sign of this difference shows that the two-configuration approximation gives smaller screening of the nuclear charge in the neighborhood of the nucleus, and larger screening far away from it, as compared with the results obtained in the one-configuration approximation.

---

[8] V. V. Kibartas, V. I. Kavetskis and A. P. Iutsis, J. Exper. Theoret. Phys. USSR 29, 623 (1955); Soviet Phys. 2, 481 (1956).

Translated by M. Hamermesh
245