theory of the isotopic effect (the terms of the lighter isotopes are placed deeper). One should keep in mind the fact that in complicated atoms

non-normal positions of the isotope terms are sometimes found as the results of perturbation.

The Double Configuration Approximation to the Two Lowest Configurations of the Boron Atom

G. K. Tsiunaitis and A. P. Iutsis
Vilna State University
Physico-technical Institute, Academy of Science, Lithuanian SSSR
(Submitted to JETP editor March 24, 1954)
J. Exper. Theoret. Phys. USSR **28**, 452-457 (April, 1955)

The solutions of the equations of the self-consistent field without exchange are presented for the configurations $1s^2 2s^2 2p$ and $1s^2 2s^2 3s$ of boron. The values of the total energy, both in single configuration as well as in the double configuration approximation $1s^2 2s^2 2p^k 3s^{1-k} - 1s^2 2p^{k+2} 3s^{1-k}$ ($k = 1, 0$) are computed with the help of these solutions. With the aid of the solutions of the equation of the self-consistent field without exchange, there are also computed the mass effect, the total dipole strength and the transition probability for the transition $1s^2 2s^2 3s - 1s^2 2s^2 2p$, both in the single configuration and the double configuration approximations.

1. INTRODUCTION

THE present work is devoted to the application of a multiple configuration approximation to the two lowest configurations $1s^2 2s^2 2p$ and $1s^2 2s^2 3s$ of the boron atom with the help of the solution of the equation of the self-consistent field without exchange. The method of analysis carried out in reference 1 shows that while we use single electron wave functions, which are determined in the single configuration approximation, the multiple configuration approximation, in practice, reduces to the double configuration approximation :
$1s^2 2s^2 2p^k 3s^{1-k} - 1s^2 2p^{k+2} 3s^{1-k}$, where $k = 1$ or 0.

The approximate solutions for the lowest configuration, which were obtained in reference 2, were used as the initial functions for the solution of the

self-consistent field equation without exchange. In both configurations, the solution was carried out to the degree of self-consistency 0.0015 [cf. Eq. (2.8) in reference 3]. The orthonormalized solutions are presented in Table I. The orthonormalization was obtained by means of Eqs. (2.2) and (2.3) of reference 4, and the values of the constants c_{ik} are also given in Table I.

2. NUMERICAL CALCULATION OF THE ENERGY

The non-diagonal matrix element of the energy, which combines the investigated configurations $1s^2 2s^2 2p^k 3s^{1-k}$ with a consideration of the configuration $1s^2 2p^{k+2} 3s^{1-k}$, can be put in the following form:

$$E_{12} = (-1)^{k+1} \frac{\sqrt{3-k}}{3} G_1 (2s, 2p)_{12} \; V^2 (1s, 1s)_{12} \; N^k$$
$$\times (2p, 2p)_{12} \; N^{1-k} (3s, 3s)_{12}, \; k = 1, 0. \quad (1)$$

[1] A. P. Iutsis and V. I. Kavertskis, J. Exper. Theoret. Phys. USSR **21**, 1139 (1951)

[2] F. W. Brown, J. H. Bartlett and C. G. Dunn, Phys. Rev. **44**, 296 (1933)

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

[4] G. K. Tsiunaitis and A. P. Iutsis, J. Exper. Theoret. Phys. USSR **25**, 679 (1953)

TABLE I

Orthonormalized solutions of the equation of the self-consistent field without exchange for the two lowest configurations of the boron atom.

r	$P(1s\|r)$	$1s^22s^22p$		$1s^22s^23s$	
		$P'(2s\|r)$	$P'(2p\|r)$	$P(2s\|r)$	$P'(3s\|r)$
0.00	0.0000	0.0000	0.0000	0.0000	0.0000
0.01	0.1976	0.0339	0.0002_6	0.0371	0.0061
0.02	0.3761	0.0645	0.0010_2	0.0706	0.0117
0.03	0.5367	0.0921	0.0022_5	0.1006	0.0167
0.04	0.6810	0.1167	0.0039	0.1275	0.0211
0.06	0.9255	0.1579	0.0084	0.1728	0.0289
0.08	1.1187	0.1899	0.0142	0.2079	0.0350
0.10	1.2684	0.2139	0.0213	0.2340	0.0394
0.12	1.3815	0.2309	0.0294	0.2525	0.0424
0.14	1.4637	0.2417	0.0383	0.2643	0.0442
0.16	1.5197	0.2472	0.0479	0.2702	0.0451
0.18	1.5539	0.2481	0.0582	0.2711	0.0453
0.20	1.5700	0.2450	0.0691	0.2678	0.0447
0.22	1.5711	0.2385	0.0804	0.2607	0.0434
0.24	1.5599	0.2290	0.0922	0.2502	0.0416
0.26	1.5387	0.2169	0.1043	0.2368	0.0393
0.28	1.5093	0.2025	0.1166	0.2209	0.0367
0.30	1.4733	0.1861	0.1292	0.2028	0.0337
0.32	1.4323	0.1681	0.1419	0.1830	0.0304
0.34	1.3875	0.1486	0.1547	0.1617	0.0269
0.36	1.3398	0.1279	0.1675	0.1389	0.0231
0.38	1.2901	0.1062	0.1804	0.1150	0.0191
0.40	1.2391	0.0837	0.1934	0.0903	0.0149
0.42	1.1874	0.0606	0.2063	0.0648	0.0106
0.44	1.1355	0.0370	0.2191	0.0388	0.0062
0.46	1.0838	0.0129	0.2319	0.0123	0.0018
0.48	1.0326	—0.0115	0.2446	—0.0144	—0.0027
0.50	0.9824	—0.0361	0.2572	—0.0413	—0.0073
0.52	0.9333	—0.0607	0.2697	—0.0682	—0.0119
0.54	0.8855	—0.0853	0.2820	—0.0952	—0.0164
0.56	0.8390	—0.1098	0.2941	—0.1221	—0.0209
0.58	0.7941	—0.1341	0.3060	—0.1488	—0.0254
0.60	0.7510	—0.1582	0.3177	—0.1752	—0.0299
0.65	0.6499	—0.2172	0.3461	—0.2396	—0.0411
0.70	0.5598	—0.2737	0.3729	—0.3011	—0.0516
0.75	0.4800	—0.3273	0.3981	—0.2593	—0.0613
0.80	0.4099	—0.3775	0.4216	—0.4138	—0.0704
0.85	0.3488	—0.4241	0.4434	—0.4641	—0.0788
0.90	0.2959	—0.4670	0.4635	—0.5101	—0.0864
0.95	0.2505	—0.5061	0.4819	—0.5518	—0.0932
1.00	0.2115	—0.5414	0.4985	—0.5892	—0.0992
1.05	0.1781	—0.5730	0.5135	—0.6224	—0.1044
1.10	0.1497	—0.6011	0.5270	—0.6514	—0.1089
1.15	0.1256	—0.6255	0.5390	—0.6764	—0.1126
1.20	0.1053	—0.6466	0.5496	—0.6978	—0.1154
1.25	0.0882	—0.6646	0.5588	—0.7155	—0.1175
1.30	0.0737	—0.6796	0.5667	—0.7297	—0.1189
1.35	0.0615	—0.6918	0.5734	—0.7407	—0.1197
1.40	0.0514	—0.7014	0.5790	—0.7488	—0.1198
1.45	0.0429	—0.7086	0.5836	—0.7542	—0.1192
1.50	0.0358	—0.7135	0.5872	—0.7570	—0.1180
1.55	0.0299	—0.7164	0.5898	—0.7575	—0.1162
1.6	0.0250	—0.7173	0.5916	—0.7560	—0.1139
1.7	0.0174	—0.7142	0.5929	—0.7472	—0.1079
1.8	0.0121	—0.7054	0.5915	—0.7321	—0.1001
1.9	0.0084	—0.6920	0.5878	—0.7120	—0.0906
2.0	0.0058	—0.6749	0.5822	—0.6880	—0.0797
2.1	0.0040	—0.6549	0.5750	—0.6610	—0.0675

TABLE I (continued)

	$P(1s|r)$	1s²2s²2p		1s²2s²3s	
		$P'(2s|r)$	$P(2p|r)$	$P'(2s|r)$	$P'(3s|r)$
2.2	0.0028	—0.6327	0.5664	—0.6320	—0.0543
2.3	0.0019	—0.6090	0.5566	—0.6017	—0.0402
2.4	0.0013	—0.5841	0.5459	—0.5705	—0.0253
2.5	0.0009	—0.5587	0.5344	—0.5390	—0.0099
2.6	0.0007	—0.5330	0.5223	—0.5076	0.0059
2.7	0.0005	—0.5073	0.5097	—0.4767	0.0222
2.8	0.0003	—0.4818	0.4967	—0.4465	0.0389
2.9	0.0002	—0.4566	0.4835	—0.4172	0.0558
3.0	0.0001	—0.4319	0.4701	—0.3889	0.0729
3.2		—0.3851	0.4430	—0.3360	0.1070
3.4		—0.3414	0.4159	—0.2882	0.1404
3.6		—0.3012	0.3891	—0.2456	0.1728
3.8		—0.2648	0.3630	—0.2082	0.2037
4.0		—0.2320	0.3377	—0.1758	0.2330
4.2		—0.2026	0.3134	—0.1478	0.2603
4.4		—0.1764	0.2902	—0.1237	0.2853
4.6		—0.1533	0.2682	—0.1032	0.3081
4.8		—0.1330	0.2473	—0.0859	0.3285
5.0		—0.1152	0.2277	—0.0713	0.3464
5.2		—0.0996	0.2092	—0.0591	0.3620
5.4		—0.0859	0.1919	—0.0488	0.3752
5.6		—0.0740	0.1758	—0.0402	0.3860
5.8		—0.0636	0.1609	—0.0331	0.3947
6.0		—0.0546	0.1470	—0.0273	0.4013
6.5		—0.0371	0.1167	—0.0169	0.4097
7.0		—0.0252	0.0919	—0.0104	0.4076
7.5		—0.0170	0.0720	—0.0064	0.3974
8.0		—0.0115	0.0561	—0.0039	0.3810
8.5		—0.0078	0.0435	—0.0024	0.3600
9.0		—0.0052	0.0336	—0.0015	0.3361
9.5		—0.0035	0.0259	—0.0010	0.3105
10.0		—0.0024	0.0198	—0.0006	0.2842
10.5		—0.0016	0.0154	—0.0004	0.2581
11		—0.0011	0.0115	—0.0002	0.2327
12		—0.0005	0.0067	—0.0001	0.1857
13		—0.0002	0.0039		0.1452
14		—0.0001	0.0023		0.1116
15		—0.0000$_5$	0.0013		0.0845
16			0.0008		0.0632
17			0.0005		0.0469
18			0.0003		0.0346
19			0.0001$_5$		0.0254
20			0.0000$_8$		0.0187
22			0.0000$_3$		0.0102
24					0.0055
26		$c_{12} = 0.0431$		$c_{12} = 0.0472$	0.0029
28				$c_{13} = 0.0151$	0.0015
30				$c_{23} = 0.119$	0.0008
32					0.0004
34					0.0002

Here the radial integral G_1 has the same definition as in Eq. (3.7) of reference 1, and $N(nl, nl)_{ij}$ coincides with C_{nlij} defined in Eq. (3.4) of reference 1. The diagonal matrix elements of the energy are expressed in the usual fashion by the radial integrals I, F and G, the definitions of which are also given in reference 1.

For the single electron wave functions of the configuration under examination, we use the corresponding functions of the configuration already investigated. Under such conditions,

$$N(nl, nl)_{ij} = 1. \qquad (2)$$

Furthermore, for the function $P(2p\,|\,r)$ of the configuration $1s^2 2p^2 3s$ we use the values of the cor-

responding function of the configuration $1s^2 2s^2 2p$. Such a procedure is based on the fact that the configuration under consideration is responsible only for a correction to the energy, which is small in comparison with the value of the total energy. Therefore, a variation in the correction of several percent involves a correspondingly smaller change in the value of the total energy of the desired configuration which was determined in the double configurational approximation.

The results of the numerical determination of the energy are given in Table II, where the experimental values of the energy, taken from references 5 and 6, are also listed.

3. DETERMINATION OF THE MASS EFFECT

The mass effect for the transition $1s^2 2s^2 3s$

TABLE II

Values of the Lagrange multipliers, radial integrals and the energies for the configurations $1s^2 2s^2 2p$ and $1s^2 2s^2 3s$ of the boron atom (in atomic units).

	$1s^22s^22p$	$1s^22s^23s$		$1s^22s^22p$	$1s^22s^23s$
$\varepsilon_{1s,\,1s}$	15.494	16.025	$G_0(1s, 2s)$	0.0299	0.0354
			$G_0(1s, 3s)$		0.0010
$\varepsilon_{2s,\,2s}$	0.8897	1.3428	$G_0(2s, 3s)$		0.0039
$\varepsilon_{2p,\,2p}$	0.4533		$G_1(1s, 2p)$	0.0327	
			$G_1(2s, 2p)$	0.2459	
$\varepsilon_{3s,\,3s}$		0.2021	$G_1(2p, 3s)^*$	0.0128	
$I(1s)$	—12.437	—12.437			
$I(2s)$	—2.5121	—2.6262	E_{11}	—24.526	—24.336
$I(2p)$	—2.1098		E_{22}	—24.022	—23.758
$I(3s)$		—0.7088	E_{12}	0.116	— 0.142
$F_0(1s, 1s)$	2.8838	2.8838	ΔE	—0.025	— 0.033
$F_0(2s, 2s)$	0.4386	0.4749	a_{12}	—0.22	0.23
$F_0(2p, 2p)$	0.3670		E_{theor}	—24.551	—24.369
$F_2(2p, 2p)$	0.1629		E_{exp}	—24.655	—24.472
$F_0(1s, 2s)$	0.6093	0.6532			
$F_0(1s, 3s)$		0.1532			
$F_0(2s, 3s)$		0.1485			
$F_0(1s, 2p)$	0.5382				
$F_0(2s, 2p)$	0.3992				
$F_0(2p, 3s)^*$	0.1460				

Note: The asterisk indicates that the first function refers to the configuration $1s^2 2s^2 2p$ and the second to $1s^2 2s^2 3s$. E_{11} denotes the energy in the single configuration approximation, E_{theor} in the double configuration approximation $1s^2 2s^2 2p^k 3s^{1-k} - 1s^2 2p^{k+2} 3s^{1-k}$ ($k = 1, 0$).

— $1s^2 2s^2 2p$ of the boron atom in the single configuration approximation was calculated by Opechowski and de Vries[7] with the aid of the approximate functions of the self-consistent field

[7] M. Opechowski and D. A. de Vries, Physica 6, 913 (1939)

[5] M. Morse L. A. Young and E. S. Haurwitz, Phys. Rev. 48, 948 (1935)

[6] R. F. Bacher and S. Goudsmit, *Atomic Energy States*, New York, 1932

without exchange. Here we shall determine this effect in the double configuration approximation with the help of the radial wave functions listed in Table I.

We find the following expression for the specific shift in the energy of the investigated configuration in the double configuration approximation $1s^2 2s^2 2p^k 3s^{1-k} - 1s^2 2p^{k+2} 3s^{1-k}$ by the method developed in reference 8:

$$\Delta_c E = \frac{1}{M} \frac{1}{1 + a_{12}^2} [kK (1s, 2p)_{11} \tag{3}$$

$$+ kK (2s, 2p)_{11}$$

$$+ 2(-1)^{k+1} \sqrt{3-k} \times a_{12} K (2s, 2p)_{12} N^2$$

$$\times (1s, 1s)_{12} N^k (2p, 2p)_{12} N^{1-k} (3s, 3s)_{12}$$

$$+ (k+2) a_{12}^2 K (1s, 2p)_{22}$$

$$+ (1-k) a_{12}^2 K (2p, 3s)],$$

where all the symbols are taken from reference 8. The numerical results are given in Table III. Equation (3.1) of reference 8 was used for the calculation of the shift in the spectral line.

4. DETERMINATION OF THE VALUES OF TRANSITION THEORY

We obtain the following expression for the total dipole strength (cf. Bolotin and Iutsis[10]) in the double configuration approximation:

$$S(1s^2 2s^2 3s \, ^2S, 1s^2 2s^2 2p \, ^2P) \tag{4}$$

$$= \frac{2}{(1 + a_{12}^2)(1 + a_{12}'^2)} [N (r2p, 3s)_{11'}$$

$$\times N^2 (1s, 1s)_{11'} N^2 (2s, 2s)_{11'}$$

$$- \sqrt{2/3} \, a_{12} a_{12}' N (r 2p, 3s)_{22'}$$

$$\times N^2 (1s, 1s)_{22'} N^2 (2p, 2p)_{22'}]$$

Here the integral $N(ml, n'l')_{ij}$ has the definition of Eq. (2.5) in reference 10. The numbers 1 and 2 refer to the configurations $1s^2 2s^2 2p$ and $1s^2 2p^3$, and $1'$ and $2'$ refer to $1s^2 2s^2 3s$ and $1s^2 2p^2 3s$, respectively; a_{12} pertains to the first two configurations, a_{12}' to the latter two.

It is convenient to use the method given by

TABLE III

The results of the determination of the mass effect for the configurations $1s^2 2s^2 2p$ and $1s^2 2s^2 3s$ of the boron atom (ν in cm^{-1}, the remaining quantities in atomic units).

	$1s^2 2s^2 2p$	$1s^2 2s^2 3s$			$1s^2 2s^2 3s - 1s^2 2s^2 2p$	
					$M_2 = 11$	$M_2 = 12$
$K(1s, 2p)$	—0,2587			$\Delta_c \nu(M_2, 10) \begin{cases} a \\ b \end{cases}$	—0,357	—0,655
$K(2s, 2p)$	—0.0675				—0,372	—0,683
$K(2s, 2p)*$		—0,0783				
$K(2p, 3s)*$		—0,0075				
$M\Delta_c E \begin{cases} a \\ b \end{cases}$	—0.326	0		$\Delta_H \nu(M_2, 10) \begin{cases} a \\ b \end{cases}$	0.208	0.382
	—0.307	0.033			0.199	0.365
$M\Delta_H E \begin{cases} a \\ b \end{cases}$	24,526	24.336		$\Delta \nu(M_2, 10) \begin{cases} a \\ b \\ c \end{cases}$	—0.149	—0,273
	24.551	24.369			—0.173	—0.317
					—0.17	

Note: The asterisk indicates that the first function refers to the configuration $1s^2 2s^2 2p$ and the second to $1s^2 2s^2 3s$, a refers to the single configuration approximation, b to the double configuration approximation, c to experimental data[9]

[9] S. Mrozowski, Z. Phys. 112, 223 (1939)

[8] A. P. Iutsis, A. S. Nakonechnyi and G. K. Tsiunaitis, J. Exper. Theoret. Phys. USSR 25, 683 (1953)

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

Racah[11] for obtaining Eq. (4), since the signs in front of the values of the matrix elements of the electrical dipole moment (in first degree) must be considered in the case of the single configuration approximation. It must be noted that the sign in front of the first term in Eq. (4) in the square brackets depends, through a_{12} and a'_{12}, on the signs of the non-diagonal matrix elements of the energy in Eq. (1).

Terms with a single a_{12} and a'_{12} do not appear in Eq. (4). Therefore, in the given case, the double configuration approximation has an insignificant effect on the values of the transition theory.

In our approximation,

$$N(r2p, 3s)_{11'} = N(r2p, 3s)_{22'} \quad \text{and} \quad (5)$$
$$N(nl, nl)_{ii'} = 1.$$

TABLE IV

Transition probability for $1s^2 2s^2 3s\,^2S - 1s^2 2s^2 2p\,^2P$ for the boron atom (probability in units of 10^8/sec, other quantities in atomic units).

$N(r2p,3s) = 1.676$			
	$S(^2S, ^2P)$	$E(^2S) - E(^2P)$	$W(^2S, ^2P)$
a	5.62	0.190	4.11
b	5.52	0.182	. 3.54

Note: a gives the single configuration approximation, b the double configuration approximation.

[11] G. Racah, Phys. Rev. 62, 438 (1942); 63, 367 (1943)

We determine the integral $N(r2p, 3s)$ with the aid of the wave functions of Table I. The numerical results are given in Table IV. In this case the transition probability is determined by Eq. (4.3) of reference 10.

5. CONCLUSIONS

It can be seen from Table II that the correction to the energy in the double configuration approximation amounts to 0.025 atomic units for the configuration $1s^2 2s^2 2p$, and 0.033 atomic units for the configuration $1s^2 2s^2 3s$.

The data in Table III show that the mass effect for the transition $1s^2 2s^2 3s - 1s^2 2s^2 2p$, determined in the double configuration approximation, amounts to the entire observed isotopic shift of the given line.

As seen from Table IV, the double configuration approximation decreases the transition probability by approximately 14% in comparison with its value determined in the single figure approximation. This decrease arises principally because of the decrease in the value of the difference between the energies of the combined terms, which enters in third degree in the expression for the transition probability.