

## Bohr-Coster diagrams for multiply ionized states of light elements in the range $Z = 10$ to $20$

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**Abstract.** Calculations in the L-S coupling approximation of the average total energies of various defect electron configurations with single or double  $K$  shell and varying number of  $L$  shell vacancies for some light elements in the range  $Z = 10$  to  $20$  are reported. The calculations show that the linear trend observed for normal Bohr-Coster diagrams ( $\sqrt{E}$  vs  $Z$  curves for the usual X-ray energy states) persists in the case of multiply ionized atomic states as well.

**Keywords.** Bohr-Coster diagrams; defect electron configurations; multiply ionized atoms.

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### 1. Introduction

The great regularity of X-ray spectral lines, first observed by Moseley (1913), led to the systematization of X-ray spectra and the understanding of the origin of X-ray emission and absorption processes. This work also enabled to arrive at the precise energy level values for the inner shells of all the atoms (Bearden and Burr 1967), a knowledge which is of fundamental importance. The diagrams which depict for the various X-ray lines the variation of  $\sqrt{\nu/R}$  (where  $\nu$  represents the frequency of a particular spectral line for different elements and  $R$  is the Rydberg constant) with atomic number  $Z$  are usually called Moseley diagrams. Similar plots for the normal inner energy levels (sometimes also called X-ray levels, e.g.  $K$ ,  $L_I$ ,  $L_{II}$ , etc, which denote the binding energy of the atoms singly ionized in the respective shells) showing the variation of square roots of energies with atomic number  $Z$  are usually referred to as Bohr-Coster diagrams in literature (Slater 1960; Kuhn 1964). To our knowledge, no such plots have been reported so far for the inner atomic states multiply ionized to different degrees. We have recently reported (Lakshmi Natarajan *et al* 1986a, b) the results of our theoretical calculations of the energies of satellites and hypersatellites for neon and magnesium. We thought it interesting to extend these calculations to some more light elements in the range  $Z = 10$  to  $20$  in order to see if the linear trend observed in the case of Bohr-Coster diagrams persists for multiply ionized atomic states as well.

Electron-ion as well as ion-ion collision processes have attracted considerable attention (Crandall 1983; Hahn 1985) in recent years because of their applications in astrophysical and fusion plasma studies. In such studies it has been shown that the multicharged ions play a more important role in the formation of intermediate excited

states than the singly charged ions. It seems therefore worthwhile to undertake a systematic study of the energy sequences of multiply ionized atoms.

## 2. Calculation of configurational average energies

In our earlier publications (Lakshmi Natarajan *et al* 1986a, b) we have described the procedure for the calculation of the average energies of the different multiply ionized configurations of two light atoms, namely neon and magnesium, making use of screened hydrogenic wavefunctions. These calculations have enabled us to draw the energy level diagrams for these elements (Lakshmi Natarajan *et al* 1986b; Lakshmi Natarajan 1986) multiply ionized to different degrees in the *K* and *L* states, which in turn directly depict the transitions responsible for the *K-LL* satellites and hypersatellites. Our results for the energies of the satellite and hypersatellite lines in X-ray as well as Auger spectra are in good agreement with experimental data wherever available (Richard *et al* 1972; Kauffman *et al* 1973; Matthews *et al* 1973; Breuckman 1979). They also agree fairly well with the theoretical calculations of Bhalla *et al* (1973). It might be mentioned here that our method of calculation gives a better picture of the processes occurring in the inner atomic shells because of the analytical wavefunctions used.

The average configurational energies of the neutral, singly ionized and multiply ionized atoms (sometimes called exotic atoms in literature) in the *L-S* coupling approximation can be calculated using the following expression due to Slater (1960)

$$E_{av} = \sum I(nl) + \sum \text{interaction energies} \\ \text{for all} \quad \text{for pairs of electrons,} \\ \text{electrons} \quad \quad \quad (1)$$

where  $I(nl)$  is the one-electron energy integral. The electrostatic interaction energy integrals called the Slater-Condon parameters are given by

$$F^k(n_1l_1, n_2l_2) = e^2 \int_{r_1=0}^{\infty} \int_{r_2=0}^{\infty} R_{n_1l_1}^2(r_1) R_{n_2l_2}^2(r_2) \frac{(r_<)^k}{(r_>)^{k+1}} r_1^2 r_2^2 dr_1 dr_2, \quad (2)$$

and

$$G^k(n_1l_1, n_2l_2) = e^2 \int_{r_1=0}^{\infty} \int_{r_2=0}^{\infty} R_{n_1l_1}(r_1) R_{n_2l_2}(r_1) \frac{(r_<)^k}{(r_>)^{k+1}} \\ \times R_{n_1l_1}(r_2) R_{n_2l_2}(r_2) r_1^2 r_2^2 dr_1 dr_2, \quad (3)$$

where  $R_{n_1l_1}$  and  $R_{n_2l_2}$  are the radial parts of the hydrogenic wavefunctions. In order to calculate the values of the integrals  $F^k$ s and  $G^k$ s, one needs the numerical values of the effective charges for wavefunctions ( $Z_{eff}$  values) for different orbitals which were calculated by us using the procedure described in the earlier publications.

**Table 1.** Effective  $Z$  values for different orbitals of elements in the range  $Z = 10$  to 20.

Element	Effective charges for wave functions					
	1s	2s	2p	3s	3p	4s
Neon (10)	9.64	7.50	6.63			
Magnesium (12)	11.52	9.25	8.48	4.95		
Aluminium (13)	12.62	10.16	9.22	5.97	5.26	
Silicon (14)	13.59	11.10	10.19	6.93	6.03	
Argon (18)	17.67	14.76	13.95	10.57	9.28	
Calcium (20)	19.63	16.13	16.06	12.59	10.96	6.40

**Table 2.** Screening produced on an electron in the different shells.

Element	K		L		M	
	by K electron	by each K electron	by each L electron	by each K electron	by each L electron	by each M electron
Neon (10)	0.36	0.75	0.27			
Magnesium (12)	0.48	0.75	0.30	0.75	0.66	0.30
Aluminium (13)	0.38	0.75	0.32	0.80	0.70	0.27
Silicon (14)	0.41	0.75	0.33	0.80	0.71	0.23
Argon (18)	0.33	0.78	0.36	0.80	0.71	0.21
Calcium (20)	0.37	0.80	0.35	0.80	0.72	0.24

### 3. Results

In table 1 we have tabulated our calculated values of  $Z_{\text{eff}}$  for different orbitals of Ne, Mg, Al, Si, Ar and Ca. In table 2 are given the screenings produced by each electron in the  $K$  and  $L$  shells on the other electrons in the  $K$ ,  $L$  and  $M$  shells respectively. In table 3 are given the average total energies of the different multiply ionized atomic states characterized by various electron defect configurations.

### 4. Discussion

The energy of a normal X-ray state according to Bohr's theory is given by

$$E = (Z - \sigma)^2 / n^2, \quad (4)$$

where  $E$  is the energy of the state in Rydbergs,  $\sigma$  the screening constant and  $n$  the principal quantum number. The slopes of the curves  $\sqrt{E}$  vs  $Z$  drawn for the  $K$  and  $L$

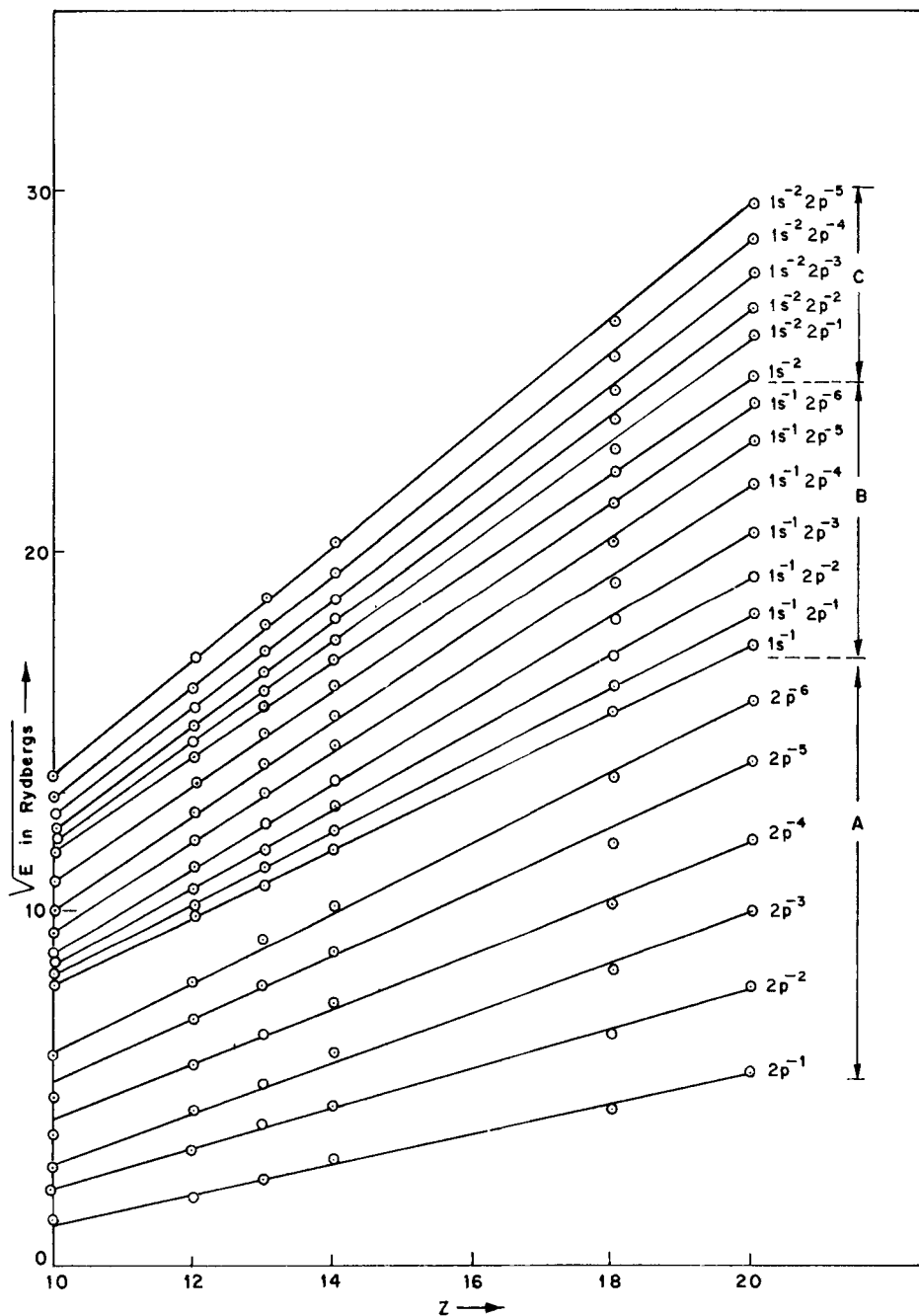
Table 3. Average total energies of multiply ionized atomic states.

Electron defect configuration	$E_{\text{average}}$ in eV					
	$_{10}\text{Ne}$	$_{12}\text{Mg}$	$_{13}\text{Al}$	$_{14}\text{Si}$	$_{18}\text{Ar}$	$_{20}\text{Ca}$
$2p^{-1}$	21.9	47.9	78.5	111.3	249.9	367.9
$2p^{-2}$	56.1	135.5	203.5	270.6	565.1	822.8
$2p^{-3}$	108.9	268.8	367.2	484.2	945.8	1332.1
$2p^{-4}$	200.3	431.1	576.9	739.8	1394.1	1933.9
$2p^{-5}$	318.4	640.5	848.3	1047.2	1904.0	2681.9
$2p^{-6}$	475.7	881.8	1128.8	1398.1	2503.0	3349.7
$1s^{-1}$	868.8	1302.0	1562.3	1846.9	3206.4	4055.5
$1s^{-1}2p^{-1}$	905.8	1396.0	1697.3	2021.4	3540.7	4534.2
$1s^{-1}2p^{-2}$	968.5	1534.7	1872.7	2248.1	3935.1	5068.0
$1s^{-1}2p^{-3}$	1068.1	1712.8	2096.0	2517.2	4404.5	5691.7
$1s^{-1}2p^{-4}$	1196.3	1936.8	2377.3	2841.1	4928.6	6463.9
$1s^{-1}2p^{-5}$	1369.5	2193.7	2674.9	3209.6	5556.7	7160.4
$1s^{-1}2p^{-6}$	1571.7	2514.6	3060.1	3635.1	6220.6	7923.4
$1s^{-2}$	1848.6	2749.0	3319.1	3905.3	6677.1	8381.6
$1s^{-2}2p^{-1}$	1914.2	2898.0	3504.7	4143.9	7087.3	8945.1
$1s^{-2}2p^{-2}$	2025.6	3087.1	3740.2	4428.7	7575.4	9592.5
$1s^{-2}2p^{-3}$	2165.2	3323.8	4035.4	4770.3	8119.2	10388.4
$1s^{-2}2p^{-4}$	2349.9	3597.8	4351.1	5155.8	8768.4	11120.7
$1s^{-2}2p^{-5}$	2566.2	3936.5	4750.5	5597.2	9455.2	11913.6

states should be 1 and 1/2, since  $n = 1$  and 2 respectively for these states. In order to see if (4) is valid for the multiply ionized states also, we have plotted in figure 1 the values of the square roots of the energies (in Rydbergs) for different multiply ionized states against atomic number. It is interesting to note that for the multiply ionized atomic states also, one obtains linear Bohr-Coster plots as for the singly ionized states. This linearity observed by us establishes the linear dependence of  $\sqrt{E}$  on  $Z$  even for the multiply ionized states.

We may group the curves in figure 1 into three groups: the group A comprises of different atomic states multiply ionized in the  $2p$  shell only, the group B comprises of the configurations with multiple ionization in the  $2p$  shell together with single ionization in the  $1s$  shell and the group C refers to the states multiply ionized in the  $2p$  shell and doubly ionized in the  $1s$  shell. We observe that with gradual increase in the degree of multiple ionization the slopes of the curves also increase progressively. It is interesting to note that in the groups B and C, the relative change in the slopes of the individual curves is small, which probably indicates that the effect of holes in the  $1s$  shell is large and the gradual increase of holes in the  $2p$  shell for the individual curves produces only a small percentage change in their slopes. On the other hand in the group A of the curves corresponding to the states with no hole in the  $1s$  shell the gradual increase of holes in the  $2p$  shell produces a larger percentage change from curve to curve.

In table 4 we have given the values of the slopes of the curves plotted in figure 1. In figure 2, we have plotted these values as a function of  $n_p$ , the number of holes in the  $2p$



**Figure 1.** Bohr-Coster diagrams for multiply ionized atomic states. The group *A* corresponds to atoms multiply ionized in the  $2p$  shell only. The groups *B* and *C* correspond respectively to atoms multiply ionized in the  $2p$  shell and singly or doubly ionized in the  $1s$  shell.

**Table 4.** Values of the slopes of the  $\sqrt{E}$  vs  $Z$  curves.

Electron defect configuration	Values of slopes	Slope <sup>-1</sup> = $n^*$
$2p^{-1}$	0.47	2.14
$2p^{-2}$	0.58	1.72
$2p^{-3}$	0.70	1.42
$2p^{-4}$	0.80	1.25
$2p^{-5}$	0.90	1.11
$2p^{-6}$	1.00	1.00
$1s^{-1}$	0.95	1.05
$1s^{-1}2p^{-1}$	1.02	0.98
$1s^{-1}2p^{-2}$	1.11	0.91
$1s^{-1}2p^{-3}$	1.17	0.85
$1s^{-1}2p^{-4}$	1.23	0.81
$1s^{-1}2p^{-5}$	1.29	0.77
$1s^{-1}2p^{-6}$	1.34	0.76
$1s^{-2}$	1.35	0.74
$1s^{-2}2p^{-1}$	1.41	0.71
$1s^{-2}2p^{-2}$	1.47	0.68
$1s^{-2}2p^{-3}$	1.54	0.65
$1s^{-2}2p^{-4}$	1.59	0.63
$1s^{-2}2p^{-5}$	1.66	0.60

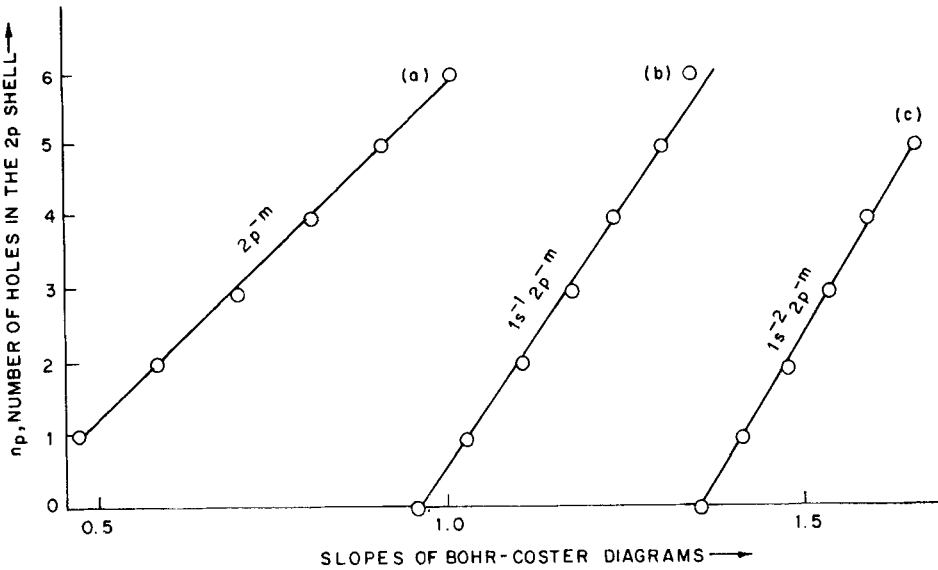
shell. In this figure the curve *a* corresponds to multiple ionization in the  $2p$  shell only, the curve *b* to single ionization in the  $1s$  shell and multiple ionization in the  $2p$  shell, while the curve *c* corresponds to double ionization in the  $1s$  shell and multiple ionization in the  $2p$  shell. We note that these plots are more or less similar to the  $E$  vs  $n_p$  plots (where  $E$  is the energy of the satellite/hypersatellite line) reported by us earlier (1986a, b). We further note that the curves *b* and *c* are nearly parallel to each other which might probably be due to ionization in the  $1s$  shell in both the cases in addition to multiple ionization in the  $2p$  shell. The curve *a* is not parallel to the *b* and *c* curves, most probably because in this case the ionization of the atoms occurs in the  $2p$  shell with no ionization in the  $1s$  shell.

It has been customary (White 1934) in optical spectra to write the following expression for the energy of the valence orbitals

$$E = \frac{(Z - \sigma)^2}{n^{*2}}. \quad (5)$$

This expression is similar to (4) except that here  $n$  is replaced by  $n^* = n - \mu$ , where  $n^*$  is called the effective principal quantum number and  $\mu$  the quantum defect. The latter is assumed to be arising out of the penetration of the outer orbitals into the core levels. The concept of the effective principal quantum number helps in defining accurately the energy of a state in the case of a complex atom.

Drawing the analogy from the valence states to the case of inner multiply ionized states we have attempted to determine the values of  $n^*$  from the energies of the multiply



**Figure 2.** Plots between the slopes of the Bohr-Coster diagrams and  $n_p$ , the number of holes in the  $2p$  shell. The curve *a* corresponds to multiple ionization in the  $2p$  shell only while the curves *b* and *c* respectively refer to multiple ionization in the  $2p$  shell along with single or double ionization in the  $1s$  shell.

ionized configurations. It must, however, be borne in mind that  $n^*$  does not have the same physical origin in the two cases. In the case of our energy states which arise because of multiple ionisation in the  $K$  as well as  $L$  levels, the principal quantum number  $n$  is neither 1 nor 2, but gets non-integral values which are effective in describing the energies of the complex states. In table 4 we have therefore included the reciprocals of the slopes yielding  $n^*$  for the different electron defect configurations. For the state  $1s^0 2p^{-1}$ , i.e. the normal  $L$  X-ray level, the value of  $n^*$  comes out to be very nearly 2 as expected, while for the configurations  $1s^0 2p^{-m}$  the value of  $n^*$  decreases from 2 to 1 as  $m$  increases from 1 to 6. Likewise, for the levels  $1s^{-1} 2p^0$ , i.e. the normal  $K$  X-ray level, the slope<sup>-1</sup> of the  $\sqrt{E}$  vs  $Z$  curve is found to be nearly 1 as expected, while for the  $1s^{-1} 2p^{-m}$  and  $1s^{-2} 2p^{-m}$  states the values of  $n^*$  gradually decrease from 1 to 0.6.

It is interesting to mention here that Uchai *et al* (1986) have very recently calculated the energy shifts of the  $L$  X-ray satellites due to multiple  $M$  vacancies for the elements in the range  $Z = 70$  to 90, using a Dirac-Fock computer programme. Their plots between  $\Delta E$  and  $Z$  are very similar to our plots. It may indirectly be concluded from their work that the Bohr-Coster diagrams are valid for multiply ionized atomic states of heavier elements also.

## 5. Concluding remarks

The results of our present calculations, although based on a few light elements only, reveal that the atomic states of multiply ionized atoms show the same trend of

behaviour as is exhibited by the normal X-ray states. Our work, however, shows that the values of the principal quantum number for the exotic atoms are no more 1, 2, 3 . . . . as for the normal  $K, L, M$  . . . . X-ray states but the concept of an effective quantum number has to be introduced to account for their energies. It seems now necessary to undertake further theoretical and experimental investigations on the nature and behaviour of exotic atoms. Fortunately with the advent of numerous heavy-ion accelerators presently available in different parts of the world, it should now be possible to carry out meaningful experiments on satellite and hypersatellite lines in X-ray and Auger spectra. Such studies will hopefully lead to a better understanding of the processes occurring in ion-atom collisions and the nature of the various transient atomic states.

It has been recently shown (Raman and Vane 1984) that the X-ray satellite spectra of chemical compounds produced by heavy ion bombardment display significant variations in satellite peaks, which are found to depend on the chemical environment of the emitting atoms. In order to understand the effects of chemical bonding in satellite spectra and to be able to derive any meaningful information from such studies, it seems necessary to first systematize and understand the data on multiply ionized atomic states of pure elements.

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