

# ATOMIC IONIZATION ENERGIES OF LOW ATOMIC NUMBER ELEMENTS CALCULATED BY SEMICLASSICAL METHOD

Gy. VARSÁNYI

Department of Physical Chemistry,  
Technical University, H-1521 Budapest

Received October 3, 1983

## Summary

A semiclassical method has been presented for the calculation of ionization energies. Basic principle is the determination and consideration of shielding and of orbital modifying interactions. Besides ionization energy, the removing and the binding energy are defined. The method is applied also for calculation of inner ionization energies. A secondary relaxation is interpreted which is taken into consideration formally by fractional number of electrons. Excitation energies of electrons can be calculated by the same method.

## 1. Relation of Binding and Ionization Energies in Atoms and Ions of Low Atomic Number Elements

### *Introduction*

Atomic ionization energies can be expressed by a formula  $(Z_{\text{eff}}^2/n^2) E_{\text{H}}$  where  $Z_{\text{eff}}$  stands for the effective nucleic charge,  $n$  for the principle quantum number, while  $E_{\text{H}}$  is the ionization energy (IE) of the hydrogen atom, 13.595 eV.  $Z_{\text{eff}}$  can be obtained by calculating the shielded charge of the nucleus by other electrons and completing this with an orbital modifying interaction.

### *The shielding*

The shielding effect of a 1s electron towards the other one can be calculated from the corresponding eigenfunction of the hydrogen atom. For this purpose the probability of a 1s electron has to be multiplied in every  $r$  distance by the integrated probability of the other 1s electron in a sphere inside this distance, then to be integrated over the whole area. No normalizing factor has to be taken into account if this integral is divided by the integral of the whole expression which is the product of both probability integrals:

$$Q = \frac{\int_0^{\infty} P_1(r) \left[ \int_0^r P_2(r) dr \right] dr}{\int_0^{\infty} P_1(r) \left[ \int_0^{\infty} P_2(r) dr \right] dr} = \frac{\int_0^{\infty} P_1(r) \left[ \int_0^r P_2(r) dr \right] dr}{\int_0^{\infty} P_1(r) dr \int_0^{\infty} P_2(r) dr} \quad (1.1)$$

If a 1s electron is shielded by a 1s electron,  $P_1 = P_2 = r^2 \exp(-2r/r_1)$  where  $r_1$  is the Bohr radius. Partial results are:

$$\int_0^{\infty} P dr = r_1^3/4$$

$$\int_0^r P dr = \frac{r_1^3}{4} - \left( \frac{r_1^3}{4} + \frac{r_1^2 r}{2} + \frac{r_1 r^2}{2} \right) \exp(-2r/r_1) \quad (1.2)$$

$$\int_0^{\infty} P \left( \int_0^r P dr \right) dr =$$

$$\begin{aligned} &= \int_0^{\infty} \left\{ \frac{r_1^3 r^2}{4} \exp(-2r/r_1) - \left[ \frac{r_1^3 r^2}{4} + \frac{r_1^2 r^3}{2} + \frac{r_1 r^4}{2} \right] \exp(-4r/r_1) \right\} dr = \\ &= \frac{r_1^6}{16} - \left( \frac{r_1^6}{128} + \frac{3r_1^6}{256} + \frac{3r_1^6}{256} \right) = \frac{r_1^6}{32} \end{aligned}$$

The denominator of (1.1) is  $r_1^6/16$ , hence:  $Q = 1/2$ . This is a trivial result as one of the electrons shields the other when it lies closer to the nucleus than the other. But this is a certain case. This certainty is shared to two electrons. Nevertheless, this consideration may be generalized for cases when the shielding does not equal 1/2 (the two electrons are not in the same orbital). Under such circumstances the sum of the shieldings of both electrons equals the unity.

Similarly, the shielding of a 1s electron by a 2s electron can be calculated as follows.  $P$  function of a 2s electron is:

$$P_2 = r^2 \left[ 4 - 4 \frac{r}{r_1} + \left( \frac{r}{r_1} \right)^2 \right] \exp(-r/r_1).$$

Partial results are:

$$\int_0^{\infty} P_2 dr = 8r_1^3$$

$$\int_0^r P_2 dr = 8r_1^3 - \left( 8r_1^3 + 8r_1^2 r + 4r_1 r^2 + \frac{r^4}{r_1} \right) \exp(-r/r_1) \quad (1.3)$$

The numerator of (1.1):  $2r_1^6 - \left( \frac{16r_1^6}{27} + \frac{16r_1^6}{27} + \frac{32r_1^6}{81} + \frac{80r_1^6}{243} \right) = \frac{22r_1^6}{243}$ .

The denominator:  $8r_1^3(r_1^3/4) = 2r_1^6$ , hence:  $Q = \frac{11}{243} = 0.04527$ . The shielding of the 2s electron by the 1s electron:  $1 - 0.04527 = 0.9547$ .

If the atom contains also 2p electrons, one has to calculate the shielding of 1s and 2s electrons by each 2p electrons. According to the eigenfunctions of the hydrogen atom, the probability function of a 2p electron is:

$\Psi^2 = N^2 \left( \frac{r}{r_1} \right)^2 \exp(-r/r_1) \cos^2 \vartheta$  where  $N$  stands for the normalizing factor and  $\vartheta$  for the polar angle. As the charge has to be integrated to the whole area the probability has to be multiplied by  $r^2 \sin \vartheta dr d\vartheta d\varphi$  and to be integrated between the corresponding limits. In the denominator of (1.1), however, the integral does not depend on the polar angle thus  $\cos^2 \vartheta$  has to be omitted:

$$Q = \frac{\int_0^{\infty} P_1 \left[ \int_0^r \frac{r^4}{r_1^2} \exp(-r/r_1) dr \right] dr \int_0^{\pi} \cos^2 \vartheta \sin \vartheta d\vartheta}{\int_0^{\infty} P_1 dr \int_0^{\infty} \frac{r^4}{r_1^2} \exp(-r/r_1) dr \int_0^{\pi} \sin \vartheta d\vartheta} \quad (1.4)$$

(Integral of  $d\varphi$  has been omitted from numerator and denominator.) The integral containing the polar angle in the numerator equals 2/3, in the denominator 2 thus the whole fraction 1/3. Partial results are:

$$\int_0^{\infty} \frac{r^4}{r_1^2} \exp(-r/r_1) dr = 24r_1^3$$

$$\int_0^r \frac{r^4}{r_1^2} \exp(-r/r_1) dr =$$

$$= 24r_1^3 - \left( 24r_1^3 + 24r_1^2 r + 12r_1 r^2 + 4r^3 + \frac{r^4}{r_1} \right) \exp(-r/r_1)$$

Substituting  $P_1$  by the probability of a 1s electron the numerator of (1.4):  $6r_1^6 - \left( \frac{32}{9}r_1^6 + \frac{32}{27}r_1^6 + \frac{240}{243}r_1^6 \right) = \frac{22}{81}r_1^6$ . The denominator:  $6r_1^6$ . The fraction containing variant  $r$  is equal to  $\frac{11}{243}$  (identical to the shielding of a 2s electron) but multiplied by the fraction containing  $\vartheta$  thus by 1/3, so the result is  $\frac{11}{729} = 0.0151$ .

Replacing the probability function of a 2s electron in  $P_1$  the numerator equals  $291r_1^6 - \left( 90r_1^6 + \frac{315}{4}r_1^6 \right) = \frac{489}{4}r_1^6$ . The denominator amounts to  $192r_1^6$  and the fraction to  $\frac{163}{256}$ . Multiplied by 1/3 the shielding  $2p \rightarrow 2s$  is equal to  $\frac{163}{768} = 0.2122$ .

#### *The orbital modifying interaction*

Shielding effect itself is an electron-electron interaction too, with the assumption, however, that the electron functions are not varied by the presence of two electrons in the same orbital or several electrons in different orbitals. Thus the shielding term has to be completed with an orbital modifying term in the expression of IE:

$$E_I = \frac{(Z - Q_{\text{eff}})^2 - E_M}{n^2} E_H \quad (1.5)$$

where  $Q_{\text{eff}}$  stands for the effective shielding and  $E_M$  for the orbital modifying energy equivalent. (In the following energies will be expressed either as the multiple of the IE of hydrogen atom like a dimensionless quantity or in electron volts.)  $E_M$  is an electron-electron repulsion which always diminishes IE in the form of a negative term. The orbital modifying energy (OME) in helium atom can be calculated from the experimental IE. The IE of helium atom amounts to  $24.580 \text{ eV} = 1.808 E_H$  [1].  $Q_{\text{eff}}$  calculated equals 0.5, hence  $E_M = 2.25 - 1.808 = 0.442$ .

The orbital modifying electron-electron interaction is inversely proportional to the average electron-electron distances. Quantum mechanical calculations also accept the special result of the Bohr model that the Bohr radius  $r_1$  is inversely proportional to the nucleic charge. Rounding the mutual OME of 1s electrons in helium atom calculated from the experimental IE up to 0.5, one can say that the OME of all 1s electrons equals  $0.25 Z$ .

The average nucleus-electron distance calculated from the 1s eigenfunction is equal to  $1.5r_1$ , the same in the 2s orbital to  $6r_1$ . This is four

times more than in the  $1s$  orbital, because of the division by  $n^2$ , however, the OME of  $2s$  electrons can be taken to be equal to  $0.25 Z$ , too.

The OME between  $1s$  and  $2s$  electrons can be determined from the mutual sinking of the orbitals relative to the total "volume" of the more extended orbital. These "volumes", however, are infinite. Usually the distance within the electron stays with a probability of 90% is given instead. If, for  $1s$  electrons:

$$\frac{\int_0^r Pdr}{\int_0^\infty Pdr} = 1 - \left[ 2\left(\frac{r}{r_1}\right)^2 + 2\frac{r}{r_1} + 1 \right] \exp(-2r/r_1) = 0.9,$$

$r = 2.661 r_1$ . Substituting this distance as upper integration limit in the corresponding expression of  $2s$  electrons:

$$\frac{\int_0^r Pdr}{\int_0^\infty Pdr} = 1 - \left[ \frac{1}{8}\left(\frac{r}{r_1}\right)^4 + \frac{1}{2}\left(\frac{r}{r_1}\right)^2 + 1 \right] \exp(-r/r_1) = 0.0588$$

thus within the distance where a  $1s$  electron stays with a probability of 90%, the probability of a  $2s$  electron is only 5.88%. The ratio of the probabilities is 0.0654. Multiplied by  $0.25 Z$ , the mutual OME  $1s-2s$  gives  $0.01635 Z$  which can be rounded down to  $0.015 Z$ .

The probability of a  $2p$  electron within the same distance:

$$\frac{\int_0^r Pdr}{\int_0^\infty Pdr} = 1 - \left[ \frac{1}{24}\left(\frac{r}{r_1}\right)^4 + \frac{1}{6}\left(\frac{r}{r_1}\right)^3 + \frac{1}{2}\left(\frac{r}{r_1}\right)^2 + \frac{r}{r_1} + 1 \right] \exp(-r/r_1) =$$

$$= 0.1313$$

The ratio of the probabilities is 0.1459. A  $2p$  electron, however, is in contact with only one third of the  $1s$  electron cloud, therefore the sinking proportion is only  $0.1459/3$ . Multiplied by  $0.25 Z$ ,  $0.01216 Z$  is obtained and the rounded value is  $0.012 Z$ .

In order to get 0.9 as the result of the last expression, the corresponding upper integration limit has to be  $7.993 r_1$ , thus the  $2p$  electron stays with 90% probability within the distance of  $7.993 r_1$ . Taking this value as upper integration limit in the expression for  $2s$  electrons, 0.8137 is obtained. Relative to 90% the overlapping would be 90.41% if the  $2p$  electron occupied the whole

area. Divided by 3 the real overlapping is only 30.14%. The overlap of  $1s-2p$  electrons has been multiplied by  $0.25 Z$ , considering, however, that the average distance of  $2s$  electrons is four times higher, the overlap of  $2s-2p$  electrons has to be multiplied only by  $\frac{0.25}{4} Z$ . The result is  $0.01884 Z$  which can be rounded up to  $0.02 Z$ .

As the orbital of three  $p$  electrons is divided into six parts by nodal planes, the interaction of  $2p$  electrons in the same orbital consisting of two equal parts the area of which is then one sixth of the total  $p$  orbitals, can be calculated by averaging the OME-s calculated for the same and for different sixth areas. The ratio of the average electron-electron distances in the case of identical sixth area can be substituted by the cube root of the orbital volume ratio. According to the former calculation the volume of three  $p$  orbitals is equal to 0.9041 volume of a  $2s$  orbital and that of a sixth area to 0.1507. Cube root of the inverse ratio is 1.879. The interaction of electrons in different sixth areas can be calculated from the ratio of the average nucleic distance of  $2s$  and  $2p$  electrons, respectively. This ratio is 6:5 thus the ratio of OME-s is 1.2. The arithmetic mean is 1.5395. Multiplied by  $0.25 Z$  one obtains  $0.3849 Z$  and the rounded value is  $0.4 Z$ .

At last the interaction of  $2p$  electrons in different orbitals can be calculated from the overlap of two different  $2p$  orbitals. This overlap (Fig. 1.1):

$$\frac{\int_{\pi/4}^{3\pi/4} \cos^2 \vartheta \sin \vartheta d\vartheta}{\int_0^{\pi} \cos^2 \vartheta \sin \vartheta d\vartheta} = \frac{\sqrt{2}}{4}$$

The result has to be divided and multiplied by 2. The division is sufficient because the overlap calculated holds for the two other  $p$  orbitals and for the present case the interaction of a  $p$  electron pair is interesting. Multiplication can neither be omitted because not only the considered electron extends over the polar angles given as limits, but also the other electron stays beyond them:  $\sqrt{2}/4$  multiplied by  $0.4 Z$  results in  $0.1414$  the rounded value of which is  $0.15 Z$ . Table 1.1 contains the mutual shieldings and OME-s.

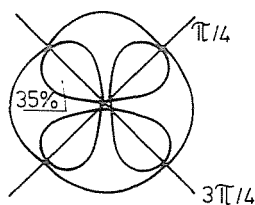


Fig. 1.1

**Table 1.1**

Shielding of  $j$ -th orbital by an  $i$ -th orbital electron ( $Q_{ij}$ ) and the  $i-j$  orbital modifying energies in  $E_H$

	1s-1s	1s-2s	1s-2p	2s-2s	2s-2p	2p <sub>x</sub> -2p <sub>y</sub>	2p <sub>x</sub> -2p <sub>x</sub>
$Q_{ij}$	0.5	0.9547	0.9849	0.5	0.7878	0.5	0.5
$E_M$	0.25 Z	0.015 Z	0.012 Z	0.25 Z	0.02 Z	0.15 Z	0.4 Z

*The effective shielding*

The shielding of electrons perturbed by orbital modifying interactions cannot be taken identical to the charge equivalents calculated from the eigenfunctions of hydrogen atom. Naturally, mutual shielding of electrons in identical orbital is always 0.5, because of the equivalence of the electrons. In the case of helium atom the OME has been calculated by subtracting the square of the effective nucleic charge 1.808 from  $(2-0.5)^2$  i.e. the difference of two charge squares has been constructed. The shielding perturbing effect of OME-s can be similarly interpreted. The OME of an electron in an  $i$ -th orbital:

$$E_M^* = (N_i Q_{ij})^2 - Q_{ij, \text{eff}}^2$$

where  $N_i$  is number of electrons in the  $i$ -th orbital,  $Q_{ij}$  the shielding of the  $j$ -th orbital by the  $i$ -th orbital's electrons calculated from the hydrogen atom eigenfunctions while  $Q_{ij, \text{eff}}$  stands for the effective shielding. The shielding perturbing effect of the OME of an electron or electron pair can only be proportional to its proper shielding effect. Being OME a Coulomb interaction it is proportional to  $e^2/r$  where  $e$  is the elementary charge.  $E_M^*$  is proportional, however, to the shielding charge square  $q_i^2 \equiv e^2 Q_i^2$ . Hence:  $E_M^* = E_M Q_i^2$ .

$$Q_{ij}^2 E_{Mi} = (N_i Q_{ij})^2 - Q_{ij, \text{eff}}^2$$

$$Q_{ij, \text{eff}} = Q_{ij} N_i \sqrt{1 - E_{Mi}/N_i^2} \tag{1.6}$$

This expression serves for the effective shielding only when  $E_{Mi}/N_i^2$  is small (for example in the case of  $2p$  electrons of nitrogen atom  $E_{Mi}$  exceeds the unity which would result in an imaginary number for  $Q_{\text{eff}}$ ). Therefore (1.6) has to be replaced by an exponential expression:

$$Q_{ij, \text{eff}} = Q_{ij} N_i \exp(-E_{Mi}/2N_i^2) \tag{1.7}$$

which goes over (1.6) if  $E_{Mi}$  is small. In the case, however, when an  $i$ -th orbital electron shields an other of the  $j$ -th orbital,  $Q_{ij}$  is modified also by the OME of

the electron or electron pair of the  $j$ -th orbital. Considering that

$$Q_{ij} + Q_{ji} = 1,$$

$$Q_{ij} = 1 - Q_{ji} \exp(-E_{Mj}/2N_j^2),$$

hence

$$Q_{ij, \text{eff}} = N_i [1 - Q_{ji} \exp(-E_{Mj}/2N_j^2)] \exp(-E_{Mi}/2N_i^2) \quad (1.8)$$

$E_{Mi}$  and  $E_{Mj}$  stands for the sum of OME-s of electrons in the  $i$ -th and  $j$ -th orbital, respectively. The half of OME, corresponding to the interaction of two electrons, belongs to one, the other half to the other electron. It follows that all OME-s belonging to the electron to be removed in ionization have to be multiplied by  $N_i/2$  and  $N_j/2$ , respectively in (1.8). Thus the exponent is simplified into  $E_{Mi}/(4N_i)$  and  $E_{Mj}/(4N_j)$ .

If the  $j$ -th orbital is a  $p$ -type one, while the  $i$ -th an  $s$  orbital, calculating  $Q_{ij, \text{eff}}$  in the  $E_{Mi}$  sum only one third of the  $s-s$  interactions has to be taken into account as these interactions can influence the shielding of the  $p$  electrons occupying one third of the area only in this proportion. The  $s-p$  interactions of other  $p$  electrons with  $s$  orbitals have not to be considered at all because another  $p$  orbital electron modifies the  $s$  orbital perpendicularly not influencing the  $s-p$  shielding to be calculated.

Table 1.2 includes the IE-s of the atoms and ions in the first two periods, giving the  $Q_{ij, \text{eff}}$  shieldings exerted to the electrons to be removed, and the sum

Table 1.2

Charge shieldings towards outer electrons, orbital modifying interactions, calculated and measured ionization energies in eV

	$Q_{1s}$	$Q_{2s}$	$Q_{2p}$	$Q_{2p^2}$	$\Sigma E_M$	$E_I$	exp. [1]
He	0.5	—	—	—	0.5	23.8	24.580
He <sup>+</sup>	—	—	—	—	—	54.4	54.403
Li	1.731	—	—	—	0.09	5.17	5.390
Li <sup>+</sup>	0.5	—	—	—	0.75	74.8	75.619
Li <sup>2+</sup>	—	—	—	—	—	122.4	122.419
						202.4	
Be	1.670	0.5	—	—	1.12	7.57*	9.320
Be <sup>+</sup>	1.675	—	—	—	0.12	18.0	18.206
Be <sup>2+</sup>	0.5	—	—	—	1	152.9	153.850
Be <sup>3+</sup>	—	—	—	—	—	217.5	217.657
						396.0	
B	1.846	1.498	—	—	0.32	8.23	8.296
B <sup>+</sup>	1.615	0.5	—	—	1.4	23.5	25.149
B <sup>2+</sup>	1.621	—	—	—	0.15	38.3	37.920
B <sup>3+</sup>	0.5	—	—	—	1.25	258.3	259.298
B <sup>4+</sup>	—	—	—	—	—	339.9	340.127
						668.2	



	$Q_{1s}$	$Q_{2s}$	$Q_{2p}$	$Q_{2p_2}$	$\Sigma E_M$	$E_I$	exp.[1]
C	1.828	1.554	0.5	—	1.284	10.9	11.264
C <sup>+</sup>	1.823	1.483	—	—	0.384	23.4	24.376
C <sup>2+</sup>	1.562	0.5	—	—	1.68	47.0	47.864
C <sup>3+</sup>	1.569	—	—	—	0.18	66.1	64.476
C <sup>4+</sup>	0.5	—	—	—	1.5	390.9	391.986
C <sup>5+</sup>	—	—	—	—	—	489.4	489.84
						<u>1027.7</u>	
N	1.809	1.608	1	—	2.548	14.0	14.54
N <sup>+</sup>	1.805	1.547	0.5	—	1.498	28.6	29.605
N <sup>2+</sup>	1.799	1.468	—	—	0.448	45.9	47.426
N <sup>3+</sup>	1.510	0.5	—	—	1.96	78.0	77.450
N <sup>4+</sup>	1.518	—	—	—	0.21	101.4	97.863
N <sup>5+</sup>	0.5	—	—	—	1.75	550.6	551.925
N <sup>6+</sup>	—	—	—	—	—	666.2	666.83
						<u>1484.7</u>	
O	1.766	1.577	1	0.5	6.112	13.1	13.614
O <sup>+</sup>	1.787	1.603	1	—	2.912	34.4	35.146
O <sup>2+</sup>	1.782	1.539	0.5	—	1.712	53.5	54.934
O <sup>3+</sup>	1.776	1.452	—	—	0.512	75.6	77.394
O <sup>4+</sup>	1.460	0.5	—	—	2.24	116.4	113.873
O <sup>5+</sup>	1.469	—	—	—	0.24	144.2	138.080
O <sup>6+</sup>	0.5	—	—	—	2	737.5	739.114
O <sup>7+</sup>	—	—	—	—	—	870.1	871.12
						<u>2044.8</u>	
F	1.743	1.591	0.5	1.5	8.226	17.7	17.418
F <sup>+</sup>	1.741	1.567	1	0.5	6.876	36.4	34.98
F <sup>2+</sup>	1.765	1.596	1	—	3.276	62.0	62.646
F <sup>3+</sup>	1.760	1.530	0.5	—	1.926	85.7	87.23
F <sup>4+</sup>	1.753	1.437	—	—	0.576	112.8	114.214
F <sup>5+</sup>	1.411	0.5	—	—	2.52	162.2	157.117
F <sup>6+</sup>	1.422	—	—	—	0.27	194.3	185.139
F <sup>7+</sup>	0.5	—	—	—	2.25	951.65	953.60
F <sup>8+</sup>	—	—	—	—	—	1101	
						<u>2723.75</u>	
Ne	1.720	1.598	—	2.5	10.64	23.3	21.559
Ne <sup>+</sup>	1.719	1.578	0.5	1.5	9.14	44.1	41.07
Ne <sup>2+</sup>	1.717	1.555	1	0.5	7.64	66.9	64
Ne <sup>3+</sup>	1.743	1.588	1	—	3.64	96.9	97.16
Ne <sup>4+</sup>	1.738	1.520	0.5	—	2.14	125.1	126.4
Ne <sup>5+</sup>	1.731	1.422	—	—	0.64	157.2	157.91
Ne <sup>6+</sup>	1.364	0.5	—	—	2.8	215.4	—
Ne <sup>7+</sup>	1.376	—	—	—	0.3	251.8	—
Ne <sup>8+</sup>	0.5	—	—	—	2.5	1193	—
Ne <sup>9+</sup>	—	—	—	—	—	1359.5	—
						<u>3533.2</u>	

\* Goscinski und cow. [2] also obtained too low ionization energy on the ground of quantum mechanical calculation (8.02 eV).

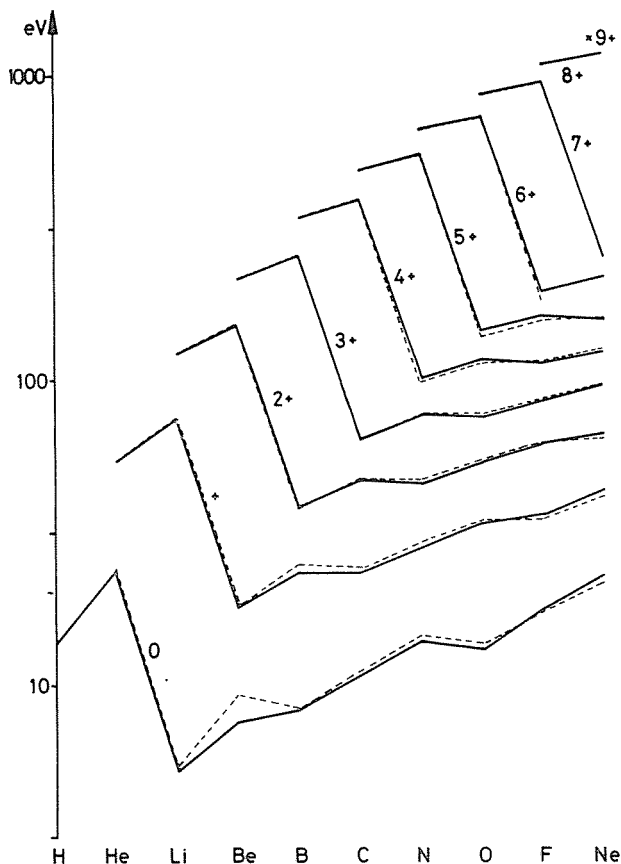


Fig. 1.2

of OME-s belonging to the same electron. Let us control for example the quantities used for the calculation of IE of an oxygen atom resulting in a local minimum with increasing atomic number. Among four  $p$  electrons two are compensated. These have the lowest IE. The OME in identical  $p$  orbital is  $0.4 \times 8 = 3.2$ . OME with the two unpaired electrons amounts to  $2 \times 8 \times 0.15 = 2.4$ . With the two  $1s$  electrons:  $2 \times 8 \times 0.012 = 0.192$ . With the two  $2s$  electrons the OME is  $2 \times 8 \times 0.02 = 0.32$ . Summing up: 6.112. Necessary data to calculate

$$Q_{1s-2p^2, \text{eff}}: \quad N_{1s} = 2, \quad Q_{2p^2-1s} = 0.0151, \quad E_{M2p^2} = 6.112,$$

$N_{2p^2} = 2$ , the OME between  $1s-1s$  electrons equals  $8 \times 0.25 = 2$  and between  $1s-2s$  electrons  $8 \times 0.015 = 0.12$ , hence

$$E_{M1s} = \frac{1}{3}(2 + 2 \times 0.12) + 0.192 = 0.9387.$$

$Q_{2p^2-1s} \exp(-E_{M_{2p^2}}/4N_{2p^2}) = 0.00703$ ;  $\exp(-E_{M_{1s}}/4N_{1s}) = 0.8893$   
 and  $2(1 - 0.00703)0.8893 = 1.766$ . Similarly calculated, for 2s shielding:  
 $Q_{2s-2p^2, \text{eff}} = 1.577$ . According to (1.5):

$$E_{I_{2p^2}} = \frac{[8 - (1.776 + 1.577 + 1.5)]^2 - 6.112}{4} = 0.9637 E_H = 13.10 \text{ eV.}$$

Fig. 1.2 represents calculated and experimental IE-s in logarithmic scale.

### *Binding energy*

The total binding energy (BE) of electrons is equal to the energy to be invested in order to remove all the electrons successively from the nucleic linkage. It is easy to comprehend, according to the shielding effects, that removing of two electrons one after the other from the same orbital requires different energies, although their BE is naturally the same. Following the chemical definition *BE is an average energy necessary to cut the system in components*. Thus BE-s can be determined from IE-s if the removing energy (RE) necessary to remove the first electron of the corresponding orbital is multiplied by a factor  $r$  the ratio of the sum of successive IE-s and RE-s of first electrons summing up for every orbital:

$$r = \frac{\sum_{j=1}^z E_{Ij}}{\sum_{i=1}^n N_i E_{Ri1}}$$

where  $n$  is the number of different orbitals,  $N_i$  the electron number in the  $i$ -th orbital,  $E_{Ri1}$  stands for the RE of the first electron from the  $i$ -th orbital and  $E_{Ij}$  for the  $j$ -th IE. Hence the BE:

$$E_{Bi} = E_{Ri1} r \quad (1.9)$$

The RE-s, shieldings and OME-s used in the calculation and BE-s calculated according to (1.9) for Li, C, O and Ne to be found in Table 1.3. RE of outer electrons is identical to IE.

Figs 1.3 demonstrate the connection between BE and IE from helium to neon. The levels correspond to BE-s. Zero energy level corresponds to ionized state, in spite of this vertical arrows representing IE-s do not reach the zero level because the BE of the corresponding electron in absolute value is higher than IE. The excess energy necessary for ionization (the distance between the point of the arrow and the zero level) is covered by the relaxation of the ion in the course of which the BE of the remaining electrons is increased.

Table 1.3

Charge shieldings towards the electron to be removed, orbital modifying interactions, calculated removing and binding energies

	$Q_{1s}$	$Q_{2s}$	$Q_{2p}$	$Q_{2p^2}$	$E_M$	$E_R$	$E_B$
			Li	$r = \frac{202.4}{136.0} = 1.488$			
2s	1.731*	—	—	—	0.09*	5.17*	7.7
1s	0.5	0.1326	—	—	0.795	65.4	97.3
			Li <sup>+</sup>	$r = \frac{197.2}{149.6} = 1.318$			
1s	0.5*	—	—	—	0.75*	74.8*	98.6
1s	—	—	—	—	—	122.4*	122.4
			C	$r = \frac{1027.7}{723.0} = 1.421$			
2p	1.828*	1.554*	0.5*	—	1.284*	10.9*	15.5
2s	1.536	0.5	0.401	—	1.92	36.6	52.0
1s	0.5	0.3775	0.1305	—	1.824	314.0	446.3
			O		$r = \frac{2044.8}{1466.6} = 1.394$		
2p <sup>2</sup>	1.766*	1.577*	1*	0.5*	6.112*	13.1*	18.3
2p	2.790	1.650	0.5	1	4.112	17.8	24.8
2s	1.395	0.5	0.2122	0.2893	2.88	96.9	135.1
1s	0.5	0.4357	0.0812	0.1156	2.624	605.5	844.0
			Ne		$r = \frac{3533.2}{2525.6} = 1.399$		
2p <sup>2</sup>	1.720*	1.598*	—	2.5*	10.64*	23.3*	32.6
2s	1.253	0.5	—	0.5286	4	188.9	264.3
1s	0.5	0.4672	—	0.2372	3.52	1004	1405

\* Data occurring also in Table 1.2.

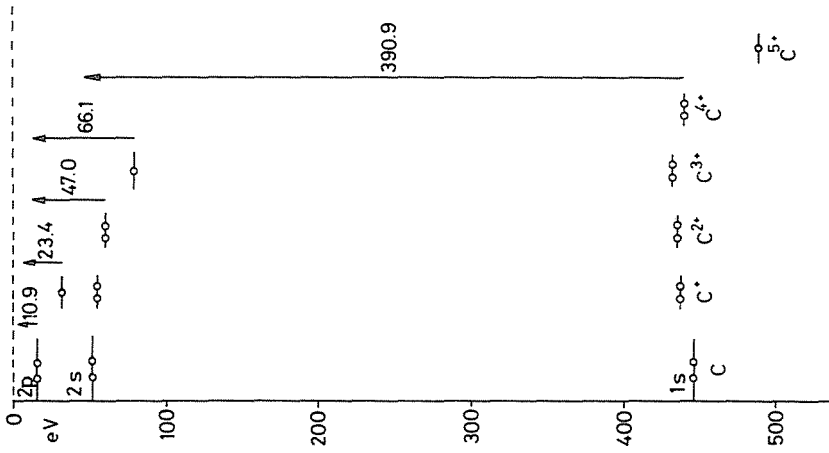


Fig. 1.3.b

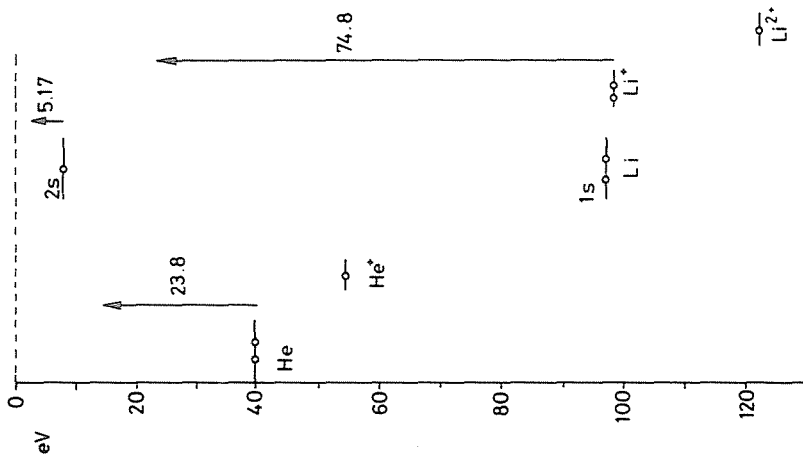


Fig. 1.3.a

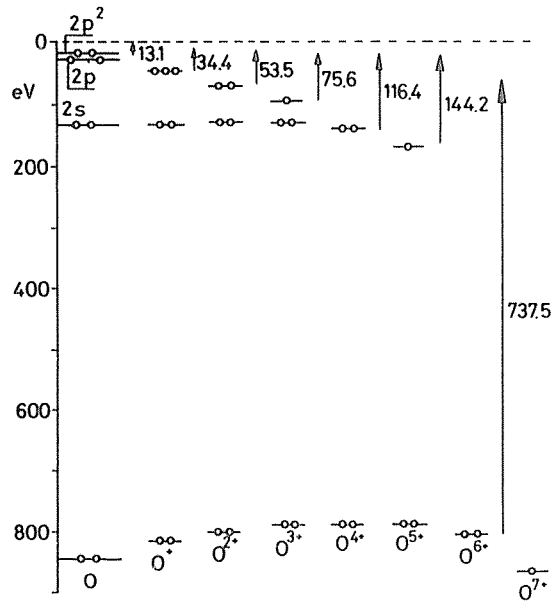


Fig. 1.3.c

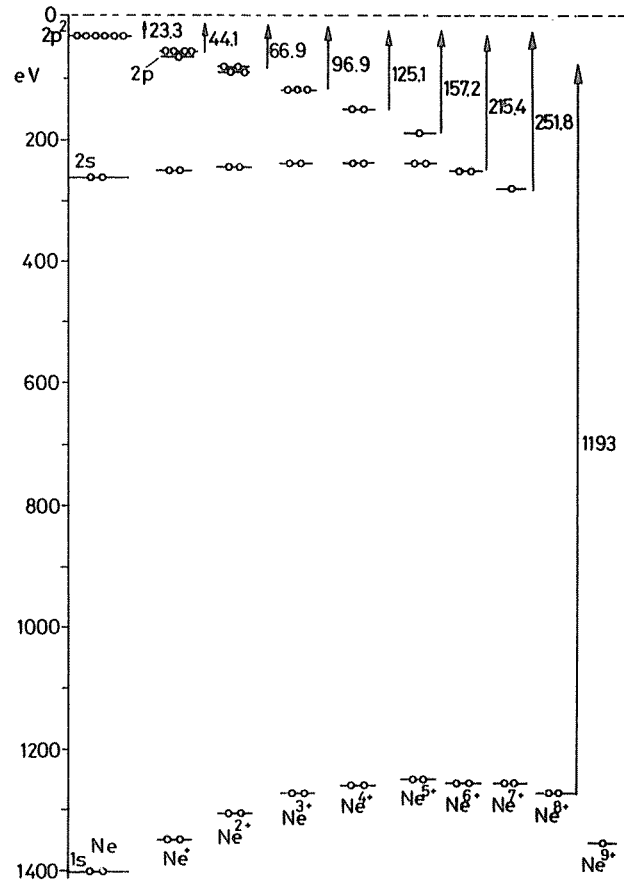


Fig. 1.3.d

## 2. Inner Ionization Energies in Atoms of Low Atomic Number Elements

With the method described in Part 1 we can try to calculate also IE-s of excited atoms. IE-s of excited atoms and ions are summarized in Table 2.1, with the details of the calculation, compared to data of vacuum UV spectra. It can be seen that with the exception of lithium ion in  $1s2s$  configuration, the calculated energies are systematically higher than the values determinable from spectra [3]. The reason of this systematic deviation will be treated later.

### *1s inner ionization energies*

Calculated with the method of Part 1 RE-s of outer electrons can only be taken identical to IE-s. Inner ionization energies (IIE) can be calculated indirectly taking into account that the total energy of ionization, when  $N$  outer electrons are removed, is independent of the order of the electrons. Therefore, if we wish to calculate IIE, when the  $n$ -th electron counted from outside is removed, we have to subtract  $\sum_{i=1}^{n-1} E_{Ii}^{\oplus}$  from the sum  $\sum_{i=1}^n E_{Ii}$  where  $E_{Ii}^{\oplus}$  stands for the  $i$ -th IE of the inner ion while  $E_{Ii}$  for the  $i$ -th IE of the atom. Fig. 2.1 schematizes the calculation of  $1s$  IIE of beryllium atom, with numerical values. If  $1s$  ionization is in question it is  $(Z - 1)$ -th counted from outside thus  $n = Z - 1$ . Outer IE-s for atoms and ions are to be found in Table 1.2, for atoms and ions ionized in  $1s$  orbital in Table 2.2. IIE-s calculated by subtracting the sums compared to experimental data are to be found in Table 2.3. It can be seen that, except lithium, calculated IIE-s are systematically higher than energies determined experimentally. In the case of neon the deviation reaches 75 eV.

Generally, if an electron is removed not from an outer but an inner shell, hole state is established which is stabilized by a secondary relaxation. Calculations demonstrated in Table 2.2 do not take this secondary relaxation into account. Hole states have been treated by Slater [4] who introduced the conception of "transition states" formally described by fractional numbers of electrons. In these cases in internally ionized atoms a fraction of  $2s$  electrons has to be taken into consideration in the  $1s$  orbital. One can easily calculate IE-s with fractional electron numbers by the method given in Part 1, partly when determining the  $N$ -s in the exponents of (1.8), partly when calculating the OME-s. If, for example in the  $1s$  orbital 1.1 and in the  $2s$  orbital 1.9 electrons are taken into account the OME  $1s - 1s$  is equal to  $0.1 \times 0.25 Z$  while the OME  $2s - 2s$  to  $0.9 \times 0.25 Z$ . In the exponent concerning  $1s$  electrons  $E_{M, 1s-2s}$  has to be multiplied by 1.9 while in the exponent of  $2s$  electrons by 1.1. At last, summing

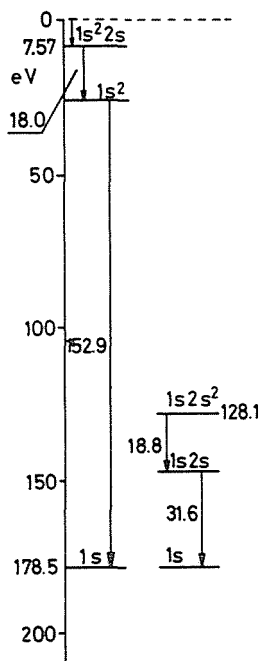


Fig. 2.1

up the IE-s the IE of the shared electron will be the weighted average of the energies of both orbitals. For example the sum  $\sum_{i=1}^{Z-2} E_{Ii}^{\oplus}$  of beryllium atom ionized in  $1s$  orbital if the effective electron configuration is  $1s^{1.1} 2s^{1.9}$  as follows:  $E_{I1} + 0.9E_{I2} + 0.1E_{I3}$ .

Recently many experimental data have been published about IIE-s of atoms [5, 6, 7], partly contradicting to older data [8]. The most recent experimental data can be reproduced with the method of Part 1 when a small fraction of  $2s$  electrons is taken into consideration in the  $1s$  orbital. This fraction, in a relatively simple expression:

$$\Delta N = 0.03(N_{2s} - 1) + 0.015N_{2p}$$

where  $N_{2s}$  is the number of  $2s$  electrons while  $N_{2p}$  stands for the *occupied*  $2p$  orbitals. In this way the maximal fraction number of electrons to be transposed (in the case of nitrogen, oxygen, fluorine and neon) is only 0.075. First, second, etc. IE-s of  $1s$  ionized atoms are collected in Table 2.4, completing these with IIE-s obtained by subtraction of energy sums. Maximal deviation is to be found for neon: 3.3 eV representing, however, an error of 0.4%. It is worth to mention



**Table 2.1**

Ionization energies of excited atoms and ions and corresponding spectroscopic terms in eV

	$Q_{1s}$	$Q_{2s}$	$Q_{2p}$	$\Sigma E_M$	$E_I$	spec [3]
1s2s						
Li <sup>+</sup>	0.9446	—	—	0.045	14.2	14.9
1s2p						
Li <sup>+</sup>	0.9762	—	—	0.036	13.8	13.4
Be <sup>2+</sup>	0.9733	—	—	0.048	31.0	30.2
B <sup>3+</sup>	0.9705	—	—	0.06	55.0	53.8
C <sup>4+</sup>	0.9676	—	—	0.072	85.8	84.2
N <sup>5+</sup>	0.9647	—	—	0.084	123.5	121.5
O <sup>6+</sup>	0.9619	—	—	0.096	168.0	165.4
F <sup>7+</sup>	0.9591	—	—	0.108	219.4	216.1
1s <sup>2</sup> 2p						
Li	1.901	—	—	0.072	3.86	3.54
Be <sup>+</sup>	1.879	—	—	0.096	15.0	14.25
B <sup>2+</sup>	1.857	—	—	0.12	33.2	31.9
C <sup>3+</sup>	1.835	—	—	0.144	58.5	56.5
N <sup>4+</sup>	1.813	—	—	0.168	90.9	87.9
O <sup>5+</sup>	1.792	—	—	0.192	130.3	126.1
F <sup>6+</sup>	1.771	—	—	0.216	176.9	171.2
1s <sup>2</sup> 2s2p						
Be	1.875	0.7734	—	0.176	5.61	4.05
B <sup>+</sup>	1.852	0.7697	—	0.22	18.5	16.0
C <sup>2+</sup>	1.829	0.7661	—	0.264	38.4	35.2
N <sup>3+</sup>	1.806	0.7624	—	0.308	65.7	61.2
O <sup>4+</sup>	1.784	0.7588	—	0.352	100.0	94.2
F <sup>5+</sup>	1.762	0.7551	—	0.396	141.5	134.8

that calculating IIE of lithium, transposition of fraction electrons into 1s orbital is not necessary (according to the formula  $\Delta N=0$ ), the calculated energy very well agrees with the experimental value. It is also interesting that the experimental value is satisfied by the RE of a 1s electron (according to Table 1.3 this is 65.4 eV), too.

### *2s inner ionization energies*

2s inner ionization energies differ from each other strongly according to *J* and *S* quantum numbers of the ion. Calculations have tried to reproduce the maximal values belonging to unvaried *L* quantum number of *p* electrons and to minimal spin quantum number. Calculating with integer electrons the

**Table 2.2**

Calculation of ionization energies of 1s inner ions not considering secondary relaxation

	$E_I/eV$		$E_I/eV$		$E_I/eV$		$E_I/eV$
Li <sup>⊕</sup>	14.2	B <sup>⊕</sup>	21.1	C <sup>⊕</sup>	26.2		
Be <sup>⊕</sup>	18.8	B <sup>⊕+</sup>	38.9	C <sup>⊕+</sup>	42.1		
Be <sup>⊕+</sup>	31.6	B <sup>⊕2+</sup>	55.8	C <sup>⊕2+</sup>	65.9		
	50.4		115.8	C <sup>⊕3+</sup>	86.9		
					221.1		
N	31.7	O <sup>⊕</sup>	33.6	F <sup>⊕</sup>	40.6	Ne <sup>⊕</sup>	48.5
N <sup>⊕+</sup>	49.6	O <sup>⊕+</sup>	49.6	F <sup>⊕+</sup>	62.2	Ne <sup>⊕+</sup>	72.1
N <sup>⊕2+</sup>	70.2	O <sup>⊕2+</sup>	79.9	F <sup>⊕2+</sup>	90.3	Ne <sup>⊕2+</sup>	97.8
N <sup>⊕3+</sup>	99.7	O <sup>⊕3+</sup>	105.3	F <sup>⊕3+</sup>	117.2	Ne <sup>⊕3+</sup>	130.2
N <sup>⊕4+</sup>	124.8	O <sup>⊕4+</sup>	140.4	F <sup>⊕4+</sup>	147.6	Ne <sup>⊕4+</sup>	161.5
	376.0	O <sup>⊕5+</sup>	169.6	F <sup>⊕5+</sup>	188.0	Ne <sup>⊕5+</sup>	196.9
			586.3	F <sup>⊕6+</sup>	221.1	Ne <sup>⊕6+</sup>	242.5
					867.1	Ne <sup>⊕7+</sup>	279.6
							1229.1

\* Data occurring also in Table 2.1.

**Table 2.3**

Calculated 1s ionization energies, not considering secondary relaxation

	$\sum_{i=1}^{z-1} E_I^i - \sum_{i=1}^{z-2} E_{Ii}^{\oplus i}$	Exp. [5]
Li:	80.0 - 14.2 = 65.8 eV	66.3 eV
Be:	178.5 - 50.4 = 128.1 eV	123.6 eV
B:	328.3 - 115.8 = 212.5 eV	200.8 eV
C:	538.3 - 221.1 = 317.2 eV	296.2 eV
N:	818.5 - 376.0 = 442.5 eV	403 eV [8]
O:	1174.7 - 586.3 = 588.4 eV	538 eV [8]
F:	1622.75 - 867.1 = 755.65 eV	694 eV [8]
Ne:	2173.7 - 1229.1 = 944.6 eV	870.1 eV

obtained results are to be found in Table 2.5. The corresponding energy sums in this case:

$$E_{I2s} = \sum_{i=1}^{z-3} E_{Ii} - \sum_{i=1}^{z-4} E_{Ii}^{\oplus} \quad (2.1)$$

The calculated results are systematically lower than the energies experimentally determined so that using the method of fractional electron numbers, just contrarywise to the former, a fraction of 1s electrons has to be transposed into the 2s orbital which is trivial considering that the lack of electrons appears now

**Table 2.4**  
Calculated 1s ionization energies

Be <sup>⊕</sup>	$\Delta N=0.03$ $E_I/\text{eV}$	B <sup>⊕</sup>	$\Delta N=0.045$ $E_I/\text{eV}$	C <sup>⊕</sup>	$\Delta N=0.06$ $E_I/\text{eV}$	N <sup>⊕</sup>	$\Delta N=0.075$ $E_I/\text{eV}$
1.	18.8	1.	21.0	1.	26.1	1.	31.6
2.	$\left\{ \begin{array}{l} 30.2 (0.97 \times E_{2s}) \\ 6.5 (0.03 \times E_{1s}) \end{array} \right.$	2.	38.9	2.	41.9	2.	49.4
	$\frac{55.5}{}$	3.	$\left\{ \begin{array}{l} 52.5 (0.955 \times E_{2s}) \\ 15.1 (0.045 \times E_{1s}) \end{array} \right.$	3.	65.9	3.	69.9
			$\frac{127.5}{}$	4.	$\left\{ \begin{array}{l} 80.5 \\ 29.0 \end{array} \right.$	4.	99.9
					$\frac{243.4}{}$	5.	$\left\{ \begin{array}{l} 113.8 \\ 49.3 \end{array} \right.$
							$\frac{413.9}{}$

O <sup>⊕</sup>	$\Delta N=0.075$ $E_I/\text{eV}$	F <sup>⊕</sup>	$\Delta N=0.075$ $E_I/\text{eV}$	Ne <sup>⊕</sup>	$\Delta N=0.075$ $E_I/\text{eV}$
1.	33.5	1.	40.5	1.	48.4
2.	57.4	2.	62.0	2.	72.0
3.	79.7	3.	90.2	3.	97.6
4.	104.9	4.	116.6	4.	130.0
5.	140.8	5.	147.1	5.	161.3
6.	$\left\{ \begin{array}{l} 155.1 \\ 64.5 \end{array} \right.$	6.	188.5	6.	196.4
	$\frac{635.9}{}$	7.	$\left\{ \begin{array}{l} 202.6 \\ 81.7 \end{array} \right.$	7.	243.4
			$\frac{929.2}{}$	8.	$\left\{ \begin{array}{l} 256.8 \\ 101.0 \end{array} \right.$
					$\frac{1306.9}{}$

	$\sum_{i=1}^{z-1} E_i - \sum_{i=1}^{z-2} E_i^{\oplus i}$	
Be:	178.5 - 55.5 = 123.0 eV	(123.6)
B:	328.3 - 127.5 = 200.8 eV	(200.8)
C:	538.3 - 243.4 = 294.9 eV	(296.2)
N:	818.5 - 413.9 = 404.6 eV	(403)
O:	1174.7 - 635.9 = 538.8 eV	(538)
F:	1622.75 - 929.2 = 693.55 eV	(694)
Ne:	2173.7 - 1306.9 = 866.8 eV	(870.1)

in the 2s orbital. Good agreements are obtained by the transposition of the following fractional number of electrons:

$$\Delta N = 0.01 + \frac{4S_p}{300} \tag{2.2}$$

where  $S_p$  stands for the resulting spin quantum number of  $p$  electrons. One has to calculate with maximal fraction for nitrogen atom, namely 0.03. The

Table 2.5

Calculation of ionization energies of 2s inner ions with integer electron numbers

	$E_I/\text{eV}$		$E_I/\text{eV}$		$E_I/\text{eV}$		$E_I/\text{eV}$		$E_I/\text{eV}$
B <sup>⊖</sup>	18.5*	N <sup>⊖</sup>	29.8	O <sup>⊖</sup>	31.8	F <sup>⊖</sup>	39.1	Ne <sup>⊖</sup>	47.4
		N <sup>⊖+</sup>	46.6	O <sup>⊖+</sup>	55.4	F <sup>⊖+</sup>	60.1	Ne <sup>⊖+</sup>	70.6
C <sup>⊖</sup>	24.3	N <sup>2+</sup>	65.7*	O <sup>⊖2+</sup>	76.4	F <sup>⊖2+</sup>	88.0	Ne <sup>⊖2+</sup>	95.6
C <sup>⊖+</sup>	38.4*			O <sup>⊖3+</sup>	100.0*	F <sup>⊖3+</sup>	113.4	Ne <sup>⊖3+</sup>	127.6
	62.7		142.1		263.6	F <sup>⊖4+</sup>	141.5*	Ne <sup>⊖4+</sup>	157.4
							442.1	Ne <sup>⊖5+</sup>	190.1
									688.7

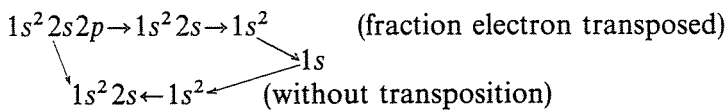
B:	$8.2+23.5-18.5=13.2$ eV	(17.4) [5]
C:	$10.9+23.4+47.0-62.7=18.6$ eV	(25.0)
N:	$14.0+28.6+45.9+78.0-142.1=24.4$ eV	(35.2)
O:	$13.1+34.4+53.5+75.6+116.4-263.6=29.4$ eV	(40.0)
F:	$17.7+36.4+62.0+85.7+112.8+162.2-442.1=34.7$ eV	(47.1)
Ne:	$23.3+44.1+66.9+96.9+125.1+157.2+215.4-688.7=40.2$ eV	(48.4)

\* Data occurring also in Table 2.1.

maximum relative deviation appears for boron atom (instead of 17.4 eV, 15.6 eV) the origin of which, however, comes from the calculation of outer IE-s in the first sum being a bit lower than the experimental energies. The calculations can be controlled in Table 2.6.

#### Outer ionization energies of excited atoms and ions

It was to be seen from Table 2.1 that calculated IE-s were higher than those determined from UV spectra. In the course of excitation a hole state is established similarly to inner ionization. For example the configuration  $1s^2 2s 2p$  corresponds to a boron atom ionized in its 2s orbital. Transposing some fraction of electrons from 1s orbital to 2s the calculated outer IE will be modified. If the 2p, 2s and the first 1s electron are successively removed, a normal  $B^{4+}$  is obtained. Considering the energy circle:



first ionization energy of the internal ion can be determined by subtracting the third and fourth IE of boron atom from the IE sum of the inner ion. According

**Table 2.6**  
Calculated 2s ionization energies

B <sup>⊖</sup>	$E_I/eV$ $\Delta N = 0.0167$	C <sup>⊖</sup>	$E_I/eV$ $\Delta N = 0.0233$	N <sup>⊖</sup>	$E_I/eV$ $\Delta N = 0.03$
1.	18.5	1.	23.9	1.	29.9
2.	38.3	2.	38.6	2.	46.7
3.	{ 0.6 (0.0167 × E <sub>2s</sub> ) 255.3 (0.9833 × E <sub>1s</sub> ) 312.7	3.	66.1	3.	65.8
		4.	{ 1.5 383.9 514.0	4.	101.4
				5.	{ 3.0 537.3 784.1

O <sup>⊖</sup>	$\Delta N = 0.0233$	F <sup>⊖</sup>	$\Delta N = 0.0167$	Ne <sup>⊖</sup>	$\Delta N = 0.01$
1.	31.8	1.	39.2	1.	47.4
2.	55.4	2.	60.1	2.	70.6
3.	76.5	3.	88.0	3.	95.6
4.	100.2	4.	113.4	4.	127.7
5.	144.1	5.	141.6	5.	157.4
6.	{ 3.3 723.3 1134.6	6.	194.2	6.	190.2
		7.	{ 3.2 938.2 1577.9	7.	251.7
				8.	{ 2.5 1182.6 2125.7

B:	328.3 – 312.7 = 15.6 eV	(17.4) [5]
C:	538.3 – 514.0 = 24.3 eV	(25.0)
N:	818.5 – 784.1 = 34.4 eV	(35.2)
O:	1174.7 – 1134.6 = 40.1 eV	(40.0)
F:	1622.75 – 1577.9 = 44.85 eV	(47.1)
Ne:	2173.7 – 2125.7 = 48.0 eV	(48.4)

to (2.2) 0.01667 electron has to be transposed in order to correspond to configuration 1s<sup>2</sup>2s2p. In the case of 1s<sup>2</sup>2p configuration best agreement is obtained with transposing 0.01, for 1s2p configuration with the transposition of 0.005 electrons. Details of the calculations can be found in Table 2.7.

*2p inner ionization energies*

Until neon, these can be interpreted only for oxygen and fluorine. I.e. only in these atoms can be compensated and uncompensated p electrons distinguished. Removing of a compensated electron requires the lowest energy: this is

Table 2.7

Outer ionization energies of excited atoms and ions

1s2p configuration $\Delta N = 0.005$							
Li <sup>+</sup>	$E_I/\text{eV}$	Be <sup>2+</sup>	$E_I/\text{eV}$	B <sup>3+</sup>	$E_I/\text{eV}$		
1.	13.7	1.	31.1	1.	55.1		
2.	$\begin{cases} 0.1 (0.005 \times E_{2s}) \\ 121.8 (0.995 \times E_{1s}) \end{cases}$	2.	$\begin{cases} 0.2 \\ 216.4 \end{cases}$	2.	$\begin{cases} 0.3 \\ 338.1 \end{cases}$		
	135.6		247.7		393.5		
C <sup>4+</sup>		N <sup>5+</sup>	O <sup>6+</sup>	F <sup>7+</sup>	$E_I/\text{eV}$		
1.	86.0	1.	123.7	1.	168.3	1.	219.7
2.	$\begin{cases} 0.4 \\ 486.9 \end{cases}$	2.	$\begin{cases} 0.6 \\ 662.7 \end{cases}$	2.	$\begin{cases} 0.8 \\ 865.6 \end{cases}$	2.	$\begin{cases} 1.1 \\ 1095.5 \end{cases}$
	573.3		787.0		1034.7		1316.3
Li <sup>+</sup>	135.6 – 122.4 = 13.2 eV					(13.4) [3]	
Be <sup>2+</sup>	247.7 – 217.5 = 30.2 eV					(30.2)	
B <sup>3+</sup>	393.5 – 339.9 = 53.6 eV					(53.8)	
C <sup>4+</sup>	573.3 – 489.4 = 83.9 eV					(84.2)	
N <sup>5+</sup>	787.0 – 666.2 = 120.8 eV					(121.5)	
O <sup>6+</sup>	1034.7 – 870.1 = 164.6 eV					(165.4)	
F <sup>7+</sup>	1316.3 – 1101 = 215.3 eV					(216.1)	
1s <sup>2</sup> 2p configuration $\Delta N = 0.01$							
Li	$E_I/\text{eV}$	Be <sup>+</sup>	$E_I/\text{eV}$	B <sup>2+</sup>	$E_I/\text{eV}$		
1.	3.9	1.	15.1	1.	33.4		
2.	$\begin{cases} 0.0 \\ 74.5 \end{cases}$	2.	$\begin{cases} 0.2 \\ 152.0 \end{cases}$	2.	$\begin{cases} 0.4 \\ 256.5 \end{cases}$		
	78.4		167.3		290.3		
C <sup>3+</sup>		N <sup>4+</sup>	O <sup>5+</sup>	F <sup>6+</sup>	$E_I/\text{eV}$		
1.	58.7	1.	91.2	1.	130.7	1.	177.3
2.	$\begin{cases} 0.6 \\ 387.9 \end{cases}$	2.	$\begin{cases} 1.0 \\ 546.2 \end{cases}$	2.	$\begin{cases} 1.4 \\ 731.4 \end{cases}$	2.	$\begin{cases} 1.9 \\ 943.6 \end{cases}$
	447.2		638.4		863.5		1122.8
Li	78.4 – 74.8 = 3.6 eV					(3.54) [3]	
Be <sup>+</sup>	167.3 – 152.9 = 14.4 eV					(14.25)	
B <sup>2+</sup>	290.3 – 258.3 = 32.0 eV					(31.9)	
C <sup>3+</sup>	447.2 – 390.9 = 56.3 eV					(56.5)	
N <sup>4+</sup>	638.4 – 550.6 = 87.8 eV					(87.9)	
O <sup>5+</sup>	863.5 – 737.5 = 126.0 eV					(126.1)	
F <sup>6+</sup>	1122.8 – 951.65 = 171.15 eV					(171.2)	

**Table 2.7** (cont.)

$1s^2 2s 2p$ configuration $\Delta N = 0.0167$					
Be	$E_I/\text{eV}$	$B^+$	$E_I/\text{eV}$	$C^{2+}$	$E_I/\text{eV}$
1.	5.6		312.7	1.	38.6
2.	18.0		(Table 2.6)	2.	66.1
3.	{ 0.3 <u>151.4</u> 175.3			3.	{ 1.1 <u>385.9</u> 491.7
$N^{3+}$		$O^{4+}$		$F^{5+}$	
1.	65.8	1.	100.1	1.	141.6
2.	101.4	2.	144.1	2.	194.2
3.	{ 1.7 <u>543.2</u> 712.1	3.	{ 2.4 <u>727.3</u> 973.9	3.	{ 3.2 <u>938.2</u> 1277.2
Be	$175.3 - 18.0 - 152.9 = 4.4 \text{ eV}$				(4.05) [3]
$B^+$	$312.7 - 38.3 - 258.3 = 16.1 \text{ eV}$				(16.0)
$C^{2+}$	$491.7 - 66.1 - 390.9 = 34.7 \text{ eV}$				(35.2)
$N^{3+}$	$712.1 - 101.4 - 550.6 = 60.1 \text{ eV}$				(61.2)
$O^{4+}$	$973.9 - 144.2 - 737.5 = 92.2 \text{ eV}$				(94.2)
$F^{5+}$	$1277.2 - 194.3 - 951.65 = 131.25 \text{ eV}$				(134.0)

the outer IE. For oxygen  $2p$  inner ionization energy can be obtained by subtracting the first IE of the inner ion from the first and second IE of the atom. Both procedures lead to an  $O^{2+}$  ion of carbon configuration. For fluorine the first two IE-s of the inner ion have to be subtracted from the first three IE-s of the atom realizing a  $F^{3+}$  of similar carbon configuration. The calculation is to be found in Table 2.8. The results serve an evidence of *no secondary relaxation*.

**Table 2.8**

Calculated  $2p$  ionization energies

$E_I/\text{eV}$		
$O^\ominus$	29.5	O: $13.1 + 34.4 - 29.5 = 18.0 \text{ eV}$ (18.6) [5]
$F^\ominus$	36.4	F: $17.7 + 36.4 + 62.0 - 93.4 = 22.7 \text{ eV}$ (23.0)
$F^{\ominus+}$	<u>57.0</u> 93.4	

### Binding energies of internal ions

BE-s can be calculated on the ground of Formula (1.9) but the IIE has to be subtracted from the numerator of  $r$ . Similarly to Figs 1.3 Figs 2.2 illustrate the procedure of internal ionization, the primary and secondary relaxation for the same elements.

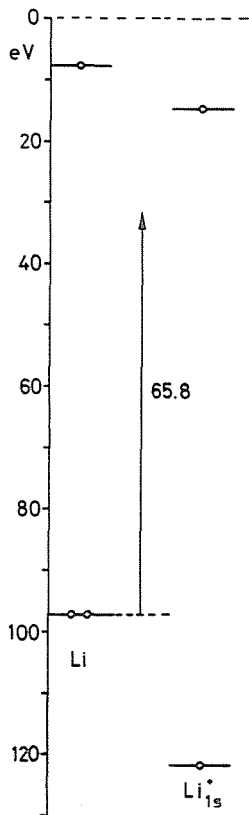


Fig. 2.2.a

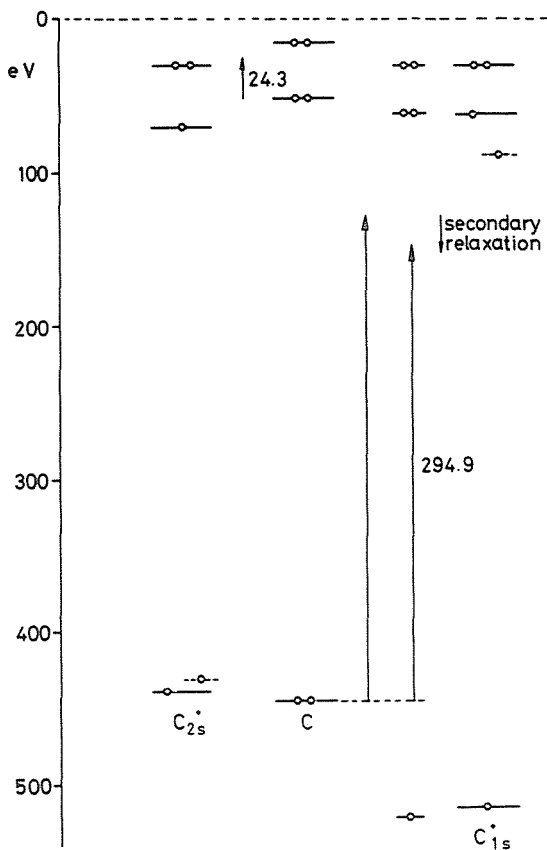


Fig. 2.2.b



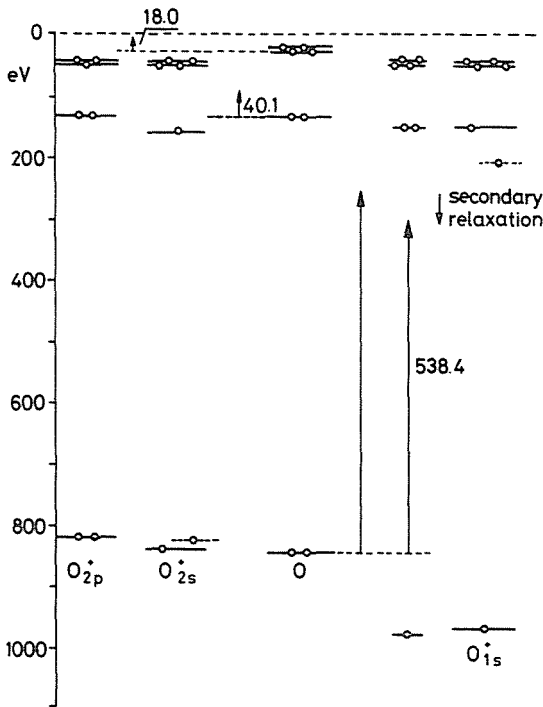


Fig. 2.2.c

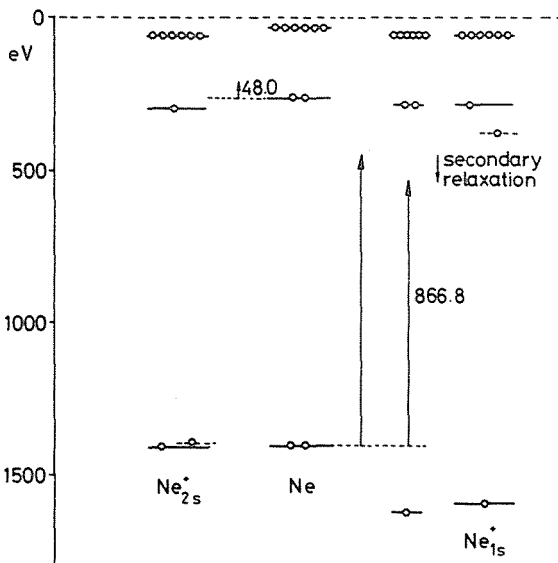


Fig. 2.2.d

**Literature**

1. MOORE, C.: Atomic Energy Levels. NSRDS—NBS 35, Vol. 1. Washington D.C. US Govt. Printing Office, 1949.
2. GOSCINSKI O.—PICKUP B. T.—PURVIS G.: Chem. Phys. Lett. 22, 167 (1973).
3. Landolt—Börnstein Tabellen. Atom- und Molekularphysik 1. Teil. Springer Verlag, Berlin, Göttingen, Heidelberg 1950.
4. SLATER J. C.: Advances in Quantum Chemistry 6, 1 (1972).
5. SIEGBAHN H.—KARLSSON L.: Handbuch der Physik XXXI, 215. Springer Verlag, Berlin, Heidelberg, New York 1982.
6. EDERER D. L.—LUCATORTO T.—MADDEN R. P.: Phys. Rev. Lett. 25, 1537 (1970).
7. KRUMMACHER S.—SCHMIDT V.—BIZAU J. M.—EDERER D. L.—DHEZ P.—WUILLEUMIER F.: J. Phys. B 15, 4363 (1982).
8. BRIGGS D.: Handbook of X-Ray and Ultraviolet Photoelectron Spectroscopy. Heyden 1977.

Prof. Dr. György VARSÁNYI H-1521 Budapest