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Valence Orbital Ionization Potentials of $1s^2\,2s^m\,2p^n$ Atoms and Ions

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The 2s and 2p valence orbital ionization potentials (VOIP) are determined systematically for atoms and ions with configurations $1s^2\,2s^m\,2p^n$, using the Anno-Teruya values of the average energies of the configurations. All the cases with possible values of m and n, in conformity with the Pauli principle, are treated. The 2s or 2p VOIP of a particular ion with the configuration of this type is almost independent of the electron configuration. The VOIP's of an isoelectronic series are fitted to a quadratic equation in terms of atomic number Z: $\mathrm{VOIP} = A_0 + A_1 Z + A_2 Z^2$, by a least-squares method. There are remarkable regularities among A_0's, A_1's or A_2's, for different isoelectronic series, which may be explained by Slater's simple expression for the total energy of an atom (or ion) with the idea of screening effect due to inner electrons. Various screening constants have been determined from the analysis of such regularities.

Unter Benutzung der Anno-Teruya-Werte für die durchschnittliche Energie der Konfigurationen werden systematisch für Atome und Ionen der Konfiguration $1s^2\,2s^m\,2p^n$ die 2s- und 2p-VOIP's bestimmt. Alle Fälle mit den nach dem Pauli-Prinzip möglichen Werten für m und n werden behandelt. Das 2s- oder 2p-VOIP eines besonderen Ions ist beinahe unabhängig von der Elektronenkonfiguration. Nach der Methode der kleinsten quadratischen Abweichung werden die VOIP's einer isoelektronischen Serie mit Hilfe einer in Z (Z = Kernladungszahl) quadratischen Gleichung bestimmt: $\mathrm{VOIP} = A_0 + A_1 Z + A_2 Z^2$. Die Koeffizienten A_0, A_1 und A_2 zeigen untereinander für verschiedene isoelektronische Serien bemerkenswerte Regelmäßigkeiten, die mit der einfachen Slaterformel für die Gesamtenergie eines Atoms oder Ions als Abschirmeffekte der inneren Elektronen erklärt werden können. Durch die Untersuchung dieser Regelmäßigkeiten konnten verschiedene Abschirmkonstanten bestimmt werden.

Les potentiels d'ionisation des orbitales de valence (VOIP) 2s et 2p sont systématiquement déterminés pour les atomes et les ions de configuration $1s^2\,2s^m\,2p^n$, en utilisant les valeurs de Anno-Teruya pour les énergies moyennes des configurations. Tous les cas possibles d'après le principe de Pauli sont traités. Le VOIP 2s ou 2p d'un ion donné avec une configuration de ce type est presque indépendant de la configuration électronique. Une relation quadratique en fonction du numéro atomique Z est ajustée pour les VOIP d'une série isoélectronique par la méthode des moindres carrés: $\mathrm{VOIP} = A_0 + A_1 Z + A_2 Z^2$. Des régularités remarquables se manifestent pour A_0, A_1, A_2 dans différentes séries isoélectroniques; ceci peut être expliqué à l'aide des expressions simples de Slater pour l'énergie totale d'un atome (ou d'un ion) avec l'idée d'un effet d'écran dû aux électrons internes. Différentes constantes d'écran ont été déterminées par l'analyse de ces régularités.

1. Introduction

The valence orbital ionization potential (VOIP) is defined as

$$\mathrm{VOIP} = E_{\mathrm{av}}^{+} - E_{\mathrm{av}} + \mathrm{IP}\,, \tag{1}$$

where E_{av} is the average energy of the configuration of the atom (or ion) as measured from its ground state and E_{av}^{+} is the similar quantity of the ion produced by removing an electron from the above-mentioned atom (or ion), while IP is the ionization potential connecting the ground states. Basch, Viste and Gray [1] have calculated VOIP for the atoms and ions of H through Kr in various configurations and in various stages of ionization and have fitted a quadratic function of the charge q

$$\mathrm{VOIP} = Aq^2 + Bq + C \tag{2}$$

to VOIP's of an isoelectronic series of ions. They have pointed out that the A value thus obtained is almost independent of what series is considered but no mention has been made of the B and the C values.

Anno and Teruya [2], on the other hand, have determined E_{av} along with the Slater-Condon parameters for isoelectronic atoms and ions in all the configurations of the type $1s^2 2s^m 2p^n$ more systematically by paying careful attention to the possibility of misassignment of the observed atomic term values. They have thus obtained E_{av}'s for those configurations which Basch *et al.* were unaccessible. Moreover, even for those configurations which Basch *et al.* were accessible, Anno and Teruya's E_{av}'s may be considered to be more accurate or reliable than those obtained and used for the calculations of VOIP by Basch *et al.* Therefore, recalculation of VOIP using Anno and Teruya's E_{av}'s is deemed advisable. It would also be interesting to see if regularities could be found not only among the coefficients of quadratic terms but among the coefficients of linear and constant terms of the functions of type of Eq. (1) fitted to the new values of VOIP's of various isoelectronic series.

It is the purpose of the present paper to give the data of VOIP, corresponding to the ionization of a $2s$ or a $2p$ electron from any configuration of the type $1s^2 2s^m 2p^n$, based on the E_{av} values of Anno and Teruya and to show that various regularities really exist among coefficients of quadratic functions fitted to the new data of VOIP along isoelectronic series. It will be also shown that such regularities can be explained remarkably well by the simple expression of the total energy of an atom (or ion) given by Slater [3] on the basis of the virial theorem and the idea of screening effect on an "outer" electron by "inner" electrons. The screening constants and the effective quantum numbers have been evaluated from the analysis of such regularities and compared with the Slater rule.

2. Results

The calculation of VOIP has been done for all the cases where E_{av} and E_{av}^{+} are available in Anno and Teruya's paper [2]. In cases where corrected or estimated values are given, these values were used rather than the uncorrected values. The IP values were taken from Moore's table [4]. The results are plotted against atomic number in Figs. 1 and 2. The following points are apparent in these figures:

(i) The VOIP's of an isoelectronic series may be correlated with the atomic number Z by a quadratic equation.

(ii) There may be a regularity among the curvatures, slopes and the relative positions of a set of VOIP/Z correlation curves corresponding to an ionization from a particular orbital ($2s$ or $2p$) of $1s^2 2s^m 2p^n$ configurations with a definite value of m but with different values of n.

(iii) Roughly speaking, $2s$ or $2p$ VOIP of a particular ion is independent of the electron configuration.

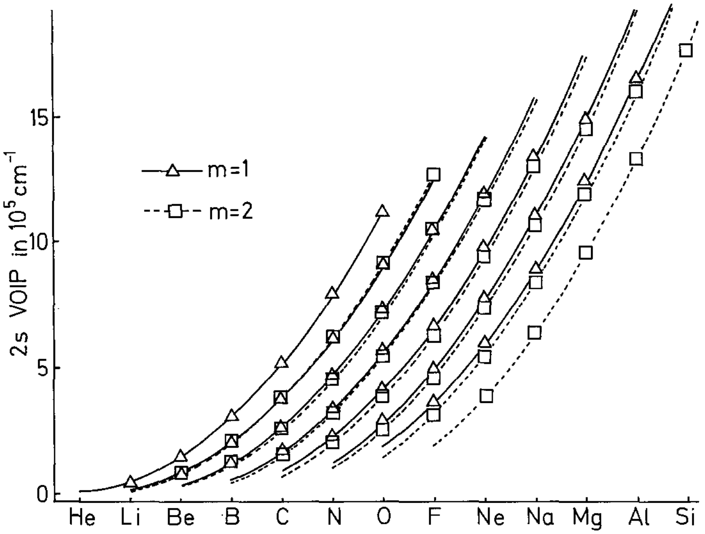

Fig. 1. 2*s* VOIP of isoelectronic ions with $1s^2 2s^m 2p^n$ configurations

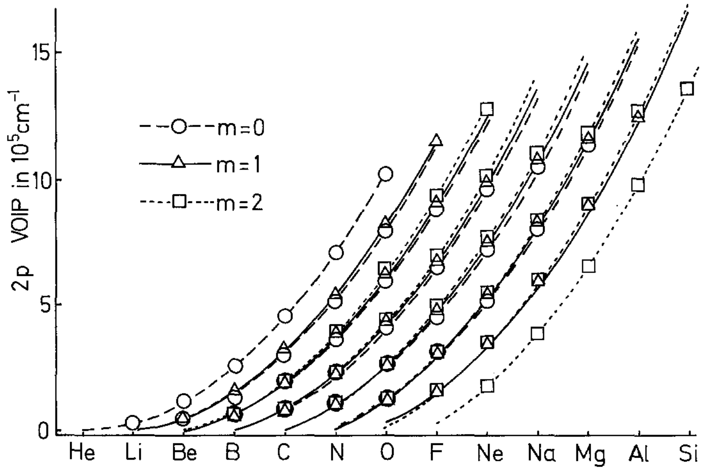

Fig. 2. 2*p* VOIP of isoelectronic ions with $1s^2 2s^m 2p^n$ configurations

In view of the observation (i) above, a quadratic equation of Z, rather than of q,

$$\mathrm{VOIP} = A_0 + A_1 Z + A_2 Z^2 \tag{3}$$

has been fitted to the VOIP's of an isoelectronic series of ions by a least-squares method. The coefficients of the equations thus obtained are given in Table 1. Since

$$q = Z - Z_0 , \tag{4}$$

where Z_0 is the number of the electrons in the atom (or ion), the following relations hold among the coefficients of Eqs. (2) and (3):

$$\left.\begin{aligned} A &= A_2\,, \\ B &= A_1 + 2A_2 Z_0\,, \\ C &= A_0 + A_1 Z_0 + A_2 Z_0^2\,, \end{aligned}\right\} \tag{5}$$

or conversely,

$$\left.\begin{aligned} A_0 &= C - BZ_0 + AZ_0^2\,, \\ A_1 &= B - 2AZ_0\,, \\ A_2 &= A\,. \end{aligned}\right\} \tag{6}$$

Table 1. *Coefficients* A_0, A_1 *and* A_2 *of* VOIP $= A_0 + A_1 Z + A_2 Z^2$ *fitted to the* VOIP's *of isoelectronic series of ions with* $1s^2 2s^m 2p^n$ *configuration* (*cm*$^{-1}$)[a]

m	n	A_0	A_1	A_2
(2*s* VOIP)				
1	0	63800 (63980)	− 89657 (− 89720)	27618 (27620)
	1	134608 (132920)	−124779 (−124160)	27776 (27720)
	2	224991 (224500)	−160182 (−160000)	27916 (27910)
	3	328059 (331800)	−194131 (−194800)	27990 (28000)
	4	447094 (457350)	−226709 (−229400)	27867 (28050)
	5	540027 ( )	−251754 (—)	27493 (—)
	6	832100 (—)	−308292 ( )	28463 (—)
2	0	116320 (116140)	−120893 (−120820)	27647 (27640)
	1	204878 (205900)	−157342 (−157600)	27801 (27820)
	2	314221 (313200)	−193979 (−193800)	27959 (27950)
	3	461385 (450640)	−234343 (−232040)	28293 (28160)
	4	551580 (572800)	−258114 (−262600)	27723 (27950)
	5	766786 (745970)	−303415 (−299560)	28245 (28070)
	6	957204 (949900)	−340066 (−338800)	28344 (28290)

[a] The values given outside of the parentheses are those which are obtained in the present work, while the values given inside of the parentheses are those obtained with Eq. (6) from the data of Basch *et al.* (Ref. [1]). Perhaps three or four significant figures only have any significance, but all the figures above the decimal point are given to avoid the effect of rounding error upon a_k's and b_k's to be given in Table 2.

Table 1 (continued)

m	n	A_0	A_1	A_2
(2p VOIP)				
0	1	100405 (110320)	−107191 (−110080)	27727 (27480)
	2	198451 (182070)	−149391 (−144460)	27936 (27570)
	3	302927 (272650)	−186075 (−178500)	27691 (27250)
	4	425926 (465860)	−221893 (−231320)	27541 (28060)
	5	615681 (—)	−267004 (—)	27787 (—)
	6	806692 (—)	−308583 (—)	27957 (—)
1	1	166966 (166860)	−140818 (−140780)	27760 (27760)
	2	283863 (287000)	−183237 (−184100)	27957 (28020)
	3	427140 (424280)	−225449 (−224410)	28107 (28030)
	4	597796 (801890)	−267392 (−306140)	28195 (30010)
	5	707220 (741440)	−291860 (−298960)	27409 (27760)
	6	1051872 (1021620)	−356003 (−350260)	28488 (28220)
2	1	249540 (249250)	−175493 (−175400)	27787 (27780)
	2	390667 (382800)	−219268 (−217200)	28080 (27950)
	3	559513 (553840)	−262387 (−261040)	28246 (28160)
	4	699193 (717560)	−293473 (−297290)	27743 (27940)
	5	938656 (923230)	−340282 (−337240)	28079 (27930)
	6	1210524 (1196900)	−387119 (−384800)	28347 (28250)

For the purpose of comparison, the A, B and the C values of Basch *et al.* have been converted into A_0, A_1 and A_2 with Eqs. (6) and are also given in Table 1 by enclosing in parentheses. It may be seen in this table that two sets of data agree fairly well with each other in cases where comparison is possible although there *are* some differences.

An approximate constancy of A, which is equal to our A_2, has already been pointed out by Basch *et al.* We are tempted to find out further regularities among A_1 and A_0 also in view of the observation (ii). In Fig. 3, A_1 and A_0 for various

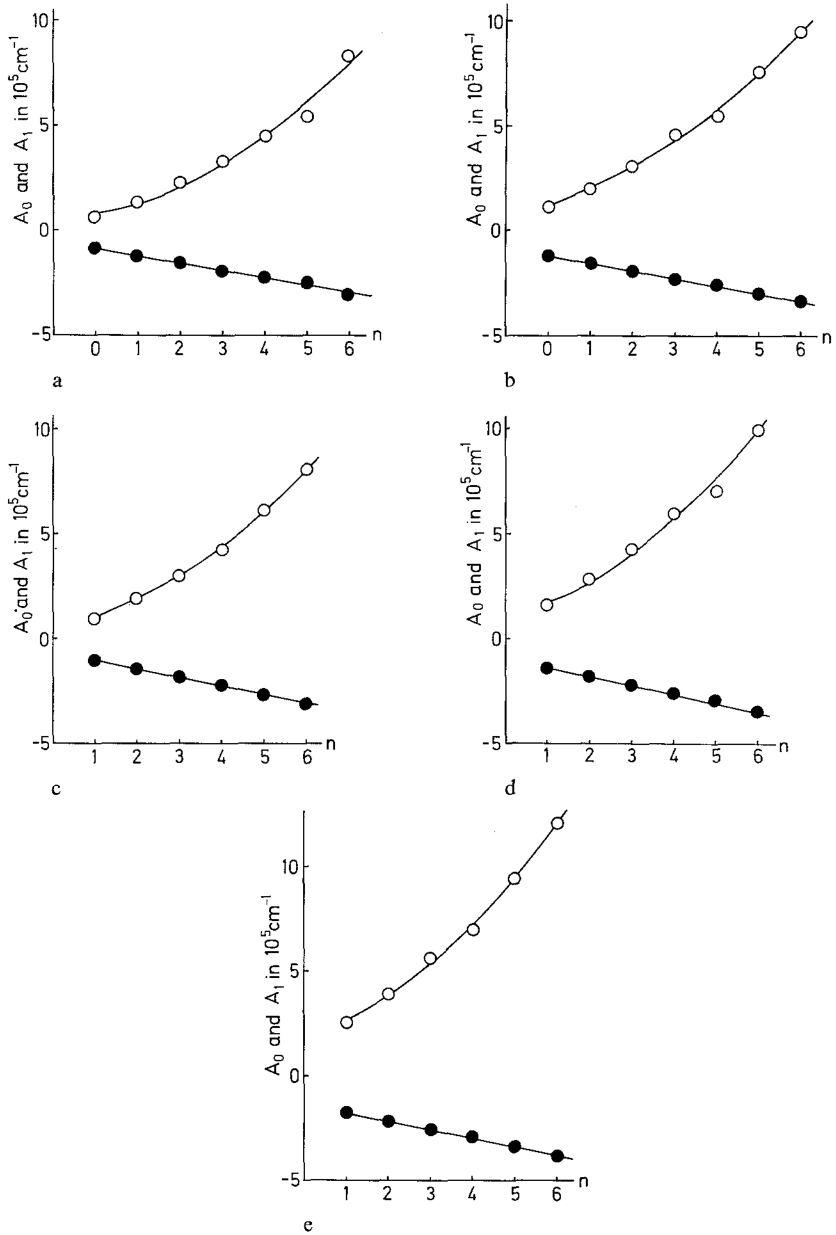

Fig. 3a–e. A_0 (–○–) and A_1 (–●–) for various isoelectronic series corresponding to configurations $1s^2 2s^m 2p^n$ with a definite number of m but with different numbers of n. (a) $2s$ VOIP, $m = 1$; (b) $2s$ VOIP, $m = 2$; (c) $2p$ VOIP, $m = 0$; (d) $2p$ VOIP, $m = 1$; (e) $2p$ VOIP, $m = 2$

isoelectronic series, corresponding to ionization of a $2s$ or a $2p$ electron from the configurations $1s^2 2s^m 2p^n$ with a definite number of m but with different numbers of n, are plotted against n. As can be seen in Fig. 3, there are actually regularities that A_1 is almost linear in n while A_0 is parabolic in n in each of the cases. The

Table 2. *Coefficients of Eq.* (7) *(in $R_\infty = 109737\ cm^{-1}$)*

	a_0	a_1	a_2	b_0	b_1
(2s VOIP)					
$m=1$	0.711942	0.337112	0.124867	−0.811314	−0.317767
$m=2$	1.099753	0.662127	0.100313	−1.103682	−0.329943
(2p VOIP)					
$m=0$	0.474390	0.359334	0.131148	−0.611716	−0.363367
$m=1$	1.092101	0.384179	0.163274	−0.909018	−0.375895
$m=2$	1.566058	0.649034	0.152341	−1.225153	−0.378114

least-squares fittings to the following equations have therefore been tried:

$$\left.\begin{aligned} A_0 &= a_0 + a_1 n + a_2 n^2 , \\ A_1 &= b_0 + b_1 n . \end{aligned}\right\} \tag{7}$$

The results are given in Table 2. Contrary to Table 1, the unit used in Table 2 is Rydberg ($R_\infty = 109737\ \mathrm{cm}^{-1}$) to facilitate the theoretical analysis to be given in the next section.

3. Interpretation by a Simplified Model

Slater gave a simplified expression for the total energy E of an atom or ion based on the virial theorem:

$$E = -\sum_i \frac{N_i (Z - s_i)^2}{n_i^2} \quad \text{in Rydbergs}^1 , \tag{8}$$

where Z is the atomic number, n_i is the principal quantum number of the i-th orbital, N_i is the number of electrons in the i-th orbital and s_i is the constant, called screening constant, representing the screening effect on an electron in the i-th orbital due to the other electrons. This screening constant s_i may be regarded as a sum of individual screening effects

$$s_i = \sum_j N_j s_{j \to i} , \tag{9}$$

where $s_{j \to i}$ represents the screening effect on an electron in the i-th orbital due to another electron in the j-th orbital. In this section, it will be shown that various facts found in the preceding section may be explained remarkably well by Eq. (8).

As is usually assumed, we assume that the screening effect on an inner electron from an outer electron is negligible. Contrary to the Slater rule on the screening constants, however, we distinguish the $2s$ and the $2p$ orbitals from each other. With this assumption, Eq. (8) becomes for an atom or ion with $1s^2 2s^m 2p^n$ configuration

$$\begin{aligned} E(1s^2 2s^m 2p^n) = &-(2/n_{1s}^2)(Z - s_{1s \to 1s})^2 \\ &-(m/n_{2s}^2)\{Z - 2s_{1s \to 2s} - (m-1)s_{2s \to 2s} - n s_{2p \to 2s}\}^2 \\ &-(n/n_{2p}^2)\{Z - 2s_{1s \to 2p} - m s_{2s \to 2p} - (n-1) s_{2p \to 2p}\}^2 . \end{aligned} \tag{10}$$

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[1] Unless stated otherwise, the energy is given in Rydberg for an infinite mass of the nucleus ($R_\infty = 109737\ \mathrm{cm}^{-1}$).

Table 3. *The expressions of B_k's of Eq.* (12) *in terms of n_i's and $s_{i\to j}$'s*

	2s VOIP	2p VOIP
B_1	$(4/n_{2s}^2)\,(s_{1s\to 2s} - s_{2s\to 2s})^2$	$(4/n_{2p}^2)\,(s_{1s\to 2p} - s_{2p\to 2p})^2$
B_2	$(1/n_{2s}^2)\,s_{2s\to 2s}(8s_{1s\to 2s} - 7s_{2s\to 2s})$	$(1/n_{2s}^2)\,s_{2p\to 2s}(4s_{1s\to 2s} - s_{2p\to 2s} - 2s_{2s\to 2s})$ $+ (4/n_{2p}^2)\,s_{2s\to 2p}(s_{1s\to 2p} - s_{2p\to 2p})$
B_3	$(4/n_{2s}^2)\,s_{2p\to 2s}(s_{1s\to 2s} - s_{2s\to 2s})$ $+ (1/n_{2p}^2)\,s_{2s\to 2p}(4s_{1s\to 2p} - s_{2s\to 2p} - 2s_{2p\to 2p})$	$(1/n_{2p}^2)\,s_{2p\to 2p}(8s_{1s\to 2p} - 7s_{2p\to 2p})$
B_4	$(3/n_{2s}^2)\,s_{2s\to 2s}^2$	$(2/n_{2s}^2)\,s_{2s\to 2s}\,s_{2p\to 2s} + (1/n_2^{2p})\,s_{2s\to 2p}^{\;2}$
B_5	$(4/n_{2s}^2)\,s_{2s\to 2s}\,s_{2p\to 2s} + (2/n_{2p}^2)\,s_{2s\to 2p}^2$	$(2/n_{2s}^2)\,s_{2p\to 2s}^2 + (4/n_{2p}^2)\,s_{2p\to 2p}\,s_{2s\to 2p}$
B_6	$(1/n_{2s}^2)\,s_{2p\to 2s}^2 + (2/n_{2p}^2)\,s_{2s\to 2p}\,s_{2p\to 2p}$	$(3/n_{2p}^2)\,s_{2p\to 2p}^2$
B_7	$(4/n_{2s}^2)\,(-s_{1s\to 2s} + s_{2s\to 2s})$	$(4/n_{2p}^2)\,(-s_{1s\to 2p} + s_{2p\to 2p})$
B_8	$-(4/n_{2s}^2)\,s_{2s\to 2s}$	$-(2/n_{2s}^2)\,s_{2p\to 2s} - (2/n_{2p}^2)\,s_{2s\to 2p}$
B_9	$-(2/n_{2s}^2)\,s_{2p\to 2s} - (2/n_{2p}^2)\,s_{2s\to 2p}$	$-(4/n_{2p}^2)\,s_{2p\to 2p}$
B_{10}	$(1/n_{2s}^2)$	$(1/n_{2p}^2)$

The energies of the ions with $1s^2\,2s^{m-1}\,2p^n$ and $1s^2 2s^m 2p^{n-1}$ configurations may be obtained similarly. These energies are considered to be the average energies of the respective configurations. The VOIP therefore becomes in this approximation as follows:

$$\left.\begin{aligned} 2s\ \text{VOIP} &= E(1s^2\,2s^{m-1}\,2p^n) - E(1s^2\,2s^m 2p^n)\,,\\ 2p\ \text{VOIP} &= E(1s^2\,2s^m\,2p^{n-1}) - E(1s^2\,2s^m\,2p^n)\,.\end{aligned}\right\} \tag{11}$$

By putting Eq. (10) and similar equations for $E(1s^2\,2s^{m-1}\,2p^n)$ and $E(1s^2\,2s^m 2p^{n-1})$ into Eqs. (11), one obtains an equation of the following form for both 2s and 2p VOIP's:

$$\begin{aligned} \text{VOIP} = B_1 &+ B_2 m + B_3 n + B_4 m^2 + B_5 mn + B_6 n^2\\ &+ (B_7 + B_8 m + B_9 n)\,Z + B_{10} Z^2\,, \end{aligned} \tag{12}$$

where B_k's ($k = 1, 2, \ldots, 10$) are constants which can be expressed in terms of various n_i's and $s_{i\to j}$'s as shown in Table 3. If one compares Eq. (12) with Eq. (3), one will easily find that

$$A_0 = B_1 + B_2 m + B_3 n + B_4 m^2 + B_5 mn + B_6 n^2\,, \tag{13a}$$

$$A_1 = B_7 + B_8 m + B_9 n\,, \tag{13b}$$

$$A_2 = B_{10}\,. \tag{13c}$$

Eq. (13a) shows that A_0 is a quadratic function of n for a definite value of m while A_1 is shown to be linear in n from Eq. (13b) for a definite value of m. Thus, Eqs. (13a) and (13b) constitute theoretical justifications for Eqs. (7). On the other hand, if both n_{2s} and n_{2p} are taken to be 2 as usually are, Eq. (13c) and the expressions of B_{10} in Table 3 give

$$A_2 = (1/4)\,\text{Rydberg} = 27434\ \text{cm}^{-1}\,, \tag{14}$$

for both the 2s and the 2p VOIP's. This is the theoretical justification of both the constancy and the numerical values of A_2 given in Table 1, as already pointed out by Basch *et al.* [1].

On the basis of Eqs. (13a)–(13c) and the expressions of B_k's in Table 3, we can proceed still further. According to Eq. (13b), the slope of A_1 *vs* n correlation line should be independent of m, although it is different for $2s$ VOIP and for $2p$ VOIP in view of the expression of B_9 in Table 3. The data given in Table 2 under the heading of b_1 bear out this theoretical expectation at least qualitatively. Similarly, a_2 of Eq. (7) should be independent of n, although it is different for $2s$ and $2p$ VOIP. The data in Table 2 bear out roughly this expectation again.

Comparing the expressions of a_k's and b_k's to be obtained from Eqs. (7) and (13) and the expressions of B_k's in Table 3 with the corresponding numerical values in Table 2, one should be able to derive the values of various screening constants. In the remaining part of this section, we are going to do actual determination of the screening constants along this line, by assuming that $n_{2s} = n_{2p} = 2$.

Now, from Eqs. (7) and (13) and the expressions of B_k's, one obtains

$$\left.\begin{aligned} b_1^{2s} &= -(1/2)(s_{2p\to 2s} + s_{2s\to 2p}), \\ b_0^{2s}(m=1) &= -s_{1s\to 2s}, \\ b_0^{2s}(m=2) &= -(s_{1s\to 2s} + s_{2s\to 2s}), \end{aligned}\right\} \tag{15}$$

where $b_0^{2s}(m=1)$ for example stands for b_0 for the $2s$ VOIP's of those configurations for which $m=1$. As for b_1, the distinction for m is not needed since b_1 is independent of m. From these equations and the data in Table 2, one obtains

$$s_{2p\to 2s} + s_{2s\to 2p} = 0.647710, \tag{16}$$

$$s_{1s\to 2s} = 0.811314, \tag{17}$$

and

$$s_{2s\to 2s} = 0.292368. \tag{18}$$

In obtaining (16), we have used the average of b_1 for $m=1$ and $m=2$.

Eqs. (13b) and (7) along with the B_k expressions in Table 3, on the other hand, give

$$b_1^{2p} = -s_{2p\to 2p}, \tag{19}$$

and

$$b_0^{2p} = -s_{1s\to 2p} + s_{2p\to 2p} - (m/2)(s_{2p\to 2s} + s_{2s\to 2p}). \tag{20}$$

Eq. (20) tells us that b_0 for $2p$ VOIP should be linear in m. It can be seen that the data in Table 2 satisfy this requirement reasonably well. A least-squares fitting of the data in Table 2 to Eq. (20) gives

$$s_{2p\to 2s} + s_{2s\to 2p} = 0.613437, \tag{21}$$

and

$$-s_{1s\to 2p} + s_{2p\to 2p} = -0.608577. \tag{22}$$

The difference between (16) and (21), which should be identical according to our theory, might be a measure of accuracy of our analysis.

From Eq. (19) and the average value of b_1^{2p} taken from Table 2, we have

$$s_{2p\to 2p} = 0.372459. \tag{23}$$

We have another way of obtaining $s_{2p\to 2p}$. By comparing Eqs. (7) and (13a), a_2 for $2p$ VOIP is found to be

$$a_2^{2p}=(3/4)\,s_{2p\to 2p}^2\,,$$

if Table 3 is consulted. By using the average value of a_2^{2p} taken from Table 2, one obtains

$$s_{2p\to 2p}=0.445602\,. \tag{24}$$

Comparison of (23) and (24) might give another measure of accuracy of our analysis. Since (23) is based on two data, while (24) is based on three data, we use the following weighted mean as the value of $s_{2p\to 2p}$ to be used in the subsequent analysis:

$$s_{2p\to 2p}=(2/5)\times 0.372459+(3/5)\times 0.445602=0.416345\,. \tag{25}$$

From a similar reason, we give the weight of 2 and 3 to (16) and (21), respectively, to obtain

$$s_{2p\to 2s}+s_{2s\to 2p}=0.627146\,. \tag{26}$$

Eqs. (22) and (25) give

$$s_{1s\to 2p}=1.024922\,. \tag{27}$$

We cannot determine the individual values of $s_{2p\to 2s}$ and $s_{2s\to 2p}$ unless we have another relation between these quantities. From Eqs. (7) and (13a) and the B_k expressions in Table 3 one obtains

$$s_{2p\to 2s}^2+2s_{2s\to 2p}\,s_{2p\to 2p}=4a_2^{2s}\,, \tag{28}$$

and

$$m[(1/2)\,s_{2p\to 2s}^2+s_{2s\to 2p}\,s_{2p\to 2p}]+2s_{1s\to 2p}\,s_{2p\to 2p}-(7/4)\,s_{2p\to 2p}^2=a_1^{2p}\,. \tag{29}$$

According to Eq. (28), a_2^{2s} should be constant, while Eq. (29) requires that a_1^{2p} should be linear in m, the slope being equal to $2a_2^{2s}$. Although the requirement of Eq. (28) is satisfied fairly well, the requirement of (29) is not satisfied by the data in Table 2, so that we use Eq. (28) along with the average of a_2^{2s} from Table 2 to obtain

$$s_{2p\to 2s}^2+2s_{2s\to 2p}\,s_{2p\to 2p}=0.450360\,. \tag{30}$$

From (25), (26) and (30), one obtains the following two sets of solutions:

$$\left.\begin{aligned} s_{2p\to 2s}&=0.734912\,,\\ s_{2s\to 2p}&=-0.107766\,,\end{aligned}\right\} \tag{31}$$

and

$$\left.\begin{aligned} s_{2p\to 2s}&=0.097778\,,\\ s_{2s\to 2p}&=0.529368\,.\end{aligned}\right\} \tag{32}$$

Another way of obtaining $s_{2p\to 2s}$ and $s_{2s\to 2p}$ is to use

$$s_{2s\to 2p}^2+2s_{2s\to 2s}\,s_{2p\to 2s}=0.650030\,, \tag{33}$$

along with (18) and (26). Eq. (33) has been obtained from a_1^{2s} in Table 2 on the basis of Eqs. (7) and (13a) and the B_k expressions in Table 3. From this way one obtains the following two sets of solutions:

$$\left.\begin{aligned} s_{2p\to 2s} &= 0.942062\,, \\ s_{2s\to 2p} &= -0.314916\,, \end{aligned}\right\} \tag{34}$$

and

$$\left.\begin{aligned} s_{2p\to 2s} &= -0.272506\,, \\ s_{2s\to 2p} &= 0.899652\,. \end{aligned}\right\} \tag{35}$$

The author is inclined, however, to think that Sets (31) and (32) are preferred to Sets (34) and (35), since (30) upon which (31) and (32) are based has been obtained from two data (a_2^{2s}, see Table 2) which should be and actually are, at least approximately, identical to each other while (34) and (35) are based upon (33) for which we do not know to what extent it should be reliable because the only data used is the *difference* between two a_1's for $2s$ VOIP.

4. Discussion

In the preceding sections, we have seen that there are remarkable regularities among A_0's, A_1's or A_2's, for different isoelectronic series, which may be explained by Slater's simple expression for the total energy of an atom (or ion) with the ideal of screening effect due to inner electrons. The various screening constants have also been obtained. In the present section, the screening constants thus obtained will be discussed, remembering that the numerical values should be regarded to be rather approximate.

The average of $s_{1s\to 2s}$ and $s_{1s\to 2p}$, given by (17) and (27), is fairly close to the value given by the Slater rule

$$s_{1s\to 2s} = s_{1s\to 2p} = 0.85\,. \tag{36}$$

The fact that our $s_{1s\to 2s}$ is smaller than $s_{1s\to 2p}$ might be explained by supposing that a $2p$ electron is less tightly bound than a $2s$ electron within one-and-the-same atom since the less tightly bound an electron is, the more screened it is by a $1s$ electron. The difference between $s_{2s\to 2s}$ and $s_{2p\to 2p}$, as can be seen in (18) and (25), might also be consistent with this idea, since two electrons in less tightly bound orbital have larger screening effect to each other than two electrons in more

Table 4. *The screening constants*

	Present work	From the Slater rule
$s_{1s\to 2s}$ [a]	0.811	0.85
$s_{1s\to 2p}$	1.025	
$s_{2s\to 2s}$	0.292	0.35
$s_{2p\to 2p}$	0.416	
$s_{2s\to 2p}$	0.529	
$s_{2p\to 2s}$	0.098	

[a] $s_{j\to i}$ represents the screening effect of an electron in orbital i due to another electron in orbital j.

tightly bound orbital as can be exemplified by the Slater values:

$$s_{1s\to 1s} = 0.30 < s_{2s\to 2s} (= s_{2p\to 2p}) = 0.35 . \qquad (37)$$

The average of our $s_{2s\to 2s}$ and $s_{2p\to 2p}$ values again are fairly close to the Slater value of 0.35.

The idea that a $2p$ electron is less tightly bound to the nucleus than a $2s$ electron is also of help in choosing the alternative sets (31) and (32) for $s_{2p\to 2s}$ and $s_{2s\to 2p}$. On this basis, we have chosen (32) rather than (31), since the screening effect from a more tightly bound electron to a less tightly bound electron should be larger than the effect in other way round. It should be noted that the average of $s_{2p\to 2s}$ and $s_{2s\to 2p}$ in (32) is fairly close to the Slater value of 0.35. In Table 4, our screening constants are tabulated together with the Slater values for comparison.

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