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The Valence Orbital Ionization Potential of the First Transition-Metal Atoms and Ions

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The $3d$, $4s$ and $4p$ valence orbital ionization potentials (VOIP) are determined for the atoms and the ions with the electron configuration $3d^{\alpha}4s^{\beta}4p^{\gamma}$, using the Anno-Teruya values of the average energies of the configurations and the experimental ionization potentials. Not all the configurations of this type are treated for lack of the data. As far as the data are available, a quadratic equation in terms of the atomic number Z is fitted to the VOIP's of an isoelectronic series: $\mathrm{VOIP} = A_0 + A_1 Z + A_2 Z^2$. The coefficients A_0's, A_1's and A_2's thus obtained are analysed in the light of Slater's simple expression for the total energy of an atom with the idea of screening effect due to inner electrons.

Mit den Anno-Teruya-Werten für die durchschnittliche Energie der Konfigurationen und den experimentellen Ionisationspotentialen werden für Atome und Ionen der Konfigurationen $3d^{\alpha}4s^{\beta}4p^{\gamma}$ die $3d$-, $4s$- und $4p$-VOIPs bestimmt. Mangels verfügbarer Daten werden nicht alle Konfigurationen dieses Typs behandelt. Sofern Daten verfügbar sind, wird den VOIPs einer isoelektronischen Reihe eine in der Kernladungszahl Z quadratische Gleichung angepaßt: $\mathrm{VOIP} = A_0 + A_1 Z + A_2 Z^2$. Dies aus dieser Gleichung gewonnenen Regelmäßigkeiten in den Koeffizienten A_0, A_1 und A_2 werden mit der einfachen Slaterformel für die Gesamtenergie eines Atoms als Abschirmeffekte der inneren Elektronen erklärt.

Les potentiels d'ionisation des orbitales de valence (VOIP) $3d$, $4s$ et $4p$ sont déterminés pour les atomes et les ions de configuration électronique $3d^{\alpha}4s^{\beta}4p^{\gamma}$ en utilisant les valeurs de Anno-Teruya des énergies moyennes des configurations et les potentiels d'ionisation expérimentaux. Par suite d'absence de données toutes les configurations de ce type ne sont pas étudiées. Dans la mesure des données existantes, une relation quadratique en fonction du numéro atomique Z est ajustée pour les VOIP d'une série isoélectronique: $\mathrm{VOIP} = A_0 + A_1 Z + A_2 Z^2$. Les coefficients A_0, A_1 et A_2 ainsi obtenus sont analysés à la lumière des expressions simples de Slater pour l'énergie totale d'un atome avec l'idée d'un effet d'écran dû aux électrons internes.

1. Introduction

In a previous paper [1], referred to as I, Anno gave the results of a systematic determination of the $2s$ and the $2p$ valence orbital ionization potentials (VOIP) of atoms and ions with the $1s^2 2s^m 2p^n$ configurations. He made a least-squares fitting of these data along an isoelectronic series to a quadratic function of the atomic number Z

$$\mathrm{VOIP} = A_0 + A_1 Z + A_2 Z^2 , \tag{1}$$

for all the possible cases of m and n values and found that the regularities existed among A_0's, A_1's and A_2's of functions of the type of (1), which were able to be explained remarkably well by the simplified theory of Slater for the total energy of an atom or an ion. In the present paper, the results of a similar attempt will be given for the atoms and ions of the first transition elements having the electron configuration of the type $3d^{\alpha}4s^{\beta}4p^{\gamma}$ [1], corresponding to the ionization of a $3d$, $4s$ or a $4p$ electron.

Gray and coworkers [2–4] have already determined $3d$, $4s$ or $4p$ VOIP of atoms and ions with $3d^{\alpha}4s^{\beta}4p^{\gamma}$ configurations and have fitted a quadratic function of the charge q

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

to VOIP's of such a series of atoms and ions that have the same set of Z, β and γ values but different α (consequently different q) values. Nevertheless, it seemed to the authors that repetition of a similar work is worthwhile, since Anno and Teruya [5] have determined the average energies E_{av} of various configurations of $3d^{\alpha}4s^{\beta}4p^{\gamma}$ type of various atoms and ions along with the Slater-Condon parameters with careful choice of those experimental term values which are free from anomaly due either to misassignment or to effect of configuration interactions, so that their E_{av} values should be more accurate than those available to Gray and coworkers. Moreover, their work is merely to fit a quadratic function of charge to VOIP of a series of atoms and ions, but the present work is to analyse the coefficients of functions of the type of Eq. (1) corresponding to various configurations in the light of I.

2. Results

The VOIP has been calculated from

$$\mathrm{VOIP} = E_{\mathrm{av}}^{+} - E_{\mathrm{av}} + \mathrm{IP}\,, \tag{2}$$

where the same notations as those used in I are used. The IP values were taken from Moore's table [6], while the E_{av}^{+} and E_{av} values were taken from Anno and Teruya's paper [5] except for the $3d^{\alpha}4p^2$ cases, which had not been treated in their paper. As was pointed out by Anno and Teruya [5], only a very few data are available for these cases. Nevertheless, we need the $4p$ VOIP of atoms or ions with the configurations of this type to some extent in the analysis to be given in the subsequent sections. For lack of the data, we had to be content with the data of the $4p$ VOIP of Ca and Sc^{+} (both in the $3d^0 4p^2$ configuration) and of Zn and Ga^{+} (both in the $3d^{10}4p^2$ configuration) only. The procedure adopted in obtaining the E_{av} values of these atoms and ions are given in the Appendix.

Now, in the case of atoms and ions to be treated in the present paper, only a few points, corresponding to a particular isoelectronic series, to which a quadratic function is to be fitted are available. At least three points are required for a quadratic function (1) to be fitted, while at most three points only are available in the cases treated in the present paper. Therefore, only in such cases the determination of A_0, A_1 and A_2 of Eq. (1) is possible. In Figs. 1–11, A_0, A_1 and A_2 thus obtained are plotted against α. They are given in open squares, circles and triangles, respectively. Contrary to the cases of the $1s^2 2s^m 2p^n$ atoms and ions (cf. Table 1 and Fig. 3 of I [1]), there are not very clear regularities. Theoretical

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[1] $3d^{\alpha}4s^{\beta}4p^{\gamma}$ is the abbreviation of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{\alpha}4s^{\beta}4p^{\gamma}$.

analysis to be given in the next section, however, shows that A_2 for VOIP's of a particular kind of orbitals should be constant, that A_1 should be linear in α, slope being a constant characteristic to the kind of orbital involved, and that A_0 should be parabolic in α. Inspection of appropriate ones of Figs. 1–11 reveals that this theoretical expectation is satisfied fairly well for A_2, but not so well for the other coefficients.

The reason why there are not very clear regularities among A_0's, A_1's and A_2's may be the fact that only three points are available for fitting an equation of the type (1), which involves three unknown parameters, to an isoelectronic series in each of the cases treated, so that even a small deviation of any of the three points from its ideal value would directly affect the values of the coefficients. As for $1s^22s^m2p^n$ ions, on the other hand, five or six points were available for the fitting, so that the effect of deviation, which is expected to be random, of individual points from their ideal values would be smoothed out through the least-squares process. Therefore if one knew the "ideal" or "true" value of one of the coefficients A_0, A_1 and A_2, fixed that coefficient to the "ideal" value and found the rest of the coefficients by the least-squares process, the regularity would be obtained

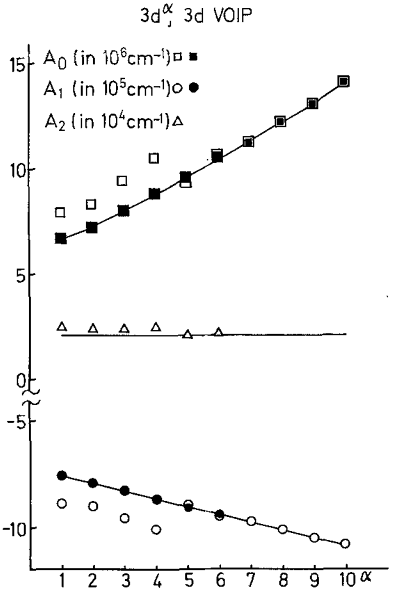

Fig. 1

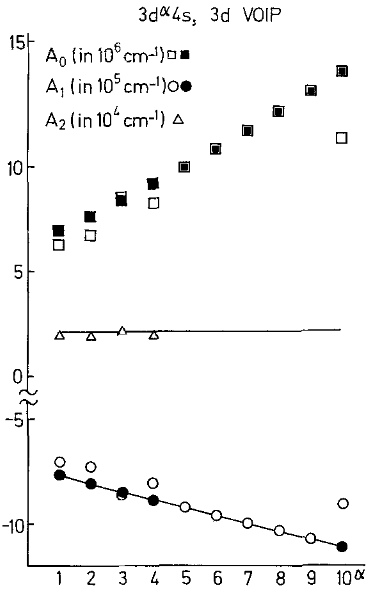

Fig. 2

Fig. 1. A_0, A_1 and A_2 of Eq. (1), fitted to the $3d$ VOIP's of isoelectronic ions with electron configuration of $3d^\alpha$, as plotted against α. The white points (□, ○, △) are resulting from the fitting where the number of data available is just equal to the number of parameters (A_0, A_1 or A_2) to be determined. The black points (▣, ●) are obtained by the fitting in which the number of data available is larger than the number of parameters to be determined. The horizontal line in the middle of the figure is drawn at the height of the A_2 value given in (3) and is considered to give the average or "ideal" value of A_2. The curved line at the top of the Figure and the straight line at the bottom of the Figure represent Eqs. (4) and (5), for A_0 and A_1, respectively. For detail, see text

Fig. 2. A_0, A_1 and A_2 of Eq. (1), fitted to the $3d$ VOIP's of isoelectronic ions with electron configuration of $3d^\alpha 4s$, as plotted against α. See also the caption to Fig. 1

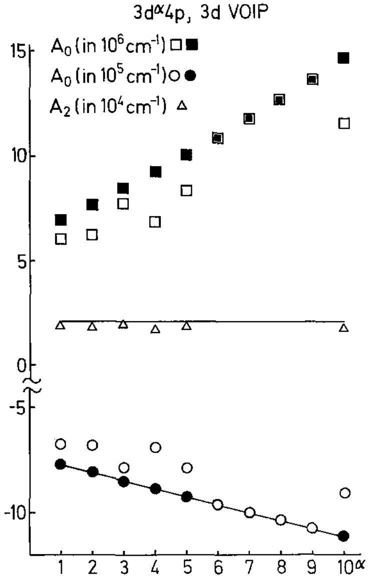

Fig. 3

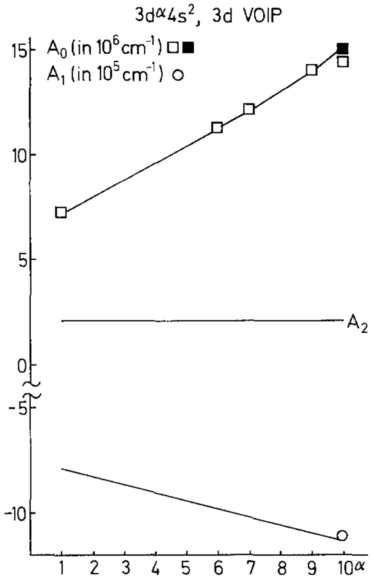

Fig. 4

Fig. 3. A_0, A_1 and A_2 of Eq. (1), fitted to the 3*d* VOIP's of isoelectronic ions with electron configuration of $3d^{\alpha}4p$, as plotted against α. See also the caption to Fig. 1

Fig. 4. A_0, A_1 and A_2 of Eq. (1), fitted to the 3*d* VOIP's of isoelectronic ions with electron configuration of $3d^{\alpha}4s^2$, as plotted against α. See also the caption to Fig. 1

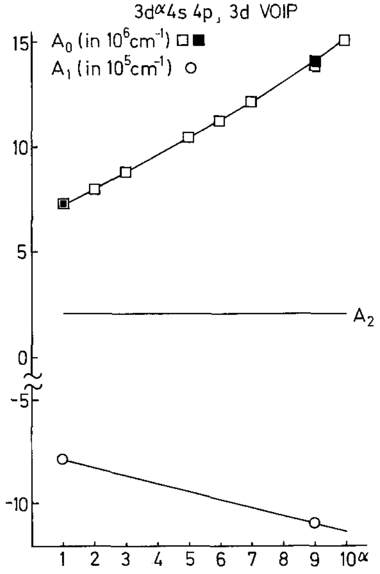

Fig. 5

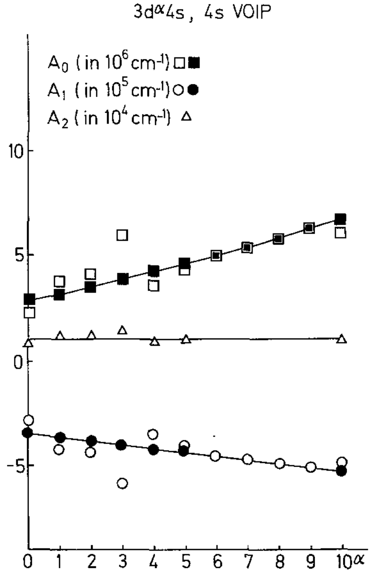

Fig. 6

Fig. 5. A_0, A_1 and A_2 of Eq. (1), fitted to the 3*d* VOIP's of isoelectronic ions with electron configuration of $3d^{\alpha}4s4p$, as plotted against α. See also the caption to Fig. 1

Fig. 6. A_0, A_1 and A_2 of Eq. (1), fitted to the 4*s* VOIP's of isoelectronic ions with electron configuration of $3d^{\alpha}4s$, as plotted against α. See also the caption to Fig. 1

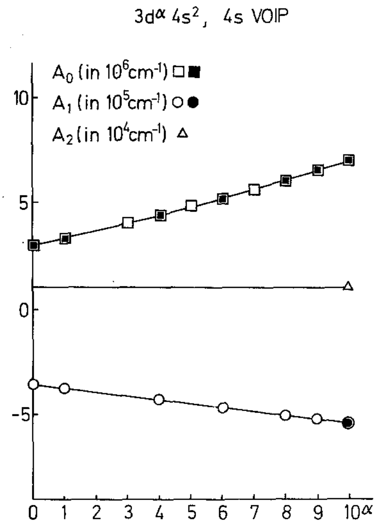

Fig. 7

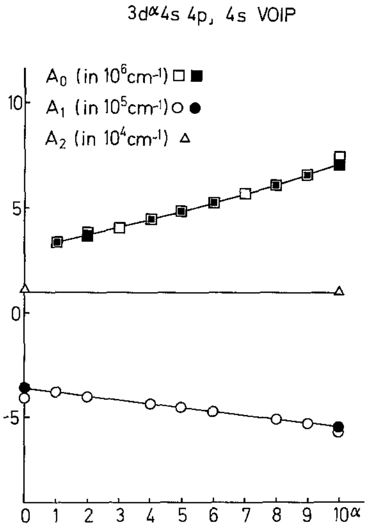

Fig. 8

Fig. 7. A_0, A_1 and A_2 of Eq. (1), fitted to the 4*s* VOIP's of isoelectronic ions with electron configuration of $3d^{\alpha}4s^2$, as plotted against α. See also the caption to Fig. 1

Fig. 8. A_0, A_1 and A_2 of Eq. (1), fitted to the 4*s* VOIP's of isoelectronic ions with electron configuration of $3d^{\alpha}4s4p$, as plotted against α. See also the caption to Fig. 1

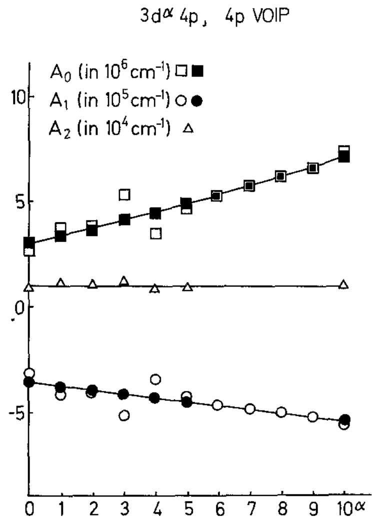

Fig. 9

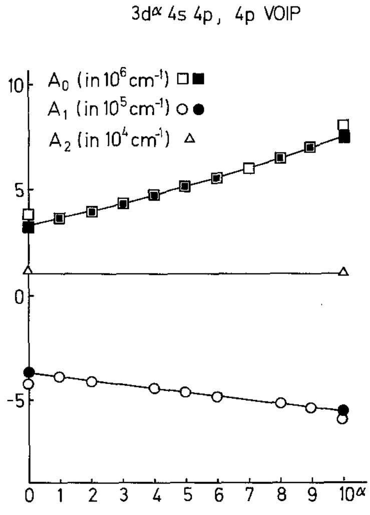

Fig. 10

Fig. 9. A_0, A_1 and A_2 of Eq. (1), fitted to the 4*p* VOIP's of isoelectronic ions with electron configuration of $3d^{\alpha}4p$, as plotted against α. See also the caption to Fig. 1

Fig. 10. A_0, A_1 and A_2 of Eq. (1), fitted to the 4*p* VOIP's of isoelectronic ions with electron configuration of $3d^{\alpha}4s4p$, as plotted against α. See also the caption to Fig. 1

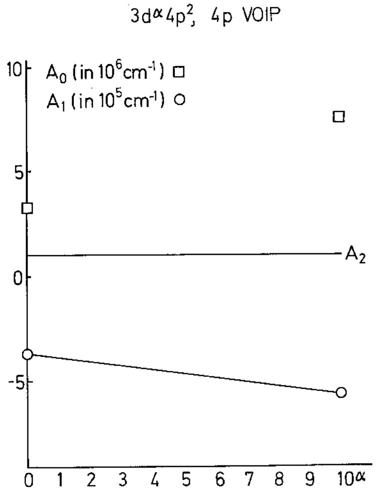

Fig. 11. A_0, A_1 and A_2 of Eq. (1), fitted to the $4p$ VOIP's of isoelectronic ions with electron configuration of $3d^\alpha 4p^2$, as plotted against α. See also the caption to Fig. 1

for these coefficients even in the cases of the transition-metal atoms and ions where only three points are available for the fitting of Eq. (1).

As mentioned above, A_2 for a particular orbital should be and is approximately constant. By averaging the data given in appropriate ones of Figs. 1–11, one obtains

$$\left.\begin{aligned} A_2 &= 21170.4\ \mathrm{cm}^{-1} \quad \text{for} \quad 3d\ \text{VOIP}, \\ \text{or} \quad &= 10342.9\ \mathrm{cm}^{-1} \quad \text{for} \quad 4s\ \text{VOIP}, \\ \text{or} \quad &= 10351.7\ \mathrm{cm}^{-1} \quad \text{for} \quad 4p\ \text{VOIP}. \end{aligned}\right\} \tag{3}$$

Eq. (1) has been fitted to the VOIP's of an isoelectronic series for which three data are available, by fixing A_2 to the appropriate value given in (3). The resulting values of A_0 and A_1 are also plotted in appropriate ones of Figs. 1–11. They are given in black squares and circles, respectively, to distinguish them from the corresponding values ("white" points) obtained without fixing A_2. As can be seen in these figures, the regularities that A_1 is linear in α and A_0 is parabolic in α have now been obtained. Quadratic and linear functions

$$A_0 = a_0 + a_1\alpha + a_2\alpha^2, \tag{4}$$

$$A_1 = b_0 + b_1\alpha \tag{5}$$

could therefore be fitted to the numerical values of A_0 and A_1 thus obtained. We shall postpone the fitting of A_0's to later part of this section. Table 1 lists the b_0 and the b_1 values obtained from the fitting of Eq. (5) to A_1's. In cases of the $3d$ VOIP in $3d^\alpha 4s^2$ and $3d^\alpha 4s4p$ configurations no reliable A_1 values can be obtained by the above-mentioned procedure, so that the b_0 and the b_1 values for these cases, which are also tabulated in Table 1 by enclosing in the parentheses, have been estimated in the manner to be explained later (Sec. 3). In the case of the $4s$ VOIP in $3d^\alpha 4s^2$ configuration, reliable A_1 value may be obtained only for

Table 1. *Coefficients of Eqs.* (4) *and* (5) (*cm*$^{-1}$)[a,b]

	a_0	a_1	a_2	b_0	b_1
($3d$ VOIP)					
$3d^{\alpha}$	5998899	637895	16788	−713770	−37914
$3d^{\alpha}4s$	6268723	676026	15403	−732521	−38141
$3d^{\alpha}4p$	6276820	675032	16017	−732098	−38315
$3d^{\alpha}4s4p$	6629100	677555	16826	(−751564)	(−38124)
$3d^{\alpha}4s^2$	6609955	672780	17284	(−750980)	(−38124)
($4s$ VOIP)					
$3d^{\alpha}4s$	2830580	314441	7243	−344101	−18514
$3d^{\alpha}4s4p$	3063068	315247	8005	−357156	−18404
$3d^{\alpha}4s^2$	3030356	321092	7695	−356000	−18595
($4p$ VOIP)					
$3d^{\alpha}4p$	3036536	328742	8446	−355447	−19098
$3d^{\alpha}4s4p$	3268943	336083	8571	−368895	−18990
$3d^{\alpha}4p^2$	3289167	337632	(8508)	−369730	−18989

[a] 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 errors upon further calculations using these a_k and b_k.

[b] Estimated values are given in parentheses (see text).

$\alpha = 10$, while no reliable A_1 values may be obtained in the case of the $4p$ VOIP in $3d^{\alpha}4p^2$ configuration, so that b_0 and b_1 of Eq. (5) would not be able to be obtained in these two cases. Unfortunately, estimination of the b_0 and the b_1 values in these cases is found to be impossible either. Therefore, A_1 values obtained from two points along each of the isoelectronic series as explained later have been used to determine the b_0 and the b_1 values in Eq. (5) in these cases, which are also given in Table 1. It may be seen that b_1 is approximately constant depending only on what orbital is involved in VOIP. This fact is in accordance with the theoretical analysis to be given in the next section.

An idea of giving an appropriate fixed value to A_2 before fitting Eq. (1) to the VOIP's of an isoelectronic series enables for us to do such a fitting even in those cases in which only two points are available for the fitting. The resulting values of A_0 and A_1 are also given in appropriate ones of Figs. 1–11 by indicating them in open squares and circles, respectively, to indicate that the number of parameters to be found equals the number of the data used for the fitting. It would be expected that the regularities are not so good for these A_0 and A_1 values. However, they do obey the regular trends, shown by A_0's and A_1's obtained from three points by fixing A_2 ("black" square and circles), fairly well.

In order to revise the A_0 values when only two points are available along isoelectronic series, Eq. (1) has been fitted to these points by fixing not only A_2 but also A_1. The values of A_1 for this purpose were calculated by Eq. (5) using the b_0 and b_1 values tabulated in Table 1. The A_0 values obtained are also plotted in appropriate ones of Figs. 1–11 in black squares. We have only one point for the fitting of Eq. (1) along isoelectronic series in some cases. If one gives appropriate fixed values to A_2 and A_1 as mentioned above, one obtains the A_0 values even in such cases. The A_0 values thus obtained are also plotted in appropriate ones of Figs. 1–11 as open squares.

Now, we are in a position to fit Eq. (4) to a series of A_0's. Unless states otherwise, A_0's used for this fitting were those which correspond to "black" squares in appropriate one of Figs. 1–11. In the cases of $3d$ VOIP in $3d^\alpha 4s^2$ and $3d^\alpha 4s4p$ configurations, A_0's corresponding to "white" squares were also used provided that no corresponding "black" A_0 values are available. The values of a_0, a_1 and a_2 thus obtained are also included in Table 1. It may be seen that a_2 is approximately constant, depending only upon what orbital is involved in VOIP. This fact will be proved by the theoretical analysis to be given in the next section. Therefore, in the case of $4p$ VOIP in $3d^\alpha 4p^2$ configurations, where only two A_0 ("white") points (corresponding to $\alpha = 0$ and 10) are available, the fitting has been done by fixing a_2 to 8508 cm^{-1}, which is the average of a_2 values for $4p$ VOIP in $3d^\alpha 4p$ and in $3d^\alpha 4s4p$ configurations.

3. Theoretical Analysis

As was done in I [1], we shall explain the regularities which exist among A_k's on the basis of Slater's simple expression for the total energy E of an atom or an ion [7]:

$$E = -\sum_i \frac{N_i\left(Z - \sum_j N_j s_{j\to i}\right)}{n_i^2} \quad \text{in Rydbergs,} \tag{6}$$

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 $s_{j\to i}$ represents the screening effect of an electron in the i-th orbital due to another electron in the j-th orbital. In applying Eq. (6), which is supposed to represent the average energy of the configuration of a transition-metal atom or ion in the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^\alpha 4s^\beta 4p^\gamma$, we assume that the $1s$, $2s$ and $2p$ electrons completely screen the effect of the nucleus on the $3d$, $4s$ or the $4p$ electrons. Our system therefore reduces to a hypothetical ion with its atomic number Z'

$$Z' = Z - 10 \tag{7}$$

and with electron configuration $3s^2 3p^6 3d^\alpha 4s^\beta 4p^\gamma$. We now give the numbering (i) to the orbitals (AO) involved in this configuration as follows:

$$\left.\begin{array}{cccccc} \text{AO} & 3s & 3p & 3d & 4s & 4p\,, \\ i & 1 & 2 & 3 & 4 & 5\,. \end{array}\right\} \tag{8}$$

With this notation, our next assumption can be written as

$$s_{j\to i} = 0 (i = 1, 2; j = 3, 4, 5)\,. \tag{9}$$

With these assumption, the $3d$, $4s$ and the $4p$ VOIP can be obtained as the differences between E of Eq. (6) as applied to the configuration $3d^\alpha 4s^\beta 4p^\gamma$ and E of $3d^{\alpha-1} 4s^\beta 4p^\gamma$, $3d^\alpha 4s^{\beta-1} 4p^\gamma$ and of $3d^\alpha 4s^\beta 4p^{\gamma-1}$, respectively, with a definite Z value. The VOIP of a particular kind of orbital of an atom or an ion with the atomic number $Z' + 10$ in a definite configuration $3d^\alpha 4s^\beta 4p^\gamma$ can thus be shown

Table 2. *Coefficients B_k's of Eq. (10) as expressed in terms of the screening constants $s_{i\to j}$ and the principal quantum number n_i.*

	$3d$ VOIP	$4s$ VOIP	$4p$ VOIP
B_1	$(4/n_3^2)\,[(s_{1\to3}+3\,s_{2\to3})-s_{3\to3}]^2$	$(4/n_4^2)\,[(s_{1\to4}+3\,s_{2\to4})-s_{4\to4}]^2$	$(4/n_5^2)\,[(s_{1\to5}+3\,s_{2\to5})-s_{5\to5}]^2$
B_2	$(4/n_3^2)\,s_{4\to3}[(s_{1\to3}+3s_{2\to3})-s_{3\to3}] + (1/n_4^2)\,s_{3\to4}[4(s_{1\to4}+3s_{2\to4})-s_{3\to4}-2s_{4\to4}]$	$(1/n_4^2)\,s_{4\to4}[8(s_{1\to4}+3s_{2\to4})-7s_{4\to4}]$	$(1/n_4^2)\,s_{5\to4}[4(s_{1\to4}+3s_{2\to4})-2s_{4\to4}-s_{5\to4}] + (4/n_5^2)\,s_{4\to5}[(s_{1\to5}+3s_{2\to5})-s_{5\to5}]$
B_3	$(4/n_3^2)\,s_{5\to3}[(s_{1\to3}+3s_{2\to3})-s_{3\to3}] + (1/n_5^2)\,s_{3\to5}[4(s_{1\to5}+3s_{2\to5})-s_{3\to5}-2s_{5\to5}]$	$(4/n_4^2)\,s_{5\to4}[(s_{1\to4}+3s_{2\to4})-s_{4\to4}] + (1/n_5^2)\,s_{4\to5}[4(s_{1\to5}+3s_{2\to5})-s_{4\to5}-2s_{5\to5}]$	$(1/n_5^2)\,s_{5\to5}[8(s_{1\to5}+3s_{2\to5})-7s_{5\to5}]$
B_4	$(1/n_3^2)\,s_{4\to3}^2+(2/n_4^2)\,s_{3\to4}\,s_{4\to4}$	$(3/n_4^2)\,s_{4\to4}^2$	$(2/n_4^2)\,s_{4\to4}\,s_{5\to4}+(1/n_5^2)\,s_{4\to5}^2$
B_5	$2[(1/n_3^2)\,s_{4\to3}\,s_{5\to3}+(1/n_4^2)\,s_{3\to4}\,s_{5\to4} + (1/n_5^2)\,s_{3\to5}\,s_{4\to5}]$	$2[(2/n_4^2)\,s_{4\to4\;5\to4}+(1/n_5^2)\,s_{4\to5}^2]$	$2[(1/n_4^2)\,s_{5\to4}^2+(2/n_5^2)\,s_{4\to5}\,s_{5\to5}]$
B_6	$(1/n_3^2)\,s_{5\to3}^2+(2/n_5^2)\,s_{3\to5}\,s_{5\to5}$	$(1/n_4^2)\,s_{5\to4}^2+(2/n_5^2)\,s_{4\to5}\,s_{5\to5}$	$(3/n_5^2)\,s_{5\to5}^2$
B_7	$(1/n_3^2)\,s_{3\to3}[8(s_{1\to3}+3s_{2\to3})-7s_{3\to3}]$	$(1/n_3^2)\,s_{4\to3}[4(s_{1\to3}+3s_{2\to3})-2s_{3\to3}-s_{4\to3}] + (4/n_4^2)\,s_{3\to4}[(s_{1\to4}+3s_{2\to4})-s_{4\to4}]$	$(1/n_3^2)\,s_{5\to3}[4(s_{1\to3}+3s_{2\to3})-2s_{3\to3}-s_{5\to3}] + (4/n_5^2)\,s_{3\to5}[(s_{1\to5}+3s_{2\to5})-s_{5\to5}]$
B_8	$2[(2/n_3^2)\,s_{3\to3}\,s_{4\to3}+(1/n_4^2)\,s_{3\to4}^2]$	$2[(1/n_3^2)\,s_{4\to3}^2+(2/n_4^2)\,s_{3\to4}\,s_{4\to4}]$	$2[(1/n_3^2)\,s_{4\to3}\,s_{5\to3}+(1/n_4^2)\,s_{3\to4}\,s_{5\to4} + (1/n_5^2)\,s_{3\to5}\,s_{4\to5}]$
B_9	$2[(2/n_3^2)\,s_{3\to3}\,s_{5\to3}+(1/n_5^2)\,s_{3\to5}^2]$	$2[(1/n_3^2)\,s_{4\to3}\,s_{5\to3}+(1/n_4^2)\,s_{3\to4}\,s_{5\to4} + (1/n_5^2)\,s_{3\to5}\,s_{4\to5}]$	$2[(1/n_3^2)\,s_{5\to3}^2+(2/n_5^2)\,s_{3\to5}\,s_{5\to5}]$
B_{10}	$(3/n_3^2)\,s_{3\to3}^2$	$(2/n_3^2)\,s_{3\to3}\,s_{4\to3}+(1/n_4^2)\,s_{3\to4}^2$	$(2/n_3^2)s_{3\to3}\,s_{5\to3}+(1/n_5^2)\,s_{3\to5}^2$
B_{11}	$-(4/n_3^2)\,[(s_{1\to3}+3s_{2\to3})-s_{3\to3}$	$-(4/n_4^2)\,[(s_{1\to4}+3s_{2\to4})-s_{4\to4}]$	$-(4/n_5^2)\,[(s_{1\to5}+3s_{2\to5})-s_{5\to5}]$
B_{12}	$-2[(1/n_3^2)\,s_{4\to3}+(1/n_4^2)\,s_{3\to4}]$	$-(4/n_4^2)\,s_{4\to4}$	$-2[(1/n_4^2)\,s_{5\to4}+(1/n_5^2)\,s_{4\to5}]$
B_{13}	$-2[(1/n_3^2)\,s_{5\to3}+(1/n_5^2)\,s_{3\to5}]$	$-2[(1/n_4^2)\,s_{5\to4}+(1/n_5^2)\,s_{4\to5}]$	$-(4/n_5^2)\,s_{5\to5}$
B_{14}	$-(4/n_3^2)\,s_{3\to3}$	$-2[(1/n_3^2)\,s_{4\to3}+(1/n_4^2)\,s_{3\to4}]$	$-2[(1/n_3^2)\,s_{5\to3}+(1/n_5^2)\,s_{3\to5}]$
B_{15}	$(1/n_3^2)$	$(1/n_4^2)$	$(1/n_5^2)$

to have the following form:

$$\begin{aligned}\mathrm{VOIP} = {} & [(B_1 + B_2\beta + B_3\gamma + B_4\beta^2 + B_5\beta\gamma + B_6\gamma^2) + (B_7 + B_8\beta + B_9\gamma)\alpha \\ & + B_{10}\alpha^2] + [(B_{11} + B_{12}\beta + B_{13}\gamma) + B_{14}\alpha]Z' + B_{15}Z'^2 ,\end{aligned} \tag{10}$$

where B_k's can be expressed in terms of various $s_{i\to j}$'s and n_i's as shown in Table 2.

Although we have now obtained a theoretical expression (10) for the VOIP's of isoelectronic ions, we have to transform it into a quadratic expression of Z rather than of Z' before using it to interpret the data given in Table 1. Putting Eq. (7) into Eq. (10) one obtains

$$\begin{aligned}\mathrm{VOIP} = {} & [B_1 - 10B_{11} + 100B_{15} + (B_2 - 10B_{12})\beta + (B_3 - 10B_{13})\gamma \\ & + B_4\beta^2 + B_5\beta\gamma + B_6\gamma^2 + (B_7 - 10B_{14} + B_8\beta + B_9\gamma)\alpha + B_{10}\alpha^2] \\ & + (B_{11} - 20B_{15} + B_{12}\beta + B_{13}\gamma + B_{14}\alpha)Z + B_{15}Z^2 .\end{aligned} \tag{11}$$

If one compares Eq. (1) with Eq. (11) and remembers that B_k's are constants characteristic to the orbital involved in the VOIP, one is now able to understand that A_2 is constant for VOIP's of a particular kind of orbitals, that A_1 is linear in α, slope being a constant characteristic to the orbital involved and A_0 should be parabolic in α. If one puts Eqs. (4) and (5) into Eq. (1) and compares the resulting equation with Eq. (11), one obtains

$$\left.\begin{aligned} a_0 &= (B_1 - 10B_{11} + 100B_{15}) + (B_2 - 10B_{12})\beta + (B_3 - 10B_{13})\gamma \\ &\quad + B_4\beta^2 + B_5\beta\gamma + B_6\gamma^2 , \\ a_1 &= (B_7 - 10B_{14}) + B_8\beta + B_9\gamma , \\ a_2 &= B_{10} , \\ b_0 &= B_{11} - 20B_{15} + B_{12}\beta + B_{13}\gamma , \\ b_1 &= B_{14} . \end{aligned}\right\} \tag{12}$$

We are now in a position to interpret the regularities among the a_k and the b_k values listed in Table 1 based on our theory and to explain how we have obtained a_k's and b_k's when direct evaluation is impossible. For the sake of brevity, we shall denote a_k for the $3d$ VOIP of an isoelectronic series of ions with electron configuration $3d^\alpha 4s^\beta 4p^\gamma$ by $a_k(3d, d^\alpha s^\beta p^\gamma)$. When the specification of the configuration is unnecessary, it will simple be written as $a_k(3d)$. The similar notations will be used also for b_k's throughout the present paper.

The fact, which was already pointed out in the previous section, that b_1 is constant characteristic to the orbital involved, is apparent from the last one of Eqs. (12) if Table 2 is consulted. Because of this fact, both $b_1(3d, d^\alpha s^2)$ and $b_1(3d, d^\alpha sp)$ have been obtained as the mean value of $b_1(3d)$'s of $3d^\alpha$, $3d^\alpha 4s$ and $3d^\alpha 4p$. Moreover, the following relations can be obtained from Eq. (12) and Table 2;

$$b_0(3d, d^\alpha s^2) - b_0(3d, d^\alpha s) = b_0(3d, d^\alpha s) - b_0(3d, d^\alpha) = b_1(4s) , \tag{13}$$

$$b_0(3d, d^\alpha sp) - b_0(3d, d^\alpha s) = b_0(3d, d^\alpha p) - b_0(3d, d^\alpha) = b_1(4p) , \tag{14}$$

$$b_0(3d, d^\alpha sp) - b_0(3d, d^\alpha p) = b_1(4s) . \tag{15}$$

From the data given in Table 1,

$$b_0(3d, d^\alpha s) - b_0(3d, d^\alpha) = -18750\,, \tag{16}$$

$$b_1(4s) = (1/2)[b_1(4s, d^\alpha s) + b_1(4s, d^\alpha sp)] = -18459\,, \tag*{(17)^2}$$

$$b_0(3d, d^\alpha p) - b_0(3d, d^\alpha) = -18327\,, \tag{18}$$

$$b_1(4p) = (1/2)[b_1(4p, d^\alpha p) + b_1(4p, d^\alpha sp)] = -19044\,, \tag*{(19)^3}$$

all in cm^{-1}. From (16)–(19), it may be seen that the second equality of Eq. (13) holds fairly well, but that of Eq. (14) does not hold so well. A probable reason for it is that $b_0(3d, d^\alpha p)$ is a little in error. To estimate $b_0(3d, d^\alpha sp)$, therefore, (14) rather than (15) was used along with (19), which is considered to be more accurate than (18) since (19) was obtained as the average of two fairly close quantities. Thus,

$$b_0(3d, d^\alpha sp) = b_0(3d, d^\alpha s) + (-19044) = -751564\ \mathrm{cm}^{-1}\,. \tag{20}$$

Similarly, if one used (13) and (17), one obtains

$$b_0(3d, d^\alpha s^2) = b_0(3d, d^\alpha s) + (-18459) = -750980\ \mathrm{cm}^{-1}\,. \tag{21}$$

The fact that a_2 is constant depending only upon what orbital is involved in VOIP was also pointed out in the preceding section. It may be seen from Eq. (12) that this fact has now been verified if Table 2 is consulted.

4. Determination of n_i's and $s_{i\to j}$'s

Since the least-squares fitting of VOIP's described in Sect. 2 is based on the true atomic number Z, while the theoretical expressions given in Sect. 3 is based on the charge of the core $Z'(=Z-10)$, it would be convenient to transform a_k's and b_k's given in Table 1 into a'_k's and b'_k's defined by

$$\mathrm{VOIP} = a'_0 + a'_1\alpha + a'_2\alpha^2 + (b'_0 + b'_1\alpha)Z' + A'_2 Z'^2\,, \tag{22}$$

before being used for the determination of n_i's and $s_{i\to j}$'s. If one puts Eq. (7) into Eq. (22) and compares the resulting equation with another equation obtained by

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[2] Although $b_1(4s, d^\alpha s^2)$ is also available in Table 1, it has not been included in this average, contrary to the case of assigning numerical value to $-2[(1/n_3^2)s_{4\to 3} + (1/n_4^2)s_{3\to 4}]$, where $b_1(4s, d^\alpha s^2)$ is also taken into account. There is an inconsistency in this respect but it would not affect the results seriously.

[3] Although $b_1(4\mathrm{p}, d^\alpha p^2)$ is also available in Table 1, it has not been included in this average, contrary to the case of assigning numerical value to $-2[(1/n_3^2)s_{5\to 3} + (1/n_5^2)s_{3\to 5}]$, where $b_1(4s, d^\alpha p^2)$ is also taken into account. There is an inconsistency in this respect but it would not affect the results seriously.

putting Eqs. (4) and (5) into Eq. (1), one obtained the following relations:

$$\left.\begin{aligned} a'_0 &= a_0 + 10b_0 + 100A_2\,, \\ a'_1 &= a_1 + 10b_1\,, \\ a'_2 &= a_2\,, \\ b'_0 &= b_0 + 20A_2\,, \\ b'_1 &= b_1\,, \\ A'_2 &= A_2\,. \end{aligned}\right\} \tag{23}$$

Table 3. *Numerical values assigned to various expressions to get simultaneous equations for the determination of n_i's and $s_{i\to j}$'s*[a]

Expression number	Expression	Numerical values assigned (cm^{-1})[b]	Source[c]
1	$1/n_3^2$	21170	$A'_2(3d)$
2	$1/n_4^2$	10343	$A'_2(4s)$
3	$1/n_5^2$	10352	$A'_2(4p)$
4	$-(4/n_3^2)s_{3\to 3}$	−38124	Average of $b'_1(3d, d^\alpha)$, $b'_1(3d, d^\alpha s)$ and $b'_1(3d, d^\alpha p)$
5	$-2[(1/n_3^2)s_{4\to 3}+(1/n_4^2)s_{3\to 4}]$	−18504	Average of $b'_1(4s, d^\alpha s)$, $b'_1(4s, d^\alpha sp)$ and $b'_1(4s, d^\alpha s^2)$
6	$-2[(1/n_3^2)s_{5\to 3}+(1/n_5^2)s_{3\to 5}]$	−19026	Average of $b'_1(4p, d^\alpha p)$, $b'_1(4p, d^\alpha sp)$ and $b'_1(4p, d^\alpha p^2)$
7	$-(4/n_3^2)[(s_{1\to 3}+3s_{2\to 3})-s_{3\to 3}]$	−290212	Average of $b'_0(3d, d^\alpha)$, $b'_0(3d, d^\alpha s) -$ ⑤ and $b'_0(3d, d^\alpha p) -$ ⑥
8	$-2[(1/n_4^2)s_{5\to 4}+(1/n_5^2)s_{4\to 5}]$	−13252	Average of $[b'_0(4s, d^\alpha sp)-b'_0(4s, d^\alpha s)]$ and $[b'_0(4p, d^\alpha sp)-b'_0(4p, d^\alpha p)]$
9	$-(4/n_4^2)(s_{1\to 4}+3s_{2\to 4})$	−137144	Average of $b'_0(4s, d^\alpha s)$ and $[b'_0(4s, d^\alpha sp) -$ ⑧$]$
10	$-(4/n_4^2)s_{4\to 4}$	− 11997	$b'_0(4s, d^\alpha s^2) -$ ⑨
11	$-(4/n_5^2)(s_{1\to 5}+3s_{2\to 5})$	−148511	Average of $b'_0(4p, d^\alpha p)$ and $[b'_0(4p, d^\alpha sp) -$ ⑧$]$
12	$-(4/n_5^2)s_{5\to 5}$	− 14185	$b'_0(4p, d^\alpha p^2) -$ ⑪
13	$(1/n_4^2)s_{3\to 4}^2+(2/n_3^2)s_{4\to 3}s_{3\to 3}$	7648	Average of $a'_2(4s, d^\alpha s)$, $a'_2(4s, d^\alpha sp)$ and $a'_2(4s, d^\alpha s^2)$
14	$(1/n_5^2)s_{3\to 5}^2+(2/n_3^2)s_{5\to 3}s_{3\to 3}$	8508	Average of $a'_2(4p, d^\alpha p)$ and $a'_2(4p, d^\alpha sp)$
15	$(1/n_4^2)[s_{5\to 4}^2+4s_{5\to 4}(s_{1\to 4}+3s_{2\to 4})]$ $+(1/n_5^2)[s_{4\to 5}^2+4s_{4\to 5}(s_{1\to 5}+3s_{2\to 5})]$	97918[d]	$a'_0(4p, d^\alpha sp)-a'_0(4p, d^\alpha p)$

[a] Simultaneous equations may be obtained by putting the expressions in the second column equal to the numerical value given in the same row.

[b] See footnote [a] to Table 1.

[c] $b'_0(3d, d^\alpha s) -$ ⑤ for example stands for the numerical value obtained by subtracting the numerical value assigned to the expression No. 5 from the $b'_0(3d, d^\alpha s)$ value.

[d] Although this quantity could also be obtained as $a'_0(4s, d^\alpha sp)-a'_0(4s, d^\alpha s)$, we preferred $a'_0(4p, d^\alpha sp)-a'_0(4p, d^\alpha p)$ since a'_0's for $4p$ VOIP is considered to be more accurate than those for $4s$ VOIP judging from the fluctuation of a'_2, which should be constant characteristic to the orbital involved in VOIP.

In transforming a_k's and b_k's into a'_k's and b'_k's, the A_2 values given in (3) were used, while the a_k and the b_k values used were those given in respective rows in Table 1. The resulting a'_k and b'_k values are not given, since the calculation is very straightforward.

We are now in a position to determine n_i's and $s_{i\to j}$'s. The n_i can easily be determined from

$$1/n_i^2 = B_{15}^i = A_2^i\,. \tag{24}$$

In Eq. (24), which is obtained from Eqs. (1) and (11), the superscript i attached to B_{15} and A_2 indicates that those for the orbital i are involved. Thus, converting the values given as (3) in Rydbergs, one obtains

$$\left.\begin{aligned} n_{3d} &= 2.277\,, \\ n_{4s} &= 3.257\,, \\ n_{4p} &= 3.256\,. \end{aligned}\right\} \tag{25}$$

To obtain $s_{i\to j}$'s, simultaneous equations are constructed by comparing the theoretical expressions and the numerical values of a'_k's or b'_k's and by putting the numerical values of (25) into the n_i's appearing in the theoretical expressions. In some cases, there are several ways of obtaining equivalent set of simultaneous equations. In such cases, those which are obtained from b'_k rather than from a'_k are adopted. This is because our b'_k is considered to be more accurate than a'_k judging from the fact that $b_1 (= b'_1)$ less fluctuate than $a_2 (= a'_2)$, which should be constant characteristic to the orbital involved in VOIP (see Table 1). In the third column of Table 3, the numerical values assigned to the expression given in the second column are given. The fourth column shows how these values are obtained. In solving the simultaneous equations, alternative sets of solutions have been obtained for each of the pairs of quantities $(s_{3\to 4}, s_{4\to 3})$, $(s_{3\to 5}, s_{5\to 3})$ and $(s_{4\to 5},$

Table 4. *The effective quantum numbers and the screening constants*

	Present work	From the Slater rule
n_{3d}	2.277	3.00
n_{4s}	3.257	3.70
n_{4p}	3.256	3.70
$s_{3s\to 3d} + 3s_{3p\to 3d}$	3.877	4.00
$s_{3s\to 4s} + 3s_{3p\to 4s}$	3.315	3.40
$s_{3s\to 4p} + 3s_{3p\to 4p}$	3.587	3.40
$s_{3d\to 3d}$	0.450	0.35
$s_{4s\to 4s}$	0.290	0.35
$s_{4p\to 4p}$	0.343	0.35
$s_{3d\to 4s}$	0.820	0.85
$s_{3d\to 4p}$	0.894	0.85
$s_{4s\to 3d}$	0.036	0.00
$s_{4s\to 4p}$	0.581	0.35
$s_{4p\to 3d}$	0.012	0.00
$s_{4p\to 4s}$	0.060	0.35

$s_{5\to4}$). In such cases, those which satisfy the condition that

$$s_{i\to j} > s_{j\to i}\,(i<j) \tag{26}$$

have been adopted since the screening effect due to an inner electron to an electron in outer orbital is considered to be larger than the screening effect in other way round. The screening constants and the effective quantum numbers thus obtained are given in Table 4 and compared with those derived from the Slater rule [7].

5. Discussions

We have now shown that there are regularities among A_k's of Eq. (1) fitted to the VOIP of isoelectronic series of atoms and ions of the first transition elements, although the regularities are not so apparent as in the cases treated in I [1]. It has also been shown that the regularities can be understood on the basis of Slater's simple theory of atoms with the idea of screening effect due to inner electrons. Contrary to the cases treated in I, the VOIP for not all the configurations are known for atoms and ions of the transition elements. We have therefore tried to calculate these unknown VOIP's on the basis of regularities found for A_k's, a_k's and b_k's but we have very frequently obtained negative values, which are unreasonable. The reproductions of *known* VOIP is not necessarily good also. In the subsequent work therefore the least-squares fitting of Eq. (10) to all the available data of VOIP will be given with the purpose of obtaining a general formula for calculating VOIP. It should be stressed that the essential achievement of the present work as well as of I are as follows: (i) to have shown *empirically* that there are regularities among A_k's of Eq. (1); (ii) to have shown that the regularities can be understood on the basis of the simple Slater theory and to have laid the foundation of the subsequent work.

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Appendix

E_{av} Values of $3d^{\alpha}4p^2$ Atoms and Ions

The E_{av} values of Ca $3d^0 4p^2$, was obtained as the weighted mean of the observed term values [8] as all the terms belonging to this configuration of Ca are observed. As for Sc$^+$ $3d^0 4p^2$, Zn $3d^{10} 4p^2$ and Ga$^+$ $3d^{10} 4p^2$, a special device is necessary, as the term values belonging to these configurations are incompletely given. Fraga and Fisk [9] have evaluated the Slater parameters of various kinds in various atoms and ions, by using the analytical Hartree-Fock AO's. Their results show that $G^1(2s, 2p)/F^2(2p, 2p)$ and $G^1(3s, 3p)/F^2(3p, 3p)$ are approximately constants depending only upon the ionic charge provided that the $2s$ and $2p$ or the $3s$ and $3p$ orbitals are the outermost orbitals of the atom or the ion occupied by electrons; $G^1(2s, 2p)/F^2(2p, 2p) \approx 1.34$ and $G^1(3s, 3p)/F^2(3p, 3p) \approx 1.40$ for the singly positive ions while they are $1.40 \sim 1.45$ and $1.42 \sim 1.43$, respectively, for the neutral atoms. From these observations, we *assume* that $G^1(4s, 4p)/F^2(4p, 4p) = 1.45$ and have obtained the $F^2(4p, 4p)$ value of a $3d^\alpha 4p^2$ ion from the $G^1(4s, 4p)$ value of the same ion in the $3d^\alpha 4s4p$ configuration obtained by Anno and Teruya [5]. If we put the $F^2(4p, 4p)$ value thus obtained and the experimental term value into the theoretical expression of the term value, we can obtain E_{av} value. In the case of Zn $3d^{10}4p^2$, observed term values are available both for ^3P and ^1D, so that the mean of the E_{av} values obtained from these two term values with the procedure outline above was taken.

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