Systematic Determination of the Slater-Condon Parameters of Atoms and Ions with $1s^2\,2s^m\,2p^n$ Configurations

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Semiempirical values of the Slater parameters $F^2(2p, 2p)$ and $G^1(2s, 2p)$ have been determined for the atoms and ions with the electron configurations $1s^2 2s^m 2p^n$ from the experimental atomic energy levels. Particular attention has been paid to get the values of the parameters to be used for semiempirical calculations on molecular electronic structure. The calculation has also yielded E_{av}'s, the average energies of configurations of these atoms. Evaluation of the semiempirical or effective value of F^0 from ΔE of an appropriate electron-transfer reaction, based on the idea presented by Anno [15], is also referred to in the present paper. The semiempirical values of the Slater parameters as well as those of ΔE's and E_{av}'s show almost linear dependence upon atomic number Z through isoelectronic series. From the overall tendency of the correlation lines, it is pointed out that the assignment of atomic energy levels of $Na^{5+}(1s^2 2p^4)$ must be wrong.

Semiempirische Werte der Slater-Parameter $F^2(2p, 2p)$ und $G^1(2s, 2p)$ wurden für die Atome und Ionen mit der Elektronenkonfiguration $1s^2 2s^m 2p^n$ aus den experimentellen atomaren Energie-termen bestimmt. Insbesondere wurden die Parameter bestimmt, die für semiempirische Berechnungen der Elektronenstruktur von Molekülen benötigt werden. Die Berechnung ergibt weiterhin Werte von E_{av}, der Durchschnittsenergie der Konfigurationen der genannten Atome. Die vorliegende Arbeit geht auch auf die Bestimmung des semiempirischen bzw. effektiven Wertes von F^0 aus ΔE einer geeigneten Elektronenübertragungsreaktion ein, die auf die Arbeit von Anno [15] zurückgeht. Die semiempirischen Werte der Slater-Parameter sowie der ΔE und E_{av} zeigen annähernd lineare Abhängigkeit von der Atomnummer Z innerhalb isoelektronischer Reihen. Aus dem Gesamtverhalten der genannten Kurven wird geschlossen, daß die Zuordnung der atomaren Energieterme von $Na^{5+}(1s^2 2p^4)$ falsch sein dürfte.

Détermination à partir des niveaux d'énergie atomiques expérimentaux des valeurs semi-empiriques des paramètres de Slater $F^2(2p, 2p)$ et $G^1(2s, 2p)$ pour les atomes et les ions ayant les configurations $1s^2 2s^m 2p^n$. On a fait particulièrement attention d'obtenir les valeurs des paramètres à utiliser pour des calculs moléculaires semi-empiriques. Le calcul a aussi fourni les énergies moyennes des configurations de ces atomes. On évoque aussi le calcul de la valeur semi-empirique ou effective de F^0 à partir du ΔE d'une réaction appropriée de transfert électronique, selon une idée de Anno [15]. Les valeurs semi-empiriques des paramètres de Slater, ainsi que celles des ΔE et E_{moy}, montrent une dépendance presque linéaire au nombre atomique Z à travers les séries isoélectroniques. A partir des tendances générales des lignes de corrélation, on remarque que l'attribution des niveaux d'énergie atomiques de $Na^{5+}(1s^2 2p^4)$ doit être fausse.

1. Introduction

There are many attempts in the literature of determining semiempirical values of the Slater-Condon parameters from the observed term values [1–10] because of the importance of these parameters in the semiempirical theory of atoms and molecules. Of the atoms and ions treated, those which have the electron configura-

tions of the type $1s^2 2s^m 2p^n$ have been studied most extensively [2, 4, 7, 9]. We refer in particular to Rohrlich [2], Pilcher and Skinner [4], Hinze and Jaffé [7] and to Edlén [9]. Rohrlich [2] has studied these atoms by amending the Slater method to include the "polarization" correction and, wherever possible, configuration interaction. Pilcher and Skinner [4] have tried to eliminate the effect of configuration interaction between $2s^2 2p^{n-2}$ and $2p^n$, while Edlén [9] has included the spin-orbit coupling effect in the Slater-type treatment.

As is well known, Slater's theory of many-electron atoms [11] is based on the Russell-Saunders coupling approximation, with a complete neglect of the spin-orbit couplings, and regards an atom as in a single configuration. Usual semiempirical theories of molecular electronic structures, such as the Pariser-Parr type [12], are based on the LCAO MO approximation. The atoms in molecules are therefore treated in such theories with the same approximation as adopted in the Slater theory mentioned above. Essential achievement of the semiempirical theory is its ability of taking account of any effect, such as the electron correlation, which usual nonempirical orbital theory is unable to include, but is present in atoms before they get into the molecule. This is done by obtaining the values of the parameters or one-center integrals to be used in the molecular calculations in such a way that they reproduce the experimental data of atoms as accurately as possible. Therefore, the experimental term values, without any corrections such as of the configuration interaction, must directly be used for the determination of the Slater-Condon parameters to be used for the molecular calculation, although the J structure of the atomic energy levels is to be averaged out since the spin-orbit coupling is neglected in the usual semiempirical molecular orbital theory. Hinze and Jaffé [7] seem to stand upon this philosophy, but they have treated atomic energy levels belonging to $1s^2 2s^2 2p^{n-2}$, $1s^2 2s 2p^{n-1}$ and $1s^2 2p^n$ configurations together. In other words, they have assumed that values of the Slater-Condon parameters are the same in such three configurations. There are reasons [13, 14] to believe that the $2p$ orbitals are "outer" than the $2s$ orbital. Therefore, the value of $F^2(2p, 2p)$, for example, must be distinguished in the three configurations mentioned above.

From the reasons described above, a systematic reevaluation of the Slater-Condon parameters of the $1s^2 2s^m 2p^n$ atoms[1] is deemed advisable. It is the purpose of the present paper to give the results of such a work. Evaluation of the semiempirical or effective values of F^0, based on the idea presented by Anno [15], is also referred to in the present paper. Comparison with the nonempirical values however are postponed to a later publication.

2. Method

As in a previous paper [10] (hereafter referred to as I), which was concerned with the first transition elements having the electron configuration of $K(2) L(8) 3s^2 3p^6 3d^\alpha 4s^\beta 4p^\gamma$, Slater's parameters, rather than Condon's parameters, are considered in the present work. Not more than one term arises for each kind,

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[1] In the present paper, "atom" means both the neutral atoms and the ions. "The $1s^2 2s^m 2p^n$ atoms" mean the atoms and ions with the electron configurations $1s^2 2s^m 2p^n$.

as specified by the multiplicity and the symmetry, for a configuration treated in the present paper. Therefore, in the notation of I, n_r is always equal to 1 and the term value ^rT of the rth kind can simply be expressed as

$$^rT = \sum_l {}^{rl}B\, G_l,\tag{1}$$

where G_l's represent either Slater's F^k or G^k or even the average energy of the configuration E_{av} and ^{rl}B's are numerical coefficients. If we take E_{av} as G_1, ^{r1}B is always equal to 1. The least-squares procedure now to be used is to adjust G_l's in such a way that the sum ε of the squares of the differences between the calculated term value ^rT, given by Eq. (1), and the corresponding experimental value $^rT^{(e)}$ be a minimum. Therefore, one obtains

$$\sum_l \left[\sum_r {}^rW{}^{rl}B\,{}^{rl}B \right] G_l = \sum_r {}^rW\,{}^{rl}B\,{}^rT^{(e)},\tag{2}$$

by differentiating partially

$$\varepsilon = \sum_r {}^rW\left({}^rT^{(e)} - \sum_l {}^{rl}B\, G_l \right)^2\tag{3}$$

with respect to $G_{l'}$. In Eqs. (2) and (3), ^rW is the weight to be given to $^rT^{(e)}$ in the least-squares treatment. Eq. (2) is a set of linear simultaneous equations, which may be solved for G_l's, if the numerical values are given for ^rW, ^{rl}B and $^rT^{(e)}$.

The ^{rl}B values are given in Slater's book [16] and have been taken from this source. The observed levels have been taken from Moore's table [17] by averaging out the fine structure, each component of a particular term being given a weight of $2J + 1$. Some of the term values quoted in Moore's table have been obtained by inter- or extrapolation through isoelectronic series of atoms. Moreover, for some of the atoms, the term values whose multiplicity is different from that of the ground state are subject to an uncertainty, which is denoted by x in Moore's table, because no intersystem combinations have been observed with any certainty. In the present calculations, however, all the term values quoted in Moore's table have been used as the "experimental" values withot discriminations. This is because of the fact that the experimental term values of the atoms treated in the present work actually show a linear dependence upon atomic number along isoelectronic series with a fairly high degree of approximation and a linear inter- or extrapolation is therefore expected to be accurate enough and that the uncertainty x is estimated to be a few hundred wave-numbers or less, which is within the limit of accuracy of the Slater-type treatment of many-electron atoms.

In the least-squares treatment, each of the "experimental" term values would have to be given a weight proportional to $(2L + 1)(2S + 1)$, where L and S are the quantum numbers of the total orbital and the spin angular momentum of the term, respectively, since the state wave function representing the term has $(2L + 1)(2S + 1)$-fold degeneracy. We have however given a constant weight to each of the term values. The reasons for this choice of the weight will be described below.

As was mentioned in the Introduction, the essential purpose of the present work is to establish the semiempirical values of the Slater-Condon parameters to be used for the molecular calculations. An atom in a molecule is in a valence

state, which is a linear combination of spectroscopic states belonging to a configuration:

$$\Phi_V = \sum_r c_r \psi_r, \tag{4}$$

where Φ_V is the valence-state wave function and ψ_r is the wave function of the rth spectroscopic state belonging to the configuration. Anno and Sakai [18] have shown that the best values of the Slater-Condon parameter for the calculation of the valence-state energy are obtained from the observed term values by putting $^rW = c_r^2$. In the usual semiempirical molecular orbital theory, however, one might prefer to use a single value for a particular parameter in a particular configuration for the sake of simplicity and the set of c_r values are different for different valence states even if they belong to one and the same configuration. The Slater-Condon parameters optimum to all the valence states belonging to one and the same configuration would be obtained by putting all the c_r's be equal, namely by taking a constant ^rW value. Therefore, we have given a constant weight to each of the term values.

3. Results for E_{av}, $F^2(2p, 2p)$ and $G^1(2s, 2p)$

The semiempirical values of the E_{av} and the Slater parameters $F^2(2p, 2p)$ and $G^1(2s, 2p)$ obtained as described in a preceding section are given in Tables 1–3, while Figs. 1 and 2 correlate the $F^2(2p, 2p)$ and the $G^1(2s, 2p)$ values with the atomic number Z. The numerical value of E_{av} depends upon the energy reference. The ground state of the atom concerned is always taken as the energy reference. As can be seen in these figures, a particular kind of Slater parameters of an isoelectronic series of ions can be correlated linearly with Z with a fairly high degree of approximation. A straight line, which is called a correlation line, has therefore been fitted to each series by a least-squares method. Correlation lines thus obtained are also shown in Figs. 1 and 2, while Table 4 lists the numerical values of coefficients a_0 and a_1 of

$$G = a_0 + a_1 Z, \tag{5}$$

which represents a correlation line of a Slater parameter G of an isoelectronic atoms. Correlation diagrams between E_{av} and Z are not given in the present paper since the numerical values of E_{av} depend upon the energy reference and the comparison of the correlation diagrams of *different* isoelectronic series have no significance. It should be mentioned however that the ground state, which is taken as the energy reference, is the same in its configuration, symmetry and multiplicity for a particular series of isoelectronic atoms treated in the present paper and that E_{av} of a particular isoelectronic series in a definite configuration is found to be linear in Z with a fairly high degree of approximation[2].

For some of the cases, the semiempirical values of the Slater parameters and E_{av} cannot be obtained for lack of the experimental data on the term values. In such cases, the $F^2(2p, 2p)$ and the $G^1(2s, 2p)$ values have been calculated with

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[2] For isoelectronic series $1s^2 2s^2 2p$ and $1s^2 2s^2 2p^5$, E_{av} shows a parabolic, *not* a linear, dependence upon Z. These two series however are only exceptional series.

Table 1. *Semiempirical values of* E_{av} *(cm^{-1})*[a–d]

q^e	0	+1	+2	+3	+4	+5
$2p$	14904	31933	48381	64556	80637	96730
$2p^2$	59115	101704	142912	183639	224378	264913
$2p^3$	(102722)	155459	209583	262244	315058	(368451)
$2p^4$	{ (148101)	(220205)	292308	(364411)	(436515)	508618
	[159626]^f	[226376]^f	—	[359356]	[428405]	[492594]
$2p^5$	(234690)	(318065)	401376	484944	568126	(651565)
$2p^6$	[292776]^f	[386031]^f	[480129]	[572530]	[664486]	[758320]
$2s2p$	27127	46360	64863	83128	101509	119574
$2s2p^2$	46506	70990	94785	118225	142036	165154
$2s2p^3$	75306	107973	139010	170546	202053	233750
$2s2p^4$	(117924)	159100	201062	242530	283744	325046
$2s2p^5$	142187	183617	225812	269136	312497	356147
$2s2p^6$	168554	217050	264449	311527	358810	406500
$2s^2 2p$	11	43	116	258	497	877
$2s^2 2p^2$	4912	7415	9862	12358	14962	17668
$2s^2 2p^3$	17962	25148	32017	38551	44888	51209
$2s^2 2p^4$	7670	10152	12640	15294	17987	20768
$2s^2 2p^5$	135	261	455	742	1147	1700

[a] The configuration of the core, i.e. $1s^2$, is omitted for brevity.

[b] The energy of the ground state of the atom or the ion in question is taken to be zero.

[c] Inter- or extrapolated values are given in parentheses, while the corrected values are given in brackets (see text).

[d] Only one state arises from each of those configurations which consist of closed-shells only or of closed-shells and an open-shell involving a single electron. Therefore, for these configurations, E_{av} is equal to the energy of the only state belonging to the configuration. Of these configurations, $1s^2$, $1s^2 2s$, $1s^2 2s^2$ and $1s^2 2s^2 2p^6$ are the ground configurations of the He-, Li-, Be- and Ne-like atoms, respectively. For these configurations the numerical value of E_{av} is therefore equal to zero, which is not included in Table 1 for brevity.

[e] q is the charge of the atom or ion. Since the atomic number Z may easily be calculated from $Z = q + 2 + m + n$ for the atoms or ions with the electron configuration $1s^2 2s^m 2p^n$, neither the atomic number nor the atomic symbol is given.

[f] These values cannot be obtained by the method described in Section 4 of text. They have therefore been obtained by a linear extrapolation along isoelectronic series.

Table 2. *Semiempirical values of* $F^2(2p, 2p)$ *(cm^{-1})*[a]

q^b	0	+1	+2	+3	+4	+5
$2p^2$	21421	49661	77259	101950	125887	150350
$2p^3$	(20445)	42868	70507	93885	115353	(140861)
$2p^4$	{ (−1994)	(49559)	101111	(152663)	(204216)	255768
	[51371]	[76241]	—	[125981]	[150851]	[175721]
$2s2p^2$	33326	51290	73325	93993	113387	138209
$2s2p^3$	45134	60301	78706	98988	118925	138621
$2s2p^4$	(55538)	74558	96348	116163	135600	154888
$2s^2 2p^2$	35699	53850	70996	87763	104302	120610
$2s^2 2p^3$	48488	68002	86624	104409	121697	138969
$2s^2 2p^4$	55685	73969	91644	109499	127025	144385

[a] See Footnotes a, c and d to Table 1.

[b] See Footnote e to Table 1.

Table 3. *Semiempirical values of* $G^1(2s, 2p)$ (cm^{-1}) [a]

q [b]	0	+1	+2	+3	+4	+5
$2s2p$	30876	54072	74977	95133	114578	134533
$2s2p^2$	44260	68062	89178	109777	129317	151085
$2s2p^3$	55635	81354	102158	122692	142846	162747
$2s2p^4$	(73111)	93128	115067	136294	156476	176341
$2s2p^5$	95300	111976	127335	149673	170818	191386

[a] See Footnotes a, c and d to Table 1.
[b] See Footnote e to Table 1.
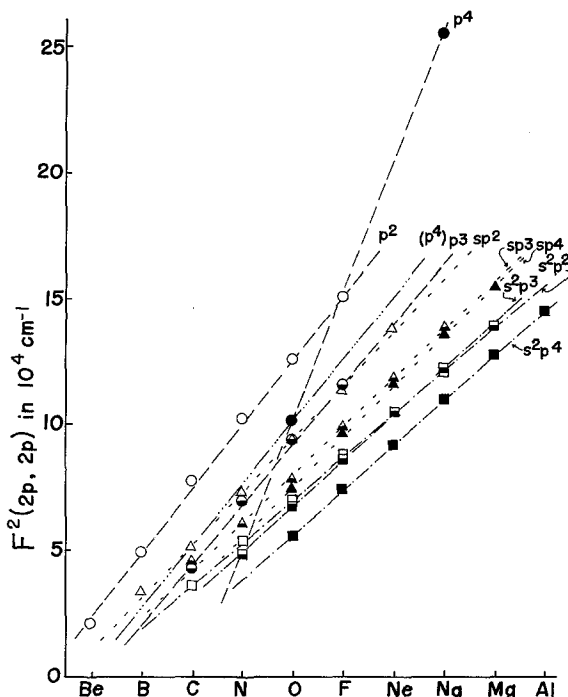
Fig. 1. $F^2(2p, 2p)$ of isoelectronic series with $1s^2 2s^m 2p^n$ (abbreviated as $s^m p^n$) configurations

— — — — p^n,   ◯ p^2,   ◗ p^3,   ● p^4;
---------------- sp^n,   △ sp^2,   ▲ sp^3,   ▲ sp^4;
— · — · — $s^2 p^n$,   □ $s^2 p^2$,   ◩ $s^2 p^3$,   ■ $s^2 p^4$;
— ·· — ·· — (p^4), corrected correlation line for p^4 (see text)
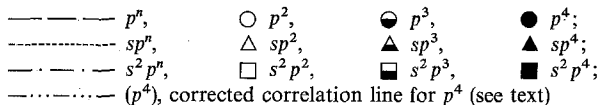
Eq. (5) and the E_{av} values have been obtained similarly by a linear inter- or extra-polation along isoelectronic series with a least-squares method[3]. The numerical values thus obtained are given in parentheses in appropriate one of Tables 1–3.

Only one state arises from each of those configurations which consist of closed-shells only or of closed-shells and an open-shell involving a single electron.

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[3] All the atoms, for which an inter- or an extrapolation is necessary, belong to those isoelectronic series for which E_{av} shows a linear dependence upon Z.
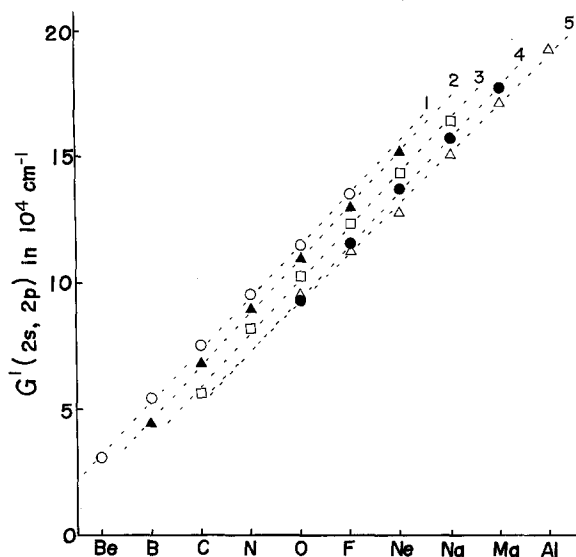
Fig. 2. $G^1(2s, 2p)$ of isoelectronic series with $1s^2 2s 2p^n$ configurations. Numeral given at the top of each of the correlation lines indicates the n value

Therefore, for these configurations, E_{av} is equal to the energy of the only state belonging to the configuration. Of these configurations, $1s^2, 1s^2 2s, 1s^2 2s^2$ and $1s^2 2s^2 2p^6$ are the ground configurations of the He-, Li-, Be- and Ne-like atoms, respectively. For these configurations, the numerical value of E_{av} is therefore equal to zero, which is not included in Table 1 for brevity.

We shall now look at Figs. 1 and 2 and shall see if there are any regularities among various correlation lines. A regularity can be seen among the correlation lines for $G^1(2s, 2p)$ of $1s^2 2s 2p^n$ configurations with various n: they run roughly parallel to one another with an approximately constant separation. This sort of regularity cannot be seen for $F^2(2p, 2p)$ except that the slopes of the correlation lines are very roughly the same. The correlation line for $F^2(2p, 2p)$ of the $1s^2 2p^4$ configuration is exceptional even in its slope as is seen in Fig. 1. As will be discussed in connection with $\Delta E(2s, 2s)$ in the next section, we believe that the probable reason for it is that the observed term value(s) of $Na^{5+}(1s^2 2p^4)$ is wrong because of misassignment or for some other reasons. A "corrected" correlation line for $F^2(2p, 2p)$ of the $1s^2 2p^4$ atoms would then be useful. Only ions with the configuration $1s^2 2p^4$ for which the data are available are O^{2+} and Na^{5+} and the data for $O^{2+}(1s^2 2p^4)$ do not seem to be wrong for reasons described in the next section. The "corrected" correlation line for $F^2(2p, 2p)$ of the $1s^2 2p^4$ atoms have therefore been drawn in such a way that it passes the O^{2+} point and has the slope which is the average of those of the $1s^2 2p^2$ and of the $1s^2 2p^3$ correlation lines. The a_0 and the a_1 values [see Eq. (5)] of this corrected correlation line are given in Table 4, while the $F^2(2p, 2p)$ values of the $1s^2 2p^4$ atoms obtained from this corrected correlation line are also given in Table 2 by enclosing in brackets.

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Table 4. *The numerical values of a_0 and a_1 of Eq. (5) (cm^{-1})* [a]

Configuration	a_0	a_1
$F^2(2p, 2p)$		
$2p^2$	$-$ 79019	25658
$2p^3$	$-$ 99972	24083
$2p^4$ [b]	{ $-$ 311308	51552
	{ [$-$ 97849]	[24870]
$2s2p^2$	$-$ 72801	20896
$2s2p^3$	$-$ 71045	18960
$2s2p^4$	$-$ 84401	19991
$2s^22p^2$	$-$ 65066	16934
$2s^22p^3$	$-$ 76648	18036
$2s^22p^4$	$-$ 85789	17729
$G^1(2s, 2p)$		
$2s2p$	$-$ 49679	20570
$2s2p^2$	$-$ 59634	21100
$2s2p^3$	$-$ 68614	21159
$2s2p^4$	$-$ 72374	20784
$2s2p^5$	$-$ 62707	19408

[a] See Footnote a to Table 1.
[b] For this configuration, a_0 and a_1 of corrected correlation line are also given in brackets (see text).

4. Determination of F^0

We are now in a position to determine F^0's by considering "electron-transfer reactions" as suggested by Anno [15]. Variuos electron-transfer reactions, necessary for the determination of F^0's of the transition elements, and the corresponding expressions for the energy changes in terms of the Slater parameters, are given in Table 3 of I [10]. For the present purpose, the expressions related to $\Delta E(ss)$, $\Delta E(pp)$ and $\Delta E(sp)$ given in that Table may be used if one puts $\alpha = 0$, $\beta = m$, $\gamma = n$ and interprets s and p as $2s$ and $2p$, respectively.

The semiempirical values of ΔE can be obtained from the E_{av} values (as measured from the ground states of respective atoms) given in Table 1 and the experimental ionization potential given in Moore's table [17]. With these values of ΔE, F^0 could be obtained by using F^k's and G^k's $(k \neq 0)$. We leave this calculation to the reader and shall confine ourselves to ΔE rather than F^0 in the remaining part of this section.

Since the calculation of ΔE from the data of Table 1 and of Moore's table [17] is also very easy to do, the numerical values of various ΔE's are not tabulated in the present paper. They are however plotted in Figs. 3–8 to show the trend of the data. Now if one looks at these Figures, one will find that ΔE's are correlated linearly with Z and that a set of correlation lines for a particular kind of ΔE, corresponding to configurations with a definite number of $2s$ electrons but with different numbers of $2p$ electrons run parallel to one another with an approximately constant separation with a few exceptions. It would be tempting therefore to assume that a set of correlation lines run really parallel to one another with a constant separation (we shall refer to this assumption as "the assumption of
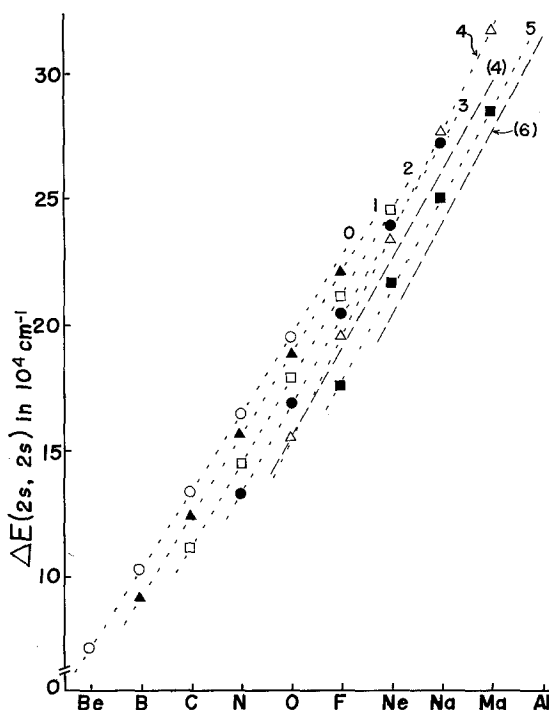
Fig. 3. $\Delta E(2s, 2s)$ of isoelectronic series with $1s^2 2s^2 2p^n$ configurations. --------------indicates correlation lines fitted to the original data, while — — —represents "corrected" or "estimated" correlation lines. Numeral given at the top of each of the correlation lines (by enclosing in the parentheses in the case of corrected or estimated correlation lines) indicates the n value

constant slope-constant separation") and that "exceptions" are resulting from wrong values of some quantities used in the calculations of ΔE's.

As an example, let us look at Fig. 3, where $\Delta E(2s, 2s)$ of the $1s^2 2s^2 2p^n$ atoms are plotted. It will then easily be seen that only exceptional correlation line in Fig. 3 is that for the $1s^2 2s^2 2p^4$ atoms. All the quantities, necessary for the calculation of $\Delta E(2s, 2s)$ of such atoms, do not seem to be wrong except E_{av} of the $1s^2 2p^4$ atoms, since the correlation lines for any of such quantities along isoelectronic series are either linear or monotonously parabolic. We suspect therefore that the adopted values for E_{av} of the $1s^2 2p^4$ atoms might be wrong.

Now, only atoms with $1s^2 2p^4$ configurations whose E_{av} have been obtained by semiempirical analysis of the experimental data, are O^{2+} and Na^{5+}. For the other atoms with this configuration, E_{av} has been obtained by assuming a linear relation between E_{av} and Z passing the O^{2+} and the $Na5^+$ points. Therefore, if either one of these points were wrong, all the inter- or extrapolated E_{av} values would be wrong. Since the point for oxygen in the $1s^2 2s^2 2p^4$ correlation line in Fig. 3 appears to be normal because it stands just halfway between the $1s^2 2s^2 2p^3$ and the $1s^2 2s^2 2p^5$ lines, we assume that what is wrong is the E_{av} value of $Na^{5+}(1s^2 2p^4)$ rather than of $O^{2+}(1s^2 2p^4)$. This assumption is supported by the fact that the
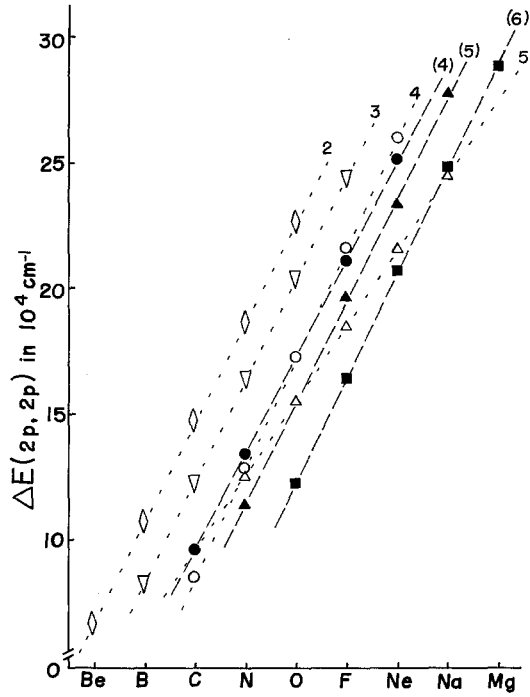
Fig. 4. $\Delta E(2p, 2p)$ of isoelectronic series with $1s^2 2p^n$ configurations. See also caption to Fig. 3
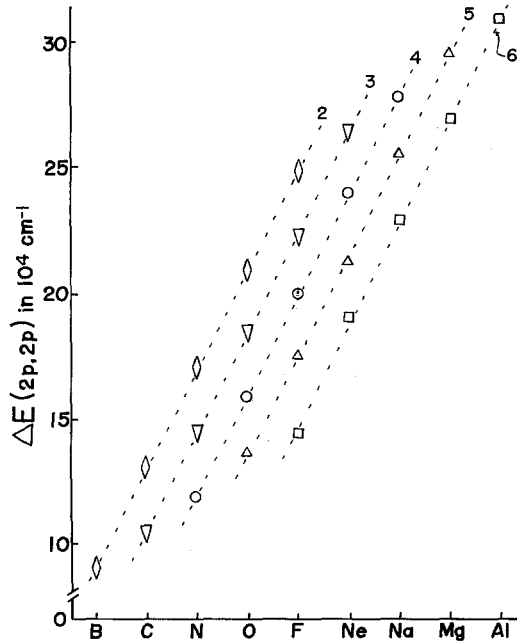

Fig. 5. $\Delta E(2p, 2p)$ of isoelectronic series with $1s^2 2s 2p^n$ configurations. See also caption to Fig. 3
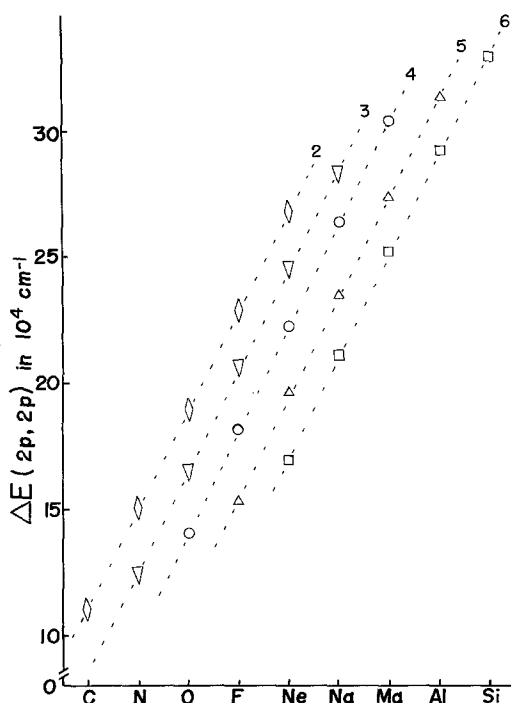
Fig. 6. $\Delta E(2p, 2p)$ of isoelectronic series with $1s^2 2s^2 2p^n$ configurations. See also caption to Fig. 3
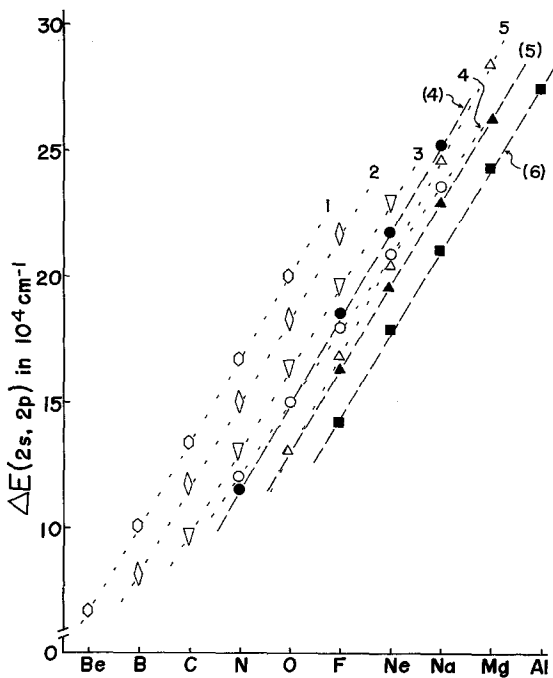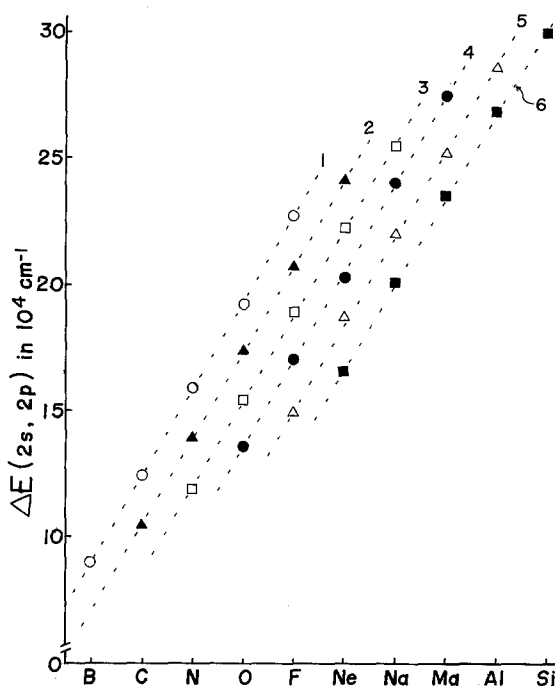

Fig. 7. $\Delta E(2s, 2p)$ of isoelectronic series with $1s^2 2s 2p^n$ configurations. See also caption to Fig. 3

Fig. 8. $\Delta E(2s, 2p)$ of isoelectronic series with $1s^2 2s^2 2p^n$ configurations. See also caption to Fig. 3

$F^2(2p, 2p)$ value of $Na^{5+}(1s^2 2p^4)$ is abnormally large as we saw in Fig. 1 and there must be something wrong in the experimental term values.

In order to get the "corrected" value of E_{av} of $Na^{5+}(1s^2 2p^4)$, the "corrected" correlation line for $\Delta E(2s, 2s)$ of the $1s^2 2s^2 2p^4$ configuration is drawn, as is shown in Fig. 3, in such a way that it passes the $O(1s^2 2s^2 2p^4)$ point with a slope which is equal to the arithmetic mean of those of the $1s^2 2s^2 2p^3$ and the $1s^2 2s^2 2p^5$ correlation lines. The $\Delta E(2s, 2s)$ values of the isoelectronic atoms with the $1s^2 2s^2 2p^4$ configuration obtained from this corrected correlation line are used to calculate the E_{av} values of the $1s^2 2p^4$ atoms, since all the rest of the quantities necessary for the calculation are available. The E_{av} values of the $1s^2 2p^4$ atoms thus obtained are given in Table 1 by enclosing in brackets.

Let us now go on to the rest of the ΔE correlation diagrams. Of these, Figs. 4 and 7 contain some "exceptional" lines. Close inspection reveals that all of these exceptional lines are related to E_{av} of the $1s^2 2p^4$ atoms and recalculation with the corrected E_{av} values of the $1s^2 2p^4$ atoms obtained as mentioned above give new correlation lines as shown in Figs. 4 and 7. It can be seen clearly in these Figures that "exceptions" have now disappeared as far as the slope is concerned. This may be taken as an additional support for our revision of E_{av} of $Na^{5+}(1s^2 2p^4)$.

From the over-all tendency of the ΔE correlation diagrams, the E_{av} values of isoelectronic atoms with the $1s^2 2p^6$ configuration may be obtained. The only term arising from this configuration is ^1S, whose term value, which is identical to E_{av} of this configuration, has not been obtained for any of the isoelectronic

atoms with this configuration. The estimation of this quantity therefore may be useful. The estimation is based on our "assumption of contant slope-constant separation", which is introduced empirically above in this section and will be proved theoretically in the next section. The idea is to get the $\Delta E(2s, 2s)$ values for the $1s^2 2s^2 2p^6$ atoms first based on this "assumption of constant slope-constant separation" (the detail is given in the Appendix) and then to calculate the E_{av} values of the $1s^2 2p^6$ atoms from the $\Delta E(2s, 2s)$ values thus obtained since the other quantities necessary for this calculation are available. The E_{av} values of the $1s^2 2p^6$ atoms thus obtained are given in Table 1 by enclosing in brackets.

To show that our estimation of E_{av} of the $1s^2 2p^6$ isoelectronic series described above is not just a speculation, further quantities have been calculated. They are $\Delta E(2p, 2p)$ of the $1s^2 2p^6$ atoms and $\Delta E(2s, 2p)$ of the $1s^2 2s 2p^6$ atoms. They are plotted against Z in Figs. 4 and 7, respectively. It can be seen in these Figures that the correlation lines of these ΔE's are in conformity with the overall trend of the other correlation lines involved in these Figures. This may be taken as an evidence to show that our estimation of E_{av} of the $1s^2 2p^6$ atoms is not far from correct.

5. Parameters to be Used for Molecular Calculations

As was mentioned in the Introduction, the essential purpose of the present paper is to establish the numerical values of the Slater parameters to be used in evaluating atomic or one-center quantities necessary for the semiempirical calculation of molecules. An atom in a molecule, in general, is in such a configuration that the electron population in its atomic orbital as judged by the Mulliken population analysis [19] is fractional, which may be regarded as some average of various configurations having integral values of electron population. Therefore, it would be convenient if a formula with the numerical value of the Slater parameter can be calculated from the electron populations (m, n in the notation of the present paper) and the atomic number Z, would be obtained for each kind of the Slater parameter. The formula must be supported not only by theoretical basis but also by empirical data.

We shall discuss F^k's and G^k's ($k \neq 0$) first. For these parameters, the "ideal correlation lines" given in I [10] for the transition elements are equivalent to such formulas. In I, the ideal correlation lines have been obtained with a least-squares method in such a way that the set of correlation lines is in conformity with the "assumption of constant slope-constant separations". This assumption as applied to F^k's and G^k's ($k \neq 0$), however, can be verified only roughly by the Slater rule if the Slater-type AO's are employed. In the case of transition element, the deviation of the individual point in the correlation diagram of the Slater parameter from the actual correlation lines (as called "final correlation line" in I) is large and "idealization" based upon such a crude theory would therefore be tolerable. In the case of the $1s^2 2s^m 2p^n$ atoms treated in the present paper, however, the isoelectronic points in the correlation diagram lie upon a straight line with a fairly high degree of approximation as stated in Section 3. "Idealization" in this case, therefore, must be based upon a much more sound theoretical basis. As will be discussed in a separate article [18], the effect of the correlation energy,

Table 5. *The numerical values of C_i's of* Eq. (7) (cm^{-1})

	C_1	C_2	C_3	C_4
$\Delta E(2s, 2s)$	-60834	0	-11725	32960
$\Delta E(2s, 2p)$	-38989	-11725	-18895	34182
$\Delta E(2p, 2p)$	-41354	-18895	-25048	39962

which is responsible for the difference between the Hartree-Fock value and the semiempirical value of the Slater parameters, is different for different configurations. Therefore, the "assumption of constant slope-constant separation" would not be supported by more accurate theories and we would suggest to use the $F^2(2p, 2p)$ and the $G^1(2s, 2p)$ values obtained from the actual correlation line (corrected correlation line must be used for $F^2(2p, 2p)$ of the $1s^2 2p^4$ atoms) for the semi-empirical calculations of the molecules.

In the case of ΔE's, situations are different. Anno [20] and Anno and Sakai [18] have shown that the effect of correlation energy upon ΔE are very small. There-fore, "idealization" based on a simpler theory would be adequate in the case of ΔE's. Now, if one looks at the expressions of Table 3 of I [10], which define our ΔE's, one will find that each of the ΔE's can be expressed as a difference between appropriate valence orbital ionization potentials (VOIP's), which are defined by

$$VOIP = E_{av}^+ - E_{av} + IP, \tag{6}$$

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. Anno and Sakai [21], on the other hand, have found that the VOIP corresponding to a removal of an electron from a particular kind of orbital can be expressed as a quadratic function of the atomic number and the occupation numbers of various valence orbitals. Therefore an equation of the following form can be obtained for each kind of ΔE's:

$$\Delta E = C_1 + C_2 m + C_3 n + C_4 Z, \tag{7}$$

which constitutes a theoretical proof of the assumption of constant slope-constant separation for the ΔE correlation lines. Furthermore, Anno and Sakai [22] have fitted their VOIP functions by a least-squares method, to the empirical values of VOIP's calculated from the E_{av} values of the present work. Therefore, the numerical values of C_i's of Eq. (7) may also be calculated. They are given in Table 5. We are thus able to calculate the ideal values of various ΔE's for any of the $1s^2 2s^m 2p^n$ atoms from Eq. (7).

6. Concluding Remarks

In the present paper, the semiempirical values of $F^2(2p, 2p)$ and $G^1(2s, 2p)$ to be used for the molecular calculation involving the $1s^2 2s^m 2p^n$ atoms are given. The semiempirical values of E_{av} are also obtained. From such E_{av} values, the ΔE's of the Anno-Teruya electron-transfer reactions [10] are calculated. Effective

values of F^0's may therefore be calculated from ΔE's and the Slater-Condon parameters thus obtained [10, 15]. Perhaps, the values to be recommended for use in the molecular calculations are those obtained from Eq. (5) for $F^2(2p, 2p)$ and $G^1(2s, 2p)$ and those from Eq. (7) for ΔE's, with the numerical values of coefficients tabulated in Tables 4 and 5, respectively. The comparison with the nonempirical values are postponed to a separate article. It should be mentioned however that a systematic determination of the nonempirical values of the Slater parameters for the $1s^2 2s^m 2p^n$ atoms have been done by the present authors by a direct integration using the analytical Hartree-Fock AO's and have been published elsewhere [23]. In that paper, references to earlier works including those of nonempirical nature may be found.

Appendix

$\Delta E(2s, 2s)$ of the $1s^2 2s^2 2p^6$ Atoms

The $\Delta E(2s, 2s)$ values for the $1s^2 2s^2 2p^6$ atoms have been obtained from the correlation line of this quantity with the atomic number Z, which is drawn as follows:

i) Draw two horizontal lines with different heights in Fig. 3.

ii) Get the average of intercepts of the horizontal line by different $1s^2 2s^2 2p^n$ lines for each of the horizontal lines.

iii) Assume this value as the separation between the $1s^2 2s^2 2p^5$ and the $1s^2 2s^2 2p^6$ lines at respective heights.

It can be shown that the $1s^2 2s^2 2p^6$ line obtained is independent of the heights of the horizontal lines adopted. The $1s^2 2s^2 2p^6$ line thus obtained is also shown in Fig. 3.

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