Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen). Bis zum 10. des Monats bei der Redaktion eingehende Manuskripte können günstigenfalls am 15. des folgenden Monats veröffentlicht werden.

Sixty Years of Kossel Isoelectronic Series—Arguments Derived from Photo-electron and Atomic Spectra *

Christian K. Jørgensen **
Département de Chimie minérale, analytique et appliquée, Université de Genève

Summary

In spite of chemical shifts (in photo-electron spectra) and interatomic relaxation by condensation of gaseous samples, the difference ΔI between the ionization energies of the monatomic entities and the compounds in the oxidation state z tends to be proportional to z. The new parameter ($\Delta I/z$) seems to indicate a superposition of electrostatic interatomic effects and the screening of the inner shell by external electrons. It is suggested to call the number of electrons in a Kossel isoelectronic series *K*.

Both chemical bonding and atomic spectral lines were profoundly foreign to classical mechanical and electromagnetic theories, but there was no obvious relation between these two enigmatic areas. At the end of the last century, Rydberg pointed out the similarity between the line spectra of gaseous atoms of the alkaline metals and monatomic ions M^+ of the alkaline-earth metals later recognized to have a single electron outside a core (Atomrumpf) of closed shells, whereas the slightly more complicated spectra of helium and neutral atoms of the alkaline-earths (including Zn, Cd, Yb and Hg) can be described by triplet and singlet energy levels formed by two external electrons. When it was realized that the persistence of a given element resides in the fact that the very small nucleus carries a positive charge (Z times that of a proton), one of the best indicators of the atomic number Z was found by Moseley in 1913 from the X-ray line spectra. To a remarkably good approximation, the X-ray spectra of

---

* Received September 16, 1976

** Prof. Dr. Ch. K. Jørgensen, Section Chimie de l'Université, 30, quai E. Ansermet, CH-1211 Geneva 4 all the elements (heavier than lithium) are alkaline-like corresponding to the absence of exactly one electron in one of the inner shells. Whereas the light emission of a sodium or a rubidium atom is due to the jump of an electron from a less strongly bound orbital to a stronger bound (but outside the core) the emission of X-rays (at much higher photon energy $h\nu$) corresponds to the displacement of the vacant position from a stronger bound, inner shell to a less strongly bound orbital, or more realistically speaking, the jump of an electron in the opposite direction. Going from one element to the next $(Z+1)$, there is a regular increase of binding energy of each inner shell, but what is much more important for the chemist, *all* the elements use the same manifold of *nl*-values (1s, 2s, 2p, 3s, ...) either as inner shells or for external electrons. Further on, the *Aufbau principle* is valid that each shell is able to contain at most $(4l+2)$ electrons, that is two s, six p, ten d or fourteen f electrons with a given n (larger than the non-negative integer l). It was recognized in X-ray spectra that positive l values correspond to two slightly different binding energies of the quantum number $j = (l+\frac{1}{2})$ and $(l-\frac{1}{2})$, the latter strongest bound. In a way, there is also an Aufbau principle allowing $(2j+1)$ electrons of each j-value. This effect of spin-orbit coupling (separating the energy of the two j-values) was also known in atomic spectra, but is usually not prominent. Thus, the difference 0.1 percent in wave-numbers of the two yellow sodium lines is due to this effect on Na 3p, and it is rarely beyond a few percent of the binding energies, with exception of 6p of the radon atom, where the first ionization energy 10.75 eV corresponds to $j = \frac{3}{2}$ whereas removal of a 6p electron with $j = \frac{1}{2}$ costs 14.58 eV. It may be noted that X-ray spectra can be observed of solid or gaseous compounds or of metallic elements, whereas the atomic line spectra are only observed of highly separated, monatomic entities.

Kossel worked with X-ray spectra [1] and got in 1916 the idea [2] that chemically stable species have electron configurations with closed shells containing a definite number K = 2, 10, 18, 28, 36, 46, 48, 54, 68, 78, 80 or 86 electrons. Though this suggestion is a generalization of the observation that noble gases have higher ionization energies I than alkaline-metal atoms, it would hardly occur to an atomic spectroscopist to compare condensed matter with the Aufbau principle, whereas it is attractive to a X-ray spectroscopist recognizing the same inner shells of a given element in different surroundings. Strictly speaking, the idea of electron configurations of *nl*-shells is related to spherical symmetry [3, 4] and there was a strong tendency before 1930 to emphasize electrostatic attractions between spherically symmetric, non-overlapping cations and anions (these two conditions permit calculations assuming point-charges) as done by Van Arkel [5] and described by Rabinowitch and Thilo [6] whereas covalent bonding was disregarded. The opposite trend prevailed between 1930 and 1950, culminating in the electroneutrality principle (the assumption that the fractional atomic charges always occur in the interval between -1 and $+1$).

There is no doubt what an *isoelectronic series* of monatomic entities is. It may be noted that no gaseous anions with more than one negative charge are stable; they always dissociate spontaneously to M^- and free electrons. Hence, their I is zero in Table 1 (see page 492). Negative I values (say for oxide) obtained from Born-Fajans-Haber expressions for heats of formation of crystalline salts from gaseous ions, or from Hartree-Fock calculations (constrained by the condition of a definite closed-shell configuration) are somewhat artificial compared with observed I values. Though many elements form stable M^- they are not included in the tables by Charlotte Moore [7] because they do not generally present sharp excited states, but their I have attracted recent attention [8, 9]. In a few isoelectronic series of monatomic entities, the configuration of the groundstate may change as a function of the ionic charge $+z$. Thus, for K = 68, the neutral erbium atom has a groundstate belonging to [Xe] $4f^{12}6s^2$, Tm^+ belonging to [Xe] $4f^{13}6s$ whereas Yb^{+2}, Lu^{+3}, ... have the unique closed-shell state [Xe] $4f^{14}$. A more subtle case [10, 11] is the series K = 67 where the groundstate of the neutral holmium atom belongs to [Xe] $4f^{11}6s^2$, of Er^+ [Xe] $4f^{12}6s$ and of Tm^{+2}, Yb^{+3}, Lu^{+4}, Hf^{+5}, Ta^{+6} and W^{+7} the lowest of the two levels of [Xe] $4f^{13}$. However, just before Re^{+8} a crossing of the 4f and 5p energies takes place, with the result that the groundstate of the latter ion belongs to $5p^5 4f^{14}$ disregarding the other (filled) shells.

The *oxidation state* of a chemical species [3] is connected with a preponderant electron configuration and is frequently, but not always, defined. The isoelectronic series introduced by Kossel in 1916 are based on K being the difference between Z and the oxidation state (in the following written z) and do not demand full electrovalent bonding with fractional atomic charges as high as z. The transition groups present many isoelectronic series, where K does not correspond to closed shells. Thus, all the K between 19 and 27 represent $(K-18)$ electrons in the partly filled 3d shell, K between 37 and 45 a partly filled 4d shell, K between 55 and 67 the 4f shell of the lanthanides, K from 69 to 76 the 5d shell, and it is now known that K between 87 and 99 correspond to a partly filled 5f shell. Nevertheless, it is striking how far longer are the chemical isoelectronic series with K representing closed shells. It has been discussed [12, 13] that K = 10 has twelve members from C(−IV) to Cl(VII), K = 28 eleven members from Mn(−III) to Br(VII), K = 46 eleven members from Ru(−II) to Xe(VIII) and K = 68 seven members from Yb(II) to Os(VIII). It must be added in all fairness that in many cases, the closed-shell K do not correspond to the most stable nor the most frequent oxidation state of a given element. Thus, neither Mn(−III) nor Mn(VII) is the most stable z of manganese, neither Ru(−II) nor Ru(VIII) of ruthenium; or Yb(II) of ytterbium, however much the overwhelming majority of lutetium, hafnium and tantalum non-metallic compounds belong to the Kossel series *K* = 68 together with W(VI), Re(VII) and Os(VIII).

The one-shot ionization energies I of inner shells determined from X-ray spectra [14, 15] are not particularly precise for penultimate orbitals, and often not known at all. This is a specific point where the study [11, 13] of *photo-electron spectra* can be of great help. It was shown by Coster [16] in 1923 that the change (dI/dZ) of I of a given shell from one element to the next can vary quite a lot. This is particularly true in the d transition groups [17] where (dI/dZ) does not increase monotonically with Z, but sharply decreases in the beginning, and even more so [18] in the lanthanides. Recently, a revised table [19] of ionization energies I_{z+1} of gaseous M^{+z} has been compiled. Table 1 compares this value in several Kossel isoelectronic series with the range of one-shot I(*nl*) (the lowest of the two values if spin-orbit coupling is perceptible) of solid and gaseous compounds. Most of the non-metallic solids were measured [20] on a Varian IEE-15 photo-electron spectrometer, and the I values corrected for charging effects, as previously discussed [21]. The gaseous compounds do not present this problem, but not all oxidation states present suitable volatile species. A large number of such molecules were discussed by Jolly and Perry [22]. In the case of other solid or gaseous compounds, Table 1 gives the literature references. On the whole, the gaseous mole-

Table 1: The ionization energies (in eV) of the *nl*-shell in gaseous monatomic entities [19], solid non-metallic compounds [20] and gaseous molecules [22] in isoelectronic series with *K* electrons, and the difference ($\Delta I/z$) which has been divided with the oxidation state. Other literature references (not already compiled [28]) are given as right-hand superscripts

K		*nl*	I_{z+1}	non-metallic solids	gaseous molecules	($\Delta I/z$)
2	Li(I)	1s	75.64	60.7–60	–	15.3±0.4
2	Be(II)	1s	153.89	121–118.5	–	17.0±0.6
2	B(III)	1s	259.37	201–192	202.8–193	20.8±1.7
2	C(IV)	1s	392.08	298–288	301.8–289.7	24±1.5
10	F(−I)	2p	3.40	14–11.5	16.5–15	10±2
10	Ne	2p	21.57	–	–	–
10	Na(I)	2p	47.29	36–35	–	11.8±0.5
10	Mg(II)	2p	80.14	56–54	–	12.6±0.5
10	Al(III)	2p	119.99	82–79	–	13.1±0.5
10	Si(IV)	2p	166.77	109.5–107.5	111.8–105.9	14.8±0.7
10	P(V)	2p	220.43	143.6–138.5	145.7–140	15.9±0.7
10	S(VI)	2p	280.93	175–174	180.4–176.5	17.0±0.5
10	Cl(VII)	2p	348.28	215–212.5	216.1	19.2±0.3
18	Cl(−I)	3p	3.61	10–9	12.7–11	7±2
18	Ar	3p	15.76	–	–	–
18	K(I)	3p	31.62	23–21.4	–	9.6±0.8
18	Ca(II)	3p	50.91	30.6–30	–	10.2±0.2
18	Sc(III)	3p	73.47	39–38	–	11.7±0.2
18	Ti(IV)	3p	99.22	44–42	–	14.0±0.5
18	V(V)	3p	128.12	47–44	–	16.5±0.3
18	Cr(VI)	3p	161.1	54--52	–	18.0±0.3
18	Mn(VII)	3p	196.46	61–60	–	19.4
19	Ti(III)	3d	43.27	–	7.9	11.8
19	V(IV)	3d	65.28	–	9.4	14.0
24	Mn(I)	3d	(13.8)	–	10.5–9	4
24	Fe(II)	3d	30.65	8–7	(6.9)	11.7
24	Co(III)	3d	51.3	10–8	10–8	14.1
26	Ni(II)	3d	35.17	9.3–7.7	(6.5)	13.6
27	Cu(II)	3d	36.83	11–10	–	13.2±0.3
28	Ni(0)	3d	(5.8)	–	9.6–8.9	–
28	Cu(I)	3d	20.29	8.9	–	11.4
28	Zn(II)	3d	39.72	17–15	19.1–17.0	11.5±1
28	Ga(III)	3d	64	26.8–25.6	–	12.5±0.5
28	Ge(IV)	3d	93.5	39–37.5	–	13.8±0.2
28	As(V)	3d	127.6	51–50.5	–	15.5±0.1
28	Se(VI)	3d	155.4	66–65	–	16.5
36	Se(−II)	4p	0	7	–	–
36	Br(−I)	4p	3.36	9–8.5	11.7–10	6.5±1.5
36	Kr	4p	14.00	–	–	–
36	Rb(I)	4p	27.28	19–18.5	–	8.5±0.3
36	Sr(II)	4p	41.64^{36}	25–24.5	–	8.5±0.3
36	Y(III)	4p	61.8	32–31	–	10.1±0.2
36	Zr(IV)	4p	81.5	39–36	–	11.0±0.4
36	Nb(V)	4p	102.6	43–41	–	12.1±0.2
36	Mo(VI)	4p	126.8	47–45	–	13.5±0.2
44	Rh(I)	4d	18.08	–	9.7	8.4
44	Pd(II)	4d	32.93	10.2–9.7	–	11.0±0.3
46	Pd	4d	8.34	–	–	–
46	Ag(I)	4d	21.49	10.5–10	–	11.2±0.3
46	Cd(II)	4d	37.48	17.4–16.8	19.6–17.3	9.9±0.7
46	In(III)	4d	54	24.3–23	–	10.0±0.2
46	Sn(IV)	4d	72.28	33–31	$34.5–30^{37}$	10.0±1
46	Sb(V)	4d	108	42.2–40	–	13.4±0.3
46	Te(VI)	4d	137	52–48	–	14.5±0.3
48	In(I)	5s	18.87	–	$9.8–8.8^{43}$	10.5
48	Sn(II)	5s	30.50	–	$10.3–9.8^{44}$	10.2
54	Sb(−III)	5p	0	5	–	–
54	Te(−II)	5p	0	6	–	–
54	I(−I)	5p	3.06	8.5–8	10.4–8	5.8±1
54	Xe	5p	12.13	–	–	–
54	Cs(I)	5p	23.17^{38}	16–15	$(18.3)^{45}$	8.3±0.5
54	Ba(II)	5p	35.79^{38}	19.5–19	–	8.2±0.2
54	La(III)	5p	45.95^{38}	25–24	–	7.1±0.2
61	Eu(II)	4f	24.70^{39}	7–5	–	9.3±0.5
61	Gd(III)	4f	44.01^{39}	15.5–12	–	10.1±0.6
61	Tb(IV)	4f	66.46^{40}	24.7	–	10.4
62	Tb(III)	4f	39.37^{41}	9.0–6	–	10.6±0.5
63	Dy(III)	4f	41.47^{39}	11–8	–	10.7±0.5
65	Er(III)	4f	42.65^{39}	12–9	–	10.7±0.5
66	Tm(III)	4f	42.69^{39}	12–8.5	–	10.8±0.6
67	Tm(II)	4f	23.68^{39}	4	–	10
67	Yb(III)	4f	43.74^{39}	14.2–12	–	10.3±0.4
68	Yb(II)	4f	25.03^{39}	6	–	9.5
68	Lu(III)	4f	45.19^{39}	15.3–12	–	10.5±0.5
68	Hf(IV)	4f	68.36^{40}	23.7–22	–	11.3±0.4
68	Ta(V)	4f	97.34^{42}	34–31	–	13.0±0.3
68	W(VI)	4f	122.02^{10}	42–40.7	46.7	13.1±0.5
78	Au(I)	5d	20.5	10.6	–	10
78	Hg(II)	5d	34.2	14.3–14	16.7–15.0	9.5±1
78	Pb(IV)	5d	68.8	25–24.4	–	11.0
80	Hg	6s	10.44	–	–	–
80	Tl(I)	6s	20.43	–	10.8–9.9	10.0±0.5
80	Pb(II)	6s	31.94	$16–15^{46}$	10.1	10

cules tend to show higher I than non-metallic solids. This is mainly due to interatomic relaxation effects [23] as also known from the condensation of atoms to metallic mercury [24] and the implantation of xenon atoms [25] in metallic copper, silver and gold, and from the chemical shifts [26] of Auger signals compared with I values. The halides isoelectronic with the noble gases present the special problem that the gaseous compounds [27] usually produce several distinct signals due to different M.0. [11,28] and the lowest (vertical) I has been selected. Hence, the average I(F2p) or I(Cl3p) is slightly higher (1 to 2 eV) than given in Table 1. With exception of indium (I) and thallium(I) halides, typical gaseous ion-pairs have not been included.

It has not previously been emphasized that the huge difference ΔI between I_{z+1} of the gaseous ion and I measured by photo-electron spectra of compounds having the same oxidation state z actually, to the first approximation, is proportional to z. Hence, the last column of Table 1 gives the quantity (ΔI/z). Though the chemical variation of I frequently has the same order of magnitude 5 eV [20] as the dissociation energies of the strongest single bonds (though it is well-known [29] that the variation of the sum of one-shot I-values hardly makes any contribution to the total energy of the system) it is completely swamped by the much larger ΔI. At this point, the lowest series (K = 2) is somewhat atypical, and it would have no meaning to consider nitrogen (V). The variation of I = 417.0 eV for gaseous NOF_3 and 404.7 eV for $N(CH_3)_3$ [22] is too small to give significance to (ΔI/5) = 28 eV one would obtain by comparing I_6 = 552.1 eV of N^{+5} with I = 412.5 to 412 eV for solid nitrates [20]. Table 1 gives the impression that there is a strong difference between beryllium(II) and boron (III) compounds, but this may be due to the fact that photo-electron spectra of organo-beryllium compounds have not been reported, whereas BF_3 and BF_4^- have considerably higher I than $B(CH_3)_3$ and $B(C_6H_5)_4^-$.

There is an obvious tendency for (ΔI/z) to increase for decreasing atomic radii. For six of the closed-shell isoelectronic series, it is a fairly good approximation to write the linear expressions for this quantity (in eV):

$$\begin{array}{l} K = 2: 11.0 + 3.3z \\ K = 10: 10.7 + 1.0z \\ K = 18: 7.5 + 1.5z \\ K = 28: 10.0 + 1.0z \\ K = 36: 7.8 + 0.8z \\ K = 68: 7.5 + 1.0z \end{array} \quad (1)$$

whereas the series K = 46 shows a shallow minimum between cadmium(II) and tin(IV). Though it might be argued that I_{z+1} of the corresponding gaseous ions are not known with great precision in this series, there is little doubt that the high (ΔI/z) = 11.2 eV for silver(I) is an example of a more general tendency for polarizable ions to show high values, as seen also from the equal value for rubidium(I) and strontium(II), or the frankly decreasing value from barium(II) to lanthanum(III), or the roughly invariant 10 eV in the many-electron series K = 78 and 80.

Transition-group compounds tend to have (ΔI/z) slightly higher than obtained by linear interpolation between pre- and post-transitional elements with the same oxidation state. The values 13.6 eV for nickel(II) compared with 11.5 eV for zinc(II), or 14.1 eV for cobalt(III) compared with 12.5 eV for gallium(III) are typical in this aspect, also discussed previously [17] in connection with certain difficulties for the concept of "ligand field stabilization". It may be noted that terbium(III) to thulium(III) have marginally higher (ΔI/3) than obtained by interpolation between $4f^7$ gadolinium(III) and $4f^{14}$ lutetium(III). There is a long tradition in inorganic chemistry to compare the variation, say of I_2 from 15.64 eV for Mn^+ to 20.29 eV for Cu^+ with the tendency toward covalent bonding in complexes (with the same ligands) from manganese(II) to copper(II) and in particular the regular variation of formation constants first pointed out by Irving and Williams. There has, obviously, been less work on correlation between I_3 and the M(II) chemistry.

The I_2 = 13.8 eV for Mn^+ and I_1 = 5.8 eV for Ni^0 given in parentheses in Table 1 refer to the ionization of the electron configurations $3d^6$ and $3d^{10}$ though they do not contain the groundstate of such gaseous species. The organometallic compounds having M–C bonds have I values, unusually high for z = 0 but rather low for z = +2. This is the reason why I for volatile iron(II) and nickel(II) cyclopentadienides are atypical and given in parentheses in Table 1.

It should be emphasized that the regularities illustrated here cannot be construed to mean a full electrovalent situation, since neutral atoms would provide roughly the same ΔI on a percentage scale. On the other hand, it is worthwhile to note that ΔI is a difference between two quantities *derived from measurements* of atomic and photo-electron spectra, respectively. Though there is a certain analogy between the hydration energy of a given gaseous ion [30] and the quantity $\varkappa z^2$ (where the parameter $\varkappa$ is 5.3 eV in the 3d group and 4.3 eV in the 4f group [31]) and the Madelung potential [3,6] varying in the alkaline halides from 12.5 eV in LiF to 6.4 eV in CsI, there is no obvious way to predict ΔI from theory. Whereas the (adiabatic) chemical ionization energy of a moderately to strongly reducing species (defined as the sum of 4.5 eV and the standard oxidation potential E^0) can be compared with the vertical (invariant internuclear distances) I of the loosest bound orbitals [11,28] there is no higher limit to I of a closed shell not loosing electronic density under any chemical conditions. Thus, it can be safely concluded from the photo-electron spectra that E^0 for caesium(I) aqua ions is around + 9V, for calcium(II) aqua ions + 23V but for lithium(I) higher than + 50V. This variation illustrates how exceedingly narrow, some 6V, the E^0 scale is between metallic sodium and fluoride. An alternative to the electrostatic picture of the quantity $(\Delta I/z)$ is that z is the number of loosely bound valence electrons in the *neutral* atom, rather than the oxidation state. Since the influence of external electrons on an inner shell is well-represented [32] by an electrostatic potential proportional (14.4 eV/Å) to the average reciprocal radius of the external electron, it can be argued that the I(Cl2p) = 348 eV of gaseous Cl^{+7} would be decreased some eight times 18.2 eV (0.67 hartree) to 201 eV in a gaseous chloride anion, actually very close to the photo-electron results for chlorides, whereas 219 eV would seem rather high for the neutral chlorine atom (the Cl_2 molecule [22] shows I = 207.64 eV).

Certain properties of inner shells are modified strongly by the presence of external electrons, such as ΔI indicates. On the other hand, the spin-orbit coupling (expressed by the Landé parameter) is surprisingly invariant. The $2p_{1/2}$ and $2p_{3/2}$ photo-electron signals of elemental sulphur are separated by 1.15 eV [33] and a large number of gaseous compounds measured in Uppsala by 1.2 eV to be compared with 1.255 eV in S^{+7} [7]. Hence, the spin-orbit coupling does not change significantly before the 2p shell contains less than five electrons. The separation [7] 0.901 eV in P^{+6} and 1.20 eV in P^{+10} shows a certain influence in the latter case, but the Sommerfeld formula for the one-electron system S^{+15} gives 2.97 eV. The series limits of Fe^{+16} 12.66 eV, Co^{+17} 15.03 eV, Zn^{+20} [34] 24.40 eV and Ge^{+22} [34] 32.66 eV are not as precise as a direct determination of the energy difference in the $2p^5$ systems Fe^{+17}, ... would be, but they are remarkably close to the values [20] derived from 2p signals, 12.9 eV for diamagnetic iron(II), 15.0 eV for cobalt(III), 23.15 eV for zinc(II) and 31.2 eV for germanium(IV) compounds. Two opposite effects may operate on the $(K = 24)$ d^6 isoelectronic series, where the distance between the two signals may be increased by the same contributions of differing interelectronic repulsion which increase the separation in nickel(II) compounds from 17.2 eV in diamagnetic to about 17.8 eV in paramagnetic cases. It must be remembered that Zn^{+20} lacks eighteen (3p and 3d) electrons, compared with Zn^{+2}. Already the 2p spin-orbit separation 2.91 eV in K^{+10} [7] is perceptibly larger than 2.65 eV [20] in potassium salts, like 3.72 eV in Ca^{+11} compared with 3.5 eV found for calcium(II). These examples of inner-shell behaviour represent an extreme extrapolation of the invariance of Landé parameters for changing occupation of outer orbitals noted by Dunn [35].

The data presented here illustrate several unexpected relations between photo-electron spectra and chemical stability of isoelectronic series. The inner shells are by no means indifferent to influences of neighbour atoms (as far goes ionization energies I) though it cannot be concluded that they contribute specifically to the chemical bonding when I is above a limit [11] which seems to vary from 50 to 15 eV according to the localized character of the shell to be ionized. The arguments of Kossel, originally derived from distinctly inner shells, have gained much support from the photo-electron spectra due to penultimate orbitals.

Acknowledgements

The writer is grateful to Dr. Hervé Berthou for six years of intensive experimental effort. The Swiss National Science Foundation provided the grant (2323-70) allowing the purchase of the photo-electron spectrometer.

References

1 *W. Kossel:* Valenzkräfte und Röntgenspektren, Julius Springer, Berlin 1921.
2 *W. Kossel:* Ann. Physik *49* (1916) 229.
3 *C. K. Jørgensen:* Oxidation Numbers and Oxidation States, Springer-Verlag, Berlin 1969.
4 *C. K. Jørgensen:* Modern Aspects of Ligand Field Theory, North-Holland Publishing Co., Amsterdam 1971.
5 *C. J. M. Rooymans* and *A. Rabenau* (editors): Crystal Structure and Chemical Bonding in Inorganic Chemistry, North-Holland Publishing Co., Amsterdam 1975.
6 *E. Rabinowitch* and *E. Thilo:* Periodisches System, Geschichte und Theorie, Ferdinand Enke, Stuttgart 1930.
7 *C. E. Moore:* Atomic Energy Levels, Nat. Bur. Stand. Circ. 467, Vol. 1, 2 and 3. Washington D. C. 1949, 1952 and 1958.
8 *R. S. Berry:* Chem. Rev. *69* (1969) 533.
9 *H. S. W. Massey:* Endeavour *35* (1976) 58.
10 *J. Sugar* and *V. Kaufman:* Phys. Rev. *A 12* (1975) 994.
11 *C. K. Jørgensen:* Structure and Bonding *30* (1976).
12 *C. K. Jørgensen:* Chimia *28* (1974) 605.
13 *C. K. Jørgensen:* Structure and Bonding *22* (1975) 49.
14 *Y. Cauchois:* J. Physique *13* (1952) 113 and *16* (1956) 253.
15 *J. A. Bearden* and *A. F. Burr:* Rev. Mod. Phys. *39* (1967) 125.
16 *D. Coster:* Naturwiss. *11* (1923) 567.
17 *C. K. Jørgensen:* Chimia *28* (1974) 6.
18 *C. K. Jørgensen:* Structure and Bonding *13* (1973) 199.
19 *C. E. Moore:* Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra. NSRDS-NBS 34, Washington D. C. 1970.
20 *C. K. Jørgensen* and *H. Berthou:* Mat. Fys. Medd. Dan. Vid. Selskab *38* (1972) No. 15.
21 *C. K. Jørgensen:* Chimia *27* (1973) 203.
22 *W. L. Jolly* and *W. B. Perry:* Inorg. Chem. *13* (1974) 2686.
23 *C. K. Jørgensen:* Adv. Quantum Chem. *8* (1974) 137.
24 *S. Svensson, N. Mårtensson, E. Basilier, P. Å. Malmqvist, U. Gelius* and *K. Siegbahn:* J. Electron Spectr. *9* (1976) 51.
25 *H. Citrin* and *D. R. Hamann:* Phys. Rev. *B 10* (1974) 4948.
26 *C. D. Wagner:* Discuss. Faraday Soc. *60* (1976) 291.
27 *D. W. Turner, C. Baker, A. D. Baker* and *C. R. Brundle:* Molecular Photoelectron Spectroscopy, Interscience, London 1970.
28 *C. K. Jørgensen:* Structure and Bonding *24* (1975) 1.
29 *C. K. Jørgensen:* Orbitals in Atoms and Molecules, Academic Press, London, 1962.
30 *C. K. Jørgensen:* Topics in Current Chemistry *56* (1975) 1.
31 *C. K. Jørgensen:* Chimia *23* (1969) 292.
32 *P. Politzer* and *K. C. Daiker:* Chem. Phys. Letters *20* (1973) 309.
33 *R. Reisfeld, C. K. Jørgensen, A. Bornstein* and *H. Berthou:* Chimia *30* (1976) 451.
34 *W. E. Behrling, L. Cohen, G. A. Doschek* and *U. Feldman:* J. Opt. Soc. Amer. *66* (1976) 376.
35 *T. M. Dunn:* Trans. Faraday Soc. *57* (1961) 1441.
36 *W. Persson* and *S. Valind:* Physica Scripta (Stockholm) *5* (1972) 187.

37 *S.C. Avanzino* and *W.L. Jolly:* J. Electron Spectr. *8* (1976) 15.
38 *J. Reader* and *G.L. Epstein:* J. Opt. Soc. Amer. *65* (1975) 638.
39 *J. Sugar* and *J. Reader:* J. Chem. Phys. *59* (1973) 2083.
40 *J. Sugar:* J. Opt. Soc. Amer. *65* (1975) 1366.
41 *N. Spector* and *J. Sugar:* J. Opt. Soc. Amer. *66* (1976) 436.
42 *V. Kaufman* and *J. Sugar:* J. Opt. Soc. Amer. *65* (1975) 302.
43 *J. Berkowitz* and *J.L. Dehmer:* J. Chem. Phys. *57* (1972) 3194.
44 *S. Evans* and *A.F. Orchard:* J. Electron Spectr. *6* (1975) 207.
45 *J. Berkowitz, J.L. Dehmer* and *T.E.H. Walker:* J. Chem. Phys. *59* (1973) 3645.
46 *M.G. Mason* and *L.J. Gerensen:* Chem. Phys. Letters *40* (1976) 476.