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SLATER–CONDON PARAMETERS FOR ATOMS AND IONS OF THE FIRST TRANSITION PERIOD*

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One of the most characteristic aspects of the semiempirical molecular orbital theory is the introduction of quantities estimated from the valence states of atoms or ions, instead of the employment of theoretical one-centre integrals[1–3]. These quantities take into account, at least to a certain degree, the intra-atomic electron correlation and give the actual electronegativity of atoms as a function of the orbital occupation numbers[4].

As it is well known, the valence state[5–7] can be assumed as formed by removing from an atom in a molecule in an adiabatic manner all other atoms with their electrons, without allowing any electronic rearrangement. In such a state the electrons have random spin distribution. Thus, it is possible to calculate valence state energies using spectroscopic data, when Slater–Condon parameters (SCP) are known. Therefore, since the evaluation of semiempirical integrals has to be made from the valence state energies, their values depend upon the SCP's.

The theory of atomic spectra developed by Slater[8–9] provides approximate expressions for the energy terms of atoms or ions as functions of certain coulomb and exchange integrals represented by the parameters F_k and G_k. These parameters may be evaluated empirically only if the spectrum of the atom or the ion is sufficiently investigated. The parameters values are commonly determined by a least squares' fitting of the available spectroscopic data to the theoretical equations.

Hartree[10] noticed that the SCP's are different in different configurations of the same atom and, therefore, it seems necessary that the F_k's and the G_k's have to be evaluated for each configuration. But, in this case the number of Slater expressions are not always sufficient to afford such calculations. Consequently, different configurations have to be pooled: the transition metals belong to such a case.

Hinze and Jaffe[11] (H.J.) investigated the uncertainties introduced by fitting various configurations and calculated extensive SCP's for the first transition series metals. They and other authors[12] concluded that the approximations in the Slater theory bear an accuracy of the same order of magnitude as the further approximation introduced by the pooling of data from several configurations. Nevertheless,

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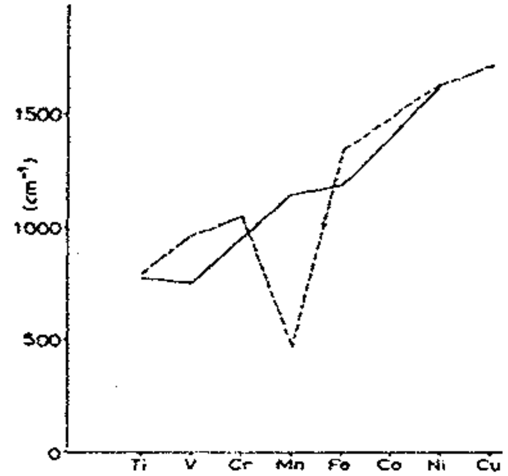


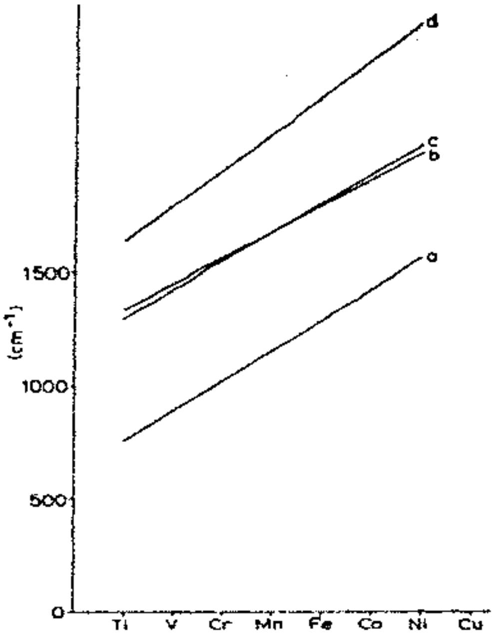


Fig. 1. Hinze-Jaffé F_2(dd) parameter (—— $q = 0$; --- $q = +1$) as a function of atomic number.

Fig. 2. F_2(dd) parameter theoretically evaluated as a function of atomic number (a, Slater AO; b, Watson AO; c, Richardson AO; d, Clementi AO[14]).

they obtained SCP values varying unreasonably with atomic number (Fig. 1).

Therefore, in addition to evaluating the SCP's on the basis of the energies of different configurations it seems important to fulfill certain theoretical conditions in order to obtain a more consistent set of values.

Thus, we have re-evaluated the SCP's by satisfying the following conditions:

(i) First of all, H.J.[13] neglected configurational interaction which is very important, especially for transition metals. In this paper configurational interaction (CI) is minimized by pooling in the SCP evaluation only those terms for which the CI's are reasonably small.

(ii) Theoretical investigations of the value of F_2(dd)[14–15] have proven that the plot of F_2(dd) against the atomic number is a straight line (Fig. 2), whose position is determined by the assumed radial wave function, (Fig. 2). Therefore, it is reasonable to assume that the F_2(dd)'s, and also the G_1(pd)'s, depend in a linear way upon the atomic number. This condition is imposed in the present SCP determinations.

(iii) Moreover, on the basis of theoretical studies[15], the F_2(dd)/F_4(dd) ratio is usually rather close to the hydrogenic function ratio. Noting now that the F_4(dd)'s and G_3(pd)'s are small terms and, therefore, do not contribute in a determinant manner to the spectroscopic energy levels, one can assume that the $F_2(\mathrm{dd})/F_4(\mathrm{dd})$ and $G_1(\mathrm{pd})/G_3(\mathrm{pd})$ ratios are those of hydrogen-like atoms.

Slater–Condon parameters calculations

Following Slater's theory, based on the central field approximation, the energy of a spectroscopic term of an atom is given by the expression:

$$E = \sum_{i=1}^{N} I(\mathrm{n}_i\mathrm{l}_i) + \sum_{i>j}^{N} \left\{J(\mathrm{n}_i\mathrm{l}_i\mathrm{m}_{l_i}\mathrm{s}_i;\, \mathrm{n}_j\mathrm{l}_j\mathrm{m}_{l_j}\mathrm{s}_j) - K(\mathrm{n}_i\mathrm{l}_i\mathrm{m}_{l_i}\mathrm{s}_i;\, \mathrm{n}_j\mathrm{l}_j\mathrm{m}_{l_j}\mathrm{s}_j)\right\} \tag{1}$$

where N denotes the total number of electrons; n, l, m_l, s are the quantum numbers; $I(\mathrm{n}_i\mathrm{l}_i)$ the kinetic and coulomb energy of the i^{th} electron; and, J and K, respectively, the coulomb and exchange integrals between the i^{th} and j^{th} electrons. Expanding J and K integrals into spherical harmonics, expression (1) reduces to:

$$\begin{aligned} E = \sum_{i=1}^{N} I(\mathrm{n}_i\mathrm{l}_i) + \sum_{i>j}^{N} \sum_{k} \{&\mathrm{a}_k(\mathrm{l}_i\mathrm{m}_{l_i};\mathrm{l}_j\mathrm{m}_{l_j})F_k(\mathrm{n}_i\mathrm{l}_i;\, \mathrm{n}_j\mathrm{l}_j) - \\ &-\delta(\mathrm{s}_i,\, \mathrm{s}_j)\mathrm{b}_k(\mathrm{l}_i\mathrm{m}_{l_i};\, \mathrm{l}_j\mathrm{m}_{l_j})G_k(\mathrm{n}_i\mathrm{l}_i;\, \mathrm{n}_j\mathrm{l}_j)\} \end{aligned} \tag{2}$$

where a_k, b_k and δ are obtained by direct integration of the angular and spin part[16], while F_k and G_k depend upon the radial part of the J and K integrals.

Slater's procedure consists of applying expression (2), to the spectroscopic energy terms of an atom or ion. In this way a system of equations is obtained, which is linear with I, F_k and G_k. Nevertheless, it is convenient to rewrite expression (2), keeping in mind that when one applies it to the terms belonging to the same configuration, integrals with the same coefficients appear in each energy term and, therefore, do not contribute to energy differences between terms. All these integrals may be united in the $W(x)$ parameters, which then have constant values for each configuration. The modified expression is thus:

$$E_i(x) = W(x) + \sum_{k} (\mathrm{c}_{ik}F_k + \mathrm{d}_{ik}G_k) \tag{3}$$

where i denotes the i^{th} term of the x^{th} configuration.

In the present paper we use $E_i(x)$'s from Moore's tables[17], and by substitution of these quantities in eq. (3), a system of linear equations is obtained. Since the terms are split by spin–orbit coupling, we have taken as energy terms the centres of gravity of the split multiplets. An exception was made for terms belonging to the fundamental designation of configurations, whose energies were corrected due to spin–orbit coupling. Explicit expressions for $W(x)$ were given in the H.J. paper[11]. Since the magnitude of the $W(x)$'s depend upon the energy scale origin we chose the energy of the spectroscopic ground state of the atom or the ion under examination as zero energy.

Then the SCP's were calculated, for atoms and singly and doubly positive-

TABLE 1

SLATER–CONDON PARAMETERS (in cm^{-1}) FOR NEUTRAL ATOMS OF THE FIRST TRANSITION PERIOD

	Ti^{I}	V^{I}	Cr^{I}	Mn^{I}	Fe^{I}	Co^{I}	Ni^{I}	Cu^{I}
$W(d^n)$	52,600	71,470	71,020	66,190	46,410	27,040	14,170	
$W(d^{n-1}s)$	26,520	39,670	66,270	65,050	38,810	17,600	2,340	0
$W(d^{n-1}p)$	46,170	60,070	89,300	98,500	72,780	52,770	33,940	30,700
$W(d^{n-2}s^2)$	7,470	18,670	46,000	68,000	46,080	30,330	13,890	12,020
$W(d^{n-2}sp)$	30,920	46,300	76,000	103,670	97,230	(79,780)	(63,240)	(58,750)
$W(d^{n-2}p^2)$	(60,050)	(76,850)	(106,000)	(137,630)	(142,000)	(129,230)	(112,590)	(105,480)
$F_2(pp)$	(220)	(240)	(260)	(280)	(300)	(320)	(340)	(360)
$F_2(pd)$	450	500	550	550	350	500	350	480
$F_2(dd)$	765	895	1,025	1,155	1,285	1,415	1,545	1,675
$F_4(dd)$	55	64.5	74	83.5	93	102.5	112	121.5
$G_1(pd)$	350	380	410	440	470	500	530	560
$G_3(pd)$	13	14.1	15.3	16.4	17.6	18.7	19.9	21
$G_1(sp)$	2,200	2,350	2,500	2,650	2,800	(2,950)	(3,100)	(3,250)
$G_2(sd)$	1,550	1,650	1,580	1,800	1,600	1,700	1,900	(2,000)
Δ^a	1,036	612	1,320	1,682	1,399	959	930	632

[a] standard deviation (see APPENDIX).

TABLE 2

SLATER–CONDON PARAMETERS (in cm^{-1}) FOR SINGLY POSITIVE CHARGED IONS

	Ti^{II}	V^{II}	Cr^{II}	Mn^{II}	Fe^{II}	Co^{II}	Ni^{II}	Cu^{II}
$W(d^n)$	18,270	34,790	65,500	58,400	29,570	13,180	0	0
$W(d^{n-1}s)$	11,800	29,990	60,500	83,360	57,770	40,293	27,490	25,750
$W(d^{n-1}p)$	40,770	60,790	94,000	120,000	108,570	91,880	78,950	76,000
$W(d^{n-2}s^2)$	24,920	(35,190)	67,500	99,200	105,570	93,510	(90,500)	86,980
$W(d^{n-2}sp)$	59,300	82,290	(112,000)	(142,500)	(154,570)	(162,980)	(158,700)	(154,500)
$W(d^{n-2}p^2)$	(93,680)	(129,390)	(156,500)	(185,800)	(203,570)	(232,450)	(226,900)	(222,020)
$F_2(pp)$	(350)	(370)	(390)	(410)	(430)	(450)	(470)	(490)
$F_2(pd)$	500	600	600	(650)	650	700	450	550
$F_2(dd)$	875	1,005	1,135	1,265	1,395	1,525	1,655	1,785
$F_4(dd)$	63	72.5	82	91.5	101	110.5	120	129.5
$G_1(pd)$	450	480	510	540	570	600	630	660
$G_3(pd)$	16.8	17.9	19.1	20.2	21.3	22.4	23.5	24.6
$G_1(sp)$	2,400	2,550	(2,700)	(2,850)	(3,000)	(3,150)	(3,300)	(3,450)
$G_2(sd)$	2,000	2,100	2,100	1,900	1,800	2,100	2,000	2,300
Δ^a	1,560	723	1,563	1,079	1,272	993	756	906

[a] standard deviation (see APPENDIX).

charged ions of the first transition period from Ti to Cu, by a least squares method and in such a way as to satisfy the previously described conditions. Results of these calculations are reported in Tables 1, 2 and 3. It must pointed out that in certain cases evaluation of the SCP's could not be carried out on the basis of the available spectroscopic data alone, and the following criteria were used:

(i) The $G_1(sp)$, $G_2(sd)$ and $F_2(pd)$ values in parentheses in Table 1 and 2 were evaluated in such a way as to follow a regular trend.

TABLE 3

SLATER–CONDON PARAMETERS (in cm^{-1}) FOR DOUBLY POSITIVE CHARGED IONS

	Ti^{III}	V^{III}	Cr^{III}	Mn^{III}	Fe^{III}	Co^{III}	Ni^{III}	Cu^{III}
$W(d^n)$	9,260	24,060	44,940	81,100	53,150	33,470	14,860	0
$W(d^{n-1}s)$	40,960	59,390	83,370	120,400	129,250	114,450	96,240	83,170
$W(d^{n-1}p)$	80,760	100,060	128,370	168,000	180,560	183,150	164,700	151,350
$F_2(pd)$	850	950	950	850	750	850	1,100	855
$F_2(dd)$	1,055	1,175	1,295	1,415	1,535	1,655	1,775	1,895
$F_4(dd)$	76	84.7	93.4	102	110.7	119.3	128	136.6
$G_1(pd)$	550	580	610	640	670	700	730	760
$G_3(pd)$	20.5	21.6	22.7	23,8	24.9	26	27.2	28.3
$G_2(sd)$	2,400	2,600	2,350	2,050	2,100	2,400	2,200	2,500
Δ^a	1,116	467	878	1,416	1,413	1,259	888	862

[a] standard deviation (see APPENDIX).

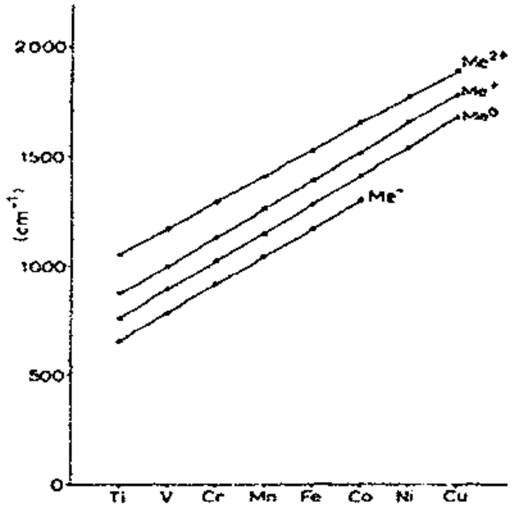
(ii) The $F_2(pp)$ values were taken from the H.J. paper[11].

(iii) The $W(d^{n-2}sp)$ for Cr^{II}, Co^{II} and Ni^{II}, and $W(d^{n-2}s^2)$ for V^{II} and Ni^{II} were evaluated by following the trend.

(iv) The $W(d^{n-2}p^2)$ for all the atoms and ions, except Ti, V and Mn, were evaluated by using the H.J. relation:

$$W(d^{n-2}p^2) \approx 2W(d^{n-2}sp) - W(d^{n-2}s^2)$$

(v) All the other $W(x)$ values in parentheses in Table 1 and 2 were calculated from the spectroscopic data on the basis of the F_k and G_k values, evaluated according to the assumed criteria (i) and (ii).



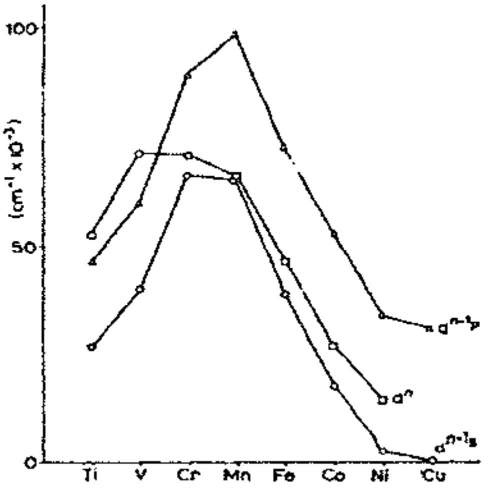


Fig. 3. $F_2(dd)$, evaluated in this work, as a function of atomic number.

Fig. 4. A plot of neutral atom $W(d^n)$, $W(d^{n-1}s)$ and $W(d^{n-1}p)$ values evaluated in this work, against atomic number.

In Figs. 3 and 4 some of the parameters obtained are plotted against the atomic numbers of the metals: F_2(dd) varies linearly, as we imposed, and the $W(x)$'s vary according to a regular trend, which is similar to that obtained by other authors for the metals of the second transition period[12]. A comparison of the parameters with the theoretical estimates of Brown[18] and Watson[19] shows that the empirical parameters are somewhat lower.

In order to test the validity of the parameters' evaluation, a comparison between the present work and H.J. data was made. For this, manganese, which is the middle point of the first transition period was chosen. In Table 4, considering the standard deviations, one can note a good agreement in reproducing spectroscopic energy terms of Mn^I by both methods, while the SCP's of the present paper reproduce the energy terms of Mn^{II} much better.

TABLE 4

COMPARISON BETWEEN THE PARAMETERS OF HINZE-JAFFÉ AND THOSE OF THE PRESENT WORK IN REPRODUCING SPECTROSCOPIC LEVELS FOR Mn° AND Mn^+.

All values are in cm^{-1}; multiplet terms are reduced to their centre of gravity.

Config.	*Desig.*	*Observed*	*H.J.*	*Present work*	*Config.*	*Desig.*	*Observed*	*H.J.*	*Present work*
d^5s^2	^6S	0	738	1,272	d^5s	^7S	0	5,509	762
	^4G	25,280	24,273	23,260		^5S	9,473	12,019	10,262
	^4P	27,244	29,095	26,892		^5G	27,576	28,361	26,750
	^4D	30,403	28,865	28,422		^5P	29,920	38,311	30,732
d^6s	^6D	17,311^a	17,057	17,813		^3G	34,892	32,267	32,450
	^4D	23,596	21,825	25,013		^3P	36,355	42,217	36,432
	^4H	34,289	34,453	34,253		^5F	43,258	35,461	42,845
	^4G	37,644	37,733	37,941	d^6	^5D	14,601^a	17,346	14,541
	^2H	38,064	36,837	37,853		^3H	30,666	35,346	30,581
d^6p	^6D	41,946^a	42,454	41,571		^3G	33,225	34,396	34,619
	^6F	43,530	43,322	44,871		^3D	37,837	33,066	40,271
	^6P	45,136	43,322	44,871	d^5p	^7P	38,605^a	34,473	39,381
	^4H	58,443	59,750	59,757		^5G	64,498	56,167	63,711
	^4I	58,853	58,819	58,599		^5H	65,662	56,563	64,378
d^7	^4F	45,061^a	43,467	42,851		^3H	67,833	63,887	67,689
	^4P	51,715	53,307	53,913		^3G	70,530	73,703	70,687
d^5p^2	^6P	57,256^a	60,007	57,256	d^4s^2	^5D	55,381^a	55,403	55,341
d^5sp	^8P	18,369^a	18,706	19,170	d^4sp	^7P	83,414^a	71,822	83,271
	^4I	61,217	57,662	56,223					
Δ^b			1,540	1,682	Δ^b			5,926	1,079

[a] The values are spin-orbit coupling free. [b] Standard deviation (see APPENDIX).

Slater–Condon parameters for negative ions

Since no spectra of negative ions are available, SCP's for negative ions cannot be determined. Nevertheless, parameters for negative ions may be determined by extrapolation, considering isoelectronic series, once one has calculated the SCP's for neutral and positively-charged atoms.

H.J., on the basis of their calculation[13], evaluated the negative ions' parameters by a linear extrapolation of the corresponding parameters of atoms and ions in an isoelectronic sequence[20]. By an examination of the H.J. results, one can note that many parameters have absurd values; *i.e.*, the F_k's are often negative, while these quantities must be positive by definition. This fact depends upon both the linear extrapolation approximation and the inaccuracy of the parameters; on the other hand, having only two points for the isoelectronic sequence, these authors are forced to adopt a linear extrapolation.

In the present paper, by introducing the SCP's for the doubly charged positive ions, a third point of the isoelectronic sequence was obtained. Using this, the SCP's for negative ions were determined in the following way:

(i) The F_k and G_k parameters, which depend in a linear manner upon the atomic and oxidation numbers[9,15], were extrapolated linearly in an isoelectronic sequence. The F_2(dd) parameters are reported in Fig. 3.

(ii) The $W(x)$ parameters, which include monoelectronic integrals, kinetics and coulombics $[I(n_i l_i)]$, and some bielectronic integrals (J and K), were consistently extrapolated parabolically in an isoelectronic sequence.

This is possible only for the d^n, $d^{n-1}s$ and $d^{n-1}p$ configurations from Ti to Fe. Moreover, the $W(x)$ extrapolations must take into account the fact that the $W(x)$'s are the greatest contributors to promotion energy from the ground state to

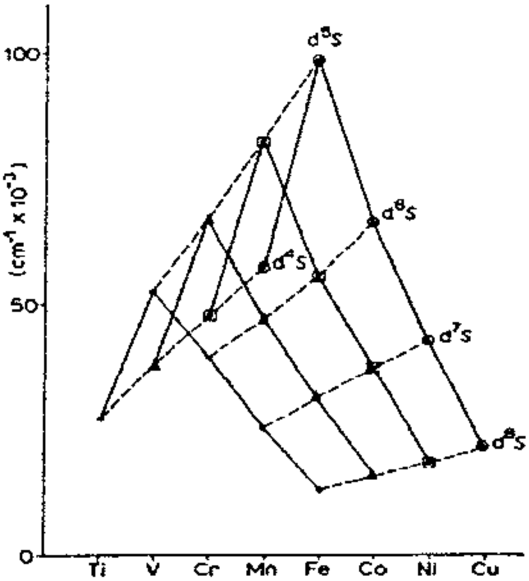


Fig. 5. Evaluation by extrapolation along isoelectronic sequences (dotted lines) of the $W(d^{n-1}s)$ parameter of negative ions (○, $q = +2$; □, $q = +1$; △, $q = 0$; ●, $q = -1$)].

the x^{th} configuration terms and that the ground state configuration for atoms and ions, which constitutes the isoelectronic sequence, does not remain constant[17]. Then, it is necessary to assume as reference state a configuration which appears along the entire isoelectronic sequence and to which the $W(x)$'s have to be referred. In our case the reference state chosen is the ground term of the $d^{n-2}s$ configuration. The choice of the $d^{n-1}s$ configuration, instead of the $d^{n-1}s^2$ one, which, generally speaking, should be the ground state of the negative ions, is related to the impossibility of determining the $W(d^{n-2}s^2)$'s for doubly positive charged ions. Thus, no parabolic extrapolation would be possible.

In Fig. 5 the extrapolations of $W(d^{n-1}s)$ for the negative ions Ti^-, V^-, Cr^-, Mn^- and Fe^- are reported.

All the SCP's calculated for negative ions are reported in Table 5; values in parentheses which cannot be extrapolated from an isoelectronic sequence, were evaluated following the general trend.

TABLE 5

SLATER–CONDON PARAMETERS (in cm^{-1}) FOR SINGLY NEGATIVE CHARGED IONS

	Ti^{-1}	V^{-1}	Cr^{-1}	Mn^{-1}	Fe^{-1}	Co^{-1}	Ni^{-1}	Cu^{-1}
$W(d^n)$	67,850	65,590	45,850	48,280	39,680	—	—	—
$W(d^{n-1}s)$	26,750	52,560	39,030	24,920	12,500	—	—	—
$W(d^{n-1}p)$	35,050	63,040	53,610	40,910	31,480	—	—	—
$F_2(pp)$	90	110	130	150	170	190	(210)	(230)
$F_2(pd)$	400	450	450	350	550	150	(300)	(400)
$F_2(dd)$	655	785	915	1,045	1,175	1,305	(1,415)	(1,565)
$F_4(dd)$	47.5	56.5	66	75	85	94	(103.5)	(113)
$G_1(pd)$	250	280	310	340	370	400	(430)	(460)
$G_3(pd)$	9.2	10.3	11.5	12.6	13.7	14.8	(15.9)	(17)
$G_1(sp)$	2,000	2,150	2,300	2,450	2,600	2,750	(2,900)	(3,050)
$G_2(sd)$	1,200	1,260	1,800	1,100	1,400	1,500	(1,700)	(1,800)

In this manner the $W(x)$'s obtained, unlike those calculated by H.J. which have no "absolute" meaning, are parameters which give the promotion energies with respect to the lowest state of the $d^{n-1}s$ configuration.

Conclusion

From the above discussion, we conclude that the approximations introduced in the evaluation of Slater–Condon parameters, although constituting a restriction, afford a set of parameter values which reproduce at least as well as the parameters in the literature[21–25] the spectroscopic energy terms. Moreover, the SCP's of the present paper have the advantage of a more regular trend, which is consistent with the properties derived from the electronic structure of the atoms and ions of the first transition period. In addition, these parameters are very useful for valence state energy calculations and for a measure of the electronegativity.

APPENDIX

The standard deviation Δ is defined as

$$\left[\frac{\sum_i d_i^2}{(n-1)}\right]^{\frac{1}{2}}$$

where d_i indicates the individual deviation between the ith energy term calculated by the SCP's and the experimental i^{th} one, and n indicates the number of calculated energy terms.

For this calculation we made use of the following configurations for the atoms and ions:

Ti$^{\text{I}}$ $d^{n-2}s^2$: $^3F, {}^1D, {}^3P, {}^1G$
$d^{n-1}s$: $^5F, {}^3F, {}^5P, {}^3G, {}^3P, {}^1P, {}^1H, {}^1F$
d^n : $^5D, {}^3G$; $d^{n-1}p$: $^5G, {}^5F, {}^3I$; $d^{n-2}p^2$: ^5G
$d^{n-2}sp$: $^5G, {}^5F, {}^5D, {}^3G$

Ti$^{\text{II}}$ $d^{n-1}s$: $^4F, {}^2F, {}^2D, {}^2G$; d^n: $^2G, {}^4P, {}^4F, {}^2H$; $d^{n-2}p^2$: ^2D
$d^{n-1}p$: $^4G, {}^4F, {}^2H$; $d^{n-2}sp$: $^4D, {}^4P$

Ti$^{\text{III}}$ d^n : $^3F, {}^1D, {}^3P, {}^1G$; $d^{n-1}s$: $^3D, {}^1D$
$d^{n-1}p$: $^1D, {}^3D, {}^1F, {}^1P, {}^3F, {}^3P$

V$^{\text{I}}$ $d^{n-2}s^2$: $^4F, {}^2G, {}^4P, {}^2H, {}^2P$; $d^{n-1}s$: $^6D, {}^4G, {}^4H, {}^2H, {}^2G$
d^n : $^6S, {}^4F$; $d^{n-1}p$: $^6P, {}^6F, {}^6D, {}^4I$; $d^{n-2}p^2$: ^6G
$d^{n-2}sp$: $^6G, {}^6F$

V$^{\text{II}}$ $d^{n-1}s$: $^5F, {}^5P, {}^3G, {}^3H, {}^1F$
d^n : $^5D, {}^3G, {}^3H, {}^3D, {}^1F, {}^1I$
$d^{n-2}sp$: $^5F, {}^5G, {}^5D$

V$^{\text{III}}$ $d^{n-1}s$: $^4F, {}^2F$; d^n: $^4F, {}^4P, {}^2G, {}^2H$
$d^{n-1}p$: $^2F, {}^4F, {}^4G, {}^2G$

Cr$^{\text{I}}$ $d^{n-2}s^2$: $^5D, {}^3H, {}^3G, {}^3D, {}^3I$
$d^{n-1}s$: $^7S, {}^5S, {}^5G, {}^3G, {}^5P, {}^5D, {}^3P, {}^3I, {}^5F$
d^n : ^5D; $d^{n-1}p$: $^7P, {}^5H$
$d^{n-2}sp$: $^7D, {}^7P, {}^7F, {}^5I$

Cr$^{\text{II}}$ $d^{n-2}s^2$: $^2G, {}^2P, {}^4P$; $d^{n-1}s$: $^6D, {}^4H, {}^2I, {}^2H, {}^4G$
d^n : $^6S, {}^4G, {}^4P, {}^4F, {}^4D, {}^2I, {}^2H, {}^2S$
$d^{n-1}p$: $^6F, {}^6P, {}^6D, {}^4I$

Cr$^{\text{III}}$ $d^{n-1}s$: $^5F, {}^3G, {}^5P, {}^3H, {}^1G$
d^n : $^5D, {}^3D, {}^3G, {}^3H, {}^1F$
$d^{n-1}p$: $^5G, {}^5F, {}^3I$

Mn$^{\mathrm{I}}$ $d^{n-2}s^2$: ^6S, ^4G, ^4P, ^4D; $d^{n-1}s$: ^6D, ^4D, ^2H, ^4H, ^4G
d^n : ^4P, ^4F; $d^{n-1}p$: ^6D, ^6P, ^6F, ^4H, ^4I
$d^{n-2}p^2$: ^8P; $d^{n-2}sp$: ^8P, ^4I

Mn$^{\mathrm{II}}$ $d^{n-2}s^2$: ^5D; $d^{n-1}s$: ^7S, ^5S, ^5G, ^5P, ^5D, ^3G, ^3P, ^3D, ^5F
d^n : ^5D, ^3H, ^3G, ^3D; $d^{n-1}p$: ^7P, ^5G, ^5H, ^3H, ^3G
$d^{n-2}sp$: ^7P

Mn$^{\mathrm{III}}$ $d^{n-1}s$: ^4D, ^6D; d^n: ^6S, ^4G, ^4P, ^4D, ^4F
$d^{n-1}p$: ^6F, ^4P, ^6D, ^6P, ^4D, ^4F

Fe$^{\mathrm{I}}$ $d^{n-2}s^2$: ^5D, ^3H, ^3G, ^1I, ^3D
$d^{n-1}s$: ^5F, ^5P, ^3G, ^1G, ^3H, ^1H
d^n : ^3F; $d^{n-1}p$: ^3I, ^1I, ^5F, ^5G
$d^{n-2}sp$: ^7D, ^7F, ^7P

Fe$^{\mathrm{II}}$ $d^{n-2}s^2$: ^6S, ^4D; $d^{n-1}s$: ^6D, ^4H, ^2H, ^4G, ^2I
d^n : ^4F, ^4P, ^2G, ^2P, ^2F, ^2H
$d^{n-1}p$: ^6D, ^6P, ^4I, ^6F
$d^{n-2}sp$: ^8P, ^4F, ^4G

Fe$^{\mathrm{III}}$ $d^{n-1}s$: ^5G, ^5P, ^5D, ^5S, ^3I, ^7S
d^n : ^5D, ^3H, ^3G, ^1I, ^3D
$d^{n-1}p$: ^7P, ^5H, ^3K

Co$^{\mathrm{I}}$ $d^{n-2}s^2$: ^4F, ^4P, ^2G, ^2P, ^2H
$d^{n-1}s$: ^4F, ^2F, ^4P, ^2P, ^2G, ^2D
d^n : ^2D; $d^{n-1}p$: ^4F, ^4G
$d^{n-1}sp$: ^6F, ^6G, ^6D

Co$^{\mathrm{II}}$ $d^{n-2}s^2$: ^5D; $d^{n-1}s$: ^5F, ^3F, ^5P
d^n : ^3F, ^3P; $d^{n-1}p$: ^5F, ^5G, ^3F, ^3G
$d^{n-2}sp$: ^5D, ^5P, ^5F

Co$^{\mathrm{III}}$ $d^{n-1}s$: ^6D, ^4D, ^4H, ^2H, ^4G, ^2G, ^2I
d^n : ^4F, ^4P, ^2G, ^2H
$d^{n-1}p$: ^6D, ^6P, ^6F, ^4I

Ni$^{\mathrm{I}}$ $d^{n-2}s^2$: ^3F, ^1D, ^3P, ^1G
$d^{n-1}s$: ^3D, ^1D
d^n : ^1S; $d^{n-1}p$: ^1F, ^1D, ^1P, ^3D, ^3P, ^3F
$d^{n-2}sp$: ^5D, ^5F, ^1G, ^5G

Ni$^{\mathrm{II}}$ $d^{n-1}s$: ^4F, ^2F, ^2D, ^2P, ^4P, ^2G
$d^{n-1}p$: ^4G, ^4F
d^n : ^2D

Ni$^{\mathrm{III}}$ $d^{n-1}s$: ^5F, ^3F, ^3P, ^5P, ^3G; d^n: ^3F, ^3P
$d^{n-1}p$: ^5F, ^5G

$\mathrm{Cu^{I}}$ $\mathrm{d}^{n-2}\mathrm{s}^2$: ${}^2D$; $\mathrm{d}^{n-1}\mathrm{s}$: ${}^2S$
$\mathrm{d}^{n-1}\mathrm{p}$: ${}^2P$; $\mathrm{d}^{n-2}\mathrm{sp}$: ${}^4F$, ${}^4P$, ${}^4D$

$\mathrm{Cu^{II}}$ $\mathrm{d}^{n-2}\mathrm{s}^2$: ${}^3F$, ${}^1D$, ${}^3P$, ${}^1G$; $\mathrm{d}^{n-1}\mathrm{s}$: ${}^3D$, ${}^1D$
d^{n} : ${}^1S$; $\mathrm{d}^{n-1}\mathrm{p}$: ${}^3P$, ${}^3F$, ${}^1F$, ${}^3D$
$\mathrm{d}^{n-2}\mathrm{sp}$: ${}^5F$

$\mathrm{Cu^{III}}$ $\mathrm{d}^{n-1}\mathrm{s}$: ${}^4F$, ${}^2F$, ${}^4P$, ${}^2G$, ${}^2D$; d^{n}: ${}^2D$
$\mathrm{d}^{n-1}\mathrm{p}$: ${}^4F$, ${}^4G$.

REFERENCES

1 R. S. Mulliken, *J. Phys. Chem.*, 56 (1952) 295.
2 R. G. Parr and R. Pariser, *J. Chem. Phys.*, 21 (1953) 466, 767.
3 C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory*, Benjamin, New York, 1964, p. 118.
4 L. Oleari, L. Di Sipio and G. De Michelis, *Mol. Phys.*, 10 (1966) 97.
5 J. H. Van Vleck, *J. Chem. Phys.*, 2 (1934) 20.
6 R. S. Mulliken, *J. Chem. Phys.*, 2 (1934) 782.
7 C. A. Coulson, *Valence*, Oxford Univ. Press, London, 1959, p. 205.
8 J. C. Slater, *Phys. Rev.*, 34 (1929) 1293.
9 J. C. Slater, *Quantum Theory of Atomic Structure*, McGraw-Hill, New York, 1960, vol. 1–2.
10 D. R. Hartree, *J. Opt. Soc. Am.*, 46 (1956) 350.
11 J. Hinze and H. H. Jaffé, *J. Chem. Phys.*, 38 (1963) 1834.
12 O. P. Charkin and M. E. Dyatkina, *Zh. Strukt. Khim.*, 5 (1964) 440.
13 J. Hinze and H. H. Jaffé, *Canad. J. Chem.*, 41 (1963) 1315.
14 D. A. Brown and N. J. Fitzpatrick, *J. Chem. Soc.*, A (1966) 941.
15 R. E. Watson, *Phys. Rev.*, 118 (1960) 1036.
16 E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra*, Cambridge Univ. Press, London, 1935, p. 174–183.
17 C. Moore, *Atomic Energy Levels*, Nat. Bur. Stand. vol. 2 (1952) circ. 467.
18 D. A. Brown, *J. Chem. Phys.*, 28 (1958) 67.
19 R. E. Watson, *Phys. Rev.*, 119 (1960) 1934.
20 F. Rohrlich, *Phys. Rev.*, 101 (1956) 69.
21 A. A. Schweizer, *Phys. Rev.*, 80 (1950) 1080.
22 G. Racah, *Phys. Rev.*, 61 (1942) 537.
23 M. A. Catalan, F. Rohrlich and A. G. Shenstone, *Proc. Roy. Soc.*, 221 (1954) 421.
24 L. E. Orgel, *J. Chem. Phys.*, 23 (1955) 1819.
25 Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, 9 (1954) 753.

Coordin. Chem. Rev., 2 (1967) 65–75