Dependence of Slater—Condon parameters on electron configuration. IV. Atoms and ions with electron configurations $K(2)L(8)3s^m3p^n$

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Approximative relations for the dependence of the Slater—Condon parameters of atoms and ions of the third period on their electron configuration are proposed here. The obtained relations are useful in semiempirical methods of quantum chemistry. They allow the extension of the parametrization of methods including the dependence of individual semiempirical integrals on electron configuration of atoms in molecules on a number of systems of chemical importance containing atoms of the third series.

В работе предложены апроксимативные соотношения для зависимостей параметров Слейтера—Кондона атомов и ионов 3-го периода от их электронной конфигурации. Полученные соотношения, применимые в полуэмпирических методах квантовой химии, позволяют расширение параметризации методов включающих зависимости отдельных полуэмпирических интегралов от электронной конфигурации атомов в молекулах на ряд химически интересных систем, содержащих атомы 3-го периода.

In [1] there are proposed approximative relations expressing the dependence of values of the Slater—Condon parameters of atoms and ions of the second series on their electron configuration. Papers [2, 3] are dealing with an analogous dependence of parameters necessary for enumeration of monocentric integrals of electron repulsion of elements of the first transition series. These dependences can be used for calculation of the electron structure of molecules by semiempirical methods of quantum chemistry with parameters dependent on the electron configuration of

Table 1
Values of coefficients B_{ij} for function $F^0(3s,3s)$ [eV]

i	j	B_{ij}
0	0	-0.96472012 x 10
1	0	0.14121115 x 10
2	0	0.56426643 x 10^{-3}
0	1	-0.22615011 x 10^{2}
0	2	0.14007312
1	1	0.33904020 x 10
1	2	-0.14651788
2	1	-0.12052849
2	2	0.84400526 x 10^{-2}

Correlation coefficient	0.9980
Standard deviation	0.250

Table 2
Values of coefficients B_{ijk} for function $F^0(3p,3p)$ [eV]

i	j	k	B_{ijk}
0	0	0	0.22998475 x 10^{3}
1	0	0	-0.29380623 x 10^{2}
2	0	0	0.99968755
0	1	0	-0.81174347 x 10^{2}
0	2	0	0.58831419 x 10^{2}
0	0	1	-0.12736007 x 10^{3}
1	1	0	0.10836516 x 10^{2}
1	2	0	-0.78933505 x 10
1	0	1	0.16114049 x 10^{2}
2	1	0	-0.35675230
2	2	0	0.26047739
2	0	1	-0.51196603
0	1	1	-0.65038156
0	2	1	0.30588598

Correlation coefficient	0.9707
Standard deviation	0.898

Table 3
Values of coefficients B_{ijk} for function $F^0(3s,3p)$ [eV]

i	j	k	B_{ijk}
0	0	0	-0.31603978 x 10^{2}
1	0	0	0.29767164 x 10
0	1	0	-0.39893539
0	0	1	0.19725670 x 10^{2}
0	0	2	-0.63861861 x 10

Table 3 (Continued)

i	j	k	B_{ijk}
1	1	0	0.43560784 x 10^{-1}
1	0	1	-0.12072288 x 10
1	0	2	0.38259084
0	1	1	-0.12573360 x 10
0	1	2	0.29136111

Correlation coefficient	0.9940
Standard deviation	0.429

Table 4
Values of coefficients B_{ij} for function $G^1(3s,3p)$ [eV]

i	j	B_{ij}
0	0	0.14968368 x 10^{2}
0	1	-0.17221322 x 10
0	2	-0.15336139 x 10
0	3	0.11887174
1	0	-0.12602465 x 10
1	1	0.50282455
1	2	0.42567364 x 10^{-1}
1	3	-0.59551330 x 10^{-2}

Correlation coefficient	0.9808
Standard deviation	0.661

Table 5
Values of coefficients B_{ijk} for function $F^2(3p,3p)$ [eV]

i	j	k	B_{ijk}
0	0	0	0.79309267 x 10^{2}
1	0	0	-0.32623620 x 10
0	1	0	-0.97726148 x 10
0	1	1	-0.66868960 x 10^{2}
0	0	2	0.10681371 x 10^{2}
0	1	1	0.65413020 x 10
0	1	2	-0.91021606
1	1	0	-0.44051473 x 10^{-1}
1	0	1	0.33382630 x 10
1	0	2	-0.55438770

Correlation coefficient	0.9818
Standard deviation	0.425

Table 6
Experimental and calculated values of $F^0(3s,3s)$ [eV]

Atom	Z	S	P	Q	Experimental	Approximative	Deviation
Mg	12	2	0	0	7.3860	7.3794	0.0066
Al	13	2	1	0	8.8339	8.8056	0.0283
	13	2	0	1	9.9200	9.5582	0.0618
Si	14	2	2	0	10.1636	10.2330	-0.0693
	14	2	1	1	11.0474	11.2031	-0.1557
	14	2	0	2	11.6700	11.6593	0.0107
P	15	2	3	0	11.5732	11.6614	-0.0882
	15	2	2	1	12.9024	12.6249	0.2775
	15	2	1	2	13.0577	13.2709	-0.2132
	15	2	0	3	13.6600	13.5996	0.0604
S	16	2	3	1	14.1716	13.8136	0.3480
	16	2	2	2	14.2431	14.4691	-0.2259
	16	2	1	3	15.0506	15.0274	0.0232
	16	2	0	4	15.5300	15.4986	0.0314
Cl	17	2	3	2	14.9014	15.2537	-0.3524
	17	2	2	3	16.1804	15.8850	0.2953
	17	2	1	4	16.7331	16.6932	0.0398
	17	2	0	5	17.6000	17.6783	-0.0783

Table 7
Experimental and calculated values of $F^0(3p,3p)$ [eV]

Atom	Z	S	P	Q	Experimental	Approximative	Deviation
Mg	12	0	2	0	5.9136	5.9431	-0.0295
Al	13	1	2	0	7.3057	7.1432	0.1624
	13	0	2	1	7.8780	8.1845	-0.3065
Si	14	2	2	0	8.8027	8.9621	-0.1593
	14	1	3	0	7.3570	7.2266	0.1304
	14	1	2	1	9.6832	9.6799	0.0034
	14	0	3	1	9.4328	8.2686	1.1642
	14	0	2	2	10.3026	10.3773	-0.0748
P	15	2	3	0	9.6759	9.8109	-0.1350
	15	1	4	0	8.5853	9.6031	-1.0178
	15	2	2	1	11.3428	10.7298	0.6130
	15	1	3	1	10.5353	10.7893	-0.2539
	15	1	2	2	11.8712	11.9754	-0.1043
	15	0	3	2	10.2209	11.6800	-1.4591
	15	0	2	3	12.8465	12.5217	0.3247
S	16	2	4	0	11.0412	11.7543	-0.7132
	16	1	5	0	12.8316	11.2007	1.6309
	16	2	3	1	12.4490	12.4301	0.0189
	16	2	2	2	13.3222	13.1059	0.2163

Table 7 (Continued)

Atom	Z	S	P	Q	Experimental	Approximative	Deviation
S	16	1	3	2	13.0725	13.0869	-0.0144
	16	1	2	3	14.1144	14.0300	0.0844
	16	0	3	3	14.4320	14.0190	0.4129
	16	0	2	4	14.5786	14.6176	-0.0390
Cl	17	2	5	0	11.8510	11.7204	0.1306
	17	2	4	1	13.7255	13.1771	0.5485
	17	2	3	2	14.6876	14.6337	0.0539
	17	1	4	2	10.4505	12.3957	-1.9451
	17	2	2	3	15.5168	16.0903	-0.5736
	17	1	3	3	15.2910	14.1196	1.1712
	17	1	2	4	15.9963	15.8435	0.1528
	17	0	3	4	15.1676	15.2856	-0.1180
	17	0	2	5	16.7901	16.6650	0.1250

Table 8
Experimental and calculated values of $F^0(3s,3p)$ [eV]

Atom	Z	S	P	Q	Experimental	Approximative	Deviation
Mg	12	1	1	0	6.6090	6.7183	-0.1092
Al	13	2	1	0	7.9136	8.1153	-0.2017
	13	1	2	0	8.1996	8.3248	-0.1252
	13	1	1	1	9.0604	8.9139	0.1465
Si	14	2	2	0	9.1445	9.3227	-0.1782
	14	1	3	0	7.8691	8.3354	-0.4663
	14	1	2	1	10.4871	10.4610	0.0261
	14	2	1	1	10.4080	10.3545	0.0535
	14	1	1	2	11.2479	11.1095	0.1383
P	15	2	3	0	10.4028	10.2820	0.1208
	15	2	2	1	11.8990	11.5024	0.3966
	15	1	3	1	12.2889	11.1773	1.1116
	15	2	1	2	12.6657	12.5937	0.0720
	15	1	2	2	12.3720	12.5972	-0.2252
	15	1	1	3	13.3759	13.3052	0.0708
S	16	2	4	0	13.2636	13.2887	-0.0251
	16	2	3	1	12.8532	13.1675	-0.3142
	16	2	2	2	13.9712	13.6822	0.2890
	16	1	3	2	13.3428	14.0192	-0.6764
	16	2	1	3	14.8853	14.8329	0.0524
	16	1	2	3	14.9834	14.7334	0.2500
	16	1	1	4	15.3795	15.5008	-0.1213
Cl	17	2	4	1	17.9818	17.6451	0.3366
	17	2	3	2	15.3117	16.0529	-0.7412
	17	2	2	3	16.2892	15.8619	0.4273
	17	1	3	3	16.8922	16.8611	0.0311
	17	2	1	4	16.7843	17.0721	-0.2878

Table 8 (Continued)

Atom	Z	S	P	Q	Experi-mental	Approxi-mative	Devia-tion
Cl	17	1	2	4	16.9439	16.8696	0.0743
	17	1	1	5	17.5714	17.6965	-0.1250

Table 9
Experimental and calculated values of $G^1(3s,3p)$ [eV]

Atom	Z	S	P	Q	Experi-mental	Approxi-mative	Devia-tion
Mg	12	1	1	0	2.4499	3.1818	-0.7319
Al	13	1	2	0	3.4228	2.4610	0.9618
	13	1	1	1	4.1609	4.6250	-0.4641
Si	14	1	2	1	5.1007	4.4931	0.6077
	14	1	1	2	5.5940	5.7966	-0.2026
P	15	1	4	0	0.9500	1.0193	-0.0693
	15	1	3	1	4.7744	4.3611	0.4133
	15	1	2	2	6.6336	6.2672	0.3664
	15	1	1	3	6.8753	6.9148	-0.0395
S	16	1	4	1	3.2376	4.2291	-0.9915
	16	1	3	2	6.9100	6.7377	0.1723
	16	1	2	3	7.8467	7.9658	-0.0119
	16	1	1	4	8.1046	8.0550	0.0496
Cl	17	1	5	1	4.0460	4.0971	-0.0511
	17	1	3	3	9.4747	9.0168	0.4579
	17	1	2	4	9.1119	9.6287	-0.5168
	17	1	1	5	9.3067	9.1497	0.1570

Table 10
Experimental and calculated values of $F^2(3p,3p)$ [eV]

Atom	Z	S	P	Q	Experi-mental	Approxi-mative	Devia-tion
Al	13	1	2	0	2.7840	2.9493	-0.1653
Si	14	2	2	0	3.1580	3.1542	0.0038
	14	1	2	1	3.8753	4.1018	-0.2265
	14	0	2	2	5.3580	5.0494	0.3086
P	15	2	3	0	3.8747	3.2759	0.5988
	15	1	4	0	2.2110	2.2110	0.0000
	15	2	2	1	4.4110	4.2627	0.1483
	15	1	3	1	1.3396	2.2774	-0.9378
	15	1	2	2	5.2069	5.2544	-0.0475
	15	0	3	2	1.6475	1.2788	0.3687
	15	0	2	3	6.3564	6.2460	0.1103

Table 10 (Continued)

Atom	Z	S	P	Q	Experi-mental	Approxi-mative	Devia-tion
S	16	2	4	0	4.5118	4.5118	0.0000
	16	2	3	1	5.0762	4.9508	0.1254
	16	2	2	2	5.5286	5.3712	0.1574
	16	1	3	2	3.9071	3.9963	-0.0892
	16	1	2	3	6.2310	6.4069	-0.1759
	16	0	3	3	2.9461	3.0417	-0.0956
Cl	17	2	4	1	5.6442	5.6442	0.0000
	17	2	3	2	6.1745	6.6256	-0.4511
	17	2	2	3	6.5892	6.4798	0.1094
	17	1	3	3	6.1960	5.7152	0.4808
	17	1	2	4	7.3370	7.5595	-0.2225

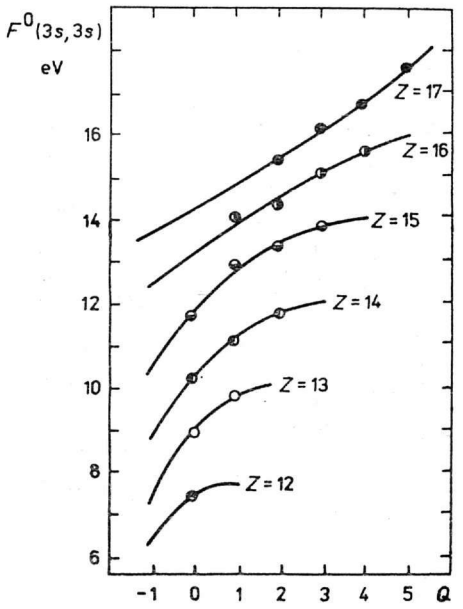

Fig. 1. Dependence of $F^0(3s,3s)$ on charge for configuration $K(2)L(8)3s^23p^n$ of atoms of the third period.

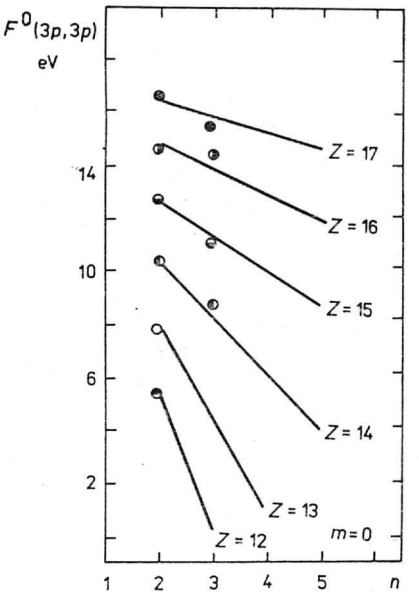

Fig. 2. Dependence of $F^0(3p,3p)$ on the number of p-electrons for configurations $K(2)L(8)3s^03p^n$ of atoms of the third period.

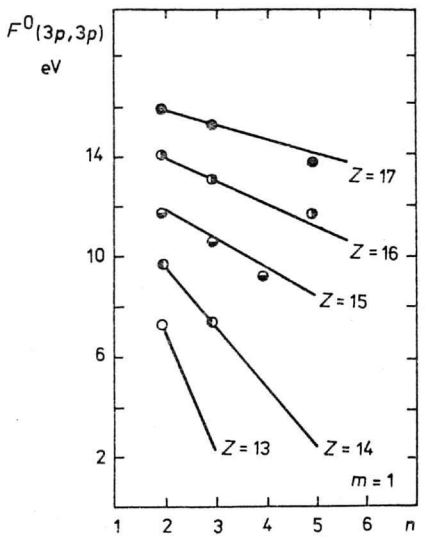

Fig. 3. Dependence of $F^0(3p,3p)$ on the number of p-electrons for configurations $K(2)L(8)3s^13p^n$ of atoms of the third period.

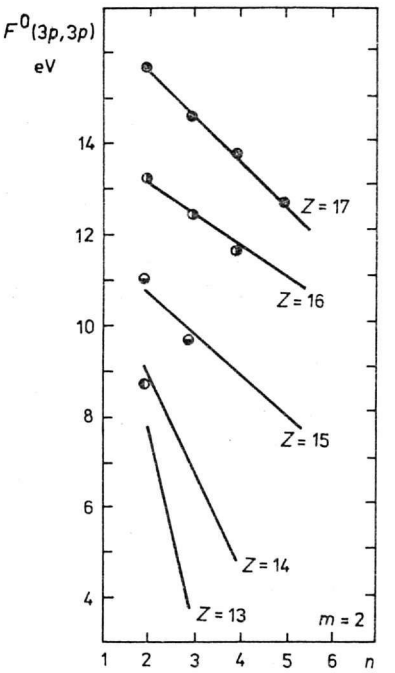

Fig. 4. Dependence of $F^0(3p,3p)$ on the number of p-electrons for configurations $K(2)L(8)3s^23p^n$ of atoms of the third period.

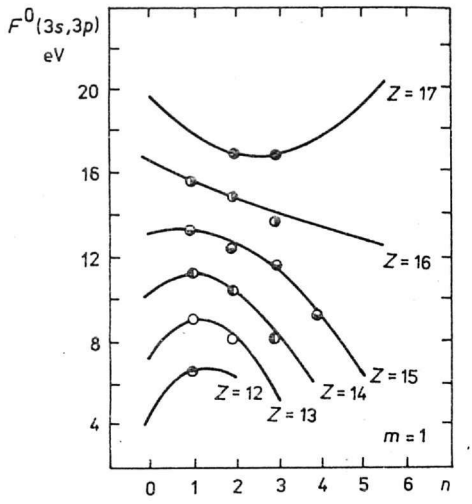

Fig. 5. Dependence of $F^0(3s,3p)$ on the number of p-electrons for configurations $K(2)L(8)3s^13p^n$ of atoms of the third period.

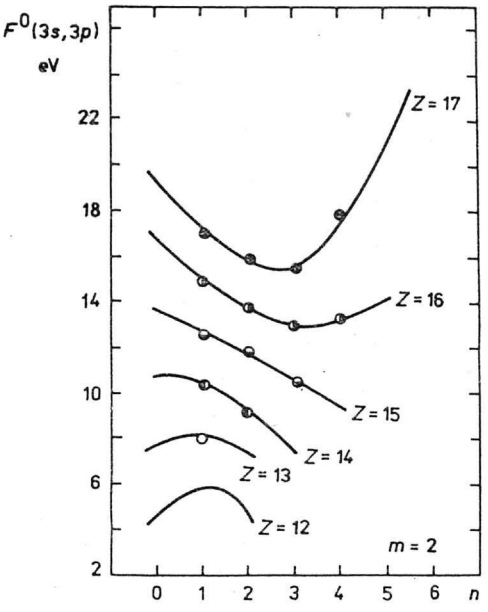

Fig. 6. Dependence of $F^0(3s,3p)$ on the number of p-electrons for configurations $K(2)L(8)3s^23p^n$ of atoms of the third period.

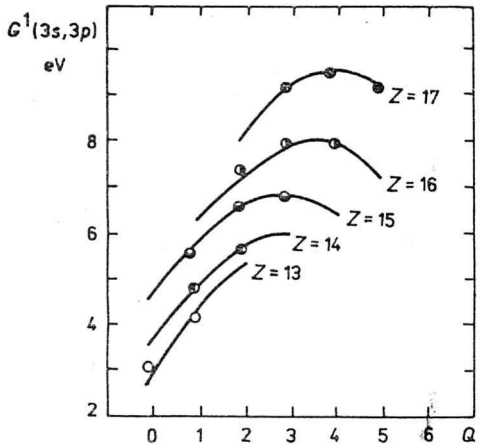

Fig. 7. Dependence of $G^1(3s,3p)$ on charge for configurations $K(2)L(8)3s^13p^n$ of atoms of the third period.

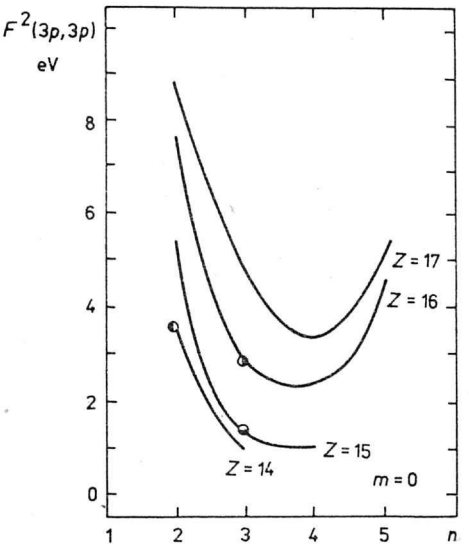

Fig. 8. Dependence of $F^2(3p,3p)$ on the number of p-electrons for configurations $K(2)L(8)3s^03p^n$ of atoms of the third period.

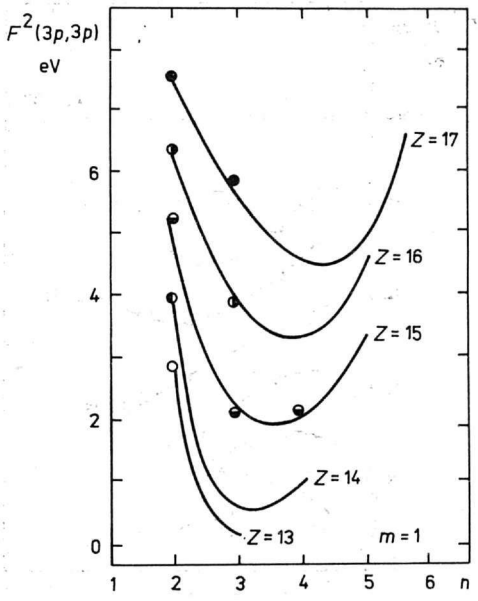

Fig. 9. Dependence of $F^2(3p,3p)$ on the number of p-electrons for configurations $K(2)L(8)3s^1 3p^n$ of atoms of the third period.

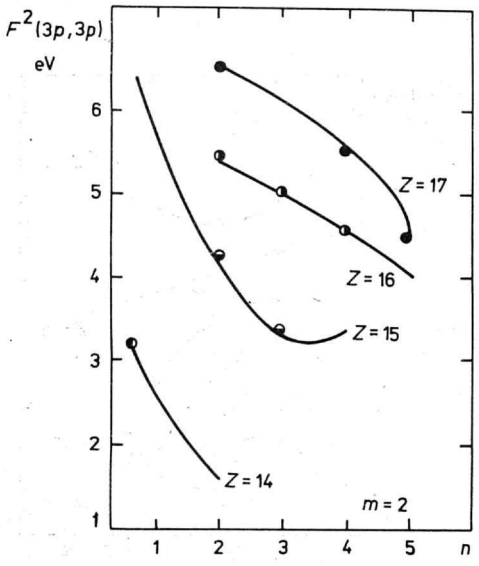

Fig. 10. Dependence of $F^2(3p,3p)$ on the number of p-electrons for configurations $K(2)L(8)3s^2 3p^n$ of atoms of the third period.

atoms in molecules [4, 5]. Because a great number of compounds of chemical importance contain also elements of the third period, in this work there is proposed analogous parametrization for these elements.

Method and results

All the available spectral values of the Slater—Condon parameters for atoms and ions with electron configuration $K(2)L(8)3s^m 3p^n$ were systematically determined using the analysis of atomic spectra [6]. The regression relations are proposed for noninteger values of electron configurations $s^x p^y$, that occur in the framework of LCAO MO SCF calculations of electron structure of molecules

$$F(Z,x,y)=\sum_{i=0}^{N_Z}\sum_{j=0}^{N_s} B_{ijo} Z^i x^j + \sum_{i=0}^{N_Z}\sum_{k=1}^{N_p} B_{iok} Z^i y^k + \\ + \sum_{j=1}^{N_s}\sum_{k=1}^{N_p} B_{ojk} x^j y^k \qquad (1)$$

$$F(Z,Q)=\sum_{i=0}^{N_Z}\sum_{j=0}^{N_Q} B_{ij} Z^i Q^j \qquad (2)$$

The values of coefficients B_{ij}, resp. B_{ijk}, and relevant statistical characteristics of dependences for individual Slater—Condon parameters are shown in Tables 1—5. In Tables 6—10 all the experimental available values of the Slater—Condon parameters are compared with values calculated using relations (*1*) and (*2*). In Figs. 1—10 there is graphically represented the course of individual regression functions.

From the presented results we can conclude that the suggested regression functions very well correlate with experimentally obtained values. Therefore, they are useful for semiempirical methods of quantum chemistry with parametrization dependent on the electron configuration of atoms in a molecule.

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