Dependence of Slater—Condon parameters on electron configuration. I. Atoms and ions with electron configurations $K(2)2s^m2p^n$

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Regression relations for the dependence of the Slater—Condon parameters of atoms and ions of the second period on their electron configuration are proposed here. The obtained relations are useful in semiempirical methods of quantum chemistry.

В работе предложены уравнения регрессии для зависимостей параметров Слейтера—Кондона атомов и ионов 2-ого периода от электронной конфигурации. Полученные соотношения можно использовать в полуэмпирических методах квантовой химии.

The success of semiempirical methods of molecular orbitals depends above all on proper parametrization. The common mark of the so far used parametrization of semiempirical methods with an explicit inclusion of the mutual electron repulsion is the choice of atomic parameters reproducing spectral characteristics of electroneutral atoms [1, 2]. In the present paper we express in an explicit way the dependence of Slater—Condon parameters on electron configuration of atoms. The consideration of dependences of this kind in calculations of an electron structure allows the configurationally dependent parametrization of semiempirical methods [3, 4].

Method and results

Anno and *Teruya* [5] have systematically determined the values of the Slater—Condon parameters $F^0(2s,2s)$, $F^0(2s,2p)$, $F^0(2p,2p)$, $G^1(2s,2p)$, and

$F^2(2p,2p)$ for atoms and ions with the electron configurations $K(2)2s^m2p^n$ by an analysis of atomic spectra. In the framework of LCAO MO approximation the electron configuration of atoms in molecules acquires the noninteger values s^xp^y. If we want to use the configurationally dependent values of the Slater—Condon parameters for LCAO MO calculation of electron structure of molecules, we must approximate the discrete functions mentioned to the continuous ones. Then we regard the individual parameters as functions of the atomic number and continuous arguments which are represented by the populations x, y of individual levels of the valence sphere of an atom or by the atomic charge Q. The dependence on the atomic number Z is included to achieve the maximum number of experimental data in the correlation.

The polynomial functions the concrete form and degree of which were obtained by maximization of the correlation coefficient are the most suitable of the functions tested. For the parameters $F^0(2p,2p)$, $F^0(2s,2p)$, and $F^2(2p,2p)$ the regression function was used

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

Because of deficiency of experimental data (only values for configurations of the type s^1p^n can be experimentally determined) it was necessary to simplify this expression for the parameters $F^0(2s,2s)$ and $G^1(2s,2p)$ into the form

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

The values of the coefficients B_{ij} or B_{ijk} as well as relevant statistical characteristics of dependences for individual Slater—Condon parameters are listed in Tables 1—5. In Tables 6—10 all the experimental accessible values of the Slater—Condon parameters, values calculated according to eqns (*1*) and (*2*), and their relative deviations are shown. Figs. 1—10 graphically demonstrate the shape of individual regression functions.

We can conclude from the presented results 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.

Table 1. Numerical values of B_{ij}'s for function $F^0(2s,2s)$ [eV]

i	j	B_{ij}
0	0	$-0.15943258 \times 10^{1}$
1	0	0.25996024×10^{1}
0	1	0.40225592×10^{1}
0	2	$-0.20935365 \times 10^{1}$
0	3	0.14523322
0	4	$0.39390213 \times 10^{-1}$
1	1	-0.47504881
1	2	0.44437713
1	3	$-0.82618805 \times 10^{-1}$
1	4	$0.17842531 \times 10^{-2}$
Correlation coefficient		0.9993
Standard deviation		0.264

Table 2. Numerical values of B_{ijk}'s for function $F^0(2p,2p)$ [eV]

i	j	k	B_{ijk}
0	0	0	$-0.39424596 \times 10^{3}$
1	0	0	0.98553204×10^{2}
2	0	0	$-0.55332171 \times 10^{1}$
0	1	0	$-0.41218100 \times 10^{1}$
0	0	1	0.31918585×10^{3}
0	0	2	$-0.64803289 \times 10^{2}$
1	1	0	-0.71656540
1	0	1	$-0.77073611 \times 10^{2}$
1	0	2	0.15450047×10^{2}
2	1	0	$0.51281676 \times 10^{-1}$
2	0	1	0.45468576×10^{1}
2	0	2	-0.91007623
0	1	1	0.29902650×10^{1}
0	1	2	-0.50554702
Correlation coefficient			0.9977
Standard deviation			0.535

Table 3. Numerical values of B_{ijk}'s for function $F^0(2s,2p)$ [eV]

i	j	k	B_{ijk}
0	0	0	$-0.56534262 \times 10^{1}$
1	0	0	0.49872707×10^{1}
0	1	0	$-0.37759204 \times 10^{1}$
0	0	1	$-0.11917546 \times 10^{1}$
0	0	2	-0.19759186
0	0	3	$-0.48837400 \times 10^{-1}$
1	1	0	0.13145794
1	0	1	-0.91120259
1	0	2	0.38891533
1	0	3	$-0.41546989 \times 10^{-1}$
0	1	1	0.28873448×10^{1}
0	1	2	$-0.14090198 \times 10^{1}$
0	1	3	0.18261151
Correlation coefficient			0.9994
Standard deviation			0.258

Table 4. Numerical values of B_{ij}'s for function $G^1(2s,2p)$ [eV]

i	j	B_{ij}
0	0	0.23489783×10^{1}
1	0	-0.38732334
2	0	0.19437843
0	1	0.18566999×10^{1}
0	2	$-0.27241670 \times 10^{1}$
0	3	0.23679638
1	1	0.45862446
1	2	0.60394323
1	3	$-0.79182408 \times 10^{-1}$
2	1	$-0.92222958 \times 10^{-1}$
2	2	$-0.23376719 \times 10^{-1}$
2	3	$0.47904852 \times 10^{-2}$
Correlation coefficient		0.9995
Standard deviation		0.171

Table 5. Numerical values of B_{ijk}'s for function $F^2(2p,2p)$ [eV]

i	j	k	B_{ijk}
0	0	0	$-0.11433797 \times 10^{2}$
1	0	0	0.92499223×10^{1}
2	0	0	-0.35097685
0	1	0	$-0.14893139 \times 10^{2}$
0	2	0	0.18836956×10^{1}
0	0	1	$-0.10549898 \times 10^{1}$
0	0	2	0.17871841
1	1	0	$-0.25111455 \times 10^{1}$
1	2	0	0.73573670
1	0	1	$-0.35951523 \times 10^{1}$
1	0	2	0.52634843
2	1	0	0.11725033
2	2	0	$-0.37869140 \times 10^{-1}$
2	0	1	0.19267329
2	0	2	$-0.27168918 \times 10^{-1}$
0	1	1	0.16571577×10^{2}
0	1	2	$-0.26510243 \times 10^{1}$
0	2	1	$-0.33682063 \times 10^{1}$
0	2	2	0.53179978
Correlation coefficient			0.9995
Standard deviation			0.176

Table 6. Experimental and calculated values of $F^0(2s,2s)$ [eV]

Z	S	P	Experimental	Approximative	Deviation
4	2	0	8.886	8.804	0.082
5	2	1	11.357	11.404	-0.047
5	2	0	12.771	12.960	-0.189
6	2	2	13.937	14.003	-0.066
6	2	1	15.420	15.447	-0.028
6	2	0	16.605	16.636	-0.031
7	2	3	16.529	16.603	-0.073
7	2	2	18.119	17.936	0.183
7	2	1	19.423	19.431	-0.008
7	2	0	20.413	20.357	0.056
8	2	4	19.323	19.202	0.121
8	2	3	20.896	20.424	0.472
8	2	2	22.336	22.226	0.110
8	2	1	23.333	23.445	-0.112
8	2	0	24.207	24.207	0.000
9	2	5	21.810	21.802	0.008
9	2	4	22.346	22.912	-0.566
9	2	3	25.204	25.020	0.184
9	2	2	26.334	26.532	-0.198
9	2	1	27.313	27.186	0.127
9	2	0	28.022	28.047	-0.025

Table 7. Experimental and calculated values of $F^0(2p,2p)$ [eV]

Z	S	P	Experimental	Approximative	Deviation
4	0	2	8.543	8.460	0.082
5	1	2	11.422	11.484	-0.062
5	0	3	9.799	9.913	-0.114
5	0	2	13.910	13.948	-0.038
6	2	2	14.064	14.043	0.021
6	1	3	13.259	13.225	0.034
6	1	2	16.715	16.660	0.055
6	0	3	15.550	15.379	0.171
6	0	2	19.119	19.277	-0.157
7	2	3	16.023	16.270	-0.247
7	1	4	11.665	11.665	0.000
7	2	2	19.245	19.112	0.133
7	1	3	18.600	18.474	0.126
7	1	2	21.861	21.779	0.082
7	0	3	20.870	20.678	0.191
7	0	2	24.254	24.445	-0.191
8	2	4	17.857	17.873	-0.016
8	1	5	17.683	17.579	0.105
8	2	3	21.227	21.508	-0.281
8	1	4	20.492	20.573	-0.081
8	2	2	24.369	24.226	0.142
8	1	3	25.811	25.660	0.151
8	0	4	23.055	23.273	-0.217
8	1	2	26.869	26.840	0.029
8	0	3	25.957	25.811	0.146
8	0	2	29.365	29.454	-0.090
9	2	5	19.664	18.702	0.962
9	1	6	18.980	19.895	-0.915
9	2	4	23.102	23.223	-0.122
9	1	5	22.725	22.806	-0.081
9	2	3	26.406	26.785	-0.379
9	1	4	25.766	25.768	-0.002
9	0	5	28.411	26.910	1.500
9	2	2	29.370	29.386	-0.016
9	1	3	28.814	28.781	0.033
9	0	4	26.779	28.313	-1.534

Table 7 (Continued)

Z	S	P	Experimental	Approximative	Deviation
9	1	2	31.974	31.845	0.129
9	0	3	31.090	30.777	0.312
9	0	2	34.441	34.304	0.138

Table 8. Experimental and calculated values of $F^0(2s,2p)$ [eV]

Z	S	P	Experimental	Approximative	Deviation
4	1	1	8.942	9.013	-0.071
5	2	1	11.985	12.110	-0.125
5	1	2	11.069	11.204	-0.135
5	1	1	13.652	13.568	0.084
6	2	2	14.157	14.336	-0.179
6	1	3	13.370	13.391	-0.022
6	2	1	16.843	16.797	0.046
6	1	2	15.853	15.723	0.130
6	1	1	18.194	18.123	0.072
7	2	3	16.369	16.211	0.158
7	2	2	18.980	18.987	-0.007
7	1	3	18.095	18.155	-0.060
7	2	1	21.571	21.483	0.088
7	1	2	20.458	20.243	0.215
7	1	1	22.689	22.678	0.011
8	2	4	18.695	18.477	0.218
8	2	3	21.157	21.106	0.051
8	1	4	20.291	20.509	-0.218
8	2	2	23.755	23.638	0.118
8	1	3	22.735	22.919	-0.184
8	2	1	26.199	26.169	0.030
8	1	2	24.914	24.762	0.152
8	1	1	27.168	27.233	-0.065
9	2	5	20.894	20.880	0.014
9	2	4	23.371	23.646	-0.275
9	1	5	21.304	21.435	-0.131
9	2	3	25.878	26.001	-0.123
9	1	4	26.287	25.547	0.740
9	2	2	28.299	28.289	0.010
9	1	3	27.163	27.682	-0.519
9	2	1	30.830	30.856	-0.025
9	1	2	29.443	29.282	0.161
9	1	1	31.626	31.787	-0.162

Table 9. Experimental and calculated values of $G^1(2s,2p)$ [eV]

Z	S	P	Experimental	Approximative	Deviation
4	1	1	3.828	3.910	-0.082
5	1	2	5.487	5.272	0.215
5	1	1	6.704	6.788	-0.084
6	1	3	6.898	7.023	-0.125
6	1	2	8.438	8.303	0.125
6	1	1	9.295	9.304	-0.009
7	1	4	9.064	9.162	-0.098
7	1	3	10.086	9.986	0.100
7	1	2	11.056	11.029	0.027
7	1	1	11.794	11.794	0.000
8	1	5	11.815	11.691	0.124
8	1	4	11.546	11.835	-0.290
8	1	3	12.665	12.662	0.003
8	1	2	13.610	13.630	-0.020
8	1	1	14.205	14.200	0.005
9	1	5	13.882	13.852	0.030
9	1	4	14.266	14.205	0.061
9	1	3	15.211	15.140	0.071
9	1	2	16.032	16.130	-0.098
9	1	1	16.679	16.130	0.450

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

Z	S	P	Experimental	Approximative	Deviation
4	0	2	2.656	2.634	0.022
5	1	2	4.132	4.158	-0.026
5	0	2	6.157	6.131	0.026
6	2	2	4.426	4.381	0.045
6	1	3	5.596	5.305	0.291
6	0	4	6.369	6.380	-0.011
6	1	2	6.359	6.309	-0.245
6	0	3	5.315	5.572	-0.257
6	0	2	9.578	9.478	0.100
7	2	3	6.011	6.245	-0.234
7	1	4	6.885	6.834	0.042
7	2	2	6.676	6.580	0.096
7	1	3	7.476	7.536	-0.060
7	0	4	9.452	9.476	-0.024
7	1	2	9.091	9.059	0.032

Table 10 (Continued)

Z	S	P	Experi-mental	Approxi-mative	Devia-tion
7	0	3	8.741	8.547	0.195
7	0	2	12.640	12.677	-0.037
8	2	4	6.904	6.853	0.051
8	2	3	8.431	8.351	0.080
8	1	4	9.244	9.315	-0.071
8	2	2	8.802	8.796	0.006
8	1	3	9.758	9.891	-0.133
8	0	4	12.536	12.542	-0.006
8	1	2	11.653	11.525	0.128
8	0	3	11.640	11,486	0.154
8	0	2	15.607	15.728	-0.121
9	2	4	9.171	9.221	-0.050
9	2	3	10.739	10.587	0.152
9	1	4	11.945	11.926	0.019
9	2	2	10.881	11.030	-0.149
9	1	3	12.272	12.369	-0.097
9	0	4	15.619	15.578	0.041
9	1	2	14.057	14.001	0.046
9	0	3	14.301	14.391	-0.089
9	0	2	18.640	18.629	0.011

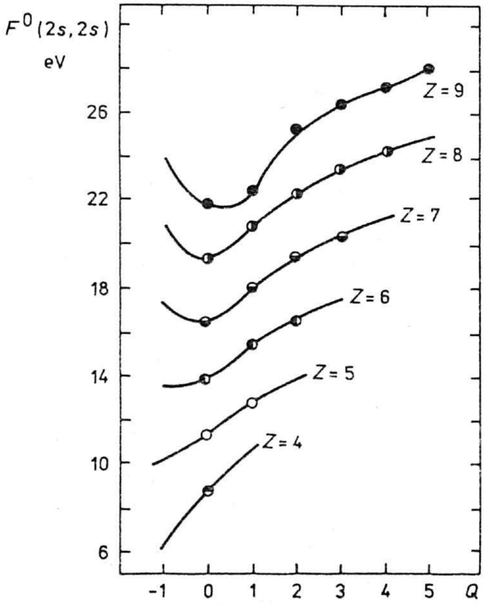

Fig. 1. Dependence of $F^0(2s,2s)$ on charge for configurations $K(2)2s^22p^n$ of atoms of the second period.

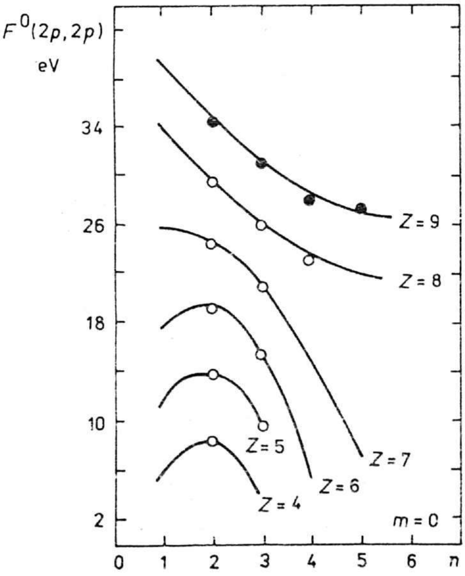

Fig. 2. Dependence of $F^0(2p,2p)$ on the number of p-electrons for configurations $K(2)2s^02p^n$ of atoms of the second period.

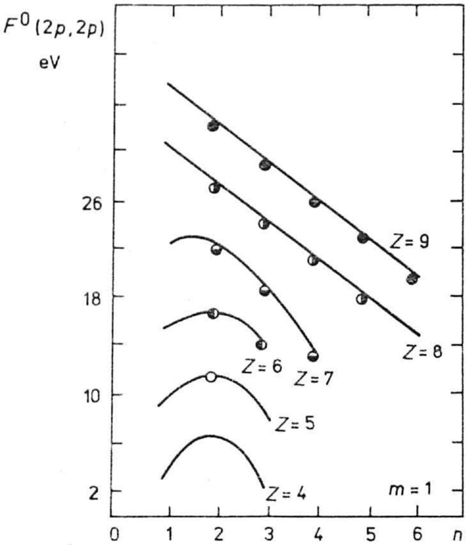

Fig. 3. Dependence of $F^0(2p,2p)$ on the number of p-electrons for configurations $K(2)2s^12p^n$ of atoms of the second period.

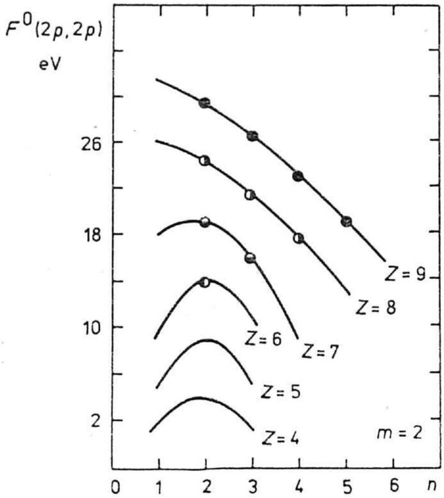

Fig. 4. Dependence of $F^0(2p,2p)$ on the number of p-electrons for configurations $K(2)2s^22p^n$ of atoms of the second period.

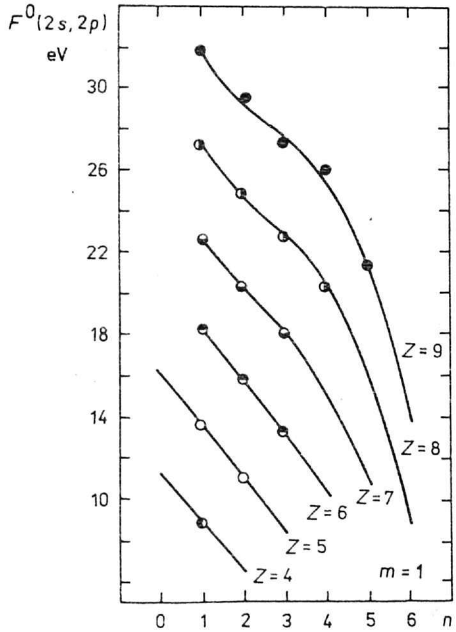

Fig. 5. Dependence of $F^0(2s,2p)$ on the number of p-electrons for configurations $K(2)2s^12p^n$ of atoms of the second period.

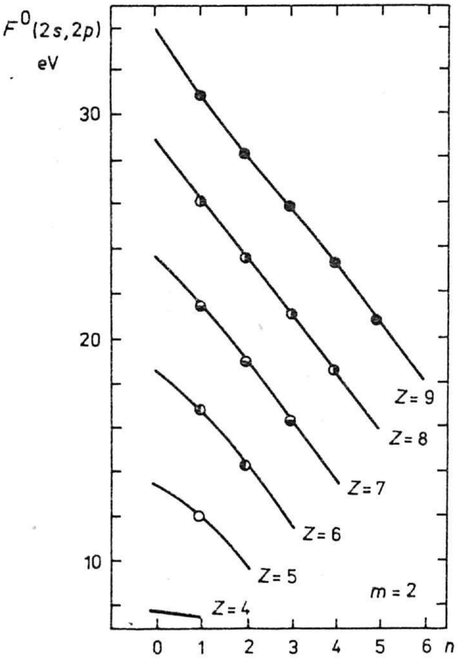

Fig. 6. Dependence of $F^0(2s,2p)$ on the number of p-electrons for configurations $K(2)2s^22p^n$ of atoms of the second period.

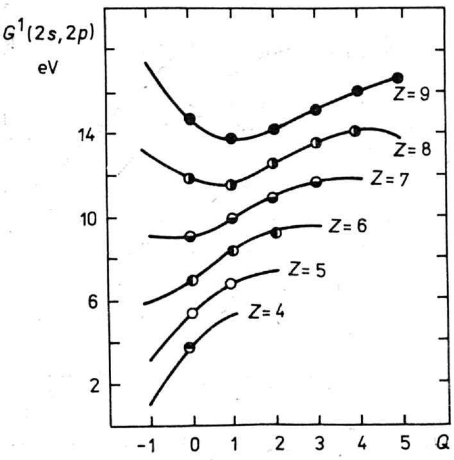

Fig. 7. Dependence of $G^1(2s,2p)$ on charge for configurations $K(2)2s^12p^n$ of atoms of the second period.

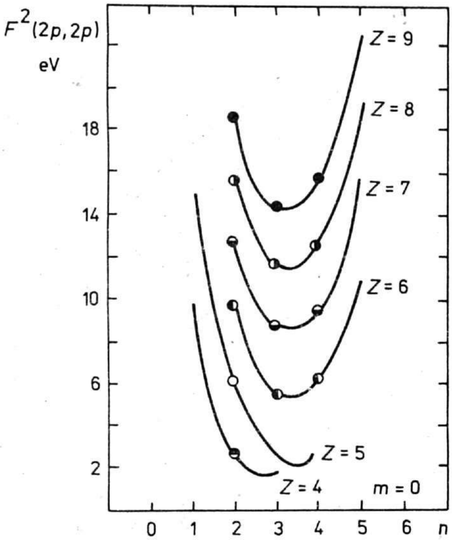

Fig. 8. Dependence of $F^2(2p,2p)$ on the number of p-electrons for configurations $K(2)2s^02p^n$ of atoms of the second period.

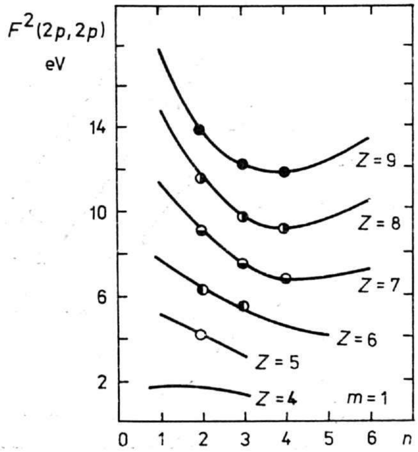

Fig. 9. Dependence of $F^2(2p,2p)$ on the number of p-electrons for configurations $K(2)2s^12p^n$ of atoms of the second period.

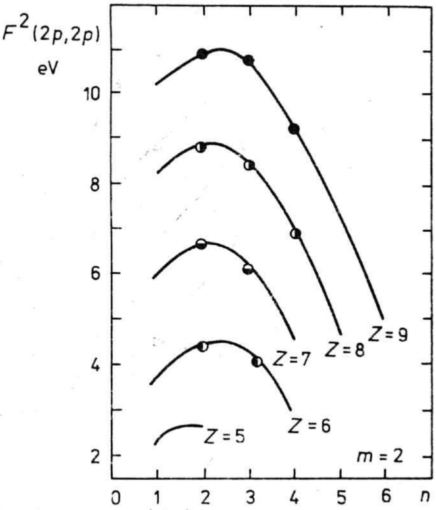

Fig. 10. Dependence of $F^2(2p,2p)$ on the number of p-electrons for configurations $K(2)2s^22p^n$ of atoms of the second period.

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