Valence orbital ionization potentials of $K(2)2s^m2p^n$ and $K(2)L(8)3s^m3p^n$ atoms and ions

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Valence orbital ionization potentials were systematically determined for the atoms and ions of the second and third periods with the electron configuration $K(2)2s^m2p^n$ and $K(2)L(8)3s^m3p^n$ respectively. For the approximation of the dependence of VOIP on the electron configuration and atomic number were used mixed polynomials having variables m, n, and Z.

It is well known that the Slater theory of many-electron atoms is based on the Russell—Saunders coupling approximation with a complete neglect of the spin-orbit coupling and considers atoms as a single configuration. Common semiempirical methods are based on the LCAO MO approximation and the atoms in molecules are therefore regarded in the same approximation as in the above Slater theory. That is the reason for a great interest in the semiempirical parameters obtained by analysis of atomic spectra, which are usable in semiempirical methods of calculating electronic structures of molecules. One of such parameters is the ionization potential of valence orbitals (VOIP).

VOIP are defined by the relation

$$\mathrm{VOIP} = E^{+}_{\mathrm{av}} - E_{\mathrm{av}} + \mathrm{IP}, \qquad (1)$$

where E_{av} is the average energy of the given electron configuration of the atom (ion) with respect to its ground state and E^{+}_{av} is the similar quantity for the ion formed by the removal of one valence electron from the atom (ion) under consideration. IP is the ionization potential of the atom (ion) in its ground state.

Anno and *Teruya* have determined E_{av} with the help of Slater—Condon parameters for atoms and ions in all electron configurations of the type $K(2)2s^m2p^n$ [1] and $K(2)L(8)3s^23p^63d^k4s^m4p^n$ [2]. Recently we have calculated [3] the E_{av} values for atoms and ions of the electron configurations $K(2)L(8)3s^m3p^n$.

Method

Basch, *Viste*, and *Gray* [4] evaluated VOIP for atoms and ions from H to Kr for various electron configurations and for different oxidation states. The depen-

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Table 1

Numerical values of C_{rt}'s [eV]

	j	k	$2s$	$2p$	$3s$	$3p$
0	0	0	1.477815	-1.334598×10^{2}	1.521112×10^{2}	1.673094×10^{2}
1	0	0	-7.441048	2.452873×10	-3.907846×10	-3.616541×10
2	0	0	3.445261	1.509719	2.666145	1.972356
3	0	0	—	—	-2.578131×10^{-2}	—
0	1	0	6.233788	-2.111729×10^{-1}	1.927201×10	1.243582×10
0	2	0	—	2.593736	—	—
0	0	1	8.339323	2.600504×10^{2}	2.095417×10^{2}	-6.254666×10
0	0	2	4.823313×10^{-1}	-1.367811×10^{2}	-5.461743×10^{2}	3.185377×10
0	0	3	-1.778742×10^{-1}	2.323340×10	2.342697×10^{2}	-1.880283
1	1	0	-3.659323	-3.615350	-2.086598	-1.610449
1	2	0	—	-1.662258×10^{-1}	—	—
1	0	1	-4.872082	-6.542306×10	-2.790699×10	1.092351×10
1	0	2	2.683286×10^{-1}	3.292460×10	9.565173×10	-5.327602
1	0	3	2.653241×10^{-2}	5.521061	-4.319176×10	4.305389×10^{-1}
2	1	0	-2.020041×10^{-2}	-3.536589×10^{-2}	-2.889904×10^{-2}	-1.159903×10^{-2}
2	2	0	—	8.801815×10^{-3}	—	—
2	0	1	6.357853×10^{-2}	3.550183	8.849363×10^{-1}	-5.226916×10^{-1}
2	0	2	-2.926522×10^{-2}	-1.930613	-5.478806	2.207884×10^{-1}
2	0	3	8.282584×10^{-5}	3.240164×10^{-1}	2.638783	-2.088997×10^{-2}
3	1	0	—	—	1.424452×10^{-3}	—
3	0	1	—	—	-1.311974×10^{-3}	—
3	0	2	—	—	1.023130×10^{-1}	—
3	0	3	—	—	-5.340999×10^{-2}	—
0	1	1	8.519657×10^{-1}	8.556154	9.162572×10^{-1}	3.743874
0	1	2	1.560795×10^{-1}	-2.872783	-6.388782×10^{-2}	-1.460695
0	1	3	-1.157059×10^{-2}	3.649397×10^{-1}	-2.617515×10^{-2}	2.002036×10^{-1}
0	2	1	—	-2.242257	—	—
0	2	2	—	1.029760	—	—
0	2	3	—	-1.298844×10^{-1}	—	—

dence of VOIP on the charge (q) of the given atom was approximated by the quadratic function

$$\mathrm{VOIP}(q) = Aq^{2} + Bq + C. \tag{2}$$

Anno and *Sakai* [5—7] have shown by theoretical analysis that the dependence of VOIP on the electron configuration can be approximated better by the function

$$\begin{aligned}\mathrm{VOIP}^{\mathrm{approx}}(m,n,Z) = {} & B_1 + B_2m + B_3n + B_4m^{2} + B_5mn + B_6n^{2} + \\ & + (B_7 + B_8m + B_9n + B_{10}Z)\,Z,\end{aligned} \tag{3}$$

where B_k's are the constants which can be determined by the least squares method and Z is the atomic number.

This method was used in [6] for enumerating VOIP for atoms and ions with electron configuration $K(2)2s^{m}2p^{n}$, in [8] for atoms and ions with electron configuration $K(2)L(8)3s^{m}3p^{n}$, and in [7] for atoms and ions with electron configuration $K(2)L(8)3s^{2}3p^{6}3d^{k}4s^{m}4p^{n}$. In the present work the mixed polynomials having variables m, n, and Z for the elements of the second and third periods were used for the approximation of the dependence of VOIP on electron configuration and atomic number.

Table 2

Numerical values of VOIP$_{2s}$'s [eV]

Atom	m	n	q	VOIP$^{\text{spect}}_{2s}$	VOIP$^{\text{polyn}}_{2s}$	Relative deviation [%]	VOIP$^{\text{approx}}_{2s}$	Relative deviation [%]
Be	2	0	0	9.320	9.384	+0.69	9.408	+0.95
	1	1	0	9.916	9.993	+0.78	9.891	−0.25
	1	0	1	18.206	18.111	−0.52	18.212	+0.03
B	2	1	0	14.042	13.979	−0.47	13.975	−0.48
	1	2	0	15.209	15.233	+0.16	15.194	−0.10
	2	0	1	25.149	25.268	+0.47	25.080	−0.27
	1	1	1	25.399	25.450	+0.20	25.411	+0.05
	1	0	2	37.920	37.836	−0.22	37.970	+0.13
C	2	2	0	19.434	19.254	−0.92	19.335	−0.51
	1	3	0	21.172	21.172	0.00	21.292	+0.57
	2	1	1	32.412	32.374	−0.12	32.336	−0.24
	1	2	1	33.363	33.468	+0.31	33.404	+0.12
	2	0	2	47.864	47.962	+0.21	47.688	−0.39
	1	1	2	47.825	47.827	0.00	47.857	+0.07
	1	0	3	64.476	64.412	−0.10	64.655	+0.28
N	2	3	0	25.570	25.474	−0.37	25.489	−0.32
	2	2	1	40.413	40.439	+0.06	40.385	−0.07
	1	3	1	42.101	42.197	+0.23	42.190	+0.21
	2	1	2	57.717	57.747	+0.05	57.623	−0.16
	1	2	2	58.520	58.575	+0.09	58.540	+0.03
	2	0	3	77.450	77.466	+0.02	77.204	−0.32
	1	1	3	77.140	77.122	−0.02	77.232	+0.12
	1	0	4	97.863	97.837	−0.03	98.266	+0.41
O	2	4	0	32.370	32.471	+0.31	32.436	+0.20
	2	3	1	49.154	49.246	+0.19	49.227	+0.15
	1	4	1	51.731	51.640	−0.18	51.770	+0.08
	2	2	2	68.349	68.455	+0.16	68.361	+0.02
	1	3	2	70.060	69.931	−0.18	70.015	−0.06
	2	1	3	89.946	89.999	+0.06	89.837	−0.12
	1	2	3	90.636	90.553	−0.09	90.602	−0.04
	2	0	4	113.873	113.779	−0.08	113.656	−0.19
	1	1	4	113.279	113.336	+0.06	113.532	+0.22
	1	0	5	138.080	138.113	+0.02	138.804	+0.52
F	2	5	0	40.167	40.158	−0.02	40.177	+0.02
	2	4	1	58.627	58.550	−0.13	58.864	+0.40
	1	5	1	61.978	61.779	−0.32	62.144	+0.27
	2	3	2	79.689	79.687	−0.01	79.893	+0.26
	1	4	2	80.974	81.722	+0.92	82.284	+1.62
	2	2	3	103.289	103.302	+0.01	103.264	−0.02
	1	3	3	104.983	104.375	−0.58	104.767	−0.21
	2	1	4	128.975	129.130	+0.12	128.980	+0.01
	1	2	4	129.533	129.403	−0.10	129.592	+0.05
	2	0	5	157.117	156.902	−0.14	157.034	−0.05
	1	1	5	156.288	156.470	+0.12	156.759	+0.30
	1	0	6	185.139	185.238	+0.05	186.269	+0.61

Table 3

Numerical values of VOIP$_{2p}$'s [eV]

Atom	m	n	q	VOIP$_{2p}^{\text{spect}}$	VOIP$_{2p}^{\text{polyn}}$	Relative deviation [%]	VOIP$_{2p}^{\text{approx}}$	Relative deviation [%]
Be	1	1	0	5.957	5.870	−1.46	5.966	+0.15
	0	2	0	5.915	5.910	−0.08	5.807	−1.83
	0	1	1	14.247	14.333	+0.60	14.287	+0.28
B	2	1	0	8.295	8.235	−0.72	8.274	−0.25
	1	2	0	8.313	8.388	+0.90	8.288	−0.30
	0	3	0	8.909	8.855	−0.61	8.175	−8.24
	1	1	1	19.402	19.438	+0.19	19.379	−0.12
	0	2	1	18.503	18.441	−0.35	18.504	+0.01
	0	1	2	31.923	31.922	−0.00	31.938	+0.05
C	2	2	0	10.666	10.694	+0.27	10.675	+0.08
	1	3	0	10.818	10.671	−1.37	10.735	−0.77
	2	1	1	24.372	24.444	+0.30	24.378	+0.03
	1	2	1	23.645	23.804	+0.67	23.675	+0.13
	0	3	1	23.010	23.233	+0.97	22.846	−0.71
	1	1	2	39.824	39.860	+0.09	39.722	−0.26
	0	2	2	38.107	37.931	−0.46	38.130	+0.06
	0	1	3	56.475	56.417	−0.10	56.518	+0.08
N	2	3	0	13.183	13.090	−0.71	13.201	+0.13
	1	4	0	16.906	16.906	0.00	13.307	−21.29
	2	2	1	28.708	28.786	+0.27	28.753	+0.16
	1	3	1	28.027	27.988	−0.14	28.096	+0.25
	2	1	2	47.415	47.489	+0.16	47.411	−0.01
	1	2	2	46.012	46.126	+0.25	45.992	−0.04
	0	3	2	44.446	44.677	+0.52	44.446	0.00
	1	1	3	67.148	67.135	−0.02	66.992	−0.23
	0	2	3	64.632	64.380	−0.39	64.684	+0.08
	0	1	4	87.871	87.819	−0.06	88.027	+0.18
O	2	4	0	15.837	15.658	−1.13	15.851	+0.09
	1	5	0	15.684	15.745	+0.39	16.004	+2.04
	2	3	1	33.184	33.171	−0.04	33.253	+0.21
	1	4	1	32.621	32.374	−0.76	32.643	+0.06
	2	2	2	53.753	53.767	+0.03	53.760	+0.01
	1	3	2	52.378	52.318	−0.11	52.387	+0.02
	0	4	2	50.950	51.133	+0.36	50.887	−0.12
	2	1	3	77.370	77.370	0.00	77.373	+0.00
	1	2	3	75.350	75.355	+0.01	75.236	−0.15
	0	3	3	72.954	73.187	+0.32	72.974	+0.03
	1	1	4	101.297	101.264	−0.03	101.191	−0.10
	0	2	4	97.992	97.789	−0.21	98.166	+0.18
	0	1	5	126.099	126.128	+0.02	126.464	+0.29
F	2	5	0	18.648	18.651	+0.02	18.627	−0.11
	1	6	0	19.296	19.185	−0.57	18.826	−2.43
	2	4	1	37.757	37.921	+0.44	37.878	+0.32
	1	5	1	37.107	37.363	+0.69	37.314	+0.56
	2	3	2	60.121	60.247	+0.21	60.234	+0.19
	1	4	2	58.819	58.904	+0.14	58.907	+0.15

Table 3 (Continued)

Atom	m	n	q	$\text{VOIP}_{2p}^{\text{spect}}$	$\text{VOIP}_{2p}^{\text{polyn}}$	Relative deviation [%]	$\text{VOIP}_{2p}^{\text{approx}}$	Relative deviation [%]
	0	5	2	56.103	56.291	+0.33	57.454	+2.41
	2	2	3	85.770	85.636	−0.16	85.696	−0.09
	1	3	3	83.721	83.661	−0.07	83.606	−0.14
	0	4	3	82.829	81.896	−1.13	81.390	−1.74
	2	1	4	114.168	114.085	−0.07	114.263	+0.08
	1	2	4	111.455	111.491	+0.03	111.410	−0.04
	0	3	4	108.271	108.764	+0.45	108.431	+0.15
	1	1	5	142.310	142.246	−0.05	142.319	+0.01
	0	2	5	138.210	138.158	−0.04	138.577	+0.27
	0	1	6	171.161	171.344	+0.11	171.829	+0.39

Results

The experimental values VOIP can be determined for all the cases for which are known the values of E_{av} and E_{av}^{+} shown in papers [1, 3]. The required values of IP are listed in Moore's table [9]. Spectral values $\text{VOIP}_{s}^{\text{spect}}(m,n,Z)$ and $\text{VOIP}_{p}^{\text{spect}}(m,n,Z)$ for all available electron configurations of atoms and ions of the second and third periods with electron configurations $K(2)2s^{m}2p^{n}$ and $K(2)L(8)3s^{m}3p^{n}$ respectively, were enumerated:

$$\text{VOIP}_{s}^{\text{spect}}(m,n,Z) = E_{\text{av}}^{+}(m-1,n,Z) - E_{\text{av}}(m,n,Z) + \text{IP}(q), \qquad (4)$$

$$\text{VOIP}_{p}^{\text{spect}}(m,n,Z) = E_{\text{av}}^{+}(m,n-1,Z) - E_{\text{av}}(m,n,Z) + \text{IP}(q), \qquad (5)$$

where $q = Z - 2 - m - n$ and $q = Z - 10 - m - n$, for atoms and ions of the second and third periods, respectively. The values of $\text{VOIP}^{\text{spect}}$ obtained in this way were used for polynomic approximation. The optimum shape of individual polynomials was obtained by maximalization of the correlation coefficient as follows

$$\text{VOIP}_{\alpha}^{\text{polyn}}(m,n,Z) = C_{0}^{\alpha} + \sum_{i=1}^{N_i^{\alpha}} C_{ii}^{\alpha} m^{i} + \sum_{j=1}^{N_j^{\alpha}} C_{jj}^{\alpha} n^{j} +$$

$$+ \sum_{k=1}^{N_k^{\alpha}} C_{kk}^{\alpha} Z^{k} + \sum_{i=1}^{N_i^{\alpha}} \sum_{j=1}^{N_j^{\alpha}} C_{ij}^{\alpha} m^{i} n^{j} + \sum_{i=1}^{N_i^{\alpha}} \sum_{k=1}^{N_k^{\alpha}} C_{ik}^{\alpha} m^{i} Z^{k} + \sum_{j=1}^{N_j^{\alpha}} \sum_{k=1}^{N_k^{\alpha}} C_{jk}^{\alpha} n^{j} Z^{k}, \qquad (6)$$

where $\alpha = 2s$, $2p$, $3s$ or $3p$ and N_i^{α}, N_j^{α}, N_k^{α} are maximal degrees of variables m, n, and Z. Coefficients C_{rt}^{α} obtained by the method of least squares are shown in Table 1. Tables 2—5 show the values VOIP obtained by the analysis of atomic spectra ($\text{VOIP}^{\text{spect}}$) as well as the values obtained by eqn (*6*) ($\text{VOIP}^{\text{polyn}}$) and their relative deviations in per cents. For comparison purposes, also the values VOIP obtained by the method of *Anno* and *Sakai* [5, 8] using eqn (*3*) ($\text{VOIP}^{\text{approx}}$) and their relative deviations are shown. The distribution of deviations from the experimental points and some other statistical characteristics of individual approximations are shown in Table 6.

Table 4

Numerical values of VOIP$_{3s}$'s [eV]

Atom	m	n	q	VOIP$_{3s}^{\text{spect}}$	VOIP$_{3s}^{\text{polyn}}$	Relative deviation [%]	VOIP$_{3s}^{\text{approx}}$	Relative deviation [%]
Mg	2	0	0	7.644	7.611	−0.44	7.477	−2.18
	1	1	0	8.951	8.881	−0.78	8.942	−0.11
	1	0	1	15.030	15.077	+0.31	14.933	−0.64
Al	2	1	0	11.317	11.438	+1.07	11.280	−0.32
	1	2	0	12.361	12.394	+0.27	12.874	+4.15
	2	0	1	18.823	18.812	−0.06	18.892	+0.36
	1	1	1	20.153	20.220	+0.33	20.328	+0.87
	1	0	2	28.440	28.420	−0.07	28.329	−0.39
Si	2	2	0	14.946	14.798	−0.99	14.854	−0.62
	1	3	0	17.531	17.531	0.00	16.577	−5.44
	2	1	1	23.801	23.865	+0.27	23.928	+0.54
	1	2	1	25.110	25.126	+0.06	25.494	+1.53
	2	0	2	33.460	33.442	−0.06	33.550	+0.27
	1	1	2	34.848	34.735	−0.32	34.958	+0.31
	1	0	3	45.130	45.137	+0.02	44.969	−0.36
P	2	3	0	18.324	17.983	−1.86	18.199	−0.68
	2	2	1	28.557	28.928	+1.30	28.736	+0.63
	1	3	1	29.897	30.238	+1.14	30.431	+1.79
	2	1	2	39.725	39.671	−0.14	39.820	+0.24
	1	2	2	41.455	41.282	−0.42	41.358	−0.24
	2	0	3	51.354	51.362	+0.01	51.451	+0.19
	1	1	3	52.791	52.566	−0.42	52.831	+0.08
	1	0	4	65.007	65.083	+0.12	64.852	−0.24
S	2	4	0	20.729	20.824	+0.46	21.316	+2.83
	2	3	1	33.946	33.735	−0.62	33.316	−1.86
	2	2	2	46.094	46.282	+0.41	45.862	−0.50
	1	3	2	48.117	47.945	−0.37	47.529	−1.22
	2	1	3	58.942	59.002	+0.10	58.956	+0.02
	1	2	3	60.337	60.591	+0.42	60.465	+0.21
	2	0	4	72.500	72.434	−0.09	72.597	+0.13
	1	1	4	73.993	73.853	−0.19	73.949	−0.06
	1	0	5	88.029	88.112	+0.09	87.979	−0.06
Cl	2	5	0	25.271	24.754	−2.04	24.204	−4.22
	2	4	1	35.325	36.997	+4.73	37.667	+6.63
	2	3	2	52.624	51.270	−2.57	51.676	−1.80
	2	2	3	66.734	66.598	−0.20	66.232	−0.75
	1	3	3	67.525	67.356	−0.25	67.871	+0.51
	2	1	4	81.250	82.007	+0.60	81.335	−0.23
	1	2	4	82.914	82.784	−0.16	82.817	−0.12
	2	0	5	96.700	96.523	−0.18	96.986	+0.30
	1	1	5	98.254	98.735	+0.49	98.310	+0.06
	1	0	6	114.270	114.076	−0.17	114.350	+0.07

Table 5

Numerical values of VOIP$_{3p}$'s [eV]

Atom	m	n	q	VOIP$^{\text{spect}}_{3p}$	VOIP$^{\text{polyn}}_{3p}$	Relative deviation [%]	VOIP$^{\text{approx}}_{3p}$	Relative deviation [%]
Mg	1	1	0	4.523	4.529	+0.13	4.476	−1.05
	0	2	0	4.901	4.968	+1.36	5.102	+4.11
	0	1	1	10.602	10.606	+0.03	10.530	−0.68
Al	2	1	0	5.977	5.725	−3.77	5.723	−4.25
	1	2	0	6.411	6.645	+3.65	6.723	+4.86
	1	1	1	13.483	13.729	+1.82	13.599	+0.86
	0	2	1	14.203	13.859	−2.43	14.063	−0.99
	0	1	2	21.770	21.706	−0.30	21.618	−0.70
Si	2	2	0	7.772	7.761	−0.14	7.858	+1.11
	1	3	0	9.314	8.790	−5.62	8.805	−5.46
	2	1	1	16.322	16.304	−0.11	16.183	−0.85
	1	2	1	16.626	16.898	+1.63	17.020	+2.37
	0	3	1	16.893	17.683	+4.68	17.432	+3.19
	1	1	2	25.981	26.204	+0.86	26.024	+0.17
	0	2	2	26.365	26.035	−1.25	26.326	−0.15
	0	1	3	36.263	36.105	−0.44	36.009	−0.70
P	2	3	0	9.710	9.278	−4.45	9.828	+1.22
	1	4	0	11.534	11.534	0.00	10.723	−7.03
	2	2	1	19.123	19.330	+1.08	19.492	+1.93
	1	3	1	19.943	20.118	+0.87	20.277	+1.68
	2	1	2	30.121	30.109	−0.04	29.946	−0.58
	1	2	2	30.292	30.414	+0.40	30.620	+1.09
	0	3	2	31.501	30.958	−1.72	30.870	−2.00
	1	1	3	41.750	41.956	+0.49	41.753	+0.01
	0	2	3	41.627	41.498	−0.31	41.892	+0.64
	0	1	4	53.967	53.803	−0.30	53.703	−0.49
S	2	4	0	11.602	11.917	+2.71	11.635	+0.28
	1	5	0	12.351	12.527	+1.43	12.478	+1.02
	2	3	1	22.286	22.267	−0.08	22.638	+1.58
	1	4	1	24.819	23.800	−4.11	23.370	−5.84
	2	2	2	34.339	34.138	−0.58	34.430	+0.27
	1	3	2	34.434	35.077	+1.87	35.052	+1.80
	2	1	3	47.231	47.166	−0.14	47.011	−0.47
	1	2	3	47.187	47.193	+0.01	47.523	+0.71
	0	3	3	46.654	47.887	+2.64	47.610	+2.05
	1	1	4	60.789	60.983	+0.32	60.784	−0.01
	0	2	4	60.843	60.247	−0.98	60.761	−0.13
	0	1	5	74.825	74.801	−0.03	74.700	−0.17
Cl	2	5	0	13.709	13.370	−2.48	13.277	−3.15
	2	4	1	25.278	26.321	+4.13	25.619	+1.35
	1	5	1	23.763	24.437	+2.83	26.299	+10.67
	2	3	2	38.552	38.864	+0.81	38.750	+0.51
	1	4	2	42.577	40.198	−5.59	39.320	−7.65
	2	2	3	52.709	52.187	−0.99	52.670	−0.08
	1	3	3	52.662	53.667	+1.91	53.130	+0.89
	2	1	4	67.708	67.476	−0.34	67.379	−0.49
	1	2	4	67.496	67.234	−0.39	67.729	+0.35
	0	3	4	68.051	68.470	+0.62	67.654	−0.58
	1	1	5	82.887	83.287	+0.48	83.118	+0.28
	0	2	5	82.835	82.281	−0.67	82.932	+0.12
	0	1	6	98.904	99.097	+0.20	99.000	+0.10

Table 6

Measure of accuracy of the fitting

Error [%] Distribution[a]	2s		2p		3s		3p	
	polyn[b]	approx[c]	polyn[b]	approx[c]	polyn[b]	approx[d]	polyn[b]	approx[d]
0.0 – 0.1	19	15	19	20	10	6	6	4
0.1 – 0.3	14	18	14	24	10	11	7	8
0.3 – 0.5	6	6	9	2	10	6	8	4
0.5 – 1.0	6	5	11	3	4	8	8	12
1.0 – 1.5	0	0	3	0	4	1	4	6
1.5 – 2.0	0	1	0	2	1	4	5	5
2.0 – 3.0	0	0	0	3	2	2	5	2
3.0 – 4.0	0	0	0	0	0	0	2	2
4.0 – 5.0	0	0	0	0	1	2	4	3
> 5.0	0	0	0	2	0	2	2	5
Total number of experimental points	45	45	56	56	42	42	51	51
Degrees of freedom	27	36	32	46	19	33	33	41
Maximal deviation [%]	0.91	1.62	1.46	21.29	4.73	6.63	5.62	10.67
Standard deviation [eV]	0.222	0.305	0.361	0.638	0.796	0.858	0.850	1.143
Correlation coefficient	0.999992	0.999980	0.999989	0.999899	0.999900	0.999822	0.999900	0.999561

a) Numbers of points in given error range.
b) This work.
c) Ref. [6].
d) Ref. [8].

From the results it is evident that the approximative expressions of VOIP suggested by us fit better in the spectral values of VOIP in comparison with the approximation made by Anno and Sakai. The obtained polynomials are applicable in semiempirical methods for calculating the electronic structure of molecules.

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