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Department of Chemistry, Columbia University, New York, New York 10027

Valence Orbital Ionization Potentials from Atomic Spectral Data

By

Harold Basch, Arlen Viste*, and **Harry B. Gray**

Average Energy of Configuration Valence Orbital Ionization Potentials (VOIPs) are reported for the elements H through Kr in various configurations and for many states of ionization. For the lighter elements the isoelectronic series are fitted to a quadratic equation, VOIP $(q) = Aq^2 + Bq + C$. The significance of the A, B, and C parameters is discussed.

Über die Konfiguration gemittelte Ionisierungsenergien der Valenzorbitale (VOIP's) werden für verschiedene Konfigurationen und Ionisierungsstufen der Elemente H bis Kr angegeben. Bei den leichteren Elementen werden die isoelektronischen Reihen durch Ausgleichsparabeln dargestellt, VOIP $(q) = Aq^2 + Bq + C$ (q = Ladung), und die Parameter A, B und C diskutiert.

Pour plusieurs configurations et états d'ionisation des éléments H jusqu'à Kr, nous présentons les potentiels d'ionisation, moyennés pour chaque configuration, des orbitales de valence (VOIPs). Pour les éléments légers, les séries isoélectroniques sont représentées par des équations VOIP $(q) = Aq^2 + Bq + C$. Les paramètres A, B et C sont discutés.

Introduction

In semi-empirical molecular orbital (MO) methods, the diagonal Hamiltonian matrix elements are usually identified with Valence State Ionization Energies (VSIEs) [*22*] or Valence Orbital Ionization Potentials (VOIPs) [*2, 1*]. Available atomic spectral data [*15*] invariably serve as the source of these energies. The VSIE of an electron in a particular orbital represents the energy needed to remove that electron from an atom in the corresponding valence state. By "valence state" is meant a (non-stationary) state of the atom in which the electrons occupy particular individual orbitals, with definite space but random spin orientations [*10, 14*]. Such a valence state is conceptually useful for a valence bond discussion of a molecule in terms of localized electron-pair bonds with suitable directional characteristics. In a molecular orbital treatment, on the other hand, imposing particular directional characteristics on the starting atomic orbitals through prior hybridization seems inappropriate, or, at least, unnecessary. It is common to analyze a molecular orbital in terms of the (non-integral) occupation numbers of the ordinary atomic orbitals from which the molecular orbital is built up [*16*]. In such a case, it seems reasonable to make use of VOIPs, since they refer to electrons with random spin and space orientations within a given configuration [*1, 2*].

As a further refinement in some calculations [*1, 2, 21*] an iterative process approximating SCF theory is carried out involving the VOIPs as functions of the charge and configuration on the individual atoms. This requires extensive tabulation of VOIPs as a function of ionization from a specified orbital for different

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* Present address: Augustana College, Sioux Falls, South Dakota.

configurations, so as to adequately represent fractional populations in two (or more) partially occupied levels simultaneously.

We have therefore computed Average Energies of Configurations (E_{av}) as defined by SLATER [20], and derived from them a set of VOIPs for the elements hydrogen through krypton in various configurations and for many stages of ionization. A detailed account of the method of calculation has been given elsewhere [1,2].*

Results

For the elements hydrogen through argon the VOIPs corresponding to ionization of an s or p electron from the isoelectronic series $s^m p^n$ (where m and n are integers consistent with the Pauli Principle) have been fitted by a least squares method to a quadratic power series expansion of the form, VOIP $(q) = Aq^2 + Bq + C$, where q is the charge. C therefore corresponds to the VOIP of the neutral atom which is considered the zeroth member of the series. The fitting for each series was begun with as many points (up to six stages of ionization) as were available from the atomic spectral data. Subsequently, any point off the computed curve by more than two standard deviations** was rejected and the points refitted. The final A, B, and C parameters in units of 1000 cm^{-1} are set out in Tab. 1.

Previous investigators have extrapolated to ground- and excited-state electron affinities [3, 9, 17] along isoelectronic series from the equation, $I\,(Z) = \alpha Z^2 + \beta Z + \gamma$, where Z is the atomic number and $I\,(Z)$ the corresponding ionization potential. The parameters α, β, and γ are related to the A, B, and C by

$$\begin{array}{ll} \alpha = A & A = \alpha \\ \beta = B - 2\,Z_0 A & B = 2\,Z_0\alpha + \beta \\ \gamma = C - BZ_0 + AZ_0^2 & C = \alpha Z_0^2 + \beta Z_0 + \gamma \end{array}$$

where Z_0 is the atomic number of the zeroth member of a series. Electron affinities derived by this and similar methods have been found to be in excellent agreement with theoretically calculated and experimentally observed values [6, 7, 8]. Other investigators [12] have used similar extrapolation formulas but with a greater number of variable parameters. The generally limited amount of accurate experimentally observed term energies, however, makes the latter formulas infeasible [8].

The VOIPs in an isoelectronic series are expressed as an ionization potential plus a sum of Slater-Condon parameters of the same type [20]. ROHRLICH [18] found that for second-row atoms the Slater-Condon parameters in an isoelectronic series have a linear Z dependence. Since a quadratic representation of ionization potentials is found to give good results, it is reasonable to assume that a quadratic representation for the VOIPs will be adequate. This assumption is supported by the present investigation.

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* Calculations using average energy of configuration (E_{av}) valence orbital ionization potentials are outlined in Appendix 8-B of [1]. Although these ionization potentials are not valence state ionization energies as defined in [10, 14], the old abbreviation VSIE was retained. We simply suggest the abbreviation VOIP for ionization potentials obtained from E_{av} values, to distinguish them from those obtained by other methods.

** The standard deviation is defined as $\left[\frac{\sum_i D_i^2}{v-1}\right]^{\frac{1}{2}}$ where D_i is the individual deviation and v is the number of points.

Table 1. *VOIP Isoelectronic Fit Parameters*[a]

Number of Electrons	Configuration	Electron	Standard Deviation	*A*[b]	*B*	*C*
1	$1s$	$1s$	0.0	109.84	219.2	109.7
2	$1s^2$	$1s$	0.1	109.82	301.7	198.4
2	$1s\,2p$	$1s$	0.1	109.96	386.8	357.85
3	$1s^2\,2p$	$1s$	0.1	110.15	467.2	524.8
1	$2s$	$2s$	0.0	27.48	54.8	27.4
3	$1s^2\,2s$	$2s$	0.1	27.62	76.0	43.4
4	(He) $2s^2$	$2s$	0.1	27.64	100.3	75.1
4	(He) $2s\,2p$	$2s$	0.3	27.76	81.3	47.9
5	(He) $2s^2\,2p$	$2s$	0.1	27.82	120.6	113.4
5	(He) $2s\,2p^2$	$2s$	0.3	27.91	119.1	122.25
6	(He) $2s^2\,2p^2$	$2s$	0.2	27.95	141.6	156.6
6	(He) $2s\,2p^3$	$2s$	0.4	28.00	141.2	171.0
7	(He) $2s^2\,2p^3$	$2s$	0.2	28.16	162.2	206.2
7	(He) $2s\,2p^4$	$2s$	0.1	28.05	163.3	226.0
8	(He) $2s^2\,2p^4$	$2s$	0.3	27.95	184.6	260.8
9	(He) $2s^2\,2p^5$	$2s$	0.5	28.07	205.7	323.6
10	(He) $2s^2\,2p^6$	$2s$	0.1	28.29	227.0	390.9
1	$2p$	$2p$	0.0	27.48	54.8	27.4
2	$1s\,2p$	$2p$	0.1	27.52	57.8	28.6
3	$1s^2\,2p$	$2p$	0.2	27.74	59.1	28.4
4	(He) $2s\,2p$	$2p$	0.2	27.72	97.6	79.8
4	(He) $2p^2$	$2p$	0.4	27.57	76.1	45.35
5	(He) $2s^2\,2p$	$2p$	0.2	27.78	102.4	66.75
5	(He) $2s\,2p^2$	$2p$	0.3	28.02	96.1	67.0
5	(He) $2p^3$	$2p$	0.1	27.25	94.0	61.4
6	(He) $2s^2\,2p^2$	$2p$	0.3	27.95	118.2	85.8
6	(He) $2s\,2p^3$	$2p$	0.4	28.03	111.95	86.9
6	(He) $2p^4$	$2p$	0.1	28.06	105.4	88.1
7	(He) $2s^2\,2p^3$	$2p$	0.2	28.16	133.2	106.4
7	(He) $2s\,2p^4$	$2p$	2.1	30.01	114.0	129.4
8	(He) $2s^2\,2p^4$	$2p$	0.4	27.94	149.75	127.4
8	(He) $2s\,2p^5$	$2p$	0.1	27.76	145.2	126.4
9	(He) $2s^2\,2p^5$	$2p$	0.4	27.93	165.5	150.4
9	(He) $2s\,2p^6$	$2p$	0.8	28.22	157.7	155.1
10	(He) $2s^2\,2p^6$	$2p$	0.3	28.25	180.2	173.9
11	(Ne) $3s$	$3s$	0.6	13.18	68.0	41.0
12	(Ne) $3s^2$	$3s$	0.5	13.13	78.2	61.25
12	(Ne) $3s\,3p$	$3s$	0.5	13.14	78.6	71.7
13	(Ne) $3s^2\,3p$	$3s$	0.8	13.15	89.0	90.8
13	(Ne) $3s\,3p^2$	$3s$	0.0[c]	9.50	103.6	89.4
14	(Ne) $3s^2\,3p^2$	$3s$	1.3	13.08	99.9	119.6
14	(Ne) $3s\,3p^3$	$3s$	2.0	11.12	118.2	111.2
15	(Ne) $3s^2\,3p^3$	$3s$	0.3	14.27	106.7	151.4
16	(Ne) $3s^2\,3p^4$	$3s$	0.3	12.23	124.0	166.7
17	(Ne) $3s^2\,3p^5$	$3s$	0.2	13.70	126.7	203.8
18	(Ne) $3s^2\,3p^6$	$3s$	0.3	13.24	138.6	235.6
11	(Ne) $3p$	$3p$	0.7	13.33	49.4	23.9
12	(Ne) $3s\,3p$	$3p$	0.6	13.21	60.5	36.0
12	(Ne) $3p^2$	$3p$	0.6	12.05	61.9	41.3
13	(Ne) $3s^2\,3p$	$3p$	0.6	13.29	71.1	47.85
13	(Ne) $3s\,3p^2$	$3p$	0.6	12.44	75.65	42.8

Table 1 (continued)

Number of Electrons	Configuration	Electron	Standard Deviation	A^b	B	C
14	(Ne) $3s^2\,3p^2$	$3p$	0.3	13.02	81.7	62.5
14	(Ne) $3s\,3p^3$	$3p$	2.8	8.82	110.7	19.4
14	(Ne) $3s^2\,3p\,4s$	$3p$	0.9	13.36	86.3	90.5
15	(Ne) $3s^2\,3p^3$	$3p$	0.0[c]	15.25	83.9	81.6
15	(Ne) $3s\,3p^4$	$3p$	1.3	14.25	83.85	100.1
15	(Ne) $3s^2\,3p^2\,4s$	$3p$	0.7	14.63	91.3	114.8
16	(Ne) $3s^2\,3p^4$	$3p$	0.7	13.17	98.5	93.4
16	(Ne) $3s\,3p^5$	$3p$	0.7	13.88	94.9	99.7
16	(Ne) $3s^2\,3p^3\,4s$	$3p$	0.4	13.57	102.4	131.6
17	(Ne) $3s^2\,3p^5$	$3p$	0.4	13.49	106.3	110.4
17	(Ne) $3s\,3p^6$	$3p$	0.0[c]	13.40	106.4	116.0
17	(Ne) $3s^2\,3p^4\,4s$	$3p$	0.2	13.36	112.0	153.3
18	(Ne) $3s^2\,3p^6$	$3p$	0.1	13.36	116.6	127.5
18	(Ne) $3s^2\,3p^5\,4s$	$3p$	0.6	13.39	121.5	175.3
19	(Ar) $3d$	$3d$	0.1	13.10	24.5	12.2
11	(Ne) $4s$	$4s$	0.3	7.47	29.0	15.5
12	(Ne) $3s\,4s$	$4s$	0.1	7.67	32.2	19.8
13	(Ne) $3s^2\,4s$	$4s$	0.2	7.65	36.1	22.85
14	(Ne) $3s^2\,3p\,4s$	$4s$	0.8	7.79	39.7	25.15
15	(Ne) $3s^2\,3p^2\,4s$	$4s$	1.0	9.30	38.5	31.8
16	(Ne) $3s^2\,3p^3\,4s$	$4s$	0.2	7.82	45.35	30.1
17	(Ne) $3s^2\,3p^4\,4s$	$4s$	0.3	8.00	48.0	32.1
18	(Ne) $3s^2\,3p^5\,4s$	$4s$	0.4	7.99	51.9	33.6
19	(Ar) $4s$	$4s$	0.4	8.09	53.5	34.7

[a] All numbers in 1000 cm^{-1}.

[b] The theoretical values for hydrogenic functions are: $n = 1$, $A = 109.7$; $n = 2$, $A = 27.4$; $n = 3$, $A = 12.2$; $n = 4$, $A = 6.9$.

[c] Only three points.

Based on the virial theorem, Slater [*19*] suggested that for wave functions with effective nuclear charges $(Z - s_i)$ and principal quantum numbers n_i the total energy of an atom with N electrons be written as $-\sum_{i=1}^{N} \frac{(Z - s_i)^2}{n_i^2}$ Rydbergs, where the s_i are screening constants. The coefficient of Z^2 in such an expansion is therefore $-\sum_{i=1}^{N} \frac{1}{n_i^2}$. As pointed out by Jørgensen [*13*], a quadratic representation of ionization potentials can be considered as the difference between two such isoelectronic series differing in one electron. The theoretical value of A (or α) is then $109{,}700 \times \frac{1}{n^2}\ \text{cm}^{-1}$, independent of the number of other electrons, their distribution (configuration), or the subshell (λ-quantum number) of the electron to be ionized. This is expected for average of configuration ionization potentials (VOIPs). Examination of Tab. 1 shows remarkably good agreement with the simple hydrogenic values. Deviations are seen to increase, however, proportional to the total number of electrons. This is in accord with the observation that the optimum value of n in the orbital exponent is n^* given by $n^* = n - \delta$ where δ is another screening constant [*19*]. It also appears from Tab. 1 that for ionization from the same orbital for different isoelectronic series of the same number of electrons, the B parameters are approximately equal. This can be attributed to the similarity in screening constants [*4, 5, 19*] for s and p electrons of the same principal quantum number n.

For the first-row transition elements, where there is an insufficient number of points for an isoelectronic analysis, the VOIPs have been smoothed by subjecting the available data across the transition series to a least squares fit for a given charge, s, and p character. The fit was quadratic if not more than two VOIPs were missing or omitted, and linear otherwise. Again the criterion of two standard deviations was invoked. The resulting and extrapolated VOIPs were then represented quadratically, VOIP $(q) = A' q^2 + B' q + C'$ (q is the charge) for ionization of an electron from a given orbital, where for a given curve, configurations for successive q's differ only in the number of d electrons. For some VOIP curves the problem of having insufficient points to fully determine the curve arose. The procedure followed was to take over A' from a related curve (ionization of the same electron) and for the $d^{v-2}p^2$ curve for $4p$, both A' and B'. The resultant A', B', and C' parameters are tabulated in Tab. 2. These are, of course, distinct from the isoelectronic A, B, and C reported for the lighter elements.

Finally, for the Ga to Kr VOIPs set out in Tab. 3 the fitting was done as outlined above for the transition elements.

The accuracy of the derived VOIPs hinges on many factors. The Russell-Saunders scheme is itself approximate. The methods of evaluating E_{av}, being based on the Russell-Saunders scheme, ignore possible complications arising from configuration interaction or spin-orbit coupling.

HINZE and JAFFÉ [*11*] concluded, after a detailed study of Slater-Condon parameters, that the uncertainties involved in fitting the Slater-Condon parameters for separate configurations are at least as great as the uncertainties contained in the further approximation of mixing configurations, although the resultant parameters may differ substantially. The E_{av}s calculated from an incomplete set of observed terms are heavily dependent on the numerical values of the Slater-Condon parameters. Ideally, all E_{av}s calculated for a given configuration from different multiplets should be identical. In practice they had to be averaged since (and especially for the transition metals) differences of a few thousand cm^{-1} were common. In some cases all of the known terms had nearly the same dependence on some particular Slater-Condon parameter. In such cases, both the Slater-Condon parameter and the E_{av} are probably less accurate than otherwise.

The tabulated VOIPs are also subject to the uncertainties in the reported [*8, 15*] ionization potentials and term distances. It is known that very reliable experimental values are available only for the first few members of a sequence. The problem is not an experimental one, but rather in assigning spectra. Incorrect identification of the observed spectral lines also affects strongly the Slater-Condon parameters which are derived by a least squares fit of the reported spectra [*11*].

Although a least squares regression does allow a different weighting factor to be introduced for each member of a series, and the variable reliability of the input data indicates such a procedure should be adopted, the weighting factor was taken to be *one* for all points. The alternative procedure of rejecting all points in variance

Table 2. *VOIP Curves for First-Row Transition Metals*[a]

VOIP curve[b]	Ti	V	Cr	Mn	Fe	Co	Ni
1	17.15	15.8	14.75	14.1	13.8	13.85	14.2
2	18.45	14.0	9.75	5.5	13.8	13.85	14.2
3	18.45	14.0	9.75	5.5	13.8	13.85	14.2
4	9.3	8.55	8.05	7.6	7.35	7.25	7.35
A' 5	9.3	8.55	8.05	7.6	7.35	7.25	7.35
6	9.3	8.55	8.05	7.6	7.35	7.25	7.35
7	7.8	7.45	7.25	7.2	7.3	7.55	7.95
8	7.8	7.45	7.25	7.2	7.3	7.55	7.95
9	7.8	7.45	7.25	7.2	7.3	7.55	7.95
1	60.85	68.0	74.75	80.8	86.2	91.15	95.5
2	77.85	87.0	95.95	105.0	101.5	106.25	110.7
3	76.75	87.3	96.95	106.0	101.9	105.55	108.2
4	50.4	54.15	57.55	60.9	63.85	66.65	69.05
B' 5	58.5	62.95	66.85	70.3	73.05	75.25	77.05
6	55.0	57.55	60.45	63.8	67.35	71.35	75.65
7	35.6	45.45	47.55	49.3	50.8	51.95	52.85
8	48.9	50.85	52.85	55.2	57.8	60.65	63.75
9	48.9	50.85	52.85	55.2	57.8	60.65	63.75
1	27.4	31.4	35.1	38.6	41.9	44.8	47.6
2	44.6	51.4	57.9	64.1	70.0	75.6	80.9
3	55.4	61.4	67.7	74.3	81.2	88.4	95.9
4	48.6	51.0	53.2	55.3	57.3	59.1	60.8
C' 5	57.2	60.4	63.3	65.9	68.3	70.5	72.3
6	66.0	70.6	74.7	78.3	81.4	84.0	86.0
7	26.9	27.7	28.4	29.2	29.9	30.7	31.4
8	35.9	36.8	37.8	38.8	39.7	40.7	41.6
9	34.4	36.4	38.1	39.4	40.3	40.8	40.9

[a] Energies in 1000 cm^{-1}.

[b] The type of electron being ionized, and the configurations, are as follows for the nine VOIP curves. 1: d, d^v. 2: d, $d^{v-1}s$. 3: d, $d^{v-1}p$. 4: s, $d^{v-1}s$. 5: s, $d^{v-2}s^2$. 6: s, $d^{v-2}sp$. 7: p, $d^{v-1}p$. 8: p, $d^{v-2}p^2$. 9: p, $d^{v-2}sp$.

Table 3. *Valence Orbital Ionization Potentials for 4s, 4p, and 5s Electrons*[a]

Ionization Configuration[b]	$4s$ $(0 \rightarrow 1)$ $4s^2\,4p^v$	$4s$ $(1 \rightarrow 2)$ $4s^2\,4p^{v-1}$	$4p$ $(0 \rightarrow 1)$ $4s^2\,4p^v$	$4p$ $(1 \rightarrow 2)$ $4s^2\,4p^{v-1}$	$5s$ $(0 \rightarrow 1)$ $4s^2\,4p^{v-1}\,5s$	$5s$ $(1 \rightarrow 2)$ $4s^2\,4p^{v-2}\,5s$
Atom v						
Ga 1	103.2	(164.7)	47.4	—	23.5	—
Ge 2	122.8	201.2	60.9	127.5	25.7	66.3
As 3	144.8	234.9	74.1	(147.3)	27.7	74.1
Se 4	168.1	265.7	87.0	166.7	29.6	79.7
Br 5	(193.8)	(243.7)	99.6	185.5	31.4	83.0
Kr 6	221.7	319.0	111.8	204.0	32.9	84.0
Standard Deviation	2.4	6.8	0.8	1.5	0.5	1.1

[a] Energies in 1000 cm^{-1}.

[b] Values in parentheses are extrapolated.

with the computed value by more than two standard deviations was adopted. Hopefully, this eliminates incorrectly assigned spectral terms and Slater-Condon parameters, as well as numerical errors.

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