

Systematic determination of the Slater—Condon parameters of atoms and ions with $K(2)L(8)3s^m3p^n$ configurations

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Semiempirical values of the Slater—Condon parameters $F^2(3p, 3p)$ and $G^1(3s, 3p)$ for atoms from Mg to Cl with electron configuration $K(2)L(8)3s^m3p^n$ were determined from experimental atomic energy levels. The Slater—Condon parameters $F^0(3s, 3s)$, $F^0(3s, 3p)$, and $F^0(3p, 3p)$ were calculated using the Anno electron transfer equations $A^+ + A^+ \rightarrow A + A^{2+}$. The obtained semiempirical values of the Slater—Condon parameters are suitable for the use in semiempirical methods of calculation of electronic structure of molecules.

Из экспериментальных значений энергетических уровней атомов были определены полуэмпирические значения Слейтер—Кондоновских параметров $F^2(3p, 3p)$ и $G^1(3s, 3p)$ для атомов начиная с Mg до Cl с электронной конфигурацией $K(2)L(8)3s^m3p^n$. Слейтер—Кондоновские параметры $F^0(3s, 3s)$, $F^0(3s, 3p)$ и $F^0(3p, 3p)$ были рассчитаны с помощью уравнения Анно для реакции переноса электрона $A^+ + A^+ \rightarrow A + A^{2+}$. Полученные полуэмпирические значения Слейтер—Кондоновских параметров пригодны для использования в полуэмпирических методах расчета электронной структуры молекул.

Many works on semiempirical values of the Slater—Condon parameters based on central energy values of atomic terms have been published [1—14]. These parameters are of significant importance in semiempirical theories of atoms and molecules.

It is well known that the Slater theory of many-electron atoms is based on Russell—Saunders coupling approximation with a complete neglect of spin-orbital coupling and considering atoms as a single configuration. The routine semiempirical methods are based on LCAO MO approximation and therefore the atoms in molecules are considered in the same approximation as in the Slater's theory of atoms. The advantage of semiempirical methods as compared with the non-empirical theories consists mainly in the fact that they include directly such effects as electronic correlation, since they are using such approximation of monocentric integrals which reproduce the experimental characteristics of atomic spectroscopy to the maximum

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possible extent. Therefore, the Slater—Condon parameters for MO calculations must be used without any corrections with respect to the configuration interaction. The J structure of atomic energy levels is to be averaged since the spin-orbital splitting is neglected.

So far, atoms and ions with electron configurations $K(2)L(8)3s^m3p^n$ were studied only to a limited extent [7, 15]. *Hinze* and *Jaffé* [7] have determined semiempirical values of the Slater—Condon parameters for the elements of the third period with electron configurations $K(2)L(8)3s^m3p^n$. However, they considered simultaneously the energy levels of configurations $K(2)L(8)3s^23p^{n-2}$, $K(2)L(8)3s^13p^{n-1}$, and $K(2)L(8)3p^n$. In other words, they assumed that the values of the Slater—Condon parameters are equal in all these electron configurations. Furthermore they have not determined the Slater—Condon parameters $F^0(3s,3s)$, $F^0(3s,3p)$, and $F^0(3p,3p)$. Therefore, we have systematically evaluated the Slater—Condon parameters for atoms from Mg up to Cl.

Method and results

In the Slater theory of the many-electron atoms the energy of the given atomic term can be expressed in the form [10]

$$E^r = W^r + \sum_i B_i^r G_i, \quad (1)$$

where G_i are the Slater—Condon parameters, F^k or G^k , B_i^r are numerical coefficients and W^r is the constant term characterizing the electron configuration of the atom or ion. Averaged energy of the configuration can be expressed as follows

$$E_{av} = \sum_r C_r E^r = \sum_r C_r (W^r + \sum_i B_i^r G_i), \quad (2)$$

where C_r is the weight of the r -th term

$$C_r = \frac{(2S_r + 1)(2L_r + 1)}{\sum_r (2S_r + 1)(2L_r + 1)} \quad (3)$$

Experimental values $E_{av}^{(e)}$ are given by the relation

$$E_{av}^{(e)} = \sum_r C_r E_r^{(e)}, \quad (4)$$

where $E_r^{(e)}$ are spectral values of the energy levels of the corresponding atomic terms. Values of the Slater—Condon parameters G_i can be determined by the least squares method, minimizing the expression

$$F(G_i) = \sum_r C_r (E_r^{(e)} - W^r - \sum_i B_i^r G_i)^2 \quad (5)$$

with respect to G_i .

The values of coefficients B_i^r were reported by *Slater* [10]. The experimental values of energy levels of atomic terms were taken from *Moore's* tables [16] and averaged through the fine structure of J levels.

The obtained $E_{av}^{(e)}$ values and the Slater—Condon parameters $F^2(3p,3p)$ and $G^1(3s,3p)$ are listed in Table 1. Numerical values of $E_{av}^{(e)}$ depend on the selection of the reference state. In all cases, the ground state of an electroneutral atom is considered as the energy reference.

Table 1

Semiempirical values of E_{av} and the Slater-Condon parameters (eV)*

Atom	m	q	E_{av}	$F^2(3p,3p)$	$G^1(3s,3p)$	$F^0(3s,3s)$	$F^0(3s,3p)$	$F^0(3p,3p)$
Mg	2	0	0	0.000	—	—	7.386	—
	1	1	0	3.121	—	2.450	—	6.495
	0	2	0	7.171	—	—	—	5.914
	1	0	1	7.644	—	—	—	—
	0	1	1	12.072	—	—	—	—
Al	0	0	2	22.674	—	—	—	—
	2	1	0	0.007	—	—	8.834	8.185
	1	2	0	4.913	2.784	3.423	—	8.362
	2	0	1	5.984	—	—	9.620	—
	1	1	1	11.324	—	4.161	—	8.971
	0	2	1	17.274	—	—	—	7.878
	1	0	2	24.807	—	—	—	—
	0	1	2	31.477	—	—	—	—
Si	0	0	3	53.247	—	—	—	—
	2	2	0	0.395	3.158	—	10.164	9.703
	1	3	0	6.027	—	—	—	8.090
	2	1	1	8.167	—	—	11.047	10.586
	1	2	1	15.341	3.875	5.101	—	10.587
	0	3	1	23.558	—	—	—	9.433
	2	0	2	24.489	—	—	11.670	—
	1	1	2	31.968	—	5.594	—	11.209
	0	2	2	40.451	5.358	—	—	10.303
	1	0	3	57.949	—	—	—	—
P	0	1	3	66.816	—	—	—	—
	0	0	4	103.079	—	—	—	—
	2	3	0	1.402	3.875	—	11.573	11.029
	1	4	0	8.191	2.211	0.950	—	8.585
	2	2	1	11.111	4.411	—	12.902	12.270
	1	3	1	19.725	1.340	4.774	—	12.358
	2	1	2	30.235	—	—	13.058	12.774
	1	2	2	39.668	5.207	6.634	—	12.425
	0	3	2	49.622	1.647	—	—	11.871
	2	0	3	60.356	—	—	13.660	10.221
	1	1	3	69.960	—	6.875	—	13.377
	0	2	3	81.123	6.356	—	—	12.846
	1	0	4	111.710	—	—	—	—
	0	1	4	122.750	—	—	—	—
S	0	0	5	176.717	—	—	—	—
	2	4	0	0.589	4.512	—	—	13.753
	1	5	0	8.967	—	—	—	12.832
	2	3	1	12.192	5.076	—	14.172	13.300
	1	4	1	21.318	—	3.238	—	9.886
	2	2	2	34.477	5.529	—	14.243	14.167
	1	3	2	46.137	3.907	6.910	—	13.372
	2	1	3	68.816	—	—	15.051	14.916
	1	2	3	80.571	6.231	7.847	—	14.975
	0	3	3	94.255	2.946	—	—	14.432
	2	0	4	116.047	—	—	15.530	—
	1	1	4	127.758	—	8.105	—	15.395
	0	2	4	140.909	—	—	—	14.579
	1	0	5	188.547	—	—	—	—
0	1	5	201.751	—	—	—	—	
0	0	6	276.576	—	—	—	—	

Table 1 (Continued)

Atom	<i>m</i>	<i>n</i>	<i>q</i>	E_{av}	$F^2(3p,3p)$	$G^1(3s,3p)$	$F^0(3s,3s)$	$F^0(3s,3p)$	$F^0(3p,3p)$
Cl	2	5	0	0.055	—	—	—	10.728	11.851
	2	4	1	13.764	5.644	—	—	18.708	13.725
	1	5	1	25.326	—	4.046	—	—	19.142
	2	3	2	39.042	6.174	—	14.901	15.689	14.688
	1	4	2	49.089	—	—	—	—	10.451
	2	2	3	77.593	6.589	—	16.180	16.300	15.517
	1	3	3	91.665	6.196	9.475	—	16.968	15.291
	2	1	4	130.302	—	—	16.733	16.724	—
	1	2	4	144.327	7.337	9.117	—	16.853	15.996
	0	3	4	159.191	—	—	—	—	15.168
	2	0	5	197.810	—	—	17.600	—	—
	1	1	5	211.623	—	9.307	—	17.591	—
	0	2	5	227.042	—	—	—	—	16.790
	1	0	6	294.510	—	—	—	—	—
	0	1	6	309.876	—	—	—	—	—
	0	0	7	408.780	—	—	—	—	—

*1 eV = 1.6021 × 10⁻¹⁹ J.

The method described does not allow a direct determination of the Slater—Condon parameters $F^0(3s, 3s)$, $F^0(3s, 3p)$, and $F^0(3p, 3p)$ since in the expressions for energies of individual atomic terms of the given electron configuration these parameters are set up with equal coefficients. From the known values $E_{av}^{(e)}$, $F^2(3p, 3p)$, and $G^1(3s, 3p)$ it is possible, however, to determine them by means of the *Anno* formula for the electron transfer [17]



For the energy balance of such reactions the following relations can be obtained

$$2A^{(q+1)+(s^{m-1}, p^n)} \rightarrow A^{q+(s^m, p^n)} + A^{(q+2)+(s^{m-2}, p^n)},$$

$$\Delta E(s, s) = F^0(s, s),$$

$$2A^{(q+1)+(s^m, p^{n-1})} \rightarrow A^{q+(s^m, p^n)} + A^{(q+2)+(s^m, p^{n-2})},$$

$$\Delta E(p, p) = F^0(p, p) - \frac{2}{25} F^2(p, p), \quad (7)$$

$$A^{(q+1)+(s^{m-1}, p^n)} + A^{(q+1)+(s^m, p^{n-1})} \rightarrow A^{q+(s^m, p^n)} + A^{(q+2)+(s^{m-1}, p^{n-1})},$$

$$\Delta E(s, p) = F^0(s, p) - \frac{1}{6} G^1(s, p).$$

The values of the Slater—Condon parameters $F^0(3s, 3s)$, $F^0(3s, 3p)$, and $F^0(3p, 3p)$ for the elements of the third period calculated in this way are also listed in Table 1.

The calculated values of the Slater—Condon parameters can be used in semiempirical methods of calculations of electronic structure of molecules. From the values of the average energies of electron configurations of atoms, the valence orbital ionization potentials can be evaluated [18—21].

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