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Relationes

Physical Properties of Many-Electron Atomic Systems Evaluated from Analytical Hartree-Fock Functions

IX. Valence State Energies*

Jon Thorhallsson, Carolyn Fisk, and Serafin Fraga

Division of Theoretical Chemistry, Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

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The promotion energies, ionization potentials, electron affinities, and orbital electronegativities for the valence states of importance in atoms of the first two rows of the periodic system have been evaluated from analytical Hartree-Fock functions for the corresponding groundstates. The agreement with existing values, determined from experimental data, is very satisfactory.

Introduction

Valence state ionization potentials and electron affinities are used as input data in semiempirical calculations of polyatomic molecules. The values usually employed are those determined by Hinze and Jaffe [4] from experimental data.

The purpose of this paper is to report the values calculated for those quantities, as well as for orbital electronegativities and promotion energies, from existing analytical Hartree-Fock functions for the groundstate of the system under consideration.

Theoretical Formulation

The energy of a spectroscopic state of an atom can be expressed, according to Slater [7], by

$$W = \sum_i H_i + \sum_{i<j} \sum_k [a_{ij}^{(k)} F_{ij}^{(k)} - b_{ij}^{(k)} G_{ij}^{(k)} \delta(m_{si}, m_{sj})] , \tag{1}$$

where the summations over i, j extend over all the electrons in the system. H_i represents the one-electron (kinetic and nuclear attraction) energy of the i-th electron, and the so-called Slater-Condon parameters, $F^{(k)}$ and $G^{(k)}$, are defined by

$$\begin{aligned} F_{ij}^{(k)} &= F^k(n_i l_i, n_j l_j) \\ &= \int\int (r_<^k / r_>^{k+1}) R_{n_i l_i}^2(r_1) R_{n_j l_j}^2(r_2) r_1^2 r_2^2 \, dr_1 \, dr_2 , \\ G_{ij}^{(k)} &= G^k(n_i l_i, n_j l_j) \\ &= \int\int (r_<^k / r_>^{k+1}) R_{n_i l_i}(r_1) R_{n_j l_j}(r_1) R_{n_j l_j}(r_2) R_{n_i l_i}(r_2) r_1^2 r_2^2 \, dr_1 \, dr_2 , \end{aligned}$$

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where R_{nl} represents the radial function of the atomic orbital denoted by the quantum numbers n, l. The parameters a_{ij}, b_{ij} depend only on the quantum numbers l, m_l of the orbitals involved; the corresponding values have veen tabulated by Condon and Shortley [2].

Eq. (1) applies to a true spectroscopic state. For the interactions between valence-shell electrons in a valence state, however, it is customary to replace $\delta(m_{s_i}, m_{s_j})$ by 1/2, on the basis that a valence state may be assumed to represent an average of the two possibilities that exist regarding the spins of the two electrons considered.

The quantities considered in this work – promotion energies (P), ionization potentials (I), electron affinities (E), and orbital electronegativities (χ_M) – are

Table 1. *Promotion energies (in eV)*

Valence electrons	Valence state	C^+	Si^+				
3	spp	7.58	6.55				
	ppp	17.64	14.99				
	$didi\pi$	6.01	5.50				
	$di\pi\pi$	12.61	10.77				
	trtrtr	5.48	5.15				
	$trtr\pi$	10.23	8.90				
	tetete	8.92	7.87				
		C	N^+	Si	P^+		
4	sppp	8.41	15.17	6.69	9.09		
	$didi\pi\pi$	7.00	13.33	5.76	7.86		
	$trtrtr\pi$	6.52	12.72	5.45	7.46		
	tetetete	6.29	12.41	5.29	7.25		
		C^-	N	O^+	Si^-	P	S^+
3	s^2ppp	0.94	1.45	1.91	0.74	1.01	1.17
	sp^2pp	10.54	15.53	20.47	8.07	11.14	14.10
	$di^2di\pi\pi$	5.74	8.49	11.19	4.40	6.08	7.63
	$didi\pi^2\pi$	9.36	13.83	18.37	7.31	10.03	12.71
	$tr^2trtr\pi$	6.81	10.08	13.35	5.29	7.27	9.17
	$trtrtr\pi^2$	8.96	13.27	17.66	7.06	9.65	12.25
	$te^2tetete$	7.25	10.74	14.25	5.67	7.77	9.82
		N^-	O	F^+	P^-	S	Cl^+
2	s^2p^2pp	0.38	0.55	0.70	0.26	0.38	0.42
	sp^2p^2p	14.08	19.20	24.38	10.05	13.06	16.00
	$di^2di^2\pi\pi$	0.38	0.55	0.70	0.26	0.38	0.41
	$di^2di\pi^2\pi$	7.23	9.87	12.54	5.16	6.72	8.21
	$didi\pi^2\pi^2$	12.64	17.26	22.02	9.12	11.79	14.47
	$tr^2tr^2tr\pi$	4.95	6.76	8.59	3.53	4.60	5.61
	$tr^2trtr\pi^2$	8.87	12.12	15.44	6.37	8.27	10.13
	te^2te^2tete	6.87	9.39	11.95	4.93	6.40	7.83
		O^-	F	S^-	Cl		
1	p	0.00	0.00	0.00	0.02		
	s	18.42	23.92	12.40	15.43		

Table 2. *Valence state ionization potentials, I_v, and electron affinities, E_v, and orbital electronegativities, χ_M (in eV)*[a]

System	Valence state	Orbital	I_v	E_v	χ_M
C (4)	sppp	s	20.01 (21.01)	8.02 (8.91)	28.04 (29.92)
		p	9.95 (11.27)	−1.58 (0.34)	8.37 (11.61)
	$\mathrm{didi}\pi\pi$	σ	16.40 (17.42)	1.81 (3.34)	18.21 (20.77)
		π	9.80 (11.19)	−1.81 (0.10)	7.99 (11.29)
	$\mathrm{trtrtr}\pi$	σ	14.50 (15.62)	0.26 (1.95)	14.76 (17.58)
		π	9.75 (11.16)	−1.89 (0.03)	7.86 (11.19)
	tetetete		13.41 (14.61)	−0.42 (1.34)	13.00 (15.95)
N (3)	$\mathrm{s^2ppp}$		15.15 (13.94)	−1.08 (0.84)	14.07 (14.78)
	$\mathrm{sp^2pp}$	s	31.83 (26.92)	12.99 (14.05)	44.82 (40.98)
		p	16.38 (14.42)	−0.70 (2.54)	15.67 (16.96)
	$\mathrm{di^2di}\pi\pi$	σ	27.17 (23.91)	5.95 (7.45)	33.12 (31.35)
		π	15.76 (14.18)	−0.89 (1.66)	14.87 (15.84)
	$\mathrm{didi}\pi^2\pi$	σ	25.80 (22.10)	4.45 (6.84)	30.25 (28.94)
		π	16.23 (14.11)	−0.95 (2.14)	15.27 (16.25)
	$\mathrm{tr^2trtr}\pi$	σ	23.51 (20.06)	2.98 (5.14)	26.49 (25.74)
		π	15.90 (14.12)	−0.94 (1.78)	14.96 (15.90)
	$\mathrm{trtrtr}\pi^2$		22.97 (19.72)	2.44 (4.92)	25.21 (24.63)
	$\mathrm{te^2tetete}$		21.66 (18.93)	1.72 (4.15)	23.38 (23.08)
O (2)	$\mathrm{s^2p^2pp}$		16.44 (17.28)	0.01 (2.01)	16.45 (19.29)
	$\mathrm{sp^2p^2p}$	s	35.09 (36.07)	18.66 (18.44)	53.75 (54.51)
		p	16.35 (18.53)	0.24 (3.40)	16.59 (21.93)
	$\mathrm{di^2di^2}\pi\pi$		16.44 (17.28)	0.01 (2.01)	16.45 (19.29)
	$\mathrm{di^2di}\pi^2\pi$	σ	29.98 (30.17)	9.33 (10.23)	39.31 (40.40)
		π	16.40 (17.91)	0.12 (2.71)	16.52 (20.61)
	$\mathrm{didi}\pi^2\pi^2$		27.66 (28.71)	7.51 (9.51)	35.17 (38.22)
	$\mathrm{tr^2tr^2tr}\pi$	σ	26.40 (26.65)	6.22 (7.49)	32.62 (34.14)
		π	16.41 (17.70)	0.08 (2.47)	16.50 (20.17)
	$\mathrm{tr^2trtr}\pi^2$		25.36 (26.14)	5.44 (7.32)	30.80 (33.47)
	$\mathrm{te^2te^2tete}$		23.67 (24.39)	4.24 (6.11)	37.91 (30.50)
F (1)	$\mathrm{s^2p^2p^2p}$		19.94 (20.86)	1.37 (3.50)	21.30 (24.36)
	$\mathrm{sp^2p^2p^2}$		43.64 (38.24)	25.29 (24.37)	68.93 (62.61)
Si (4)	sppp	s	15.97 (17.31)	6.90 (6.94)	22.87 (24.24)
		p	7.52 (9.19)	−0.43 (2.82)	7.09 (12.01)
	$\mathrm{didi}\pi\pi$	σ	12.67 (14.06)	2.31 (4.07)	14.98 (18.12)
		π	7.40 (9.18)	−0.60 (2.20)	6.80 (11.38)
	$\mathrm{trtrtr}\pi$	σ	11.11 (12.61)	1.11 (3.20)	12.22 (15.80)
		π	7.36 (9.17)	−0.65 (2.00)	6.71 (11.17)
	tetetete		10.24 (11.82)	0.58 (2.78)	10.82 (14.59)
P (3)	$\mathrm{s^2ppp}$		9.47 (10.73)	0.20 (1.42)	9.66 (12.15)
	$\mathrm{sp^2pp}$	s	20.51 (20.20)	10.33 (8.48)	30.84 (28.68)
		p	9.75 (12.49)	0.55 (1.98)	10.30 (14.46)
	$\mathrm{di^2di}\pi\pi$	σ	17.43 (17.53)	5.27 (4.95)	22.70 (22.49)
		π	9.61 (11.61)	0.37 (1.68)	9.98 (13.29)

Table 2 (continued)

System	Valence state	Orbital	I_v	E_v	χ_M
P (3)	$\mathrm{didi}\pi^2\pi$	σ	16.25 (16.78)	4.32 (4.77)	20.57 (21.55)
		π	9.65 (11.89)	0.36 (2.02)	10.01 (13.91)
	$\mathrm{tr}^2\mathrm{trtr}\pi$	σ	14.83 (15.59)	3.20 (3.74)	18.02 (19.33)
		π	9.61 (11.64)	0.35 (1.80)	9.96 (13.44)
	$\mathrm{trtrtr}\pi^2$		14.28 (15.18)	2.74 (3.76)	17.02 (18.94)
	$\mathrm{te}^2\mathrm{tetete}$		13.51 (14.57)	2.30 (3.24)	15.82 (17.80)
S (2)	$\mathrm{s}^2\mathrm{p}^2\mathrm{pp}$		11.82 (12.39)	1.28 (2.38)	13.10 (14.77)
	$\mathrm{sp}^2\mathrm{p}^2\mathrm{p}$	s	25.32 (20.08)	13.96 (11.54)	39.28 (31.62)
		p	12.07 (13.32)	1.56 (3.50)	13.64 (16.83)
	$\mathrm{di}^2\mathrm{di}^2\pi\pi$		11.82 (12.39)	1.28 (2.38)	13.10 (14.78)
	$\mathrm{di}^2\mathrm{di}\pi^2\pi\pi$	σ	21.34 (17.78)	7.62 (6.96)	28.96 (24.74)
		π	11.95 (12.86)	1.42 (2.94)	13.37 (15.80)
	$\mathrm{didi}\pi^2\pi^2$		19.96 (17.42)	6.50 (6.80)	26.46 (24.22)
	$\mathrm{tr}^2\mathrm{tr}^2\mathrm{tr}\pi$	σ	18.79 (16.33)	5.51 (5.43)	24.29 (21.76)
		π	11.90 (12.70)	1.38 (2.76)	13.28 (15.46)
	$\mathrm{tr}^2\mathrm{trtr}\pi^2$		18.20 (16.27)	5.04 (5.49)	23.24 (21.76)
	$\mathrm{te}^2\mathrm{te}^2\mathrm{tete}$		16.96 (15.50)	4.21 (4.77)	21.17 (20.27)
Cl (1)	$\mathrm{s}^2\mathrm{p}^2\mathrm{p}^2\mathrm{p}$		14.38 (15.03)	2.60 (3.73)	16.97 (18.76)
	$\mathrm{sp}^2\mathrm{p}^2\mathrm{p}^2$		30.49 (24.02)	18.00 (14.45)	48.49 (38.47)

[a] The values of Hinze and Jaffe [4] are given in parentheses.

defined by

$$P_v = W_v - W_g\,, \tag{2a}$$

$$I_{v(0)} = W_{v(+)} - W_{v(0)}\,, \tag{2b}$$

$$E_{v(0)} = W_{v(0)} - W_{v(-)}\,, \tag{2c}$$

$$\chi_M = I_{v(0)} + E_{v(0)}\,, \tag{2d}$$

where the subscripts v and g denote the valence and groundstates, respectively, and the subindices $(+)$, $(-)$ label the quantities corresponding to the ion with one electron less or more, respectively, than the system considered, for which the subindex (0) is used. Eq. (2d) is the definition of orbital electronegativity given by Mulliken [6].

Results of the Calculations

The calculations of the quantities defined by Eq. (2) have been carried out for the atoms C, N, O, F, Si, P, S, and Cl, and their positive and negative ions, using the analytical Hartree-Fock functions of Clementi [1] and Malli [5].

The one-electron energies have been calculated directly from these functions, while for the Slater-Condon parameters the values, calculated by Fisk and Fraga [3] from the same functions, have been used.

The results of these calculations are presented in Tables 1–2. In Table 2, comparison is made with the results given by Hinze and Jaffe [4].

It can be observed that the agreement for the ionization potentials is, in general, very satisfactory. For the electron affinities, however, the situation is different. The Hartree-Fock values are of the order of 2 eV, as an average, lower than the values given by Hinze and Jaffe [4]. In this connection it must be mentioned first of all that, due to lack of experimental results, the data for the negative ions were approximated by Hinze and Jaffe [4] by extrapolation. Another source of discrepancy, of course, is the fact that the Hartree-Fock functions for negative ions are not as accurate as those for neutral atoms, as it has already been pointed out by Thorhallsson, Fisk, and Fraga [8].

For the orbital electronegativities, the agreement is also very satisfactory, due to the fact that the ionization potentials make the main contribution.

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Professor S. Fraga
Department of Chemistry
The University of Alberta
Edmonton, Canada