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Calculating atomic charges in molecules and crystals by a new electronegativity equalization method

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ABSTRACT

The new method of the electronegativity equalization of atoms in molecules and crystals based on Mulliken' scale is proposed. Calculating the atomic charges by this method gives results which are in accordance with the chemical intuition and empirical estimations.

1. Introduction

The principle of electronegativity equalization (ENE) proposed by Sanderson [1] (when two or more atoms with different electronegativity combine, they become adjusted to the same intermediate electronegativity within the compound) inspired numerous works of empirical [2–6] and quantum-chemical [7–12] types and now is one of a most popular approach in theoretical chemistry. At the same time, this method is open for a further improvement because of a number of reasons. First of all, the physical dimensions of electronegativity (EN) in different scales are different. So, in Mulliken' scale [13] the physical dimension is the energy (or potential), the Pauling' scale [14] has the dimension of the square root of energy, Sanderson' one [1] is the relative electron density, and Parr et al. [15] defined the absolute electronegativity as the electronic chemical potential, and so on. Respectively, there exists no unique method for the calculation of EN, for an each scale of ENs one must use the specific calculation scheme, for example, as it is made by Bratsch for Pauling' scale [5].

The aim of this paper is to develop the simple and physically well-founded method of ENE for calculating atomic charges in compounds MX by means orbital radii and Mulliken's EN of atoms in the valence states (VS). Because VS of atoms in molecules and crystals are different, it allows us to calculate atomic charges both the molecular and crystalline compounds.

2. Methods and equations

Let us equalize the electronegativity (χ) of atoms M and X in the M–X bonds by means of the simple law:

$$\chi_M \times f = \chi_X/f \tag{1}$$

where f is the factor of an equalization:

$$f = \sqrt{\chi_X/\chi_M} \tag{2}$$

and χ is the Mulliken electronegativity computed as

$$\chi = 1/2(I_{vs} + A_{vs}) \tag{3}$$

here I and A are the ionization potential and electron affinity of atoms, respectively. Apparently, f will influence the interatomic distance, decreasing the M size in the M–X separation by the expression

$$r_{q+} = r_o/f \tag{4}$$

where r_o is the orbital radius of the electro-neutral atom [16] and r_{q+} is the radius of this atom with a charge q.

Experimental (bonded, r_b) radii of cations (Be, Mg, Ca, Mn, Co, Ni, Al) determined as the distances between the nuclei of ions and the minimal electron density on the bond lines are larger their ionic radii (r_{cat}) and less than the covalent radii. The bonded radii of the oxide ions show the inverse dependence and Johnson [17] established a direct correlation between polarizing power of cations with the oxide ion radius. In this correlation, r_b(O) decreases

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Table 1
Orbital radii (Å) of the metal atoms (r_o) and their cations (r_{cat}).

M	r_o	r_{M+}	M	r_o	r_{M++}
Li	1.586	0.186	Be	1.040	0.138
Na	1.713	0.278	Mg	1.279	0.247
K	2.162	0.593	Ca	1.690	0.539
Rb	2.287	0.735	Sr	1.836	0.685
Cs	2.518	0.922	Ba	2.060	0.869
Cu	1.191	0.325	Zn	1.065	0.311
Ag	1.286	0.536	Cd	1.184	0.508
Au	1.187	0.634	Hg	1.126	0.584

linearly from ~1.4 Å when O bonded to Rb down to ~0.8 Å when it bonded to Be. Johnson also reported a similar correlation for the sulfide ion with its radius decreasing linearly from ~1.8 Å in the Rb–S bond down to ~ 1.4 Å when S bonded to Be. Thus, r_b(O) and r_b(S) decrease in a regular way as the partial ionic character of the bonds decreases. Authors of [18] established a dependence of r_b(O) on electronegativities of metals in the M–O bonds. Gibbs et al. [19] showed that the bonded radii of metals in sulfides being higher than those in oxides, for example r_b(Mg) = 0.92 Å in MgO and 1.28 Å in MgS; similarly: r_b of K and Cu in MBr are larger than in MCl. Hence, the real atomic radii depend on the bond polarity. As a first approximation, the atomic radii of the metal atoms in molecules with the fractional charges we will calculate by the linear extrapolation between radii of the neutral atoms M^o (r_o) and corresponding cations M^+ or M^{++} (r_{cat}),

$$i = \frac{r_o - r_{q+}}{r_o - r_{cat}} \tag{5}$$

3. Results and discussion

Atomic radii used in this work are listed in Table 1, but electronegativities and radii of atoms with the partial charges in molecules and crystalline compounds are given in Tables 2 and 3.

Table 2
Electronegativities, orbital atomic radii (Å) and the bond ionicity in molecules MX.

M	χ	H (7.176)		F (12.20)		Cl (9.35)		Br (8.63)		I (8.00)	
		r_{q+}	i_{mol}	r_{q+}	i_{mol}	r_{q+}	i_{mol}	r_{q+}	i_{mol}	r_{q+}	i_{mol}
Li	3.005	1.026	0.400	0.787	0.571	0.899	0.491	0.936	0.464	0.972	0.439
Na	2.844	1.078	0.442	0.827	0.617	0.945	0.535	0.983	0.509	1.021	0.482
K	2.421	1.256	0.577	0.963	0.764	1.100	0.677	1.145	0.648	1.189	0.620
Rb	2.332	1.304	0.633	1.000	0.829	1.142	0.738	1.189	0.707	1.235	0.678
Cs	2.183	1.389	0.707	1.065	0.910	1.217	0.815	1.266	0.784	1.315	0.754
Cu	4.477	0.941	0.289	0.721	0.543	0.824	0.424	0.858	0.384	0.891	0.346
Ag	4.439	1.011	0.367	0.776	0.680	0.886	0.533	0.922	0.485	0.958	0.437
Au	5.767	1.064	0.222	0.816	0.671	0.932	0.461	0.970	0.392	1.008	0.324
		O (9.63)		S (7.44)		Se (6.99)		Te (6.46)			
Be	4.65	0.723	0.351	0.822	0.242	0.848	0.213	0.882	0.175		
Mg	4.11	0.836	0.429	0.951	0.318	0.981	0.289	1.020	0.251		
Ca	3.29	0.988	0.610	1.124	0.492	1.159	0.461	1.206	0.420		
Sr	3.07	1.037	0.694	1.179	0.571	1.217	0.538	1.266	0.495		
Ba	2.79	1.109	0.798	1.261	0.671	1.301	0.637	1.354	0.593		
Zn	4.99	0.767	0.395	0.872	0.256	0.900	0.219	0.936	0.171		
Cd	4.62	0.820	0.538	0.933	0.371	0.963	0.327	1.001	0.271		
Hg	5.55	0.855	0.500	0.972	0.284	1.003	0.227	1.044	0.151		

Table 3
Electronegativities, orbital atomic radii (Å) and the bond ionicity in crystals MX.

M	χ	F_{oc} (15.82)		Cl_{oc} (11.22)		Br_{oc} (10.52)		I_{oc} (9.51)	
		r_{q+}	i_{cr}	r_{q+}	i_{cr}	r_{q+}	i_{cr}	r_{q+}	i_{cr}
Li	3.005	0.691	0.639	0.821	0.546	0.848	0.527	0.891	0.496
Na	2.844	0.726	0.688	0.862	0.593	0.891	0.573	0.938	0.540
K	2.421	0.846	0.839	1.004	0.738	1.037	0.717	1.091	0.683
Rb	2.332	0.878	0.908	1.043	0.801	1.077	0.780	1.132	0.744
Cs	2.183	0.935	0.992	1.111	0.882	1.147	0.859	1.206	0.822
		F_{te} (17.63)		Cl_{te} (12.15)		Br_{te} (11.46)		I_{te} (10.26)	
Cu	4.477	0.600	0.682	0.723	0.540	0.744	0.516	0.787	0.466
Ag	4.439	0.645	0.855	0.777	0.679	0.800	0.648	0.846	0.587
Au	5.767	0.679	0.919	0.818	0.667	0.842	0.624	0.890	0.537
		O_{oc} (12.56)		S_{oc} (9.04)		Se_{oc} (8.64)		Te_{oc} (7.83)	
Mg	4.11	0.732	0.530	0.862	0.404	0.882	0.385	0.927	0.341
Ca	3.29	0.865	0.717	1.019	0.583	1.043	0.562	1.095	0.517
Sr	3.07	0.908	0.806	1.070	0.665	1.094	0.645	1.150	0.596
Ba	2.79	0.971	0.914	1.144	0.769	1.171	0.746	1.230	0.697
		O_{te} (14.02)		S_{te} (9.84)		Se_{te} (9.48)		Te_{te} (8.52)	
Be	4.65	0.599	0.489	0.715	0.360	0.728	0.346	0.768	0.302
Zn	4.99	0.635	0.570	0.758	0.407	0.773	0.387	0.815	0.332
Cd	4.62	0.680	0.745	0.811	0.552	0.826	0.530	0.872	0.461
Hg	5.55	0.708	0.771	0.846	0.517	0.862	0.487	0.909	0.400

Table 4
Comparison of calculated and empirical values of the bond ionicity in molecules and crystals MX; upper lines: p and i_{mol}, lower lines: e^* and i_{cr}; left columns correspond to empirical values, right columns – to calculated magnitudes.

M	F		Cl		Br		I	
Li	0.84	0.57	0.73	0.49	0.70	0.46	0.65	0.44
	0.81	0.64	0.77	0.55	0.74	0.53	0.54	0.50
Na	0.88	0.62	0.79	0.54	0.79	0.51	0.71	0.48
	0.83	0.69	0.78	0.59	0.75	0.57	0.74	0.54
K	0.82	0.76	0.80	0.68	0.78	0.65	0.74	0.62
	0.92	0.84	0.81	0.74	0.77	0.72	0.75	0.68
Rb	0.78	0.83	0.78	0.74	0.77	0.71	0.75	0.68
	0.97	0.91	0.84	0.80	0.80	0.78	0.77	0.74
Cs	0.70	0.91	0.74	0.81	0.73	0.78	0.73	0.75
	0.96	0.99	0.85	0.88	0.82	0.86	0.78	0.82
Cu	0.69	0.54	0.53	0.42				
		0.68	0.66	0.54	0.64	0.52	0.60	0.47
Ag	0.65	0.68	0.55	0.53				
	0.89	0.86	0.71	0.68	0.67	0.65	0.61	0.59
MO	Be	Mg	Ca	Sr	Ba	Zn	Cd	Hg
i_c	0.49	0.53	0.72	0.81	0.91	0.57	0.74	0.77
$e^*/2$	0.55	0.59	0.62	0.64	0.74	0.60	0.59	0.57