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Electronegativity scales and electronegativity-bond ionicity relations: A comparative study

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ABSTRACT

Electronegativity (χ) and bond ionicity are very important concepts in chemistry and other branches of science. Due to the lack of a precise definition, several χ scales have been introduced, based on a variety of chemical and physical quantities. On the other hand, many empirical relations have been devised to estimate the bond ionicity from χ of the bonding atoms. In this work, the bond ionicity in an extensive list of $A^N B^{8-N}$ compounds, obtained by employing the Abu-Farsakh and Qteish ionicty scale (q_i), are used as a benchmark to investigate the performance of the widely accepted and promising χ scales and frequently adopted χ-ionicity relations. The employed ionicty scale is based on the centers of the maximally localized Wannier functions and has several advantages. It has been demonstrated that the bond ionicity is better expressed in terms of normalized $\Delta\chi$, rather than $\Delta\chi$, and the best χ-ionicity relation has been unambiguously identified. The Allred-Rochow (AR) electronegativity scale is found to outperform the other considered electronegativity measures. The discrepancies between q_i and bond ionicity (p_i), obtained by using the best χ-ionicity relation and the AR scale, are found to have clear trends, which may imply that the AR values of some atoms are inaccurate. Corrections to the AR values, to minimize the discrepancies between q_i and p_i, lead to a highly reasonable set of χ values of the involved atoms that satisfy the main χ rules.

1. Introduction

Electronegativity (χ) is a very important concept in chemistry, physics and other branches of science. Allen [1,2] has suggested that χ is the missing third dimension of the Periodic Table. Many fundamental properties can be understood and modeled for evaluation in terms of χ, such as bond polarities and dipole moments, bond energies, force constants and the inductive effects [3]. An outstanding correlation between the superconducting transition temperature and χ has been observed for both solid elements and high-temperature superconductors [4–6]. A strong correlations have also been found between χ and the chemical shift in NMR spectroscopy [7] and the Isomer shift in Mössbauer spectroscopy [8]. Recently, the electronegativity concept has been utilized in chemical informatics [9] and material design [10].

Electronegativity is proved to be a difficult concept. As defined by Pauling [11], χ is the ability of the atom to attract an electron to itself, when interacts with other atoms to form molecules or solids. Therefore, χ lacks a precise definition (unlike, e.g., electron affinity) because it is not a property of the atom in isolation. The χ scales that adopt this point of view will be referred to as empirical scales. The first empirical χ scale introduced by Pauling [11] is based on thermochemical data. Several other empirical approaches are introduced [3]. The most widely cited one is that of Allred and Rochow [12] (AR), based on the electrostatic force between the effective nucleus charge of the atom and an electron at its covalent radius. On the other hand, Allen [1,2] has argued that χ is a property of the isolated atom, and introduced a χ scale based on the configuration energy of the valence electrons. Modern computational techniques, based of the density functional theory, are employed to compute the atomic χ, based on the chemical potential [14], mean valence density radius [13] and electrophilicity [15] of isolated atoms. These χ measures will thus be referred to as absolute scales.

Another related important concept is the bond ionicity (hereafter referred to as ionicity), which also lacks a precise definition. Several ionicity scales have been introduced since the original work of Pauling [11], in 1932. In the Pauling ionicity scale, the ionicity (p_i) is expressed in terms of the difference in χ ($\Delta\chi$) of the bonded atoms. For this purpose, several empirical relations are devised to estimate p_i from $\Delta\chi$ (see for example, Refs. [15] and [18]). It has been argued by Nethercot [16,17] and Barbe [18] that p_i could not be a simple function of $\Delta\chi$, and proposed relations that express p_i in terms of normalized $\Delta\chi$. This approach will be referred to collectively as Pauling ionicity scale. The other ionicity measures are based on spectroscopy (the famous Phillips ionicity scale [19]), ensemble of effective charges (see Ref. [20]),

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Table 1
Abu-Farsahk and Qteish (q_i) [21,23], Phillips [19] (f_i) and Pauling [11] (p_i) ionicity in the considered group-IV solids and III-V compounds, crystalizing in the zinc-blende structure. Those of Pauling are calculated using Allred-Rochow [12] (AR) and corrected AR (c-AR) χ values. The ionicity difference ($q_i - p_i$) is also shown in parentheses.

Compound	q_i	f_i	$p_{i,5}$@AR	$p_{i,5}$@c-AR
SiC	0.318	0.177	0.175(0.143)	0.310(0.008)
SiGe	0.020	0.002	0.030(-0.010)	0.021(-0.001)
BN	0.421	0.221	0.437(-0.018)	0.392(0.029)
BP	0.077	0.032	0.251(-0.179)	0.252(-0.175)
BAs	0.107	0.044	0.259(-0.153)	0.250(-0.143)
AlN	0.604	0.449	0.672(-0.068)	0.595(0.009)
AlP	0.417	0.307	0.356(0.061)	0.407(0.010)
AlAs	0.410	0.274	0.399(0.011)	0.399(0.011)
AlSb	0.265	0.250	0.293(-0.028)	0.305(-0.040)
GaN	0.551	0.500	0.512(0.039)	0.570(-0.019)
GaP	0.375	0.327	0.266(0.109)	0.381(-0.007)
GaAs	0.383	0.310	0.287(0.096)	0.374(0.009)
GaSb	0.304	0.261	0.250(0.054)	0.285(0.018)
InN	0.591	0.578	0.662(-0.071)	0.592(-0.001)
InP	0.421	0.421	0.348(0.075)	0.403(0.018)
InAs	0.357	0.357	0.390(0.067)	0.395(-0.038)
InSb	0.321	0.321	0.288(0.076)	0.302(0.019)

charge density [13] and centers of the maximally localized Wannier functions (MLWFs) [21].

The modern ionicity scale of Abu-Farsakh and Qteish [21] (q_i), based on the centers of MLWFs, has four main advantages. First, it is a fully self-consistent approach, based on accurate DFT calculations. Second, it is a direct ionicity measure (i.e., based on a bond property). This is because the MLWFs can be thought of as σ-bond orbitals [22]. Third, the ionicity is expressed solely in terms of physical parameters (i.e., free from adjustable parameters). Fourth, the performance of this ionicity scale has very recently been investigated [23] by applying it to an extensive list of 72 $A^N B^{8-N}$ compounds, shown in Tables 1–3. The considered systems range from group-IV solids to I-VII compounds and crystallize in the tetrahedral (zincblende or wurtzite) or octahedral (rocksalt) structures. This measure is proved to be highly competitive to the most widely accepted ionicity scales of Phillips [19] and Pauling [11], and it overcomes their shortcomings.

In this work, the reported [23] values of q_i for the above extended list of $A^N B^{8-N}$ compounds, are used as a benchmark to investigate the performance of the various χ scales and empirical electronegativity-ionicity relations. As for χ, the two most famous empirical (namely, Pauling and AR) and three absolute (namely, Allen [1,2], Garcia and Cohen [13], and Noorizadeh and Shakerzadeh [15]) scales have been considered. The last two absolute measures are based on first-principles calculations. For the electronegativity-ionicity relations, we consider the eight relations reported in Refs. [18] and [15]. We anticipate that the AR scale provides the best performance. Finally, some trends in the difference between q_i and the best p_i values are observed, which could arise from inaccuracies in the employed AR values of some atoms. A new set of the electronegativity values for involved atoms is provided.

2. Background

2.1. Abu-Farsakh and Qteish ionicity scale

Recently, Abu-Farsakh and Qteish [21] have introduced an ionicity scale based on the centers of the MLWFs. For elemental group-IV solids in the diamond structure, there is a symmetric MLWF associated with each bond, centered at the middle of the bond. By going to $A^N B^{8-N}$ compounds crystallizing in the ZB phase, the MLWFs become asymmetric with their centers ($\mathbf{r}_n$) lie between the bond center and the anion, at a fixed distance from bond center. The MLWFs of the $A^N B^{8-N}$ compounds have roughly the character of the σ-bond orbitals [22]. To evaluate the shift in $\mathbf{r}_n$ of these systems, away from the bond center, a parameter β is defined as $\beta = r_n/d$, where r_n is the magnitude of the displacement between $\mathbf{r}_n$ and the cation position, and d is the bond length. In the case of the RS phase, there are four MLWFs and six bonds per primitive unit cell. The orientation of the MLWFs is found to be similar to those of the ZB phase (i.e., along four of the [111] directions), and their centers are located very close to the anions. Thus, the MLFWs in this case are thought of as superposition's of some kind of

Table 2
As in Table 1, but for the considered II-VI compounds. The adopted crystal structures [zinc-blende (ZB) or rock-salt (RS)] are also shown.

Compound	q_i	f_i	$p_{i,5}$@AR	$p_{i,5}$@c-AR
ZB-ZnO	0.771	0.616	0.798(-0.027)	0.763(0.008)
ZB-ZnS	0.653	0.623	0.596(0.057)	0.653(0.000)
ZB-ZnSe	0.640	0.630	0.604(0.042)	0.644(-0.004)
ZB-ZnTe	0.581	0.609	0.524(0.057)	0.593(-0.012)
RS-CdO	0.937	0.785	0.902(0.035)	0.872(0.065)
ZB-CdS	0.688	0.685	0.655(0.032)	0.705(-0.017)
ZB-CdSe	0.672	0.699	0.664(0.008)	0.696(-0.024)
ZB-CdTe	0.651	0.717	0.563(0.088)	0.644(0.007)
ZB-HgS	0.717	0.790	0.661(0.056)	0.713(0.004)
ZB-HgSe	0.701	0.680	0.670(0.031)	0.704(-0.003)
ZB-HgTe	0.656	0.650	0.568(0.088)	0.653(0.004
ZB-BeO	0.726	0.602	0.850(-0.124)	0.731(-0.004)
ZB-BeS	0.615	0.312	0.652(-0.037)	0.618(-0.003
ZB-BeSe	0.605	0.299	0.660(-0.055)	0.609(-0.004)
ZB-BeTe	0.549	0.169	0.561(-0.011)	0.561(-0.011)
RS-MgO	0.931	0.841	0.941(-0.010)	0.900(0.031)
RS-MgS	0.916	0.000	0.825(0.091)	0.837(0.079
RS-MgSe	0.917	0.000	0.831(0.086)	0.832(0.085)
ZB-MgTe	0.671	0.554	0.633(0.038)	0.698(-0.027)
RS-CaO	0.941	0.913	0.966(-0.025)	0.964(-0.023)
RS-CaS	0.925	0.902	0.874(0.051)	0.927(-0.002)
RS-CaSe	0.925	0.900	0.880(0.045)	0.924(0.001
RS-CaTe	0.915	0.894	0.806(0.112)	0.901(0.017)
RS-SrO	0.945	0.926	0.972(-0.027)	0.966(-0.021)
RS-SrS	0.929	0.914	0.887(0.042)	0.931(-0.002)
RS-SrSe	0.927	0.917	0.893(0.034)	0.928(-0.001)
RS-SrTe	0.921	0.903	0.821(0.100)	0.906(0.015)
RS-BaO	0.950	0.878	0.974(-0.024)	0.969(-0.019)
RS-BaS	0.934	0.886	0.893(0.041)	0.937(-0.003)
RS-BaSe	0.934	0.880	0.898(0.036)	0.934(-0.000)
RS-BaTe	0.927	0.876	0.827(0.100)	0.913(0.014)

Table 3
As in Tables 1 and 2, but for the considered I-VII compounds.

Compound	q_i	f_i	$p_{i,5}$@AR	$p_{i,5}$@c-AR
ZB-CuF	0.899	0.766	0.929(-0.030)	0.901(-0.001)
ZB-CuCl	0.859	0.746	0.824(0.035)	0.859(0.000)
ZB-CuBr	0.844	0.735	0.815(0.029)	0.854(-0.009)
ZB-CuI	0.826	0.692	0.768(0.057)	0.825(0.001)
RS-AgF	0.976	0.894	0.975(0.000)	0.961(0.014)
RS-AgCl	0.966	0.856	0.917(0.048)	0.940(0.026)
RS-AgBr	0.964	0.850	0.911(0.052)	0.937(0.028)
ZB-AgI	0.843	0.770	0.808(0.035)	0.880(-0.037)
RS-LiF	0.970	0.915	0.995(-0.025)	0.979(-0.010)
RS-LiCl	0.963	0.903	0.967(-0.004)	0.964(-0.002)
RS-LiBr	0.963	0.899	0.963(0.000)	0.962(0.001)
RS-LiI	0.960	0.890	0.930(0.030)	0.949(0.010)
RS-NaF	0.971	0.946	0.994(-0.020)	0.982(-0.008)
RS-NaCl	0.974	0.935	0.963(0.004)	0.968(-0.002)
RS-NaBr	0.966	0.934	0.959(0.005)	0.966(-0.002)
RS-NaI	0.964	0.927	0.924(0.039)	0.954(0.009)
RS-KF	0.963	0.955	0.996(-0.018)	0.984(-0.007)
RS-KCl	0.978	0.953	0.973(-0.003)	0.972(-0.001)
RS-KBr	0.970	0.952	0.969(0.001)	0.970(-0.000)
RS-KI	0.970	0.950	0.939(0.027)	0.959(0.008)
RS-RbF	0.966	0.960	0.997(-0.018)	0.986(-0.007)
RS-RbCl	0.979	0.955	0.975(-0.003)	0.975(-0.003)
RS-RbBr	0.972	0.957	0.971(0.000)	0.973(-0.002)
RS-RbI	0.968	0.951	0.942(0.026)	0.963(0.005)