

Quantum-chemical definition of the atomic valence in molecules and crystals

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Summary. A new quantum-chemical definition is given of the full atomic valence taking into account both the covalent and ionic parts of the chemical bonds formed by an atom in molecules and crystals. Full valence is close to formal (“classical”) valence of an atom in a wide row of compounds. The theoretical consideration and the CNDO calculations of molecules and crystals are made to justify the validity of the full valence definition.

Key words: Valency – Electron structure – CNDO calculation

1. Introduction

The widely spread definition of valency or oxidation number of an atom in a compound is based on using some formal rules and assumption that any atom in a compound is capable of connecting a definite number of atoms of other kinds. If the oxidation number of atoms of one kind in a compound is unknown it may be calculated using the electroneutrality of a compound as a whole.

Atomic valence defined in such a way uses the stoichiometric formula of a compound and is applicable only for a restricted number of compounds. Its applicability is questionable for complex compounds, for compounds with several atoms of variable valence [1]. Moreover, the integer classical valence values do not allow one to take into account the differences in the reaction capacity of compounds containing atoms with formally constant valence. Therefore in the considerations mentioned it seems expedient to establish the connection between the formal (classical) atomic valence definitions and the electron density distribution in a compound which may be found as a result of quantum-chemical calculation.

A quantum-chemical definition of the valence of an atom in a compound presupposes, in some or another way, finding the connection between the electron density distribution and the number of electrons attributed to an atom and involved in chemical bonds formed by this atom [2]. Such a connection can be found by different ways. Apparently the preference has to be given to such a valence definition which allows one to obtain the calculated atomic valence values close to the corresponding formal valence of an atom in a wide series of compounds.

Till now the quantum-chemical definitions of an atomic valence are introduced in fact only for purely ionic compounds (electrovalence E_A) or for compounds with covalent nonpolar bonds (covalence C_A [3, 4]). The majority of compounds have mixed (ionic-covalent) chemical bonds. The numerical values of both E_A and C_A for these compounds differ essentially from the formal valence of an atom. However, the correct quantum-chemical definition of the atomic valence for the compounds with mixed chemical bonds is missing till now.

In this paper a new quantum-chemical definition is given of the atomic valence taking into account both the covalent and ionic parts of chemical bonds formed by an atom in molecules and crystals. The introduced valence V_A may be called the full valence of an atom in a compound.

In the framework of CNDO approximation the atomic full valence V_A is calculated in different molecules and crystalline solids. The numerical values of V_A are compared with covalence and electrovalence values found in the same approximation.

2. Electro- and covalency

In the quantum-chemical LCAO calculations of the electron structure of molecules one obtains the density matrix P . In the case of closed shell systems, the density matrix elements P_{ab} between atomic orbitals a on atom A and b on atom B are given by:

$$P_{ab} = 2 \sum_i^{occ.} C_{ia} C_{ib}. \quad (1)$$

In Eq. (1) i is the number of occupied molecular or crystalline orbitals.

An analogous expression of density matrix elements in the band model of crystals in the LCAO approach was considered in Ref. [5] and may be used for the definition of valence in crystals.

Let the atomic orbitals in the minimal basis form the orthonormal set generated by Löwdin transformation from nonorthogonal ones [6]. In the case of an extended atomic orbital basis one can define atomic charges in other ways, for example within Natural Atomic Orbital formalism [7].

The total electron charge N_A on atom A is given by the sum:

$$N_A = \sum_a^A P_{aa}. \quad (2)$$

The ionic part of the chemical bond is defined by the atomic charge $Q_A = Z_A - N_A$, where Z_A is the A-atom core charge.

In the hypothetical case of a purely ionic compound the atomic charge Q_A coincides with the formal oxidation number of an atom. (Hereafter, the absolute value of oxidation number of atom A in polar compounds we denote by \mathcal{E}_A .) In real compounds with mixed ionic-covalent bonds some part of electronic density is localized in the interatomic region so that the numerical values of electrovalence $E_A \equiv |Q_A|$ and of \mathcal{E}_A may differ essentially.

When describing the electron density localized on interatomic covalent bonds the Wiberg bond index is used [8]:

$$W_{AB} = \sum_a^A \sum_b^B P_{ab}^2. \quad (3)$$

The numerical value of bond index W_{AB} correlates with the number of electron pairs localized on the bond A–B.

When using one-determinate approximation and the orthogonal atomic basis the electron density matrix P is idempotent, i.e. $P^2 = 2P$. The idempotency condition allows one to connect the electron charge N_A on atom A with the orders of the bonds formed by this atom:

$$N_A = \sum_a^A P_{aa} = 1/2 \sum_a^A \sum_c P_{ac} P_{ca} = 1/2 \sum_a^A \sum_B \sum_b^B P_{ab} P_{ba} = 1/2 \sum_B W_{AB}. \quad (4)$$

The sum in Eq. (4) is taken over all the B atoms of the molecule or crystal, including the item W_{AA} . The latter corresponds to nonbonding orbitals of the A-atom, all the other items in the sum of Eq. (4) correspond to a number of electrons given away by A-atom to form the covalent bonds with other atoms.

In the case of covalent nonpolar compounds ($Q_A = 0$), any electron pair is localized in the bonds region (the order of this bond is taken as equal to 1). These covalent bonds may be considered as formed equally by electrons of both bonded atoms.

Therefore, in the covalence expression one has to include twice the number of A-atom electrons, localized on the bonds [3, 9].

$$C_A = 2 \left(1/2 \sum_{B \neq A} W_{AB} \right) = \sum_{B \neq A} W_{AB}. \quad (5)$$

As a result, the sum of covalencies C_A over all the atoms in a molecule is twice greater than the total number of electrons involved in the forming of the chemical bonds.

Introduced for the nonpolar covalent compounds, the concept of atomic covalence C_A cannot be directly extended to compounds with mixed ionic-covalent bonds.

When the bond ionicity increases, both the number of electrons localized in the interatomic region and, as a result, the covalencies of atoms decrease. Thus, in the limit case of purely ionic compounds the covalencies of all atoms are equal to zero, which makes no sense.

Evidently in compounds with mixed bonding the calculated atomic valencies have to include both the electrovalent (ionic) part and covalent part. The “full” valence V_A of an atom must be independent on the relation between the ionic and covalent parts of chemical bonding (the ionicity degree). In two limit cases of purely ionic and covalent nonpolar bonding, the full valence V_A must coincide with electrovalence and covalence, respectively.

3. The full atomic valency

In the compounds with a purely ionic chemical bonding the valencies of atoms coincide with their electrovalence as all the valence electrons forming chemical bonds are strongly localized near the atomic cores.

Let us suppose that the part ΔQ_A of valence electron charge on atom A is delocalized over the covalent bonds of this atom with other ones (with the corresponding bond orders ΔW_{AB}). Decreasing ΔQ_A of the electrovalence means a corresponding increase αC_A of the A-atom covalence (because the oxidation number of atom A does not change).

For small ΔQ_A values the multiplier α value may be defined strictly. Indeed, let the full atom valence V_A^z in the compound with mixed ionic-covalent bonding be written as:

$$V_A^z = |Q_A| + \alpha C_A. \quad (6)$$

For an atom with nonvariable valence the oxidation number Ξ_A is connected with the atom's position in the Periodic Table. Let an atom give all its valence electrons to form a closed-shell configuration, for example nontransition metals (K(I), Ca(II), Al(III)):

$$\Xi_A = Z_A. \quad (7a)$$

For the negatively charged atom (H(I), F(I), O(II)):

$$\Xi_A = 2n_A - Z_A, \quad (7b)$$

where n_A is the number of valence atomic orbitals of atom A.

The density matrix elements defined in Löwdin's symmetrically orthogonalized atomic basis in the purely ionic compound ($C_A = 0$) may be written in the form:

$$p_{aa'}^{ion} = \begin{cases} 0, & \text{if } a = a' \quad Q_A > 0 \\ 2, & \text{if } a = a' \quad Q_A < 0 \\ 0, & \text{if } a \neq a' \end{cases} \quad (8)$$

Equation (7) is fulfilled strictly for the density matrix of Eq. (8).

Let us turn to the compounds with relatively high degrees of ionicity, those compounds for which the density matrix elements $p_{aa'}$ are closed to $p_{aa'}^{ion}$ (corresponding to Eq. (8)) and therefore one can neglect the quantities $(p_{aa'} - p_{aa'}^{ion})^2$. Substituting Eq. (6) into Eq. (7a) one obtains for positively charged atom A:

$$V_A^z - \Xi_A = (2\alpha - 1) \sum_a^A p_{aa} - \alpha \sum_a^A p_{aa}^2 - \alpha \sum_{a \neq a'}^A p_{aa'}^2 = 0. \quad (9a)$$

Neglecting in Eq. (9a) the small quantities $p_{aa'}^2$ we obtain $\alpha = 1/2$. Introducing $\tilde{p}_{aa} \equiv 2 - p_{aa}$ and comparing Eq. (6) with Eq. (7b) one can obtain for the negatively charged atom A:

$$V_A^z - \Xi_A = (2\alpha - 1) \sum_a^{n_A} \tilde{p}_{aa} - \alpha \sum_a^A \tilde{p}_{aa}^2 - \alpha \sum_{a \neq a'}^A p_{aa'}^2 = 0. \quad (9b)$$

Neglecting, as above, the small quantities $p_{aa'}^2$ and $(2 - p_{aa})^2$ we get $\alpha = 1/2$.

Thus, the numerical values of the oxidation number or valence of an atom in a compound with relatively high ionicity are close to the value:

$$V_A^{(1/2)} = |Q_A| + 1/2 \cdot C_A. \quad (10)$$

Equation (10) was obtained assuming that the coefficient α in Eq. (6) is independent on the ionicity of bonding. This assumption may be justified only for the essentially ionic compounds. Indeed, Eq. (10) gives for the nonpolar covalent compounds ($|Q_A| = 0$) the atomic valence values which are two times smaller than the classical valence values: $V_A^{(1/2)} = 1/2 \cdot C_A$.

Let us consider a compound with a hydrogen-type atom H with one valence electron on the single atomic orbital (H may be hydrogen or an alkali-metal

atom). In this simple case the atomic charge Q_H and the covalence C_H of the atom H depends only on the single density matrix element $P_{hh} = p$:

$$\begin{aligned} Q_H &= Z_H - p = 1 - p \\ C_H &= 2N_H - W_{HH} = 2p - p^2. \end{aligned}$$

As the formal oxidation number of this hydrogen-type atom is equal to unity in any compound, we have:

$$\Xi_H \equiv 1 = |Q_H| + \alpha C_H = |Q_H| + \alpha(2(1 - Q_H) - (1 - Q_H)^2) \quad (11)$$

or $\alpha = 1/(1 + |Q_H|)$.

For $Q_H = 0$ and α value equals 1 so that the valence of Eq. (6) coincides with the covalence C_A .

When the ionic contribution to bonding is relatively large, the coefficient α value is practically independent on the atomic charge value and may be taken as equal to 1/2 which corresponds to Eq. (10). It is easy to check up that when the charge $|Q_H|$ changes in the interval $0.55 < |Q_H| < 1.00$ the $V_H^{(1/2)}$ value changes only in the interval 0.90–1.00.

The coefficient α in Eq. (6): (i) is practically independent on the type of atom, (ii) actually does not depend on the absolute but on the relative charge value: $|Q_A|/\Xi_A$.

Indeed let AB_n be a molecule or molecular cluster in which the bonds between atoms A and B may be considered as approximately equivalent and the bond order W_{BB} between different B-type atoms (which have the same charges and large B–B' bond length) is negligibly small.

Using Eq. (6) we have:

$$\begin{aligned} V_A^z &= |Q_A| + \alpha_A \cdot \sum_{B \neq A} W_{AB} \approx n|Q_B| + n\alpha_A W_{AB} \\ V_B^z &= |Q_B| + \alpha_B \cdot \left(\sum_{B \neq B'} W_{BB'} + W_{AB} \right) \approx |Q_B| + \alpha_B W_{AB}. \end{aligned}$$

According to the classical valence theory, the A-atom oxidation number in the compound AB_n is n times greater than oxidation number of B-atom. $V_A = nV_B$, so that $\alpha_A = \alpha_B$. Besides it was already shown that the coefficient α is equal 1/2 in the case of highly ionic bond. This is fulfilled if $|Q_H|$ in Eq. (11) is not greater than 1, thus:

$$\alpha = 1/(1 + |Q_A|/\Xi_A). \quad (12)$$

Putting in Eq. (12) $\Xi_A \approx V_A$ and using Eq. (6) we obtain the quadratic equation for V_A :

$$V_A = |Q_A| + C_A/(1 + |Q_A|/V_A). \quad (13)$$

The positive root of Eq. (13) is:

$$V_A = (C_A + (C_A^2 + 4Q_A^2)^{1/2})/2. \quad (14)$$

Equation (14) may be considered as one possible definition of the full atomic valence V_A , which in limit cases of the nonpolar covalent and purely ionic bonding gives the values C_A and E_A , respectively.

4. Discussion of results

In the preceding section some model systems were considered. The density matrix elements for these systems have special form that allows one to find the bounds of applicability of the different valence definitions of Eqs. (5), (10) and (14). Naturally, the final conclusion about the correctness of either valence definition may be made only based on an analysis of the numerical values calculated for a wide range of compounds.

Tables 1–4 give the numerical values of atomic charges (Q_A), covalencies (C_A) and full valencies ($V_A^{(1/2)}$ and V_A), found as a result of electronic structure calculations of molecules and crystals.

There are three groups of compounds included in these tables. The first group (marked by a letter) includes those molecules for which the full atomic valence values are calculated from the values of atomic charges Q_A and covalencies C_A published in the literature [10, 11].

The second group consists of those molecules for which the electronic structure calculation was made by us in the framework of CNDO approximation with parameters taken from Ref. [12] or from our preceding crystals calculations. We used in the CNDO calculations the experimental interatomic distances [13].

At last, the third group of compounds (marked by the symbol “*”) consists of those crystals for which we made the electronic structure self-consistent density matrix calculations of crystals [14, 15].

Table 1. Valence of halogen and oxygen atoms

$\Xi_A = 1$	Q_A	C_A	$V_A^{(1/2)}$	V_A	$\Xi_A = 2$	Q_A	C_A	$V_A^{(1/2)}$	V_A
PbJ ₂	0.24	1.17	0.82	1.22	SnO	0.34	2.41	1.55	2.46
PbBr ₂	0.33	1.09	0.87	1.18	PbO	0.50	2.25	1.62	2.36
^a HF	0.37	0.89	0.81	1.02	^b H ₂ O	0.69	1.76	1.57	2.00
PbCl ₂	0.41	1.00	0.91	1.15	SnO ₂	0.75	1.71	1.61	1.99
^a H ₄ F ₅ ⁻	0.46	0.83	0.87	1.03	Tl ₂ O	0.87	1.85	1.80	2.19
^a H ₃ F ₄ ⁻	0.49	0.79	0.88	1.02	*Pb ₃ O ₄	1.05	1.58	1.84	2.10
SiF ₂	0.50	0.91	0.96	1.13	CaO	1.14	0.97	1.62	1.72
TlJ	0.51	0.88	0.95	1.11	*Pb ₃ O ₄	1.24	1.34	1.91	2.08
SnF ₂	0.56	0.79	0.96	1.08	*Y ₂ Cu ₂ O ₅	1.38	1.13	1.94	2.06
^a H ₂ F ₃ ⁻	0.56	0.68	0.90	1.00	*Y ₂ Cu ₂ O ₅	1.41	1.09	1.95	2.06
TlCl ₃	0.58	0.74	0.95	1.06	*ZrO ₂	1.45	1.02	1.96	2.05
^a H ₄ F ₅ ⁻	0.58	0.84	1.00	1.14	*YBa ₂ Cu ₃ O ₇	1.51	0.83	1.92	1.98
TlCl	0.59	0.75	0.96	1.07	*Cu ₄ O ₃	1.55	0.82	1.96	2.01
PbCl ₄	0.62	0.67	0.96	1.04	*La ₂ O ₃	1.59	0.77	1.98	2.02
^a H ₂ F ₃ ⁻	0.63	0.71	0.99	1.08	*CuO	1.60	0.74	1.97	2.01
SiF ₄	0.65	0.63	0.96	1.04	*La ₂ CuO ₄	1.62	0.71	1.98	2.01
^a HF ₂ ⁻	0.69	0.55	0.97	1.02	*La ₂ CuO ₄	1.65	0.66	1.98	2.01
SnF ₄	0.76	0.46	0.99	1.02	*La ₂ O ₃	1.68	0.61	1.98	2.01
PbF ₂	0.78	0.42	0.99	1.02	*Cu ₄ O ₃	1.70	0.49	1.95	1.96
PbF ₄	0.85	0.29	1.00	1.01	*YCuO ₂	1.71	0.56	1.99	2.01
YF ₃	0.86	0.27	1.00	1.01	*LaCuO ₂	1.73	0.52	1.99	2.01
*LaF ₃	0.92	0.15	1.00	1.00	*SrCuO ₂	1.77	0.42	1.98	1.99
ZrCl ₄	0.93	0.13	1.00	1.00	*Sr ₂ CuO ₃	1.86	0.26	1.99	1.99
KF	0.99	0.01	1.00	1.00	*Cu ₂ O	1.94	0.12	2.00	2.00

^a Ref. [10], ^b Ref. [11], * crystal

Table 2. Valence of positively charged atoms with constant oxidation states

$\Xi_A = 1$	Q_A	C_A	$V_A^{(1/2)}$	V_A	$\Xi_A = 2$	Q_A	C_A	$V_A^{(1/2)}$	V_A
^a LiH	0.45	0.80	0.85	1.00	SrO	1.14	0.98	1.63	1.73
^a CH ₃ Li	0.68	0.50	0.93	0.97	CaO	1.17	0.97	1.65	1.75
Li ₂ O	0.77	0.41	0.97	1.00	*SrCuO ₂	1.94	0.12	2.00	2.00
^a LiF	0.80	0.39	1.00	1.02	*CaF ₂	1.99	0.01	2.00	2.00
*KCuO ₂	0.99	0.02	1.00	1.00	*Sr ₂ CuO ₃	1.99	0.02	2.00	2.00
$\Xi_A = 3$	Q_A	C_A	$V_A^{(1/2)}$	V_A	$\Xi_A = 4$	Q_A	C_A	$V_A^{(1/2)}$	V_A
*Y ₂ Cu ₂ O ₅	2.03	1.71	2.88	3.06	*ZrO ₂	2.90	1.95	3.87	4.03
*La ₂ CuO ₄	2.40	1.15	2.98	3.04	ZrCl ₄	3.73	0.50	3.98	3.99
*La ₂ O ₃	2.43	1.08	2.97	3.03	ZrO ₂	3.85	0.29	3.99	4.00
*YBa ₂ Cu ₃ O ₇	2.48	0.99	2.97	3.02	ZrF ₄	3.87	0.26	4.00	4.00
YF ₃	2.58	0.80	2.98	3.01					

^a Ref. [11], *crystal**Table 3.** Valence of atoms with variable oxidation states^a

$\Xi_A = 1$	Q_A	C_A	$V_A^{(1/2)}$	V_A	$\Xi_A = 3$	Q_A	C_A	$V_A^{(1/2)}$	V_A
Tl ₂ O	0.43	1.04	0.95	1.19	TlCl ₃	1.73	1.94	2.70	2.95
TlI	0.51	0.88	0.95	1.11					
TlCl	0.59	0.75	0.96	1.07					
TlF	0.78	0.42	0.99	1.02					
$\Xi_A = 2$	Q_A	C_A	$V_A^{(1/2)}$	V_A	$\Xi_A = 4$	Q_A	C_A	$V_A^{(1/2)}$	V_A
SnO	0.34	2.41	1.55	2.46	^b CH ₄	0.52	3.92	2.48	3.99
PbJ ₂	0.48	2.20	1.58	2.30	^b CH ₃ Li	1.01	3.40	2.71	3.68
PbO	0.50	2.25	1.62	2.36	^b ClI ₄	1.29	3.57	3.07	3.99
PbBr ₂	0.67	2.04	1.69	2.24	SnO ₂	1.49	3.05	3.01	3.66
*Pb ₃ O ₄	0.74	2.11	1.79	2.34	PbCl ₄	2.46	2.41	3.66	3.94
PbCl ₂	0.82	1.87	1.75	2.18	SiF ₄	2.61	2.25	3.73	3.97
*PbO	0.91	2.07	1.94	2.41	*SiO ₂	2.68	2.18	3.77	3.98
*Pb ₂ O ₃	0.94	1.94	1.91	2.32	*PbO ₂	2.78	1.99	3.78	3.95
SiF ₂	1.00	1.67	1.84	2.14	*Pb ₂ O ₃	2.80	1.95	3.78	3.94
SnF ₂	1.12	1.49	1.87	2.09	SnF ₄	3.02	1.70	3.87	3.99
PbF ₂	1.56	0.81	1.96	2.02	*Pb ₃ O ₄	3.09	1.57	3.87	3.97
					PbF ₄	3.40	1.09	3.95	3.99

^a The crystal structure of the miscellaneous oxides: Pb₂O₃, Pb₃O₄ and Cu₄O₃ contain two different kinds of metal atoms (with different formal valence)^b Ref. [11], *crystal

As it is seen from the tables, the atomic covalence C_A (usually named valence in the literature) has the numerical values close to those of the classical valence only for the compounds with the small ionicity degree. Moreover, the covalence C_A values of the same atom are close in the compounds with a priori different oxidation numbers of this atom (for comparison C_A is equal to 1.49 and 1.70 in SnF₂ and SnF₄ molecules, respectively).

Table 4. Valence of copper atoms^a

	Q_A	C_A	$V_A^{(1/2)}$	V_A
*Cu ₄ O ₃	0.95	0.13	1.01	1.02
*Cu ₂ O	0.97	0.12	1.03	1.03
*LaCuO ₂	0.97	0.09	1.01	1.02
*YCuO ₂	0.98	0.15	1.06	1.06
*Sr ₂ CuO ₃	1.38	0.76	1.76	1.81
*Li ₂ CuO ₂	1.43	0.86	1.86	1.92
*SrCuO ₂	1.43	0.92	1.89	1.96
*Cu ₄ O ₃	1.55	0.99	2.05	2.12
*CuO	1.60	1.00	2.10	2.18
*Y ₂ Cu ₂ O ₅	1.60	1.09	2.14	2.24
*La ₂ CuO ₄	1.76	1.15	2.34	2.43
*LaCuO ₃	1.81	1.49	2.55	2.70
*NaCuO ₂	1.89	1.16	2.47	2.56
*KCuO ₂	2.08	1.14	2.65	2.73

^a See footnote to Table 3

*crystal

Based on an analysis of atomic covalence C_A values [16] an attempt was made to consider the change of the molecules reactivity. The dependence of some properties of molecules (rotation barriers, substitution effects, reactivity properties) on the atomic valence numerical value is evident. But the change of covalence C_A itself may be due to the change of the bond ionicity degree. Therefore it seems to be more consistent to seek for the connection between mentioned properties of molecules and full atomic valence.

It is seen from the tables that the values of the full valence $V_A^{(1/2)}$ are close to the classical valence values for the molecules and crystals with relatively high ionicity degree of bonding. However, in more covalent compounds the values of $V_A^{(1/2)}$ are underestimated in comparison with the classical atomic valence values.

The full atomic valence definition of Eq. (14) is more complicated than the definition of Eq. (10) but appears to be more appropriate since it reproduces correctly the atomic valence for any values of atomic charges Q_A (i.e., it is independent on the bond ionicity) and is applicable both for atoms with constant and variable valencies. Moreover, this valence definition seems to be most fruitful in those compounds where stoichiometric formula analysis does not allow one to find the atomic valencies at all. As an example the tables give the results of our calculation for the crystalline mixed oxides Cu₄O₃, Pb₂O₃, Pb₃O₄. Earlier we calculated the atomic valencies also in the high- T_c superconductors YBa₂Cu₃O_x ($x = 6, 7$) [14].

5. Conclusion

We have presented in this paper a new atomic valence definition (called full valence) which seems to be applicable to molecules and crystals with any ionicity degree of bonds. As far as we know this is the first attempt to give a quantum-chemical definition and to calculate an atomic valence in crystalline solids. Applications of the approach presented are in progress.

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