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REGULAR ARTICLE

R. Ponec

Chemical bonding in solids. On the generalization of the concept of bond order and valence for infinite periodical structures

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Abstract A simple model allowing the description and the visualization of the bonding in solids in terms of classical chemical concepts of bond order and valence was proposed. The model is based on the straightforward generalization of the Wiberg indices, which are known to mimic the pattern of bonding interactions in ordinary isolated molecules, to infinite periodical structures. The picture of bonding based on the applications of this model to idealized 1D, 2D and 3D lattices is remarkably reminiscent of the model proposed a long time ago by Pauling to describe the nature of the metallic bonding. It implies that in addition to small fraction of valence electrons involved in the covalent bonding with the nearest neighbors, the majority have the character of "mobile" electrons, which are responsible for the build-up of metallic properties in the studied solids.

1 Introduction

Material science, as the realm of the design and the synthesis of new advanced materials with unusual mechanical, electrical, optical or magnetic properties is one of the most rapidly expanding fields of contemporary research. As most of these advanced materials are solids, their design and the synthesis relies considerably on the dialogue between solid state physicists, who possess the mathematical tools for the description of the solid state, and chemists whose task is the actual synthesis of these materials. Despite its importance, such a dialogue is still a little hindered by the fact that the language which chemists and physicist use for the description of the systems they are working with is considerably different. While physicist's approach to solids is based on a mathematical description in terms of Brillouin zones and k-states [1], the approach of chemists is much more intuitive and relies on the classical concepts of bonds, bond orders, valences etc., terms of which chemists are traditionally used to describing molecules and their structures.

In order to overcome this barrier, and to allow both groups to understand each other better, considerable effort has been devoted in recent years to the reconciliation of both approaches. An example in this respect can be, for example, the books by Harrison [2], Cox [3] and Hoffmann [4], in which the principles of solid state chemistry are being explained with the chemists audience in mind. Our aim in this study is to pursue this chemist oriented approach to the description of the structure of the solids and to demonstrate that even such very chemical concepts as bond order and valence, originally introduced in the realm of classical chemistry, can quite straightforwardly be generalized also to infinite periodical structures. In this connection it is perhaps worth mentioning that similar and in fact the first attempt to generalize the bond order to solids was proposed some time ago by Hoffmann [4] in his concept of crystal orbital overlap population (COOP), but in contrast to this concept which is closely related to the definition of bond order by Coulson [5], our approach relies on the generalization of the so-called Wiberg index [6]. In the following part the basic ideas of our generalization will be presented.

2 Theoretical

The concept of bond order was introduced into chemical theory as a theoretical counterpart of the classical concept of bond multiplicity. The most widely used definition of bond order is due to Wiberg [6], who defined it in terms of the square of the elements of charge density-bond order matrix [5] (Eq. 1).

$$W_{AB} = \sum_{\mu}^{A} \sum_{\nu}^{B} p_{\mu\nu}^{2} \,. \tag{1}$$

This original definition is applicable not only for orthogonal basis sets, but also to generalization to non-orthogonal basis sets reported by Mayer [7]. The important feature of Wiberg as well as of Mayer generalized bond orders is that their values mimic the pattern of bonding interactions in a molecule as depicted in the classical structural formula remarkably well. Thus, for example, the fact that a given pair of atoms is formally linked by a bond in the classical structural

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R. Ponec
Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Prague 6, Suchdol, 165 02, Czech Republic

formula finds its reflection in the nonnegligible value of the corresponding bond order. Moreover, the numerical values of calculated bond orders between formally bonded atoms often surprisingly coincide with classical bond multiplicities. On the other hand, the bond orders between the atoms which are not formally linked are practically negligible. Wiberg's definition of bond orders served subsequently also as a basis for the generalization of another classical chemical concept, namely the concept of valence. This generalization was proposed by Gopinathan and Jug [8] who defined the valence of the atom A as: (Eq. 2)

$$V_A = \sum_{B \neq A} W_{AB} \,, \tag{2}$$

and the calculated values of valences do indeed correspond fairly well with the classical chemical expectations.

After having reminded the definition of bond order and valence for "ordinary" molecules, let us demonstrate that basically the same formulas can be applied also to infinite periodical structures. For this purpose it is convenient to first rewrite the original formula (1) into the alternative form (3) [9],

$$\begin{aligned} F_{AB} &= 2\sum_{i}^{\text{occ}} \langle i \,|\rangle_A \, \langle j \,| i \rangle_B \quad , \\ W_{AB} &= 2F_{AB} \,, & (3) \\ \langle i \,| j \rangle_A &= \int_{\Omega_A} \varphi_i^*(r)\varphi_j(r)\mathrm{d}r \,, & (4) \end{aligned}$$

where the integration of the overlap integral of two occupied molecular orbitals i and j is over the atomic domains resulting from Bader's virial partitioning [10] of the electron density function $\rho(r)$. The formula (3) can thus be regarded as the AIM generalized definition of bond order.

This generalized formula reduces to the original definition if the overlap integrals (4) are approximated using a kind of Mulliken-like approximation according to which the electron is assumed to be in the region of the atom A, if it resides in the orbital localized on that atom. As it will be shown, similar approximation will also be used in our generalization of the concept of bond order to infinite periodical structures.

This generalization is based on the straightforward parallel between discrete molecular orbitals of isolated molecules and quasi-continuum of k-states in the solid state. On the basis of this parallel, the original definition of the bond order (1) can be rewritten in the form (5)

$$\begin{aligned} F_{AB}^{\text{solid}} &= 2\sum_{k}^{\text{occ}}\sum_{k'}^{\text{occ}} \langle k|k'\rangle_A \langle k|k'\rangle_B \\ &\cong 2\int_0^{k_F}\int_0^{k'_F} \langle k|k'\rangle_A \langle k|k'\rangle_B \mathrm{d}k\mathrm{d}k' \,, & (5) \\ W_{AB}^{\text{solid}} &= 2F_{AB}^{\text{solid}} \,. \end{aligned}$$

In the following part the application of this formula to several simple periodic structures will be reported.

The simplest form of infinite periodical system is a linear chain in which each atom contributes to the bonding by one electron in a single 1s orbital χ. This model is, of course, a bit idealized as in the real situation such a chain would undergo a Peierls distortion [11], but for the purpose of the demonstration of the principles of this approach, this simple model seems plausible.

Under the above assumptions, the one-electron orbitals of this system are given by the Bloch functions of the form (6)

$$\psi_k(r) = \frac{1}{\sqrt{N}} \sum_m \mathrm{e}^{i\vec{k}\cdot\vec{r}_m} \chi(\vec{r} - \vec{r}_m) \,, \tag{6}$$

where N is the total number of the atoms, and the summation runs over the individual atoms in the chain. Assuming now, without the loss of generality, the orthogonality of atomic orbitals in the chain, the integrals over the atomic domains in the formula (4) can be approximated as (6).

$$\begin{aligned} \langle k|k'\rangle_A &= \frac{1}{N}\sum_m\sum_n \mathrm{e}^{i\vec{k}\cdot\vec{r}_m}\mathrm{e}^{-i\vec{k}'}\cdot\vec{r}_n \\ &\times \int_{\Omega_A} \chi^*(r - r_n)\chi(r - r_m)\mathrm{d}r \cong \frac{1}{N}\mathrm{e}^{i(\vec{k}-\vec{k}'})\vec{r}_A & (7) \end{aligned}$$

Within this approximation, the formula for the bond order between the pair of atoms A and B reduces to (8)

$$W_{AB}^{\text{chain}} = \frac{4}{N}\int_0^{k_F}\int_0^{k'_F} \mathrm{e}^{i(\vec{k}'-\vec{k})(\vec{r}_B-\vec{r}_A)}\mathrm{d}k\mathrm{d}k' \,. \tag{8}$$

Taking into account that for the linear chain with the lattice separation a the difference $(r_B - r_A)$ can be written as j.a $(j = 1, 2, 3 \ldots.)$, and that the wave vectors k and k' can be alternatively expressed as (9)

$$k = \frac{2\pi n}{Na}, k' = \frac{2\pi n'}{Na} \quad (n = 0, 1, 2, 3 \ldots ..\mathrm{N} - 1) \,, \tag{9}$$

the bond order between the pair of neighboring atoms is given by formula (10)

$$W_{A(A+1)} = \frac{4}{N}\int_0^{N/2} \mathrm{e}^{-i\frac{2\pi n}{N}}\mathrm{d}n \int_0^{N/2} \mathrm{e}^{i\frac{2\pi n'}{N}}\mathrm{d}n' = \frac{4}{\pi^2} \,. \tag{10}$$

Similarly, it can be shown that the bond order $\mathrm{W}_{A(A+2)}$ between the next nearest neighbors as well as between all pairs of atoms A, A+2j $(j = 1, 2, ...)$ equals identically zero, while bond orders between the atoms A, A+$(2j + 1)$ is given by (11)

$$W_{A(A+(2j+1))}^{\text{solid}} = \frac{4}{\pi^2} \cdot \frac{1}{j^2} \,. \tag{11}$$

Taking into account that the monoatomic term W_{AA}^{solid} is equal to 1, the above bond orders can be shown to satisfy the normalization condition (12)

$$\frac{1}{2}\sum_A W_{AA}^{\text{solid}} + \sum_{A<B} W_{AB}^{\text{solid}} = N\left(1/2 + \frac{4}{\pi^2}\left(1 + \frac{1}{3^2} + \frac{1}{5^2} + \frac{1}{7^2} + \dots\right)\right) = N\,, \tag{12}$$

which is the straightforward counterpart of the similar normalization valid for the ordinary Wiberg indices in isolated molecules.

On the basis of this parallel it is possible to introduce the solid state counterpart of the atomic valence by the formula (13)

$$V_A^{\text{solid}} = \sum_{B\neq A} W_{AB}^{\text{solid}} \tag{13}$$

Let us now attempt to explore the concept of the valence further. As it is straightforwardly evident, the atomic valence of any of the atom in the chain is, consistent with the expectation, equal to 1. More detailed inspection of the individual terms contributing to the total valence shows that the valence electron of each atom in the chain is engaged in bonding interactions not only with its nearest neighbors but that a certain nonnegligible contributions come also from the interactions with more distant atoms. This situation is quite different from what was typical for "ordinary" molecules where the bond orders between classically nonbonded atoms are generally very small. This implies that due to the existence of nonnegligible bond orders between non-nearest neighbors, the bonding in the chain is much more delocalized than in isolated molecules. This suggests that it may be useful to partition the total atomic valence in solids into localized covalent part which accounts for the bonding to nearest neighbors and the "mobile" part which reflects the existence of long-distance bonding interactions. This result is very interesting since the existence of "mobile" electrons was anticipated already long time ago in free-electron model of metals [1]. The only difference is, that while free-electron model assumes that the "mobile" electrons are all the valence electrons of the metal, the above approach demonstrates that at least part of the valence electrons is still involved in localized covalent interactions with the nearest neighbors.

In the case of our simple model, the contribution of long-distance "mobile" bonding covers roughly 20% of the total bonding capacity of each atom in the chain.

$$V_A^{\text{mobile}} = V_A^{\text{solid}} - \sum_{B\neq A}^{\text{nearest}} W_{AB}^{\text{solid}} = 1 - \frac{2\cdot 4}{\pi^2} \cong 0.20\,. \tag{14}$$

This, of course, is not very much, but as it will be shown, the amount of mobile electrons dramatically increases on going from simple linear chain to 2D and 3D solids. In this connection it is interesting to remind that a qualitatively similar model of bonding was proposed a long time ago by Pauling to explain the nature of the so-called metallic bond [12]. According to his model, the metallic bond is closely related to the ordinary covalent or electron pair bond. The only difference is that because the number of available electrons is usually less than the number of nearest neighbors, the bonds must resonate among all available positions. The effect of such a resonance is the effective decrease of the bond order with the bonded neighbors so that greater fraction of valence electrons remains available as "mobile" electrons.

In order to demonstrate the gradual build-up of metallic character let us analyze first the bonding in simple square planar lattice with the lattice separation a, in which each atoms contributes again by one electron in single 1s orbital.

The Bloch functions for this simple model lattice have the form

$$\psi_k(\vec{r}) = \frac{1}{N}\sum_{m,n} \mathrm{e}^{i\vec{k}\cdot\vec{r}_{mn}}\varphi(\vec{r}-\vec{r}_{mn})\,, \tag{15}$$

where

$$\vec{r}_{mn} = ma\vec{i} + na\vec{j}\,, \tag{16}$$

denotes the position of the atom in the direct lattice and k is the wave vector

$$\vec{k} = \frac{2\pi n_1}{Na}\vec{i} + \frac{2\pi n_2}{Na}\vec{j}\,. \tag{17}$$

Assuming again the orthogonality of the basis orbitals in the lattice and using the Mulliken-like approximation of the integrals $\langle k' \mid k\rangle_A$ (17)

$$\langle k|k'\rangle_A = \frac{1}{N^2}\mathrm{e}^{i(\vec{k}-\vec{k}')}\cdot\vec{r}_A\,, \tag{18}$$

The bond order between the nearest neighbors is given by (18)

$$W_{AB}^{\text{square}} = \frac{4}{N^4}\left(\frac{N}{2}\right)^2 \int_0^{N/2} \mathrm{e}^{i\frac{2\pi n'}{N}}\mathrm{d}n' \int_0^{N/2} \mathrm{e}^{-i\frac{2\pi n}{N}}\mathrm{d}n = \frac{2}{4\pi^2}(1-\cos\pi) = \frac{1}{\pi^2} \cong 0.101\,. \tag{19}$$

As each atom of the lattice contributes 1 electron and at the same time has four nearest neighbors, the total amount of "mobile" electrons is roughly equal to 0.6 (20)

$$V_A^{\text{mobile}} = V_A^{\text{solid}} - 4\cdot\frac{1}{\pi^2} \cong 0.60\,. \tag{20}$$

As it can be seen the number of mobile electrons is indeed higher than in the case of the linear chain and a further increase is observed on extending the above model to 3D. Thus, for example, the same approach applied to the 3D solid with simple cubic cell yields the bond order between the nearest neighbors equal to $1/4\pi^2$ (20)

$$W_{\text{AB}}^{\text{cubic}} = \frac{4}{N^6}\left(\frac{N}{2}\right)^4 \frac{N^2}{4\pi^2}2(1-\cos\pi) = \frac{1}{4\pi^2} \cong 0.025\,. \tag{21}$$

This implies that because each atom is now surrounded by 6 nearest neighbors, the total amount of "mobile" electrons increases to 85%.

$$V_A^{\text{mobile}} = 1 - 6 \cdot 0.025 \doteq 0.85\,. \tag{22}$$

We can thus see that the transition from simple linear chain to 3D solid is connected with the gradual increase in the amount of "mobile" electrons and, consequently, to the build-up of metallic character. As it will be shown below, the same general trend holds also for other more realistic structures. As an example of such a system let us analyze the nature of the bonding in alkali metals whose elementary cell is of bcc type.

For this purpose let us introduce the basis vectors of the direct lattice (23)

$$\begin{aligned}\vec{a}_1 &= \frac{a}{2}(\vec{i} - \vec{j} + \vec{k})\,,\\ \vec{a}_2 &= \frac{a}{2}(\vec{i} + \vec{j} - \vec{k})\,,\\ \vec{a}_3 &= \frac{a}{2}(-\vec{i} + \vec{j} + \vec{k})\,,\end{aligned} \tag{23}$$

and let us assume that each elementary cell contains just one atom which contributes to the bonding by one electron. The Bloch functions characterizing the individual k-states can be written as (24)

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{N^3}} \sum_{m,n,o} e^{i\vec{k}\cdot\vec{r}_{\text{mno}}} \varphi(\vec{r} - \vec{r}_{\text{mno}})\,, \tag{24}$$

where $\vec{r}_{\text{mno}}$ characterizes the position of the atom in the lattice

$$\vec{r}_{\text{mno}} = m\vec{a}_1 + n\vec{a}_2 + o\vec{a}_3, \tag{25}$$

and the wave vector $\vec{k}$ can be expressed using basis vectors of the reciprocal lattice as (24)

$$\vec{k} = \frac{n_1}{N}\vec{b}_1 + \frac{n_2}{N}\vec{b}_2 + \frac{n_3}{N}\vec{b}_3 \tag{26}$$

Adopting now, as in the previous cases, the above-mentioned Mulliken-like approximation, bond order between the nearest neighbors can straightforwardly be calculated. But in contrast to the previous two examples, the situation here is a slightly different because the specification of the neighboring atoms requires one to distinguish between two cases. One of them corresponds to the neighbors at the position (25)

$$\Delta\vec{r}_{1,2} = (m \pm 1)\vec{a}_1 + (n \pm 1)\vec{a}_2 + (o \pm 1)\vec{a}_3\,, \tag{27}$$

while the other one involves six remaining neighbors localized at (26)

$$\begin{aligned}\Delta\vec{r}_{3,4} &= (m \pm 1)\vec{a}_1\,,\\ \Delta\vec{r}_{5,6} &= (n \pm 1)\vec{a}_2\,,\\ \Delta\vec{r}_{7,8} &= (o \pm 1)\vec{a}_3\,,\end{aligned} \tag{28}$$

Substituting these position vectors into the general definition of bond order (5) it is possible to show, that bond orders between the neighbors localized at positions (25) equals to (27)

$$W_{AB_{1,2}}^{bcc} = \frac{4}{N^6}\left(\frac{N^2}{4\pi^2}\right)^3 [2(1 - \cos\pi)]^3 = \frac{4}{\pi^6} \cong 0.004\,, \tag{29}$$

while bond orders between the neighbors localized at the positions (26) are equal to (28)

$$\begin{aligned}W_{AB_{3,4,5,6,7,8}}^{bcc} &= \frac{4}{N^6}\left(\frac{N}{2}\right)^4 \left(\frac{N^2}{4\pi^2}\right)[2(1 - \cos\pi)]\\ &= \frac{1}{4\pi^2} \cong 0.025\,.\end{aligned} \tag{30}$$

On the basis of these values it is then useful to introduce the weighted mean of bond orders as (29)

$$\overline{W}_{AB}^{\text{bcc}} = \frac{4/\pi^6 + 3/4\pi^2}{4} = \frac{1}{\pi^6} + \frac{3}{16\pi^2} \cong 0.020\,. \tag{31}$$

Taking now into account that each atom in bcc cell is surrounded by eight nearest neighbors, the amount of electrons engaged in the covalent bonding with the neighbors exhausts only about 16% of the total bonding capacity while 84% are again available as "mobile" electrons for the build-up of the metallic character.

Similarly it is possible to analyze bonding in another simple metallic structure, like fcc, which is characteristic for rare metals as Cu, Ag and Au. The situation here is, however, a bit more complex as the electrons of the filled d-shell also contribute to bonding, but a first rough idea of the bonding situation can be obtained by assuming again that each atom contributes just one singly occupied valence orbital. Under this assumption the mean bond order between nearest neighbors can be found to be 0.0175. This implies that with 12 nearest neighbors, the amount of electrons involved in the covalent bonding with these neighbors is about 21%, while remaining 79% are again available as "mobile" electrons.

These results are very interesting. They demonstrate, namely, that despite its simplicity, the proposed model is indeed able to reveal the most basic features of the bonding in solids, like, for example, the existence of "mobile" electrons in metals. The above approach is, however, quite general and can be applied also to other types of solids at a more realistic level of the theory and we believe that such an application can contribute to the reconciliation of physically and chemically oriented approach to the description of the bonding in these systems.

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