Bond Indices in Solids. A Numerical Approach to Analytical Model

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A NUMERICAL APPROACH TO ANALYTICAL MODEL.

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Some time ago a simple analytical model allowing to evaluation of the bond indices especially in metallic solids was proposed by one of us [1]. The model was based on the straightforward generalization of the formula for the calculation of delocalization or shared-electron distribution (SEDI) indices [2,3] indices in ordinary molecules.

$$W_{AB} = 2F_{AB}$$

$$F_{AB} = 2\sum_{i}^{occ}\sum_{j}^{occ}\langle i|j\rangle_A \langle j|i\rangle_B \qquad (1)$$

$$\langle i|j\rangle_A = \int_{\Omega_A} \varphi_i^*(r)\varphi_j(r)dr$$

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 can be rewritten in the form (2)

$$F_{AB}^{solid} = 2\sum_{k}^{occ}\sum_{k'}^{occ}\langle k|k'\rangle_A \langle k'|k\rangle_B \cong 2\int_{k_{occ}}\int_{k_{occ}}\langle k|k'\rangle_A \langle k'|k\rangle_B dkdk'$$

$$W_{AB}^{solid} = 2F_{AB}^{solid} \qquad (2)$$

The practical use of the above formula can be best demonstrated on a simple case of linear 1-D chain in which each atom contributes to the bonding by one electron in a single 1s orbital χ. Under the above assumptions, the one-electron orbitals of this system are given by the Bloch functions of the form (3)

$$\psi_k(r) = \frac{1}{\sqrt{N}} \sum_m e^{ik \cdot r_m} \chi(r - r_m) = \frac{1}{\sqrt{N}} \sum_m e^{ikma} \chi_m,$$ (3)

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 (3) can be approximated as (4).

$$\langle k' | k \rangle_A = \frac{1}{N} \sum_m \sum_n e^{ik \cdot r_m} e^{-ik' \cdot r_n} \cdot \int_{\Omega_A} \chi^*(r - r_n) \chi(r - r_m) dr \cong \frac{1}{N} e^{i(k-k') \cdot r_A}$$ (4)

Within this approximation, the formula for the bond index between the pair of neighbouring atoms A and A+1 can be rewritten as (5)

$$W_{A,A+1}^{chain} = \frac{4}{N^2} \int_{k_{occ}} \int_{k'_{occ}} e^{i(k'-k)a} dk dk'$$ (5)

Using this approximation, and taking into account that the labels k can alternatively be expressed as

$$k = \frac{2\pi}{Na} g; k' = \frac{2\pi}{Na} g' \quad \text{where } (g; g' = 0,1,2,3.....N-1)$$ (6)

the formula (5) reduces to:

$$W_{A,A+1}^{solid} = 2F_{A,A+1} = \frac{4}{N^2} \int_0^{N/2} e^{i\frac{2\pi g}{N}} dg \int_0^{N/2} e^{-i\frac{2\pi g'}{N}} dg' = \frac{4}{N^2} \left(\frac{N^2}{4\pi^2} \right) (2 - 2\cos\pi) = \frac{4}{\pi^2}$$ (7)

The approximations underlying the above analytical model were checked in the recent study [4] by comparing with the values resulting from the real solid state calculations on a model chain of H atoms and such a comparison showed the complete quantitative agreement between both approaches. Unfortunately, such a nice agreement was observed just in the case of linear 1-D chain. In the case of similar comparison for square-planar 2-D and simple cubic 3-D lattices, the

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systematic deviations of both approaches were observed which manifested themselves in the systematic overestimation of the fraction of the mobile electrons responsible for the build-up of the metallic character. The detailed scrutiny of the observed deviations revealed that they mainly arise from too straightforward replacement of the summation over occupied orbitals in the general formula (1) by the integration over quasi-continuum of k-states in infinite structures. This is not the problem in 1-D lattice where the integration was trivial and involved just N/2 states of lowest energy (eq. 9), but the extension to more dimensions is a bit more tricky and deserves a more detailed clarification

For this purpose let us discuss the in more details the simple case of NxN square planar lattice. In such a case the Bloch functions are given by the formula (8)

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{N}\sum_{m}\sum_{n}e^{i\mathbf{k}\mathbf{r}_{mn}}\chi(\mathbf{r}-\mathbf{r}_{mn}) \tag{8}$$

where

$$\mathbf{r}_{mn} = ma\mathbf{i} + na\mathbf{j} \tag{9}$$

denotes the position of the individual atoms in the direct lattice and $\mathbf{k}$ is the wave vector

$$\mathbf{k} = \frac{2\pi}{Na}g_{1}\mathbf{i} + \frac{2\pi}{Na}g_{2}\mathbf{j} \tag{10}$$

Assuming again the orthogonality of the basis orbitals in the lattice and using the same approximation for the calculation of the integrals as in Eq. (5) one gets,

$$\left\langle \mathbf{k}'\middle|\mathbf{k}\right\rangle_{A} = \frac{1}{N^{2}}e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}_{A}} \tag{11}$$

where $\mathbf{r}_{A}$ denotes the position of an atom A in the array. Focusing on the nearest neighbour atoms B whose positions are given by the vectors (14)

$$\mathbf{r}_{A} = A_{1}a\mathbf{i} + A_{2}a\mathbf{j}$$
$$\mathbf{r}_{B} = (A_{1} \pm 1)a\mathbf{i} + A_{2}a\mathbf{j} \tag{12}$$

the formula for the bond index W_{AB} is given by (eq. (13))

$$F_{AB}^{square} = \frac{2}{N^2} \int_{k_{occ}} e^{ik_1 a} dk_1 dk_2 \int_{k'_{occ}} e^{-ik'_1 a} dk'_1 dk'_2$$

$$W_{AB}^{square} = 2F_{AB}^{square}$$

(13)

and the only what remains to be specified are the integration domains for the individual components of k-vector. In the original model the limits of the integration were arbitrarily chosen from 0 to N/2 for both components of k-vector.

$$F_{AB}^{square} = \frac{2}{N^2} \int_0^{N/2} e^{i\frac{2\pi}{N}g_1} dg_1 \int_0^{N/2} dg_2 \int_0^{N/2} e^{-i\frac{2\pi}{N}g'_1} dg'_1 \int_0^{N/2} dg'_2$$

$$W_{AB}^{square} = \frac{1}{\pi^2} \cong 0.101$$

(14)

The resulting value was about one half of the „exact" value 0.19 reported in the study [4] and similar underestimation, by the factor of 4, was observed also for 3-D simple cubic lattice (0.025 vs 0.12 respectively). The detailed analysis of the observed shortcomings of the original model has revealed that they are directly related to the implications resulting from the arbitrary choice of the integration limits. One of them is the systematic underestimation of the number of occupied states but in addition to this there is another problem that concerns the possible bias in the selection of occupied k-states. The selection of the integration domains determines, namely, the shape of the Fermi surface so that arbitrarily chosen integration limits may result in the distorted form of this surface and, consequently in the inclusion of some formally unoccupied k-states. To remedy the above problem we recently suggested a simple criterion for the selection of the occupied states based, similarly as in the case of 1-D lattice on the energy. Thus, e.g., in the case of 2-D square planar lattice, the energy of the system is given by (Eq. 18) [5]

$$E = \alpha + 2\beta(\cos(k_x a) + \cos(k_y a))$$

(15)

where β is the resonance integral describing in the tight binding approximation the interaction between nearest neighbours. Based on the energy criterion, the

choice of the occupied states is straightforward and manifests itself in imposing certain restrictions on the integration domains. To demonstrate these restrictions let us first rewrite, similarly as in the 1-D case, label k using the alternative expressions

$$k_x = \frac{2\pi}{Na} g_1; k_y = \frac{2\pi}{Na} g_2; k_x{}' = \frac{2\pi}{Na} g_1{}'; k_y{}' = \frac{2\pi}{Na} g_2{}'$$

$$(g_1, g_2 = 0,1,2,3.....N-1; g_1{}', g_2{}' = 0,1,2,3.....N-1)$$

(15)

If now, the points corresponding to individual states are plotted in the square diagram with coordinates g_1 and g_2, the domains of positive and negative energies concentrate into separate regions from which the limits for the integration over occupied states are straightforwardly evident. In the case of the above 2-D lattice, the corresponding diagram is shown in the Scheme I.

Scheme I
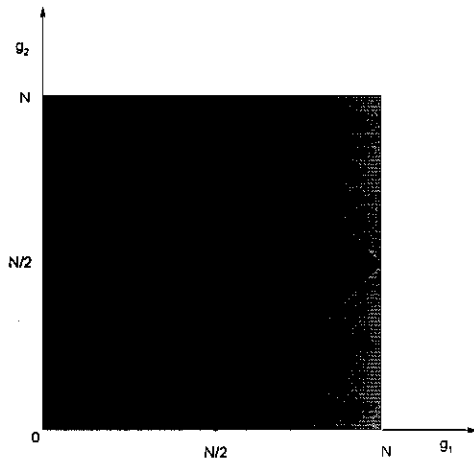
In this scheme, the domain of „occupied" states is highlighted in green while the red domain correspond to energetically unfavorable states. Based on this scheme, the formula (13) for the bond index between nearest neighbours can be rewritten as (Eq. (16)),

$$F_{AB}^{square} = \frac{2}{N^4} \iint\limits_{\Omega_{green}} e^{i\frac{2\pi}{N}g_1} dg_1 dg_2 \cdot \iint\limits_{\Omega_{green}} e^{-i\frac{2\pi}{N}g_1{}'} dg_1{}' dg_2{}'$$

(16)

Actual calculations based on the formula (18) then give the value of the index

$$W_{AB}^{square} = 2F_{AB}^{square} = \frac{16}{\pi^4} = 0.164 \qquad (17)$$

which closely agrees with the value 0.16 resulting from the integration over Fermi sphere [12] and reasonably close is also agreement with the value 0.19 resulting from the real calculations [12]. We can thus see that the suggested energy criterion together with the underlying implications for the specification of the domain of integration over the occupied k-states is indeed able to improve predictions of the original model and in spite its simplicity is indeed able to provide reasonably realistic eastimate of the electron sharing in solids.

Unfortunately the above straightforward procedure for the determination of the integration domains is not practically applicable in other cases. Thus, e.g., already in the case of simple cubic cell, the application of the energy criterion specified by (Eq. 20)

$$E = \alpha + 2\beta(\cos(\frac{2\pi}{N} g_1) + \cos(\frac{2\pi}{N} g_2) + \cos(\frac{2\pi}{N} g_3)) \qquad (20)$$

shows that the shapes of the Fermi surface is much more tricky (Scheme II)
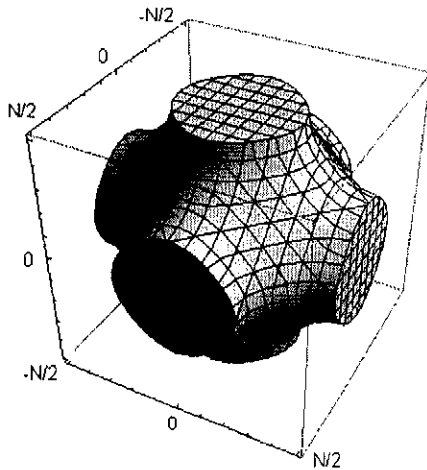
so that the explicit specification of the integration domains, required for the application of the analytical approach, is impossible. To overcome this problem we proposed as a feasible alternative the numerical calculations using the explicit summation over N/2 of low energy states. Such an approach gives for the index between nearest neighbour atoms the value 0.111, which well agrees with the „exact" value 0.12 reported in the study [12]. This result is very important as

it demonstrates that the numerical remedy of the problems with the specification of integration domains does indeed represents a feasible strategy for the calculation of bond indices in solids and examples of the applications to other types of unit cells will be discussed.

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