



Valence Illustration for Large Structure: A Fast Empirical Approach Based on Bond-Valence Method

Hoang Nam Nhat*

*Faculty of Engineering Physics and Nanotechnology, VNU University of Engineering and Technology,
E4 Building, 144 Xuan Thuy, Cau Giay, Hanoi, Vietnam*

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Abstract: Modelling of large structures by using the quantum-mechanical approach is still not accessible, especially for many heavy atoms complexes, as these tasks require vast computational resources that are not often available. This article introduces a procedure for modelling of large structures using a structural approach usually referred to as a bond-valence method. This empirical method minimalizes the computation costs and facilitates the construction of complex 3D images of thermally dependent electron density even for very large periodic structures. This method also provides a convenient way to visualize the carrier density, defect locations, and valence dynamics under thermal fluctuation.

Keywords: Bond-valence, defects, modelling, tools.

1. Introduction

The reconstruction of electric field gradient and valence structure plays an important role in understanding the properties of materials at microscopic level. Unfortunately, the modelling illustration is not available for many large structures due to complexity in computation. As known, there are many different field-dependent gradient-based methods for illustration purposes but one among the most efficient ones is a method called a bond-valence method, which was proposed by I. D. Brown [1] decades ago. As this method requires an *a priori* known crystal structure of materials - the information that was not often available for many compounds in the past, its application was limited to some simple structures and metallo-organic compounds where such data are accessible. The recent renaissance of this method follows from its wide application range and simplicity in use for large structures. According to its definition, a chemical valence, or may be called a chemical valence gradient (*de facto* electron density per length) which is related to a particular bond $\{i\}$ is called a bond-

* Tel.: 84-913097735.

Email: namnhat@gmail.com

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valence v_i and is modelled as a exponent function of the bonding distance R_i . The final atomic valence is defined as a sum of overlapping exponential functions [2, 3]:

$$v = \sum_{i=1}^n v_i = \sum_{i=1}^n v_{0i} \exp\left(\frac{R_i - R_0}{B}\right) \quad (1)$$

where n is the coordination number surrounding a given atom, R_0 is an equidistance, v_{0i} is a equivalence, and B is a constant. For each particular atomic types, the constant v_{0i} and B are tabulated [1]. These empirical values were obtained on the basis of the linear fitting of extensive set of data for this atomic type. As reported, the accuracy of this method exceeds 95% for the metallo-organic compounds. The recent studies showed that it can be used to reverse a model (crystal) structure obtained by the other techniques such as the Monte-Carlo into a valence band structure [4, 5]. In its deep theoretical concerns, the decomposition of atomic valence into the bond valences is a special case of de Prony's problem of spectral analysis of overlapping exponential functions which is well-known in many other areas of experimental physics [6, 7]. This paper attempts to extend the use of bond-valence method for a construction of colour 3D valence map, and related electric gradient, to demonstrate the valence dynamics under temperature fluctuation.

Evidently, the electric field gradient defined by a relation (1) is not an exact field gradient as obtained by the lower level theories like the Density Functional Theory, but for its simplicity it can be used for very large structures. For periodic structures we require that a valence given by (1) will satisfy also a condition of periodicity (\vec{T} is a real lattice translation vector):

$$v(\vec{R} + \vec{T}) = v(\vec{R}) \quad (2)$$

2. Valence and electric field under thermal fluctuation

To estimate a valence, or a bonding electron density, at arbitrary fixed point in a space between two atoms, we assume that a thermal fluctuation of atoms at certain temperature T follows a symmetric isothermal mode, *i.e.* there is only one constant B_{ISO} that determines the average width of a Gaussian distribution of atomic positions (Fig. 1). For this purpose, let us define a valence density as a valence per length unit $\rho(v_i) = v_i / r_i$. Now consider a thermal fluctuation of atoms around their crystallographic positions. Let denote a probability of an atom I to occur at a position a by $p_I(a)$ and

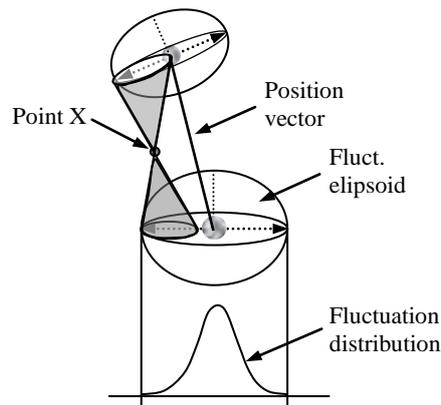


Fig.1. A fluctuation of interatomic distances determines all possible valence values (*alias* electron density) at arbitrary point X in the space between two atoms.

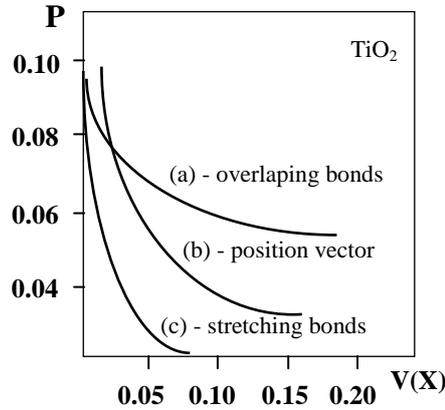


Fig. 2. The exponential distributions of $v(X)$ for the two atoms case showing a low probability for higher valencies.

of atom 2 at a position b by $p_2(b)$. The probability that both atoms occur simultaneously at a and b positions will be given by a product of these probabilities, *i.e.* by $P_{12}(a,b) = p_1(a)p_2(b)$. In a simplest case, $p_1(a)$ and $p_2(b)$ are the Gaussian functions whose half width is set by the particular isotropic temperature factors B_{ISO} retrieved from the structural analysis. Therefore a density $v(X)$ at a given point X in the space between two atoms also follows a probability distribution $p[v(X)] = p_1(a)p_2(b)$.

In 3D illustration (see Fig.1), all the lines connecting two atoms lie within a cone whose top is a point X . Since the valence is a function of length, these lines determine all possible valence values between the two given atoms, so an electron valence density at X . A typical distribution for the two atoms case is showed in Fig. 2.

Because the particular probabilities $p_1(a)$ and $p_2(b)$ are the quantities smaller than 1, the final product probability $p[v(X)]$ is usually small for X not lying along the position vectors (position vectors are the connecting lines between the two atoms). However, as interatomic distances may reduce radically during the thermal fluctuation, the values of $v(X)$ may be far greater than the nominal value of valence which is associated with the length of position vectors.

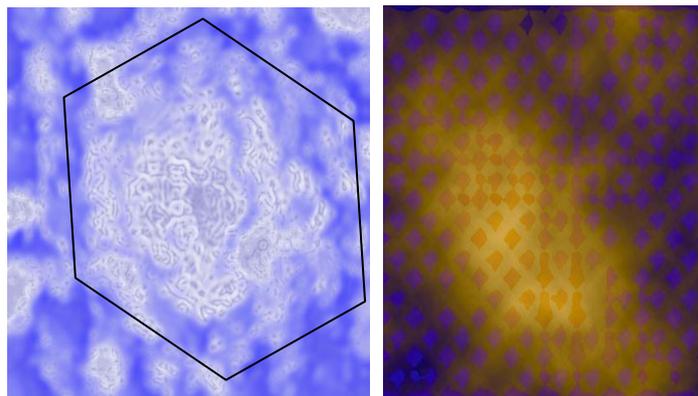


Fig.3. (Left) The 2D valence contours constructed for ZnO: there are 3 different areas of valence density: 1-bond intersection, 2-position vector and 3- dark region (no valence). (Right) Enhancement of electric field over the silicon carbide (SiC) surface layer due to organic solvent.

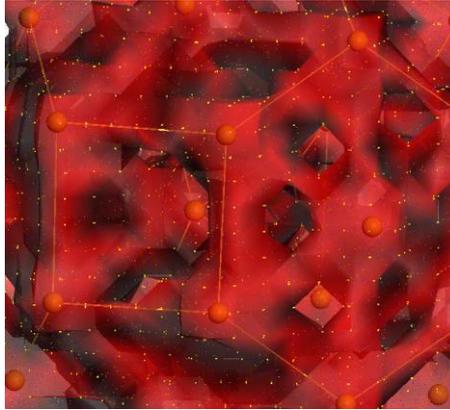


Fig. 4. K^+ vacancy in $CaCl_2/KCl$. The blank areas show the vacancies whose electron density is around +0.25. The valence over Ca^{2+} sites is +1.75. The neighbors of the vacancy sites are merely deformed.

Another important factor is that the probability $p[v(X)]$ depends on location of X , so it will vary between different points. To illustrate, we show in Fig. 3 the static 2D construction of valence map for ZnO where the different values of $v(X)$ are distinguished by colours. As seen, there are 3 interesting areas: (i) the first corresponds to the intersections where Zn-O bonds overlap, this effect raises the valence density above its nominal value and gives a certain way to imagine the dimension of atomic radius; (ii) the second area is lying along a position vector Zn-O whose valence itself is not large but due to a higher probability the average density is better visible; (iii) and the third area covers the blank space between the atoms where a little or no valence was encountered.

By their nature, the electron density in these blank areas is near 0 so the areas are neither negative nor positive with no trapping function. The 2D images themselves are dynamic images according to temperature as a half width of probability distribution of position fluctuation depends on temperature. For a simplicity, we assume a linear dependence of $B_{ISO}(T)$ on temperature.

As seen in Fig. 3 the areas with same colors feature the same electron densities, so we can reveal a part of the band structure related to the Brillouin zone, if the vectors of the reciprocal lattice are drawn. However, the valence density images cannot differentiate between the valence bands densities and this is a main drawback of this method.

Another example of the application of the method is showed in Fig. 4, where the occurrence of lattice vacancies depending on the activation energy of creating pairs of positive and negative ionic sites according to the Boltzmann probability distribution $n = Ne^{-E_v/2k_B T}$ is shown (N is a total number of positions, n is the number of vacancy pairs, k_B stands for the Boltzmann constant). The reconstructed valence map for $CaCl_2/KCl$ shows that such occurrence changes valence distribution among atoms and causes deformation of neighbouring bonding spheres. This relocation of valence has a recognizable effect in reducing the charge imbalance creating by K^+ vacancies, so that the total positive charge over K^+ center is lower than +1 and over Ca^{2+} center is lower than +2. As a consequence, the trap capacity of vacancies (i.e. detectable trap concentration) is lower than their theoretical value. The calculation for a case in Fig. 4 resulted in about 30% lower trap concentration than that given by $n = Ne^{-E_v/2k_B T}$.

3. Conclusion

The bond-valence method for modelling valence structure can be used in a wide class of materials. This allows us to illustrate the dynamics of valence relocation due to various factors, including structure deformation, temperature fluctuation and forming of vacancies. The advantage of this method is two fold: it offers the statistical average fits for valences and full information about probability distribution of valences at each point in coordination space, so opens up the way for a real-time simulation of dynamics of valence relocation process under thermal fluctuation. Among the main disadvantages belongs the fact that its densities are only position-related but not band-related values.

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