Balanced crystal orbital overlap population—a tool for analysing chemical bonds in solids

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Abstract
A new tool for analysing theoretically the chemical bonding in solids is
proposed. A balanced crystal orbital overlap population (BCOOP) is an
energy resolved quantity which is positive for bonding states and negative
for antibonding states, hence enabling a distinction between bonding and
antibonding contributions to the chemical bond. Unlike the conventional crystal
orbital overlap population (COOP), BCOOP handles correctly the situation of
crystal orbitals being nearly linear dependent, which is often the case in the solid
state. Also, BCOOP is much less basis set dependent than COOP. A BCOOP
implementation within the full-potential linear muffin tin orbital method is
presented and illustrated for Si, TiC and Ru. Thus, BCOOP is compared to
the COOP and crystal orbital Hamilton population (COHP) for systems with
chemical bonds ranging from metallic to covalent character.

1. Introduction

In the last few decades the Kohn–Sham (KS) method [1], based on the density functional
theory (DFT) [2], has become a standard tool to calculate physical and chemical properties
of molecules and solids. Numerous DFT codes have been written. The method has been
demonstrated to have great accuracy in reproducing experimental values of the equilibrium
volumes [3], cohesive energy [4], elastic constants [5], structural properties [6], and phase
stability [7]. Typically experimental data are reproduced to within 10%. Although this is a
very important step in providing a theoretical tool for analysing and understanding materials
properties, there is often a problem in extracting vital information from a calculation as to what
microscopic mechanism is actually responsible for a specific observed property. Hence, DFT
calculations are sometimes criticized for providing only numbers and not understanding.

Most of the properties obtainable from a DFT calculation are in one way or another
reflecting the chemical bonding between the different atoms of the material. The microscopic
understanding of a calculated (or observed) property of a material, almost always turns into
an analysis of the nature of the chemical bonds between the atoms, and it becomes crucial to
develop a tool that reflects these bonds. Given the success of DFT calculations it is desirable to

use information from these calculations for analysing the chemical bonds. Hence Hughbanks and Hoffmann [8] suggested a quantity called the crystal orbital overlap population (COOP), for distinguishing bonding from antibonding orbitals. Other methods used for chemical bonding analysis include COHP [9] and E_{cov} [10], which are essentially COOP-like; as well as completely different approaches involving electron localization functions [11] and Wannier functions [12].

Unfortunately, the COOP (as well as COHP and E_{cov}) is a basis set dependent quantity and therefore is not an absolute bonding indicator. It is not an expectation value of any quantum mechanical operator. Traditionally, COOP has been used with tight-binding versions of linear combination of atomic orbitals (LCAO) or linearized muffin tin orbital (LMTO) methods [13]. Such methods have a minimal and well-localized basis set that is ideal for analysing different types of chemical bonding (e.g. covalency). However, in order to describe solids with open crystal structure correctly, full-potential methods for band-structure calculations are desired. In this manuscript we will demonstrate that in the most general computational scheme, not only involving minimal basis functions, the method of [8] is less suitable, and we propose instead a related method that in a more robust way reflects the nature of the chemical bonds of a material. Due to its close connection to COOP, we name the new method 'balanced COOP' or BCOOP.

2. Definition of COOP and COHP

The computationally most demanding equation to solve in a DFT calculation, the KS equation, is an effective one-electron Schrödinger-like equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{eff} - \epsilon_n(\mathbf{k}) \right)|\psi\rangle = 0, \tag{1}$$

where V_{eff} is an effective potential which should be determined self-consistently.

The COOP of Hughbanks and Hoffmann [8] is defined as an orbital-population weighted density of states:

$$\text{COOP}_{ij}(\epsilon) = \sum_{nk} \delta(\epsilon - \epsilon_n(\mathbf{k}))c_i^* c_j O_{ij}, \tag{2}$$

where

$$\sum_{nk} \equiv \sum_n \int_{BZ} \frac{v_0 \, d\mathbf{k}}{(2\pi)^3}, \tag{3}$$

$$O_{ij} = \langle e_i | e_j \rangle \tag{4}$$

is the overlap matrix, and c_i are eigenvector components defined by:

$$|\psi_n(\mathbf{k})\rangle = \sum_i c_i |e_i\rangle, \tag{5}$$

where $|\psi_n(\mathbf{k})\rangle$ is the KS eigenvector corresponding to the eigenvalue $\epsilon_n(\mathbf{k})$.

In order to give meaningful chemical information, the basis set $\{|e_i\rangle\}$ should consist of atomic-like orbitals, localized on certain atoms in the unit cell. Usually they also have quantum numbers l, m, σ (orbital and magnetic quantum number and spin projection, respectively). Such basis functions are used in the LCAO and LMTO methods. $\text{COOP}(\epsilon)$ is an energy resolved quantity, which is positive for bonding combinations of orbitals $|e_i\rangle$ and $|e_j\rangle$ and negative for antibonding combinations. COOP has a sum rule

$$\sum_{ij} \text{COOP}_{ij}(\epsilon) = \text{DOS}(\epsilon), \tag{6}$$

where the sum is taken over all possible contributions to COOP, including the diagonal ones $COOP_{ii}(\epsilon)$, which do not correspond to any chemical bonds.

COHP is defined in a way similar to equation (2), but with Hamiltonian matrix elements H_{ij} instead of overlap matrix elements O_{ij}.

$$COHP_{ij}(\epsilon) = \sum_{nk} \delta(\epsilon - \epsilon_n(\mathbf{k})) c_i^* c_j H_{ij}. \tag{7}$$

The well-known drawback of COHP [9, 10] is the fact that it depends on the position of the origin of the energy scale of the DFT calculation (energy zero) and cannot be defined in an unambiguous way. Indeed, upon transformation $\epsilon \to \epsilon + \Delta\epsilon$, the Hamiltonian transforms as $H_{ij} \to H_{ij} + \Delta\epsilon\, O_{ij}$, and, consequently

$$COHP_{ij}(\epsilon) \to COHP_{ij}(\epsilon) + \Delta\epsilon\, COOP_{ij}(\epsilon). \tag{8}$$

The idea behind COHP assumes that H_{ij} and O_{ij} have opposite sign, and that negative COHP corresponds to bonding states. However, this fact is also dependent on the choice of energy zero. Note that while the units of COOP are energy^{-1} (same as DOS), COHP is dimensionless.

As we have already mentioned, COOP and COHP are basis set dependent. They give good results for tight-binding LCAO and LMTO methods, methods that use minimal (i.e. one basis function for a given atom and l, m) and well localized basis sets. Different basis sets, e.g. the full potential linearized muffin tin orbital (FP-LMTO) [14], are less localized, and in addition the FP-LMTO method normally uses two or more basis functions (with different kinetic energy κ^2 of the envelope functions) per atom, l and m (see discussion in [15]). The main difference between these types of basis sets is that minimal basis set functions are almost orthogonal while the 'complete' basis sets are close to linear dependence. In particular, the off-diagonal overlap matrix elements are small in the former case: $O_{ij}^2 \ll O_{ii} O_{jj}$, while in the latter case often $O_{ij}^2 \approx O_{ii} O_{jj}$ holds true.

The main goal of this paper is to investigate how the orbital population and the COOP behave in the case of arbitrary O_{ij}, including a near-linear-dependent basis. We start with a simple model system, which will be solved analytically within the LCAO method, namely a hydrogen-like molecule with arbitrary off-diagonal overlap. Then we proceed to solid state systems (Si, TiC and Ru) treated with the FP-LMTO method [14]. It will be shown that the orbital population gives incorrect results in the near-linear-dependent case, namely it reaches large values $|c_i^* c_j O_{ij}| \gg 1$ and usually it overestimates antibonding compared to bonding strengths, and the COOP inherits this problem as well. A solution in the form of the balanced COOP (BCOOP) will be suggested below.

Before moving any further, an important remark has to be made. Since we are dealing here with crystals, all basis functions must be Bloch functions. Therefore, in a strict sense equation (2) only defines bonding between certain atom types rather than individual atoms. Hence, if $|\mathbf{R}_i\rangle$ is an orbital centred on $\mathbf{R}_i$, the basis function $|e_i\rangle$ is a Bloch sum:

$$|e_i\rangle = \frac{1}{\sqrt{N_i}} \sum_{\mathbf{R}_i} e^{i\mathbf{k}\mathbf{R}_i} |\mathbf{R}_i\rangle. \tag{9}$$

Inserting (9) into (2) gives:

$$\begin{aligned}
COOP_{ij}(\epsilon) &= \sum_{nk} \delta(\epsilon - \epsilon_n(\mathbf{k})) c_i^* c_j \frac{1}{\sqrt{N_i N_j}} \sum_{\mathbf{R}_i, \mathbf{R}_j} e^{i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_i)} \langle \mathbf{R}_i | \mathbf{R}_j \rangle \\
&= \frac{1}{\sqrt{N_i N_j}} \sum_{\mathbf{R}_i, \mathbf{R}_j} \sum_{nk} \delta(\epsilon - \epsilon_n(\mathbf{k})) (c_i^* e^{-i\mathbf{k}\mathbf{R}_i})(c_j e^{i\mathbf{k}\mathbf{R}_j}) \langle \mathbf{R}_i | \mathbf{R}_j \rangle \\
&= \frac{1}{\sqrt{N_i N_j}} \sum_{\mathbf{R}_i, \mathbf{R}_j} COOP_{\mathbf{R}_i, \mathbf{R}_j}(\epsilon). \tag{10}
\end{aligned}$$

Therefore, the $COOP_{i,j}$ is indeed a properly normalized sum of contributions from all pairs $(\mathbf{R}_i, \mathbf{R}_j)$, provided that we define

$$c_{\mathbf{R}_i} = e^{i\mathbf{k}\mathbf{R}_i} c_i. \tag{11}$$

The expression for the COOP between the atom centred orbitals is then

$$COOP_{\mathbf{R}_i,\mathbf{R}_j}(\epsilon) = \sum_{nk} \delta(\epsilon - \epsilon_n(\mathbf{k})) c^*_{\mathbf{R}_i} c_{\mathbf{R}_j} \langle \mathbf{R}_i | \mathbf{R}_j \rangle. \tag{12}$$

3. Orbital population of an H_2-like molecule

To test the concept of the orbital population $OP_{ij} = c^*_i c_j O_{ij}$, it is reasonable to start with the simplest possible case, namely a hydrogen-like molecule, with a basis of two s orbitals. The LCAO equation in this case is

$$(\hat{H} - \epsilon \hat{O}) \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{13}$$

with

$$\hat{H} = \begin{bmatrix} 0 & -|h| \\ -|h| & 0 \end{bmatrix}, \qquad \hat{O} = \begin{bmatrix} 1 & S \\ S & 1 \end{bmatrix}. \tag{14}$$

There are two solutions to this equation: a bonding state

$$\epsilon_b = \frac{-|h|}{1+S}, \qquad |b\rangle = \frac{1}{\sqrt{2(1+S)}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \tag{15}$$

and an antibonding state

$$\epsilon_a = \frac{|h|}{1-S}, \qquad |a\rangle = \frac{1}{\sqrt{2(1-S)}} \begin{pmatrix} -1 \\ 1 \end{pmatrix}. \tag{16}$$

It is important that the eigenvectors in (15) and (16) are normalized.

The orbital populations are:

$$OP_b = \frac{S}{2(1+S)}, \qquad OP_a = \frac{-S}{2(1-S)} \neq -OP_b. \tag{17}$$

In the limit of linear dependence $S \to 1$ and the bonding OP becomes $+1/2$, while the OP for the antibonding state diverges as $-1/2(1-S)$. The reason for this may be seen in figure 1, where we show Ψ_b and Ψ_a as orthogonal and normalized state vectors, composed from basis functions $\mathbf{e}_1$ and $\mathbf{e}_2$ that are far from being orthogonal. As figure 1 shows, c_1 and c_2 for the antibonding state must become very large when the angle between $\mathbf{e}_1$ and $\mathbf{e}_2$ is small, which results in a divergent OP for the antibonding state.

In order to remedy this problem we propose here a balanced orbital population, defined as

$$BOP_{12} = \frac{c^*_1 c_2 O_{12}}{O_{11}|c_1|^2 + O_{22}|c_2|^2}. \tag{18}$$

This quantity differs only in sign between bonding and antibonding states

$$BOP_b = -BOP_a = \frac{S}{2}, \tag{19}$$
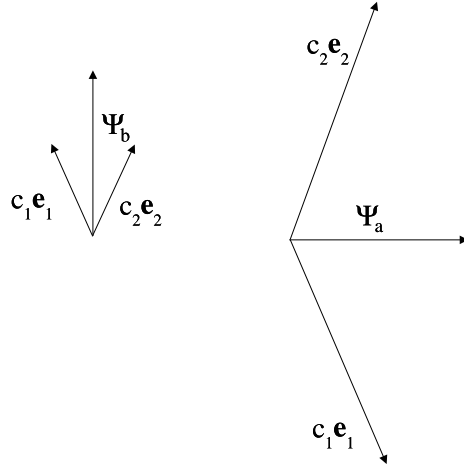
and this balance in magnitude motivates the name.

Figure 1. Bonding and antibonding states of a hydrogen-like molecule with a large overlap S presented graphically as 2D vectors. The antibonding eigenstate is labelled Ψ_a and the bonding eigenstate Ψ_b. For definition of other quantities see the text. Since the eigenvector ψ is normalized, the eigenvector components become large in the antibonding case $|c_1| = |c_2| \gg 1$.

4. Definition of the BCOOP

We define the balanced crystal orbital overlap population (BCOOP) for solid state materials as the DOS, weighted with a balanced overlap population. There are different ways to define it. The simplest version is the diagonal-balanced COOP (DBCOOP):

$$\text{DBCOOP}_{ij}(\epsilon) = \sum_{nk} \delta(\epsilon - \epsilon_n(\mathbf{k})) \frac{c_i^* c_j O_{ij}}{\sum_{i'} O_{i'i'} |c_{i'}^*|^2}. \tag{20}$$

The more general definition is the balanced COOP:

$$\text{BCOOP}_{\alpha_1, \alpha_2}(\epsilon) = \sum_{nk} \delta(\epsilon - \epsilon_n(\mathbf{k})) \frac{\sum_{i' \in A(\alpha_1)} \sum_{j' \in A(\alpha_2)} c_i^* c_j O_{ij}}{\sum_{\alpha} \sum_{i', j' \in A(\alpha)} c_{i'}^* c_{j'} O_{i'j'}}, \tag{21}$$

where the compound quantum number α includes all chemically important quantum numbers (e.g. the atom type t and the orbital quantum number l). For example, in the example of TiC given below, α can be one of six different values: $\alpha = \text{Ti } s$, Ti p, Ti d, C s, C p or C d. The set of all basis functions with given α (and arbitrary values of other quantum number) is denoted $A(\alpha)$. Definition (21) can be rewritten in a more compact way

$$\text{BCOOP}_{\alpha_1, \alpha_2}(\epsilon) = \sum_{nk} \delta(\epsilon - \epsilon_n(\mathbf{k})) \frac{\langle \alpha_1 | \alpha_2 \rangle}{\sum_{\alpha} \langle \alpha | \alpha \rangle} \tag{22}$$

provided that we define the different contributions to the eigenvector as

$$|\alpha\rangle = \sum_{i \in A(\alpha)} c_i |e_i\rangle, \qquad \sum_{\alpha} |\alpha\rangle = |\psi_n(\mathbf{k})\rangle. \tag{23}$$

It is very important that vectors $|\alpha\rangle$ are not orthogonal to each other.

BCOOP no longer fulfils the sum rule of the COOP, equation (6). Instead, it sums up to some quantity which is different from the DOS:

$$\sum_{\alpha_1, \alpha_2} \text{BCOOP}_{\alpha_1, \alpha_2}(\epsilon) = \sum_{nk} \delta(\epsilon - \epsilon_n(\mathbf{k})) \frac{1}{\sum_{\alpha} \langle \alpha | \alpha \rangle}. \tag{24}$$

Therefore, one might question the use of the word 'population' in 'BCOOP'. However, because the definition of BCOOP is genetically related to COOP, there is motivation to make as few changes to the nomenclature as possible, and we propose the term BCOOP.

Note also that in the limit of a near-orthogonal basis set, the denominators in the BCOOP and DBCOOP become equal to 1 and they become identical to the COOP. For an exactly orthogonal basis, the COOP and BCOOP would vanish and one would rather use the COHP as a chemical bonding indicator. However, exactly orthogonal basis functions (e.g. plane waves) are normally extended in space. The authors are not aware of any exactly orthogonal basis set of atomic-like (atom, l, m) functions, which can be used in DFT calculations, although near orthogonal basis functions have been proposed [16]. The usefulness in the BCOOP lies in the opposite limit, of strongly non-orthogonal (or even near-linear-dependent) basis set.

5. Details of calculations

In order to test the possibility of using the COOP-related indicators in the full-potential methods, we implemented the BCOOP, DBCOOP, COOP and COHP in the FP-LMTO method [14]. In our implementation of the BCOOP we take $\alpha = (t, l)$, while the other quantum numbers of the FP-LMTO method, namely magnetic quantum number (m), atom index (within type t), energy set and energy tail were included in the summations $\sum_{i \in A(\alpha)}$. All the COOP-related values are defined between two atom types rather than between two atoms in real space.

As the main test system we have chosen semiconducting silicon in the diamond structure (lattice constant $a = 10.263$ a.u.), since the bonding in this system is well known (see e.g. [9]). The local density approximation (LDA) has been used in all FP-LMTO calculations in this paper. First, we performed a self-consistent (SC) calculation in order to obtain the converged KS potential. At this point we used the Gaussian smearing method for the Brillouin zone (BZ) integration. The $8 \times 8 \times 8$ k-point mesh included 23 k-points in the irreducible part of the Brillouin zone (IBZ) and 256 k-points in the whole BZ. The $32 \times 32 \times 32$ fast-Fourier transform (FFT) mesh has been used. We used the double basis set with tail energies $\kappa^2 = -0.3$; $+0.1$ Ryd for the SC calculation.

Once the SC potential was obtained, we made one last iteration to calculate the DOS, COOP, BCOOP, etc. On this iteration the linear tetrahedon method has been used for the BZ integration with a large k-point mesh (385 points in the IBZ, 6859 in the whole BZ) in order to achieve maximum accuracy of the BCOOP curves. To test the basis set dependence of COOP and BCOOP, we performed a calculation with a single-tail (minimal) basis set with tail energy $\kappa^2 = -0.5$ Ryd. We also performed two additional calculations, with a two-tail (double) basis set, with tail energies $\kappa^2 = -0.05$; -0.4 Ryd and with $\kappa^2 = -0.1$; -0.5 Ryd.

In addition we performed calculations for semi-metallic titanium carbide (TiC) and metallic ruthenium (Ru). TiC has a NaCl crystal structure with lattice constant $a = 8.159$ a.u. For the SC calculation we use 35 k-points in the IBZ (729 in the BZ), $24 \times 24 \times 24$ FFT mesh and tails $\kappa^2 = -0.1$; -0.5 Ryd. Additional tails $\kappa^2 = -1.0$; -1.5 Ryd have been used for semicore Ti 3s, 3p states, but these do not play any significant role in the valence band region where we plot our COOP curves. In the COOP calculation for TiC we used 120 k-points in the IBZ (3375 in the BZ) and different choices of tail energy: one single tail calculations with $\kappa^2 = -0.5$ Ryd; and two double tail calculations, one with $\kappa^2 = -0.1$ Ryd; -0.5 Ryd and another with $\kappa^2 = -0.05$ Ryd; -0.4 Ryd (only the latter case is presented on the figures below). Ruthenium has an hcp structure with $a = 5.113$ a.u. and $c = 8.091$ a.u. We used 285 k-points in the IBZ (1352 in the full BZ) for the SC calculation, and 462 k-points in the IBZ (2250 in the full BZ) for the COOP and the same FFT mesh and tail energies as for TiC (albeit with no semicore states).
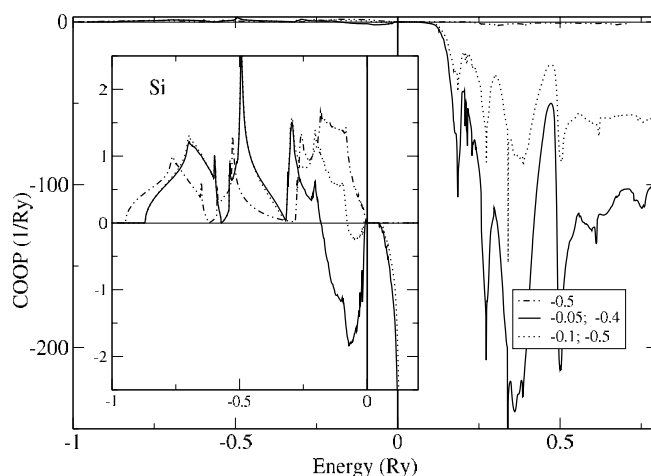
Figure 2. COOP(ϵ) for silicon in the diamond structure. The Fermi level is at $E = 0$ (vertical line). The legend box contains tail energies κ^2 in Ryd. The inset shows the valence band region.

6. Numerical results

Figures 2 and 3 present the COOP and BCOOP, respectively, calculated between the two sublattices of the Si atoms in the diamond structure (summed over all l-quantum numbers). One can indeed observe huge negative values of the COOP (figure 2) in the conduction band, a direct consequence of the orbital population divergence for antibonding states discussed above. The l-resolved COOP curves (not shown) demonstrate that the huge negative peaks are almost exclusively caused by the s–s contribution, since the overlap between two s orbitals is much larger than the s–p or p–p overlap. Also, as may be noted from the figure, the basis set dependence is significant, even for two different double basis sets, with some choices of tails giving negative values for the COOP in some parts of the valence band. The negative antibonding peaks become much larger in magnitude for a double basis set, since they represent a situation closer to linear dependence, and also they are more extended for smaller $|\kappa^2|$ and for positive κ^2 (less localized orbitals).

On the other hand, the BCOOP (figure 3) gives the same order of magnitude for bonding states (conduction band) and antibonding states (valence band) and a much smaller basis set dependence. The two double basis set curves are almost identical and are in excellent agreement with the COHP result for silicon, calculated with a minimal basis set, given by the TB-LMTO method [9]. The minimal basis set curve has erroneous band width and band gap values, but this is just the result of the crudeness of the KS band structure, obtained from the FP-LMTO method using one tail. The DBCOOP curves (not shown) have a shape similar to the BCOOP but with a smaller overall magnitude.

The COHP curves for silicon (figure 4) have the same problems as the COOP curves in figure 2, including the non-physical antibonding region just below the Fermi level. We presented the COHP curves with a natural choice of energy zero (average potential of the FP-LMTO method [14]), plus one curve with the energy zero shifted by a somewhat arbitrary value of $\Delta\epsilon = -0.4563$ Ryd. The latter curve has the deepest antibonding peaks (down to -220), because, according to equation (8), there is a COOP contribution that is added to it.

In order to assess the quality of the COOP and BCOOP analyses for a broad spectrum of materials with different types of chemical bonding, we also investigated TiC (NaCl structure,
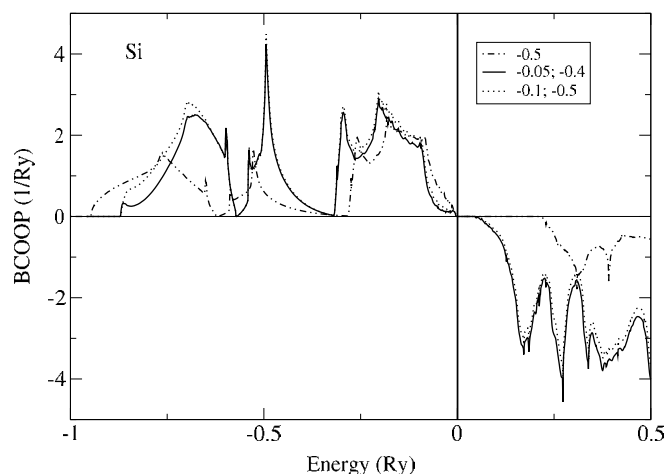
Figure 3. BCOOP(ϵ) for silicon in the diamond structure. The Fermi level is at $E = 0$ (vertical line). The legend box contains tail energies κ^2 in Ryd.
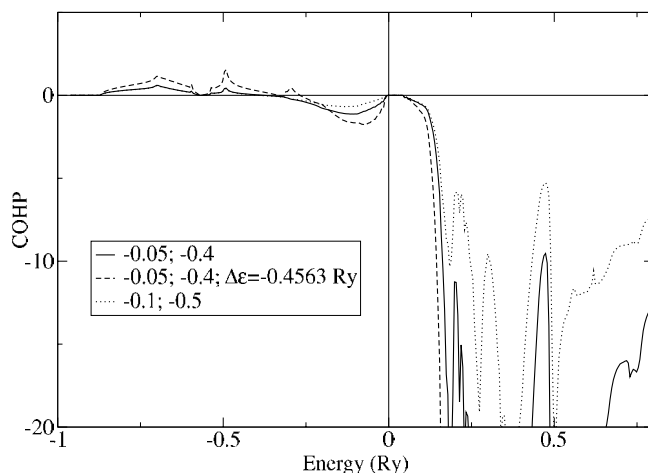

Figure 4. COHP(ϵ) for silicon in the diamond structure. The Fermi level is at $E = 0$ (vertical line). The legend box contains tail energies κ^2 in Ryd. A curve with an artificially shifted energy origin ($\Delta\epsilon = -0.4563$ Ryd) is also presented.

focusing on the Ti d–C p bond) and ruthenium (hcp structure, studying the Ru–Ru d-bond). The results are presented in figures 5 and 6, respectively. As in the case of Si, there are for both materials huge peaks in the COOP calculations that are avoided by the BCOOP. Starting with hcp Ru, we note that the BCOOP curve shows that the states corresponding to less than a half-filled d-band have a positive BCOOP, representing bonding states, and states corresponding to more than half filling have a negative BCOOP, representing antibonding states. Most of the bonding in Ru is known to be due to the d-states and the calculated BCOOP curve in figure 6 is consistent with the Friedel model [17]. Concerning TiC, the bonding character is known to be mainly of Ti d–C p character [17]. As figure 5 shows, the electronic structure of TiC is dominated by C-p states in the energy range between -0.5 and 0 Ryd and the Ti-d states are situated between 0 and 0.5 Ryd. The hybridization between these orbitals has been shown to
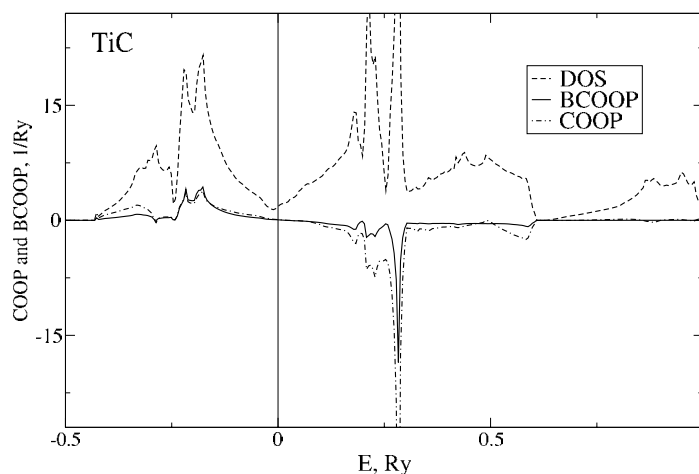
Figure 5. COOP(ϵ), BCOOP(ϵ) and DOS for TiC in the NaCl structure, illustrating the Ti d–C p bond. The Fermi level is at $E = 0$ (vertical line).

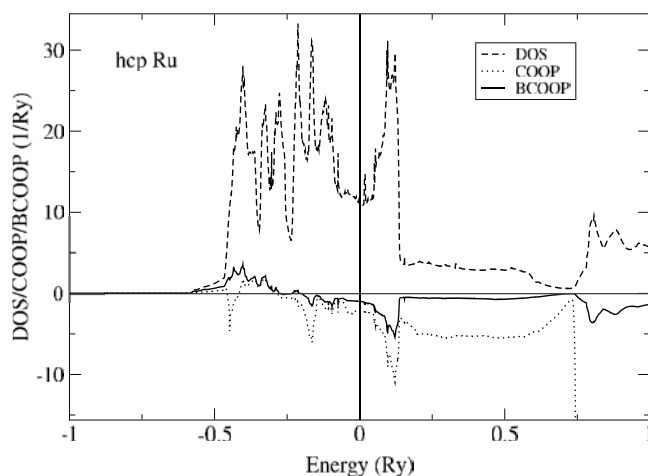**Figure 6.** COOP(ϵ), BCOOP(ϵ) and DOS for hcp ruthenium, illustrating the Ru–Ru bond between two sublattices. The height of the COOP peak at +1 Ryd is -660 1 Ryd^{-1}. The Fermi level is at $E = 0$ (vertical line).

result [18] in the strong covalent bonds of this material. The transition between bonding and antibonding states has been analysed to take place close to the Fermi level of TiC [18]. The BCOOP curve reproduces these features, with a positive contribution in the C-p band region and a negative contribution in the Ti-d band region.

7. Discussion and conclusion

In this paper we put existing chemical bonding indicators, such as the COOP and COHP, to a test to see if they are sufficiently robust to be used with full-potential DFT codes, such as FP-LMTO, which have non-minimal basis sets. Upon implementation of the COOP in the FP-LMTO code, we found, in agreement with [15], that the COOP cannot be used with the FP-LMTO method in a straightforward way.

The difficulties involve huge antibonding peaks, a large basis set dependence, and drastic over estimation of bonding/antibonding contributions to the total bond, coming from orbitals with low values of l (s, p), as compared to higher values of l. It has been found that the origin of the problem lies in the fact that the basis set of the FP-LMTO method is strongly non-orthogonal and in fact often lies close to linear dependence (at least for certain parts of the BZ). On the other hand, the COOP gives good results when the basis set is nearly orthogonal (such as TB-LCAO or TB-LMTO minimal basis sets).

The analysis made above shows how to get around the linear-dependence problem for the H_2-like molecule by introducing what we call 'balanced overlap population'. We used this idea to define BCOOP as a modified version of COOP. Our numerical test show that BCOOP is much less basis set dependent and can be used even with highly non-orthogonal basis sets. Namely, our tests for Si, TiC and Ru show that the BCOOP gives a significant improvement over the COOP. The BCOOP results are in good agreement with traditional views about the chemical bonding in these materials and existing COOP and COHP calculations, that were based on a minimal basis set techniques.

We were also interested in whether the COHP could perform any better than the COOP for the difficult case of a non-minimal (FP-LMTO) basis set. Despite the common belief that the COHP has smaller basis set dependence than the COOP, our results demonstrate that the COHP has essentially the same problems as the COOP: huge antibonding peaks, significant basis set dependence, and, in addition, a large dependence on the choice of energy zero. The power of the COHP seems to be in the opposite limit of a nearly orthogonal basis set when it is indeed preferable to the COOP or BCOOP.

Our conclusion is, therefore, that the BCOOP is a more robust chemical bonding indicator than the COOP or the COHP in the case of a highly non-orthogonal basis set, and that it can be used in practice in e.g. FP-LMTO calculations.

Acknowledgments

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