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REGULAR ARTICLE

R. A. Evarestov · V. P. Smirnov · D. E. Usvyat

Wannier-type atomic orbitals for periodic systems

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Abstract The results of an application of Wannier-type atomic orbitals for calculations of local properties of electronic structure for periodic systems (atomic charges and covalencies, bond orders and total valencies), published earlier by the authors, are summarized. The numerical results are given for bulk crystals with the perovskite structure $ATiO_3$, A=Sr,Ba,Pb and $LaMnO_3$ (the Bloch functions are calculated in LCAO basis), for bulk MgO crystal (the Bloch functions are calculated both in LCAO and PW basis) and for the two periodic slab models of surfaces (001) of MgO and (110) of rutile TiO_2.

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1 Introduction

Chemical bonding in crystals (as well as in molecules) is commonly analysed in terms of the local properties of the electronic structure, such as: the electronic population of atoms, atomic charges, bond orders, covalences and valences of atoms [1,2]. Since they are essential ingredients of a number of theories and models, their estimation is of great importance and may be indirectly compared with experimental data. Therefore, a correct definition and a method to calculate these quantities are vital.

The local properties of electronic structure are obtained from a one-electron density matrix, written on a localized basis of randomly chosen atomic-like functions. When the electronic structure of a crystal is calculated in the approximation of linear combinations of atomic orbitals (LCAO), traditionally, the same atomic orbitals are also used to define the local properties [1]. However since such a basis usually consists of non-orthogonal atomic functions, there exist two possible schemes of population analysis – according to Mulliken and to Lowdin (the latter implies a preliminary symmetrical orthogonalization of the basis functions). However, this approach is not always reliable, since the results of the population analyses are often strongly dependent on an inclusion of diffuse orbitals into the basis (useful for the band structure calculations) and on the scheme chosen for the population analysis.

When the plane wave (PW) basis is used in the calculations of crystalline electronic structures, the above approach cannot be used due to the delocalized nature of plane waves. For this case, a special procedure of population analyses was suggested [3]. Within this procedure, the atomic-like functions are generated using the pseudopotentials chosen for the band structure calculations. Such functions are neither orthonormal nor complete in the sense of spanning the space of the occupied states. To measure how completely the localized atomic orbitals represent the eigenstates, a so-called spilling parameter is introduced, which varies between 1 and 0. If the spilling parameter is nonzero, a special projection procedure is needed to correctly define the density operator for the incomplete basis of atomic-like functions [3]. Since thus constructed localized basis is not orthogonal, as in the case of LCAO calculations, both Mulliken and Lowdin schemes may be used. However, in the case of PW calculations the population analysis, performed according the above described scheme, often gives results, which do not provide a reasonable chemical interpretation even for uncomplicated periodic systems [3].

Recently, [4] localized quasiatomic minimal basis orbitals (QUAMBO) for Si and Al in diamond and fcc structures have been constructed. The electron states of these crystals were calculated in PW basis and atomic functions in a crystal were found by minimization of their mean square deviation

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R. A. Evarestov (✉) · D.E. Usvyat
Department of Quantum Chemistry, St. Petersburg State University,
26 Universitetskii Prospekt, Stary Petergof,
St. Petersburg, Russia, 198504
E-mail: evarest@hm.csa.ru

V. P. Smirnov
Department of Mathematics, Institute of Fine Mechanics and Optics,
14 Sablinskaya Ulitsa, St. Petersburg, Russia, 197101

from the corresponding free-atom orbitals. This approach seems to be mostly appropriate for the essentially covalent systems.

Recently we suggested an approach based on Wannier functions (WFs) use [5]. This approach seems to be much less basis-set-dependent than the conventional ones. The population analysis in this case is done using the density matrix given in the minimal valence basis of Wannier-type atomic orbitals (WTAOs) – Wannier functions centered on atoms and having the behavior of atomic valence states in the cores of atoms [5,6]. WTAOs are analogous to atomic functions in form and by symmetry but, in contrast to the initial LCAO basis, they are directly connected with the electronic band structure and the Bloch states involved. WTAOs are constructed from the occupied and some vacant states. The latter are chosen so that they assure the maximal localization for the corresponding WTAOs.

In this paper, we summarize results published earlier [5–9] of WTAO application for the calculations of local properties of the electronic structure of periodic systems. In Sect. 2, the variational method of WTAOs generation and their use for population analysis are shortly described. In Sect. 3, the WTAO application for three periodic systems is considered both when LCAO and PW basis were used for Bloch function calculations. In Sect. 4, WTAOs are applied for two periodic slab models of a crystal surface.

2 Wannier-type atomic orbitals generation and use for population analysis

The one-electron Wannier functions $W_m(\mathbf{r}-\mathbf{a_n})$ ($\mathbf{r}$ is an electron coordinate, $\mathbf{a_n}$ is a translation vector and the index m numbers the functions belonging to the same primitive unit cell) are defined as a Fourier transform over the quasi-Bloch functions $\psi_{m\mathbf{k}}(\mathbf{r})$ ($\mathbf{k}$ is a wave vector from the first Brillouin zone (BZ)), which are connected with the canonical Bloch orbitals $\varphi_{\tau\mathbf{k}}(\mathbf{r})$ (the index τ labels energy bands) via the transformations $U(\mathbf{k})$:

$$\begin{aligned} W_m(\mathbf{r}-\mathbf{a_n}) &= L^{-1/2}\sum_{\mathbf{k}} \mathrm{e}^{-i\mathbf{k}\mathbf{a_n}} \sum_{\tau} U_{\tau,m}(\mathbf{k})\,\varphi_{\tau\mathbf{k}}(\mathbf{r}) \\ &= L^{-1/2}\sum_{\mathbf{k}} \mathrm{e}^{-i\mathbf{k}\mathbf{a_n}} \psi_{m\mathbf{k}}(\mathbf{r}), \end{aligned} \tag{1}$$

$$\begin{aligned} \varphi_{\tau\mathbf{k}}(\mathbf{r}) &= L^{-1/2}\sum_{m} U^{\dagger}_{m,\tau}(\mathbf{k}) \sum_{\mathbf{n}} \mathrm{e}^{-i\mathbf{k}\mathbf{a_n}} W_m(\mathbf{r}-\mathbf{a_n}) \\ &= L^{-1/2}\sum_{m} U^{\dagger}_{m,\tau}(\mathbf{k})\,\psi_{m\mathbf{k}}(\mathbf{r}). \end{aligned} \tag{2}$$

The expressions (1) and (2) correspond to the cyclic model of a crystal consisting of L unit cells. In the model of an infinite crystal, the $\mathbf{k}$-summations in Eq. (1) are substituted by integrations over BZ.

Wannier-type atomic orbitals are defined as the Wannier functions, which are constructed from a set of specially chosen occupied and vacant bands and have a definite symmetry (they are centered on atoms and transform via irreducible representations (irreps) of the corresponding site groups). Thus, the index m may be substituted by several indices – i, j, a, β, μ – which reflect the symmetry properties of the WTAOs – $W^{(\beta,\mu)}_{ija}(\mathbf{r}-\mathbf{a_n})$: the index a marks the symmetrically non-equivalent atoms, the index j runs through the set of symmetrically equivalent atoms of the type a; the Wyckoff positions of these atoms $\mathbf{q}_a$ are characterized by their site groups, whose irreps are labelled by the index β, the index i numbers the basis orts of the irrep β and the index μ discriminates between the independent sets of the functions transforming according to the same irrep β. The requirement for WTAOs to have fixed symmetry properties implies additional restrictions on the matrices $U(\mathbf{k})$. These restrictions can be completely taken into account by using, instead of canonical Bloch orbitals, their linear combinations, symmetrized according to the desired irreps of the site symmetry groups of atoms [5].

Wannier-type atomic orbitals were generated by the variational method [6], which allows obtaining both orthogonal $W^{(\beta,\mu)}_{ija}(\mathbf{r}-\mathbf{a_n})$ and non-orthogonal $V^{(\beta,\mu)}_{ija}(\mathbf{r}-\mathbf{a_n})$ sets of symmetry-adapted WTAOs. In this method, the functional

$$I_{\beta a} = \int \omega_{\beta a} \left| V^{(\beta,1)}_{11a}(\mathbf{r}) \right|^2 \mathrm{d}\mathbf{r}, \tag{3}$$

with the weight function

$$\omega_{\beta a} = \left(\pi r^2_{\beta a}\right)^{-3/2} \exp\left(-\frac{(\mathbf{r}-\mathbf{q}_a)^2}{2r^2_{\beta a}}\right) \tag{4}$$

is maximized ($r^2_{\beta a}$ is a parameter, for which we used a value of 1 Å). The orthogonal WTAOs $W^{(\beta,\mu)}_{ija}(\mathbf{r}-\mathbf{a_n})$ are obtained from the non-orthogonal ones $V^{(\beta,\mu)}_{ija}(\mathbf{r}-\mathbf{a_n})$ via Lowdin's procedure:

$$\mathbf{W} = \mathbf{V}\left(S^{(V)}\right)^{-1/2}, \tag{5}$$

where $S^{(V)}$ is the overlap matrix of non-orthogonal WFs $V^{(\beta,\mu)}_{ija}(\mathbf{r}-\mathbf{a_n})$, and $\mathbf{W}$ and $\mathbf{V}$ are row vectors constituted by the sets of the orthogonal and non-orthogonal WFs, correspondingly. The orthogonalization procedure can be performed either in the indirect or reciprocal space. The latter is computationally faster.

Before constructing the minimal basis of WTAOs, one should choose the energy bands, whose states are to be used in the process of the WTAOs, generation. For each of the WTAOs, a band or a group of bands is chosen according to the following criteria: the band states should be compatible with the corresponding WTAOs by symmetry (in the context of the induced representations (indreps) theory [10]) and provide the maximal localization for them. Hereafter, we mark such bands by the type of WTAOs corresponding to them (e.g. s-band of the oxygen atom: the s-WTAOs centered on oxygen and constructed from the states of this band appear to be the most localized comparing to the ones constructed from any other states). After the desired bands for all the WTAOs are chosen, the final WTAOs are constructed using the states from this group of bands. When the WTAOs (orthogonal or non-orthogonal) are found, the density matrix is calculated in the localized basis of these functions. The local properties are expressed via matrix elements of this matrix.

WTAOs' analog of Mulliken population analysis is made using non-orthogonal WTAOs: let us now consider WTAOs $V_{\nu a}\left(\mathbf{r}-\mathbf{a}_{\mathbf{n}}\right)$ (υ-th WTAO of atom a in the $\mathbf{n}$-th cell) as linear combinations of Bloch functions:

$$V_{\nu a}\left(\mathbf{r}-\mathbf{a}_{\mathbf{n}}\right) = \sum_{\tau\mathbf{k}} b_{\tau\mathbf{k},ia\mathbf{n}}\varphi_{\tau\mathbf{k}}\left(\mathbf{r}\right), \quad \text{or} \quad \mathbf{V}=\varphi b, \varphi=\mathbf{V}b^{-1}, \tag{6}$$

where Bloch functions $\varphi_{\tau\mathbf{k}}\left(\mathbf{r}\right)$ are given in LCAO or PW basis. The density matrix in the corresponding basis $\rho^{(V)}$ can be written in the following way:

$$\rho^{(V)}=2\bar{b}^{-1}\bar{b}, \tag{7}$$

where $\bar{b}$ is the truncated matrix b with rows corresponding only to the occupied states.

For the orthogonalized WTAOs:

$$W_{\nu a}\left(\mathbf{r}-\mathbf{a}_{\mathbf{n}}\right) = \sum_{\tau\mathbf{k}} d_{\tau\mathbf{k},ia\mathbf{n}}\varphi_{\tau\mathbf{k}}\left(\mathbf{r}\right), \quad \text{or} \quad \mathbf{W}=\varphi d, \quad \varphi=\mathbf{V}d^{\dagger}, \tag{8}$$

the density matrix $\rho^{(V)}$ is given by

$$\rho^{(V)}=2\bar{d}^{\dagger}\bar{d}. \tag{9}$$

The electronic population $N_{a\mathbf{n}}$ of an atom a in the $\mathbf{n}$-th primitive cell and an order of the bond $B_{a\mathbf{0},a'\mathbf{n}}$ between an atom a of the reference cell and an atom a' in the $\mathbf{n}$-th cell can be obtained from the density matrix:

$$N_{a\mathbf{n}}=N_{a0}=\sum_{\nu}\rho_{\nu\nu}^{a0,a0}, \tag{10}$$

$$B_{a0,a'\mathbf{n}}=\sum_{\mu\nu}\rho_{\mu\nu}^{a0,a'\mathbf{n}}\rho_{\nu\mu}^{a'\mathbf{n},a0}. \tag{11}$$

Using these quantities, one can obtain the atomic charge Q_a of an atom a, and the covalence C_a and total valence V_a [1] of this atom:

$$Q_{a\mathbf{n}}=Q_{a0}=Z_a-N_{a0}, \tag{12}$$

where Z_a is the nuclear charge of the atom a in all-electron calculations or charge of the core in the case of pseudopotential approximation,

$$C_{a\mathbf{n}}=C_{a0}=\sum_{a'\neq a}B_{a0,a'0}+\sum_{\mathbf{n}\neq 0}\sum_{a'}B_{a0,a'\mathbf{n}}, \tag{13}$$

$$V_{a0}=\frac{1}{2}\left(C_{a0}+\sqrt{C_{a0}^2+4Q_{a0}^2}\right). \tag{14}$$

3 Use of WTAO for three periodic systems: chemical bonding in bulk crystals

3.1 LCAO approximation in Bloch function calculation

To demonstrate the efficiency of WTAO use for chemical bonding analysis, we consider at first the cubic crystals with the perovskite structure [7].

In the LCAO approximation, we used ab initio Hartree–Fock (HF) and density functional theory (DFT) methods to calculate the electronic structure of bulk $SrTiO_3$ (STO), $BaTiO_3$(BTO), $PbTiO_3$(PTO) and $LaMnO_3$ (LMO) crystals. The CRYSTAL computer code [11] was used to calculate the band structure and the Bloch functions. The Hay-Wadt pseudopotentials [12] were adopted: small-core for Ti, Sr, Ba, La and Mn atoms, large-core for Pb atoms. The oxygen atoms were included with the all-electron basis set. The optimized Gaussian-type atomic basis was taken from [13], where the same pseudopotentials were used. The basis optimization made it possible to obtain the lattice constant, bulk modulus and elastic constants of the considered crystals being in good agreement with the experimental data. For the exchange-correlation functional, we used the hybrid HF-DFT form (B3PW), as it reproduces, for optimized basis sets, optical band gaps close to the experimental values [13].

The Monkhorst-Pack [14] mesh of $4\times4\times4=64$ **k**-points, used in our calculations, corresponds to a cyclic model with 64 primitive unit cells in the direct lattice [10]. An increase in this number in the band structure calculations up to $8\times8\times8=512$ does not lead to any significant changes in the values of the one-electron energies.

The cubic structure of perovskite-like ABO_3 compounds is characterized by the primitive cubic lattice with the O_h^1 (Pm3m) space group. The A-atoms and B-atoms occupy the Wyckoff positions ***a*** (0,0,0) and ***b*** (0.5,0.5,0.5), correspondingly, with the site groupO_h. The oxygen atoms occupy ***c*** (0.5,0.5,0) positions, site groupD_{4h}. The minimal atomic-like basis for the crystals under consideration consists of s- and p-type functions of the oxygen atoms, s- and d-type functions of the Ti atoms and s- and p-type functions of Sr, Ba and Pb in STO, BTO, PTO or s- and d-type functions of La and Mn in LMO. So, these are the types of WTAOs to be used in the population analysis for the compounds under consideration. Table 1 lists the symmetries of these functions. The notations for the induced representations of space group O_h^1 are taken from ref. [10].

Once the types of WTAOs are determined, one should find the energy bands states corresponding to these WTAOs. Firstly, the bands to be chosen should be symmetry compatible with the corresponding WTAOs (see ref. [6] for details). Secondly, the WTAOs constructed from the Bloch states of the chosen bands should be principally the most localized

Table 1 The symmetry properties of the WTAOs of the minimal valence basis for STO, BTO, PTO and LMO crystals

Atom	Function's type	Symmetry
Sr, Ba, Pb	s	$(\boldsymbol{a}, a_{1g})$
	p	$(\boldsymbol{a}, t_{1u})$
La	s	$(\boldsymbol{a}, a_{1g})$
	d	$(\boldsymbol{a}, t_{2g}) + (\boldsymbol{a}, e_g)$
Ti, Mn	s	$(\boldsymbol{b}, a_{1g})$
	d	$(\boldsymbol{b}, t_{2g}) + (\boldsymbol{b}, e_g)$
O	s	$(\boldsymbol{c}, a_{1g})$
	p	$(\boldsymbol{c}, a_{2u}) + (\boldsymbol{c}, e_u)$

Table 2 Atomic charges in cubic $SrTiO_3$

Method of electronic structure calculation	Population analysis scheme	Atomic charges, |e|		
		Sr	Ti	O
HF	Nonorthogonal WTAO	2.00	3.20	−1.73
	Orthogonal WTAO	2.00	3.13	−1.71
	Mulliken	1.92	2.76	−1.56
DFT	Nonorthogonal WTAO	2.00	2.68	−1.56
	Orthogonal WTAO	2.00	2.63	−1.54
	Mulliken	1.87	2.35	−1.40

Table 3 Atomic charges in cubic $BaTiO_3$

Method of electronic structure calculation	Population analysis scheme	Atomic charges, |e|		
		Ba	Ti	O
HF	Nonorthogonal WTAO	2.00	3.19	−1.73
	Orthogonal WTAO	2.00	3.16	−1.72
	Mulliken	1.86	2.82	−1.56
DFT	Nonorthogonal WTAO	2.00	2.65	−1.55
	Orthogonal WTAO	2.01	2.60	−1.54
	Mulliken	1.80	2.37	−1.39

Table 4 Atomic charges in cubic $PbTiO_3$

Method of electronic structure calculation	Population analysis scheme	Atomic charges, |e|		
		Pb	Ti	O
HF	Nonorthogonal WTAO	1.99	3.27	−1.75
	Orthogonal WTAO	1.89	3.14	−1.68
	Mulliken	1.59	2.79	−1.46
DFT	Nonorthogonal WTAO	1.99	2.72	−1.57
	Orthogonal WTAO	1.93	2.64	−1.52
	Mulliken	1.34	2.34	−1.23

WTAOs of the corresponding type. Our analysis of the electronic structure of STO and BTO has shown (excluding the semicore states from consideration) that the oxygen s- and p-bands and the Sr (Ba) atom p-bands form 15 upper valence bands states. The Ti atom d-states form the five lowest conduction bands, while the Sr (Ba) and Ti atoms s-states are located among vacant conduction band states very high in energy. In the case of PTO, the difference in the location of the bands is that the Pb atom s-band is one of the valence bands and the Pb atom p-bands are vacant and lie high in the conduction band. This agrees with the results of DFT local density approximation (LDA) calculations [15].

Unlike STO, BTO and PTO, the electronic structure of cubic LMO is metallic both in HF and DFT calculations (a nonzero band gap in LMO appears only if an orthorhombic structure with four formula units in the primitive cell is considered). The s- and p-bands of the oxygen atoms are occupied. Like in STO and BTO, the s-bands of the metal atoms are located at high energies. However, the d-bands of both metal atoms are located in the region of the Fermi energy. These bands are partly occupied and partly vacant, which is caused by the metallic nature of the calculated electronic structure.

The WTAOs that are used in the population analysis are built from the space of all the chosen bands taken together. The density matrix is then calculated using the coefficients connecting the orthogonal or non-orthogonal WTAOs and the occupied Bloch states [5].

In Tables 2–4, the atomic charges for STO, BTO, PTO, correspondingly, calculated by the WTAOs technique, and using the traditional Mulliken population analysis scheme are compared. The Mulliken atomic charges coincide with those given in [13]. The results of the WTAO population analysis in these three crystals show the following.

1. The results of the population analysis performed on orthogonal and non-orthogonal WTAOs are close.
2. The fully ionic charge (+2 |e|) for the Sr, Ba or Pb atoms remains practically the same for both methods of the electronic structure calculation – Hartree–Fock and DFT. The only exception is the orthogonal WTAOs analysis in PTO, but even in this case the charge is very close to +2. The reason for such a high ionicity is related to the high-energy location of the s-bands of the Sr and Ba atoms and the p-bands of Pb atom, which leads to a negligible contribution of the corresponding WTAOs to the covalence of these atoms. The switch from the HF calculations to DFT practically does not affect the location of high-lying vacant bands of the Sr, Ba and Pb atoms and, therefore, no covalence for these atoms appears. On the

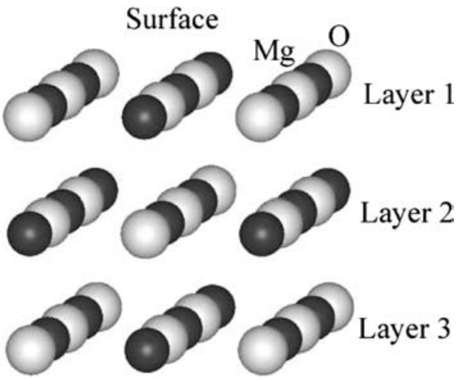

Fig. 1 Three layer slab model of (001) surface of MgO crystal

contrary, the traditional Mulliken analysis displays some covalence for these atoms, which increases in the case of DFT calculations. This is especially noticeable in a PTO crystal.

3. The Ti and O atom charges differ from the purely ionic ones (indicating a partial covalence of the Ti and O atoms). For these atoms, the covalence is higher in DFT calculations than in HF ones. This correlates with the decrease in the band gaps in DFT calculations compared to the HF ones (in DFT calculations the d-bands of the Ti atom shift down and become closer to the valence oxygen bands). As a result, mixing of the vacant states of the Ti atom d-bands with the oxygen WTAOs increases, generating the larger values of the covalence for these atoms.
4. The results of the WTAO analysis demonstrate a mixed (ionic-covalent) character of chemical bonding in ABO_3 crystals. However, the ionicity, calculated by the WTAOs method, appears to be larger than that obtained in the traditional Mulliken population analysis.
5. The values of atomic charges in all the three considered perovskite type crystals are close.

The values of some other local characteristics of the electronic structure of STO, BTO and PTO – bond orders, covalences and valences of atoms – are listed in Tables 5–7, respectively. The values in these tables correspond to the non-orthogonal WTAOs analysis. The results of Tables 5–7 allow concluding the following.

1. The numerical values of the local characteristics of the electronic structure of the cubic STO, BTO and PTO are very close.
2. The covalence in these crystals appears only in the nearest-neighbor Ti–O bonds (all the other bonds manifest almost no covalence both in HF and DFT calculations). Each Ti atom has six bonds of this type, and each oxygen atom two bonds. In DFT calculations, the value of the bond order is larger than in HF ones.
3. Both in the DFT and HF calculations, the values of the total calculated valence of the metal atoms practically coincide with the values of the oxidation state used by chemists for these compounds.

The population analysis is not entirely correct for metallic crystals, because they are characterized by a special metallic type of bonding. But since the non-conducting state in LMO arises within already small distortions from the cubic structure, a formal population analysis performed on the cubic structure can show some tendencies in the local properties. Their values for the cubic LMO obtained with the help of the orthogonal WTAOs in HF calculations are given in Table 8. Analysing these values, one can conclude the following.

1. Some of the results are principally different from the ones of STO, BTO and PTO. These are a non-zero covalence of the A (La) atom, a non-zero La–O bond order, the calculated valence of the B (Mn) atom is different from the expected one. Probable reasons for these results are connected with the metallic nature of the considered crystal in cubic structure and with the difference of the LMO crystal from STO, BTO or PTO.
2. On the other hand, the value of the La atomic charge is relatively close to the fully ionic one (+3 |e|). Besides, the calculated valences of the La and oxygen atoms are similar to the ones obtained in STO, BTO and PTO crystals. This indicates the similarity between these crystals and LMO, manifested in spite of the metallic nature of the latter.

Table 5 Ti–O bond orders, covalence and valence of atoms in $SrTiO_3$

Method of electronic structure calculation	Order of Ti–O bond	Covalence			Total valence		
		Sr	Ti	O	Sr	Ti	O
HF	0.24	0.00	1.47	0.51	2.00	4.01	2.01
DFT	0.36	0.00	2.28	0.82	2.00	4.06	2.02

Table 6 Ti–O bond orders, covalence and valence of atoms in $BaTiO_3$

Method of electronic structure calculation	Order of Ti–O bond	Covalence			Total valence		
		Ba	Ti	O	Ba	Ti	O
HF	0.24	0.00	1.46	0.51	2.00	4.01	2.01
DFT	0.37	0.01	2.33	0.83	2.01	4.06	2.02

Table 7 Ti–O bond orders, covalence and valence of atoms in $PbTiO_3$

Method of electronic structure calculation	Order of Ti–O bond	Covalence			Total valence		
		Pb	Ti	O	Pb	Ti	O
HF	0.22	0.02	1.35	0.47	2.00	4.01	2.01
DFT	0.35	0.04	2.23	0.80	2.02	4.06	2.02

Table 8 Local properties of electronic structure of cubic $LaMnO_3$

Atomic charges			Bond orders		Covalence			Total valence		
La	Mn	O	La–O	Mn–O	La	Mn	O	La	Mn	O
2.48	2.09	−1.53	0.08	0.16	1.00	2.48	0.80	3.04	3.68	1.98

3. The largest value of a bond order in LMO corresponds to the nearest-neighbor Mn–O bond. This correlates with the interatomic charge distribution in STO, BTO and PTO. The difference is in the value of the bond order – in LMO this bond order is smaller – while the covalence (which is, actually, the sum of all the bond orders) of the Mn atoms practically coincides with the one of the Ti atoms in the other three considered crystals. This is, apparently, a consequence of the metallic nature of LMO, which leads to smearing of the nearest-neighbor Mn-O bond charge over the other bonds.

Finally, we note that the local properties of STO, BTO and PTO not that close to each other might be obtained if non-cubic low-temperature phases are studied. It is especially important to consider the orthorhombic phase of LMO since in this phase LMO is no longer metallic.

3.2 Plane-wave basis in Bloch functions calculations

Wannier-type atomic orbitals population analysis can be made also using the Bloch functions found in the calculations with plane wave basis (the majority of modern computer codes for periodic systems calculations use this basis and DFT Hamiltonian). We compared [9] the results of chemical bonding analysis for crystal MgO, performed via the conventional and WF schemes of population analysis. The MgO crystal is a good testing system for studying the accuracy of such methods, since on the one hand, the nature of chemical bonding in it is well known to be ionic, and on the other hand, some of the methods give contradictory results of chemical bonding analysis in this crystal (see below and Refs. [3,4]).

The electronic structure of the MgO crystal was calculated both on the basis of atomic orbitals (LCAO approximation) using the CRYSTAL code [11] and on the PW basis using the CASTEP code [16]. In both cases, the calculations were done by the DFT method in the local density approximation (LDA). The Monkhorst–Pack [14] $4 \times 4 \times 4$ set of special points of the Brillouin zone (BZ), which allows obtaining a convergence (relating to extended special points sets) in the calculations of electronic structure, was used in both cases. For the LCAO calculations, Durand–Barthelat pseudopotential [17] with 2–1 (sp) basis atomic orbitals for the Mg atoms and 3–1 (sp), for the oxygen atoms [18] was adopted. In the case of PW calculations, we used norm-conserving pseudopotential and a PW kinetic energy cutoff of 300 eV.

For construction of the WTAOs, we used the variational method and delta-functions as the weight functions (4) in the variational functional (3). In this case, the variational procedure is equivalent to projecting the delta functions onto the space of the states of chosen energy bands and demands a very low computational effort.

In both types of calculations, the s-and p-bands of oxygen atoms form the four valence bands. The s-band of the Mg in the case of LCAO basis is the highest possible (twelfth) conduction band. For the PW calculations, we examined the lower 32 conduction bands. This analysis showed that the s-band of the Mg atom in PW calculations is also located among high-energy conduction bands. If one considers more than 32 conduction bands, the location of the s-band of the Mg atom can only increase, which would not affect the results of the population analysis.

The calculations showed that the WTAOs, corresponding to the LCAO and PW bases, are essentially different in their form. This distinction is probably caused mainly by the difference in the structure of the bases used for the LCAO and PW calculations. All the WTAOs, excluding the s-WTAO of the Mg atom in the PW calculations, are well localized. The poor localization of the latter is probably due to considering only 32 lower bands, while the actual s-band of the Mg atom might lie higher in the energy than the examined ones. Anyway, the difference in the WTAOs' form and localization level does not affect the results of WTAO-based population analysis for MgO.

The atomic charges and covalences, calculated within the conventional approaches and WTAOs method, are given in Tables 9 and 10. The spilling parameter for the projection procedure in the PW calculations was 2.5×10^{-3}. It is seen from these tables that among the traditional schemes, only the Mulliken analysis performed for the LCAO calculations exhibits a more or less ionic picture of chemical bonding in MgO. All the other conventional methods give the results corresponding to the mixed ionic-covalent type of bonding, which is actually quite unnatural for MgO. Besides, for the traditional methods the values of the atomic charges and covalences are significantly different depending on the scheme and the type of the basis.

Table 9 Calculated atomic charges on the Mg atom in MgO

Basis	Population analysis	Charge on Mg atom, |e|
LCAO	Mulliken	1.93
	Lowdin	1.54
PW	Mulliken	1.06
	Lowdin	0.90
LCAO	Nonorthogonal WTAOs	2.00
	Orthogonal WTAOs	1.97
PW	Nonorthogonal WTAOs	2.00
	Orthogonal WTAOs	1.93

Table 10 Calculated atomic covalencies for MgO

Basis	Population analysis	Atomic covalency	
		Mg	O
LCAO	Mulliken	0.15	0.30
	Lowdin	0.88	1.13
PW	Mulliken	1.63	1.65
	Lowdin	1.90	1.89
LCAO	Nonorthogonal WTAOs	0.00	0.00
	Orthogonal WTAOs	0.05	0.05
PW	Nonorthogonal WTAOs	0.00	0.05
	Orthogonal WTAOs	0.13	0.14

On the contrary, the method based on orthogonal or nonorthogonal WTAOs correctly demonstrates the ionic nature of chemical bonding in MgO crystal, whatever basis is used for the electronic structure calculations. The values, obtained within the different types of the basis, are close and correspond to practically pure ionic character of bonding in this crystal. Though the LDA band structure calculations for the MgO crystal in LCAO and PW bases give different values for the total energy and band-gap width and the forms of corresponding WTAOs are quite dissimilar, nevertheless, the results of population analysis performed on the basis of WTAOs are practically the same. This is a consequence of a high-energy location of the s-band of the Mg atom in both types of calculations.

4 Use of WTAO for two-periodic slab model of the surface

Investigation of chemical bonding on a crystalline surface is important for being an essential factor in the study of surface stability, relaxation, polarization, adsorption, etc. A periodic slab model is one of convenient models when studying the electronic structure properties of crystalline surfaces. When the LCAO approximation is used for calculations, both single (two-periodic – 2D) and repeating (three-periodic – 3D) slabs [19] are considered.

Let us consider application of WTAOs for the calculation of local properties of the electronic structure of unrelaxed MgO (001) and TiO_2 (110) surfaces. Firstly, WFs, corresponding to valence bands, may be used as a tool, allowing one to estimate the values for the slab parameters needed to adequately model the surface electronic structure. And secondly, a minimal valence basis of WTAOs, which are the Wannier functions, generated from occupied and vacant Bloch states and centered on atoms can be used for the analysis of chemical bonding at the surfaces under study.

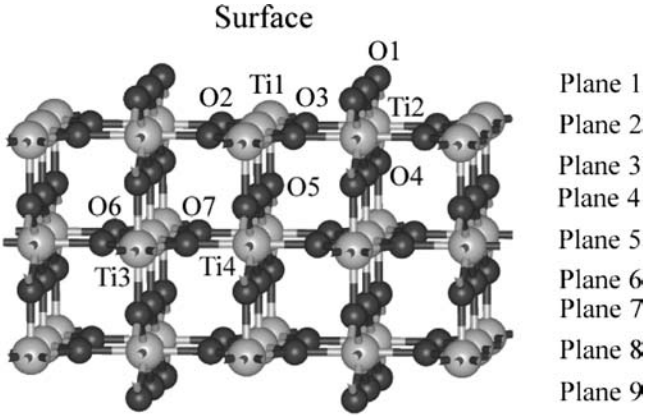

Fig. 2 Three layer (nine planes) slab model of (110) surface of rutile TiO_2 crystal

The electronic structure for the bulk crystals and slab models of surfaces MgO and TiO_2 was calculated in the LCAO approximation by the HF method using the CRYSTAL code [11]. For the MgO crystal, an all-electron basis was chosen. In the case of the TiO_2 crystal, Durand-Barthelat pseudopotential [17] and the corresponding basis consisting of (4–1)/1 (d/sp) AOs for the titanium atoms and 3–1 (sp), for the oxygen atoms was adopted. For the bulk crystals, the Monkhorst–Pack (MP) [14] $4\times4\times4$ mesh of special points of the BZ was used. For surface modelling, we considered single slabs containing three (001)-type atomic planes for MgO (Fig. 1) and nine (110)-type atomic planes for TiO_2(Fig. 2).

In the case of a single-slab model, the space group is two periodic and contains only in-plane proper translations. This fact should be taken into account at the stage of the symmetry analysis. Such space groups correspond to two-dimensional BZ. Traditional methods for WFs generation are based on the 3D-periodicity of conventional crystals [20, 21], and thus cannot be applied for the slab model. Some methods [22, 23], which combine crystal and molecular localization schemes, may be used in this case. But since the latter methods do not utilize the symmetry of the system, they are not quite appropriate for construction of WTAOs, which are characterized by a predefined symmetry. The variational method, used in the present paper, is, on the one hand, symmetry-oriented and, on the other, universal and can be used both in the bulk crystal and slab model calculations as well. Therefore, this method is very useful in the problem of WFs and WTAOs generation in the single-slab model.

For construction of WTAOs for the minimal valence basis, the corresponding energy bands are to be chosen. The s- and p-bands of oxygen atoms form the higher valence bands in both considered slabs. In the case of the TiO_2 slab, the d-bands of the titanium atoms are the lower conduction bands, while the s-bands of the metal atoms in both slabs are located among vacant states high in the energy. The latter makes the contribution of s-WTAOs of the metal atoms to the covalence of theses atoms negligible.

One can estimate the slab thickness needed for surface modelling by a preliminary qualitative analysis of the behavior of WFs, corresponding to valence bands of bulk crystal. Indeed, the off-diagonal elements of the density matrix of a bulk crystal fall off with distance as Wannier functions of valence bands or faster (exponentially in case of insulators). Thus, beyond a sufficiently large domain of the crystal (basic domain) the values of Wannier functions, assigned to the central unit cell of the domain, are negligible. Consequently, truncation of the rest of the crystal and imposition of the periodical boundary conditions on the domain edge atoms practically do not affect the electron density distribution inside the domain chosen. The basic domain of the crystal corresponds to a special set of **k**-points, which provides a convergence of the calculation results relative to the extension of this set [24].

A similar ideology can be used for the slab model. Let us consider the slab consisting of the finite number of atomic planes. Let at the surface planes of the slab chosen the numerical values of bulk valence band WFs be close to zero. The corresponding number of atomic planes determines the minimal thickness of a slab for the studied surface, which can be expected to provide the convergence of the results relative to increasing its thickness. However, the convergence might not occur for the chosen thickness of the slab due to an absence of periodical boundary conditions at the slab surface. However, if the slab WFs, localized in its central part, are close to the bulk ones and the localization of the slab WFs, centered near the slab edge, is to a certain extent the same as in the bulk crystal, the electron density in the mid part of the slab does not differ much from the bulk electron density, and would not change when the thickness of the slab is increased. Thus, the analysis of bulk WFs can help in estimating the slab thickness, which allows obtaining the bulk-like results in the central planes of the slab and thus corresponds to more or less adequate surface modelling. Still this is only a qualitative and estimative analysis.

Let us illustrate the aforesaid by the results obtained for MgO and TiO_2 crystals. Wannier functions for the valence bands of the bulk MgO crystal calculated along the [001] direction are practically completely localized inside a domain containing just three (001) atomic planes. Further, according to calculations the difference between these WFs and the WFs generated for the slab and centered on the plane 2 is negligible. This means that the three-plane slab is convenient for modelling the (001)-surface properties of MgO. This consideration is in principal confirmed by thorough calculations of MgO slabs with a varied thickness – the surface energy and other characteristics converge at the three-plane slab.

In the case of TiO_2, the bulk WFs do not fit into nine atomic planes. As a result, the WFs, calculated from the slab states and localized in the 'central' region of the slab, are different to the corresponding bulk WFs. Consequently, nine planes are not sufficient for correct modelling of the TiO_2 crystalline surface. This result correlates with the results of the calculations in [19].

Table 11 Atomic charges for the single MgO 3-plane (001)-surface slab and bulk crystal

Atoms	Atomic charges, |e|			
	Nonorth. WTAOs	Orth. WTAOs	Mulliken	Lowdin
O 1, Surface	−1.98	−1.96	−1.96	−1.83
Mg 1, Surface	2.00	1.97	1.96	1.83
O 2	−1.99	−1.96	−1.97	−1.82
Mg 2	1.97	1.95	1.97	1.82
O Bulk	−2.00	−1.98	−1.98	−1.82

Table 12 Atomic charges for the single TiO_2 nine-plane (110)-surface slab and bulk crystal

Planes	Atoms	Atomic charges, |e|			
		Nonorth. WTAOs	Orth. WTAOs	Mulliken	Lowdin
1	O 1, surface	−1.33	−1.30	−1.13	−0.88
2	Ti 1, surface	2.99	2.87	2.62	1.84
	Ti 2	2.86	2.79	2.54	1.63
	O 2,3, surface	−1.48	−1.44	−1.35	−0.86
3	O 4	−1.57	−1.51	−1.38	−0.91
4	O 5	−1.54	−1.45	−1.28	−0.82
5	Ti 3	3.06	2.95	2.66	1.72
	Ti 4	3.01	2.93	2.65	1.73
	O 6,7	−1.50	−1.46	−1.33	−0.87
Bulk	Ti	2.76	2.70	2.66	1.72
	O	−1.38	−1.35	−1.33	−0.86

As seen from Table 11, the values of atomic charges for the MgO slab correspond to the purely ionic type of chemical bonding both at the surface and inside the slab. The charges in the slab model practically coincide with the bulk ones. The results, obtained by the WTAOs method and according to the traditional Mulliken and Lowdin schemes, are nearly the same.

For the TiO_2 slab, the Mulliken and Lowdin population analysis give contradictory results. Particularly, as noted in Table 12, the values of atomic charges at the surface planes of the slab, calculated according to the Mulliken scheme, are smaller in magnitude than the ones inside the slab. This corresponds to a lower ionicity at the crystalline surface than the bulk. An opposite tendency is demonstrated in the Lowdin analysis, where the surface charges are larger or the same as in the bulk. Besides, the absolute values of the charges obtained according to both the traditional schemes are quite different from each other. The analysis performed by the orthogonal and non-orthogonal WTAOs gives approximately the same results. They show the tendency of increasing the ionicity level at the surface, which is similar to the results of the Mulliken analysis.

Let us consider the values of atomic charges obtained for the central planes of the slab (planes 3–7). Due to the symmetry of the slab, the planes 6 and 7 are equivalent to the planes 4 and 3, correspondingly. As was shown in the previous section and as is confirmed by other studies [24], a nine-plane slab is not sufficient to model TiO_2 surface, as the electron density at the central planes of the slab is different from of

Table 13 Orders of the bonds between the near-neighbor Ti and O atoms in the single TiO$_2$ nine-plane (110)-surface slab and bulk crystal

Atom	Neighbor atoms			Bond orders			
	Atom	N	Distance (a.u.)	Nonorth. WTAO	Orth. WTAO	Mulliken	Lowdin
O 1	Ti 2, in-surface	2	3.687	0.54	0.55	0.80	0.79
Ti 1	O 2,3, in-surface	4	3.687	0.37	0.39	0.42	0.62
	O 5	1	3.727	0.17	0.25	0.62	0.63
Ti 2	O 1, in-surface	2	3.687	0.54	0.55	0.80	0.79
	O 4	2	3.687	0.27	0.29	0.47	0.50
	O 2,3	2	3.727	0.11	0.13	0.17	0.40
O 2,3	Ti 1, in-surface	2	3.687	0.37	0.39	0.42	0.62
	Ti 2	1	3.727	0.11	0.13	0.17	0.40
O 4	Ti 2	2	3.687	0.27	0.29	0.47	0.50
	Ti 3	1	3.727	0.17	0.21	0.52	0.54
O 5	Ti 4	2	3.687	0.30	0.32	0.52	0.54
	Ti 1	1	3.727	0.17	0.25	0.62	0.63
Ti 3	O 6,7	4	3.687	0.31	0.32	0.34	0.54
	O 4	2	3.727	0.17	0.21	0.52	0.54
Ti 4	O 5	4	3.687	0.30	0.32	0.52	0.54
	O 6,7	2	3.727	0.22	0.23	0.34	0.53
O 6,7	Ti 3	2	3.687	0.31	0.32	0.34	0.54
	Ti 4	1	3.727	0.22	0.23	0.34	0.53

the bulk crystal. However, the values of atomic charges calculated according to both the Mulliken and Lowdin schemes practically coincide with the bulk ones (Table 12). In contrast to these results, the population analysis based on WTAOs reproduces this slab-bulk misfit: the values for the charges of atoms of the inner planes in the slab and the bulk crystal noticeably differ.

When analyzing the Ti–O bond orders, which are given in Table 13, one can conclude the following. The values, obtained by the two traditional schemes, can be hardly interpreted. Some of the bonds have the same orders in both schemes (Ti1–O5, Ti2–O1, Ti3–O4, Ti4–O5), while the others are essentially different (Ti1–O2, Ti2–O2, Ti3–O6, Ti4–O6). As to the results obtained by orthogonal and non-orthogonal WTAOs, they are close for all the bonds under consideration.

Every oxygen atom (excluding the atoms O1) has two neighboring titanium atoms at a distance of 3.687 a.u. and one at 3.727 a.u. (three-coordinated atoms). The O1 atoms are two-coordinated and have neighbors only at 3.687 a.u. The titanium atoms are six-coordinated (Ti2, Ti3, Ti4) or five-coordinated (Ti1) and have four neighboring oxygen atoms at 3.687 a.u. and two or one – at 3.727 a.u., correspondingly. Only for some of the atoms (Ti2, O2, Ti4) the Mulliken and Lowdin schemes allow obtaining the larger orders for the shorter bonds (among the nearest neighbor Ti–O bonds). For other atoms, the values of the shorter bond orders are approximately of the same magnitude as the longer ones (O6) or even significantly smaller (Ti3, O4, O5), which is unreal from the chemical point of view. The WTAOs method for all the atoms gives the expected tendency – the shorter is a bond, the larger is the value of the corresponding bond order. Also, WTAOs analysis gives noticeably larger values for the in-surface bonds. This agrees with the decreased values of the atomic charges at the surface relative to the ones at the inner part of the slab.

The results of the calculations of atomic covalences are presented in Table 14. Again, the Mulliken and Lowdin methods demonstrate contradictory and obscure bulk-surface tendencies. For some atoms, the values of the covalences, calculated according to the Mulliken scheme, are close to the Lowdin ones, for the other they differ significantly. Thus, these coincidences of the Mulliken and Lowdin results can be regarded as casual. And since the nine-plane slab does not provide the bulk-like electron density in the middle of the slab, the correspondence between the values for the covalences of the bulk and slab atoms, obtained by the traditional population analysis schemes, also cannot be considered as reliable.

The WTAOs method, in turn, allows one to obtain the values of atomic covalences in the slab, which can be physically interpreted. Firstly, the values, calculated with the orthogonal and non-orthogonal WTAOs, are alike. Secondly, the in-slab atoms have a covalence different to that of the bulk. This result can be expected due to the insufficient thickness of the nine-plane slab for the TiO$_2$(110) surface modelling.

And last but not least, the results of the WTAOs population analysis clearly show the increase in the covalence at the surface of the slab when compared to the in-slab values. The surface atom O1 has the maximal covalence among all the oxygen atoms of the slab. This effect is even sharper, if it is remembered that this atom is only two-coordinated, while the others are three-coordinated. The large value of the covalence is also observed for the surface atoms O2/O3, but it is not that pronounced as for the atom O1. The atom Ti1, which can be regarded as a surface atom, has a smaller covalence than the atom Ti2, but taking into account that the former is only five-coordinated, one can conclude that the effect of higher covalence at the surface is valid for this atom as well.

The values of local characteristics of the slab electronic structure, differing from the bulk, may indicate the possibility of significant structural relaxation of the studied TiO$_2$

Table 14 Atomic covalences for the single TiO_2 nine-plane (110)-surface slab and bulk crystal

Planes	Atoms	Atomic covalences			
		Nonorth. WTAOs	Orth. WTAOs	Mulliken	Lowdin
1	O 1, surface	1.20	1.24	1.86	1.88
2	Ti 1, surface	1.74	1.91	2.44	3.35
	Ti 2	1.92	2.03	2.36	3.02
	O 2,3, surface	0.95	1.02	1.28	2.01
3	O 4	0.80	0.90	1.76	1.95
4	O 5	0.85	0.99	1.92	2.07
5	Ti 3	1.64	1.82	2.49	3.47
	Ti 4	1.73	1.85	2.87	3.45
	O 6,7	0.92	0.99	1.27	2.03
Bulk	Ti	2.06	2.16	2.15	3.46
	O	1.11	1.17	1.24	2.04

slab. This relaxation would involve in-surface and intra-slab atoms, since the TiO_2 nine-plane slab at its inner planes does not reproduce the bulk electronic structure. Taking into account the results of the WTAO population analysis, one can assume that the atoms would shift so that the length of the bonds would increase or decrease to compensate the excessive or deficient values of covalence, correspondingly. These considerations correlate with the studies of the geometry optimization in TiO_2 slabs [25].

From the use of WTAOs in the slab calculations, we conclude the following.

1. The bulk Wannier functions, corresponding to valence bands, allowed us to estimate that the three-plane slab of MgO is sufficient and the nine-plane (three-layer) slab of TiO_2 is insufficient for modelling the surface properties of the studied crystals.
2. The traditional Mulliken and Lowdin schemes, as well the WTAOs approach, show the purely ionic nature of chemical bonding at the MgO (001)-surface.
3. Unlike the results of Mulliken and Lowdin analysis, which are contradictory and unreliable, the WTAOs method results can be physically interpreted. Calculated by the latter method, local characteristics of the electronic structure of nine-plane (110)-surface slab of TiO_2 are different from the bulk values for all the atoms in the slab. Generally, the type of chemical bonding in the TiO_2 slab is of a mixed ionic-covalent character. At the surface of the slab, the degree of the covalence increases. The results of chemical bonding analysis may be interpreted as an indication of a definite structural relaxation for the studied slab.

5 Conclusion

In the preceding sections, it was demonstrated that use of WTAOs for the chemical bonding analysis in crystals is an efficient and flexible approach: it is fruitful both for the bulk and surface calculations and is applicable for LCAO or PW basises, used in Bloch functions calculations. Wannier-functions are also suited for transferring to the periodic systems the local correlation methods developed for molecules [26].

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References

1. Veryazov VA, Leko AV, Evarestov RA (1999) Phys Solid State 41:1286
2. Mayer I (1986) Int J Quantum Chem 29:73
3. Segall MD, Shah R, Pickard CJ, Payne MC, Dawson I (1996) Phys Rev B 54:16317
4. Lu WC, Wang CZ, Chan TL, Ruedenberg K, Ho KM (2004) Phys Rev B 70:041101
5. Smirnov VP, Evarestov RA, Usvyat DE (2002) Int J Quantum Chem 88:642
6. Evarestov RA, Usvyat DE, Smirnov VP (2003) Phys Solid State 45:459
7. Evarestov RA, Smirnov VP, Usvyat DE (2003) Solid State Commun 127:423
8. Evarestov RA, Smirnov VP, Usvyat DE (2004) Int J Quantum Chem 96:95
9. Evarestov RA, Smirnov VP, Usvyat DE (2004) Phys Stat Sol (b) 241:R35
10. Evarestov RA, Smirnov VP (1997) Site symmetry in crystals: theory and applications, Springer series in solid state sciences. 2nd ed. Springer, Berlin Heidelberg New York Vol 108, 280 p
11. Dovesi R, Saunders VR, Roetti C, Causa M, Harrison NM, Orlando R, Apra E (1996) Crystal 95 User's Manual. Torino University, Torino
12. Hay PJ, Wadt WR (1984) J Chem Phys 82:270
13. Piskunov S, Heifets E, Eglitis R, Borstel G (2004) Comput Mater Sci 29:165
14. Monkhorst HJ, Pack JD (1976) Phys Rev B 13:5188
15. Veithen M, Gonze X, Chosez M (2002) Phys Rev B 66:235113
16. Payne MC (1992) Rev Mod Phys 64:1045
17. Durand P, Barthelat J (1975) Theor Chem Acta 38:283
18. CRYSTAL (2003) Web page. http://www.crystal.unito.it
19. Evarestov RA, Bandura AV (2004) Int J Quantum Chem 96:282
20. Sporkman B, Bross H (1994) Phys Rev B 49:10869
21. Marzari N, Vandebildt D (1997) Phys Rev B 56:12847
22. Zicovich-Wilson CM, Dovesi R, Saunders VR (2001) J Chem Phys 115:9708
23. Mayer I, Rather G, Suhai S (1998) Chem Phys Lett 293:81
24. Evarestov RA,Tupitsyn II (2002) Phys Sol State 44:1656
25. Bates SP, Kresse G, Gillan MG (1997) Surf Sci 385:386
26. Pisani C (2003) J Molec Struct (THEOCHEM) 621:141