PHYSICAL REVIEW B **72**, 075138 (2005)

Symmetry analysis for localized function generation and chemical bonding in crystals: $SrZrO_3$ and MgO as examples

V. P. Smirnov*
St. Petersburg University of Information Technology, Mechanics and Optics, Sablinskaya ul. 14, 197101 St. Petersburg, Russia

R. A. Evarestov†
St. Petersburg University, 198904, St. Petersburg, Petrodvoretz, Russia

(Received 17 May 2005; published 26 August 2005)

Different criteria of localization of one-electron states in crystals are discussed and relations between them are established. A new localization criterion determined only by the localized orbital (LO) itself is formulated. The importance of the symmetry analysis in the procedure of the generation of maximally LOs in crystals is shown. It is suggested that the numerical parameters of the LOs corresponding to the valence energy bands of the crystal can be used in the theory of chemical bonding only if these functions form bases of *irreducible* representations of site symmetry groups of atoms and bonds in crystals. General considerations are illustrated on the examples of LOs corresponding to the valence energy bands in $SrZrO_3$ and MgO crystals. There is in $SrZrO_3$ a LO describing a partly covalent bond between oxygen and zirconium atoms with the degree of covalency $K=0.46$. When applied to the MgO crystal the suggested approach confirms a purely ionic nature of chemical bonding in this crystal.

DOI: 10.1103/PhysRevB.72.075138 PACS number(s): 71.20.−b, 71.15.−m

I. INTRODUCTION

There are known two approaches to the analysis of the chemical bonding in crystals. In the first approach, Mulliken[1] or Löwdin[2] population analysis is applied in the basis of atomic orbitals (AOs) used to approximate Bloch functions (extended AO basis) or generated by projection procedure when Bloch functions calculations were made on the basis of plane waves (minimal AO basis is usually used). Shortcomings of this traditional population analysis are well known: the results essentially depend on the choice of the initial nonorthogonal or orthogonal (after Lowdin symmetrical orthogonalization procedure[3]) basis set; moreover the results are sensitive to the inclusion of diffuse AOs in the basis. The use of Wannier-type atomic orbitals[4] (WTAO) makes this approach free from the drawbacks of the traditional scheme. Both in traditional and WTAO population analysis the number of AOs used is more than the number of valence bands states at every wave vector **k** and requires the inclusion of the conduction bands Bloch states.

The second approach[5] does not use population analysis at all, as it is connected with the generation of localized functions only from the occupied Bloch states found in LCAO basis and with the calculation of the numerical indexes of localized orbitals to describe the chemical bonding in a crystal. In this paper we discuss some details of this second approach concerning one of important indexes of the LO—its centroid position. The latter is considered also in the widely extended Wannier functions generation method[6] using Bloch states obtained in plane wave calculations. We suggest some improvements of the theory important for noncontradictory chemical interpretation of the LOs obtained. This paper is organized as follows.

The symmetry of LOs in crystals in connection with the band representations (BRs) of space groups is discussed in Sec. II. The LOs generation in crystals based on the use of different localization criteria is considered in Sec. III. The importance of the irreducibility of the representation on the basis of LOs is cleared up in Sec. IV. In Secs. IV A and IV B, the general theory is applied to the generation of localized orbitals from occupied (valence) band states calculated in the LCAO approximation and illustrated by the chemical bonding analysis in $SrZrO_3$ and MgO crystals. Concluding remarks are given in Sec. V.

II. SYMMETRY OF LOCALIZED ORBITALS AND BAND REPRESENTATIONS OF SPACE GROUPS

Independently on methods (basis LCAO, plane waves or others), computer codes for electron structure calculations in crystals give usually, besides other information, the profiles of energy bands [energy levels on some array of **k**-points in the Brillouin zone (BZ)] and the total and projected densities of states. Let us take, for example, the $SrZrO_3$ crystal. The configurations of valence electrons in free atoms are

$$\text{O-}2s^2 2p^4, \quad \text{Sr-}4p^6 5s^2, \quad \text{Zr-}4d^2 5s^2. \tag{1}$$

The semicore $4p$-states of the Sr atom are included in (1) as they take part in the valence band structure. The cubic phase of $SrZrO_3$ with the space group $Pm3m$ (O_h^1, a simple cubic lattice) consists of one formula unit (5 atoms) in the primitive unit cell. Atoms Sr, Zr, and O occupy Wyckoff positions (Cartesian coordinates are given in units of lattice constant of the crystal) $b(1/2,1/2,1/2)$, a (0,0,0) (site group O_h for both), and $d(0,0,1/2)$ (site group D_{4h}), respectively.[7]

The CRYSTAL-03 computer code[8] was used for the calculation of the electronic structure of this crystal.[9] The details of this calculation are given in Sec. IV A. 30 electrons per primitive unit cell of $SrZrO_3$ crystal occupy 15 one electron

TABLE I. BR of upper valence bands in the $SrZrO_3$ crystal induced from Sr 4p-, O 2s-, and O 2p-atomlike states.

Atom states	**q**-basis	Γ	R	M	X
Sr 4p-	(b,t_{1u})	4^-	5^+	2^-5^-	1^+5^+
O 2s-	(d,a_{1g})	1^+3^+	4^-	1^+5^-	$1^+2^+3^-$
O 2p_z-	(d,a_{2u})	4^-	1^+3^+	$1^+2^+3^-$	1^+5^-
O 2$p_{x,y}$-	(d,e_u)	4^-5^-	4^+5^+	$3^+4^+5^\pm$	$3^-4^-5^\pm$

levels for each **k**-point in the BZ. 15-sheeted valence band consists of two subbands (6 and 9 sheets). The analysis of the projected densities of states shows that the lower 6-sheeted subband is formed by Sr 4p- and O 2s-states, the upper 9-sheeted band is connected mainly with O 2p-states. These free atoms electron states are transformed by the interatomic interaction in crystalline LOs. The latter basis (just as the basis of canonical Bloch one electron states) may be used to describe the electronic structure of the crystal and calculate its properties.

According to the BR theory,[10–12] there exists the symmetry connection between Bloch one-electron states and LOs. In our example of the $SrZrO_3$ crystal, two induced BRs correspond to six- and nine-sheeted bands. As it is seen from Table I, the states of six-sheeted band are induced by LO of the symmetry a_{1g} of oxygen site symmetry group D_{4h} (Wyckoff position d) and by LOs of the symmetry t_{1u} of the Sr-atom site symmetry group O_h (Wyckoff position b), i.e., by O 2s- and Sr 4p-atomiclike states. The states of nine-sheeted band are induced by LOs of the symmetry a_{2u} and e_u of oxygen site symmetry group D_{4h}, i.e., by O 2p-atomiclike states.

The background of LOs symmetry analysis is the theory of BRs of space groups G. This analysis is equally applicable to localized Wannier orbitals (LWOs), i.e., to an orthonormal set of LOs. We describe the main principles of this theory related to the examined problem. One can get acquaintance with it in detail in Refs. 10–12, for example.

The LOs $V_{i1p}^{(\beta)}(\mathbf{r}) \equiv V_i^{(\beta)}(\mathbf{r}-\mathbf{q}_1^{(p)})$ are the basis functions of the irreducible representation (IR) β of the site symmetry group $L_{\mathbf{q}^{(p)}} \subset G$ corresponding to their centering point (centroid) $\mathbf{q}_1^{(p)}$ (index p distinguishes the symmetry nonequivalent points in the space of the crystal):

$$(l \upharpoonright \mathbf{v}_l) V_{i1p}^{(\beta)}(\mathbf{r}) = \sum_{i'} d_{i'i}^{(\beta)}(l) V_{i'1p}^{(\beta)}(\mathbf{r}), \tag{2}$$

where $(l|\mathbf{v}_l) \in L_{\mathbf{q}^{(p)}}$, $d^{(\beta)}(l)$ is the matrix mapping the element $(l|\mathbf{v}_l)$ in the IR β. In the crystal $SrZrO_3$ index $p=1,2,3$ numbers symmetry nonequivalent Sr, Zr and one of three oxygen atoms. Applying symmetry operations $(g_j|\mathbf{v}_j+\mathbf{a}_\mathbf{n})$ (where $\mathbf{a}_\mathbf{n}$ are lattice translations) from the decomposition of the group G into the left cosets with respect to the site group $L_{\mathbf{q}^{(p)}}$

$$G = \sum_j (g_j|\mathbf{v}_j + \mathbf{a}_\mathbf{n}) \cdot L_{\mathbf{q}^{(p)}}, \tag{3}$$

to the functions $V_{i1p}^{(\beta)}(\mathbf{r})$,

$$V_{ijp}^{(\beta)}(\mathbf{r} - \mathbf{a}_\mathbf{n}) \equiv (g_j|\mathbf{v}_j + \mathbf{a}_\mathbf{n}) V_{i1p}^{(\beta)}(\mathbf{r}), \tag{4}$$

one can obtain the complete basis in the space $\Omega_p^{(\beta)}$ of the reducible representation of the group G induced from the IR β of the group $L_{\mathbf{q}^{(p)}}$. The functions $V_{ijp}^{(\beta)}(\mathbf{r}-\mathbf{a}_\mathbf{n}) \equiv V_i^{(\beta)}(\mathbf{r}-\mathbf{q}_{j,\mathbf{n}}^{(p)}-\mathbf{a}_\mathbf{n})$ are centered at the points $\mathbf{q}_{j,\mathbf{n}}^{(p)} \equiv (g_j|\mathbf{v}_j+\mathbf{a}_\mathbf{n})\mathbf{q}_1^{(p)} = g_j\mathbf{q}_1^{(p)}+\mathbf{v}_j+\mathbf{a}_\mathbf{n}$. Such a basis consisting of the LOs $V_{ijp}^{(\beta)}(\mathbf{r}-\mathbf{a}_\mathbf{n}) \equiv V_\tau(\mathbf{r}-\mathbf{a}_\mathbf{n}) \equiv V_t(\mathbf{r})$ is called the **q**-basis. The index τ replaces i,j,β,p, and the index t replaces $\tau,\mathbf{n}$ to simplify a traditional group-theoretical notation. This basis is fully determined by its any single representative [for example, $V_{11p}^{(\beta)}(\mathbf{r})$]. All the other basis functions of the same BR can be obtained from it by the symmetry operations (2), (4). A BR is characterized in **q**-basis by the site $\mathbf{q}^{(p)}$ [the centroid of $V_{i1p}^{(\beta)}(\mathbf{r})$] and the IR β of the site group $L_{\mathbf{q}^{(p)}}$:$[\mathbf{q}^{(p)},\beta]$ is a symbol of the BR in the **q**-basis.

In the $SrZrO_3$ crystal oxygen 2s-functions transform according to $\beta = a_{1g}$ IR of the site symmetry group $L_{\mathbf{q}^{(3)}} = D_{4h}$ and decomposition (3) consists of 3 terms as the point group of the crystal is O_h. The functions $V_{ijp3}^{(a_{1g})}(\mathbf{r}-\mathbf{a}_\mathbf{n})$ are centered at the oxygens in a whole direct lattice ($j=1,2,3$ numbers oxygens in one primitive cell). This is an example of **q**-basis corresponding to 3-sheeted BR, induced by O 2s-type atomic states. This basis is fully determined by 2s-function of one of three oxygens in the primitive cell and may be labelled by the symbol (d,a_{1g}) as oxygen atoms occupy Wyckoff position d in space group O_h^1.

Resolving this BR into IRs of the space group G, one gets the indices of the BR in **k**-basis (Bloch basis). The short symbol of the BR in the **k**-basis contains only the indices of the small IRs for the most symmetrical points of the BZ, because the indices for all other IRs contained in the BR are determined with the help of compatibility relations. For example, in Table I the BR (d,a_{1g}) is given in the **k**-basis $(\Gamma,R,M,X$ are the symmetry points of the BZ).

There exists simple and composite BRs. A BR is simple if it does not consist of two or more BRs of a smaller dimension. All simple BRs for a given space group are generated by the IRs of site symmetry groups of just a few points in the Wigner-Seitz cell of the direct lattice. Tables of BRs for all space groups can be found in Ref. 13 and for some of the most important space groups in Ref. 12.

In our example, the BR corresponding to the 6-sheeted valence band is a composite one as it is formed by two simple BRs (d,a_{1g}) and (b,t_{1u}) induced by O 2s- and Sr 4p-states, respectively.

From the theory of BRs of space groups, it follows that the generation of LOs corresponding to a given simple or composite energy band is possible only if the canonical (Bloch) orbitals of this band form the basis of some simple or composite BR. This analysis permits not only to establish the principal possibility to construct LOs, but also to define the possible positions of their centroids $\mathbf{q}^{(p)}$ and their symmetry with respect to the site symmetry group $L_{\mathbf{q}^{(p)}}$. The latter is not always unambiguous due to the fact that there are the BRs which have different symbols in **q**-basis, but the same index in **k**-basis[14] or there are the composite BRs which can be decomposed in simple ones by several ways (see the details in Ref. 12).

Thus, the symmetry analysis consists of a procedure of identifying LOs symmetry from the symmetry of the canonical orbitals of the energy band under consideration, or of establishing the fact that the construction of LOs from the canonical orbitals chosen is impossible for the reasons of symmetry.

When calculating the electronic structure of a crystal it is used in its cyclic model,[12,15] i.e., the model of a finite crystal with periodic boundary conditions (a supercell) consisting of N unit cells. Generally, when a numerical integration over the BZ is carried out as a summation over a set of special points of the BZ, it means that a cyclic model of a certain size is introduced for the crystal. The relation between the symmetry group G of the model of an infinite crystal and the symmetry group $G^{(N)}$ of a corresponding cyclic model and their IRs and BRs has been studied in detail in Ref. 15. LOs of the model of an infinite crystal are well approximated by LOs of cyclic models with the size slightly exceeding the region of their localization.[16]

We assume that the canonical delocalized orbitals $\varphi^{(\gamma)}_{m\mu}(\mathbf{k},\mathbf{r}) \equiv \varphi_\sigma(\mathbf{k},\mathbf{r}) \equiv \varphi_s(\mathbf{r})$ (the index m numbers the basis vectors of IR γ with wave vector $\mathbf{k}$, μ discriminates between the independent bases of equivalent IRs; the index σ replaces γ, m, μ, and s replaces $\sigma, \mathbf{k}$) of an energy band under consideration form a basis in the space Ω of some simple BR of the group $G^{(N)}$ of a crystal (index p is omitted for simplicity). The same space Ω is spanned also by the set of LOs $V^{(\beta)}_{ij}(\mathbf{r}-\mathbf{a_n}) \equiv V_t(\mathbf{r})$. The delocalized and localized bases are bounded by a linear transformation in the space Ω,

$$V_\tau(\mathbf{r}-\mathbf{a_n}) = \sum_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{a_n}) \sum_{\sigma} U_{\sigma,\tau}(\mathbf{k})\varphi_\sigma(\mathbf{k},\mathbf{r}), \quad (5a)$$

or

$$V_t(\mathbf{r}) = \sum_s U_{st}\cdot\varphi_s(\mathbf{r}) \quad \text{with} \quad U_{st} = U_{\sigma,\tau}(\mathbf{k})\cdot\exp(-i\mathbf{k}\mathbf{a_n}). \quad (5b)$$

If the matrix U is unitary and the functions $\varphi_s(\mathbf{r})$ are orthonormalized, the functions $V_t(\mathbf{r})$ form an orthonormal system of LWOs $V_t(\mathbf{r}) = W_t(\mathbf{r})$.

Their localization extent depends on the choice of the matrix $U_{\sigma,\tau}(\mathbf{k})$ in Eq. (5a) [U_{st} in Eq. (5b)]. The existence of Wannier functions decreasing exponentially at infinity (for the model of an infinite crystal) is established in many cases listed in Ref. 17. It proved the uniqueness of these functions for nondegenerate bands in crystals with centers of inversion.[17,18] In this case Wannier functions correspond to a special choice of phase factors $U(\mathbf{k}) = \exp(i\alpha(\mathbf{k}))$ of Bloch orbitals $\varphi^{(\gamma)}_{m\mu}(\mathbf{k},\mathbf{r}) = \varphi_s(\mathbf{r})$ in Eq. (5b). Any other choice of phase factors destroys either symmetry properties of the Wannier functions, or their reality, or both.[17–19] Obviously these functions are as maximally localized as possible (fall off exponentially in the model of infinite crystal). If the choice of phase factors in Eq. (5b) is not correct, the Wannier functions lose the exponential character of their decreasing and, therefore, are not maximally localized according to any reasonable criterion of localization.

III. LOCALIZATION CRITERIA AND GENERATION OF LOCALIZED ORBITALS IN CRYSTALS

At the present time there exists different methods of generation of maximally LOs via canonical Bloch orbitals $\varphi_s(\mathbf{r})$ of some energy bands (5b). They differ at first by explicitly or implicitly used localization criterion. Usually the LOs are found as extremals of the functional

$$J(V) = \int \omega(\mathbf{r})\cdot|V(\mathbf{r})|^2 d\mathbf{r}, \quad (6)$$

satisfying the supplementary condition,

$$\int |V(\mathbf{r})|^2 d\mathbf{r} = 1. \quad (7)$$

The weight function $\omega(\mathbf{r}) \geqslant 0$, which is supposed to be invariant under the operations from the site symmetry group $L_\mathbf{q}$, determines the localization region of the function $V(\mathbf{r})$. Particular choices of the weight function are[20]

(1)

$$\omega(\mathbf{r}) = (\pi r_o^2)^{-3/2} \exp\left(-\frac{(\mathbf{r}-\mathbf{q})^2}{r_o^2}\right) \quad (8)$$

which underlines the contribution in (6) of the values of the function $|V(\mathbf{r})|^2$ inside the sphere of radius r_o. The maximally LO corresponds to a maximum of the functional (6),

(2)

$$\omega(\mathbf{r}) = \begin{cases} 1, & \text{if } \mathbf{r} \in \Delta; \\ 0, & \text{if } \mathbf{r} \notin \Delta; \end{cases} \quad (9)$$

where Δ is some region surrounding the point $\mathbf{q}$ of symmetry localization of the function $V^{(\beta)}_0(\mathbf{r})$. The maximally LO corresponds to a maximum of the functional (6),

(3)

$$\omega(\mathbf{r}) = (\mathbf{r}-\mathbf{q})^2. \quad (10)$$

(Refs. 6 and 21–23). The maximally LO corresponds to a minimum of the functional (6).

As a special case of Eq. (8) for $r_o \to 0$ one has $\omega(\mathbf{r}) = \delta(\mathbf{r}-\mathbf{q})$. The weight function in Eq. (10) can be also considered as a special case of Eq. (8). When the region of localization of $V(\mathbf{r})$ is much smaller than r_o, the weight function (8) in functional (6) can be replaced approximately by $(\pi r_o^2)^{-3/2}(1-[(\mathbf{r}-\mathbf{q})^2/r_o^2])$, and the extremal of (6) with $\omega(\mathbf{r})$ (8) corresponds to a minimum of (6) with $\omega(\mathbf{r})$ (10).

The extremal $V(\mathbf{r})$ of the functional (6) [a set of the coefficients U in Eq. (5b)] is a solution of the system of equations

$$\sum_{s'} \langle \varphi_s(\mathbf{r})|\omega(\mathbf{r})|\varphi_{s'}(\mathbf{r})\rangle U_{s'} = \lambda U_s. \quad (11)$$

The solution of the variational problem (6), (7), gives a nonorthogonal set of LOs. The procedure of symmetrical orthogonalization[3] of these functions generates the corresponding orthonomal set of LWOs. If one finds the solution of the variational problem in the class of unitary transformations U (5b), one obtains directly the orthonormal set of maximally LWOs.[5,6]

Another way to formulate the localization criterion is to search $V(\mathbf{r})$ (5b) as the function which minimizes the functional[24,25]

$$I(V) = \int |V(\mathbf{r}) - V_a(\mathbf{r})|^2 d\mathbf{r}, \tag{12}$$

where $V_a(\mathbf{r})$ is some atomiclike function (for example, a function of a free atom). As a matter of fact, the latter determines the least difference of $V(\mathbf{r})$ from $V_a(\mathbf{r})$ as a criterion of localization.

It is well known that the coefficients U_s of linear combination (5b) imparting a minimum to the functional (12) coincide with Fourier coefficients $U_s^{(a)}$ of the function $V_a(\mathbf{r})$ with respect to the set of $\varphi_s(\mathbf{r})$: $U_s = U_s^{(a)} = \langle \varphi_s(\mathbf{r}) | V_a(\mathbf{r}) \rangle$.

The extremals of the functionals (6) and (12) are the LOs generated in the same space Ω of Bloch functions $\varphi_s(\mathbf{r})$ of some energy bands, but corresponding to different localization criteria.

Let us consider particular limit cases when $|V_a(\mathbf{r})| \to \delta(\mathbf{r} - \mathbf{r}_0)$ and $\omega(\mathbf{r}) \to \delta(\mathbf{r} - \mathbf{r}_0)$. In these limit cases

$$U_s = U_s^{(a)} = \langle \varphi_s(\mathbf{r}) | V_a(\mathbf{r}) \rangle = \varphi_s^*(\mathbf{r}_0) \tag{13}$$

and the system (11) transforms in the system

$$\varphi_s^*(\mathbf{r}_0) \sum_{s'} \varphi_{s'}(\mathbf{r}_0) U_{s'} = \lambda U_s \tag{14}$$

the solution of which is $U_s = C\varphi_s^*(\mathbf{r}_0)$ with $\lambda = \Sigma_{s'} |\varphi_{s'}(\mathbf{r}_0)|^2 = (1/C)V(\mathbf{r}_0)$. The constant C can be found from normality condition (7),

$$C = \left(\sum_{s'} |\varphi_{s'}(\mathbf{r}_0)|^2 \right)^{-1/2}. \tag{15}$$

Then

$$J_{\max} = \lambda = C^{-2} = \sum_{s'} |\varphi_{s'}(\mathbf{r}_0)|^2,$$

$$V(\mathbf{r}_0) = \sqrt{\sum_{s'} |\varphi_{s'}(\mathbf{r}_0)|^2} = \sqrt{J_{\max}}. \tag{16}$$

Therefore, the projection of a deltalike function on the space Ω followed by the normalization gives the same LO as the variational method (6) and (7) with a deltalike weight function. The degree of localization of the function $V(\mathbf{r})$ depends on the choice of $\mathbf{r}_0$. The relation (16) shows that the most LO in the frame of the chosen localization criterion corresponds to $\mathbf{r}_0$ at which the electron density in valence energy bands

$$\rho(\mathbf{r}) = \sum_{s'} |\varphi_{s'}(\mathbf{r})|^2 \tag{17}$$

has an absolute maximum. This does not mean that this function will be the mostly localized if the other localization criterion is chosen. Therefore, it is desirable to formulate the localization criterion in such a way that it does not depend on any factors except the function itself looked for. This requirement is satisfied, for example, by the criterion (6) at $\omega(\mathbf{r}) = |V(\mathbf{r})|^2$, i.e., the functional

$$\tilde{J}(V) = \int |V(\mathbf{r})|^2 \cdot |V(\mathbf{r})|^2 d\mathbf{r} = \int |V(\mathbf{r})|^4 d\mathbf{r} \tag{18}$$

is supplied with a maximum by the function $V(\mathbf{r})$ at a supplementary normality condition (7). The solution of this problem can be realized by the method of successive approximations

$$\tilde{J}_n(V) = \int |V_{n-1}(\mathbf{r})|^2 \cdot |V_n(\mathbf{r})|^2 d\mathbf{r} \tag{19}$$

choosing the function $V_o(\mathbf{r})$ determined by the way described earlier

$$V_o(\mathbf{r}) = \frac{\sum_{s'} \varphi_{s'}^*(\mathbf{r}_0)\varphi_{s'}(\mathbf{r})}{\left(\sum_{s'} |\varphi_{s'}(\mathbf{r}_0)|^2\right)^{-1/2}} \tag{20}$$

as an initial approximation.

IV. CENTROID POSITION AND SYMMETRY OF LOCALIZED ORBITALS

In the approach proposed in Ref. 5 the centroid position $\bar{\mathbf{r}}_i$ of a LWO $W_i(\mathbf{r})$ (a mean value of $\mathbf{r} = \Sigma_s x_s \mathbf{e}_s$) is introduced as a numerical characteristic of the chemical bonding in crystals

$$\bar{\mathbf{r}}_i = \int \mathbf{r} |W_i(\mathbf{r})|^2 d\mathbf{r} = \sum_s \bar{x}_{si} \mathbf{e}_s, \quad \bar{x}_{si} = \int x_s |W_i(\mathbf{r})|^2 d\mathbf{r}. \tag{21}$$

Centroid position $\bar{\mathbf{r}}_i$ of the LWO $W_i(\mathbf{r})$ determines the so-called polarization fraction[5] for $W_i(\mathbf{r})$,

$$p_i = \left| 2\frac{(\bar{\mathbf{r}}_i - \mathbf{r}_A)(\mathbf{r}_B - \mathbf{r}_A)}{|\mathbf{r}_B - \mathbf{r}_A|^2} - 1 \right|, \quad (0 \leqslant p_i \leqslant 1), \tag{22}$$

which is proposed to estimate the degree of ionicity and covalency of the chemical bonding between atoms A and B ($\mathbf{r}_A$ and $\mathbf{r}_B$ are their position vectors). This parameter takes the value $p_i = 1$ for pure ionic bond and $p_i = 0$ for pure covalent bond. A and B atoms are supposed to give the two largest contributions of the Mulliken atomic population to the LWO $W_i(\mathbf{r})$.

In the general case, the LWOs are centered on some center $\mathbf{q}$ and transform according to some representation Re (in general case reducible) of the site symmetry group $L_{\mathbf{q}}$ of this center. Let us represent these functions as linear combinations of the LWOs $\tilde{W}_j^{(\beta)}(\mathbf{r})$ transforming according to IRs β of the site group $L_{\mathbf{q}}$,

$$W_i(\mathbf{r}) = \sum_{\beta,j} \alpha_{\beta j,i} \tilde{W}_j^{(\beta)}(\mathbf{r}), \quad \alpha^T \alpha = E. \tag{23}$$

The transformation with the help of the matrix α is orthogonal as it relates to two orthonormal bases in the space of the representation Re (E is a unit matrix). Inserting Eq. (23) in Eq. (21), one obtains

$$\bar{x}_{si} = \sum_{\beta\beta' jj'} D^{(s)}_{\beta j,\beta' j'} \alpha^{*}_{\beta j,i} \alpha_{\beta' j',i}, \tag{24}$$

where the number of independent values $D^{(s)}_{\beta j,\beta' j'} = \langle \tilde{W}_j^{(\beta)}(\mathbf{r}) | x_s | \tilde{W}_{j'}^{(\beta')}(\mathbf{r}) \rangle$ is equal[12] to the number of irreducible components of the vector representation contained in the symmetric square $\{\mathrm{Re} \times \mathrm{Re}^*\}^{(+)}$ of the representation Re. If $W_i(\mathbf{r})$ coincide with their irreducible components ($\alpha_{\beta j,i} = \delta_{\beta j,i}$), then $\bar{\mathbf{r}}_i = 0$ for centrosymmetrical site groups $L_{\mathbf{q}}$ as all $D^{(s)}_{\beta j,\beta' j'} = 0 (\bar{x}_{si} = 0)$. In general case, as seen from Eq. (24), $\bar{\mathbf{r}}_i \neq 0$ and their lengths and orientations depend on the value of the coefficients $\alpha_{\beta j,i}$. Being function of the centroid position, the polarization fractions p_i (22) depend also on the value of the coefficients $\alpha_{\beta j,i}$. It is obvious that in general case one can not attribute to the centroid of a LWO some physical meaning. But a particular choice of LOs can attach to the centroid a commonon sense useful in the theory of chemical bonding.

LWOs $W_a(\mathbf{r})$ cited on atoms describe lone pairs or a purely ionic bonding ($p_i = 1$). LWOs $W_b(\mathbf{r})$ cited on interatomic bonds mean the presence of a covalent component of the chemical bonding ($0 < p_i \leqslant 1$), the degree of covalency being determined by the value of the polarization fraction p_i which takes the form

$$p_i = \left| 2\frac{d_i - d_A}{d_B - d_A} - 1 \right|, \tag{25}$$

where d_A, d_B, and d_i are positions of atoms A, B, and the centroid of the LWO $W_i(\mathbf{r})$ on the bond line A-B counted off some arbitrary point on it. In latter case, the BR associated with the valence bands of the crystal has to include the BR induced from some IR β of the site symmetry group $L_{\mathbf{q}_b}$ of the bond. The value $p_i = 0$ corresponds to a pure covalent bond.

Note that this BR is a composite one. Indeed, the group $L_{\mathbf{q}_b}$ is a subgroup of the site group $L_{\mathbf{q}_A}$ of the atom A (and of the site group $L_{\mathbf{q}_B}$ of the atom B) lying on the bond. The IR β induces in the groups $L_{\mathbf{q}_A}$ some reducible representation which, in its turn, induces in the space group G a composite BR.[12] There is an exception when a middle point of the bond is a symmetry point. In this case the IR of the site group of this point induces in the space group G a simple BR. This situation takes place, for example, in the Si crystal,[20] where the IR a_{1g} of the site group D_{3d} of the middle point of the bond Si-Si (Wyckoff position c) induces in the space group O_h^7 of the crystal the BR with $\mathbf{q}$-basis consisting of the canonical Bloch states of the four-sheeted upper valence band. This LWO describes the purely covalent bond ($p = 0$).

We propose to introduce not only centroids position, but also the following numerical characteristics of the chemical bond related to the LWO $W_i(\mathbf{r})$:

(1) Contributions $Q_i^{(A)}$ and $Q_i^{(B)}$ to charges on atoms A and B related to the LWO $W_i(\mathbf{r})$ (in $|e|$ units)

$$Q_i^{(A)} = 2\frac{d_i - d_B}{d_B - d_A}, \quad Q_i^{(B)} = 2\frac{d_A - d_i}{d_B - d_A}, \quad -2 \leqslant Q_i^{(A)}, Q_i^{(B)} \leqslant 0. \tag{26}$$

An electron charge $Q_i^{(A)} + Q_i^{(B)} = -2$ associated with the fully occupied LWO $W_i(\mathbf{r})$ is partitioned between atoms A and B inversely proportional to the distances between the centroid position and the atoms.

(2) Degree of ionicity I_i of the bond A-B related to the LWO $W_i(\mathbf{r})$,

$$I_i = \left| \frac{2d_i - d_A - d_B}{d_B - d_A} \right| = \frac{1}{2} |Q_i^{(A)} - Q_i^{(B)}|, \quad 0 \leqslant I_i \leqslant 1. \tag{27}$$

(3) Degree of covalency K_i of the bond A-B related to the LWO $W_i(\mathbf{r})$,

$$K_i = 1 - \left| \frac{2d_i - d_A - d_B}{d_B - d_A} \right| = 1 - \frac{1}{2} |Q_i^{(A)} - Q_i^{(B)}|, \quad 0 \leqslant K_i \leqslant 1. \tag{28}$$

Ionicity I_i coincides with polarization fraction p_i (25). For pure ionic bonding $Q_i^{(A)} = -2$, $Q_i^{(B)} = 0$ (or vice versa), $K = 0$, $I = 1$. For pure covalent bonding $Q_i^{(A)} = Q_i^{(B)} = -1$, $K = 1$, $I = 0$.

We suggest the following procedure to describe the chemical bonding in crystals by analyzing only occupied valence states in the basis of LWOs:

(1) A symmetry analysis of valence bands states is carried out. The purpose of this analysis is to find the $\mathbf{q}$-basis indexes of the BR corresponding to the valence states of the crystal. These indexes can consist of:

(a1) the IRs of the site groups of the bonds (including those of symmetry points on the bond lines, if there is any);

(a2) the IRs of site groups of atoms;

If a composite BR has several variants to be represented as a sum of more simple ones,[12] the preference has to be given to BR s induced from site groups of bonds.

The results of this symmetry analysis allow to find the centroids positions (on atoms or on bonds) of the LWOs to be generated from Bloch canonical valence states. The numerical characteristics of only these LWOs are suggested to give a non-contradictory unambiguous interpretation of chemical bonding in crystals.

(2) Projection of the space Ω of the states of all the valence energy bands on the spaces Ω_i of IR of the site symmetry groups related to the components of the BR in $\mathbf{q}$-basis established above.

(3) Generation from the canonical Bloch valence states maximally LWOs in the spaces Ω_i by any known procedure (see Sec. III).

(4) Calculation of numerical characteristics of the chemical bonding on the base of these LWOs.

There exists approaches where LWOs are generated directly from Bloch valence states without any preliminary symmetry analysis.[5,6] In this case one obtains LWOs which have the centroids positions in the vicinities of some points of the direct lattice of the crystal occupied by atoms or being midpoint between the pairs of symmetry equivalent atoms. As it follows from the theory of BR, these LWOs are in fact to be bases of some representations (in general case reducible) of site symmetry groups of these Wyckoff positions (of atoms and bonds), the preference has to be given also to BR s induced from site groups of bonds. So, in this case the points 2 and 3 have to be replaced by

(2′) Generation maximally LWOs in the space Ω of the canonical Bloch valence states by any known procedure.

(3′) A proper symmetrization of generated LWOs according to the results of the symmetry analysis of point (1).

We shall illustrate this on the examples of the $SrZrO_3$ and MgO crystals. Point group symmetry of the localized function is taken into account in Ref. 26.

A. Centroid positions of LWOs and chemical bonding in the $SrZrO_3$ crystal

In our DFT-LCAO calculations of the $SrZrO_3$ crystal,[9] the CRYSTAL-03 computer code[8] was used with small-core Hay-Wadt pseudopotentials[27] and the corresponding basis sets for Sr and Zr atoms, whereas the O atom was treated as all electrons.[28] The Monkhorst-Pack[29] $8\times8\times8$ set of special points was used in the BZ sampling, PBE-GGA density functional[30] was adopted. The lower valence bands are composed of Sr $4p$-and O $2s$-states (six sheets), whereas the upper valence band is produced mainly by the O $2p$-atomic orbitals (nine sheets). The symmetry of all these valence band states and the atomic nature of the projected density of states is the same both in these DFT-LCAO and in former DFT-PW (plane wave) calculations.[31]

Using the computer code,[8] the iterative procedure was applied to generate LWOs using crystal orbitals of these 15 occupied bands. The Bloch functions for Γ point of BZ are taken as the starting LWOs. As a result, the iterative procedure gives 15 LWOs. Three of them are centered on Sr atom and are connected with Sr atom $4p$-states. The remaining 12 LWOs are connected with the three symmetry equivalent oxygen atoms in the crystal, four LWOs with the centroid positions near the each oxygen atom.

To analyze the nature of chemical bonding with these LWOs, we used the given in Table I information about the symmetry of the band states induced from Sr $4p$-, O $2s$-, and O $2p$-states forming two upper valence bands. It is seen that these states form a basis of composite BR described in $\mathbf{q}$-basis by the symbol

$$(b,t_{1u})+(d,a_{1g}+a_{2u}+e_u). \tag{29}$$

TABLE II. Centroids positions (x_{1i},x_{2i},x_{3i}) (in a.u.) and polarization fractions p_i for functions $W_i(\mathbf{r})$ in the $SrZrO_3$ crystal localized according to Wannier-Boys mixed scheme (Ref. 5).

$W_i(\mathbf{r})$	x_{1i}	x_{2i}	x_{3i}	p_i
$W_1(\mathbf{r})$	−0.039	0.465	−0.002	0.999
$W_2(\mathbf{r})$	0.465	−0.039	−0.002	0.999
$W_3(\mathbf{r})$	−0.211	−0.211	0.774	0.610
$W_4(\mathbf{r})$	−0.215	−0.215	−0.769	0.612

Therefore, four LWOs $W_i(\mathbf{r})$ with the centroid positions near the each oxygen atom form a basis of four-dimensional representation $a_{1g}+a_{2u}+e_u$ of the site group D_{4h} of the oxygen atom. Let us denote LWOs which are the basis functions of these IRs as follows: $\widetilde{W}_1(\mathbf{r})=\widetilde{W}_1^{(d,e_u)}(\mathbf{r})$, $\widetilde{W}_2(\mathbf{r})=\widetilde{W}_2^{(d,e_u)}(\mathbf{r})$, $\widetilde{W}_3(\mathbf{r})=\widetilde{W}^{(d,a_{2u})}(\mathbf{r})$, $\widetilde{W}_4(\mathbf{r})=\widetilde{W}^{(d,a_{1g})}(\mathbf{r})$. Then, instead of Eq. (23), one has

$$W_i(\mathbf{r})=\sum_{j=1}^{4}\alpha_{ji}\widetilde{W}_j(\mathbf{r}),\quad i=1,2,3,4. \tag{30}$$

The starting LWOs of the computer code[8] result in $W_i(\mathbf{r})$ (30) with some definite values of the coefficients α_{ji}. In this case $\mathrm{Re}=e_u+a_{2u}+a_{1g}$, the representation $\{\mathrm{Re}\times\mathrm{Re}\}^{(+)}=3a_{1g}+b_{1g}+b_{2g}+e_g+e_u+a_{2u}$ contains only one time two irreducible components of the vector representation (e_u+a_{2u}), i.e., there are only two independent parameters in Eq. (24),

$$\bar{\mathbf{r}}_i=\sum_{s=1}^{3}\bar{x}_{si}\mathbf{e}_s,\quad \bar{x}_{si}=D_s\alpha_{4i}\alpha_{si}, \tag{31}$$

where

$$D_1=2\langle\widetilde{W}_4(\mathbf{r})|x_1|\widetilde{W}_1(\mathbf{r})\rangle=D_2=2\langle\widetilde{W}_4(\mathbf{r})|x_2|\widetilde{W}_2(\mathbf{r})\rangle,$$

$$D_3=2\langle\widetilde{W}_4(\mathbf{r})|x_3|\widetilde{W}_3(\mathbf{r})\rangle. \tag{32}$$

In Table II are given the Cartesian coordinates $\bar{x}_{si}$ of centroid positions and the polarization fractions p_i for LWOs $W_i(\mathbf{r})$ $(i=1-4)$ evaluated by the computer code.[8] It is evident [see Eq. (31)] that the other choice of the starting LWOs can, in principle, give other centroid positions and other values of p_i.

Let us note that the BR $(d,a_{1g}+a_{2u})$ is a composite one. The points on the line binding Zr and O atoms (Wyckoff position e) have the site symmetry C_{4v}. The IR a_1 of this group induces in the group D_{4h} (the site symmetry group of the oxygen atom) the representation $a_{1g}+a_{2u}$: $a_1(C_{4v})\uparrow D_{4h}=a_{1g}+a_{2u}(D_{4h})$. Therefore instead of Eq. (29) one can write another symbol in $\mathbf{q}$-basis

$$(b,t_{1u})+(d,e_u)+(e,a_1) \tag{33}$$

for the same BR corresponding to the 15-sheeted band chosen. Note that the IR a_1 of C_{4v} induces also the representation $a_{1g}+e_g+t_{1u}$ of the site group O_h of the Zr atom—the second atom on the bond line Zr-O: $a_1(C_{4v})\uparrow O_h=a_{1g}+e_u+t_{1u}(O_h)$. Thus, one can attribute one more symbol in the $\mathbf{q}$-basis to the BR corresponding to the same 15-sheeted energy band,

$$(b,t_{1u})+(d,e_u)+(a,a_{1g}+e_g+t_{1u}). \tag{34}$$

It is seen that the part $(b,t_{1u})+(d,e_u)$ is common for three symbols (29), (33), (34) of the BR under consideration. They correspond to LWOs, localized on Sr and oxygen atoms. The rest of the BR is given by different ways in three its labels (29), (33), (34). The symmetry considerations show that it is possible to generate from the states of valence bands of the $SrZrO_3$ crystal the LWOs centered on zirconium and on oxygen atoms. These LWOs form the bases of *reducible* representations of the site groups of Zr and O atoms, $a_{1g}+e_g+t_{1u}$ of O_h and $a_{1g}+a_{2u}$ of D_{4h}, respectively. Linear combinations of functions of any of these bases are equivalent from the group-theoretical point of view, but will give *different* values for the numerical characteristics of chemical bonding (see Sec. IV). However, there is only *one* possibility to conciliate these two bases. Both bases are induced from the same IR a_1 of the common subgroup C_{4v} (the site group of the Wyckoff position e on the bond line Zr-O) of the groups O_h and D_{4h}.

The BR with **q**-basis (33) corresponds to a particular choice of the linear combinations of $\widetilde{W}_j(\mathbf{r})$ (30): two of them are transformed according to the IR e_u of the site group (D_{4h}) of the oxygen atom, the linear combination $\widetilde{W}_{+}^{(e,a_1)}=(1/\sqrt{2})(\widetilde{W}^{(d,a_{1g})}+\widetilde{W}^{(d,a_{2u})})$ of two others engenders the LWO sited on the bond line Zr-O and transforming according to IR a_1 of the symmetry group C_{4v} of the bond. This LWO induces another one $\widetilde{W}_{-}^{(e,a_1)}=(1/\sqrt{2})(\widetilde{W}^{(d,a_{1g})}-\widetilde{W}^{(d,a_{2u})})$ centered on the Zr-O bonding line but at the other side of the same oxygen atom. In the whole the number of LWOs per unit cell remains the same. These functions describe the covalent bonding of the oxygen atom with two its neighboring Zr atoms. The numerical value of covalency can be evaluated from the centroid positions of these LWOs counted off the oxygen atom.

To find the centroid positions of the LWOs $\widetilde{W}_i(\mathbf{r})$ it is sufficient to symmetrize the calculated LWOs $W_i(\mathbf{r})$ by the usual group-theoretical methods. Instead of extracting the LWO s themselves from the results of computer code[8] application we used another way to find the coefficients α_{ji} in Eq. (30) and centroid positions corresponding to LWOs $\widetilde{W}_i(\mathbf{r})$.

The relations (31) with the normality condition $(\Sigma_{j=1}^{4}\alpha_{ji}^2=1)$ give

$$\alpha_{4i}=\sqrt{\frac{1}{2}-\sqrt{\frac{1}{4}-\left(\frac{\bar{x}_{1i}^2+\bar{x}_{2i}^2}{D_1^2}+\frac{\bar{x}_{3i}^2}{D_3^2}\right)}},$$

$$\alpha_{si}=\frac{\bar{x}_{si}}{D_s\alpha_{4i}},\quad s=1,2,3;\quad i=1,2,3,4 \tag{35}$$

as functions of the parameters D_1 and D_3 [the matrix $\alpha=\alpha(D_1,D_3)$]. The values of these parameters were found to be $D_1=1.336$, $D_3=1{,}825$ from the condition of minimum of the function

$$\sum_{i,j=1}^{4}(\alpha^T(D_1,D_3)\alpha(D_1,D_3)-E)_{i,j}^2 \tag{36}$$

to assure the orthogonality of the matrix α which is found to be

$$\alpha=\begin{pmatrix}-0.077 & 0.923 & -0.264 & -0.269\\ 0.923 & -0.077 & -0.264 & -0.269\\ -0.003 & -0.003 & 0.709 & -0.706\\ 0.377 & 0.377 & 0.598 & 0.598\end{pmatrix}. \tag{37}$$

It is seen from Eq. (30) with the matrix (37) that LWOs $W_i(\mathbf{r})$ $(i=1,2)$ almost coincide with $\widetilde{W}_i^{(d,e_u)}(\mathbf{r})$ although they have a noticeable admixture of LWO $\widetilde{W}^{(d,a_{1g})}(\mathbf{r})$. LWOs $W_i(\mathbf{r})$ $(i=3,4)$ are formed essentially by $\widetilde{W}^{(d,a_{2u})}(\mathbf{r})$ and $\widetilde{W}^{(d,a_{1g})}(\mathbf{r})$ although they have a noticeable admixture of LWO $\widetilde{W}_i^{(d,e_u)}(\mathbf{r})$.

Using (32), we obtain $\langle\widetilde{W}^{(d,a_{1g})}(\mathbf{r})|x_3|\widetilde{W}^{(d,a_{2u})}(\mathbf{r})\rangle=0.912$. The centroid positions relative to oxygen atoms for the LWOs $\widetilde{W}_i(\mathbf{r})$ $(i=1,2,3,4)\bar{\mathbf{r}}_i-\mathbf{r}_{\mathrm{O}}=0$, and the corresponding polarization fraction $p_i=1$ for all four LWOs. In particular, for $\widetilde{W}_1^{(d,e_u)}(\mathbf{r})$ and $\widetilde{W}_2^{(d,e_u)}(\mathbf{r})p=1$. They describe lone pairs on the oxygen atom in the crystal. But for the linear combinations $\widetilde{W}_{\pm}^{(e,a_1)}(\mathbf{r})$ (the IR a_1 of the site group C_{4v} of the Wyckoff position e on the bond line Zr-O), $\bar{\mathbf{r}}_{\pm}-\mathbf{r}_{\mathrm{O}}=\pm 0.912\ \mathbf{e}_3$ (in a.u.) and the polarization fractions $p_{\pm}=0{,}54$. These LWOs describe partly covalent binding of atoms O and Zr in the crystal $SrZrO_3$. The other numeric characteristics (26) and (27) of this bond are: $Q^{(\mathrm{O})}=-1.54$, $Q^{(\mathrm{Zr})}=-0.46$, $I_{\text{O-Zr}}=0.54$, $K_{\text{O-Zr}}=0.46$.

Taking into account (1), atomic cores have the charges: +6(O), +8(Sr), +4(Zr). According to the **q**-basis index of the BR (33) the electron structure of the crystal can be represented by 15 LWOs per primitive cell every orbital being occupied by two electrons:

(1) Three orbitals $\widetilde{W}^{(b,t_{1u})}(\mathbf{r})$ of symmetry t_{1u} (p-type) are localized on Sr (site group O_h) and bring to it the charge −6. Finally, atom Sr has in the crystal the charge +2(=8−6) rigorously.

(2) Six orbitals $\widetilde{W}^{(d,e_u)}(\mathbf{r})$ of symmetry e_u (p_x,p_y-type) are localized on O atoms (site group D_{4h}, three atoms per primitive cell and bring to every atom the charge −4.

(3) Six orbitals $\widetilde{W}^{(e,a_1)}(\mathbf{r})$ of symmetry a_1 (sp_z-type) are localized on the bonding line O-Zr (site group C_{4v}, six bonding lines per primitive cell). The charge −2 associated with every orbital is partitioned between oxygen (−1.54) and zirconium (−0.46) atoms. As there are two bonds for the oxygen atom, its charge in the crystal is $-1.08(=+6-4-1.54\times 2)$. Equally for the zirconium atom, one has $+1.24$ $(=+4-0.46\times 6$; 6 bonds for Zr).

B. Centroid positions of LWOs and chemical bonding in the MgO crystal

In the MgO crystal (space group O_h^5) atoms Mg and O occupy the positions $b(0,0,1/2)$ and a (0,0,0) (site group O_h for both), correspondingly. The electronic structure and the insulating gap of the crystal was calculated by the restricted Hartree-Fock (RHF) method using the CRYSTAL-03 computer code.[8] Both Mg and O atoms were treated as all electron.[28] The $8\times 8\times 8$ Monkhorst-Pack set of special points[29] was used in the BZ sampling.

The electronic structure is characterized by two uppermost valence energy bands consisting of 3 and 1 energy sheets for O $2p$- and O $2s$-bands, respectively. From group-theoretical point of view the Bloch states of these bands form a basis of composite BR which has in **q**-basis the symbol,

$$(a, a_{1g} + t_{1u}). \tag{38}$$

Electronic states of these energy bands are originated certainly from $2s, 2p$-O atomic states. The points on the bond line of the atoms Mg and O (Wyckoff position e) have the symmetry C_{4v}. Even the one-dimensional IR a_1 of this group induces in the group O_h the six-dimensional representation $a_{1g}+e_g+t_{1u}$: $a_1(C_{4v})\uparrow O_h = a_{1g}+e_g+t_{1u}(O_h)$. This means, that there exists no LWO centered on this bond which could generate four-sheeted valence energy band in the MgO crystal. One can say the same about the LWOs centered on the Wyckoff position $f(x,x,x)$ (site group C_{3v}): they could engender eight-sheeted energy band.

Therefore there is no other alternative but (38) for the BR corresponding to valence bands in the MgO crystal. For reasonable interpretation of bonding in the crystal only the functions $\widetilde{W}_1(\mathbf{r}) = \widetilde{W}^{(a,a_{1g})}(\mathbf{r})$, $\widetilde{W}_2(\mathbf{r}) = \widetilde{W}_1^{(a,t_{1u})}(\mathbf{r})$, $\widetilde{W}_3(\mathbf{r}) = \widetilde{W}_2^{(a,t_{1u})}(\mathbf{r})$, $\widetilde{W}_4(\mathbf{r}) = \widetilde{W}_3^{(a,t_{1u})}(\mathbf{r})$ are suited. They are centered on oxygen atom and $\overline{\mathbf{r}}_i = \mathbf{r}_{\mathrm{O}}$, $Q_i^{(\mathrm{O})} = -2$, $I_i = p_i = 1$, $K_i = 0$ $(i=1,2,3,4)$. The centroid positions and the values of other numeric characteristics of chemical bonding are not changed evidently for any linear combination of the functions $\widetilde{W}_i(\mathbf{r})$ $(i=2,3,4)$ in the space of IR t_{1u}. The charges on atoms are: +2(Mg), −2(O) strongly.

V. CONCLUSIONS

In the present paper we demonstrate the importance of the symmetry analysis in the procedure of the generation of LWOs in crystals. The theory of space group BR gives a powerful tool to determine the centroid positions of LWOs.

(1) If this centroid is at the symmetry point in the direct lattice, its position is defined exactly by the BR theory. If this position is occupied by an atom, the corresponding LWO describes an ionic bond or a lone pair. This is the case for the MgO crystal and the LWOs $\widetilde{W}_1^{(d,e_u)}(\mathbf{r})$ and $\widetilde{W}_2^{(d,e_u)}(\mathbf{r})$ in the SrZrO$_3$ crystal. If it is a middle point between two atoms, the corresponding LWO describes a pure covalent bond. This is the well known example of the Si crystal.

(2) If the centroid is located on a symmetry line (possible site groups are C_{6v}, C_{4v}, C_{3v}, C_{2v}, C_6, C_4, C_3, C_2), its exact position cannot be defined by the BR theory, and numeric calculations are necessary. The corresponding LWO describes a two-atomic partly covalent bond. This is the case of the LWO $\widetilde{W}^{(e,a_1)}(\mathbf{r})$ (site group C_{4v}) in the SrZrO$_3$ crystal with the following numeric characteristics of the bond: $I_{\text{O-Zr}} = p_{\text{O-Zr}} = 0.54$, $K_{\text{O-Zr}} = 0.46$, $Q^{(\mathrm{O})} = -1.54$, $Q^{(\mathrm{Zr})} = -0.46$.

(3) If the centroid is located at a symmetry plane (possible site group is C_s), its exact position cannot be defined by the BR theory, and numeric calculations are also necessary. The corresponding LWO describes a three- and more-atomic bond.

Note added in proof. Through a private communication from S. Casassa, we became aware that *a posteriori* symmetrization of a set of localized Wannier functions is presented by Casassa *et al.* (Ref. 32).

ACKNOWLEDGMENTS

One of authors (R.A.E.) thanks the Russian Foundation of Basic Research (Grant No. 05-03-32002-a) for support.

---

*Electronic address: smirnov36@mail.ru
†Electronic address: evarest@hm.csa.ru

[1] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).
[2] P. O. Löwdin, Adv. Quantum Chem. **5**, 185 (1970).
[3] P. O. Löwdin, Adv. Phys. **5**, 1 (1956).
[4] V. P. Smirnov, R. A. Evarestov, and D. E. Usvyat, Int. J. Quantum Chem. **88**, 642 (2002).
[5] C. M. Zicovich-Wilson, A. Bert, C. Roetti, R. Dovesi, and V. R. Saunders, J. Chem. Phys. **116**, 1120 (2002).
[6] N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997).
[7] B. J. Kennedy, C. J. Howard, and B. C. Chakoumakos, Phys. Rev. B **59**, 4023 (1999).
[8] V. R. Saunders, R. Dovesi, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, N. M. Harrison, K. Doll, B. Civalleri, I. J. Bush, Ph. D'Arco, and M. Llunell, *Crystal 2003 User's Manual* (University of Turin, Turin, 2003).
[9] R. A. Evarestov, A. V. Bandura, V. E. Alexandrov, and E. A. Kotomin, Phys. Status Solidi B **242**, R11 (2005).
[10] J. Des Cloizeaux, Phys. Rev. **129**, 554 (1963).
[11] O. V. Kovalev, Fiz. Tverd. Tela (S.-Peterburg) **17**, 1700 (1975).
[12] R. A. Evarestov and V. P. Smirnov, *Site Symmetry in Crystals: Theory and Applications*, Vol. 108, in Springer Series in Solid State Sciences, 2nd ed. (Springer, Berlin, 1997).
[13] O. V. Kovalev, *Representations of the Crystallographic Space Groups: Irreducible Representations, Induced Representations and Corepresentations*, 2nd ed. (Gordon and Breach, Philadelphia, 1993).
[14] H. Bacry, L. Michel, and J. Zak, Lect. Notes Phys. **313**, 291 (1988).
[15] R. A. Evarestov, A. V. Leko, and V. P. Smirnov, Phys. Status Solidi B **128**, 275 (1985).
[16] R. A. Evarestov and V. P. Smirnov, Phys. Status Solidi B **180**, 441 (1993).
[17] J. Des Cloizeaux, Phys. Rev. **135**, A698 (1964).
[18] W. Kohn, Phys. Rev. **115**, 809 (1959).
[19] V. P. Smirnov and D. E. Usvyat, Phys. Rev. B **59**, 9695 (1999).
[20] V. P. Smirnov and D. E. Usvyat, Phys. Rev. B **64**, 245108 (2001).
[21] E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13, p. 305.
[22] B. Sporkmann and H. Bross, Phys. Rev. B **49**, 10869 (1994).
[23] B. Sporkmann and H. Bross, J. Phys.: Condens. Matter **9**, 5593 (1997).

[24] D. Sanchez-Portal, E. Artacho, and J. M. Soler, Solid State Commun. **95**, 685 (1995).

[25] W. C. Lu, C. Z. Wang, T. L. Chan, K. Ruedenberg, and K. M. Ho, Phys. Rev. B **70**, 041101(R) (2004).

[26] C. Pisani *et al.*, J. Chem. Phys. **122**, 094113 (2005).

[27] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 270 (1985).

[28] R. Dovesi *et al.*, Crystal Atomic Functions Basis Sets, Theoretical Chemistry Group, University of Turin,-URL: http://www.crystal.unito.it/Basis_Sets/ptable.html; Updated 03-02-2004.

[29] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188, (1976).

[30] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[31] E. Mete, R. Shaltaf, and S. Ellialtioglu, Phys. Rev. B **68**, 035119 (2003).

[32] S. Casassa, C. M. Zicovich-Wilson, and C. Pisani, Theor. Chem. Acc. (to be published).