

Local characteristics of crystal electronic structure in the Hartree–Fock method

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The formalism developed in molecular theory for calculation of local electronic-structure characteristics in a nonorthogonal atomic basis is generalized to systems with translational symmetry. Expressions have been derived to describe the bond orders, covalency, and valence in a crystal for restricted and unrestricted Hartree–Fock methods. Nonempirical electronic-structure calculations and an analysis of chemical bonding in the TiO₂, Ti₂O₃, and TiO titanium oxide crystals have been performed. © 1999 American Institute of Physics. [S1063-7834(99)01108-9]

The band theory of solids is usually employed to consider characteristics of the electronic structure of a crystal which are associated with the potential periodicity and the corresponding electronic-state delocalization over the crystal, namely, the electronic energy bands, effective masses, etc. At the same time crystals, like molecules, are made up of atoms interacting with one another, which gives rise to electronic density localization along bonds (covalent crystals), around atomic nuclei (ionic crystals), or to the more complex and most widespread pattern of electronic density distribution.

In the recent decade, the Hartree–Fock (HF) method in the LCAO approximation, which had been already successfully employed for a long time in molecular theory, has gained wide acceptance in calculations of the electronic structure of crystals.¹ The HF method compares well in accuracy with other approaches while being, at the same time, the best starting approximation to take into account electronic correlations.² This method enables nonempirical calculations of both band and local characteristics of the electronic structure of a crystal and can be extended readily to cover systems with lower-order periodicity (polymers and crystal surfaces in the plate model).¹⁾

The density matrix obtained in the calculation permits one to derive the characteristics employed usually when describing chemical bonding in molecules or crystals (the electronic configuration of an atom, atomic charges Q_A , atomic-bond orders W_{AB} and covalency C_A , and the total and free atomic valences V_A).

In molecular theory, the local electronic-structure characteristics were defined for the orthogonalized atomic basis used in approximate calculations, with subsequent generalization to the case of a nonorthogonal basis employed in HF calculations.^{3,4}

The first attempts at a theoretical determination of local electronic-structure characteristics of crystals have been made only quite recently, and then only for the orthogonal basis^{5–7} used in semiempirical versions of the HF method.

Note that determination of local characteristics by traditional methods of band theory for solids, which make use, as a rule, of the plane-wave basis (OPW, APW, density func-

tional), involves additional approximations to calculate electronic-density-matrix elements in an atomic basis.⁸

The present work generalizes the existing methods of determination of local electronic-structure characteristics to crystalline systems, which are calculated in terms of the band model in the LCAO approximation using a nonorthogonal atomic basis. An analysis is made of the one-determinant approximation for a multi-electron wave function of a crystal within the restricted (RHF) and unrestricted (UHF) HF approaches.

Section 1 considers the electronic-density operator and matrix in the atomic-orbital basis and derives an expression which relates the density-matrix elements in the atomic basis and the Bloch basis taking into account the translational symmetry of a crystal.

Section 2 introduces definitions of local electronic-structure characteristics in a nonorthogonal atomic basis for different versions of the HF method.

Section 3 discusses the results of nonempirical HF calculations of the local electronic-structure characteristics of crystalline titanium oxides for various degrees of oxidation.

1. CRYSTAL ELECTRONIC-DENSITY OPERATOR AND MATRIX IN THE LCAO APPROXIMATION

Consider the most widespread version of the HF method, where, for the multi-electron wave function of a molecule or crystal, one takes a determinant constructed from single-electron wave functions, i.e., spin orbitals $\psi_i^\sigma(\mathbf{r})$, where $\sigma = \alpha, \beta$ are spin functions.

The single-electron functions are calculated by solving the HF equations²

$$\left(-\frac{1}{2}\Delta + V(\mathbf{r}) + \int \frac{\rho_{\mathbf{r}\mathbf{r}'}}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' \right) \psi_i^\sigma(\mathbf{r}) - \frac{1}{2} \int \frac{\rho_{\mathbf{r}\mathbf{r}'}}{|\mathbf{r}-\mathbf{r}'|} \psi_i^\sigma(\mathbf{r}') d^3\mathbf{r}' = E_i^\sigma \psi_i^\sigma(\mathbf{r}). \quad (1)$$

The two-electron part of the Fock operator depends on the density matrix, which for a one-determinant wave function can be expressed through spin orbitals

$$\rho_{\mathbf{r}\mathbf{r}'} = \rho_{\mathbf{r}\mathbf{r}'}^\alpha + \rho_{\mathbf{r}\mathbf{r}'}^\beta = \sum_{\sigma} \sum_i^{\text{occ}} \psi_i^\sigma(\mathbf{r}) \psi_i^{\sigma*}(\mathbf{r}'). \quad (2)$$

The summation in Eq. (2) is carried out over the spin orbitals corresponding to occupied single-electron states.

Closed-shell systems are analyzed using the RHF method, which requires coincidence of the spatial orbitals corresponding to spins α and β [$\psi_i^\alpha(\mathbf{r}) = \psi_i^\beta(\mathbf{r})$]. In the RHF method, the spinless density operator $\hat{\rho} = 2 \sum_i^{\text{occ}} |\psi_i\rangle\langle\psi_i|$ satisfies the conditions of duodempotency

$$\begin{aligned} \hat{\rho}^2 &= 2 \sum_i^{\text{occ}} |\psi_i\rangle\langle\psi_i| 2 \sum_j^{\text{occ}} |\psi_j\rangle\langle\psi_j| \\ &= 4 \sum_{ij}^{\text{occ}} |\psi_i\rangle\delta_{ij}\langle\psi_j| = 2\hat{\rho}. \end{aligned} \quad (3)$$

In the UHF method, the orbitals for spins α and β are considered independently, i.e., one takes into account spin polarization for electrons with opposite spins. The density operators $\hat{\rho}_\alpha$ and $\hat{\rho}_\beta$ for electrons with spins α and β and the total-density operator $\hat{\rho}$ satisfy the relations

$$\begin{aligned} \hat{\rho} &= \hat{\rho}_\alpha + \hat{\rho}_\beta; \quad \hat{\rho}_\alpha^2 = \hat{\rho}_\alpha; \\ \hat{\rho}_\beta^2 &= \hat{\rho}_\beta; \quad \hat{\rho}^2 = (\hat{\rho}_\alpha + \hat{\rho}_\beta)^2 = 2\hat{\rho} - \hat{\rho}_s^2, \end{aligned} \quad (4)$$

where $\hat{\rho}_s = \hat{\rho}_\alpha - \hat{\rho}_\beta$ is the spin-density operator.

The single-electron functions ψ_i^σ used in the LCAO approximation for molecules are presented in the form of a linear combination of basis atomic orbitals

$$\psi_i^\sigma = \sum_\lambda C_{i\lambda}^\sigma \varphi_\lambda. \quad (5)$$

By applying the density operator $\hat{\rho}_\sigma$ to the atomic orbital φ_μ one obtains

$$\begin{aligned} \hat{\rho}_\sigma |\varphi_\mu\rangle &= \sum_i^{\text{occ}} |\psi_i^\sigma\rangle\langle\psi_i^\sigma| \varphi_\mu\rangle = \sum_i^{\text{occ}} \sum_\nu \sum_\lambda C_{i\nu}^{\sigma*} C_{i\lambda}^\sigma S_{\lambda\mu} \varphi_\nu \\ &= \sum_\nu (P^\sigma S)_{\nu\mu} \varphi_\nu, \end{aligned} \quad (6)$$

where $S_{\mu\nu} = \int \varphi_\mu^*(\mathbf{r}) \varphi_\nu(\mathbf{r}) d\mathbf{r}$ are elements of the overlap matrix S , and $P_{\nu\lambda}^\sigma = \sum_i^{\text{occ}} C_{i\nu}^{\sigma*} C_{i\lambda}^\sigma$. Equation (6) means that the density operator $\hat{\rho}_\sigma$ in the LCAO basis is presented by the $(P^\sigma S)$ matrix.⁴

The operator relations (3) and (4) can be used to derive matrix relations

$$(PS)^2 = 2(PS), \quad (7)$$

$$(PS)^2 = 2(PS) - (P^s S)^2, \quad (8)$$

for the RHF and UHF methods, respectively, with $P = P^\alpha + P^\beta$ and $P^s = P^\alpha - P^\beta$.

The crystal orbitals $\Psi_i^\sigma(\mathbf{k}, \mathbf{r})$ for systems with translational symmetry are presented in the LCAO approximation in the form of a linear combination of Bloch sums of the $\Phi_i(\mathbf{k}, \mathbf{r})$ atomic functions

$$\Psi_i^\sigma(\mathbf{k}, \mathbf{r}) = \sum_\mu C_{i\mu}^\sigma(\mathbf{k}) \Phi_\mu(\mathbf{k}, \mathbf{r}), \quad (9)$$

$$\Phi_\mu(\mathbf{k}, \mathbf{r}) = \sum_n \exp(i\mathbf{k}\mathbf{R}_n) \varphi_\mu(\mathbf{r} - \mathbf{R}_A - \mathbf{R}_n). \quad (10)$$

The $\varphi_\mu^{A_n}(\mathbf{r}) = \varphi_\mu(\mathbf{r} - \mathbf{R}_A - \mathbf{R}_n)$ atomic orbital is centered on atom A in the unit cell with a translation vector \mathbf{R}_n . The density operator for the crystal can be written

$$\hat{\rho}_\sigma = \frac{2}{V_{BZ}} \int_{BZ} \sum_i^{\text{occ}} |\Psi_i^\sigma(\mathbf{k}, \mathbf{r})\rangle\langle\Psi_i^\sigma(\mathbf{k}, \mathbf{r})| d\mathbf{k}. \quad (11)$$

Integration in Eq. (11) is performed over the vectors \mathbf{k} in the first Brillouin zone.

Taking into account Eq. (9), we obtain

$$\hat{\rho}_\sigma \varphi_\mu^{A0}(\mathbf{r}) = \sum_{\lambda n} (P^\sigma S)_{\lambda\mu}^{Bn, A0} \varphi_\lambda^{Bn}(\mathbf{r}), \quad (12)$$

where

$$(P^\sigma S)_{\lambda\mu}^{Bn, A0} = \frac{1}{V_{BZ}} \int_{BZ} (P^\sigma(\mathbf{k}) S(\mathbf{k}))_{\lambda\mu} \exp(i\mathbf{k}\mathbf{R}_n) d\mathbf{k}. \quad (13)$$

The matrix elements $S_{\mu\nu}(\mathbf{k})$ and $P_{\mu\nu}^\sigma(\mathbf{k})$ in the basis of Bloch sums $\Phi_\mu(\mathbf{k}, \mathbf{r})$ are calculated by the expressions

$$\begin{aligned} S_{\mu\nu}(\mathbf{k}) &= \sum_n \exp(-i\mathbf{k}\mathbf{R}_n) \\ &\times \int \varphi_\mu^*(\mathbf{r} - \mathbf{R}_A) \varphi_\nu(\mathbf{r} - \mathbf{R}_B - \mathbf{R}_n) d\mathbf{r}, \end{aligned} \quad (14)$$

$$P_{\mu\nu}^\sigma(\mathbf{k}) = \sum_i^{\text{occ}} C_{i\mu}^{\sigma*}(\mathbf{k}) C_{i\nu}^\sigma(\mathbf{k}). \quad (15)$$

The expansion coefficients $C_{i\mu}^\sigma(\mathbf{k})$ are calculated by solving matrix equations of the CO LCAO method for the crystal

$$F^\sigma(\mathbf{k}) C^\sigma(\mathbf{k}) = S(\mathbf{k}) C^\sigma(\mathbf{k}) E^\sigma(\mathbf{k}), \quad (16)$$

where $F^\sigma(\mathbf{k})$ is the Fock operator matrix, and $E^\sigma(\mathbf{k})$ is the single-electron energy vector. Self-consistent solution of Eqs. (16) involves calculation of the $F^\sigma(\mathbf{k})$ and $S(\mathbf{k})$ matrices over a finite special-point set in the Brillouin zone, and integration over the zone required to calculate the elements of the $F^\sigma(\mathbf{k})$ matrix is replaced by summation over the point set.⁹

2. LOCAL CHARACTERISTICS OF THE CRYSTAL ELECTRONIC STRUCTURE

Because of the normalization of the multi-electron wave function, $\text{Sp}(\hat{\rho}) = N^{\text{tot}}$ (N^{tot} is the total number of electrons in the system, $\hat{\rho} = \hat{\rho}_\alpha + \hat{\rho}_\beta$). In view of the translational symmetry of the crystal, one can introduce density normalization per unit cell. Denoting by N the number of electrons per cell, we write in the matrix form

$$\begin{aligned} \text{Sp}(PS) &= \frac{1}{V_{BZ}} \int_{BZ} \sum_\mu (PS)_{\mu\mu}(\mathbf{k}) d\mathbf{k} \\ &= \sum_\mu (PS)_{\mu,\mu}^{A0,A0} = N. \end{aligned} \quad (17)$$

This relation permits one to use the diagonal elements of matrix (PS) to describe the electronic-density distribution among the atoms in the system. In accordance with the definition of Mulliken,¹⁰ the electronic population of an atom is a sum of the elements of matrix (PS) over the basis orbitals of this atom

$$\begin{aligned} N_{An} &= N_{A0} = \sum_{\mu \in A} (PS)_{\mu\mu}^{A0,A0} \\ &= \sum_{\mu \in A} \left(\sum_n \sum_{\lambda} P_{\mu\lambda}^{A0,Bn} S_{\lambda\mu}^{Bn,A0} \right) \\ &= \sum_{\mu \in A} P_{\mu\mu}^{A0,A0} + \sum_{B \neq A} R_{A0,B0} + \sum_{n \neq 0} \sum_B R_{A0,Bn}, \end{aligned} \quad (18)$$

where the quantities

$$R_{A0,Bn} = \sum_{\mu \in A} \sum_{\lambda \in B} P_{\mu\lambda}^{A0,Bn} S_{\lambda\mu}^{Bn,A0} \quad (19)$$

are called overlap populations. The charge on the atom is given by

$$Q_{A0} = Z_{A0} - N_{A0}, \quad (20)$$

where Z_{A0} is the nuclear charge for an all-electron calculation or the core charge if the pseudopotential approximation is used. The absolute value $|Q_{A0}|$ is called also the electrovalence of an atom.

Recalling relation (8), the expression for atomic populations within the unrestricted HF method can be recast in the form

$$\begin{aligned} N_{A0} &= \frac{1}{2} \sum_{\mu \in A} \left(((PS)^2)_{\mu\mu}^{A0,A0} + ((P^s S)^2)_{\mu\mu}^{A0,A0} \right) \\ &= \frac{1}{2} \sum_{\mu \in A} \left(\sum_n \sum_{\lambda} (PS)_{\mu\lambda}^{A0,Bn} (PS)_{\lambda\mu}^{Bn,A0} \right. \\ &\quad \left. + (P^s S)_{\mu\lambda}^{A0,Bn} (P^s S)_{\lambda\mu}^{Bn,A0} \right) \\ &= \frac{1}{2} \left(B_{A0,A0} + \sum_{B \neq A} B_{A0,B0} + \sum_{n \neq 0} \sum_B B_{A0,Bn} \right), \end{aligned} \quad (21)$$

where the quantities

$$\begin{aligned} B_{A0,Bn} &= \sum_{\mu \in A} \sum_{\lambda \in B} \left((PS)_{\mu\lambda}^{A0,Bn} (PS)_{\lambda\mu}^{Bn,A0} \right. \\ &\quad \left. + (P^s S)_{\mu\lambda}^{A0,Bn} (P^s S)_{\lambda\mu}^{Bn,A0} \right) \end{aligned} \quad (22)$$

are actually a generalization to crystals of the definition of bond order in a nonorthogonal atomic basis introduced⁴ earlier for molecules.

When using an orthonormalized set of basis functions, the overlap matrix S is an identity matrix, which simplifies considerably Eqs. (20)–(22). The method most widely used to obtain an orthonormalized basis is symmetric orthogonalization of atomic basis functions by Löwdin.¹¹ The density matrix \tilde{P} in the Löwdin basis can be obtained from the P matrix using the relation $\tilde{P} = S^{1/2} P S^{1/2}$. In this case, Eqs. (20)

and (22) are actually a definition of charge when analyzing populations by Löwdin¹¹ or of the bond order by Wiberg.¹²

It appears natural to define the covalency C_{A0} of atom A in a crystal as a sum of the orders of all bonds of this atom

$$C_{A0} = \sum_{B \neq A} B_{A0,B0} + \sum_{n \neq 0} \sum_B B_{A0,Bn}. \quad (23)$$

Using Eq. (21), one can readily express the covalency only through the elements of matrix (PS) in the basis of orbitals of atoms A :

$$\begin{aligned} C_{A0} &= 2N_A - B_{A0,A0} = 2 \sum_{\mu \in A0} (PS)_{\mu\mu}^{A0,A0} \\ &\quad - \sum_{\mu \in A0} \sum_{\mu' \in A0} (PS)_{\mu\mu'}^{A0,A0} (PS)_{\mu'\mu}^{A0,A0} \\ &\quad - \sum_{\mu \in A0} \sum_{\mu' \in A0} (P^s S)_{\mu\mu'}^{A0,A0} (P^s S)_{\mu'\mu}^{A0,A0}. \end{aligned} \quad (24)$$

The restricted HF method may be considered as a particular case of the unrestricted one, for which the spin density P^s in Eqs. (22) and (24) is zero.

An expression for the total valence of an atom taking into account both the ionic and covalent components of chemical bonding was proposed¹³

$$V_{A0} = \frac{1}{2} (C_{A0} + \sqrt{C_{A0}^2 + 4Q_{A0}^2}). \quad (25)$$

An analysis of a large number of compounds with ionic-covalent bonding showed that this relation permits obtaining reasonable values of the valence.⁵ The validity of the definition introduced was buttressed, however, by semiempirical calculations made on an orthogonalized atomic basis. This work is a first systematic investigation of the validity of this relation for nonempirical calculations on a nonorthogonal atomic basis made with the use of Eqs. (20) and (24) for atomic charges and covalencies.

3. ELECTRONIC STRUCTURE AND CHEMICAL BONDING IN CRYSTALLINE TITANIUM OXIDES

The above formalism for calculation of local electronic-structure characteristics of crystals was applied by us to a number of titanium oxides with the metal atom oxidized to various degrees. Although the quadrivalent state of the titanium atom is the most stable, the existence of oxygen com-

TABLE I. Crystal structure of titanium oxides: space group, number of formula units per cell Z , and nearest interatomic distances.

Structural characteristics	TiO(hex)	Ti ₂ O ₃	TiO ₂ (r)	TiO ₂ (a)	TiO ₂ (b)
Group	$P\bar{6}m2$	$R\bar{3}c$	$P4_2/mnm$	$I4_1/amd$	$Pbca$
Z	2	2	2	2	8
R_{Ti-Ti} , Å	3.03 3.24	2.58 2.99	3.00 3.55	3.10 3.76	2.95 3.06
R_{Ti-O} , Å	2.38 3.86	2.02 2.07	1.95 1.97	1.94 1.99	1.86 1.92

TABLE II. Local electronic-structure characteristics of titanium oxides in the Hartree–Fock method.

Crystal	Mulliken				Löwdin			
	P_d	Q_{Ti}	V_{Ti}	V_O	P_d	Q_{Ti}	V_{Ti}	V_O
TiO(hex)	2.38	1.62	2.14	2.04	2.70	1.27	2.30	2.15
Ti ₂ O ₃	1.82	2.26	3.61	2.05	2.50	1.43	3.98	2.30
TiO ₂ (r)	1.46	2.66	3.94	2.08	2.18	1.73	4.18	2.36
TiO ₂ (a)	1.47	2.65	3.98	2.08	2.19	1.72	4.23	2.36
TiO ₂ (b)	1.49	2.63	3.97	2.09	2.21	1.70	4.23	2.38

pounds of titanium in formal oxidation states of III and II, as well as of a series of nonstoichiometric compounds was established.

Table I presents the space-group symbol, the number of formula units in the cell, and the shortest Ti–Ti and Ti–O distances for TiO,¹⁴ Ti₂O₃,¹⁵ and TiO₂ in the rutile (*r*), anatase (*a*), and brookite (*b*) modifications.

For the TiO₂ and Ti₂O₃ crystals, band structure calculations were carried out earlier both in the Hartree–Fock^{16,17} and local exchange¹⁸ approximations. We are not aware of the existence of any electronic structure calculations for TiO. The available publications focus attention primarily on description of the band structure of titanium oxides and restrict the discussion of the nature of chemical bonding in these compounds to an analysis of atomic charges.

We have used in this work both the restricted and unrestricted HF treatments implemented in the CRYSTAL-95 program.¹⁹ The core states were described in the calculations by the pseudopotentials and on the atomic bases proposed in Ref. 16. A self-consistent electronic-density calculation was done over a grid of 216 BZ points. Self-consistent solutions obtained with different starting density matrices were considered for each compound by the scheme proposed in Ref. 20. Tables II and III list the values corresponding to insulator solutions with the lowest total crystal energy.

Table II presents local electronic-structure characteristics of the titanium oxides obtained by the RHF method, namely, the Ti *d*-orbital populations P_d and atom charges Q_{Ti} , as well as the atomic valences V_A . Also given are the

local characteristics calculated using Eqs. (20)–(22) in a nonorthogonal atomic basis and a basis orthogonalized according to Löwdin. As follows from a comparison of the results obtained from population analyses by Mulliken and Löwdin, the Löwdin analysis shows the chemical bonding in the crystals under study to be largely covalent, with the total valences of the titanium and oxygen atoms differing substantially from the expected stoichiometric values. It was shown²¹ that the calculations made using a valence atomic basis (without polarizing functions) in the Löwdin population analysis agree better with the expected values. The population analysis by Mulliken made in a nonorthogonal basis was found to be less sensitive to the inclusion of polarizing functions into the calculation.

As seen from Table III, the results obtained with the restricted and unrestricted HF methods for TiO₂ (with a formal titanium configuration d^0) do not differ practically from one another. The results of a calculation of the local properties of the TiO₂ modifications shows them to be only weakly sensitive to structural changes.

The largest difference between the calculations made in the RHF and UHF approximations was found for Ti₂O₃ with a formal titanium atom configuration d^1 , where one can expect substantial spin polarization effects.

As seen from Table III, the RHF method predicts a high bond order between titanium atoms, which, in its turn, results in an overestimated titanium valence. This pattern of chemical bonding is not borne out by experiments.

As follows from Table III, an increase in the degree of Ti oxidation from II to IV gives rise to an increase in the charge on the titanium atom, but the relative ionicity and the absolute value of the charge on the oxygen atom decrease. UHF calculations show that, in all the above insulator oxygen compounds of titanium, there is no strong covalent interaction among the metal atoms.

The valences of titanium and oxygen calculated with Eqs. (20)–(25) practically coincide with the expected stoichiometric values. This gives one grounds to hope that the above relations will prove to be applicable to an analysis of the valence states of atoms in nonstoichiometric titanium compounds.

Thus our study of titanium oxides shows that the scheme proposed here for the analysis of chemical bonding permits description of the local electronic-structure characteristics in accordance with the common chemical concepts. The above consideration suggests that, when used in describing the electronic structure of poorly studied compounds, the local characteristics of chemical bonding may be treated as addi-

TABLE III. Local properties of chemical bonding in titanium oxide crystals in the restricted and unrestricted HF methods: titanium *d*-orbital populations P_d , atomic charges Q_A , covalencies C_A , atomic valences V_A , and bond orders B_{AB} for nearest-neighbor atoms.

Local electronic-structure	TiO(hex)		Ti ₂ O ₃		TiO ₂ (r)
	RHF	UHF	RHF	UHF	RHF
P_d	2.38	2.34	1.82	1.77	1.46
Q_{Ti}	1.63	1.67	2.26	2.32	2.66
C_{Ti}	0.90	0.69	2.19	1.23	2.15
V_{Ti}	2.14	2.05	3.61	3.01	3.94
Q_O	-1.63	-1.67	-1.51	-1.55	-1.33
C_O	0.74	0.66	0.94	0.88	1.24
V_O	2.04	2.03	2.05	2.05	2.08
B_{Ti-Ti}	0.03	0.01	0.89	0.03	0.01
	0.00	0.00	0.00	0.01	0.01
B_{Ti-O}	0.11	0.10	0.20	0.19	0.36
	0.00	0.00	0.21	0.19	0.30

Note. For the TiO₂ crystal, the RHF and UHF results coincide.

tional quantities, whose analysis may provide an evaluation of the validity of the approach employed.

An appreciable role in transition-metal compounds is played by electron-correlation effects, which may be considered within the framework of multi-configurational methods employing the cluster model of the crystal. In this case, local characteristics can be calculated using the approach developed in Ref. 22.

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¹⁾In the literature dealing with the theory of solids, the LCAO approximation for crystal-field orbitals is sometimes erroneously identified with the tight-binding method, which is conventionally used as an interpolation scheme in calculations made with more rigorous methods.

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