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The linear muffin-tin orbitals/tight-binding/direct-screening method for the calculation of the electronic structure of crystals

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Abstract. A new version of the tight-binding representation of the linear muffin-tin orbitals method based on the direct-screening of the muffin-tin orbitals (LMTO-TB-DS) is presented. The equations for the screened basis wavefunctions, the screened structure matrix and the corresponding Hamiltonian are obtained. Test calculations of the chromium and $\text{YBa}_2\text{Cu}_3\text{O}_7$ band structures proved the validity and accuracy of the method.

1. Introduction

The tight binding representation of the linear muffin-tin orbitals method (LMTO-TB) has proved to be one of the best approximations for treating defects and surfaces in crystals. At the same time the method as was first formulated by Andersen and Jepsen [1] is not a closed one because it needs a previous calculation of the structure matrix with the traditional LMTO method. Such a calculation as well as the following calculation of the screened structure matrix becomes very complex and time-consuming for crystals with a complex unit cell, e.g. the crystals of high- T_c superconductors.

To avoid these difficulties, to minimize the calculation time and to make the LMTO-TB method self-contained, we were forced to formulate a version of the LMTO-TB method with direct screening of the wavefunctions (LMTO-TB-DS).

We construct the basis wavefunctions from linear combinations of the linearized muffin-tin orbitals, centred on groups of neighbouring atoms. The linear combinations are chosen in a special way to cancel themselves everywhere outside these groups of atoms. The basis wavefunctions are localized and therefore satisfy the tight-binding approximation.

The way of building the basis wavefunctions and the screened structure matrix is described in section 2 of this work. Section 3 is devoted to the construction of the Hamiltonian and its features.

In section 4 we give a description of the test calculations of the band structures of chromium and of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$. The application of the method to the electronic structure of semi-infinite crystals, which was the main purpose of the work, will be described elsewhere.

2. The screened basis functions and structure constants

In the traditional LMTO method the wavefunctions of the basis set look like [2]

$$\chi_{Ln}(r) = (S_n/2)^{-1/2} \begin{cases} i^l Y_L(\hat{r}_n) \Phi_{ln}^-(r_n) / \Phi_{ln}^-(S_n) & r_n \leq S_n \\ N_{Ln}(r_n) & r_n > S_n \end{cases} \quad (1)$$

where S_n is the n th muffin-tin (MT) sphere radius, Y_L is the spherical harmonic, $L = \{l, m\}$ is the combination of angular quantum numbers, $r_n = r - R_n$,

$$\Phi_{ln}^-(r) = \varphi_{vn}(r) + \omega_{vn}^- \dot{\varphi}_{vn}(r) \quad (2)$$

φ_{vn} is the solution of the radial Schrödinger equation inside the n th MT sphere for the energy $E = E_v$, $\dot{\varphi}_{vn}$ is its energy derivative, ω_{vn}^- is chosen to ensure continuous behaviour of the radial part of χ_{Ln} function and its first derivative on the sphere, which, as we see later, is equivalent to the matching of function

$$P_{Ln}^-(r) = i^l Y_L(\hat{r}) \Phi_{ln}^-(r) / \Phi_{ln}^-(S_n)$$

inside the sphere with the function

$$K_{Ln}(r) = i^l Y_L(\hat{r}) (r/S_n)^{-l-1}$$

outside of it.

Outside of its own MT sphere the K_{Ln} function may be represented as

$$K_{Ln}(r_n) = - \sum_{L'} S_{Ln;L'm} J_{L'}(r_m) / 2(2l' + 1) \quad m \neq n, r_m \leq S_m \quad (3)$$

$$J_{L'm}(r) = i^{l'} Y_{L'}(\hat{r}) (r/S_m)^{l'}$$

The function N_{Ln} from expression (1) is a generalization of the K_{Ln} function: it and its first derivative coincide with those of K_{Ln} function on the MT spheres but they differ inside of them. Such generalization is obtained by the decomposition of $N_{Ln}(r)$ inside any MT sphere:

$$N_{Ln}(r_n) = - \sum_{L'} S_{Ln;L'm} i^{l'} Y_{L'}(\hat{r}) \Phi_{L'm}^+(r_m) / 2(2l' + 1) \Phi_{L'm}^+(S_m) \quad m \neq n, r_m \leq S_m \quad (4)$$

where the structure constants $S_{Ln;L'm}$ are taken from expression (3). Here

$$\Phi_{lm}^+(r) = \varphi_{vm}(r) + \omega_{vm}^+ \dot{\varphi}_{vm}(r) \quad (5)$$

and ω^+ is chosen to ensure matching of the function $P_{Ln}^+(r) = i^l Y_L(\hat{r}) \Phi_{ln}^+(r) / \Phi_{ln}^+(S_n)$ with the function $J_{Lm}(r)$ on the MT sphere. Explicit expressions for the structure constant matrix elements were presented by Skriver [2].

The slow decrease of the functions (3) with r causes the slow decrease of the structure constants $S_{Ln;L'm}$ with $|R_m - R_n|$, which in turn, yields large values of the Hamiltonian matrix elements placed far from the main diagonal. To avoid this difficulty, which is significant for calculations of surfaces and defects, Andersen and Jepsen [1] have proposed to use some linear combinations of functions (1) as the basis wavefunctions to obtain a fast decrease of the structure matrix elements with radius. The possibility of such a representation is seen from a simple electrostatic analogy: the functions $K_{Ln}(r)$ behave like electric potentials of charges with multipolarity l and value $(S_n)^{l+1}$. So these

fields can be screened by multipoles with opposite charge placed at the neighbouring atoms. So, Andersen and Jepsen have defined the screened structure matrix as

$$T = S(I - \alpha S)^{-1} \tag{6}$$

where α coefficients are chosen to obtain the fastest decrease of T with radius.

The direct calculation of expression (6) is very difficult, because it needs previous calculations of the non-screened structure constants and inversion of infinite-range matrices with simultaneous fitting of the α parameters. Andersen and Jepsen [1] have proposed an interpolation scheme, which supposes that the non-diagonal T -matrix elements are independent of the lattice geometry and depend only on the relative distances between the atoms. This scheme works for cubic lattices with simple unit cells, but its reliability for complex crystals is not evident.

To rid the LMTO-TB method of these difficulties we shall use as functions of the new basis set linear combinations of the usual MTO (1):

$$\Psi_{L_n}(\mathbf{r}) = \chi_{L_n}(\mathbf{r}) + \sum_{L',m,\neq n} \Lambda_{L_n;L'm} \chi_{L'm}(\mathbf{r}) \quad \mathbf{R}_m \in \mathbb{R}_n \tag{7}$$

where \mathbb{R}_n is a group of atoms placed inside the sphere with centre in \mathbf{R}_n and radius R_s , and Λ coefficients are chosen to make the function Ψ_{L_r} equal to zero everywhere outside the radius of screening R_s . R_s is chosen to reach a compromise between the quality of the screening and the calculation expenditure. Usually it includes some dozens of atoms (from two to 10–15 coordination spheres).

For the calculation of the screening coefficients Λ , we shall construct the auxiliary function

$$\begin{aligned} \Psi_{L_n}^0(\mathbf{r}) &= \chi_{L_n}^0(\mathbf{r}) + \sum_{L',m,\neq n} \Lambda_{L_n;L'm} \chi_{L'm}^0(\mathbf{r}) \quad \mathbf{R}_m \in \mathbb{R}_n \\ \chi_{L_n}^0(\mathbf{r}) &= (S_n/2)^{-1/2} \begin{cases} P_{L_n}^-(r_n) & r_n \leq S_n \\ K_{L_n}(r_n) & r_n \geq S_n \end{cases} \end{aligned} \tag{8}$$

where K_{L_n} is substituted instead of N_{L_n} . Let us demand that the function $\Psi_{L_n}^0$ be zero together with its first and second derivatives in the centres of all the atoms outside the radius of screening:

$$\begin{aligned} K_{L_n}(\mathbf{R}_{kn}) + \sum_{L',m} K_{L'm}(\mathbf{R}_{km}) \Lambda_{L_n;L'm} &= 0 \\ \frac{\partial}{\partial x_i} K_{L_n}(\mathbf{R}_{kn}) + \sum_{L',m} \frac{\partial}{\partial x_i} K_{L'm}(\mathbf{R}_{km}) \Lambda_{L_n;L'm} &= 0 \\ \frac{\partial^2}{\partial x_i \partial x_j} K_{L_n}(\mathbf{R}_{kn}) + \sum_{L',m} \frac{\partial^2}{\partial x_i \partial x_j} K_{L'm}(\mathbf{R}_{km}) \Lambda_{L_n;L'm} &= 0 \end{aligned} \tag{9}$$

where x_i are orthogonal coordinates, $\mathbf{R}_{kn} = \mathbf{R}_k - \mathbf{R}_n$, $\mathbf{R}_k \notin \mathbb{R}_n$. The $K_{L_n}(\mathbf{r})$ functions satisfying the Laplace equation

$$\Delta K_{L_n}(\mathbf{r}) = 0 \tag{10}$$

so only five of six equations (9), containing the second derivatives, are independent.

According to the commonly used set of independent d functions d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_z^2 , we shall use in (9) five combinations of the second derivatives:

$$\partial^2/\partial x\partial y \quad \partial^2/\partial y\partial z \quad \partial^2/\partial x\partial z \quad \partial^2/\partial x^2 - \partial^2/\partial y^2 \quad \partial^2/\partial z^2.$$

From (3) and (8) we conclude that (9) leads to the condition that the new screened structure constants

$$T_{Ln;L'm} = S_{Ln;L'm} + \sum_{L^*k} \Lambda_{Ln;L^*k} S_{L^*k;L'm}$$

become zero everywhere outside the radius of screening:

$$T_{Ln;L'm} \equiv 0 \quad R_m \notin \mathbb{R}_n. \tag{11}$$

Actually, the function $K(r)$ in the centre of a MT sphere can be represented by a Taylor expansion. Taking into account (10) we obtain

$$K(r) = \left[K(R) + \frac{\partial}{\partial x} K(R)x + \dots + \frac{\partial^2}{\partial x \partial y} K(R)xy + \dots + \frac{1}{4} \left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} \right) K(R)(x^2 - y^2) + \frac{1}{4} \frac{\partial^2}{\partial z^2} K(R)(2z^2 - x^2 - y^2) \right] \tag{12}$$

$|r - R| \leq S \quad (x, y, z) = r - R.$

On the other hand, if we substitute explicit expressions for $J_{Ln}(r)$ into (3), we obtain

$$K_{Ln}(r) = \frac{-1}{2} \left[S_{Ln;sm} \left(\frac{1}{4\pi} \right)^{1/2} + S_{Ln;p_xm} \left(\frac{3}{4\pi} \right)^{1/2} \frac{x}{3S_m} + \dots + S_{Ln;d_{xy}m} \left(\frac{15}{4\pi} \right)^{1/2} \frac{xy}{5S_m^2} + \dots + S_{Ln;d_{x^2-y^2}m} \left(\frac{15}{16\pi} \right)^{1/2} \frac{x^2 - y^2}{5S_m^2} + S_{Ln;d_z^2m} \left(\frac{5}{16\pi} \right)^{1/2} \frac{2z^2 - x^2 - y^2}{5S_m^2} \right]. \tag{13}$$

Comparison of (12) and (13) shows that the non-screened structure constants are proportional to the values of functions $K(r)$ and their derivatives:

$$\begin{aligned} S_{Ln;sm} &= -2(4\pi)^{1/2} K_{Ln}(R_{nm}) \\ S_{Ln;p_xm} &= -6(4\pi/3)^{1/2} S_m \frac{\partial}{\partial x} K_{Ln}(R_{mn}) \\ &\vdots \\ S_{Ln;d_{xy}m} &= -10(4\pi/15)^{1/2} S_m^2 \frac{\partial^2}{\partial x \partial y} K_{Ln}(R_{mn}) \\ &\vdots \\ S_{Ln;d_{x^2-y^2}m} &= -10(16\pi/15)^{1/2} S_m^2 \frac{1}{4} \left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} \right) K_{Ln}(R_{mn}) \\ S_{Ln;d_z^2m} &= -10(16\pi/5)^{1/2} S_m^2 \frac{1}{4} \frac{\partial^2}{\partial z^2} K_{Ln}(R_{mn}). \end{aligned} \tag{14}$$

Therefore, if the relations (9) are satisfied, then (11) is also valid. So not only the

function (8)

$$\begin{aligned} \Psi_{L_n}^0(\mathbf{r}) &= K_{L_n}(\mathbf{r}_n) + \sum_{L',k} \Lambda_{L_n;L'k} K_{L'n}(\mathbf{r}_k) \\ &= \sum_{L'} \left(S_{L_n;L'm} + \sum_{L',k} \Lambda_{L_n;L'k} S_{L'k;L'm} \right) J_{L'm}(\mathbf{r}_m) \\ &= \sum_{L'} T_{L_n;L'm} J_{L'm}(\mathbf{r}_m) \equiv 0 \quad \mathbf{R}_m \notin \mathbb{R}_n \end{aligned} \tag{15}$$

but also the original functions (7) become zero outside the radius of screening

$$\begin{aligned} \Psi_{L_n}(\mathbf{r}) &= N_{L_n}(\mathbf{r}_n) + \sum_{L',k} \Lambda_{L_n;L'k} N_{L'k}(\mathbf{r}_k) \\ &= \sum_{L'} T_{L_n;L'm} P_{L'm}^+(\mathbf{r}_m) \equiv 0 \quad \mathbf{R}_m \notin \mathbb{R}_n. \end{aligned} \tag{16}$$

Since functions $K(R)$ depend only on the crystal structure, it follows from (9) that the coefficients Λ and the matrix T are dependent only on the structure and are independent of the crystal potential.

The full number of independent linear equations (9) or (11) is not limited because they can be formulated in the centre of any atom outside the radius of screening. In any case, their number may be more than the number of unknown coefficients Λ and the system (9) or (11) will have no exact solution. Such an 'overabundant' system can be solved approximately by the least-squares method (see for example [3]). According to the method, a set of equations with the number of equations larger than the number of unknowns

$$\sum a_{nj} x_j + b_n = 0 \quad n \leq N, \quad j \leq M < N$$

can be replaced approximately by the set of equations with equal numbers of equations and unknowns

$$\sum A_{ij} x_j + B_i = 0 \quad i, j \leq M$$

where $A_{ij} = \sum a_{ni} a_{nj}$, $B_i = \sum a_{ni} b_n$. Solving these equations, we shall find the screening coefficients Λ and the new basis wavefunctions. However, it is useful to include in (9) a number of additional equations, connected with an electrostatic analogy. To obtain the fast decrease (faster than $1/r^3$) of the basis wavefunctions at large radii, it is necessary to demand the cancelling of the total 'monopole', 'dipole' and 'quadrupole' moments of the groups of atoms taking part in the screening. These conditions look like

$$\begin{aligned} S_n \delta_{L,s} + \sum_m S_m \Lambda_{L_n;sm} &= 0 \quad (\text{monopole moment}) \\ S_n^2 \sqrt{3} \delta_{L,p_x} + \sum_m (X_{mn} S_m \Lambda_{L_n;sm} + S_m^2 \sqrt{3} \Lambda_{L_n;p_x m}) &= 0 \quad (\text{dipole moments}) \\ S_n^3 \sqrt{15} \delta_{L,d_{xy}^+} \sum_m (X_{mn} Y_{mn} S_m \Lambda_{L_n;sm} + Y_{mn} S_m^2 \sqrt{3} \Lambda_{L_n;p_x m} \\ &+ X_{mn} S_m^2 \sqrt{3} \Lambda_{L_n;p_y m} + S_m^3 \sqrt{15} \Lambda_{L_n;d_{xy}^-}) = 0 \quad (\text{quadrupole moments}) \end{aligned} \tag{17}$$

$(X_{mn}, Y_{mn}, Z_{mn}) = \mathbf{R}_{mn}$.

When the screening coefficients Λ and the screened structure matrix T are determined, we can represent the decomposition of functions (7) centred at \mathbf{R}_n , inside any other MT sphere, as

$$\Psi_{L_n}(\mathbf{r}) = (S_n/2)^{-1/2} \sum_{L'} \Lambda_{L_n;L'm} P_{L'm}^-(\mathbf{r}_m) + T_{L_n;L'm} P_{L'm}^+(\mathbf{r}_m) \quad r_m \leq S_m. \tag{18}$$

This decomposition is also valid at $m = n$, if we define $\Lambda_{Ln;L'n} = \delta_{LL'}$. Outside the radius of screening ($R_m \notin \mathbb{R}_n$) $T_{Ln;L'm} = 0$ according to (11), $\Lambda_{Ln;L'm} = 0$ according to its definition (7), so $\Psi_{Ln}(R_m) = 0$. Therefore, the functions (7) preserve all the advantages of the linearized muffin-tin orbitals, as they were described by Skriver [2], and they are also localized in space. They satisfy the tight-binding approximation and are available for inhomogeneous crystal calculations.

3. The screened Hamiltonian and its hermiticity

The Hamiltonian matrix elements in the basis of functions (7) can be easily expressed through the matrix elements of the traditional LMTO Hamiltonian and the screened structure constants. Taking into account (18) we obtain

$$\begin{aligned} H_{L'm;Ln} &= \langle \Psi_{L'm} | H - E_\nu | \Psi_{Ln} \rangle \\ &= \sum_{L',k} (\Lambda_{L'm;L'k}^* \Lambda_{Ln;L'k} \langle P_{L'k}^- | H - E_\nu | P_{L'k}^- \rangle \\ &\quad + \Lambda_{L'm;L'k}^* T_{Ln;L'k} \langle P_{L'k}^- | H - E_\nu | P_{L'k}^+ \rangle \\ &\quad + T_{L'm;L'k}^* \Lambda_{Ln;L'k} \langle P_{L'k}^+ | H - E_\nu | P_{L'k}^- \rangle \\ &\quad + T_{L'm;L'k}^* T_{Ln;L'k} \langle P_{L'k}^+ | H - E_\nu | P_{L'k}^+ \rangle) \end{aligned} \quad (19)$$

where the sum is taken over all the MT spheres of the crystal. The matrix elements on the right-hand side of (19) are the matrix elements of the non-screened LMTO Hamiltonian, and explicit expressions for them are presented in [2]. The overlap matrix elements are obtained in this way. They differ from (19) only in the substitution of the unit operator for $(H - E_\nu)$.

When we go from the node representation, which has been used up till now, to the Bloch one, it is sufficient to build the Bloch matrices Λ and T ,

$$\begin{aligned} \Lambda_{Ln;L'm}(k) &= \sum_a \exp(-ik \cdot a) \Lambda_{Ln;L'm} \\ T_{Ln;L'm}(k) &= \sum_a \exp(-ik \cdot a) T_{Ln;L'm} \end{aligned} \quad (20)$$

and to substitute them in (18) and (19). Here n and m belong to the same unit cell. a is a translation vector. We may restrict the sum in (20) by the condition $R_{m'} = R + a \in \mathbb{R}_n$, since $\Lambda_{nm'}$ and $T_{nm'} = 0$ when $|R_n - R_{m'}|$ is greater than the radius of screening of the site n due to the definition.

The $\Lambda(k)$ and $T(k)$ matrices are not Hermitian because the screening coefficients $\Lambda_{Ln;L'm}$ are calculated independently for each L, n and they are not connected with the coefficients $\Lambda_{L'm;Ln}$. Nevertheless, the Λ and T matrices are connected with a Hermitian non-screened structure matrix S . If we define $\Lambda_{Ln;L'n} = \delta_{LL'}$, the definition of matrix T will be like the following:

$$T_{Ln;L'm} = \sum_{\substack{L',k \\ R_k \in \mathbb{R}_n}} \Lambda_{Ln;L'k} S_{L'k;L'm} \quad R_m \notin \mathbb{R}_n. \quad (21)$$

If we substitute this definition into (20) we obtain

$$T_{Ln;L'm}(k) = \sum_{\substack{a \\ R_{m'} = R_m + a \in \mathbb{R}_n}} \exp(-ik \cdot a) \sum_{\substack{L',j' \\ R_{j'} \in \mathbb{R}_n}} \Lambda_{Ln;L'j'} S_{L'j';L'm}. \quad (22a)$$

Now let us represent $R_{j'} = R_j + a'$, where R_j lies in the same unit cell as R_n, R_m , and a' is

a translation vector. Because of the translation symmetry, $S_{L^j;L^m} \equiv S_{L^j;L^m}$, where $R_m = R_m - a' = R_m + a''$ and $a'' = a - a'$. Then

$$\begin{aligned}
 T_{Ln;L^m}(k) &= \sum_{R_m \in \mathbb{R}_n} \exp(-ik \cdot a) \sum_{\substack{L^j, a' \\ R_j \in \mathbb{R}_n}} \Lambda_{Ln;L^j} S_{L^j;L^m} \\
 &= \sum_{L^j} \sum_{a'} \exp(-ik \cdot a') \Lambda_{Ln;L^j} \sum_a \exp[-ik \cdot (a - a')] S_{L^j;L^m} \\
 &= \sum_{L^j} \sum_{\substack{a' \\ R_j \in \mathbb{R}_n}} \exp(-ik \cdot a') \Lambda_{Ln;L^j} \sum_{\substack{a'' \\ R_m + a' \in \mathbb{R}_n}} \exp(-ik \cdot a'') S_{L^j;L^m}. \tag{22b}
 \end{aligned}$$

Comparing this expression with that for the product of the Bloch matrices Λ and S ,

$$\sum_{L^j} \Lambda_{Ln;L^j}(k) S_{L^j;L^m}(k) = \sum_{L^j} \sum_{\substack{a' \\ R_j \in \mathbb{R}_n}} \exp(-ik \cdot a') \Lambda_{Ln;L^j} \sum_{a''} \exp(-ik \cdot a'') S_{L^j;L^m} \tag{23}$$

we can see that they differ only in the area of the sum over a'' (in (23) it is performed over all the lattice). The relation (11) permits us to spread the sum over a, a'' in (20) and (22) to the entire crystal lattice, and thus the expressions (22) and (23) coincide.

The obtained equality

$$T(k) = \Lambda(k)S(k) \tag{24}$$

can serve as a criterion of the accuracy of the screening. If the basis wavefunctions (7) do not cancel exactly outside the radius of screening, the relation (21) will be valid at $R_m \notin \mathbb{R}_n$ as well as (24).

If the screening is exact, we can rewrite (18) and (19) as

$$\begin{aligned}
 \Psi_{Ln}(r) &= \Lambda_{Ln;L^m} [P_{L^m}^-(r_m) + S_{L^m;L^j} P_{L^j}^+(r_j)] = \Lambda_{Ln;L^m} \chi_{L^m}(r) \\
 H_{L^m;Ln} &= \Lambda_{L^m;L^j}^* H_{L^j;L^m}^0 \Lambda_{Ln;L^m}
 \end{aligned} \tag{25a}$$

and in the Bloch representation

$$\begin{aligned}
 \Psi_{Ln}(r, k) &= \Lambda_{Ln;L^m}(k) [P_{L^m}^-(r_m) + S_{L^m;L^j}(k) P_{L^j}^+(r_j)] = \Lambda_{Ln;L^m}(k) \chi_{L^m}(r) \\
 H_{L^m;Ln}(k) &= \Lambda_{L^m;L^j}^*(k) H_{L^j;L^m}^0(k) \Lambda_{Ln;L^m}(k)
 \end{aligned} \tag{25b}$$

where $H_{L^j;L^m}^0 = \langle \chi_{L^j} | H - E_\nu | \chi_{L^m} \rangle$ is the non-screened LMTO Hamiltonian. This Hamiltonian is Hermitian by definition, but the screened Hamiltonian (19) would be Hermitian only if the relations (25) are valid, so the hermiticity of the constructed Hamiltonian may also be a criterion of the screening accuracy and the reliability of the method.

We have shown that the LMTO-TB-DS method can be reduced to the linear transformation of the basis set of the linearized muffin-tin orbitals and to the corresponding transformation of the LMTO Hamiltonian with the help of the specially determined matrix Λ . Matrix Λ depends only on the crystal structure and is independent of the crystal potential. The main purpose of the method was to construct the localized wavefunctions and the short-range Hamiltonian that are necessary for inhomogeneous crystal calculations. At the same time we have also reduced the calculation time, since the main part of the calculation is the node representation calculation (constructing of equations (9) for the Λ coefficients, their solution and the T matrix construction (21)). The Bloch

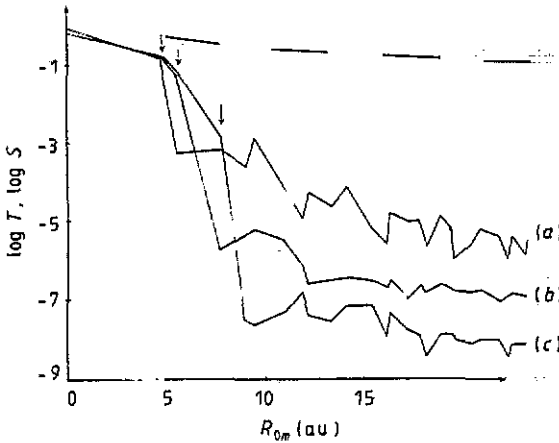


Figure 1. Screening in the chromium crystal. The screened structure constants $T_{s0,sm}$ (full lines) and non-screened structure constants $S_{s0,sm}$ (broken line) as functions of the distance $|R_{0m}|$: (a) one, (b) two and (c) three coordination spheres take part in the screening. The corresponding radii of screening are marked by the arrows.

matrices $\Lambda(k)$, $T(k)$ and the Hamiltonian are easily built in every point of k -space because the sum over only a few dozen atoms is necessary. This is especially useful for precise calculations with a large number of k -points in the Brillouin zone. In the traditional LMTO method, at the same time, the Bloch structure constants $S(k)$ are calculated separately in any point of the Brillouin zone, and this calculation needs the sum over a large number of points in both r - and k -space, especially for complex crystal structures.

4. The test calculations and accuracy

To test the accuracy and reliability of the method, the band structure of chromium (BCC lattice) was calculated. To build the Hamiltonian we have used the self-consistent potential parameters [2]. The calculation was provided for several radii of screening R_s , so that one, two, three and four coordination spheres (8, 14, 26 and 50 atoms respectively) took part in the screening. The set of equations (11) and (17), which were written down for approximately 500 sites, have been solved.

From the dependence of the screened structure constants T on the radius (figures 1 and 2) we can see that the atoms of a single coordination sphere do not provide effective screening. Indeed, although the T_{ss} constants decrease significantly, the T_{ds} , for example, remain of the same order of magnitude as the non-screened structure constants (figure 2). To reach an effective (3–7 orders of magnitude) suppression of the basis wavefunctions and the screened structure constants outside the radius of screening, we need two or more coordination spheres. The T -matrix elements remain small in the points that were not included in equations (9) and for which the screening was not demanded directly. So the described approach to the construction of the localized basis wavefunctions proves itself to be reliable.

The drastic decrease of the basis wavefunctions is not sufficient to ensure the accuracy of the calculation. Owing to this we used two quantitative criteria of accuracy.

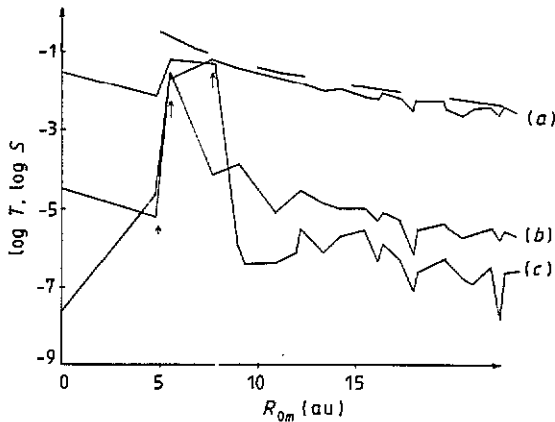


Figure 2. Screening in the chromium crystal. The screened structure constants $T_{d_2^2;sm}$ and non-screened structure constants $S_{d_2^2;sm}$. All the notations are as in figure 1.

Table 1. Some results of chromium band-structure calculation (in Ryd)^a.

Spheres	Γ		Z			
	E_{min}	E_{max}	E_{min}	E_{max}	$H_{c,max}$	$H_{a,max}$
One	0.13698 (0.21377)	3.75614 (3.73809)	0.58087 (0.50162)	3.15500 (3.20626)	51.80 (53.25)	2.7×10^{-1} (3.2×10^{-2})
Two	0.21379 (0.21379)	3.74018 (3.73798)	0.50070 (0.50038)	3.20873 (3.20968)	81.53 (81.35)	1.6×10^{-2} (2.4×10^{-4})
Three	0.21379 (0.21379)	3.73910 (3.73911)	0.50030 (0.50028)	3.21102 (3.21087)	76.36 (76.25)	3.6×10^{-3} (4.7×10^{-6})
Four	0.21379 (0.21379)	3.73796 (3.73798)	0.50038 (0.50038)	3.20983 (3.20968)	98.47 (98.48)	1.7×10^{-4} (3.7×10^{-6})
LMTO ^b	0.21382	3.73901	0.50030	3.21175		

^a The second rows (in parentheses) show the calculation with correction of the non-screened 'tails' of the basis wavefunctions.

^b The standard LMTO calculation (see [2]).

First, we controlled the Hamiltonian hermiticity. The Hamiltonian was represented as $H = H_c + H_a$, where H_c was Hermitian and H_a anti-Hermitian ($H_a^+ = -H_a$). The calculation was thought to be an exact one when the anti-Hermitian part of the Hamiltonian was negligible.

Secondly, as pointed out above, since (11) can be satisfied only approximately, we have calculated for each matrix Λ the real values of matrix elements of T outside the radius of screening at about 400 lattice sites. Then these constants were taken into account in the Bloch matrix $T(k)$ and the Hamiltonian to introduce the corrections caused by the 'tails' of the functions (7), remaining after screening. The Hamiltonian with this correction changes insignificantly but its anti-Hermitian part reduces itself

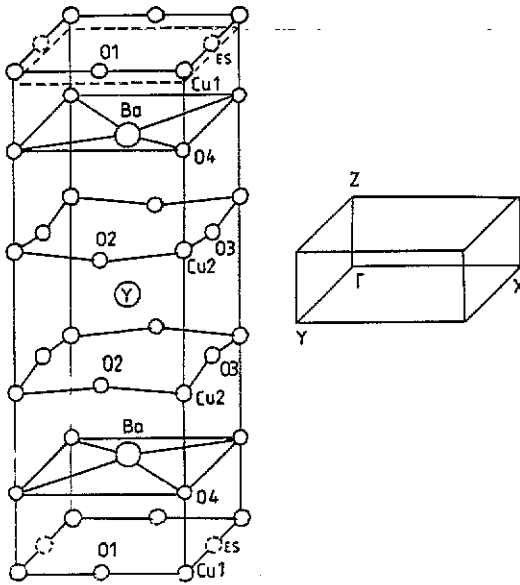


Figure 3. The unit cell and the Brillouin zone of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ crystal. es are empty muffin-tin spheres.

strongly. The calculation was considered to be reliable when such a correction did not affect the eigenvalues of the Hamiltonian.

In table 1 are presented the minimum and maximum eigenvalues in Γ and Z points of the Brillouin zone, the maximum Hermitian and anti-Hermitian Hamiltonian matrix elements in the Z point. We can see that the accuracy of screening increases with the number of atoms taking part in the screening (the anti-Hermitian part of the Hamiltonian without correction decreases, and the influence of the correction also reduces). When more than three coordination spheres take part in the screening, the following change of the eigenvalues is negligible and the resulting discrepancy of our method with the usual LMTO method is about 0.02%. The eigenvectors behave themselves with the improvement of the screening just as the eigenvalues, and the final partial weights of the s, p and d states, which depend on the eigenvectors, differ from the LMTO results also by 0.02–0.05%.

To calculate the band structure of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$, the screened basis wavefunctions were constructed, as described in section 2. The non-screened basis set contained the s, p and d functions for the Y, Ba and Cu atoms, s and p functions for the O atoms and s functions for the empty MT spheres, placed at the oxygen vacancies (figure 3). The different radii of screening were used for different atoms to ensure the best screening and, if possible, to minimize the calculation time. So each atom was screened by 40–60 neighbours. The sets of equations for each atom of the unit cell were constructed as for chromium.

The behaviour of the screened structure constants (figure 4) demonstrates the screening efficiency. The screened wavefunctions and structure constants are suppressed by 3–7 orders of magnitude outside the radius of screening. The obtained screening was used in the self-consistent band-structure calculation for the $\text{YBa}_2\text{Cu}_3\text{O}_7$ crystal. The band structure was calculated in 27 points of the Brillouin zone.

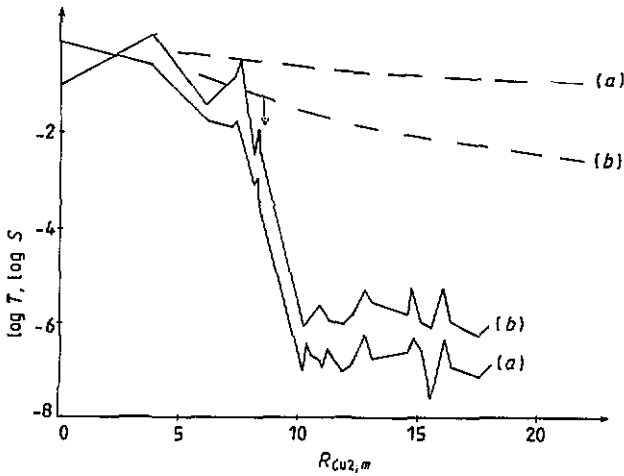


Figure 4. Screening in the $\text{Ba}_2\text{Cu}_3\text{O}_7$ crystal. The screened structure constants $T_{L\text{Cu}_2:L'm}$ as the functions of the distance $|R_{\text{Cu}_2,m}|$. The radius of screening is marked by the arrow. (a) $L = s, L' = s$; (b) $L = d_2^2, L' = s$.

Table 2. Some results of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ band-structure calculations (in Ryd).

		LMTO-TB-DS	LMTO-TB-DS ^a	LMTO ^b
Γ	E_1	-1.6306	-0.7388	-0.7474
	E_{37}	-0.0193	0.0285	0.0286
	E_{73}	0.8799	0.9009	0.8767
	$H_{e,\text{max}}$	245.0	245.0	
	$H_{a,\text{max}}$	1.0×10^{-1}	1.0×10^{-3}	
X	E_1	-0.6960	-0.6960	-0.7048
	E_{37}	0.0262	0.0261	0.0215
	E_{73}	0.7232	0.7234	0.7262
	$H_{e,\text{max}}$	886.9	887.0	
	$H_{a,\text{max}}$	0.3×10^{-1}	0.7×10^{-3}	
Y	E_1	-0.6988	-0.6988	-0.7066
	E_{37}	0.0199	0.0200	0.0124
	E_{73}	0.7320	0.7321	0.7275
	$H_{e,\text{max}}$	401.8	401.9	
	$H_{a,\text{max}}$	0.5×10^{-1}	0.7×10^{-3}	
Z	E_1	-0.7370	-0.7370	-0.7465
	E_{37}	0.0225	0.0224	0.0161
	E_{73}	0.8894	0.8861	0.8901
	$H_{e,\text{max}}$	245.0	245.0	
	$H_{a,\text{max}}$	1.0×10^{-1}	0.8×10^{-3}	

^a The calculation with correction of the non-screened 'tails' of the basis wavefunctions.

^b The standard LMTO calculation (see [2]).

Some results of this calculation, which demonstrate the calculation accuracy, are presented in table 2. Three eigenvalues (E_1 , E_{37} and E_{73}) are compared with the standard LMTO method in Γ , X, Y and Z points (figure 3) of the Brillouin zone. As for chromium, we have also made an additional calculation with the non-screened 'tails' correction. Near the Γ point this correction changes the eigenvalues significantly, but in the rest of the Brillouin zone it is negligible. In any case, the results with correction show good agreement with the results of the standard LMTO method. So all the self-consistent calculations were done with this correction. The eigenvalue discrepancies do not exceed 0.01–0.02 Ryd (2–3%) and only for the 6–8 highest bands (from 83) do they reach 0.05–0.15 Ryd.

5. Conclusions

We can conclude that the LMTO-TB-DS method demonstrates its reliability for crystal electronic structure calculations. The direct screening procedure ensures efficient screening of the basis wavefunctions and structure constant matrix. To estimate the reliability of the calculation, numerical criteria for screening accuracy can be applied.

The results of test calculations of chromium and $\text{YBa}_2\text{Cu}_3\text{O}_7$ band structures show that for simple crystal lattices the LMTO-TB-DS method causes no additional uncertainties in comparison with the usual LMTO method, and for complex crystal structures it keeps a satisfactory accuracy.

Acknowledgment

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References

- [1] Anderson O K and Jepsen O 1984 *Phys. Rev. Lett.* **53** 2571
- [2] Skriver HL 1984 *The LMTO Method, Muffin-Tin Orbitals and Electronic Structure* (New York: Springer)
- [3] Wilkinson J H and Reinsch C 1970 *Handbook for Automatic Computation Linear Algebra* (Berlin: Springer)