PHYSICAL REVIEW B VOLUME 46, NUMBER 24 15 DECEMBER 1992-II

Calculation of Wannier functions for the *d-s* band of Cu by a modified variational method

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(Received 7 July 1992)

A modified variational method is used to calculate the Wannier functions for the *d-s* band of Cu. Energies at high-symmetry points in the Brillouin zone and the density of states calculated with the use of Wannier functions are compared with the exact values. The effect of the number of nearest-neighbor shells is taken into account, and other approximations introduced into these calculations are discussed.

I. INTRODUCTION

Direct calculations of Wannier functions based on the variational principle satisfied by these functions have been performed only for a very limited number of three-dimensional crystals.[1-10] The Wannier functions for periodic systems can be, in principle, obtained by the Fourier transformation of Bloch functions. However, the choice of an arbitrary phase in Bloch functions[11,12] and the fact that the analytical dependence of Block functions on the **k** vector is not known make the transformation difficult. On the other hand, direct calculations of Wannier functions for periodic systems allow one to verify approximations that are frequently made in approximate considerations of the band structures of solids; furthermore, such calculations are relatively easy to generalize for a crystal with the surface and a crystal containing an impurity.[13-18]

The present calculations for the copper *d-s* band are performed by the modified variational method previously used for the crystal with the Mathieu potential[18,19] and for the *d* band of Ni and Cu.[9,10] The modification of the variational method suggested by Kohn [20] consists in a very accurate calculation of the Wannier function in the region surrounding the lattice site on which the function is localized. In this region the trial functions taken to construct the Wannier functions are arbitrary variational functions defined by differential equations derived from the expression for the total energy.

The crystal potential used in the present paper is not calculated self-consistently. The potential taken from the work of Moruzzi, Janak, and Williams[21] is used and both band energies and the density of states (DOS) can be directly compared with the results given in Ref. 21. The use of this potential[21] makes it possible to examine the effects of other approximations, unrelated to the construction of the potential, on band energies and DOS obtained with the aid of Wannier functions.

This paper is organized in the following way. The method of calculation is described in Sec. II. In that section emphasis is placed on the changes and improvements introduced to the method in comparison with the calculation performed for the *d* band in Ref. 9 (hereafter referred to as paper I). Section III provides the results of calculations and their discussion. Section IV contains conclusions.

II. METHOD OF CALCULATIONS

A. The basic equations

We seek for the set of Wannier functions $a_{m\mathrm{L}}$ which minimizes the energy functional for the composite *d-s* band,

$$E(a_{1\mathrm{L}_0},\ldots,a_{6\mathrm{L}_0})=\sum_{m=1}^{6}(a_{m\mathrm{L}_0},\hat{H}a_{m\mathrm{L}_0})\ , \tag{2.1}$$

where $\hat{H}$ is the Hamiltonian of the system, $a_{m\mathrm{L}_0}(\mathbf{r})$, with $m=1,2,\ldots,5$, are Wannier functions localized on site $\mathrm{L}_0=(0,0,0,)$ for the *d* band and a_{6,L_0} is the Wannier function for the *s* band of the metal, and the symbol (,) denotes the integration over the whole space. The Wannier functions are in turn expressed in terms of trial functions,

$$a_{m\mathrm{L}_0}(\mathbf{r})=\sum_{m_1,\mathrm{L}_1}N_{m_1}^{-1/2}f_{m_1\mathrm{L}_1}(\mathbf{r})G^{-1/2}_{m_1\mathrm{L}_1,m\mathrm{L}_0}\ , \tag{2.2}$$

where $f_{m\mathrm{L}}(\mathbf{r})=f_m(\mathbf{r}-\mathbf{L})$ is the trial function of the correct symmetry localized on the lattice site **L** and $N_m^{-1/2}$ is a normalization factor. The matrix elements $G^{-1/2}_{m_1\mathrm{L}_1,m\mathrm{L}_0}$ are chosen so that Wannier functions form the orthogonal set. It turned out[22] that the orthogonalization procedure suggested by Löwdin[23] and used in paper I cannot be used in the case of a *d-s* band because overlap integrals for *s* trial functions are too large and the expansion of $G^{-1/2}$ suggested by Löwdin is out of the range of its convergence. The matrix elements $G^{-1/2}$ were therefore calculated directly from orthogonalization relations of Wannier functions (see Appendix A),

$$(a_{m_1\mathrm{L}_1},a_{m_2\mathrm{L}_2})=\delta_{m_1,m_2}\delta_{\mathrm{L}_1,\mathrm{L}_2}\ . \tag{2.3}$$

Now the energy functional can be expressed in terms of trial functions,

$$E(\{f_{m_i\mathrm{L}_i}\})=\sum_{\substack{m,m_1,m_2\\ \mathrm{L}_1,L_2}}N_{m_1}^{-1/2}N_{m_2}^{-1/2}G^{-1/2}_{m_2\mathrm{L}_2,m\mathrm{L}_0}\times H_{m_2\mathrm{L}_2,m_1\mathrm{L}_1}G^{-1/2}_{m_1\mathrm{L}_1,m\mathrm{L}_0}\ , \tag{2.4}$$

where

$$H_{m_1\mathrm{L}_1,m_2\mathrm{L}_2}=(f_{m_1\mathrm{L}_1}(\mathbf{r})\ ,\hat{H}f_{m_2\mathrm{L}_2}(\mathbf{r}))\ . \tag{2.5}$$

Since the matrix elements H and $G^{-1/2}$ (see Appendix A) are not independent, the total energy can be expressed in terms of the set of independent matrix elements[24,25] and Eq. (2.4) can be reduced to the following form:

$$E(\{f_{m_iL_i}\})=\sum_{m,i,j,k} C_{m\mathbf{L}_0,m\mathbf{L}_0}(i,j,k)G_i^{-1/2}N_j^{-1}H_jG_k^{-1/2} , \tag{2.6}$$

where $G_i^{-1/2}$ and H_j denote independent matrix elements of $G^{-1/2}$ and H, respectively, $N_j^{-1}=N_{n_j}^{-1/2}\ N_{m_j}^{-1/2}$, the summation is over all d and s Wannier states and over all independent matrix elements, and $C_{m\mathbf{L}_0,m\mathbf{L}_0}$ has the same meaning as in paper I and can be calculated only once for the set of orbitals and the lattice of a given symmetry. The set of independent matrix elements $G^{-1/2}$ and H consists of matrix elements listed for d orbitals in paper I and additional matrix elements between d and s, and between s states. The whole set of independent matrix elements is listed in Table I. Table I contains all independent matrix elements between d states and d and s states up to second-nearest neighbors and independent matrix elements between s states up to eighth-nearest neighbors (the notation of Slater and Koster[24] appropriate for Hamiltonian matrix elements can be easily deduced.)

Now we assume that

$$f_{m\mathbf{L}}(\mathbf{r})\equiv f_m(\mathbf{r}-\mathbf{L})=N_\eta^{-1/2}r_{\mathbf{L}}^{-1}R_{\eta\mathbf{L}}(r)Y_{m\mathbf{L}}(\vartheta,\phi) , \tag{2.7}$$

where $r_{\mathbf{L}}=|\mathbf{r}-\mathbf{L}|$, $R_{\eta\mathbf{L}}(r)=R_\eta(|\mathbf{r}-\mathbf{L}|)$, $\eta=1$ for $m\leq 5$ and 2 otherwise, and $Y_{m\mathbf{L}}$ are the cubic harmonics centered on the $\mathbf{L}$ lattice site ($Y_{m\mathbf{L}}$ for $m\leq 5$ have the same form as in paper I and $Y_{6\mathbf{L}}$ is equal to unity). Equation (2.7) means that we assume, as in paper I, that the variations in the function $f_{m\mathbf{L}}$ are confined to variations in the functions $R_{\eta\mathbf{L}}(r)$ and the function $R_{1\mathbf{L}}(r)$ is the radial function common to all trial functions of e_g and t_{2g} symmetry. We further assume that the functions $R_{\eta\mathbf{L}}(r)$ are arbitrary variational functions inside the muffin-tin sphere and simple analytical functions outside the sphere,

$$R_{\eta,\mathbf{L}}(\mathbf{r})=\begin{cases} R_{\eta\mathbf{L}}(r) , & r_{\mathbf{L}}\leq r_0 \\ R_{\eta\mathbf{L}}(\{\beta_i\};r) , & r_{\mathbf{L}}\geq r_0 , \end{cases} \tag{2.8}$$

where

$$R_{\eta\mathbf{L}}(\{\beta_i\};r)=\beta_{\eta,0}r_{\mathbf{L}}^{n_\eta}\exp(-\beta_{\eta,\mathbf{L}}r) , \tag{2.9}$$

$n_1=3$, $n_2=4$, and r_0 is the muffin-tin radius. Since the functions are to be admissible variational functions, the functions $R_{\eta\mathbf{L}}$ and their derivatives must be continuous functions at $r_{\mathbf{L}}=r_0$.

Following the method described in Ref. 19, the condition for the minimum of the functional (2.6) can be written in the form of the following set of equations:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{1}{2}\frac{l_\eta(1_\eta+1)}{r^2}+V(r)+\varepsilon_\eta\right]R_\eta(r)=X_\eta(r)+(\eta-1)\sum_{n=1}^{3}\lambda_{\eta,n}R_{ns}(r) , \quad \eta=2,l \tag{2.10}$$

$$\varepsilon_\eta=-a_\eta^{-1}N_\eta^{-1}\left\{\sum_{i,j,k}C_t(i,j,k)\left[G_i^{-1/2}N_j^{-1}\gamma_{\eta,j}H_jG_k^{-1/2}+N_j^{-1}H_j\sum_{n\neq 1,2,16}(\omega_{i,n}G_k^{-1/2}+G_i^{-1/2}\omega_{k,n})\gamma_{\eta,n}S_n\right]\right\} , \tag{2.11}$$

TABLE I. The independent matrix elements M_i of the operator $\hat{M}$ having the full symmetry of the lattice. The functions in the first column of the table are localized on the $\mathbf{L}_0=(0,0,0)$ lattice site, the functions in rows of the table are localized on the $\mathbf{L}$ lattice site.

$\mathbf{L}=(0,0,0)$	yz	zx	xy	x^2-y^2	$3z^2-r^2$	s
yz	M_1					
zx		M_1				
xy			M_1			
x^2-y^2				M_2		
$3z^2-r^2$					M_2	
s						M_{16}
$\mathbf{L}=(1,1,0)$	yz	zx	xy	x^2-y^2	$3z^2-r^2$	s
yz	M_3	M_8				
zx	M_8	M_3				
xy			M_4		M_7	M_{13}
x^2-y^2				M_5		
$3z^2-r^2$			M_7		M_6	M_{14}
s			M_{13}		M_{14}	M_{17}
$\mathbf{L}=(0,0,2)$	yz	zx	xy	x^2-y^2	$3z^2-r^2$	s
yz	M_9					
zx		M_9				
xy			M_{10}			
x^2-y^2				M_{11}		
$3z^2-r^2$					M_{12}	M_{15}
s					M_{15}	M_{18}
$\mathbf{L}=(1,1,2)$	s					
s	M_{19}					
$\mathbf{L}=(0,2,2)$	s					
s	M_{20}					
$\mathbf{L}=(0,1,3)$	s					
s	M_{21}					
$\mathbf{L}=(2,2,2)$	s					
s	M_{22}					
$\mathbf{L}=(1,2,3)$	s					
s	M_{23}					
$\mathbf{L}=(0,0,4)$	s					
s	M_{24}					

where

$$X_\eta(r)=-a_\eta^{-1}N_\eta^{-1}\left\{\sum_{\substack{i,j,k\\(j\neq 1,2,16)}} C_t(i,j,k)\left[G_i^{-1/2}N_j^{-1}\gamma_{\eta,j}G_k^{-1/2}\bar{H}_j(r)\right.\right.$$

$$\left.\left.+N_j^{-1}H_j\sum_{n\,(\neq 1,2,16)}(\omega_{i,n}G_k^{-1/2}+G_i^{-1/2}\omega_{k,n})\gamma_{\eta,n}\bar{S}_n(r)\right]\right\}\ , \tag{2.12}$$

$$C_t(i,j,k)=3C_{1\mathbf{L}_0,1\mathbf{L}_0}(i,j,k)+2C_{4\mathbf{L}_0,4\mathbf{L}_0}(i,j,k)+C_{6\mathbf{L}_0,6\mathbf{L}_0}(i,j,k)\ , \tag{2.13}$$

$$a_1=\sum_{i,k}[C_t(i,1,k)+C_t(i,2,k)]G_i^{-1/2}N_1^{-1}G_k^{-1/2}\ , \tag{2.14}$$

$$a_2=\sum_{i,k}C_t(i,16,k)G_i^{-1/2}N_{16}^{-1}G_k^{-1/2}\ , \tag{2.15}$$

$$\bar{H}_j(r)=\int d\Omega\, Y_{n_j}(r)\hat{H}f_{m_j}(r)\ , \tag{2.16}$$

$$\bar{S}_j(r)=\int d\Omega\, Y_{n_j}(r)f_{m_j}(r)\ , \tag{2.17}$$

$$S_n=N_{m_n}^{-1/2}N_{p_n}^{-1/2}(f_{m_n},f_{p_n})\ , \tag{2.18}$$

$$\gamma_{1,n}=\begin{cases}1\ , & n\leq 12\\ \frac{1}{2}\ , & 12<n<16\\ 0\ , & n\geq 16\ ,\end{cases} \tag{2.19}$$

$$\gamma_{2,n}=1-\gamma_{1,n}\ . \tag{2.20}$$

$l_1=2$, $l_2=0$, the integration over $d\Omega$ denotes the integration over the solid angle, and $R_{ns}(r)$ and $\lambda_{\eta,n}$ appearing in Eq. (2.10) denote the core states of s symmetry and the Lagrange multipliers ensuring the orthogonality of the conduction-band s state to the core states, respectively. While the d states are automatically orthogonal to the core states localized on the same lattice site because of the angular parts of the functions, the orthogonality of the conduction-band s state must be imposed as an additional constraint. The Lagrange multipliers can be calculated in the following way. The core states can be considered with a good approximation as the states orthogonal to the core states localized on adjacent lattice sites. They therefore satisfy the equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+V(r)+\varepsilon_{ns}\right]R_{ns}(r)=0\ , \tag{2.21}$$

with the continuity equations analogical to these satisfied by $R_{\eta L}$. By multiplying Eq. (2.21) by $R_2(r)$ and Eq. (2.10) by $R_{ns}(r)$, integrating over the muffin-tin sphere and adding the integrals of analytical parts of the functions over remaining parts of the space, we get

$$(\varepsilon_2-\varepsilon_{ns})(R_2,R_{ns})=\tilde{H}_{ns,2}-\tilde{H}_{2,ns}+\tilde{X}_2+\lambda_{ns}\tilde{S}_{ns}\ , \tag{2.22}$$

where

$$\tilde{H}_{i,j}=\int_{r_0}^{\infty}dr\, R_i(r)\left[-\frac{1}{2}\frac{d^2}{dr^2}+V(r)+\varepsilon_j\right]R_j(r)\ , \tag{2.23}$$

$$\tilde{X}_{2,ns}=\int_0^{r_0}dr\, X_2(r)R_{ns}(r)\ , \tag{2.24}$$

$$\tilde{S}_{ns}=\int_0^{r_0}dr\, R_{ns}^2(r)\ , \tag{2.25}$$

and we assumed that

$$\int_0^{r_0}dr\, R_{n_1s}(r)R_{n_2s}(r)\cong(R_{n_1s},R_{n_2s})=0\ ,\quad n_1\neq n_2\ . \tag{2.26}$$

Since $\varepsilon_2\neq\varepsilon_{ns}$, it is sufficient that

$$\lambda_{ns}=-\tilde{S}_{ns}^{-1}(\tilde{H}_{ns,2}-\tilde{H}_{2,ns}+\tilde{X}_{2,ns}) \tag{2.27}$$

to ensure the orthogonality of R_2 to core states localized on the same lattice site.

Equations (2.10) and (2.11), together with the continuity conditions at r_0, fully define the trial functions both inside and outside the muffin-tin sphere. Similarly as in paper I, the set of the equations was solved in two-center approximation. However, three-center contributions were included into the final calculations of matrix elements of the Hamiltonian.

Three-center contributions to the matrix elements of the Hamiltonian come from the integrals of the form

$$\int f_{m_1\mathbf{L}_1}(\mathbf{r})V(\mathbf{r}-\mathbf{L}_2)f_{m_2\mathbf{L}_3}(\mathbf{r})d\tau \tag{2.28}$$

for $\mathbf{L}_2$ not equal to either $\mathbf{L}_1$ or $\mathbf{L}_3$. The three-center corrections also result from the nonorthogonality of the trial functions both of d and s symmetry to core states localized on adjacent lattice sites. The angular dependence of the trial functions in the case of *d* orbitals and the Lagrange multipliers introduced into Eq. (2.10) ensure the orthogonality of the trial functions to the core states localized on the same lattice site but the functions must be orthogonalized to the core states on other lattice sites. The method of calculations of three-center contributions is described in Appendix B. It should be mentioned that nonorthogonality effects reduce three-center corrections connected with integrals (2.28) and are particularly large in the case of the extended conduction-band *s* states. The effect is similar to the replacement of the bare potentials $V(\mathbf{r}-\mathbf{L})$ by pseudopotentials.

B. Numerical details

As in paper I the basic equations (2.10) and (2.11) for calculating the trial functions have been solved by an iterative method. However, the iterative procedure was slightly modified. First, Eqs. (2.10) were solved by replacing in the initial iteration the inhomogeneous parts of the equations by zero and assuming reasonable values of eigenvalues. The Herman-Skillman integration mesh[26] was adopted for the first four blocks and the integration in the remaining part of the interval $[0,r_0]$ was performed for fixed interval Δr equal to the interval Δr in the fourth block. The whole interval $[0,r_0]$ was divided into 20 blocks. In the next step of the calculations the parameters of the analytical parts of the trial functions were found from the continuity conditions and the inhomogeneous parts and eigenvalues were calculated. The calculations were repeated until the values of the total energy obtained in the current and preceding iterations differed by less than the assumed accuracy criterion (in the present calculation the criterion was $|E_i-E_{i-1}|/E_i \leq 10^{-5}$).

III. RESULTS AND DISCUSSION

The calculations have been performed for the *d*-*s* band of copper and the crystal potential was taken from Ref. 21. The matrix elements between the functions of *d* symmetry and those between the functions of *d* and *s* symmetry were neglected for the lattice sites more distant than second-nearest neighbors. The matrix elements between the functions of *s* symmetry were calculated up to the eighth nearest neighbors in the lattice. The matrix elements obtained in the Wannier-function basis for two atomic shells ($i=2$) and for the maximum number of neighbors ($i=8$) taken into account in the present calculation are listed in Table II. The table contains, for both values of *i*, two sets of values of matrix elements. The second and the fourth column contain the values obtained when the three-center corrections are calculated for nearest neighbors, that is the three-center corrections are neglected when either $|\mathbf{L}_2-\mathbf{L}_1|$ or $|\mathbf{L}_2-\mathbf{L}_3|$ in Eq. (2.28) is greater than the distance between nearest neighbors in the lattice. For consistency, the nonorthogonality

TABLE II. Hamiltonian matrix elements calculated in Wannier-function basis (in Ry). *i* denotes the number of atomic shells taken into account for the *s* states. Three-center corrections are calculated for nearest neighbors (*n*) and up to the second nearest neighbors (*s*). The Slater notation is used.

	$i=2$		$i=8$	
Element	(*n*)	(*s*)	(*n*)	(*s*)
$E_{yz,yz}(000)$	0.4185	0.4185	0.4179	0.4178
$E_{x^2-y^2,x^2-y^2}(000)$	0.4158	0.4158	0.4156	0.4157
$E_{yz,yz}(110)$	0.0072	0.0072	0.0073	0.0073
$E_{xy,xy}(110)$	−0.0214	−0.0214	−0.0214	−0.0214
$E_{x^2-y^2,x^2-y^2}(110)$	0.0168	0.0169	0.0169	0.0169
$E_{3z^2-r^2,3z^2-r^2}(110)$	−0.0082	−0.0082	−0.0080	−0.0080
$E_{xy,3z^2-r^2}(110)$	0.0107	0.0106	0.0107	0.0107
$E_{zx,yz}(110)$	0.0079	0.0080	0.0082	0.0083
$E_{yz,yz}(002)$	−0.0011	−0.0011	−0.0009	−0.0009
$E_{xy,xy}(002)$	−0.0006	−0.0006	−0.0005	−0.0005
$E_{x^2-y^2,x^2-y^2}(002)$	0.0019	0.0020	0.0021	0.0021
$E_{3z^2-r^2,3z^2-r^2}(002)$	−0.0044	−0.0043	−0.0044	−0.0044
$E_{s,zy}(110)$	0.0394	0.0390	0.0382	0.0377
$E_{s,3z^2-r^2}(110)$	−0.0228	−0.0234	−0.0218	−0.0225
$E_{s,3z^2-r^2}(002)$	0.0091	0.0090	0.0116	0.0114
$E_{s,s}(000)$	0.5818	0.5873	0.5356	0.5460
$E_{s,s}(110)$	−0.0804	−0.0827	−0.0767	−0.0806
$E_{s,s}(002)$	−0.0118	−0.0093	−0.0012	0.0039
$E_{s,s}(112)$			0.0167	0.0164
$E_{s,s}(022)$			0.0108	0.0122
$E_{s,s}(013)$			−0.0024	−0.0033
$E_{s,s}(222)$			−0.0083	−0.0079
$E_{s,s}(123)$			−0.0020	−0.0020
$E_{s,s}(004)$			0.0048	0.0050

of the Wannier functions to core states localized on more distant lattice sites than the nearest neighbors was also ignored. The third and the last column in the table contain the results obtained in the case of the three-center corrections calculated up to second-nearest neighbors. The comparison of these two sets of values shows that while the three-center corrections to the matrix elements between d states coming from more distant lattice sites are negligibly small, the three-center corrections for the matrix elements involving more extended s states should be calculated at least up to second-nearest neighbors. The role played by the potential and the orthogonality effect in the three-center contributions can be illustrated by the following example. The value of the matrix element $E_{s,s}(0,0,0)$ for $i=8$ obtained without three-center corrections is equal to 0.6239 Ry and the value calculated with contributions from integrals (2.28) involving potentials localized on neighboring sites (up to second-nearest neighbors) is reduced to -0.0954 Ry. The orthogonality to core states imposed on the Wannier functions gives finally the value 0.5460 Ry listed in Table II. Thus the orthogonalization to core states plays a similar role as the calculation of matrix elements in conventional band-structure calculations for a pseudopotential instead of a bare potential reducing the magnitude of three-center corrections. The comparison between results for $i=2$ and 8 shows that the increase of the number of atomic shells taken into account in the calculations significantly affects the values of matrix elements between Wannier functions localized on less-distant lattice sites particularly in the case of matrix elements involving Wannier functions of s symmetry.

The matrix elements between extended s states decrease slowly with the distance between lattice sites on which two Wannier functions involved in the matrix element are localized. This result is in agreement with previous results for metallic hydrogen,[1] but precludes the possibility of an accurate description of the ds band of transition metals by a model Hamiltonian based on Wannier functions and confined to second-nearest neighbors. This conclusion is corroborated further by a comparison of band energies at high-symmetry points in the Brillouin zone shown in Table III. The band energies obtained in the present work at various levels of accuracy are com-

TABLE III. The comparison of band energies obtained in the present calculations (i) with exact band energies given in Ref. 21. The successive energy values at the Γ point (e.g., -0.453, 0.385 and 0.460) correspond to Γ_1 state, Γ_{25}' states and to Γ_{12} states, respectively. i denotes the number of shells taken into account in the calculation of the Wannier function of the s symmetry, **k** is expressed in $2\pi/a$ units where a is the lattice constant. In (a), three-center corrections are calculated for nearest neighbors; in (b), three-center corrections are calculated up to the second-nearest neighbors.

Symmetry point	Band energies in Rydbergs (relative to muffin-tin zero)						
			(a)				
Γ [**k**=(0,0,0)]	−0.453	0.385	0.385	0.385	0.460	0.460	($i=2$)
	−0.599	0.385	0.385	0.385	0.462	0.462	($i=3$)
	−0.073	0.386	0.386	0.386	0.462	0.462	($i=6$)
	−0.051	0.386	0.386	0.386	0.462	0.462	($i=8$)
	−0.064	0.390	0.390	0.390	0.451	0.451	(exact)
X [**k**=(0,0,1)]	0.235	0.270	0.491	0.499	0.499	0.888	($i=2$)
	0.232	0.268	0.490	0.498	0.498	0.796	($i=3$)
	0.224	0.269	0.490	0.499	0.499	0.74	($i=6$)
	0.241	0.270	0.490	0.499	0.499	0.895	($i=8$)
	0.241	0.284	0.494	0.509	0.509	0.748	(exact)
L [**k**=(0.5,0.5,0.5)]	0.197	0.385	0.385	0.494	0.494	0.816	($i=2$)
	0.168	0.384	0.384	0.495	0.495	0.716	($i=3$)
	0.220	0.384	0.384	0.494	0.494	0.865	($i=6$)
	0.227	0.384	0.384	0.494	0.494	0.897	($i=8$)
	0.242	0.386	0.386	0.497	0.497	0.544	(exact)
W [**k**=(0.5,0,1)]	0.333	0.389	0.389	0.452	0.501		($i=2$)
	0.332	0.387	0.387	0.453	0.501		($i=3$)
	0.332	0.388	0.388	0.456	0.501		($i=6$)
	0.333	0.388	0.388	0.455	0.501		($i=8$)
	0.297	0.354	0.354	0.448	0.509		(exact)
K [**k**=(0.75,0.75,0.75)]	0.285	0.354	0.455	0.464	0.487		($i=2$)
	0.274	0.352	0.454	0.463	0.487		($i=3$)
	0.289	0.353	0.454	0.464	0.487		($i=6$)
	0.289	0.353	0.454	0.464	0.487		($i=8$)
	0.286	0.311	0.413	0.416	0.494		(exact)

TABLE III. (*Continued*).

Symmetry point	Band energies in Rydbergs (relative to muffin-tin zero)						
			(b)				
Γ [**k**=(0,0,1)]	−0.461	0.385	0.385	0.385	0.460	0.460	($i=2$)
	−0.625	0.385	0.385	0.385	0.462	0.462	($i=3$)
	−0.088	0.386	0.386	0.386	0.462	0.462	($i=6$)
	−0.064	0.386	0.386	0.386	0.462	0.462	($i=8$)
	−0.064	0.390	0.390	0.390	0.451	0.451	(exact)
X [**k**=(0,0,1)]	0.235	0.270	0.492	0.499	0.499	0.918	($i=2$)
	0.235	0.268	0.490	0.498	0.498	0.866	($i=3$)
	0.230	0.269	0.491	0.499	0.499	0.820	($i=6$)
	0.244	0.269	0.491	0.499	0.499	0.979	($i=8$)
	0.241	0.284	0.494	0.509	0.509	0.748	(exact)
L [**k**=(0.5,0.5,0.5)]	0.197	0.385	0.385	0.494	0.494	0.806	($i=2$)
	0.164	0.384	0.384	0.494	0.494	0.698	($i=3$)
	0.222	0.384	0.384	0.494	0.494	0.857	($i=6$)
	0.229	0.384	0.384	0.494	0.494	0.890	($i=8$)
	0.242	0.386	0.386	0.497	0.497	0.544	(exact)
W [**k**=(0.5,0,1)]	0.333	0.389	0.389	0.452	0.501		($i=2$)
	0.332	0.387	0.387	0.453	0.501		($i=3$)
	0.332	0.388	0.388	0.456	0.501		($i=6$)
	0.333	0.388	0.388	0.455	0.501		($i=8$)
	0.297	0.354	0.354	0.448	0.509		(exact)
K [**k**=(0.75,0.75,0.75)]	0.285	0.354	0.455	0.465	0.487		($i=2$)
	0.276	0.352	0.454	0.463	0.487		($i=3$)
	0.290	0.353	0.454	0.464	0.487		($i=6$)
	0.290	0.353	0.454	0.464	0.487		($i=8$)
	0.286	0.311	0.413	0.461	0.494		(exact)

pared with the exact values obtained directly[21] for the same crystal potential. The comparison clearly shows the necessity of taking into account in calculations the matrix elements between more-distant neighbors to get a reasonable agreement between low-lying band energies. That higher band energies are not reproduced equally well is probably connected with the omission of p functions in the present calculations. On the other hand, the comparison between the values in parts (a) and (b) of Table III seems to indicate that three-center contributions calculated in the nearest-neighbor approximation give sufficiently accurate matrix elements for a correct description of the band structure.

The method for band-structure description in terms of the model Hamiltonians based on Wannier functions, originally suggested by Bross,[27] is widely used (see, for example, Refs. 28 and 29); this description is usually limited to matrix elements between neighbors up to second order. In light of the present results, it seems that the conduction band in transition metals cannot be described accurately within this approximation. On the other hand, the model Hamiltonians based on nonorthogonal functions[29,30] which are also limited to the second-nearest neighbors, are in a better position to give an accurate description of conduction band in transition metals not only because they introduce a greater number of parameters to fit the structure of the band but also because they are equivalent to the model Hamiltonians based on orthogonal Wannier functions with a greater number of atomic shells taken into account.

Having calculated the matrix elements in the Wannier-function basis we can directly calculate the density of states for the *d*-*s* band. The method of calculation given in Ref. 31 and adapted for the fcc lattice[32] was used. DOS obtained for $i=2$ and 8 is compared in Fig. 1 with the exact DOS taken from Ref. 21. The DOS obtained in the present calculation for $i=8$ is close to the exact DOS. The positions of peaks are in good agreement and the differences can be probably ascribed to the neglect of p functions in the present calculation. The DOS obtained for $i=2$ and 8 are very close to each other. The differences occur mainly for higher energies when the only contributions come from *s*-symmetry states. It seems to indicate that if the main aim of a calculation is to obtain the shape of the *d* band of transition metals, a calculation limited to second-nearest neighbors and to the *d*-*s* complex band can be a good approximation.

IV. CONCLUSIONS

Direct calculations of the Wannier functions for the *d*-*s* band in copper show that the modified variational

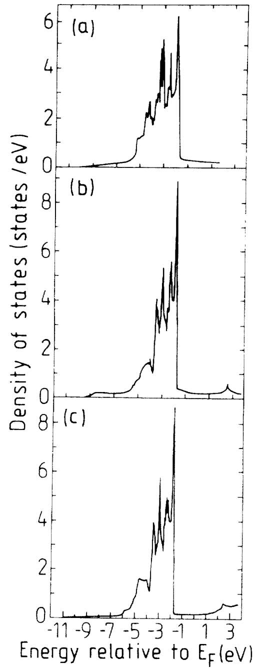

FIG. 1. Density of states (DOS) curves for Cu. (a) The exact DOS taken from Ref. 21. (b) The DOS obtained in the case when the matrix elements for Wannier functions of the *s* symmetry are calculated up to the eighth-nearest neighbors. (c) The matrix elements are calculated up to the second-nearest neighbors. Energy is expressed in eV relative to Fermi energy [assumed to be equal (Ref. 21) to 0.628 Ry].

method can be applied even to wide conduction bands in transition metals. The calculations reveal the role of three-center corrections in the calculation of the matrix elements and show the importance of the orthogonality of Wannier functions to core states. The matrix elements between extended *s* states decrease slowly with the distance between the lattice sites on which Wannier functions involved in the matrix element are localized. The matrix elements between the Wannier functions localized on more-distant lattice sites are important for an accurate description of the band structure, but an approximate description of the DOS is possible within the scope of a model limited to second-nearest neighbors.

APPENDIX A. THE CALCULATION OF THE COEFFICIENTS $G^{-1/2}_{m_1\mathbf{L}_1,m_2\mathbf{L}_2}$ IN THE EXPANSION OF WANNIER FUNCTIONS IN TERMS OF THE TRIAL FUNCTIONS

First, it will be shown that coefficients $G^{-1/2}$ in expansion (2.2) can be expressed in terms of independent matrix elements of the matrix $G^{-1/2}$ in the same way as matrix elements of any operator invariant under the operations of the point group of the crystal, provided that both the trial functions and the Wannier functions in Eq. (2.2) span the same representation of the point group. By acting on both sides of Eq. (2.2) with the operator $\mathcal{P}(T)$ of the symmetry group, we get

$$\begin{aligned}\mathcal{P}(T)a_{\mu\mathbf{L}}(\mathbf{r}) &= \sum_{\nu,\mathbf{L}'} G^{-1/2}_{\nu\mathbf{L}',\mu\mathbf{L}}\mathcal{P}(T)f_{\nu\mathbf{L}'}(\mathbf{r}) \\ &= \sum_{\nu,\mathbf{L}'} G^{-1/2}_{\nu\mathbf{L}',\mu\mathbf{L}} \sum_{\tau} \mathcal{D}_{\tau\nu}(T)f_{\tau T\mathbf{L}'}(\mathbf{r}) \ , \end{aligned} \tag{A1}$$

in which the notation of Ref. 25 has been adopted. On the other hand,

$$\begin{aligned}\mathcal{P}(T)a_{\mu\mathbf{L}}(\mathbf{r}) &= \sum_{\tau} \mathcal{D}_{\tau\mu}(T)a_{\tau T\mathbf{L}}(\mathbf{r}) \\ &= \sum_{\tau} \mathcal{D}_{\tau\mu}(T) \sum_{\nu,\mathbf{L}''} G^{-1/2}_{\nu\mathbf{L}'',\tau T\mathbf{L}} f_{\nu\mathbf{L}''}(\mathbf{r}) \ . \end{aligned} \tag{A2}$$

By introducing $\mathbf{L}''=T\mathbf{L}'$, summing over $\mathbf{L}'$ instead of $\mathbf{L}''$, and interchanging names of the summation indices, we get

$$\mathcal{P}(T)a_{\mu\mathbf{L}}(\mathbf{r}) = \sum_{\tau,\nu,\mathbf{L}'} \mathcal{D}_{\nu\mu}(T)G^{-1/2}_{\tau T\mathbf{L}',\nu T\mathbf{L}} f_{\tau T\mathbf{L}'}(\mathbf{r}) \ . \tag{A3}$$

By comparing right-hand sides of Eq. (A1) and (A3) and taking into account that (since the functions $f_{\tau\mathbf{L}}$ are arbitrary functions) the coefficients at the same function have to be equal, we get

$$\sum_{\nu} G^{-1/2}_{\nu\mathbf{L}',\mu\mathbf{L}}\mathcal{D}_{\tau\nu}(T) = \sum_{\nu} \mathcal{D}_{\nu\mu}(T)G^{-1/2}_{\tau T\mathbf{L}',\nu T\mathbf{L}} \ . \tag{A4}$$

By multiplying Eq. (A4) by $\mathcal{D}^*_{\tau\mu}(T)$, summing up over τ, and taking into account that $\mathcal{D}(t)$ is the unitary matrix, we finally get

$$G^{-1/2}_{\mu'\mathbf{L}',\mu\mathbf{L}} = \sum_{\tau,\nu} \mathcal{D}^*_{\tau\mu'}(T)\mathcal{D}_{\nu\mu}(T)G^{-1/2}_{\tau T\mathbf{L}',\nu T\mathbf{L}} \ . \tag{A5}$$

Equation (A5) has exactly the same form as the equations derived in Ref. 25 to establish the set of independent matrix elements of an operator invariant under the operations of the point group of the crystal. The overlap matrix elements in the Wannier-function basis can therefore be expressed in terms of the independent matrix elements,

$$(a_{m_1\mathbf{L}_0}, a_{m_2\mathbf{L}}) = \sum_{i,j,k} C_{m_1\mathbf{L}_0,m_2\mathbf{L}}(i,j,k)G_i^{-1/2}S_jG_k^{-1/2} \ , \tag{A6}$$

where $G_i^{-1/2}$ and S_i denote the independent matrix elements of the matrix $G^{-1/2}_{m_1\mathbf{L}_0,m_2\mathbf{L}}$ and of the overlap matrix $S_{m_1\mathbf{L}_0,m_2\mathbf{L}}$ calculated in the trial-function basis, respectively.

Since the overlap matrix elements in the Wannier-function basis can be also expressed in terms of independent matrix elements, the orthogonality condition of Wannier functions can be reduced to the set of equations (A6) for the independent matrix elements. The set of equations (A6) was solved by an iterative method: the equations were linearized by replacing one of $G_i^{-1/2}$ appearing in the quadratic form by initial values in the first step and by the average values of $G_i^{-1/2}$ obtained in the current and the preceding iteration in the successive steps of the iteration procedure.

The set of equations (A6) also served as a starting point for the calculation of the variation $\delta G_i^{-1/2}$. Since the orthogonality of the Wannier function is the constraint imposed on the variation of the trial functions,

$$\delta(a_{m\mathbf{L}_0},a_{m_2\mathbf{L}})=0 \tag{A7}$$

for any variation of the trial functions. If we expand $\delta G_i^{-1/2}$ in terms of the variation δS_j,

$$\delta G_i^{-1/2}=\sum_j \omega_{ij}\,\delta S_j \;, \tag{A8}$$

we get from Eqs. (A6)–(A8) the set of linear equations defining the coefficients ω_{ij},

$$\sum_i \alpha_{li}\omega_{in}=d_{ln} \;, \tag{A9}$$

where

$$a_{li}=\sum_{j,k}[C_l(i,j,k)S_jG_k^{-1/2}+C_l(k,j,i)S_jG_k^{-1/2}] \;, \tag{A10}$$

$$d_{ln}=\sum_{j,k}C_l(i,n,k)G_i^{-1/2}G_k^{-1/2} \;, \tag{A11}$$

where l is a shorthand for all pairs $m_1\mathbf{L}_0,m_2\mathbf{L}$ which form the set of independent matrix elements of the overlap matrix.

APPENDIX B. THE CALCULATION OF THREE-CENTER CONTRIBUTIONS

The three-center contributions to the matrix elements stem from the integrals of the form (2.28) and from the nonorthogonality of the Wannier functions to core states localized on adjacent lattice sites. Let us consider first the corrections connected with the integrals (2.28). In this approximation the independent matrix element can be expressed as the sum of the matrix element calculated in two-center approximation and three-center contribution,

$$H_j=H_j^d+H_j^t \;, \tag{B1}$$

where H_j^t is the sum of integrals (2.28),

$$H_j^t=\sum_{\mathbf{L}_1\,(\neq\mathbf{L}_0,\mathbf{L}_j)}\int d\tau\, f_{\mu_j\mathbf{L}_0}(\mathbf{r})V(\mathbf{r}-\mathbf{L}_1)f_{\nu_j\mathbf{L}_j}(\mathbf{r})$$

$$=\sum_{\mathbf{L}_1\,(\neq\mathbf{L}_0,\mathbf{L}_j)}\int d\tau\, f_{\mu_j\mathbf{L}_0-\mathbf{L}_1}(\mathbf{r})V(\mathbf{r})f_{\nu_j\mathbf{L}_j-\mathbf{L}_j}(\mathbf{r}) \;. \tag{B2}$$

The cubic harmonics contained in the functions f_μ can be expressed in terms of spherical harmonics and the latter can in turn be expressed in rotated frame of reference,[33]

$$Y_{lm}(\vartheta',\phi')=\sum_{m'=-1}^{l}Y_{lm'}(\vartheta,\phi)\mathcal{D}^{(l)}_{m'm}(\alpha,\beta,\gamma) \;, \tag{B3}$$

where Y_{lm} is the spherical harmonic, α, β, and γ are Euler angles describing the rotation, and the method of calculation of the matrix $\mathcal{D}^{(l)}_{m'm}$ is described in Ref. 33. By using (B3), the three-center correction H^t can be written in the following form:

$$H_j^t=\sum_{\mathbf{L}_1\,(\neq\mathbf{L}_0,\mathbf{L}_j)}\sum_{m_1,m_2}T^*_{\mu,m_1}T_{\nu,m_2}\sum_{m_1'}\mathcal{D}^{(l_\mu)}_{m_1'm_1}(\alpha_0,\beta_0,\gamma_0)$$

$$\times\sum_{m_2'}\mathcal{D}^{(l_\nu)}_{m_2'm_2}(\alpha_j,\beta_j,\gamma_j)\int d\tau\, Y^*_{l_\mu m_1';\mathbf{L}_0-\mathbf{L}_1}(\vartheta,\phi)\mathbf{r}^{-1}_{\mathbf{L}_0-\mathbf{L}_1}R_{\mu,\mathbf{L}_0-\mathbf{L}_1}V(\mathbf{r})$$

$$\times Y_{l_\nu m_2';\mathbf{L}_0-\mathbf{L}_1}(\vartheta,\phi)\mathbf{r}^{-1}_{\mathbf{L}_0-\mathbf{L}_1}R_{\nu,\mathbf{L}_0-\mathbf{L}_1} \;, \tag{B4}$$

where μ and ν denote the pair of the functions involved in the matrix element H_j, the matrix T is the transformation matrix from cubic to spherical harmonics $\alpha_0,\beta_0,\gamma_0$ and $\alpha_j,\beta_j,\gamma_j$ are the Euler angles describing the rotation of the frame of reference so that the z axis is directed along $\mathbf{L}_0-\mathbf{L}_1$ and $\mathbf{L}_j-\mathbf{L}_1$, respectively, and the additional index at Y indicates the localization and the frame of reference connected with the spherical harmonic. Now we can expand the function $r_{\mathbf{L}}^{-1}Y_{lm;\mathbf{L}}R_{\mu\mathbf{L}}$ around the displaced center using the method given in Ref. 34,

$$H_j^t=\sum_{\mathbf{L}_1\,(\neq\mathbf{L}_0,\mathbf{L}_j)}\sum_{m_1,m_2}T^*_{\mu,m_1}T_{\nu,m_2}\sum_{m_1'}\mathcal{D}^{(l_\mu)}_{m_1'm_1}(\alpha_0,\beta_0,\gamma_0)\sum_{m_2'}\mathcal{D}^{(l_\nu)}_{m_2'm_2}(\alpha_j,\beta_j,\gamma_j)$$

$$\times\int d\tau\, r^{-2}\sum_{l_1,l_2}Y^*_{l_1m_1'}(\vartheta',\phi')\alpha_{l_1}(n_{\mu'}l_{\mu'}m_1'|a_p,r)$$

$$\times V(\mathbf{r})Y_{l_2m_2'}(\vartheta'',\phi'')\alpha_{l_2}(n_{\nu'}l_{\nu'}m_1'|a_q,r) \;, \tag{B5}$$

where the function α_1 has the same meaning as in Ref. 34, n_μ and n_ν are the exponentials occurring in the analytical parts of trial functions f_μ and f_ν, respectively, ϑ', ϕ', and ϑ'',ϕ'' are expressed in the frames of reference in which the z axis is directed along $\mathbf{L}_0-\mathbf{L}_1$ and $\mathbf{L}_j-\mathbf{L}_1$, respectively, $a_p=|\mathbf{L}_0-\mathbf{L}_1|$ and $a_q=|\mathbf{L}_j-\mathbf{L}_0|$. The last step in the calculation of H_j^t consists of the reciprocal rotations of the frames of reference used for the first and the second function occurring in the integrand. Since the function α_l depends on the distance between two centers involved it is convenient to replace the summation over $\mathbf{L}_1$ by the summations over shells in which $\mathbf{L}_1$ is the nearest-neighbor position with respect to both $\mathbf{L}_0$ and $\mathbf{L}_j$, $\mathbf{L}_1$ is the nearest-neighbor position of $\mathbf{L}_0$ and the second-nearest-neighbor position of $\mathbf{L}_j$, and so on. In this way the three-center correction H_j^t can be finally written in the following form:

$$H_j^t = \sum_{\substack{l,m_1',m_2'\\p,q}} M_j(l,m_1',m_2',p,q)F_j(l,m_1',m_2',p,q) , \qquad \text{(B6)}$$

where

$$F_j(l,m_1',m_2',p,q)=\int_0^{r_0} dr\, V(r)\alpha_1(n_{\mu'}l_{\mu'}m_1'|a_p,r)\alpha_1(n_{\nu'}l_{\nu'}m_2'|a_q,r) , \qquad \text{(B7)}$$

$$M_j(l,m_1',m_2',p,q)= \sum_{m_1=-l_\mu}^{l_\mu} \sum_{m_2=-l_\nu}^{l_\nu} \sum_{m''=-l}^{l} \sum_k \{ T^*_{\mu,m_1} T_{\nu,m_2} \mathcal{D}^{(l_\mu)*}_{m_1'm_1}(\alpha_{0k},\beta_{0k},\gamma_{0k})\mathcal{D}^{(l_\nu)}_{m_2'm_2}(\alpha_{jk},\beta_{jk},\gamma_{jk})$$
$$\times \mathcal{D}^{(l)*}_{m''m_1'}(\alpha^r_{0k},\beta^r_{0k},\gamma^r_{0k})\mathcal{D}^{(1)}_{m''m_2'}(\alpha^r_{jk},\beta^r_{jk},\gamma^r_{jk})\} , \qquad \text{(B8)}$$

the summation over k denotes the summation over all sets of Euler angles which result from the summation over $\mathbf{L}_1$ and correspond to the geometrical arrangements in which $\mathbf{L}_1$ is the neighbor of the order p with respect to $\mathbf{L}_0$ and, at the same time, $\mathbf{L}_1$ is the neighbor of the order q with respect to $\mathbf{L}_j$ and the Euler angles with index r correspond to the rotations restoring the original frame of reference.

It should be mentioned that the matrix M_j need be calculated only once for a given crystal lattice and a given set of trial functions. It turned out that with good accuracy the summation over l can be truncated beyond $l=4$.

The orthogonality of the Wannier functions to core states localized on adjacent lattice sites has been achieved by the orthogonalization of the trial functions to the core states. The Wannier functions formed according to Eq. (2.2) from such functions will be also orthogonal to the core states. By using Schmidt orthogonalization procedure and assuming that the core states localized on different lattice sites are mutually orthogonal, the trial functions orthogonalized to the core states can be written in the following form:

$$f^0_{\mu\mathbf{L}_0}(\mathbf{r})=c_\mu \left[f_{\mu\mathbf{L}_0}(\mathbf{r}) - \sum_{\nu_\beta,\Delta} \kappa_{\mu,\nu_\beta}(\Delta)\phi_{\nu_\beta,\mathbf{L}_0+\Delta}(\mathbf{r}) \right] , \qquad \text{(B9)}$$

where

$$\kappa_{\mu,\nu_\beta}(\Delta)=(\phi_{\nu_\beta\mathbf{L}_0+\Delta},f_{\mu\mathbf{L}_0}) , \qquad \text{(B10)}$$

$$c_\mu = \left[1-\sum_{\nu,\Delta} \kappa^2_{\mu,\nu_\beta}(\Delta) \right]^{-1/2} , \qquad \text{(B11)}$$

and ϕ_{ν_β} are the core states. It can be shown that the function $f^0_{\mu\mathbf{L}}$ span the irreducible representation of the point group provided that the original functions $f_{\mu\mathbf{L}}$ do so.

The overlap matrix and the Hamiltonian matrix elements can now be recalculated in the orthogonalized trial function basis,

$$S^0_j=c_\mu c_\nu \left[S_j - \sum_{\nu_\beta,\Delta} \kappa_{\mu,\nu_\beta}(\Delta)\kappa_{\nu,\nu_\beta}(\mathbf{L}_0+\Delta-\mathbf{L}_j) \right] , \qquad \text{(B12)}$$

$$H^0_j=c_\mu c_\nu \left[H_j - \sum_{\nu_\beta,\Delta} \varepsilon_{\nu_\beta}\kappa_{\mu,\nu_\beta}(\Delta)\kappa_{\nu,\nu_\beta}(\mathbf{L}_0+\Delta-\mathbf{L}_j) \right] , \qquad \text{(B13)}$$

where S_j and H_j are the matrix elements calculated with the use of the original functions $f_{\mu\mathbf{L}}$ and we assumed that

$$\hat{H}\phi_{\nu_\beta\mathbf{L}}=\varepsilon_{\nu_\beta}\phi_{\nu_\beta\mathbf{L}} . \qquad \text{(B14)}$$

In order to simplify the calculations the sum of products $\kappa_{\mu,\nu_\beta}\kappa_{\mu,\nu_\beta}$ can be expressed in terms of independent elements of the overlap matrix between the trial functions and the core states. Following the method used in paper I to obtain matrix elements expressed in terms of independent matrix elements, we get

$$S^0_j=c_\mu c_\nu \left[S_j - \sum_{l,k_1,k_2} B(j,l,k_1,k_2)\sum_n \kappa_{nl\mu}(k_1)\kappa_{nl\nu}(k_1) \right] , \qquad \text{(B15)}$$

$$H^0_j=c_\mu c_\nu \left[H_j - \sum_{l,k_1,k_2} B(j,l,k_1,k_2) \times \sum_n \varepsilon_{nl}\kappa_{nl\mu}(k_1)\kappa_{nl\nu}(k_1) \right] , \qquad \text{(B16)}$$

where

$$B(j,l,k_1,k_2)=(2\pi)^{-3}\int_{-\pi}^{\pi} d\rho_x \int_{-\pi}^{\pi} d\rho_y \int_{-\pi}^{\pi} d\rho_z \sum_{p_1,p_2} \{\omega_{\mu,l,p_1,k_1}(\rho)\omega_{\nu,l,p_2,k_2}(\rho)\exp[(i\rho(\mathbf{L}_j-\mathbf{L}_0)]\} , \qquad \text{(B17)}$$

$$\sum_\Delta \kappa_{\mu\nu_\beta}(\Delta)\exp(i,\rho\Delta)=\sum_{p,k}\omega_{\mu,l,p,k}(\rho)\kappa_{nl\mu}(k) , \qquad \text{(B18)}$$

$$\sum_{\Delta} \kappa_{\nu\nu_\beta}(\Delta)\exp(-i\rho\Delta)=\sum_{p,k}\omega_{\nu,l,p,k}(\rho)\kappa_{nl\nu}(k)\ , \tag{B19}$$

the core states are specified by two quantum numbers n and l, and k runs over the number of independent matrix elements of the overlap matrix $\kappa_{nl,\mu}$. The matrix B need be calculated only once for crystal and trial functions of a given symmetry.

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