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Modified method of variational calculations of Wannier functions: The Wannier functions for *d* bands of Cu and paramagnetic Ni

P. Modrak and R. Wojnecki
Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, PL-01-224 Warsaw, Poland

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The method of the direct variational calculation of the Wannier functions consisting of the variation of the energy functional with respect to the trial functions in the region surrounding the lattice site on which the functions are centered, and with respect to parameters describing the exponential tails of the trial functions for the remaining volume of the crystal is generalized for the case of composite bands. The calculations are performed for *d* bands of copper and paramagnetic nickel.

I. INTRODUCTION

The calculations of Wannier functions are still far less developed than the calculations of Bloch functions, particularly for three-dimensional crystals. The direct calculations of Wannier functions for metallic hydrogen,[1] for semiconductors,[2–7] and for thallous halides[8] are the only calculations for three-dimensional crystals based on the variational principle satisfied by these functions. The Wannier functions for periodic crystals can be, in principle, obtained by the Fourier transformation of the Bloch functions. However, the choice of an arbitrary phase in Bloch functions makes the transformation difficult[9,10] and, moreover, this method cannot be used if the translational symmetry of the system is broken. On the other hand, the method of variational calculation of Wannier functions can directly provide interaction (hopping) integrals between different orbitals localized on different lattice sites needed in various approximate calculations, and can be easily generalized for a crystal with the surface and a crystal containing an impurity.[11–15]

The calculations reported in the present paper are the first direct calculations of the Wannier functions for the *d* band of transition metals. The method used in the present work is the method applied before to the crystal with Mathieu potential[16] generalized for the composite band. The main approximation introduced consists in neglecting the *s*-*d* hybridization. This approximation simplifies the calculation, but the method can be easily generalized to give the full description of *s*-*d* composite bands of transition metals. In spite of this approximation, the results obtained give some insight into relations between various energy matrix elements calculated for *d*-band Wannier functions and allow us to estimate the validity of two-center approximation in the calculations of these matrix elements. The interaction energy integrals can be compared with the results of the previous approximate calculations and with the energy matrix elements obtained by the linear combination of atomic orbitals (LCAO) model Hamiltonian method.[17–31]

This paper is arranged in the following way. The method of the calculation is described in the following section. Section III gives the results of calculations for copper and nickel, the comparison with the previous results, and its discussion. Section IV contains conclusions.

II. THE METHOD OF CALCULATIONS OF WANNIER FUNCTIONS FOR COMPOSITE BANDS

A. The basic equations

The method used in the present paper to obtain the Wannier functions for the *d* band of transition metals is the modified variational method[16] generalized for the composite band. According to Kohn's suggestion[32] we seek for the set of Wannier functions $a_{m,\mathbf{L}}$ which minimizes the energy functional for the composite band,

$$\varepsilon(a_{1,\mathbf{L}_0},a_{2,\mathbf{L}_0},\ldots,a_{M,\mathbf{L}_0})=\sum_{m=1}^{M}\langle a_{m,\mathbf{L}_0}(\mathbf{r}),\hat{H}a_{m,\mathbf{L}_0}(\mathbf{r})\rangle \ , \tag{2.1}$$

where $\hat{H}$ is the Hamiltonian of the system, $a_{n,\mathbf{L}_0}(r)$ is the Wannier function localized on the $\mathbf{L}_0=(0,0,0)$ lattice site, and M is the number of Wannier functions belonging to the composite band. The Wannier functions are in turn represented in the form of the linear combination of the trial functions,

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

where $f_{m\mathbf{L}}(\mathbf{r})=f_m(\mathbf{r}-\mathbf{L})$ is the trial function of the correct symmetry localized on the lattice site $\mathbf{L}$ and the coefficients $G^{-1/2}_{m_1\mathbf{L}_1,m_2\mathbf{L}_2}$ are chosen so that the Wannier functions form the orthonormal set. We follow the orthogonalization procedure suggested by Löwdin[33] to obtain $G^{-1/2}$,

$$\begin{aligned}G^{-1/2}_{m_1\mathbf{L}_1,m\mathbf{L}_0}=\delta_{m_1,m}\delta_{\mathbf{L}_1,\mathbf{L}_0}-\tfrac{1}{2}N_{m_1}^{-1/2}N_m^{-1/2}S_{m_1\mathbf{L}_1,m\mathbf{L}_0}\\+\tfrac{3}{8}N_{m_1}^{-1/2}N_m^{-1/2}\sum_{m_2,\mathbf{L}_2}N_{m_2}^{-1}S_{m_1\mathbf{L}_1,m_2\mathbf{L}_2}\\\times S_{m_2\mathbf{L}_2,m\mathbf{L}_0}-\cdots \ ,\end{aligned} \tag{2.3}$$

where

$$N_m = \langle f_{m\mathbf{L}}(\mathbf{r}), f_{m\mathbf{L}}(\mathbf{r})\rangle \tag{2.4}$$

and

$$S_{m_1\mathbf{L}_1,m_2\mathbf{L}_2} = \langle f_{m_1\mathbf{L}_1}(\mathbf{r}), f_{m_2\mathbf{L}_2}(\mathbf{r})\rangle (1-\delta_{m_1m_2}\delta_{\mathbf{L}_1\mathbf{L}_2}) . \tag{2.5}$$

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

$$\begin{aligned}\varepsilon(\{f_{m_i\mathbf{L}_i}\}) = {} & \sum_m N_m^{-1} H_{m\mathbf{L}_0,m\mathbf{L}_0} - \sum_{m,m_1,\mathbf{L}} N_m^{-1} N_{m_1}^{-1} H_{m\mathbf{L}_0,m_1\mathbf{L}} S_{m_1\mathbf{L},m\mathbf{L}_0} \\ & + \sum_{m,m_1,m_2,\mathbf{L}_1,\mathbf{L}_2} N_m^{-1} N_{m_1}^{-1} N_{m_2}^{-1} H_{m\mathbf{L}_0,m_1\mathbf{L}_1} S_{m_1\mathbf{L}_1,m_2\mathbf{L}_2} S_{m_2\mathbf{L}_2,m\mathbf{L}_0} - \cdots ,\end{aligned} \tag{2.6}$$

where

$$H_{m_1\mathbf{L}_1,m_2\mathbf{L}_2} = \langle f_{m_1\mathbf{L}_1}(\mathbf{r}), \hat{H} f_{m_2\mathbf{L}_2}(\mathbf{r})\rangle , \tag{2.7}$$

and in the derivation of Eq. (2.6) we have made use of the Hermicity of the Hamiltonian and of the fact that the trial functions are chosen to be real.

Equation (2.6), even truncated after the first three terms, is very difficult to evaluate because of the presence of multiple sums over lattice sites. However, we can make use of the fact that all matrix elements $H_{m_1\mathbf{L}_1,m_2\mathbf{L}_2}$ and $S_{m_1\mathbf{L}_1,m_2\mathbf{L}_2}$ can be expressed in terms of the set of independent matrix elements[34,35] and the number of the latter is much less than the number of the former. Thus we can reduce Eq. (2.6) to the following form:

$$\begin{aligned}\varepsilon(\{f_{m_i\mathbf{L}_i}\}) = {} & \sum_\alpha d_\alpha N_{\mu_\alpha}^{-1} H_{\mu_\alpha\mathbf{L}_0,\mu_\alpha\mathbf{L}_0} - \sum_j N_j^{-2} A_j H_j S_j + \sum_\alpha N_{\mu_\alpha}^{-1} H_{\mu_\alpha\mathbf{L}_0,\mu_\alpha\mathbf{L}_0} \sum_j N_j^{-2} A_j^\alpha S_j^2 \\ & + \sum_{i,j,k} N_i^{-1} N_j^{-1} N_k^{-1} B_{ijk} H_i S_j S_k - \cdots ,\end{aligned} \tag{2.8}$$

where d_α is the order of the representation which is spanned by the set of functions $\{f_{\mu_\alpha,\mathbf{L}_0}\}$, $f_{\mu_\alpha,\mathbf{L}_0}$ is one of the functions belonging to the basis of the representation α, H_j and S_j are the independent matrix elements of the Hamiltonian and overlap matrices, respectively, $N_j = N_{m_j}^{1/2} N_{m_j'}^{1/2}$ where m_j and m_j' denote the pair of trial functions involved in the matrix element H_j or S_j, the coefficients A_j, A_j^α, and $B_{i,j,k}$ are the coefficients independent of the form of trial functions which can be calculated only once for a given band and a given structure of the lattice (see Appendix A), and the last sum in Eq. (2.8) does not include the matrix elements of the Hamiltonian between the trial functions localized on the same lattice site.

The full (not truncated) expression (2.8) is the exact expression for the energy of the system. The calculation of $\varepsilon(f)$ requires, however, the following approximations to be introduced: (i) the number of terms in Eq. (2.8) must be finite, (ii) the number of Wannier functions belonging to the composite band must be defined, and (iii) the infinite summations over $i,j,k,\ldots$ must be truncated (the interactions between only a finite number of neighbors in the lattice can be taken into account). In the present work we neglect all terms not written in the expansion (2.8) and the *s*-*d* hybridization assuming M to be equal to 5 for the composite *d* band. Assuming the Hamiltonian to be of the form

$$\hat{H} = \hat{T} + \sum_{\mathbf{L}} V(\mathbf{r}-\mathbf{L}) , \tag{2.9}$$

where $\hat{T}$ is the kinetic energy operator and $V(\mathbf{r}-\mathbf{L})$ is the potential localized on the $\mathbf{L}$ lattice site, we will neglect all contributions from the integrals containing the potential term localized on the lattice site other than the lattice site on which at least one of the trial functions is localized. All calculations of the energy matrix elements show that such contributions are considerably less than the matrix elements calculated in the two-center approximation (or in the one-center approximation in the case when both functions are localized on the same lattice site). Beside that, all such contributions neglected at this stage of calculations can be included into the final calculation of the energy matrix elements between the Wannier functions. Assuming further that the trial functions have a common radial part and differ only in the dependence on angle variables, and neglecting all interaction matrix elements except for those for the nearest neighbors and the second nearest neighbors, we can reduce Eq. (2.8) to the following form:

$$\begin{aligned}\varepsilon(f) = {} & 5N_1^{-1}H_1 - \sum_{j=3}^{12} N_j^{-2} H_j S_j + N_1^{-1} H_1 \sum_{j=3}^{12} N_j^{-2} A_j S_j^2 \\ & + \sum_{i,j,k=3}^{12} N_i^{-1} N_j^{-1} N_k^{-1} B_{ijk} H_i S_j S_k .\end{aligned} \tag{2.10}$$

Table I explains how H_1, S_1, and matrix elements of other operators appearing in the paper are related to the independent matrix elements between the functions of a given symmetry localized on two, in general, different lattice sites (the relations between H_i and other notations used for interaction matrix elements are given in Appendix B). It should be mentioned that $H_1 = H_2$ in the approximation in which the energy functional is calculated.

The energy functional (2.10) is to be minimized in respect to the trial functions $f_{m\mathbf{L}}(r)$. As in Ref. 16 we assume that

$$f_{mL}(\mathbf{r})\equiv f_m(\mathbf{r}-\mathbf{L})=r_{\mathbf{L}}^{-1}R_{\mathbf{L}}(r)Y_{m,\mathbf{L}}(\vartheta,\varphi)\ , \tag{2.11}$$

where $r_L=|\mathbf{r}-\mathbf{L}|$, $R_L(r)=R(|\mathbf{r}-\mathbf{L}|)$,

$$Y_{m\mathbf{L}_0}(\vartheta,\varphi)=\begin{cases}\dfrac{\sqrt{15}}{2\sqrt{\pi}}\dfrac{yz}{r^2}\\[4pt] \dfrac{\sqrt{15}}{2\sqrt{\pi}}\dfrac{zx}{r^2}\\[4pt] \dfrac{\sqrt{15}}{2\sqrt{\pi}}\dfrac{xy}{r^2}\\[4pt] \dfrac{\sqrt{15}}{4\sqrt{\pi}}\dfrac{x^2-y^2}{r^2}\\[4pt] \dfrac{\sqrt{5}}{4\sqrt{\pi}}\dfrac{3z^2-r^2}{r^2}\ ,\end{cases} \tag{2.12}$$

and $Y_{m\mathbf{L}}$ is the function $Y_{m\mathbf{L}_0}(\vartheta,\varphi)$ centered on the $\mathbf{L}$ lattice site. We further assume that the variations in the function $f_{m\mathbf{L}}$ are confined to variations in the function $R_{\mathbf{L}}(r)$ and the function $R_{\mathbf{L}}(r)$ is assumed to be of the form

$$R_{\mathbf{L}}(r)=\begin{cases}R_{\mathbf{L}}(r), & r_{\mathbf{L}}\le r_0\\ R_{\mathbf{L}}(r;\{\beta_i\}), & r_{\mathbf{L}}\ge r_0\end{cases} \tag{2.13}$$

where $R_{\mathbf{L}}(r;\{\beta_i\})$ is the analytical function dependent on the set of variational parameters. The radius r_0 of the sphere in which $R_{\mathbf{L}}(r)$ is an arbitrary variational function will be chosen to be equal to the muffin-tin radius r_m of the potential. In the present work the analytical part of the function $R_{\mathbf{L}}$ is assumed to be of the form of the Slater orbital,

TABLE I. The relations between M_i and the independent matrix elements of the operator $\hat{M}$ for the functions of the d symmetry. $\hat{M}$ denotes any operator 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 the first row of the table are localized on the $\mathbf{L}$ lattice site.

$\mathbf{L}=(0,0,0)$	yz	zx	xy	x^2-y^2	$3z^2-r^2$
yz	M_1				
zx		M_1			
xy			M_1		
x^2-y^2				M_2	
$3z^2-r^2$					M_2
$\mathbf{L}=(1,1,0)$	yz	zx	xy	x^2-y^2	$3z^2-r^2$
yz	M_3	M_8			
zx	M_8	M_3			
xy			M_4		M_7
x^2-y^2				M_5	
$3z^2-r^2$			M_7		M_6
$\mathbf{L}=(0,0,2)$	yz	zx	xy	x^2-y^2	$3z^2-r^2$
yz	M_9				
zx		M_9			
xy			M_{10}		
x^2-y^2				M_{11}	
$3z^2-r^2$					M_{12}

$$R_{\mathbf{L}}(r,\{\beta_i\})=\beta_0 r_{\mathbf{L}}^3 e^{-\beta_1 r_{\mathbf{L}}}\ . \tag{2.14}$$

Now, following the method described in Ref. 16, the condition for the minimum of the functional (2.10) can be written in the form of the following set of equations:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{1}{2}\frac{2\times 3}{r^2}+V(r)+\lambda\right]R(r)=X(r)\ , \tag{2.15}$$

$$\begin{aligned}\lambda N^{\beta}+H_1^{\beta}=\left[5+N^{-2}\sum_{j=3}^{12}A_jS_j^2\right]^{-1}\Bigg[&N^{-1}\sum_{j=3}^{12}A_j(H_j^{\beta}S_j+H_jS_j^{\beta})-2N^{-2}H_1\sum_{j=3}^{12}A_jS_jS_j^{\beta}\\&-N^{-2}\sum_{i,j,k=3}^{12}B_{i,j,k}S_j(H_i^{\beta}S_k+2H_iS_k^{\beta})\Bigg]\ ,\end{aligned} \tag{2.16}$$

where

$$\begin{aligned}X(r)=\left[5+N^{-2}\sum_{j=3}^{12}A_jS_j^2\right]^{-1}\Bigg[&N^{-1}\sum_{j=3}^{12}A_j[S_j\bar{H}_j(r)+H_j\bar{S}_j(r)]-2N^{-2}H_1\sum_{j=3}^{12}A_jS_j\bar{S}_j(r)\\&-N^{-2}\sum_{i,j,k=3}^{12}B_{i,j,k}S_j[S_k\bar{H}_i(r)+2H_i\bar{S}_k(r)]\Bigg]\ ,\end{aligned} \tag{2.17}$$

$$N=\int_0^{\infty}R^2(r)dr\ , \tag{2.18}$$

$$\bar{H}_n(r)=\int d\omega\, rY_{\mu_n\mathbf{L}_0}(\vartheta,\varphi)\hat{H}r_{\mathbf{L}_n}^{-1}Y_{v_n\mathbf{L}_n}(\vartheta,\varphi)R_{\mathbf{L}_n}(r)\ , \tag{2.19}$$

$$\bar{S}_n(r)=\int d\omega\, rY_{\mu_n\mathbf{L}_0}(\vartheta,\varphi)r_{\mathbf{L}_n}^{-1}Y_{v_n\mathbf{L}_n}(\vartheta,\varphi)R_{\mathbf{L}_n}(r)\ , \tag{2.20}$$

$$H_n^\beta = \int_{r_0}^{\infty} dr\, R(r) \bar{H}_n(r) , \tag{2.21}$$

$$S_n^\beta = \int_{r_0}^{\infty} dr\, R(r) \bar{S}_n(r) , \tag{2.22}$$

$$N^\beta = \int_{r_0}^{\infty} dr\, R^2(r) . \tag{2.23}$$

The subscripts of the functions appearing in the integrand in Eqs. (2.19) and (2.20) are ascribed to n according to Table I and the integration over $d\omega$ denotes the integration over the full solid angle. In the derivation of Eqs. (2.15) and (2.16) we have assumed that the potential has the spherical symmetry in the muffin-tin sphere, i.e., $V(\mathbf{r}-\mathbf{L}) = V(r_\mathbf{L})$.

Equations (2.15) and (2.16) together with the boundary conditions,

$$R_\mathbf{L}(r_0) = R_\mathbf{L}(r_0;\{\beta_i\}) , \tag{2.24}$$

$$R_\mathbf{L}^{-1}(r_0) \left. \frac{dR_\mathbf{L}(r)}{dr_\mathbf{L}} \right|_{r_\mathbf{L}=r_0} = R_\mathbf{L}^{-1}(r_0;\{\beta_i\}) \left. \frac{dR(r_\mathbf{L}\{\beta_i\})}{dr_\mathbf{L}} \right|_{r_\mathbf{L}=r_0} , \tag{2.25}$$

fully define the trial functions, and the method of their solution will be outlined in the following subsection.

Having calculated the trial functions we can calculate the matrix elements of $G^{-1/2}$ and the Wannier functions localized on an arbitrary lattice site. If we take into account only contributions to the Wannier functions from the trial functions localized on the lattice sites up to (and including) the second nearest neighbors, it is sufficient to calculate 12 independent matrix elements,

$$\begin{aligned} G^{-1/2}_{\mu_n \mathbf{L}_n, \nu_n \mathbf{L}_0} = {} & \delta_{\mu_n,\nu_n} \delta_{\mathbf{L}_n,\mathbf{L}_0} - \tfrac{1}{2} S_n + \tfrac{3}{8} \sum_{i,j} B_{\mu_n \mathbf{L}_0, \nu_n \mathbf{L}_n}(i,j) S_i S_j \\ & - \tfrac{5}{16} \sum_{i,j,k} C_{\mu_n \mathbf{L}_0, \nu_n \mathbf{L}_n}(i,j,k) S_i S_j S_k + \tfrac{35}{128} \sum_{i,j,k,l} D_{\mu_n \mathbf{L}_0, \nu_n \mathbf{L}_n}(i,j,k,l) S_i S_j S_k S_l , \end{aligned} \tag{2.26}$$

where the trial functions are assumed to be normalized and the coefficients $B_{\mu_n \mathbf{L}_0, \nu_n \mathbf{L}_n}(i,j)$, $C_{\mu_n \mathbf{L}_0, \nu_n \mathbf{L}_n}(i,j,k)$, and $D_{\mu_n \mathbf{L}_0, \nu_n \mathbf{L}_n}(i,j,k,l)$ can be calculated once for a given structure of the lattice (see Appendix A). Similarly, there are 12 independent matrix elements of the Hamiltonian calculated in the basis of the Wannier functions,

$$H_n^a = \sum_{i,j,k=1}^{12} C_{\mu_n \mathbf{L}_0, \nu_n \mathbf{L}}(i,j,k) G_i^{-1/2} H_j G_k^{-1/2} , \tag{2.27}$$

where the superscript a in the symbol H^a means that the matrix elements of the Hamiltonian are calculated in the Wannier function basis.

It should be mentioned that H_i^a cease to fulfill the relations valid in two-center approximation even if H_i are calculated in two-center approximation. It is connected with the fact that the Wannier functions contain contributions from the trial functions localized on various lattice sites.

B. Numerical details

The basic equations for calculating the trial functions, Eqs. (2.15) and (2.16) of the preceding subsection, have been solved by the iterative method. The iterative procedure consists of the following steps.

(i) The first step of the calculation. The radial part of the trial functions is assumed to be given (for example in the form of the Slater orbital for the whole crystal) or is taken from the preceding iteration. All matrix elements H_i and S_i and the functions $\bar{H}_n(r)$ and $\bar{S}_n(r)$ are then calculated. The method described in Ref. 36 is used to get the expansions of the trial functions about a displaced center,

$$\frac{R_\mathbf{L}(r)}{r_\mathbf{L}} Y_l^m(\theta,\phi) = \sum_{l'} \frac{1}{r} \alpha_{l'}(n,l,m \mid b,r) Y_{l'}^m(\vartheta,\varphi) , \tag{2.28}$$

where Y_l^m are the spherical harmonics, θ,ϕ and ϑ,φ are the coordinates in the axis systems with $\mathbf{L}$ and $\mathbf{L}_0$ as their origins, respectively, $\alpha_{l'}$ denotes the radial functions in the new axis system displaced by a distance $b = |\mathbf{L}-\mathbf{L}_0|$, the z axis in both axis systems is directed along the vector $\mathbf{L}-\mathbf{L}_0$, and n denotes the exponent of r in the Slater orbital. The method of calculating α_l is given in Ref. 36 and in order to get the expansion of the trial functions about a displaced center it is sufficient to express the angular parts of the trial functions in terms of spherical harmonics quantized in respect to the axis joining two lattice sites on which the trial functions are localized. It should be mentioned that α_l is the analytical function of r because the trial functions are analytical functions of $r_\mathbf{L}$ outside the muffin-tin sphere. The matrix elements of the Hamiltonian and overlap matrices are calculated first for the trial functions assumed in the form of Slater orbitals in the whole region and then the contributions from the muffin-tin spheres surrounding two centers in two-center integrals are calculated.

The calculation of the inhomogenous part of Eq. (2.15) and the coefficients of H_i^β and S_i^β in Eq. (2.16) complete the first step of the computation.

(ii) The solution of the differential equation. The solution of Eq. (2.15) is performed by Numerov's method starting from $r=0$ and from the muffin-tin radius r_m. Herman and Skillman's[37] mesh for integration is adopted with a small correction resulting from the assumption that the region $[0,r_m]$ is divided on an integer number of blocks. The first two values of $R(r)$ needed to start the solution from $r=0$ are obtained by two-term expansion of R into the power series,

$$R(r)=Ar^3(1+C_1 r)\ . \qquad (2.29)$$

The constant C_1 is obtained from the equation relating the coefficients at the lowest powers of r resulting from Eq. (2.15). The constant A and the eigenvalue λ are used to match the solutions obtained from the integration from $r=0$ and r_m and to fulfill the normalization condition for $R(r)$. The first two values for the backward integration are supplied by the values of $R(r,\{\beta_i\})$ for $r=r_m$ and $r=r_m-\Delta r$, where Δr is the step of the integration in the last block of the integration mesh.

(iii) The calculation of β_1. Equation (2.16) is used as the equation determining β_1. The Newton-Raphson method is used to solve Eq. (2.16). The new trial functions in which β_0 is adjusted to fulfill the continuity condition $R(r_m)=R(r_m\{\beta_i\})$ are then renormalized and are used as the initial trial functions in step (i) of the computations.

Steps (i)–(iii) are repeated until the eigenvalues and the values of β_1 obtained in the current and preceding iterations differ less than assumed criteria of accuracy (in the present calculation the criterion for the eigenvalue was $\eta_1=(\lambda_i-\lambda_{i-1})/\lambda_i=2.5\times10^{-4}$ and $\eta_2=(\beta_{1,i}-\beta_{1,i-1})/\beta_{1,i}=2.5\times10^{-4}$, where λ_i and $\beta_{1,i}$ are the values of λ and β_1 obtained in ith iteration.

The matrix elements of the Hamiltonian occurring in Eqs. (2.15) and (2.16) were calculated in two-center approximation. However, Eq. (2.28) applied to two trial functions allows us to calculate the integrals of the form

$$I_{\mu\nu}(\mathbf{L}_1,\mathbf{L}_2,\mathbf{L}_3)=\int d\tau\, V(\mathbf{r}-\mathbf{L}_1)f_{\mu,\mathbf{L}_2}(r)f_{\nu,\mathbf{L}_3}(r)\ . \qquad (2.30)$$

The integrals of this form were calculated to obtain three-center contributions to the matrix elements calculated in two-center approximation.

III. THE RESULTS AND DISCUSSION

The calculations have been performed for d bands of copper and paramagnetic nickel. The potentials were taken from Ref. 38 and the values of the potentials needed at the points of the integration mesh were obtained by the interpolation.

The resulting trial functions allow us to directly calculate the overlap matrix S and the Hamiltonian matrix H. The number of terms in the expansion of $G^{-1/2}$ needed

TABLE II. The results obtained for the d band of copper (all values in this and following tables are given in rydbergs). The last column of the table contains the Slater and Koster notation for the independent matrix elements of the Hamiltonian.

	Two-center approx.		Three-center approx.		Slater's
i	H_i	H_i^a	H_i	H_i^a	notation
1	0.404 21	0.409 14	0.392 41	0.397 01	$E_{xy,xy}(000)$
2	0.404 21	0.408 79	0.397 20	0.402 12	$E_{x^2-y^2,x^2-y^2}(000)$
3	0.004 18	0.007 52	0.005 00	0.008 21	$E_{yz,yz}(110)$
4	−0.010 09	−0.021 18	−0.010 27	−0.021 12	$E_{xy,xy}(110)$
5	0.011 09	0.020 02	0.013 26	0.021 90	$E_{x^2-y^2,x^2-y^2}(110)$
6	−0.005 18	−0.010 12	−0.005 55	−0.010 37	$E_{3z^2-r^2,3z^2-r^2}(110)$
7	0.004 26	0.009 82	0.004 58	0.009 83	$E_{xy,3z^2-r^2}(110)$
8	0.006 90	0.012 61	0.003 58	0.009 18	$E_{zx,yz}(110)$
9	0.002 12	0.003 88	0.004 34	0.006 18	$E_{yz,yz}(002)$
10	−0.000 29	−0.000 86	−0.000 40	−0.000 74	$E_{xy,xy}(002)$
11	−0.000 29	0.000 05	−0.001 02	−0.000 63	$E_{x^2-y^2,x^2-y^2}(002)$
12	−0.004 10	−0.005 36	−0.005 22	−0.006 30	$E_{3z^2-r^2,3z^2-r^2}(002)$
$(dd\sigma)_1$		−0.026 71		−0.026 50	
		−0.026 84		−0.026 80	
		−0.027 12		−0.027 40	
$(dd\sigma)_{\mathrm{av}}$		−0.026 89		−0.026 90	
$(dd\pi)_1$		0.020 02		0.021 90	
		0.020 13		0.017 39	
$(dd\pi)_{\mathrm{av}}$		0.020 08		0.019 65	
$(dd\delta)_1$		−0.005 09		−0.000 97	
		−0.004 18		−0.004 09	
		−0.004 59		−0.004 99	
		−0.004 45		−0.004 69	
$(dd\delta)_{\mathrm{av}}$		−0.004 58		−0.003 69	

to achieve a good accuracy in calculating the matrix elements in the Wannier function basis was tested by checking the orthogonality of Wannier functions localized on different lattice sites. It turned out that the use of four-term expansion in (2.26) ensured that all overlap integrals between the Wannier functions localized on different lattice sites were less than 2×10^{-5} and the norms of the Wannier functions differed from unity by less than 5×10^{-6} both for copper and nickel.

The independent matrix elements of the matrices H and H^a are listed in Tables II and III for copper and nickel, respectively. The values of H_i in the second columns of the tables are calculated in the two-center approximation. The differences between H_i and H_i^a are connected with the fact that the Wannier functions cease to be one-center functions. It causes the interaction matrix elements $(dd\sigma)_1$, $(dd\pi)_1$, and $(dd\delta)_1$ for the nearest neighbors to depend on which matrix elements H_i^a are taken for their calculation (see Appendix B). The differences between interaction matrix elements thus obtained show to what extent the two-center approximation is valid for the nearest neighbors in the case when the matrix elements H_i are calculated in the two-center approximation. In the two-center approximation H_{10}^a should be equal to H_{11}^a. Since they are significantly different the conclusion is that the two-center approximation is certainly not a good approximation for the second nearest neighbors.

The last two columns of the tables contain the matrix elements H_i and H_i^a calculated in three-center approximation. Equation (2.30) was used to calculate the main three-center (two-center in the case of H_1 and H_2) contributions stemming from integrals (2.30) containing the potential $V(\mathbf{r}-\mathbf{L})$ localized on all nearest neighbors of both lattice sites on which the trial functions involved are localized, and then the matrix elements H_i^a were recalculated. The comparison of H_i calculated in two- and three-center approximations shows *ex post facto* to what extent the two-center approximation made in the calculation of the energy functional was valid. The differences between most matrix elements H_i calculated in these two approximations for the nearest neighbors are small enough to justify the validity of the two-center approximation in the calculation of the energy functional. The only exception for the nearest neighbors is the difference in the case of H_8. The larger magnitude of three-center contributions in this case seems to be connected with space distributions of values of trial functions involved, with respect to the localization of the potential. Much larger relative differences between the values of H_i for the second nearest neighbors should affect the calculation of trial functions to a lesser extent because their contribution to the total energy is considerably less than that of the nearest neighbors.

All conclusions derived from the comparison of the values listed in Tables II and III seem to be, to a large extent, independent of the main approximation (neglecting *s-d* hybridization) made in the calculations. The hy-

TABLE III. The results obtained for the *d* band of paramagnetic nickel. The last column of the table contains the Slater and Koster notation for the independent matrix elements of the Hamiltonian.

	Two-center approx.		Three-center approx.		Slater's notation
i	H_i	H_i^a	H_i	H_i^a	
1	0.544 95	0.554 49	0.528 14	0.536 93	$E_{xy,xy}(000)$
2	0.544 95	0.554 18	0.534 95	0.544 84	$E_{x^2-y^2,x^2-y^2}(000)$
3	0.003 94	0.010 50	0.005 11	0.011 42	$E_{yz,yz}(110)$
4	−0.008 25	−0.028 45	−0.008 50	−0.028 26	$E_{xy,xy}(110)$
5	0.011 27	0.028 80	0.014 40	0.031 36	$E_{x^2-y^2,x^2-y^2}(110)$
6	−0.005 01	−0.014 31	−0.005 56	−0.014 61	$E_{3z^2-r^2,3z^2-r^2}(110)$
7	0.002 81	0.012 53	0.003 28	0.012 43	$E_{xy,3z^2-r^2}(110)$
8	0.007 32	0.018 64	0.002 53	0.013 60	$E_{zx,yz}(110)$
9	0.003 08	0.006 77	0.006 32	0.010 18	$E_{yz,yz}(002)$
10	−0.000 47	−0.001 82	−0.000 63	−0.001 48	$E_{xy,xy}(002)$
11	−0.000 47	0.000 31	−0.001 53	−0.000 66	$E_{x^2-y^2,x^2-y^2}(002)$
12	−0.005 02	−0.007 83	−0.006 65	−0.009 09	$E_{3z^2-r^2,3z^2-r^2}(002)$
$(dd\sigma)_1$		−0.035 52		−0.035 09	
		−0.035 69		−0.035 44	
		−0.036 01		−0.036 14	
$(dd\sigma)_{\text{av}}$		−0.035 74		−0.035 56	
$(dd\pi)_1$		0.028 80		0.031 36	
		0.029 14		0.025 02	
$(dd\pi)_{\text{av}}$		0.028 97		0.028 19	
$(dd\delta)_1$		−0.008 15		−0.002 19	
		−0.006 74		−0.006 73	
		−0.007 24		−0.007 78	
		−0.007 07		−0.007 43	
$(dd\delta)_{\text{av}}$		−0.007 30		−0.006 03	

bridization can certainly change slightly the values of matrix elements between d-band Wannier functions, but the relative values of the three-center contributions should remain qualitatively unchanged.

The best values of the interaction energies to compare with the present results would be the matrix elements obtained from the interpolation scheme based on the Wannier functions[39,40] fitted to the band structure for the same potential as was used in the present calculations. Since such results are not available we have chosen for the comparison three sets of results: the results given in Refs. 30 and 31 obtained from the interpolation scheme based on the Wannier functions for copper, and the results of Johnston *et al.*[28] for copper and nickel obtained by the model Hamiltonian method, in which the model Hamiltonian was represented in the mixed basis but the band structure fitted was calculated for the same potential as is used in the present paper. All these results are listed in Table IV.

As could be expected, the agreement between our values of H_1^a and H_2^a with the values of Johnston *et al.*[28] is much better than that between ours and the remaining two sets of results. It is easily explained by the fact that H_1^a and H_2^a are most sensitive to the choice of the potential; for example, a change of the muffin-tin zero shifts their values in the same way while conserving the difference between them. However, the difference between H_1^a and H_2^a as well as the other matrix elements for the nearest neighbors are closer to the results obtained from the interpolation scheme based on the Wannier functions than to the results of Johnston *et al.* Moreover, the relative differences between matrix elements of Refs. 30 and 31 and our results are, approximately, of the same magnitude, whereas the discrepancy between our value of H_5 and that obtained in Ref. 28 is much greater than differences between other matrix elements. The differences between our and Johnston *et al.*'s results seem to indicate that the Mueller type[21] of the model Hamiltonian method does not give the matrix elements of the Hamiltonian calculated in the basis of symmetry-adapted and best-localized d-band Wannier functions. It would also explain why, in particular, the values of $(dd\pi)_1$ listed in Tables II and III differ considerably from the values previously quoted (see, for example, Refs. 21 and 29). As long as the values of $(dd\sigma)_1$, $(dd\pi)_1$, and $(dd\delta)_1$ are considered to be the parameters of an interpolation scheme used to fit a band structure, their values can be arbitrarily chosen. However, if one wants to consider their values or the values of the matrix elements H_i^a as the hopping integrals between the localized orbitals, our results as well as the results of Refs. 30 and 31 are certainly more suitable. The approximate relations[22,24,26,27] derived for integrals $(dd\sigma)$, $(dd\pi)$, and $(dd\delta)$ seem also to be better fulfilled by the values obtained from the Mueller type of the interpolation scheme.

The agreement between our results and the results of Refs. 30 and 31 for the second nearest neighbors is

TABLE IV. The comparison of the present results for Cu (a) and paramagnetic Ni (b) with the results obtained by the model Hamiltonian method. The results of Johnston *et al.* (Ref. 28) are obtained for the same crystal potential as used in the present paper but by the Mueller type of interpolation scheme, the results given in Refs. 30 and 31 are obtained by the interpolation schemes based on Wannier functions but for different crystal potentials.

	Present results	Ref. 28	Ref. 30	Ref. 31
		(a) Cu		
H_1^a	0.397 01	0.4230	−0.579 92	−0.630 42
H_2^a	0.402 12	0.4190	−0.575 70	−0.630 56
H_3^a	0.008 21	0.0066	0.006 76	0.008 35
H_4^a	−0.021 12	−0.0215	−0.019 66	−0.019 30
H_5^a	0.021 90	0.0134	0.018 21	0.021 21
H_6^a	−0.010 37	−0.0081	−0.009 42	−0.011 18
H_7^a	0.009 83	0.0104	0.011 12	−0.008 59[a]
H_8^a	0.009 18	0.0103	0.012 39	0.013 20
H_9^a	0.006 18		0.003 90	0.003 43
H_{10}^a	−0.000 74		−0.000 04	0.001 58
H_{11}^a	−0.000 63		0.000 60	0.000 34
H_{12}^a	−0.006 30		−0.007 25	−0.004 35
		(b) Ni		
H_1^a	0.536 93	0.5760		
H_2^a	0.544 84	0.5694		
H_3^a	0.011 42	0.0089		
H_4^a	−0.028 26	−0.0288		
H_5^a	0.031 36	0.0184		
H_6^a	−0.014 61	−0.0108		
H_7^a	0.012 43	0.0130		
H_8^a	0.013 60	0.0101		

[a] The sign of H_7^a for Cu in Ref. 31 is probably misprinted.

worse than that for the first eight matrix elements H_i^a. The values of matrix elements for the second nearest neighbors are affected to a larger extent by all approximations made in our calculations, particularly by the assumption of the analytical part of the radial function in very simple form. However, it is worth noticing that the two-center approximation certainly ceases to be valid for the second nearest neighbors. This should be taken into account in interpolation schemes if the parameters occurring in a scheme are to have a physical meaning.

IV. CONCLUSIONS

The calculations reported in the present paper show that the modified variational method can give a quite good description of *d* bands of transition metals even if the *s-d* hybridization is neglected. The method allows us to avoid the calculation of the Bloch functions, the iteration procedure involved converges quickly, and the method seems to be the easiest and the quickest way to obtain the approximate description of the *d* band and to calculate the *d*-band Wannier functions at the same time.

The method can be easily extended to include the *s-d* hybridization. It would result in the necessity of solving two coupled sets of equations similar to that derived for the radial part of the *d*-band trial functions. The asymptotic form of the radial function can also be enriched and the only limitation of the method consists in the assumption that the radial and angular parts of the trial functions can be separated.

APPENDIX A: THE CALCULATION OF COEFFICIENTS IN THE EXPANSIONS OF MATRIX ELEMENTS OF OPERATORS CALCULATED IN THE WANNIER FUNCTION BASIS

An arbitrary sum of products,

$$\Pi^{(n)}_{\mu_0\mathbf{L}_0,\mu\mathbf{L}}=\sum_{\{\mu_i\},\{\mathbf{L}_i\}} M_{\mu_0\mathbf{L}_0,\mu_1\mathbf{L}_1}S_{\mu_1\mathbf{L}_1,\mu_2\mathbf{L}_2}\cdots S_{\mu_n\mathbf{L}_n,\mu\mathbf{L}} , \tag{A1}$$

can be reduced to the following form:

$$\Pi^{(n)}_{\mu_0\mathbf{L}_0,\mu\mathbf{L}}=\sum_{\{\mu_i\},\{\boldsymbol{\Delta}_i\}} M_{\mu_0\mathbf{L}_0,\mu_1\boldsymbol{\Delta}_1}S_{\mu_1\mathbf{L}_0,\mu_2\boldsymbol{\Delta}_2}\cdots S_{\mu_n\mathbf{L}_0,\mu\boldsymbol{\Delta}n} , \tag{A2}$$

where $\boldsymbol{\Delta}_i=\mathbf{L}_i-\mathbf{L}_{i-1}$, provided that the matrix elements $M_{v_1L_1,v_2L_2}$ are translationally invariant and that

$$\sum_i \boldsymbol{\Delta}_i=\mathbf{L}-\mathbf{L}_0 . \tag{A3}$$

Let us introduce the Kronecker delta

$$\delta_{\sum_i \boldsymbol{\Delta}_i,\mathbf{L}-\mathbf{L}_0}=\frac{1}{\Omega}\int d\boldsymbol{\rho}\exp\left[i\boldsymbol{\rho}\cdot\left[\sum_i\boldsymbol{\Delta}_i-\mathbf{L}+\mathbf{L}_0\right]\right] , \tag{A4}$$

where, for cubic lattices, $\Omega=(2\pi)^3$ and the domains of integrations over ρ_x, ρ_y, and ρ_z are $[-\pi,\pi]$. The use of (A4) allows us to remove the restriction (A3) imposed on the summations over $\boldsymbol{\Delta}_i$ in Eq. (A2) and to rewrite (A1) in the following form:

$$\Pi^{(n)}_{\mu_0L_0,\mu_nL}=\frac{1}{\Omega}\sum_{\{\mu_i\}}\int d\boldsymbol{\rho}\,M_{\mu_0,\mu_1}S_{\mu_1,\mu_2}\cdots \times S_{\mu_n,\mu}e^{-i\boldsymbol{\rho}\cdot(\mathbf{L}-\mathbf{L}_0)} , \tag{A5}$$

where

$$M_{\mu_i,\mu_j}=\sum_{\boldsymbol{\Delta}} M_{\mu_i\mathbf{L}_0,\mu_j\boldsymbol{\Delta}}e^{i\boldsymbol{\rho}\cdot\boldsymbol{\Delta}} , \tag{A6}$$

$$S_{\mu_i,\mu_j}=\sum_{\boldsymbol{\Delta}} S_{\mu_i\mathbf{L}_0,\mu_j\boldsymbol{\Delta}}e^{i\boldsymbol{\rho}\cdot\boldsymbol{\Delta}} . \tag{A7}$$

The matrix elements M_{μ_i,μ_j} and S_{μ_i,μ_j} can be in turn expressed in terms of independent matrix elements M_i and S_i,

$$M_{\mu_i,\mu_j}=\sum_l M_l\varphi_l(\boldsymbol{\rho};\mu_i,\mu_j) , \tag{A8}$$

$$S_{\mu_i,\mu_j}=\sum_l S_l\varphi_l(\boldsymbol{\rho};\mu_i,\mu_j) , \tag{A9}$$

where φ_l are simple linear combinations of trigonometrical functions similar to those given for energy matrix elements in Table II of Ref. 34 for the sc lattice. For example,

$$\begin{aligned}M_{yz,yz}=&M_1+M_3(4\cos\rho_x\cos\rho_y+4\cos\rho_x\cos\rho_z)\\&+M_4(4\cos\rho_y\cos\rho_z)+M_9(2\cos2\rho_y+2\cos\rho_z)\\&+M_{10}(2\cos2\rho_x)\end{aligned} \tag{A10}$$

and the remaining φ_l are equal to zero. In this way we can express the coefficients A_l, A_l^α, B_{l_1,l_2,l_3}, $B_{\mu L,vL_0}(l_1,l_2)$, $C_{\mu L,vL_0}(l_1,l_2,l_3)$, and $D_{\mu L,vL_0}(l_1,l_2,l_3,l_4)$ appearing in this paper in terms of simple integrals of trigonometrical functions,

$$A_l=\sum_{\mu_1,\mu_2}\frac{1}{(2\pi)^3}\int d\boldsymbol{\rho}\,\varphi_l(\boldsymbol{\rho};\mu_1;\mu_2)\varphi_l(\boldsymbol{\rho};\mu_2,\mu_1) , \tag{A11}$$

$$A_l^\alpha=\sum_{\mu_1^\alpha,\mu_2}\frac{1}{(2\pi)^3}\int d\boldsymbol{\rho}\,\varphi_l(\boldsymbol{\rho};\mu_1^\alpha,\mu_2)\varphi_l(\boldsymbol{\rho};\mu_2,\mu_1^\alpha) , \tag{A12}$$

$$B_{i,j,k}=\sum_{\mu_1,\mu_2,\mu_3}\frac{1}{(2\pi)^3}\int d\rho\,\varphi_i(\rho;\mu_1,\mu_2)\varphi_j(\rho;\mu_2,\mu_3)\varphi_k(\rho;\mu_3,\mu_1)\;, \tag{A13}$$

$$B_{\mu L,\upsilon L_0}(l_1,l_2)=\sum_{\mu_1}\frac{1}{(2\pi)^3}\int d\rho\,\varphi_{l_1}(\rho;\mu,\mu_1)\varphi_{l_2}(\rho;\mu_1,\upsilon)e^{i\rho\cdot(\mathbf{L}-\mathbf{L}_0)}\;, \tag{A14}$$

$$C_{\mu L,\upsilon L_0}(l_1,l_2,l_3)=\sum_{\mu_1,\mu_2}\frac{1}{(2\pi)^3}\int d\rho\,\varphi_{l_1}(\rho;\mu,\mu_1)\varphi_{l_2}(\rho;\mu_1,\mu_2)\varphi_{l_3}(\rho;\mu_2,\upsilon)e^{i\rho\cdot(\mathbf{L}-\mathbf{L}_0)}\;, \tag{A15}$$

$$\begin{aligned}D_{\mu L_0,\upsilon L}(l_1,l_2,l_3,l_4)=\sum_{\mu_1,\mu_2,\mu_3}\frac{1}{(2\pi)^3}\int d\rho\,&\varphi_{l_1}(\rho;\mu,\mu_1)\varphi_{l_2}(\rho;\mu_1,\mu_2)\varphi_{l_3}(\rho;\mu_2,\mu_3)\\&\times\varphi_{l_4}(\rho,\mu_3,\upsilon)e^{i\rho\cdot(\mathbf{L}-\mathbf{L}_0)}\;.\end{aligned} \tag{A16}$$

The summation over μ_1^α in Eq. (A12) denotes the summation over all μ_1 belonging to the representation α so that

$$A_l=\sum_\alpha A_l^\alpha\;. \tag{A17}$$

APPENDIX B: NOTATIONS USED FOR THE INDEPENDENT MATRIX ELEMENTS OF THE HAMILTONIAN AND THE RELATIONS BETWEEN INTERACTION INTEGRALS $(dd\eta)$ AND MATRIX ELEMENTS H_i^a

The notation used in the present paper is explained in Table I. The relations with the notations used by Slater and Koster,[34] by Fletcher[19] which is also used in Ref. 28, and by Mueller[21] are given in Table V.

The interaction integrals $(dd\eta)$ can be expressed in terms of the independent matrix elements H_i^a in the following way:

$$(dd\sigma)_1=\begin{cases}\frac{3}{2}H_4^a-\frac{1}{2}H_6^a\\ H_4^a-\frac{1}{\sqrt{3}}H_7^a\\ H_6^a-\sqrt{3}H_7^a\;,\end{cases} \tag{B1}$$

$$(dd\pi)_1=\begin{cases}H_5^a\\ H_3^a+H_8^a\;,\end{cases} \tag{B2}$$

and

$$(dd\delta)_1=\begin{cases}H_3^a-H_8^a\\ H_4^a+\sqrt{3}H_7^a\\ \frac{3}{2}H_6^a-\frac{1}{2}H_4^a\\ H_6^a+\frac{1}{\sqrt{3}}H_7^a\;.\end{cases} \tag{B3}$$

TABLE V. Comparison of our notation and that of Slater and Koster (Ref. 34), Fletcher (Ref. 19), and Mueller (Ref. 21).

	Notation of		
Ours	Slater and Koster	Fletcher	Mueller
H_1^a	$E_{xy,xy}(000)=E_{yz,yz}(000)=E_{xz,xz}(000)$	E_0	P_1
H_2^a	$E_{x^2-y^2,x^2-y^2}(000)=E_{3z^2-r^2,3z^2-r^2}(000)$	$E_0+\Delta$	P_2
H_3^a	$E_{yz,yz}(110)=E_{xy,xy}(011)$	A_2	P_4
H_4^a	$E_{xy,xy}(110)$	$-A_1$	P_3
H_5^a	$E_{x^2-y^2,x^2-y^2}(110)$	A_4	P_8
H_6^a	$E_{3z^2-r^2,3z^2-r^2}(110)$	$-\frac{4}{3}(\frac{1}{4}A_4+A_5)$	P_7
H_7^a	$E_{xy,3z^2-r^2}(110)$	$2/\sqrt{3}A_6$	P_6
H_8^a	$E_{zx,yz}(110)=E_{xy,yz}(101)$	A_3	P_5
H_9^a	$E_{yz,yz}(002)$		
H_{10}^a	$E_{xy,xy}(002)$		
H_{11}^a	$E_{x^2-y^2,x^2-y^2}(002)$		
H_{12}^a	$E_{3z^2-r^2,3z^2-r^2}(002)$		

If the two-center approximation is valid, Eqs. (B1), (B2), and (B3) should give the same values for $(dd\sigma)$, $(dd\pi)$, and $(dd\delta)$, respectively. The values of the interaction integrals calculated in different ways are listed in Tables II and III and differences between the values thus obtained show to what extent the two-center approximation is valid.

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