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Scattered impurity states in transition metals. I. Exploitation of the point-group symmetry for the linear-combination-of-atomic-orbitals method

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Localized impurities in crystals break down the translational symmetry, but the point-group symmetry of the crystal may often be preserved. To describe this situation the linear-combination-of-atomic-orbitals method is generalized to a scheme in which the wave functions of the unperturbed crystal can be calculated as the basis functions of the crystal point group, while in the traditional scheme they are the basis functions of the translational subgroup. In this new scheme the wave functions have a standing-wave-like character. The coefficient functions building up both kinds of the wave functions satisfy the same set of Wannier-Slater differential equations and the standing-wave-like wave functions are obtained from the Bloch's traveling wave functions by means of the projection-operator technique. In effect, the band structure of an ideal metal obtained when many electron states are considered is identical in both approaches. It is shown that a substantial reduction of the number of parameters entering the Hamiltonian as well as the perturbation matrices can be obtained providing the crystal point-group symmetry is exploited. Because of future applications, the calculation of the projected standing-wave-like wave functions as well as the reduction of the number of matrix parameters are illustrated for the example of cubic metals, in which several kinds of the atomic states, viz., *s*, *p*, and *d*, are taken into account.

I. INTRODUCTION

The linear-combination-of-atomic-orbitals (LCAO) method, introduced for perfect crystals by Bloch[1] and refined later by Slater and Koster,[2] has turned out to be a very useful tool for the calculation of the electronic structure of many crystals, including transition metals.[3–17] A predominant success of the LCAO method has been in the description of perfect crystals; nevertheless—beginning with the series of papers by Koster and Slater[18–20]—a considerable effort has been applied toward a description of the impurity states in metals with the aid of the LCAO approximation. The difficulty for the impurity states was the calculation of the perturbed wave function, which had to be represented with the aid of a Green's function expressed in the basis of the wave functions obtained for the perfect crystal. An exact calculation of a function of this kind is usually a very tedious task. It has been fully accomplished only in one special case when (a) the metal lattice is simple cubic, (b) the interaction between lattice atoms is limited to the nearest atomic neighbors, (c) electrons on the atoms are *s* type, and (d) the area of the impurity potential is extended over only one lattice site.[21] For any other impurity states in metals only simplified LCAO calculations have been done. One of the simplifications was based on a treatment of the Green's function with the aid of a stationary-phase method.[19,21,22] This method represented the electron wave function at large distances from the impurity center as a combination of the original LCAO wave function of the perfect metal and the scattered part which, in its mathematical form, was similar to the scattered free-electron wave function. Besides difficulties connected with the calculation of the coefficient multiplying the scattered part, this approximation could not be considered satisfactory because the scattered part of the perturbed LCAO wave function had coefficients at the atomic orbitals which did not satisfy the difference equations dictated by the crystal potential. Other LCAO methods applied to the treatment of the problem of an isolated impurity, or an impurity area in a metal, tried to exploit the point-group symmetry of the matrix as well as that of the impurity problem.[23,24] In this case the idea was to combine, linearly, the orbitals of the atoms equidistant from the impurity into the basis functions of irreducible representations of the crystal point group. This procedure, however, required a separate construction of the basis functions for any coordination sphere of the equidistant atoms. Another difficulty was the combination of the functions calculated for separate coordination spheres into one wave function representing the electron state in the whole metal.

The purpose of the present paper is to formulate a LCAO method for the treatment of metal impurities which is simpler than the former methods of the same, viz., LCAO, kind. For the first step we suggest LCAO wave functions for the perfect metal which are different from the Bloch LCAO wave functions. This suggestion is based on the observation that the Wannier-Slater (WS) equation[25,26] which has to be satisfied by the coefficient functions of the LCAO wave functions can be fulfilled by a larger class of the functions than the Bloch coefficient functions. This allows us to construct—instead of the traveling-wave functions of Bloch—a new set of wave functions which have the character of standing waves. These are no longer basis functions of the translational subgroup, but transform according to irreducible representations of the crystal point group. A step towards this construction has been done before with the aid of diagonalization of the WS operator.[27-32] This calculation was limited to s electrons only and was done with the lattice (cubic) harmonics times the Bessel spherical functions taken as trial functions. The calculation of the crystal states required no information about the Brillouin zone, but the diagonalization process turned out to be a tedious task, especially because of the large size of the functional basis that had to be taken into account. In effect, the convergence of the method was satisfactory only in a limited interval of the energy band, and the calculations which considered the whole band, for example, the total electron charge carried by the states within it, gave defective results.

We try to overcome this difficulty in the present paper. After a review and generalization of the LCAO method done in Sec. II, we construct in Secs. III and V the standing-wave-like LCAO wave functions with the aid of the projection technique applied to the Bloch wave functions; at the same time it is shown in Sec. IV how the basis of the atomic states considered can be extended arbitrarily. Since both kinds of crystal wave functions satisfy the same set of WS equations, the spectrum of the eigenenergies calculated within both approaches is the same. This allows us to avoid the convergence difficulties connected with certain areas of the energy spectrum and considerably simplifies the calculation of the required coefficient functions. In Sec. VI we use the point-group symmetry of the problem, which is the same for both the ideal and perturbed crystal. This allows us to relate the matrix elements of the Hamiltonian calculated between different pairs of the atomic orbitals. These matrix elements are often considered as adjustable parameters; therefore a method is given which establishes a set of independent parameters. A convenient procedure, avoiding summation over many site positions, is developed for the calculation of the Bloch Hamiltonian matrix elements in Sec. VII. The matrix elements of the perturbation calculated in the basis of the standing-wave-like coefficient functions are expressed in a convenient form in Sec. VIII. In the following paper,[33] hereafter referred to as II, the coefficient functions obtained in the present paper are submitted to scattering processes and then applied to the calculation of a crystal with impurities.

II. GENERALIZED LCAO METHOD

In this section we describe the LCAO approximation for the one-electron problem, which is more general than a traditional approach of this kind. Both an ideal crystal and a crystal perturbed by an impurity are considered. The trial wave function $\Psi(\mathbf{r})$ is expressed as a linear combination of atomic orbitals Φ_μ which are functions centered at each atomic site $\mathbf{R}_L$:

$$\Psi(\mathbf{r})=\sum_{L,\mu} A_{\mu L}\Phi_\mu(\mathbf{r}-\mathbf{R}_L)\ , \tag{2.1}$$

where

$$\mathbf{R}_L=L_1\mathbf{a}_1+L_2\mathbf{a}_2+L_3\mathbf{a}_3\ ,$$
$$L=(L_1,L_2,L_3),\quad L_j=0,\pm1,\pm2,\ldots \tag{2.2}$$

$\mathbf{a}_j$ are elementary translations, and

$$A_{\mu L}\equiv A_\mu(\mathbf{R}_L) \tag{2.3}$$

is called, henceforth, the coefficient function of the lattice-site position $\mathbf{R}_L$. For simplicity we consider Bravais lattices only. Subscript μ labels the type of the atomic orbital. In general, μ is characterized by five indices $\mu=\{b,l,\alpha,\beta,\zeta\}$; here, b is the principal quantum number, l is the orbital quantum number, α is the label of the irreducible representation of the crystal point group, β is the partner index within a set of the basis functions for the representation α, and ζ distinguishes between different functions belonging to the same α and β. Very often it is sufficient to abbreviate μ as, for example, $\mu=3s,4s,4x,4y,4z,3(x^2-y^2),3(3z^2-r^2),\ldots$; see Sec. IV for details. A usual simplification of the LCAO method is that a finite number σ of atomic orbitals is used in the calculations of (2.1). The choice of the set of atomic orbitals depends on the band problem and the desired accuracy of its solution. We suppose that atomic orbitals are normalized and orthogonal,

$$\langle\Phi_{\mu L}\mid\Phi_{\mu' L'}\rangle\equiv\int d^3r\,\Phi^*_\mu(\mathbf{r}-\mathbf{R}_L)\Phi_{\mu'}(\mathbf{r}-\mathbf{R}_{L'})=\delta_{LL'}\delta_{\mu\mu'}\ . \tag{2.4}$$

This requirement presents, in fact, no restriction because any originally nonorthogonal set of functions can be made orthogonal, with no change of symmetry.[34] Using Eq. (2.1) we reduce the one-electron Schrödinger equation

$$\hat{H}(\mathbf{r})\Psi(\mathbf{r})=E\Psi(\mathbf{r}) \tag{2.5}$$

to the matrix eigenequation

$$\sum_{L',\mu'} H_{\mu L,\mu' L'}A_{\mu' L'}=EA_{\mu L}\ , \tag{2.6}$$

where

$$H_{\mu L,\mu' L'}=\langle\Phi_{\mu L}\mid\hat{H}\mid\Phi_{\mu' L'}\rangle\equiv\int d^3r\,\Phi^*_\mu(\mathbf{r}-\mathbf{R}_L)\hat{H}(\mathbf{r})\times\Phi_{\mu'}(\mathbf{r}-\mathbf{R}_{L'})\ . \tag{2.7}$$

A special case of the LCAO method is the tight-binding approximation, in which the matrix elements (2.7) are assumed negligible when the positions $\mathbf{R}_L$ and $\mathbf{R}_{L'}$ are not the same lattice site, nor the nearest neighbors (NN's) to each other. No "range" of the interaction has to be specified in the present method.

As far as an ideal (periodic) crystal is considered, the property $\hat{H}(\mathbf{r}+\mathbf{R}_L)=\hat{H}(\mathbf{r})$ implies that

$$H_{\mu L,\mu' L'}=H_{\mu 0,\mu'(L'-L)}=H_{\mu(L-L'),\mu' 0}\ . \tag{2.8}$$

Therefore Eq. (2.6) may be rewritten as a difference equation

$$\sum_{L',\mu'} H_{\mu 0,\mu' L'}A_{\mu'(L+L')}=EA_{\mu L}\ , \tag{2.9}$$

where, in practice, the summation over L' involves only a very limited number of sites (e.g., **0** and NN's).

We may consider $A_\mu(\mathbf{R})$ as a continuous and infinitely differentiable function of $\mathbf{R}$, so

$$\begin{aligned}A_{\mu(L+L')} &\equiv A_\mu(\mathbf{R}_L+\mathbf{R}_{L'})\\ &= \left[A_\mu(\mathbf{R})+\frac{1}{1!}\mathbf{R}_{L'}\frac{\partial}{\partial\mathbf{R}}A_\mu(\mathbf{R})+\cdots\right]_{\mathbf{R}=\mathbf{R}_L}\\ &=[e^{\mathbf{R}_{L'}\cdot(\partial/\partial\mathbf{R})}A_\mu(\mathbf{R})]_{\mathbf{R}=\mathbf{R}_L}\ . \qquad (2.10)\end{aligned}$$

Hence the eigenequation (2.9) may be replaced by

$$\sum_{\mu'}\hat{W}_{\mu\mu'}(\mathbf{R})A_{\mu'}(\mathbf{R})=EA_\mu(\mathbf{R}) \quad \text{for } \mathbf{R}=\mathbf{R}_L\ . \qquad (2.11)$$

Here we introduced the so-called Wannier-Slater operator

$$\hat{W}_{\mu\mu'}(\mathbf{R})=\sum_{L'}H_{\mu 0,\mu' L'}e^{\mathbf{R}_{L'}\cdot(\partial/\partial\mathbf{R})}\ , \qquad (2.12)$$

which is a differential operator in $\mathbf{R}$ space and a $\sigma\times\sigma$ matrix in the space of the indices of the atomic orbitals.

One set of the solutions of (2.9) or (2.11) has the Bloch form

$$A_{\mu L}=A_\mu^{\mathbf{k}}(\mathbf{R}_L)=\frac{1}{\sqrt{N}}e^{i\mathbf{k}\cdot\mathbf{R}_L}a_\mu^{\mathbf{k}} \qquad (2.13)$$

(N is the total number of atoms in the crystal). Then the eigenvectors $a_\mu^{\mathbf{k}\lambda}$ and eigenvalues $E^{\mathbf{k}\lambda}$ [λ is the branch (band) label] satisfy the equation

$$\sum_{\mu'=1}^{\sigma}H_{\mu\mu'}^{\mathbf{k}}a_{\mu'}^{\mathbf{k}\lambda}=E^{\mathbf{k}\lambda}a_\mu^{\mathbf{k}\lambda},\quad \mu,\lambda=1,2,\ldots,\sigma \qquad (2.14)$$

where the Bloch Hamiltonian matrix is

$$H_{\mu\mu'}^{\mathbf{k}}=\sum_{L}H_{\mu 0,\mu' L}e^{i\mathbf{k}\cdot\mathbf{R}_L}\ . \qquad (2.15)$$

Comparing (2.12) and (2.15), we see that the Wannier-Slater operator is

$$\hat{W}_{\mu'\mu}(\mathbf{R})=H_{\mu'\mu}^{\partial/i\partial\mathbf{R}}\ , \qquad (2.16)$$

i.e., it can be obtained readily from the Bloch Hamiltonian matrix $H_{\mu\mu'}^{\mathbf{k}}$ through the substitution

$$\mathbf{k}\to\frac{\partial}{i\partial\mathbf{R}}\ . \qquad (2.17)$$

It should be stressed that besides the functions (2.13), other sets of solutions of (2.11) are possible. From this point of view Eq. (2.11) represents a more general approach to the LCAO method than those based on the Bloch LCAO wave functions. In the case of a one-dimensional crystal the new solutions are discussed in Sec. II of paper II, whereas the new solutions for three dimensions are presented in the next section. The coefficient functions given in the Bloch form (2.13) are orthonormal,

$$\sum_{L,\mu}A_{\mu L}^{*\mathbf{k}'\lambda'}A_{\mu L}^{\mathbf{k}\lambda}=\delta_{\mathbf{k}'\mathbf{k}}\delta_{\lambda'\lambda}\ , \qquad (2.18)$$

provided the Bloch eigenvectors for a given $\mathbf{k}$ are orthogonal and normalized, i.e.,

$$\sum_{\mu}a_\mu^{*\mathbf{k}\lambda'}a_\mu^{\mathbf{k}\lambda}=\delta_{\lambda'\lambda}\ . \qquad (2.19)$$

So far we have considered an ideal crystal, giving the basic equations concerning it and introducing the corresponding notation. Now we are going to consider the perturbed crystal, which is obtained from the perfect one by the replacement of the host atom at the crystal center ($L=0$) by an impurity atom; in general, a cluster of impurity atoms can be substituted for the atoms located around the crystal center. In any case the atomic orbitals of the impurity atoms are assumed to be of the same symmetry (although of different $|\mathbf{r}|$ dependence) as the host atoms. We will denote all quantities pertaining to the perturbed crystal by the same symbols we use for the ideal one, but with the superscript "per." In particular, the eigenequation (2.6) in the case of a perturbed crystal is

$$\sum_{L',\mu'}H_{\mu L,\mu' L'}^{\text{per}}A_{\mu' L'}^{\text{per}}=E^{\text{per}}A_{\mu L}^{\text{per}}\ . \qquad (2.20)$$

We will call a perturbation matrix the difference

$$V_{\mu L,\mu' L'}=H_{\mu L,\mu' L'}^{\text{per}}-H_{\mu L,\mu' L'}\ . \qquad (2.21)$$

It should be noted that this matrix includes effects due to the perturbation in the Hamiltonian as well as those due to the differences in the atomic orbitals connected with the substitution of the impurities. Denoting $\hat{H}^{\text{per}}=\hat{H}+\delta\hat{H}$ and $\Phi_{\mu L}^{\text{per}}=\Phi_{\mu L}+\delta\Phi_{\mu L}$, we have

$$\begin{aligned}V_{\mu L,\mu' L'}&=\langle\Phi_{\mu L}+\delta\Phi_{\mu L}\,|\,\hat{H}+\delta\hat{H}\,|\,\Phi_{\mu' L'}+\delta\Phi_{\mu' L'}\rangle-\langle\Phi_{\mu L}\,|\,\hat{H}\,|\,\Phi_{\mu' L'}\rangle\\ &=\langle\Phi_{\mu L}\,|\,\delta\hat{H}\,|\,\Phi_{\mu' L'}\rangle+\langle\delta\Phi_{\mu L}\,|\,\hat{H}\,|\,\Phi_{\mu' L'}\rangle+\langle\Phi_{\mu L}\,|\,\hat{H}\,|\,\delta\Phi_{\mu' L'}\rangle+\cdots\ . \qquad (2.22)\end{aligned}$$

Because of the short-range character of the interaction of the impurity atoms and the small number (one or few) of these atoms, the nonzero perturbation elements $V_{\mu L,\mu' L'}$ extend over a small number of positions $\mathbf{R}_L,\mathbf{R}_{L'}$ close to $\mathbf{0}$. We call this the perturbed region. Outside this region $H_{\mu L,\mu' L'}^{\text{per}}=H_{\mu L,\mu' L'}$, so the perturbed coefficient functions $A_{\mu L}^{\text{per}}$ and the corresponding eigenenergies E^{per} fulfill there the unperturbed equation (2.9) or (2.11).

III. SOLUTIONS POSSESSING PARTICULAR SYMMETRY PROPERTIES OBTAINED FOR AN IDEAL CRYSTAL

When impurities are introduced into an ideal crystal, they break its translational symmetry. But if this perturbation is in the form of a substitution of one atom, or a symmetric cluster of atoms, the point-group symmetry may be preserved completely or, at least, may be limited to a certain subgroup. Therefore, it is reasonable to classify the electron states of an unperturbed crystal according to the representations of the crystal point group $\mathcal{G}_0$.

This classification may be done in a systematic way using projection operator $\hat{\mathcal{O}}^{\omega}$. The superscript ω denotes the symmetry properties which are represented by three indices, so $\omega=\{\alpha,\beta,\gamma\}$; here, α labels the irreducible representation of the crystal point group $\mathcal{G}_0$; the symbols β and γ label, respectively, the row and column of this representation. The crystal is invariant upon the group of the point transformations, or rotations, $\hat{T}_j$,

$j=1,2,\ldots,d_g$, so the projection operator may be written in the form

$$\hat{\mathcal{O}}^{\alpha\beta\gamma}=C_{\alpha\beta\gamma}\sum_{j=1}^{d_g}D^{*}_{\alpha\beta\gamma}(T_j)\hat{\mathcal{P}}_{T_j} \ . \tag{3.1}$$

Here, $D_{\alpha\beta\gamma}(T_j)$ is the (β,γ) element of the unitary matrix of the αth representation of the point group, $C_{\alpha\beta\gamma}$ is the normalization factor, and $\hat{\mathcal{P}}_T$ is the operator whose action "rotates" the function:

$$\hat{\mathcal{P}}_T\Psi(\mathbf{r})=\Psi(\hat{T}^{-1}\mathbf{r}) \ . \tag{3.2}$$

Any wave function which transforms according to the βth row and γth column of the αth irreducible representation can be obtained from an arbitrary wave function with the aid of the projection

$$\Psi^{\omega}(\mathbf{r})\equiv\Psi^{\alpha\beta\gamma}(\mathbf{r})=\hat{\mathcal{O}}^{\alpha\beta\gamma}\Psi(\mathbf{r}) \ . \tag{3.3}$$

Because we are interested in the LCAO form (2.1) of the wave functions, we first examine the transformation properties of the atomic orbitals:

$$\begin{aligned}\hat{\mathcal{P}}_T\Phi_\mu(\mathbf{r}-\mathbf{R}_L)&=\Phi_\mu(\hat{T}^{-1}\mathbf{r}-\mathbf{R}_L)\\&=\Phi_\mu(\hat{T}^{-1}(\mathbf{r}-\hat{T}\mathbf{R}_L))\\&=\sum_\nu D_{\nu\mu}(T)\Phi_\nu(\mathbf{r}-\hat{T}\mathbf{R}_L) \ .\end{aligned} \tag{3.4}$$

The last equality in (3.4) expresses the fact that any rotated atomic orbital may be represented as a linear combination of the unrotated orbitals, which leads to the reducible—in general—representation $D_{\nu\mu}(T)$ (see examples given in Sec. IV):

$$\hat{\mathcal{P}}_T\Phi_\mu(\mathbf{r})=\sum_\nu D_{\nu\mu}(T)\Phi_\nu(\mathbf{r}) \ . \tag{3.4a}$$

Because the atomic orbitals form an orthonormal set (2.4), the induced representation $D_{\nu\mu}(T)$ is unitary. Now let us rotate the LCAO function (2.1):

$$\begin{aligned}\hat{\mathcal{P}}_T\Psi(\mathbf{r})&=\sum_{L,\mu}A_\mu(\mathbf{R}_L)\hat{\mathcal{P}}_T\Phi_\mu(\mathbf{r}-\mathbf{R}_L)\\&=\sum_{\nu,\mu}D_{\nu\mu}(T)\sum_L A_\mu(\mathbf{R}_L)\Phi_\nu(\mathbf{r}-\hat{T}\mathbf{R}_L) \ .\end{aligned} \tag{3.5}$$

We assume the crystal has the form of an enlarged Wigner-Seitz cell which contains N atoms. When the Born—von Kármán conditions are used, the space is filled up with these adjacent cells. We may change the order of labeling of the atom positions $L\rightarrow L'$ in such a way that $\mathbf{R}_{L'}=\hat{T}\mathbf{R}_L$. The label L' runs over all atoms belonging to the large cell, as was true in the case of the label L. Therefore we have, from (3.5),

$$\hat{\mathcal{P}}_T\Psi(\mathbf{r})=\sum_{L',\nu}\left[\sum_\mu D_{\nu\mu}(T)A_\mu(\hat{T}^{-1}\mathbf{R}_{L'})\right]\Phi_\nu(\mathbf{r}-\mathbf{R}_{L'}) \ , \tag{3.6}$$

since $\mathbf{R}_L=\hat{T}^{-1}\mathbf{R}_{L'}$.

As a final step we can perform a projection on the Bloch LCAO function which has coefficients $A^{\mathbf{k}\lambda}_{\mu L}$ and corresponds to the wave vector **k** and branch (band) λ:

$$\begin{aligned}\Psi^{\alpha\beta\gamma\mathbf{k}\lambda}(\mathbf{r})=C_{\alpha\beta\gamma}&\sum_{L,\mu,\nu,j}D^{*}_{\alpha\beta\gamma}(T_j)D_{\nu\mu}(T_j)\frac{1}{\sqrt{N}}\\&\times e^{i\mathbf{k}\cdot(\hat{T}_j^{-1}\mathbf{R}_L)}a^{\mathbf{k}\lambda}_\mu\Phi_\nu(\mathbf{r}-\mathbf{R}_L) \ .\end{aligned} \tag{3.7}$$

The argument of the exponential function may be transformed as

$$\begin{aligned}\mathbf{k}\cdot(\hat{T}_j^{-1}\mathbf{R}_L)&=(\hat{T}_j\mathbf{k})\cdot[\hat{T}_j(\hat{T}_j^{-1}\mathbf{R}_L)]\\&=(\hat{T}_j\mathbf{k})\cdot\mathbf{R}_L=\mathbf{R}_L\cdot\hat{T}_j\mathbf{k}\end{aligned} \tag{3.8}$$

since the scalar product remains invariant upon rotation. In effect, the projected wave function written in terms of the standing-wave-like projected coefficients (SWLPC's) $A^{\omega\mathbf{k}\lambda}_\nu(\mathbf{R}_L)$ is

$$\Psi^{\omega\mathbf{k}\lambda}(\mathbf{r})=\sum_{L,\nu}A^{\omega\mathbf{k}\lambda}_\nu(\mathbf{R}_L)\Phi_\nu(\mathbf{r}-\mathbf{R}_L) \ , \tag{3.9}$$

with

$$A^{\omega\mathbf{k}\lambda}_\nu(\mathbf{R})=\frac{C_\omega}{\sqrt{N}}\sum_\mu\mathcal{N}^{\omega}_{\nu\mu}(\mathbf{k},\mathbf{R})a^{\mathbf{k}\lambda}_\mu \tag{3.10}$$

and

$$\mathcal{N}^{\alpha\beta\gamma}_{\nu\mu}(\mathbf{k},\mathbf{R})=\sum_{j=1}^{d_g}e^{i\mathbf{R}\cdot\hat{T}_j\mathbf{k}}D^{*}_{\alpha\beta\gamma}(T_j)D_{\nu\mu}(T_j) \ . \tag{3.11}$$

The value of the normalization factor

$$C_{\alpha\beta\gamma}\equiv C_\alpha=(d_\alpha/d_g)^{1/2} \tag{3.11a}$$

will be justified below; d_α is the dimension of the representation α. The coefficients $A^{\omega\mathbf{k}\lambda}_\nu(\mathbf{R})$ are the standing-wave-like functions because, when calculated according to the formula (3.11), they become linear combinations of products of sine or cosine functions with arguments $k_nR_{n'}$, where $n,n'=x,y,z$ (see Sec. IV).

Now let us apply the Hamiltonian operator to the projected wave function (3.3) obtained with the aid of (3.1):

$$\hat{H}(\mathbf{r})\Psi^{\omega\mathbf{k}\lambda}(\mathbf{r})=C_\omega\sum_j D^{*}_\omega(T_j)\hat{H}(\mathbf{r})\hat{\mathcal{P}}_{T_j}\Psi^{\mathbf{k}\lambda}(\mathbf{r}) \ . \tag{3.12}$$

Because the crystal is invariant under the rotation T_j, the Hamiltonian must commute with the rotation operator

$$\hat{H}(\mathbf{r})\hat{\mathcal{P}}_{T_j}=\hat{\mathcal{P}}_{T_j}\hat{H}(\mathbf{r}) \ . \tag{3.13}$$

Therefore, from (3.12),

$$\hat{H}(\mathbf{r})\Psi^{\omega\mathbf{k}\lambda}(\mathbf{r})=E^{\mathbf{k}\lambda}\Psi^{\omega\mathbf{k}\lambda}(\mathbf{r}) \ , \tag{3.14}$$

so the eigenenergy $E^{\mathbf{k}\lambda}$ is the same as for the Bloch solution (2.14) and does not depend on the label ω. Applying transformations (2.5)—(2.11) to the function (3.9), we obtain, from (3.14), the following equation satisfied by the SWLPC's:

$$\sum_\nu\hat{W}_{\mu\nu}(\mathbf{R})A^{\omega\mathbf{k}\lambda}_\nu(\mathbf{R})=E^{\mathbf{k}\lambda}A^{\omega\mathbf{k}\lambda}_\mu(\mathbf{R}) \ . \tag{3.15}$$

The fact that the eigenenergy $E^{\mathbf{k}\lambda}$ of Eqs. (3.14) or (3.15) does not depend on ω reflects a well-known property that the band energy is the same for any member of the star of the vector $\mathbf{k}$, so this energy is d_g-fold degenerate:

$$E^{(\hat{T}_j\mathbf{k})\lambda}=E^{\mathbf{k}\lambda},\quad j=1,\ldots,d_g\ . \tag{3.16}$$

The subscript ω runs over the d_g different combinations of α, β, and γ, because, as shown in group theory,

$$d_g=\sum_{\alpha} d_\alpha^2\ . \tag{3.17}$$

Therefore the number of electron states remains unchanged if instead of $N\sigma$ Bloch solutions $A_\mu^{\mathbf{k}\lambda}(\mathbf{R})$, where $\mathbf{k}\in \mathrm{v}_{\mathrm{BZ}}$, we take $d_g(N/d_g)\sigma$ projected solutions $A_\mu^{\omega\mathbf{k}\lambda}(\mathbf{R})$, where $\mathbf{k}\in \mathrm{v}_{\mathrm{IBZ}}$. Symbol v_{BZ} denotes the region of the reciprocal space known as the Brillouin zone (BZ), and $\mathrm{v}_{\mathrm{IBZ}}$ the irreducible part of it; v_{BZ} and $\mathrm{v}_{\mathrm{IBZ}}$ are related by

$$\mathrm{v}_{\mathrm{BZ}}=\sum_{j=1}^{d_g}\hat{T}_j\mathrm{v}_{\mathrm{IBZ}}\ . \tag{3.17a}$$

We conclude this section by the examination of the orthogonality and normalization properties of SWLPC's; use is made here of (3.9)—(3.11). We obtain

$$\begin{aligned}\int d^3r\,\Psi^{*\omega'\mathbf{k}'\lambda'}(\mathbf{r})\Psi^{\omega\mathbf{k}\lambda}(\mathbf{r})&=\sum_{L,\nu}A_\nu^{*\omega'\mathbf{k}'\lambda'}(\mathbf{R}_L)A_\nu^{\omega\mathbf{k}\lambda}(\mathbf{R}_L)\\&=\sum_{\mu,\mu',j,j'}\frac{(d_{\alpha'}d_\alpha)^{1/2}}{d_g}\left[\sum_L\frac{1}{N}e^{i(\hat{T}_j\mathbf{k}-\hat{T}_{j'}\mathbf{k}')\cdot\mathbf{R}_L}\right]D_{\omega'}(T_{j'})D_\omega^*(T_j)\left[\sum_\nu D_{\nu\mu'}^*(T_{j'})D_{\nu\mu}(T_j)\right](a_{\mu'}^{*\mathbf{k}'\lambda'}a_\mu^{\mathbf{k}\lambda})\ .\end{aligned} \tag{3.18}$$

The sum over L given inside the first pair of large parentheses leads to $\delta_{(\hat{T}_j\mathbf{k}),(\hat{T}_{j'}\mathbf{k}')}$, which for $\mathbf{k}\in\mathrm{v}_{\mathrm{IBZ}}$ and $\mathbf{k}'\in\mathrm{v}_{\mathrm{IBZ}}$, goes to $\delta_{j'j}\delta_{\mathbf{k}'\mathbf{k}}$. So the sum over ν in the second pair of large parentheses has to be calculated for $j'=j$. Taking into account that the matrices $D_{\mu\nu}$ are unitary and form a representation, we have

$$\begin{aligned}\sum_\nu D_{\nu\mu'}^*(T_j)D_{\nu\mu}(T_j)&=\sum_\nu D_{\mu'\nu}^\dagger(T_j)D_{\nu\mu}(T_j)\\&=\sum_\nu D_{\mu'\nu}(T_j^{-1})D_{\nu\mu}(T_j)\\&=D_{\mu'\mu}(T_j^{-1}T_j)=\delta_{\mu'\mu}\ .\end{aligned} \tag{3.19}$$

Because of the $\delta_{\mu'\mu}$ and $\delta_{\mathbf{k}'\mathbf{k}}$ obtained above, the sum over μ taken for the last pair of parentheses in (3.18) gives $\delta_{\lambda'\lambda}$ [see (2.19)]. Therefore, we have, for (3.18),

$$\left[\sum_j\frac{(d_{\alpha'}d_\alpha)^{1/2}}{d_g}D_{\alpha'\beta'\gamma'}(T_j)D_{\alpha\beta\gamma}^*(T_j)\right]\delta_{\mathbf{k}'\mathbf{k}}\delta_{\lambda'\lambda}\ . \tag{3.20}$$

The remaining sum over j is—owing to the orthogonality relation of the irreducible representations [see Eq. (5.2)]—equal to $\delta_{\alpha'\alpha}\delta_{\beta'\beta}\delta_{\gamma'\gamma}\equiv\delta_{\omega'\omega}$. Finally,

$$\sum_{L,\nu}A_\nu^{*\omega'\mathbf{k}'\lambda'}(\mathbf{R}_L)A_\nu^{\omega\mathbf{k}\lambda}(\mathbf{R}_L)=\delta_{\omega'\omega}\delta_{\mathbf{k}'\mathbf{k}}\delta_{\lambda'\lambda}\ . \tag{3.21}$$

This proves that the SWLPC's are exactly orthonormal.

IV. SYMMETRY PROPERTIES OF ATOMIC ORBITALS AND THEIR USE

The projection-operator technique considered in Sec. III will be discussed here and in the next section in detail, and will be illustrated with the example of Bravais crystals, which are invariant under the operations of the point group O_h; these are the sc, fcc, and bcc lattices. The group O_h consists of $d_g=48$ elements (rotations). There are ten irreducible representations for this group. In Table I we list their symbols α as used by different authors, their dimensions d_α, and the basis functions $\phi_{\alpha\beta}(\mathbf{r})$ which generate the representations $D_{\alpha\beta\gamma}(T_j)$ according to the formula

TABLE I. Basis functions $\phi_{\alpha\beta}(\mathbf{r})$ generating the irreducible representations $D_{\alpha\beta\gamma}(T_j)$ of the cubic point group O_h.

		α						
a	b	c	d	Our	d_α	$\phi_{\alpha1}(\mathbf{r})$	$\phi_{\alpha2}(\mathbf{r})$	$\phi_{\alpha3}(\mathbf{r})$
Γ_1	α	A_{1g}	Γ_1	1^+	1	1		
Γ_2	β'	A_{2g}	Γ_2	2^+	1	$x^4(y^2-z^2)+\cdots$		
Γ_{12}	γ	E_g	Γ_3	3^+	2	$(x^2-y^2)/2$	$(3z^2-r^2)/\sqrt{12}$	
$\Gamma_{15'}$	δ'	T_{1g}	Γ_4	4^+	3	$yz(y^2-z^2)$	$zx(z^2-x^2)$	$xy(x^2-y^2)$
$\Gamma_{25'}$	ϵ	T_{2g}	Γ_5	5^+	3	yz	zx	xy
$\Gamma_{1'}$	α'	A_{1u}	Γ_1'	1^-	1	$xyz[x^4(y^2-z^2)+\cdots]$		
$\Gamma_{2'}$	β	A_{2u}	Γ_2'	2^-	1	xyz		
$\Gamma_{12'}$	γ'	E_u	Γ_3'	3^-	2	$xyz(3z^2-r^2)$	$-xyz(x^2-y^2)\sqrt{3}$	
Γ_{15}	δ	T_{1u}	Γ_4'	4^-	3	x	y	z
Γ_{25}	ϵ'	T_{2u}	Γ_5'	5^-	3	$x(y^2-z^2)$	$y(z^2-x^2)$	$z(x^2-y^2)$

[a] Bouckaert, Smoluchowski, and Wigner (Ref. 35).

[b] Von der Lage and Bethe (Ref. 36).

[c] Molecular physics.

[d] Bethe (Ref. 37) and Overhauser (Ref. 38).

$$\hat{\mathscr{P}}_{T_j}\phi_{\alpha\gamma}(\mathbf{r})=\sum_{\beta=1}^{d_\alpha} D_{\alpha\beta\gamma}(T_j)\phi_{\alpha\beta}(\mathbf{r}) \ ,$$

$$\gamma=1,2,\ldots,d_\alpha,\ \ j=1,2,\ldots,d_g \ . \tag{4.1}$$

The operator $\hat{\mathscr{P}}_T$ is defined through Eq. (3.2). The basis functions, chosen in Table I, warrant all induced representations to be *unitary* and *real.* Tables of these representations may be found in Ref. 39, p. 231, for $\alpha=1^\pm,2^\pm,3^\pm,4^\pm$, while for $\alpha=5^\pm$ we have

$$D_{5^\pm\beta\gamma}(T_j)=D_{2^\pm 11}(T_j)D_{4^+\beta\gamma}(T_j) \ .$$

It should be noted that the matrices of the representation $\alpha=4^-$ coincide with the matrices of rotations,

$$T_{j\gamma\beta}=D_{4^-\gamma\beta}(T_j) \ , \tag{4.2}$$

where

$$\hat{\mathscr{P}}_{T_j^{-1}}r_\gamma=(\hat{T}_j\mathbf{r})_\gamma=\sum_\beta T_{j\gamma\beta}r_\beta \ . \tag{4.3}$$

The property (4.2) follows from the fact that the basis of the representation $\alpha=4^-$ consists of the Cartesian coordinates of the argument vector $\mathbf{r}=(r_1,r_2,r_3)\equiv(x,y,z)$; cf. also (4.1) and (3.2).

Atomic orbitals are—in general—the basis functions of the rotational group. They can be easily transformed into a set of the basis functions of the crystal point group, for example, a cubic group. Then the angular part of the atomic orbital is a lattice harmonic, for example, a cubic harmonic;[36,40] the transformed atomic orbitals are

$$\Phi_\mu(\mathbf{r})\equiv\Phi_{bl\alpha\beta\zeta}(\mathbf{r})=\Phi_{bl}(r)\phi^{l\zeta}_{\alpha\beta}(\mathbf{r}/r)$$

$$=\Phi_{bl}(r)\sum_{m=-l}^{l} C^{lm}_{\alpha\beta\zeta}Y_{lm}(\mathbf{r}/r) \ . \tag{4.4}$$

Here, $Y_{lm}(\mathbf{r}/r)$ is a spherical harmonic of orbital quantum number l and magnetic quantum number m. Index b represents the principal quantum number, α is the irreducible representation, and its row is β. Index ζ distinguishes between different functions (4.4) belonging to the same representation and the same row; this index occurs for $l\geq 5$ only.

Some angular parts $\phi^{l\zeta}_{\alpha\beta}(\mathbf{r}/r)$ of the functions (4.4) may be found among the basis functions $\phi_{\alpha\beta}(\mathbf{r})$ given in Table I (normalization factors are omitted there). The value of l equals the degree of the polynomial in $\mathbf{r}$. The functions given in Table I represent a full set of the basis functions $\phi^{l\zeta}_{\alpha\beta}(\mathbf{r})$ for $l=0=s$ (see $\alpha=1^+$), $l=1=p$ ($\alpha=4^-$), and $l=2=d$ ($\alpha=5^+$ and 3^+), while for higher l other basis functions are necessary.

It is convenient to use the functions $\Phi_{bl\alpha\beta\zeta}(\mathbf{r})$ given in Eq. (4.4) as the atomic orbitals for the LCAO expansions, instead of the original $\Phi_{bl}(r)Y_{lm}(\mathbf{r}/r)$ functions. In practice, the full index $\mu=\{b,l,\alpha,\beta,\zeta\}$ may be abbreviated to b and the formula of the basis function, e.g., $\mu=\{3,2,5^+,2\}$ is replaced by $3zx$, $\{4,1,4^-,1\}$ by $4x$, $\{4,0,1^+,1\}$ by $4s$, etc. Also, the principal quantum number may be omitted if only one value of b is used for a given LCAO expansion. In the further formulas, where the symmetry properties of the basis functions are taken into account, we use an abbreviation in which the index b represents three indices (b,l,ζ), without losing generality. Therefore, henceforth, $\mu=\{b,\alpha,\beta\}$.

Owing to the choice of the atomic orbitals in the form (4.4), the representation $D_{\nu\mu}(T)$ defined by Eq. (3.4) has a block-diagonal form, being a direct sum of the corresponding irreducible representations:

$$D_{\mu'\mu}(T)\equiv D_{b'\alpha'\beta',b\alpha\beta}(T)=\delta_{b'b}\delta_{\alpha'\alpha}D_{\alpha\beta'\beta}(T) \ . \tag{4.5}$$

Therefore the general formulas (3.9)—(3.11), defining the SWLPC functions, may be simplified to

$$\Psi^{\omega\mathbf{k}\lambda}(\mathbf{r})=\sum_{L,b',\alpha',\beta'} A^{\omega\mathbf{k}\lambda}_{b'\alpha'\beta'}(\mathbf{R}_L)\Phi_{b'\alpha'\beta'}(\mathbf{r}-\mathbf{R}_L) \ , \tag{4.6}$$

where

$$A^{\omega\mathbf{k}\lambda}_{b'\alpha'\beta'}(\mathbf{R})=\left[\frac{d_\alpha}{d_gN}\right]^{1/2}\sum_{\gamma'}\mathscr{N}^{\ \omega}_{\alpha'\beta'\gamma'}(\mathbf{k},\mathbf{R})a^{\mathbf{k}\lambda}_{b'\alpha'\gamma'} \tag{4.7}$$

and

$$\mathscr{N}^{\ \omega}_{\omega'}(\mathbf{k},\mathbf{R})\equiv\mathscr{N}^{\ \alpha\beta\gamma}_{\alpha'\beta'\gamma'}(\mathbf{k},\mathbf{R})$$

$$=\sum_{j=1}^{d_g} D^*_{\alpha\beta\gamma}(T_j)D_{\alpha'\beta'\gamma'}(T_j)e^{i\mathbf{R}\cdot\hat{T}_j\mathbf{k}} \ . \tag{4.8}$$

We see that the $d_g\times d_g$ matrix $\{\mathscr{N}^{\ \omega}_{\omega'}\}$, composed of the functions dependent on $\mathbf{k}$ and $\mathbf{R}$, is sufficient to obtain all SWLPC functions based on an arbitrarily large set of the atomic orbitals.

V. CONSTRUCTION OF THE STANDING-WAVE-LIKE COEFFICIENT FUNCTIONS

The properties and the form of the functions $\mathscr{N}^{\ \omega}_{\omega'}(\mathbf{k},\mathbf{R})$, Eq. (4.8), determining the SWLPC functions, Eq. (4.7), are discussed in this section. In the case of $\mathbf{R}=0$, or $\mathbf{k}=0$, the function $\mathscr{N}^{\ \omega}_{\omega'}(\mathbf{k},\mathbf{R})$ may be easily calculated,

$$\mathscr{N}^{\ \omega}_{\omega'}(\mathbf{k},0)=\mathscr{N}^{\ \omega}_{\omega'}(0,\mathbf{R})=\frac{d_g}{d_\alpha}\delta_{\omega\omega'} \ , \tag{5.1}$$

owing to the orthogonality relation of the irreducible representations

$$\sum_{j=1}^{d_g} D^*_{\alpha\beta\gamma}(T_j)D_{\alpha'\beta'\gamma'}(T_j)=\frac{d_g}{d_\alpha}\delta_{\alpha\alpha'}\delta_{\beta\beta'}\delta_{\gamma\gamma'} \ . \tag{5.2}$$

According to (4.7) and (5.1), the SWLPC function calculated at the position of the central atom is

$$A^{\alpha\beta\gamma\mathbf{k}\lambda}_{b'\alpha'\beta'}(0)=\left[\frac{d_g}{d_\alpha N}\right]^{1/2}\delta_{\alpha\alpha'}\delta_{\beta\beta'}a^{\mathbf{k}\lambda}_{b'\alpha\gamma} \ . \tag{5.3}$$

This expression is diagonal with respect to the representation indices α and α' and the row indices β and β'; it is also independent of β. The corresponding contribution to the electron number is

$$\rho^{\alpha\beta\gamma\mathbf{k}\lambda}(0)=\sum_{b',\alpha',\beta'}|A^{\alpha\beta\gamma\mathbf{k}\lambda}_{b'\alpha'\beta'}(0)|^2=\frac{d_g}{d_\alpha N}\sum_{b'}|a^{\mathbf{k}\lambda}_{b'\alpha\gamma}|^2 \ . \tag{5.4}$$

The sum of (5.4) over all contributions due to different symmetry indices gives

$$\rho^{\mathbf{k}\lambda}(\mathbf{0})=\sum_{\alpha,\beta,\gamma}\rho^{\alpha\beta\gamma\mathbf{k}\lambda}(\mathbf{0})$$
$$=\frac{d_g}{N}\sum_{b,\alpha,\gamma}|a_{b\alpha\gamma}^{\mathbf{k}\lambda}|^2\left[\sum_{\beta=1}^{d_\alpha}\frac{1}{d_\alpha}\right]=\frac{d_g}{N}\;. \qquad (5.5)$$

In the last step the normalization of the Bloch vector $a_\mu^{\mathbf{k}\lambda}$ has been taken into account; see Eq. (2.19). The coefficient d_g occurring in the result (5.5) renders the fact that any state labeled by $\mathbf{k}\in v_{\mathrm{IBZ}}$ represents a contribution of d_g vectors $(\hat{T}_j\mathbf{k})\in v_{\mathrm{BZ}}$, where $j=1,2,\ldots,d_g$. We note that

$$\rho^{\mathbf{k}\lambda}(\mathbf{0})=\sum_{\omega,\mu}|A_\mu^{\omega\mathbf{k}\lambda}(\mathbf{0})|^2$$

is the expression which occurs in the denominators of Eqs. (4.3) and (4.13) of the following paper (II).

For arbitrary $\mathbf{k}$ and $\mathbf{R}$ the functions $\mathcal{N}_{\omega'}^{\omega}(\mathbf{k},\mathbf{R})$ may be readily calculated according to the formula (4.8) using the known matrices $D_{\alpha\beta\gamma}(T_j)$. If representations are *real*,

$$D_\omega^*(T)=D_\omega(T)\;, \qquad (5.6)$$

as it is chosen in the case of the group O_h, then the matrix $\{\mathcal{N}_{\omega'}^{\omega}\}$ is symmetrical with respect to the interchange of ω and ω':

$$\mathcal{N}_{\omega}^{\omega'}(\mathbf{k},\mathbf{R})=\mathcal{N}_{\omega'}^{\omega}(\mathbf{k},\mathbf{R})\;. \qquad (5.7)$$

Further particular properties of this matrix for the cubic group O_h follow from the fact that $O_h=O\otimes C_i$, where group O includes all proper rotations T_j, $j=1,2,\ldots,24$, and group C_i consists of the identity E and inversion I operations. Let us denote the representation of the group O by $D_{\alpha\beta\gamma}(T_j)$, $\alpha=1,2,\ldots,5$, $j=1,2,\ldots,24$. Among ten representations of the group O_h, five of them, denoted α^+, are *even* with respect to inversion,

$$D_{\alpha^+\beta\gamma}(T_j)=D_{\alpha\beta\gamma}(T_j),\quad D_{\alpha^+\beta\gamma}(IT_j)=+D_{\alpha\beta\gamma}(T_j)\;, \qquad (5.8a)$$

whereas five representations α^- are *odd*,

$$D_{\alpha^-\beta\gamma}(T_j)=D_{\alpha\beta\gamma}(T_j),\quad D_{\alpha^-\beta\gamma}(IT_j)=-D_{\alpha\beta\gamma}(T_j)\;. \qquad (5.8b)$$

It is evident from Table I that the parity of a representation coincides with the parity of its basis functions. Using (5.8) for the evaluation of (4.8), we find that $\mathcal{N}_{\omega'}^{\omega}$ is purely real when representations involved in its indices have the same parity,

$$\mathcal{N}_{\alpha'^+\beta'\gamma'}^{\alpha^+\beta\gamma}(\mathbf{k},\mathbf{R})=\mathcal{N}_{\alpha'^-\beta'\gamma'}^{\alpha^-\beta\gamma}(\mathbf{k},\mathbf{R})=\mathcal{N}_{\alpha\beta\gamma,\alpha'\beta'\gamma'}^{\cos}(\mathbf{k},\mathbf{R})\;, \qquad (5.9)$$

and purely imaginary when representations have different parities,

$$\mathcal{N}_{\alpha'^-\beta'\gamma'}^{\alpha^+\beta\gamma}(\mathbf{k},\mathbf{R})=\mathcal{N}_{\alpha'^+\beta'\gamma'}^{\alpha^-\beta\gamma}(\mathbf{k},\mathbf{R})=i\mathcal{N}_{\alpha\beta\gamma,\alpha'\beta'\gamma'}^{\sin}(\mathbf{k},\mathbf{R})\;, \qquad (5.10)$$

where

$$\mathcal{N}_{\alpha\beta\gamma,\alpha'\beta'\gamma'}^{f}(\mathbf{k},\mathbf{R})=\sum_{j=1}^{24}D_{\alpha\beta\gamma}(T_j)D_{\alpha'\beta'\gamma'}(T_j)2f(\mathbf{R}\cdot\hat{T}_j\mathbf{k}) \qquad (5.11)$$

for $f=\cos,\sin$. Thus the full 48×48 matrix $\{\mathcal{N}_{\omega'}^{\omega}\}$ is partitioned into four 24×24 submatrices,

$$\{\mathcal{N}_{\omega'}^{\omega}\}=\begin{bmatrix}\{\mathcal{N}_{\omega\omega'}^{\cos}\} & i\{\mathcal{N}_{\omega\omega'}^{\sin}\}\\ i\{\mathcal{N}_{\omega\omega'}^{\sin}\} & \{\mathcal{N}_{\omega\omega'}^{\cos}\}\end{bmatrix}\;, \qquad (5.12)$$

each submatrix being symmetrical, according to (5.11),

$$\mathcal{N}_{\omega\omega'}^{f}=\mathcal{N}_{\omega'\omega}^{f}\;. \qquad (5.13)$$

Therefore the matrix $\mathcal{N}_{\omega'}^{\omega}$ is defined by $24\times(24+1)/2=300$ elements of the upper triangle of $\mathcal{N}_{\omega\omega'}^{\cos}$ and the same number of elements of $\mathcal{N}_{\omega\omega'}^{\sin}$.

Owing to some properties of the representations $D_{\alpha\beta\gamma}(T_j)$ of the group O occurring in Eq. (5.11), the number of independent elements is less than 600, mentioned above. By direct inspection of the tables of $D_{\alpha\beta\gamma}(T_j)$ [see the inferences below Eq. (4.1)], the following properties are established:

$$[D_{211}(T_j)]^2=D_{111}(T_j)=1\;, \qquad (5.14a)$$

$$D_{5\beta\gamma}(T_j)=D_{211}(T_j)D_{4\beta\gamma}(T_j)\;, \qquad (5.14b)$$

$$\begin{aligned}D_{322}(T_j)&=D_{211}(T_j)D_{311}(T_j)\;,\\ D_{321}(T_j)&=-D_{211}(T_j)D_{312}(T_j)\;.\end{aligned} \qquad (5.14c)$$

Therefore the following relations between different matrix elements hold:

$$\mathcal{N}_{211,211}^{f}=\mathcal{N}_{111,111}^{f} \qquad (5.15a)$$

from (5.14a),

$$\mathcal{N}_{4\beta'\gamma',5\beta\gamma}^{f}=\mathcal{N}_{4\beta\gamma,5\beta'\gamma'}^{f}\;, \qquad (5.15b)$$

$$\mathcal{N}_{5\beta\gamma,5\beta'\gamma'}^{f}=\mathcal{N}_{4\beta\gamma,4\beta'\gamma'}^{f}\;, \qquad (5.15c)$$

$$\mathcal{N}_{211,4\beta\gamma}^{f}=\mathcal{N}_{111,5\beta\gamma}^{f}\;, \qquad (5.15d)$$

$$\mathcal{N}_{211,5\beta\gamma}^{f}=\mathcal{N}_{111,4\beta\gamma}^{f}\;, \qquad (5.15e)$$

from (5.14b) and (5.14a), and

$$\begin{aligned}&\mathcal{N}_{211,311}^{f}=\mathcal{N}_{111,322}^{f},\quad \mathcal{N}_{211,321}^{f}=-\mathcal{N}_{111,312}^{f}\;,\\ &\mathcal{N}_{211,322}^{f}=\mathcal{N}_{111,311}^{f},\quad \mathcal{N}_{211,312}^{f}=-\mathcal{N}_{111,321}^{f}\;,\end{aligned} \qquad (5.15f)$$

$$\begin{aligned}&\mathcal{N}_{322,322}^{f}=\mathcal{N}_{311,311}^{f},\quad \mathcal{N}_{321,322}^{f}=-\mathcal{N}_{311,312}^{f}\;,\\ &\mathcal{N}_{312,312}^{f}=\mathcal{N}_{321,321}^{f},\quad \mathcal{N}_{312,322}^{f}=-\mathcal{N}_{311,321}^{f}\;,\end{aligned} \qquad (5.15g)$$

$$\begin{aligned}&\mathcal{N}_{311,5\beta\gamma}^{f}=\mathcal{N}_{322,4\beta\gamma}^{f},\quad \mathcal{N}_{321,5\beta\gamma}^{f}=-\mathcal{N}_{312,4\beta\gamma}^{f}\;,\\ &\mathcal{N}_{322,5\beta\gamma}^{f}=\mathcal{N}_{311,4\beta\gamma}^{f},\quad \mathcal{N}_{312,5\beta\gamma}^{f}=-\mathcal{N}_{321,4\beta\gamma}^{f}\;,\end{aligned} \qquad (5.15h)$$

from (5.14c) and (5.14a).

Relations (5.15) reduce the number of independent matrix elements $\mathcal{N}_{\omega'}^{\omega}(\mathbf{k},\mathbf{R})$ to 312.

Because of the factor $\cos(\mathbf{R}\cdot\hat{T}_j\mathbf{k})$ or $\sin(\mathbf{R}\cdot\hat{T}_j\mathbf{k})$ present in (5.11), any function $\mathcal{N}_{\omega\omega'}^{f}(\mathbf{k},\mathbf{R})$ may be written in a form of a linear combination of the functions $P_t(\mathbf{k},\mathbf{R})$ with constant coefficients:

$$\mathscr{N}^f_{\omega\omega'}(\mathbf{k},\mathbf{R})=\sum_t C^f_{\omega\omega'}(t)P_t(\mathbf{k},\mathbf{R})\ . \tag{5.16}$$

A typical example of $P_t(\mathbf{k},\mathbf{R})$ is

$$P_{C\beta\gamma S\beta'\gamma' C\beta''\gamma''}(\mathbf{k},\mathbf{R})=\cos(R_\beta k_\gamma)\sin(R_{\beta'}k_{\gamma'})\cos(R_{\beta''}k_{\gamma''})\ . \tag{5.17}$$

The letters C or S, occurring three times in the above notation for t, represent a cosine or sine factor, respectively. The sets of indices (β,β',β'') and $(\gamma,\gamma',\gamma'')$ are some permutations of (1,2,3). Because the value of the function (5.17) is independent of the order of its three factors, the corresponding indices t are considered to be equivalent, e.g., $t_1=C23S31S12$ is equivalent to $t_2=S12C23S31$, etc. There are 48 inequivalent indices t, because there are eight combinations of C and S and six permutations of $(\gamma,\gamma',\gamma'')$ for any fixed set (β,β',β''), say $(\beta,\beta',\beta'')=(1,2,3)$, taken as a standard one.

The coefficients $C^f_{\alpha\beta\gamma,\alpha'\beta'\gamma'}(t)$, calculated for the expansions (5.16), are listed in the following tables: for $\alpha,\alpha'=1,2,3$ in Table II; for $\alpha=3,\alpha'=4$ and $f=\cos$ in Table III; and for $\alpha=3,\alpha'=4$ and $f=\sin$ in Table IV.

In the case of $\alpha=1$ and $\alpha'=4,5$, the functions $\mathscr{N}^f_{\alpha\beta\gamma,\alpha'\beta'\gamma'}(\mathbf{k},\mathbf{R})$ may be written explicitly as

$$\mathscr{N}^{\cos}_{111,4\beta\gamma}=\epsilon_{\beta\beta'\beta''}\epsilon_{\gamma\gamma'\gamma''}(-8P_{C\beta\gamma S\beta'\gamma' S\beta''\gamma''}+8P_{C\beta\gamma S\beta'\gamma'' S\beta''\gamma'})\ , \tag{5.18}$$

$$\mathscr{N}^{\cos}_{111,5\beta\gamma}=-8P_{C\beta\gamma S\beta'\gamma' S\beta''\gamma''}-8P_{C\beta\gamma S\beta'\gamma'' S\beta''\gamma'}\ , \tag{5.19}$$

$$\mathscr{N}^{\sin}_{111,4\beta\gamma}=+8P_{S\beta\gamma C\beta'\gamma' C\beta''\gamma''}+8P_{S\beta\gamma C\beta'\gamma'' C\beta''\gamma'}\ , \tag{5.20}$$

$$\mathscr{N}^{\sin}_{111,5\beta\gamma}=\epsilon_{\beta\beta'\beta''}\epsilon_{\gamma\gamma'\gamma''}(+8P_{S\beta\gamma C\beta'\gamma' C\beta''\gamma''}-8P_{S\beta\gamma C\beta'\gamma'' C\beta''\gamma'})\ , \tag{5.21}$$

while in the case of $\alpha,\alpha'=4,5$ as

$$\mathscr{N}^f_{\alpha\beta\gamma,\alpha'\beta'\gamma}=\mathscr{N}^f_{\alpha\beta\gamma,\alpha'\beta\gamma'}=0\ , \tag{5.22}$$

$$\mathscr{N}^{\cos}_{4\beta\gamma,4\beta\gamma}=8P_{C\beta\gamma C\beta'\gamma' C\beta''\gamma''}+8P_{C\beta\gamma C\beta'\gamma'' C\beta''\gamma'}\ , \tag{5.23}$$

$$\mathscr{N}^{\cos}_{4\beta\gamma,5\beta\gamma}=\epsilon_{\beta\beta'\beta''}\epsilon_{\gamma\gamma'\gamma''}(8P_{C\beta\gamma C\beta'\gamma' C\beta''\gamma''}-8P_{C\beta\gamma C\beta'\gamma'' C\beta''\gamma'})\ , \tag{5.24}$$

$$\mathscr{N}^{\sin}_{4\beta\gamma,4\beta\gamma}=\epsilon_{\beta\beta'\beta''}\epsilon_{\gamma\gamma'\gamma''}(-8P_{S\beta\gamma S\beta'\gamma' S\beta''\gamma''}+8P_{S\beta\gamma S\beta'\gamma'' S\beta''\gamma'})\ , \tag{5.25}$$

$$\mathscr{N}^{\sin}_{4\beta\gamma,5\beta\gamma}=-8P_{S\beta\gamma S\beta'\gamma' S\beta''\gamma''}-8P_{S\beta\gamma S\beta'\gamma'' S\beta''\gamma'}\ , \tag{5.26}$$

TABLE II. Coefficients $C^f_{\alpha\beta\gamma,\alpha'\beta'\gamma'}(t)$ for $\alpha,\alpha'=1,2,3$.

		$f=\cos$					
ω $\alpha\beta\gamma$	ω' $\alpha'\beta'\gamma'$ t	$C11C22C33$	$C11C23C32$	$C12C23C31$	$C12C21C33$	$C13C21C32$	$C13C22C31$
111	1 1 1	+8	+8	+8	+8	+8	+8
111	2 1 1	+8	−8	+8	−8	+8	−8
111	3 1 1	+8	+4	−4	−8	−4	+4
	2 1	0	$-4\sqrt{3}$	$+4\sqrt{3}$	0	$-4\sqrt{3}$	$+4\sqrt{3}$
	1 2	0	$-4\sqrt{3}$	$-4\sqrt{3}$	0	$+4\sqrt{3}$	$+4\sqrt{3}$
	2 2	+8	−4	−4	+8	−4	−4
311	3 1 1	+8	+2	+2	+8	+2	+2
	2 1	0	$-2\sqrt{3}$	$-2\sqrt{3}$	0	$+2\sqrt{3}$	$+2\sqrt{3}$
	1 2	0	$-2\sqrt{3}$	$+2\sqrt{3}$	0	$-2\sqrt{3}$	$+2\sqrt{3}$
	2 2	+8	−2	+2	−8	+2	−2
21	2 1	0	+6	+6	0	+6	+6
	1 2	0	+6	−6	0	−6	+6

		$f=\sin$					
ω $\alpha\beta\gamma$	ω' $\alpha'\beta'\gamma'$ t	$S11S22S33$	$S11S23S32$	$S12S23S31$	$S12S21S33$	$S13S21S32$	$S13S22S31$
111	1 1 1	−8	+8	−8	+8	−8	+8
111	2 1 1	−8	−8	−8	−8	−8	−8
111	3 1 1	−8	+4	+4	−8	+4	+4
	2 1	0	$-4\sqrt{3}$	$-4\sqrt{3}$	0	$+4\sqrt{3}$	$+4\sqrt{3}$
	1 2	0	$-4\sqrt{3}$	$+4\sqrt{3}$	0	$-4\sqrt{3}$	$+4\sqrt{3}$
	2 2	−8	−4	+4	+8	+4	−4
311	3 1 1	−8	+2	−2	+8	−2	+2
	2 1	0	$-2\sqrt{3}$	$+2\sqrt{3}$	0	$-2\sqrt{3}$	$+2\sqrt{3}$
	1 2	0	$-2\sqrt{3}$	$-2\sqrt{3}$	0	$+2\sqrt{3}$	$+2\sqrt{3}$
	2 2	−8	−2	−2	−8	−2	−2
21	2 1	0	+6	−6	0	−6	+6
	1 2	0	+6	+6	0	+6	+6

TABLE III. Coefficients $C^{\cos}_{\alpha\beta\gamma,\alpha'\beta'\gamma'}(t)$ for $\alpha=3$, $\alpha'=4$.

ω	ω'	t					
$\alpha\beta\gamma$	$\alpha'\beta'\gamma'$	$C11S22S33$	$C11S23S32$	$C12S23S31$	$C12S21S33$	$C13S21S32$	$C13S22S31$
311	4 1 1	-8	$+4$	0	0	0	0
	1 2	0	0	$+4$	-8	0	0
	1 3	0	0	0	0	$+4$	$+4$
21	1 1	0	$-4\sqrt{3}$	0	0	0	0
	1 2	0	0	$-4\sqrt{3}$	0	0	0
	1 3	0	0	0	0	$+4\sqrt{3}$	$+4\sqrt{3}$
12	1 1	0	$-4\sqrt{3}$	0	0	0	0
	1 2	0	0	$+4\sqrt{3}$	0	0	0
	1 3	0	0	0	0	$-4\sqrt{3}$	$+4\sqrt{3}$
22	1 1	-8	-4	0	0	0	0
	1 2	0	0	$+4$	$+8$	0	0
	1 3	0	0	0	0	$+4$	-4

ω	ω'	t					
$\alpha\beta\gamma$	$\alpha'\beta'\gamma'$	$S11C22S33$	$S11C23S32$	$S12C23S31$	$S12C21S33$	$S13C21S32$	$S13C22S31$
311	4 2 1	0	0	0	-8	$+4$	0
	2 2	-8	0	0	0	0	$+4$
	2 3	0	$+4$	$+4$	0	0	0
21	2 1	0	0	0	0	$+4\sqrt{3}$	0
	2 2	0	0	0	0	0	$+4\sqrt{3}$
	2 3	0	$-4\sqrt{3}$	$-4\sqrt{3}$	0	0	0
12	2 1	0	0	0	0	$-4\sqrt{3}$	0
	2 2	0	0	0	0	0	$+4\sqrt{3}$
	2 3	0	$-4\sqrt{3}$	$+4\sqrt{3}$	0	0	0
22	2 1	0	0	0	$+8$	$+4$	0
	2 2	-8	0	0	0	0	-4
	2 3	0	-4	$+4$	0	0	0

ω	ω'	t					
$\alpha\beta\gamma$	$\alpha'\beta'\gamma'$	$S11S22C33$	$S11S23C32$	$S12S23C31$	$S12S21C33$	$S13S21C32$	$S13S22C31$
311	4 3 1	0	0	$+4$	0	0	$+4$
	3 2	0	$+4$	0	0	$+4$	0
	3 3	-8	0	0	-8	0	0
21	3 1	0	0	$-4\sqrt{3}$	0	0	$+4\sqrt{3}$
	3 2	0	$-4\sqrt{3}$	0	0	$+4\sqrt{3}$	0
	3 3	0	0	0	0	0	0
12	3 1	0	0	$+4\sqrt{3}$	0	0	$+4\sqrt{3}$
	3 2	0	$-4\sqrt{3}$	0	0	$-4\sqrt{3}$	0
	3 3	0	0	0	0	0	0
22	3 1	0	0	$+4$	0	0	-4
	3 2	0	-4	0	0	$+4$	0
	3 3	-8	0	0	$+8$	0	0

$$\mathcal{N}^{\cos}_{4\beta\gamma,4\beta'\gamma'}=-8P_{S\beta\gamma S\beta'\gamma' C\beta''\gamma''}\,, \tag{5.27}$$

$$\mathcal{N}^{\cos}_{4\beta\gamma,5\beta'\gamma'}=\epsilon_{\beta\beta'\beta''}\epsilon_{\gamma\gamma'\gamma''}(-8)P_{S\beta\gamma S\beta'\gamma' C\beta''\gamma''}\,, \tag{5.28}$$

$$\mathcal{N}^{\sin}_{4\beta\gamma,4\beta'\gamma'}=\epsilon_{\beta\beta'\beta''}\epsilon_{\gamma\gamma'\gamma''}8P_{C\beta\gamma C\beta'\gamma' S\beta''\gamma''}\,, \tag{5.29}$$

$$\mathcal{N}^{\sin}_{4\beta\gamma,5\beta'\gamma'}=8P_{C\beta\gamma C\beta'\gamma' S\beta''\gamma''}\,. \tag{5.30}$$

The sets (β,β',β'') and $(\gamma,\gamma',\gamma'')$ entering Eqs. (5.18)—(5.30) form some permutations of (1,2,3), whereas $\epsilon_{\xi\xi'\xi''}=+1$ for (ξ,ξ',ξ'') forming an even permutation of (1,2,3), while $\epsilon_{\xi\xi'\xi''}=-1$ in the case of an odd permutation. Relations (5.9), (5.10), (5.13), (5.15), and (5.16), and Tables II—IV, together with formulas (5.18)—(5.30), allow us to write $\mathcal{N}^{\omega}_{\omega'}(\mathbf{k},\mathbf{R})$ in terms of $P_t(\mathbf{k},\mathbf{R})$ for any combination of ω and ω'.

Several sum rules allowing a check on the correctness

TABLE IV. Coefficients $C^{\sin}_{\alpha\beta\gamma,\alpha'\beta'\gamma'}(t)$ for $\alpha=3, \alpha'=4$.

ω	ω'			t			
$\alpha\beta\gamma$	$\alpha'\beta'\gamma'$	$S11C22C33$	$S11C23C32$	$S12C23C31$	$S12C21C33$	$S13C21C32$	$S13C22C31$
311	4 1 1	+8	+4	0	0	0	0
	1 2	0	0	−4	−8	0	0
	1 3	0	0	0	0	−4	+4
21	1 1	0	$-4\sqrt{3}$	0	0	0	0
	1 2	0	0	$+4\sqrt{3}$	0	0	0
	1 3	0	0	0	0	$-4\sqrt{3}$	$+4\sqrt{3}$
12	1 1	0	$-4\sqrt{3}$	0	0	0	0
	1 2	0	0	$-4\sqrt{3}$	0	0	0
	1 3	0	0	0	0	$+4\sqrt{3}$	$+4\sqrt{3}$
22	1 1	+8	−4	0	0	0	0
	1 2	0	0	−4	+8	0	0
	1 3	0	0	0	0	−4	−4

ω	ω'			t			
$\alpha\beta\gamma$	$\alpha'\beta'\gamma'$	$C11S22C33$	$C11S23C32$	$C12S23C31$	$C12S21C33$	$C13S21C32$	$C13S22C31$
311	4 2 1	0	0	0	−8	−4	0
	2 2	+8	0	0	0	0	+4
	2 3	0	+4	−4	0	0	0
21	2 1	0	0	0	0	$-4\sqrt{3}$	0
	2 2	0	0	0	0	0	$+4\sqrt{3}$
	2 3	0	$-4\sqrt{3}$	$+4\sqrt{3}$	0	0	0
12	2 1	0	0	0	0	$+4\sqrt{3}$	0
	2 2	0	0	0	0	0	$+4\sqrt{3}$
	2 3	0	$-4\sqrt{3}$	$-4\sqrt{3}$	0	0	0
22	2 1	0	0	0	+8	−4	0
	2 2	+8	0	0	0	0	−4
	2 3	0	−4	−4	0	0	0

ω	ω'			t			
$\alpha\beta\gamma$	$\alpha'\beta'\gamma'$	$C11C22S33$	$C11C23S32$	$C12C23S31$	$C12C21S33$	$C13C21S32$	$C13C22S31$
311	4 3 1	0	0	−4	0	0	+4
	3 2	0	+4	0	0	−4	0
	3 3	+8	0	0	−8	0	0
21	3 1	0	0	$+4\sqrt{3}$	0	0	$+4\sqrt{3}$
	3 2	0	$-4\sqrt{3}$	0	0	$-4\sqrt{3}$	0
	3 3	0	0	0	0	0	0
12	3 1	0	0	$-4\sqrt{3}$	0	0	$+4\sqrt{3}$
	3 2	0	$-4\sqrt{3}$	0	0	$+4\sqrt{3}$	0
	3 3	0	0	0	0	0	0
22	3 1	0	0	−4	0	0	−4
	3 2	0	−4	0	0	−4	0
	3 3	+8	0	0	+8	0	0

of Tables II—IV as well as Eqs. (5.18)—(5.30) can be established. The definition (4.8) and arguments similar to those applied in obtaining Eqs. (3.18) and (3.19) give

$$\frac{1}{N}\sum_{L}\mathcal{N}^{*\omega_1}_{\omega_2}(\mathbf{k},\mathbf{R}_L)\mathcal{N}^{\omega_3}_{\omega_4}(\mathbf{k},\mathbf{R}_L) =\sum_{j}D_{\omega_1}(T_j)D^{*}_{\omega_2}(T_j)D^{*}_{\omega_3}(T_j)D_{\omega_4}(T_j)\ , \qquad (5.31)$$

so

$$\sum_{\beta_2}\frac{1}{N}\sum_{L}\mathcal{N}^{*\omega_1}_{\alpha_2\beta_2\gamma_2}(\mathbf{k},\mathbf{R}_L)\mathcal{N}^{\omega_3}_{\alpha_2\beta_2\gamma_4}(\mathbf{k},\mathbf{R}_L)=\frac{d_g}{d_{\alpha_1}}\delta_{\omega_1\omega_3}\delta_{\gamma_2\gamma_4} \qquad (5.32)$$

or

$$\sum_{\gamma_2}\frac{1}{N}\sum_{L}\mathcal{N}^{*\omega_1}_{\alpha_2\beta_2\gamma_2}(\mathbf{k},\mathbf{R}_L)\mathcal{N}^{\omega_3}_{\alpha_2\beta_4\gamma_2}(\mathbf{k},\mathbf{R}_L)=\frac{d_g}{d_{\alpha_1}}\delta_{\omega_1\omega_3}\delta_{\beta_2\beta_4}\ . \qquad (5.33)$$

Using orthonormality relations for functions $P_t(\mathbf{k},\mathbf{R}_L)$,

$$\frac{1}{N}\sum_L P_t(\mathbf{k},\mathbf{R}_L)P_{t'}(\mathbf{k},\mathbf{R}_L)=\tfrac{1}{8}\delta_{tt'}\ , \tag{5.34}$$

and expressions (5.16), we obtain from (5.32) and (5.33) the sum rules

$$\sum_{\beta_2,t} C^f_{\omega_1,\alpha_2\beta_2\gamma_2}(t)C^f_{\omega_3,\alpha_2\beta_2\gamma_4}(t)=\frac{8\times 48}{d_{\alpha_1}}\delta_{\omega_1\omega_3}\delta_{\gamma_2\gamma_4}\ , \tag{5.35}$$

$$\sum_{\gamma_2,t} C^f_{\omega_1,\alpha_2\beta_2\gamma_2}(t)C^f_{\omega_3,\alpha_2\beta_4\gamma_2}(t)=\frac{8\times 48}{d_{\alpha_1}}\delta_{\omega_1\omega_3}\delta_{\beta_2\beta_4}\ . \tag{5.36}$$

In order to illustrate the application of the formalism discussed above, we consider now an example of a transition metal, say Ni, whose LCAO wave function is constructed of six types of atomic orbitals $\Phi_\mu(\mathbf{r})$: one s-like orbital, $\mu=01^+1\equiv s$ and five d-like orbitals, $\mu=25^+1\equiv yz$, $25^+2\equiv zx$, $25^+3\equiv xy$, forming the basis of the representation $\alpha'=5^+$, and $\mu=23^+1\equiv x^2-y^2$, $23^+2\equiv 3z^2-r^2$, forming the basis of $\alpha'=3^+$. Then the wave function transforming according to the βth row and γth column of the irreducible representation α, i.e., the function having the index $\omega=\alpha\beta\gamma$, is [see Eqs. (4.6) and (4.7)]

$$\begin{aligned}\Psi^{\omega\mathbf{k}\lambda}(\mathbf{r})=\sum_L[\,&A_s^{\omega\mathbf{k}\lambda}(\mathbf{R}_L)\Phi_s(\mathbf{r}-\mathbf{R}_L)+A_{yz}^{\omega\mathbf{k}\lambda}(\mathbf{R}_L)\Phi_{yz}(\mathbf{r}-\mathbf{R}_L)+A_{zx}^{\omega\mathbf{k}\lambda}(\mathbf{R}_L)\Phi_{zx}(\mathbf{r}-\mathbf{R}_L)\\&+A_{xy}^{\omega\mathbf{k}\lambda}(\mathbf{R}_L)\Phi_{xy}(\mathbf{r}-\mathbf{R}_L)+A_{x^2-y^2}^{\omega\mathbf{k}\lambda}(\mathbf{R}_L)\Phi_{x^2-y^2}(\mathbf{r}-\mathbf{R}_L)+A_{3z^2-r^2}^{\omega\mathbf{k}\lambda}(\mathbf{R}_L)\Phi_{3z^2-r^2}(\mathbf{r}-\mathbf{R}_L)]\ ,\end{aligned} \tag{5.37}$$

with

$$\begin{aligned}
A_s^{\omega\mathbf{k}\lambda}(\mathbf{R})&=\left[\frac{d_\alpha}{48N}\right]^{1/2}\mathcal{N}^{\omega}_{1^+11}(\mathbf{k},\mathbf{R})a_s^{\mathbf{k}\lambda}\ ,\\
A_{yz}^{\omega\mathbf{k}\lambda}(\mathbf{R})&=\left[\frac{d_\alpha}{48N}\right]^{1/2}[\mathcal{N}^{\omega}_{5^+11}(\mathbf{k},\mathbf{R})a_{yz}^{\mathbf{k}\lambda}+\mathcal{N}^{\omega}_{5^+12}(\mathbf{k},\mathbf{R})a_{zx}^{\mathbf{k}\lambda}+\mathcal{N}^{\omega}_{5^+13}(\mathbf{k},\mathbf{R})a_{xy}^{\mathbf{k}\lambda}]\ ,\\
A_{zx}^{\omega\mathbf{k}\lambda}(\mathbf{R})&=\left[\frac{d_\alpha}{48N}\right]^{1/2}[\mathcal{N}^{\omega}_{5^+21}(\mathbf{k},\mathbf{R})a_{yz}^{\mathbf{k}\lambda}+\mathcal{N}^{\omega}_{5^+22}(\mathbf{k},\mathbf{R})a_{zx}^{\mathbf{k}\lambda}+\mathcal{N}^{\omega}_{5^+23}(\mathbf{k},\mathbf{R})a_{xy}^{\mathbf{k}\lambda}]\ ,\\
A_{xy}^{\omega\mathbf{k}\lambda}(\mathbf{R})&=\left[\frac{d_\alpha}{48N}\right]^{1/2}[\mathcal{N}^{\omega}_{5^+31}(\mathbf{k},\mathbf{R})a_{yz}^{\mathbf{k}\lambda}+\mathcal{N}^{\omega}_{5^+32}(\mathbf{k},\mathbf{R})a_{zx}^{\mathbf{k}\lambda}+\mathcal{N}^{\omega}_{5^+33}(\mathbf{k},\mathbf{R})a_{xy}^{\mathbf{k}\lambda}]\ ,\\
A_{x^2-y^2}^{\omega\mathbf{k}\lambda}(\mathbf{R})&=\left[\frac{d_\alpha}{48N}\right]^{1/2}[\mathcal{N}^{\omega}_{3^+11}(\mathbf{k},\mathbf{R})a_{x^2-y^2}^{\mathbf{k}\lambda}+\mathcal{N}^{\omega}_{3^+12}(\mathbf{k},\mathbf{R})a_{3z^2-r^2}^{\mathbf{k}\lambda}]\ ,\\
A_{3z^2-r^2}^{\omega\mathbf{k}\lambda}(\mathbf{R})&=\left[\frac{d_\alpha}{48N}\right]^{1/2}[\mathcal{N}^{\omega}_{3^+21}(\mathbf{k},\mathbf{R})a_{x^2-y^2}^{\mathbf{k}\lambda}+\mathcal{N}^{\omega}_{3^+22}(\mathbf{k},\mathbf{R})a_{3z^2-r^2}^{\mathbf{k}\lambda}]\ .
\end{aligned} \tag{5.38}$$

The Bloch eigenvector $a_\mu^{\mathbf{k}\lambda}$, together with the corresponding eigenenergy $E^{\mathbf{k}\lambda}$, is the member λ belonging to the set of $\sigma=6$ solutions of the secular eigenequation (2.14). Here it should be stressed that the general eigenproblem represented by Eqs. (2.11)–(2.12) leads to the same secular equation for an $a_\mu^{\mathbf{k}\lambda}$ represented by Eq. (2.14) irrespective of the fact whether we use the Bloch coefficient functions (2.13) or the standing-wave-like coefficient functions (3.10) at the starting point. The explicit form of the 6×6 Hamiltonian matrix $H^{\mathbf{k}}_{\mu\mu'}$, for different cubic lattices and different types of interactions between atomic neighbors, may be found, e.g., in Ref. 2, where the matrix elements are denoted by (μ/μ'). In Sec. VII we develop a general procedure allowing a simplified evaluation of $H^{\mathbf{k}}_{\mu\mu'}$ and give some examples of it.

To specify the example of the standing-wave-like LCAO function given above, we write some $\mathcal{N}^{\omega}_{\omega'}$ terms of the SWLPC function which transform according to an odd one-dimensional representation, say $\alpha=1^-$. From Table II we obtain an element for an s-type orbital,

$$\begin{aligned}\mathcal{N}^{1^-11}_{1^+11}(\mathbf{k},\mathbf{R})=i\mathcal{N}^{\sin}_{111,111}(\mathbf{k},\mathbf{R})=i\,8\{&\sin(R_1k_1)[\sin(R_2k_3)\sin(R_3k_2)-\sin(R_2k_2)\sin(R_3k_3)]\\&+\sin(R_1k_2)[\sin(R_2k_1)\sin(R_3k_3)-\sin(R_2k_3)\sin(R_3k_1)]\\&+\sin(R_1k_3)[\sin(R_2k_2)\sin(R_3k_1)-\sin(R_2k_1)\sin(R_3k_2)]\}\ .\end{aligned} \tag{5.39}$$

From Table II we obtain a typical element for a d-type orbital of $\alpha'=3^+$:

$$\begin{aligned}\mathcal{N}^{1^-11}_{3^+12}(\mathbf{k},\mathbf{R})=i\mathcal{N}^{\sin}_{111,312}(\mathbf{k},\mathbf{R})=i\,4\sqrt{3}\{&-\sin(R_1k_1)\sin(R_2k_2)\sin(R_3k_3)+\sin(R_1k_2)\sin(R_2k_3)\sin(R_3k_1)\\&-\sin(R_1k_3)[\sin(R_2k_1)\sin(R_3k_2)-\sin(R_2k_2)\sin(R_3k_1)]\}\ ,\end{aligned} \tag{5.40}$$

and from Eq. (5.21) a typical element for a d-type orbital of $\alpha'=5^+$:

$$\mathcal{N}^{1-11}_{5+32}(\mathbf{k},\mathbf{R})=i\mathcal{N}^{\sin}_{111,532}(\mathbf{k},\mathbf{R})=i\,8\sin(R_3k_2)[\cos(R_1k_3)\cos(R_2k_1)-\cos(R_1k_1)\cos(R_2k_3)]\ . \tag{5.41}$$

VI. INDEPENDENT PARAMETERS FOR THE HAMILTONIAN MATRIX

The matrix elements $H_{\mu L,\mu' L'}$ of the unperturbed Hamiltonian, Eq. (2.7), and the elements $V_{\mu L,\mu' L'}$ of the perturbation matrix, Eq. (2.21), may be calculated directly according to their definitions, providing the operators $\hat{H}(\mathbf{r})$ and $\hat{H}^{\,\text{per}}(\mathbf{r})$ and the appropriate atomic orbitals $\Phi_\mu(\mathbf{r})$ and $\Phi^{\text{per}}_\mu(\mathbf{r})$ are known. However, very often, particularly for the impurity problem, these matrix elements are considered parameters whose values are obtained by fitting the results of the LCAO calculations to some experimental data or to results of other calculations.[41] In this case the number of parameters should be as small as possible, and a substantial reduction of this number may be obtained by symmetry considerations.

Let $M(\mathbf{r})$ denote an operator invariant under the operations of the point group $\mathcal{G}_0$ of the crystal:

$$\hat{\mathcal{P}}_{T_j}\hat{M}(\mathbf{r})=\hat{M}(\mathbf{r})\hat{\mathcal{P}}_{T_j},\ \ j=1,2,\ldots,d_g\ . \tag{6.1}$$

Examples of $\hat{M}(\mathbf{r})$ could be $\hat{H}(\mathbf{r})$ and $\hat{H}^{\,\text{per}}(\mathbf{r})$. We are going to establish the relations between different components of the matrix

$$\begin{aligned}M_{\mu L,\mu' L'}&=\langle\Phi_{\mu L}\,|\,\hat{M}\Phi_{\mu' L'}\rangle\\&=\int d^3r\,\Phi^*_\mu(\mathbf{r}-\mathbf{R}_L)\hat{M}(\mathbf{r})\Phi_{\mu'}(\mathbf{r}-\mathbf{R}_{L'})\ .\end{aligned} \tag{6.2}$$

Because a scalar product is invariant under the rotation we have

$$\begin{aligned}\langle\Phi_{\mu L}\,|\hat{M}\Phi_{\mu' L'}\rangle&=\langle\hat{\mathcal{P}}_T\Phi_{\mu L}\,|\,\hat{\mathcal{P}}_T\hat{M}\Phi_{\mu' L'}\rangle\\&=\langle\hat{\mathcal{P}}_T\Phi_{\mu L}\,|\hat{M}\hat{\mathcal{P}}_T\Phi_{\mu' L'}\rangle\ .\end{aligned} \tag{6.3}$$

In the last step the commutation relation (6.1) was used. The effect of the rotation operator on the atomic orbital was already found in Eq. (3.4). Therefore, from (6.3) it follows that

$$M_{\mu L,\mu' L'}=\sum_{\nu,\nu'}D^*_{\nu\mu}(T)D_{\nu'\mu'}(T)M_{\nu(TL),\nu'(TL')}\ , \tag{6.4}$$

where we introduced the notation

$$\mathbf{R}_{TL}=\hat{T}\mathbf{R}_L\ . \tag{6.5}$$

The relation (6.4) may be reversed using unitarity of the representation $D_{\nu\mu}(T)$:

$$M_{\nu(TL),\nu'(TL')}=\sum_{\mu,\mu'}D_{\nu\mu}(T)D^*_{\nu'\mu'}(T)M_{\mu L,\mu' L'}\ . \tag{6.6}$$

Choosing atomic orbitals whose angular parts transform according to the irreducible representations of the point group $\mathcal{G}_0$, Sec. IV, we have $D_{\nu\mu}$ in the reduced form; cf. Eq. (4.5). Then Eq. (6.6) may be rewritten as

$$M_{b\alpha\beta(TL),b'\alpha'\beta'(TL')}=\sum_{\gamma,\gamma'}D_{\alpha\beta\gamma}(T)D^*_{\alpha'\beta'\gamma'}(T)M_{b\alpha\gamma L,b'\alpha'\gamma' L'}\ . \tag{6.7}$$

This is an important equation since it allows us to calculate the matrix elements connected with position vectors $\hat{T}\mathbf{R}_L$ and $\hat{T}\mathbf{R}_{L'}$ from the elements connected with positions $\mathbf{R}_L$ and $\mathbf{R}_{L'}$. The property of hermicity of the operator $\hat{M}$ allows us to find the matrix elements having a reversed order of position vectors

$$M_{\mu L',\nu L}=M^*_{\nu L,\mu L'}\ . \tag{6.8}$$

Let us define group $\mathcal{G}_0(\mathbf{R}_L,\mathbf{R}_{L'})$ of the vectors $\mathbf{R}_L$ and $\mathbf{R}_{L'}$, being a subgroup of the crystal point group $\mathcal{G}_0$, as a set of such rotations $T_{\nu n}$ which leave these vectors unchanged,

$$\hat{T}_{\nu n}\mathbf{R}_L=\mathbf{R}_L\ \text{ and }\ \hat{T}_{\nu n}\mathbf{R}_{L'}=\mathbf{R}_{L'}\ ,\qquad n=1,2,\ldots,d_g(\mathbf{R}_L,\mathbf{R}_{L'})\ . \tag{6.9}$$

The order of this group is denoted by $d_g(\mathbf{R}_L,\mathbf{R}_{L'})$. Then, from (6.7) it follows that

$$M_{b\alpha\beta L,b'\alpha'\beta' L'}=\sum_{\gamma,\gamma'}D_{\alpha\beta\gamma}(T_{\nu n})D^*_{\alpha'\beta'\gamma'}(T_{\nu n})M_{b\alpha\gamma L,b'\alpha'\gamma' L'}. \tag{6.10}$$

This set of $d_g(\mathbf{R}_L,\mathbf{R}_{L'})$ equations imposes restrictions on the matrix elements of $\hat{M}$ having fixed indices $b\alpha L$ and $b'\alpha' L'$, and allows us to determine the independent matrix elements.

In order to illustrate this possibility, let us first consider the matrix elements with indices $\mathbf{R}_L=\mathbf{R}_{L'}=\mathbf{0}$. In this case $\mathcal{G}_0(\mathbf{0},\mathbf{0})$ coincides with the full point group of the crystal $\mathcal{G}_0$, whose irreducible representations are $D_{\alpha\beta\gamma}(T)$. After summing up both sides of Eq. (6.10) over T_j and applying the orthogonality relation (5.2), we get

$$M_{b\alpha\beta 0,b'\alpha'\beta' 0}=\delta_{\alpha\alpha'}\delta_{\beta\beta'}\frac{1}{d_\alpha}\sum_{\gamma=1}^{d_\alpha}M_{b\alpha\gamma 0,b'\alpha\gamma 0}\ . \tag{6.11}$$

Because the left-hand side does not depend on the value of β, therefore the summation over γ is trivial and we obtain a known result

$$M_{b\alpha\beta 0,b'\alpha'\beta' 0}=\delta_{\alpha\alpha'}\delta_{\beta\beta'}M^{0\alpha}_{bb'}\ , \tag{6.12a}$$

where

$$M^{0\alpha}_{bb'}=M_{b\alpha 10,b'\alpha 10}=M_{b\alpha 20,b'\alpha 20}=\cdots\ . \tag{6.12b}$$

So, for fixed quantum numbers b and b' characterizing atomic orbitals, there is connected with each representation α only one parameter $M^{0\alpha}_{bb'}$ instead of possible $(d_\alpha)^2$ parameters.

If one or both position vectors $\mathbf{R}_L$ and $\mathbf{R}_{L'}$ are not zero, then the group $\mathcal{G}_0(\mathbf{R}_L,\mathbf{R}_{L'})$ of the vectors $\mathbf{R}_L$ and

$\mathbf{R}_{L'}$ is a proper subgroup of $\mathscr{G}_0$. Therefore the representations $D_{\alpha\beta\gamma}(T)$ are, in general, reducible with respect to $\mathscr{G}_0(\mathbf{R}_L,\mathbf{R}_{L'})$. Only after their reduction may the relations similar to (6.12) be obtained. This procedure will be shown on example of the group $\mathscr{G}_0(\mathbf{R}_L,\mathbf{R}_{L'})$ for $\mathbf{R}_L=\mathbf{0}$ and $\mathbf{R}_{L'}=(0,0,u)$, which are positions of the central atom and its nearest neighbor in the sc lattice (or the second-nearest neighbor in the fcc or bcc lattice). There are eight operations T_{vn} leaving invariant these vectors: identity E, rotation C_4 through $\pi/2$ about the (0,0,1) axis, its powers C_4^2,C_4^3, operation IC_{4x}^2, the rotation through the angle $2\times(\pi/2)$ about the (1,0,0) axis followed by an inversion I, operation IC_{4y}^2, which is the previous one but about the (0,1,0) axis, operation IC_2, the rotation through π about the (1,1,0) axis, followed by inversion, and operation $IC_{2'}$, which is like the previous one but about the $(1,-1,0)$ axis. In Table V are given the representations $\underline{D}_\alpha(T)$ with $\alpha=1^+,4^-,5^+,3^+$ for these operations. These representations define the symmetry properties of all *s*-, *p*-, and *d*-like atomic orbitals entering the matrix elements. As mentioned in Eq. (4.2), the representation $\underline{D}_{4^-}(T)$ coincides with the operation matrix $\underline{T}$. The bar under the symbol of a representation, a transformation, etc. is introduced to denote the matrix, e.g., $\underline{D}_\alpha$ is a matrix composed of the elements $D_{\alpha\beta\gamma}$.

The group $\mathscr{G}_0(\mathbf{0},(0,0,u))$ is already known, since it is identical with the group $\mathscr{G}_0(\mathbf{k})$ of the wave vector $\mathbf{k}=\mathbf{\Delta}=(0,0,u)$.[35] Its irreducible representations, called Δ_j, consist of four one-dimensional representations: Δ_1, Δ_2, $\Delta_3=\Delta_2'$, and $\Delta_4=\Delta_1'$, and one two-dimensional representation, Δ_5. The characters of these representations, given first by Bouckaert *et al.*,[35] are presented also in

TABLE V. Representations $\underline{D}_\alpha(T)$ of the group $\mathscr{G}_0(\mathbf{R}_L,\mathbf{R}_{L'})$ for the vectors $\mathbf{R}_L=\mathbf{0}$, $\mathbf{R}_{L'}=\mathbf{\Delta}=(0,0,u)$, and characters χ of the irreducible representations $\underline{\Delta}_j(T)$ of the group $\mathscr{G}_0(\mathbf{k})$ for the wave vector $\mathbf{k}=\mathbf{\Delta}=(0,0,u)$.

T	E	C_{4z}^2	C_{4z}	C_{4z}^3
$\underline{D}_{1^+}(T)$	1	1	1	1
$\underline{D}_{4^-}(T)$	$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}0&-1&0\\1&0&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}0&1&0\\-1&0&0\\0&0&1\end{bmatrix}$
$\underline{D}_{5^+}(T)$	$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}0&1&0\\-1&0&0\\0&0&-1\end{bmatrix}$	$\begin{bmatrix}0&-1&0\\1&0&0\\0&0&-1\end{bmatrix}$
$\underline{D}_{3^+}(T)$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$
$\chi(\underline{\Delta}_1(T))$	1	1	1	
$\chi(\underline{\Delta}_2(T))$	1	1	-1	
$\chi(\underline{\Delta}_3(T))$	1	1	-1	
$\chi(\underline{\Delta}_4(T))$	1	1	1	
$\chi(\underline{\Delta}_5(T))$	2	-2	0	

T	IC_{4x}^2	IC_{4y}^2	IC_2	$IC_{2'}$
$\underline{D}_{1^+}(T)$	1	1	1	1
$\underline{D}_{4^-}(T)$	$\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}0&-1&0\\-1&0&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}$
$\underline{D}_{5^+}(T)$	$\begin{bmatrix}1&0&0\\0&-1&0\\0&0&-1\end{bmatrix}$	$\begin{bmatrix}-1&0&0\\0&1&0\\0&0&-1\end{bmatrix}$	$\begin{bmatrix}0&-1&0\\-1&0&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}$
$\underline{D}_{3^+}(T)$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$
$\chi(\underline{\Delta}_1(T))$	1		1	
$\chi(\underline{\Delta}_2(T))$	1		-1	
$\chi(\underline{\Delta}_3(T))$	-1		1	
$\chi(\underline{\Delta}_4(T))$	-1		-1	
$\chi(\underline{\Delta}_5(T))$	0		0	

Table V. The examination of $\underline{D}_\alpha$ and $\chi(\Delta_j)$ in Table V allows us to conclude that some representations $\underline{D}_\alpha$ are already in the reduced form:

$$\underline{D}_{1^+}(T)=\underline{\Delta}_1(T)\ , \tag{6.13}$$

$$\underline{D}_{4^-}(T)=\begin{bmatrix}\underline{\Delta}_5(T) & \underline{0}\\ \underline{0} & \underline{\Delta}_1(T)\end{bmatrix}\ , \tag{6.14}$$

$$\underline{D}_{3^+}(T)=\begin{bmatrix}\underline{\Delta}_2(T) & \underline{0}\\ \underline{0} & \underline{\Delta}_1(T)\end{bmatrix}\ , \tag{6.15}$$

while the representation $\underline{D}_{5^+}$ may be reduced to

$$\underline{S}_{5^+}^{-1}\underline{D}_{5^+}(T)\underline{S}_{5^+}=\begin{bmatrix}\underline{\Delta}_5(T) & \underline{0}\\ \underline{0} & \underline{\Delta}_3(T)\end{bmatrix} \tag{6.16}$$

with the help of a similarity transformation

$$\underline{S}_{5^+}=\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & 0\\ 0 & 0 & 1\end{bmatrix}\ . \tag{6.17}$$

It is now convenient to rewrite Eq. (6.10) in the matrix form

$$\underline{M}_{\alpha L,\alpha' L'}=\underline{D}_\alpha(T_{\nu n})\underline{M}_{\alpha L,\alpha' L'}\underline{D}^{\dagger}_{\alpha'}(T_{\nu n})\ . \tag{6.18}$$

The indices b and b', which are not influenced by the symmetry operations, are henceforth omitted for the sake of brevity. Note that L,L' and α,α' are fixed indices for the both sides of Eq. (6.18). Equations (6.13)–(6.15) can be written in the same form as Eq. (6.16), providing the notation

$$\underline{S}_\alpha=\underline{1}\quad\text{for } \alpha=1^+,4^-,3^+ \tag{6.19}$$

is introduced. By applying transformations $\underline{S}_\alpha$ and $\underline{S}_{\alpha'}$ to Eq. (6.18), we get

$$\underline{S}_\alpha^{-1}M_{\alpha L,\alpha' L'}\underline{S}_{\alpha'}=[\underline{S}_\alpha^{-1}D_\alpha(T_{\nu n})\underline{S}_\alpha](\underline{S}_\alpha^{-1}M_{\alpha L,\alpha' L'}\underline{S}_{\alpha'})\times[\underline{S}_{\alpha'}^{-1}\underline{D}_{\alpha'}(T_{\nu n})\underline{S}_{\alpha'}]^{\dagger}\ . \tag{6.20}$$

The property of unitarity $\underline{S}_\alpha^{\dagger}=\underline{S}_{\alpha'}^{-1}$ has been used. For fixed indices L,α,L',α', let us denote by $\underline{m}$ the matrix occurring on the left-hand side of Eq. (6.20):

$$\underline{m}=\underline{S}_\alpha^{-1}\underline{M}_{\alpha L,\alpha' L'}\underline{S}_{\alpha'}\ ; \tag{6.21}$$

$\underline{m}_{jj'}$ are the submatrices (blocks) of $\underline{m}$. Subscript j assumes the values of the indices j of the irreducible representations Δ_j and runs in the same order as these representations occur in the reduced form of the representation $\underline{D}_\alpha$ [see Eqs. (6.13)–(6.16)], for example, $j=5,1$ for $\alpha=4^-$; subscript j' has the same meaning, but concerns $\underline{D}_{\alpha'}$. The number of rows and columns within the block $\underline{m}_{jj'}$ equals the dimension of Δ_j and $\Delta_{j'}$, respectively. As follows from (6.20), each block $\underline{m}_{jj'}$ satisfies the equation

$$\underline{m}_{jj'}=\underline{\Delta}_j(T_{\nu n})\underline{m}_{jj'}\underline{\Delta}_{j'}(T_{\nu n})\ . \tag{6.22}$$

We may sum up both sides of Eq. (6.22) over all the operations $T_{\nu n}$ and apply the orthogonality relation concerning irreducible representations $\underline{\Delta}_j(T_{\nu n})$; we obtain a result similar to that obtained in (6.12), namely

$$\underline{m}_{jj'}=\delta_{jj'}m^j\underline{1}\ , \tag{6.23}$$

i.e., each block $\underline{m}_{jj'}$ is either a zero matrix (for $j\neq j'$) or is proportional to a unit matrix (for $j=j'$) with its proportionality coefficient (parameter) denoted by m^j. Therefore the block is characterized either by a single parameter or no parameter at all. Having determined all blocks $\underline{m}_{jj'}$ according to Eq. (6.23), the matrix $\underline{M}_{\alpha L,\alpha' L'}$ may be found by a reversal of the relation (6.21):

$$\underline{M}_{\alpha L,\alpha' L'}=\underline{S}_\alpha\underline{m}\,\underline{S}_{\alpha'}^{-1}\ . \tag{6.24}$$

The above considerations may be illustrated on an example of $\alpha=4^-$ and $\alpha'=5^+$. Since the reduced form of $\underline{D}_{4^-}$ has blocks $\underline{\Delta}_5$ and $\underline{\Delta}_1$ and the reduced form of $\underline{D}_{5^+}$ has $\underline{\Delta}_5$ and $\underline{\Delta}_3$, the structure of the matrix $\underline{m}$ is as follows:

$$\underline{m}=\begin{bmatrix}\underline{m}_{55} & \underline{m}_{53}\\ \underline{m}_{15} & \underline{m}_{13}\end{bmatrix}\ , \tag{6.25}$$

where $\underline{m}_{55}$ is a 2×2 submatrix and $\underline{m}_{13}$ is a 1×1 submatrix, etc. Using (6.23) we get

$$\underline{m}=\begin{bmatrix}m & 0 & 0\\ 0 & m & 0\\ 0 & 0 & 0\end{bmatrix}\ , \tag{6.26}$$

where $\underline{m}=\underline{m}^5$, and from (6.24) we finally obtain

$$\underline{M}_{4^-0,5^+\Delta}=\underline{S}_{4^-}\underline{m}\underline{S}_{5^+}=\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}m & 0 & 0\\ 0 & m & 0\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & 0\\ 0 & 0 & 1\end{bmatrix}=\begin{bmatrix}0 & m & 0\\ m & 0 & 0\\ 0 & 0 & 0\end{bmatrix}\ . \tag{6.27}$$

For the case of $\alpha=5^+$ and $\alpha'=3^+$, the result must be zero, because the representations $\underline{\Delta}_5$ and $\underline{\Delta}_3$ entering the reduced form of $\underline{D}_{5^+}$, see (6.16), are different then $\underline{\Delta}_2$ and $\underline{\Delta}_1$ entering $\underline{D}_{3^+}$, see (6.15):

$$\underline{M}_{5^+0,3^+\Delta}=\underline{0}\ . \tag{6.28}$$

In the same way, any combination of α and α' taken from the set $1^+,4^-,5^+,3^+$ can be considered. All results obtained for $M_{\mu 0,\mu'\Delta}$ are collected in Table VI. The matrix elements for $\mathbf{\Delta}$ replaced by the other neighbors of site $\mathbf{0}$, say $\mathbf{\Delta}'=(u,0,0)$ or $\mathbf{\Delta}''=(0,u,0)$, can be obtained according to Eq. (6.7).

In order to determine the independent matrix elements for the case of the central site $\mathbf{R}_L=\mathbf{0}$ and the site $\mathbf{R}_{L'}=(u,u,0)$ (which can be a nearest-neighbor position in the fcc lattice or the second-nearest-neighbor position in the sc lattice, or a third-nearest-neighbor position in the bcc lattice), the group $\mathcal{G}_0(\mathbf{0},(u,u,0))$ must be considered; this group is identical to the group $\mathcal{G}_0(\mathbf{k})$ for the wave

TABLE VI. Matrix elements $M_{\mu L,\mu' L'}$ for $\mathbf{R}_L=\mathbf{0}$ and $\mathbf{R}_{L'}=\mathbf{\Delta}=(0,0,u)$ in terms of 15 independent parameters M^i, $i=1,2,\ldots,15$.

			l'	s	p			d				
			α'	1^+	4^-			5^+			3^+	
			β'	1	1	2	3	1	2	3	1	2
			μ'	s	x	y	z	yz	zx	xy	x^2-y^2	$3z^2-r^2$
l	α	β	μ									
s	1^+	1	s	M^1	0	0	M^3	0	0	0	0	M^8
p	4^-	1	x	0	M^2	0	0	0	M^{10}	0	0	0
		2	y	0	0	M^2	0	M^{10}	0	0	0	0
		3	z	M^{13}	0	0	M^3	0	0	0	0	M^{11}
d	5^+	1	yz	0	0	M^{14}	0	M^4	0	0	0	0
		2	zx	0	M^{14}	0	0	0	M^4	0	0	0
		3	xy	0	0	0	0	0	0	M^5	0	0
	3^+	1	x^2-y^2	0	0	0	0	0	0	0	M^6	0
		2	$3z^2-r^2$	M^{12}	0	0	M^{15}	0	0	0	0	M^7

vector $\mathbf{k}=\mathbf{\Sigma}=(u,u,0)$.[35] There are four elements in the group. The corresponding representations $\underline{D}_\alpha(T)$ are given in Table VII, together with the characters $\chi(\Sigma_j)$ of the irreducible representations $\Sigma_j(T)$, $j=1,2,\ldots,5$, which are all one dimensional. The following reductions are obtained from Table VII:

$$\underline{S}_{1^+}^{-1}\underline{D}_{1^+}(T)\underline{S}_{1^+}=\Sigma_1(T)\ , \tag{6.29}$$

$$\underline{S}_{4^-}^{-1}\underline{D}_{4^-}(T)\underline{S}_{4^-}=\begin{bmatrix}\Sigma_1(T) & 0 & 0\\ 0 & \Sigma_4(T) & 0\\ 0 & 0 & \Sigma_3(T)\end{bmatrix}, \tag{6.30}$$

$$\underline{S}_{5^+}^{-1}\underline{D}_{5^+}(T)\underline{S}_{5^+}=\begin{bmatrix}\Sigma_3(T) & 0 & 0\\ 0 & \Sigma_2(T) & 0\\ 0 & 0 & \Sigma_1(T)\end{bmatrix}, \tag{6.31}$$

$$\underline{S}_{3^+}^{-1}\underline{D}_{3^+}(T)\underline{S}_{3^+}=\begin{bmatrix}\Sigma_4(T) & 0\\ 0 & \Sigma_1(T)\end{bmatrix}, \tag{6.32}$$

with the help of the similarity transformations

$$\underline{S}_{1^+}=\underline{\mathbb{1}},\ \underline{S}_{3^+}=\underline{\mathbb{1}}\ , \tag{6.33}$$

$$\underline{S}_{4^-}=\underline{S}_{5^+}=\begin{bmatrix}1/\sqrt{2} & -1/\sqrt{2} & 0\\ 1/\sqrt{2} & 1/\sqrt{2} & 0\\ 0 & 0 & 1\end{bmatrix}. \tag{6.34}$$

TABLE VII. Representations $\underline{D}_\alpha(T)$ of the group $\mathcal{G}_0(\mathbf{R}_L,\mathbf{R}_{L'})$ for the vectors $\mathbf{R}_L=\mathbf{0}$ and $\mathbf{R}_{L'}=\mathbf{\Sigma}=(u,u,0)$, and characters χ of the irreducible representations $\Sigma_j(T)$ of the group $\mathcal{G}_0(\mathbf{k})$ for the wave vector $\mathbf{k}=\mathbf{\Sigma}=(u,u,0)$.

T	E	C_2	IC_4^2	$IC_{2'}$
$\underline{D}_{1^+}(T)$	1	1	1	1
$\underline{D}_{4^-}(T)$	$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}0&1&0\\1&0&0\\0&0&-1\end{bmatrix}$	$\begin{bmatrix}1&0&0\\0&1&0\\0&0&-1\end{bmatrix}$	$\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}$
$\underline{D}_{5^+}(T)$	$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}0&-1&0\\-1&0&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}$
$\underline{D}_{3^+}(T)$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$
$\chi(\Sigma_1(T))$	1	1	1	1
$\chi(\Sigma_2(T))$	1	1	-1	-1
$\chi(\Sigma_3(T))$	1	-1	-1	1
$\chi(\Sigma_4(T))$	1	-1	1	-1

As in the previous case $[\mathbf{R}_{L'}=(0,0,u)=\mathbf{\Delta}]$, for each pair of indices α,α' the matrix $\underline{m}$ is constructed from the blocks $\underline{m}_{jj'}$, which are, in the present case, 1×1 matrices. As an example, the matrix $\underline{m}$ for $\alpha=3^+$ and $\alpha'=4^-$ is

$$\underline{m}=\begin{bmatrix} m_{41} & m_{44} & m_{43} \\ m_{11} & m_{14} & m_{13} \end{bmatrix}=\begin{bmatrix} 0 & m^4 & 0 \\ m_1 & 0 & 0 \end{bmatrix}, \tag{6.35}$$

the second step because of (6.23). Applying (6.24) together with (6.33) and (6.34), we arrive at a final result,

$$\underline{M}_{3^+0,4^-\mathbf{\Sigma}}=\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} 0 & m^4 & 0 \\ m^1 & 0 & 0 \end{bmatrix}\begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}=\frac{1}{\sqrt{2}}\begin{bmatrix} -m^4 & m^4 & 0 \\ m^1 & m^1 & 0 \end{bmatrix}. \tag{6.36}$$

Similar considerations may be performed for any other pair α,α'. The results are collected in Table VIII.

Finally, the case of $\mathbf{R}_L=\mathbf{0}$ and $\mathbf{R}_{L'}=(u,u,u)$ can be also considered; here, $\mathbf{R}_L$ is the central site and $\mathbf{R}_{L'}$ is a nearest-neighbor position in the bcc lattice (or the third-nearest-neighbor position in the sc lattice). The corresponding group $\mathcal{G}_0(\mathbf{R}_L,\mathbf{R}_{L'})$, identical with the group $\mathcal{G}_0(\mathbf{k})$ for $\mathbf{k}=\mathbf{\Lambda}=(u,u,u)$,[35] consists of six elements; its three irreducible representations are called $\underline{\Lambda}_j(T)$, see Table IX for details. Table X contains the matrix elements $M_{\mu 0,\mu'\Lambda}$ obtained in the same way as in the previous cases, using the following reductions:

$$\underline{S}_{1^+}^{-1}\underline{D}_{1^+}(T)\underline{S}_{1^+}=\underline{\Lambda}_1(T)\ , \tag{6.37}$$

$$\underline{S}_{3^+}^{-1}\underline{D}_{3^+}(T)\underline{S}_{3^+}=\underline{\Lambda}_3(T)\ , \tag{6.38}$$

$$\underline{S}_{4^-}^{-1}\underline{D}_{4^-}(T)\underline{S}_{4^-}=\underline{S}_{5^+}^{-1}\underline{D}_{5^+}(T)\underline{S}_{5^+}=\begin{bmatrix} \underline{\Lambda}_1(T) & \underline{0} \\ \underline{0} & \underline{\Lambda}_3(T) \end{bmatrix}, \tag{6.39}$$

where

$$\underline{S}_{1^+}=\underline{\mathbb{1}},\ \ \underline{S}_{3^+}=\underline{\mathbb{1}}\ , \tag{6.40}$$

$$\underline{S}_{4^-}=\underline{S}_{5^+}=\frac{1}{\sqrt{6}}\begin{bmatrix} \sqrt{2} & \sqrt{3} & -1 \\ \sqrt{2} & -\sqrt{3} & -1 \\ \sqrt{2} & 0 & 2 \end{bmatrix}. \tag{6.41}$$

The above analysis of $M_{\mu L,\mu' L'}$, based on the property (6.1), is valid also for the perturbation matrix $V_{\mu L,\mu' L'}$, Eq. (2.21), because the property (6.1) is true both for the operator $\hat{H}(\mathbf{r})$ and $\hat{H}^{\text{per}}(\mathbf{r})$, and because the atomic orbitals $\Phi_{\mu L}^{\text{per}}(\mathbf{r})$ were assumed to have the same symmetry properties as the orbitals $\Phi_{\mu L}(\mathbf{r})$. No more constraints on the structure and number of independent elements of the perturbation matrix $V_{\mu L,\mu' L'}$ may be imposed from symmetry considerations.

On the other hand, the Hamiltonian $\hat{H}(\mathbf{r})$ of the unperturbed crystal also possesses, besides the property (6.1), translational symmetry,

$$\hat{H}(\mathbf{r}+\mathbf{R}_L)=\hat{H}(\mathbf{r})\ , \tag{6.42}$$

which leads to the relations (2.8). Using these relations together with (6.8) and taking (6.7) for $T=I$, which is an inversion operation, we perform a chain of transformations

$$H_{b\alpha\beta 0,b'\alpha'\beta' L}=H_{b\alpha\beta(-L),b'\alpha'\beta' 0}=H^{*}_{b'\alpha'\beta' 0,b\alpha\beta(-L)}=\sum_{\gamma,\gamma'} D^{*}_{\alpha'\beta'\gamma'}(I)D_{\alpha\beta\gamma}(I)H^{*}_{b'\alpha'\gamma' 0,b\alpha\gamma L}\ . \tag{6.43}$$

TABLE VIII. Matrix elements $M_{\mu L,\mu' L'}$ for $\mathbf{R}_L=\mathbf{0}$ and $\mathbf{R}_{L'}=\mathbf{\Sigma}=(u,u,0)$ in terms of 25 independent parameters M^i, $i=1,2,\ldots,25$.

			l'	s	p			d				
			α'	1^+	4^-			5^+			3^+	
			β'	1	1	2	3	1	2	3	1	2
			μ'	s	x	y	z	yz	zx	xy	x^2-y^2	$3z^2-r^2$
l	α	β	μ									
s	1^+	1	s	M^1	M^{13}	M^{13}	0	0	0	M^{10}	0	M^{11}
p	4^-	1	x	M^{21}	M^2	M^4	0	0	0	M^{14}	M^{16}	M^{17}
		2	y	M^{21}	M^4	M^2	0	0	0	M^{14}	$-M^{16}$	M^{17}
		3	z	0	0	0	M^3	M^{15}	M^{15}	0	0	0
d	5^+	1	yz	0	0	0	M^{23}	M^5	M^7	0	0	0
		2	zx	0	0	0	M^{23}	M^7	M^5	0	0	0
		3	xy	M^{18}	M^{22}	M^{22}	0	0	0	M^6	0	M^{12}
	3^+	1	x^2-y^2	0	M^{24}	$-M^{24}$	0	0	0	0	M^8	0
		2	$3z^2-r^2$	M^{19}	M^{25}	M^{25}	0	0	0	M^{20}	0	M^9

TABLE IX. Representations $\underline{D}_\alpha(T)$ of the group $\mathscr{G}_0(\mathbf{R}_L,\mathbf{R}_{L'})$ for the vectors $\mathbf{R}_L=\mathbf{0}$ and $\mathbf{R}_{L'}=\mathbf{\Lambda}=(u,u,u)$, and characters χ of the irreducible representations $\Lambda_j(T)$ of the group $\mathscr{G}_0(\mathbf{k})$ for the wave vector $\mathbf{k}=\mathbf{\Lambda}=(u,u,u)$. Notation for coefficients: $c=-\frac{1}{2}$, $s=\sqrt{3}/2$.

<table>
<tr><th>T</th><th>E</th><th>C_3</th><th>C_3^2</th></tr>
<tr><td>$\underline{D}_{1^+}(T)$</td><td>1</td><td>1</td><td>1</td></tr>
<tr><td>$\underline{D}_{4^-}(T)=\underline{D}_{5^+}(T)$</td><td>$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}$</td><td>$\begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix}$</td><td>$\begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix}$</td></tr>
<tr><td>$\underline{D}_{3^+}(T)$</td><td>$\begin{bmatrix}1&0\\0&1\end{bmatrix}$</td><td>$\begin{bmatrix}c&-s\\s&c\end{bmatrix}$</td><td>$\begin{bmatrix}c&s\\-s&c\end{bmatrix}$</td></tr>
<tr><td>$\chi(\underline{\Delta}_1(T))$</td><td>1</td><td colspan="2">1</td></tr>
<tr><td>$\chi(\underline{\Delta}_2(T))$</td><td>1</td><td colspan="2">1</td></tr>
<tr><td>$\chi(\underline{\Delta}_3(T))$</td><td>2</td><td colspan="2">-1</td></tr>
<tr><th>T</th><th>IC_{2x}</th><th>IC_{2y}</th><th>IC_{2z}</th></tr>
<tr><td>$\underline{D}_{1^+}(T)$</td><td>1</td><td>1</td><td>1</td></tr>
<tr><td>$\underline{D}_{4^-}(T)=\underline{D}_{5^+}(T)$</td><td>$\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix}$</td><td>$\begin{bmatrix}0&0&1\\0&1&0\\1&0&0\end{bmatrix}$</td><td>$\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}$</td></tr>
<tr><td>$\underline{D}_{3^+}(T)$</td><td>$\begin{bmatrix}-c&-s\\-s&c\end{bmatrix}$</td><td>$\begin{bmatrix}-c&s\\s&c\end{bmatrix}$</td><td>$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$</td></tr>
<tr><td>$\chi(\underline{\Delta}_1(T))$</td><td colspan="3">1</td></tr>
<tr><td>$\chi(\underline{\Delta}_2(T))$</td><td colspan="3">$-1$</td></tr>
<tr><td>$\chi(\underline{\Delta}_3(T))$</td><td colspan="3">0</td></tr>
</table>

This imposes additional constraints on the matrix elements of $\hat{H}$. In the case of cubic crystals we may choose these elements to be real. As follows from (5.8), the matrix $D_{\alpha\beta\gamma}(I)$ is

$$D_{\alpha\beta\gamma}(I)=D_{\alpha\beta\gamma}(IE)=\pm\delta_{\beta\gamma}\ , \tag{6.44}$$

where the upper sign holds for even representations ($\alpha=1^+,2^+,\dots$), while the lower sign holds for odd representations ($\alpha=1^-,2^-,\dots$). Therefore Eq. (6.43) may be simplified for cubic crystals as

$$H_{b\alpha\beta 0,b'\alpha'\beta' L}=\pm H_{b'\alpha'\beta' 0,b\alpha\beta L}\ , \tag{6.45}$$

with the upper sign in the case of α and α' having the same parity and the lower sign in the opposite case.

The relation (6.45) reduces the number of the independent parameters for $H_{\mu L,\mu' L'}$ as compared with those obtained for $M_{\mu L,\mu' L'}$.

TABLE X. Matrix elements $M_{\mu L,\mu' L'}$ for $\mathbf{R}_L=\mathbf{0}$ and $\mathbf{R}_{L'}=\mathbf{\Lambda}=(u,u,u)$, in terms of 18 independent parameters M^i, $i=1,2,\dots,18$. Notation for coefficients: $c=-\frac{1}{2}$, $s=\sqrt{3}/2$.

			l'	s	p			d				
			α'	1^+	4^-			5^+			3^+	
			β'	1	1	2	3	1	2	3	1	2
			μ'	s	x	y	z	yz	zx	xy	x^2-y^2	$3z^2-r^2$
l	α	β	μ									
s	1^+	1	s	M^1	M^9	M^9	M^9	M^7	M^7	M^7	0	0
p	4^-	1	x	M^{15}	M^2	M^3	M^3	M^{10}	M^{11}	M^{11}	sM^{12}	cM^{12}
		2	y	M^{15}	M^3	M^2	M^3	M^{11}	M^{10}	M^{11}	$-sM^{12}$	cM^{12}
		3	z	M^{15}	M^3	M^3	M^2	M^{11}	M^{11}	M^{10}	0	M^{12}
d	5^+	1	yz	M^{13}	M^{16}	M^{17}	M^{17}	M^4	M^5	M^5	sM^8	cM^8
		2	zx	M^{13}	M^{17}	M^{16}	M^{17}	M^5	M^4	M^5	$-sM^8$	cM^8
		3	xy	M^{13}	M^{17}	M^{17}	M^{16}	M^5	M^5	M^4	0	M^8
	3^+	1	x^2-y^2	0	sM^{18}	$-sM^{18}$	0	sM^{14}	$-sM^{14}$	0	M^6	0
		2	$3z^2-r^2$	0	cM^{18}	cM^{18}	M^{18}	cM^{14}	cM^{14}	M^{14}	0	M^6

Consider the case of $\mathbf{R}_L=\mathbf{0}$ and $\mathbf{R}_{L'}=\mathbf{\Delta}=(0,0,u)$. Matrix elements $H_{\mu 0,\mu'\Delta}$ can be expressed in terms of 11 independent parameters H^i, $i=1,2,\ldots,11$, instead of 15 parameters M^i. The table for $H_{\mu 0,\mu'\Delta}$ can be obtained readily with the help of $M_{\mu 0,\mu'\Delta}$ given in Table VI and the following substitutions, based on (6.45):

$$\begin{aligned} &M^i=H^i \quad \text{for } i=1,2,\ldots,11\ ,\\ &M^{12}=H^8\ , \\ &M^i=-H^{i-4} \quad \text{for } i=13,14,15\ . \end{aligned} \tag{6.46}$$

For the case of $\mathbf{R}_L=\mathbf{0}$ and $\mathbf{R}_{L'}=\mathbf{\Sigma}=(u,u,0)$ there are 17 independent parameters H^i, $i=1,2,\ldots,17$. The matrix elements $H_{\mu 0,\mu'\Sigma}$ can be obtained from Table VIII with the aid of the substitutions

$$\begin{aligned} &M^i=H^i \quad \text{for } i=1,2,\ldots,17\ ,\\ &M^i=H^{i-8} \quad \text{for } i=18,19,20\ , \\ &M^i=-H^{i-8} \quad \text{for } i=21,22,\ldots,25\ . \end{aligned} \tag{6.47}$$

Finally, the matrix elements $H_{\mu 0,\mu'\Lambda}$ can be expressed in terms of 12 independent parameters H^i, $i=1,2,\ldots,12$. These matrix elements are obtained from Table X with the aid of the substitutions

$$\begin{aligned} &M^i=H^i \quad \text{for } i=1,2,\ldots,12\ ,\\ &M^i=H^{i-6} \quad \text{for } i=13,14\ , \\ &M^i=-H^{i-6} \quad \text{for } i=15,16,17,18\ . \end{aligned} \tag{6.48}$$

Further use of the relation (6.7) for $H_{\mu L,\mu' L'}$ entering the expressions for energy is made in the next two sections.

VII. POINT-GROUP ANALYSIS OF THE BLOCH HAMILTONIAN

In the calculation of the matrix elements $H^{\mathbf{k}}_{\mu\mu'}$ of the Bloch Hamiltonian, Eq. (2.15), the advantage of the point-group symmetry may be taken into account if the sum over the atomic positions $\mathbf{R}_L$ is arranged according to the sets of the atomic neighbors equidistant from site $\mathbf{0}$; these sets are called coordination spheres:

$$H^{\mathbf{k}}_{\mu\mu'}=\sum_L H_{\mu 0,\mu' L}e^{i\mathbf{k}\cdot\mathbf{R}_L}=H^{\mathbf{k}}_{\mu\mu'}(\mathbf{0})+H^{\mathbf{k}}_{\mu\mu'}(\mathbf{R}_{L_1}) +H^{\mathbf{k}}_{\mu\mu'}(\mathbf{R}_{L_2})+\cdots\ , \tag{7.1}$$

where

$$H^{\mathbf{k}}_{\mu\mu'}(\mathbf{0})=H_{\mu 0,\mu' 0}e^{i\mathbf{k}\cdot\mathbf{0}}\ , \tag{7.2}$$

$$H^{\mathbf{k}}_{\mu\mu'}(\mathbf{R}_{L_s})=\sum_{m=1}^{n_s} H_{\mu 0,\mu'(T_{sm}L_s)}e^{i\mathbf{k}\cdot\hat{T}_{sm}\mathbf{R}_{L_s}}\ . \tag{7.3}$$

Here, $\mathbf{R}_{L_s}$ denotes the position of a typical atom belonging to the sth sphere, e.g., $\mathbf{R}_{L_1}=(a/2,a/2,0)$ represents a member of the first coordination sphere for the fcc lattice. Operations $\hat{T}_{sm}$, acting on the vector $\mathbf{R}_{L_s}$, transform it into another member of the sth coordination sphere, Eq. (6.5). The number of atoms belonging to the sth coordination sphere is denoted by n_s (so $n_s=n_1=12$ in the above example).

We are going to prove that the sum over the subset $\hat{T}_{sm}$ of rotations in (7.3) may be replaced by the sum over all $\hat{T}_j$ belonging to $\mathcal{G}_0$, divided by $d_g(s)$:

$$H^{\mathbf{k}}_{\mu\mu'}(\mathbf{R}_{L_s})=\frac{1}{d_g(s)}\sum_{j=1}^{d_g} H_{\mu 0,\mu'(T_jL_s)}e^{i\mathbf{k}\cdot\hat{T}_j\mathbf{R}_{L_s}}\ ; \tag{7.4}$$

here, $d_g(s)$ is the order of the group

$$\mathcal{G}_0(\mathbf{R}_{L_s})\equiv\mathcal{G}_0(\mathbf{0},\mathbf{R}_{L_s})$$

of the vector $\mathbf{R}_{L_s}$; see (6.9). The members of this group are denoted $\hat{T}_{vsm'}\in\mathcal{G}_0(\mathbf{R}_{L_s})$, $m'=1,2,\ldots,d_g(s)$. Then we decompose a group $\mathcal{G}_0$ into left cosets with respect to its subgroup $\mathcal{G}_0(\mathbf{R}_{L_s})$. In this way we find the operations $\hat{T}_{sm}$ with the aid of which any $\hat{T}_j\in\mathcal{G}_0$ is represented in a unique way as

$$\hat{T}_j=\hat{T}_{sm}\hat{T}_{vsm'}\ . \tag{7.5}$$

The number of cosets (operations $\hat{T}_{sm}$) is n_s. This is the number of the atoms in the coordination sphere. The n_s satisfies the relation

$$d_g=n_sd_g(s)\ . \tag{7.6}$$

Therefore Eq. (7.4) may be rewritten as

$$H^{\mathbf{k}}_{\mu\mu'}(\mathbf{R}_{L_s})=\frac{1}{d_g(s)}\sum_{m=1}^{n_s}\sum_{m'=1}^{d_g(s)} H_{\mu 0,\mu'(T_{sm}T_{vsm'}L_s)} \times e^{i\mathbf{k}\cdot\hat{T}_{sm}\hat{T}_{vsm'}\mathbf{R}_{L_s}}\ . \tag{7.7}$$

However, operators $\hat{T}_{vsm'}$ which occur in (7.7) may be omitted because when they act on $\mathbf{R}_{L_s}$ they do not change it. This ends the proof that (7.4) and (7.3) are identical. Expression (7.4) may be easily calculated if we recall the property (6.7):

$$H^{\mathbf{k}}_{b\alpha\beta,b'\alpha'\beta'}(\mathbf{R}_{L_s})=\frac{1}{d_g(s)}\sum_{\gamma,\gamma'}\left[\sum_j D_{\alpha\beta\gamma}(T_j)D^*_{\alpha'\beta'\gamma'}(T_j)e^{i\mathbf{k}\cdot\hat{T}_j\mathbf{R}_{L_s}}\right]H_{b\alpha\gamma 0,b'\alpha'\gamma' L_s}\ . \tag{7.8}$$

The expression in large parentheses is very similar to (4.8). If we change the order of summation there, replacing T_j by T_j^{-1} and make use of the unitarity of $D_{\alpha\beta\gamma}(T_j^{-1})$ as well as of Eq. (3.8), we finally obtain

$$H^{\mathbf{k}}_{b\alpha\gamma,b'\alpha'\gamma'}(\mathbf{R}_{L_s})=\frac{1}{d_g(s)}\sum_{\beta,\beta'}\mathcal{N}^{\alpha\beta\gamma}_{\alpha'\beta'\gamma'}(\mathbf{k},\mathbf{R}_{L_s})H_{b\alpha\beta 0,b'\alpha'\beta' L_s}\ . \tag{7.9}$$

We see that the functions $\mathcal{N}^{\omega}_{\omega'}(\mathbf{k},\mathbf{R})$, introduced for SWLPC functions, Eqs. (4.6)–(4.8), are useful also for the calculation of the elements of the Bloch Hamiltonian matrix. Equation (7.9) is an important result because it shows that the contribution of the sth coordination sphere to the matrix element $H^{\mathbf{k}}_{\mu\mu'}$ may be calculated with the aid of the Hamiltonian matrix elements $H_{v0,vL}$ taken for one representative position $\mathbf{R}_L = \mathbf{R}_{L_s}$ only, instead of forming a combination of such elements taken for n_s different positions, as in the case of the original formula (7.3).

In practice, it is sufficient to calculate the matrix elements $H^{\mathbf{k}}_{\mu\mu'}(\mathbf{R}_{L_s})$ with the help of Eq. (7.9) applied in the case of the subscripts belonging to the upper triangle of the square matrix only. The remaining elements are obtained from the property of hermiticity:

$$H^{\mathbf{k}}_{\mu'\mu}(\mathbf{R}_{L_s}) = [H^{\mathbf{k}}_{\mu\mu'}(\mathbf{R}_{L_s})]^* \ . \tag{7.10}$$

The relation (7.10) may be derived formally from (6.45) and (5.13) together with (5.14).

As an example we calculate, according to (7.1) and (7.9), some matrix elements $H^{\mathbf{k}}_{\mu\mu'}$ of the Bloch Hamiltonian for the fcc crystal in the tight-binding approximation (i.e., zeroth and first coordination spheres are only assumed). This is done using (6.12) and Table VIII together with (6.47) for parameters $H_{\mu L,\mu' L'}$ and Tables II–IV and Eqs. (5.18)–(5.30) for the functions $\mathcal{N}^{\omega}_{\omega'}(\mathbf{k},\mathbf{R})$. With the notation $\mathbf{k}=(k_1,k_2,k_3)$ and $\mathbf{\Sigma}=(a/2)(1,1,0)$, we obtain

$$\begin{aligned} H^{\mathbf{k}}_{ss} &= H^{\mathbf{k}}_{1+1,1+1} = H_{1+10,1+10} + \tfrac{1}{4}\mathcal{N}^{1+11}_{1+11}(\mathbf{k},\mathbf{\Sigma})H_{1+10,1+1\mathbf{\Sigma}} \\ &= H_{s0,s0} + \tfrac{1}{4}H_{s0,s\mathbf{\Sigma}}8(P_{C11C22C33}+P_{C11C23C32}+P_{C12C23C31}+P_{C12C21C33}+P_{C13C21C32}+P_{C13C22C31}) \\ &= H_{s0,s0} + 4H_{s0,s\mathbf{\Sigma}}\left[\cos\left[\frac{a}{2}k_2\right]\cos\left[\frac{a}{2}k_3\right]+\cos\left[\frac{a}{2}k_3\right]\cos\left[\frac{a}{2}k_1\right]+\cos\left[\frac{a}{2}k_1\right]\cos\left[\frac{a}{2}k_2\right]\right] , \end{aligned} \tag{7.11}$$

$$\begin{aligned} H^{\mathbf{k}}_{x^2-y^2,x^2-y^2} &= H^{\mathbf{k}}_{3+1,3+1} = H_{3+10,3+10} + \tfrac{1}{4}\sum_{\beta,\beta'}\mathcal{N}^{3+\beta 1}_{3+\beta' 1}(\mathbf{k},\mathbf{\Sigma})H_{3+\beta 0,3+\beta'\mathbf{\Sigma}} \\ &= H_{3+10,3+10} + \tfrac{1}{4}(\mathcal{N}^{3+11}_{3+11}H_{3+10,3+1\mathbf{\Sigma}} + \mathcal{N}^{3+21}_{3+21}H_{3+20,3+2\mathbf{\Sigma}}) \\ &= H_{(x^2-y^2)0,(x^2-y^2)0} + \tfrac{1}{4}H_{(x^2-y^2)0,(x^2-y^2)\mathbf{\Sigma}}(8P_{C11C22C33}+2P_{C11C23C32}+2P_{C12C23C31} \\ &\qquad +8P_{C12C21C33}+2P_{C13C21C32}+2P_{C13C22C31}) \\ &\quad + \tfrac{1}{4}H_{(3z^2-r^2)0,(3z^2-r^2)\mathbf{\Sigma}}(6P_{C11C23C32}+6P_{C12C23C31}+6P_{C13C21C32}+6P_{C13C22C31}) \\ &= H_{(x^2-y^2)0,(x^2-y^2)0} + 4H_{(x^2-y^2)0,(x^2-y^2)\mathbf{\Sigma}}\cos\left[\frac{a}{2}k_1\right]\cos\left[\frac{a}{2}k_2\right] \\ &\quad + (H_{(x^2-y^2)0,(x^2-y^2)\mathbf{\Sigma}} + 3H_{(3z^2-r^2)0,(3z^2-r^2)\mathbf{\Sigma}})\cos\left[\frac{a}{2}k_3\right]\left[\cos\left[\frac{a}{2}k_1\right]+\cos\left[\frac{a}{2}k_2\right]\right] , \end{aligned} \tag{7.12}$$

$$\begin{aligned} H^{\mathbf{k}}_{x^2-y^2,zx} &= \mathbf{H}^{\mathbf{k}}_{3+1,5+2} = \tfrac{1}{4}\sum_{\beta,\beta'}\mathcal{N}^{3+\beta 1}_{5+\beta' 2}(\mathbf{k},\mathbf{\Sigma})H_{3+\beta 0,5+\beta'\mathbf{\Sigma}} = \tfrac{1}{4}\mathcal{N}^{3+21}_{5+32}H_{3+20,5+3\mathbf{\Sigma}} \\ &= \tfrac{1}{4}H_{5+30,3+2\mathbf{\Sigma}}(4P_{S11S23C32}+4P_{S13S21C32})\sqrt{3} \\ &= 2\sqrt{3}H_{(xy)0,(3z^2-r^2)\mathbf{\Sigma}}\sin\left[\frac{a}{2}k_1\right]\sin\left[\frac{a}{2}k_3\right] . \end{aligned} \tag{7.13}$$

Matrix elements $H^{\mathbf{k}}_{\mu\mu'}$ obtained above are equivalent to the (μ/μ') calculated in Ref. 2.

VIII. EVALUATION OF THE MATRIX ELEMENTS OF PERTURBATION

Solutions for the perturbed crystal obtained by means of the perturbation theory applied in the SWLPC-function representation, are expressed generally in terms of the following matrix elements:

$$V^{\omega_0'\mathbf{k}'\lambda',\omega_0\mathbf{k}\lambda} = \sum_{L',\mu',L,\mu} A^{*\omega_0'\mathbf{k}'\lambda'}_{\mu'}(\mathbf{R}_{L'})V_{\mu'L',\mu L}A^{\omega_0\mathbf{k}\lambda}_{\mu}(\mathbf{R}_L) \ . \tag{8.1}$$

Here, $A^{\omega_0\mathbf{k}\lambda}_{\mu}(\mathbf{R}_L)$ is the SWLPC function, see Eqs. (4.7) and (4.6), while $V_{\mu'L',\mu L}$ is the perturbation matrix, see Eqs. (2.21), (2.22), and (2.7). It is convenient to separate, in Eq. (8.1), the summation over position indices L' and L from the summation over orbital indices μ' and μ:

$$V^{\Omega} = \sum_{L',L} V^{\Omega}_{L'L} \ , \tag{8.2}$$

where

$$V^{\omega_0'\mathbf{k}'\lambda',\omega_0\mathbf{k}\lambda}_{L',L} = \sum_{\mu',\mu} A^{*\omega_0'\mathbf{k}'\lambda'}_{\mu'}(\mathbf{R}_{L'})V_{\mu'L',\mu L}A^{\omega_0\mathbf{k}\lambda}_{\mu}(\mathbf{R}_L) \ ; \tag{8.3}$$

the superscript Ω means a collection of the indices $\omega_0'\mathbf{k}'\lambda'$ and $\omega_0\mathbf{k}\lambda$. The symmetry of the crystal may help to simplify the summation over all pairs of the lattice positions entering (8.2). This is so because—as was done in the calculation of $H^{\mathbf{k}}_{\mu\mu'}$ [Eqs. (7.1)–(7.3)]—the terms related by a rotation of their position indices may be grouped together into sets:

$$V^{\Omega}=\sum_{s}\left[\sum_{m=1}^{n_s} V^{\Omega}_{T_{sm}L'_s,T_{sm}L_s}\right] . \tag{8.4}$$

Here notation (6.5) was used. Within the sth set of the atomic pairs, let $(\mathbf{R}_{L'_s},\mathbf{R}_{L_s})$ be a typical pair. This pair can be transformed by the operation $\hat{T}_{sm}\in\mathcal{G}_0$ into another pair $(\hat{T}_{sm}\mathbf{R}_{L'_s},\hat{T}_{sm}\mathbf{R}_{L_s})$; there are n_s different pairs in the sth set. The pair of the vector $(\mathbf{R}_{L'_s},\mathbf{R}_{L_s})$ defines the subgroup $\mathcal{G}_0(\mathbf{R}_{L'_s},\mathbf{R}_{L_s})$ of the point group $\mathcal{G}_0$, as a set of operations $\hat{T}_{vsm'}$, $m'=1,2,\dots,d_g(s)$, which leaves $\mathbf{R}_{L'_s}$ and $\mathbf{R}_{L_s}$ unchanged, so

$$\hat{T}_{vsm'}\mathbf{R}_{L'_s}=\mathbf{R}_{L'_s} \quad\text{and}\quad \hat{T}_{vsm'}\mathbf{R}_{L_s}=\mathbf{R}_{L_s} . \tag{8.5}$$

Therefore each term occurring in Eq. (8.4) may be expressed as

$$\begin{aligned} V^{\Omega}_{T_{sm}L'_s,T_{sm}L_s} &= V^{\Omega}_{T_{sm}T_{vsm'}L'_s,T_{sm}T_{vsm'}L_s}\\ &=\frac{1}{d_g(s)}\sum_{m'=1}^{d_g(s)} V^{\Omega}_{T_{sm}T_{vsm'}L'_s,T_{sm}T_{vsm'}L_s} . \end{aligned} \tag{8.6}$$

If we recall the decomposition of the group $\mathcal{G}_0$ into left cosets with respect to the subgroup $\mathcal{G}_0(\mathbf{R}_{L'_s},\mathbf{R}_{L_s})$, Eq. (7.5), we obtain, from Eq. (8.4) and (8.6),

$$V^{\Omega}=\sum_{s}\frac{1}{d_g(s)}\sum_{j=1}^{d_g} V^{\Omega}_{T_jL'_s,T_jL_s} . \tag{8.7}$$

Notice that the second sum runs now over all the operations of the full point group $\mathcal{G}_0$. Further progress will be possible if we express the element with the rotated position indices in terms of the elements with the unrotated position indices. Thus we are going to prove the following relation, in which the group representations are induced (for convenience, $T_j=T_0^{-1}$ and $L'_s=L'$, $L_s=L$ are chosen):

$$V^{\alpha'_0\beta'_0\gamma'_0\mathbf{k}'\lambda',\alpha_0\beta_0\gamma_0\mathbf{k}\lambda}_{T_0^{-1}L',T_0^{-1}L}=\sum_{\xi'_0,\xi} D^{*}_{\alpha'_0\xi'_0\beta'_0}(T_0)D_{\alpha_0\xi_0\beta_0}(T_0)V^{\alpha'_0\xi'_0\gamma'_0\mathbf{k}'\lambda',\alpha_0\xi_0\gamma_0\mathbf{k}\lambda}_{L',L} . \tag{8.8}$$

In order to prove (8.8), let us recall the definition of $A^{\omega\mathbf{k}\lambda}_{\mu}(\mathbf{R})$, Eq. (4.7), and apply it to (8.3), with the same indices as were used on the left-hand side of (8.8):

$$V^{\omega'_0\mathbf{k}'\lambda',\omega_0\mathbf{k}\lambda}_{T_0^{-1}L',T_0^{-1}L}=\frac{(d_{\alpha'_0}d_{\alpha_0})^{1/2}}{d_gN}\sum_{\alpha',\beta',\gamma',\alpha,\beta,\gamma}\mathcal{N}^{*\omega'_0}_{\alpha'\beta'\gamma'}(\mathbf{k},\hat{T}_0^{-1}\mathbf{R}_{L'})\mathcal{N}^{\omega_0}_{\alpha\beta\gamma}(\mathbf{k},\hat{T}_0^{-1}\mathbf{R}_L)\left[\sum_{b,b'}a^{*\mathbf{k}'\lambda'}_{b'\alpha'\gamma'}V_{b'\alpha'\beta'(T_0^{-1}L'),b\alpha\beta(T_0^{-1}L)}a^{\mathbf{k}\lambda}_{b\alpha\gamma}\right] . \tag{8.9}$$

The perturbation matrix with rotated position vectors must be calculated according to (6.7),

$$V_{b'\alpha'\beta'(T_0^{-1}L'),b\alpha\beta(T_0^{-1}L)}=\sum_{\xi',\xi}D_{\alpha'\beta'\xi'}(T_0^{-1})D^{*}_{\alpha\beta\xi}(T_0^{-1})V_{b'\alpha'\xi'L',b\alpha\xi L} . \tag{8.10}$$

Let us substitute (8.10) into (8.9), using also the property of unitarity $D_{\alpha\beta\xi}(T_0^{-1})=D^{*}_{\alpha\xi\beta}(T_0)$:

$$\begin{aligned} V^{\omega'_0\mathbf{k}'\lambda',\omega_0\mathbf{k}\lambda}_{T_0^{-1}L',T_0^{-1}L}=\frac{(d_{\alpha'_0}d_{\alpha_0})^{1/2}}{d_gN}&\sum_{\alpha',\xi',\gamma',\alpha,\xi,\gamma}\left[\sum_{\beta'}D^{*}_{\alpha'\xi'\beta'}(T_0)\mathcal{N}^{*\omega'_0}_{\alpha'\beta'\gamma'}(\mathbf{k},\hat{T}_0^{-1}\mathbf{R}_L)\right]\\ &\times\left[\sum_{\beta}D_{\alpha\xi\beta}(T_0)\mathcal{N}^{\omega_0}_{\alpha\beta\gamma}(\mathbf{k},\hat{T}_0^{-1}\mathbf{R}_L)\right]\left[\sum_{b,b'}a^{*\mathbf{k}'\lambda'}_{b'\alpha'\gamma'}V_{b'\alpha'\xi L',b\alpha\xi L}a^{\mathbf{k}\lambda}_{b\alpha\gamma}\right] . \end{aligned} \tag{8.11}$$

The term in the second pair of large parentheses can be now calculated with the help of (4.8),

$$\begin{aligned} \left[\sum_{\beta}D_{\alpha\xi\beta}(T_0)\mathcal{N}^{\alpha_0\beta_0\gamma_0}_{\alpha\beta\gamma}(\mathbf{k},\hat{T}_0^{-1}\mathbf{R}_L)\right]&=\sum_{\beta,T}D_{\alpha\xi\beta}(T_0)D^{*}_{\alpha_0\beta_0\gamma_0}(T)D_{\alpha\beta\gamma}(T)e^{i(\hat{T}_0^{-1}\mathbf{R}_L)\cdot(\hat{T}\mathbf{k})}\\ &=\sum_{T}D^{*}_{\alpha_0\beta_0\gamma_0}(T_0^{-1}T_0T)\left[\sum_{\beta}D_{\alpha\xi\beta}(T_0)D_{\alpha\beta\gamma}(T)\right]e^{i\mathbf{R}_L\cdot(\hat{T}_0\hat{T})\mathbf{k}}\\ &=\sum_{T}\sum_{\xi_0}D^{*}_{\alpha_0\beta_0\xi_0}(T_0^{-1})D^{*}_{\alpha_0\xi_0\gamma_0}(T_0T)D_{\alpha\xi\gamma}(T_0T)e^{i\mathbf{R}_L\cdot(\hat{T}_0\hat{T})\mathbf{k}}\\ &=\sum_{\xi_0}D_{\alpha_0\xi_0\beta_0}(T_0)\sum_{T}D^{*}_{\alpha_0\xi_0\gamma_0}(T_0T)D_{\alpha\xi\gamma}(T_0T)e^{i\mathbf{R}_L\cdot(\hat{T}_0\hat{T})\mathbf{k}}\\ &=\sum_{\xi_0}D_{\alpha_0\xi_0\beta_0}(T_0)\mathcal{N}^{\alpha_0\xi_0\gamma_0}_{\alpha\xi\gamma}(\mathbf{k},\mathbf{R}_L) , \end{aligned} \tag{8.12}$$

since $D^{*}_{\alpha_0\beta_0\xi_0}(T_0^{-1})=D_{\alpha_0\xi_0\beta_0}(T_0)$. In the last step, the summation over T was replaced by summation over T_0T, with T_0 fixed. A similar expression can be obtained for the term in the first pair of large parentheses in (8.11). If we apply the definition of $V_{L',L}^{\alpha_0'\xi_0'\gamma_0'\mathbf{k}'\lambda',\alpha_0\xi_0\gamma_0\mathbf{k}\lambda}$, which is analogous to (8.9), we obtain, from (8.11) and (8.12), the relation (8.8). After substitution of (8.8) into (8.7), the summation over j is easily performed using the orthogonality relations (5.2) for representations:

$$V^{\alpha_0'\beta_0'\gamma_0'\mathbf{k}'\lambda',\alpha_0\beta_0\gamma_0\mathbf{k}\lambda}=\sum_s \frac{1}{d_g(s)}\sum_{\xi_0',\xi_0}\frac{d_g}{d_{\alpha_0}}\delta_{\alpha_0'\alpha_0}\delta_{\beta_0'\beta_0}\delta_{\xi_0'\xi_0}V_{L_s',L_s}^{\alpha_0\xi_0\gamma_0'\mathbf{k}'\lambda',\alpha_0\xi_0\gamma_0\mathbf{k}\lambda} . \tag{8.13}$$

From Eqs. (8.13) and (7.6) follows the final result

$$V^{\Omega}=\sum_s V^{\Omega}(\mathbf{R}_{L_s'},\mathbf{R}_{L_s}) , \tag{8.14}$$

where

$$V^{\Omega}(\mathbf{R}_{L_s'},\mathbf{R}_{L_s})\equiv V^{\alpha_0'\beta_0'\gamma_0'\mathbf{k}'\lambda',\alpha_0\beta_0\gamma_0\mathbf{k}\lambda}(\mathbf{R}_{L_s'},\mathbf{R}_{L_s})=\delta_{\alpha_0'\alpha_0}\delta_{\beta_0'\beta}\frac{n_s}{d_{\alpha_0}}\sum_{\xi_0}V_{L_s',L_s}^{\alpha_0\xi_0\gamma_0'\mathbf{k}'\lambda',\alpha_0\xi_0\gamma_0\mathbf{k}\lambda} . \tag{8.15}$$

Owing to relations (8.14) and (8.15), the contribution coming from the sth set of atomic pairs needs a calculation of $V_{L',L}^{\Omega}$ for one pair of atomic positions only, instead of the calculation required for n_s pairs belonging to this set, as in the case of (8.4).

From (8.14) and (8.15) the usual selection rule may be easily obtained:

$$V^{\alpha_0'\beta_0'\gamma_0'\mathbf{k}'\lambda',\alpha_0\beta_0\gamma_0\mathbf{k}\lambda}=\delta_{\alpha_0'\alpha_0}\delta_{\beta_0'\beta_0}V^{\alpha_0 1\gamma_0'\mathbf{k}'\lambda',\alpha_0 1\gamma_0\mathbf{k}\lambda} . \tag{8.16}$$

This means the matrix element of the perturbation is diagonal in the representation indices α_0' and α_0 and the row indices β_0' and β_0, and it does not depend on the value of the row index β_0.

As an example, for an application of (8.14), let us consider the perturbation of the tight-binding character in the fcc crystal. There are three sets of pairs of position indices in (8.14): the one-member set $(\mathbf{0},\mathbf{0})$, the twelve-member set with a typical pair $(\mathbf{0},\mathbf{\Sigma})$, and the twelve-member set with $(\mathbf{\Sigma},\mathbf{0})$, where $\mathbf{\Sigma}=(a/2)(1,1,0)$ can be taken as a representative site. Therefore,

$$V^{\Omega}=V^{\Omega}(\mathbf{0},\mathbf{0})+V^{\Omega}(\mathbf{0},\mathbf{\Sigma})+V^{\Omega}(\mathbf{\Sigma},\mathbf{0}) . \tag{8.17}$$

With the help of the definition of $V_{L'L}^{\Omega}$ given in (8.3), the value of $A_{\mu}^{\omega\mathbf{k}\lambda}(\mathbf{0})$ in (5.3), $A_{\mu}^{\omega\mathbf{k}\lambda}(\mathbf{R})$ in (4.7), and $V_{\mu'0,\mu0}$ obtained from (6.12a), we find, from (8.15),

$$V^{\alpha_0 1\gamma_0'\mathbf{k}'\lambda',\alpha_0 1\gamma_0\mathbf{k}\lambda}(\mathbf{0},\mathbf{0})=\frac{d_g}{Nd_{\alpha_0}}\sum_{b',b}a_{b'\alpha_0\gamma_0'}^{*\mathbf{k}'\lambda'}V_{b'b}^{0\alpha_0}a_{b\alpha_0\gamma_0}^{\mathbf{k}\lambda} , \tag{8.18}$$

$$V^{\alpha_0 1\gamma_0'\mathbf{k}'\lambda',\alpha_0 1\gamma_0\mathbf{k}\lambda}(\mathbf{0},\mathbf{\Sigma})=\frac{12}{N}\sum_{\alpha,\beta,\gamma}\frac{1}{d_{\alpha_0}}\sum_{\beta_0}\mathcal{N}_{\alpha\beta\gamma}^{\alpha_0\beta_0\gamma_0}(\mathbf{k},\mathbf{\Sigma})\left[\sum_{b',b}a_{b'\alpha_0\gamma_0'}^{*\mathbf{k}'\lambda'}V_{b'\alpha_0\beta_0 0,b\alpha\beta\Sigma}a_{b\alpha\gamma}^{\mathbf{k}\lambda}\right] , \tag{8.19}$$

and

$$V^{\alpha_0 1\gamma_0'\mathbf{k}'\lambda',\alpha_0 1\gamma_0\mathbf{k}\lambda}(\mathbf{\Sigma},\mathbf{0})=[V^{\alpha_0 1\gamma_0\mathbf{k}\lambda,\alpha_0 1\gamma_0'\mathbf{k}'\lambda'}(\mathbf{0},\mathbf{\Sigma})]^{*} . \tag{8.20}$$

Here index 1 replaces any representation row index β_0. The form and dependence of the perturbation matrix $V_{\mu0,\mu'\Sigma}$ on the independent parameters is the same as that of the matrix $M_{\mu0,\mu'\Sigma}$ given in Table VIII.

From (8.18) and (8.19) we see that $V^{\Omega}=0$ for those α_0 which do not enter the indices of the atomic orbitals used for a given model.

We specify further our example for a transition metal, whose LCAO functions are constructed of six atomic orbitals, s-like and d-like, as they were introduced at the end of Sec. V. We notice immediately that $V^{\Omega}=0$ for α_0 different than 1^+, 5^+, or 3^+. Let us calculate, e.g., the matrix element between functions transforming according to the representation $\alpha_0=1^+$:

$$V^{1^+11\mathbf{k}'\lambda',1^+11\mathbf{k}\lambda}(\mathbf{0},\mathbf{0})=\frac{48}{N}a_s^{*\mathbf{k}'\lambda'}V_{s0,s0}a_s^{\mathbf{k}\lambda} , \tag{8.21}$$

$$
\begin{aligned}
V^{1+11\mathbf{k}'\lambda',1+11\mathbf{k}\lambda}(0,\boldsymbol{\Sigma}) &= \frac{12}{N}a_s^{*\mathbf{k}'\lambda'}\biggl\{V_{s0,s\Sigma}a_s^{\mathbf{k}\lambda}\mathcal{N}^{1+11}_{1+11}(\mathbf{k},\boldsymbol{\Sigma}) \\
&\qquad + \sum_{\gamma=1}^{3} V_{s0,(xy)\Sigma}a^{\mathbf{k}\lambda}_{5+\gamma}\mathcal{N}^{1+11}_{5+3\gamma}(\mathbf{k},\boldsymbol{\Sigma}) + \sum_{\gamma=1}^{2} V_{s0,(3z^2-r^2)\Sigma}a^{\mathbf{k}\lambda}_{3+\gamma}\mathcal{N}^{1+11}_{3+2\gamma}(\mathbf{k},\boldsymbol{\Sigma})\biggr] \\
&= \frac{12}{N}a_s^{*\mathbf{k}'\lambda'}\Biggl[V_{s0,s\Sigma}a_s^{\mathbf{k}\lambda}16\biggl[\cos\Bigl[\frac{a}{2}k_2\Bigr]\cos\Bigl[\frac{a}{2}k_3\Bigr]+\cos\Bigl[\frac{a}{2}k_3\Bigr]\cos\Bigl[\frac{a}{2}k_1\Bigr]+\cos\Bigl[\frac{a}{2}k_1\Bigr]\cos\Bigl[\frac{a}{2}k_2\Bigr]\biggr] \\
&\qquad - V_{s0,(xy)\Sigma}16\biggl[a^{\mathbf{k}\lambda}_{yz}\sin\Bigl[\frac{a}{2}k_2\Bigr]\sin\Bigl[\frac{a}{2}k_3\Bigr]+a^{\mathbf{k}\lambda}_{zx}\sin\Bigl[\frac{a}{2}k_3\Bigr]\sin\Bigl[\frac{a}{2}k_1\Bigr] \\
&\qquad\qquad + a^{\mathbf{k}\lambda}_{xy}\sin\Bigl[\frac{a}{2}k_1\Bigr]\sin\Bigl[\frac{a}{2}k_2\Bigr]\biggr] \\
&\qquad + V_{s0,(3z^2-r^2)\Sigma}8\biggl[a^{\mathbf{k}\lambda}_{x^2-y^2}\cos\Bigl[\frac{a}{2}k_3\Bigr]\Bigl[\cos\Bigl[\frac{a}{2}k_2\Bigr]-\cos\Bigl[\frac{a}{2}k_1\Bigr]\Bigr] \\
&\qquad\qquad + a^{\mathbf{k}\lambda}_{3z^2-r^2}\biggl\{\cos\Bigl[\frac{a}{2}k_1\Bigr]\Bigl[\cos\Bigl[\frac{a}{2}k_2\Bigr]-\cos\Bigl[\frac{a}{2}k_3\Bigr]\Bigr] \\
&\qquad\qquad\qquad + \cos\Bigl[\frac{a}{2}k_2\Bigr]\Bigl[\cos\Bigl[\frac{a}{2}k_1\Bigr]-\cos\Bigl[\frac{a}{2}k_3\Bigr]\Bigr]\biggr\}\biggr]\Biggr]\,.
\end{aligned}
\tag{8.22}
$$

In the calculation of (8.22) we made use of Table VIII for independent $V_{\mu0,\mu'\Sigma}$ in the first step, and Table II, together with Eq. (5.21), in the second step. The analogous matrix elements for $\alpha_0=5^+$ and 3^+ may be found.

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