Clebsch–Gordan Coefficients for Space Groups*

D. B. LITVIN AND J. ZAK
Department of Physics, Technion—Israel Institute of Technology, Haifa, Israel

(Received 6 June 1967)

It is shown that to find Clebsch–Gordan coefficients of space groups (both single and double), the representations of the groups of **k** alone are required. This is another example demonstrating the well-accepted fact that in applications of space groups it is sufficient to know the representations of the groups of **k**. Final formulas are derived that enable the calculation of the Clebsch–Gordan coefficients from the representations of the groups of **k**. As an example the spin-orbit coupling in solids is considered.

I. INTRODUCTION

In applications of group theory in physics the problem very often arises of decomposing a direct product of two irreducible representations into a sum of irreducible parts. A classical example is the addition of angular momentum in quantum mechanics. In the theory of solid-state physics such a decomposition is required in defining selection rules in scattering processes in crystals.[1] Sometimes more detailed information is needed, as when one has to express a product of two wavefunctions $\psi_i^{(\alpha)}\psi_j^{(\beta)}$, which are specified according to irreducible representations of some symmetry group, α being the index of the representation and i of the row, by means of functions $\psi_k^{(\gamma)}$ that undergo transformations according to irreducible representations of the same group. The elements of the matrix that gives the connection between $\Psi_i^{(\alpha)}\psi_j^{(\beta)}$ and $\psi_k^{(\gamma)}$ are called the Clebsch–Gordan coefficients. These coefficients are of general interest for each specific symmetry group. For example, they are of very great use for the three-dimensional rotation group and different kinds of SU groups.

In solids the symmetry groups are space groups, and this paper deals with the question of finding the Clebsch–Gordan coefficients for them. The method used is one developed by Koster[2] for finite groups. It is shown that the finding of Clebsch–Gordan coefficients for space groups can be reduced to formulas containing only the representations of groups of the vector **k**. A similar result was obtained before, for the decomposition of direct products of representations of space groups when one is interested in selection rules in crystals.[3]

As an example, it is shown how the Clebsch–Gordan coefficients are obtained for the spin-orbit coupling in solids.

II. GENERAL FORMALISM

Any space group G can be decomposed for a specific **k**, a vector in the first Brillouin zone, into q left cosets

$$G = (\alpha_0 \mid \mathbf{A}_0)\mathcal{K} + (\alpha_i \mid \mathbf{A}_1)\mathcal{K} + \cdots + (\alpha_{q-1} \mid \mathbf{A}_{q-1})\mathcal{K},$$

where $(\alpha_0 \mid \mathbf{A}_0) = (\epsilon \mid 0)$ is the unit element and $\mathcal{K}$, the little group of the vector **k**, is the set of elements $\{(\beta \mid \mathbf{B})\}$ with the property that $\beta\mathbf{k} = \mathbf{k}$ or $\beta\mathbf{k} = \mathbf{k} + \mathbf{K}$ where **K** is a lattice vector of k space. We will denote these two relations by $\beta\mathbf{k} \doteq \mathbf{k}$. The set of elements $\{(\alpha_i \mid \mathbf{A}_i)\}$, the representing elements, has the property that $\alpha_i\mathbf{k} = \mathbf{k}_i$ where $\mathbf{k}_i \not\doteq \mathbf{k}$. The q vectors $\mathbf{k}_i$, i.e., $\mathbf{k}_0 = \mathbf{k}, \mathbf{k}_1, \cdots, \mathbf{k}_{q-1}$, form the star of the vector **k** denoted by S_k.

The elements of G can be written as

$$(\alpha \mid \mathbf{A}) = (\alpha \mid \mathbf{v}(\alpha) + \mathbf{a}) = (\epsilon \mid \mathbf{a})(\alpha \mid \mathbf{v}(\alpha)),$$

where **a** is a primitive translation and $\mathbf{v}(\alpha)$ is either zero or a nonprimitive translation associated with the operator α. We note that $\mathbf{v}(\epsilon) = 0$.

An irreducible representation of the space group G is characterized by the vector **k** and its star, and the irreducible representation of the group of the vector **k**. We denote an irreducible representation of the space group G by $D_{k^*}^r$, where k^* denotes the specific vector **k** in the Brillouin zone and its star, and r denotes the irreducible representation of the group of the vector **k**. The irreducible representation $D_{k^*}^r$ is a $n = dq$ dimensional irreducible representation, q is the number of vectors in the star of **k**, and d the dimension of the rth irreducible representation of the little group of the vector **k**.

We take the irreducible representation of G in the standard form, i.e., the representation of the elements of the invariant subgroup of translations is of the

* Based on a thesis submitted by D. B. Litvin to the Graduate School of the Technion—Israel Institute of Technology, in partial fulfilment of the requirements for the degree of Master of Science, January 1967.

[1] E. J. Elliott and R. Loudon, J. Phys. Chem. Solids **15**, 146 (1960).
[2] G. F. Koster, Phys. Rev. **109**, 227 (1958).
[3] J. Zak, J. Math. Phys. **3**, 1278 (1962).

Downloaded 28 Oct 2004 to 128.118.81.52. Redistribution subject to AIP license or copyright, see http://jmp.aip.org/jmp/copyright.jsp

following form[4]:

$$D^{r}_{k^*}[\epsilon \mid \mathbf{a}] = \begin{pmatrix} e^{-i\mathbf{k}\cdot\mathbf{a}}I & & & & \\ & e^{-i\mathbf{k}_1\cdot\mathbf{a}}I & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & e^{-i\mathbf{k}_{q-1}\cdot\mathbf{a}}I \end{pmatrix}$$

The unit matrix I is of dimension d. For a general element $D^r_{k^*}(G)$ is divided into blocks of dimension d. There will be q rows and columns of blocks. We say then that $D^r_{k^*}(G)$ has $n = dq$ rows (columns) and q block rows (block columns).

The $\theta\mu$th block of $D^r_{k^*}(G)$, denoted by $D^r_{k^*\theta\mu}(G)$, is nonzero, when for all $\mathbf{a}$

$$e^{i\alpha\mathbf{k}_\mu\cdot\mathbf{a}} = e^{i\alpha_\theta\mathbf{k}\cdot\mathbf{a}}.$$

We have for this nonzero block of dimension d:

$$D^r_{k^*\theta\mu}[\alpha \mid \mathbf{v}(\alpha) + \mathbf{a}] = D^r_k[\beta_{\theta\mu} \mid \mathbf{v}(\beta_{\theta\mu}) + \mathbf{b}_{\theta\mu}], \quad (1)$$

where $D^r_k[\beta_{\theta\mu} \mid \mathbf{v}(\beta_{\theta\mu}) + \mathbf{b}_{\theta\mu}]$ is the d-dimensional irreducible representation of the little group of the vector $\mathbf{k}$ and $(\beta_{\theta\mu} \mid \mathbf{v}(\beta_{\theta\mu}) + \mathbf{b}_{\theta\mu})$ is found from the relation

$$\begin{aligned}(\alpha \mid \mathbf{v}(\alpha) + \mathbf{a})(\alpha_\mu \mid \mathbf{v}(\alpha_\mu) + \mathbf{a}_\mu) \\ = (\alpha_\theta \mid \mathbf{v}(\alpha_\theta) + \mathbf{a}_\theta)(\beta_{\theta\mu} \mid \mathbf{v}(\beta_{\theta\mu}) + \mathbf{b}_{\theta\mu}). \quad (2)\end{aligned}$$

Hence $(\alpha_\mu \mid \mathbf{v}(\alpha_\mu) + \mathbf{a}_\mu)$ and $(\alpha_\theta \mid \mathbf{v}(\alpha_\theta) + \mathbf{a}_\mu)$ are the representing elements, such that $\alpha_\mu\mathbf{k} = \mathbf{k}_\mu$ and $\alpha_\theta\mathbf{k} = \mathbf{k}_\theta$; we assume that $\mathbf{a}_\mu = \mathbf{a}_\theta = 0$.

Defining the nonprimitive translation associated with $\beta_{\theta\mu}$ as

$$\mathbf{v}(\beta_{\theta\mu}) = \alpha_\theta^{-1}(\alpha\mathbf{v}(\alpha_\mu) + \mathbf{v}(d) - \mathbf{v}(d_\theta)),$$

we derive from Eq. (2) that

$$\alpha\alpha_\mu = \alpha_\theta\beta_{\theta\mu} \quad (3)$$

and

$$\mathbf{b}_{\theta\mu} = \alpha_\theta^{-1}\mathbf{a}. \quad (4)$$

Rewriting Eq. (1) and using Eq. (4), we have for the nonzero blocks of $D^r_{k^*}$

$$\begin{aligned}D^r_{k^*\mu\theta}[\alpha \mid \mathbf{v}(\alpha) + \mathbf{a}] &= D^r_k[\beta_{\theta\mu} \mid \mathbf{v}(\beta_{\theta\mu}) + \alpha_\theta^{-1}\mathbf{a}] \\ &= e^{-i\mathbf{k}_\theta\cdot\mathbf{a}} D^r_k[\beta_{\theta\mu} \mid \mathbf{v}(\beta_{\theta\mu})], \quad (5)\end{aligned}$$

where $\beta_{\theta\mu}$ and $\mathbf{v}(\beta_{\theta\mu})$ are given by Eqs. (3) and (4), respectively.

If the direct product of two irreducible representations of the space group G is reducible, we have

$$D^r_{k^*} \times D^{r'}_{k'^*} = \sum_{mn} c_{mn} D^{r''_n}_{k''_m{}^*},$$

[4] G. F. Koster, *Space Groups and their Representations* (Academic Press Inc., New York, 1957).

where c_{mn} is the number of times the irreducible representation appears in the reduced form.

We calculate c_{mn} from

$$c_{mn} = \frac{1}{gh} \sum_G \mathrm{X}^r_{k^*}(G)\mathrm{X}^{r'}_{k'^*}(G)\mathrm{X}^{r''_n}_{k''_m{}^*}(G)^*,$$

where $\mathrm{X}^r_{k^*}(G)$ is the character of $D^r_{k^*}(G)$, and gh is the order of the space group G; h is the order of the invariant subgroup of translations T, and g the order of the factor group G/T.

The direct product is put into reduced form by a similarity transformation using a unitary matrix U:

$$U^{-1}[D^r_{k^*} \times D^{r'}_{k'^*}]U = \begin{pmatrix}\text{reduced form of the} \\ \text{direct product}\end{pmatrix}.$$

We assume that the irreducible representation $D^{r''_1}_{k''_1{}^*}$, a $n'' = q''d''$ dimensional representation, appears c times in the reduced form. (In general the dimension of $D^{r''_n}_{k''_m{}^*}$ is denoted as $n''_{mn} = q''_m d''_n$ and its multiplicity in the reduced form as c_{mn}; when referring to $D^{r''_1}_{k''_1{}^*}$, for typographical reasons only, we will drop the indexes m and n from the dimensionality and multiplicity.) If these are the first irreducible representations in the reduced form, i.e., the first irreducible representations along the diagonal of the reduced form, then the first $cq''d''$ columns of U are calculated from the equation[2]

$$\begin{aligned}\frac{d''q''}{gh}\sum_G [D^r_{k^*}(G) \times D^{r'}_{k'^*}(G)]_{mn}[D^{r''_1}_{k''_1{}^*}(G)]^*_{i''j''} \\ = U_{mi''}U^*_{nj''} + U_{m(d''q''+i'')}U^*_{n(d''q''+j'')} \\ + U_{m(2d''q''+i'')}U^*_{n(2d''q''+j'')} \\ + U_{m([c-1]d''q''+i'')}U_{n([c-1]d''q''+j'')}. \quad (6)\end{aligned}$$

This gives the elements of the first $cq''d''$ columns of U in terms of the known quantities

$$\frac{d''q''}{gh}\sum_G [D^r_{k^*}(G) \times D^{r'}_{k'^*}(G)]_{mn}[D^{r''_1}_{k''_1{}^*}(G)]^*_{i''j''}.$$

We also know that

$$[D^r_{k^*}(G) \times D^{r'}_{k'^*}(G)]_{mn} \equiv D^r_{k^*}(G)_{ij}D^{r'}_{k'^*}(G)_{i'j'},$$

where m and n are used as an abbreviation for the double indices (i, i') and (j, j'), respectively. The possible values of the indices are as follows:

$$\begin{aligned} m, n &= 1, 2, \cdots, qdq'd', \\ i, j &= 1, 2, \cdots, qd, \\ i', j' &= 1, 2, \cdots, q'd', \\ i'', j'' &= 1, 2, \cdots, q''d''. \end{aligned}$$

qd is the dimension of the irreducible representation

Downloaded 28 Oct 2004 to 128.118.81.52. Redistribution subject to AIP license or copyright, see http://jmp.aip.org/jmp/copyright.jsp

$D^r_{k^*}$, $q'd'$ of $D^{r'}_{k'^*}$, $q''d''$ of $D^{r_1''}_{k_1''^*}$, and $qdq'd'$ of the direct product $D^r_{k^*} \times D^{r'}_{k'^*}$.

Let us introduce a new indexation which will show clearly the division of the irreducible representations into blocks. $D^r_{k^*}$ is a qd-dimensional irreducible representation which is divided into $q \times q$ blocks of dimension $d \times d$. Let θ be the index of the block rows, and μ be the index of the block columns. A specific block of $D^r_{k^*}$ is denoted by (θ, μ), the intersection of the θth block row and the μth block column.

The ith row of $D^r_{k^*}$ can be denoted as the ηth row of the θth block row, and the jth column denoted as the πth column of the μth block column, that is,

$$i = \theta d + \eta, \quad \theta, \mu = 0, 1, \cdots, q - 1,$$
$$j = \mu d + \pi, \quad \eta, \pi = 1, 2, \cdots, d. \tag{7}$$

Using this indexation, the (i, j)th element of $D^r_{k^*}$ is denoted as the $(\theta d + \eta)(\mu d + \pi)$th element. It is the $(\eta\pi)$th element of the $(\theta\mu)$th block of $D^r_{k^*}$. The rows and columns of $D^{r'}_{k'^*}$ and $D^{r_1''}_{k_1''^*}$ are denoted in a similar manner.

Recalling that $G = \{(\alpha \mid \mathbf{v}(\alpha) + \mathbf{a})\}$ and using Eqs. (1) and (5), we can write

$$D^r_{k^*}(G)_{(\theta d+\eta)(\mu d+\pi)} = e^{-i\mathbf{k}_\theta \cdot \mathbf{a}} D^r_k[\beta_{\theta\mu} \mid \mathbf{v}(\beta_{\theta\mu})] \delta(\alpha\alpha_\mu - \alpha_\theta\beta_{\theta\mu}). \tag{8}$$

The $(\theta\mu)$th block of $D^r_{k^*}(G)$ is nonzero only if α fulfills the condition written in the delta function. Two similar expressions can be written for elements of the irreducible representations $D^{r'}_{k'^*}$ and $D^{r_1''}_{k_1''^*}$.

Using the new indexation, and writing the sum on the elements of the space group G as

$$\sum_G = \sum_{(\epsilon|\mathbf{a})} \sum_{(\alpha|\mathbf{v}(\alpha))}$$

we then rewrite Eq. (6) in the following form:

$$\begin{aligned} &\frac{1}{h} \sum_{(\epsilon|\mathbf{a})} e^{-i(\mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}_1''{}_{\theta''}) \cdot \mathbf{a}} \frac{d''q''}{g} \sum_{(\alpha|\mathbf{v}(\alpha))} D^r_k[\beta_{\theta\mu} \mid \mathbf{v}(\beta_{\theta\mu})]_{\eta\pi} \\ &\times D^{r'}_{k'}[\beta'_{\theta'\mu'} \mid \mathbf{v}(\beta'_{\theta'\mu'})]_{\eta'\pi'} D^{r_1''}_{k_1''}[\beta''_{\theta''\mu''} \mid \mathbf{v}(\beta''_{\theta''\mu''})]^*_{\eta''\pi''} \\ &\qquad \times \delta(\alpha\alpha_\mu - \alpha_\theta\beta_{\theta\mu}) \\ &\qquad \times \delta(\alpha\alpha'_{\mu'} - \alpha'_{\theta'}\beta'_{\theta'\mu'}) \delta(\alpha\alpha''_{\mu''} - \alpha''_{\theta''}\beta''_{\theta''\mu''}) \\ &\quad = U_{(\theta d+\eta;\theta' d'+\eta')(\theta'' d''+\eta'')} U^*_{(\mu d+\pi;\mu' d'+\pi')(\mu'' d''+\pi'')} \\ &\qquad + \cdots + U_{(\theta d+\eta;\theta' d'+\eta')([c-1]d''q''+\theta'' d''+\eta'')} \\ &\qquad \times U^*_{(\mu d+\pi;\mu' d'+\pi')([c-1]d''q''+\mu'' d''+\pi'')}. \end{aligned} \tag{9}$$

The basis functions of the irreducible representation $D^r_{k^*}$ are $\psi^{\mathbf{k}_\theta}_\eta$, and transform under elements of the space group as follows:

$$(\alpha \mid \mathbf{A})\psi^{\mathbf{k}_\theta}_\eta = \sum_{\mu,\pi} D^r_{k^*}[\alpha \mid \mathbf{A}]_{(\mu d+\pi)(\theta d+\eta)} \psi^{\mathbf{k}_\theta}_\pi. \tag{10}$$

The functions $\psi^{\mathbf{k}}_\eta$, $\theta = 0$, form the basis functions of the irreducible representation D^r_k of the little group $\mathcal{K}$. The functions $\psi^{\mathbf{k}_\theta}_\eta$ are related to the functions $\psi^{\mathbf{k}}_\eta$ by the following relation[4]:

$$\psi^{\mathbf{k}_\theta}_\eta = (\alpha_\theta \mid \nu(\alpha_\theta))\psi^{\mathbf{k}}_\eta, \tag{11}$$

where $(|\alpha_\theta \ \mathbf{v}(\alpha_\theta))$ are the representing elements of the group G. Similar relations hold for the basis functions $\psi^{\mathbf{k}'_{\theta'}}_{\eta'}$ and $\psi^{\mathbf{k}_1''{}_{\theta''}}_{\eta''}$ of the irreducible representations $D^{r'}_{k'^*}$ and $D^{r''}_{k_1''^*}$, respectively.

The basis functions of the direct product are $\psi^{\mathbf{k}_\theta}_\eta \psi^{\mathbf{k}'_{\theta'}}_{\eta'}$. The elements of U give the coefficients of the linear combinations of these functions, which form the basis functions of the c irreducible representations $D^{r_1''}_{k_1''^*}$ appearing in the reduced form, that is,

$$\psi^{\mathbf{k}_1''{}_{\theta''}}_{\eta''} = \sum_{\substack{\theta\theta' \\ \eta\eta'}} U_{(\theta d+\eta;\theta' d'+\eta')(ld''q''+\theta'' d''+\eta'')} \psi^{\mathbf{k}_\theta}_\eta \psi^{\mathbf{k}'_{\theta'}}_{\eta'}, \tag{12}$$

where $l = 0, 1, \cdots, c - 1$.

The columns of U calculated in Eq. (9) can be shown to be divided into blocks. The $cq''d''$ columns are divided into sections, and each section divided into $qq' \times q''$ blocks of dimension $dd' \times d''$. A specific block is denoted by $(\theta\theta')(lq'' + \theta'')$, the $(\theta\theta')(\theta'')$th block of the lth section.

Equation (9) facilitates the calculation of the set of c blocks $(\theta\theta')(lq'' + \theta'')$, $l = 0, 1, \cdots, c - 1$, for each trio of values of θ, θ', and θ''. Once we have chosen a specific trio we may perform the first sum in the equation, for

$$\frac{1}{h} \sum_{(\epsilon|\mathbf{a})} e^{-i(\mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}_1''{}_{\theta''}) \cdot \mathbf{a}} = \begin{cases} 0 & \text{if} \quad \mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}''_{1\theta''} \not\doteq 0 \\ 1 & \text{if} \quad \mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}''_{1\theta''} \doteq 0. \end{cases} \tag{13}$$

By choosing in Eq. (9) the indices $\mu\mu'\mu''$ and $\pi\pi'\pi''$, equal to $\theta\theta'\theta''$ and $\eta\eta'\eta''$, respectively, and using Eq. (13), one finds that sums of the squares of elements of the $(\theta\theta')(lq'' + \theta'')$th blocks are equal to zero if $\mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}''_{1\theta''} \not\doteq 0$. Consequently, the elements of the blocks for which $\mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}''_{1\theta''} \not\doteq 0$ are zero. In the following we assume that $\mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}''_{1\theta''} \doteq 0$. We also note that in the second sum of Eq. (9) we do not have to sum over all α, but only over those that simultaneously fulfill the three delta conditions.

Let us begin by calculating the first block column of each section, that is, the $(\theta\theta')(lq'')$th blocks, where we have taken $\theta'' = 0$. We first choose $\theta = \theta' = \theta'' = 0$ and calculate the $(00)(lq'')$th blocks, using Eq. (9.)

We have assumed that $\mathbf{k} + \mathbf{k}' - \mathbf{k}''_1 \doteq 0$, where $\mathbf{k}$ is the first vector of the star of $\mathbf{k}$, $\mathbf{k}'$ the first vector of the star of $\mathbf{k}'$, and $\mathbf{k}''_1$, the first vector of the star of $\mathbf{k}''_1$.

Downloaded 28 Oct 2004 to 128.118.81.52. Redistribution subject to AIP license or copyright, see http://jmp.aip.org/jmp/copyright.jsp

In our notation we have

$$\mathbf{k}_0 = \mathbf{k}, \quad \alpha_0 = \epsilon;$$
$$\mathbf{k}'_0 = \mathbf{k}', \quad \alpha'_0 = \epsilon;$$
$$\mathbf{k}''_{1_0} = \mathbf{k}''_1, \quad \alpha''_0 = \epsilon.$$

We choose $\mu = \mu' = \mu'' = 0$ and with this choice, the three delta conditions in Eq. (9) are

$$\alpha = \beta, \quad \alpha = \beta', \quad \alpha = \beta''.$$

Let us denote the elements of G which simultaneously fulfill the three delta conditions by $\hat{\beta}$. We have then:

$$\{\hat{\beta}\} = \{\beta\} \cap \{\beta'\} \cap \{\beta''\}. \tag{14}$$

The set of elements $\{\hat{\beta}\}$ is the intersection of the point groups associated with the three little groups $\mathcal{K}$, $\mathcal{K}'$, and $\mathcal{K}''$.

To find the elements $\hat{\beta}$ the following remark is useful. One can define the direct product of two stars, $S_{\mathbf{k}} \times S_{\mathbf{k}'}$, the star $S_{\mathbf{k}}$ of the vector $\mathbf{k}$ times the star $S_{\mathbf{k}'}$ of the vector $\mathbf{k}'$ as the aggregate of all vectors formed by adding vectorally one vector of the star of $\mathbf{k}$ and one vector of the star of $\mathbf{k}'$.[5] One may write

$$S_{\mathbf{k}} \times S_{\mathbf{k}'} = \sum_m \epsilon_m S_{\mathbf{k}_m''},$$

where ϵ_m is the number of times the star $S_{\mathbf{k}_m''}$ appears in the direct product $S_{\mathbf{k}} \times S_{\mathbf{k}'}$. Two types of stars appear in the reduced form of the direct product of the two stars. If $\epsilon_m = 1$ we speak of $S_{\mathbf{k}_m''}$ as a star of the first kind, and if $\epsilon_m > 1$, as a star of the second kind.

It is clear that the elements of G which simultaneously leave the vectors $\mathbf{k}$ and $\mathbf{k}'$ invariant also leave $\mathbf{k}_1''$ invariant. Now, if $S_{\mathbf{k}_1''}$ is a star of the first kind, then the point group $\{\beta''\}$ contains only these elements, and relation (11) reduces to

$$\{\hat{\beta}\} = \{\beta''\}. \tag{15}$$

However, if $S_{\mathbf{k}_1''}$ is a star of the second kind, then $\{\beta''\}$ contains additional elements that, while leaving $\mathbf{k}_1''$ invariant, do not leave $\mathbf{k}$ and $\mathbf{k}'$ invariant. Relation (11) reduces in this case to (see Appendix A):

$$\{\hat{\beta}\} = \{\beta\} \cap \{\beta''\}. \tag{16}$$

We are now in a position to use Eq. (9) to calculate the $(00)(lq'')$ blocks; this equation becomes

$$\frac{d''q''}{g} \sum_{(\hat{\beta}|\mathbf{v}(\hat{\beta}))} D^{\tau}_{\mathbf{k}}[\hat{\beta} \mid \mathbf{v}(\hat{\beta})]_{\eta\pi} D^{\tau'}_{\mathbf{k}'}[\hat{\beta} \mid \mathbf{v}(\hat{\beta})]_{\eta'\pi'} D^{\tau_1''}_{\mathbf{k}_1''}[\hat{\beta} \mid \mathbf{v}(\hat{\beta})]^*_{\eta''\pi}$$
$$= U_{(\eta\eta')(\eta'')} U^*_{(\pi\pi')(\pi'')} + U_{(\eta\eta')(d''q''+\eta'')} U^*_{(\pi\pi')(d''q''+\pi'')}$$
$$+ \cdots + U_{(\eta\eta')([c-1]d''q''+\eta'')} U^*_{(\pi\pi')([c-1]d''q''+\eta'')}, \tag{17}$$

where the elements $\{\hat{\beta}\}$ are given by Eq. (12) or (13).

[5] J. L. Birman, Phys. Rev. **127**, 1093 (1962).

If the irreducible representation $D^{\tau_1''}_{\mathbf{k}_1''*}$ appears only once in the reduced form of the direct product, i.e., $c = 1$ then to calculate the (00)(0)th block of the $q''d''$ columns of U associated with $D^{\tau_1''}_{\mathbf{k}_1''*}$ we use Eq. (17) for the case $c = 1$. The right-hand side of (17) is then

$$U_{(\eta\eta')(\eta'')} U^*_{(\pi\pi')(\pi'')}. \tag{18}$$

According to Koster[1] one finds specific values of $\pi\pi'\pi''$ and $\eta\eta'\eta''$ such that the left-hand side of Eq. (17) is nonzero, and then holds $\pi\pi'\pi''$ to these specific values and lets $\eta\eta'\eta''$ run over their possible values. For each trio of values of $\eta\eta'\eta''$ one uses Eq. (17) with Eq. (18) to calculate $U_{(\eta\eta')(\eta'')} U^*_{(\pi\pi')(\pi'')}$, and thereby one derives $dd'd''$ equations for the $dd'd''$ elements of the (00)(0)th block of the columns of the matrix U. The general case for an arbitrary c is obtained in a similar manner.[2]

Now we find the other blocks in the first block columns of each section, the $(\theta\theta')(lq'')$th blocks, for which $\mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}_1'' \doteq 0$.[6]

At the beginning of this section, the space group G was divided for a chosen vector $\mathbf{k}$ into q left cosets. The vector $\mathbf{k}$ defined the aggregate of vectors $\alpha_\theta \mathbf{k} = \mathbf{k}_\theta$, the star of the vector $\mathbf{k}$. If we were to choose any other of the vectors $\mathbf{k}_\theta$ we could again divide the space group G into q left cosets and define the star of the vector $\mathbf{k}_\theta$. The stars of the vectors $\mathbf{k}$ and $\mathbf{k}_\theta$ are identical, the star is defined by giving any one of its vectors; but the division of the space group G is in general different.

We redefine the first star by the vector $\mathbf{k}_\theta$ instead of $\mathbf{k}$, and define the little group of the vector $\mathbf{k}_\theta$. The functions $\psi^{\mathbf{k}_\theta}_\eta$, for the specific θ, form the basis functions of $D^{\tau}_{\mathbf{k}_\theta}$, the irreducible representation of the little group of the vector $\mathbf{k}_\theta$. The second star is redefined by $\mathbf{k}'_{\theta'}$ instead of $\mathbf{k}'$, and the star of the vector $\mathbf{k}_1''$ remains defined by the vector $\mathbf{k}_1''$.

The irreducible representation $D^{\tau_1''}_{\mathbf{k}_1''*}$ again appears c times in the reduced form of the direct product of the irreducible representations in the redefinition. To solve for the $(\theta\theta')(lq'')$th blocks of U is equivalent to finding the $(00)(lq'')$th blocks of the matrix $\bar{U}$, which reduces the direct product of the irreducible representations in the redefinition (see Appendix B).

$$\bar{U}_{(\eta\eta')(lq''d''+\eta'')} = U_{(\theta d+\eta;\theta' d'+\eta')(lq''d''+\eta'')} \tag{19}$$

holds for all values of the indexes η, η', η'', and l.

[6] If $S_{\mathbf{k}_m''}$ is defined by $\mathbf{k} + \mathbf{k}' - \mathbf{k}_m'' \doteq 0$ and is a star of the first kind, then the $(00)(lq'')$th blocks are the only nonzero blocks of the first block columns. If $S_{\mathbf{k}_m''}$ is a star of the second kind, then additional nonzero blocks, $(\theta\theta')(lq'')$ for which $\mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}_m'' \doteq 0$, are in general such that $\theta = \theta'$.

Downloaded 28 Oct 2004 to 128.118.81.52. Redistribution subject to AIP license or copyright, see http://jmp.aip.org/jmp/copyright.jsp

Following steps (1) to (17) we have in our redefinition

$$\frac{d''g''}{g}\sum_{(\hat\beta|\mathbf{v}(\hat\beta))} D^{r}_{\mathbf{k}_\theta}[\hat\beta\,|\,\mathbf{v}(\hat\beta)]_{\eta\pi}$$
$$\times D^{r'}_{\mathbf{k}'\theta'}[\hat\beta\,|\,\mathbf{v}(\hat\beta)]_{\eta'\pi'} D^{r_1''}_{\mathbf{k}_1''}[\hat\beta\,|\,\mathbf{v}(\hat\beta)]_{\eta''\pi''}$$
$$= \bar U_{(\eta\eta')(\eta'')}\bar U^{*}_{(\pi\pi')(\pi'')} + \bar U_{(\eta\eta')(d''q''+\eta'')}\bar U^{*}_{(\pi\pi')(d''q''+\pi'')}$$
$$+ \cdots + \bar U_{(\eta\eta')([c-1]d''q''+\eta'')}\bar U^{*}_{(\pi\pi')([c-1]d''q''+\pi'')}. \quad (20)$$

If the star of the vector $\mathbf{k}_1''$ is of the first kind, then

$$\{\hat\beta\} = \{\beta''\},$$

and if of the second kind,

$$\{\hat\beta\} = \{\alpha_\theta\beta\alpha_\theta^{-1}\} \cap \{\alpha'_{\theta'}\beta'\alpha'^{-1}_{\theta'}\}. \quad (21)$$

Again, by finding specific values of $\pi\pi'\pi''$ such that the left-hand side of Eq. (20) is nonzero, the number of trios of $\pi\pi'\pi''$ depending on the value of c, we find the elements of the $(00)(lq'')$ blocks of $\bar U$, and therefore by Eq. (19) the $(\theta\theta')(lq'')$ blocks of U.

We have shown a method to calculate the blocks in the first block column of each section, i.e., the $(\theta\theta')(lq'')$th blocks, $\theta''=0$, for which $\mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}_1'' \doteq 0$. In both Eqs. (17) and (20) it is necessary to know only the irreducible representations of the factor group $\mathcal{K}/T$, $\mathcal{K}'/T$, and $\mathcal{K}''/T$, where T is the invariant subgroup of translations.

Instead of using Eq. (9) to calculate the remaining nonzero blocks of elements, it is advantageous to review the structure of the basis functions of irreducible representations of space groups. Using properties of this structure we derive an alternative method to calculate the remaining blocks.

For the sake of simplicity we consider only the first of the c sections which we are calculating. The results are, of course, applicable to every section.

The basis functions of the direct product are $\psi^{\mathbf{k}\theta}_\eta\psi^{\mathbf{k}'\theta'}_{\eta'}$. The elements of U give the coefficients of the linear combinations of these functions which form the basis functions of the irreducible representation $D^{r_1''}_{\mathbf{k}_1''*}$; we rewrite Eq. (12) by

$$\psi^{\mathbf{k}_1''\theta''}_{\eta''} = \sum_{\substack{\theta\theta'\\ \eta\eta'}} U_{(\theta d+\eta;\theta'd'+\eta')(\theta''d''+\eta'')}\psi^{\mathbf{k}\theta}_\eta\psi^{\mathbf{k}'\theta'}_{\eta'}. \quad (22)$$

The sum is not on all possible values of θ and θ', but only on those values which fulfill the condition $\mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}''_{1\theta''} \doteq 0$. To denote this, we replace the sign of summation $\sum_{\theta\theta'}$ with $\sum^{\mathbf{k}_1''\theta''}_{\theta\theta'}$, where $\mathbf{k}'_{1\theta''}$ denotes that θ and θ' take only those values for which the condition is fulfilled.

In particular, for $\theta''=0$, we have

$$\psi^{\mathbf{k}_1''}_{\eta''} = \sum^{\mathbf{k}_1''}_{\substack{\theta\theta'\\ \eta\eta'}} U_{(\theta d+\eta;\theta'd'+\eta')(\eta'')}\psi^{\mathbf{k}\theta}_\eta\psi^{\mathbf{k}'\theta'}_{\eta'}. \quad (23)$$

The basis function of $D^{r_1''}_{\mathbf{k}_1''*}$ must fulfill relation (11), that is

$$\psi^{\mathbf{k}_1''\theta''}_{\eta''} = (\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''}))\psi^{\mathbf{k}_1''}_{\eta''}. \quad (24)$$

For a specific θ'' we have, using Eq. (22), that

$$\psi^{\mathbf{k}_1''\theta''}_{\eta''} = \sum^{\mathbf{k}_1''\theta''}_{\substack{\mu\mu'\\ \pi\pi'}} U_{(\mu d+\pi;\mu'd'+\pi')(\theta''d''+\eta'')}\psi^{\mathbf{k}\mu}_\pi\psi^{\mathbf{k}'\mu'}_{\pi'}, \quad (25)$$

where the values of μ and μ' are constrained by the condition $\mathbf{k}_\mu + \mathbf{k}'_{\mu'} - \mathbf{k}''_{1\theta''} \doteq 0$. On the other hand, substituting (23) into (24), we have

$$\psi^{\mathbf{k}_1''\theta''}_{\eta''} = \sum^{\mathbf{k}_1''}_{\substack{\theta\theta'\\ \eta\eta'}} U_{(\theta d+\eta;\theta'd'+\eta')(\eta'')}(\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''}))\psi^{\mathbf{k}\theta}_\eta\psi^{\mathbf{k}'\theta'}_{\eta'}. \quad (26)$$

For Eqs. (25) and (26) to be consistent, we must have

$$(\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''}))\psi^{\mathbf{k}\theta}_\eta\psi^{\mathbf{k}'\theta}_{\eta'}$$
$$= \sum^{\mathbf{k}_1''\theta''}_{\substack{\mu\mu'\\ \pi\pi'}} D^{r}_{\mathbf{k}*}[\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''})]_{(\mu d+\pi)(\theta d+\eta)}$$
$$\times D^{r'}_{\mathbf{k}'*}[\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''})]_{(\mu'd'+\pi')(\theta'd'+\pi')}\psi^{\mathbf{k}\mu}_\pi\psi^{\mathbf{k}'\mu'}_{\pi'}$$
$$= \sum^{\mathbf{k}_1''\theta''}_{\substack{\mu\mu'\\ \pi\pi'}} (D^{r}_{\mathbf{k}*}[\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''})]$$
$$\times D^{r'}_{\mathbf{k}'*}[\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''})])_{(\mu d+\pi,\mu'd'+\pi')(\theta d+\eta;\theta'd'+\eta')}\psi^{\mathbf{k}\mu}_\pi\psi^{\mathbf{k}'\mu'}_{\pi'}. \quad (27)$$

Substituting this into (26), we have

$$\psi^{\mathbf{k}_1''\theta''}_{\eta''} = \sum^{\mathbf{k}_1''\theta''}_{\substack{\mu\mu'\\ \pi\pi'}}\sum^{\mathbf{k}_1''}_{\substack{\theta\theta'\\ \eta\eta'}} (D^{r}_{\mathbf{k}*}[\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''})]$$
$$\times D^{r'}_{\mathbf{k}'*}[\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''})])_{(\mu d+\pi;\mu'd'+\pi')(\theta d+\eta;\theta'd'+\eta')}$$
$$\times U_{(\theta d+\eta;\theta'd'+\eta')(\eta'')}\psi^{\mathbf{k}\mu}_\pi\psi^{\mathbf{k}'\mu'}_{\pi'},$$

and comparing this to Eq. (25), we see that

$$U_{(\mu d+\pi;\mu'd'+\pi')(\theta''d''+\eta'')}$$
$$= \sum^{\mathbf{k}_1''}_{\substack{\theta\theta'\\ \eta\eta'}} (D^{r}_{\mathbf{k}*}[\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''})]$$
$$\times D^{r'}_{\mathbf{k}'*}[\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''})])_{(\mu d+\pi;\mu'd'+\pi')(\theta d+\eta)(\theta'd'+\eta')}$$
$$\times U_{(\theta d+\eta;\theta'd'+\eta')(\eta'')}. \quad (28)$$

By this important relation the $(\theta''d''+\eta'')$th column of elements is related to the elements of the (η'')th column. Once the elements of the first block column are known, the remaining elements of the section are calculated using Eq. (28).

In the general case when $D^{r_1''}_{\mathbf{k}_1''*}$ appears c times in the reduced form of the direct product, we can generalize Eq. (28) as

$$U_{(\mu d+\pi;\mu'd'+\pi')(ld''q''+\theta''d''+\eta'')}$$
$$= \sum^{\mathbf{k}_1''}_{\substack{\theta\theta'\\ \eta\eta'}} (D^{r}_{\mathbf{k}*}[\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''})]$$
$$\times D^{r'}_{\mathbf{k}'*}[\alpha''_{\theta''}\,|\,\mathbf{v}(\alpha''_{\theta''})])_{(\mu d+\pi;\mu'd'+\pi')(\theta d+\pi;\theta'd'+\pi')}$$
$$\times U_{(\theta d+\eta;\theta'd'+\eta')(ld''q''+\eta'')}. \quad (29)$$

Downloaded 28 Oct 2004 to 128.118.81.52. Redistribution subject to AIP license or copyright, see http://jmp.aip.org/jmp/copyright.jsp

Once the first block column of each section has been calculated, the remaining elements of each section are derived, using Eq. (29), and thus the first $cq''d''$ columns of U are calculated.

If the c irreducible representations $D_{k_1''*}^{r_1''}$ are not the only irreducible representations appearing in the reduced form of the direct product $D_{k*}^{r} \times D_{k'*}^{r'}$, then there is a second one, $D_{k_m''*}^{r_n''}$, that appears c_{mn} times. We assume these are the c_{mn} irreducible representations following the c irreducible representations $D_{k_1''*}^{r_1''}$. The dimension of $D_{k_m''*}^{r_n''}$ is $n''_{mn} \doteq q''_m d''_n$. We divide the $C_{mn}q''_m d''_n$ columns of U following the $cq''d''$ columns previously calculated into blocks of dimension $dd' \times d''_n$ and c_{mn} sections. The elements of the blocks of these c_{mn} sections are calculated in the same manner as the blocks of the c sections of the first $cd''q''$ column of U.

If there are additional irreducible representations appearing in the reduced form, we repeat the above procedure until we have exhausted all the irreducible representations that appear in the reduced form of the direct product $D_{k*}^{r} \times D_{k'*}^{r'}$.

Thus we have obtained a method to calculate the elements of the matrix U, the Clebsch–Gordan coefficients: with each irreducible representation $D_{k_m''*}^{r_n''}$, that appears c_{mn} times in the reduced form of the direct product $D_{k*}^{r} \times D_{k'*}^{r'}$, we associate $c_{mn}d''_n q''_m$ columns of U. These columns are divided into blocks of dimension $dd' \times d''_n$ and into c_{mn} sections. The nonzero blocks $(\theta\theta')(lq''_m + \theta'')$ must fulfill the condition $\mathbf{k}_\theta + \mathbf{k}'_{\theta'} - \mathbf{k}''_{m\theta''} \doteq 0$. The nonzero blocks in the first block column of each section are calculated, using Eq. (17) or (20); and finally, the elements of the remaining nonzero blocks are calculated, using Eq. (29). In the calculation of the Clebsch–Gordan coefficients it is not necessary to know the irreducible representations of the space group G. In both Eqs. (17) and (20) only the irreducible representations of the factor groups $\mathcal{K}/T$, $\mathcal{K}'/T$, and $\mathcal{K}''/T$ enter into the calculations.

So far the formalism is quite general, applicable also for nonsymmorphic space groups on the boundary of the Brillouin zone. There are, however, simplifications for symmorphic groups and nonsymmorphic groups in the interior of the Brillouin zone.

Equation (5) for nonsymmorphic groups in the interior of the Brillouin zone may be written as

$$D_{k*\theta\mu}^{r}[\alpha \mid \mathbf{v}(\alpha) + \mathbf{a}] = e^{-i\mathbf{k}\cdot\mathbf{v}(\beta_{\theta\mu})} e^{-i\mathbf{k}_\theta\cdot\mathbf{a}} \Gamma_k^r(\beta_{\theta\mu}), \quad (30)$$

where we have used

$$D_k^r[\beta_{\theta\mu} \mid \mathbf{v}(\beta_{\theta\mu})] = e^{-i\mathbf{k}\cdot\mathbf{v}(\beta_{\theta\mu})} \Gamma_k^r(\beta_{\theta\mu}).$$

Γ_k^r is an irreducible representation of the point group associated with the factor group $\mathcal{K}/T$.

In subsequent calculations, for each irreducible representation whose vector $\mathbf{k}$ is in the interior of the Brillouin zone, instead of

$$D_k^r[\hat{\beta} \mid \mathbf{v}(\hat{\beta})]_{\eta\pi},$$

we write

$$e^{-i\mathbf{k}\cdot\mathbf{v}(\hat{\beta})} \Gamma_k^r(\hat{\beta})_{\eta\pi}.$$

In the case where all three vectors $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{k}''$ are in the interior of the Brillouin zone, the left-hand side of Eq. (17) will read

$$\frac{d''q''}{g} \sum_{(\hat{\beta}|\mathbf{v}(\hat{\beta}))} e^{-i(\mathbf{k}+\mathbf{k}'-\mathbf{k}_m'')\cdot\mathbf{v}(\hat{\beta})} \Gamma_k^r(\hat{\beta})_{\eta\pi} \Gamma_{k'}^{r'}(\hat{\beta})_{\eta'\pi'} \Gamma_{k_m''}^{r_n''}(\hat{\beta})^*_{\eta''\pi''}. \quad (31)$$

This can further be simplified by noting that

$$e^{-i(\mathbf{k}+\mathbf{k}'-\mathbf{k}_m'')\cdot\mathbf{v}(\hat{\beta})} = \begin{cases} 1 & \text{if } \mathbf{k} + \mathbf{k}' - \mathbf{k}''_m = 0, \\ e^{-i\mathbf{K}\cdot\mathbf{v}(\hat{\beta})} & \text{if } \mathbf{k} + \mathbf{k}' - \mathbf{k}''_m = \mathbf{K}, \end{cases}$$

where $\mathbf{K}$ is a reciprocal lattice vector.

Therefore Eq. (31) becomes

$$\frac{d''q''}{g} \sum_{(\hat{\beta})} \Gamma_k^r(\hat{\beta})_{\eta\pi} \Gamma_{k'}^{r'}(\hat{\beta})_{\eta'\pi'} \Gamma_{k_m''}^{r_n''}(\hat{\beta})^*_{\eta''\pi''}, \quad (32)$$

if $\mathbf{k} + \mathbf{k}' - \mathbf{k}''_m = 0$, or

$$\frac{d''q''}{g} \sum_{(\hat{\beta}|\mathbf{v}(\hat{\beta}))} e^{-i\mathbf{K}\cdot\mathbf{v}(\hat{\beta})} \Gamma_k^r(\hat{\beta})_{\eta\pi} \Gamma_{k'}^{r'}(\hat{\beta})_{\eta'\pi'} \Gamma_{k_m''}^{r_n''}(\hat{\beta})^*_{\eta''\pi''}, \quad (33)$$

if $\mathbf{k} + \mathbf{k}' - \mathbf{k}''_m = \mathbf{K}$.

In the same manner, the left-hand side of (20) becomes

$$\frac{d''q''}{g} \sum_{(\hat{\beta})} \Gamma_{k_\theta}^r(\hat{\beta})_{\eta\pi} \Gamma_{k'_{\theta'}}^{r'}(\hat{\beta})_{\eta'\pi'} \Gamma_{k_m''}^{r_n''}(\hat{\beta})^*_{\eta''\pi''}, \quad (34)$$

if $\mathbf{k} + \mathbf{k}' - \mathbf{k}''_m = 0$, or

$$\frac{d''q''}{g} \sum_{(\hat{\beta}|\mathbf{v}(\hat{\beta}))} e^{-i\mathbf{K}\cdot\mathbf{v}(\hat{\beta})} \Gamma_{k_\theta}^r(\hat{\beta})_{\eta\pi} \Gamma_{k'_{\theta'}}^{r'}(\hat{\beta})_{\eta'\pi'} \Gamma_{k_m''}^{r_n'}(\hat{\beta})^*_{\eta''\pi''}, \quad (35)$$

if $\mathbf{k} + \mathbf{k}' - \mathbf{k}''_m = \mathbf{K}$.

For symmorphic groups we know that $\mathbf{v}(\alpha) = 0$ for all α. Equation (30) then reads

$$D_{k*\theta\mu}^{r}[\alpha \mid \mathbf{a}] = e^{-i\mathbf{k}_\theta\cdot\mathbf{a}} \Gamma_k^r(\beta_{\theta\mu}),$$

and denoting $(\hat{\beta} \mid 0)$ simply as $(\hat{\beta})$, the left-hand side of (17) reads

$$\frac{d''q''}{g} \sum_{(\hat{\beta})} \Gamma_k^r(\hat{\beta})_{\eta\pi} \Gamma_{k'}^{r'}(\hat{\beta})_{\eta'\pi'} \Gamma_{k_m''}^{r_n''}(\hat{\beta})^*_{\eta''\pi''}. \quad (36)$$

The left-hand side of Eq. (20) for symmorphic groups becomes

$$\frac{d''q''}{g} \sum_{(\hat{\beta})} \Gamma_{k_\theta}^r(\hat{\beta})_{\eta\pi} \Gamma_{k'_{\theta'}}^{r'}(\hat{\beta})_{\eta'\pi'} \Gamma_{k_m''}^{r_n''}(\hat{\beta})^*_{\eta''\pi''}. \quad (37)$$

Downloaded 28 Oct 2004 to 128.118.81.52. Redistribution subject to AIP license or copyright, see http://jmp.aip.org/jmp/copyright.jsp

We see, therefore, that for symmorphic groups and nonsymmorphic groups in the interior of the Brillouin zone, the Clebsch–Gordan coefficients of space groups can be obtained using only the irreducible representations of point groups.

In conclusion of this section let us note that the formalism developed here is applicable to both single and double space groups.

III. SPIN-ORBIT COUPLING

As an example of the application of the general theory developed in the previous section, let us treat the spin-orbit coupling in solids. Although the group-theoretical aspects of this problem have been considered before,[7] it is worthwhile to give an approach to it from the point of view of Clebsch–Gordan coefficients of the whole space group, which is the subject of this paper.

The Schrödinger equation of an electron moving in a crystal with a periodic potential V is

$$\left[\frac{\mathbf{P}^2}{2m} + V\right]\psi = \epsilon\psi. \tag{38}$$

The potential V has both the point and translation symmetry of the lattice, and the symmetry of the space group G associated with the lattice.

The Schrödinger equation when spin-orbit interaction is taken into account is[7]

$$\left[\frac{\mathbf{P}^2}{2m} + V + \frac{\hbar}{4m^2c^2}(\nabla V \times \mathbf{P})\cdot\boldsymbol{\sigma}\right]\Phi = E\Phi, \tag{39}$$

where $\boldsymbol{\sigma}$ are the Pauli-spin matrices. With the inclusion of spin, the symmetry group of the Hamiltonian is $\bar{G}$, the double group[7] of G.

Consider now the problem that arises when one has to find the eigenfunctions of Eq. (39) in the lowest order of perturbation theory. Let us denote by $\psi_\eta^{\mathbf{k}\theta}$ the orbital eigenfunctions of Eq. (38), and by $\psi_{\eta'}^{0}$ the spin function of the electron. The superscript $\mathbf{k}' = 0$ of $\psi_{\eta'}^{0}$ is a consequence of the fact that spin functions are invariant under translations. The functions $\psi_\eta^{\mathbf{k}\theta}$ and $\psi_{\eta'}^{0}$ can be looked upon as belonging to bases of irreducible representations of the double space group $\bar{G}$. Assume that the orbital function transforms according to a representation $D_{k^*}^{r}(\bar{G})$. The spin function $\psi_{\eta'}^{0}$ undergoes a transformation according to $D_0^{\frac{1}{2}}(\bar{G})$. In the lowest order of perturbation theory the eigenfunctions Φ of Eq. (39), say $\psi_{\eta''}^{\mathbf{k}\theta''}$, are linear combinations of the products $\psi_\eta^{\mathbf{k}\theta}\psi_{\eta'}^{0}$. The correct eigenfunctions $\psi_{\eta''}^{\mathbf{k}\theta''}$ of Eq. (39) in the lowest order of perturbation theory are those linear combinations of $\psi_\eta^{\mathbf{k}\theta}\psi_{\eta'}^{0}$ that transform according to irreducible representations of $\bar{G}$. The problem of finding the correct $\psi_{\eta''}^{\mathbf{k}\theta''}$ is therefore the reduction of direct products which was worked out in the previous section of this paper.

The functions $\psi_\eta^{\mathbf{k}\theta}\psi_{\eta'}^{0}$ form the basis of the direct product representation $D_{k^*}^{r}(\bar{G}) \times D_0^{\frac{1}{2}}(\bar{G})$. $D_{k^*}^{r}$ being an irreducible representation of the group G is also an irreducible representation of the double group $\bar{G}$. If the direct product is irreducible, the spin-orbit interaction causes no splitting, and eigenfunctions $\psi_{\eta''}^{\mathbf{k}\theta''}$ are equal to the product functions $\psi_\eta^{\mathbf{k}\theta}\psi_{\eta'}^{0}$. If the direct product is reducible, then

$$D_{k^*}^{r}(\bar{G}) \times D_0^{\frac{1}{2}}(\bar{G}) = \sum_n c_n D_{k^*}^{r_n''}(\bar{G}). \tag{40}$$

Since $\mathbf{k}' = 0$, the only star appearing in the reduced form is the star of the vector $\mathbf{k}$.

c_n is calculated from

$$c_n = \frac{1}{2gh}\sum \mathrm{X}_{k^*}^{r}(\bar{G})\mathrm{X}_0^{\frac{1}{2}}(\bar{G})\mathrm{X}_{k^*}^{r_n''}(\bar{G})^*,$$

where gh is the order of the single group G, h being the order of the invariant subgroup of translations T, and g the order of the factor group G/T. Following Zak[3,8], this reduces to

$$c_n = \frac{q}{2g}\sum_{(\delta|\mathbf{v}(\delta))} \xi_k^{r}[\delta \mid \mathbf{v}(\delta)]\mathrm{X}_0^{\frac{1}{2}}(\delta)\xi_k^{r_n''}[\delta \mid \mathbf{v}(\delta)]^*, \tag{41}$$

where $\mathrm{X}_0^{\frac{1}{2}}(\delta)$ is the character of $D_0^{\frac{1}{2}}(\delta)$, $\xi_k^{r}[\delta \mid \mathbf{v}(\delta)]$ is the character of $D_k^{r}(\delta \mid \mathbf{v}(\delta))$, and $\xi_k^{r_n''}[\delta \mid \mathbf{v}(\delta)]$ is the character of $D_k^{r_n''}[\delta \mid \mathbf{v}(\delta)]$; q is the number of vectors in $S_{\mathbf{k}}$, the star of the vector $\mathbf{k}$. All the representations in Eqs. (40) and (41) are now representations of double space groups.

It is known[7] that

$$D_0^{\frac{1}{2}}(\bar{\beta}) = -D_0^{\frac{1}{2}}(\beta)$$

and

$$\mathrm{X}_0^{\frac{1}{2}}(\bar{\beta}) = -\mathrm{X}_0^{\frac{1}{2}}(\beta), \tag{42}$$

where $\bar{\beta}$ is the "barred" element of the double group. Since $D_{k^*}^{r}(G)$ is an irreducible representation of the single group as well, one has

$$D_k^{r}[\bar{\beta} \mid \mathbf{v}(\beta)] = D_k^{r}[\beta \mid \mathbf{v}(\beta)]$$

and

$$\xi_k^{r}[\bar{\beta} \mid \mathbf{v}(\beta)] = \xi_k^{r}[\beta \mid \mathbf{v}(\beta)]. \tag{43}$$

This being the case, to obtain a nonzero c_n it is necessary that the irreducible representation $D_{k^*}^{r_n''}(\bar{G})$ be such that

$$D_k^{r_n''}[\bar{\beta} \mid \mathbf{v}(\beta)] = -D_k^{r_n''}[\beta \mid \mathbf{v}(\beta)],$$

and

$$\xi_k^{r_n''}[\bar{\beta} \mid \mathbf{v}(\beta)] = -\xi_k^{r_n''}[\beta \mid \mathbf{v}(\beta)]. \tag{44}$$

[7] R. J. Elliott, Phys. Rev. 96, 280 (1954).

[8] J. Zak, Phys. Rev. 151, 464 (1966).

Downloaded 28 Oct 2004 to 128.118.81.52. Redistribution subject to AIP license or copyright, see http://jmp.aip.org/jmp/copyright.jsp

By dividing the sum in Eq. (41) into two, the sum on the elements $[\beta \mid \mathbf{v}(\beta)]$ and the sum on the elements $[\bar{\beta} \mid \mathbf{v}(\beta)]$ [both of which are equal by Eqs. (42), (43), and (44)], Eq. (41) reduces to

$$c_n = \frac{q}{g} \sum_{(\beta|\mathbf{v}(\beta))} \xi_k^r[\beta \mid \mathbf{v}(\beta)] X_0^{\frac{1}{2}}(\beta) \xi_k^{r_n''}[\beta \mid \mathbf{v}(\beta)]. \quad (45)$$

Now let us use the results obtained in the preceding sections: The blocks of U are denoted by $(\theta)(lq + \theta'')$; since $D_0^{\frac{1}{2}}(\bar{G})$ is not divided into blocks we have dropped the index θ'. The only nonzero blocks are those for which $\theta = \theta''$. To calculate the $(0)(lq)$th blocks we use Eq. (17), the left-hand side of this equation being in our case

$$\frac{d''q}{2g} \sum_{(\delta|\mathbf{v}(\delta))} D_k^r[\delta \mid \mathbf{v}(\delta)]_{\eta\pi} D_0^{\frac{1}{2}}(\delta)_{\eta'\pi'} D_k^{r_n''}[\delta \mid \mathbf{v}(\delta)]_{\eta''\pi''}.$$

Using Eqs. (42), (43), and (44), this becomes

$$\frac{d''q}{g} \sum_{(\beta|\mathbf{v}(\beta))} D_k^r[\beta \mid \mathbf{v}(\beta)]_{\eta\pi} D_0^{\frac{1}{2}}(\beta)_{\eta'\pi'} D_k^{r_n''}[\beta \mid \mathbf{v}(\beta)]_{\eta''\pi''}. \quad (46)$$

To calculate the remaining nonzero blocks we use Eqs. (10), (11), (27), and (28):

$$U_{(\theta d+\eta;\eta')(\theta d''+\eta'')} = D_0^{\frac{1}{2}}(\alpha_\theta)_{\eta'1} U_{(\eta'1)(\eta'')} + D_0^{\frac{1}{2}}(\alpha_\theta)_{\eta'2} U_{(\eta 2)(\eta'')}. \quad (47)$$

For an irreducible representation $D_{k*}^{r_n''}$ appearing c_n times in the reduced form of the direct produce, Eq. (47) is used to calculate the $(0)(lq)$th blocks, and the remaining nonzero blocks, the $(\theta)(lq + \theta)$th blocks, are calculated, using Eq. (48). This process is repeated for all irreducible representations appearing in the reduced form, and thus we calculate the matrix U, which reduces the direct product $D_{k*}^r(\bar{G}) \times D_0^{\frac{1}{2}}(\bar{G})$.

As mentioned before, the eigenfunctions Φ of Eq. (39), in the lowest order of perturbation theory, are the functions which form the basis functions of one of the c_n irreducible representations $D_{k*}^{r_n''}$ which appear in the reduced form of the direct product. The qd_n'' columns of U corresponding to this irreducible representation give the linear combinations of the product functions $\psi_\eta^{\mathbf{k}\theta}\psi_{\eta'}^0$ which form these functions, that is,

$$\psi_{\eta''}^{\mathbf{k}\theta''} = \sum_{\eta\eta'} U_{(\theta d+\eta;\eta')(lqd_n''+\theta''d_n''+\eta'')} \psi_\eta^{\mathbf{k}\theta}\psi_{\eta'}^0,$$

where $l = 0, 1, \cdots, c_n - 1$.

The method as given above is quite general, applicable for symmorphic and nonsymmorphic space groups with $\mathbf{k}$ on the boundary of or in the interior of the Brillouin zone. But for symmorphic groups and for nonsymmorphic groups within the interior of the Brillouin zone Eqs. (45) and (46) can be appreciatively simplified, using the results obtained in the previous section.

For symmorphic groups and nonsymmorphic groups with $\mathbf{k}$ in the interior of the Brillouin zone, Eq. (45) reduces to

$$c_n = \frac{q}{g} \sum_{(\beta)} \xi_k^r(\beta) X_0^{\frac{1}{2}}(\beta) \xi_k^{r_n''}(\beta), \quad (48)$$

where $\xi_k^r(\beta)$ is the character of $\Gamma_k^r(\beta)$, the irreducible representation of the point group formed by the set of elements $\{(\beta \mid 0)\}$.

It can be verified by inspection of the character tables of the point groups,[9] that for any point group excepting C_1 and C_i, c_n is either one or zero. For the point groups C_1 and C_i, c_n is either two or zero. Equation (17) will thus become [we have used Eq. (46) and dropped d'']

$$\frac{q}{g} \sum_{(\beta)} \Gamma_k^r(\beta)_{\eta\pi} D_0^{\frac{1}{2}}(\beta)_{\eta'\pi'} \Gamma_k^{r_n''}(\beta)^* = U_{(\eta\eta')(\eta'')} U^*_{(\pi\pi')(\pi'')} \quad (49)$$

for all point groups excepting C_1 and C_i. For these two latter point groups the right-hand side is replaced by

$$U_{(\eta\eta')(\eta'')} U^*_{(\pi\pi')(\pi'')} + U_{(\eta\eta')(d''q+\eta'')} U^*_{(\pi\pi')(d''q+\pi'')}.$$

In either case the sum is on the point group $\{(\beta \mid 0)\}$, the point group associated with the group of the vector $\mathbf{k}$, since the nonprimitive translations take no part in the calculation.

We see then that only for nonsymmorphic space groups with $\mathbf{k}$ on the boundary of the Brillouin zone do the nonprimitive translations enter into the calculations. For symmorphic groups and nonsymmorphic groups in the interior of the Brillouin zone only the properties of the irreducible representations of the point group enter into the calculation.

Finally, let us point our that the matrix U is completely determined by a matrix that reduces the direct product of representations of point groups. Indeed, we use Eq. (48) to calculate the number of times the irreducible representation $D_{k*}^{r_n''}(\bar{G})$ appears in the reduced form of the direct product $D_{k*}^r(\bar{G}) \times D_0^{\frac{1}{2}}(\bar{G})$. Equation (48) is also the equation necessary to calculate the number of times the irreducible representation $\Gamma_{k*}^{r_n''}(\beta)$ appears in the reduced form of the direct product $\Gamma_k^r(\beta) \times D_0^{\frac{1}{2}}(\beta)$. In addition, since g/q is the order of the point group

[9] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-two Point Groups* (Massachusetts Institute of Technology Press, Cambridge, Mass., 1963).

Downloaded 28 Oct 2004 to 128.118.81.52. Redistribution subject to AIP license or copyright, see http://jmp.aip.org/jmp/copyright.jsp

$\{(\beta \mid 0)\}$, Eq. (49) is also the equation for the elements of the section associated with the irreducible representation $\Gamma_k^{r_n''}(\beta)$ of the unitary matrix V, which reduces the direct product $\Gamma_k^r(\beta) \times D_0^{\frac{1}{2}}(\beta)$. Therefore, each section of V associated with the irreducible representation $\Gamma_k^{r_n''}(\beta)$ of the point group is the (0)(0)th block of the section of U association with $D_{k^*}^{r_n''}(\bar{G})$. The calculation of the unitary matrix V is a strictly point-group problem.

If $D_0^{\frac{1}{2}}(\beta)$ is an irreducible representation of the point group $\{(\beta \mid 0)\}$, $\Gamma_k^r(\beta) \times D_0^{\frac{1}{2}}(\beta)$ is then the direct product of two irreducible representations of the point group, and the matrix is known.[9] When $D_0^{\frac{1}{2}}(\beta)$ is irreducible,[10] by inspection of the character tables of the thirty-two point groups one finds that $\Gamma_k^r(\beta)$ is a one-dimensional representation, and the matrix V is then a two-dimensional unit matrix. In both cases then the (0)(0)th block of each section of U is known. The remaining nonzero blocks of each section of U are calculated using Eq. (47). Once U has been calculated, the eigenfunctions $\psi_\eta^{\mathbf{k}_\theta r''}$ of Eq. (39) can be calculated.

APPENDIX A

Here we show that when $S_{\mathbf{k}_m''}$ is a star of the first or second kind, Eq. (14) reduces to Eq. (15) or (16), respectively.

If λ is an element such that

$$\lambda \subset \{\beta\} \cap \{\beta'\},$$

then from $\mathbf{k} + \mathbf{k}' = \mathbf{k}_m''$ we have by multiplying from the left by λ

$$\lambda(\mathbf{k} + \mathbf{k}') = \lambda\mathbf{k}_m'',$$
$$\lambda\mathbf{k} + \lambda\mathbf{k}' = \lambda\mathbf{k}_m'',$$
$$\mathbf{k} + \mathbf{k}' = \lambda\mathbf{k}_m'',$$
$$\mathbf{k}_m'' = \lambda\mathbf{k}_m''.$$

Therefore

$$\lambda \subset \{\beta''\}$$

and

$$\{\beta\} \cap \{\beta'\} \subset \{\beta''\}. \quad \text{(A1)}$$

If λ is an element such that

$$\lambda \subset \{\beta''\},$$

then from $\mathbf{k} + \mathbf{k}' = \mathbf{k}_m''$ again multiplying from the left by λ,

$$\lambda\mathbf{k} + \lambda\mathbf{k}' \doteq \lambda\mathbf{k}_m'',$$
$$\lambda \ + \lambda\mathbf{k}' \doteq \mathbf{k}_m''. \quad \text{(A2)}$$

We have either

$$\lambda\mathbf{k} \not\doteq \mathbf{k},$$
$$\lambda\mathbf{k}' \not\doteq \mathbf{k}',$$

or (A3)

$$\lambda\mathbf{k} \doteq \mathbf{k},$$
$$\lambda\mathbf{k}' \doteq \mathbf{k}'.$$

[We cannot have

$$\lambda\mathbf{k} \doteq \mathbf{k}$$
$$\lambda\mathbf{k}' \not\doteq \mathbf{k}'$$

for inserting this into (A2) we would have

$$\mathbf{k} + \lambda\mathbf{k}' \doteq \mathbf{k}_m'',$$
$$\mathbf{k} + \lambda\mathbf{k}' \doteq \mathbf{k} + \mathbf{k}',$$
$$\lambda\mathbf{k}' \doteq \mathbf{k}',$$

which is a contradiction.]

We will then have, either

$$\mathbf{k}_\theta + \mathbf{k}_{\theta'}' \doteq \mathbf{k}_m''$$

or

$$\mathbf{k} + \mathbf{k}' \doteq \lambda\mathbf{k}_m'',$$

where $\lambda\mathbf{k} = \mathbf{k}_\theta$ and $\lambda\mathbf{k}' = \mathbf{k}_{\theta'}'$.

For $\mathbf{k}''$, which belongs to a star of the first kind, the first possibility in (A3) is forbidden by definition of a star of the first kind; the star $S_{\mathbf{k}_m''}$ and consequently the vector $\mathbf{k}_m''$ defined by $\mathbf{k} + \mathbf{k}' = \mathbf{k}_m''$ appears only once in the direct product $S_\mathbf{k} \times S_{\mathbf{k}'}$. Therefore we have for stars of the first kind

$$\mathbf{k} + \mathbf{k}' \doteq \mathbf{k}_m''.$$

This means that

$$\lambda \subset \{\beta\} \cap \{\beta'\}$$

and therefore

$$\{\beta''\} \subset \{\beta\} \cap \{\beta'\}. \quad \text{(A4)}$$

From Eqs. (A1) and (A4) we have for stars of the first kind

$$\{\beta''\} = \{\beta\} \cap \{\beta'\}$$

and therefore Eq. (14) reduces to

$$\{\hat{\beta}\} = \{\beta''\}. \quad \text{(A5)}$$

For stars of the second kind, (A4) is not applicable, and using only (A2), Eq. (14) becomes

$$\{\hat{\beta}\} = \{\beta\} \cap \{\beta'\}. \quad \text{(A6)}$$

APPENDIX B

Here we prove Eq. (19), that is, by redefining the stars $S_\mathbf{k}$ and $S_{\mathbf{k}'}$ by the vectors $\mathbf{k}_\theta$ and $\mathbf{k}_{\theta'}'$, respectively, the $(00)(lq'')$th block of $\bar{U}$, the unitary matrix that reduces the direct $D_{k_\theta^*}^r(G) \times D_{k_{\theta'}'^*}^{r'}(G)$, is equal to the $(\theta\theta')(lq'')$th block of the unitary matrix U, which reduces the direct product $D_{k^*}^r(G) \times D_{k'^*}^{r'}(G)$.

[10] $D_0^{\frac{1}{2}}(\beta)$ is a reducible representation for the point groups C_1, C_i, C_2, C_s, C_{2h}, C_4, S_4, C_{4h}, C_3, C_{3i}, C_6, C_{3h}, and C_{6h}; it is an irreducible representation for the remainder of the point groups.

Downloaded 28 Oct 2004 to 128.118.81.52. Redistribution subject to AIP license or copyright, see http://jmp.aip.org/jmp/copyright.jsp

Let V be the unitary transformation that reorders the basis functions of $D^{r}_{k^*}(G)$ to form the basis functions of $D^{r}_{k_\theta^*}(G)$. We have

$$V \begin{pmatrix} \cdot \\ \cdot \\ \cdot \\ \psi_\eta^{\mathbf{k}\theta} \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} = \begin{pmatrix} \psi_\eta^{\mathbf{k}\theta} \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \end{pmatrix}, \qquad \text{(B1)}$$

where the new basis is some permutation of the old basis with the functions $\psi_\eta^{\mathbf{k}\theta}$ in the top position.

Equation (B1) implies that the structure of V is of the following form:

$$\begin{pmatrix} 0 & \begin{matrix} 1 & & \\ & \ddots & \\ & & 1 \end{matrix} & 0 \\ & 0 & \end{pmatrix}, \qquad \text{(B2)}$$

where the large center zero denotes the θth block column. The irreducible representation $D^{r}_{k^*}(G)$ in the new basis is

$$V D^{r}_{k^*}(G) V^{-1} = D^{r}_{k_\theta^*}(G). \qquad \text{(B3)}$$

In the same manner we define a unitary matrix W, which transforms the irreducible representation $D^{r'}_{k'^*}(G)$ into $D^{r'}_{k'_{\theta'}^*}(G)$.

$\bar{U}$ is defined as the unitary matrix which reduces the direct product $D^{r}_{k_\theta^*}(G) \times D^{r'}_{k'_{\theta'}^*}(G)$, that is,

$$\bar{U}^{-1}[D^{r}_{k_\theta^*}(G) \times D^{r}_{k'_{\theta'}^*}(G)]\bar{U} = (\text{reduced form}). \qquad \text{(B4)}$$

Using Eq. (B3) and the comparable relation for $D^{r'}_{k'_{\theta'}^*}(G)$, we see that the left-hand side of the (B4) can be written as

$$\bar{U}^{-1}[V D^{r}_{k^*}(G) V^{-1} \times W D^{r'}_{k'^*}(G) W^{-1}]\bar{U} = \bar{U}^{-1}(V \times W)[D^{r}_{k^*}(G)](V \times W)^{-1}\bar{U}.$$

Using this and the definition of (B4) becomes

$$\bar{U}^{-1}(V \times W)U \,(\text{reduced form})\, U^{-1}(V \times W)^{-1}U = (\text{reduced form}).$$

Therefore

$$\bar{U}^{-1}(V \times W)U = I$$

and

$$\bar{U} = (V \times W)U. \qquad \text{(B5)}$$

We now use (B5) to calculate an element of the $(00)(lq'')$th block of the first $cq''d''$ column of $\bar{U}$:

$$\bar{U}_{(\eta\eta')(lq''d''+\eta'')} = \sum_{\substack{aa'\\bb'}} V_{(\eta)(ad+b)} W_{(\eta')(a'd'+b')} \times U_{(ad+b;a'd'+b')(lq''d''+\eta'')}. \qquad \text{(B6)}$$

From the structure of V and W we have

$$V_{(\eta)(ad+b)} = \delta(\theta - a)\delta(\eta - b),$$
$$W_{(\eta')(a'd'+b')} = \delta(\theta' - a')\delta(\eta' - b'),$$

and inserting this into (B6), we have

$$\bar{U}_{(\eta\eta')(lq''d''+\eta'')} = \sum_{\substack{aa'\\bb'}} U_{(ad+b;a'd'+b')(lq''d''+\eta'')} \times \delta(\theta - a)\delta(\eta - b)\delta(\theta' - a')\delta(\eta' - b')$$

and

$$\bar{U}_{(\eta\eta')(lq''d''+\eta'')} = U_{(\theta d+\eta;\theta' d'+\eta')(lq''d''+\eta'')}.$$

This last relation is Eq. (19).

Downloaded 28 Oct 2004 to 128.118.81.52. Redistribution subject to AIP license or copyright, see http://jmp.aip.org/jmp/copyright.jsp