BLOCH THEOREM FOR CRYSTALS WITH STRUCTURAL DISTORTIONS

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ABSTRACT

A new Bloch Theorem, based on wreath group symmetry, is formulated for crystals with structural distortions. This new Bloch Theorem is applied to determine the form and corresponding charge density of one-electron eigenfunctions in the nearly free electron approximation for crystals with periodic structural distortions.

1. WREATH GROUPS

The use of wreath groups for the classification of color functions and spin functions defined on crystals was first introduced by Koptsik and Kotzev [1-3]. Recent reviews on the classification of color and spin functions have been given by Kotzev [4] and Opechowski [5]. Wreath groups have recently also been used in the classification of crystals with structural distortions by Koptsik [6-8] and Litvin [9]. It is an application of the theory of wreath groups to the derivation of a Bloch Theorem for crystals with structural distortions which is the topic of this contribution.

Let $E(3) = \{P, V_E(3)\}$ be a three-dimensional Euclidean point space consisting of the point space P and the Euclidean vector space $V_E(3)$. Let R denote the positions of atoms of a crystal, in P, whose symmetry group $\mathfrak{F}$ is one of the 230 three-dimensional space groups, and let $\vec{D}(R)$ denote a vector function defined on the crystal which maps points R into vectors of the vector space $V_E(3)$. $\vec{D}(R)$ represents the structural distortion of the position of the atom which in the undistorted crystal is at the position R.

The wreath group symmetry of a crystal with structural distortions $\vec{D}(R)$ is defined as the group of all operator pairs $(\vec{V}_F(R)|F)$, where $\vec{V}_F(R)$ is a vector function defined on the crystal which maps points R into vectors of $V_E(3)$, paired with an element F of the space group $\mathfrak{F}$ of the crystal and such that [9,10]:

$$(\vec{V}_F(R)|F)\vec{D}(R) = \vec{D}(F^{-1}R) + \vec{V}_F(R) = \vec{D}(R)$$

The product of two such operator pairs is:

$$(\vec{V}_{F_1}(R)|F_1)\ (\vec{V}_{F_2}(R)|F_2) = (\vec{V}_{F_1}(R) + \vec{V}_{F_2}(F_1^{-1}R)|F_1F_2)$$

The wreath group is a subgroup of the semi-direct product $\Omega_V\, s\Omega_F$, where

Ω_V is the group of all operators $(\vec{V}(R)|E)$ and Ω_F the group of all operators $(E|F)$. This semi-direct product is called the wreath product $V_E(3)\ w\Omega_F$ [11,12].

2. BLOCH THEOREM FOR CRYSTALS WITH STRUCTURAL DISTORTIONS

The Bloch Theorem for crystals whose symmetry group is one of the 230 three-dimensional space groups [13] is a statement concerning the structure of eigenfunction $\Psi(r)$ of the electronic Schrodinger equation $H\Psi(r) = E\Psi(r)$ of the crystal. The Bloch Theorem states that the structure of eigenfunctions $\Psi_k(r)$ are such that:

$$\Psi_k(r) = e^{-ik\cdot r}\, U_k(r) \quad ; \quad \{t\}U_k(r) = U_k(r)$$

where t is a translation of the space group $\mathbb{F}$ of the crystal and k is a vector in the first Brillouin Zone.

We define operators $\{V(r)|F\}$ which act on the space of all scalar functions U(r) defined on the point space P of E(3) in the following manner: First, we define the vector functions $\vec{W}(r)$ and $\vec{V}(r)$ defined on P which map all points r into vectors of the vector space $V_E(3)$. We define operators $(\vec{V}(r)|F)$ on the space of all vector functions $\vec{W}(r)$ such that:

$$(\vec{V}(r)|F)\vec{W}(r) = \vec{W}(F^{-1}r) + \vec{V}(r)$$

Second, we define the mappings $\langle\vec{V}(r)|F\rangle$ of the point space P onto itself. A mapping $\langle\vec{V}(r)|F\rangle$ maps the point r into the point denoted by $\langle\vec{V}(r)|F\rangle r$ and defined by:

$$\langle\vec{V}(r)|F\rangle r = Fr + \vec{V}(r)$$

Finally, we define the operators $\{V(r)|F\}$ on the space of all scalar functions U(r) defined on P:

$$\{\vec{V}(r)|F\}\ U(r) = U(\langle\vec{V}(r)|F\rangle^{-1}r)$$

Because of an isomorphism which exists between the operators $(V(r)|F)$, $\langle\vec{V}(r)|F\rangle$, and $\{\vec{V}(r)|F\}$, and typographical reasons, we shall denote all these operators by $(\vec{V}(r)|F)$.

We assume the following relationship between the wreath group symmetry of the crystal with structural distortions and an invariance wreath group of the Hamiltonian: There exists an invariance wreath group of the Hamiltonian consisting of operator pairs $(\vec{V}_F(r)|F)$, one such pair for each element F of $\mathbb{F}$, such that restricting the functions $\vec{V}_F(r)$ to $\vec{V}_F(R)$, the resulting operators $(\vec{V}_F(R)|F)$ constitute the wreath group of the crystal with structural distortions $\vec{D}(R)$. This invariance wreath group contains a subgroup $\mathbb{T}_w$ of operator pairs $(\vec{V}_t(r)|t)$ one such pair for each translation t of the translational subgroup $\mathbb{T}$ of $\mathbb{F}$. $\mathbb{T}_w$ is isomorphic to $\mathbb{T}$ and the irreducible representation of $\mathbb{T}_w$ are then $\Gamma^k(\vec{V}_t(r)|t) = \exp(ik\cdot t)$.

We construct eigenfunctions $\Psi_k(r)$ of the Hamiltonian which are basis functions of the irreducible representations Γ^k of $\mathfrak{T}_w$ using a projection operator proceedure:

$$\Psi_k(r) = \sum_{t'} e^{-ik\cdot t'} (\vec{V}_{t'}, (r)|t')\phi(r)$$

where $\phi(r)$ is an arbitrary eigenfunction of the Hamiltonian. The eigenfunctions $\Psi_k(r)$ are basis functions of irreducible representations Γ^k of $\mathfrak{T}_w$:

$$(\vec{V}_t(r)|t)\Psi_k(r) = \sum_{t'} e^{-ik\cdot t'} (\vec{V}_t(r)|t)\ (\vec{V}_{t'}(r)|t')\phi(r)$$

$$= \sum_{t'} e^{-ik\cdot t'} (\vec{V}_{t+t'}(r)|t+t')\phi(r)$$

$$= e^{ik\cdot t} \sum_{t''} e^{-ik\cdot t''} (V_{t''}(r)|t'')\phi(r)$$

$$= e^{ik\cdot t}\Psi_k(r)$$

The Bloch Theorem for crystals with structural distortions follows from writing the eigenfunctions $\Psi_k(r)$ as:

$$\Psi_k(r) = e^{-ik\cdot r}U_k(r)$$

where, from the above, one finds:

$$(\vec{V}_t(r)|t)U_k(r) = e^{-ik\cdot \vec{V}_t(r)}U_k(r)$$

3. NEARLY FREE ELECTRON APPROXIMATION

In the nearly free electron approximation $U_k(r)$ is given by the fourier integral:

$$U_k(r) = \int A_k(p)e^{ip\cdot r}dp$$

The coefficients $A_k(p)$ are given by the inverse fourier integral:

$$A_k(p) = \int U_k(r)e^{-ip\cdot r}dr$$

Using the Bloch Theorem for crystals with structural distortions on the first of the two above equations, substituting into the second, and summing on all elements of the wreath group $\mathfrak{T}_w$, one derives an integral equation for the coefficients $A_k(p)$. Assuming that the structural distortions are of the form $\vec{D}(R) = \vec{D}\sin(Q\cdot R)$, summing over t and integrating over r, one obtains:

$$A_k(p) = (2\pi)^3 \sum_{m,m'} \int J_m(\vec{D}\cdot(k-p))J_{m'}(-\vec{D}\cdot(k-p))A_k(p')x$$

$$\delta(K-p'-mQ)\ \delta(p'-p+(m+m')Q)dp'$$

where J_m are Bessel functions of the first kind, and K is a reciprocal lattice vector of the translational subgroup $\tilde{T}$ of $\tilde{F}$. $A_k(p)$ is equal to zero if the two delta functions in the above equation are not simultan-

eously satisfied. It follows that:

$$A_k(p) = 0 \quad \text{if} \quad p \neq K + mQ$$

Consequently, in the nearly-free electron approximation, the eigenfunctions of a one-electron Schrodinger equation for a crystal with periodic structural distortions $\vec{D}(R) = \vec{D}\sin(Q\cdot R)$ are given by:

$$\Psi_k(r) = e^{-ik\cdot r} \sum_{K,m} A_k(K,m) e^{i(K + mQ)\cdot r}$$

The charge density $\delta_k(r) = |\Psi_k(r)|^2$ corresponding to the kth eigenfunction $\Psi_k(r)$ can be calculated from the above. This charge density can be written in the form:

$$\rho_k(r) = \rho_k^o(r) + \sum_{m\neq o} \rho_k^m(r)\cos(mQ\cdot r)$$

where the functions $\rho_k^m(r)$, m=0,1,..., are functions invariant under translations t of $\mathfrak{T}$, i.e. $\rho_k^m(r + t) = \rho_k^m(r)$. Consequently, the charge density in the nearly-free electron approximation for a crystal with periodic structural distortions is a modulated charge density, consisting of charge densities having the translational periodicity of the undistorted crystal modulated by functions cos(mQ·r).

ACKNOWLEDGEMENTS

Financial support for this work by the Faculty Scholarship Support Fund - Phase IV of The Pennsylvania State University for a visit to the University of British Columbia, and by Dr. H. W. Perkins, Director, Berks Campus, The Pennsylvania State University, for travel funds to attend this colloquium, is greatfully acknowledged.

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