Multipole expansion of the density of states about a crystal cell*

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We construct the expansion of a Bloch wave with energy E into a complete set of multipole waves around a "center" of a crystal as an analog of the expansion in spherical waves in free space. Crystal point group symmetry is used to classify the set. The density of states in a cell is then analyzed into multipole components whose magnitude depends on the cell's distance from the "center."

1. INTRODUCTION

The band theory of crystalline solids considers a single expression for the electronic density of states of each band, states which are regarded as fully delocalized with periodic probability over the whole crystal. Emphasis on delocalized states becomes, however, inappropriate when treating phenomena which select a particular lattice site, as, for example, in the presence of an isolated impurity or in photoabsorption from inner shells which leaves a localized hole. Experimental evidence of the nonuniqueness of the relevant density of final states can be seen, for example, in the difference between K and L spectra of solid Al,[1] which has been accounted for recently in a qualitative way by Hayes and Sen.[2] In effect, the introduction of a "center" spoils the translational invariance of the lattice and shifts the analysis toward a local point of view.

Central symmetry is, of course, essential to the states of isolated atoms. Here, orbital momentum eigenstates represent a very natural basis for analysis. Indeed one can resolve the density of states into contributions from separate orbital momenta. In crystals, however, anisotropy spoils the conservation of angular momentum and a corresponding analysis of the density of states requires the construction of a new suitable basis. Orbital momentum eigenstates are replaced in a crystalline medium by states that transform according to the irreducible representations of the appropriate crystal group. However, the number of representations of finite groups and their dimensionality are finite in contrast to the infinity of angular momentum eigenvalues. In a crystal, therefore, a complete basis must include an infinity of states which transform according to the same row of the same irreducible representation. What we need, then, is a systematic classification of such states. The "appropriate" crystal groups we consider in this paper for the classification of the new set of states are the isogonal point groups of the space groups, whose elements, together with the inversion, transform the constant energy surface onto itself.

A solution to this problem has been sketched in a brief communication.[3] In this paper we develop the solution in some detail, with explicit application of the point group symmetry, and with the specific aim of resolving the density of states in a cell into contributions from different multipole waves. Further applications remain to be developed.

2. MULTIPOLE WAVE EXPANSION OF THE DENSITY OF STATES

In accordance with the local character of impurity effects and related phenomena, we consider a set of localized Wannier wavefunctions $\langle \mathbf{r}|t\mathbf{n}\rangle$ of an electron, where t is a band index and $\mathbf{n}$ is a lattice vector. We shall drop the band index throughout since all our considerations will refer to a simple band. A Bloch wave, eigenfunction of the perfect lattice Hamiltonian corresponding to the energy E, can be expressed as a superposition of Wannier functions:

$$\langle \mathbf{r}|\mathbf{k}\rangle_E = \sum_{\mathbf{n}} \langle \mathbf{r}|\mathbf{n}\rangle \langle \mathbf{n}|\mathbf{k}\rangle_E,$$
$$\langle \mathbf{n}|\mathbf{k}\rangle_E = w_E^{1/2}(\mathbf{k}) \exp(i\mathbf{n}\cdot\mathbf{k}). \tag{2.1}$$

The wave vector $\mathbf{k}$ is restricted to the first Brillouin zone and ranges over the constant energy surface defined by the dispersion relation

$$D(E;\mathbf{k}) = 0, \tag{2.2}$$

which we assume to be known and which incorporates the crystal field properties relevant to our problem. The amplitude $\langle \mathbf{n}|\mathbf{k}\rangle_E$ includes both the phase factor appropriate to the $\mathbf{n}$th lattice point and a normalization coefficient. The definition (2.1) sets the phase of the Bloch wave at zero in the central cell, $\mathbf{n}=0$, in accordance with the recent work of Kohn.[4] Since we will work at a fixed energy E, the Bloch wave (2.1) will be normalized per unit range of energy and of the solid angle centered around the wave vector's direction $\mathbf{k}$. The density of states is thus incorporated in the normalization of the wavefunctions, by identifying the coefficient of (2.1) as:

$$w_E(\mathbf{k}) = \frac{\Omega_c}{(2\pi)^3} \left(\frac{\partial(E,\hat{k})}{\partial(k_x,k_y,k_z)} \right)^{-1}$$
$$= \frac{\Omega_c}{(2\pi)^3} \frac{k^2}{|\hat{k}\cdot\nabla_{\mathbf{k}} E(\mathbf{k})|}, \tag{2.3}$$

where Ω_c is the volume of the unit cell (which we take as the symmetrical Wigner–Seitz cell) and the last factor takes into account the obliquity of the constant energy surface. The Jacobian of the transformation is evaluated from the dispersion relation (2.2).

The points of the constant energy surface are in one to one correspondence with two continuous parameters (the polar angles of $\mathbf{k}$). Our goal is to replace the two-

parameter set of Bloch waves (2.1) of given energy by a new set, whose elements will be called multipole waves because of their analogy to the orbital momentum eigenstates of free space. These waves will be labeled by indices which are discrete but must run over an infinite range of values. Their construction by a unitary transformation of the set (2.1) will preserve the normalization per unit energy.

The space variables of the new set of multipole waves are the coordinates $\mathbf{n}$ of the Bravais lattice nodes, whose point-symmetry elements form the holosymmetric point group of the crystal system. This group always includes the space inversion. However, since we are constructing the multipole waves at fixed energy E, we will classify them according to the irreducible representations of the symmetry group of the constant energy surface $E(\mathbf{k}) = E$ which is a subgroup of the holosymmetric group. We call Γ an irreducible representation and i one of its rows. As previously noted, the set of Γ and i is finite and, therefore, insufficient to classify a complete set. Thus, *for each* Γ *and* i, we require a further set of *two* discrete indices L and q which can run over an infinite range of values and whose meaning remains to be determined.

The matrix elements $\langle \Gamma i L q \,|\, \mathbf{k}\rangle_E$ of the unitary transformation, which we seek to construct, constitute the coefficients of the expansion of the Bloch wave amplitudes,

$$\langle \mathbf{n} \,|\, \mathbf{k}\rangle_E = \sum_{\Gamma i} \sum_{Lq} \langle \mathbf{n} \,|\, \Gamma i L q\rangle_E \langle \Gamma i L q \,|\, \mathbf{k}\rangle_E, \tag{2.4}$$

into multipole waves $\langle \mathbf{n} \,|\, \Gamma i L q\rangle_E$; each of these waves will in fact be constructed by working out the inverse expansion:

$$\langle \mathbf{n} \,|\, \Gamma i L q\rangle_E = \int d\hat{k}\, \langle \mathbf{n} \,|\, \mathbf{k}\rangle_E \langle \mathbf{k} \,|\, \Gamma i L q\rangle_E. \tag{2.5}$$

The integration extends over the solid angle subtended by the constant energy surface. Both the varying radius of this surface and its obliquity are taken into account in the integrand of Eq. (2.5), in particular through the factor $w_E(\mathbf{k})$ which appears in the expression (2.1) of $\langle \mathbf{n} \,|\, \mathbf{k}\rangle_E$ and will also appear in $\langle \mathbf{k} \,|\, \Gamma i L q\rangle_E$.

The role of these multipole waves in the analysis of the density of states can be described even before their actual construction. The translational invariance of the crystal ensures that the total density of states $N(E)$ is a sum of equal contribution $N(E;\mathbf{n})$ from the various cells of the crystal, where

$$N(E;\mathbf{n}) = \frac{\Omega_c}{(2\pi)^3} \int \frac{dS_E}{|\nabla_{\mathbf{k}} E(\mathbf{k})|} = \int d\hat{k}\, w_E(\mathbf{k}) = \int d\hat{k} \langle \mathbf{n} \,|\, \mathbf{k}\rangle_E \langle \mathbf{k} \,|\, \mathbf{n}\rangle_E. \tag{2.6}$$

If we substitute here the expansion (2.4) of $\langle \mathbf{n} \,|\, \mathbf{k}\rangle_E$ into multipole waves,

$$N(E;\mathbf{n}) = \sum_{\Gamma i} \sum_{Lq} \sum_{\Gamma' i'} \sum_{L' q'} \int d\hat{k} \langle \mathbf{n} \,|\, \Gamma i L q\rangle_E \langle \Gamma i L q \,|\, \mathbf{k}\rangle_E \times \langle \mathbf{k} \,|\, \Gamma' i' L' q'\rangle_E \langle \Gamma' i' L' q' \,|\, \mathbf{n}\rangle_E, \tag{2.7}$$

the unitarity of the transformation

$$\int d\hat{k} \langle \Gamma i L q \,|\, \mathbf{k}\rangle_E \langle \mathbf{k} \,|\, \Gamma' i' L' q'\rangle_E = \delta_{\Gamma\Gamma'} \delta_{ii'} \delta_{LL'} \delta_{qq'} \tag{2.8}$$

reduces $N(E;\mathbf{n})$ to the form:

$$N(E;\mathbf{n}) = \sum_{\Gamma i} \sum_{Lq} |\langle \mathbf{n} \,|\, \Gamma i L q\rangle_E|^2. \tag{2.9}$$

This expression subdivides the density of states per cell into contributions from the various multipoles. The squared magnitude of the multipole wave $\langle \mathbf{n} \,|\, \Gamma i L q\rangle_E$ thus represents the density of states belonging to the $\Gamma i L q$-multipole at the $\mathbf{n}$ cell. The expression (2.6) of $N(E;\mathbf{n})$ can also be interpreted as a "sum rule" for the set of multipoles waves.

The "local" density of states—as defined, e.g., by Heine and Weaire[5]—is similarly subdivided by transforming the multipole waves and (2.9) itself to the position representation by means of the Wannier functions,

$$n(E;\mathbf{r}) = \sum_{\Gamma i} \sum_{Lq} |\langle \mathbf{r} \,|\, \Gamma i L q\rangle_E|^2, \tag{2.10}$$

where

$$\langle \mathbf{r} \,|\, \Gamma i L q\rangle_E = \sum_{\mathbf{n}} \langle \mathbf{r} \,|\, \mathbf{n}\rangle \langle \mathbf{n} \,|\, \Gamma i L q\rangle_E. \tag{2.11}$$

3. CONSTRUCTION OF THE TRANSFORMATION $\langle \mathbf{k} \,|\, \Gamma i L q\rangle_E$

The set of Bloch waves with energy E reduces to plane waves with the same energy when the crystal becomes isotropic (empty lattice). In this limit the constant energy surface is a sphere of radius $|\mathbf{k}| = \sqrt{2mE}/\hbar$ whose symmetry group is the full rotation group so that the indices Γ and i coincide with the indices L and m of the angular momentum theory. The transformation $\langle \mathbf{k} \,|\, \Gamma i L q\rangle_E$ consists then simply of the spherical harmonics $Y_{Lm}(\hat{k})$ which indeed form a complete set of orthonormal functions with weight factor 1 over a sphere of arbitrary radius. What we want now is to construct a generalization of the set of spherical harmonics for a nonspherical surface with the symmetry discussed above. The functions of the new set must, however, depend both on the direction and the magnitude of $\mathbf{k}$ because this magnitude varies over the surface.

(a) To allow for the variation of $|\mathbf{k}|$ explicitly, we rewrite the condition of unitarity, Eq. (2.8), by extending the integration formally over the whole Brillouin zone and then restricting it to the constant energy surface by insertion of a factor $\delta[E - E(\mathbf{k})]$ which represents the surface equation $E(\mathbf{k}) = E$. Indicating the analogs of the spherical harmonics by $P_{Lq}^{(\Gamma i)}(\mathbf{k})$, we write then the orthonormality condition in the form

$$[\Omega_c/(2\pi)^3] \int d\mathbf{k}\, P_{Lq}^{(\Gamma i)}(\mathbf{k})\, P_{L'q'}^{(\Gamma' i')}(\mathbf{k})\, \delta[E - E(\mathbf{k})] = \int d\hat{k}\, P_{Lq}^{(\Gamma i)}(\mathbf{k})\, w_E(\mathbf{k})\, P_{L'q'}^{(\Gamma' i')}(\mathbf{k}) = \delta_{\Gamma\Gamma'} \delta_{ii'} \delta_{LL'} \delta_{qq'}. \tag{3.1}$$

Comparison with Eq. (2.8) shows that the nonspherical shape of the surface requires the unitary transformation to include a weight factor $w_E^{1/2}(\mathbf{k})$:

$$\langle \mathbf{k} \,|\Gamma i L q\rangle_E = w_E^{1/2}(\mathbf{k})\, P_{Lq}^{(\Gamma i)}(\mathbf{k}), \tag{3.2}$$

while the remaining factor $P_{Lq}^{(\Gamma i)}(\mathbf{k})$ may reduce to a polynomial as it does for a spherical surface.

(b) Following a general procedure of mathematical physics, we determine the $P_{Lq}^{(\Gamma i)}(\mathbf{k})$ as *orthogonal polynomials belonging to the weight function* $w_E(\mathbf{k})$ which is positive over the constant energy surface. The procedure starts from *any* convenient set of linearly independent homogeneous polynomials in the components of $\mathbf{k}$. In our case we want the polynomials to be symmetry-adapted, that is, each of them should transform according to a row i of an irreducible representation Γ of the point group. We make explicit the symmetry of the polynomial by factoring out its angular part as a symmetry-adapted spherical harmonic $X_{\Gamma i\lambda}^{(l)}(\hat{k})$, which is the λth linear combination of spherical harmonics of degree l that transforms according to the Γi irreducible representation of the point group (see, e.g., Bradley and Cracknell 1972 [6]). Symmetry-adapted homogeneous polynomials in $\mathbf{k}$ are then obtained by multiplying the $X_{\Gamma i\lambda}^{(l)}(\hat{k})$ with the invariant quantity $|\mathbf{k}|^l$ and any additional power of $|\mathbf{k}|^2$, which is itself an invariant polynomial in k_x, k_y, k_z.

Proceeding now to regroup *all* the polynomials which are homogeneous of degree l in $\mathbf{k}$, we identify $\frac{1}{2}(l+1)\,(l+2)$ symmetry-adapted polynomials for each l which we write as:

$$\begin{aligned} &v_{ls\lambda}^{(\Gamma i)}(\mathbf{k}) = A(l,s)\,|\mathbf{k}|^l\, X_{\Gamma i\lambda}^{(l-2s)}(\hat{k}), \\ &A(l,s) = \{4\pi/[2(l-s)+1]!!\,(s!)2^s\}^{1/2}, \end{aligned} \tag{3.3}$$

where $s = 0, 1, \ldots, [\frac{1}{2}l]$ (integer part of $\frac{1}{2}l$). The coefficients $A(l,s)$ are so chosen that the expansion of the plane wave $\exp(i\mathbf{r}\cdot\mathbf{k})$ has the form

$$\exp(i\mathbf{r}\cdot\mathbf{k}) = \sum_l i^l l!^{-1}(\mathbf{r}\cdot\mathbf{k})^l = \sum_{\Gamma i}\sum_{ls\lambda} i^l v_{ls\lambda}^{(\Gamma i)}(\mathbf{r}) v_{ls\lambda}^{(\Gamma i)}(\mathbf{k}), \tag{3.4}$$

with each term factored into identical polynomials in $\mathbf{r}$ and $\mathbf{k}$. The series (3.4) represents a rearrangement of the usual expansion of a plane wave into spherical waves, designed for easy adaptation to nonspherical symmetries. Successive terms of the power expansion of each spherical Bessel function $j_{l'}$ have been incorporated, in Eq. (3.4), into the various polynomials $v_{ls\lambda}^{(\Gamma i)}$ with equal $l' = l - 2s$ and different l. This parcelling out of the Bessel series was made necessary by the fact that each factor $|\mathbf{k}|^2$ is no longer independent of $\hat{k}$ in a crystal.

It is emphasized that for nonspherical surfaces over which $|\mathbf{k}|$ is not constant there are

$$\sum_{s=0}^{[l/2]} [2(l-2s)+1] = \tfrac{1}{2}(l+1)\,(l+2) \tag{3.5}$$

linearly independent polynomials $v_{ls\lambda}^{(\Gamma i)}$ homogeneous in $\mathbf{k}$ with degree l, in contrast to the familiar number $2l+1$ of harmonic polynomials $|\mathbf{k}|^l Y_{lm}(\hat{k})$ for the case of a spherical surface. In the spherical case the orthogonalization problem requires no special attention because different l values correspond to different group representations.

(c) The determination of the orthogonal polynomials $P_{Lq}^{(\Gamma i)}(\mathbf{k})$ is worked out separately for each Γ and for each i because both the constant energy surface and the weight function $w_E(\mathbf{k})$ are group-invariant. Moreover, each of the irreducible representations Γ is even (+) or odd (−) under inversion since the groups we deal with include this operation. The degree l of the symmetry-adapted polynomials $v_{ls\lambda}^{(\Gamma i)}(\mathbf{k})$ is similarly even or odd for each Γ.

The orthogonalization of the $P_{Lq}^{(\Gamma i)}(\mathbf{k})$ will be carried out, as usual, by recursion, starting with the lowest degree, l_0, that occurs for the given Γ in the process of symmetry-adapting the spherical harmonics. This value is given in the compatibility tables for the representations of the full orthogonal group and the representations of the point group (e.g., Bradley and Cracknell [6]). Generally, there is a single symmetry-adapted polynomial of degree l_0, $v_{l_0 0}^{(\Gamma i)}(\mathbf{k})$, for each Γ and i, and we can set

$$P_{l_0}^{(\Gamma i)}(\mathbf{k}) = d^{(l_0)} v_{l_0 0}^{(\Gamma i)}(\mathbf{k}), \tag{3.6}$$

where the indices q and λ, which distinguish polynomials of the same degree, have been dropped as superfluous in this particular case. (For the cases when the irreducible representation Γ occurs more than once at l_0, orthogonalization of the corresponding $P_{l_0 q}^{(\Gamma i)}(\mathbf{k})$ should present no difficulty.) The normalization coefficient $d^{(l_0)}$ is determined by (3.1) as

$$d^{(l_0)} = \langle v_{l_0 0} \,|W_E(\Gamma i)\,|\, v_{l_0 0}\rangle^{-1/2}; \tag{3.7}$$

the matrix elements

$$\begin{aligned} &\langle v_{ls\lambda}\,|W_E(\Gamma i)\,|\,v_{l's'\lambda'}\rangle \\ &\quad = \int d\hat{k}\; v_{ls\lambda}^{(\Gamma i)}(\mathbf{k}) w_E(\mathbf{k}) v_{l's'\lambda'}^{(\Gamma i)}(\mathbf{k}) \end{aligned} \tag{3.8}$$

constitute the essential structural parameters for our problem.

For each $L > l_0$, we set up the orthogonalization procedure by representing each polynomial $P_{Lq}^{(\Gamma i)}(\mathbf{k})$ as the sum of one group of terms homogeneous of degree L and of a second group of terms of lower degree designed to insure the orthogonalization to all $P_{L'q'}^{(\Gamma i)}(\mathbf{k})$ with $L' < L$. Thus we set:

$$P_{Lq}^{(\Gamma i)}(\mathbf{k}) = \sum_{s\lambda} v_{Ls\lambda}^{(\Gamma i)}(\mathbf{k})\, d_{s\lambda}^{(Lq)} + \sum_{L'q'}^{L'<L} P_{L'q'}^{(\Gamma i)}(\mathbf{k})\, g_{L'q'}^{(Lq)}, \tag{3.9}$$

where the coefficients $g_{L'q'}^{(Lq)}$ will be determined by Schmidt orthogonalization and the $d_{s\lambda}^{(Lq)}$ by a separate procedure. The orthogonality condition for $L' < L$ reads:

$$\begin{aligned} &\langle P_{L'q'}\,|W_E(\Gamma i)\,|\,P_{Lq}\rangle \\ &\quad = \sum_{s\lambda} \langle P_{L'q'}\,|W_E(\Gamma i)\,|\,v_{Ls\lambda}\rangle d_{s\lambda}^{(Lq)} \\ &\qquad + \sum_{L''q''}^{L''<L} \langle P_{L'q'}\,|W_E(\Gamma i)\,|\,P_{L''q''}\rangle g_{L''q''}^{(Lq)} = 0. \end{aligned} \tag{3.10}$$

Owing to the previous orthonormalization of the $P_{L'q'}^{(\Gamma i)}(\mathbf{k})$ with $L' < L$, this condition gives simply

$$g_{L'q'}^{(Lq)} = -\sum_{s\lambda} \langle P_{L'q'}\,|W_E(\Gamma i)\,|\,v_{Ls\lambda}\rangle d_{s\lambda}^{(Lq)}. \tag{3.11}$$

Substitution of this result in (3.9) reduces the orthonormalization condition on the $P_{Lq}^{(\Gamma i)}(\mathbf{k})$ with equal degree L to the form:

$$\langle P_{Lq_1}|W_E(\Gamma i)|P_{Lq_2}\rangle = \sum_{s\lambda}\sum_{s'\lambda'} d_{s\lambda}^{(Lq_1)}\Big\{\langle v_{Ls\lambda}|W_E(\Gamma i)|v_{Ls'\lambda'}\rangle - \sum_{L'q'}^{L'<L}\langle v_{Ls\lambda}|W_E(\Gamma i)|P_{L'q'}\rangle \times\langle P_{L'q'}|W_E(\Gamma i)|v_{Ls'\lambda'}\rangle\Big\} d_{s'\lambda'}^{(Lq_2)} = \delta_{q_1q_2}. \tag{3.12}$$

The construction of the polynomials of each degree L thus reduces to the determination of the eigenvectors $\mathbf{d}^{(Lq)}$ of the symmetric and real matrix

$$\langle v_{Ls\lambda}|\overline{W}_E(\Gamma i)|v_{Ls'\lambda'}\rangle = \langle v_{Ls\lambda}|W_E(\Gamma i)|v_{Ls'\lambda'}\rangle - \sum_{L'q'}^{L'<L}\langle v_{Ls\lambda}|W_E(\Gamma i)|P_{L'q'}\rangle\langle P_{L'q'}|W_E(\Gamma i)|v_{Ls'\lambda'}\rangle. \tag{3.13}$$

The order of this matrix equals the number of symmetry-adapted polynomials $v_{Ls\lambda}^{(\Gamma i)}(\mathbf{k})$ of degree L. The normalization of the eigenvectors $\mathbf{d}^{(Lq)}$, implied by (3.12), coincides with that given by (3.7) for the special case $L=l_0$. Examples of the construction of the $P_{Lq}^{(\Gamma i)}(\mathbf{k})$ are shown in the Appendix.

4. PROPERTIES OF THE MULTIPOLE WAVES

Entering the symmetry-adapted expansion of the plane wave (3.4) into the expression (2.5) of the multipole wave $\langle \mathbf{n}|\Gamma i L q\rangle_E$, yields

$$\langle \mathbf{n}|\Gamma i L q\rangle_E = \int d\hat{k}\,\exp(i\mathbf{n}\cdot\mathbf{k})w_E(\mathbf{k})P_{Lq}^{(\Gamma i)}(\mathbf{k}) = \sum_{ls\lambda} i^l v_{ls\lambda}^{(\Gamma i)}(\mathbf{n})\langle v_{ls\lambda}|W_E(\Gamma i)|P_{Lq}\rangle. \tag{4.1}$$

Because of the orthogonality of $P_{Lq}^{(\Gamma i)}(\mathbf{k})$ to the entire space of polynomials of degree lower than L, the expansion (4.1) starts with terms of degree $l=L$. This property was introduced by Fano[3] as the characteristic of the dependence of each multipole wave on the distance from the "center".

This result permits us now to specify that the first term of the series expansion of the multipole wave $\langle \mathbf{n}|\Gamma i L q\rangle_E$ is

$$i^L\sum_{s\lambda}\sum_{s'\lambda'} v_{Ls\lambda}^{(\Gamma i)}(\mathbf{n})\,\overline{W}_E(\Gamma i)|v_{Ls'\lambda'}\rangle d_{s'\lambda'}^{(Lq)}. \tag{4.2}$$

Recalling that $\mathbf{d}^{(Lq)}$ is eigenvector of the matrix $\langle v_{Ls\lambda}|\overline{W}_E(\Gamma i)|v_{Ls'\lambda'}\rangle$ corresponding to the eigenvalue $\overline{W}_{\Gamma Lq}$, we obtain that the first term of the series expansion of the density of states $|\langle \mathbf{n}|\Gamma i L q\rangle_E|^2$ belonging to the $\Gamma i L q$-multipole is of degree $2L$ and is given by

$$\Big\{\overline{W}_{\Gamma Lq}\sum_{s\lambda} v_{Ls\lambda}^{(\Gamma i)}(\mathbf{n})\,d_{s\lambda}^{(Lq)}\Big\}^2. \tag{4.3}$$

Since the eigenvectors $\mathbf{d}^{(Lq)}$ are normalized in accordance with (3.12), we conclude that (4.2) is linear, rather than quadratic, in the eigenvalue $\overline{W}_{\Gamma Lq}$ of the matrix (3.13).

This conclusion represents the central result of the paper; we have shown how the density of states around a center cell in a crystalline medium can be characterized in practice by a few parameters only of the constant energy surface, namely the eigenvalues $\overline{W}_{\Gamma Lq}$ for rather low L. More specifically, the structural similarity of the polynomials $v_{Ls\lambda}^{(\Gamma i)}(\mathbf{n})$ and of the Bessel functions $j_L(|\mathbf{n}|)$ shows that $v_{Ls\lambda}^{(\Gamma i)}(\mathbf{n})\ll 1$ whenever $|\mathbf{n}|\ll L$. However, we regard this result as the first step of a broader investigation of physical parameters appropriate to the study of phenomena with local character.

This point of view is close to that which motivated Kohn[4] and collaborators to express energy band properties of solids directly in terms of Wannier functions and of such local quantities as the matrix elements $\langle O|H_c|\mathbf{n}\rangle$, where H_c is the 1-electron Hamiltonian of the crystal. As an example of the connection of the two approaches, the equation of the constant energy surface, which is given by Kohn as a Fourier series with coefficients $\langle O|H_c|\mathbf{n}\rangle$, can be expressed in terms of the symmetry-adapted polynomials belonging to Γ_1^+:

$$E(\mathbf{k}) = \sum_{ls\lambda} E_{ls\lambda} v_{ls\lambda}^{(\Gamma_1^+)}(\mathbf{k}), \tag{4.3}$$

where

$$E_{ls\lambda} = i^l\sum_{\mathbf{n}}\langle O|H_c|\mathbf{n}\rangle v_{ls\lambda}^{(\Gamma_1^+)}(\mathbf{n}). \tag{4.4}$$

Owing to the localization of the Wannier functions, the sum over $\mathbf{n}$ extends in effect only to a limited number of cells around the center. Owing, once again, to the properties of the polynomials $v_{ls\lambda}$, the sum in (4.3) also converges rapidly with increasing l.

APPENDIX: EXAMPLES OF ORTHOGONAL POLYNOMIALS FOR THE GROUP O_h

We use the notation of Bradley and Cracknell[6]:

$$Y_l^{m,c} = (2)^{-1/2}(Y_l^m + Y_l^{-m}),\quad Y_l^{m,s} = -i(2)^{-1/2}(Y_l^m - Y_l^{-m}).$$

Case 1: Γ_1^+

(a) $l=0$, $v_{00}(\mathbf{k})=1$, $P_0(\mathbf{k}) = \langle v_{00}|W_E|v_{00}\rangle^{-1/2}$.

(b) $l=2$, $v_{21}(\mathbf{k}) = (6)^{-1/2}|\mathbf{k}|^2$,

$$P_2(\mathbf{k}) = \langle v_{21}|\overline{W}_E|v_{21}\rangle^{-1/2}[v_{21}(\mathbf{k}) - P_0(\mathbf{k})\langle P_0|W_E|v_{21}\rangle].$$

(c) $l=4$

$$v_{40}(\mathbf{k}) = (4\pi/945)^{1/2}|\mathbf{k}|^4[(\tfrac{7}{12})^{1/2} Y_4^0(\hat{k}) + (\tfrac{5}{12})^{1/2} Y_4^{4,c}(\hat{k})],$$

$$v_{42}(\mathbf{k}) = (120)^{-1/2}|\mathbf{k}|^4,$$

$$P_{4\pm}(\mathbf{k}) = \overline{W}_{4\pm}^{-1/2}[(\overline{W}_{4\pm} - \langle v_{40}|\overline{W}_E|v_{40}\rangle)^2 + \langle v_{40}|\overline{W}_E|v_{42}\rangle^2]^{-1/2}[\langle v_{40}|\overline{W}_E|v_{42}\rangle u_{40}(\mathbf{k}) + (\overline{W}_{4\pm} - \langle v_{40}|\overline{W}_E|v_{40}\rangle)u_{42}(\mathbf{k})],$$

where

$$u_{4s}(\mathbf{k}) = v_{4s}(\mathbf{k}) - P_2(\mathbf{k})\langle P_2|W_E|v_{4s}\rangle$$

$$- P_0(\mathbf{k})\langle P_0|W_E|v_{4s}\rangle \quad (s=0,2),$$

and $\overline{W}_{4\pm}$ are the roots of the quadratic equation

$$(\langle v_{40}|\overline{W}_E|v_{40}\rangle - \overline{W}_{4q})(\langle v_{42}|\overline{W}_E|v_{42}\rangle - \overline{W}_{4q}) = \langle v_{40}|\overline{W}_E|v_{42}\rangle^2.$$

Case 2: Γ_4^-

(a) $l=1$, $\left.\begin{matrix} v_{10}^{(1)}(\mathbf{k}) \\ v_{10}^{(2)}(\mathbf{k}) \\ v_{10}^{(3)}(\mathbf{k}) \end{matrix}\right\} = \left(\frac{4\pi}{3}\right)^{1/2} |\mathbf{k}| \left\{\begin{matrix} Y_1^{1,c}(\hat{k}) \\ Y_1^{1,s}(\hat{k}) \\ Y_1^{0}(\hat{k}) \end{matrix}\right. = \left\{\begin{matrix} k_x, \\ k_y, \\ k_z, \end{matrix}\right.$

$$P_1^{(i)}(\mathbf{k}) = \langle v_{10}|W_E(i)|v_{10}\rangle^{-1/2} v_{10}^{(i)}(\mathbf{k}) \quad (i=1,2,3).$$

(b) $l=3$, $\left.\begin{matrix} v_{30}^{(1)}(\mathbf{k}) \\ v_{30}^{(2)}(\mathbf{k}) \\ v_{30}^{(3)}(\mathbf{k}) \end{matrix}\right\}$

$$= \left(\frac{4\pi}{105}\right)^{1/2} |\mathbf{k}|^3 \left\{\begin{matrix} (\tfrac{3}{8})^{1/2} Y_3^{1,c}(\hat{k}) - (\tfrac{5}{8})^{1/2} Y_3^{3,c}(\hat{k}), \\ (\tfrac{3}{8})^{1/2} Y_3^{1,s}(\hat{k}) + (\tfrac{5}{8})^{1/2} Y_3^{3,s}(\hat{k}), \\ - Y_3^{0}(\hat{k}), \end{matrix}\right.$$

$$\left.\begin{matrix} v_{31}^{(1)}(\mathbf{k}) \\ v_{31}^{(2)}(\mathbf{k}) \\ v_{31}^{(3)}(\mathbf{k}) \end{matrix}\right\} = \left(\frac{4\pi}{30}\right)^{1/2} |\mathbf{k}|^3 \left\{\begin{matrix} Y_1^{1,c}(\hat{k}), \\ Y_1^{1,s}(\hat{k}), \\ Y_1^{0}(\hat{k}), \end{matrix}\right.$$

$$P_{3\pm}^{(i)}(\mathbf{k}) = \overline{W}_{3\pm}^{-1/2}[(\overline{W}_{3\pm} - \langle v_{30}|\overline{W}_E(i)|v_{30}\rangle)^2 + \langle v_{30}|\overline{W}_E(i)|v_{31}\rangle^2]^{-1/2} \times[\langle v_{30}|\overline{W}_E(i)|v_{31}\rangle u_{30}^{(i)}(\mathbf{k}) + (\overline{W}_{3\pm} - \langle v_{30}|\overline{W}_E(i)|v_{30}\rangle) u_{31}^{(i)}(\mathbf{k})] \quad (i=1,2,3),$$

where

$$u_{3s}^{(i)}(\mathbf{k}) = v_{3s}^{(i)}(\mathbf{k}) - P_1^{(i)}(\mathbf{k})\langle P_1|W_E(i)|v_{3s}\rangle \quad (s=0,1),$$

and $\overline{W}_{3\pm}$ are the roots of the quadratic equation

$$(\langle v_{30}|\overline{W}_E(i)|v_{30}\rangle - \overline{W}_{3q})(\langle v_{31}|\overline{W}_E(i)|v_{31}\rangle - \overline{W}_{3q}) = \langle v_{30}|W_E(i)|v_{31}\rangle^2.$$

Case 3: Γ_3^+

(a) $l=2$, $\left.\begin{matrix} v_{20}^{(1)}(\mathbf{k}) \\ v_{20}^{(2)}(\mathbf{k}) \end{matrix}\right\} = \left(\frac{4\pi}{15}\right)^{1/2} |\mathbf{k}|^2 \left\{\begin{matrix} Y_2^{0}(\hat{k}), \\ Y_2^{2,c}(\hat{k}), \end{matrix}\right.$

$$P_2^{(i)}(\mathbf{k}) = \langle v_{20}|W_E(i)|v_{20}\rangle^{-1/2} v_{20}^{(i)}(\mathbf{k}) \quad (i=1,2).$$

(b) $l=4$ $\left.\begin{matrix} v_{40}^{(1)}(\mathbf{k}) \\ v_{40}^{(2)}(\mathbf{k}) \end{matrix}\right\}$

$$= \left(\frac{4\pi}{945}\right)^{1/2} |\mathbf{k}|^4 \left\{\begin{matrix} (\tfrac{5}{12})^{1/2} Y_4^{0}(\hat{k}) - (\tfrac{7}{12})^{1/2} Y_4^{4,c}(\hat{k}), \\ - Y_4^{2,c}(\hat{k}), \end{matrix}\right.$$

$$\left.\begin{matrix} v_{41}^{(1)}(\mathbf{k}) \\ v_{41}^{(2)}(\mathbf{k}) \end{matrix}\right\} = \left(\frac{4\pi}{210}\right)^{1/2} |\mathbf{k}|^4 \left\{\begin{matrix} Y_2^{0}(\hat{k}), \\ Y_2^{2,c}(\hat{k}), \end{matrix}\right.$$

$$P_{4\pm}^{(i)}(\mathbf{k}) = \overline{W}_{4\pm}^{-1/2}[(\overline{W}_{4\pm} - \langle v_{40}|\overline{W}_E(i)|v_{40}\rangle)^2 + \langle v_{40}|\overline{W}_E(i)|v_{41}\rangle^2]^{-1/2} \times[\langle v_{40}|\overline{W}_E(i)|v_{41}\rangle u_{40}^{(i)}(\mathbf{k}) + (\overline{W}_{4\pm} - \langle v_{40}|\overline{W}_E(i)|v_{40}\rangle) u_{41}^{(i)}(\mathbf{k})] \quad (i=1,2),$$

where

$$u_{4s}^{(i)}(\mathbf{k}) = v_{4s}^{(i)}(\mathbf{k}) - P_2^{(i)}(\mathbf{k})\langle P_2|W_E(i)|v_{4s}\rangle \quad (s=0,1),$$

and $\overline{W}_{4\pm}$ are the roots of the quadratic equation

$$(\langle v_{40}|\overline{W}_E(i)|v_{40}\rangle - \overline{W}_{4q})(\langle v_{41}|W_E(i)|v_{41}\rangle - \overline{W}_{4q}) = \langle v_{40}|\overline{W}_E(i)|v_{41}\rangle^2.$$

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