Multipole Waves in Periodic Lattices*

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The concept of a spherical wave is extended for application to anisotropic crystalline fields. The construction and labeling of such waves are outlined for a schematic model. Possible applications are indicated.

A multipole source radiates into isotropic surroundings a spherical wave which is an eigenfunction of the square of angular momentum. Expansion into such waves is basic to the theory of scattering by small objects, as well as to the study of bound states that extend into the surrounding medium.

The anisotropy of crystals spoils the conservation of angular momentum and has thus hindered the application of spherical-wave techniques to problems concerning radiation from localized sources or impurity effects in crystals. More specifically, the motion of an electron in the lattice surrounding an impurity is generally studied by considering separately its interactions with individual lattice atoms, whereas the same interactions can be treated globally in the construction of Bloch states, by taking advantage of translational symmetry. Callaway has attempted to remedy this situation by a theory of impurity scattering analogous to atomic theory, replacing the angular momentum classification of spherical waves by a point-group classification. However, labeling of waves by point-group symmetry does not suffice to classify a complete set of waves of given energy; applications were then carried out under a restriction to spherical energy surfaces.[1]

This Letter points out that the quantum number L of a 2^L-pole wave characterizes not only its angular momentum, but also the lowest term of its expansion into powers of the distance from the center of coordinates. This second criterion applies irrespective of anisotropy. It preserves the essential feature that only low-L waves interact appreciably with a localized source or perturber. It also provides for labeling of a complete set of spherical-type waves. On this basis we introduce a multipole-wave approach to problems of crystal physics.

The work originates from efforts to interpret large and extensive structures in the inner-shell photoabsorption spectra of crystals. These structures depend on the parity and multipolarity of the photoemission (into $s,p,\ldots$ channels) and hence cannot be reproduced by multiplying an atomic spectrum by a single normalization factor proportional to the density of final states in the crystal.[2] To this problem we contribute here only a qualitative remark because detailed application to any one crystal phenomenon would require further development while restricting needlessly the focus of attention. We concentrate instead on demonstrating the construction of multipole waves for the schematic example of a two-dimensional "tight-binding" model. This example will suffice to show that a localized perturbation interacts with a multipole wave in proportion to a normalization coefficient which depends on the multipolarity and coincides with the density of states only for a monopole. (Indeed photoabsorption is usually shown to be proportional to the density of states by assuming that it yields a pointlike source of electrons, equally coupled to plane waves traveling in all directions.)

Our restriction to a very schematic model has the purpose of minimizing notations. Extension to three dimensions and to more realistic wave functions is straightforward, except for the introduction of irregular functions mentioned further below. The use of point-group symmetry, which is central to the approach of Ref. 1, appears in the present treatment as a simplification whose relevance and role will be indicated but whose explicit development is deferred, as is also the development of many other points.

We consider, then a two-dimensional crystalline lattice of cells identified by pairs of integer indices (m,n). To each cell there pertains a Wannier wave function $u(\vec{r}-\vec{R}_{mn})$, where $\vec{R}_{mn}$ is a reference point in the cell; no band index is required for our purposes. An eigenfunction of an electron with energy E in the crystal is represented by a superposition

$$\Psi(E,\vec{r})=\sum_{mn}\psi(E;m,n)u(\vec{r}-\vec{R}_{mn}). \quad (1)$$

The translational invariance of the lattice leads

to the existence of Bloch states with

$$\psi(E;m,n)=w^{1/2}(E;\alpha,\beta)e^{i(\alpha m+\beta n)}. \quad (2)$$

Here w is a normalization coefficient and α and β are wave-vector components (in units of the basis vectors of the reciprocal lattice) related to each other and to E by a dispersion relation

$$D(E;\alpha,\beta)=0, \quad (3)$$

which defines the constant-energy curve on the (α,β) plane. (The properties of the functions D and u are not relevant here. A study of the construction of D in terms of unit-cell parameters, irrespective of tight-binding approximations, is in progress and will be reported elsewhere.)

The amplitude $w^{1/2}$ of the plane wave (2) depends on its normalization. Normalization per unit α and β would lead to $w=(2\pi)^{-2}$. We intend, however, to normalize per unit of the fixed energy E. Accordingly we choose as a pair of independent variables the energy E and a direction parameter φ of the plane wave. Normalization per unit E and φ requires that

$$w(E;\alpha,\beta)=(2\pi)^{-2}\partial(\alpha,\beta)/\partial(E,\varphi), \quad (4)$$

where the Jacobian is calculated from (3) and from $\tan\varphi=\beta/\alpha$. The coefficient (4) is the density of states differential in E and φ. (For a square lattice, φ is the direction angle of the plane wave.)

Multipole waves will now be constructed as superpositions of plane waves (2) with equal E and different φ. We define

$$\psi_{Lq}(E;m,n)=\int_0^{2\pi}d\varphi\, c_{Lq}(\alpha,\beta)w^{1/2}(E;\alpha,\beta)e^{i(\alpha m+\beta n)}, \quad (5)$$

with the intention of selecting coefficients c_{Lq} such that the power expansion of (5) contains no terms $m^r n^s$ with $r+s<L$. The index q will distinguish different waves with the same L. {In the isotropic case, where D and w are independent of φ, the problem is solved by $c_{Lq}\propto\cos L\varphi$, and ψ_{Lq} reduces to the familiar form $J_L((\alpha^2+\beta^2)^{1/2}(m^2+n^2)^{1/2})\cos L\chi$ with $\tan\chi=n/m$.} The integrals in the expansion

$$\psi_{Lq}(E;m,n)=\sum_{rs}i^{r+s}[m^r n^s/(r!s!)]\int_0^{2\pi}d\varphi\, c_{Lq}(\alpha,\beta)w^{1/2}(E;\alpha,\beta)\alpha^r\beta^s \quad (6)$$

will then be made to *vanish for all* $r+s<L$. This condition identifies the functions c_{Lq} as the set obtained by orthogonalization to the sequence of $\alpha^r\beta^s$ arranged in order of increasing $r+s$, with the weight function $w(E;\alpha,\beta)$. Ordering at equal $r+s$ may remain unspecified.

The orthogonalization problem is solved by setting

$$c_{Lq}(\alpha,\beta)=w^{1/2}(E;\alpha,\beta)\sum_{\rho,\sigma}^{\rho+\sigma\le L}d_{\rho\sigma}^{(Lq)}\alpha^\rho\beta^\sigma, \quad (7)$$

where the coefficients d of the polynomials remain to be determined. Equation (7) transforms (6) into

$$\psi_{Lq}(E;m,n)=\sum_{rs}i^{r+s}\frac{m^r n^s}{r!s!}\sum_{\rho,\sigma}^{\rho+\sigma\le L}M_{rs,\rho\sigma}\,d_{\rho\sigma}^{(Lq)}, \quad (8)$$

where the matrix elements

$$M_{rs,\rho\sigma}=\int_0^{2\pi}d\varphi\, w(E;\alpha,\beta)\alpha^{r+\rho}\beta^{s+\sigma} \quad (9)$$

are moments of the distribution of (α,β) over the curve of constant E and are the essential ingredients of the present theory. The expansion (8) starts with terms of Lth degree provided

$$\sum_{\rho\sigma}^{\rho+\sigma\le L}M_{rs,\rho\sigma}d_{\rho\sigma}^{(Lq)}=0 \text{ for all } r+s<L. \quad (10)$$

This system of equations permits elimination of all $d_{\rho\sigma}^{(Lq)}$ with $\rho+\sigma<L$, insures that the c_{Lq} with different L are orthogonal over $0\le\varphi<2\pi$, and reduces the orthonormality of the c_{Lq} with equal L to

$$\sum_{\rho\sigma}^{\rho+\sigma=L}\sum_{\rho'\sigma'}^{\rho'+\sigma'=L}\bar{M}_{\rho\sigma,\rho'\sigma'}^{(L)}d_{\rho\sigma}^{(Lq)}d_{\rho'\sigma'}^{(Lq')*}=\delta_{qq'}. \quad (11)$$

Here $\bar{M}^{(L)}$ is the matrix

$$\bar{M}^{(L)}=P^{(L)}MP^{(L)}-P^{(L)}MQ^{(L)}(Q^{(L)}MQ^{(L)})^{-1}Q^{(L)}MP^{(L)}, \quad (12)$$

obtained by eliminating $\rho+\sigma<L$ using the projection operators

$$P_{\rho\sigma,\rho'\sigma'}{}^{(L)}=\delta_{\rho+\sigma,L}\delta_{\rho'\rho}\delta_{\sigma'\sigma},$$

$$Q^{(L)}=\sum_{\bar{L}=0}^{L-1}P^{(\bar{L})}.$$

Equation (11) has no unique solution for $L>0$, but one may choose a standard base set of ψ_{Lq} by requiring the $d_{\rho\sigma}{}^{(Lq)}$ to be eigenvectors of $\bar{M}^{(L)}$. Each orthonormal set of ψ_{Lq} with given L is at first view of the same order as the matrix $\bar{M}^{(L)}$, equal to the number $L+1$ of pairs of integers (ρ, σ) with $\rho+\sigma=L$; for a three-dimensional system the corresponding number is $\frac{1}{2}(L+1)(L+2)$. This *multiplicity differs from that of isotropic systems*, which is familiarly twofold in two dimensions (for $L\neq 0$) and $(2L+1)$-fold in three dimensions. Physically, the difference occurs because the number of independent multipole fields is restricted by symmetry in isotropic media. (For example, in three-dimensional isotropic space the quadrupole fields $\nabla_x{}^2r^{-1}$, $\nabla_y{}^2r^{-1}$, and $\nabla_z{}^2r^{-1}$ add up to zero.) Formally a reduction of the number of independent multipole waves results from any reduction of the rank of the matrices $\bar{M}^{(L)}$.

Such a reduction may result from *symmetries* which "reduce" the matrix M into separate diagonal blocks, in the sense of group theory. Firstly, time-reversal invariance always causes $w(\alpha, \beta)$ to be even under the inversion $(\alpha,\beta)\rightarrow(-\alpha,-\beta)$. Because of this symmetry, (9) vanishes for all odd values of $r+s+\rho+\sigma$, thus restricting the polynomials in (7) to even values of $L-\rho-\sigma$ and the expansion (8) of ψ_{Lq} to terms with even values of $r+s-L$. The matrices M and $\bar{M}^{(L)}$ reduce further in accordance with the point-symmetry group of the cell array, expressed through symmetries of D and w, whereby the coefficients $d_{\rho\sigma}{}^{(Lq)}$ and the waves ψ_{Lq} with different q are sorted out into the various symmetry species. Thus, e.g., in the isotropic limit the $M_{rs,\rho\sigma}$ are proportional to the averages of $\cos^{r+\rho}\varphi\sin^{s+\sigma}\varphi$, and are easily evaluated for all pairs with $r+s$ or $\rho+\sigma$ equal to 0 or 2; one then verifies that $\bar{M}^{(2)}$ is of order 3 but of rank 2 and that there are only two independent waves ψ_{2q}.

The treatment of an impurity at $m=n=0$ requires the matching of its wave function to those of the surrounding crystal lattice. To do this one needs not only wave functions ψ_{Lq} regular at $m=n=0$ but also the corresponding irregular functions. The latter may be introduced by generalizing the procedure used for Bessel functions,[3] considering that $w(E;\alpha,\beta)$ is periodic in φ and assuming that it remains bounded when $\varphi\rightarrow\infty$ in the complex plane; this assumption holds at least for a broad class of models. The steps of the procedure are these: (a) Define φ_0 by setting $m=h\sin\varphi_0$ and $n=-h\cos\varphi_0$, whereby $\alpha m+\beta n$ vanishes for $\varphi=\varphi_0$. (b) Extend the path of integration in Eq. (5) to run along six legs into the complex field, as indicated by

$$\int_{\varphi_0+i\infty}^{\varphi_0}+\int_{\varphi_0}^{\varphi_0+\pi}+\int_{\varphi_0+\pi}^{\varphi_0+\pi-i\infty}+\int_{\varphi_0+\pi-i\infty}^{\varphi_0+\pi}+\int_{\varphi_0+\pi}^{\varphi_0+2\pi}+\int_{\varphi_0+2\pi}^{\varphi_0+2\pi+i\infty}. \qquad (13)$$

(c) Note that under the assumptions for w, the first and last legs, as well as the third and fourth, cancel in pairs thus leaving the total integral equal to (5); also, each leg remains finite except for $m=n=0$. (d) Split the integral into separate sums of the first three and of the last three legs; the separate sums represent ingoing and outgoing progressive waves, respectively, while their difference yields the desired irregular standing wave.

The wave function of a photoelectron ejected from an atom with angular momentum l need not match a single multipole wave of the surrounding crystal with $L=l$, but must anyhow be matched to a superposition of waves of the same point-group symmetry. The photoemission rate will depend on the phase matching, as it does for free atoms, and may thus exhibit resonances when the phases are sensitive to energy. The rate also depends linearly on the squared coefficients,

$$\Big|\sum_{\rho\sigma}^{\rho+\sigma=L}\bar{M}_{rs,\rho\sigma}{}^{(L)}d_{\rho\sigma}{}^{(Lq)}\Big|^2,$$

of the lowest terms in the expansion of the relevant multipole wave. From the normalization equation (11) one sees that these squared coefficients, in turn, depend linearly on the eigenvalues of $\bar{M}^{(L)}$. Proportionality of photoemission to the usual density of states, i.e., to $M_{00,00}$, is thus restricted to $L=0$ as anticipated above; for $L\neq 0$ photoemission depends also on moments $M_{rs,\rho\sigma}$ of the density of states, of order $r+s+\rho+\sigma\neq 0$.

The construction of multipole waves by superposition of plane waves applies also to light in crystals. Thus, e.g., the angular distribution of light emitted by an atomic dipole in a crystal does not obey the Hertz formula but is given by the asymptotic expansion of a ψ_{1q} wave for $(m,n)\rightarrow\infty$. It is thus proportional to the value of $|c_{1q}(\alpha,\beta)|^2$ evaluated at the point of *stationary phase*, where $\partial(\alpha m+\beta n)/\partial\varphi=0$. This remark should open the way for theory and experiments on the

angular distribution of fluorescence by crystal impurities, analogous to the well-established studies of radiations from single atoms and from nuclei.

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Coulomb Effects on the Gain Spectrum of Semiconductors

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We have investigated the effect of Coulomb interactions on the gain spectra of highly excited semiconductors, specifically GaAs. It is shown that at low temperatures there is an enhancement of the direct excitation of approximately a factor of 2 and a sideband due to particle-hole pair excitations that extends into the gap. As the temperature increases, it is argued by analogy to the electron-phonon problem that the sideband changes into an Urbach tail with gain of the order of 10–100 cm^{-1}.

Stimulated recombination in direct-gap semiconductors has been under intensive study in the last decade.[1,2] There exist extensive calculations of gain versus temperature and degree of inversion based on independent-particle models taking into account band-structure effects[3] and impurity-band tailing.[4,5] Recently, direct measurements of the gain spectrum have become available for optically pumped systems at low temperature and for a variety of pump powers.[2] One of the most striking features is that gain begins only at one or two exciton energies below the gap. This effect has been explained[6,7] as being a result of exchange and correlation. We discuss in this paper two additional effects due to this Coulomb interaction: (i) an enhancement of the band-to-band gain, and (ii) emission below the band-to-band processes that takes the form of a plasmon sideband at low temperatures and a self-induced band tail at high temperatures. We argue that this band tail may be quite important in understanding the properties of undoped or lightly doped ($<10^{18}$ cm^{-3}) GaAs lasers operating at room temperature. This sideband effect has previously been discussed.[8] However, there are large cancelations omitted by previous authors, and consequently our results are very different.

We shall limit ourselves to isotropic electron and hole bands described by effective density-of-states masses m_e and m_h. We shall also specialize to GaAs as an illustration and take $m_h/m_e = 9.5$. The absorption and gain of an inverted semiconductor is given by the imaginary part of the dielectric function. This is calculated to lowest order in the dynamically screened Coulomb interaction, $V(q) = (4\pi e^2/q^2)[\epsilon(q, \omega)]^{-1}$, by summing the three diagrams shown in Fig. 1. The dielectric function $\epsilon(q, \omega)$ of the electron-hole plasma is further approximated by the single-plasmon-pole approximation that has been used extensively by Hedin and Lundquist.[9] However, in order to attempt to represent the true spectrum of a zinc-blende material,[10] we broaden the plasmon into a Lorentzian whose width is $\frac{1}{10}$ of the plasma frequency. When the gain spectrum is calculated, we find an enhancement of the band-to-band recombination. This enhancement varies somewhat with frequency and is approximately a factor of 2 at low temperature. The slightly distorted gain spectrum is compared with the single-particle result in the lower right-hand corner of Fig. 1 for a typical electron-hole density at low temperature. It is seen that the enhancement is considerably reduced compared to that of the exciton problem[11] because of the screening of the Coulomb interaction. We have crudely estimated the effects of multiple scattering by using the work of Mahan[12] and found them to be small. In the same calculation, we can look at Auger processes involving the emission