

Multipole wavefunctions for photoelectrons in crystals. IV. The irregular functions and the matching to an impurity^{a)}

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Extension of the method of partial waves to scattering by an impurity center in a crystal requires the construction of energy eigenfunctions of the unperturbed crystal that are irregular at the center. These irregular solutions of a nonseparable problem are constructed by utilizing the expansion of the Green's function into the regular solutions symmetry-adapted about the impurity center, which have been obtained earlier. The wavefunction within an impurity can thus be continued throughout the surrounding crystal by matching it at the impurity boundary to a superposition of regular and irregular solutions. This procedure is compared to the current EXAFS treatment of photoabsorption.

I. INTRODUCTION

This paper develops a mathematical framework for matching the wavefunctions of a localized impurity and of its surrounding unperturbed crystalline medium. The matching constitutes the interface for connecting atomic and band properties. Our method extends to crystals the partial wave expansion which is familiar for spherical symmetry. This paper deals with certain aspects of the solutions of the Schrödinger equation with potential fields that possess point group symmetry about an impurity center as well as translational crystal symmetry except for the presence of this center.

We divide the crystal into an *internal* region where the perturbing potential is effective, and an *external* region where the crystal is unperturbed. In previous papers¹⁻⁴ we considered a complete set of solutions in the external region, symmetry-adapted to the point group, which remain bounded when continued into the center of the internal region. For this reason we call them *regular* multipole wavefunctions. However, the matching of an impurity wavefunction and of its normal derivative at the boundary of the internal region requires also the knowledge of the corresponding set of *irregular* multipole wavefunctions, that is, of functions which would become singular when continued into the center of the internal region. The construction of these irregular functions constitutes the main task of this paper.

The regular multipole wavefunctions result from a unitary transformation of the Bloch waves with real \mathbf{k} vectors,³ analogous to the construction of the spherical Bessel functions by superposition of plane waves. Irregular multipole wavefunctions could then be constructed by analogy to the corresponding construction of the spherical Neumann functions, namely, by the integral representation in terms of plane waves,

$$n_l(kr) = \frac{1}{4i^{l+1}} \int_C d\theta \sin\theta e^{ikr\cos\theta} P_l(\cos\theta), \quad (\text{I.1})$$

where C is a suitable path in the complex θ plane.⁵ However, in the crystal situation the nonseparability of angular varia-

bles makes it difficult to identify the appropriate path in the three-dimensional complex domain of \mathbf{k} vectors. Moreover, even though Bloch waves with complex \mathbf{k} vectors can be defined by analytic continuation,⁶ degeneracies among bands make their constructive definition unpractical. On the other hand, the Neumann functions can also be defined by a Green's function formalism,⁷ which depends only on general properties of partial differential equations rather than on the separation of variables for spherical symmetry. Extension of this procedure proves feasible.

In spherical symmetry a wavefunction can be expanded into spherical partial waves in both the internal and the external region. The matching at the spherical boundary can thus be performed by considering one partial wave at a time, working with radial wavefunctions only. An equivalent statement is that the portion of the boundary contained in the *basic domain*⁸ in spherical symmetry reduces to a single point, so that it suffices to perform the matching at any one reference point on the sphere, the symmetry taking care of the rest. When the symmetry is lowered to a point group, the portion of the boundary surface contained in the basic domain has *finite* extension; an *infinite* number of functions is then needed to perform the matching for each symmetry species.

The impurity wavefunction in the internal region could be calculated by an extension of the cellular method of band theory, e.g., in the formulation of Altmann *et al.*⁹ Alternatively, a variational calculation within the internal region would apply regardless of nonsphericity of the internal region, and, most of all, would also enable one to treat the internal region as a many-particle problem. This approach to the impurity problem in crystals would thus eventually converge to an R -matrix calculation.¹⁰

Full specification of the impurity potential would require taking into account the relaxation of the medium about the impurity so as to screen completely the effect of the impurity outside the internal region. This problem exceeds the scope of this paper and will be treated separately.

The plan of the paper is as follows. Section II summarizes properties of the regular multipole wavefunctions. Section III solves the one-electron Schrödinger equation with

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an impurity center formally, while Sec. IV recasts the solutions in a form that holds in the external region only. Section V introduces a set of harmonics of the boundary of the internal region. The matching of the impurity wavefunction and of its normal derivative is treated in Sec. VI. Section VII compares the present approach with current EXAFS theories of photoabsorption.

II. PROPERTIES OF THE REGULAR MULTIPOLE WAVEFUNCTIONS

This section summarizes properties of the regular multipole wavefunctions $\mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}; E_\mu)$ to be used in the following and discusses their analytic dependence on the energy E .

The \mathcal{R} functions are obtained by unitary transformation of the set of Bloch waves $\varphi_\mu(\mathbf{r}; \mathbf{k})$ with energy $E_\mu(\mathbf{k}) = E^3$:

$$\begin{aligned} \mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}; E_\mu) &= \frac{1}{i^L \Omega^{1/2}} \int_{\Omega} d\mathbf{k} \delta[E - E_\mu(\mathbf{k})] \varphi_\mu(\mathbf{r}; \mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{t}_\mu) \\ &\times \sum_{i=1}^{\dim(\Gamma')} P_{Lq}^{(\Gamma' i)}(\mathbf{k}; E_\mu) (\Gamma' i', \Gamma(\mu) | \Gamma i), \end{aligned} \quad (\text{II.1})$$

where Ω stands both for the Brillouin zone and for its volume. The coupling coefficients $(\Gamma' i', \Gamma(\mu) | \Gamma i)$, which were implied but not explicitly indicated in Ref. 4, serve to reduce the Kronecker product representation $\Gamma(\mu) \times \Gamma'(\mu)$ being the one-dimensional irreducible representation of the Wannier function $a_\mu(\mathbf{r})$.⁴ As in Refs. 3 and 4, we confine ourselves to crystals with a single atom per unit cell and with the atom at the cell's center. The role of the various factors in the integral of Eq. (II.1) and the specification of the phase of the Bloch waves have been discussed in Ref. 4. We need only to recall here that the functions \mathcal{R} :

- (i) are real, that is, they correspond to standing-wave type solutions of the unperturbed crystal Hamiltonian, H_0 ;
- (ii) transform according to the i th row of the irreducible representation Γ of the crystal point group acting at $\mathbf{r} = 0$, that is, at the position of the impurity;
- (iii) are normalized according to

$$\begin{aligned} \int d\mathbf{r} \mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}; E_\mu) \mathcal{R}_{Lq'}^{(\Gamma')}(\mathbf{r}; E_{\mu'}) &= \delta(E - E') \delta_{\mu\mu'} \delta_{LL'} \delta_{qq'}, \end{aligned} \quad (\text{II.2})$$

where the integration extends over the whole (infinite) crystal;

- (iv) are complete in the sense that

$$\sum_{\mu} \int_{\min(E_\mu)}^{\max(E_\mu)} dE \sum_{\Gamma L q} \mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}; E_\mu) \mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}'; E_\mu) = \delta(\mathbf{r} - \mathbf{r}'). \quad (\text{II.3})$$

The factor i^{-L} has been included, as noted in Sec. X of Ref. 4, to make the \mathcal{R} real.

The \mathcal{R} functions have an alternative representation in terms of Wannier functions⁴:

$$\begin{aligned} \mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}; E_\mu) &= \sum_{\mathbf{n}} a_\mu(\mathbf{r} - \mathbf{n}) \sum_{i=1}^{\dim(\Gamma')} \langle \mathbf{n} + \mathbf{t}_\mu | \Gamma' i' L q \rangle_{E_\mu} \\ &\times (\Gamma' i', \Gamma(\mu) | \Gamma i), \end{aligned} \quad (\text{II.4})$$

with coefficients (called *lattice multipoles*)

$$\begin{aligned} \langle \mathbf{n} + \mathbf{t}_\mu | \Gamma' i' L q \rangle &\equiv \frac{1}{i^L \Omega} \\ &\times \int_{\Omega} d\mathbf{k} \delta[E - E_\mu(\mathbf{k})] P_{Lq}^{(\Gamma' i)}(\mathbf{k}; E_\mu) \exp[i\mathbf{k} \cdot (\mathbf{n} + \mathbf{t}_\mu)]. \end{aligned} \quad (\text{II.5})$$

These coefficients converge to zero for any given \mathbf{n}

$$\lim_{L \rightarrow \infty} \langle \mathbf{n} + \mathbf{t}_\mu | \Gamma' i' L q \rangle_{E_\mu} = 0, \quad (\text{II.6})$$

and for any given L

$$\langle \mathbf{n} + \mathbf{t}_\mu | \Gamma' i' L q \rangle_{E_\mu} = O(1/|\mathbf{n}|). \quad (\text{II.7})$$

One may also show that

$$\langle \mathbf{n} + \mathbf{t}_\mu | \Gamma' i' L q \rangle_{E_\mu} \leq [D_\mu(E)]^{1/2} G_L^{(\Gamma)}(\mathbf{n} + \mathbf{t}_\mu), \quad (\text{II.8})$$

where $D_\mu(E)$ is the density of states of the unperturbed crystal contributed by the μ th band per crystal cell, and $G_L^{(\Gamma)}(\mathbf{n} + \mathbf{t}_\mu)$ is a geometrical factor. This factorization permits one to show that lattice multipoles with high L have vanishing amplitude in the proximity of the central cell, $\mathbf{n} = 0$. Moreover, because, for small $|\mathbf{r}|$, $\lim_{|\mathbf{n}| \rightarrow \infty} |a_\mu(\mathbf{r} - \mathbf{n})| = 0$, we expect that the \mathcal{R} functions with high L will also have vanishing amplitude for small $|\mathbf{r}|$, say on the boundary of the internal zone. The maximum value of L , L_{\max} , that one needs to consider will then depend essentially on the convergence of the Wannier expansion (II.4).

The series (II.4) is uniformly convergent over the interval $[\min(E_\mu), \max(E_\mu)]$. The \mathcal{R} functions are, therefore, continuous functions of E in that interval and vanish at the band edges. One can also show that the lattice multipoles (II.5) are analytic functions of E within the range of the band except at critical energies E_C where they exhibit singularities not worse than those of the density of states $D_\mu(E)$.¹¹ We can consider the \mathcal{R} functions to have the same dependence on E as the lattice multipoles because, for practical applications the series (II.4) will include a finite number of terms.

III. THE SCATTERING BY AN IMPURITY

Our task is to solve the one-electron Schrödinger equation

$$(H_0 + V) \Psi_{\epsilon, \lambda}^{(\Gamma)}(\mathbf{r}) = \epsilon \Psi_{\epsilon, \lambda}^{(\Gamma)}(\mathbf{r}), \quad (\text{III.1})$$

where H_0 is the Hamiltonian of the unperturbed crystal and V is the perturbing impurity potential. V is assumed to be nonvanishing in the internal region only, as discussed in the Introduction, and to possess the point group symmetry of the crystal about $\mathbf{r} = 0$. The discrete index λ distinguishes

eigensolutions with the same energy ϵ and symmetry species Γ_i . In this Section we will solve Eq. (III.1) in a formal way by adapting standard techniques of scattering theory. In Sec. IV we will specialize the solutions to a form that holds in the external region only.

Because the \mathcal{R} functions form a complete system and because the perturbing potential V possesses the crystal point group symmetry, we can represent each $\Psi_{\epsilon,\lambda}^{(\Gamma_i)}(\mathbf{r})$ by an expansion into \mathcal{R} functions belonging to the same symmetry species:

$$\Psi_{\epsilon,\lambda}^{(\Gamma_i)}(\mathbf{r}) = \sum_{\mu} \int_{\min(E_{\mu})}^{\max(E_{\mu})} dE \times \sum_{Lq} \mathcal{R}_{Lq}^{(\Gamma_i)}(\mathbf{r}; E_{\mu}) D_{Lq,\lambda}^{(\Gamma_i)}(E_{\mu}; \epsilon), \quad (\text{III.2})$$

thus reducing the Schrödinger equation (III.1) to the form

$$(E' - \epsilon) D_{Lq',\lambda}^{(\Gamma_i)}(E_{\mu}; \epsilon) + \sum_{\mu} \int_{\min(E_{\mu})}^{\max(E_{\mu})} dE \times \sum_{Lq} \langle Lq', E_{\mu}' | V | Lq, E_{\mu} \rangle^{(\Gamma_i)} D_{Lq,\lambda}^{(\Gamma_i)}(E_{\mu}; \epsilon) = 0. \quad (\text{III.3})$$

Here we have set

$$\langle Lq', E_{\mu}' | V | Lq, E_{\mu} \rangle^{(\Gamma_i)} \equiv \int d\mathbf{r} \mathcal{R}_{Lq'}^{(\Gamma_i)}(\mathbf{r}; E_{\mu}') V \mathcal{R}_{Lq}^{(\Gamma_i)}(\mathbf{r}; E_{\mu}), \quad (\text{III.4})$$

where the range of V limits the integration to the internal region.

We are interested in *values of ϵ within the allowed range of a band*. The quantity $(E' - \epsilon)$ in Eq. (III.3) may, therefore, vanish. Equation (III.3) can thus be cast in the form of a linear integral equation¹²

$$D_{Lq',\lambda}^{(\Gamma_i)}(E_{\mu}; \epsilon) = \delta(\epsilon - E') \alpha_{Lq',\lambda}^{(\Gamma_i)}(\epsilon_{\mu}') + \frac{\mathcal{P}}{(\epsilon - E')} \sum_{\mu} \times \int_{\min(E_{\mu})}^{\max(E_{\mu})} dE \sum_{Lq} \langle Lq', E_{\mu}' | V | Lq, E_{\mu} \rangle^{(\Gamma_i)} \times D_{Lq,\lambda}^{(\Gamma_i)}(E_{\mu}; \epsilon), \quad (\text{III.5})$$

where \mathcal{P} means that the principal part is to be taken in any integration over the singularity, and the coefficients α are to be determined by boundary conditions. Equation (III.5) generates an infinite Neumann's series,¹³ and its formal solution is

$$D_{Lq',\lambda}^{(\Gamma_i)}(E_{\mu}; \epsilon) = \delta(\epsilon - E') \alpha_{Lq',\lambda}^{(\Gamma_i)}(\epsilon_{\mu}') + \frac{\mathcal{P}}{(\epsilon - E')} \times \sum_{\{\mu\}, Lq} \langle Lq', E_{\mu}' | K | Lq, \epsilon_{\mu} \rangle^{(\Gamma_i)} \times \alpha_{Lq,\lambda}^{(\Gamma_i)}(\epsilon_{\mu}). \quad (\text{III.6})$$

Here the symbol $\{\mu\}_{\epsilon}$ means that the summation is extended only to those bands whose energy range includes ϵ . Equation (III.6) defines the K matrix.¹⁴ The two terms on the right-hand side of Eq. (III.6) represent contributions "on the energy shell" and "off the energy shell," respectively.

We now insert the solution (III.6) into the expansion (III.2) and get

$$\Psi_{\epsilon,\lambda}^{(\Gamma_i)}(\mathbf{r}) = \sum_{\{\mu\}, Lq} \widehat{\mathcal{R}}_{Lq}^{(\Gamma_i)}(\mathbf{r}; \epsilon_{\mu}) \alpha_{Lq,\lambda}^{(\Gamma_i)}(\epsilon_{\mu}), \quad (\text{III.7})$$

where

$$\widehat{\mathcal{R}}_{Lq}^{(\Gamma_i)}(\mathbf{r}; \epsilon_{\mu}) = \mathcal{R}_{Lq}^{(\Gamma_i)}(\mathbf{r}; \epsilon_{\mu}) + \sum_{\mu'} \frac{\mathcal{P}}{E' - \epsilon} \int_{\min(E_{\mu'})}^{\max(E_{\mu'})} dE' \sum_{Lq'} \mathcal{R}_{Lq'}^{(\Gamma_i)}(\mathbf{r}; E_{\mu}') \times \frac{1}{\epsilon - E'} \langle Lq', E_{\mu}' | K | Lq, \epsilon_{\mu} \rangle^{(\Gamma_i)}. \quad (\text{III.8})$$

(The principal-value integrals in this equation and in the following are mathematically well defined for all ϵ within a band owing to the analytical behavior of the \mathcal{R} as functions of E . Furthermore, integrals of this type have been evaluated numerically without difficulty.)¹⁵ The effect of the impurity is thus to modify each \mathcal{R} function with energy ϵ by adding to it the second term of Eq. (III.8), which consists of functions $\mathcal{R}(E')$ with $E' \neq \epsilon$, and hence orthogonal and linearly independent of $\mathcal{R}(\epsilon)$ itself.

The orthonormalization condition of the functions $\Psi_{\epsilon,\lambda}^{(\Gamma_i)}(\mathbf{r})$ can be worked out either by using operator techniques, as in Ref. 14, or, more directly, by using Eq. (III.5). Attention must be then paid when integrating through the double principal part singularity, as shown in detail in Appendix A of Ref. 16. The result is:

$$\int d\mathbf{r} \Psi_{\epsilon,\lambda}^{(\Gamma_i)}(\mathbf{r}) \Psi_{\epsilon',\lambda'}^{(\Gamma_i)}(\mathbf{r}) = \sum_{\mu} \int_{\min(E_{\mu})}^{\max(E_{\mu})} dE \sum_{Lq} D_{Lq,\lambda}^{(\Gamma_i)}(E_{\mu}; \epsilon) D_{Lq,\lambda'}^{(\Gamma_i)}(E_{\mu}; \epsilon') = \delta(\epsilon - \epsilon') \sum_{\{\mu\}, Lq} [\alpha_{Lq,\lambda}^{(\Gamma_i)}(\epsilon_{\mu}) \alpha_{Lq,\lambda'}^{(\Gamma_i)}(\epsilon_{\mu}) + \beta_{Lq,\lambda}^{(\Gamma_i)}(\epsilon_{\mu}) \beta_{Lq,\lambda'}^{(\Gamma_i)}(\epsilon_{\mu})], \quad (\text{III.9})$$

where

$$\beta_{Lq,\lambda}^{(\Gamma)}(\epsilon_\mu) \equiv \pi \sum_{\{\mu'\}} \sum_{Lq'} \langle Lq, \epsilon_\mu | K | Lq', \epsilon_{\mu'} \rangle^{(\Gamma)} \alpha_{Lq',\lambda}^{(\Gamma)}(\epsilon_{\mu'}). \quad (\text{III.10})$$

The eigenfunctions $\Psi_{\epsilon,\lambda}^{(\Gamma)}(\mathbf{r})$ are thus properly orthonormalized by setting

$$\alpha_\lambda(\epsilon) \cdot \alpha_{\lambda'}(\epsilon) + \beta_\lambda(\epsilon) \cdot \beta_{\lambda'}(\epsilon) = \delta_{\lambda\lambda'}. \quad (\text{III.11})$$

at each ϵ , where $\alpha_\lambda(\epsilon) \equiv \{ \alpha_{Lq,\lambda}^{(\Gamma)}(\epsilon_\mu) \}$. Note that we have taken the coefficients α of the expansion (III.7) to be real. The β 's, which are defined in terms of the real and symmetric K matrix on the energy shell,¹⁴ are then real, too.

IV. SYMMETRY-ADAPTED GREEN'S FUNCTIONS AND IRREGULAR FUNCTIONS

In Sec. III we have represented the eigenfunctions of the full Hamiltonian $H_0 + V$ in a form [Eq. (III.7)] that holds *everywhere* in space, that is, both in the internal and the external region. In this Sec. we recast Eq. (III.7) into a more compact form that holds *in the external region only*. The internal region will be treated instead by a different approach.

We start by rewriting the elementary solutions (III.8) into the equivalent form:

$$\begin{aligned} \tilde{\mathcal{R}}_{Lq}^{(\Gamma)}(\mathbf{r}; \epsilon) &= \mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}; \epsilon_\mu) \\ &+ \int d\mathbf{r}' G_\epsilon^{(\Gamma)}(\mathbf{r}; \mathbf{r}') V \tilde{\mathcal{R}}_{Lq}^{(\Gamma)}(\mathbf{r}'; \epsilon_\mu). \end{aligned} \quad (\text{IV.1})$$

Here $G_\epsilon^{(\Gamma)}(\mathbf{r}; \mathbf{r}')$ is the *symmetry-adapted principal-value Green's function*

$$\begin{aligned} G_\epsilon^{(\Gamma)}(\mathbf{r}; \mathbf{r}') &= \sum_\mu \mathcal{P} \int_{\min(E_\mu)}^{\max(E_\mu)} dE \\ &\times \sum_{Lq} \mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}; E_\mu) \frac{1}{\epsilon - E} \mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}'; E_\mu). \end{aligned} \quad (\text{IV.2})$$

This function is symmetry-adapted in that it transforms according to the i th row of the irreducible representation Γ of the crystal point group under group transformations of *either* \mathbf{r} *or* \mathbf{r}' . Since the Green's function is singular at $\mathbf{r} = \mathbf{r}'$, the bilinear expression on the right-hand side of Eq. (IV.2) converges to $G_\epsilon^{(\Gamma)}(\mathbf{r}; \mathbf{r}')$ in the distribution sense, that is, only when integrated over some test function.

Equation (IV.2) constitutes an eigenfunction expansion of the Green's function $G_\epsilon^{(\Gamma)}(\mathbf{r}; \mathbf{r}')$. In the usual context of problems fully separable, e.g., in spherical coordinates, the Green's function can be represented *either* by an expansion analogous to Eq. (IV.2) *or*, alternatively, in its "closed form," i.e., as product of the regular and the irregular solutions of a one-dimensional equation.¹⁷ For instance, when H_0 is the free space Hamiltonian,

$$\begin{aligned} \frac{1}{r r'} g_l(r; r') &= \frac{2}{\pi} \mathcal{P} \int_0^\infty dk' j_l(kr) \frac{k'^2}{k^2 - k'^2} j_l(kr') \\ &= k n_l(kr) j_l(kr'), \quad r > r'. \end{aligned} \quad (\text{IV.3})$$

We want to generalize Eq. (IV.3) to the crystal situation where the variables cannot be separated.

The following considerations hold irrespectively of separation of variables:

(i) Owing to the definition, Eq. (IV.2), and to the completeness of the \mathcal{R} functions, Eq. (II.2), the full principal-value Green's function

$$G_\epsilon(\mathbf{r}; \mathbf{r}') = \sum_{\Gamma} G_\epsilon^{(\Gamma)}(\mathbf{r}; \mathbf{r}') \quad (\text{IV.4})$$

satisfies the inhomogeneous equation

$$(H_0 - \epsilon) G_\epsilon(\mathbf{r}; \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}'), \quad (\text{IV.5})$$

where H_0 operates either on \mathbf{r} or on \mathbf{r}' . For $\mathbf{r} \neq \mathbf{r}'$, $G_\epsilon(\mathbf{r}; \mathbf{r}')$ thus satisfies the corresponding homogeneous equation with the boundary condition of being regular at either $\mathbf{r} = 0$ or $\mathbf{r}' = 0$. These two properties hold as well for *each separate term* of Eq. (IV.4), $G_\epsilon^{(\Gamma)}(\mathbf{r}; \mathbf{r}')$.

(ii) Because the principal value integration in Eq. (IV.2) excludes contributions "on the energy shell," the second term on the right-hand side of Eq. (IV.1) represents a function which is *linearly independent* of all \mathcal{R} functions with energy ϵ . At the same time, this term is a solution of H_0 in the external region corresponding to the *same* eigenvalue ϵ .

Therefore, in analogy with Eq. (IV.3), we can represent the symmetry-adapted principal-value Green's function $G_\epsilon^{(\Gamma)}(\mathbf{r}; \mathbf{r}')$, for \mathbf{r} in the external region and \mathbf{r}' in the internal region, as

$$G_\epsilon^{(\Gamma)}(\mathbf{r}; \mathbf{r}') = \pi \sum_{\{\mu'\}} \sum_{Lq} \mathcal{I}_{Lq}^{(\Gamma)}(\mathbf{r}; \epsilon_\mu) \mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}'; \epsilon_\mu). \quad (\text{IV.6})$$

This expansion *defines* the set of *irregular multipole wavefunctions* $\mathcal{I}_{Lq}^{(\Gamma)}(\mathbf{r}; \epsilon_\mu)$ which are linearly independent of the multipole wavefunctions $\mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}; \epsilon_\mu)$, which have the same energy ϵ but are constrained to be regular. The actual construction of this set will be discussed below.

Substitution of Eq. (IV.6) into Eq. (IV.1) expresses the elementary solutions, for \mathbf{r} in the external region, as

$$\begin{aligned} \tilde{\mathcal{R}}_{Lq}^{(\Gamma)}(\mathbf{r}; \epsilon_\mu) &= \mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}; \epsilon_\mu) + \pi \sum_{\{\mu'\}} \sum_{Lq'} \mathcal{I}_{Lq'}^{(\Gamma)}(\mathbf{r}; \epsilon_{\mu'}) \\ &\times \langle Lq', \epsilon_{\mu'} | K | Lq, \epsilon_\mu \rangle^{(\Gamma)}. \end{aligned} \quad (\text{IV.7})$$

The corresponding formula for the general solution (III.7) is then

$$\Psi_{\epsilon,\lambda}^{(\Gamma)}(\mathbf{r}) = \sum_{|\mu|} \sum_{Lq} [\mathcal{R}_{Lq}^{(\Gamma)}(\mathbf{r}; \epsilon_\mu) \alpha_{Lq,\lambda}^{(\Gamma)}(\epsilon_\mu) + \mathcal{I}_{Lq}^{(\Gamma)}(\mathbf{r}; \epsilon_\mu) \beta_{Lq,\lambda}^{(\Gamma)}(\epsilon_\mu)] \quad (\text{IV.8})$$

with the β 's defined in Eq. (III.10). This expression generalizes to a crystal field the familiar expression of the wavefunction outside the range of a spherically symmetric scatterer, as a linear superposition of regular and irregular solutions of the residual Hamiltonian H_0 . Note how the dependence on the perturbing potential V is now included in the coefficients β .

The actual construction of the irregular functions \mathcal{I} from the defining equations (IV.2) and (IV.6) requires us to disentangle them from the infinite sum over L in Eq. (IV.6). To this end, notice that, because the \mathcal{R} functions of \mathbf{r}' in the internal region converge to zero as $L \rightarrow \infty$, they are not all linearly independent within this region. As a *measure of linear independence* we consider the Gram determinant of the N \mathcal{R} functions with lowest values of L .¹⁸ The value of this determinant decreases steadily as a function of increasing N for large N . Consider a value of N , N_{\max} , at which the Gram determinant has fallen below a preestablished low level. The value of L , L_{\max} , corresponding to N_{\max} limits a subset of \mathcal{R} functions with $L \leq L_{\max}$. We can then construct a set of functions "reciprocal" (i.e., orthogonalized) to this subset of \mathcal{R} functions over the internal region.¹⁹ Successive integration over the internal region of the product of Eqs. (IV.2), or (IV.6), and of each reciprocal function will thus furnish each of the irregular functions \mathcal{I} with $L \leq L_{\max}$. Only this subset of \mathcal{I}_{Lq} is, in fact, required in Eq. (IV.8) because the coefficients β_{Lq} vanish for large L . An alternative procedure will be found appropriate for our boundary problem, in Sec. VI, because only the value of \mathcal{I} and of its normal derivative on the boundary are actually needed.

V. THE HARMONICS OF THE BOUNDARY

The coefficients α and β of Eq. (IV.8) must be chosen to satisfy the boundary conditions of continuity of the wavefunction and of its normal derivative *across the boundary* Σ of the internal region. Σ can be the boundary surface of the Wigner-Seitz unit cell containing the impurity, or, more generally, of a number of these cells; that is, Σ is a piecewise smooth surface, consisting of a finite number of plane surfaces. As discussed in the Introduction, we confine the actual matching to the portion of Σ within a single basic domain, because Σ possesses the point group symmetry of the crystal and because the wavefunctions in both the internal and the external region are classified according to symmetry.

We shall perform the matching by expanding the wavefunction and its normal derivative on both side of Σ into a *complete and orthonormal set of harmonics of the boundary surface*. In other words, we shall perform the matching by the method of least squares rather than at a chosen mesh of points over Σ . The harmonics of the boundary surface can be determined by a procedure analogous to that employed in

Refs. 2 and 3 to calculate the harmonics of the constant-energy surface in \mathbf{k} -space. We then indicate the harmonics of Σ by $Q_{\mathcal{L}q}^{(\Gamma)}(\mathbf{r}; \Sigma)$, the discrete indices $\mathcal{L}q$ being analogs of the Lq of Refs. 2 and 3. The Q 's are:

$$(i) \text{ orthonormalized with unit weight over } \Sigma, \text{ that is, } \oint_{\Sigma} d\sigma Q_{\mathcal{L}q}^{(\Gamma)}(\mathbf{r}; \Sigma) Q_{\mathcal{L}'q'}^{(\Gamma)}(\mathbf{r}; \Sigma) = \delta_{\mathcal{L}\mathcal{L}'} \delta_{qq'}; \quad (\text{V.1})$$

(ii) *complete* over Σ , that is, any piecewise smooth function $f^{(\Gamma)}(\mathbf{r})$ can be expressed over Σ as

$$f^{(\Gamma)}(\mathbf{r})|_{\Sigma} = \sum_{\mathcal{L}q} Q_{\mathcal{L}q}^{(\Gamma)}(\mathbf{r}; \Sigma) f_{\mathcal{L}q}^{(\Gamma)}, \quad (\text{V.2})$$

the coefficients $f_{\mathcal{L}q}^{(\Gamma)}$ being determined as usual by

$$f_{\mathcal{L}q}^{(\Gamma)} \equiv \langle \mathcal{L}q | f \rangle_{\Sigma} = \oint_{\Sigma} d\sigma Q_{\mathcal{L}q}^{(\Gamma)}(\mathbf{r}; \Sigma) f^{(\Gamma)}(\mathbf{r}). \quad (\text{V.3})$$

Consider, e.g., the surface of an fcc Wigner-Seitz unit cell. The portion of Σ within the basic domain ($2b \geq y \geq x \geq z \geq 0$) has equation $x + y = 2b$ with $b = a/4$, a being the lattice constant. The integral over Σ of any group invariant function then reduces to

$$\oint_{\Sigma} d\sigma f(x,y,z) = 48\sqrt{2} \int_0^b d\eta \int_0^{b-\eta} dz f(b-\eta, b+\eta, z) \quad (\text{V.4})$$

The overlap integrals entering the expansion of the Q into polynomials in x , y , and z ^{2,3} can be now calculated analytically in a lengthy but straightforward way. For stance, $Q_2^{(A_1)}(\mathbf{r}; \Sigma)$ is proportional to $(r/b)^2 - 5/2$.

VI. THE MATCHING TO AN IMPURITY

In this section we sketch two alternative methods for calculating the impurity wavefunctions in the internal region and for matching them to the wavefunctions (IV.8) of the external region. Since every energy eigenvalue in the continuum possesses an infinite multiplicity, each method involves boundary conditions that identify a set of solutions uniquely.

A. Outward integration of the Schrödinger equation

Following Altmann *et al.*,⁹ one may expand both the centrosymmetric impurity potential and the impurity wavefunctions in the internal region into spherical harmonics symmetry-adapted to the crystal point group about $\mathbf{r}=0$. The Schrödinger equation (III.1) thus reduces to a system of coupled differential equations for the radial wavefunctions. This systems is integrated from $\mathbf{r}=0$ up to the surface of a sphere circumscribing the internal region. Each solution, λ , is identified by initial conditions at $\mathbf{r}=0$. This procedure specifies the values of $\Psi_{\epsilon,\lambda}^{(\Gamma)}(\mathbf{r})$ and of $(\partial/\partial\nu)\Psi_{\epsilon,\lambda}^{(\Gamma)}(\mathbf{r})$ on the inner face of Σ for each λ . The eigensolutions can be then continued into the surrounding unperturbed crystalline medium by Eq. (IV.8) with coefficients α and β so adjusted that the values of $\Psi_{\epsilon,\lambda}^{(\Gamma)}(\mathbf{r})$ and $(\partial/\partial\nu)\Psi_{\epsilon,\lambda}^{(\Gamma)}(\mathbf{r})$ coincide on the outer and inner faces of Σ .

The problem of finding the coefficients α and β can be

reduced to an inhomogeneous system of algebraic equations by expanding $\Psi_{\epsilon,\lambda}^{(\Gamma)}(\mathbf{r})$ and $(\partial/\partial\nu)\Psi_{\epsilon,\lambda}^{(\Gamma)}(\mathbf{r})$ on both faces of Σ into the harmonics $Q_{\mathcal{L}q}^{(\Gamma)}(\mathbf{r}; \Sigma)$ introduced in Sec. V. With the notation of Eq. (V.3), the system reads

$$\begin{aligned} \mathcal{N}_{\epsilon,\lambda}^{(\Gamma)} \langle \mathcal{L}q | \Psi_{\epsilon,\lambda}^{\text{int}} \rangle_{\Sigma}^{(\Gamma)} \\ = \sum_{\{\mu\}} \sum_{Lq} [\langle \mathcal{L}q | \mathcal{R}_{Lq}(\epsilon_{\mu}) \rangle_{\Sigma}^{(\Gamma)} \alpha_{Lq,\lambda}^{(\Gamma)}(\epsilon_{\mu}) \\ + \langle \mathcal{L}q | \mathcal{F}_{Lq}(\epsilon_{\mu}) \rangle_{\Sigma}^{(\Gamma)} \beta_{Lq,\lambda}^{(\Gamma)}(\epsilon_{\mu})], \end{aligned} \quad (\text{VI.1})$$

and²⁰

$$\begin{aligned} \mathcal{N}_{\epsilon,\lambda}^{(\Gamma)} \left\langle \mathcal{L}q \left| \frac{\partial}{\partial\nu} \Psi_{\epsilon,\lambda}^{\text{int}} \right. \right\rangle_{\Sigma}^{(\Gamma)} \\ = \sum_{\{\mu\}} \sum_{Lq} \left[\left\langle \mathcal{L}q \left| \frac{\partial}{\partial\nu} \mathcal{R}_{Lq}(\epsilon_{\mu}) \right. \right\rangle_{\Sigma}^{(\Gamma)} \alpha_{Lq,\lambda}^{(\Gamma)}(\epsilon_{\mu}) \right. \\ \left. + \left\langle \mathcal{L}q \left| \frac{\partial}{\partial\nu} \mathcal{F}_{Lq}(\epsilon_{\mu}) \right. \right\rangle_{\Sigma}^{(\Gamma)} \beta_{Lq,\lambda}^{(\Gamma)}(\epsilon_{\mu}) \right]. \end{aligned} \quad (\text{VI.2})$$

The normalization factor $\mathcal{N}_{\epsilon,\lambda}^{(\Gamma)}$ of the wavefunctions $\Psi_{\epsilon,\lambda}^{\text{int}}$ will be determined by the requirement that the α 's and β 's satisfy Eqs. (III.9) and (III.11).

In Eqs. (VI.1) and (VI.2) the indices \mathcal{L} and L range in principle over an infinite set of values. However, truncation of the sums on the right-hand side to include only the first N terms with lowest L can be guided by the discussion at the end of Sec. IV. Each equation then contains $2N$ unknowns, that is, the $2N$ ratios α/\mathcal{N} and β/\mathcal{N} . These $2N$ ratios are determined uniquely by Eqs. (VI.1) and (VI.2) by including exactly N terms in the expansions into Q 's. Alternatively one might include a larger number of Q 's and obtain an approximation for the α 's and β 's by least squares.²¹ Knowledge of N solutions ($\alpha_{\lambda}, \beta_{\lambda}$) ($\lambda = 1, \dots, N$) is equivalent to calculating the $N \times N$ submatrix of K , Eq. (III.10), "on the energy shell." These N solutions should, in general, be orthonormalized to satisfy Eq. (III.11).

The overlap integrals $\langle \mathcal{L}q | \mathcal{F}_{Lq}(\epsilon_{\mu}) \rangle_{\Sigma}^{(\Gamma)}$ and $\langle \mathcal{L}q | (\partial/\partial\nu) \mathcal{F}_{Lq}(\epsilon_{\mu}) \rangle_{\Sigma}^{(\Gamma)}$ are to be determined by projecting Eqs. (IV.2) and (IV.6) onto the boundary Σ . In view of the singularities of the Green's function at $\mathbf{r} = \mathbf{r}'$, one may consider initially two slightly separate surfaces, $\Sigma_{<}$ for \mathbf{r}' and $\Sigma_{>}$ for \mathbf{r} , which then converge onto Σ . Projection onto a pair of harmonics of these surfaces, $Q_{\mathcal{L}'q'}^{(\Gamma)}(\mathbf{r}'; \Sigma_{<})$ and $Q_{\mathcal{L}q}^{(\Gamma)}(\mathbf{r}; \Sigma_{>})$, gives

$$\begin{aligned} \sum_{\mu} \mathcal{P} \int_{\min(E_{\mu})}^{\max(E_{\mu})} dE \\ \times \sum_{Lq} \langle \mathcal{L}q | \mathcal{R}_{Lq}(E_{\mu}) \rangle_{\Sigma}^{(\Gamma)} \frac{1}{\epsilon - E} \langle \mathcal{R}_{Lq}(E_{\mu}) | \mathcal{L}'q' \rangle_{\Sigma}^{(\Gamma)} \\ = \pi \sum_{\{\mu\}} \sum_{Lq} \langle \mathcal{L}q | \mathcal{F}_{Lq}(\epsilon_{\mu}) \rangle_{\Sigma}^{(\Gamma)} \langle \mathcal{R}_{Lq}(\epsilon_{\mu}) | \mathcal{L}'q' \rangle_{\Sigma}^{(\Gamma)}. \end{aligned} \quad (\text{VI.3})$$

As the left-hand side of Eq. (VI.3) is finite, the series on the right-hand side may be truncated after the first N terms. Considering also N harmonics Q only, Eq. (VI.3) reduces to N inhomogeneous systems, each of N equations, for the N^2 unknown matrix elements $\langle \mathcal{L}q | \mathcal{F}_{Lq}(\epsilon_{\mu}) \rangle_{\Sigma}^{(\Gamma)}$, which can thus be determined uniquely. One can proceed similarly to determine $\langle \mathcal{L}q | (\partial/\partial\nu) \mathcal{F}_{Lq}(\epsilon_{\mu}) \rangle_{\Sigma}^{(\Gamma)}$, noting that the surface integrals remain finite in spite of the sharper singularity of the gradient of the Green's function.

B. Variational calculation within the internal region

A variational method can be used alternatively to calculate the impurity wavefunction within the internal region. In fact, variational methods are particularly suited to deal with nonseparable Schrödinger equations.

For our continuous spectrum where the energy eigenvalue ϵ is specified in advance within the allowed range of a band, we look for the extrema of the integral²²

$$J[\Psi] = \int_{\nu} d\mathbf{r} [(\nabla\Psi)^2 + (V_c + V - \epsilon)\Psi^2], \quad (\text{VI.4})$$

with the subsidiary condition:

$$\oint_{\Sigma} d\sigma \Psi^2 = 1. \quad (\text{VI.5})$$

Here $V_c + V$ represents the sum of the unperturbed crystal potential and of the impurity effect, and ν and Σ stand for the volume and the surface of the internal region. A necessary condition for an extremum of $J[\Psi]$ is that Ψ satisfies the Schrödinger equation (III.1) with the natural boundary condition

$$\left[\frac{\partial\Psi}{\partial\nu} - b\Psi \right]_{\Sigma} = 0. \quad (\text{VI.6})$$

The constant parameter $b = b_{\lambda}$ plays the role of eigenvalue of the normal derivative.²² At any given energy ϵ , the set of boundary values of the corresponding eigenfunctions Ψ_{λ} is then complete and orthonormal over the boundary surface,

$$\oint_{\Sigma} d\sigma \Psi_{\lambda} \Psi_{\lambda'} = \delta_{\lambda\lambda'}. \quad (\text{VI.7})$$

The matching to the wavefunction in the external region, Eq. (IV.8), can proceed in analogy to Sec. VI A. The boundary values of the variational eigenfunctions Ψ_{λ} may serve here as the harmonics of the boundary surface. Equations (VI.1) and (VI.2) thus become

$$\begin{aligned} \mathcal{N}_{\epsilon,\lambda}^{(\Gamma)} \delta_{\lambda\lambda'} = \sum_{\{\mu\}} \sum_{Lq} [\langle \lambda' | \mathcal{R}_{Lq}(\epsilon_{\mu}) \rangle_{\Sigma}^{(\Gamma)} \alpha_{Lq,\lambda}^{(\Gamma)}(\epsilon_{\mu}) \\ + \langle \lambda' | \mathcal{F}_{Lq}(\epsilon_{\mu}) \rangle_{\Sigma}^{(\Gamma)} \beta_{Lq,\lambda}^{(\Gamma)}(\epsilon_{\mu})], \end{aligned} \quad (\text{VI.8})$$

$$\begin{aligned} \mathcal{N}_{\epsilon,\lambda}^{(\Gamma)} b_{\lambda} \delta_{\lambda\lambda'} \\ = \sum_{\{\mu\}} \sum_{Lq} \left[\left\langle \lambda' \left| \frac{\partial}{\partial\nu} \mathcal{R}_{Lq}(\epsilon_{\mu}) \right. \right\rangle_{\Sigma}^{(\Gamma)} \alpha_{Lq,\lambda}^{(\Gamma)}(\epsilon_{\mu}) \right. \\ \left. + \left\langle \lambda' \left| \frac{\partial}{\partial\nu} \mathcal{F}_{Lq}(\epsilon_{\mu}) \right. \right\rangle_{\Sigma}^{(\Gamma)} \beta_{Lq,\lambda}^{(\Gamma)}(\epsilon_{\mu}) \right], \end{aligned} \quad (\text{VI.9})$$

where the matrices on the left-hand side of Eqs. (VI.1) and (VI.2) are replaced by $\delta_{\lambda\lambda'}$ and by $b_{\lambda}\delta_{\lambda\lambda'}$.

The alternative methods of Secs. VI A and VI B might complement each other in practical calculations. For example, the outward integration method might provide a set of N functions at a coarse mesh of values of ϵ . These functions might, in turn, be used as trial functions for a Rayleigh–Ritz variational calculation at a finer mesh of ϵ .

VII. DISCUSSION

Photoabsorption cross sections have been generally obtained as products of squared dipole matrix elements and of the density of states. It has been increasingly recognized²³ that the density of states should be apportioned among channels of different symmetries and should reflect local impurity effects for each channel. The allotment of the “local” density of states among the various channels was considered earlier in Ref. 2. Here we have identified the relevant density as the square of the normalization factor $\mathcal{N}_{\epsilon,\lambda}^{(D)}$ of Sec. VI, with the understanding that the matrix element is calculated with the internal final state function $\Psi_{\epsilon,\lambda}^{\text{int}}$. This normalization factor incorporates the effects of the band structure in the external region. The dependence of $\mathcal{N}_{\epsilon,\lambda}^{(D)}$ on the energy ϵ will thus modulate the photoabsorption profile by reflecting the influence of the external region on the rate of escape of the photoelectron.

The current EXAFS theories²⁴ ascribe the modulation of photoabsorption to interference between the wavefunction of the escaping electron and the waves backscattered by the surrounding crystal structure. In our approach the effects of these reflections are incorporated in the conditions over the boundary of the internal region; thereby, multiple scatterings are taken into account to all orders because the wavefunction in the external region takes full account of the crystal field. Our approach is thus particularly suited to energies close to the threshold, while the EXAFS is suited to escape energies $\approx 30\text{--}50$ eV.

The formalism of this paper can also be applied to the calculation of scattering processes in crystals since Eq. (III.10) provides the K matrix on the energy shell.

Our approach should eventually be extended to include a many-particle treatment of the internal region. This could be done, in analogy with atomic calculations,²⁵ by a many-body variational procedure which would also have to take into account the relaxation of the medium around the hole. A detailed procedure for this purpose remains, however, to be developed.

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