Multichannel multiple-scattering theory with general potentials

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We outline a many-body description of the photoemission and photoabsorption processes that incorporates the multichannel treatment of the atomic dynamical excitations into the framework of multiple-scattering (MS) theory. This generalization is a most natural one, in that the internal structure of the atomic constituents of the physical system under study is taken into account by the introduction of an interchannel atomic t matrix that fixes the probability amplitude of a particular excitation (channel) of the internal degrees of freedom of the atom by the photoelectron impinging on it. For the rest the MS structure of the theory is left unchanged, provided the propagation vector of the photoelectron between successive scattering events is changed according to the energy loss suffered. In this way the interplay between excitation dynamics and electronic and geometrical structure of the ground state is elucidated. At the same time this approach provides a theoretical model for the study of the evolution from the adiabatic to the sudden regime. In this context we describe a new MS expansion that reproduces the results of the sudden approximation for photoemission and photoabsorption cross sections in the limit of high photoelectron energies. As expected, the expansion parameter that controls the crossover between the two regimes is substantially the maximum eigenvalue of the interchannel atomic t matrix $(T_a)_{LL'}^{\alpha\alpha'}(\alpha \neq \alpha')$, where α is a channel index and L is an angular-momentum index: If this quantity is much less than one, then the deviations from the sudden approximation are negligible. Physical applications of the theory are briefly described.

I. INTRODUCTION

The study of the electronic and structural properties of matter has received, in the recent past, a big impulse due to the increasing exploitation of synchrotron radiation. In fact, the unique properties of the electromagnetic radiation emitted by electrons (or positrons) circulating in a storage ring, like the intensity, brilliance, polarization, tunability and collimation, to cite a few, coupled with highly sophisticated data-acquisition techniques have made possible the explosive growth of many kinds of spectroscopies. Among them, photoemission and photoabsorption have gained more and more attention as a source of information concerning both the empty and occupied electronic states of the systems under study, their relation with the underlying geometrical structure and, in general, the dynamics of the excitation process.

The realization of the potentialities of these techniques has stimulated a parallel development of the theoretical schemes needed to interpret and analyze the experimental observations. As an example, the multiple-scattering (MS) theory has developed a unifying scheme of interpretation that encompasses a wide variety of physical cases and provided the necessary tools for extracting useful structural as well as electronic information from experimental data. The field of application ranges from molecules in the gas phase to adsorbates, from extended periodic systems, like crystals, to disordered and amorphous materials, from large atomic clusters to small ones. Combined with the local-density approximation for evaluating Dyson's self-energies, it has provided a practical and convenient way for calculating both occupied and unoccupied electronic states in the large variety of systems mentioned above. The price paid for this generality, however, is that the field of application of theory is restricted to those cases that are amenable to a description in terms of an effective one-particle scheme. Even though correlation effects can be taken into account in an average way in the framework of the local-density scheme through the introduction of an exchange-correlation po-

tential, there are cases in which such an approximation is not sufficient to describe in a satisfactory way the physical processes under study.

In fact, all the phenomena connected with the excitation dynamics, like screening, polarization, relaxation, autoionization, and decay, especially in the presence of a certain degree of electronic localization, fall outside the realm of effective one-electron theory. An approach based on configuration interaction and on general many-body theories is needed in this case. As a consequence, the understanding of those systems where electronic correlations and localization effects are important, requires a more elaborate theory than the simple one-particle approach. Such a comprehension is obviously essential if one wants to understand the electronic properties of these systems, but becomes equally important in structural studies, since structural information tends to be distorted or obscured by electronic correlation effects. The case of mixed-valent compounds is emblematic of such systems.

Therefore, it would be highly desirable to develop a theory that incorporates both aspects of the problem, i.e., the description of the geometrical arrangement of the atomic constituents of the system under study and the electronic dynamics of the excitation process. The aim of this paper is to show that the multichannel generalization of the MS theory provides such an interpretative scheme. This generalization is a most natural one, in that the internal structure of the atomic constituents of the physical system is taken into account by the introduction of an interchannel atomic t matrix that gives the probability amplitude of a particular excitation (channel) of the internal degrees of freedom of the atom by an electron impinging on it. For the rest, the MS structure of the theory is left unchanged, provided the propagation vector of the photoelectron between successive scattering events is changed according to the energy loss suffered. Besides local electronic excitations, other nonlocalized (or collective) excitations are possible in the system, like extrinsic plasmon losses. In principle, as shown in Sec. II, it is possible to include such losses in the multichannel formalism, provided one knows the real-space eigenstates (or a reasonable approximation to them) corresponding to such excitations. In practice, such losses are better taken into account through the introduction of an optical imaginary potential modifying the N-channel potential matrix relative to the N particular configurations chosen, usually describing local excitations. This point will be touched upon in Sec. IV. The mathematical formalism of the multichannel approach used here is equivalent to the close-coupling scheme widely used in the field of electron-molecule collisions and to the configuration-interaction method used by Fano[1] and Davis and Feldkamp[2] to describe interaction effects between bound and continuum configurations in photoemission and photoabsorption spectroscopies of atomic systems. The novelty here is that one can generalize such a scheme for extended systems, allowing at the same time for the description of the atomic geometrical arrangement in real space. This is what is needed for the realistic treatment of an intermediate valence (IV) system where one has two or

more localized atomic configurations interacting with conduction states.

In this paper, we shall limit ourselves to photoemission and photoabsorption from inner-shell states. The limitation to inner shells, with the inherent simplification brought about by the localized and dispersionless initial state, has made simpler the theoretical interpretation of the experimental results, which, in turn, have exploited the selectivity power of the incoming radiation both in terms of the type of atom to excite and the type of final state to reach. Nonetheless, a generalization of the formalism presented here to arbitrary initial states is straightforward, although the practical implementation of the calculation scheme might not be that easy, especially in the presence of electronic correlations.

II. MULTICHANNEL THEORY

A. Introduction to multichannel theory

During an absorption process from an N-electron atom, in the final state of the system photoelectron plus excited $(N-1)$-electron atom, this latter can end up in several final stationary states because of the different ways it can relax. Each of the final states of the excited $(N-1)$-electron atom is called a channel. By taking into account exchange processes, this definition is seen to include rearrangement channels. It seems natural to adopt the same definition for extended systems as well. In principle, the multichannel theory enables one to take a quantitative account of all possible outcomes of the photoemission process. A very clear introduction to multichannel theory can be found in Ref. 3.

In atomic units for lengths and Rydberg units for energies, used throughout this paper, the total absorption cross section for many-body initial and final states and light polarized in the ϵ direction is given by

$$\sigma = 4\pi^2\alpha\omega\sum_f |\langle \Psi_f^N|\epsilon\cdot\sum_j \mathbf{r}_j|\Psi_i^N\rangle|^2\delta(E_f - E_i - \omega) \ ,$$

where N is the number of electrons in the system, $|\Psi_i^N\rangle$ is the initial state of the system, $|\Psi_f^N\rangle$ is a final state, and the sum $\sum_j \mathbf{r}_j$ is carried out over all the N electrons. As usual, a summation is performed over all the final N-electron states of energy $E_f = E_i + \omega$. The quantity $\alpha = \frac{1}{137}$ is the usual fine-structure constant.

To take account of the possibility of configuration interaction in the initial state, which is observed in mixed-valent systems, for example, we shall write the initial state as

$$\Psi_i^N(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1}, \mathbf{r})$$

$$= \sqrt{N!}\sum_n c_n\mathcal{A}\,[\varphi_c(\mathbf{r})\Phi_n^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})] \ ,$$

where $\mathcal{A}$ is the antisymmetrizing operator $[\mathcal{A} = (1/N!)\sum_P(-1)^P P]$, $\varphi_c(\mathbf{r})$ represents the core orbital, and $\Phi_n^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})$ a Slater determinant describing a particular configuration of the other electrons. The above expression can also be written

$$\Psi_i^N(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1}, \mathbf{r}) = \sqrt{N!}\mathcal{A}\,[\varphi_c(\mathbf{r})\Psi_G^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})]$$

with

$$\Psi_G^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) = \sum_n c_n \Phi_n^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) \ .$$

In the following, we shall refer, for brevity, to the excited core electron as to "the photoelectron," ignoring exchange effects which, however, are taken into account in the formalism. The remaining electrons will be described by the $(N-1)$-electron Hamiltonian:

$$H_{N-1} = -\sum_{i=1}^{N-1} \nabla_i^2 - \sum_{i=1}^{N-1} \sum_{k=1}^{N_a} \frac{2Z_k}{|\mathbf{r}_i - \mathbf{R}_k|}$$

$$+ \sum_{\substack{i<j \\ 1 \le i,j \le N-1}} \frac{2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

with the usual notation, N_a being the number of atomic centers with charge Z_k and

$$\sum_{k=1}^{N_a} Z_k = N \ .$$

Therefore, without loss of generality, we can write the final-state wave function as

$$\Psi_f^N(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}, \mathbf{r})$$

$$= \sqrt{N!} \mathcal{A} \left[\sum_\alpha f_\alpha(\mathbf{r}) \Psi_\alpha^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) \right] \ ,$$

where the $(N-1)$-electron wave function $\Psi_\alpha^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1})$ is an eigenfunction of H_{N-1} with eigenvalues E_α^{N-1}. This means that we allow a sort of configuration interaction in the final state as well. Each term in the sum represents the photoelectron leaving the absorbing system in a different state. The quality of single-channel calculation dictates the number of terms that must be kept in the sum. If needed, each Ψ_α^{N-1} is assumed to be approximated by a linear combination of Slater determinants. They are obviously fully relaxed around the core hole.

The N-electron Hamiltonian can now be written as

$$H_N = -\nabla_r^2 + V(\mathbf{r}, \mathbf{r}_i) + H_{N-1} \ ,$$

where

$$V(\mathbf{r}, \mathbf{r}_i) = \sum_{i=1}^{N-1} \frac{2}{|\mathbf{r} - \mathbf{r}_i|} - \sum_{k=1}^{N_a} \frac{2Z_k}{|\mathbf{r} - \mathbf{R}_k|} \ .$$

With the above notation, the Schrödinger equation for the N-electron system becomes

$$[-\nabla_r^2 + V(\mathbf{r}, \mathbf{r}_i) + H_{N-1}] \mathcal{A} \left[\sum_\alpha f_\alpha(\mathbf{r}) \Psi_\alpha^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) \right] = E \mathcal{A} \left[\sum_\alpha f_\alpha(\mathbf{r}) \Psi_\alpha^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) \right] \ .$$

By multiplying the left-hand side by Ψ_α^{N-1} and integrating, we obtain the set of coupled equations

$$(\nabla^2 + E - E_\alpha^{N-1}) f_\alpha(\mathbf{r}) = \sum_{\alpha'} [V_{\alpha\alpha'}^d(\mathbf{r}) + V_{\alpha\alpha'}^{ex}(\mathbf{r})] f_{\alpha'}(\mathbf{r}) \ ,$$

where the right-hand-side (rhs) potential has been split into two contributions: a direct contribution

$$V_{\alpha\alpha'}^d(\mathbf{r}) = \int d^3 r_1 \dots d^3 r_{N-1} \Psi_\alpha^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) V(\mathbf{r}; \mathbf{r}_1, \dots, \mathbf{r}_{N-1}) \Psi_{\alpha'}^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) \ ,$$

and an exchange and nonlocal contribution. If we impose the condition that the function $f_\alpha(\mathbf{r})$ be orthogonal to all the one-particle states present in the configurations entering in the description of the Ψ_α^{N-1}'s, we obtain that the exchange contribution writes

$$V_{\alpha\alpha'}^{ex}(\mathbf{r}_N) = \frac{1}{f_\alpha(\mathbf{r}_N)} \int d^3 r_1 \dots d^3 r_{N-1} \Psi_\alpha^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) V(\mathbf{r}_N; \mathbf{r}_1, \dots, \mathbf{r}_{N-1})$$

$$\times \sum_{P \ne E} (-1)^P f_{\alpha'}(\mathbf{r}_{P(N)}) \Psi_\alpha^{N-1}(\mathbf{r}_{P(1)}, \dots, \mathbf{r}_{P(N-1)}) \ .$$

If this assumption is not made, the result is still more complicated. In general, $V_{\alpha\alpha'}^{ex}(\mathbf{r}_N)$ is a complex, nonlocal, energy-dependent potential. In practical calculations, $V_{\alpha\alpha'}^d(\mathbf{r}) + V_{\alpha\alpha'}^{ex}(\mathbf{r})$ is known as the optical potential for the channels considered and has been studied extensively in nuclear physics. Two types of nonlocality arise in the optical potential: the exchange nonlocality, coming from the antisymmetrization of the wave functions[4,5] and the dynamic nonlocality due to the dynamical polarization processes of the system.[6] Nuclear physicists have devised systematic methods to replace this complicated optical potential by an "equivalent" local potential.[7]

Therefore, we shall assume that

$$V_{\alpha\alpha'}(\mathbf{r}) = V_{\alpha\alpha'}^d(\mathbf{r}) + V_{\alpha\alpha'}^{ex}(\mathbf{r})$$

has been transformed into a local potential. We shall also assume that the matrix in the channel indices is Hermitian (conservation of incident flux), although we shall consider in Sec. IV the possibility of having a complex absorptive part in each channel.

Since $E = \omega + E_g^N$ we can write

$$E - E_\alpha^{N-1} = \omega - I_c - \Delta E_\alpha \equiv \kappa_\alpha^2 \ ,$$

where $I_c = E_g^{N-1} - E_g^N$ is the ionization potential for the core state [E_g^N and E_g^{N-1} are, respectively, the ground-state energies of the N-electron Hamiltonian and the

$(N-1)$-electron Hamiltonian] and $\Delta E_\alpha = E_\alpha^{N-1} - E_g^{N-1}$ is the excitation energy left behind to the $(N-1)$-particle system. Therefore, the coupled equations can be rewritten in the following way:

$$(\nabla^2 + \kappa_\alpha^2) f_\alpha(\mathbf{r}) = \sum_{\alpha'} V_{\alpha\alpha'}(\mathbf{r}) f_{\alpha'}(\mathbf{r}) . \qquad (1)$$

B. Boundary condition and density of states

Once the equation is found, we must still write the boundary conditions. These are most easily established by treating the case of an electron-molecule collision and then considering a photoemission and photoabsorption process. Since the equation for $f_\alpha(\mathbf{r})$ is not diagonal, κ_α^2 cannot be considered to be the energy of $f_\alpha(\mathbf{r})$. However, the incident electron in channel β is still represented as a plane wave with energy κ_β^2 and direction $\hat{\kappa}_\beta$: $\varphi_0(\mathbf{r}, \kappa_\beta) = \exp(i\kappa_\beta \cdot \mathbf{r})$. It is an electron with wave vector κ_β impinging on the system in state Ψ_β^{N-1}. Now, it can be checked that the wave function $f_\alpha^+(\mathbf{r}, \kappa_\beta)$ which is the solution of the Lippmann-Schwinger equation

$$f_\alpha^+(\mathbf{r}, \kappa_\beta) = \varphi_0(\mathbf{r}, \kappa_\beta) \delta_{\alpha,\beta}$$
$$+ \int d^3 r' G_0^\alpha(\mathbf{r} - \mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}(\mathbf{r}) f_{\alpha'}^+(\mathbf{r}, \kappa_\beta)$$

is a solution of the coupled Schrödinger equation (1), with

$$G_0^\alpha(\mathbf{r}) = (-1/4\pi) \exp(i\kappa_\alpha r)/r .$$

This equation means that an incident plane wave $\exp(i\kappa_\beta \cdot \mathbf{r})$ in channel β is scattered by the potential into a set of waves, $f_\alpha^+(\mathbf{r}, \kappa_\beta)$ being the part of the scattered wave that belongs to channel α. Now, repeating the standard argument of the one-channel case,[7,8] one easily obtains that the asymptotic form of $f_\alpha^+(\mathbf{r}, \kappa_\beta)$ is

$$f_\alpha^+(\mathbf{r}, \kappa_\beta)_{r \to \infty} \sim \exp(i\kappa_\beta \cdot \mathbf{r}) \delta_{\alpha,\beta} + f^+(\kappa_\alpha, \kappa_\beta) \exp(i\kappa_\alpha r)/r$$

with

$$\kappa_\alpha = \kappa_\alpha \hat{\mathbf{r}}$$

which means that an electron represented by a plane wave with wave vector κ_β in the incoming channel β is scattered in the outgoing channels α with energy loss or gain $\Delta E = \Delta E_\alpha - \Delta E_\beta$. Notice that, in principle, interaction of continuum states with bound states of the total N-electron system can be taken into account by imposing that the channel β is closed so that $\lim_{r \to \infty} f_\alpha^+(\mathbf{r}, \kappa_\beta) = 0$ [i.e., there is no homogeneous terms $\varphi_0(\mathbf{r}, \kappa_\beta)$ in the Lippmann-Schwinger equation]. Very often, as for the Fano effect, these states should be included in the expansion for Ψ_f^N.

When dealing with an absorption process, in the Golden Rule formula we must sum over all the final states of the process. In this case, we do not observe any feature of the photoelectron state, therefore we must sum over a complete set of final states. The asymptotic completeness theorem for multichannel scattering[9] ensures that we obtain a complete set of final states by finding the scattering states corresponding to a complete set of incident waves in each channel. Therefore, in our case, we must sum over all the (open) energy channels κ_β^2 and over all the corresponding photoelectron directions $\hat{\kappa}_\beta$. Moreover, because of the isometry of the Møller operator, the density of states of the final states is the same as the density of states of the corresponding incident waves.

Now, in our case the full incident wave is

$$\exp(i\kappa_\beta \cdot \mathbf{r}) \Psi_\beta^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})$$

(the antisymmetrization being irrelevant), which represents a free electron traveling towards the $(N-1)$-electron system in the state Ψ_β^{N-1}. If the $(N-1)$ electrons of $\Psi_\beta^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})$ are in a bound state, the density of states coming from this part of the total wave function is simply $\delta(E - E_\beta^{N-1})$. The density of states coming from the incident plane wave is the usual factor $\kappa_\beta/16\pi^3$ (in atomic units). The present treatment can be extended to the case when Ψ_β^{N-1} is not a bound state, provided the continuum electrons of Ψ_β^{N-1} are properly taken into account, as in the postcollision-interaction approach.[10-12] Therefore, the absorption cross section is written:

$$\sigma = (\alpha\omega/4\pi) \sum_\beta \kappa_\beta \int d\hat{\kappa}_\beta \left| \left\langle N! \mathcal{A} \left[\sum_\alpha f_\alpha^+(\mathbf{r}, \kappa_\beta) \Psi_\alpha^{N-1} \right] \middle| \boldsymbol{\epsilon} \cdot \sum_j \mathbf{r}_j \middle| \varphi_c(\mathbf{r}) \Psi_G^{N-1} \right\rangle \right|^2 .$$

The sum over β is a sum over all the open channels. This can be best understood by thinking in terms of the photoemission process. If we were not summing over κ_β and $\hat{\kappa}_\beta$ and were using $f_\alpha^-(\mathbf{r}, \kappa_\beta)$ instead of $f_\alpha^+(\mathbf{r}, \kappa_\beta)$,[13] we would obtain the probability that the x ray would eject an electron from the core orbital $\varphi_c(\mathbf{r})$ and transform it into a photoelectron with energy κ_β propagating in direction $\hat{\kappa}_\beta$, leaving an ion in the state Ψ_β^{N-1}. The corresponding photoemission cross section would, in fact, be

$$\frac{d\sigma}{d\hat{\kappa}_\beta} = S(\alpha\omega/4\pi) \kappa_\beta \left| \left\langle N! \mathcal{A} \left[\sum_\alpha f_\alpha^-(\mathbf{r}, \kappa_\beta) \Psi_\alpha^{N-1} \right] \middle| \boldsymbol{\epsilon} \cdot \sum_j \mathbf{r}_j \middle| \varphi_c(\mathbf{r}) \Psi_G^{N-1} \right\rangle \right|^2 .$$

The different energies κ_β^2 that are possible correspond to the different states in which the remaining ion can be left, and that are compatible with energy conservation $\omega - I_c - \Delta E_\beta = \kappa_\beta^2 \geq 0$, so that ΔE_β is the binding energy

referred to the lowest photoemission transition $\omega - I_c$.

In an absorption experiment, we do not observe the energy nor the direction of the photoelectron. Therefore, we must sum over the final photoelectron directions *and*

and energies that are possible. Moreover, since this summation is over a complete set of scattering states, we may replace $f_\alpha^-(\mathbf{r}, \boldsymbol{\kappa}_\beta)$ with $f_\alpha^+(\mathbf{r}, \boldsymbol{\kappa}_\beta)$. Note that the number of open channels increases with the incident photon energy. The wave function $f_\alpha^-(\mathbf{r}, \boldsymbol{\kappa}_\beta)$ will be used when dealing with photoemission spectroscopy. In the rest of this paper, we use $f_\alpha^+(\mathbf{r}, \boldsymbol{\kappa}_\beta)$ and drop the superscript $+$ for convenience. The argument $\boldsymbol{\kappa}_\beta$ in the photoelectron wave function $f_\alpha(\mathbf{r}, \boldsymbol{\kappa}_\beta)$ reminds the reader that this scattered wave corresponds to an incident plane wave $\exp(i\boldsymbol{\kappa}_\beta \cdot \mathbf{r})$ in channel β.

III. THE MULTICHANNEL MULTIPLE-SCATTERING EQUATION

A. The no-outer-sphere case

From the Lippmann-Schwinger equation we have written above, we shall derive a multiple-scattering equation valid for the multichannel case. A preliminary treatment of this problem has been given in Refs. 14 and 15.

In the present section, we follow the notations and line of reasoning presented in Ref. 16. First, we must partition the space into N_a atomic nonoverlapping spheres Ω_k, the interstital region being denoted by

$\Delta\Omega = \mathbb{R}^3 - \sum_k \Omega_k$. Each sphere $\Omega_k (k=1, \ldots, N_a)$ is centered on the atomic nucleus k located at $\mathbf{R}_k$ and its radius is denoted by ρ_k. The potential $V_{\alpha\alpha'}$ is written as a sum of potentials $V_{\alpha\alpha'}^k$ and $V_{\alpha\alpha'}^I$ acting respectively within Ω_k and $\Delta\Omega$. With this partition of space and potential, the Lippmann-Schwinger equation becomes

$$f_\alpha(\mathbf{r}) = \exp(i\boldsymbol{\kappa}_\beta \cdot \mathbf{r})\delta_{\alpha,\beta}$$
$$+ \sum_k \int_{\Omega_k} d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^k(\mathbf{r}') f_{\alpha'}(\mathbf{r}')$$
$$+ \int_{\Delta\Omega} d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{\alpha'}(\mathbf{r}') \ .$$

The wave function $f_\alpha(\mathbf{r})$ depends on $\boldsymbol{\kappa}_\beta$ but for notational convenience we drop this index. When the specification of the incident wave $\exp(i\boldsymbol{\kappa}_\beta \cdot \mathbf{r})$ is required, we shall use the notation $f_\alpha(\mathbf{r}; \beta)$. From the coupled equations (1) for $f_\alpha(\mathbf{r})$ we know that we can also write

$$f_\alpha(\mathbf{r}) = \exp(i\boldsymbol{\kappa}_\beta \cdot \mathbf{r})\delta_{\alpha,\beta}$$
$$+ \int_V d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}')(\nabla_{r'}^2 + \kappa_\alpha^2) f_\alpha(\mathbf{r}') \ .$$

If $\hat{\mathbf{n}}'$ is the outward normal to the boundary S_V of the volume V, Green's theorem

$$\int_V d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}')(\nabla_{r'}^2 + \kappa_\alpha^2) f_\alpha(\mathbf{r}') = \int_V d^3r' f_\alpha(\mathbf{r}')(\nabla_{r'}^2 + \kappa_\alpha^2) G_0^\alpha(\mathbf{r}-\mathbf{r}')$$
$$+ \int_{S_V} [G_0^\alpha(\mathbf{r}-\mathbf{r}')\nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}')\nabla_{r'} G_0^\alpha(\mathbf{r}-\mathbf{r}')] \cdot \hat{\mathbf{n}}' d\sigma' \tag{2}$$

together with the defining relation for the free Green's function

$$(\nabla_{r'}^2 + \kappa_\alpha^2) G_0^\alpha(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}'-\mathbf{r})$$

leads to the following equations:
(i) Inside atomic spheres $(\mathbf{r} \in \sum_k \Omega_k)$

$$0 = \exp(i\boldsymbol{\kappa}_\beta \cdot \mathbf{r})\delta_{\alpha,\beta} + \sum_k \int_{S_{\Omega_k}} [G_0^\alpha(\mathbf{r}-\mathbf{r}')\nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}')\nabla_{r'} G_0^\alpha(\mathbf{r}-\mathbf{r}')] \cdot \hat{\mathbf{n}}_k' d\sigma_k'$$
$$+ \int_{\Delta\Omega} d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{\alpha'}(\mathbf{r}') \ . \tag{3a}$$

(ii) In the interstitial region $(\mathbf{r} \in \Delta\Omega)$

$$f_\alpha(\mathbf{r}) = \exp(i\boldsymbol{\kappa}_\beta \cdot \mathbf{r})\delta_{\alpha,\beta} + \sum_k \int_{S_{\Omega_k}} [G_0^\alpha(\mathbf{r}-\mathbf{r}')\nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r})\nabla_{r'} G_0^\alpha(\mathbf{r}-\mathbf{r}')] \cdot \hat{\mathbf{n}}_k' d\sigma_k'$$
$$+ \int_{\Delta\Omega} d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{\alpha'}(\mathbf{r}') \ . \tag{3b}$$

Now we treat each equation separately. We shall use real spherical harmonics throughout.

1. Inside atomic spheres

Here, we take $\mathbf{r}$ inside the sphere Ω_i. We need an expression for the solution of the system of Schrödinger equations inside each atomic sphere Ω_k. Writing

$$f_\alpha(\mathbf{r}) = \sum_L f_L^\alpha(r) Y_L(\hat{\mathbf{r}}) \ ,$$

inserting into the coupled equation, and projecting onto $Y_L(\hat{\mathbf{r}})$ we find

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \kappa_\alpha^2 - \frac{l(l+1)}{r^2} \right] f_L^\alpha(r)$$
$$= \sum_{\alpha'L'} V_{LL'}^{k\alpha\alpha'}(r) f_{L'}^{\alpha'}(r) \ ,$$

where we have assumed that, around each center k,

$$V^k_{\alpha\alpha'}(\mathbf{r}_k)=\sum_{L''}V^{k\alpha\alpha'}_{L''}(r_k)Y_{L''}(\hat{\mathbf{r}}_k)$$

so that

$$V^{k\alpha\alpha'}_{LL'}(r_k)=\sum_{L''}C^L_{L'L''}V^{k\alpha\alpha'}_{L''}(r_k) ,$$

putting $\mathbf{r}_k=\mathbf{r}-\mathbf{R}_k$ and using definition (A12) in Appendix A for the Gaunt coefficients $C^L_{L'L''}$.

As in Ref. 16, if we use a finite number l_m of azimuthal quantum numbers and a finite number ν of channels, we can find $\nu(l_m+1)^2$ linearly independent vector solutions of the form $f^{k\alpha\alpha'}_{LL'}(r)$ regular at the origin which, for given $\alpha'L'$, can be interpreted as vector solutions whose components are labeled by αL. To start the integration, we might take, near the origin,[16,17]

$$f^{k\alpha\alpha'}_{LL'}(r_k)\sim r^l_k\delta_{LL'}\delta_{\alpha\alpha'} .$$

Note that $f^{k\alpha\alpha'}_{LL'}(r_k)$ does not depend on the input channel β.

Consequently, the general solution inside sphere Ω_k can be put into the form

$$f^k_\alpha(\mathbf{r}_k)=\sum_{\alpha'LL'}C^{k\alpha'}_L(\kappa_\beta)f^{k\alpha\alpha'}_{LL'}(r_k)Y_L(\hat{\mathbf{r}}_k) , \qquad (4)$$

where we have made explicit the fact that the amplitudes $C^{k\alpha'}_L$ correspond to an incident plane wave $\exp(\kappa_\beta\cdot\mathbf{r})$.

In order to perform the surface integrals in Eq. (3a) around the spheres Ω_k centered at $\mathbf{R}_k$ we make use of the expansions (A8a) and (A10) derived in Appendix A:

$$G^\alpha_0(\mathbf{r}-\mathbf{r}')=\kappa_\alpha\sum_{LL'}J_L(\kappa_\alpha\mathbf{r}_i)H^{ij\alpha}_{LL'}J_{L'}(\kappa_\alpha\mathbf{r}'_j)$$

which is valid for $j\neq i$,

$$G^\alpha_0(\mathbf{r}-\mathbf{r}')=-i\kappa_\alpha\sum_{L'}J_L(\kappa_\alpha\mathbf{r}_i)H^+_L(\kappa_\alpha\mathbf{r}'_i)$$

valid because $r_i<r'_i$.

Inserting these expressions into the transformed Lippmann-Schwinger equation, taken for $\mathbf{r}\in\Omega_i$, and using the identity (valid when the normal to the sphere is outward)

$$\int_{S_{\Omega_k}}Y_L(\hat{\mathbf{r}}')\nabla_{r'}[g(r')Y_{L'}(\hat{\mathbf{r}}')]\cdot\hat{\mathbf{n}}'_k\,d\sigma'_k=\rho^2_k g'(\rho_k)\delta_{LL'} ,$$

we obtain

$$0=\sum_L J_L(\kappa_\alpha\mathbf{r}_i)\left[\kappa_\alpha\rho^2_i\sum_{\alpha'L'}W[-ih^+_l(\kappa_\alpha\rho_i),f^{i\alpha\alpha'}_{LL'}(\rho_i)]C^{i\alpha'}_{L'}(\kappa_\beta)+\sum_{k\alpha'}\sum_{L'L''}\kappa_\alpha\rho^2_k H^{ik\alpha}_{LL'}W[j_{l'}(\kappa_\alpha\rho_k),f^{k\alpha\alpha'}_{L'L''}(\rho_k)]C^{k\alpha'}_{L''}(\kappa_\beta)\right]$$
$$+\exp(i\kappa_\beta\cdot\mathbf{r})\delta_{\alpha,\beta}+\int_{\Delta\Omega}d^3r'G^\alpha_0(\mathbf{r}-\mathbf{r}')\sum_{\alpha'}V^I_{\alpha\alpha'}(\mathbf{r}')f_{\alpha'}(\mathbf{r}') ,$$

where the sum over k is not restricted to $k\neq i$ because we set by definition $H^{ii\alpha}_{LL'}=0$. We have used the following notation for the Wronskian of two functions f and g at the point ρ:

$$W[f(\rho),g(\rho)]\equiv\{f(\rho)[g'(r)]|_{r=\rho}-g(\rho)\}[f'(r)]|_{r=\rho} .$$

If we define the matrices

$$W[-ih^+,f^i]^{\alpha\alpha'}_{LL'}\equiv W[-ih^+_l(\kappa_\alpha\rho_i),f^{i\alpha\alpha'}_{LL'}(\rho_i)]$$

and

$$W[j,f^i]^{\alpha\alpha'}_{LL'}\equiv W[j_l(\kappa_\alpha\rho_i),f^{i\alpha\alpha'}_{LL'}(\rho_i)]$$

and the vector

$$B^{k\alpha}_L(\kappa_\beta)\equiv\rho^2_k\sum_{\alpha'L''}W[j,f^k]^{\alpha\alpha'}_{L'L''}C^{k\alpha'}_{L''}(\kappa_\beta) , \qquad (5)$$

we get

$$\rho^2_k C^{k\alpha'}_L(\kappa_\beta)=\sum_{\alpha''L''}(W[j,f^k]^{-1})^{\alpha'\alpha''}_{L'L''}B^{k\alpha''}_{L''}(\kappa_\beta) .$$

With these notations the equation becomes

$$0=\sum_L J_L(\kappa_\alpha\mathbf{r}_i)\left[\kappa_\alpha\sum_{\alpha'L'}W[-ih^+,f^i]^{\alpha\alpha'}_{LL'}(W[j,f^i]^{-1})^{\alpha'\alpha''}_{L'L''}B^{i\alpha''}_{L''}(\kappa_\beta)+\sum_{kL'}\kappa_\alpha H^{ik\alpha}_{LL'}B^{k\alpha}_L(\kappa_\beta)\right]$$
$$+\exp(i\kappa_\beta\cdot\mathbf{r})\delta_{\alpha,\beta}+\int_{\Delta\Omega}d^3r'G^\alpha_0(\mathbf{r}-\mathbf{r}')\sum_{\alpha'}V^I_{\alpha\alpha'}(\mathbf{r}')f_{\alpha'}(\mathbf{r}') .$$

We now introduce the generalized inverse atomic t matrix

$$[(T^i_a)^{-1}]^{\alpha\alpha'}_{LL'}\equiv-\kappa_\alpha\sum_{\alpha''L''}W[-ih^+,f^i]^{\alpha\alpha''}_{LL''}(W[j,f^i]^{-1})^{\alpha''\alpha'}_{L''L'}$$

whose meaning will be discussed later on, use the well-known angular-momentum expansion of a plane wave:

$$\exp(i\kappa_\beta \cdot \mathbf{r}) = 4\pi \sum_{L_\beta} i^{l_\beta} Y_{L_\beta}(\hat{\kappa}_\beta) J_{L_\beta}(\kappa_\beta \mathbf{r}) \ ,$$

which is referred to the center of the coordinates and reexpand it around site i with the help of Eq. (A27), obtaining

$$\exp(i\kappa_\beta \cdot \mathbf{r}) \delta_{\alpha,\beta} = 4\pi \sum_{L_\beta L} i^{l_\beta} Y_{L_\beta}(\hat{\kappa}_\beta) J_{LL_\beta}^{i0\alpha} J_L(\kappa_\alpha \mathbf{r}_i) \delta_{\alpha,\beta} \ .$$

Similarly, to exploit the linearity of the multiple-scattering expansion, we write the amplitudes of the scattered waves as

$$B_L^{k\alpha}(\kappa_\beta) = 4\pi \sum_{L_\beta} i^{l_\beta} Y_{L_\beta}(\hat{\kappa}_\beta) B_L^{k\alpha}(L_\beta) \ . \tag{6}$$

In this way, due the linearity of the Lippmann-Schwinger equation, all the quantities indexed by L_β now correspond to an incident spherical wave $J_{L_\beta}(\kappa_\beta \mathbf{r})$ (in channel β), as all the quantities indexed by κ_β corresponded before to an incident plane wave $\exp(\kappa_\beta \cdot \mathbf{r})$. This gives us the equation

$$0 = \sum_{LL_\beta} J_L(\kappa_\alpha \mathbf{r}_i) \left[-\sum_{\alpha'L'} [(T_\alpha^i)^{-1}]_{LL'}^{\alpha\alpha'} \cdot B_{L'}^{i\alpha'}(L_\beta) + \sum_{kL'} \kappa_\alpha H_{LL'}^{ik\alpha} B_{L'}^{k\alpha}(L_\beta) + J_{LL_\beta}^{i0\alpha} \delta_{\alpha,\beta} \right] i^{l_\beta} Y_{L_\beta}(\hat{\kappa}_\beta) 4\pi$$

$$+ \int_{\Delta\Omega} d^3 r' G_0^\alpha(\mathbf{r} - \mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{\alpha'}(\mathbf{r}') \ . \tag{7a}$$

For obtaining the multiple-scattering equations, we still have to transform the integral over the interstitial potential.

2. In the interstitial region

In the interstitial region ($\mathbf{r} \in \Delta\Omega$) we have $|\mathbf{r} - \mathbf{R}_k| > |\mathbf{r}' - \mathbf{R}_k|$ if $\mathbf{r}'$ is to be on the surface of the sphere Ω_k. Therefore, one must use the expansion (A17)

$$G_0^\alpha(\mathbf{r} - \mathbf{r}') = G_0^\alpha(\mathbf{r}_k - \mathbf{r}_k') = -i\kappa_\alpha \sum_L J_L(\kappa_\alpha \mathbf{r}_k') H_L^+(\kappa_\alpha \mathbf{r}_k) \ .$$

Using the expansion of Eq. (4) for $f_\alpha(\mathbf{r})$ and the relation of Eq. (6) between $B_L^{k\alpha}(\kappa_\beta)$ and $B_L^{k\alpha}(L_\beta)$ yields

$$\int_{S_{\Omega_k}} [G_0^\alpha(\mathbf{r} - \mathbf{r}') \nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}') \nabla_{r'} G_0^\alpha(\mathbf{r} - \mathbf{r}')] \cdot \hat{\mathbf{n}}_k' d\sigma_k' = -i\kappa_\alpha \sum_{LL_\beta} H_L^+(\kappa_\alpha \mathbf{r}_k) B_L^{k\alpha}(L_\beta) i^{l_\beta} Y_{L_\beta}(\hat{\kappa}_\beta) 4\pi \ .$$

Therefore, Eq. (3b) for the interstitial region becomes

$$f_\alpha(\mathbf{r}) = \sum_{L_\beta} i^{l_\beta} Y_{L_\beta}(\hat{\kappa}_\beta) 4\pi \left[J_{L_\beta}(\kappa_\beta \mathbf{r}) \delta_{\alpha,\beta} - i\kappa_\alpha \sum_{kL} H_L^+(\kappa_\alpha \mathbf{r}_k) B_L^{k\alpha}(L_\beta) \right] + \int_{\Delta\Omega} d^3 r' G_0^\alpha(\mathbf{r} - \mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{\alpha'}(\mathbf{r}') \ .$$

To proceed further, we shall introduce the functions $f_{IL}^{k\alpha}(\mathbf{r})$ and $f_I^{0\alpha}(\mathbf{r}; L_\beta)$, solutions of the Lippmann-Schwinger equations

$$f_{IL}^{k\alpha}(\mathbf{r}) = -i\kappa_\alpha H_L^+(\kappa_\alpha \mathbf{r}_k) + \int_{\Delta\Omega} d^3 r' G_0^\alpha(\mathbf{r} - \mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{IL}^{k\alpha'}(\mathbf{r}') \ ,$$

$$f_I^{0\alpha}(\mathbf{r}; L_\beta) = J_{L_\beta}(\kappa_\beta \mathbf{r}) \delta_{\alpha,\beta} + \int_{\Delta\Omega} d^3 r' G_0^\alpha(\mathbf{r} - \mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_I^{0\alpha'}(\mathbf{r}'; L_\beta) \ .$$

By direct inspection, one can see that the function

$$\sum_{L_\beta} i^{l_\beta} Y_{L_\beta}(\hat{\kappa}_\beta) 4\pi \left[f_I^{0\alpha}(\mathbf{r}; L_\beta) + \sum_{kL} B_L^{k\alpha}(L_\beta) f_{IL}^{k\alpha}(\mathbf{r}) \right]$$

satisfies the same Lippmann-Schwinger equation as $f_\alpha(\mathbf{r}; \kappa_\beta)$ in the interstitial region. Therefore, since, in our case, the Lippmann-Schwinger equation has a unique solution,[18] one has

$$f_\alpha(\mathbf{r}; \kappa_\beta) = \sum_{L_\beta} i^{l_\beta} Y_{L_\beta}(\hat{\kappa}_\beta) 4\pi \left[f_I^{0\alpha}(\mathbf{r}; L_\beta) + \sum_{kL} B_L^{k\alpha}(L_\beta) f_{IL}^{k\alpha}(\mathbf{r}) \right] \ . \tag{7b}$$

3. Back inside the atomic spheres

If we introduce this form into

$$\int_{\Delta\Omega} d^3 r' G_0^\alpha(\mathbf{r} - \mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{\alpha'}(\mathbf{r}')$$

of Eq. (7) and take again $r \in \Omega_i$, we can use the reexpansion formula Eq. (A8a)

$$G_0^\alpha(r-r') = G_0^\alpha(r_i - r_i') = -i\kappa_\alpha \sum_L J_L(\kappa_\alpha r_i)H_L^+(\kappa_\alpha r_i') \ ,$$

valid because $r_i < r_i'$ (since $r_i' \in \Delta\Omega$), obtaining

$$\int_{\Delta\Omega} d^3r' G_0^\alpha(r-r') \sum_{\alpha'} V_{\alpha\alpha'}^I(r')f_{\alpha'}(r')$$

$$= \sum_L J_L(\kappa_\alpha r_i)(-i\kappa_\alpha)\sum_{L_\beta} i^{l_\beta} Y_{L_\beta}(\hat{k}_\beta) \sum_{\alpha'} \left[\int_{\Delta\Omega} d^3r' f_I^{0\alpha'}(r';L_\beta)V_{\alpha\alpha'}^I(r')H_L^+(\kappa_\alpha r_i') \right.$$

$$\left. + \sum_{kL'} B_{L'}^{k\alpha'}(L_\beta) \int_{\Delta\Omega} d^3r' f_{IL'}^{k\alpha'}(r')V_{\alpha\alpha'}^I(r')H_L^+(\kappa_\alpha r_i') \right] \ .$$

The last step is performed by defining, as in the single-channel case,

$$(\Theta_I)_{LL'}^{ik\alpha\alpha'} \equiv -i\kappa_\alpha \int_{\Delta\Omega} d^3r' H_L^+(\kappa_\alpha r_i')V_{\alpha\alpha'}^I(r')f_{IL'}^{k\alpha'}(r')$$

$$= -\kappa_\alpha \kappa_{\alpha'} \int_{\Delta\Omega} d^3r\, d^3r' H_L^+(\kappa_\alpha r_i)T_I^{\alpha\alpha'}(r,r')H_{L'}^+(\kappa_{\alpha'} r_k) \ ,$$

$$(\Theta_I)_{LL_\beta}^{i0\alpha\beta} \equiv -i\kappa_\alpha\kappa_\beta \int d^3r' H_L^+(\kappa_\alpha r_i') \sum_{\alpha'} V_{\alpha\alpha'}^I(r')f_I^{0\alpha'}(r';L_\beta)$$

$$= -i\kappa_\alpha\kappa_\beta \int_{\Delta\Omega} d^3r' H_L^+(\kappa_\alpha r_i)T_I^{\alpha\beta}(r,r')J_{L_\beta}(\kappa_\beta r) \ ,$$

where $T_I^{\alpha\beta}(r,r')$ is the t matrix of the interstitial potential. This gives us the multichannel multiple-scattering equation for general potentials:

$$\sum_{\alpha'kL'} \{[(T_a^i)^{-1}]_{LL'}^{\alpha\alpha'}\delta_{ik} - (\Theta_I)_{LL'}^{ik\alpha\alpha'} - \kappa_\alpha H_{LL'}^{ik\alpha}\delta_{\alpha\alpha'}\}B_{L'}^{k\alpha'} = J_{LL_\beta}^{i0\alpha}\delta_{\alpha,\beta} + (1/\kappa_\beta)(\Theta_I)_{LL_\beta}^{i0\alpha\beta} \tag{8}$$

or, in a more compact form,

$$\sum_{\alpha'kL'} (\tau^{-1})_{LL'}^{ik\alpha\alpha'}B_{L'}^{k\alpha'} = J_{LL_\beta}^{i0\alpha}\delta_{\alpha,\beta} + (1/\kappa_\beta)(\Theta_I)_{LL_\beta}^{i0\alpha\beta} \ ,$$

where, with obvious notation and introducing the diagonal matrix

$$(\kappa)_{LL'}^{ik\alpha\alpha'} \equiv \kappa_\alpha \delta_{\alpha,\beta}\delta_{ik}\delta_{LL'} \ ,$$

$$(\tau)_{LL'}^{ik\alpha\alpha'} = [(T_a^{-1} - \kappa H - \Theta_I)^{-1}]_{LL'}^{ik\alpha\alpha'} \tag{9}$$

is the general scattering path operator discussed in Appendix C.

B. The case with outer sphere

We now treat the case when an outer sphere, denoted Ω_0 (having radius ρ_0 and centered at site 0), encloses all the atomic spheres. Strictly speaking the introduction of an outer sphere is only necessary when dealing with long-range potentials (e.g., Coulombic), in order to impose the appropriate boundary conditions at infinity. It is, however, a useful expedient even for short-range potentials, since it helps reduce the volume of the interstitial region and consequently the strength of the interstitial potential. The interstitial region is now $\Delta\Omega = \Omega_0 - \sum_k \Omega_k\, C\Omega_0$ and denotes the exterior of the outer sphere. The potential $V_{\alpha\alpha'}$ is written as a sum of the potentials $V_{\alpha\alpha'}^k$, $V_{\alpha\alpha'}^I$, and $V_{\alpha\alpha'}^0$ acting, respectively, within Ω_k, $\Delta\Omega$, and $C\Omega_0$. We prefer to make a separate treatment for the case of the outer sphere because the boundary conditions are not the same as for the above case.

The problem is twofold. Firstly, for a short-range potential, the transformation of the Lippmann-Schwinger equation with the Green's theorem gives, for the outer sphere, a contribution at infinity that cancels the incident wave. Secondly, the Lippmann-Schwinger equation valid for long-range potentials has no incident wave.[19] Therefore, we cannot follow the previous treatment, and shall use a consequence of the Green's theorem which is valid for short-range as well as long-range potentials. In fact, by applying the Green's theorem Eq. (2) taken for $V = \Omega_0$ and using Eq. (1), we obtain

$$\sum_{\alpha'} \int_{\Omega_0} d^3r' G_0^\alpha(r-r')V_{\alpha\alpha'}(r')f_\alpha(r') - \int_{S_{\Omega_k}} [G_0^\alpha(r-r')\nabla_{r'}f_\alpha(r') - f_\alpha(r')\nabla_{r'}G_0^\alpha(r-r')]\cdot\hat{n}'d\sigma' = f_\alpha(r)$$

if $r \in \Omega_0$, and zero in the rhs if $r \in C\Omega_0$.

By separating the domain Ω_0 into $\sum_k \Omega_k + \Delta\Omega$ and by applying the Green's theorem to the atomic spheres Ω_k we obtain

$$0 = \sum_k \int_{S_{\Omega_k}} [G_0^\alpha(\mathbf{r} - \mathbf{r}') \nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}') \nabla_{r'} G_0^\alpha(\mathbf{r} - \mathbf{r}')] \cdot \hat{\mathbf{n}}'_k d\sigma'_k$$

$$- \int_{S_{\Omega_k}} [G_0^\alpha(\mathbf{r} - \mathbf{r}') \nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}') \nabla_{r'} G_0^\alpha(\mathbf{r} - \mathbf{r}')] \cdot \hat{\mathbf{n}}'_0 d\sigma'_0$$

$$+ \int_{\Delta\Omega} d^3 r' G_0^\alpha(\mathbf{r} - \mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{\alpha'}(\mathbf{r}') \quad \text{for } \mathbf{r} \in \Omega_i \text{ or } \mathbf{r} \in C\Omega_0 , \tag{10a}$$

$$f_\alpha(\mathbf{r}) = \sum_k \int_{S_{\Omega_k}} [G_0^\alpha(\mathbf{r} - \mathbf{r}') \nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}') \nabla_{r'} G_0^\alpha(\mathbf{r} - \mathbf{r}')] \cdot \hat{\mathbf{n}}'_k d\sigma'_k$$

$$- \int_{S_{\Omega_k}} [G_0^\alpha(\mathbf{r} - \mathbf{r}') \nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}') \nabla_{r'} G_0^\alpha(\mathbf{r} - \mathbf{r}')] \cdot \hat{\mathbf{n}}'_0 d\sigma'_0$$

$$+ \int_{\Delta\Omega} d^3 r' G_0^\alpha(\mathbf{r} - \mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{\alpha'} \quad \text{for } \mathbf{r} \in \Delta\Omega . \tag{10b}$$

The main difference between these equations and Eqs. (3a) and (3b) used for the no-outer-sphere case is that the present equations are homogeneous. Therefore, the normalization and completeness of the $f_\alpha(\mathbf{r})$ are not automatically ensured by that of the incident waves and must be obtained "by hand," guided by the previous results. We shall do this by imposing the asymptotic form of the wave function. For the time being, we want to find the general solution and we expand the photoelectron wave function outside the outer sphere over the solutions of the Schrödinger equation for the long-range potential

$$f_\alpha(\mathbf{r}) = \sum_{\alpha' L L'} [A_{L'}^{0\alpha'} f_{LL'}^{0\alpha\alpha'}(r) + C_{L'}^{0\alpha'} \gamma_{LL'}^{0\alpha\alpha'}(r)] Y_L(\hat{\mathbf{r}}) ,$$

where the radial solutions have the asymptotic behavior

$$f_{LL'}^{0\alpha\alpha'}(r)_{r \to \infty} \sim (1/\kappa_\alpha r) \sin(\kappa_\alpha r - l\pi/2 + \omega_l) \delta_{LL'} \delta_{\alpha\alpha'} ,$$

$$\gamma_{LL'}^{0\alpha\alpha'}(r)_{r \to \infty} \sim -(1/\kappa_\alpha r) \exp[i(\kappa_\alpha r - l\pi/2 + \omega_l)] \delta_{LL'} \delta_{\alpha\alpha'} ,$$

and the extra phase shift ω_l has been introduced for dealing with long-range potentials. We make use of the same reexpansions as for the previous case, with two additional expressions corresponding to the presence of the outer sphere [see Eqs. (A13) and (A15) of Appendix A]:

$$G_0^\alpha(\mathbf{r} - \mathbf{r}') = -i\kappa_\alpha \sum_{LL'} J_L(\kappa_\alpha \mathbf{r}_i) J_{LL'}^{i0\alpha} H_{L'}^+(\kappa_\alpha \mathbf{r}_0')$$

valid for $\mathbf{r} \in \Omega_i$, $\mathbf{r}'$ on S_{Ω_0},

$$G_0^\alpha(\mathbf{r} - \mathbf{r}') = -i\kappa_\alpha \sum_{LL'} H_L^+(\kappa_\alpha \mathbf{r}_0) J_{LL'}^{0i\alpha} J_{L'}(\kappa_\alpha \mathbf{r}_i')$$

valid $\mathbf{r} \in C\Omega_0$, $\mathbf{r}'$ on S_{Ω_i}. From Eq. (10a) we derive, for $\mathbf{r} \in \Omega_i$,

$$0 = \sum_L J_L(\kappa_\alpha \mathbf{r}_i) \left[\kappa_\alpha \rho_i^2 \sum_{\alpha' L'} W[-i h_l^+(\kappa_\alpha \rho_i), f_{LL'}^{i\alpha\alpha'}(\rho_i)] C_{L'}^{i\alpha'} + \sum_{k\alpha'} \sum_{L'L''} \kappa_\alpha \rho_k^2 H_{LL'}^{ik\alpha} W[j_{l'}(\kappa_\alpha \rho_k), f_{L'L''}^{k\alpha\alpha'}(\rho_k)] C_{L''}^{k\alpha'} \right.$$

$$\left. - \kappa_\alpha \rho_0^2 \sum_{\alpha' L'L''} J_{LL'}^{i0\alpha} \{ W[-i h_{l'}^+(\kappa_\alpha \rho_0), f_{L'L''}^{0\alpha\alpha'}(\rho_0)] A_{L''}^{0\alpha'} + W[-i h_{l'}^+(\kappa_\alpha \rho_0), \gamma_{L'L''}^{0\alpha\alpha'}(\rho_0)] C_{L''}^{0\alpha'} \} \right]$$

$$+ \int_{\Delta\Omega} d^3 r' G_0^\alpha(\mathbf{r} - \mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{\alpha'}(\mathbf{r}') .$$

From the same equation we derive, for $\mathbf{r} \in C\Omega_0$,

$$0 = -i \sum_L H_L^+(\kappa_\alpha \mathbf{r}_0) \left[\sum_{k\alpha'} \sum_{L'L''} \kappa_\alpha \rho_k^2 J_{LL'}^{0k\alpha} W[j_{l'}(\kappa_\alpha \rho_k), f_{L'L''}^{k\alpha\alpha'}(\rho_k)] C_{L''}^{k\alpha'} \right.$$

$$\left. - \kappa_\alpha \rho_0^2 \sum_{\alpha' L'} \{ W[j_l(\kappa_\alpha \rho_0), f_{LL'}^{0\alpha\alpha'}(\rho_0)] A_{L'}^{0\alpha'} + W[j_l(\kappa_\alpha \rho_0), \gamma_{LL'}^{0\alpha\alpha'}(\rho_0)] C_{L'}^{0\alpha'} \} \right]$$

$$+ \int_{\Delta\Omega} d^3 r' G_0^\alpha(\mathbf{r} - \mathbf{r}') \sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}') f_{\alpha'}(\mathbf{r}') .$$

Finally, from Eq. (10b) we obtain, for $\mathbf{r} \in \Delta\Omega$,

$$f_\alpha(\mathbf{r}) = -i\sum_{kL} H_L^+(\kappa_\alpha r_k) \left[\sum_k \kappa_\alpha \rho_k^2 \sum_{\alpha'L'} W[j_l(\kappa_\alpha\rho_k), f_{LL'}^{k\alpha\alpha'}(\rho_k)] C_{L'}^{k\alpha'} \right.$$

$$\left. -\sum_L J_L(\kappa_\alpha r_0)\kappa_\alpha\rho_0^2 \sum_{\alpha'L'} \{ W[-ih_l^+(\kappa_\alpha\rho_0), f_{LL'}^{0\alpha\alpha'}(\rho_0)]A_{L'}^{0\alpha'} + W[-ih_l^+(\kappa_\alpha\rho_0), \gamma_{LL'}^{0\alpha\alpha'}(\rho_0)]C_{L'}^{0\alpha'} \} \right]$$

$$+ \int_{\Delta\Omega} d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}')\sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}')f_{\alpha'}(\mathbf{r}') \ .$$

If, to the quantities defined in Eq. (5) for the case without outer sphere (OS), we add

$$B_L^{0\alpha} \equiv -\rho_0^2 \sum_{\alpha'L'} \{ W[-ih_l^+(\kappa_\alpha\rho_0), f_{LL'}^{0\alpha\alpha'}(\rho_0)]A_{L'}^{0\alpha'} + W[-ih_l^+(\kappa_\alpha\rho_0), \gamma_{LL'}^{0\alpha\alpha'}(\rho_0)]C_{L'}^{0\alpha'} \} \ ,$$

we obtain the following equations:

$$0 = \sum_L J_L(\kappa_\alpha r_0) \left[\sum_{\alpha'L'} -[(T_a^i)^{-1}]_{LL'}^{\alpha\alpha'} B_{L'}^{i\alpha'} + \kappa_\alpha \sum_{kL'} H_{LL'}^{ik\alpha} B_{L'}^{k\alpha} + \kappa_\alpha\sum_{L'} J_{LL'}^{i0\alpha} B_{L'}^{0\alpha} \right]$$

$$+ \int_{\Delta\Omega} d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}')\sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}')f_{\alpha'}(\mathbf{r}') \quad \text{for } \mathbf{r}\in\Omega_i \ , \tag{11a}$$

$$0 = -i\sum_L H_L^+(\kappa_\alpha r_0) \left[-\sum_{\alpha'L'} D_{LL'}^{\alpha\alpha'} A_{L'}^{0\alpha'} - \sum_{\alpha'L'} [(T_{OS}^0)^{-1}]_{LL'}^{\alpha\alpha'} B_{L'}^{0\alpha'} + \sum_{kL'} \kappa_\alpha J_{LL'}^{0k\alpha} B_{L'}^{k\alpha} \right]$$

$$+ \int_{\Delta\Omega} d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}')\sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}')f_{\alpha'}(\mathbf{r}') \quad \text{for } \mathbf{r}\in C\Omega \ , \tag{11b}$$

$$f_\alpha(\mathbf{r}) = -i\kappa_\alpha\sum_{kL} H_L^+(\kappa_\alpha r_k)B_L^{k\alpha} + \kappa_\alpha\sum_L J_L(\kappa_\alpha r_0)B_L^{0\alpha}$$

$$+ \int_{\Delta\Omega} d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}')\sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}')f_{\alpha'}(\mathbf{r}') \quad \text{for } \mathbf{r}\in\Delta\Omega \ , \tag{11c}$$

where we have defined

$$[(T_{OS}^0)^{-1}]_{LL'}^{\alpha\alpha'} \equiv -\kappa_\alpha \sum_{\alpha''L''} W[j,\gamma^0]_{LL''}^{\alpha\alpha''}(W[-ih^+,\gamma^0]^{-1})_{L''L'}^{\alpha''\alpha'} \ , \tag{12a}$$

$$D_{LL'}^{\alpha\alpha'} \equiv \kappa_\alpha\rho_0^2 \left[(W[j,f^0])_{LL'}^{\alpha\alpha'} - \sum_{\Lambda\Lambda'}\sum_{\beta\beta'} (W[j,\gamma^0])_{L\Lambda}^{\alpha\beta}(W[-ih^+,\gamma^0]^{-1})_{\Lambda\Lambda'}^{\beta\beta'}(W[-ih^+,f^0])_{\Lambda'L'}^{\beta'\alpha'} \right]$$

$$= (1/\kappa_\alpha\rho_0^2)((W[-ih^+,\gamma^{0*}]^{-1})^T)_{LL'}^{\alpha\alpha'} \ , \tag{12b}$$

this last step being derived in Appendix B.

To solve Eq. (11c) for $\mathbf{r}\in\Delta\Omega$, we proceed as before: we define

$$f_{IL}^{k\alpha}(\mathbf{r}) = -i\kappa_\alpha H_L^+(\kappa_\alpha r_k)$$

$$+ \int_{\Delta\Omega} d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}')\sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}')f_{IL}^{k\alpha'}(\mathbf{r}') \ ,$$

$$f_{IL}^{0\alpha}(\mathbf{r}) = \kappa_\alpha J_L(\kappa_\alpha r_0)$$

$$+ \int_{\Delta\Omega} d^3r' G_0^\alpha(\mathbf{r}-\mathbf{r}')\sum_{\alpha'} V_{\alpha\alpha'}^I(\mathbf{r}')f_{IL}^{0\alpha'}(\mathbf{r}') \ ,$$

then we show that

$$f_\alpha(\mathbf{r}) = \sum_L f_{IL}^{0\alpha}(\mathbf{r})B_L^{0\alpha} + \sum_{kL} f_{IL}^{k\alpha}(\mathbf{r})B_L^{k\alpha}$$

by considering Eq. (11c) as a Lippmann-Schwinger equation for which the incident waves φ_0 are $-i\kappa_\alpha H_L^+(\kappa_\alpha r_k)$ and $\kappa_{\alpha'}J_L(\kappa_\alpha r_0)$. Therefore, from the well-known relation $V\psi = T\varphi_0$, we can define the additional t-matrix elements by

$$(\Theta_I)_{LL'}^{0k\alpha\alpha'} \equiv \kappa_\alpha \int_{\Delta\Omega} d^3r' J_L(\kappa_\alpha r')V_{\alpha\alpha'}^I(\mathbf{r}')f_{IL'}^{k\alpha'}(\mathbf{r}')$$

$$= -i\kappa_\alpha\kappa_{\alpha'} \int_{\Delta\Omega} d^3r\, d^3r' J_L(\kappa_\alpha r)T_I(\mathbf{r},\mathbf{r}')H_{L'}^+(\kappa_{\alpha'}r_k') \ ,$$

$$(\Theta_I)_{LL'}^{00\alpha\alpha'} \equiv \kappa_\alpha \int_{\Delta\Omega} d^3r' J_L(\kappa_\alpha r')V_{\alpha\alpha'}^I(\mathbf{r}')f_{IL'}^{0\alpha'}(\mathbf{r}')$$

$$= \kappa_\alpha\kappa_{\alpha'} \int_{\Delta\Omega} d^3r\, d^3r' J_L(\kappa_\alpha r)T_I(\mathbf{r},\mathbf{r}')J_{L'}(\kappa_{\alpha'}r) \ .$$

In this way, Eqs. (11a) and (11b) give us, respectively,

$$0 = \sum_{\alpha'L'} [(T_a^i)^{-1}]_{LL'}^{\alpha\alpha'} B_{L'}^{i\alpha'} - \sum_{kL'} \kappa_\alpha H_{LL'}^{ik\alpha} B_{L'}^{k\alpha}$$

$$-\kappa_\alpha\sum_{L'} J_{LL'}^{i0\alpha} B_{L'}^{0\alpha} - \sum_{k(=0)}\sum_{L'\alpha'} (\Theta_I)_{LL'}^{ik\alpha\alpha'} B_{L'}^{k\alpha'} \ , \tag{13a}$$

$$0 = \sum_{\alpha'L'} D_{LL'}^{\alpha\alpha'} A_{L'}^{0\alpha'} + \sum_{\alpha'L'} [(T_{OS}^0)^{-1}]_{LL'}^{\alpha\alpha'} B_{L'}^{0\alpha'}$$

$$-\sum_{kL'} \kappa_\alpha J_{LL'}^{0k\alpha} B_{L'}^{k\alpha} - \sum_{k(=0)}\sum_{L'\alpha'} (\Theta_I)_{LL'}^{0k\alpha\alpha'} B_{L'}^{k\alpha'} \ , \tag{13b}$$

where the notation $k(=0)$ means that the outer sphere must be included in the sum over k. These are the final multichannel multiple-scattering equations for general potentials with an outer sphere.

To find the proper normalization and boundary condi-

tions, we now follow the results of the no-outer-sphere case. By taking the exciting amplitude $A_L^{0\alpha} = \delta_{\alpha\beta}\delta_{LL_\beta}$ for each incoming channel β and angular momentum L_β, the corresponding wave functions $f_\alpha(\mathbf{r};L_\beta)$ will span a complete set of states corresponding to incident spherical waves [with the same normalization as $J_{L_\beta}(\kappa_\beta \mathbf{r})$]. Alternatively, one can combine the above functions according to

$$f_\alpha(\mathbf{r};\kappa_\beta) = 4\pi \sum_{L_\beta} i^{l_\beta} Y_{L_\beta}(\hat{\kappa}_\beta) f_\alpha(\mathbf{r};L_\beta)$$

so that the wave functions $f_\alpha(\mathbf{r};\kappa_\beta)$ will correspond to incident waves $\exp(i\kappa_\beta \cdot \mathbf{r})$.

The definition of the scattering path operator τ in the presence of an outer sphere, corresponding to Eqs. (8) and (9), valid in the case of no outer sphere, is easily derived by eliminating the amplitude $B_L^{0\alpha}$ in Eqs. (13a) and (13b), so that only atomic-site indices appear explicitly. Taking $A_L^{0\alpha} = \delta_{\alpha\beta}\delta_{LL_\beta}$, the result is seen to be

$$\sum_{\alpha'kL'} (\tau^{-1})_{LL'}^{ik\alpha\alpha'} B_L^{k\alpha'} = \sum_{\alpha'\alpha''} \sum_{L'L''} [\kappa_{\alpha'} J_{LL''}^{i0\alpha} \delta_{\alpha\alpha'} + (\Theta_I)_{LL'}^{i0\alpha}]$$
$$\times \theta_{L'L''}^{00\alpha'\alpha''} D_{L''L_\beta}^{\alpha''\beta} ,$$

where

$$(\tau)_{LL'}^{ik\alpha\alpha'} \equiv [(T_a^{-1} - \kappa H - \Theta_I - \kappa J \theta \kappa J - \kappa J \theta \Theta_I$$
$$- \Theta_I \theta \kappa J - \Theta_I \theta \theta \Theta_I)^{-1}]_{LL'}^{ik\alpha\alpha'} . \qquad (14)$$

Here, we have defined

$$\theta_{LL'}^{ik\alpha\alpha'} \equiv [(T_{OS}^{-1} - \Theta_I^{00})^{-1}]_{LL'}^{ik\alpha\alpha'} \delta_{i0}\delta_{k0}$$

and

$$J_{LL'}^{ik\alpha\alpha'} \equiv J_{LL'}^{ik\alpha} \delta_{\alpha\alpha'} ,$$

so that, for example,

$$(\kappa J \theta \Theta_I)_{LL'}^{ik\alpha\alpha'} = \sum_{\alpha''} \sum_{\Lambda\Lambda'} \kappa_{\alpha''} J_{L\Lambda}^{i0\alpha} \theta_{\Lambda\Lambda'}^{00\alpha\alpha''} (\Theta_I)_{\Lambda'L'}^{0k\alpha''\alpha'} .$$

It can be shown that Eqs. (9) and (14) are indeed identical when due account is taken of the different extension of the interstitial region in the two cases. It can also be checked that Eqs. (13a) and (13b) formally reduce to Eq. (8) when the potential is zero outside the outer sphere. In this case we have

$$\gamma_{LL'}^{0\alpha\alpha'}(r) = -ih_l^+(\kappa_\alpha r)\delta_{LL'}\delta_{\alpha\alpha'}$$

and

$$f_{LL'}^{0\alpha\alpha'}(r) = j_l(\kappa_\alpha r)\delta_{LL'}\delta_{\alpha\alpha'} ,$$

so that Eq. (13b) gives $B_L^{0\alpha} = (1/\kappa_\alpha)A_L^{0\alpha}$ which, when inserted in Eq. (13a) gives, in turn, Eq. (8) provided $A_L^{0\alpha} = \delta_{\alpha\beta}\delta_{LL_\beta}$.

IV. CALCULATION OF THE PHOTOEMISSION AND PHOTOABSORPTION CROSS SECTIONS

This section will be devoted to giving physical insight to the formal results we have obtained. First we shall illustrate the meaning of the various quantities we have defined for the case of a single atom. If we define a new normalization to the radial functions $\underline{f}_{LL'}^{\alpha\alpha'}(r)$ by

$$\underline{f}_{LL'}^{\alpha\alpha'}(r) = \rho^{-2} \sum_{\alpha''L''} f_{LL''}^{\alpha\alpha''}(r)(W[j,f]^{-1})_{L''L'}^{\alpha''\alpha'} , \qquad (15)$$

then the solution outside the atom can be written

$$f_\alpha(\mathbf{r};\kappa_\beta) = \exp(i\kappa_\beta \cdot \mathbf{r})\delta_{\alpha,\beta}$$
$$- 4\pi\kappa_\alpha \sum_{LL_\beta} i^{l_\beta+1} H_L^+(\kappa_\alpha r)B_L^\alpha(L_\beta)Y_{L_\beta}(\hat{\kappa}_\beta) . \qquad (16)$$

From the definition of the t matrix, the quantity $B_L^\alpha(L_\beta)$ in Eq. (16) is proportional to the atomic scattering amplitude

$$(T_a)_{LL_\beta}^{\alpha\beta} = B_L^\alpha(L_\beta)$$
$$= \frac{-1}{\kappa_\alpha} \sum_{\alpha''L''} W[j,\underline{f}]_{LL''}^{\alpha\alpha''}(W[-ih^+,\underline{f}]^{-1})_{L''L_\beta}^{\alpha''\beta}$$
$$= \frac{-1}{\kappa_\alpha} \sum_{\alpha''L''} W[j,f]_{LL''}^{\alpha\alpha''}(W[-ih^+,f]^{-1})_{L''L_\beta}^{\alpha''\beta} . \qquad (17)$$

Now, inside the muffin-tin sphere,

$$f_\alpha(\mathbf{r}) = 4\pi\sum_{\alpha'L}\sum_{L'L_\beta} i^{l_\beta} Y_{L_\beta}(\hat{\kappa}_\beta)B_{L'}^\alpha(L_\beta)\underline{f}_{LL'}^{\alpha\alpha'}(r)Y_L(\hat{r}) . \qquad (17a)$$

In other words, the choice of normalization (15) for the regular solutions of the system of radial Schrödinger equations has the important consequence that the quantity controlling the amplitude of the wave function $f_\alpha(\mathbf{r};\kappa_\beta)$ inside the muffin-tin sphere is the same quantity that controls the amplitudes of the spherical waves in the asymptotic region, i.e., it is the scattering amplitude. This fact will be extremely useful, when calculating the absorption cross section, for establishing the connection between the wave-function approach and the Green's-function or density-of-state approach, through the application of the generalized optical theorem.

From Eqs. (17) and (A2), one derives the relation

$$[(T_a)^{-1}]_{LL'}^{\alpha\alpha'} = [(K_a)^{-1}]_{LL'}^{\alpha\alpha'} + i\kappa_\alpha\delta_{LL'}\delta_{\alpha\alpha'} , \qquad (18a)$$

where

$$[(K_a)^{-1}]_{LL'}^{\alpha\alpha'} \equiv -\kappa_\alpha \sum_{\alpha''L''} W[n,f^i]_{LL'}^{\alpha\alpha''}(W[j,f^i]^{-1})_{L''L'}^{\alpha''\alpha'} \qquad (18b)$$

is the reactance matrix. Notice that K_a is Hermitian.

When there are several atoms located at sites k and there is no interstitial potential, outside the cluster region we obtain the expression

$$f_\alpha(\mathbf{r};\kappa_\beta)=\exp(i\kappa_\beta\cdot\mathbf{r})\delta_{\alpha,\beta}$$

$$-4\pi\kappa_\alpha\sum_k\sum_{LL_\beta}i^{l_\beta+1}H_L^+(\kappa_\alpha\mathbf{r}_k)$$

$$\times B_{L'}^{k\alpha}(L_\beta)Y_{L_\beta}(\hat{\kappa}_\beta) . \qquad (19)$$

In Eq. (19), the quantities $B_{L'}^{k\alpha}(L_\beta)$ now describe the amplitude of the spherical waves emanating from the atom located at site k and corresponding to the incident spheri-

cal wave $J_{L_\beta}(\kappa_\beta\mathbf{r})$.

When an interstitial potential is present, the wave function outside the muffin-tin spheres no longer has the simple form (19), but the physical meaning of the t-matrix elements and of the amplitudes $B_{L'}^{k\alpha}(L_\beta)$ is unchanged. In particular, $B_L^{k\alpha}(L_\beta)$ is the scattering amplitude in response to the exciting wave $f_I^{0\alpha}(\mathbf{r};L_\beta)$, as seen from Eq. (7a).

With this in mind, let us now turn to the calculation of the absorption cross section

$$\sigma=(1/4\pi)\alpha\omega\sum_\beta\kappa_\beta\int d\hat{\kappa}_\beta\left|\left\langle N!\mathcal{A}\left[\sum_\alpha f_\alpha(\mathbf{r},\kappa_\beta)\Psi_\alpha^{N-1}\right]\right|\epsilon\cdot\sum_j\mathbf{r}_j\left|\varphi_c(\mathbf{r})\Psi_G^{N-1}\right\rangle\right|^2$$

(we shall henceforth assume summation over the appropriate spin and magnetic quantum number of the initial core state). This expression represents the x-ray absorption by all the electrons of all the atoms in the cluster. In the experimental procedure one can isolate, by setting the energy and performing the proper background removal of the spectra, the contribution of a specific core orbital of a specific atomic species $\varphi_c(\mathbf{r})$. Therefore, in the dipole operator, only the contribution due to $\epsilon\cdot\mathbf{r}$ is conserved. Now, in the corresponding expression for the absorption cross section, all the permutations that involve the coordinate $\mathbf{r}$ have terms of the form

$$\langle f_\alpha(\mathbf{r}_k,\kappa_\beta)|\varphi_G^k(\mathbf{r}_k)\rangle\langle\varphi_\alpha^k(\mathbf{r})|\epsilon\cdot\mathbf{r}|\varphi_c(\mathbf{r})\rangle$$

which represent processes in which the core electron goes to a bound orbital $\varphi_\alpha^k(\mathbf{r})$ of the $(N-1)$-particle state Ψ_α^{N-1}, while another ground-state electron $\varphi_G^k(\mathbf{r}_k)$ is ejected to the continuum. These processes are usually small, so that only the permutations that do not change $\mathbf{r}$ must be considered. These contributions can be exactly eliminated by imposing the orthogonality of the state $f_\alpha(\mathbf{r}_k,\kappa_\beta)$ to all the ground-state orbitals making up the configurations present in Ψ_G^{N-1} when solving Eq. (1). Since the $(N-1)$-electron wave functions $|\Psi_\alpha^{N-1}\rangle$ and $|\Psi_G^{N-1}\rangle$ are already antisymmetrized we obtain

$$\sigma=(1/4\pi)\alpha\omega\sum_\beta\kappa_\beta\int d\hat{\kappa}_\beta\left|\sum_\alpha S^{\alpha0}\langle f_\alpha(\mathbf{r},\kappa_\beta)|\epsilon\cdot\mathbf{r}|\varphi_c(\mathbf{r})\rangle\right|^2 ,$$

where we have defined $S^{\alpha0}\equiv\langle\Psi_\alpha^{N-1}|\Psi_G^{N-1}\rangle$.

By expanding $f_\alpha(\mathbf{r},\kappa_\beta)$ as in Eq. (17a) and performing the integral over $\hat{\kappa}_\beta$ we obtain (assuming that the ejected core electron belongs to site i)

$$\sigma=4\pi\alpha\omega\sum_\beta\kappa_\beta\sum_{L_\beta}\sum_{\alpha\alpha'}S^{\alpha0}(S^{\alpha'0})^*\sum_{\gamma\gamma'}\sum_{LL'}[B_L^{i\gamma}(L_\beta)]^*B_{L'}^{i\gamma'}(L_\beta)M_L^{\alpha\gamma}[M_{L'}^{\alpha'\gamma'}]^* , \qquad (20)$$

where we have defined the atomic matrix elements

$$M_L^{\alpha\gamma}\equiv\sum_\Lambda\langle\underline{f}_{\Lambda L}^{\alpha\gamma}(r_i)Y_\Lambda(\hat{\mathbf{r}}_i)|\epsilon\cdot\mathbf{r}_i|\varphi_c(\mathbf{r}_i)\rangle .$$

In Appendix C we prove the validity of the generalized optical theorem

$$\sum_\beta\kappa_\beta\sum_{L_\beta}[B_L^{i\gamma}(L_\beta)]^*B_{L'}^{i\gamma'}(L_\beta)=\frac{-1}{2i}\{\tau_{L'L}^{ii\gamma'\gamma}(\kappa)-[\tau_{LL'}^{ii\gamma\gamma'}(\kappa)]^*\}$$

which relates to the scattering amplitude character of the quantities $B_L^{i\gamma}(L_\beta)$. This leads to writing the photoabsorption cross section as

$$\sigma=-4\pi\alpha\omega\,\text{Im}\left[\sum_{\alpha\alpha'}S^{\alpha0}(S^{\alpha'0^*})\sum_{\gamma\gamma'}\sum_{LL'}M_L^{\alpha\gamma}\tau_{LL'}^{ii\gamma\gamma'}(\kappa)[M_{L'}^{\alpha'\gamma'}]^*\right]$$

[where κ refers to the elastic channel $\kappa^2=(\hbar\omega-I_c)$] or

$$\sigma=-4\pi\alpha\omega\sum_{\gamma\gamma'}\sum_{LL'}\text{Im}\{\tau_{LL'}^{ii\gamma\gamma'}(\kappa)\overline{M}_L^\gamma[\overline{M}_{L'}^{\gamma'}]^*\} , \qquad (21)$$

where we have defined the effective atomic dipole matrix elements by

$$\overline{M}_L^\gamma\equiv\sum_\alpha S^{\alpha0}M_L^{\alpha\gamma} .$$

The form (21) is what one would obtain by starting from a Green's-function approach to the problem, as shown in Appendix C. In this way, the exact equivalence between the scattering and the Green's-function approach is established.

Along similar lines, one can show that the differential cross section for emission of a photoelectron with energy κ_β^2 along the direction $\hat{\kappa}_\beta$ consequent to an incident photon of energy ω is, since

$$\psi^-(\mathbf{r},\hat{\kappa})=[\psi^+(\mathbf{r},-\hat{\kappa})]^*$$

when spin is neglected,[8]

$$\frac{d\sigma(\omega,\kappa_\beta)}{d\Omega_\beta}=(1/4\pi)\alpha\omega\kappa_\beta\left|\sum_\alpha S^{\alpha 0}\langle f_\alpha^*(\mathbf{r},-\kappa_\beta)|\epsilon\cdot\mathbf{r}|\varphi_c(\mathbf{r})\rangle\right|^2$$

$$=4\pi\alpha\omega\kappa_\beta\left|\sum_{L_\beta}i^{l_\beta}Y_{L_\beta}(-\hat{\kappa}_\beta)\sum_{\gamma L}B_L^{j\gamma}(L_\beta)\overline{M}\,\chi\right|^2\ . \tag{22}$$

For simplicity we treat the case of no interstitial potential. In this case we know that

$$B_L^{j\gamma}(L_\beta)=\sum_{L'j}\tau_{LL'}^{ij\gamma\beta}J_{L'L_\beta}^{j0\beta}\ .$$

Therefore,

$$\sum_{L_\beta}i^{l_\beta}Y_{L_\beta}(-\hat{\kappa}_\beta)B_L^{j\gamma}(L_\beta)=\sum_{L'j}\tau_{LL'}^{ij\gamma\beta}\sum_{L_\beta}J_{L'L_\beta}^{j0\beta}i^{l_\beta}Y_{L_\beta}(-\hat{\kappa}_\beta)\ .$$

Using the definition (A14) and the relation

$$\sum_{L_\beta}C_{L'}^{L_\beta}Y_{L_\beta}(-\hat{\kappa}_\beta)=Y_{L'}(-\hat{\kappa}_\beta)Y_{L''}(-\hat{\kappa}_\beta)\ ,$$

which follows from the definition (A12), we can apply the identity (A4) to find

$$\sum_{L_\beta}J_{L'L_\beta}^{j0\beta}i^{l_\beta}Y_{L_\beta}(-\hat{\kappa}_\beta)=-i^{l'}Y_{L'}(\hat{\kappa}_\beta)\exp(\kappa_\beta\cdot\mathbf{R}_{0j})\ .$$

As a consequence

$$\frac{d\sigma(\omega,\kappa_\beta)}{d\Omega_\beta}=4\pi\alpha\omega\kappa_\beta\left|\sum_{\gamma L}\sum_{jL'}\tau_{LL'}^{ij\gamma\beta}i^{l'}Y_{L'}(\hat{\kappa}_\beta)\exp(\kappa_\beta\cdot\mathbf{R}_{0j})\overline{M}\,\chi\right|^2\ , \tag{22a}$$

which can be used to analyze photoemission and photoelectron diffraction data. In the presence of an interstitial potential, all one has to do is to add the interstitial potential to the sum over atomic sites j. This gives, in the notation of Appendix C,

$$\frac{d\sigma(\omega,\kappa_\beta)}{d\Omega_\beta}=4\pi\alpha\omega\kappa_\beta\left|\sum_{\gamma L}\left[\sum_{jL'}\tau_{LL'}^{ij\gamma\beta}i^{l'}Y_{L'}(\hat{\kappa}_\beta)\exp(\kappa_\beta\cdot\mathbf{R}_{0j})+\tau_{LL}^{iI\gamma\beta}i^{l}Y_L(\hat{\kappa}_\beta)\right]\overline{M}\,\chi\right|^2\ . \tag{22b}$$

The term $\tau_{LL}^{iI\gamma\beta}$ describes the scattering of the photoelectron by the interstitial potential. It has no exponential factor since the center of the interstitial region is usually at site 0.

Equation (22) provides a multichannel multiple-scattering description of photoelectron diffraction, which is becoming more and more important with the advent of ARPEFS (angle-resolved photoemission extended fine structure). Previous treatments of this effects were limited to the single-channel single-scattering approximation.[20–22]

V. THE GENERALIZED MULTIPLE-SCATTERING EXPANSION

In expression (21), the structural information is contained in the scattering path matrix τ in a rather involved

way that intermingles dynamics as well as structure, through the presence of the structure matrix elements $H_{LL'}^{jk\alpha}$ in Eq. (14). It turns out, however, that under certain circumstances, to be discussed shortly, one can expand the various cross sections in a convergent series, the general term of which has a simple and direct physical meaning. In fact, we have proved in Appendix C that the scattering path matrices can be written

$$\tau=(T_a^{-1}-R)^{-1}=(1-T_aR)^{-1}T_a\ ,$$

where R can be found from the various expressions of the scattering path operators given therein (e.g., for the muffin-tin case with no interstitial potential $R=\kappa H$). Therefore, if the spectral radius (the maximum modulus of the eigenvalues) of the matrix (T_aR) is less than one, then the absorption cross section can be expanded in an absolutely convergent series

$$\sigma(\omega) = \sum_{n=0}^{\infty} \sigma_n(\omega) \ ,$$

where

$$\sigma_0 = -4\pi a \omega \sum_{\gamma\gamma'} \sum_{LL'} \mathrm{Im}\{(T_a)_{LL'}^{i\gamma\gamma'} \overline{M} \, {\overset{\gamma}{L}} [\overline{M} \, {\overset{\gamma'}{L'}}]^*\}$$

is a smoothly varying atomic cross section and

$$\sigma_n = -4\pi a \omega \sum_{\gamma\gamma'} \sum_{LL'} \mathrm{Im}\{[(T_a R)^n T_a]_{LL'}^{ii\gamma\gamma'} \overline{M} \, {\overset{\gamma}{L}} [\overline{M} \, {\overset{\gamma'}{L'}}]^*\}$$

represents the contribution to the photoabsorption cross section coming from the process where the photoelectron, before being ejected at infinity, leaves the photoabsorbing atom, located at site i, with angular momentum L and channel state γ, is scattered $(n-1)$ times by the surrounding atoms and returns to site i with angular momentum L' and channel state γ'. All these events will eventually be multiplied by the corresponding effective atomic matrix elements $\overline{M} \, {\overset{\gamma}{L}}$ and summed together to give the nth-order contribution. It is clear that this term bears information on the n-particle correlation and therefore is sensitive to the geometrical arrangement around the photoabsorbing atom.

The multiple-scattering analysis can, in principle, proceed in a way similar to the single-channel case although the situation is now much more complex due to the new feature introduced by the internal dynamics of the atoms in the system. In fact, at each scattering event the photoelectron can change its channel state and consequently its propagation vector κ_α. Even assuming a channel structure only for the photoabsorbing atom, one is faced with a superposition of different oscillating multiple-scattering signals of the type

$$A(\kappa_\alpha)\sin[\kappa_\alpha R_{\mathrm{tot}} + \varphi(\kappa_\alpha)] \ ,$$

each one with a different threshold energy corresponding to the energy loss ΔE_α suffered by the photoelectron to excite channel α [remember that $\kappa_\alpha = (\hbar\omega - I_c - \Delta E_\alpha)^{1/2}$]. It might be not at all easy to discriminate between such signals. However, the functional form suggested by the theory resolves an old ambiguity regarding whether or not to use different threshold energies in the analysis of mixed-valent homogeneous compounds[23] and in so doing helps the experimental analysis by reducing the number of unknowns.

A similar multiple-scattering expansion is also possible to study photodiffraction phenomena. For instance, we can expand $\tau_{LL'}^{ij\gamma\beta}$ into a multiple-scattering series up to second order

$$\tau_{LL'}^{ij\gamma\beta} = [T_a]_{LL'}^{i\gamma\beta}\delta_{ij} + \sum_{\alpha\Lambda\Lambda'} [T_a]_{L\Lambda}^{i\gamma\alpha} R_{\Lambda\Lambda'}^{ij\alpha} [T_a]_{\Lambda'L'}^{\alpha\beta}$$

$$+ \sum_{\alpha\alpha'k}\sum_{\Lambda\Lambda'}\sum_{\Lambda''L''} [T_a]_{L\Lambda}^{i\gamma\alpha} R_{\Lambda\Lambda'}^{ik\alpha} [T_a]_{\Lambda'\Lambda''}^{k\alpha\alpha'}$$

$$\times R_{\Lambda''L''}^{kj\alpha'}[T_a]_{L''L'}^{j\alpha'\beta} + \cdots$$

and insert the expansion into the photoemission cross-section formula (22). From the resulting expression, it can be seen that the photoemission signal is obtained from scattering paths beginning at the photoabsorbing

site and ending anywhere in the system, as it is obvious since the photoelectron is detected outside, in free space. The structural analysis is more complicated than in the photoabsorption case, but it can still be done and is giving its fruits.[21] The present formulation incorporates the multichannel structure, which can help in analyzing photodiffraction experiments with more completeness.

In general, the existence of an energy range where the multiple-scattering series converges follows from the asymptotic behavior of the scattering amplitudes at high photoelectron energy, since

$$\lim_{\kappa_a \to \infty} [T_a]_{LL'}^{i\alpha\alpha'} = 0 \ .$$

It is fairly obvious that in this regime one can write

$$[T_a]_{LL'}^{i\alpha\alpha'} \simeq (-1/\kappa_a) t_l^{i\alpha}\delta_{\alpha\alpha'}\delta_{LL'}$$

and   (23)

$$M_L^{\alpha\alpha'} \simeq M_L^\alpha \delta_{\alpha\alpha'}\delta_{LL'}$$

since the photoelectron is sensitive only to atomic cores, which are spherically symmetric and only the "incoming" channel is relevant. The argument runs as follows. At high energy $\kappa_a^2 \gg |V^{\alpha\alpha}| \gg V^{\alpha\alpha'}$ $(\alpha \neq \alpha')$, so that to a first approximation we can neglect off-diagonal terms of the potential in the rhs of Eq. (1). Together with the boundary conditions, this implies that $f_{LL'}^{k\alpha\alpha'} \simeq f_L^{k\alpha}\delta_{\alpha\alpha'}\delta_{LL'}$ in Eq. (4) to first order in the potential.

The fact that in this limit the MS matrix τ becomes diagonal in the channel indices (and therefore block diagonal in all the indices) strongly suggests another kind of expansion which sheds light onto a new aspect of the present theory. From Eq. (18a) we observe that the various channels interfere through the off-diagonal elements of the inverse of the reactance matrix $[K_a^{-1}]_{LL'}^{i\alpha\alpha'}(\alpha \neq \alpha')$. In the high-energy limit, these matrix elements go to zero, due to Eq. (23) so that in the expression (21) for photoabsorption the different channels decouple and one recovers the result of the sudden approximation.[24] In other words, the quantities $[K_a^{-1}]_{LL'}^{i\alpha\alpha'}$ control the crossover from the adiabatic to the sudden regime. By lowering the photoelectron energy, off-diagonal terms of the matrix solutions $f_{LL'}^{i\alpha\alpha'}$ in Eq. (4), and therefore of the matrix K_a^{-1} come slowly into play. Specifically one expects in this case that the amplitudes diagonal in the channel indices $[T_a]_{LL'}^{i\alpha\alpha}$ be substantially bigger than the off-diagonal amplitudes $[T_a]_{LL'}^{i\alpha\alpha'}(\alpha \neq \alpha')$. As a consequence, since from Eq. (18a) we have $1 - i\kappa T_a = T_a K_a^{-1}$, if the amplitude $[T_a]_{LL'}^{i\alpha\alpha'}(\alpha \neq \alpha')$ is small, so is $[T_a K_a^{-1}]_{LL'}^{i\alpha\alpha'}$. Choosing the case of a muffin-tin potential without interstitial potential for simplicity, we can then perform the following partition of τ^{-1} in Eq. (9):

$$[\tau^{-1}]_{LL'}^{ij\alpha\alpha'} = [T_a^{-1}]_{LL'}^{i\alpha\alpha}\delta_{ij} - \kappa_a H_{LL'}^{ij\alpha}\delta_{\alpha\alpha'}$$

$$- (1 - \delta_{\alpha\alpha'})\delta_{ij}[K_a^{-1}]_{LL'}^{i\alpha\alpha'}$$

$$= [\tau_c^{-1}]_{LL'}^{\alpha ij}\delta_{\alpha\alpha'} - (1 - \delta_{\alpha\alpha'})\delta_{ij}[K_a^{-1}]_{LL'}^{i\alpha\alpha'}$$

using the relation (18a) between the t and k matrices for the off-diagonal elements. Here τ_c^α is a block-diagonal

scattering path operator matrix describing the multiple-scattering structure relative to channel α. By assuming that the spectral radius of $\tau_c K_a^{-1}$ is less than unity we then find

$$\tau = (1 - \tau_c K_a^{-1})^{-1} \tau_c = \sum_{n=0}^{\infty} (\tau_c K_a^{-1})^n \tau_c \ .$$

Remembering Eq. (21) the photoabsorption can be written again

$$\sigma(\omega) = \sum_{n=0}^{\infty} \sigma_n(\omega)$$

$$= -4\pi\alpha\omega \sum_{n=0}^{\infty} \sum_{\alpha\alpha'} \sum_{LL'} \sum_{\Lambda j} \mathrm{Im}\{ [(\tau_c K_a^{-1})^n]_{L\Lambda}^{\alpha\alpha'ij}$$

$$\times [\tau_c]_{\Lambda L'}^{\alpha'ji} \overline{M}_L^{\alpha} [\overline{M}_{L'}^{\alpha'}]^* \} \ .$$

(24)

In this expansion the term $n=0$ gives the sudden approximation, since τ_c is diagonal in the channel indices

$$\sigma_0 = -4\pi\alpha\omega \sum_{\alpha} \sum_{LL'} \mathrm{Im}\{ (\tau_c)_{LL'}^{ii\alpha} \overline{M}_L^{\alpha} [\overline{M}_{L'}^{\alpha}]^* \} \ . \qquad (24a)$$

For the next first-order term one obtains

$$\sigma_1 = -4\pi\alpha\omega \sum_{\alpha\neq\alpha'} \sum_{LL'} \sum_{\Lambda\Lambda'j} \mathrm{Im}([\tau_c]_{L\Lambda}^{\alpha ij} [K_a^{-1}]_{\Lambda\Lambda'}^{j\alpha\alpha'}$$

$$\times [\tau_c]_{\Lambda'L'}^{\alpha'ji} \overline{M}_L^{\alpha} [\overline{M}_{L'}^{\alpha'}]^*) \ .$$

(24b)

In this latter expression we have retained for simplicity the full expression for the effective atomic matrix elements, although in the high-energy limit some sort of complicated expansion of $M_L^{\alpha\gamma}$ should exist in terms of $V_L^{i\alpha\alpha'}$ and indirectly of $[K_a^{-1}]_{LL'}^{i\alpha\alpha'}$ due to Eqs. (1) and (23). Expression (24), however, encompasses the more general case in which in some energy range the off-diagonal elements of the matrix solution (15) are not small, although the matrix elements $[K_a^{-1}]_{LL'}^{i\alpha\alpha'} (\alpha \neq \alpha')$ are. This is a fairly possible situation which enlarges the energy range where the expansion (24) is feasible.

When the state $\Psi_{\alpha'}^{N-1}$ is identified with an extended excitation of the system (like plasmons in a metal), Eq. (24b) represents the contribution of the interference between intrinsic and extrinsic losses, obtained by Hedin and Bardyszewski.[25(a)] These authors have developed an alternative approach for treating the effect of many-body interaction in x-ray absorption and photoemission. Like us, they use final states of the $(N-1)$-electron system that are fully relaxed in the presence of the core hole (which in our case are the most relevant in the expansion of Ψ_f^N), but they describe the interaction of valence electrons with photoelectrons and core holes within a boson-fermion coupling model. They also neglect exchange between the photoelectron and the remaining $(N-1)$ electrons.

In our approach, we can also treat localized atomic excitations throughout the system which likewise interfere with the primary "elastic" channel ($\kappa^2 = \omega - I_c$). However, it might be difficult to treat extended plasmonic excitations in configuration space. A reasonable scheme of

calculation would perhaps be to treat explicitly, in a close-coupling scheme, the localized configurations (channels) relevant to the problem, incorporating the extrinsic losses in an absorptive part added to the interchannel potentials. This method is used by nuclear physicists in treating nuclear reactions.[7] In other words, the interaction with the neglected channels is taken into account through the definition of effective optical potentials for the channels that are treated explicitly. Alternatively, one can explicitly treat plasmonic channel in real space by adopting the random-phase-approximation–boson representation of the plasmon states as done by Fujikawa in Ref. 25(b). This author has, in fact, developed a theory for treating intrinsic and extrinsic excitation effects in deep core x-ray-photoemission-spectroscopy (XPS) and x-ray-absorption-spectroscopy (XAS) spectra based on a many-body scattering theory,[25(b)] as well as lifetime effects.[25(c)] Although the formalism used is quite different from ours, in reality the physics described is the same and the results arrived at are very similar to ours. Our formalism, however, should be more transparent and easier to follow.

We can also try to relate photoemission and photoabsorption measurements. By integrating the photoemission cross section Eq. (22) over the photoelectron directions $\hat{\kappa}_\beta$ one has

$$\sigma(\omega, \kappa_\beta) = 4\pi\alpha\omega\kappa_\beta \sum_{L\beta} \left| \sum_{\gamma L} [B_L^{i\gamma}(L_\beta)] \overline{M}_L^{\gamma *} \right|^2 \ . \qquad (25)$$

Comparing Eqs. (20) and (25), one sees that the integrated photoemission cross section for ejection of one electron with binding energy ΔE_β equals the partial contribution to the total photoabsorption cross section of channel β.

The general formula (25) simplifies when the various channels decouple

$$\sigma(\omega, \kappa_\beta) \simeq 4\pi\alpha\omega\kappa_\beta \sum_{L\beta} \left| \sum_{L} [B_L^{i\beta}(L_\beta)] \overline{M}_L^{\beta *} \right|^2$$

$$= -4\pi\alpha\omega \, \mathrm{Im} \left[\sum_{LL'} [\tau_c(\kappa_\beta)]_{LL'}^{ii\beta} \overline{M}_L^{\beta} [\overline{M}_{L'}^{\beta}]^* \right] \qquad (26)$$

since the optical theorem can be applied to the amplitudes $B_L^{i\beta}(L_\beta)$ which are now diagonal in channel.

By averaging over sample orientations, assuming spherical symmetry and a single predominant final l state, we obtain

$$\sigma^l(\omega, \kappa_\beta) = \sigma_0^l(\omega, \kappa_\beta) \chi_\beta^l(\omega, \kappa_\beta) \ ,$$

where

$$\sigma_0^l(\omega, \kappa_\beta) \equiv 4\pi\alpha\omega |\overline{M}_l^{\beta}|^2 \sin^2(\delta_l^\beta)^l / \kappa_\beta \ ,$$

$$\chi_\beta^l(\omega, \kappa_\beta) = \frac{-\kappa_\beta}{(2l+1)\sin^2(\delta_l^\beta)} \mathrm{Im} \left[\sum_m [\tau_c(\kappa_\beta)]_{lmlm}^{ij\beta} \right] \ .$$

If one sums over all the final-state channels, and if one assumes that the functional form of $\chi_\beta^l(\omega, \kappa_\beta)$ does not depend very much on the channel, we obtain an approximate formula for the absorption cross section taking into account multielectronic effects:

$$\sigma(\omega,\kappa)=\sum_\beta \sigma_0^l[\omega,(\kappa^2-\Delta E_\beta)^{1/2}]\chi^l[\omega,(\kappa^2-\Delta E_\beta)^{1/2}] \ ,$$

(27)

where χ^l embodies all structural information. This is the relation used by Chou et al.[24] to discuss the role of multielectron excitation in the extended x-ray-absorption fine structure (EXAFS) of the Br_2 molecule in the framework of the sudden approximation and by Hammond et al. to discuss XAS spectra in mixed-valent systems.[26(a)] On the other hand, Eq. (26) has provided the rationale for determining the f-electron occupancy in homogeneous mixed-valent rare-earth compounds by measuring the integrated intensities of the various photoemission or photoelectron L_{III} lines corresponding to the different final-state channels. The relation between peak intensity and f count can be more complicated than a simple 1:1 ratio and depends obviously on the structure of Ψ_g^{N-1} and Ψ_α^{N-1} which intervene in the definitions of $S^{\alpha 0}$ and $\overline{M}$ in Eqs. (20) and (22). We refer the reader to Ref. 26(b) and citations therein for a full discussion of this point in the case of Ce compounds. See also the discussion in the next section.

Expansion (24) shows clearly the interchannel structure of the theory. Although we have justified its derivation starting from the high-energy limit, its validity is not restrained to this energy regime, as already anticipated above. Even in the near-edge region the interchannel atomic matrix elements $[T_a]_{LL'}^{i\alpha\alpha'}(\alpha\neq\alpha')$ might happen to be negligible compared to the diagonal ones. This situation parallels that encountered in the case of Cu and, in general, free-electron metals, where the diagonal matrix elements $[T_a]_{LL'}^{i\alpha\alpha}$ are themselves small at low (≤ 50 eV) photoelectron kinetic energy, so that a single-scattering EXAFS approximation is sufficient to describe the near-edge structure.[27] In such cases the sudden approximation would be valid right at the near-edge region, obviously only for those channels which are open at that particular energy.

It would be extremely interesting to explore experimentally the validity of these speculations. In the next section we shall show an application of these considerations to mixed-valent compounds.

VI. APPLICATIONS OF THE THEORY AND CONCLUSIONS

The theory set forth above makes definite predictions about the role of the various channels present in a photoabsorption spectrum. In the sudden approximation limit, all channels are decoupled (they do not interfere) and have identical or reasonably similar multiple-scattering structure, depending on the slight difference of the atomic t matrix among the various channel states. Experimental evidence for such MS structure associated with excitations with double-electron excitations would provide more convincing support to the theory.[28]

Another aspect worth pursuing is the study of the absolute amplitude of the signal coming from the elastic channel ($\Delta E_\alpha=0$). A success in this field would give more interpretative power to MS (in particular, EXAFS)

structural analysis.[24]

In the case of mixed-valent compounds the theory provides a clue to the resolution of the threshold puzzle and to the discrimination between homogeneous and inhomogeneous systems. In fact, in the case of inhomogeneous rare-earth compounds (static admixture of 2+ and 3+ ions), the total absorption coefficient is given by an incoherent sum of two absorption spectra with weight C_0^2 and C_1^2, the relative concentration of the two types of ions:

$$\sigma(\omega)=C_0^2\sigma_0(\omega)\chi_1^0(\kappa_0)+C_1^2\sigma_1(\omega)\chi_1^1(\kappa_1) \ ,$$

where $\sigma_0(\omega)$ is the absorption coefficient of the 2+ ion and $\sigma_1(\omega)$ that of the 3+ ion. As a good approximation

$$\sigma_p(\omega)\simeq |S^{0p}|^2|\langle f_p(r)|r|\varphi_c(r)\rangle|^2/\kappa_p \quad (p=0,1) \ .$$

For simplicity we assume a single-l final state and average over sample orientations. The wave numbers κ_0 and κ_1 are given by $\kappa_p=(\hbar\omega-I_p)^{1/2}$, where I_p is the ionization threshold for the two types of ions, and

$$\chi_1^p(\kappa_p)\simeq\kappa_p\sum_m \text{Im}[(\tau_c)_{lmlm}^{ii\alpha_p}]$$

describes the multiple-scattering structure. We assume that only the channels α_p are predominant, having taken account of the remaining channels through an appropriate optical potential.

The case of the homogeneous compounds is quite different. Here at least two configurations are mixed in the ground state, so that

$$\Psi_g=\sqrt{N!}\mathcal{A}\{\varphi_c(\mathbf{r})[a\Psi_0(4f^{n-1}(5d\,6s)^{m+1})$$
$$+b\Psi_1(4f^n(5d\,6s)^m)]\} \ ,$$

whereas for the excited final states we can approximately write

$$\Psi_f=\sqrt{N!}\mathcal{A}[f_0^\gamma(\mathbf{r})\Psi_0^*+f_1^\gamma(\mathbf{r})\Psi_1^*] \ ,$$

where Ψ_p^* indicates the relaxed configurations corresponding to Ψ_p and γ ($=0,1$) labels the two independent final-state solutions. As a matter of fact, since the states $5d\,6s$ are spread into a band, we should write $\sum_k a_k\Psi_{1k}^*$, k indexing the electron promoted from the f state to the band. For simplicity, we neglect this further complication, although the generalization of the following argument is immediate. See Refs. 26 and 29 for a complete treatment of this point.

In order to write the photoabsorption cross section, we need $\overline{M}_L^\gamma\equiv\sum_\alpha S^{\alpha 0}M_L^{\alpha\gamma}$ of Eq. (22). By putting $P^{pp'}=\langle\Psi_p^*|\Psi_{p'}\rangle$ we find

$$\sum_{\alpha=0}^1 S^{\alpha 0}[M_L^{\alpha\gamma}]=(aP^{00}+bP^{01})[M_L^{0\gamma}]+(aP^{10}+bP^{11})[M_L^{1\gamma}]$$

$$\simeq aP^{00}[M_L^{0\gamma}]+bP^{11}[M_L^{1\gamma}]$$

(28)

neglecting the overlap factor P^{01} with respect to P^{00} and P^{11}.

To the zero order of the expansion (24) and in the high-energy limit, using Eqs. (23) and (27), we easily find for the absorption coefficient

$$\sigma^l(\omega) = a^2 \sigma_0^l(\omega) \chi_l^0(\kappa_0) + b^2 \sigma_1^l(\omega) \chi_l^1(\kappa_1) \,, \tag{29}$$

where

$$\sigma_0^l(\omega) \simeq |P^{pp} M_{L'}^{pp}| \sin^2 \delta_l^p / \kappa_p$$

is the atomic absorption coefficient for the configuration p, $\kappa_0^2 = \hbar\omega - I_c$, and $\kappa_1^2 = \hbar\omega - I_c - \Delta E_1$ (where ΔE_1 is the energy splitting of the two $4f$ configurations in the final state). This settles down the question of the "threshold puzzle"[23] since two threshold energies must be used to analyze x-ray spectra in these compounds. Notice that in this limit the ratio $a^2 \sigma_0^l(\omega)/b^2 \sigma_1^l(\omega)$ and the splitting ΔE_1 can be obtained from x-ray absorption or XPS core-level spectra.

Therefore, at this level of approximation, by identifying $C_0^2 = a^2$ and $C_1^2 = b^2$ as the $4f$ occupancy in the ground state, one can use the same formula to analyze homogeneous as well as inhomogeneous systems. Moreover, by taking advantage of the rescaling properties of the photoabsorption spectra with respect to change in coordination bond length, it should be possible to analyze lattice relaxation effects in the final state of homogeneous compounds using inhomogeneous systems of similar composition and structure as standards. In other words, by combining XPS and EXAFS analyses one should be able to measure the $4f$ occupancy in the ground state, the splitting ΔE_1 of the $4f$ configurations in the final state, and lattice relaxation effects, if present, in homogeneous mixed-valent compounds. These results were already foreseen by an experimental group,[30] based on the analysis of mixed-valent compounds x-ray absorption spectra. The present work now sets the theoretical framework and the approximations involved in this approach, and it is hoped it will facilitate this type of analysis.

The same Eq. (29) has been extended to the low-energy x-ray appearance near-edge structure (XANES) region and applied to the analysis of homogeneous $SmS_{0.85}As_{0.15}$ and inhomogeneous $SmS_{0.85}As_{0.15}$ compounds with satisfactory results.[30-32] The problem in such an extension is that, even assuming that the sudden approximation is valid in the low-energy regime, Eqs. (23) are not. Consequently, the effective atomic matrix elements $\overline{M}_{L'}^p$ are different in the low- and high-energy limit and we cannot use XPS results (usually at high photoelectron kinetic energy) to fix the relative weight of the two channels in the final state. One can still use Eq. (29), but in this case the relation of the weights to the f counts is more involved and the separation between atomic and structural contributions not so clear cut, as seen from Eqs. (24) and (28). To add more complications, one expects the sudden approximation not to be valid, in general, in the low-energy regime. It certainly does not hold for Ce metal in the α phase and intermetallic compounds, CeO_2, etc., where the $4f^0$, $4f^1$, and $4f^2$ configurations interact very strongly both in the initial and final states.[26,32,33]

The investigation of all these questions constitutes a field of still active research and can potentially provide a deeper understanding of two main problems facing today core-level x-ray spectroscopy: the evolution from the adiabatic to the sudden regime and the interplay between excitation dynamics and structure.

APPENDIX A

In order to perform the surface integrals in Sec. III we need various one- or two-center expansions of the free Green's function ($\kappa = \sqrt{E}$).

$$G_0^+(\mathbf{r} - \mathbf{r}'; E) = \frac{1}{(2\pi)^3} \int d^3k \frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}}{E - k^2 + i\epsilon}$$

$$= -\frac{1}{4\pi} \frac{e^{i\kappa \cdot |\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} (\epsilon \to 0^+) \,. \tag{A1}$$

Here, for convenience of the reader, we provide a quick derivation of these expansions, to be used in the text. Henceforth, we shall drop the superscript $+$ of the free Green's function, assuming implicitly outgoing wave boundary conditions.

We shall use real spherical harmonics throughout and spherical Bessel, Neumann and Hankel functions $j_l(\rho)$, $n_l(\rho)$, and $h_l^\pm(\rho)$ as defined in Ref. 34 (with slightly different notation). Notice the relations

$$h_l^\pm(\rho) = j_l(\rho) \pm in_l(\rho), \quad j_l(-\rho) = (-1)^l j_l(\rho) \,,$$

$$h_l^-(-\rho) = (-1)^l h_l^+(\rho), \quad n_l(-\rho) = (-1)^{l+1} n_l(\rho) \,. \tag{A2}$$

Moreover, we shall put, for short,

$$J_L(\boldsymbol{\rho}) \equiv j_l(\rho) Y_L(\hat{\boldsymbol{\rho}}) \,,$$

$$N_L(\boldsymbol{\rho}) \equiv n_l(\rho) Y_L(\hat{\boldsymbol{\rho}}) \,, \tag{A3}$$

$$H_L^\pm(\boldsymbol{\rho}) \equiv h_l^\pm(\rho) Y_L(\hat{\boldsymbol{\rho}}) \,,$$

where $L \equiv l, m$ and $\boldsymbol{\rho} \equiv k\mathbf{r}$ or $\kappa\mathbf{r}$.

We start from the basic plane-wave expansion:

$$\exp(i\mathbf{p}\cdot\mathbf{r}) = 4\pi \sum_L i^l j_l(\kappa r) Y_L(\hat{\mathbf{r}}) Y_L(\hat{\mathbf{k}}) \tag{A4}$$

to derive the angular-momentum representation of $G_0(\mathbf{r}-\mathbf{r}')$:

$$G_0(\mathbf{r}-\mathbf{r}') = \sum_L Y_L(\hat{\mathbf{r}}) G_0^l(r, r') Y_L(\hat{\mathbf{r}}') \,. \tag{A5}$$

Inserting Eq. (A4) into Eq. (A1) and performing the angular intergrations we obtain

$$G_0(\mathbf{r}-\mathbf{r}') = \sum_L Y_L(\hat{\mathbf{r}}) \frac{2}{\pi} \int_0^\infty k^2 dk \frac{j_l(kr) j_l(kr')}{E - k^2 + i\epsilon} Y_L(\hat{\mathbf{r}}') \,. \tag{A6}$$

Under the assumption that $r' > r$, by comparing Eqs. (A6) and (A5) and using the relations (A2) we find

$$G_0^l(r,r') = \frac{1}{\pi} \int_0^\infty k^2 d\kappa \frac{j_l(kr)[h_l^+(kr') + h_l^-(kr')]}{E - k^2 + i\epsilon}$$

$$= \frac{1}{\pi} \int_{-\infty}^{+\infty} k^2 dk \frac{j_l(kr) h_l^+(kr')}{E - k^2 + i\epsilon}$$

$$= -i\kappa j_l(\kappa r) h_l^+(\kappa r') \tag{A7}$$

closing the contour in the upper half-plane. Therefore, for $r' > r$,

$$G_0(\mathbf{r} - \mathbf{r}') = -ik \sum_L J_L(\kappa \mathbf{r}) H_L^+(\kappa \mathbf{r}') . \tag{A8a}$$

Similarly for $r' < r$,

$$G_0(\mathbf{r} - \mathbf{r}') = -ik \sum_L J_L(\kappa \mathbf{r}') H_L^+(\kappa \mathbf{r}) . \tag{A8b}$$

In order to derive a two-center expansion around sites i and j located at $\mathbf{R}_i$ and $\mathbf{R}_j$, we observe that

$$\mathbf{r} - \mathbf{r}' = \mathbf{r} - \mathbf{R}_i - (\mathbf{r}' - \mathbf{R}_j) + \mathbf{R}_i - \mathbf{R}_j$$

$$= \mathbf{r}_i - \mathbf{r}_j' + \mathbf{R}_{ij} \tag{A9}$$

with obvious definitions of the symbols. We have the following different cases.

(a) $\mathbf{r} \in \Omega_i$ and $\mathbf{r}'$ on S_{Ω_j} (i,j atomic sites). Then $R_{ij} > r_i + r_j'$. Then, proceeding as in Eq. (A7):

$$G_0(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int d^3k \frac{\exp[i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)]\exp(i\mathbf{k}\cdot\mathbf{R}_{ij})}{E - k^2 + i\epsilon}$$

$$= 8 \sum_{LL'} \sum_{L'} \int d^3k i^{l-l'+l''} \frac{J_L(k\mathbf{r}_i) Y_L(\hat{\mathbf{k}}) J_{L'}(k\mathbf{r}_j') Y_{L'}(\hat{\mathbf{k}}) J_{L''}(k\mathbf{R}_{ij}) Y_{L''}(\hat{\mathbf{k}})}{E - k^2 + i\epsilon}$$

$$= 8 \sum_{LL'} \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} \int_0^\infty k^2 dk \frac{J_L(k\mathbf{r}_i) J_{L'}(k\mathbf{r}_j') J_{L''}(k\mathbf{R}_{ij})}{E - k^2 + i\epsilon}$$

$$= -4\pi i\kappa \sum_{LL'} \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} H_{L''}^+(\kappa\mathbf{R}_{ij}) J_L(\kappa\mathbf{r}_i) J_{L'}(\kappa\mathbf{r}_j')$$

$$= \kappa \sum_{LL'} J_L(\kappa\mathbf{r}_i) H_{LL'}^{ij} J_{L'}(\kappa\mathbf{r}_j') , \tag{A10}$$

where, by comparison,

$$H_{LL'}^{ij} = -4\pi i \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} H_{L''}^+(\kappa\mathbf{R}_{ij}) \tag{A11}$$

having defined the Gaunt coefficients

$$C_{LL''}^{L'} \equiv \int d\Omega_k Y_L(\hat{\mathbf{k}}) Y_{L'}(\hat{\mathbf{k}}) Y_{L''}(\hat{\mathbf{k}}) . \tag{A12}$$

(b) $\mathbf{r} \in \Omega_i$ (i atomic site) and $\mathbf{r}'$ on S_{Ω_0} (0 outer sphere). Then $r_0' > r_i + R_{i0}$. Therefore,

$$G_0(\mathbf{r} - \mathbf{r}') = G_0(\mathbf{r}_i - \mathbf{r}_0' + \mathbf{R}_{i0})$$

$$= 8 \sum_{LL'} \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} \int_0^\infty k^2 dk \frac{J_L(k\mathbf{r}_i) J_{L'}(k\mathbf{r}_0') J_{L''}(k\mathbf{R}_{i0})}{E - k^2 + i\epsilon}$$

$$= -4\pi i\kappa \sum_{LL'} \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} J_{L''}(\kappa\mathbf{R}_{i0}) J_L(\kappa\mathbf{r}_i) H_{L'}^+(\kappa\mathbf{r}_0')$$

$$= -i\kappa \sum_{LL'} J_L(\kappa\mathbf{r}_i) J_{LL'}^{i0} H_{L'}^+(\kappa\mathbf{r}_0') , \tag{A13}$$

where

$$J_{LL'}^{i0} = 4\pi \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} J_{L''}(\kappa\mathbf{R}_{i0}) . \tag{A14}$$

(c) $\mathbf{r} \in C\Omega_0$ and $\mathbf{r}'$ on S_{Ω_i}. Then $r_0 > r_i' + R_{0i}$. As for Eq. (A13) we find

$$G_0(\mathbf{r} - \mathbf{r}') = G_0(\mathbf{r}_0 - \mathbf{r}_i' + \mathbf{R}_{0i})$$

$$= -i\kappa \sum_{LL'} H_L^+(\kappa\mathbf{r}_0) J_{LL'}^{0i} J_{L'}(\kappa\mathbf{r}_i') \tag{A15}$$

with

$$J_{LL'}^{0i} = 4\pi \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} J_{L''}(\kappa\mathbf{R}_{0i}) . \tag{A16}$$

(d) $\mathbf{r} \in \Delta\Omega$ and $\mathbf{r}'$ on S_{Ω_i}. In this case $r_i > r_i'$, so that, using Eq. (A8)

$$G_0(\mathbf{r} - \mathbf{r}') = G_0(\mathbf{r}_i - \mathbf{r}_i')$$

$$= -i\kappa \sum_L H_L^+(\kappa\mathbf{r}_i) J_L(\kappa\mathbf{r}_i') . \tag{A17}$$

(e) $r \in \Delta\Omega$ and $\mathbf{r}'$ on S_{Ω_0}. In such a case $r_0' > r_0$, so that, using Eq. (A8) again

$$G_0(\mathbf{r} - \mathbf{r}') = G_0(\mathbf{r}_0 - \mathbf{r}_0')$$

$$= -i\kappa \sum_L H_L^+(\kappa \mathbf{r}_0') J_L(\kappa \mathbf{r}_0) \ . \tag{A18}$$

Since, from Eq. (A2),

$$-ih_l^+(\rho) = n_l(\rho) - ij_l(\rho) \ ,$$

we easily find the decomposition (i,j atomic sites)

$$H_{LL'}^{ij} = -4\pi i \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} H_{L''}^+(\kappa \mathbf{R}_{ij})$$

$$= 4\pi \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} [N_{L''}(\kappa \mathbf{R}_{ij}) - iJ_{L''}(\kappa \mathbf{R}_{ij})]$$

$$= N_{LL'}^{ij} - iJ_{LL'}^{ij} \ . \tag{A19}$$

Notice that from this definition $N_{LL'}^{ij}$ and $J_{LL'}^{ij}$ have the following properties:

$$J_{LL'}^{ij} = J_{L'L}^{ji}, \quad N_{LL'}^{ij} = N_{L'L}^{ji} \tag{A20}$$

and that

$$J_{LL'}^{ii} = \delta_{LL'} \ , \tag{A21}$$

i denoting an atomic site or the center of the outer sphere.

Another property worth noticing is the addition formula

$$\sum_{L''} J_{LL''}^{ii'} J_{L''L'}^{i'j} = J_{LL'}^{ij} \tag{A22}$$

which comes from the addition property of the exponential function $\exp(i\mathbf{k}\cdot\mathbf{R})$ and the integral representation of $J_{LL'}^{ij}$:

$$J_{LL'}^{ij} = \int d^3k(1/k^2)\delta(k-\kappa)Y_L(\hat{\mathbf{k}})\exp(i\mathbf{k}\cdot\mathbf{R}_{ij})Y_{L'}(\hat{\mathbf{k}})i^{l-l'}$$

$$= 4\pi \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} J_{L''}(\kappa \mathbf{R}_{ij}) \ . \tag{A23}$$

Since $\mathbf{R}_{ij} = \mathbf{R}_{ii'} + \mathbf{R}_{i'j}$, where i' is any site, we find

$$J_{LL'}^{ij} = \int d^3k(1/k^2)\delta(k-\kappa)Y_L(\hat{\mathbf{k}})\exp(i\mathbf{k}\cdot\mathbf{R}_{ii'})\exp(i\mathbf{k}\cdot\mathbf{R}_{i'j})Y_{L'}(\hat{\mathbf{k}})i^{l-l'}$$

$$= \int d^3k(1/k^2)\delta(k-\kappa)Y_L(\hat{\mathbf{k}})\exp(i\mathbf{k}\cdot\mathbf{R}_{ii'})\int d^3k'\delta(k-k')\exp(i\mathbf{k}'\cdot\mathbf{R}_{i'j})Y_{L'}(\hat{\mathbf{k}}')i^{l-l'}$$

$$= \int d^3k(1/k^2)\delta(k-\kappa)Y_L(\hat{\mathbf{k}})\exp(i\mathbf{k}\cdot\mathbf{R}_{ii'})\int d^3k'(1/k'^2)\delta(k-k')\delta(\Omega_k - \Omega_{k'})\exp(i\mathbf{k}'\cdot\mathbf{R}_{i'j})Y_{L'}(\hat{\mathbf{k}}')i^{l-l'}$$

$$= \int d^3k(1/k^2)\delta(k-\kappa)Y_L(\hat{\mathbf{k}})\exp(i\mathbf{k}\cdot\mathbf{R}_{ii'})\int d^3k'(1/k'^2)\delta(k-k')\sum_{L''} Y_{L''}(\hat{\mathbf{k}})Y_{L''}(\hat{\mathbf{k}}')\exp(i\mathbf{k}'\cdot\mathbf{R}_{i'j})Y_{L'}(\hat{\mathbf{k}}')i^{l-l''}i^{l''-l'}$$

$$= \sum_{L''} J_{LL''}^{ii'} J_{L''L'}^{i'j} \ .$$

For completeness we give also the integral representation for $H_{LL'}^{ij}$:

$$H_{LL'}^{ij} = \frac{2}{\pi\kappa} \int dk^3 \frac{j_l(kr)}{j_l(\kappa r)} \frac{Y_L(\hat{\mathbf{k}})\exp(i\mathbf{k}\cdot\mathbf{R}_{ij})Y_{L'}(\hat{\mathbf{k}})}{E-k^2+i\epsilon} \frac{j_{l'}(kr')}{j_{l'}(\kappa r')} i^{l-l'}$$

$$= -4\pi i \sum_{L''} i^{l-l'+l''} C_{LL''}^{L'} H_{L''}^+(\kappa \mathbf{R}_{ij}) \ , \tag{A24}$$

and note that, by writing $\mathbf{R}_{ij} = \mathbf{R}_{ii'} + \mathbf{R}_{i'j}$ and exploiting again the additivity of the exponential,

$$H_{LL'}^{ij} = \sum_{L''} H_{LL''}^{ii'} J_{L''L'}^{i'j} \quad \text{if } R_{ii'} > R_{i'j} \tag{A25a}$$

or

$$H_{LL'}^{ij} = \sum_{L''} J_{LL''}^{ii'} H_{L''L'}^{i'j} \quad \text{if } R_{ii'} < R_{i'j} \ . \tag{A25b}$$

Finally, by starting from Eqs. (A8) and (A1) written as

$$-i\kappa \sum_L H_L^+(\kappa \mathbf{r}_i') J_L(\kappa \mathbf{r}_i) = \frac{1}{(2\pi)^3} \int d^3k \frac{\exp(i\mathbf{k}\cdot\mathbf{r}_i')\exp(-i\mathbf{k}\cdot\mathbf{r}_i)}{E-k^2+i\epsilon}$$

$$= \frac{4\pi}{(2\pi)^3} \sum_{L'} i^{-l'} \int d^3k \frac{\exp(i\mathbf{k}\cdot\mathbf{r}_i')J_{L'}(k\mathbf{r}_i)Y_{L'}(\hat{\mathbf{k}})}{E-k^2+i\epsilon}$$

and taking r'_i to be $r_i + R_{ij} = r_j$, we derive the reexpansion relations

$$-iH_L^+(\kappa \mathbf{r}_j) = \sum_{L'} J_{L'}(\kappa \mathbf{r}_i) H_{L'L}^{ij} \quad \text{if } |\mathbf{r}_i - \mathbf{r}_j| = R_{ij} > r_i \ ,$$

(A26a)

$$-iH_L^+(\kappa \mathbf{r}_j) = -i\sum_{L'} H_{L'}^+(\kappa \mathbf{r}_i) J_{L'L}^{ij} \quad \text{if } R_{ij} < r_i \ ,$$

(A26b)

from which, by taking the imaginary part of both members, we obtain

$$J_L(\kappa \mathbf{r}_j) = \sum_{L'} J_{L'}(\kappa \mathbf{r}_i) J_{L'L}^{ij}$$

(A27)

valid whatever $\mathbf{r}_i$, $\mathbf{r}_j$, $\mathbf{R}_{ij}$. These relations are also special cases of Eqs. (A25a) and (A25b). In deriving Eqs. (A10) and (A13) we have taken advantage of the fact that $l + l' + l'' = 2n$ ($n = 0, 1, \ldots$) which is imposed by Eq. (A12), in order to extend the radial integral over the entire axis.

APPENDIX B

In this appendix, we prove a transformation of the quantity $D_{LL'}^{\alpha\alpha'}$ in Eq. (12b) that can also be applied to transform Eq. (2.49) in Ref. 16. We directly treat the multichannel case. The key quantity to manipulate in this transformation is the t matrix in Eq. (12a) which, in matrix notation, can be rewritten with the help of Eq. (A2) as

$$-\kappa^{-1}(T_{\mathrm{OS}}^0)^{-1} = W[j,\gamma^0](W[n,\gamma^0] - iW[j,\gamma^0])^{-1}$$

$$= (W[n,\gamma^0]W[j,\gamma^0]^{-1} - i)^{-1} \ . \quad (B1)$$

Here $\gamma_{LL'}^{0\alpha\alpha'}$ form a set of independent irregular solutions of the system of radial Schrödinger equations

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \kappa_\alpha^2 - \frac{\lambda(\lambda+1)}{r^2} \right] \varphi_\Lambda^\alpha(r)$$

$$= \sum_{\alpha'\Lambda'} V_{\Lambda\Lambda'}^{\alpha\alpha'}(r)\varphi_{\Lambda'}^{\alpha'}(r) \quad (B2)$$

and $V_{\Lambda\Lambda'}^{\alpha\alpha'}(r)$ is, in general, Hermitian in the indices α and Λ. In the one-channel case $V_{\Lambda\Lambda'}(r)$ is real if one uses real spherical harmonics, so that $V_{\Lambda\Lambda'}(r) = V_{\Lambda'\Lambda}(r)$. Following Eqs. (16a) and (16b) the matrix $W[n,\gamma^0]W[j,\gamma^0]^{-1}$ is the inverse of the reactance matrix which, according to a general theorem in scattering theory, is Hermitian [real symmetric if $V_{\Lambda\Lambda'}^{\alpha\alpha'}(r)$ is such]. Therefore,

$$W[n,\gamma^0]W[j,\gamma^0]^{-1} = (W[j,\gamma^{0*}]^{-1})^T(W[n,\gamma^{0*}])^T \ ,$$

(B3)

where superscript T indicates transposition. This property can also be verified directly. Hence

$$-\kappa^{-1}(T_{\mathrm{OS}}^0)^{-1} = ((W[j,\gamma^{0*}]^{-1})^T(W[n,\gamma^{0*}])^T - i)^{-1}$$

$$= (W[-ih^+,\gamma^{0*}]^{-1})^T(W[j,\gamma^{0*}])^T \ .$$

(B4)

Using this relation, we find

$$(1/\kappa_\alpha\rho_0^2)D_{LL'}^{\alpha\alpha'} = (W[j,f^0])_{LL'}^{\alpha\alpha'} - \sum_{\beta\gamma}\sum_{\Lambda\Lambda'}(W[j,\gamma^0])_{L\Lambda}^{\alpha\beta}(W[-ih^+\gamma^0]^{-1})_{\Lambda\Lambda'}^{\beta\gamma}(W[-ih^+,f^0])_{\Lambda'L'}^{\gamma\alpha'}$$

$$= (W[j,f^0])_{LL'}^{\alpha\alpha'} - \sum_{\beta\gamma}\sum_{\Lambda\Lambda'}((W[-ih^+,\gamma^{0*}]^{-1})^T)_{L\Lambda}^{\alpha\beta}(W[j,\gamma^{0*}]^T)_{\Lambda\Lambda'}^{\beta\gamma}(W[-ih^+,f^0])_{\Lambda'L'}^{\gamma\alpha'}$$

$$= ((W[-ih^+,\gamma^{0*}]^{-1})^T(W[-ih^+,\gamma^{0*}]^TW[j,f^0] - W[j,\gamma^{0*}]^TW[-ih^+,f^0]))_{LL'}^{\alpha\alpha'} \ .$$

Now,

$$(W[-ih^+,\gamma^{0*}]^TW[j,f^0] - W[j,\gamma^{0*}]^TW[-ih^+,f^0])_{LL'}^{\alpha\alpha'} = \sum_{\beta\Lambda}\{W[-ih_\lambda^+(\kappa_a\rho_0),(\gamma_{\Lambda L}^{0\beta\alpha})^*]W[j_\lambda(\kappa_a\rho_0),f_{\Lambda L'}^{0\beta\alpha'}]$$

$$- W[j_\lambda(\kappa_a\rho_0),(\gamma_{\Lambda L}^{0\beta\alpha})^*]W[-ih_\lambda^+(\kappa_a\rho_0),f_{\Lambda L'}^{0\beta\alpha'}]\}$$

$$= \sum_{\beta\Lambda}W[-ih_\lambda^+(\kappa_a\rho_0),j_\lambda(\kappa_a\rho_0)]W[(\gamma_{\Lambda L}^{0\beta\alpha})^*,f_{\Lambda L'}^{0\beta\alpha'}]$$

$$= (1/\kappa_a\rho_0^2)\sum_{\beta\Lambda}W[f_{\Lambda L'}^{0\beta\alpha'},(\gamma_{\Lambda L}^{0\beta\alpha})^*] \ .$$

This last quantity can be easily evaluated by noting that $f_{\Lambda L'}^{0\beta\alpha'}$ and $\gamma_{\Lambda L}^{0\beta\alpha}$ are regular and irregular vector solutions, respectively, of Eq. (B2). Therefore, a customary argument leads to

$$(d/dr)\left[r^2\sum_{\beta\Lambda}W[f_{\Lambda L'}^{0\beta\alpha'},(\gamma_{\Lambda L}^{0\beta\alpha})^*]\right] = 0$$

which entails that the quantity in large parentheses is a constant. Evaluation of this constant in the asymptotic region gives

$$\sum_{\beta\Lambda}W[f_{\Lambda L'}^{0\beta\alpha'},(\gamma_{\Lambda L}^{0\beta\alpha})^*] = (1/\kappa_a\rho_0^2)\delta_{LL'}\delta_{\alpha\alpha'} \ .$$

The final result is

$$D_{LL'}^{\alpha\alpha'} = (1/\kappa_\alpha\rho_0^2)((W[-ih^+,\gamma^{0*}]^{-1})^T)_{LL'}^{\alpha\alpha'} .$$

In the one-channel case, as in Refs. 16 and 35, we find the same result for the quantity $D_{LL''}^0$ in Eq. (2.49):

$$D_{LL''}^0 = (1/\pi\rho_0^2)((W[-ih^+,\gamma^{0*}]^{-1})^T)_{LL''}$$

taking into account the different normalization of f^0 and γ^0.

APPENDIX C

This appendix establishes a connection between the wave-function approach used in this article and an adaptation of the scattering path operator formalism[36,37] to multichannel problems. This connection will enable us to provide an alternative proof of the generalized optical theorem established in Ref. 16 which will be useful in making contact with the Green's-function approach to the problem of calculating photoabsorption cross sections. To avoid the confusing use of too many indices, we shall first demonstrate the optical theorem for the single-channel case. Then, we will describe the modifications required by the multichannel problem.

1. Scattering path operators in the single-channel case

Let $G^+(\kappa)$ be the advanced Green's function corresponding to the Hamiltonian H. $G^+(r,r';\kappa)$ satisfies the equation

$$[\kappa^2 + \Delta - V(r)]G^+(r,r';\kappa) = \delta(r-r') .$$

If we write the potential $V(r)$ as a sum of nonoverlapping potentials

$$V(r) = \sum_i V^i(r) ,$$

then one can define scattering path operators $\bar\tau^{ij}(\kappa)$ by

$$\bar\tau^{ij}(\kappa) \equiv V^i\delta_{ij} + V^i G^+(\kappa)V^j .$$

We shall also use a sum of scattering path operators that will be related to the amplitude B_L^i

$$\bar\tau^i(\kappa) \equiv \sum_j \bar\tau^{ij}(\kappa) .$$

The scattering path operators were introduced by Gyorffy and Stott.[36] Physically, $\bar\tau^{ij}(\kappa)$ gives the sum of all scattering paths that begin at atom i and terminate at

atom j. From the definition of the scattering path operators, one sees that $\bar\tau^{ij}(r,r';\kappa) = 0$ if r (r') is out of the range of atom i (j), i.e., in a region where $V^i(r)$ [$V^j(r')$] is zero, and that they are valid for any kind of potential (nonspherical and non-muffin-tin). Moreover, if a region of space I is subdivided in smaller regions I^j, then we find the useful property

$$\bar\tau^{II}(\kappa) = \sum_{I_i I_j} \bar\tau^{I_iI_j}(\kappa) . \tag{C1}$$

As can be seen from the definition of the scattering path operators, we have

$$\sum_{ij} \bar\tau^{ij}(\kappa) = T(\kappa) , \tag{C2}$$

where $T(\kappa)$ is the t matrix of the full potential.

Therefore, the scattering path operators are obtained from a space partioning of the t matrix. We shall work mainly in the harmonic representation $|\kappa L\rangle$ defined in the real-space representation by $\langle r|\kappa L\rangle \equiv J_L(\kappa r)$. In this representation, we can define the matrix elements

$$\bar\tau_{LL'}^{ij}(\kappa) = \langle \kappa L|\bar\tau^{ij}(\kappa)|\kappa L'\rangle$$

$$= \int d^3r\, d^2r'\, J_L(\kappa r)\bar\tau^{ij}(r,r';\kappa)J_{L'}(\kappa r') .$$

2. The optical theorem for scattering path operators

The proof of the optical theorem follows standard arguments.[38] From the definition of the scattering path operators we obtain

$$\langle \kappa L|\bar\tau^{ij}(\kappa)|\kappa L'\rangle = \langle \kappa L|V^i|\kappa L'\rangle\delta_{ij}$$

$$+ \langle \kappa L|V^i G^+(\kappa)V^j|\kappa L'\rangle .$$

If we insert a resolution of the identity in scattering states (the presence of bound states can be easily taken into account[8,38]),

$$1 = \int d\kappa' \sum_{L''} |\psi_{L''}^+(\kappa')\rangle(2\kappa'^2/\pi)\langle \psi_{L''}^+(\kappa')| ,$$

where $|\psi_{L''}^+(\kappa')\rangle$ is the solution of the Lippmann-Schwinger equation

$$|\psi_{L''}^+(\kappa')\rangle = |\kappa'L''\rangle + G_0^+(\kappa')V|\psi_{L''}^+(\kappa')\rangle ,$$

we obtain

$$\langle \kappa L|\bar\tau^{ij}(\kappa)|\kappa L'\rangle = \langle \kappa L|V^i|\kappa L'\rangle\delta_{ij} + \sum_\Lambda \int \frac{2\kappa'^2 d\kappa'}{\pi} \frac{\langle \kappa L|V^i|\psi_\Lambda^+(\kappa')\rangle\langle \psi_\Lambda^+(\kappa')|V^j|\kappa L'\rangle}{\kappa^2 - \kappa'^2 + i\epsilon} .$$

In the last equation, we make use of the relation $V^i|\psi_\Lambda^+(\kappa')\rangle = \bar\tau^i(\kappa')|\kappa'\Lambda\rangle$, obtaining

$$\langle \kappa L|\bar\tau^{ij}(\kappa)|\kappa L'\rangle = \langle \kappa L|V^i|\kappa L'\rangle\delta_{ij} + \sum_\Lambda \int \frac{2\kappa'^2 d\kappa'}{\pi} \frac{\langle \kappa L|\bar\tau^i|\kappa'\Lambda\rangle\langle \kappa L'|\bar\tau^j|\kappa'\Lambda\rangle^*}{\kappa^2 - \kappa'^2 + i\epsilon} .$$

and then interchange i and j, L and L', and take the complex conjugate. Subtracting the resulting equation from the original one gives the optical theorem

$$\langle \kappa L | \bar{\tau}^{ij}(\kappa) | \kappa L' \rangle - \langle \kappa L' | \bar{\tau}^{ji}(\kappa) | \kappa L \rangle^*$$

$$= -2i\kappa \sum_\Lambda \langle \kappa L | \bar{\tau}^i | \kappa \Lambda \rangle \langle \kappa L' | \bar{\tau}^j | \kappa \Lambda \rangle^* \; ,$$

where we have made use of the distribution identity

$$\frac{1}{\kappa^2 - \kappa'^2 + i\epsilon} - \frac{1}{\kappa^2 - \kappa'^2 - i\epsilon} = -2i\pi\delta(\kappa^2 - \kappa'^2)$$

$$= \frac{-i\pi}{\kappa}\delta(\kappa - \kappa') \; .$$

In a real spherical harmonics basis, the symmetry of the Green's function[39]

$$G^+(\mathbf{r},\mathbf{r}';\kappa) = G^+(\mathbf{r}',\mathbf{r};\kappa)$$

leads to the additional relation

$$\langle kL | \bar{\tau}^{ij}(\kappa) | k'L' \rangle = \langle k'L' | \bar{\tau}^{ji}(\kappa) | kL \rangle \; ,$$

so that the optical theorem for scattering path operators takes the simpler form

$$\mathrm{Im}\langle \kappa L | \bar{\tau}^{ij}(\kappa) | \kappa L' \rangle$$

$$= -\kappa \sum_{L''} \langle \kappa L | \bar{\tau}^i(\kappa) | \kappa L'' \rangle \langle \kappa L' | \bar{\tau}^j(\kappa) | \kappa L'' \rangle^* \; .$$

The scattering path operators used in practice are not $\bar{\tau}^{ij}$ but operators centered on the corresponding sites and defined by

$$\tau^{ij}(\mathbf{r} - \mathbf{R}_i, \mathbf{r}' - \mathbf{R}_j) = \bar{\tau}^{ij}(\mathbf{r},\mathbf{r}') \; ,$$

so that now, the matrix elements become

$$\tau_{LL'}^{ij}(\kappa) = \langle \kappa L | \tau^{ij}(\kappa) | \kappa L' \rangle$$

$$= \int d^3r \, d^3r' J_L(\kappa \mathbf{r}) \tau^{ij}(\mathbf{r},\mathbf{r}';\kappa) J_{L'}(\kappa \mathbf{r}')$$

$$= \sum_{\Lambda\Lambda'} J_{L\Lambda}^{i0} \bar{\tau}_{\Lambda\Lambda'}^{ij}(\kappa) J_{\Lambda'L'}^{0j} \; . \qquad (C3)$$

The operator $\tau_{LL'}^{ij}$ has been calculated in Sec. III A. For the single-channel case and within the (nonspherical) muffin-tin approximation, the interstitial contribution is zero in Eq. (9) and we obtain the standard muffin-tin equation (Ref. 40 and references therein)

$$\sum_{jL'} \tau_{LL'}^{ij} [(T_a^{-1})_{L'L''}^j \delta_{jk} - \kappa H_{L'L''}^{jk}] = \delta_{ik}\delta_{LL''} \; . \qquad (C4)$$

Now the equation giving the amplitudes $B_L^j(L_0)$ is, still for nonspherical-muffin-tin potentials

$$\sum_{Lj} [(T_a^{-1})_{LL'}^i \delta_{ij} - \kappa H_{LL'}^{ij}] B_{L'}^j(L_0) = J_{L'L_0}^{i0} \; .$$

By application of Eqs. (A27) and (C3), we then find

$$B_L^i(L_0) = \sum_{L'j} \tau_{LL'}^{ij} J_{L'L_0}^{j0}$$

$$= \sum_{L'j} J_{LL'}^{i0} \langle \kappa L' | \bar{\tau}^{ij}(\kappa) | \kappa L_0 \rangle$$

$$= \sum_{L'} J_{LL'}^{i0} \langle \kappa L' | \bar{\tau}^i(\kappa) | \kappa L_0 \rangle \; .$$

In particular, if the photoabsorbing site is at the origin of coordinates, we have

$$B_L^0(L_0) = \langle \kappa L | \bar{\tau}^0(\kappa) | \kappa L_0 \rangle \; .$$

Since $\bar{\tau}^i(\kappa)$ is independent on the way the total potential is divided [it depends only on $V^i(\mathbf{r})$ and $V(\mathbf{r})$], the above result can be generalized to a non-muffin-tin potential: it is sufficient to fill the space with empty spheres to establish Eq. (8), as we shall shortly see. With these notations, making use of Eq. (A22), the optical theorem reads

$$\sum_{L_0} B_L^i(L_0)[B_{L'}^j(L_0)]^* = (-1/2i\kappa)(\tau_{LL'}^{ij} - \tau_{L'L}^{ji*})$$

$$= (-1/\kappa)\mathrm{Im}(\tau_{LL'}^{ij}) \; ,$$

the last step holding in the real harmonic representation.

3. Applications of the scattering path operators

To give further insight into the power of the scattering path operators, we shall show that they enable us to derive the non-muffin-tin equation (9) from the muffin-tin one (C4). We shall be restricted to the single-channel case, but the extension to the general case is straightforward. The trick is to fill the interstitial region with virtual spheres. Then we are back to the muffin-tin case, and we can write the equation for the scattering path operators as

$$(T_s^{-1} - \kappa H^{ss})\tau^{ss} = 1 \; ,$$

where the index s refers collectively to all the spheres. Now the set of spheres can be divided into atomic spheres a and interstitial spheres i. The muffin-tin equation is therefore

$$\begin{bmatrix} T_a^{-1} - \kappa H^{aa} & -\kappa H^{ai} \\ -\kappa H^{ia} & T_i^{-1} - \kappa H^{ii} \end{bmatrix} \begin{bmatrix} t^{aa} & \tau^{ai} \\ \tau^{ia} & \tau^{ii} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \; ,$$

where indices a and i refer collectively to the atomic and interstitial spheres. By eliminating the scattering path operators involving the interstitial indices we find

$$[T_a^{-1} - \kappa H^{aa} - \kappa^2 H^{ai}(T_i^{-1} - \kappa H^{ii})^{-1} H^{ia}]\tau^{aa} = 1 \; .$$

We can identify the terms of the last equation with those of Eq. (9). Notice that $(T_i^{-1} - \kappa H^{ii})^{-1}$ represents the scattering path operators of the spheres of the interstitial region (without atoms). Therefore, the term

$$\kappa^2 H^{ai}(T_i^{-1} - \kappa H^{ii})^{-1} H^{ia}$$

describes the way outgoing waves from atomic centers are transported to the interstitial region ($-\kappa H^{ia}$), scattered by the interstitial potential ($T_i^{-1} - \kappa H^{ii})^{-1}$, and brought back to the atoms ($-\kappa H^{ai}$). Furthermore, for i and j in the interstitial region and k and l referring to atomic sites one has, by Eq. (C4) for the interstitial potential and by Eqs. (A26) and (C3),

$$\sum_{\Lambda\Lambda'} \kappa^2 H_{L\Lambda}^{ki} [(T_a^{-1})_{\Lambda\Lambda'}^i \delta_j - \kappa H_{\Lambda\Lambda'}^{ij}]^{-1} H_{\Lambda'L'}^{jl}$$

$$= -\kappa^2 \int d^3r \, d^3r' H_L^+(\kappa \mathbf{r}_k) \bar{\tau}^{ij}(\mathbf{r},\mathbf{r}') H_{L'}^+(\kappa \mathbf{r}_l') \; ,$$

where $\tilde{\tau}^{ij}(\mathbf{r},\mathbf{r}')$ refers to the scattering path operators of the interstitial spheres alone. Then, the virtual spheres are disposed of by noticing that, according to Eqs. (C1) and (C2),

$$\sum_{ij} \tilde{\tau}^{ij}(\mathbf{r},\mathbf{r}') = T^I(\mathbf{r},\mathbf{r}') \; ,$$

where $T^I(\mathbf{r},\mathbf{r}')$ is the t matrix of the interstitial potential. With the last identity, we recover the definition of $(\Theta_I)_{LL'}^{kl}$,

$$(\Theta_I)_{LL'}^{kl} = \sum_{\Lambda\Lambda'} \sum_{ij} \kappa^2 H_{L\Lambda}^{ki} [(T_a^{-1})_{\Lambda\Lambda'}^i \delta_{ij} - \kappa H_{\Lambda\Lambda'}^{ij}]^{-1} H_{\Lambda'L'}^{jl}$$

$$= -\kappa^2 \int_{\Delta\Omega} d^3r\, d^3r'\, H_L^+(\kappa\mathbf{r}_k) T^I(\mathbf{r},\mathbf{r}') H_{L'}^+(\kappa\mathbf{r}_l') \; .$$

In the same way, the additional term on the right-hand side of Eq. (8) can be identified with a term

$$\kappa H^{ai}(T_i^{-1} - \kappa H^{ii})^{-1} J^{i0}$$

which describes how the incident spherical wave is scattered by the interstitial potential into an incident wave on the atomic sites. Therefore, we again find the single-channel definition of the interstitial matrix elements $(\Theta_I)_{LL'}^{k0}$

$$(\Theta_I)_{LL'}^{k0} = \sum_{\Lambda\Lambda'} \sum_{ij} \kappa^2 H_{L\Lambda}^{ki} [(T_a^{-1})_{\Lambda\Lambda'}^i \delta_{ij} - \kappa H_{\Lambda\Lambda'}^{ij}]^{-1} J_{\Lambda'L'}^{j0}$$

$$= -i\kappa^2 \int_{\Delta\Omega} d^3r\, d^3r'\, H_L^+(\kappa\mathbf{r}_k) T^I(\mathbf{r},\mathbf{r}') J_{L'}(\kappa\mathbf{r}')$$

[we have used the notation $(\Theta_I)_{LL'}^{kl}$ instead of $(T_I)_{LL'}^{kl}$ because the scalar product is not taken with basis states $|\kappa L\rangle$]. In other words, by packing the interstitial region with spheres and using the properties of the scattering path operators, we have found the equation giving the (atomic site) scattering path operators in the presence of an interstitial potential:

$$\tau_{LL'}^{kl} = [(T_a^{-1} - \kappa H - \Theta_I)^{-1}]_{LL'}^{kl} \; .$$

Analogously, it is possible to take into account an outer sphere by starting from the muffin-tin equation with outer sphere. We fill the interstitial region with virtual spheres and we use the equation giving the scattering path operators with outer sphere

$$\begin{bmatrix} T_s^{-1} - \kappa H^{ss} & -\kappa J^{s0} \\ -\kappa J^{0s} & T_{OS}^{-1} \end{bmatrix} \begin{bmatrix} \tau^{ss} & \tau^{s0} \\ \tau^{0s} & \tau^{00} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \; .$$

Then one again splits the centers s into a (atomic) and i (interstitial), eliminates the scattering path operators involving interstitial and outer sphere indices, and finds an equation which includes all the previous cases:

$$\tau^{aa} = (T_a^{-1} - \kappa H^{aa} - \Theta_I^{aa} - \kappa^2 J^{a0}\theta^{00}J^{0a} - \kappa J^{a0}\theta^{00}\Theta_I^{0a}$$

$$- \kappa\Theta_I^{a0}\theta^{00}J^{0a} - \Theta_I^{a0}\theta^{00}\Theta_I^{0a})^{-1}$$

with the additional definitions

$$(\Theta_I)_{LL'}^{0l} = \sum_{\Lambda\Lambda'} \sum_{ij} \kappa^2 J_{L\Lambda}^{0i} [(T_a^{-1})_{\Lambda\Lambda'}^i \delta_{ij} - \kappa H_{\Lambda\Lambda'}^{ij}]^{-1} H_{\Lambda'L'}^{jl}$$

$$= -i\kappa^2 \int_{\Delta\Omega} d^3r\, d^3r'\, J_L(\kappa\mathbf{r}) T^I(\mathbf{r},\mathbf{r}') H_{L'}^+(\kappa\mathbf{r}_l') \; ,$$

$$(\Theta_I)_{LL'}^{00} = \sum_{\Lambda\Lambda'} \sum_{ij} \kappa^2 J_{L\Lambda}^{0i} [(T_a^{-1})_{\Lambda\Lambda'}^i \delta_{ij} - \kappa H_{\Lambda\Lambda'}^{ij}]^{-1} J_{\Lambda'L'}^{j0}$$

$$= \kappa^2 \int_{\Delta\Omega} d^3r\, d^3r'\, J_L(\kappa\mathbf{r}) T^I(\mathbf{r},\mathbf{r}') J_{L'}(\kappa\mathbf{r}') \; ,$$

$$\Theta^{00} = (T_{OS}^{-1} - \Theta_I^{00})^{-1} \; .$$

The importance of the scattering path operators stems from the fact that they can be used to evaluate the full Green's function, from which most properties can be evaluated. The diagonal part of the Green's function writes[40]

$$G(\mathbf{r}_i,\mathbf{r}_i') = \sum_{LL'} \sum_{\Lambda\Lambda'} Y_\Lambda(\hat{\mathbf{r}}_i) \underline{f}_{\Lambda L}^i (r_i) \tau_{LL'}^{ii} Y_{\Lambda'}(\hat{\mathbf{r}}_i') \underline{f}_{\Lambda'L'}^i (r_i')$$

$$- \sum_{L\Lambda} Y_\Lambda(\hat{\mathbf{r}}_<) \underline{f}_{\Lambda L}^i (r_<) g_L^i(\mathbf{r}_>) \; , \qquad (C5)$$

where $r_<$ ($r_>$) refers to the smaller (greater) of r_i and r_i', and where $g_L^i(\mathbf{r})$ is the wave function inside the sphere Ω_i that matches smoothly to $J_L(\mathbf{r})$ across the sphere, and where $\mathbf{r}_i$ and $\mathbf{r}_i'$ are within the sphere Ω_i. For completeness, the nondiagonal part of the Green's function is[40]

$$G(\mathbf{r}_i,\mathbf{r}_j') = \sum_{LL'} \sum_{\Lambda\Lambda'} Y_\Lambda(\hat{\mathbf{r}}_i) \underline{f}_{\Lambda L}^i (r_i) \tau_{LL'}^{ij} Y_{\Lambda'}(\hat{\mathbf{r}}_j') \underline{f}_{\Lambda'L'}^j (r_j') \; .$$

$$(C6)$$

Note that Faulkner and Stocks have established the expressions (C5) and (C6) for the muffin-tin case, but by filling the interstitial region with empty spheres, one can show that it is true in general.

For instance, the absorption cross section is given by[36,37]

$$\sigma = -4\pi\alpha\omega\langle \varphi_c(\mathbf{r}_i)|\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}_i|\mathrm{Im}[G(\mathbf{r}_i,\mathbf{r}_i')]|\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}_i'|\varphi_c(\mathbf{r}_i')\rangle \; ,$$

or, with complex spherical harmonics

$$\sigma = -4\pi\alpha\omega\, \mathrm{Im}[\langle \varphi_c(\mathbf{r}_i)|\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}_i|G(\mathbf{r}_i,\mathbf{r}_i')|\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}_i'|\varphi_c(\mathbf{r}_i')\rangle]$$

from which we again find the expression (21) in the single-channel case. It might be useful to state that the above two equations are true also when using complex potentials, σ is then the total absorption (elastic plus inelastic). All the results established above can be transposed to the multichannel case, as we demonstrate now for the optical theorem.

4. Multichannel case

The modifications required to treat the multichannel case are relatively straightforward. First, all the operators will now be matrices of operators indexed by the channel numbers. For instance, we define the Hamiltonian operator by

$$H^{\alpha\beta} = -\Delta + (E_\alpha^{N-1} - E_g^{N-1})\delta_{\alpha\beta} + V_{\alpha\beta} \; .$$

We assume it to be Hermitian so that $V_{\alpha\beta} = V_{\beta\alpha}^*$. The onset of the continuum spectrum is the ground state of the

$(N-1)$-body problem.[38] Therefore, there exists a channel γ, called the elastic channel, for which $E_\gamma^{N-1}=E_g^{N-1}$. Let κ be the wave number of the elastic channel $(\kappa^2=E-E_g^{N-1})$. The components of the wave-function vectors will be denoted by $|f_\alpha(\kappa,\beta,L)\rangle$ which is the αth component of the scattered wave function corresponding to an incident spherical wave $|\kappa_\beta L\rangle$ (with $\kappa_\beta^2=\kappa^2-E_\beta^{N-1}+E_g^{N-1}$) in channel β. $|f_\alpha(\kappa,\beta,L)\rangle$ is the solution of the Lippmann-Schwinger equation

$$|f_\alpha(\kappa,\beta,L)\rangle=|\kappa_\beta L\rangle\delta_{\alpha\beta}+\sum_{\alpha'}G_0^\alpha(\kappa_\alpha)V_{\alpha\alpha'}|f_{\alpha'}(\kappa,\beta,L)\rangle\ .$$

This yields

$$\sum_{\alpha'}H^{\alpha\alpha'}|f_{\alpha'}(\kappa,\beta,L)\rangle=\kappa^2|f_\alpha(\kappa,\beta,L)\rangle\ .$$

The Green's function becomes a matrix $G^{\alpha\beta}(\mathbf{r},\mathbf{r}';\kappa)$ satisfying

$$\sum_\beta(\kappa^2-H^{\alpha\beta})G^{\beta\gamma}(\mathbf{r},\mathbf{r}';\kappa)=\delta(\mathbf{r}-\mathbf{r}')\delta_{\alpha\gamma}$$

and the scattering path operators are matrices whose elements are defined by

$$\bar\tau^{ij\alpha\beta}(\kappa)\equiv V_{\alpha\beta}^i\delta_{ij}+\sum_{\alpha'\beta'}V_{\alpha\alpha'}^iG^{\alpha'\beta'}(\kappa)V_{\beta'\beta}^j\ .$$

When the interstitial potential is taken into account, we can also define scattering path operators involving it. For instance we have

$$\bar\tau^{iI\alpha\beta}(\kappa)\equiv\sum_{\alpha'\beta'}V_{\alpha\alpha'}^iG^{\alpha'\beta'}(\kappa)V_{\beta'\beta}^I\ .$$

The proof of the optical theorem is exactly parallel to the single-channel treatment. The only changes are the expression

$$\sum_{\alpha'}V_{\alpha\alpha'}^i|f_{\alpha'}(\kappa,\beta,L)\rangle=\bar\tau^{i\alpha\beta}(\kappa)|\kappa_\beta L\rangle\ ,$$

where

$$\bar\tau^{i\alpha\beta}(\kappa)=\sum_j\bar\tau^{ij\alpha\beta}(\kappa)$$

(the sum including the interstitial potential), and the resolution of the identity

$$1\delta_{\alpha\beta}=\sum_\gamma\int d\kappa'_\gamma\sum_L f_\alpha(\kappa',\gamma,L)\rangle(2\kappa_\gamma'^2/\pi)\langle f_\beta(\kappa',\gamma,L)|$$

(C7)

which can be obtained from the closure relation for the N-electron wave functions, or by noticing that Eq. (C7) is obvious for the free solutions and can be transposed to the interacting case by using the isometric property of Møller operators.[3] Again, the presence of bound states of the potential can be dealt with easily. With these notations, one can repeat the reasoning of the single-scattering case, noticing that

$$-2i\pi\delta(\kappa^2-\kappa_\gamma'^2)\frac{2\kappa_\gamma'^2d\kappa_\gamma'}{\pi}=-2i\pi\delta(\kappa_\gamma^2-\kappa_\gamma'^2)\frac{2\kappa_\gamma'^2d\kappa_\gamma'}{\pi}$$

$$=-2i\kappa_\beta\delta(\kappa_\gamma-\kappa_\gamma')\ ,$$

and one obtains the optical theorem for multichannel scattering path operators:

$$\langle\kappa_aL|\bar\tau^{ij\alpha\beta}(\kappa)|\kappa_\beta L'\rangle-\langle\kappa_\beta L'|\bar\tau^{ji\beta\alpha}(\kappa)|\kappa_\alpha L\rangle^*=-2i\sum_\gamma\kappa_\gamma\sum_\Lambda\langle\kappa_\alpha L|\bar\tau^{i\alpha\gamma}(\kappa)|\kappa_\gamma\Lambda\rangle\langle\kappa_\beta L'|\bar\tau^{j\beta\gamma}(\kappa)|\kappa_\gamma\Lambda\rangle^*\ .$$

As for the single-channel situation, one obtains

$$B_L^{i\alpha}(L_\beta)=\sum_{L'j}\tau_{LL'}^{ij\alpha\beta}J_{L'L_\beta}^{j0\beta}$$

$$=\sum_{L'j}J_{LL'}^{i0\alpha}\langle\kappa_\alpha L'|\bar\tau^{ij\alpha\beta}(\kappa)|\kappa_\beta L_\beta\rangle\ ,$$

where the sum over j now includes the interstitial potential. This leads to

$$B_L^{i\alpha}(L_\beta)=\sum_{L'}J_{LL'}^{i0\alpha}\langle\kappa_\alpha L'|\bar\tau^{i\alpha}(\kappa)|\kappa_\beta L_\beta\rangle\ ,$$

so that the optical theorem yields

$$\sum_\beta\kappa_\beta\sum_{L_\beta}[B_L^{i\gamma}(L_\beta)]^*B_{L'}^{i\gamma'}(L_\beta)$$

$$=\frac{-1}{2i}\{\tau_{L'L}^{ji\gamma'\gamma}(\kappa)-[\tau_{LL'}^{ij\gamma\gamma'}(\kappa)]^*\}\ ,$$

which is the result required to establish Eq. (21). The optical theorem can also be proved by the more direct methods developed in Ref. 16.

In a real sphereical harmonics basis and with real potentials, we have the additional relation

$$\langle\kappa_\alpha L|\bar\tau^{ij\alpha\beta}(\kappa)|\kappa_\beta L'\rangle=\langle\kappa_\beta L'|\bar\tau^{ji\beta\alpha}(\kappa)|\kappa_\alpha L\rangle$$

and the optical theorem takes the simpler form

$$\mathrm{Im}\langle\kappa_\alpha L|\bar\tau^{ij\alpha\beta}(\kappa)|\kappa_\beta L'\rangle$$

$$=-\sum_\gamma\kappa_\gamma\sum_\Lambda\langle\kappa_\alpha L|\bar\tau^{i\alpha\gamma}(\kappa)|\kappa_\gamma\Lambda\rangle\langle\kappa_\beta L'|\bar\tau^{j\beta\gamma}(\kappa)|\kappa_\gamma\Lambda\rangle^*\ .$$

As a consequence one has

$$\sum_\beta\kappa_\beta\sum_{L_\beta}[B_L^{i\gamma}(L_\beta)]^*B_{L'}^{i\gamma'}(L_\beta)=-\mathrm{Im}\tau_{L'L}^{ji\gamma'\gamma}(\kappa)$$

$$=-\mathrm{Im}\tau_{LL'}^{ij\gamma\gamma'}(\kappa)\ .$$

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