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ABSTRACT

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 the multiple scattering theory. 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. We derive a new multiple scattering expansion that takes into account interchannel transitions as well. As an application we discuss the homogeneous and inhomogenous mixed-valent compounds, where the theory provides a clue at the resolution of the "threshold puzzle" and sheds light onto the relation between photoemision and photoabsorption spectroscopy.

1. INTRODUCTION

The study of the electronic and structural properties of matter has received in the recent past a great impulse due to the advent of synchrotron radiation. The unique properties of this radiation source, like its intensity, brilliance, polarization, tunability and collimation, to cite a few, coupled with sophisticated data acquisition techniques have made possible the explosive growth of all kinds of spectroscopic research. In particular inner shell photoemission and photoabsorption spectroscopies have

received progressively more and more attention as a source of information about the electronic and structural properties of physical systems. Strangely enough, these high energy spectroscopies have been shown to be able to provide useful information on both the excited as well as the ground state of the systems under investigation.

The realization of these potentialities has stimulated a parallel development of the theoretical schemes needed to interpret and analyse the experimental observations. On the structural side, for example, the multiple scattering (m.s.) theory has offered a unifying scheme of interpretation that encompasses a wide variety of physical cases, ranging from molecules in gas phase to adsorbates, from extended periodic systems, like crystals, to disordered or amorphous materials, from large atomic clusters to small ones. The price paid for this generality is the restriction of the fields of application of the theory to those cases that are amenable to a description in terms of an effective one particle scheme. This approach is certainly viable when both the initial and final states can be reasonably described in terms of a single Slater determinant (or configuration).

However all the phenomena connected to the excitation dynamics, like screening, polarization, relaxation, autoionization and decay fall outside the realm of the one electron approach. Configuration interaction and in general many-body techniques are called for in this case. As a consequence the understanding of those systems where electronic correlation 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 obscured by electronic correlation effects.

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 costituents 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 m.s. 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 m.s. 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.

It turns out that this multichannel m.s. approach is substantially equivalent to the configuration interaction method used by FANO, DAVIS and FELDKAMPS [1] to describe the interaction effects of bound and continuum configurations in the photoabsorption and photoemission spectra of atomic systems. The novelty here is that one can incorporate such a scheme in an extended system, allowing at the same time the description of the atomic geometrical arrangement in the real space. This is what

is needed for the realistic treatment of an intermediate valence (I.V.) system where one has two or more localized atomic configurations interacting with conduction states. In the photoabsorption process of an inner shell electron one is substantially observing the projection of this complicated many-body ground state onto the photoabsorbing site. This fact allows one to look at the local electronic structure of the ground state and to derive information about the configurations present in it.

A good understanding of the physics of these systems and a satisfactory description of the photoemission and photoabsorption spectra has been achieved by KOTANI, GUNNARSON and SCHONHAMMER [2] on the basis of the Anderson impurity model, using a fitting procedure for the Hamiltonian parameters.

The theory to be presented here will allow a first principle calculation of the spectra of I.V. systems. At the same time it will elucidate the relation between structure and electronic dynamics on one hand and the mechanism of transition from the adiabatic to the sudden regime on the other. These problems ask indeed interesting theoretical questions which are not yet well understood. It is hoped that the theoretical framework provided by the multichannel multiple scattering theory may help to clarify these points.

2   THE MULTICHANNEL MULTIPLE SCATTERING THEORY

The derivation of the multichannel m.s. equations follows very closely the analogous method used in the case of non muffin-tin potentials by NATOLI et al.[3]. The reader is referred to this paper and to ref.[4] for further details and for the general treatment.

We begin with the total absorption cross section, given by

$$\sigma(\omega)=4\pi^2\alpha\hbar\omega \ \Sigma_f \ | \ (\Psi_f^N | \, \epsilon \cdot \sum_{i=1}^{N} \, \mathbf{r}_i \, |\Psi_i^N) |^2 \, \delta \, (\hbar\omega - E_f + E_i) \qquad (2.1)$$

where $\Psi_{i,f}^N$ are the many-body initial and final state wave functions for N electrons in the system and the sum over the final states Σ is intended also over all directions of the photoemitted electrons. $\hbar\omega$ is the incoming photon energy and ϵ its polarization.

For transitions from a core state we assume that, to a good approximation,

$$\Psi_i^N = \sqrt{N!} \, A \ \phi_c \, (\mathbf{r}) \Sigma_n \, c_n \Phi_n^{N-1} \, (\mathbf{r}_1 ... \mathbf{r}_{N-1})$$

$$= \sqrt{N!} A \phi_c \, (\mathbf{r}) \, \Psi_G^{N-1} \, (\mathbf{r}_1 ... \mathbf{r}_{N-1}) \qquad (2.2)$$

where A is the usual antisymmetrizing operator: $A = (1/N!) \Sigma_p (-1)^P P$ $(A^2 = A)$ and $\Phi_n^{N-1}(\mathbf{r}_1 ... \mathbf{r}_{N-1})$ are

Slater determinants describing the configurations present in the initial state wave function Ψ_i^N. Normalization imposes $\Sigma_n |c_n|^2 = 1$, if $\langle \phi_c | \phi_c \rangle = 1$.

Similarly we assume that, by expanding $\Psi_f^N(r, r_1 \ldots r_{N-1})$ in terms of the complete set $\Psi_\alpha^{N-1}(r_1 \ldots r_{N-1})$, we can write

$$\Psi_f^N = \sqrt{N!} \, A \sum_\alpha f_\alpha(r) \, \Psi_\alpha^{N-1}(r_1 \ldots r_{N-1}) \qquad (2.3)$$

We take the functions Ψ_α^{N-1} to be eigenstates of the N-1 electron Hamiltonian

$$H_{N-1} = -\sum_{i=1}^{N-1} \nabla_i^2 - \sum_{i=1}^{N-1} \sum_{k=1}^{P} \frac{2Z_k}{|r_i - R_k|} + \sum_{i<j}^{1 \le i, j \le N-1} \frac{2}{|r_i - r_j|} \qquad (2.4)$$

with eigenvalues E_α^{N-1}:

$$H_{N-1} \, \Psi_\alpha^{N-1} = E_\alpha^{N-1} \, \Psi_\alpha^{N-1} \qquad (2.5)$$

where $\sum_{k=1}^{P} Z_k = N$, R_k denotes the nuclear positions and Z_k are the associated charges.

We use throughout atomic units of length and Rydberg units of energy. The factor $\sqrt{N!}$ in Eq. (2.3) again assumes that we can approximate Ψ_α^{N-1} by a linear combination of Slater determinants, belonging to a continuum spectrum if Ψ_α^{N-1} does. In any case we assume for simplicity all continuum states normalized into a box enclosing the system: one may eventually take the limit of the box linear dimensions to infinity and transform the sum in Eq. (2.3) into an integral.

The final state wave function Ψ_f is an eigenstate, with energy $E = \hbar\omega + E_i^N$, of the N-electron Hamiltonian

$$H_N = -\nabla_r^2 + \sum_{i=1}^{N-1} \frac{2}{|r - r_i|} - \sum_{k=1}^{P} \frac{2Z_k}{|r - R_k|} + H_{N-1}$$

$$= -\nabla_r^2 + V(r, r_i, R_k) + H_{N-1} \qquad (2.6)$$

Therefore

$$H_N \, \Psi_f^N = E \, \Psi_f^N \qquad (2.7)$$

and we shall henceforth assume that $E_i^N = E_g^N$ is the ground state of the system.

The insertion of Eq. (2.3) into Eq. (2.7) gives

$$(-\nabla^2_r + V(\mathbf{r},\mathbf{r}_i,\mathbf{R}_k) + H_{N-1}) \, A\Sigma_\alpha f_\alpha(\mathbf{r})\Psi_\alpha^{N-1}(\mathbf{r}_1...\mathbf{r}_{N-1}) =$$

$$= E \, A\Sigma_\alpha f_\alpha(\mathbf{r})\Psi_\alpha^{N-1}(\mathbf{r}_1...\mathbf{r}_{N-1}) \qquad (2.8)$$

and by multiplying on the left by Ψ_α^{N-1} and integrating we obtain the set of equations

$$(\nabla^2 + E - E_\alpha^{N-1}) \, f_\alpha(\mathbf{r}) = \Sigma_{\alpha'}[\, V_{\alpha\alpha'}(\mathbf{r},\mathbf{R}_k) + W_{\alpha\alpha'}(\mathbf{r},\mathbf{R}_k)\,]\, f_{\alpha'}(\mathbf{r}) \qquad (2.9)$$

where

$$V_{\alpha\alpha'}(\mathbf{r},\mathbf{R}_k) = \int \prod_{i=1}^{N-1} d^3r_i \Psi_\alpha^{N-1}(\mathbf{r}_1...\mathbf{r}_{N-1})$$

$$V(\mathbf{r},\mathbf{r}_i,\mathbf{R}_k) \, \Psi_{\alpha'}^{N-1}(\mathbf{r}_1...\mathbf{r}_{N-1}) \qquad (2.10)$$

is a direct potential term and we have lumped all the exchange terms into the quantities $W_{\alpha\alpha'}(r,R_k)$ which are thus complicated, non local, exchange potentials for which a suitable, local approximation has to be found. If we impose the condition, as we shall do, that the functions $f_\alpha(r)$ be orthogonal to all the one particle states present in the configurations making up the ground state wave function (so as to ensure the orthogonality condition $(\Psi_f^N \mid \Psi_g^N)=0$) as well as to those configurations that enter in all the Ψ_α^{N-1}, then the exchange term is given by

$$W_{\alpha\alpha'}(\mathbf{r},\mathbf{R}_k) = 1/f_\alpha(\mathbf{r}) \int \prod_{i=1}^{N-1} d^3r_i \Psi_\alpha^{N-1}(\mathbf{r}_1...\mathbf{r}_{N-1}) V(\mathbf{r},\mathbf{r}_i,\mathbf{R}_k)$$

$$\sum_{P(\neq E)} (-1)^P \, Pf_{\alpha'}(\mathbf{r}_i)\Psi_{\alpha'}^{N-1}(\mathbf{r}_1...\mathbf{r}...\mathbf{r}_{N-1}) \qquad (2.11)$$

We refer to the appropriate literature for the transformation of this non local operator into a local one [5]. Henceforth we shall assume that this transformation has been performed and that our problem is to solve the set of coupled Schrödinger equations with local potentials.

Since $E=\hbar\omega + E_g^N$ we can write in Eq. (2.9)

$$E - E_\alpha^{N-1} = \hbar\omega + E_g^N - E_\alpha^{N-1} = \hbar\omega + E_g^N - E_g^{N-1} - (E_\alpha^{N-1} - E_g^{N-1})$$

$$= \hbar\omega - I_c - \Delta E_\alpha = k_\alpha^2 \qquad (2.12)$$

since $E_g^{N-1} - E_g^N = I_c$ is the ionization potential for the core state and $\Delta E_\alpha = E_\alpha^{N-1} - E_g^{N-1}$ is the excitation energy left behind in the (N-1)-particle system. Therefore k_α is the wave-vector of the final state photoelectron.

Eqs. (2.9) can then be rewritten as

$$(\nabla^2 + k_\alpha^2)\ f_\alpha(\mathbf{r}) \ = \ \Sigma_{\alpha'}\ V_{\alpha\alpha'}(\mathbf{r}, \mathbf{R}_k)\ f_{\alpha'}(\mathbf{r}) \tag{2.13}$$

where for sake of brevity we have put $V_{\alpha\alpha'} = V_{\alpha\alpha'} + W_{\alpha\alpha'}$.

The functions $f_\alpha(\mathbf{r})$ have a simple physical meaning in the case of electron-molecule scattering. Through the asymptotic conditions

$$f_\alpha(\mathbf{r}) \ \underset{r\to\infty}{\sim} \ (e^{i\mathbf{k}_\alpha\cdot\mathbf{r}}\,\delta_{\alpha\underline{\alpha}} + f_\alpha(\hat{\mathbf{r}},\hat{\mathbf{k}}_\alpha)\ \frac{e^{ik_\alpha r}}{r}\ )\ N_\alpha \tag{2.14}$$

where the factor $N_\alpha = (k_\alpha/\pi)^{1/2}/(4\pi)$ is necessary to ensure normalization to one state per Rydberg, they describe an electron in the incoming channel $\underline{\alpha}$ with wave vector $\mathbf{k}_{\underline{\alpha}}$ which can be scattered in any outgoing channel α, with wave vector $\mathbf{k}_\alpha$, after loosing the energy ΔE_α. In the photoemission process we have to take the time-reversed state of Eq. (2.3) (complex conjugate if spin is neglected) so that the outgoing channels become incoming channels which interfere constructively in the wave packet describing the photoelectron so as to give an asymptotic plane wave propagating out to infinity with wave number $\mathbf{k}_{\underline{\alpha}}$.

Therefore Eqs. (2.13) are to be supplemented with the boundary conditions Eqs. (2.14) written by replacing $f_\alpha(\mathbf{r})$ with $f_\alpha^*(\mathbf{r})$. It would be more appropriate to write $f_\alpha(\mathbf{r})$ as $f_\alpha(\mathbf{r}\,;\mathbf{k}_{\underline{\alpha}})$ to make explicit the dependence on the boundary conditions. We shall introduce this more complete expression where necessary, otherwise the simpler form will be used.

It is fairly obvious then that in the expansion (2.3) the most important (N-1)-particle states are the excited states Ψ_α^{N-1} with a core hole corresponding to the photoejected electron, for which $E_g^{N-1}\text{-}E_g^N = I_c$, so that $k_\alpha^2 = \hbar\omega - I_c - \Delta E_\alpha$ is small compared to $V_{\alpha\alpha'}$. In this sense the Ψ_α^{N-1} are the relaxed excited states of H_{N-1}. The argument runs as follows. If $k_\alpha^2 \gg \hbar\omega - I_c = k_0^2$ and $k_\alpha^2 \gg |V_{\alpha\alpha'}(r_c)|$, where r_c is the radius of the atomic core, then to a first approximation we can neglect the potentials in the r.h.s. of Eqs. (2.13), so that, together with the boundary conditions Eqs. (2.14), we obtain

$$f_\alpha(\mathbf{r}) \ \sim \ e^{i\mathbf{k}_\alpha\cdot\mathbf{r}}\,\delta_{\alpha\underline{\alpha}}\ . \tag{2.15}$$

The procedure for solving Eqs. (2.13) with boundary conditions (2.14) (in the end we shall take the complex conjugate) closely follows Ref. [3]. Here we limit ourselves to present the relevant results deferring the interested reader to ref. [4] for a complete derivation. We describe any physical system as a collection of atoms whose dynamics is described by the potentials $V_{\alpha\alpha'}(r)$ as defined in Eqs. (2.10) and (2.11). For semplicity of presentation these latter are assumed to be zero beyond an effective muffin-tin radius, although the presence of intestitial potentials describing the dynamics of the medium in the region between the muffin-tin spheres would not modify the physical picture based on the

multiple scattering approach, it would only change the definitions of the propagators and the atomic T-matrices.

The results are best illustrated by beginning with the case of a single atom. The solution in the region outside the atom $\rho(r \in \Delta\Omega)$ can be written as

$$f_\alpha(r) = N_\alpha e^{ik_\alpha \cdot r} \delta_{\alpha\alpha}$$

$$- k_\alpha \Sigma_{LL} i^{l+1} h^+_l(k_\alpha r) Y_L(\hat{r}) \; B^\alpha_L(\underline{\alpha};\underline{L}) \; Y_L(\hat{k}_\alpha) \qquad (2.16)$$

whereas inside the muffin-tin sphere Ω of radius $\rho(r \in \Omega)$

$$f_\alpha(r;k_\alpha) =$$

$$\Sigma_L \; \Sigma_{\alpha'L'} \; \Sigma_L \; B^{\alpha'}_{L'}(\underline{\alpha};\underline{L}) \; i^l \; Y_L(\hat{k}_\alpha) \; f_{LL'}{}^{\alpha\alpha'}(r) Y_L(\hat{r}) \qquad (2.17)$$

Here the functions $f_{LL'}{}^{\alpha\alpha'}(r)$, for given α', L', are particolar vector solution components of index α,L of the system of radial equations derived from the system of Schrödinger equations (2.13) by writing

$$f_\alpha(r) = \Sigma_L \; f^\alpha_L(r) \; Y_L(\hat{r}) \qquad (2.18)$$

inserting into Eq. (2.13) and projecting onto Y_L. One finds

$$[1/r(d^2/dr^2)r + k_\alpha^2 - l(l+1)/r^2]f^\alpha_L(r) =$$

$$\Sigma_{\alpha'L'} \; V_{LL'}{}^{\alpha\alpha'}(r) \; f^{\alpha'}_{L'}(r) \qquad (2.19)$$

where it has been assumed that the expansion

$$V_{\alpha\alpha'}(r) = \Sigma_L \; V_L{}^{\alpha\alpha'}(r) Y_L(\hat{r}) \qquad (2.20)$$

is possible so that

$$V_{LL'}{}^{\alpha\alpha'}(r) = \Sigma_{L''} \; C_L{}^{L'}{}_{L''} \; V_{L''}{}^{\alpha\alpha'}(r) \qquad (2.21)$$

$C_L{}^{L'}{}_{L''}$ being the usual Gaunt coefficient defined as (using real spherical harmonics)

$$C_L{}^{L'}{}_{L''} = \int Y_L(\Omega) \; Y_{L'}(\Omega) \; Y_{L''}(\Omega) \; d\Omega \qquad (2.22)$$

If α runs from 1 to n_α and l from 0 to l_{max}, Eqs. (2.19) are a set of $n_\alpha(l_{max}+1)^2$ equations and consequently one can construct this number of linearly independent solutions $f_{LL'}{}^{\alpha\alpha'}(r)$ regular at the origin which, for given $\alpha'L'$ can be interpreted as vector solutions whose components are labelled by

αL. To start the integration one might take, for example, near the origin

$$f_{LL'}{}^{\alpha\alpha'}(r) \simeq r^{l}\, \delta_{LL'}\, \delta_{\alpha\alpha'}. \tag{2.23}$$

In one introduces the matrix $W(j,f)_{LL'}{}^{\alpha\alpha'}$ defined as

$$W(j,f)_{LL'}{}^{\alpha\alpha'} = W[j_{l}, f_{LL'}{}^{\alpha\alpha'}] \tag{2.24}$$

where $W[f,g]$ is the wronskian of the functions $f(r)$ and $g(r)$ calculated at $r=\rho$

$$W[f,g]=f(r)\,(d/dr)\,g(r) - g(r)\,(d/dr)\,f(r)\,|_{r=\rho} \tag{2.25}$$

and $j_l(k_\alpha r)$ is the usual spherical Bessel function of argument $k_\alpha r$, then

$$f_{LL''}{}^{\alpha\alpha''}(r) = \rho^{-2}\Sigma_{\alpha'L'}\, f_{LL'}{}^{\alpha\alpha'}(r)\,[W(j,f)^{-1}]_{L'L''}{}^{\alpha'\alpha''} \tag{2.26}$$

The general solution $f_\alpha(r)$ inside the muffin-tin sphere is therefore given by the linear combination

$$f_\alpha(r;k_\alpha) = \Sigma_L Y_L(r)\, \Sigma_{\alpha'L'}\, C_{L'}{}^{\alpha'}(k_\alpha)\, f_{LL'}{}^{\alpha\alpha'}(r) \tag{2.27}$$

By matching smoothly this solution with the solution (2.16) in the outer region at the muffin-tin radius ρ, one obtains an expression for $B_L{}^\alpha(\alpha,L)$, given below, and the relation

$$C_{L'}{}^{\alpha'}(k_\alpha) = \Sigma_L\, B_{L'}{}^{\alpha'}(\alpha,L)\, i^{l+1}\, Y_L(\hat{k}_\alpha) \tag{2.28}$$

The quantity $B_L{}^{\alpha'}(\alpha,L)$, by definition, is proportional to the atomic scattering amplitude $(Ta)^{\alpha\alpha}{}_{LL}$ into the angular momentum L and channel state α in response to an excitation with angular momentum L and channel state α. In terms of the matrix (2.24) and the analogous matrix $W(-ih^+,f)_{LL'}{}^{\alpha\alpha'}$ constructed with the Hankel function $h^+_l(k_\alpha r)$, one finds

$$-B^\alpha_L(\alpha;L) = (k_\alpha/\pi)^{1/2}(T_a)^{\alpha\alpha}{}_{LL} =$$

$$= (k_\alpha/\pi)^{1/2}\Sigma_{\alpha'L'}\,[W(j,f)]_{LL'}{}^{\alpha\alpha'}(k_\alpha)^{-1}\,[W(-ih^+,f)^{-1}]_{L'L}{}^{\alpha'\alpha} \tag{2.29}$$

This expression is obviously invariant under the transformation (2.26). One has in fact $W(j,f)_{LL'}{}^{\alpha\alpha'}= \rho^{-2}\,\delta_{\alpha\alpha'}\,\delta_{LL'}$ and

$$[W(-ih^+,f)^{-1}]_{LL'}{}^{\alpha\alpha'}= \underset{\alpha''L''}{\Sigma}\, W(j,f)_{LL''}{}^{\alpha\alpha''}\,[W(-ih^+,f)^{-1}]_{L''L'}{}^{\alpha''\alpha'}\,\rho^2.$$

Remembering that $-ih_l = n_l - ij_l$, where n_l is the Neuman function, one derives the relation

$$(T_a^{-1})^{\alpha\alpha'}{}_{LL'} \ = \ k_\alpha \Sigma_{\alpha''L''} [W(-ih^+,f)]_{LL''}{}^{\alpha\alpha''} [W(j,f)^{-1}]_{L''L'}{}^{\alpha''\alpha'} =$$

$$= \ k_\alpha \Sigma_{\alpha''L''} \ [W(n,f)]_{LL''}{}^{\alpha\alpha''} \ [W(j,f)^{-1}]_{L''L'}{}^{\alpha''\alpha'} - ik_\alpha \delta_{LL'} \cdot \delta_{\alpha\alpha'}$$

$$= \ (K_a^{-1})^{\alpha\alpha'}{}_{LL'} - ik_\alpha \delta_{LL'} \cdot \delta_{\alpha\alpha'} \qquad\qquad (2.30)$$

where K_a is the reactance matrix. This relation will be useful in the following. Notice that K_a is hermitian.

The choice (2.26) for the normalization of the regular solutions (2.23) of the system of radial Schrodinger equations (2.19) has the important consequence that the quantity controlling the amplitude of the wave function $f_\alpha(r)$ inside the muffin-tin sphere Ω in Eq. (2.17) is the same quantity that controls in Eq. (2.16) 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 Green's function or density of state approach, through the application of a generalized optical theorem.

When there are several atoms located at sites R_k, the same expressions (2.16) and (2.17) carry over to the many centre case, provided one introduces the quantities $B^\alpha{}_{kL}(\alpha,L)$ which describe the scattering amplitudes for spherical waves emanating from the atom located at R_k, and sums over all sites:

$$f_\alpha(r) = N_\alpha e^{ik_\alpha \cdot r} \delta_{\alpha\alpha}$$

$$- k_\alpha \Sigma_k \ \Sigma_{LL} \ i^{l+1} \ h^+{}_l (k_\alpha r_k) Y_L(\hat{r}_k) B^\alpha{}_{kL}(\alpha;L) \ Y_L(\hat{k}_\alpha) \qquad (2.16a)$$

where $r_k = r - R_k$, and r is referred to the origin of the coordinates.

Similarly, inside the muffin-tin sphere Ω_i of radius ρ_i, one has

$$f_\alpha{}^i (r_i; k_\alpha) \ =$$

$$\Sigma_L \Sigma_{\alpha'L'} \Sigma_L B^{\alpha'}{}_{iL'}(\alpha;L) i^l \ Y_L(\hat{k}_\alpha) f_{i;LL'}{}^{\alpha\alpha'} (r_i) Y_L(\hat{r}_i) \qquad (2.17a)$$

where now all coordinates are referred to R_i.

The new scattering amplitudes $B^\alpha{}_{iL}(\alpha,L)$ are now obtained as solutions of the multiple scattering equations

$$\sum_{\alpha'L'} (T_{ai}^{-1})^{\alpha\alpha'}{}_{LL'} \; B^{\alpha'}{}_{iL'} \, (\underline{\alpha};\underline{L}) \; +$$

$$+ \; \sum_{k \, (\neq i)} \sum_{L'} \; G^{\alpha}{}_{iL,kL'} \; B^{\alpha}{}_{kL'} \, (\underline{\alpha};\underline{L}) \; = - \; J^{\alpha}{}_{iL,oL} \; \delta_{\alpha\underline{\alpha}} (1/(k_\alpha \pi))^{1/2} \qquad (2.31)$$

one for each site i, which in fact describe the self-consistency conditions for their simultaneous existence, since now the scattering amplitude emanating from one site becomes an exciting amplitude for all other sites.

In Eqs. (2.31) the quantities $G^{\alpha}{}_{iL,kL'}$ are the usual spherical waves propagators with wave vectors k_α, given by

$$G^{\alpha}{}_{iL,kL'} \quad = \; 4\pi \; k_\alpha \; \sum_{L''} \; i^{1''+1-1'} C_L{}^{L'}{}_{L''} \, [-ih^+{}_{1''} (k_\alpha R_{ik})] \; Y_{L''} (\hat{R}_{ik})$$

$$= \; N^{\alpha}{}_{iL,kL'} \; - \; i \; J^{\alpha}{}_{iL,kL'} \qquad\qquad (2.32)$$

where $R_{ik}=R_i-R_k$, and $N^{\alpha}{}_{iL,kL'}$, $J^{\alpha}{}_{iL,kL'}$ have been defined in terms of the decomposition $-ih_l^+ = n_l - ij_l$. Moreover $(T_{ai})^{\alpha\alpha'}{}_{LL'}$ is the atomic T-matrix for the atom located at site i and o denotes the origin of the coordinates so that $R_{ko} = R_k$.

The quantities N and J, when considered as matrices in the site and angular momentum indices, are real symmetric. Notice the relations

$$J^{\alpha}{}_{iL,iL'} \; = \; k_\alpha \delta_{LL'} \qquad\qquad (2.33a)$$

$$\sum_{L} \; J^{\alpha}{}_{iL,oL} \; J^{\alpha}{}_{kL',oL} \; = \; k_\alpha J^{\alpha}{}_{iL,kL'} \qquad\qquad (2.33b)$$

Eqs. (2.31) can also be written in compact form

$$\sum_{k} \; \sum_{\alpha'L'} \; S^{\alpha\alpha'}{}_{iL,kL'} \; B^{\alpha'}{}_{kL'} \, (\underline{\alpha},\underline{L}) \; = \; -J^{\alpha}{}_{iL,oL} \, \delta_{\alpha\underline{\alpha}} / (k_\alpha \pi)^{1/2} \qquad (2.34)$$

and the multiple scattering matrix $S^{\alpha\alpha'}{}_{iL,kL'}$ can be cast into the form

$$S^{\alpha\alpha'}{}_{iL,kL'} \quad = (T_{ai}^{-1})^{\alpha\alpha'}{}_{LL'} \; \delta_{ik} + (1- \delta_{ik}) \; \delta_{\alpha\alpha'} \, G^{\alpha}{}_{iL,kL'}$$

$$= (K_{ai}^{-1})^{\alpha\alpha'}{}_{LL'} \; \delta_{ik} + (1- \delta_{ik}) \delta_{\alpha\alpha'} N^{\alpha}{}_{iL,kL'} - i\delta_{\alpha\alpha'} \, J^{\alpha}{}_{iL,kL'}$$

$$= M^{\alpha\alpha'}{}_{iL,kL'} - i\Delta^{\alpha\alpha'}{}_{iL,kL'} \qquad\qquad (2.35)$$

having used Eq. (2.33a). Here M and Δ are hermitian matrices; actually Δ is real symmetric. By solving Eqs. (2.34) with respect to $B^{\alpha}{}_{kL}(\underline{\alpha},\underline{L})$ and using Eq.(2.33b) one can now derive a generalized optical theorem, which will be used shortly,

$$\Sigma_{\alpha L} \; B^{\alpha}_{iL} (\underline{\alpha}; L) \; [B^{\alpha}_{kL'} (\underline{\alpha}; L)]^{*} \; = 1/\pi \; [(M-i\Delta)^{-1}\Delta \; (M+i\Delta)^{-1}]^{\alpha\alpha'}_{iL, kL'}$$

$$= 1/\pi \; \text{Im} \; [(M-i\Delta)^{-1}]^{\alpha\alpha'}_{iL, kL'} = 1/\pi \; \text{Im} \; \tau^{\alpha\alpha'}_{iL, kL'} \qquad (2.36)$$

where we have put $(M-i\Delta)^{-1} = S^{-1} = \tau$, which is the scattering path operator in the multichannel case. Taken for the diagonal elements, this equation gives the anticipated relation between the square of the wave function amplitude and the local projected density of states.

In order to obtain the total photoabsorption cross section, we have to sum over all possible photoelectron final states labelled by the index $\underline{\alpha}$ and integrate over all possible direction of emission $k_{\underline{\alpha}}$. If we assume that the initial core state is localized at site i, we need $f_{\alpha}^{i}(r_i, k_{\underline{\alpha}})$ of Eq.(2.17a). Since these wave functions are normalized to one state per Rydberg, we find, using Eqs. (2.1-3) and the projection properties $A^2 = A$,

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \; \Sigma_{\underline{\alpha}}$$

$$\int d\hat{k}_{\underline{\alpha}} \; | \; (\Sigma_{\alpha} f_{\alpha}^{i}(r; k_{\underline{\alpha}}) \Psi_{\alpha}^{N-1} \; | \; \varepsilon \cdot \overset{N}{\underset{m=1}{\Sigma}} \; r_m \; | N ! A \phi_c^{i}(r) \Psi_G^{N-1}) \; |^2$$

$$= 4\pi^2 \alpha \hbar \omega \; \Sigma_{\underline{\alpha}} \int d\hat{k}_{\underline{\alpha}} \; | \; (\Sigma_{\alpha} f_{\alpha}^{i}(r; k_{\underline{\alpha}}) \; | \; \varepsilon \cdot r \; | \phi_c^{i}(r)) \; S_{\alpha 0} |^2 \qquad (2.37)$$

The last step follows from the fact that we have assumed the orthogonality of the scattering states $f_{\alpha}^{i}(r_i, k_{\underline{\alpha}})$ to all the single particle orbitals appearing in the Ψ_{α}^{N-1}'s. We have also introduced the quantity $S_{\alpha 0} = (\Psi_{\alpha}^{N-1} | \Psi_G^{N-1})$ which represents the projection of Ψ_{α}^{N-1} onto the occupied configurations present in the initial ground state.

By introducing the expression (2.17a) into Eq.(2.37) performing the angular integration over $k_{\underline{\alpha}}$ and defining the atomic matrix elements

$$M^{\alpha\alpha'}_{LL'} = (f^{\alpha\alpha'}_{LL'}(r_i) Y_L(\hat{r}_i) \; | \varepsilon \cdot r | \; \phi_c^{i}(r_i)) \qquad (2.38)$$

we can rewrite Eq.(2.37) as

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \; \Sigma_{\underline{\alpha}L} \; \Sigma_{\alpha \cdot \alpha} \Sigma_{\beta \cdot \beta} \; \underset{L_f L'_f}{\Sigma} \Sigma_{LL'} \; S_{\alpha 0} \; M^{\alpha\beta}_{L_f L} \; B^{\beta}_{iL} (\underline{\alpha}; L)$$

$$[B^{\beta'}_{iL'} (\underline{\alpha}; L) \; M^{\alpha'\beta'}_{L'_f L'} \; S_{\alpha' 0}]^{*} \qquad (2.39a)$$

or

$$\sigma(\omega) = 4\pi \alpha \hbar \omega \; \Sigma_{\alpha \alpha'} \Sigma_{\beta \beta'} \; \underset{L_f L'_f}{\Sigma} \; \Sigma_{LL'} \; S_{\alpha 0} \; M^{\alpha\beta}_{L_f L}$$

$$\{ \text{Im} \; \tau^{\beta\beta'}_{iL, iL'} \} \; [M^{\alpha'\beta'}_{L'_f L'} \; S_{\alpha' 0}]^{*} \qquad (2.39b)$$

using the generalized optical theorem Eq.(2.36).

In a similar way, from Eq.(2.17a) it is immediate to write down an expression for the photoemission cross section for ejection of an electron into the state k_α with energy $k_\alpha^2 = \hbar\omega - I_c - \Delta E_\alpha$

$$d\sigma(\Delta E_\alpha)/ d\hat{k}_\alpha \, d\Delta E_\alpha = 4\pi^2 \alpha \hbar\omega \, | \, (\Sigma_\alpha f_\alpha^i(r;k_\alpha) \, | \, \varepsilon \cdot r \, | \, \phi_c^i(r) \,) \, S_{\alpha 0} |^2$$

$$= 4\pi^2 \alpha \hbar\omega \, | \, \sum_{\alpha L_f} \Sigma_{\alpha' L'} \, \Sigma_L \, B^{\alpha'}{}_{iL} \cdot (\alpha;L) \, i^\perp \, Y_L(\hat{k}_\alpha) \, M^{\alpha\alpha'}_{L_f L'} \, S_{\alpha 0} |^2 \qquad (2.40)$$

where the quantity ΔE_α represents now the binding energy. Notice that now it is no longer possible to take advantage of the generalized optical theorem (2.36). In both cases the sum over L_f is over the final angular momenta allowed by the dipole selection rule in Eq.(2.38).

The expressions (2.39) and (2.40) can be used to establish in some limiting cases a relation between photoemission and photoabsorption cross sections.

3. THE GENERALIZED MULTIPLE SCATTERING EXPANSIONS

In the expressions (2.39), (2.40) the structural information is contained in the inverse $\tau = S^{-1}$ of the multiple scattering matrix Eq. (2.35) in a rather involved way that intermingles dynamics as well as structure, through the presence of the structure matrix elements $G^\alpha{}_{iL,kL'}$. 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, remembering the notation introduced in section 2, we have

$$\tau = S^{-1} = (T_a^{-1} + G)^{-1} = (I + T_a G)^{-1} T_a$$

so that if the spectral radius $\rho (T_a G)$ of the matrix $T_a G$ is less than one, where $\rho (A)$ is the maximum modulus of the eigenvalues of A, then

$$(I + T_a G)^{-1} = \sum_{n=0}^{\infty} (-1)^n (T_a G)^n \qquad (3.1)$$

the series on the right being absolutely convergent relative to some matrix norm. For short we shall henceforth define $G^\alpha{}_{iL,iL'} \equiv 0$ to account for the factor $(1-\delta_{ik})$ in Eq. (2.35).

As a consequence the photoabsorption cross section Eq. (2.39b) can be expanded in an absolutely convergent series

$$\sigma(\omega) = \sum_{n=0}^{\infty} \sigma_n(\omega) \qquad (3.2)$$

where

$$\sigma_0(\omega) = 4\pi\alpha\hbar\omega \, \Sigma_{\alpha\alpha'} \, \Sigma_{\beta\beta'} \sum_{L_f L'_f} \Sigma_{LL'} \, (M_{eff})^{\beta}_{L_f L} \, Im(T_{ai})^{\beta\beta'}_{iL,iL'}$$

$$[(M_{eff})^{\beta'}_{L'_f L'}]^* \qquad (3.3a)$$

is a smoothly varying atomic cross section and

$$\sigma_n(\omega) = 4\pi\alpha\hbar\omega \, \Sigma_{\beta\beta'} \sum_{L_f L'_f} \Sigma_{LL'} \, (M_{eff})^{\beta}_{L_f L}$$

$$Im[(-1)^n \, (T_a G)^n \, T_a]^{\beta\beta'}_{iL,iL'} [(M_{eff})^{\beta'}_{L'_f L'}]^* \qquad (3.3b)$$

represents the contribution to the photoabsorption cross section coming from process where the photoelectron, before being ejected at infinity, leaves the photoabsorbing atom, located at site i, with angular momentum L and channel state β, is scattered (n-1) times by the surrounding atoms and returns to site i with angular momentum L' and channel state β'. All these events are eventually to be multiplied by the corresponding effective atomic matrix elements

$$(M_{eff})^{\beta}_{L_f L} = \sum_{\alpha} S_{\alpha 0} \, M^{\alpha\beta}_{L_f L} \quad \text{and} \quad (M_{eff})^{\beta}_{L'_f L'} = \sum_{\alpha} S_{\alpha' 0} \, M^{\alpha'\beta'}_{L'_f L'} \qquad (3.4)$$

and summed together to give the n-th 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 one channel case [6] 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 k_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 $A(k_\alpha) Sin[k_\alpha R_{tot} + \phi(k_\alpha)]$, each one with a different threshold energy corresponding to the energy loss ΔE_α suffered by the photoelectron to excite channel α (remember that $k_\alpha = [\hbar\omega - I_c - \Delta E_\alpha]^{1/2}$). 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 wether or not to use different threshold energies in the analysis of mixed valent homogeneous compounds [7] and in so doing helps the experimental analysis by reducing the number of unknowns.

In general the existence of an energy range where the condition $\rho(T_a G) < 1$ is satisfied, follows from the asimptotic behaviour of the scattering amplitudes at high photoelectron energy, since $\lim(k_\alpha \to \infty)|(T_a)^{\alpha\alpha'}{}_{LL'}| = 0$. Actually in this regime one can write

$$(T_a)^{\alpha\alpha'}{}_{LL'} \simeq t^\alpha{}_{al}\delta_{LL'}\delta_{\alpha\alpha'} \quad \text{and} \quad M^{\alpha\alpha'}{}_{LL'} \simeq M^\alpha{}_L \delta_{LL'}\delta_{\alpha\alpha'} \tag{3.5}$$

since the photoelectron is sensitive only to the atomic cores, which are spherically symmetric and only the "incoming" channel $f_\alpha(r)$ in Eq. (2.14) is relevant, following the same argument leading to (2.15).

The fact that in this limit the m.s. matrix S in Eq. (2.35) 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 the same Eq. (2.35) and Eq. (2.30) we in fact observe that the various channels interfere through the off-diagonal elements of the inverse of the reactance matrix $(K_a^{-1})^{\alpha\alpha'}{}_{LL'}(\alpha \neq \alpha')$. In the high energy limit, these matrix elements go to zero, due to Eqs. (3.5), so that in the expression (2.39) for photoabsorption the different channels decouple and one recover the result of the sudden approximation [8]. In other words the quantities $(K_a^{-1})^{\alpha\alpha'}{}_{LL'}$ control the cross-over from the adiabatic to the sudden regime. By lowering the photoelectron energy, off-diagonal terms of the matrix solution $f^{\alpha\alpha'}{}_{LL'}$ in Eq. (2.32), and therefore of the matrix K_a^{-1}, come slowly into play. Specifically one expects in this case that the amplitudes $(T_{ai})^{\alpha\alpha}{}_{LL'}$, diagonal in the channel indices be substantially bigger than the off-diagonal $(\alpha \neq \alpha')$ amplitudes $(T_{ai})^{\alpha\alpha'}{}_{LL'}$. As a consequence, since from Eq. (2.30) $T_a^{-1} = K_a^{-1} - ik$, we have $1 + iT_a k = T_a K_a^{-1}$, so that if $(T_a)^{\alpha\alpha'}{}_{LL'}(\alpha \neq \alpha')$ is small, so is $(T_a K_a^{-1})^{\alpha\alpha'}{}_{LL'}$. One can then perform the following partition of the m.s. matrix $S^{\alpha\alpha'}{}_{iL,kL'}$ in Eq. (2.47)

$$S^{\alpha\alpha'}{}_{LL,KL'} = [(T_{ai}^{-1})^{\alpha\alpha}{}_{LL'} \delta_{ik} + G^\alpha{}_{iL,kL'}]\delta_{\alpha\alpha'} + (K_{ai}^{-1})^{\alpha\alpha'}{}_{LL'}(1-\delta_{\alpha\alpha'})\delta_{ik}$$

$$= (\tau_b^{-1})^\alpha{}_{iL,kL'} \delta_{\alpha\alpha'} + (K_{ai}^{-1})^{\alpha\alpha'}{}_{LL'}(1-\delta_{\alpha\alpha'})\delta_{ik} \tag{3.6}$$

using the relation (2.30) between T_{ai} and K_{ai} for the off diagonal elements. Here τ_b is a block-diagonal matrix describing the m.s. structure relative to channel α. By assuming that $\rho(\tau_b K_a^{-1}) < 1$ we then find

$$\tau = S^{-1} = (I + \tau_b K^{-1})^{-1}\tau_b = \sum_{n=0}^{\infty} (\tau_b K^{-1})^n \tau_b \tag{3.7}$$

Remembering Eq. (2.39b) the photoabsorption cross section can be written as

$$\sigma(\omega) = 4\pi\hbar\omega\alpha \sum_{\alpha\alpha'} \sum_{L_f L'_f} \sum_{LL'} (M_{eff})^\alpha{}_{L_f L} \, \text{Im}\, \tau^{\alpha\alpha'}{}_{iL,iL'} (M^*_{eff})^{\alpha'}{}_{L'_f L'} \tag{3.8}$$

Then, using Eq. (3.7), we can expand $\sigma(\omega)$ in an absolutely convergent series

$$\sigma(\omega) = \sum_{n=0}^{\infty} \sigma_n(\omega) = 4\pi\hbar\omega \sum_{\alpha\alpha'} \sum_{L_fL'_f} \sum_{LL'} (M_{eff})^{\alpha}_{L_fL} (M^*_{eff})^{\alpha'}_{L'_fL'} \, \text{Im} \sum_{n=0}^{\infty} (-1)^n$$

$$[(\tau_b K_a^{-1})^n \tau_b]^{\alpha\alpha'}_{iL,iL'} \qquad (3.9)$$

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

$$\sigma_0(\omega) = 4\pi\hbar\omega\alpha \sum_{\alpha} \sum_{L_fL'_f} \sum_{LL'} (M_{eff})^{\alpha}_{L_fL} (M^*_{eff})^{\alpha}_{L'_fL'} \, \text{Im}(\tau_b)^{\alpha}_{iL,iL'} \qquad (3.10)$$

For the first next order term one obtains

$$\sigma_1(\omega) = -4\pi\hbar\omega\alpha \sum_{\alpha\alpha'} \sum_{L_fL'_f} \sum_{LL'} \sum_{\underline{LL}'} (M_{eff})^{\alpha}_{L_fL} \, \text{Im}[(\tau_b)^{\alpha}_{iL,i\underline{L}} (K_{ai}^{-1})^{\alpha\alpha'}_{\underline{LL}'} (\tau_b)^{\alpha'}_{i\underline{L}',iL'}]$$

$$(M^*_{eff})^{\alpha'}_{L'_fL'} \qquad (3.11)$$

and we expect this to be the dominant term of the series (3.7).

In this latter expansion we have retained for simplicity the full expression (3.4) for the effective atomic matrix elements, although in the high energy limit some sort of complicated expansion of $M^{\alpha\alpha'}_{LL'}$ should exist in terms of $V^{\alpha\alpha'}_{LL'}(r)$ and indirectly of $(K_a^{-1})^{\alpha\alpha'}_{LL'}$, due to Eqs. (2.19) and (3.5). The expression (3.9) however encompasses the more general case in which in some energy range the off-diagonal elements of the matrix solution (2.26) are not small, although the matrix elements $(K_a^{-1})^{\alpha\alpha'}_{LL'}(\alpha\neq\alpha')$ are. This is a fairly possible situation which enlarges the energy range where the expansion (3.9) is feasable.

In the sudden approximation limit a useful relation can be established between the photoabsorption and the photoemission cross sections. From Eq. (2.40) one finds in this limit

$$\frac{d\sigma(\Delta E_\alpha)}{d\Delta E_\alpha d\hat{k}_\alpha} = 4\pi^2\alpha\hbar\omega \, |\sum_{L} \sum_{L_fL'} B^{\alpha}_{iL'}(\underline{\alpha},\underline{L}) \, i^{L}y_{L}(\hat{k}_\alpha) (M_{eff})^{\alpha}_{L_fL'}|^2 \qquad (3.12)$$

By integrating over $d\hat{k}_\alpha$ one has

$$\frac{d\sigma(\Delta E_\alpha)}{d\Delta E_\alpha} = 4\pi\alpha\hbar\omega \sum_{L_fL'_f} \sum_{LL'} (M_{eff})^{\alpha}_{L_fL} (M^*_{eff})^{\alpha}_{L'_fL'} \, \text{Im}(\tau_b)^{\alpha}_{iL,iL'}$$

$$= I(\omega;\Delta E_\alpha) \qquad (3.13)$$

since now Eq. (2.36) reduces to

$$\sum_{L} B^{\alpha}_{iL} (\underline{\alpha}, L) [B^{\alpha}_{kL'} (\underline{\alpha}, L)]^{*} = \frac{1}{\pi} Im(\tau_{b})^{\alpha}_{iL, kL'} \qquad (3.14)$$

Comparing Eqs. (3.10) and (3.13), one sees that the integrated photoemission cross section for ejection of one electron with binding energy ΔE_{α} equals the partial contribution to the total photoabsorption cross section of channel $\underline{\alpha}$, as expected when the various channels decouple. This fact can be used in different ways. By taking, for example, the high energy limit, using Eqs. (3.5) and remembering that in this limit $t_{ai}^{\alpha} \ll 1$, we can write from Eq. (3.6)

$$(\tau_{b})^{\alpha}_{iL, iL'} =$$

$$= ([I + t_{a}^{\alpha} G^{\alpha}]^{-1} t_{a}^{\alpha})_{iL, iL'} \cong (t_{ai}^{\alpha})_{1} \delta_{LL'} = e^{i\delta_{1}^{\alpha}} sin(\delta_{1}^{\alpha})/k_{\alpha} \qquad (3.15)$$

neglecting any structural contribution. Then

$$\frac{d\sigma(\Delta E_{\alpha})}{d\Delta E_{\alpha}} = 4\pi\alpha\hbar\omega \sum_{L_{f}} (M_{eff})^{\alpha}_{L_{f}} (M_{eff}^{*})^{\alpha}_{L_{f}} sin^{2} (\delta_{1_{f}}^{\alpha})/k_{\alpha} \qquad (3.16)$$

$$= I_{as}(\omega; \Delta E_{\alpha})$$

Since in the same limit

$$\sigma(\omega) = 4\pi\alpha\hbar\omega \sum_{\alpha} \sum_{L_{f}} (M_{eff})^{\alpha}_{L_{f}} (M_{eff}^{*})^{\alpha}_{L_{f}} Im(\tau_{b})^{\alpha}_{iL_{f}, iL_{f}} \qquad (3.17)$$

we finally get, assuming predominance of one final L_{f} component and a negligible dipendence of $(M_{eff})^{\alpha}_{L}$ on the photon energy $\hbar\omega$,

$$\sigma(\omega) = 4\pi\hbar\omega \sum_{\alpha L_{f}} (M_{eff})^{\alpha}_{L_{f}} (M_{eff}^{*})^{\alpha}_{L_{f}} sin^{2}\delta^{\alpha}_{L_{f}} \frac{k_{\alpha}}{k_{\alpha} sin^{2}\delta^{\alpha}_{L_{f}}} Im(\tau_{b})^{\alpha}_{iL_{f}, iL_{f}}$$

$$= \sum_{\alpha} I_{as}(\omega; \Delta E_{\alpha}) \chi_{L_{f}} (\omega - I_{c} - \Delta E_{\alpha}) \qquad (3.18)$$

where $\chi_{L}(\omega)$ embodies all structural information. This is the relation used by Chou et al. [8] to discuss the role of multielectron excitation in the EXAFS structure of the Br_{2} molecule in the framework of the sudden approximation and by Hammond et al. [9] to discuss XAS spectra in mixed-valent systems. On the other hand Eq. (3.13) has provided the rationale for determining the f-electron occupancy in homogeneous mixed-valent rare earth (R.E.) compounds, by measuring the integrated intensities of the various photoemission lines in L_{III} photoemission spectra corresponding to the different final state

channels. The relation between peak intensity and f-count can be more complicated then a simple 1:1 ratio and depends obviously on the structure of Ψ^{N-1}_G and Ψ^{N-1}_α which intervene in the definitions of $S_{\alpha 0} = (\Psi^{N-1}_\alpha | \Psi^{N-1}_G)$ and M_{eff} Eq. (3.4). We refer to Ref. [10] and citations therein for a full discussion of this point in the case of Ce compounds. See also the discussion in the next section.

The expansion (3.9) 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 $(T_{ai})^{\alpha \alpha'}_{LL'} (\alpha \neq \alpha')$ 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 $(T_a)^{\alpha \alpha}_{LL'}$ are themselves small at low ($\leq$ 40 eV) photoelectron kinetic energy, so that a single scattering EXAFS approximation is sufficient to describe the near edge structure [6]. 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.

4. 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^α-matrix among the various channel states. Experimental evidence for such m.s. structure associated with double electron excitations would provide more convincing support to the theory [11].

Another aspect worth persuing 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 m.s. (in particular EXAFS) structural analysis [8].

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 R.E. 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:

$$\alpha(\omega) = C_0^2 \, \alpha_0(\omega) \chi_1^0(k_0) + C_1^2 \, \alpha_1(\omega) \chi_1^1(k_1) \tag{4.1}$$

where $\alpha_0(\omega)$ is the atomic absorption coefficient of the 2^+ ion and $\alpha_1(\omega)$ that of the 3^+ ion. As a good approximation $\alpha_p(\omega)= | S_{p0}|^2 | (f_p(r) | r | \phi_c(r)) |^2 / k_p$ (p=0,1). For simplicity we assume a single l final state and average over sample orientations. The wave vectors k_0 and k_1 are given by $k_p = [\hbar\omega - I_p]^{1/2}$ (p=0,1) where I_p is the ionization threshold for the two types of ions, and $\chi_l^p(k) = k_p \Sigma_m$ Im $(\tau_b)^\alpha p_{ilm,ilm}$ describes the m.s. structure. We assume that only the elastic channel α_p is predominant, having taken account of the remaining channels through an appropriate optical potential.

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

$$\Psi_G = \sqrt{N!} A\phi_c(\mathbf{r}) \{a\Psi_0[4f^{n-1}(5d6s)^{m+1}]+b\Psi_1[4f^n(5d6s)^m]\} \tag{4.2}$$

whereas for the excited final state we can approximately write

$$\Psi_f = \sqrt{N!} A\{f_0(\mathbf{r})\Psi_0^*+f_1(\mathbf{r})\Psi_1^*\} \tag{4.3}$$

where Ψ_p^* (p=0,1) indicates the relaxed configurations corresponding to Ψ_p. As a matter of fact, since the states 5d6s are spread into a band, we should write e.g. $\Sigma_k a_k \Psi^k_1$, 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 ref. [10] for a complete treatment of this point.

In order to write the photoabsorption cross section we need $(M_{eff})^\beta L_f = \Sigma_\alpha S_{\alpha 0} M_l^{\alpha\beta}$ of Eq. (3.4). By putting $P_{0p} = (\Psi_0^*|\Psi_p)$ and similarly $P_{p0}=(\Psi_p^*|\Psi_0)$ for p=0,1, we easily find

$$\sum_{\alpha=0}^{1} S_{\alpha 0} M^{\alpha\beta}_{L_f L} = (aP_{00} + bP_{01})M^{0\beta}_{1_f} + (aP_{01} + bP_{11})M^{1\beta}_{1_f}$$

$$\approx aP_{00} \, M^{0\beta}_{1_f} + bP_{11} \, M^{1\beta}_{1_f} \tag{4.4}$$

neglecting the off-diagonal overlap factor P_{01} with respect to P_{00} and P_{11}.

To the zero the order of the expansion (3.9) and in the high energy limit, using Eqs. (3.5) and (3.18), we easily find for the absorption coefficient $\alpha_0^{tot}(\omega)$, writing I for I_f,

$$\alpha_0^{tot}(\omega) = a^2 \, \alpha_0^1(\omega) \chi_1(k_0) + b^2 \, \alpha_1^1(\omega) \chi_1(k_1) \tag{4.5}$$

where $\alpha_p^I(\omega) \propto |P_{pp}M_f^{pp}|^2 \sin^2\delta^p_I / k_p$ is the atomic absorption coefficient for the configuration p, $k^2_0 =$ $\hbar\omega - I_c$, where $I_c = E^N_G - E^{N-1}_G$ is the photoemission binding energy of the initial core state, and $k^2_1 =$ $\hbar\omega - I_c - \Delta E_1$, 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" [7], since two threshold energies must be used to analyze X-ray spectra in these compounds. Notice that in this limit the ratio $a^2\alpha_0(\omega)/b^2\alpha_1(\omega)$ and the splitting ΔE_1 can be obtained from XPS core 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 analyse 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 analyse 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 analysis one should be able to measure the f occupancy in the ground state, the splitting of the f configuration ΔE_1 in the final state and lattice relaxation effects, if present, in homogeneous mixed-valent compounds. This analysis is currently being done by some experimental groups [12], although uncertainties in the Debye-Waller factor and a lack of a clear theoretical background have complicated and made ambiguous the interpretation of the results. Eq. (4.5) sets now the correct theoretical framework and it is hoped it will facilitate this type of analysis.

The same Eq. (4.5) has been extended to the low energy XANES region and applied to the analysis of homogeneous $SmS_{0.85}As_{0.15}$ and inhomogeneous $SmS_{0.96}As_{0.04}$ compounds with satisfactory results [13,14]. The problem in such extension is that, even if the sudden approximation is valid in the low energy regime, Eqs. (3.5) are not. Consequently the effective atomic matrix elements $(M_{eff})^\alpha_{LL'}$ 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. (4.5), but in this case the relation of the weights to the f-counts is more involved and the separation between atomic and structural contribution not so clear-cut, as seen from Eqs. (4.4) and (3.10). To add more complication, 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 γ-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 in the final state [10,14].

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 adiabatric to the sudden regime and the interplay between excitation dynamics and structure.

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