Laboratori Nazionali di Frascati

LNF-87/83(PT)
28 Agosto 1987

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INNER SHELL X-RAY PHOTOABSORPTION AS A STRUCTURAL AND ELECTRONIC PROBE OF MATTER

Lectures given at the
"NATO Advanced Study Institute"
30 August - 12 September 1987, Vimeiro (Portugal)

Servizio Documentazione
dei Laboratori Nazionali di Frascati
P.O. Box, 13 - 00044 Frascati (Italy)

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ABSTRACT

A many-body description of the photoemission and photoabsorption processes is outlined that incorporates the multichannel treatment of the atomic dynamical excitations into the framework of the multiple scattering theory.

In this context the interplay between excitation dynamics and electronic and geometrical structure of the ground state is elucidated. A new multiple scattering expansion is derived that takes into account interchannel transitions as well. An application to the analysis of photoabsorption spectra of mixed valence compounds is outlined.

The same approach is shown to provide a theoretical model for the study of the evolution from the adiabatic to the sudden regime. Limiting, asymptotic cases are discussed.

Finally the unifying approach provided by the multiple scattering theory in the description of photoemission and photoabsorption processes in condensed and gaseous phase matter is illustrated.

KEYWORDS: multichannel / multiple scattering / XANES / EXFAS

1. INTRODUCTION

Electromagnetic radiation has been historically the most widely used tool in the investigation of the properties of the physical state of matter. The reason lies in the smalleness of the fine structure constant $\alpha=(e^2/\hbar c)=(1/137)$ that governs the coupling of the radiation with matter. The resulting weak interaction has a twofold advantage: on one hand the perturbation on the system under study is negligible so that one is able to investigate the properties of the unperturbed system; on the other hand from a theoretical point of view one can use the linear response theory as an interpretative scheme in which to frame the experimental observations.

The study of the electronic excitation dynamics in the various states of the matter benefits of this fortunate circumstance. There is however a price to pay for this simplification in the investigation of the structural properties of matter. Due to the smallness of the coupling constant scattering experiments can only probe the pair correlation function of observables that couple to the electromagnetic probe, like the local density $\rho(\mathbf{r})$ or the current density $j_i(\mathbf{r})$. Except for periodic systems, where this information is usually sufficient to reconstruct the spatial organization of the atoms, in any other instance one has no clue to the atomic geometrical arrangement in the system under study.

The advent of the extensive use of synchrotron radiation has given a tremendous impulse to both areas of research. 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 development of all kinds of spectroscopic research.

On the side of electronic excitation dynamics a deeper understanding has been achieved in the way an excited system reacts to the excitation probe. Screening, polarization, relaxation, autoionization and decay mechanics have been elucidated in a variety of cases, both because of higher quality data and better theoretical treatment.

On the structural side the photoabsorption process has been progressively recognized and used as a technique capable of providing structural information beyond the pair correlation function relative to the absorbing atom even in non periodic systems. In fact it has been realized that, even though the primary probe, the radiation, couples weakly with matter, the secondary probe generated in the photoabsorption process, i.e. the photoelectron, can couple strongly with the atoms of the system and therefore can carry supplementary information through final state interactions.

As a consequence photoabsorption and photoemission measurements, especially from inner shell states, have been progressively used for structural purposes. 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 selective power of the incoming radiation both in terms of the type of atom to excite and the type of final state to reach.

Another reasons for using deep core states has been the reduction, in the final state, of the amount of electronic correlation effects which in general tend to obscure the informational content relating to the structural arrangement of the atoms in the system.

However relaxation processes and double excitations are, to some extent, always present in the final state of inner shell photoabsorption. Therefore a theoretical scheme for interpreting the interplay between structural properties and electronic correlation dynamics would be highly desirable. This scheme is provided by the multichannel multiple scattering (m.s.) theory[1,2] which forms the objects of these lecture notes.

2. - THE MULTICHANNEL MULTIPLE SCATTERING THEORY

We begin with the total absorption cross section, given by

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

where $\Psi^N_{i,f}$ 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,

$$\begin{aligned}\Psi_i^N &= \sqrt{N!}\,\mathcal{A}\phi_c(\mathbf{r})\Sigma_n c_n\Phi_n^{N-1}(\mathbf{r}_1\ldots\mathbf{r}_{N-1})\\ &= \sqrt{N!}\,\mathcal{A}\phi_c(\mathbf{r})\Psi_G^{N-1}(\mathbf{r}_1\ldots\mathbf{r}_{N-1})\end{aligned} \qquad (2.2)$$

where $\mathcal{A}$ is the usual antisymmetrizing operator $\mathcal{A}=(1/N!)\,\Sigma_p(-1)^p P$ ($\mathcal{A}^2=\mathcal{A}$) and $\Phi_n^{N-1}(\mathbf{r}_1\ldots\mathbf{r}_{N-1})$ 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 $(\phi_c|\phi_c)=1$.

Similarly we assume that, by expanding $\Psi_f^N(\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_{N-1})$ in terms of the complete set $\Psi_\alpha^{N-1}(\mathbf{r}_1\ldots\mathbf{r}_{N-1})$

$$\Psi_f^N=\sqrt{N!}\,\mathcal{A}\sum_\alpha f_\alpha(\mathbf{r})\,\Psi_\alpha^{N-1}(\mathbf{r}_1\ldots\mathbf{r}_{N-1}) \qquad (2.3)$$

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

$$H_{N-1}=-\sum_{i=1}^{N-1}\nabla_i^2-\sum_{i=1}^{N-1}\sum_{k=1}^{P}\frac{2Z_k}{|\mathbf{r}_i-\mathbf{R}_k|}+\sum_{i<j}^{1\le i,j\le N-1}\frac{2}{|\mathbf{r}_i-\mathbf{r}_j|} \qquad (2.4)$$

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 $\sum_{k=1}^{P} Z_k = N$, $\mathbf{R}_k$ 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 $E=\hbar\omega+E^N_i$, of the N-electron Hamiltonian

$$H_N = -\nabla_r^2 + \sum_{i=1}^{N-1} \frac{2}{|\mathbf{r}-\mathbf{r}_i|} - \sum_{k=1}^{P} \frac{2Z_k}{|\mathbf{r}-\mathbf{R}_k|} + H_{N-1} \tag{2.6}$$

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

Therefore

$$H_N \Psi^N_f = E \Psi^N_f \tag{2.7}$$

and we shall henceforth assume that $E^N_i=E^N_g$ is the ground state of the system.

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

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

$$= E \mathcal{A}\Sigma_\alpha f_\alpha(\mathbf{r}) \Psi_\alpha^{N-1}(\mathbf{r}_1 \ldots \mathbf{r}_{N-1}) \tag{2.8}$$

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

$$(\nabla^2 + E - E_\alpha^{N-1}) f_\alpha(\mathbf{r}) =$$

$$= \Sigma_{\alpha'} [V_{\alpha\alpha'}(\mathbf{r},\mathbf{R}_k) + W_{\alpha\alpha'}(\mathbf{r},\mathbf{R}_k)] f_{\alpha'}(\mathbf{r}) \tag{2.9}$$

where

$$V_{\alpha\alpha'}(\mathbf{r},\mathbf{R}_k) = \int \prod_{i=1}^{N-1} d^3r_i \Psi_\alpha^{N-1}(\mathbf{r}_1\ldots\mathbf{r}_{N-1}) \; V(\mathbf{r},\mathbf{r}_i,\mathbf{R}_k)\; \Psi_{\alpha'}^{N-1}(\mathbf{r}_1\ldots\mathbf{r}_{N-1}) \tag{2.10}$$

is a direct potential term and we have lumped all the exchange terms into the quantities $W_{\alpha\alpha'}(\mathbf{r},\mathbf{R}_k)$ 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 $f_\alpha(\mathbf{r})$ 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 $(\Psi_f^N|\Psi_g^N)=0$) as well as to those configurations that enter in all the Ψ_α^{N-1}, then the exchange term is given by

$$W_{\alpha\alpha'}(\mathbf{r},\mathbf{R}_k) = 1/f_\alpha(\mathbf{r}) \int \prod_{i=1}^{N-1} d^3r_i \Psi_\alpha^{N-1}(\mathbf{r}_1\ldots\mathbf{r}_{N-1}) V(\mathbf{r},\mathbf{r}_i,\mathbf{R}_k) \sum_{P(\neq E)} (-1)^P P f_{\alpha'}(\mathbf{r}_i) \Psi_{\alpha'}^{N-1}(\mathbf{r}_1\ldots\mathbf{r}\ldots\mathbf{r}_{N-1}) \tag{2.11}$$

We refer to the appropriate literature for the transformation of this non local operator into a local one[3]. Henceforth we shall assume that this transformation has been performed and that our problem is to solve the coupled set of Schrödinger equations with local potentials.

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

$$E-E_\alpha^{N-1} = \hbar\omega + E_g^N - E_\alpha^{N-1} = \hbar\omega + E_g^N - E_g^{N-1} - (E_\alpha^{N-1}-E_g^{N-1}) = \hbar\omega - I_c - \Delta E_\alpha = k_\alpha^2 \tag{2.12}$$

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 to 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

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

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

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

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

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 $k_{\underline{\alpha}}$ which can be scattered in any outgoing channel α, with wave vector k_α, after loosing the energy $\Delta E_{\underline{\alpha}}$. 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 at infinity with wave number $k_{\underline{\alpha}}$.

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 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 $E_g^{N-1}-E_g^N = I_c$, so that $k_\alpha^2 = \hbar\omega - I_c - \Delta E_\alpha$ is small compared to $\mathbf{V}_{\alpha\alpha'}$. 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

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

The procedure for solving Eqs. (2.13) with boundary conditions (2.14) (in the end we shall take the complex conjugate) closely follows Ref. 2. We first transform Eq.

(2.10) into a Lippman-Schwinger equation

$$f_\alpha(\mathbf{r}) = N_\alpha e^{i\mathbf{k}_\alpha\cdot\mathbf{r}}\delta_{\alpha\underline{\alpha}} + \int G^{\alpha}{}_0(\mathbf{r}-\mathbf{r}')\ \Sigma_{\alpha'} V_{\alpha\alpha'}(\mathbf{r}') f_{\alpha'}(\mathbf{r}')\, d^3r'$$

$$= N_\alpha e^{i\mathbf{k}_\alpha\cdot\mathbf{r}}\delta_{\alpha\underline{\alpha}} + \sum_{k=1}^{p}\int_{\Omega_k} G^{\alpha}{}_0(\mathbf{r}-\mathbf{r}')\Sigma_{\alpha'} V^{k}_{\alpha\alpha'}(\mathbf{r}') f_{\alpha'}(\mathbf{r}')\, d^3r' \qquad (2.16)$$

$$+\int_{\Delta\Omega} G^{\alpha}{}_0(\mathbf{r}-\mathbf{r}')\Sigma_{\alpha'} V^{I}_{\alpha\alpha'}(\mathbf{r}') f_{\alpha'}(\mathbf{r}')\, d^3r'$$

where we have partitioned the space in non overlapping spheres Ω_k around the atomic nuclei and an interstitial region $\Delta\Omega$. An outer sphere Ω_0 enclosing all atomic spheres can be added by replacing $\Sigma_{k=1}$ with $\Sigma_{k=0}$. Also $V^{k}_{\alpha\alpha'}(\mathbf{r}') \equiv V_{\alpha\alpha'}(\mathbf{r}')$ for $\mathbf{r}' \in \Omega_k$. Moreover

$$(\nabla^2 + k_\alpha)\, G^{\alpha}{}_0(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \qquad (2.17)$$

whose solution is[2]

$$G^{\alpha}{}_0(\mathbf{r}-\mathbf{r}') = -(1/4\pi)\frac{e^{ik_\alpha|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} = -ik_\alpha \Sigma_L\ j_l(k_\alpha r_<)\, Y_L(\hat{\mathbf{r}}_<)\, h_l^{+}(k_\alpha r_>)\ Y_L(\hat{\mathbf{r}}_>) \qquad (2.18)$$

$$= -ik_\alpha \Sigma_L\ J^{\alpha}{}_L(\mathbf{r}_<)\, H^{+\alpha}{}_L(\mathbf{r}_>)$$

where L stands for (l,m), $r_>(r_<)$ refers to the greater (lesser) of $|\mathbf{r}|$ and $|\mathbf{r}'|$ and j_l, n_l, h_l^{+} are spherical Bessel, Neumann and Hankel functions, respectively, with $h_l^{+} = j_l + in_l$. We shall use real spherical harmonics and put for brevity $J^{\alpha}{}_L(\mathbf{r}) = j_l(k_\alpha r) Y(\hat{\mathbf{r}})$, etc...$G^{\alpha}{}_0(\mathbf{r}-\mathbf{r}')$ is the free Green's function with momentum $\hbar k_\alpha$ and outgoing wave boundary conditions.

Use of Eq. (2.13) allows us to write

$$f_\alpha(\mathbf{r}) = N_\alpha e^{i\mathbf{k}_\alpha\cdot\mathbf{r}}\delta_{\alpha\underline{\alpha}} + \int G^{\alpha}{}_0\ (\mathbf{r}-\mathbf{r}')\ (\nabla_{r'}{}^2 + k_\alpha{}^2) f_\alpha(\mathbf{r}')\, d^3r' \qquad (2.19)$$

which, together with the Green's theorem

$$\int_V [G^{\alpha}_0(\mathbf{r}-\mathbf{r}')\,(\nabla_{r'}^2 + k_\alpha^2)\, f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}')\,(\nabla_{r'}^2 + k_\alpha^2)\, G^{\alpha}_0(\mathbf{r}-\mathbf{r}')]\, d^3r' \qquad (2.20)$$

$$= \int_{S_V} [G^{\alpha}_0(\mathbf{r}-\mathbf{r}')\,\nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}')\,\nabla_{r'} G^{\alpha}_0(\mathbf{r}-\mathbf{r}')]\cdot \mathbf{n}\, d\sigma'$$

leads to the following equations

$$f_\alpha(\mathbf{r}) = N_\alpha e^{i\mathbf{k}_\alpha\cdot\mathbf{r}}\delta_{\alpha\underline{\alpha}} + \sum_{k=1}^{P}\int_{S_{\Omega_k}} [G^{\alpha}_0(\mathbf{r}-\mathbf{r}')\;\nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}')\;\nabla_{r'} G^{\alpha}_0(\mathbf{r}-\mathbf{r}')]\cdot\mathbf{n}\, d\sigma' \qquad (2.21a)$$

$$+ \int_{\Delta\Omega} G^{\alpha}_0(\mathbf{r}-\mathbf{r}')\,\Sigma_{\alpha'}\mathbf{V}^{I}_{\alpha\alpha'}(\mathbf{r}')\, f_{\alpha'}(\mathbf{r}')\, d^3r' \qquad \text{if } \mathbf{r}\notin\Sigma_k\Omega_k$$

$$0 = N_\alpha e^{i\mathbf{k}_\alpha\cdot\mathbf{r}}\delta_{\alpha\underline{\alpha}} + \sum_{k=1}^{P}\int_{S_{\Omega_k}} [G^{\alpha}_0(\mathbf{r}-\mathbf{r}')\,\nabla_{r'} f_\alpha(\mathbf{r}') - f_\alpha(\mathbf{r}')\,\nabla_{r'} G^{\alpha}_0(\mathbf{r}-\mathbf{r}')]\cdot\mathbf{n}\, d\sigma' \qquad (2.21b)$$

$$+ \int_{\Delta\Omega} G^{\alpha}_0(\mathbf{r}-\mathbf{r}')\,\Sigma_{\alpha'}\mathbf{V}^{I}_{\alpha\alpha'}(\mathbf{r}')\, f_{\alpha'}(\mathbf{r}')\, d^3r' \qquad \text{if } \mathbf{r}\in\Sigma_k\Omega_k$$

In order to perform the surface integrals around the spheres Ω_k centered at $\mathbf{R}_k$ we make use of the usual expansion[2]

$$G^{\alpha}_0(\mathbf{r}-\mathbf{r}') = \Sigma_{LL'}\, j_l(k_\alpha r_i)\, Y_L(\hat{\mathbf{r}}_i)\, G^{\alpha}_{iL,jL'}\, j_{l'}(k_\alpha r_j)\, Y_{L'}(\hat{\mathbf{r}}_j) \qquad (2.22)$$

$$= \Sigma_{LL'}\, J^{\alpha}_{L}(\mathbf{r}_i)\, G^{\alpha}_{iL,jL'}\, J^{\alpha}_{L'}(\mathbf{r}_j)$$

where

$$G^{\alpha}_{iL,jL'} = 4\pi\, k_\alpha \sum_{L''} i^{l''+l-l'} C_L{}^{L'}{}_{L''}\, [-ih^{+}_{l''}(k_\alpha R_{ij})]\, Y_{L''}(\hat{\mathbf{R}}_{ij})$$

$$= N^{\alpha}_{iL,jL'} - i\, J^{\alpha}_{iL,jL'} \qquad (2.23)$$

with

$$C_L{}^{L'}{}_{L''} = \int Y_L(\Omega)\, Y_{L'}(\Omega)\, Y_{L''}(\Omega)\, d\Omega \qquad (2.24)$$

and putting $\mathbf{r}_j=\mathbf{r}-\mathbf{R}_j$, $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$. Unless explicitly stated, we shall henceforth assume this meaning for $\mathbf{r}_j$. The matrices N and J are defined by decomposing $-ih^+_l=n_l-ij_l$.

Moreover we need also an expression for the solution of the system of Schrödinger equations (2.13) inside each sphere Ω_k. Writing

$$f_\alpha(\mathbf{r}) = \Sigma_L f^\alpha{}_L(r)\, Y_L(\hat{\mathbf{r}}) \tag{2.25}$$

inserting into Eq. (2.13) and projecting onto Y_L we find

$$[1/r(d^2/dr^2)r + k_\alpha{}^2 - l(l+1)/r^2]f^\alpha{}_L(r) = \Sigma_{\alpha'L'} V_{k;LL'}{}^{\alpha\alpha'}(r)\; f^{\alpha'}{}_{L'}(r) \tag{2.26}$$

Here we have assumed that around each center k,

$$\mathbf{V}^k{}_{\alpha\alpha'}(\mathbf{r}) = \Sigma_L V_{k;L}{}^{\alpha\alpha'}(r)\, Y_L(\hat{\mathbf{r}}) \tag{2.27}$$

so that

$$V_{k;LL'}{}^{\alpha\alpha'}(r) = \Sigma_{L''} C_L{}^{L'}{}_{L''}\, V_{k;L''}{}^{\alpha\alpha'}(r) \tag{2.28}$$

If α runs from 1 to n_α and l from 0 to l_{max}, this is a set of $n_\alpha(l_{max}+1)^2$ equations and consequently we 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, we might take, for example, near the origin,

$$f_{LL'}{}^{\alpha\alpha'} \simeq r^l\, \delta_{LL'}\, \delta_{\alpha\alpha'} \tag{2.29}$$

Consequently the general solution can be written as

$$f_L{}^\alpha(r) = \Sigma_{\alpha'L'} C_{L'}{}^{\alpha'} f_{LL'}{}^{\alpha\alpha'}(r) \tag{2.30}$$

so that without loss of generality, inside the sphere Ω_i, we can write

$$f_\alpha{}^i(\mathbf{r}_i) = \Sigma_{\alpha'} \Sigma_{LL'} C_{iL'}{}^{\alpha'} f_{i;LL'}{}^{\alpha\alpha'}(r_i)\; Y_L(\hat{\mathbf{r}}_i) \tag{2.31}$$

Inserting this expression into Eq. (2.21b), taken for $\mathbf{r}\in\Omega_i$, remembering Eq. (2.22), one obtains

$$0 = \Sigma_L J^{\alpha}{}_L(\mathbf{r}_i)\{k_\alpha \rho_i^2 \Sigma_{\alpha' L'} W[-ih^+{}_l, f_{i;LL'}{}^{\alpha\alpha'}]C_{iL'}{}^{\alpha'}$$

$$+ \sum_{k(\neq i)} \Sigma_{\alpha'} \Sigma_{L'L''} \rho_k^2 G^{\alpha}{}_{iL,kL'} W[j_{l'}, f_{k;L'L''}{}^{\alpha\alpha'}]C_{kL''}{}^{\alpha'}\} \qquad (2.32)$$

$$+ \int_{\Delta\Omega} G^{\alpha}{}_0(\mathbf{r}-\mathbf{r}')\Sigma_{\alpha'} V^I{}_{\alpha\alpha'}(\mathbf{r}') f_{\alpha'}(\mathbf{r}')\, d^3r' + N_\alpha\, e^{ik_\alpha\cdot r}\delta_{\alpha\underline{\alpha}}$$

Here we have introduced ρ_k, the radius of sphere Ω_k, and defined the wronskian

$$W[f,g]=f(r)(d/dr)g(r) - g(r)(d/dr)f(r)\,\big|_{r=\rho_k} \qquad (2.33)$$

calculated for $r = \rho_k$.

We now put

$$B^{\alpha}{}_{kL'} = \rho_k^2 \Sigma_{\alpha' L''} W[j_{l'}, f_{k;L'L''}{}^{\alpha\alpha'}]C_{kL''}{}^{\alpha'} =$$

$$= \rho_k^2 \Sigma_{\alpha' L''} W(j, f_k)_{L'L''}{}^{\alpha\alpha'} C_{kL''}{}^{\alpha'} \qquad (2.34)$$

and invert this relation to obtain

$$\rho_k^2\, C_{kL'}{}^{\alpha'} = \Sigma_{\alpha'' L''}[W(j, f_k)^{-1}]_{L'L''}{}^{\alpha'\alpha''} B^{\alpha''}{}_{kL''} \qquad (2.35)$$

with obvious notation.

Then Eq. (2.32) becomes

$$0 = \Sigma_L J_L{}^{\alpha}(\mathbf{r}_i)\{\Sigma_{\alpha' L'}\Sigma_{\alpha'' L''} k_\alpha [W(-ih^+, f_i)]_{LL'}{}^{\alpha\alpha'}$$

$$[W(j, f_i)^{-1}]_{L'L''}{}^{\alpha'\alpha''} B^{\alpha''}{}_{iL''} + \sum_{k(\neq i)} \Sigma_{L'} G^{\alpha}{}_{iL,kL'} B^{\alpha}{}_{kL'}\} \qquad (2.36)$$

$$+ N_\alpha e^{ik_\alpha\cdot r}\delta_{\alpha\underline{\alpha}} + \int_{\Delta\Omega} G_0{}^{\alpha}(\mathbf{r}-\mathbf{r}')\Sigma_{\alpha'} V^I{}_{\alpha\alpha'}(\mathbf{r}') f_{\alpha'}(\mathbf{r}')\, d^3r'$$

We now introduce the generalized inverse atomic $T_{ai}{}^{-1}$-matrix whose meaning we shall discuss later

$$(T_{ai}^{-1})^{\alpha\alpha'}_{LL'} = k_\alpha \Sigma_{\alpha"L"} [W(-ih^+, f_i)]_{LL"}^{\alpha\alpha"} [W(j, f_i)^{-1}]_{L"L'}^{\alpha"\alpha'} \tag{2.37}$$

and use the usual development (remember that $N_\alpha = (k_\alpha/\pi)^{1/2}/(4\pi)$)

$$\begin{aligned} N_\alpha e^{ik_\alpha \cdot r} &= (k_\alpha/\pi)^{1/2} \Sigma_L i^l J^\alpha{}_L(\mathbf{r}) Y_L(\hat{\mathbf{k}}_\alpha) = \\ &= (1/k_\alpha\pi)^{1/2} \Sigma_L i^l Y_L(\hat{\mathbf{k}}_\alpha) \Sigma_{L'} J^\alpha{}_{iL',oL} J^\alpha{}_{L'}(\mathbf{r}_i) \end{aligned} \tag{2.38}$$

where we have reexpanded the function $J^\alpha{}_L(\mathbf{r}) \equiv J^\alpha{}_L(\mathbf{r}_o)$, which is defined with respect to the origin of the coordinates o, around site i through the quantity $J^\alpha{}_{iL',oL}$ defined in Eq. (2.23)[2].

Since the solution of Eq. (2.36) is linear in the source term $N_\alpha e^{ik_\alpha \cdot r}$, we can put in Eq. (2.38)

$$(1/k_\alpha\pi)^{1/2} i^l Y_L(\hat{\mathbf{k}}_\alpha) = \delta_{LL'} (1/k_\alpha\pi)^{1/2} \tag{2.39}$$

so that finally we can write

$$\begin{aligned} 0 = \Sigma_L J^\alpha{}_L(\mathbf{r}) \{ & \Sigma_{\alpha'L'} (T_{ai}^{-1})^{\alpha\alpha'}_{LL'} B^{\alpha'}{}_{iL'}(\underline{\alpha};\underline{L}) \\ & + \sum_{k(\neq i)} \Sigma_{L'} G^\alpha{}_{iL,kL'} B^\alpha{}_{kL'}(\underline{\alpha};\underline{L}) + J^\alpha{}_{iL,oL} \delta_{\alpha\underline{\alpha}} (1/k_\alpha\pi)^{1/2} \} \\ & + \int_{\Delta\Omega} G^\alpha{}_0(\mathbf{r}-\mathbf{r}') \Sigma_{\alpha'} V^I{}_{\alpha\alpha'}(\mathbf{r}') f_{\alpha'}(\mathbf{r}') d^3r' \end{aligned} \tag{2.40}$$

Notice that we have now affected the quantities $B^\alpha{}_{iL}(\underline{\alpha};\underline{L})$ by the indices $\underline{\alpha},\underline{L}$, marking the dependence on the inhomogeneous term $\delta_{\alpha\underline{\alpha}}\delta_{L\underline{L}}$. Therefore in Eq. (2.36)

$$B^\alpha{}_{iL} = \Sigma_{\underline{L}} i^l B^\alpha{}_{iL}(\underline{\alpha};\underline{L}) Y_L(\hat{\mathbf{k}}_{\underline{\alpha}}) \tag{2.41}$$

Let us neglect, for the moment, the interstitial potential, i.e. let us put $V^I{}_{\alpha\alpha'}(\mathbf{r})=0$. Then the Eqs. (2.40), one for each i, determine the coefficients $B^\alpha{}_{iL}(\underline{\alpha};\underline{L})$, which through the relations (2.35) and (2.31), provide the functions $f_\alpha(\mathbf{r}_i)$ needed to calculate the transition matrix elements.

To interpret the $B^\alpha{}_{iL}(\underline{\alpha};\underline{L})$, we need to consider Eq. (2.21a)

for $\mathbf{r} \notin \Sigma_k \Omega_k$ and use Eq. (2.18). Performing the surface integral and remembering the definition (2.35) we find

$$f_\alpha(\mathbf{r}) = N_\alpha e^{i\mathbf{k}_\alpha \cdot \mathbf{r}} \delta_{\alpha\underline{\alpha}}$$

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

$$+ \int_{\Delta\Omega} G^\alpha{}_0 (\mathbf{r}-\mathbf{r}') \Sigma_{\alpha'} V^I_{\alpha\alpha'}(\mathbf{r}') f_{\alpha'}(\mathbf{r}') d^3r' \qquad (2.42)$$

Assuming again $V^I_{\alpha\alpha'}(\mathbf{r})=0$, this equation clearly shows the meaning of the $B^\alpha{}_{kL}(\underline{\alpha};\underline{L})$'s as scattering amplitudes into the channel α with angular momentum L emanating from site k in response to an excitation with angular momentum $\underline{L}$ into the channel $\underline{\alpha}$.

It is interesting to derive an explicit formula for the $B^\alpha{}_{iL}$'s in the atomic case, which is obtained by suppressing the terms $k\neq i$ in Eqs. (2.40) and (2.42) and putting i=o.

From Eq. (2.40) in such a case we obtain, since[2] $J^\alpha{}_{oL,o\underline{L}} = \delta_{L\underline{L}} k_\alpha$,

$$\Sigma_{\alpha'L'} (T_a^{-1})^{\alpha\alpha'}{}_{L\underline{L}'} B^{\alpha'}{}_{L'}(\underline{\alpha};\underline{L}) = - \delta_{L\underline{L}} \delta_{\alpha\underline{\alpha}} (k_{\underline{\alpha}}/\pi)^{1/2} \qquad (2.43)$$

giving

$$-B^\alpha{}_L(\underline{\alpha};\underline{L}) = (T_a)^{\alpha\underline{\alpha}}{}_{L\underline{L}} (k_{\underline{\alpha}}/\pi)^{1/2} = \qquad (2.44)$$

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

This explains the definition in Eq. (2.37). The quantities $(T_a)^{\alpha\alpha'}{}_{L\underline{L}'}$ are the natural generalization of the usual atomic T_a-matrices for non spherically symmetric potential in the multichannel case.

For the many center case the interpretation of the coefficients $B^\alpha{}_{iL}(\underline{\alpha};\underline{L})$ as scattering amplitudes is indeed confirmed by the physical meaning of the m.s. equations:

$$\Sigma_{\alpha'L'} (T_{ai}^{-1})^{\alpha\alpha'}{}_{L\underline{L}'} B^{\alpha'}{}_{iL'}(\underline{\alpha};\underline{L}) + \qquad (2.45)$$

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

which can also be written as

$$B^{\alpha}{}_{iL}(\underline{\alpha};\underline{L}) = -\Sigma_{\alpha'L'}(T_{ai})^{\alpha\alpha'}{}_{LL'} \sum_{k(\neq i)} \Sigma_{L''} G^{\alpha'}{}_{iL',kL''} B^{\alpha'}{}_{kL''}(\underline{\alpha};\underline{L})$$

$$- \Sigma_{L'} (T_{ai})^{\alpha\underline{\alpha}}{}_{LL'} J^{\underline{\alpha}}{}_{iL',o\underline{L}}(1/(k_{\underline{\alpha}}\pi))^{1/2} \qquad (2.46)$$

Since, from Eq. (2.38), $J^{\underline{\alpha}}{}_{iL,o\underline{L}}$ is the exciting amplitude of the $\underline{L}$ angular momentum component of a plane wave impinging on the origin as seen from site i, Eq. (2.46) shows that $B^{\alpha}{}_{iL}(\underline{\alpha};\underline{L})$ is the sum of the scattering amplitude originated directly at site i by the exciting amplitude plus all the scattering amplitudes generated by the waves that are scattered by all other sites $k(\neq i)$ and propagate from site k to site i, where they are finally scattered into the final state.

If is interesting to look at the structure of the m.s. matrix Eq. (2.45):

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

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

$$= M^{\alpha\alpha'}{}_{iL,kL'} - i\Delta^{\alpha\alpha'}{}_{iL,kL'} \qquad (2.47)$$

where M and Δ are hermitian matrices (actually Δ is real symmetric). We have introduced the reactance atomic K_{ai}-matrix related to the T_{ai}-matrix by the usual relation

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

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

$$- ik_{\alpha}\delta_{LL'}\delta_{\alpha\alpha'}$$

$$= (K_{ai}{}^{-1})^{\alpha\alpha'}{}_{LL'} - iI\,k_{\alpha} \qquad (2.48)$$

remembering that $-ih^{+}{}_{l} = n_l - ij_l$. The term $iI\,k_{\alpha} = i\,\delta_{\alpha\alpha'}\,\delta_{LL'}\,k_{\alpha}$ has been incorporated in Δ by lifting the restriction $i\neq k$ and using the relation $J^{\alpha}{}_{iL,iL'} = k_{\alpha}\delta_{LL'}$. In Eq. (2.47) we have used the decomposition (2.23).

By exploiting the sum rule[2]

$$\Sigma_L \; J^{\alpha}_{iL,oL} \, J^{\alpha}_{kL',oL} = k_{\alpha} J^{\alpha}_{iL,kL'} = k_{\alpha} \; \Delta^{\alpha\alpha'}_{iL,kL'} \, \delta_{\alpha\alpha'} \qquad (2.49)$$

it is now easy to derive a generalized optical theorem for the amplitudes $B^{\alpha}_{iL}(\underline{\alpha};\underline{L})$:

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

$$= 1/\pi \; \mathrm{Im} \; [(M-i\Delta)^{-1}]^{\alpha\alpha'}_{iL,kL'} = 1/\pi \; \mathrm{Im} \; \tau^{\alpha\alpha'}_{iL,kL'} \qquad (2.50)$$

which we shall need in the following. For convenience we have put $(M-i\Delta)^{-1}=S^{-1}=\tau$, which is known as the scattering path operator.

The presence of an interstitial potential $V^{I}_{\alpha\alpha'}(\mathbf{r})$ merely modifies the quantities T_{ai}^{-1} and G in Eq. (2.45). However the general structure of the m.s. equations as well as the validity of the generalized optical theorem (2.50) remain unchanged. This is also true in presence of an outer sphere. We refer the reader to the already cited articles for details[1,2].

If we assume that the initial core state is localized at site i, we need the vave function $f_{\alpha}(\mathbf{r})$ inside the sphere Ω_i. From Eqs. (2.31) and (2.35) we obtain

$$f^{i}_{\alpha}(\mathbf{r}) = \Sigma_{\alpha'} \, \Sigma_{LL'} \, C_{iL,\alpha'} f_{i;LL'}^{\alpha\alpha'}(r_i) Y_L(\hat{\mathbf{r}}_i)$$

$$= \Sigma_{\alpha'} \, \Sigma_{LL'} \, \Sigma_{\alpha''L''} \, \rho_i^{-2} [W(j,f_i)^{-1}]_{L'L''}^{\alpha'\alpha''} \qquad (2.51)$$

$$B^{\alpha''}_{iL''} \, f_{i;LL'}^{\alpha\alpha'}(r_i) \; Y_L(\hat{\mathbf{r}}_i)$$

By defining the functions

$$f_{LL''}^{\alpha\alpha''}(r) = \rho_i^{-2} \Sigma_{\alpha'L'} f_{LL'}^{\alpha\alpha'}(r) \, [W(j,f)^{-1}]_{L'L''}^{\alpha'\alpha''} \qquad (2.52)$$

we can also write, making explicit the dependence on the incident wave vector k_{α} and using Eq. (2.41),

$$f_{\alpha}^{\,i}(\mathbf{r};\mathbf{k}_{\underline{\alpha}}) = \Sigma_{L}\,\Sigma_{\alpha' L'}\, B^{\alpha'}{}_{iL'}\, \underline{f}_{LL'}^{\alpha\alpha'}(r_i)\, Y_L(\hat{\mathbf{r}}_i)$$

$$= \Sigma_{L}\,\Sigma_{\alpha' L'}\,\Sigma_{\underline{L}}\, B^{\alpha'}{}_{iL'}(\underline{\alpha};\underline{L})\; i^{\underline{L}}\, Y_{\underline{L}}(\hat{\mathbf{k}}_{\underline{\alpha}})\; \underline{f}_{i;LL'}^{\alpha\alpha'}(r_i)\, Y_L(\hat{\mathbf{r}}_i) \tag{2.53}$$

To obtain the total cross section we have to sum over all possible photoelectron final states labelled by the index $\underline{\alpha}$. Since the wave functions f^{i}_{α} are normalized to one state per Rydberg we have, using the projection property $\mathcal{A}^2=\mathcal{A}$,

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

$$\int d\hat{\mathbf{k}}_{\underline{\alpha}} \left| (\Sigma_{\alpha} f_{\alpha}^{\,i}(\mathbf{r};\mathbf{k}_{\underline{\alpha}})\Psi_{\alpha}^{N-1}) \left| \boldsymbol{\varepsilon}\cdot \sum_{m=1}^{N} \mathbf{r}_m \right| N!\mathcal{A}\phi_c^{\,i}(\mathbf{r})\Psi_G^{N-1}) \right|^2$$

$$= 4\pi^2\alpha\hbar\omega\,\Sigma_{\underline{\alpha}} \int d\hat{\mathbf{k}}_{\underline{\alpha}} \left| (\Sigma_{\alpha} f_{\alpha}^{\,i}(\mathbf{r};\mathbf{k}_{\underline{\alpha}}) \left| \boldsymbol{\varepsilon}\cdot\mathbf{r} \right| \phi_c^{\,i}(\mathbf{r})) S_{\alpha 0} \right|^2 \tag{2.54}$$

The last step follows from the orthogonality of f^{i}_{α} to all the initially occupied orbitals and the fact that we assume the arthogonality of $\phi_c^{\,i}(\mathbf{r})$ to all the orbitals appearing in the Ψ_{α}^{N-1}'s. $S_{\alpha 0}=(\Psi_{\alpha}^{N-1}|\Psi_G^{N-1})$ is the projection of Ψ_{α}^{N-1} onto the occupied configurations present in the initial state.

By introducing the expression (2.53) into Eq. (2.54), performing the angular integration over $\hat{\mathbf{k}}_{\underline{\alpha}}$ and introducing the atomic matrix elements

$$M^{\alpha\alpha'}{}_{LL'} = (\underline{f}^{\alpha\alpha'}{}_{LL'}(r_i)\, Y_L(\mathbf{r}_i) \;\; |\boldsymbol{\varepsilon}\cdot\mathbf{r}| \;\; \phi_c^{\,i}(\mathbf{r}_i)) \tag{2.55}$$

we can rewrite Eq. (2.54) as

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

$$\left[B^{\beta'}{}_{iL'}(\underline{\alpha};\underline{L})\;\; M^{\alpha'\beta'}_{L'_f L'}\; S_{\alpha' 0} \right]^{*} \tag{2.55a}$$

$$= 4\pi\alpha\hbar\omega\,\Sigma_{\alpha\alpha'}\,\Sigma_{\beta\beta'}\; \sum_{L_f L'_f}\;\; \Sigma_{LL'}\, S_{\alpha 0}\;\; M^{\alpha\beta}_{L_f L}$$

$$\{\mathrm{Im}\;\tau^{\beta\beta'}{}_{iL,iL'}\}\; \left[\; M^{\alpha'\beta'}_{L'_f L'}\;\; S_{\alpha' 0}\;\right]^{*} \tag{2.55b}$$

using the generalized optical theorem Eq. (2.50).

From Eq. (2.53) it is immediate to write down an expression

for the photoemission cross section for ejection of an electron into the state $\mathbf{k}_\alpha$ with energy $k_\alpha^2 = \hbar\omega - I_c - \Delta E_\alpha$

$$d\sigma(\omega)/d\hat{\mathbf{k}}_\alpha = 4\pi^2\alpha\hbar\omega \left| (\Sigma_\alpha f_\alpha^{\,i}(\mathbf{r};\mathbf{k}_\alpha) \,|\, \boldsymbol{\epsilon}\cdot\mathbf{r} \,|\, \phi_c^{\,i}(\mathbf{r})) S_{\alpha 0} \right|^2$$

$$= 4\pi^2\alpha\hbar\omega \left| \sum_{\alpha L_f} \Sigma_{\alpha' L'} \Sigma_L B^{\alpha'}{}_{iL'}(\underline{\alpha};\underline{L})\; i^l\, Y_L(\hat{\mathbf{k}}_\alpha)\; M^{\alpha\alpha'}{}_{L_f L'} S_{\alpha 0} \right|^2 \qquad (2.56)$$

In both cases the sum over L_f indicates the sum over the final angular momenta allowed by the dipole selection rule in Eq. (2.55). Notice that in Eq. (2.56) it is not possible to take advantage of the generalized optical theorem.

It is interesting to compare the expression (2.55) with the total cross section for electron molecule scattering. The general definition of scattering T-matrix in the multichannel case is derived by looking at the asymptotic behavior of the electron wave function

$$f_\alpha(\mathbf{r}) \underset{r\to\infty}{\sim} \Sigma_L\, 4\pi\, Y_L(\hat{\mathbf{k}}_\alpha)\, i^l \left[J^\alpha{}_L(\mathbf{r})\delta_{\alpha\underline{\alpha}} - ik_\alpha \Sigma_{L'} H^{+\alpha}{}_{L'}(\mathbf{r}) T^{\underline{\alpha}\alpha}{}_{L'L} \right] \qquad (2.57)$$

where $\mathbf{r}$ is referred to the center of the coordinates.

This expression has to be compared with Eq. (2.42), with $\mathbf{V}^I_{\alpha\alpha'}=0$, after all coordinates $\mathbf{r}_k=\mathbf{r}-\mathbf{R}_k$ have been referred to the origin. To this purpose we use the reexpansion formula[2]

$$-ik_\alpha h^+{}_l(k_\alpha r_k) Y_L(\hat{\mathbf{r}}_k) = -i \Sigma_{L'} h^+{}_{l'}(k_\alpha r) Y_{L'}(\hat{\mathbf{r}})\; J^\alpha{}_{oL',kL} \qquad (2.58)$$

valid for $|\mathbf{r}_k-\mathbf{r}|=|\mathbf{R}_k| < |\mathbf{r}|$ since we look at $|\mathbf{r}|\to\infty$

Substituting this relation into Eq. (2.42) we obtain

$$f_\alpha(\mathbf{r}) \underset{r\to\infty}{\sim} \Sigma_L\, 4\pi\, Y_L(\hat{\mathbf{k}}_\alpha)\, i^l \left[N_{\underline{\alpha}}\, J^{\underline{\alpha}}{}_L(\mathbf{r})\delta_{\alpha\underline{\alpha}} \right.$$

$$\left. -i/4\pi \Sigma_{kL} \Sigma_{L'} h^+{}_{l'}(k_\alpha r) Y_{L'}(\hat{\mathbf{r}})\; J^\alpha{}_{oL',kL} B^\alpha{}_{kL}(\underline{\alpha};\underline{L}) \right]$$

$$= \Sigma_L\, 4\pi\, Y_L(\hat{\mathbf{k}}_\alpha)\, i^l\, N_{\underline{\alpha}} \left[J^{\underline{\alpha}}{}_L(\mathbf{r})\; \delta_{\alpha\underline{\alpha}} \right.$$

$$\left. -i/(4\pi N_{\underline{\alpha}}) \Sigma_{L'} H^{+\alpha}{}_{L'}(\mathbf{r})\; \Sigma_{kL} J^\alpha{}_{oL',kL} B^\alpha{}_{kL}(\underline{\alpha};\underline{L}) \right] \qquad (2.59)$$

This gives for $T^{\alpha\underline{\alpha}}{}_{L\underline{L}}$ the expression

$$T^{\alpha\underline{\alpha}}{}_{L\underline{L}} = \Sigma_{kL'} J^{\alpha}{}_{oL,kL'} B^{\alpha}{}_{kL'}(\underline{\alpha};\underline{L}) (\pi/k_\alpha^3)^{1/2} \qquad (2.60)$$

The total scattering cross section into any channel α' starting from channel α is given by

$$\sigma^{\alpha}{}_{el}(E_\alpha) = 4\pi \Sigma_{\alpha'L'}\Sigma_L |T^{\alpha'\alpha}{}_{L'L}|^2 = 4\pi \Sigma_{\alpha'L'} \Sigma_L |T^{\alpha\alpha'}{}_{LL'}|^2 \qquad (2.61)$$

using the detailed balance relation[4].

Using Eq. (2.60) we find

$$\Sigma_{\underline{\alpha}\underline{L}} |T^{\alpha\underline{\alpha}}{}_{L\underline{L}}|^2 = (TT^+)^{\alpha\alpha}{}_{LL} =$$

$$= \pi/k_\alpha^3 \Sigma_{\underline{\alpha}\underline{L}} \Sigma_{kL'} J^{\alpha}{}_{oL,kL'} B^{\alpha}{}_{kL'}(\underline{\alpha};\underline{L}) [\Sigma_{k'L''} J^{\alpha}{}_{oL,k'L''} B^{\alpha}{}_{k'L''}(\underline{\alpha};\underline{L})]^*$$

$$= \pi/k_\alpha^3 \Sigma_{kL'} \Sigma_{k'L''} J^{\alpha}{}_{oL,kL'} \mathrm{Im}\ \tau^{\alpha\alpha}{}_{kL',kL''} J^{\alpha}{}_{oL,k'L''}$$

$$= 1/k_\alpha \mathrm{Im}\ T^{\alpha\alpha}{}_{LL} \qquad (2.62)$$

since $J^{\alpha}{}_{oL,kL'}$ is real and we have exploited the relation, derived from Eq. (2.45)

$$(k_\alpha\pi)^{1/2} B^{\alpha}{}_{kL}(\alpha;L) = \Sigma_{k'L'} \tau^{\alpha\alpha}{}_{kL,k'L'} J^{\alpha}{}_{oL,k'L'} \qquad (2.63)$$

Eq. (2.62) is nothing else that the optical theorem for the scattering T-matrix. As a consequence Eq. (2.61) takes the form

$$\sigma^{\alpha}{}_{el}(E_\alpha) = 4\pi/k_\alpha \Sigma_L \mathrm{Im}\ T^{\alpha\alpha}{}_{LL} \qquad (2.64)$$

$$= 4\pi/k_\alpha^3 \mathrm{Im} \Sigma_{L''} \Sigma_{kL} \Sigma_{k'L'} J^{\alpha}{}_{oL'',kL} \tau^{\alpha\alpha}{}_{kL,k'L'} J^{\alpha}{}_{k'L',oL''}$$

exploiting the relation $J^{\alpha}{}_{oL,kL'} = J^{\alpha}{}_{kL',oL}$.

We shall discuss the relation of this expression with Eq. (2.55) in the next section.

3. THE GENERALIZED MULTIPLE SCATTERING EXPANSION

In the expressions (2.55), (2.64) the structural information is contained in the inverse $\tau = S^{-1}$ of the multiple scattering matrix Eq. (2.47) through the presence at the structure matrix elements $G^{\alpha}_{iL,kL'}$, in a rather involved way that intermingles dynamics as well as structure.

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

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

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

$$(I+T_aG)^{-1} = \sum_{n=0}^{\infty} (-1)^n\, (T_aG)^n \tag{3.1}$$

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. (2.47).

As a consequence the photoabsorption cross section Eq. (2.55) can be expanded in an absolutely convergent series

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

where

$$\sigma_0(\omega) = 4\pi\alpha\hbar\omega\, \Sigma_{\alpha\alpha'}\, \Sigma_{\beta\beta'} \sum_{L_fL'_f} \Sigma_{LL'} S_{\alpha 0}\, M^{\alpha\beta}_{L_fL}\, \mathrm{Im}(T_{ai})^{\beta\beta'}_{iL,iL'}$$

$$[M^{\alpha'\beta'}_{L'_fL'}\, S_{\alpha' 0}]^* \tag{3.3}$$

is a smoothly varying atomic cross section and

$$\sigma_n(\omega) = 4\pi\alpha\hbar\omega \sum_{\alpha\alpha'} \sum_{\beta\beta'} \sum_{L_f L'_f} \sum_{LL'} S_{\alpha 0} M^{\alpha\beta}_{L_f L} \quad \mathrm{Im}[(-1)^n (T_a G)^n T_a]^{\beta\beta'}_{iL,iL'} [M^{\alpha'\beta'}_{L'_f L'} S_{\alpha' 0}]^* \tag{3.3}$$

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 amplitudes

$$S_{\alpha 0} M^{\alpha\beta}_{L_f L} \quad \text{and} \quad S_{\alpha'} M^{\alpha'\beta'}_{L'_f L'}$$

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.

In order to better illustrate these concepts let us treat some asymptotic cases. It is obvious that the condition $\rho(T_a G)<1$ is satisfied at high photoelectron energy since

$$\lim_{k_\alpha \to \infty} |(T_a)^{\alpha\alpha'}_{LL'}| = 0.$$

In this regime one can safely 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 $f_\alpha(\mathbf{r})$ in Eq. (2.14) is relevant, following the same argument leading to (2.15).

As a consequence the asymptotic cross section $\sigma_{as}(\omega)$ is given by

$$\sigma_{as}(\omega) = 4\pi\alpha\hbar\omega \sum_{\alpha} |S_{\alpha 0} M^{\alpha}_{l}|^2 \sum_{m} \mathrm{Im}\, \tau^{\alpha}_{ilm,ilm} \tag{3.6}$$

where, for simplicity, we have assumed a single l final state

and $\tau^{\alpha}_{iL,kL'}$ is the inverse of S^{α}, the submatrix of S relative to the channel α:

$$[(\tau^{\alpha})^{-1}]_{iL,kL'} = S^{\alpha}_{iL,kL'} = (t^{\alpha}_{ail})^{-1}\,\delta_{ik}\,\delta_{LL'} + G^{\alpha}_{iL,kL'} \qquad (3.7)$$

In other words the different channels decouple and they have identical m.s. structure, apart from the trivial dependence on the photoelectron propagation vector k_{α} and on the atomic scattering matrices t^{α}_{al}.

Eq. (3.6) is the form used by Rehr et al[6] to discuss the role of multielectron excitations in the EXAFS structure of the Br_2 molecule in the framework of the "sudden approximation".

The total cross section is therefore an incoherent sum of photoabsorption cross sections relative to different channels, so that we can limit ourselves to a single channel. On a theoretical basis, born out by experiments, one expects the predominance of a single channel in the sum (3.6) when the ground state of the system contains one single dominant configuration. In this case the biggest overlap factor among the $S_{\alpha'0}$'s is S_{00}, corresponding to the same relaxed configuration in the final state and to $\Delta E_{\alpha}=0$ in Eq. (2.12). Depending on the systems, one has $0.7 < |S_{00}|^2 < 0.8$ so that one single channel accounts for 70~80 per cent of the spectrum. We shall see in a moment how to account for the rest in an approximate way.

In the energy region where Eq. (3.6) is valid we can also expand τ^{α} as

$$\tau^{\alpha} = (I + t^{\alpha}_{a}\,G^{\alpha})^{-1}\,t^{\alpha}_{a} = \sum_{n=0}^{\infty} (-1)^n\,(t^{\alpha}_{a}\,G^{\alpha})^n\,t^{\alpha}_{a} \qquad (3.8)$$

so that

$$\sigma_{as}(\omega) = 4\pi\alpha\hbar\omega \sum_{\alpha} |S_{\alpha 0}\,M^{\alpha}_{1}|^2 \sum_{n} \sum_{m} (-1)^n\,\mathrm{Im}\,[(t^{\alpha}_{a}\,G^{\alpha})^n\,t^{\alpha}_{a}]_{ilm,ilm}$$

$$= \sum_{n=0}^{\infty} \sum_{\alpha} \sigma^{\alpha}_{nas}(\omega) \qquad (3.9)$$

Analytic expressions for the m.s. terms, based on the Eq. (2.23) for the matrix elements $G_{iL,kL'}$, are available in the

literature[7,8]. For our purpose it is sufficient to observe that each $G^{\alpha}_{iL,kL'}$ carries a factor $\exp\{ik_{\alpha}R_{ik}\}$ independent of L,L' contained in the Hankel function appearing in the definition (2.23), which can be better taken account of by defining the reduced matrix

$$\underline{G}^{\alpha}_{iL,kL'} = e^{-ik_{\alpha}R_{ik}} G^{\alpha}_{iL,kL'}$$

$$\underline{G}^{\alpha}_{iL,iL'} = 0 \qquad (3.10)$$

For the n-th order term in Eq. (3.9), we find

$$\sum_m [(t^{\alpha}_a G^{\alpha})^n t^{\alpha}_a]_{ilm,ilm} = \sum_m \sum_{k_1L_1} \cdots \sum_{k_{n-1}L_{n-1}} t^{\alpha}_{ilm} \; G^{\alpha}_{ilm,k_1L_1} \; t^{\alpha}_{k_1l_1} \cdots \qquad (3.11)$$

$$\cdots \; t^{\alpha}_{k_{n-1}\,l_{n-1}} \; G^{\alpha}_{k_{n-1}L_{n-1},ilm} \; t^{\alpha}_{ilm}$$

The set $k_1 \ldots k_{n-1}$ defines a path p_n of order n that begins and ends at the central atom (located at site i), to which we can associate a total path length

$$R^{tot}_{p_n} = \sum_{m=1}^{n-1} R_{k_m k_{m+1}} \qquad (3.12)$$

Therefore, putting

$$A^{l}_{n}(k_{\alpha}, R^{p_n}_{ik}) \exp[i\phi^{l}_{n}(k_{\alpha}, R^{p_n}_{ik})] \qquad (3.13)$$

$$= \Sigma_m \sum_{L_1} \cdots \sum_{L_{n-1}} t^{\alpha}_{ilm} \; \underline{G}^{\alpha}_{ilm,k_1L_1} \cdots \underline{G}^{\alpha}_{k_{n-1}L_{n-1},ilm} \; t^{\alpha}_{ilm}$$

we can finally write

$$\Sigma_m [(t^{\alpha}_a G^{\alpha})^n t^{\alpha}_a]_{ilm,ilm} =$$

$$= \Sigma_{p_n} A^{l}_{n}(k_{\alpha}, R^{p_n}_{ik}) \exp\{i[k_{\alpha}R^{tot}_{p_n} + \phi^{l}_{n}(k_{\alpha}, R^{p_n}_{ik})]\} \qquad (3.14)$$

so that the functional contribution of the n-th order m.s.

term to the photoabsorption cross section in channel α is

$$\sum_{p_n} A^1{}_n(k_\alpha, R_{ik}^{p_n}) \sin\,[k_\alpha R_{p_n}^{tot} + \phi^1{}_n(k_\alpha, R_{ik}^{p_n})] \qquad (3.15)$$

This means that each path contributes an oscillatory signal in the cross section of period $2\pi/R^{tot}{}_{p_n}$ and amplitude $A^1{}_n(k_\alpha, R^{p_n}{}_{ik})$.

The quantities $A^1{}_n(k_\alpha, R^{p_n}{}_{ik})$ and $\phi^1{}_n(k_\alpha, R^{p_n}{}_{ik})$ are slowly varying functions of k_α, so that, indicating by $k_0=[\hbar\omega-I_c]^{1/2}$ the photoelectron wave vector of the primary channel, we can write approximatively in Eq. (3.14)

$$\Sigma_m [(t^\alpha{}_a G^\alpha)^n t^\alpha{}_a]_{ilm,ilm} =$$

$$\sum_{p_n} A^1{}_n(k_0, R_{ik}^{p_n}) \exp\{i[k_0 R_{p_n}^{tot} + \phi^1{}_n(k_0, R_{ik}^{p_n})]\} \qquad (3.16)$$

$$\exp\{i(k_\alpha - k_0)[R_{p_n}^{tot} + (d/dk)\phi^1{}_n(k, R_{ik}^{p_n})|_{k=k_0}]\}$$

If we then define the complex number

$$B^1{}_n(k_0)\; e^{i\psi^1{}_n(k_0)} = |S_{00}\, M_1^{\alpha_0}|^{-2} \Sigma_\alpha |S_{\alpha 0}|^2$$

$$\exp\{i(k_\alpha - k_0)[R_{p_n}^{tot} + (d/dk)\phi^1{}_n(k, R_{ik}^{p_n})|_{k=k_0}]\} \qquad (3.17)$$

we can finally write

$$\sigma_{as}(\omega) = \Sigma_n \Sigma_\alpha \sigma^\alpha{}_n(\omega) = 4\pi\alpha\hbar\omega\, |S_{00}\, M_1^{\alpha_0}|^2 \Sigma_n \sum_{p_n} (-1)^n B^1{}_n(k_0)$$

$$A^1{}_n(k_0, R_{ik}^{p_n}) \sin[k_0 R_{p_n}^{tot} + \phi^1{}_n(k_0, R_{ik}^{p_n}) + \psi^1{}_n(k_0)] \qquad (3.18)$$

This is the generalization of the result arrived at in Refs. 5,6. The modification needed when there are two or more configurations present in the ground state with comparable amplitudes, is straightforward. We easily find in this case

$$\sigma_{as}(\omega) = 4\pi\alpha\hbar\omega \Sigma_\beta |S_{\beta 0} M^\beta{}_1|^2 \Sigma_n \sum_{p_n} (-1)^n B^1{}_n(k_\beta) A^1{}_n(k_\beta, R^{p_n}_{ik})$$

$$\sin [k_\beta R^{tot}_{p_n} + \phi^1{}_n(k_\beta, R^{p_n}_{ik}) + \psi^1{}_n(k_\beta)] \qquad (3.19)$$

where the Σ_β is over the corresponding relaxed configurations in the final state.

It should then be possible to discriminate in the experimental analysis between the various oscillatory signals appearing in the spectrum due to the presence of different main channels β.

However the formula (3.19) is only asymptotic and deviations from the sudden approximation (3.5) must be considered if one wants to exploit a larger energy range.
The general expansion to use in this case is given in Eq. (3.4). The lowest order term is n=2, since $G^\alpha{}_{iL,iL'}=0$. This is the usual EXAFS contribution given by

$$\sigma_2(\omega) = 4\pi\alpha\hbar\omega \Sigma_{\alpha\alpha'} S_{\alpha 0} M^\alpha{}_1 \Sigma_m \Sigma_{kL'} \sum_{\alpha_1\alpha_2} (T_{ai})_1{}^{\alpha\alpha_1} G^{\alpha_1}{}_{iL,kL'}$$

$$(T_{ak})_1{}^{\alpha_1\alpha_2} G^{\alpha_2}{}_{kL',iL} (T_{ai})_1{}^{\alpha_2\alpha'} [M^{\alpha'}{}_1 S_{\alpha' 0}]^* \qquad (3.20)$$

where for simplicity we have assumed $(T_{ai})^{\alpha\alpha'}{}_{LL'} = (T_{ai})_1{}^{\alpha\alpha'} \delta_{LL'}$ and set $M^{\alpha\alpha'}{}_{LL'} \simeq M^\alpha{}_1 \delta_{\alpha\alpha'} \delta_{LL'}$, since terms proportional to $M^{\alpha\alpha'}{}_{LL'} (\alpha \neq \alpha')$ would be of higer order in this expansion.

The new feature now is given by the fact that at each scattering event the photoelectron can change its channel state, and consequently its propagation vector k_α. This fact can make difficult the detection of, say, a two channel in the EXAFS signal of fluctuating mixed valence compounds, especially for the first coordination shell whose atoms can participate to the relaxation effect of the photoabsorber.

However it is likely that there is no relaxation beyond the first shell so that one can write $(T_{ak})_1{}^{\alpha_1\alpha_2} \sim (T_{ak})_1{}^{\alpha_1} \delta_{\alpha_1\alpha_2}$ for atoms located in the second shell. Eq. (3.20) then implies that there are only two EXAFS signals, originating from this shell, each one with a definite propagation vector. Since for higher order shells the period of oscillation in k is shorter,

it should be easier to detect the two signals. Recently interesting results concerning lattice relaxation in homogeneous and inhomogeneous mixed-valent materials have been obtained by the use of a two channel EXAFS analysis[9].

Equations like the one in (3.19) constitute the basis for a structural analysis of photoabsorption spectra. This analysis is in many way complicated by the need of taking configurational averages both dynamical (over the phonon spectrum) and structural, when it is the case (as in amorphous systems). The way to do this averaging processes is still a matter a research.

It is interesting at this point to compare the photoabsorption cross section Eq. (2.55b) which reduces to the following

$$\sigma(\omega) \simeq 4\pi\hbar\,\omega\,\Sigma_{\alpha\alpha'}\, S_{\alpha 0} M^{\alpha}{}_{L}\, \{\mathrm{Im}\ \tau^{\alpha\alpha'}{}_{iL,iL}\}\ [M^{\alpha'}{}_{L}\, S_{\alpha' 0}]^{*} \qquad (3.21)$$

if one takes the most important terms ($M^{\alpha\alpha'}{}_{LL'} \sim M^{\alpha}{}_{L}\,\delta_{\alpha\alpha'}$, where L represents the l channel selected by the dipole matrix element with initial core electron angular momentum l-1), with the expression (2.64) for electron- molecule (i.e. cluster of atoms total cross section, which we rewrite here for convenience

$$\sigma^{\alpha}{}_{el}(E_{\alpha}) = \qquad (3.22)$$

$$= 4\pi/k_{\alpha}{}^{3}\ \mathrm{Im}\ \Sigma_{L''}\ \Sigma_{kL}\Sigma_{k'L'}\, J^{\alpha}{}_{oL'',kL}\ \tau^{\alpha\alpha}{}_{kL,k'L'}\ J^{\alpha}{}_{k'L',oL''}$$

The greater structural and angular momentum selectivity of the photoabsorption cross section is apparent. In Eq. (3.21) only paths beginning and ending at the photoabsorbing site with the same angular momentum are possible. No such selection rule exists in Eq. (3.22). Moreover in the greatest majority of cases, when only one single configuration is dominant in the ground state, only the primary channel α_0 matters, the effect of the remaining channels resulting into a smoothing action on the primary transition. Therefore, as a structural probe, photoabsorption has to be preferred to electron collisions.

It is also interesting to compare Eq. (3.21) with the photoemission cross section Eq. (2.56), which under the same assumptions reduces to

$$\frac{d\sigma}{d\hat{k}_\alpha} \simeq 4\pi^2\hbar\omega \, | \Sigma_\alpha \Sigma_L \, B^\alpha{}_{iL} \, (\alpha;L) \, i^l \, Y_L(\hat{k}_\alpha) \, M^\alpha{}_L \, S_{\alpha 0} \, |^2 \qquad (3.23)$$

By using the solution (2.63) for $B^\alpha{}_{iL}$, together with the definition (2.23) for $J^\alpha{}_{oL,kL'}$ and the relation (2.38), we find

$$\begin{aligned} &\Sigma_L \, B^\alpha{}_{iL} \, (\alpha; L) \, i^l \, Y_L(\hat{k}_\alpha) \\ &\quad = (k_\alpha/\pi)^{1/2} \, \Sigma_{kL'} \, \tau^{\alpha\alpha}{}_{iL,kL'} \, i^{l'} \, Y_{L'}(\hat{k}_\alpha) \, e^{\,ik_\alpha \cdot R_{ko}} \\ &\quad = (k_\alpha/\pi)^{1/2} \, \Sigma_{kL'} \, [(I + T_a G)^{-1} \, T_a]^{\alpha\alpha}{}_{iL,kL'} \, i^{l'} \, Y_{L'}(\hat{k}_\alpha) \, e^{\,ik_\alpha \cdot R_{ko}} \end{aligned} \qquad (3.24)$$

At "high" photoemission energies, again

$$(I+T_aG)^{-1} \, T_a \simeq [I - T_aG + (T_aG)^2 + \ldots] \, T_a$$

retaining only terms up to the second.

Within this approximation and putting for simplicity $(T_{ai})^{\alpha\alpha'}{}_{LL'} \simeq (T_{ai})_1{}^{\alpha\alpha'} \, \delta_{LL'}$, we derive

$$\begin{aligned} \Sigma_L \, B^\alpha{}_{iL}(\alpha; L) \, i^l \, Y_L \, (\hat{k}_\alpha) \; &= \; (k_\alpha/\pi)^{1/2} \, \Sigma_{\alpha'} \, (T_{ai})_1{}^{\alpha\alpha'} \\ &\{ i^l \, Y_L(\hat{k}_\alpha) \; \delta_{ik} \, \delta_{\alpha\alpha'} - \Sigma_{kL'} \, G^{\alpha'}{}_{iL,kL'} \, (T_{ak})_1{}^{\alpha'\alpha} \, i^{l'} \, Y_{L'}(\hat{k}_\alpha) \\ &+ \Sigma_{\alpha''} \, \Sigma_{kL'} \, \Sigma_{jL''} \, G^\alpha{}_{iL,jL''} \, (T_{aj})_{1''}{}^{\alpha'\alpha''} \, G^{\alpha''}{}_{jL'',kL'} \\ &(T_{ak})_1{}^{\alpha''\alpha} \, i^{l'} \, Y_{L'}(\hat{k}_\alpha) + \ldots \} e^{\,ik_\alpha \cdot R_{ko}} \end{aligned} \qquad (3.25)$$

which has to be inserted in Eq. (3.23).

As can be seen from this equation, now there are contributions coming from 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 can still be done and is giving its fruits[10]. The expression (3.25) incorporates the multichannel structure which can help analysing photodiffraction experiments with more completeness.

Of practical importance in the structural analysis is an accurate approximation to the exact, but computationally cumbersome, expression (2.23).

The following approximation

$$G^{\alpha}_{iL,kL'} = -4\pi\, k_{\alpha}\, i^{l-l'} Y_{L}(\hat{\mathbf{R}}_{ik})\, Y_{L'}(\hat{\mathbf{R}}_{ik})\, G(\rho^{\alpha}_{ik};\ \alpha_{ll'},\beta_{ll'}) \qquad (3.26)$$

where

$$g(\rho;\alpha,\beta) = [1+\alpha/(2\rho)^2]^{1/2}\, J_0(\beta/\rho)\ 1/\rho \exp\{i\rho[1+(\alpha/(2\rho)^2]\} \qquad (3.27)$$

with

$$\alpha_{ll'} = 2[l(l+1)+l'(l'+1)]; \qquad \beta_{ll'} = [l(l+1)\,l'(l'+1)]^{1/2}; \qquad \rho^{\alpha}_{ik} = k_{\alpha}R_{ik} \qquad (3.28)$$

gives rather accurate results for m.s. paths of low order (n=2,3,4) when compared with the exact expressions. In Eq. (3.27) $J_0(\rho)$ is the Bessel function of order zero[8,11].

The nice feature of Eq. (3.26) is the proportionality to $Y_L Y_{L'}$, which allows to close intermediate angular momentum summations through the addition theorem for spherical harmonics

$$(2l+1)/(4\pi)\ P_l(\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2) = \Sigma_m\ Y_{lm}(\hat{\mathbf{R}}_1)\, Y_{lm}(\hat{\mathbf{R}}_2) \qquad (3.29)$$

For example the second term in Eq. (3.25), putting the origin o at site i, becomes

$$-\Sigma_{kL'}\, G^{\alpha'}_{iL,kL'}\, (T_{ak})_{l'}^{\alpha'\alpha}\, i^{l'} Y_{L'}(\hat{\mathbf{k}}_{\alpha})\, e^{\,i\mathbf{k}_{\alpha}\cdot\mathbf{R}_{ki}}$$

$$= 4\pi\, k_{\alpha'}\, i^{l}\, Y_{L}(\hat{\mathbf{R}}_{ik})\, \Sigma_{kL'} Y_{L'}(\hat{\mathbf{R}}_{ik})\, g(\rho^{\alpha'}_{ik};\alpha_{ll'},\beta_{ll'})\ (T_{ak})_{l'}^{\alpha'\alpha}\, Y_{L'}(\hat{\mathbf{k}}_{\alpha})\, e^{\,i\mathbf{k}_{\alpha}\cdot\mathbf{R}_{ki}} \qquad (3.30)$$

$$= \Sigma_k \, i^l \, Y_L(\hat{\mathbf{R}}_{ik}) \; \Sigma_{l'} \, (2l'+1) P_{l'}(\hat{\mathbf{k}}_\alpha \cdot \hat{\mathbf{R}}_{ik})$$

$$g(\rho^{\alpha'}{}_{ik};\ \alpha_{ll'},\ \beta_{ll'}) \; k_{\alpha'} \, (T_{ak})_{l'}{}^{\alpha'\alpha} \; e^{\,i\mathbf{k}_\alpha \cdot \mathbf{R}_{ki}}$$

$$= \Sigma_k \, i^l \, Y_L \, (\hat{\mathbf{R}}_{ik}) \, f_{eff}(\rho^{\alpha'}{}_{ik};\ \hat{\mathbf{k}}_\alpha \cdot \hat{\mathbf{R}}_{ik}) \; e^{\,i\mathbf{k}_\alpha \cdot \mathbf{R}_{ki}} \qquad (3.30)$$

where $f_{eff}(\rho^{\alpha'}{}_{ik};\ \hat{\mathbf{k}}_\alpha \cdot \hat{\mathbf{R}}_{ik})$ is an effective scattering amplitude off the atom located at site k, calculated at the angle arcos $(\hat{\mathbf{k}}_\alpha \cdot \hat{\mathbf{R}}_{ik})$ between the vector joining the photoabsorbing site i with the scattering atom and the direction $\hat{\mathbf{k}}_\alpha$ of escape of the photoejected electron. A similar form is valid for the third term if one introduces an effective scattering amplitude off atoms located at site k and j.[12]

The expression (3.26) can also be efficiently used for computing m.s. terms like those in Eq. (3.13) for photoabsorption. We refer the interested reader to Refs. 8,11.

Until now we have simply assumed that $\rho(T_a G)<1$ and given an argument $(|T_{ai})^{\alpha\alpha'}{}_{LL'}| \to 0$ for $k_\alpha \to \infty$) to show that there exists an energy regime for which this relation holds.

However, by simply considering the behavior of $\rho(T_a G)$ as a function of $\hbar\omega$ (hence of the various k_α), one can predict some general features of photoabsorption spectra.

In fact the spectral radius $(T_a G)$ is a continuous function of $\hbar\omega$ and, as already observed, goes to zero for $\hbar\omega \to \infty$. At the other extreme however, i.e. near threshold ($\hbar\omega \sim I_c$), it is reasonable to assume that $\rho(T_a G) \to \infty$, due to the singularity of the Hankel functions $h^+_l(k_\alpha R_{ij})$ appearing in the definition (2.23) of the matrix elements of G (the product $k_\alpha h^+_l(k_\alpha R_{ij})$ goes like k_α^{-1}). Consequently $\rho(T_a G)$ must cross at least once the value $\rho=1$ in the range $I_c < \hbar\omega < \infty$. Moreover, the nearer to 1 is its value, the slower is the convergence of the m.s. series.

On the basis of this simple consideration we can therefore conclude that there are at least three regimes in a photoabsorption spectrum: a full multiple scattering regime (FMS) ($\rho(T_a G) \gtrsim 1$), where a great number of m.s. paths of high order contribute significantly to shape up the photoabsorption spectrum or even an infinite number of them, depending on

whether the m.s. series converges or not; an intermediate multiple scattering regime (IMS) where only a few m.s. paths of low order are relevent (typically n<4) so that interatomic configurational correlations of this order are accessible; a single scattering (SS) regime where only the lowest order term of the m.s. series (n=2) is detectable and provides information on the atomic pair correlation function.

The energy extent and even the sequential order, as a function of increasing photon energy, of the regimes described above are obviously system dependent. Usually the FMS regime precedes the IMS which, in turn, merges into the SS region. This is the normal situation; however there are exceptions to this. In copper K-edge spectrum, for example, in the first ~50 eV above the absorption edge the EXAFS like $\sigma_2(\omega)$ term alone is capable of reproducing the experimental spectrum and the exact band calculation. However a substantial discrepancy shows up in the energy range 50÷200 eV, where clearly m.s. contributions of order higher that two are present[11].

This behavior can be understood on the basis of the peculiarity of the relevant atomic phase shifts that are small (modulo π, by Levinson theorem) at low energy and must cross $\pi/2$ (again modulo π) before going to zero at high energy. At the crossing $|t_{a1}|=|\sin\delta_1|\sim 1$, so that the coupling of the photoelectron with matter becomes again substantial.

Summarizing, since the magnitude of $\rho(T_aG)$ depends on the interplay between the atomic T-matrices and the structure factors G, both ingredients must be considered in discussing a photoabsorption spectrum. The bearance of the multichannel structure of T_a on the magnitude of ρ is still an interesting subject open to research.

Experimental analysis based on the preceeding considerations is confirming that structural information can indeed be obtained from the SS and IMS energy region of the spectrum[13,14]. In the FMS region the presence of many scattering paths in a limited energy range (usually 2-5 Rydbergs) makes it impossible to derive any detailed information whatsover on the various paths. However it is an empirical experimental fact that clusters of similar atoms (in the sense that they have similar scattering power, i.e. atomic phase shifts, like

atoms in neighboring or corresponding positions along the periodic table) with the same geometrical arrangement give quite similar features, like fingerprints in photoabsorption spectra.

This is quite evident in molecules where these particular features have been named "cage" or "shape resonances"[15]. They afford a kind of global information about both the structure and the type of atoms participating in the resonance

These resonances are the cluster analogues of the scattering or photoabsorption resonances which are well known in the single atom scattering case. They have been mainly asssociated with the presence of some effective repulsive potential that creates a sort of cage that traps the final state electron in a quasi-bound state decaying away with a lifetime $\tau=\hbar\Gamma_\gamma^{-1}$ connected with the tunneling probability through the barrier. In reality this is only a partial, model view of the potential resonance theory[16]. Be as it may be, these resonances, which show up as more or less sharp maxima in the cross section, are associated with a singularity of the reactance matrix k related to the atomic t-matrix by the relation (see Eq. (2.48) for the general case)

$$t_l = (1/k_0)e^{i\delta_l}\sin\delta_l;\ k^{-1}{}_l = \cot g\ \delta_l = t_l^{-1} + ik_0$$

$$t_l = k_l/(1-ik_0 k_l) \qquad (3.31)$$

where we have indicated by k_0 the wave vector of the electron and introduced the potential phase shift δ_l.

Since the cross section is proportional to Im t_l (see Eq. 2.55b) we find

$$\text{Im } t_l = (1/k_0)\sin^2\delta_l = k_0/(k_0^2 + k_l^{-2}) \qquad (3.32)$$

so that at a maximum

$$k_l^{-1} = k_0 \cot g\delta_l = 0 \rightarrow \delta_l = \pi/2 \text{ (modulo } \pi)$$

This implies that at a resonance k_l is singular.

It is easy to convince oneself that quite similarly, in the

cluster case, resonances are associated with singularities of the cluster K_c-matrix which can be shown to be given by

$$(K_c)^{\alpha\alpha'}_{LL'} = \Sigma_{kL'} \Sigma_{jL''} J^{\alpha}_{oL,kL'} (M^{-1})^{\alpha\alpha'}_{kL',jL''} J^{\alpha}_{jL'',oL'} \qquad (3.33)$$

where the matrix M has been defined in Eq. (2.47), and to be related to the cluster T_c matrix Eq. (2.64) by the usual relation, analogous to (3.31)

$$(T_c)^{\alpha\alpha'}_{LL'} = [\,(I - i\,\underline{k}\,K_c)^{-1} K_c\,]^{\alpha\alpha'}_{LL'} \qquad (3.34)$$

where we have introduced the diagonal matrix $\underline{k} = k_\alpha\,\delta_{\alpha\alpha'}\,\delta_{LL'}$.

The matrix K_c is hermitian, so that its real eigenvalues λ_m can be identified with the tangent of the eigenphase shifts: $\lambda_m = \tan\,\delta_{\lambda m}$.

Therefore in the electron molecules scattering, as in the atomic case, resonances occur whenever some eigenvalue λ_m goes to infinity ($\delta_{\lambda m} \to \pi/2$), i.e. whenever

$$\text{Det}\,\|\,M\,\| = \text{Det}\,\|\,(K_{ai})^{\alpha\alpha'}_{LL'}\,\delta_{ik} + (1-\delta_{ik})\,\delta_{\alpha\alpha'} N^{\alpha}_{iL,kL'}\,\| = 0 \qquad (3.35)$$

due to (3.33). Similarly for the photoabsorption case Eq. (2.55b) where the cross section is proportional to

$$\text{Im}\,\tau = \text{Im}\,(M - i\Delta)^{-1} = \text{Im}(I - iM^{-1}\Delta)^{-1}M^{-1}\ .$$

The sharpness of the resonance depends on how fast, as a function of energy, the eigenphase δ_m increases through an odd multiple of $\pi/2$.

Eq.(3.35) is the natural generalization to the multichannel case of the resonance condition already discussed in Ref. 16 for the one channel case. It gives the wanted, global relation between scattering power of the constituent atoms and their geometrical organization in the molecule or cluster. In the one channel case, under the assumption that the relevant atomic phase shifts are non resonating and actually depend smoothly on the energy, it leads to the rule $k_r R$=constant, where k_r denotes the resonance wavevector and R the average coordination bond length, in molecules or clusters with

identical angular geometrical arrangement but different bond length scale. This follows from the fact that the structure matrix elements $N_{iL,kL'}$ depend on energy only through the combination kR.We refer for applications and more details to Refs. (16,17).

As a final remark, we note that the condition Det $\|M\|=0$ does not entail necessarily the other condition $\rho(T_aG)>1$. Stated differently, at a resonance the m.s. series might even converge, although one is always in the FMS regime where $\rho\simeq 1$.

4. THE ONE CHANNEL APPROXIMATION AND THE OPTICAL POTENTIAL

The multichannel m.s. theory approach to the description of photoabsorption and photoemission processes in condensed matter is a relatively recent development that makes use of concepts already known in atomic or molecular physics. This approach is substantially equivalent to the configuration interaction method (Fano, Davis, Feldkamp)[18]. For the relation of this latter approach to some aspects of the many-body calculational approach, see Chang and Fano[19], although in the general case this relation can be quite involved.

As a general trend, however, the calculation of the EXAFS signal in photoabsorption and photoelectron diffraction processes in condensed matter or molecular physics has been traditionally based on an effective one particle approach, that is one particle moving in an effective (real or complex) potential. Multielectron excitations effects are added on top, so to say[6].

In this section we want to illustrate the relation of this one particle approach to the general theory of section 2 and show how the multiple scattering approach provides the unifying scheme in which to frame the different ways of solving the one particle problem.

The first reduction procedure one can think of is to eliminate in the set of equations (2.13), supplemented by the boundary conditions (2.14), all the "inelastic channels", i.e. those with $\alpha \neq \alpha'$ and such that $\Delta E_\alpha \neq 0$, in favour of the "elastic" one. This elimination is in principle possible and

leads to an effective Schrödinger equation with a complex potential, which in fact describes exactly the effect of the eliminated channels. This potential is known as optical potential. The contribution of the inelastic channels to the total absorption cross section is neglected altogether. Actually, since the optical potential is quite complicated, approximate forms based on ad hoc theoretical considerations are used in practical calculations, where quite often the imaginary part is neglected.

As a further approximation one reduces the potential to a muffin-tin form, although this is done only for computational convenience. In order to keep the discussion and the notation simple we shall assume this form for the potential, so that the relations (3.5) apply. The necessary generalization of the following considerations for non muffin-tin potentials is left to the reader.

The problem is therefore reduced to the calculation of the quantity

$$\sigma(\omega) = 4\pi^2\alpha\hbar\omega \, \Sigma_f \, |(\phi_f|\varepsilon\cdot\mathbf{r}|\phi_i)|^2 \, \delta(h\omega - E_f + E_i) \qquad (4.1)$$

where now $|\phi_f)$ and $|\phi_i)$ refer to one particle eigenstates with energies E_f and E_i respectively, of the effective one-electron Hamiltonian. For the final state

$$(k^2 - H)\phi_f = (\Delta + k^2 - V(\mathbf{r}))\phi_f = 0 \qquad (4.2)$$

where $V(\mathbf{r}) = \Sigma_k V_k(\mathbf{r})$ is a collection of muffin-tin potentials and $k^2 = \hbar\omega - I_c$ is the photoelectron energy.

Three methods have been used to calculate the quantity in Eq.(4.1):

a) the scattering method, where one calculates the time reversed scattering wave function ϕ^-_k for ϕ_f, with energy k^2 and normalized to one state per Rydberg. Then

$$\sigma_{sc}(\omega) = 4\pi^2\alpha\hbar\omega\,|(\phi^-_k(\mathbf{r})|\varepsilon\cdot\mathbf{r}|\phi_i(\mathbf{r}))|^2 \qquad (4.3)$$

with

$$(\nabla^2 + k^2 - V(\mathbf{r}))\ \phi^-_k = 0$$

$$\phi^-_k \underset{r\to\infty}{\simeq} (1/4\pi)\,(k/\pi)^{1/2}\ [e^{-i\mathbf{k}\cdot\mathbf{r}} + f^*(\mathbf{k}',\mathbf{k})\,(e^{-ikr}/r)]$$

b) the Green's function method, whereby one transforms Eq.(4.1) as ($T = \varepsilon\cdot\mathbf{r}$)

$$\sigma_{GF}(\omega) = 4\pi^2\alpha\hbar\omega\,(1/\pi)\,\mathrm{Im}(\phi_i|T^+(k^2-H)^{-1}\,T|\phi_i) \qquad (4.4)$$

$$= 4\pi\alpha\hbar\omega\,\mathrm{Im}\int d\mathbf{r}^3 d\mathbf{r}'^3\ \phi_i(\mathbf{r})\ \varepsilon\cdot\mathbf{r}\ G^-(\mathbf{r},\mathbf{r}')\ \varepsilon\cdot\mathbf{r}'\ \phi_i(\mathbf{r}')$$

where $(k^2-H)G^- = I$ or in the coordinate representation

$$[\nabla^2 + k^2 - V(\mathbf{r})]\ G^-(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \qquad (4.5)$$

G^- being the Green's function operator, with incoming wawe boundary conditions.

c) the band structure approach for periodic systems, whereby the scattering states are replaced by Bloch states $\phi_{\mathbf{q}}^{\,n}(\mathbf{r})$, where $\mathbf{q}$ indicates the wave vector in the reduced Brillouin zone (BZ) and n is the band index. Then Eq.(4.1) becomes

$$\sigma_{BS}(\omega) = 4\pi^2\alpha\hbar\omega\,\Sigma_n\ v/(2\pi)^3 \qquad (4.6)$$

$$\int_{BZ} d^3q\ \delta(k^2 - \varepsilon_n(\mathbf{q}))\ |(\phi_{\mathbf{q}}^{\,n}(\mathbf{r})\,|\varepsilon\cdot\mathbf{r}|\,\phi_i(\mathbf{r}))|^2$$

where $\varepsilon_n(\mathbf{q})$ gives the dispersion low for the band of index n and v is the volume of the unit primitive cell.

It is not at all immediate that the three expressions can be cast into the same final form for identical systems. We shall show that this is possible in the framework of the m.s. theory.

We can obtain the result of the scattering approach by performing the necessary index reduction in Eq.(2.55a). We obtain, assuming i≡o

$$\sigma_{BS}(\omega) = 4\pi^2\alpha\hbar\omega\,\Sigma_{L_f L'_f}\ M_{L_f}\ \Sigma_{\underline{L}}\ B_{oL_f}(\underline{L})\ B^*_{oL'_f}(\underline{L})\ M^*_{L'_f} \qquad (4.7)$$

where

$$M_L = (R^o_L(\mathbf{r}) | \boldsymbol{\varepsilon}\cdot\mathbf{r} | \phi_o(\mathbf{r})) \tag{4.8}$$

$$R^o_L(\mathbf{r}) = R^o_l(r)\ Y_L(\hat{\mathbf{r}}) \tag{4.9}$$

and $R^o_l(r)$ is that solution of the radial Schrödinger equation that matches smoothly to $j_l(kr)\,\mathrm{ctg}\delta_l - n_l(kr)$ at the radius of the muffin-tin sphere of the absorbing atom and behaves like $r^l(1 + \ldots)$ at the origin. It can be shown to be identical with the reduced form of the function $f^{\alpha\alpha}_{LL'}$ introduced in Eq.(2.52).

If the potential $V(\mathbf{r})$ is real, by using the optical theorem (2.19) we obtain the alternative form (2.55b)

$$\sigma_{sc}(\omega) = 4\pi\alpha\hbar\omega \sum_{L_f L'_f} M_{L_f}\ \mathrm{Im}\ \tau_{oL_f, oL'_f}\ M_{L'_f} \tag{4.10}$$

where we have dropped the star on $M_{L'}$, since in this case $R_L(\mathbf{r})$ is real. This form will be useful for comparison with the Green's function approach.

The solution of Eq.(4.5) for a collection of muffin-tin potentials is given by (but see Ref. 21 for a more complete definition)

$$G^+(\mathbf{r},\mathbf{r}') = -\Sigma_{LL'} R_L(\mathbf{r}_o)\ \tau_{oL,oL'}\ R_{L'}(\mathbf{r}'_o) - \Sigma_L R_L(\mathbf{r}_o) S_L(\mathbf{r}'_o)$$
$$\text{for } \mathbf{r},\mathbf{r}' \in \Omega_o \tag{4.11a}$$

$$G^+(\mathbf{r},\mathbf{r}') = -\Sigma_{LL'} R_L(\mathbf{r}_i)\ \tau_{iL,kL'}\ R_{L'}(\mathbf{r}'_k)$$
$$\text{for } \mathbf{r} \in \Omega_i,\ \mathbf{r}' \in \Omega_k \tag{4.11b}$$

where $S_L(\mathbf{r}) = S_l(r) Y_L(\hat{\mathbf{r}})$ and $S_l(r)$ is that solution of the radial Schrödinger equation that matches smoothly to $j_l(kr)$ at ρ_o and is singular at the origin. We need only the expression (4.11a), since $\phi_o(r)$, being a core state, is localized at site o. Its insertion in Eq.(4.4) gives, since $G^- = (G^+)^*$,

$$\sigma_{GF}(\omega) = 4\pi\alpha\hbar\omega \sum_{L_f L'_f} \mathrm{Im}\{M_{L_f}\ \tau_{oL_f, oL'_f}\ M_{L'_f} + M_{L_f}\ \underline{M}_{L'_f}\} \tag{4.12}$$

where

$$\underline{M}_L = (S_L(\mathbf{r}) | \boldsymbol{\varepsilon}\cdot\mathbf{r} | \phi_o(\mathbf{r})) \tag{4.13}$$

For real potentials, since M_L and $\underline{M}_L$ are real, we recover Eq. (4.10).

Finally, in an infinite regular lattice, where for simplicity we assume all sites to be equivalent, the KKR method writes the Bloch function as

$$\phi^n_{\mathbf{q}}(\mathbf{r}) = \Sigma_L \, \alpha^n{}_L(\mathbf{q}) \; R_L(\mathbf{r}) \tag{4.14}$$

with the same definition of $R_L(\mathbf{r})$ as before.

The coefficients $\alpha^n{}_L(\mathbf{q})$ satisfy the homogeneous equations

$$\Sigma_{L'}(t^{-1}{}_l \; \delta_{LL'} - G_{LL'}(\mathbf{q})) \; \alpha^n{}_L(\mathbf{q}) = 0 \tag{4.15}$$

where $t_l = e^{i\delta_l} \sin\delta_l$ is the usual l wawe atomic t-matrix, common to all sites, and

$$\begin{aligned} G_{LL'}(\mathbf{q}) &= (1/N) \; \Sigma_{ik} \; e^{-\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_k)} \; G_{iL,kL'} \\ &= \sum_{k(\neq o)} e^{-\mathbf{q}\cdot(\mathbf{R}_o - \mathbf{R}_k)} \; G_{oL,kL'} \end{aligned} \tag{4.16}$$

since now the second term is independent of the initial site o.

A non trivial solution of Eq.(4.15) demands that

$$\text{Det} \; \| \, t^{-1}(\varepsilon) - G(\mathbf{q};\varepsilon) \, \| = 0 \tag{4.17}$$

which determines the band dispersion $k^2 = \varepsilon = \varepsilon_n(\mathbf{q})$. Correspondently Eqs. (4.15) provide $\alpha^n{}_L(\mathbf{q})$. Using the expression (4.14) for the final state wave function, the Eq. (4.6) gives

$$\sigma_{BS}(\omega) = 4\pi^2\alpha\hbar\omega \, \Sigma_{L_f L'_f} M_{L_f} M_{L'_f} \, \Sigma_n \, v/(2\pi)^3$$

$$\int_{BZ} d^3q \; \delta(k^2 - \varepsilon_n(\mathbf{q})) \; \alpha^n{}_{L_f}(\mathbf{q}) \, [\alpha^n{}_{L'_f}(\mathbf{q})]^* \tag{4.18}$$

Now this expression is nothing else that

$$\sigma_{BS}(\omega) = 4\pi\alpha\hbar\omega$$

$$\mathrm{Im} \int dr^3\, dr^3\, \phi_o(\mathbf{r})\ \varepsilon\cdot\mathbf{r}\ G_{BS}(\mathbf{r},\mathbf{r}')\ \varepsilon\cdot\mathbf{r}'\ \phi_o(\mathbf{r}') \tag{4.19}$$

where

$$\mathrm{Im}\ G_{BS}(\mathbf{r},\mathbf{r}') = \mathrm{Im}\ \Sigma_q \Sigma_n \frac{[\phi^n_q(\mathbf{r})]^*\ \phi^n_q(\mathbf{r}')}{k^2 - \varepsilon_n(q)} =$$

$$= \pi \Sigma_q \Sigma_n [\phi^n_q(\mathbf{r})]^*\ \phi^n_q(\mathbf{r}')\ \delta(k^2 - \varepsilon_n(q)) \tag{4.20}$$

But the function $G_{BS}(\mathbf{r},\mathbf{r}')$ is a solution of the Schrödinger equation

$$(\nabla + k^2 - V(\mathbf{r}))\ G_{BS}(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{4.21}$$

which satisfies periodic boundary conditions

$$G_{BS}(\mathbf{r}+\mathbf{R}_k, \mathbf{r}'+\mathbf{R}_k) = G_{BS}(\mathbf{r},\mathbf{r}') \tag{4.22}$$

due to the property of the Bloch states

$$\phi^n_q(\mathbf{r}+\mathbf{R}_k) = e^{i\mathbf{q}\cdot\mathbf{R}_k}\ \phi^n_q(\mathbf{r})$$

Such a solution is provided by the function defined in Eq. (4.11), where now $\tau_{iL,kL'}$ depends only on the difference $\mathbf{R}_i - \mathbf{R}_j$ due to the periodicity of the lattice. When inserted in Eq. (4.19) this solution provides the usual result (4.10), since $V(\mathbf{r})$ is assumed to be real in band structure calculations.

The equivalence of the three approaches, just proved, reconciles the apparently different point of view of the chemist, who usually thinks in terms of wave function amplitude, with the physicist attitude, who is inclined to think in terms of density of unoccupied states. In fact Im $G(\mathbf{r},\mathbf{r}')$, for $\mathbf{r},\mathbf{r}' \in \Omega_o$, is proportional to the local projected density of states, of which a particular l character is selected when performing the weighted trace in Eq. (4.4). This

equivalence is not surprising, since the presence of a potential modifies at the same time the amplitude of the wave function and the density of the available states.

When the potential is complex, there is no more equivalence between the scattering and the Green's function approach. In fact the generalized optical theorem Eq. (2.50) does not hold in this case. One must then resort to theoretical considerations to know which method to use.

The imaginary part of the complex optical potential describes the reduction of the wavefunction amplitude of the elastic channel due to transitions to all the other channels.

As it is known in scattering theory[4], the imaginary part of the forward scattering amplitude is greater than the integral of its modulus, the difference giving the flux of particles scattered in the inelastic channels. So for the electron-molecule scattering the form (2.64) is still to be used for the total cross section, elastic plus inelastic.

In the photoabsorption process we add an electron to the ground state of the (Z+1)-equivalent atom, therefore we neeed to describe the propagation of the added electron in the presence of all the other electrons of the system. The amplitude of this propagation is the probability amplitude that the added electron remains in the original state in which it has been added to the system. Its imaginary part, as in the scattering case, gives the total probability of scattering in and out the initial state.

This propagation is described by the one particle Green's function $G(\mathbf{r},\mathbf{r}';E)$ which obeys an effective one particle Schrödinger equation, better known as Dyson equation,

$$(\nabla^2+E- V_c(\mathbf{r}))\ G(\mathbf{r},\mathbf{r}';E)- \tag{4.23}$$

$$\int d^3r''\ \Sigma(\mathbf{r},\mathbf{r}'';E)\ G(\mathbf{r}'',\mathbf{r}';E) = \delta(\mathbf{r}-\mathbf{r}')$$

where $\Sigma(\mathbf{r},\mathbf{r}';E)$ is an energy dependent, complex and in general non local, effective exchange and correlation potential, whereas $V_c(\mathbf{r})$ is the usual Coulomb or Hartree potential. Therefore in calculating the photoabsorption cross section we

have to replace Eq. (4.5) with Eq. (4.23) and use formula (4.12).

Much work has gone into approximating the self-energy Σ in a way suitable for numerical applications. Hedin and Lundqvist[22], by incorporating the Sham-Kohn[23] density-functional formalism for excited states within the single-plasmon pole approximation of the electron-gas dielectric function, have produced a useful, theoretically sound, local approximation to Σ given by

$$V_{xc}(\mathbf{r}) \simeq \Sigma_h(p(\mathbf{r}), E - V_c(\mathbf{r}); \rho(\mathbf{r})) \tag{4.24}$$

Here Σ_h is the self-energy of an electron in an homogeneous electron gas with momentum $p(\mathbf{r})$, energy $E - V_c(\mathbf{r})$ and density $\rho(\mathbf{r})$, the local density of the actual physical system.

The local momentum $p(\mathbf{r})$ is defined as

$$p^2(\mathbf{r}) = k^2 + k^2_F(\mathbf{r}) - \mu_F \tag{4.25}$$

where k^2 is the photoelectron energy, $k^2_F(\mathbf{r}) = [3\pi^2\rho(\mathbf{r})]^{1/3}$ is the local Fermi momentum and μ_F is the Fermi energy of the system as a whole. For molecules it should be the first ionization energy.

Since $E - V_c(\mathbf{r}) \sim p^2(\mathbf{r})$ we can write with Lee and Beni[24]

$$V_{xc}(\mathbf{r}) \simeq \Sigma_h(p(\mathbf{r}), p^2(\mathbf{r}); \rho(\mathbf{r})) \tag{4.26}$$

To calculate Σ_h, one uses Eq.s (25.14) and (25.15) of Ref. 25

$$\mathrm{Re}\ \Sigma_h(\mathbf{p},\omega) = -\int \frac{d^3q}{(2\pi)^3} \frac{4\pi}{q^2} \frac{f(\mathbf{p}+\mathbf{q})}{\varepsilon(\mathbf{q}, (\mathbf{p}+\mathbf{q})^2 - \omega)}$$

$$-\omega_p \int \frac{d^3q}{(2\pi)^3} \frac{1}{2\omega_1(\mathbf{q})} \frac{1}{\omega_1(\mathbf{q}) - \omega + (\mathbf{p}+\mathbf{q})^2}$$

$$\text{Im}\ \Sigma_h\ (\mathbf{p},\omega) = \frac{\pi\,\omega_p^{\,2}}{2} \int \frac{d^3q}{(2\pi)^3}\ \frac{4\pi}{q^2}\ \frac{1}{\omega_1(\mathbf{q})}$$

$$\{\, f(\mathbf{p}+\mathbf{q})\ \ \delta[\,(\mathbf{p}+\mathbf{q})^2 - \omega_1(\mathbf{q})\ - \omega]$$

$$-\ [1-f(\mathbf{p}+\mathbf{q})]\ \ \delta[\,(\mathbf{p}+\mathbf{q})^2 + \omega_1(\mathbf{q})\ - \omega]\,\}$$

where the dielectric function is approximated by

$$[\varepsilon\ (\mathbf{p},\omega)\,]^{-1} = 1 + \frac{\omega_p^{\,2}}{[\omega^2 - \omega_1^{\,2}(\mathbf{q})\,]}$$

$$\omega_1^{\,2}(\mathbf{q}) = \omega_p^{\,2} + \varepsilon_F^{\,2}\,[\,(4/3)\ (q/k_F)^2 + (q/k_F)^4]$$

ω_p is the plasmon frequency and $f(\mathbf{k})$ is the Fermi distribution function. A useful analytical approximation to these equations is given in ref. 6 where other approximate forms of effective potentials are discussed, like the X-α and the Dirac-Hara potentials[26].

5. CONCLUSIONS

The multichannel multiple scattering theory outlined in section 2 provides a simple, natural scheme in which to study two main problems that are still a subject of active research: the evolution from the adiabatic to the sudden regime and the interplay between excitation dynamics and structure.

In fact the nature of the crossover from sudden to adiabatic behavior is an interesting theoretical question which is not yet well understood. We refer to ref. 27 for a review discussion on this point, mainly based on the articles of Fano and Cooper[28] and Lee and Beni[24]. A more quantitative attempt is contained in the work by Chou et al[6] (but se also references therein) and in ref. 29.

In our formulation we see from Eq.(2.47) that the driving terms that control the crossover are the off-diagonal (i.e. interchannel) $(K_{ai})^{\alpha\alpha'}{}_{LL'}$ matrix elements of the atomic reactance matrices. It is not the purpose of the present notes to develop this aspect of the theory which is still a matter of investigation.

Another aspect which is clarified by the present theory is that of the relation between excitation dynamics and geometrical and electronic structure of the ground state. It is not surprising, looking at the structure of the m.s. matrix Eq. (2.47) and the resonance condition Eq. (3.35) that the general shape of a photoabsorption spectrum is determined mainly by the geometrical structure of the ground state and by the configurations present in it.

Certainly many applications are needed to establish the relative role of the various factors that contribute to a photoabsorption or to a photoemission spectrum. What was missing was a unifying interpretative scheme which we think is now provided by the multichannel multiple scattering theory.

After the completion of this notes I became aware of the fact that the questions treated here had been addressed by Bardyszewski and Hedin in a different scheme provided by a novel perturbation theory approach, with applications to photoemission and X-ray spectroscopy[30]. Their conclusions are qualitatively similar to those presented here although further study is needed to established the relation between the two approaches.

AKNOWLEDGMENTS

It is a pleasure to aknowledge the stimulating collaboration of Dr. M. Benfatto during which a large part of the results presented here have been obtained.

I also want to thank Mrs. L. Invidia for her patience and valuable suggestions in editing the manuscript.

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