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THE USE OF GENERAL POTENTIALS IN MULTIPLE SCATTERING THEORY

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Abstract

A mathematically clear and simple derivation of the multiple scattering equations valid for a general non muffin-tin potential, as applied to clusters of atoms, with and without a surrounding outer sphere, is presented. These equations are shown to be a natural generalization of the analogous equations valid for muffin-tin potentials, to which they reduce in this latter case. An application to the calculation of phototabsorption cross sections in this general case is given. A connection with the Green function approach to the problem is established via a generalized optical theorem shown to be valid for scattering amplitudes. An expression for the photoabsorption cross section in the framework of the multiple scattering theory valid for a general potential is derived for the first time, providing the necessary generalization for the similar expression valid in the muffin-tin case.

1. Introduction

The multiple scattering theory approach to the calculation of the electronic structure of molecules and clusters of atoms, although quite successful in many applications, has suffered from the restriction to potentials of the muffin-tin type, i.e. potentials spherically symmetric inside the atomic spheres and constant in the interstitial region.

The difference between the true potential and its muffin-tin form can be quite serious in those instances in which there is an effect of building up of charge density along a bond or when most of the charge is left in the interstitial region, as is the case of short bonds between low Z atoms. The monopole approximation of the potential inside the atomic spheres in the first case and the approximation of the potential in the interstitial region by a constant in the second case constitute a very poor representation of the real state of affairs.

The purpose of this paper is to give a general formulation of the multiple scattering equations (MSE) for any (local) potential that can be represented by a multipole expansion around the atomic centers. The final result will turn out to be a straightforward generalization of the equations valid for the muffin-tin case, easily amenable to computer programming.

Attempts to lift the restrictions imposed by the form of the potential used in the calculations already exist in the literature. Siegel, Dill and Dehmer¹⁾ have given a formulation of the MSE for a nonspherically symmetric potential inside the atomic spheres, while still assuming its constancy in the interstitial region. They came to the conclusion that this generalization entails a doubling of the linear system of equations to be solved. Moreover their formulation for this case loses the physical transparency which was present in the muffin-tin case. Our formulation on the contrary will show that the extension to general potentials does not require such sacrifices.

A much more complete review of the multiple scattering theory in condensed matter with original contributions was given by Lloyd and Smith²⁾. The extension of the method to local potentials of general type is indeed contained in their paper if one is willing to put together bits and pieces scattered throughout the various sections. However a mathematically clear, simple and unified derivation of the MSE in the general case, as applied

to clusters of atoms, especially in the presence of a surrounding outer sphere, necessary for example in problems of scattering by a long range potential (e. g. Coulomb tail in problems of photoionization) is to our knowledge still missing. The present paper is intended to fill this gap.

Section 2 is devoted to the derivation of the MSE in the general case following the Green function approach as used by Belezny and Lawrence³⁾ to introduce non zero interstitial potentials in the calculation of electronic band structure. Section 3 contains instead on application of the MS method to the calculation of the photoabsorption cross section by a cluster of atoms with no approximation for the one-electron potential. A general expression is derived which should prove very useful to estimate the errors introduced by the often used muffin-tin approximation to the potential. Via a generalized optical theorem satisfied by the scattering amplitudes B_L^i defined below we make contact with the Green function approach to the problem which deals in terms of projected density of excited states onto the photoabsorbing site. This last formulation enables us to rapidly estimate in section 4 the correction introduced by the interstitial potential in the MS expansion for the cross section, which is shown to be absolutely convergent under certain conditions. These corrections are estimated to be important for open structures and not too high photoelectron energies ($\leq 100 - 150\text{eV}$).

2. The modified multiple scattering matrix

Being mainly interested in scattering problems, we shall first consider the Lippman-Schwinger equation

$$\psi(\vec{r}) = \phi_0(\vec{r}) + \int_V G_0^+(\vec{r}, \vec{r}') V(\vec{r}') \psi(\vec{r}') d^3 r' \quad (2.1)$$

associated to the Schrödinger equation

$$(\Delta + E)\psi(\vec{r}) = V(\vec{r})\psi(\vec{r}) \quad (2.2)$$

where $\phi_0(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$ ($k^2 = E$, using atomic units for lengths and Ryd units for energies) is the solution of the free equation $(\Delta + E)\phi_0(\vec{r}) = 0$, $G_0^+(\vec{r}, \vec{r}')$ is the free Green function appropriate to outgoing waves, satisfying

$$(\Delta + E)G_0^+(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}') \quad (2.3)$$

and $V(\vec{r})$ is a general local potential which we assume can be represented as a multipole expansion around a given centre ($L \equiv l, m$)

$$V(\vec{r}) = \sum_L V_L(r) Y_L(\hat{r}) \quad (2.4)$$

The spherical harmonics $Y_L(\hat{r})$ are defined according to Condon and Shortley⁴).

As usual in the multiple scattering theory, we partition the whole space V in nonoverlapping spheres Ω_j centered around the atomic site j and a remaining interstitial region $\Delta\Omega$. For simplicity, in order to make simple the derivation of the MSE in the general case, we shall defer to a later stage the inclusion of an outer sphere Ω_o enclosing all the atomic ones.

By introducing the potentials $V_j(\vec{r}) \equiv V(\vec{r})$ for $\vec{r} \in \Omega_j$ and $V_j(\vec{r}) = 0$ for $\vec{r} \notin \Omega_j$, $V_I(\vec{r}) \equiv V(\vec{r})$ for $\vec{r} \notin \sum_j \Omega_j$ and $V_I(\vec{r}) = 0$ for $\vec{r} \in \sum_j \Omega_j$, we can write Eq.(2.1) as

$$\psi(\vec{r}) = \phi_0(\vec{r}) + \sum_j \int_{\Omega_j} G_0^+(\vec{r}, \vec{r}') V_j(\vec{r}') \psi(\vec{r}') d^3 r' + \int_{\Delta\Omega} G_0^+(\vec{r}, \vec{r}') V_I(\vec{r}') \psi(\vec{r}') d^3 r' \quad (2.5)$$

Use of Green's theorem in the form

$$\int_V [F(\nabla^2 + E)G - G(\nabla^2 + E)F] d\tau = \int_{S_V} (F\vec{\nabla}G - G\vec{\nabla}F) \cdot \vec{n} d\sigma \quad (2.6)$$

where S_V is the surface enclosing the volume V , when applied to the volume integrals over Ω_j in Eq. (2.5) leads to the following relations:

$$\begin{aligned} \psi(\vec{r}) = \phi(\vec{r}) + \sum_j \int_{S_{\Omega_j}} [G_0^+(\vec{r}, \vec{r}') \vec{\nabla} \psi(\vec{r}') - \psi(\vec{r}') \vec{\nabla}_{r'} G_0^+(\vec{r}, \vec{r}')] \cdot \vec{n}_j d\sigma_j \\ + \int_{\Delta\Omega} G_0^+(\vec{r}, \vec{r}') V_I(\vec{r}') \psi(\vec{r}') d^3 r' \quad \text{if } \vec{r} \notin \sum_j \Omega_j \end{aligned} \quad (2.7a)$$

$$\begin{aligned} 0 = \phi(\vec{r}) + \sum_j \int_{S_{\Omega_j}} [G_0^+(\vec{r}, \vec{r}') \vec{\nabla} \psi(\vec{r}') - \psi(\vec{r}') \vec{\nabla}_{r'} G_0^+(\vec{r}, \vec{r}')] \cdot \vec{n}_j d\sigma_j \\ + \int_{\Delta\Omega} G_0^+(\vec{r}, \vec{r}') V_I(\vec{r}') \psi(\vec{r}') d^3 r' \quad \text{if } \vec{r} \in \sum_j \Omega_j \end{aligned} \quad (2.7b)$$

In deriving these equations we have made the identification $F \equiv G_0^+(\vec{r}, \vec{r}')$ and $G \equiv \psi(\vec{r})$ in Eq.(2.6), using Eq.(2.2) to rewrite $\nabla^2 \psi$ as $(\Delta + E)\psi$ in Eq.(2.5) and remembering Eq.(2.3).

To perform the surface integrals in Eq.(2.7b) for $\vec{r} \in \Omega_i$, we need to rewrite the free Green function as

$$G_0^+(\vec{r}, \vec{r}') \equiv G_0^+(\vec{r} - \vec{r}') = \frac{-\exp(ik|\vec{r} - \vec{r}'|)}{4\pi|\vec{r} - \vec{r}'|} = \begin{cases} -ik \sum_L j_l(kr_{<}) Y_L(\hat{r}_{<}) h_l^+(kr_{>}) Y_L^*(\hat{r}_{>}) & (2.8a) \\ -ik \sum_L j_l(kr_{<}) Y_L^*(\hat{r}_{<}) h_l^+(kr_{>}) Y_L(\hat{r}_{>}) & (2.8b) \end{cases}$$

where $r_{>}$ ($r_{<}$) refer to the greater (the lesser) of $|\vec{r}|$ and $|\vec{r}'|$, in terms of coordinates referred to different sites (j_l, n_l, h_l^+ are spherical Bessel, Neumann and Hankel functions, respectively, with $h_l^+ = j_l + in_l$).

We find, with reference to fig.1, defining $\vec{R}_{ij} \equiv \vec{R}_i - \vec{R}_j$, $\vec{r}_i \equiv \vec{r} - \vec{R}_i$,

$$G_0^+(\vec{r} - \vec{r}') = G_0^+(\vec{r}_i + \vec{R}_{ij} - \vec{r}'_j) = -ik \sum_L j_l(kr_i) Y_L(\hat{r}_i) h_l^+(k|\vec{r}'_j - \vec{R}_{ij}|) Y_L^*(\hat{r}'_j - \vec{R}_{ij}) \quad (2.9)$$

since, when \vec{r} is inside Ω_i and \vec{r}' on the surfaces S_{Ω_j} , $|\vec{r}'_j - \vec{R}_{ij}| = |\vec{r}' - \vec{R}_i| > |\vec{r} - \vec{R}_i|$

Using the reexpansion theorem²⁾, noting that $|\vec{R}_{ij}| > |\vec{r}'_j|$, when \vec{r}' is on S_{Ω_j} , we have

$$-ih_l^+(k|\vec{r}'_j - \vec{R}_{ij}|) Y_L(\hat{r}'_j - \vec{R}_{ij}) = \sum_{L'} j_{l'}(kr'_j) Y_{L'}(\hat{r}'_j) H_{LL'}^i \quad (2.10)$$

where

$$\begin{aligned} H_{LL'}^i &= 4\pi \sum_{\underline{L}} i^{l+l'-l} C_{L'L}^{\underline{L}} [-ih_{\underline{L}}^+(kR_{ji})] Y_{\underline{L}}(\hat{R}_{ji}) \\ &= \sum_{\underline{L}} i^{l+l'-l} (-1)^m [4\pi(2l'+1)(2l+1)(2\underline{l}+1)]^{\frac{1}{2}} \begin{pmatrix} l' & l & \underline{l} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l & \underline{l} \\ m' & -m & \underline{m} \end{pmatrix} [-ih_{\underline{L}}^+(kR_{ji})] Y_{\underline{L}}(\hat{R}_{ji}) \end{aligned} \quad (2.11)$$

since⁵⁾

$$\begin{aligned} C_{L'L}^{\underline{L}} &= \int Y_{L'}(\Omega) Y_L^*(\Omega) Y_{\underline{L}}(\Omega) d\Omega \\ &= (-1)^m [(2l'+1)(2l+1)(2\underline{l}+1)/4\pi]^{1/2} \begin{pmatrix} l' & l & \underline{l} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l & \underline{l} \\ m' & -m & \underline{m} \end{pmatrix} \end{aligned} \quad (2.12)$$

Inserting Eq.(2.10) into Eq.(2.9) we finally have the result,

$$G_0^+(\vec{r} - \vec{r}') = G_0^+(\vec{r}_i + \vec{R}_{ij} - \vec{r}'_j) = k \sum_{LL'} j_l(kr_i) Y_L(\hat{r}_i) H_{LL'}^i j_{l'}(kr'_j) Y_{L'}^*(\hat{r}'_j) \quad (2.13)$$

for \vec{r} inside the sphere Ω_i and \vec{r}' on the surfaces of the spheres Ω_j ($j \neq i$). To derive Eq.(2.13) we have taken into account that $Y_{lm}^* = (-1)^m Y_{l-m}$ and that $(-1)^{m+m'} H_{LL'}^i = H_{l'-m' l-m}^i$ which follows from the definition (2.11).

Next we need an expression for the solution of the Schrödinger equation (2.2) inside each sphere Ω_j . Writing

$$\psi(\vec{r}) = \sum_L \phi_L(r) Y_L(\hat{r})$$

and inserting in Eq.(2.2) together with expansion (2.4), using the orthogonality properties of the spherical harmonics, we find that the functions $\phi_L(\vec{r})$ satisfy the following set of coupled differential equations:

$$\left(\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + E - \frac{l(l+1)}{r^2} \right) \phi_L(r) = \sum_{L'} V_{LL'}(r) \phi_{L'}(r) \quad (2.14)$$

where

$$V_{LL'}(r) = \sum_{L''} C_{L'L''}^L V_{L''}(r) \quad (2.15)$$

with $C_{L'L''}^L$ defined in Eq. (2.12).

Now Eqs.(2.14) constitute a set of $(l_{max} + 1)^2$ coupled equations if we truncate the L -expansion to an l_{max} allowed angular momentum. As is well known, we can construct $(l_{max} + 1)^2$ linearly independent solutions $R_{LL'}(r)$ regular at the origin, by using this number of different initial boundary conditions.

Under the assumption that the matrix elements $V_{LL'}(r)$ have no singularity of order two or greater, we can take near the origin

$$R_{LL'}(r) \simeq r^{l+1} \delta_{LL'} \quad (2.16)$$

For a given L' , $R_{LL'}(r)$ is a vector solution of Eq.(2.14) of $(l_{max} + 1)^2$ dimensions, L labelling the vector components.

Consequently the general solution $\phi_L(r)$ can be written as

$$\phi_L(r) = \sum_{L'} C_{L'} R_{LL'}(r) \quad (2.17)$$

so that, in all generality, inside the spheres Ω_j , we can write

$$\psi(\vec{r}_j) = \sum_{LL'} C_{L'}^j R_{LL'}(r_j) Y_L(\hat{r}_j) \quad (2.18)$$

Insertion of Eq.(2.13) and (2.18) into Eq.(2.7b), assuming \vec{r} inside the sphere Ω_i and performing the surface integrals, gives

$$0 = \sum_L j_l(kr_i) Y_L(\hat{r}_i) \left(k \rho_i^2 \sum_{L'} W[-ih_i^+, R_{LL'}^i] C_{L'}^i + \sum_{j \neq i} \sum_{L''} k \rho_j^2 H_{LL''}^j W[j_\nu, R_{L''L''}^j] C_{L''}^j \right) + \phi_0(\vec{r}) + \int_{\Delta\Omega} G_0^+(\vec{r}, \vec{r}') V_I(\vec{r}') \psi(\vec{r}') d^3 r' \quad (2.19)$$

where ρ_j is the radius of sphere Ω_j and we have introduced, e. g., the Wronskians $W[j_l(kr_j), R_{LL'}^j(r_j)] = j_l(kr_j) \frac{d}{dr_j} R_{LL'}^j(r_j) - R_{LL'}^j(r_j) \frac{d}{dr_j} j_l(kr_j)$ calculated at $r_j = \rho_j$.

By putting

$$B_{L'}^j = k \rho_j^2 \sum_{L''} W[j_\nu, R_{L''L''}^j] C_{L''}^j \quad (2.20)$$

and introducing the matrices of the Wronskians

$$W[j, R^j]_{LL'} \equiv W[j_l, R_{LL'}^j], \quad W[-ih^+, R^j]_{LL'} \equiv W[-ih_l^+, R_{LL'}^j], \quad (2.21)$$

we can solve for the coefficients C_L^j in Eq.(2.20), obtaining

$$k \rho_j^2 C_L^j = \sum_{L'} (W[j, R^j]_{LL'})_{LL'}^{-1} B_{L'}^j \quad (2.23)$$

Upon definition of the atomic quantities

$$(T_a^j)_{LL'}^{-1} = \sum_L W[-ih^+, R^j]_{LL} (W[j, R^j]_{LL'})_{LL'}^{-1} \quad (2.24)$$

and expansion of the incoming wave $\phi_0(\vec{r})$, which is referred to the origin o of the coordinates, around center i ,

$$\phi_0(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} = 4\pi \sum_{L'} i^{l'} j_{l'}(kr) Y_{L'}(\hat{r}) Y_{L'}^*(\hat{k}) = 4\pi \sum_{L'} i^{l'} Y_{L'}^*(\hat{k}) \sum_L j_l(kr_i) Y_L(\hat{r}_i) J_{LL'}^i \quad (2.25)$$

we can write Eq. (2.19) as

$$0 = \sum_L j_l(kr_i) Y_L(\hat{r}_i) \left(\sum_{jL'} [(T_a^i)_{LL'}^{-1} B_{L'}^i \delta_{ij} + (1 - \delta_{ij}) H_{LL'}^i B_{L'}^i + J_{LL'}^i 4\pi i^{l'} Y_{L'}^*(\hat{k})] \right) + \int_{\Delta\Omega} G_0^+(\vec{r}, \vec{r}') V_I(\vec{r}') \psi(\vec{r}') d^3 r' \quad (2.26)$$

In deriving Eq. (2.25) we have made use of the expansion²⁾

$$j_l(kr_i) Y_L(\hat{r}_i) \equiv j_l(k|\vec{r}_j - \vec{R}_{ij}|) Y_L(\vec{r}_j - \vec{R}_{ij}) = \sum_{L'} j_{l'}(kr_j) Y_{L'}(\hat{r}_j) J_{LL'}^i \quad (2.27)$$

valid under no restriction on \vec{r}_i , \vec{r}_j and \vec{R}_{ij} , where

$$J_{LL}^i = 4\pi \sum_{\underline{L}} i^{L+L'-1} C_{L'L}^L j_L(kR_{ji}) Y_{\underline{L}}(\hat{R}_{ji}) \quad (2.28)$$

Under the assumption that $V_I(\vec{r}) = 0$, Eq. (2.26) gives the usual multiple scattering equations²⁾ for non spherically symmetric potentials $V_j(\vec{r})$, provided the exciting amplitude $4\pi i^L Y_L^*(\hat{k})$ is set equal to δ_{LL} :

$$\sum_{jL'} [(T_a^j)_{LL'}^{-1} B_{L'}^i \delta_{ij} + (1 - \delta_{ij}) H_{LL'}^i B_{L'}^j] = -J_{LL}^i \quad (2.29)$$

We show in Appendix A that the quantities $(T_a^j)_{LL'}$ in Eq. (2.24) are indeed the atomic t-matrices in angular momentum representation relative to the potentials $V_j(\vec{r})$ as defined by Evans and Keller⁶⁾ in their Appendix 1.

When $V_j(\vec{r}) \equiv V_j(|\vec{r}|)$ is spherically symmetric, then in Eq. (2.18) $R_{LL'}^j \rightarrow R_L^j \delta_{LL'}$, so that $(T_a^j)_{LL'} \rightarrow t_L^j \delta_{LL'}$, where

$$t_L^j = W[j_L, R_L^j] / W[-ih_L^+, R_L^j] \quad (2.30)$$

which is the usual definition of the atomic t-matrices in the spherical case⁷⁻⁹⁾.

When $V_I(\vec{r}) \neq 0$, we need to consider Eq.(2.7a) for $\vec{r} \notin \sum_j \Omega_j$. If \vec{r} is in the interstitial region, then $|\vec{r} - \vec{R}_j| > |\vec{r}' - \vec{R}_j|$ if \vec{r}' is to be on the surface of the sphere Ω_j . Hence, using Eq. (2.8b) in the form

$$G_0^+(\vec{r} - \vec{r}') = G_0^+(\vec{r}_j - \vec{r}'_j) = -ik \sum_L j_L(kr'_j) Y_L^*(\hat{r}'_j) h_L^+(kr_j) Y_L(\hat{r}_j) \quad (2.31)$$

inserting in Eq. (2.7a), using again Eq. (2.18) and performing the surface integrals we find

$$\psi(\vec{r}) = -i \sum_{jL} h_L^+(kr_j) Y_L(\hat{r}_j) B_L^j + \phi_0(\vec{r}) + \int_{\Delta\Omega} G_0^+(\vec{r} - \vec{r}') V_I(\vec{r}') \psi(\vec{r}') d^3r' \quad (2.32)$$

remembering the definitions (2.20).

Notice that, when $V_I(\vec{r}) = 0$, the solution of Eq. (2.29) yields the coefficients B_L^j of the scattered waves in the interstitial region. Eqs (2.20) provide the relation between these coefficients and the coefficients C_L^j in Eq. (2.18) of the solution inside the atomic spheres. It is the straightforward generalization of the similar relation valid for the spherical case⁸⁻⁹⁾ and does not seem to be contained in the literature. Notice also that in the nonspherical

case no doubling of the dimensions of the multiple scattering matrix (2.29) is necessary.

Coming back to the case $V_I(\vec{r}) \neq 0$ we can use Eq. (2.32) to determine $\psi(\vec{r})$ in the interstitial region to substitute in Eq. (2.26), in order to obtain the MSE in the general case.

As it is, Eq. (2.32) is the Lippmann-Schwinger equation relative to the potential $V_I(\vec{r})$, with incoming waves given by

$$\tilde{\phi}_0(\vec{r}) = -i \sum_{jL} h_L^+(kr_j) Y_L(\hat{r}_j) B_L^j + \phi_0(\vec{r}) \quad (2.33)$$

By introducing the T-matrix relative to the interstitial potential $V_I(\vec{r})$ defined by the equation

$$T_I = V_I + V_I G_0^+ T_I = V_I + T_I G_0^+ V_I \quad (2.34)$$

so that

$$T_I \tilde{\phi}_0 = V_I \psi \quad (2.35)$$

we can write the last term in Eq. (2.26) as

$$\int_{\Delta\Omega} G_0^+(\vec{r} - \vec{r}') V_I(\vec{r}') \psi(\vec{r}') d^3 r' = \int_{\Delta\Omega} \int_{\Delta\Omega} G_0^+(\vec{r} - \vec{r}') T_I(\vec{r}', \vec{r}'') \tilde{\phi}_0(\vec{r}'') d^3 r' d^3 r'' \quad (2.36)$$

since Eq. (2.34) shows that $T_I(\vec{r}, \vec{r}')$ is different from zero only for \vec{r} and \vec{r}' in the interstitial region.

For \vec{r} inside Ω_i , as appropriate in Eq. (2.26) and \vec{r}' in the interstitial region, as demanded by Eq. (2.26), we have $|\vec{r}_i| < |\vec{r}'_i|$, so that we can write

$$G_0^+(\vec{r} - \vec{r}') = -ik \sum_L j_L(kr_i) Y_L(\hat{r}_i) h_L^+(kr'_i) Y_L^*(\hat{r}'_i) \quad (2.37)$$

Use of this relation into Eq. (2.36), remembering Eq. (2.33) and (2.25) referred to the center o , gives

$$\int_{\Delta\Omega} G_0^+(\vec{r} - \vec{r}') V_I(\vec{r}') \psi(\vec{r}') d^3 r' = \sum_L j_L(kr_i) Y_L(\hat{r}_i) \left[\sum_{jL'} T_{LL'}^j B_{L'}^j + \sum_{L'} \Theta_{LL'}^i 4\pi i^L Y_{L'}^*(\hat{k}) \right] \quad (2.38)$$

where we have defined

$$T_{LL'}^j = k \int_{\Delta\Omega} \int [-ih_L^+(kr_i) Y_L^*(\hat{r}_i) T_I(\vec{r}, \vec{r}') [-ih_{L'}^+(kr'_j) Y_{L'}(\hat{r}'_j) d^3 r d^3 r'] \quad (2.39)$$

$$\Theta_{LL'}^i = k \int_{\Delta\Omega} \int [-ih_l^+(kr_i)] Y_L^*(\hat{r}_i) T_I(\vec{r}, \vec{r}') j_l(kr'_o) Y_L(\hat{r}'_o) d^3r d^3r' \quad (2.40)$$

Insertion of Eq.(2.38) into Eq.(2.26) provides the desired generalization of the MSE, in the absence of an outer spheres; after equating to zero the coefficient of $j_l(kr_i)Y_L(\hat{r}_i)$ and putting again $4\pi i^l Y_L^*(\hat{k}) = \delta_{LL}$:

$$\sum_{jL'} ((t^i)_{LL'}^{-1} + T_{LL'}^i) B_{L'}^j \delta_{ij} + (1 - \delta_{ij})(H_{LL'}^i + T_{LL'}^i) B_{L'}^j = -J_{LL}^i - \Theta_{LL}^i \quad (2.41)$$

Had we worked in K -matrix normalization ($-ih_l^+ \rightarrow n_l$) instead of T -matrix normalization, we would have recovered the analogous generalization of the MSE with the mere substitution, in all the above formulae, of the outgoing wave $-ih_l^+$ with the standing wave n_l . In this case Eq.(2.41) would constitute the generalization of the MSE by Dehmer and Dill⁹⁾ to non muffin-tin potentials, with the same definition of the coefficient B_L^j .

To solve for this latter quantities, we need to know the matrix elements $T_{LL'}^i$ in Eq.(2.41), which is tantamount the T_I -matrix for the interstitial potential. If $V_I(\vec{r})$ cannot support a bound state, than a Born expansion of Eq.(2.34) provides the desired result. If instead $V_I(\vec{r})$ is strong enough to support a bound state, one can use some of the tricks already known in the literature¹⁰⁾. The simplest of all is suggested by the observation that there is a reasonable chance that with a judicious choice of the constant \bar{V}_{int} , the potential $V_I(\vec{r}) - \bar{V}_{int}$ does not bind. Generalization to this case of the above formulae is then immediate. Indeed now Eq.(2.2) should read

$$(\Delta + E - \bar{V}_{int})\psi(\vec{r}) = (V(\vec{r}) - \bar{V}_{int})\psi(\vec{r}) \quad (2.42)$$

If we choose the true Green's function as the solution of the equation

$$(\Delta + E - \bar{V}_{int})G_0^+(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}')$$

then all the above derivation is valid, provided we replace $k = \sqrt{E}$ with $\kappa = [E - \bar{V}_{int}]^{\frac{1}{2}}$ and $V_I(\vec{r})$ with $V_I(\vec{r}) - \bar{V}_{int}$. However the solution of the Schrödinger equation inside the atomic spheres Ω_j , $R_{LL}(r_j, E)$, should still calculated at the energy E , since in Ω_j the solution of Eq.(2.42) is the same as the one of Eq.(2.2).

The presence of an outer sphere Ω_o , enclosing all the atomic spheres, having radius ρ_o and centered at site o , does not introduce any major complication in the derivation

of the MSE. Strictly speaking the introduction is only necessary when dealing with long-range potentials (e.g. coulombic), in order to impose the appropriate boundary conditions at infinity. It is however a useful expedient even for short-range potentials, since it helps reduce the volume of the interstitial region and consequently the strength of the interstitial potential.

In analogy with above we define $V_o(\vec{r}) \equiv V(\vec{r})$ for $r \in \mathcal{C}\Omega_o$, where $\mathcal{C}\Omega_o$ is the region of the space complementary to Ω_o and $V_o(\vec{r}) \equiv 0$ for $r \in \Omega_o$. Similarly we take $V_j(\vec{r}) \equiv V(\vec{r})$ for $r \in \Delta\Omega' \equiv \Omega_o - \sum_{j=1}^N \Omega_j$, which now defines the interstitial region, N being the number of the atomic spheres, and $V_j(\vec{r}) \equiv 0$ elsewhere.

As before use of the Green's theorem Eq.(2.1) leads again to the Eq.(2.7a) for $r \notin \mathcal{C}\Omega_o + \sum_{j=1}^N \Omega_j$ and to Eq.(2.7b) for $r \in \mathcal{C}\Omega_o + \sum_{j=1}^N \Omega_j$, the summation \sum_j over the surface integrals including now a contribution from the outer sphere surface S_{Ω_o} . The free part $\phi_0(\vec{r})$ can be now dropped since the outgoing wave condition can be imposed directly on $\mathcal{C}\Omega_o$. In this region we can write, in analogy with Eq.(2.18)

$$\psi(\vec{r}) = \sum_{LL'} [A_{LL'}^o f_{LL'}^o(r_o) + C_{LL'}^o \gamma_{LL'}^o(r_o)] Y_L(\vec{r}_o) \quad (2.43)$$

where $f_{LL'}^o$ and $\gamma_{LL'}^o$ are determined by inward integration in $\mathcal{C}\Omega_o$ through their asymptotic behavior, normalized to one state per Ryd.

$$\lim_{r_o \rightarrow \infty} f_{LL'}^o(r_o) \approx \delta_{LL'} \frac{1}{kr_o} \sin(kr_o - \frac{1}{2}l\pi + \omega_l) \quad (2.44a)$$

$$\lim_{r_o \rightarrow \infty} \gamma_{LL'}^o(r_o) \approx -\delta_{LL'} \frac{1}{kr_o} \cos(kr_o - \frac{1}{2}l\pi + \omega_l) - i f_{LL'}^o(r_o) \quad (2.44b)$$

The extra phase shift ω_l has been introduced for dealing with long-range potentials.

In Eq.(2.43) A_L^o is the exciting amplitude, to be set equal to δ_{LL} and C_L^o is to be determined by solving the MSE. To evaluate the outer sphere contribution to the surface integrals in Eq.(2.7) we need the free Green's function G_0^+ rewritten either as

$$G_0^+(\vec{r} - \vec{r}') \equiv G_0^+(\vec{r}_i - \vec{R}_{oi} - \vec{r}') = k \sum_{LL'} [-ih_l^+(kr'_o)] Y_L(\vec{r}_o) J_{LL}^o j_l(kr'_i) Y_L^*(\vec{r}'_i) \quad (2.45a)$$

for $\vec{r} \in \Omega_i$ and \vec{r}' on S_{Ω_o} ($|\vec{r}'_o| > |\vec{r}_o|$), or as

$$G_0^+(\vec{r} - \vec{r}') \equiv G_0^+(\vec{r}_o + \vec{R}_{oi} - \vec{r}') = k \sum_{LL'} [-ih_l^+(kr_o)] Y_L(\vec{r}_o) J_{LL}^o j_l(kr'_i) Y_L^*(\vec{r}'_i) \quad (2.45b)$$

for $\vec{r} \in \mathcal{C}\Omega_o$ and \vec{r}' on S_{Ω_o} ($|\vec{r}_o| > |\vec{r}'_o|$). These relations (2.45) easily follow from an application of Eq.(2.8) and subsequent use of Eq.(2.27).

By defining, in keeping with Eq.s (2.21), the matrices of the Wronskians

$$W[-ih^+, \gamma^o]_{LL'} \equiv W[-ih^+, \gamma^o_{LL'}], \quad W[-ih^+, f^o]_{LL'} \equiv W[-ih^+, f^o_{LL'}] \quad (2.46a)$$

$$W[j, \gamma^o]_{LL'} \equiv W[j, \gamma^o_{LL'}], \quad W[j, f^o]_{LL'} \equiv W[j, f^o_{LL'}] \quad (2.46b)$$

putting

$$-k\rho_o^2 \sum_{L'} (W[-ih^+, \gamma^o]_{LL'} C_{L'}^o + W[-ih^+, f^o]_{LL'} A_{L'}^o) = B_L^o \quad (2.47)$$

we obtain for $\vec{r} \in \Omega_i$ the same equation (2.26), provided the exciting amplitude $4\pi i^l Y_L^*(\hat{k})$ is replaced by B_L^o .

Similarly for \vec{r} in the interstitial region ($\vec{r} \notin \mathcal{C}\Omega_o + \sum_j \Omega_j$), we recover Eq.(2.32) provided $\phi_o(\vec{r})$ is replaced by $\sum_L j_l(kr_o) Y_L(\hat{r}_o) B_L^o$.

These two equations are to be combined with a further relation obtained when $\vec{r} \in \mathcal{C}\Omega_o$:

$$0 = -i \sum_L h_l^+(kr_o) Y_L(k\hat{r}_o) \left(\sum_{jL'} J_{LL'}^o B_{L'}^o + \sum_{L'} (T_{os}^o)_{LL'}^{-1} B_{L'}^o - \sum_{L'} D_{LL'}^o A_{L'}^o \right) + \int_{\Delta\Omega'} G_o^+(\vec{r}, \vec{r}') V_I(\vec{r}') \psi(\vec{r}') d^3r' \quad (2.48)$$

having defined, in analogy with Eq.(2.24) (but notice the inversion of j with $-ih^+$)

$$(T_{os}^o)_{LL'}^{-1} = \sum_L W[j, \gamma^o]_{LL} W[-ih^+, \gamma^o]_{LL'}^{-1} \quad (2.49)$$

and

$$D_{LL}^o = k\rho_o^2 \left(W[j, f^o]_{LL} - \sum_{L'L''} W[j, \gamma^o]_{LL'} W[-ih^+, \gamma^o]_{L'L''}^{-1} W[-ih^+, f^o]_{L''L} \right) \quad (2.50)$$

The derivation of the MSE proceeds now as before. The final result is:

$$\sum_{jL'} ((T_{os}^o)_{LL'}^{-1} + T_{LL'}^o) B_{L'}^o \delta_{ij} + (1 - \delta_{ij}) [H_{LL'}^o + T_{LL'}^o] B_{L'}^o + \sum_{L'} [J_{LL'}^o + \Theta_{LL'}^o] B_{L'}^o = 0 \quad (2.51a)$$

$$\sum_{jL'} [J_{LL'}^o + \Theta_{LL'}^o] B_{L'}^o + \sum_{L'} ((T_{os}^o)_{LL'}^{-1} + \Theta_{LL'}^o) B_{L'}^o = D_{LL}^o \quad (2.51b)$$

where the quantities $T_{LL'}^o$ and $\Theta_{LL'}^o$ are defined as in Eq.s (2.39) and (2.40), the integration

being now extended to the new interstitial region $\Delta\Omega'$. By similarity $\Theta_{LL'}^o j$ and $\Theta_{LL'}^o o$ are obtained by Eq.(2.40) through the replacement $-ih^+ \rightarrow j$ whenever the site j is replaced by the outer sphere site o and viceversa. Again the exciting amplitude A_L^o has been set equal to δ_{LL}

Notice that the MSE in (2.41) already contain the contribution of the outer sphere region $\mathcal{C}\Omega_o$ since in this case the interstitial region $\Delta\Omega$ includes $\mathcal{C}\Omega_o$. The MSE in (2.51) makes explicit this contribution to the matrix element $T_{LL'}^i j$, coming from $\mathcal{C}\Omega_o$. The two sets of equations are indeed alternative ways to solve the same problem.

For spherically symmetric potentials and constant interstitial potential, Eq.s (2.51) reduce to the MSE of ref.9 when written for T-matrix normalization, since in this case

$$D_{LL}^o \rightarrow \delta_{LL} W[f_l^o, \gamma_l^o] / W[j_l, \gamma_l^o]$$

With the replacement $\gamma_l^o \rightarrow g_l^o$ (real part of γ_l^o) and $-ih_l^+ \rightarrow n_l$ the sets of equations (2.51) reduce identically to the MSE of ref.9, which are written for K-matrix normalization.

In absence of spin dependent potentials, the complex conjugate solution of the Lippman-Schwinger equation (2.1) can be used to treat the photoemission problems. Indeed, according to Breit and Bethe¹¹⁾, to describe this latter process we need to impose incoming wave boundary conditions, which in absence of spin entail the replacement $G_0^+ \rightarrow G_0^-$ and $-ih_l^+ \rightarrow ih_l^-$, i.e. complex conjugation.

Finally, by dropping the inhomogeneous term ϕ_0 in the Lippman-Schwinger equation (2.1), making the analytic continuation $k \rightarrow ik$, $E \rightarrow -E$ wherever necessary, in particular in the expression for the function G_0^+ and the T-matrix for interstitial region, using the reexpansion theorems for modified Bessel, Neumann and Hankel functions, imposing decay-ing wave boundary conditions on the outer sphere region $\mathcal{C}\Omega_o$ ($A_L^o = 0$), we obtain the MSE for bound states in the case of general potentials.

3. The photoabsorption cross section and the generalized optical theorem.

We now use the results of section 2. to derive an expression for the total photoabsorption cross section valid in the MS formulation for general potential, which generalizes the analogous expression of ref.9 for muffin-tin potentials. At the same time we shall establish a generalized optical theorem for the wave function amplitudes B_L^j which will allow us to

make connection with the Green function approach to the problem.

Following ref.9, the expression for the photoabsorption cross section by a cluster of atoms of light polarized in the $\hat{\epsilon}$ direction is given, in the dipole approximation, by

$$\sigma(E; \vec{\epsilon}) = k/\pi (4\pi^2 h\omega\alpha) \sum_{\underline{L}} |D_{\underline{L}}^-(E; \vec{\epsilon})|^2$$

where

$$D_{\underline{L}}^-(E; \vec{\epsilon}) = (\psi_{\underline{L}}^-(E) | \vec{r} \cdot \vec{\epsilon} | \psi_{in})$$

and $\psi_{\underline{L}}^-(E)$ is the solution of the Lippman-Schwinger equation (2.1) with incoming wave boundary conditions, energy E and relative to exciting wave \underline{L} . Assuming the initial state ψ_{in} to be a core state localized at site i we need only the expression of $\psi_{\underline{L}}^-$ at site i . Hence using Eq.s (2.18) and (2.23)

$$\begin{aligned} D_{\underline{L}}^-(E; \vec{\epsilon}) &= \sum_{L_f} \sum_L C_L^i(R_{L_f L}^i Y_{L_f} | \vec{r} \cdot \vec{\epsilon} | \psi_{in}) \\ &= (k\rho_i^2)^{-1} \sum_{L_f} \sum_{LL'} W[j, R^i]_{LL'}^{-1} B_{L'}^i(\underline{L}) (R_{L_f L}^i | \vec{r} \cdot \vec{\epsilon} | \psi_{in}) \end{aligned}$$

where $B_{L'}^i(\underline{L})$ indicates that vector solution of the MSE (2.41) relative to the particular exciting wave \underline{L} and L_f the final L selected by the dipole selection rule.

Introducing the wave function

$$\underline{R}_{LL'}^i = (k\rho_i^2)^{-1} \sum_{L''} R_{LL''}^i W[j, R^i]_{L''L'}^{-1}$$

which is real for real potential and matches smoothly to

$$\begin{aligned} \sum_{L''} j_l W[-ih^+, R^i]_{LL''} W[j, R^i]_{L''L'}^{-1} - ih_l^+ = \\ \sum_{L''} j_l W[n, R^i]_{LL''} W[j, R^i]_{L''L'}^{-1} - n_l \end{aligned}$$

putting

$$M_{L_f L}(\vec{\epsilon}) = (\underline{R}_{L_f L}^i Y_{L_f} | \vec{r} \cdot \vec{\epsilon} | \psi_{in})$$

we can write

$$\sigma(E; \vec{\epsilon}) = 4\pi h k \omega \alpha \sum_{\underline{L}} \sum_{L_f L} M_{L_f L}^*(\vec{\epsilon}) B_{\underline{L}}^{i*}(\underline{L}) \sum_{L_f L'} M_{L_f L'}(\vec{\epsilon}) B_{\underline{L}}^i(\underline{L}) \quad (3.1)$$

This is the wanted generalization of the photoabsorption cross section to the case of general potentials. To make contact with the Green function approach and solution to the problem we should prove a generalized optical theorem for the amplitude $B_L^i(\underline{L})$ analogous to that already shown in the case of muffin-tin potentials¹²⁾.

The theorem takes the form

$$\sum_L B_L^{i*}(\underline{L}) B_L^i(\underline{L}) = \frac{1}{2i} \left([(T + H)^{-1}]_{LL}^{ij*} - [(T + H)^{-1}]_{LL}^{ij} \right) \quad (3.2)$$

where, for short, we have indicated by $T + H$ the MS matrix in Eq.(2.41):

$$(T + H)_{LL'}^{ij} = ((T_a)_{LL'}^{-1} + T_{LL'}^{ij}) \delta_{ij} + (1 - \delta_{ij})(H_{LL'}^{ij} + T_{LL'}^{ij}) \quad (3.3)$$

Using this theorem, the expression for the cross section reads

$$\sigma(E; \vec{\epsilon}) = -4\pi h \omega \alpha k \sum_{L, L'} \sum_{L', L''} M_{L, L'}(\vec{\epsilon}) \text{Im} [(T + H)^{-1}]_{L'L}^{ij} M_{L', L''}(\vec{\epsilon}) \quad (3.4)$$

which is the generalization to non-muffin-tin cases of the similar Green function expression valid for muffin-tin potentials¹²⁾⁻¹³⁾. We have used the fact that $M_{L, L'}(\vec{\epsilon})$ is real for real potentials.

The existence of the theorem (3.2) rests on the possibility of a particular decomposition of the MS matrix (3.3) in such a way that

$$T + H = \underline{M} - i\underline{\Delta} \quad (3.5)$$

where \underline{M} and $\underline{\Delta}$ are hermitian matrices and

$$\Delta_{LL'}^{ij} = \sum_L (J_{LL}^{i0} + \Theta_{LL}^{i0})(J_{L'L}^{j0*} + \Theta_{L'L}^{j0*}) \quad (3.6)$$

Under this assumption, from Eq.s (2.41) we have

$$B_L^i(\underline{L}) = - \sum_{jL'} [(M - i\underline{\Delta})^{-1}]_{L'L}^{ij} (J_{L'L}^{j0} + \Theta_{L'L}^{j0})$$

so that

$$\begin{aligned}
 \sum_{\underline{L}} B_{\underline{L}}^{i*}(\underline{L}) B_{\underline{L}'}^i(\underline{L}) &= \\
 &= \sum_{\underline{L}} \sum_{k\underline{L}''} \left([(\underline{M} - i\underline{\Delta})^{-1}]_{\underline{L}\underline{L}''}^{ik} (J_{\underline{L}''\underline{L}}^k + \Theta_{\underline{L}''\underline{L}}^k) \right)^* \sum_{h\underline{L}''} [(\underline{M} - i\underline{\Delta})^{-1}]_{\underline{L}'\underline{L}''}^{jh} (J_{\underline{L}''\underline{L}'}^h + \Theta_{\underline{L}''\underline{L}'}^h) \\
 &= [(\underline{M} - i\underline{\Delta})^{-1} \underline{\Delta} (\underline{M} + i\underline{\Delta})^{-1}]_{\underline{L}'\underline{L}}^{ji} \\
 &= \frac{1}{2i} [(\underline{M} + i\underline{\Delta})^{-1} - (\underline{M} - i\underline{\Delta})^{-1}]_{\underline{L}'\underline{L}}^{ji} \\
 &= \frac{1}{2i} \left([(\underline{T} + \underline{H})^{-1}]_{\underline{L}\underline{L}'}^{ij*} - [(\underline{T} + \underline{H})^{-1}]_{\underline{L}'\underline{L}}^{ij} \right)
 \end{aligned} \tag{3.7}$$

which proves the generalized optical theorem. In deriving (3.7) we have used the fact that

$$[(\underline{M} - i\underline{\Delta})^{-1}]_{\underline{L}\underline{L}'}^{ij*} = [(\underline{M} + i\underline{\Delta})^{-1}]_{\underline{L}'\underline{L}}^{ji}$$

which follows from the hermiticity of \underline{M} and $\underline{\Delta}$. That the decomposition (3.5) is actually possible is shown in Appendix B.

We do not need to prove the generalized optical theorem in the presence of an outer sphere, since Eq. (2.41) already describe the most general case. Hence the theorem holds true also for the amplitudes $B_{\underline{L}}^i(\underline{L})$ solutions of the MSE (2.51). The MS matrix to use in Eq. (3.2) in this latter case is obtained after elimination of the amplitude $B_{\underline{L}}^0$ from the set of Eq. (2.51)

$$\begin{aligned}
 (\underline{T} + \underline{H})_{\underline{L}\underline{L}'}^{ij} &= (T_{\underline{L}\underline{L}'}^i)^{-1} \delta_{ij} + H_{\underline{L}\underline{L}'}^{ij} (1 - \delta_{ij}) + T_{\underline{L}\underline{L}'}^{ij} \\
 &\quad + \sum_{\underline{L}''} (J_{\underline{L}\underline{L}''}^i + \Theta_{\underline{L}\underline{L}''}^i) [(T_{\underline{L}''\underline{L}''}^0)^{-1} + \Theta_{\underline{L}''\underline{L}''}^{00}]^{-1} (J_{\underline{L}''\underline{L}'}^0 + \Theta_{\underline{L}''\underline{L}'}^0)
 \end{aligned} \tag{3.8}$$

remembering that now the matrix elements $T_{\underline{L}\underline{L}'}^{ij}$ refer to a reduced interstitial region.

4. The MS expansion in the general case

Starting from Eq. (3.4) a generalized MS expansion can be set up for a non muffin-tin potential similar to the one already used for the muffin tin case. This expansion rests on a particular decomposition of the MS matrix Eq. (2.41)

$$\underline{T}_{\underline{L}\underline{L}'}^i = [(T_{\underline{L}\underline{L}'}^i)^{-1} + T_{\underline{L}\underline{L}'}^{ii}] \delta_{ij} \tag{4.1a}$$

$$\underline{H}_{\underline{L}\underline{L}'}^i = (H_{\underline{L}\underline{L}'}^i + T_{\underline{L}\underline{L}'}^{ii})(1 - \delta_{ij}) \tag{4.1b}$$

so that the matrix elements (4.1a) describe the non propagating smooth part of the photoelectronic wave emanating from the photoabsorber located at site i .

Provided the condition $\rho(\underline{T}^{-1}\underline{H})$ is satisfied for a certain energy range, where $\rho(A)$ is the maximum eigenvalue of the matrix A , in that range we can write

$$(\underline{T} + \underline{H})^{-1} = (I + \underline{T}^{-1}\underline{H})\underline{T}^{-1} = \sum_{n=0}^{\infty} (\underline{T}^{-1}\underline{H})^n \underline{T}^{-1} \quad (4.2)$$

the series being absolutely convergent relative to some matrix norm. As a consequence the photoabsorption cross section Eq. (3.1) can be expanded in an absolutely convergent series

$$\sigma(E; \vec{\epsilon}) = \sum_{n=0}^{\infty} \sigma_n(E; \vec{\epsilon}) \quad (4.3)$$

where

$$\sigma_0(E; \vec{\epsilon}) = -4\pi h\omega\alpha k \sum_{L,L'} \sum_{L',L''} M_{L,L'}(\vec{\epsilon}) \text{Im}(\underline{T}^{-1})_{LL'}^{i,i} M_{L',L''}(\vec{\epsilon}) \quad (4.4)$$

is a smoothly varying "atomic" cross section, which takes into account the contribution of the interstitial region and

$$\sigma_n(E; \vec{\epsilon}) = -4\pi h\omega\alpha k \sum_{L,L'} \sum_{L',L''} M_{L,L'}(\vec{\epsilon}) \text{Im}[(\underline{T}^{-1}\underline{H})^n \underline{T}^{-1}]_{LL'}^{i,i} M_{L',L''}(\vec{\epsilon}) \quad (4.5)$$

represents the contribution to the photoabsorption cross section coming from processes where the photoelectron has been scattered $n - 1$ times by the surrounding atoms before returning to the photoabsorbing site. The presence of an interstitial potential modifies the free amplitude of propagation $H_{LL'}^{i,j}$ of spherical waves components from site i and angular momentum L to site j and angular momentum L' through the appearance of the matrix element $T_{LL'}^{i,j}$ in Eq. (4.1b).

In order to estimate this modification we write in Eq. (2.39), referring to site i as origin ($\vec{r} \equiv \vec{r}_i$)

$$T_I(\vec{r}, \vec{r}') = \sum_{LL'} Y_L^*(\hat{r}) T_{LL'}^I(r, r') Y_{L'}(\hat{r}') \quad (4.6)$$

and use the reexpansion theorem

$$\begin{aligned} -ih_l^+(kr_j) Y_L(\hat{r}_j) &= \sum_{L'} j_{\nu}(kr_i) Y_{L'}(\hat{r}_i) H_{LL'}^{i,j} & \text{for } |\vec{r}_i - \vec{r}_j| = |\vec{R}_{ij}| > |\vec{r}_i| \\ &= -i \sum_{L'} h_l^+(kr_i) Y_{L'}(\hat{r}_i) J_{LL'}^{i,j} & \text{for } |\vec{r}_i - \vec{r}_j| = |\vec{R}_{ij}| < |\vec{r}_i| \end{aligned}$$

Hence, remembering that $T_I(\vec{r}, \vec{r}') \neq 0$ only for $\vec{r}, \vec{r}' \in \Delta\Omega$

$$T_{LL'}^{ij} = k \int_{\rho_4}^{\infty} r^2 dr [-ih_l^+(kr)] \int_{\rho_4}^{R_{ij}} r'^2 dr' \sum_{L''} T_{LL''}^l(r, r') j_{l''}(kr') H_{L'L'}^i j_{L'}^i + \int_{R_{ij}}^{\infty} r'^2 dr' \sum_{L''} T_{LL''}^l(r, r') [-ih_{l''}^+(kr')] J_{L'L'}^i j_{L'}^i \quad (4.7)$$

where the upper limit of integration is to be changed accordingly in presence of an outer sphere. If the muffin-tin constant \bar{V}_{int} can be chosen in such a way that $V_l(\vec{r}) - \bar{V}_{int} = \sum_{\underline{L}} \bar{V}_{\underline{L}}(r) Y_{\underline{L}}(\hat{r})$ is weak enough, then to a reasonable approximation $T_l(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}') \bar{V}_l(\vec{r})$ and

$$T_{LL'}^l(r, r') = \frac{1}{r^2} \delta(r - r') \sum_{\underline{L}} \bar{V}_{\underline{L}}(r) C_{\underline{L}L'}^L$$

in Eq.(4.6), since $\sum_{L'} C_{L'L}^L Y_{L'}(\hat{r}) = Y_{\underline{L}}(\hat{r}) Y_{\underline{L}}^*(\hat{r})$. Substitution into Eq.(4.7) gives

$$T_{LL'}^{ij} = k \sum_{\underline{L}L'} \int_{\rho_4}^{R_{ij}} r^2 dr [-ih_l^+(kr)] \bar{V}_{\underline{L}}(r) j_{l'}(kr) C_{\underline{L}L'}^L H_{\underline{L}L'}^i j_{L'}^i + k \sum_{\underline{L}L'} \int_{R_{ij}}^{\infty} r^2 dr [-ih_l^+(kr)] \bar{V}_{\underline{L}}(r) [-ih_{l'}^+(kr)] C_{\underline{L}L'}^L J_{\underline{L}L'}^i j_{L'}^i \quad (4.8)$$

To proceed further, we use an approximate expression for the quantities $H_{\underline{L}L'}^i$ and $J_{\underline{L}L'}^i = \frac{1}{2}(H_{\underline{L}L'}^i - H_{\underline{L}'L}^i)$. It has been shown¹³⁾ that to a good approximation

$$H_{\underline{L}L'}^i \approx -4\pi Y_{\underline{L}}^*(\hat{R}_{ij}) Y_{L'}(\hat{R}_{ij}) f(R_{ij}) i^{l-l'} \quad (4.9a)$$

so that

$$J_{\underline{L}L'}^i \approx -4\pi Y_{\underline{L}}^*(\hat{R}_{ij}) Y_{L'}(\hat{R}_{ij}) \text{Im}[f(R_{ij}) i^{l-l'}] \quad (4.9b)$$

where

$$f(R_{ij}) = [1 + \frac{\beta}{(2kR_{ij})^2}]^{\frac{1}{2}} \frac{1}{(kR_{ij})} \exp(ikR_{ij}[1 + \frac{\beta}{(2kR_{ij})^2}])$$

and $\beta = 2[l(l+1) + l'(l'+1)]$.

Remembering Eq.(2.12), the first integral in (4.8) becomes

$$\begin{aligned} & -4\pi \sum_{\underline{L}L'} \int_{\rho_4}^{R_{ij}} r^2 dr [-ih_l^+(kr)] \bar{V}_{\underline{L}}(r) j_{l'}(kr) \int d\Omega Y_{\underline{L}}^*(\Omega) Y_{\underline{L}}(\Omega) Y_{L'}(\Omega) Y_{\underline{L}}^*(\hat{R}_{ij}) Y_{L'}(\hat{R}_{ij}) f(R_{ij}) i^{l-l'} \\ & = -4\pi \int_{\Delta(\rho_4, R_{ij})} d^3r [-ih_l^+(kr)] Y_{\underline{L}}^*(\hat{r}) \bar{V}(\vec{r}) e^{ik\vec{r} \cdot \hat{R}_{ij}} f(R_{ij}) Y_{L'}(\hat{R}_{ij}) i^{-l'} \\ & = [4\pi i^l Y_{\underline{L}}^*(\hat{R}_{ij})]^{-1} \int_{\Delta(\rho_4, R_{ij})} d^3r [-ih_l^+(kr)] Y_{\underline{L}}^*(\hat{r}) \bar{V}(\vec{r}) e^{ik\vec{r} \cdot \hat{R}_{ij}} H_{\underline{L}L'}^i j_{L'}^i \end{aligned} \quad (4.10)$$

where $\Delta(\rho_i, R_{ij})$ is that part of the interstitial region comprised between the two concentric spheres of radii ρ_i and R_{ij} .

A similar derivation shows that the second integral in Eq.(4.8) yields

$$-[4\pi i^l Y_L^*(\hat{R}_{ij})]^{-1} \int_{C\Delta'(R_{ij})} d^3r [-ih_l^+(kr)] Y_L^*(\hat{r}) \bar{V}(\vec{r}) \mathcal{N}(\vec{r} \cdot \vec{R}_{ij}) J_{LL}^i J_{LL}^j, \quad (4.11)$$

where $\mathcal{N}(\vec{r} \cdot \vec{R}_{ij}) = -4\pi \sum_L i^{l+1} h_l^+(kr) Y_L^*(\hat{r}) Y_L(\hat{R}_{ij})$ and $C\Delta'(R_{ij})$ denotes the interstitial region outside the sphere of radius R_{ij} centered at site i . In this region we can use the asymptotic expansion for $h_l^+(kr) \approx i^{-(l+1)} \frac{e^{ikr}}{(kr)}$ so that roughly the quantity in (4.11) becomes

$$(-1)^{l+1} \int_{R_{ij}}^{\infty} r^2 dr \frac{e^{2ikr}}{(kr)^2} \bar{V}(r, \hat{R}_{ij}) J_{LL}^i J_{LL}^j, \quad (4.12)$$

where the integral is to be taken along the line connecting the two centers i and j .

The two expressions (4.10) and (4.12) provide a useful estimate of the order of magnitude of the correction terms due to the presence of a non constant interstitial potential. They represent the zero order term of a series expansion originated by the Born series for the interstitial T-matrix $T_I = \sum_{n=0}^{\infty} V_I (G_0^+ V_I)^n$, assumed to be convergent. Higher order terms can then be evaluated along the same lines as above, exploiting the multicenter expansion of the free Green function G_0^+ . We expect the correction terms to be relevant for open structures (with large interstitial volume) and for not too high energies of the final state photoelectron ($\leq 100 - 150$ eV).

Appendix A

We want to show here the equivalence between the expression (2.24) for the atomic t-matrix (T_a^i) relative to the potential $V_i(\vec{r})$ and the expression for the similar quantity as defined by Evans and Keller⁶⁾ in their Appendix 1.

For a single center i we have to match smoothly the general solution inside the sphere Ω_i

$$\psi_{\vec{k}}(\vec{r}) = \sum_L \phi_L(\vec{r}) Y_L(\hat{r}) = \sum_{LL'} C_{L'} R_{LL'}(\vec{r}) Y_L(\hat{r}) \quad (A1)$$

to the general solution in the external region $C\Omega_i$

$$\psi_{\vec{k}}(\vec{r}) = \sum_L A_L^{\vec{k}} [i^l j_l(kr) Y_L(\hat{r}) - ik \sum_{L'} i^{l'} h_{l'}^+(kr) T_{L'L} Y_{L'}(\hat{r})] \quad (A2)$$

where, by definition, $T_{LL'}$ is the atomic t-matrix.

The exciting amplitude $A_L^{\vec{k}}$ is determined by asking that asymptotically

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + f(\vec{k}, \vec{k}') e^{ikr}/r$$

so that $A_L^{\vec{k}} = 4\pi Y_L^*(\hat{k})$. The suffix \vec{k} refers to the direction of the incident wave.

Equation (A2) can be rewritten as

$$\psi_{\vec{k}}(\vec{r}) = \sum_L A_L^{\vec{k}} [i^l j_l(kr) - i B_L^{\vec{k}} h_l^+(kr)] Y_L(\hat{r}) \quad (A3)$$

where

$$B_L^{\vec{k}} = k \sum_{L'} T_{LL'} A_{L'}^{\vec{k}} \quad (A4)$$

The matching conditions at the radius ρ_i of Ω_i

$$\sum_{L'} R_{LL'} C_{L'} = i^l [A_L^{\vec{k}} j_l(k\rho_i) - i B_L^{\vec{k}} h_l^+(k\rho_i)] \quad (A5a)$$

$$\sum_{L'} R'_{LL'} C_{L'} = i^l [A_L^{\vec{k}} j'_l(k\rho_i) - i B_L^{\vec{k}} h_l^{+\prime}(k\rho_i)] \quad (A5b)$$

where the prime indicates derivation with respect to r , determine the coefficients C_L and $B_L^{\vec{k}}$.

In matrix form they read

$$Gx = d$$

where

$$G \equiv \begin{pmatrix} \frac{R_{LL'}}{i^l j_l(k\rho_s)} & \frac{ih_l^+(k\rho_s)}{j_l(k\rho_s)} \\ \frac{R'_{LL'}}{i^l j_l'(k\rho_s)} & \frac{ih_l^{+'}(k\rho_s)}{j_l'(k\rho_s)} \end{pmatrix}$$

$$x = \begin{pmatrix} C_L \\ B_L^{\bar{k}} \end{pmatrix} \quad d = \begin{pmatrix} A_L^{\bar{k}} \\ A_L^{\bar{k}'} \end{pmatrix}$$

By introducing

$$G^{-1} = \begin{pmatrix} M & N \\ P & Q \end{pmatrix}$$

we can write the solution x as $x = G^{-1}d$, or

$$C_L = \sum_{L'} (M_{LL'} + N_{LL'}) A_{L'}^{\bar{k}}$$

$$B_L^{\bar{k}} = \sum_{L'} ((P_{LL'} + Q_{LL'}) A_{L'}^{\bar{k}'})$$

By comparison with Eq. (A4) we get

$$T_{LL'} = \frac{1}{k} (P_{LL'} + Q_{LL'})$$

which is the solution by Evans and Keller.

We can however solve Eq.s (A5) in an alternative way by eliminating in turn $A_L^{\bar{k}}$ and $B_L^{\bar{k}}$ in Eq. (A5a) as obtained from Eq. (A5b). The result is, remembering the definition of the Wronskian given in the text,

$$\sum_{L'} W[j_l, R_{LL'}] C_{L'} = W[j_l, -ih_l^+] i^l B_L^{\bar{k}} = \frac{i^l}{k\rho_s^2} B_L^{\bar{k}} \quad (A6a)$$

$$\sum_{L'} W[-ih_l^+, R_{LL'}] C_{L'} = -W[j_l, -ih_l^+] i^l A_L^{\bar{k}} = -\frac{i^l}{k\rho_s^2} A_L^{\bar{k}} \quad (A6b)$$

By introducing the matrices of the wronskians as in Eq. (2.21) we solve for the C_L in (A6b) and substitute in (A6a), to obtain

$$\sum_{L'L''} W[j, R]_{LL''} W[-ih^+, R]_{L''L'}^{-1} A_{L'}^{\bar{k}} = -B_L^{\bar{k}}$$

or

$$T_{LL'} = -\frac{1}{k} \sum_{L''} W[j, R]_{LL''} W[-ih^+, R]_{L''L'}^{-1}$$

or

$$(T^{-1})_{LL'} = -k \sum_{L''} W[-ih^+, R]_{LL''} W[j, R]_{L''L'}^{-1}$$

which is the expression (2.24) apart from the factor $-k$.

Appendix B

We show here that the multiple scattering matrix $\underline{T} + \underline{H}$ in the presence of a non constant interstitial potential can be decomposed as

$$\underline{T} + \underline{H} = \underline{M} - i \underline{\Delta}$$

where \underline{M} and $\underline{\Delta}$ are hermitian matrices and

$$\begin{aligned} \Delta_{LL'}^i &= \sum_L (J_{LL}^i + \Theta_{LL}^i) (J_{L'L}^{i*} + \Theta_{L'L}^{i*}) \\ &= J_{LL'}^i + \Theta_{LL'}^i + \Theta_{L'L}^{i*} + \sum_L \Theta_{LL}^i \Theta_{L'L}^{i*} \end{aligned} \quad (B1)$$

The second step follows from the hermiticity of $J_{LL'}^i = J_{L'L}^{i*}$, which is a consequence of the definition (2.28), from the validity of the sum rule

$$J_{LL'}^i = \sum_L J_{LL}^i J_{L'L}^{i*} = \sum_L J_{LL}^i J_{LL'}^{i*} \quad (B2)$$

which is a consequence of (2.25), (2.27) and the property of the exponential

$$e^{i\vec{k} \cdot \vec{r}_i} e^{-i\vec{k} \cdot \vec{r}_j} = e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)}$$

as shown in ref.[2], and from the fact that

$$\Theta_{LL'}^i = \sum_L \Theta_{LL}^i J_{L'L}^{i*} = \sum_L \Theta_{LL}^i J_{LL'}^{i*} \quad (B3)$$

which is a consequence of the definition (2.40) and the relation (2.27).

The MS matrix $\underline{T} + \underline{H}$, following Eq. (2.41), can be written as

$$(\underline{T} + \underline{H})_{LL'}^i = (T_a^i)_{LL'}^{-1} \delta_{ij} + H_{LL'}^i (1 - \delta_{ij}) + T_{LL'}^i$$

Now, according to the definition (2.11), remembering that $-ih_l^+ = n_l - ij_l$, we can write

$$H_{LL'}^i = N_{LL'}^i - iJ_{LL'}^i \quad (B4)$$

where $J_{LL'}^i$ is defined in (2.28) and $N_{LL'}^i$ is similarly defined by making the substitution $j_l \rightarrow n_l$. They are both hermitian matrices.

Moreover the atomic t-matrix $(T_a^i)_{LL'}$ is known to be related to the hermitian atomic k-matrix $(K_a^i)_{LL'}$ by the relation²⁾

$$(T_a^i)_{LL'}^{-1} = (K_a^i)_{LL'}^{-1} - i$$

Finally, to accomplish a similar decomposition for T we first observe that

$$T = \frac{1}{2}(T + T^\dagger) - i\frac{1}{2i}(T^\dagger - T)$$

where $\frac{1}{2}(T + T^\dagger)$ and $\frac{1}{2i}(T^\dagger - T)$ are hermitian. Moreover

$$\frac{1}{2}(T + T^\dagger) = -\frac{1}{2}(T + T^\dagger) + (\underline{\Theta} + \underline{\Theta}^\dagger) - i(\underline{\Theta} + \underline{\Theta}^\dagger)$$

the last step following from the definition (2.39) for $T_{LL'}^i$, and the fact that $-ih_l^\dagger = n_l - i j_l$, having introduced, in analogy with (2.40), the matrix

$$\underline{\Theta} \equiv \underline{\Theta}_{LL'}^i = k \int_{\Delta\Omega} \int [-ih_l^\dagger(kr_i)] Y_L^*(\hat{r}_i) T_l(\vec{r}, \vec{r}') n_\nu(kr'_j) Y_{L'}(\hat{r}'_j) d^3r d^3r'$$

Remembering that $J_{LL'}^i = \delta_{LL'}$, we finally achieve the decomposition

$$\begin{aligned} (\underline{T} + \underline{H})_{LL'}^i &= (K_a^i)_{LL'}^{-1} \delta_{ij} + (1 - \delta_{ij}) N_{LL'}^i - \frac{1}{2}(T + T^\dagger)_{LL'}^i + (\underline{\Theta} + \underline{\Theta}^\dagger)_{LL'}^i \\ &\quad - i[J_{LL'}^i + (\underline{\Theta} + \underline{\Theta}^\dagger)_{LL'}^i + \frac{1}{2i}(T^\dagger - T)_{LL'}^i] \\ &= \underline{M}_{LL'}^i - i\underline{\Delta}_{LL'}^i \end{aligned}$$

where the matrix $\underline{\Delta}_{LL'}^i$ is identical to the expression in (A1), taking into account that the optical theorem for the t-matrix for any potential, and in particular for the interstitial potential reads²⁾

$$\frac{1}{2i}(T^\dagger - T)_{LL'}^i = \sum_{\underline{L}} \Theta_{LL}^{i\circ} \Theta_{L'L}^{i\circ*}$$

This last step completes the proof.

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