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Use of general potentials in multiple-scattering theory

C. R. Natoli and M. Benfatto
Laboratori Nazionali di Frascati dell' Istituto Nazionale di Fisica Nucleare, P. O. Box 13, 00044-Frascati, Italy

S. Doniach
Department of Applied Physics, Stanford University, Stanford, California 94305

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A mathematically transparent 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. An expression for the photoabsorption and electron scattering cross section in the framework of the multiple-scattering theory valid for a general potential is derived for what may be the first time, providing the necessary generalization for the similar expression valid in the muffin-tin case. A connection with the Green-function approach to the problem is also established via a generalized optical theorem.

I. 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., to potentials which are 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 a 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, and is 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 Dehmer[1] 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. In contrast, our formulation provides an extension to general potentials which does not require such sacrifices.

A much more complete review of multiple-scattering theory in condensed matter with original contributions was given by Lloyd and Smith.[2] The extension of the method to local potentials of general type is in fact contained in their paper if one is willing to put together bits and pieces scattering 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, which is necessary for example in problems of scattering by a long-range potential (e.g., Coulomb tail in problems of photoionization), is still missing as far as we are aware. The present paper is intended to fill this gap.

Section II is devoted to the derivation of the MSE in the general case following the Green-function approach as used by Beleznay and Lawrence[3] to introduce nonzero interstitial potentials in the calculation of electronic band structure. Section III contains an application of the MS method to the calculation of the photoabsorption and electron scattering 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 in estimating 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 is formulated in terms of the projected density of excited states onto the photoabsorbing site. This approach enables us to provide an estimate in Sec. IV of 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 photoelectron energies which are not too high ($\leq 100-150$ eV). Finally, Sec. V discusses the difficulties involved in numerically implementing the formulation of the theory and makes comparison with other methods. In this connection it is shown that the extension of the theory to nonlocal potentials does not pose unsurmountable problems, only adds greater computational complication.

II. THE MODIFIED MULTIPLE-SCATTERING MATRIX

Since we are mainly interested in scattering problems, we shall first consider the Lippmann-Schwinger equation

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

resulting from the Schrödinger equation

$$(\Delta+E)\psi(\mathbf{r})=V(\mathbf{r})\psi(\mathbf{r})\ , \tag{2.2}$$

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

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

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

$$V(\mathbf{r})=\sum_L V_L(r)Y_L(\mathbf{r})\ . \tag{2.4}$$

The spherical harmonics $Y_L(r)$ are defined following Condon and Shortley.[4]

As usual in the multiple scattering theory, we partition the whole space V into nonoverlapping spheres Ω_j centered around the atomic site j and a remaining interstitial region $\Delta\Omega$. 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 spheres.

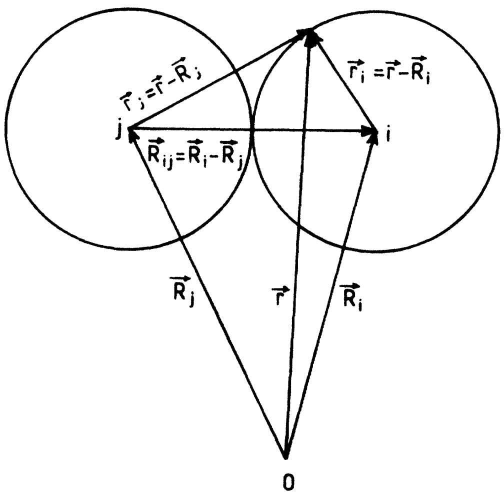

FIG. 1. Vector diagram for reexpansion formulas [Eqs. (2.9) and (2.10)].

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

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

Use of Green's theorem in the form

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

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:

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

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

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

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

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

where $r_>$ ($r_<$) refers to the greater (lesser) of $|\mathbf{r}|$ and $|\mathbf{r}'|$, in terms of coordinates referred to different sites (j_l, n_l, and 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 $\mathbf{R}_{ij}\equiv\mathbf{R}_i-\mathbf{R}_j$, $\mathbf{r}_i\equiv\mathbf{r}-\mathbf{R}_i$,

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

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

Using the reexpansion theorem,[2] and noting that $|\mathbf{R}_{ij}|>|\mathbf{r}'_j|$, when $\mathbf{r}'$ is on S_{Ω_j}, we have

$$-ih_l^+(k\,|\mathbf{r}'_j-\mathbf{R}_{ij}|)Y_L(\mathbf{r}'_j-\mathbf{R}_{ij})=\sum_{L'} j_{l'}(kr'_j)Y_{L'}(\mathbf{r}'_j)H^{ji}_{L'L}\ , \tag{2.10}$$

where

$$\begin{aligned}H^{ji}_{L'L}&=4\pi\sum_{L''} i^{l''+l'-l}C^{L}_{L'L''}[-ih^+_{l''}(kR_{ji})]Y_{L''}(\mathbf{R}_{ji})\\&=\sum_{L''} i^{l''+l'-l}(-1)^m[4\pi(2l'+1)(2l+1)(2l''+1)]^{1/2}\\&\quad\times\begin{bmatrix}l' & l & l''\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}l' & l & l''\\ m' & -m & m''\end{bmatrix}[-ih^+_{l''}(kR_{ji})]Y_{L''}(\mathbf{R}_{ji})\end{aligned} \tag{2.11}$$

since[5]

$$\begin{aligned}C^{L}_{L'L''}&=\int Y_{L'}(\Omega)Y^*_L(\Omega)Y_{L''}(\Omega)d\Omega\\&=(-1)^m[(2l'+1)(2l+1)(2l''+1)/4\pi]^{1/2}\\&\quad\times\begin{bmatrix}l' & l & l''\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}l' & l & l''\\ m' & -m & m''\end{bmatrix}\ .\end{aligned} \tag{2.12}$$

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

$$\begin{aligned}G_0^+&(\mathbf{r}-\mathbf{r}')\\&=G_0^+(\mathbf{r}_i+\mathbf{R}_{ij}-\mathbf{r}'_j)\\&=k\sum_{L,L'} j_l(kr_i)Y_L(\mathbf{r}_i)H^{ij}_{LL'}j_{l'}(kr'_j)Y^*_{L'}(\mathbf{r}'_j)\ ,\end{aligned} \tag{2.13}$$

for $\mathbf{r}$ inside the sphere Ω_i and $\mathbf{r}'$ on the surfaces of the spheres Ω_j $(j\neq i)$. To derive Eq. (2.13) we have taken into account that $Y^*_{lm}=(-1)^mY_{l\,-m}$ and that $(-1)^{m+m'}H^{ij}_{LL'}=H^{ji}_{l'-m'\,l-m}$ 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

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

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

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

where

$$V_{LL'}(r)=\sum_{L''}C^{L}_{L'L''}V_{L''}(r) \tag{2.15}$$

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 2 or greater, we can take near the origin

$$R_{LL'}(r)\simeq r^l\delta_{LL'}\ . \tag{2.16}$$

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

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

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

so that, without loss of generality, inside the spheres Ω_j, we can write

$$\psi(\mathbf{r}_j)=\sum_{L,L'}C^j_{L'}R^j_{LL'}(r_j)Y_L(\mathbf{r}_j) \tag{2.18}$$

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

$$\begin{aligned}0=\sum_L j_l(kr_i)Y_L(\mathbf{r}_i)&\left[k\rho_i^2\sum_{L'}W[-ih_l^+,R^i_{LL'}]C^i_{L'}+\sum_{j\,(\neq i)}\sum_{L',L''}k\rho_j^2H^{ij}_{LL'}W[j_{l'},R^j_{L'L''}]C^j_{L''}\right]\\&+\phi_0(\mathbf{r})+\int_{\Delta\Omega}G_0^+(\mathbf{r},\mathbf{r}')V_I(\mathbf{r}')\psi(\mathbf{r}')d^3r'\ ,\end{aligned} \tag{2.19}$$

where ρ_j is the radius of sphere Ω_j and we have introduced the Wronskians

$$W[j_l(kr_j),R^j_{LL'}(r_j)]=j_l(kr_j)\frac{d}{dr_j}R^j_{LL'}(r_j)-R^j_{LL'}(r_j)\frac{d}{dr_j}j_l(kr_j)$$

calculated at $r_j=\rho_j$.

By putting

$$B^j_{L'}=k\rho_j^2\sum_{L''}W[j_{l''},R^j_{L'L''}]C^j_{L''} \tag{2.20}$$

and introducing the matrices of the Wronskians

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

we can solve for the coefficients C^j_L in Eq. (2.20), obtaining

$$k\rho_j^2C^j_L=\sum_{L'}(W[j,R^j])^{-1}_{LL'}B^j_{L'}\ . \tag{2.22}$$

Defining of the atomic quantities

$$(T^j_a)^{-1}_{LL'}=\sum_{L''}(W[-ih^+,R^j])_{LL''}(W[j,R^j])^{-1}_{L''L'} \tag{2.23}$$

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

$$\phi_0(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}=4\pi\sum_{L'}i^{l'}j_{l'}(kr)Y_{L'}(\mathbf{r})Y^*_{L'}(\mathbf{k})=4\pi\sum_{L'}i^{l'}Y^*_{L'}(\mathbf{k})\sum_{L}j_l(kr_i)Y_L(\mathbf{r}_i)J^{io}_{LL'} \tag{2.24}$$

we can write Eq. (2.19) as

$$0=\sum_L j_l(kr_i)Y_L(\mathbf{r}_i)\left[\sum_{j,L'}[(T^i_a)^{-1}_{LL'}B^i_{L'}\delta_{ij}+(1-\delta_{ij})H^{ij}_{LL'}B^j_{L'}+J^{io}_{LL'}4\pi i^{l'}Y^*_{L'}(\mathbf{k})]\right]$$
$$+\int_{\Delta\Omega}G_0^+(\mathbf{r},\mathbf{r}')V_I(\mathbf{r}')\psi(\mathbf{r}')d^3r'\ . \tag{2.25}$$

In deriving Eq. (2.24) we have made use of the expansion[2]

$$j_l(kr_i)Y_L(\mathbf{r}_i)\equiv j_l(k\,|\mathbf{r}_j-\mathbf{R}_{ij}|\,)Y_L(\mathbf{r}_j-\mathbf{R}_{ij})$$
$$=\sum_{L'}j_{l'}(kr_j)Y_{L'}(\mathbf{r}_j)J^{ji}_{L'L} \tag{2.26}$$

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

$$J^{ji}_{L'L}=4\pi\sum_{L''}i^{l''+l'-l}C^L_{L'L''}j_{l''}(kR_{ji})Y_{L''}(\mathbf{R}_{ji})\ . \tag{2.27}$$

Under the assumption that $V_I(\mathbf{r})=0$, Eq. (2.25) gives the usual multiple-scattering equations[2] for nonspherically symmetric potentials $V_j(\mathbf{r})$, provided the exciting amplitude $4\pi i^lY^*_L(\mathbf{k})$ is set equal to $\delta_{LL''}$:

$$\sum_{j,L'}[(T^i_a)^{-1}_{LL'}B^i_{L'}\delta_{ij}+(1-\delta_{ij})H^{ij}_{LL'}B^j_{L'}]=-J^{io}_{LL''}\ . \tag{2.28}$$

We show in Appendix A that the quantities $(T^j_a)_{LL'}$ in Eq. (2.23) are indeed the atomic t matrices in angular momentum representation relative to the potentials $V_j(\mathbf{r})$ as defined by Evans and Keller[6] in their Appendix 1.

When $V_j(\mathbf{r})\equiv V_j(\,|\mathbf{r}|\,)$ is spherically symmetric, then in Eq. (2.18) $R^j_{LL'}\rightarrow R^j_L\delta_{LL'}$, so that $(T^j_a)_{LL'}\rightarrow t^j_L\delta_{LL'}$, where

$$t^j_L=W[j_l,R^j_l]/W[-ih_l^+,R^j_l] \tag{2.29}$$

which is the usual definition of the atomic t matrices in the spherical case.[7–9]

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

$$G_0^+(\mathbf{r}-\mathbf{r}')=G_0^+(\mathbf{r}_j-\mathbf{r}'_j)$$
$$=-ik\sum_L j_l(kr'_j)Y^*_L(\mathbf{r}'_j)h_l^+(kr_j)Y_L(\mathbf{r}_j)\ , \tag{2.30}$$

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

$$\psi(\mathbf{r})=-i\sum_{j,L}h_l^+(kr_j)Y_L(\mathbf{r}_j)B^j_L+\phi_0(\mathbf{r})$$
$$+\int_{\Delta\Omega}G_0^+(\mathbf{r}-\mathbf{r}')V_I(\mathbf{r}')\psi(\mathbf{r}')d^3r' \tag{2.31}$$

remembering the definitions (2.20).

Notice that, when $V_I(\mathbf{r})=0$, the solution of Eq. (2.28) yields the coefficients B^j_L of the scattered waves in the interstitial region. Equations (2.20) provide the relation between these coefficients and the coefficients C^j_L in Eq. (2.18) of the solution inside the atomic spheres. It is the straightforward generalization of the similar relation valid for the spherical case[8,9] 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 (2.28) is necessary.

Coming back to the case $V_I(\mathbf{r})\neq 0$ we can use Eq. (2.31) to determine $\psi(\mathbf{r})$ in the interstitial region to substitute in

Eq. (2.25), in order to obtain the MSE in the general case.

As it is, Eq. (2.31) is the Lippmann, Schwinger equation relative to the potential $V_I(\mathbf{r})$, with incoming waves given by

$$\tilde{\phi}_0(\mathbf{r})=-i\sum_{j,L} h_L^+(kr_j)Y_L(\mathbf{r}_j)B_L^j+\phi_0(\mathbf{r}) . \tag{2.32}$$

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

$$T_I=V_I+V_IG_0^+T_I=V_I+T_IG_0^+V_I \tag{2.33}$$

so that

$$T_I\tilde{\phi}_0=V_I\psi \tag{2.34}$$

we can write the last term in Eq. (2.25) as

$$\int_{\Delta\Omega}G_0^+(\mathbf{r}-\mathbf{r}')V_I(\mathbf{r}')\psi(\mathbf{r}')d^3r' =\int\int_{\Delta\Omega}G_0^+(\mathbf{r}-\mathbf{r}')T_I(\mathbf{r}',\mathbf{r}'')\tilde{\phi}_0(\mathbf{r}'')d^3r'd^3r'' \tag{2.35}$$

since Eq. (2.33) shows that $T_I(\mathbf{r},\mathbf{r}')$ is different from zero only for $\mathbf{r}$ and $\mathbf{r}'$ in the interstitial region.

For $\mathbf{r}$ inside Ω_i, as appropriate in Eq. (2.25) and $\mathbf{r}'$ in the interstitial region, as demanded by Eq. (2.25), we have $|\mathbf{r}_i|<|\mathbf{r}_i'|$, so that we can write

$$G_0^+(\mathbf{r}-\mathbf{r}')=-ik\sum_L j_l(kr_i)Y_L(\mathbf{r}_i)h_l^+(kr_i')Y_L^*(\mathbf{r}_i') . \tag{2.36}$$

Use of this relation into Eq. (2.35), remembering Eq. (2.32) and (2.24) referred to the center o, gives

$$\int_{\Delta\Omega}G_0^+(\mathbf{r}-\mathbf{r}')V_I(\mathbf{r}')\psi(\mathbf{r}')d^3r' =\sum_L j_l(kr_i)Y_L(\mathbf{r}_i)\left[\sum_{j,L'}T_{LL'}^{ij}B_{L'}^j+\sum_{L'}\Theta_{LL'}^{io}4\pi i^{l'}Y_{L'}^*(\mathbf{k})\right] , \tag{2.37}$$

where we have defined

$$T_{LL'}^{ij}=k\int\int_{\Delta\Omega}[-ih_l^+(kr_i)]Y_L^*(\mathbf{r}_i)T_I(\mathbf{r},\mathbf{r}')\times[-ih_{l'}^+(kr_j')]Y_{L'}(\mathbf{r}_j')d^3r\,d^3r' , \tag{2.38}$$

$$\Theta_{LL'}^{io}=k\int\int_{\Delta\Omega}[-ih_l^+(kr_i)]Y_L^*(\mathbf{r}_i)T_I(\mathbf{r},\mathbf{r}')\times j_{l'}(kr_o')Y_{L'}(\mathbf{r}_o')d^3r\,d^3r' . \tag{2.39}$$

Insertion of Eq. (2.37) into Eq. (2.25) provides the desired generalization of the MSE, in the absence of an outer spheres, after equating the coefficient of $j_l(kr_i)Y_L(\mathbf{r}_i)$ to zero and putting $4\pi i^lY_L^*(\mathbf{k})=\delta_{LL''}$:

$$\sum_{j,L'}\{[(T_a^i)_{LL'}^{-1}+T_{LL'}^{ii}]B_{L'}^j\delta_{ij} +(1-\delta_{ij})(H_{LL'}^{ij}+T_{LL'}^{ij})B_{L'}^j\}=-J_{LL''}^{io}-\Theta_{LL''}^{io} . \tag{2.40}$$

If we had 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 substitution, in all the above formulas, of the standing wave n_l in place of the outgoing wave $-ih_l^+$. In this case Eq. (2.40) would constitute the generalization of the Dehmer and Dill[9] version of MSE to non-muffin-tin potentials, with the same definition of the coefficient B_L^j.

To solve for this latter quantity, we need to know the matrix elements $T_{LL'}^{ij}$ in Eq. (2.40), which is tantamount to the T_I matrix for the interstitial potential. If $V_I(\mathbf{r})$ cannot support a bound state, then a Born expansion of Eq. (2.33) provides the desired result. If instead $V_I(\mathbf{r})$ is strong enough to support a bound state, one can use some of the tricks already known in the literature.[10] The simplest of these is suggested by the observations that there is a reasonable chance that with a judicious choice of the constant $\overline{V}_{\text{int}}$, the potential $V_I(\mathbf{r})-\overline{V}_{\text{int}}$ does not bind. Generalization to this case of the above formulas is then immediate. Indeed now Eq. (2.2) should read

$$(\Delta+E-\overline{V}_{\text{int}})\psi(\mathbf{r})=[V(\mathbf{r})-\overline{V}_{\text{int}}]\psi(\mathbf{r}) . \tag{2.41}$$

If we choose the free Green function as the solution of the equation

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

then all the above derivation is valid, provided we replace $k=\sqrt{E}$ with $\kappa=(E-\overline{V}_{\text{int}})^{1/2}$ and $V_I(\mathbf{r})$ with $V_I(\mathbf{r})-\overline{V}_{\text{int}}$. However, the solution of the Schrödinger equation inside the atomic spheres Ω_j, $R_{LL'}(r_j,E)$, should still be calculated at the energy E, since in Ω_j the solution of Eq. (2.41) 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 $V_o(\mathbf{r})\equiv V(\mathbf{r})$ for $r\in\mathscr{C}\Omega_o$, where $\mathscr{C}\Omega_o$ is the region of the space complementary to Ω_o and $V_o(\mathbf{r})\equiv 0$ for $r\in\Omega_o$. Similarly we take $V_I(\mathbf{r})\equiv V(\mathbf{r})$ 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 $V_I(\mathbf{r})\equiv 0$ elsewhere.

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

$$\psi(\mathbf{r})=\sum_{L,L'}[A_{L'}^of_{LL'}^o(r_o)+C_{L'}^o\gamma_{LL'}^o(r_o)]Y_L(\mathbf{r}_o) , \tag{2.42}$$

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

$$\lim_{r_o\to\infty} f^o_{LL'}(r_o)\approx\delta_{LL'}\left[\frac{1}{k\pi}\right]^{1/2}\frac{1}{r_o}\sin(kr_o-\tfrac{1}{2}l\pi+\omega_l)\ , \tag{2.43a}$$

$$\lim_{r_o\to\infty} \gamma^o_{LL'}(r_o)\approx-\delta_{LL'}\left[\frac{1}{k\pi}\right]^{1/2}\frac{1}{r_o}\cos(kr_o-\tfrac{1}{2}l\pi+\omega_l)-if^o_{LL'}(r_o)\ . \tag{2.43b}$$

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

In Eq. (2.42) A^o_L is the exciting amplitude, to be set equal to $\delta_{LL''}$ and C^o_L 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 function G^+_o rewritten either as

$$G^+_0(\mathbf{r}-\mathbf{r}')\equiv G^+_0(\mathbf{r}_i-\mathbf{R}_{oi}-\mathbf{r}'_o)=k\sum_{L,L''}[-ih^+_l(kr'_o)]Y_L(\mathbf{r}'_o)\times J^{oi}_{LL''}j_{l''}(kr_i)Y^*_{L''}(\mathbf{r}_i) \tag{2.44a}$$

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

$$G^+_0(\mathbf{r}-\mathbf{r}')\equiv G^+_0(\mathbf{r}_0+\mathbf{R}_{oi}-\mathbf{r}'_i)=k\sum_{L,L''}[-ih^+_l(kr_o)]Y_L(\mathbf{r}_o)\times J^{oi}_{LL''}j_{l''}(kr'_i)Y^*_{L''}(\mathbf{r}'_i) \tag{2.44b}$$

for $\mathbf{r}\in\mathscr{C}\Omega_o$ and $\mathbf{r}'$ on S_{Ω_o} $(|\mathbf{r}_o|>|\mathbf{r}'_o|)$. These relations easily follow from an application of Eq. (2.8) and subsequent use of Eq. (2.26).

Defining, in keeping with Eqs. (2.21), the matrices of the Wronskians

$$\begin{aligned}(W[-ih^+,\gamma^o])_{LL'}&\equiv W[-ih^+_l,\gamma^o_{LL'}]\ ,\\ (W[-ih^+,f^o])_{LL'}&\equiv W[-ih^+_l,f^o_{LL'}]\ ;\end{aligned} \tag{2.45a}$$

$$\begin{aligned}(W[j,\gamma^o])_{LL'}&\equiv W[j_l,\gamma^o_{LL'}]\ ,\\ (W[j,f^o])_{LL'}&\equiv W[j_l,f^o_{LL'}]\end{aligned} \tag{2.45b}$$

and putting

$$-k\rho_o^2\sum_{L'}\{(W[-ih^+,\gamma^o])_{LL'}C^o_{L'}+(W[-ih^+,f^o])_{LL'}A^o_{L'}\}=B^o_L \tag{2.46}$$

we obtain for $\mathbf{r}\in\Omega_i$, the same equation, (2.25), provided the exciting amplitude $4\pi i^lY^*_L(\hat{\mathbf{k}})$ is replaced by B^o_L. Similarly, for $\mathbf{r}$ in the interstitial region $(\mathbf{r}\notin\mathscr{C}\Omega_o+\sum_j\Omega_j)$, we recover Eq. (2.31) provided $\phi_0(\mathbf{r})$ is replaced by $\sum_L j_l(kr_o)Y_L(\mathbf{r}_o)B^o_L$. These two equations are to be combined with a further relation obtained when $\mathbf{r}\in\mathscr{C}\Omega_o$:

$$0=-i\sum_L h^+_l(kr_o)Y_L(\mathbf{r}_o)\left[\sum_{j,L'}J^{oj}_{LL'}B^j_{L'}+\sum_{L'}(T^o_{os})^{-1}_{LL'}B^o_{L'}-\sum_{L'}D^o_{LL'}A^o_{L'}\right]+\int_{\Delta\Omega'}G^+_0(\mathbf{r},\mathbf{r}')V_I(\mathbf{r}')\psi(\mathbf{r}')d^3r' \tag{2.47}$$

having defined, in analogy with Eq. (2.23) (but notice the inversion of j_l with $-ih^+_l$)

$$(T^o_{os})^{-1}_{LL'}=\sum_{L''}(W[j,\gamma^o])_{LL''}(W[-ih^+,\gamma^o])^{-1}_{L''L'} \tag{2.48}$$

and

$$D^o_{LL'''}=k\rho_o^2\left[(W[j,f^o])_{LL'''}-\sum_{L',L''}(W[j,\gamma^o])_{LL''}(W[-ih^+,\gamma^o])^{-1}_{L''L'}(W[-ih^+,f^o])_{L'L'''}\right]\ . \tag{2.49}$$

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

$$\sum_{j,L'}\{[(T^i_a)^{-1}_{LL'}+T^{ii}_{LL'}]B^i_{L'}\delta_{ij}+(1-\delta_{ij})(H^{ij}_{LL'}+T^{ij}_{LL'})B^j_{L'}\}+\sum_{L'}(J^{io}_{LL'}+\Theta^{io}_{LL'})B^o_{L'}=0\ , \tag{2.50a}$$

$$\sum_{j,L'}(J^{oj}_{LL'}+\Theta^{oj}_{LL'})B^j_{L'}+\sum_{L'}[(T^o_{os})^{-1}_{LL'}+\Theta^{oo}_{LL'}]B^o_{L'}=D^o_{LL''}\ , \tag{2.50b}$$

where the quantities $T^{ij}_{LL'}$ and $\Theta^{io}_{LL'}$ are defined as in Eqs. (2.38) and (2.39), and the integration is now extended to the new interstitial region $\Delta\Omega'$. Similarly $\Theta^{oj}_{LL'}$ and $\Theta^{oo}_{LL'}$ are obtained by Eq. (2.39) through the replacement $-ih^+_l\to j_l$ whenever the site j is replaced by the outer sphere site o and vice versa. Again the exciting amplitude A^o_L has been set equal to $\delta_{LL''}$.

Notice that the MSE in (2.40) already contain the contribution of the outer sphere region $\mathscr{C}\Omega_o$ since in this case the interstitial region $\Delta\Omega$ includes $\mathscr{C}\Omega_o$. The MSE in (2.50) make explicit this contribution to the matrix element $T^{ij}_{LL'}$, coming from $\mathscr{C}\Omega_o$. The two sets of equations are indeed alternative ways to solve the same problem.

For spherically symmetric potentials and constant interstitial potential, Eqs. (2.50) reduce to the MSE of Ref. 9 when written for T-matrix normalization, since in this case

$$D^o_{LL'}\to\delta_{LL'}W[f^o_{l'},\gamma^o_{l'}]/W[j_{l'},\gamma^o_{l'}]\ .$$

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 (2.50) 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 Lippmann-Schwinger equation (2.1) can be used to treat the photoemission problems. Indeed, according to Breit and Bethe,[11] 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 Lippmann-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 the interstitial region, using the reexpansion theorems for modified Bessel, Neumann, and Hankel functions, and imposing decay wave boundary conditions on the outer sphere region $\mathscr{C}\Omega_o$ ($A_L^o = 0$), we obtain the MSE for bound states in the case of general potentials.

III. THE PHOTOABSORPTION AND ELECTRON SCATTERING CROSS SECTIONS AND THE GENERALIZED OPTICAL THEOREM

We now use the results of Sec. II to derive expressions of the total photoabsorption and electron scattering cross sections valid in the MS formulation for the general potential, which generalize the analogous expressions 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^i 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

$$\sigma(E;\epsilon) = \frac{k}{\pi}\left[4\pi^2 \hbar\omega\alpha \sum_{L''} |D_{L''}^-(E;\epsilon)|^2\right],$$

where

$$D_{L''}^-(E;\epsilon) = \langle \psi_{L''}^-(E) | \mathbf{r}\cdot\epsilon | \psi_{\text{in}} \rangle$$

and $\psi_{L''}^-(E)$ is the solution of the Lippmann-Schwinger equation (2.1) with incoming wave boundary conditions, energy E, and relative to an exciting wave L''. The quantity k/π, which comes from normalizing $\psi_{L''}^-(E)$ to one state per Ry, has been explicitly factorized. Assuming the initial state ψ_{in} to be a core state localized at site i we need only the expression for $\psi_{L''}^-$ at site i. Hence using Eqs. (2.18) and (2.22)

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

where $B_L^i(L'')$ indicates that vector solution of the MSE (2.40) relative to the particular exciting wave L'', and L_f is 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 a real potential and matches smoothly to

$$\begin{aligned} \sum_{L''} j_l (W[-ih^+,R^i])_{LL''} (W[j,R^i])_{L''L'}^{-1} - ih_{l'}^+ \\ = \sum_{L''} j_l (W[n,R^i])_{LL''} (W[j,R^i])_{L''L'}^{-1} - n_{l'}, \end{aligned}$$

and putting

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

we can write

$$\begin{aligned} \sigma(E;\epsilon) = 4\pi k\hbar\omega\alpha \sum_{L''} \sum_{L_f,L} M_{L_f L}(\epsilon) [B_L^i(L'')]^* \\ \times \sum_{L'_f,L'} M_{L'_f L'}(\epsilon) B_{L'}^i(L''). \end{aligned} \tag{3.1}$$

This is the generalization of the photoabsorption cross section to the case of general potentials which we have been seeking. To make contact with the Green-function approach to the problem we should prove a generalized optical theorem for the amplitude $B_L^i(L'')$ analogous to that already shown in the case of muffin-tin potentials.[12]

The theorem takes the form

$$\begin{aligned} -\sum_{L''} [B_L^i(L'')]^* B_{L'}^j(L'') \\ = \frac{1}{2i}\left(\{[(\underline{T}+\underline{H})^{-1}]_{LL'}^{ij}\}^* - [(\underline{T}+\underline{H})^{-1}]_{L'L}^{ji}\right), \end{aligned} \tag{3.2}$$

where, for short, we have indicated by $\underline{T}+\underline{H}$ the MS matrix in Eq. (2.40):

$$\begin{aligned} (\underline{T}+\underline{H})_{LL'}^{ij} = [(T_a^i)_{LL'}^{-1} + T_{LL'}^{ii}]\delta_{ij} \\ + (1-\delta_{ij})(H_{LL'}^{ij} + T_{LL'}^{ij}). \end{aligned} \tag{3.3}$$

Using this theorem, the expression for the cross section reads

$$\begin{aligned} \sigma(E;\epsilon) = -4\pi k\hbar\omega\alpha \sum_{L_f,L} \sum_{L'_f,L'} M_{L_f L}(\epsilon) \operatorname{Im}[(\underline{T}+\underline{H})^{-1}]_{L'L}^{ii} \\ \times M_{L'_f L'}(\epsilon) \end{aligned} \tag{3.4}$$

which is the generalization to non-muffin-tin cases of the similar Green-function expression valid for muffin-tin potentials.[12,13] We have used the fact that $M_{L_f L}(\epsilon)$ 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

$$\underline{T}+\underline{H}=\underline{M}-i\underline{\Delta}\ , \tag{3.5}$$

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

$$\underline{\Delta}\,{}^{ij}_{LL'}=\sum_{L''}(J^{io}_{LL''}+\Theta^{io}_{LL''})[(J^{jo}_{L'L''})^*+(\Theta^{jo}_{L'L''})^*]\ . \tag{3.6}$$

Under this assumption, from Eqs. (2.40) we have

$$B^i_L(L'')=-\sum_{j,L'}[(\underline{M}-i\underline{\Delta})^{-1}]^{ij}_{LL'}(J^{jo}_{L'L''}+\Theta^{jo}_{L'L''})$$

so that

$$\begin{aligned}\sum_{L''}[B^i_L(L'')]^*B^j_{L'}(L'')&=\sum_{L''}\left[\sum_{k,L'''}\{[(\underline{M}-i\underline{\Delta})^{-1}]^{ik}_{LL'''}(J^{ko}_{L'''L''}+\Theta^{ko}_{L'''L''})\}\right]^*\\&\quad\times\left[\sum_{h,L'''}[(\underline{M}-i\underline{\Delta})^{-1}]^{jh}_{L'L'''}(J^{ho}_{L'''L''}+\Theta^{ho}_{L'''L''})\right]\\&=[(\underline{M}-i\underline{\Delta})^{-1}\underline{\Delta}(\underline{M}+i\underline{\Delta})^{-1}]^{ji}_{L'L}\\&=-\frac{1}{2i}[(\underline{M}+i\underline{\Delta})^{-1}-(\underline{M}-i\underline{\Delta})^{-1}]^{ji}_{L'L}\\&=-\frac{1}{2i}(\{[(\underline{T}+\underline{H})^{-1}]^{ij}_{LL'}\}^*-[(\underline{T}+\underline{H})^{-1}]^{ji}_{L'L})\end{aligned} \tag{3.7}$$

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

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

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. (2.40) already describes the most general case. Hence the theorem holds true also for the amplitudes $B^j_L(L'')$ solutions of the MSE (2.50). The MS matrix to use in Eq. (3.2) in this latter case is obtained after elimination of the amplitude B^o_L from the set of Eq. (2.50)

$$\begin{aligned}(\underline{T}+\underline{H})^{ij}_{LL'}&=(T^i_a)^{-1}_{LL'}\delta_{ij}+H^{ij}_{LL'}(1-\delta_{ij})+T^{ij}_{LL'}\\&\quad+\sum_{L'',L'''}(J^{io}_{LL''}+\Theta^{io}_{LL''})[(T^o_{os})^{-1}+\Theta^{oo}]^{-1}_{L''L'''}\\&\qquad\times(J^{oj}_{L'''L'}+\Theta^{oj}_{L'''L'})\end{aligned} \tag{3.8}$$

remembering that the matrix elements $T^{ij}_{LL'}$ now refer to a reduced interstitial region.

The unpolarized electron scattering cross section by a cluster of atoms is given in Ref. 9 as

$$\sigma_{\text{ES}}(E)=4\pi\sum_{L,L'}|\,T^c_{LL'}\,|^2\ ,$$

where the k^2 factor in the denominator of Eq. (48) of Ref. 9 has been incorporated in the definition of $T^c_{LL'}$, which is the T matrix of the whole cluster defined as in Eq. (A2). In the absence of the outer sphere this quantity is derived from Eq. (2.31) by referring the intervening functions to the origin of the coordinates using the appropriate expansion theorems and following the same steps leading to Eq. (2.37). The net result is that in the interstitial region and for $r_o\to\infty$ the wave function has the form

$$\begin{aligned}\psi(\mathbf{r}_o)&=\phi_o(\mathbf{r})\\&\quad-i\sum_L h_l^+(kr_o)Y_L(\mathbf{r}_o)\\&\qquad\times\left[\sum_{j,L'}(J^{oj}_{LL'}+\Theta^{oj}_{LL'})B^j_{L'}(L'')+\Theta^{oo}_{LL''}\right]\end{aligned}$$

which shows, by comparison with Eq. (A2), that

$$T^c_{LL''}=\frac{1}{k}\left[\sum_{j,L'}(J^{oj}_{LL'}+\Theta^{oj}_{LL'})B^j_{L'}(L'')+\Theta^{oo}_{LL''}\right]\ .$$

In presence of outer sphere, using Eqs. (2.42) and (2.46) with $A^o_{L'}=\delta_{L'L''}$, one obtains

$$\begin{aligned}T^c_{LL''}&=\frac{1}{k}C^o_L(L'')\\&=-\frac{1}{k}\sum_{L'}(W[-ih^+,\gamma^o])^{-1}_{LL'}\\&\qquad\times\left[\frac{B^o_{L'}(L'')}{(k\rho_o^2)}+(W[-ih^+,f^o])_{L'L''}\right]\ ,\end{aligned}$$

where $B^o_{L'}(L'')$ is to be derived by solving Eqs. (2.50).

The generalized optical theorem of Eq. (3.7) can then be used to derive the usual optical theorem for $T^c_{LL''}$ under the form

$$\sum_{L'}T^c_{LL'}(T^c_{L'L''})^\dagger=-\frac{1}{k}\operatorname{Im}T^c_{LL''}$$

so that

$$\sigma_{\text{ES}}(E)=-\frac{4\pi}{k}\sum_{L,L'}\operatorname{Im}T^c_{LL'}\ .$$

IV. 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. (2.40),

$$\underline{T}^{ij}_{LL'}=[(T^i_a)^{-1}_{LL'}+T^{ii}_{LL'}]\delta_{ij} , \tag{4.1a}$$

$$\underline{H}^{ij}_{LL'}=(H^{ij}_{LL'}+T^{ij}_{LL'})(1-\delta_{ij}) \tag{4.1b}$$

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

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

$$\begin{aligned}(\underline{T}+\underline{H})^{-1}&=(I+\underline{T}^{-1}\underline{H})\underline{T}^{-1}\\ &=\sum_{n=0}^{\infty}(-1)^n(\underline{T}^{-1}\underline{H})^n\underline{T}^{-1} ,\end{aligned} \tag{4.2}$$

where the series is 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

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

where

$$\begin{aligned}&\sigma_0(E;\epsilon)\\ &\quad=-4\pi k\hbar\omega\alpha\sum_{L_f,L}\sum_{L'_f,L'}M_{L_fL}(\epsilon)\mathrm{Im}(\underline{T}^{-1})^{ii}_{LL'}M_{L'_fL'}(\epsilon)\end{aligned} \tag{4.4}$$

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

$$\begin{aligned}\sigma_n(E;\epsilon)=&-4\pi k\hbar\omega\alpha(-1)^n\\ &\times\sum_{L_f,L}\sum_{L'_f,L'}M_{L_fL}(\epsilon)\mathrm{Im}[(\underline{T}^{-1}\underline{H})^n\underline{T}^{-1}]^{ii}_{LL'}\\ &\times M_{L'_fL'}(\epsilon)\end{aligned} \tag{4.5}$$

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 $H^{ij}_{LL'}$ of spherical-wave components from site i and angular momentum L to site j and angular momentum L' through the appearance of the matrix element $T^{ij}_{LL'}$ in Eq. (4.1b).

In order to estimate this modification we write in Eq. (2.38), referring to site i as origin ($\mathbf{r}\equiv\mathbf{r}_i$),

$$T_I(\mathbf{r},\mathbf{r}')=\sum_{L,L'}Y^*_L(\mathbf{r})T^I_{LL'}(r,r')Y_{L'}(\mathbf{r}') \tag{4.6}$$

and use the reexpansion theorem

$$\begin{aligned}-ih_l^+(kr_j)Y_L(\mathbf{r}_j)&=\sum_{L'}j_{l'}(kr_i)Y_{L'}(\mathbf{r}_i)H^{ij}_{L'L}\quad\text{for } |\mathbf{r}_i-\mathbf{r}_j|=|\mathbf{R}_{ij}|>|\mathbf{r}_i|\\ &=-i\sum_{L'}h^+_{l'}(kr_i)Y_{L'}(\mathbf{r}_i)J^{ij}_{L'L}\quad\text{for } |\mathbf{r}_i-\mathbf{r}_j|=|\mathbf{R}_{ij}|<|\mathbf{r}_i| .\end{aligned}$$

Hence, remembering that $T_I(\mathbf{r},\mathbf{r}')\neq0$ only for $\mathbf{r},\mathbf{r}'\in\Delta\Omega$

$$\begin{aligned}T^{ij}_{LL'}=k\int_{\rho_i}^{\infty}r^2dr[-ih_l^+(kr)]&\int_{\rho_i}^{R_{ij}}r'^2dr'\sum_{L''}T^I_{LL''}(r,r')j_{l''}(kr')H^{ij}_{L''L'}\\ &+\int_{R_{ij}}^{\infty}r'^2dr'\sum_{L''}T^I_{LL''}(r,r')[-ih^+_{l''}(kr')]J^{ij}_{L''L'} ,\end{aligned} \tag{4.7}$$

where the upper limit of integration is to be changed accordingly in presence of on outer sphere. If the muffin-tin constant $\overline{V}_{\text{int}}$ can be chosen in such a way that $V_I(\mathbf{r})-\overline{V}_{\text{int}}=\sum_{L''}\overline{V}_{L''}(r)Y_{L''}(\mathbf{r})$ is weak enough, then to a reasonable approximation $T_I(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}')\overline{V}_I(\mathbf{r})$ and

$$T^I_{LL'}(r,r')=\frac{1}{r^2}\delta(r-r')\sum_{L''}\overline{V}_{L''}(r)C^L_{L''L'}$$

in Eq. (4.6), since $\sum_{L'}C^L_{L''L'}Y_{L'}(\mathbf{r})=Y_{L''}(\mathbf{r})Y^*_L(\mathbf{r})$. Substitution into Eq. (4.7) gives

$$\begin{aligned}T^{ij}_{LL'}=&k\sum_{L'',L'''}\int_{\rho_i}^{R_{ij}}r^2dr[-ih_l^+(kr)]\overline{V}_{L''}(r)j_{l'''}(kr)C^L_{L''L'''}H^{ij}_{L'''L'}\\ &+k\sum_{L'',L'''}\int_{R_{ij}}^{\infty}r^2dr[-ih_l^+(kr)]\overline{V}_{L''}(r)[-ih^+_{l'''}(kr)]C^L_{L'',L'''}J^{ij}_{L'''L'} .\end{aligned} \tag{4.8}$$

To proceed further, we use an approximation expression for the quantities $H^{ij}_{LL'}$ and $J^{ii}_{LL'}=(i/2)[H^{ij}_{LL'}-(H^{ii}_{L'L})^*]$. It has been shown[14] that to a good approximation

$$H^{ij}_{LL'}\approx-4\pi Y^*_L(\mathbf{R}_{ij})Y_{L'}(\mathbf{R}_{ij})f(R_{ij})i^{l-l'} \tag{4.9a}$$

so that

$$J^{ij}_{LL'} \approx -4\pi Y^*_L(\mathbf{R}_{ij}) Y_{L'}(\mathbf{R}_{ij}) \mathrm{Im}[f(R_{ij}) i^{l-l'}] \tag{4.9b}$$

where

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

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

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

$$\begin{aligned} -4\pi \sum_{L'',L'''} \int_{\rho_i}^{R_{ij}} r^2 dr[-ih_l^+(kr)] \bar{V}_L(r) j_{l'''}(kr) \int d\Omega\, Y^*_L(\Omega) Y_{L''}(\Omega) Y_{L'''}(\Omega) Y^*_{L'''}(\mathbf{R}_{ij}) Y_{L'}(\mathbf{R}_{ij}) f(R_{ij}) i^{l'''-l'} \\ = -4\pi \int_{\Delta(\rho_i,R_{ij})} d^3r[-ih_l^+(kr)] Y^*_L(\mathbf{r}) \bar{V}(\mathbf{r}) e^{ik\mathbf{r}\cdot\hat{\mathbf{R}}_{ij}} f(R_{ij}) Y_{L'}(\mathbf{R}_{ij}) i^{-l'} \\ = [4\pi i^l Y^*_L(\mathbf{R}_{ij})]^{-1} \int_{\Delta(\rho_i,R_{ij})} d^3r[-ih_l^+(kr)] Y^*_L(\mathbf{r}) \bar{V}(\mathbf{r}) e^{ik\mathbf{r}\cdot\hat{\mathbf{R}}_{ij}} H^{ij}_{LL'} \ , \end{aligned} \tag{4.10}$$

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

$$-[4\pi i^l Y^*_L(\mathbf{R}_{ij})]^{-1} \int_{\mathscr{C}\Delta'(r_{ij})} d^3r[-ih_l^+(kr)] Y^*_L(\mathbf{r}) \bar{V}(\mathbf{r}) \mathscr{H}(\mathbf{r}\cdot\mathbf{R}_{ij}) J^{ij}_{LL'} \ , \tag{4.11}$$

where $\mathscr{H}(\mathbf{r}\cdot\mathbf{R}_{ij}) = -4\pi \sum_L i^{l+1} h_l^+(kr) Y^*_L(\mathbf{r}) Y_L(\mathbf{R}_{ij})$ and $\mathscr{C}\Delta'(R_{ij})$ 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 $h_l^+(kr) \approx i^{-(l+1)} e^{ikr}/(kr)$ so that the quantity in (4.11) becomes roughly

$$(-1)^{l+1} \int_{R_{ij}}^{\infty} r^2 dr \frac{e^{2ikr}}{(kr)^2} \bar{V}(r, \hat{\mathbf{R}}_{ij}) J^{ij}_{LL'} \ , \tag{4.12}$$

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 nonconstant 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 energies of the final-state photoelectron which are not too high ($\le$ 100–150 eV).

V. NUMERICAL IMPLEMENTATION AND COMPARISON WITH OTHER METHODS

All major theoretical methods devised up to now to calculate molecular photoabsorption or electron-molecule collision cross sections and even in the more sophisticated version of the multichannel scattering theory, sooner or later reduce to the solution of a system of coupled second-order elliptic differential (integro-differential) equations of the Schrödinger type in a local (nonlocal) potential whose essential peculiarity is its multicenter anisotropic nature. Usually for the solution of this problem a single-center expansion of the wave functions and of the potential is used. The disadvantage of this approach is that only small molecules with light atoms (except perhaps the central one) can be treated, since a reasonably manageable single-center expansion is usually not sufficient for reproducing the singularities of the potential far away from the center or for representing wave functions well localized around a distant nuclear charge.

The multicenter expansion method that is typical of the MS approach to the problem corrects for this drawback, since the expansion is made around each singularity of the potential. Hence bigger molecules with heavy atoms can be successfully treated. Another advantage over the existing methods is that it is a non-basis-set method that directly solves the Lippmann-Schwinger equation for any energy of the final-state electron. As a consequence, questions regarding the completeness of the basis chosen are automatically bypassed.

As is apparent from the derivation of Sec. II, the MS method breaks the solution of the problem into two steps: finding the individual T_a matrices for the various potentials $V_o(\mathbf{r})$ and $V_j(\mathbf{r})$ or the T_I matrix for $V_I(\mathbf{r})$ and then solving the algebraic equations for the coefficients B^i_L.

The numerical solution of Eq. (2.14) inside the atomic spheres does not pose any major problem for local potentials. By putting $R_{LL'}(r) = (1/r) X_{LL'}(r)$ $[R(r) = (1/r) X(r)$ in matrix notation] and introducing

$$G(r) \equiv G_{LL'}(r) = \left[\frac{l(l+1)}{r^2} - E\right] \delta_{LL'} + V_{LL'}(r)$$

the system of coupled Schrödinger equations

$$X''(r) - G(r) X(r) = 0$$

can be solved very efficiently by using the matrix Numerov procedure

$$\begin{aligned} &[I - \tfrac{1}{12} h^2 G(r_{n+1})] X(r_{n+1}) \\ &\quad = [2I + \tfrac{10}{12} h^2 G(r_n)] X(r_n) \\ &\qquad - [I - \tfrac{1}{12} h^2 G(r_{n-1})] X(r_{n-1}) \ , \end{aligned} \tag{5.1}$$

where $h = r_n - r_{n-1}$ is the mesh size and I is the unit matrix. Actually, the number of operations involved can be further reduced, with a consequent reduction of computational time, by putting

$$Y(r)=[I-\tfrac{1}{12}h^2G(r)]X(r)$$

and rewriting Eq. (5.1) as

$$Y(r_{n+1})=12[I-\tfrac{1}{12}h^2G(r_n)]^{-1}Y(r_n)-[10Y(r_n)+Y(r_{n-1})] \qquad (5.2)$$

so that at each step both $Y(r)$ and $X(r)=[I-\frac{1}{12}h^2G(r)]^{-1}Y(r)$ are calculated.

By using the asymptotic form of the matrix solution at $r\to 0$ for the atomic spheres or at $r\to\infty$ for the outer sphere [see Eqs. (2.16) and (2.43)] one can generate by outward or inward integration of Eqs. (5.2) the wanted solution from which to calculate the atomic $t^j_{LL'}$ matrices.

The numerical computation of the quantities $T^{ij}_{LL'}$ ($\Theta^{io}_{LL'}$) is best achieved by solving for the quantity ψ^j_L (ψ^o_L) satisfying the equations

$$\psi^j_L(\mathbf{r})=-ih_l^+(kr_j)Y_L(\mathbf{r}_j)+\int_{\Delta\Omega}G_0^+(\mathbf{r}-\mathbf{r}')V_I(\mathbf{r}')\psi^j_L(\mathbf{r}')\,, \qquad (5.3a)$$

$$\psi^o_L(\mathbf{r})=j_l(kr_o)Y_L(\mathbf{r}_o)+\int_{\Delta\Omega}G_0^+(\mathbf{r}-\mathbf{r}')V_I(\mathbf{r}')\psi^o_L(\mathbf{r}')\,, \qquad (5.3b)$$

which are derived from Eq. (2.31) by putting $B^i_{L'}=\delta_{ij}\delta_{LL'}$ [$B^i_{L'}=0$ and $4\pi i^{l'}Y_{L'}(\mathbf{k})=\delta_{LL'}$] at the points of a Gaussian quadrature using a single-center expansion for all the functions involved and a linear-algebraic approach along the lines of that suggested by Schneider and Collins[15] for a similar problem, the electron molecule collision. The solution at such points can then be used to evaluate, by the same technique of single-center expansion and Gaussian quadrature at the same points, the integrals

$$T^{ij}_{LL'}=\int_{\Delta\Omega}[-ih_l^+(kr_i)]Y_L(\mathbf{r}_i)V_I(\mathbf{r})\psi^j_{L'}(\mathbf{r})d^3r\,,$$

$$\Theta^{ij}_{LL'}=\int_{\Delta\Omega}[-ih_l^+(kr_i)]Y_L(\mathbf{r}_i)V_I(\mathbf{r})\psi^o_{L'}(\mathbf{r})d^3r\,.$$

We notice that the expansion of $V_I(\mathbf{r})=\sum_L V_I^L(r)Y_L(\mathbf{r})$ around the center of the cluster should not in principle cause much trouble in this case, since now $V_I(\mathbf{r})$ has only finite size discontinuities at the sphere radii ρ_i and ρ_o. Such discontinuities can even be reduced in strength, if necessary, by introducing $\overline{V}_{\text{int}}$ as discussed in Sec. II [see Eq. (2.41) following]. Also, at the price of adding empty spheres, one can minimize the effect of the interstitial region, if this is needed.

Regarding the convergence of the L angular momentum expansion, there is a natural cutoff given by the size of the potential $V_j(\mathbf{r})$, so that around each center j the maximum l needed at energy E is roughly $k\rho_j$. Similarly, for the outer sphere and the interstitial region $l_{\max}$ is the order of $k\rho_o$. This is due to the fact that a spherical wave with angular momentum l and momentum k is not scattered by a potential of radius ρ if its classical impact parameter $k\rho<l$. These cutoff values are quite low for atomic spheres (for a typical value $\rho=3$ a.u. and a photoelectron energy as high as 16 Ry, $l_{\max}\approx 12$). For the outer sphere, assuming a rather large value of 10 a.u., at the same energy $l_{\max}\approx 40$, a typical value used in the single-center expansion calculation for small molecules.

Finally, the point group symmetry of the cluster around the photoabsorber can be effectively used to reduce the dimensions of the secular matrix to be solved. Details of the symmetrized version of the MS equations will be given elsewhere. The extension of the MS method to a nonlocal potential does not present conceptual difficulties, it only adds greater complication. In this case one has to solve a set of integro-differential equations inside the atomic spheres and many methods of solution are available in the literature for such a problem. For the interstitial region one can still use the method of Ref. 15 which was originally devised to treat this more general case. It is clear, however, that the use of a local potential greatly facilitates the solution of the ionization problem. Hence in the context of the MS method the choice of the local density potential of the type proposed by Hedin and Lundqvist,[16] based on the free-electron-gas approximation of the Dyson self-energy of the real system under study, comes in very handy. This potential is energy dependent and incorporates the effect of the free-electron-gas exchange, the Coulomb correlation hole, and the screened exchange. Its complex part describes in an average way the inelastic processes that damp the photoelectron wave in the final state. Simpler versions, always in the spirit of the local-density approximation, are the $X\alpha$ potential and the Dirac-Hara free-electron-gas exchange potential, used by various authors to calculate photoionization and electron-molecule cross sections for small molecules (see Lane for a review[17]).

An improvement on this approach has been proposed by Zangwill and Soven,[18] in that they incorporate in a self-consistent way the effect of the time-dependent field induced by the external radiation field on the photoionization cross section. This approach, known as the time-dependent local-density approximation, takes into account polarization-type many-body effects influencing the photoresponse of small electronic system. The method has been applied to rare-gas atoms but it is clear that it can be extended to molecules, provided the multicenter peculiarity of the induced field is taken into account. The multiple-scattering method presented here can readily cope with such an extension. It is difficult to assess the relationship of the local-density method to other methods currently used to solve the photoionization problem, like the Stieltjes moment theory by Langhoff[19] or the Schwinger variational method by McKoy *et al.* (see Ref. 20 for a review). These latter methods, although with different techniques, both try to solve the Hartree-Fock (HF) equations for a continuum orbital in the static exchange approximation, in which interelectronic correlations are neglected but the nonlocality of the exchange and the orthogonality constraints are fully taken into account at the HF level. The assessment of the accuracy of the exchange approximation in the local-density methods relative to its nonlocal HF counterpart is not easy; it requires careful comparison between model results in both cases. Also, the local-density methods can include in an average way electron correlation effects which are neglected at the HF level. As a general rule we expect that the two approaches give qualitatively similar results in the semiclassical regime, i.e., at those energies of the final-state electron where the density of the available final channels is so high that an average description of the system is appropriate. At low energies where the effect of a single final-state channel is important at the quantum level both approaches are insufficient although the treatment of exchange is more realistic in the HF approximation. A multichannel extension of the scattering problems is essential in such a case. It turns out that it is possible to extend the Schwinger variational principle in this direction[20] and calculations have been performed on small molecules using this method. No such extension exists, to our knowledge, for the local-density method. The next step is to extend the MS method to this general case.

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APPENDIX A

We show here the equivalence between the expression (2.23) for the atomic T matrix (T_a^i) relative to the potential $V_i(\mathbf{r})$ and the expression for the similar quantity as defined by Evans and Keller[6] in their Appendix 1.

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

$$\psi_{\mathbf{k}}(\mathbf{r})=\sum_{L}\phi_L(\mathbf{r})Y_L(\mathbf{r})=\sum_{L,L'}C_{L'}R_{LL'}(\mathbf{r})Y_L(\mathbf{r}) \tag{A1}$$

to the general solution in the external region $\mathscr{C}\,\Omega_i$

$$\psi_{\mathbf{k}}(\mathbf{r})=\sum_{L}A_L^{\mathbf{k}}\left[i^l j_l(kr)Y_L(\mathbf{r})-ik\sum_{L'}i^{l'}h_{l'}^{+}T_{L'L}\,Y_{L'}(\mathbf{r})\right], \tag{A2}$$

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

The exciting amplitude $A_L^{\mathbf{k}}$ is determined by requiring that

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

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

Equation (A2) can be rewritten as

$$\psi_{\mathbf{k}}(\mathbf{r})=\sum_{L}A_L^{\mathbf{k}}[i^l j_l(kr)-iB_L^{\mathbf{k}}h_l^{+}(kr)]Y_L(\mathbf{r}) , \tag{A3}$$

where

$$B_L^{\mathbf{k}}=k\sum_{L'}T_{LL'}A_{L'}^{\mathbf{k}} . \tag{A4}$$

The matching conditions at the radius ρ_i of Ω_i

$$\sum_{L'}R_{LL'}C_{L'}=i^l[A_L^{\mathbf{k}}j_l(k\rho_i)-iB_L^{\mathbf{k}}h_l^{+}(k\rho_i)] , \tag{A5a}$$

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

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

In matrix form they read

$$Gx=d ,$$

where

$$G\equiv\begin{bmatrix}\dfrac{R_{LL'}}{i^l j_l(k\rho_i)} & \dfrac{ih_l^{+}(k\rho_i)}{j_l(k\rho_i)}\\[2ex] \dfrac{R'_{LL'}}{i^l j'_l(k\rho_i)} & \dfrac{ih_l^{+\prime}(k\rho_i)}{j'_l(k\rho_i)}\end{bmatrix},$$

$$x=\begin{bmatrix}C_L\\ B_L^{\mathbf{k}}\end{bmatrix},\quad d=\begin{bmatrix}A_L^{\mathbf{k}}\\ A_L^{\mathbf{k}}\end{bmatrix} .$$

By introducing

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

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

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

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

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

$$\sum_{L'}W[j_l,R_{LL'}]C_{L'}=W[j_l,-ih_l^{+}]i^l B_L^{\mathbf{k}}=\frac{i^l}{k\rho_i^2}B_L^{\mathbf{k}} , \tag{A6a}$$

$$\begin{aligned}\sum_{L'}W[-ih_l^{+},R_{LL'}]C_{L'}&=-W[j_l,-ih_l^{+}]i^l A_L^{\mathbf{k}}\\ &=-\frac{i^l}{k\rho_i^2}A_L^{\mathbf{k}} .\end{aligned} \tag{A6b}$$

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

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

or

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

or

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

which is the expression (2.23) apart from the factor $-k$.

APPENDIX B

We show here that the multiple-scattering matrix $\underline{T}+\underline{H}$ in the presence of a nonconstant 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

$$\begin{aligned}\underline{\Delta}{}^{ij}_{LL'}&=\sum_{L''}(J^{io}_{LL''}+\Theta^{io}_{LL''})[(J^{jo}_{L'L''})^*+(\Theta^{jo}_{L'L''})^*]\\&=J^{ij}_{LL'}+\Theta^{ij}_{LL'}+(\Theta^{ji}_{L'L})^*+\sum_{L''}\Theta^{io}_{LL''}(\Theta^{jo}_{L'L''})^*\ .\end{aligned}\tag{B1}$$

The second step follows from the Hermiticity of $J^{ij}_{LL'}=(J^{ji}_{L'L})^*$, which is a consequence of the definition (2.27), resulting from the validity of the sum rule

$$J^{ij}_{LL'}=\sum_{L''}J^{io}_{LL''}(J^{jo}_{L'L''})^*=\sum_{L''}J^{io}_{LL''}J^{oj}_{L''L'}\tag{B2}$$

which is a consequence of (2.24), (2.26), and the property of the exponential

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

as shown in Ref. 2, and from the fact that

$$\Theta^{ij}_{LL'}=\sum_{L''}\Theta^{io}_{LL''}(J^{jo}_{L'L''})^*=\sum_{L''}\Theta^{io}_{LL''}J^{oj}_{L''L'}\tag{B3}$$

which is a consequence of the definition (2.39) and the relation (2.26).

The MS matrix $\underline{T}+\underline{H}$, following Eq. (2.40), can be written as

$$(\underline{T}+\underline{H})^{ij}_{LL'}=(T^i_a)^{-1}_{LL'}\delta_{ij}+H^{ij}_{LL'}(1-\delta_{ij})+T^{ij}_{LL'}\ .$$

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

$$H^{ij}_{LL'}=N^{ij}_{LL'}-iJ^{ij}_{LL'}\ ,\tag{B4}$$

where $J^{ij}_{LL'}$ is defined in (2.27) and $N^{ij}_{LL'}$ is similarly defined by making the substitution $j_l\rightarrow n_l$. They are both Hermitian matrices.

Moreover the atomic T matrix $(T^i_a)_{LL'}$ is known to be related to the Hermitian atomic K matrix $(K^i_a)_{LL'}$ by the relation[2]

$$(T^i_a)^{-1}_{LL'}=(K^i_a)^{-1}_{LL'}-i\ .$$

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

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

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

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

the last step following from the definition (2.38) for $T^{ij}_{LL'}$ and the fact that $-ih_l^+=n_l-ij_l$, having introduced, in analogy with (2.39), the matrix

$$\begin{aligned}\underline{\Theta}\equiv\underline{\Theta}{}^{ij}_{LL'}=k\int\int_{\Delta\Omega}&[-ih_l^+(kr_i)]Y_l^*(\mathbf{r}_i)T_I(\mathbf{r},\mathbf{r}')\\&\times n_{l'}(kr_j')Y_{L'}(\mathbf{r}_j')d^3r\,d^3r'\ .\end{aligned}$$

Remembering that $J^{ii}_{LL'}=\delta_{LL'}$, we finally achieve the decomposition

$$\begin{aligned}(\underline{T}+\underline{H})^{ij}_{LL'}&=(K^i_a)^{-1}_{LL'}\delta_{ij}+(1-\delta_{ij})N^{ij}_{LL'}-\tfrac{1}{2}(T+T^\dagger)^{ij}_{LL'}\\&\quad+(\underline{\Theta}+\underline{\Theta}^\dagger)^{ij}_{LL'}-i\left[J^{ij}_{LL'}+(\Theta+\Theta^\dagger)^{ij}_{LL'}+\frac{1}{2i}(T^\dagger-T)^{ij}_{LL'}\right]\\&=\underline{M}{}^{ij}_{LL'}-i\underline{\Delta}{}^{ij}_{LL'}\ ,\end{aligned}$$

where the matrix $\underline{\Delta}{}^{ij}_{LL'}$ is identical to the expression in (B1), taking into account that the optical theorem for the T matrix for any potential, and in particular for the interstitial potential, reads[2]

$$\frac{1}{2i}(T^\dagger-T)^{ij}_{LL'}=\sum_{L''}\Theta^{io}_{LL''}(\Theta^{jo}_{L'L''})^*\ .$$

This last step completes the proof.

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[1] J. Siegel, D. Dill, and J. L. Dehmer, J. Chem. Phys. **64**, 3204 (1976).

[2] P. Lloyd and P. V. Smith, Adv. Phys. 21, 69 (1972).

[3] F. Beleznay and M. J. Lawrence, J. Phys. C 1, 1288 (1968).

[4] E. U. Condon and G. H. Shortly, *The Theory of Atomic Spectra* (Cambridge University, Cambridge, England, 1959).

[5] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, N.J., 1957).

[6] R. Evans and J. Keller, J. Phys. C 4, 3155 (1971).

[7] G. Baym, *Lectures on Quantum Mechanics* (Benjamin, New York, 1969).

[8] K. Johnson, Adv. Quantum Chem. 7, 143 (1973).

[9] J. L. Dehmer and D. Dill, J. Chem. Phys. **61**, 692 (1974).

[10] R. G. Newton, *Scattering Theory of Waves and Particles* (McGraw-Hill, New York, 1966).

[11] G. Breit and H. A. Bethe, Phys. Rev. **93**, 888 (1954).

[12] C. R. Natoli and J. Rehr (unpublished).

[13] P. J. Durham, J. B. Pendry, and C. H. Hodges, Comput. Phys. Commun. 25, 193 (1982).

[14] J. Rehr, R. Albers, C. R. Natoli, and E. Stern, Phys. Rev. B **34**, 4350 (1986).

[15] B. I. Schneider and L. A. Collins, J. Phys. B **14**, L101 (1981).

[16] L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[17] N. F. Lane, Rev. Mod. Phys. 52, 29 (1980).

[18] A. Zangwill and P. Soven, Phys. Rev. A 21, 1561 (1980).

[19] P. W. Langhoff and C. T. Corcoran, J. Chem. Phys. **61**, 146 (1974); P. W. Langhoff, J. Sims, and C. T. Corcoran, Phys. Rev. A **10**, 829 (1974).

[20] R. Lucchese, K. Takatsuka, and V. McKoy, Phys. Rep. **131**, 149 (1986).