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Basis-independent multiple-scattering theory for electron spectroscopies: General formalism

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I present here a general formalism that allows the construction of the cross section of any electron spectroscopy in a straightforward and transparent way. This approach does not make any assumption concerning the choice of the basis functions used to expand the wave function of the electron. In this sense, it generalizes existing theories. It allows us to keep the physics well in view and offers, due to the relationship between operators and parts of a pictorial representation of the experiments, a type of a graphical interface to the problem at hand. Moreover, it does not assume any particular shape for the potential.

I. INTRODUCTION

Electron spectroscopy techniques are now a well-established tool for the study of surfaces. They have become more and more popular over the years both because they are nondestructive probes and as a result of the theoretical and computational effort that transformed them into very accurate and powerful methods. Historically, low-energy electron diffraction[1–3] (LEED) was the first to establish itself as an essential technique for surface crystallography. With the advent of synchrotron radiation, x-ray absorption spectroscopy (XAS) developed rapidly as a new spectroscopic method capable of giving both electronic structure orientated (x-ray absorption near edge structure, XANES) and crystallographic orientated information either for bulk (extended x-ray absorption fine structure, EXAFS) or surfaces (surface EXAFS, SEXAFS).[4] Then, photoelectron diffraction[5–9] (PhD) and Auger electron diffraction[10] (AED) were developed for crystallographic purposes. Finally, electron energy loss spectroscopy (EELS), which was originally considered as an electronic structure tool[11] capable of giving information on collective excitations such as plasmons[12] or phonons,[13] has now been shown to be able to give surface crystallographic parameters as well.[14] Simultaneously, inverse methods such as bremstrahlung isochromat spectroscopy[15] (BIS) or inverse photoelectron diffraction[16] were developed to study both empty states and crystallography depending on the energy. All these tools, from which a great variety of knowledge about a crystal can be obtained, commonly use, in one way or another, electrons as the source of information.

The term *electron spectroscopy* is used here in a very general way: it simply means that the spectra obtained from the experiments contain, directly or indirectly, the information that is sought as a result of the scattering processes undergone by an electron inside a crystal. In that sense, the electron need not be the particle entering the detector, provided that the resulting signal is related somehow to the behavior of an electron.

From the point of view of crystallography, it is possible to divide electron spectroscopies into two categories according to the type of parameters they depend upon, and hence on the kind of information they will be able to provide. Namely, one can distinguish between localized and nonlocalized crystallographic probes. I will call here localized probes those originating from an excitation process occuring on a particular atom. This is typically the case of XAS, core PhD, and AED or EELS. As a result, these spectroscopies will be mainly sensitive to the immediate surrounding of the atom on which the excitation has taken place. On the other hand, nonlocalized spectroscopies will essentially reflect the long-range structure of the system under study. Actually, the term nonlocalized can be understood in two ways. It can either mean that there is no excitation process or that the excitation process involves a delocalized level. The first case corresponds to LEED, where a beam of incoming electrons is elastically scattered by the atoms of the crystal with the resulting beam entering the detector. Valence photoelectron diffraction[17] is a good example of the second case.

Traditionally, there are two ways to tackle the problem of the modelization of electron spectroscopies. One uses a cluster approach and an expansion of the wave function of the traveling electron into spherical waves. Historically, it was developed for localized spectroscopies such as XAS,[18,19] PhD,[5–9] or EELS,[20] with some refinements proposed later that use a shell partitioning of the crystal.[21,22] The reason for such a choice of basis probably lies in the fact that spherical waves are localized functions and thus thought more suited to describe the physical process. The other approach, which can be called the slab appraoch, involves a partitioning of the crystal into planes so that the periodicity of each plane can be taken into account. Consequently, the wave function incident upon a plane is expanded into a set of discrete plane waves satisfying the Born–Von Kármán cyclic conditions of the corresponding plane. This is the case in LEED,[1–3] where the use of plane waves, which are inherently nonlocalized, is particularly adapted to the nature of the problem. In this sense, LEED theories can be viewed as the spectroscopic equivalent to the layer Korringa-Kohn-Rostoker (KKR) theory.[23] Mixed approaches have, however, been developed such as cluster theories of LEED[24,25] or slab theories of PhD[26,27] or EELS.[28] But at all events, all the existing methods rely either on spherical waves or on plane waves. These bases have the advantage of being both simple and flexible. Yet they have an important drawback: their use is energetically limited due to the rate of convergence of the corre-

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sponding expansions, which varies considerably with energy. If this rate is too slow, many basis functions will be needed to achieve convergence, and hence a computational bottleneck will soon be reached. Let me give an example to illustrate the problem. As is well known the convergence of the spherical-wave expansion is controlled by the upper value l_{max} of the angular momentum index l given by the relation[29] $kr_a \sim \sqrt{l_{max}(l_{max}+1)}$, where k is the wave number of the electron and r_a the radius of the potential centered on atom a around which the expansion is made. The number of basis functions used in the expansion corresponds to the number of values of (l,m), which is $(l_{max}+1)^2$. Low-energy PhD (as an example) can be described exactly by inverting the multiple scattering matrix[30] expressed in a spherical wave basis. Let me suppose now, to simplify the reasoning, that crystal symmetries are not taken into account. Obviously, the inclusion of symmetries will reduce the size of the problem, especially when combined with an appropriate partitioning of the cluster, either into planes[26] (case of translational symmetry) or into shells[28] (point group symmetry). The size of the matrix that has to be inverted is then $N_{at}(l_{max}+1)^2 \times N_{at}(l_{max}+1)^2$, where N_{at} is the number of atoms in the cluster. Consequently, the storage of the matrix will increase with the square of energy and the calculation will soon become impossible. Indeed, for a kinetic energy $E_k \sim 35$ eV, l_{max} is of the order of 4 and the number of basis functions necessary to expand the photoelectron wave function around a particular atomic center is about 25. On the other hand, when the kinetic energy reaches 1 keV, the number of basis functions becomes of the order of 400, therefore preventing the exact calculation of the cross section. This is why high-energy photoelectron diffraction has to be described using a series expansion, i.e., by performing analytically, instead of numerically, the inversion and truncating it to a certain order, which is always a very time-consuming procedure. As a consequence, spherical waves are well suited to low energies (because there the wave function of the electron resembles a spherical wave and hence few nonzero coefficients are left in the expansion) but not to medium or high energies.

Another approach to photoelectron diffraction has been made recently,[31] which uses a reflection high-energy electron diffraction (RHEED)-type formalism, i.e., an expansion of the photoelectron wave function into a set of discrete plane waves reflecting the periodicity conditions of the crystal. In the range of energies used in RHEED, which is a few tens of keV, the number of plane waves necessary to achieve convergence is about 10. This is why plane waves are particularly suited to RHEED, which is a direct consequence from the fact that at these energies, the wave function of the electron is close to a plane wave. Then, when the energy is decreased to x-ray photoelectron diffraction (XPD) energies, that is, to 1 keV or so, the number of basis functions needed increases to about 300. Note that these plane waves are related to planes and not to atoms as the spherical waves are. However, the expected gain in CPU time is counterbalanced here by the fact that the calculation has to be redone for each angle point in contrast to spherical waves where the use of a scattering path operator model disconnects what happens to the electron inside the crystal from its escape towards the detector.

This comparison between the two approaches means that neither spherical waves nor plane waves are really adapted to the 1 keV range for electron spectroscopies. Therefore, there is clearly a need for another approach, at least in this energy range, that covers a majority of the work that can be found in the literature. Indeed, the energy dependence of the cutoff governing the expansion of the usual basis functions considerably limits the complexity of the systems studied, either by memory (exact calculation) or by CPU time (series expansion) requirements.

To overcome this problem, I propose here an alternative approach that generalizes both the cluster and slab theories. The basic idea is to develop a theory of electron spectroscopy techniques that does not make any assumption concerning the choice of the basis. Thus, a general formalism will be described that allows the derivation of cross sections using only operators. Therefore, the choice of the basis is left to the computing strategy (it will be the object of a forthcoming article) and can be tailored to the problem at hand. Note as well that no particular shape will be assumed for the potential to keep the generality of the method. Spherical-wave cluster theories will then be only a particular case of this general framework, and so will be plane-wave slab theories, provided that the cluster, and hence the corresponding operators have been appropriately partitioned as a preliminary to the introduction of the plane-wave basis functions. This important question of the basis-independant partitioning will be the subject of another article. The interesting point here is that other choices can be made that will simplify the calculations. Some, such as screened spherical waves,[32] have already been shown to be very successful in electronic structure calculations. Note that this philosophy is not too distant from the actual debate in the electronic structure community where people are seeking the best choice of a basis for the so called $O(N)$ methods[33](i.e., methods for which the CPU time and the memory scale linearly with the dimension N of the problem), and for which it has been demonstrated that only localized bases are good candidates.[34]

In addition, this approach in terms of operators has a further advantage: operators are directly connected to a physical process (of which matrix elements are only a particular representation) and hence can serve as a graphical interface between the physics behind the experiments and the equations. In other words, the present theory will allow us in a straightforward manner to translate a sketch of the experiment into an operator equation and then into the cross section. The physics behind the equations becomes therefore very easy to identify and the manipulation of these equations is more transparent.

In order to devise this framework, I will divide the physical problem corresponding to a given electron spectroscopy technique into a series of building blocks. Two of these building blocks can be considered as the basis blocks: the excitation and the propagation. The propagation block, which is nothing but the well-known scattering path operator[35] and has already been recognized by Gunnella *et al.*[25] as giving a unified description of electron spectroscopy techniques. I will show here how the excitation block can be defined and the way to match these two building blocks. A sub-block of the propagation block, which can be termed the closed-loop propagation block, will also be introduced as a standard building block to describe absorption processes. All electron spectroscopies can then be constructed by combination of these blocks.

In Sec. II, I will recall some basic definitions of scattering theory. They can be found in more detail in any textbook on the subject[36] but as some of them, such as the Møller wave operator, have never been used in the field of electron spectroscopies (at least to my knowledge); this will greatly help the understanding of the making of the building blocks. Then, I will show in Sec. III how the blocks can be constructed. An example of application, core photoelectron diffraction, will be given in Sec. IV. Finally, in the Conclusion I will draw some perspectives that will be illustrated in forthcoming articles.

II. BASIC DEFINITIONS

I will give here only the main results necessary for the building of the present framework. A more detailed account will be found in standard texbooks on scattering theory[36] to which the reader is referred. From now on, I will suppose the atomic potentials V_i to be both local and real. In other words, V_i will be considered as a Hermitian operator. I will use reduced units throughout the text, i.e., all operators are supposed to be divided by $\hbar^2/2m$, where m is the mass of the electron involved in the process. Moreover, I will make the further assumption that the potentials converge faster than $1/r$ at infinity, which is the mathematical condition[37] for the Møller wave operator to exist over the entire Hilbert space. More precisely, I will suppose that they can be truncated somewhere, this value defining the range of these potentials. But, except as otherwise stated, I will not assume any particular shape for these potentials. In other words, the present formalism is very general and not restricted to the so called muffin-tin potential.

A. Case of a single potential V

Let me consider first the case of an electron in the presence of a single potential V. Any electronic state must therefore satisfy the Schrödinger equation

$$(H_o+V)\,|\psi_k\rangle = k^2\,|\psi_k\rangle. \tag{2.1}$$

If the solution of the Schrödinger equation in the abscence of V is called $|\varphi_k\rangle$, the states $|\psi_k\rangle$ are given by the well-known Lippmann-Schwinger equation

$$|\psi_k^{\pm}\rangle = |\varphi_k\rangle + G_0^{\pm}\,V\,|\psi_k^{\pm}\rangle. \tag{2.2}$$

Here, $G_0^{\pm}$ is the free-electron propagator. The ± solutions originate from the fact that the Green operator $G_0(z)\equiv(z-H_0)^{-1}$ is not defined when z is a positive real number. Therefore, G_0 has to be constructed either by approaching the real axis from above (+ solution) or from below (− solution). The corresponding states are then outgoing states for the + solution and ingoing states for the − solution.

Equivalently, one has, in terms of the propagators, the Dyson equation

$$\begin{aligned} G^{\pm} &= G_0^{\pm} + G_0^{\pm}\,V\,G^{\pm} \\ &= G_0^{\pm} + G^{\pm}\,V\,G_0^{\pm}, \end{aligned} \tag{2.3}$$

where $G(z)\equiv(z-H)^{-1}$. It is important to note here that the definition of G implies that its poles correspond to the eigenvalues of H. Consequently, all the information we are looking for is contained in G. Reasoning in terms of G is therefore equivalent to solving the Schrödinger equation (2.1).

Introducing the transition operator $T^{\pm}$ by

$$T^{\pm} = V + V\,G^{\pm}\,V, \tag{2.4}$$

which obviously has the same poles as $G^{\pm}$, the Lippmann-Schwinger equation (2.2) can then be recast as

$$\begin{aligned} |\psi_k^{\pm}\rangle &= [I + G^{\pm}\,V]\,|\varphi_k\rangle \\ &= [I + G_0^{\pm}\,T^{\pm}]\,|\varphi_k\rangle, \end{aligned} \tag{2.5}$$

where I is the identity of the Hilbert space associated with the electron, and the corresponding Dyson equation as

$$\begin{aligned} G^{\pm} = G_0^{\pm} + G_0^{\pm}\,T^{\pm}\,G_0^{\pm} &= [I + G_0^{\pm}\,T^{\pm}]\,G_0^{\pm} \\ &= G_0^{\pm}[I + T^{\pm}\,G_0^{\pm}]. \end{aligned} \tag{2.6}$$

The interpretation of this equation is straightforward when noticing that $G_0^{\pm}$ describes the propagation of a free electron and $T^{\pm}$ the effect of the potential V upon the incoming electron.

Let me turn now to the expression (2.5) of the Lippmann-Schwinger equation. The Møller wave operator $\Omega^{(\pm)}$ can be defined as the operator transforming a free state $|\varphi_k\rangle$ into a scattering state $|\psi_k^{\pm}\rangle$. In other words,

$$\begin{aligned} \Omega^{(\pm)} &= I + G^{\pm}\,V \\ &= I + G_0^{\pm}\,T^{\pm}. \end{aligned} \tag{2.7}$$

Note in particular that although $\Omega^{(\pm)}$ is not unitary, it satisfies

$$\Omega^{(\pm)\,\dagger}\,\Omega^{(\pm)} = I. \tag{2.8}$$

The dagger † indicates here the Hermitian conjugate.

Actually, a scattering state corresponds, by definition, to a wave function of an electron located outside the range of the potential. But this wave function matches smoothly (and so does its derivative) to an inner wave function corresponding to a continuum state of the potential V. It is therefore possible to analytically continue $\Omega^{(\pm)}$ within the potential, and it is this prolongated operator that I will use from now on. $|\psi_k^{\pm}\rangle$ will therefore describe either the outer scattering states or the inner continuum states. But note that, in addition to the continuum states, there exist as well bound states that will satisfy the Schrödinger equation (2.1) but that will not match to any scattering state outside V. As a consequence, it will not be possible to reach them with $\Omega^{\pm}$.

Now, the Lippmann-Schwinger equation (2.5) can be rewritten as

$$|\psi_k^{\pm}\rangle = \Omega^{(\pm)}|\varphi_k\rangle \tag{2.9}$$

and the Dyson equation as

$$G^{\pm} = \Omega^{(\pm)}G_0^{\pm} = G_0^{\pm}\Omega^{(\mp)\,\dagger}. \tag{2.10}$$

$|\varphi_k\rangle$ is called an asymptotical state with respect to V.[38]

Multiplying Eq. (2.5) by V and using the definition (2.4) of $T^{\pm}$, one obtains

$$V\,|\psi_k^{\pm}\rangle = T^{\pm}\,|\varphi_k\rangle. \tag{2.11}$$

This is a fundamental result for the construction of the formalism. It means that T acts on an *asymptotical state* while V acts on an *inner state* with both actions giving the same result. Inserting now Eq. (2.9) into Eq. (2.11) leads to the equivalent expression

$$T^{\pm} = V\,\Omega^{(\pm)} = \Omega^{(\mp)\,\dagger}\,V. \tag{2.12}$$

Again, this equation is of great importance for our purpose. Indeed, excitation always takes place via a potential. Consequently, *an asymptotical state with respect to V*—which is basically the kind of state obtained after the propagation of an electron within the cluster—*has to be transformed by Ω into an inner state so that the perturbation V can act upon it*.

Equation (2.12) can be transformed into

$$V^{-1} = \Omega^{(\pm)}\,T^{\pm\,-1} = T^{\pm\,-1}\,\Omega^{(\mp)\,\dagger}. \tag{2.13}$$

This quantity will appear frequently in the present theory and I will therefore write it as

$$\begin{aligned}\tilde{\Omega}^{(\pm)} &= \Omega^{(\pm)}\,T^{\pm\,-1}\\ &= T^{\pm\,-1} + G_0^{\pm}\end{aligned} \tag{2.14}$$

and call it the renormalized Møller wave operator.

As V has been supposed to be a real operator, $\tilde{\Omega}^{(\pm)}$ will also be real, which means that its matrix elements in a real basis will be real. This choice of V real is not a true limitation as most of the previous results still hold for complex potentials, as I will demonstrate it in a forthcoming article. Indeed, the Dyson equations for G, T, and Ω remain valid, and it is still possible to define $+$ and $-$ solutions with respect to the branch cut, although the latter will not be on the real axis anymore. The main difference now is that the relation between the $+$ and $-$ operators (and hence between $+$ and $-$ states) will change according to

$$A^{(+)\,\dagger}(z) = A^{(-)}(z^*) \tag{2.15}$$

instead of

$$A^{(+)\,\dagger}(z) = A^{(-)}(z) \tag{2.16}$$

for any operator A.

B. Case in which V is a superposition of potentials

Let me turn now to the case of an assembly of atoms such as a cluster. It is generally possible to write the cluster potential as a superposition of local potentials centered on the atomic sites. This is true as long as the optical potential, which accounts for the inelastic losses and has been neglected here by making the assumption that V is real, is considered as local. In this case, it has been demonstrated[39] that the general scattering expressions do not depend on the particular shape of the potential, and in particular, that they still hold true for a collection of generally shaped, space-filling potentials. But care must be taken here: when there was only one potential V, it was implicitly assumed that the origin of space was at the center of this potential. This is not the case anymore. However, it is easy to verify that all the preceding results still hold provided that any operator A_i attached to a certain atomic site i is replaced by its origin centered counterpart

$$\overline{A_i} = \mathcal{T}(\mathbf{R}_i)\,A_i\,\mathcal{T}(-\mathbf{R}_i) \tag{2.17}$$

where $\mathcal{T}(\mathbf{R}_i)$ is the translation operator and $\mathbf{R}_i$ the position of site i with respect to an arbitrary origin. The unitary translation operator is defined by[40]

$$\mathcal{T}(\mathbf{R}_i) = e^{-\mathbf{R}_i\cdot\boldsymbol{\nabla}_i} \tag{2.18}$$

and verifies

$$\begin{aligned}\mathcal{T}(\mathbf{R}_i)|\mathbf{r}\rangle &= |\mathbf{r}+\mathbf{R}_i\rangle,\\ \langle\mathbf{r}|\mathcal{T}(\mathbf{R}_i) &= \langle\mathbf{r}-\mathbf{R}_i|,\end{aligned} \tag{2.19}$$

and

$$\mathcal{T}^{\dagger}(\mathbf{R}_i) = \mathcal{T}^{-1}(\mathbf{R}_i) = \mathcal{T}(-\mathbf{R}_i). \tag{2.20}$$

With the previous equation, it is clear that Eq. (2.17) is the usual unitary transform expression for operators,[41] i.e.,

$$T[A] = T\,A\,T^{\dagger}, \tag{2.21}$$

the transform being here the translation of $\mathbf{R}_i$. $T[A]$ is the T transform of A.

Actually, Eq. (2.17) can be interpreted in two ways. As a matter of fact, the wave function $\psi(\mathbf{r})$ is constructed, in Dirac's notation, from the scalar product of a ket particle state $|\psi\rangle$ and a bra space state $\langle\mathbf{r}|$, namely, $\langle\mathbf{r}|\psi\rangle$, with $\langle\mathbf{r}|$ referred to the arbitrary origin. If $\overline{A}_{\mathrm{i}}$ is made to act upon $|\psi\rangle$, it simply means that a $|\psi\rangle$ state located in the vicinity of atom i will be translated close to the origin by $\mathcal{T}(-\mathbf{R}_i)$, and then A_i can act upon it as in the case of a single potential, and the resulting state is then transferred back near the atom i by $\mathcal{T}(\mathbf{R}_i)$. Reasoning in space, i.e., from left to right, Eq. (2.17) means now that the origin is translated to i by $\mathcal{T}(\mathbf{R}_i)$; then A_i can act and finally, the origin is transferred back to its real location by $\mathcal{T}(-\mathbf{R}_i)$. Both views are equivalent. $\overline{A_i}$ thus defined acts on states centered at the origin while A_i acts on states centered on atom i.

Equation (2.17) is an important piece in the building of the formalism. In fact, it is the operator's equivalent to the well-known addition theorems[42] used when thinking in terms of wave functions. The connection between the two is presented in Appendix A.

With this in mind, we can adapt the results of the previous subsection to the case of a collection of potentials. Keeping the definition (2.4) of $T^{\pm}$ and definition (2.7) of $\Omega^{(\pm)}$, we can partition these operators accordingly to V. As a direct consequence of the notion (2.17) of origin-centered atomic based operators, it is possible to write

$$\overline{T^{\pm}} = \sum_i \overline{\mathcal{T}_i^{(\pm)}}, \tag{2.22}$$

$$\overline{\Omega}^{(\pm)}=\sum_i \overline{\omega}_i^{(\pm)}.$$

Let me point out here that $\overline{\mathcal{T}}_i$ is not the atomic transition operator associated with site i, nor is $\overline{\omega}_i$ the Møller wave operator corresponding to site i. These atomic operators will be noted here as $\overline{T}_i$ and $\overline{\Omega}_i$, respectively.

From Eq. (2.12), we see that $\overline{\mathcal{T}}_i$ is related to $\overline{V}_i$ by

$$\overline{\mathcal{T}}_i^{(\pm)}=\overline{V}_i\,\overline{\Omega}^{(\pm)}=\overline{\Omega}^{(\mp)\,\dagger}\,\overline{V}_i, \tag{2.23}$$

where $\overline{\Omega}^{(\pm)}$ is the total Møller wave operator. Moreover, it satisfies the relation

$$\overline{\mathcal{T}}_i^{(-)\,\dagger}=\overline{\mathcal{T}}_i^{(+)}. \tag{2.24}$$

It is convenient at this stage to introduce a further partitioning of the T operator, which defines the scattering path operator,[35] by

$$\overline{\mathcal{T}}_i^{(\pm)}=\sum_j \overline{\tau}^{ji\,(\pm)}=\sum_j \overline{\tau}^{ij\,(\pm)}. \tag{2.25}$$

Clearly, the origin centered scattering path operator can be expressed as[43]

$$\overline{\tau}^{ji\,(\pm)}=\mathcal{T}(\mathbf{R}_j)\,\tau^{ji\,(\pm)}\,\mathcal{T}(-\mathbf{R}_i). \tag{2.26}$$

From the definition (2.4) of T, one can deduce that

$$\overline{\tau}^{ji\,(\pm)}=\overline{V}_i\,\delta_{ij}+\overline{V}_j\,G^{\pm}\,\overline{V}_i \tag{2.27}$$

and from Eq. (2.23) that

$$\overline{\tau}^{ji\,(\pm)}=\overline{V}_j\,\overline{\omega}_i^{(\pm)}=\overline{\omega}_j^{(\mp)\,\dagger}\,\overline{V}_i. \tag{2.28}$$

Note in particular that Eq. (2.27) implies that

$$\overline{\tau}^{ij\,(-)\,\dagger}=\overline{\tau}^{ji\,(+)}. \tag{2.29}$$

We can establish now the well-known expression of the scattering path operator as a function of the atomic T operators. If we define the atomic propagators by

$$G_i^{\pm}=G_0^{\pm}+G_0^{\pm}\,\overline{T}_i^{(\pm)}\,G_0^{\pm}, \tag{2.30}$$

it can be shown[44] in the case of two potentials that

$$G^{\pm}=G_1^{\pm}+G_1^{\pm}\,\overline{V}_2\,G^{\pm}=G_1^{\pm}+G^{\pm}\,\overline{V}_2\,G_1^{\pm}. \tag{2.31}$$

Equivalent expressions are obtained by exchanging the roles of the two potentials. The generalization to a collection of potentials is straightforward by setting $\overline{V}_1=\overline{V}_i$ and $\overline{V}_2=\Sigma_{j\neq i}\overline{V}_j$ and leads to

$$G^{\pm}=G_i^{\pm}+\sum_{j\neq i} G_i^{\pm}\,\overline{V}_j\,G^{\pm} \tag{2.32}$$

and its mirror counterpart. Making use of Eq. (2.10), multiplying by $G_0^{\pm\;-1}$ on the right-hand side and noticing from Eqs. (2.23) and (2.10) that $\overline{V}_jG^{\pm}=\overline{\mathcal{T}}_j^{(\pm)}G_0^{\pm}$, gives

$$\overline{\Omega}^{(\pm)}=\overline{\Omega}_i^{(\pm)}+\sum_{j\neq i} \overline{\Omega}_i^{(\pm)}\,G_0^{\pm}\,\overline{\mathcal{T}}_j^{(\pm)}. \tag{2.33}$$

From this expression, we can deduce

$$\overline{\omega}_i^{(\pm)}=\overline{\Omega}_j^{(\pm)}\,\delta_{ij}+\sum_{k\neq j} \overline{\Omega}_j^{(\pm)}\,G_0^{\pm}\,\overline{\tau}^{ki\,(\pm)}. \tag{2.34}$$

Now, if we multiply this equation by $\overline{V}_j$ on the left-hand side, and use Eq. (2.28), we obtain the expression for the scattering path operator as a function of the atomic transition operators

$$\overline{\tau}^{ji\,(\pm)}=\overline{T}_j^{(\pm)}\,\delta_{ij}+\sum_{k\neq j} \overline{T}_j^{(\pm)}\,G_0^{(\pm)}\,\overline{\tau}^{ki\,(\pm)}. \tag{2.35}$$

The mirror equation

$$\overline{\tau}^{ji\,(\pm)}=\overline{T}_j^{(\pm)}\,\delta_{ij}+\sum_{k\neq i} \overline{\tau}^{jk\,(\pm)}\,G_0^{(\pm)}\,\overline{T}_i^{(\pm)} \tag{2.36}$$

can be worked out in a similar way.

Iteration of any of the above equations shows that $\overline{\tau}^{ji}$ represents the set of all the terms in the Born development starting with $\overline{T}_i$ (i is then called the entrance point) and ending with $\overline{T}_j$ (j is the exit point). Therefore, it is the sum of all the scattering paths connecting i to j and containing the scattering by the two extremity potentials. As a consequence, $\overline{\tau}^{ji}$ describes completely the propagation of an electron between i and j. It will then serve as one of the building blocks. Note as well that $\overline{\tau}^{ji}$ can be considered as a photograph of the geometry of the cluster. With this in mind, the definition (2.25) and Eq. (2.23) have now a simple interpretation: $\overline{\mathcal{T}}_i^{(\pm)}$ represents all the scattering paths starting or ending at atom i. Here, the + sign indicates that the paths are followed progressively, while the − sign means that the propagation is made ‘‘backward in time.’’ $\overline{\mathcal{T}}_i$ was originally introduced by Velicky̆, Kirkpatrick, and Ehrenreich.[45]

Let me now come back to the expression (2.27) of $\overline{\tau}^{ji}$ in terms of V_i and V_j. We can multiply it by $\widetilde{\overline{\Omega}}_j^{(-)\,\dagger}$ on the left and $\widetilde{\overline{\Omega}}_i^{(+)}$ on the right, or equivalently, by $\widetilde{\overline{\Omega}}_j^{(+)}$ on the left and $\widetilde{\overline{\Omega}}_i^{(-)\,\dagger}$ on the right. Recalling, according to Eq. (2.13), that these quantities are nothing but the inverse of the potential operator, one obtains straightforwardly

$$\begin{aligned}G^{+}&=-\widetilde{\overline{\Omega}}_j^{(+)}\,\delta_{ij}+\widetilde{\overline{\Omega}}_j^{(-)\,\dagger}\,\overline{\tau}^{ji\,(+)}\,\widetilde{\overline{\Omega}}_i^{(+)}\\&=-\widetilde{\overline{\Omega}}_j^{(+)}\,\delta_{ij}+\widetilde{\overline{\Omega}}_j^{(+)}\,\overline{\tau}^{ji\,(+)}\,\widetilde{\overline{\Omega}}_i^{(-)\,\dagger}.\end{aligned} \tag{2.37}$$

This important result is the operator's equivalent to that originally derived for the Green function by Beeby[46] and generalized by Faulkner and Stocks.[47] The recovery of the latter expression is given in appendix A. With the definition (2.14) of the renormalized atomic Møller wave operator $\widetilde{\overline{\Omega}}_i^{(\pm)}$, the first of these equations corresponds exactly to the result derived by Vvendensky.[48] However, no physical interpretation of this result has been given in the literature, at least to my knowledge. The introduction of the renormalized atomic Møller wave operators provides here an elegant way

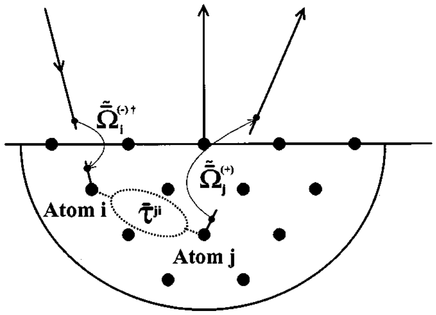

FIG. 1. Geometrical interpretation of the development of the propagator G^+ in terms of the scattering path operator $\overline{\tau}^{j\,i}$.

to interpret it. Let us consider the second equation (2.37) and suppose that i is different from j. Developing the renormalized Møller wave operators, it can be rewritten as

$$G^+ = (I + G_0^+ \overline{T_j^+})\, \overline{T_j^+}^{\;-1}\, \overline{\tau}^{ji\,(+)}\, \overline{T_i^+}^{\;-1}\, (I + \overline{T_i^+} G_0^+). \tag{2.38}$$

Now, if we suppose, as is sketched in Fig. 1, an electron incoming on a cluster represented by its asymptotic state with respect to the cluster potential, $\overline{\tilde{\Omega}}_i^{(-)\dagger}$ will transform this state into an asymptotical state with respect to potential $\overline{V}_i$ prior to the scattering by atom i. It can be viewed as a localization of the state of the incoming electron right before i. This is a direct consequence of the definition of $\overline{\tilde{\Omega}}_i^{(-)\dagger}$ which, as can be seen from Eq. (2.38), starts by propagating the state of the outer electron towards atom i before renormalizing it so that the matching condition is satisfied. Then $\overline{\tau}^{ji}$ will propagate it to j including the scattering by this latter atom, that is, transform it into an asymptotical state with respect to $\overline{V}_j$ after scattering by j. Finally, $\overline{\tilde{\Omega}}_j^{(+)}$ will transform it back into an asymptotic state outside the cluster, i.e., delocalize it from atom j. Again, this is a consequence of the construction of $\overline{\tilde{\Omega}}_j^{(+)}$, which renormalizes the state first and then propagates it elsewhere. Therefore, the atomic renormalized Møller wave operator $\overline{\tilde{\Omega}}_i$ acts as a localization, or delocalization, operator connecting an outer state to an asymptotical state with respect to the potential $\overline{V}_i$.

It is important to note at this stage that although both expressions in Eq. (2.37) are mathematically equivalent (the two renormalized Møller wave operators are equal and in practice will lead to the same wave functions), only the last one has a simple physical explanation. G^+ is known to contain all the electronic structure information of the crystal as its imaginary part is proportional to the density of states.[49] Equation (2.37) shows as well that the crystallographic information, contained in $\overline{\tau}^{ji}$, can also be easily extracted from it.

III. THE BUILDING BLOCK MODEL

In the forthcoming discussion, I will consider only the case where a core atom is involved in an excitation process. It simplifies the reasoning and still keeps the generality of the method, as all the necessary ingredients can be found in this example. More precisely, I will suppose, for the time being, that an electron undergoing an excitation on an atom labeled 0 will then travel inside the crystal towards another part that may be the vacuum.

As I developed the idea in the introductory section, at least two building blocks are necessary to construct an operator's theory of electron spectroscopy: one for the excitation of an electron and one for its propagation within a collection of scatterers. The last one is obviously related to the scattering path operator. After the excitation, the subsequent propagation can be described by

$$\overline{\mathcal{T}}_0 = \sum_j \overline{\tau}^{j0}, \tag{3.1}$$

following the interpretation of this operator given previously. I recall that the left-hand side index in the scattering path operator has been chosen to be the exit point, while the right-hand side index is the entrance point. Now, because $\overline{\mathcal{T}}_0$ consists of a Born expansion of atomic transition operators, it will act on states that are asymptotic with respect to atom 0. Let me call V_0^{ex} the perturbation responsible for the excitation. Its effect is to promote an electron originally into a bound state $|\overline{\varphi_0^b}\rangle$ of atom 0 to a continuum state $|\overline{\psi_0^{ex}}\rangle$ of the same atom. Note that the latter has to be a continuum state if propagation is considered afterwards (or prior to the excitation). $|\overline{\psi_0^{ex}}\rangle$ matches the corresponding scattering state outside the potential $\overline{V}_0$ of atom 0. $\overline{\mathcal{T}}_0$ cannot act directly upon it as $|\overline{\psi_0^{ex}}\rangle$ is not an asymptotical state with respect to $\overline{V}_0$. According to the interpretation of the Møller wave operator, $\overline{\Omega}_0^\dagger\, |\overline{\psi_0^{ex}}\rangle$ is such an asymptotical state, but it already contains the effect of $\overline{V}_0$ as does $\overline{\mathcal{T}}_0$. Therefore, the matching of the two blocks is not directly possible. However, a simple physical argument indicates that $\overline{\Omega}_0^\dagger$ and $\overline{\mathcal{T}}_0 \overline{T}_0^{-1}$ can match to form the product operator. Indeed, there is always the possibility, in quantum scattering theory, that the incoming electron does not ''feel'' the perturbing potential, in contrast to classical theory. This can be seen easily in the Lippmann-Schwinger equation (2.2). In the Møller wave operator, it is accounted for by the presence of the identity operator I. This property must survive the matching of the operators. $\overline{\mathcal{T}}_0$ can be written, following Eq. (2.35), as

$$\begin{aligned} \overline{\mathcal{T}}_0 &= \overline{\tau}^{00} + \sum_{j\neq 0} \overline{\tau}^{j0} \\ &= \overline{T}_0 + \sum_{j\neq 0} (I + \overline{T}_0 G_0^+)\, \overline{\tau}^{j0} = \overline{T}_0 + \sum_{j\neq 0} \overline{\Omega}_0^{(-)\dagger}\, \overline{\tau}^{j0}, \end{aligned} \tag{3.2}$$

and it is clear that $\overline{\mathcal{T}}_0 \overline{T}_0^{-1}$ will satisfy this property.

This can be demonstrated more formally. Let us consider now an electron initially in a state $|\overline{\varphi_{in}}\rangle$ incident upon a cluster. In the abscence of the excitation, this electron will be, after scattering by atom 0, in the state $\overline{\mathcal{T}}_0 |\overline{\varphi_{in}}\rangle$. If we turn on the perturbation V_0^{ex}, the electron will undergo a transition on atom 0 and, following the argument given before, should be, after the whole process, in the state

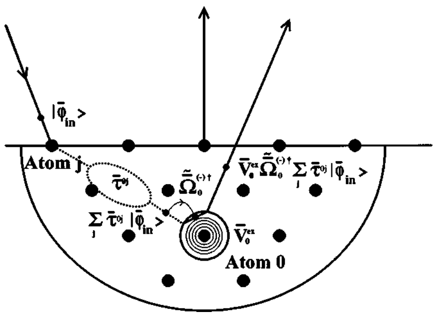

FIG. 2. Pictorial representation of the matching of the two building blocks.

$$(\overline{V}_0+\overline{V}_0^{ex})\,\overline{\Omega}_0\,\overline{T}_0^{-1}\,\overline{\mathcal{T}}_0\,|\overline{\varphi}_{in}\rangle, \tag{3.3}$$

as the potential the electron ''feels'' on atom 0 is $\overline{V}_0+\overline{V}_0^{ex}$. In practice, $\overline{V}_0$ is omitted because it cannot induce the transition. Here, however, we want to check the validity of Eq. (3.3), and hence we must make $\overline{V}_0^{ex}$ tend continuously towards zero and see if we recover $\overline{\mathcal{T}}_0\,|\overline{\varphi}_{in}\rangle$. In this case, the transition will also tend to zero, and therefore, $\overline{V}_0$ must be kept in Eq. (3.3). As, according to Eq. (2.12)

$$\overline{V}_0\,\overline{\Omega}_0=\overline{T}_0, \tag{3.4}$$

we see immediately that

$$\lim_{\overline{V}_0^{ex}\to 0}\ (\overline{V}_0+\overline{V}_0^{ex})\,\overline{\Omega}_0\,\overline{T}_0^{-1}\,\overline{\mathcal{T}}_0\,|\overline{\varphi}_{in}\rangle=\overline{\mathcal{T}}_0\,|\overline{\varphi}_{in}\rangle, \tag{3.5}$$

which demonstrates the validity of Eq. (3.3). The matching condition is illustrated in Fig. 2.

Now we have the two matching bricks together and we must choose where to draw the frontier between them. $\overline{V}_0^{ex}\,\overline{\Omega}_0$ and $\overline{\mathcal{T}}_0$ are obviously blocks, but a decision has to be made about the renormalization operator $\overline{T}_0^{-1}$ that can equally well be attached to any of the two blocks. To be consistent with the existing literature, I will include it in the excitation block. Therefore, the two building blocks become $\overline{V}_0^{ex}\,\tilde{\overline{\Omega}}_0$ and $\overline{\mathcal{T}}_0$ with $\tilde{\overline{\Omega}}_0$ being the renormalized Møller wave operator. In the case of certain electron spectroscopies such as XAS or EELS, the sub-block $\overline{\tau}^{00}$ of $\overline{\mathcal{T}}_0$ will also be needed. It describes closed-loop propagation from and to atom 0.

IV. EXAMPLE: CORE PHOTOELECTRON DIFFRACTION

As an example to illustrate the use of this formalism, let me take the case of core photoelectron diffraction. A more thorough derivation of the cross sections of the most popular electron spectroscopies, including those involving two electrons and delocalized levels, will be given elsewhere.[50]

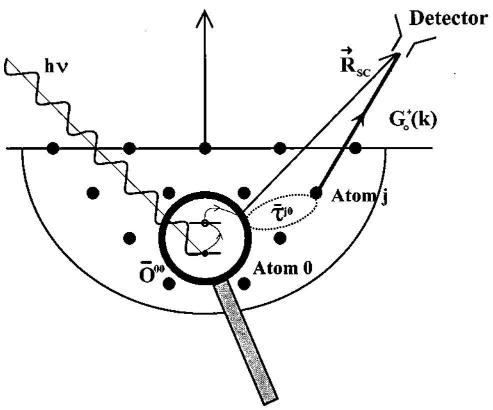

FIG. 3. Schematic of a photoelectron diffraction experiment. Each part has been associated with its corresponding operator.

In a PhD experiment, a beam of monochromatic light incident upon a sample excites core electrons that can escape this sample and reach a detector positioned along a given direction. By carefully choosing the energy of the electrons entering the detector, it is possible to select only those originating from a certain core level on a particular chemical species. This physical process is illustrated in Fig. 3 where the optical excitation operator responsible for the promotion of the core electron has been labeled $\overline{\mathcal{O}}^{00}$. It is obviously related to the interaction Hamiltonian $(e/m)\,\mathbf{A}\cdot\mathbf{p}$ (the Coulomb gauge is used here), where $\mathbf{A}$ is the vector potential of the electromagnetic field and $\mathbf{p}$ the momentum of the electron. In reduced units, the excitation potential becomes

$$\overline{V}_0^{ex}=\frac{2e}{\hbar^2}\mathcal{T}(\mathbf{R}_0)\,\mathbf{A}\cdot\mathbf{p}\,\mathcal{T}(-\mathbf{R}_0)=\frac{2e}{\hbar^2}\,\overline{(\mathbf{A}\cdot\mathbf{p})}_0. \tag{4.1}$$

As the process here is the time reversal of the process used to establish Eq. (3.3), the optical excitation operator is

$$\overline{\mathcal{O}}^{00}=\frac{2e}{\hbar^2}A\,\tilde{\overline{\Omega}}_0^{(-)\dagger}\,\overline{(\hat{\boldsymbol{\epsilon}}\cdot\mathbf{p})}_0. \tag{4.2}$$

A is the modulus of the potential vector and $\hat{\boldsymbol{\epsilon}}$ its unit vector. With the initial state $|i\rangle$ and the continuum state being eigenstates of the same Hamiltonian, one can use the well-known result[51]

$$\hat{\boldsymbol{\epsilon}}\cdot\mathbf{p}=im\omega_q\,\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}, \tag{4.3}$$

where ω_q is the angular frequency of the incident photon, to transform $\overline{\mathcal{O}}^{00}$ into

$$\overline{\mathcal{O}}^{00}=i\,\frac{2me}{\hbar^2}A\,\omega_q\,\tilde{\overline{\Omega}}_0^{(-)\dagger}\,\overline{(\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r})}_0. \tag{4.4}$$

Then, using the two building blocks previously defined, the wave function of the electron reaching the analyzer located at $\mathbf{R}$ from the origin can be written as

$$\langle\mathbf{R}|\psi\rangle=\langle\mathbf{R}|G_0^+\,\overline{\mathcal{T}}_0^{(-)\dagger}\,\overline{\mathcal{O}}^{00}\,\mathcal{T}(\mathbf{R}_0)\,|i\rangle. \tag{4.5}$$

If $|i\rangle$ is the initial state of the excited electron, with respect to atom 0, then $\mathcal{T}(\mathbf{R}_0)\,|i\rangle$ is the corresponding state referred to the origin of the coordinates with $\mathbf{R}_0$ being the position of atom 0. G_0^+ describes the propagation of the electron from the last scatterer encountered to the analyzer, and $\overline{\mathcal{T}}_0^{(-)\dagger}\equiv\overline{\mathcal{T}}_0^{(+)}$ the propagation of this electron from atom 0 to the last scatterer within the cluster.

As $\mathbf{R}$ is large compared to interatomic distances, one can write

$$\langle \mathbf{R}|G_0^+ = -\sqrt{\frac{\pi}{2}}\,\frac{e^{ikR}}{R}\langle \mathbf{k}|, \tag{4.6}$$

with the definition $\mathbf{k}=k\hat{\mathbf{R}}$. This result is obtained by developing the Green function $\langle \mathbf{R}|G_0^+|\mathbf{r}\rangle$ to the first order in r/R whatever the value of r.

The cross section is defined by

$$\frac{d\sigma}{d\Omega} = R^2 \frac{d\phi_{sc}}{d\phi_{in}}, \tag{4.7}$$

where $d\phi_{in}$ and $d\phi_{sc}$ are, respectively, the incoming and scattered flux. The incoming flux of photons can be shown to be[52]

$$d\phi_{in} = \frac{N_q c}{(2\pi)^3}. \tag{4.8}$$

Here, N_q is the number of photons of energy $\hbar\omega_q$ contained in the incoming beam and c the speed of the light. With a normalization to a δ "function," the modulus of the potential vector is[53]

$$A = \frac{1}{(2\pi)^{3/2}}\left(\frac{N_q \hbar}{2\epsilon_0 \omega_q}\right)^{1/2}, \tag{4.9}$$

where ϵ_0 is the dielectric constant of the vacuum.

The scattered flux through a unit surface positioned at $\mathbf{R}$ is given by

$$d\phi_{sc}(\mathrm{R}) = \frac{\hbar}{m}\,\mathrm{Im}\left[\psi^*(\mathbf{R})\,\frac{\partial\psi(\mathbf{r})}{\partial r}\bigg|_{r=R}\right], \tag{4.10}$$

where Im indicates the imaginary part. In case of a spherical wave $U(\hat{\mathbf{R}})\,e^{ikR}/R$, the scattered flux becomes

$$d\phi_{sc} = \frac{\hbar k}{m}\,\frac{|U(\hat{\mathbf{R}})|^2}{R}. \tag{4.11}$$

Combining these results with expression (4.5) of the wave function gives the photoelectron diffraction cross section independent of the basis,

$$\frac{d\sigma}{d\hat{\mathbf{k}}} = 8\pi^2\,\alpha\,k\,\frac{m\omega_q}{\hbar}\sum_0 \sum_{m_{l_i}} \left|\langle \mathbf{k}|\,\overline{\mathcal{T}}_0^{(-)\,\dagger}\,\tilde{\tilde{\Omega}}_0^{(-)\dagger}\,(\overline{\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}})_0 \times \mathcal{T}(\mathbf{R}_0)\,|i\rangle\right|^2 \tag{4.12}$$

or, equivalently

$$\frac{d\sigma}{d\hat{\mathbf{k}}} = 8\pi^2\,\alpha\,k\,\frac{m\omega_q}{\hbar}\sum_0 \sum_{m_{l_i}} \left|\sum_{\mathrm{j}} \langle \mathbf{k}|\,\mathcal{T}(\mathbf{R}_j) \times \tau^{j\,0}\,\tilde{\Omega}_0^{(-)\dagger}\,(\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r})\,|i\rangle\right|^2, \tag{4.13}$$

$\alpha=e^2/4\pi\epsilon_0\hbar c$ is the fine-structure constant and the summations are over the different absorbers 0 and m_{l_i}, the angular momentum index of the core initial state $|i\rangle\equiv|n_i,l_i,m_{l_i}\rangle$. The final result has been multiplied by 2 to take the spin into account. These expressions further simplify if the cluster is translationally invariant as shown in Appendix B.

Extension of Eq. (4.12) to one of the spin-orbit components $|n_i,j_i,m_{j_i}\rangle$, if they can be resolved, is trivial and gives

$$\frac{d\sigma}{d\hat{\mathbf{k}}} = 4\pi^2\,\alpha\,k\,\frac{m\omega_q}{\hbar}\sum_0 \sum_{m_{j_i},m_{s_k}} \left|\langle \tfrac{1}{2},m_{s_k}| \otimes \langle \mathbf{k}|\,\overline{\mathcal{T}}_{0\,\otimes}^{(-)\,\dagger}\,\tilde{\tilde{\Omega}}_{0\,\otimes}^{(-)\dagger}\,(\overline{\hat{\boldsymbol{\epsilon}}\cdot\mathbf{R}})_{0\,\otimes}\,\mathcal{T}(\mathbf{R}_0)\,|n_i,j_i,m_{j_i}\rangle\right|^2. \tag{4.14}$$

The summation over the spin of the outgoing electron comes from the fact that the detector has been assumed not to be able to differentiate spin orientations, in which case,

$$\frac{d\sigma}{d\hat{\mathbf{k}}} = \frac{d\sigma}{d\hat{\mathbf{k}}}(+) + \frac{d\sigma}{d\hat{\mathbf{k}}}(-). \tag{4.15}$$

The index $\otimes$ indicates that the operator acts in the product space. If the spin dependance of the potential is neglected, the product operators $\overline{A}_{i\,\otimes}$ reduce to

$$\overline{A}_{i\,\otimes} = \overline{A}_i \otimes I_S, \tag{4.16}$$

where I_S is the identity in the spin space.

Equations (4.12) and (4.14) are valid whatever the shape of the atomic potentials, as the only assumption that was made about them is that their superposition coincides with the crystal potential. It is interesting to see now how the usual spherical wave cluster result[30] can be recovered from the general result (4.12).

Obviously, the way to introduce the basis into the previous expressions is through the closure relation of the selected basis. Therefore, it is preferable to work with the orthonormal basis so that this closure relation equals the identity of the Hilbert space of the electron, that is to say in the case of spherical waves

$$\int \sum_L |kL\rangle\,\langle kL|\,dk = I, \tag{4.17}$$

where L stands for the two angular momentum indices (l,m). Consequently, I will define free spherical waves by

$$\langle \mathbf{r}|kL\rangle = k\,\sqrt{\frac{2}{\pi}}\,i^l\,j_l(kr)\,Y_L(\hat{\mathbf{r}}). \tag{4.18}$$

Here $j_l(kr)$ is the spherical Bessel function of order l. The spherical waves in the literature are, most of the time, not normalized. In general, they are chosen so that the matrix elements of the transition operator T reduce to the simple form $t_l=(\sin\delta_l)\,e^{i\delta_l}$, where δ_l is the lth phase shift of the potential V taken, in this case, to be spherically symmetric. Here, the matrix elements of T are, for a spherically symmetric potential,

$$\langle k_2 L_2|T^+|k_1 L_1\rangle = -\frac{2k}{\pi}(\sin\delta_{l_1})\,e^{i\delta_{l_1}}\,\delta_{L_1 L_2}\,\delta(k_2-k_1) \times \delta(k_1-k), \tag{4.19}$$

where k is the wave number associated with T^{+}. The Dirac δ ''functions'' in this expression ensure the conservation of energy throughout the whole scattering process. The use of normalized plane waves, i.e.,

$$\langle\mathbf{r}|\mathbf{K}\rangle=\frac{1}{(2\pi)^{3/2}}e^{i\mathbf{K}\cdot\mathbf{r}} \tag{4.20}$$

imposes the following relation under the change of the basis:

$$\langle\mathbf{K}|kL\rangle=\frac{1}{k}Y_{L}(\hat{\mathbf{K}})\ \delta(k-K). \tag{4.21}$$

Introducing Eqs. (2.25) in Eq. (4.12) and expressing the origin-centered atomic operators in terms of their atomic-centered counterparts according to Eq. (2.17) immediately leads to

$$\frac{d\sigma}{d\hat{\mathbf{k}}}=8\pi^{2}\,\alpha\,k\,\frac{m\omega_{q}}{\hbar}\sum_{0}\ \sum_{m_i}\left|\sum_{j}\ e^{-i\mathbf{k}\cdot\mathbf{R}_j}\right.$$
$$\left.\times\langle\mathbf{k}|\ \tau^{j0}\,\tilde{\Omega}_{0}^{(-)\dagger}\,\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}\,|i\rangle\right|^{2}. \tag{4.22}$$

The insertion of the closure relation of the basis $\{|k_0L_0\rangle\}$ and $\{|k_jL_j\rangle\}$ centered, respectively, on atom 0 and atom j allows the direct recovery of the usual equation[30]

$$\frac{d\sigma}{d\hat{\mathbf{k}}}=8\pi^{2}\,\alpha\,\frac{m\omega_{q}}{\hbar k}\sum_{0}\ \sum_{m_{l_i}}\left|\sum_{L_0}\ M^{00}_{L_0L_i}\right.$$
$$\left.\times\sum_{j,L_j}\ \tau^{j0}_{L_jL_0}\,Y_{L_j}(\hat{\mathbf{k}})\,e^{-i\mathbf{k}\cdot\mathbf{R}_j}\right|^{2}, \tag{4.23}$$

with the matrix elements

$$M^{00}_{L_0L_i}=\langle \mathrm{k}_0L_0|\tilde{\Omega}_0^{(-)\dagger}\,\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}|i\rangle. \tag{4.24}$$

This is the starting point of all spherical-wave cluster theories that can be found in the literature. Note that with the normalization (4.18), $\langle\mathbf{r}|\tilde{\Omega}_0^{(-)}|k_0L_0\rangle$ is the continuum state that matches smoothly to

$$-\sqrt{\frac{\pi}{2}}t_{l_0}^{-1}\,i^{l_0}[j_{l_0}(kr)+it_{l_0}h^{(1)}_{l_0}(kr)]\,Y_{L_0}(\hat{\mathbf{r}})\ \delta(k_0-k)$$
$$=-\sqrt{\frac{\pi}{2}}\tilde{R}_L^{(\pm)}(\mathbf{r})\ \delta(k_0-k)$$

across the limit of the bounding sphere of the potential. Note as well that due to the use of normalized free-electron wave functions, $\tau^{j0}_{L_jL_0}$ differs by a factor $-2k/\pi$ from the expression found in the literature. Taking these two differences into account will change the coefficient before the modulus in the cross section into $8\pi\alpha\hbar\omega_q k(2m/\hbar^2)$. The term $(2m/\hbar^2)$ here comes from the fact that reduced units have been used to establish the cross section. When multiplied by the δ function that is omitted here and that accounts for the k^2 conservation, it will eventually give $\delta(\hbar\omega_q-E_k-E_i)$ with E_i being the binding energy of the core electron promoted to a scattering state with kinetic energy E_k.

V. CONCLUSION

I have presented in this paper a very general framework to build the multiple scattering theory of electron spectroscopy. This formalism does not make any assumption concerning the choice of the basis used to expand the wave function of the electron. As such, it is a generalization of existing theories. Indeed, both spherical-wave cluster theories and plane-wave slab approaches are particular cases of it. However, in the latter case, a partitioning of the scattering path operator (as it is done in the layer KKR theory[23]) has to be carried out prior to the use of the plane-wave basis. Work on the different modes of partitioning is currently in progress.

The first advantage of the present formalism lies in the fact that any basis of the Hilbert space can be used—it is not limited to the standard basis. Therefore, the choice of the basis can be made to minimize the computational effort. In particular, a new basis remains to be found in the medium-energy range (around 1 keV). This will be the subject of a forthcoming study.

Its second advantage is that, when dealing with operators that have a well-defined physical meaning, the equations become more transparent. As a consequence, this formalism can serve as a graphical interface between experiments and calculations, as each part of a sketch of the experimental process can be associated with a well-identified building block composed of one or two operators. Hence, the derivation of the cross section of a given electron spectroscopy reduces to the combining of these building blocks according to the sketch of the experiment. This has been illustrated in the case of core photoelectron diffraction. The basis-independent theory of the other major electron spectroscopy techniques will be the subject of a forthcoming paper. Finally, the last advantage of this general framework is to replace the fastidious addition theorems by the more friendly translation operator.

ACKNOWLEDGMENT

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APPENDIX A: THE RECOVERY OF THE ADDITION THEOREMS AND OF THE FAULKNER-STOCKS RESULT

In this appendix, I want to show how well-known results such as the addition theorems for spherical waves,[42] or the Faulkner-Stocks formula,[47] can be naturally deduced from the translation operator's approach. Let me point out first that the translation operator for any translation vector $\mathbf{R}_i$ commutes with the propagator G_0^{+}, i.e.,

$$[G_0^{+},\mathcal{T}(\mathbf{R}_i)]=0. \tag{A1}$$

This important property will prove most useful here. I will use throughout this appendix normalized spherical waves as defined by Eq. (4.18). Before proceeding further, we need to find the scattered wave functions $\langle\mathbf{r}|G_0^{+}(k)|k_1L_1\rangle$. Recalling that, by definition of $G_0^{+}(k)$,

$$G_0^{+}(k)\,|\mathbf{K}\rangle=\lim_{\epsilon\rightarrow 0^{+}}\frac{|\mathbf{K}\rangle}{k^2-K^2+i\epsilon}, \tag{A2}$$

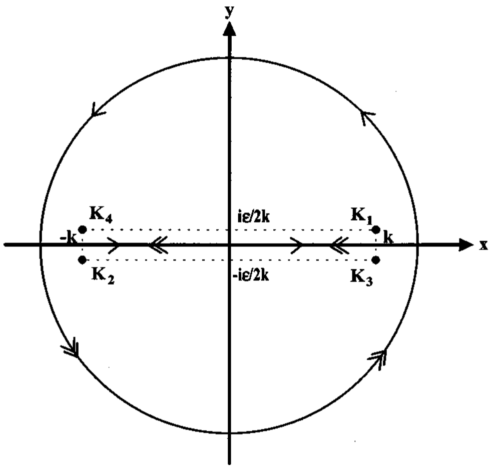

FIG. 4. Integration contour for the calculation of $\alpha(\epsilon)$ and $\beta(\epsilon)$. K_1 and K_2 correspond to $\alpha(\epsilon)$ with the upper single arrowed contour while K_3 and K_4 with the lower double arrowed contour correspond to $\beta(\epsilon)$.

the insertion of the closure relation of the plane-wave basis into the definition of the scattered wave function immediately leads to

$$\langle \mathbf{r}|G_0^+(k)|k_1L_1\rangle = \sqrt{\frac{2}{\pi}}\, i^{l_1}\, Y_{L_1}(\hat{\mathbf{r}}) \lim_{\epsilon\to 0^+} \times \int_0^{+\infty} \frac{K\, j_{l_1}(Kr)\;\delta(k_1-K)}{k^2-K^2+i\epsilon}\, dK. \tag{A3}$$

Owing to the δ function, the integral, hereafter named $I(\epsilon)$, can be extended to $-\infty$. If we decompose the spherical Bessel function according to

$$j_{l_1}(z) = \frac{1}{2}\left[h_{l_1}^{(1)}(z) + h_{l_1}^{(1)*}(z)\right]. \tag{A4}$$

$I(\epsilon)$ is transformed into

$$I(\epsilon) = \frac{1}{2}\left[\alpha(\epsilon) + \beta(\epsilon)\right] \tag{A5}$$

with

$$\alpha(\epsilon) = \int_{-\infty}^{+\infty} \frac{K\, h_{l_1}^{(1)}(Kr)\;\delta(k_1-K)}{k^2-K^2+i\epsilon}\, dK, \tag{A6}$$

$$\beta(\epsilon) = \int_{-\infty}^{+\infty} \frac{K\, h_{l_1}^{(1)*}(Kr)\;\delta(k_1-K)}{k^2-K^2+i\epsilon}\, dK = \alpha^*(-\epsilon).$$

These two integrals can be calculated by using a classical contour integration as shown in Fig. 4 combined with the residue theorem.[54] Here, $\alpha(\epsilon)$ is computed with the single arrowed contour and poles K_1 and K_2, while the calculation of $\beta(\epsilon)$ makes use of the double arrowed contour with K_3 and K_4. This calculation eventually leads to

$$\alpha(0^+) = -i\pi\, h_{l_1}^{(1)}(kr)\;\delta(k_1-k), \tag{A7}$$

$$\beta(0^+) = -i\pi\, h_{l_1}^{(1)*}(-kr)\;\delta(k_1+k),$$

k_1 and k being positive real numbers, $\beta(0^+)$ is zero and hence

$$\langle \mathbf{r}|G_0^+(k)|k_1L_1\rangle = -i\sqrt{\frac{\pi}{2}}\, i^{l_1}\, h_{l_1}^{(1)}(kr)\; Y_{L_1}(\hat{\mathbf{r}})\;\delta(k_1-k). \tag{A8}$$

We need now to consider the separable representation of the Green function. As found in any textbook,[36] it is written as

$$\langle \mathbf{r}'|G_0^+(k)|\mathbf{r}\rangle = -ik\sum_L\; j_l(kr_<)\; h_l^{(1)}(kr_>)\; Y_L(\hat{\mathbf{r}}')\; Y_L^*(\hat{\mathbf{r}}), \tag{A9}$$

where $r_<$ ($r_>$) designates the smaller (larger) of r and r'. It is necessary for convergence that $r_<$ is the argument of the spherical Bessel function. With Eqs. (4.18) and (A8), its demonstration becomes trivial by inserting the closure relation of the spherical-wave basis in $\langle \mathbf{r}|G_0^+(k)|\mathbf{r}'\rangle$. The only knowledge we need from the standard proof is where to insert this closure relation. Clearly, we can accept as a general rule that when dealing with free-electron propagators and space vectors, the closure relation must be inserted between G_0^+ and the smaller of the space vectors.

Now, starting from a scattered wave centered on atom i, we can write, if $\mathbf{r}_i = \mathbf{r} - \mathbf{R}_{0i}$ ($\mathbf{R}_{0i}$ is the vector connecting 0 to j) is a position referred to this atom,

$$\begin{aligned}\langle \mathbf{r}_i|G_0^+(k)|L_i\rangle &= \langle \mathbf{r}_j + \mathbf{r}_i - \mathbf{r}_j|G_0^+(k)|L_i\rangle\\ &= \langle \mathbf{r}_j + \mathbf{R}_{ij}|G_0^+(k)|L_i\rangle\\ &= \langle \mathbf{r}_j|\mathcal{T}(-\mathbf{R}_{ij})\; G_0^+(k)|L_i\rangle\\ &= \langle \mathbf{r}_j|G_0^+(k)\;\mathcal{T}(-\mathbf{R}_{ij})|L_i\rangle,\end{aligned} \tag{A10}$$

with $\mathbf{R}_{ij} = \mathbf{r}_i - \mathbf{r}_j = \mathbf{R}_{0j} - \mathbf{R}_{0i}$ and using the fact that G_0^+ commutes with the translation operator. According to the above-mentioned general rule, we deduce

$$\begin{aligned}\langle \mathbf{r}_i|G_0^+(k)|L_i\rangle &= \sum_{L_j}\;\langle \mathbf{r}_j|L_j\rangle\,\langle L_j|\mathcal{T}(-\mathbf{R}_{ij})\; G_0^+(k)|L_i\rangle\\ &\qquad \text{if}\;\; R_{ij} > r_j\\ &= \sum_{L_j}\;\langle \mathbf{r}_j|G_0^+(k)|L_j\rangle\,\langle L_j|\mathcal{T}(-\mathbf{R}_{ij})|L_i\rangle\\ &\qquad \text{if}\;\; R_{ij} < r_j.\end{aligned} \tag{A11}$$

Here, I have suppressed the integral in the closure relation because it disappears with the δ contained either in $\langle \mathbf{r}_j|G_0^+(k)|k_jL_j\rangle$ or in $\langle k_jL_j|\mathcal{T}(-\mathbf{R}_{ij})G_0^+(k)|k_iL_i\rangle$.

The matrix elements of the translation operator and of the propagator can be easily calculated and their value is

$$T^{j\,i}_{L_jL_i}=\langle L_j|\mathcal{T}(-\mathbf{R}_{ij})|L_i\rangle$$

$$=4\pi\sum_{L} i^l\, j_l(kR_{ij})\, Y_L(\hat{\mathbf{R}}_{ij})\, G(L_jL|L_i), \qquad \text{(A12)}$$

$$G^{j\,i}_{L_jL_i}=\langle L_j|\mathcal{T}(-\mathbf{R}_{ij})G_0^+|L_i\rangle$$

$$=-\frac{2i\pi^2}{k}\sum_{L} i^l\, h_l^{(1)}(kR_{ij})\, Y_L(\hat{\mathbf{R}}_{ij})\, G(L_jL|L_i),$$

where $G(L_jL|L_i)$ is a Gaunt coefficient.[55] The replacement of these matrix elements by their value in Eq. (A11) leads to the addition theorems derived by Danos and Maximon.[42]

In addition, this formalism greatly simplifies the development of the Green function around two centers which is a central issue in multiple scattering theory. Indeed, if we define again $\mathbf{r}_i=\mathbf{r}-\mathbf{R}_{0i}$ where $\mathbf{R}_{0i}$ is the position of site i with respect to the origin 0,

$$\langle\mathbf{r}|G_0^+(k)|\mathbf{r}'\rangle=\langle\mathbf{r}_i+\mathbf{R}_{0i}|G_0^+(k)|\mathbf{r}'_j+\mathbf{R}_{0j}\rangle$$

$$=\langle\mathbf{r}_i|\mathcal{T}(-\mathbf{R}_{0i})\, G_0^+(k)|\mathbf{r}'_j+\mathbf{R}_{0j}\rangle$$

$$=\langle\mathbf{r}_i|G_0^+(k)|\mathbf{r}'_j+\mathbf{R}_{ij}\rangle$$

$$=\sum_{L_i}\langle\mathbf{r}_i|L_i\rangle\,\langle L_i|G_0^+(k)|\mathbf{r}'_j+\mathbf{R}_{ij}\rangle$$

$$\text{if}\ \ r_i<|\mathbf{r}'_j+\mathbf{R}_{ij}|$$

$$=\sum_{L_i}\langle\mathbf{r}_i|L_i\rangle\,\langle L_i|\mathcal{T}(-\mathbf{R}_{ij})\, G_0^+(k)|\mathbf{r}'_j\rangle$$

$$=\sum_{L_i,L_j}\langle\mathbf{r}_i|L_i\rangle\, G^{i\,j}_{L_iL_j}\,\langle L_j|\mathbf{r}'_j\rangle$$

$$\text{if}\ \ r'_j<R_{ij}, \qquad \text{(A13)}$$

which corresponds to the classical result.[56] Similarly, the Faulkner-Stocks expansion of the Green function can be established easily. Indeed, we have, for example, in the case where $\mathbf{r}$ and $\mathbf{r}'$ are inside cells i and j respectively,

$$\langle\mathbf{r}'|G^+(k)|\mathbf{r}\rangle=\langle\mathbf{r}'|[-\overline{\tilde{\Omega}}_i^{(+)}\,\delta_{ij}+\overline{\tilde{\Omega}}_j^{(+)}\,\overline{\tau}^{ji\,(+)}\,\overline{\tilde{\Omega}}_i^{(-)\,\dagger}]|\mathbf{r}\rangle$$

$$=-\langle\mathbf{r}'_i|\tilde{\Omega}_i^{(+)}|\mathbf{r}_i\rangle\,\delta_{ij}$$

$$+\langle\mathbf{r}'_j|\tilde{\Omega}_j^{(+)}\,\tau^{ji\,(+)}\,\tilde{\Omega}_i^{(-)\,\dagger}|\mathbf{r}_i\rangle. \qquad \text{(A14)}$$

Here, it can be shown that, to be consistent with the converging expansion (A9) of the free-electron Green function, the closure relation has to be inserted between $\tilde{\Omega}$ and the *larger* of $\mathbf{r}_i$ and $\mathbf{r}'_i$ in the first term in the right-hand side of Eq. (A14). This eventually leads to the Faulkner-Stocks expansion

$$\langle\mathbf{r}'|G^+(k)|\mathbf{r}\rangle=k\sum_{L_i}\tilde{\mathcal{R}}^{i\,(+)}_{L_i}(\mathbf{r}_{i\,<})\,\mathcal{J}^*_{L_i}(\mathbf{r}_{i\,>})\,\delta_{ij}$$

$$+\frac{\pi}{2}\sum_{L_i,L_j}\tilde{\mathcal{R}}^{i\,(+)}_{L_i}(\mathbf{r}_i)\,\tau^{ij}_{L_iL_j}\,\tilde{\mathcal{R}}^{j\,(-)}_{L_j}{}^*(\mathbf{r}_j) \qquad \text{(A15)}$$

with the convention

$$\langle\mathbf{r}|\tilde{\Omega}_i^{(\pm)}|L\rangle=-\sqrt{\frac{\pi}{2}}\,\tilde{\mathcal{R}}^{i\,(\pm)}_{L}(\mathbf{r})=-\sqrt{\frac{\pi}{2}}\,t_l^{i\,-1}\,\mathcal{R}^{i\,(\pm)}_{L}(\mathbf{r}), \qquad \text{(A16)}$$

with $\mathcal{R}^{(+)}_L(\mathbf{r})$ matching to $J_L(\mathbf{r})+it_lH^+_L(\mathbf{r})$ and $\mathcal{J}_L(\mathbf{r})$ to $J_L(\mathbf{r})$ outside the bounding sphere. Here, $F_L(\mathbf{r})=i^lf_l(kr)Y_L(\hat{\mathbf{r}})$ where f_l is any of the spherical Bessel functions.

APPENDIX B: CASE OF A TRANSLATIONALLY INVARIANT CLUSTER

Let me suppose that $\mathbf{R}_n-\mathbf{R}_0$ is a translation that leaves the crystal unchanged. Here, n designates another absorber situated at $\mathbf{R}_n$ from the origin. Clearly, for any atom j and its $\mathcal{T}(\mathbf{R}_n-\mathbf{R}_0)$-transformed i, the scattering path operator must satisfy

$$\tau^{i\,n}=\tau^{j\,0} \qquad \text{(B1)}$$

and hence

$$\mathcal{T}_n=\mathcal{T}_0. \qquad \text{(B2)}$$

As a consequence,

$$\mathcal{T}(\mathbf{R}_i)\,\tau^{i\,n}=\mathcal{T}(\mathbf{R}_i)\,\tau^{j\,0}$$

$$=\mathcal{T}(\mathbf{R}_i-\mathbf{R}_j)\,\mathcal{T}(\mathbf{R}_j)\,\tau^{j\,0}$$

$$=\mathcal{T}(\mathbf{R}_n-\mathbf{R}_0)\,\mathcal{T}(\mathbf{R}_j)\,\tau^{j\,0}. \qquad \text{(B3)}$$

The cross section corresponding to absorber n can be rewritten as

$$\left(\frac{d\sigma}{d\hat{\mathbf{k}}}\right)_n=8\pi^2\,\alpha\,k\,\frac{m\,\omega_q}{\hbar}\sum_{m_{l_i}}\left|e^{-i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_0)}\right.$$

$$\left.\times\sum_j\langle\mathbf{k}|\,\mathcal{T}(\mathbf{R}_j)\,\tau^{j\,0}\,\tilde{\Omega}_0^{(-)\dagger}\,(\cdot\mathbf{r})\,|i\rangle\right|^2$$

$$=\left(\frac{d\sigma}{d\hat{\mathbf{k}}}\right)_0, \qquad \text{(B4)}$$

where use has been made of the relation

$$\langle\mathbf{k}|\mathcal{T}(\mathbf{a})=e^{-i\mathbf{k}\cdot\mathbf{a}}\langle\mathbf{k}|. \qquad \text{(B5)}$$

Accordingly, the total cross section becomes

$$\frac{d\sigma}{d\hat{\mathbf{k}}}=8\pi^2\,\alpha\,k\,\frac{m\,\omega_q}{\hbar}\sum_p\sum_{0_p}D_{0_p}\sum_{m_{l_i}}\left|\sum_j\langle\mathbf{k}|\,\mathcal{T}(\mathbf{R}_j)\right.$$

$$\left.\times\,\tau^{j\,0_p}\,\tilde{\Omega}_{0_p}^{(-)\dagger}\,(\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r})\,|i\rangle\right|^2. \qquad \text{(B6)}$$

While in Eq. (4.13) the summation was over *all* the absorbing atoms in the cluster, here it reduces to the inequivalent absorbers 0_p of plane p. This considerably diminishes the amount of calculations that have to be done. D_{0_p} is the density of absorbers of type 0_p in the plane p.

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