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A UNITARY VIEW OF THE PARTITION TECHNIQUE BASED ON THE SCATTERING THEORY

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Abstract. We propose here a unitary view of partitioning based on scattering theory. The theory we develop allows to decompose a complex problem into a certain number of independent subproblems and reconstruct the full solution of the original problem from the knowledge of the solutions of the various subproblems. This decomposition, known generally as a partition, is chosen so that the solutions of the subproblems are much easier to obtain, either analytically or numerically.

Key words: scattering theory, partition, LEED algorithm, KKR algorithm.

1. INTRODUCTION

Partitioning is an essential tool in physics that is often used as a numerical trick to speed up computing rather than as the true solving method it is. We propose here to derive its theory by considering it as a general tool which can be used to solve complex problems. Partitioning consists in dividing a complicated problem into smaller, independent, easier to solve subproblems and reconstructing the solution of the initial problem from the knowledge of the solutions of the subproblems and the connections between them. This kind of idea can obviously be applied to almost any kind of problem.

Our approach will be based on a scattering theoretic view. This is not however a strong limitation to the generality of our purposes as scattering theory is not limited to potential scattering as often considered. Indeed, as discussed by Akhiezer and Glazman [1], almost any system that can be described by a

characteristic operator A could, in principle, be treated within the scattering theory framework. Let us suppose that this system is described at a given moment (the initial state for instance) by the eigenequation $A_o|a_o\rangle = a_o|a_o\rangle$ and at another moment by $A|a\rangle = a|a\rangle$. Then, whenever the change in the system $(A - A_o)$ is bounded (it needs not be a perturbation as such), it is possible to define resolvent operators by $R_A(z) = (z - A)^{-1}$ and $R_{A_o}(z) = (z - A_o)^{-1}$. It we assume that the system described by A_o is fully known and that we are trying to characterize its final state represented by A, then $A = A_o + (A - A_o)$ can be associated to a Dyson-type of equation for R_A and a Lippmann-Schwinger equation for $|a\rangle$ that will allow the calculation of these quantities in terms of the known quantities R_{A_o} and $|a_o\rangle$. As a consequence, all the tools of scattering theory (transition operators, wave operators, ...) can be used to solve the problem.

Section 3 which is the core of this article will be devoted to the recovery of all particular results we have been able to find in the literature, thereby showing that they can be considered as particular cases of our general theory. We have obviously not explored the whole corpus of physics literature but have restricted ourselves to our own research area. This is why all the particular cases belong either to the theory of electron spectroscopies or to that of the electronic structure of materials. Nevertheless, we are confident that the general views we present here can be applied to many other areas of physics. Possible use of these ideas to particular domains of our research fields are discussed in the conclusion.

2. GENERAL PARTITIONING THEORY

Let us consider a given problem which is either too complex to be solved directly or for which computing the complete solution will take a lot of time. To keep a common view of scattering theory, and have therefore a straightforward physical meaning, we will model or image the problem as the interaction of a particle with a collection of potentials (atoms for instance), but as discussed in the introduction, our results will have in fact the generality of the scattering approach. We will use the cluster model essentially as a guideline to the eyes in this section.

In this view, the operator A is therefore the hamiltonian H of the system and $(A - A_o)$ is the potential. Modelled in this manner, our problem is a standard multiple scattering problem as we have to consider the interaction of the particle with all the potentials to solve it. The resolution of such a problem is well-known but most of the time extremely tedious, complicated and time consuming. The complexity of the problem is directly related to the number of the multiple scattering events that have to be taken into account to compute the final solution,

and to the number of "atoms" they involve. Therefore, a straightforward way to simplify the resolution of the problem is to group the "atoms" into a small number of sets, solve the multiple scattering problem for each group and combine the solutions obtained for the various groups in a suitable way to construct the whole solution. This is at the core of the partitioning technique.

Following the standard mathematical terminology [2], we will call partition any decomposition of the cluster of "atoms" into a set of non intersecting groups, or classes. Labelling these classes with greek letters, a partitioning $\mathcal{P}=(\alpha,\beta,\gamma,\cdots)$ of P will be defined by

$$\begin{cases} P=\alpha\cup\beta\cup\cdots \\ \alpha\cap\beta=\varnothing \quad \text{for any } \alpha \text{ and } \beta. \end{cases}$$

The case of intersecting classes [3], although interesting in certain cases, will not be treated here but will be the subject of a forthcoming publication.

It should be noted at this point of the discussion that the language we will use in the remainder of this article is very close to that of multichannel scattering theory [4]. There is however a fundamental difference. In multichannel scattering theory, one is interested in the transition from one partition $\mathcal{P}_1=(\alpha_1,\beta_1,\gamma_1,\cdots)$ of the system P to another partition $\mathcal{P}_2=(\alpha_2,\beta_2,\gamma_2,\cdots)$ of the same system. The indices occuring in the operators will represent partitions. Here, we are interested in the multiple scattering between the elements α, β, γ, … of the same partition $\mathcal{P}$ of the system and the indices will be class indices.

2.1. TWO-CLASS SYSTEM

Let us first consider the simple case of a two-class system. If we label α one of the classes, then by definition the other class is the complement $\complement_\alpha$ in P. If A is an arbitrary operator of scattering theory, we will call A_α the corresponding operator restricted to the class α and A^α its counterpart for the complement class. As discussed by Sébilleau [5], when dealing with more than one class, class operators should be replaced by

$$\bar{A}_\alpha=\mathcal{T}(\vec{\mathbf{R}}_\alpha)A_\alpha\mathcal{T}(-\vec{\mathbf{R}}_\alpha), \tag{2.1}$$

where $\mathcal{T}(\vec{\mathbf{R}}_\alpha)$ is the translation operator of vector $\vec{\mathbf{R}}_\alpha$ and $\vec{\mathbf{R}}_\alpha$ is the position of the chosen origin of class α with respect to the system origin. Equation (2.1) is nothing else than the operator equivalent of the so-called addition theorems [6] which allow to express functions centered on a given point in terms of functions centered on another point of space.

For the sake of simplicity, we take again the cluster picture to represent the system under study. In this case, the hamiltonian can be written as

$$H = H_o + \bar{V}_\alpha + \bar{V}^\alpha = \bar{H}_\alpha + \bar{V}^\alpha, \tag{2.2}$$

where $\bar{V}_\alpha$ is the potential of subset α and $\bar{V}_\alpha$ that of its complement.

The system potential is then partitioned according to $V = \bar{V}_\alpha + \bar{V}^\alpha$. The subset resolvent is introduced as

$$\bar{G}_\alpha(z) = (z - \bar{H}_\alpha)^{-1} \tag{2.3}$$

and we will call it a propagator to keep the terminology of scattering theory by a potential. The transition operator $\bar{T}_\alpha$ of subset α is defined as the restriction of the system transition operator T to α, namely

$$\bar{T}_\alpha(z) = \bar{V}_\alpha + \bar{V}_\alpha \bar{G}_\alpha(z) \bar{V}_\alpha. \tag{2.4}$$

Likewise, the Møller wave operator is given by

$$\bar{\Omega}_\alpha(z) = I + G_o(z) \bar{T}_\alpha(z). \tag{2.5}$$

$G_o(z)$ is the propagator corresponding to the system described by H_o. If $|\varphi_o\rangle$ is an eigenstate of H_o for a given eigenvalue (energy, belonging to the continuum), and $|\bar{\psi}_\alpha\rangle$ an eigenstate of $\bar{H}_\alpha$ for the same eigenvalue, the Møller wave operator maps the $\{|\varphi_o\rangle\}$ onto the continuum eigenstates of $\bar{H}_\alpha$, *i.e.*

$$|\bar{\psi}_\alpha^\pm\rangle = \bar{\Omega}_\alpha^{(\pm)} |\varphi_o\rangle. \tag{2.6}$$

Here, the sign ± comes from the fact that when z tends to a continuum eigenvalue of $\bar{H}_\alpha$, equation (2.3) becomes divergent when crossing the branch cut to which this eigenvalue belongs. Therefore, it has to be calculated by taking the limit either from above (+ sign) or from below (– sign). It should be noted that equation (2.6) is in fact a compact form of the Lippmann-Schwinger equation as can be seen directly by inserting the definition (2.5) into it. So, equations (2.4)–(2.6) allow us to calculate directly the subset quantities from the corresponding quantities of its constituents (atoms for instance). What we need now to complete our theory is a way to construct the system quantities T, Ω or $|\psi^\pm\rangle$ from the knowledge of the subset quantities $\bar{T}_\alpha$, $\bar{\Omega}_\alpha$ or $|\bar{\psi}_\alpha\rangle$. For this, we introduce first a partitioning of the system T operator similar to that of the potential V

$$T = \bar{T}_\alpha + \bar{T}^\alpha. \tag{2.7}$$

$\bar{\mathcal{T}}_\alpha$ differs from the subset transition operator $\bar{T}_\alpha$ as it must contain some interaction with the complement subset for equation (2.7) to be true. For this reason, we will call $\bar{\mathcal{T}}_\alpha$ the distorted transition operator of subset α, or in other words, the transition operator of subset α in the presence of the complement subset. This is in contrast with $\bar{T}_\alpha$ which is the transition operator of subset α in the absence of any other subset. From these definitions, we see that $\bar{\mathcal{T}}_\alpha$ must be related to $\bar{T}_\alpha$ somehow. Following Tandy and Thaler [7], we introduce the distortion operator $\bar{W}^\alpha$ as the operator relating these two transition operators

$$\bar{\mathcal{T}}_\alpha = \bar{T}_\alpha \bar{W}^\alpha. \tag{2.8}$$

The upper index here indicates that it is the complement subset that is responsible for the distortion. From equation (2.7) and the standard definition $T = V + VGV$ of transition operators, we deduce that we have either $\bar{\mathcal{T}}_\alpha = \bar{V}_\alpha + {+}\bar{V}_\alpha GV$ or $\bar{\mathcal{T}}_\alpha = \bar{V}_\alpha + VG\bar{V}_\alpha$. We choose the first expression as our definition of $\bar{\mathcal{T}}_\alpha$. The second would lead to an equivalent theory as for hermitian operators $(\bar{V}_\alpha + VG^{\pm}\bar{V}_\alpha) = (\bar{V}_\alpha + \bar{V}_\alpha G^{\mp}V)^{\dagger}$.

Similarly, we can introduce a distorted wave operator $\bar{W}^\alpha$ that maps the subset eigensolutions onto the system solutions $|\psi\rangle$

$$\left|\psi^{\pm}\right\rangle = \bar{\mathcal{W}}^{\alpha(\pm)}\left|\bar{\psi}^{\pm}_{\alpha}\right\rangle.$$

It can be shown [3] that the distortion operator and the distorted wave operator are related by

$$\bar{W}^{\alpha\pm} = \bar{\Omega}^{(\pm)\dagger}_{\alpha}\bar{\mathcal{W}}^{\alpha(\pm)}\bar{\Omega}^{(\pm)}_{\alpha}. \tag{2.9}$$

For the sake of convenience, we also introduce the so-called Lovelace operator [8] by

$$\bar{T}^{\alpha\alpha} = \bar{V}^\alpha + \bar{V}^\alpha G \bar{V}^\alpha.$$

and the corresponding expression for the lower position of the indices. This transition-like operator satisfies the Dyson equation

$$G = \bar{G}_\alpha + \bar{G}_\alpha \bar{T}^{\alpha\alpha}\bar{G}_\alpha. \tag{2.10}$$

We deduce directly from this expression that

$$T^{\pm} = \bar{T}^{\pm}_{\alpha} + \bar{\Omega}^{(\mp)\dagger}_{\alpha}\bar{T}^{\alpha\alpha\pm}\bar{\Omega}^{(\pm)}_{\alpha}. \tag{2.11}$$

This is a central result to our approach. A similar result has been derived by MacMillan and Redish [9] in the context of multichannel scattering theory. Here, it

allows to calculate the system T operator as the sum of the T operator of subset α plus a correction term that account for the existence of the complement subset. The Møller wave operator of the system is then obtained from its α-subset restriction by

$$\Omega^{(\pm)} = \bar{\mathcal{W}}^{\alpha(\pm)} \bar{\Omega}_\alpha^{(\pm)} = \bar{\Omega}_\alpha^{(\pm)} \bar{W}^{\alpha\pm}. \tag{2.12}$$

So we have derived a way to reconstruct the system operators T, Ω (and therefore $|\psi\rangle$) from the knowledge of the subset operators $\bar{T}_\alpha$, $\bar{\Omega}_\alpha$. The reconstruction algorithm involves new operators $\bar{W}^\alpha$, $\bar{\mathcal{W}}^\alpha$ and $\bar{T}^{\alpha\alpha}$ which we have now to express in terms of known quantities for calculation purposes. Let us first note that in addition to equation (2.9), these new operators are also related by

$$\begin{cases} \bar{T}^{\alpha\alpha\pm} = \bar{V}^\alpha \bar{W}^{\alpha(\pm)} \\ \bar{W}^{\alpha\pm} = I + G_o^\pm \bar{T}^{\alpha\alpha\pm} \bar{\Omega}_\alpha^{(\pm)} \end{cases} \tag{2.13}$$

and

$$\begin{cases} \bar{W}^{\alpha\pm} = I + G_o^\pm \bar{T}^{\alpha\pm} \\ \bar{\mathcal{W}}^{\alpha(\pm)} = I + G_o^\pm \bar{T}^{\alpha\mp\dagger}. \end{cases} \tag{2.14}$$

From equations (2.8) and (2.14), we deduce that the distortion operator $\bar{W}^\alpha$ satisfies the coupled equations

$$\begin{cases} \bar{W}_\alpha = I + G_o \bar{T}_\alpha \bar{W}^\alpha \\ \bar{W}^\alpha = I + G_o \bar{T}^\alpha \bar{W}_\alpha. \end{cases}$$

Hence, the distortion operator can be expressed in terms of the known subset transition operators $\bar{T}_\alpha$ and $\bar{T}^\alpha$ as

$$\bar{W}^\alpha = \left[I - G_o \bar{T}^\alpha G_o \bar{T}_\alpha \right]^{-1} \bar{\Omega}^\alpha \tag{2.15}$$

and likewise for $\bar{W}_\alpha$. And from the second expression of the system (2.13), we have

$$\bar{T}^{\alpha\alpha} = \left[I - \bar{T}^\alpha G_o \bar{T}_\alpha G_o \right]^{-1} \bar{T}^\alpha = \bar{T}^\alpha \left[I - G_o \bar{T}_\alpha G_o \bar{T}^\alpha \right]^{-1}. \tag{2.16}$$

Equations (2.15), (2.16) and (2.9) allow a complete calculation of $\bar{W}^\alpha$, $\bar{T}^{\alpha\alpha}$ and $\bar{\mathcal{W}}^\alpha$ in terms of the individual transition operators of the two subsets. Then, the full system quantities are obtained through (2.10)–(2.12).

2.2. SEVERAL CLASSES SYSTEM

Up to now, we have only considered a two-class partitioning. Obviously, the case of several classes can be obtained from the previous theory by iterating the

process: the complement to α is itself divided into two subsets and $\bar{T}^{\alpha}$ and related quantities can be obtained from the same equations applied to this new two subset system. The process is then ended when the right number of subsets is reached. Many particular cases in the literature rely on this approach as we will review it in the next section. Here however, we want to generalize the results of the previous subsection to the case of a *N*-subset system. Let us suppose therefore that

$$V = \bar{V}_{\alpha} + \bar{V}_{\beta} + \bar{V}_{\gamma} + \cdots.$$

As before, we can introduce a Lovelace transition operator by

$$\bar{T}^{\alpha\beta} = \bar{V}_{\alpha} + V_{\alpha} G \bar{V}_{\beta}.$$

Note that there exist also a non equivalent definition with $\bar{V}^{\beta} + V^{\alpha} G \bar{V}^{\beta}$ as we loose the symmetry of the formula now. Then, using the same kind of approach as developped in subsection 1, equation (2.11) can be generalized in

$$T^{\pm} = \bar{T}_{\alpha}^{\pm} + \bar{\Omega}_{\alpha}^{(\mp)\dagger} \bar{T}^{\alpha\beta\pm} \bar{\Omega}_{\beta}^{(\pm)}. \tag{2.17}$$

Unfortunately, we have not been able to find a simple and suitable algorithm such as (2.16) to compute $\bar{T}^{\alpha\beta\pm}$ and therefore this result is not convenient for calculation. There is however another way to tackle the problem that will make the connection with some other particular applications that are found in the literature (see section 3).

Following the partitioning of the potential *V*, we can partition the transition operator accordingly

$$T = \bar{\mathcal{T}}_{\alpha} + \bar{\mathcal{T}}_{\beta} + \bar{\mathcal{T}}_{\gamma} + \cdots.$$

We can identify $\bar{\mathcal{T}}_{\alpha}$ as the α-component of *T* in the (α, β, γ, …) partition. As we have seen it before, $\bar{\mathcal{T}}_{\alpha}$ is the *T* operator of subset α in the presence of all the other subsets. It therefore contains contributions of the other subsets as well as that of $\bar{T}_{\alpha}$, the contributions of the former being contained into the distortion operator $\bar{W}^{\alpha}$ as expressed by equations (2.8) and (2.15). So, it can be useful to make these contributions more apparent by partitioning $\bar{\mathcal{T}}_{\alpha}$ itself, *i.e.*, by expanding it onto the partition. To this purpose, we introduce the scattering path operator [10] as the component of $\bar{\mathcal{T}}_{\alpha}$ onto the partition

$$\bar{\mathcal{T}}_{\alpha} = \sum_{\beta} \bar{\tau}_{\alpha\beta}.$$

With this definition, we see that $\bar{\tau}_{\alpha\beta}$ results from a double partitioning of *T*

$$T = \sum_{\alpha,\beta} \bar{\tau}_{\alpha\beta}. \tag{2.18}$$

We deduce from this expression that the scattering path operator must be expressed as

$$\bar{\tau}_{\alpha\beta} = \bar{V}_\alpha \delta_{\alpha\beta} + \bar{V}_\alpha G \bar{V}_\beta.$$

It satisfies the equation of motion

$$\bar{\tau}_{\alpha\beta} = \bar{T}_\alpha \delta_{\alpha\beta} + \sum_{\gamma\neq\alpha} \bar{T}_\alpha G_o \bar{\tau}_{\gamma\beta}. \tag{2.19}$$

This equation provides a convenient way to calculate $\bar{\tau}_{\alpha\beta}$ and from this T. It is noteworthy that the scattering path operator coincides with the Lovelace operator when $\alpha = \beta$ but not otherwise.

There is, however, another way of computing the path operators $\bar{\tau}_{\alpha\beta}$: The mirror counterpart of equation (2.19)

$$\bar{\tau}_{\alpha\beta} = \bar{T}_\beta \delta_{\alpha\beta} + \sum_{\gamma\neq\beta} \bar{\tau}_{\alpha\gamma} G_o \bar{T}_\beta \tag{2.20}$$

is also true. Rewriting it in a convenient form and using definitions (2.5) and (2.14) we can write

$$G_o \bar{\tau}_{\alpha\beta} \bar{\Omega}_\beta = \bar{W}_\alpha G_o \bar{T}_\beta. \tag{2.21}$$

If we imagine that the cluster is built by adding iteratively the subsets α, β, … one by one, we can prove [3] that, when we add the "k"-th subset, the corresponding $\bar{W}_k$ operator can be obtained by

$$\bar{W}_k = \left[I - G_o \bar{T}_k \bar{\Omega}_k \bar{W}_1^{(k-1)} \ldots \bar{W}_{k-1}^{(k-1)} \right]^{-1} \tag{2.22}$$

using the $\bar{W}_j^{(k-1)}$ distortion operators calculated (at the previous step of iteration, when the "$k-1$" subset was added) for the "j"-th subset in the situation when only $k-1$ subsets exist. With these results, we can build an iterative algorithm for iterative calculation of path operators.

2.3. PARTITIONING SCHEMES

In the case of a general partitioning, we have outlined two ways to obtain the transition operator T of the system. One involves an iterative partitioning with T calculated by (2.11) and (2.16). The second one treats all subsets on an equal

footing and makes use of the scattering path operator through (2.18) and (2.19). As discussed briefly by Gavaza and Sébilleau [11] and in more details by Gavaza [3], these two particular algorithms can be further understood from a topological point of view. Let us consider two subsets α and β within the partition $\mathcal{P}$. If we take again the image of a particle scatterred by the subsets as a guideline, there are two possibilities for this particle to reach γ from α: (i) the particle can do it without encountering any other subset β, (ii) it must cross another subset β to travel from α to γ. These two alternatives are sketched in Fig. 1. In the case of Fig. 1(a), we have a paving-like structure for the partition : all subsets are on an equal footing from a classical point of view, any of them can be reached without encountering another, and before the others. Fig. 1(b) with its onion-like shape leads to a very different structure where the classical particle goes through the subshells in a certain order and only adjacent subsets can be passed through without intersecting a third subset. From this point of view, we see that 1(a) is the natural structure of an algorithm of type (i) while 1(b) can be associated very transparently to (ii). But of course this is only a connection based on a classical (topological) view. Nothing prevents to use an algorithm of type (ii) to compute T within a partitioning of type 1(a) and conversely (i) with 1(b). The algorithms (i) and (ii) have been discussed in some detail by Gavaza and Sébilleau [11] and Gavaza [3], so we will not discuss them any further and we refer the reader to these references for a more detailed account.

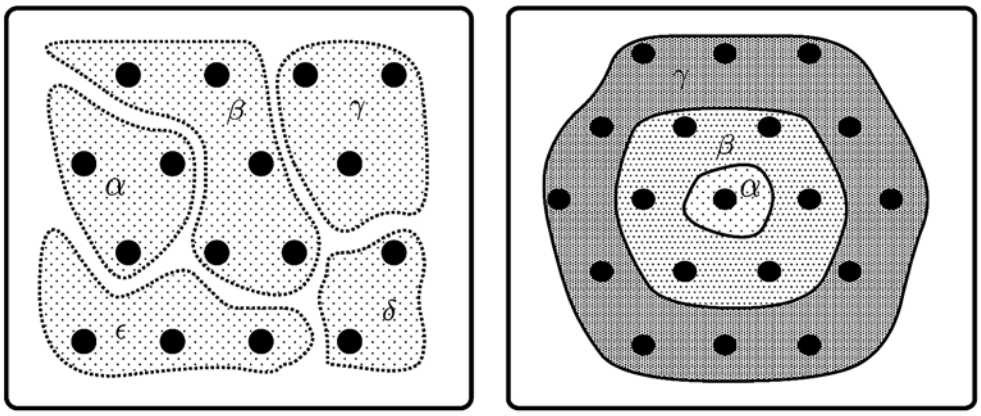

Fig. 1 – (a): paving-like type of partitioning, (b): onion-like type of partitioning.

3. RECOVERY OF THE ALGORITHMS USED IN ELECTRON SPECTROSCOPIES

Up to now, the theory we have derived is very general. Although we often took the image of the scattering of a particle by atoms to illustrate and guide our

derivation, the results we have obtained are much more general. In the present section, we will specialize our multiple scattering theory to the case of electron spectroscopies and electronic structure methods to show how standard theories of the literature can be considered as particular cases of our present approach.

3.1. THE CONCENTRIC SHELL ALGORITHM

This algorithm, originally devised for X-ray Absorption Spectroscopy (XAS) by Durham and coworkers [15, 16], was then extended to Low-Energy Electron Diffraction (LEED) by Saldin and Pendry [17] and then to Photoelectron Diffraction (PhD) and Auger Electron Diffraction (AED) by Saldin, Harp and Chen [18]. In this approach, which for simplicity we will call PDS (Pendry-Durham-Saldin), the cluster of atoms used to model these spectroscopies is divided into concentric shells, thereby leading to an onion-like structure such as the one sketched in Fig. 1(b). Assuming that the scattering contributions within each shell have been calculated by one way or another, the wave function of the electron travelling from one shell to another is expressed in terms of four reflection/ transmission coefficients and sets of spherical waves centered on each shell. If we label by *I* and *O* respectively the ingoing and outgoing waves corresponding to a given spherical shell *k*, it is rather straightforward to show that the four PDS coefficients will write in our theory as

$$\begin{cases} \bar{T}_k^{OO} = G_o \bar{T}_k \\ \bar{T}_k^{OI} = G_o \bar{T}_k G_o \\ \bar{T}_k^{IO} = \bar{T}_k \\ \bar{T}_k^{II} = \bar{T}_k G_o . \end{cases} \tag{3.23}$$

In these PDS equations, the first exponent corresponds to the incident wave. It is not the place here to rederive all the PDS equations from the equivalence system (3.23). This has been done by Gavaza [3]. But all the PDS equations can be obtained from the iterative algorithm of section 1 and (3.23). Here however, we have some extra flexibility with our theory as, by exchanging the roles of α and its complement in the equations of section 1, or using the distorted wave operator $\bar{\mathcal{W}}^{\alpha}$ instead of the distortion operator $\bar{W}^{\alpha}$ in the expression (2.12) of the system Møller wave operator we have in fact four different algorithms at our disposal instead of the one provided by the PDS equations.

3.2. THE STANDARD LEED ALGORITHM

Standard LEED theory was historically the first electron spectroscopy theory to be developped and it is well documented. We refer the reader to the two classical

textbooks by Pendry [19] and by Van Hove, Weinberg and Chan [20] for its complete derivation. There, as long-range order is necessary, symmetry is extensively used. The crystal is decomposed into a finite set of infinite planes and the wave function of any electron incident upon any of these planes is expanded in terms of plane waves satisfying the symmetry conditions of the plane considered. Again, as in the PDS theory, assuming the scattering operator of each plane (subset) already computed, the interplane scattering processes are described with the transmission/reflection coefficients of each plane. Therefore, this approach can be seen as a limiting case of the PDS model, with the curvature of each shell tending to infinity. Let us call A any such plane and note r_A (t_A) the reflection (transmission) coefficient of this plane to use the Pendry/Van Hove-Weinberg-Chan (PVWC) notation. The connection to our theory is made through the recognition that

$$\begin{cases} \overline{t}_{AA}^{++} = \overline{\Omega}_A^{(+)} \\ \overline{t}_{AA}^{--} = \overline{\Omega}_A^{(-)\dagger} \\ \overline{r}_A^{-+} = \overline{T}_A^{+} \\ \overline{r}_A^{+-} = G_o^{+} \overline{T}_A^{+} G_o^{+}. \end{cases} \tag{3.24}$$

The lefthand sign corresponds to the scattered wave and the righthand side one to the wave incident upon plane A. In contrast to the PDS theory, transmission without scattering through a layer is taken into account in the definition of the t_A coefficient. This adds the identity operator in the $\overline{T}_k^{OO}$ and $\overline{T}_k^{II}$ expressions in (3.23) which allows us to identify them to the Møller wave operators $\overline{\Omega}_A^{(+)}$ and $\overline{\Omega}_A^{(-)\dagger}$.

The most popular algorithm to combine the scattering contributions of each plane in LEED is probably the layer doubling method [19, 20]. It is an iterative process where at each step the two layers from the previous step are combined to form a new single layer. This algorithm can be deduced in a straightforward manner from the theory we developped in section 2. If we call AB the layer formed by combining plane A and plane B, then the reflection and transmission coefficients of this bilayer are simply

$$\begin{cases} \overline{T}^{++} = \overline{\Omega}_{AB}^{(+)} \\ \overline{R}^{-+} = \overline{T}_{AB}^{+}. \end{cases}$$

$\overline{T}^{--}$ and $\overline{R}^{+-}$ are obtained by exchanging the roles of A and B. Equations (2.11) and (2.12) allow to compute them directly to recover the results of the PVWC theory as exposed by Van Hove, Weinberg and Chan [20]. The exponential terms appearing in their equations come from the fact that they are using layer-

centered operators which, according to (2.1) are related to our origin-centered operators through translation operators. The complete derivation has been given by Gavaza [3].

3.3. THE CLUSTER APPROACH

This is probably the most straightforward way to compute the cross-section in electron spectroscopies. It is often referred to as the multiple scattering approach although the previous methods do rely as well on multiple scattering (between planes or shells and within them). It would be therefore more proper to call it atomic multiple scattering as it does not make any use of partitioning at all. Or, to view it in another way, each atom in this method is a subset in itself. It uses the scattering path operator algorithm generalized in section 2 to the case of subsets. However, it should be noted that nothing prevents the use of the iterative algorithm of section 1 to compute the cross-section in this case, or a mixed approach such as the iterative calculation of the scattering path operator proposed by Gavaza [3]. Apart from this latter idea, that has not been used for calculations yet, two ways to calculate the scattering path operator can be found in the literature. One called multiple scattering series expansion is based on the iteration of the equation of motion (2.19) applied to subsets restricted to single atoms. If we label the individual atoms by i, j, k, … this iteration leads to

$$\overline{\tau}_{ij} = \overline{T}_i \, \delta_{ij} + \overline{T}_i G_o \overline{T}_j + \sum_{k \neq i,j} \overline{T}_i G_o \overline{T}_k G_o \overline{T}_j + \cdots . \tag{3.25}$$

This method requires the construction and computation of the contribution of each possible scattering pathway from i to j, truncated to a certain order, and is therefore extremely time consuming. Moreover, it does not necessarily converge at low energies (typically below 50 eV).

The second method is called full multiple scattering and is obtained by factorizing the equation of motion (2.19). Writing the operators in matrix notation, we obtain

$$\boldsymbol{\tau} = \boldsymbol{T}(\boldsymbol{I} - \boldsymbol{G}_o \boldsymbol{T})^{-1}.$$

It should be noted that equation (3.25) is recovered by expanding the inverse in the previous equation

$$\boldsymbol{\tau} = \boldsymbol{T}(\boldsymbol{I} + \boldsymbol{G}_o \boldsymbol{T} + (\boldsymbol{G}_o \boldsymbol{T})^2 + \cdots).$$

This expansion shows the limits on the convergence (see Natoli and Benfatto [21] for a complete discussion of the convergence).

Therefore, this matrix inversion method does not suffer from the drawback of the series expansion method (3.25). However, being a matrix method, its use is

strongly limited by the size of the matrix $(\boldsymbol{I}-\boldsymbol{G}_o\boldsymbol{T})$, called the multiple scattering matrix, that has to be inverted. As a consequence, it is restricted to small clusters and low energies. It is these limitations that have led Ankudinov and coworkers [22] to use a special partitioning of the cluster to compute XAS spectra. Owing to the fact that the XAS spectra are dominated by contributions from the near neighbours of the absorbing atom but still influenced by more distant scatterers, they divided their cluster of atoms into a small spherical subset surrounding the absorber and a larger one containing all the more distant ones. The dominant contribution of the small subset is then computed exactly by matrix inversion, which is possible because of the small number of atoms contained in this subset, while scattering by the other atoms is calculated perturbatively with the series expansion method. Their partitioning algorithm then takes care of combining properly the two contributions to reconstruct the XAS spectrum. Actually, this algorithm is exactly equivalent to

$$G=\bar{G}_\alpha+\bar{G}_\alpha\left[I-\bar{T}^\alpha G_o\bar{T}^\alpha G_o\right]^{-1}\bar{T}^\alpha\bar{G}_\alpha$$

which is equation (2.10) combined with (2.16) when identifying subset α to the small inner subset where full matrix inversion is performed.

3.4. THE FUJIKAWA METHOD

The inversion of the multiple scattering matrix is strongly limited by the size of this matrix. One way to extend the use of this method that has been practised for a long time is to use a block inversion, *i.e.*, to partition the matrix into four blocks which are inverted as separate entities. Indeed, according to standard matrix theory [23], if a matrix $\boldsymbol{M}$ is divided into

$$\boldsymbol{M}=\begin{pmatrix}\boldsymbol{a} & \boldsymbol{b}\\ \boldsymbol{c} & \boldsymbol{d}\end{pmatrix}$$

with $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$, and $\boldsymbol{d}$ being matrices, the inverse matrix $\boldsymbol{M}^{-1}$ can be reconstructed according to

$$\mathbf{M}^{-1}=\begin{pmatrix}(\boldsymbol{a}-\boldsymbol{b}\boldsymbol{d}^{-1}\boldsymbol{c})^{-1} & -\boldsymbol{a}^{-1}\boldsymbol{b}(\boldsymbol{d}-\boldsymbol{c}\boldsymbol{a}^{-1}\boldsymbol{b})^{-1}\\ -\boldsymbol{d}^{-1}\boldsymbol{c}(\boldsymbol{a}-\boldsymbol{b}\boldsymbol{d}^{-1}\boldsymbol{c})^{-1} & (\boldsymbol{d}-\boldsymbol{c}\boldsymbol{a}^{-1}\boldsymbol{b})^{-1}\end{pmatrix}$$

If this approach allows to extend sensibly the size of the problems that can be treated by full inversion, it still does not allow to cover the whole range of energies encountered in electron spectroscopies. To further improve, *albeit* to the price of a more complex algorithm, Fujikawa [24, 25] has proposed to divide the multiple scattering matrix into nine blocks instead of four. From the point of view of our

partitioning theory, this amounts to considering a three subset problem and finding a suitable algorithm. This can be solved directly from equations (2.10) and (2.16) by iterating only once to write $\overline{V}^{\alpha} = \overline{V}_{\beta} + \overline{V}_{\gamma}$. Using the formulas of section 2.1, this gives [3]

$$\overline{T}^{\alpha} = \overline{T}_{\beta} + \left[\overline{T}_{\gamma}^{-1} - G_o \overline{T}_{\beta} G_o\right]^{-1} + \overline{T}_{\beta} G_o \left[\overline{T}_{\gamma}^{-1} - G_o \overline{T}_{\beta} G_o\right]^{-1} + \\ + \left[\overline{T}_{\gamma}^{-1} - G_o \overline{T}_{\beta} G_o\right]^{-1} G_o \overline{T}_{\beta} + \overline{T}_{\beta} G_o \left[\overline{T}_{\gamma}^{-1} - G_o \overline{T}_{\beta} G_o\right]^{-1} G_o \overline{T}_{\beta}$$

which, after regrouping some of the terms and considering a first-order approximation, gives exactly the results obtained by Fujikawa from matrix theory.

3.5. THE LAYER KKR ALGORITHM

The layer KKR (KKR is named after Kohn, Korringa and Rostoker) method [26, 27, 28, 29] is a very efficient calculation scheme to compute the electronic structure of surfaces and interfaces. Like the previous algorithm, it is based on a three subset partitioning of the system, but with an iteration scheme where at each step three layers are combined to form a new layer according to an algorithm that we have termed within our general theory the sandwich algorithm [3].

The central layer being formed of the three layers of the previous step, we can write the *T* operator of the new layer as

$$T = \mathcal{T}_{\alpha} + \mathcal{T}_{\beta} + \mathcal{T}_{\gamma}.$$

where α, β, and γ represent the three layers to be combined. If we write the restriction of $\mathcal{T}_{\alpha}$ to the subset $\alpha \cup \beta$ as $\mathcal{T}_{\alpha}^{(\alpha\cup\beta)}$, it is straightforward to show, being the standard two subset case of section 2.1 that

$$\mathcal{T}_{\alpha}^{(\alpha\cup\beta)} = \left[I - \overline{T}_{\alpha} G_o \overline{T}_{\beta} G_o\right]^{-1} T_{\alpha} \overline{\Omega}_{\beta}. \tag{3.26}$$

As demonstrated by Tandy and Thaler [7], the distorted transition operator $\mathcal{T}_{\alpha}$ can be written in the general case of a *N*-subset partition

$$\mathcal{T}_{\alpha} = \mathcal{T}_{\alpha}^{(\alpha\cup\beta)} \left[I + G_o \sum_{\gamma \neq \alpha,\beta} \mathcal{T}_{\gamma} \right].$$

In the three subset case, this leads to a system of three equations with three unknowns which is easily solved giving

$$\mathcal{T}_{\alpha} = \left[I - \mathcal{T}_{\alpha}^{(\alpha\cup\beta)} G_o \mathcal{T}_{\gamma}^{(\beta\cup\gamma)} G_o\right]^{-1} \mathcal{T}_{\alpha}^{(\alpha\cup\beta)} \left[I + G_o \mathcal{T}_{\gamma}^{(\beta\cup\gamma)}\right].$$

with $\mathcal{T}_\alpha^{(\alpha\cup\beta)}$ given by (3.26) and $\mathcal{T}_\gamma^{(\beta\cup\gamma)}$ obtained by permutation of the indices. $\mathcal{T}_\beta$ and $\mathcal{T}_\gamma$ are obtained in a similar way. Expressing these equations in terms of the notations of MacLaren and coworkers [27] gives directly the fundamental equations of the layer KKR method as was shown by Gavaza [3].

4. CONCLUSION

In this article, we have proposed a general theory of partitioning within a multiple scattering framework. This theory is very general and, although we used as a guideline to the derivation the image of the repeated scattering of a particle by a collection of potentials, it goes well beyond this and does not need potentials or perturbations to be valid. Its limitations are purely those of scattering theory. The basic idea of this theory is to propose alternative algorithms to solve a complex problem by dividing it in non intersecting subproblems that are then solved independently. The reconstruction algorithms discussed in sections 2.1 and 2.2 provide an elegant and systematic way to reconstruct the full solution by taking properly into account the connections between the subproblems resulting from the partitioning.

We have then shown how different techniques used for electron spectroscopies or electronic calculation methods are in fact particular cases of the present theory of multiple scattering within a partitioned space. The list we have presented in section 3 is obviously not exhaustive as partitioning can have applications in many other domains.

The only constraint we put on the decomposition is that of a partition, *i.e.*, of non intersecting subproblems. The case of intersecting subsets, although extremely useful in certain cases, is more complicated and outside the scope of this article. It has been however treated in full by Gavaza [3].

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