Multiple scattering theory for non-local and multichannel potentials

Calogero R Natoli[1,2]**, Peter Krüger**[1]**, Keisuke Hatada**[2,3]**,**
Kuniko Hayakawa[2,4]**, Didier Sébilleau**[5] **and Ondřej Šipr**[6]

[1] ICB, UMR 6303 Université de Bourgogne—CNRS, BP 47870, F-21078 Dijon, France
[2] INFN Laboratori Nazionali di Frascati, Via E Fermi 40, c.p. 13, I-00044 Frascati, Italy
[3] CNISM, School of Science and Technology, Physics Division, University of Camerino, I-62032 Camerino (MC), Italy
[4] Centro Fermi, Compendio Viminale, Roma I-00184, Italy
[5] Institut de Physique de Rennes, UMR UR1-CNRS 6251, Campus de Beaulieu, Université de Rennes1, F-35042 Rennes-cedex, France
[6] Institute of Physics, Academy of Sciences of the Czech Republik, Cukrovarnicka 10, 162 53 Praha 6, Czech Republic

E-mail: pkruger@u-bourgogne.fr

Abstract

Methodological advances in multiple scattering theory (MST) in both wave and Green's function versions are reported for the calculation of electronic ground and excited state properties of condensed matter systems with an emphasis on core-level photoemission and absorption spectra. Full-potential MST is reviewed and extended to non-local potentials. Multichannel MST is reformulated in terms of the multichannel density matrix whereby strong electron correlation of atomic multiplet type can be accounted for in both ground and excited states.

1. Introduction

Electron spectroscopies using synchrotron radiation are playing an increasingly important role for the in-depth investigation of structural and electronic properties of matter. For example, resonant x-ray scattering, in the elastic or inelastic mode, is rapidly becoming the crucial technique for understanding the subtleties of the microscopic mechanism relating to magnetic and electronic (orbital) degrees of freedom in strongly correlated systems and for studying their low-energy excitations. X-ray absorption and natural circular dichroism are used to access structural and electronic details in many systems of interest in material science, including molecular and organic materials of interest in biophysics (e.g. proteins), while magnetic circular and linear dichroism are able to carry information on the magnetic properties of many systems, from the traditional ones (for which the information is complementary to that derived by neutrons) to the newly developed materials such as nano-structures, thin films and multilayers, where the use of synchrotron radiation

is essential to obtain the desired information. In this context a successful theoretical interpretation of these spectroscopies is of paramount importance for extracting the rich electronic and structural information contained in the experimental spectra.

Moreover, significant progress into the preparation, characterization and industrial exploitation of new magnetic materials based on transition metals and/or rare earths has spurred new research. As a consequence, we have witnessed the explosion of the nano-revolution aimed at developing new technologies, devices and synthesis routes. At present, many research groups working in both basic and applied research move their interest to the new nano-science and nanotechnology fields. Now, the change in the size scale of the new materials implies both the modification of their properties and the appearance of new physical phenomena, since in these systems correlation effects are most pronounced due to their reduced dimensionality. Another field where correlation effects are important for the same reasons is surface science, which encompasses the important field of catalysis. Therefore, a satisfactory description of the

electronic correlations, both in the ground and in the excited states probed by x-rays in Synchrotron Radiation (SR) spectroscopy, is one of the major challenges in condensed matter physics.

The purpose of this paper is to present a theoretical framework, based on multiple scattering theory (MST), able to provide a unified description of the electronic ground state as well as the excited states of a physical system, taking into account correlation effects, at least at a local level, beyond what can be reached in a description based on density functional theory (DFT). The key ingredient in this approach is the knowledge of the Green's function (GF) which provides information on both the ground state and the excited ones. Needless to say, the knowledge of the properties of the ground state is of paramount importance in the interpretation of the excited states as observed in SR spectroscopy.

At its most basic, multiple scattering theory is a technique for solving a linear partial differential equation (or a system thereof) over a region of space with certain boundary conditions. It is implemented by dividing the space into non-overlapping domains (cells), solving the differential equation separately in each of the cells and then assembling together the partial solutions into a global solution that is continuous and smooth across the whole region and satisfies the given boundary conditions.

As such MST has been applied to the solution of many problems drawn from classic as well as quantum physics, ranging from the study of membranes and electromagnetism to the quantum-mechanical wave equation. In quantum mechanics it has been widely used to solve the Schrödinger equation (or the associated Lippmann–Schwinger equation) for both scattering and bound states.

One of the early applications of the theory, from which the name was derived, was in nuclear theory for the calculation of the scattering cross-section of a neutron impinging onto an atomic nucleus composed of many nucleons. The idea was based on imagining the nucleons frozen at certain positions in space, calculating the successive scatterings of the incoming particle from this configuration (whence the name multiple scattering) and then performing the average over all space configurations with a probability distribution based on the nuclear wavefunction. This is very similar to a photoemission (PE) process in matter. Instead of coming from a source external to the system, the impinging particle (the electron in this case) is generated internally and in its way out of the system is scattered by the atoms constituting the sample, which are at fixed positions in space.

The transition from this non-stationary process to a stationary one, as needed for the calculation of bound states in a solid, was a straightforward step. The theory indeed was soon proposed by Korringa and by Kohn and Rostoker (KKR) as a convenient method for calculating the electronic structure of solids [1, 2] and was later extended to polyatomic molecules by Slater and Johnson [3].

A characteristic feature of the method is the complete separation between the potential aspect of the material under study, embodied in the cell scattering power, from the structural aspect of the problem, reflecting the geometrical position of the atoms in space.

Applications of the KKR method were first made within the so-called muffin-tin approximation for the potential. In this approximation the potential is confined within non-overlapping spheres, where it is spherically symmetrized, and takes a constant value in the interstitial region. Despite this approximation the method was complicated and demanding from a numerical point of view and as a band-structure method was therefore superseded by more efficient linearized methods, such as the linearized muffin-tin-orbital method (LMTO) [4] and the linearized augmented-plane-wave method (LAPW) [5].

Full-potential versions of these band methods have also been introduced in recent years. However, none of these methods can match the power and versatility of a full-potential method based on the formalism of MST, either in terms of providing a complete solution of the Schrödinger equation or in the range of problems that could be treated. In particular, none of these methods leads easily to the construction of the Green's function which is invaluable in the study of a number of properties of many physical systems. Moreover, the same GF can be used to calculate spectroscopic response functions, since it includes the information on excited state as well, as anticipated above.

For these reasons, in the last two decades, the KKR method has experienced a revival in the framework of the Green's function method (KKR-GF). Indeed, due to the introduction of the complex energy integration, it was found that the method is well suited for ground state calculations, with an efficiency comparable to typical diagonalization methods. A host of problems became in this way tractable, ranging from solids with reduced symmetry (e.g. isolated impurities in ordered crystals, surfaces, interfaces, layered systems, etc) to randomly disordered alloys in the coherent potential approximation. A very recent comprehensive review on the KKR-GF is contained in [6].

At the same time, it soon became clear that the muffin-tin approximation was not adequate for the treatment of systems with reduced symmetry or for the calculation of lattice forces and relaxation. In order to deal with these problems a number of groups developed a full-potential KKR-GF method, obtaining very good results, comparable with the full-potential LAPW method, as concerns total energy calculations, lattice forces and relaxation around an impurity ([7–11] and references therein).

Instead, applications to states well above the Fermi energy, as required in the simulations of x-ray spectroscopies, such as absorption, photoemission, anomalous scattering, etc, have been scarce and proceeded slowly. In the words of [12], 'the feeling that one should calculate the "near-field corrections", coupled with the need to solve a fairly complicated system of coupled differential equation to determine the local (cell) solutions (based on the phase function method) has contributed greatly to the slow development of a Full-Potential method based on MST'. It was only after it was realized that near-field corrections are not necessary and a new method to generate local solutions was found that progress became faster, at least in the calculation of the electronic structure of solids.

For all the above reasons full-potential codes based on MST for the calculation of x-ray spectroscopies are not very numerous. We mention here the work by Huhne and Ebert [13] on the calculation of x-ray absorption spectra using the full-potential spin-polarized relativistic MST and that of Ankudinov and Rehr [14] in the scalar relativistic approximation.

Very recently we have developed a derivation of a real space full-potential multiple scattering theory, both for continuum and bound states, that is free from the drawbacks that up to now have impaired its development (in particular the need to use cell shape functions and rectangular matrices), under conditions for space-partitioning that are not excessively restrictive and easily implemented [15–17]. This approach provides a straightforward extension of MST in the muffin-tin approximation, with only one truncation parameter given by the classical relation $l_{max} = kR_b$, where k is the electron wavevector (either in the excited or ground state of the system under consideration) and R_b the radius of the bounding sphere of the scattering cell. It was also shown that the theory converges absolutely in the $l_{max} \to \infty$ limit. As a consequence the method provides a firm ground to the use of full-potential MST as a viable method for electronic structure calculations and makes possible the computation of x-ray spectroscopies, notably photo-electron diffraction, absorption and anomalous scattering among others, with the ease and versatility of the corresponding muffin-tin theory.

This development was essential for establishing the limitations of the effective quasi-particle description of x-ray spectroscopy based on a complex optical potential [18]. Due to the fact that now the single-particle Schrödinger equation is solved exactly (within some numerical precision) without approximation for the geometrical shape of the potential, it becomes possible to test the performance of a particular optical potential to describe the average effects of the so-called neglected channels, that is to say the effect of all the inelastic events that accompany the photoemission (photoabsorption) process.

On the other hand, in the calculation of the ground state properties in the framework of the DFT approach, the possibility of an exact solution of the Kohn and Sham [19] orbitals has allowed us to test the reliability of the starting density functional. In this way it was found that DFT, although based on the exact ground state theorem of Hohenberg and Kohn [20], in practice describes electronic correlations in an average way, due to the fact that the exact form of the associated functional is unknown (henceforth, when talking about DFT, we shall mean the practical implementations of the theory (i.e. local (spin) density approximation (L(S)DA) or generalized gradient approximation (GGA)) [21]). A well known case of failure of DFT is in the description of the electronic properties of transition metal compounds. Their physics is strongly related to the particular nature of their 3d valence states. On the one hand the 3d states are partly localized and thus retain some electron correlation effects of the free atom, e.g. Hund's rule coupling responsible for the formation of magnetic moments. On the other hand they are considerably hybridized (i.e. delocalized) and

thus strongly participate in solid state phenomena such as bonding, electronic transport and magnetic ordering. The failure of DFT to predict properties of the ground states in these materials reflects itself in the corresponding failure of effective independent particle theories (i.e. in the framework of an optical potential) in the description of x-ray spectroscopies. The case of the non-statistical branching ratio of the $L_{2,3}$ edges in these materials is paradigmatic [22]. We know however that an approach based on atomic multiplet theory works [23]. This is a configuration interaction method and thus accounts well for (local) electron correlation effects. Solid state effects are treated by adding to the atomic Hamiltonian either an effective crystal field or the hybridization with a few near-neighbor ligand orbitals, in which case one arrives at the charge transfer cluster model. The atomic multiplet and charge transfer cluster model approaches have been extremely successful in describing and understanding the XAS and related spectroscopies of transition metal compounds [23]. However, all extra-atomic terms (crystal field and hybridization) are usually introduced through empirical parameters, which limits considerably the predictive power of this scheme. Even though cluster calculations for $L_{2,3}$ edge XAS of transition metal oxides using a full *ab initio* quantum chemistry method have obtained good agreement with experiments without introducing any empirical parameters [24], it is clear that quantum chemistry methods are limited to very small systems. Consequently long range effects, which are especially important in metallic and covalently bonded systems (periodic and non-periodic), cannot be handled in this framework.

As a general consideration, whenever local electronic correlations are important, be it the case of extended systems, systems of reduced dimensionality, surfaces, etc, a theoretical scheme able to encompass both aspects of space extension and electronic interaction is highly needed. A step forward toward this goal in the framework of MST for the description of excited states was provided by Natoli *et al* [25] and is known as multichannel multiple scattering theory. It is a generalization of the multiple scattering method to correlated N-electron wavefunctions in the framework of the configuration interaction method. In this scheme the atoms become dynamical entities that can exchange energy with an incoming electron (be it a test electron or a photo-electron in a photoemission and absorption experiment) in such a way that in each collision the total energy of the projectile and the target is conserved: while the atom jumps between its possible quantum states the electron loses or gains energy accordingly, changing its kinetic energy from one scattering event to the next. The various possible quantum atomic excitations can be identified with the local atomic multiplets and are called channels, so that to each channel there corresponds a particular propagation wavevector of the electron. This situation is very similar to an electron–molecule collision described by quantum molecular dynamics, where the same terminology is employed [26]. The amplitude probability for changing channel in a collision process is described by the interchannel atomic T-matrix, which is the natural generalization of the atomic t-matrix of the usual MST, in

which the atom is described by a static potential. Indeed the multichannel MST turns out to be a straightforward generalization of the usual MST: it is sufficient to add a channel index to the atomic T-matrix and take into account that in the free propagation from one atom to the next the wavevector of the electron does not change; in other words, the free propagation is diagonal in the channel index. For more details the reader is referred to [25]. Krüger and Natoli reformulated the theory, providing its first implementation for the description of the $L_{2,3}$-edge absorption spectra using a particle–hole wavefunction [27] and obtaining very good agreement with experiments.

In the present paper we intend to show that the multichannel approach can be used to introduce local correlations not only in the excited states to calculate spectroscopic response functions but also in the ground state wavefunction, using the analyticity of the corresponding Green's function. In so doing we shall be confronted with the necessity of introducing non-local potentials. Even though in DFT the ground state energy is a functional of only the local density, so that a local effective potential is obtained by a functional differentiation of the energy with respect to the density, our ignorance about the form of this functional compels us to use approximate expressions, including non-local quantities such as the one-particle density matrix, in order to obtain accurate representations of the exchange energy (cf the use of Hartree–Fock–Kohn–Sham orbitals in [21], section 8.4). However, in the practical implementation of the theory and in a trade-off of accuracy for simplicity, the use of approximate local potentials is preferred, since this is very convenient for numerical calculations, as in L(S)DA.

Moreover in section 3 below a simple estimate of the range of non-locality of the one-particle density matrix based on the known analytic form for a free electron gas provides a range between 3 and 10 au for valence states, showing that the local approximation might be rather crude. The local approximation is indeed the main source of error in L(S)DA calculations of the correlation energy (see e.g. section 8.7 of [21] and references therein). The generalized gradient approximation by Perdew and Yue, introducing a non-locality correction still in the framework of a local potential, improves this situation considerably. However, its performance has not been studied in strongly correlated extended systems, the properties of which we intend to address in this paper, especially in the case of almost filled bands of 3d or 4f character. Moreover, since the exchange energy is between one and two orders of magnitude higher than the correlation energy, even a small error in the first might be comparable with a substantial fraction of the latter.

In the present paper, our goal is the formulation of a quasi-particle- or many-particle-theory that allows the calculation of both ground and excited state properties such as probed in electron spectroscopies. Therefore, in the calculation of ground state properties, we prefer not to approximate the exchange energy and to work with non-local potentials in the framework of MST, by analogy with the Hartree–Fock–Kohn–Sham method of DFT, which provides

an exact functional form for the exchange [21]. For excited states, non-local potentials are a necessary means both to describe quantum-mechanical exchange and to represent all the degrees of freedom eliminated in the reduction process of the quasi-particle formulation. In this way it is hoped to go beyond DF theory in the description of the physical properties of correlated systems in their ground state and to improve our ability to analyze their SR spectroscopies.

Section 2 presents a new derivation of the solution of the Lippmann–Schwinger equation in the framework of MST for non-local potentials, suitable for a straightforward extension to the multichannel case. Section 2.1 gives the derivation for scattering states, while section 2.2 calculates the Green function and illustrates how it can be used to calculate both the properties of the ground state and the spectroscopic response functions related to excited states. Finally section 3 extends the theory to the multichannel case, illustrates the reduction to the single channel case, calculates the relevant spectroscopic response functions for photoemission and photoabsorption and introduces the multichannel GF as a key ingredient for performing ground state self-consistent calculations taking into account local electronic correlations. To this purpose a generalization of the usual Kohn–Sham implementation of DFT is given in the case where many configurations are present in the ground state wavefunction. Section 4 summarizes the results.

2. Multiple scattering method for scattering and bound states: quasi-particle approach

In this section we assume that we have already reduced the excitation problem to an effective independent particle problem via the knowledge of an effective optical potential $V(\mathbf{r}; \mathbf{r}')$ which is in general non-local. The reduction process will be sketched in section 3. Throughout the paper we shall use real spherical harmonics and shall put for short $J_L(\mathbf{r}; k) \equiv j_l(kr)Y_L(\hat{\mathbf{r}})$, $N_L(\mathbf{r}; k) \equiv n_l(kr)Y_L(\hat{\mathbf{r}})$ and $\tilde{H}_L^+(\mathbf{r}; k) \equiv -\mathrm{i}kh_l^+(kr)Y_L(\hat{\mathbf{r}})$, where j_l, n_l, h_l denote respectively spherical Bessel, Neumann and Hankel functions of order l and L stands for l, m.

2.1. Scattering states

In the quasi-particle approach, we need to solve the Schrödinger equation (in Rydberg units)

$$(\nabla^2 + E)\psi(\mathbf{r}; \mathbf{k}) - \int V(\mathbf{r}; \mathbf{r}')\psi(\mathbf{r}'; \mathbf{k})\, \mathrm{d}^3 r' = 0 \qquad (1)$$

supplemented by the outgoing boundary conditions

$$\psi(\mathbf{r}; \mathbf{k}) \simeq \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} + f(\hat{\mathbf{r}}; \mathbf{k})\frac{\mathrm{e}^{\mathrm{i}kr}}{r} \qquad (2)$$

where $\mathbf{k} = \sqrt{E}$ is the photo-electron wavevector and $f(\hat{\mathbf{r}}; \mathbf{k})$ is the scattering amplitude. We have omitted for simplicity an overall factor $(k/(16\pi^3))^{\frac{1}{2}}$ which takes into account the normalization of the scattering states to one state per Ryd. We assume that $V(\mathbf{r}; \mathbf{r}')$ is a most general optical potential,

i.e. it may be non-local, complex and energy dependent. Its non-local part may be long range, in the sense that it extends well beyond nearest neighbors, although decaying not slower than $1/r^2$ with $r = |\mathbf{r} - \mathbf{r}'|$, which is the behavior of the density matrix in a free electron gas [21].

By introducing the free electron Green function, the solution of the equation

$$(\nabla^2 + E)G_0^+(\mathbf{r} - \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}') \qquad (3)$$

we can transform the differential equation (1) with the boundary condition (2) into an integral equation, known as the Lippmann–Schwinger equation, easier to solve and of more transparent physical interpretation. This equation describes the response of the system, described by the potential $V(\mathbf{r}; \mathbf{r}')$, to an exciting plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ and is given by

$$\psi(\mathbf{r}; \mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}} + \int G_0^+(\mathbf{r} - \mathbf{r}'; E)V(\mathbf{r}'; \mathbf{r}'')$$
$$\times \, \psi(\mathbf{r}''; \mathbf{k}) \, d^3r' \, d^3r''. \qquad (4)$$

By applying the operator $(\nabla^2 + E)$ to the left-hand side, taking into account equation (3) and that $(\nabla^2 + E)e^{i\mathbf{k}\cdot\mathbf{r}} = 0$, we easily find that the solution (4) obeys equation (1). As for the boundary conditions, we use the fact that the solution of equation (3) is given at large $\mathbf{r}$ by

$$G_0^+(\mathbf{r} - \mathbf{r}'; E) = -\frac{1}{4\pi} \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$$
$$\approx \frac{e^{ikr(1-\mathbf{r}\cdot\mathbf{r}'/r^2)}}{r} \qquad (r \to \infty) \qquad (5)$$

which, when inserted in (4), provides an explicit expression for the scattering amplitude $f(\hat{\mathbf{r}}; \mathbf{k})$. Its modulus squared is the cross-section of an impinging electronic plane wave onto the scattering potential. Due to the expansions [25]

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_L i^l Y_L(\hat{\mathbf{k}}) J_L(\mathbf{r}; k) \qquad (6)$$

$$G_0^+(\mathbf{r} - \mathbf{r}'; E) = \sum_L J_L(\mathbf{r}; k)\tilde{H}_L^+(\mathbf{r}'; k) \qquad (r < r') \ (7)$$

$$= \sum_L J_L(\mathbf{r}'; k)\tilde{H}_L^+(\mathbf{r}; k) \qquad (r > r') \ (8)$$

and the linearity of equation (4), we can write the corresponding solution as

$$\psi(\mathbf{r}; \mathbf{k}) = \sum_L A_L(\mathbf{k})\psi_L(\mathbf{r}; k) \qquad (9)$$

where $A_L = 4\pi i^l Y_L(\hat{\mathbf{k}})$ and $\psi_L(\mathbf{r}; k)$ is the wavefunction in response to an exciting wave with angular momentum (AM) L, satisfying the equation

$$\psi_L(\mathbf{r}; k) = J_L(\mathbf{r}; k) + \int G_0^+(\mathbf{r} - \mathbf{r}'; k)V(\mathbf{r}'; \mathbf{r}'')$$
$$\times \, \psi_L(\mathbf{r}''; k) \, d^3r' \, d^3r''. \qquad (10)$$

Remembering the relations (6)–(8), we see that at great distances

$$\psi_L(\mathbf{r}; k) = J_L(\mathbf{r}; k) + \sum_{L'} \tilde{H}_{L'}^+(\mathbf{r}; k)$$
$$\times \int J_{L'}(\mathbf{r}'; k)V(\mathbf{r}'; \mathbf{r}'')\psi_L(\mathbf{r}''; k) \, d^3r' \, d^3r''$$
$$= J_L(\mathbf{r}; k) + \sum_{L'} \tilde{H}_{L'}^+(\mathbf{r}; k)T_{L'L} \qquad (11)$$

where we have defined $T_{L'L}$ as

$$T_{L'L} = \int J_{L'}(\mathbf{r}; k)V(\mathbf{r}; \mathbf{r}')\psi_L(\mathbf{r}'; \mathbf{k}) \, d^3r \, d^3r'. \qquad (12)$$

The quantity $T_{L'L} = T_{LL'}$ is known as the T-matrix of the potential and measures the scattering response to an incident wave of angular momentum L into one with angular momentum L'.

In MST we now partition the space in terms of non-overlapping space-filling cells Ω_j with surfaces S_j and origins at $\mathbf{R}_j$ and introduce local variables $\mathbf{r}_j = \mathbf{r} - \mathbf{R}_j$. The partition is assumed to satisfy the requirement that the shortest inter-cell vector $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ joining the origins of the nearest neighbor cells i and j is larger than any intra-cell vector $\mathbf{r}_i$ or $\mathbf{r}_j$, when $\mathbf{r}$ is inside cell i or cell j. If necessary, empty cells can be introduced to satisfy this requirement. We also assume that there exists a finite neighborhood around the origin of each cell lying in the domain of the cell [28].

Accordingly, we split the potential V as $\bar{V} + \Delta V$, where $\bar{V}(\mathbf{r}; \mathbf{r}')$ is different from zero only for $\mathbf{r}, \mathbf{r}'$ inside the same cell. $\bar{V}$ is partitioned into cell potentials, such that $\bar{V}(\mathbf{r}; \mathbf{r}') = \sum_j \bar{v}_j(\mathbf{r}_j; \mathbf{r}_j')$, where $\bar{v}_j(\mathbf{r}_j; \mathbf{r}_j')$ takes the value of $\bar{V}(\mathbf{r}; \mathbf{r}')$ for $\mathbf{r}, \mathbf{r}'$ inside cell j and vanishes elsewhere. In the following we disregard the part ΔV of the non-local potential extending beyond the cell, which will be included in a second step.

We introduce as well local scattering solutions of the form of equation (10), but referred to the center R_j of cell Ω_j and relative to the potential $\bar{v}_j(\mathbf{r}_j)$

$$\bar{\psi}_L(\mathbf{r}_j; k) = J_L(\mathbf{r}_j; k)$$
$$+ \int_{\Omega_j} G_0^+(\mathbf{r}_j - \mathbf{r}_j'; k)\bar{v}_j(\mathbf{r}_j'; \mathbf{r}_j'')\bar{\psi}_L(\mathbf{r}_j''; k) \, d^3r_j' \, d^3r_j'' \qquad (13)$$

so that the global solution $\psi(\mathbf{r}; \mathbf{k})$ in (4) can be represented locally in each cell Ω_j by the expression [28]

$$\bar{\psi}(\mathbf{r}_j; \mathbf{k}) = \sum_L \bar{C}_L^j(\mathbf{k})\bar{\psi}_L(\mathbf{r}_j; k). \qquad (14)$$

The coefficients $\bar{C}_L^j(\mathbf{k})$ are to be determined by the condition that the global solution be smoothly continuous at the common boundaries of contiguous cells.

A simple way to obtain this condition is to rewrite equation (4) referred to a particular center $\mathbf{R}_i$, so that we have

$$\bar{\psi}(\mathbf{r}_i; \mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}_i} e^{i\mathbf{k}\cdot\mathbf{R}_i}$$
$$+ \int_{\Omega_i} G_0^+(\mathbf{r}_i - \mathbf{r}_i'; k)\bar{v}_i(\mathbf{r}_i'; \mathbf{r}_i'')\bar{\psi}(\mathbf{r}_i''; k) \, d^3r_i' \, d^3r_i''$$
$$+ \sum_{j\neq i} \int_{\Omega_j} G_0^+(\mathbf{r}_j - \mathbf{r}_j'; k)\bar{v}_j(\mathbf{r}_j'; \mathbf{r}_j'')$$
$$\times \, \bar{\psi}(\mathbf{r}_j''; k) \, d^3r_j' \, d^3r_j''. \qquad (15)$$

By using the local representation (14) and equation (13) we find

$$\sum_L \bar{C}_L^i(\mathbf{k}) J_L(\mathbf{r}_i; k) = \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_i} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{R}_i}$$

$$+ \sum_{j\neq i} \int_{\Omega_j} G_0^+(\mathbf{r}_j - \mathbf{r}_j'; k) \bar{v}_j(\mathbf{r}_j'; \mathbf{r}_j'')$$

$$\times \sum_L \bar{C}_L^j(\mathbf{k}) \bar{\psi}_L(\mathbf{r}_j''; k) \, \mathrm{d}^3 r_j' \, \mathrm{d}^3 r_j''.$$

$$(16)$$

The derivation now proceeds along the lines of traditional MST [28, 12, 15]. We take r_i in the neighborhood of the origin of cell Ω_i and use the two center re-expansion of the free GF [25]

$$G_0^+(\mathbf{r} - \bar{\mathbf{r}}'; k) = \sum_{LL'} J_L(\mathbf{r}_i; k) G_{LL'}^{ij} J_{L'}(\mathbf{r}_j; k) \qquad (17)$$

which converges absolutely and uniformly in both cells provided $R_{ij} > r_i + r_j$. This is a condition satisfied for muffin-tin cells, but not in general for space-filling cells. In [16, 17] it is shown that a rigorous derivation of the MS equations can be achieved by assuming the weaker condition $R_{ij} > \max(r_i, r_j)$, separately for each pair of cells, a relation assured by the conditions assumed above for the partition of the space. Since we can take r_i arbitrarily near to the origin of cell i, the absolute convergence of the expansion (17) is always assured. In equation (17) $G_{LL'}^{ij}$ are the free electron propagator in the site and angular momentum basis (KKR real space structure factors) given by

$$G_{LL'}^{ij} = 4\pi \sum_{L''} C(L, L'; L'') \mathrm{i}^{l-l'+l''} \tilde{H}_{L''}^+(\mathbf{R}_{ij}; k) \qquad (18)$$

where

$$C(L, L'; L'') = \int Y_L(\Omega) Y_{L'}(\Omega) Y_{L''}(\Omega) \, \mathrm{d}\Omega. \qquad (19)$$

Projecting equation (16) onto the spherical harmonics (SH) $Y_L(\hat{\mathbf{r}})$, eliminating the common factor $j_l(kr_i)$ and remembering the definition (12) for the cell $\bar{T}^j$-matrix relative to the potential $\bar{V}$, we find the following algebraic equations for the coefficients $\bar{C}_L^i(\mathbf{k})$:

$$\bar{C}_L^i(\mathbf{k}) = I_L^i(\mathbf{k}) + \sum_{j\neq i} \sum_{L'L''} G_{LL'}^{ij} \bar{T}_{L'L''}^j \bar{C}_{L''}^j(\mathbf{k}) \qquad (20)$$

where

$$I_L^i(\mathbf{k}) = \sqrt{\frac{k}{\pi}} \mathrm{i}^l Y_L(\hat{\mathbf{k}}) \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{R}_i}. \qquad (21)$$

Notice that in the last expression we have reinserted the factor $(k/(16\pi^3))^{\frac{1}{2}}$ necessary to normalize the scattering states to one state per Ryd, which had been omitted for simplicity in equation (2). These relations describe the propagation of the site and angular momentum amplitudes $C_L^i(\mathbf{k})$ from one site to another analogous to that described by the Lippmann–Schwinger equation (4) for the point amplitudes $\psi(\mathbf{r}; \mathbf{k})$, except that now the scattering power of the potential at point $\mathbf{r}$ is replaced by the corresponding scattering strength

$T_{LL'}^j$ of the cell at site j. They can be viewed as a Dyson equation for the expansion coefficients $C_L^i(\mathbf{k})$.

Reference [17] gives a new scheme to calculate the scattering amplitudes $T_{LL'}^j$ in the case of a local potential, based on a method to generate local basis functions for truncated potential cells that is simple, fast, efficient, valid for any shape of the cell and does not make use of cell shape functions expanded in spherical harmonics, reducing in this way to the minimum their number in the expansion of the scattering wavefunction. Such a method has overcome the major stumbling block for the development of a full-potential MS theory. For a non-local potential the solution can be found along the same lines as for the Hartree–Fock equations by an iterative procedure starting from the local solution. If necessary, a local exchange can be added and subtracted in order to make the iterative procedure converge faster. It is interesting to note that the non-locality of the potential $\bar{V}$ does not affect the intuitive interpretation of MST, since in the Dyson equation (20) only the physical scattering amplitudes of the various cells intervene.

In MST it is expedient to work with other amplitudes $\bar{B}_L^j(\mathbf{k})$ such that

$$\bar{B}_L^j(\mathbf{k}) = \sum_{L'} \bar{T}_{LL'}^j \bar{C}_{L'}^j(\mathbf{k}) \qquad (22)$$

by expanding locally the scattering function in terms of new basis functions given by

$$\bar{\Phi}_L(\mathbf{r}_j; k) = \sum_{L'} [T^j]_{L'L}^{-1} \bar{\psi}_{L'}(\mathbf{r}_j; k) \qquad (23)$$

so that now

$$\bar{\psi}(\mathbf{r}_j; \mathbf{k}) = \sum_L \bar{B}_L^j(\mathbf{k}) \bar{\Phi}_L(\mathbf{r}_j; k). \qquad (24)$$

On the basis of equation (20), the new MS equation are easily seen to be

$$\sum_{L'} (\bar{T}^i)_{LL'}^{-1} \bar{B}_{L'}^i(\mathbf{k}) - \sum_{j,L'}^{j\neq i} G_{LL'}^{ij} \bar{B}_{L'}^j(\mathbf{k}) = I_L^i(\mathbf{k}) \qquad (25)$$

from which we derive the solution

$$\bar{B}_L^i(\mathbf{k}) = \sum_{jL'} \tau_{LL'}^{ij} I_{L'}^j(\mathbf{k}) = \sqrt{\frac{k}{\pi}} \sum_{jL'} \tau_{LL'}^{ij} \mathrm{i}^{l'} Y_{L'}(\hat{\mathbf{k}}) \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{R}_i} \quad (26)$$

in terms of the scattering path operator $\boldsymbol{\tau}$, the inverse of the MS matrix $(\bar{\mathbf{T}}^{-1} - \mathbf{G})$

$$\boldsymbol{\tau} = (\bar{\mathbf{T}}^{-1} - \mathbf{G})^{-1}. \qquad (27)$$

As usual, we have introduced matrices labeled by the site and angular momentum indices. Equations (26) and (25) show that the quantities $B_L^i(\mathbf{k})$ are scattering amplitudes, which in the case of real potentials satisfy the generalized optical theorem [29, 25]

$$\int \mathrm{d}\hat{\mathbf{k}} \, \bar{B}_L^i(\mathbf{k}) [\bar{B}_{L'}^j(\mathbf{k})]^* = -\frac{1}{\pi} \mathrm{Im}\tau_{LL'}^{ij}. \qquad (28)$$

This relation is very important, since it establishes the connection between the photoemission and the photoabsorption

cross-section [17]. Moreover, $-\text{Im}\,\tau_{LL}^{ii}$ is proportional to the L-projected density of states onto site i. All this is obviously valid for a non-local potential with support only inside each cell.

The solution for the whole potential V, including the non-local long range part ΔV, can now be found in the following way. Writing in equation (10) $|\psi_L\rangle = |\bar{\psi}_L\rangle + |\Delta\psi_L\rangle$ we have, in operator form,

$$|\bar{\psi}_L\rangle + |\Delta\psi_L\rangle = |J_L\rangle + G_0^+(\bar{V} + \Delta V)(|\bar{\psi}_L\rangle + |\Delta\psi_L\rangle) \quad (29)$$

where $|\bar{\psi}_L\rangle = |J_L\rangle + G_0^+\bar{V}|\bar{\psi}_L\rangle$ is the solution of equation (10) already found in terms of MST. Therefore $|\Delta\psi_L\rangle$ obeys the following equation:

$$|\Delta\psi_L\rangle = G_0^+\bar{V}|\Delta\psi_L\rangle + G_0^+\Delta V|\bar{\psi}_L\rangle + G_0^+\Delta V|\Delta\psi_L\rangle. \quad (30)$$

Neglecting for the moment the last term in this equation we have

$$|\Delta\psi_L\rangle = G_0^+\bar{V}|\Delta\psi_L\rangle + G_0^+\Delta V|\bar{\psi}_L\rangle. \quad (31)$$

This is an equation similar to (10) with a kernel $G_0^+\bar{V}$ and an inhomogeneous term given by $G_0^+\Delta V|\bar{\psi}_L\rangle$. Projecting the solution onto cell Ω_i, noticing that ΔV is zero inside Ω_i by definition and remembering equation (17), this term takes the form

$$\sum_L J_L(\mathbf{r}_i)K_L^i(\mathbf{k}) \quad (32)$$

where, indicating by S the whole space,

$$K_L^i(\mathbf{k}) = \sum_{jL'} G_{LL'}^{ij} \int_{S-\Omega_i} J_{L'}(\mathbf{r}_j)\Delta V(\mathbf{r}_j;\mathbf{r}')\bar{\psi}_L(\mathbf{r}')\,\mathrm{d}^3r_j\,\mathrm{d}^3r'. \quad (33)$$

Notice that a convergence problem might arise for cells Ω_j, nearest neighbors of cell Ω_i, where, for points near the cell boundaries, $r_i + r_j$ might be greater than R_{ij}. The way to bypass this difficulty is to use the displaced cell approach (see, for example, section 6.5.3 of [12] and appendix G of [17]), whereby one can write

$$\sum_L J_L(\mathbf{r}_i)K_L^i(\mathbf{k}) \equiv \sum_{j\Lambda} \left\{ \sum_{LL'} J_{L\Lambda}(\mathbf{b})J_L(\mathbf{r}_i)G_{\Lambda L'}(\mathbf{R}_{ij}+\mathbf{b}) \right.$$
$$\left. \times \int_{S-\Omega_i} J_{L'}(\mathbf{r}_j)\Delta V(\mathbf{r}_j;\mathbf{r}')\bar{\psi}_L(\mathbf{r}')\,\mathrm{d}^3r_j\,\mathrm{d}^3r' \right\} \quad (34)$$

obtaining a convergent result, provided $|\mathbf{R}_{ij}+\mathbf{b}| > R_i^b + R_j^b$ (where again R_i^b is the bounding sphere of cell Ω_i) and the sums inside the curly brackets are performed first. Equation (34) can serve as a definition for $K_L^i(\mathbf{k})$ by projection onto the complete set of functions $J_L(\mathbf{r}_i)$. Here $J_{LL'}(\mathbf{b})$ is the usual translation operator in MST as defined in [12]. Notice that the vector $\mathbf{b}$ depends only on the geometry of the partition of the space in cells and is independent of L. Equation (34) reduces to equation (33) at points for which $r_i + r_j < R_{ij}$.

With this proviso we can expand $|\Delta\psi_L\rangle$ in terms of the same basis functions as for $|\bar{\psi}_L\rangle$. Following the same lines as the solution illustrated above, the new scattering amplitudes

$B_L^i(\mathbf{k})$ that include the correction introduced by ΔV are given by

$$B_L^i(\mathbf{k}) = \sum_{jL'} \tau_{LL'}^{ij}(t_{L'}^j(\mathbf{k}) + K_{L'}^j(\mathbf{k}))$$
$$= \sqrt{\frac{k}{\pi}} \sum_{jL'} \tau_{LL'}^{ij}(i^{l'} Y_{L'}(\hat{\mathbf{k}})e^{i\mathbf{k}\cdot\mathbf{R}_i} + K_{L'}^j(\mathbf{k})). \quad (35)$$

Now, in order to take into account the last neglected term in (30) we use this expression for $B_L^i(\mathbf{k})$ in place of the old amplitudes (26) to calculate $\bar{\psi}_L(\mathbf{r}')$ in (33) and iterate this procedure until self-consistence. This procedure should converge if the perturbation ΔV is 'small' enough, i.e. if the trace of $\text{Tr}(G_0^- \Delta V^\dagger G_0^+ \Delta V) < 1$ for energies E not on the real axis.

Expression (35) can be used to calculate the response functions for core spectroscopies. But in this case the presence of the extra term $K_{L'}^j(\mathbf{k})$ invalidates the generalized optical theorem so that to calculate absorption spectra it is preferable to use the expression for the complete GF, which is calculated in the next section 2.2. Here we also give an alternative method to calculate $|\psi_L\rangle$ in terms of the Green's function for the potential $\bar{V}$.

2.2. Green's function

As already anticipated in section 1, one of the major advantages of MST is the direct access to the Green's function of the system. Having an explicit expression for this quantity is of the utmost importance both for writing down spectroscopic response functions (see [18]) and for the calculation of ground state properties through contour integration in the complex energy plane (see e.g. [10] and references therein).

The GF is a solution of the Schrödinger equation with a source term

$$(\nabla^2 + E)G^\pm(\mathbf{r}, \mathbf{r}'; E)$$
$$- \int \mathrm{d}^3r'' V(\mathbf{r}, \mathbf{r}'')G^\pm(\mathbf{r}'', \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}'). \quad (36)$$

It is known that a formal solution of this equation is given by

$$G^\pm(\mathbf{r}, \mathbf{r}'; E) = \sum_n \frac{\psi_n^\star(\mathbf{r})\psi_n(\mathbf{r}')}{E - E_n \pm i\eta} \quad (37)$$

where the sum runs over all eigenfunctions ψ_n, whether discrete or continuous, of the associated Schrödinger equation (1). Henceforth, we shall omit the indication of the analyticity behavior, unless necessary. From this expression it is clear that in the complex energy plane

$$\frac{1}{2\pi} \oint_C G(\mathbf{r}, \mathbf{r}; E)\,\mathrm{d}E = \sum_{n\in C} |\psi_n(\mathbf{r})|^2 \quad (38)$$

where now the sum runs over the states with energy inside the contour C. Moreover, the density of states can be found simply as

$$-\frac{1}{\pi}\text{Im} \int \mathrm{d}^3r\, G^+(\mathbf{r}, \mathbf{r}; E) = \sum_n \delta(E - E_n). \quad (39)$$

As for the wavefunction, we observe that equation (36) can be transformed into the corresponding Lippmann–Schwinger equation

$$G(\mathbf{r}, \mathbf{r}'; E) = G_0(\mathbf{r} - \mathbf{r}'; E)$$
$$+ \int G_0(\mathbf{r} - \mathbf{r}_1; E) V(\mathbf{r}_1; \mathbf{r}_2) G(\mathbf{r}_2, \mathbf{r}'; E) \, d^3 \mathbf{r}_1 \, d^3 \mathbf{r}_2. \quad (40)$$

Following the partition of the potential $V = \bar{V} + \Delta V$ introduced in the previous section, we first solve for $\bar{V}$ in the framework of MST. The solution corresponding to equation (40) for this potential can be found by the procedure used by Zeller [30]. The result is

$$\bar{G}(\mathbf{r}_i, \mathbf{r}'_j; E) = \sum_{LL'} \bar{\psi}_L(\mathbf{r}_i)[(\mathbf{I} - \mathbf{G\bar{T}})^{-1}\mathbf{G}]^{ij}_{LL'} \bar{\psi}_{L'}(\mathbf{r}'_j)$$
$$+ \delta_{ij} \sum_L \bar{\psi}_L(\mathbf{r}_<) \Psi_L(\mathbf{r}_>) \quad (41)$$

where $\mathbf{r}_<$ ($\mathbf{r}_>$) indicates the lesser (the greater) of r_i and r'_i. The function $\Psi_{L'}(\mathbf{r})$ is the irregular solution in cell i that matches smoothly to $\tilde{H}^+_{L'}(\mathbf{r})$ at R^i_{b}.

The solution G for the entire potential is then seen to satisfy the equation

$$G = \bar{G} + \bar{G}\Delta V G = \bar{G} + G\Delta V \bar{G} \quad (42)$$

remembering that by definition $(\Delta + E - \bar{V})\bar{G} = I$, and can be obtained by iteration if again $\mathrm{Tr}(\bar{G}^- \Delta V^\dagger \bar{G}^+ \Delta V) < 1$. The first few iterations should be sufficient.

We notice, *en passant*, that $|\psi\rangle$, the wavefunction obeying the Lippmann–Schwinger equation for the full potential V, satisfies an equation equivalent to (42),

$$|\psi\rangle = |\bar{\psi}\rangle + \bar{G}\Delta V|\psi\rangle \quad (43)$$

the solution of which can again be found by iteration. The zeroth order approximation of this equation provides the same solution as (31) with G_0 replaced by $\bar{G}$ and constitutes a preferred starting point for an iterative procedure. We shall discuss in section 3 the range of the non-local potential ΔV.

As mentioned above, the solution of (40), together with equation (38), constitutes the basis for the self-consistent calculations of the ground state either of periodic systems (by working in Fourier space) [10] or in real space [31] in the framework of the local density approximation to DF theory. In this case the MS solution for the Green's function $\bar{G}$ in (41) is sufficient.

In practice, given an initial potential constructed on the basis of an initial density $\rho_0(\mathbf{r})$ according to a certain functional expression, one constructs the GF (41) and finds the associated density according to the relation

$$-\frac{1}{\pi} \mathrm{Im} \int_{-\infty}^{E^1_{\mathrm{F}}} G^+(\mathbf{r}, \mathbf{r}; E) \, dE = \rho_1(\mathbf{r}) \quad (44)$$

where the integral can be calculated by deforming the integration path in the complex plane and E^1_{F} is obtained from the relation

$$\int d^3\mathbf{r} \, \rho_1(\mathbf{r}) = N. \quad (45)$$

N being the total number of electrons in the system. This new density can serve to build a second potential to generate a second GF and a second E^2_{F} and so on, until self-consistency. It can be shown that this procedure minimizes also the ground state energy. Moreover, calculations in periodic and finite systems can now be done efficiently in full-potential mode [10, 17].

The knowledge of the self-consistent GS density is convenient for calculating the effective optical potential in the local density approximation in emission spectroscopy where, according to the final state rule, the final state to be considered is the GS of the system. However, the procedure can also be useful for excited states with a deep core hole in absorption spectroscopy, since with good approximation these can be considered as the GS of the system for the $Z + 1$ impurity atom. In this way one can assess e.g. relative edge shifts in compounds where the photoabsorber enters with different formal valences, and in general investigate effects related to the self-consistent density. Moreover, it is known that in the absorption cases where the excited photo-electron almost fills up a final state band (e.g. CuO) the Pauli principle blocks charge screening, so the LD optical potential should be constructed using the GS density.

It is clear from equation (37) that the GF contains information not only on the occupied states of the system but also on the unoccupied ones, so it can be used to construct the response function for core electron spectroscopies. We refer the reader to [17] for the treatment of this subject in the case of local general potentials.

3. Multichannel multiple scattering theory

3.1. Multichannel spectroscopies: scattering states

To fix the ideas we start by calculating the angular-resolved photoemission cross-section in the many-body case, which is the basis for all other x-ray spectroscopies. In this experiment, photo-electrons of energy $E = k^2$ are detected along a direction $\hat{\mathbf{k}}$ determined by the user. In this section, for the convenience of the reader, we shall use the notations of [25] for the statement of the problem, so that it will be easier to underline similarities and differences with the previous paper.

The expression for the photoemission cross-section for the ejection of a photo-electron of final momentum $\mathbf{k}$ and kinetic energy k^2 along the direction $\hat{\mathbf{k}}$ can be written as [18]

$$\frac{d\sigma(\omega)}{d\hat{\mathbf{k}}} = 4\pi^2 \alpha \hbar \omega \left| \langle \Theta \Psi^N_{\mathbf{k}} | \hat{\boldsymbol{\varepsilon}} \cdot \sum_{i=1}^N \mathbf{r}_i | \Psi^N_{\mathrm{g}} \rangle \right|^2 \quad (46)$$

where $\Psi^N_{\mathbf{k}}$ is the many-body final scattering state, normalized to one state per energy interval unit, for the N-electron system with one electron of momentum $\mathbf{k}$ traveling to infinity, and Ψ^N_{g} its ground state with respective energies E^N_k and E^N_{g}. Here α is the fine structure constant, $\hbar\omega$ the incoming photon energy and $\hat{\boldsymbol{\varepsilon}}$ its polarization. Energy conservation imposes that $\hbar\omega = E^N_k - E^N_{\mathrm{g}}$. According to Breit and Bethe [32], in order to satisfy the correct boundary conditions for the ejected photo-electron (no electron in a continuum state in the remote past), we must

take the time-reversed scattering state by application of the time-reversal operator Θ.

In the case of photoemission from a deep core state $\phi_{L_0}^c$ of angular momentum $L_0 = (l_0, m_0)$, we assume that, to a good approximation,

$$
\begin{aligned}
\Psi_g^N(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) &= (N!)^{1/2} A \phi_{L_0}^c(\mathbf{r}) \\
&\times \sum_n c_n \Phi_n^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) \\
&= (N!)^{1/2} A \phi_{L_0}^c(\mathbf{r}) \Psi_g^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})
\end{aligned} \tag{47}
$$

where A is the usual antisymmetrizing operator ($A = 1/N! \sum_P (-1)^P P$, with $A^2 = A$, P being the permutation operator) and $\Phi_n^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})$ are Slater determinants describing the configurations present in the ground state of the system. Normalization imposes $\sum_n |c_n|^2 = 1$ if $\langle \phi_c | \phi_c \rangle = 1$ and for simplicity of presentation we shall omit spin variables, though their introduction into the theory would be straightforward. Moreover, we treat here only the non-relativistic case, although the method could be extended with some labor to the relativistic one.

In a similar way, we can write without loss of generality

$$
\begin{aligned}
\Psi_f^N(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) &= (N!)^{1/2} A \\
&\times \sum_\alpha \phi_\alpha^f(\mathbf{r}) \tilde{\Psi}_\alpha^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})
\end{aligned} \tag{48}
$$

where α labels any complete basis set and where the functions ϕ_α^f, ignoring exchange effects, can be thought to describe the excited photo-electron while the $\tilde{\Psi}_\alpha^{N-1}$ states are normalized eigenstates of the Hamiltonian H^{N-1} describing the remaining $(N-1)$-electron system with eigenvalues $\tilde{E}_\alpha^{N-1}$:

$$
H^{N-1} \tilde{\Psi}_\alpha^{N-1} = \tilde{E}_\alpha^{N-1} \tilde{\Psi}_\alpha^{N-1}. \tag{49}
$$

The tilde over them stands as a reminder that in the expansion (48) the relaxed states around the core hole are dominant. If needed, they can be in turn expanded in terms of Slater determinants describing the intervening configurations in the final state. The expansion in (48) is akin to the eigenfunction-expansion method in quantum molecular dynamics [26, 33]. For example, in electron–molecule scattering, the total scattering wavefunction is expanded in terms of eigenfunctions of the target state (the molecule). In a photoemission experiment, the photo-electron plays the role of the impinging electron (which in this case is generated inside the system), while the rest of the $(N-1)$-particle system represents the target. Borrowing the term from electron–molecule scattering theory, we call the states $\tilde{\Psi}_\alpha^{N-1}$ final state channels. This similarity is not surprising, since in the photoemission process the time-reversed scattering wavefunction appears in equation (46). We sketch the analogy between photoemission and electron scattering in section B. Here and henceforth the index f in the final state Ψ_f^N can be replaced by $\mathbf{k}$ whenever we deal specifically with the scattering state $\Psi_\mathbf{k}^N$.

The wavefunction Ψ_f^N is an eigenstate of the total Hamiltonian H^N with eigenvalue $E_f^N = E_g^N + \hbar\omega$, i.e.

$$
H^N \Psi_f^N = E_f^N \Psi_f^N. \tag{50}
$$

Moreover,

$$
\begin{aligned}
H^N &= -\nabla_\mathbf{r}^2 + \sum_i^{1,N-1} \frac{2}{|\mathbf{r} - \mathbf{r}_i|} - \sum_{k=1}^{N_a} \frac{2Z_k}{|\mathbf{r} - \mathbf{R}_k|} + H^{N-1} \\
&= -\nabla_\mathbf{r}^2 + \sum_i^{1,N-1} V(\mathbf{r}, \mathbf{r}_i) + \Phi_Z(\mathbf{r}) + H^{N-1}.
\end{aligned} \tag{51}
$$

N_a being the number of atomic sites and $\Phi_Z(\mathbf{r})$ the total nuclear potential.

By inserting (48) into (50), projecting onto the states $\tilde{\Psi}_\alpha^{N-1}$ and using (49), one obtains for the amplitude functions ϕ_α^f the set of coupled equations

$$
\begin{aligned}
(\nabla^2 &+ k_\alpha^2) \left(\phi_\alpha^f(\mathbf{r}) - \sum_\beta \int \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}') \phi_\beta^f(\mathbf{r}') \mathrm{d}\mathbf{r}' \right) \\
&= \sum_\beta \int V_{\alpha\beta}^1(\mathbf{r}, \mathbf{r}') \phi_\beta^f(\mathbf{r}') \, \mathrm{d}\mathbf{r}' \\
&+ \sum_\beta \int V_{\alpha\beta}^2(\mathbf{r}, \mathbf{r}') \phi_\beta^f(\mathbf{r}') \, \mathrm{d}\mathbf{r}'
\end{aligned} \tag{52}
$$

where

$$
\begin{aligned}
k_\alpha^2 &= \hbar\omega - (E_g^{N-1} - E_g^N) - (\tilde{E}_\alpha^{N-1} - E_g^{N-1}) \\
&= \hbar\omega - I_c - \Delta E_\alpha.
\end{aligned} \tag{53}
$$

I_c being the ionization potential for the core state and ΔE_α the excitation energy left behind in the $(N-1)$-particle system. In equation (52) the second non-local term in the left-hand side comes from the presence of the antisymmetrizing operator A in the expansion (48) and is expressed in terms of the interchannel one-particle density matrix

$$
\begin{aligned}
\rho_{\alpha\beta}(\mathbf{r}'; \mathbf{r}) &= \rho_{\beta\alpha}^*(\mathbf{r}; \mathbf{r}') = (N-1) \\
&\times \int \tilde{\Psi}_\alpha^{(N-1)*}(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N-1}) \\
&\times \tilde{\Psi}_\beta^{N-1}(\mathbf{r}', \mathbf{r}_2, \ldots, \mathbf{r}_{N-1}) \, \mathrm{d}\mathbf{r}_2 \cdots \mathrm{d}\mathbf{r}_{N-1}.
\end{aligned} \tag{54}
$$

The non-local interchannel potentials $V_{\alpha\beta}^1(\mathbf{r}, \mathbf{r}')$ are the matrix elements between states $\tilde{\Psi}_\alpha^{N-1}$ and $\tilde{\Psi}_\beta^{N-1}$ of the interaction potential $V(\mathbf{r}, \mathbf{r}_i)$ plus the external nuclear potential $\Phi_Z(\mathbf{r})$ and include local terms as well as non-local exchange terms originating from the exchange interaction. Explicitly, in terms of the density matrix (54), we have $V_{\alpha\beta}^1(\mathbf{r}, \mathbf{r}') = V_{\alpha\beta}^d(\mathbf{r}, \mathbf{r}') + V_{\alpha\beta}^{\mathrm{exc}}(\mathbf{r}, \mathbf{r}')$, where

$$
\begin{aligned}
V_{\alpha\beta}^d(\mathbf{r}, \mathbf{r}') &= \delta(\mathbf{r} - \mathbf{r}') \\
&\times \left[\int \rho_{\alpha\beta}(\mathbf{r}''; \mathbf{r}'') \frac{2}{|\mathbf{r} - \mathbf{r}''|} \, \mathrm{d}\mathbf{r}'' + \Phi_Z(\mathbf{r}) \delta_{\alpha\beta} \right] \\
V_{\alpha\beta}^{\mathrm{exc}}(\mathbf{r}, \mathbf{r}') &= -\rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}') \\
&\times \left[\frac{2}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2}(\Phi_Z(\mathbf{r}) + \Phi_Z(\mathbf{r}')) \right].
\end{aligned} \tag{55}
$$

Moreover

$$V_{\alpha\beta}^2(\mathbf{r}, \mathbf{r}') = -\int \rho_{\alpha\beta}^2(\mathbf{r}, \mathbf{r}''; \mathbf{r}', \mathbf{r}'')$$
$$\times \left(\frac{2}{|\mathbf{r}'' - \mathbf{r}|} + \frac{2}{|\mathbf{r}'' - \mathbf{r}'|} \right) d\mathbf{r}'' \quad (56)$$

is given in terms of the two-particle density matrix

$$\rho_{\alpha\beta}^2(\mathbf{r}', \mathbf{r}''; \mathbf{r}, \mathbf{r}'') = (N-1)(N-2)/2$$
$$\times \int \tilde{\Psi}_\alpha^{(N-1)*}(\mathbf{r}, \mathbf{r}'', \ldots, \mathbf{r}_{N-1})$$
$$\times \tilde{\Psi}_\beta^{N-1}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}_{N-1}) d\mathbf{r}_3 \cdots d\mathbf{r}_{N-1} \quad (57)$$

which, if necessary, can be approximated in terms of one-particle density matrices, as shown in section 3.3. In equations (55) and (56) we have symmetrized respectively the external potential $\Phi_Z(\mathbf{r})$ and the Coulomb interaction $2/|\mathbf{r}'' - \mathbf{r}|$ due to the fact that when summed over β in equation (52) the two terms give the same contribution. This shows explicitly the hermiticity of the interchannel potential. Likewise one can show that

$$(\nabla_{\mathbf{r}}^2 + k_\alpha^2) \sum_\beta \int \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}') \phi_\beta^f(\mathbf{r}') d\mathbf{r}'$$
$$= \sum_\beta \int [(\nabla_{\mathbf{r}'}^2 + k_\beta^2) \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')] \phi_\beta^f(\mathbf{r}') d\mathbf{r}' \quad (58)$$

where $\nabla_{\mathbf{r}'}^2$ acts only on ρ. This implies that this term is also Hermitian. These properties of the density matrix are shown in section A.

The difference between the present approach and that of two earlier papers on the same subject lies in the fact that in [25] a local density approximation of the exchange interchannel potential was assumed to be feasible, without however specifying the actual procedure for performing such an operation, while in [27] the non-locality (and the orthogonalization of the photo-electron final state wavefunction to the initially occupied states) was imposed only inside the photoabsorbing cell. No good approximation was found in the first case at low photo-electron energies, whereas the second approach was found to be good in the nearly empty band case (Ca and Ti compounds, for example [27, 34]) but failed, although not too badly, in the nearly full band case, as in the CuO compound. The need to also orthogonalize the excited electron wavefunction on the ligand was quite evident. A simple argument bears this out. We can estimate the correlation length of $\rho_{\alpha\alpha}(\mathbf{r}; \mathbf{r}')$ for valence states in terms of a free electron gas model, whereby (see page 107 of [21])

$$\rho_{\alpha\alpha}(\mathbf{r}; \mathbf{r}') = \rho\left(\frac{\mathbf{r} + \mathbf{r}'}{2}\right) \frac{\sin t - t \cos t}{t^3} \quad (59)$$

where $\rho(\mathbf{r})$ is the density at point $\mathbf{r}$, $t = k_F(\mathbf{r})|\mathbf{r} - \mathbf{r}'|$ and $k_F(\mathbf{r}) = (3\pi^2 \rho(\mathbf{r}))^{1/3} = 1/(0.52 r_s)$, r_s being the electron gas parameter given by $r_s = (\frac{3}{4\pi\rho})^{1/3}$. At valence states densities, typically $r_s \approx 2$ au, so that $k_F \approx 1 (\text{au})^{-1}$. This means that at a distance of only 3 au ≈ 1.5 Å from point $\mathbf{r}$ the exchange

decreases by a factor of ≈ 3 or 10 (according to the value of t), implying a non-locality at least extended up to nearest neighbors.

Coming back to the photoemission problem, the set of equations (52) is to be supplemented with the boundary conditions related to the behavior of the photo-electron at infinity and to the state of the $(N-1)$-electron system according to the partition of the total energy $E_f^N = E_g^N + \hbar\omega$ between them. To each different partition there corresponds a different set of boundary conditions leading to a different solution of the set of (52). For example, if we are interested in a particular photoemission channel γ with kinetic energy k_γ^2 leaving behind the energy ΔE_γ into the system, in the limit $r \to +\infty$ we should impose the scattering conditions

$$\phi_\alpha(\mathbf{r}; \mathbf{k}_\gamma) \simeq \left(\frac{k_\alpha}{16\pi^3}\right)^{\frac{1}{2}} e^{i\mathbf{k}_\gamma \cdot \mathbf{r}} \delta_{\alpha\gamma} + f_\alpha(\hat{\mathbf{r}}, \mathbf{k}_\gamma) \frac{e^{ik_\alpha r}}{r} \quad (60)$$

where we have made explicit the dependence of ϕ_α on k_γ as an argument rather than an upper index. Here, as usual, $\delta_{\alpha\gamma}$ is the Kronecker symbol, f_α is the scattering amplitude and the factor $(k_\alpha/16\pi^3)^{1/2}$ takes care of the normalization of the photo-electronic plane wave at the detector to one state per Rydberg.

Using equations (46)–(48), defining the overlap density matrix

$$\rho_{\alpha g}(\mathbf{r}'; \mathbf{r}) = (N-1) \int \tilde{\Psi}_\alpha^{(N-1)*}(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N-1})$$
$$\times \Psi_g^{N-1}(\mathbf{r}', \mathbf{r}_2, \ldots, \mathbf{r}_{N-1}) d\mathbf{r}_2 \cdots d\mathbf{r}_{N-1} \quad (61)$$

and introducing the orthogonalized core initial state

$$\tilde{\phi}_\alpha^c(\mathbf{r}) = \phi_\alpha^c(\mathbf{r}) - S_\alpha^{-1} \int \rho_{\alpha g}(\mathbf{r}; \mathbf{r}') \phi_\alpha^c(\mathbf{r}') d\mathbf{r}' \quad (62)$$

we can rewrite the photoemission cross-section as

$$\frac{d\sigma(\omega)}{d\hat{\mathbf{k}}} = 8\pi^2 \alpha \hbar\omega \sum_{m_0} \left| \sum_\alpha S_\alpha \langle \phi_\alpha^-(\mathbf{r}; \mathbf{k}_\beta) | \hat{\boldsymbol{\varepsilon}} \cdot \mathbf{r} | \tilde{\phi}_{l_0 m_0}^c(\mathbf{r}) \rangle \right|^2 . \quad (63)$$

Here and in equation (62) we have introduced the overlap integrals $S_\alpha = \langle \Theta \tilde{\Psi}_\alpha^{N-1} | \Psi_g^{N-1} \rangle$ of the passive electrons and indicated by ϕ_α^- the time-reversal of ϕ_α^f (in practice the complex conjugate, if spin is neglected). Spin–orbit splitting in the initial core state has been ignored for simplicity, although it can be easily added, and spin degeneracy (in the case of non-magnetic systems) has been taken into account by an extra factor of 2.

The set of equations in (52) contains the complete description of all the outcomes of the photoemission process, be it of intrinsic origin (i.e. consequent to the relaxation of the system around the core hole) or extrinsic (excitations created by the photo-electron in its way out of the system). Their complete solution is out of the question; however, one can analyze their implications in particular cases. The simplest one is when the excited photo-electron interacts weakly with the rest of the system, e.g. when the final state is an extended wide band. This case lends itself to structural analysis, in both

photoemission and photoabsorption. To a good approximation we need only to consider the completely relaxed or elastic channel (i.e. the one for which $\Delta E_\gamma = 0$), because it carries most of the weight and is usually used for structural analysis. Indeed, using for this channel the index $\alpha = 0$, we have as a typical value $|S_0|^2 = |\langle \Theta \tilde{\Psi}_0^{N-1} | \Psi_g^{N-1} \rangle|^2 \approx 0.9$ [35].

With this in mind, we can then think of solving the set of coupled Schrödinger equations (52) by eliminating all unwanted channels in favor of the elastic one [18]. The result is a single equation for the channel function $\phi_0(\mathbf{r})$ at energy $E = k_0^2$ with an effective complex energy-dependent non-local optical potential of the kind

$$[\nabla^2 + E - \Phi_Z(\mathbf{r}) - V_c(\mathbf{r})]\phi_0(\mathbf{r})$$
$$= \int \Sigma^{opt}(\mathbf{r}, \mathbf{r}'; E)\phi_0(\mathbf{r}') \, d\mathbf{r}' \tag{64}$$

where we have isolated its local Coulomb part (V_c) and indicated the energy dependence coming from the eliminated channels by the argument E in Σ^{opt}. Notice that, although not explicitly indicated, this equation should be solved with the constraint that the channel function $\phi_0(\mathbf{r})$ be orthogonal to the one-particle states constituting the configurations present in the ground state. Usually this condition is neglected, but its effects might be quite important near the edge, at low photo-electron energies. In fact the exchange effects described by Σ^{opt} do not contain this kind of constraint, but only the reflection of it on the interparticle potential. A widespread approximation for Σ^{opt} is that based on the local density single plasmon pole approximation of a GW self-energy by Hedin and Lundqvist [36, 37] (see [38] for an explicit expression of it), or a generalization of it [39]. These exchange–correlation potentials ignore the description of intrinsic losses (presumably small in the case of weak interaction of the photo-electron with the rest of the system) and describe the exchange at a local level.

Obviously different is the case when the interaction of the photo-electron with the core hole and the rest of the system is strong. In this instance, effects of single quantum states become important and contribute features to the spectrum which are not of structural origin. We need to solve the set of coupled Schrödinger equations (52) with scattering boundary conditions (60). As in the single channel case, this is best done by passing to the corresponding Lippmann–Schwinger equations

$$\phi_\alpha^f(\mathbf{r}) = \left(\frac{k_\gamma}{16\pi^3}\right)^{\frac{1}{2}} e^{i\mathbf{k}_\gamma \cdot \mathbf{r}} \delta_{\alpha\gamma}$$
$$+ \sum_\beta \int G_0(\mathbf{r} - \mathbf{r}'; k_\alpha)\tilde{V}_{\alpha\beta}(\mathbf{r}', \mathbf{r}'')\phi_\beta^f(\mathbf{r}'') \, d\mathbf{r}' \, d\mathbf{r}'' \tag{65}$$

where the free Green function $G_0(\mathbf{r} - \mathbf{r}'; k_\alpha)$ in channel α is the solution of the free equation

$$(\nabla^2 + k_\alpha^2)G_0(\mathbf{r} - \mathbf{r}'; k_\alpha) = \delta(\mathbf{r} - \mathbf{r}') \tag{66}$$

with energy k_α^2. Notice that now in equation (65) the potential $\tilde{V}_{\alpha\beta}$ also incorporates the effect of the exchange term in the left-hand side (lhs) of equation (52), so that

$$\tilde{V}_{\alpha\beta}(\mathbf{r}; \mathbf{r}') = V_{\alpha\beta}^1 + V_{\alpha\beta}^2 + (\nabla_\mathbf{r}^2 + k_\alpha^2)\rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}'). \tag{67}$$

With this in mind, equation (65) clearly reduces to (52) upon application on both sides of the operator $(\nabla^2 + k_\alpha^2)$ with the correct boundary conditions (60).

The procedure for applying the MS method and taking into account the non-locality of $\tilde{V}_{\alpha\beta}^{exc}(\mathbf{r}, \mathbf{r}')$ then follows the same lines as in section 2.1.

Calling $\bar{\mathbf{V}}$ again the restriction of $\tilde{\mathbf{V}}$ to cell exchange, equation (65) can be written in vector form

$$\bar{\Phi}^f(\mathbf{r}; \mathbf{k}_\gamma) = \mathbf{I}(\mathbf{k}_\gamma)$$
$$+ \int \mathbf{G}_0(\mathbf{r} - \mathbf{r}'; \mathbf{k})\bar{\mathbf{V}}(\mathbf{r}', \mathbf{r}'')\bar{\Phi}^f(\mathbf{r}'') \, d\mathbf{r}' \, d\mathbf{r}'' \tag{68}$$

where in the channel space Φ^f is a vector with components Φ_α^f, $\mathbf{I}(\mathbf{k}_\gamma)$ is a vector with components $(\frac{k_\gamma}{16\pi^3})^{\frac{1}{2}} e^{i\mathbf{k}_\gamma \cdot \mathbf{r}} \delta_{\alpha\gamma}$, $\mathbf{k}$ is a vector with components k_α, $\mathbf{G}_0(\mathbf{k})$ is a diagonal matrix with elements $G_0(\mathbf{r} - \mathbf{r}'; k_\alpha)\delta_{\alpha\beta}$ and finally $\bar{\mathbf{V}}$ is the potential matrix. As before we introduce local (cell) scattering solutions in response to an exciting partial L-wave in channel γ. Defining the vector $\mathbf{J}_L(\mathbf{r}_j; \mathbf{k}_\gamma)$ with components $J_L(\mathbf{r}_j; k_\gamma)\delta_{\alpha\gamma}$ we have

$$\bar{\Psi}_L(\mathbf{r}_j; \mathbf{k}_\gamma) = \mathbf{J}_L(\mathbf{r}_j; \mathbf{k}_\gamma)$$
$$+ \int \mathbf{G}_0^+(\mathbf{r}_j - \mathbf{r}_j'; \mathbf{k})\bar{\mathbf{V}}^j(\mathbf{r}_j', \mathbf{r}_j'')\bar{\Psi}_L(\mathbf{r}_j''; \mathbf{k}_\gamma) \, d^3 r_j' \, d^3 r_j'' \tag{69}$$

so that in any individual cell the global solution can be expanded in terms of these local solutions as

$$\bar{\Phi}^f(\mathbf{r}_j; \mathbf{k}_\gamma) = \sum_L \bar{\mathbf{C}}_L^j(\mathbf{k}_\gamma)\bar{\Psi}_L(\mathbf{r}_j; \mathbf{k}_\gamma) \tag{70}$$

where $\bar{\mathbf{C}}_L^j$ is a vector with components $\bar{C}_{L\alpha}^j$. In terms of the interchannel matrix

$$\bar{\mathbf{T}}_{L\alpha L'\beta}^j = \int J_L(\mathbf{r}_j; k_\alpha)\bar{V}_{\alpha\beta}^j(\mathbf{r}_j', \mathbf{r}_j'')\Psi_{L'\beta}(\mathbf{r}_j''; \mathbf{k}_\gamma) \, d^3 r_j' \, d^3 r_j''$$
$$\tag{71}$$

and putting together site, angular momentum and channel indices we finally obtain the multichannel MS equations for the amplitudes $\bar{C}_{L\alpha}^j(\mathbf{k})$ written in matrix form

$$\bar{\mathbf{C}}(\mathbf{k}_\gamma) = \mathbf{I}(\mathbf{k}_\gamma) + \mathbf{G}_0(\mathbf{k})\bar{\mathbf{T}}\bar{\mathbf{C}}(\mathbf{k}_\gamma) \tag{72}$$

where

$$\bar{\mathbf{C}}(\mathbf{k}_\gamma) = (\bar{C}_{L\alpha}^j(\mathbf{k}_\gamma)\delta_{ij})$$
$$\mathbf{I}(\mathbf{k}_\gamma) = \left(\sqrt{\frac{k_\gamma}{\pi}} i^l Y_L(\hat{\mathbf{k}}_\gamma) e^{i\mathbf{k}_\gamma \cdot \mathbf{R}_i} \delta_{\alpha\gamma} \delta_{ij} \delta_{LL'}\right)$$
$$\mathbf{G}_0(\mathbf{k}) = (G_{LL'}^{ij}(k_\alpha)\delta_{\alpha\beta}) \tag{73}$$
$$\bar{\mathbf{T}} = (\bar{\mathbf{T}}_{L\alpha L'\beta}^j \delta_{ij}).$$

This is the straightforward generalization of the single channel MS equations, in that now the cell potential is no longer static and can react to the impinging photo-electron by changing its energy (and therefore its propagation channel).

There is one last point to clarify. Up to now we have assumed that the functions $\rho_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ in equation (54) are known. The eigenfunctions $\tilde{\Psi}_\alpha^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})$ of the $(N-1)$-particle problem are obviously unknown. However, what

we need is a density matrix, i.e. an integrated property of the $(N-1)$-particle functions, which can be reasonably approximated. For example in a $3d^n$ transition metal with one atom per cell we might take

$$\tilde{\Psi}_\alpha^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) \approx A \Pi_j \tilde{\Psi}_\alpha^j(\mathbf{r}_{j1}, \ldots, \mathbf{r}_{jn})$$
$$\times \Phi(\mathbf{r}_{N_c n+1}, \ldots, \mathbf{r}_{N-1}) \quad (74)$$

where $\tilde{\Psi}_\alpha^j(\mathbf{r}_{j1}, \ldots, \mathbf{r}_{jn})$ is one of the local multiplet wavefunctions centered at site j for the $3d^n$ configuration. They are linear combinations of Slater determinants made up of single-particle functions calculated in a relaxed one-particle mean field potential, N_c is the number of cells and $\Phi(\mathbf{r}_{N_c n+1}, \ldots, \mathbf{r}_{N-1})$ is the uncorrelated Slater determinant relative to the remaining electrons in the system. This is the approach used in [27], where the problem of calculating the non-local exchange–correlation potential in each cell was elegantly bypassed by calculating the interchannel T^j-matrix in the R-matrix approach [27], so that the antisymmetrizer A was acting only inside the cell. Notice that also the excitation energies k_α^2 are not known, but, in keeping with the ansatz (74), they can be reasonably approximated by the multiplet energy splittings. The same approximation might be used to calculate the two-particle density matrix or one might resort to some kind of decoupling (see section 3.2).

Continuing with the multichannel theory, we can introduce as before **B**-amplitudes via the relation

$$\bar{B}_{L\alpha}^j(\mathbf{k}_\gamma) = \sum_{L'\beta} \bar{T}_{L\alpha L'\beta}^j \bar{C}_{L'\beta}^j(\mathbf{k}_\gamma) \quad (75)$$

for which the generalized optical theorem again holds

$$\sum_\gamma \int d\hat{\mathbf{k}}_\gamma \, \bar{B}_{L\alpha}^i(\mathbf{k}_\gamma)[\bar{B}_{L'\beta}^j(\mathbf{k}_\gamma)]^* = -\frac{1}{\pi} \mathrm{Im}\boldsymbol{\tau}_{L\alpha L'\beta}^{ij} \quad (76)$$

where, as before, $\boldsymbol{\tau} = (\bar{\mathbf{T}}^{-1} - \mathbf{G})$ in the extended multichannel space. In this space equation (76) can be derived in the same way as in appendix D of [17], provided the inhomogeneous term $\mathbf{I}(\mathbf{k}_\gamma)$ is of the form given in equation (73). Similar derivations can be found in [25, 27].

As before, we can introduce new local basis functions

$$\bar{\Phi}^f(\mathbf{r}_j; \mathbf{k}_\gamma) = \sum_{L\beta} \bar{B}_{L\beta}^j(\mathbf{k}_\gamma) \bar{\Phi}_{L\beta}(\mathbf{r}_j; \mathbf{k}_\gamma) \quad (77)$$

so that the photoemission cross-section (63) becomes

$$\frac{d\sigma(\omega)}{d\hat{\mathbf{k}}_\gamma} = 8\pi^2 \alpha\hbar\omega \sum_{m_0} \left| \sum_{L\beta} S_\beta^* \tilde{M}_{L_c L\beta} \bar{B}_{L\beta}^j(\mathbf{k}_\gamma) \right|^2 \quad (78)$$

with similar definition of the atomic matrix element $\tilde{M}_{L_c L\beta}$ in terms of the orthogonalized core initial state (62) given by

$$\tilde{M}_{L_c L\beta} = \langle \bar{\Phi}_{L\beta}(\mathbf{r}; \mathbf{k}_\beta)|\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{r}|\tilde{\phi}_{l_0 m_0}^c(\mathbf{r})\rangle. \quad (79)$$

By integrating over the emission direction $\mathbf{k}_\gamma$ we obtain the total absorption cross-section

$$\sum_\gamma \int d\hat{\mathbf{k}}_\gamma \frac{d\sigma}{d\hat{\mathbf{k}}_\gamma} = -8\pi\alpha\hbar\omega$$
$$\times \sum_{L\beta L'\beta'} S_\beta^* \tilde{M}_{L_c L\beta}^*(E)(\mathrm{Im}\tau_{L\beta L'\beta'}^{ii})\tilde{M}_{L_c L'\beta'}(E)S_{\beta'} \quad (80)$$

which is the generalization of the single channel expression. These expressions are valid if we can neglect the effect of the non-local potential ΔV.

To take this latter into account we use the matrix generalization of equation (29) and following, but again this procedure would spoil the generalized optical theorem in the multichannel case. Alternatively, we can use the expression for the complete GF (see section 3.5).

3.2. Multichannel equations for the ground state

In trying to extend the multichannel method to investigate properties of the ground state we start from the wavefunction

$$\Psi_g^N(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) = (N!)^{1/2}A$$
$$\times \sum_\alpha \phi_\alpha(\mathbf{r})\Psi_\alpha^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) \quad (81)$$

and try to optimize the single-particle $\phi_\alpha(\mathbf{r})$ using the variational principle

$$\frac{\delta E_{av}}{\delta\phi_\alpha^*} = \frac{\delta}{\delta\phi_\alpha^*}\left(\frac{\langle\Psi_g^N|H|\Psi_g^N\rangle}{\langle\Psi_g^N|\Psi_g^N\rangle}\right) \quad (82)$$

assuming for the time being that the Ψ_α^{N-1} are known and satisfy the same equation as (49)

$$H^{N-1}\Psi_\alpha^{N-1} = E_\alpha^{N-1}\Psi_\alpha^{N-1} \quad (83)$$

this time without a tilde, since we are dealing with ground state properties.

Resorting to the same projection technique used to arrive at equation (52) we find

$$\langle\Psi_g^N|H|\Psi_g^N\rangle = \sum_\alpha \int \phi_\alpha^*(\mathbf{r})(-\nabla^2 + E_\alpha^{N-1})\phi_\alpha(\mathbf{r})\, d\mathbf{r}$$
$$- \sum_{\alpha\beta} \int \phi_\alpha^*(\mathbf{r})(-\nabla_\mathbf{r}^2 + E_\alpha^{N-1})\rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')\phi_\beta(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}'$$
$$+ \sum_{\alpha\beta} \int \phi_\alpha^*(\mathbf{r})(V_{\alpha\beta}^1(\mathbf{r}; \mathbf{r}') + V_{\alpha\beta}^2(\mathbf{r}; \mathbf{r}'))\phi_\beta(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}'$$

$$(84)$$

and

$$\langle\Psi_g^N|\Psi_g^N\rangle = \sum_\alpha \int \phi_\alpha^*(\mathbf{r})\phi_\alpha(\mathbf{r})\, d\mathbf{r}$$
$$- \sum_{\alpha\beta} \int \phi_\alpha^*(\mathbf{r})\rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')\phi_\beta(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}'. \quad (85)$$

The symmetrization argument of section A shows that, despite its appearance, the energy (84) is real, as it should be. Moreover, by analogy with the Hartree–Fock procedure, we impose not only the usual normalization condition $\langle\Psi_g^N|\Psi_g^N\rangle = 1$ but also the orthogonality conditions

$$\int \phi_\alpha^*(\mathbf{r})\rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')\phi_\beta(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' \equiv \langle\phi_\alpha|\rho|\phi_\beta\rangle = 0 \quad (86)$$

for all α and β. Introducing the Lagrange multipliers $\mu + E_g^{N-1}$ and $\epsilon_{\alpha\beta}$, we need to minimize the expression

$$\frac{\delta}{\delta\phi_\alpha^*}\left(\langle\Psi_g^N|H|\Psi_g^N\rangle - (\mu + E_g^{N-1})\langle\Psi_g^N|\Psi_g^N\rangle\right.$$

$$\left. - \sum_{\alpha\beta}\epsilon_{\alpha\beta}\langle\phi_\alpha|\rho|\phi_\beta\rangle\right) = 0 \qquad (87)$$

which leads to the following set of equations:

$$(\boldsymbol{\nabla}^2 + k_\alpha^2)\phi_\alpha(\mathbf{r}) = (\boldsymbol{\nabla}_\mathbf{r}^2 + k_\alpha^2)\sum_\beta\int\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}'$$

$$+ \sum_\beta\epsilon_{\alpha\beta}\int\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}'$$

$$+ \sum_\beta\int V_{\alpha\beta}^1(\mathbf{r},\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}'$$

$$+ \sum_\beta\int V_{\alpha\beta}^2(\mathbf{r},\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}' \qquad (88)$$

where now the one- and two-particle density matrices are referred to the $(N-1)$-particle wavefunctions without tilde (i.e. without core hole) and

$$k_\alpha^2 = \mu + E_g^{N-1} - E_\alpha^{N-1} = \mu - \Delta E_\alpha^{N-1} \qquad (89)$$

μ being the chemical potential of the system (when $\langle\Psi_g^N|\Psi_g^N\rangle = 1$) and ΔE_α^{N-1} the excitation energies of the $(N-1)$-electron system.

In a standard variational scheme, equations (88) are to be solved by assuming that the one- and two-particle density matrices are known, even in an approximate way, in terms of local multiplet wavefunctions, as mentioned in section 3. However, the single-particle wavefunctions used to build them would not contain the effect of the environment of the solid. The remedy to this drawback will be described in section 3.3.

Equation (88) represents the propagation of a test electron throughout the system, passing from a state described by $\phi_\alpha(\mathbf{r})$ to another one described by $\phi_\beta(\mathbf{r})$ under the action of the interchannel potentials $V_{\alpha\beta}^1 + V_{\alpha\beta}^2$. Notice the presence of a further kinetic term on the right-hand side of equation (88), analogous to the same term in equation (52) describing excited states. This term is a kind of exchange correction to the kinetic energy arising from the antisymmetrization of the test electron wavefunction to the rest of the system.

It is interesting to investigate the nature of the interchannel potential. The analysis is complicated by the presence of the two-particle density matrix in V^2. To this purpose we put

$$2\rho_{\alpha\beta}^2(\mathbf{r},\mathbf{r}'';\mathbf{r}',\mathbf{r}'') = (\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}')\rho_{\alpha\beta}(\mathbf{r}'';\mathbf{r}'')$$
$$- \rho_{\alpha\beta}(\mathbf{r}'';\mathbf{r}')\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}''))$$
$$\times (1 + h_{\alpha\beta}(\mathbf{r};\mathbf{r}')) \qquad (90)$$

where the second exchange term preserves the antisymmetry between the couples of variables on each side of the semicolon on the left-hand side and $h_{\alpha\beta}(\mathbf{r};\mathbf{r}')$ is a symmetric function in

the two variables that describes a kind of correlation hole [21]. Neglecting this correlation, we find

$$(\boldsymbol{\nabla}^2 + k_\alpha^2)\phi_\alpha(\mathbf{r}) = (\boldsymbol{\nabla}^2 + k_\alpha^2)\sum_\beta\int\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}'$$

$$+ \sum_\beta\epsilon_{\alpha\beta}\int\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}'$$

$$+ \sum_\beta\int V_{\alpha\beta}'(\mathbf{r},\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}' \qquad (91)$$

where

$$V_{\alpha\beta}'(\mathbf{r},\mathbf{r}') = V_{\alpha\beta}^d(\mathbf{r},\mathbf{r}') + V_{\alpha\beta}^{\mathrm{exc}}(\mathbf{r},\mathbf{r}') \qquad (92)$$

is given in terms of

$$V_{\alpha\beta}^d(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$$
$$\times\left[\int\rho_{\alpha\beta}(\mathbf{r}'';\mathbf{r}'')\frac{2}{|\mathbf{r}-\mathbf{r}''|}\,\mathrm{d}\mathbf{r}'' + \Phi_Z(\mathbf{r})\delta_{\alpha\beta}\right]$$
$$V_{\alpha\beta}^{\mathrm{exc}}(\mathbf{r},\mathbf{r}') = -\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}')\left[\frac{2}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}(\Phi_Z(\mathbf{r})+\Phi_Z(\mathbf{r}'))\right]$$
$$- \frac{1}{2}\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}')\int\rho_{\alpha\beta}(\mathbf{r}'';\mathbf{r}'')$$
$$\times\left(\frac{2}{|\mathbf{r}''-\mathbf{r}|} + \frac{2}{|\mathbf{r}''-\mathbf{r}'|}\right)\,\mathrm{d}\mathbf{r}''$$
$$+ \frac{1}{2}\int\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}'')\rho_{\alpha\beta}(\mathbf{r}'';\mathbf{r}')$$
$$\times\left(\frac{2}{|\mathbf{r}''-\mathbf{r}|} + \frac{2}{|\mathbf{r}''-\mathbf{r}'|}\right)\,\mathrm{d}\mathbf{r}''. \qquad (93)$$

Notice that $\rho_{\alpha\alpha}(\mathbf{r},\mathbf{r})$ is normalized to $N-1$, since the states Ψ_α^{N-1} are normalized to one. Neglecting, for short, symmetrization, we now observe that equation (91) can be rewritten as

$$(\boldsymbol{\nabla}^2 + k_\alpha^2 - \Phi_Z(\mathbf{r}))\left[\phi_\alpha(\mathbf{r}) - \sum_\beta\int\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}'\right]$$

$$= \sum_\beta\int\rho_{\alpha\beta}(\mathbf{r}'';\mathbf{r}'')\frac{2}{|\mathbf{r}-\mathbf{r}''|}\,\mathrm{d}\mathbf{r}''$$

$$\times\left[\phi_\beta(\mathbf{r}) - \int\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}'\right]$$

$$- \sum_\beta\int\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}'')\frac{2}{|\mathbf{r}-\mathbf{r}''|}\,\mathrm{d}\mathbf{r}''$$

$$\times\left[\phi_\beta(\mathbf{r}'') - \int\rho_{\alpha\beta}(\mathbf{r}'';\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}'\right]$$

$$+ \sum_\beta\epsilon_{\alpha\beta}\int\rho_{\alpha\beta}(\mathbf{r};\mathbf{r}')\phi_\beta(\mathbf{r}')\,\mathrm{d}\mathbf{r}'. \qquad (94)$$

In the case of only one channel ($\alpha = \beta = 1$) with no electronic correlations, $\Psi_1^{N-1} = [(N-1)!]^{1/2}A\,\Pi_i^{1,N-1}\phi_i(\mathbf{r}_i)$ is equal to the Slater determinant of the remaining $N-1$ particles, $\rho_{\alpha\alpha}(\mathbf{r},\mathbf{r}') = \sum_i^{1,N-1}\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')$, and the relation (90) becomes exact with $h = 0$ [21]. Then equation (94) reduces to the usual Hartree–Fock (HF) equations, the last term imposing the orthogonality of $\phi_\alpha(\mathbf{r})$ on all the remaining single-particle wavefunctions.

For many channels, equation (91) is the generalization of the HF equations to the case where we mix different configurations of the entire system, described by Ψ_α^{N-1}, something like the case in a multiconfiguration HF. Actually, one can view these equations as a kind of Euler–Lagrange equation for the Hartree–Fock–Kohn–Sham orbitals $\phi_\alpha(\mathbf{r})$, in which all terms with $\beta \neq \alpha$ in the effective potentials represent a sort of functional derivative of the correlation energy, the exchange part being represented exactly by the $\beta = \alpha$ term (cf e.g. equation (8.4.4) in [21]). This point of view will be elaborated in more depth in section 3.3.

It is interesting to note that the present scheme is free from self-interaction problems and that the pure HF potential is modified via the presence of many channels and the two-particle correlation function.

3.3. The ground state energy as a functional of the multichannel density matrix

In this section we want to tackle the problem of the self-consistent determination of the one-particle density matrix and present a more fundamental point of view for minimizing the ground state energy.

The starting point is the realization that the most general one-particle density matrix derived from antisymmetric wavefunctions can be represented as

$$\rho(\mathbf{r}; \mathbf{r}') = \sum_i n_i \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}') \quad (95)$$

where $\phi_i(\mathbf{r})$ is an orthonormal set of natural orbitals and n_i are occupation numbers such that $0 \leq n_i \leq 1$ [21]. They are respectively eigenstates and eigenvalues of the operator $\rho(\mathbf{r}; \mathbf{r}')$. This representation of the density is also the basis for the Kohn–Sham (KS) implementation of DFT and for its generalization (see the Hartree–Fock–Kohn–Sham method; section 8.4 in [21]).

In an endeavor to find an extension of the HF-KS method that takes into account a multiconfiguration (multichannel) scheme, such as the one we have described through this paper, we define a matrix 'density matrix' as a vector generalization of equation (95)

$$\rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}') = \sum_i n_i \phi_{i\alpha}(\mathbf{r}) \phi_{i\beta}^*(\mathbf{r}') \quad (96)$$

or in operator form in channel space

$$\Gamma(\mathbf{r}; \mathbf{r}') = \sum_i n_i |\Phi_i(\mathbf{r})\rangle \langle \Phi_i(\mathbf{r}')| \quad (97)$$

where the vector function $|\Phi_i(\mathbf{r})\rangle$ has components $\phi_{i\alpha}(\mathbf{r})$. In analogy with expression (95) they are eigenstates of $\Gamma(\mathbf{r}; \mathbf{r}')$. Notice that

$$\sum_\alpha \rho_{\alpha\alpha}(\mathbf{r}; \mathbf{r}) \equiv \rho(\mathbf{r}) = \sum_{i\alpha} |\phi_{i\alpha}(\mathbf{r})|^2 \quad (98)$$

and, provided

$$\sum_\alpha \int |\phi_{i\alpha}(\mathbf{r})|^2 \, d\mathbf{r} \equiv \langle \Phi_i(\mathbf{r})|\Phi_i(\mathbf{r})\rangle = 1 \quad (99)$$

we have for the total number of electrons N

$$N = \sum_i n_i. \quad (100)$$

In keeping with the expression (84) for the ground state energy and the definition (96) we write the following energy functional:

$$\begin{aligned}
E(\{n_i, \phi_{i\alpha}\}) &= \sum_{i\alpha} n_i \int \phi_{i\alpha}^*(\mathbf{r})(-\nabla^2)\phi_{i\alpha}(\mathbf{r}) \, d\mathbf{r} \\
&- \frac{1}{4} \sum_{i\alpha\beta} n_i \int \phi_{i\alpha}^*(\mathbf{r})(-\nabla_\mathbf{r}^2 - \nabla_{\mathbf{r}'}^2)\rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')\phi_{i\beta}(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \\
&+ \frac{1}{2} \sum_{i\alpha\beta} n_i \int \phi_{i\alpha}^*(\mathbf{r})(V_{\alpha\beta}^1(\mathbf{r}; \mathbf{r}') \\
&+ \frac{2}{3} V_{\alpha\beta}^2(\mathbf{r}; \mathbf{r}'))\phi_{i\beta}(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \quad (101)
\end{aligned}$$

where the potentials V^1 and V^2 are the same as defined in equations (55) and (57). In comparison with equation (84), we have dropped here the terms E_α^{N-1}, which are supposed to be taken into account by the introduction of all the other orbitals different from the one under consideration. The factor $\frac{1}{2}$ takes into account double counting, as does the factor of $\frac{2}{3}$ in front of V^2, since ρ^2 is proportional to the product $\rho^1 \rho^1$ (see equation (90)). The guiding idea is that the variational equations obeyed by the $\phi_{i\alpha}(\mathbf{r})$ should be similar to those satisfied by the wavefunctions $\phi_\alpha(\mathbf{r})$ of the test electron in equation (88).

By rewriting equation (101) in terms of only the density matrices defined in equation (96) we find

$$E(\{n_i, \phi_{i\alpha}\}) \equiv E(\{\rho_{\alpha\beta}\}) = T_1 + T_2 + V_d^1 + V_{\text{exc}}^1 + V^2 \quad (102)$$

where

$$T_1 = -\sum_\alpha \int d\mathbf{r} \, \nabla_\mathbf{r}^2 \rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}')\Big|_{\mathbf{r}=\mathbf{r}'} \quad (103)$$

is the usual kinetic term operator of the Kohn–Sham reference non-interacting system,

$$\begin{aligned}
T_2 &= \frac{1}{4} \sum_{\alpha\beta} \int \rho_{\alpha\beta}^*(\mathbf{r}; \mathbf{r}')(-\nabla_\mathbf{r}^2 - \nabla_{\mathbf{r}'}^2)\rho_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \\
&= -\frac{1}{4} \sum_{\alpha\beta} \int (|\nabla_\mathbf{r}\rho_{\alpha\beta}(\mathbf{r}, \mathbf{r}')|^2 + |\nabla_{\mathbf{r}'}\rho_{\alpha\beta}(\mathbf{r}, \mathbf{r}')|^2) \, d\mathbf{r} \, d\mathbf{r}'
\end{aligned}$$
$$(104)$$

is a correction term to T_1 arising from the presence of correlation in the basis functions Ψ_α^{N-1} (it would be zero if such a function were a Slater determinant),

$$\begin{aligned}
V_d^1 &= \frac{1}{2} \sum_{\alpha\beta} \int \rho_{\alpha\beta}^*(\mathbf{r}; \mathbf{r}) \frac{2}{|\mathbf{r} - \mathbf{r}'|} \rho_{\alpha\beta}(\mathbf{r}'; \mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \\
&+ \sum_\alpha \int \Phi_Z(\mathbf{r}) \rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}) \, d\mathbf{r} \quad (105)
\end{aligned}$$

is the direct term of V^1, whereas

$$V_{\text{exc}}^1 = -\frac{1}{2} \sum_{\alpha\beta} \int |\rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')|^2$$

$$\times \left(\frac{2}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2}(\Phi_Z(\mathbf{r}) + \Phi_Z(\mathbf{r}')) \right) \, d\mathbf{r} \, d\mathbf{r}' \quad (106)$$

is the corresponding exchange contribution, where the term with $\Phi_Z(\mathbf{r})$ has the same origin as in T_2. Finally,

$$V^2 = -\frac{1}{3} \sum_{\alpha\beta} \int \rho_{\alpha\beta}^*(\mathbf{r}; \mathbf{r}') \rho_{\alpha\beta}^2(\mathbf{r}, \mathbf{r}''; \mathbf{r}', \mathbf{r}'')$$

$$\times \left(\frac{2}{|\mathbf{r}'' - \mathbf{r}|} + \frac{2}{|\mathbf{r}'' - \mathbf{r}'|} \right) \, d\mathbf{r} \, d\mathbf{r}' \, d\mathbf{r}'' \quad (107)$$

is the term coming from the two-particle density matrix. Using the relation (90) we can then rewrite V^2 as

$$V^2 = -\frac{1}{6} \sum_{\alpha\beta} \int \{ |\rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')|^2 \rho_{\alpha\beta}(\mathbf{r}''; \mathbf{r}'')$$

$$- \rho_{\alpha\beta}^*(\mathbf{r}; \mathbf{r}') \rho_{\alpha\beta}(\mathbf{r}''; \mathbf{r}') \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}'') \}$$

$$\times \left(\frac{2}{|\mathbf{r}'' - \mathbf{r}|} + \frac{2}{|\mathbf{r}'' - \mathbf{r}'|} \right) (1 + h_{\alpha\beta}(\mathbf{r}; \mathbf{r}')) \, d\mathbf{r} \, d\mathbf{r}' \, d\mathbf{r}''$$

$$(108)$$

where the function h is left unspecified for the moment and, in the practical implementation of the theory, could either be neglected or considered a fixed function independent of the density and the channel indices [21].

　　Having expressed the energy in terms of the n_i and $\phi_{i\alpha}(\mathbf{r})$, we can obtain the ground state energy by minimizing $E(n_i, \phi_{i\alpha})$ with respect to n_i and $\phi_{i\alpha}(\mathbf{r})$. Therefore, for a fixed set of n_i, the set of the functions $\phi_{i\alpha}(\mathbf{r})$ must satisfy the Euler equations

$$\frac{\delta}{\delta\phi_{i\alpha}(\mathbf{r})}$$

$$\times \left\{ E(n_i, \phi_{i\alpha}) - \sum_i \epsilon_i' \left(\int \sum_\alpha |\phi_{i\alpha}(\mathbf{r})|^2 \, d\mathbf{r} - 1 \right) \right\} = 0$$

$$(109)$$

imposing the normalization (99) through the Lagrange multipliers ϵ_i'. This variational procedure leads to the following set of coupled integro-differential equations for the set of functions $\phi_{i\alpha}(\mathbf{r})$

$$(\nabla_{\mathbf{r}}^2 + \epsilon_i) \phi_{i\alpha}(\mathbf{r})$$

$$= \frac{1}{2} \sum_\beta \int [(\nabla_{\mathbf{r}}^2 + \nabla_{\mathbf{r}'}^2) \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')] \phi_{i\beta}(\mathbf{r}') \, d\mathbf{r}'$$

$$+ \sum_\beta \int V_{\alpha\beta}^{\text{eff}}(\mathbf{r}; \mathbf{r}') \phi_{i\beta}(\mathbf{r}') \, d\mathbf{r}' \quad (110)$$

which can be rewritten in matrix form and with obvious notations as

$$\int \{ \delta(\mathbf{r} - \mathbf{r}')(\nabla_{\mathbf{r}'}^2 + \epsilon_i) \mathbf{I} - \frac{1}{2}[(\nabla_{\mathbf{r}}^2 + \nabla_{\mathbf{r}'}^2) \Gamma(\mathbf{r}; \mathbf{r}')]$$

$$- \mathbf{V}^{\text{eff}}(\mathbf{r}; \mathbf{r}') \} |\Phi_i(\mathbf{r}')\rangle \, d\mathbf{r}' = 0. \quad (111)$$

In this equation we have put $\epsilon_i = \epsilon_i'/n_i$, exploiting the fact that each term of the functional derivative is proportional to $n_i \neq 0$. Moreover, the Laplacian term comes from T_1, the second from T_2, whereas $V_{\alpha\beta}^{\text{eff}}$ comes from the functional derivative of $V_d^1 + V_{\text{exc}}^1 + V^2$. Notice that, due to the hermiticity of these operators, vector solutions corresponding to different eigenvalues ϵ_i are orthogonal, so we do not need to impose this constraint. For short, in the following, we shall incorporate the term $\frac{1}{2}(\nabla_{\mathbf{r}}^2 + \nabla_{\mathbf{r}'}^2)\Gamma(\mathbf{r}; \mathbf{r}')$ into the definition of $\mathbf{V}^{\text{eff}}(\mathbf{r}; \mathbf{r}')$.

　　Explicitly, we find

$$V_{\alpha\beta}^{\text{eff}}(\mathbf{r}; \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$$

$$\times \left[\int \rho_{\alpha\beta}(\mathbf{r}''; \mathbf{r}'') \frac{2}{|\mathbf{r} - \mathbf{r}''|} d\mathbf{r}'' + \Phi_Z(\mathbf{r}) \delta_{\alpha\beta} \right]$$

$$- \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}') \left[\frac{2}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2}(\Phi_Z(\mathbf{r}) + \Phi_Z(\mathbf{r}')) \right]$$

$$- \frac{1}{3} \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}') \int \rho_{\alpha\beta}(\mathbf{r}''; \mathbf{r}'')$$

$$\times \left(\frac{2}{|\mathbf{r}'' - \mathbf{r}|} + \frac{2}{|\mathbf{r}'' - \mathbf{r}'|} \right) d\mathbf{r}''$$

$$+ \frac{1}{6} \int \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}'') \rho_{\alpha\beta}(\mathbf{r}''; \mathbf{r}')$$

$$\times \left(\frac{2}{|\mathbf{r}'' - \mathbf{r}|} + \frac{2}{|\mathbf{r}'' - \mathbf{r}'|} \right) d\mathbf{r}''$$

$$- \frac{1}{3} \delta(\mathbf{r} - \mathbf{r}') \int |\rho_{\alpha\beta}(\mathbf{r}''; \mathbf{r}_1)|^2 \frac{2}{|\mathbf{r} - \mathbf{r}''|} d\mathbf{r}'' d\mathbf{r}_1$$

$$+ \frac{1}{3} \int \rho_{\alpha\beta}^*(\mathbf{r}; \mathbf{r}'') \rho_{\alpha\beta}(\mathbf{r}''; \mathbf{r}')$$

$$\times \left(\frac{2}{|\mathbf{r}'' - \mathbf{r}|} + \frac{2}{|\mathbf{r}'' - \mathbf{r}'|} \right) d\mathbf{r}''$$

$$+ \frac{1}{2}(\nabla_{\mathbf{r}}^2 + \nabla_{\mathbf{r}'}^2) \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}'). \quad (112)$$

Notice that here $\rho_{\alpha\alpha'}$ refers to an N-particle density matrix. Due to this, the interchannel potential (112) is not free from self-interaction effects, in analogy with the scalar KS procedure. For simplicity, we have dropped the correlation term h in (108).

　　The set of coupled equations (110) constitutes the vector generalization of the usual Kohn–Sham equations to the case where we take into account several configurations in the ground state. Similarly to the scalar counterpart, they are to be solved self-consistently, since $\rho_{\alpha\beta}$ and $V_{\alpha\beta}^{\text{eff}}$ are themselves expressed in terms of the $\phi_{i\alpha}(\mathbf{r})$. The general problem of finding the minimum of the energy upon variation of both the $\phi_{i\alpha}(\mathbf{r})$ and the n_i has not found a solution yet ([21], section 7.6). We follow the Kohn–Sham approach and take $n_i = 1$ for the lowest N eigenstates of equation (111) and zero otherwise.

3.4. The multichannel Green's function

What remains to be done is to indicate an iteration scheme leading both to the self-consistent solution of equation (111) and to the minimization of the ground state energy. To

this purpose we introduce the multichannel Green's function obeying the equation

$$(\nabla^2 + E)G_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}')\delta_{\alpha\alpha'}$$
$$+ \sum_\beta \int V_{\alpha\beta}^{\text{eff}}(\mathbf{r}, \mathbf{r}'')G_{\beta\alpha'}(\mathbf{r}'', \mathbf{r}'; E)\, d\mathbf{r}''. \quad (113)$$

In terms of the vector solutions $|\Phi_i(\mathbf{r})\rangle$ of equation (111) corresponding to the eigenvalue ϵ_i, we can immediately generalize the formal solution of equation (37), obtaining

$$\mathbf{G}^\pm(\mathbf{r}, \mathbf{r}'; E) = \sum_i \frac{|\Phi_i(\mathbf{r})\rangle\langle\Phi_i(\mathbf{r}')|}{E - \epsilon_i \pm i\eta}$$
$$G_{\alpha\alpha'}^\pm(\mathbf{r}, \mathbf{r}'; E) = \sum_i \frac{\phi_{i\alpha}^\star(\mathbf{r})\phi_{i\alpha'}(\mathbf{r}')}{E - \epsilon_i \pm i\eta}. \quad (114)$$

Passing to the corresponding Lippmann–Schwinger equation, equation (113) can also be written as

$$G_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}'; E) = G_0^\alpha(\mathbf{r} - \mathbf{r}'; k_\alpha(E))\delta_{\alpha\alpha'}$$
$$+ \sum_\beta \int G_0^\alpha(\mathbf{r} - \mathbf{r}''; k_\alpha(E))V_{\alpha\beta}^{\text{eff}}(\mathbf{r}'', \mathbf{r}''')$$
$$\times G_{\beta\alpha'}(\mathbf{r}''', \mathbf{r}'; E)\, d\mathbf{r}''\, d\mathbf{r}''' \quad (115)$$

which in operator form becomes

$$\mathbf{G} = \mathbf{G}_0 + \mathbf{G}_0\mathbf{V}^{\text{eff}}\mathbf{G}. \quad (116)$$

This equation is the vector generalization of equation (40), so the solution follows the same patterns. Splitting again the MC potential $\mathbf{V}^{\text{eff}}$ as $\mathbf{V}^{\text{eff}} = \bar{\mathbf{V}}^{\text{eff}} + \Delta\mathbf{V}^{\text{eff}}$, we explicitly find in terms of the scattering solutions (69)

$$\bar{G}_{\alpha\alpha'}(\mathbf{r}_i, \mathbf{r}_j'; E) = \sum_{L\beta L'\beta'} \bar{\Psi}_{L\beta}(\mathbf{r}_i; k_\alpha)$$
$$\times [(\mathbf{I} - \mathbf{G}_0\bar{\mathbf{T}})^{-1}\mathbf{G}_0]_{L\beta L'\beta'}^{ij}\bar{\Psi}_{L'\beta'}(\mathbf{r}_j'; k_{\alpha'})$$
$$+ \delta_{ij}\sum_{L\beta}\bar{\Psi}_{L\beta}(\mathbf{r}_<; k_\alpha)\tilde{\bar{\Psi}}_{L\beta}(\mathbf{r}_>; k_{\alpha'}) \quad (117)$$

where we have now indicated by $\tilde{\bar{\Psi}}_{L\alpha}(\mathbf{r}_>; k_{\alpha'})$ the irregular solution in cell i that matches smoothly to $\tilde{H}_L^+(\mathbf{r}; k_\alpha)\delta_{\alpha\alpha'}$ at R_{b}^i. Using instead the basis functions defined by (77), we find

$$\bar{G}_{\alpha\alpha'}(\mathbf{r}_i, \mathbf{r}_j'; E) = \sum_{L\beta L'\beta'} \bar{\Phi}_{L\beta}(\mathbf{r}_i; k_\alpha)\tau_{L\beta L'\beta'}^{ij}\bar{\Phi}_{L'\beta'}(\mathbf{r}_j'; k_{\alpha'})$$
$$+ \delta_{ij}\sum_{L\beta}\bar{\Phi}_{L\beta}(\mathbf{r}_<; k_\alpha)\tilde{\bar{\Lambda}}_{L\beta}(\mathbf{r}_>; k_{\alpha'}) \quad (118)$$

where now $\tilde{\bar{\Lambda}}_{L\alpha}(\mathbf{r}_>; k_{\alpha'})$ joins smoothly to $J_L^+(\mathbf{r}; k_\alpha)\delta_{\alpha\alpha'}$ at R_{b}^i.

The solution $\mathbf{G}$ for the entire potential can be found again as before by iteration of

$$\mathbf{G} = \bar{\mathbf{G}} + \bar{\mathbf{G}}\Delta\mathbf{V}^{\text{eff}}\mathbf{G} = \bar{\mathbf{G}} + \mathbf{G}\Delta\mathbf{V}^{\text{eff}}\bar{\mathbf{G}}. \quad (119)$$

The procedure for a self-consistent calculation now proceeds as follows. We start from a DFT solution of the system under study that provides the initial Kohn–Sham orbitals by which to construct the initial set of single-particle

density matrices $\rho_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$. To this purpose, we discretize by suitable normalization [40] the extended one-electron KS orbitals $\phi_\alpha(\mathbf{r})$ having the relevant orbital character (e.g. 3d or 4f), so as to generate in the corresponding energy range $2(2l + 1)$ discrete orbitals, and construct the $n_c = \binom{2(2l+1)}{n}$ Slater determinants (SD) Φ_i ($i = 1, n_c$) formed by these extended orbitals for a definite n-electron configuration suggested by the physical situation under consideration. In this basis we diagonalize the total n-electron Hamiltonian (including therefore the Coulomb interaction), restricting the various space integrals to the cell(s) where we intend to introduce local electronic correlations. In this way we generate local multiplet wavefunctions that are used to construct initial density matrices. The relations (112) then generate the starting interchannel potentials, so that the corresponding multichannel GF, obtained according to the equations (117)–(119) above, generates a new set of density matrices and a new chemical potential μ by contour integral

$$-\frac{1}{\pi}\text{Im}\int_{-\infty}^\mu G_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}'; E)\, dE = \rho_{\alpha\alpha'}^N(\mathbf{r}, \mathbf{r}') \quad (120)$$

where μ is determined by the condition

$$\sum_\alpha \int \rho_{\alpha\alpha}^N(\mathbf{r}, \mathbf{r})\, d^3\mathbf{r} = N. \quad (121)$$

This new set of quantities is then used to construct a new set of interchannel potentials and so on, until self-consistency. At each iteration the value of the ground state energy is given by [41]

$$E_{\text{g}} = -\frac{1}{\pi}\text{Im}\int d^3\mathbf{r}$$
$$\times \sum_\alpha \int_{-\infty}^\mu G_{\alpha\alpha}(\mathbf{r}, \mathbf{r}; E)(E + \rho(E) - \mu)/2\, dE \quad (122)$$

where $\rho(E)$ is the density of states of the non-interacting particles, i.e. with only the external potential $\Phi_Z(\mathbf{r})$.

This procedure should describe correlations present in the ground state beyond their current treatment in DFT. Again, including spin variables in the formalism is not a problem, although essential to describe physical reality. This could be done in the framework of spin-density-functional theory ([21], chapter 8).

Before leaving this section, we would like to observe that, even though the KS orbitals are auxiliary quantities used to construct the density of the system, they are usually interpreted as quasi-particle wavefunctions with energies corresponding to the Lagrange multipliers ϵ_i. This is the case of the mapping of band states in periodic systems. Similarly, by an application of the above generalization of the KS theory, we might think of the correlated band states of 3d transition metals as given by the poles of the multichannel GF (117) or the zeros of the determinant of the MS matrix $\text{Det}|\mathbf{I} - \mathbf{G}_0(\mathbf{k}_{\text{BZ}}; \mathbf{k}; E)\bar{\mathbf{T}}(E)|$, where $\mathbf{G}_0(\mathbf{k}_{\text{BZ}}; \mathbf{k}; E)$ is the Fourier transform of the usual free electron propagator $G_{LL'}^{ij}(k_\alpha)$ in angular momentum representation calculated at the wavevector k_{BZ} of the Brillouin zone.

A further interesting application in real space is the possibility of introducing the electronic correlation only on one atom or cluster of atoms and leaving the rest of the system uncorrelated, which is obtained by keeping the interchannel dynamics only on the atom(s) of interest and describing the rest by their usual static *t*-matrices. This approach has been used with success for the calculation of the $L_{2,3}$ absorption edges in Ca, CaF_2, CaO and TiO_2 under its various forms (rutile, anatase, etc), where the photoabsorbing atom plays the natural role of a dynamic impurity to which the rest of the system is coupled via a reflectivity function [27, 34]. In investigating ground state properties, this method would be akin to the dynamical mean field theory (DMFT) approach, but conceptually easier to implement.

3.5. Absorption cross-section in terms of multichannel GF

Putting for short $D = \hat{\boldsymbol{\varepsilon}} \cdot \sum_{i=1}^{N} \mathbf{r}_i$, we calculate the dipole absorption cross-section expressed in terms of the *N*-particle GF as

$$\sigma_{\text{tot}}(\omega) = 4\pi^2 \alpha \hbar \omega \sum_f |\langle \Psi_f|D|\Psi_g\rangle|^2 \delta(\hbar\omega + E_g - E_f)$$

$$= -4\pi \alpha \hbar \omega \text{Im} \sum_f \langle \Psi_g|D^\dagger \frac{|\Psi_f\rangle\langle\Psi_f|}{E - E_f + i\eta} D|\Psi_g\rangle$$

$$= -4\pi \alpha \hbar \omega \text{Im} \langle \Psi_g|D^\dagger G^N(E)D|\Psi_g\rangle \quad (123)$$

where as usual $G^N(E)$ satisfies the equation $(E - H^N)G^N(E) = I^N$ and is calculated at $E = \hbar\omega - I_c$.

As in the wavefunction case described in section 3.1, we want to single out the motion of the final state photo-electron (modulo exchange terms) so that, in analogy with the procedure used in treating the electron–molecule scattering process illustrated in section C, we expand $G^N(E)$ in terms of the complete basis of $N-1$ particle $\tilde{\Psi}_\alpha^{N-1}$ already introduced

$$G^N(E) = AA' \sum_{\alpha\alpha'} \tilde{\Psi}_\alpha^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})$$

$$\times G_{\alpha\alpha'}^{\text{phe}}(\mathbf{r}, \mathbf{r}'; E) \tilde{\Psi}_{\alpha'}^{\star N-1}(\mathbf{r}'_1, \ldots, \mathbf{r}'_{N-1}) \quad (124)$$

where A' and A are antisymmetrizer operators acting respectively on the primed and unprimed variables.

The multichannel equations satisfied by $G_{\alpha\alpha'}^{\text{phe}}(\mathbf{r}, \mathbf{r}'; E)$ are derived in section C and are given by equations (C.6) and (C.7).

Then, on the basis of the expressions (123) and (124) and in terms of the orthogonalized initial core state wavefunctions defined by equation (62) we find

$$\sigma_{\text{tot}}(\omega) = -8\pi \alpha \hbar \omega \theta(\hbar\omega - I_c)$$

$$\times \sum_{m_c} \sum_{\alpha\alpha'} \text{Im} \int S_\alpha^* S_{\alpha'} \langle \tilde{\phi}_{L_c}^c(\mathbf{r})|\hat{\boldsymbol{\varepsilon}}^* \cdot \mathbf{r}|$$

$$\times G_{\alpha\alpha'}^{\text{phe}}(\mathbf{r}, \mathbf{r}'; \hbar\omega - I_c)|\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{r}'|\tilde{\phi}_{L_c}^c(\mathbf{r}')\rangle \, d^3\mathbf{r} \, d^3\mathbf{r}'$$

$$(125)$$

with the usual definition of the θ function and taking into account again spin degeneracy.

The photo-electron $\mathbf{G}^{\text{phe}}$ is different from the one calculated in the preceding section with the interchannel potential $\mathbf{V}^{\text{eff}}$ for two reasons. First, the density matrix $\Gamma(\mathbf{r}; \mathbf{r}')$ refers to the ground state, but it would be not difficult to use a kind of $Z + 1$ approximation. Second, $\mathbf{V}^{\text{eff}}$ and the potential in equation (C.6) are not exactly the same, since the first one comes from a generalized KS variational procedure. Nonetheless, we feel that the two approaches would give roughly similar spectra. In both cases we can use MST to obtain solutions of the form (118), if the correction $\Delta\mathbf{V}$ can be neglected. In this case equation (125) reduces to (80), since the singular part in (118) is real, due to the hermiticity of the many-body Hamiltonian. By contrast, in the general case, equation (125) can be used without restrictions.

4. Conclusions

In the framework of MST, we have presented a unifying scheme for calculating x-ray spectroscopic response functions and ground state properties of condensed matter systems, based on the Green's function approach, in both the single and multichannel scheme. Core-excited spectra are often strongly modified by electron correlation effects that cannot be described in an effective single-particle approach, such as density functional theory. Well-known examples are charge transfer and multiplet splittings in x-ray absorption and photoemission spectra of transition metal and rare earth compounds, where strong configuration mixing takes place. Multichannel MST is a promising approach to this problem since it can quite naturally account for local configuration interaction through the off-diagonal elements of the multichannel *T*-matrix. The progress of multichannel MST theory was limited by the conceptual problems for the calculation of the interchannel potential or multichannel *T*-matrix. Here we have devised a practically feasible, yet fully general, method for calculating the interchannel potential via the multichannel density matrix. We have shown how strong electron correlation can be accounted for in both the ground and core-excited states by means of multichannel MST both in the wavefunction and the Green's function formulation. In the case of the ground state we have generalized the usual KS equation to the case where several configurations (channels) are present in the ground state. We have therefore developed a self-consistent procedure to minimize the ground state energy in a way similar to the KKR-GF method, by introducing the multichannel GF associated with the generalized KS orbitals. In view of the fact that the local approximation to the exchange energy is the main source of error in LDA calculations, we have opted to represent exactly the exchange contribution to the energy functional. For this reason we have extended both single channel and multichannel MST theory to fully non-local potentials.

Acknowledgments

Appendix A. Hermiticity of the interchannel potentials

In projecting the N-body Hamiltonian (51) onto states Ψ_α^{N-1} we use here for convenience $\mathbf{r}_i$ coordinates where i runs from 1 to N, with the identification $\mathbf{r}_1 \equiv \mathbf{r}$. Then a typical projection term looks like

$$
\int \Psi_\alpha^{*N-1}(\mathbf{r}_2, \ldots, \mathbf{r}_N)
$$
$$
\times \left[H^1(\mathbf{r}_1) + H^{N-1}(\mathbf{r}_2, \ldots, \mathbf{r}_N) + \sum_{i \neq 1}^{1,N} V(\mathbf{r}_1, \mathbf{r}_i) \right]
$$
$$
\times (I - T_{1,2}) \phi_\beta(\mathbf{r}_1) \Psi_\beta^{N-1}(\mathbf{r}_2, \ldots, \mathbf{r}_N)\, \mathrm{d}\mathbf{r}_2 \cdots \mathrm{d}\mathbf{r}_N \quad \text{(A.1)}
$$

where $T_{1,2}$ is the transposition of elements 1 and 2 and we have singled out the coordinate $\mathbf{r}_1$ in splitting H^N.

Exploiting the complete symmetry of the Hamiltonian under interchange of all coordinates we can instead single out the coordinate 2, so that equation (A.1) gives the same result as

$$
\int \Psi_\alpha^{*N-1}(\mathbf{r}_2, \ldots, \mathbf{r}_N)
$$
$$
\times \left[H^1(\mathbf{r}_2) + H^{N-1}(\mathbf{r}_1, \mathbf{r}_3, \ldots, \mathbf{r}_N) + \sum_{i \neq 2}^{1,N} V(\mathbf{r}_2, \mathbf{r}_i) \right]
$$
$$
\times (I - T_{1,2}) \phi_\beta(\mathbf{r}_1) \Psi_\beta^{N-1}(\mathbf{r}_2, \ldots, \mathbf{r}_N)\, \mathrm{d}\mathbf{r}_2 \cdots \mathrm{d}\mathbf{r}_N. \quad \text{(A.2)}
$$

From this property the equality of the two terms in equation (58) follows. As a consequence, one can symmetrize the interchannel potentials with respect to $\mathbf{r}$ and $\mathbf{r}'$, showing explicitly their hermiticity property.

By the same property one can also show that in equation (84)

$$
\sum_{\alpha\beta} \int \phi_\alpha^*(\mathbf{r})(-\nabla_\mathbf{r}^2 + E_\alpha^{N-1}) \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}') \phi_\beta(\mathbf{r}')\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'
$$
$$
= \sum_{\alpha\beta} \int \phi_\alpha^*(\mathbf{r}) \phi_\beta(\mathbf{r}')(-\nabla_{\mathbf{r}'}^2 + E_\beta^{N-1}) \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'
$$
$$
\text{(A.3)}
$$

so that

$$
\frac{1}{2} \left\{ \sum_{\alpha\beta} \int \phi_\alpha^*(\mathbf{r}) \phi_\beta(\mathbf{r}')(-\nabla_\mathbf{r}^2 - \nabla_{\mathbf{r}'}^2 + E_\alpha^{N-1} + E_\beta^{N-1}) \right.
$$
$$
\left. \times \rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}' \right\} \quad \text{(A.4)}
$$

is manifestly real.

Appendix B. Analogy with electron–molecule scattering

For the convenience of the reader we want to underline here the analogy between equation (52) for the excited photo-electron and the analogous expression in the case of electron–molecule scattering [26]. In both cases, using the same notations, the total Hamiltonian is

$$
H^N = -\nabla_\mathbf{r}^2 + \Phi_Z(\mathbf{r}) + \sum_i^{1,N-1} V(\mathbf{r}, \mathbf{r}_i) + H^{N-1}
$$
$$
= H_0 + H^{N-1} + V_{\text{int}} \quad \text{(B.1)}
$$

where $-\nabla_\mathbf{r}^2$ is the kinetic operator of the projectile, $\Phi_Z(\mathbf{r})$ the external potential due to the atomic nuclei of the target, H^{N-1} describes the internal degrees of freedom of the target and V_{int} is the interaction potential that couples the motion of the projectile with the target and allows an energy exchange between the two subsystems.

If we now assume that the projectile and the target are distinguishable (this might be a physical case if the projectile is a positron), we can expand the total scattering wavefunction Ψ_s^N in terms of a complete set of states of the target (called channels)

$$
H^{N-1} \Psi_\alpha^{N-1} = E_\alpha^{N-1} \Psi_\alpha^{N-1} \quad \text{(B.2)}
$$

so that

$$
\Psi_s^N(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) = \sum_\alpha \phi_\alpha(\mathbf{r}) \Psi_\alpha^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1}). \quad \text{(B.3)}
$$

For the total scattering wavefunction we have

$$
H^N \Psi_s^N = E \Psi_s^N \quad \text{(B.4)}
$$

where $E = k^2 + E_g^{N-1}$ is the sum of the kinetic energy of the projectile at infinity and the initial state of the target assumed in its ground state. Projecting this equation onto the eigenstates of the target, we easily obtain a set of coupled (channel) equations for the projectile

$$
(\nabla^2 + k_\alpha^2 - \Phi_Z(\mathbf{r})) \phi_\alpha(\mathbf{r}) = \sum_\beta V_{\alpha\beta}(\mathbf{r}) \phi_\beta(\mathbf{r}) \quad \text{(B.5)}
$$

or in matrix form

$$
[(\nabla^2 - \Phi_Z(\mathbf{r}))\mathbf{I} + \mathbf{k}^2] \mathbf{\Phi}(\mathbf{r}) = \mathbf{V}(\mathbf{r}) \mathbf{\Phi}(\mathbf{r}) \quad \text{(B.6)}
$$

where $\mathbf{k}^2$ is a diagonal matrix with matrix elements

$$
k_\alpha^2 = E - E_\alpha^{N-1} = k^2 - \Delta E_\alpha^{N-1}. \quad \text{(B.7)}
$$

$\mathbf{\Phi}(\mathbf{r})$ is a column vector with components $\phi_\alpha(\mathbf{r})$ and $\mathbf{V}$ is the interchannel potential matrix with matrix elements

$$
V_{\alpha\beta}(\mathbf{r}) = \langle \Psi_\alpha^{N-1} | V_{\text{int}} | \Psi_\beta^{N-1} \rangle. \quad \text{(B.8)}
$$

Since the asymptotic state of the total scattering wavefunction Ψ_s^N is

$$
\Psi_s^N \to \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \times \Psi_\gamma^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) \quad \text{(B.9)}
$$

where Ψ_γ^{N-1} corresponds to the ground state of the target, equation (B.5) are to be solved with the asymptotic boundary

conditions

$$\phi_\alpha(\mathbf{r}) \to e^{i\mathbf{k}_\gamma \cdot \mathbf{r}} \delta_{\alpha\gamma} + f_\alpha(\hat{\mathbf{r}}; \mathbf{k}) \frac{e^{ikr}}{r}. \quad (B.10)$$

Notice that under the assumption that the projectile and the target are distinguishable, the interchannel potential is local. However, this assumption leads to wrong predictions in the case of the electron–molecule scattering, since the impinging electron and the electrons of the molecule are indistinguishable in the interaction region of the molecule. We therefore should insert an antisymmetrizing operator in equation (B.3), so that by repeating the projection procedure we arrive at equation (52). It is customary in molecular dynamics to approximate the exchange part of the non-local potential with local quantities [42]. However, serious discrepancies with experiments still remain, especially at low energies of the projectile. This is one of the reasons why we retain the exact form of the exchange, both in the case of photo-electron (absorption) spectroscopy and in the study of the ground state, where the test electron can be assimilated to an excited photo-electron.

Appendix C. The multichannel Green's function in electron–molecule scattering

Using the eigenfunction-expansion technique it is possible to express the Green's function (GF) of the total Hamiltonian H^N in terms of only the projectile coordinates (or the test electron in the study of the ground state of a system). We treat first the case of distinguishable particles.

Starting from the defining equation for the GF

$$(E - H^N)G^N(E) = I^N \quad (C.1)$$

we can expand the total GF in terms of eigenstates of the target Hamiltonian H^{N-1} as

$$G^N(E) = \sum_{\mu\nu} \Psi_\mu^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) G_{\mu\nu}(\mathbf{r}, \mathbf{r}'; E)$$
$$\times \Psi_\nu^{\star N-1}(\mathbf{r}_1', \ldots, \mathbf{r}_{N-1}'). \quad (C.2)$$

Likewise, for the unity operator $\mathbf{I}^N$ in equation (C.1) in the configuration space of N particles, we can write

$$\mathbf{I}^N \equiv \delta(\mathbf{r} - \mathbf{r}') \Pi_{i=1}^{N=1} \delta(\mathbf{r}_i - \mathbf{r}_i')$$
$$\equiv \delta(\mathbf{r} - \mathbf{r}') \sum_\mu \Psi_\mu^{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1})$$
$$\times \Psi_\mu^{\star N-1}(\mathbf{r}_1', \ldots, \mathbf{r}_{N-1}') \quad (C.3)$$

where in the space of $N-1$ particles we have limited ourselves to the subspace of the completely antisymmetric functions. Projecting equation (C.1) onto the states $\langle \Psi_\alpha^{N-1}|$ on the left and $|\Psi_{\alpha'}^{N-1}\rangle$ on the right and remembering equation (B.2) we find, putting again $k_\alpha^2 = E - E_\alpha^{N-1}$,

$$\sum_\beta [(\nabla_\mathbf{r}^2 + k_\alpha^2 - \Phi_Z(\mathbf{r}))\delta_{\alpha\beta} - V_{\alpha\beta}(\mathbf{r})]$$
$$\times G_{\beta\alpha'}(\mathbf{r}, \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}')\delta_{\alpha\alpha'} \quad (C.4)$$

or in matrix form

$$[(\nabla_\mathbf{r}^2 - \Phi_Z(\mathbf{r}))\mathbf{I} + \mathbf{k}^2 - \mathbf{V}(\mathbf{r})]\mathbf{G}(\mathbf{r}, \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}')\mathbf{I} \quad (C.5)$$

where now $\mathbf{I}$ is the unit matrix in the channel space.

If we now drop the assumptions of distinguishable particles, we have to insert an antisymmetrization operator at each side of equation (C.2) for both the primed and unprimed variables. Repeating the projection procedure onto states α and α' we obtain

$$(\nabla_\mathbf{r}^2 + k_\alpha^2)\tilde{G}_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}'; E)$$
$$- (\nabla_\mathbf{r}^2 + k_\alpha^2) \sum_\beta \int \rho_{\alpha\beta}(\mathbf{r}''; \mathbf{r}) \tilde{G}_{\beta\alpha'}(\mathbf{r}'', \mathbf{r}'; E)$$
$$- \sum_\beta \int V_{\alpha\beta}'(\mathbf{r}, \mathbf{r}'') \tilde{G}_{\beta\alpha'}(\mathbf{r}'', \mathbf{r}'; E)\, d\mathbf{r}'$$
$$= \delta(\mathbf{r} - \mathbf{r}')\delta_{\alpha\alpha'} \quad (C.6)$$

where we have assumed the relation (90) so that, with $h = 0$, $V_{\alpha\beta}'$ is the interchannel potential defined in equations (92) and (93). Notice that we have introduced the auxiliary function $\tilde{G}_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}'; E)$, which is related to the original $G_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}'; E)$ by

$$\tilde{G}_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}'; E) = \sum_\beta \left(\delta_{\alpha'\beta} - \int \rho_{\beta\alpha'}(\mathbf{r}'; \mathbf{r}'') \right)$$
$$\times G_{\alpha\beta}(\mathbf{r}, \mathbf{r}''; E)\, d\mathbf{r}''. \quad (C.7)$$

This complication arises from the presence of the antisymmetrizing operators acting also on the primed variables. In these equations the density matrix $\rho_{\alpha\beta}(\mathbf{r}; \mathbf{r}')$ can be obtained by a self-consistent calculation, as outlined in section 3.3, either for the ground state (in the case of electron–molecule scattering) or for a relaxed state around a core hole (in the case of photoemission or photoabsorption).

References

[1] Korringa J 1947 *Physica* **13** 392–400
[2] Kohn W and Rostoker N 1954 *Phys. Rev.* **94** 1111–20
[3] Slater J C and Johnson K H 1972 *Phys. Rev. B* **5** 844–53
[4] Andersen O 1975 *Phys. Rev. B* **12** 3060–83
[5] Koelling D and Arbman G 1975 *J. Phys. F: Met. Phys.* **5** 2041
[6] Ebert H, Ködderitzsch D and Minár J 2011 *Rep. Prog. Phys.* **74** 096501
[7] Bei der Kellen S and Freeman A J 1996 *Phys. Rev. B* **54** 11187–98
[8] Huhne T, Zecha C, Ebert H, Dederichs P and Zeller R 1998 *Phys. Rev. B* **58** 10236–46
[9] Asato M, Settels A, Hoshino T, Asada T, Blügel S, Zeller R and Dederichs P 1999 *Phys. Rev. B* **60** 5202–10
[10] Papanikolau N, Zeller R and Dederichs P 2002 *J. Phys.: Condens. Matter* **14** 2799–823
[11] Ogura M and Akai H 2005 *J. Phys.: Condens. Matter* **17** 5741–55
[12] Gonis A and Butler W H 2000 *Multiple Scattering in Solids* (New York: Springer) and references therein
[13] Huhne T and Ebert H 1999 *Solid State Commun.* **109** 577–82
[14] Ankudinov A L and Rehr J J 2005 *Phys. Scr.* **T115** 24–7
[15] Hatada K, Hayakawa K, Benfatto M and Natoli C R 2007 *Phys. Rev. B* **76** 060102
[16] Hatada K, Hayakawa K, Benfatto M and Natoli C R 2009 *J. Phys.: Condens. Matter* **21** 104206

[17] Hatada K, Hayakawa K, Benfatto M and Natoli C R 2010 *J. Phys.: Condens. Matter* **22** 185501

[18] Sébilleau D, Gunnella R, Wu Z Y, Matteo S D and Natoli C R 2006 *J. Phys.: Condens. Matter* **18** R175–230

[19] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133–8

[20] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864–71

[21] Parr R G and Yang W 1989 *Density Functional Theory of Atoms and Molecules* (New York: Oxford University Press)

[22] Zaanen J, Sawatzky G A, Fink J, Speier W and Fuggle J C 1985 *Phys. Rev.* B **32** 4905

[23] Groot F D and Kotani A 2008 *Core Level Spectroscopy of Solids* (London: CRC Taylor and Francis)

[24] Ogasawara K, Iwata T, Koyama Y, Ishii T, Tanaka I and Adachi H 2001 *Phys. Rev.* B **64** 115413

[25] Natoli C R, Benfatto M, Brouder C, RuizLópez M F and Foulis D L 1990 *Phys. Rev.* B **42** 1944–68

[26] Zhang J Z H 1999 *Theory and Application of Quantum Molecular Dynamics* (Singapore: World Scientific)

[27] Krüger P and Natoli C R 2004 *Phys. Rev.* B **70** 245120

[28] Butler W H, Gonis A and Zhang X G 1992 *Phys. Rev.* B **45** 11527–41

[29] Natoli C R, Benfatto M and Doniach S 1986 *Phys. Rev.* A **34** 4692–4

[30] Zeller R 1987 *J. Phys. C: Solid State Phys.* **20** 2347–60

[31] Ankudinov A, Ravel B, Rehr J J and Conradson S 1998 *Phys. Rev.* B **58** 7565–75

[32] Breit G and Bethe H A 1954 *Phys. Rev.* **93** 888–90

[33] Mott N F and Massey H S W 1965 *The Theory of Atomic Collisons* 3rd edn (New York: Oxford University Press)

[34] Krüger P 2010 *Phys. Rev.* B **81** 125121

[35] de Leon J M, Rehr J J, Zabinsky S I and Albers R C 1991 *Phys. Rev.* B **44** 4146–56

[36] Hedin L and Lundqvist B I 1971 *J. Phys. C: Solid State Phys.* **4** 2064–83

[37] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629–42

[38] Natoli C R, Benfatto M, Longa S D and Hatada K 2003 *J. Synchrotron Radiat.* **10** 26–42

[39] Kas J J, Sorini A P, Prange M P, Cambell L W, Soininen J A and Rehr J J 2007 *Phys. Rev.* B **76** 195116

[40] Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (Berkeley, CA: University of California Press) chapter 18

[41] Kadanoff L P and Baym G 1962 *Quantum Statistical Mechanics* (New York: Benjamin)

[42] Riley M E and Truhlar D G 1975 *J. Chem. Phys.* **63** 2182