

# Chapter 9

## $(e,2e)$ Impact Ionization Processes for Surface Science

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**Abstract** We present a scattering theoretic approach to the calculation of the cross-section of  $(e,2e)$  impact spectroscopy where all the electrons involved are treated within the real space multiple scattering framework. This approach is particularly suited to the reflection geometry at low kinetic energies, with the ejection of a core-level electron. In this case, we expect  $(e,2e)$  spectroscopy can be turned into an extremely sensitive surface structure probe.

### 9.1 Introduction

$(e,2e)$  has a long history, especially in atomic and molecular physics. Originally derived for the  $(p, 2p)$  spectroscopy in nuclear physics [1], where  $p$  represents a proton, it was proposed in 1966 by Smirnov and coworkers [2] for the investigation of atomic wave functions [3], upon the replacement of the protons by electrons. Since then, it has enjoyed a widespread popularity and is often termed *electron momentum spectroscopy* [4]. Indeed, in the high energy regime (primary energy  $\sim 10$ – $50$  keV), we can represent the electron by a plane wave. If in addition, the momentum transfer is large ( $\mathbf{K} = \mathbf{k}_{\text{in}} - \mathbf{k}_{\text{sc}} \approx \mathbf{k}_{\text{ex}}$ ), the collision between the impinging electron and

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the target electron can be described as a *single binary collision* (i.e. many-body interactions are approximated by consecutive two-body interactions) and therefore, the impact approximation is valid [5]. This approximation assumes that the incoming electron interacts only with the ejected electron and neither affects the target nor is affected by it (the *spectator electrons* are frozen). Within this so-called Plane Wave Impulse Approximation (PWIA), the momentum opposite to the recoil ion momentum vector is interpreted as the bound electron momentum. In this case, the cross-section is proportional to the *spectral momentum density*  $\varrho(\mathbf{q}, \epsilon) = |\phi(\mathbf{q}, \epsilon)|^2$  where  $\mathbf{q}$  is the momentum of the bound electron and  $\epsilon$  its binding energy.  $\phi(\mathbf{q}, \epsilon)$  is the Fourier transform of the wave function  $\phi(\mathbf{r}, \epsilon)$  before the collision.  $\varrho(\mathbf{q}, \epsilon)$  is the probability of finding a bound electron of momentum  $\mathbf{q}$  and energy  $\epsilon$ . Hence the name of *wave function mapping* spectroscopy [6, 7] often given to  $(e,2e)$ .

Although proposed since the very beginning of  $(e,2e)$ , the application of the technique to solids [2] has long been hampered by the low count rate. It is only rather recently that technical developments in the devising of new analyzers, such as the time-of-flight technique [8], have made it possible to use it as a probe of condensed matter.

$(e,2e)$  in reflection mode was proposed back in 1978 in order to study surfaces by D'Andrea and Del Sole in a theoretical paper [9]. The first experiment was performed in 1992 by Kirschner and coworkers [10] on W(110). But it is not before 1995 that the feasibility of this binding-energy spectroscopy with quasimomentum discrimination was firmly established [11]. However, in this case, as we need to be sensitive to the surface, the experiments have to be performed for primary beams of low energy and grazing incidence in order to minimize the inelastic mean free path and the escape depth of the outgoing electrons. In the case of surfaces, the use of  $(e,2e)$  can give us important information on many different processes. For instance, in their seminal paper, D'Andrea and Del Sole [9] demonstrated that the computed  $(e,2e)$  spectra were very sensitive to the surface reconstruction. It is with this type of applications in mind that we develop here a real space multiple scattering framework to model  $(e,2e)$  experiments. Previous approaches were more interested in the excitation of valence states; we focus here on core states.

## 9.2 Reduction of the Cross-Section

The cross section of  $(e,2e)$  can be written as

$$\frac{d^3\sigma}{dE_1 d\Omega_{\mathbf{k}_{sc}} d\Omega_{\mathbf{k}_{ex}}} = \frac{1}{8} (2\pi)^4 \left(\frac{2m}{\hbar^2}\right)^3 \frac{k_{sc}k_{ex}}{k_{in}} \sum_{av} |\langle \Phi_{\mathbf{k}_{sc}\mathbf{k}_{ex}}^{N+1} | T_I | \Phi_{\mathbf{k}_{in}}^{N+1} \rangle|^2. \quad (9.1)$$

Here, we have noted  $\mathbf{k}_{in}$ ,  $\mathbf{k}_{sc}$  and  $\mathbf{k}_{ex}$  respectively the direction of the incoming, scattered and excited (ejected) electron. By convention, the scattered electron is the faster of the two outgoing electrons and the ejected (or excited) electron is the slower.

The sum over the states noted av is a sum over degenerate final states and an average over degenerate initial states.

Here,  $|\Phi_{k_{in}}^{N+1}\rangle$  and  $|\Phi_{k_{sc}k_{ex}}^{N+1}\rangle$  are eigenstates of the *asymptotic Hamiltonian*, i.e. of the Hamiltonian  $H_0$  *without interaction*. ( $N + 1$ ) is the total number of electrons, the target being assumed to contain  $N$  electrons. We can express the initial state as

$$|\Phi_{k_{in}}^{N+1}\rangle = |\varphi_g^{N-1}\rangle |\phi_0\rangle \otimes |\phi_{k_{in}}\rangle, \quad (9.2)$$

where  $|\phi_0\rangle$  is the initial wave state of the electron that will be excited,  $|\phi_{k_{in}}\rangle$  is the wave state of the incoming electron and  $|\varphi_g^{N-1}\rangle$  is the ground state of the remaining ( $N - 1$ ) system. Here,  $\otimes$  represents the product in the two-electron space.

Likewise, we write the final state as

$$|\Phi_{k_{sc}k_{ex}}^{N+1}\rangle = |\varphi_{ion}^{N-1}\rangle |\phi_{k_{sc}k_{ex}}\rangle, \quad (9.3)$$

where  $|\varphi_{ion}^{N-1}\rangle$  is the residual ion state and  $|\phi_{k_{sc}k_{ex}}\rangle$  is the outgoing two-electron state.

With these notations, the cross-section becomes

$$\frac{d^3\sigma}{dE_1 d\Omega_{k_{sc}} d\Omega_{k_{ex}}} = \frac{1}{8} (2\pi)^4 \left(\frac{2m}{\hbar^2}\right)^3 \frac{k_{sc}k_{ex}}{k_{in}} \times \sum_{av} |\langle \varphi_{ion}^{N-1} | \langle \phi_{k_{sc}k_{ex}} | T_I | \varphi_g^{N-1} \rangle |\phi_0\rangle \otimes |\phi_{k_{in}}\rangle|^2. \quad (9.4)$$

At this stage, we make a first approximation called *the frozen core approximation* or *the sudden approximation*. This approximation assumes that the ejected electron leaves the atom in a time much less than the time it takes for the remaining electrons of the ion to readjust. In other words, these atoms can be considered as *spectators* of the interaction process. This approximation implies

$$\frac{d^3\sigma}{dE_1 d\Omega_{k_{sc}} d\Omega_{k_{ex}}} = \frac{1}{8} (2\pi)^4 \left(\frac{2m}{\hbar^2}\right)^3 \frac{k_{sc}k_{ex}}{k_{in}} \sum_{av} |S_0^{N-1}|^2 |T_{fi}|^2, \quad (9.5)$$

where we have noted

$$T_{fi} = \langle \phi_{k_{sc}k_{ex}} | T_I | \phi_0 \rangle \otimes |\phi_{k_{in}}\rangle. \quad (9.6)$$

We are then left with a three-body problem plus the overlap term  $|S_0^{N-1}|^2 = |\langle \varphi_{ion}^{N-1} | \varphi_g^{N-1} \rangle|^2$  which is independent of the interaction process.  $\langle \varphi_{ion}^{N-1} | \varphi_g^{N-1} \rangle$  is usually called the *structure factor* while  $\langle \phi_{k_{sc}k_{ex}} | T_I | \phi_0 \rangle \otimes |\phi_{k_{in}}\rangle$  is called the *collision factor*. The separation of the total matrix element into these two contributions is called the *factorization approximation*. For the rest of the discussion, we will consider the structure factor as constant and take it out of the sum. In this approximation,  $T_I$  is a two-body transition operator.

### 9.3 The Two-Electron Differential Cross-Section

We recall that a  $N$ -body  $T$ -matrix element can be written as [12]

$$\begin{cases} T_{fi} = \langle \Phi_f | V_f | \Psi_i^+ \rangle = \langle \Phi_f | V_f \Omega_i^{(+)} | \Phi_i \rangle & \text{post form} \\ = \langle \Psi_f^- | V_i | \Phi_i \rangle = \langle \Phi_f | \Omega_f^{(-)\dagger} V_i | \Phi_i \rangle & \text{prior form} \end{cases} \quad (9.7)$$

where  $|\Psi^\pm\rangle$  is an eigenket of  $H$ , the full Hamiltonian,  $|\Phi_f\rangle$  an eigenstate of  $H_f = H - V_f$  and  $|\Phi_i\rangle$  an eigenstate of  $H_i = H - V_i$ .  $V_i$  and  $V_f$  are the interaction potentials respectively in the *initial channel* and the *final channel*.  $\Omega^{(\pm)}$  are Møller wave operators.

Each continuum electron interacts with the cluster potential through

$$V_{xxS} = \sum_{n=1}^{N_{\text{at}}} V_{xxn} \quad (9.8)$$

where  $N_{\text{at}}$  is the number of atoms in the cluster. Here, xx stands for in, sc or ex, and S for the sample. Within this 3-body approach (incoming electron, bound/ejected electron, cluster), we can define the interactions in the initial and final channel as

$$\begin{cases} V_i = V_{\text{in}S} + V_{\text{in}co} + V_{coS} \\ V_f = V_{scS} + V_{exS} + V_{scex} \end{cases} \quad (9.9)$$

We note that we can suppress the interaction potential  $V_{coS}$  between the core state and the sample in the expression of  $V_i$ . Indeed, if the calculation of the sample potential  $V_S$  and of the wave function  $\phi_{co}(\mathbf{r})$  have been done properly, this has already been accounted for.

Let us consider now the prior form of (9.7). As the interaction between the incoming electron and the system  $V_{\text{in}S}$  cannot excite the bound electron, we can reduce  $V_i$  to  $V_{\text{in}co}$  in (9.7) so that we have now  $|\Phi_i\rangle$  eigenstate of  $H_i = H - V_{\text{in}co} = H_0 + V_{\text{in}S}$ . To keep the standard distorted wave notation, we will write it as  $|\chi_i^\pm\rangle \otimes |\phi_{co}\rangle$ . Therefore, (9.7) becomes

$$T_{fi} = \langle \Phi_f | \Omega_f^{(-)\dagger} V_{\text{in}co} |\chi_i^+\rangle \otimes |\phi_{co}\rangle \quad (9.10)$$

where according to (9.9),  $|\Phi_f\rangle$  is an eigenstate of  $H_0$ .  $|\chi_i^+\rangle$  is the result of the interaction of the incoming electron with the sample through the potential  $V_{\text{in}S}$ . It is therefore a *multiple scattering state* which we will rewrite  $|\chi_{\text{in}}^\pm\rangle$  to make the difference with the multiple scattering states in the final channel.

As the matrix elements of  $T$  involve multiple scattering states  $|\chi^\pm\rangle$ , let us introduce the multiple scattering Møller wave operators  $\omega_{xx}^{(\pm)}$  associated to the Hamiltonian

$H_{xx} = H_0 + V_{xx}$  S by

$$\omega_{xx}^{(\pm)} |\Phi\rangle = (\omega_{xx}^{(\pm)} \otimes I) |\mathbf{k}_{xx}\rangle \otimes |\phi\rangle . \quad (9.11)$$

We can now rewrite our result (9.10) in terms of the initial state and final state plane waves solutions of  $H_0$  as

$$T_{fi} = \langle \mathbf{k}_{sc} | \otimes \langle \mathbf{k}_{ex} | \Omega_f^{(-)\dagger} V_{in\ co} (\omega_{in}^{(+)} \otimes I) |\mathbf{k}_{in}\rangle \otimes |\phi_{co}\rangle . \quad (9.12)$$

This expression is an *exact result* within our 3-body impact approximation.

An important issue in ( $e,2e$ ) spectroscopy is to find a proper description of the so-called *post-collision interaction* (PCI), i.e. the interaction between the two outgoing electrons. In our formulation, this effect is embedded within the final channel Møller wave operator  $\Omega_f^{(-)\dagger}$ . We know how to compute the individual wave operators  $\omega_{xx}^{(\pm)}$ , all multiple scattering codes can do it, but  $\Omega_f^{(\pm)}$  is a complicated operator taking into account all the interactions in the final state at the same time. However, we can use the simple first order approximation derived by Briggs [12]

$$\Omega^{(\pm)} \approx \prod_{n=1}^N \omega_n^{(\pm)} . \quad (9.13)$$

We will call this result *Briggs' first order approximation* (Br1 in the equations). We find then

$$\Omega_f^{(-)\dagger} \Big|_{\text{Br1}} = (\omega_{sc\ S}^{(-)\dagger} \otimes I) (I \otimes \omega_{ex\ S}^{(-)\dagger}) \omega_{sc\ ex}^{(-)\dagger} = (\omega_{sc\ S}^{(-)\dagger} \otimes \omega_{ex\ S}^{(-)\dagger}) \omega_{sc\ ex}^{(-)\dagger} , \quad (9.14)$$

where the order of the wave operators is indifferent.  $\omega_{sc\ ex}^{(-)\dagger}$  is the PCI wave operator which describes the (screened Coulomb) interaction between the two outgoing electrons.

Therefore, we can rewrite now the transition matrix element as

$$T_{fi} \Big|_{\text{Br1}} = \underbrace{\langle \mathbf{k}_{sc} | \otimes \langle \mathbf{k}_{ex} | \omega_{sc\ ex}^{(-)\dagger}}_{\text{PCI scattering state}} (\omega_{sc\ S}^{(-)\dagger} \otimes \omega_{ex\ S}^{(-)\dagger}) V_{in\ co} (\omega_{in}^{(+)} \otimes I) |\mathbf{k}_{in}\rangle \otimes |\phi_{co}\rangle . \quad (9.15)$$

The neglect of PCI amounts to the replacement of the Møller wave operator  $\omega_{sc\ ex}^{(-)\dagger}$  by the identity  $I_{\otimes}$  in the two-electron space.

In order to simplify the notation, let us write as usual

$$\omega_{xx}^{(\pm)} |\mathbf{k}_{xx}\rangle = |\chi_{\mathbf{k}_{xx}}^{\pm}\rangle , \quad (9.16)$$

and the Coulomb interaction in the initial channel as  $V_C$  as there is no ambiguity (the one in the final channel is contained into the PCI wave operator). Note that  $V_C$  is

a short-hand notation for the antisymmetrized operator ( $\mathcal{A}_{\otimes}^{\dagger} V_C \mathcal{A}_{\otimes}$ ), where  $\mathcal{A}$  is the antisymmetrizer.

We can now rewrite (9.15) as

$$T_{fi} \Big|_{\text{BrI}} = \langle \chi_{k_{sc}}^{-} | \otimes \langle \chi_{k_{ex}}^{-} | \omega_{sc\ ex}^{(-)\dagger} V_C | \chi_{k_{in}}^{+} \rangle \otimes | \phi_{co} \rangle , \quad (9.17)$$

where the  $|\chi^{\pm}\rangle$  are the multiple scattering states computed by the multiple scattering codes.

We can now inject this result into the cross-section

$$\frac{d^3\sigma}{dE_1 d\Omega_{k_{sc}} d\Omega_{k_{ex}}} \Big|_{\text{BrI}} = 2\pi^4 \left( \frac{2m}{\hbar^2} \right)^3 \frac{k_{sc} k_{ex}}{k_{in}} |S_0^{N-1}|^2 \sum_{av} |T_{fi}|^2 , \quad (9.18)$$

to obtain a workable formula within the first Briggs approximation.

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