Electron-electron coincidences experiments on surfaces, status and perspective of a new spectroscopy

G. Stefani

Unitá INFM Roma 3 and Dipartimento di Fisica E. Amaldi, Universitá di Roma Tre, via della Vasca Navale 84, 00146 Roma, Italy

Abstract. The past decade has witnessed a sizeable increase of activity in the field of electron-electron coincidence on surfaces.
Electron collision and photon absorption have been exploited to perform correlated experiments in a variety of kinematics and involving valence as well as core electrons. In these break-up experiments the kinematics of the ionising event is fully determined. In this talk I shall concentrate on those experiments performed in reflection geometry as they are thought to be particularly suited to investigate surface rather than bulk properties. To understand which is the dominant mechanism that leads to ejection of pairs of electron from the surface and what novel information is yielded by these spectroscopies is the main aim of this work. This issue will be discussed in two cases :
a) the grazing and normal incidence (e,2e) experiments performed at low and intermediate energies,
b) the first angle resolved Auger-photoelectron coincidence experiment.
It will be shown that for both classes of experiments, depending on the kinematics chosen, the correlated behaviour of the pairs of electrons detected might prevail on the independent particle one.

1. INTRODUCTION

Electron-electron coincidence spectroscopies have been extensively applied to atomic and molecular physics since early seventies and ever since then they have grown in number and relevance. This conference itself testifies the constant flourishing growth of this sector. To apply this methodology to solids and surfaces has been a major target since the beginning but the time needed to complete a coincidence experiment has hampered its attainment. This time is usually too long when compared with the speed at which a clean surface gets contaminated, even in a state of the art ultra high vacuum system. This handicap has been surmounted during the past decade by the help of new high luminosity multicoincidence apparatuses and high brilliance light sources. Once again, innovative instrumentation opens up new applications to established methodologies.
Similarly to what has happened for atoms and molecules, these coincidence experiments can be used to study the dynamics of the electron interaction with and within a solid. This will be the focus of this talk and I shall concentrate on two examples: (e,2e) experiments in reflection geometry and Angle Resolved Auger-Photoelectron Coincidence experiments (AR-APECS).
In these break-up experiments the kinematics of the ionising event is fully determined and two main issues are and have always been at stake : i) which is the dominant mechanism that leads to ejection of electron pairs from a solid surface, ii) which information, not already available from currently used spectroscopies, is yielded by these "exotic" spectroscopies.
For both classes of experiments, depending on the kinematics chosen, the correlated behaviour of the electron pairs might prevail on the independent particle one.

2. REFLECTION GEOMETRY LOW ENERGY (e,2e)

The experimental aim is to determine the kinematics of the electron collision as fully as possible and the goal is achieved by detecting coincident in time the two final electrons. The reaction is initiated by a slow monochromatic electron impinging onto the surface, momenta and energies of the two final electrons are

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measured as well. The first experiment of this kind was performed few years ago [1]. By this experiment it has been shown that it is possible to obtain a full picture of the collision dynamics and, more importantly, to do this in sufficiently a short time to allow highly reactive surfaces to be investigated as well as the more inert ones. The crucial breakthrough lies in combining the time-of-flight and coincidence detection with a pulsed current. This allows the complete energy spectrum of the electron pairs emerging from the surface to be measured simultaneously, and hence with great efficiency, at given angles. The investigations that have followed this first experiment, on various targets and with various kinematics, speak in favour of a direct electron-electron scattering, rather than a cascade process of secondary electrons, as the dominant mechanism for electron pair creation at low-intermediate energies.

A recent study [2] shows that, at least at low energy, the pair of final electrons ejected from the surface in a reflection (e,2e) event can be described by a quasi-particle with an internal degree of freedom. The energy distribution of the pair reveals structures that might be interpreted as resulting from diffraction of the quasi-particle from the crystal lattice. This gives the unique chance to study the dynamics of direct electron collisions a few electron volts above the vacuum level.

3. REFLECTION GEOMETRY INTERMEDIATE ENERGY (e,2e)

For energies well above the vacuum level, the (e,2e) event is also dominated by direct impact processes and provides a "portrait" of the electrons moving in the initial bound state that can not be given by any other kind of electron spectroscopy. Based on the experience gained in atomic physics, it is now well established that (e,2e) has the unique capability of measuring the momentum distribution of the initial state directly. Although angle resolved photoemission spectroscopy can yield accurate determinations of the energy versus momentum dispersion, it can not measure momentum distributions. Compton scattering can give momentum distributions, albeit with limited binding energy discrimination and negligible surface sensitivity.

The potential capability of high energy (e,2e) to measure surface momentum densities was recognised as long ago as the late 1960's, but it was not until recently that the Rome's group has succeeded in performing the first momentum density determination in grazing angle reflection geometry [3]. The experiment, performed on a sample of pyrolitic graphite (HOPG) using 300 eV energy incident electrons and a grazing angle of 7°, established the feasibility of a spectroscopy that could shed light on binding energy and momentum density of solid surfaces. In order to measure the momentum density the collisional model must be reliable. In the case of (e,2e) experiments in transmission kinematics and of energies of several KeV, the interaction mechanism is simple and well established ; the Plane Wave Impulse Approximation, already applied in the atomic case, holds very well [4]. The model adopted and successfully applied till now for the grazing angle reflection geometry, is based on the First Born approximation. The projectile is treated as a plane wave whereas the target electron initial and final states are described by one-electron wave functions in the momentum space representation. Similarly to the three step model of volume photoionisation from solids, the ejected electron wave function within the solid matches the energy and the parallel component of the momentum of the plane wave in the vacuum. Within first Born approximation and using plane waves for the ejected electron the cross-section factorises in the product of a kinematical factor times the Mott factor times the momentum density of the initial state.

. Of the various dynamical models suggested to describe the grazing reflection (e,2e) experiment we accept only one dominating mechanism in which the projectile reflects specularly from the target and then scatters inelastically from the bound electron [5]. This assumption is corroborated by recent experimental evidences obtained by measuring excitation spectra of HOPG by electron impact at intermediate energies and in specular reflection geometry [6]. This work shows that the dominant collision mechanism consists of two independent interactions, an elastic one with the crystal lattice that is followed or preceded by an inelastic one with the valence electrons. The two channels of the double scattering event can be isolated, one from the other, suitably coshing the kinematics of the experiment. Other mechanisms in which the (e,2e) event is caused directly by the incident electron have much larger momentum transfer and are strongly suppressed by the Mott factor which is proportional to the inverse forth power of the momentum transfer.

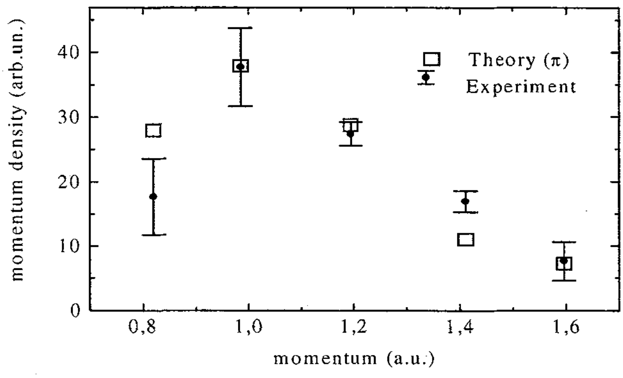

Figure 1. Comparison between (e,2e) measured (solid circles) and theoretical (open squares) momentum distribution for π band electrons in highly oriented pyrolotic graphite.

Results of the (e,2e) experiments on HOPG are compared with a calculated momentum density of the π band that adopts the Linear Muffin Thin Orbital method to describe the solid bound states. In figure 1 the momentum density as measured for the π band adopting the aforementioned double scattering collision model in conjunction with the plane wave first Born approximation is compared with the one calculated in LMTO approximation. In the experiment the ejected electrons are collected within the hollow cone accepted by a cylindrical mirror analyser, hence the measured momentum density is averaged over a sizeable fraction of the first Brillouin zone [3]. The shape of the two curves agrees fairly well but for the lowest momentum, for which the plane wave approximation might be too crude.

Experimentally, it would be more advantageous to resolve fully the ejected electron momentum and perform an (e,2e) reaction on the surface of crystalline rather than rotationally disordered HOPG. These developments in theory and experiment [7] are currently under way and promise a better understanding of the physics of the electron impact ionisation of solids.

4. ANGLE RESOLVED APECS SPECTROSCOPY

In recent years there has been a growing interest and activity in the field of Auger-Photoelectron coincidence experiments (APECS) applied to solids. The unique capability of this technique to disentangle signals originated from different sites within the solid or from overlapping spectral features, together with its high surface sensitivity make it very attractive for surface analysis [8]. Until now these experiments have always been performed in angle integrated mode. Correlation in energy of the two final electrons (Auger and photoelectron) has been shown to be relevant both in atoms and in solids. Correlation in momentum of the final pair has been modelled and measured only in isolated atoms and at low energies, where the continuum final state effects dominate [9]. To extend angle resolved APECS to higher energies and to solid targets it is a major task and is not at all clear what will be the interplay between the "atomic like" angular distribution of the two final electrons and the scattering from neighbouring atoms.

The first step towards attainment of this target has been recently made by an experiment performed on the $L_3M_{45}M_{45}$ transition of the Cu(111) surface. This pioneering experiment was performed at ELETTRA with the ALOISA beam line that is at present, with its multicoincidence system, the only apparatus capable of efficiently performing such experiments fully resolved in angle. By this experiment it has been measured the angular distribution of the Cu $L_3M_{45}M_{45}$ Auger electrons detected in coincidence with Cu $2p_{3/2}$ photoemission line tuned at a diffraction maximum and minimum alternatively. The most relevant finding of this investigation being that the APECS angular distribution exhibit a shape not always reducible to the incoherent combination of the individual angular distributions of the two final electrons. In other words, this result clearly speaks for inadequacy of the two step model that is commonly accepted for non

coincident experiments performed at the same energy and on the same process of core hole creation and relaxation. In particular, the largest discrepancy between the two step uncorrelated model and the experiment has been found for the photoelectron set at a minimum of the diffraction pattern [10].
To properly describe the result of this experiment, theory should account, at the same time and within a single step model framework, for both initial state electron correlation and diffraction from the crystal lattice of the final state correlated wavefunction of the emitted electron pair [11]. In this model, the intermediate ionic state is seen as a continuum distribution over all possible core hole states plus the photoelectron wavefunction and the whole process is treated as a resonance in the double photoionisation.

CONCLUSIONS

Electron-electron coincidence experiments on surfaces have been demonstrated to be possible with both electron and photon excitation. These experiments are proving to be very surface sensitive and characterised by a very high degree of discrimination of the atomic site and of the chemical environment.
Besides the enhanced discrimination and sensitivity they posses some unique characteristics not shared with other electron spectroscopies. Among them the capability to perform momentum spectroscopy of the (e,2e) experiments and the possibility to investigate new aspects of electron correlation in bound and continuum states of the angle resolved APECS. Many interesting future developments are in sight for both these novel spectroscopies

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