Multi-electron correlation spectroscopy of atoms and molecules

Delphine Lebrun
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Introduction

Motivation

Correlated many-particle dynamics in Coulombic systems is one of today’s grand challenges in physics. In order to address this task, the electronic structure and electron correlations of multiply ionised systems are studied in this thesis, aiming to obtain information on the dynamics of electron emission processes at unprecedented ease and high resolution. State-of-the-art multi-electron correlation spectrometers are used, which were originally developed at Oxford University, UK, and which are now frequently in use at the Ångström laboratory in Uppsala, Sweden.

The research is so far based mainly on single-photon excitations using laboratory light sources and synchrotron radiation facilities, and expands now gradually into non-linear and time-resolved studies of atoms, molecules and clusters using high intensive Free Electron Lasers (FEL) in the Vacuum Ultra-Violet (VUV) and X-ray spectral region. This development is highly relevant for even more deep-going applications regarding the ion and excited-state balance in the Earth’s outer atmosphere and in astrophysical contexts, for photochemistry and biochemistry, for materials science, and to test current atomic and molecular structure theories to their limits.

We will focus on the multiple ionization of the buckminsterfullerene (C_{60}) which is of scientific interest as an exceptionally stable and symmetric cluster. Its applications are quite large in nanotechnologies.

Single and multiple-ionization processes

Photoelectric effect

Matter exposed to high energy light may emit electrons. The first observation of this phenomenon known to us today as the photoelectric effect was made by Heinrich Rudolf Hertz in 1887, who explored that the incidence of ultra-violet (UV) light on a spark gap facilitated the passage of the electrical spark. Later on, Aleksandr Stoletov discovered the direct proportionality between the intensity of the light and the induced photo-electric current. Furthermore, at the beginning of the 20th century, Philipp Lenard realized the possibility to ionize a gas with UV light. He found that the calculated maximum electron kinetic energy is determined by the frequency of the light. The theoretical explanation of all these observations was given by Albert Einstein in 1905\(^1\). In his paper he introduced the idea that light is composed of “quanta” of energy: “The body’s surface layer is penetrated by energy quanta whose energy is converted at least partially into kinetic energy of the electrons. The simplest conception is that a light quantum transfers its entire energy to a single electron”\(^2\). These light quanta –named later on photons- justify the assertion that the energy of light is discontinuously distributed in space and are the basis for today’s understanding of light-matter interaction.

Einstein provided an equation for the photoelectric effect which fit the experimental data and concluded that the energy of photoelectrons was dependent only on the frequency of the incident light and not on its intensity:

\[
KE_{\text{max}} = h\nu - \varphi \quad [\text{eV}] \quad (\text{eq}1)
\]

Here, \(KE_{\text{max}}\) denotes the maximum kinetic energy of the photoelectron ejected, \(h\nu\) the energy of the light (quantized) and \(\varphi\), in case of condensed matter the work function, i.e. the energy needed to
move an electron from the Fermi level into vacuum, and in case of free atoms and molecules the binding energy of the released electron.

Photoionization, which is schematically illustrated in figure 1, implies the emission of an electron when matter is exposed to radiation. The frequency of the radiation determines if an electron will be ejected and from which orbital. The kinetic energy of the ejected electron is directly linked to the photon energy according to Einstein’s photoelectric law (cf. eq. (1)). As a consequence, a vacancy, also often called a ‘hole’, is created in the electronic shells of the atom, and may undergo further reactions.

The situation before and after the photoionization process can briefly be denoted as equation (2), where $A$ stands for a neutral atom and $h\nu$ the photon energy absorbed by the system:

$$A + h\nu \rightarrow A^+ + e^- \quad (eq2)$$

The principle of energy conservation leads to:

$$KE = h\nu - (A^+ - A) \quad (eq3)$$

The difference in energy between the singly-ionized atom $A^+$ (also denoted as cation) and the neutral atom $A$ can be understood as the binding energy (BE) of the electron, in particular if the recoil energy of the ion is negligibly small, which is often valid to a very good approximation.

Generally, the outer shells in an atomic system, are called valence levels and the inner shells are called core levels.

![Schematic illustration of the photoionization process: a photon is absorbed and a photoelectron leaves the system](image)

If a core electron is removed, the ionized state of the atom $A$ is not stable (lifetime of remaining state approximate $10^{-8}$ s). The remaining electrons of the atom will screen the hole and several processes can occur: an electron from an higher lying orbital can relax into the hole by emission of a photon (radiative decay) or the excess energy can be transferred to another electron which leaves the atom (Auger decay, see also below); the final state of the atom is therefore $A^{2+}$. But these relaxations are not straightforward, since the cross section of the process and the size of the atom play a role, and some interactions between the emitted electrons and the electron cloud can occur (shake up). The probability of a photon ionizing an atom is high when the energy difference
between the photon and the binding energy of the electron is small (~0.1 – 1.0 eV), close to the ionization threshold; and decreases with decreasing wavelength.

A photoelectron which has not lost energy is referred to as a direct photoelectron; in contrast, a photoelectron which has lost energy is an indirect photoelectron (by processes as, e.g., the already mentioned Auger decay). Measurement of the intensities and energies of the outgoing electrons with an electron spectrometer produces a photoemission spectrum that mirrors the distribution of filled levels in the matter.

To calculate the binding energy of an electron, one can make use of Koopmans’s theorem:

\[ BE = E_{\text{final}(n-1)} - E_{\text{initial}(n)} \]  

which is only an approximation, since it does not take into account relaxation effects of the system. This implies a rearrangement of the electron cloud in order to reduce the total energy, taking into account the positive hole. Some other aspects may come into play during the photoemission process such as relativistic effects and electron correlation. Koopmans’s theorem is a useful tool to get roughly an idea of which electrons can be removed at a given photon energy. More sophisticated calculations involve quantum mechanical and quantum chemical methods like, e.g. density functional theory (DFT).

Also the spin-orbit splitting effect, which occurs when electrons can have different spin configurations on the same orbital, is important in this context. For instance, an electron from a p-orbital can lead to a total angular momentum \( j = 1/2 \) or \( j = 3/2 \), splitting the core-level into a doublet (which can be resolved in an electron spectrum).

Auger decay

Enlighted in 1922 by Lise Meitner\(^5\) in one of her articles on nuclear physics, and fully described later on by Pierre Auger in an independent experiment based on a Wilson chamber, the emission of an additional electron subsequent to the release of a photoelectron was revealed. This is known today as the Auger effect. As Auger understood it himself\(^6\), this process is not restricted to the emission of a single electron. Auger decay is the prominent process if electron rearrangement, driven by Coulomb interaction between remaining electrons, is faster than the radiative decay in atoms\(^7\).

A useful characteristic of the Auger electron is its independence on the photon energy due to the nature of the underlying process, as illustrated Figure 2. Upon creation of a core-hole, the vacancy may be filled by an outer electron and the excess energy transferred to the later Auger electron, with a well-defined kinetic energy determined by the energy difference of the binding energy of the Auger electron, the binding energy of the core hole and binding energy of the relaxed electron\(^8\).
Alternatively, instead of an Auger electron, an X-ray fluorescence photon may be observed, as systematically studied early on by Henry Moseley at Oxford and later on refined by Manne Siegbahn in Uppsala. In these early spectroscopic studies, a letter nomenclature for the electronic shell structure has been introduced as is summarized in Table 1. It is often used also in the context of Auger decay processes in the following way: the letter corresponding to the shell of the first electron (the photoelectron), the letter corresponding to the shell of the decaying electron and the letter corresponding to the shell of the outgoing electron are used to classify the pathway. For example, if the photoelectron originates from the $1s$ shell, the $2p$ electron fills the vacancy and another $2p$ electron is ejected, then the spectroscopic notation is: KLL.

<table>
<thead>
<tr>
<th>Main quantum number</th>
<th>Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K</td>
</tr>
<tr>
<td>2</td>
<td>L</td>
</tr>
<tr>
<td>3</td>
<td>M</td>
</tr>
<tr>
<td>4</td>
<td>N</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
</tr>
</tbody>
</table>

### Table1: spectroscopic notations

Auger decay can also involve inner shells: it is then called the Inner Rydberg Auger effect. A special type of Auger transition, which is called the Coster-Kronig transition, involves the filling of the primary vacancy by an electron from the same main shell (that is same principal quantum number) but a different subshell (corresponding to different orbital momentum quantum number).

One can define the Auger yield as:

$$a = \frac{P_A}{P_A + P_{CK} + P_R} \quad (eq5)$$

where $P_A$ denotes the probability of Auger decay, $P_{CK}$ the probability of a Coster-Kronig decay and $P_R$ the probability of radiative emission. The Auger yield decreases with increasing atomic number.

Generally, the recorded electron spectra\textsuperscript{10} can be composed of Auger and photoelectron peaks. The lower-binding energy peaks may quite often involve ejection of an electron from the valence band, while the higher-binding energy peaks correspond to the emission of a core electron. By varying the photon energy, the Auger peaks will stay constant on the kinetic energy scale, while the peak
positions of the photoelectron lines move according to the photoelectric law (cf eq.(1)). In condensed matter, Auger peaks are often broadened by small energy losses from the electron escape. Losses may also occur due to interband transitions and creation of electron-hole pairs.

Electron dynamics

Associated with the initial photoionization, different processes can be observed. For example, the departing electron can interact with other electrons when leaving the atom. It can lose energy and give rise to an excited state of the atom, where an electron has been transferred to an unoccupied state. This process is referred to as *shake-up*.

The departing electron may even knock-out another electron and give it enough energy to allow for leaving the atom. This process is referred to as *shake-off*. Such an ejection changes the local electric field very suddenly.

Another process can be mentioned, it is the Post-Collision Interaction (PCI)\(^{11}\). If the first ejected electron (photoelectron) has less energy than the second electron (Auger), then the Auger electron may overtake the photoelectron, and the two particles may exchange energy by Coulomb interaction. The faster electron (Auger electron) will gain energy since it will be shielded from the core by the slower electron. The slower electron will lose energy due to the additional positive charge it will experience.

Multiple ionization

As we have seen so far, single-photon absorption can lead to multiple electron emission. This multiple ionization can be either direct or indirect.

Direct multiple ionization is the simultaneous emission of all ionized electrons via a shake off process and the photoelectric effect. These electrons are correlated. Therefore, they share the excess energy arbitrarily, and hence the energy distribution is expected to be continuous (flat).

In contrast to that, indirect multiple ionization is the stepwise emission of electrons via intermediate states. In atoms, the predominant process is, as discussed above, the Auger decay. Depending on the photon energy chosen and the system studied, indirect multiple ionization may be the dominant process.

Experimental setup

Light sources

The kinetic energy of an electron can be measured either by means of an electrostatic energy analyzer or by means of a time of flight energy analyzer. The latter choice\(^ {12}\) implies the use of a pulsed light source and sets constraints on the minimum inter-pulse period (which, ideally is longer than the slowest particle’s flight time). The light has to be sufficiently intense at a suitably high repetition rate, and also a narrow pulse width is needed. For the experiments to be discussed in the following, we make use of radiation from, either a Helium discharge lamp, a synchrotron or an ultrafast free electron laser (FEL).
He gas-discharge lamp

The Helium lamp is based on a discharge in a hollow cathode. The heart of a hollow cathode lamp consists of a glass or ceramic tube which contains a buffer gas, in our case He. A high voltage applied across the gas will excite and/or ionize it, thus leading to a plasma. As the excited atoms decay to lower states, they will emit photons which can then be detected, and a spectrum can be determined. In the case of our He lamp, we can make use of spectral lines in the photon energy range $21 – 48$ eV. The first experiments used only a capacitor and the Helium lamp, but in order to pulse the emission, a hydrogen thyratron is now used. A thyratron is basically a high energy electrical switch$^{13}$. With such a device, the switching can be done with kHz repetition rate. A grating monochromator is used to select one wavelength in the ultraviolet range. The Helium lamp we use is shown in figure 3.

Synchrotron radiation

Synchrotron radiation is a useful tool for many experiments because it offers photons at high flux in the infrared to hard X-ray spectral region. Essential components to create this kind of radiation in a laboratory are an electron source (electron gun) and a storage ring. The electrons are accelerated in a booster ring up to GeV energies before they are injected to the storage ring. The storage ring consists of bending magnets, used to bend the trajectory of the electrons, and straight sections where insertion devices such as undulators are placed. Undulators (cf fig.5 & fig.6) are composed of a double array of magnets with alternating polarity (north and south consecutively). An electron passing through the undulator will be forced by this magnetic field, to move on a wiggled trajectory. Because the electrons travel close to the speed of light, they experience a Lorentz contraction in space and also feel a Doppler effect, as schematically illustrated in figure 4. It is therefore of no need to have an undulator of kilometer length. The distance between the two rows of magnets is used to change the magnetic field strength experienced by the electron. By changing this distance, it is possible to change the energy of the emitted photons (see eq.6
The emission of this so-called synchrotron radiation decelerates the electrons in the bunch. Applying regularly voltage in form of a radio-frequency field allows the electrons to circulate in the storage ring for some hours. This radio-frequency field causes electrons to accumulate in bunches. Two different operation modes are possible in a synchrotron facility: single bunch or multi bunch operation.

The electrons emit light, passing an undulator, at a wavelength depending on the magnetic field $B$, according to:

$$\lambda \sim \left( \frac{\lambda_p}{2\gamma^2} \right) \times (1 + bB^2) \quad (eq6)$$

Here $\lambda_p$ denotes the spatial period of the magnetic field, $\gamma$ the Lorentz factor, $B$ the magnetic field and $b$ is a dimensional factor.
In order to extract the synchrotron radiation from the storage ring and guide it to the experimental stations, beam lines are used. Beam lines consist of several different optical elements such as mirrors and gratings. The heart of the beam line is a monochromator which selects a certain wavelength of the emitted light. The beam line is typically under ultra high vacuum (10^{-9} mbar). Various sections of the beam line are equipped with valves for security purposes. The user can control many aspects of the beam line such as the entrance slit, the photon energy set by the monochromators and the width of the exit slit. The software of the beam line computer states the photon energy based on frequently performed calibration checks. The photon flux depends on the entrance slit dimension, the separation between the rows of the undulator and also the monochromator bandwidth associated with the photon energy.

![Image of undulator segment](image.png)

6: View of an undulator segment (9 poles, 10 magnets) 

**Free Electron Laser**

A Free Electron Laser (FEL) is a novel type of light source in the VUV and X-ray spectral region. The principle is rather simple and builds on undulator radiation. As in the case of a synchrotron radiation facility, an electron beam is produced by an electron gun and passes through an electron accelerator, before entering a long series of undulators, where the light produced at an earlier instant of the undulators can interfere with the light emitted at further distances.

Undulator radiation can mathematically be described by following equation:

\[
\lambda_s = \frac{\lambda_U}{2\gamma^2} \left[ 1 + \frac{K^2}{2} + (\gamma \theta)^2 \right] \text{[cm]} \quad (eq7)
\]

where \( \lambda_s \) is the positive interference wavelength, \( \lambda_U \) the undulator period, \( \theta \) the angle between the emitted light and the central orbit, \( K \) the undulator strength parameter and \( \gamma \) the relativistic parameter. The latter one is defined as:

\[
\gamma = \frac{1}{\sqrt{1 - (\frac{v}{c})^2}} \quad (eq8)
\]

where \( c \) is the speed of light and \( v \) the particle velocity.
The undulator strength parameter $K$ can be expressed as:

$$K = \frac{\lambda_u e B_0}{2\pi m_e c \gamma} \quad (eq.9)$$

where $B_0$ is the magnetic field strength, $e$ the elementary charge and $m_e$ the electron charge.

The undulator equation (eq.7) reflects positive interferences of the radiation at a given wavelength. This wavelength is tunable via machine parameters such as the electron beam energy and the magnetic field strength, whereby the latter depends in practice on the distance between the two arrays of magnets$^{14}$.

The most important effect for understanding the principle of an FEL is the interaction between the electron beam and the radiation field. Spontaneous radiation is emitted by the electron travelling along the undulator, and is as such comparatively weak and incoherent$^{16}$. Because the beam is narrow and does not deflect too much from the central direction of propagation, the electron beam can interact with the emitted light.

If the electron and the light field are in phase, and are pointing in the same direction, the electron loses energy which is transferred to the light field$^{16}$. If the phases are different, the electron gains energy. After a short time, the more-energetic electrons catch-up the less-energetic ones; the electron beam consists now of bunches of electrons spaced with the light wavelength. The waves radiated by the initially random electron then add in phase with one another. The bunches are in phase with the incident light field, the emission of the bunches adds coherently to the light field and amplifies it.

This interaction is called micro-bunching and is illustrated in figure 7. At resonant conditions, the electron beam and the radiation field can exchange energy over several undulator periods, which can lead to a net gain of energy in the radiation field$^{14}$. 

One of the major features of an FEL is its high brilliance, notably in the X-ray region which is not available at other light sources. And because of its transverse (consists of oscillations occurring perpendicular to the direction of energy transfer) coherence, the FEL is diffraction limited (at saturation). The longitudinal (waves that have the same direction of vibration as their direction of travel) coherence is comparatively poor and affect the repeatability of the pulse structure, i.e. each pulse is different. The high brilliance makes it challenging to find suitable materials for measuring the emitted light, splitting the light or even measure calibration spectra directly.

As illustrated in figure 8, a new generation of FEL consists of two series of undulators separated by a chicane, where the conversion between energy and density modulation can be done. Different parts of the bunch take different paths through the chicane, realized by two bending magnets that deflect away and return the beam along the original path. A laser pulse can also be introduced to induce a modulation and thus seed the photon emission. This technique is called High-Gain Harmonic-Generation (HGHG), and is designed to convert the fundamental frequency of the laser to a much higher frequency. The first undulator is used as a modulator, the chicane compresses the bunches (which enhances further the density modulation), and it is in the second undulator where the lasing process occurs. This geometry gives an intense fundamental mode which is narrow, and the shot-to-shot repeatability is also better.

Some efforts are made also to provide beam splitters and light detectors (or attenuators) for the beam diagnostics which is inevitable for any experiment carried out at an FEL.
Principle of a magnetic bottle electron spectrometer

Résumé of magnetism

From the theory of electromagnetism, it is known that a solenoid supplied by a current results in a magnetic field. Oersted studied early on the influence of a current on a magnetic needle, which formed the basis for Ampère to observe the complementary phenomenon on a solenoid. Maxwell equations relate the electric and magnetic field vectors $\vec{E}$ and $\vec{B}$ and their sources which are electric charges and currents. They express the unification between an electric field and a magnetic field:

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad , \quad (eq10)$$

where $t$ denotes the time and $\partial$ the first derivative.

According to Faraday, induced electromagnetic force in a solenoid can be expressed as:

$$\varepsilon = -N \frac{d\phi_B}{dt} \quad , \quad (eq11)$$

where the magnetic flux is given by:

$$\phi_B = B \times A \quad . \quad (eq12)$$

Here $B$ denotes the magnetic field, $A$ the area cross section and $N$ the number of turns of the solenoid.

The Faraday law tells us in our case, that a solenoid will produce an electromagnetic force which will be proportional to its length and to the current which passes through. For a long solenoid, the magnetic field is given by:

$$B = \mu_0 \frac{NI}{l} \quad (eq13)$$
where $B$ is the magnetic field, $\mu_0$ the vacuum permeability, $I$ the electric current, $N$ the number of turns of the solenoid and $l$ the length.

A solenoid can simply be formed by a conductive wire spiral connected to a DC power supply. The electromagnetic field produced is radially uniform inside, as illustrated in figure 9. In a magnetic bottle electron spectrometer, one uses this effect to guide the charged particles, according to the Lorentz force:

$$\vec{F} = q \left( \vec{E} + (\vec{v} \times \vec{B}) \right) \quad (eq 14)$$

Here, $q$ is the charge of the particle, $\vec{E}$ the electrical field vector, $\vec{v}$ the speed of the particle and $\vec{B}$ the magnetic field vector.

If one produces a uniform and directed electromagnetic field, by using this force, one can lead charged particles to a certain position in space where, e.g., a detector is located.

Another way to guide electrons is to use a permanent magnet which produces a comparatively strong magnetic field (several Tesla). For the present discussion, we simply recall that permanent magnets possess a hysteresis behavior due to their characteristics and that we use it to keep the material in its remanent magnetization state.

The equation of motion of an electron in a magnetic field reads as:

$$\dot{\vec{k}} = -\frac{e}{\hbar^2} (\nabla_k \varepsilon) \times \vec{B} \quad (eq 15)$$

Where $\dot{\vec{k}}$ is the motion of an electron, $\nabla_k$ the gradient in $k$, $e$ is the elementary charge, $\hbar$ the Planck constant, $\varepsilon$ the energy and $\vec{B}$ the magnetic field vector. This equation shows that an electron experiencing a magnetic field will change both trajectory and velocity.

In 1989, Kruit and Read\textsuperscript{19} published a paper on the magnetic influence on charged particles. They studied electrons passing from a high inhomogeneous magnetic field region to a low homogenous magnetic field region and found an increase of the longitudinal part of the velocity, and, accordingly, a decrease of the transverse part of the velocity (cf fig.10). Due to this parallelization process in the strong inhomogeneous magnetic field, the initial angular information of the emitted electrons gets complex. According to Kruit and Read, the time of flight of the electrons is quasi-independent of the angle of incidence of the charged particle if the low-field evolves adiabatically.
The major contribution to the variation of the time of flight comes from the high-field region. A compromise has to be made for the design of the magnetic fields. The thigh-field region needs to be kept short in order to reduce the broadening of the time of flight, and the so-called adiabatic parameter, which reflects the gradient between the two field regions, must also be small. The shape of the permanent magnet is preferably chosen to be cone-like with the tip truncated, allowing to direct the electrons more straightforward.

**10:** Schematic diagram showing the helical motion of an electron moving in a magnetic field that changes gradually from a strong field $B_i$ to a weaker uniform field $B_f$, according to the work of Kruit and Read.

**Magnetic bottle**

A magnetic bottle spectrometer is based on the idea of using a combination of high and low magnetic fields to direct all electrons created in a photoionization process to a distant detector and record the arriving time in comparison to a time reference. Since the travel distance and the electron mass are known, the time of flight can be converted to the kinetic energy of the detected electrons. The flight tube consists of several components (cf fig.11). The outer tube is surrounded by a μ-metal which protects the electrons from the undesired influence of the Earth magnetic field (which has a field strength in the order of 24 nTesla to 66 nTesla). A μ-metal is a nickel-iron alloy (approximately 75% nickel, 15% iron, plus copper and molybdenum) that has very high magnetic permeability. The magnetic shielding properties rely on maintaining a large crystalline grain size of around 100 μm or more in the material. Static or slowly varying magnetic fields can only be redirected, not created or removed; each material has a magnetic saturation, which determines the magnetic field strength that can effectively be shielded.
The electron flight tube itself is made of stainless steel around which a copper wire is wrapped. The copper wire forms the solenoid to produce the homogeneous magnetic field inside the tube by applying an electric current (referred to last chapter). In order to decelerate or accelerate the electrons, a so-called inner-tube (also “flight tube” or “drift tube”) is installed which is electrically insulated from the other tube. Indeed, as we can see from the definition of the unit “electron volt”, it is the amount of kinetic energy gained by a single unbound electron when it gets accelerated through an electric potential difference of one Volt\textsuperscript{13}. Therefore, when we apply a potential difference at the entrance of the inner tube, one can remove energy or add energy to the charged particles. It is important to influence the spectral resolution. Generally, if a particle has a very high kinetic energy, its time of flight is very short and hence the resolution is worse in a time-of-flight spectrometer, compared to lower kinetic energies. I.e. if one can retard high kinetic energy particles, it is possible to study them at a good resolution, too. Furthermore, this inner tube is also useful to accelerate particles with kinetic energies close to zero without having to change the photon energy.

Above we already discussed that an electron spirals around the magnetic field lines, whereby the electron (or charged particles) follows a helical trajectory in going from the strong-field region
(permanent magnet) to the low-field region (solenoid). When it enters the inner tube, the electron trajectory starts to be linear (but the electron still describes a spiral around the magnetic field lines) because the magnetic field lines inside the solenoid are parallel to its axis\textsuperscript{19}. Of course, it is possible to have electrons without a straightforward pathway since they are emitted in all directions, and even electrons which do not hit the detector.

A critical angle can be defined for which electrons are not reflected backwards\textsuperscript{8}:

\[ \theta_{\text{crit}} = \arcsin \left( \frac{B_{\text{magnet}}}{B_{\text{tube}}} \right) \quad (eq16) \]

Electrons can also reach the detection region on a trajectory of length different from an integer number of turns around the magnetic lines and hence may not be counted. The equations linked to the trajectories are not simple but one can express the flight length of an electron as follows\textsuperscript{22}:

\[ \text{flight length} = n \times d \quad (eq17.1) \]

where \( n \) is an integer and \( d \) is the longitudinal distance for an electron making a complete turn which can be expressed as:

\[ d = t \times v_{\text{longitudinal}} \quad (eq17.2) \]

with \( t \) being the time needed to complete a full turn and \( v \) is the longitudinal velocity.

We know that the longitudinal part of the velocity contributes mainly to the kinetic energy (KE):

\[ v_{\text{longitudinal}} = \sqrt{\frac{2KE}{m}}. \quad (eq17.3) \]

We now need to express the time of a complete turn:

\[ t = \frac{2\pi R}{v_{\text{transversal}}}, (eq18) \]

where \( R \) is the radius of the electron trajectories.

To express the transversal velocity, one needs to combine the Lorentz force and the centrifugal force:

\[ F_{\text{Lorentz}} = e \times B_{\text{longitudinal}} \times v_{\text{transversal}} \quad (eq19) \]

\[ F_{\text{centrifugal}} = \frac{mv_{\text{transversal}}^2}{R} \quad (eq20) \]

\[ v_{\text{transversal}} = \frac{eRB_{\text{longitudinal}}}{m} \quad (eq21) \]

Summarizing all these results, we get:

\[ \text{flight length} = n \times \frac{2\pi m}{B_{\text{longitudinal}}} \times \sqrt{\frac{2KE}{m}} \quad (eq22) \]
The kinetic energy is the one which the electron has just after entering into the flight tube (so with or without any additional voltage).

Technical review

Review of the spectrometer set-up

The spectrometer set-up can be divided into the following parts: light source, interaction chamber, flight tube and detector, as illustrated in figure 11 above.

Suitable light sources, such as Helium lamps, synchrotron radiation facilities and FELs have been discussed above and hence do not need any further considerations here.

The interaction chamber comprises a light detector based on MCP plates, a permanent magnet and either a gas needle or an evaporative oven source. The light detector is used to monitor the ionizing light pulse. The role of the permanent magnet was already discussed above. To recapitulate briefly; it is used to direct all the electrons created towards the drift tube. The needle is used to introduce into the chamber a certain amount of gas in form of a narrow jet. The oven is an alternative sample source, used to evaporate condensed samples, such as C_{60}. The oven is essentially a container heated by the Joule effect with a narrow opening for the vapor formed during the heating process. The surface of the needle and the magnet were painted by colloidal graphite to lower their reflectivity and to avoid local electric charge accumulation. The flight tube is about 2.2m long which the electrons need to travel before they reach the detector. The detection is done with a set of microchannel plates (MCPs) and fast timing electronics.

Detector

We use a MCP detector to count the electrons emitted after ionization of the gas sample. A microchannel plate (cf fig.12) is a piece of glass pierced by thousands of miniature electron multipliers aligned parallel to each other. A typical channel has a diameter of few to hundreds of micrometers. Each channel acts as an independent, continuous dynode multiplier. A dynode multiplier is a vacuum tube structure that multiplies incident charges by the so-called Avalanche effect, i.e. a single electron can induce emission of several other electrons when it bombards the walls of such a tube. In a MCP, the multiplication takes place under a strong electrical field. The amplification of the signal determines the gain. For charged particle detection, high gain is reachable (10^6 to 10^8), define the parameters of the ratio between the length over the diameter of the individual channels and the applied voltage (increase linearly until a plateau value is reached).
Several MCPs are oriented in certain configurations such as Chevron or Z-stacks, suppressing the positive ions feedback (ions generated by the electron from the interaction with the channel walls, which can produce secondary electrons at the cathode). The dead time of the detector and the subsequent electronics set limitations with respect to the ultimately achievable time resolution. In the present set-up, we encounter a typical dead time of about 10-20 ns, which prohibits detection of electrons with exactly the same kinetic energy.

**Manipulators**

We used micrometer-based XYZ manipulators for the magnet and the needle, which enables us to move precisely the magnet and the needle to position them adequately in the interaction chamber, and relative to the light beam.

The interest of moving the magnet and the needle is for optimizing the resolution of the spectrometer. When the needle is too far away, the gas may spread out and the interaction point becomes large, increasing the number of particles which are not taking a proper path to the flight tube. The position of the permanent magnet plays a role with respect the trajectories of the particles; as discussed above, it needs not to be too close to the flight tube (magnetic field gradient). By moving the magnet further back from the interaction region, it is possible to increase the count rate. But of course, if the magnet is too far away from the light, then its strength decreases and the particle collection efficiency and the resolution decreases, too. One has to vary carefully the position of these two parts of the instrument and study the influence on the spectra. It is part of the optimization procedure prior to calibration of the experimental setup. For these purposes, we usually use Xenon gas because it is has a well-known abundant Auger spectrum.
BESSY experiments

Coincidence detection and analysis

The present experiments involve the coincidence detection of several particles from a single event, by measuring their arriving times at a single detector. A paper from McCulloh et al. published 1965 describes an experiment on doubly charged ions using a related coincidence technique. They describe the coincidence as: “A single ionization (event) is marked by a pulse from the ion detector which follows a pulse from the ejected-electron detector, the time interval between pulses being equal to the difference of travel times of these particles”.

Based on this, to determine “true” coincidences, it is important to look at a time window in which every single count can be assumed to come from the same event. This time window is a critical choice, where the duration of the event, the time of flight of the particles and the period of the light source have to be taken into account. As schematically illustrated in figure 14 below, a timing set-up is needed: pulses from the electron detector and the radio-frequency cavity of the storage ring are amplified and shaped by regenerative amplitude discriminators. Then a delay is applied on the light pulse (in our case 7000 ns) before being register in a Time-to-Digital Converter (TDC). In this case, a card with high temporal resolution (<100 ps) is needed. The electron detector pulse is also delayed (~ 60 ns) before being sent to the TDC card. From the same event a signal is sent to the TDC card to start the counting. There is a dead time of around 10-20 ns; to avoid detection of rebounds in the electron signal of electrons with nearly the exact time-of-flight. This is one possible electrical arrangement for PEPECO, which, generally, needs a period of light source longer than the maximum electron time of flight (~ 5 µs). In the case of a synchrotron, like BESSY-II, where the into-pulse period is much shorter than the flight time of slow electrons (cf fig.13), the electron pulse is used not only as a start signal but also as a “filter” for the light signal: if the light signal does not correspond to an electron signal the light pulse is cancelled. The time of flight (TOF) of the first arriving electron is well-known:

\[ \text{TOF} = \text{ringperiod} - t_{\text{ring}}, (eq23) \]

where \( t_{\text{ring}} \) is the arriving time relative to the start of a light pulse from the storage ring.

13: Timing principles of TOF experiments based on a long magnetic bottle
The ring period corresponds to approximately 21 eV electron kinetic energy; meaning that an electron with energy below this value will not be recorded with the correct TOF.

Simple classical physics are applied to link TOF and kinetic energy:

\[ KE = \frac{m_e v^2}{2} = \frac{m_e (l/t)^2}{2} \sim \frac{d^2}{t^2} \text{ [eV]} \quad (eq24) \]

where KE is the kinetic energy, \( m_e \) the mass of the electron, \( v \) the particle velocity, \( l \) the length of the flight tube, \( t \) the TOF and \( d \) a constant related to the length of the electron flight path.

But to be closer to real experimental conditions, it is important to take into consideration the calibration: there is a small offset in time, \( t_0 \) and in energy, \( E_0 \).

\[ KE = \frac{d^2}{(t - t_0)^2} + E_0 \text{ [eV]} \quad (eq25) \]

The offset in time has to be the same for each similar experiment since it arises basically from the electronical setup. The energy offset originates from contact potentials in the spectrometer, which changes depending on the samples studied. The calibration is done using very well-know electron lines, as already mentioned above. The parameters that can be modified in order to fit are: \( d \), \( t_0 \) and \( E_0 \).

![Diagram of TDC and electron detection with synchrotron light source]

A true coincidence event corresponds to electrons originating from a photon ionization event from the same particle. False coincidence events remain from: electron-electron scattering, background electron emission and other ionizations occurring in different particles. A way to get rid of false coincidences is to make a 2D map: false coincidence electrons will contribute to the overall background since there is no correlation between such electrons. One should also remember that Auger electrons have fixed kinetic energies independent of the light wavelength whereas the photoelectron kinetic energy varies. The inherent limit of the TOF coincidence method is that electrons with nearly the same energy will not be all detected. The total collection detection efficiency is around 40-50\%\textsuperscript{28}.
Experimental details

Preparation of the experiment

To connect our experimental setup to a beam line at the synchrotron radiation facility BESSY, we used a differential pumping stage with two powerful turbo pumps, which create a pressure gradient between the $10^{-9}$ mbar pressure environment of the beam line and our $10^{-7}$ mbar experimental chamber. The spectrometer was aligned to the beam line by using the visible white light part of the synchrotron radiation (which is the zero order). For the experiment, we needed also bright and well focused light, so we carefully avoided the light getting reflected at the entrance pin hole of our chamber.

To monitor the pressure in our chamber, we used Pirani and cold cathode gauges (see Appendix for details on such vacuum components). Pictures of the experimental setup are displayed in figures 15 & 16.

![Photographs of the magnet and needle set-ups](image)

Rotary pumps were then connected to the turbo pumps and pressure gauges were mounted in between these pumps. Additional pressure gauges were used for controlling the pressure in different parts of the gas inlet system. The dry rotary pumps were all connected by a plastic tube to the air exhaust line of the BESSY-II facility.

To be able to apply a voltage on the needle and the magnet, power supplies were connected. A bake out of a few hours at 150°C was applied to the differential pumping section. For security reasons, dangerous gases were enclosed in a specific cabinet, and were transferred through a tube to the gas inlet system. We built a high pressure reservoir for these gases to lower substantially the risk of accidents.

Once the optical alignment of the set-up was done (through a glass window), we used the light detector to measure the light intensity and adjusted more precisely the spectrometer relative to the beam line. Then the electronical connections were made for the detection system (for further detail
A data acquisition computer was connected to the read-outs of the electrons and a home-made software was used to record the spectra.

For the study of vapor from liquid samples, the system was modified by attaching a glass tube to the needle set-up. Furthermore, for the studies of C<sub>60</sub>, which we will discuss further below, the needle set-up was replaced by an oven (cf fig. 17).

The oven is resistively heated; a copper wire is connected to a little container which is thermally insulated from the manipulator by a ceramic plate. Thermocouples are used to control the temperature of the oven and a small needle. The needle is connected to a plastic tube and is used to introduce a reference gas – for the calibration. Using the oven is completely different from the needle because the pressure is hard to control and essentially unknown. For our experiment, we used a cold trap opposite to the oven, filled with liquid Nitrogen, to be able to condense the evaporated C<sub>60</sub> and thus avoiding pollution of the spectrometer. For C<sub>60</sub> experiments, the oven was operated at a temperature of around 510°C. The potential applied on the needle was about -0.25V and it was about -0.5V on the magnet. The spectra were collected during a typical acquisition time of a few hours (2~5 hours, depending on the experiment).
BESSY-II facility

BESSY-II is a third generation synchrotron radiation source located in Berlin (Germany) and is schematically illustrated in figure 18. For the present experiments, we used the facility when operated in single bunch mode. This mode gives light pulses in the order of 50 ps or better at an inter-light-pulse spacing of 800.5 ns \(^2\) (i.e. the light pulse repetition rate is about 1.25 MHz). The beam line is composed of straight vacuum tubes, valves, pressure gauges and a monochromator which selects the wavelength usually as part of a certain harmonic of the undulator in order to ensure a high photon flux. One can use slits to adjust the light intensity exposed to the experiment. This may also affect the resolution, but for the present experiment usually the slits were so narrow that the photon energy resolution was superior to the resolution of our electron spectrometer. The available energy range at this beam line is 86 eV to about 2 keV, with photon fluxes in the range of \(10^9\text{ to }10^{13}\) s\(^{-1}\), depending on the bandwidth chosen. The beamline which we used is called U49/2-PM-2.
During the experimental campaign carried out in spring 2011, we studied a variety of different samples. As an example of the results obtained, we shall discuss in this report $C_{60}$. For calibration purposes, Xenon gas was ionized at 105 eV photon energy which leads to triply ionized states by emission of a primary photoelectron and two subsequent Auger electrons.

The calibration is achieved by such Xenon gas measurements before and after each experimental run.

$C_{60}$ buckminsterfullerene
In what follows, we will focus mostly on the analysis of the C_{60} results obtained with the multi-electron coincidence set-up described above. The full name of C_{60} is Buckminsterfullerene, and its geometric structure is illustrated schematically in figure 19.

In 1985, a group of researchers created C_{60} by laser vaporization of graphite. They concluded, using time-of-flight mass spectrometry, that C_{60} takes a truncated icosahedron shape (soccerball of carbon atoms), a polygone with 60 vertices, 32 faces – 12 of which are pentagonal and 20 are hexagonal. It is a very stable system with all valence shells satisfied by two single bonds and one double bond (carbon electron configuration: 1s^2 2s^2 2p^2). It is a natural element because it is very stable even if formed under violent conditions. This structure has great interest in Nanotechnology due to its shape (used as wheels), its electrical properties, its magnetic properties (most likely unproved yet), and its large diameter (~7Å), providing an inner-cavity which can accept a guest atom or molecule. The C_{60} C1s ionization potential is known to be 290.1 eV in the gas phase and 289.75 eV in the solid phase. Some data of the characteristics of C_{60} are summarized in Table 2.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average C-C distance</td>
<td>1.44 Å</td>
</tr>
<tr>
<td>C60 mean ball diameter</td>
<td>6.83 Å</td>
</tr>
<tr>
<td>C60 ball outer diameter</td>
<td>10.18 Å</td>
</tr>
<tr>
<td>C60 ball inner diameter</td>
<td>3.48 Å</td>
</tr>
<tr>
<td>Binding energy per atom</td>
<td>7.4 eV</td>
</tr>
<tr>
<td>Ionization potential (1^{st})</td>
<td>7.58 eV</td>
</tr>
<tr>
<td>Ionization potential (2^{nd})</td>
<td>11.5 eV</td>
</tr>
<tr>
<td>Spin- orbit splitting C2p</td>
<td>0.0022 eV</td>
</tr>
<tr>
<td>Boiling point</td>
<td>Sublimes at 800K</td>
</tr>
<tr>
<td>Resistivity</td>
<td>1014 ohms m^{-1}</td>
</tr>
</tbody>
</table>

Table 2

Theoretical calculations have been performed to get a picture of the molecular orbitals of the buckminsterfullerene (cf fig.20).
Single-particle energy level spectrum of C\textsubscript{60}, levels sorted by symmetry\textsuperscript{40}

Due to its particular shape, a truncated icosahedron, the C\textsubscript{60} possesses a high symmetry (I\textsubscript{h} group with 120 symmetry elements\textsuperscript{41}) and a closed-shell structure. Due to these characteristics, the HOMO-LUMO (Highest Occupied Molecular Orbital – Lowest Unoccupied Molecular Orbital) gap is expected to be high (~1.1 and 2.04 eV, depending on the literature\textsuperscript{42\&43}). It is interesting to know that the HOMO-LUMOs are symmetry forbidden transitions. The 90 C-C bonds are not all similar: two types of bonds can be found. Thirty bonds are shared by two hexagons and have a double bond character (\(\pi\) bonds) and sixty bonds are placed between a hexagon and a pentagon which is a single bond (\(\sigma\) bonds)\textsuperscript{44}. The bond lengths are therefore not equal: a difference of 0.07\textsubscript{Å} to 0.09\textsubscript{Å} was computed\textsuperscript{45}. The \(\pi\) bonds are, at around 97\%, coming from radial 2\textit{p} electrons and the \(\sigma\) bonds are made from 2\textit{s} and tangential 2\textit{p} electrons\textsuperscript{46}.

Data analysis and Discussions

To analyze the data, obtained with our data acquisition system, we use home-written, off-line data analysis software (written in “Ruby” language\textsuperscript{45}). This software allows us to take into account the physics behind the raw data numbers: a calibration can be made by using, e.g., the 4\textit{d} photoionization data of Xenon. Furthermore, the TOF conversion to kinetic energy and kinetic energy to binding energy can also easily be made.

2D coincidence maps can be plotted with this software. The maps are usually based on kinetic energy scales\textsuperscript{8}. For instance, in the case of triple ionization studies, the total kinetic energy of all three emitted electrons can be plotted versus the energy sum of the second and third arriving electron. Such a map gives deep insight into various possible triple ionization processes. As mentioned before, the photoelectron energy will depend on the photon energy whereas the Auger electron’s energy will remain constant. This method can also be used to distinguish double Auger decay and direct double photoionization. Indeed, two directly emitted Auger electrons can also share their energy arbitrarily, thus leading to a continuous intensity distribution which appears as a horizontal line in the map. In contrast to that, sequential Auger decay will appear as dots in the map. A map can be used to remove false peaks from the data. It has to be mentioned that the energy
versus energy map will inevitably have a narrow dead zone because electron pairs with exactly the same energy cannot be distinguished. Unfortunately, the maps of C\textsubscript{60} look very complicated and are therefore not shown here.

Instead, we study triple ionization and double core hole formation of C\textsubscript{60} in form of conventional spectral plots. Two experiments were conducted on C\textsubscript{60}\textsuperscript{3+} by studying the double Auger decay (photon energy of 296 eV) and core-valence double ionization followed by single Auger decay (photon energy of 360 eV). The first experiment is the study of one core hole created by one photon filled by an electron and followed by the emission of two Auger electrons. The second experiment is based on single core hole creation and the simultaneous emission of a valence electron. In addition to that, the creation of two core holes by one single photon was studied, which subsequently decays by the emission of two Auger electrons to quadruply ionized C\textsubscript{60} (photon energy 800 eV).

**Xe calibration**

Before discussing the C\textsubscript{60} results, we should discuss in further details the Xe-calibration carried out at the photon energy of 105 eV. At this photon energy, one observes in the “first arriving electron” spectrum the position of the peaks corresponding to 5p\textsuperscript{-1}, 5s\textsuperscript{-1} (very weak) and 5d\textsuperscript{-1}ionization. Then, on the second arriving electron spectrum, one can find the position of the peaks corresponding to the Auger decay of 4d\textsuperscript{-1}. If the resolution is good enough, the “third arriving electron” spectrum can be used to get electron peak positions associated with 5p\textsuperscript{-3} formation. Table 3 summarizes the peak energies. Knowing the expected kinetic energies, the TOF are then used to calculate \(d, t_0\) and \(\varepsilon_0\) to be included in the treatment of the C\textsubscript{60} data.

<table>
<thead>
<tr>
<th>Xe\textsuperscript{+}</th>
<th>eV</th>
<th>Xe\textsuperscript{2+} 4d\textsuperscript{-1}</th>
<th>eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>5p\textsuperscript{-1}</td>
<td>12.13 &amp; 13.44</td>
<td>Peak 1</td>
<td>34.36</td>
</tr>
<tr>
<td>5s\textsuperscript{-1}</td>
<td>23.39</td>
<td>Peak 2</td>
<td>33.33</td>
</tr>
<tr>
<td>4d\textsuperscript{-1}</td>
<td>67.55 &amp; 69.54</td>
<td>Peak 3</td>
<td>32.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peak 4</td>
<td>29.967</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peak 5</td>
<td>21.665</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peak 6</td>
<td>19.689</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peak 7</td>
<td>17.249</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peak 8</td>
<td>16.146</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peak 9</td>
<td>15.270</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peak 10</td>
<td>14.169</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peak 11</td>
<td>10.279</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peak 12</td>
<td>8.300</td>
</tr>
</tbody>
</table>

*Table 3*

Figures 21 and 22 show the spectra of the first and second arriving electrons, respectively, of Xe at the photon energy of 105 eV for a solenoid current of 1.2 A. Figure 21 gives an assignment of the Xe\textsuperscript{+} data and figure 22 gives an identification of the Xe\textsuperscript{2+} data (cf. Table 3).
First electron data from Xe ionization

Time of flight spectrum of electrons ejected from Xe 4d hole

Depending on the experiment carried out, the solenoid currents was either 1.2 A or 1.7 A. For each solenoid current, the calibrations have been made and are summarized in Table 4:

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>( t_0 ) (ns)</th>
<th>( \varepsilon_0 ) (eV)</th>
<th>d (( \sqrt{eV \cdot ns} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>-69.8 +/- 0.8</td>
<td>-0.53 +/- 0.05</td>
<td>3760.4 +/- 8.4</td>
</tr>
<tr>
<td>1.7</td>
<td>-68.9 +/- 1.0</td>
<td>-0.63 +/- 0.06</td>
<td>3763.1 +/- 11.0</td>
</tr>
</tbody>
</table>

These values are then entered into the program to be able to determine the spectra as accurate as possible.
Single ionization

The X-ray Photoelectron Spectroscopy (XPS) of gas phase C$_{60}$ can be extracted, e.g., from our “Double Auger” run, where the photon energy was set to 296 eV. As shown in figure 23, the C1s peak position is around 290.4 eV which is close to the known literature value\textsuperscript{38} of 290.1 eV. This observed shift (of around 0.3 eV) can be explained by two possible (physical) reasons. Since the photoelectric law (cf eq.1) leads to an electron kinetic energy of 5.9 eV and since the Auger electrons are much faster (~ 200 eV kinetic energy), we reckon that this photoelectron spectrum may be affected by the so-called PCI effect (cf above for the explanation of the PCI effect). Also, the calibration may not be very accurate, since in our Xe spectra we are lacking information about the low kinetic energy peaks which are associated with $5p^5$ formation.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{C60_XPS.png}
\caption{C$_{60}$ C1s ionization energy from XPS measurements (see also reference\textsuperscript{48})}
\end{figure}

Double ionization

The “core-valence” run was recorded to reveal doubly-ionized states of C$_{60}$ with one vacancy in the core and another vacancy in the valence shell. To measure such states, the photon energy was set to 360 eV. Figure 24 shows the core-valence spectrum of C$_{60}$ which is comparatively weak. This spectrum was obtained by treating the triple data of the “core-valence” run and by selecting the last two arriving electrons, since the valence electron and the photoelectron have slowest flight times.
In order to understand this spectrum, one can compare it to an ordinary valence photoelectron spectrum\(^{49}\) of \(\text{C}_{60}\). The shape of our spectrum is similar to the gas-phase valence band spectrum of \(\text{C}_{60}\), both in terms of relative energies and relative intensities of the features observed. It is shifted in binding energy in comparison to the core-valence spectrum\(^{50}\) of \(\text{CS}_2\) where the first core-valence peak is at around 310.8 eV. This shift can be explained by looking at the difference in the C1s ionization energies (3 eV). Also, the first valence peak (called HOMO) in the gas-phase \(\text{C}_{60}\) is around 7.6 eV binding energy (cf. Table 2 above) whereas the HOMO of \(\text{CS}_2\) is around 10 eV binding energy\(^{51}\), comforting our idea that the core-valence spectrum of \(\text{C}_{60}\) should be shifted towards lower binding energies than in the case of the \(\text{CS}_2\). From the similarities in intensity and in relative energies compared to the valence spectrum of \(\text{C}_{60}\), we identify three peaks which should involve following valence orbitals: the HOMO at around 300.3 eV, at 1.4 eV from it the HOMO-1 and, at 3.9 eV from the first peak, the C \(\pi^+\sigma\) peak. Indeed, in the valence spectrum the distance between the first and the second peak is about 1.4 eV and the distance between the first and the third peak is about 3.7 eV.

Therefore, the interaction between core and valence electrons is mostly Coulombic type. The valence spectrum\(^{49}\) allowed us to extract the HOMO binding energy, situated at around 7.6 eV. From our experiments, we know that the first core-valence double ionization energy is situated at around 300.3 eV. This leads to an energy difference of 292.7 eV, and if we remove the C1s ionization energy\(^{38}\) (290.1 eV), we obtain a value of the interaction energy of a core and a valence electron in \(\text{C}_{60}\) of about 2.6 eV.

**Triple ionization**

The double Auger run reveals signs of a direct double Auger process but is dominated by cascade processes involving inner-valence electrons in a first step followed by autoionization\(^{52}\). The first process implies a direct process where the two electrons are ejected at the same time and share...
continuously the available excess of energy. The second process occurs sequentially, where the doubly charged ion state populated in the first Auger decay is autoionizing and releases a second electron. This double Auger process is less intense than “normal” single Auger decay but is not negligible. The study of double Auger decay provides valuable information about correlations in atoms since the process occurs only due to electron–electron correlations.

The double Auger decay can be described as:

\[ h\nu + A \rightarrow A^{+*} + e_{ph} \rightarrow A^{3+} + e_{ph} + e_{A1} + e_{A2} \quad \text{(eq26)} \]

where \( h\nu \) is the photon energy, \( A \) the atom, \( e_{ph} \) the photoelectron and \( e_A \) the Auger electrons.

Therefore:

\[ \text{IP}(A^{3+}) = h\nu - (e_{ph} + e_{A1} + e_{A2}) \quad \text{(eq27)} \]

Generally speaking, the direct double Auger process can be observed in a map with \( (e_{A2} - e_{A1}) \) on the x axis and \( (e_{A2} + e_{A1}) \) on the y axis, in form of a continuous energy distribution between the two electrons for a selected final state (horizontal line). These lines can reveal several spots where most of the coincidence counts are concentrated, which then means then that the double Auger decays are dominated by cascade processes. In the direct process, the two Auger electrons share continuously the excess energy between the core-excited state and the final ionic state which is determined by the energy conservation principle, and electron correlation has to be considered to describe such a multielectron process. This energy sharing leads to a continuous distribution between the two Auger electrons with a pronounced preference for a U-shaped asymmetric energy sharing that corresponds to the emission of a slow and a fast Auger electron. In the case of indirect double Auger decay, each electron has a discrete energy which depends on the energy difference between the initial, intermediate, and final states.

To focus on the triply ionized final states of \( C_{60} \), we select the energy range of the C1s peak on the time of flight spectrum of all electrons. Then, we plot, in this energy range (equivalent to time of flight), the difference between the photon energy and the sum of all electrons, that is to say the binding energy. Two different photon energies have been examined for this purpose: 296 eV and 360 eV. Even if the \( C_{60} \) ends up in triply ionized states, the pathways (or intermediate states) may be different. With 296 eV photon energy (oven temperature: \( \sim 509^\circ\text{C} \) and solenoid current: 1.7A), the core photoelectron escape and a double Auger decay occur and lead to \( C_{60}^{3+} \) state. At 360 eV (oven temperature: \( \sim 510^\circ\text{C} \) and solenoid current: 1.2A), the same pathway is possible and the corresponding spectrum is shown in the upper panel of figure 25. Alternatively, at 360 eV photon energy, the core electron can shake off a valence electron and single Auger decay may follow, leading also to \( C_{60}^{3+} \). The spectrum obtained in this way is shown in the upper panel of figure 26.
From all these measurements, one can extract a minimum triple ionization energy for gas-phase C₆₀ and compare it to previously published results obtained with different techniques. The energy range of the lowest triple ionization energy determined from the double Auger data sets is between 32 eV and 38 eV, though the shape of the two spectra are not the same.

The ionization potentials of C₆₀ can be estimated according to:

\[ IP(C_{60}^{q+}) = 7.108 + 3.252 \times q^2 [eV] \]  (eq28)

For triply ionized C₆₀, one would expect 36.38 eV, which is well in agreement with our results.

As mentioned above, one can also extract a triple ionization spectrum through the core-valence pathway, by selecting, in the triple coincidences, the pair of electrons within a binding energy range of 298-305 eV, corresponding to the expected energy of the “core-valence” states (cf figure 24 above). Figure 26 shows such a spectrum denoted as single Auger decay of CV in comparison to the one obtained by the Double Auger decay.
The minimum triple ionization energy of C$_{60}^{3+}$ is clearly different from the “Double Auger” run compared to the “core-valence” run. The minimum triple ionization energy for a Double Auger decay pathway is around 32 eV whereas for a core-valence-single Auger decay it appears to be around 95 eV, which means that the contribution of triply ionized C$_{60}$ from this pathway is situated at much higher energy. A similar result, even though less different in terms of energy, was found earlier for the triple ionization of methane, where J. H. D. Eland et al. observed a shift in the triple ionization energy relatively to the pathway experienced, as illustrated in figure 27.
Double core hole spectroscopy

In principle we could compare our experimental results on double core hole (DCHs) in $C_{60}$ to \textit{ab initio} calculations, where relaxation effects, the correlation energy and the Coulomb repulsion (for two core holes see as two positive charges) are taken into account if they were available. Double core hole states are interesting to study because they exhibit much larger orbital relaxation effects than the corresponding single core hole states\(^{28}\). In what follows, we assume the double core holes on the same shell.

The single core hole ionization potential is for the formation of vacancy $S^{-1}$:

$$ IP(S^{-1}) = -\varepsilon_S - RC(S^{-1}) \quad (eq29) $$

where $\varepsilon_S$ the orbital energy and RC the relaxation and correlation energy (Hartree-Fock and SCF calculations).

And the double ionization potential of double core hole on the same shell $S$:

$$ DIP(S^{-2}) \equiv -2\varepsilon_S - RC(S^{-2}) - V_{ssss} \quad (eq30) $$

with $V_{ssss}$ the repulsion integral which needs to be obtained from \textit{ab initio} calculations for further considerations.

To be able to reveal a double core hole spectrum from our experimental data, some treatment was necessary because of the limitations in statistics. Focusing on the triply ionized states considered as a part of the subsequent decay of double core holes, with one core hole and two valence holes (CVV), one can reduce the energy window where the actual DCH should appear. This was done, for instance, by J. H. D. Eland et al.\(^{28}\) for the case of CH$_4$. We focused on the quadruple data in the present case, and to reduce the background, we removed the electron with kinetic energy lower than 20 eV. Also, we assigned a certain CVV energy range (335-370 eV). Then, the last two arriving electrons (the last pair) binding energies are plotted in the energy range of 600 to 800 eV to get the double core hole spectrum, as shown in figure 28.
As expected, the statistics are comparatively low due to the weakness of this kind of states, but these data reveal a first signature of the C1s\(^2\) state in C\(_{60}\) which is located at an ionization energy of around 645 eV. It would be very interesting to compare this experimental finding to numerical calculations akin to the work of J. H. D. Eland et al.\(^{55}\).
Due to the comparatively low repetition rate of today’s free electron laser, true coincidence experiments are not practicable. However, as shown by Frasinski et al. in 1989 in home-laboratory laser assisted ion-ion fragmentation experiments, the correlation between charged particles created in a photoionization process can be revealed by the method of covariance mapping.

In order to study double core holes in molecular systems in a more efficient way, we developed, as part of this thesis, a new magnetic bottle electron spectrometer, which will be used in August 2011 at LCLS for covariance mapping experiments.

Covariance analysis method

Covariance is a number following the variation of variables and, then, determines the independence between them.

\[ \text{cov}(X,Y) \equiv E[(X - E[X])(Y - E[Y])] \quad \text{(unit of } XY) \quad (eq31) \]

where \( E[\cdot] \) is the expectation value operator and \( X \) and \( Y \) are real random variables. In the present context, \( X(x) \) and \( Y(y) \) are the TOF-spectra, where a particular value of \( x \) or \( y \) corresponds to a created TOF-value, and \( C(X,Y) \) represents a two-dimensional map. Provided the fragments are measured by a single detector, \( X \) and \( Y \) are the same and, in this case, \( C(X,Y) \) is the auto-covariance. When more than two ionization products are detected, the multi-dimensional covariance map is found as:

\[ \text{cov}(X,Y,Z,...) = E[(X - E[X])(Y - E[Y])(Z - E[Z])...](\text{unit of } XYZ...) \quad (eq32) \]

One has to mention that if the fluctuations in the TOF-spectra are not inherently statistical but also due to the light source instability (like, for instance, at an FEL source), then the covariance formula has to take this also into account.

Experimental details

Free electron laser beam line

The SASE process will produce pulses of coherent FEL X-ray radiation at LCLS (The Linac Coherent Light Source) undulator with a harmonic spectrum that is adjustable over a large wavelength range. The LCLS is designed to accelerate electrons to a final energy that is adjustable within the operational range between 4.54 GeV and 14.35 GeV. The undulator consists of 33 individual undulator segments (Type: Planar Halbach Hybrid Undulator, \( \lambda_u = 0.03 \) m, Undulator parameter \( K=3.71 \), effective \( B = 1.325 \) Tesla, undulator length: 3-4 m) that are separated from each other by about 20 to 40 cm long breaks, to provide space for focusing, steering, diagnostics and vacuum components. Focusing quadrupoles and electron beam diagnostics are located in between the undulator segments. The total length of the LCLS undulator is 121 m. In addition to the intensity fluctuations produced by the statistical nature of the SASE process, there will be an intensity jitter in the X-ray radiation due to a variation of electron beam parameters.

There are several different experimental stations available at LCLS, and the one which is of concern here is the so-called Atomic, Molecular and Optical (AMO) instrument. It is situated on one of the
soft X-ray branches of the LCLS that delivers intense ultra short pulses of X-rays from the FEL. Details of this instrument are shown in figure 29. It has an energy range of about 480-2000 eV. Our magnetic bottle spectrometer will be attached to the High Field Physics (HFP) chamber of AMO including the magnet, the gas needle and the detector.

Design of a new magnetic bottle instrument

The apparatus is similar to the instrument used at BESSY-II, but is all completely new and it will work at ultra-high vacuum (<10⁻⁹ Torr). A complete technical overview of the new instrument is displayed in figure 30.
30: The new magnetic bottle instrument dedicated for LCLS experiments

The flight tube is composed of an inner tube (cf fig. 31), which is electrically insulated by ceramic legs from the outer tube which itself is surrounded by the solenoid and a \( \mu \)-metal shielding.

31: time-of-flight tube (details)
Conclusion

In this thesis, the technique of and two set-ups for multi-electron correlation experiments were described. One of the set-ups was developed for LCLS free electron laser experiments to be carried out in August 2011. The other, already existing, set-up has been used at BESSY-II for experiments on gas-phase C$_{60}$. As one of the main results, we found experimentally the minimum triple ionization energy through Double Auger decay to be around 32 – 38 eV which is in agreement with both theoretical calculations and previous experiments. We also obtained the first core-valence spectrum of C$_{60}$ and compared it to the valence band photoelectron spectrum known in the literature. From this study, we established the interaction energy of a valence and a core electron in C$_{60}$ to be in the order of 2.5 eV. Furthermore, we revealed the first double core hole electron spectrum of C$_{60}$, which suggests the C1s$^2$ energy to be around 645 eV.
Appendix

The pressure on a surface can be defined as the ratio between the forces applied to this surface and the area of the surface itself. The atmospheric pressure is 1013 mbar (or 1 atm). In removing gas from a closed area, the outside gas exerts on the walls a huge force. This brings us to the definition of vacuum: a space in which the pressure is below atmospheric pressure.

The gas pressure can be expressed using the laws of thermodynamics:

\[ P = nk_B T \]  

(eqA1)

Where \( P \) is the gas pressure (N/m\(^2\)), \( n \) the molecular number density (m\(^{-3}\)), \( k_B \) the Boltzmann’s constant (J/K) and \( T \) the temperature (K).

The pressure is linked to the number of molecules, knowing that a volume of 22.414L at 0°C and 1 atm, contains \( 6.022 \times 10^{23} \) particles (Avogadro number). There is never a total void, even for ultra high vacuum.

Vacuum pumps work at different level of pressures, and experience different types of flow, like, e.g., continuous, Knudsen and molecular flows, respectively, which is illustrated in figure 32.

![Different types of flows](image)

32: Different types of flows

The volume flow rate (or pumping speed) of pumps is constant:

\[ S = \frac{dV}{dt} \]  

(eqA2)

where \( S \) is the pumping speed, \( V \) the volume and \( t \) the time.

By stating the flow in terms of throughput \( Q \), one receives a unit which relates directly to the actual density of gaseous matter in the flow:

\[ Q = PS \]  

(eqA3)

The experiments discussed in this thesis work at high or ultra-high vacuum, meaning at pressures in the range of \( 10^{-6} \) to \( 10^{-11} \) mbar. To be able to reach this good quality vacuum, we use different types of pumps, like oil-sealed mechanical rotary pump and turbomolecular pumps.

The principle of oil pumps is to remove the gas from the chamber by rotating a blade in a stator, pushing the incoming gas to an exhaust valve. The oil is used for lubrication, sealing, cooling and...
as a corrosive protector. A filter system is used to avoid the suck-back of oil in the vacuum. These pumps are used to reach a so-called forevacuum in the $10^{-3}$ mbar range, which is needed for proper operation of the turbomolecular pumps. See figure 33 for the scheme of a rotary pump.

![Figure 33: Oil rotary pump](image)

The turbomolecular pump is a gas transfer pump which compresses the gas by a succession of high speed rotary blades and stationary blades (cf fig. 34). If the turbomolecular pump receives too many particles, and also a lot of light particles, the turbopump can be damaged. The molecules hit the blades and acquire an additional velocity component in the direction of the pitched blades. The stator blades are also pitched, preferentially in the left direction of the rotor blade and oriented axially downwards in the pump. These blades avoid the molecules to move in the reverse direction, called back-diffusion. The blades’ speed is roughly the same as the molecular speed. Therefore, the rotor blades run at around 60 000 turns per minute and if they are fixed mechanically they need a cooling source. The best solution is to levitate the blades with a magnetic field, because then the frictions disappear.

![Figure 34: turbomolecular pump](image)

We use the turbomolecular pump because they do not disturb the analysis chamber and they easily result in high vacuum or even ultra-high vacuum.

The pumping system is always limited by the surface gases released, including vaporization (the wall surface emit molecules by evaporation), desorption (physisorbed and chemisorbed), diffusion (molecules inside the walls reach the surface and escape) and permeation (outside molecules entering inside the chamber through the porous wall).
The permeation manifests itself first at pressures below $10^{-8}$ mbar. The permeation gas flow is proportional to the pressure gradient $p_0/d$ (d is the wall thickness and $p_0$ the atmospheric pressure) and to the permeation constants for the various materials $k_{perm}$ (which depend on the solubility and the diffusion constant of the gas in the material).

To control the pressure inside the chamber, one has to use pressure gauges at strategic points. Three different types of gauges are available: mechanical, transport and ionization phenomena gauges. We use Pirani (transport type) and cold cathode gauge (ionization type).

The Pirani gauge, working at $5 \times 10^{-4}$ mbar to $10^3$ mbar, uses the pressure dependency of the ability of a gas to conduct heat. A current is passed through a filament, exposed to the pressure to be measured. If the pressure is high, there will be frequent collisions between gas molecule and the filament; the filament will transfer heat to the molecules which transfer it to the walls of the gauge head.

The cold cathode transmitter, working at $10^{-9}$ mbar to 0.01 mbar, consists of two electrodes, a cathode and an anode, between which a high voltage is applied. Negatively charged electrons leave the cathode, moving at high velocity toward the anode, therefore they ionize the neutral gas which ignites a gas discharge. The ion current formed is displayed on a meter and is proportional to the pressure in the gauge head.

In our apparatus we use a combination of Pirani and cold cathode gauges which work in the $10^{-9}$ mbar to $10^3$ mbar range. Figure 35 shows two pressure gauges, namely a Pirani (left) and a cold cathode (right).

Once high vacuum is reached, it may still not be possible to conduct the experiment and the vacuum needs to be improved further as is the case for the FEL experiments. The vacuum system is powerful enough only to remove the gas particles and the physisorbed particles on the surfaces. Physisorption is a Van der Waals interaction between a molecule and a surface, typically water on the wall of the chamber. But some other species might have interacted more strongly with the walls like in the case of chemisorptions. Chemisorption implies greater overlap between the wave functions of the molecule and the surface; the bonding energy is in the order of tens eV (few meV for Physisorption). Therefore, one needs to degas the system for few hours; usually this is done by baking the desired parts of the system at around 120°C or more, using heating tape and Aluminum foil, following the Joule effect:

$$P = RI^2 \quad (eqA4)$$

where $P$ denotes the thermal power, $R$ the resistance and $I$ the electric current.
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