The hollow atoms

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This site is dedicated to a review of already published scientific results of the Laboratory of Atomic and Nuclear Physics - Radium Institute, of the University Pierre and Marie Curie, Sorbonne University (Paris), on the interaction of Highly Charged Ions with surfaces and the properties of the hollow atoms.

Last Edition: January 2019
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**The hollow atoms**

The structure of the atoms seems today definitively well known. Most common experiments or observations of the atoms mainly deal with the manipulation of their outermost (valence) electron(s), which may be excited in higher states, all innermost shell electrons being considered as an inner frozen core. Physicists daily observing or manipulating atoms are then actually only dealing with atoms in an extremely restricted number of configurations. It is now possible to fully ionize, at thermal velocities, any atom up to uranium, which may be later on refed, allowing removing or adding, on demand, any number of electrons, in any excited states of atoms. These new techniques which allow the observation of an unlimited number of new atomic states and unforeseen atomic events, open new astonishing scientific or technical opportunities: the atomic manipulations.

**Introduction**

The electron of the hydrogen atom may be excited into an infinite number of discrete quantum states labeled by quantum numbers, such as e.g. (n, l, m). This electron may be more or less well localized around its nucleus, as pictorially shown in one of the oldest text books of atomic physics (Fig.1). The localization of the electrons in states of lower quantum numbers shows up very diffuse electron clouds around the nucleus, while electrons in very excited states (Rydberg states) move in more well defined and restricted areas. Quantum mechanics tending asymptotically to classical mechanics when all quantum numbers tend to infinity, the electrons excited in states of high quantum numbers may alternatively approximately also be described by classical mechanics, as moving on relatively well-defined trajectories.

![Fig.1: Spatial localization of one electron in given n, l, m orbitals according to White [1].](image)

The atoms are made of a given number of electrons characterized by the same quantum numbers than for hydrogen, which label the symmetries and the radial and azimuthal properties of the atomic clouds. These electrons couple each other’s in many different allowed ways, leading to the formation of large varieties of different merged electron clouds.

In the ground state of the atom these electrons occupy all states of the lowest quantum numbers. The quantum states of the atoms have mainly been experimentally explored promoting
only one or two outermost electrons in excited states, thus only providing a very limited insight on the atomic allowed structures.

It is now possible, as discussed below, thanks to nuclear techniques, to set around a nucleus any number of electrons (smaller than the nuclear charge...), in any state (according to the Pauli Exclusion Principle), opening an immense and fascinating virgin new field to explore. One can then now play with an incredible number of different atomic configurations, discovering new atomic arrangements of unexpected and original properties making atomic physics much funnier. One may now for instance remove all electrons of an atom and capture new ones in given excited states. Among the most amazing examples of exotic species are the hollow atoms, atomic configurations in which the innermost shells are empty, all electrons lying in outermost shells e.g. Ar atoms whose K and L shells are empty, all electrons being localized in the M and N shell (Fig.2 A), i.e. atoms in a generalized state of inversion of population.

The atom while being singly excited (one of its electrons being promoted into an outershell state) decays by emission of a photon; in the visible or UV range, if the excited electron comes from its (valence) outermost shell, or in the X ray range when it comes from an innershell. In this latter case the excitation energy of the atom is always larger than the energy of its outside (valence) electron (first ionization potential). It then owns enough energy to spontaneously expel one electron and then auto ionizes. All atomic states owning inner shell vacancies are then auto ionizing, the sum of all repulsive forces between the electrons being always stronger than those due to their attraction by the nucleus. The decay of these excited atoms may then also proceeds through Auger transitions rather than through photon emission. These Auger transitions (Fig.2 B) that obey fully different scaling laws and selection rules than photons, not only move down one electron from a state to another one, but also expel a second electron, auto-ionizing the atoms, thus changing, at each step of e.g. the cascade decaying a multi excited atom, the number of electrons attached to the ion and their repartition in the excited levels.

![Hollow atom with inner shell vacancies](image1)

**Fig.2:** A) Hollow atom. B) A KLM Auger transition: the K hole is filled by an L electron and an M electron is expelled.
It is the purpose of this review to present selected examples of these atomic manipulations with a special emphasis to the decay cascades of these exotic species that may show up a diaporama of never explored curious quantum states, but also provide extremely fast videos of many newly discovered atomic events.

**How to fully strip atoms?**

The building up of such exotic atomic species may be achieved e.g. by quickly removing or exciting inner-shell electrons of a neutral atom, and capturing electrons in given excited states of these ionized atoms. Ionization is a violent and not very selective process while capture is a much more delicate operation, sometime more selective. In many cases (but not exclusively) the strategy will then be to first fully remove all electrons of a neutral atom and then recapture electrons in selected states.

The very first technique used to prepare Highly Charged Ions (HCI) was to accelerate at very high energy ion beams of low charge state, and to direct them through thin foils, in such a way that the ions must be stripped in a very short time (shorter than the typical times of capture processes), getting out the foils in a higher charge state, the so called beam foil technique. These more highly charged ions may then be further reaccelerated at higher energies, and sent once more through another thin foil to be ultimately stripped (Fig.3).

![Diagram of the beam foil stripping technique](image)

**Fig.3:** Schematics of the beam foil stripping technique: a) A beam of singly ionized atoms provided by a conventional ion source is sent into an accelerator. b) After being accelerated the ions pass through a thin foil where they are stripped. c) One selects in a bending magnet among all ionized species produced one given ion. d) These ions are then directed into a second accelerator where they gain energy. e) The ions are once more stripped in a thin foil. f) One selects one ion among the more ionized particles exiting the foils and so on.
The main difficulty of such techniques is that the ionization cross section of these ions is maximal when their velocity is close to that of the electron to be removed. The velocity of the most strongly bound electrons of the atoms (K electrons) being of the order of 1% of the velocity of the light for hydrogen and up to more than 90% for uranium, these heavy ions must be accelerated at enormous kinetic energies, up to hundreds of GeV for uranium. The second main experimental difficulty is then that one has to deal when carrying experiments, with ions of velocities close to that of the light… Many interesting experiments with such HCI have been performed to study high energy ion collisions, or spectroscopic properties of e.g H-like or H-like ions for fundamental purposes (QED or relativity).

In the 80\textsuperscript{ies} new techniques have been developed to produce such HCI directly at low velocities, opening a completely new field in physics. In vacuum, positive ions in their fundamental states are stable, but nature does not like ions: as soon as an electron has been removed the atom becomes a positive ion, attracting the most abundant negative particles of our world: the electrons. To prepare highly charged ions one must then find experimental situations allowing the ionization processes to be faster than the capture processes. The fastest way to fully ionize atoms would then to find a process allowing to remove all or most electrons in a single event (Coulomb explosion), instead of removing the electrons one after the other. Such ‘Coulomb explosions’ have been observed during collisions of extremely ionized ions, at extremely high velocities, impinging atoms of a gas target. It has never been however possible to prepare, in a single event, fully stripped ions of atomic number higher than 18. Moreover such technique requests ion beams delivered by the most powerful accelerators, of ions much more ionized than those produced in the gas target …

The most efficient way to ionize atoms is to bombard them with electrons; electrons are abundant and easy to manage, and their ionization cross section is maximal when their energy is only twice that of the binding energy of the electron of the atom to be removed i.e. easy to reach. In such a case however single electron capture dominates because after having expelled a first electron from the atom the energy needed to ionize the next one is much larger, strongly reducing the capture cross section. It is really astonishing considering, as discussed below, that fully stripped ions up to uranium at low kinetic energy are actually essentially produced by stepwise ionization processes, all electrons being removed one after the other from 1+ up to 92+ (Physics World \cite{2}).

The principle of the low energy ion beam sources is to stepwise ionize with energetic electrons ions trapped in vacuum, in such a way that they could not escape the collision area, or be neutralized by collision with the neutral atoms of the residual vacuum. The ions must be at the same time ionized and trapped either

- inside the incoming electron beam itself (EBIS: Ion Beam Electron Sources) where they may be confined in the negative charge space made by the beam itself (a poison process in accelerator techniques)
- or in a hot plasma confined in a magnetic structure (ECRIS: Electron Cyclotron Resonance Ion Sources), the trapped ions being ionized by the free electrons in a plasma heated at very high temperatures by radiofrequencies at the cyclotron resonance.

The first technique provides low intensity currents of the most ionized ions up to U^{91+}, while the second one provides high ionic currents of lower charge states. In both cases these ions have to be extracted from the electron beam or the plasma by a suitable electrostatic device accelerating the ions at typical energies of the order of 5 to 20 keV/q, and may be fully decelerated in the experimental sets up down to few eV/q. Highly charged ion beams are now routinely available for scientists in a certain number of facilities through the world.
How to recapture electrons?

Highly charged ions (HCl) may capture bound electrons from free atoms or molecules in vacuum or inside solids; these electrons are captured, for energy conservation, in very excited states of the ions (Rydberg states), but one cannot expect to capture much more than one electron per atom, the binding energies of the electrons of the atom strongly increasing with the charge of the considered atom. A much faster process allowing capturing many electrons, quasi at the same time, holds during the approach of an ion close to a metal surface which constitutes an infinite reservoir of equivalent electrons. The capture of electrons then proceeds through a field effect process analog to what happens in an electron gun. The Child Langmuir law has even been successfully used to describe the gross features of this process [3]. In quantum mechanics the target electrons are considered as crossing or overcoming the potential barrier between the ion and the conduction electrons in the box made by the solid, and then resonantly transfer these electrons into an excited state of the ion of comparable energy i.e. into a very excited state of the ion of quantum number n # q (q charge of the ion) (Fig.4). The distance $z_0$ at which the exodus of the target electrons to the ion starts may then be easily calculated [4][5] and found to be of the order of nm or few nm for ions of atomic numbers close to that of Ar.

Fig.4: Potential energy curve of the ion-metal system leading to the resonant neutralization.

One may then imagine [6] that the ion may capture, quasi at the same time, many electrons in highly excited states of the ion forming exotic unknown, incredible, atomic species in full inversion of population. A detailed quantum mechanical treatment of this capture process for light ions, the over the barrier model, has been given by Burgdorfer et al. [7]. The way these expected exotic species may be formed, or even their fundamental existence, faces however conceptual and experimental difficulties.

The main experimental difficulty to overcome to observe what happens above the surface is that the time allowed to the ions to travel the distance from $z_0$ to the surface is very small compared to that of most processes of decay of these expected very excited species. To increase
the time passed by the ions above the surface below \( z_0 \) one must then either ultimately decelerate them at normal incidence or direct them to the surface at grazing incidence. Such deceleration is however limited owing to the fact that the ion is attracted by its own electric image, gaining an irreducible amount of kinetic energy \([8]\) and must, in any case, hit the surface even at zero given kinetic energy. The highly excited ions, in a weakly bound state, might not have enough time to decay to its ground state to allow e.g. the observation of the x-rays emitted at the end of their decay cascade, prior to touching the surface where they are peeled off.

![Diagram](image)

Fig. 5: From left to right: 0) An ion approaches a surface. 1) Below \( z_0 \) it starts capturing many electrons in high \( n \) states. 2) Forms a hollow atom. 3) Is peeled off while hitting the surface. 4) Recaptures electrons in the solid, but in lower \( n \) state. 5) Forms another kind of hollow atom.

The existence of such exotic species in a full inversion of population, the hollow atoms, has been demonstrated \([9]\) while studying the interaction of \( \text{Ar}^{17+} \) ions (and later on \( \text{Ar}^{18+} \) ions \([10]\) \([11]\)) impinging surfaces at kinetic energies of the order of 20 keV/q. In these experiments clear spectroscopic signatures have been observed, at high x-ray resolution, of atoms whose K and L shells are empty, while all or most electrons to neutralize the ion lie in the M (N) shell. At such relatively high kinetic energies of the ion the time passed by the hollow atom above the surface is so small that it was not possible to observe its outside decay, and these findings were attributed to hollow atoms formed below the surface. The atoms re-ionized at the surface \([10]\) then recapture electrons inside the target (Fig. 5), through another kind of close collision process, but in lower excited states \((n = 3 \text{ or } 4)\), forming very nicely characterized hollow atoms as shown below. Later on similar experiments, but at very low kinetic energies, have been carried out in order to explore the possible existence of ‘above the surface hollow atoms’ formed in more excited states as discussed below. There are then two different kinds of hollow atoms formed above and below the surfaces.

The interaction of the highly charged ions with surfaces may be studied in various ways, looking at the spontaneous emissions of the ions (x-rays or Auger transitions), measuring the number of electrons ejected from the surface, looking at ion trajectories etc.\ldots \([12]\). These highly excited hollow atoms decay through long cascades of spontaneous transitions, sometime interrupted by electron captures. The Auger rates scaling as the inverse of the third power of the energy of the emitted electrons, these transitions between very excited ion levels, i.e. very close...
in energy, mainly proceed through Auger emissions and only with a very low probability with x-rays in the innermost shells of the ions at the end of the cascade. Most of the experiments in the field have then been carried out in Auger spectrometry (summarized e.g in review papers [12][13]), and very rarely in x-ray spectroscopy [14][15][16]. In the present paper we will review the experiments carried out in x-ray spectroscopy i.e. these less probable emissions (with fluorescence yields \( \omega \) most of the time of the order of \( 10^{-3-4} \)) but totally insensible to the electric fields present nearby the surfaces, by the Laboratory of Atomic and Nuclear Physics - Radium Institute of the University Pierre and Marie Curie, Sorbonne University (Paris), in collaboration with many groups through the world listed below.

Most of the excited states of these hollow atoms decaying via Auger emission our main goal was then to have access to the ion sources delivering the most intense ion beams, and to develop x-ray detectors of the highest transmission, and the highest resolution owning to the large number of emitted x-rays of close energies during these long decay cascades. These techniques and ion deceleration techniques used in these specific experiments, are described in Ref.[17].

Two different kinds of x-ray detectors have been used. Bragg spectrometers with curved or flat crystals, which allow detecting x-rays with an ultimate resolution, of the order of the natural width of the lines, but an extremely low transmission, of the order of \( 10^{-8-10} \), and solid state detectors (SiLi or Ge), easy to manipulate, of transmission of the order of \( 10^{-1-2} \), but a resolution of the order of 65-130 eV, allowing e.g. to perform coincidence experiments signing the time correlation between the detected x-rays. Most of the experiments described in the present review have been carried out in Bragg spectroscopy using Highly Orientated Pyrolitic Graphite (HOPG) mosaic crystals, in a given geometry described in ref.[17], which improves the transmission of pure flat crystals by one or two orders of magnitude, for a resolution comparable to that of intrinsic crystals. With such Bragg spectrometers it was possible to get typical spectra in one or few hours, and in few minutes with solid state detectors. The experiments described in this review have been carried out using alternatively solid state detectors and these original Bragg spectrometers.

The hollow atoms below the surfaces

The spectroscopic data allowing diagnosing the formation of hollow atoms (Fig.6) has been first observed with Ar\(^{17+}\) ions looking, at very high resolution, at the characteristic K\(_\alpha\) x-rays emitted by the ions while filling its unique K vacancy [9]. The energy of the observed K\(_\alpha\) x-ray line (L \( \rightarrow \) K transition) is known to linearly depend on the number of present L electrons, an increase of one more L electron decreasing the energy by about 25 eV, a value that has to be compared to a typical experimental energy resolution of the order of few eV. If the filling of the K hole holds in presence of any number of L electrons one may observe statistically as shown in Fig.6 all KL\(^x\) lines (x number of L electrons), signing the filling of the K hole, at all steps of the filling of the L shell. A precise measurement of the energies of these lines shows that these KL\(^x\) lines correspond to ions owning a closed M shell with the exception of the very first ones where less M electrons are present, but in that case one observes on the L and K\(_\gamma\) spectra clear signatures of the presence of N electrons, all these findings leading to the conclusion that the M and N shells are quasi closed (neutralized) at all steps of the decay of hollow atoms.
The relative intensity of these KL\(^{\alpha}\) lines depends on the relative rates for the filling of the 8 holes of the L shell and of the unique vacancy in the K shell. The stepwise filling of the L shell proceeding, by steps of roughly equal periods of time of the order of 0.3-0.5 fs \([9]\), plays then the role of an atomic clock, while the emission of the K x-ray plays the role of a snapshot displaying (Fig.7) the actual level of filling of the L shell (the so called Atomic Clock Property of the Hollow Atoms ACPHA). This property may be exploited to study the time evolution of the hollow atoms as shown in Fig.8. This figure displays the characteristic KL\(^{\alpha}\) array of satellites to be observed when the filling of the L shell is much faster or much slower than that of the filling of the K hole. In the first case the K hole is filled when the L shell is quasi closed, the distribution peaking on the KL\(^{\theta}\) satellite; in the opposite case as soon as a first electron reaches the L shell a K x-ray may be emitted; in that case the distribution strongly peaks on the KL\(^{\gamma}\) satellite. The first case may correspond e.g. to what happens below a metal surface where free conduction electrons quickly fill the M (N) shell, and the opposite case i.e. when hollow atoms may be formed above a

![A Sand glass](image)

**The atomic clock**

The M electrons drop into the L shell like in a sandglass at a rate of \# 0.3-0.5 fs

Fig.7: The Atomic Clock Property of the Hollow Atoms: the stepwise filling of the L shell plays the role of a sandglass, while the K x-ray that of a snapshot displaying the level of filling of this L shell.
surface in very highly excited states, i.e. slowly filling the L shell, or below a dielectric surface where it takes a longer time for valence electrons to fill the M (N) shells than for conduction electrons, and correlativey for populating the L shell.

![Fig.8: The Atomic Clock Property of the Hollow Atoms.](image)

One presents in Fig.9 the KL\textsuperscript{x} x-ray spectra observed below the surface of Au and SiO\textsubscript{2} targets [18] where one can see that the L shell is much faster filled in metals than in dielectrics which clearly illustrates the above quoted atomic clock property of the hollow atoms. It is then possible just by looking at these KL\textsuperscript{x} spectra to characterize the electrical nature (conductive or isolative) of the first few layers of a surface.

![Fig 9: KL\textsuperscript{x} spectra observed below very clean metal and dielectric surfaces.](image)

Similar experiments have been carried out using Ar\textsuperscript{18+} ions i.e. ions owning two K vacancies. In that case one may observe the two KL\textsuperscript{x} x-ray spectra stepwise filling the two K holes. For neutral atoms twice ionized in the K shell these lines are usually referred as hypersatellite: filling of the first K hole, and satellite for the filling of second K hole; for the most ionized atoms (with zero or one K electron and e.g. one L electron) these lines are also often simply referred as hydrogenlike (Hlike) and Heliumlike (Helike) ions. We present in Fig. 10 the K x-ray spectra observed with Ar\textsuperscript{18+} ions of 10 keV/q energy impinging Si and Au targets.

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The second main and also obvious feature observed on these spectra is that above metal, the filling of both K holes holds in presence of a higher number of L spectator electrons than in dielectrics, like in the case of Ar\textsuperscript{17+} (Fig.9). This finding must however be considered as qualitative because these experiments have been performed in different ion facilities through the world where the vacuum in the beam pipes was different, leading to different qualities of the metal surfaces. In the followings we will mainly concentrate on the study of the interaction of these ions on the most well characterized Si targets whose surfaces were passivated according to the usual techniques in microelectronics.

The comparison of the KL\textsuperscript{x} spectra of the hypersatellite line of Ar\textsuperscript{18+} ions on Si with that of the KL\textsuperscript{x} lines observed with Ar\textsuperscript{17+} ion (Fig.6) is that the KL\textsuperscript{x} array of lines of the hypersatellite transition is strongly concentrated onto the KL\textsuperscript{2}, KL\textsuperscript{3}, KL\textsuperscript{4}, KL\textsuperscript{5} and KL\textsuperscript{6} lines compared to what is observed with Ar\textsuperscript{17+} ions where the distribution of the KL\textsuperscript{x} lines is much more uniform, and also that the KL\textsuperscript{7} and KL\textsuperscript{8} lines are strongly weakened also compared to those observed with Ar\textsuperscript{17+}. This last finding may then provide an estimate of the decay time of the hypersatellite (the
delay time between the emission of the hypersatellite and the satellite) that corresponds at the meantime needed to add about 2 or 3 more L electrons (of the order of one fs), in good agreement with the calculated meantime for filling one L hole and the calculated lifetime of the hypersatellite [9] [11].

It is also worth noting that the energy of the lowest energetic hypersatellite $K^0 L^8 M^8$ line which is known to show up a complex very characteristic spectroscopic original property [19] [20] for atoms such as Ar (the inversion population of the spin doublet of the $K\alpha$ line the so-called $K\alpha^2$) clearly shows up that the double K vacancy may survive long enough to the full filling of the L shell.

We have studied these mechanisms of capture with bare or Hlike ions of atomic numbers higher than for Ar, up to Bi ($Z = 83$), and lower atomic numbers down to C ($Z = 6$). For such ions the energy of the emitted photons is too large or too small to allow the use of crystal spectrometry, and it was not possible to observe separately the $KL^x$ lines emitted during the filling of the K hole. We nevertheless studied the K, L, and M x-ray spectra emitted by these ions with SiLi or GeLi detectors i.e. at a lower energy resolution (see e.g. Fig.11). In most cases it was however possible to measure, e.g. in the $K\alpha$, $K\beta$, $K\gamma$ spectra, the mean number of L vacancies of the L shells at the time of the filling of the K hole(s). It has then be found for high Z ion that in all kinds of targets the emission of the K x-ray holds in presence of a very small number of L electrons, the $KL^x$ strongly peaking to the smallest values of $x$ compared to what is observed for lighter ions where all $KL^x$ lines are observed. This finding may be easily explained taking account of the fact that the filling of the L shell mainly holds via LMM Auger emission, a process that does not scale with the atomic number $Z$, while the rate of the K x-ray emission scales like $Z^4$. The K x-ray is then emitted much faster than the stepwise filling of the L shell, weakening the usefulness of the Atomic Clock Property of the Hollow Atoms (ACPHA), based on the observation of the relative intensity of the 8 $KL^x$ lines. The second main finding studying the evolution of the capture processes with the atomic number of H and He like ions is that capture holds below the surface in slightly higher levels (never exceeding $n = 5$) of slightly larger size to form stationary state in solids of the same interatomic distances as discussed below.

![Fig. 11: Fe$^{26+}$ and Kr$^{36+}$ spectra observed with Ge detector.](image)
While it was not possible experimentally to observe separately all KL\textsuperscript{x} individual components of the x-ray spectra of these more highly charged ions with solid states detectors (SiLi or Ge), these techniques allowed to carry out coincidence experiments between the hypersatellite and satellite transitions \([21]\) i.e. showing up the time correlation between each of these two KL\textsuperscript{x} transitions, e.g. any K\textsubscript{α}, K\textsubscript{β}, K\textsubscript{γ} lines of the hypersatellite with any of the K\textsubscript{α}, K\textsubscript{β}, K\textsubscript{γ} lines of the satellite transition during the filling of the second K hole. This experiment (Fig.12) then clearly illustrates the time sequences of the great many number of real stationary states happening during the decay of the hollow atoms formed during the interaction highly charged ions below surface.

![Biparametric coincidence plane of the hypersatellite satellite cascade of Fe\textsuperscript{26+} ions.](image1)

The x and y axis correspond to increasing x-ray energies in detector one (e.g. x) and two (y). Dark regions correspond to the time correlated x-rays between a given hypersatellite line and another one of the satellite)

For lighter elements the x-ray energies are much too low to allow the use of Bragg spectrometry. One presents in Fig.13 -14 the K x-ray spectra of N, O and Ne ions, observed with a SiLi detector \([22]\). For these atoms which own a smaller number of L electrons than for Ar, the mean number of electrons present at the time of the filling of a K hole is obviously more

![KL\textsuperscript{x} spectra observed at low resolution (SiLi detectors).](image2)

Fig.12: Biparametric coincidence plane of the hypersatellite satellite cascade of Fe\textsuperscript{26+} ions. The x and y axis correspond to increasing x-ray energies in detector one (e.g. x) and two (y). Dark regions correspond to the time correlated x-rays between a given hypersatellite line and another one of the satellite)

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The mechanisms of formation of hollow atoms below a surface

As above quoted, electron capture by highly charged ions above metal surfaces proceeds through a field effect (over the barrier model), feeding very excited (Rydberg) states of the ion with conduction electrons of the target. The electron capture below a surface, which leads to the formation of hollow atoms, but in lower excited states than above the surface (M and N shells in the case of Ar), obviously proceeds through different collisional processes.

The most remarkable feature of the x-ray spectra observed (Fig.6) during the interaction of Ar$^{17+}$ below surfaces, which leads to the observation of hollow atoms [9], is that all K$\alpha$L$^x$ lines have been found to be emitted by ions always owning a quasi-full M (N) shell(s) (i.e. quasi fully neutralized). The filling of the L shell has then been attributed to be mainly due to very fast LMM Auger transitions (top feeding), in agreement with calculations [9].

This filling of the L shell by the M electrons has also been observed [25] looking at the L x-rays (M to L radiative transitions) as shown in Fig.15. The very large intensity observed for these L x-ray lines, whose fluorescence yields are extremely small ($\omega_L \# 10^{-3.4}$ compared to $\omega_K \# 10^{-1}$), also clearly demonstrates that the L shell is mainly filled with electrons coming from the M and N shells of the ion.

At the low ion kinetic energies considered in the present experiments where the ion velocity is always close to that of the outermost shell electrons of the atoms of the solid, the interaction of the ions with the solid may be described in the frame of the Born Oppenheimer...
approximation i.e. considering that the ions may transiently form quasi-stationary states with the whole solid or with individual atoms of the solid.

![Figure 15: K and L spectra observed during the interaction of Ar$^{17+}$ ions on Si targets.](image)

The neutralization of the ion through a process of capture filing the M and N excited states of the ion (top feeding), may be attributed [26] to an already known process happening during the interaction of very slow singly ionized ions impinging metal surfaces, first introduced and observed by Hagstrum [27][28]: the Auger neutralization process (AN). In this process (Fig.16) the ion is supposed, at the lowest ion kinetic energies, to form a quasi-stationary state with the solid. AN is an Auger process in which one conduction (or valence) electron of the solid is ejected into the continuum while another one fills one vacancy of the ion. The Auger process, whose rate is known to dramatically increase with the decrease in energy of the ejected electron, must then fill the ion level the closest to the conduction or valence band of the solid i.e. the highest available stationary state of the ion while being inside the solid, explains then the formation of hollow atoms. The size of the outermost shell of an ion moving inside a solid must obviously be smaller than the interatomic distances in the considered solid. In the case of Ar ions AN then selectively fills the M and N shells of the ion, the highest allowed stationary states of such ions inside a solid.

The interaction of ions inside a solid, at the lowest ion kinetic energies, may be also described as a collision of the ions with individual atoms or molecules of the solid. The collisions of multi-charged ions with individual atoms in vacuum are usually described as forming, during the penetration of the ion inside the atom, transient molecular compounds whose molecular levels evolved in time, to lead, at the exit of the incoming ion from the quasimolecule, to the direct non radiative transfer of holes and electrons between the two partners of the collision (the so called electron promotion model). Such model requests however the existence of some resonant energy matchings between some levels of the ion and of the target atom.
At the early times of the studies of the interaction of highly charged ions with surfaces the main concern of the community working in this field was to try to observe signatures of the existence of the predicted atomic multi highly excited states, in full inversion of population, supposed to be formed during the interaction of highly charged ions above the surfaces and not what may happen below the surface where the interaction was supposed to be much too complex to own any real interest. The main goal was then at that time to try to observe, with ions of very low velocities in order to give the supposedly formed hollow atom above the surface enough time to decay before hitting the surface, looking at the ion Auger transitions filling their empty K and L shell, the last steps of the relatively long cascade of transitions decaying these hollow atoms above the surface.

In 1990 Folkerts and Morgenstern studied the K and L Auger transitions emitted by light H-like ions, during their interaction with metal (Ta) surfaces, at a kinetic energy of 600 eV, i.e. low enough to allow a small fraction of the ions to decay above the surface. These authors then observed a number of LMM Auger transitions two times lower than that of the KLL transitions, which means that the L shell was not only filled via the cascade following the capture of conduction electrons of the target into highly excited level of the ion (top feeding), a process which they then called ‘side feeding’. They then suggested that this side feeding of the ion L shell may come from inner shell electrons of the atoms of the Ta target i.e. of an ion atom collision with the formation of a quasi-molecule.

There are then two possible mechanisms of filling the ion vacancies in ion surface interactions, a non radiative filling of the inner shell ion vacancies with inner shell electrons of the target (side feeding,) which may not lead to the formation of hollow atoms, or the capture of target conduction or valence electrons in the outermost available excited levels of the ion: top feeding, leading to the formation of hollow atoms. The relative intensity of these two processes depends on the nature of the ions and of the targets (energy matchings).

The electron capture process holding via the formation of quasi-molecules which transfers electrons of the target into e.g. the empty L shell of the incoming highly charged ions or, in other words, transfers holes of the ion into inner shells of the target, without any emission of Auger or x-ray of the ion (whose energy is transferred in this case as kinetic energy of the ion), must then lead to the emission of characteristic target Auger electrons or x-rays, providing undoubtful proof of a process capture holding via the formation of quasi-molecules. In such a case one must then
observe e.g. x-rays of the target instead of x-rays of the projectile. The target x-rays may however also be due to the fluorescence of the target atoms provoked by the photoionisation induced by the very great number of Auger electrons ejected inside the solid during e.g. the decay cascade.

In the case of Ar\textsuperscript{17+} ions interacting with Si targets where the filling of the L shell mainly comes, as above quoted, from M or N ion electrons (top feeding), we never observed any Si K x-ray when these ions interact with Si target, while some ion-atom energy matchings might be considered for such very close atoms: Ar (Z = 18) and Si (Z = 14). Vinecki et al. [15] studying the interaction of Ar\textsuperscript{17+} ions with carbon targets suggested that the filling of the ion L shell by M (N) electrons) may proceed through the formation of a C-Ar quasimolecule, owning to an energy matching between the C K shell and the Ar M shell. We carefully studied [30] the interaction of Ar ions of various ionization states (9, 10, 12, 14, 16, 17+ i.e. all states of the L shell filling) with C targets and actually clearly observed the emission of C K x-rays, but with an intensity two orders of magnitude lower than expected. A simple calculation showed that the observed line may safely be attributed to the photoionization of the target atoms by the LMM Auger electrons emitted during the filling the ion L shell below the surface.

For heavier ions owning a quite large number of electrons (instead of H or Helike ions) Pesic et al. [16] studying the interaction of Pb\textsuperscript{53-58+} (Z = 82) with Ta targets (Z = 73), two atoms owning then clear energy matchings, calculated that the electron promotion model undoubtedly explained their observed transfer of Ta innershell electrons into the n = 7 and 8 levels of incoming Pb ions i.e. the formation of quasi-molecules made of two big bags containing many electrons penetrating each other. Both side and top feeding processes then hold for ions penetrating solid targets according to the exact nature of the two partners (atomic number, initial charge, and electric properties of the target: insulator or conductors).

Here: soon coming comments of the Wilhelm et al. experiments

The radiative electron capture

The filing of the ion vacancies might also a priori proceed through Radiative Electron Capture (REC): capture of a free electron into a vacant state of an ion leading to the simultaneous emission of a photon of energy \(h\nu = B_i + E_e\) (\(B_i\) binding energy of the ion vacancy, \(E_e\) kinetic energy of the electron). The REC process (emission of one photon during the capture of one electron) being the inverse process of photoionisation (extraction during the absorption of a photon of a ‘free’ electrons trapped in a metal box), its cross section may easily be calculated using the inverse balance theorem. Radiative Electron Capture is a basic essential process of atomic physics: the capture of a free electron approaching an ion showing up how to build an atom with a free electron and e.g. a bare nucleus. The probability of this process quickly increasing with the binding energy of the level in which the electron may be captured, REC then mainly fills the innermost vacant state of the ion (e.g. the K level for Hlike or bare nucleus), and its cross section quickly decreases with the kinetic energy of the electron \(E_e\). This process has originally been observed in plasmas where both particles move erratically at very low velocity (cold plasmas) i.e. when its cross section is maximal.

As it is quasi impossible to study experimentally the Radiative Electron Capture collisions sending an electron beam of given kinetic energy onto a target of trapped free ions at rest, this process has actually mainly been studied in collisions of very fast ion beams impinging the
electrons of target atoms, of much slower velocities, supposed to be at rest [31]. The energy of
the emitted photons, $B_i + E_e$, instead of being well defined (monoenergetic) reflects then in this
case the energy spread $E_e$ of the captured electrons. Another similar situation has also been
observed during the channeling of ions in crystals [32]. Ion beams entering a crystal along a
string or a crystallographic plane may be channeled i.e. progressively ‘focused’ along the center
of the channel, and then interacting with the atoms of the solid at the largest impact parameters.
In such a case the charge exchange processes (formation of quasi molecules) which hold during
the deep penetration of the ion inside the target atom, i.e. at the smallest impact parameters of the
atoms of the solid, becomes negligible and REC the dominant process of capture of valence
(quasi at rest) electrons. The filling of the K hole of the ions inside the solid may then proceed
either from spontaneous transitions of L, M, N, (O) outershells electrons of the excited ion into
the K hole, or from the capture of free electrons (of negligible energy, few eV in our case) leading
to the emission of a photon of energy $\# B_{K}$ i.e. just above the last $K_{\gamma}$ line (Fig.17).

Fig. 17: electron capture processes and corresponding x-ray transitions emitted during the
interaction of Ar ions below a surface. REC fills essentially the innermost shell of the ion, the K
shell in the present case, and AN neutralization the top levels. Black insert: observed radiative
cascade following top feeding.

This radiative electron capture process has been observed [33] in the x-ray spectra emitted
by the hollow atoms formed by slow Ar$^{17+}$ ions travelling inside solids. We present in Fig.18 the
part of the K x-ray spectrum showing up the $K_{\beta\gamma}$ lines corresponding to the KL$^{5-8}$ states of the ion
(the most illustrative part of the spectrum ; the second part second part - the KL$^{1-5}$ lines - may be
found in ref.[33]). It is worth noting that the observed REC lines, of energy close to $B_i$ ($E_e \#$ few
eV being negligible), which corresponds to a process in which one photon is emitted at each
radiative capture, are much more intense that the $K_{\beta}$ lines which corresponds to the decay of a
given state of the ion which owns a low fluorescence yield.
The second striking feature of this spectrum is the quasi linear increase of the intensity of the KLx lines with decreasing values of x. This finding may be explained by the fact that the ions moving below the surface are quasi neutralized, the higher the number of L vacancies, the larger the number of M, N available valence electrons to be captured.

It must also be noticed that the intensity of the Kβ line compared to that of the Ka one is always much lower in the considered cases than in neutral atoms, a finding that may be easily explained considering that the M shell obviously decay preferentially through the very fast LMM Auger to the L vacancies in the considered cases than through the emission of Kβ transitions in neutral atoms.

The hollow atoms above the surfaces

The main property of the Auger decay is that its rate dramatically varies with the energy of the emitted electron: the lower the energy, the higher the transition rate. The Auger process then strongly favors transitions between the closest levels energetically allowed (by contrast to x-ray transitions whose rates increase as the third power of the energy difference between the initial and final state i.e. the photon energy). The energy of the atomic states varying as the inverse of the square of their quantum number n (# 1/n²), the energy difference between the highly excited levels also dramatically decreases for the most excited levels. The Auger decay is then the dominant decay process of ions owning many electrons in highly excited states, and each level of the cascade populates its closest level (n→ n-1 → n-2…). The decay of the ions owning many electrons in highly excited levels then mainly proceeds through a long cascade of Auger transitions, obviously ending when the ion only owns one excited electron and may only decay via x-ray emission.

The full decay of slow hollow atoms formed above a surface, which proceeds through this cascade of a very large number of steps of Auger transitions, ionizing the ion after each transition, and recapturing electrons during their approach to the surface, is then a very long process, whose length is very difficult to evaluate. It has to be compared to the meantime for the hollow atoms to travel, at the lowest available velocity # 10⁴ m s⁻¹ (E = 1 eV/q), from the distance z₀ (# 1.5 nm) at

Fig.18: The Kβ, Kγ, and REC x-rays observed during the interaction of Ar¹⁷⁺ on metal surfaces.
which it starts capturing electrons, to the surface where it is peeled off, which is of the order of 150 fs. At these very low kinetic energies the ion stays then above the surface a certain time, allowing the observation of some of the last x-ray transitions of the decay cascade emitted above the surface.

The quick neutralization of incoming slow highly charged ions, supposed to fill quasi instantaneously very excited Rydberg states of this ion, opens however fundamental conceptual questions. The rate of the Auger effect is known to scale like the square of the number of excited electrons. At the early beginning of this cascade the decay rate of the hollow atoms formed above the surfaces is then incredibly large. The time between these very first steps of a cascade between so many stationary (?) states, is then so small, that one may then be puzzled trying to describe such situations in quantum mechanics.

The very first signal of the formation above a metal surface of highly excited ions following the capture of electrons by strongly decelerated highly charged ions, has been first observed, in Auger spectroscopy by F. Meyer et al. [28], and confirmed some time later [14][34][35] in x-ray spectrometry. The main feature of the KLx x-ray spectra emitted by Ar17+ ions (Fig.19) at the lowest ion energies (down to # 1 eV/q) i.e. when the probability of observing above the surface signals is maximal, is that this KLx distribution dramatically peaks to the lines corresponding to the lowest numbers of L spectator electrons (KL1 and KL2). This finding is then in good agreement with the above quoted Atomic Clock Property of Hollow Atoms because the filling of the L shell is quite slow and lasts a meantime comparable to that of the filling of the K hole. These spectra exhibit however dramatic differences in shape above metal and dielectric surfaces (Fig.19).

![Fig.19: KLx spectra at the lowest ion kinetic energies above metal and dielectric surfaces.](image)

Above dielectrics, at the lowest ion kinetic energies, the KLx distribution strongly peaks on a KL1 line of energy undoubtedly signing a transition in an ion owning no or extremely few outershell M, N, O, P... electrons, by contrast to what happens below the surfaces where the ion is quasi fully neutralized. This finding has been tentatively explained considering that above dielectrics the very fast exodus of a great many number of electrons leads to the local formation of static positive repulsive charges on the surface (leading sometimes to local permanent marks [36]), which cannot be evacuated fast enough during the interaction time, and may overcome the image acceleration. The ions may then be backscattered [34][35] at the lowest ion given kinetic energies, the so called trampoline effect, and never touch the surface, giving the ion an infinite time to decay. While being backscattered the ions then exit the capture area to freely decay in vacuum, not being re-fed any longer. The spontaneous decay of these very excited states quasi
exclusively proceeding through Auger transitions, the ion loses then one electron at each step of the cascade and spontaneously re-ionizes. The final charge state of the ion depends then on the relative number of excited electrons and the number of steps needed for the electrons to reach the ground state. If the number of electrons is lower than the number of the steps to reach the ground state, the ion is fully re-ionized, losing all its electrons but one (the Auger transitions need obviously two excited electrons) and mandatory ends its decays via the emission of the characteristic x-rays of an ‘one excited electron ion’ (Helike in the present case of Hlike Ar\textsuperscript{17+} projectile ions), in agreement with the above quoted findings. In the, very unlikely, opposite case the ion ends the cascade still with a certain number of electrons, and then a lower charge state, emitting KL\textsuperscript{x} x-rays of slightly lower energy, corresponding to an ion owning few electrons in its outershells. By contrast to what happens with hollow atoms formed below the surfaces where capture holds in states of the ions of low quantum numbers (n = 3 and 4 for Ar ions), and all steps of the decay (M→L→K) may be observed in x-ray spectroscopy, the capture holds above the surfaces in much more highly excited levels and the observed M→L→K x-ray cascade only corresponds to the last steps of the outside decay. One presents in Fig.20 the evolution of the KL\textsuperscript{x} spectra versus the kinetic energy of the ion which shows up the continuous decrease of the outside formation and decay of the excited ions with increasing ion energy [25].

![KL\textsuperscript{x} spectra emitted with Ar\textsuperscript{17+} ions impinging SiH solid targets at various kinetic energies.](image)

Above metals where the ion mandatory hits the surface owing to its electric image acceleration, one observes an x-ray spectrum made of transitions emitted by the ion above, at and below the surface, whose relative contributions vary according to the kinetic energy of these ions. One observes at the lowest ion given kinetic energy, i.e. when the contribution of the above the
surface decay is maximum, a KL spectrum peaking on KL$^1$ and KL$^2$ lines whose energies and widths correspond to transitions in ions owning a certain number (unknown but likely quite large) of M or outershell electrons.

The KL$^1$ lines corresponding to ions free of any outershell electrons, which cannot then decay by Auger transitions, owns a quite long lifetime (# 30 fs) and a fluorescence yield of unity. The lifetime of this state which may only decay via the emission of a K x-ray, may be however shortened as soon as outermost shell electrons are present, opening a new (Auger) decay channel in the ion.

The KL$^2$ lines corresponding to ions free of any outershell electrons, which cannot then decay by Auger transitions, owns a quite long lifetime (# 30 fs) and a fluorescence yield of unity. The lifetime of this state which may only decay via the emission of a K x-ray, may be however shortened as soon as outermost shell electrons are present, opening a new (Auger) decay channel in the ion.

The decay of the hollow atoms in their KL$^2$ states mainly proceeds for these ions of relatively low atomic number via Auger transitions (e.g. KLL Auger). There are then many more ions decaying while being in this KL$^2$ state (of low fluorescence yield), than it seems by just looking at the x-ray spectra.

We do not know a priori however which of the KL$^1$ and KL$^2$ states observed transitions are emitted above, at the surface or after penetrating this surface. The formation of these two states is however time ordered. The KL$^1$ states, of the largest lifetime, are formed before the KL$^2$ states which own a shorter lifetimes. The decay of the KL$^2$ state then holds after the formation of a KL$^1$ state which has not decayed via any kind of filling of the K vacancy, waiting for one more transition filling one more vacancy of the L shell. (by contrast to what happens below the surface where the filling of the K hole may hold at any time of the filling of the L shell , the lifetime for the filling of the K shell being of the same order of magnitude for the filling of the L shell).

We only have then at our disposal, for the time being, a very poor amount of experimental information about what happens to the hollow atoms formed above metal surface, and what may be observable, an archeologic issue!

**Above the surface decay of the hollow atoms formed with Ar$^{18+}$ ions**

The behavior of hollow atoms above dielectric surfaces has been studied with bare Ar$^{18+}$ ions in two kinds of experiments where the hollow atoms may freely escape the capture area. Ar$^{18+}$ ions owning two K vacancies decay, below a surface, emitting two KL$^x$ x-rays. The observed x-ray spectrum is then made of two well separated groups of lines, similar to those shown in Fig.10, distant of about 210 eV, corresponding to the stepwise filling of the two K holes in presence of a certain number of L electrons. In these two experiments the emitted x-rays have been detected using SiLi spectrometers of lower energy resolution (130 eV). It was not then possible with these detectors to separate all the KL$^x$ components of each group of x-rays, but only to measure the mean value of the number of L spectator electrons present at the time of the filling of each K hole.

In the first experiment [37] an ion beam of 10 keV/q kinetic energy is decelerated in a dedicated ion optics down to energies close to zero, biasing the surface of the target at a variable potential slightly lower than 10 kV (Fig.8). At ion given energies low enough to allow the backscattering, the ion comes back upstream in the same ion optic, and is then reaccelerated to its initial energy. In order to detect the backscattered ion one just provokes a small misalignment of the reflected beam by slightly tilting the angle of the target with respect to the axis of the beam pipe, in such a way that the backscattered ion hits the edge of the slit. In order to follow the travel of the ions inside the beam pipe three SiLi x-ray detectors in coincidence, i.e. allowing detecting the time correlation between the detected signal emissions, have been placed along the ion
trajectories: two in front of the target and one in front of the area where the backscattered ion is supposed to hit the edge of the slit as shown in Fig. 21.

At an ion energy large enough to oblige the ion hitting and penetrating the surface, one may then observe coincidences between the two K x-rays in the two detectors (1 and 2) located in front of the target. At decreasing ion kinetic energies down to zero, when the ions may be backscattered, one starts observing the apparition in detector 3 of the characteristic spectrum currently observed at the largest ion energies with Ar$^{17+}$ ions, and the rate of coincidences between detectors 1 and 2 decreases. At the same time one then simultaneously starts detecting coincidence events between detector 3 and any of the detectors 1 and 2, exactly delayed by the travel time of the ion between the target and the slit. The transition filling the first K hole is then emitted in front of the surface and the second one is emitted, after being backscattered while touching the edge of the slit. These findings may then be explained following the above quoted scenario of the free decay in vacuum of ‘above the surface’ hollow atoms: the ion first penetrates the capture area where it captures a certain number of electrons in highly excited levels, loses all of them but one in a cascade of auto-ionizing transitions to become an excited Ar$^{17+}$ ion, radiatively filling nearby the surface its first K vacancy and escaping the capture area as an Ar$^{17+}$ ion in its ground state i.e. not having enough electron to fill the last K vacancy. This ion is then reaccelerated in the beam line by the decelerating electrostatic device and hits (penetrates) the edge of the slit at its initial kinetic energy, emitting the above showed up characteristic K x-rays of ‘below the surface hollow atoms’.

In the second experiment Ar$^{18+}$ ions of 10 keV/q kinetic energy have been sent onto a C$_{60}$ vapor beam [38] i.e. skimmed past a small spherical carbon surface. Two different kinds of collisions may be considered. At impact parameters b lower than the radius r (0.35 nm) of the cage of the C$_{60}$ (head on collisions) the ion always penetrates the body of the molecule (Fig.22) and break it. For collisions at impact parameters higher than r and lower than $z_0$ (the maximal distance of capture from a surface, # 2 nm in the present case) the ion captures electrons while crossing the sphere of radius $z_0$ (interacting then with a small surface of carbon), and escapes this capture area to freely decay outside where it is, as discussed above, fully auto-ionized. The geometrical cross section for electron capture from the surface of the bucky ball being much
larger (92%) than that for a head on collision with the cage, most of the observed collisions are then due to ‘above the $C_{60}$ surface’ interactions

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**Fig.22: Interaction of a highly charged ion with a $C_{60}$ molecule.**

The events holding during these collisions have been studied looking at the ion x-rays emitted in the collision area with a SiLi detector in coincidence with charged fragments of the broken $C_{60}$ molecule resulting of the relatively large removal of electrons compared to the number of atoms in the bucky ball, and which signs the occurrence of a collision. With $Ar^{18+}$ ions, which own two K vacancies, one mainly observes the characteristic x-rays signing the filling of the ‘first’ K hole (Hlike ion) and only very few x-rays signing the filling of the ‘second’ K hole (Helike ion). This result then means that the ion, at the end of its decay cascade escaping the capture area, does not have enough electrons to fill the second K hole (only filled when the ion touches or penetrates the surface where it is permanently refed (quasi neutralized). These findings then clearly show that the number of steps to reach the L shell is higher than the number of captured electrons allowing getting an estimate of the minimum n state in which the electrons are captured following a full neutralization of the ion while crossing the capture area.

**Conclusions**

The fundamental quest at the origin of the study of the interaction of highly charged ions above surfaces was to know if these expected, incredible, exotic species, made of a very great number of electrons in highly excited states and few or none in the innermost shells, really exists. While such exotic species, the hollow atoms, had been observed below surfaces [9], it was soon realized that if such highly excited atomic species would be formed above surfaces they may not be really observable owning to the extremely short time they would have to decay along their trajectories from the distance at which where they may be formed (# few nm) and the surface where they are destroyed.

The ions above dielectrics are backscattered, and one may observe in vacuum the full free decay of the ion, looking at the x-rays emitted in the last steps of the cascade allowing getting information on the approximate number of captured electrons and in which states they have been captured. The existence of this backscattering led at the beginning of the study of the interaction of highly charged ions above dielectrics to controversies [39] [40], some authors claiming that, according to their calculations and models the ion backscattering could not be theoretically possible. This controversy is now over the backscattering trajectory of the ions above dielectrics
having been experimentally directly observed, in the coincidence experiment [37], as shown above. The backscattering of the ions above dielectrics holds when the repulsive forces induced by the positive charges remaining on the surface during the interaction, becomes stronger than the image acceleration. This backscattering must then obviously vanish for ions of lowest charge state; we found [41] that this backscattering does not hold for Ne$^{9+}$ ions, meaning that this cancellation holds for ionic charges between 10 (Ne) and 18 (Ar). Most experiments studying the possible formation of hollow atoms above a surface having been carried out with C, N, O and Ne ions, this may explain why this backscattering, sometime theoretically contested, had never been observed before [42] [43].

These interactions above the surface may however often be satisfactorily described simply using scaling laws and orders of magnitude, and even sometime quite well described using simple tutorial elementary school problems such as calculating the water level in a sink with a tap and a plug hole to describe the last above quoted experiments. It is worth noting however that the interaction of highly charged ions with surfaces lead to cascades of an extremely large number of steps i.e. of possible scenarios, for a limited number of experimental data (we, most of the time, only observed the last steps of the decay cascades) and quite a lot of very refined theoretical calculations. These experiments show up new, attracting and amazing views of the atoms, allowing imagining new experiments or improving the teaching of atomic physics providing new and amazing views of the atoms. They may also open the way to many original applications in solid state physics, discovering new techniques in nanotechnologies and materials preparations and diagnostics.

The atomic manipulations and their applications

The approach of a surface by highly charged ions may lead to structural modifications of the surfaces. Above metal the local quick removal of many electrons does not provoke any visible permanent modification of the surface, the removed electrons being quickly replaced. By contrast above dielectrics the positive charges locally left after the fast migration of lot of electrons, which cannot be evacuated fast enough, have been found to create permanent surface structural modifications, dots or blisters [36]. It has been for instance demonstrated that the impact of a highly charged ion on a silicon surface passivated by a single atomic conductive layer of hydrogen prints, when exposed to oxygen nanometric dots of, isolative, SiO$_2$ [44] [45], or that above an, isolative, surface of diamond the same ions may create nanometric, conductive, dots of graphite, or even more exciting that nanodiamond dots created on graphite surfaces may own field emission properties[46] [47]; an immense and very promising field to explore.

The original property of the hollow atoms formed below the surfaces is that they spontaneously decay in a stepwise manner following a long series of transitions extending in time up to tens of fs. The ion being moving at controlled velocities (between $10^2$ and $10^6$ ms$^{-1}$) this sequence of events, which may in certain cases exceeds hundreds of steps, holds along paths of lengths of the order of up to tens of nm. Beyond the interest of these new atomic situations in fundamental physics the original properties of these manipulations may also be used in many technical applications.

The capture processes below surfaces as shown above dramatically depends on the electric properties of the solid (conductive or isolative). It has been recently demonstrated [48] that the x-rays emitted by these hollow atoms below a surface hold along a range of the order of # 2 nm in metals, but more than ten times longer in dielectrics. One may then take advantage of these long
decay cascades of the hollow atoms to characterize the nature and depth of shallow atomic layers present above surfaces, an important issue in nanotechnology. The interaction of these highly charged ions may even, as demonstrated, allow the full macroscopic transformation of graphite surfaces into diamond and vice et versa [49], an exciting issue in surface physics (and for jewelers!).

Here soon coming comments on recent experiments on Graphene

Such a technique has recently been successfully used studying e.g. the surfaces of carbon made materials such as diamond and graphite. It has then been demonstrated for instance that it may be possible with highly charged ion beams of just few tens of nA, to detect ‘live’ the presence of graphitic atomic layers build (reconstructed) on the surfaces, just by looking at the x-rays emitted by the ions penetrating these surfaces (the Atomic Clock Property of the Hollow Atoms ACPHA), an interesting non-destructive technique of exploration of the surfaces [50].

References

These experiments have been carried out using either ECR or EBIS source facilities through the world, selected to their ability to provide either the most intense ion beams (ECR) of medium atomic numbers (Z = 6 to 18), or the most highly charged ions (EBIS), in close collaboration with the physicists who developed these sources.

The first experiments started, in 1988-90 in Grenoble, in collaboration with Richard Geller who first developed the ECR sources and who first prepared ion beams of Ar$^{17+}$ ions. The first goal of these experiments was to study the interaction of these ions with free atoms in gas targets soon followed, by curiosity, by the study of the interaction of these ions with solid targets, an a priori much too complex system to be a promising domain of research, but was soon found to be a manageable field of physics which leads to the discovery of the hollow atoms in 1990 [9]. This series of experiment on Ar ions continued at the EBIS source in Kansas State University, built in Orsay, not allowed locally to be used in atomic physics, in close collaboration with Pat Richard and Martin Stockli. In the next few years ions of much higher charge states become available at the Super EBIT developed in Livermore where a series of experiments on ions up to Hlike Bi have been carried out, in a long term collaboration with Dieter Schneider and his team. New experiments have then also been carried out at ECR sources of the Cyclotron of the Lawrence Berkeley Laboratory where the most intense ion beams through the world became available in collaboration with Dieter Schneider, Dan Xie and Mike Prior. Later on, after the shutdown of the Livermore EBIT, new experiments on the mechanism of formation of the hollow atoms have been conducted in Collaboration with John Gillapsy at the NIST EBIS source in Gaithersburg, Maryland, and after the shutdown of the cyclotron in Berkeley, at the GTS ECR source of the CEN de Grenoble with G. Melin, A. Girard and D. Hitz, at GANIL in Caen, and with the ECR sources developed in Santa Clara by the company Berkeley Ion Equipment (BIE) Inc., founded and managed by Dan Xie in collaboration with the Université Pierre et Marie Curie, Paris. Later on we were offered a permanent beamline at the ECR source of the University of Nevada, Reno in very close collaboration with Ron Phaneuf, shutdown now since 2014. The last experiment has been carried out at GANIL in Caen in collaboration with V. Kostroun and D. Xie.

All these experiments have been carried out by the searchers of the Laboratoire de Physique Atomique et Nucléaire (LPAN), alias Equipe de Recherche Ions Surfaces (ERIS): B. D’Etat, L. de Billy, P. Charles, G. Giardino, J. Merot, and J.P. Desclaux of the CEN Grenoble and PhD students listed below.

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