Resonance phenomena in electron-ion and photon-ion collisions

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Abstract. Intermediate autoionizing states can be formed during electron-ion and photon-ion collisions. Depending on the decay of these multiply excited states by electron and/or photon emission the associated indirect processes can contribute to net electron-ion recombination, elastic or inelastic electron scattering, to excitation, to single or to multiple ionization of the initial ion. Intermediate states give rise to distinct features in the associated cross sections and, in particular, narrow resonances can occur. These sharp features facilitate access to level energies and transition rates of ions from which detailed information about quantum electrodynamic, relativistic, nuclear, and field effects can be extracted.

1. Introduction
The physics of resonant intermediate autoionizing states populated during photon-ion or electron-ion collisions is reviewed. Resonances can occur when the energy available in the collision matches intrinsic energies in the ion. Formation and decay processes of such resonances are numerous and involve intricate effects on the associated cross sections. While resonances in photon-ion interactions are associated with electron excitation mediated by the photo effect, their counterparts in electron-ion collisions involve non-radiative (dielectronic) capture of the projectile electron with simultaneous excitation of the ion core. In both cases, the subsequent relaxation of the intermediate excited state by radiative decay or electron emission determines the final observation channel. Although viewed as academically interesting phenomena, resonant contributions to photonic and electronic collisions have often been neglected in theoretical attempts to assess cross sections because resonances are generally associated with multi-step processes which are expected to be unlikely.

Recent progress in the field has become possible by the combination of intense, high quality photon and electron beams with well prepared ionic targets. By using advanced ion source technology, storage ring capabilities and trapped ion techniques a wide spectrum of target species is accessible to studies of ionic resonances ranging from negative to highly charged positive ions and even to ions encapsulated within fullerene molecules.

It was recognized early that electron-ion recombination in a plasma is dominated by dielectronic recombination resonances provided the ion has at least one core electron. Later, investigations of electron-impact excitation and ionization and even of elastic electron scattering revealed unexpected strengths of resonant contributions to the associated cross sections. Similarly, the importance of resonances in photon-matter interactions has been recognized,
particularly also for photoionization of atoms, molecules and ions, where an incoming photon can produce multiply excited states which subsequently decay by autoionization and thus contribute to net ionization of the target particle. Again, such resonances can dominate the cross sections for photoionization and, hence, influence the state and emission characteristics of a plasma as well as the opacity of matter exposed to electromagnetic radiation.

Beside the resulting applied importance of indirect resonant contributions to collision cross sections, the spectroscopy of resonances offers unique opportunities for studying the structure and dynamics of atoms, molecules, including fullerenes, and clusters as well as their ions. Photoionization is time-inversed electron-ion recombination. This can be exploited to obtain very detailed information on the relevance of individual intermediate excited states for the observed processes. Collisional spectroscopy of such states has reached a very high level of precision. It has recently been demonstrated to be even sensitive to nuclear properties such as the charge radius and the spin of the atomic nucleus. The precision of such spectroscopy has been shown to be competitive with or even superior to optical methods and thus provides new possibilities, e.g., for sensitive tests of quantum electrodynamics in high fields.

Early work on resonances in electron-atom and electron-molecule collisions, i.e., on the formation and decay of multiply excited intermediate negative-ion states has been reviewed by Schulz [1, 2]. A later review by Buckman and Clark [3] addressed new developments and also included resonances excited by interactions of photons with negative atomic ions. More recently, the physics of negative ions including resonance phenomena was comprehensively reviewed by Andersen [4].

Resonances in the photoabsorption by atoms and molecules have been studied for many decades. Seminal papers have been published by Beutler [5] and, after the advent of the first synchrotron radiation sources, by Madden and Codling [6] and Codling and Madden [7]. A comprehensive review of photoionization of atoms was given by Schmidt [8].

The first observation of resonance structure in a negative-ion photodetachment cross section was made by Patterson et al [9] using light from a tunable dye laser. Work following up on these first photon–negative-ion resonance studies is included in the reviews by Buckman and Clark [3] and by Andersen [4]. Photoabsorption by positive ions became accessible to experiments by introducing the dual laser plasma technique. The development and the successful use of this technique has been reviewed by Kennedy et al [10]. Photon–positive-ion work employing merged beams of ions and synchrotron radiation was pioneered by Lyon et al [11]. The field was reviewed by West [12] and, more recently, by Kjeldsen [13].

Dielectronic recombination was the first subfield of electron-ion collisions to yield to the observation of resonances. Pioneering work has been published 1983 in a series of Physical Review Letters by Mitchell et al [14], Belić et al [15], and by Dittner et al [16]. First experimental observations of resonances in electron-impact single and multiple ionization of ions followed [17, 18]. A comprehensive overview of electron-ion collisions with emphasis on resonance phenomena has been published recently [19].

2. Experimental aspects of ionic resonances
A well characterized target ensemble of ions [20] exposed to a beam of photons or electrons would be the method of choice to study electron-ion and photon-ion interactions. A stationary target of ions, however, is not as easily produced as a gas target. The space charge of the ions drives the ensemble apart. Without additional forces to confine the ions such a target cannot but explode. Stationary ion targets can thus only be produced with suitable electromagnetic traps. Such a scheme for electron-ion or photon-ion experiments has been realized, for example, in electron beam ion trap (EBIT) devices [21]. Recently, a Fourier Transform Ion Cyclotron Resonance trap was employed to irradiate ions with synchrotron radiation [22]. Important progress of photoionization of multi-charged ions produced and trapped in an EBIT is reported by Simon
Alternatively, the ion target is provided by a beam of ions that is crossed or merged with the photon or electron beam. The merged-beam geometry has advantages through the possible interaction path length and, in electron-ion collisions, through kinematic effects supporting high energy resolution. It is interesting to note that storage rings for ions and electrons provide the most favorable conditions for studying narrow resonance features. Stored and cooled beams of ions in an ion storage ring are characterized by high brightness and low energy spreads. The combination of an electron cooler in the ion storage ring and a beam of ultracold electrons as available at the Max-Planck-Institute for Nuclear Physics in Heidelberg are ideal for high-resolution studies of electron-ion resonance phenomena. On the other hand, storage rings for electrons with GeV energies and advanced insertion devices provide the brightest quasi-continuous (practically DC) sources of high-energy photons. The combination of ion beams and synchrotron radiation from such third generation light sources has been exploited in the last decade to study resonances in the photoionization of ions with unprecedented energy resolution and statistical quality. The future of photon-ion interaction and resonance studies will be determined by the availability of free electron lasers (FEL). A first round of successful experiments carried out at the FLASH facility (Free electron LASer in Hamburg) has been published and was recently reviewed. Several new high-brightness FELs are under construction worldwide. Their brightness is or will be orders of magnitude higher than that of third generation synchrotron light sources during the short FEL pulses. However, the repetition rate for such pulses is limited and the duty cycle is comparatively low.

In spite of great progress in experimental techniques the investigation of interactions between free electrons and ions often suffers from low signal rates. The limitations in the free-electron density can partly be overcome by using quasi-free electrons bound in atoms or molecules. At sufficiently high projectile velocities (\(v_{\text{ion}} \gg v_{\text{orb}}\) with \(v_{\text{ion}}\) the velocity of the incident ion and \(v_{\text{orb}}\) the orbital electron velocity) the electrons bound in target atoms can be treated as free particles, a concept that has been used with great success for almost a century to describe high-energy atomic collisions.

The importance of recombination and excitation measurements for plasma applications and the necessity to test and to guide theory together with the appealing subject of observing resonance features in atomic collisions led to a very important development of accelerator-based ion-neutral-target collision studies of resonance phenomena related to electron-ion collisions. The dielectronic-capture–related process of resonant transfer with excitation (RTE) was unambiguously demonstrated for the x-ray emission channel by Tanis et al. Similarly, the ion-atom equivalent to resonant elastic electron scattering from ions was found by Itoh et al. who observed the Auger decay channel of resonant-transfer-with-excitation resonances. This technique has been extended to measurements of differential cross sections for inelastic and super-elastic scattering processes. Resonant-transfer-with-excitation was studied for the highest accessible ion charge states by Graham et al. who observed RTE resonances in the total one-electron capture cross section of \(U^{90+}\) in He and by Ma et al. who succeeded to obtain cross sections for RTE in \(U^{91+}\) differential in the angle of photon emission.

### 3. Mechanisms of Resonances

Resonances in atomic processes can occur when the projectile energy matches intrinsic characteristic energies of the target system. In electron-ion collisions the formation of a resonance involves the radiationless capture of the incoming electron while one or several target electrons are simultaneously excited (see figure 1)

\[
e + A^{q+} \rightarrow [A^{(q-1)+}]^{**}.
\]
The decay of the intermediate autoionizing state determines the reaction channel in which the resonance can be observed. Decay processes can involve the emission of one or more photons stabilizing the initial capture of the projectile electron. The associated process is resonant recombination. The dominant resonant recombination process is dielectronic recombination which involves two active electrons, the projectile and a core electron in the target ion. In contrast to that, trielectronic recombination proceeds via the interaction of three active electrons, the projectile and two target electrons. Apart from photons, a number \( n \) of electrons can be ejected from the intermediate, possibly highly excited state. For \( n=1 \) the net result of the process is elastic or inelastic electron scattering. For \( n>1 \) the net result of formation and decay is net \((n-1)\)-fold ionization of the target. The emission of electrons mostly occurs in successive single Auger processes. Without a suitable intermediate autoionizing state present in the transient \( A^{q+} \) ion also the simultaneous correlated emission of two electrons from the \( [A^{(q-1)+}]^{**} \) ion can be observed. For a detailed review of resonance mechanisms in electron-ion interactions see reference [19].

Photons can be absorbed by the photo effect involving direct ejection of a target electron. The related cross sections have a sharp onset at threshold and above that they slowly decrease with a relatively smooth energy dependence. When the photon energy exactly matches a discrete excitation energy of the target system (where one or more electrons can be excited; see figure 1) a resonance can be observed in the absorption spectrum. In a wider sense, photoexcitation of discrete bound states leads to resonances. In the present context, the discussion of resonances in photon interactions is restricted to photoionization, i.e., the photons have an energy sufficient to ionize the target. Then the smooth cross section for net single or multiple ionization can show resonances associated with excitation of more than one electron or, alternatively, the excitation of an inner-shell electron to an outer shell

\[
h\nu + A^{q+} \rightarrow [A^{q+}]^{**}. \tag{2}\]

By such processes, multiply excited states can be populated which are identical with dielectronic resonances. Again, \( n \) electrons can be ejected from such resonant states with \( n=0,1,2,3... \)

A particularly interesting group of resonance phenomena is that associated with the formation and decay of hollow ions where, for example, both K-shell electrons are excited. In such cases, there can be decay paths associated with simultaneous emission of two electrons. An example is the double detachment from the He\(^-\) \((1s2s2p\ ^4P)\) ion proceeding via one-electron photoexcitation.
to $\text{He}^-(2s2p^2 \ ^4P)$ and subsequent two-electron emission [38]. The detected final ion is $\text{He}^+(1s)$ which cannot be reached from $\text{He}^-(2s2p^2 \ ^4P)$ by sequential Auger processes. The experimental cross section is shown in Fig. 2.

Double-excitation of the K-shell of He-like ions has also been observed. In photoionization of Li$^+(1s^2)$ intermediate configurations such as Li$^+(2s2p)$ can be produced which contribute to net single ionization by Auger decay [41]. Similarly, double excitation of Li$^+$ ions is also possible by electron impact at energies beyond the related double-excitation threshold. When the electron energy is just below that threshold, the formation of a hollow state is still possible, but then the projectile electron looses so much energy that it becomes trapped in the target potential. This process is termed trielectronic capture and is the first step in the trielectronic recombination discussed above. The resulting resonances can be of the type Li$(2s^22p)$ or Li$(2s2p^2)$. These hollow lithium atoms can then, at least in principle, decay by photon emission and, by that, stabilize the neutral charge state. Most likely, the hollow states decay by a single Auger process and subsequent photon emission producing an ion, Li$^{+}$, that has not changed its initial charge state. In addition, a (second) correlated three-electron process is possible in which one of the L-shell electrons falls into the K-shell while the two others simultaneously leave the atom, thus producing the final Li$^{2+}(1s)$ product ion. The latter processes have been observed in electron-ion crossed beams experiments [42].

In complex many-electron systems also collective electron motions can be excited. Giant resonances in the 10 to 20 MeV region were observed in nuclear excitations already more than 60 years ago. They are interpreted as collective motions of the protons versus the neutrons in a nucleus. Broad resonance features with large cross sections observed in photon interactions with Xe and Ba atoms were similarly termed ‘giant resonances’. They are associated with the excitation of 4d-shell electrons. The topic has received considerable attention and has been reviewed by Kjeldsen [13]. Cross sections for electron-impact double ionization of Xe$^+$ ions associated with 4d vacancy production were found by Achenbach et al. [39] to exhibit a broad

**Figure 2.** Cross section for photo-double-detachment from $\text{He}^- (1s2s2p \ ^4P)$ proceeding via photoexcitation of $\text{He}^- (1s2p^2 \ ^4P)$ [38]. The solid line is a Voigt fit yielding a photon energy spread of 5.5 meV and a natural width of the intermediate $\text{He}^-(1s2p^2 \ ^4P)$ resonant state $\Gamma = 9.7 \pm 2$ eV as well as the resonance energy 37.668 $\pm 0.007$ eV.

**Figure 3.** Inferred cross section for a 4d giant resonance contribution to electron impact double ionization of Xe$^+$ ions. From the measured cross sections [39, 40] a smooth curve representing the non-resonant contributions was subtracted to obtain the displayed data. Error bars are statistical only.
resonance feature similar to that observed in photoionization of the Xe atom (see figure 3). Similar resonance features were seen in single ionization of xenon ions, especially in Xe$^{3+}$ [43]. The observation of ‘giant resonances’ in ionizing electron collisions with ions of I, Xe, Cs, Ba, La and Ce was reviewed by Müller [44].

A giant resonance was also found in the single-photon absorption spectrum of neutral C$_{60}$ at energies near 20 eV [45, 46]. This resonance is associated with the collective motion of the 240 delocalized valence electrons that form a negatively charged cloud around the positively charged ion cage of the C$_{60}$ molecule and can oscillate relative to the positive charge of the carbon ion cores that form the C$_{60}$ molecular cage. This oscillation is associated with a so-called surface plasmon resonance. It was observed in single ionization of C$_{60}^+$ ions [47]. In addition to the dominant peak centered at 22 eV, a higher order resonance was found in C$_{60}^+$ near 40 eV and was associated with a ‘volume plasmon’ [47, 48]. Similar plasmon contributions at almost identical energies are found in the photoionization of other fullerene ions [49, 50].

Recently, an exotic electron-ion resonance process has been proposed [51] and studied theoretically: the radiationless capture of a free electron by a completely stripped ion with excitation of the nucleus. Depending on the decay of the intermediate resonant state the final observation channel is resonant recombination [52] or resonant elastic electron scattering [53]. The cross sections for such processes are typically well below $10^{-27}$ cm$^2$.

4. Time reversal symmetry

Identical resonant states in a given ion can be populated via different doorway states. For example, photoionization of C$^{3+}$($1s^22s$) can proceed via photo–inner-shell excitation to the doubly excited C$^{3+}$($1s2s2p\ 2P_{1/2,3/2}$) states which then decay to C$^{4+}$($1s^2$) by an Auger process. The time-reversed process is dielectronic recombination proceeding via the identical fine-structure $2P_{1/2,3/2}$ resonances

$$h\nu + C^{3+}(1s^22s\ 2S) \leftrightarrow C^{3+}(1s2s2p\ 2P) \leftrightarrow C^{2+}(1s\ 1S) + e^- 64.4939\ eV.$$  \hspace{1cm} (3)

The interactions that dominate electron-ion and photon-ion collisions conserve time-reversal symmetry. Hence, the Hamiltonian of the system does not depend on the direction of time’s arrow. As a result, the principle of detailed balance can be applied. Cross sections for reactions proceeding in one direction can be calculated from the cross section for the time-inverse process. The cross section $\sigma_{i\rightarrow f}^{(PR)}(E_e)$ for photorecombination

$$e + \mid i \rangle \rightarrow \mid f \rangle + \gamma + I_{bind}$$  \hspace{1cm} (4)

of an ion in state $\mid i \rangle$ can be calculated from the cross section $\sigma_{f\rightarrow i}^{(PI)}(E_\gamma)$ for photoionization of an ion in state $\mid f \rangle$. The energies are related via the binding energy $I_{bind}$ of the electron in state $\mid f \rangle$

$$E_\gamma = h\nu = E_e + I_{bind}.$$  \hspace{1cm} (5)

$E_\gamma$ is the energy of the photon and $I_{bind}$ is the ionization potential of state $\mid f \rangle$. With these definitions the principle of detailed balance provides the relation between associated cross sections for photoionization and photorecombination on a state-to-state basis. For nonrelativistic photon energies $h\nu \ll m_e c^2$ the relation is

$$\sigma_{f\rightarrow i}^{(PR)}(E_e) = \frac{(h\nu)^2}{2m_e c^2 E_e g_i} \frac{g_i}{g_f} \sigma_{i\rightarrow f}^{(PI)}(h\nu)$$  \hspace{1cm} (6)

where $E_e$ is the energy in the electron-ion center-of-mass frame [54]. The quantities $g_i$ and $g_f$ are the statistical weights of the ionic initial and final states, respectively. Eq. 6 also holds when
there are intermediate resonances involved, however, it can only be employed on a state to state basis ($|i\rangle \leftrightarrow |f\rangle$).

Examples where time-reversal symmetry has been exploited to obtain more details of photoionization and electron-ion recombination resonances are scarce. The reason is in the stabilization of resonances by photoemission. Different from the example of Eq. 3, doubly excited states usually decay by the emission of two photons producing a stable recombined ion. Time reversal would then imply simultaneous absorption of two photons which cannot easily be accessed in photon-ion experiments. Published examples of time reversal studies deal with doubly excited resonances in C$^{2+}$ ions [55] and in Sc$^{2+}$ ions [56, 57].

5. Line shapes and interference phenomena

For electron-ion and photon-ion processes associated with undisturbed resonances $|d\rangle$ the related resonant cross section contribution $\sigma_{d,f}$ can be represented by the product of the resonance formation cross section $\sigma_d$ and the branching ratio $\omega_{d,f}$ for the particular decay path to the final channel observed in the experiment

$$\sigma_{d,f} = \sigma_d \omega_{d,f} = S_{d,f} \frac{\Gamma_d}{2\pi} \frac{1}{(E - E_{res})^2 + \Gamma_d^2/4}. \tag{7}$$

$S_{d,f}$ is the resonance strength, $E$ is the energy of the incident electron or photon and $E_{res}$ the resonance energy for populating the state $|d\rangle$. $\Gamma_d$ is the total width of $|d\rangle$

$$\Gamma_d = \hbar \left[ \sum_{k'} A_a(d \rightarrow k') + \sum_{f'} A_r(d \rightarrow f') \right] \tag{8}$$

where $A_a(d \rightarrow k')$ is the Auger rate for transitions from $|d\rangle$ to state $|k'\rangle$ and $A_r(d \rightarrow f')$ denotes the rate for the radiative transition from $|d\rangle$ to state $|f'\rangle$. The summation indices $k'$ and $f'$ run over all states which can be reached from $|d\rangle$ either by autoionization or by radiative transitions, respectively.

In general, the appearance of resonances is not as simple as described above because of the possible interference of resonant and direct reaction channels. In the general case, there are several reaction pathways to the final result of a collision that cannot always be distinguished from one another. One can imagine two reaction mechanisms which start from a given initial state, characterized by an electron with a defined energy and an ion, for example, in its ground state. After the collision there may be photons, electrons and a product ion in a given final electronic state. When in two different pathways the final numbers of electrons and photons as well as their energies are identical and when the final electronic state of the target is also the same for both pathways, i.e., when the different pathways starting from a defined initial state end up in the same final state, then (and only then) the pathways cannot be distinguished from one another and their amplitudes can interfere. This is similar to the observation of light scattered from a double-slit arrangement. The photons cannot be traced back in their pathway through one or the other slit. The result is, that the amplitudes describing the two different pathways can interfere. The shape of an interfering-resonance cross section as a function of energy is then no longer Lorentzian (see Eq. (7)) but becomes distorted ([58, 59]). The resonance acquires a shape given by

$$F(E) = \frac{S_{d,f}}{Q^2 \Gamma_d^2 \pi} \left[ \left( \frac{Q + \varepsilon}{1 + \varepsilon^2} \right)^2 - 1 \right] \tag{9}$$

with $\varepsilon = 2(E - E_{res})/\Gamma_d$, the resonance energy $E_{res}$, the resonance width $\Gamma_d$, and the asymmetry parameter $Q$. The term -1 inside the square brackets ensures that $F(E) \rightarrow 0$ for $E \rightarrow \infty$. Low
values of $|Q|$ correspond to strongly destructive interference and $Q = 0$ produces a symmetric dip in the cross section at the resonance energy, a so-called window resonance. In the limit $Q \to \infty$ the Fano profile as defined by Eq. (9) approaches the symmetric Lorentzian line profile of Eq. 7.

![Figure 4](image)

**Figure 4.** Sample of resonances observed in electron-impact single ionization showing interference patterns. The left panel shows data for $B^{2+}$ ions in the vicinity of the $1s2s3s3d \, ^3D$ resonance (A). The middle panel shows data for $C^{3+}$. The dominant resonances are $1s2s2p \, ^3P$ (A), $1s2s2p \, ^3D$ (B), and $1s2s2p \, ^1D$ (C). The right panel displays window resonances observed with ground-state parent $Li^+$ ions. The two dominant resonances are associated with $2s2p \, ^2P$ (A) and $2s2p \, ^2D$ (B) states. The solid lines are Gaussian-convoluted Fano-profile fits to the experimental data. Contributions from direct single ionization were subtracted in the data for $C^{3+}$ and $Li^+$, hence the occurrence of "negative cross sections". The figure is adopted from Ref. [19].

Another scenario for interfering pathways in an electron-ion collision is of a more subtle nature. It is related to the finite widths of excited states. When two resonant states $|d_1\rangle$ and $|d_2\rangle$ of equal symmetry overlap one another, i.e., when the energy gap between the two states is smaller than the sum of the widths $\Gamma_{d_1}$ and $\Gamma_{d_2}$, interference is also possible because one cannot decide from the initial and final states which reaction pathway has been taken during the collision.

Interference phenomena in the formation and decay of resonances are ubiquitous. They can be easily found in the photoionization of ions and many examples have been observed. In electron-ion collisions it is more difficult to clearly see interference patterns in measured cross sections [19]. The reason is mainly in the limited potential of interacting beams experiments to measure differential or partial cross sections. Usually several different channels contribute to the observed cross section and their possible individual interference patterns get washed out with the summation of non-differentiated channels.

Unperturbed resonances have a Lorentz-shaped cross section with the natural line width $\Gamma_d = \hbar/\tau_d$ where $\tau_d$ is the lifetime of the resonant state $|d\rangle$. Also the Fano profiles given by Eq. 9 depend on the width $\Gamma_d$ and, hence, also on the lifetime of the resonant state. By employing high-resolution photoexcitation with experimental energy spreads smaller than the...
natural width \( \Gamma \) the lifetime of the associated resonance can be determined. Measurements with a finite energy resolution, i.e., non-zero energy spread, find the Lorentz profiles convoluted with the experimental energy distribution function. Usually, this experimental function can be well represented by a gaussian distribution with a specified width. The convoluted resonance shape is a Voigt profile [60]. In the case of interference the resulting Fano profile also has to be convoluted with the experimental energy distribution function (typically a gaussian) to describe experimental observations.

Figure 4 shows examples of resonances observed in electron impact single ionization of \( \text{B}^{2+} \), \( \text{C}^{3+} \), and \( \text{Li}^+ \) ions. For \( \text{B}^{2+} \) a resonance feature is shown [61] that can be associated with the dielectronic capture process \( e+\text{B}^{2+} \rightarrow \text{B}^+ (1s2s3s3d \; ^3\text{D}) \) and subsequent sequential Auger decay to \( \text{B}^{3+} (1s^2) + e+e \). The middle panel shows resonances that can only contribute to the ionization of \( \text{C}^{3+} \) ions by dielectronic capture to \( 1s2s2l2l' \) intermediate states that decay by double-Auger processes in which two electrons are ejected simultaneously [62]. The right panel displays resonances in the single ionization of ground-state \( \text{Li}^+ \) ions. These are populated by trielectronic capture to \( 2s^22p \) and \( 2s2p^2 \) states in neutral \( \text{Li} \) which subsequently decay by simultaneous emission of two electrons [42]. In all cases, pronounced interference of the resonant with non-resonant channels is observed.

6. Effects of external electromagnetic fields
It is known since a long time that autoionization rates are influenced by external electromagnetic fields. The dominant effect at moderate field strengths is caused by electric fields which mix states with different orbital angular-momentum quantum numbers \( \ell \). Magnetic field components perpendicular to an electric field mix, in addition, states with different orientation quantum numbers \( m \). The effects of different combinations of external fields on autoionizing states have been extensively investigated by Gallagher’s group ([63] and references therein). The production and decay of core-excited barium Rydberg atoms studied in that work is closely related to the process of dielectronic recombination. Effects of external electric and magnetic fields on dielectronic recombination of singly and multiply charged ions have been reviewed by Müller and Schippers [64]. Experimental observation of the effect of a static external electric field on the photoexcitation and autoionization of doubly excited states in helium was reported by Harries et al [65].

7. Resonance spectroscopy
The detailed observation of resonances in photon-ion and electron-ion interactions opens possibilities to determine resonance energies \( E_{\text{res}} \), resonance widths \( \Gamma \) and associated lifetimes \( \tau \) of the resonant state, as well as resonance areas and associated oscillator strengths. Figures 5 and 6 highlight the parameter space covered in electron-ion recombination measurements. The highest charge states and highest resonance energies were first accessed in RTE experiments. Figure 5 shows the result of the RTE contribution to the total one-electron capture cross section in \( \text{U}^{90+}+\text{H}_2 \) collisions [35]. The observed cross section is shown as a function of the electron energy equivalent to the ion energy in the ion-atom collision. The natural widths of some of the resonances are of the order of 50 eV while the experimental width of the peaks is roughly 3 keV which is predominantly due to the Compton profile, i.e., the distribution of orbital velocities of the \( \text{H}_2 \) target electrons along the axis of the ion beam. Storage ring recombination experiments with \( \text{U}^{91+} \) ions interacting with free electrons came about 15 years later [66]. While energies up to 90 keV were covered in those experiments establishing the highest resonance energies investigated so far in electron-ion collisions, the next example addresses the region of the lowest resonance energies found in dielectronic recombination experiments. In the regime of electron-ion center-of-mass energies below 1 eV the strength of the merged-beam technique can be fully exploited for high-resolution measurements [67]. Fig. 6 shows high-resolution dielectronic recombination
data obtained by Lestinsky et al. [68] for Sc$^{18+}$ ions at energies below 0.1 eV measured with an energy spread as low as 0.7 meV.

The observation of narrow resonances provides access to the measurement of experimental energy distribution functions which are usually assumed to be of gaussian shape. This is not the case in electron-ion merged beams experiments using energetic ion beams. There, the experimental shape of narrow low-energy resonances is determined by a flattened Maxwellian distribution of the electron-ion collision velocities [69, 70]. Resonance energies can be used to determine electron transition energies, for example by following up Rydberg series of resonances which eventually converge to a series limit equal to a core-electron excitation threshold. Resonance energies are sensitive to the properties of the atomic nucleus, since the bound atomic electrons probe the magnetic-moment and Coulomb-potential distribution of the nucleus. Resonances are also sensitive to the chemical and physical environment in which the atom/ion resides.

Photon-ion interactions can be studied with very good energy resolution making use of the high brilliance of modern radiation sources. For the energy range of interest in this overview, third generation synchrotron light sources and free electron laser sources are the facilities of choice. Yet, signal rates are often quite limited when ionic targets are studied. Therefore, the energy resolution, although principally achievable by closing slits on a monochromator of sufficient quality, often has to be restricted in order to facilitate sufficiently high signal rates. The narrowest resonance features observed in photon-ion interactions are near 1 meV width [57].

Energy spreads in electron beams can be reduced also to several meV by employing suitable energy selectors. Intensities resulting from such sources are typically too low to facilitate measurements on ionic targets. Energy-selected electron beams from thermal cathodes have
been employed in ionization experiments with a minimum energy spread of slightly below 100 meV [71]. Intense electron beams typically have energy spreads of at least 300 to 400 meV. Dilute beams of electrons produced with a cooled laser-irradiated photocathode may have energy spreads of as low as several meV without energy selection.

Energy spreads in electron-ion collision experiments can be partly offset by employing the merged-beams technique which offers substantial kinematical advantages by reducing laboratory energy spreads in the required transformation of experimental cross sections to the electron-ion center-of-mass system. Experiments with cooled stored beams of ions and ultra-cold electron beams have recently resulted in considerable progress in electron-ion energy resolution. By using liquid-nitrogen cooled photocathodes, adiabatic acceleration and adiabatic radial expansion in a decreasing magnetic field electron beams with internal temperatures $k_B T_{\perp} = 1$ meV and $k_B T_{\parallel} = 25 \mu$eV have been prepared for a precision measurement of dielectronic recombination of Li-like Sc$^{18+}$($1s^2 2s$) [68]. The resulting data at energies below 0.1 eV are shown in figure 6. Energy spreads in the electron-ion center-of-mass system were lower than 3 meV at the lowest-energy resonances. This was sufficient to resolve the hyperfine structure splitting of the $2s$ core electron. Moreover the excitation energy $2s - 2p_{3/2}$ could be determined with an uncertainty of 200 $\mu$eV which is less than 1% of the screened radiative corrections to quantum electrodynamic calculations of the transition energy.

Spectroscopy of dielectronic recombination resonances has also been exploited to measure energy shifts between spectra of different isotopes of Li-like Nd$^{57+}$ ions [72]. Such shifts provide direct access to the difference of the charge radii of the $^{142}$Nd and $^{150}$Nd nuclei. Advantages of using collisional spectroscopy of stored highly charged energetic ions for such measurements are the relatively simple electronic structure of the few-electron systems that can be employed and the potential for in-situ measurements with radioactive isotopes produced just before their injection into a storage ring. Measurements on Cu-like Pb$^{53+}$ [73] have previously demonstrated the potential of storage ring collisional spectroscopy to study hyperfine shifts. The future combination of a high-energy storage ring with an electron cooler plus a cold electron-beam target at FAIR (Facility for Antiproton and Ion Research) in Darmstadt, Germany, is a promising tool for studies at the border line between atomic and nuclear physics [74].

8. Resonances of caged ions
Recent developments in the production of endohedral-fullerene ions such as Ce@C$_{82}^+$ [75, 49] are opening new possibilities to study resonances of ions caged within a fullerene molecule. The Ce@C$_{82}$ complex is stabilized by the Ce atom donating three electrons to the C$_{82}$ cage. Hence the complex can also be described as Ce$^{3+}$@C$_{82}^-$. Resonance structures characteristic for the excitation of a 4d inner-shell electron in Ce$^{3+}$ could be observed in the single- and double-photoionization channels of Ce@C$_{82}^+$ ions. Less than half of the 4d-oscillator strength observed in the photoionization of free atomic Ce$^{3+}$ ions is found in the experiments with Ce$^{3+}$ encapsulated within the fullerene sphere [76]. Apparently, substantial redistribution of 4d-oscillator strength occurs in the caged-ion–fullerene system.

Acknowledgments
The author is grateful to all colleagues who ever published work together with him on electron-ion and photon-ion resonance phenomena. Among them, special thanks go to Gordon H. Dunn, Ronald A. Phaneuf and Stefan Schippers. Support by Deutsche Forschungsgemeinschaft (DFG) and Bundesministerium für Bildung und Forschung (BMBF) is gratefully acknowledged.

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