Atomic negative ions: structure, dynamics and collisions

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Abstract

This paper reviews the knowledge of the structure, dynamics and collisions of atomic negative ions, as accumulated at the end of 2003, and describes how the research exploring these ions developed during the last decade. New experimental information has mainly been obtained from photon–negative-ion interactions using lasers and more recently also synchrotron radiation as the photon source. Additional insights have been gained from the use of new experimental techniques like heavy-ion storage rings, which made long-time observations of negative ions possible and promoted the study of electron–negative ion-interactions. Substantial progress has also appeared on the theoretical side with computational methods leading to reliable predictions for many of the lighter negative ions.

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1. Introduction

Negative ions represent a special niche of atomic physics and offer excellent opportunities for studies of atomic structure, dynamics and interactions in systems characterized by the binding of an extra electron to a neutral atom in a short-range potential. While the electrons in neutral atoms and positively charged ions are bound in the long-range Coulomb potential, which is proportional to $r^{-1}$, $r$ being the separation between the electron and the nucleus, the excess electron in negative ions is bound in a short-range potential, of the order of $r^{-4}$, with the H$^-$ ion as the only exception. The short-range potential gives rise to a number of exotic properties of negative ions unlike those of neutral atoms or positive ions. Whereas nearly 90% of atoms are able to form stable negative ions in the gas phase by attaching an electron to the ground state electron configuration, the short-range potential can usually only bind the fine- or hyperfine-structure states of the ground state term or in case of several terms of the energetic lowest lying one, while the Coulomb potential supports an infinite number of bound states, converging into Rydberg series at the ionization threshold. Due to its dipole potential, which decays as $r^{-2}$, the H$^-$ ion deviates to a certain extent from the common description of negative atomic ions, since this potential can support an infinite series of states, converging to the H($n$) = 2, 3, 4, etc. thresholds.

Electronically excited states in a negative atomic ion are expected to lie energetically above the ground state of the parent neutral atom. Such excited ions (singly, doubly, or triply excited) may be called temporary anions since they are unstable with respect to electron detachment. Their lifetimes are usually rather short, in the range $10^{-11}$–$10^{-16}$ s and they reveal themselves as autodetaching resonances. However, electronically excited bound states, located below the ground state of the parent neutral atom and therefore unable to decay via electron emission, could perhaps exist for a few of the elements possessing a complex atomic structure, such as the heavier transition elements or the lanthanides. This expectation has very recently been proved to be correct [1].
Another well-understood result of the short-range potential is the variation of the photodetachment cross section with energy. The cross section is zero at threshold and rises in a manner that only depends on the angular momentum of the detached electron \([2,3]\), unlike the photoionization cross section of neutral atoms, which is non-zero at threshold. This threshold behaviour is vital for experimental methods designed for accurate binding energy measurements (see Section 2.4), e.g. the laser photodetachment method utilizing resonance ionization detection of the excited neutral atom produced by the detachment process \([4–6]\). The zero cross section value at threshold also facilitated the first absolute measurements of a photodetachment cross section of an 1s electron in a free negative ion by means of synchrotron radiation \([7,8]\).

A third speciality of negative ions is the filling of the electronic subshells for which the filling may not be following the same ordering as for the neutral atoms, as already pointed out by Bates \([9]\) more than 50 years ago. The Ca\(^{−}\) ion and the Sc atom are good representatives for the different filling rules, which lead to a 4s\(^2\)4p valence configuration for the stable Ca\(^{−}\) ion \([10,11]\), but to 4s\(^2\)3d for the isoelectronic Sc atom.

A small number of atoms cannot form stable negative ions due to their closed shell or subshell structures, but some of these atoms are able to form metastable excited states of negative ions by binding an extra electron to an excited state configuration. With lifetimes of the order of \(10^{-3}–10^{-6}\) s metastable ions like He\(^{−}\) or Be\(^{−}\) can be studied experimentally which has been attractive during the last decade \([12–24]\).

In contrast to neutral atoms and positively charged ions, electron correlation effects often account for most of the binding energy in atomic negative ions. The comparison of experimentally determined binding energies of the ground states, the energy positions of excited states (resonances), or lifetimes of metastable negative ions, to sophisticated theoretical models thus provides a very sensitive probe into their ability to model electron correlations in atomic systems. In recent years this aspect of negative-ion research has attracted a good deal of interest from both experimentalists and theorists particularly after new experimental techniques became available yielding more accurate data for negative ion properties than obtainable before and made it possible to distinguish between various theoretical approaches.

Today, it is well established that negative atomic ions play an important role in various branches of physics, ranging from astrophysics, atmospheric and plasma physics to surface physics and accelerator physics. In addition, negative ions form the basis for advanced analytical methods such as ultrasensitive accelerator mass spectroscopy, now routinely used for dating samples of archaeological or geophysical interest, but also for oceanography, hydrology, or biomedicine (for a review see Ref. \([25]\)).

1.1. Historical background

Research on the physics of free atomic negative ions has a long history beginning with J.J. Thomson’s pioneering studies \([26]\) of mass spectra of positive and negative ions in 1913. A significant stimulation to explore the physics of negative ions came rather early from geophysics and astrophysics \([27]\). With the discovery of the ionizing layers of the upper atmosphere, it became evident that the O\(^{−}\) ion, which was known from theoretical as well as experimental studies to be a stable negative ion in contrast to the N\(^{−}\) ion, might play an important role in reactions with O\(^{+}\) or N\(^{2+}\) ions, resulting in observable radiation from the night-sky. A remarkable proposal for the presence
of the atomic negative hydrogen ion in the Solar photosphere was put forward in 1939 [28] and later proved to be correct. Examples like these clearly illustrated that negative atomic ions were not only a curiosity of academic interest, but could play an important role in various branches of physics and chemistry as evident today. The existence of $\text{H}^-$ as a bound system had already been proposed theoretically by Bethe [29] in 1929, whereas predictions based on simple perturbational or variational methods had failed, even though these methods were well suited to predict the gross properties of the isoelectronic systems such as He, Li$^+$, Be$^{2+}$, etc. (for a review of the history of the H$^-$ ion see [30]).

A combination of experimental, theoretical, and empirical methods had already in 1950 [27] established a reasonable set of electron affinity (EA) values for the atoms belonging to the first two rows of the periodic system (H–Ar). The binding energy of the lowest lying hyperfine state of a negative ion relative to the lowest lying hyperfine state of the corresponding neutral atom is termed the electron affinity (EA) of the neutral atom. EA values, derived from extrapolation of known ionization potentials of neutral atoms and the positive ions isoelectronic with the negative ions, showed that stable negative ions could not be expected to exist for elements like He, N, Ne, Mg, or Ar. The extrapolated EA values were generally smaller than the values established today [31] and e.g. the weakly bound B$^-$ ion was predicted to be unstable.

In the 1950s renewed attention was drawn to the physics of free negative ions by pressing problems in various fields of physics and chemistry [32]. The nuclear physicists wanted to apply high-current negative-ion sources to double the effective energy of electrostatic accelerators; binding energies of negative ions were often important links in closed cycles of reaction energies from which the physical chemist could determine important data such as dissociation energies or heat of vaporations, and the study of atmospheric gases at very high temperatures involved formation of negative ions, which influenced the thermodynamic properties of the gas. Basic properties as the electron affinities were still difficult to establish experimentally with a reasonable accuracy for many atoms and direct theoretical methods were considered to be too difficult or too tedious for quantitative calculations. The only exception was atomic hydrogen for which a variational calculation [33] yielded a value of 0.754 eV in excellent agreement with much later calculations [31]. The indirect experimental methods used [34] were often unsatisfactory except for atoms possessing very large affinities as the halogens. Near the end of the decade, however, Branscomb and Smith [35,36] introduced direct measurements of EA values from photon–negative ion studies by observing the optical threshold for electron detachment from negative ions. They established the values $O(EA) = 1.48(10)$ eV and $EA(S) = 2.07(7)$ eV, which within the error bars given are in good agreement with the more accurate values available today [31], and they became the pioneers of one of the most reliable methods developed so far for obtaining accurate EA values. At the time Branscomb and Smith performed their studies the laser was not invented, so light from classical light sources had to be used combined with suitable filtering.

1.2. Previous review articles

Progress in negative atomic ion physics has been reviewed from time to time. In the 1970s Schulz [37] described “Resonances in electron impact on atoms”, whereas Massey [38,39] in the book “Negative Ions” [38] along with his updated article from 1979 [39] summarized nearly everything that was known at that time about atomic negative ions. Even though a quarter of a century has
passed since Massey’s monograph [38] appeared it is still a useful source of information. The progress obtained during the 1980s has been described by Bates [40], who treated the atomic structure and spectra, by Esaulov [41] who focussed on the collisional aspects, and by Buckman and Clark [42], who in a very comprehensive review entitled “Atomic negative-ion resonances” updated the famous article by Schulz [37] from the early 1970s.

Classification of atomic negative-ion resonances has been a controversial topic for many years [42]. Traditionally, resonances created in photodetachment or electron–atom scattering experiments were divided into two groups, named Feshbach and shape resonances. The latter type arises from the trapping of the electron transitorily by the potential created by the neutral core of the atom, provided this potential had a proper shape. Shape resonances were usually very short lived and should be considered as a one-electron phenomenon with energies above the energy of the parent atom. Contrary to shape resonances, Feshbach resonances were keeping the excited electron bound for a rather long time, on the scale of atomic times, which could be attributed to the reorganization of the atomic core allowing an extra electron to be part of the outer electron shell, usually in the form of a highly correlated state. Since the decay of a Feshbach resonance involves the transfer of energy from the atomic core to the electron being emitted, these resonances should be found below the corresponding energy levels of the parent atom. Such a classification scheme represents, however, an idealization of the real situation and can only be of use as a descriptive sub-division of atomic negative-ion resonances [42,43]. The trapping of an extra electron cannot leave the atomic core totally unchanged, and the reorganization of the atomic shells to allow for an extra electron cannot be so extensive that it becomes very different from the parent state of the atom. Thus it is not surprising that alternative classification schemes have been introduced.

Buckman and Clark [42] preferred to adopt the terminology originally introduced by Schulz [37], with the nicknames the “parent” and the “grandparent” models, for their review of atomic negative-ion resonances. The resonances were described as the result of the binding of either one electron to a neutral parent state or two electrons to a positive-ion parent state, respectively. With focus on the H− or He− ions and with the purpose to gain more insight to the nature of the resonances special descriptions of the outer shell of the negative ion have been introduced successfully, such as the hyperspherical coordinates [44–47], which will be used in the more detailed description of the H− ion in Section 4.1.

Special aspects of atomic negative-ion properties, such as the binding energies and fine-structure splittings of the ground states, were critically reviewed and compiled by Hotop and Lineberger in 1975 [48] and 1985 [49] and this series was updated recently [31]. The progress in the understanding of the important negative hydrogen ion was covered by Bryant and Halka [50], metastable excited states in negative ions by Nicolaides et al. [51], while Ivanov [52] reviewed many-body effects in negative ion photodetachment. Several shorter and often more specialized reviews focussing on recent understanding of structure, spectra, lifetimes or other properties of negative atomic ions have also appeared in the 1990s [43,53–63] and are continuing at the beginning of the new century [64–67].

1.3. Plan for the review

It is the aim of the present paper to present a review of the knowledge of the structure and dynamics of negative ions, as accumulated at the end of 2003, and to describe how this field of research has developed since Buckman and Clark [42] wrote their paper. The new experimental
information has mainly been obtained from studies of photon–negative ion interactions using lasers and more recently also synchrotron radiation as the photon source. The development during the 1990s of new and often sophisticated linear and non-linear laser techniques, sometimes combined with very sensitive detection techniques [4,68] have yielded significant new insight to a number of negative ions and provided information covering the ground state properties as well as the resonance structures, with the lighter negative ions being the preferred objects. Additional information has come from the use of heavy-ion storage rings [63] or small ion-traps [69], allowing long-time observations of negative ions leading to determination of lifetimes of metastable excited ions; heavy-ion storage rings have also made it possible to promote the study of interactions between electrons and negative ions. The various new experimental methods will be treated in the following chapter together with a short presentation of the previously developed, but still used techniques. The latters have contributed to the recent development, but to a less extent; electron–atom collisions [42] with information about temporary anions, collisions between energetic stable negative ions and rare gases [70] with new data about doubly excited states not accessible by photon excitation from the ground state of the ions, and the beam-foil technique [71] with evidence for optical transitions in negative ions and thereby for electronically excited states with lifetimes of the order of $10^{-9}$ s.

The progress in the understanding of negative-ion properties is to a large extent the result of the active interplay between experimental and computational studies. Section 3 will review the theoretical methods. The present knowledge about negative atomic ions belonging to the various groups of elements of the periodic system will be treated in Section 4 provided that new information has become available since Buckman’s and Clark’s paper [42] was written. For some negative ions the knowledge available today is nearly the same as described in their review and for such ions the reader should consult their paper. This is particularly the case for the resonance structures of the negative ions, which do not exist as stable or long lived, metastable ions with lifetimes of the order needed for beam experiments. Temporary anions of the rare gases Ne, Kr, and Xe, belong to this category, which also includes elements like N, Zn, Cd and Hg. Very recently [67] tentative classifications have been proposed for several of the resonant states previously observed, but not identified for Zn, Cd, and Hg; the new classifications were obtained combining earlier experimental observations with new theoretical calculations, based on the $R$-matrix technique.

During the last decade, electron-impact detachment from negative ions has been a theme of significant interest for both experiment and theory, and this will be covered in Section 5, while the final Section 6 will deal with the influence of external fields on negative ions.

2. Experiment

This section describes the various experimental techniques used during the last decade with emphasis on the methods developed since 1990.

2.1. Production of negative ions

The main methods for production of negative ions are:

1. charge exchange of an initially positive beam in a gas or a metal vapour,
(2) direct extraction of negative ions from a Penning-type or a plasma source, 
(3) sputtering from a caesium contaminated surface.

The need for negative-ion beams in connection with tandem accelerators entailed already in the 1970s [72,73] a significant development of negative-ion source technology, which continued in the 1980s [74,75]. The aim was to develop a universal negative-ion source, which could produce ion beams with intensities ranging from 100 nA to 1 mA. This goal was reached for many elements by means of sputter ion sources [72,73,75], now commonly used in laboratories performing negative ion research. In the 1970s Penning-type ion sources [76] were often utilized to produce beams of stable negative ions from the main groups of the periodic system [49].

The sputter source technology is, however, unsuited for production of negative ions with very low binding energies. For such ions the classical method for producing negative ions, the charge exchange process, which transforms a positive-ion beam to a negative-ion beam by passage of a gas or metal vapour cell [77], is still to be preferred. Weakly bound negative ions, such as Ca$^-$, Sr$^-$ or Ba$^-$, and the metastable negative ions, He$^-$ or Be$^-$, are produced by this technique. The competing electron-capture and electron-loss processes suffered by energetic atomic ions in collisions with a gas or a metal vapour target will lead to a statistical distribution of the charge states of the ions in the emergent beam. At sufficiently high target thickness, equilibrium between the competing processes will be attained and the resulting equilibrium charge state distribution will be independent of the target thickness. It was already pointed out in the 1960s [78] that large negative-ion fractions could be expected from charge exchange in metal vapours.

The formation of the negative beam by the charge-exchange technique is usually a two-step process in which the projectile ion captures an electron, leading to the formation of an excited state or the ground state of the fast neutral beam, followed by a second capture process resulting in the formation of the negative ion. There are several factors to take into account to optimize the negative-ion formation [77], such as the projectile–target combination leading to as low-energy defect as possible in the two separate electron capture processes. This favours target atoms with low ionization potentials, such as the alkalis. The fully resonant process can, however, not be obtained since the lowest ionization potential for a metal (Cs) is larger than the even the largest EA value. Thus the yield of negative ions formed by charge exchange is generally only of the order of 0.1–1%, which, however, is sufficient for most studies dealing with the weakly bound negative ions. Other parameters with strong influence on the efficiency are the density of target atoms and the centre of mass energy.

Direct extraction of a negative-ion beam from a Penning-type ion source [76] or a plasma ion source [79] is possible by reversing the polarity for extraction. The plasma ion source developed by Almén and Nielsen [79] for production of positive-ion beams can also handle less volatile elements as metals by heating these sufficiently, but for the large majority of atoms the sputter ion sources are clearly superior.

The various types of sputter sources have the common feature that the negative ions are formed on a low work function solid surface [72]. A large range of solid surfaces sputtered by positive caesium ions will emit a significant fraction of negative ions and addition of neutral caesium to the surface strongly enhances the yield of negative ions since this depresses the work function of the surface. The presence of caesium on the surface of the sputtering cathode is normally regulated by adsorption–desorption processes and by the bombardment with the positive caesium ions, used as the
sputtering projectile. As the caesium on the surface will be sputtered mostly as positive ions, a large fraction of the sputtered caesium will be driven back to the surface by the cathode potential drop. This mechanism tends to stabilize the caesium coverage and limits the caesium consumption of the source [73]. The design of the sputtering cathode, which usually is placed in a discharge opposite the outlet of the ion source, can be very important to ensure a highly efficient beam formation by focusing the negatively charged, sputtered ions onto the outlet opening. The negative ions formed by the sputter technique will usually have to undergo a mass analysis before being injected into the experimental section of a negative-ion equipment.

2.2. Photon sources

The photon sources used for negative-ion studies can be divided into two groups:

(1) Lasers for low-energy photons (below 15 eV),
(2) Synchrotron radiation for photons above 15 eV.

Studies of photon–negative ion interactions can only be performed with low-density targets. Thus, the development and use of photon sources able to deliver high photon flux (at narrow bandwidth) have had an important influence on the history of negative ions. During the last three to four decades we have witnessed a development from crossed ion-photon beam geometry with fixed frequency pulsed or cw lasers, via the use of tunable dye lasers to the more recent use of collinear geometry and the appearance of new laser sources, particularly in the infrared region e.g. the titanium-sapphire laser or the generation of intense coherent, Raman-shifted, infrared radiation produced from tunable dye laser radiation [31,48,49]. High-resolution studies of negative ions have benefited from this development and pulsed tunable dye lasers (including frequency doubling) with band widths between 0.05 and 1 cm\(^{-1}\) have, during the last decade, been the main source to explore the energy region from 1.3 to 6 eV. Intense coherent infrared radiation, produced by Raman-shifting of tunable dye laser radiation in a molecular hydrogen cell, has been essential to explore the energy range from 0.25 to 1.3 eV with a bandwidth around 0.1 cm\(^{-1}\) [31].

Previously, photon–negative ion studies were based exclusively on single-photon techniques. During the last decade, however, multi-photon techniques have been applied routinely in combination with new detection techniques, such as resonant ionization spectroscopy (RIS). In addition, strong laser fields have been used both to introduce “forbidden” transitions between electronic states possessing the same parity [31,64] and thereby opening up for studies which were previously not possible, and for excess photon absorption studies [43]. Multi-photon studies involving up to four different photon frequencies have been reported in connection with the study of the excited Ca\(^-\)(4p\(^3\) 4S) state [80]. Two photons were used to populate the negative-ion state via resonant transitions from the ground state, whereas the identification of the neutral Ca atom state, formed by autodetachment of the excited 4S state, demanded additional two different photons.

The exploration of resonance structures located more than 6 eV above the ground state of negative ions has not been in focus so far mainly due to the experimental problems associated with producing the energetic photons combined with the demands for unambiguous identification of the resonance states. An exception is the fundamental H\(^-\) ion even the study of its resonance structures demands higher photon energies than described above, ranging from approximately 9.5 to 14.5 eV. In the
experimental investigation of the H$^-$ ion Bryant and co-workers [81] introduced in 1977 a technique, which for two decades has provided a remarkable amount of spectroscopic information about this ion (for a review see [50]). The energetic photons were obtained using standard lasers in the visible or UV range and the frequency was up-shifted by as much as a factor of 3.4 by employing the large Doppler-shift associated with the high-velocity H$^-$ beam provided by the Los Alamos Meson Physics Facility. The 800 MeV H$^-$ beam energy was fixed, as was the photon energy of the lasers applied; tunability was achieved by adjusting the angle of interaction between the laser and ion beams. A very large photon energy range could be covered by this technique and used for studying the gross behaviour of the cross section, as well as detailed studies of resonances near the various H(n) thresholds. The same principle was also used in connection with the two-photon absorption study [82] of resonances possessing the same parity as the ground state. The resolution of the one-photon experiments was about 8 meV, mainly limited by the momentum spread of the relativistic ion beam and the angular divergence of the crossed-beam geometry.

The main disadvantage of the technique described above to study the H$^-$ ion is the limited resolution, which prohibits a study of the much narrower H$^-$ resonances, located near the H(n = 2) threshold, which would be stringent tests of the many theoretical predictions available for the positions of the resonances [83–92] and their widths [83–85,88–90,92–95]. An alternative approach of Doppler-tuned spectroscopy was utilized by Balling et al. [96–99], who applied collinear ion–photon beams combined with a strongly reduced energy spread of the H$^-$ ions. Fixed frequency laser light at 118 nm (close to 11 eV) was produced as the 9th harmonic of the fundamental 1064 nm output from a pulsed, seeded Nd:YAG laser. Non-linear crystals were used to generated the 3’harmonic, which was further frequency shifted a factor of three in Xe gas using four-wave mixing. The tunability of this laser source was obtained by applying small changes in energy to the stored H$^-$ (or D$^-$) beam. The experimental resolution was improved a factor of 40 [99], compared with the experiments performed by Bryant et al., making it possible to explore some of the narrow resonances located near the H(n = 2) thresholds, see Section 4.1.

The photo-induced processes in negative atomic ions by means of various laser techniques are all concerned with outer-shell electrons, whereas inner-shell excitation processes are outside the present range of conventional lasers and no inner-shell electron excitation or detachment in a free negative atomic ion had been reported before 2001. The reason was probably a combination of the very low densities which can be obtained for negative ions, the limiting photon flux available from bending magnets at synchrotron radiation facilities and the relatively small cross section for photodetachment. However, during the second half of the 1990s synchrotron radiation beam lines started to be equipped with insertion devices called undulators, which could improve the photon flux at selected photon ranges by several orders of magnitude. During 2001–2002 the first studies of 1s electron excitation in free negative atomic ions were reported dealing with the Li$^-$ [7,8], He$^-$ [100], and C$^-$ ions [101].

The 1s experiments have been performed at the Advanced Light Source, Berkeley and at the ASTRID storage ring, Aarhus using collinear geometry. The photon energies have ranged from the upper 30’s eV (He$^-$) to close to 300 eV (C$^-$). Synchrotron radiation is tunable over a very large energy range and undulator radiation is presently available from approximately 10 eV to about 500 eV, but these limits may be extended in the future. Even though the undulator radiation is two–three orders of magnitude more intense than synchrotron radiation from bending magnets the intensity/meV bandwidth is still much lower than available from lasers. If we compare the photon
flux/meV generated by the 9th harmonics from a Nd:YAG laser at 118 nm and applied to study resonances in the H\(^-\) ion [98] with the photon flux/meV applied in the first inner-shell electron experiment of Li\(^-\) [7] there is approximately a ratio of 10\(^5\) between them. Thus, it is necessary to accumulate data from a large number of scans in the inner-shell excitation studies and then add them together. In the first Li\(^-\) experiment an accumulation time of 13 min per data point was used for energies below 60 eV. It should be noted that the rather low photon flux/meV for synchrotron radiation may to some extent be compensated by the properties of the resonances formed by 1s excitation. These may be well separated in energy and in addition be rather broad.

The main experimental problem in connection with the inner-shell studies has been the large background signal due to collisions between the negative-ion beam and the rest gases leading to formation of singly charged positive ions, Li\(^+\) ions in case of a Li\(^-\) beam, in spite of the pressure at the interaction region was as low as 2\(\times\)10\(^{-10}\) Torr. Inner-shell photon excitation of an 1s electron will also lead to formation of double detachment, since the highly excited negative ion or the excited neutral atom formed by detachment of the 1s electron quickly will undergo autodetachment processes leading to formation of singly charged positive ions. Inner-shell studies may, however, be easier to conduct in the near future, when single-pass free electron lasers (FELs) are available as a new source for experiments in the VUV and X-ray region. The FEL devices are based on the principle of self-amplified spontaneous emission, allowing very large gain up to a saturation in a single pass through a long periodic magnetic structure. It is expected that intense, sub-picosecond laser pulses for a wide, continuous range of wavelengths down to approximately 0.1 nm (or photon energies of the order of 1 keV) will be available.

2.3. Single-photon studies using fixed frequency lasers

Single-photon studies utilizing a fixed frequency laser yielding photons with energies below 4 eV were routinely performed in the 1970s and 1980s in combination with high-resolution electron energy analysers, to explore the binding energies of a large number of negative atomic ions [48,49]. Up to 1985 most of the reported EA values were obtained by means of laser photodetachment electron spectrometry (LPES) [49] with uncertainties ranging from 2 to 20 meV. The fixed frequency lasers were usually the cw Ar\(^+\) laser, operated at 514.5, 488.0 or at 351.1 nm, or the Nd:YAG laser which emits 1064 nm photons. However, in the period from 1985 and up to the end of the century the LPES method added rather little to the knowledge about atomic negative ions. New methods for determination of the binding energy of negative ions were developed (see Section 2.4) and the previous EA values based on LPES measurements were replaced by more accurate values obtained by various tunable laser photodetachment threshold (LPT) methods [31]. A remarkable exception was, however, the discovery of the stable Ca\(^-\) ion [10], which involved energy analysis of photodetached electrons, emitted parallel or anti-parallel to the direction of a 70 keV Ca\(^-\) beam. It had generally been believed that the alkaline earth atoms, Be, Mg, Ca, Sr, and Ba, were unable to bind an extra electron to their ground state configurations, which are characterized by closed s-electron shells. The binding energy, 43(7) meV, reported for the Ca\(^-\) ion was in good agreement with the theoretical prediction of 45 meV reported in parallel work [11]. Subsequent investigations showed, however, that the correct binding energy was nearly 20 meV lower [5], indicating the difficulties associated with the transformation from the observed electron signal to the binding energy [49], but also the reliability of theoretical predictions for heavier ions at that time [11]. In Section 4.5 the negative-ion
research following the original discovery of the Ca\(^-\) ion will be reviewed illustrating the important development in the study of negative ions, which took place both experimentally and theoretically in the 1990s.

The LPES method has been revitalized at the end of the last decade by Thompson and co-workers in connection with studies of negative ions of lanthanides [102–105]. These ions can be expected to have a rather complex structure, possessing up to several excited states located below the energy of the ground state of the parent neutral atom. In order to establish the gross structure of these ions it is attractive to use the LPES technique to obtain the EA values even though the accuracy will be limited to approximately 25 meV. When the gross structure is established it is easier to perform EA measurements using LPT methods and thereby reducing the uncertainties. Fig. 1 shows a photoelectron kinetic energy spectrum for photodetaching Ce\(^-\) using an argon ion laser (514.5 nm). The energy scale for the Ce\(^-\) photoelectron spectra in the laboratory frame was transformed into the ion rest frame using the Cu\(^-\) photoelectron spectra as a reference and interpreted using spectroscopic data for the neutral atom [106]. The electrons photodetached in the interaction region were energy analysed using a spherical sector, 160\(^o\) electrostatic kinetic energy analyser, which operated in a fixed pass-energy mode. The structure labelled 3 is the most intense structure, and since there are no discernible higher energy structure, it was assumed to be associated with the ground state to ground state transition and studied in more detail at higher resolution, see Section 4.13.

Single-photon studies using fixed frequency lasers were also applied, as described above in Section 2.2, to explore the structure of the H\(^-\) ion, but tunability of the laser light was then obtained using Doppler-shift methods.

2.4. Single-photon studies using tunable lasers

Single-photon and multi-photon studies using tunable lasers have dominated the experimental negative-ion studies during the 1990s.
2.4.1. Laser photodetachment threshold (LPT) spectroscopy

By measuring the threshold photon frequency of the transition from the ground state of the negative ion to the ground state of the neutral atom plus a threshold electron the binding energy of a negative ion can be established. Up to year 2000 [31] the binding energies measured covered the energy range from approximately 25 meV (Ca\(^-\)) to 3.61 eV (Cl\(^-\)). If the rather few negative ions with binding energies below 150 meV were excluded, it should be possible to determine the binding energies of the remaining stable negative ions, more than 60, utilizing single-photon absorption from tunable lasers combined with recording the rate of formation of the detachment products, the neutral atoms, the emitted electrons, or both, as a function of the frequency. Tunable laser photodetachment threshold (LPT) spectroscopy is well suited for such studies, utilizing UV, visible or IR tunable laser light. LPT spectroscopy using visible laser light was already established in 1970 [107] in combination with crossed ion-laser beam geometry, and later improved utilizing coaxial beams [108,109]. It is, however mainly within the last decade that tunable IR radiation has been applied to the study of negative ions. Binding energies of many negative stable ions are of the order of 1 eV or below [31]; tunable IR laser light is therefore advantageous for photodetachment studies, especially for detachment studies to the ground state of the neutral atoms.

In a series of experiments Haugen and coworkers from the McMaster University group introduced and applied tunable IR laser photodetachment threshold (LPT) spectroscopy in a crossed beam set-up to measure a large amount of precise EA values [31] covering elements like B [110], C [111], Al [112], Si [111], Cr [113], Co [114], Ni [114], Cu [113], Ge [111], Mo [113], Ru [115], Rh [114], Pd [114] and even some heavier ones [31]. Nd:YAG pumped dye laser light was used to generate light with wavelengths ranging from 400 to 980 nm with typical pulse energies up to 50 mJ. The tunable IR radiation covering the range up to 5.2 µm was obtained using Raman conversion of the dye laser light in a high-pressure (22 bar) molecular hydrogen cell [31,64]. The IR radiation technique was originally developed by Bischel and Dyer [116]. Under the experimental conditions applied by the McMaster group, the first Stokes falls in the wavelength range of 950–1650 nm, the second in the range 1.6–5.2 µm. The relatively simple molecular hydrogen cell applied produced good quality light of the first Stokes light, whereas the second Stokes light could suffer from lower beam quality associated with the four-wave mixing [111,113]. With the continuing development in laser capabilities significant improvement may be expected in the future, which greatly will improve the IR-laser light for negative ion studies. The accuracy of the tunable IR laser photodetachment threshold measurements has been reported to reach 20–25 µeV (0.15–0.20 cm\(^{-1}\)) for ions like B\(^-\), C\(^-\), and Al\(^-\).

Assuming that the transition from the negative-ion ground state to the ground state of the neutral atom is identified without ambiguity, the determination of the threshold position can be obtained by extrapolation from the frequency dependence of the detachment product rate in agreement with Wigner’s law [2]. Since the presence of a neutral core perturbs the motion of the emitted electron only in a limited volume, the final state of the photoelectron can be considered as the one of a free electron for which the wavefunction is a plane-wave. This “free-electron” approximation leads to the general behaviour of the detachment cross section at threshold. The partial photodetachment cross section, \(\sigma_l\), is proportional to \(\epsilon^{l+1/2}\) with \(l\) being the angular momentum of the outgoing electron and \(\epsilon\) its kinetic energy. Wigner’s law is derived under the assumption that the potential experienced by the outgoing electron vanishes faster than \(r^{-2}\) and is therefore a low-order expansion valid
only in the energy region close to threshold. The energy range over which the relationship given by Wigner’s law is valid to describe the threshold behaviour is not known from theory. It may therefore be necessary to apply correction terms associated with the long-range interaction between the electron and the neutral atom. If the dipole polarizability of the final atomic state is large then it is necessary to take the residual-dipole point–charge interaction into account and the partial photodetachment cross section \( \sigma_i \) will then also contain a first order correction term proportional to the dipole polarizability [117].

For most neutral atoms in the ground state, the dipole polarizability [118] is limited and the simple version of the partial photodetachment cross section is valid. If it is favourable to measure the onset of the photodetachment process at an excited state rather than the ground state of the neutral atom, then the EA value for the neutral atom can be obtained by subtracting the accurately known excited energy of the neutral atom; however, then it may be necessary to evaluate and perhaps take the correction term into account. It is well known that Rydberg states can possess high polarizabilities and thus Wigner’s law will only be valid in a rather narrow region for detachment to such states. For metastable negative ions like the He\(^-\)(1s\(^2\)s\(^2\)p\(^4\)P) ion it is, however, necessary to detach to a Rydberg state in order to measure the binding energy [13].

According to Wigner’s law the shape of the partial photodetachment cross section close to threshold will be markedly different for an outgoing s-electron (\( l = 0 \)) than for an electron with angular momentum larger than zero. The tangent to the cross section curve at threshold will be vertical for \( l = 0 \), but horizontal for \( l = 1, 2, \) etc. The onset of the cross section at threshold will therefore be sharp for an s-electron emission in contrast to the smooth onset appearing for a p-electron emission. For a precise determination of the threshold position an s-electron emission is to be preferred. Fortunately, s-electron emission is possible for a large number of negative atomic ions, such as B\(^-\), C\(^-\), or O\(^-\), see Fig. 2, whereas ions like H\(^-\) or Li\(^-\) will emit a p-electron, see Fig. 3. This obstacle can be overcome for the Li\(^-\)ion by using photodetachment to an excited state, combined with resonance ionization detection [68] (see Section 2.4), but not for the H\(^-\) ion.

Besides the necessary extrapolation of the cross section to threshold another critical aspect of any accurate determination of the binding energy is a precise measurement of the photon frequency. This problem arises due to the fast moving ions used in negative-ion studies. The photon frequency needed to detach the negative ion at threshold in the laboratory frame will be different from the frequency in the rest frame. The relationship between the two frequencies depends on the velocity of the negative-ion beam relative to the velocity of light and the angle of intersection \( \alpha \) between the two beams

\[
v = v_{\text{Lab}}(1 - (v/c) \cos \alpha) \left[ 1 - (v/c)^2 \right]^{-1/2} .
\]

Measurements based on collinear technique utilize threshold frequency measurements for both parallel and anti-parallel ion and laser beams in order to eliminated the first-order Doppler shift and take advantage of the fact that the threshold frequency \( v_{EA} \) simply can be obtained as the square root of the product of the laboratory frequencies, determined for the parallel and anti-parallel beams [119,120], respectively, and thus in a way independent of the beam velocity [49]. The second-order correction term is usually too small to influence the result at the present level of accuracy, and the recoil threshold shift associated with the photon absorption is negligible.
Fig. 2. Photodetachment yield vs. photon energy for the B$^-$ ion [110]. The measurements are performed by tuneable infrared spectroscopy. The solid line represents an analysis of the data using a Wigner s-wave fit including the leading correction term.

Crossed beam experiments are usually carried out choosing $\alpha=90^\circ$ to avoid the first-order Doppler effects, if not it is important that the angle of intersection is known very precisely. To eliminate the first-order Doppler shift Blondel and coworkers [121] reported an elegant method for nearly perpendicular laser and ion beams. They applied a corner cube reflector to generate two interactions of the pulsed laser beam with the negative-ion beam so the incident and returning laser wave vectors were exactly anti-parallel. Thus, the first order Doppler shifts had the same absolute value, but opposite signs, at the two interaction points. Recording the detachment signals from the two intersection points, which were well separated, allowed the thresholds from the two interaction regions to be sampled individually, and consequently the transition frequency needed for the binding energy determination to be evaluated.

Finally, precision measurements of the laser wavelength (in vacuum) are needed. The methods chosen depend usually on the laser used, cw single mode, multimode cw lasers or pulsed lasers [31]. The latter, which has been used predominantly in the last decade, are normally characterized by a wavelength comparison with a calibrated system, such as molecular iodine vapour ([122] and references therein) or by optogalvanic spectroscopy of atomic transitions in one of the rare gases in conjunction with wavelength markers from a calibrated Fabry–Perot interferometer or etalon [123].
Due to the experimental difficulties mentioned above with the H$^-$ ion in connection with threshold frequency determination (emission of p-wave) it has not been reasonable to select this ion as the reference standard for binding energies of negative atomic ions; the O$^-$ ion [49] has been adopted. The very precise binding energy reported by Neumark et al. [124] for the O$^-$ ion with a relative uncertainty of $5 \times 10^{-7}$, obtained from coaxial laser photodetachment threshold (LPT) spectroscopy, was for more than a decade considered to be the proper reference standard, since it was considered to be the most accurately known of all measured atomic electron affinities [49]. The recent development of the laser photodetachment microscope (LPM) [125] and its use for determining the electron affinity of the $^{16}$O atom [126,127] have, however, caused some reconsiderations concerning selection of the O$^-$ ion as the reference standard [31], since the LPM and LPT results deviate by 0.032 cm$^{-1}$ or 4 eV. This issue will be further addressed in connection with the negative oxygen ion, see Section 4.10.

2.4.2. Laser photodetachment microscopy (LPM)

Photodetachment microscopy can directly image the spatial distribution of electrons photodetached from a negative ion in the presence of a uniform electric field [125,128]. Provided the electric field is small compared to the internal field of the atom, which is the usual situation when dealing with negative atomic ions in the laboratory, the electron is emitted from the ion in the form of a spherical wave of energy $\epsilon$, which will be folded back onto itself by the external field. The two halves of the wave will interfere and produce a pattern cylindrically symmetric around the electric field direction. Since the spectral resolution of the excitation scheme usually is of the order of 0.02 cm$^{-1}$ and the spectral resolution experimentalists can achieve with electron detectors never is much better than
0.1 mm, the ring pattern can be observed provided the following conditions are present: The kinetic energy at which the electron is brought above the detachment threshold is in the range 0.1–3 cm$^{-1}$ [129], the electric field remains in the $10^2$–$10^4$ V m range, and a high spatial resolution electron detector is included in the experimental set-up [125,126].

The electron energy can be determined from the pattern radius since the radius increases as $\varepsilon^{1/2}$. One can, however, also measure the accumulated phase or the number of rings, both of which have an $\varepsilon^{3/2}$ variation with energy, which makes them more sensitive to energy variation than the spot radius. Furthermore, the latter two are dimensionless quantities, which means that no absolute calibration of the electron image sizes will be needed. Counting the bright and dark rings immediately yields the number of rings. A more quantitative analysis is usually performed by fitting the formula for the radial oscillation of the electron current with the experimental data. Fig. 4 shows the scheme of the experimental set-up and illustrates the expansion of the electron wavefunction from the region of the photodetachment zone to it reaches the high spatial resolution detector [126]. The properties and usefulness of the photodetachment microscopy and its application to atomic and more recently also molecular negative-ion studies have been reported in a series of papers by the group from Laboratoire Aime-Cotton, Orsay [125–127,129–132]. The accuracy of the electron affinities determined by the LPM method has reached values of 2–3 µeV, or 0.016–0.024 cm$^{-1}$.

Since the photoelectron energy must be very small (in the range 10–300 µeV), the technique is effectively limited to negative atomic ions for which the detachment cross section is high even close to the detachment threshold, namely s-wave detaching ions. It should be noted that of two recent studies of the binding energy of the Si$^-$ ion, the LPM method yielded a result [131], which was improved an order of magnitude over the LPT measurement [111].

2.4.3. Resonance structures

In connection with the study of binding energies of the alkali negative ions, Rb$^-$ [133] and Cs$^-$ [134], it was observed that these ions possessed resonance structures located in the energy region just below the first excited state of the neutral atoms. The resonance structures appeared in the cross section for neutral atom formation recorded as function of the photon frequency. The cross section varied dramatically over a very narrow region and the resonance, of the “window” type (called so, since the cross section drops to near zero and consequently the ions are nearly transparent at specific photon frequencies), was attributed to the existence of an autodetaching state, that was optically connected to the ground state of the negative ion. For the negative Rb ion, the observed state was assumed to be $5p6s \, ^1P$, representing a doubly excited state with respect to the $5s^2 \, ^1S$ ground state.

Analogous studies of cross sections and resonance structures, located very near the first excited neutral atom threshold, have more recently been reported for a series of negative ions, including the He$^-$ [135], Li$^-$ [136–138], B$^-$ [139], C$^-$ [68], Al$^-$ [140], Si$^-$ [141], and Ca$^-$ [142,143]-ion systems. The experimental studies have been concerned with lighter negative atomic ions for which a significant amount of theoretical calculations was available, for a recent review see [52].

Resonance structures appearing in the vicinity of higher lying neutral thresholds can be difficult to study using single-photon technique. The resonance signals will usually be superimposed on an increasing background caused by the photodetachment channels to the lower lying thresholds. Thus it has been more attractive to use multi-photon techniques, allowing selective detection of
the population of a specific neutral threshold (see Section 2.5). However, for ions like H\(^-\) [50] and He\(^-\) [19] it has been possible to benefit from special experimental possibilities. The neutral H\((n = 2–8)\) atoms, formed during the photodetachment of the 800 MeV H\(^-\) beam at the Los Alamos Meson Facility could be identified separately by means of field ionization, utilizing the laboratory motional field from a strong magnet, with the resulting protons being detected downstream, so the decay to a particular H\((n)\) channel could be monitored. The selective detection of the various Rydberg atoms yielded a wealth of information about resonances [50,144,145] in the H\(^-\) ion up to the energy of approximately 300 meV below the two-electron detachment limit.
For neutral thresholds located very near to the two-electron escape thresholds it may be possible to combine single-photon excitation with state-selective electric field ionization to study energetic high lying resonance structures by selectively monitoring the neutral Rydberg atoms formed. By proper design of an electric field ioniser Petrunin et al. [19] could perform a photodetachment study of the He\(^-\)(1s2s2p \(^3\)P) ion in the vicinity of the two-electron escape threshold by selective monitoring the formation of He(1sn\(^3\)L) Rydberg states for \(n\) being 11–14, which are located only 50–100 meV below the He\(^+\) limit. The Rydberg atoms were reaction products from very weak reaction channels, representing only \(10^{-6}–10^{-7}\) of the total detachment yield.

Resonance structures have also been observed in connection with inner-shell excitation studies of negative ions using far more energetic photons than considered above. In the negative carbon ion [101] a pronounced shape resonance structure was observed just above 281 eV. The synchrotron radiation-induced excitation and detachment studies could benefit from the subsequent Auger-decay processes leading to formation of positive ions, which can be separated from the collinear photon and negative-ion beams.

### 2.4.4. Photodetachment cross sections and angular distributions

For structural studies of negative atomic ions absolute cross photodetachment sections are of great interest, but not always needed and relative cross sections can be sufficient. However, absolute photodetachment cross sections for negative atomic ions are essential for testing the many theoretical predictions available dealing with many-body effects in negative-ion photodetachment (for a recent review see [52]).

Photoionization is a fundamental process of importance in many areas of science and technology and photoionization cross sections of neutral atoms and positive ions are needed to model different types of plasmas, especially, but by no means only, in astrophysics. Therefore, considerable effort has been devoted to the calculation of photoionization cross sections for almost every element from hydrogen to iron, in all ionization stages, see e.g. the Opacity project [146,147]. The experimental testing of the theoretical data has been in progress during recent years [148,149]. Experimental data on photodetachment cross sections, including photoelectron angular distributions and polarization parameters, are very limited compared with the data on neutral atoms and positive ions. For inner-shell studies this situation seems, however, to be changing with the first absolute inner-shell photodetachment cross sections being reported in 2001 [7,8] for the Li\(^-\) ion. The experimental method adopted for photodetachment cross sections of inner-shell electrons is identical to the one used for photoionization cross sections of positive ions by Lyon et al. [150,151].

A beam of a the Li\(^-\) ion is overlapped collinearly with an intense synchrotron radiation beam of VUV photons over a distance of about 50 cm. The absolute cross section is derived from the photoinduced yield of Li\(^+\) ions, the density of the Li\(^-\) target ions, the interaction length and the absolute photon flux. The detectors for Li\(^+\) ions and for the photon flux, respectively, are absolute calibrated, and several sets of slit-scanners applied to determine the profile of both photon and parent-ion beams, to establish their shapes, sizes and degree of overlap. Absolute photodetachment cross sections can be determined with an accuracy of 10–15%.

Absolute photodetachment cross sections for laser-induced detachment processes are usually relying on measuring the saturation behaviour of neutral atom production as a function of laser intensity at selected energies. As the intensity of the laser is increased, the neutral atom production saturates,
and the cross section can be obtained from the shape of the curve. This technique has been in use for single as well as multi-photon detachment studies [152–154]. The saturation method has the advantage that it is not necessary to know the detection efficiency of the neutral atoms nor the current of the negative ions, but information about the overlap between the laser and ion beams is needed, since the ion beam is not stationary and the laser flux not constant over the beam spot. If the velocity of the ions and the inhomogeneity of the laser flux have to be included then one has to consider explicitly the trajectory of the ions through the laser beam [154], but still it is not necessary to know the detection efficiency, since the shape of the curve determines the cross section. Absolute cross sections using this method have been reported to be accurate within 10%.

To avoid many of the complications related to photon–negative ion absolute cross section measurements relative measurements are often performed and made absolute by measuring the neutral atom production from the negative-ion beam of interest relative to that from an O\(^-\) ion beam. Measurements of the cross section of O\(^-\) have been reported long ago by Branscomb et al. [155] in the energy region from 1.5 and to 4 eV. This procedure has been applied to several photodetachment studies in the 1990s, e.g. for the B\(^-\) ion [139], with the absolute cross section data claimed to have an accuracy of better than 10%.

Angular distributions of photoelectrons produced by single-photon detachment may be measured to give a valuable supplement to cross section data. The measurements are usually performed at a few selected wavelengths using a crossed laser-ion beam apparatus, see e.g. the measurements concerning the negative ions of Al, Si, and P [156] or the negative C ion (Section 4.7).

2.5. Multi-photon studies

Multi-photon studies have had an important impact on negative-ion studies during the last 15 years. As neutral atoms, negative ions can undergo multi-photon excitation in sufficiently intense fields. Even though the first two-photon detachment experiment was performed already in 1965 [157], it was not before the end of the 1980s and the beginning of the 1990s that multi-photon experiments with negative atomic ions really were taking off, at the beginning directed towards strong laser fields studies and based on absorption of two or more photons possessing the same frequency [158–160]. The field quickly developed to be very fertile taking advantages of the many possibilities for combinations of photon frequencies [43,64]. Particularly two areas of negative-ion research have benefited from this development, the structures of atomic negative ions [31,64] and photon–negative-ion collisions [43].

2.5.1. Resonant ionization spectroscopy (RIS)

State selective techniques have proved to be extremely valuable to overcome some of the problems associated with threshold measurements using single-photon studies, (see Section 2.4). Since the determination of binding energies is accomplished by measuring the threshold photon energy of the transition from the negative ion state to the parent state of the neutral atom or to an excited state in the latter, it is possible both to avoid the use of p-wave thresholds and to measure binding energies well below 150 meV, if state selective techniques are introduced. One such technique is resonant ionization spectroscopy (RIS), which was introduced to negative-ion research in 1995 [4].

Utilizing RIS, the negative ion is first photodetached with a tunable laser source as in LPT spectroscopy (Section 2.4), and the neutral atoms produced in the detachment process are excited by
a second photon into a known state, often a Rydberg state, which subsequently is either photoionized or electric field ionized. The positive ions produced are subsequently detected. Photodetachment of a negative ion to an excited state of the neutral atom had been used for many years to obtain binding energies of negative ions, such as the alkalies, but the accuracy of the values obtained was lower than could be obtained with detachment to the ground state [49]. The reason was that changes in the photodetachment cross section, from the opening of a new detachment channel, would be superimposed on the much larger photodetachment cross section for the lower lying atomic states. This is particularly the case if the new detachment channel is associated with emission of a p-electron and the detection of the neutral atoms has to rely on the conventional methods for neutral particles [49]. A significant improvement could then be obtained utilizing only s-electron emission channels and detection of the excited state atoms produced by the opening of a new detachment channel by the sensitive resonant laser photoionization method [161], which originally was developed for isotope separation. The RIS method facilitates the distinction between close lying photodetachment channels as well as between different negative ion states. The use of RIS to detect excited neutral atoms offers the following advantages: high efficiency, very high optical selectivity, and strong suppression of the background induced via collisions between the negative ions and the rest gases. Thus, even very weak photodetachment channels can be studied.

Fig. 5 illustrates schematically the experimental set-up used at the University of Aarhus for studies of negative ions based on the application of RIS. A beam of positive alkaline earth ions is transformed to negative ions via a two-step charge-exchange process in alkali metal vapour. The positive ions are extracted from a plasma ion source, mass and charge analysed before entering the metal vapour cell. The beam current is usually in the range from 0.1 to 1 μA and the conversion coefficient for producing the negative ions $10^{-2}$–$10^{-4}$. After separation of the different charge state components by electric fields the negative beam enters a 1 m long field free drift region in which the ions are overlapped with the output from a pulsed laser system, consisting of two dye lasers pumped by the second harmonics of a Nd:YAG laser. The first dye laser is used to detach the negative ions, the second to probe the neutral atoms with pulses delayed 10–20 ns with respect to the detaching pulses taking advantages of RIS of the neutral atoms generated. At the exit of the interaction region the beam is again undergoing charge-state analysis using a second electrostatic deflector. The latter step in the experiment is important for elimination of the positive ions produced via collisions with the background gases, which otherwise would influence the final detection. The second deflector also
has the purpose to act, at higher voltages, as a state-selective electron-field ionized optimized for detection of specific Rydberg states.

Fig. 6 shows the schematic energy diagram of Be\(^-\) and Be states with the detachment and excitation channels indicated. The experiment was performed by Kristensen et al. [21] and resulted in the determination of the binding energy of the longest-living fine-structure component of the Be\(^-\)(2s2p\(^3\) 4P) state, which is \(J = 3/2\). The first photon detaches the electron at the Be(2s3p\(^3\)P) state, whereas the second photon excites this state to the 2s15d\(^3\)D Rydberg state in the neutral Be atom, subsequently followed by electric field ionization of the latter resulting in Be\(^+\) ions. The Be\(^+\) yield is recorded as a function of the detachment photon frequency and shown in Fig. 7; it is easy to identify the opening of the detachment channel characterized by s-electron emission. By means of the RIS method it was possible to improve the accuracy of the binding energy of the Be\(^-\) ion by two orders of magnitude compared to the value published a few years before [162], which was obtained by photodetached electron spectroscopy (see Section 2.3). The RIS technique has been used
Fig. 7. Be⁺-yield following photodetachment of the Be⁻(4P_3/2) ion to the Be(2s3p 3P) state, which subsequently is monitored by resonant ionization via the Be(2s15d 3D) Rydberg state [21].

to obtain binding energies with high accuracy for several negative atomic ions such as the He⁻ [13], Li⁻ [68], K⁻ [163], and the alkaline earths, Be⁻ [21], Ca⁻ [5], Sr⁻ [6], and Ba⁻ [4] ions.

The RIS method has also been very important for the exploration of the resonance structures belonging to the He⁻(1s2s2p 4P) ion and located in the energy region of the He(1snl 3L) thresholds with \( n = 3–5 \) [14–16]. Additional studies have covered the Li⁻ ion in the energy region below the Li(6p) threshold [164–167], the Na⁻ ion below the Na(5p) threshold [168], and the K⁻ ion below the K(7p) threshold [169]. These studies have all stimulated theoretical studies of the relevant ions and the comparisons between the experimental results and the theoretical predictions will be discussed in Sections 4.2 and 4.3. Furthermore, the state-selective detection method also plays an important role in combination with non-linear laser techniques, see Section 2.5.3 [170,171].

2.5.2. Non-resonant multi-photon detachment

The access to strong laser fields created in the beginning of the 1990s an interest for exploring the impact of strong laser fields on negative atomic ions [43,54]. At that time strong laser field studies of neutral atoms had been performed for more than a decade, but due to the atomic structure of neutral atoms and the influence of the Coulomb potential on the outgoing electron non-resonant multi-photon detachment studies of negative atomic ions offered possibilities for studying electron emission under quite different and sometime much better conditions. First of all it would be possible to select negative ions, like the halogen ions, so the studies could performed without interfering effects from excited states, secondly the emitted electrons would not be under influence of the Coulomb field. Thus, non-resonant multi-photon detachment provided conditions which, from a theoretical point of view, would be very attractive with a perfect non-resonant bound-free multi-photon transition. During the first years of these studies the focus was on measurements of total multi-photon detachment cross sections, but it was often difficult to achieve the cross sections sufficiently accurate to allow for
Fig. 8. Schematic of experimental cross-beam apparatus employed in the non-resonant excess photon detachment work on the Au\textsuperscript{−} ion.

a clear distinction between existing theories [43]. It was more successful to study

1. Excess-photon absorption in negative ions.
3. Multi-photon detachment with different polarization of the laser light.

Fig. 8 shows a set-up used for non-resonant photon detachment studies of negative ions [54]. The negative ions, supplied from a sputter ion source, are introduced to an ultrahigh vacuum chamber (UHV) after undergoing acceleration and mass and charge-state analyses. By deflecting the negative-ion beam about 15° within the UHV chamber, at a pressure of \(10^{-8}–10^{-9}\) mbar, the collisionally produced neutral atoms are eliminated. At the centre of the UHV chamber the negative ions are crossed by a focussed laser beam and after subsequent electric field analysis the detached neutral atoms and positive ions are recorded by electron multipliers. The electrons emitted from the photon–ion detachment process can be analysed by a magnetically shielded time-of-flight (TOF) spectrometer, equipped with tandem-channel plates [54].

Three publications appeared within a few weeks in 1991 all reporting the observation of excess photon absorption in either negative F [158], Cl [159], or Au ions. [160]. In the case of the Au-ions (Fig. 9), two 1.165 eV photons from a Nd:YAG laser were sufficient to exceed the detachment threshold with about 20 meV. According to Wigner’s threshold law [2], the two-photon detachment cross section will be suppressed just above threshold and it was therefore easier to search for higher order excess-photon processes in negative ions than in neutral atoms [54]. In all three experiments mentioned above it was possible to reach at the same qualitative conclusion, that non-resonant excess photon absorption is an important process in a negative atomic ion at laser intensities of the order of TW/cm\textsuperscript{2}. In the negative Au ion experiment the first order excess-photon process
Fig. 9. Energy level diagram of Au\(^{−}\). A mode-locked Nd:YAG laser was employed, such that the 2-photon absorption barely exceeds thresholds [54].

Fig. 10. Angular distribution of four-photondetached electrons from F\(^{−}\), at the wavelength of 1064 nm; three-photons are enough to detach the negative ion. The qualitative correspondence with the plane-wave approximation (dashed line) is a precise signature of excess-photon detachment [43].

(three photon absorption), and the second order excess-photon processes (four photon absorption) were estimated to represent 5% and 0.6%, respectively, of the total electron yield at an irradiation intensity of \(3 \times 10^{12} \text{ W/cm}^2\). In the F\(^{−}\) experiment the angular distributions of excess-electron detached electrons were measured. Fig. 10 shows the angular distribution of four-photon detached electrons from F\(^{−}\) ion at the wavelength of 1064 nm [158]. Three photons are sufficient to detach the F\(^{−}\) ion at this wavelength, so the shape of the angular distribution gives a precise signature of excess-photon detachment. The figure illustrates the correspondence between the experimental data and the plane-wave approximation for the electron emitted after four-photon absorption. The measurement of the angular distribution of the electrons emitted as a consequence of multi-photon detachment has the advantages, too, that these data provide precise challenges for theories [172] trying to reproduce the experimental results.
2.5.3. Resonant multi-photon detachment: resonances above the detachment limit

Resonant multi-photon detachment methods have been developed during the last decade and may be subdivided into two groups,

1. The resonant state is located above the detachment limit.
2. The resonant state is located below the detachment limit.

The exploration of resonant multi-photon detachment as an experimental method to study negative ions was pioneered by Haugen and co-workers [54,173,174]. Resonant phenomena can occur in negative ions in several ways. The first experiments took advantages of the resonances located above the detachment limit, such as the doubly excited states in the heavier negative ions of the alkalis [133,134]. Fig. 11(a) shows a simplified energy level diagram for the Cs\(^-\) ion and the Cs atom indicating the multi-photon processes. Excess photon detachment from the ground state of the Cs\(^-\) ion is strongly enhanced when the first photon reaches an energy corresponding to the Cs\(^-\)\((6p_{1/2}7s)\) state, where the cross section for single-photon detachment reaches a minimum, caused by the interference between the excited Cs\(^-\) state and the continuum [173]. This minimum facilitates absorption of additional photons by suppressing the depletion of the ground state during the
rise time of the laser pulse; in addition the doubly excited state is expected to favour the absorption of additional photons. As indicated on the figure absorption of an additional photon by the negative ion will lead to population of an excited Cs atom state, which subsequently can be ionized by absorption of one additional photon. Fig. 11(b) shows the variation in the Cs atom signal compared with the Cs\(^+\) signal. The minimum in the yield of Cs atoms is coinciding with a maximum in the production of positive Cs ions.

The Cs\(^-\) \(\rightarrow\) Cs\(^+\) double ionization process (Fig. 11) was due to sequential electron removal. Very recently, Greenwood et al. [175] have studied double ionization of atomic negative ions (Al\(^-\), Ag\(^-\), I\(^-\), C\(^-\)) in an intense laser field (power density of 10\(^14\) W/cm\(^2\)). The yields of positive ions as a function of intensity were not consistent with sequential electron removal. Although the laser pulses applied were very long by modern standards, and tend to produce sequential ionization in atoms, the positive ion yields from the negative ions do not depend predictably on the ionization potentials. The authors suggest that there may be an alternative mechanism enhancing double ionization at low laser intensity. This mechanism may involve resonant enhancement via doubly or multiply excited states.

Excess-photon absorption via an autodetaching state was further developed, combining low laser intensities and resonant ionization spectroscopy (RIS), to a powerful technique [171] to obtain spectroscopic information about autodetaching states. The high sensitivity of the RIS detection method allows the observation of the resonant excess photon absorption process at much lower laser intensities (four to five orders of magnitude less) than applied in the experiment described above. Thus, it is possible to avoid the influence of saturation effects due to depletion of the negative-ion target, an effect which otherwise would influence both the position and the width of the excess photon absorption signal even at very low fluences. By means of this technique spectroscopic information was obtained for autodetaching states in negative ions of Sr and Ba, respectively [171].

An alternative non-linear laser technique, state-selective depletion spectroscopy [170], allowed spectroscopic information to be obtained about the autodetaching nsnp\(^2\) 4P levels in the alkaline earths ions. This multi-photon technique relies on the use of three pulsed nanosecond lasers, see Fig. 12. The first laser pulse is used to explore the detachment cross section in the energy region around the 4P autodetaching state. The second laser pulse is a probe pulse, with a small time delay (approximately 10 ns) after the first laser pulse, and used to probe the remaining population of the ns\(^2\)np \(^2\)P ground state levels. The energy of the probe pulse is sufficient to transfer the remaining population of the ground state levels to the neutral atom nsnp \(^3\)P \((J=0, 1 \text{ or } 2)\) levels, with the \(^2\)P\(_{1/2}\) ground state population being represented by the \(^3\)P \((J=0)\) population, and the \(^2\)P\(_{3/2}\) ground state level population by the \(^3\)P \((J=2)\) population. The population of the neutral atom \(J=0\) or 2 levels can then be measured separately using RIS technique. This detection scheme provides independent measurements of the absolute photodetachment cross section for the two ground state levels of the negative ion by monitoring the decrease in population of each of these levels after interaction with the detachment beam (the first laser pulse). By recording the positive ion signal as a function of wavelength of the laser pulse used to induce the transition from one of the \(^2\)P ground state levels to one of the autodetaching 4P levels the photodetachment cross section will display a Fano interference pattern [176] which contains comprehensive information above the negative-ion properties, such as binding energy and lifetime of the autodetaching levels, fine-structure intervals, and the absolute strengths of the inter-combination transitions [170]. This technique was developed to resolve the long-lasting dispute concerning the Ca\(^-\) ion.
The Ca\(^{−}\)(4s\(n\)p\(^2\)\(^4\)P) state has played a very important role in the process leading to the present understanding of the Ca\(^{−}\) ion. Before 1987 the existence of the negative Ca ion was considered to be due to the \(^4\)P state, which was assumed to be long lived and metastable like the homologous state in the Be\(^{−}\). The discovery of the stable Ca\(^{−}\) ion [10] dismissed this assumption, but subsequent studies [177] still claimed that a long lived, metastable component was present in negative Ca-beams and that this component most likely should be attributed to Ca\(^{−}\)(4s4p\(^2\)\(^4\)P) ions. The state-selective depletion spectroscopy study by Kristensen et al. [170] finally dismissed these claims and showed that the lifetimes of the autodetaching \(^4\)P\(_J\) levels were of the order of 10–100 ps, for more details see Section 4.5.

More recently, resonant multicolour spectroscopy in the photodetachment continuum [80] was introduced, combining two-photon resonant absorption from the ground state, using photons of different energies, together with the RIS detection method. The first photon is used to reach an autoionizing state from which a second autoionizing state could be populated by the second photon. The RIS technique is applied to monitor the autodetachment of the second excited state. Fig. 13 shows
a schematic energy level diagram of the negative calcium ion and the corresponding parent atom used. The first excited autodetaching state was Ca\(^{-}(4s4p^2 \, ^4P)\), the second Ca\(^{-}(4p^3 \, ^4S)\), which subsequently was monitored by RIS via the Ca\((4s4p \, ^1P)\) state. Fig. 14 shows the Ca\(^{+}\) photon–ion yield, reflecting the population of the Ca\((4s4p \, ^1P)\) state by the two-photon detachment process, with the \(\lambda_2\) laser being scanned in the region of the \(^4P_{1/2} - ^4S_0\) transition in the negative Ca ion. This experiment yielded information about the energy and lifetimes (autodetachment and radiative lifetimes) of the Ca\(^{-}(4p^3 \, ^4S)\) state and also explained why it has not been possible to observe the optical \(^4S - ^4P\) transition in the Ca\(^{-}\) ion before even though the homologous optical transition in the negative Be ion had been observed already in 1989 [178] using the beam-foil technique.

2.5.4. Resonance multi-photon detachment: resonances below the detachment limit

Resonant multi-photon detachment can also occur in another way taking advantages of the resonant states located below the detachment limit. Several negative ions exhibit fine structure in their ground electronic state with both the fine structure levels being located below the detachment limit; the
Fig. 14. Ca\(^+\) photo-ion yield, reflecting the population of the Ca(4s4p \(^1\)P) level generated by the two-photon detachment process with the \(\lambda_2\) laser (Fig. 13) being scanned in the region of the 4s4p\(^2\) \(^3\)P\(_{1/2}\)–4p\(^3\) \(^1\)S transition in the Ca\(^-\) ion [80].

electronic configuration of the ground state can also possess more than one bound term. In both cases it is possible to benefit from resonant multi-photon detachment methods to obtain structural information about the negative ions. The first of the two possibilities was studied by multi-photon detachment in a Raman coupling regime [179] with the aim to measure the fine-structure splitting in the ground state of the Te\(^-\) ion.

If two laser fields are applied and matched such that the difference in photon energies is equal to the energy splitting of the fine-structure components of the ground state electronic configuration (Raman condition), then a modification of the multi-photon detachment probability can generally be expected. Fig. 15 shows a schematic energy level diagram of the Te\(^-\) ion illustrating the (2+1)-photon detachment of the Te\(^-\) \(^2\)P\(_{1/2}\) level when the Raman condition is fulfilled. The Raman coupling of the two fine-structure levels occurs via a virtual bound state. In the Te experiment the two laser fields were created by the fundamental laser wavelength at 1064 nm from a Nd:YAG laser (\(\omega_{IR}\)) and a dye laser operating around 694 nm. By recording the neutral atom signal as a function of the wavelength of the dye laser a strong enhancement was observed when the Raman condition was fulfilled. This method can lead to fine-structure splittings [179–181] with an accuracy of the order of 0.2 cm\(^{-1}\).

The principle of stimulated Raman scattering (SRS) detachment should make it applicable to many negative ions possessing a fine-structure splitting as the negative Se or Te ions. However, attempts to use the 2+1 photon Raman method to explore the properties of the negative ions of Ir and Pt have failed, indicating that the multi-photon cross sections may be very much smaller for these ions than for the Se and Te ions, which could seriously limit the use of the SRS method [31].

With the exception so far of the Os\(^-\) ion [1], the transition between negative-ion states located below the detachment limit will be between states possessing the same parity. Even though the transitions will be “optical forbidden” and the transition probabilities therefore much smaller (a factor of 10\(^6\)–10\(^7\)) than for allowed electric dipole (E1) transitions it has successfully been demonstrated that it is possible to drive these transitions either as single-photon magnetic dipole (M1) or as electric quadropole (E2) transitions (for recent reviews see [31,64]). The McMaster group has applied
“forbidden” transitions to study a range of heavier negative ions of elements like Sn [114], Sb [182], Te [180], Ir and Pt [181,183] to obtain information about the binding energies of excited, but bound negative-ion states including fine-structure states, located below the detachment limit. The transitions between the bound states of same parity can easily be probed by the detection of the neutral atoms produced in the subsequent photodetachment from the upper ionic state. Fig 16 illustrates the many possibilities for photodetachment processes possible considering the negative Sb-ion [182]. By means of single-, two-, and three-photon detachment processes it was possible to measure the energies of the fine-structure levels belonging to the ground state as well as the energy of the excited 1D term.

The resonant multi-photon methods are very well suited to yield information about the binding energies of excited states, which have little or no population and consequently cannot be explored using the LPT methods. Furthermore, resonant multi-photon detachment may be applied to search for bound excited states of opposite parity of the ground state configuration, since such states should be noticeable due to a large transition probability from the ground state. It was the observation of a much larger transition probability than expected for an M1 transition that indicated the presence of a bound excited state of opposite parity to the ground state configuration in the Os\(^{-}\) ion [1]. A few years before, a similar resonant multi-photon detachment experiment had shown [184] that the previously assumed best suited candidate for possessing a bound excited state of opposite parity...
to the ground state configuration, the Cs\(^-\) ion, had its 6s6p \(^3\)P\((J = 0)\) level displaced only 8 meV above the detachment limit.

Future development of the resonant multi-photon techniques could well lead to methods able to yield information about the lifetimes of these states [64].

2.6. Electron collisions with atoms or negative atomic ions

Electron-impact spectroscopy has been a unique method to study atomic negative-ion resonances and provided a large amount of the knowledge we have about the excited negative-ion states. An informative and extensive review dealing with atomic negative-ion resonances was reported by Buckman and Clark [42], who stated that electron-impact spectroscopy had provided the majority of new information about negative-ion resonances in the period from about 1970 to 1990. They also described the experimental electron-impact techniques in some detail, predominantly for electron–atom collisions.

Negative-ion resonances formed by electron impact on atoms are studied by detecting reaction products in one or more of the decay channels energetically available to the compound state (the negative-ion resonance). Usually, such studies involve the measurement of either the total or differential scattering cross section as a function of the incident electron energy. Two types of experiments are dominating: transmission studies and crossed beam studies [42]. The former relies on the measurement of a total cross section for an electron beam through a gas cell and detecting those electrons that are not scattered by the gas, whereas the latter is preferred in experiments aimed at detecting the scattered electrons. Electron impact on atoms with the aim to obtain new information about negative-ion resonances has not been an active research field during the 1990s; the interest is now directed towards electron–atom ionization, together with electron–molecule, electron–cluster, electron–positive ion, and electron–negative ion collisions. The latter type is of interest for the present review.
Whereas electron-impact ionization of atoms and positive ions has been studied since the early days of quantum mechanics, and much of our understanding of the structure of atoms has emerged from electron scattering experiments, the situation has been completely different with respect to electron detachment from negative atomic ions. Only very few electron–negative atomic ion experiments have been conducted and only a few elements studied, before storage rings dedicated to atomic and molecular research became available (see Section 2.8 about storage rings). Tisone and Branscomb [185,186] and Dance et al. [187] studied the impact of 10–500 eV electrons on the $H^-$ ion, whereas the studies by Peart et al. [188–190] in addition to $H^-$ also included ions like $C^-$, $O^-$ and $F^-$. From an experimentalist's point of view, negative ions may be difficult to work with since the cross section for collisions with rest gases is large, leading to detachment of the negative ions. This results in a significant background signal from neutral atoms which should be distinguished from the neutral atoms resulting from electron-induced impact of the negative-ion target. Electron–negative-ion impact studies have been revitalized due to several experimental achievements related to storage rings, such as high-energy negative-ion beams, good vacuum, a dense electron source and efficient counting of the neutral atoms [63,65,191]. The experiments performed since the beginning of the 1990s have been carried out at the heavy-ion storage rings ASTRID at University of Aarhus and CRYRING at Stockholm. They have mainly focussed on low-energy electron impact, covering the energy region from zero to about 30 eV. This has been possible by using merged beam technique in which MeV negative atomic ions are merged with an intense beam of electrons possessing the same velocity as the ions and recording the formation of neutral atoms. The experiments, which will be discussed further in Section 5, have focussed on two items: The cross section behaviour (i) near threshold and (ii) well above threshold (10–30 eV), the latter since earlier studies have claimed the existence of short lived, doubly charged atomic negative ions. Whereas the threshold behaviour for photon impact on negative ions is well established by Wigner’s law [2], the situation is far more complex for electron impact in the region close to threshold, since there are three particles in the final state (two electrons and a neutral atom) see [192,193] and references therein. Rost [192] showed that the description of threshold fragmentation under long-range repulsive forces has much in common with the principles used by Wannier [194] for describing threshold ionization under attractive forces.

When a free electron approaches a negative atomic ion, it will experience a repulsive field (Coulomb), which strongly will influence its trajectory. It is not enough that the incoming electron possesses an energy equal to the binding energy of the negative ion, typically 1 eV, since the closest approach at that energy will be 27 a.u. The incoming electron must provide sufficient energy to release the loosely bound electron of the negative ion, but also enough kinetic energy for the two outgoing continuum electrons that repel each other [191]. The threshold energy needed to complete detachment is therefore typical a factor of two to three larger than the binding energy. This situation is very different from neutral atoms or positive ions. In the case of positive ions, the electron will gain kinetic energy, since it is accelerated towards the nucleus of the positive ion. The consequence could be that the incoming electron may be able to excite one of the core electrons, and, in addition, the incoming electron could be captured in some highly excited state. The same scenario could perhaps happen for a negative atomic ion target, but the situation will be more complicated due to the large amount of Coulomb energy inherent in the system. So far the experiments performed with electron impact on negative atomic ions like $H^-$ [195] and $O^-$ [196] at storage rings have
dismissed the previous claims [197–199] for the existence of doubly charged, negative atomic ions (see Section 5), produced by electron scattering from ground state negative atomic ions.

2.7. Negative-ion–atom collisions

Heavy-particle collisions, using fast negative ion–atom or positive ion–solid interactions (solids in the form of thin carbon foils) as projectile–target combinations, have proved to yield valuable information about doubly excited states of simple negative ions, which otherwise are difficult to study due to lack of selective excitation techniques. The negative ion–atom collision experiments were introduced by Edwards and co-workers in the 1970s, for a review see [70], and were performed by interacting momentum analysed and focussed negative-ion beams, having energies in the keV range, with atomic (He, Ne, etc.) or molecular (H₂) gases. The experiments were carried out under conditions usually applied to heavy-ion collisions at that time, so ultra-high vacuum was not used. The electrons resulting from the different collision processes were energy analysed using various types of energy analysers. Only electrons originating from excitation of either the projectile or the target will lead to structures in the yield of electrons as a function of energy. Doubly excited negative-ion states can be generated both in the projectile negative ion due to excitation, but also in the target due to charge exchange and excitation. By proper selection of target and collision energy it is possible, however, to eliminate the latter and only focus on the projectile; at low-energy it is also possible to control, to some extent, the doubly excited states created.

The starting point for interpretation of inelastic processes in low-energy (1–10 keV) heavy-ion collisions is the diabatic molecular orbital-correlation diagram for the projectile–target pair. Fig. 17 shows schematically such a diagram for the F⁻–He collision, constructed from the Barat–Lichten rules [200]. Only the filled orbitals are indicated. The main feature to observe is that two 2p F⁻ electrons may be promoted along the 3dσ orbitals and end up in excited states after the collision, whereas the 2s electrons cannot be excited within this scheme. The remaining F⁻ core will have the configuration K 2s²2p⁴ which may couple to a 3P, 1D or 1S state in order of increasing energy. Since the two promoted electrons have opposite spins, the 3P core cannot be excited. According to the spin-conservation rule for low-energy collisions, the total spin before and after the collision will be the same, i.e. in the case of F⁻ the spin will be zero. Since the target gas He is not excited at these low energies, only doubly excited F⁻ singlet states are expected and mainly with the 1D core. Consequently, the lowest lying doubly excited F⁻ state to be observed should be the 2p⁶(1D)3s² 1D state, which would be expected to decay to the F-ground state by emitting energetic electrons (14.85 eV). Only this autodetaching state in F⁻ had been reported before 1986 on the basis of electron spectra containing electrons with energies larger than 0.6 eV [201]. In 1986 Grouard et al. [202] observed in F⁻–He collisions a group of low-energy electrons with energies ranging from 90 to 250 meV, which also originated from excited F⁻ ions, but the autodetaching state was not identified. By means of low energy electron–photon coincidence technique [203] these low-energy electrons were subsequently proved to originate from the 2p⁶(1D)3s² doubly excited state, too; the doubly excited state decayed to the excited 2p⁶(3P)3p 3P and 2D states in neutral F (note the change of the core), in addition to the ground state of F. Thus only one doubly excited state was populated. The same conclusion was reached for collisions involving the Cl⁻ [204] and the O⁻ ion [205].

Collision studies have also been performed at larger collision energies for which the Barat–Lichten rules may not be applicable [206] leading to a breakdown of the spin-conservation rule.
Light sources based on heavy-ion collisions as the fast beam-foil/gas sources have been shown to efficiently populate multiple excited states. The beam-foil technique relies on the passage of an energetic (keV–MeV) positively charged ion beam through a thin carbon foil with subsequent observation of the light emitted from the particles passing the foil. By varying the energy of the projectile ions it is possible to influence the charge distribution of the beam after its passage of the foil. The beam-foil technique has mainly been used to study: Atomic spectra of highly charged ions, multiply excited states in few electron systems (for a review of the three electron systems see [207]), and lifetimes of excited states decaying by photon emission. Since negative ions were not considered to possess excited states able to decay by photon emission it was never suggested before 1980 that optical spectra recorded from beam-foil experiments could contain spectral lines originating from negative ions. However, that year Bunge [208,209] predicted on the basis of very accurate calculations that an unidentified spectral line in Li-beam foil spectra at 349.0 nm originated from a transition in the core excited Li$^-$ ion, which very quickly was confirmed experimentally [71,210,211]. At the end of the 1980s and the beginning of the 1990s additional optical transitions in negative ions were identified, the first belonging to the Be$^-$ ion [178], the second to the He$^-$ ion [212,213]. Among these three optical transitions the one belonging to the negative Be ion has
proved to be very valuable in connection with the characterization of the structural and dynamic properties of the metastable $\text{Be}^- (2s2p^2 \ 4P)$ state [21,22].

The collisional aspects of keV negative ion–atom collisions were studied in the 1970s and 1980s and reviewed by Esaulov [41]. The dominant process was single-electron detachment, which theoretically could be accounted for within an “independent scattering model” in which a simple picture of the negative ions was used, consisting of a loosely bound electron and a core of the neutral atom. It was assumed that the electron and the core collided independently with the target [214–216]; a critical experimental test of this model was performed more recently [217] by comparing the orientation and alignment of the $\text{Li}(2p^3\text{P})$ states created in $\text{Li}–\text{He}$ and $\text{Li}^-–\text{He}$ collisions, using polarised photon-scattered particle coincidence technique. Such complete scattering experiments have contributed significantly to the study of positive ion–atom, atom–atom and electron–atom collisions, but similar experiments with negative ions are rare.

Negative-ion–atom collisions at low energies (below 10 eV) can lead to associative detachment with the formation of a neutral molecule and detachment of the extra electron. The molecules can be generated in various vibrational and rotational states; a detailed analysis of the energy spectra of the emitted electrons can yield valuable insight to the collision process, see Section 4.10.2.

2.8. Storage rings and ion traps

Storage rings had served as tools in nuclear and particle physics for many years before attracting the interest of the atomic and molecular physics community. A small number of magnetic heavy-ion storage rings dedicated to research in atomic and molecular physics became operative at the beginning of the 1990s in Europe and Japan. The general purpose of a heavy-ion storage ring is to accumulate, recycle, accelerate or decelerate, and cool ions before they are used in various experiments. The storage rings are usually dedicated to experiments with positive ions, but the ASTRID storage ring at University of Aarhus was also adapted to negative ions. Prior to the first negative ion experiments at ASTRID only storage of $50 \text{ MeV H}^-$ ions had been reported [218] using the low-energy antiproton ring LEAR at CERN; useful lifetimes in the $50–100$ s range could be obtained. The ASTRID storage ring is designed for lower beam energies with most of the negative-ion beams having energies equal to the injection energy, which could be varied from 10 to 150 keV. The lighter negative ions can be accelerated to MeV energies by means of radio-frequency technique, which permits a significant Doppler shift of applied laser light. It also allows the negative ions to be merged with a beam of electrons of about equal velocity and thereby to study low-energy negative ion–electron collisions.

Storage times of atomic negative ions, like $\text{C}^-$, $\text{O}^-$ and $\text{F}^-$, were observed to be in the range of $2–5$ s at $100 \text{ keV}$ [219], at a rest gas pressure of $4 \times 10^{-11}$ mbar, with the storage times being limited by collision-detachment processes. Storage times of s implied, however, that qualitative new experiments with negative ions would be possible, including measurements of autodetachment lifetimes for metastable negative ions having lifetimes in the range of $\mu$s–ms, like $\text{He}^-$ and $\text{Be}^-$, photoexcitation of $\text{H}^-$ ions allowing narrow resonances to be studied, and low-energy negative ion–electron collisions by means of merged beams, for a review see [63].

Fig. 18 shows the essential features of ASTRID. The ring has a circumference of 40 m, two bending magnets in each of the four corners, 16 quadrupole magnets and 16 correction dipoles. The negative ions are prepared outside the ring, in ion sources as described in Section 2.1, and injected, by using a magnetic septum and a kicker, into ASTRID and stored at the injection energy.
Fig. 18. The storage ring ASTRID. Shown are some of the essential features for the experiments with negative ions. The 16 quadrupoles and correction dipoles are not shown.

The intensity of the stored beam is typically monitored by Schottky pick-ups, but in order to greatly extend the sensitivity of beam monitoring, neutral atom detectors were installed at the corners of the ring. Whereas most of the negative-ion experiments were performed using nA or more intense beams, the sensitive detection technique allowed for experiments with pA beams, too. The count rate of neutral particles detected behind one of the magnets was recorded as a function of time after injection. This provides not only a method to follow the beam storage, but also allows for an easy method to measure the lifetimes of negative, metastable atomic ions that decay by electron emission, on a time scale considerably shorter than the storage time.

By circulating a metastable negative-ion beam for periods of seconds it is possible by time-of-flight technique to make measurements of lifetimes in the range from about 10 μs to 100 ms at the ASTRID storage ring [12,20,56,63]. The short time limit is due to the round-trip of the ion, the long time by negative ion-rest gas collisions leading to destruction of the ion. The advantages of using a storage ring rather than a single-pass beam [220] to study lifetimes of metastable negative ions are: data can be extracted over a much greater time range out to several lifetimes with a good signal-to-noise ratio; slit scattering is essentially eliminated in the ring, and ultrahigh vacuum conditions render collisional quenching entirely negligible.

For photon- or electron-impact studies, the ions are accelerated to MeV energies before being exposed to VUV laser photons or merged with the electron beam from the electron cooler, respectively. The acceleration procedure can be performed within a few seconds, before the negative ions interact with 118 nm photons in the case of the H\(^-\) ion (see Section 4.1) or are merged with mA electron beams with energies ranging from 50 eV to 2 keV. The electron beam is essentially uniform with a density of the order of 10\(^7\) cm\(^{-3}\) [196,221]. It is important that the electron velocity distribution is known, particularly when threshold behaviour or resonances are studied.

The electron cooler, which is mounted on one of the straight sections of ASTRID consists of an electron gun, a 1 m interaction region, and an electron collector. A 4–5 mA electron beam is emitted by a tungsten cathode and accelerated through a grid to about 450 V. The electron beam
is guided in and out of the interaction region by solenoid magnetic fields of 100–200 G connected with two deflection toroids. Since the electrons are continuously renewed, the electron cooler may be considered a heat exchanger in which the velocity spread of an ion beam with longitudinal velocity equal to that of the electron beam is reduced as the ions moving too fast (slow) are decelerated (accelerated) by collisional energy transfer [222]. By the cooling process an equilibrium situation with equal ion- and electron-beam temperatures is approached, implying a velocity spread of the ion beam which is reduced with respect to that of the electron beam by a factor \((M/m)^{1/2}\), with \(M\) and \(m\) representing the ion- and electron masses, respectively, provided Maxwellian velocity distributions can be assumed. The longitudinal electron temperature will be reduced by the acceleration process to approximately 1 meV [221], while the transverse temperature can be reduced from its original value, given by the cathode temperature, by adiabatically expanding the electron beam [223]. In the cooling of the \(H^-\) ion [99] the transverse temperature was determined to be 26 meV, which represented a reduction by a factor of 4.3.

From an atomic physics point of view the use of a magnetic storage ring for lifetime studies may have some disadvantages, since the steering quadrupoles magnets can cause mixing of magnetic substates originating from different, but close-lying fine-structure components with the same \(M_J\) quantum number. This effect complicates both the measurements and the interpretation of the data in lifetime studies, as seen in the case of the He\(^{2-}\) ion [12]. On the technical side, magnetic rings are usually large-scale devices with limited access to control, for instance, of the temperature in connection with the study of the influence of blackbody radiation-induced photodetachment of weakly bound negative ions, like the Ca\(^+\) ion [224]. These difficulties have, among others, been avoided in the more recently developed electrostatic storage ring Electrostatic Ion Storage Ring, Aarhus (ELISA) [225], in which heavy ions are stored using purely electrostatic deflection and focussing elements.

An important difference between the electrostatic ring and its magnetic counterpart is that the strength of the bending forces “felt” by the ions depends on their kinetic energy and not on their momentum [18,225]. This allows high-intensity beams to be used to set up the storage ring before turning to the desired low-intensity beam of a different mass as long as the charge to the kinetic energy ratio is conserved, a feature which was very important for the first ELISA experiments. The ELISA storage ring may be considered as a small “table-top” ring; Fig. 19 shows a schematic diagram of the ring with injector. The race-trap shaped ring has a circumference of nearly 8 m.
The electrostatic lattice confining the ions is defined by two 160° cylindrical deflectors, each having a 10° parallel-plate deflector and a quadrupole doublet for horizontal and vertical focussing on each side. Position sensitive pickups are used to monitor the circulating beam. Due to its limited size it is possible to cool the entire vacuum system below −50°C simply by placing an isolating box around the ring and cooling the inside by inlet of liquid nitrogen. This was important for the study of the influence of blackbody radiation on the lifetime measured for the He− (1s2s2p 4P) ion [18].

An alternative to storage rings for negative-ion research is ion-traps, for a review of ion-traps see [226]. In most cases the ions are stored with very low kinetic energy (a few eV) in a combination of electrostatic and magnetostatic or time-dependent fields. The ions are confined in a relatively small region of space, and their trajectories are often complex functions of the fields and geometry of the electrodes. Ion traps have been applied in connection with photodetachment studies of the S− ion in a strong magnetic field [227,228] and for measurements of photodetachment cross sections of the Au− ion [229].

An electrostatic hybrid-storage device, which combines the advantages of the ion traps (inexpensive, small, and simple to operate) with the advantages of the storage rings (beams with well-defined direction and energy and the possibility of single-particle counting) was developed by Zajfman et al. [69]. The fast-ion trap is designed like an optical resonator, whose electron configuration allows for a very large field-free region, an easy access into the trap by various probes, a simple loading technique, and a broad acceptance range for the initial kinetic energies of the ions [69]. A model has recently been proposed, which can describe the motion of the ions in the ‘Zajfman trap’ [230].

The lifetimes of the metastable He−(1s2s2p 4P) and Be−(2s2p2 4P) ions have been studied using all three storage techniques, the magnetic storage ring ASTRID [12,20], the electrostatic storage ring ELISA [18,24], and the electrostatic trap [17,23]. The most precise lifetime values have been obtained using the electrostatic ring, which yielded results in agreement with the lifetimes obtained at the magnetic storage ring. The uncertainty of 0.2% for the Be− lifetime [24] determined at ELISA represents an improvement of a factor of 50 compared to the original magnetic storage ring experiment [20], which can be accounted for by the absence of magnetic fields in the electrostatic storage ring and its shorter circumference providing a larger dynamical range. The lifetime values obtained at the electrostatic storage ring were 3–6% longer than reported from the electrostatic trap, indicating a less perfect storage of the negative ions or an unidentified loss mechanism in the ion trap experiments.

2.9. Accelerator mass spectroscopy (AMS)

Accelerator mass spectroscopy (AMS) using tandem accelerators is a well-established technique applied for C-14 dating, but it can also be a valuable tool for studies of negative atomic or molecular ions, particularly of elements or compounds for which the experimental evidence has not yet been established. For atomic ions the lanthanides [231] and actinides [231–233] may be typical examples, for molecular ions the long-lived state of the negative molecular nitrogen ion [234,235]. Unambiguous identification of an atomic negative ion and its mass can usually be obtained using AMS.

For weakly bound, negative ions, like Ca−, the binding energy could be obtained using AMS together with electric field dissociation [236,237], for slightly stronger bound ions, like Sr−
by combining AMS with laser photodetachment [238]. The electric field technique has also provided preliminary binding energies for negative ions of Tm and Dy [231] and Yb [239]. The latter was reported to have a binding energy of only 10(3) meV, which would have been the lowest binding energy known for a stable negative atomic ion. However, a reinvestigation [240] of the Yb$^-$ ion has dismissed the claim for the existence of a stable Yb$^-$ ion and also for a long-lived, metastable one.

3. Theoretical approaches

The theoretical analysis and description of negative ions have followed two more or less independent, but interacting, directions one being predominantly computational, the other predominantly modelistic. Buckman and Clark [42] have given a very good survey of the various methods within both directions and their survey may be consulted for a more extensive description of the theoretical methods used most often during the last decade.

3.1. Computational methods

Theoretical models of neutral atoms are generally based on the central-field approximation, according to which each electron moves in a spherical symmetric potential representing the interaction with the nucleus and the average effect of the interaction with the remaining electrons. If the electronic motions are only weakly coupled, so the introduction of spherical symmetric potentials can account for the major part of the electron–electron interaction term of the Hamiltonian, then the remaining part can be treated as a perturbation. The configuration assignment which is associated with the use of the symmetric potential will then still make sense, but the energy levels associated with a given configuration will split into a multiplet of fine-structure components.

For negative atomic ions in the ground or multiply excited states the electron correlation is so large that the above perturbative approach no longer applies. The energy level can, however, still be associated with a mixture of different configurations and the wave function written as a linear combination of Slater determinants, which is the idea behind the configuration interaction (CI) and multi-configurational Hartree–Fock (MCHF) method. The additional configurations are often chosen to represent singly, doubly, triply or higher excited states of the dominant configuration applied in the Hartree–Fock procedure. In the MCHF approach the radial wave functions of the single-electron orbitals are optimized variationally in addition to the coefficients entering the configuration expansion of the total wave function, whereas the radial functions are kept fixed in the simpler CI approach.

The configurations (or Slater determinants) may also be chosen independently, i.e. without representing excitations of the same basic configuration, and then the method is called a multi-reference (MR) MCHF or MRCI. For heavier negative ions many calculations were originally performed in the frozen core-approximation in which the excitations are limited to the outermost bound valence electrons, which then represents the complete active space (CAS) and the method is then called CASSCF, the MC character being implicitly implied by the presence of CAS. At the beginning of the last decade it was realized that the interaction between the core and the valence electrons could not be neglected, if the purpose was to predict rather accurate binding energies for negative
atomic ions. In principle, energy levels can be calculated numerically to arbitrarily high accuracy by inclusion of an arbitrary number of configurations, but the calculation quickly become cumbersome and a large number of configurations is required for reasonable convergence. It is possible to minimize the computational efforts by including terms in the expansion of the total wave function, which depend on the interelectronic distances, i.e. from the outset accounts for a larger part of the electronic correlation. This is the idea behind the two-electron Hylleraas wave functions and the elaborations towards the development of possible candidates of correlated wave functions applicable to larger systems [241].

The electron affinities of the first- and second-row atoms have often been used as benchmarks for high-level electronic structure methods since many of these values are known experimentally to a very high precision [31], complications as geometric relaxation are not involved, and the computational demands required are still relatively modest [242]. For the hydrogen atom the electron affinity can be calculated ab initio far better than obtained experimentally, see Section 4.1. A, and for He the electron affinity of He(1s2s 3S) was calculated to an accuracy of $5 \times 10^{-3}$ meV, which is comparable with the obtained experimental accuracy [31], see Section 4.2. The difficulties the ab initio theoretical calculations have to deal with when the number of electrons increases, resulting in less accurate predictions, can be illustrated by the data available for the following elements, Li, Be, and B, for which the deviations between the calculated and the precise measured electron affinities increase reaching 1 meV for Be and 2 meV for B, see [31] and references therein. Recently, this level of accuracy has also been obtained for ab initio calculations of the electron affinities of the first (B–F) and second row (Al–Cl) atoms [242] based on CCSDT (coupled cluster with all single, double, and triple excitations [243]) calculations. The calculations involve basis sets of spdfgh quality, extrapolations to the one-particle basis set limit, and a combination of the coupled cluster with all single, double and triple excitations together with full configuration-interaction electron correlation. Scalar relativistic and spin–orbit coupling effects were taken into account.

Many electron affinity calculations for heavier atoms have been performed during the last decade using a selection of many-body perturbation-theory calculations, see Section 4.5. with Ca as a good example. Here it has been possible to reduce the deviation between the calculated and experimental electron affinity to a few meV, but the experimental value is known with an accuracy of 0.1 meV. For heavier atoms than Ca, calculations of electron affinities often have to be simplified due to the increasing number of electrons. The goals for such calculations have usually been an accuracy of the order of 10–20 meV when the predicted values are compared with the experimental data. Even this level of accuracy can be very demanding to reach with the consequence, that it can be extremely difficult to predict whether a very weakly bound negative ion is indeed existing as a stable ion or only in the form of a short-lived resonance; the alkaline-earth like Yb− ion (see Section 4.12) is a good example. If the complexity of the atomic structure is large as expected for the negative ions of the lanthanides (see Section 4.12) the calculations have sometimes been performed using a rather simple description of the electronic structure. Thus, it is not surprising that rather large discrepancies appear between the predicted electron affinities and the experimental results obtained within the last few years. The discrepancies can be of the order of 0.5–1 eV.

The approaches described above can also be used for calculations of resonance properties, in addition to the bound state properties, by inclusion of the continuum states in the configuration expansion. More than three decades ago Nicolaides [244] considered three principal approaches to resonance computation, which still may be considered appropriate [42]: (i) computation of the wave
function of continuum states from which the resonance parameters are obtained via the analysis of scattering matrices or eigenphase shifts; (ii) direct calculation of complex energies of decaying states by treating the resonance as an eigenfunction of a non-Hermitian system, and (iii) computations that treat resonances like ordinary bound states and neglect interactions with the continuum as a first approximation [42].

Many of the methods applied during the last decade were developed previously [42]. Particularly two of these methods have attracted interest; the R-matrix method, which belongs to the first of the three categories mentioned by Nicolaides, has been used extensively with great success to describe the photodetachment cross sections for many of the lighter negative ions ranging from hydrogen to calcium (see Section 4) in the region below double-electron detachment. Over the last number of years many different approximations have been successfully applied to the evaluation of accurate photodetachment cross sections. These techniques include the close-coupling R-matrix method, many-body perturbation theory (MBPT), multi-channel quantum theory, the random-phase approximation with exchange (RPAE), and more recently, the relativistic random-phase approximation (RRPA); these methods have recently been described and compared in a review article by Ivanov [52] plus references therein.

The other example is the complex-rotation method, which belongs to the second of the three categories. It has been used to obtain accurate structural information about the properties of resonance parameters, such as energies and widths.

**The R-matrix method:** The underlying idea of the R-matrix theory is that it is possible to separate the configuration space into two regions, an inner region often called the reaction volume and an outer region. For the energy region below the double-detachment threshold, negative ions like H\(^-\) are described as exactly as possible, taking all known interactions into account; for negative alkali metal ions it may be adequately to treat the ions as two active electrons moving in a central field resulting from the nuclear charge and the frozen inner shell electrons. In the outer region, only one electron is allowed to move, and thus only single-detachment processes are considered. The R-matrix method was already developed in the 1970s [245,246] particularly at the Queen’s University of Belfast and subsequently applied to predict a large number photo ionization cross sections for positive ions of astrophysical interest within the Opacity project [247]. Experimental tests of the Opacity projects results have first been experimentally possible in recent years [148,149] and the calculated cross sections reproduce in general the experimental data very accurately.

The eigenchannel R-matrix method [248–250] aims to determine variationally an orthogonal and complete basis set of wave functions, named the eigenchannel wave functions, at a given energy \(E\), whose logarithmic derivatives are constant across a reaction surface \(S\) enclosing a reaction volume \(V\). For treatment of two-electron excitations, the reaction volume \(V\) is that part of a six-dimensional configuration space for which both electrons lie within a sphere of radius \(r_0\). For each range of excitation energy \(r_0\) is chosen to be sufficiently large that the probability of both electrons being outside \(r_0\) is negligible, and thus \(r_0\) has to be large enough to encompasses all possible doubly excited-state wave functions in the energy range considered. The many-electron interactions within the reaction volume \(V\) can be treated by bound state, configuration interaction (CI) technique applying a basis of independent electron orbital wavefunctions obtained often from a model potential for the singly charged, positive-ion core and LS coupling to represent the many-electron wavefunctions. The applicability of the model potential is tested by calculating the energies of excited states belonging to the positive ion; a very good agreement with the experimental energies can usually be obtained which
indicates that the applied wave functions are suitable for the problem studied. At a given energy \( E \), the wave function inside the reaction volume is then described as a linear combination of the eigenchannel wave functions generated.

In the outer region all the long-range interactions are treated numerically by close-coupling procedures to obtain a basis set of multi-channel wave functions that can describe the outgoing electron and the residual neutral atom with the effects due to the polarization of the residual atom included. Finally, the linear combinations of the multi-channel basis functions for the inner and outer regions are matched at the reaction surface to obtain the exact final-state wave function that satisfies the incoming wave boundary conditions. The method described above has been used with significant success by Starace and coworkers to study the photodetachment cross sections of He\(^-\) and the alkali metal ions Li\(^-\), Na\(^-\), and K\(^-\), see Sections 4.2 and 4.4.

Depending on the complexity of the photodetachment spectra the resonance energies and widths can then be obtained either by fitting of the calculated partial cross section to a resonance profile formula, or one may analyse the eigenphase sum as a function of energy. The characterization of the doubly excited state for the resonances in the cross section spectra is achieved by using a projection operator method. The radius of the \( R \)-matrix sphere, \( r_0 \) was for He\(^-\) and the alkali metal ions chosen to be 180 a.u., large enough to encompass the doubly excited states in the energy range considered.

To give an impression of the numerical details applied to calculate the photodetachment cross section for He\(^-\) (1s2s2p \( ^4P \)), see Section 4.2, 58 closed type (i.e. zero at \( r_0 \)) and two open-type (i.e. non-zero at \( r_0 \)) one-electron orbital wave functions were calculated for each of the orbital angular momenta \( l \), where \( l \) can range from zero to six. In total 1912 closed-type two-electron configurations were included in the calculation for the final state wave function used to describe the dominating \( ^4P_e \) channels.

The \( R \)-matrix method has also been applied to describe multi-photon detachment rates within the \( R \)-matrix-Floquet theory, which combines the \( R \)-matrix theory of atomic processes with the Floquet ansatz [251,252]. In both the inner and outer regions, the Schrödinger equation can be transformed into a system of time-independent coupled equations by using the Floquet–Fourier expansion [251]. The \( R \)-matrix Floquet theory of multi-photon processes, in which the coupling of the negative ion and the laser field is described non-perturbatively, have been used to investigate multi-photon processes for a number of negative atomic ions, such as H\(^-\) (see Section 4.1) and the halogen ions (Section 4.10). The calculations have also treated the effects of autodetaching resonances on the multi-photon spectra.

**Complex-coordinate rotation:** The complex-coordinate rotation method was developed in the 1970s [253–256]. It allows a resonant state to be calculated as a bound square-integrable state of a complex rotated Hamilton with a complex eigenvalue. The theoretical aspects of the complex rotation method have been discussed previously, see e.g. [42,257]. The method utilizes a rotation of the particle radial coordinates into the complex plane, \( r \rightarrow re^{i\theta} \). The transformed Hamiltonian, \( H(\theta) \) may then support discrete eigenfunctions with complex energies, \( ce^{i\phi} \), provided that \( \theta \) is larger than \( \phi/2 \). The complex energies are independent of \( \theta \), and may correspond to resonances.

The rotation of the particle radial coordinates will influence the continuum that starts at each threshold, since the continuum will be rotated \( 2\theta \). This will leave any bound state unaffected, but if the continuum is rotated far enough it might reveal complex eigenvalues that correspond to the poles in the \( S \)-matrix, which will correspond to resonant states. The real part corresponds to the position of the resonance, whereas the imaginary part corresponds to the half-width.
The complex-coordinate rotation method has been used rather extensively and with significant success to predict energies and widths of doubly excited states in negative ions, particularly for ions with two active electrons, such as $\text{H}^-$, $\text{He}^-$, or the negative alkali ions, see Sections 4.1, 4.2 and 4.4. For ions like $\text{Li}^-$, the interaction between the two active electrons and the $1s^2$ core is described by a Hartree–Fock potential plus a polarization potential.

The difference between the treatment of the two-electron system like $\text{H}^-$ and the three electron system of $\text{He}^-$ is mainly in the size of the problem, and this has been a challenge to theorists. To treat three electrons fully is at the limit of what many computers can handle at the present time. Especially, it is important to keep the number of one-electron eigenfunctions to a minimum. For this purpose the so-called B splines are introduced [258]. The crucial point in the three-electron calculations is the approximation made by describing the radial coordinates with a certain set of B splines. The angular integrals are usually performed analytically using Racah algebra [259,260], which also can handle the special problems related to three equivalent electrons using coefficients of fractional parentage. Within the last few years, it has been possible to perform accurate predictions for resonances belonging to triply excited state in $\text{He}^-$, see Section 4.2.

3.2. The hyperspherical-coordinate approach

The numerical methods discussed above are to a significant extent developed from the independent-particle approximation and not particularly tailored to deal with the electron correlation. They are, in principle, capable of predicting a negative-ion spectrum to an arbitrarily high accuracy, but they do not provide the link to an understanding or a visualization of the underlying electronic structure responsible for the spectrum. It would be valuable if the understanding and classification of the negative-ion structure, especially of the doubly excited states, in terms of quantum numbers could be accomplished by models in which the electron correlation was build in from the outset. The final goal would then be a model, which combines the two assets, numerical accuracy and qualitative understanding. This goal has still not been reached.

The hyperspherical model [261–263] has provided a much better understanding of the properties of the electronic system for which electron correlations plays an important role, like $\text{H}^-$, but it is not competitive with the computational methods with respect to numerical accuracy. An alternative, which also treats the three-body system as a whole, sets up a correspondence between $\text{H}^-$ and $\text{H}_2^+$, using the language of molecular orbitals and potential wells to establish a quasimolecular model [264,265]. Both these approaches have common elements and been useful in understanding doubly excited states. The description given below is intended only to be sufficiently detailed to give a taste of the origin of the quantum numbers used for labelling the $\text{H}^-$ resonances (see Section 4.1).

In the hyperspherical-coordinate approach the six coordinates required to describe the two electrons in $\text{H}^-$ are chosen to be: the hyper-radius $R = (r_1^2 + r_2^2)^{1/2}$, which reflects the size of the system with $r_1$ and $r_2$ being the two electron-nuclear radii, the hyper-angle $\alpha = \arctan(r_2/r_1)$, which is a dimensionless quantity related to the radial correlation of the system, the angle $\theta_{12}$ between the position vectors of the two electrons, plus three Euler angles to describe the localization of the triangle nucleus and electrons in space. When expressed in terms of these coordinates, the two-electron Schrödinger equation is separable into a set of hyper-radial equations that can be solved in the adiabatic approximation where the motion in the hyper-radius is assumed to be much slower than that in the angles; the dependence on $R$ enters through adiabatic potentials,
analogous to those arising in the Born–Oppenheimer approximation for molecules. For a given \( R \) the potential energy of the system can be represented by an effective charge, which is a function of \( \alpha \) and \( \theta_{12} \) [266].

A resonant state is obtained in a situation where the two electrons are bound to the nucleus, i.e. they remain at finite distance and hence, in the hyperspherical representation, at a finite hyper-radius. A resonance is then described as a state bound in one of the adiabatic hyperspherical potential curves. For large \( R \), the adiabatic potentials converge on those appropriate for the description of one distant electron bound in an induced dipole potential, associated with a neutral-atom threshold of a given main quantum number \( n \). For small \( R \), the potential curves exhibit different behaviours depending on the symmetry of the associated wave functions, normally characterized by the quantum number \( A \).

The \( A = + \) curves correspond to resonances that have an approximate antinode near \( \alpha = 45^\circ \), while those with \( A = - \) have a node under similar conditions. The \( A = + \) and \( A = - \) states correspond, respectively, to the electrons being radially in phase or out of phase when approaching the nucleus, as in the symmetric and asymmetric stretch modes, respectively, of a linear tri-atomic molecule. The adiabatic hyperspherical potential curves for the \( A = 0 \) states are generally repulsive for all \( R \) and thus hold no bound states. The wave functions for \( A = 0 \) states are highly asymmetric with one of the electrons being located close to the nucleus and the other far away; furthermore there is little radial correlation associated with the \( A = 0 \) states [267].

Among the \( ^1P^o \) curves associated with each \( H(n) \) threshold, there is a single \( A = 0 \) curve, while there are \( n - 1 \) curves of \( A = + \) and \( A = - \) character, respectively. The resonant states supported by a specific potential curve form a series or channel and are labelled according to their symmetry properties. Quite generally, both the \( A = + \) and \( A = - \) curves have minima that support resonances. The minima of the \( A = + \) curves are located at smaller \( R \) than those associated with the \( A = - \). Consequently, the \( A = + \) resonances are excited more easily from the ground state of \( \text{H}^- \) than the \( A = - \) resonances, since the wave functions of the \( A = + \) resonant states more closely resemble the localized ground state wave function. In the lowest level of a given channel of the \( A = + \) type (denoted by \( m = n \)) the two electrons spend considerable time at a comparable distance to the nucleus. They interact strongly and the state is thus quite unstable, resulting in rapid autodetachment. For higher lying resonances in the channel (i.e., for a given \( A = + \) curve) the states labelled by \( m = n + 1, n + 2 \ldots \), form a series of resonances converging on the associated threshold that become increasingly dipole-like. A resonance associated with an \( A = - \) curve can roughly be characterized by one electron being fairly distant from the excited, neutral hydrogen atom. The interaction between the electrons is weak, primarily through the induced dipole moment, and thus the resonance is more stable against autodetachment. There is again an infinity of resonances denoted \( m = n + 1, n + 2 \ldots \), converging on the neutral atom threshold, corresponding to an infinite dipole series.

A consequence of the strong correlation in the doubly excited states under consideration is the inadequacy of the one-electron angular momenta quantum numbers. Instead Herrick and Sinanoglu [268,269] proposed the use of the \((K,T)\) quantum numbers as collective quantum numbers that describe the angular correlation. \( K \) is proportional to the average \( \langle r_\varphi \cos \theta_{12} \rangle \), where \( r_\varphi \) is the distance to the inner electron. The \( T \) quantum number can be interpreted as the projection of the angular momentum \( L \) on the inter-electronic axis. These quantum numbers are used to label the different hyperspherical potential curves discussed above, i.e., they specify the different channels. A resonance of parity \( \pi \) can be described by the symbol \( \kappa(K,T)_m^{2S+1}L^\pi \), where the last part denotes the usual term.
4. Review of specific results by elements

4.1. Hydrogen

The H\(^{-}\) ion occupies a special role in the study of negative atomic ions. It is the simplest ion of this type, its dipole potential can support an infinite series of states converging to the H\((n)=2, 3, 4,\) etc. thresholds, and it represents one of the few available three-body two-electron atomic systems. Among the latter the H\(^{-}\) ion is the most interesting, since the electron correlations are especially strong for this ion. The H\(^{-}\) ion has therefore attracted a very large interest from theorists both before and after the Buckman–Clark review appeared a decade ago [42] and theory has so far been able to explain or predict the general behaviour of the H\(^{-}\) ion, e.g. the photodetachment cross section and the positions and widths of its resonances.

Experimentally, the H\(^{-}\) ion presents many difficulties since the resonance structures are located more than 10 eV above the ion ground state, which has severely limited the experimental studies. Whereas electron-scattering and heavy particle collisions still were used in the 1980s to obtain experimental information about the H\(^{-}\) ion [42], allowing several experimental groups to contribute to the experimental research of this ion, the higher resolution demanded for more detailed investigations called for experimental approaches based on photon-impact, which only have been available to a few groups. Most of the experimental information available about the H\(^{-}\) ion was obtained before 1992 by Bryant and coworkers [50] using the relativistic H\(^{-}\) beams at the Los Alamos Meson Physics Facility combined with conventional lasers; more recently the use of the ASTRID storage ring has been explored in combination with energetic laser light produced by high harmonic generation [96,98], see Section 2.2 where the two-photon techniques are described.

Bryant and Halka [50] have given a comprehensive review of the experimental data obtained at the Los Alamos Facility, whereas Buckman and Clark’s review [42] also includes the experimental results obtained from electron scattering and a survey of the theoretical studies. The experimental H\(^{-}\) studies performed at the ASTRID storage ring are summarized by Balling et al. [98]; these studies have, however, so far been limited to the photon energy region near the H\((n=2)\) threshold.

\(\text{H}^{-}\) (1s\(^2\) 1S): Elaborate numerical calculations [31,270] have yielded a very accurate electron affinity of the hydrogen atom (0.754 203 75(4) eV) [31], a value which is orders of magnitude more accurate than the best experimental value available (0.754 195(20) eV) [271], obtained by laser photodetachment threshold technique with emission of a p-electron. Recent attempts to improve the experimental value have so far not been successful [31,272] and it seems unlikely that a determination of the electron affinity for hydrogen can benefit from the new methods described in Section 2.

Calculation of the ground state energies for H\(^{-}\) and other three-particle systems like He by variational and other means have provided benchmark tests of the relative accuracies and efficiencies of various methods of calculation. Traditionally, the best results have been obtained by variational calculations in Hylleraas coordinates and the theoretical value quoted above was obtained by Drake et al. [31,270] using a triple basis set in Hylleraas coordinates to describe the wave function.

The H\(^{-}\) ion has two bound states: the ground 1s\(^2\) 1S state and the doubly excited 2p\(^2\) 3P state. The latter has not been observed till date. It was predicted computationally nearly 40 years ago and its energy computed repeatedly, most recently and very precise by Bylicki and Bednarz [273]. There is no doubt about its existence, but the experimental non-appearance is linked to the lack of an initial state from which it can be reached [273].
4.1.1. Resonance structures

Resonances of $\text{H}^-$ near $\text{H}(n=2)$: In the unique series of experiments performed by Bryant et al. before 1992 the gross behaviour of the photodetachment cross section as well as detailed studies of $^1\text{P}$ resonances near the $n=2$–8 thresholds were explored. The initial observations of the lower lying resonances were in remarkably good agreement with the calculations by Broad and Reinhardt [274]. The detailed investigations of the higher lying resonances prompted theoretical investigations in the relevant energy regions [42,50] and again the agreement was good. More recently, the New-Mexico group has also explored the application of two-photon detachment technique to study a $^1\text{D}$ resonance located just below the $n=2$ threshold [82] and extended this work to include isotope shifts [275,276], see below.

The specific properties of atomic hydrogen lead to a degeneracy of different angular momentum states for the excited states and therefore the existence of the linear Stark effect of this atom. An immediate consequence of this phenomenon is that the excited hydrogen states in an electric field can possess a permanent electric dipole moment. The resulting potential will then be a dipole potential, which has a distinct $r^{-2}$ character. Considering an electron approaching a hydrogen atom excited to $n=2$, the electric field from the distant electron will polarize the atom and the incoming electron will feel a potential, which consists of a repulsive centrifugal term and an attractive dipole potential, both of which behave as $r^{-2}$. Depending on the relative strength of the two terms, the electron may or may not be bound to the excited state. This problem was first treated by Gailitis and Damburg [277], who showed that an infinite series of $\text{H}^-$ resonances converging to the excited state threshold could be expected to exist. The infinite series satisfies an interesting recurrence relation, which predicts that both the binding energies of the states and their widths become exponentially smaller going up the series [98].

The resolution in most of the one-photon studies at Los Alamos was roughly 8 meV, set by the combined contributions from the momentum spread of the relativistic ion beam and the angular divergence of the crossed-beam geometry. While this technique was extremely versatile and provided a great deal of information about broad resonances, it was clear from the on-going theoretical development that the narrower features in the cross section could not be resolved. However, a new approach, which improves the resolution in the region near the $\text{H}(n=2)$ threshold, was introduced at the ASTRID storage ring in 1996 as described in Section 2.2. This approach was based on the use of high harmonic generation of laser light with an energy close to 11 eV combined with a strongly reduced energy spread of the $\text{H}^-$ (or $\text{D}^-$) ions. Initially the resolution was improved by a factor of about 40 [98]; later it was possible to reduce the relative velocity spread of the uncooled beam still more using electron cooling of the negative hydrogen beam [99]. Hereby it became possible to measure the width of the lowest lying $^1\text{P}$ resonance.

In the hyperspherical-coordinate description the doubly excited $\text{H}^-$ states are described by the symbol $\sigma(K,T)_m^{2S+1}L^e$ using the collective quantum numbers $K$, $T$, and $A$ (see Section 3) with $n$ being the main quantum number of the neutral atom threshold, whereas the dipole states are denoted by $m$ ($m$ does not refer directly to a quantum number of the outer electron, since $m=4$ represents the main quantum numbers 7–9 of the outer electron for $n=2$). A slightly more compact notation is often used, when $(K,T)$ is replaced by $v=1/2(n-1-K-T)$ to describe the angular correlation, where $v$ is the bending vibrational quantum number of the three-body rotor [46]. The observed $\text{H}^-$ resonances observed so far have $v=0$ [46].
Bryant and coworkers [50] observed the first $^1P$ members of the two series $2\{0\}_m^-$ and $2\{0\}_m^+$ in the 1980s, the former as a small and narrow structure located below the threshold, the latter as a larger and rather broad structure (shape resonance) located above threshold. The short range attraction should be strong enough to form a dipole series of $A=-$ resonances located below the threshold, but too weak to form a similar series above threshold [98], where only a single resonance can be expected to appear. Due to the limited experimental resolution Bryant and coworkers were able only to observe the first member of the $A=-$ series, and the energy quoted for this resonance (10.9264(6) eV) disagreed from most of theoretical expectations by about 2 meV or four times the experimental uncertainty [98].

By means of about 11 eV laser light, produced via high harmonic generation, Balling et al. [98,97] observed two narrow (Feshbach) resonances $2\{0\}_3^-$ and $2\{0\}_4^-$ below the threshold and the broad $2\{0\}_2^+$ resonance above (for the $A=-$ resonances the $m$ numbering is $m=n+1$, $n+2$, etc., whereas the $A=+$ resonances have the numbering $m=n$, $n+1$, etc.). Fig. 20 shows the relative photodetachment cross section vs. the effective photon energy in the energy region around the $H(n=2)$ threshold.

The energies of the narrow resonances (10.9243(2) and 10.9519(2) eV, respectively,) are in excellent agreement with the most recent theoretical predictions [98]; the disagreement between the previous experiment and theory for the first Feshbach resonance was hereby eliminated. The ratio between their energies relative to the threshold was predicted to be close to 30 [98], which was in good agreement with the experimental results (ratio 26(5)). The energies of the two narrow resonances can be used to predict the position of the next member in this dipole series, $2\{0\}_5^-$, which should be located about 40 μeV from the $H(n=2)$ threshold. This energy is, however, comparable to the fine-structure splitting of the $H(2p)$ state of the neutral atom, and thus one can no longer neglect the effect of the relativistic interaction and QED effects. The proper inclusion of these terms leads to a lifting of the degeneracy, destroying the dipole potential. This problem has been studied in detail by Lindroth et al. [94] and by Purr et al. [278,279]. They concluded that the dipole series is terminated after the third member and that this $2\{0\}_5^-$ state is shifted closer to the threshold, only 0.19 μeV below the $H(2p_{1/2})$ state. It will be very difficult experimentally to observe the third member of this dipole series, since its intensity will be nearly a factor of $30^2$ smaller than the intensity of the first member.

The resolution needed to study the width of the $2\{0\}_3^-$ resonance demanded electron cooling of the applied $D^-$ ion beams [99]. The resolution of the uncooled beam was about 180 μeV (FWHM), which did not allow a detailed test of the predicted width. Successful cooling improved the resolution by a factor of about 6. Fig. 21 shows the relative photodetachment cross section vs. effective photon energy in the vicinity of the $^1P\ 2\{0\}_3^-$ resonance with the solid curve representing the best fit to a Fano profile convolved with the experimental resolution. The width was determined to be 37(3) μeV and the slight asymmetry of the structure yielded an asymmetry parameter $q$ of $-16(3)$. Within the quoted error bars the experimental results were in good agreement with several of the available theoretical predictions, such as Lindroth et al. [94], Venuti and Declava [93] and several others, see [99]. The width of the $2\{0\}_4^-$ could not be measured with the resolution obtained by electron cooling; the width is expected to be about a factor of 30 smaller, or in the range of $1$–$2$ μeV. The theoretical calculations had correctly predicted the properties of the negative hydrogen ion with a high accuracy; the complex-rotation method applied in several variants by Ho [83], Lindroth et al. [90,94], Kuan et al. [89], and Chen [95] seems to provide a very good description of the structure of the negative hydrogen ion.
Fig. 20. Relative photodetachment cross section for D− vs effective photon energy [97]. (a) The measured cross section has been normalized to theoretical results of Lindroth [86] (solid curve). The data of the 2{0}−3 resonance at 10.9277 eV exceeds the vertical scale of the plot. (b) Blow-up of the region near the 2{0}−3 resonance; the solid curve is a fit to a Fano profile convolved with the photon energy resolution. (c) Blow-up of the region near the 2{0}−4 resonance at 10.9553 eV. Here the solid curve is a fit to a Gaussian profile.

The hydrogen experiments can be performed applying either H− or D− ions, which allows for an investigation of the isotope effects. The very narrow A=− structures permit a study of even small shifts. Both the experimental and the theoretical efforts have been centred towards determining the so-called specific mass shift (or mass polarization), since the other terms contributing to the isotope effect can be accounted for by rescaling of the energies according to the appropriate reduced mass [98]. While a rather large specific mass shift of 486 μeV has been calculated for the 1S ground state of H− by Drake [280], Lindroth et al. [94] predicted very small mass shifts (only about 10 μeV) for the 2{0}−3 resonance. This prediction was confirmed by the experimental data obtained at the ASTRID storage ring [98,97].

The shape resonance located just above the H(n = 2) threshold (see Fig. 20) and classified as 2{0}+2 is the largest resonance in the H− photodetachment spectra and has played an important role in the understanding of electron correlations [50,281]. It is unique that its potential has three classical
turning points and that it is the only resonance of its type observed in the H\(^-\) photodetachment spectra. The energy of this resonance has been predicted in good agreement with the observed one of 10.971 eV, but the resonance width still causes some problems. The width has been calculated to be within the range of 16.9–18.6 meV [84–86,90,282], whereas the experimental results of 21(1) or 30(1) meV reported by the New-Mexico group [281] and the more recent value of 25(2) meV, obtained at the ASTRID storage ring [283], are indicating a somewhat larger width. In the latter experiment a new-positioning method was applied to prevent changes in the overlap between laser and ion beams over the large kinetic-energy range employed. In order to establish the width, the energy and asymmetry of the shape resonance a function is needed which coincides well with the experimental data. Traditionally, a Fano function [176] has been used to fit the observed data; this function requires, however, that the parameters (such as the width) should be constant with respect to energy across the width of the resonance. This may not be the case for this resonance as pointed out by Halka et al. [281].

The lowest lying resonances in H\(^-\)(\(^1\)S, \(^3\)P and \(^1\)D) were already studied in 1972 by electron transmission spectroscopy [284], but only one of these, the \(^1\)D resonance, has been investigated applying photoexcitation technique [82,275,276]. Stintz et al. [82] observed this resonance by means of two-photon technique and the data have later been improved [275,276] so the energy now is established as 10.873 2(27) eV above the ground state of H\(^-\) with a width of 8.9(12) meV. The position and width of this resonance agree very well with the predictions made by several theoretical groups [285–288] and with the later very precise calculation by Chung and Chu [289]. The latter were also able to reproduce the peak cross section for the two-photon detachment cross section (3.1 \(\times\) \(10^{-49}\) cm\(^4\)). It should be noted, however, that the isotope effect reported for the \(^1\)D resonance [275,276], with a specific mass shift of −2.4 (11) meV, disagrees significantly from several theoretical estimates, which only predict a specific mass shift value about −0.1 meV [275].
One-photon excitation of $\text{H}^{-}$ ions present in their ground state can only lead to population of $^{1}\text{P}$ states, whereas two-photon excitation can lead to population of $^{1}\text{D}$ or $^{1}\text{S}$ states, but so far $^{1}\text{S}$ states have not been observed. In the energy region close to the $\text{H}(n=2)$ threshold triplet states are also present, but the selection rules for photon impact prohibit the exploration of such states, which previously have been observed in elastic electron-scattering experiments [42]. Theoretical calculations, which have been proved to yield excellent agreement with the experimental photon-impact data available, have been used to generate energies and widths of several of the resonance states which have not been observed so far. Several methods have been used for this purpose (see [98]), such as the saddle-point complex-rotation method used by Chen [87] or the numerically accurate Harris–Nesbet variational method applied by Gien [88].

**Resonances of $\text{H}^{-}$ near $\text{H}(n=3–8)$:** Several series of doubly excited $\text{H}^{-}$ resonances were observed by Harris et al. [144] in the energy region covering the $\text{H}(n=3–8)$ thresholds and these pioneering data and their identification were reviewed by Bryant and Halka [50] as well as by Buckman and Clark [42]. At least three Feshbach-type resonances were clearly visible converging on each of the thresholds $n=5$, 6, 7, and 8. There has, however, been no new experimental data related to this energy region since 1990. The high-resolution technique applied to study the narrow $A=-$ resonances below $\text{H}(n=2)$ [98,99] at the ASTRID storage ring could also be applied to investigate some of the narrow resonances predicted below the $\text{H}(n=3)$ threshold. The main experimental problem will be the intensity of these resonances, which for the most intense one is expected to be a factor of 20–30 smaller than for the observed $2\{0\}^{-}_{3}$ resonance or similar to the $2\{0\}^{-}_{4}$ one.

In contrast to the lack of new experimental data there has been a significant activity of several theoretical groups. Some of the theoretical studies mentioned in connection with the resonances located near the $\text{H}(n=2)$ threshold, e.g. Lindroth [86] and Venuti and Decleva [93], also contain predictions for resonances located below the $\text{H}(n=3)$ and $\text{H}(n=4)$ thresholds. Similar studies have been reported by Chen [290], Ho [291], Ho and Bhatia [282], Kuan et al. [89], Tang et al. [85], Ndao et al. [292], and Odgers et al. [293].

The most extensive studies have, however, been performed by Bylicki and Nicolaides covering the entire $\text{H}^{-}$ resonance spectrum up to the $\text{H}(n=4)$ threshold [294,295]. Their calculations were performed by implementing the theory of resonances which is expressed as a complex eigenvalue Schrödinger equation (see [296] and references therein), using as the cut-off criterion states with widths down to about 3 neV. In order to observe such narrow resonances the present high-resolution laser technique has to be improved by one to two orders of magnitude. However, the limiting factor in the case of the $2\{0\}^{-}_{3}$ resonance was not the lasers, but the velocity spread of the negative $\text{D}^{-}$ ions limiting the width studies to about 30 μeV or four orders of magnitude larger than the width-limit given above. 76 resonances having $^{1}\text{P}^{o}$, $^{1}\text{D}^{o}$, or $^{1}\text{F}^{o}$ symmetries [294] were identified and characterised (energies and widths), together with 70 resonances with $^{1}\text{S}$ and $^{1}\text{D}$ symmetries [295]. In addition a large number of $^{1}\text{P}^{e}$ [297], $^{3}\text{P}^{o}$ [298] or $^{3}\text{P}^{e}$ resonances [299] were reported to appear in the $\text{H}^{-}$ resonance spectrum up to $\text{H}(n=5)$. The overwhelming majority of these resonances have not been detected experimentally and many of these will be extremely difficult if not impossible to observe since they will demand ultra-sensitive techniques, not yet available, capable of dealing with the small widths. The results obtained by Bylicki and Nicolaides were classified according to the Gailitis–Damburg model of dipole resonances [277] (a product of the $r^{-2}$-like potential) and there are unperturbed as well as perturbed series present, in analogy with Rydberg spectra of neutrals.
Fig. 22. Detachment data for the $e^- + D^-$ collision process obtained at the ASTRID storage ring [195] compared with previously reported results [199], the latter connected by means of a solid line.

and positive ions. The perturbed series result from interchannel coupling and the remaining electron correlation.

4.1.2. Search for $H_2^-$

Doubly charged negative atomic ions have several times been reported to exist as stable ions, but none of these observations have been able to stand the test of time. The large repulsive energy of two electrons confined within a single atom means that it is unlikely that such ions should exist with lifetimes long enough to be observed with conventional methods. The most extreme case would be $H_2^-$ with three negative charges and only one positive. In the early 1970s this ion was reported to exist [197–199], because collisions between electrons and $H^-$ ions resulted in short-lived resonances located at 14.5 and 17.8 eV, which is above the threshold for complete breakup (0.75 + 13.6 eV). The resonance features had widths of approximately 1 eV (or a lifetime of the order of $10^{-15}$ s). They were attributed to doubly-excited states in the $H_2^-$ ion such as the $2s^22p\,^2P$, and the $2p^3\,^2P$ or $^2D$ states [300,301].

In 1994 the previously assumed agreement between experiment and theory was questioned [302] and R-matrix calculations could not support the original predictions showing no evidence of the resonances previously reported to exist. Calculations [303] also ruled out the possible existence of triply excited $H_2^-$ states with $^2P^e$ symmetry.

The experimental reinvestigation of the $H_2^-$ ion was carried out by Andersen et al. [195], who performed a merged $e^-–H^-$ beam experiment using the electron cooler at the ASTRID storage ring. Fig. 22 shows their data compared with the previously reported single-beam pass results [199]. No resonance structures can be seen in the storage ring data, and consequently electron scattering on ground state $H^-$ ions does not result in resonance structures. The possible existence of short-lived $H_2^-\,^2L$ states was hereby eliminated. The experimental rejection of the existence of doublet $H_2^-$ states was also the conclusion of a subsequent experimental study by Tanabe et al. [304]
using the Tokyo storage ring. The previously reported resonance structures were most likely experimental art effects, as first suggested by Robicheaux et al. [302].

The issue of resonances in \( \text{H}_2^- \) was, however, far from over. Sommerfeld et al. [305,306] performed large-scale calculations in the framework of the complex-rotated Hamiltonian, which indicated strong correlation effects in this ion. They reported that a resonance state with three equivalent electrons and one proton should exist; the triply excited \( 2p^3 \ 4S \) state of \( \text{H}_2^- \) should be located 1.4 eV above the \( 2p^2 \ 3P \) threshold of \( \text{H}^- \) (which is below the two-electron detachment limit) and with a lifetime of \( 3.8 \times 10^{-16} \) s (a width of about 1.6 eV). The predicted resonance was not in contradiction with the experimental data, since the merged beam experiments mentioned above only could populate doublet states. The observation of this \( 4S \) resonance will, however, be difficult since it involves electron scattering of \( \text{H}^- \) ions present in the excited \( 2p^2 \ 3P \) state, but this state has never been observed.

Morishita et al. [307] performed a reinvestigation the existence of resonances in \( \text{H}_2^- \) ions and calculated the hyperspherical adiabatic potential curves for \( \text{H}_2^- \). For \( ^4S^o \) symmetry all the potential curves are repulsive, and thus no bound or resonance states should exist. This conclusion clearly contradicted the results reported by Sommerfeld et al. as mentioned above. Furthermore, Morishita et al. also calculated the potential curves for several values of the nuclear charge \( Z \) ranging between 1 and 2 and showed that no resonance or bound state can exist for \( Z \) less than 1.6. Morishita et al. concluded that the \( ^4S \) resonance proposed by Sommerfeld et al. [305,306] was the result of an artifact of their numerical calculation. This statement stimulated additional interest in properties of the \( \text{H}_2^- \) ion.

Bylicki and Nicolaides [308] performed complex coordinate calculations showing that the \( \text{H}_2^- \) spectrum has at least two complex eigenvalues corresponding to quasi-localized \( ^4S \) states. The first is localised 1.43 eV above the \( \text{H}(n = 2) \) threshold, the second 0.46 eV above \( \text{H}(n = 3) \) with the widths of the resonances being rather large, about 1.7 and 0.29 eV, respectively. The energy and width of the former of the two resonances are in good agreement with the original prediction of a \( ^4S \) state given by Sommerfeld et al. [305,306]. The authors conclude that although the complex eigenvalue for the lowest \( ^4S \) state exists, its characteristics still challenge both theory and experiment through questions such as: can we expect with certainty that this broad state close to the threshold is observable and how—and to what extent will the calculated property be related to the expected energy-dependent features of the resonance structure, should it be observed? The final contribution to the exploration of the \( \text{H}_2^- \) ion has clearly not yet appeared.

Under special conditions, however, it may be possible to create multiply charged negative ions of hydrogen. Duijn et al. [309] have predicted, that such ions may be induced by super-intense laser fields. Using the high-frequency Floquet theory of laser–atom interaction they predict that a proton in super-intense laser fields can bind more than two electrons. The authors state that the fields and frequencies needed for binding \( \text{H}_2^- \) are within reach of lasers under construction and that even more highly charged negative hydrogen ions lies within experimental reach. These negative ions are stabilized against ionization from their very appearance.

4.1.3. Photon impact collisions

\( \text{H}^- \) has been the selected negative atomic ion for studies of collisions between negative ions and photons, electrons or heavy particles. These studies have mainly focussed on the cross sections for
one- and two-electron ejection from H$^-$ as a function of the energy of the collision partner (photon, electron, etc.). Single photon–H$^-$ collisions leading to one-electron ejection have played an important role in the history of H$^-$ [30]. The abundant presence of both hydrogen atoms and low-energy electrons in the ionized atmosphere of the Sun and other stars argues for the formation of H$^-$ by electron attachment. At the same time, subsequent photodetachment back to hydrogen atoms and electrons for photon energies larger than the binding energy of H$^-$ points to the importance of the opacity of these atmospheres to the passage of electromagnetic radiation [30]. Besides photodetachment, other collision processes involving H$^-$ are also important in stellar atmospheres. Prominent among these are collisions with neutral hydrogen or with protons that are abundantly present [30].

The single-photon detachment cross section of H$^-$ has previously received a considerable amount of attention for low photon energies, see [30,50,89,310] and references therein, and the main collision processes between H$^-$ and heavier particles have been reviewed by Esaulov [41]. In this and the following sections only the more recent development will be covered for photon- or heavy particle impact, whereas collisions between electrons and H$^-$ ions will be treated in Section 5 of this review.

Single-photon-impact collisions: Studies of single-photon two-electron ejection from H$^-$ at photon energies above the double escape threshold at 14.35 eV has been far more limited than those of the isoelectronic neutral He atom. The threshold behaviour for double photodetachment of H$^-$ has been explored both theoretically [311] and experimentally [312], but these studies have been restricted to just the first 1 or 2 eV above the threshold, a region also studied theoretically more recently by Nicolaides et al. [313].

There exists so far no experimental data for higher photon energies even these now may be obtainable at synchrotron facilities, and only a few theoretical studies have been reported. Broad and Reinhardt [274] conducted in 1976 a pioneering study covering photon energies in the range up to 69 eV, making a prediction of the branching ratio between double and single detachment of H$^-$ possible. This branching ratio has recently attracted a good deal of interest for two electron systems, particularly for He, and the analogous branching ratios for other projectiles have also been explored.

In 1997 Meyer et al. [314] reported cross section calculations, based on the eigenchannel $R$-matrix method, of two-electron photoejection of H$^-$ and He, covering the range 14.4–110 eV for the former and 79–460 eV for the latter. The ratio for double- to single-electron ejection reaches a maximum for H$^-$ in the photon range of 25–35 eV of 0.094(6), a value 25–40% larger than predicted by Broad and Reinhardt [274]; at higher photon energies the ratio decreases reaching a value of about 0.044 at 110 eV. The calculations indicate that the maximum value for the branching ratio for H$^-$ mentioned above is about three times as large as the value for helium (0.037(1)). Furthermore, the maximum value occurs at an energy approximately six times smaller for H$^-$ than for He, relative to the double escape threshold; similar results have also been reported by Nicolaides et al. [313]. This is consistent with the small binding energy of H$^-$, since a smaller energy is required to remove one electron in H$^-$, and more energy is then available to remove the remaining electron.

The one- and two-electron ejections from H$^-$ at still larger photon energies (1–10 keV) were studied by Qiu et al. [315] using an accurate Hylleraas initial-state wave function and a correlated so-called 3C final state wave function [316], which consists of a sum of products describing the incoming Coulomb waves of the two electrons and a Coulomb distortion factor describing the electron–electron correlation. In the high-energy limit, the double-electron ejection is dominated only by the initial-state correlation, resulting in the asymptotic limit of 0.015 for the double- to single-electron ejection ratio. At the largest energy studied, 10 keV, the final-state correlation is found still to be
important, giving rise to an $E^{-1}$ high-energy behaviour for the double to single-electron ejection ratio. It should be noted that the asymptotic value for the branching ratio for H$^-$ (0.015) is lower than for helium (0.0167) although one might expect otherwise because of the stronger role of electron–electron correlation for smaller nuclear charge ($Z$). Several explanations for this behaviour have been proposed [314,315].

Multi-photon-impact collisions: During the last decade, intense lasers have made it possible to observe effects of multi-photon-absorption (Section 2.5) by atoms and ions, including the negative hydrogen ion [30,50]. Among notable effects are “above-threshold ionization” wherein more photons are absorbed than necessary to break up the system, the extra energy going to increase the kinetic energy of the ejected photo electron by multiples of the photon energy [30]. Experimental studies were first reported for H$^-$ by Tang et al. [317,318], who applied a CO$_2$ laser beam of laboratory photon energy of 0.117 eV in combination with the relativistic Doppler shift of the Los Alamos 800 MeV H$^-$ beam to excite the H$^-$ beam with photon-energies ranging from 0.08 to 0.39 eV, depending on the angle between the photon momentum and the H$^-$ beam (see Section 2.2). Detachment, which requires 0.75 eV, takes place therefore as the result of the absorption of two to nine photons or more. It was noted that the two-photon detachment data revealed intensity-dependent shifts of the H$^-$ electron detachment threshold energy; the threshold was located at larger photon energies as a function of the laser intensity, an effect known as due to the ponderomotive energy [50].

As pointed out in Section 2.5 negative atomic ions, and particularly the three particle H$^-$ system, are theoretically simpler systems for studies of multi-photon absorption than neutral atoms with their Coulomb fields and spectra. This has resulted in a significant number of theoretical multi-photon studies involving H$^-$ ions, far outnumbering the experimental investigations, and the theoretical studies have covered a much larger part of the multi-photon spectra than experimentally studied, which will be illustrated below. The difficulties associated with a precise determination of absolute multi-photon cross sections (see Section 2) have to some extent been responsible for this difference between theory and experiment, but multi-photon studies with negative ions as H$^-$ are experimentally often demanding due to the low density of the ion target.

The two-photon detachment cross section of H$^-$ for photon energies up to the one-photon threshold can illustrate the situation described above. There does not exist an experimental measurement of the two-photon detachment cross section in this energy range (0.75–1.50 eV), but many theoretical predictions, see [319,320] and references therein. The calculated two-photon detachment cross section, Fig. 23, raises sharply above the one-photon detachment threshold at 0.75 eV and reaches a maximum of $2.3 \times 10^{-48}$ cm$^4$ s at a total photon energy of about 1.12 eV ($2 \times 0.56$ eV) before decreasing to about $1.9 \times 10^{-48}$ cm$^4$ s at 1.50 eV ($2 \times 0.75$ eV). There is a very good agreement between many of the calculations of this cross section using different approaches such as the many-electron, many-photon theory (MEMPT) [321], the complex Sturmian function [322], the B-spline method [323], and the more recently reported variationally stable, coupled-channel hyperspherical approach [319], whereas the variationally stable, uncoupled adiabatic hyperspherical channel result of Liu et al. [324] and the $R$-matrix Floquet result by Dörr et al. [325] are about 8–10% higher in the region of the cross section maximum.

Starting out in the H$^-$ ($^1S$) ground state, two-photon detachment can produce electrons of either s or d character. The electron angular distribution contains information about the relative strength and the phase between the two channels. The contributions to the total two-photon detachment
Fig. 23. Left: Two-photon detachment cross section of H\textsuperscript{−} using linearly polarized light as a function of the photoelectron kinetic energy $\varepsilon_f$. $N_c$ is the number of coupled channels within each term level of the initial, intermediate, and final states [319]. Right: Contribution to the total two-photon detachment cross section from $L = 0$ and 2 partial waves with four coupled channels (1 a.u. = 27.196 eV).

cross section from the partial waves ($L = 0$ and 2) exhibit very different behaviour as a function of the photon energy. The cross section for detachment to final $^1\text{S}_\text{c}$ states is dominating for small values of the photoelectron energy, but for higher energies the final $^1\text{D}_\text{c}$ states become increasingly important and eventually become dominant, see Fig. 23 [319]. There is a good agreement concerning the contributions to the total two-photon detachment cross section between the various calculations, based on either perturbation theory [323,326–328], the non-perturbative Floquet method [289,329], or the hyperspherical approach [329].

Experimentally Præstegård et al. [330] utilized an imaging electron spectrometer to study the electron angular distribution for the two-photon process in the vicinity of the one-photon threshold (total photon energy is $2 \times 0.75$ eV) and showed that the distribution resembles that of a pure $d$ wave, in very good agreement with all the predictions. The experiment took advantage of the suppression of the one-photon process just above threshold to enhance the probability for observation of the non-resonant two-photon excess-photon detachment of H\textsuperscript{−}. Higher excess photon detachment channels were not observed in this study due to the saturation of the two-photon process. This was, however, achieved by Reichle et al. [331] a few years later (see below).

Two-photon detachment of H\textsuperscript{−} with 1064 nm (1.165 eV) laser light had previously been reported by Zhao et al. [332], who concluded that the process at this photon energy, which is located far above threshold, branches 90(10)\% into the outgoing $d$ wave, in agreement with the calculation of Telnov and Chu [329]. However, Zhao et al. did not provide the important parameter which contains information about the relative phase shift of the outgoing $s$ and $d$ waves. This was however, obtained a few years later by the same group [333]; the relative phase angle between the $S$ and $D$ amplitudes was determined to be less than 59\º.

Gulley et al. [333] also attempted to measure the three-photon detachment cross section of H\textsuperscript{−} using 1.165 eV photons from a Nd:YAG laser at peak intensities of $10^{11}$ W/cm\textsuperscript{2}, but could only estimate an upper limit on what the cross section could be. It was reported to be less than $4.4 \times 10^{-79}$ cm\textsuperscript{6} s\textsuperscript{2} in good agreement with the cross section of $8 \times 10^{-80}$ cm\textsuperscript{6} s\textsuperscript{2} calculated by
Fig. 24. Angular integrated photoelectron energy spectrum showing the results of absorption of 2–5 photons in $\text{H}^-$; solid curve: theoretical results, dots: experimental data. Angular distributions at energies labelled $a$ and $b$, respectively, are shown in Fig. 25. The inset shows the higher energy peaks in greater detail [331].

Nikolopoulos and Lambropoulos [327]. A few years later Reichle et al. [331] used intense IR light at 2.15 $\mu$m (0.577 eV) from a femtosecond laser to observe three- and four-photon detachment of $\text{H}^-$; hereby they could overcome the saturation problems caused by the long interaction time using pulses from Nd:YAG lasers. Previously, Nicolaides et al. [334,335] had calculated the multi-photon detachment rates of $\text{H}^-$ for IR-laser photons with energies ranging from 0.136 to 0.326 eV and intensities in the range $2.5 \times 10^{10} - 10^{11}$ W/cm², covering three- to seven-photon detachment rates, by means of the many-electron, many-photon theory (MEMPT), and obtained cross sections indicating that it should indeed be possible to observe several of the higher order detachment channels.

Reichle et al. [331,336] studied the angular distribution of the photoelectrons produced in two-, three-, and four-photon detachment of $\text{H}^-$. The infrared light used required absorption of at least two photons to overcome the binding energy of $\text{H}^-$. Fig. 24 shows the photoelectron spectrum, which reveals at least three prominent excess photon detachment channels. An analysis of the angular distribution of the photoelectrons revealed an unusual dependence of the angular distribution on the electron kinetic energy. This effect was most pronounced in the two-photon detachment channel near the threshold of photodetachment. Fig. 25 shows the angular distributions of photoelectrons in the two-photon detachment channel at two different laser intensities, $1.3 \times 10^{11}$ W/cm² for the upper part (a), and $6.5 \times 10^{11}$ W/cm² for the lower part (b). The corresponding kinetic energies are marked as $a$ and $b$ in Fig. 24. The distribution at the lower intensity (a) can be described by a superposition of $s$ and $d$ waves with their relative phase taken into account. At the higher intensity the distribution has a shape with a maximum pointing perpendicular to the laser polarization. Gribakin and Kuchiev [337] have described such a behaviour in terms of quantum interference of electron trajectories. An electron can tunnel into the continuum at different times within a period of the field oscillation, and the corresponding continuum wavefunctions will carry the phase of the field at which the electron is emitted. The interference effect results from the superpositions of the wavefunctions [331].

The two-photon detachment cross section of $\text{H}^-$ has also been extended to the energy regions below the $\text{H}(n=2)$ and $\text{H}(n=3)$ thresholds, where $^1\text{S}$ and $^1\text{D}$ resonances may appear. As described in the section about $\text{H}^-$ resonances, a $^1\text{D}$ resonance located below the $\text{H}(n=2)$ threshold was observed and characterized [82,275,276] in good agreement with several theoretical predictions.
Resonant and non-resonant two-photon absorption at still larger photon energies (8 eV or above) have been calculated by several groups [338,339]. Du et al. [338] calculated the cross section for resonant two-colour, two-photon detachment of $^1P_3{^2}0$ resonance located below the H$(n = 2)$ threshold, whereas the second photon scans the energy region above the same threshold where long-range dipole-field induced cross section oscillations are predicted to occur, but so far not observed experimentally. It should be noted that the resonant two-colour, two-photon detachment cross section is 8–9 orders of magnitude larger than the corresponding non-resonant single-colour, two-photon detachment cross section. Pindzola and Robicheaux [339] considered the complete photo fragmentation of the H$^-$ ion by means of two 8 eV photons. The calculations included the analogous process in He using 45 eV photons. The development of bright light synchrotron sources may perhaps make it possible to test these predictions within the coming decade.

Results of calculations investigating the effects of autodetaching resonances on multi-photon detachment spectra of H$^-$, assuming laser intensities of $10^{11}$ W/cm$^2$, have been reported by Hart and Fearnside [340] using the R-matrix Floquet method in which the coupling of the ion with the laser field is described non-perturbatively. The frequency ranges were chosen such that the lowest autodetaching states of the H$^-$ are excited through two- or three photon transitions from the ground state and the detachment rates are compared to previous results obtained using perturbation theory. In the intense laser fields considered ($10^{11}$ W/cm$^2$) resonances may induce structure in parts of the continuum, where no structure exists in the absence of the field. This phenomenon is known as light-induced continuum structure (LICS) and has been studied in neutral atoms.

The multi-photon studies described above rely on the use of linearly polarised laser light. The application of elliptically polarised laser light fields may add a new dimension to the study of multi-photon processes in negative ions including H$^-$. This topic was first addressed theoretically by Nikolopoulos and Lambropoulos [327]. Very recently Manakov et al. [341] described multi-photon detachment of a negative ion by an elliptically polarized, monochromatic laser field and illustrated numerically the various predicted effects for the H$^-$ ion. Multi-photon detachment studies using...
elliptically polarised laser light have been reported for the negative halogen ions and reviewed by Blondel [43], but so far no experimental data are available dealing with $\text{H}^-$.  

4.1.4. Heavy particle-impact collisions  
Collisions between $\text{H}^-$ and an atom, molecule or ion have been studied quite extensively for several decades [30,41,342], but to a less extent during the last decade. The importance of collisions between $\text{H}^-$ and a positive ion has been recognized for long time within astrochemistry, planetary atmospheres and astrophysical processes, and for generation of intense neutral hydrogen beams employed in the heating of magnetically confined fusion [343]. In stellar atmospheres with temperatures above 8000 K and in lower temperature stars with lower surface gravity [30] the interaction between $\text{H}^-$ and $\text{H}^+$ will lead to charge exchange and the formation of neutral H atoms, a process which will dominate over associative detachment between $\text{H}^-$ and $\text{H}$ leading to formation of hydrogen molecules.

Recent studies of interaction between $\text{H}^-$ and a positive ion have been performed with $\text{H}^+$ [344–346], $\text{He}^+$ [347–349], multiple charged ions like $\text{He}^{2+}$ [343], $\text{Ne}^{4+}$ or $\text{Ar}^{4+}$ [350–352], and $\text{H}_2^+$ [353]. These studies have covered a number of reactions, such as transfer ionization and detachment [344,346], neutralization [349], and associative ionization [347], depending on the relative velocities of the interacting particles. Often the experimental results have been available for some time and theoretical calculations are now becoming available yielding a better understanding of the various reactions. In the case of multiply charged ions interaction with $\text{H}^-$ the latter can often be viewed as an active loosely bound electron around a H(1s)-like core, while the inner electron is considered as a spectator. The active electron experiences the weak short-range potential of the neutral core and the long-range electrostatic attraction of the projectile ion. Various rather simple models are often able to reproduce the experimental cross sections surprisingly well [352].

The reaction between $\text{H}_2^+$ and $\text{D}^-$ [353] represents the simplest mutual neutralization involving a molecular ion and consequently is an important test for theory describing this process as well as for the understanding of the chemistry of the early universe. The cross section measured by Peart et al. [353] appeared to be independent of the initial vibrational state population of the $\text{H}_2^+$ ions. The measurements were performed for centre-of-mass energies between 3 and 460 eV and differed at the lower energies significantly from the results of the Landau–Zener calculation by Eerden et al. [354], but converged at the high interaction speeds with the results for the atomic pairs $\text{H}^+–\text{H}^-$, $\text{He}^+–\text{H}^-$ and $\text{Li}^+–\text{H}^-$.  

The interaction between $\text{H}^-$ and He or the other noble gases still attracts interest experimentally [355–357] as well as theoretically [358,359] with emphasis on the single- and double-electron detachment from $\text{H}^-$ at collision energies (5–100 keV), where an impulse approximation for the scattering of the loosely bound electron yields a reasonable description of the collision. These collision systems have been studied for several decades and a consistent picture seems now available.

For collision energies below 1 keV an adiabatic molecular picture is commonly used to describe the interaction between $\text{H}^-$ and neutral atoms. Martín and Berry [360] have calculated theoretical cross sections for Penning detachment of $\text{H}^-$ from excited Li and Ca atoms for very low impact energies (25 meV to 20 eV). Penning detachment is the name used by these authors for a process in which a negative ion ($\text{H}^-$) collides with an electronically excited energy donor (Li(3$I$) or Ca(4$s$5$s$ 1$S$) atoms) and the excitation energy passes from the donor to the negative ion and sets the excess
electron free. The Penning detachment is shown to be enhanced when several decay channels are open and the target (Li or Ca) is left preferentially in the nearest excited state.

Angular distributions of neutral hydrogen atoms following electron detachment from \( H^- \) ions interacting with molecular hydrogen or nitrogen at 2–6 MeV have been studied experimentally and reported rather recently [361]. The measurements were, however, performed already in 1985, but the data were classified for more than 10 years. The experimental distributions are found to be in good agreement with existing Born approximation theory for scattering processes [362].

Single- and double-electron detachment in collisions of two negative atomic ions has been studied experimentally [363,364] and theoretically [364,365] for \( H^- \). Since the single-detachment cross section reaches a magnitude of \( 10^{-14} \) cm\(^2\) at 10 keV centre-of-mass collision energy these collisions can play an important role in electromagnetic storage rings (see Section 2.8) and be responsible for loss of negative ion beams due to intrabeam scattering, an effect noticed at the ELISA storage ring during the running-in period.

Finally measurements of \( H^- \), \( H^0 \), and \( H^+ \) yields produced by foil stripping of 800 MeV \( H^- \) ions have been performed passing \( H^- \) ions through foils of carbon or Al\(_2\)O\(_3\) [366–368]. The time of interaction is less than a femtosecond, when \( H^- \) is experiencing a pulse of the “matter field” [30]. Since this is the appropriate orbital period of loosely bound electrons, complicated energy transfer and chaotic processes may occur. A significant fraction of the incident \( H^- \) ions emerge unscathed, but neutral hydrogen atoms in excited states and \( H^+ \) ions are also observed. The principal results of these experiments are the relative yields of \( H(n) \) states vs. beam thickness for \( n \) ranging from 1 to 11 [50] and the populations of the individual \( H^0 \) Stark states, which depart significantly from the statistical weighting with the abundance of \( m = 0 \) states being increased relative to the other Stark states. A detailed theory able to account for the various observations with foil stripping is not yet available.

4.2. Helium

It is not possible to attach an electron to the ground state of the helium atom to form a stable negative ion, but it is well established that there exists many \( He^- \) resonances associated with singly and doubly excited states of He [42]. The first group of resonances, \( 1snln'l' \), are located at about 19–24.5 eV above the ground state of He, whereas the second group, \( nln'l'n'l' \), for which the main quantum numbers can be 2 or larger, are located more than 57 eV above the He ground state. The three electron \( He^- \) ion can either have spin 1/2 or 3/2 leading to two sets of resonances, \( 2L \) and \( 4L \). The former can be generated by electron–He scattering and have been explored in great detail since Schulz [369] observed and identified the \( He^- 1s(2s^2) ^2S \) resonance at 19.37 eV. Buckman and Clark [42] have given a comprehensive review of the \( 2L \) resonances located below the first ionization limit of He, and since then there has only be rather few studies of this resonance system. The \( 2L \) resonances located above the \( He^+ \) limit and associated with the doubly excited He states were also reviewed by Buckman and Clark; these resonances have recently attracted more interest.

An electron can be attached to the \( 1s2s \) \(^3S \) excited state of the helium atom leading to the formation of the metastable \( He^- (1s2s2p ^4P) \) ion, which exhibits differential metastability with respect to autodetachment. The three \(^4P_J \) levels are forbidden to decay via the Coulomb interaction; the \(^4P_{3/2,1/2} \) levels can decay by spin–orbit and spin–spin interaction, whereas the \(^4P_{5/2} \) level only decays by spin–spin interaction [220,370]. With a lifetime exceeding 300 \( \mu \)s the \( He^- (1s2s2p ^4P_{5/2}) \)
ion has become an attractive negative ion to study. Storage ring and ion trap experiments have yielded accurate lifetimes of the metastable ion, interaction with lasers detailed information about the photodetachment cross section below the He$^+$ limit from which the binding energy of the ion and the energies and widths of excited $1s^2ln'nl'$ $^4$L resonances with $n$ and $n'$ reaching 15 have been obtained, whereas interaction with synchrotron radiation provides information about the photodetachment cross section and resonances located above the He$^+$ limit. Here the only other bound state of He$^-$, $2p^3~^4S$, is located, see [371] and references therein.

4.2.1. Below the He$^+$ limit

The negative-ion spectrum of helium has probably been the subject of the most extensive experimental and theoretical investigation of any element in the periodic table [42] and the knowledge about the many $^2$L resonances has been accumulated over a period of four decades resulting in energies and widths with accuracies about 1 meV for the former and 0.5 meV for the latter. The $1s(2s^2)~^2S$ resonance is located at 19.365(1) eV above the He ground state with a width of 11.2(5) meV according to the most recent experimental study by Gopalan et al. [372]. They improved the accuracy of the energy and obtained a width in good agreement with the one reported by Kennerly et al. [373], but larger than claimed more recently by Dubé et al. [374]. The paper by Gopalan contains 19 references to previous experimental investigations of the $1s(2s^2)~^2S$ resonance and 17 to theoretical studies. Gopalan et al. [372] also reported numerical calculations based on the $R$-matrix method with pseudo-state approach, as described by Bartschat et al. [375] and Bartschat [376], and obtained results for the energy and width of the He$^-$ ($^2S$) resonance agreeing with the experimental values within their error limits. Theoretical studies have also been reported by Chrysos et al. [377] with the aim to calculate the energies and partial widths of the He$^-$ $^2S$ two-electron ionization ladder resonances and by Bylicki [378], who focussed on the $^2P$ and $^2D$ Feshbach resonances, but none of the latter mentioned resonances have so far been identified.

The metastable He$^-$ ($ls2s2p~^4P$) ion has received considerable attention since its discovery by Hiby in 1939 [379]. Its binding energy, fine-structure splittings, and the lifetimes of the J-levels were studied before 1990, but the new experimental laser methods developed since then created new interest in this ion. The binding energy was determined by Kristensen et al. [13], who utilized the $\epsilon$s-wave threshold associated with photodetachment to the He($ls3s~^3S$) state, which was monitored by resonant ionization spectroscopy, to obtain the precise binding energy of 77.516(6) meV with respect to the He($ls2s~^3S$) state. This value is in excellent agreement with the ab initio calculation performed by Chung [13], yielding 77.518(11) meV. The use of an $\epsilon$s-wave threshold combined with selective monitoring of the He atoms allowed the accuracy to be improved by a factor of 20 compared to previous values. A few years before, the experimental binding energy value was reported to be 77.67(12) meV [135], obtained from photodetachment to the He ($ls2p~^3P$) state with emission of a p-electron and without selective monitoring of the population of the excited He state. This binding energy value was, however, in slight disagreement with the best theoretical value (77.51(4) meV) available [380] at that time.

With the He$^-$($ls2s2p~^4P$) state located below the first excited state of the He atom its possible decay routes to the ground state of He can only take place via so-called forbidden transitions, either by photon or electron emission. Being embedded in the doublet continuum, the ion can autodetach only via the relatively weak magnetic interactions. The spin–orbit-induced coupling between the $^4P$
Fig. 26. Lifetime data recorded for He\(^-\) (1s2s2p \(^4\)P\(_{5/2}\)) at the ASTRID storage ring [12]. The neutral He atom signal from a tandem-channel plate detector is shown as a function of time following beam injection.

and \(^2\)P levels of the 1s2s2p configuration, with the doublet levels being allowed to decay promptly via the Coulomb interaction, is responsible for the lifetimes of the \(J = 1/2\) and \(3/2\) levels being decreased relative to the \(J = 5/2\) level. The coupling between the \(^4\)P and \(^2\)P levels complicates the theoretical predictions of the lifetimes for the \(J = 1/2\) and \(3/2\) levels; for the \(J = 5/2\) level the interaction Hamilton is explicitly known, so the calculation of the lifetime of this metastable level is simpler.

Before the storage rings were introduced to atomic physics the lifetimes of the He\(^-\) \(^4\)P) levels could only be obtained from single-pass experiments at a direct beam line. Blau et al. [220] reported the lifetime of the longest living level (\(J = 5/2\)) to be 345(90) \(\mu\)s, whereas the calculated lifetimes before 1992 ranged from 266 to 550 \(\mu\)s, being very dependent on the precise form of the wavefunction in both the initial and final state. The more advanced calculations, see [12], were yielding lifetimes for the \(J = 5/2\) component with an average value about 450 \(\mu\)s, whereas the lifetimes for the \(J = 1/2\) and \(3/2\) levels were of the order of 10 \(\mu\)s. By using the ASTRID storage ring Andersen et al. [12] measured the \(J = 5/2\) lifetime to be 350(15) \(\mu\)s by time-of-flight technique. Blackbody-induced photodetachment of the weakly bound level was shown to influence the decay rate by nearly 20%, but also magnetic-field-induced effects (Zeeman mixing of magnetic substates with same magnetic quantum number, but originating from different, close lying fine-structure levels), caused by the magnetic lattice of the storage ring, influenced the lifetime data. Fig. 26 shows the measured He\(^-\) decay rate as a function of the time following ion–beam injection [12]. In first-order perturbation theory, the mixing amplitudes will be proportional to the magnetic field strength (Zeeman coupling); thus the decay rate is expected to depend quadratically on the field strength or linearly on the beam energy at sufficiently low energies. The experimental data in Fig. 26 had to be fitted to a function, which consisted of the sum of three contributions, the natural decay rate, the temperature-dependent blackbody radiation-induced decay rate at room temperature, and the magnetic field-dependent contribution [12], yielding a natural lifetime of 350(15) \(\mu\)s after the blackbody contribution was estimated from experiments performed at elevated temperatures. The lifetime obtained at the magnetic...
The storage ring lifetime stimulated new theoretical research [383]. Three factors were considered as being responsible for the fact that the previously calculated lifetimes were too long: the auto-detachment mechanism, the electron correlation effects in the initial state, and in the final state. The analysis revealed that it was the correlations in the initial 1s2s2p 4P state, which had to be better accounted for, whereas correlations in the final He(1s2 1S) state are negligible. In the multiconfiguration Hartree-Fock approximation, correlations is accounted for by mixing in other configurations with the original 1s2s2p 4P wavefunction. Most important are the contributions from the 1s2p3d and 2s3s2p configurations with the strongest interaction being introduced via the interaction between the 1s2s2p and 2s3s2p configurations; this interaction brings a radial correlation to the 1s orbital and significantly reduces the lifetime. The final lifetime was calculated to be 345 μs with an estimated accuracy of 10 μs, which is in good agreement with the experimental magnetic storage ring value and also with the later value of 343(10) μs reported by Wolf et al. [17] using an electrostatic trap, but applying the same correction for blackbody radiation as used by Andersen et al. [12]. The trap experiment also allowed the average lifetime for the 4P3/2,1/2 levels to be measured yielding a value of 8.9(2) μs, somewhat below the estimated value of 11.4 μs [384].

Recently, Pedersen et al. [18] reinvestigated the lifetime of the He− (1s2s2p 4Pj) levels using the electrostatic storage ring ELISA (Section 2.8). This storage rings allows the lifetime measurements to be performed without the influence of magnetic fields, and at temperatures below −50°C, which reduces the photodetachment of the He− ion due to blackbody radiation quite significantly, and finally it has a circumference allowing also the average lifetime of the two shorter-lived components to be obtained. Fig. 27 illustrates the He− 4P3/2 lifetime data at eight different temperatures ranging from room temperature to below −50°C. The lifetime is clearly increasing going to lower temperatures.

Fig. 27. He− (1s2s2p 4P5/2) lifetime data recorded at eight different temperatures of the ELISA storage ring [18]. Open circles: measured data, full circles: data corrected for blackbody radiation. Solid line: mean weighted value of the corrected data, whereas the dotted lines indicate the uncertainty limits.
and correction for the blackbody-induced photodetachment leads to a consistent set of lifetimes in the range 360–370 μs from which the final lifetime of 365(3) μs was obtained, whereas the average lifetime of the two shorter lived components was measured to be 11.1(3) μs. The lifetime results obtained at the two storage rings are in good agreement within their uncertainties, whereas the electrostatic ion trap lifetimes are shorter, probably due to a less perfect storage of the negative ions or an unidentified loss mechanism in the ion trap experiment. This statement was supported by experiments at the ELISA storage ring, where it was possible to obtain results in agreement with the ion trap data by using less optimal storage conditions [18].

Photodetachment studies of the He− (1s2s2p 4P) ion have been a very active field since the Buckman–Clark review was written [42]. Up to 1995 the experimental results on photodetachment concerned only production of He(n=2) states, see [135] and references therein. Most noticeable was the 1s2p2 4P shape resonance located 12.3 meV above the He(1s2p 3P) threshold at 20.963 eV with a cross section maximum of 80(10) Mb and a width of about 8 meV. Many-body calculations within the Dyson equation method were performed by Ivanov et al. [385] and could reproduce most of the experimental evidence for 2s and 2p photodetachment of the He− (1s2s2p 4P) ion available at that time. However, the experimental techniques applied by Walter et al. [135], photodetachment by laser light followed by detection of the neutral He atoms formed, or autodetachment electron spectroscopy of the collisionally populated shape resonance [386], could not be utilized to cover higher lying resonances, since the detachment channels were too weak. Selective monitoring of He(1snl 3L) states was needed and this technique (resonant ionization spectroscopy) was first introduced to negative ions at the end of 1995 [4]. Shortly after the Gothenburg group performed detailed studies of the higher energy region, in the vicinity of the He(1snl 3L) thresholds for n=3 or larger with focus on the effects of quartet doubly excited resonances.

Klinkmüller et al. [14] measured the He(1s2s 3S) partial cross section in the vicinity of a 4S resonance, associated with the He(n=3) threshold, and assigned it to be the He− (1s3s4s 4S) state. The energy and width of this resonance were in good agreement with the theoretical prediction by Xi and Froese Fischer [387], but the width was 20% wider than calculated by Ramsbottom and Bell [388]. Subsequently, Klinkmüller et al. [15] measured the partial photodetachment cross section for production of He(1s2p 3P) in the vicinity of three quartet Feshbach resonances associated with the He(n=3) thresholds. Whereas the energy location of these resonances (1s3s4s 4S, 1s3p2 4P, and 1s3p4p 4P) agreed with most of the recent theoretical predictions [387–389] the experimental widths of the two 4P resonances differed considerably from the predicted values [387–389].

A third study of He− quartet resonances was also performed by the Gothenburg group [16], measuring the partial cross section for production of He(1s3p 3P) in the vicinity of the He (1snl) thresholds with n being 4 and 5. This study resulted in the observation of 12 previously unknown resonances. Fig. 28 shows the experimental data (partial cross sections) for photodetachment of He− via the He (1s3p 3P) + εp channel. It should be noted that the data also will include the He (1s3p 3P) + εf channel, which contributes to the cross section containing 4D resonances, but the experiment is not able to distinguish between the two channels. The energies and widths of all 12 resonances were measured, but only 8 identified.

The resonances marked a, c, e, g, i, j, k, were proposed as belonging to two Rydberg series of 4P intra-shell resonances, with a, c, and e representing He− (1s4pn p) states (n=4–6) and g, i, j, and k He− (1s5pn p) states (n=5–8), whereas resonance b was due to the He− (1s4s5s 4S) state. Four of the features, marked d, f, h, and l, respectively, were left unidenified ‘due to a lack of theoretical
Fig. 28. Partial cross sections for photodetachment via the He(1s3p \(^3\)P) + e\(^-\) (\(\epsilon\)p) channel [16]. The upper and lower spectra show the regions below the He(\(n = 4\)) and He(\(n = 5\)) thresholds, respectively. The insets show the regions near the thresholds in greater detail.

input’. Most likely some of these resonances could have \(^4\)S or \(^4\)D symmetry, since they did not appear in the calculations of \(^4\)P resonances by Bylicki [389]. These and the previous observations clearly called for a comprehensive theoretical study covering all the resonance features as well as the partial cross sections for photodetachment of He\(^-\)(1s2s2p \(^4\)P) in the vicinity of He(1sn/l) thresholds with \(n = 3, 4\) and 5.
Liu and Starace [390] performed a comprehensive $R$-matrix study of the photodetachment of the He$^-$ ($1s2s2p\,^4P$) ion in the vicinity of the three thresholds mentioned above. The calculated He ($1s2s\,^3S$) and He ($1s2p\,^3P$) partial cross section results were in excellent agreement with the relative measurements of Klinkmüler et al. [14,15]. Near the He ($1snl = 4l$ and $5l$) thresholds Liu and Starace predicted the presence of about 30 quartet Feshbach resonances and four quartet shape resonances which had not been observed or predicted before; the calculated He ($1s3p\,^3P$) partial cross section was also in excellent agreement with the measurements of Kiyan et al. [16]. Of the 12 observed resonances 11 were identified.

The measured $\sigma(3p)$ partial cross section is a sum of three partial cross sections $\sigma(3p,\,^4L)$ with L being S, P or D. By decomposing the $\sigma(3p)$ cross section in this way it was possible to accurately characterize the term value of the doubly excited state responsible for the observed resonance structure (see Fig. 29). The labels (a–f) used in Figs. 28 and 29 are the same. The upper part of Fig. 27 shows the excellent agreement reached between experiment and theory. The $\sigma(3p,\,^4P)$ partial cross section gives the largest contribution to the $\sigma(3p)$ partial cross section and the $^4P$ resonances are the ones which dominate the $\sigma(3p)$ spectrum, whereas a series of very narrow $^4S$ resonances exists situated on top of a nearly constant background. The calculations show that both the feature b and d should be assigned to resonances with $^4S$ symmetry, confirming the calculations by Brandefelt and Lindroth [391], who had searched for resonances of $^4S$ symmetry in He$^-$ and reported energies and widths of four such resonances located below the He ($1s5s\,^3S$) threshold. The energies and widths
of the resonances were calculated using the complex rotation method combined with the use of B splines in a spherical cavity to describe the negative ion and its decay channels. The calculations had confirmed the original identification of the 1s3s4s and 1s4s5s resonances, (the latter is marked b in Fig. 28), but also identified the narrow resonance marked d as due mainly to the 1s4d5d configuration.

Liu and Starace used the group theoretical classification scheme \[392,393] in which the b and d resonances are \( A = -\) resonances, whereas the resonances named a, c, e, and f, all having \( 4P \) symmetry were classified as \( A = +\) resonances. It should be noted that \( A = -\) resonances also were observed in the photodetachment spectra of H\(^-\) as narrow resonances; in the negative alkali ions \( A = -\) resonances are present too, but these are not necessarily narrow. Clearly, the field of the He\(^+(1s)\) core is much closer to the Coulomb field of the H\(^+\) core than are those of the singly ionized alkali atom cores, like Li\(^+\)(1s\(^2\)) \[390\].

Finally, the resonances marked (g-l) were analysed using similar methods as described above \[390\]. The calculated partial photodetachment cross sections show that these resonances (unless the resonance marked k) have \( 4P \) symmetry and can be classified as \( A = +\) resonances. In the region near the He\((1s5l\;\;\;3L)\) thresholds resonances having \( 4S \) symmetry are weak and cannot be observed, whereas \( 4P \) and \( 4D \) resonances overlap to some extent. The \( \sigma(3p,\;\;4P) \) cross section is the main contributor to the partial \( \sigma(3p) \) cross section but the \( \sigma(3p,\;\;4D) \) cross section also contributes.

The major resonance structures discussed above in the total cross section reflect the propensity rules for radiative and non-radiative transitions. The principal series of resonances, having \( (K, T)^4 = (n - 2, 1)^+ \), fulfills the conditions for propensity-favoured transitions. Members of this series with \( 4P \) and \( 4D \) symmetries generally exhibit stronger transition amplitudes and broader widths. The propensity-allowed series of \( 4S \) symmetry, having \( (K, T)^4 = (n - 1, 0)^- \) also exhibit strong transition amplitudes, but are generally narrow due to their \( A = -\) type. Series like \( (n - 4, 1)^+ \) or \( (n - 3, 0)^- \) are also prominent in the He\(^-\) photodetachment spectrum, although such states have little effect in photodetachment of H\(^-\) \[390\]. The results obtained by Liu and Starace \[390\] were later to a large extent confirmed by Sanz-Vicario et al. \[394\] using a complex scaled configuration-interaction approach.

Recently experimental photodetachment of the He\(^-\) ion has been extended to still larger photon energies reaching the vicinity of the two-electron escape threshold \[19\]. This energy region can be reached with a single laser operating in the optical domain, but a highly sensitive detection scheme is needed to observe and characterize the double Rydberg quartet He\(^-\) states present. This was achieved using state-selective electric field ionization to selectively monitor the He\((1snl\;\;3L)\) Rydberg states with \( n = 11-14 \). The data \[19\] covering the He\((3S)\) thresholds did not exhibit a variation in the signal over the thresholds showing that the reaction channels containing He\(^-(1snn'\;4S)\) double Rydberg states, decaying by emission of s-electrons, or He\(^-(1snn'\;4D)\) states, decaying by emission of d-electrons, are weak (denoting the double Rydberg states only by their principal quantum numbers since the strong angular correlations enforce a pronounced \( l \) mixing). Contrary a significant signal increase was observed passing over the He\((3P)\) thresholds and to a minor extent over the He\((3D)\) ones, which can be explained as due to significant population of the reaction channels containing He\(^-(1spnn'l'p'\;4P)\) double Rydberg states, which can decay emitting either \( s \) or \( d \) electrons. The population of He\((3D)\) Rydberg states via reaction channels containing He\(^-(1snsnl'd'\;4D)\) double Rydberg states will be negligible according to calculations of an analytical model for electron–electron correlation—the so-called doubly excited symmetry basis (DESB) \[268\].
The data from the vicinity of two-electron escape threshold [19] exhibit the same tendency as
seen at the lower lying He(1s3p 3P) state by Kiyan et al. [16]; it is 4P double Rydberg states,
which are the dominating resonance structures populated in photodetachment of the He−(1s2s2p 4P)
ion. The energies and widths of a few intra-shell He− (4P) resonances in the \( n = 13–15 \) mani-
folds were reported, but so far theoretical calculations for comparison are only available for smaller
\( n \)-values [395]. The experimental data also revealed the presence of several broad and some very
narrow resonance structures, the latter with widths down to 0.1 meV. Some of the resonances are
strongly bound and obviously belong to channels different from the lowest one within a hydrogenic
manifold [46].

Concurrent with the experimental and computational studies attempting to locate, identify, and
characterize the He− resonances additional insights to the He− resonances have been searched for
using the hyperspherical method within the adiabatic approximation [396]. In this approach, bound
and resonance states are not calculated directly. Instead the hyperspherical adiabatic potential curves
are first calculated. If a potential curve has a relatively deep well, then it is likely that some bound or
resonance states can be found. If the potential curve is fully repulsive, then it cannot support bound
states. This method has been fully developed for two-electron systems and extended for three-electron
atoms and first applied for the He− ion by Le Dourneuf and Watanabe [397], who treated the He−
ion doubly excited states as a two-electron system, where the two outer electrons move in the field
from a He+(1s) core.

The study by Morishita and Lin [396] applies the three-electron hyperspherical approach, which
allows investigation of all states in the He− system, including excitation of one, two or three
electrons, all together at the same time. Potential curves that support 1s2l2l′ doubly excited states and
2l/l′2l′′ triply excited states were analysed to interpret the possible existence and the nature of these
states. Among the doublet states in the 19–21.5 eV region above the He ground states only the 2S
state is a clear-cut Feshbach resonance, whereas the 2P and 2D resonances or structures (see [42]) are
less evident and cannot be viewed as associated with a single channel, at least in the hyperspherical
sense. Within the same energy region, the two quartet resonances, 1s2s2p 4P and 1s2p 2 4P, can
be identified as the bound state or shape resonance associated with a single hyperspherical potential
curve. This study also proved that it is possible to classify the doubly excited states of He− using
the same quantum numbers \( K, T \) and \( A \) that were applied for classifying the doubly excited states
of the H− ion. This was utilized by Liu and Starace [390] as mentioned above.

4.2.2. Above the \( \text{He}^+ \) limit

During the last decade there has been substantial interest in the observation and description of
triply excited states in the spectrum of neutral lithium—the so-called hollow atoms. Despite these
recent activities, the first observation of such states occurred already in the 1960s when triply ex-
cited states of He−, with all three electrons in the \( n = 2 \) shell, were observed by Kuyatt et al. [398]
in elastic electron scattering experiments on He. The triply excited states offer a very fertile field
for studies of electron correlation effects, particularly in the negative He ion, as the presence of
the extra electron implies that the motion of the three excited electrons must be even more highly
correlated than in neutral lithium in order for them to share and mutually screen the charge of the
ion. Despite the advantages that these studies offer there has been relatively little work on triply
excited He− resonances [42]. The triply excited resonances are only weakly excited in electron
scattering experiments from the ground state of He and they occur in a region of the spectrum (57–71 eV) where the existence of overlapping, doubly excited autoionizing He states greatly complicates their observation and unambiguous classification [399]. At the time of the Buckman–Clark review [42], five triply excited He− (2L) states were considered classified and this number has only been slightly increased during the past decade.

The triply excited negative-ion states may be divided into two classes, the so-called intra-shell and the intershell or non-valence resonances. Unambiguous confirmation of the original classification [400] of the two lowest lying 2L intra-shell resonances, He− 2s2p 2P at 57.22 eV and 2s2p2 2D at 58.30 eV [42], was reported in 1999 by Trantham et al. [399], who measured the electron-impact excitation function for the $n = 2$ singly excited states of He as a function of the scattering angle.

Intra-shell resonances are expected to decay strongly and preferentially to the low-$n$ neutral excited states [42]. Previously, Batellaan et al. [401] had questioned the certainty of the classification of the 2D feature, noting that its proximity to the 2s2p 3P autoionizing state could complicate the interpretation as a result of possible post collision interaction effects. The 2s2p 2P resonance has also been studied theoretically [402,403]; the energy was predicted in good agreement with the experimental observations, whereas the width was calculated to be about 70 meV with the only accurate experimental value being 90(14) meV [404].

Additional intra-shell resonances, which should be located within the same energy region (57–60 eV) as the two mentioned above, have been predicted by Nicolaides et al. [405] and assigned to 2s2p2 2P at 59.71 eV and 2p3 2D at 59.46 eV, but none of these have so far been observed. The theoretical study was initiated of the experimental investigation performed by Gosselin and Marmet [406], who reported high-resolution measurements of He− triply excited resonances located at 58.41 and 58.48 eV in addition to the well-known 2s2p2 2D resonance mentioned above. Gosselin and Marmet proposed the two resonances to be the 2p3 4S and 2D states, but both these assignments were dismissed by calculations [405], and the experimental data are still unidentified.

In addition to intra-shell resonances a second group of resonances, named intershell resonances, is existing and formed by an electron being weakly bound in the polarization potential associated with a doubly excited He state. In contrast to intra-shell resonances these resonances will only give rise to structures in the excitation functions for high-$n$ neutral excited states, as these states are favoured in the decay of autoionizing levels near threshold because of post collision interaction effects. The intershell resonances were originally proposed to exist by van der Burgt and Heideman [42,407] and the lowest lying intershell resonance was observed at 57.80 eV [408], at the threshold of the doubly excited He(2s2) 1S autoionizing level and classified as 2s2p [42]. This notation should indicate that the resonance has 2P symmetry and is located at the threshold of the He(2s2) 1S autoionizing level. Recently, however, Piangos and Nicolaides [409] reported new calculations dealing with the 2s2p resonance. It lies only 5 meV below the He(2s2p) 2P threshold with a width about 9.5 meV. The intershell resonance is considered as resulting from strong electron correlation in the intra-shell 2s2p 2P resonance and from weak binding due to long-range interactions of an s-electron with a He(2s2p) type core. The s-electron cannot be identified with a 3s electron since its orbital is very diffuse with a calculated radius of about 50 a.u., having its largest overlap with the 5s orbital of He(1s5s) 1S.

Long time may pass from the experimental observations of triply excited He− states to reliable calculations are available, which can give a more detailed characterization of the states than usually available in experimental papers. Roy [410] observed in 1977 three features in the region about 69–70 eV above the He ground state in e-He scattering experiments and attributed these to two
resonances, the first being located at 68.98(7) eV with the label 3s\(^2\)3p \(^2\)P, the second at 69.67(8) eV was proposed to be the 3s3p\(^2\) \(^2\)D resonance. Roy mentioned that the first resonance had an unexpected broadening which could indicate the contribution or the overlapping of another resonance in this region. Nearly, a quarter of a century later Nicolaides and Pingos [411, 412] performed large-scale calculations in the framework of the state-specific theory of resonance states, taking all localized electron correlations into account. They predicted that 11 triply excited resonances of He\(^{−}\) may appear in the energy region between 68.7 and 70.3 eV. A few of these are essentially overlapping and their zero-order representations consist of strongly mixed \(n=3\) configurations. The experimental features located below 69 eV and accounted for by Roy as due to one triply excited state originate from two states, the lowest lying \(^2\)P and \(^2\)D states, which have the 3s\(^2\)3p and 3s3p\(^2\) configurations as the leading components, respectively, but also contain significant contributions from other configurations such as 3p\(^3\), 3s3p \((^3\)P)3d and 3s3p \((^3\)P)3d for the \(^2\)P resonance. The feature at 69.67 eV covers the position of three essentially overlapping resonances with additional two very close, so an unambiguous assignment is not possible and much higher experimental resolution is needed to obtain new insight to triply excited He\(^{−}\) \(^2\)L states. Additional information about these triply excited resonances has been reported by Chung [413] and by Morishita and Lin [414].

Recently there has been significant progress in the study of triply excited quartet He\(^{−}\) states. The 2p\(^3\) \(^4\)S state had already been observed by beam-foil spectroscopy [213] in 1992 and predictions were also available for the 2s2p\(^3\) \(^4\)P state [415, 416], but significant progress came with the first synchrotron radiation experiment [100]. Photodetachment of the He\(^{−}\)-(1s2s2p \(^4\)P) ion above the He\(^{−}\) 1s ionization threshold and below the He\(^{+}\) \((n=2)\) threshold, involving \(K\)-shell detachment and triply excited quartet states of a He\(^{−}\) ‘hollow ion’, could now be studied experimentally. So far data from the experiment [100] and several theoretical calculations [394, 417–421] are available all dealing with the photon energy region 38–45 eV, corresponding to about 57–64 eV above the ground state of He.

The theoretical papers have applied different calculation techniques. Xi and Froese Fischer [418] applied the so-called Galatrin-MCHF method, Zhou et al. [419] the \(R\)-matrix method, and Sanz-Vicario [394] the complex scaled configuration-interaction method. In the former two the He threshold energies are calculated separately and as accurate as possible. Then the various channels are constructed in a close-coupling sense and small corrections to the energies may be added. The method applied by Sanz-Vicario et al. [394] yields the He threshold directly by the three-electron configuration interaction calculation and additional corrections are not introduced.

Fig. 30 shows a comparison between the experimental data and the theoretical results of Refs. [418, 419] with the He thresholds and He\(^{−}\) resonances indicated by hatched lines and arrows, respectively. The \(R\)-matrix calculation reproduces the experimental spectrum rather well, after shifting the calculated thresholds +\(106\) meV to be aligned with the experimental thresholds, unless at the lowest energies, whereas there are noticeable deviations between the calculated spectrum reported by Xi and Froese Fischer [418] and the observed one. The calculated spectrum by Sanz-Vicario et al. [394] confirms basically the theoretical results of Zhou et al. [419], but some minor deviations in the position of resonances have been noticed. The deviation observed between experiment and theory at photon energies close to the 1s threshold was accounted for by Sanz-Vicario et al. [394] taking post-collision interaction effects into account.

The experimental data are obtained by measuring the yield of He\(^{+}\) ions, since photoexcitation of the 1s electron will lead to triply excited, quartet He\(^{−}\) states, which subsequently will decay to
He$^+$ ions via a two-step process. Just above the first threshold an electron will be emitted with low excess energy. When the remaining doubly excited He atom undergoes Auger decay, a very fast second electron is ejected and the first electron will suddenly feel the potential from the He$^+$ ion. Sanz-Vicario et al. [394] calculated the effect of this post-collision interaction (PCI) using classical methods and obtained close agreement with the experimental data. The structures seen in the experimental data in Fig. 30 were previously assumed to be non-resonant structures, but this has been dismissed [100,394], i.e. they are true triply excited quartet He$^-$ states, and their properties have been calculated in good agreement with the experimental data. The feature close to threshold is not representing a resonance, but the large hump originates from the cross section for photodetachment of a negative ion being zero at threshold, and therefore the cross section will raise quickly above threshold and then fall off as known from photoionization studies of positive ions or neutral atoms, which have non-zero cross section at threshold.

There are a number of ways in which triply excited states can be viewed. Morishita and Lin [396] proposed a picture of three electrons which form an equilateral triangle with the nucleus at the centre. The energy differences in these states should arise as a result of rotational excitations of this structure. An alternative view is that they are formed by a single electron which is attached to a large, but weakly bound doubly excited state of the neutral atom. An additional alternative view is that they are formed from two electrons being in a doubly excited configuration about an excited Coulomb core. Trantham et al. [399] find it most acceptable to identify the intra-shell resonances they studied (see above) in terms of the latter structure, i.e. a correlated pair of electrons external to an excited core, whereas the intershell resonances may be better understood from the picture of a very loosely bound electron attached to a doubly excited He core by long-range interactions. Further studies, both experimental and theoretical ones, are clearly needed to obtain a better knowledge about the triply excited He$^-$ resonances.
4.3. The noble gases

The heavier noble gases, Ne, Ar, Kr, and Xe, are often treated separately to He, as the spectrum of negative-ion resonances for these atoms reflects the significant differences in the nature of the their positive-ion cores from that of He [42]. The consequence is that the ion cores of the heavier noble gases are split by the spin–orbit interaction but in addition also have different parity and angular momenta to that of He, leading to the use of different electron-coupling schemes. This is important for the description of the many resonances observed in the previous decades by elastic electron scattering from the heavier noble gases, for a comprehensive review see Buckman and Clark’s article [42]. During the 1990s these atoms have attracted far less interest, since it is not possible to utilize the new photon-based methods to explore the properties of their negative ions due to lack of long-lived negative-ion states.

The noble gases are unable to form stable negative ions due to the low polarizability of their closed-shell $^1S$ ground state configuration. Their metastable triplet states may be able to bind an extra electron to form a bound, spin-aligned quartet negative-ion state as described for He. In all the heavier noble gases, metastable atoms are formed by promoting a $p$-electron to the lowest vacant $s$-shell resulting in an $np^5(n+1)s^3P$ state. According to non-relativistic configuration-interaction calculations by Bunge et al. [422] Ne is unable to form metastable negative ions, whereas Ar$^-$ ($3p^54s^4p^4S$) should exist and be bound by more than 135 meV with respect to the Ar($3p^54s^3P$) state (or 70 meV below the $^3P_2$ level). Thus Ar$^-$ is a suitable object for a laser-based study, which also in 1998 was performed by Pedersen et al. [423]. Like Ne, Kr and Xe can probably not form long-lived negative-ion states even though Haberland et al. [424] have claimed the observation of a long-lived component of Xe$^-$ with a lifetime exceeding 0.1 ms.

A study of the resonance structures corresponding to the $1s2s^2\,^2S$ in He$^-$ and the $np^5\,(^2P_{3/2,1/2}) (n+1)s^2\,(^1S)$ states in Ne$^-$, Ar$^-$, Kr$^-$, and Xe$^-$ with $n = 2$ for Ne and 5 for Xe have been performed by Zubek et al. [425] using elastic electron scattering over an angular range from 100° to 180°. A new experimental technique [426,427] was introduced to allow for the studies in the previously inaccessible region close to 180°. Measurements of elastic electron scattering at large angles are important for the determination of the phase shifts of the partial waves involved and this is especially useful for the heavier gas atoms, for which more partial waves are present than for the lighter atoms He and Ne. These characteristics have been exploited to determine the energy positions and widths of the resonances in Kr and Xe [425].

The energy positions of the $3p^54s^2\,^2P_{3/2,1/2}$ negative-ion states of argon have also been improved by Hammond [428], who reported values with an uncertainty of less than 1 meV, which was at least a factor of ten better than had been achieved previously. These benchmark energies were obtained by accurately fitting, with a minimum of assumptions, a concurrently measured near-threshold electron-impact excitation cross section of the metastable $3p^54s\,^3P_2$ state of argon, which is of known excitation energy. The near-threshold cross section was found to be dominated by s-wave scattering in the first 25 meV above the $^3P_2$ metastable state threshold. This calibration method is applicable to all atomic targets for which the Wigner form of the above-threshold cross section can be assumed.

Dubé et al. [374] studied the Feshbach resonances located below the first inelastic thresholds in the rare gases performing measurements with an electron spectrometer capable of simultaneous measurements at up to 19 angles ranging from 18° to 162°. For each gas the data allowed a precise
evaluation of the first three or four phase shifts and the resonance width. The agreement with theory is generally good, but not perfect at small or large scattering angles.

4.3.1. Argon

The Ar\(^-\)\((3p^54s4p\ \ ^4S)\) state was first observed by Bae et al. [429], who reported the decay of a single component with a lifetime of 350(150) ns, a value later improved by Ben-Itzhak et al. [430] to 260(25) ns. More recently, the binding energy of the Ar\(^-\)\((\ ^4S)\) state was measured by Pedersen et al. [423] using laser photodetachment threshold technique.

Due to the short lifetime of the Ar\(^-\) ions, which were produced via charge exchange in K vapour, only about 1% of the metastable Ar\(^-\) ions arrived at the laser-interaction region, where the photodetachment took place followed by monitoring by resonant ionization spectroscopy of the excited Ar\((3p^54p\ \ ^3D_3)\) atoms formed, see Fig. 31 [423]. Due to the limited current of Ar\(^-\) ions it was necessary to select the strongly populated Ar\((3p^54p\ \ ^3D_3) + \epsilon p\) reaction channel rather than an \(\epsilon s\) emission channel, which may have yielded a more accurate binding energy value.

The binding energy was determined to be 32.5(1.0) meV with respect to the Ar\((3p^54s\ \ ^3P_2)\) level [423]. The lifetime of the negative-ion state was proved to be consistent with the lifetime values given above. The experiment established that the long-lived Ar\(^-\) ion originated from a quartet state, which was bound with respect to the Ar\((3p^54s\ \ ^3P)\) term. Since the dominant detachment channel was due to Ar\((3p^54p\ \ ^3D_3) + \epsilon p\) it was most likely that the negative Ar ion stems from the 3p\(^5\)4s4p
configuration rather than from the potentially possible $3p^53d4s$; the latter would give rise to an emitted s electron in contradiction with the observed threshold behaviour. This conclusion was in agreement with the prediction by Bunge et al. [422] and with the theoretical study by Veseth [423]. Both calculations assigned $^4S^o$ symmetry to the observed metastable state. Veseth calculated the binding energy by using many-body perturbation theory to third order and obtained 24.9 meV, which is in reasonable good agreement with the experimental value. When comparing theory and experiment, it is important to recall the difficult character of the three open-shell configuration that gives rise to the metastable $\text{Ar}^-$ ion. To test the validity of the many-body method used by Veseth the binding energies of the ground state and the excited $\text{Ca}^-$ ion, respectively, were also calculated yielding results in very good agreement with experiments.

4.3.2. Xenon and ekaradon

The state-selective laser technique, applied in the $\text{Ar}^-$ study described above, would also be applicable to the study of the metastable $\text{Xe}^-$ ion reported by Haberland et al. [424]. It was, however, not possible for Pedersen et al. [423] nor previously for Bae et al. [429] to produce metastable $\text{Xe}^-$ ions using the charge-exchange technique. It should be noted that Haberland et al. applied a special production technique involving interaction between a pulsed electron beam and a pulsed supersonic gas beam consisting of a mixture of 5–10% Xe in about equal amounts of Ar and $\text{N}_2$. Even though special ion sources have proved to be important for formation of some metastable molecular negative ions [431] it seems not likely that metastable $\text{Xe}^-$ ions, if existing, should be so sensitive to the production method unless a high-spin state is involved [31]. A possible existence of a metastable $\text{Xe}^-$ ion, created by excitation of one of the inner-shell electrons, can also be ruled out. Furthermore, theoretical studies have not been able to support the claim for the existence of a long-lived $\text{Xe}^-$ state [432,433]. The signal attributed to metastable $\text{Xe}^-$ ions by Haberland et al. is most likely due to a molecular contamination.

Even though the polarizabilities are increasing going from Ne to Rn by more than a factor of 10, the values are still of the same order as known for Zn, Cd and Hg, for which no stable negative ion has been observed and a factor of five below the polarizability of Ca, which only forms a very weakly bound stable negative ion. The electron affinity of the noble gas ekaradon, element 118, which so far has not been produced, may however be positive! Eliav et al. [434] calculated the electron affinity of this element by means of the relativistic coupled cluster method based on the Dirac–Coulomb–Breit Hamiltonian with the use of a large basis set and incorporating electron correlation between the external 40 electrons. Taking both relativistic effects and correlations into account an electron affinity of 56(10) meV was predicted.

4.4. Alkali metals

The alkali metals are able to form stable negative ions with configurations consisting of closed shell cores and a $ns^2$ valence shell, $n$ being 2 for Li and 6 for Cs. The $\text{Li}^-$ ion and to some extent also the heavier alkali metal negative ions may be considered homologous to $\text{H}^-$ ion in the “frozen core” approximation and are therefore considered to be effective two-electron systems.

Two electron atomic systems are ideal systems for investigating the interplay of the electron–nucleus and electron–electron interactions. This is particularly true if both the electrons in the system are excited. Electron correlation effects are more enhanced in negative ions than in the isoelectronic
atoms and positive ions since the negative ion is the lowest member of the sequence and the electron–nucleus interaction is weakest relative to the electron–electron interaction. Thus studies of doubly excited states in H$^-$, as described in Section 4.1, and of doubly excited states in negative alkali metal ions can yield new insight to fundamental aspects of atomic physics. However, doubly excited states in the Li$^-$ ion had not been observed even at the time when the Buckman–Clark review was written [42], whereas the photodetachment cross section near the Li(2p) threshold had been studied. One of the main achievements in recent negative-ion research has been the detailed studies of the photodetachment spectra of the lighter alkali metal ions, Li$^-$, Na$^-$ and K$^-$, and the possibility to compare the photodetachment spectra of the H$^-$ and Li$^-$ ions with the purpose to explore to what extent the existing theories for two-electron systems are applicable to pseudo-two-electron systems having finite cores.

The experimental studies of valence shell photodetachment spectra of the alkali metal ions have been performed by the Gothenburg group [164–169], utilizing the resonance ionization detection technique to explore the higher excited states. Contrary to the H$^-$ ion, the doubly excited states of the negative alkali metal ions can be studied using conventional lasers and the focus has been on the $^1P$ resonances excited by one-photon absorption from the ground states. Temporary negative ion states of Na, K, Rb, and Cs have also been explored by Johnston and Burrow [435] using electron-transmission spectroscopy; they observed that there was a strong “familiar” resemblance among the resonances of the heavier alkali metals and made tentative assignments for some of the observed features.

In 2001 the first inner-shell photodetachment studies of a negative atomic ion, Li$^-$, were reported [7,8] taking advance of the intense synchrotron radiation from insertion devices at synchrotron storage rings. The experimental studies were strongly stimulated and challenged by the ongoing theoretical studies [8,436,437], which predicted that the experiments would reveal dramatic structure, differing substantially both qualitative and quantitative from the corresponding processes above the 1s ionization threshold in Li and Li$^+$. Recently, inner-shell photo detachment of the Na$^-$ ion has also been reported [438].

4.4.1. Lithium

The electron affinity of Li is determined to be 0.618 049(20) eV, combining collinear laser-ion beam spectroscopy with resonant ionization detection of the residual Li(2p $^2P$) atoms [68] and utilizing photoionization via an intermediate Rydberg state. The state-selective detection method improved the accuracy of the electron affinity value established only a few years before by an order of magnitude [137]. The experimental value is slightly larger than the best theoretical value of 0.617 64 eV [439].

Low lying resonance states in Li$^-$ were predicted theoretically already in the 1970s [42], most noticeable the 2s2p $^3P$ state, which never was observed in electron scattering experiments. The observation became possible applying fast collisions between Li$^-$ ions and gas targets [206]; a shape resonance located at 50(6) meV above the detachment limit and with a width of 64(25) meV could be identified as the 2s2p $^3P$ resonance, for which the energy was predicted to be about 60 meV and the width in the range 57–77 meV [440,441].

Photo-induced resonances below Li$^+$: Parallels between doubly excited state spectra in H$^-$ and Li$^-$ photodetachment were already predicted to exist [442] before the first observation of resonance structure in Li$^-$ was reported by Benzinsh et al. [164]. The energy region studied was between the
Li(3s) and Li(3p) thresholds. Fig. 32 shows the experimental data compared with the calculated photodetachment cross section. The experimental data exhibit three significant features, a small and narrow dip in the cross section just at the 3p threshold arising from the opening of a new detachment channel, a narrow resonance structure just below the threshold, and finally a very broad resonance that occupies a large part of the region between the 3s and 3p thresholds.

The broad resonance is mainly associated with a doubly excited state at 4.32 eV above the ground state of Li− with a width of 0.36 eV. It should be noted that the width is overlapping the narrow resonance as well as the Li(3p) threshold and to some extent even the Li(3s) threshold. Hence the interference results in a narrower structure in the spectrum compared to what would arise from an isolated doubly excited state of similar width [86]. The Li− state appears to be analogous to the symmetrically excited \(^1\)P state in H− that lies 12.647 eV above the ground state with a width of 33 meV and originally was observed by Hamm et al. [443]. The H− resonance was described as member of an \(A = +\)Feshbach series, which converges on the \(n = 3\) neutral thresholds, with the two electrons residing at approximately equivalent distances from the core [42]. The broad Li− resonance may also be associated with a symmetrically excited, intra-shell doubly excited state and it has a very similar energy relative to the double detachment limit as the H− resonance, but it is approximately one order of magnitude broader than the H− state. This broadening arises from the strong coupling to the 3s\(\ell\)p continuum, a continuum which is not available below the H(\(n = 3\)) threshold in H− [86]. The Li− resonance state is dominated by the configurations 3p3d and 4s3p, whereas there is no significant contribution to the localized part of the wave function from configurations with one electron in the 3s orbital, which also is in contrast to the case of H− [86].

The narrow structure located just below the Li(3p) threshold (Fig. 32) is due to two asymmetrically excited Rydberg-like states located rather close and with their widths overlapping each other [86]. Rydberg-like resonant states are also known from the calculated spectrum of H− and are bound by the strong dipole field between the two electrons arising due to the degeneracy of the H(3\(l\)) states.
resulting in nearly equal admixtures of 3snp and 3pns configurations in their compositions [164].

The Rydberg-like Li− states, however, do have a different character. They are completely dominated by 3pn\(l\) configurations with \(n\) being somewhat larger than 3, and the dipole field is in this case insignificant. Benzinsh et al. [164] pointed out that the explanation for the existence of the Rydberg states in Li− is the inability of the monopole part of the electron–electron interaction to screen the singly charged core completely, whereas the residual nuclear attraction binds the states below the Li(3p) threshold.

The Gothenburg group extended the study of the Li− photodetachment cross section to cover the Li(4p) and Li(5p) threshold regions by measuring the relative partial cross section for photodetachment via the Li(3s) + e−(\(\ell p\)) channel [165]. Resonant ionization detection of Li(3s) atoms was applied to secure high spectral resolution. At higher levels of excitation the core effects should become smaller, resulting in near degeneracy of the Li excited state thresholds and the Li− spectrum will then more resemble that of H−. Fig. 33 shows a comparison between the experimental data obtained in the two energy regions and theoretical calculations by Pan et al. [444], who utilized the \(R\)-matrix method. The upper part of the figure represents the region below the Li(4p) threshold for which there is an excellent agreement between the experimental and theoretical (solid line) data, whereas noticeable differences appear in the lower figure, which represents the energy region below the Li(5p) threshold. Here the discrepancy appears to increase the further the resonance is from threshold, and the observed strengths of some of the resonances deviate from the predictions.

The resonance parameters (energies and widths) for the first two resonances located in the upper part of Fig. 33 were calculated by Lindroth [86], who derived the parameters from complex rotation calculations, whereas the \(R\)-matrix calculations by Pan et al. [444] do not explicitly yield the resonance parameters. The agreement between the calculated and observed values is very good; the energy was predicted to be 5.115 eV for the first resonance with a width of 73 meV, whereas the experimental values were 5.1132(4) eV and 74(5) meV, respectively [165].

The discrepancies between the experimental and calculated data in the lower part of Fig. 33 initiated new calculations by Liu and Starace [445], who used a much larger \(R\)-matrix radius than applied in the previous calculations by Pan et al. [444,446]. The new calculations resulted in a much better agreement with the experimental data [165] and account for nearly all the prior discrepancies between theory and experiment unless in the energy region around 5.421 eV. At this energy theory predicts a resonance structure not clearly observed or experimentally identified. This resonance was attributed by Liu and Starace to a \(s\{1\}\(6\) doubly excited state with angular symmetry. This state is quasi forbidden in H− by propensity rules, but it has a significant effect on all Li− photodetachment partial cross sections owing to the non-Coulomb Li+ core.

Haefer et al. [166] extended the study of the Li− resonance structures below the Li(4p) threshold by recording the Li(4s) + e−(\(\ell p\)) partial photodetachment cross section and comparing the new data with the spectrum presented in the upper part of Fig. 33, which represents the Li(3s) + e−(\(\ell p\)) partial cross section. The two spectra were found to be mirror images of each other, a behaviour already predicted by Pan et al. [444]. The new data confirmed the resonance parameters obtained before [165], but the widths appear to some extent to be affected by the overlap of adjacent resonances.

Most recently, the studies have been extended to include the energy region below the Li(6p) threshold [167] and the experimental data have been compared with a complex rotation calculation
allowing identification of the strongly correlated, doubly excited states of Li\(^-\) responsible for the observed resonances. Fig. 34 shows the comparison between the experimental and calculated Li\(^-\) data and with the calculated photodetachment cross section of H\(^-\) below the H\((n=6)\) threshold, included in the lower part of the figure.

The analysis of the experimental data revealed that the resonances marked a–g do not belong to a common series, since they are too closely spaced in energy. The resonances marked b, d, f and g are members of a \(^1\text{P}^0\) series corresponding to the \(\sigma(K,T)=\sigma(4,1)^+\) series in the H\(^-\) spectrum, whereas the resonances a and e are members of the \((3,0)^-\) series below \(n=6\) threshold. The “+” series having \(K=n-2\) dominates the Li\(^-\) spectrum as well as the H\(^-\) spectrum [50]. Resonances with “-” character were not identified in the photodetachment spectra of Li\(^-\) at lower level of excitation (below the Li\((5p)\) threshold), but theoretically predicted by Liu and Starace [445], see above. The weak resonance marked c in Fig. 34 was assigned to be a member of the \(\sigma(2,1)^+\) series, which corresponds to \(K=n-4\), a series not observed in the H\(^-\) spectrum.
Fig. 34. Top part: Experimental Li(3s) + e^−(e p) partial photodetachment cross section for Li^− below the Li(6p) threshold. The solid line represents a fit based on Shore parametrization to the experimental data [167]. Middle part: Calculated total photodetachment cross section using the method of complex rotation to handle the autodetaching states. Bottom part: Calculated total photodetachment cross section of H^− below the H(n = 6) threshold. The energy scale at the top is relative to the Li^− ground state and applies to the two upper curves, whereas the energy scale at the bottom shows the energy relative to the Li(6p) threshold (top and middle part) and the H(n = 6) threshold (bottom part).

It is possible to make a comparison between the series observed in the photodetachment of the Li^− and H^− ions and obtain information about the influence of the core electrons on the photodetachment processes by comparing the spectra shown in Fig. 34 [167]. The H^− spectrum is dominated by the two intense window resonances marked B and D (analogous to b and d in the Li^− spectrum) and are members of the (4,1)^+ series. The tiny features marked A and E (the latter is hardly visible in the spectrum) are members of the (3,0)^− series. Thus the pattern in H^− is broken, since even though photoexcitation of Li^− to the (K = n − 2, T = 1)^+ states still dominates like in H^− the excitation to the (K = n − 3, T = 0)^− states is significant in Li^−, but not in H^−.
In the case of \( H^- \), the motions of the electrons in a highly correlated, doubly excited state were shown to be similar to those in a floppy three-body rotor, consisting of a proton situated between the two excited electrons \([264,447]\). In this model the “+” series corresponds to the ground state bending vibrational mode \((v = 0)\), whereas the “−” series corresponds to an excited state \((v = 1)\) of this motion. The latter type of excitation is present in the photodetachment spectra of \( Li^- \) and thus represents a violation of the propensity rules established for \( H^- \), since this type of excitation is not observed in the experimental \( H^- \) data \([50]\).

**Inner-shell excitation and detachment of \( Li^- \):** Inner-shell excitation of \( Li^- \) ions was first observed in beam-foil spectra, see Section 2.7, but the \( Li^- \) \( 1s2p^3 \, ^3S^- 1s2p^2 \, ^5P \) optical transition remained for a long time an unidentified transition or was assumed to belong to the core excited neutral \( Li \) spectrum. The energies of the two \( Li^- \) states and the lifetime of the upper state could be obtained from the beam-foil data, but in spite of several later attempts to measure the lifetime of the lower state or its fine or hyperfine structure these properties are still unknown due to lack of experimental methods to selectively populate the quintet \( P \) state.

Deep inner-shell photodetachment of a negative atomic ion was investigated both experimentally \([7,8]\) and theoretically \([8,436]\) in 2001 with the \( Li^- \) ion as the selected system, since it is the simplest multi-shell negative atomic ion and experimentally reasonable to deal with. Zhou et al. \([436]\) predicted that the photodetachment of the \( Li^- \) ion would differ qualitatively and quantitatively from the corresponding process in \( Li \) and \( Li^+ \). The calculations were performed using an augmented \( R \)-matrix methodology, and revealed numerous structures over a broad energy region including a new phenomenon, Auger decay of a shape resonance.

Concurrent with the theoretical study by Zhou et al. \([436]\), Kjelsenn et al. \([7]\) performed absolute cross section measurements for photodetachment of \( Li^- \) ions near the \( 1s \) threshold by measuring the \( Li^+ \) production by overlapping a beam of \( Li^- \) ions with synchrotron radiation from an undulator at the ASTRID storage ring. Multiple excitation to the core-excited \( Li \) \( 1s(2s2p \, ^3P)\, ^2P \) and \( Li \) \( 1s(2p3s \, ^3P)\, ^2P \) states, i.e. conjugate shakeup, was found to be much stronger than observed for any neutral or positive ion, reflecting the dominant influence of electron correlation for negative ions. The cross section for multiple excitation was significantly larger than for single excitation. The main conclusions from the experimental study and the theoretical predictions were in very good agreement. It was, however, predicted that the one-electron detachment cross section should exhibit a large cross section with a maximum of approximately \( 16 \) \( Mb \) right after the \( 1s \) threshold at \( 56.9 \) \( eV \) due to the \( Li \) \( 1s2s^2 \) formation. This prediction was, however, not in agreement with the experimental data by Kjeldsen et al. nor with the photodetachment data reported later in 2001 by Berrah et al. \([8]\).

Fig. 35 shows the total double photodetachment cross section of \( Li^- \) giving rise to \( Li^+ \) in the vicinity of the \( 1s \) threshold. The solid curve is an \( R \)-matrix calculation superimposed on the experimental data by Berrah et al. \([8]\), the later being normalised to the calculations at \( 62 \) \( eV \). The arrows indicate neutral \( Li \) thresholds. The main features are the same in the experimental data by Kjeldsen et al. \([7]\) and by Berrah et al. \([8]\), and both data sets are deviating from the theoretical calculation near the \( Li \) \( 1s2s^2 \) threshold. The reason for this deviation has been identified very recently as due to post-collision interaction. By including recapture of slow photoelectrons following Auger decay of an inner-vacancy state in the \( R \)-matrix calculation it was possible to obtain an excellent agreement between experiments and theory \([437]\).

Collisional detachment of \( Li^- \) by rare gases was studied in the beginning of the 1980s, and later followed by a critical investigation of the independent scattering model \([216]\), which treats the
negative ion as consisting of a loosely bound electron and a neutral core atom, which independently of each other can interact with the rare gas. The experimental test [217] compared the population of the excited Li(2p 3P) state for keV Li–He and Li−–He collisions.

In the region of maximum excitation probability, a strong preference for population of the magnetic sublevel \( m = -1 \) was observed for both types of collisions; the shape of the excited electron cloud and its alignment with respect to the projectile axis were identical for the two collision processes, yielding support to the independent scattering model. The degree of polarization, however, showed that the electron correlation of the two outer electrons in Li− should be taken into account to account for all the properties related to the electron detachment process.

4.4.2. Sodium

During the last decade the Na− ion has not attracted a similar great interest as the Li− ion. The binding energy of the Na− was already well established in the 1980s [49] and in contrast to the relative large number of studies of highly excited two-electron states in photodetachment spectra of H− and later Li− the Na− photodetachment spectrum and, more specifically, the spectrum of excited two electron states in Na−, was relatively unexplored until a few years ago [168,448]. Only the energy region from the Na(3s) threshold to the Na(3p) threshold had been studied before, experimentally and theoretically [42,449]. The photodetachment cross section raises rapidly above the ground-state threshold and exhibits a prominent cusp structure at the first excited state threshold, Na(3p). The cusp behaviour is well understood on the basis of the Wigner threshold laws [261].

In 1999 Haefliger et al. [168] reported experimental measurements of the Na− partial cross section of the photodetachment of the Na− ion for the Na(4s) + e−(ɛp) channel for energies ranging from the vicinity of the Na(5s) threshold to the vicinity of the Na(4d) threshold. This study was followed by a detailed theoretical investigation of the photodetachment spectra of Na− by Liu and Starace.
Fig. 36. Na(4s) + e\(^{-}\) (ep) photodetachment for Na\(^{-}\) in the photon region from the Na(5s) to the Na(5p) threshold. The data points [168] are normalized to the theoretical result [390] between the Na(5s) and Na(4d) thresholds. The vertical dashed lines indicate the location of the thresholds.

[448], who reported partial as well as total cross sections covering the energy region up to the Na(5p) threshold. The cross sections were calculated by the eigenchannel \( R \)-matrix method, which previously had been used successfully to predict the H\(^{-}\) and Li\(^{-}\) photodetachment spectra [444–446]. The photo electron angular distribution asymmetry parameter for photodetachment of Na\(^{-}\) leading to Na(3p) + e\(^{-}\) formation was also calculated over the same energy range. The analyses focussed on the identification of the \(^1\)P\(^0\) resonance structures and the comparison with corresponding ones in H\(^{-}\) and Li\(^{-}\).

Fig. 36 shows a comparison between the experimental [168] and calculated [448] cross sections in the range covering the Na(5s) and Na(5p) thresholds after the experimental data have been normalized to the calculated cross section in the region between the 5s and 4d thresholds. Five doubly excited \(^1\)P doubly excited states, having three different kinds of radial and angular symmetry, are responsible for the structure in the spectrum. The non-hydrogenic nature of the Na\(^{+}\) core leads to prominence of doubly excited resonances that are absent in H\(^{-}\) photodetachment spectra, as was also found in analysis of the Li\(^{-}\) photodetachment spectrum [444–446]. Whereas the “+” type states completely dominate the H\(^{-}\) photodetachment spectrum and “−” type states only appear as extremely narrow resonances (see Section 4.1) there is a prominence of “−” type resonances in the Na\(^{-}\) spectrum. This is accounted for by a mixing of different angular symmetries among the doubly excited states in Na\(^{-}\), which may be attributed to the non-Coulomb Na\(^{+}\) core that the excited pair of electrons in Na\(^{-}\) see [448].

Vinci et al. [450] extended the study of the photodetachment of Na\(^{-}\) to include both single- and multi-photon detachment using the \( R \)-matrix Floquet approach, which can yield additional information on the negative ion, for example, two-photon excitation of \(^1\)S\(^0\) and \(^1\)D\(^0\) resonances come into play. In the low-photon intensity limit agreement for single detachment was obtained over a wide frequency range with other theoretical work and with experiments. At higher photon
intensity ($10^{10}$ W/cm$^2$) two- and three-photon detachment rates have been calculated at low frequencies, where multi-photon absorption is the lowest-order process, and at higher frequencies where two- and three-photon absorption are studied as above threshold processes. Similar theoretical studies have previously also been performed for the Li$^-$ ion [451], but so far there are no experimental data to compare with for either of the negative ions.

Photodetachment of the Na$^-$ using XUV photons with energies in the range 30–51 eV has been studied [438] at the advanced light source (ALS) at the Lawrence Berkeley National Laboratory. At these photon energies, electron detachment leads prominently to the production of Na$^+$ ions. The structures in the measured cross section are associated with correlated processes involving detachment or excitation of a 2p electron, processes that often are accompanied by the excitation of one or more valence electrons and thereby showing that multiple excitation, as previously observed for inner-shell excitation of Li$^-$ [7], is the dominant process in inner-shell excitation of a negative atomic ion. The most prominent feature in the Na$^-$ cross section is a strong resonance at 36.292 eV associated with excitation of a 2p electron from the core and a 3s valence electron leading to the Na$^-$ 2p$^2$3s4s $^2$Po doubly excited state. So far the inner-shell photodetachment of Na$^-$ has not been studied theoretically.

4.4.3. Potassium

The K$^-$ ion has recently attracted new interest following the success of the studies of the lighter negative alkali metal ions. Previous studies of the K$^-$ ion were mainly based on electron scattering experiments [42,435], but the lack of resolution sometimes prohibited unambiguous assignment of the observed structures. The use of photon-impact has made more detailed studies possible dealing with the photodetachment spectrum from threshold to nearly 4 eV above. The binding energy of K$^-$ was improved by Andersson et al. [163] using laser photodetachment threshold spectroscopy combined with selective detection of the excited K(4p) atoms generated. The binding energy value of 0.501 459(12) eV represented an improvement in accuracy of nearly an order of magnitude compared with the previous value [31].

The spectrum of $^1$Po doubly excited states in the K$^-$ ion has been the object of an experimental photodetachment study by the Gothenburg group [169]. The energy region studied covered the K(5d), K(7s) and K(5f) thresholds, which are located between 4.2 and 4.3 eV above the ground state of K$^-$. The experimental technique used was similar to the one applied to study the higher lying Li$^-$ resonances and included measurement of the partial photodetachment cross section for the K(5s) + e$^-$ channel. Seven resonances were observed and six of these could be assigned to two series, one consisting of two states (a–b) located below the K(5d) threshold the other of four states(d–g) located below the K(5f) threshold, see Fig. 37. The fits of the data to sums of Shore profiles [452] with linear backgrounds are shown by solid lines. The energy region between 4.1 and 4.2 eV, where the K(6p) threshold is located, was investigated too, but no prominent resonance structures were observed in this region.

Identification of the K$^-$ resonances in Fig. 37 was facilitated using a semi-classical formula for the energies of doubly excited states in nonhydrogenic negative ions [453], which relates the resonance energy $E(n)$ with respect to the threshold by the equation

$$E(n) = -2C_0^4 \left( n_{\text{max}} - n \right)^4/\alpha ,$$
where $C_0$ is a numerical constant (1.848), $n$ is the principal quantum number for the outer electron, $\alpha$ the dipole polarizability of the parent atomic state, and the integer part of the parameter $n_{\text{max}}$ represents the maximum number of states that can be bound to the given atomic state. It should be noted that $n$ refers to the quantum number of the outer electron in the model polarization potential and thus one should assign $n=1$ to the lowest state of a given series, such as resonance $a$ converging on the K(5d) threshold and resonance $d$ converging on K(5f).

The widths of the resonances along a given series such as $d-g$ are decreasing by nearly an order of magnitude from one member to the next. The resonances $d-f$ have widths of 10(2), 1.5(2) and 0.10(8) meV, respectively [169]. Kiyan [453] has developed a semi-classical model to describe the two-electron dynamics of the process of autodetachment from which a formula can be derived for the partial width of a doubly excited state as a product of an amplitude and phase factors. The phase factor reflects phase matching between the semi-classical phase of the outer electron in the initial
state and the phase of the continuum wave of the outgoing electron. This factor is nearly constant at small energies below the threshold, where the functional behaviour of widths can be described by the amplitude factor determined by the wave function normalization coefficient. The semi-classical model describes reasonably well the experimental \( K^- \) data and is also able to account for the width of the last resonance in the series \( d - g \). It is located close to the threshold and has a width of 0.30(3) meV, which deviates considerably from the decreasing trend mentioned above. The model predicts that in the case where the outer electron has a high angular momentum, the width can have an anomalous behaviour near threshold.

The experimental \( K^- \) study [169] was quickly followed of a detailed theoretical study [454], which calculated the photodetachment cross section over the energy region from the \( K(5s) \) threshold to the \( K(7p) \) threshold using \( R \)-matrix technique; thus the entire region explored experimentally was covered. The calculated spectrum is in good agreement with the experimental observations by Kiyana et al. [169] and the \( 1P^o \) resonances could all be identified with \( K^- \) doubly excited states and characterized by their energies and widths. The calculations show that the resonance marked a in Fig. 37 is due to two overlapping resonances, but appears as a single window feature in the experimental data, which indicates that fitting the measured cross section to a resonance profile formula might not always be sufficient in determining the resonance parameters.

Comparing the \( K^- \) results with the prior studies of the lighter alkali metal negative ions and of \( \text{He}^- \) it is evident that, as the alkali-metal negative ions become heavier, the approximate symmetry of pure three-body systems breaks down, being replaced by a more complicated interchannel coupling [454]. The asymptotic behaviour of electron–atom interaction plays a decisive role in the spectrum of negative ions, but a pure induced-dipole potential is not sufficient to describe the structure and dynamics of non-hydrogenic negative ions. It is necessary to take effects due to interchannel coupling and electron correlation in the region close to the nucleus into account [454].

Later Vinci et al. [455] calculated the single- and multi-photon detachment rates for \( K^- \) using the \( R \)-matrix Floquet approach. At lower laser intensities \( (10^9 \text{ W/cm}^2) \) the authors obtain good agreement with the experimental and theoretical data described above. The two-photon detachment rates are calculated at low frequencies, where multi-photon absorption is the lowest-order process, and compared with the two-photon detachment study of \( \text{Na}^- \) [450] performed by the same authors. It should be noted that the signature of the \( K^-(5s^2 \; 1S) \) doubly excited state is clearly visible in the calculated two-photon detachment rate, which may encourage multi-photon experiment to be performed in the future with the lighter negative alkali metal ions [455]. Multi-photon experiments have been reported for \( \text{Rb}^- \) [174] and \( \text{Cs}^- \) [173], as described below, but only at specific photon energies.

4.4.4. Rubidium, caesium, and francium

In contrast to the lighter negative alkali metals ions, the experimental studies performed during the last decade with the \( \text{Rb}^- \) and \( \text{Cs}^- \) ions have been limited and not included systematic studies of the single-photon detachment cross section nor improvement of the binding energy values presented by Hotop and Lineberger in 1985 [31,49]. Negative ions of Fr have so far not been studied.

Resonance structures in the photodetachment spectra of \( \text{Rb}^- \) [133] and \( \text{Cs}^- \) [134] were already established in the 1970s, when it was observed that the photodetachment cross section nearly vanished over a small wavelength range just below the first excited state thresholds. This behaviour could be
explained by the existence of a resonance in the $^1P$ channel just below the respective excited state thresholds. Resonances above the first excited neutral atom states have also been observed in electron scattering experiments [42], but detailed experimental single-photon detachment data covering the energy region above the first excited state thresholds have not yet been reported.

Scheer et al. [184] localized the Cs$^-$($6s6p \textit{^3P}_J$) states just above the ground state of Cs. Since the transition from the Cs$^-$($6s^2 \textit{^1S}$) ground state to the excited $6s6p \textit{^3P}_1$ is forbidden in the LS coupling scheme, the photoexcitation becomes very sensitive to the spin–orbit interaction. Photo detachment spectroscopy and the ASTRID storage ring were used to search for $^3P_J$ low-lying states, which previously had been proposed to be possible bound state candidates (see Section 2.5.4). The $J=1$ resonance was observed in the photodetachment spectrum and proved to be located 8.0(3) meV above the Cs($6s$) ground state having a width of 5.0(5) meV. The $J=0$ fine structure state, which is located at lower energy, was calculated by Thumm and Norcross [456] and Bartschat [457] to be located about 3.5 meV below the $J = 1$ state; thus it should also be located in the continuum. A storage ring experiment was conducted searching for the $J=0$ state. If it were located below the Cs ground state, the $J=0$ state could be observable in the decay rate of the stored ions as a consequence of blackbody-induced photodetachment radiation, but only the signal attributed to the ground state of Cs$^-$ was observed. Thus the storage ring experiment supported the theoretical estimates for the location of the Cs$^-$($6s6p \textit{^3P}_0$) state just above the continuum limit. Very recently Khuskivadze et al. [458] performed a theoretical study of the static electric-field effects of the photodetachment cross section of Cs$^-$ at the $^3P$ resonance region. They reported, that it should be possible to obtain more favourable experimental conditions for the observation of the lowest $^3P$ resonance by studying the near-threshold photodetachment cross section of Cs$^-$ in the presence of a dc electric field.

The Cs$^-$ ion was at the middle of the 1990s assumed to be the best candidate for a negative ion possessing bound states with different parity. A few years later the Os$^-$ ion was proved to exhibit these properties [1].

Experimental multi-photon absorption studies of the Rb$^-$ [174] and Cs$^-$ ions [173] have been explored showing that photoabsorption via the window resonances occurs very efficiently and that multi-photon absorption leads to double ionization of the negative ions primarily as the result of a sequential removal of the two electrons via an excited neutral atom state, in the case of the Rb$^-$ ion the excited state is Rb(8s) or Rb(6d) [174]. The Cs$^-$ study was described in Section 2.5.3 as an example of resonant multi-photon study above the detachment limit. It has not been the purpose of these multi-photon experiments to search for resonances above the first excited thresholds and such resonances have not been observed.

Theoretically the resonances, which may be detected in near-threshold photodetachment spectra of the Rb$^-$, Cs$^-$ and Fr$^-$ ions and in slow-electron-heavy alkali metal atom scattering, have been studied rather intensively during recent years by Bahrim et al. [459–463]. The photodetachment calculations were carried out using $R$-matrix methods and suggested that none of the negative ions of Rb, Cs or Fr has an excited bound state [459]. For Cs$^-$ the photodetachment cross section near threshold has even been calculated in very good agreement with the experimental observation by Scheer et al. [184] after tuning the resonance position by 2–4 meV [462]. For Rb$^-$ and Fr$^-$ the resonance contribution to the near-threshold photodetachment cross section has been estimated be much smaller than for Cs$^-$ [462,463].

Bahrim et al. [460] also analysed negative-ion resonances in elastic and inelastic total scattering cross section for slow electron collisions with Rb, Cs or Fr. These calculations were based on the
Dirac-R matrix method described by Thumm and Norcross [456]. For incident electron energies up to 2.8 eV kinetic energy, the resonance structures located between the continuum limit, the neutral atom ground state, and the first excited threshold of the atomic target were investigated. In addition to the low-lying $^3P_0$ shape resonance discussed above the studies are dealing with $^3P_e$, $^1P_0$ and $^1D_0$ Feshbach resonances, located below the first excited threshold.

Just above the first excited threshold in the neutral alkali metal atoms a $^3F_0$ shape resonance has been observed [42]. Bahrim and Thumm [461] calculated the angle-dependent and momentum-transfer cross sections for elastic scattering on Rb, Cs, and Fr at impact energies below 3 eV. They found for Cs a Cs$^-$($^3F_0$) shape resonance at 1.528 eV in excellent agreement with the experimental data [464].

The last decade has yielded significant progress in the understanding of the structure and dynamics of the negative alkali metal ions, but further studies are indicated such as experimental studies using intense lasers or systematic studies of the photodetachment cross section of the heavier negative alkali metal ions.

4.5. The alkaline earths

Next to the fundamental hydrogen ion, the negative ions of the alkaline earths elements have been at the centre of negative ion research for more than a decade after Pegg et al. [10] in 1987 discovered the stable Ca$^-$ ion. Before that time it was generally accepted that the alkaline earths elements, Be, Mg, Ca, Sr, and Ba, all having a closed s-electron shell in their ground state electronic configuration, would be unable to form stable negative ions. Since the filling of electronic sub-shells may not be following the same ordering for negative atomic ions as for neutral atoms, some surprises could, however, be expected and one of these appeared with the stable Ca$^-$ ion. This ion possesses a 4s$^2$4p valence shell in the ground state in contrast to 4s$^2$3d present in the isoelectronic Sc atom. Since the polarizability of the alkaline earth atoms increases from Be to Ba, it could be expected that both Sr and Ba would form stable negative ions with binding energies somewhat larger than for Ca.

The Ca$^-$, Sr$^-$, and Ba$^-$ ions are all weakly bound with binding energies below 150 meV [31], which has made them attractive test objects for atomic theory. Only a proper description of the electron correlation can match the experimental binding energies. The first attempts to calculate the binding energies of the heavier negative alkaline earths ions focussed on the contribution from the valence electrons, whereas contributions from the core electrons or among core and valence electrons were neglected, leading to binding energies that later were shown to be significantly larger than the measured values. This development was undoubtedly due to the fact that the binding energy reported for the negative Ca-ion in 1987 [10] was a factor two too large [4].

4.5.1. Beryllium

The Be$^-$ ion has been known to exist since 1966, when it was observed in the mass spectra from negative-ion sources [465]. The electron configuration 1s$^2$2s2p$^2$ and the term $^4P$ were assigned to the observed Be$^-$ ion at the beginning of the 1980s as a result of a series of experimental and theoretical studies [422,466–470]. Calculations showed, that the negative Be-ion could not be formed by adding an electron to the Be atom in its 1s$^2$2s$^2$ ground state configuration, but only to the excited Be(2s2p$^3$P) state. In addition, two other metastable states were predicted to exist [442,469,470], the 1s$^2$2p$^3$ $^4S$ and the core excited 1s2s2p$^3$ $^6S$. 
Be\(^-\)(2s2p\(^2\) 4P): The observation of the metastable 1s\(^2\)2s2p\(^2\) 4P state was quickly followed by calculations of its binding energy, fine and hyperfine structure, and the lifetimes of the three P\(_J\) levels [384,470–474]. These can undergo direct autodetachment only via intermediate coupling, and the lifetimes of the J-levels can be expected to be rather different with the J = 3/2 level having a lifetime considerable longer than the J = 5/2 and 1/2 levels. Brage and Froese Fischer [384] explained the longer J = 3/2 lifetime as a consequence of destructive interference between the direct relativistic and relativistically induced Coulomb detachment. It should be noted that the decay mechanism for the metastable Be\(^-\)(4P) ion is very different from the decay mechanism for the metastable He\(^-\)(1s2s2p4P) ion, for which the J = 5/2 level has the longest lifetime of the J-levels [12].

Before 1990 the binding energy of the Be\(^-\) (4P) ion was predicted to be in the range from 275–285 meV [422,471], but the only experimental value available was 190(110) meV [467], which could not challenge the predictions. In 1993 the binding energy was determined more accurately by laser photodetached electron spectroscopy to be 261(10) meV [475], but this value was also below the theoretical estimates. Furthermore, extensive calculations with cautious treatment of the core–core and core–valence contributions to the electron correlation showed [476,477] that the binding energy might be even larger than previously assumed with 289.1(1.0) meV being the most accurate prediction so far [477]. Finally, the development of resonant ionization spectroscopy and its application to the Be\(^-\) ion (see Section 2.5.1, where the Be-experiment is described) established the binding energy of the 4P state with respect to the 2s2p 3P state in Be to be 290.99(10) meV [21].

Before magnetic storage rings were introduced to negative-ion research the lifetimes of the metastable Be\(^-\)(2s2p\(^2\) 4P\(_J\)) levels were only available from theoretical estimates [384,472,473], which predicted the J = 3/2 component to have a lifetime between 0.1 and 2 ms, whereas the J = 5/2 and 1/2 components were expected to have lifetimes shorter than 1 \(\mu\)s. From a single-pass beam experiment Bae and Peterson [466] had reported that the decay of Be\(^-\)(2s2p\(^2\) 4P\(_J\)) ions exhibits at least two components, one with a lifetime of the order of 100 \(\mu\)s, which now may be attributed to the J = 3/2 level, the other with a lifetime a magnitude lower.

The measurement of the lifetime of the J = 3/2 level was among the first experiments performed at the storage ring ASTRID [20] (Section 2.8). The decay rate of the metastable, negative Be ions was measured with a tandem-channel-plate detector, which monitored the fast neutral atoms (Be) produced along one of the straight sections of the ring. Fig. 38 shows a typical plot of the neutral atom signal vs. time for a beam energy of 50 keV. The time interval between the data points depends on the operation mode of the storage ring. With a 40 m circumference of the ring and a beam energy of 50 keV there will only be a limited number of data points as indicated on the figure. The decay rate could be accurately fitted by a single exponential, representing the lifetime of the J = 3/2 level, whereas the two shorter lived, fine-structure levels decay during the first roundtrip of the ions. The J = 3/2 lifetime was determined to be 45(5) \(\mu\)s, which was considerably below the theoretical estimates.

The magnetic fields in the storage ring can influence the measurement of the lifetime. The field in the dipole magnets, a few hundred gauss, is strong enough to mix magnetic substates from different fine-structure components with the same M\(_J\) number. In first-order perturbation theory, the mixing amplitudes will be proportional to the magnetic field strength (Zeeman coupling), and consequently the decay rate is expected to depend quadratically on the field strength, i.e. linearly on the beam energy at sufficiently low energies. An analysis of the decay rate as a function of the beam energy...
exhibited the expected linear dependence, allowing an extrapolation of the decay rate to zero beam energy and a determination of the $J=3/2$ lifetime. From the analysis of the influence of the magnetic field it was also possible to get some information about the short lived components ($J=5/2$ and $1/2$); taking into account that the $J=5/2$ component will be the dominantly populated of these two its lifetime could be estimated to be $0.25(15)$ µs [20].

The use of a magnetic storage ring to measure lifetimes of metastable, negative atomic ions with lifetimes longer than $10$ µs was a significant step forward compared with lifetime methods based on single-pass beam techniques. However, the influence from the magnetic fields may limit the accuracy obtainable, but contrary can provide some information about decay rates for the shorter lived $J$-levels, which otherwise are eliminated during the first roundtrip of the ions in the ring.

It is evident that a storage ring based on pure electrostatic storage would be more favourable for measurements of lifetimes of negative atomic ions, like Be$^-$, leading to a much improved accuracy. This has recently been demonstrated [24] using the electrostatic storage ring ELISA.

In between the two storage ring measurements Knoll et al. [23] reported the lifetime value $42.07(12)$ µs for the Be$^-$(4P$_{3/2}$) ion, obtained using an electrostatic hybrid ion trap [69]. This lifetime value is in good agreement with the result from the magnetic storage ring and the uncertainty represents an improvement of a factor of 40 with respect to the storage ring experiment. Shortly after the electrostatic storage ring ELISA became operative allowing tests of the previous measured lifetimes for metastable, negative ions, such as He$^-$ and Be$^-$. Even though the two reported experimental lifetimes for the Be$^-$ ion agree within the quoted error bars, ELISA offers possibilities to determine the lifetime of the $J=3/2$ level much more accurately than at the magnetic storage ring. Furthermore, it is well established that imperfect storage of ions can appear in ion traps as well as in storage rings resulting in lifetimes shorter than the true one. If the lifetimes measured at ion traps or storage rings deviate, it is reasonable to assume that the longest lifetime value is in best agreement with the true value, since most conceivable effects, which can influence the measurement, will lead to an increase of the decay rate.

Fig. 38. Autodetachment yield of Be atoms vs. time for Be$^-$ ions stored in the ASTRID storage ring at 50 keV. The straight line represents a fit to the experimental data. Statistical error bars are shown for the experimental points for which the error bars are larger than the size of the dots.
Fig. 39. Autodetachment decay of Be\(^-\)\(2s2p^2\,{}^4\text{P}_{3/2}\) ions. The neutral Be signal is shown as a function of time after the injection of the Be\(^-\) ions into the ELISA storage ring [24]. The solid line represents a single exponential decay component plus a small background.

The decay rate measurements at the ELISA storage ring were independent of the kinetic energy of the Be\(^-\) ions as expected as no magnetic fields is present, and in addition the decay rate is insensitive to blackbody radiation from the surrounding walls since the binding energy is about 291 meV. A detailed statistical analysis of the data (see Fig. 39) [24], which could be fitted to a single exponential, yields a final lifetime value of 43.40(10) \(\mu\)s for the \(J = 3/2\) component, which is 3% longer than reported from the ion trap experiment mentioned above. It should be noted that the 3% represents more than 10 standard deviations and consequently indicates a discrepancy between the two lifetime measurements. At the present time the precise Be\(^-\)\(4\text{P}_{3/2}\) lifetime, obtained at the electrostatic storage ring, may be used as a suitable reference standard for future lifetime measurements of metastable, negative atomic ions.

The most recent calculation of the \(J = 3/2\) lifetime has been performed by Aspromallis et al. [478]. They based their calculations on the golden rule formula, Breit–Pauli Hamiltonian and quasi-relativistic wavefunctions, which took the effects of electron correlation, core polarization and resonances via intermediate coupling into account. A lifetime of 33 \(\mu\)s was obtained, which is considerably shorter than the previously calculated lifetimes [384,473] and close to the experimental result taking the complexity of the calculation into account.

The lifetimes of the two shorter-lived fine-structure components of the Be\(^-\)\(4\text{P}_J\) ion, \(J = 5/2\) and 1/2, which were predicted to have lifetimes shorter than 1 \(\mu\)s, cannot be determined using storage rings. Single-pass beam technique combined with selective monitoring of the fine-structure levels is needed. State-selective two-photon detachment studies of Be\(^-\) ions, formed by double-capture of Be\(^+\) ions in Na vapour, combined with resonant ionization detection of the resulting neutral Be atoms was utilized [22] to obtain these lifetimes together with the fine-structure splittings of the three \(4\text{P}_J\) levels. Fig. 40 shows an energy level diagram of the relevant states in the Be\(^-\) ion and the Be atom and indicates the experimental method used. The probe lasers \(\lambda_1\) and \(\lambda_2\) perform selective photodetachment and ionization of the Be\(^-\)\(4\text{P}_J\) levels, while the pump laser \(\lambda_p\) can redistribute the ions from the long-lived \(4\text{P}_{3/2}\) level to the complete multiplet. The time ordering of
the laser pulses is indicated on the figure. Andersen et al. [22] applied two methods to obtain the lifetimes of the $J = 5/2$ and $1/2$ levels. The first relies on studying the decay of the fine-structure components produced immediately after the charge-exchange cell in which the ions are produced, the second benefits from redistribution of the level population by means of the pump laser via the $2p^3 \, ^4S$ level and probing of the populations of the short-lived fine-structure components with different delays between the pump and the probe lasers. The lifetime for the $J = 5/2$ level was measured to be $0.33(6) \, \mu s$ in good agreement with the first estimate of this lifetime from the magnetic storage ring [20], whereas the $J = 1/2$ level has a lifetime of $0.73(8) \, \mu s$. The theoretical calculation by Aspromallis et al. [478] also predicted the lifetime of the $J = 1/2$ level to be longer-lived than for the $J = 5/2$ level, with the lifetime of the latter ($0.43 \, \mu s$) being close to the experimental value. The measured fine-structure splittings between the three $J$-levels are in good agreement
with the calculations available \[470,477\], but the experimental accuracy is too low to distinguish between them.

The outer-shell photodetachment process of the $\text{Be}^-(1s^22s2p^2\,^4P)$ metastable state has been studied experimentally by Bae and Peterson \[466\] and Pegg et al. \[479\], who measured the total cross section and the angular distribution at selected photon energies between 1.5 and 2.5 eV. Theoretical studies have been reported by Sinanis et al. \[480\] and Ramsbottom and Bell \[481\] for photon energies ranging from threshold to 4.6 eV. No resonance structure was observed in this region. More recently, Xi and Froese Fischer \[482\] and Zeng et al. \[483\] have performed calculations ranging from threshold to 7.5 eV, whereas the study by Sanz-Vicario and Lindroth \[484\] covers the region up to about 10 eV. The former reports partial and total photodetachment cross sections, angular distribution parameters, and analysis of possible resonance structures in this energy region, which covers energies below the $n = 4$ threshold, where $n$ is the principal quantum number of the outermost electron of the Be target.

The only experimental value available for the angular asymmetry parameter \[479\] is in excellent agreement with the calculation, whereas there are significant discrepancies between the total cross section data, with the values measured by Bae and Peterson \[466\] being a factor of 4 below the calculated ones, for Pegg et al. \[479\] a factor of 1.3 which, however, may be reduced using new normalization data \[483\].

Sanz-Vicario and Lindroth \[484\] calculated the outer-shell photodetachment cross section using a complex scaled configuration interaction method. All the final symmetries exhibit resonant features, four $^4P^o$, seven $^4D^o$ and two $^4S^o$ resonances, six of these are corresponding to resonant triply excited states, including the two $^4P^o$ resonances reported by Zeng et al. \[483\]. The various theoretical calculations performed for the photodetachment of the $\text{Be}^-(2s2p^2\,^4P)$ ion are in rather good agreement. However, the minor differences may be used to test the ability of the different methods to achieve accurate results. The experimental data needed for testing the calculations are still lacking at the present time. Experiments involving beryllium species have almost disappeared from laboratories due to the strict regulations to manipulate dangerous substances.

Very recently, the partial and total cross sections for photodetachment of the metastable $\text{Be}^-(2s2p^2\,^4P)$ ion have been calculated for a range of initial photon energies across and beyond the 1s detachment threshold by Carlin et al. \[485\] using a multi-channel close-coupling $R$-matrix approximation, where sophisticated configuration interaction wavefunctions were used to represent the initial and final states. Twelve target eigenstates were included in the expansion of the total wavefunction describing the neutral Be atom. A number of prominent resonance structures were identified in the partial cross sections, but there are so far no experimental data to compare with nor other theoretical results describing inner-shell photodetachment of the negative ion of beryllium.

$\text{Be}^-(2p^3\,^4S)$: The $\text{Be}^-(^4S)$ state was first observed in 1989 by means of beam-foil spectroscopy \[178\], and its lifetime determined by following the optical decay at 265.30 nm to the lower lying $2s2p^2\,^4P$ state yielding the lifetime to be $1.25(10)$ ns. Due to the limited resolution of beam-foil data, the transition wavelength is later improved applying laser technique \[21,22\] resulting in $265.331(3)$ nm. The laser technique used is indicated in Fig. 40, utilizing a short delay (50 ns) between the pump laser and the probe lasers. The $^4P$–$^4S$ wavelength was the object of several calculations before the transition was observed, ranging from 263.8(6) to 267.1(1.2) nm \[380,422,469,470\]. The most recent value is 265.370(68) nm \[477\], which leads to a binding energy of the $^4S$ state of $295.0(7)$ meV with respect to the $\text{Be}(2p^2\,^3P)$ state, in excellent agreement with the measured value of 295.72(11) meV \[22\].
Possessing only 5 electrons the Be$^-$ ion attracts a good deal of interest as test object for theoretical calculations, some of which are aimed at accurate binding energies, but obtained using simpler calculations [486,241] than the large-scale configuration interaction calculations performed to obtain the binding energy of $295.0(7)$ meV mentioned above [477]. Hart [486] performed a $B$-spline configuration interaction calculation and reported $291.4$ meV, whereas Bertini et al. [241] presented a new form of explicitly correlated wavefunctions in quantum Monte Carlo calculations and obtained $292(2)$ meV.

The lifetime of the $^4S$ state was predicted to be $1.49$ ns, neglecting decay mechanisms other than electric-dipole transition. Taking radiative autoionization into account the lifetime would be $10–15\%$ shorter, i.e. approximately $1.3$ ns [469], which is in good agreement with the observed value [178]. The presence of two metastable states of opposite parity in the Be$^-$ ion, separated by an energy covered by conventional lasers, has offered good possibilities for structural and dynamic studies of this negative ion comparable to the ones existing for studies of neutral atoms. The Be$^-$ ion is, however, in this respect probably an exception among the negative ions.

$\text{Be}^-(1s2s2p^3\textit{6}S)$: The highly excited Be$^-(\textit{6}S)$ state is expected to be metastable. It has so far not been observed, but its properties, like binding energy and Auger electron energies, have been predicted [422,469,472,487].

The three Be$^-$ ions described above all have spin values of $3/2$ or $5/2$. The exploration of temporary anions of Be with spin value $1/2$, using electron scattering on Be-vapour, has not been attempted in the 1990s due to the well-known unhealthy properties of Be-vapour. The knowledge about the low-spin states is therefore still unchanged since Buckman and Clark [42] published their review.

### 4.5.2. Magnesium

Similar to beryllium, the binding energy for the Mg$^-$ ground state is negative. Temporary anion states with spin $1/2$ were studied in the 1970s and 1980s [42] and more recently also by Sullivan et al. [67,488], but the detection of a metastable Mg$^-$ ion with spin $3/2$, homologous to one of the metastable Be$^-$ ions described above, has so far been unsuccessful.

$\text{Mg}^-(3s3p^2\textit{4}P)$: Long-lived states of Mg$^-$ have been claimed to be observed in Penning ion sources [465] and their energies calculated by Weiss [468]. The observation was explained as due to the presence of the Mg$^-(3s3p^2\textit{4}P)$ ion, and the long-lifetime accounted for as a consequence of forbidden autodetachment in LS coupling. However, the experimental observation has been invalidated by later studies [489,490]. The experimental techniques applied in all the experiments demanded lifetimes of at least one of the $P_J$ levels to be longer than $10\mu$s and calculations by Beck [491] in the Hartree–Fock approximation predict the lifetimes to be much shorter, less than $10$ ns. If the lifetime is as short as indicated by the calculation it explains the negative results. Nicolaides et al. [51] have, however, pointed out that the Hartree–Fock predictions may be unreliable since the lifetimes are sensitive to a variety of electron correlation and cancellation effects as seen for the homologous Be$^-$ ion. It should be noted that the long lifetime of the Be$^-(\textit{4}P_{3/2})$ level is due to a specific cancellation effect, which is not present in case of the homologous Mg$^-$ ion. The Mg$^-(\textit{4}P)$ lifetimes are therefore expected to be shorter lived than the ones observed for other Be$^-(\textit{4}P)$ levels (less than $1\mu$s), since the spin–orbit coupling is increasing from Be to Mg leading to faster decays via autodetachment. An alternative experimental approach for detecting the Mg$^-(\textit{4}P)$ ion would be
to search for the optical decay from the excited 3p^3 4S state and estimate the lifetime from an analysis of the spectral line width.

Photodetachment of the Mg\(^-\) (3s3p^2 4P) ion has recently been treated by Zeng et al. [483] who predicted a rather smooth cross section below 3.5 eV; only a 4P resonance is predicted in this energy region and assigned to the 3s4s4p 4P state. The possibility for testing these calculations are limited due to the short lifetime of the target.

Mg\(^-\) (3p^3 4S): The Mg\(^-\) (4S) state is predicted to decay mainly by optical emission [422,474,491,492] with a radiative lifetime of 1.4 ns. According to Beck’s calculation [492] the 4S–4P transition would appear at 292.1(4) nm, whereas a more detailed investigation [474], predicted 289.5 nm. Froese Fischer [474] studied variational procedures for predicting energy differences for many-electron systems and included calculations of the transition wavelengths for the Li\(^-\) and Be\(^-\) ions, respectively, in addition to the unknown wavelength for the Mg\(^-\) ion. The calculations were based on the energy differences between the parent states in the neutral atoms combined with the expected or known electron affinities including contributions from the valence electrons and the core–valence interaction. For the Be\(^-\) ion the calculated transition wavelength agreed with the observed one within 0.05 nm, for Li\(^-\) within 0.2 nm.

Since the two theoretical estimates for the optical transition in the negative Mg-ion were deviating by nearly 3 nm, an experimental search had to cover a wavelength region ranging from about 286 nm to 295 nm [493]. The search [493] was based on the use of beam-foil and beam-gas spectroscopy, the latter applied to study the step-wise formation of the possible Mg\(^-\) (4S) ion from the initial Mg\(^+\) ion via charge exchange processes, considering Mg(3p^2 3P) atoms as the intermediate state. The analysis of the optical spectra showed that the cross section for production of the Mg\(^-\) (4S) ion by this mechanism is very much lower, by a factor of 30, than for formation of the homologous negative Be ion. The beam-foil spectra reveal a large number of spectral lines in the investigated wavelength region, but none of these could be assigned to a negative ion. While the possibility for observing the 4S–4P transition near 292.1 nm can be excluded, the region around 289.5 nm is more congested with a rather intense spectral line at 289.6 nm, which was shown to originate from the quintet spectrum of neutral Mg [493,494]. This Mg I line may perhaps cover a much weaker spectral line from the negative Mg ion. It should be noted, that if the cross section for producing the Be\(^-\) (4S) state was reduced by a factor of 30, it would have been extremely difficult to observe the optical transition in this ion using beam-foil technique [178].

4.5.3. Calcium

Peterson stated in 1992 [495] that “the Ca\(^-\) ion has proven to be a formidable and moving target for both experimental and theoretical attempts to determine its properties”, when he summarized the knowledge about this negative ion, which at that time already had attracted interest for nearly 10 years. Two electronic states of Ca\(^-\) were considered to have been observed, the stable ground state, 4s^24p 2P, and a metastable 4s4p^2 4P state. This was also the situation when Buckman and Clark wrote their review [42], in which a detailed description of the studies performed before that time is given. The development since then has led to a significant modification of the 1992 status. Now the properties of the stable ground state are well established; the excited 4s4p^2 4P state has finally been observed and characterized, disproving previous claims for its observation, and the doubly excited 4p^3 4S state has more recently been observed and characterized. In addition, the total cross section for photodetachment of the stable Ca\(^-\) ion has attracted a good deal of interest.
$Ca^- (4s^24p^2P)$: Pegg et al. [10] and Froese Fischer et al. [11] gave the study of the $Ca^-$ ion a new start in 1987 when they experimentally and theoretically, respectively, proved that the $Ca^-$ ion existed as a stable negative ion with a binding energy less than 50 meV. Both studies reported the binding energy for the $4s^24p$ ion to be close to 45 meV. In the following years these studies had a significant impact on many theoretical groups devoting their research to the properties of the negative ions of the heavier alkaline-earth elements. Many of the calculations following from 1989 to 1991 [496–501] yielded binding energies in the range 45–82 meV for the $Ca^-$ ion, whereas only a few [502,503] predicted values below the result reported by Pegg et al. [10].

In 1992, Walter and Peterson [504] reinvestigated the properties of the $Ca^-(2P)$ ground state, using laser photodetachment threshold technique (LPT) in contrast to laser photodetachment electron spectroscopy (LPES) used by Pegg et al. The measured binding energy of 18.4(2.5) meV was substantially smaller than the value (43(7) meV) reported by Pegg et al. [10]. Walter and Petersons work was soon after supported by two independent studies; the first applied electric field dissociation at a tandem accelerator [236,237] and obtained 21.5 (2.5) meV, the second was based on the observation of the decay rate for a stable $Ca^-$ beam in a storage ring [224]. Even though it was a stable ion, which was injected into the ASTRID storage ring, the $Ca^-$ ions decayed with a lifetime of only 490 μs. The observed decay rate, which could be attributed to the effect of blackbody induced photodetachment of the ground state negative $Ca$ ions at room temperature, was inconsistent with a binding energy of 43 meV, but in good agreement with a binding energy of the order of 20 meV.

Before the binding energy for the $Ca^-$ ground state was finally settled by Petrunin et al. [5] by means of multi-photon technique combined with resonant ionization detection, an alternative method of obtaining the binding energy of a weakly bound negative ion, like $Ca^-$, was proposed. On the basis of a theoretical study by Fabrikant [505], McLaughlin and Duquette [506] reported that the binding energy for the ground state of the negative $Ca$ ion could be obtained from studies of the electron transfer processes between $Ca(4s^2)$ ground state atoms and $Ca(4s(nd)$ Rydberg atoms, with $n$ values around 25, leading to formation of ion pairs, which consisted of $Ca^+$ ions in the 4s ground state and $Ca^- (4s^24p)$ ions. The initial calculations demonstrated a dramatic increase in the ion-pair formation when the binding energy of the Rydberg atom matched the electron affinity. Since the 4s(nd) Rydberg states around $n = 25$ are separated by approximately 1 meV it was the hope that the binding energy by this method could be obtained with a similar uncertainty. The binding energy was reported [506] to be 24(1.4) meV, obtained for $n = 25$.

It was, however, surprising that the ion-pair experiment was unable to observe the two fine-structure components of the $Ca^- (2P)$ ion, taking the good resolution claimed into account. The ion-pair result was therefore received with some scepticism and a reinvestigation of the experiment was undertaken at JILA [507]. It was here observed that the resonant formation of $Ca^+$ ions, the quantity measured by McLaughlin and Duquette [506], was not due to the ion-pair process, but to a three photon absorption process via the $Ca(4s25d \, ^1D)$ Rydberg state leading to autoionization of $Ca$ atoms from a doubly excited $Ca(3d_{3/2}9f_{3/2})$ state, located above the ionization limit.

In a later experiment [508] collisions between $Ca$-ground state atoms and Ne-Rydberg states, have yielded a significant peak in the $Ca^-$ production for Rydberg states with effective quantum number $n^* = 11.68$ for S states, and 11.5 for D states, in good agreement with the theoretical study of a decay model by Fabrikant [509], and with more recent close-coupling calculations by Fabrikant and Chibisov [510]. Collision between Rydberg atoms and ground state atoms can be an efficient way of producing negative ions with small binding energies. Experimental measurements of the rate
Fig. 41. Ca\(^+\) yield following photodetachment of the Ca\(^-\)\((4s^24p\;^2P_{1/2,3/2})\) ground state levels to the Ca\((4s5s\;^3S_1)\) level, which subsequently is monitored by resonant ionization via the Ca\((4s15p\;^3P_2)\) Rydberg level. Arrows indicate location of the thresholds [4].

of this process as a function of the principal quantum number \(n\) can also yield information about electron affinities of weakly bound atoms and molecules [511–513], which otherwise may be difficult to obtain. For the Ca\(^-\) ion the combination of photodetachment and resonant ionization spectroscopy (RIS) (see Section 2.5.1) of the excited Ca atom [5] has, however, proved to be superior to the methods mentioned above.

For Ca\(^-\), a small part of the ground state ions was photodetached to the Ca\((4s5s\;^3S)\) state, which was monitored by RIS via the 4s15p \(^3P_2\) Rydberg level. The data obtained are shown in Fig. 41, allowing an accurate determination of the binding energies of both fine-structure components, 24.55(10) meV for the \(J = 1/2\) and 19.73(10) meV for the \(J = 3/2\) component, together with a determination of the fine-structure splitting, 4.81(10) meV [5]. The accuracy of the binding values was limited to 0.10 meV by the frequency control during laser scans, whereas the contribution from the bandwidth of the applied laser and the effect of power broadening were negligible in this comparison. The experimental binding energies were in good agreement with the calculation reported by Bauschlicher et al. [502] in 1989, but this calculation was performed without taking polarization or relativistic effects into account, effects now known to play an important role for a proper description of a negative ion, so the close agreement with experiment can only be considered as accidental. The fine-structure splitting predicted by Vosko et al. [514] of 5.4 meV reproduced the experimental result rather well.

Concurrent with the experimental progress in the 1990s concerning the binding energy of the stable negative Ca ion, theory focussed on various methods to determine the properties of two and three electrons outside polarizable closed electron shells [515–520]. It is a formidable problem for atomic calculations to obtain precise values for energy levels in strongly correlated systems and beyond the capacity of the most sophisticated methods and approaches. This is also true for calculations of negative ions, since a high precision is needed to obtain values which can be close to the measured
binding energies in weakly bound ions. Among these calculations the ones being in best agreement with the experimental binding energies are performed by Salomonson et al. [518], who evaluated the many-body self-energy potential beyond the second order in perturbation theory and obtained 19 meV for the binding energy of the $J = 1/2$ level, and by Avgoustoglou and Beck [520] who reported 22 meV for the same level as the result of an all-order relativistic many-body calculation. More recent calculations like the many-body approach used by Veseth [423] or the configuration interaction by Osanai et al. [521] have also reported binding energies in good agreement with the experimental values. Osanai et al., however, state in their conclusion that the final value for the calculated binding energy still has not been obtained; the excellent agreement between their calculated binding energy of 22 meV and the weighted average of the two experimental values [5] of 21.33(10) meV should not be considered as an agreement on the 1 meV level. To attain such an accuracy it will be necessary to solve the full configuration interaction for 10 electrons for Ca and 11 for Ca$^-$, respectively, but also to include minor effects from the coupling between the electron correlation and relativistic effects and contributions from the inner core containing the 2s and 2p electrons to the differential correlation energies.

Attempts to calculate the binding energy by simpler methods have been reported such as a modified density function theory by Guo-xin et al. [522], who obtained a binding energy of 26 meV, which is close to the experimental value; their binding energy values for several other negative ions including H$^-$, Be$^-$ or O$^-$ deviate, however, considerably from the experimental results, so the close agreement for Ca$^-$ ion cannot be considered as a general trend.

Based on the observation that many-body perturbation-theory calculations overestimate the correlation potential by 10–15%, Dzuba and Gribakin [523] proposed to use scaling factors in the correlation potential to reproduce the experimental binding energy of the Ca$^-$(2P$_{1/2}$) component and via this procedure be able to predict the fine-structure intervals with high accuracy for the heavier alkaline earth negative ions. The most accurate experimental, fine-structure splitting value for the Ca$^-$ ground state reported is presently 4.865(14) meV [170], obtained by state-selective depletion spectroscopy (see Section 2.5.1).

Measurements of the photodetachment cross section of the negative Ca ion can be traced back to the experiment by Heinicke et al. [524] nearly 30 years ago. They observed structures in the energy interval 0.5–3.2 eV such as a Cooper minimum near 1.2 eV, a shoulder near 2.0 eV and a pronounced peak around 3.0 eV. More recently, the relative cross section from 1.1 to 3.1 eV was measured with a much improved resolution [495,504]. The position of the Cooper minimum was determined more precisely, and a sharper shape resonance peak established just above the Ca(4s4p 1P) threshold. Additional absolute photodetachment cross sections, obtained at a few photon energies, have become available from Kristensen et al. [170], using the state selective depletion method technique, and from Lee et al. [142,143] applying the saturation technique.

Theoretical studies of the photodetachment of the negative Ca ion have been reported by Gribakin et al. [498], Froese Fischer and Hansen [525], Ivanov [60,61], and more recently by Yuan and Fritsche [526] and Yuan [527]. The latter study, which probably is the most advanced of these, has been based on the $R$-matrix method and includes a five-state close-coupling calculation of the photodetachment of Ca$^-$ with photon energies below 4 eV. It is found that the so-called core–valence correlation, included by exciting one of the 3p electrons to the valence orbital, is quite crucial to the prediction of the position of the Cooper minimum and the distinct behaviour of the photodetachment cross section near the Ca(4s4p 3P and 1P) thresholds. Fig. 42 shows a comparison
Fig. 42. Total photodetachment cross section for Ca\(^{-}\). The thick solid and dashed lines represent, respectively, the length and velocity forms of the core–valence correlation result, whereas the thin solid and dashed lines represent the same forms of a valency-only calculation [527]. The calculated cross sections are compared with experimental data [143,170,495,504].

between the calculations by Yuan [527] and the experimental data available; the agreement is rather good, particularly below 2 eV. The absolute cross section values calculated at 1.39 and 1.903 eV lie within the error bars of the experiments at these energies [143,170], and the resonance at 3 eV is also reproduced with shape and width of the peak in good agreement with the experiment [495,504]. The study of the photodetachment of the Ca\(^{-}\) ion shows very clearly, that correct binding energies, position of Cooper minima or shape resonances, and the absolute magnitude of the total cross section, all rely on a proper description of the electron correlation. Without including the core–valence correlation or core polarization, the binding energies will be overestimated and the Cooper minimum appear at an incorrect photon energy. In addition, core–core and relativistic interactions may also have a distinct influence on the binding energies. Some of these effects, such as the core–valence electron correlation, are also important for a proper description of low-energy electron-Ca atom scattering [528].

Ca\(^{-}\)(4s4p\(^2\) 4P): From the early days of negative-ion research, the Ca\(^{-}\)(4s4p\(^2\) 4P) ion has proved to be a most elusive object. For many years it was assumed that a long lived Ca\(^{-}\) ion could exist only if it had this configuration. Later the lifetime, 290(100) \(\mu\)s, and the binding energy, 562(5) meV, were reported [177,495,504], but these data have been completely revised since 1992. Serious criticism was advocated of the interpretation of the experimental data (see [495]) since Hanstorp et al. [177] assigned the long lifetime to the \(^4\)P\(_{5/2}\) level, in analogy with the long lived He\(^-\)(1s2s2p \(^4\)P\(_{5/2}\)) level, discussed in Section 4.2. This analogy is, however, not valid, since the three \(J\) levels in the Ca\(^{-}\)(\(^4\)P\(_J\)) ion all can be mixed via spin–orbit interaction with \(J\) levels from doublet states (\(^2\)D, \(^2\)P, \(^2\)S) of the 4s4p\(^2\) configuration, leading to fast autodetachment and thereby short lifetimes. This possibility
Fig. 43. Fano-profile observed when exciting the Ca\(^-\) (4s4p\(^2\)P\(_{3/2}\)) level from the Ca\(^-\) (4s\(^2\)4p\(^2\)P\(_{3/2}\)) level with the population of the latter being monitored as Ca\(^+\) ions [170], using a detection technique similar to the one described in connection with Fig. 12 of this review.

does not exist for the \(J = 5/2\) level of the He\(^-\) ion. A few years later Froese Fischer et al. [529] predicted the binding energy to be about 40 meV below the experimental value reported. Looking back, it seems likely that the Ca\(^-\) (4P) ion never has been observed before 1997, when Kristensen et al. [170] developed state-selective depletion spectroscopy and applied it to the Ca\(^-\) ion.

The state-selective depletion experiment [170] was based on the use of a fast negative Ca-ion beam being overlapped by three pulsed laser ns beams within a 1 m long interaction zone. Fig. 12 in this review showed a schematic energy level diagram of the Ca\(^-\) ion and the laser–ion interactions described in connection with the experimental technique used, see Section 2.5.3. By recording the positive ion signal, obtained by resonant excitation of the Ca(4s4p \(^3\)P\(_2\) or \(^3\)P\(_0\)) levels, as a function of the laser wavelength used to induce the transition from the \(^2\)P ground state to one of the \(^4\)P\(_J\) levels, the positive ion signal will display a Fano profile [176] as shown in Fig. 43, since the \(^4\)P levels are energy degenerate with the \(^1\)S + \(\epsilon l\) continuum.

The binding energy was now established to be 521.84(10) meV for the centre of gravity in good agreement with the theoretical estimates [499,529], which also had predicted the fine-structure splittings correctly. The autodetachment lifetimes were determined to be: 9(2) ps for the \(J = 5/2\) level and 55(15) ps for the \(J = 3/2\) level, respectively, which is an order of magnitude shorter than the predictions [384], whereas the lifetime of the \(J = 1/2\) level was reported to be within the range 0.1–10 ns, also much shorter than the 137 ns predicted by Miecznik et al. [530].

Zeng et al. [483] have calculated the photodetachment cross section for the Ca\(^-\) (4P) ion from threshold to about 3.5 eV, but the short lifetimes discussed above will probably prohibit a test of these data. However, the calculated cross section does not support the existence of a rapid increase in the photodetachment cross section near 2.57 eV, as claimed by Hanstorp et al. [177] and Peterson [495] and ascribed to the Ca(4s5s \(^3\)S) threshold. The calculated photodetachment cross section is consistent with the conclusion of Petrunin et al. [5] that metastable Ca\(^-\) ions were not observed in the experiment of Hanstorp et al. [177].

Ca\(^-\) (4P\(^3\) \(^4\)S): The Ca\(^-\) (4S) state, which has the same parity as the ground state of the Ca\(^-\) ion, cannot be populated by single photon-absorption technique from the latter. To populate the Ca\(^-\) (4S) state it will be necessary to absorb more photons than needed to liberate an electron. To avoid
the use of strong laser fields, which will influence the spectroscopic data, excess-photon absorption via an autodetaching state is a suitable technique to gain spectroscopic information about the doubly excited Ca$^-$($4p^3\,^4S$) state. Combining resonant ionization with non-linear resonant multicolour spectroscopy Petrunin et al. [80] obtained information about the Ca$^-$($^4S$) state (see Section 2.5.3, where this technique is described with the present experiment as an example). The binding energy was determined to be 586.86(10) meV with respect to the parent Ca($4p^2\,^3P$) state, deviating only 3 meV from the prediction (589.6 meV) by Hart [486], who used a $B$-spline configuration approach to calculate the binding energy. Taking relativistic interactions into account the theoretical value will be reduced by about 6 meV [486], which also was the effect of relativistic interactions on the calculated binding energies of the Ca$^-$ ground state and the metastable $^4P$ state [496,529].

The binding energy for the Ca$^-$($^4S$) ion is roughly 250 meV larger than the one for the homologous Be$^-$ ion, which can be ascribed to the much stronger interaction with the $3d^24p$ configuration [486] for the Ca-ion. The lifetimes of the Be$^-$($^4S$) and Ca$^-$($^4S$) ions are also very different, with the lifetime of the former to be 1.25(10) ns [178], whereas the latter was determined to be of the order of 10 ps [80]. The dominant decay mechanism for the Ca-ion is electron emission in contrast to photon emission for the Be-ion.

4.5.4. Strontium

Despite the lack of measurements of the binding energy of the Sr$^-$ ground state before 1995, the ion was the object of several calculations [496–501,503,519,531,532]. Most of these were performed at a time when the importance of core–valence correlation for predicting reliable binding energies was not yet realised. More recently, Salomonson et al. [518], Avgoustoglov and Beck [520], and Guo-xin et al. [522] predicted binding energies close to the finally established ones of 52.06(6) meV and 32.17(3) meV for the Sr$^-$($5s^25p\,^2P_{1/2,3/2}$) levels, respectively, with a fine-structure splitting in the ground state of 19.89(3) meV [6,170]. The binding energies were determined using laser photodetachment threshold technique combined with state selective detection (RIS).

Experimental binding energy values for the Sr$^-$ ion were first reported in 1995 by Berkovits et al. [238] from an experiment combining photodetachment with accelerator mass spectroscopy, yielding a value of 48(6) meV and a fine-structure splitting of 26(8) meV. Shortly after the experimental methods utilizing resonant ionization detection technique were applied and improved the accuracy by two orders of magnitude leading to the values given above [6,170]. The fine-structure splitting was smaller than most of the published theoretical values; subsequently scaling of the polarization potential [523], to reproduce the experimental binding energy of the $J=1/2$ component, has resulted in a fine-structure splitting of 19.9 meV, which is in good agreement with the experimental result obtained using state-selective depletion spectroscopy [170]. This spectroscopic technique also yielded information about the excited Sr$^-$($5s5p\,^4P$) state with a binding energy of 532.38(3) meV and fine-structure splittings of 15.01(3) meV and 24.23(3) meV for the $3/2–1/2$ and $5/2–3/2$ intervals, respectively. Furthermore, the autodetachment lifetimes were established with values being in the range of 10 ps together with the absolute cross sections for photodetachment. The spectroscopic data for the $^4P$ state have been confirmed by Petrunin et al. [171] using the excess-photon absorption method via an autodetaching state by combining low laser intensities with resonant ionization detection.

Of the theoretical values available the binding energy result of 540 meV, reported by Cowan and Wilson [499], is in rather good agreement with the experimental result, whereas the agreement
between the calculated [498] and measured cross sections may be considered fortuitous, since the former differs considerably in the length and velocity forms. Theoretical data [486,533] are also available for the 5p^3 4S and 5s4d5p 4F states, respectively, but none of these states have so far been observed experimentally.

4.5.5. Barium and radium

The experimental proof for the existence of a long-lived metastable or stable Ba\(^-\) ion was already available at the time, when Buckman and Clark published their review in 1994 [42], but the experiments [534,535] had not been able to distinguish between the two types of possible ions. Based on the observation of a stable Ca\(^-\) ion, a similar Ba\(^-\) ion could be expected to exist with a 6s^26p ground state configuration. Many estimates of its binding energy were available ranging from 110 to 220 meV [496–501,503,516,536] with a fine-structure splitting of approximately 55 meV.

The Ba\(^-\) ion is not only of interest from an atomic physics point of view, but also for accelerator mass spectroscopy (AMS) studies of the very long lived \(^{135}\)Cs isotope, which is considered a potential tracer for oceanographic studies [537]. Knowledge about the isobar \(^{135}\)Ba\(^-\) ion is therefore essential, so a possible Ba\(^-\)—contamination can be eliminated.

\(\text{Ba}^- (6s^26p \, ^2P)\): Photodetachment of Ba\(^-\) ions followed by state-selective photoionization of the neutral atoms was used to characterize the composition of the Ba\(^-\) ion beam applied in the experimental study of the negative Ba-ion by Petrunin et al. [4] and also to determine the binding energies of its long lived components. Ba\(^+\) ions, produced in a plasma ion source [79], were converted to Ba\(^-\) ions using the charge-exchange technique. The expected Ba\(^-\)(6s^26p) ion was the dominant component (85%) of the negative-ion beam, but surprisingly it contained also another component, which could be identified as the metastable Ba\(^-\)(5d6s6p 4F\(_9/2\)) ion. Fig. 44 shows a schematic energy diagram for the Ba and Ba\(^-\) states of interest in connection with the experimental study.

The binding energies for the two fine-structure components of the 6s^26p \(^2\)P ground state were measured utilizing the s-electron threshold signal, which can be obtained using the 5d6s \(^1\)D detachment channel. This channel constitutes, however, only 0.5% of the total amount of photodetached Ba atoms at the photon energies needed (approximately 1.557 eV), and such a weak channel can only be detected using the resonant ionization technique, which was introduced to negative-ion research in connection with this study. Fig. 45 shows the Ba\(^+\) yield following the photodetachment of the Ba\(^-\)(6s^26p \(^2\)P\(_{1/2}\)) component to the Ba(5d6s \(^1\)D\(_2\)) state. The binding energies could be obtained with an accuracy of 0.06 meV, which represented a significant improvement in accuracy for binding energies compared with the alternative methods used at that time. The binding energies were reported to be 144.62(6) meV for the \(J = 1/2\) ground state level and 89.60(6) meV for the \(J = 3/2\) level, leading to a fine-structure splitting of 55.02(9) meV.

The average binding energy of the two \(^2\)P components is 108 meV, which is very close to the theoretical prediction by Hart et al. [516] of 110 meV, whereas all the other calculations mentioned above predicted larger binding energies. The close agreement between experiment and the theoretical prediction by Hart et al. may, however, be fortuitous as pointed out by Sundholm and Olsen [517], since the theoretical value was obtained via extrapolation from the calculated Ca\(^-\) binding energy, for which neither the core–core correlation nor the relativistic effects were taken into account. In a later calculation Sundholm [532] reported a binding energy which still deviates 25% from the experimental result, indicating the difficulties present for theoretical calculations of binding
energies of weakly bound, heavier negative ions. However, a more recent all-order many-body calculation [520] has yielded binding energies (145 and 96 meV for $J = 1/2$ and $3/2$, respectively,) in good agreement with the experimental data.

Storage ring experiments revealed that the Ba$^-$ beams contained at least two components with storage times of 1.75(10) and 10.5(2) ms, respectively. Petrunin et al. [4] attributed the two components to the $J(3/2$ and 1/2)-levels belonging to the stable 6s$^2$6p $^2$P ion, whereas the minor component, Ba$^-$($^4$F$_{9/2}$), could not be observed. The metastable Ba$^-$($^4$F$_{9/2}$) ion could either be so long lived that its lifetime only would be limited by the blackbody radiation-induced photodetachment similar to the $^2$P ground state levels and it would then decay with a lifetime equivalent to the storage times (ms) of the stable ion, or the lifetime was so short that the ion decayed during the first roundtrip in the storage ring. The authors proposed the latter explanation and the Ba$^-$($^4$F$_{9/2}$) ion was reported to have a natural lifetime below 100 µs and may be even an order of magnitude lower. This was, however, not correct as discussed below.

Experimental cross sections for photodetachment of the stable Ba$^-$ ion have so far not been reported, whereas several theoretical studies are available [52]. It is expected that polarization effects will play a dominant role for the photodetachment of the Ba$^-$ ion; furthermore, it will be necessary

Fig. 44. Schematic energy-level diagram of Ba and Ba$^-$ with the detachment and detection channels indicated as dashed and solid lines, respectively [4].
to perform relativistic calculations, taking account of many-electron effects, to obtain an appropriate description of the cross section.

\( \text{Ba}^- (5d6s6p \ ^4F_{9/2}) \): By irradiating \( \text{Ba}^- \) beams with the fundamental IR radiation from a Nd:YAG laser Petrunin et al. [4] observed a significant population of the \( \text{Ba}(5d6s \ ^3D_3) \) level, and some population of the \( \text{Ba}(6s6p \ ^3P_2) \) level, whereas the other \(^3D\) or \(^3P\) levels hardly were populated. Since the IR radiation of the \( \text{Ba}^- (^2P) \) ground state levels only can lead to population of the \( \text{Ba}(6s^2) \) ground state, see Fig. 44, these observations were clear evidence for the presence of a metastable \( \text{Ba}^- \) ion in the beam possessing the \( 5d6s6p \) configuration. This configuration supports many term and levels, but since strong population of the \( \text{Ba}(5d6p \ ^3F_4) \) state was observed using detaching laser light with an energy around 1.90 eV the observed long-lived metastable component could be identified as the \(^4F_{9/2}\) level. The binding energy was measured to be 144.2(5) meV, relative to the \( \text{Ba}(5d6s \ ^3D_3) \) level, which is nearly the same value obtained for the \( \text{Ba}^- (^2P(J=1/2)) \) ground state level, but the uncertainty is larger, since the binding energy was measured using a p-electron emission channel.

Fig. 44 shows that the \( \text{Ba}^- (^4F_{9/2}) \) level is energetically located below the first excited state of the \( \text{Ba} \) atom and it can therefore only decay via photon emission to the \( \text{Ba}^- (6s^26p \ ^3P) \) ground state or via electron emission to the \( \text{Ba}(6s^2 \ ^1S) \) ground state by emitting an \( h \) electron. Both the proposed decay channels will lead to a rather long lifetime for the \(^4F_{9/2}\) level. Petrunin et al. [4] stated that its lifetime was longer than 5 \( \mu s \), but were unable to report an upper limit. Later Andersen et al. [62] pointed out, that the lifetime might exceed 1 ms. In order to test this proposal experiments were performed at the storage ring ASTRID using different isotopes of the negative \( \text{Ba}^- \) ion. Whereas the even-mass \(^{136}\text{Ba}\) and \(^{138}\text{Ba}\) isotopes have zero nuclear angular momenta, the odd-mass \(^{135}\text{Ba}\) and \(^{137}\text{Ba}\) isotopes have a nuclear moment of \( 3/2 \). Via hyperfine interaction, the electronic system may exchange angular momentum with the nucleus; thus the \( \text{Ba}^- (^4F_{9/2}) \) state can interact with lower \( J \) states and couple to doublet states, which are allowed to auto detach via the strong Coulomb interaction.

The experimental data [538] indicated that the short-lived component in the storage ring with a storage time of the order of 2 ms was influenced when odd-mass \( \text{Ba} \) isotopes were utilized. This

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**Fig. 45.** \( \text{Ba}^+ \) yield following the photodetachment of the \( \text{Ba}^- (^2P_{1/2}) \) component to the \( \text{Ba}(5d6s \ ^1D_2) \) state, see Fig. 44. The solid line represents a Wigner s-wave fit to the experimental data [4].
suggests that the short-lived component contains two independent decay components with slightly different lifetimes. The two components represent the blackbody induced decay of the \( \text{Ba}^- (^{2P}_{3/2}) \) level and the autodetachment rate for the odd-mass isotopes of the metastable \( \text{Ba}^- (^{4F}_{9/2}) \) level. The lower limit of the metastable lifetime is therefore a few ms and the \( \text{Ba}^- (^{4F}_{9/2}) \) ion by far the longest-living metastable negative atomic ion observed so far.

\( \text{Ba}^- (6s6p^2 \, {}^2P_{J=2}) \): The excited \( \text{Ba}^- (6s6p^2 \, {}^2P_{J=2}) \) level, which is located below the \( \text{Ba}(6s6p \, {}^3P_0) \) level, is connected to the ground state of the \( \text{Ba}^- \) ion by an electric dipole transition. Due to the autodetachment selection rules it cannot decay to the ground state of the Ba atom via Coulomb autodetachment, whereas this is possible to the \( \text{Ba}(5d6s) \) states by emitting an \( \epsilon d \)-electron. The \( {}^2P_{1/2} \) level was studied in connection with the development of spectroscopic techniques based on the use of excess-photon absorption via an autodetaching state [171] (see Section 2.5.3) leading to determination of its binding energy and lifetime.

\( \text{Ra}^- (7s7p \, {}^2P) \): The \( \text{Ra}^- \) ion has been observed in accelerator mass spectroscopy studies [231, 232]. Its binding energy was first estimated to be larger than 50 meV, later increased to be 0.17 eV, which is similar to the value for \( \text{Ba}^- \). These values were obtained relating the probability for producing negative ions by sputtering to the electron affinity of the element. Dzuba and Gribakin [523] have predicted that only the \( J = 1/2 \) level will be stable with a binding energy about 100 meV, whereas the \( J = 3/2 \) level will be located approximately 16 meV above the detachment limit.

4.6. Group III elements

Stable negative atomic ions exist for all the elements of group III, B, Al, Ga, In and Tl, with \( ns^2np^2 \) ground state configurations, \( n \) being 2 for B and 6 for Tl. The binding energies of these ions have all been investigated during the last decade using laser photodetachment threshold spectroscopy for B and Al and laser photodetachment electron spectroscopy for Ga, In and Tl [31] leading to much improved accuracies compared to the values available at the beginning of the 1990s [49]. The lighter negative ions, B\(^-\) and Al\(^-\), have also been the objects of more detailed investigations covering photodetachment studies in the energy region near the first excited thresholds.

4.6.1. Boron

\( \text{B}^- (2s^2p^2 \, {}^3P) \): The binding energy of the stable \( \text{B}^- \) ion was reported in 1981 to be 277(10) meV [539], obtained with laser photodetachment electron spectroscopy. A 400-fold increase in accuracy was obtained in 1998, when Scheer et al. [110] utilized a tunable IR laser source within the laser photodetachment threshold method (Section 2.4.1) and reported 279.723(25) meV for the \( {}^3P_0 \) level, measured with respect to the \( \text{B}(2s^2p \, {}^2P_{1/2}) \) ground state level.

The experimental data are presented in Fig. 2 of this review as an illustration of the technique used (LPT). The fine structure of the ionic and neutral ground states produces a series of six closely spaced cascaded thresholds in the photodetachment spectrum, from which the fine-structure intervals can be determined [31, 110]. Due to the conspicuous nature of the s-wave threshold law, the photodetachment background observed from underlying detachment channels does not pose excessive difficulties. The fine-structure intervals for the \( \text{B}^- ({}^3P_J) \) ground state were measured to be 3.23(15) and 5.18(15) cm\(^{-1}\), respectively, with the \( J = 0–1 \) splitting being associated with the former value.

The low binding energy of the \( \text{B}^- \) ion combined with the limited number of electrons involved made the \( \text{B}^- \) ion an attractive object for theoretical studies after Feigerle et al.’s value [539] had
appeared in 1981. Among the theoretical calculations reported [540–547] three of these were aiming at accuracies better than 10 meV. Noro et al. [543] performed a large-basis-set multi-reference single and doubly excited configuration-interaction calculation and obtained a binding energy of 278 meV, whereas two large-scale finite element multi-configuration Hartree–Fock (MCHF) calculations [544,545] yielded values of 268.6(1.7) and 273.2(2) meV, respectively. The latter were obtained without taking core polarization effects into account. When Froese Fischer et al. [545] included contributions from core–valence and core–core correlations, the predicted value increased to 279.5(2.0) meV, whereas Sundholm and Olsen [544] calculated the binding energy to be lowered to 267.8(2.0) meV taking the core polarization effects into account. The disagreement between the two calculations can be attributed to the different approaches used in estimating the effects of core–core and core–valence correlations. The experimental value of 279.723(25) meV [110] resolved this discrepancy being in excellent agreement with the calculation reported by Froese Fischer et al. [545].

The binding energy of B$^-$ ion has also attracted interest from theory after the experimental value was finally settled. Most important is the benchmark ab initio and density-functional theory study of electron affinities of atoms ranging from B to F and from Al to Cl by de Oliveira et al. [242]. The values reported agree within 1.5 meV or better with the experimental values, unless for P, for which the results deviate by 1.8 meV. The ab initio study used basis sets of spdfgh quality for the B$^-$ ion, extrapolations to the one-particle basis set limit, and a combination of the coupled cluster method with all single, double and triple excitations taken into account together with full configuration-interaction electron correlation methods. There has also been several attempts to obtain the electron affinities for the first 18 elements of the periodic system using methods demanding less computations, but still providing reliable results agreeing with the experimental results within 10–20 meV, see [548,549] and references therein. These calculations are often related to the ongoing development of computational methods in quantum chemistry where full ab initio calculations still may be a too demanding task.

The B$^-$ ground state binding energy studies show very clearly the importance of properly calculated core–core and core–valence correlation in order to obtain an accurate treatment of this six-electron system.

B$^-$($2p^2^1D$): The other terms belonging to the B$^-$ ground state configuration, $^1D$ and $^1S$ are located above the detachment limit. Fast collisions between 100 keV B$^-$ ions and He or Ar gas targets have been used to search for these resonance structures. Lee et al. [206] reported the energy (104(8) meV) and width (68(25) meV) for a B$^-$ resonance and tentatively assigned the values to the B$^-$($2p^2^1D$) state, whereas several other observed resonances still remain without identification. Sinanis et al. [550] confirmed the tentative identification of the B$^-$($2p^2^1D$) resonance by a state specific configuration interaction in the continuum calculation, taking electron correlation into account. They obtained the energy (95 meV) and width (54 meV) in good agreement with the experimental results, which illustrates that it is possible to compute the properties of shape resonances in polyelectronic atoms to a high degree of accuracy.

B$^-$($2s2p^3^3D$): Photodetachment of the B$^-$ ($2s^22p^2^3P$) ion has also been performed at larger photon energies than needed for the detachment of the ground state and close to the first excited boron state, B($2s2p^2^4P$) [139], where quasi-bound B$^-$($2s2p^3^3P$ and $^3D$) resonance states may be located and appear in the photodetachment cross section. An experimental photodetachment study of the B$^-$ ion was initiated after experimental studies of the Si$^-$ ion [141] confirmed the prediction [551,552], that intra-shell correlation between the $ns$ and the $np$ electrons in negative ions possessing a half-filled
Fig. 46. Photodetachment cross section of B\(^-\) at the vicinity of the B(2s) threshold. Experimental data points: open circles [556], dark squares [139]. Theory 1: R-matrix calculation [555]; theory 2 and 3: Combined many-body method results [557], with the length and velocity forms shown, respectively.

\(np^3\) subshell, \(n = 3\) for Si\(^-\), would create dramatic deviations from the independent-electron picture in the photodetachment cross section. The experimental Si\(^-\) photodetachment cross section exhibited a significant window resonance in good agreement with the prediction. Similar interference structures were predicted for the homologous C\(^-\) [552] and Ge\(^-\)-ions [553], too, and will be discussed in Section 4.7.

A theoretical prediction [554] of the photodetachment cross section for B\(^-\) was available before the experiment was performed. It was based on many-body calculations in the framework of the spin-polarized random-phase approximation with exchange (SPRPAE) and thereby analogous to the calculations performed for the negative ions of C, Si, and Ge. The calculation predicted a similar behaviour for the B\(^-\) cross section as observed for the Si\(^-\)-ion, a window resonance just below the B(2s2p\(^2\) ^4P) threshold. It was, however, pointed out that significant deviations from this prediction could happen due to the limitation of the calculation method, which was developed for half-filled shells and not for open shells like the B\(^-\) ion; the latter represents a system inherently much more difficult to describe with the SPRPAE method.

The experimental photodetachment cross section was measured from 3.4 to 4.8 eV [139] and did not reveal the window resonance structure predicted above. Much better agreement between calculation and experiment was achieved with an R-matrix calculation by Ramsbottom and Bell [555], see Fig. 46, when the theoretical curve is slightly shifted towards larger energies. The experimental cross section data reported by Lee et al. [556] are also included. Later Kashenock and Ivanov [557] reinvestigated the collective effects in B\(^-\) photodetachment using many-body theory taking interchannel interactions, dynamic-core polarization and screening effects into account. The resulting cross sections, calculated with the dipole operator in length and velocity form, are also included in
Fig. 46. The results for the length and velocity forms differ, however, because the method applied is not self-consistent; the results may, however, be considered as a first step in the direction of calculating the total and the partial photodetachment cross sections taking all relevant physical effects into account and it gives a reasonable accurate account of the dominant Be$^-(2s2p^3 3D)$ shape resonance in the photodetachment of the negative B-ion [557]. The energy and width of the $^3D$ resonance can be extracted from the experimental data to be 4.31 and 1.16 eV, respectively.

Highly excited $B^-$ resonances, $B^{2-}$, and collisions: Highly excited bound states of B$^-$ have been considered theoretically by Piangos and Nicolaides [558], who calculated the binding energies of states for which all electron spins are unpaired and the nuclear charge partially unscreened. They obtained positive binding energies for two septet states, 27 meV for the B$^-$ (1s2s2p$^33s3p 7P$) state, and 8 meV for the B$^-$ (1s2s2p$^53p^2 7S$) state. These states are located several hundreds eV above the ground state, and may be difficult to observe experimentally.

It has been suggested [306] that addition of an extra electron to the ground state of the B$^-$ ion might form a resonance state of the dianion B$^{2-}$ (1s$^22s2p3^3$) with $^4S$ symmetry. This suggestion was reported [306] together with a prediction of the 2p$^3$ $^4S$ resonance state in the H$^{2-}$ ion. None of these predictions have been confirmed by experiments. Andersen et al. [559] measured the cross section for electron impact detachment from B$^-$, but no resonances were observed in the detachment cross section and hence no sign of an equivalent shortlived B$^{2-}(2p^3)$ state.

The collisional aspects of electron impact on B$^-$ and other negative atomic ions will be discussed in connection with Section 5. Electron detachment from negative ions in energetic collisions with charged particles has also attracted interest during the last decade [560] including theoretical investigation of B$^-$ neutralization cross section from collisions between B$^-$ ions and charged bare projectiles [561]. These studies can via scaling relations be extrapolated to other negative ions with loosely bound s and p electrons.

4.6.2. Aluminum

During the 1990s studies of the negative Al-ion have focussed on the properties of the ground state configuration, 3s$^23p^2$, and on resonance features appearing just below the Al(3s$^24s 2S$) threshold.

Al$^{-}(3s^23p^2 3P)$: Already at the beginning of the 1980s Feigerle et al. [539] reported the binding energy of the Al$^-$ (3s$^23p^2 3P$) ion to be 442(10) meV and found the Al$^-$($^1D_2$) level to lie 332(10) meV above the $^3P$ ground state, with a binding energy of 110(10) meV. In the 1990s two independent experimental studies have been performed with the aim to determine the binding energy of the negative Al-ion more precisely. Both studies [112,562] applied the laser photodetachment threshold method; Calabrese et al. [562] measured the binding energy to be 440.94 (+0.66/−0.48) meV utilizing a tunable F-centre laser and a coaxial ion-laser equipment. They were, however, not able to investigate the actual threshold region and the associated fine structure, but compensated for lack of data in this region via extrapolation from higher photon energy data.

Scheer et al. [112] applied tunable IR laser spectroscopy in a crossed beam setup and obtained a binding energy of 432.83(5) meV, which is in substantial disagreement with the result of Calabrese et al. [562]. Even though the two experiments have much in common there are also striking differences, since Calabrese et al. were not able to perform measurements at or below the threshold region due to an upper limit on the wavelength scan for the colour centre laser used. They could not explore the multiple thresholds due to fine-structure splittings, see Fig. 47, and were unable to obtain data...
Fig. 47. Photodetachment yield vs. photon energy for Al\(^-\) \[112\]. The data are analysed using a Wigner s-wave fit including the leading correction term (solid line). The difference between close lying dotted lines represents the contribution from the correction term.

below 3585 cm\(^{-1}\) (or below 444.4 meV). The figure shows how important it is to be able to follow the detachment process even to below the threshold.

Although the Al\(^-\) ion possesses 14 electrons it has attracted interest from several theoretical groups. Arnau et al. \[563\] applied a configuration interaction method with pseudo-potentials and obtained a binding energy of 450 meV, Woon and Dunning \[564\] employed a similar calculation with correlation-consistent basis sets and reported 437 meV, whereas Wijesundera \[546\] with a multiconfiguration Dirac–Fock method obtained 433 meV. The theoretical values all have uncertainties of the order of 10 meV and the latter two are therefore in good agreement with the measured value by Scheer et al. \[112\]. The recent benchmark ab initio study by de Oliveira et al. \[242\] has yielded a binding energy, which agrees with the experimental value by Scheer et al. within 0.1 meV. The detailed calculation considered all effects influencing the final binding energy, such as valence and inner-shell correlations, spin–orbit and relativistic effects.

The experimental data from Fig. 47 yield the \(J = 0–1\) and \(1–2\) fine-structure splittings to be 22.7(3) and 45.7(2) cm\(^{-1}\), respectively, which essentially is in agreement with the results previously obtained via isoelectronic extrapolations \[49\]. The properties of the Al\(^-\)(1\(D_2\)) level have not been explored recently even though this might be possible using one of the multi-photon detachment schemes described in Section 2.5.4.

\(Al^- (3s^24s^2p^3P)\): Photodetachment of the Al\(^-\) ground state ion in the vicinity of the Al(3s\(^2\)4s\(^2\)S) threshold has been studied experimentally and theoretically \[140\]. A large, narrow and nearly symmetric resonance signal was observed about 25 meV below this threshold with a width of 13.4 meV. \(R\)-matrix calculations for photodetachment of Al\(^-\), using an approximation in which only the outer-two electrons are active, provided predictions for the cross section up to the Al (3s\(^2\)4s\(^2\)S) threshold. Just below the threshold the calculations predict a sharp, nearly symmetric resonance at the same energy as observed experimentally. The theoretical line shape for this resonance agrees qualitatively with the experimental one, but is narrower, which may be due to neglect of the intershell
transitions involving the 3s subshell. The calculation indicates that the resonance may be classified as a doubly excited negative-ion state having predominantly 3s^24s4p ^3P character. It should be noted that this resonance in contrast to many other negative-ion resonances only interacts with a very small portion of the underlying continuum; thus the resonance profile sits atop the continuum.

4.6.3. Gallium, indium, thallium

The stable negative ions of Ga, In, and Tl have been studied both experimentally and theoretically during the last decade with emphasis on the binding energies of these ions. Before 1998 the experimental binding energies [49] relied on photodetachment threshold studies using classical light sources, which resulted in binding energies of about 0.2–0.3 eV with an uncertainty of similar magnitude. The experimental binding energies have now been established with much improved accuracy using laser photoelectron spectroscopy leading to the following values: 0.43(3) eV for Ga^- [565], 0.404(9) eV for In^- [566], and 0.377(13) eV for Tl^- [567]. Before the improved experimental values became available, several theoretical studies, using different calculation techniques, such as the multiconfiguration Dirac–Fock method or the relativistic coupled cluster method, were reported [522,546,547,563,568].

Whereas the binding energy for the negative In and Tl ions were well predicted [522,547], none of the calculations for the Ga^- ion are in agreement or even close to the reported experimental binding energy. New ab initio calculations by Sundholm et al. [569] have confirmed a binding energy value for the Ga^- ground state of approximately 0.30 eV as obtained by three of the calculations mentioned above, but this value is also much smaller than the measured one. It is difficult to explain why several different theoretical calculations can predict binding energies for In^- and Tl^- in good agreement with the experimental results, but in strong disagreement with the Ga^- binding energy. In the review article “Binding Energies in Atomic Negative Ions: III” [31] it is proposed that the experimental EA value for Ga may be somewhat too high and that taking the effect of the unresolved fine structure into account will reduce the experimental value to 0.41(4) eV. However, even this value is significantly larger than any of the calculated values.

Photodetachment cross section and photoelectron angular distribution for In^- have been calculated within the Relativistic Random Phase Approximation from threshold up to 20 eV by Ipatov and Ivanov [570]. The cross section is dominated by the 5p_{1/2} → e d_{3/2} transition. An interesting feature located in the vicinity of the 5s_{1/2} threshold is attributed to inner-electron transition into vacant states in the 5p_{3/2} subshell. There exists no experimental study which can confirm the predictions.

4.7. Group IV elements

Group IV elements form rather stable negative ions, due to the half-filled np shell in the ground state configuration, with binding energies larger than 1 eV for C, Si, Ge, and Sn, whereas the heaviest element, Pb, deviates from this trend and has a lower binding energy, mainly due to the influence of the large fine-structure splitting in the ground state of the parent atom, Pb(^3P) [31]. During the 1990s the negative ions of the first four members of group IV have been studied experimentally and theoretically with focus on the structural properties of the ground states [31] and on the photodetachment cross sections. The cross section studies have included photodetachment of valence as well as inner shell electrons.
4.7.1. Carbon

C\(^{−}(2^s 2^p \, ^4S \text{ and } ^2D)\): The C\(^{−}\) ion is easy to produce and its binding energy was established already in the 1970s [48,49] with Feldmann's value of 1.2629(3) eV [571] being considered to be the most precise for the \(^4S\) state. It was obtained from his pioneering infrared laser photodetachment threshold measurements, and only slightly corrected by Scheer et al. [111] more than 20 years later to be 1.262 119(20) eV, using essentially the same technique. The excited, bound \(^2D\) state was also observed by Feldmann and its binding energy determined to be 33(1) meV. C\(^{−}(^2D)\) ions can be produced in significant amounts via charge-exchange of positive carbon ions, whereas they are destroyed in a sputter ion source like the one used by Scheer et al. The 1977 binding value for the \(^2D\) state is therefore still the best available, whereas no experimental information is available about the \(^2P\) state, which is located in the continuum.

Accurate ab initio calculations of the binding energy of C\(^{−}(^4S)\) ion were reported in 1999 [242], but calculations with uncertainties of a few meV existed before [543,548,549]. The C\(^{−}\) binding energy has been studied by many theoretical groups over the last two decades, see [242] starting with deviations of the order of 50 meV, but being reduced to 1–2 meV at the end of the 1990s. The value calculated by de Oliveira et al. [242] is 1.2629 eV, identical to the value reported by Feldmann [571], and 0.7 meV above the more accurate experimental result by Scheer et al. [111].

Since it is possible to produce a significant amount of C\(^{−}(^2D)\) ions photodetachment cross sections have been measured for both the \(^4S\) and the \(^2D\) ions as targets. The first study dates back to 1962 when Seman and Branscomb [572] measured the cross section for photodetachment of the C\(^{−}(^4S)\) ion at photon energies ranging from 1.6 to 3.1 eV, dealing with detachment of a 2p electron. The experimental studies being performed since 1996 include photodetachment studies of 2p [573,574], 2s [68], and most recently 1s electrons [101]. The experimental studies have all been performed in close cooperation with theoretical investigations of the cross section and resonance structures in the continuum [52,101,552,575–578].

The dominant photoinduced process just above threshold is 2p \(\rightarrow\) \(\epsilon\)s, followed by 2p \(\rightarrow\) \(\epsilon\)d, which at higher energies quickly dominates the cross section. At photon energies above 5.44 eV, the energy of the C(1s\(^2\)2s2p\(^3\) \(^5\)S) threshold, the photodetachment process 2s \(\rightarrow\) \(\epsilon\)p starts to be important and above 6 eV it contributes most to the total cross section. The threshold for photodetachment of an 1s electron is the energy of the C(1s2s\(^2\)2p\(^3\) \(^5\)S) state, 281.415 eV, so synchrotron radiation is needed for these studies [101].

Lee et al. [573] and Brandon et al. [574] performed spectroscopic studies of 2p electrons photodetached from C\(^{−}\) ions at a specific photon energy, 2.08 eV and determined the partial cross sections and asymmetry parameters for both the C\(^{−}(^4S)\) and the C\(^{−}(^2D)\) targets. The asymmetry parameters were obtained from the ratio of the electron yields recorded with the linear polarization vector of the laser light being parallel or perpendicular to the electron collection direction. The experimental cross sections were in good agreement with calculations by Ramsbottom et al. [575] and the asymmetry parameters with calculations by Cooper and Zare [579]. The good agreement between experiment and theory at 2.08 eV was in contrast to the studies of the photodetachment of the 2s electrons described below.

C\(^{−}(2s 2p\(^4\) \(^4\)P)\): Photodetachment of open-shell negative ions is among the most stringent tests of the theoretical description of electron correlation in atomic systems, in particular for processes involving inner-shell electrons, and various methods were developed during the beginning of the 1990s
to treat open-shell systems. Gribakin et al. [552] used the spin-polarized version of the random-phase approximation with exchange (SPRPAE) and calculated the cross section for the first three elements of group IV. For C−, the calculations predicted a maximum of the order of 50 Mb in the photodetachment cross section, located approximately 0.6 eV above the C(2s2p3 5S) threshold at 5.44 eV. Ramsbottom et al. [575] adopted the R-matrix multi-channel theory for free–free transitions of an electron in the presence of an atomic system to describe the photodetachment process. Their calculation predicted a very sharp Feshbach resonance with a maximum value of nearly 100 Mb, located below the 5S threshold. Le Dourneuf et al. [576] also applied the R-matrix method but utilized a more elaborate description of the C−(4S) target. The latter calculation rejected the existence of a resonance structure below the threshold, but predicted a shape resonance maximum of 30 Mb approximately 1 eV above the threshold. This result could be explained by the opening of a new photodetachment channel at the C(2S) threshold and the presence of a C−(2s2p4 4P) shape resonance located 1 eV above the threshold.

The experimental photodetachment cross section data reported by Haeffler et al. [68] covered the C(5S) threshold region and up to 0.6 eV above. The data contradicted the predictions based on the limited R-matrix theory [575] as well as the random-phase calculation [552], since the cross section was entirely flat in the region studied. Due to limitation in the photon energies available it was not possible to explore the cross section above 6 eV. The more elaborate R-matrix calculation by Le Dourneuf et al. [576] was in better agreement with the observed cross section, but a new R-matrix calculation by Miura et al. [577] has located the C−(2s2p4) resonance at still higher energy, 1.5 eV above the relevant threshold. Similar results were reported by Kashenock and Ivanov [578], who used a method based on many-body theory, which permitted analysis of the contributions from different many-electron interactions to the photodetachment process. Fig. 48 compares some of the recent calculations with the experimental data available. It would clearly be of interest to perform experimental studies above 6 eV to test the most recent calculations.

C−(1s2s22p4 4P): Very recently Gibson et al. [101] performed K-shell photodetachment from C− in the photon energy range between 280 and 285 eV using the merged ion–photon beam technique at the Advanced Light Source, Berkeley. The relative cross section was measured and compared with theoretical R-matrix calculations. The spectrum contains a resonance near 281.7 eV, which was attributed to the C−(1s2s22p4 4P) shape resonance being located just above the C(1s2s2p3 5S) threshold. The width of the resonance is only 0.2 eV and it is predicted to decay mainly by low-energy electron emission to the C(5S) threshold state. The rather narrow width may indicate that the resonance can have a mixed character, since it is located above the C(1s2s2p3 5S) threshold, but below the C(1s2s2p3 3D, 3P, 3S) ones.

The studies of photodetachment of 1s and 2s electrons, respectively, exhibit several similarities, but also some deviations. Rather elaborate R-matrix calculations are needed to avoid the appearance of a superficial resonance (Feshbach) below the relevant thresholds and to place a resonance above these. Whereas the resonance in case of the 2s study was rather broad and clearly would be named a shape resonance, the narrow width of the 1s resonance may need further studies to characterize it unambiguously.

Highly excited states and collisions: Very highly excited states of C− with all the electrons having unpaired spins, like 1s2s2p3 3s3p or 3p2, have been predicted to exist as bound states [558], but it will probably be difficult to observe these states with the present experimental methods.
The negative ions of group IV elements have been studied with emphasis on collisional detachment by the interaction with He, Ne or Ar gases at relative velocities ranging from 0.2 to 2.2 a.u. [580,581]. It was observed that it is possible to scale all the cross sections into a single curve of total cross section for each noble gas. This observation is in agreement with previous studies of collisional detachment cross sections of H\(^-\) and the alkali ions, Li\(^-\), Na\(^-\), and K\(^-\) ions, which showed a similar multiplicative scaling, but for which the understanding may be simpler due to the ns\(^2\) configurations of these ions [582].

Electron impact double ionization of C\(^-\) ions has also attracted interest. This process has been studied experimentally from threshold to several keV. The absolute cross section peaks near 50 eV with a value of about 80 Mb [583], which is significantly larger than predicted theoretically [584,585]. In negative ions like C\(^-\) or O\(^-\) double ionization can proceed along different paths utilizing intermediate excited (autoionizing) states. Rost and Pattard [586] have shown that the measured cross sections for double ionization of negative ions (H\(^-\), C\(^-\) and O\(^-\)) possess a universal shape when plotted in suitable dimensionless units, which demonstrates that direct double ionization dominates the cross sections for these ions.

4.7.2. Silicon

Si\(^-\)(3s\(^2\)3p\(^3\) 4S, 2D, and 2P): The 3s\(^2\)3p\(^3\) configuration leads for the Si\(^-\) ion to three bound terms, 4S, 2D, and 2P. Their binding energies were already established by Kasdan et al. [587] using laser photodetachment electron spectroscopy (LPES) and the binding energy for the 2P term of 29(5) meV is still the best available [31]. For the two other terms the binding energies and the 2D fine-structure splitting have been the objects for detailed studies using single- and multi-photon
infrared laser photodetachment threshold spectroscopy (LPT) [114, 588] and laser photodetachment microscopy (LPM) [131] resulting in much improved accuracy, changing the uncertainty for the binding energies from 5 meV [587] to 2.4 µeV [131], or by more than three orders of magnitude. The binding energy value for the $^{28}\text{Si}^{-}(4\text{S})$ state is reported to be $1.3895220(24)\text{ eV}$ [131], which makes it among the most accurate binding energies reported so far for a negative ion [31]. It should be noted that Blondel et al. [131] using LPM were able to improve the rather accurate binding energy value reported by Scheer et al. [114] using LPT by one order of magnitude, which clearly demonstrates the potential of the photodetachment microscope.

The binding energy of the $\text{Si}^{-}$ ground state ion has also attracted interest from several theoretical groups in recent years [242, 549, 568, 589] using very different approaches and with de Oliveira et al. [242] ab initio calculation being far the most accurate, deviating only 1 meV from the experimental result.

The lifetimes for the $^2\text{P}_{1/2}$ and the $^2\text{D}_{3/2}$ levels have been calculated to be 24 and 162 s, respectively, whereas the $^2\text{D}_{5/2}$ level should have a much longer lifetime, of the order of 27 h [590].

$\text{Si}^{-}(3s3p^4)$: Strong and complicated intershell interactions can manifest themselves in the photodetachment of negative atomic ions with open subshells [52]. The main features of these ions, with $\text{Si}^{-}$ as an example, are related to the production of different terms in the final state and to the formation of quasi-bound states in the vicinity of inner-shell thresholds. Thus it is necessary for such ions to use a multichannel description of the photodetachment process taking inter-channel interactions into account, which can lead to pronounced resonance structures in the photodetachment cross section. The negative Si-ion is a good example for such an interference feature.

According to calculations by Amusia et al. [551] and Gribakin et al. [552], based on the spin-polarized version of the random phase approximation with exchange, the photodetachment cross section in the vicinity of 5 eV should exhibit a pronounced interference structure with a deep minimum, which should be due to the interference between the two detachment channels:

\[
\text{Si}^{-}(3s^23p^3\text{ 4S}) + h\nu \rightarrow \text{Si}(3s^23p^2\text{ 3P}) + \epsilon d,
\]

\[
\text{Si}^{-}(3s^23p^3\text{ 4S}) + h\nu \rightarrow \text{Si}(3s3p^3\text{ 5S}) + \epsilon p
\]

and the presence of a $3s3p^4$ autodetaching resonance in the $\epsilon p$ continuum. The latter corresponds to the transition of a 3s electron to the quasi-bound 3p shape resonance [141]. A shape resonance is usually located above the corresponding threshold, in this case Si($3s3p^3\text{ 5S}$), but for the $\text{Si}^{-}$-ion it is shifted below the threshold by channel interaction [552]. In the independent electron approximation the $\epsilon p$ channel does not interact with other channels, so the presence of a resonance structure is a clear evidence of electron correlation in the negative Si-ion. It should be noted that the first of the two detachment channels mentioned above also can occur with emission of an s-electron, but this channel will only be slightly affected by channel interaction [552] and its major role is as a contributor to total cross section at the minimum position.

Balling et al. [141] performed a photodetachment study of the $\text{Si}^{-}(3s^23p^3\text{ 4S})$ ion in the photon energy range close to the 3s threshold. The threshold is located 5.52 eV above the ground state of $\text{Si}^{-}$ and the experiment covered the photon range from 4.63 to 5.42 eV. The single photodetachment cross section revealed as predicted a deep window resonance. It was located at 5.18 eV, nearly 0.5 eV above the prediction, whereas the width and asymmetry parameters obtained, assuming the resonance could be described with a Fano profile, were in better agreement with the predictions [552].
Fig. 49. Photodetachment cross section of Si$^-$ in the vicinity of the window resonance. The experimental data are indicated by crosses [141]. The solid curves (1) and (2) represent calculated cross sections applying various modifications of the random phase approximation (RPAE) [52].

Fig. 49 shows a comparison between the experimental data and two calculations both performed within the random phase approximation with exchange, using frozen-core wavefunctions or by taking static rearrangement effects into account [52,552]. The location of the experimental data in between the two theoretical curves shows that it is necessary to take other many-electron processes into account to obtain a better agreement between experiment and theory, as done more recently for the photodetachment of the homologous C$^-$ ion [577,578].

4.7.3. Germanium and tin

The binding energies of the bound s$^2$p$^3$ terms, $^4$S and $^2$D, and the $^2$D fine-structure splittings for the negative Ge and Sn ions have been investigated by Thøgersen et al. [588] and Scheer et al. [114] using a combination of single- and multi-photon tunable infrared laser techniques. The binding energies of the $^4$S states had already been established in the 1980s with an accuracy of 3–4 meV by laser photodetachment electron spectroscopy [591], whereas the information about the $^2$D states was very uncertain [49]. The recent binding energies of the $^4$S ground state terms and of the excited $^2$D terms, including their fine-structure splittings, constituted improvements in accuracy over previous
experimental values of up to four orders of magnitude and provided the first experimental data for the \( ^2D \) fine-structure splittings [31].

Veseth [589] performed a many-body perturbation study of the photodetachment cross section of Ge\(^-\) and included a calculation of the binding energies of the two stable terms, \( ^4S \) and \( ^2D \). The binding energies were obtained from a single-reference perturbation expansion complete to third order, which yielded agreement with experiment for the \( ^4S \) state within 5 meV, whereas the calculated binding energy for the \( ^2D \) state shows that it is necessary to go beyond third order in the perturbation expansion to obtain a result of similar accuracy for this state. O’Malley and Beck [592] performed a relativistic configuration interaction calculation for the Sn\(^-\) ion with the aim to determine the energies of the \( ^2D \) levels relative to the \( ^4S_{3/2} \) ground state level. Whereas the energy of the \( J = 5/2 \) level is in good agreement with experiment the calculated fine-structure splitting is 25% too low, illustrating the complexities of the 51-electron Sn\(^-\) system [114].

The photodetachment cross section for Ge\(^-\) has been the object of several calculations [553, 552, 589] based either on the random phase approximation with exchange or on many-body perturbation theory. The three calculations predict, as for Si\(^-\) discussed above, a deep and rather narrow minimum (window resonance), but its location and the absolute value of the cross section in the resonance region are rather deviating; so far there is no experimental data available to test these predictions.

Whereas the photodetachment cross sections of Ge\(^-\) and Sn\(^-\), respectively, have not yet been studied experimentally there exists measurements of the photoelectron angular distribution of Ge\(^-\) [593] and Sn\(^-\) [594] at several photon energies in the visible range, but no theoretical investigation of the measured photoelectron asymmetry parameters to compare with. It should, however, be noted that the asymmetry parameters for the negative ions of group IV elements are rather similar and that a description of photoelectron distributions based on the independent particle approximation is adequate for describing photodetachment processes for an ion as heavy as Sn\(^-\) [594].

4.8. Group V elements

Of group V elements, N, P, As, Sb, and Bi, nitrogen is unable to form a stable or a longer-lived metastable ion, which has limited the experimental studies of this ion, whereas P, As, Sb, and Bi all form stable negative ions with binding energies for the \( np^4 \, ^3P_2 \) ground state levels ranging from 0.7465(3) eV for P\(^-\) to 1.047 401(20) eV for Sb\(^-\) [31]. The experimental and theoretical studies of group V elements performed since 1990 have mainly been dealing with the ground state configurations.

4.8.1. Nitrogen

At the time when Buckman and Clark’s review article appeared in 1994 [42] it was well established that N\(^-\) did not exist as a stable ion, whereas metastable states with lifetimes exceeding 1 \( \mu \)s were claimed to have been observed. The metastable states had, however, not been spectroscopically identified and were generally assumed to be due to N\(^-\) 2p\(^4\) \(^1\)D and \(^1\)S states. It is of great importance for the accelerator mass spectroscopy (AMS) \(^14\)C dating method, that longer-lived N\(^-\) ions do not exist, since they could strongly hamper the dating method. The argumentation for the existence of longer-lived N\(^-\) 2p\(^4\) \(^1\)D and \(^1\)S ions has usually been, that these negative-ion states are bound with respect to the 2p\(^3\) \(^2\)D and \(^2\)P states of N by at least 0.5 eV [48]. Thus the negative ions can only decay via autodetachment to the 2p\(^3\) \(^4\)S \( \epsilon \)l continuum, which is a spin forbidden process in the LS
approximation. It should be noted that the observation of longer-lived \( N^- \) species first appeared in connection with dissociative collisions of nitrogen containing molecules (as \( N_2 \) or NO), whereas it was impossible to detect any longer-lived negative nitrogen ion using \( N^+ \) ions and a gas phase two-step electron capture process [489].

In 1994 it was realized by Müller et al. [595] that ion-surface collisions provided an alternative way to implement the two-step procedure. If a low work-function surface was applied, such as W(110) covered by a monolayer of Cs, low-energy electron spectra induced in slow collisions of \( N^+ \) or \( N_2^+ \) could be interpreted in a consistent manner by assuming the electron emission was observed from the autodetachment of the \( N^- \) 2p\(^1\) 1D ions to the neutral N(2p\(^3\) 4S) ground state. The excitation energy of the 1D ions was determined to be 1.4 eV with respect to the 4S ground state of \( N^- \). Subsequently, Müller et al. [596] reported that 200 ns would be an upper limit to the lifetime of the metastable negative \( N^- \) ions, whereas Cowan et al. [597] estimated, on the basis of the same experiment, that a lower limit would be 3 ps. It was clearly of interest to obtain more accurate estimates of the natural lifetimes.

Cowan et al. [597] performed detailed calculations of the energies and lifetimes of the \( N^- \) states belonging to the 2p\(^4\) configuration. Systematic multiconfiguration-interaction Hartree–Fock (MCHF) procedures were applied to study the energies of the 1D and 1S states relative to the N(2p\(^3\) 2D) state. The calculations showed that the binding energy of \( N^- \) (1D) state was 0.817(2) eV, which is identical to a location of 1.513 eV above the ground state of neutral nitrogen, whereas the 1S term is located 1.390(1) eV above the 1D term. The value for 1D is in good agreement with the experimental observation of 1.4(1) eV from the ion-surface experiments [595,596], whereas there are no experimental data for the 1S state to compare with. Both the negative ion states can only decay via magnetic interactions. The calculations of the lifetimes yielded 0.1 and 0.07 ns for the 1D and 1S states, respectively. Even the real lifetimes may deviate a factor of five from the calculated ones it seems reasonable to state [597] that the calculated lifetimes definitively rule out lifetimes in the \( \mu \)s range, which also would have had a serious impact on \( ^{14} \)C dating by AMS, since a typical drift time in modern tandem AMS accelerators is about 8 \( \mu \)s. The calculations by Cowan et al. [597] also confirmed that the \( N^- \) 3P ground state has a lifetime of the order of \( 10^{-14} \) s.

The binding energy of the \( N^- \) (3P\(_2\)) level has been calculated by Wijesundera and Parpia [598] using the multi configuration Dirac–Fock method, but neglecting core–core and core–valence correlation effects. The purpose of this study was, however, not to obtain the most accurate binding energy for the \( N^- \) ion, but to understand the significant difference in binding energy between the \( N^- \) and \( P^- \) ions, which will be discussed below. The existence of a highly excited bound state of \( N^- \), having all the electrons with unpaired spins, has been predicted by Piangos and Nicolaides [558], but so far not observed.

4.8.2. Phosphorous, arsenic, antimony, and bismuth

Experimental as well as theoretical studies of the negative ions of P, As, Sb, and Bi have been rather limited during the 1990s and only the binding energies of terms or levels belonging to ground state configurations have been studied. By means of laser photodetachment electron spectroscopy the binding energy and the fine-structure splittings of the As\(^-\) ion [599,600] were investigated yielding the binding energy and fine-structure splittings with an accuracy of 5–10 meV, whereas studies of Sb\(^-\) [182] and Bi\(^-\) [601] were performed using infrared laser photodetachment threshold
Wijesundera and Parpia [598] performed multi-configuration Dirac–Fock calculations of the electron affinities of atoms with open p-electron shell within the first (B–F) and second (Al–Cl) row of the periodic system in order to gain some insight to the marked difference between the binding energies of the N\(^-\) and P\(^-\) ions. The Dirac–Fock method provides a qualitative understanding of general features of atoms and negative ions and it is able to account for the trends of the electron affinities among the elements belonging to the first and second row of the periodic system. The investigation showed that the marked difference between the electron affinities of N and P should be attributed to the exchange interaction between the 2p electrons and the three outer electrons (3p\(^3\)) in neutral phosphorous, which significantly reduces the screening effect on the P-atom and enhances its electron affinity.

The binding energy of P\(^-\)(3p\(^4\) 3P) has later been calculated by ab initio calculations [242], which yielded a value of 0.7467 eV in perfect agreement with the experimental value available. A similar good agreement was also obtained from a simple modified density function theory calculation performed by Guo-xin et al. [522].

The experimental study of the Sb\(^-\) ion [182] proved that a combination of one-, two-, and three-photon detachment experiments can be used to completely and accurately determine the energies of the bound terms (3P and 3D) and the fine-structure levels of the 3P term. This study clearly demonstrated the potential of utilizing forbidden transitions in optical studies of negative ions. A schematic level diagram of Sb\(^-\) and the different detachment schemes used to obtain the structural information about the bound terms and levels of this ion was presented in Fig. 16. The experimental determinations of the binding energies were complicated due to line broadening of the resonances observed in Sb\(^-\), see Fig. 50 as an example, which illustrates the 3P\(_2\) → 1D magnetic dipole (M1) resonance in the two-photon detachment yield. The broadening cannot be explained on the basis of laser bandwidth and Doppler effects alone, but hyperfine structure effects have to be taken into

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**Fig. 50.** M1 resonance in the two-photon detachment yield after excitation of the Sb\(^-\)(5p\(^4\) 3P\(_2\)) ground state level via the Sb\(^-\)(5p\(^4\) 1D\(_2\)) excited state to above the detachment limit. The solid line represents the simulated resonance profile, whereas the vertical lines indicate positions and relative strengths of individual hyperfine components [182].
account. The solid line in Fig. 50 represents a simulated resonance profile, whereas the vertical lines indicate the positions and relative strengths of the individual hyperfine components, which could be determined on the basis of calculated hyperfine structure constants. The large amount of hyperfine components is due to the presence of both the $^{121}\text{Sb}$ and $^{123}\text{Sb}$ isotopes in the experiment, which contribute 18 and 26 hyperfine structure components, respectively, to the M1 resonance. The hyperfine structure parameters were calculated by Beck [182] using relativistic configuration interaction calculations, which also yielded energy values for the $^3\text{P}_1$, $^3\text{P}_0$, and $^1\text{D}_2$ levels in good agreement with the experimentally determined energy splittings.

Very recently this type of study has been extended to include the Bi$^-$ ion [601], but only the binding energy of the lowest negative-ion hyperfine structure level $(6p^3\text{ 4S}_3/2, F = 6)$ was determined relative to the Bi$(6p^3\text{ 4S}_3/2, F = 6)$ level yielding a value of $0.942 \pm 0.01(13)$ eV, whereas the hyperfine-averaged threshold is slightly larger (by $8 \mu$eV).

4.9. Group VI elements

The stable negative ions belonging to group VI, O$^-$, S$^-$, Se$^-$, and Te$^-$, were all well known and studied by laser photodetachment threshold spectroscopy during the 1970s and 1980s leading to accurate binding energies [49], whereas information about O$^-$ resonances was obtained from O$^-$–He collisions and electron scattering on atomic oxygen [42]. The resonances could be attributed to excitation of two 2p electrons leading to resonances with $2p^3(4\text{S}, 2\text{D} \text{ or } 2\text{P})$ cores, and $3s^2$, $3s3p$ or $3p^2$ valence electrons. In addition the O$^-$($2s2p^6$) resonance was claimed to be observed in O$^-$–He collisions, but the observed width of about $200 \text{ meV}$ was in contradiction with calculations [42], which predicted the width to be an order of magnitude larger. This dilemma has been eliminated in the 1990s by studying the angular distribution of the autodetached electrons from doubly excited O$^-$ states [205].

Investigations of negative-ion resonances in this group of elements have so far only been performed by negative-ion–atom collisions or electron–atom scattering, since more energetic photons are needed for photodetachment studies than available from commercial lasers. With the access to more intense synchrotron radiation sources a study of photoexcitation of inner electrons in negative ions is possible and the O$^-$ ion could be a suitable target.

The laser-based techniques developed during the 1990s such as laser photodetachment microscopy or resonance multi-photon detachment using non-linear laser techniques (see Section 2) have been used rather extensively to gain precise information about the properties of the bound levels of the negative ions belonging to group VI.

4.9.1. Oxygen

O$^-$($2s^22p^5\text{ 2P}$): Laser photodetachment threshold spectroscopy had already in 1985 [124] yielded rather accurate information about the binding energies of the two O$^-$($2s^22p^5\text{ 2P}$) fine-structure levels. The electron affinity (EA) of the $J = 3/2$ level for the $^{16}\text{O}$ isotope was reported to be $11784.645(6) \text{ cm}^{-1}$, later corrected to $11784.648(6) \text{ cm}^{-1}$ or $1.461 1107(17)$ eV [43] by proper evaluation of the Doppler-shifted thresholds. At this level of accuracy even the conversion from cm$^{-1}$ to eV adds significantly to the relative uncertainty. The O(EA) value was considered to be the most accurate experimental determination of a negative-ion binding energy and as such considered the appropriate reference for EA studies. In the recent review of atomic EA values
[31] it was, however, pointed out that the Doppler shifted thresholds reported for parallel and anti-parallel laser and ion beams extracted from the figures in [124] deviated slightly from the values given in the text, which could be due to an unmentioned recalibration of the respective photon energy scales. The possibility that such a recalibration may have caused an error in the reported EA values cannot be excluded since recent reinvestigations of the EA value for oxygen by laser photodetachment microscopy (LPM) [127,129] and laser photodetachment threshold spectroscopy(LPT) [602] both yielded larger values, 11784.680(16) and 11784.690(23) cm\(^{-1}\), respectively. The new measurements agree within their uncertainties, but deviate from the value given by Neumark et al. [124].

Theoretical calculations of the \(^{16}\)O electron affinity are also available with the value reported by de Oliveira et al. [242] deviating less than 1 meV from the experimental results, but calculations cannot resolve the discrepancy between the experimental values mentioned above for which the deviations are only a few \(\mu\)eV.

Blondel et al. [127] have also performed detailed studies of the electron affinities (EA) for the \(^{17}\)O and \(^{18}\)O isotopes. The determination of EA for \(^{17}\)O demanded knowledge about the hyperfine structure of the \(^{17}\)O\(^{-}\) ion. The hyperfine averaged \(^{17}\)O value was shown to lie at the expected position between the EA values of the two even isotopes (\(^{16}\)O and \(^{18}\)O), and confirms the negative specific mass shift predicted by calculation. Furthermore, the fine-structure splitting for the \(^{16}\)O\(^{-}\) ion was measured to be 177.084(14) cm\(^{-1}\), improving the recommended value of 177.10(4) cm\(^{-1}\) [31], together with the hyperfine structure parameters for the \(^{17}\)O\(^{-}\) ion. Many-body calculations performed by Godefroid and Froese Fischer [603] have yielded theoretical results in good agreement with the measured isotope shift and fine-structure splitting. The photodetachment microscopy study of the negative oxygen ion indicates that it should be possible within a few years to obtain still more accurate energy values for negative atomic ions such as binding energies and fine structure splittings.

\(O^{-}(2s^22p^3)\rightarrow O^{-}(2s^22p^3nl^n'l'^{'}n'')\): The doubly excited \(O^{-}(2s^22p^3nl^n'l'^{'}n'')\) ion can be formed with three different cores, \(2p^3\) (\(4S\), \(2D\) and \(3P\)), which all have been observed in electron–atom scattering experiments [42,604], whereas only the doublet core resonances are formed in low-energy \(O^{-}\)–He collisions due to the spin–conservation rule (see Section 2.8). The spectrum of ejected electrons resulting from 5 keV \(O^{-}\)–He collisions [205] is shown in Fig. 51. The \(O^{-}(2s2p^6\ 2S)\) state was originally assigned [605] to the dominant line located just above 10 eV, the \(O^{-}(2p^3(2D)3s^2\ 2D)\) state to the line at 12 eV and both assignments were supported by theoretical calculations [42]. These assignments would lead to near degeneracy of the two excited \(O^{-}\) states, which should decay as follows:

\[
O^{-}(2p^3(2D)3s^2\ 2D) \rightarrow O(2p^4\ 3P) + \epsilon p\ 12\ eV , \\
O^{-}(2s2p^6\ 2S) \rightarrow O(2p^4\ 1D) + \epsilon d\ 10\ eV .
\]

Thus, the emitted electrons should be different. An important point in favour of this proposal was that the energy difference between the two peaks was measured [605] to be 2.01(2) eV and not 1.97 eV, which is the \(3P–1D\) splitting in the ground state configuration of oxygen. The energy-difference measurement dismissed the possibility that the two negative-ion resonances could represent the branching between autodetachment decays from the \(O^{-}(2p^3(2D)3s^2\ 2D)\) state to the \(3P\) and \(1D\) states in the neutral oxygen ground state configuration. Furthermore the branching mechanism was also dismissed, since an estimation of the branching ratio resulted in values larger than 20, in clear disagreement with the experimental data. If, however, the interpretations given above were incorrect
and the two electron resonances did represent the branching between the dismissed autodetachment channels, only p electrons would be emitted.

Dahl et al. [205] performed a combined experimental and theoretical investigation of the O$^-$ system with emphasis on the decay mechanisms proposed. The energy separation between the two intense resonance peaks was determined to be 1.97(1) eV, which deviates from the 2.01 eV previously reported [605], but is consistent with the energy separation between the $^1$D and $^3$P states in the oxygen ground state configuration. The intensity ratio between the two resonance peaks was independent of impact energy and showed a ratio of 1.58(8), in good agreement with a multiconfigurational Hartree–Fock calculation, which yielded 1.3 with an estimated 20% uncertainty. The final proof for the branching mechanism came from the angular distributions of the emitted electrons, see Fig. 52 [205]. The solid lines represent least squares fits to the experimental points, using the theoretical form of the angular-distribution functions [205], which assumes $^j_\text{p}$ electron emission only. The calculation predicted the angular dependences to be roughly mirror images of each other for the autodetaching process

$$2\text{p}^3(^2\text{D})\text{3s}^2~^2\text{D} \rightarrow \text{O}(2\text{p}^4~^3\text{P},~^1\text{D}) + \epsilon_\text{p}$$

but not for the $2\text{s}2\text{p}^6~^2\text{S} \rightarrow 2\text{p}^4~^1\text{D} + \epsilon_\text{d}$ process. Thus, the claim for observation of the inner shell excited O$^-$($2\text{s}2\text{p}^6~^2\text{S})$ state was dismissed.

**Highly excited states and collisions:** The discussion above shows that the O$^-$($2\text{s}2\text{p}^6$) resonance so far has not been observed, but this may be possible using the intense synchrotron radiation sources now available; the same is valid for the resonance formed by photo exciting the 1s electron, which would demand photon energies above 500 eV. Simultaneous excitation of a 1s and 2s electron may also be possible and perhaps result in the highly excited, but bound O$^-$ state, proposed by Piangos and Nicolaides [558].

Electron-impact on O$^-$ ions has been explored to search for a possible doubly charged O$^{2-}$ ion [196] with a closed 2p shell, but this ion was proved not to exist. The collision processes
have also been investigated covering the electron energies from threshold to several keV [196,583]. The low-energy electron collision processes will be treated in more detail in Section 5. The higher energy electron-negative-ion collisions will lead to single and double ionization of the negative ion and autoionizing, neutral states have been shown to play an important role in these processes [583]. However, Rost and Pattard [586] have shown that direct double photoionization still dominates the measured cross section for an ion like O−.

Electron detachment and charge transfer collisions between O− ions and atomic hydrogen have been studied at relative collision energies ranging from 0.1 to 15 eV [606] with the purpose to obtain experimental cross sections. Associative attachment is considered to be an important mechanism for formation of OH in the interstellar space and this process displays no energy barrier. At the low collision energies used the experimental cross sections could be accounted for by simple models such as a Langevin orbiting or a curve-crossing model [606].

4.9.2. Sulphur, selenium, and tellurium

During the last decade the laser based structural studies of the negative ions of S, Se, and Te, have focussed on the properties of the ground state configurations. Only very recently the first inner-shell photodetachment study was reported for the latter of these ions, Te− [607]. Since the negative ions of group VI elements can be produced rather easily, further inner-shell studies may be expected in the near future.

The ground state properties of the S− ion were already established by Larson and Stoneman [49,228] using laser photodetachment threshold spectroscopy and these data have not been improved during the last two decades. The electron affinity for sulphur is related to the 32S isotope. The uneven isotopes like 33S would complicate the EA determination due to the hyperfine structure splitting of the ground state 2P3/2 level, but the hyperfine structure of the 33S− ion has been measured [608] using optical probing of microwave transitions. Hyperfine-split Zeeman resonances were observed using state-selective photodetachment to probe the 2P3/2 state of the 33S− ions, which were stored
in a Penning ion trap, leading to a determination of the dipole and quadropole hyperfine structure constants of this ion.

The photodetachment of the $S^-$ ion in the presence of a static electric field has been studied by Gibson et al. [609] and will treated in more detail in Section 6 of this review. Excitation and collisional detachment processes occurring in $S^-$ collisions with atoms and molecules have been studied by Boumsellek et al. [610] using electron spectroscopy, but the aim was to gain information about excited autoionizing states of neutral S, which play an important role for the production of $S^+$ ions in these collisions.

The $Se^-$ and $Te^-$ ions for which the binding energies are well established from laser photodetachment threshold spectroscopy [31,611,612] have been test cases in connection with the development of multi-photon techniques for negative-ion studies of the resonances located below the detachment limit (see Section 2.5.4) [110,179,181]. The fine-structure splittings of the $^2P$ ground state terms have been obtained by single-photon detachment and three-photon detachment in a Raman coupling scheme and compared directly in the study by Thøgersen et al. [181]. In the case of the $Se^-$ ion, the two techniques yield results which are mutually consistent and are of the same level of accuracy. Since the fine-structure splitting in $Se^-$ is not too large (2278.2 cm$^{-1}$ [181]), both fine-structure levels are populated to a reasonable extent and a serious limitation on the single-photon work is not encountered. The situation is very different for $Te^-$. In this case the Raman approach is clearly superior. The population of the upper $^2P_{1/2}$ level of $Te^-$ is usually so low that this clearly affects the accuracy which can be obtained with the single-photon technique.

Inner-shell photodetachment of $Te^-$ has been studied from 34 to 140 eV covering the entire 4d-excitation region by synchrotron radiation applying the merged ion–photon beam technique and the ASTRID storage ring [607]. The absolute cross sections for $Te^+$ and $Te^{2+}$ ions production were determined. The photo excitation processes led to $4d \rightarrow 5p$ and $4d \rightarrow \epsilon f$ transitions. Both reaction channels will contribute to the formation of $Te^+$ ions by autodetaching processes, the former via the $Te^-$ ($4d^95s^25p^6 \ 3D_{5/2,3/2}$) resonances located at 37.37 and 38.84 eV, respectively, whereas the latter is manifested by the broad giant-resonance structure peaking at 90 eV, see Fig. 53. The $^2D$ resonances (Feshbach) are located 2.95 and 1.48 eV, respectively, below the 4d detachment limit for $Te^-$ and the $^2D_{5/2}$ resonance level is therefore more effectively bound with respect to its parent state than the ground state level of $Te^-$. The $^2D$ resonances are rather narrow with natural widths about 200 meV [607]. The $4d \rightarrow \epsilon f$ detachment process produces a core excited $Te$ state that with almost 100% probability decays by Auger decay with the final product being ionic, like $Te^+$ or $Te^{2+}$. The yields of the two ions are very similar, which shows that double-Auger and single-Auger decays in this case occur with almost equal probability.

4.10. The halogens

The negative halogen ions possess large binding energies (above 3 eV), are easy to produce, and have been used as targets in many experimental studies involving negative ions such as collisions between negative halide ions and atoms or electrons, laser-based multi-photon absorption and more recently single-photon inner-shell photodetachment studies. Being isoelectronic to the noble gases with $np^6 \ 1S$ closed shell systems the negative halogen ions are also attractive to theoretical calculations as proving ground for theories of atomic photoabsorption. Laser techniques have been applied to negative halogen ions for nearly four decades from the pioneering multi-photon I$^-$ experiment
by Hall et al. [157] to the recent laser photodetachment study of $F^-$ in a strong infrared laser pulse [613]. The binding energies of the negative ions are well established with high accuracies (2–27 μeV) [31,121,131,614,615], and theoretical calculations for $F^-$ and $Cl^-$ have reached a level of accuracy of 1–2 meV [242].

4.10.1. Fluorine

$F^-(2p^6 \, ^1S)$: The binding energy of the $F^-$ ion has been studied by LPT [121] and LPM [131] techniques. The values obtained were in good agreement and the recommended binding energy is now 3.401 1895(25) eV [131]. The theoretical methods applied to calculate binding energies of strongly bound negative ions, like fluorine, [242,548,549] can reproduce the binding energy within 1 meV [242].

$F^-(2p^4 \, ^3S^2 \, ^1D)$: Due to the large energy gap between the ground state level of the $F^-$ ion and the first excited state in neutral fluorine single-photon laser techniques have not been used to explore the properties of autodetaching states in $F^-$. As described in Section 2.7 a doubly excited $F^-$ state, $2p^4(1D) \, 3s^2 \, ^1D$, was already observed in the 1970s in $F^-–He$ collisions. It was, however, a bit of a surprise that this resonance state decayed via low-energy electrons (0.09–0.25 eV) to the $2p^4(3P)3p \, ^2P$ and $^2D$ states in neutral fluorine [203], by changing the $2p^4 \, ^1D$ core, as well as decaying to the ground state of the neutral atom.

The low-energy electrons were observed by Grouard et al. [202] at the end of the 1980s and could either be attributed to decays from the $F^- \, 2p^4 \,(1D)3s^2 \, ^1D$ state or originate from $F^- \,(2p^4 \, ^1D)3p^2 \, ^1L$ states, with L ranging from zero (S-state) to four (G-state) [203], but these states had not been observed before. The $^1L$ states could account for the low-energy electrons by decays to the $F(2p^4 \, ^1D)3p(2D \text{ and } ^2F)$ states, because the energy splittings between the $(^1D) \, 3p(^2D \text{ and } ^2F)$ levels...
are nearly identical to the energy splittings between the F 2p⁴ (3P) 3p(2P and 2D) levels. Poulsen et al. [203] resolved this problem by use of electron–photon coincidence technique, which proved that all the autodetached electrons originated from the same upper level, F⁻ 2p⁴ (1D)3s² 1D. In addition, calculations showed [203] that the decay process emitting low-energy electrons was at least as favourable as decay to the ground state of the F atom even though a change of core was involved. This result was in good agreement with the experimental data since the branching ratio was determined to be close to unity.

Excitation of the F⁻(1D) resonance state is far from being the dominant excitation process in low-energy F⁻–He or Ne collisions. Poulsen et al. [203] reported that the cross section for populating the F⁻ 2p⁴ (1D) 3s² 1D state was one order of magnitude lower than the cross section for collisional population of F(1D)nl states, which again only accounted for a minor part of the F atoms produced in the collisions. The neutral F atoms are mainly formed by detachment processes leaving the projectile and target atoms in their respective ground states.

Photon and electron collisions: The interaction between strong light fields and negative ions has been a major research topic over the last decade, both from an experimental and theoretical viewpoint. In a strong laser field, the probability of absorbing more photons than required becomes significant and among the first demonstration of excess-photon detachment from a negative ion was the F⁻ study by Blondel et al. [158] as mentioned in Section 2.5.2 of this review. For most experiments investigating multi-photon physics in negative ions, halide ions have been employed due to their large electron affinities and easy production. Blondel [43] has given an overview of experiments on negative ions in strong light fields.

A simple analytical solution to the problem of multi-photon detachment of electrons from negative ions by a linearly polarized laser field was found by Gribakin and Kuchiev [337,616], who followed the original approach of Keldysh [617]. It gives reliable quantitative results for a wide range of intensities and frequencies of the laser field, from the weak-field regime, where the process can be described by the perturbation theory, to the strong fields, where it proceeds as tunnelling. The theory is valid when the number of photons is large, but usually gives reasonable good results as soon as the number of photons absorbed is equal to or larger than two. Very recently the theory very was able qualitatively to reproduce the energy and angle resolved spectrum of electrons produced by photodetachment of F⁻ in a strong infrared laser pulse. The spectrum involved contributions from more than 23 excess photon detachment channels [613].

The experimental study by Kiyan and Helm [613] has stimulated new theoretical research leading to a Keldysh-type theory, that includes rescattering of the detached electron on the parent atom [618] and to a model-independent quantum approach [619], both of which yield predictions in good agreement with the earlier theoretical results at the low-energy part of the spectra.

A comparison between measured and calculated three-photon cross sections for the halogen ions shows in general a very good agreement concerning their relative magnitudes, but the calculated cross sections are consistently larger than those obtained experimentally.

Multi-photon detachment of negative ions can be studied using linearly or elliptically polarized light [620] with most studies being performed with linearly polarized laser light. Very recently multi-photon detachment by intense elliptically polarized light has attracted new interest in connection with negative ions, since unusual threshold effects have been found theoretically in the frequency and intensity dependence of the electron angular distributions produced by an elliptically polarized laser as well as in the elliptic dichroism parameter, which measures the angular distribution [621].
So far these predictions have not been tested experimentally for negative ions, but asymmetries in above threshold ionization electron angular distributions from rare gas atoms have been observed applying elliptically polarized light [622].

A few years ago Hart [623] applied the R-matrix Floquet approach to examine two- and three-photon detachment cross sections for electron-correlation effects. Using different expansions the influence of the overlap between the F and F\textsuperscript{−} wavefunctions was found to be very important for determining cross sections at the onset of the open channels. By including only a limited number of interactions it was possible to get good agreement with experiment, but the author states that a full inclusion of all possible interactions is required to guarantee a proper result. It is, however, clear that correlation effects have a significant influence on the multi-photon detachment behaviour of F\textsuperscript{−}. Correlation effects involving excitations to electron shells with higher angular momenta influence in particular the properties for outgoing electrons with low angular momenta and close to threshold, whereas these effects are less dramatic, but still important at higher energies [623].

Electron impact detachment of the F\textsuperscript{−} ion has been performed at the heavy ion storage ring CRYRING at Stockholm with the purpose to determine the cross section [624]. Electron impact on negative ions will be treated in more detail in Section 5 of this review.

4.10.2. Chlorine

Cl\textsuperscript{−} (3p\textsuperscript{6} 1S): The chlorine atom possesses the largest known atomic electron affinity, 3.612 724(27) eV [614]. The accuracy of this value was improved during the 1990s changing it by 4 meV from the value recommended in 1985 [49], but is still a factor of ten lower than obtained for the homologous F\textsuperscript{−} ion. The theoretical binding energy has also been improved in recent years [242] and now only deviates 1–2 meV from the experimental result. In addition, the isotope shift between the electron affinities of the two Cl isotopes (35Cl and 37Cl) has been established [614].

Since the binding energies of the negative halide ions are so large, the ground state wavefunctions and the photoabsorption cross sections are rather similar to those in the neutral atoms of the noble gases [52]. Although the threshold behaviour of cross sections is different due to the different residual-core charge the photodetachment processes in the negative halide ions exhibit the same collective nature as known for photoionization of the noble gases [52]. The photodetachment cross section for the Cl\textsuperscript{−} valence electrons was studied experimentally already in the 1970s [625] and since then it has been a testing ground for theoretical calculations of atomic photoionization, starting with single-particle model calculations by Robinson and Geltman [626], via many-body perturbation theory calculations to the relativistic random-phase approximation (RRPA) calculations [627,628].

Cl\textsuperscript{−} (3p\textsuperscript{4} 1D) 4s\textsuperscript{2} 1D): Several doubly excited states belonging to the Cl\textsuperscript{−} ion were reported by Cunningham and Edwards [629] to be populated in Cl\textsuperscript{−}–He collisions. The assignments of these states were performed with the help of theoretical calculations by Matese et al. [630]. The assignments have been rather convincing and quoted in several reviews [38,41,42]. However, a reinvestigation by Andersen et al. [204] completely changed the previous interpretation and assignments. Only the 3p\textsuperscript{4}(1D) 4s\textsuperscript{2} 1D state, homologous to the observed doubly excited state in F\textsuperscript{−}, is populated in Cl\textsuperscript{−}–He collisions, whereas all the additional peaks in the electron spectra, considered as evidence for doubly excited states such as 3p\textsuperscript{4}(3P) 4p\textsuperscript{2} or 3p\textsuperscript{4}(1S) 4s\textsuperscript{2}, were proved to belong to 3s3p\textsuperscript{5}nl′ or 3s\textsuperscript{2}3p\textsuperscript{3}nl′l′ excited neutral Cl states [240,631]. Collisional detachment of the Cl\textsuperscript{−} ions, leading to formation of Cl atoms during the passage from the ion source to the He-interaction region, was
responsible for the original, but incorrect interpretations. Thus, the collisional properties of the Cl\(^{-}\) and F\(^{-}\) ions are very similar with respect to population of doubly excited states. If molecular targets such as H\(_2\) were used it is also possible to populate the Cl\(^{-}\) 3p\(^4\)(1S)4s\(^2\) resonance state [42,629], whereas the 3p\(^4\)(1S)4s\(^2\) resonance still remains unobserved.

**Photon, electron and atomic collisions:** Like F\(^{-}\), the Cl\(^{-}\) ion has often been an object in multi-photon detachment studies both experimentally and theoretically, for reviews see [43,632] and references therein. The experimental studies have aimed at absolute cross sections and angular parameters measured at selected photon energies. The number of photons needed to reach the detachment threshold could be expected to increase with increasing wavelength, and the intensity to saturate the photodetachment process should behave correspondingly. Surprisingly, Crance [633] reported calculations indicating that multi-photon detachment saturation intensities could decrease when the number of photons required to detach increased, and Davidson et al. [634] have claimed that they have observed such an effect in multi-photon detachment of Cl\(^{-}\). Blondel [43] has, however, pointed out that this interpretation of the multi-photon detachment signal as a function of intensity may not be possible, since intricate effects such as inhomogeneity of the laser beam and the finite rise time of the laser pulse prohibit such an unambiguous conclusion to be reached. Whereas rather few experimental, multi-photon detachment studies have appeared in the literature in recent years multi-photon processes in Cl\(^{-}\) are still attracting a good deal of theoretical interest [632,635,636].

Very recently, electron-impact detachment of Cl\(^{-}\) has been studied over a collision energy range of 0–95 eV at the CRYRING storage ring [637]. Absolute single-, double- and triple-electron detachment cross sections were measured with the shapes of these showing striking similarities. The ratio between the single- and double-detachment cross sections, measured about 10 eV above their respective thresholds, is approximately seven, and the same is valid for the ratio between the double- and triple-detachment cross sections.

Interactions between halide ions and atomic hydrogen or deuterium have recently attracted new interest for low-energy collisions (below 8 eV) leading to associative attachment, a process important in many plasmas. Associative attachment results in molecule formation concurrent with detachment of electrons. The energy spectra of the detached electrons can yield detailed information about the vibrational and rotational states the molecules are formed in. The shapes of the electron spectra exhibit significant structures [638,639], which can be accounted for as due to ro-vibrational thresholds or are a consequence of interchannel coupling.

### 4.10.3. Bromine and iodine

The heavier halide ions, Br\(^{-}\) and I\(^{-}\), have been studied to establish accurate binding energies [31], to explore the formation of doubly excited states populated in negative ion–atom collisions [42], and to obtain single- or multi-photon cross sections and asymmetry parameters [43] using synchrotron radiation or intense laser sources. Whereas binding energies and multi-photon studies could benefit from the laser development in the 1990s there has not been reported new collision studies. In contrast to F\(^{-}\)–He and Cl\(^{-}\)–He collisions, Br\(^{-}\)–He and I\(^{-}\)–He collisions can lead to population of doubly excited negative-ion resonances with p\(^4\)(3P) core in addition to p\(^4\)(1D) core [42].

Recently the I\(^{-}\) ion has also been the object for an experimental photodetachment study [640] dealing with detachment from the closed 4d subshell, whereas theoretical predictions have been available for some time [52,641,642]. The experiments were performed at the ASTRID storage
ring applying the merged beam technique with energetic photons (40–160 eV) from a synchrotron source. The purpose was to study the contraction of the 4f wavefunction along the isoelectronic Xe sequence by comparing 4d photoexcitation of the ions and neutral atoms ranging from I\(^-\) to Ba\(^{2+}\). The assumption that a gradual contraction of the 4f wavefunction occurs along the isoelectronic sequence was supported, whereas the previously claimed abrupt collapse could be dismissed.

Exposing I\(^-\) ions to energetic photons will cause excitation and detachment of electrons from the 4d\(^{10}\) electron shell and result in the 4d → \(\epsilon nf\) resonance phenomenon. Since the photoexcitation process to a high degree of accuracy can be described as a one-electron process, the single-electron detachment process is expected to be dominant. In the present case, however, the filling of the 4d hole will, with almost 100% probability, lead to additional loss of one or two electrons via Auger or double-Auger decays resulting in I\(^+\) and I\(^{2+}\) ions, respectively. The partial cross sections for formation of these ions exhibit maxima at 95 eV, but as expected they do not contain narrow resonance lines.

An important conclusion from the synchrotron radiation study was that the total oscillator strength over the 4d energy region is close to 10 for all species studied in the Xe isoelectronic sequence, which shows that the 4d shell is fairly unperturbed by other electron shells. Thus correlations involving the 4d and other electron shells are relatively minor, since it is unlikely that there can be correlations that do not involve a transfer of oscillator strength [640]. Since the I\(^-\) ion has a noble gas structure the absolute total photodetachment cross section could be described very well by the relativistic random phase approximation including exchange [52,640–642].

### 4.11. Transition elements

Of the 30 elements classified as transition elements starting with scandium and ending with mercury 23 have been proved to form stable negative ions. Elements, like Zn, Cd, and Hg with \((n-1)d^{10}ns^2\) ground state configurations, cannot form stable negative ions, but a large amount of information about negative-ion resonance states of these elements is available [42] and is still being extended [643]. It is also well established that a stable Mn\(^-\) ion cannot be formed (Mn possesses a half filled 3d shell), whereas this should be possible for the homologous 4d (Tc) and 5d (Re) elements [644], but not yet confirmed experimentally. In addition, the existence of a stable Hf\(^-\) ion is still an open question. Of the 23 elements forming stable negative ions 13 have been studied during the last decade some of them for the first time like Ru, La, and Os. The main object has been to obtain accurate binding energies and fine-structure splittings of the bound levels [31]. The knowledge available about the remaining 10 elements is still as described by Hotop and Lineberger in 1985 [49].

For a few of the transition metal ions, Cu\(^-\), Ag\(^-\), Au\(^-\), Cr\(^-\), and Pd\(^-\) experimental [154,229] and/or theoretical [52,551,646,648] studies of the process of photodetachment have been performed, but the focus on this type of studies has been rather limited compared with the ions belonging to the main groups of the periodic system. This can be explained as due to the more complicated atomic structures associated with the open d-shells, which are characteristic for the negative ions of the transition elements. The complex structures may, however, also contain some surprises, such as the existence of negative ions with bound states of opposite parities [1].

Nearly all the experimental electron affinity studies have been based on the use of tunable infrared laser sources for single-photon and/or multi-photon resonance detachment (LPT) studies
(Sections 2.4.1 and 2.5.4). These studies have been performed by the McMaster group \cite{1,31,111,113–115,649} and cover 12 of the negative transition element ions, which all can be characterized by possessing five or more electrons in the outer d shell, including e.g. the platinum metals. Information about the La\textsuperscript{−} ion, which only has two 5d electrons, was obtained from laser photodetachment electron spectroscopy (LPES) \cite{102}. The LPT technique leads to more accurate EA values than LPES with uncertainties ranging from about 0.05–0.1 meV for ions like Pt\textsuperscript{−}, Pd\textsuperscript{−}, Cr\textsuperscript{−}, and Ni\textsuperscript{−}, to 20 meV for the La\textsuperscript{−} ion \cite{31}. The use of the LPT experimental techniques improved the accuracy of many previously measured EA values \cite{49} with two orders of magnitude or more. For a few of the transition elements theoretical studies have also been reported, such as for Ru\textsuperscript{−} \cite{115}, Tc\textsuperscript{−} \cite{644}, or La\textsuperscript{−} \cite{650}; some of which will be discussed further below.

Negative ions like Cr\textsuperscript{−} or Cu\textsuperscript{−} only possess one level in the ground state term and are thus easier to study than the ions having fine-structure splitting like Co\textsuperscript{−} or Ni\textsuperscript{−} \cite{31} or possess more than one bound configuration like Pd\textsuperscript{−} \cite{31}. The limitations of the LPT approach to the more complex negative ions possessing several bound levels are mainly associated with the large backgrounds resulting from overlapping thresholds, particularly when p electrons are emitted, which was the case for the 12 transition elements studied by the McMaster group \cite{31,64}.

4.11.1. Lanthanum and osmium

Negative ions possessing more than one bound term or level can usually attribute these to the same configuration, and the terms or levels thus have the same parity. For ions like Pd\textsuperscript{−} and Pt\textsuperscript{−} for which more than one bound state configuration can be expected to exist \cite{31,601}, e.g. 4d\textsuperscript{10}5s\textsuperscript{1} and 4d\textsuperscript{9}5s\textsuperscript{2} for Pd\textsuperscript{−}, the parity of the two configurations will be the same. The possible existence of negative ions possessing bound configurations with even as well as odd parities has attracted a great deal of interest. A number of theoretical calculations indicated rather early that the Cs\textsuperscript{−} ion was a possible candidate (see Section 4.3), but this was disproved experimentally; the three fine-structure levels belonging to the excited 6s6p 3P state were situated in the continuum, just above the detachment limit, so only the 6s\textsuperscript{2} 1S state was bound.

La\textsuperscript{−} was proposed as an alternative candidate after Vosko et al. \cite{651} put forward the idea that La\textsuperscript{−} ions could be formed by p as well as d attachment to the La(5d6s\textsuperscript{2}) ground state configuration. O’Malley and Beck \cite{650} elaborated further on this proposal, performing relativistic configuration-interaction calculations, including valence and some shallow core–valence correlations. The calculations indicated that La\textsuperscript{−} should possess 11 bound states of which seven odd states originated from 6p attachment, whereas the remaining four were attributed to even states from 5d attachments. The ground state term of La\textsuperscript{−} was predicted to be 1D and to originate from the 6p attachment with a binding energy of 462 meV, whereas the lowest lying 5d attachment state (3F\textsubscript{2}) was placed less than 30 meV above. The La\textsuperscript{−} had been studied experimentally using LPES \cite{102}, but such studies do not reveal the parity of states and therefore the predictions remain unconfirmed. The electron affinity of lanthanum was measured to be 0.47(2) eV with an excited state having an electron affinity with respect to the ground state of lanthanum of 0.17(2) eV \cite{102}. The identity of the ground state configuration of La\textsuperscript{−} cannot be decided unambiguously on the basis of the information available today and the 5d\textsuperscript{2}6s\textsuperscript{2} 3F\textsubscript{2} assignment \cite{31} still has to be confirmed. It would be valuable to study the La\textsuperscript{−} ion using infrared photodetachment spectroscopy in both a single- and multi-photon regime, in order to achieve much higher resolution and thereby to verify or dismiss the existing interpretation of this complex system.
A recent laser spectroscopy experiment revealed, however, the presence of two unexpected states in the Os\(^-\) ion\[1\]. Whereas the 5d\(^7\)6s\(^2\) \(4F_{9/2}\) ground state level of the Os\(^-\) ion has a binding energy above 1 eV (1.077 80(12) eV)\[31\]) and the remaining three fine-structure levels belonging to the \(4F\) term have been observed, two unexpected states appeared very close to threshold. One was bound with 11.48(12) meV with respect to the Os(5d\(^6\)6s\(^2\) \(5D_4\)) level the other was located only 3.52(12) meV above, see Fig. 54. Here the two states are labelled a and b, respectively, with the position of the detachment threshold indicated between the two resonances. The Einstein coefficients for the transitions from the ground state level have been estimated on the basis of saturation techniques and determined to be of the order of \(10^4/s\) for these two levels close to the detachment threshold. This is far too large to be explained as magnetic dipole transitions at these wavelengths, but should be attributed to electric dipole transitions. The new state has not been identified so far, but the resonances are tentatively assigned to 5d\(^6\)6s\(^2\)6p \(6D_{9/2,11/2}\) levels with \(J = 11/2\) being the level above the detachment limit.

4.11.2. Technetium and rhenium

The complex nature of the negative ions of some of the transition elements is noticeable along the Mn, Tc, and Re sequence. In the early days of negative ion research and prior to some of the electron affinity (EA) measurements for transition elements semiempirical EA values were provided viewing the negative transition element ions as an s electron attachment to a \(nd^m(n+1)s\) atomic state with \(m\) being 6 and \(n\) being 3–5, respectively, for the three elements mentioned above\[48\]. The semiempirical method often provided EA values, which later proved to be in reasonable agreement with the measured ones\[48,49\].

For both Mn\(^-\) and Tc\(^-\) the semiempirical values were close to 1 eV, whereas the Re\(^-\) value was about 1.6 eV\[644\]. However, since the ground states of the Mn, Tc, and Re atoms originate
from \( nd^{m-1}(n+1)s^2 \) configurations it was necessary to adjust by the energy difference to the excited \( nd^m(n+1)s \) states resulting in a negative binding energy for \( Mn^- \), about 0.5 eV for \( Tc^- \) and close to zero for \( Re^- \) [644]. This was also the status when the newest review of binding energies for atomic ions appeared in 1999 [31]. It is noticeable that it is the element with the open 4d shell (Tc), which has the largest binding energy, a trend also recognized for the Ti, Zr, Hf and V, Nb, Ta sequences [644].

In the interest to improve the semiempirical estimates O'Malley and Beck [644] performed relativistic configuration-interaction calculations predicting the binding energies for the \( Tc^- (4d^65s^2\text{ }^5D_J) \) levels to range from 636 meV for \( J = 4 \) to 460 meV for \( J = 0 \). Similar calculations for the \( Re^- (5d^66s^2\text{ }^5D_4) \) level suggest that this level is slightly unbound (of the order of 10 meV), whereas the calculations confirm that the \( Mn^- \) ion should be unbound by more than 1 eV. Whereas the experimental verification of the prediction for the radioactive Tc element seems less likely to be performed in the near future it may be possible to test the prediction for the \( Re^- \) ion.

4.11.3. Iridium and platinum

The heavier platinum metals, Ir and Pt, have been the objects for several recent laser studies [140,181,183,645,649] all directed towards obtaining accurate binding energies of the respective negative ions. Such values have now been established [649] using laser photodetachment threshold (LPT) spectroscopy. It should, however, be noted that some of the EA values reported during the last decade deviated more than the quoted experimental uncertainties. A careful investigation of possible experimental reasons for these deviations concluded [649] that the most likely reason was that the experimental data could not be fitted appropriately to the Wigner threshold law [2]. A significant systematic deviation was observed for both the negative Ir and Pt ions and remains unexplained under the current available threshold models, which also include correction terms due to the polarizability of the neutral atom. This indicates that improvements in the threshold models may be necessary even for photodetachment ranges close to the threshold. It seems particularly needed for p-wave detaching electrons because of the zero-slope onset at the threshold, which makes them very sensitive to deviations from the threshold behaviour. Since the early work of Hotop and Lineberger [152] very few experiments have aimed at explicitly establishing the range of validity of the threshold laws and the ranges could be very dependent on specific properties of the negative ion.

4.11.4. Copper, silver and gold

The negative ions of the elements Cu, Ag, and Au, only possess one bound state \((^1S)\), which originates from the \( nd^{10}(n+1)s^2 \) configurations with \( n \) being 3 for Cu. So far there is very limited information available revealing information about structures due to resonances for any of these ions. The absolute photodetachment cross section for an ion as \( Cu^- \) could, however, be of significant value since it is an important parameter in the modelling of partly ionized Cu vapour as applied in the copper vapour laser [646]. The need for further development of high-power Cu-lasers also stimulated the recent study of absolute electron detachment cross sections for 8–30 keV \( Cu^- – He, Ne, \) and \( Ar \) collisions [647].

Photodetachment cross sections of \( Cu^- \) have been calculated by Scheibner and Hazi [646], who performed ab initio close coupling calculations based on \( R \)-matrix theory. They applied two different descriptions of atomic copper with the first including a five configuration ground state, a single
configuration 3d\(^{10}\)4p \(^2\)P state and a three-configuration approximation for each of the two \(^2\)D states belonging to 3d\(^{10}\)4s\(^2\) and 3d\(^{10}\)4d, whereas the second approach in addition included the six lowest terms from the 3d\(^9\)4s4p configuration. Both calculations predicted that a Cu\(^-\) shape resonance, 3d\(^{10}\)4s4p \(^1\)P, located about 1.7 eV above the ground state of Cu\(^-\)\[652\], would manifest itself as a large and broad peak in the cross section, but the peak height and width would be dependent on the approximation used.

Balling et al.\[154\] measured the absolute photodetachment cross section of Cu\(^-\) at three different laser wavelengths to test the predictions above\[646\]. The cross sections were obtained by studying the saturation of neutral atom production versus laser intensity. The experimental data confirmed the importance of the shape resonance, but also indicated that the position of the shape resonance should be shifted towards higher energies. This has later been confirmed by Ivanov\[52,60\], who obtained the theoretical results using the random phase approximation including exchange and pointed out that the position and shape of the Cu\(^-\) \(^1\)P shape resonance is very sensitive to the polarization interaction between the outgoing electron and the core electrons.

Whereas there exists experimental photodetachment cross section data for Cu\(^-\) only theoretical data are available for Ag\(^-\)\[551\] for the energy region above the threshold. In the Ag\(^-\)(4d\(^{10}\)5s\(^2\)) ion the many electron 4d subshell is quite close to the outer 5s subshell and the intershell correlations are predicted to lead to two maxima in the photodetachment cross section, a prediction which has not yet been tested experimentally. Neither Cu\(^-\) or Ag\(^-\) are predicted to possess resonance structures (window resonances) as observed for Rb\(^-\) and Cs\(^-\).

The Au\(^-\) ion has been used as target for both single- and multi-photon studies. Champeau et al.\[229\] measured the photodetachment cross section of Au\(^-\) ions, which were stored in a radio frequency trap, from about 0.5 to 1.7 eV above the detachment limit. The photodetachment cross section exhibits a strong window resonance, located 2.92 eV above the ground state of Au\(^-\), and a fainter one at 3.00 eV. The two resonances can be represented by Fano profiles and were tentatively attributed to \(J = 1\) states belonging to the 5d\(^{10}\)6s6p and 5d\(^{10}\)6s\(^2\)6p configurations, but Ivanov\[52\] suggests that the resonance features could be related to some other states. He also points out that many-body effects like interchannel and polarization interactions between the electrons are very important to describe the photodetachment process.

The multi-photon Au\(^-\) studies showed that non-resonant excess photon absorption is an important process in a negative ion at laser intensities of the order of TW/cm\(^3\)\[160\], see Fig. 9 and Section 2.5.2, where the Au\(^-\) experiment was discussed. More recently, Bilodeau et al.\[653\] demonstrated, that it is possible to dramatically change the energy dependence of the near threshold photodetachment cross section in the two-photon detachment of the Au\(^-\) ion via laser polarization. Whereas the expected s-wave threshold behaviour was observed with linearly polarized light, it was possible to close the s-wave channel by using circular polarization, allowing the observation of a d-wave threshold in a negative atomic ion for the first time. The control of the near-threshold photodetachment cross section via laser polarization can be of value for future investigations of negative ions possessing near-threshold structures.

4.12. Lanthanides

Negative ions of the rare earth elements, ranging from cerium to lutetium, have been the objects of growing interest during the 1990s and it has recently been possible to establish accurate values for
the binding energies of Ce\(^-\) \[105\], Pr\(^-\) \[104\], Tm\(^-\) \[103\], and Lu\(^-\) \[654\] by laser photodetachment electron spectroscopy (LPES). Semi-empirical extrapolations established already in the 1970s and 1980s \[49\] that is should be possible to add 5d or 4f electrons to the rare earth elements leading to stable negative ions with binding energies in the range 0.2–0.8 eV. Computational studies \[655–658\] performed more recently indicated, however, that it is be more likely that the extra electron will be a 6p electron leading to lower electron affinities than previously assumed.

The experimental proofs for the existence of stable or long-lived metastable negative ions of the rare earth elements came from accelerator mass spectroscopy (AMS) groups \[231–233\], reporting that at least 11 of the 14 elements could form negative ions detectable with AMS technique. The only exceptions were holmium and erbium, whereas the radioactive promethium (Pm) had not been investigated. Nadeau et al. \[231\] reported lower limits for the electron affinities of a number of rare earths elements by assuming that the probability for producing negative ions by sputtering, given by the ratio of the negative ions produced to the sputtered neutral atoms, could be expressed by a rather simple function, which included the work function of the sputtered surface, the electron affinity of the sputtered species, and the mass of the sputtered particles. The negative ions were expected to be generated in the ground state, if not, the lower limit of the binding energy would deviate considerably from the real one. Large sputtering yield was only obtained for Ce indicating that this ion had a large binding energy or a great part of the negative ions was formed in excited, but bound states. For Tm\(^-\), Dy\(^-\), and Yb\(^-\) ions, the sputtering yields were low and the binding energies expected to be below 100 meV; more precise values could be obtained applying electric dissociation technique in combination with AMS. Subsequent studies of Tm\(^-\) \[103\] and Yb\(^-\) \[240\] have, however, disproved the AMS results, since the Tm\(^-\) ion has a rather large binding energy, whereas the Yb\(^-\) ion does not exist as a stable or long-lived negative ion.

4.12.1. Cerium and praseodymium

The complex atomic structure of the lanthanides makes it difficult to perform reliable calculations of the negative ions. The recent calculation performed for the Ce\(^-\) ion by O’Malley and Beck \[659\] illustrates this. They performed a relativistic configuration interaction calculation, which starts with a zeroth-order multiconfigurational Dirac–Fock (MCDF) reference functions using the Desclaux \[660\] program. Two Ce thresholds were considered, 4f5d6s\(^2\) and 4f5d\(^2\)6s, with 6p electron attachment to the former and 5d to the latter, leading to Ce\(^-\) bound states with the configurations [Xe] (4f5d\(^3\)6s) and [Xe] (4f5d\(^2\)6s6p), respectively. The calculations predicted an electron affinity for the Ce (4f5d\(^2\)6s \(^1\)G) ground state term to be 0.428 eV, but the LPES study by Davis and Thompson \[105\] yielded a much larger value, 0.955(26) eV. The experimental data were presented as Fig. 1 of this review as an illustration of the LPES technique. The figure shows the presence of three photoelectron peaks, each of which contains contributions from more than one photodetachment channel. The rather narrow peak marked 3 was shown to contain at least 6 transitions of which the strongest represents the actual electron affinity of Ce\(^\pm\)G. The many components are indicative of excited states in the Ce\(^-\) ion and the binding energies of two of these could also be extracted from the analysis of peak 3. These bound states of Ce\(^-\) must be long-lived since the flight time to the interaction region for the ions in the beam was estimated to be approximately 55 \(\mu\)s. It is not possible unambiguously to identify the configurations or terms of the two excited states on the basis of the data available, but laser photodetachment threshold spectroscopy may yield further information about this question.
It should be noted that the AMS study by Nadeau et al. [231] estimated the binding energy for Ce\(^-\) to be larger than 0.5 eV, whereas an AMS study combined with laser excitation [661] indicated that the binding energy may be approximately 0.7 eV, but both results are somewhat away from the 0.955 eV obtained by Davis and Thompson [105], which illustrates that a reasonable high resolution is needed in this type of studies to obtain accurate results.

For praseodymium an analogous situation exists. A theoretical prediction by Dinov and Beck [658] yielded an electron affinity of 0.128 eV; Nadeau et al. [231] reported a lower limit of 0.1 eV, whereas a LPES study by Davis and Thompson [104] resulted in an electron affinity value of 0.962(24) eV, with respect to the Pr(4f\(^3\)6s\(^2\) 4I\(_{9/2}\)) ground state level. The ground state configuration of the negative ion is expected to be [Xe] (4f\(^3\)6s\(^2\)6p), but neither the ground state term nor the excited Pr\(^-\) states observed have been identified.

4.12.2. Thulium, ytterbium, and lutetium

Stable, but weakly bound Tm\(^-\) and Yb\(^-\) ions were claimed to exist by the Toronto AMS group [231,239] with binding energies of 32(7) meV and 10(3) meV, respectively. Davis and Thompson [103] reported from LPES experiments, however, that the electron affinity of Tm (4f\(^{13}\)6s\(^2\) 2F\(_{7/2}\)) was much larger, 1.029(22) eV, and that the Tm\(^-\) ion also possesses an excited state located 50 meV above the ground state level, which is assumed to represent the other 2F fine-structure level. The experimental electron affinity and the fine-structure splitting are both nearly an order of magnitude larger than predictions by Chevary and Vosko [662], but the experimental data do support the prediction that the negative ion is formed by attachment of a 6p electron.

With a closed 4f shell and a [Xe] (4f\(^{14}\)6s\(^2\)) ground state configuration the ytterbium atom possesses an outer electron configuration similar to the alkaline earths and may be expected to form negative ions by attachment of a 6p electron rather than a 5d electron. Early calculations by Sen et al. [663] and Bratsch [664] dismissed the existence of a stable Yb\(^-\) ion with a [Xe] (4f\(^{14}\)5d6s\(^2\)) configuration, whereas Vidolova-Angelova et al. [665], on the basis of a relativistic perturbation calculation, reported that attachment of a 6p electron would lead to a stable negative ion with a binding energy larger than 1 eV. Later calculations by Vosko et al. [514] using density functional theory and by Gribakina et al. [552], who applied the Dyson equation, obtained lower binding energies, in the range 50–100 meV. None of these studies indicated, however, that the binding energy could be as low as 10(3) meV as claimed by Litherland et al. [239] on the basis of their experimental study.

After the binding energy of the Ca\(^-\) ion, at the beginning of the 1990s, was shown to be close to 20 meV and the extra electron proved to be a p electron the possible existence of a still weaker bound Yb\(^-\) ion attracted new theoretical interest. Dzuba and Gribakin [666] used a relativistic correlation-potential method and reported the binding energy for the 2P\(_{1/2}\) component to be 36 meV; Wijesundera and Parpia [667] obtained 20 meV using a Dirac–Fock calculation, whereas Avgoustoglou and Beck [520] performed a relativistic many-body calculation, which indicated that the negative ytterbium ion most likely was unbound, but they could not exclude a positive binding energy lower than 10 meV. Considering that the electron affinities of the heavier alkaline earths, Ca, Sr, and Ba, scale linearly with the static atomic polarizability, an extrapolation to Yb suggests that this element should not be able to form a stable negative ion [31,668]. A reinvestigation of the experimental proof for a stable Yb\(^-\) ion was clearly needed.
Andersen et al. [240] performed a detailed investigation of the possible existence of a stable \( \text{Yb}^- \) ion using the ASTRID storage ring and a single-pass beam facility in combination with tunable laser photodetachment spectroscopy. After a careful search using different experimental approaches to generate and observe a possible long-lived \( \text{Yb}^- \) ion it was concluded that if a stable \( \text{Yb}^- \) ion do exist, its binding energy would be lower than 3 meV, a limit given by the electric fields present. This conclusion was supported by the later finding that it was not possible to form \( \text{Yb}^- \) ions in collisions between \( \text{Yb} \) ground state and Rydberg atoms for principal quantum numbers up to 30, suggesting that the binding energy would be lower than 2 meV [31,669]. The study by Andersen et al. [240] also showed that an error in the mass calibration of the original AMS study of the \( \text{Yb}^- \) ion [239] could explain the misinterpretation of the original data.

The experimental rejection of a long-lived \( \text{Yb}^- \) ion was followed by strong theoretical evidence against stability of the negative ytterbium ion [668]. It was predicted that the lowest negative ion state, \( \text{Yb}^- (4f^{14}6s^2 6p^2 P_{1/2}) \) is a narrow shape resonance in the electron–atom continuum at 20 meV. These results were obtained from many-body theory calculations with the electron–atom correlation potential appropriately scaled to reproduce the experimental data for the isoelectronic neutral lutetium atom. The most conclusive evidence for the absence of a stable \( \text{Yb}^- \) ion would be obtained if the narrow, but low lying shape resonances \( p_{1/2} \) and \( p_{3/2} \), predicted [668] to appear at 20 and 80 meV, respectively, could be detected in elastic scattering from the ground state of \( \text{Yb} \).

The last rare earth atom is lutetium, which has a ground state configuration of \([\text{Xe}] (4f^{14}6s^25d)\) with a closed 4f shell and an outer 6s^25d electron structure similar to lanthanum, for which a stable negative ion is known to exist with a binding energy of 0.47(2) eV [31,102]. By adding a 6p electron to the neutral ground state a stable \( \text{Lu}^- \) ion can most likely be formed with a binding energy of similar magnitude as for \( \text{La}^- \). This has been confirmed by Davis and Thompson using LPES technique obtaining a binding energy 0.34(1) eV [654], which is somewhat larger than the predictions made by Vosko and Chevary [656] and by Eliav et al. [657] yielding 0.19(11) and 0.257 eV, respectively.

The complexity of the rare earth elements will probably still for some time prohibit accurate calculations, which can reproduce the binding energies of the negative rare earth ions within 10–20 meV.

5. Electron-impact on negative ions

Electron-impact detachment from negative atomic ions has received a good deal of interest during the last decade since modern experimental technique (see Sections 2.6 and 2.8) allows accurate cross section measurements in the near threshold region. The field of electron scattering on negative ions, covering atomic and molecular ions, has been reviewed in recent years by Andersen [63,65,191].

Detachment from \( \text{H}^- \) (or \( \text{D}^- \)) has been of special interest in this connection due to earlier reported signatures of short-lived \( \text{H}_2^- \) states [197–199]. Electron-impact on \( \text{H}^- \) or \( \text{D}^- \) [195,304], \( \text{B}^- \) [559], \( \text{O}^- \) [196], \( \text{F}^- \) [65], \( \text{S}^- \) [670], and \( \text{Cl}^- \) [637] has been studied experimentally since 1995 using storage rings with electron sources attached, but none of these ions were able to bind an additional electron and form doubly charged ions, either stable or as resonances. Most important was the study of the negative hydrogen ion, see Section 4.1. The experimental cross section data
Fig. 55. Electron-impact detachment cross section of $D^-$ as a function of energy. The model calculation is compared with the experimental data for three different values of the radius of the reaction zone [195].

usually cover the range from threshold to about 30 eV above with the single detachment cross section being nearly two orders of magnitude larger than the double detachment cross section, which can be observed at the higher energies for ions like $B^-$ [559]. Electron energies up to 95 eV have been applied to study $e^-\text{--}Cl^-$ collisions [637] with the aim to study single-, double- and triple-detachment cross sections.

The single detachment data, see Fig. 55, presented a challenge to theory since previous work dealing with electron detachment from negative ions, see references in [671], appeared to be of limited applicability in the near-threshold region. The electron-impact detachment of weakly bound negative ions exemplifies one of the more important processes in physics: the breaking of a target by a projectile giving at least three distinct bodies in the final state, two electrons and a neutral atom [193], but this process can be difficult to describe theoretically. There has been several methods used to describe electron impact detachment of negative ions in the threshold region, including classical, semi-classical as well as quantum calculations [63].

A classical, phenomenological technique was used by Andersen et al. [195] in the paper presenting the experimental data for $D^-$. The total detachment cross section was estimated assuming that detachment takes place only when the incoming electron gets inside a reaction volume with radius $R$, where $R$ is related to the threshold energy $E_{\text{th}}$ as $R = E_{\text{th}}^{-1}$. The reaction volume is defined as the region in space in which the perturbing force exceeds the binding force and thus over-the-barrier transitions become allowed. The radius $R$ and the reaction volume are obtained from fits to the experimental detachment cross section. The threshold behaviour obtained by this method is
well known from nuclear and molecular calculations and this classical “reaction model” reproduces the general behaviour of the experimental data rather well.

The classical calculations were quickly followed by a number of semi-classical techniques [671–674] in which the projectile electron was treated as a classical particle, whereas the electron that is attached to the atom was treated quantum mechanically. A theoretical description of the detachment process may be based on a rather simple field-ionization concepts. It is, however, important to account for quantum tunnelling effects at large separations as well as for saturation effects that appear when the incident electron comes close to the negative ion. Quantum tunnelling and classical over-barrier models were applied by Ostrovsky and Taulbjerg [671] to describe the detachment process and similar simple models based on a non-stationary wavepacket approach were investigated by Kazinsky and Taulbjerg [672]. These semi-classical models did not aim at a complete description of the detachment process and their shortcomings are also noticeable [193]. It is not possible to include electron exchange in these methods nor is it possible to make successive improvements in the main approximation of a classical incident electron. Robicheaux [193] has also pointed out that it is difficult correctly to describe the final state dynamics using the classical electron approximation since the projectile does not change its energy and does not respond to changes in the negative ion target state during the collision process.

Rost [192] considered how the threshold detachment proceeds since the impacting electron does not even reach the atom at very low energies and is repelled by the loosely bound electron. The experimental detachment threshold is therefore significantly larger than the binding energy of the negative ion, often a factor of 2–3. Rost analyses the problem by decomposing the cross section into a product of a background part and a barrier penetration probability resulting from the repulsive Coulomb interaction. This tunnelling probability contains the dominant energy variation, as also noted in the semi-classical studies mentioned above, and it can be calculated analytically based on the same principles as the famous Wannier description [194] for threshold ionization under attractive forces [192].

Using a standard quantum-mechanical treatment Pindzola [675] calculated the detachment cross section based on lowest-order distorted-wave theory. A similar method had previously also been used to calculate ionization cross sections for atoms and positive ions. The calculations showed that it was important to include and select the best possible polarization potential for the continuum-distorted waves. Pindzola calculated the detachment cross section for both H$^-$ and O$^-$ and obtained surprisingly good agreement with the experimental data for the latter; this is perhaps somewhat fortuitous, as the importance of polarization may indicate that higher-order perturbation terms might also be important [675].

More recently, Robicheaux [193,676] presented a completely different method for treating the double electron continuum. He considered the problem in two different coordinate systems, one for the initial bound system and another for the continuum final state. The most important parameters needed to calculate the cross section are then the so-called $T$-matrix elements, which were calculated and summed for 10–20 partial waves. As shown in Fig. 56 this approach yields cross sections which are in very good agreement with the experimental data for the H$^-$ and B$^-$ ions. Robicheaux [193] also calculated the cross sections differential in energy which gave some insight to the dynamics that controls the detachment process, which mainly occurs when the incident electron is at its minimum distance from the weakly bound electron. The ejected-energy differential and total integrated cross sections for electron impact on H$^-$ were also studied by Pindzola and Robicheaux [677] by means of
time-dependent close-coupling theory. The total cross sections obtained are in very good agreement with the experimental storage ring data [195], while the differential cross sections confirm the Monte Carlo perturbation theory results obtained by Robicheaux [193,676]. Experimental differential cross section data are, however, not available for comparison.

Electron-impact studies on H⁻ at energies well above the threshold region have attracted theoretical interest in recent years stimulated by the progress obtained in the experimental study of (e,2e) processes associated with neutral targets. In order to describe the shape and magnitude of the triple-differential cross section it is necessary to account for both the initial and final channel effects [678]. Negative ions are excellent targets for a theoretical study of (e, 2e) processes, because the description required in the final state is simple compared to that of a neutral target. Through (e, 2e) studies on H⁻ it may be possible to gain more insight to the initial state mechanisms involved in more general (e, 2e) processes. In case of the H⁻ ion the final state interaction will be the one between the two continuum electrons. Lucey et al. [678] showed that the size and shape of the triple-differential cross section for this process is extremely sensitive to the form of the approximation used for the H⁻ wavefunction.

Fully differential cross sections for (e, 3e) processes with rare gases have now become available, which has initiated a theoretical study of the (e, 3e) process on H⁻ [679] using a correlated wavefunction for the target and a partially correlated double continuum in the final channel. Unlike previous theoretical studies for this process, the long-range Coulomb interaction arising between the projectile and the target ion was fully taken into account [679] in a consistent manner in both channels within the framework of the Coulomb–Born approximation. The calculations refer to incident electron energies, which are quite high (about 5 keV), compared with the energies discussed at the beginning of this section.
6. Negative ions in external electric and magnetic fields

Negative-ion states can be influenced by external electric and magnetic fields leading to the well-known Stark and Zeeman effects, which cause splitting of degenerate fine-structure levels in the weak field limit. The external fields are usually classified as weak, intermediate, or strong fields depending on the relative strength of the external effect compared with the properties of the atomic state investigated; if the separation between two fine-structure levels is large compared with the effect of the external magnetic field the latter is classified as weak, as intermediate if the effect is comparable with the splitting, and large when the Lorentz force caused by the external magnetic field is of the order of magnitude or greater than the Coulomb binding force.

6.1. Electric fields

Adding an electric field to an atom or negative ion will increase the probability for electron tunnelling and thereby influence the lifetime of the system [680]. This is particularly noticeable for the weakly bound, negative atomic ions, which become unstable even at moderate laboratory fields. Electric fields can strip electrons from weakly bound negative ions, which has been utilized to determine the binding energy of ions as Ca− [236] having a binding energy of 24 meV. Electric fields will also limit the existence of much weaker bound negative ions (binding energies of a few meV or less) or complicate the search for such ions, as seen for the negative Yb ion [240], since the low binding energy imposes constrains on the strength of bending magnets and beam energies of accelerators to be used.

The main interest with external fields has been in connection with the way static electric and magnetic fields can modify the one-photon detachment process and this field of research has been active for more than two decades [30,42,66,681]. Some of the effects observed are due to the influence of the external field on the initial state (e.g., Zeeman splitting), and some are due to the interaction of the electron with the external field in the final state. Effects of the latter type have been observed both for magnetic and electric fields. In the case of a pure electric field a “ripple-type” structure was observed in the photodetachment cross section for H− by Bryant et al. [682,683], which quickly attracted a significant theoretical interest [684–689]. The first observation of the ripple structure was in 1978 [690], appearing in the photodetachment cross section of Rb−, but the origin of the ripple structure was not understood; the explanation was given a decade later by Greene and Rouze [691].

The theoretical analyses could account for the principal observed effects: a finite cross section at the zero-field detachment threshold of 0.75 eV, an exponential falloff of the cross section for lower photon energies due to detachment aided by tunnelling through the static electric field’s potential, and the oscillations in the cross section about the zero-field value for energies above 0.75 eV, see Fig. 57. The oscillations may be viewed as the interference between the electron wave reflected by the potential barrier formed by the electric field and the unreflected wave [692] or as an effect of the sloping static field potential on the outgoing p wave (so-called “Airy-function oscillations” [30,693]). The cross section for photodetachment in the presence of the external electric field could therefore be described in a simple form as a product of the zero-field cross section and a modulation factor, where the latter depends on the momentum of the outgoing electron. Simple analytical expressions for the modulation factor were developed [684,686] and very good agreement between theory and the experimental data was obtained.
Fig. 57. Photodetachment of $\text{H}^-$ just above the detachment threshold at 0.75 eV (dashed line) and in the presence of a strong electric field $F$ (solid line). Note that the detachment sets in below 0.75 eV in the presence of the electric field and that field-induced modulations appear at higher photon energies. The arrow marks the data point that was normalized to the theoretical result of Rau and Wong [30,684].

Du [687] and Kondratovich and Ostrovsky [694] have pointed out, that the ripple structure can be related to the interference pattern observed in photodetachment microscopy (see Fig. 4). When the photon energy is increased, the microscope picture will either exhibit a bright spot inflated in the middle of the pattern or a dark, destructive interference spot; the former can be related to the maximum slope in the ripple structure, the latter to the zero slope. More recently, Kramer et al. [695,696] have given an explicit derivation of the total photodetachment current in the framework of a Green function calculation; they commented the staircase look of the total current as the remaining imprint of a remarkable interference pattern distribution. The same authors have also shown [696] how similar the expression of the total photoelectron current is to the total current density at the very centre of the interference pattern, which illustrates the close relationship between both quantities (same Airy function, same argument).

The oscillations mentioned above can be manipulated by adding a static magnetic field [681,687, 697,698]; alternatively, at fixed excitation frequency these quantum interference effects may be controlled by changing the duration of the laser pulse or by using two or more short laser pulses [697–699]. With the advent of intense lasers, there has been an interest in multi-photon detachment and non-perturbative phenomena due to the dynamic electric field of the detaching laser, in particular since Gao and Starace [700] reinvestigated the problem through an exact solution for the outgoing electron in combined static and dynamic electric fields. When applied to the $\text{H}^-$ ion, they claimed that a cross term between the two fields leads to a somewhat different result from previous studies even in the weak-laser field limit, the cross section near the zero-static field detachment threshold being lowered [693]. What exactly is going on very near threshold created a strong disagreement between theoretical groups [66]. Contrary to Gao and Starace [700], subsequent calculations by Rangan and Rau [693] and Zhao et al. [701] did not support the claims of lowered cross sections arising from a cross term between static and dynamic fields, but the final solution to this problem is still not available [702,703].
Bryant [66] has recently performed a comparison between the original experimental data, obtained at 64, 80, and 143 KV/cm, and four of the theoretical calculations [686,693,700,704] covering the critical region of high fields near threshold. The comparison shows that the recent calculation by Manakov et al. [704], in which rescattering is added to the original contributions given by Gao and Starace [700], is in best agreement with the experimental H$^-$ data. A few years before Bao et al. [705] had pointed out, that rescattering effects, originally neglected by Gao and Starace [700], are small for one-photon detachment, but important in describing two-photon detachment. However, Bryant points out [66] that it seems unlikely that any of the presently available theories, which recently were reviewed by Manakov et al. [704], are right since a realistic model of the residual atom has been omitted. In all the theoretical work, the hydrogen potential is taken in the zero-range approximation, where the potential is a delta function. New experiments with better experimental resolution accompanied by more realistic theoretical calculations, including work at much larger fields, are recommended by Bryant [66], who adds that electron correlations must be taken into account.

Experimental studies of photodetachment in static electric fields were also performed with the negative ions of Cl and S [609,706], as representative for s-wave photodetachment, and with Au$^-$ [707] (p-wave detachment). Detachment below threshold and oscillations on the cross sections above threshold were observed near the S$^-$ and Cl$^-$ thresholds. The phase of the oscillations in the S$^-$ and Cl$^-$ data was in good agreement with predictions for s-wave photodetachment in a static electric field, whereas the amplitude of the oscillations was observed to be slightly reduced, but not for Au$^-$. This difference between s- and p-wave detachment was attributed to rescattering, since this effect would be most pronounced for s-wave detachment. Near-threshold photodetachment of the S$^-$ ion was recently studied both theoretically and experimentally [708] for combined parallel magnetic and electric fields. The theory predicts both a loss of contrast in the detachment rate and a shift of the photocurrent maxima towards higher laser frequencies as a consequence of adding an electric field parallel to a magnetic field. The experimental results are supporting the theoretical predictions.

Experiments investigating the effects of static electric fields on H$^-$ have not been limited to energies near the one-electron detachment threshold at 0.75 eV. Bryant and coworkers [42,50] had already in the 1970s and 1980s studied the electric field effects on the doubly excited resonances located near the H($n = 2–4$) thresholds and more recently Halka et al. [709] extended these studies to the photon energy range from 13.4 to 14.2 eV, which covers the H($n = 4–6$) thresholds. The electric field effects on the lower lying resonances could generally be understood as the result of the Stark effect, leading to sublevel splitting at increasing electric fields or causing mixing of different parity states. During the 1990s Ho [710] and Ho and Callaway [711] have calculated the electric field effects on the Feshbach and shape resonances located near the H($n = 2–4$) thresholds using the method of complex-coordinate rotation and obtained data for the energies and widths as a function of the electric field strength. There is generally a good agreement between the calculated and observed values, particularly at lower field strengths. At higher field strengths the uncertainties of the experimental data are often large and do not allow for a proper test of the calculated data.

The onset of excited hydrogen production for photon energies above 13.4 eV [709] was observed to be downshifted with increasing field strength, which agreed with the hyperspherical coordinate interpretation of Zhou and Lin [712]. Stronger fields (above 50 kV/cm) generated resonance structures in the cross section below and above the zero-field threshold region, the former being attributed to field-assisted tunnelling of a Feshbach resonance, the latter to a field-induced shape resonance.
In the photon energy region near the $H(n = 4)$ threshold the experimental data indicate that mixing of $^1P^o$ states with $^1S^o$ and $^1D^o$ states becomes possible at increasing field strengths.

6.2. Magnetic fields

Magnetic fields can also influence the lifetimes of negative ions, as seen in connection with the determination of the lifetimes of the metastable $He^-(1s2s2p \,^4P_J)$ levels [12]; the magnetic fields in the ASTRID storage ring caused Zeeman-mixing of magnetic sublevel populations originating from different finestructure states having lifetimes deviating by more than order of magnitude. Otherwise the influence of magnetic fields on the lifetimes of negative ion resonances demands field strengths which cannot be reached in the laboratory, see [713] and references therein, but only in astrophysical objects like neutron stars or white dwarfs [714].

The influence of magnetic fields on the one-photon detachment process was observed to lead to Landau resonances which were well accounted for experimentally [227,715] and theoretically [716,717] in the previous decade.

According to our present knowledge it is most likely that singly charged negative ions in the absence of a magnetic field only possess one stable ground state configuration, for $H^-$ the $1s^2 \,^1S$ electronic state; a rigorous proof that this is also the only possible bound and stable state was given by Hill [718]. On the other hand one can expect [719] that in the presence of a strong magnetic field new discrete states of negative ions may appear. This conclusion was formulated more than two decades ago on the basis of a formal mathematical treatment by Avron et al. [720], who did not provide a physical picture of the appearance of the infinite sequence of bound states nor estimated the corresponding energies [719]. Recently bound states of negatively charged ions induced by strong magnetic fields have attracted new interest [714,719,721].

Bezchastnov et al. [719] confirmed that the number of bound states of negatively charged ions in the presence of a strong magnetic field is infinite in the approximation of an infinitely heavy nucleus and described by a simple physical picture the appearance of such states as the attachment of the external electron to the atom with different values of its angular momentum along the magnetic field. The number of such possible values is infinite and for each value a different effective potential appears. This potential determines the motion of the external electron along the field and can bind the electron in at least one quantum state. When applied to the $H^-$ ion the binding energies obtained [719] are indeed very small, of the order of $\mu eV$ for the state with zero angular momentum of the external electron and a magnetic field of 30 T; the binding energy is even three orders of magnitude smaller for quantum states with the quantum number $s = 1$, where $s$ is the negative of the magnetic quantum number of the excited electron [719]. The binding energies will, however, be larger, but still rather small, for heavier atoms which have polarizabilities significantly larger than the hydrogen atom, such as the Cs atom for which the resulting electron affinity to this atom for the $s = 1$ state at 30 T is estimated to be $0.2 \, \mu eV$.

The influence of the centre-of-mass motion in a magnetic field was subsequently studied by Al-Hujaj and Schmelcher [714] and by Bezchastnov et al. [721]. It was demonstrated that coupling of the centre-of-mass motion of an atom to the external electronic motion dramatically influences the properties of the negative ions. If this motion is taken into account a series of infinitely bound states is terminated and bound states are turned into short-lived resonance states. The lifetime of the energetically lowest magnetically induced state of $H^-$ is calculated to be 2 ns at a field strength of
1 T. Since the number of bound, magnetically induced ionic states depends on the product of mass and polarizability of the neutral system and the applied magnetic field the authors [721] hope that negative ions, which do not exist in free-field space, like Xe\(^{-}\), may be detected in the presence of strong magnetic fields.

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