

Spectroscopic studies of the structure of highly ionised atoms

I. MARTINSON and L. J. CURTIS

Studies of atomic structure are being extended into highly ionised regimes in which relativistic and quantum electrodynamic interactions and effects due to the finite size of the nucleus may dominate the dynamical structure of the ions. These highly ionised atoms have important applications in astrophysics, fusion plasma and X-ray laser technology, and provide new tests of computational atomic theory.

1. Introduction

The field of atomic physics is now in the midst of a period of intense activity, in which the experimental measurement and theoretical formulation of highly ionised atoms is being extended to regimes which were not previously accessible. These systems have both many electrons stripped away and some electrons remaining, and their dynamical structure is often dominated by interactions that are negligible in neutral systems and lightly ionised systems (i.e. where only a few electrons have been removed).

There is much motivation for the study of highly ionised systems. They are important for high precision metrology of atomic structure and for tests of basic atomic theory; they sensitively probe interelectron correlations, relativistic and quantum electrodynamic interactions, and effects due to the finite size of the nucleus. They have applications in the interpretation of spectra from space, the diagnostics of fusion plasma impurities, the development of X-ray lasers and the modelling of stellar atmospheres.

In this article we shall review briefly the historical development of these studies, describe some of the unusual properties of highly ionised systems, indicate the experimental and theoretical approaches being used and provide some examples of recent findings.

2. Historical development

In the mid 1930s it was discovered that more than twenty electrons could be removed from a complex atom such as tin (Sn) in a vacuum spark light source and the line radiation emitted from such a highly ionised atom could

be precisely measured by means of a grating spectrograph. The spectral lines were classified, i.e. assigned to definite energy levels, by means of semiempirical extrapolation from corresponding systems of lower ionisation. The leading centre for such work at that time was Manne Siegbahn's laboratory at the University of Uppsala, and some of the early work—which resulted in many publications—has been summarised by Edlén (1947, 1984). In the 1930s it seemed highly improbable that such ions would be found elsewhere 'in heaven or on earth', and there appeared to be little motivation for pursuing these studies further (Edlén 1984). However, a startling discovery was then made showing that atoms of 10–15 times ionised Ca, Fe and Ni were present in the solar corona (Edlén 1942), thereby indicating that the temperature of the corona was 2×10^6 K, much higher than previously assumed. This early demonstration of the natural existence of these highly ionised systems hinted at a significance that has only recently been comprehensively explored.

Observations of solar and stellar spectra in the vacuum ultraviolet (VUV) and soft X-ray regions (approximately in the wavelength interval 2000 – 1 Å) using rocket-borne or satellite-borne instrumentation were begun after World War II, and provided great impetus to the study of highly ionised atoms. More recently, these studies have been greatly aided by the development of new excitation methods and light sources. Among these are new experimental methods involving heavy-ion accelerators, high-power lasers, Tokamaks and other plasma discharges. The vacuum spark source, used in the early work, has also undergone important developments. Some additional light sources which produce slow, highly ionised atoms are also being successfully introduced.

Much of the impetus for recent studies is a result of exciting technical applications of the spectra of highly ionised atoms. For example, such ions are observed in

Authors' addresses: I. Martinson, Department of Physics, University of Lund, S-223 62 Lund, Sweden, and L. J. Curtis, Department of Physics and Astronomy, University of Toledo, Toledo, Ohio 43606, U.S.A.

high-temperature laboratory plasmas (such as Tokamak discharges) as unwanted and basically harmful impurities, as well as being deliberately introduced for diagnostic purposes into the hot plasma. Similarly, in recent years spectacular breakthroughs have been made in constructing lasers that operate in the extreme ultraviolet and soft X-ray regions, and several of the operating designs are based on highly ionised atoms.

3. Some properties of highly ionised atoms

Highly ionised atoms have several properties that differ from those of neutral and lightly ionised atoms. Since the nuclear charge Z greatly exceeds that of the remaining electrons, the electrostatic attraction is predominantly central, which might mislead one to conclude that the structure will resemble that of neutral hydrogen. However, the high value of Z causes large relativistic shifts in the energies of all atomic orbitals that penetrate the core deeply. There also appear cases in which the magnetic effects become larger than the electrostatic ones, i.e. the 'fine structure' splittings exceed electrostatic 'gross structure' separations. The reason for this is as follows: suppose that Z is the nuclear charge and S the screening parameter which is a measure of the screening of the nucleus by the passive electrons. Then the energy difference between two levels scales approximately as $(Z - S)$ or $(Z - S)^2$ —depending on whether the principal quantum number n of the two levels is the same or different—whereas the magnetic (spin-orbit) interaction energy is proportional to $(Z - S)^4$. Figure 1 shows how the energy level structure changes for four-electron (Be-like) ions

when Z increases from 10 to 100 (Kononov and Safronova 1977). In the high- Z limit the LS -coupling approximation, valid at the beginning of the sequence, will be replaced by jj -coupling.

A similar change with increasing degree of ionisation takes place for the rates of transitions between energy levels. In neutral and lightly ionised atoms, electric dipole (E1) or 'allowed' transitions dominate. 'Forbidden' transitions, of other multiplicities, such as magnetic dipole (M1) or electric and magnetic quadrupole (E2 and M2, respectively), are also possible, but their transition probabilities are usually extremely low. However, the decay rates of forbidden transitions scale with higher powers of Z than those of E1 processes, and situations can arise in which forbidden transitions dominate over allowed ones. Some examples of allowed and forbidden transitions between $n = 2$ and $n = 1$ levels in He-like ions are shown in figure 2. The approximate scaling of the transition probabilities with the nuclear charge Z is also indicated. In more accurate treatments Z should be replaced by $(Z - S)$, the effective nuclear charge.

Furthermore, the effects of quantum electrodynamics (QED), such as the Lamb shift (caused by electron self-energy and vacuum polarisation) which are small although of fundamental importance in neutral and lightly ionised atoms, also scale as a high power of Z —the first term is here proportional to $(\alpha Z)^4$, where α is the fine-structure constant—and they thus become substantial in highly ionised atoms. Until some years ago, most theoretical studies of QED effects dealt with one-electron systems. However, studies of recent date have demonstrated that highly ionised atoms with more than one

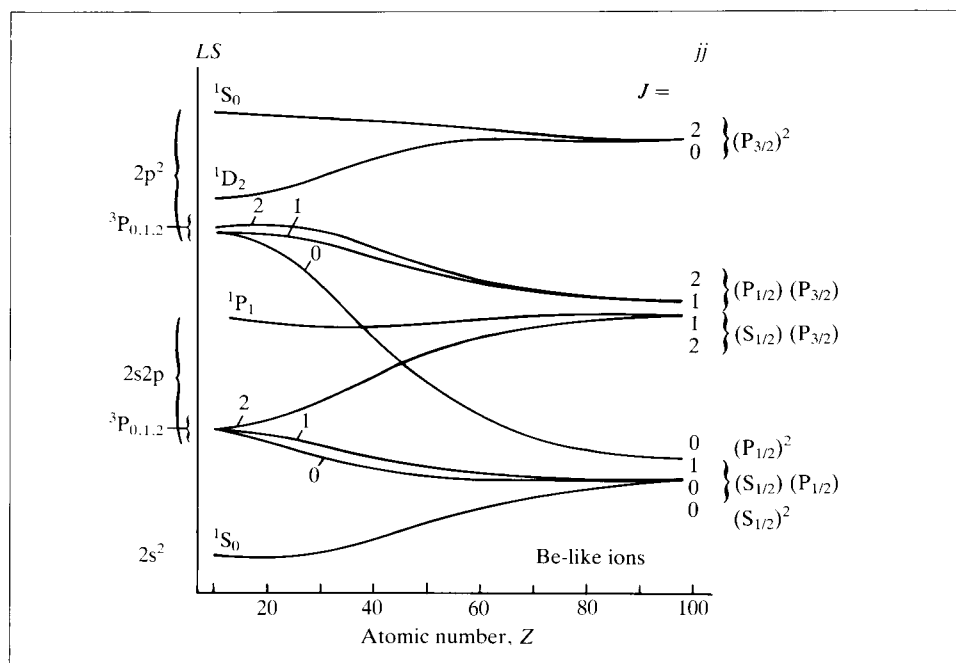


Figure 1. Theoretical energy structure of the low-lying configurations $2s^2$, $2s2p$ and $2p^2$ in Be-like ions (after Kononov and Safronova 1977). Notice the gradual transition from LS to jj coupling conditions.

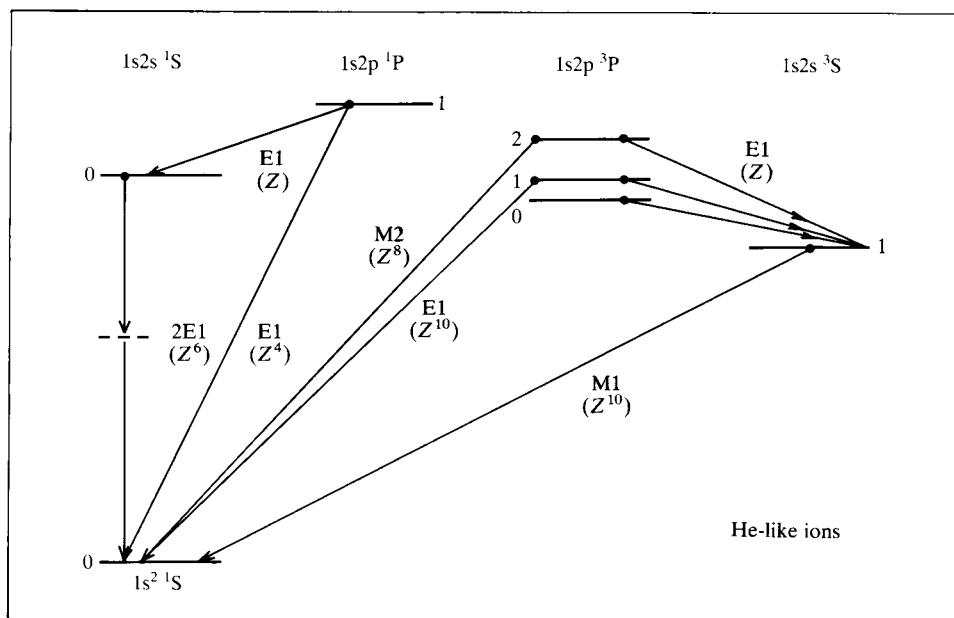


Figure 2. Energy level diagram for He-like ions, showing transitions between $n = 2$ and $n = 1$. In addition to the 'allowed' E1 transitions there is also a 'spin-forbidden' E1 decay mode (from $1s2p \ ^3P_1$ to $1s^2 \ ^1S_0$) which violates the $\Delta S = 0$ selection rule. It scales as Z^{10} . Examples of some forbidden decays and their Z -dependences are also shown.

electron remaining have some properties that simplify the observations and make possible very accurate measurements of these effects (Sapirstein 1987, Silver 1988).

The interplay of electron correlation—an effect of electrostatic interaction between the electrons—and relativistic as well as QED effects is particularly important in highly ionised atoms. For example, the inner-shell electrons in such systems undergo relativistic contraction which can greatly change the potential that the outer electrons move in, producing an indirect relativistic effect. Thus, by studying the inner electrons in a highly stripped atom, the specification of neutral atoms can be improved.

To account correctly for relativistic effects, it is important to have accurate wavefunctions for the regions of small r . Furthermore, the effect of nuclear structure on the potential experienced by the electrons cannot be adequately treated by perturbation theory. The finite size of the nucleus produces very large effects at small distances and requires a radical reconstruction of the wavefunction there. This would violate the basic assumptions of the perturbation approach, so for large Z the finite size of the nucleus should therefore be introduced from the very beginning and not added later as a correction.

High-precision spectroscopic measurements are now available over a sufficiently large range of ionisation stages that it is possible to treat the nuclear charge Z as a tuning parameter, which can be varied while all other properties of the system are held constant. This is the basis of the concept of 'isoelectronic sequence', in which data for ions with a given number of electrons are arranged in increasing order of Z . One such example has already been shown in figure 1. The scalings of the central

electrostatic attraction, the interelectron repulsion, the magnetic interactions, exchange interactions, QED effects, nuclear size corrections, etc., with different but characteristic powers of $(Z - S)$, noted above, make it possible to identify and investigate their contributions through the study of isoelectronic sequences.

One dramatic change that can be observed in isoelectronic studies concerns the reordering of the levels. Near the neutral end of the sequence, states of low angular momentum (highly elliptic orbits in the Bohr picture) are usually more tightly bound than other states of the same principal quantum number. This is largely modified in highly ionised systems, where levels having the same principal quantum numbers tend to cluster in energy and finally become asymptotically degenerate. This explains the phenomenon of 'plunging levels', in which isoelectronic configurations of low principal quantum numbers undergo an increase in their binding energy that scales as a high power of Z , and hence they 'plunge' toward the ground state through other levels.

Plunging levels can lead to local level crossings, in which two different states are nearly degenerate in energy for a specific value of Z , and so cause strong configuration interaction effects (that is, the physical states are a quantum-mechanical admixture of the labelled basis states). They can also cause isoelectronic sequences to change character markedly. As an example, consider the K isoelectronic sequence (19 electrons). In K I (neutral K) the ground state, $3s^2 3p^6 4s$, and the structure are quite simple, because there is only one electron outside the closed $3p^6$ shell. As Z increases the ground configuration will be $3s^2 3p^6 3d$; this is already the case for Sc^{2+} (Sc III), and for highly stripped 19-electron ions configurations

such as $3s^23p^53d^2$ (which consists of many energy levels) also play an important role. Thus, the initially simple system later becomes very complicated and difficult to analyse. The opposite change occurs for the 61-electron Pm sequence. At the low- Z end of this sequence the spectra are extremely complex because of the partially filled 4f shell—in Pm I the ground configuration is $4f^55s^25p^66s^2$ —but with increasing Z the $n = 5$ and 6 electrons will occupy 4f orbitals and beyond Ir^{16+} the $4f^{14}5s$ configuration plunges through the last of the open-inner-subshell configurations and becomes the ground state of a new alkali-like sequence (Curtis and Ellis 1980).

In addition to the concept of isoelectronic sequences—the most frequently used approach—a number of other generic groupings of data are being investigated. Homologous studies compare systems with similar valence electron configurations, but differing principal quantum numbers. Thus the Li, Na, and Cu isoelectronic sequences are homologous alkali-like systems, and the Be, Mg, and Zn sequences are homologous alkaline earth sequences. Ions of different elements with the same degree of ionisation (an isoionic sequence) and ions of the same element, but different degrees of ionisation (an isonuclear sequence), can also yield useful insights. Within a specific element and ionisation stage, studies are often performed for a Rydberg series or along an *yrast* chain (a ‘circular orbit’, or one for which $l = n - 1$, i.e. the maximum value of l for a given value of n).

4. Experimental methods

4.1. LIGHT SOURCES

In early studies of highly ionised atoms the light source was usually an open spark, consisting of two electrodes connected to a capacitor which was charged to a high voltage until electric breakdown took place. Later a modification of this source, the low-inductance vacuum spark, was introduced (Feldman *et al.* 1967). In this device the inductance in the circuit was minimised, whereas the capacitance was 10–20 times higher than in the original vacuum spark. Very hot plasmas were thereby produced, and transitions in, for instance, He-like Mo (or Mo LXI) were observed (Beier and Kunze 1978).

For more than 20 years pulsed lasers, usually Nd(YAG) solid-state lasers, have been successfully used to produce highly ionised atoms (Fawcett *et al.* 1966). The laser radiation is usually focused on a solid and, since the power density can be quite high ($10^{13} \text{ W cm}^{-2}$ or more), a hot and rapidly expanding plasma is formed (Carroll and Kennedy 1981). Comparatively modest laboratory lasers, with a pulse energy of a few J and a pulse length of 1–10 ns are already quite useful for

producing atoms ionised 10–20 times. On the other hand, transitions have also been studied in this way in atoms ionised more than 50 times (see e.g. Seely *et al.* 1986), by means of very large laser systems, developed for laser fusion research.

We have already stated the importance of the spectroscopy of highly ionised atoms to programmes in plasma physics including fusion research as well as in astrophysics. However, work in these two fields also yields results of interest to basic atomic physics, particularly with regard to highly ionised species. Tokamak reactors, various pinch discharges, and other plasma light sources, as well as the solar chromosphere, corona and solar flares are all excellent light sources for highly ionised atoms, being characterised by high temperatures and rather low electron and ion densities. The temperatures in solar flares can exceed 10^7 K , and spectral observations have shown Fe and Ni in very high ionisation stages, including H-like and He-like ones (Doschek 1985). The same holds for large Tokamaks such as the machines JET in Culham and TFTR in Princeton. Spectroscopic studies have here yielded important information about the structure of multiply ionised atoms, see e.g. Peacock (1984) and Denne and Hinnov (1987).

In figure 3 (Doschek 1985), two X-ray spectra of Fe, one observed at the PLT device in Princeton (Bitter *et al.* 1979) and the other from solar flares (Doschek *et al.* 1980), are depicted. The transitions are from $n = 2$ to $n = 1$ in He-like Fe XXV and their satellites. Both the similarities (concerning electron temperatures and densities) and differences (e.g. macroscopic plasma effects) can be concluded from this comparison.

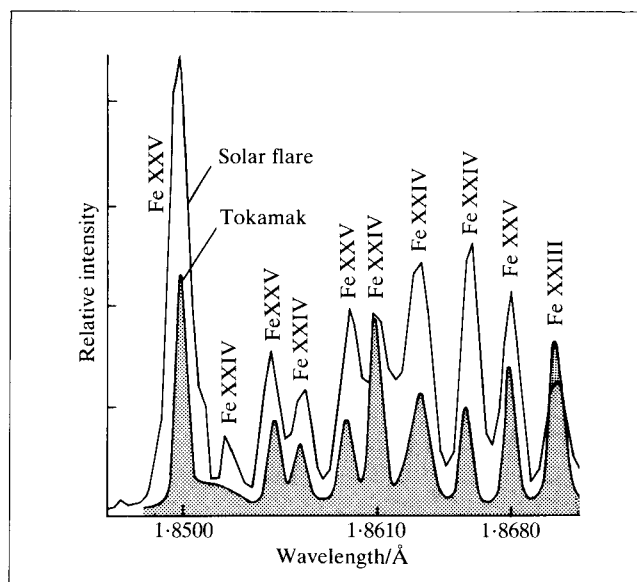


Figure 3. Comparison of high-resolution X-ray spectra of highly ionised iron (Doschek 1985), from astrophysical and terrestrial plasma light sources.

Beams of fast ions from an accelerator, excited in a target consisting of a thin foil or a gas also constitute an efficient light source for highly stripped ions. The ion-solid or ion-gas collisions result in further ionisation as well as excitation of the projectiles. The decay of their excited states can be studied by optical or electron spectroscopy. This method, often called beam-foil spectroscopy, was introduced by Kay (1963) and Bashkin (1964). It is now a standard method for the spectroscopy of highly stripped ions. A variety of heavy ion accelerators has been used, from relatively modest isotope separators to extremely powerful large facilities, mainly used for research in relativistic heavy-ion physics. A beam-foil spectrum, observed by means of a tandem accelerator in the intermediate range, is shown in figure 4 (Hutton *et al.* 1988a). Here Fe ions of 24 MeV kinetic energy were used. Most of the transitions observed also appear in the spectra of the solar corona and flares. In the very large heavy-ion facilities, such as the linear accelerators SUPER-HILAC at Berkeley, GSI-UNILAC at Darmstadt and the cyclotron system GANIL at Caen, the ion energies amount to 5–40 MeV per amu which makes it possible to produce more than 50 times ionised atoms. At the BEVALAC facility in Berkeley, work on beam-foil spectroscopy at even higher energies has been under-

taken. Thus, using beams of U, accelerated to over 50 GeV energy, Munger and Gould (1986) were able to observe radiative transitions in U^{90+} and U^{91+} , He-like and H-like U.

In recent years ion sources for positive ions have undergone striking developments, to provide beams of atoms ionised 20–50 times. These ions can be extracted from the source and either accelerated in an electrostatic field or directly used for spectroscopy by directing them into a gas target. Of the two types mainly used, the electron beam ion source (EBIS) and the electron cyclotron resonance ion source (ECRIS), (for a discussion of these sources see Arianer and Geller (1981)) the former seems to be capable of yielding higher degrees of ionisation, but the ion beam currents are relatively low. The ECRIS source provides much higher currents which are particularly useful for optical spectroscopy.

4.2. COMMENTS ON RECORDING TECHNIQUES

The line radiation emitted by highly ionised atoms lies predominantly in the VUV and soft X-ray regions. It is analysed with vacuum spectrographs or spectrometers, equipped with concave gratings. In some experiments, particularly those using ion beams, multiply excited or

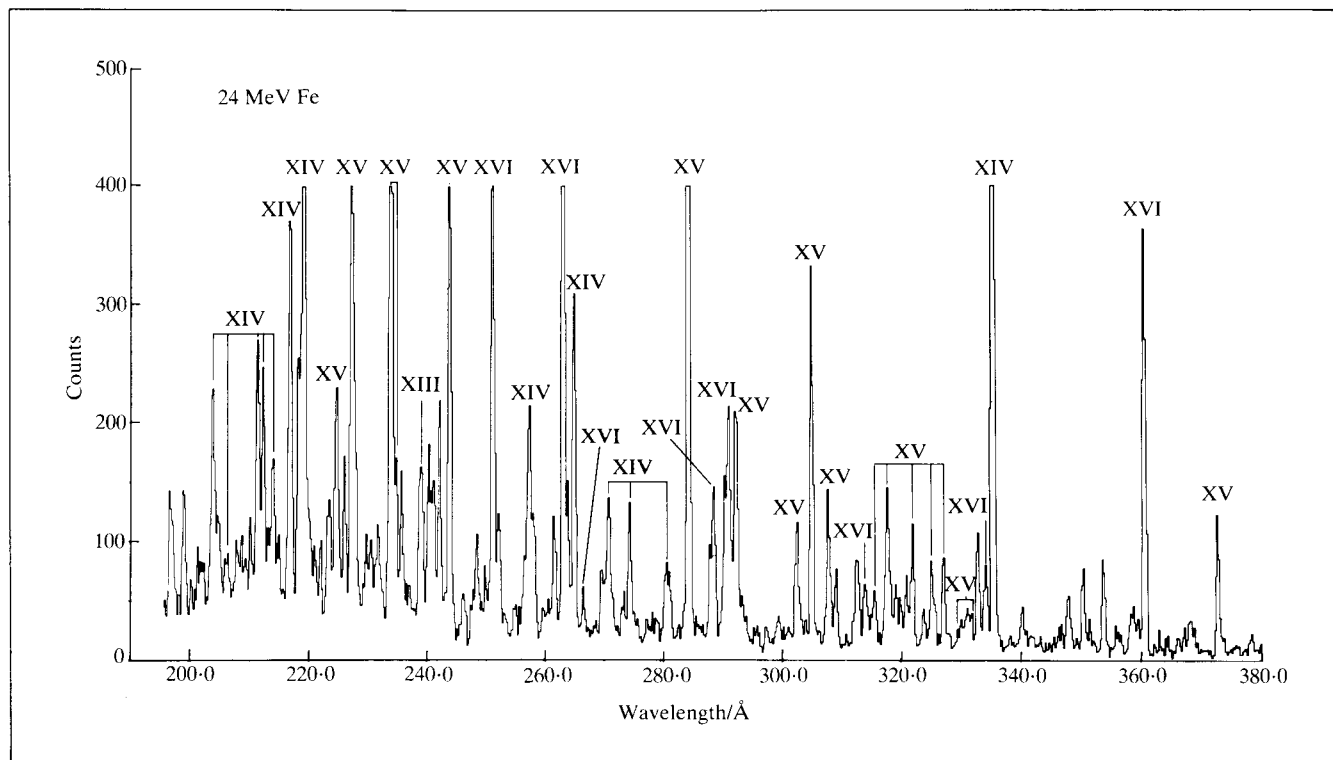


Figure 4. Beam-foil spectrum of iron (Hutton *et al.* 1988a). Ions of 24 MeV energy from a tandem accelerator were excited in a thin carbon foil, and the radiation was analysed with a 2.2 m grazing incidence monochromator. The ionisation stages of the strongest lines are indicated. For example, Fe XVI stands for Fe^{15+} , and the two strong lines at 335.4 and 360.8 Å are due to the $3p\ ^2P \rightarrow 3s\ ^2S$ resonance transition in Na-like Fe XVI, being isoelectronic to the yellow Na doublet.

inner-shell excited states are abundantly populated and these tend to decay by electron emission, autoionisation or Auger effect. Electron spectroscopy is therefore an important complement to optical and X-ray spectroscopy (Stolterfoht 1987).

In all spectroscopic work it is desirable to strive for the highest possible accuracy of wavelength and energy. In the spectroscopy of highly ionised atoms the limiting factors are usually caused by Doppler effects, from the motion of the highly stripped, excited particles in the light source. In photon spectroscopy of highly ionised atoms typical energy (wavelength) uncertainties are 10–50 ppm. In electron spectroscopy, these uncertainties are larger, usually in the 0.1–0.5% range. Besides measuring the energies of the observed transitions, it is also desirable to determine the line intensities, by use of an intensity-calibrated detection system. For optical and soft X-ray spectroscopy this can be achieved by means of synchrotron radiation, the intensity distribution of which can be accurately calculated (Ansaldò 1977).

5. Computational predictions

5.1. *AB INITIO* METHODS

Recent developments have removed some of the boundaries between theoretical and experimental atomic physics, by making large scale atomic structure computer codes generally available. These are flexible and user-friendly, and this fact, together with the access to (remote) supercomputing facilities has stimulated new approaches to atomic research. The programmes include fully relativistic multiconfiguration Dirac-Fock (MCDF) procedures as well as nonrelativistic multiconfiguration Hartree-Fock (MCHF) procedures with relativistic corrections included to first order ($\alpha^2 Z^2$), i.e. the so-called Breit-Pauli approximation. The latter approach (MCHF-BP), permits a more detailed inclusion of electron correlation effects in the calculations, whereas MCDF is particularly efficient for very highly stripped atoms where relativistic effects can no longer be treated as perturbations. It is now possible for a researcher to perform *ab initio* calculations that are custom tailored to optimise the predictive accuracy of a specific interaction being studied experimentally. This is fortunate, because highly ionised systems are complex, correlated, and strongly relativistic, and they tend to pose difficult challenges to existing theoretical methods.

When applied to highly ionised systems over a wide range of charge states, all existing *ab initio* methods suffer from limitations. The MCDF calculations treat the electrostatic and spin-orbit interactions in a fully relativistic manner, which is important for high stages of ionisation, but at present they do not describe adequately the

correlation effects, and treat interorbital magnetic effects in a perturbative rather than a self-consistent approach. Nonrelativistic MCHF calculations can readily include electron correlation effects, which are often important, particularly near crossings of plunging levels, but the inclusion of magnetic fine structure effects, which become large at high Z , are not treated in a rigorous relativistic manner.

Most *ab initio* theoretical approaches seek wavefunctions that optimise the prediction of the gross energy (arising primarily from the $1/r$ central Coulomb interaction), and treat perturbatively the finite-range interactions that fall off more steeply with r . However, in highly ionised atoms, interactions that fall off as $1/r^3$ or faster (e.g. the spin-orbit and spin-spin interactions, relativistic mass correction, hyperfine effects, etc.) become very significant. Furthermore, in spectroscopic measurements the separations between energy levels can be more important than their energies relative to the ground state or to the ionisation limit. Some of the most precisely measured spectroscopic data in highly ionised atomic systems strongly reflect the charge distribution of the inner core region, where standard theoretical wavefunctions are not very well specified. It is therefore not surprising that systematic studies of term splittings (magnetic fine structure and electrostatic direct and exchange electron-electron energies in the *LS* picture) may show regularities, linearities, and discontinuities that are not predicted by existing *ab initio* theories. For this reason, *ab initio* methods are often used in conjunction with semiempirical ones.

5.2. SEMIEMPIRICAL SYSTEMATISATIONS

The search for systematic behaviour in existing data and the use of previously discovered systematics in the interpretation of new data has always been a key feature of atomic spectroscopy. The high precision achieved in and required for spectroscopic measurements has repeatedly led to new insights into the nature of physical laws. Modern studies extending to very high stages of ionisation have accelerated these tendencies by their broad scope. A particular spectral feature can now be examined along an isoelectronic, isonuclear, or homologous sequence, over a Rydberg sequence, or along an *yrast* ($l = n - 1$) chain. The evolution of the feature while a single quantity (such as nuclear charge, degree of ionisation, principal or angular momentum quantum number, etc.) is progressively modified can reveal sensitive and subtle regularities, or sudden departures from regularity that would otherwise go unnoticed.

This sensitivity to small changes can be further enhanced through the use of semiempirical methods, in which many-body interactions are forced to reside in an

empirical parameter embedded in a quasi one-electron model. Examples of this approach are briefly referred to below, but an understanding of them is not essential for our present purpose. Among the methods used are the quantum defect method, the Ritz expansion, the core polarisation and core penetration models, and screening parametrisations.

In the quantum defect method the energy associated with a given spectral line is written as the difference in energy of a set of levels, each of which resembles the Bohr expression for the energy of an excited hydrogen atom. To take account of the fact that the attractive centre is not just a proton, but is a nucleus with screening electrons around it, the expression for the energy is modified by a so-called quantum defect i.e. instead of writing R/n^2 (where R is the Rydberg constant and n the principal quantum number) we write $R\zeta/(n - \delta)^2$. δ is the quantum defect and ζ is the net charge of the nuclear core. Thus we write

$$T_{nl} = E_i - E_{nl} = \frac{R\zeta^2}{(n - \delta)^2}, \quad (1)$$

where T_{nl} is called the term value, E_i and E_{nl} are the ionisation and excitation energies, respectively, and $\zeta = 1$ for the neutral atom, 2 for the +1 ion, etc. A simple Ritz formula for the quantum defect is

$$\delta = a + bt_{nl} + ct_{nl}^2 + \dots \quad (2)$$

Here a , b and c are parameters to be determined from experiment while t_{nl} is given by $t_{nl} = T_{nl}/R\zeta^2$. For non-penetrating orbits, i.e. those with sufficiently high values of the quantum numbers n and l , the energies are practically hydrogenic. However, the electrostatic field of the highly excited outer electron can polarise the core of the passive electrons, leading to an increase in binding energy of the outer electron, as given by the polarisation formula

$$\Delta p = T_{nl} - T_H = \alpha_d R \langle r^{-4} \rangle + \alpha_q R \langle r^{-6} \rangle. \quad (3)$$

Here Δp is the polarisation energy, T_H the relativistically corrected hydrogenic value, α_d and α_q the dipole and quadrupole polarisabilities of the core and $\langle r^{-4} \rangle$ and $\langle r^{-6} \rangle$ hydrogenlike radial expectation values. In the screening approximation, finally, the screening parameter S (mentioned in Section 3) is expressed as

$$S = A + \frac{B}{Z - S}, \quad (4)$$

where A and B are constants that can be determined empirically. For a detailed discussion of these and other important relations (cf. Edlén 1964). The use of such expressions often reveals regularities (sometimes unex-

pected) and linearities that permit extrapolative and interpolative predictions with accuracies as high as those of the available data base, and these regularities provide clues that can lead to improvements in *ab initio* approaches.

The semiempirical approach has a number of advantages: it allows interpolations for missing data and extrapolations beyond the range of available measurements, it reveals misidentifications and questionable measurements, it allows blocks of related data to be smoothed, and so provide a data set with higher accuracy than that of any single data point and it is a sensitive indicator of perturbing influences.

6. Transitions and energy levels

Although atomic energy levels have been studied for several decades by applying photon spectroscopy, the available information is often surprisingly fragmentary, especially concerning high ionisations stages. This is illustrated in figure 5, which shows the number of experimentally determined energy levels in various ions of nickel (Sugar and Corliss 1985). It should be noted that highly ionised Ni is important in astrophysical light

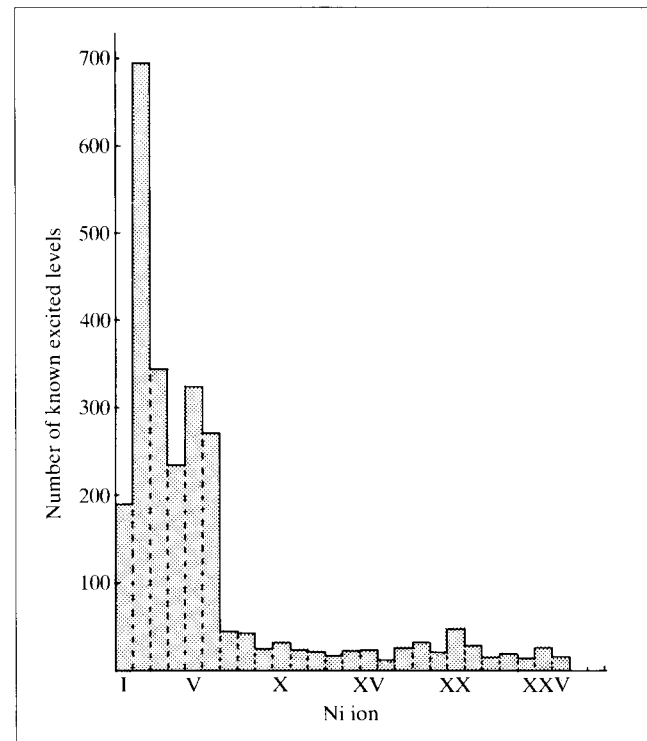


Figure 5. Number of known excited levels in various spectra of nickel, according to a compilation by Sugar and Corliss (1985). Notice the drastic reduction of the data as the degree of ionisation increases. In such ions usually only low-lying states have been experimentally determined.

sources (solar corona and flares) and Ni is also a dominant metal impurity in Tokamak devices. Other elements (e.g. Zn, Ga), which are of minor significance in astrophysics and plasma physics, have indeed been much less investigated than Ni.

The studies of highly ionised atoms have usually concentrated on transitions between low-lying levels. These have been identified for many ions in several isoelectronic sequences. In the case of Be-like ions (see figure 1) experimental data are thus available for Z as high as 40 and the situation is similar for some other sequences, as can be seen from a recent review by Edlén (1987). Most data originate from astrophysical observations and laboratory work, using laser-produced plasmas, sparks, accelerated ions and Tokamaks. Two of the most eagerly studied cases are highly stripped Ne-like and Ni-like ions, largely because their relevance to laser research. In Ne-like ions the ground state is $2p^6\ ^1S$ and the two lowest, excited configurations are $2p^53s$ and $2p^53p$. Two of the four $3s$ levels (with angular momentum $J = 1$) have much shorter radiative lifetimes than those of the $3p$ levels which feed them, and this fact makes it possible to obtain inverted populations. The situation is analogous for Ni-like ions where the ground state is $3d^{10}\ ^1S$ and other low configurations are $3d^94p$ and $3d^94d$. Here, also, inverted populations may arise. Figure 6 shows some relevant energy levels for Ne-like Mo XXXIII and Ni-like Eu XXXVI where lasing at wavelengths between 65 and 104 Å has been successfully demonstrated (MacGowan *et al.* 1987*a, b*). These examples show the importance of detailed energy-level studies for the identification of the laser transitions.

Recent theoretical work (e.g. based on the MCDF approach) has further demonstrated that the transition wavelengths for highly ionised Ne-like ions can be predicted to within 1 or 2 Å. However, although the energy level structure now appears to be well understood for these systems, the observed intensity ratios of the laser lines may differ markedly from those theoretically expected (e.g., see Matthews *et al.* 1987).

Another frequently studied case is the Cu I isoelectronic sequence. Here there is only one electron outside the $3d^{10}$ core, and transitions such as $4p \rightarrow 4s$, $4d \rightarrow 4p$, $4f \rightarrow 4d$ result in strong, easily identifiable spectral lines which have been followed over very many charge states, up to Cu-like U, as shown in figure 7. This figure originates from Edlén (1987), with the data of Seely *et al.* (1986) for $Z = 79, 82, 83, 90$ and 92 added. Notice the regular trend for all the energy levels and the variation of the relative positions of the levels with increasing Z . For example, the ratio of the 'regular' doublet ($^2P_{1/2} - ^2P_{3/2}$) interval to the 'irregular' doublet ($^2S_{1/2} - ^2P_{1/2}$) interval is very small for low ionisation stages and large for high ionisation stages. The doublet fine-structure separations, for $4p\ ^2P$, $4d\ ^2D$ and other terms, have also been studied by semiempirical techniques (Curtis 1988). It was thereby found that the linear $(Z - S)^{-1}$ dependence of the screening parameter S , see equation (4), persists over a large interval of nuclear charge, but for $Z > 60$ a sudden departure from this linearity appears, possibly due to a redistribution of the charge in the inner core (Curtis 1988). It should also be noted that for very high values of Z the energy levels are affected not only by quantum electrodynamics (QED), but also by the finite size of the

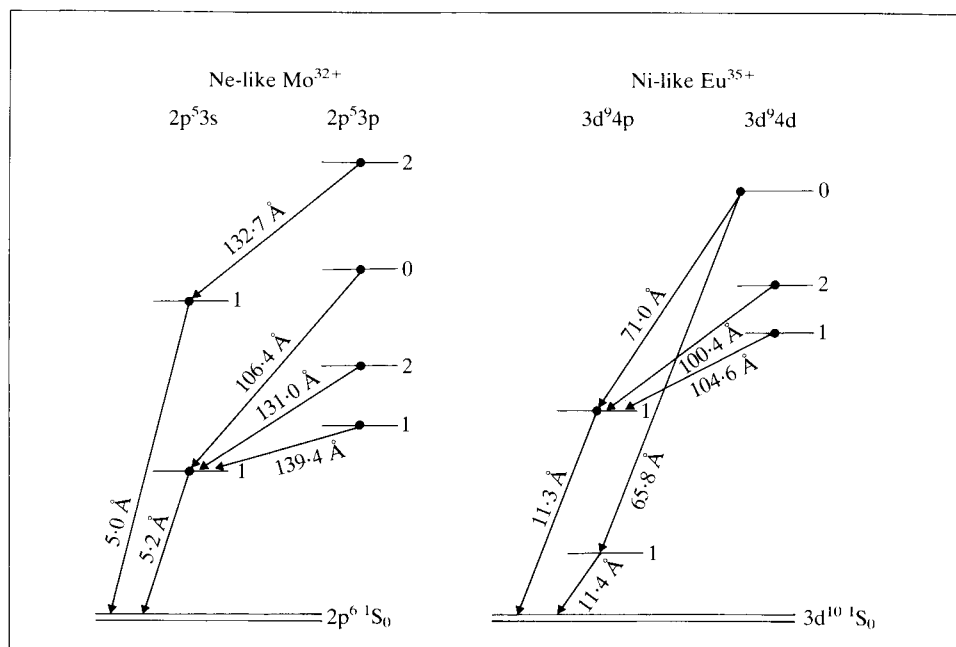


Figure 6. Energy levels for Ne-like Mo^{32+} and Ni-like Eu^{35+} , showing laser transitions between $3p$ and $3s$ (MacGowan *et al.* 1987*a*) and between $4d$ and $4p$ (MacGowan *et al.* 1987*b*). The $3s$ and $4p$ levels have lifetimes that are much shorter than those of the levels feeding them ($3p$ and $4d$, respectively) which can result in inverted populations. (The figure is schematic and the energy axis not to scale).

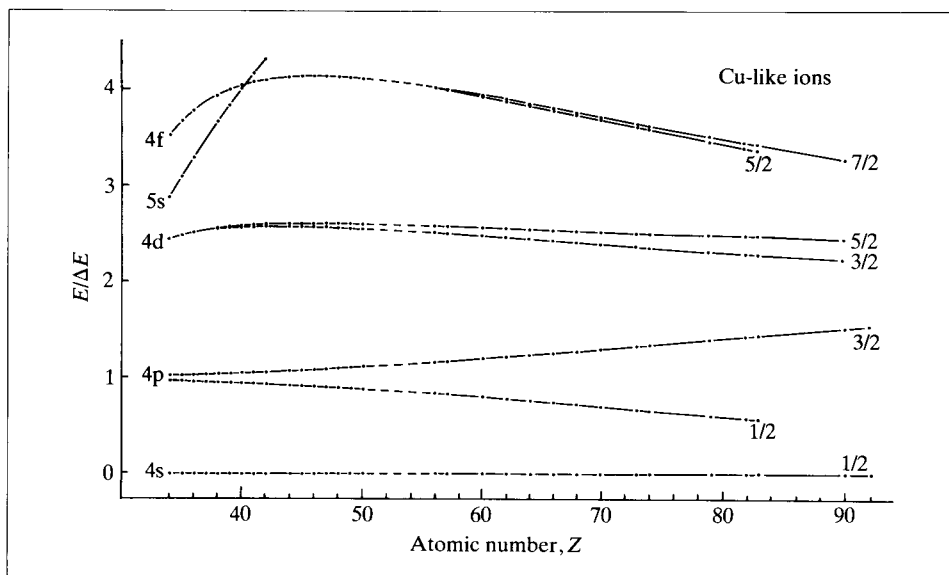


Figure 7. Isoelectronic comparison of the energies of 4s, 4p, 4d and 4f levels in Cu-like ions (from Edlén (1987) with the recent data of Seely *et al.* (1986) added). The excitation energies E , with reference to the 4s 2S ground state, are divided by the mean value of the energy of the 4p $^2P \rightarrow 4s$ 2S doublet, ΔE . Notice that the 5s level follows an entirely different trend.

nucleus (Cheng and Wagner 1987) which introduces measurable level shifts.

7. Ionisation potentials and core polarisabilities

In addition to the primary measurements of transition wavelengths and the establishment of level excitation energies, spectroscopic data are also used to specify general atomic structure properties of a given ion, such as its ionisation potential E_i and core polarisability α_d . These quantities are needed in many applications. Thus, the ionisation potential determines the charge states that will be present in a plasma at a given temperature, and the polarisability indicates the induced dipole moment, appearing as the ion is placed in an external electric field. Such data are also useful as input parameters in other atomic structure calculations. For example, semiempirical codes exist which use energy levels, ionisation potentials, and core polarisabilities as inputs to generate improved wavefunctions, the latter being used in the computation of, for instance, atomic transition probabilities.

Ionisation potentials can be determined from spectroscopic data to very high precision by two methods: a Ritz parameter quantum defect extrapolation of one or more low l Rydberg series to infinite n or a core polarisation parametrisation of levels with high values of n and l . In either case the formulation establishes a set of levels relative to the ionisation limit, which must be connected to the ground state through a chain of measured transitions. In high density sources of highly ionised atoms, electric fields depopulate states with high values of n and l through Stark mixing, and quantum defect extrapolations are the only approach available. However, low

density sources such as beam-foil excitation copiously populate states with high values of n and l , and these decay with radiative transitions, to provide a determination both of the ionisation potential and of the core polarisability.

An outer orbital electron of sufficiently high n and l serves as a gentle but sensitive probe of the inner core of the atom. In such a case the core electrons can be treated collectively as a continuously deformable distribution of charge that is distorted by the electrostatic field of the outer orbital. According to equation (3) the binding energy of the orbital electron is given by its hydrogenic term value T_H with corrections for the polarisabilities α_d and α_q , made with hydrogenlike radial expectation values $\langle r^{-4} \rangle$ and $\langle r^{-6} \rangle$. (It should be noted that the core polarisabilities refer to an ion of one charge higher than that to which the energy levels and ionisation potentials pertain).

Effective values for the dipole and quadrupole polarisabilities can be deduced from the measured data, and these two quantities then specify the binding energies of all states with suitably high values of n and l . In cases where theoretical calculations exist, their agreement with measured values is often found to be quite close for dipole polarisabilities, but extremely poor for quadrupole polarisabilities. This is undoubtedly a result of core penetration effects, which tend to mimic the n dependence of the quadrupole polarisation energy.

For highly charged ions, the polarisation energy grows with increasing ionicity, but not as rapidly as does the ionisation energy. The effective dipole and quadrupole polarisabilities are smoothly varying isoelectronically, and can readily be interpolated or extrapolated through charge scaling. In this manner, values have been obtained

for the ionisation potentials of the entire Na (11 electron) and Cu (29 electron) sequences, and for the corresponding polarisabilities for the Ne (10 electron) and Ni (28 electron) sequences.

8. Lifetimes of excited levels

8.1. INTRODUCTORY REMARKS

Excited states in atoms and ions decay spontaneously, with a characteristic transition probability A_{if} and lifetime τ_i . In the electric dipole (E1) approximation the following relation is valid:

$$\tau_i^{-1} = A_{if} = \frac{4\omega^3}{3\hbar c^3} |\langle \phi_i | e\mathbf{r} | \phi_f \rangle|^2. \quad (5)$$

The energy of the transition is $\hbar\omega$, ϕ_i and ϕ_f are the wavefunctions of the states and $e\mathbf{r}$ is the dipole operator. This is the standard quantum mechanical expression for the probability of the transition. The rate of emission of energy is just this multiplied by $\hbar\omega$. This leads to an ω^4 dependence, which is entirely analogous to the power emitted by a classical electric dipole. (Similar expressions can also be derived for forbidden decays). A convenient unit is the oscillator strength or f -value, numerically related to A_{if} as follows

$$f = 1.499 \times 10^{-16} \lambda^2 A_{if} \frac{g_i}{g_f}. \quad (6)$$

Here λ is the wavelength (in Å units) and g_i and g_f the statistical weights of the levels. The unit for A_{if} is s^{-1} whereas the f -value is dimensionless. Experimental values for τ_i , A_{if} or f constitute valuable checks of quantum mechanical calculations of atomic structure. Such data are also needed for the diagnostics of astrophysical and laboratory plasmas, in particular when determining absolute and relative abundances of various chemical elements present in these plasmas.

In neutral and lightly ionised atoms, many techniques are available for measurement of τ_i and A_{if} . The methods include delayed coincidence, using electron or photon beam excitation, modulated beam phase shift measurements, Hanle effect, beam-laser excitation and beam-foil excitation, see Imhof and Read (1977). However, most of these methods cannot be applied to highly ionised atoms. Here only the beam-foil method generally can be used. In this technique the speed of the ions v (which usually can be determined to within $\pm 1\%$) provides a time-resolved source, and the emitted intensity of individual spectral lines is measured as a function of time t after excitation. In practice this is achieved by detecting photons at a variable distance $x = vt$, downstream from the foil. In the

'ideal' case, i.e. where there is no cascading from higher levels (see below) and possible quantum beats due to the excitation coherence are absent, the lifetime, τ_i is then obtained from the simple relation

$$I(x) = I(0) \exp\left(-\frac{x}{v\tau_i}\right), \quad (7)$$

where $I(0)$ and $I(x)$ are the counting rates (intensities) at the foil and at a distance x .

Foil excitation of a fast ion beam provides access to nearly any ionisation stage of any atom, although not all excited states within a given ion are amenable to lifetime determinations. The high-density excitation conditions in the foil cause a large fraction of the beam particles to be excited and produce copious multiple electron excitation, but also lead to nonselective excitation and associated problems with cascading and blending. In such cases the simple equation (7) has to be replaced by a sum of exponentials, and their decomposition may involve difficult numerical problems and often result in systematic errors. However, these difficulties have now largely been eliminated (Curtis 1976) and many high-quality measurements have been reported in recent years. Such work has benefitted from the good wavelength resolution (typically 0.05 Å in the region 500–2000 Å) and excellent time resolution (10^{-11} s or even better), nowadays available. Other advantages include the low-density conditions in the source which practically eliminate radiation trapping or collisional effects and Stark quenching of high n , l states. Even metastable states have time to decay spontaneously. The method has been reviewed by many authors, see e.g. Berry (1977), Martinson (1985), and only a few recent examples will be mentioned here.

8.2. ALLOWED INTRASHELL RESONANCE TRANSITIONS

Lifetimes of the $np \rightarrow ns$ resonance transitions in alkali-like isoelectronic sequences provide a challenging confrontation between theory and experiment. Although these systems consist basically of a single electron outside a closed shell, the intrashell nature of these transitions produces both theoretical and experimental subtleties. The relative positions of the levels have a strong isoelectronic variation, as shown, for example, in figure 7, and this causes lifetimes and even initial populations of the individual levels to have a similarly strong Z -dependence. The magnitudes of effects such as core polarisation and other types of electron correlation, spin-orbit coupling and additional relativistic interactions also vary with Z , and all this means that the relative advantages of the Breit-Pauli approximation and fully relativistic treatments (as discussed in section 5.1) can vary with the

degree of ionicity. The experimentally determined decay curves for alkali-like ions that have been ionised several times exhibit strong cascading effects, and lifetime determinations by simple, multiexponential fitting procedures are known to be unreliable for these systems. Recently, more rigorous experimental procedures have been reported for highly ionised Na-like ions, up to Ni XVIII (Hutton *et al.* 1988b), and the data are in excellent agreement with recent theoretical results (Theodosiou and Curtis 1988).

In comparing theory and experiment it is often instructive to study how the f -value for a given transition varies with Z in an isoelectronic sequence. In the 'normal' case this variation should be smooth, but level perturbations may result in more irregular trends. An example of a smooth variation, for the $2s2p\ ^1P \rightarrow 2s^2\ ^1S$ transition in Be-like ions is shown in figure 8. Beam-foil results are here available for many ions, up to Be-like Fe XXIII (Reistad and Martinson 1986, Träbert 1988), and they agree well with modern theoretical data. Among the latter, the results of Sims and Whitten (1973) are particularly important, because they also include rigorous error limits to the theoretical f -values (see figure 8). Some of the early beam-foil work yielded data that fell below the theoretical lower limit, but this has been explained as the result of insufficient cascade corrections. In the future it would be worthwhile to extend experimental studies to values of Z higher than 30, to test MCDF theories which

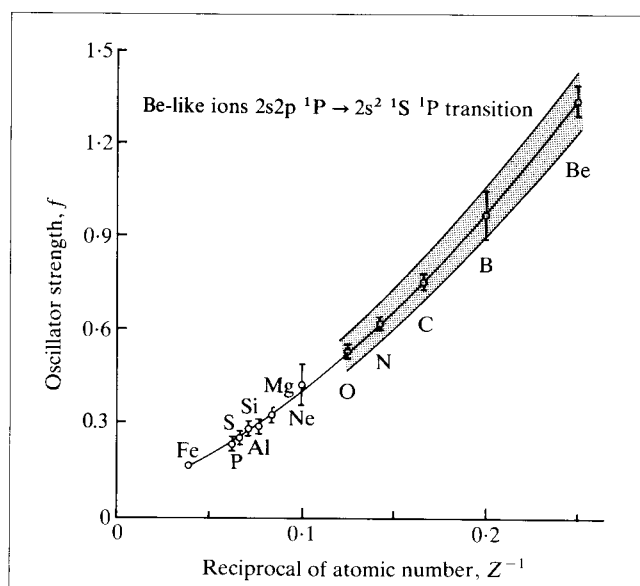


Figure 8. Oscillator strengths of the $2s2p\ ^1P \rightarrow 2s^2\ ^1S$ resonance transition in Be-like ions, from Be I to Fe XXIII. All data are from beam-foil experiments (for references, see Reistad and Martinson 1986, Träbert 1988). The shaded area shows the theoretically derived rigorous upper and lower bounds, (after Sims and Whitten 1973).

predict an increase of the f -value in the relativistic regime.

8.3. FORBIDDEN TRANSITIONS

Many authors have also carried out lifetime measurements for levels that decay by forbidden processes, in particular for He-like ions (see figure 2). Because of the strong Z -dependence, such transitions are conveniently measurable using heavy-ion accelerators of high energy (Marrus and Mohr 1978). Recently, a number of new, interesting experimental results have been obtained in these ions.

Conservation of angular momentum strictly forbids single photon transitions between two levels that both have zero total angular momentum. Two interesting examples of states which are inhibited by this $J = 0$ to $J = 0$ selection rule involve the $1s2s\ ^1S_0$ and $1s2p\ ^3P_0$ levels in highly ionised members of the helium isoelectronic sequence (see figure 2). These systems have recently been studied both theoretically and experimentally.

In the case of the $1s2p\ ^3P_0$ state the principal decay channel is to $1s2s\ ^3S_1$. However, when the nuclear spin I is nonzero, the coupling of I and J can make the transition from $1s2p\ ^3P_0$ to $1s^2\ ^1S_0$ possible, and this additional decay mode shortens the $1s2p\ ^3P_0$ lifetime, a process known as 'hyperfine quenching'. Since the dominant stable isotopes of the various elements tend to have $I = 0$ for even Z and $I > 0$ for odd Z , hyperfine quenchings shorten the 3P_0 lifetimes with a peculiar sawtooth isoelectronic pattern. In addition, the effect tends to become very pronounced for $Z > 21$, where nuclear dipole effects become substantial. Calculations have been made of these effects (Mohr 1976), and these results have been confirmed in several beam-foil experiments, (for references, see Marrus and Mohr 1978, Martinson 1985).

The $1s2s\ ^1S_0$ levels decays to the $1s^2\ ^1S_0$ ground state by the simultaneous emission of two photons (2E1) which have a continuous energy distribution. Calculations of the probability of this two-photon decay (Drake 1986) indicate that it is quite sensitive to relativistic corrections. Measurements for He-like Kr^{35+} (Marrus *et al.* 1986) and Ni^{26+} (Dunford *et al.* 1988) are in reasonable agreement with theory, but higher experimental accuracy is needed for more stringent tests. In a recent measurement of Ni^{26+} (Dunford *et al.* 1989) the two photons were detected in coincidence which eliminated a number of uncertainties present in single-photon measurements.

As a final example, figure 9 shows a decay measurement for the $1s2s\ ^3S_1 \rightarrow 1s^2\ ^1S_0$ transition in He-like U^{90+} (Munger and Gould 1986). From this experiment information was obtained about the $n = 2$ Lamb shift, i.e.

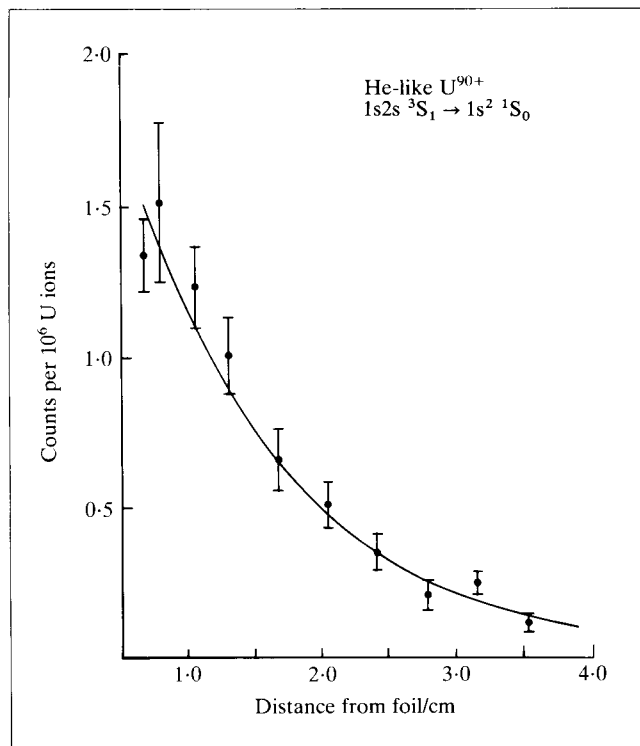


Figure 9. Decay curve of the $1s^2\ ^1S_0 \rightarrow 1s2s\ ^3S_1$ transition in He-like U^{90+} (Munger and Gould 1986). The plot is linear and each point was normalized to 10^6 U ions. From this measurement a value of the $n = 2$ Lamb shift in H-like U^{91+} was deduced.

the energy difference between the $2s\ ^2S_{1/2}$ and $2p\ ^2P_{1/2}$ levels in H-like U^{91+} . This result demonstrates that statements such as 'electronic transitions in any ion between H and U can now be experimentally studied' are no longer utopian.

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Further reading

Several of the references mentioned in the text are review articles, containing much information about highly ionised atoms. For authoritative treatments of various problems we would also recommend the following articles and monographs:

Brown, R., and Lang, J. (editors), 1988, *Astrophysical and Laboratory Spectroscopy* (Edinburgh: Scottish Universities School in Physics). Contains reviews of atomic structure and collisions, astrophysical observations, laboratory plasmas and various experimental methods.

Series, G. W. (editor), 1988, *The Spectrum of Atomic Hydrogen—Advances* (Singapore: World Scientific).

Deals not only with neutral hydrogen but also with highly ionised one-electron systems, with reviews of e.g. experimental techniques and theoretical and experimental studies of QED effects.

Cowan, R. D., 1981, *The Theory of Atomic Structure and Spectra*, (Berkeley: University of California Press).

An extensive survey of theoretical methods used in atomic spectroscopy and discussions of experimental problems.

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A review of contemporary experimental and theoretical methods, with emphasis on very high charge states.

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A compact review of experimental and theoretical studies with discussions also of plasma effects and the influence of strong magnetic fields.

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Professor L. J. Curtis carried out undergraduate studies at the University of Toledo and graduate studies at the University of Michigan, completing his PhD work in 1963. He is presently Professor of Physics and Astronomy at the University of Toledo, and has held visiting scientist positions at the Woods Hole Oceanographic Institution, the Research Institute for Physics in Stockholm, the University of Lyon, Princeton University, the Free University of Berlin, the University of Arizona, Aarhus University, Argonne National Laboratory, Brookhaven National Laboratory, and has held the position of Docent at the University of Lund. His research has centred on atomic spectroscopy and transition probability determination using fast ion beam, pulsed electron beam delayed coincidence, and modulated electron beam phase shift methods.

Professor I. Martinson did his graduate work at the Research Institute for Physics, Stockholm, and received his Fil. dr. degree in 1971. From 1968 to 1970 he was a research associate at the University of Arizona, and between 1970 and 1975 a research scientist at the Research Institute for Physics. Since 1975 he is Professor of Atomic Physics at the University of Lund. He has held the position of visiting professor at the University of Toledo. His work is in atomic structures and accelerator-based atomic physics, with applications to problems in astrophysics and fusion research.