Current trends in atomic spectroscopy

Using modern experimental and theoretical techniques, an old field has come alive, motivated by applications in a wide variety of areas, ranging from measurement in fundamental physics to elemental analysis in astrophysics.

James J. Wynne

The last three decades have seen a renaissance in atomic spectroscopy. After many years of important advances in pursuit of its own intellectual goals, the field began a major expansion in the 1950s as urgent demands for spectral data came from industry, the atomic-energy program, the space program and the defense department. Today, atomic spectroscopy is a modern, active and basic science. Atomic spectroscopists study the effects of collisions, electric and magnetic fields, photoionization, and other interactions between atoms and their environment in ways that would have been impossible or forbiddingly complex just a few years ago. They routinely use such experimental tools as lasers, synchrotron light sources, electron spectrometers, ion traps and fast ion beams (figure 1). They use such theoretical tools such as quantum-defect theory, many-body perturbation theory and group theory to study the structure of isolated atoms in greater detail and with greater precision than ever before. An important result of this new work is that atomic spectroscopy has increased its impact on diverse areas of physics as well as on its traditional area of contribution—the study of the electronic structure of atoms.

Atomic spectroscopy is a field with a long and successful history. At the end of the 19th century, Johann Balmer and Johannes Rydberg discovered key regularities and systematics in atomic spectra, which led to Niels Bohr's quantum theory of the hydrogen atom. The 1920s were a golden age for atomic spectroscopy, with the emergence of quantum mechanics and the development of a quantum-mechanical model of atomic structure. By 1935, physicists had established a basic foundation[1] for the theory of atomic spectra, and many turned their attention to the newly emerging problems of nuclear physics and electronics. During the next several decades, although atomic spectroscopy seemed to be in partial eclipse, a small group of workers analyzed the complex spectra of open-shell atoms and developed new theoretical procedures for their interpretation. The renaissance that began in the 1950s really gained momentum around 1960, triggered by the development of new light sources, new detection methods and, more subtly, new theoretical methods.

In this article, I will reflect upon the current status as well as the future of atomic spectroscopy, covering both the work that constitutes the field and how it is applied to other fields. Let us begin with a definition.

Atomic spectroscopy is the study of atoms and ions through their interaction with electromagnetic radiation, in particular, interactions in which the radiation is absorbed or emitted with an internal rearrangement of the atom's electrons. Spectroscopists pay particular attention to the dependence of these processes on the frequency (or, equivalently, wavelength) of the radiation. With this definition, we may look at current research to see if it *is* atomic spectroscopy.

At the heart of atomic spectroscopy are the systematics, which are particularly important to the organization and interpretation of the data that are produced. The beauty of atomic spectroscopy is that quantum mechanics not only established the systematics of the energy-level structure of a single electron moving in a Coulomb potential, but provided a framework for systematic investigation of the many-electron atom. It is this many-electron atom and its exquisite mysteries that continue to draw scientists to atomic spectroscopy.

We may classify the methods of atomic spectroscopy under the broad categories of theoretical and experimental techniques. Research in atomic spectroscopy produces primary data, such as the positions, widths and strengths of spectral lines, and structural information derived from these data, such as atomic energy levels and ionization limits. When these findings are organized into data banks containing refined, evaluated information, they provide a base of knowledge upon which we may build new understanding. The data, together with systematics and theoretical and experimental techniques, constitute the central core of atomic spectroscopy. It is a core that continues to develop through the refinement of standard techniques. An equally important source of progress, however, is the development of new approaches prompted by expansion into new areas of research and by applications to other fields.

The techniques of atomic spectroscopy have long been recognized as useful to other areas of scientific and technological investigation. In many instances, atomic spectroscopy has been the proving ground where techniques were tested and refined before being applied to other fields. Similarly, atomic spectroscopic data have provided the information base for investigations in other fields. As the table at the left on page 56 indicates, atomic spectroscopy has applications to many areas of importance to society. These applications in turn contribute much to the vitality of the field.

Wide-ranging impact

Advances in atomic spectroscopy contribute significantly to progress in other fields of science, areas of modern technology, and society in general. In the following paragraphs, I discuss a few highlights of the vast number of applications of atomic spectroscopy, and I try to indicate the many fertile areas that are sure to bear fruit in the next few years. I begin with a look at applications in fundamental physics.

Atomic spectroscopists provided the first experimental challenges to the classical understanding of particle dynamics, and thus helped usher in today's quantum era. Progressively more precise experiments on atomic fine structure led to the development of relativistic quantum theory, the discovery of particle spins, the discovery of the electron's anomalous magnetic moment and the Lamb shift, and the

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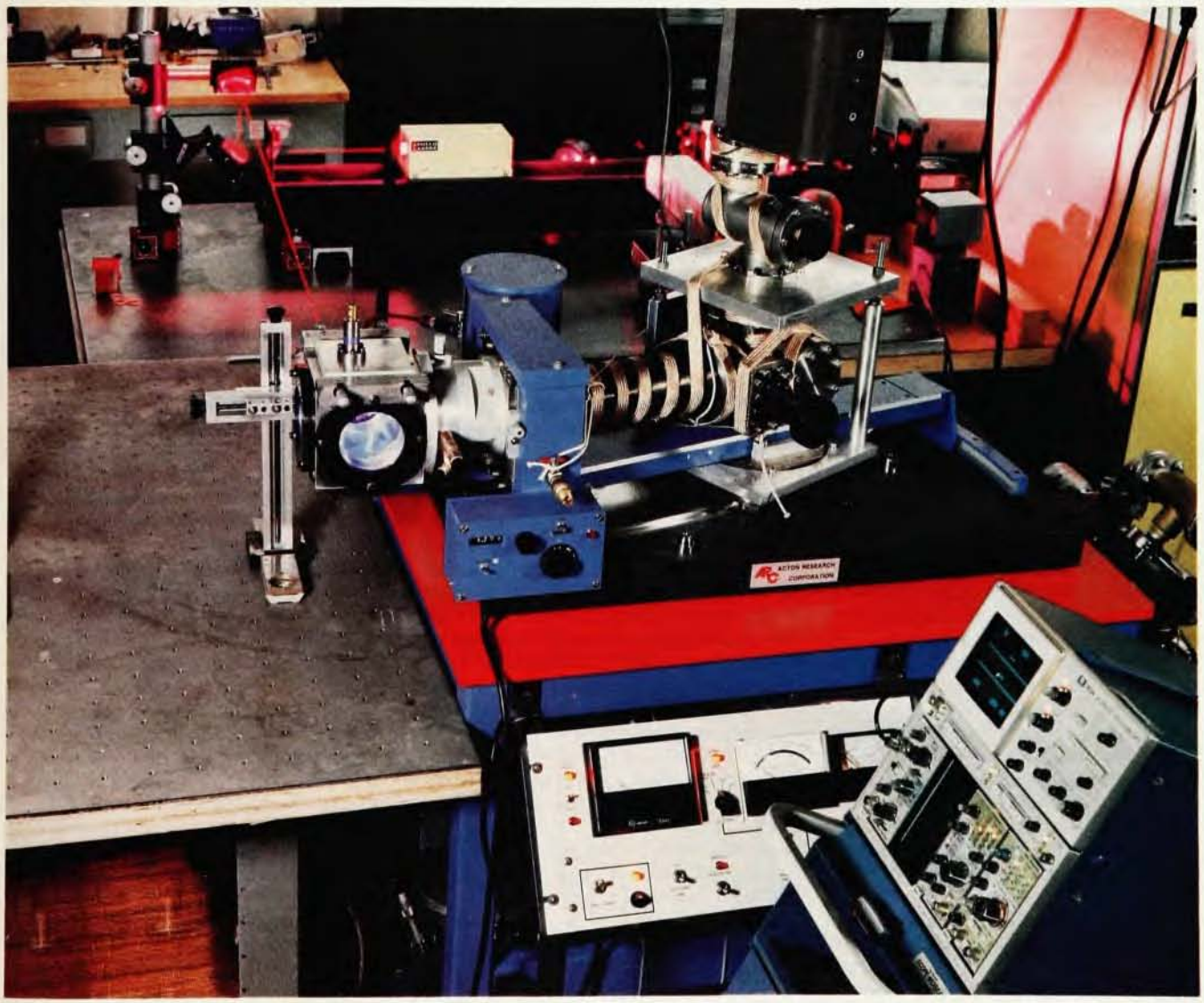
development of modern quantum electrodynamics. Soon, the generally comfortable agreement between fundamental atomic experiment and theory is likely to be disturbed once again by striking advances in the traditional testing grounds of atomic spectra, namely two- and three-particle atoms. One example is the long-awaited observation of the 1s–2s positronium transition.[2] This experiment has the potential for a thousand-fold improvement in measuring the Lamb shift in a *purely leptonic system*, a system free from the theoretically troubling effects of nuclear size. Precise laser spectroscopy of this and other exotic atoms, such as the muonium systems, will likely provide some of the most rigorous tests of QED.

To carry out many of these fundamental measurements will require further improvements in instrumental resolution. The theoretical limiting linewidths of lasers are in the millihertz range. Several laboratories are making rapid progress in stabilization, noise reduction and calibration, and linewidths of a few hertz, stable over many seconds, have been observed. The chief causes of line broadening are collisions, perturbations in external fields, Doppler shifts, transit-time effects and recoil due to photon momentum. As an example of successful reduction of these effects, experimenters are now able to isolate a single ion in a trap, let it cool radiatively, and store it for hours at a kinetic temperature of a few millikelvin.[3]

Generating coherent light. The discovery of the earliest lasers would have been difficult, if not impossible, without the detailed knowledge of energy levels, oscillator strengths and other basic parameters derived from atomic, molecular and solid-state spectra. The first laser, operating with a ruby crystal, is a prime example. Because chromium ions retain their atomic characteristics when imbedded in solid matrices such as sapphire (Al_2O_3), knowledge of chromium-ion spectra was essential in formulating the laser model. The discovery of the first gas laser—the helium–neon laser—was also made possible by the availability of relevant atomic spectroscopic data. The development of coherent sources at wavelengths not currently available—in the infrared, the ultraviolet, the vacuum ultraviolet and even shorter wavelengths—can benefit significantly from an increased data base of atomic spectroscopic information.

Surfaces and microelectronics. Investigators are just beginning to apply the

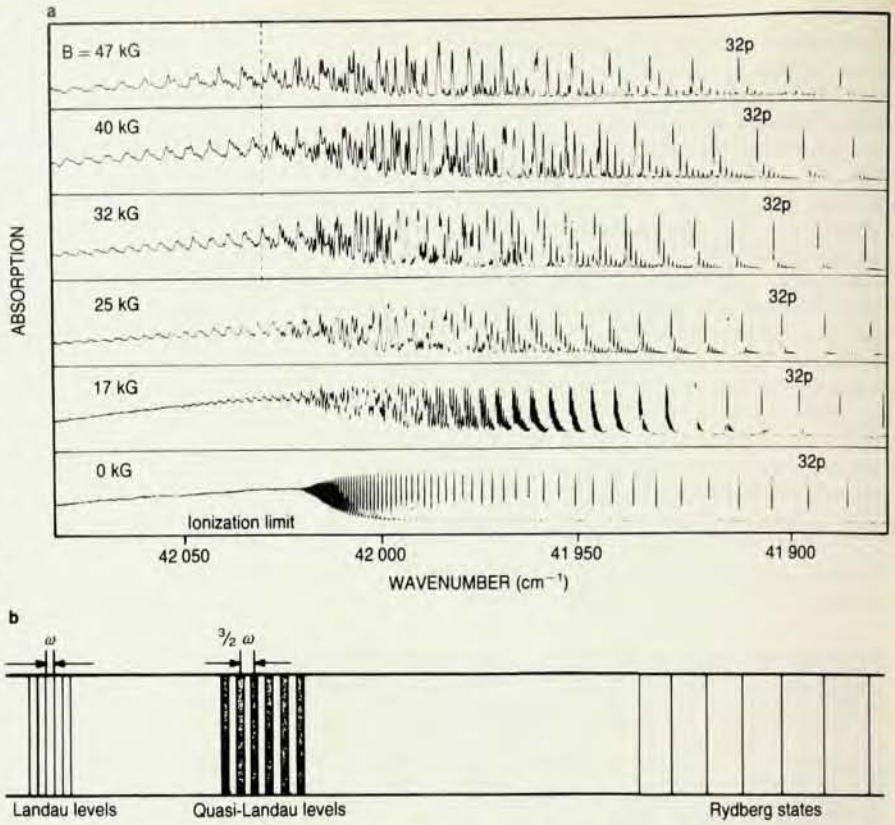


Modern vacuum-ultraviolet spectrometer. A beam from a high-power ruby laser (top) strikes a target, generating a pulse of broadband vacuum-ultraviolet radiation from the laser-produced plasma. After passing through a sample (not shown), this radiation enters a grazing-incidence spectrometer of 1.5-meter focal length (the blue object in the middle of the photo). The dispersed light is directed to a diode array sensitive to vacuum-ultraviolet radiation. The array is connected to an optical multichannel analyzer (the vertical assembly to the right of the blue object). (Photograph courtesy of National Bureau of Standards.) Figure 1

techniques of atomic spectroscopy to research in surface science and microelectronics. (See the article by Joe Demuth and Phaedon Avouris on page 62.) New and exciting studies in surface science feature the spectroscopic investigation of atoms in positions adjacent to surfaces. Similar spectroscopic investigations are revealing much about the dry processing techniques used extensively to make microelectronic circuits. This parallel development is appropriate, because one of the chief motivations for studying surfaces is that microelectronic technology depends on the interaction between solid surfaces and gases. Microelectronics chips are fabricated by a series of dry processing steps such as etching, oxidation, doping and deposition, all of which involve the interaction of solid surfaces with gases, plasmas or beams of atomic ions. Highly sensitive state- and species-selective laser spectroscopic methods such as induced fluorescence, absorption and ionization yield valuable information about these processes.

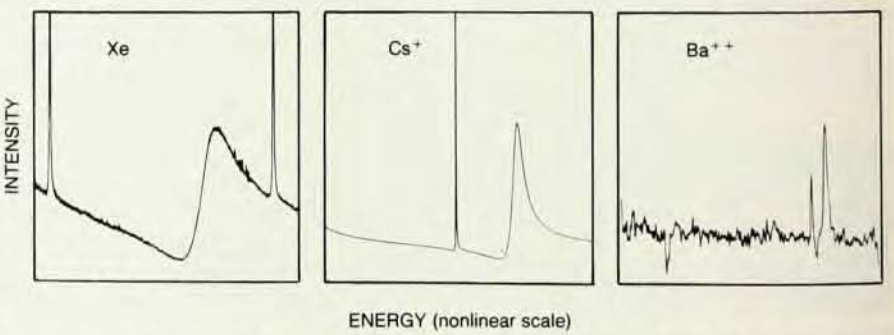
Isotope enrichment. Sequential, multiple-photon excitation experiments are able to ionize and detect *a single atom* selectively in the midst of more than an atmosphere's pressure of other atoms and molecules. An increase in our knowledge of multiphoton ionization cross sections of atoms will lead to significant improvement in the efficiency of schemes for isotope enrichment and resonance-ionization mass spectrometry. The importance of laser isotope separation for uranium and plutonium is self-evident.

Nuclear physics. Atomic spectroscopy has been an important tool for the investigation of nuclear structure since the earliest days of nuclear physics. For example, data on nuclear spins and moments from atomic-beam magnetic-resonance experiments, and knowledge of optical hyperfine structure, helped to establish the nuclear shell model. Tunable lasers have greatly increased the ability of atomic spectroscopy to contribute to studies of nuclear structure. One can orient very-short-lived nuclei by pumping the appropriate atom or ion with a laser, and one can detect the resulting orientation by anisotropies in the nuclear decay radiation. (See the article by Fay Ajzenberg-Selove and Ernest K. Warburton on page 26.) It is possible to produce very intense sources of polarized deuterons and tritons by laser pumping of appropriate atoms, and this technique is being considered for enhancing fusion rates in tokamaks and other magnetic-confinement devices. Similar optical pumping methods are being developed to produce dense targets of polarized nuclei. Nuclear physicists searching for weak intranuclear interactions that violate fundamental conservation laws such as parity, time reversal or charge conjugation, are using spin-polarized nuclei produced by some of these spectroscopic techniques.



Spectra revealing electron energy levels in combined Coulomb and magnetic fields. **a**: Absorption spectra of neutral barium, showing a Rydberg series at various magnetic field strengths B. The equally-spaced resonances around the ionization limit are quasi-Landau levels. **b**: Schematic rendering of the 25 kG spectrum. The Rydberg levels are at lower energies, where the Coulomb field dominates. The Landau levels, with spacing equal to the cyclotron frequency ω, occur at much higher energies, where the magnetic field dominates. For the quasi-Landau levels, neither field dominates.[4] Figure 2

Astrophysics rests on the interpretation of radiation reaching Earth, and most of our knowledge of the elemental composition, ionization state, temperature and density of the atmospheres of stars and of interstellar matter comes from detailed application of information derived from atomic spectroscopy. Rapid advances in the sensitivity, resolution and wavelength range of astronomical observation demand more extensive and more precise spectroscopic data. There is a continuing need for data on a very large number of transition frequencies and oscillator strengths for analysis of spectra of the Sun and all but the hottest stars. Such analyses of elemental abundances form the basis of a key part of our understanding of the evolution of the universe—the creation, out of hydrogen, of all the other elements. Extension of



Isoelectronic sequence. These are photoabsorption spectra made in the autoionization continuum. The energy scales have been normalized for this comparsion. The narrowing of the broad peak as one moves from xenon to barium marks a redistribution of oscillator strength. (From reference 5.) Figure 3

astronomical observations into the infrared, ultraviolet and x-ray regions of the spectrum has placed new demands on atomic spectroscopists. This trend is sure to continue with the launch of the Space Telescope and other satellites.

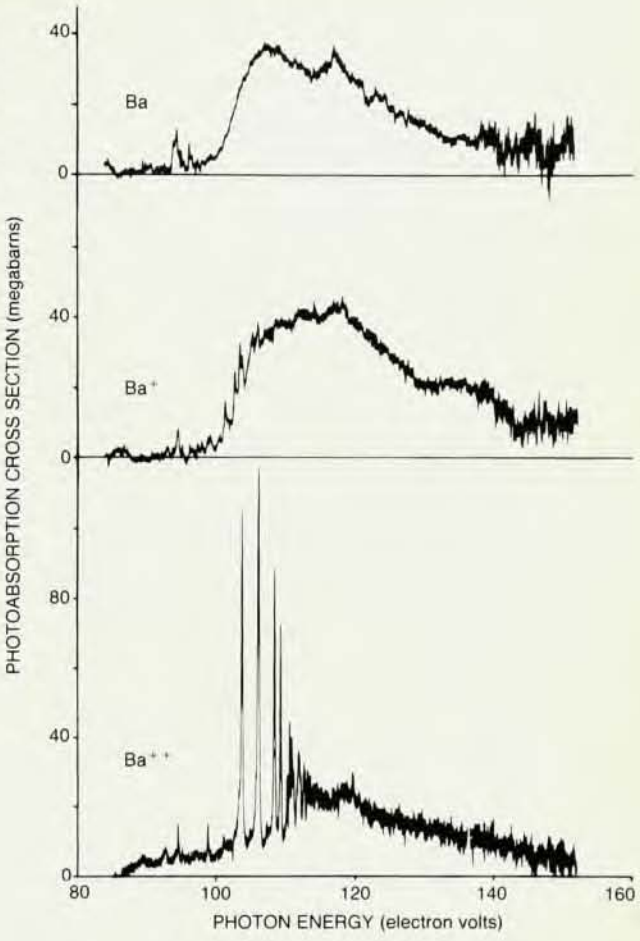
I have highlighted above some of the areas for which data from atomic spectroscopy are useful. The table at the right on page 56 summarizes the kinds of spectroscopic data needed in particular areas of applied science, and the table at the left summarizes what is needed in broader areas of society. In some cases, the needed data already exist but are hidden in the literature. In other cases, additional measurements are required. The need for better and more complete compilations is obvious. As the interesting applications change and as the needs of society evolve, so too do the requirements for data from atomic spectroscopy.

Systematics

Systematics—Nature's regular patterns of behavior—have repeatedly yielded vital new knowledge of physical laws. Rydberg's formula for atomic spectral series started physicists on the road to quantum theory, and further studies of systematics led to discoveries of the Pauli exclusion principle and electron spin, just to name two well-known examples. Additionally, the independent-particle model of atoms, indeed of all macroscopic matter, and atomic systematics are closely intertwined. However, modern study of atomic systematics has repeatedly demonstrated that the standard independent-particle model must be augmented by new concepts, reformulated in terms appropriate to new spectral regions, or, in many instances, abandoned altogether. The search for new conceptual frameworks within which to fit data of ever-increasing precision in ever-wider spectral regions forms the key intellectual challenge of atomic spectroscopy in general, and atomic systematics in particular. This search is greatly aided by the probing of regularities and, perhaps even more importantly, the conspicuous *ir*regularities of atomic spectral distributions.

With the help of novel experimental techniques, one can now select atomic species and atomic states to control the relative strengths of different interactions and thus focus on features that need to be incorporated into the conceptual framework. The charge of the nucleus, the number of its neutrons, and the valence shell structure of the atom are parameters that one can select and vary over a wide range of ionic or atomic species so as to exhibit the evolution of spectral properties as these quantities are progressively modified. The following examples illustrate some systematic studies.

Isonuclear sequence. Plotted are cross sections for the photoexcitation of a 4d electron in various barium species. The striking difference in the Ba^{++} spectrum indicates a partial contraction of the 4f orbital in the absence of barium's two outer electrons. (From reference 6.) Figure 4



We can study the interaction of the electron and the atomic core, and the effects of external fields and collisions, with unprecedented levels of precision by preparing and manipulating a wide variety of weakly bound species, including negative ions and atoms in high Rydberg levels. Rydberg atoms have an outer electron that is only weakly bound to the positive core (consisting of the atomic nucleus and the inner electrons). In this respect, we can consider Rydberg atoms as systems in which a low-energy electron is scattered off the core, allowing us to extract very valuable information about the properties of the core.

A newly developed possibility for Rydberg atoms is to vary their size almost continuously by exciting the outer electron closer and closer to the ionization limit. With laser and atomic-beam techniques, studies are currently underway on excited states whose orbitals are as large as a fraction of a micron (a biological size!) and whose binding energies are sub-thermal. Spectroscopic properties related to atomic size and binding energy are quantitatively very different for quantum states in this region than for states that lie much lower. For example, the interaction between relatively small electric or magnetic fields and the outer electron can become of the same order of magnitude or even larger than the $1/r$ Coulomb interaction between the ion core and the outer electron, leading to an extremely strong modification of the spectrum. Figure 2 shows the results of a study using an external magnetic field. Here we see the Rydberg spectrum evolve into a Landau-like spectrum (characterized by resonances of approximately equal spacing, that spacing being proportional to the magnetic field) as the electron energy increases continuously past the ionization level. The theory of this effect is still incomplete, and the basic problem of a hydrogen atom in the presence of a magnetic field of arbitrary strength is still not solved in its full generality.[4]

The comparison of spectra along several types of sequences has proved fruitful for systematic studies. Important sequences are

- Isoelectronic sequences, in which successive ionic species have the same number of electrons. One example is the series H^-, He, Li^+ and so on.
- Isonuclear sequences, in which species have identical nuclei but different numbers of external electrons. An example is the series Li, Li^+, Li^{++}.
- Homologous sequences, in which atomic species have the same number of valence electrons. The alkali metals,

Table 1. Data needs of areas of society

Data needed	Physical sciences	Industry	National defense	Environmental studies	Energy sources and utilization	Biomedicine	Metrology and fundamental constants	New sources of light
Line positions	■	■	■	■	■	■	■	■
Line strengths	■	■	■	■	■	■	■	■
Line shapes	■	■	■	■	■	■	■	■
Energy levels	■	■	■	■	■	■	■	■
Lifetimes	■	■	■		■		■	■
Ionization limits	■	■	■	■	■	■		■
Photoionization cross sections	■	■	■	■	■	■		■
Multiphoton cross sections	■	■	■	■	■		■	■
Recombination rates	■	■	■		■			■
Isotope shifts	■	■	■	■	■	■	■	■
Hyperfine splittings	■	■	■		■		■	■
External field effects	■	■	■		■	■	■	■
Collisional properties	■	■	■		■			■

Table 2. Data needs of various fields

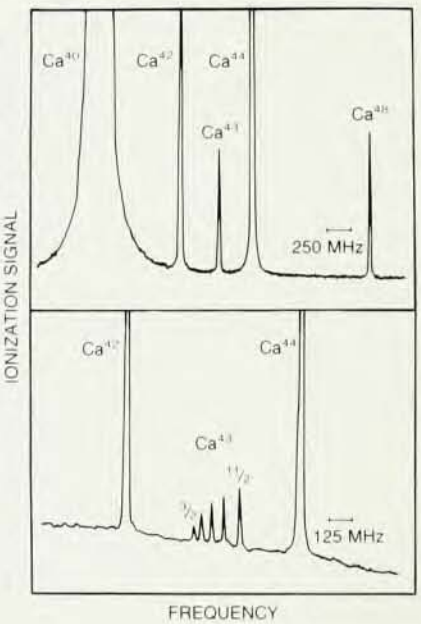
Data needed	Fundamental physics	Coherent light generation	Surface science	Microelectronics technology	Laser isotope separation	Atomic analysis	Solar and astrophysics	Plasma diagnostics	Nuclear physics	Solid-state physics
Line positions	■	■	■	■	■	■	■	■	■	■
Line strengths	■	■	■	■	■	■	■	■	■	■
Line shapes	■	■			■	■	■	■		■
Energy levels	■	■	■	■	■	■	■	■	■	■
Lifetimes	■	■	■	■	■	■	■	■		
Ionization limits	■	■	■	■	■	■	■	■	■	■
Photoionization cross sections	■	■	■	■	■	■	■	■		■
Multiphoton cross sections	■	■		■	■	■		■		
Recombination rates		■			■	■	■	■		
Isotope shifts	■	■			■	■	■	■	■	
Hyperfine splittings	■	■			■	■			■	
External field effects	■	■			■	■	■	■		■
Collisional properties		■	■	■	■	■	■	■		■

Li, Na, K and so on, are an example of such a sequence.

Comparison of photoabsorption from the ground states of members of the isoelectronic sequence Xe, Cs^+ and Ba^{++} reveals that the interaction of the excited electron with the atomic core changes dramatically along the sequence, as illustrated in figure 3 by the narrowing of an "autoionizing" resonance as one moves from Xe to Ba^{++}. Autoionization follows the excitation of two or more electrons, each having an excitation energy less than that required for ionization, but with a total excitation energy exceeding the ionization limit. The study of the sequence in figure 3 depended on the ability to prepare specific ionic species by laser-driven ionization, as well as on the development of theoretical methods capable of treating the observed spectra.[5]

Comparison of photoabsorption that excites a 4d electron in the isonuclear sequence Ba, Ba^+, Ba^{++} illustrates the expected similarity between Ba and Ba^+, but a striking difference in Ba^{++} (figure 4). Again, this observation is made possible by laser ionization of barium to produce selected ionic species. We can understand the observed redistribution in terms of the sudden contraction of the unoccupied 4f orbitals after the removal of barium's outer electrons.[6]

For the homologous sequence of noble gas atoms—Ne, Ar, Kr and Xe—the properties of complex Rydberg and autoionization spectra have been successfully characterized by multichannel quantum-defect theory, a method that treats the Rydberg spectra and the autoionizing continuum in a unified way.[7] The extension of such studies to the alkaline earth atoms (the beryllium group) reveals an interesting and general effect, namely the hybridization of singly- and doubly excited states, not only for low-lying states but also in the highly excited and continuum regions. The perspective gained from spectroscopic studies of excited states should lead to a better understanding of the chemical reactions of electronically excited atoms.



High-resolution excitation spectra of neutral calcium. The high resolution is made possible through the use of two-photon absorption from counterpropagating laser beams, which eliminates Doppler broadening. The upper trace shows transitions from the $4s^2\ ^1S_0$ ground state to the 4s10s $^1S_0$ excited stated for various isotopes of calcium. The lower shows well-resolved lines for different isotopes and hyperfine components, corresponding to transitions from the ground state to the 4s12d $^1D_2$ state. The hyperfine components are labeled by their total angular momentum, which ranges from $^3/_2$ to $^{11}/_2$. Only Ca^{43} has a nuclear spin, and its effect on the "$^1D_2$" state is explained as singlet–triplet mixing: The observed hyperfine structure corresponds to a small addition of triplet character to the singlet wavefunction. As a consequence, one can determine singlet–triplet mixing very precisely using the hyperfine structure as the probe. (Courtesy of Rene Beigang, Free University of Berlin.) Figure 5

Theoretical techniques

The continued refinement of standard theoretical techniques to give more accurate values for quantities of spectroscopic interest is a vital part of atomic spectroscopy. Equally important is the fact that the established techniques for working out atomic structure apply to other spectroscopies as well, whether it be for excitons, impurity states and two-dimensional systems in condensed-matter physics, or "charmonium" and other "quarkonium" states in particle physics. (See the article by Nathan Isgur and Gabriel Karl on page 36.) All these bound states are described in the same language, and their eigenvalues and wavefunctions are calculated in the same way as in atoms. The study of atomic

systems, where the basic interactions are well understood, yields insights into general properties of dynamical systems that are represented by nonseparable equations. Such systems are of much current interest elsewhere in physics, as in the study of chaos.

Even though the basic interactions are known, the long range of the Coulomb interaction leads to difficulties in theoretical calculations. First, a very large number of states is involved, particularly with increasing excitation, and correlations and interaction extend over large distances. Second, in a heavy atom, the outer electrons are often poorly described. This is particularly apparent when one asks detailed questions about the wavefunction, such as its behavior near the origin. These details of the wavefunction may contribute little to the energy, but knowledge of them is crucial for applications in nuclear and particle physics where one wants to calculate hyperfine structure and weak-interaction parity-violation effects. Thus, theoretical work is still challenging, with each application requiring new and specific theoretical developments. The following examples illustrate how new theoretical techniques in atomic spectroscopy arise to address questions generated by new experimental developments.

With increasingly higher excitations in many-electron atoms, the correlation between electrons—that is, the effect of the motion of one electron on that of all the others—has to be treated to increasing levels of significance. The general development of theory in atomic spectroscopy features a departure from the basic independent-particle picture of atomic electrons, in favor of a description that focuses on pairs or larger groups of electrons as the fundamental entity.

Near the ionization threshold, we can approach the problem with scattering or collision theory, where we treat not individual energy states but a whole group of them. With such an approach we can give a theoretical description of the extremely rich spectra both below and above ionization thresholds (there are an infinity of energy levels) using only a small number of parameters that characterize the non-Coulomb interactions. Such a treatment in the framework of the theory of electron–ion collisions is the basis of multichannel quantum-defect theory.[7]

With even higher excitations, particularly in the vicinity of doubly excited states, the correlations between electrons become entirely dominant, suggesting that the theory be recast in terms of pictures that focus on pairs of electrons at the outset. In one approach, the so-called "hyperspherical" coordinate method, an alternate choice

of coordinates provides for partial separation of the two-electron Schrödinger equation, and successfully accounts for the energies and widths of low-lying doubly excited states.[8]

Another approach to treating the many-electron atom starts with a group-theoretical description of the excited states of the one-electron atoms He^+ and H. Such states display the symmetry properties of the four-dimensional rotation group O(4). This symmetry approach has uncovered many regularities that are otherwise "hidden." Most important are progressions of increasing angular momentum and groupings of levels that are very similar to rotations and vibrations of a linear triatomic molecule. The O(4) symmetry ideas have thus forged a new link between coupled states of atoms in molecules, on the one hand, and strongly correlated electronic states in atoms, on the other hand.[9]

Spectroscopy with lasers introduces new methods and concepts. The narrow spectral width of the laser allows it to act on a few energy levels selectively, and these may be strongly modified by the high optical fields. The high intensities of lasers severely limit the applicability of perturbation approaches. The spectral distribution of spontaneous emission is modified, and optical pumping effects become an essential part of the phenomena. To describe these effects, one must add to the treatment of atomic levels the quantum states of the electromagnetic field and consider the coupled system of atom and electromagnetic field—the so-called "dressed atom."

Experimental techniques

Atomic spectroscopy originated in the measurement of the properties of spectral lines, and such basic measurements remain a strong necessity and an active part of the field. However, this area has evolved with the new experimental techniques made possible by new light sources, precise control of the atomic environment, novel methods of source preparation, state-of-the-art electronics, and computers. These techniques have allowed scientists to achieve higher precision in the determination of line positions, higher time resolution in the measurement of dynamic properties, and higher sensitivity to small numbers of atoms or photons. Moreover, the application of such new methods continues to lead to discoveries of qualitatively new physical processes.

The availability of tunable, coherent radiation from lasers has given rise to an exciting range of new techniques for measurements with high resolution, high precision and high sensitivity.[10] Two-photon absorption with counterpropagating beams, and methods using saturation of inhomogeneously broadened lines (saturation spectroscopy), remove Doppler broadening, as figure 5 shows. The observation of polarization changes in transmitted beams (polarization spectroscopy), and the observation of intensity modulation when one sideband of a frequency-modulated beam is changed in intensity or phase (modulation spectroscopy), provide high sensitivity to absorption. The effect of radiation from lasers on the current in hollow-cathode discharges (opto-galvanic spectroscopy) provides high sensitivity to transitions from excited levels in atoms and ions of refractory materials.

Spectroscopy without lasers has advanced significantly because of improvements in techniques for data acquisition, and because of new sources of excited atoms and highly stripped ions. Both laser and non-laser techniques will profit from the availability of new detectors and from the development of efficient mirrors, gratings and other coated optics for the far-ultraviolet and soft-x-ray regions. In general, we can expect laser techniques to provide qualitatively new approaches to spectral studies, while conventional spectroscopy remains the major source of new data.

The dye laser has revolutionized spectroscopy in the entire region from the near infrared to the near ultraviolet by providing a source of tunable, spectrally narrow radiation of unprecedented brightness. The literature of the past decade abounds with novel spectroscopic studies made possible by dye lasers. Frequency-doubling techniques routinely provide coherent light up to wavenumbers of about 46 000 cm^{-1}. However, the lack of crystals suitable for frequency doubling into the vacuum ultraviolet has led scientists to explore other techniques. One method is based on coherent, nonlinear optical mixing of dye-laser radiation in a phase-matched atomic vapor. This method has achieved coverage from about 50 000 cm^{-1} to about 100 000 cm^{-1}. One obtains spectra by using this light as a bright source for absorption or photoionization studies.

The use of synchrotron storage rings and laser-generated plasmas as vuv light sources has opened up the study of transitions in atomic systems with excited core electrons and in systems that are multiply excited. In addition to giving us new information on the positions of energy levels, the combination of vuv excitation and electron-energy analysis allows us to distinguish the various paths of excitation. A recently introduced technique—selective laser excitation of atoms in a beam or a vapor, followed by the absorption of short wavelength radiation—has allowed exciting studies of the interaction between valence electrons and core electrons.[11]

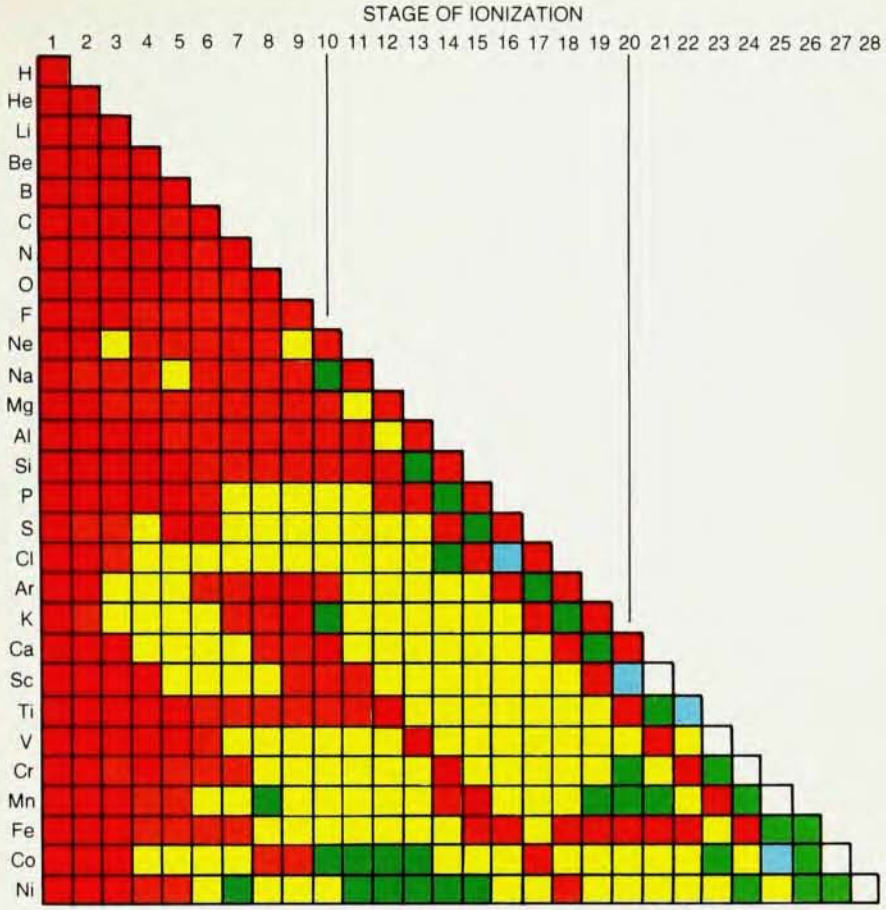
Light sources capable of producing atomic ions in extremely high stages of ionization have made it possible to observe spectra of ionization stages not previously seen in the lab. Low-inductance sparks, beam-foil excitation and pinched discharges are examples of such sources. A particularly desirable feature of these sources is their capability for preferentially exciting atoms to high stages of ionization to the relative exclusion of lower stages, thereby simplifying the interpretation of the spectra.

The advent of Fourier transform spectroscopy has revolutionized the observation of low stages of ionization, which was traditionally carried out with grating spectrometers. In this technique, one passes radiation from a steady source through a Michelson interferometer and measures the transmitted light while varying the path-length difference between the arms. State-of-the-art Fourier transform spectroscopy can record spectra between 200 cm^{-1} and 40 000 cm^{-1}.

While we know a great deal about line positions, only for a few simple atoms do we have accurate data on transition rates—lifetimes and line strengths. Measurements of relative strengths by techniques involving absorption and emission in neutral and singly ionized atoms have uncertainties ranging from a few percent, in a small number of cases, to 50% or worse. One accurate method of measuring atomic lifetimes is time-resolved fluorescence of atoms whose energy levels have been selectively populated. Recent measurements of the decay times of the lithium and sodium resonance transitions used a fast atomic beam excited by a crossed laser beam, and were accurate to a precision of 0.2%. These results represent at least an order of magnitude improvement in experimental precision over previous methods. Ion storage in traps[3] is the basis for a new and versatile technique for the direct, accurate measurement of the lifetimes of metastable and forbidden states of singly and multiply charged ions.

Compilations and tabulations

Data banks containing the best values of the measurable quantities of a field are an indispensable addition to the primary literature. In atomic spectroscopy, these data banks include refined and evaluated information on quantitites such as line positions, line strengths and energy levels. The entries either come from laboratory measurements or from various theoretical or empirical calculations. Evaluated data are important to the scientific community for a number of reasons, including the following:



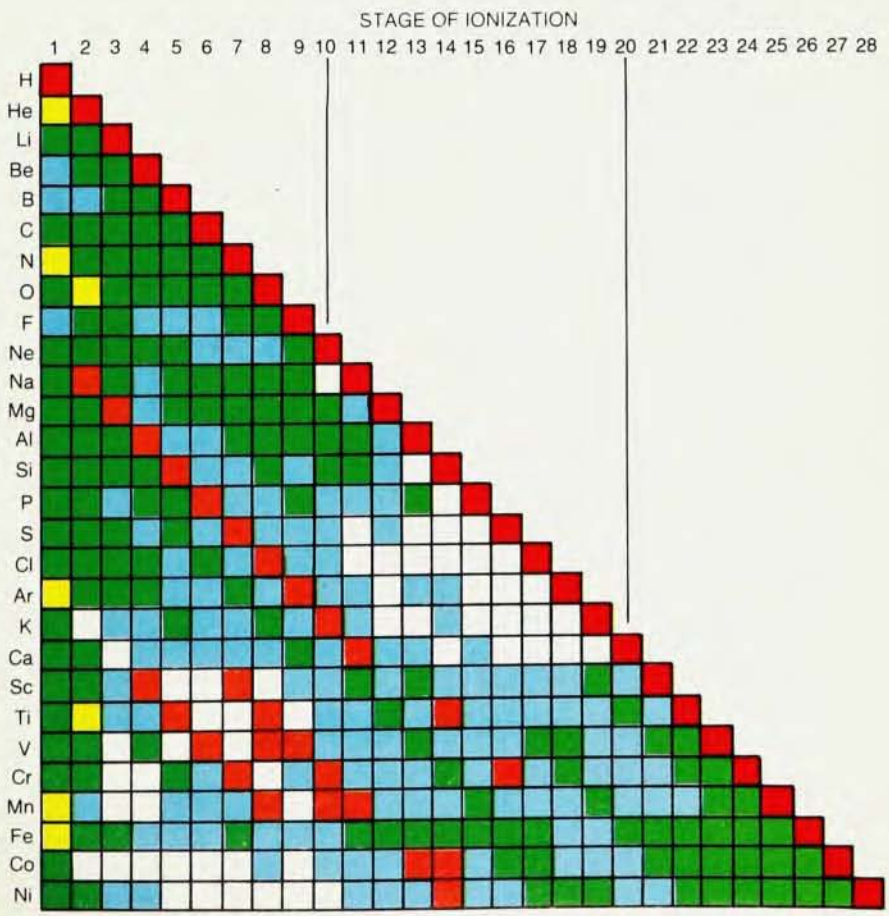
Status of analysis of atomic spectra. Colors indicate the state of our knowledge of the energy levels of various ions as follows. Red: analysis essentially complete—further progress would be difficult. Orange: all of the lowest configurations and portions of higher ones are known. Yellow: about two dozen levels are known. Green: for moderately complex spectra, about a dozen levels are known. Blue: fragmentary analysis—two to five energy levels are known. White: no analyzed data are available. Figure 6

- The process of compilation often reveals fundamental inconsistencies or conflicts in the data
- Applied spectroscopists require a rapid means for obtaining reference data
- The compilations are a pathway to the primary literature, which presents the experimental and computation work
- Theorists depend on reliable data with which to develop models and compare their predictions
- The compilations indicate the state of our knowledge.

Charlotte E. Moore's tables[12] of atomic energy levels are an outstanding example from the 1950s of spectroscopic compilation, and they have stimulated advances in every area touched upon by this article. In addition to showing the regularities and irregularities of the energy levels of atoms and ions, they reveal the incompleteness of each analysis and provide a jumping-off point for new research.

There are a number of compilations of critically evaluated data, and others are in progress or are planned for the near future.[13] The data that are incorporated into these compilations vary widely in number and quality for the various quantities tabulated. In some cases, the paucity of evaluated data is due to lack of research results in the primary literature. In other cases, it reflects the allocation of resources to the more rapid growth of the primary data base.

Figures 6 and 7 summarize the current status of evaluated data on atomic energy levels and transition probabilities for all stages of ionization of the elements hydrogen through nickel. In



Knowledge of oscillator strengths, from observation of line strengths or from calculation. Colors indicate the abundance of critically evaluated data. Red: hydrogenic spectra—strengths are calculated accurately from wavefunctions. Yellow: data of relatively high accuracy are reasonably abundant. Green: a fair number of data of relatively high accuracy, or a large number of data of moderate accuracy are available. Blue: a small number of high-accuracy data or a large number of low-accuracy data are available. Orange: data of low accuracy are available for a few transitions. White: no evaluated data are available. Figure 7

figure 6 we see that the classification and quantification of energy levels, as derived from the analysis of experimental spectra, are extensive, but are generally characterized by decreasing availability and accuracy with increasing atomic number or stage of ionization. The data on oscillator strengths (figure 7), which for ions beyond the second stage of ionization are derived primarily from theoretical calculations, are generally far less complete and less accurate than data on energy levels, with the exception of the hydrogenic spectra. Much work remains to be done.

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