Highly Excited Atoms

They are floppy, fragile and huge. Some of them have been found to have a diameter of almost a hundredth of a millimeter, which is 100,000 times the diameter of an atom in its lowest energy state

by Daniel Kleppner, Michael G. Littman and Myron L. Zimmerman

The emblem for the planetary model of the atom introduced in 1913 by Niels Bohr has become a symbol of our times. Since the 1930's, when the symbol was adopted by modernist sculptors and architects, the familiar pattern of electrons orbiting a nucleus has stood for scientific knowledge and progress. Perhaps the persistence of the ubiquitous symbol reflects its ancestry: Bohr's atomic theory imitates in part Newton's planetary theory, and the symbol could easily pass for an abstract plan of a solar system. Whatever the reason, the curious blend of traditional and modern ideas that underlies Bohr's theory has given it a remarkable vitality. The language and the spirit of Bohr's work have persisted in physical thought long after the model itself was commonly acknowledged (by Bohr among others) to have served its purpose.

Bohr's theory of the hydrogen atom had a scientifically useful life of a little more than a decade. The creation of quantum mechanics in the mid-1920's marked its demise. In the past few years, however, a new field of atomic physics has emerged from the no-man's-land between 19th-century classical physics and 20th-century quantum mechanics that was central to Bohr's early work. It is the physics of atoms in which an electron is excited to an exceptionally high energy level. Much of the appeal of the study of highly excited atoms comes from the clarity with which the atoms illustrate the continuity of thought between the world of classical physics and the world of quantum physics.

The highly excited atoms are often called Rydberg atoms, after the Swedish spectroscopist Johannes Rydberg. Any atom can be made into a Rydberg atom by promoting its outermost electron to a very high energy level. Rydberg atoms have a wealth of exotic properties. In the first place they are gigantic: Rydberg atoms have been detected whose diameter approaches a hundredth of a millimeter, which is 100,000 times the diameter of an atom in the ground state, or lowest energy level. The Rydberg atoms are so large that they can engulf other atoms. Rydberg atoms are also remarkably long-lived. An ordinary excited atom generally returns to the ground state in less than a ten-millionth of a second. On the time scale of atomic phenomena Rydberg atoms live almost forever; lifetimes from a thousandth of a second to a second are common. Ordinary atoms are scarcely affected by an applied electric field or magnetic field; Rydberg atoms can be strongly distorted and even pulled apart by a relatively weak electric field, and they can be squeezed into unexpected shapes by a magnetic field.

Powerful new experimental techniques for studying Rydberg atoms became available about six years ago, and laboratories in North America, Western Europe and the U.S.S.R. are now engaged in Rydberg-atom studies. At the Massachusetts Institute of Technology we have been particularly interested in the structure of Rydberg atoms in electric fields and magnetic fields. Our experiments have enabled us to witness dramatic atomic phenomena that had not been observed before. The experiments have also yielded some surprising new insights into the properties of simple atoms.

Rydberg atoms are like hydrogen in their essential properties. The similarity can be understood from the most elementary ideas of atomic structure. Every atom consists of a massive nucleus with an electric charge of $+Z$ (the total charge of Z protons, each having a charge of $+1$) surrounded by Z electrons, each having a charge of -1. Z is the atomic number of the atom. Hydrogen, for which Z is 1, consists of a single electron that is attracted to a nucleus composed of a single proton. If the outermost electron of an atom other than hydrogen is promoted to a very high energy level, it takes up a large orbit, well outside the orbit of all the other electrons. Hence the excited electron is attracted by a compact ionic core (made up of the nucleus and all the inner electrons) whose net charge is $+1$, the charge of a hydrogen nucleus. As long as the excited electron does not come too close to the core, the motion of the electron is the same as it would be in a hydrogen atom. Thus the physics of Rydberg atoms is essentially the physics of hydrogen.

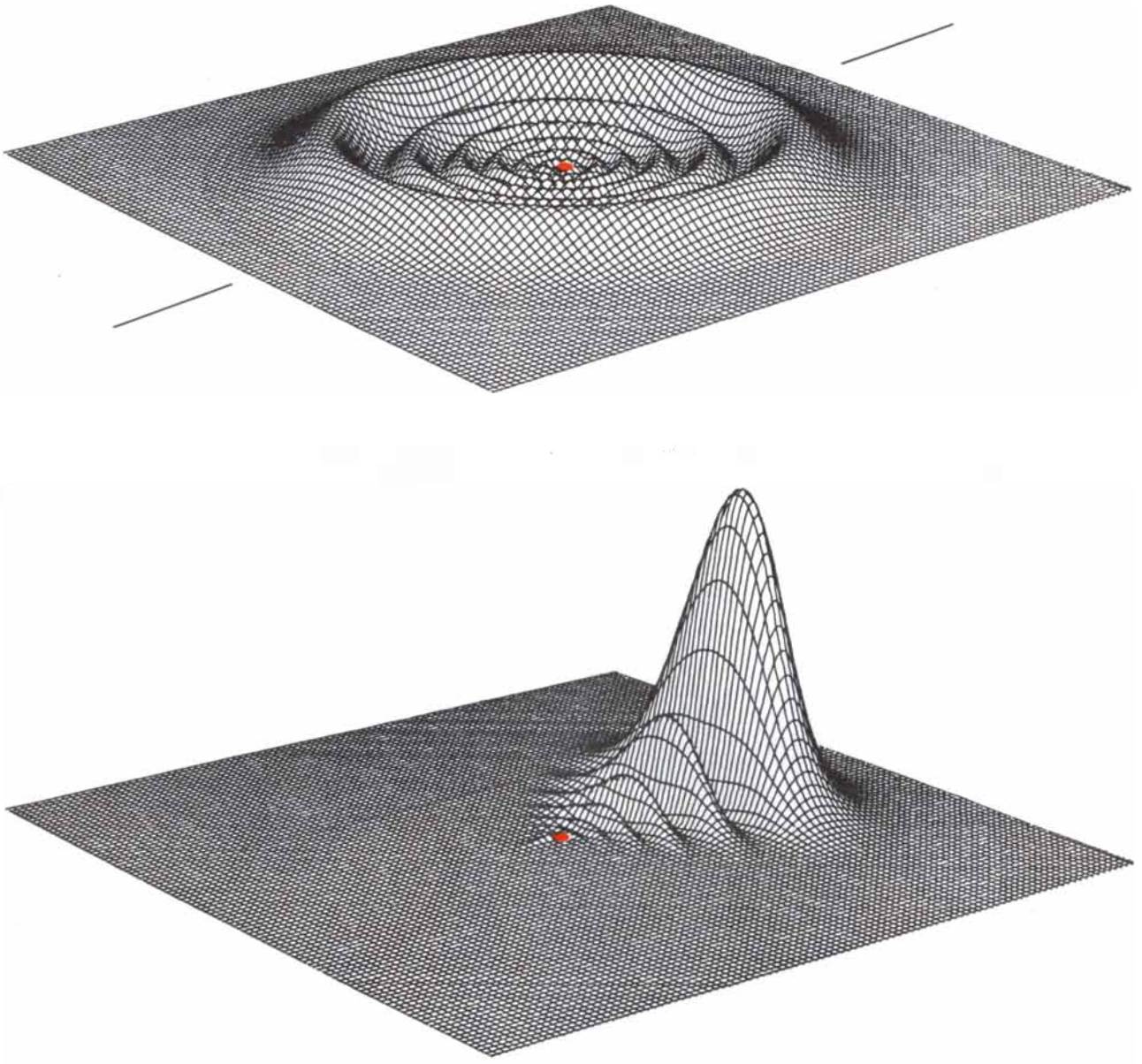
According to the Bohr theory, the hydrogen atom is a solar system in microcosm. The gravitational attraction that binds a planet to the sun and the electrostatic attraction, or Coulomb force, that binds an electron to a proton depend on distance in the same way: both forces decrease as the square of the distance. For this reason the motion of an electron around a proton is identical in form with the motion of the earth around the sun. Nevertheless, the analogy between planetary motion and the motion of the electron in a hydrogen atom is not exact. According to classical electromagnetic theory, the orbiting electron would rapidly lose energy by radiating light and would eventually crash into the nucleus.

In order to overcome this problem Bohr introduced the extraordinary idea that atoms exist only in stationary states, that is, in certain allowed energy levels. The electron cannot spiral into the nucleus. It can lose energy only by "jumping" from a higher level to a lower level, giving off the excess energy as electromagnetic radiation, until it reaches the ground state. From this lowest level no further loss of energy is possible. These simple ideas enabled Bohr to account for the stability of hydrogen as well as for its spectrum: the distinctive pattern of sharply defined wavelengths the atom radiates.

The allowed energies of the electron in a hydrogen atom are given by the expression $-E_0/n^2$, where E_0 is a constant and n is a positive integer called the principal quantum number, which designates the energy level of the electron. The constant E_0 has a value of about 13.6 electron volts. (One electron volt is the energy an electron gains when it is

accelerated through a potential difference of one volt.) The energy is negative because work must be done to overcome the Coulomb force in separating the electron from the proton. The value $n = 1$ designates the ground state, and so the electron of a hydrogen atom in the ground state has an energy of -13.6 electron volts. The energy is determined by the combination of the electrostatic attraction between the electron and the proton and the kinetic energy of the electron as it whirls around the proton. Higher energy levels are designated by increasing values of n. As n approaches infinity the energy approaches zero, which is the energy of an electron and a proton that are far apart and at rest.

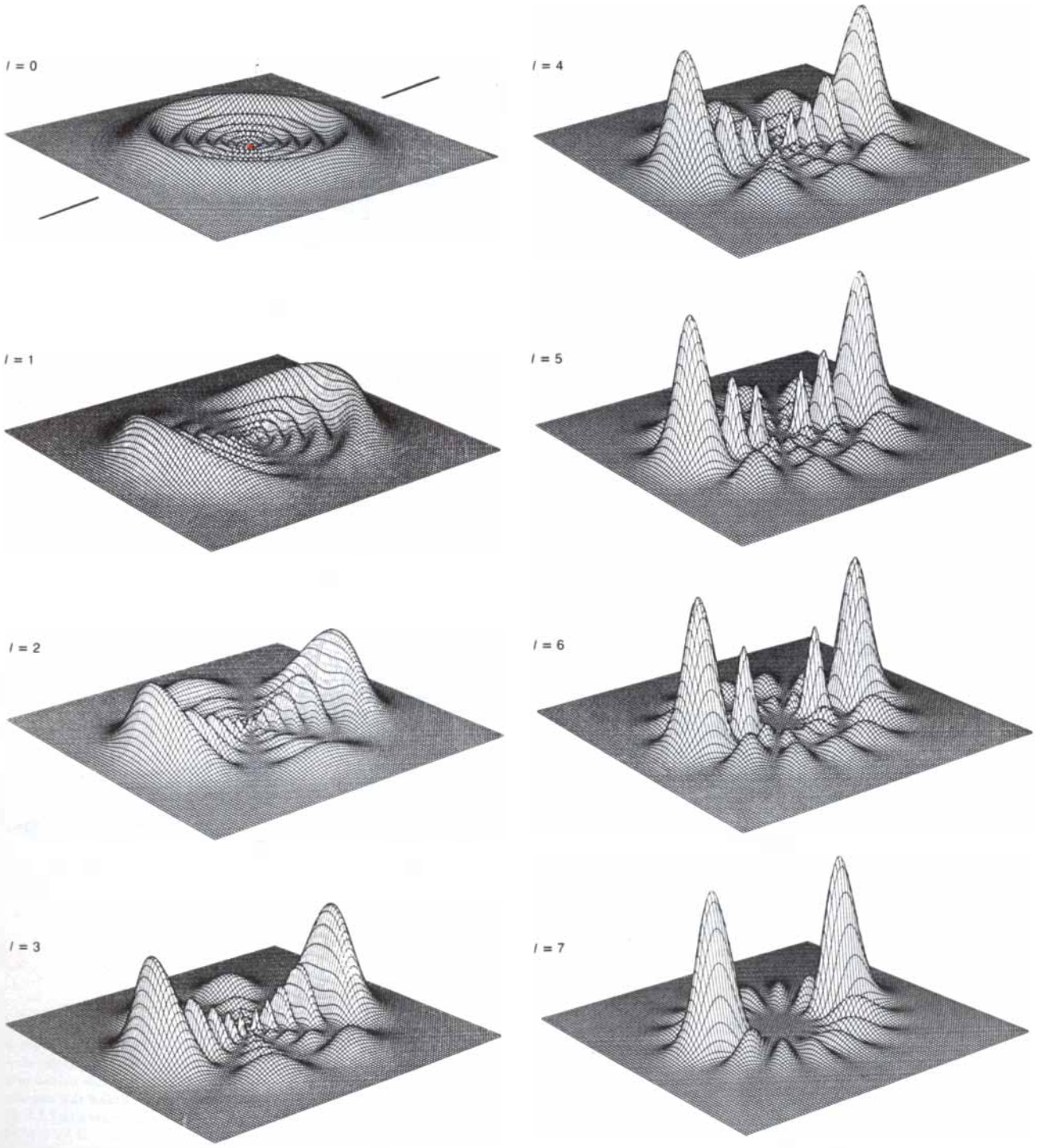
A Rydberg atom is an atom with a single electron in a state with a large principal quantum number. Atoms in states with n as large as 350 have been detected in outer space by radio astronomers, but in laboratory experiments n typically lies in the range between 10 and 100. Most of the interesting properties of Rydberg atoms depend on n in a simple way. The radius of a Bohr orbit is proportional to n^2, and so the area of the orbit is proportional to n^4. The separa-



ELECTRON-CHARGE DENSITY OF HYDROGEN is graphed on a plane passing through the single proton that forms the nucleus of the atom (*colored dot*). The states of hydrogen are described by the three quantum numbers n, l and m; n is a positive integer that designates the energy level of the electron, l is an integer between 0 and $n - 1$ that corresponds to the magnitude of the eccentricity (or angular momentum) of the electron's orbit and m is an integer between $-l$ and $+l$ that describes the orbit's orientation. In the state where $n = 8$, $l = 0$ and $m = 0$ (*upper graph*) charge density is a series of concentric wavelike peaks. In three dimensions the charge density can be visualized as a series of spherical shells formed by rotating the graph about an axis passing through the nucleus. The distance from the nucleus to the edge of the plane corresponds to 2×10^{-6} centimeter, which is 380 times the Bohr radius (the radius of a hydrogen atom in the lowest energy state). In a weak electric field (*lower graph*) the electron in an $n = 8$ state of hydrogen "stands" far to one side of the proton, forming an electric dipole. (In this state $m = 0$ and the angular momentum is a mixture of all possible values of l from zero to 7.) A dipole consists of two equal and opposite charges separated by a fixed distance. Many atoms act as dipoles, but most of them are not true dipoles: there is no separation of charges but only a slight distortion of the charge cloud. In the diagrammed state the separation is real. An atom whose outermost electron has been excited to a high energy level is often called a Rydberg atom. All Rydberg atoms are true dipoles.

tion of adjacent energy levels varies as $1/n^3$ and the number of energy levels in a small range of energies increases as n^5. The dramatic properties of a Rydberg atom follow from their dependence on large powers of n. For example, when n equals 30, the area of the electron's orbit in a Rydberg atom is almost a million times the area in an ordinary atom.

In considering the analogy between the motion of an electron around a nucleus and the motion of a planet around the sun it is important to keep in mind that the most general planetary orbit is elliptical. The period of motion of a planet (that is, the length of the planet's year) depends on the major diameter of the ellipse but not on its eccentricity, or shape. This law, which was formulated by Johannes Kepler at the beginning of the 17th century, has a parallel in the



STATES OF HYDROGEN with $n = 8$ and $m = 0$ vary in angular momentum from $l = 0$ to $l = 7$. Although charge density may seem complex, the nodal lines (where the charge density is zero) are always either circles centered on the nucleus or straight lines passing through the nucleus. In three dimensions the nodal surfaces are spheres or cones. The charge-density graphs were made with the aid of a computer by William P. Spencer of the Massachusetts Institute of Technology. To make the graphs easier to interpret the charge density was multiplied by r^2, where r is the distance to the nucleus. The innermost node of the charge density is too close to the nucleus to be seen.

dynamics of the Bohr atom. The energy of an electron in a given level is identical for orbits that have the same major diameter, no matter what the eccentricity.

Because there are infinitely many different ellipses with the same major diameter, there might be an infinite number of atomic states with the same energy. Bohr argued that only a finite number of orbits should be possible for each value of n. The orbits are distinguished geometrically by their eccentricities. The physical variable corresponding to the eccentricity is the angular momentum of the electron, and Bohr postulated that the angular momentum can have only values given by $lh/2\pi$, where l is any integer from 0 to $n-1$ and h is Planck's constant.

In creating his atomic theory Bohr invoked an original and ingenious argument, subsequently named the correspondence principle, that enabled him to derive the equations governing the hydrogen atom without any knowledge of the underlying quantum-mechanical laws. The idea of quantum jumps was so alien to traditional physics that it provided no means of predicting atomic spectra from first principles. Bohr overcame this obstacle by considering highly excited states of the hydrogen atom, or in other words Rydberg states. He argued that if n is very large, the effect of changing n by one unit must in some sense be small. For example, the jump from $n = 100$ to $n = 99$ should be much less drastic than the jump from $n = 2$ to $n = 1$. Thus changes in energy between two highly excited states should be smooth compared with the abrupt change in energy between two low-lying states.

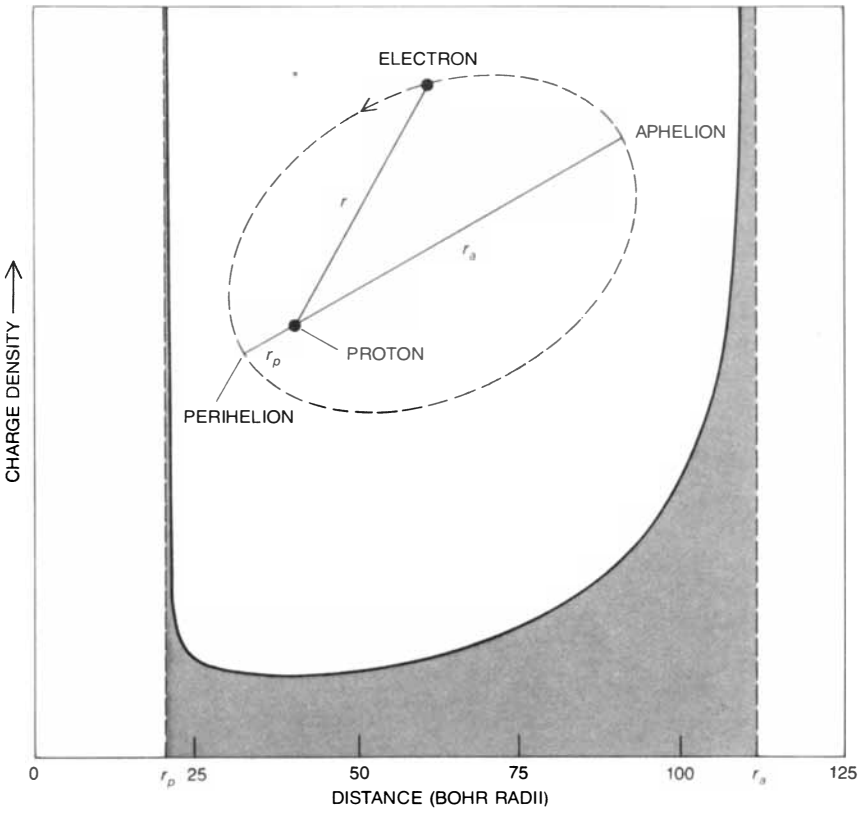
Smooth changes are characteristic of classical systems, where energy can vary continuously. The similarity suggests that highly excited atoms should have classical properties. In particular an electron in an atom should emit electromagnetic radiation with a frequency equal to the orbital frequency. The correspondence principle suggests that the frequency of electromagnetic radiation emitted as a Rydberg atom jumps to a nearby state should approach the frequency at which the electron revolves around the proton. This clue was the key to the problem. It led Bohr to the correct mathematical description of the hydrogen spectrum and to the correct expression for the energy of the electron.

Bohr's simple model accounted for the most conspicuous features of the spectrum of hydrogen, but the model incorporated such a jumble of traditional concepts and radical ideas that it could not be generalized or extended. A new point of view was needed. This point of view, which is alien to the classical outlook of Bohr's theory, was provided by quantum mechanics. The picture of an electron as a particle was replaced by an abstract vision of probability theory. According to the new mode of thought, knowledge of the electron is best expressed in terms of a wave function: a mathematical expression whose value varies in both space and time. The probability of finding the electron in some small volume V is proportional to the product of V and the intensity of the wave function there. In classical physics there is no need to speak of probability. If an electron is prepared in a known way at a given time, one can predict with certainty whether or not it will be in V at any future time. In quantum mechanics, however, if one prepares the electron in the same way and repeats the experiment many times, sometimes the electron will be found in V and sometimes it will not.

A simple artifice makes it possible to describe the electron without the encumbrance of probability theory. The idea is to view the electron not as a charged particle but as a cloud of charge. One can then imagine a fractional charge in a volume V that is the product of V and the charge density. Any single measurement of the charge in V must find either one electron or none, but if the electron is prepared in the same way and the measurement is repeated many times, the average of all the results will be the same as the fractional charge calculated from the charge density. Hence knowledge of the charge density is equivalent to knowledge of the probability that the electron is in V.

At first the concept of charge density in an atom seems to bear little resemblance to Bohr's picture of an electron orbiting the nucleus, but the two views are closely related. Consider the probability of finding an electron in some thin spherical shell surrounding the nucleus. In quantum mechanics the probability is proportional to the product of the shell's volume and the intensity of the wave function in that volume. In classical physics the average charge density is proportional to the time the electron spends in the shell. The faster the electron moves through the shell, the less time the electron spends in it and therefore the less the average charge in the shell is. In short, the classical charge density varies inversely as the speed of the electron.

In a classical elliptical orbit the distance from the nucleus to the electron varies between two extremes: aphelion

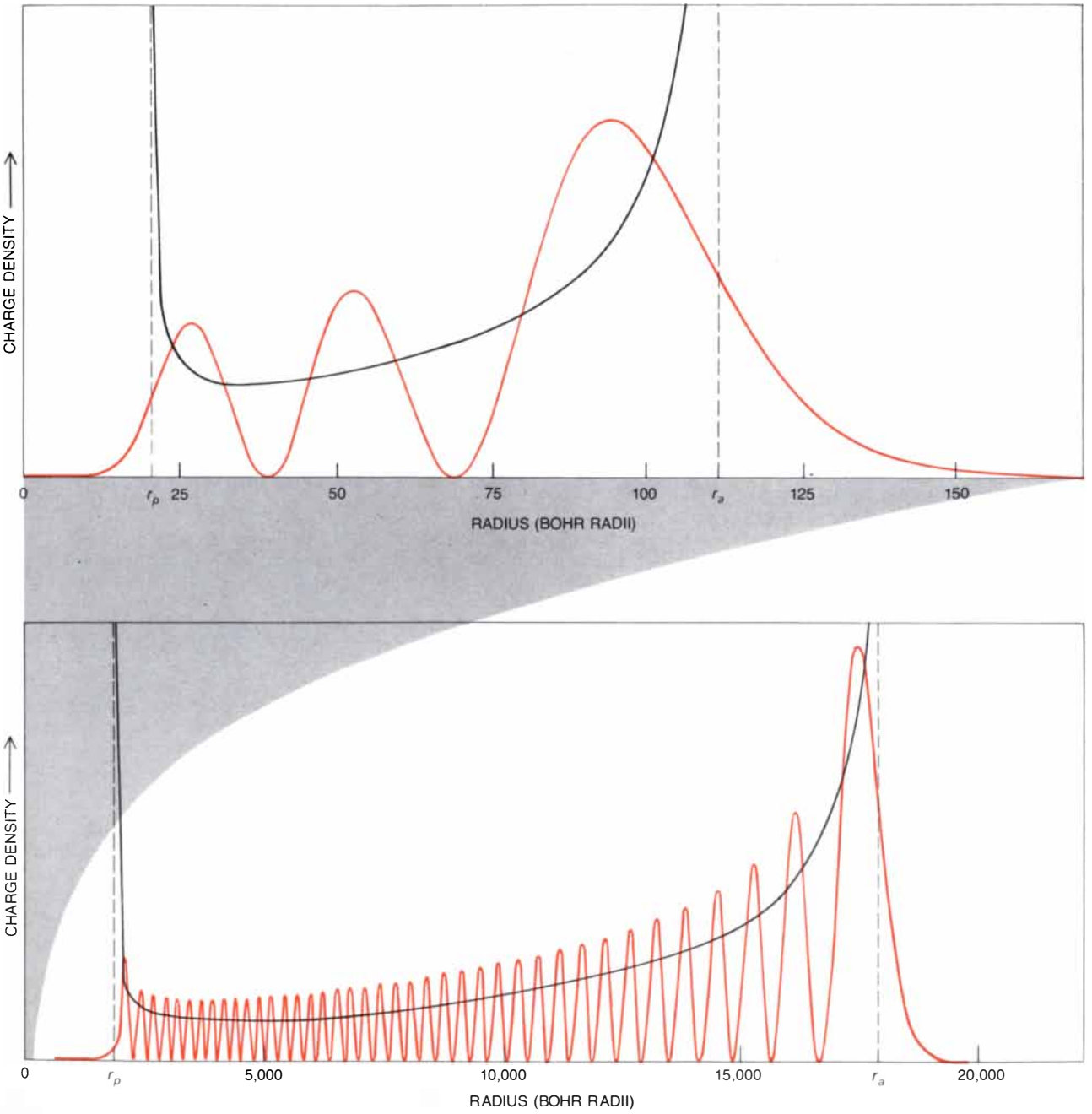


CLASSICAL BOHR ORBIT for the $n = 8$, $l = 5$ state of hydrogen is a squat ellipse (*inset illustration*). The diameter of the ellipse is 128 times the Bohr radius. As the electron moves in its orbit around the proton the orbital radius r varies between the aphelion distance r_a and the perihelion distance r_p. The classical charge density (*graph*) is proportional to the relative amount of time the electron spends at a distance r from the proton. The charge density varies inversely with the radial speed of the electron. The classical charge density diverges at aphelion and at perihelion, where the radial speed falls to zero as the electron reverses radial direction.

and perihelion, to borrow the planetary terminology. The radial speed of the electron falls to zero as it reverses radial direction at these extremes, and so the charge density has a peak there. The charge density has a minimum where the radial speed is greatest, which is close to perihelion. The charge density is zero at distances less than perihelion and greater than aphelion, where the electron never ventures.

The classical and the quantum-mechanical charge densities have little in common in a low-lying state of hydrogen such as $n = 8$, $l = 5$. As the correspondence principle predicts, however, the two charge densities are similar in a highly excited state such as $n = 100$, $l = 60$ [*see illustration below*]. Nevertheless, even in these states there are important differences between the two kinds of charge density. The quantum-mechanical charge density has wavelike features, including nodes and rounded peaks, that reflect the underlying wave properties of the electron. In the classical description the wavelike features are absent. Moreover, in quantum mechanics the electron can penetrate regions of space that are inaccessible to it in classical physics. For example, the electron can venture slightly beyond the aphelion distance.

The existence of Rydberg atoms has been known since before the turn of the century. In 1906 R. W. Wood, an American spectroscopist, observed absorption lines in sodium gas for transitions to states as high as $n = 60$. According to the Bohr theory, an atom can absorb light if the frequency of the light



QUANTUM-MECHANICAL CHARGE DENSITY (*color*) is different from the classical charge density (*black*) in a low-lying state of hydrogen such as $n = 8$, $l = 5$ (*upper graph*). In an energetic state such as $n = 100$, $l = 50$ (*lower graph*) charge densities have a similar shape.

multiplied by Planck's constant is equal to the energy difference between the initial state of the electron and an allowed excited state. When light from a lamp is passed through a gas and dispersed with a spectroscope, dark lines appear where the light has been absorbed at the frequencies satisfying the Bohr condition. There are impediments, however, to the study of Rydberg atoms by this method. Highly excited atoms are so large and so weakly bound that they rapidly break apart when they collide in a gas.

Isolated Rydberg atoms were first observed deep in interstellar space. In 1965 B. Höglund and Peter G. Mezger of the National Radio Astronomy Observatory detected radiation from hydrogen atoms undergoing transitions between levels near $n = 100$. For such large values of n the radiation is not in the optical region of the electromagnetic spectrum but in the microwave region.

Deep space might seem to be an unlikely place for finding Rydberg atoms; actually it is almost ideal because the density of atoms is so low that collisions are rare. Of course, the density must not be too low: there must be enough atoms to provide a detectable signal. A radio telescope can look so far into space that there are many atoms along the line of sight in spite of the low density. The atoms are created when free electrons and protons recombine to form hydrogen. This process of recombination is one of the dynamical mechanisms that govern the delicate balance between neutral matter and charged particles in the galaxy. The atoms radiate as they cascade to lower Rydberg states. Such recombination radiation is emitted from many regions of the galaxy.

Rydberg atoms can be created in the laboratory by a number of techniques. The bombardment of a gas with charged particles promotes atoms in the gas into a wide range of excited states, including Rydberg ones. Many laboratories, however, including our own, rely on another technique. A tunable laser is used to excite the atoms. This method makes it possible to select a particular Rydberg state, an advantage that has revolutionized the field.

Most experiments with Rydberg atoms have been done with the atoms of the alkali metals: lithium, sodium, potassium, rubidium and cesium. These elements are commonly chosen because they are easily turned into a gas, because their spectral absorption lines are at wavelengths conveniently generated by laser light and because they absorb light efficiently. The alkali metals are the workhorses of atomic physics.

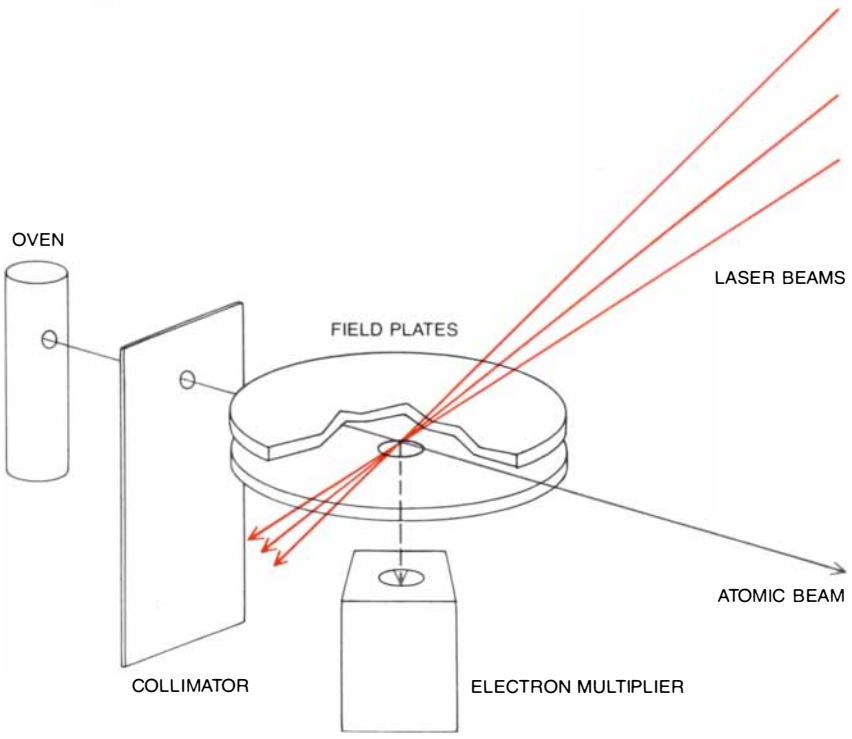
In our laboratory we excite the alkali atoms to Rydberg states with pulsed tunable dye lasers. The lasers generate brief but intense flashes of highly monochromatic light. Usually we excite an atom with pulses from three lasers. The first two pulses excite the electron to an intermediate state, and the final pulse "kicks" the atom into a Rydberg state. In lithium, for example, two lasers excite the electron to the state $n = 3, l = 0$, and the third laser, whose frequency can be tuned over a wide range, drives the electron into a Rydberg state with a large value of n and with l equal to 1. The lasers are fired about 10 times per second, and each pulse lasts for about 5×10^{-9} second. The light is so bright that most of the atoms in the interaction region (whose volume is a cubic millimeter) can be made into Rydberg atoms.

In order to keep the Rydberg atoms from colliding we do the experiments with an atomic beam. In the case of lithium the metal is turned into a vapor by heating in an oven to a temperature of about 650 degrees Celsius. The vapor flows through a small hole into a vacuum chamber; a blocking plate with a small aperture collimates the vapor to form the atomic beam. The vacuum is good enough for an atom to cross the chamber without a single collision.

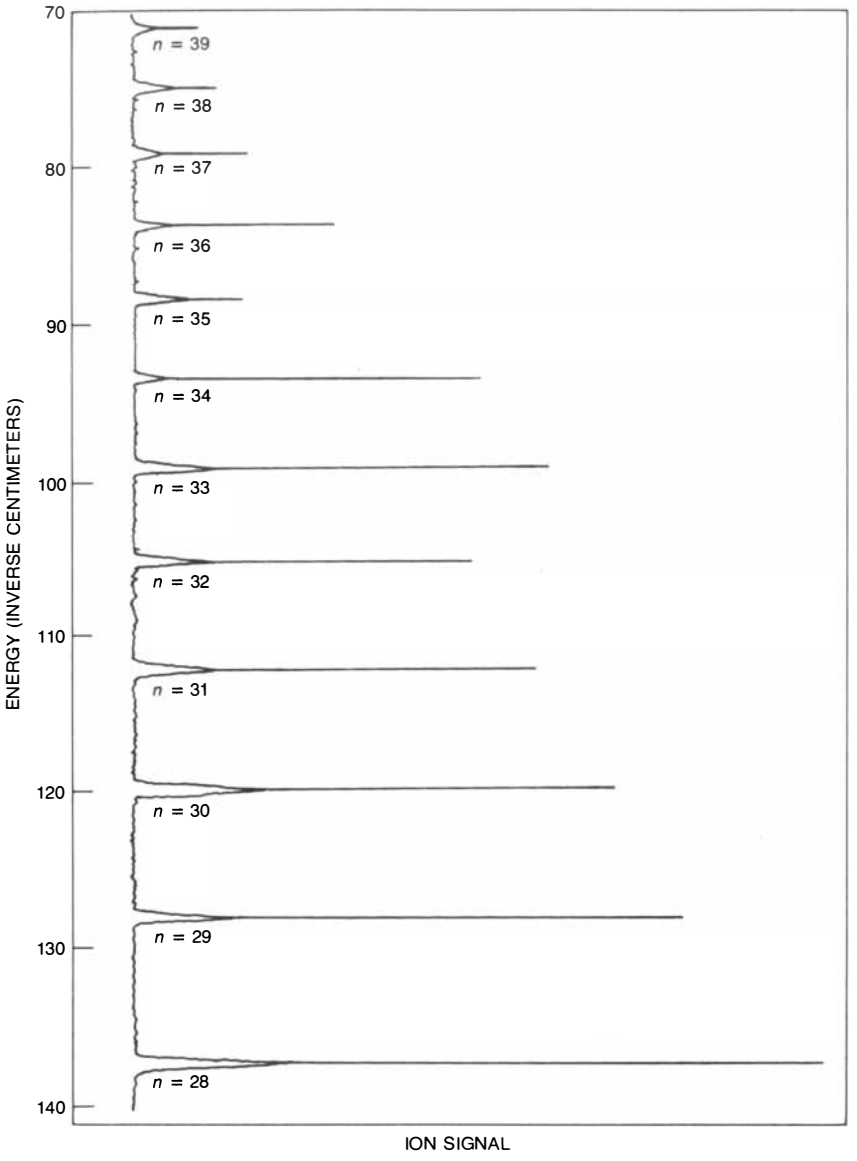
The detection of electrically neutral atoms is usually a troublesome problem, but that is not the case with Rydberg atoms. We ionize them by applying an electric field large enough to tear away the excited electron. Ionizing a ground-state atom requires an extraordinarily large field (perhaps 300 million volts per centimeter), but a field of only a few hundred volts per centimeter is sufficient to ionize many Rydberg atoms. The field is generated by applying a pulse of voltage across two parallel conducting plates centered on the interaction region. The freed electron or the ion passes through a grid in one of the plates and actuates a detector. The technique, which is called field ionization, is so sensitive that we can do experiments with one Rydberg atom per laser pulse, although we usually detect thousands of atoms per pulse.

To display a series of Rydberg-atom energy levels we slowly vary the frequency of the third laser and record the field-ionization current. Whenever the laser frequency multiplied by Planck's constant equals the energy needed to excite an atom to an allowed state, some atoms are converted into Rydberg states and are then promptly ionized. The result is an experimental "picture" of the energy levels.

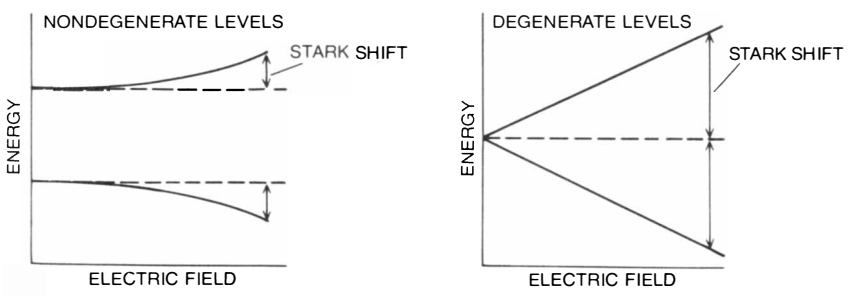
We have employed these techniques to study a fascinating aspect of Rydberg atoms: their properties in an electric field. If an electric field is applied to



THREE LASERS are employed to excite atoms of the alkali metals (lithium, sodium, potassium, rubidium and cesium) to Rydberg states in the authors' laboratory at M.I.T. The metal is heated in an oven to convert it into a vapor. The vapor flows through a small hole into a vacuum where the density is low enough for an atom to cross the entire apparatus without collision. A collimator forms the vapor into an atomic beam. Two or three laser pulses excite an atom to a Rydberg state. The Rydberg atoms are easily detected by the technique called field ionization. A pulse of high voltage is applied across two plates centered on the interaction region.



RYDBERG STATES OF LITHIUM are displayed experimentally by slowly varying the frequency of the light in the final laser pulse and recording the field-ionization current. When the frequency corresponds to the energy needed to excite an atom, the atom can absorb a photon, or quantum of light, and become a Rydberg atom, which is promptly ionized. The vertical axis corresponds to the energy, so that a sharp horizontal peak appears at the position of each energy level. The small irregularities are a result of fluctuations in the power of the laser. The energy is graphed in spectroscopic units, which have the dimension of inverse centimeters.



STARK EFFECT is a shift in the energy levels of an atom in an electric field. The extent of the shift depends on whether or not the energy levels are degenerate. Degenerate levels are states with different quantum numbers that nonetheless have the same energy. In nondegenerate states (*left*) the Stark effect is small and varies with the square of the applied field. Adjacent energy levels tend to repel each other: the upper level is shifted up and the lower level is shifted down. In degenerate states (*right*) the Stark effect is large and varies linearly with the applied field. Rydberg atoms have many degenerate states that often have a large Stark effect.

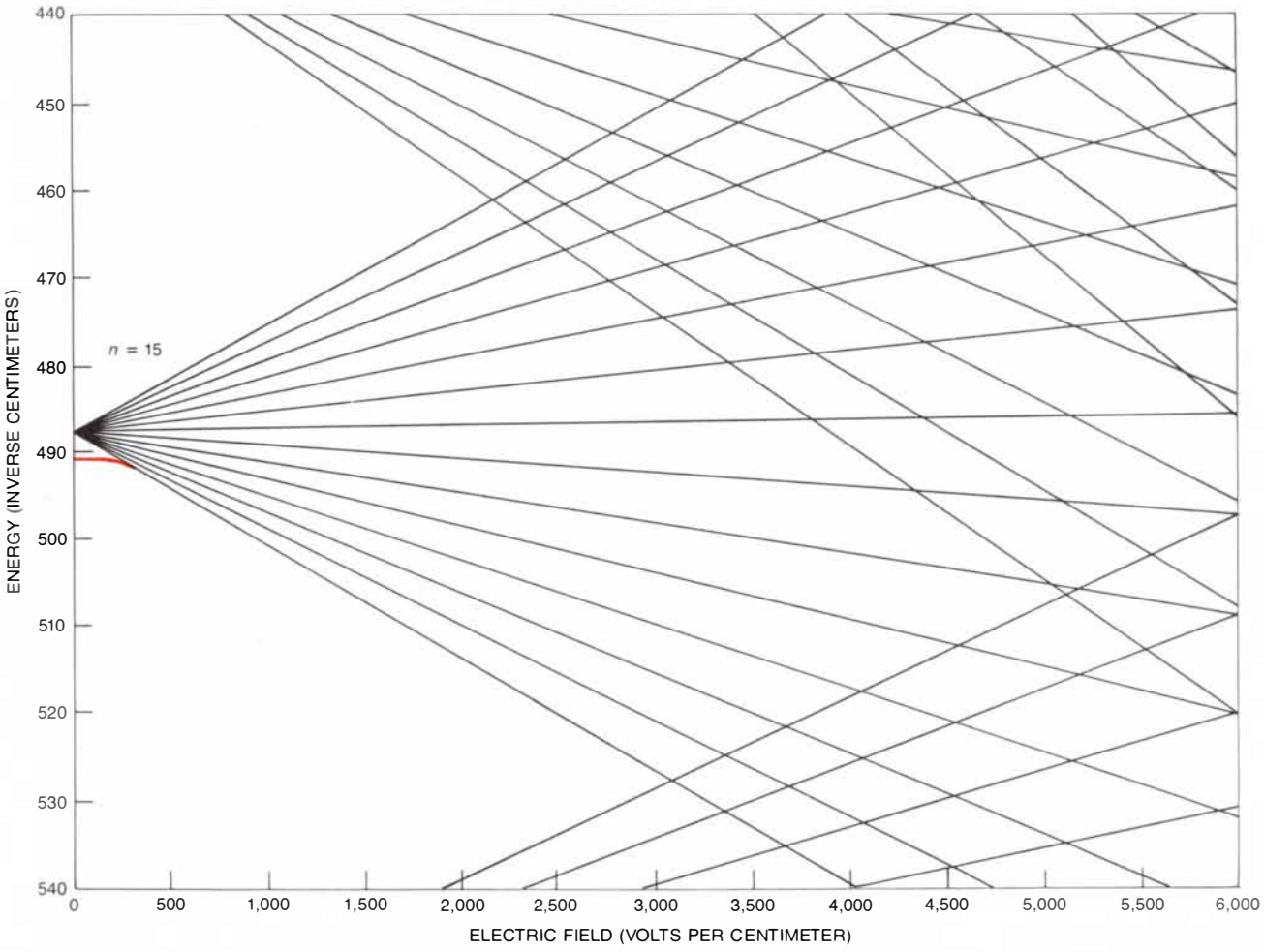
an ordinary atom, its energy levels are shifted slightly; the shift is called the Stark effect. The amount by which a given level is shifted depends chiefly on the proximity of a neighboring level. The nature of the shift is altered radically if the energy levels happen to be degenerate. Two states are said to be degenerate if they are physically distinct (that is, if they have different quantum numbers) but nonetheless have the same energy. In nondegenerate states the Stark effect is small and varies quadratically, or as the square of the applied electric field. In degenerate states the Stark effect is large and varies linearly, or by simple proportionality, with the field. Rydberg atoms are highly degenerate, and they can display spectacular Stark effects.

The degeneracy of Rydberg states follows from a unique property of hydrogen: for a given principal quantum number the states of different angular momentum all have the same energy (given by $-E_0/n^2$). The states of hydrogen are also degenerate with respect to another quantum number, m, that describes how the angular momentum is oriented in space. The value of m can be any integer from $-l$ to $+l$. Thus the state of a hydrogen atom is specified by the three quantum numbers n, l and m. (Other quantum numbers are needed to describe the spin of the electron and the spin of the nucleus, but they can be neglected here.) In hydrogen, for each value of n the states with all possible values of l and m are degenerate.

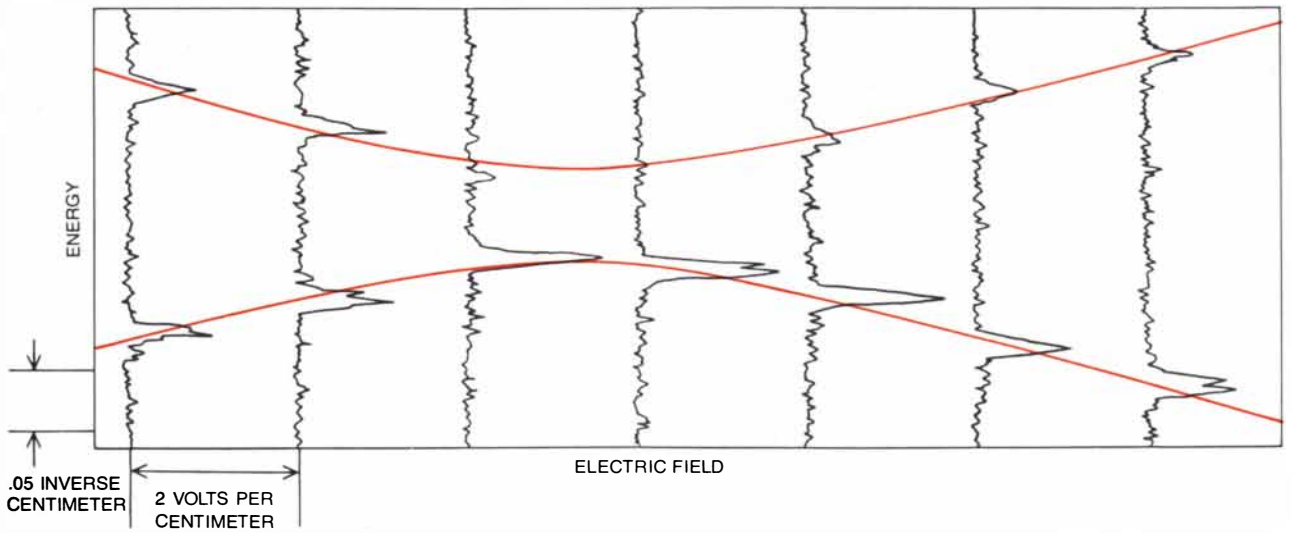
Rydberg states of hydrogen and many Rydberg states of other atoms have gigantic Stark effects because of the high degree of degeneracy and the large size of the atoms. In an electric field the degenerate levels for each value of m split into a series of groups, each group having a single value of m. If the energy of a group is graphed as a function of the electric field, the levels form a fanlike pattern in which some levels increase with the field and others decrease.

A Rydberg atom of an alkali metal such as lithium has a Stark effect that seems similar to that of hydrogen, although there are differences. Among the $m = 1$ levels, for example, the states in which l is greater than 1 resemble the states of hydrogen: they are degenerate and have a linear Stark effect. An electron in the state $l = 1$, however, passes so close to the core of the atom that the electron's energy is slightly lowered. As a result the $l = 1$ state is nondegenerate and has a typical quadratic Stark effect at low fields. In higher fields the shift becomes linear and the entire system resembles hydrogen.

We have studied the Stark effect in Rydberg atoms by applying a steady voltage across the plates centered on the interaction region. Again we slowly varied the frequency of the laser and detected the excited atoms by ionizing them



FANLIKE PATTERN is generated when the Stark effect splits the degenerate energy levels of a Rydberg atom. For hydrogen a series of levels with $n = 15$, $m = 1$ and a mixture of values of l is shown. In addition levels with $n = 14$ and $m = 1$ enter the map from below and levels with $n = 16$ and $m = 1$ enter it from above. The Stark-effect map of the comparable states of lithium resembles the map of hydrogen except for two features. If there is no external field, the $n = 15$, $l = 1$ state of lithium is not degenerate with the other angular-momentum states where n equals 15. The reason is that the $l = 1$ orbit approaches the ionic core (the inner electrons and the nucleus). As a result an electron with l equal to 1 is subject to a slightly stronger field than it is in a hydrogen atom. The $l = 1$ state is not precisely degenerate in a weak field, so that it is subject not to a large linear Stark shift but to a small quadratic one (*color*). In a field stronger than 300 volts per centimeter the shift becomes linear and the $l = 1$ state resembles the corresponding state of hydrogen. The other difference between the two maps is subtle but significant. In the Stark-effect map of lithium the energy levels never cross, as they always do in the map of hydrogen.



AVOIDED CROSSING in the Stark-effect map of the lithium atom is shown in a high-resolution view of the close approach of an $n = 18$ level and an $n = 19$ level. The colored lines represent theoretical calculations of the Stark-shifted energy levels made by the authors.

with a high-voltage pulse a microsecond or two after the lasers were turned off. The energy-level diagram was recorded and the process was repeated at increasing values of the applied field. A map of the shifted energy levels made from the data resembles a map we constructed from the theoretical methods of quantum mechanics [*see illustration below*].

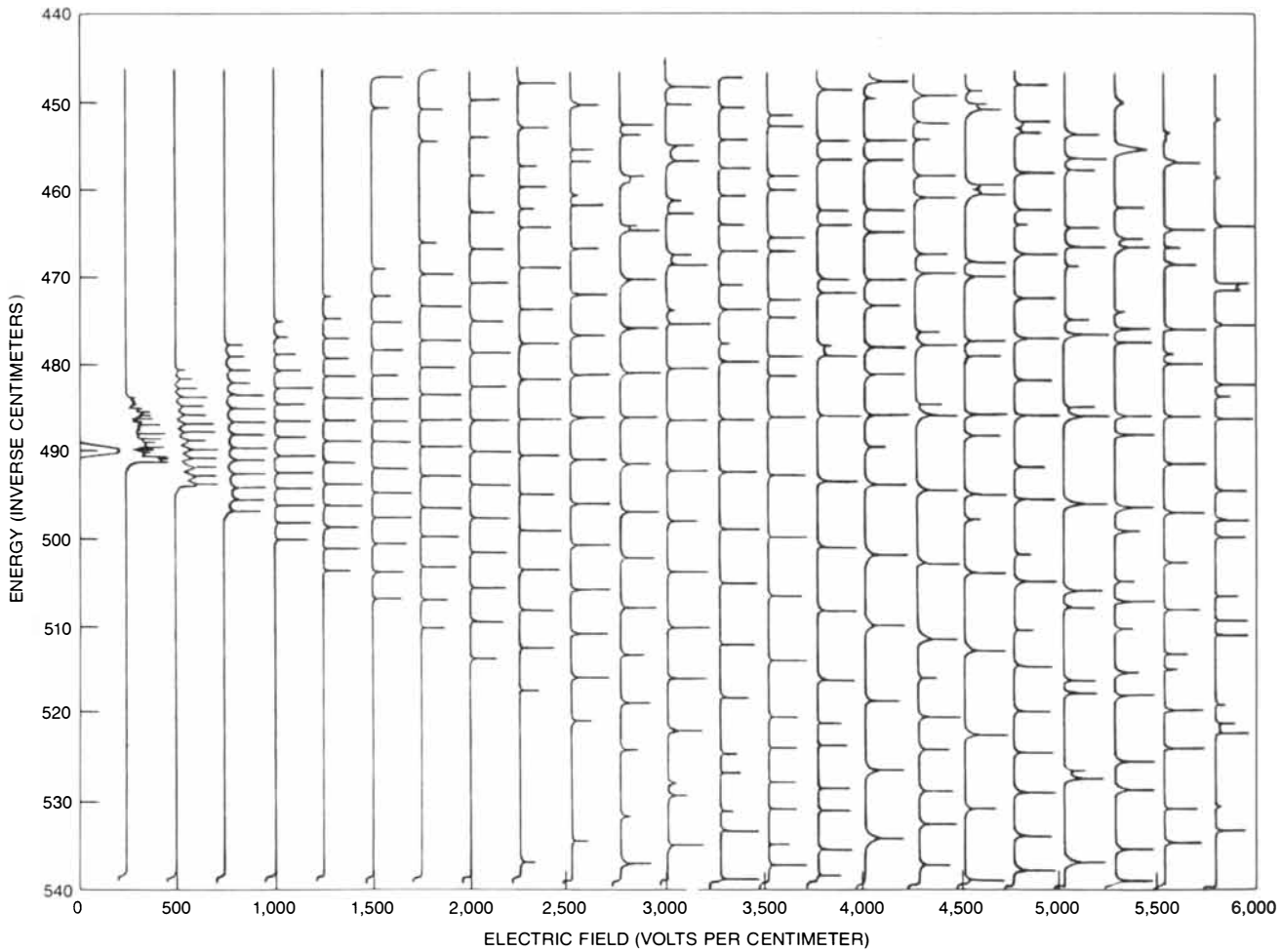
There is a subtle but important difference between the Stark structure of hydrogen and that of lithium. As the applied electric field increases, the energy levels of hydrogen cross one another. At a value of the field where two levels cross they are degenerate. It should be emphasized that degeneracies are not the rule in quantum mechanics but the exception. Wherever a degeneracy is found there is some underlying symmetry, or simplicity, in the problem. For example, the degeneracy in hydrogen of all the angular-momentum states of a given n follows from the exact inverse-square nature of the Coulomb force.

An analogous symmetry in planetary motion is connected with the fact that the orbit of a planet is an ellipse whose orientation is fixed in space. If the inverse-square gravitational force is even slightly perturbed, however, the orientation is no longer constant; the ellipse slowly precesses, or changes its direction in space. The precession of the perihelion of Mercury is a famous example caused in part by small relativistic effects.

If the pure Coulomb field is slightly perturbed, the underlying symmetry of the Stark structure is lost. Such is the case in lithium. Near the ionic core of lithium (or of any atom other than hydrogen) the inverse-square law does not hold exactly because of the influence of the core electrons. The consequences are dramatic: when the levels are shifted by the Stark effect, none of them cross. Two levels can come close, but at some point they repel each other and turn away. By observing such avoided crossings we can obtain a sensitive test of the accuracy of our calculations. Alternatively we can use the data to reveal the presence or absence of an underlying symmetry of the system.

Although the energy-level map of the Stark structure may look complex, it illustrates a simple idea about the distribution of the electric charge in a Rydberg atom. The most striking feature of the map is the linear variation of the energy with the field. Such a variation is characteristic of an electric dipole: a configuration of two equal and opposite charges separated by a fixed distance. Many atomic and molecular systems exhibit the characteristics of a dipole, but most such systems are not true dipoles: there is no actual separation of charges but only a slight distortion in the shape of a charge cloud. In Rydberg atoms, however, the separation of charges is quite real [*see illustration on page 131*].

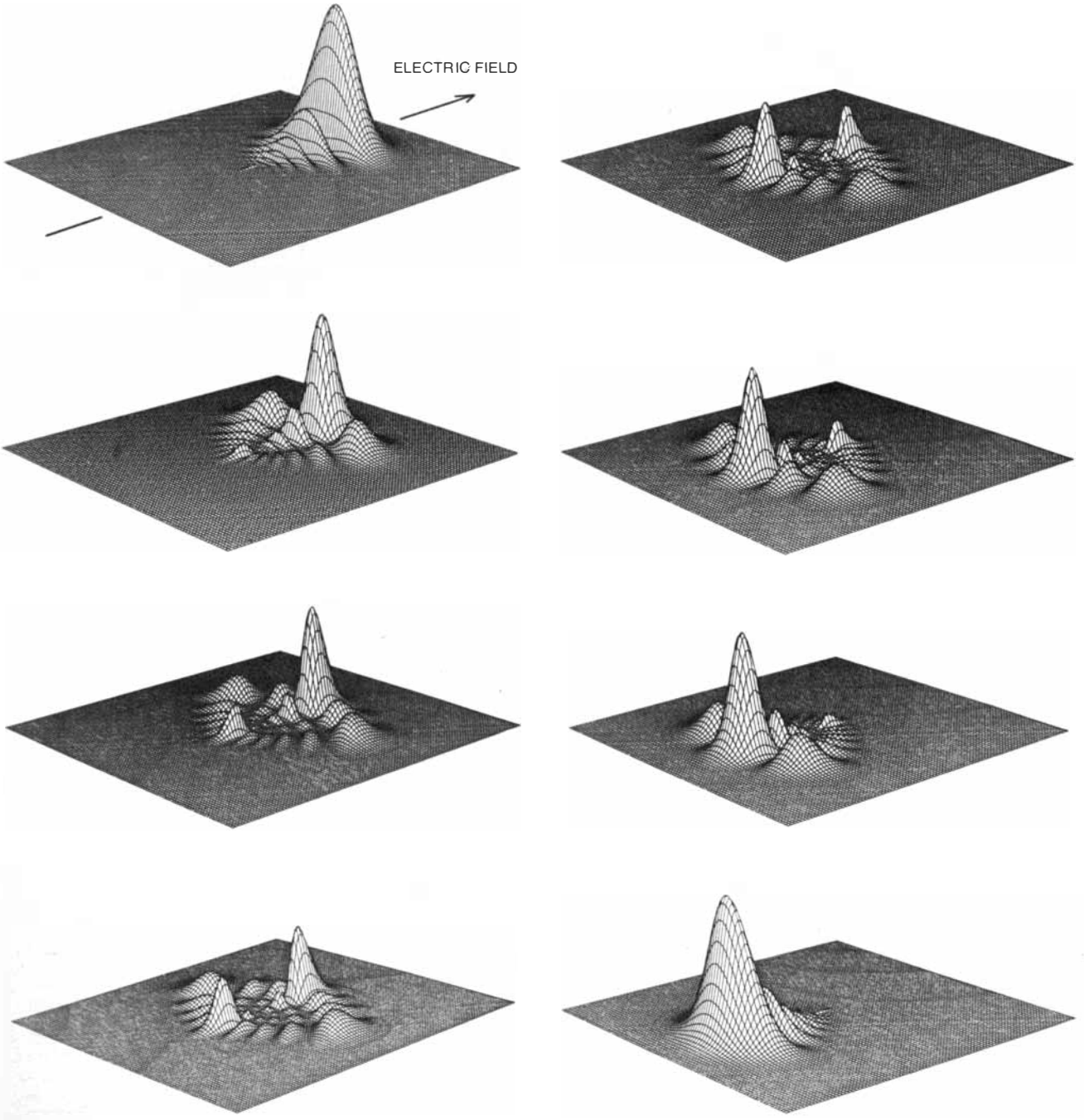
Field ionization is often employed to detect Rydberg atoms because it is simple, efficient and essentially free of noise. The physical process that underlies field ionization is quite interesting in itself. It is the process of tunneling, which is purely quantum-mechanical;



STARK-EFFECT MAP OF LITHIUM is made by recording the field-ionization signal as the electric field increases in strength. The horizontal peaks mark the ion signals that are generated when the frequency of the final laser pulse, which is slowly varied, matches an energy level of the atom. The energy levels (that is, the straight lines along which the horizontal peaks fall) can be clearly seen by turning the page sideways and looking along the surface. The levels are the same as the ones in the top illustration on the preceding page.

there is nothing like it in classical mechanics. Tunneling is the motion of a particle through a region where classical mechanics does not allow it to be.

In both quantum mechanics and classical mechanics the total energy of a particle has two components: kinetic energy and potential energy. For a hydrogen atom both components of the energy can be represented in a graph that gives the energy of the electron as a function of distance from the nucleus [*see illustration on page 142*]. Since the total energy, $-E_0/n^2$, is constant for any given value of n, it is plotted as a horizontal line. The potential energy varies inversely with distance and forms a hyperbola. Where the curves representing the total energy and the potential energy intersect, the kinetic energy is necessarily zero, and so the electron's velocity is also zero. An electron moving away from the proton comes to rest there and then starts falling back toward the proton under the attraction of the Coulomb force. The intersection is called a turning point. According to



HYDROGEN ATOM IN AN ELECTRIC FIELD can assume many shapes because of its high degree of degeneracy. The charge distribution for the $n = 8$, $m = 0$ states can have any of the eight shapes shown. In each state the angular momentum has a mixture of values from $l = 0$ to $l = 7$. The specific shape a Rydberg atom assumes depends on the experimental conditions under which it is formed. The same family of states is shown in the illustration on page 132. The electron-charge cloud is displaced from the proton, giving rise to a linear Stark effect. The Stark effect is proportional to the average distance between the proton and the electron, which is different for each state. In three dimensions the charge distribution has a cylindrical symmetry about colored axis; nodal surfaces are paraboloids of revolution.

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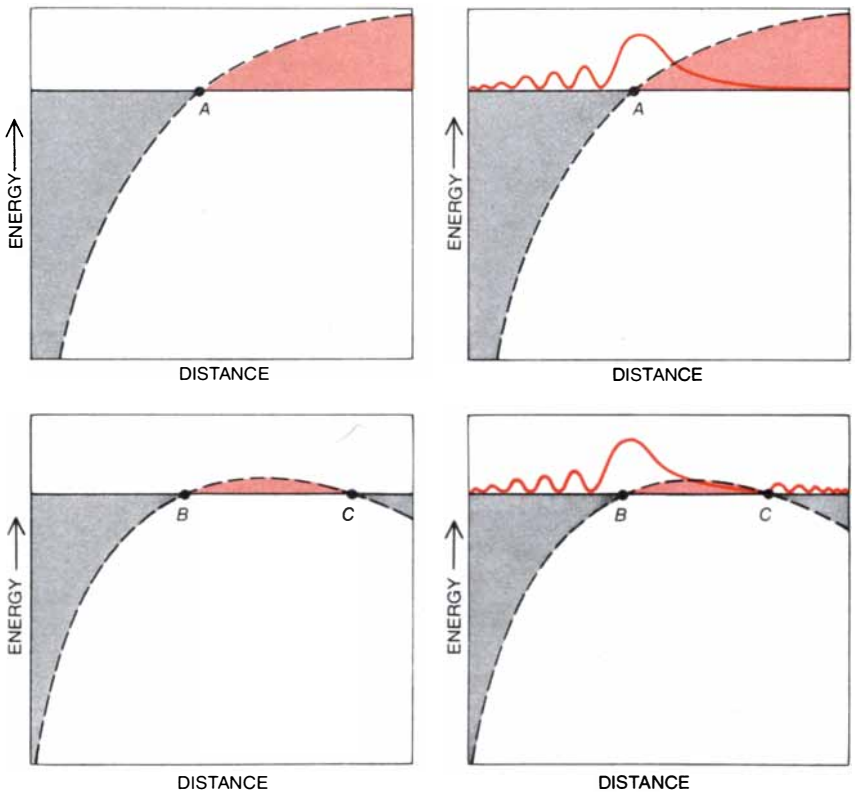
classical physics, the electron cannot go beyond the turning point because the kinetic energy would be negative there. (The kinetic energy is proportional to the square of the velocity. In classical physics it can never be negative.)

The energy diagram must be modified somewhat when a hydrogen atom is put in an electric field. Near the origin the force on the electron stems chiefly from the influence of the proton, but at large distances, where the Coulomb force is small, the force associated with the applied field dominates. The potential-energy curve, which is determined by both the Coulomb force and the applied field, has a maximum where the two forces balance. If the total energy is less than the maximum, the potential-energy curve forms a barrier to the motion of the electron. The horizontal line representing the total energy meets the potential-energy curve at both an inner turning point and an outer one. An electron at rest at the outer turning point would start to move radially outward, accelerated by the applied field. In classical physics an electron that is between the proton and the inner turning point is trapped forever by the potential barrier; it cannot escape unless its energy is boosted to a level higher than the top of the barrier.

When the quantum-mechanical distribution of charge is superposed on the energy diagram, the "tail" of the distribution extends beyond the outer turning point, which indicates that the electron can escape from the atom. The quantum-mechanical state is no longer a stationary state; sooner or later the electron will tunnel through the barrier and be carried away by the applied field.

Tunneling is the fundamental mechanism of field ionization. It also governs physical phenomena ranging from the radioactive decay of nuclei to the emission of electrons from a sharply pointed conductor. The lifetime of the electron (the average time for it to tunnel through the barrier) varies with the height of the potential barrier in a spectacular way. In the case of alpha-particle emission by a nucleus the lifetime ranges from microseconds to billions of years depending on the energy of the alpha particle. In the field ionization of a Rydberg atom the lifetime typically decreases by a factor of a million when the field is increased by only 20 percent.

The Rydberg atom is an ideal system in which to study tunneling because the lifetimes can be calculated precisely and can be varied simply by turning the knob that controls the applied voltage. In our laboratory we have measured the lifetimes of Rydberg states of sodium. The experiment is simple in concept. A Rydberg atom is formed in the applied field by a short laser pulse, and the time it takes for an ion to appear is measured by an electronic timer. The measurement is repeated thousands of times and the average lifetime is calculated. To avoid confusion no more than one atom is observed in each laser pulse. (As we mentioned above, single-atom experiments are quite practical.) Our results are in good agreement with theoretical predictions. We have found that the measured lifetimes are so sensitive to changes in the strength of the field that the lifetimes can be employed to determine the field with a high degree of accuracy.



TUNNELING OF AN ELECTRON through a potential-energy barrier is the quantum-mechanical mechanism that underlies field ionization. At the top left is a graph of the total energy (*solid line*) and the potential energy (*broken line*) of the electron in the hydrogen atom. The energy is graphed as a function of the electron's distance from the nucleus. The kinetic energy (the difference between the total energy and the potential energy) can never be negative in classical mechanics, and so the electron is confined to the region (*gray*) between the proton and the turning point (*A*), where the potential energy is equal to the total energy. According to classical physics, an electron moving away from the proton would come to rest at the turning point and then start falling back toward the proton; the electron cannot pass into the region beyond the turning point (*color*). At the top right the quantum-mechanical charge density is superposed on the energy diagram. The charge distribution has a "tail" that extends beyond the turning point, and so there is a finite probability of finding the electron in the classically forbidden region. At the bottom is the energy diagram for a hydrogen atom in an electric field. The potential-energy curve is determined by both the Coulomb-force field and the applied electric field, and as a result there are two turning points (*B, C*). At the bottom left is the situation in classical physics. An electron cannot go from the region between the proton and the inner turning point (*B*) to the region beyond the outer turning point (*C*) because it would have to pass through the forbidden region (*color*). The electron is permanently bound to the proton. The quantum-mechanical charge density at the bottom right shows that the tail of the charge distribution extends beyond the outer turning point. Therefore the electron can tunnel through the potential barrier and escape from the atom. That happens when the atom is ionized by an electric field.

Unlike atoms in strong electric fields, atoms in strong magnetic fields are not well understood. It is surprising that such an elementary problem in atomic physics remains unsolved. In the case of hydrogen the physical system (an electron, a proton and a magnetic field) is not complex and the equations that describe the system are simple. General methods for solving the equations have not yet been developed, however, and much of the physics remains a mystery. It is a mystery worth some effort to solve, because it will almost certainly lead to the discovery of interesting new phenomena.

An electric field tends to pull an atom apart, and when the field exceeds some critical strength, the atom simply ionizes. In contrast, a magnetic field squeezes an atom, which remains stable

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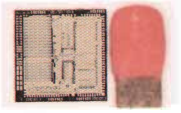

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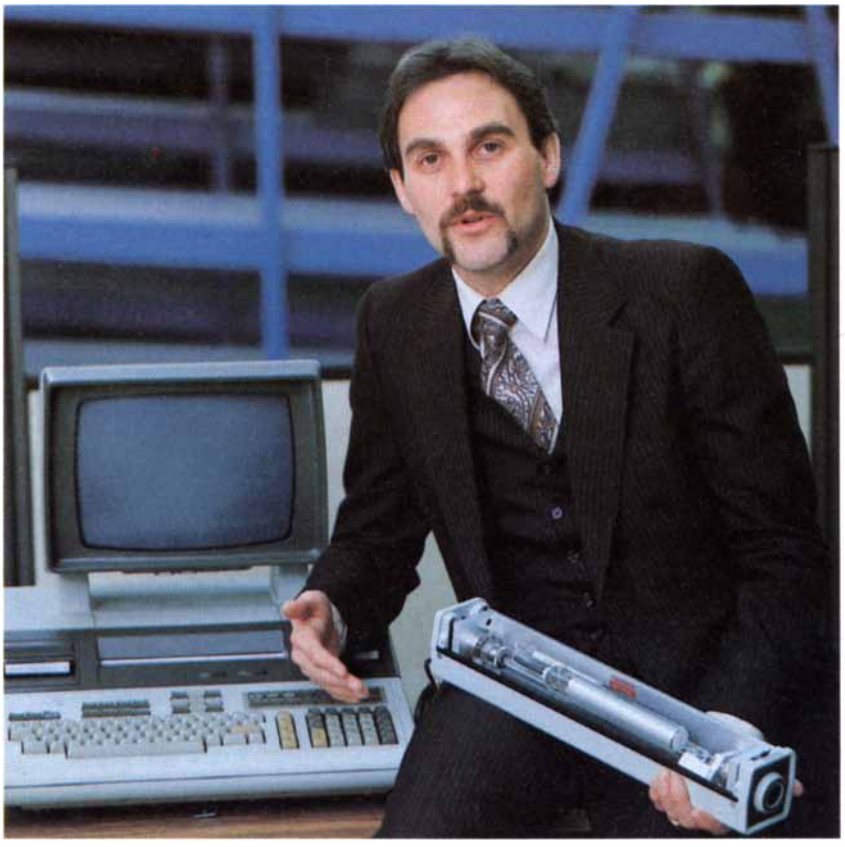

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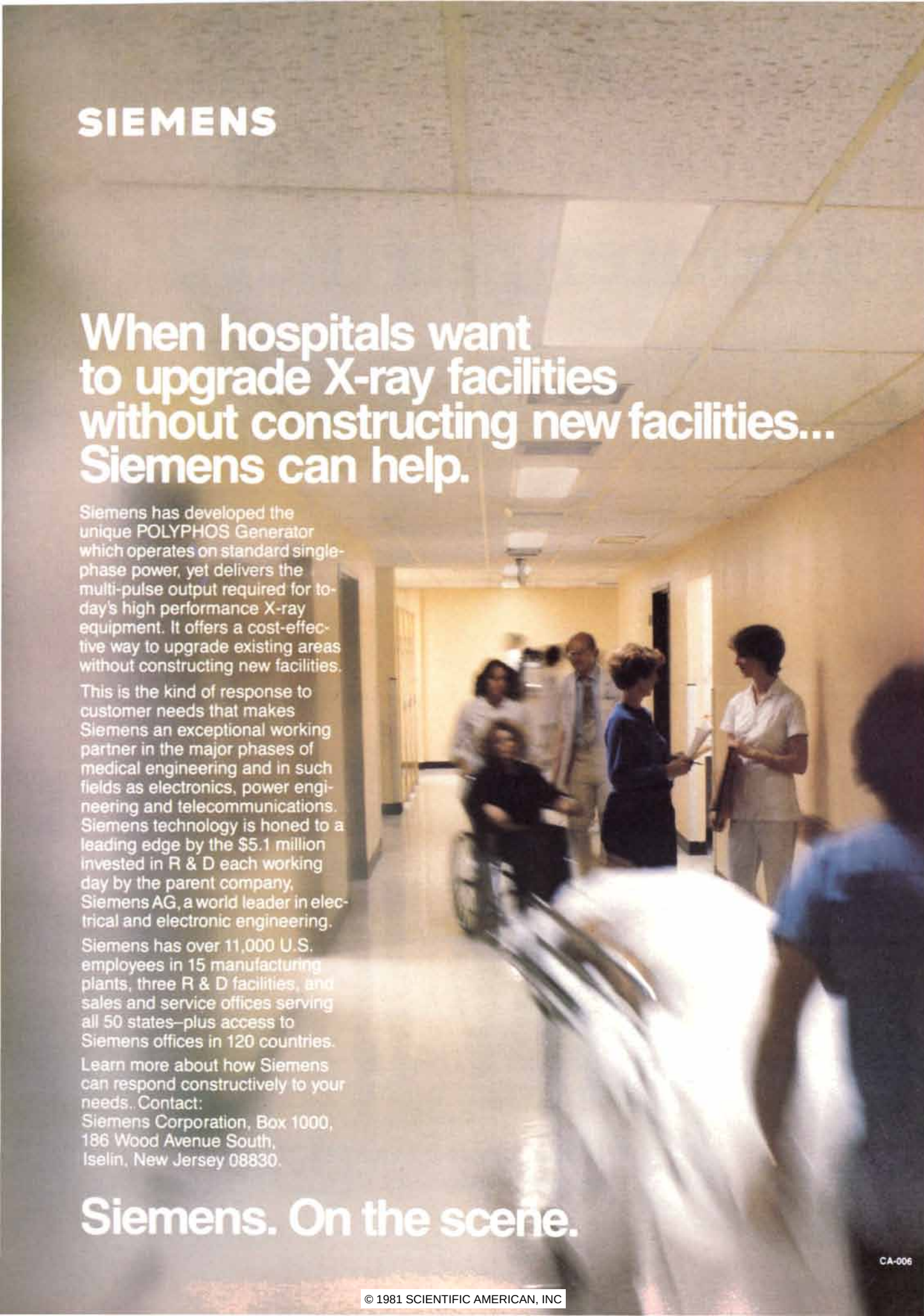

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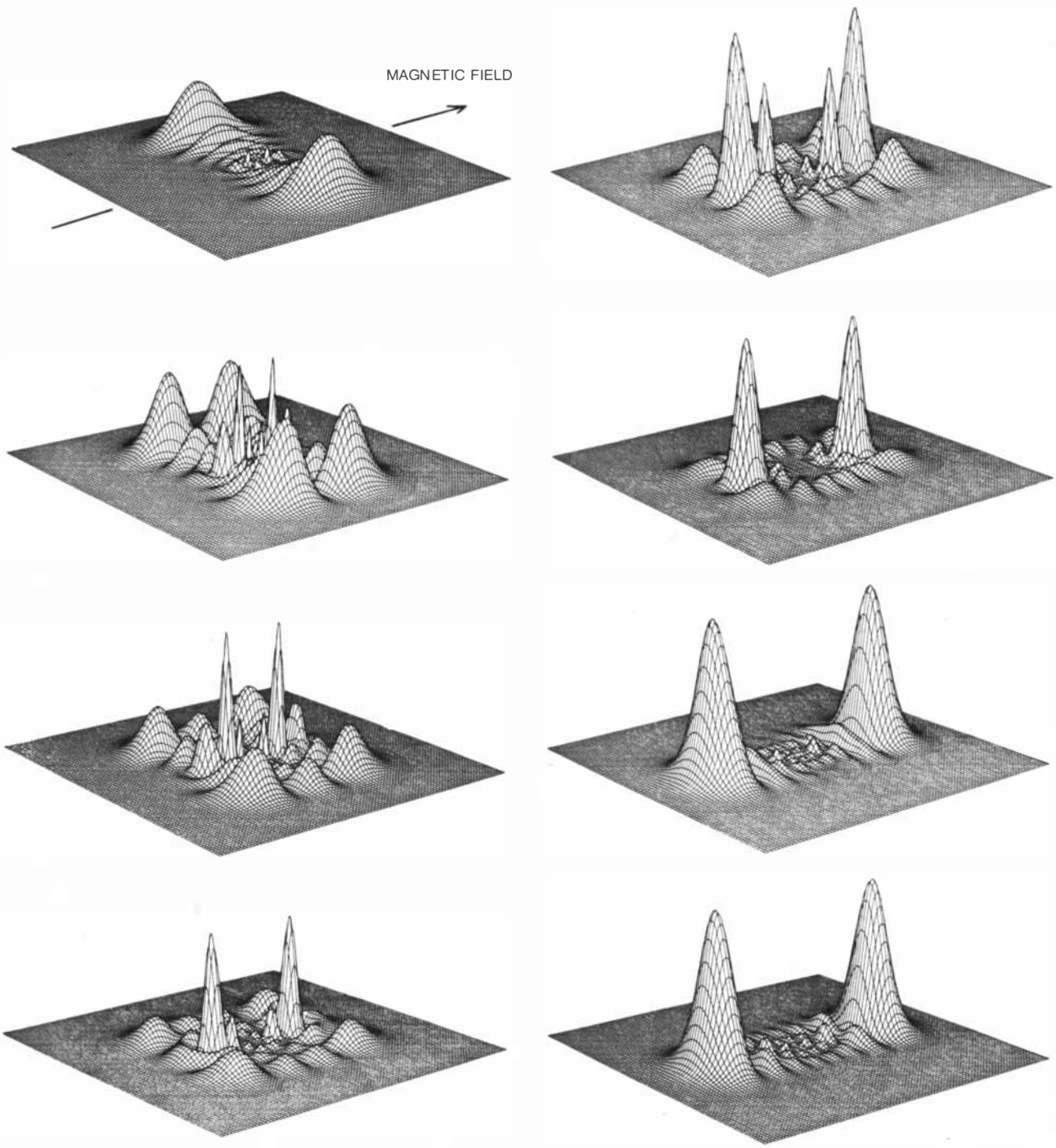
even in an arbitrarily strong field. Eventually the magnetic force exceeds the Coulomb force and the electron charge cloud assumes a new shape. Atoms under these conditions are sometimes called magnetic atoms.

Magnetic atoms are a tempting subject of study because their structure is quite different from that of ordinary atoms. They have not been studied in detail mainly because the magnetic field needed to convert a ground-state atom into a magnetic atom is more than 1,000 times as strong as the strongest field that can be created in the laboratory. Nevertheless, the subject has attracted considerable interest.

Some years ago it was discovered that when a solid-state analogue of the hydrogen atom called an exciton is put in a magnetic field, it exhibits the properties



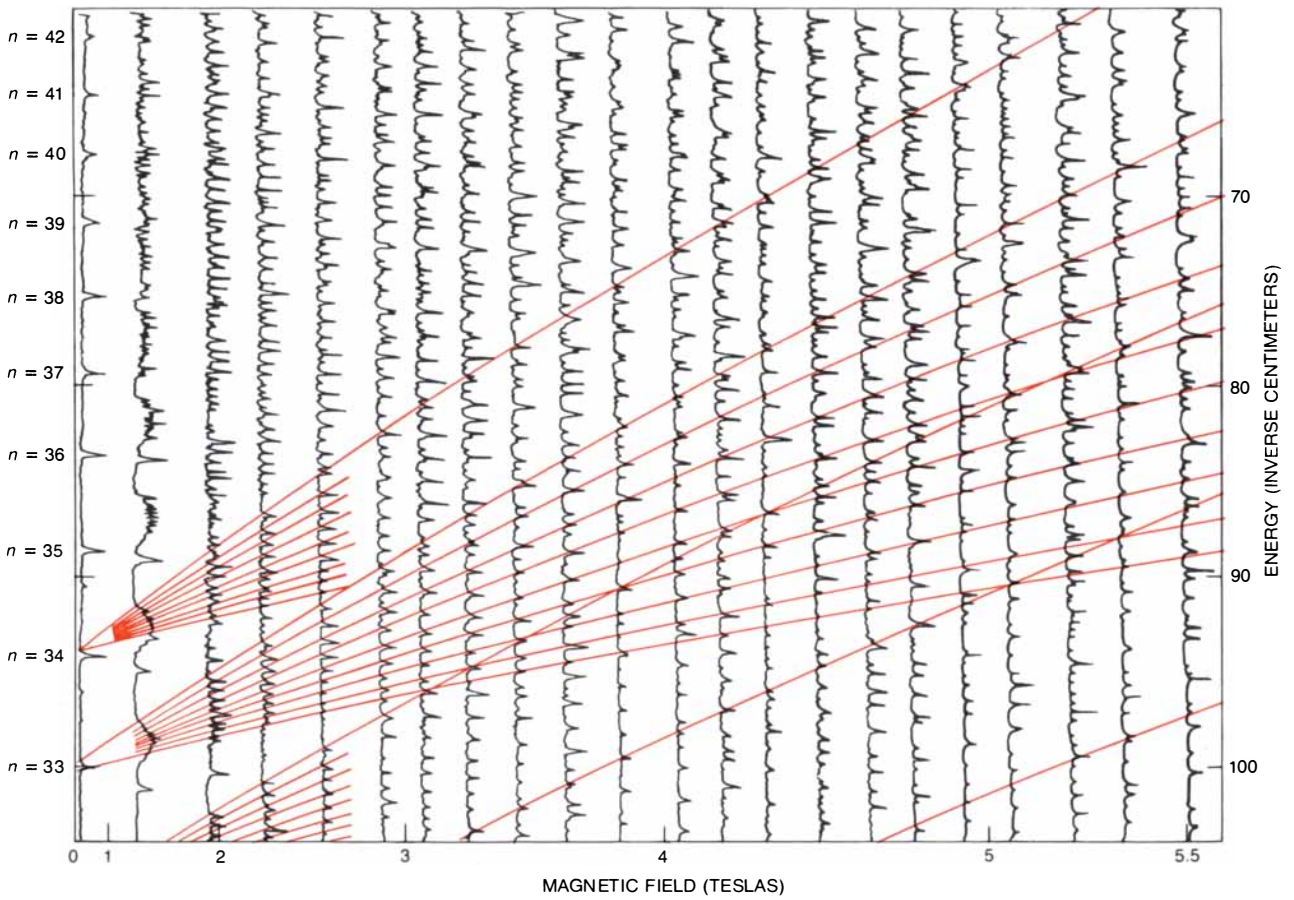
HYDROGEN IN A MAGNETIC FIELD can assume a third set of shapes for the family of $n = 8$, $m = 0$ states, where the angular momentum has a mixture of values from $l = 0$ to $l = 7$. (Other shapes for the same family of states are shown to the same scale in the illustrations on pages 132 and 140.) Little is known about the properties of atoms in a strong magnetic field. In the hydrogen atom the system is quite simple and the equations describing the system are easily stated, but no general methods for solving the equations are known. The difficulty in developing a general theory of magnetic atoms is in part that the nodal lines cannot be described by any known coordinate system. Near the proton the nodal surfaces are spherical because the Coulomb force dominates, but far from the proton the nodal surfaces are cylindrical because the magnetic force is more important. (The magnetic force is directed not toward the proton but to the axis of the field.)

of a magnetic atom. (Excitons are observed in semiconductors, where charge is carried both by electrons and by "holes," the positively charged voids formed by the absence of an electron. An exciton consists of a single electron and a single hole bound by the Coulomb force. Significantly, the exciton is an exceptionally large atom.) More recently astrophysicists realized that neutron stars (stars so dense that the electrons of their atoms have been squeezed onto the protons, neutralizing their electric charge) can have a magnetic field up to 10 million times stronger than the strongest field man can create. These discoveries have stimulated much theoretical work on the structure of magnetic atoms. Relatively little spectroscopic information has been obtained from excitons or from stellar objects with strong magnetic fields, so that much of the theory remains untested.

In the past few years magnetic atoms have been formed in the laboratory by applying a moderate magnetic field to Rydberg atoms. To understand the properties of Rydberg atoms in magnetic fields it is helpful to view atomic magnetism from the elementary perspective of the Bohr theory. Two magnetic interactions are associated with an electron in a Bohr orbit. (We shall neglect some small effects that are the result of electron spin and nuclear magnetism.) The first interaction comes from the orbital motion of the electron. An electron moving in an orbit is equivalent to a small current flowing in a loop of wire; the moving electron is a tiny electromagnet. The strength of the magnet, called the magnetic moment, is so small that even in a strong applied field the interaction is feeble. Nevertheless, the interaction can be detected: it causes the lines of the atomic spectrum to be shifted in frequency, although the shifts are so small that some skill is needed to observe them. They were first seen by the Dutch physicist Pieter Zeeman and are called the Zeeman effect.

The second magnetic interaction is a result of the law of electromagnetic induction formulated by Michael Faraday: A changing magnetic field gives rise to an electric field. If a magnetic field perpendicular to a loop of wire increases, the induced electric field causes a current to flow in the loop. The current is proportional to the area of the loop and is called the diamagnetic current. Similarly, the diamagnetic current induced in a Rydberg atom by an external magnetic field is proportional to the area of the orbit of the excited electron. Since the area of a Rydberg orbit increases as n^4, the diamagnetic interaction also increases as n^4. On the other hand, the electrostatic energy that binds the electron to the nucleus varies as $1/n^2$. Thus the ratio of the magnetic energy to the electrostatic binding energy increases as n^6. For $n = 30$ the ratio is almost a billion times larger than it is for $n = 1$. The ratio for $n = 30$ is so large that the magnetic force can no longer be thought of as a small perturbation to the electric force of the nucleus. On the contrary, it is the electric force that is the small perturbation.

The situation is actually more compli-



MAGNETIC STRUCTURE of a Rydberg atom is found by varying the strength of the applied magnetic field and recording the ionization signal. The energy-level diagram may seem chaotic, but actually it has strong regularities. The energy levels form families of smoothly varying curves. Colored lines have been drawn through several of the curves. The lines can be seen best by viewing the illustration diagonally from the lower left. The fact that the energy levels cross without any visible repulsion indicates there is an underlying symmetry in the system. The symmetry is not known, but if it could be identified, it might provide the key to a general solution to the magnetic-field problem. The data were gathered by Jarbas C. Castro and Randall G. Hulet of M.I.T. The horizontal scale has been made proportional to the square of the magnetic field because the interaction of the atom with the field is proportional to the square of the field.

cated. The magnetic force on the electron is huge when the electron moves perpendicular to the magnetic field, but it is zero when the electron moves parallel to the magnetic field. Therefore the magnetic force dominates motion in the plane perpendicular to the field, whereas in the third dimension (that is, in the direction of the field) the electric force reigns. As a result the motion is extraordinarily complicated and the present theoretical understanding of it is incomplete. It seemed to us, however, that a system as basic as an electron, a proton and a magnetic field should not be complex but simple. We decided to measure the energy levels of Rydberg atoms in strong magnetic fields in the hope that the data would lead to some new understanding.

We plotted the energy levels at numerous values of the magnetic field in much the same way as we took data in the case of an electric field. The results came as a pleasant surprise [*see illustration on opposite page*]. The energy-level map has so much structure that to the casual eye there is no rhyme or reason (as one might expect for some extremely complicated motion); actually, however, the map shows great regularities. If one views the energy levels from the proper perspective, a simple pattern emerges. Each energy level is shifted as the magnetic field increases, but the sequence of shifted levels forms a pattern of straight lines. Furthermore, the levels from different groups appear to cross freely. As we pointed out in our discussion of Stark structure, levels can cross only when there is some special symmetry in the problem. The existence of such a symmetry suggests that there is an underlying regularity in the motion. If we could identify the regularity, it should provide the key to a complete solution to the problem.

Our findings came as a surprise because no one has been able to identify a special symmetry in the magnetic-field problem, and it is widely thought that none exists. Our findings do not actually contradict this view, because we have found that the symmetry is not exact. If we examine not Rydberg states but low-lying states, the symmetry is conspicuously absent: the energy levels are disordered and the system looks discouragingly complex. The symmetry is never exact, but it becomes a better approximation as n increases. For the values of n we studied, the symmetry is exact for all practical purposes.

We are still searching for the symmetry and attempting to understand the implications of our findings. Whether or not we manage to solve the magnetic-field problem, the experiments have already taught us much. Apparently nature still has surprises in store even in the simplest systems, provided we make the effort to look.