Some Contemporary Advances in Physics—VIII
The Atom-Model, First Part[1]

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A. INTRODUCTORY REMARKS ABOUT ATOM-MODELS

MORE than any other word of the language, the word *atom* is implicated with the history of human speculations concerning the nature of things. It is introduced when people cease to content themselves with observing, and begin to philosophize. There are many of the fundamental and essential writings of the literature of physics in which it does not appear, or appears without warrant. These are the descriptions of things observed, the accounts of experiments, the records of measurements, on which the edifice of theoretical physics is founded. There are many articles of what is commonly called the "theoretical" sort in which it does not occur. Such are the papers on the motions of planets, on the vibrations of elastic solids, on the currents in electrical networks, on the courses of light-rays through optical systems—papers which are essentially descriptions, although they give the impression of being something greater and deeper because they relate to idealized cases, and are phrased in the laconic language of mathematics. When the word *atom* appears justifiably in a discourse, it means that the author has departed from the safe routine of describing observed and observable events, however selectively, however skilfully, however intelligently. It signifies that he has gone beyond the limits of observation, and has entered upon the audacious adventure of constructing by the side of the real universe an ideal one, which shall act as the real one does, and be intelligible through and through.

Atoms are the building stones of this art-world or image-world, which is intended to represent the actual world, imperfectly indeed for the time being, perhaps completely at some distant day. Some few experiments, it is true, prove (as well as anything can prove anything else) the existence of very minute particles of matter having the minute charges, the minute masses, the minute magnetic moments

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[1] This part, the first of two composing the article, is devoted chiefly to the facts of observation which the favorite atom-model of the physicists of today—the atom-model known by the names of Rutherford and of Bohr—is designed to interpret. A brief description of this atom-model is included; but the detailed account of the peculiar features, of the strange and important limitations which are imposed upon it to adjust it to all the phenomena mentioned, is reserved for the second part. Owing to the great quantity of information which it is desirable to present, the article needs all the benefit it can derive from a careful and obvious organization, and I have sacrificed fluency to a quite formal arrangement under headings and sub-headings.

which it is found expedient to ascribe to the atoms. These experiments are enormously important, for they invest the atom with a reality which nothing else could give it. To some they have given the hope that all the properties of the atom may one day be demonstrated unquestionably by direct evidence. There is little reason to expect that we shall see that day. The atom is no longer entirely a product of the scientific imagination; but neither is it entirely an object of experience. Most of its properties are invented, not discovered. Whether this invented and imagined entity is "real" is a difficult question. Perhaps it is best to evade such a question by asking the questioner what he means by "reality". As a matter of fact, it is not possible to discuss atomic theories thoroughly without raising and settling such formidable questions as, what is a theory? and, what is an explanation? and even, what is reality? perhaps eventually, what is truth? I do not aspire to answer these questions. But there are some common misconceptions about atoms which it is prudent to clear away at the beginning.

In the first place, one does not utter an atomic theory by saying that a substance is made up of small pieces, each exactly like a large piece of the substance in every respect except size. We should achieve nothing by saying that iron is made of black lustrous conductive magnetic atoms, or that glass is built of colorless transparent brittle insulating atoms, or that an apple consists of white soft sweet juicy atoms. The atoms must be endowed with fewer and simpler properties than the substance they are meant to compose, else they are futile. One must select some of the properties of the substance to be attributed to its atoms, and set the others aside to be explained by those.

Again, it is not obvious which properties should be selected for the atom; these depend largely on the fantasy of the atom-builder. However, certain qualities such as viscosity and plasticity, conductance for heat and conductance for electricity, opacity and transparency and lustre, warmth and flavor and fragrance, are not usually assigned to atoms. In general, the more a quality of a substance varies with its state, the less it is suited to be made an atomic quality. Ferromagnetism is a quality which one would assign almost instinctively to the iron atom; but it is possible to deprive iron altogether of this quality by a simple heat treatment, and hence it is not generally supposed to be a feature of the atom. But the rule is not an absolute one. The visible radiations from gaseous iron are supposed to be characteristic above all other things of the atom itself, yet they cease when the iron is condensed. It is supposed that in the condensed phases the atoms are so close together that they distort one another—a permissible idea if used with discretion, yet an atomic theory could easily become a meaningless form of words if this device were employed without limit. Of all the properties of matter, mass alone appears to be entirely exempt from change. For this reason all atom-models involve mass as an essential property of the atom; and this is the only respect in which they all agree.

Few and simple, therefore, must be the properties of the atom; yet we must not rush to the other extreme, and contrive atoms simplified into uselessness. The chemists know of eighty-eight different elements, sufficiently unlike to be distinguished; and we all know how great is the contrast between carbon and gold, hydrogen and lead, fluorine and helium. It is scarcely likely that such differences as these can be explained by atoms which are simply hard pellets differing only in size and shape and weight, like those of Lucretius and Newton, or by atoms which are abstract centres of force, like those of Boscovich. We are forced to invent atoms more complicated that these; and from this it is not far to say that we must imagine a structure for the atom; and from this scarcely farther to say that we must imagine an atom built of parts.

At this point we meet with a clamor from a number of excellent people, many of them otherwise quite innocent of Hellenic culture, who have it firmly fixed in their minds that *atom* is the Greek word for *indivisible*; whence they conclude that when the physicist speaks of subdividing his atoms, he is contradicting his own terms, he is violating the rules of his own game, and has forfeited his right to be heard.[2] The premise may be right, but the conclusion is absurd. If some of the properties of gold are explained by assuming it made of atoms with fewer properties, and later the explanation is improved and extended by assuming these atoms made of still smaller particles with still fewer properties, the second step is not less legitimate than the first. It may be contended, with some reason, that the name *atom* should be transferred at once to the smaller particles. At best this would be one of the changes which are desirable in principle but cause more trouble than they are worth. The contention is, however, weakened by the fact that some at least of the smaller particles of which we imagine gold atoms to be made are not imagined to be peculiar to gold, but are conceived as particles of a fundamental substance common to all elements. That the "atoms" of the many

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[2] I should have put this passage even more strongly, but that Schuster tells that Kelvin himself inveighed on one occasion against the idea of subdividing atoms. He was answered by a young man who said, "There you see the disadvantages of knowing Greek." This seems as good an answer as any.

elements should be systems of "atoms" of one or a few fundamental materials is a thoroughly pleasing idea, although at present an unrealized ideal. It is unknown how far our descendants will find it expedient to dissect the atom; but it is certain that they will not be stopped by etymology.

Another fact about atom-models is that they are not always displaced by their successors; several may and do persist side by side, each adapted to a certain set of facts and observations. Every atom is designed in view of a very small fraction of the available knowledge about properties of matter; and this applies to the latest model as well as the earliest. The chemists of the nineteenth century were most impressed by the immutable weight of matter and by the laws of chemical combination; hence their atoms were merely weighted particles equipped with hooks to catch the hooks of other atoms. To the physicists of fifty years ago the physical properties of gases seemed the easiest phenomena to interpret, and they imagined atoms as rigid elastic spheres with radii of some 10^{-8} centimetre; by the masses and motions of such atoms they explained the pressure, elasticity, viscosity, diffusion and specific heats of gases. The physicists of the next generation attended chiefly to the emission, the refraction, the dispersion of vibratory radiations by luminous gases, and conceived the atom as a framework holding vibrators, like a belfry with a carillon of bells. This third model is inferior to the second in explaining the properties of gases, inferior to the first in explaining the laws of chemical combination; each of the three is superior in its own field to the atom-model to which this article is chiefly devoted, and which in its turn is primarily adapted to a field of its own. Still other atom-models have been devised, endowed with other properties, to account for other phenomena; and it is altogether probable that many more will be presented before the eventual one is attained, if it ever is. For instance, we may some day behold an atom-model devised to explain the conduction of electricity in solids, very competent in its field and quite unlike these others. In the eventual atom-model the essential qualities of all of these, and of many others, must be happily combined; it does not matter about the inessential ones.[3]

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[3] Now and then an article appears in a physical or chemical journal, in which an oddly unconventional atom-model is proposed to interpret some such property of matter as the thermoelectric effects, or supra-conductivity, or valence, or some other with which the Rutherford-Bohr atom-model has not as yet been matched. It is easy for a physicist to ignore such articles, on the ground that any model departing from that of Rutherford and Bohr must be wrong. This is certainly a mistaken policy. Any partially competent atom-model deserves to be examined with care; its essential features must reappear in the eventual model. But, of course, the essential feature is not always the conspicuous one.

In awaiting that eventual atom-model, it is best to regard the atoms of the present day as mutable and transitory. Like railway time-tables, atom-models should be inscribed "subject to change without notice." Nothing is irrevocable in physics, except the record of past events; and we who have seen the undulatory theory of light assailed and shaken may well hesitate to put unquestioning faith in any atom-model. Even if there is no danger of change, it is a virtue to keep data and theories sharply separated in one's mind. In no field is this more difficult and important than in the field of this article, where the very language used to describe the data is saturated with the spirit of a particular conception of the atom, and it is customary to expound the theory before the facts. For these reasons I shall go to the opposite extreme, and treat the contemporary atomic theory with an exaggerated reserve which in many places will seem excessive to the reader and in some to the writer himself.

The favorite atom-model of the physicists of today is a structure of electrons, congregated about a positively-charged nucleus. The data which this atom is designed primarily to interpret were discovered before 1913, or else since 1913 by methods developed before that time. These discoveries are due largely to Rutherford, whose name the model often bears. The sections of this article which are labelled *B*, *C* and *D* are devoted to these data, and to the inferences from them. In 1913 a great change in the situation was wrought by a brilliant idea of Niels Bohr. Bohr did not discover new data; he taught a new way of interpreting old ones, he showed men how to read spectra. Through this interpretation of spectra, and through data which were discovered by men inspired with his idea, a previously-unknown property of matter was disclosed. This is expressed by saying that each atom possesses many distinct Stationary States. The largest section of this First Part of the article, the section *E*, is devoted to the knowledge of these Stationary States. Had these been discovered earlier, an atom-model might have been devised to explain them and them alone. Rutherford's atom-model was already in the field, and it was modified so that it might interpret the new knowledge. To these modifications, of which some are of a remarkable simplicity and beauty, the Second Part of this article will be devoted.

B. THE ELECTRON[4]

The *electron* is the atom of negative electricity. An individual electron can be captured upon a droplet of oil or mercury, or a minute

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[4] This section is drastically curtailed, for the chief facts about the electron should by this time be common knowledge. Millikan's book "The Electron" (now in its second edition) may be consulted.

solid particle, and the amount of its charge determined. This amount is $4.774.10^{-10}$ in electrostatic units, according to Millikan. It is designated by the symbol e. When a magnetic field is applied to a stream of electrons all moving with the same speed, the electrons are deflected all to the same degree, which shows that they all have the same mass. This mass is practically equal to 9.10^{-28} in grammes, unless the electron is moving at a very uncommonly high speed, in which case it is appreciably greater.

These facts of experience are about all that is definitely known or needs to be known about the electron, in order to appreciate its role in modern atomic theory. There is no good way of determining its size, although the length of its mean free path in certain gases indicates, perhaps definitely proves, that it is much smaller than an atom. If the electron is a spherule of negative electricity uniformly dense, then its radius cannot be less than 2.10^{-13} cm, for if it were, the electromagnetic mass of the spherule would exceed the observed mass of the electron.[5] This size is much smaller than the one which it is expedient to attribute to the atom, happily for us, since otherwise it would be difficult to conceive of atoms containing electrons.

Since electrons can be coaxed or forced out of substances of every kind—elements and compounds, metals and non-metals, liquids and solids and gases—the atoms are supposed to contain one or more electrons apiece. This argument was formerly fortified by the fact that the light emitted from glowing gases is in many respects such as oscillating electrons would emit. This second argument is for the present under a cloud.[6]

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[5] This is a short way of saying that, if the electron were a particle of smaller radius than 2.10^{-13} cm., more energy would have to be supplied to it to increase its speed than is actually required. For, in order to set an electrified particle into motion, energy must be supplied to build up the magnetic field which surrounds a moving electric charge; this energy U is additional to the kinetic energy $\frac{1}{2}mv^2$ required to set the mass m associated with the charge into motion with speed v, and it may be regarded as the kinetic energy associated with an extra "electromagnetic" mass $2U/v^2$ which the particle possesses by virtue of its charge. This quantity $2U/v^2$ can be calculated, for a given size and shape of the electron; if we make the electron too small, $2U/v^2$ comes out larger than its observed mass, which is a *reductio ad absurdum*. This illustrates the rather surprising fact that we are not permitted to imagine the electron as an infinitely small particle, a mere geometrical point loaded with an infinitely concentrated charge and mass. Speculations about its size and shape and the distribution of charge within it are not necessarily trivial; some may even be verifiable. We also meet with this dilemma: how does the electron, a piece of negative electricity of which each part should repel every other, keep from exploding?

[6] Perhaps I ought to mention that F. Ehrenhaft of Vienna has been ardently contending for about fifteen years that there is no such thing as an electron. He maintains that he can demonstrate negative charges much smaller in amount than

C. Positively-Charged Particles Accepted as Atoms[7]

Positively-charged particles are found in abundance in gases in which an electrical discharge is or has lately been maintained, and they may be produced under well-controlled circumstances by pouring a stream of electrons with properly-adjusted speeds into a gas, and in other ways. Only the ratio of the charge to the mass can be determined for these particles, not the charge individually nor the mass individually. But particles of apparently the same substance show distinct values of this ratio, which stand to one another as the numbers 1, 2, 3, . . . and the intermediate values do not occur. This supports the quite natural idea that these particles are atoms which have lost one or two or three or more of their electrons. If we make this supposition, we thereby assume values for the charges, and can calculate the masses of the particles from these and the observed values of the charge-mass ratio. The masses lie between 10^{-24} and 10^{-21} (in grammes) for particles occurring in the vapors of the various chemical elements, and they lie in the same order as the combining-weights of the chemical elements. This is powerful testimony that the particles indeed deserve the name of "atoms".

There is one sort of positive particle for which the charge can be measured directly. This is the alpha-particle, which cannot be produced at will but is supplied by Nature from radio-active substances. Counting the number of these particles emitted from a bit of radioactive substance in a given time, and measuring the total electrical charge lost by the substance in the same time, and dividing the latter figure by the former, Rutherford and Regener obtained the charge of the alpha-particle, which is twice the electron-charge (with reversed sign) within the limits of experimental error. This suggests that the alpha-particle is an atom of something or other, which has lost two electrons. As an evacuated tube into which alpha-particles are admitted is presently found to contain helium, the "something or other" is supposed to be helium. The mass of the alpha-particle can be determined directly from its charge and charge-mass ratio. It amounts to $6.60 \cdot 10^{-24}$, and this agrees with the mass inferred in the foregoing way for the positive particles found in helium.

$4.774 \cdot 10^{-10}$. Anyone interested in his case may find it presented in the April, 1925, number of the *Philosophical Magazine*. The question is for experimental physicists to discuss; but it is not likely that the edifice of modern physics is liable to be ruined by a flaw at its very foundation, such as this would be.

[7] The material of this section may be found much more extensively presented in my fourth article, in which I have also written about isotopes, a subject omitted here for the sake of brevity.

The alpha-particle is supposed, like the electron, to be much smaller than an atom; partly because it can go through a thin sheet of metal, chiefly because of evidence to be expounded in the next paragraph.

Collisions between alpha-particles and other particles of similar mass are occasionally observed; the mass of the struck particle can be deduced from the directions in which it and the alpha-particle fly off after the impact, assuming only that conservation of momentum and conservation of kinetic energy prevail during the impact. In this way it is possible to determine the masses of tiny particles (presumably atoms) of hydrogen, helium, oxygen and nitrogen (perhaps eventually of other elements) in terms of the mass of the alpha-particle, which is determined from its charge-mass ratio and its charge, which are determined directly. If all the properties of the elements could be explained by atoms possessing no features except charge and mass, all the foundations of science might be laid down already.

The alpha-particle is one of the most valuable and powerful instruments in the physicist's equipment. It is a sort of hyper-microscope, penetrating and revealing the arrangements of systems so minute that microscopic objects are universes compared with them. Rutherford's development of the technique of using the alpha-particle is to be ranked among his greatest works.

Positively-charged particles with masses as low as that of the electron have never been observed; the least massive of the known positively-charged particles has 1,840 times the mass of the electron.

D. THE NUCLEAR ATOM-MODEL

Since we have met with positively-charged particles which are accepted as atoms deprived of one or more of their electrons, and since these incomplete atoms are much greater in mass than the electrons, it is natural to suppose that the completed atom consists of a positively-charged particle or *nucleus* in which almost its entire mass is concentrated, and one or more electrons which compensate the charge of the positive particle but add little to the mass of the atom. If we further suppose that the dimensions of the electrons and of the positively-charged particle are small in comparison with the distance between them, we invent the *nuclear atom-model.*[8]

The direct evidence for the nuclear atom-model consists of a very

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[8] Commonly known as the Rutherford atom-model, after the physicist who invented it and discovered most of the evidence for it; occasionally as Nagaoka's, after another physicist who suggested it; occasionally as the Saturnian model, as some have supposed that the electrons lie in flat rings around the nucleus like the rings of Saturn around that planet.

small but a beautiful and convincing series of experiments, of which the first and the most were performed by Sir Ernest Rutherford and his pupils.[9] These experiments are designed to show that the orbit of a minute charged particle (usually an alpha-particle), flying through a thin film of metal, is in certain cases very like the hyperbolic orbit of a comet around the sun. Such an orbit is the path of a particle moving near to an immobile particle, for instance a light particle moving close to a much more massive one, which attracts it or repels it by a force varying inversely as the square of their distance apart. If these experiments show what they are designed to show, then they indicate that the atom includes a particle much more massive than an electron, bearing an electric charge, and sufficiently isolated from the other charges in the atom (such as the electrons) so that its field of force in a measurable space around it is not disturbed by theirs. We cannot, however, trace the entire path of an individual flying charged particle as it swings around through an atom, and are forced to make up for this deficiency by a statistical study of the visible portions of the paths of a great multitude of charge particles.

Let us consider exactly what these experiments show; for whatever they do prove is the most securely proved of all the beliefs about atoms. In the first place, they show that there is a nucleus; and a vacant space surrounding it, in which an inverse-square force centred upon the nucleus prevails; and they indicate the dimensions of this vacant space. This commences within 10^{-12} cm. of the nucleus, which is another way of saying that the diameter of the nucleus is less than 10^{-12} cm.; and it extends beyond a distance given (to take instances) as 14.10^{-12} cm. for platinum and 10^{-9} cm. for argon, which is another way of saying that nearly all of the negative charge of the atom lies still farther out from the nucleus. If the negative charge is indeed subdivided into electrons, then the atom is formed like a hollow cloud of electrons, with a massive positively-charged nucleus at the centre of the interior hollow.

The diameter of this cloud of electrons is not furnished by the experiments on alpha-particle deflections; but considering that the distance between adjacent atoms locked into a crystal lattice is generally a small multiple of 10^{-8} cm., it cannot be much greater than 10^{-8} cm. unless we are prepared to admit interpenetration or violent distortion of atoms; nor does it seem likely that the diameter is very much smaller than this amount. I have already mentioned that some of the properties of gases are adequately explained by assuming

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[9] For the mathematical theory of these experiments, the second article of this series may be consulted.

that the atoms are elastic rigid spheres with a diameter of about 10^{-8} cm. Unlike as an elastic rigid sphere and a cloud of electrons seem, this agreement between so differently made estimates is probably no mere coincidence. It will be noticed that all of the figures about sizes at which we have arrived in such various ways (diameters for the electron and the nucleus, for the vacant space inside the electron-cloud, for the entire atom) are quite compatible with one another. If the value derived for the diameter of the interior hollow had been ten times the spacing of atoms in a crystal, or a tenth the diameter of a spherule of electricity with the same electromagnetic mass as an electron, we should indeed be in trouble.

In the second place, these studies of the deflections of alpha-particles yield numerical values for the nuclear charge: $(77.4\pm1)e$ for platinum, $(46.3\pm0.7)e$ for silver, $(29.3\pm0.7)e$ for copper, $19e$ for argon, $6.5e$ for "air" (a sort of statistical average of the values for oxygen and nitrogen).[10] To these must be added the value $+2e$ for the nuclear charge of helium; for we have already seen the evidence that the alpha-particle is what is left of a helium atom when two electrons are removed, and these last-cited experiments show that it is itself a nucleus, hence a helium nucleus. This nuclear charge must be balanced by negative charges within the atom; if this balancing negative charge is subdivided into electrons, then the numerical factors of e occurring in these numerical values are equal respectively to the number of electrons belonging to each atom. We thus have fairly accurate estimates of the number of constituent electrons within each of four or five atoms.

These estimates agree, within their experimental uncertainties, with the famous and splendid idea of van den Broek and Moseley: that the number of electrons in each atom, and the nuclear charge measured as a multiple of the electron-charge, "is the same as the number of the place occupied by the element in the periodic table". This idea is also supported by rough measurements of alpha-particle deflections by a few other atoms, and by the extent to which different atoms scatter X-rays; but the most important of the additional evidence will find its appropriate place in the second section of this article.

These conclusions are almost all that can be deduced from the data. The arrangement of electrons within the electron-cloud is almost

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[10] References for these data are given in the fourth article of this series. The data obtained by E. S. Bieler (Proc. Roy. Soc., 105A, pp. 434–450, 1924) show incidentally, if I do not misread his article, that the nuclear charges of Mg and A1 have the desired values $12e$ and $13e$, respectively, within a few per cent. Rutherford's studies of encounters between alpha-particles and hydrogen atoms prove a nuclear charge of e for the latter.

entirely concealed. It is not altogether inaccessible; for the deflections suffered by alpha-particles and electrons flying through atoms are influenced by the electrons of the atom, not by the nucleus exclusively; and from the degree in which the observed deflections differ from what the nucleus alone would compel, it is possible to draw some conclusions about the way in which the electrons are arranged. The mathematical difficulties, as the reader will readily admit, are tremendous; the problem of determining the path of a flying electron through a cloud of electrons, probably themselves in motion, is enough to make the best of mathematicians despair; yet some progress in this direction has already been achieved, as I narrated in the second article of this series. Again, the scattering of X-rays by atoms should depend on the manner in which their electrons are arranged; and some measurements and some deductions have already been made, although the researches have been in abeyance for some years, probably because the newest discoveries about X-ray scattering make it extremely doubtful what the mechanism of the effect really is.

The study of deflections of alpha-particles by atoms has thus brought precious guidance to the atom-builder, and imposed severe limitations upon him, yet only partial ones. He is constrained to erect his atom according to certain fundamental rules, and yet has an extremely free hand in arranging the details. He is practically compelled to build the atom of an element which occupies the Nth place in the periodic system, out of N electrons and a much more massive nucleus with a positive charge Ne. The data which I have cited do not absolutely enforce these numerical values; but there is no other model which they permit which could possibly rival this one in respect of convincing simplicity. He may not make the electrons go more than a few times 10^{-8} cm. from the nucleus; he is constrained to leave a small vacant space around the nucleus, and within this space he may not tamper with the inverse-square law of force (a restriction which has eliminated several favored atom-models of the decade before 1910).[11] Having conformed to these restrictions he

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[11] Except that he may and must alter the inverse-square law of force to just the extent that further and more delicate experiments of this type require. Thus Bieler (*l.c. supra*) concludes, from a study of deflections of alpha-particles passing close to the nuclei of aluminium atoms, that within about 10^{-12} cm. of the aluminium nucleus the inverse-square repulsion which it exerts upon an alpha-particle is supplemented by an attractive force—perhaps an inverse-fourth-power attraction, just balancing the repulsion at a distance of $3.44 \cdot 10^{-13}$ cm. from the centre of the nucleus. Rutherford earlier found anomalies in the encounters between hydrogen nuclei and alpha-particles, which suggested to Darwin that the latter might be considered as a disc-shaped hard particle, or an oblate spheroid of semi-axes 4.10^{-13} and 8.10^{-13} cm.; this would repel hydrogen nuclei according to the inverse-square law so long as it did not actually strike them.

may do very nearly as he pleases with the electrons and the region they occupy. No data can be invoked to support him nor to confute.

Having expounded the merits of the nuclear atom, I will proceed to undo my work in part by pointing out its great and grave defect. No less a defect than this, that it is impossible. It cannot exist. Even if it were brought into existence miraculously at an instant, it could not survive, for it carries the seeds of its own dissolution within itself. For if at that initial instant all of the electrons were at rest relatively to the nucleus, they would immediately start towards it, fall into it, and expire. Of course, this consequence is so obvious that the notion of stationary electrons would not even occur to anyone having a bowing acquaintance with mechanics. Such a person would immediately assume that the electrons were in motion around the nucleus as the planets are around the sun; he would convert the nuclear atom-model into what I might call a *sun-and-planets atom-model,* the nucleus playing the role of the sun, the electrons those of the planets. Such an idea is alluring in the extreme; it implies that Nature acts similarly in great things and in small, copying the solar system within the atom; and this is most acceptable, partly because of its philosophical beauty and partly because it enables us to use the intellectual methods and habits acquired in the study of astronomy, relieving us of the labor of acquiring new ones. Unfortunately it is as untenable as the idea that the electrons stand still. For owing to the radiation of energy which continually goes on from accelerated electrified particles, an electron cannot describe a circle or an ellipse about a nucleus, as a planet may about the sun; it can only describe a narrowing spiral, ending in a collision between electron and nucleus. The nuclear atom is not stable nor enduring; and the dilemma is complete.

The only recourse is to make some entirely new and unprecedented assumption; for instance, that the electrons, in spite of everything, can stand still in certain positions without falling into the nucleus; or that they, in spite of everything, can revolve interminably in certain closed orbits without spiralling into the nucleus. Such a modification of the nuclear atom is, of course, essentially a denial of it. An atom composed of masses and electrostatic charges, plus certain restrictive rules or arbitrary assertions, is no longer simply an atom composed of masses and electrostatic charges. Instead of giving to our ultimate particles a few properties selected from among the ones which matter *en masse* displays to our senses or our instruments, we have to invent some new ones for them. This seems regrettable, but only because our expectations were too high.

Another circumstance leads us to another dilemma. Suppose that we could circumvent that difficulty about the revolving electron, which radiates part of its energy at each revolution and slides down a spiral path into the nucleus; suppose that we could find justification for saying that no radiation occurs, that the electron like a planet may revolve forever in an ellipse. If two atoms collided, as in a gas they must very frequently do, would not the electrons all be disarranged, disorganized, flung over from one orbit into another? This we should certainly expect; yet if it happens, no two atoms in a gas can be exactly alike, nor can any atom retain its character for more than a fraction of a second. If this is so, then the various sharply-defined properties of a gas must, each and every one of them, be statistical properties—not themselves properties of individual atoms, but the results of other properties of individual atoms, held in different amounts by different atoms and all averaged together. In some cases this is unobjectionable; the pressure and the temperature of a gas are sharply definite properties, resulting from the mass and the motion of the atoms, and the latter of these properties is not necessarily the same for any two atoms at the same moment nor for any atom at different moments. But one would be reluctant to treat the spectrum of a gas as such a property; according to all the traditions of physics this is one of the properties of the individual atoms. But the spectrum is very constant, sharp, immutably defined; we must therefore assume either that it depends only on the number of electrons in the atom and not upon their motion nor position, an idea which would be difficult to carry through; or that the electrons are ineluctably constrained to certain orbits or certain positions, so that the atom retains its personality and its character.

We have now made the acquaintance of two ideas which will be exceedingly prominent in the second division of this article. The nuclear atom-model is of itself unstable; therefore stability must be enforced upon it by outright assumption, it must be made stable by fiat. But this stability may not be extended to all conceivable arrangements or configurations of the model; it must be reserved for one or a few, that the atom may possess a fixed character and a personality.

We now arrive at the phenomena by means of which these vaguely-expressed ideas are to be sharpened and hardened into definite doctrines.

E. The Stationary States

E 1. *The Direct Evidence for the Stationary States*

Imagine a tube filled with gaseous helium, and containing a hot filament from which electrons emerge. By means of an accelerating potential applied between the filament and a fine-meshed gauze close in front of it, the electrons are speeded up, and pass through the gas with an energy which is accurately controlled by the accelerating-potential. A third electrode is maintained at a potential only slightly higher than that of the filament. To reach this electrode, the electrons must sacrifice nearly all of the energy which they acquired in coming up to the gauze. If they lose little or no energy in their progress through the gas, they can win their way to the third electrode, like water rising again to the level of its source. If, however, they lose a notable amount of energy to the atoms with which they collide, they cannot reach the third electrode, as water which has turned a mill-wheel cannot climb again to the level whence it fell.

By measuring the current into the third electrode in the helium-filled tube, it is found that if the electrons have an amount of energy lower than 19.75 equivalent volts, they lose scarcely any of it in their progress through the gas; but if the energy of an electron is just equal to 19.75 equivalent volts, it may and frequently does lose its energy altogether; and if the energy of an electron surpasses 19.75, it may and frequently does surrender just 19.75 equivalent volts to the gas, retaining the residuum itself. Imagining that the electron collides with atoms of helium on its way across the gas, we conclude that the helium atom can receive exactly 19.75 of these units of energy, no lesser quantity and (within certain limits) no greater. From similar experiments it appears that the mercury atom can receive 4.66 equivalent volts of energy, no smaller amount and (within certain limits) no larger. It appears that the sodium atom can receive 2.1 equivalent volts, no less and (within certain limits) no more—and the list can be extended to some thirty elements.

Another way of saying the same thing is this: the helium atom may exist (at least transiently) in its normal state, *or also* in a second state in which its energy is greater by 19.75 equivalent volts than in its normal state,—but not, so far as we can find evidence, in any state with any intermediate value of energy. Let us call this second state an "excited state." The mercury atom then has, in addition to its normal state of undefined energy, an excited state of energy greater by 4.66 equivalent volts. The sodium atom has, in addition to its normal state, an excited state of energy greater by 2.1 equivalent volts—and so with a number of others. I give these and a few other values in the following table:

TABLE I

	He	Ne	Na	Cs	Mg	Hg
Energy-value of the						
Normal state	0	0	0	0	0	0
First excited state	19.75	16.65	2.1	1.45	2.7	4.66
Other excited states	20.55	18.45			4.4	4.86 5.43 6.7
Ionized atom	24.5	21.5	5.12	3.9	7.6	10.4

It will be noticed that values are given for several excited states in the same column; these rest upon evidence of the same sort as does the first excited state, so that in general the atom must be considered to possess not one only, but several possible states in addition to its normal state.

It will be noticed also that values are given for the "ionized atom." These are the amounts of energy just sufficient (when applied by means of an impinging electron) to detach an electron from the atom. When electrons with so much energy or more are poured into the gas in question, positively-charged particles, such as I previously mentioned and characterized as the residues of atoms deprived of an electron apiece, appear in it. It is not absurd to call this an "excited state." If it takes just 24.5 equivalent volts of energy to detach an electron from a helium atom, then the system formed of an ionized helium atom and a free electron has a potential energy of 24.5 equivalent volts. Any experiment, therefore, in which the energy required to detach an electron from an atom is measured—any experiment for determining the *ionizing-potential*, as this energy when expressed in equivalent volts is called—is essentially an experiment for locating one of the excited states of the atom.

In this sense the energy-values of the last line in Table I are to be taken. I introduce them here for two reasons. In the first place, the fact that this energy-value is greater than any of the others in the same column suggests this interpretation for the excited states: that they correspond each to a certain *partial* lifting-out of an electron, to a certain stage of *incomplete separation*, while the energy-value of the ionized atom corresponds to the *total* lifting-out or to the *complete separation*. This idea is fortified by the fact that a helium atom may be ionized by two consecutive blows from electrons each with

20 equivalent volts of energy, if the blows fall closely enough together—as if the energy spent in raising the atom to its first excited state were paid into account, and could be used toward detaching the electron when the deficiency is supplied. This fact is exceedingly important for the theory, and I mention it here as a passing anticipation. In the second place it is desirable—for a reason which will presently appear—to measure the energy-values of the normal and of the excited states not from the energy of the normal state, as I have done in Table I, but from the energy of the ionized atom as zero-value. This is done in Table II.

TABLE II

	He	Ne	Na	Cs	Mg	Hg
Energy-value of the Ionized atom......	0	0	0	0	0	0
Non-ionized atom					−3.2	− 3.7
Excited states....	− 3.95	− 3.0				− 4.97
						− 5.54
First excited state.	− 4.75	− 4.85	−3.0	−2.45	−4.9	− 5.74
Normal state.....	−24.5	−21.5	−5.1	−3.9	−7.6	−10.4

With this convention, all the energy-values for the non-ionized atom become negative—a source of confusion, but not of nearly so much confusion as the previous convention would eventually entail. It is well to remember tenaciously that, in at least nine cases out of ten in the literature, the energy-values of the normal state and the excited states are referred to the energy of the ionized atom as zero, and that they all should always bear the minus sign, though generally it is left off.

For the excited states and for the normal state, I will employ the common general name of *Stationary States;* occasionally, for the sake of variety, the alternative name *levels.* Another common word is *term*, the origin of which will appear in the next section.[12]

As the reader will be forced to make himself familiar with schematic representations of the Stationary States, he may as well begin at once with a simple one. Fig. 1 is a diagram showing the stationary states listed for helium in the foregoing tables. The levels are represented by horizontal lines, separated by distances proportional to the

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[12] Anyone who reads the physical literature of today soon becomes familiar with the phrase "the electron is in the . . . orbit" used instead of "the atom is in the . . . state." This phrase expresses theory rather than facts of observation, and does not always express theory adequately; I have avoided it in this article.

differences between their energy-values (usually, however, these distances are distorted for convenience). The energy-values, expressed in equivalent volts, are affixed to the lines; on the left, they are measured from the normal state of the neutral atom as zero of

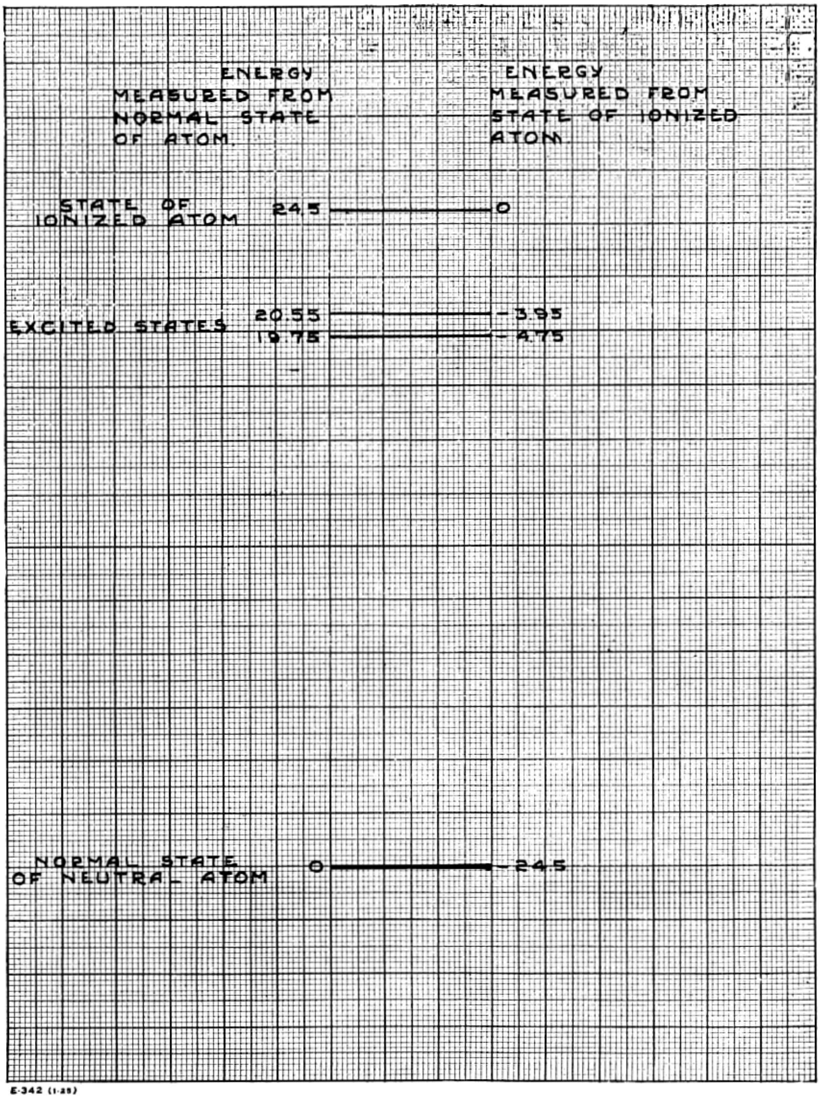

Fig. 1—Diagram of the stationary states of helium, determined by the method of electron-impacts

energy; on the right, they are measured from the state of the ionized atom (which is the more common practice)[13].

E 2. *Bohr's Interpretation of Spectra*

In 1912, the evidence to which the foregoing section is devoted was still entirely undiscovered, the Stationary States were unknown. That evidence was sought and found because Niels Bohr had divined the Stationary States in developing a new and brilliant interpretation of spectra. Until then, all physicists had wished to interpret the frequencies forming the spectrum of an atom as the natural resonance-frequencies of an elastic system. Bohr supplanted this idea with an idea of his own, one of the most novel, fecund and potent in all the long evolution of physics. Several of the ideas incorporated in the contemporary atom-model are due to Bohr; among them all this is the primary and fundamental one, and certainly the most secure.

Consider the spectrum of hydrogen. In the visible region, this spectrum consists of a "line-series"—that is to say, a procession of lines converging upon a limit, falling at intervals ever narrower and narrower, these intervals so smoothly diminishing that they bear witness to a common character and a mutual origin of all the lines. This line-series is shown in Fig. 2. Not only to the eye is it of a wonderful regularity; the frequencies of its consecutive lines are bound together in a simple numerical law. They are equal successively to

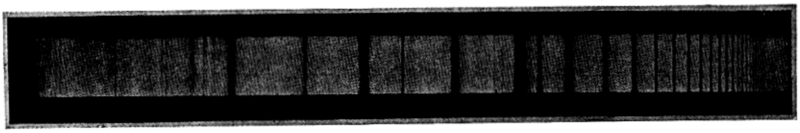

Fig. 2—Balmer series of lines in the hydrogen spectrum. (R. H. Curtiss, from Foote & Mohler, "Origin of Spectra")

$$\nu_{lim}-R/3^2,\ \nu_{lim}-R/4^2,\ \nu_{lim}-R/5^2,\ \nu_{lim}-R/6^2,\ \text{etc.} \qquad (1)$$

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[13] This method of locating stationary states by observing transfers of energy from electrons at atoms is called the *method of inelastic impacts*; for the impacts of electrons against atoms are elastic (by definition) so long as there is no transfer of energy into the internal economy of the atom, and are inelastic when such transfers occur. When an atom returns into its normal state from an excited state, it usually emits radiation; hence a method for detecting the first commencement of radiation is usually (perhaps not always) equivalent to a method for detecting the first commencement of inelastic impacts. As it is generally easier to set up apparatus for detecting radiation than to seek evidence for elastic impacts, direct observations upon these last are not so abundant as they should be. Nobody really knows how many stationary states might be discovered by the method of inelastic impacts, although Franck and Einsporn detected over a dozen for mercury (of which those given in Table II are some). In fact they detected more than could conveniently be ascribed to mercury atoms, so that it was necessary to attribute some of them to molecules.

in which

$$\nu_{lim} = \text{frequency of the limit of the series} = R/4$$

R standing for a certain constant. There is another series of lines in the ultraviolet part of the same spectrum, whereof the frequencies are equal consecutively to

$$\nu = \nu_{lim} - R/4,\ \nu_{lim} - R/9,\ \nu_{lim} - R/16,\ \text{etc.} \tag{2}$$

in which

$$\nu_{lim} = R,$$

R having the same value as before. The utter simplicity of the terms to be subtracted from ν_{lim} in each of these cases, not to speak of the related form of the expressions for ν_{lim}, suggests like simple laws in other fields of physics that in this formulation of the facts something highly important has been partially unveiled. There are certain other series in the spectrum of hydrogen, and inspecting them all one is led to the rule that *every frequency emitted by the hydrogen atom can be calculated by inserting different pairs of integers in the places of* m *and* n *in the formula*

$$\nu = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \tag{3}$$

The case of the ionized-helium[14] atom is quite as simple. Every frequency emitted by this atom can be calculated by assigning different pairs of integer values to the constants m and n in the formula

$$\nu = 4R\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \tag{4}$$

Line-series have been found in the spectra of many other elements. Some of them are as strikingly outstanding as the line-series in the spectrum of hydrogen, and converge upon limits scarcely less easy to locate; for instance, the "principal" series of the spectrum of sodium (Fig. 3). Most are by no means so obvious; often they are involved in the midst of a luxuriant jungle of unrelated or otherwise-related lines. Most spectra conceal their structures from the unpractised eye, as a tone-poem of Strauss its themes or an opera of the Ring its *Leitmotiv* from the inexperienced ear. Long training and a skilled judgment are required in the deciphering of spectra, except in the few untypically simple cases; and usually the arrangement of lines into series which the spectroscopist presents must be

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[14] The reader may take this, for the time being, simply as the name of a particular element.

accepted by the theorist without question and without suggestion, for he is not competent to analyze the data for himself.

Having grouped a certain number of lines into a series, having guessed as well as possible the convergence-frequency ν_{lim} of this series, the spectroscopist has still the task of finding the numerical law to which the consecutive frequencies conform. As a matter of course, all the frequencies can be expressed by a formula generalized from (1) and (2):

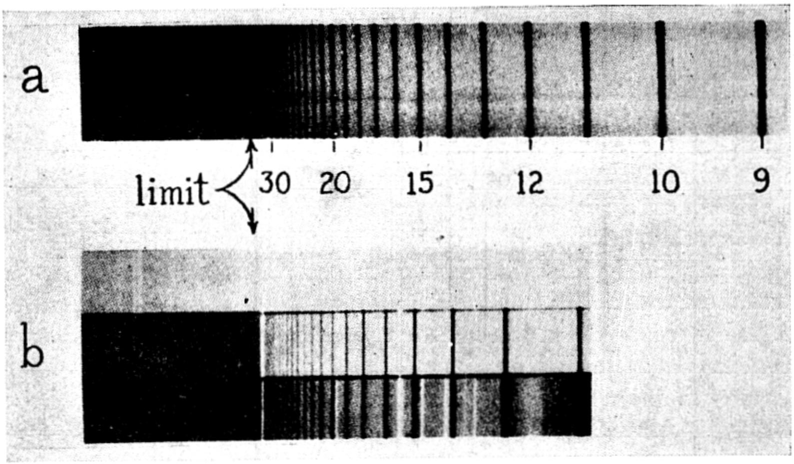

Fig. 3—Principal series of sodium (two photographs). (G. R. Harrison, *Physical Review*)

$$\nu_i = \nu_{lim} - f(i) \tag{5}$$

in which i is the order-number distinguishing each line, and $f(i)$ is a different quantity for each of the lines, which approaches zero as we pass along the series to the limit. This means nothing by itself; the question is, does the function $f(i)$ have a simplicity comparable with the simplicity of the subtrahenda in (1) and (2) which suggested that they are the symbols of something deeply important? In general, the function $f(i)$ is not so simple as the function which occurs in the series of the spectra of hydrogen and ionized helium. In many cases, however, it is almost as simple, in others a little more complicated, in others a little more complicated yet, and so forth; so that the eventual result is this, that the formula (3) appears to be the proper way of describing the lines of series spectra, even in cases where the series is so irregular and the form of the function $f(i)$ so intricate that if it were the only series in existence, no one would attach any particular importance to it.[15]

To the physicists of a generation ago, who regarded the spectrum frequencies as natural vibration-frequencies of the atom, and tried hard to invent a mechanical model of which the vibration-frequencies should conform to the formula (3) or the more general formula (5), the character of these formulae was an insurmountable obstacle. Elsewhere [16] I have given a brief account of the vain attempts to contrive such a model. Bohr abandoned this procedure altogether; and taking equation (3), he multiplied both sides of it by Planck's constant h $(=6.56 \cdot 10^{-27})$.

$$h\nu = hR\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \qquad (6)$$

The significance of this act depends on the meaning of h. Planck had found it expedient, in developing an adequate theory of radiation, to assume that solid hot bodies are populated with multitudes of oscillating electrons of all the various frequencies, possessing a very curious and inexplicable property; this being, that an oscillator vibrating with frequency ν can emit radiant energy of that same frequency ν only in units or *quanta* of amount $h\nu$. Einstein had found it expedient, in describing the photoelectric effect and other phenomena, to assume that radiant energy of the frequency ν goes about in units or quanta of the amount $h\nu$, emitted integrally, absorbed integrally, travelling integrally. Suppose then that we assume that the quantity $h\nu$, standing on the left-hand side of the equation (6), represents the amount of radiant energy emitted by the hydrogen

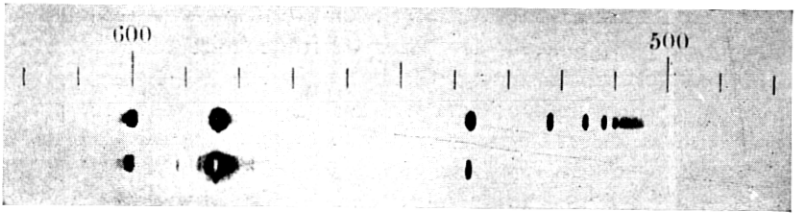

Fig. 4—Principal series of helium (singlet system). (T. Lyman, *Astrophysical Journal*)

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[15] As a matter of fact, the series-limit is not generally so obvious to the eye that it can be located at once; it is determined after and by means of a careful choice of the most suitable form for the function $f(i)$. This is one of the difficulties of the spectroscopist's task.

[16] In the seventh article of this series (footnote 9).

atom in the process of pouring out radiation of the frequency ν. The right-hand side is the difference between two terms. One term is the energy of the hydrogen atom before it emits the radiation of frequency ν; the other is the energy of the atom after the emission is concluded. *The radiation of frequency ν is emitted by reason of a transition between two stationary states of the hydrogen atom; the energies of these states are equal to the terms whereof the frequency ν is the difference, each term multiplied by h.* The terms of the spectrum formulae are the energy-values of the stationary states of the atom, when translated into the same units by multiplying them by h. When translated into proper units, *the terms are energies, and the energies are terms.* This is Bohr's great and memorable idea.

Once this idea is accepted, the known stationary states of the atom increase enormously in number. The paltry one, two, or half-dozen, which are all that have been detected by observing the energy-losses of rebounding electrons, are multiplied into hundreds and thousands. The accuracy with which each energy-value is known is augmented tenfold or a hundredfold, sometimes far more; for spectroscopic measurements are among the most accurate in physics, although the necessity of extrapolating the observed frequencies to arrive at the series-limit neutralizes some of their precision.

One point must be kept clearly and always in mind, at the peril of infinite confusion. *The energy-values which the spectrum terms supply are* not the energy-values of the stationary states measured from the normal state, as might seem natural; they are *the energy-values measured from the state of the ionized atom.* These being negative, it is the negative term-value which is significant. Equation (6) must therefore be rewritten in this fashion:

$$h\nu = Rh\left(-\frac{1}{n^2}\right) - Rh\left(-\frac{1}{m^2}\right). \tag{7}$$

The energies of the successive stationary states of the hydrogen atom are $-Rh$, $-Rh/4$, $-Rh/9$, $-Rh/16$, and so forth, relatively to the energy of the ionized atom as zero. They are not Rh, $Rh/4$, $Rh/9$, and so forth, relatively to the normal state of the atom as zero. Anyone who entertains this last idea is doomed to trouble.

The stationary states of the hydrogen atom are shown in Fig. 5, which is constructed like Fig. 1, with the energy-values of the various levels measured downwards from the state of the ionized atom, and affixed on the right. The distances from the various levels to the zero-line are proportional to these energy-values (this feature will henceforth be found too inconvenient to maintain).

The energy-value of a stationary state, when obtained by analyzing a spectrum, is generally given not in equivalent volts, but in a unit called the "wave-number." This unit is $1/hc$ times as great as an erg, and $300hc/e$ (about .0001237) times as great as an equivalent volt. When the energy-values of two stationary states are expressed in

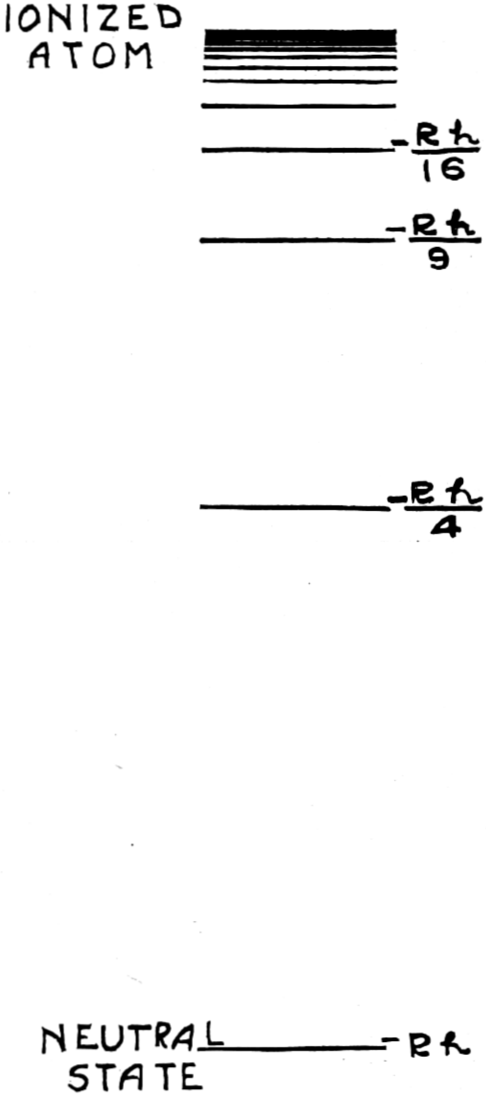

Fig. 5—Diagram of the stationary states of hydrogen, deduced from its spectrum

this unit, the difference between them is equal to $1/c$ times the frequency of the line which corresponds to the transition from one to the other.

A spectrum-line corresponding to a transition between two stationary states is symbolized, on a diagram of stationary states, by an arrow connecting the dashes (or whatever marks are used) which symbolize the two levels. This is illustrated in Fig. 6.

I pause at this point to remark that each of what I have been calling the "stationary states" is in fact usually a group of two or more stationary states, often but not always exceedingly close together; just as many stars in the sky are in fact groups of stars too close together for any but an excellent telescope to discriminate. This will be discussed at length in a later section; at present it is expedient to regard each of these groups as one stationary state.

The experimental test of Bohr's method for identifying stationary states consists in comparing the stationary states inferred from the spectrum, according to Bohr's procedure, with the stationary states derived directly by the study of electron-impacts. The agreement is perfect wherever the experiments by the latter method can be carried out. By a curious fatality, this is impracticable for hydrogen and ionized helium, as neither sort of atom occurs in gas quiescent enough for experiments on energy-transfers from electrons to atoms.

For about fifteen other elements, the comparison has been made for two or more of the Stationary States. Every energy-value given in Table II was obtained by the method of electron impacts, and confirmed by analyzing the spectrum of the element.

E 3. The Classification of Stationary States by Utilizing "Rules of Selection"

I have said that every line in a spectrum, at least of those arranged in series, may be represented by an arrow connecting two stationary states. If arrows are drawn from every one of the stationary states to every other, will every arrow correspond to a line actually observed in the spectrum? Every line has an arrow; does every arrow have a line? By no means; the answer is definitely and strongly negative. If the wave lengths deduced from all the possible arrows are sought in the spectrum, most of them are found unoccupied by lines. The great majority of the apparently possible transitions either do not occur at all, or if they do occur, the energy which is liberated is disposed of in some other way than by radiation. There is reason for believing that the atom may embrace this last alternative if it col-

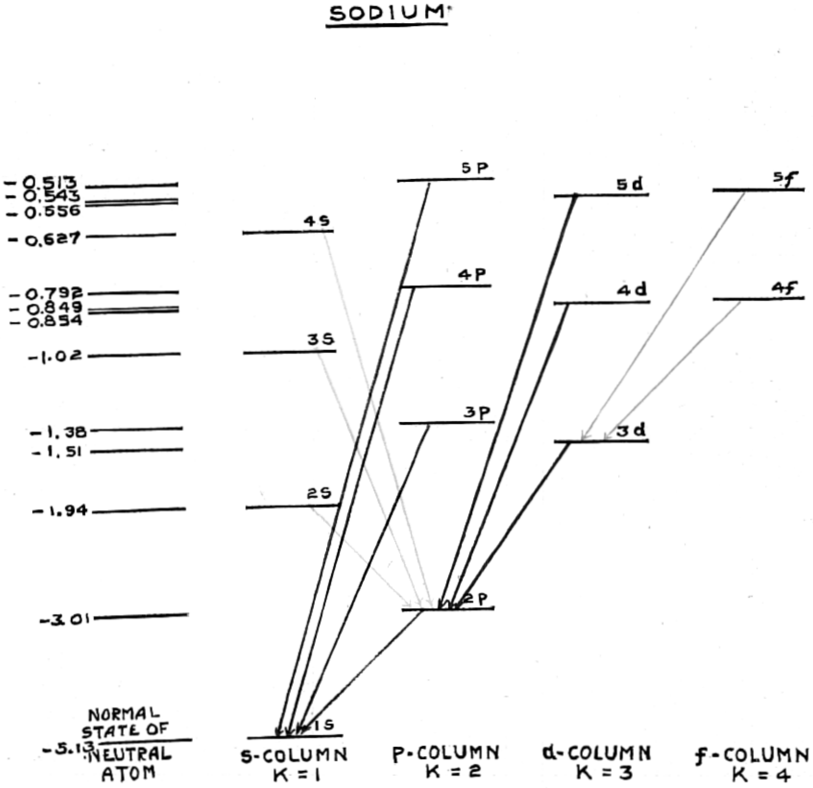

Fig. 6—Diagram of the stationary states of sodium, sorted out into columns by applying the selection-principle. Arrows represent various lines (blue for principal, yellow for sharp, red for diffuse and green for Bergmann series)

lides with another atom or with an electron. Otherwise, it seems that if the atom cannot radiate the energy liberated in a transition, the transition itself cannot happen at all. If, therefore, the line corresponding to an arrow is missing, the transition corresponding to the arrow must be inhibited by some agency as yet unknown. Many transitions must be inhibited, for many lines are missing.

These missing lines are precious to the student of spectra and to the architect of atom-models. Whatever explanation is devised for the stationary states must include a reason for the occurrence of some transitions and the non-occurrence of some others. This is good rather than bad fortune, since if such a reason is demanded, it may be found in one and not in another of two competing theories which otherwise would stand on an equal footing; the missing lines may even suggest a theory. At all events they suggest a system of classification; and, while the hardened theorizer may regard a system of classification as merely the forerunner of a theory, a theory is itself often nothing more than a classification stated in the language of an artificial analogy. It is, in fact, possible to arrange the stationary states, not in a single column as in Figs. 1 or 5, but in several as in Fig. 6; this arrangement being so contrived, that any transition can be identified in a moment as belonging among those which occur, or among those which are missing, whichever its case may be.

The mere fact that such an arrangement can be contrived shows that the missing lines are not distributed at random, but subject to some sort of a rule. Such rules are known as *principles of selection*. The missing lines are commonly called *verboten* lines by the German physicists, possibly because that was the most conspicuous word in the official German language before the war. It is not a happily-chosen word, neither are the English equivalents "forbidden" and "prohibited"; since while we know that the lines are missing, we do not definitely know what circumstance is responsible; and, whatever that circumstance may be, it is highly unconventional for a physicist to say that it "forbids" the lines. The same objection applies with extra force to the phrase "forbidden by the selection-principle". It is much better to accept the fact that certain lines are missing as a fact of experience, and the selection-principles as rules of experience whereby the facts are codified.

E 4. The Families of Stationary States (for Other Atoms than Hydrogen)

There is a far-reaching contrast between the spectra of all atoms but hydrogen and ionized helium, on the one hand, and the spectra of these two atoms on the other. The selection-principles at first accentuate this contrast, and later to a certain extent aid to explain it away. I commence with the atoms other than hydrogen, and take sodium as the specific instance.

A few of the stationary states of the sodium atom are exhibited in a single column on the left of Fig. 6. The energy-value of each level, measured from the energy of the ionized atom as zero, is affixed at the left; but the practice of drawing the levels at distances proportional to their energy-values has had to be discarded for the sake of lucidity. In this case, the distances are proportioned to the differences between the logarithms of the energy-values. Drawing arrows from each of the levels to every other, and ascertaining which of them correspond to actual and which to missing lines, we find that the missing lines are such that the stationary states can be sorted out into several families, to be arranged in parallel columns as on the right of Fig. 6. There are at least seven of these, but it is of no advantage to us to consider more than the first four. The feature of this arrangement is, that *transitions between stationary states in adjacent columns correspond to actual lines*; *but the lines corresponding to all other transitions are missing.*

This is a principle of selection. It may be phrased in an equivalent but pregnant way, in this manner. Let me attach to the several columns the numerals 1, 2, 3, 4 . . . , as they are indicated at the bases; and let me use k as the general symbol for each and all of these numerals. Then this particular selection-principle may be phrased thus:

> *The only transitions which correspond to actual spectrum lines are those in which* k *changes by unity*; $\Delta k = \pm 1$.

The numeral k bears the ponderous name of *azimuthal quantum-number*. This is a name derived from theory and not from experience, as will be made clear in due time. The principle of selection which has just been stated is the selection-principle for the azimuthal quantum-number.

Exceptions to this rule occur; the *verboten* lines, like other *verboten* things, occasionally evade the prohibition. This happens particularly when the atoms are subjected to intense electric fields, or to violent spasmodic electrical discharges in which strong transient fields are produced; in these circumstances great numbers of the missing lines leap suddenly into sight. In Fig. 11 some of these lines appear elicited by a strong electric field. Some lines corresponding to changes of k by two units or by none, which by the foregoing rule should be absent, do actually occur even when there is no obvious reason whatever for thinking that the atoms are subject to unusual stresses.[17] The exceptions, however, are not numerous enough to jeopardize the rule.

Two other features of the columns should be pointed out; first, that the successive levels in each column are not scattered at random, but form a converging series approaching the top of the column as limit (their energy-values form a sequence converging to zero); and second, that there is nothing arbitrary about the order of the columns, since the column at the extreme left admits of transitions to only one other column and therefore is unmistakable, and all the others follow after it in an immutable order.

E 5. A Digression About Notation

The symbol for a transition between two stationary states, and for the spectrum line which corresponds to that transition, consists of the symbols for the two states separated by an arrow, or a dash, or a semicolon, or any convenient mark. The final state is commonly written first. Thus the line due to the transition from a state B to a state A is designated thus: $(A)-(B)$. Chess-players will be reminded of the "Continental" system of describing moves at chess, in which symbols for the squares from which and to which the piece is moved are written down one before the other.

The notation for spectrum lines thus flows easily and naturally from the notation for stationary states. This notation is not in principle very difficult, but it has become confused and confusing, largely because of the alterations which have been wrought upon it to make it express not the facts, but divers theoretical interpretations of the facts. Alterations in names and notations generally produce an evil effect in physics even when justified in the highest degree, for the old systems and the new persist side by side and cause interminable trouble; all the more is this so when the alterations are based on uncertain grounds and impermanent. The notation for stationary states has already suffered much in this manner, and probably the worst is yet to come.

The classification of levels which I have just described enables and requires us to give a twofold symbol to each level; the symbol must designate the column in which the level stands, and its order-number or serial number in that column. The columns are generally desig-

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[17] Foote, Meggers and Mohler observed a line corresponding to a change of two units in k (the line $(1,s)-(3,d)$, in the notation to be explained in section E5) under circumstances in which it seemed impossible to believe in an abnormally large electric field.

nated by the letters *s*, *p*, *d*, *f* (or their capital, or Gothic, or Greek equivalents).[18] A spectroscopist using these symbols generally writes the serial number of the level before the letter, with a comma between, thus: (1,*s*) and (2,*p*) and (3,*d*). Or the columns may be designated by their values of the numeral *k*, which is then commonly written as a subscript to the serial number. These symbols have at least the advantage of being comparatively fixed. It is far otherwise with the serial numbers. One might expect that the level having the greatest energy-value in a particular column would be called Number 1, and the successive ones Number 2, Number 3, and so forth towards the convergence-limit. Unfortunately (though for not a bad reason) the habit is to designate the first levels of the successive columns by the order-numbers 1, 2, 3 and 4, successively; so that their respective symbols are (1,*s*); (2,*p*); (3,*d*) and (4,*f*). These are the symbols I have affixed in Fig. 6; but they are not the only ones, as the order-numbers have jumped up and down several times to satisfy the exigencies of new atom-models. It would be unprofitable to confuse the reader with further details, at least at this point. The important things to remember are three: that the symbol for each stationary state must contain one index for its column and another for its place in its column—that the former index is usually one of the specified letters—that the latter index is a number, usually beginning with 1, 2, 3, 4 for the first level in the *s*, *p*, *d*, *f* columns, respectively, and ascending along the column in unit steps.

E 6. Names and Features of the Most Noted Line-Series

Every line in every series, according to Bohr's fundamental idea, corresponds to a transition or "combination" between two stationary states of the atom—to a transition from an initial state to a final state. The atom possesses more energy in the initial state than in the final state (we are speaking of emission-spectra only). Hence the energy-value of the initial state, reckoned as it usually is from the energy of the ionized atom as zero, is algebraically higher and arithmetically lower than the energy-value of the final state.

The various lines of any one line-series have this in common: they correspond to transitions from various initial states which however all lie in one and the same column, into one final state which is the same for all and lies in an adjacent column. Each line-series thus

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[18] The symbol *b* is sometimes used instead of *f*. For the columns following to the right of the *f*-column there are various notations, particularly f', f'', f''' and *g*, *h*, *i*. See also footnote 21.

belongs to one particular final state, and to one particular column of initial states.

The line-series consisting of transitions into the state (1,*s*), or *terminating upon* (1,*s*) as the phrase sometimes is, bears the name of *principal series*. Its consecutive lines are: (1,*s*) – (2,*p*); (1,*s*) – (3,*p*); (1,*s*) – (4,*p*) and so forth. They are signified by the blue arrows of

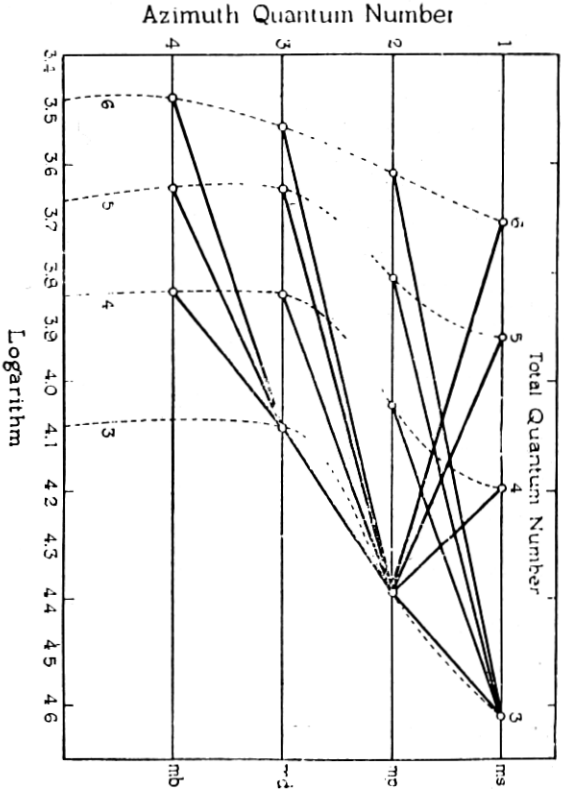

Fig. 7—Another way of mapping the stationary states of sodium

Fig. 6. The general symbol for this series is (1,*s*) – (*m*,*p*); which will be quite intelligible. The (1,*s*) level is the normal state of the atom; consequently, the various lines of the principal series correspond to transitions, by which the atom regains its normal state after a temporary exile from it. It is probably for this reason that the series is prominent enough to have received the name *principal* from the spectroscopists.

Two series terminate upon the (2,*p*) level. One of these consists of transitions from various levels of the s-column. This is the *sharp* (or second) *subordinate* series, and its symbol is $(2,p)-(m,s)$. The other series consists of transitions from various levels of the d-column; it is the *diffuse* (or first) *subordinate* series, and its symbol is $(2,p)-(m,d)$. Yellow and red arrows signify these series, respectively, in Fig. 6. Of the two line-series terminating upon the $(3,d)$ level, only one has been endowed with a name; this is the series $(3,d)-(m,f)$, known alternatively as the *Bergmann* or the *fundamental* series (the second name is a bad one) and symbolized by green arrows in Fig. 7.

These series seem to be the only ones which impressed themselves strongly enough upon the minds of spectroscopic experts to receive names [19] from them. However, many other series have been identified, and emphasized, especially since Bohr's manner of thinking took root among the students of spectra; for instance, series terminating upon $(2,s)$ and $(3,s)$, which are conspicuous in the spectrum of helium, and such line-series as $(3,d)-(m,p)$, and $(4,f)-(m,d)$.

Several rules about line-series, which are very prominent in accounts spectra, become self-evident when the rules governing the stationary states are mastered (of course, this is only because the latter rules are based upon the former). For instance, there is a rule that the sharp and the diffuse series have the same limiting-frequency; and there is a rule that the difference between this limiting-frequency and the limiting-frequency of the principal series is equal to the frequency of the first line of the principal series. The reader may derive these by inspecting Fig. 6.

Such rules do not apply to the spectra of hydrogen and of ionized-helium, which are profoundly different from the spectra of sodium and other elements; and it is perilous to attach such names as *principal* or *subordinate* to the line-series of those first elements. The stationary states of those elements are known by their energy-values, and the series by the names of their discoverers or interpreters.

E 7. Further Analysis of the Stationary States of Hydrogen and Ionized Helium; Fine Structure

In our earlier analysis of the spectrum of hydrogen and the spectrum of ionized helium, we inferred from each of these spectra a family of stationary states, the energy-values of which follow one upon the other in a very regular procession governed by a simple numerical law. This makes it practically impossible to divide up these stationary states into classes; all of the levels for each of the atoms must

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[19] The reader will recognize, in the initials of these names, the letters s, p, d, b, and f used to designate the several columns of levels.

inevitably be arranged in a single column, as it was done in Fig. 5. But in this arrangement the selection-principle of the foregoing paragraph is apparently contravened. For, when the levels of the sodium atom were arranged into columns, the transitions between levels belonging to one and the same column were among the inhibited transitions, the lines corresponding to these were among the missing lines. But the transitions between the levels in the single column which contains all of them for the hydrogen atom, correspond to the actual lines which constitute the entire hydrogen spectrum.

This discord is only apparent. It vanishes when we recall the fact, already once mentioned as a forewarning and then neglected for ease of exposition, that the stationary states of the hydrogen atoms are compound—that what has been called a "stationary state" in the preceding pages is really an ensemble of adjacent stationary states. Every line of the Balmer series, the series $R(1/m^2-1/2^2)$, is actually a close doublet; the frequency-differences between the components of all the doublets are approximately the same. Interpreted in the new fashion, this means that what we have called the stationary state of energy $-Rh/4$ is actually a pair of "component" stationary states very close together—so close together, that if the energy of one were exactly $-Rh/4$, the energy of the other would depart from that value by less than one part in forty thousand. Further in analyzing the spectrum of hydrogen we cannot go, probably because the minute details (if there are any) of the structure of its lines overtax the resolving-power of our spectroscopes. The spectrum of ionized helium, however, is spread out in a more generous scale; and some of its lines were analyzed by Paschen. Among these were the lines of frequency $4R(1/3^2-1/4^2)$; $4R(1/3^2-1/5^2)$; and $4R(1/3^2-1/6^2)$. They were resolved respectively, into six, five, and three components; and the line $4R(1/4^2-1/5^2)$ resolved into four.

Interpreted in the new manner, these data mean that what we have called the stationary states of energy-values $-4Rh/9$, $-4Rh/16$, $-4Rh/25$, and $-Rh/36$, are really ensembles of "component" stationary states lying very closely together. It would scarcely be possible to infer from these data, independently and without extraneous guidance, just how many "components" belong to each of the four ensembles. Fortunately or unfortunately, Paschen's measurements were preceded and inspired by a specific prediction of the number of components in each ensemble—a prediction that what we have called the nth stationary state should be a group of n "component" stationary states. This prediction is graphically set forth in the second column of Fig. 8, in which the level of energy-value

$-4Rh$ is drawn as a single dash, the next level as two dashes, the next as three, and so forth. Paschen's data were therefore compared with this prediction.

The data and the prediction were found compatible. If arrows are drawn from every "component" stationary state to every other "component" stationary state, it is found that each of the lines which was observed corresponds to one of the arrows (but it is necessary to assume that, in some places, two or more adjacent lines are fused apparently into one by reason of the insufficient resolving-power of the spectroscope). Some of the arrows, however, correspond to missing lines. Evidently some sort of inhibiting agency is at work; some sort of a selection-principle is adumbrated. Furthermore, some and perhaps all of the missing lines appear when the electric field strength acting upon the radiating atoms is increased, and this, it will be remembered, is the behavior of the missing lines in the sodium spectrum. Whether the selection-principle could ever have been inferred from these data alone seems doubtful. Naturally one proceeds to try out the same principle as served for the previous case. Can the component stationary states of the ionized-helium atom be sorted out into parallel columns, in such a manner that transitions between levels in adjacent columns correspond to actual, all the other transitions to missing, lines?

This is attempted in the manner shown in Fig. 8. The result is fairly satisfactory. The lines due to transitions between levels in adjacent columns should by this principle be visible, and they are. The lines corresponding to transitions between levels in the same column, or more than one column apart, should be missing; and some of them are, but also some of them undeniably can be seen. To account for these unwelcome guests, it is necessary to assume that some of the radiating atoms are subject to a strong electric field which might, but would not be likely to, exist in the discharge. This is an uncomfortable solution; but there are other numerical agreements between the prediction and the data, which it is not expedient to describe at this point, but which are good enough to excuse that deficiency to some extent. *En somme*, the evidence presents no insuperable objection to our arranging the component stationary states of the ionized-helium atom in parallel columns, and declaring that the only transitions which occur (except in strong electric fields) are those between members of adjacent columns; and this is just what we did with the sodium atom, and can in general do with every other kind of atom whereof the spectrum has been interpreted. This being granted, we can assert that the spectra and the stationary states of the ionized-helium atom (and presumably those of the hydrogen atom) are not so radically different from those of the sodium atom as they seemed to be; some of the apparent differences being traceable to the fact that corresponding levels in the *f*, the *d*, the *p*

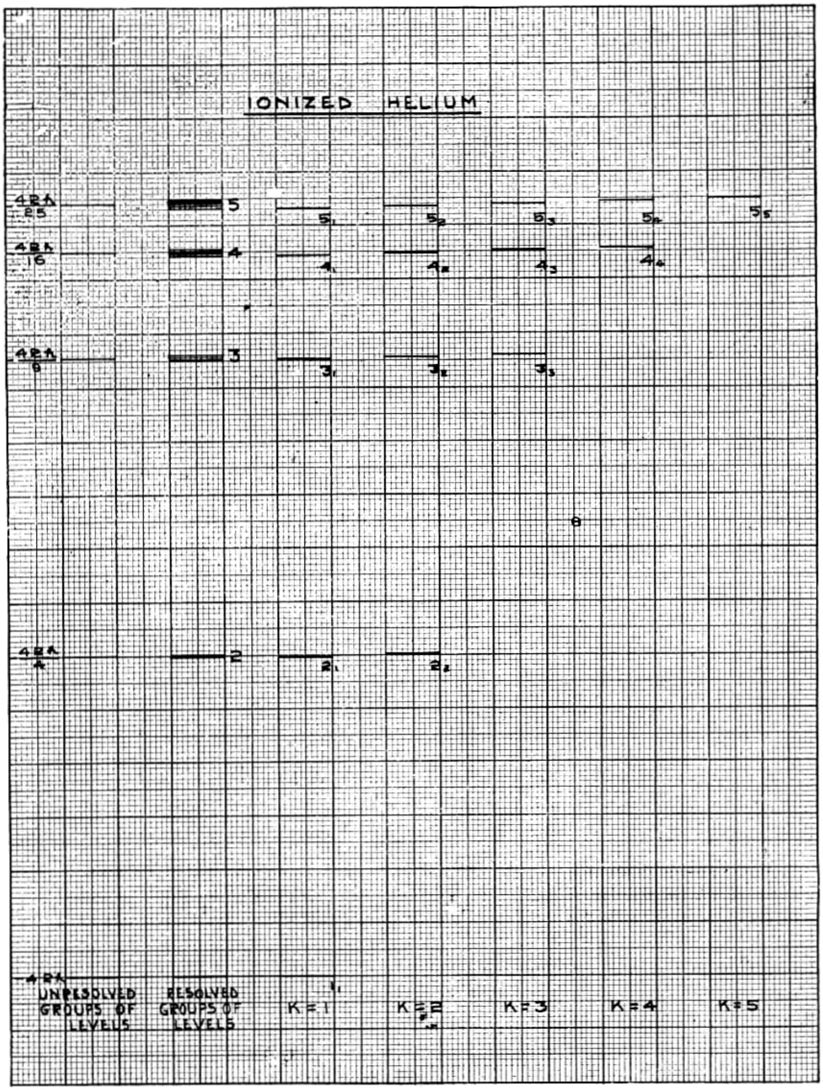

Fig. 8—Diagram of the stationary states of ionized helium, resolved to account for the fine structure of the spectrum lines

and the *s*-columns, which in the sodium atom are widely separated, are in the former atoms so closely crowded together that lines, which in the sodium spectrum are far apart, are in the former spectra packed into all-but-irresoluble groups. This is probable, but not certain. Further data about other lines in the ionized-helium spectrum would be gratefully received.[20]

The notation for the various "component" stationary states of the ionized-helium atom is shown in Fig. 8. The successive columns are denoted by the numerals 1, 2, 3, 4 . . . for which the general symbol is k, as previously. This numeral is written as a subscript to the serial number of the level in its column, which commences with 1 in the first column, 2 in the second, 3 in the third, and so forth. By inspecting the figure, the reader will see a reason for using these different values of the serial-number for the first levels of the different columns. The serial-number is designated by n and called the *total-quantum-number*. The numeral k is called the *azimuthal-quantum number*, as before. These heavily long names are imposed by the theory and not by the data.

E 8. Further Analysis of the Stationary States of Other Elements than Hydrogen and Ionized Helium; Multiplets

Having performed a two-stage analysis of the spectra of ionized helium and of hydrogen, we return to the spectra of the other elements for a second attack.

Let us consider the reasons for making these analyses in two stages. When the mid-Victorian physicist trained his spectroscope upon a tube full of glowing hydrogen, he saw the spectacle of Fig. 2—the converging procession of distinct bright lines, of which the frequencies form that delightfully smooth numerical progression which we have already met. Later physicists with better instruments discovered that each of these "lines" was in fact a pair of lines. Now in strict truth, this discovery showed that the "lines" of the Balmer series were no lines at all; for a doublet is not a line. But the physicists continued to refer to the "lines" of the Balmer series, chiefly no doubt because to anyone equipped with an ordinary spectroscope the doublets do appear as single lines. By itself this is little reason; but the usage is not altogether faulty. Few people would hesitate to admit that each of these doublets is not a couple of casual neighbors, not two

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[20] It would be particularly interesting to settle beyond question whether the missing lines demand the selection-principle already explained in section E4, rather than the one to be explained in section E8. This is one of the reasons for wanting to produce and examine the spectrum of doubly-ionized lithium, in which the evidence would probably be much clearer.

unrelated lines fortuitously close together, but a pair of lines sharing some deeply fundamental quality in common. This is indicated chiefly by the facts that the distance (measured in frequency) between the components of a doublet is the same for all the doublets, and very small compared with the distance between consecutive doublets. For this reason the doublets are treated as entities, and they require a name; which is what physicists have preserved for them, in continuing to call them "lines." "Doublet" would be better than "line", and "group" would be better yet; but we cannot ever be sure that even the apparently-single lines are not very close groups, and yet it would be silly to call every line a group. Sirius appears as a double star in a few of the most powerful telescopes, but nobody would insist on calling it a double star when pointing it out in the night sky.

All this is not so trivial as it sounds. It is easy enough to speak of doublets when looking at lines which appear single except when viewed in the most powerful spectroscope, and then are resolved into components much closer together than the nearest similar line is to either. Such lines occur not in the spectra of hydrogen and ionized helium only, but in the spectra of sodium and other elements generally. But the spectroscopist is constantly applying such names as "doublet" and "triplet" and "quadruplet", and the inclusive name "multiplet" to groups of lines which lie far apart in the spectrum, with scores of others intervening. Here his function is not to split apparent lines into narrow groups, but to unite widely-scattered lines into wide groups. This he does not because of propinquity of the lines, but because of resemblances or analogies or fixed intensity-relations between them, or because he finds it possible to construct a series of such groups with identical frequency-differences between corresponding lines within them, or because of analogies with other elements with more perspicuous spectra, or theoretical predictions, or intuitions or clairvoyance. Groups such as these are not generally termed lines, except in very abstract discussions; it is difficult to call a group a line, when it is clearly resolved by any instrument worthy the name of spectroscope. But they are like the lines of the Balmer series, treated as entities because their lines are believed to share some deeply fundamental quality in common.

What I have said about lines and groups of lines is transferable in substance to stationary states and groups of stationary states. What we had originally called the levels of hydrogen and ionized helium, with their energy-values $-Rh/n^2$ and $-4Rh/n^2$ ($n=1, 2, 3 \ldots$), were resolved into groups of levels in order to interpret the fine structure of the lines. But owing to the propinquity and to certain numerical relations of the levels in a group, and to certain qualities of the transitions between them, it was felt that the levels of each group share some deeply fundamental quality in common. For this reason we used a system of classification in which each level is represented by two symbols, one for its group and one for its place in its group; and we numbered the levels in succession, not 1 and 2 and 3 and 4 and 5 and so forth, but 1_1 and 2_1 and 2_2 and 3_1 and 3_2 and 3_3 and so forth. Interpreting the groups of lines in the spectra of sodium and other atoms, we infer groups of levels. The levels in one of these groups are often far apart. They may be eighteen or more in number, other levels may lie between; but by reason of the resemblances between the lines whence they were inferred, by reason of certain numerical relations between the levels themselves, they are believed to have some deeply fundamental quality in common. If this is vague, so also at times is the interpretation.

The statements in the foregoing sections about the stationary states of sodium are now to be understood as relating to groups of stationary states. It is the *groups of stationary states which are arranged in parallel columns, designated by numerals* k, *such that no transition takes place unless in it* k *changes by one unit.* It is the group of stationary states which is marked by a pair of numerals, one to designate its column and the other its place in its column; or by a letter to designate its column and a numeral to designate its place in its column. It is the group of stationary states which is denoted by (3_2) or $(1,s)$ or $(5,d)$.

To denote a particular stationary state we must add, to the symbols for its group, a third symbol for its place in its group. This symbol is generally a numeral, hung on as a subscript to the letter designating the column (thus: $(2,p_1)$ and $(2,p_2)$) or as an additional subscript to the two numerals (thus: 3_{21} and 3_{22}).[21] The most common general symbol for this numeral is j. Geometrically, the stationary states may be represented by lines or dots arranged, not in one row of several parallel columns as in Fig. 7, but in several rows of parallel columns. Readers with three-dimensional imaginations in good working order may develop this idea *ad libitum*. The systems for assigning the values of j are shifted around every few months to correspond to new atom-models, and are scarcely worth memorizing.

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[21] The notation suggested by Saunders and Russell, evidently in concord with a number of other experts, is built in this way: Designate the column to which a group belongs by the letters suggested in section E5, capitalized (i.e., S, P, D, F, G, H for $k=1, 2, 3, 4, 5, 6$); write the serial-number of the group before the letter, and append the value of j as a subscript to the letter. If it is desired to state what sort of a system (cf. section E10) a level belongs to, one may add an index to the left of the letter and above it.

The best of them, however, are adjusted so as to express a new and additional selection-principle, which is coequal with the other selection-principle we met a few pages above.

This principle is derived in the same way as the first one. The groups of levels are established by inference from the groups of lines; then arrows are drawn from every level to every other, the corresponding spectrum-lines are sought, and most of them are not found. Some of these missing lines are those which would contravene the first selection-principle, as they correspond to transitions in which the numeral k changes by more than one unit, or not at all. Putting these aside, there are still a number of missing lines, to which the first selection-principle has offered no objection. Now it is found possible to choose the numeral j in such a manner that the only transitions which correspond to actual spectrum lines are those in which j changes by one unit or not at all ($\Delta j = O, \pm 1$). Furthermore it is possible to adjust the values of j in such a manner that the lines corresponding to transitions, in which j is initially zero and remains unchanged, are missing.

This is the *selection-principle for the inner quantum number*; for the numeral j, when adjusted in this manner, is known as the inner quantum number. This again is a name imposed by theory and not by the data of experience.

As the two selection-principles are effective concurrently, the pair of them may be fused into this one:

Of the three numerals n, k *and* j, *which specify a stationary state completely, two* (k *and* j) *may be so chosen that the only transitions which correspond to actual lines are those in which*: *first,* $\Delta \mathrm{k} = \pm 1$; *second,* $\Delta \mathrm{j} = O, \pm 1$; *third,* j *is not zero both before and after the transition.*

This complicated rule is evidently the sign of some very important principle, the full nature of which thus far escapes us. It will probably seem difficult to grasp and fix in mind; but difficulty of this sort is likely to abound in the physics of the near future. Not so many years ago the physicist's path lay among differential equations; the defter he was in integrating hard specimens of these, the better he was fitted for his profession. I should not care to say that this is no longer true; but he will probably have to cultivate a sense for problems such as this.

It remains to give some idea about the number of stationary states in the various groups. For sodium, as laid out in Fig. 6, the groups in the s-column are merely single levels (this sounds like a contradiction in terms, but may be borne for the sake of the generality); the groups in the other columns are pairs of levels, or "doublet terms."

This is the common character of the alkali elements Li, Na, K, Rb and Cs, which occupy the first column of the periodic table; probably also for the noble metals which share this column, but the data are few. For elements of the second column of the periodic table there are two complete systems of stationary states, each having its own *s*-column, its own *p*-column, its own *d*-column, and all the rest. In one system, all the groups in every column reduce to single levels; it is a *singlet system*; in the other, all the groups in the *s*-column are single levels, all the groups in the other column are triads of levels or "triplet terms;" it is a "triplet system." The complexity mounts up stage by stage as we cross the periodic table of the elements from left to right, and soon becomes terrific.

E 9. *Effect of Magnetic Field on the Stationary States*

When a magnetic field is applied to a radiating gas, most of the lines of its spectrum are replaced by triplets (Fig. 9), or by even richer groups of lines (Fig. 10). By a somewhat loose usage the lines are said to be *resolved* into three or more components. This is the "Zeeman effect." There is a multitude of empirical rules about these components, their spacings, the way in which their number and their spacings vary from one line to another, and other features. According to the new fashion, however, we focus our attention not on the component lines, but on the stationary states which are inferred from them.

The effect of a magnetic field may be described by saying that it replaces each stationary state (with a few exceptions) by two or more new ones. Each of these new states requires four symbols to designate it; the symbols n, k and j for the original stationary state, and a new symbol m to denote its place in the resulting group. As heretofore, when every stationary state is connected with every other by an arrow and the corresponding lines are sought, it is found that some of the lines are missing. Still another selection principle is therefore to be sought, and the values of the new numeral m are to be so adjusted—if possible—that the selection-principle can be read easily from them. When so adjusted m is called the *magnetic quantum-number*.

In certain cases the empirical rules for the components whereby the magnetic field replaces the individual lines are simple; and the derived rules for the new stationary states which arise out of the original ones when the magnetic field is applied are correspondingly simple. These are the cases of "normal" Zeeman effect (the adjective "normal" may be an entirely misleading choice). Let ΔU_m

represent the energy-difference between the new stationary state denoted by the index m, and the original stationary state. The rules are comprised in the formula,

$$\Delta U_m = m\omega Hh \tag{8}$$

and in the selection-principle. In the formula H stands for the magnetic field; ω is a factor equal within experimental error to $e/4\pi\mu c$ (μ = mass of the electron) and commonly identified with it. m has two or more values spaced one unit apart (for instance, 1 and 0, or $\frac{1}{2}$ and $-\frac{1}{2}$, or 1 and 0 and -1).

The selection principle is as follows: *The only transitions which correspond to actual lines are those in which* m *changes by unity or not at all*: $\Delta m = 0, \pm 1$. This is the *selection-principle for the magnetic quantum number.*

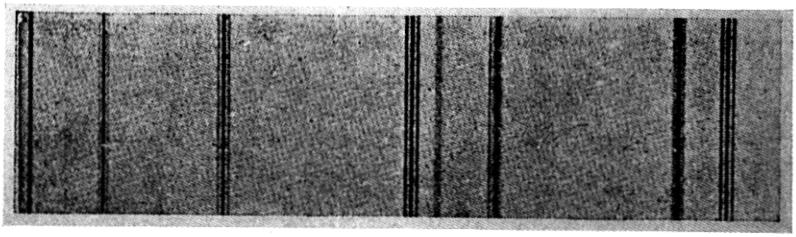

Fig. 9—Effect of magnetic field on spectrum lines. (P. Zeeman, *Journal of the Franklin Institute*)

If we allow m to assume only two values, this principle becomes nugatory. If on the other hand, we adopt the principle, m can assume any number of values whatever, provided only they are spaced at unit intervals; it makes no difference with the observed lines whether there are two or two hundred new stationary states for every original one. This is convenient for theorizing. In dealing with the Zeeman effect in general, and not merely with these special "normal" cases, it is necessary to assume that ω is not restricted to the particular value

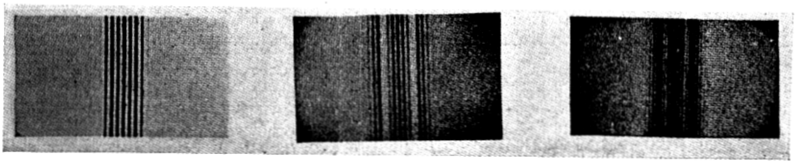

Fig. 10—More complicated effects of magnetic fields on spectrum lines. (P. Zeeman, *l.c.*)

just given, but depends on the stationary state in question; and that m depends on the value of j for the stationary state in question.

Very strong magnetic fields treat a group of stationary states as if they were one single state—as if they were first all fused together into one, and this one then resolved according to equation (8). This is the *Paschen-Back effect.* It evidently means a great deal.

The light emitted from a gas exposed to a magnetic field is polarized. Some of the new lines are circularly polarized about the direction of the magnetic field as axis; others are plane-polarized, with the electric vector parallel to the direction of the magnetic field. The lines corresponding to transitions in which m changes by one unit are all polarized in the former way; the lines corresponding to transitions in which m does not change are all polarized in the latter way.[22]

E 10. *Interrelations of Multiplets and Zeeman Effect*

I insert this section chiefly for the benefit of such readers as may be preparing for a thoroughgoing study of atomic theory. Others may do well to pass it over, as the statements it contains can scarcely be apprehended with any vividness, except by the aid of pencil and paper and hours of reiteration. For those who omit this section I will merely say, that the material described in it goes far to show that the numerical values which we have been assigning to k and j are not quite arbitrary, but are determined by something fundamental; although the ones heretofore assigned are not necessarily the most expressive.

I begin with a description of the various known systems of stationary states, condensed into Table III. To make this table clear I will explain the fourth line; this line contains the statement that a "quartet system" of stationary states consists of an s-column of single levels, a p-column of groups of three levels each, and a d-column, an f-column, and additional columns of groups of four levels each.

TABLE III

Name of System	s	p	d	f	f'	f''
Singlet	1	1	1	1	1	1
Doublet	1	2	2	2	2	2
Triplet	1	3	3	3	3	3
Quartet	1	3	4	4	4	4
Quintet	1	3	5	5	5	5
Sextet	1	3	5	6	6	6
Septet	1	3	5	7	7	7
Octet	1	3	5	7	8	8

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[22] The effect of a magnetic field on resonance-radiation, discovered by Wood and Ellett, will be described in the Second Part.

Elements of the first column of the periodic table possess a doublet system of stationary states; elements of the third column, a doublet system and in addition a quartet system. It is inferred that elements of the fifth column possess these and a sextet system in addition; elements of the seventh, these three and an octet system in addition. Elements of the second column of the periodic table possess a singlet system and in addition a triplet system. It is inferred that elements of the fourth column possess these two and a quintet system in addition; elements of the sixth column, these three and a septet system; elements of the eighth, these four and a nonet system. These inferences have been partially verified. For titanium, in the fourth column of the periodic table, the triplet and quintet systems have been discovered; for vanadium (fifth column) the quartet and sextet; for chromium (sixth) the quintet and septet; for manganese (seventh) the quartet, sextet, and octet; for iron (eighth) the triplet, quintet, and septet. Apparently it is by no means certain that the unmentioned systems are really missing, as the difficulties of analyzing these complex spectra are terrific.

There are certain rules governing the number of levels in a group, and the effect of a magnetic field upon these levels. These rules were discovered chiefly by Landé; I give them in his notation. I recall, to begin, that we have designated each group of levels by a numeral k, which is 1 for all the groups in the s-column, 2 for all groups in the p-column, 3 for all groups in the d-column, and so forth. We have further distinguished the different levels in a group by assigning them different values of another numeral j; the manner in which these values of j are chosen was described in section E8. Landé introduces a numeral K which is smaller than k by $\frac{1}{2}$; K thus is $\frac{1}{2}$ for all groups in the s-column, $1\frac{1}{2}$ for all groups in the p-column, and so forth. He also introduces a numeral J which is greater than j by $\frac{1}{2}$; and a numeral R which is $\frac{1}{2}$ for every level belonging to a singlet system, 2/2 for every level belonging to a doublet system, 3/2 for every level belonging to a triplet system, and so forth.

These are Landé's rules:

(1) The total number of levels in a group characterized by the numeral K, belonging to a system characterized by the numeral R, is twice the smaller of the two numerals R and K (that is, it is $2R$ if $R<K$; $2K$ if $R>K$; $2R=2K$ if $R=K$).

(2) In the formula (8) for the Zeeman effect, the factor ω is equal to $e/4\pi\mu c$ multiplied by a factor g, which depends on the numerals R, K, and J for the level in question in the following manner:

$$g=3/2+(R^2-K^2)/2(J^2-\tfrac{1}{4}) \qquad (9)$$

(3) In the same formula, the magnetic quantum-number m depends on the numeral J for the level in question; it assumes $2J$ values altogether, commencing at the maximum value $(J-\frac{1}{2})$ and going downwards across zero to $(-J+\frac{1}{2})$.

These rules form a beautiful little problem for the designer of atom-models. They have often been tested and verified (it is not easy to find out just how far), and at present are widely used in the deciphering of spectra. It appears, however, that some spectra—particularly those of the inert gases—are too complicated even for these rules, and possess a structure even more elaborate. Considering how difficult it is to grasp the structures already described, one may be excused for feeling some dismay at the prospect.

E 11. Effect of Electric Field on the Stationary States

When an electric field is applied to a radiating gas, the lines of its spectrum are replaced by groups of lines, often rich and complicated. (Fig. 11.) From these we infer, as heretofore, that the stationary states are replaced by groups of stationary states. The atom-model proposed for hydrogen and ionized helium has been extraordinarily successful in describing the effect of electric field upon their spectra,

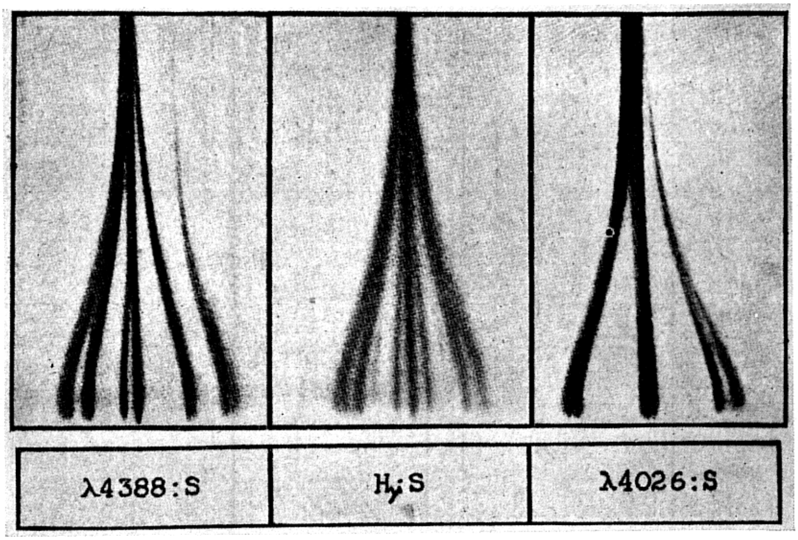

Fig. 11—Resolution of spectrum-lines into groups, displacement of lines, and emergence of missing lines, produced by a strong electric field (increasing from the top downwards to nearly the bottom of the picture). (J. S. Foster, *Physical Review*)

and therefore I shall violate the rule I have heretofore followed, and postpone the description of the phenomena until the theory is stated. Atoms of other kinds are affected in at least two ways; the stationary states are displaced, and the "missing lines" are evoked, as I have said already.

E 12. *Intensity-Ratios*

The relative intensities of the various lines of a doublet, or triplet, or multiplet are often equal within the (fairly large) uncertainties of measurement to simple ratios, such as 1 : 2, 2 : 3, 3 : 4. This happens too often to be easily put down as a mere coincidence, and indicates that the occurrence of transitions is governed by simple laws. Our selection-principles are themselves indications of the same type, since they may be taken as signifying that the intensity-ratio of certain lines to certain others is zero. This problem may be more difficult than the ones I have stressed hitherto, since each line involves two stationary states and is not a quality of one only. This applies to other properties of lines, such as their sharpness or diffuseness.

E 13. *Excitation of Individual Frequencies*

So long as an atom is conceived as a belfry full of bells of various pitches, it would probably be argued that a shock to the atom would set all the bells to jangling, and a gas bombarded by electrons would emit all of its natural frequencies if any. The interpretation of spectra to which these pages are devoted leads to a very different idea. A spectrum-line of frequency ν is emitted when the atom passes from a stationary state B to a stationary state A. The energy-value of state B by itself does not determine ν; this is controlled by the difference between the energy-values of B and A, which is $h\nu$. But the energy-value of B has everything to do with whether or not the frequency ν is emitted under given conditions; for it will not be emitted at all unless the atom is first put into state B. If the gas is bombarded with electrons of energy insufficient to raise an atom from its normal state to state B, then the line in question, and all of the other lines which result from transitions from B to other levels of lower energy-value, will fail to appear. If the energy of the electrons is raised past the critical value (the difference between the energy-value of B and the energy-value of the normal state) all of these lines suddenly appear.

This is illustrated by Fig. 12, relating to magnesium. An electron striking a magensium atom and having an energy equal to 3.2 equivalent volts is able to put the atom into a particular excited state; the atom emits radiation of wavelength 4571 in returning to its normal state. To get the atom to emit another sort of radiation, the electron must possess 6.5 equivalent volts to put it into another excited state. Any excited state can be reached if the electron has 10 equivalent volts to pass over to the atom.

In a gas sustaining an electrical discharge, the atoms are subject to stimuli of such variegated force and type that the distinctions between different lines are not so clearly marked; but it can be seen that mild discharges favor lines for which the initial level is adjacent or close to the normal level, while other lines require a more violent stimulus. Furthermore, when a gas is steadily heated to higher and higher temperatures, various lines of its spectrum appear in more or less the order of the stationary states which are the initial states of the transitions responsible for these lines. Accordingly a "temperature classification" of spectrum lines has been developed at Mount Wilson Observatory and elsewhere, and is valuable in deciphering intricate spectra.

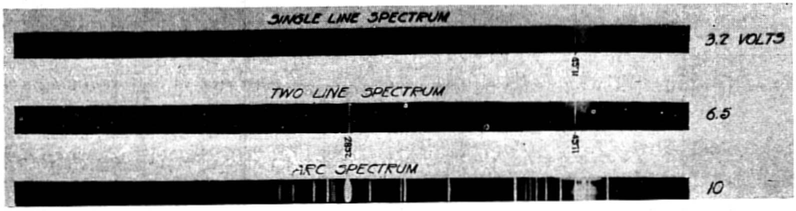

Fig. 12—Successive excitation of lines requiring electron-impacts of successively greater violence to bring atoms into the necessary initial states. (Foote, Meggers, and Mohler, *Philosophical Magazine*)

E 14. Absorption-Spectra

An atom which will emit a frequency ν when it is originally in a state B and passes over into a state A, will absorb light of the same frequency if it is initially in the state A. This has the important consequence that the lines which a gas absorbs, when lying at rest and unexcited, are those which it emits in passing from any and every other state *into the normal state*. The lines emitted when an atom passes from one of its stationary states into another which latter is not the normal state, are not absorbed by the gas lying quiescent and undisturbed. For this reason helium and neon and argon are quite transparent to all visible light, although they have many emission-lines in this region of the spectrum; for each of these lines corresponds to a transition into some other than the normal state and the lines which correspond to transitions into the normal state lie far off in the ultraviolet. But if such a gas is made the theatre of a self-sustaining electrical discharge, the other lines likewise are absorbed; for the discharge puts the atoms of the gas temporarily but frequently into various abnormal states. This incidentally is one of the bits of evidence that an atom may sojourn for a finitely long time in another stationary state than the normal one. If the gas is heated, the same effect occurs; for the violent collisions between atoms in a hot gas occasionally bring atoms into excited states.

By observing the absorption-spectrum of a quiescent gas one learns which lines in the emission-spectrum correspond to transitions into the normal state—a valuable piece of information in the cases of elements of which the spectra are complicated and obscure.

E 15. Spectra of Ionized Atoms

In a violent electrical discharge, such as a spark, the gas emits many lines which cannot be fitted into the system of series of the usual spectrum of the gas. These may also be produced by bombarding the gas with electrons possessing more than enough energy to ionize its atoms. They are believed to emanate from ionized atoms, or from atoms deprived of one electron. The spectrum of ionized-helium has been very important in these pages. In very violent sparks many more lines emerge, and these are associated with atoms deprived of two, three, or even more electrons.

The spectrum of the ionized atom of an element resembles, in its system of series, and in more minute details, the spectrum of the neutral atom of the element preceding it in the periodic system. The spectrum of an atom deprived of n electrons resembles the spectrum of the neutral atom preceding it by n places in the periodic system. This confirms the belief that the spectrum and the other properties of an element are determined chiefly by the number of electrons which its atom contains.

E 16. X-ray Spectra

The difference between the X-ray spectra to which we now come, and the "optical" spectra which we have been discussing seemed profound and vital in the era of very defective knowledge, but it has faded steadily away with the deepening of understanding. Twelve or fifteen years ago the contrast was multiform and very sharp; for the optical spectra were produced chiefly by maintaining an electrical discharge in a gas, the X-ray spectra invariably by bombarding a solid body with exceedingly fast-moving electrons or with other X-rays; the optical frequencies could be diffracted and refracted, the X-rays not at all or almost imperceptibly little; the optical frequencies were all inferior to 3.10^{15}, the X-ray frequencies all clearly more than a thousand times as great. Since then, rays of almost all the intermediate frequencies and with intermediate properties have been generated in a variety of ways, and the distinction is no longer trenchant, except between the extremes. To make it so, one must seek a theoretical reason—and perhaps there is none to be found.

There is, however, apparently good ground for introducing a theoretical distinction. I have pointed out heretofore that the energy which an atom loses, when it radiates one of the lines of its "optical" spectrum, is less than the ionizing-energy. Or, turning this statement around and amplifying it a little: the energy which an atom absorbs, when it absorbs one of the rays of its optical spectrum, is less than what is required to detach the loosest electron from it. Therefore it is possible to assume, at least as a trial hypothesis, that the energy is spent in lifting the loosest electron partway out—a hypothesis fortified by the fact that, when the atom has just absorbed some energy in this manner, the electron can be detached by supplying the atom with enough extra energy to bring the total amount up to the ionizing-energy. But if we take one of the typical X-ray frequencies, and multiply it by h to ascertain how much energy the atom gains in the process of absorbing that frequency, we find that the quantity $h\nu$ exceeds the ionizing-energy tremendously. This circumstance makes it quite out of the question to imagine that the X-rays are due to changes in the position or the motion of the loosest electron alone. We may therefore define the X-ray frequencies as those which cannot be explained as due to transitions of the loosest electron, from one motion or position to another, unaccompanied by other changes. By this definition, every frequency ν for which the quantum-energy $h\nu$ is greater than the ionizing-energy, goes into the X-ray spectrum. For the remaining frequencies the question is more dubious, perhaps never quite to be settled unless and until complete theoretical classification of all the lines is attained. In this section, however, I shall speak only of frequencies hundreds or thousands of times greater than the ionizing-frequency.

Gazing upon typical X-ray emission spectra one sees that they consist of groups of lines with wide intervals between. Going from higher frequencies towards lower, the groups are known successively as the K group, the L group, the M group and the N group. The word *series* is more commonly used than *group*; but this is a misfortune, for it suggests a dangerously misleading analogy with the series in the optical spectra which we have studied with so much care.[23] The process of measuring these lines and classifying them

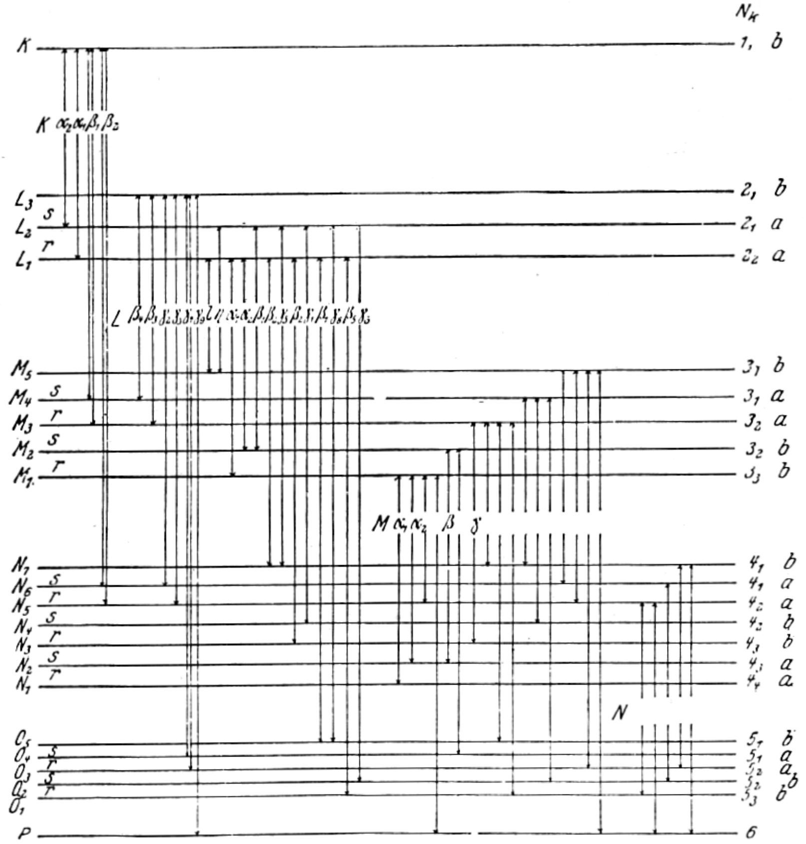

Fig. 13—Diagram of stationary states designed to account for the X-ray spectrum of uranium. (From Siegbahn, after Coster)

was carried out after the dissemination of Bohr's great idea that each line-frequency should be multiplied by h and the product interpreted as the difference between the energy-values of two stationary states of the atom. The complete analysis of an X-ray spectrum

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[23] In fact the usage is inverted. A series, in the optical spectrum, is a set of lines having the same *final* state in common; but the "*k-series*" is a group of lines having the same *initial* state in common, the L-series a set of 3 groups corresponding to 3 initial states.

thus culminates in a diagram of stationary states, as for the optical spectra.

Such a diagram is shown in Fig. 13, which is for an element far up in the periodic system, therefore with a rich system of X-ray lines and stationary states. In comparing it with one of the diagrams made for optical spectra, it must be remembered that its scale is enormously more compressed—the distance from top to bottom corresponds to about one hundred thousand equivalent volts. Each line in the X-ray spectrum corresponds to an arrow between two of the levels, but not every arrow corresponds to a line. Again there is a selection-principle, and this selection-principle is partly expressed by attaching a double index to each of the levels. When the indices are assigned as in Fig. 13, transitions between levels for which the second numeral differs by one unit include the only ones which actually occur. But this is not the complete selection-principle; it is necessary to add that in any actually occurring transition, the first numeral must change by one or more units; and further, that transitions may occur only between levels to which different letters are attached. The first numeral is designated by n, the second by k; they are called the total and the azimuthal quantum-number.

The levels are also frequently known by letters with subscript numerals, as the diagram shows. The letters by now are pretty definitely fixed, but the subscripts are still being shuttled around. The notation for the X-ray lines is in a terrible state.

A curious and evidently important feature of these levels is, that when an atom is put into any one of them—say into the K level, or the L_1 level, or the L_2 level—it extrudes an electron. Or, in other words, each of these stationary states is a state in which the atom lacks one of its electrons—like the "ionized-atom" state from which we previously measured the energy-values in dealing with the optical spectra. All of them, at least the highest ones, are in fact "ionized-atom states." Since, however, they are all different, it is natural to suppose that a different electron is missing, or that an electron is missing from a different place, in each of the different cases. Apparently an atom cannot enter into a stationary state with so high an energy, and remain neutral.

We must pause to consider from what standard state the energy-values of these stationary states are measured. In the previous case of the optical spectra, the energy-values of the stationary states were measured, so to speak, *downwards* from the state of the ionized atom to the normal state of the neutral atom; the energy of the ionized atom was set equal to zero, that of the neutral atom in its normal state then had a certain negative value, all the other energy-values were negative and scattered between these two. In this case of the X-ray spectra, the energy-values of the stationary states are measured *upwards* from the normal state of the neutral atom, to which the energy-value zero is assigned, while all the other energies are positive. In Fig. 13 this zero-line must be imagined just under the level marked P.

The exact position of this zero-line for the high energy stationary states is not very accurately known; although the distance between any two levels is determined with all the usually very great exactitude of X-ray wavelength-measurements, the distance from any level to the zero-line is uncertain within a few tens of volts. This uncertainty is not great enough to be important when dealing with the high-frequency X-rays.

This point being attended to, we are now in position to consider the striking difference between X-ray emission-spectra and X-ray absorption spectra—striking indeed when one looks at typical photographs, apparently altogether a different matter from the contrast between optical emission-spectra and optical absorption-spectra, yet in principle very much the same thing. In dealing with optical spectra, I remarked that while an atom *may* absorb any frequency which it can emit—while the complete absorption-spectrum of a gas is identical with its complete emission-spectrum, yet the absorption-spectra one ordinarily sees contain only a small selection of the emission-lines. This occurs because when a gas is being examined for its absorption-spectrum in the laboratory, by sending light through it, it is generally in an untroubled and quiescent condition, each of its atoms being in the normal state; therefore it absorbs only such frequencies as provoke transitions from the normal state to the various excited states, and not such frequencies as would induce transitions from one excited state to another, for few or none of the atoms are in any one of the excited states to start with. Such also is the case with the X-ray spectra. Quiescent atoms absorb only such X-ray frequencies as produce transitions from the normal state into one of the stationary states designated by K, or L_1, or L_2, and so forth—they do not absorb such frequencies as would produce the transitions from L_1 or L_2 to K, for instance, for the atoms are not initially in the states L_1 or L_2. This is quite the same behavior as is observed in the response of atoms to radiations in their optical spectra. It is much more pronounced, however; for, while it is possible to make a gas absorb frequencies which produce transitions from one excited state to another, by maintaining the gas in a state of intense electrical excitation, this has never been done with metals or gases exposed to X-ray frequencies.

Atoms therefore do not absorb such X-ray frequencies as are represented by the downward-pointing arrows in Fig. 13. They do absorb such frequencies as would be represented by arrows drawn from the very bottom of the diagram—a little below the level marked P—up to the various levels; and (it may seem, unexpectedly) they also absorb frequencies somewhat higher than these. This however does not mean that the atom may be put into an excited state of higher energy than the K state, for instance; it means simply, as direct evidence proves, that the extruded electron receives the extra energy and goes away with it. Owing to this fact, the X-ray absorption-spectrum consists not of sharp absorption-lines at the several frequencies corresponding to a transfer of the atom into the K-state, the L_1-state, and so forth, but of continuous bands commencing with sharp edges at these frequencies, and trailing out gradually towards higher frequencies.

Another curious feature of the X-ray spectra is that transitions from the various excited states of high energy-values, such as the K-state and the L-states, directly into the normal state, apparently do not occur.

E 17. Band-spectra

Band-spectra are the spectra of molecules,—that is to say, of clusters of two or more atoms, such as appear in certain gases. This is proved by the fact that they are displayed by gases which are known in other ways (gramme-molecular volume, specific heat) to consist of molecules; by the fact that the band-spectrum of such a gas disappears when the gas is heated to the point where its molecules are dissociated into atoms; and by the general successfulness of the quantitative theory based on the assumption that they are due to molecules. Occasionally band-spectra are displayed by gases which are not otherwise known to contain molecules, such as helium and potassium; it is supposed that they are due to molecules too few to be detected by the other accepted methods. Usually they are easy to distinguish at first glance from the optical spectra of atoms, although there are exceptions, such as the band-spectrum of the hydrogen molecule. Like the spectra we have discussed, they consist of lines; the term "band-spectrum" describes the manner in which these lines are grouped. Again like the spectra we have discussed, they are analyzed according to Bohr's fundamental principle, by interpreting the lines as the results of transitions between stationary states.

F. MAGNETIC MOMENTS OF ATOMS

Of the enormous and chaotic variety of facts about the magnetic properties of materials, only a few of the least conspicuous have been serviceable to atom-builders; the notorious ones have helped very little or not at all. The famous and characteristic magnetic properties of iron, nickel, cobalt, depend on the arrangement of the atoms and on the temperature of the metal, and cannot safely be attributed to the atoms themselves. Diamagnetism, an inconspicuous and rarely-mentioned quality of certain elements, is in some instances quite independent of temperature, and may well be a property of the atoms. Paramagnetism, an almost equally inconspicuous quality of certain other elements, depends on temperature, but in such a way that it may sometimes be explained by assuming that each atom has a characteristic magnetic moment, the same for all the atoms of a substance. The value of this magnetic moment of the atom may be calculated from measurements on the paramagnetism of the substance; the process of calculation involves certain assumptions, at least one of which is at the present open to question.

Direct measurements upon the magnetic moments of certain atoms are now being made by Gerlach; and they are among the most important achievements of these years. In a small electric oven, a metal such as silver is vaporized; a beam of the outflowing atoms, passing through a small orifice in the wall of the oven and through others beyond this one, eventually travels across a strong magnetic field with a strong field-gradient and falls upon a plate. Suppose that each atom is a bar-magnet, oriented with its length parallel to the magnetic field. If the field were uniform, the bar-magnet would not be deflected, it would travel across the field in a straight line; for although its north pole would be drawn sidewise by a force, its south pole would be pushed by an exactly equal force in the exactly opposite direction. That the atom may be drawn aside, the field must be perceptibly different at two points as close together as the two poles of the magnet. When one considers how small an object the atom is, it is clear that the field must change very rapidly from one point of space to another, its gradient must be enormous. Gerlach succeeded in contriving so great a magnetic field with so great a gradient that the beam of flying atoms was perceptibly drawn aside. The most-deflected atoms are those of which the magnetic axes are most nearly parallel to the magnetic field. From their deflections, the field, and the field-gradient, the magnetic moment of the atom can be computed very simply. The values thus obtained are of the order of 10^{-10} in *CGS* units.

I shall comment in the second part of this article upon other inferences from these experiments, which are as valuable as the experiments upon the transfer of energy from electrons to atoms. At this point it is sufficient to realize that these experiments prove that atoms, or at least the atoms of some elements, possess magnetic moment. If magnetic moment is due to electric current flowing in closed orbits, as Ampere and Weber guessed a century ago, the atom must be supposed to contain such currents; if the atom consists of a nucleus and electrons, some at least among the electrons must be supposed to circulate. And if the electrons are assumed to circulate in a particular manner the magnetic moment of the atom so designed can be computed, and thereupon tested by experiment.

This completes the list of the phenomena, the properties of matter, which are used in designing the contemporary atom-model. Nobody will require to be convinced that it is not a list of all properties of matter, nor of all phenomena. These are not among the obvious and familiar qualities of matter; and no one meets any of them in everyday life, nor perceives any of them with his unaided senses. They are phenomena of the laboratory, discovered after a long and painstaking development of laboratory technique. Lucretius did not know them, and they were inaccessible even to Newton and to Dalton. They are a very limited selection from among the phenomena of nature, but not for that the less important. The atom-model which is devised to explain them is at best a partial atom-model; thus far it serves for no other phenomena than these, but these it does interpret with an elegance and a competence quite without precedent among atom-models. I have said that some of these phenomena are explained by conceiving an atom made of a positively-charged nucleus and a family of electrons around it; but this conception is not tenable if unmodified. It can be modified so as to interpret the rest of these phenomena; but this means little by itself. The important fact is this, that the modifications which are demanded appear in some cases to be endowed with a beauty and a simplicity, which indicate that they are the expressions of an underlying principle of Nature. To these the following article will be devoted.