3000 members and guests of the American Institute of Physics met in the Chicago Civic Opera House last October 25th for the Symposium on Physics Today, during the AIP's 20th Anniversary meeting. The following article, based on the second of six invited papers presented during the symposium, is the third to appear in this journal. The fourth, by John C. Slater, will be found on page 10. Papers by Drs. Darrow and Fletcher appeared in November and December, 1951, respectively.

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ONE CAN ALWAYS TELL which part of physics is advancing most rapidly by consulting a few numbers of *The Physical Review*. Judged by this criterion, the heroic period of the physics of the atom may be taken to be roughly the two decades from 1915 to 1935. (Such dates are never exact.) Prior to 1915 there had been much speculation about the electrical nature of the atom, and Rutherford's work on alpha particle scattering and Bohr's first work on a quantum theory of the atom came a little before 1915. By 1915, however, physicists had really caught the scent of an exciting new forward surge of discovery and were preparing to exploit it fully.

By 1935 a tremendous amount of progress had been made so that physicists felt that they were in good command of an understanding of all the properties of matter in the monatomic gaseous form. The successes of theory in interpreting every detail were becoming rather monotonous, and so it was inevitable that about this time the interest in research turned away from work on individual atoms to the fruitful cultivation of the fields represented by the two other speakers [Enrico Fermi and J. C. Slater] on this morning's symposium: the nucleus and the solid state. Of course, the nucleus is part of the atom; but, as Fermi's talk has made clear to us, the phenomena involving nuclear properties are sufficiently distinct from those involving behavior of the extra-nuclear electronic structure that it will probably always be useful to regard nuclear physics and atomic physics as reasonably separate branches of the science. Likewise, there had been, even before 1915, a great deal of earlier development of the physics of the solid state in the way of definition and measurement of elastic, thermodynamic, electrical, and optical properties. The discovery of x-ray diffraction made possible an entirely new outlook for crystallography. But it was not until the early 1930's, when the modern quantum-mechanical theory of the atom was well launched, that the physics of the solid state really began to profit from the extensive use for its problems of the detailed knowledge of atomic structure. The details of these exciting developments are going to be put in their proper perspective for us by Slater in the next talk.

Between the physics of individual atoms and that of the behavior of macroscopic aggregates of them in the solid states there lies a rather large and important domain which is not explicitly recognized in today's program; I refer to the physics of chemistry: that is, the application of atomic models to giving an understanding of the forces which hold atoms together in various kinds of chemical bond in molecules and the mechanics of the processes by which chemical reactions occur. This is such a big field in itself, and such an important one, that perhaps it is best to ignore it completely rather than to deal with it inadequately. I mention it only that we may all be conscious of an important omission.

LET US BEGIN by running quickly over the most basic facts of our subject even though in so doing we are repeating things which are well known to all beginning students of physics. All of the enormous progress of recent years has been based on the general view that:

1. All matter is made of aggregates of atoms, such that there are 6×10^{23} of them in any gram-atomic weight of any elementary substances.

2. All atoms are built on a similar pattern, consisting of a central positively charged particle called the

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By *E. U. Condon*

nucleus, about 10^{-12} cm. or less in diameter, and containing all but about 0.001 or less of the mass of the atom, this nucleus being surrounded by enough negatively charged electrons to make the whole atom electrically neutral.

3. Atoms of different chemical elements differ with regard to the nuclear charge expressed in electron units and with regard to the number of electrons outside the nucleus. This number, denoted by Z, is called the atomic number. Each chemical element is characterized by a value of Z from $Z = 1$ for hydrogen, 2 for helium, on up to 92 for uranium, and several units higher for the recently-discovered artificial elements which do not occur in nature.

4. The dynamical behavior of the electrons in relation to each other, to the nucleus, and to external force fields, is governed by the principles of quantum mechanics as developed in the years 1924–26. These principles differ radically from the behavior which would follow from Newtonian dynamics although the differences become small in certain limiting situations, a fact which facilitated the discovery of quantum mechanics.

Let us now try to trace the development of our ideas about atomic structure in somewhat more detail. First, we may begin by asking what kinds of observational data concerning atoms are available to guide us and, in turn, require to be interpreted.

We get a little, very crude, information about atomic sizes from the density of matter in the solid state and from collision cross-sections of atoms moving with thermal velocities. From this, it appears that the atoms

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are remarkably alike in size, about 10^{-8} cm. in diameter for the smallest up to only several times that for the largest. This comes about, on the theoretical view before us, by the fact that as Z increases the increasing nuclear charge tends to bind the electrons more closely together which nearly compensates for the increased number of them.

Of greatest importance, because of the great amount and precision of it, are the data obtained from spectroscopy, of the frequencies of the essentially monochromatic radiations emitted by atoms when suitably excited. For each kind of atom hundreds if not thousands of characteristic numbers, capable of measurement to six-decimal place accuracy and more when the needs warrant doing so, are provided by the measurement of these frequencies, usually expressed as wave-numbers of the emitted radiations. The atoms also exist under special circumstances of excitation in which one or more of the extra-nuclear electrons have been stripped off, leaving ions, which are also capable of emitting radiations which can be studied spectroscopically. These radiations extend from the infrared through the visible and ultraviolet and into the x-ray region. They are affected by external electric and magnetic fields which may be applied to the radiating atoms and the details of these Stark and Zeeman effects have also been important for development of atomic theory.

The significance of the emitted radiations becomes even greater when these are studied in relation to the conditions of excitation of the atoms. The prototype of all experiments of this kind are those of Franck and Hertz, in which the emission spectrum is studied when the atoms are excited to emit by a stream of electrons of definite and measured kinetic energy. In this way, it is learned that the electrons are incapable of exciting any radiation at all unless their kinetic energy exceeds a definite minimum amount known as the first critical or the excitation potential. When the electrons have energy only slightly in excess of the excitation potential, only one or two lines of the spectrum are emitted. As the kinetic energy of the electrons is gradually raised other lines are emitted and the complexity of the spectrum actually emitted becomes greater and greater.

ALL OF THESE GENERAL PHENOMENA find their interpretation as follows: The atom as a dynamical system, made up of the nucleus and surrounding electrons, is only capable of existing by itself in certain discrete allowed states of total (kinetic + potential) energy. These are known as the allowed energy levels. In order for an atom to pass from one of these allowed levels to another, it must be coupled to some kind of outside system so that, properly speaking, it is a part of a larger system. For example, when an atom in an excited state (that is, one having more than the minimum energy of the lowest allowed level) emits radiation, it does so because it is really coupled to the electromagnetic field. The total energy of atom plus field remains constant. Initially, the atom has the energy of excitation. After the transition the atom no longer has such energy, but it has gone into one of the degrees of freedom of the field. The electromagnetic field is dynamically equivalent to a lot of harmonic oscillators of various frequencies, ν, whose allowed energy levels are spaced in energy by $h\nu$ where h is Planck's quantum constant. In order to conserve energy over-all, only those degrees of freedom of the field can be excited whose $h\nu$ is equal to the change in energy of the atom. If the atom is initially in a state of energy, W_1, and makes a transition to a state of energy, W_2, then the frequency of the light emitted must satisfy Bohr's frequency condition,

$$h\nu = W_1 - W_2$$

At ordinary temperatures the mean thermal energy of a degree of freedom is only about 1/40 electron-volt. In spectroscopy we are usually dealing with energy differences greater than one volt and often many times that. Hence, at such temperatures a negligible number of atoms are in states from which visible radiations can be emitted. When the atoms are excited by electron impact, it is found that the critical potentials, V, are such that the energy, Ve, which can be given to excite the atom is in agreement with the amounts needed to excite the various spectral lines as estimated from Bohr's frequency condition.

Along these lines it is possible to represent the observed emission and absorption lines of atomic spectra in terms of transitions between empirically determined allowed energy levels characteristic of that atom. When this is done, an extraordinary number of regularities in the arrangements of these levels is observed. The main problem of atomic theory has been to interpret the details of the energy level scheme of an atom to the quantum mechanical treatment of the nuclear model of the atom.

Before going on to outline the main facts about the allowed levels and their relation to the atom-model, there is one more matter of general principle that needs to be touched upon. The most casual inspection of a spectrum shows that not all of the lines are of equal intensity. On careful study it is found that the lines corresponding to transitions between some pairs of levels seem to be so weak as to be totally lacking: they are less than a millionth as strong as the main lines of the spectrum. Without for the moment discussing the meaning of variations in brightness of the lines actually observed, let us consider the main facts about which lines are observed and which are so faint as to escape observation under ordinary circumstances. It is found that the selection rule governing this can be conveniently stated as follows:

A number, denoted by J, can be ascribed to each energy level. For atoms or ions containing an even number of electrons J is an integer for all levels. For atoms or ions containing an odd number of electrons J is half an odd integer for all levels. It is then found that the lines actually observed are those for transitions in which J changes by 0 or $\pm$ 1, with the additional proviso that lines are missing in which J is zero in the initial and final states.

In terms of the atom model this rule has a simple interpretation. A free atom in a given stationary state has a definite amount of resultant angular momentum. In quantum mechanics this is always a simple multiple of the basic unit $h/2\pi$ or $\hbar$. Orbital angular momentum always comes in integral multiples of $\hbar$. The intrinsic spin angular momentum of each electron is $\frac{1}{2}\ \hbar$. So the total resultant angular momentum of the electrons as a whole must be either an integer of half-an-odd integer multiple of $\hbar$. If the nucleus itself has no angular momentum then J is the total angular momen- of the free atom expressed in units of $\hbar$.

When a transition occurs in which the atom's angular momentum changes, there must be over-all conservation of angular momentum. The excitation of the electromagnetic field produced in the emission process must be of such a nature as to take up the angular momentum lost by the atom. This at once makes it clear why no spectral lines corresponding to $0 \rightarrow 0$ transitions in J are observed. The electromagnetic field does not have any states corresponding to zero angular momentum: the least allowed value is 1. Therefore, there are no states of the field compatible with the change $0 \rightarrow 0$ in the atom. At first sight it might seem that this argument would also exclude $J \rightarrow J$ in which a nonvanishing J does not change in amount; these, however, are permitted because J is really a vector and it is possible for there to be a change whose magnitude is 1 in J, the vector, without a change in the magnitude of J simply by having a change in its orientation.

The electromagnetic field does, however, have states of angular momentum corresponding to all integral values other than zero, and from this it follows that spectral lines could appear for which ΔJ is 2 or more. Such lines are not absolutely absent, but merely very much weaker than the ordinary lines for which $\Delta J = 0, \pm 1$. This comes about in the following way. The linear momentum of a light-quantum of wavelength λ is h/λ and so, speaking classically, the impact parameter, d, or distance of closest approach to the origin for a quantum of angular momentum is:

$$d = \hbar \div (h/\lambda) = \lambda/2\pi$$

This is usually large compared to the size of the atom and therefore we can say that classically the quantum is not able to get close to the atom which emits it. The whole interaction with the atom comes about as a result of quantum mechanical deviations from this classical result which rapidly becomes very much smaller for larger values of the angular momentum of the emitted light quantum. Thus atomic transitions for which $\Delta J = 2$ are not absolutely forbidden; they are, however, very much less probable than those for which $\Delta J = 0, \pm 1$. They are actually observed under some circumstances and give rise to what is known as quadrupole radiation, the usual transitions giving dipole radiation.

WE NOW TURN to a brief outline of the results of a more detailed application of the atom model to an interpretation of the energy level scheme of the atoms. Except for the hydrogen atom we are now confronted with problems whose exact solution have not been found and must therefore proceed by the use of perturbation methods. Such approximation procedures, while inexact, have the merit that since they do not produce exact answers automatically, they force us to examine carefully the physical nature of the various aspects of the problem and thereby to learn which features are relatively more important than others.

In quantum mechanics, any dynamical system is described by a Hamiltonian operator representing the kinetic and potential energies of all its parts. The allowed energy levels of the system are the values W for which the Schrödinger wave equation

$$H\psi = W\psi$$

possesses solutions ψ satisfying appropriate boundary conditions.

In the nuclear atom model the important terms are: (1) the sum of the kinetic energies of the electrons; (2) the Coulomb potential energy of each electron's interaction with the nucleus; (3) the Coulomb potential energy of each electron with each of the others; (4) the magnetic interaction of each electron's magnetic moment with the magnetic field arising from its motion relative to the other charged particles; (5) the magnetic interaction of the nuclear magnetic moment, if any, with the magnetic field due to the electrons' spin and orbital motion; and (6) the interactions of the external electrons with departures of the nuclear electrostatic field from spherical symmetry in the case of nuclei having quadrupole moments. In connection with (1) it should be noted that the difference between the classical and relativistic forms for the kinetic energy becomes quite large in the case of the atoms of higher Z.

The starting point of all theory for the energy levels is a model in which the magnetic and nonspherical nuclear effects are neglected initially and in which the Coulomb interaction of the electrons with each other is represented roughly by a spherically symmetric space charge distribution. This means that in the main each electron moves in a central field of force described by the potential function $\phi(r)$ where for $r \rightarrow 0$

$$\phi(r) \rightarrow +\frac{Ze}{r} + C$$

and for $r \rightarrow \infty$

$$\phi(r) \rightarrow \frac{e}{r}$$

for a neutral atom. The change-over from one form to the other takes place in the range of value of r where the electrons are found. A considerable part of the theoretical literature is concerned with describing methods for making judicious choices of good initial assumptions for $\phi(r)$.

But whatever assumption is made, the calculation starts by assuming that each electron moves mainly in a spherically symmetric field and therefore it has meaning to assign individual values of the orbital angular momentum, l, to each individual electron. For historical reasons these are usually expressed in terms of a code:

Code:	s	p	d	f
$l=$	0	1	2	3

An s electron is one having zero orbital angular momentum and a d electron is one having two units of orbital angular momentum, and so on. For a central field of the general type mentioned the allowed energy levels are given by a scheme having these properties: (1) for each l the levels can be arranged in series converging to the same limit, (2) the lowest value of the principal quantum number n in the l^{th} series is $(l+1)$, and (3) as l increases the series tend toward the values characteristic of the hydrogen atom:

$$W_n = -\frac{Rhc}{n^2}$$

where $R = 109737\ \text{cm}^{-1}$ is the Rydberg constant.

WHILE SPECTROSCOPY gives us important information about all the excited levels of each atom, it is the nature of its normal or lowest energy state which is of the greatest interest in connection with its chemical molecule-forming properties and its behavior in the solid state. At first it might seem that the lowest state will be obtained on this model by putting each individual electron into a 1s state. Examination of the known facts from analysis of spectra shows that this is not the case. At this stage in the development, the physicists would have discovered the Periodic Table of the Elements, if it were not for the fact that a chemist, Mendelejeff, had done it about seventy-five years earlier. Let us proceed as we might have done if we had never heard of Mendelejeff. From analysis of the spectra alone we can learn the quantum numbers of each electron for the atoms in the normal state. In a central field problem for an electron with spin there are four quantum numbers. There is n, the principal quantum number, which has to do with the extent of the motion in and out on the radial coordinate. There is l, the orbital angular momentum, as magnitude of a vector and m, which gives the value of the projection of this vector along a reference axis. For a given l, this m (sometimes called the magnetic quantum number) can assume the $(2l+1)$ values: $-l, -l+1, \cdots -1, 0, +1 \cdots +l$. Finally there is a quantum number s, capable of assuming only two values, say $\pm \frac{1}{2}$, which give the orientation of the electron spin relative to a fixed axis. The quantum state of an electron in a central force field is thus specified by giving (n, l, m, s). In the absence of an external field, the energy depends only on n and l. Therefore, the energy value $W(n, l)$ really is represented not by one state but by a cluster of $2(2l+1)$ states all having the same energy.

In considering now what is the electron configuration of the lowest state of an atom, we have to take into account another quantum mechanical rule known as the Pauli Exclusion Principle, on which the Fermi-Dirac statistics of a degenerate electron gas is built. According to this, states of a multi-electron system are not allowed in which more than one electron occupies the same one-electron state; i.e., two electrons cannot be assigned the same set of four quantum members.

This rule means that we can not have more than two electrons in any s state, nor more than six in any p state, nor more than ten in any d state. When we now try to determine the lowest energy level of a multi-electron atom by putting the electrons in the lowest state possible consistent with this rule, the entire structure of the chemist's periodic table of the elements falls out almost automatically. Elements of like chemical properties are those having like groups of electrons in their outer parts in their normal states.

The "periodicity" of the periodic table is rather forced in places as is evidenced by the large number of different arrangements which have been proposed. Hydrogen and helium make a very short period of their own, followed by the two usual short periods of eight:

n	s	s^2	p	p^2	p^3	p^4	p^5	p^6
1	H	He						
2	Li	Be	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	A

Up to argon, the sequence goes along quite clearly. But to know what happens next calls for a somewhat more careful analysis, in order to know whether the 4s state is more firmly bound that the 3d state. Actually these two are bound with nearly equal firmness so the next twelve elements correspond to the filling of the 4s and 3d shells; after that the first long period is completed by filling the 4 p shell:

s	s^2	d	d^2	d^3	d^4	d^5	d^6	d^7
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co
d^8	d^9	d^{10}	p	p^2	p^3	p^4	p^5	p^6
Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

Actually the picture is a little more complicated than this in the iron group. There is not much difference in the binding energy of a 4s and a 3d electron. In fact, the difference is small compared to the energies of electrostatic interaction which are neglected in the central-field approximation and therefore, for example, energy levels due to d^5s^2 in manganese are not much lower than those due to d^6s, and similarly for other elements. This fact is intimately related to the chemical properties of such elements.

Similarly, the second long period is developed by the elements from Rb^{37} to Xe^{54}, and involves the filling of the 5*s* and 4*d* shells, followed by the filling of the 5*p* shell. The third long period is extra long. It extends from Cs^{55} to Rn^{86}. Besides involving the filling of the 6*s* and 5*d* shells followed by the 6*p* shell as with the other two long periods, this period involves fourteen more elements in the filling of the 4*f* shell. Since the 4*f* states are somewhat internal to the other parts of the atom, those electrons do not have an important effect on the chemical properties of the elements, which accounts for the fact that these rare earth elements are quite similar in chemical properties.

TO SUMMARIZE: the periodic table of the chemical elements finds its interpretation in the following propositions: first, elements have similar chemical properties if their normal state external electron configurations are similar as to number having different amounts of orbital angular momentum; second, the normal state is largely determined by the Pauli principle according to which but one electron can occupy a particular quantum state.

The Pauli exclusion principle finds its analytic expression in the requirement that the wave function must be an antisymmetric function of the coordinates of any two electrons. That is, $\psi(\cdots\ x_r,\ x_s\ \cdots) = -\psi(\cdots\ x_s,\ x_r\ \cdots)$ where x_r and x_s are written for the coordinates of the *r*th and *s*th electrons respectively. If, however, the *r*th and *s*th electrons were in the same state, such an interchange would not alter the value for the wave function, so it would vanish identically.

The fact that the Pauli principle requires that ψ be anti-symmetric in all the coordinates, the spin as well as the position coordinates, provides the interpretation of some facts which had been very puzzling. These are all of the nature of strong apparent magnetic coupling between electron spins. In individual atoms this manifests itself as energy differences between related singlet and triplet levels which are very much greater than could be expected on any view that the energy difference is due to direct interaction of the magnetic moments of the electrons. In chemical molecule formation it shows itself in the almost complete absence of any stable compounds which are not diamagnetic, indicating that the formation of stable chemical compounds is closely correlated with electronic states of molecules in which the resultant spin angular momentum of the electrons is zero. In the solid state we find evidence of an extraordinarily strong spin-spin energy coupling of electrons in the energies of interaction which give rise to the saturated magnetization of the domains of the ferromagnetic materials.

All three of these seemingly widely different phenomena find their explanation in terms of the dependence of the wave function on the ***positional*** coordinates of the electrons, on the resultant ***spin*** of the electrons, because of the requirement that the over-all wave function ψ must be antisymmetric in all coordinates. In consequence the Coulomb electrostatic interaction of the electrons—which is much stronger than any direct magnetic interaction—depends on the resultant spin and gives rise to an apparent strong magnetic coupling of the electrons.

Because of the mathematical complexities involved, the only atoms for which we have exact solutions of the wave equation are the one-electron atoms. For all others, it is necessary to resort to various special approximating procedures for choice of an appropriate effective central field, after which perturbation theory is applied to an essentially first-order calculation of the more detailed effects. While this procedure leaves much to be desired, it has been extraordinarily fruitful in interpreting many details of the complex energy level systems of all the atoms as revealed by spectroscopy.

Similar methods applied to approximate wave functions for electrons in molecules have also done much to deepen our understanding of the valence forces between atoms and to relate these to observations of the band spectra of such molecules.

There has recently been a strong tendency for physicists to regard these topics as so well developed as hardly to merit more detailed cultivation, and yet it is always possible that there may be some surprises in store for us, as was exemplified by the discovery by Lamb and Retherford three years ago of a slight interval between the $2^2S_{1/2}$ and $2^2P_{1/2}$ levels of atomic hydrogen due to some rather finer points in the way an electron is coupled to the radiation fields.

In recent years, therefore, the study of atomic theory has been carried on more from the point of view of applying its results to other branches of physics than for its own sake. The coupling of the outer electron structure with the magnetic dipole and quadrupole moments of the nuclei has been studied by molecular beam and by hyperfine spectroscopy methods in order to learn more about these nuclear properties and the interpretation of such experiments has called for more detailed calculations of the wave functions of the electrons at close range to the nucleus. More exact calculations have been made of wave functions at the outer parts of the atom for application to theories of molecule and crystal formation. The astrophysicists have had to pick up where the physicists left off, in order to extend the calculations of theoretical transition probabilities and relative strengths of lines so that they may interpret solar and stellar spectra in terms of the temperature, pressure and composition of the atmospheres in which these spectra are formed.

At this time, therefore, we are in possession of a theory of the structure of the atom which has been able to give a good, often accurately quantitative, account of all the phenomena relating to the detailed electronic structure of atoms. In the years to come it will probably be used with very little basic modification to give the answers to an increasing range of detailed questions in this part of physics and chemistry.