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Selected Topics in Modern Chemistry

Electronic
Structure,
Properties, and the
Periodic Law

ELECTRONIC STRUCTURE, PROPERTIES, AND THE PERIODIC LAW

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PREFACE

MODERN CHEMISTRY is indeed a complex and multifaceted body of knowledge. So varied are the topics treated that it seems difficult to find a single theme to characterize the field. However, when the developments of the past few decades of chemical research are carefully considered, it becomes apparent that, in *all* areas of chemistry, there has been a strong and continued trend toward the building of a series of theoretical concepts in terms of which it is possible to correlate the results of manifold observations of our physical surroundings with a consistent and dependable picture of the sub-microscopic structure of the material world. With each passing year theories of the structures of atoms, molecules, and crystals have become more refined, and use of these concepts to explain experimental results and to predict the results of experiments as yet untried has become more effective. Far from being the purely empirical science of the 19th century, the chemistry of today is growing ever more deductive. It is, therefore, of greatest importance for the student to taste the excitement of the new chemistry early in his study so that as he develops his knowledge of the body of chemical information, he may also breathe the spirit which gives life and unity to this most challenging field of study.

In this small textbook, we shall examine first the manner in which the structures of the various atoms change with atomic number, and hence with position in the Periodic System. We shall, in due course, find in this examination the explanation for the Periodic Law. Having laid this base for

further study, we shall consider some of the more fundamental properties of elements and the manner in which they vary with change in structural parameters. Thus, we shall seek to develop facility in the prediction of these properties in terms of the positions of the atoms in the Periodic System. In so doing we will take a most important step in learning to think as the modern chemist does when he is investigating the frontiers of our ever-broadening knowledge of the chemical world.

As this is being written, I recall the excitement with which I first discovered that the apparently very complex and confusing world of matter and energy is invested with a magnificent order and simplicity. It is my fond hope that this volume may assist the student in experiencing the same intellectual exhilaration.

I would like to express my appreciation to Mrs. Barbara Joan Novogradac and Mrs. Penelope Ansell for typing the manuscript for this volume, to Mr. Robert Beach for preparing the copy for many of the illustrations to be found herein, and to Mrs. Rachel VanderWerf for preparing the index.

I would also like to acknowledge the permission of The Macmillan Company to use several illustrations from the second edition of "College Chemistry—a Systematic Approach" by Sisler, VanderWerf, and Davidson. In addition to those indicated in the appropriate captions, the illustrations of the sodium chloride and carbon dioxide crystals in Table 3.2 were taken from the above-named text.

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ELECTRONIC STRUCTURES OF ATOMS AND THE PERIODIC LAW

MODERN CHEMISTRY is distinguished from the highly empirical science of several decades ago by the rapidly growing ability of the chemist to explain experimental observations in terms of a well-developed and self-consistent theory of the structure of matter in its various forms. *An outstanding example of this has been the successful delineation and explanation of the Periodic Law in terms of the electronic structures of the atoms of the various elements.* This will be our theme. Many chemists believe it to be the most important theme in the whole of chemistry.

If we understand the manner in which the properties of the elements may be correlated with their electronic structures and hence with their positions in the Periodic Chart, we can predict the types of bonds which various atoms form with each other; and knowing the relationship between properties of compounds and the types of chemical bonds which they contain, we can also predict the properties of a multitude of compounds. Of course, our theory of atomic and molecular structure is far from perfect, and there are many limitations on our ability to correlate structure and properties and to predict the properties of previously unknown species. Never-

theless, great progress has been made, and accomplishments of the immediate past most certainly point toward an even more exciting future.

The Nuclear Atom

From the outset we will assume that the reader is familiar with the qualitative aspects of the nuclear theory of atomic structure. In brief review it may be pointed out that the alpha particle scattering experiments of Ernest Rutherford combined with the classical researches of J. J. Thomson on the electronic nature of atoms, and of H. G. J. Moseley on the nuclear charges of atoms, as well as other studies, led to the development of the following principal postulates of atomic structure:

(1) The major portion of the mass of an atom is concentrated in an exceedingly minute, positively charged body at the center of the atom. This positively charged body is called the *nucleus* of the atom.

(2) There are distributed about this central nucleus at relatively large distances from it negatively charged bodies, called electrons, which constitute only a very small fraction of the mass of the atom. These particles have electrical charges equivalent to the smallest quantity of electrical charge ever observed. The electronic mass = 9.107×10^{-28} g. = 0.00005486 atomic mass unit (one atomic mass unit = 1/12th of the weight of the most abundant variety of carbon atoms found in nature). Hence, the electronic charge (1.602×10^{-19} coulomb) is considered to be the unit of electrical charge. Since any atom in its normal state is as a whole electrically neutral, it follows that the number of electrons in any atom must be equal to the number of unit positive charges on its nucleus. Since the nature of these electronic distributions is of great interest to chemists, we shall examine this topic more carefully below.

(3) The radii of atoms are of the order of magnitude of

10^{-8} cm., but the nuclei have radii in the range of 10^{-13} to 10^{-12} cm. It is thus evident that almost all of the mass of an atom is concentrated in an exceedingly small fraction of its volume.

(4) The number of electrons in a neutral atom, which is equal to the number of unit positive charges on its nucleus, is the characteristic which distinguishes all the atoms of a given element. This number, called the atomic number, has the value 1 for hydrogen (the lightest of all the elements), and increases step by step as we proceed through the Periodic System.

(5) Although all atoms of a given element have the same nuclear charge, their nuclear masses may differ considerably. Thus, most hydrogen atoms have masses of approximately 1 a.m.u.; however, a few hydrogen atoms have masses of approximately 2 a.m.u., and a very few have masses that are approximately 3 a.m.u. Atoms having different masses but the same nuclear charge are called *isotopes*. Most elements exist in the form of more than one isotope. Although the nuclear properties of the various isotopes of a given element may vary widely, the ordinary chemical properties treated within the scope of this book are almost the same for the various isotopes of a given element. A possible exception to this statement is H^1 , H^2 , and H^3 , which differ considerably in chemical properties. However, the percentage differences in mass of these isotopes are very great. We shall, therefore, not be greatly concerned with nuclear masses or with the details of nuclear structure. We shall, however, discuss at length the electronic configurations of the various elements and the relationship of these configurations to the chemical properties of the elements.

The Wave Mechanical Theory of the Atom

The study of the spectra of excited atoms has shown that the atoms of the various elements are capable of existing only in certain "allowed," definite energy states (Fig. 1.1)

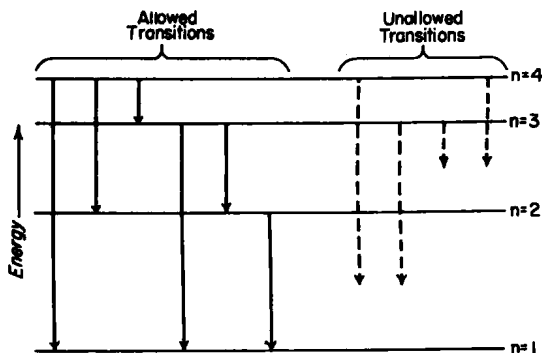


Fig. 1.1. Diagram illustrating quantization of an atom.

and are capable of absorbing or emitting energy only in certain definite quantities, corresponding to the differences in these energy states. Thus, the atom is said to be quantized. Our knowledge of these energy states is derived from the study of the absorption and emission of energy by the atoms as observed in their spectra. Further, the various energy states have been correlated with the electronic configurations of the atoms and have, in fact, provided the principal clue to establishing these configurations. This topic has been discussed in some detail by Prof. G. E. Ryschkewitsch in another volume in this series* to which the reader is referred. However, to provide the immediate basis for the discussion in this volume, it will be necessary to recapitulate and enlarge upon some of the points presented in the above reference.

The presently held theory of the electronic configurations of atoms and molecules is based on the postulate first advanced by the French physicist Louis de Broglie in 1924, that *matter is not only corpuscular in nature, but that each particle possesses*

*Ryschkewitsch, G. E., "Chemical Bonding and the Geometry of Molecules," Chap. 2, Reinhold Publishing Corporation, New York, 1963.

also wave characteristics, having a wave length given by the equation

$$\lambda = h/mv$$

where h = Planck's constant, m = the mass of the particle, and v = the velocity of the particle. This postulate, which has since been amply confirmed by a variety of experimental data, was used by the Austrian physicist Erwin Schrödinger as the basis for a new system of mechanics on which all modern atomic and molecular theory is based. The mathematical details of this new system of mechanics, now known as the *wave mechanics*, are too complex to be appropriate to our present discussion. In simple terms, however, Schrödinger proceeded as follows: Using the classical equation for the motion of standing waves (as, for example, in a vibrating string) and applying de Broglie's postulate that $\lambda = h/mv$, and further specifying that the electron to which the equation refers shall not be at infinity nor shall there be a volume unit at a finite distance from the nucleus in which there is not a finite probability of the electron's existence, Schrödinger derived an equation, called the *wave equation*, relating an amplitude function for the electron wave (commonly represented by the Greek letter ψ and called a *psi function* or *wave function*) to the kinetic and potential energies of the electron and to the space coordinates in terms of which the system is described. Various wave functions (expressions for ψ) constitute solutions to this equation, and to these allowed wave functions there correspond definite values for the energy of the system. Thus, the various energy states of the atom arise naturally out of the wave equation.

At this point let us consider specifically the significance of the wave function ψ . The intensity (number of photons per unit volume) of a beam of electromagnetic radiation has been shown to be proportional to the square of the amplitude of the electrical vector in the electromagnetic wave. Thus, the den-

sity of photons in a beam of light is related to the square of the amplitude function of the light wave.

It seems reasonable to place a similar interpretation on the wave function ψ for "matter waves." Where the wave function refers to a single particle (such as, for example, an electron in an atom), then ψ^2 represents the "probability density" corresponding to a given element of volume $dx dy dz$. Thus, the probability of finding the electron in a given element of volume $dx dy dz$ in space is proportional to the value of $\psi^2 dx dy dz$ for the particular electron at that point. Another way of looking at the problem is to imagine that the motion of the electron is observed over a period of time. The function ψ^2 will then indicate the time average of the distribution of electrical charge resulting from the motion of the electron. If the function ψ^2 is interpreted in this way, we may think of the electron in terms of an electrically negative charge cloud, the shape of which is determined by the wave function and for which the charge density in any element of volume $dx dy dz$ is proportional to $\psi^2 dx dy dz$.[†] It should be noted that $\psi^2 dx dy dz$ is *proportional* to the probability of the electron being in the element of volume $dx dy dz$, and is not necessarily *equal* to the probability. However, since it can be shown mathematically that if ψ is an acceptable solution to the wave equation then $A\psi$ where A is a constant is also an acceptable solution, we can multiply our wave functions by suitable constants so that $(A\psi)^2 dx dy dz$ is not only proportional to but is equal to the probability of the electron being in the volume element $dx dy dz$. Such a wave function is said to have been normalized. If the electron ex-

[†]In some cases wave functions (ψ) contain the imaginary number i ($= \sqrt{-1}$) and are, therefore, complex numbers. The probability of the electron being in a given element of volume $dx dy dz$ must, however, be a real number. Therefore, the product of ψ and its complex conjugate ψ^* is used rather than ψ^2 . The product $\psi\psi^*$ will always be real whereas ψ^2 can in certain instances be a complex number. If, for example, ψ is a complex quantity $a + ib$, ψ^* is $a - ib$ and $\psi\psi^*$ is $a^2 + b^2$. If, on the other hand, ψ is a real number, $\psi^* = \psi$ and $\psi\psi^*$ is equivalent to ψ^2 .

ists, it is a certainty that it is somewhere in space. This corresponds to a value of one for the probability. Hence, for a normalized wave function the summation of the values of $A^2\psi^2 dx dy dz$ over all the volume elements in space will be equal to one. In the language of the calculus this corresponds to the mathematical statement

$$\int A^2\psi^2 dx dy dz = 1$$

The above interpretation of the significance of ψ and ψ^2 is not rigorously derivable from any established principles, but is a postulate which depends for its acceptance on the fact that, insofar as it has been possible to test it experimentally, it corresponds to experimental data.

Each solution to the wave equation is characterized by a set of definite values for four numbers, called quantum numbers, commonly represented by the letters n , l , m , and s . These numbers can assume the following values:

$$n = 1, 2, 3, 4, 5, \dots, \text{any integer}$$

$$l = 0, 1, 2, 3, 4, \dots, n - 1$$

$$m = +l, (l - 1), (l - 2), \dots, 0, \dots, (-l + 2), (-l + 1), -l$$

$$s = +\frac{1}{2}, -\frac{1}{2}$$

An acceptable wave function ψ for an electron in an atom exists for each set of values for these four quantum numbers, and an energy state corresponds to each of these acceptable wave functions. Since each combination of allowed values for these four numbers represents an energy state for an electron in an atom, it will be interesting to review briefly and qualitatively the significance of each of these four quantum numbers.

The number n is known as the *main quantum number*. For single-electron atoms in the absence of a magnetic field, this number determines almost entirely the energy corresponding

to a given state. In other words, the energy of an electron in a single-electron atom in the absence of a magnetic field is almost independent of the values of the other three quantum numbers l , m , and s .

The number l is known as the *angular momentum quantum number* and indicates the angular momentum of the electron. The smaller the value of l , the less the angular momentum of the electron, and the higher the probability that it will be near the nucleus; the larger the value of l , the higher the angular momentum, and the higher the probability that the electron will be at distances far from the nucleus. The number l determines the shape of the electron probability distribution (see Figs. 1.7, 1.8 and 1.9).

The quantum number m may be thought of as determining the direction in space relative to an applied magnetic field in which the electron would have the highest probability of being found. Thought of in another way—the movement of an electrical charge (such as the electron in a cyclic path) has a magnetic field associated with it. The *magnetic quantum number* m represents the possible orientations of this magnetic field with respect to an arbitrarily applied magnetic field. It can assume the integral values $-l$, $-l + 1$, $-l + 2$, \dots , 0 , \dots , $l - 2$, $l - 1$, l . In the absence of an applied magnetic or electric field, electrons differing only in their values of m , in a given atom have the same energy.

Finally, it appears that not only is there a magnetic field arising out of the orbital motion of the electron, but there is an additional magnetic effect which can only be attributed to the spinning of the electron about an axis. If we presume that the electron possesses a finite volume, such spinning would be equivalent to a circulating electrical charge, and the spinning electron would have a magnetic field associated with it. The *spin quantum number* s has been shown to be capable of assuming two values, viz. $+\frac{1}{2}$ or $-\frac{1}{2}$, corresponding to

orientation of the magnetic field associated with the electron spin parallel with or opposed to an applied magnetic field.

Since each set of values for the four quantum numbers corresponds to a solution of the wave equation, characterized by a wave function ψ , and hence, to a possible energy state of the atom, a table of the possible sets of values for these numbers will indicate various possible energy states for an electron in an atom. A list of such sets of values corresponding to $n = 1, 2, 3$, and 4 is provided in Table 1.1.

The Hydrogen Atom According to Wave Mechanics

Reference to Table 1.1 will indicate that for each value of the main quantum number n there are a number of sets of values for the four quantum numbers—two for $n = 1$, eight for $n = 2$, eighteen for $n = 3$, and thirty-two for $n = 4$. However, for single-electron atoms such as hydrogen the energy of the atom depends almost entirely upon the value of n in the absence of a magnetic field, the energy being given by the equation

$$E_n = -\frac{2\pi^2 Z^2 e^4 m}{h^2 n^2}$$

derived by solving the Schrödinger wave equation for a single electron atom, where e = the charge on the electron, m = the mass of the electron, Z = the positive charge on the atomic nucleus and h = Planck's constant.

It should be noted that according to this equation all values of n yield negative values for E_n . This arises from the energy of the electron being defined as the energy absorbed when the electron is brought from a very large distance (infinity) into the electron energy state corresponding to the given value of n . Since in this process energy is actually evolved, E_n is negative. When $n = \infty$, $E_n = 0$, and as the value of n decreases, E_n becomes more negative (Fig. 1.2). In the presence of a magnetic field, however, the energy levels corresponding to each value

TABLE 1.1. Sets of Values for the Four Quantum Numbers (for values of n up to $n = 4$)

n	l	m	s	No. of Sets of Values and Notation	
1	0	0	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$	2	(1s) } 2
2	0	0	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$	2	(2s) }
	1	+1	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$	6	(2p) } 8
		0	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$		
		-1	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$		
3	0	0	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$	2	(3s) }
	1	+1	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$	6	(3p) }
		0	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$		
		-1	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$		
	2	+2	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$	10	(3d) }
		+1	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$		
		0	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$		
		-1	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$		
		-2	$\left. \begin{matrix} +\frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\}$		

TABLE 1.1 (continued)

n	l	m	s	No. of Sets of Values and Notation			
4	0	0	$+\frac{1}{2}$	2	$(4s)$	32	
			$-\frac{1}{2}$				
	1	+1	$+\frac{1}{2}$	6	$(4p)$		
			$-\frac{1}{2}$				
		0	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
		-1	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
	2	+2	$+\frac{1}{2}$	10	$(4d)$		
			$-\frac{1}{2}$				
		+1	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
		0	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
		-1	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
		-2	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
	3	+3	$+\frac{1}{2}$	14	$(4f)$		
			$-\frac{1}{2}$				
		+2	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
		+1	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
		0	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
		-1	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
		-2	$+\frac{1}{2}$				
			$-\frac{1}{2}$				
		-3	$+\frac{1}{2}$				
			$-\frac{1}{2}$				

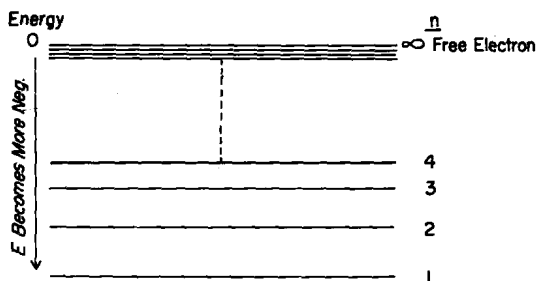


Fig. 1.2. Diagram showing relationship of energy states and values of n .

of the main quantum number are split as a result of the various possible interactions of the orbital and spin magnetic fields with the applied magnetic field as indicated by the various values of the quantum numbers m and s . The result of this splitting of energy levels is that lines in the spectrum of hydrogen (as well as other elements) are split into groups of closely spaced lines. This effect was first observed by Zeeman in 1896 and is commonly known as the Zeeman effect. This effect is illustrated in Fig. 1.3.

The lowest energy state of the hydrogen atom and the state in which we would expect to find an unexcited hydrogen atom is that corresponding to $n = 1$. The wave function ψ , corresponding to this energy state, is of the form which would indicate a high probability of finding the electron near the nucleus. We have seen (p. 6) that the mathematical form of the wave function ψ is such that it can be interpreted in either of two ways. ψ^2 can be viewed as a function which measures the probability of the electron being at a specific point in space; or, if one imagines making an observation of the movement of the electron over a relatively long period of time, ψ^2 would measure the time average of the distribution of electrical charge in space resulting from the motion of the electron. This charge distribution is commonly called the