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By use of the electron contiguration of atoms, derived from quantum mechanics, a better understanding of the atom is available. Some of the simple explanations that can be based on this arrangement of the electrons are: bond types, geometry of the molecule, complex ions, transition metals, atom size, screening properties of electrons and effective nuclear charge.

mon H. ADVISER'S APPROVAL

BASIC PRINCIPLES AND APPLICATIONS OF QUANTUM MECHANICS

By

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INTRODUCTION

The nuclear atom describes a physical model. A small, dense, positively charged nucleus surrounded by electrons.¹ The atom has striking similarities to the solar system with several major exceptions. The solar system resembles a saucer with the planets all lying in approximately the same plane, whereas the atom is more spherical, which results in a cloud of electrons or a hazy fog of negative electricity of non-uniform density.² The electrons are considered to be in constant motion and their location within the sphere is in terms of the probability of finding them at a particular spot at a given time.²

Two thermodynamic difficulties in comparing the atom to the solar system are;

- 1. An accelerating charged body must radiate energy. The electron is charged and accelerating, therefore it must radiate energy. The loss of energy should make it spiral into the nucleus.
- 2. All particles should contribute to the heat capacity of the atom commonly referred to as the Law of Equipartition of Energy.¹

BOHR'S THEORY

Bohr accepted the planetary model and first considered circular orbits.¹ He proposed a revolutionary theory that provided a basis for determining the electronic structure of atoms. He also proposed that an electron, as it moves around the nucleus, can attain only certain energy levels. An atom whose electrons all possess specific energies is said to be in a stationary state. In the stationary state called the ground state, the electrons possess the energy values which make the energy for the atom a minimum. States having more energy than the ground state are called activated states.³

Bohr's big mistake in his experiments was the selection of the simplest atom, hydrogen, to work with. However, his theories made it possible to do more accurate work on the more complex atoms.

When the light from a hydrogen lamp is passed through a spectroscope, a number of narrow colored lines separated by dark regions appear.⁴ One line was found in the red region, which is the longest wave length, one in the blue, one in the violet, the fourth close to the ultraviolet region, and five lines in the ultraviolet region.⁵ The spectroscope can be focussed so that a given colored line coincides with cross hairs in the eye piece. This marks an angle on a circular scale that is definite, reproducible, and characteristic of that particular line. From auxiliary measurements, it is possible to correlate this angle with a quantity called the wavelength of the light.

Bohr successfully explained the known series of spectral lines for hydrogen and by the end of the 19th century, many of the spectral lines of hydrogen had been measured and classified into what appeared to be groups of associated wavelengths.⁴

It was Bohr's theory that a single electron was responsible for the production of these spectral lines. Hydrogen is like a solar system with one planet and the planet could revolve in fixed tracks in space or in different energy levels; K, L, M, N, and O.⁵ The quantum theory, postulated by Bohr and Rutherford, states that systems can possess only certain definite amounts of energy; E₁, E₂, and E₃. If the body changes from one energy level to another, then energy must either be emitted or absorbed in amounts given by the equation

$E_1 - E_2 = \frac{hc}{\lambda_1}$

where c is the velocity of light, λ the wavelength of the energy emitted or absorbed, and h is Plank's Constant.

Bohr suggested that the electron can move in a circular orbit without losing energy, which was contary to the belief at the time. He contended that small particles did not operate as large particles in their relation to the electrical theory. It was also his idea that electron and proton systems can possess only certain definite energies and that when the energy of the system changes it does so in certain specified jumps.⁴ This situation reminds us of an elevator, if we suppose that by automatic control, the elevator can stop only at the floor levels, not between floors. The elevator, normally waiting for passengers on the ground level, can by the absorption of energy, be lifted to any floor above, then when it falls back to lower floors, energy is released, the greater the fall, the

greater the energy released.⁵

He proceeded to show that if the electron jumped from one circular orbit to another, the energy of the atom changed by an amount

 $E_1 - E_2 = \frac{h_c}{\lambda_1}$, $E_2 - E_3 = \frac{h_c}{\lambda_2}$ The wavelengths, λ , λ_2 , were to be related to the wavelengths of the light emitted by hydrogen in the discharge tube. Hydrogen emits light of only certain wavelengths because the atom can only possess certain well defined energies.⁴

As a crude analogy, we may examine the static distribution of magnetized needles as they float on water in an unright position, supported by corks. If we place at the center of a dish of water a permanent magnet or establish a magnetic field in the same place by means of a coil of wire wound about the dish, we then have something that is analogous to the positive charge of the atomic nucleus. If we now float in the dish a single cork bearing a vertical magnetized needle, we find that the needle will approach the center of the dish because of the attraction of the neighboring unlike poles. If we use two needles, we find that they repel each other, and, since both are attracted to the center, they take up positions diametrically opposite each other, When a third needle is added, the needles take up positions at the corners of an equilateral triangle. With four needles, we find that the figure assumed by the mobile system is a square, and with five needles a pentagon. As the figure expands, however, all of the needles become

further removed from the center of attraction because of their mutual repulsion. Eventually the polygon must become so unstable that it will give away to a system consisting of a small group of needles inside a larger group. Thus with six needles we are likely to find that one needle moves to the center of a pentagon and seven needles would produce a hexagon with a needle in the center. With eight needles, two move to the center of a hexagon and with ten needles the usual arrangement is an octagon arranged about two central needles. These arrangements of needles illustrate the fact that, under conditions of mutual repulsion and central attraction, a large hollow geometric figure is improbable.

If the attracting or retaining magnetic field is decreased, the needles all move away from each other and the geometric figures assume larger dimensions, but the shape remains the same. As we increase the strength of the magnetic field, the figure is drawn into a more compact form.²

WAVE MECHANICS

The hydrogen atom is not as simple as Bohr's model. The electron is not confined to a circular or elliptical orbit, but there is a definite chance of finding the electron anywhere outside of the nucleus. A "census" of the number of times we "see" an electron in a given area gives us regions of high and low density.⁴

Bohr's theory did not explain the whole story. In 1924, Louis de Broglie suggested that the electron not be treated as a charged ball, but as possessing wavelike properties. In 1926, Heisenberg postulated his "principle of uncertainty" which states that the momentum and the position cannot be simultaneously specified more closely than a certain approximation. The more precisely we know the momentum, the less precisely we know the position of the electron and conversely.

Also in the mid 1920's, Schroedinger proposed a theory that deals less sharply with the details of the motion of the electron with respect to the proton and it gives information not on where an electron is but on the probability of finding the electron somewhere in the space surrounding the proton. This theory is less precise about the energy which is in accord with Heisenberg's Principle.⁴

In quantum mechanics, the motion of electrons around a nucleus is described in terms of mathematical functions called wave functions. The wave function for a particular electron called its orbital wave function indicates the mathematical probability of finding that electron at different distances from the nucleus.³

This new theory retained the idea that atoms possess only certain definite energies and this theory specified what these energies are.⁴ Energy, like matter, is not continuous, but is made up of "pieces" or "bunches" called quanta. The magnitude of energy in a quantum is directly

proportional to the frequency of light, mathematically expresses as

E=hv

where E is the energy of the electron transition in ergs, h is Plank's Constant (6.60 X 10^{-27} erg-seconds), and v is the frequency of the emitted light in cycles per second.

The frequency of light is inversely proportional to the wave length. Quanta of long waves, like radio waves, carry little energy, and short waves, like X-ray and cosmic rays, possess high energy.⁵ Therefore, the greater the energy change, the higher the frequency of the emitted light, and the shorter the wave length or²

> Frequency (v) = Velocity (Plank's Constant) Wave length

Depending upon the energy content, quanta may appear as infrared, visible, or ultraviolet light. Waves of low frequency and low energy will appear in the infrared region of the spectrum, while waves of high frequency and energy will appear in the ultraviolet region.²

Since the energy levels for each element is different, the light emitted by excited atoms has a characteristic frequency or color that can be used for positive identification. For instance, the codium vapor lamp is yellow as is the flame test and the characteristic color of neon lights is due to the excited electrons of the gas.²

Line spectra forced scientist to believe electrons exist in discrete energy levels.² Sodium has one outer electron loosely held, which is similar to hydrogen. Therefore, we should expect the spectral lines to be similar. But, instead of one set of converging spectral lines, four sets are observed. Detailed study of the spectral lines for the different elements reveals that the second, third, fourth, and additional outer levels are actually split into subshells whose energies are almost equal and electron transition from a subshell of one shell to another subsnell in a different shell gives rise to extra spectral lines. Hence, we speak of a main level or shell characterized by the value <u>n</u> and sublevels designated by the symbols <u>s</u>, <u>p</u>, <u>d</u>, and <u>f</u> from sharp, principle, diffuse, and fundamental which were used by early spectroscopists to describe various series of spectral lines.³



The x-rays studied by Mosely were called K x-rays and we now know that these are due to disturbances resulting in the transfer of electrons from higher shells to the first or K shell.⁴ K_{α} spectral lines were produced by electrons dropping from the L level to the K level and K_{β} lines were caused by electrons dropping from the M level to the K level. When vacancies occurred in the K level due to removal by electron beam bombardment, electrons from higher levels would drop down, emitting light with characteristic frequency

and energy. The differences in frequency that Mosely found when he tested the various elements stems from the influence of greater nuclear charge on the attraction between the electrons and the nucleus.³

All transitions from higher states to the ground state (n=1) gives rise to spectral lines in the Lyman series. These frequencies are quite high which results in short wave lengths and the spectral lines appear in the ultraviolet region of the spectrum. Transitions from higher states to the first excited state (n=2) results in the Balmer series, spectral lines that are visible but near the ultraviolet region. Transitions from higher states to those states for which n=3, 4, and 5 gives rise to the Paschen, Brackett, and Pfund spectral series respectively. All three series are in the infrared region of the spectrum.¹

Figure 1 shows an energy level diagram of hydrogen and indicates the changes in energy levels which gives rise to the several series of spectral lines.

Remember that the Lyman series results from an electron dropping from one of the higher levels to the lowest energy level. Also included in this figure are the first fiveenergy levels for the electron and their energies in terms of electron volts. The electron volt (ev) is the kinetic energy acquired by an electron in falling through a potential difference of one volt. One mole of electrons (6.023 X 10^{23} electrons) falling through a potential difference of one volt will acquire a total kinetic energy equal to 23,900 calories.





From the diagram, an electron moving spontaneously from the fourth level to the second level, will emit 2.5 ev. of energy in the form of radiant energy similar to light. If it drops from the second level to the first, the radiation emitted has 10.1 ev. of energy. From the fourth to the first level, 12.6 ev. of energy will be released.

To lift the electron from lower to higher energy levels requires the same energy as was emitted by the electron in its descent to the lower level. If the energy supplied to the electron in the first level is 13.6 ev. or more, the electron will move entirely out of the atom and form

the hydrogen ion. The smallest amount of energy required to remove an electron entirely out of the atom is the ionization energy or ionization potential.³

QUANTUM NUMBERS

In quantum theory, certain numbers called quantum numbers are associated with each energy level.³ Quantum numbers are always whole intergers as they determine the energy of electrons, which must exist in definite, discrete energy levels.² To the various energy levels, we assign quantum numbers 1(K), 2(L), 3(M), 4(N), 5(O), 6(P), and 7(Q).

It is seen that more energy is needed to raise the electron from its lowest level to the second than from the second to the third, etc. Differences between levels becomes progressively smaller as we proceed to higher levels. This is in agreement with Bohr's theory.⁴ As the total quantum number of the initial state becomes large, the states crowd together and hence, the spectral lines do also.

As <u>n</u> approaches infinity, the continum of states is reached and the spectral lines are replaced by regions of continuous emission. Bohr's formula predicted this wave length to be 3647.05 A° .¹

There are results describing the probability of finding the electron which are best expressed in the language of mathematics, but can be approximately represented by physical models. For hydrogen, in the lowest level, the probability

is quite high that the electron will be found in the volume close to the surface of a sphere with a definite radius, but with a fuzzy outline at the surface. The electron density pattern is called an orbital, the region in space about a nucleus in which the probability of finding the electron is the greatest.⁴



Figure 2

The increased energy involved in locating electrons in orbitals of higher energy corresponds to an increase in the effective size of the atom. The higher the quantum number, the further are the electron densities associated with that quantum number removed from the nucleus. The number of orbitals will also increase with the principal quantum number because there is room for more orbitals the further we move from the nucleus.⁴

Orbitals are arranged using symbol $\underline{1}$ representing numbers 0, 1, 2, 3, ... or by using letters s, p, d, f, ... from the first initial used to describe the spectroscopy of the sub-shells. The values that $\underline{1}$ may assume for a given \underline{n} value may be n-1, n-2, ... 0 and the maximum number of electrons in any orbital is equal to $2(2 \ \underline{1} + 1)$.

Example:

M shell - Krypton (n=3)

Subshells may	r hav	re values	s oí	Ē							
n-1=2	3rd	orbital	or	d		2(2	Х	2	÷	1)=]	LO
n-2=1	2nd	orbital	or	p		2(2	Х	1	-[-	1)=	6
n-3=0	lst	orbital	or	S	teres Second	2(2	Χ	0	+	1)=	2

Energy levels are subdivided into orbitals with a specific number of electrons in each orbital and are designated by specifying the values of \underline{n} and \underline{l} .

lst	shell	s(2)				1963 P.	2
2nd	shell	s(2)	p(6)			0.09 G/14	8
3rd	shell	s(2)	p(6)	d(10)			18
4th	shell	s(2)	p(6)	d(10)	f(14)	400 1 0	32

By adding the number of electrons in each orbital of a shell, you determine the number of electrons that each shell may contain.

The energy of an electron in a <u>d</u> or <u>f</u> orbital is greater that that of an electron in the <u>s</u> or <u>p</u> subshell of the next higher main shell.⁵

The order of energy then is dependent upon <u>n</u> and <u>l</u> numbers and to some extent on the multiplet, such that the energy levels in increasing order are as follows: ls,2s,2p,3s,3p,(4s,3d),4p,(5s,4d),(4f,5p,6s,5d)
The orbitals in brackets have energies that are very nearly
the same and do not completely follow the regular pattern
of filling with electrons.

Two simple methods for establishing the order of increasing energy can be explained. The first is simply the addition of the <u>n</u> and <u>l</u> numbers, if the lowest energy level is considered to be 1, the next 2, etc. The <u>l</u> numbers assume the numerical values of s=0, p=1, d-2, and f=3. The lowest sum of the <u>n</u> and <u>l</u> numbers will be the lowest energy level.

If different orbitals have the same sum, then the orbital with the lower \underline{n} is considered to be the lowest energy level. This rule holds true except at the start of the Lanthanide Series.

Figure 3 illustrates a second method used to determine the order of increasing energies.



It is customary in speaking of hydrogen-like atoms in a specified state indicated as 1s, 2s, and 3s states. In these terms, one may conclude from radial distribution curves that for a given nucleus, electrons of a given type specified by the letters s, p, d, and f are progressively further removed from the nucleus as the principal quantum number increases. But, the energies of the general atomic orbitals depends upon both the n and 1 numbers. Thus the energies of the 3s, 3p, and 3d atomic orbitals are not identical, but increase in the indicated order. For a given value of \underline{n} , the energy increases with increasing values, of 1, and this spread of energy for each given principalquantum number may become so great for higher values of n. that the sub-shells overlap for different values of n. For a given n number, the s electron is the farthest from the nucleus and the p, d, and f electrons are progressively Thus, an electron in a given state may be located closer. on the average nearer the nucleus than an electron of lower energy (n smaller) provided the first electron is in a state of sufficiently large angular momentum ($\underline{1}$ large).¹

However, for a given value of <u>n</u>, the <u>s</u> electrons penetrate most deeply of all; the electrons are the least completely screened and most tightly held. This results in the energies of the atomic orbitals increasing in order s, p, d, and f for a given value of the principal quantum number.¹

The following diagram (Figure 4) shows the radial

probability for lower states of hydrogen



The reason for the variation of energy with 1 lies in what is called screening of the outer electrons from the nucleus by the inner electrons. The outer electrons are acted upon by an effective field arising from the nucleus and the inner electrons, the latter acting in effect, to diminish the nuclear field. Those electrons which do not penetrate near the nucleus are well screened by inner electrons and hence are more loosely held than are electrons which approach the nucleus closely, and are thereby less well screened. The probability distribution function for various sets of quantum numbers show that an electron whose behavior is described by the d orbital does not in general penetrate as near the nucleus as one described by a p orbital for the same value of n; in like manner, the electron described by a p orbital lie on the average, outside s orbitals.

Besides the principal quantum numbers (n) and the secondary quantum numbers (1), two other quantum numbers are used to characterize each distinct dynamical state of the system. The m or me number determines the component of angular momentum along the Z axis or simply the direction in space and the shape of the orbital. The m number is dependent on the 1 number and may have any integral value between +1 and -1 including 0. The m number therefore, has 2 1 + 1 possible values. The shape of the elliptical orbital may approximately be determined by allowing the 1 number to represent the radius of the minor axis of the ellipse and the n number the radius of the major axis. The most eccentric orbital is 1=1, where the electron may pass very close to the nucleus. Theoretically, the electron would pass through the nucleus if $\underline{1}=0$ or there was no angular momentum.¹

In 1925, Uhlenbeck and Goudsmit showed that certain properties associated with atomic spectra can be explained if it is assumed that the electrons in the atom can be considered to have spin. Two types of spin possible are negative and positive, clockwise and counterclockwise.⁴ So the fourth and final quantum number is <u>s</u> or <u>m</u>_s which determines the pairing of electrons in an orbital. Actually, the electrons do not spin in the true usual meaning of the word.

This now brings us to the Pauli Exclusion Principle, which states that no two electrons in an atom can have the same values for all the quantum numbers that are necessary

to completely describe the state of an electron. This is because not two electrons can occupy the same space at the same time.²

The principle leads to a periodic structure of the elements since successive electrons must occupy the successive energy levels in accordance with the development of the numbers.

To briefly summarize, each energy state is specified by a particular value of <u>n</u>. In general, however, there are for each value of <u>n</u> several possible different values of <u>1</u> (0,1,...n-1). Furthermore, for each <u>1</u> value, there are $2\underline{1} + 1$ different values of <u>m</u> possible (-1...0...+1). For each <u>m</u> there is a spin property associated such that the spins must be opposite, therefore, there are two values for each <u>m</u> designated as $\pm 1/2$ and $\pm 1/2$.¹ Finally, no two electrons can have the same four quantum numbers. Therefore, it is possible to sum up the number of different electrons in each shell, as is partially shown in Figure 5.

<u>n</u>	<u>Shell</u>	1	Subshell	m	S	<u>Combinations</u>
1	K	0	S	0	+1/2 -1/2	2
2	L	0	S	0	+1/2 -1/2	2
		1	p	+]	+1/2 -1/2	
•				0	+1/2 -1/2	6
				-1	-1/2 -1/2	
3	М	0	S	0	+1/2 -1/2	2

Figure 5

If we were to examine the inert gas Radon, with 86 electrons (2,8,18,32,18,8) we would find something significant about the completed electron shells having observed numbers of electrons. The completed shells, 2,8,18 and 32, fit a general scheme of $2n^2$ where <u>n</u> has the values of 1,2,3, and 4.² This formula is used to determine the total number of electrons that each shell may hold.

QUANTUM NUMBERS AND THE PERIODIC TABLE

The maximum number of electrons in the first level is two and they have at least one quantum number that is different. This number is associated with the spin of the electron for the two electrons in the first level spin in opposite directions. In an atom, any two electrons that have the same quantum numbers except for the spin numbers are called pairs.³

In the second level, there are four possibilities or orbitals. One of these is spherically symmeterical but further removed from the proton than the lowest energy level. The symbol, 2s, is used to distinguish its energy and shape. The other three possibilities are mutually perpendicular orbitals which are described as pairs of spheres touching each other at the proton and are described as $2p_x$, $2p_y$, and $2p_z$.⁴ In higher shells, the shape of the <u>s</u> and <u>p</u> orbitals are the same but further removed from the nucleus. The <u>d</u> orbitals have five possible arrangements, described as d_{xy} , d_{yz} , d_{zx} , d_x^2 . They all are

four directional in space, shaped like four ellipses, all touching at the proton. The first three are in orientation about the axis of a three dimensional graph. The fourth is turned to coincide with the x and y axis and the fifth has two large lobes corresponding to the z axis and two smaller lobes perpendicular to these larger lobes. The <u>f</u> state has seven possible arrangements, but is too complicated to illustrate here.

If there are an insufficient number of electrons in an atom to fill all the orbitals in a shell with pairs, then the electrons tend to arrange themselves with one electron per orbital. Only after each orbital has one electron do the electrons begin to pair off with opposite spins.

A simple shorthand method is used to indicate electron configuration.

Oxygen $ls^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1 = 2$ pair - 2 singles Carbon has two possible arrangements because of its ability to form hybrids.² It may exist as one pair and two singles or as four singles, the latter being more common.

The building up of complex atoms is seen to follow a simple and regular pattern for the first twenty elements, and then to exhibit somewhat more erratic behavior. It must be remembered that the order of energies is not exactly the same for all atoms and there will be a few discrepancies or deviations from the expected order in the case of atoms of moderate to large atomic number.

The first twenty electrons fill the ls,2s,2p,3s,3p,

and 4s subshells. The 21st electron goes into the 3s subshell which is not the valence or outer shell. The 3d level fills with 10 electrons (21 to 29) before the 4p sub-shell begins to fill and electrons again go into the valence shell. This gives a series of ten elements with only two electrons in the outer shell and a partly filled inner sub-shell. Under these conditions, the series is called a short transition metal series. Two similar series occur from yttrium to silver (39 to 47) where the 4d sub-shell is filling and lutetium to gold (71 to 79) where the 5d level is filling. Two long transition series with fourteen electrons in each series also occur. The Lanthanide Series (57 to 71) is formed as the 4f level is being filled. A similar series, called the Actinide Series, starts at element 89, where the 5f sub-shell starts to fill.⁵ At present, the Actinide Series is not complete. Theoretically, when it is completed, another short transition series of ten elements will fill the 6d level and the shell will be completed at element 118 with the filling of the 7p representative elements. Element 118 should be an inert gas as are all the elements that have complete s and p orbitals.³

In none of the elements how known or likely to be prepared in the near future does the O shell become completely filled, since it requires 110 electrons to fill it and the electrons enter the sixth and the seventh shells before the fifth shell becomes filled.⁴ That such

large atoms do not exist seems not to result from chemical factors concerning the extranuclear electrons and the stability of the nucleus-electron system, but rather from physical considerations of stability within the atomic nucleus itself.

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