Atomic Structure and Chemical Bonding

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Atomic Structure and Chemical Bonding

A NON-MATHEMATICAL INTRODUCTION

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Foreword to English Edition

Seel's *Atombau und Chemische Bindung* which was first published in 1956 has now reached its 4th German edition and has already been translated into several languages. Professor Seel's intention was to write a concise, straightforward account of the modern theory of chemical bonding which would give both perspective and significance to this subject for students taking it up for the first time. The immediate and continuing popularity of his book on the Continent testifies to the success with which he has achieved this aim. The treatment is non-mathematical and relies on the skilful use of simple pictorial models. In order to emphasize the essential unity of chemical theory the subject matter has been divided not according to the traditional fields of chemistry (inorganic, organic, and physical) but according to the four basic types of chemical bonding – ionic, covalent, metallic, and intermolecular. Modern concepts such as ligand field theory and charge transfer complexes have been introduced with a simplicity and directness which will undoubtedly stimulate the reader to delve further into these subjects.

A novel feature for English readers is the discussion of chemical reactivity in terms of bonding theory, and the Author has introduced many important ideas of his own into this section of the book. The relation between chemical bonding and physical properties such as hardness, conductivity and colour is also well handled.

In preparing this edition the Translators have, with the Author's consent, modified the text slightly in a few places, and have also made some minor corrections and additions. It is their belief that the book provides an excellent introduction to modern ideas of atomic structure and chemical bonding. A bibliography for further reading is provided at the end of the book.

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Contents

Part 1 Atomic Structure

Part 2 The Nature of the Chemical Bond

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PART 1

Atomic Structure

1. The structure of extranuclear electrons

An understanding of the nature of chemical bonding depends on a knowledge of atomic structure. Atoms are composed of electrically charged particles: a positively charged *nucleus* and up to about 100 negative 'atoms of electricity' or *electrons*. In a neutral atom the total charge on the electrons just balances the charge of the nucleus. If there are fewer electrons the atom has a net positive charge; if there are more electrons the net charge is negative. Such electrically charged atoms are called *ions*.

In order to discuss the energy of such systems it is necessary to define a uniquely determined standard state. To do this let us consider that the atom is completely separated into its component nucleus and electrons; the particles should be at rest and so far apart that all the work necessary for their separation has been performed. In the simplest case, the hydrogen atom, there is a nucleus and one electron. The system in this state has *potential energy* (or energy of position) because the particles have been separated against their attractive forces, but no *kinetic energy* (energy of movement) since they are at rest.

When an atom is built up from the separated particles the initial potential energy of the system diminishes because the distance between the oppositely charged particles decreases. Potential energy is thereby gained but not all of this is available as binding energy since the particles cannot remain at rest. Motion is necessary for a stable atomic system to ensure that the electrons do not fall into the nucleus which attracts them. To a first approximation we can assume that the atomic nucleus, which contains almost the entire mass of the atom, remains at rest and that the electrons are set in motion. To achieve this electronic motion, some of the potential energy which is liberated when the nucleus and the electrons combine must be converted into kinetic energy. The exact proportion depends on the type of interaction between the particles and in the case of electrical interaction it amounts to one-half. The remainder of the energy can be considered as the *energy of formation* of the atom from the initial standard state. This is shown in Figure 1.

At one time it was thought that electrons moved round the atomic nucleus in exactly prescribed circular or elliptical orbits in the same way that planets move round the sun (the *Bohr–Sommerfeld* model of the atom). However it is not possible to assign precise orbits to the electrons because it is not possible to define simultaneously both the position and the velocity of particles as small as electrons (*Heisenberg uncertainty principle*). Nevertheless the movement of the electrons is not completely arbitrary and they occupy certain preferred regions of space around the nucleus.

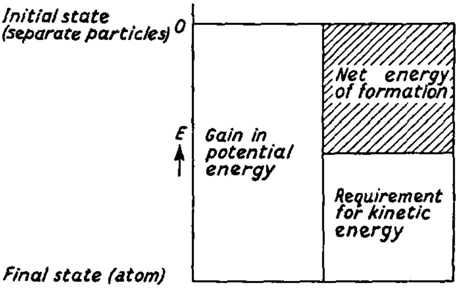

FIG. 1. Conversion of energy during the formation of atoms.

To a first approximation these regions of space can be regarded as a system of cells which surround the nucleus. The electrons in each cell trace out a particular pattern or *orbital* which imparts specific properties to the chemical elements. The orbitals are grouped into shells which are named K, L, M, N . . . and numbered 1, 2, 3, 4 . . . . The number of the shell is called the *principal quantum number*, *n*. Orbitals in each shell are further divided into *subshells* designated by the symbols *s*, *p*, *d*, *f*, depending on the values of a second quantum number, l, the *orbital quantum number*, which has the values 0, 1, 2, 3 respectively. Whether letters or numbers are used in a particular context is merely a matter of convention; their relationship may be summarized as follows:

Principal quantum number, n	*Orbital quantum number, l*
$1 \leftrightarrow \mathrm{K}$	$0 \leftrightarrow s$
$2 \leftrightarrow \mathrm{L}$	$1 \leftrightarrow p$
$3 \leftrightarrow \mathrm{M}$	$2 \leftrightarrow d$
$4 \leftrightarrow \mathrm{N}$	$3 \leftrightarrow f$

Thus a $3p$-electron is one for which $n = 3$ and $l = 1$; it is in the M-shell.

The total number of orbitals in a given shell K, L, M etc., is $Z_n = n^2$, and in each shell the number of orbitals of any one type *s*, *p*, *d* etc., is given by $Z_l = (2l+1)$. The number of values of l is limited by the relation $l \leqslant n-1$. Thus, the K-shell consists of a single orbital, the L-shell contains four orbitals and the M-shell nine. This can be seen in the following way, For the K-shell n is 1 and there is therefore only one possible value of l namely 0. For the L-shell, n is 2 so that l can be 0 or 1; the case $l = 0$ corresponds to an *s*-orbital; for $l = 1, Z_l = 3$ so there are three *p*-orbitals. For the M-shell, n is 3 and so l can take on the values 0, 1, or 2. The M-shell therefore consists of an *s*-orbital, three *p*-orbitals and five *d*-orbitals, ($l = 2, Z_l = 5$). These numerical relations are summarized in Table 1 and are represented schematically in Figure 2*a*.

TABLE 1

The structure of extranuclear electron clouds

Electron shell	n	$l \leqslant n-1$	*Type of orbital*	*Number of orbitals* $Z_n = n^2$
K	1	0	s	1
L	2	0, 1	s, p	$1+3 = 4$
M	3	0, 1, 2	s, p, d	$1+3+5 = 9$
N	4	0, 1, 2, 3	s, p, d, f	$1+3+5+7 = 16$

To complete the description of the electron we also need information about its *spin*. This is perhaps best understood by considering the electron as a small sphere which is capable of rotation in either direction about an axis (see Figure 2*b*). The concept of electron spin allows us to develop a theory of the magnetic properties of matter. One can imagine that the self-rotation of the electrons produces circular electric currents which in turn produce a magnetic field like that of an electromagnet; this field can align itself in the direction of the lines of force of an external magnetic field in such a way as to enhance the external field considerably (*paramagnetism*). Paramagnetism is also occasionally produced by the orbital motion of the *p*-, *d*-, *f*-electrons providing this is not cancelled by a corresponding electron with opposed movement. If pairs of electrons spin in opposite directions with equal velocity their magnetic fields will cancel out. An external magnetic field produces orientation in this case also, the self-rotation in one direction being accelerated and in the other retarded so as to weaken slightly the external field (*diamagnetism*).

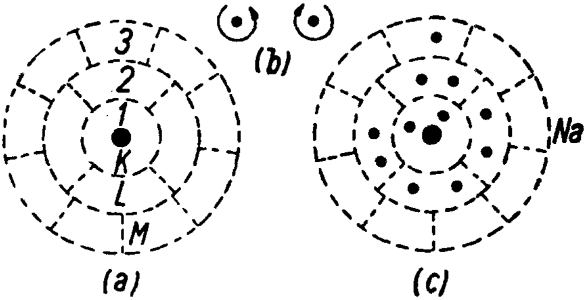

FIG. 2. Schematic representation of the structure of extranuclear electron-shells.

It is found that two electrons in an atom never have the same detailed *distribution patterns*; i.e. each orbital can only be occupied by at most two electrons and these must then spin in opposite directions. The spins are then said to be *antiparallel*. This rule, the so-called *Pauli* *exclusion principle*, immediately leads to the possible electron distributions within an atom. For example, the most stable electronic arrangement for the sodium atom is shown schematically in Figure 2*c*.

2. The Aufbau principle

The distribution pattern of an electron influences considerably the energy of formation of an atom. For an atom or ion with a single extranuclear electron e.g., H, He^+, Li^{2+} etc., the energy of formation is determined only by the principal quantum number n of the shell which

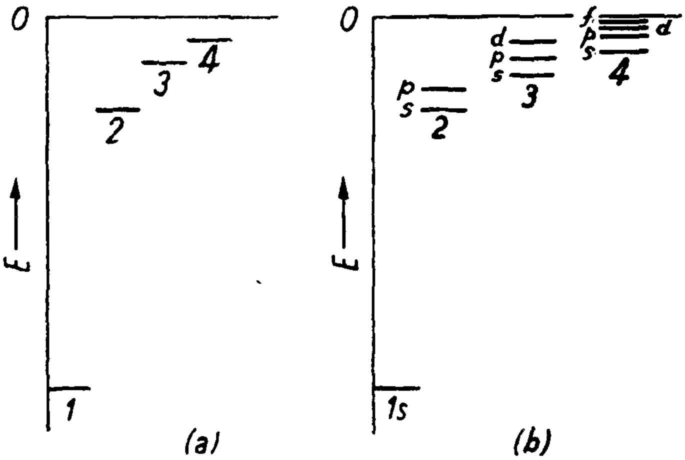

FIG. 3. Sequence of electron energy-levels (*a*) for the hydrogen atom, (*b*) for an atom with several electrons.

the electron occupies (see Figure 3*a*). Thus $E_n = E_1/n^2$ where E_1 is the energy value for $n = 1$. For 1 gram atom of hydrogen (that is $6{\cdot}02 \times 10^{23}$ hydrogen atoms) E_1 has the value 312 kcal. E_n decreases rapidly with increasing n since $E_1 : E_2 : E_3 \ldots$ varies as $1 : \frac{1}{4} : \frac{1}{9} \ldots$. It can be seen that for a one-electron atom the various orbitals which are distinguished by the symbols s, p, d, f within a given shell all have the same energy. Such energy levels are said to be *degenerate*.

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In atoms containing more than one electron the energy levels are no longer independent of the orbital quantum number, l. The sequence of energy levels within the atom then follows the sequence $(n+l)$, and if two configurations lead to an equal numerical value for $(n+l)$ then the one with the lower n-value is the more stable. Thus, in any shell, an electron in an s-orbital has a lower energy than one in a p- or d-orbital. This is shown in Figure 3*b* from which it can also be seen that the energy level for a $4s$-orbital $(n+l=4)$ is less than that for a $3d$-orbital $(n+l=5)$.

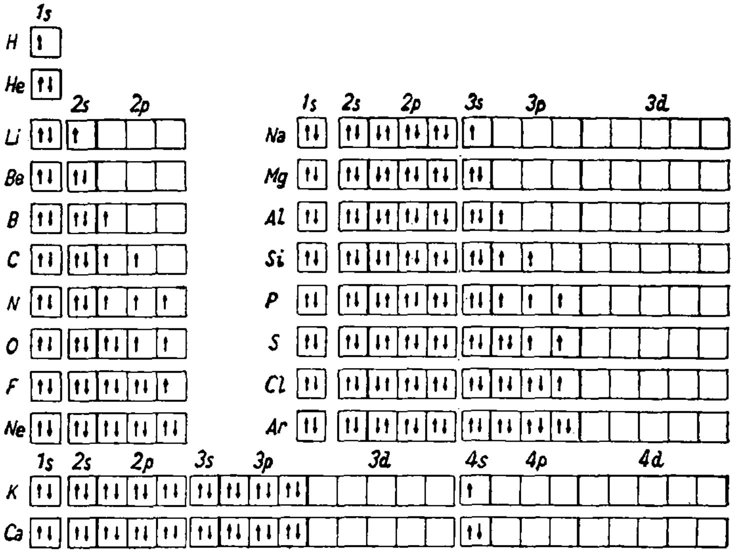

FIG. 4. Ground states of elements from hydrogen to calcium.

This method of building up a sequence of energy levels for the extranuclear electrons is called the *Aufbau Principle*. If each orbital is doubly occupied in the correct sequence until the nuclear charge is just compensated by the electron charges, the *ground state* or lowest energy state of the atom is obtained. If an electron distribution does not correspond to the ground state, the atom can radiate energy and thereby return to the ground state; conversely it can absorb more energy and thereby become 'excited' into a state of still higher energy. In terms of the symbolism just developed, and using superscripts to denote the number of electrons in a given orbital, the ground state and one of the *excited states* of a carbon atom can be represented as follows:

$$\mathrm{C}:\ 1s^2\,2s^2\,2p^2, \quad \mathrm{C}^*:\ 1s^2\,2s\,2p^3$$

In Figure 4 the details of the ground states of the first twenty atoms are given. The orbitals are depicted as small squares and each electron is symbolized by an arrow to indicate the direction of the spin. Figure 4 also illustrates a further point, namely that degenerate electron states (electron states which have the same energy) only become doubly occupied after each has first been singly occupied, and electrons in the singly occupied orbitals have their spins aligned parallel (cf. page 12).

The electronic ground states of all the elements and their relative energies are presented schematically in Figure 5. Both Figure 4 and Figure 5 give a clear impression of the periodicity which results from the progressive occupation of the electron shells. We are thus led to the *Periodic Table* of the elements which was established one hundred years ago by *Mendeleev*, *Meyer*, and others who observed regularities in the properties of the elements.

3. The shape of orbitals

In order to discuss the nature of the chemical bond it is necessary to have some knowledge of the detailed structure or shape of orbitals. Atomic orbitals have exactly the same shapes as the patterns generated by a pulsating dust-cloud which is confined within an elastic sphere. However, it is simpler to consider first an analogous two-dimensional system, e.g. a vibrating circular membrane such as the skin of a drum. If the membrane is covered with a fine powder and the drum is struck, the membrane divides into regions separated by lines (so-called *nodal lines*) along which the powder accumulates since the membrane does not vibrate there. Some of the possible *modes of*

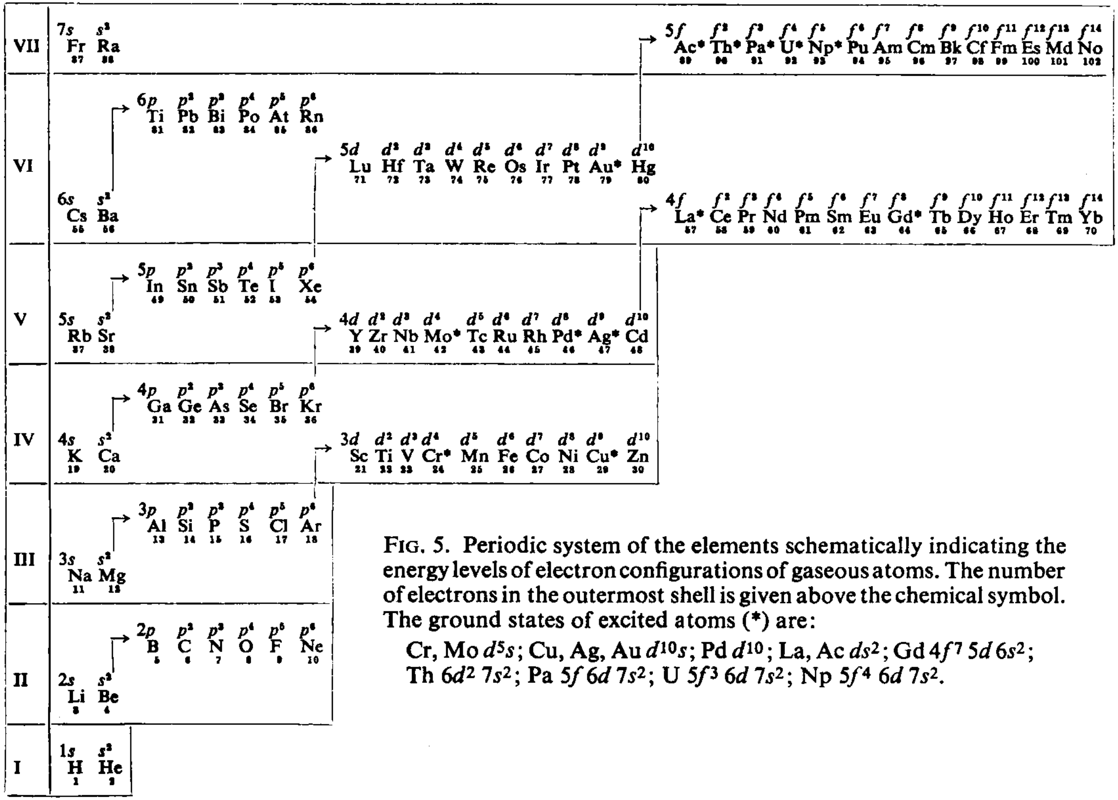

FIG. 5. Periodic system of the elements schematically indicating the energy levels of electron configurations of gaseous atoms. The number of electrons in the outermost shell is given above the chemical symbol. The ground states of excited atoms (*) are:

Cr, Mo d^5s; Cu, Ag, Au $d^{10}s$; Pd d^{10}; La, Ac ds^2; Gd $4f^7\,5d\,6s^2$;
Th $6d^2\,7s^2$; Pa $5f\,6d\,7s^2$; U $5f^3\,6d\,7s^2$; Np $5f^4\,6d\,7s^2$.

vibration of a circular membrane are shown in Figure 6 from which it is clear that the nodal lines can be either concentric circles or diameters. Each vibrational state of the membrane is characterized by the number of nodal lines and their type. If we call the total number of nodes including the edge of the membrane n and the total number of nodal lines l we obtain the notation given in Figure 6. For instance, the top left-hand membrane has only one circular node so that $n = 1$ and $l = 0$ whereas the membrane in the lower right-hand corner of Figure 6 has three nodes $(n = 3)$ of which two are linear $(l = 2)$. Once again we have the relationship $l \leqslant n - 1$. There are, in fact, an infinite number of vibrational modes for each given number of linear nodes since the patterns on the membrane can always be rotated by any arbitrary amount. However, all such vibrational modes can be built up by the appropriate superposition of two independent modes and Figure 6 shows only these independent modes.

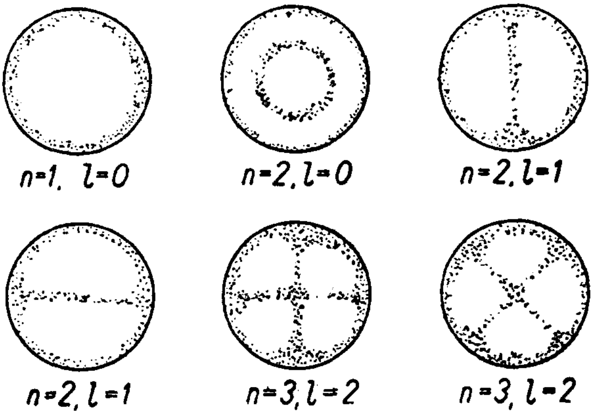

FIG. 6. Independent modes of vibration of a circular membrane.

In passing from a two-dimensional membrane to the three-dimensional pulsating sphere it is necessary to replace the circular nodes by concentric *spherical nodes* and the linear nodes by *nodal planes* which pass through the centre of the sphere. Again the total number of nodes including the outer spherical shell is called n and for each value of n there is a finite number of independent vibrational modes. However, for a given number of spherical and planar nodes the number of independent vibrations is no longer two as in the case of the circular membrane but is $(2l+1)$ where l, the total number of planar nodes, must again be $\leqslant n-1$.

Our model of the atom is closely related to the pulsating spherical dust-cloud. Each pattern into which the pulsating dust-cloud can be subdivided corresponds to an orbital and each independent mode of vibration corresponds to an electronic state of the atom. In this way we obtain a pictorial interpretation of the quantum numbers n and l with which we have numbered the electron shells and orbitals, and we can see how it comes about that a shell is composed of n^2 orbitals and a sub-shell of $(2l+1)$ orbitals respectively.

4. ψ-functions

An extranuclear electron can be regarded as an electrical charge distribution which surrounds the nucleus like a *cloud.* The shapes of the clouds formed by the individual electrons are determined by the structure of the orbitals whose nodes subdivide the charge cloud. In Figure 7 the shapes of the *s*-, *p*-, and *d*-orbitals are represented pictorially. The shaded areas indicate the regions of space in which there is the greatest *probability* of finding the electrons characterized by $l = 0$, 1, and 2 respectively. The + and − signs refer to the sign of the so-called ψ-function. In the case of the pulsating spherical dust-cloud this function gives the amplitude of vibration of a dust particle from its mean position as specified by the coordinates x, y, z. In the atomic model ψ is a mathematical function such that $\psi^2{}_{n,l}\Delta V$ gives the probability of finding an electron in the small element of volume ΔV, the electron being characterized by the quantum numbers n and l. For the 1*s*-, 2*s*-, and 2*p*-orbitals the variation of ψ along the x-axis is shown in Figure 7.

We see that the *s*-electron cloud is spherical, the *p*-cloud resembles a dumb-bell, and the *d*-cloud a rosette. The coordinate symbols x, y, z have been chosen deliberately as the subscripts to distinguish the three *p*-clouds since these each have the same shape but differ in their orientation in space. In the corresponding ψ-functions, x, y, z appear as factors which destroy the spherical symmetry of the electron cloud and the same is true for the subscripts used to distinguish the *d*-electrons. The remaining part of the ψ-function depends only on the

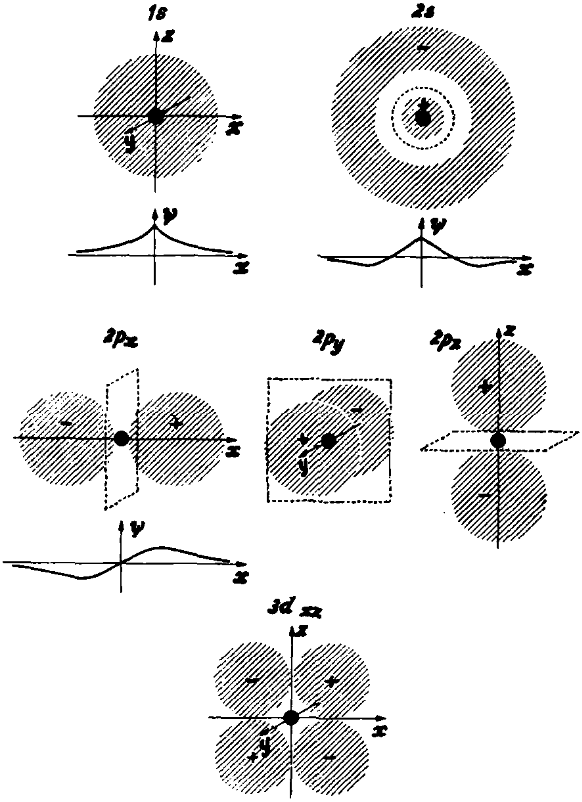

FIG. 7. Orbital shapes for extranuclear electrons.

distance r of the point x, y, z from the nucleus. Hence, the *charge density distribution* of an electron in a p_x-orbital, for example, is greatest in the direction of the x-axis and drops to zero in the yz-plane $(x = 0)$.

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