# CHEMICAL MATTER: ELEMENTS AND THEIR CLASSIFICATION THROUGH THE PERIODIC SYSTEM

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## Summary

The building up of the periodic table of the elements, based on the *aufbau* principle, Pauli exclusion principle, and Hund's rule is described and explained on the basis of a preliminary introduction to the electronic structure of atoms.

The periodic trends of ionization energies, sizes of atoms, electron affinities, and of the electronegativity of the elements are discussed together with some periodical chemical properties, such as binding energies, electrochemical properties of metals, and the shift along the periodic table from metals to nonmetals.

## 1. Introduction

Chemistry is an experimental science that involves an enormous number of observations and requires the investigation of all the various aspects of the properties of matter. For such a reason, from the beginning of the development of chemistry as a science at the end of the eighteenth century it was essential to try to rationalize the complexity of the elements' physical and chemical behavior, which at first sight were completely casual. Initially, the first elementary attempts at rationalization were based on the differentiation between metals and nonmetals. Only when the atomic weights of a good

number of elements were determined with a certain accuracy—between the years 1800 and 1860—did the basic elements of a periodic description of such a complexity became apparent. Already in 1829 the German chemist Johann Döbereiner (1780–1849) pointed out the existence of some triads: elements such as chlorine, bromine, and iodine, or calcium, strontium, and barium not only showed similar properties, but in addition the atomic weight of bromine was roughly the mean value of the atomic weights of chlorine and iodine; also the atomic weight of strontium responded to a similar trend. Later, the English chemist John Newlands (1837–1898) showed that when the elements are organized according to their atomic weight, it is possible to observe that at every eighth element—at that time noble gases were not known—one can find an element with properties similar to those of the first element of the previous eight. Such observations were the basis for understanding the periodical organization of the chemical behavior and physical properties of the various elements.

Thereafter—in the period 1860–1880—first, the German chemist Julius von Meyer (1830–1895) and then, finally, the Russian chemist Dmitri Mendeleev (1834–1907) were able to evidence and prove such a periodic hypothesis. Mendeleev, who proposed for the first time a well-defined periodic table of the elements, followed the hypothesis that the chemical behavior and physical properties of the elements are a periodic function of their atomic weights. Therefore, he organized all the elements in vertical rows—according to their similar chemical behavior and physical properties—and in horizontal rows—following the increase of their atomic weights.

Mendeleev had to base this hypothesis on the 62 elements then known; therefore, in order to complete his periodical arrangement he was compelled to predict the existence and properties of several elements. Interestingly, later on his predictions were confirmed by the discovery of elements that showed the chemical behavior and physical properties suggested by him.

| Series | Group I - $R_2O$ | Group II - RO | Group III - $R_2O_3$ | Group IV RH$_4$ $RO_2$ | Group V RH$_3$ $R_2O_5$ | Group VI RH$_2$ $RO_3$ | Group VII RH $R_2O$ | Group VIII - $RO_4$ |
|---|---|---|---|---|---|---|---|---|
| 1 | H = 1 | | | | | | | |
| 2 | Li = 7 | Be = 9 | B = 11 | C = 12 | N = 14 | O = 16 | F = 19 | |
| 3 | Na = 23 | Mg = 24 | Al = 27 | Si = 28 | P = 31 | S = 32 | Cl = 35.5 | |
| 4 | K = 39 | Ca = 40 | ? = 44 | Ti = 28 | V = 51 | Cr = 52 | Mn = 55 | Fe = 56 Co = 59 Ni = 59 |
| 5 | Cu = 63 | Zn = 65 | ? = 68 | ? = 72 | As = 75 | Se = 78 | Br = 80 | |
| 6 | Rb = 85 | Sr = 87 | Y = 88 | Zr = 90 | Nb = 94 | Mo = 96 | ? = 100 | Ru = 104 Rh = 104 Pd = 106 |
| 7 | Ag = 108 | Cd = 112 | In = 113 | Sn = 118 | Sb = 122 | Te = 128 | I = 127 | |
| 8 | Cs = 133 | Ba = 137 | Di = 138 | Ce = 140 | | | | |
| 9 | | | | | | | | |
| 10 | | | Er = 178 | La = 180 | Ta = 182 | W = 184 | | Os = 195 Ir = 197 Pt = 198 |
| 11 | Au = 199 | Hg = 200 | Tl = 204 | Pb = 207 | Bi = 208 | | | |
| 12 | | | | Th = 231 | | U = 240 | | |

Figure 1. The original periodic table of Mendeleev. The numbers indicate the atomic weight of the 62 known elements. The ? refers to the predicted elements that were still to be discovered; for example, ? = 68 is the element now known as gallium.

The Mendeleev rationalization of the periodic properties of the elements, which is one of the major achievement of modern science, was based on a compact arrangement of eight vertical rows (groups) and of several horizontal rows (series and later periods) (see Figure 1).

The elements of the same groups were characterized by a similar chemical behavior and by related physical properties, while both chemical behavior and physical properties changed in the same, repeated, periodic manner along each series.

The periodical table of the elements, as first proposed by Mendeleev, was completed in the following years when the elements lacking were discovered, and their chemical and physical properties defined. Finally, when the electronic structures of atoms had been established, the long form of the periodic table was organized into seven periods (three small and four long) and 18 groups. The latter were first divided in seven groups A and seven groups B, one large group VIII and one group O. Two separate rows were added at the end of the table, starting with lanthanum and actinium, respectively, and called the series of lanthanides and actinides. Only recently the subdivision of groups into A and B, as originally proposed, has been suppressed. Groups are classified in the long form of the periodic table (see Figure 2) from 1 to 18.

Figure 2. The actual long form of the periodic table

Therefore, while originally based only on an intuition, after the discovery of the electronic structure of the atoms the origin of such a periodical behavior was fully clarified. By successively adding electrons to the available energy levels of the gaseous atoms, one can build up the pattern of the electronic structure of the elements and, therefore, of their chemical and physical properties from the lightest to the heaviest one currently known. Interestingly, this approach follows perfectly the order of the atomic mass, which was the basis of the original intuition of Mendeleev.

Each group is characterized by the same configuration of the external electrons, while in each period or series specific electron levels are completed step by step by adding electrons.

In conclusion, the periodicity is an order related to the sequence of the electronic energy levels, so the chemical behavior and also many physical properties are dictated by the energy of the most external electronic levels. In this way one can explain easily why the elements of the same group show a similar chemical behavior and many comparable physical properties, while along a period the chemical behavior and the physical properties change abruptly from one element to the other, although they become the same after completion of the period itself.

## 2. Introduction to the Electronic Structure of Atoms

Although the subject of the electronic structures of atoms, molecules, and solids will be discussed in detail elsewhere, it will be worthwhile here to give the basic concepts of the electronic structure of atoms in order to introduce a basic understanding of the

energy of the electronic levels, which is necessary in order to describe the building up of the periodic table.

Quantum mechanics has shown that an electron may be described either as a particle or as a wave through a mathematical function called wavefunction, $\psi$, which is related to the energy, E, of the system via the Schrödinger equation:

$$\bar{H}\Psi = E\Psi \qquad (1)$$

where $\bar{H}$ is a mathematical operator called the Hamiltonian operator, which represents the general mathematical form of the kinetic and potential energies, and E is the numerical value of the energy associated with a given wavefunction, $\psi$ (see *Schrödinger Equation and Quantum Chemistry*). In the case of the hydrogen atom with one electron only attracted by a nucleus carrying the single charge of a proton the Schrödinger equation can be solved for certain wavefunctions—called eigenfunctions—and the associated energies are not given by a continuum but by a series of separated energy levels (called eigenvalues), which can be occupied by the electron. Each eigenfunction is characterized by a set of numbers n, m, and l, called quantum numbers, defined as follows:
n = 1,2,3,4,5,6,7…
l = all the integer values up to $(n–1)$
m = all the integer values between $(–l)$ and $(+l)$

- n is the principal quantum number, which mainly defines the energy and the main distance of the electron from the nucleus.
- l is the secondary or azimutal quantum number, which defines the angular momentum of the motion of the electron. Therefore, it defines the so-called shape of the eigenfunction.
- m is the magnetic quantum number associated with the magnetic moment generated by the motion of the electron around the nucleus. It defines the component of this magnetic moment along an external magnetic field.

The wavefunctions of the hydrogen atom, written in terms of polar coordinates r, $\theta$, and $\phi$ are split up to a radial component $R_{n,l}(r)$ and an angular component $\Phi_{l,m}(\theta, \phi)$, where $|R_{n,l}(r)|^2$ gives the probability of finding the electron at a distance r from the nucleus. The energy for a certain set n, l, m of quantum numbers is given by:

$$E = -\frac{Z^2 e^2}{2a_o h^2 n^2} \qquad (2)$$

where the nuclear charge Z is +1 for hydrogen, or +2, or +3 for hydrogen-like systems, such as the ions $He^+$ and $Li^{2+}$, e is the charge of the electron and the quantity $a_o$ is given by:

$$a_o = \frac{h^2}{4\pi m e^4} \qquad (3)$$

where m is the mass of the electron and h the Planck constant.

Clearly only the principal quantum number n, which characterizes the main distance of the electron from the nucleus, defines the various energy levels available to the single electron of the hydrogen atom. The wavefunctions, $\psi_{n, l, m}$, of the hydrogen atom are known as orbitals, broadly classified by their shape, therefore, according to the value of l. When l = 0 we have an s orbital that is spherically symmetrical, when l = 1 we have a p orbital with a nodal point in the nucleus, when l = 2 we have a d orbital with two nodal points in the nucleus, and, finally, when l = 3 we have an f orbital with three nodal points in the nucleus. A nodal point means that the probability of finding an electron on the nucleus is nil. In addition, p orbitals have three orthogonal orientations in space depending on the value of m, which can be 1, 0, or –1. Similarly, there are five possible orientations of d orbitals (m = 2, 1, 0, –1, or –2), and finally, seven possible orientations of f orbitals (m = 3, 2, 1, 0, –1, –2, or –3) (see *Molecular Energetics: Valence Bond and Molecular Orbital Methods* and *Density Functional Theory of Atoms and Molecules*).

Orbitals are usually represented by drawing the region of space in which there is a high probability of finding the electron (see Figure 3).
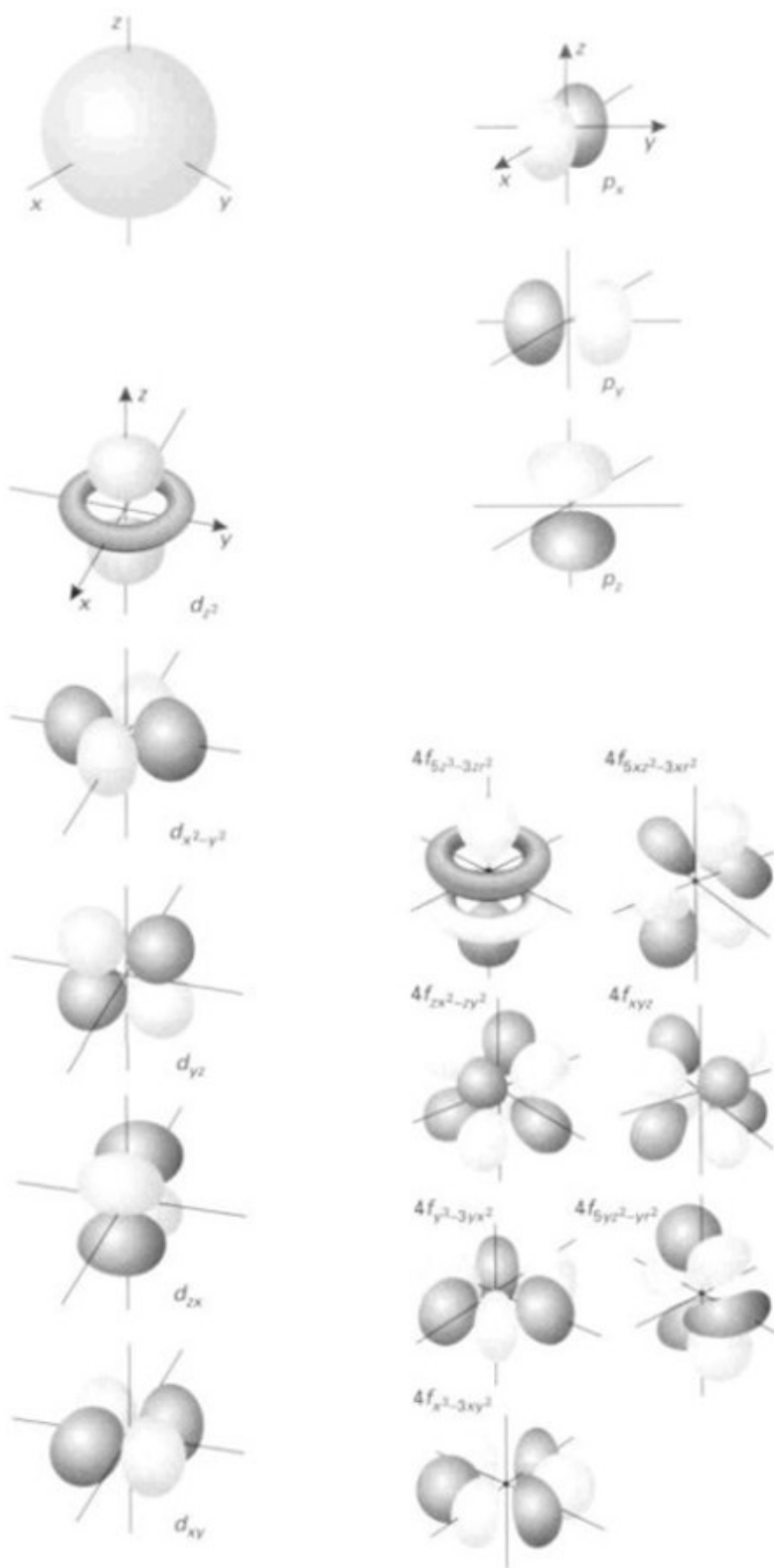
Figure 3. The drawing of the orbitals s, p, d, and f

These drawings represent only the directional character and are not intended to represent the actual shapes of the orbitals.

However, the single electron is not only characterized by the three quantum numbers of the wavefunction in which it is located, but in addition it may regarded as spinning about its own axis, generating an angular momentum and, therefore, a magnetic moment that is quantized and may assume only two directions. This means that the component of the magnetic moment in the direction of an external magnetic field is given by the quantity $s\dfrac{h}{2\pi}$, where s is the spin quantum number, which can only have the values of +½ or –½.

In conclusion, the motion, localization, and magnetic properties of the electron in the hydrogen atom are defined by four quantum numbers, but its energy is dependent only on the principal quantum number n, which defines the energy of the so-called electron shells. However, in atoms with more than one electron the energy of electrons is not anymore dependent only on the principal quantum number n, but also, for example, as in the semi-empirical approach of Slater, on the effective nuclear charge $Z^*$. In this semi-empirical approach the effective nuclear charge $Z^*$, which is felt by an electron, in a many electrons atom, is not the actual charge Z of the nucleus, but it depends on the ability of the other electrons, in particular those in orbitals penetrating towards the nucleus, to screen the electron in question from the nuclear charge Z. An empirical constant $\sum\limits_{i}^{n}\sigma_i$ represents the cumulative extent to which the other n single i electrons screen the particular electron; therefore, $Z^*$ is given by:

$$Z^* = Z - \sum_{i}^{n}\sigma_i \tag{4}$$

The screening depends first on the type of orbital in which the electron in question is housed, and also on the screening constant $\sigma_i$ of the other i electrons, calculated using a set of empirical rules, which are related to the penetration toward the nucleus of the orbitals in which the i electrons are located and of the orbital in which the electron in question is located.

By this semi-empirical approach, the single electron is considered to be an hydrogen-like system characterized by a nuclear charge $Z^*$, therefore, the energy of this electron is given by:

$$E = -\frac{(Z^*)^2 e^2}{2a_o h^2 n^2} \tag{5}$$

where the effective nuclear charge $Z^*$ is dependent not only on n but also on the quantum numbers l of the orbital in which the electron is housed.

It follows that in the hydrogen atom or hydrogen-like ions (such as $Li^{2+}$, $He^+$, and so on) the 1s orbital is more stable than the 2s orbital because the former is closer to the

nucleus than the latter, but 2s and 2p orbitals have identical energies. This is not true, however, in the case in polyelectronic atoms.

Let us look at the lithium atom carrying three electrons. The two electrons in the first 1s orbital are firmly held by the nuclear charge, which cannot be 3+ because the single electron is partially shielded by the other electron that stays in the 1s orbital. The electron in the outer orbitals with n = 2 has its greater density outside the 1s orbital; so it is strongly shielded from the nuclear charge by the two electrons in the 1s orbital that are penetrating with respect to the nucleus, being located quite close. The external electron with n = 2, therefore, "feels" an effective nuclear charge only of a little more than 1+, because it can penetrate only to a limited extent within the boundary of the 1s orbital. Now, if the outside electron is located in the 2s orbital it penetrates the 1s shield to a greater extent that it does if located in the 2p orbital. This can be easily inferred from the representation of orbitals of type s or p; electrons in orbitals of type s have a certain probability to be on the nucleus, while electrons in orbitals of type p have zero probability because they have a nodal point in the nucleus. It follows that the 2s orbital must be energetically more stable than the 2p orbital because its effective nuclear charge is higher due its higher penetration and, therefore, its energy of attraction is higher. Differing from hydrogen-like systems, the electron configuration $1s^2 2s^1$ of the lithium atom is more stable than the electron configuration $1s^2 2p^1$.

In general, according to the Slater rules, if the secondary quantum number l is constant the orbital with the lower principal quantum n number is more stable, which means that the stability decreases as follows: 1s>2s>3s>4s, and so on. Similarly, if n is constant the orbital with lower l number is more stable, which means that the stability decreases as follows: 4s>4p>4d>4f, and so on.

In conclusion, in an atom with many electrons the energy of the different orbitals are dependent on the number of electrons, that is, on the nuclear charge and how the electron is shielded with reference the single orbital under consideration. In the periodic table each new element adds one more nuclear charge than the preceding element; this charge is only partially neutralized by the addition of an electron that has fed into the lowest energy orbital available, therefore, the energy of all the electrons is more stabilized.

Orbitals with different n and with different l quantum numbers are characterized by different energies, according to Eq.(5), because they are influenced by a significantly different principal quantum number and effective nuclear charge. The levels of orbitals, characterized by different n and l quantum numbers, decrease their energy, which means they become more stable, by increasing the number of electrons as expected from the increase of the real and effective nuclear charge (Figure 4).
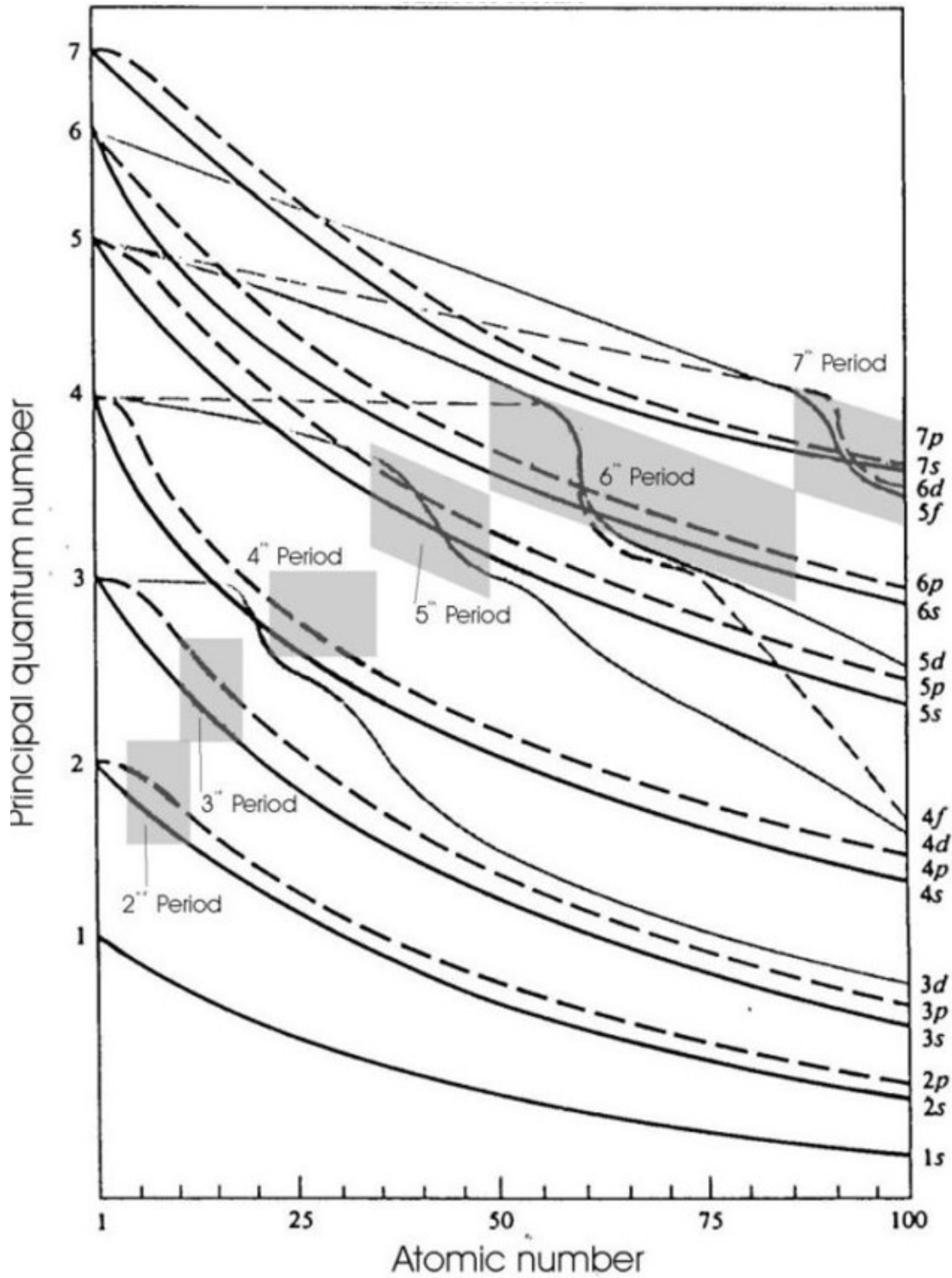
Figure 4. The trends of the energy levels of orbitals with different n e l quantum numbers in relation to the increasing atomic numbers

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**Bibliography**

Hoffman R. (1988). *Solid and Surfaces: A Chemist's View of Bonding in Extended Structures*. NY Weinheim: VCH Publishers. [A very interesting little book stressing the effectiveness of the intuitive approach of the chemist to bonding in molecules.]

Porterfield W.W. (1993). *Inorganic Chemistry. A Unified Approach*. Academic Press. [A comprehensive book on different conceptual aspects of inorganic chemistry, including periodical properties.]

Puddephatt R.J. (1972). *The Periodic Table of the Elements*. Oxford: Clarendon Press. [A valuable reference for studying the different aspects and subtleties of the periodic table.]

Sanderson R.T. (1960). *Chemical Periodicity*. New York: Van Nostrand-Reinhold. [An interesting operative approach to chemistry framed on the periodic table of elements.]

Sutton A.P. (1993). *Electronic Structure of Materials*. Oxford: Clarendon Press. [A valuable book centered on the modern realistic description of the electronic structure of matter.]

**Biographical Sketch**

**Renato Ugo** was born on June 18 1938. He holds a degree in Industrial Chemistry *cum laude* (1961); the *libero docente* was awarded prior to the prescribed term by virtue of his superior scientific merits (1966). He became a full professor, first of Analytical Chemistry (1973) and then of Inorganic Chemistry (1982) at Milan University, Italy. He is an elected member of the National Academy of the Lincei; and author and coauthor of more than 200 scientific articles and reviews. He is also the editor of two series of international journals: *Aspects of Homogeneous Catalysis* and *Catalysis by Metal Complexes,* published by Kluwer. He has been invited to give the plenary lectures in international conferences and symposia on the coordination of organometallic chemistry as well as catalysis. In this latter area of research he is the only scientist to have been invited to give plenary lectures at three major international congresses and symposia. He is currently President of AIRI (the National Association Industrial Research) and Vice-president of Assobiotec (the Association of Italian Industries for the Development of Biotechnology).