

1 Atomic Orbitals, Electronic Configurations

1.1 Atomic Orbitals

Physical experiments (electron diffraction, COMPTON effect) provide evidence that *electrons* do not only behave as *particles* but as *standing waves* as well. Mathematically, the wave nature of the electron is described by the SCHRÖDINGER equation (1). This differential equation correlates the *wave function* ψ of the electron with its total energy E .

$$H \psi = E \psi \quad (1)$$

(E : total energy, ψ : wave function, H : HAMILTON operator)

The SCHRÖDINGER equation (1) is only resolvable for *selected values of the energy* E . These values correspond to the *energy levels* of the electron in an atom, defined by the quantum numbers 1, 2, 3, Electronic energy is said to be *quantized*. The wave function ψ of an electron on a particular energy level E is the solution of the SCHRÖDINGER equation for that specific energy E . While this particular wave function ψ of the electron does not have any concrete meaning, its square, ψ^2 , describes the space around the atomic nucleus where the electron is most likely to be found. This "space of residence" or simply the "living room" of an electron described by ψ^2 is referred to as the *atomic orbital* (electron cloud).

1.2 s and p Orbitals

Spherically symmetric atomic orbitals with the atomic nucleus as center are referred to as s orbitals (Fig. 1.1).

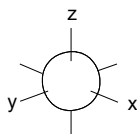


Fig. 1.1. s orbital: spherically symmetric distribution of the electron about the atomic nucleus

On the lowest energy level E_1 (quantum number $n = 1$) the electron occupies the 1s orbital; this applies for the hydrogen atom. The 2s orbital following at the second energy level E_2 ($n = 2$) concentrically envelops the 1s orbital. The 2s orbital is occupied by an electron in the lithium atom, following the helium atom of the first row of the periodic table (Table 1.1) with a doubly occupied 1s orbital.

Beginning with the second energy level E_2 ($n = 2$), there are *three additional dumbbell-shaped atomic orbitals* on energy levels slightly elevated relative to the 2s orbital (Fig. 1.2). In contrast to the spherical s orbitals, these orbitals are *directed*, extending along the axes x , y and z ; therefore, they are called the $2p_x$, $2p_y$ and $2p_z$ orbitals. All three 2p orbitals possess the same energy and for this reason they are said to be *degenerate*.

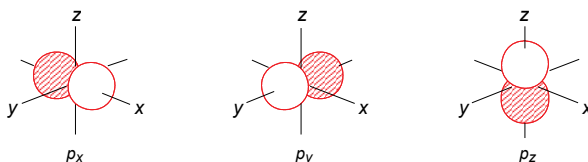


Fig. 1.2. p Orbitals (p_x , p_y , p_z) along the coordinate axes; p orbital halves in the range of negative sign are shaded

1.3 Electron Spin and PAULI Principle

In addition to their negative charge and their impulse to circumrotate the nucleus, electrons possess a *spin* (electron spin). They may spin either clockwise or counterclockwise. When two electrons spin in the same manner, they are said to have *parallel spins* and this situation is symbolized by two arrows in the same direction ($\uparrow\uparrow$). When, however, two elec-

trons spin in opposite directions, they are said to have *antiparallel spins*, and this is symbolized by two arrows in opposite direction ($\uparrow\downarrow$). Electrons with antiparallel spin are also said to be *paired*.

Only two electrons can occupy the same orbital, provided they have antiparallel spins ($\uparrow\downarrow$). This restriction is known as the PAULI principle.

1.4 Electronic Configuration of Light Atoms

The distribution of electrons in the orbitals of an atom is called the *electronic configuration* of that atom. The electronic configuration represents the *ground state* of an atom, that is the state of lowest potential energy and highest stability. The main constituent atoms C, H, O, N of organic compounds are among the light elements of the periodic table. Their electrons occupy only s and p orbitals. Three rules regulate the occupation of orbitals by electrons:

- The orbitals are occupied in order of increasing energy: first 1s, then 2s, followed by $2p_x$, $2p_y$, $2p_z$.
- Only up to two electrons can occupy the same orbital. Double occupation requires electronic spins to be antiparallel (PAULI principle).
- When a set of degenerate orbitals is available, for instance the three 2p orbitals, single occupation takes place before any of these orbitals becomes doubly occupied (HUND rule, cf. the electronic configuration of the elements C, N, O in Table 1.1).

The electronic configuration of an atom (Table 1.1) is described by quoting the occupied orbitals in the order of increasing energy. The number of electrons in each orbital, 1 or 2, is indicated by the superscript ¹ or ² at the corresponding orbitals; the ¹ for single occupation is usually omitted. Boron as an example has the electronic configuration $1s^2 2s^2 2p$ ($1s^2 2s^2 2p^1$), indicating double occupation for the 1s and 2s orbitals and single occupation for one 2p orbital.

Table 1.1. Electronic configuration of light atoms in the ground state

atom	1s	occupation			representation	
		2s	$2p_x$	$2p_y$	$2p_z$	
H	\uparrow					1s
He	$\uparrow\downarrow$					$1s^2$
Li	$\uparrow\downarrow$	\uparrow	\circ	\circ	\circ	$1s^2 2s$
Be	$\uparrow\downarrow$	$\uparrow\downarrow$	\circ	\circ	\circ	$1s^2 2s^2$
B	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\circ	\circ	$1s^2 2s^2 2p$
C	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	\circ	$1s^2 2s^2 2p^2$
N	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	$1s^2 2s^2 2p^3$
O	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	$1s^2 2s^2 2p^4$
F	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	$1s^2 2s^2 2p^5$
Ne	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$1s^2 2s^2 2p^6$ ($1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$)

Chapter 1 permits answers to the following:

- (1.1) What is an atomic orbital?
- (1.2) How do p orbitals differ from s orbitals?
- (1.3) How do p orbitals differ among themselves?
- (1.4) Write the orbital occupancy for the atoms in the first two rows of the periodic table.
- (1.5) Is the tetravalency of carbon in accordance with the electronic configuration of carbon in Table 1.1?