

## Chapter 7. Atomic Structure

### 7.1. Cosmology

The experimental investigation of material objects has progressed historically in an analytical fashion, that is, by breaking substances down into their smaller parts. Conceptual science, on the other hand, tends to build things up from their more primitive components. One cosmological<sup>1</sup> model postulates a dense fireball of radiation at the beginning of time, which expanded instantaneously (the Big Bang) causing cooling and conversion into simple matter, the fundamental particles of physics. Further cooling caused condensation into light atoms and accretion into stars, giving birth to heavier elements through nuclear reactions.

It is assumed that the strength of interactions between material objects decreases with increasing separation between the objects. Accordingly, it should be possible to discuss and investigate *isolated systems*. This simplifies the considerations enormously as the alternative would require consideration of the universe as a whole. Nevertheless, there is no reason to believe that interactions are ever totally negligible, and some researchers would insist that honest models of isolated matter can only be considered a convenient approximation to a broader holistic model of the material universe.

Our discussion of the structure of matter will assume that systems can be isolated from the rest of the universe and we will reconstruct matter from the simple to the complex. This is in contrast to the historical development of the understanding of the material universe (from the complex to the simple). In the case of chemical matter, the story begins with three fundamental particles.

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<sup>1</sup> Cosmology - the study of the *cosmos* (Greek for the orderly world), or origin and development of the universe.

## 7.2. Subatomic Particles

Understanding chemical behavior in fundamental terms has benefited from probing into molecules and atoms to reveal their internal structure. What follows is a constructive presentation of the understanding of atomic structure and behavior which emerged over a half century of investigation.

**Matter** refers to any ponderable object, i.e. any object having mass (and therefore attracted through gravitational force to other material bodies such as the earth). The **fundamental particles** of nature are the smallest material objects.<sup>2</sup> They are principally (but not exclusively) the objects of study of physics. Fundamental particles and radiation are the only objects known to exist at extremely high (thermonuclear) energies, such as exist above billions of degrees. At lower temperatures (such as found in stars), fundamental particles may condense into combinations bound together by strong (nuclear or electrical) attractions. **Atoms** are bound combinations of three fundamental **sub-atomic** particles<sup>3</sup>: positively-charged **protons** (Greek *protos* for first), neutral **neutrons** (Latin *neuter* for neither) of nearly equal mass, and negatively-charged **electrons** (Greek *elektron* for amber) of mass 1840 times less than protons and neutrons. Precise values are listed in Constants and Conversions. Elementary particle charges are measured in terms of the **atomic charge unit**, or *acu*, defined as  $1.6021773 \times 10^{-19}$  C (SI charge units, or Coulombs), equal to  $1.5189073 \times 10^{-14}$  (Jm)<sup>1/2</sup>. At still lower temperatures (such as that of planets), atoms combine to form stable collections called **molecules**. Molecules, in turn, accumulate into ponderable amounts of matter.

In an atom, the protons and neutrons (collectively called nucleons) are collected together into a **nucleus** (Latin *nucis* for kernel, nut), which is surrounded by electrons. The nucleus has a charge in atomic charge units equal to the number of protons and occupies only about one ten-thousandth the volume of the discernible atom. *Nuclei dominate the mass of matter, while electrons determine chemical properties.*

Chemical **elements** are pure forms of matter consisting of collections of atoms *all having the same number of protons*. The lightest element has one proton; the heaviest could

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<sup>2</sup> Cf. Section 4.5.

<sup>3</sup> Protons were speculated by William Prout in 1815 and discovered in 1915 by Ernest Rutherford, electrons were speculated by Faraday in 1832 and discovered by J. J. Thompson in 1897, and neutrons were speculated by Rutherford in 1913 and discovered in 1932 by James Chadwick and Harold Urey.

have an unlimited number of protons, but the heaviest known element has about one hundred protons. The fact that nature has presented us with only a rather small, finite number of different kinds of fundamental particles and atoms has facilitated our understanding of the structure of matter.

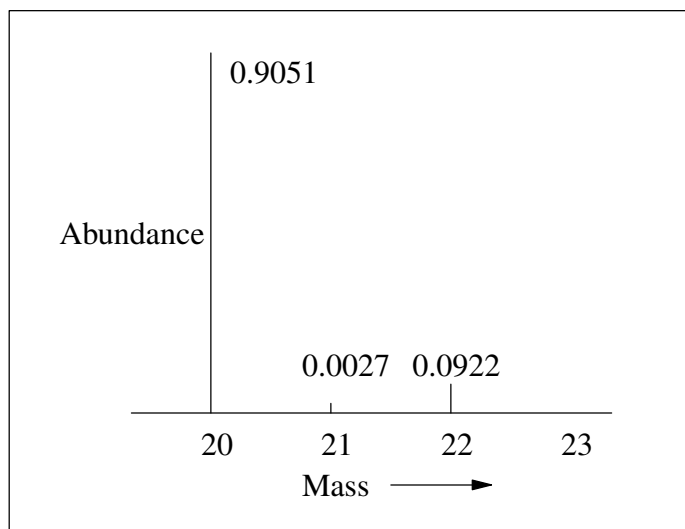
Although all atoms of a given element have a given number of protons, atoms may have varying numbers of electrons and neutrons. Atoms and molecules having equal numbers of electrons and protons are electrically **neutral**, while those with an imbalance are called **ions** (Greek *ion*, to go); those with more electrons than protons are negatively-charged **anions** (pronounced “an-ions”) (Greek *anion*, to go up), and those with fewer electrons than protons are positively-charged **cations** (pronounced “cat-ions”) (Greek *kata+ion*, downward going). Atoms of an element (each with the same number of protons) having different numbers of neutrons are called **isotopes** (Greek *isos+topos* for equal place (in the chemical periodic table)) of the element. Many naturally-occurring elements have more than one isotope, distributed according to observed *natural abundance* fractions. The number of protons an atom contains is called the **atomic number** and the number of protons plus neutrons is called the **mass number**. The **average atomic mass** of an element is the average mass of mixtures of isotopes of the element.

$$\text{Average atomic mass} = \sum_{i=1}^m f_i \text{AM}_i \quad (7.1)$$

where  $m$  is the number of different naturally occurring isotopes,  $f_i$  is the fraction of the  $i$ th isotope, and  $\text{AM}_i$  is the observed atomic mass of the  $i$ th isotope.

Accurate measurements of masses and abundances of atomic-sized particles can be obtained from instruments called *mass spectrometers*, which consist of three components acting on the particles in stages of generation, separation and detection. In the generation stage, collections of molecules are *fragmented* and *ionized* by bombardment (“blasting”) with electrons. In the second stage, the ionized particles are *accelerated* through circular paths with electric and magnetic fields; *separation* of the fragments occurs because the radii of the paths depend on the mass-to-charge ratio of the particles. Since charged particles expose photographic film in a manner similar to light, their final positions and intensities can be measured using photographic film as a *detector* (although more sophisticated detection devices are ordinarily used nowadays). The amounts of deflection as determined from the arrangement

of the equipment can then be inserted into equations of electricity and magnetism from physics. These equations can be solved for the masses of the ions, given their charges. Relative amounts of different ions are determined from the intensities of the particle beams at the detector. Fig. 7.1 shows a schematic view of the experimental mass spectrum of the element neon, showing the relative abundance of its three naturally-occurring isotopes.<sup>4</sup>



**Fig. 7.1** The Mass Spectrum of Elemental Neon

In the following example we will apply Eq. (7.1) to the analysis of elemental neon using a mass spectrometer.

**12xample 7.1** What is the average atomic mass of the element neon, which has a natural abundance isotope distribution of 90.51%  $^{20}\text{Ne}$  (AM = 19.99244), 0.27%  $^{21}\text{Ne}$  (AM = 20.99395), and 9.22%  $^{22}\text{Ne}$  (AM = 21.99138)?

<sup>4</sup> The analysis of molecules will be treated in a later chapter (Section 12.3).

$$\text{Average AM} = 0.9051 \times 19.99244 + 0.0027 \times 20.99395 + 0.0922 \times 21.99138 = 20.179$$

### 7.3. Element Symbols

An **element symbol** uses an element *name abbreviation*, symbolized here by E, embellished with the *atomic number*, symbolized by Z, written as a left-hand subscript, a *mass number*, symbolized by A, written as a left-hand superscript, and a *charge*, symbolized by q, written as a right-hand superscript.<sup>5</sup> The mass number equals the sum of the atomic (proton) number plus the number of neutrons (N). A right-hand subscript may be used to indicate the *number of atoms*, symbolized by n, bound together in the case of *polyatomic* (many-atom) element molecules. The general form of an element symbol and the relationships between element parameters are:

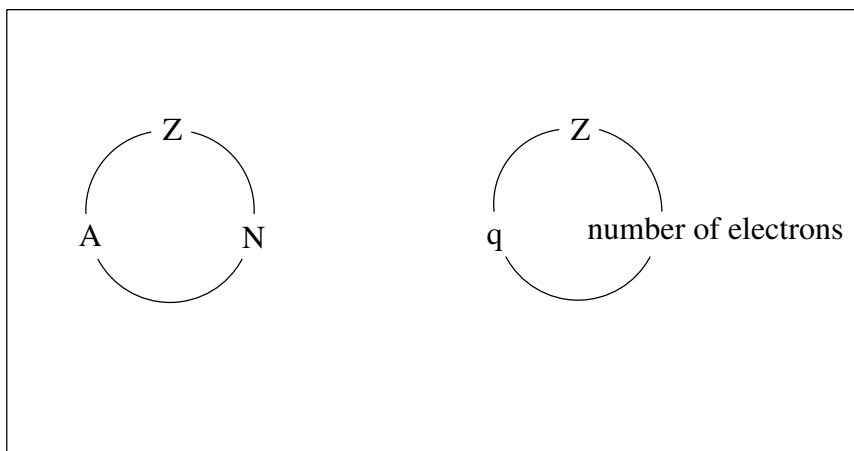
$$\text{General element symbol: } {}^A_Z E_n^q \quad (7.2)$$

$$A = Z + N \quad (7.3)$$

$$q = Z - \text{number of electrons} \quad (7.4)$$

Fig. 7.2 depicts these relationships between the atomic parameters.

<sup>5</sup> Sometimes the charge of a cation is indicated with a Roman numeral in parentheses following the name abbreviation.



**Fig. 7.2** Relationships Between Atomic Number ( $Z$ ), Atomic Mass ( $A$ ), Neutron Number ( $N$ ), Charge ( $q$ ), and Number of Electrons.

If no mass number ( $A$ ) is given, the element symbol represents the average of the masses of the various isotopes of the element occurring in nature. If no charge ( $q$ ) is given, it is assumed to be zero. If no atom subscript ( $n$ ) is given, it is assumed either to be unity in the case of **monatomic** (single atom) elements, or to represent an extremely large number in the case of polyatomic aggregate elements, such as metals. The atomic number ( $Z$ ) is optional as it conveys the same information as the element name abbreviation (i.e. number of protons).

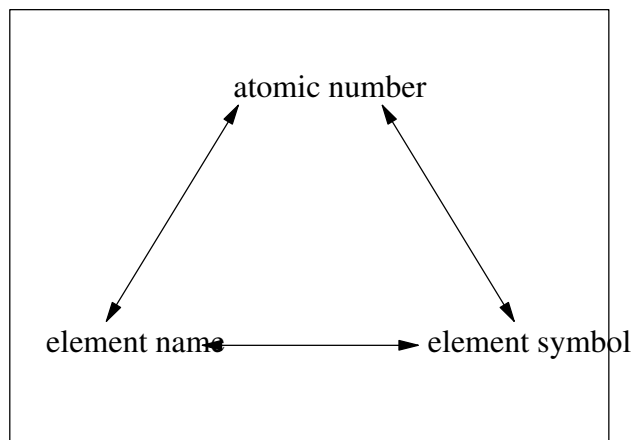
Problems dealing with the relationships of the element parameters are based on Eqs. (7.3) and (7.4).

**Example 7.2** How many protons, neutrons and electrons has  ${}^{235}_{92}\text{U}^{3+}$ ?

$Z = 92$ ,  $N = Z - A = 235 - 92 = 143$ , number of electrons =  $Z - q = 92 - 3 = 89$ .

Chemical element nomenclature deals with the three equivalent ways to represent an element: name, abbreviation and atomic number. Since chemical names and symbols are tabulated either alphabetically or by atomic number, the algorithm for translating between the representations is table lookup, that is, given one of the representations, look up the others in

a reference source. The Periodic Table (front inside cover) lists element symbols and corresponding atomic numbers.



**Fig. 7.3** Relationship Between Atomic Number, Element Name and Element Symbol.

Figures 7.2 and 7.3 represent relationships between various atomic parameters and symbols and conversion maps from one value to another. The following algorithm states verbally how to make the conversions.

### Element Identification and Parameters Algorithm

**Purpose:** To derive complementary information from partial element information.

**Procedure:**

1. Given partial identification information for an element in the form of name, symbol or atomic number, derive remaining information from a list or table, such as the periodic table.
2. Given two element subatomic parameter values from the list of atomic number, mass number and neutron number, derive the third from the relation that mass number is the sum of atomic number and neutron number.
3. Given two element subatomic parameter values from the list of atomic number, charge and electron number, derive the third from the relation that atomic number is the sum of charge and electron number.

**Example 7.3** What are the atomic number, chemical symbol and atomic mass of the element germanium?

According to the alphabetical entry titled *THE ELEMENTS* of the *CRC Handbook of Chemistry and Physics*<sup>6</sup>, germanium has atomic number 32, atomic symbol Ge, and natural abundance atomic mass 72.59.

**Example 7.4** The element symbols for naturally occurring dichlorine (each molecule having two atoms), uranium isotope 235, and iron (III) cation are  $\text{Cl}_2$ ,  $^{235}\text{U}$ , and  $\text{Fe}^{3+}$ , respectively.

#### 7.4. Atomic Spectra

The properties of atoms can be explained in terms of the *arrangement* of their subatomic particles, protons, neutrons and electrons. Chemical mass relationships, such as element and isotope mass, are dominated by the dense nucleus, but chemical *energy* relationships, such as chemical bonding and reactivity, are dominated by the electrons external to the

<sup>6</sup> *CRC Handbook of Chemistry and Physics*, CRC Press, Inc., Boca Raton, Florida, 75th. ed., 1994.



nucleus. A theoretical basis for atomic behavior has been worked out in terms of the electronic structure of atoms, based on the laws of physics for subatomic particles, namely *quantum mechanics*.

One of the properties of the elements scientists sought to understand in the Nineteenth Century was **atomic spectra** (Latin *spectrum*, for image), the colors of light absorbed by atoms when energetically “excited” (**absorption spectra**), or emitted when excited atoms relax (**emission spectra**). Atoms can be excited by a variety of energy sources, including light energy, electrical energy, heat energy and chemical energy. A significant experimental feature of atomic spectra is that *Absorption and emission spectra (colors) are the same in all cases, characteristic of the element*. This suggests a connection between discrete atomic energy differences and absorption and emission of discrete colors of light (see Fig. 7.7 below). Familiar examples of atomic emission spectra are seen in firework displays where chemical combustion reactions release energy as light.

According to Newton “white” light, as from the sun or an incandescent light bulb, is composed of a *continuous* rainbow of colors, each color characterized by a wavelength. Atomic spectra on the other hand, consist of *discrete lines* (colors or wavelengths). A glass prism may be used to display spectra and contrast the continuous emission spectra of glowing filament light bulbs and electric heaters on stoves with the discrete emission spectra of sodium and mercury vapor street lamps and natural gas burner heaters on stoves. Both continuous and discrete spectra are found in highly resolved observations of the spectrum of sunlight, in which continuous light of all frequencies generated in the interior of the sun (where the temperature is millions of degrees) must pass through the much cooler surface (at 6,000 degrees), where atoms absorb some of the light at discrete frequencies.<sup>7</sup>

Atomic line spectra, although not continuous, can be enormously complicated, with thousands of lines produced by a single element, especially when the range of observation is extended beyond the spectrum visible to the human eye into the *infrared* (beyond red wavelengths, > 700 nm) and the *ultraviolet* (below violet wavelengths, < 400 nm) regions. The line spectrum of each element is different and characteristic of the element; dominant (high intensity) visible colors are yellow for sodium (589 nm), blue for copper (522 nm),

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<sup>7</sup> In fact, the element helium was observed in the spectrum of the sun before it was detected on earth, hence the name (Greek *helios*, the sun).

green for barium (554 nm), and orange-red for neon (580 and 640 nm). Elements can be identified by observing their emission spectra after excitation through electric discharge and flames (spectrochemical analysis). The simplest element, hydrogen, with just one proton and one electron is found to have the simplest spectrum, composed of overlapping series, with each series converging to a different wavelength limit.

At the time of the investigations into atomic line spectra in the Nineteenth Century, light was thought to consist of some form of vibrating disturbance (of the aether), with the color of the light characterized by a corresponding frequency, or wavelength of the disturbance. An analogy may be drawn with wave motion in water propagating some disturbance (cf. Section 4.4 on Wave Models).

According to quantum mechanics, energy is carried by particles of light, that have associated frequencies obeying the *Planck-Einstein* equation (cf. Eqs. (5.19) and (5.22))

$$|\Delta E| = h\nu = \frac{hc}{\lambda}, \quad (7.5)$$

where  $|\Delta E|$  represents the energy of the photon and  $h$  is an universal proportionality constant, called **Planck's constant**, with value  $6.626076 \times 10^{-34}$  J s. The absolute value of energy appears because frequencies have only positive values, independently of whether the transition involves an absorption ( $\Delta E < 0$ ) or emission ( $\Delta E > 0$ ) of light energy. In a sense, Einstein did for light what Dalton had done a century earlier for matter (as discussed in the previous chapter), namely hypothesized a discrete nature at the fundamental level. The magnitudes of the energies associated with various frequencies of light may be appreciated from the fact that ultraviolet light (UV) causes suntan (and sunburn) by disrupting chemical bonds in the skin; on the other hand, it is not possible to get a suntan by standing in front of a fireplace for any length of time, because combustion yields only visible and infrared (heat) radiation energies, which are insufficient to disrupt the chemical bonds in the skin.

**Example 7.5** The energy of ultraviolet light of 400 nm wavelength is

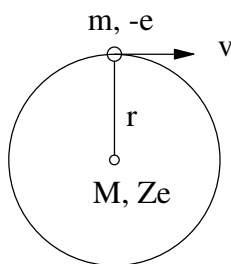
$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626076 \times 10^{-34} \text{ J s})(2.99792458 \times 10^8 \text{ m/s})}{(400 \times 10^{-9} \text{ m})} = 4.966 \times 10^{-19} \text{ J/photon}$$

To compare with chemical energies, which are measured in kJ/mol of molecules, the energy is

$$4.966 \times 10^{-19} \frac{\text{J}}{\text{photon}} \frac{(6.0221 \times 10^{23} \text{ photon})}{(1 \text{ mol photon})} \frac{(1 \text{ kJ})}{(1000 \text{ J})} = 299 \text{ kJ/mol photons}$$

This is of the order of chemical bond energies (Table 12.2), so ultraviolet light is capable of damaging substances.

Ernest Rutherford's<sup>8</sup> work on subatomic particles at the beginning of the Twentieth Century suggested a *planetary model* of atoms, consisting of a massive nucleus containing protons surrounded by orbiting electrons. Fig. 7.4 shows the motion in a one-electron planetary atom with electron of mass  $m$ , electron charge  $-e$ , moving with velocity  $v$  relative to a nucleus of nuclear mass  $M$  and nuclear charge  $Ze$ .



**Fig. 7.4** The Planetary Atomic Model

For his doctoral dissertation of 1913, Neils Bohr<sup>9</sup> explained the discrete (line) nature of atomic spectra in terms of a “quantized” planetary model of the atom. Negative electrons are permitted to orbit the positive nucleus in *particular* orbits, with transitions between the

<sup>8</sup> Ernest Rutherford (New Zealand, 1871-1937) ranked with Faraday as one of the greatest experimentalists of all time, characterized  $\alpha$  particles, discovered the nucleus, protons, neutrons, transmutation. Nobel Prize in chemistry, 1908. Ten of his students received Nobel Prizes as well.

<sup>9</sup> Neils Henrik David Bohr (Danish, 1885-1962) Nobel Prize in physics, 1922. Bohr attempted to bridge quantum and classical mechanics through principles of *complementarity* (waves and particles complement each other) and *correspondence* (classical behavior is the limit of quantum behavior).

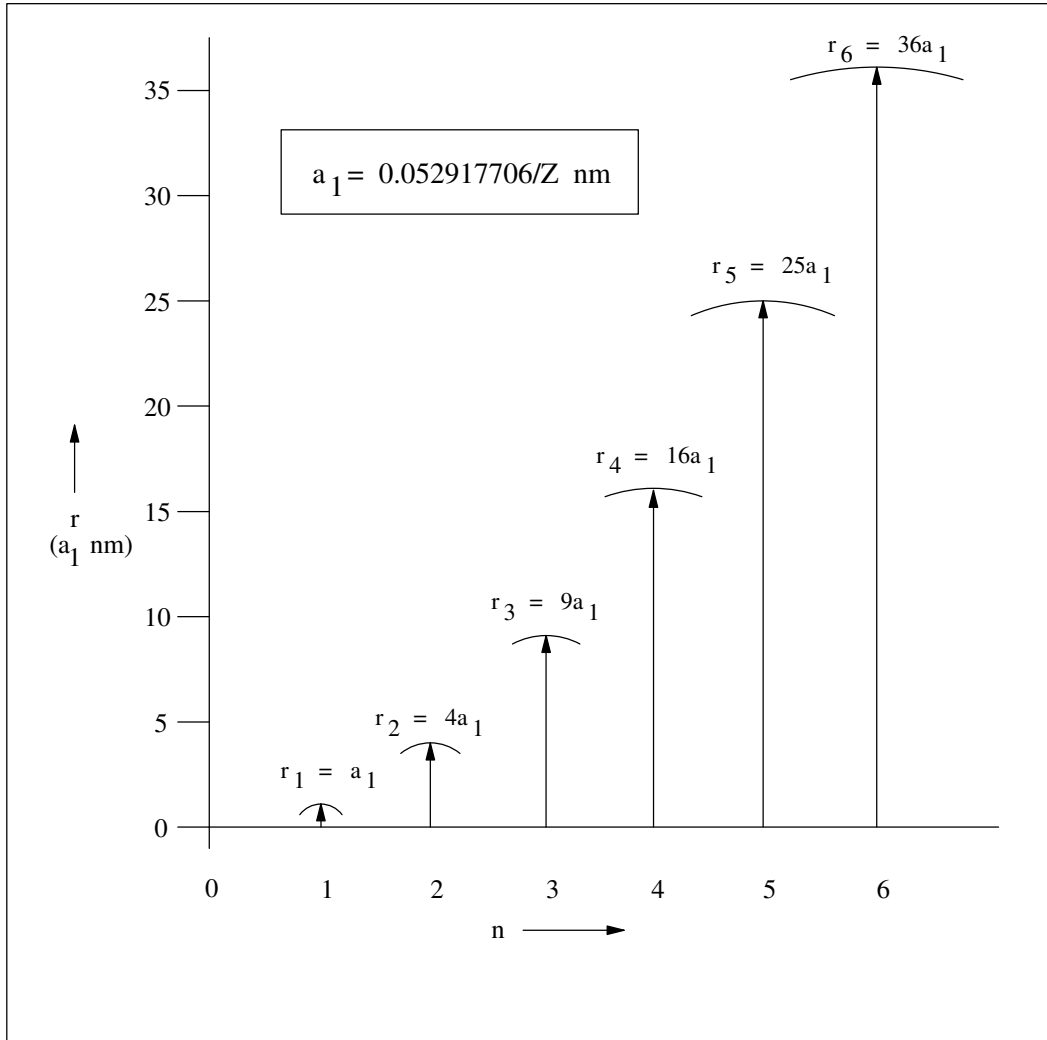
orbits absorbing or releasing energy, corresponding to moving further or closer to the nucleus. **Bohr's equations** (derived in Appendix A to this chapter) for the potential energy, radius and velocity of one-electron atoms as functions of quantum number  $n$  are:

$$v_n = \frac{2\pi Ze^2}{nh} = \frac{Z\alpha}{n}, \quad (7.6)$$

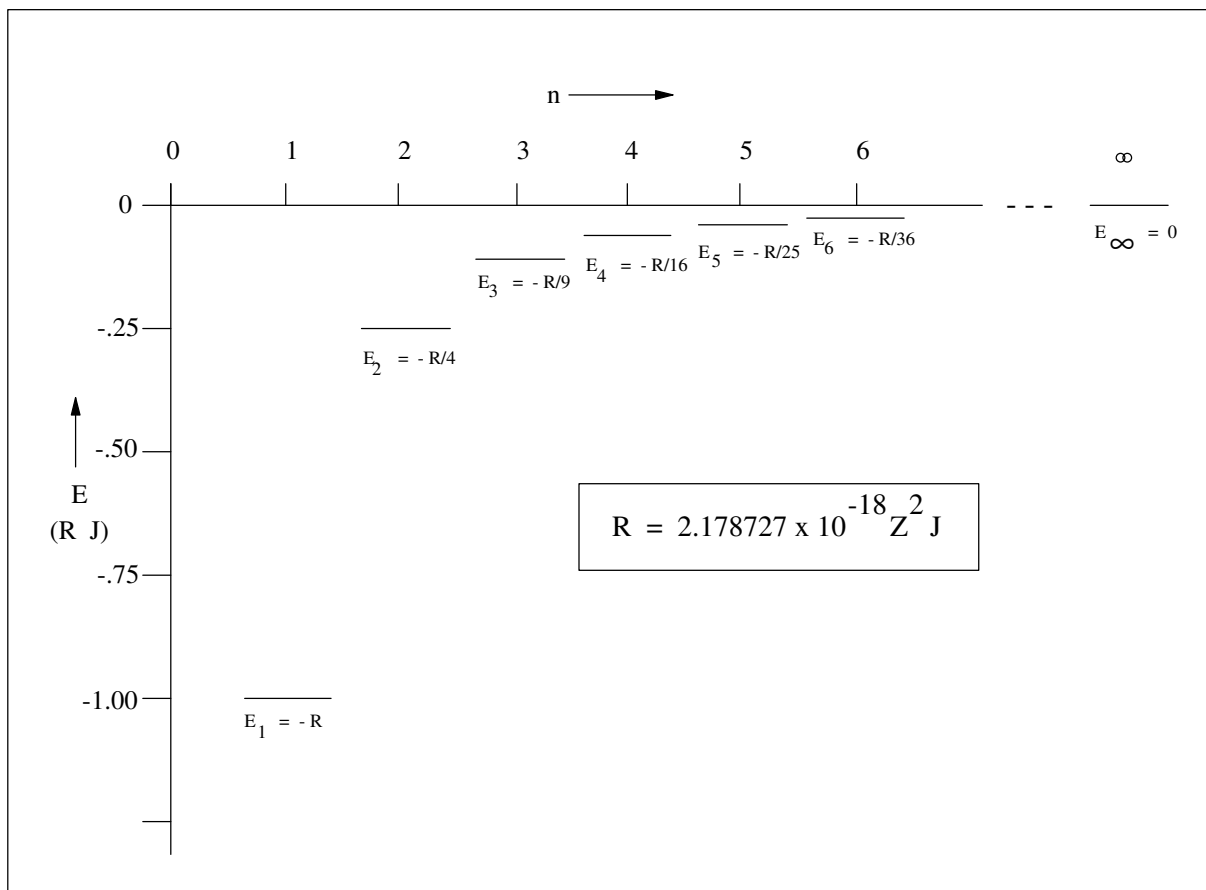
$$r_n = \frac{1}{Z} \mu \left( \frac{nh}{2\pi e} \right)^2 = \frac{Ze^2}{\mu v_n^2} \equiv a_1 n^2 \quad (7.7)$$

$$E_n = -\frac{2\pi^2 \mu Z^2 e^4}{h^2 n^2} = -\frac{Ze^2}{2r_n} \equiv -\frac{R}{n^2} \quad (7.8)$$

where  $\mu = m_e m_{\text{nucleus}} / (m_e + m_{\text{nucleus}}) \approx m_e$  is the reduced mass of an electron/nucleus pair (Section 5.4),  $e$  its charge, and  $v$  its velocity,  $Z$  the nuclear proton charge ( $Z = 1$  for hydrogen) and  $n$  is a positive integer defining the orbit, called a **quantum number**. The parameter  $\alpha$  is called the *fine structure constant*, equal to  $1/137.036$ ,  $a_1$  is called the first *Bohr radius*, equal to  $0.052917706/Z$  nm, and  $R$  is a constant called the *Rydberg constant*, with value  $R = 2.178727 \times 10^{-18} Z^2$  J. The lowest energy state corresponds to  $n = 1$  and is called the **ground state, or level**; higher states  $n > 1$  are called **excited states, or levels**, with  $n = \text{infinity}$  describing the **ionized state**. The highest energy state corresponds to infinite radius, or ionization and is assigned a potential energy value of zero. Energies below ionization are called **bound states** and are negative. Note that for a given nuclear charge  $Z$  (element), energies increase from the ground state inversely proportional to  $n^2$ , while radii increase directly proportional to  $n^2$ , as shown in Figs. 7.5 and 7.6. As the nuclear charge  $Z$  increases (from one element to the next) all the energy levels are shifted downward by a factor of  $Z^2$ , and all the radii are shifted to smaller values and velocities increased by a factor of  $Z$ .



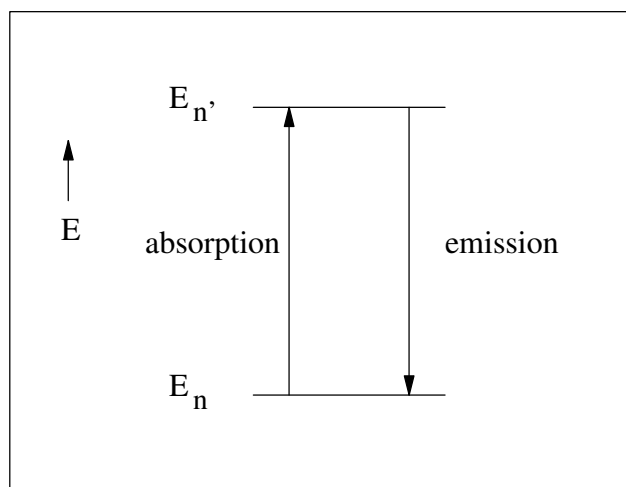
**Fig. 7.5** One-Electron Bohr Radii as a Function of Quantum Number  $n$ .



**Fig. 7.6** One-Electron Bohr Energies as a Function of Quantum Number  $n$ .

The magnitude (absolute value) of the difference in energy in changing orbits is manifest as light with frequency given by Eq. (7.5). It is the nature of quantum transitions that energy can be absorbed ( $\Delta E \geq 0$ ) or emitted ( $\Delta E \leq 0$ ) only in *discrete* differences

corresponding to different values of  $n$  in the Bohr equation, much like a ball releasing (or gaining) energy by bouncing down (or up) stairs, but not in continuous amounts by rolling down (or up) a ramp. See Fig. 7.7. In this way, Bohr was able to account for the observed lines of the hydrogen spectrum. In addition, for the first time since the discovery of subatomic particles, explanations could be given for the finite size of atoms (quantum rules exclude collapse into the nucleus as  $n = 0$  is not allowed), and for the variation in size of atoms of different elements (higher-energy electrons in different elements move in larger orbits).



**Fig. 7.7** Quantum Energy ( $E$ ) Levels and Transitions

**Example 7.6** The wavelength of light emitted when an electron in the third excited state of hydrogen falls to the ground state is found from Eqs. (7.5) and (7.6) as follows ( $R_H$  means  $R$  for  $Z = 1$ ):

$$|\Delta E| = h\nu = \frac{hc}{\lambda} = R_H \left| \frac{1}{3^2} - \frac{1}{1^2} \right| = \frac{8}{9} R_H = 2.203313 \times 10^{-18} \text{ J}$$

$$\lambda = \frac{9hc}{8R_H} = \frac{(9)(6.626076 \times 10^{-34} \text{ J s})(2.99792458 \times 10^8 \text{ m/s})}{(8)(2.178727 \times 10^{-18} \text{ J})} = 102.5215 \text{ nm}$$

Three comments: first, the wavelength agrees extremely well with experimental observation, justifying the use of quantum mechanics; second, the values of  $\Delta E$  and  $\lambda$  are typical of atom chemical energies and colors; third, although the Bohr model is successful for *one-electron* atoms, such as H and the  $\text{He}^+$  ion, it can not be extended to *any* system containing *more* than one electron.

## 7.5. Wave Mechanics

An extension of quantum mechanics to multiple-electron atoms in 1925 by Erwin Schrödinger led to a *dualistic* model for the electron, a particle with wave characteristics (cf. Section 4.4 on Wave Mechanics). Quantum wave mechanics produced a new model for electronic structure; clouds of electronic charge in discrete energy states, called *energy levels*. Four attributes of classical electron orbits are *size*, *shape*, *orientation* (in space) and *spin* (see Fig. 7.8 below). Corresponding electron cloud nomenclature is *shell*, *subshell*, *orbital* and *spin*. Each of the four attributes is measured by an integer, or half-integer in the case of spin, called the **quantum number**. The *ranges* of values of the quantum numbers are governed by the quantum mechanics of the hydrogen atom. The *shell quantum number*,  $n$  can be any positive integer, 1, 2, 3, ... . The *subshell quantum number*,  $l$  is restricted by the value of the shell quantum number, and has  $n$  different integer values ranging between 0 and  $n - 1$ . The *orbital quantum number*,  $m$  is restricted by the magnitude of the subshell quantum number, and has  $2l + 1$  integer values ranging between  $-l$  and  $+l$ . The *spin quantum number*,  $s$  is constrained to just two values,  $-\frac{1}{2}$  and  $+\frac{1}{2}$ . Altogether there are  $n$  values of  $l$  for a given value of  $n$ ,  $2l + 1$  values of  $m$  for a given value of  $l$  and thus  $2n^2$  different sets of  $l$ ,  $m$ , and  $s$ , called **quantum states**, for a given value of  $n$ . Symbols from Nineteenth Century spectroscopy notation are often used in place of the shell, subshell and orbital quantum numbers, with *the letters K, L, M, N, ... representing  $n$  values of 1, 2, 3, ..., respectively*,  *$s, p, d, f, ...$  representing  $l$  values of 0, 1, 2, 3, ..., respectively*, and  *$x, y, z$  in place of  $m$  values of  $-1, 0, +1$ , etc.* Up and down arrows are sometimes used to represent the spin quantum values, with  $\uparrow$  for  $+\frac{1}{2}$  and  $\downarrow$  for  $-\frac{1}{2}$ .<sup>10</sup> The properties of quantum numbers are summarized in Table 7.1.

<sup>10</sup> Quantum mechanics has been extended to more fundamental (or "elementary") particles, such as quarks and leptons, having additional quantized properties. Since the models are mathematically abstract, quantum



**Table 7.1 Properties of the Quantum Numbers**

Quantum Number	Name [Interpretation]	Range [Symbol]	Number of Values
n	shell [size]	1,2,... $\infty$ [K,L,M,...]	$\sum_{l=0}^{n-1} 2(2l+1) = 2n^2/\text{shell} = 2,8,18,32, \dots$
l	subshell [shape]	0,1... n-1 [s,p,d,f...]	$2(2l+1)/\text{subshell} = 2,6,10,14, \dots$
m	orbital [orientation]	-1...+1 [x,y,z,x <sup>2</sup> -y <sup>2</sup> , z <sup>2</sup> , xy, yz, xz...]	2/orbital
s	spin [direction]	-1/2, +1/2 [ $\uparrow, \downarrow$ ]	1/state

Sets of values for the four quantum numbers specify the states, or **configurations** of electrons in atoms. As with the Bohr model, the lowest energy state is called the *ground electronic state* and corresponds to the minimum set of quantum numbers  $n = 0$  and  $l = 0$  (m has only one possible value and s can have two values, which cannot be distinguished in isotropic space.) *Excited states* are higher in energy corresponding to other values of the quantum numbers. For example, the set  $\{n, l, m, s\} = \{2, 1, -1, -1/2\}$  describes the state of an electron in an excited state of hydrogen in the second shell, first subshell, -1 orbital and spin  $-1/2$ . An alternate notation for the state, or configuration of the electron would be  $2p_x \downarrow$ .

In the case of hydrogen-like atoms, wave mechanics shows that the energy of the (single) electron is determined by the shell quantum number (n) only, and *wave mechanics gives identical energies as the Bohr theory for one-electron atoms*. Thus in Bohr's quantum theory a single quantum number was sufficient to describe the major features of the hydrogen spectrum (even minor features could be accounted for by extension to elliptic orbits). Wave mechanics differs from the Bohr model in the number and interpretation of the shape of the electron orbits, however - *the classical motion of discrete particles in Bohr theory become probabilistic charge clouds in wave mechanics*. A consequence of the quantum nature of matter is that *the position and velocity of a particle cannot simultaneously be precisely known*, called the (Heisenberg) **uncertainty principle**. This explains why the initial

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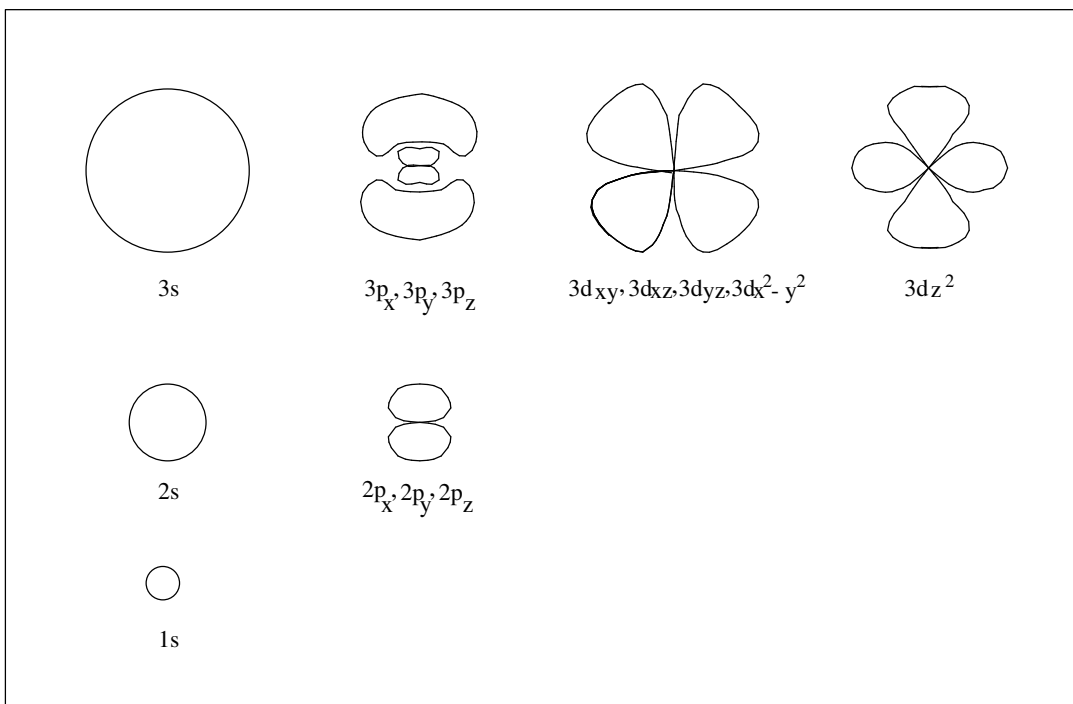
values of +1, -1 and 0 have been associated with geometric attributes like up, down and sideways, collectively called *strangeness*. More complete descriptions have added quantized properties arbitrarily named topness (or truth), bottomness (or beauty), charm, color and flavor, each having three values.

quantum value for  $n$  cannot be zero, as it would correspond to an electron at rest at the nucleus, in violation of the uncertainty principle.

For a given value of  $n$ , there are  $2n^2$  values of  $l$ ,  $m$ , and  $s$  (states), which all have the same energy called **degenerate** states in the case of hydrogen atoms in the absence of electric and magnetic fields. An **orbital**<sup>11</sup> is defined by a set of  $n$ ,  $l$  and  $m$  quantum values (ignoring the spin) and describes the spatial properties of the electron cloud. Fig. 7.8 shows cross sections of the lower energy orbitals of an hydrogen atom. The lines demark contours encompassing 99% of the orbital charge clouds (according to the interpretation of wave mechanics, charge clouds never die completely away with distance from the nucleus, but approach zero density asymptotically.) The profiles illustrate the sizes (relative to 42 Bohr radii for the hydrogen 1s orbital) and shapes of the different types of orbitals. Orbital orientations are indicated by subscripts: no subscript indicates spherical symmetry,  $x$  indicates a major (longest) axis along the  $x$  axis (and similarly for  $y$  and  $z$ ),  $xy$  and  $x^2 - y^2$  indicate major axes lying in the  $x$ - $y$  plane (and similarly for  $xz$ ,  $yz$ );  $z^2$  indicates a major axis along the  $z$  axis. The three-dimensional spatial structure of the orbitals are derived from the cross sections by rotating about the major axes of the figures.

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<sup>11</sup> Or *spatial* orbital to be distinguished from a *spin orbital*, defined by the set  $\{n,l,m,s\}$ .



**Fig. 7.8** Hydrogen Atom Atomic Orbital Profiles

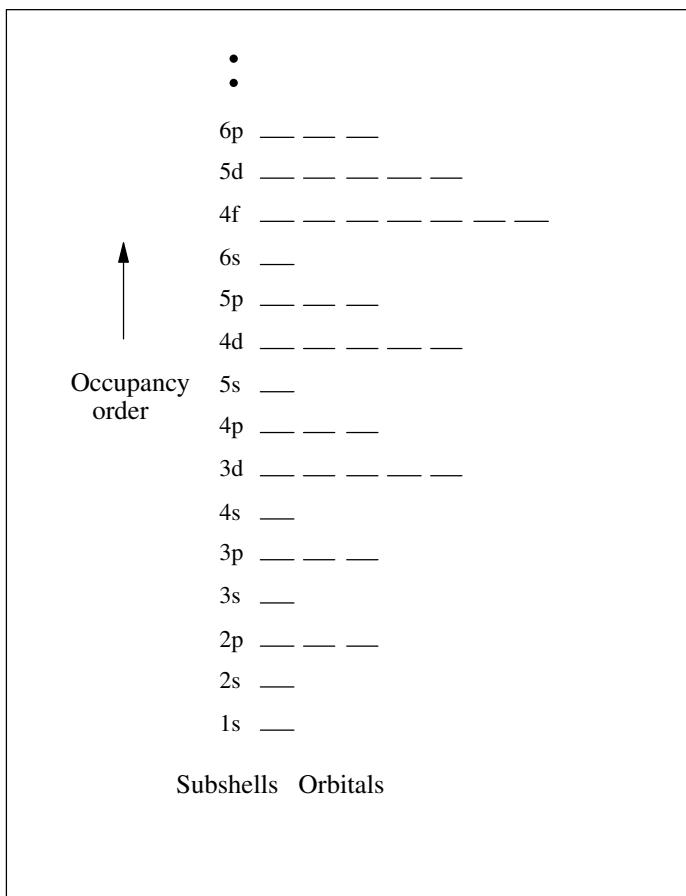
In the case of atoms with more than one electron, electron-electron interaction removes the degeneracy of the subshell ( $l$ ) quantum states, and many more energy levels appear, limited only by the range of  $l$ :  $0 \leq l < n$ . The wave nature of electrons precludes thinking of them as independent particles “occupying” orbitals. A more accurate picture is a cloud of charge of varying density in space for the whole system. Nevertheless, wave mechanical calculations show that to a first approximation, the *independent orbital occupation model* is justified, and the total atomic electronic configuration of the electrons can be approximated as a sum of individual electron configurations. This leads to a heuristic for describing the arrangement of electrons in many-electron systems.

## 7.6. Electronic Configurations

Consider the structure of a multi-electron atom in the orbital approximation. The atom contains a nucleus and some number of extra-nuclear electrons in some configuration approximated as a composite of individual electron configurations, each characterized by a set of quantum numbers. Electron interactions require that *in a multi-electron atom each electron must be in an unique state (have an unique set of quantum numbers)* (Pauli's **exclusion principle**.) *The total electronic configuration of an atom is given by the set of configurations (states, quantum numbers) for all the electrons in the atom.* The atom can be thought of as constructed from a nucleus to which the electrons are added, one at a time. This **aufbau** (building up) heuristic of electronic configurations is based on the ground state of the atom being the lowest energy state, so the *order in which the electrons are added to multi-electron systems corresponds to the ordering of increasing orbital energy states.* The order of increasing energy with quantum state has been determined by solving Schrödinger's wave equation for multi-electron atoms and agrees with experimental spectra. From this evidence, *the order of increasing energy of subshells obeys, to first approximation, the rule  $(n-3)f < (n-2)d < (n-1)p < (n)s$ , where the subshells exist according the range of  $l$  for a given  $n$  ( $l < n$ ).*<sup>12</sup> Explicitly, the order of increasing subshell energy is  $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d \dots$  This is illustrated schematically in Fig. 7.9. The vertical spacing between subshells indicates the relative ordering of the energies of the subshell electrons, but not the relative magnitudes, which tend to grow closer together with increasing subshell. In addition, as the nuclear charge of different elements increases, *all* the subshells are lowered in energy, consistent with the attraction of all the electrons to a higher nuclear charge. These trends (decreasing energy difference for a given atom and a shift to lower energies for increasing atomic charge) are described by Eq. 7.8 for one-electron atoms.

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<sup>12</sup> Occasional exceptions occur where multiple configurations are close in energy.



**Fig. 7.9** Multielectron Atomic Aufbau Energy Subshell Ordering

Further analysis of the wave equation in the orbital approximation as well as comparisons with experimental spectral show that *within each subshell, electrons occupy orbitals singly with the same value of spin quantum number (“unpaired electrons”) until all orbitals in the subshell are occupied, then additional electrons must assume the opposite spin*

quantum number, causing the electrons to “pair up” within the orbitals (**Hund’s rule**).

The number of electrons that exist in a shell, subshell or orbital is called the **occupancy** of the shell, subshell or orbital. Since there are only two values of spin quantum number, and each electron must have an unique set of quantum numbers, *the maximum occupancy of any orbital is two*. Since there are  $2l+1$  orbitals in a subshell, *the maximum occupancy of a subshell with quantum number  $l$  is  $2(2l+1)$* . Summing the maximum occupancy of subshells in a shell shows that *the maximum occupancy of a shell is  $2n^2$* . Thus the maximum occupancies of the s,  $p_x$ ,  $p_y$ ,  $p_z$ , etc. orbitals are 2, the maximum occupancies of the s, p, d, f, etc. subshells are 2, 6, 10, 14, etc, and the maximum occupancies of the K, L, M, N, etc. shells are 2, 8, 18, 32, etc. These rules are collected into the following heuristic for determining the electronic configuration of a multiple-electron system in the orbital approximation.

### The Aufbau Electronic Configuration Heuristic

**Purpose:** To construct the orbital electronic configuration of an atom or ion.

**Procedure:** Given some number of electrons in the atom or ion,

1. Add electrons to the atom in the subshell order  $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d \dots$ , with maximum occupancies for the s, p, d, f, ( $l = 0, 1, 2, \dots, n-1$ ) etc. subshells of 2, 6, 10, 14, etc.
2. Within each subshell, assign the same value of spin to up to one-half the maximum allowed occupancy of the subshell ( $2l+1$ ). Remaining electrons (up to  $2(2l+1)$  in number) are assigned the opposite value of the spin.

**Example 7.7** The electronic configuration for the lowest energy state of eight electrons is:

1.  $1s^2 2s^2 2p^4$ .
2.  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ , corresponding to  $\{n_i, l_i, m_i, s_i\}$  values in the order in which they are added:
   
 $\{1,0,0,-1/2\} \{1,0,0,+1/2\} \{2,0,0,-1/2\} \{2,0,0,+1/2\} \{2,1,-1,-1/2\} \{2,1,0,-1/2\} \{2,1,1,-1/2\}$ 
  
 $\{2,1,-1,+1/2\} \{2,1,0,+1/2\}$ .

Note how the  $2p_y$  ( $\{2,1,-1\}$ ) and  $2p_z$  ( $\{2,1,0\}$ ) orbitals are unfilled with unpaired electrons, while the  $2p_x$  ( $\{2,1,+1\}$ ) orbital is filled with two paired electrons. Unpaired electrons are attracted to magnetic fields, a phenomenon called **paramagnetism**, so species containing unpaired electrons can be easily detected experimentally. Species with all electrons paired are not attracted to magnets and are called **diamagnetic**. In the absence of an external field, any atom (containing paired or unpaired electrons) does not orient in any particular direction, and the selection of which p orbital to be doubly occupied ( $p_x$ ,  $p_y$  or  $p_z$ ) is arbitrary. Note also that this electronic configuration is for eight electrons, independent of the number of protons. Thus it would be the ground state electronic configuration for a neutral oxygen atom (with 8 protons and 8 electrons), or a  $N^-$  anion (with 7 protons with 8 electrons), or a  $F^+$  cation (with 9 protons with 8 electrons), etc. Species with identical electronic configurations are said to be **isoelectronic** (Greek *iso* for equal).

**Example 7.8** The electronic configuration for Cu ( $Z = 29 =$  number of electrons), which follows Ar in the Periodic Table, happens to be  $[Ar]3d^{10}4s^1$ , not  $[Ar]3d^94s^2$ . This exception is due to the added stability of one filled and one half-filled subshell over one filled subshell. However, the two electronic states are quite close in energy, and both are paramagnetic. Two ionic states are observed in chemical compounds of copper,  $Cu^+$  and  $Cu^{2+}$ , corresponding to removing the outer shell electrons of the two close ground state configurations. (Which ionic state is paramagnetic?)

The aufbau heuristic only summarizes detailed knowledge of electronic configurations. Experiments and complex calculations provide the details. Electrons in atoms are not independent particles but community members of a complex electronic structure. Nevertheless, the orbital model is supported by experimental *photoelectron emission spectra*. Electrons can be ejected from independent gas atoms by high-energy photons, analogous to the emission of electrons from active metals by ultraviolet light. The observed energy differences between the bombarding photons and the kinetic energies of the emitted electrons measures the energies absorbed when the atoms are ionized.

**Example 7.9** According to the Aufbau Heuristic, oxygen atoms have the electronic configuration  $1s^22s^22p^4$ . The photoelectron spectrum shows photons are absorbed at 51,500, 2370 and 830 kJ/mol, corresponding to ionization from the 1s subshell, 2s subshell, and 2p subshell of the atoms.

Note the order of magnitude increase in binding energy of the inner-shell electron over that of the outer shell, supporting a shell model of electronic structure and suggesting a

distinction between the behavior of tightly-bound inner-shell electrons and the more energetically accessible outer-shell electrons. This consideration plays an important role in chemical bonding (Chapter 12).

### *Summary*

Elements are the simplest form of chemical matter and are distinguished by the number of protons in their atoms, called atomic number. Isotopes of an element have nearly identical chemical properties but different mass and are distinguished by the number of neutrons in their atoms.

The electrons in atoms determine their chemical properties, and obey the laws of quantum mechanics, which determine their energies and spatial arrangements. The electronic configuration of an atom describes the number and arrangement of the electrons in space in terms of occupancy of quantum orbitals, grouped into quantum subshells and shells.

Chemists have enjoyed a love/hate relationship with wave mechanics. On the one hand, the theory can reproduce experimental results as precisely as they can be measured. On the other hand, the mathematical complexity of wave mechanics increases significantly with the number of subatomic particles involved. To work around the computational barrier, chemists have developed qualitative and semi-quantitative heuristics (models) which approximate the results of the exact calculations. Although exact theoretical results for many-electron systems are complicated and difficult to obtain, the simple aufbau heuristic, based on the theory of the hydrogen atom explains the basic properties of chemical atoms in terms of electronic structure.



### Appendix: The Bohr Atom Model

The Bohr model of the one electron atom as a quantized planetary system is based on the laws of classical mechanics, electricity and one assumption. It is straightforward to arrive at the results using only algebra. The situation is described pictorially in Fig. 7.4.

We begin by equating Coulomb's force of attraction between two charged particles (nucleus of charge  $Z$  and electron of charge  $e$  and reduced mass  $\mu$ ) (Section 5.2) to the Newton's centrifugal force of bodies (electron and nucleus) orbiting with velocity  $v$  at distance  $r$  (Section 5.4):

$$-\frac{Ze^2}{r^2} = -\frac{\mu v^2}{r} \quad (7A.1)$$

which yields by clearing fractions

$$\mu v^2 r = Ze^2 \quad (7A.2)$$

The bohr velocity equation comes from an assumption that the angular momentum ( $\mu v r$ ) is *quantized*, that is, proportional to Planck's constant by a quantum number  $n = 1, 2, \dots$

$$\mu v r = \frac{n h}{2\pi} \quad (7A.3)$$

Dividing Eq. (7A.1) by Eq. (7A.2) gives

$$v = \frac{2\pi Z e^2}{n h} \quad (7A.4)$$

Substituting the value of  $v$  into Eq. (7A.2) and solving for  $r$  produces

$$r = \frac{1}{Z} \mu \left( \frac{n h}{2\pi e} \right)^2 \quad (7A.5)$$

The Bohr total energy results from summing classical expressions for kinetic and Coulombic potential energy and substituting the value of  $r$  from Eq. (7A.5):

$$E = \frac{1}{2} \mu v^2 - \frac{Ze^2}{r} = -\frac{Ze^2}{r} = -\frac{2\pi^2 \mu Z^2 e^4}{h^2 n^2} \quad (7A.6)$$

**STRUCTURE OF MATTER EXERCISES**

1. Mass spectrometric measurements of chlorine show two isotopes of mass 34.969 and 36.967, in an abundance ratio of 3.1271 to 1. What is the average atomic mass of chlorine?
2. How many electrons does  $\text{H}^+$  have?
3. How many protons and electrons has  $\text{Na}^+$ ?
4. What is the energy of an ultraviolet photon?
5. What is the velocity of an electron in the first Bohr orbit?
6. What is the electronic configuration in letter symbols corresponding to the set  $\{n, l, m, s\} = \{4, 0, 0, 1/2\}$ ?
7. Write the electronic configuration for the  $\text{Pb}^{2+}$  ion.
8. Discuss the relative sizes of  $\text{S}^{2-}$ ,  $\text{Cl}^-$ , Ar,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ .

**STRUCTURE OF MATTER EXERCISE HINTS**

1. The sum of the abundances must total 100%.
2. Start by finding the atomic number of hydrogen.
3. Does sodium gain charge by *gaining* or *losing* electrons?
4. Ultraviolet light has wavelengths shorter than the shortest visible light, which ranges between about 400 nm and 700 nm.
5. Bohr could work this problem.
6. Look up the letter equivalents to quantum numbers.
7. First compute the number of electrons in  $\text{Pb}^{2+}$ .
8. Write the electronic configuration for each species.

