Electronic Structure of Atoms

1

1.1 Introduction

In this chapter the electronic structure of single atoms will be discussed. A few quantum concepts will be introduced, as they are necessary for the understanding of many aspects in solid-state physics and device applications.

In Chap. 1, we saw that matter was composed of atoms in the periodic table shown in Fig. 1.2. Until 1911, atoms were considered the simplest constituents of matter. In 1911, it was discovered that atoms had a structure of their own and Rutherford proposed the nuclear model of the atom in which almost all the mass of the atom is concentrated in a positively charged nucleus and a number of negatively charged electrons are spread around the nucleus. It was later found that the nucleus is itself made up of protons (positively charged) and neutrons (neutrally charged). The number of protons is the atomic number (Z) while the total number of protons and neutrons is the mass number of the element. Apart from the electrostatic repulsion between nuclei, all of the major interactions between atoms in normal chemical reactions (or in the structures of elemental and compound substances) involve electrons. It is therefore necessary to understand the electronic structure of atoms. The term electronic structure, (or configuration) when used with respect to an atom, refers to the number and the distribution of electrons about the central nucleus.

The following discussion traces the steps of the scientific community toward a description of the electronic structure of atoms. The reader should not be stopped by the new concepts that arise from this discussion, because they will become clearer after understanding the quantum mechanics presented in Chap. 4.

Much of the experimental work on the electronic structure of atoms done prior to 1913 involved measuring the frequencies of electromagnetic radiation (e.g., light) that are absorbed or emitted by atoms. It was discovered that atoms absorbed or emitted only certain, sharply defined frequencies of electromagnetic radiation. These frequencies were also found to be characteristic of each particular element in the periodic table. And the absorption or emission spectra, i.e., the ensemble of

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frequencies, were more complex for heavier elements. Before being able to understand the electronic structures of atoms, it was natural to start studying the simplest atom of all, the hydrogen atom, which consists of one proton and one electron.

1.2 Spectroscopic Emission lines and Atomic Structure of Hydrogen

It was experimentally observed that the frequencies of light emission from atomic hydrogen could be classified into several series. Within each series, the frequencies become increasingly closely spaced, until they converge to a limiting value. Rydberg proposed a mathematical fit to the observed experimental frequencies, which was later confirmed theoretically:

$$\frac{\upsilon}{c} = \frac{1}{\lambda} = Ry\left(\frac{1}{n^2} - \frac{1}{(n')^2}\right) \tag{1.1a}$$

with $n = 1, 2, 3, 4,...$ and $n' = (n + 1), (n + 2), (n + 3),...$

In this expression, λ is the wavelength of the light (in units of distance, and typically cm in this expression), υ is the frequency of the light emitted, c ($c = 2.99792 \times 10^8$ m·s^{-1} = 2.99792×10^{10} cm·s^{-1}) is the velocity of light in vacuum, and Ry is the fit constant, called the Rydberg constant, and was calculated to be 109,678 cm^{-1}. n is an integer, corresponding to each of the series mentioned above. n' is also an integer, larger than or equal to $(n + 1)$, showing that the frequencies become more closely spaced as n' increases.

The energy of the electromagnetic radiation is related to its wavelength and frequency by the following relation:

$$E = \frac{hc}{\lambda} = h\upsilon \tag{1.1b}$$

where h ($h = 6.62617 \times 10^{-34}$ J·s) is Planck's constant. The SI (Système International, or International System) unit for energy is the Joule (J). However, in solid-state physics, it is common to use another unit: the electron volt (eV) which is equal to 1.60218×10^{-19} J. The reason for this new unit will become clear later in the text and reflects the importance of the electron in solid-state physics.

The expression in Eq. (1.1a) shows that the emission of light from the hydrogen atom occurs at specific discrete values of frequencies ν, depending on the values of integers n and n'. The Lyman series of spectral lines corresponds to $n = 1$ for which the convergence limit is 109,678 cm^{-1}. The Balmer series corresponds to $n = 2$, and the Paschen series to $n = 3$. These are illustrated in Fig. 1.1, where the energy of the light emitted from the atom of hydrogen is plotted as arrows.

Although the absorption and emission lines for most of the elements were known before the turn of the twentieth century, a suitable explanation was not available, even for the simplest case of the hydrogen atom. Prior to 1913, the explanation for

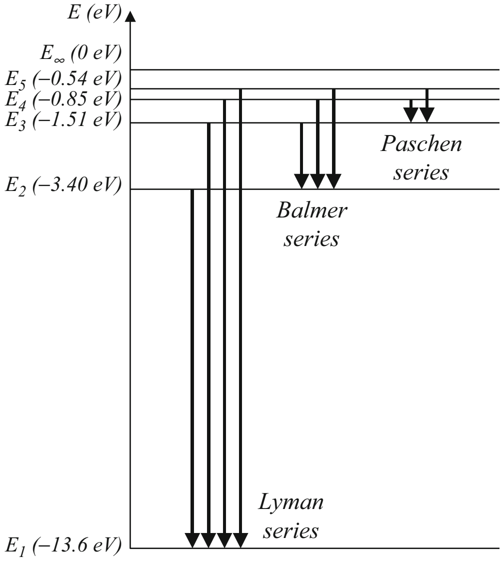


Fig. 1.1 Energies of the light emitted from the hydrogen atom (shown by arrows). The Lyman series corresponds to $n = 1$ in Eq. (1.1a), the Balmer series corresponds to $n = 2$, and the Paschen series corresponds to $n = 3$

this spectroscopic data was impossible because it contradicted the laws of nature known at the time. Indeed, very well-established electrodynamics could not explain two basic facts: that atoms could exist at all and that discrete frequencies of light were emitted and absorbed by atoms. For example, it was known that an accelerating charged particle had to emit electromagnetic radiation. Therefore, in the nuclear model of an atom, an electron moving around the nucleus has acceleration and thus has to emit light, lose energy, and fall down to the nucleus. This meant that the stability of elements in the periodic table, which is obvious to us, contradicted classical electrodynamics. A new approach had to be followed in order to resolve this contradiction, which resulted in a new theory, known as quantum mechanics. Quantum mechanics could also explain the spectroscopic data mentioned above and adequately describe experiments in modern physics that involve electrons and atoms and ultimately solid-state device physics.

Niels Bohr first explained the atomic absorption and emission spectra in 1913. His reasoning was based on the following assumptions, which cannot be justified within classical electrodynamics:

1. Stable orbits (states with energy E_n) exist for an electron in an atom. While in one of these orbits, an electron does not emit any electromagnetic radiation. An individual electron can only exist in one of these orbits at a time and thus has an energy E_n.
2. The transition of an electron from an atomic orbit of energy state E_n to that of energy state $E_{n'}$ corresponds to the emission ($E_n > E_{n'}$) or absorption ($E_n < E_{n'}$) of electromagnetic radiation with an energy $|E_n - E_{n'}|$ or frequency $\upsilon = \frac{|E_n - E_{n'}|}{h}$.

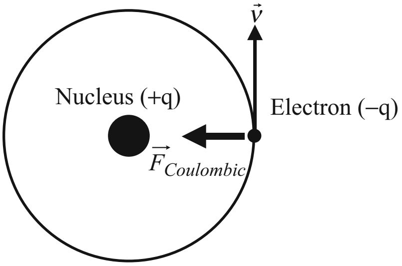


Fig. 1.2 Schematic diagram showing the electron orbit, the attractive coulombic force between the positively charged nucleus and the orbiting negatively charged electron, and the velocity of the electron which is always tangential to its circular orbit

With Sommerfeld, Bohr implemented these postulates into a simple theory. Assumption (1) of stable orbits meant that the values of angular momentum L and thus the electron orbit radius $\vec{r}$ were quantized, i.e., integer multiples of a constant. For the simple hydrogen atom with a circular electron orbit, the Bohr postulate (1) can be expressed mathematically in the following manner:

$$L_n = m\nu r_n = n\frac{h}{2\pi}, \quad n = 1, 2, \ldots \tag{1.2a}$$

where m is the mass of the electron, ν is the linear electron velocity, and n is an integer expressing the quantization and used to index the electron orbits. Since the orbit is circular, the electron experiences a centripetal acceleration ν^2/r_n. The coulombic force between the electron and nucleus provides this acceleration, as illustrated in Fig. 1.2.

Therefore, according to Newton's second law, equating Coulomb force with the mass times the centripetal acceleration, we can write:

$$\frac{q^2}{4\pi\varepsilon_0 r_n^2} = \left|\vec{F}_{\text{coulombic}}\right| = \frac{m\nu^2}{r_\text{n}} \tag{1.2b}$$

where ε_0 ($\varepsilon_0 = 8.85418 \times 10^{-12}$ F·m^{-1}) is the permittivity of free space and q ($q = 1.60218 \times 10^{-19}$ C) is the elementary charge.

Combining Eqs. (1.2a and 1.2b), one obtains the discrete radius of an electron orbit:

$$r_n = \frac{\varepsilon_0 n^2 h^2}{\pi m q^2} \tag{1.3}$$

The total electron energy E_n in the various orbits is the sum of the kinetic and (coulombic) potential energies of the electron in the particular orbit:

$$E_n = \frac{1}{2}\frac{q^2}{4\pi\varepsilon_0 r_n} - \frac{q^2}{4\pi\varepsilon_0 r_n} = -\frac{1}{8}\frac{q^2}{\pi\varepsilon_0 r_n} \tag{1.4}$$

With Eq. (1.3) we finally have:

$$E_\text{n} = \frac{-m\,q^4}{8\,(\varepsilon_0 n\,h)^2} = -\frac{13.6}{n^2} \text{ in units of electron} - \text{volts (eV)} \tag{1.5}$$

This theory thus provided an explanation for each series of spectroscopic lines in the emission spectrum from atomic hydrogen as shown in Fig. 1.1. An electron has the lowest (i.e., most negative) energy when it is in the orbit $n = 1$. The radius of this orbit can be calculated using Eq. (1.3) and is $a_0 = 0.52917$ Å. If an electron is excited to an orbit with higher energy ($n' \geq 2$) and returns to the ground state ($n = 1$), electromagnetic radiation with the frequency $c \times Ry\left[\left(\frac{1}{1^2}\right) - \left(\frac{1}{n'^2}\right)\right]$ is emitted, where c is the velocity of light in vacuum and Ry the Rydberg constant. In this case, the Lyman series of spectroscopic lines in Fig. 1.1 is observed. The other series arise when the electron drops from higher levels to the levels with $n = 2$ (Balmer series) and $n = 3$ (Paschen series), as shown in Fig. 1.1. Therefore, the Bohr-Sommerfeld theory could accurately interpret the observed, discrete absorption/emission frequencies in the hydrogen atom. Despite its success for the hydrogen atom, this theory still had to be improved for a number of reasons. One major reason was that it could not successfully interpret the spectroscopic data for atoms more complex than hydrogen. However, the results of Bohr's model can be extended to other structures similar to the hydrogen atom, called hydrogenoid systems. For example, the energy levels of several ionized atoms that have only a single electron (e.g., He^+ or Li^{++}) can be easily predicted by substituting the nuclear charge q of Bohr's model with Zq where Z is the atomic number.

The simple picture developed by Niels Bohr for electrons in atoms was among the first attempts to explain experimental data with assumptions based on the discrete (or quantum) nature of the electromagnetic field.

A typical example of the interaction between an electromagnetic field and matter is a blackbody, which is an ideal radiator of electromagnetic radiation. Using classical arguments, Rayleigh and Jeans tried to explain the observed blackbody spectral irradiance, which is the power radiated per unit area per unit wavelength, shown in Fig. 1.3. However, as can be seen in the figure, their theoretical predictions could only fit the data at longer wavelengths. In addition, their results also indicated that the total irradiated energy (integral of the irradiance over all the possible wavelengths) should be infinite, a fact that was in clear contradiction with experiment. In 1901, Max Planck provided a revolutionary explanation based on the hypothesis that the interaction between atoms and the electromagnetic field could only occur in discrete packets of energy, thus showing that the classical view that always allows a continuum of energies was incorrect. Based on these ideas, a more sophisticated and self-consistent theory was created in 1920 and is now called quantum mechanics (see Chap. 4 for more details).

1.3 Atomic Orbitals

Bohr's model solved the problem of the energy levels in the hydrogen atom but had several drawbacks: it could neither explain some of the other properties of hydrogen atoms nor correctly predict the energy levels of more complex atoms. In addition, a few years later, new experiments pointed out that particles could behave as waves,

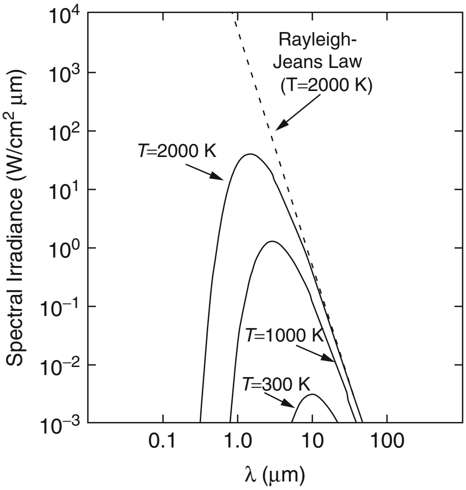


Fig. 1.3 Spectral irradiance of a blackbody at different temperatures. When the temperature is at or below room temperature, the radiation is mostly in the infrared spectral region, undetectable by the human eye. When the temperature is raised, the emission power increases and its peak shifts toward shorter wavelengths. One of the more successful interpretations, yet inaccurate because it was based on classical mechanics, was conducted by Rayleigh and Jeans but could only fit the experimental data at longer wavelengths

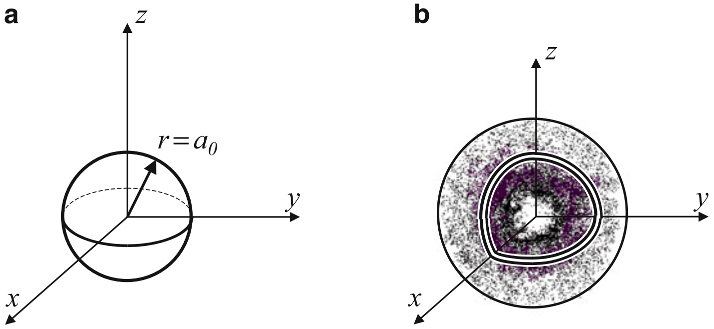


Fig. 1.4 (**a**) The precise spherical orbit of an electron in the first Bohr orbit, for which the radius is $a_0 = 0.52917$ Å, as calculated by Bohr's model. (**b**) The electron probability density pattern for the comparable atomic orbital using a quantum mechanical model. The darker areas indicate a higher probability of finding the electron at that location. The center cutout shows the interior of the orbital. The outer sphere delineates the region where the electron exists 90% of the time

and therefore their position could not be determined exactly. In Bohr's model, the radius of the first Bohr orbit in the hydrogen atom was calculated to be exactly $a_0 = 0.52917$ Å (Angstrom, abbreviated as Å, is equal to 10^{-10} m). This distance is a constant called the Bohr radius and is shown in Fig. 1.4a as a spherical surface with radius a_o.

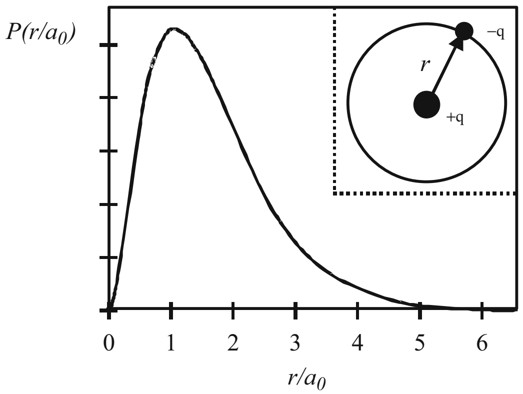


Fig. 1.5 The electron radial probability density function $P(r/a_0)$, which describes the probability of finding an electron in a spherical surface at a distance r from the nucleus in the hydrogen atom (for $n = 1$). This probability has a maximum value when the electron is at a distance equal to the Bohr radius: $r = a_0$

A new approach was clearly needed in order to describe matter on the atomic scale. This new approach was elaborated during the next decade and is now called quantum mechanics. In quantum mechanics an electron cannot be visualized as a point particle orbiting with a definite radius, but rather as a delocalized cloud with inhomogeneous probability density around a nucleus as illustrated in Fig. 1.4b. The probability density gives the probability of finding the electron at a particular point in space. In this picture, the Bohr radius can be interpreted as the radius a_0 of the spherical surface where the maximum in the electron probability distribution occurs or, in other words, the spherical orbit where the electron is most likely to be found. This can be further illustrated by Fig. 1.5 where the electron probability density function $P(r)$, which is the probability to find an electron at a distance r from the nuclei, is plotted as a function of r (for the lowest energy state of hydrogen atom $n = 1$). This function reaches its maximum at the value of Bohr's first orbit a_0.

We saw earlier that there were several stable orbits for an electron in the hydrogen atom which are distinguished by the energy given in Eq. (1.5). The orbit or energy is not enough to characterize the properties of an electron in an atom. The spatial shape and direction of the orbit are also important, as it is not always spherical, and so the term "orbital" is employed. Each orbital is assigned a unique set of quantum numbers, which completely specifies the orbital's properties. The orbital designation and its corresponding set of three quantum numbers n, l, and m_l are listed in Table 1.1 along with the electron spin quantum number m_s.

The principal quantum number n may take integral values from 1 to ∞, although values larger than 7 are spectroscopically and chemically unimportant. It is the value of this quantum number n that determines the size and energy of the principal orbitals. Orbitals with the same n are often called "shells."

For a given value of n, the angular momentum quantum number l may take integer values within $[0, 1, 2, 3, \ldots, (n-1)]$. It is this quantum number that determines the shape of the orbital. A letter designation is used for each orbital shape: s for $(l = 0)$, p for $(l = 1)$, d for $(l = 2)$, f for $(l = 3)$, etc. followed alphabetically by the letter designations g, h, and so on.

Table 1.1 Quantum numbers and atomic orbital designations for electrons in the four lowest values of *n*. When *n* increases, the scheme continues to develop with the same basic rules

Orbital	n	l	m_l	m_s
1 *s*	1	0	0	–½, +½
2 *s*	2	0	0	–½, +½
2*p*	2	1	−1, 0, +1	–½, +½
3 *s*	3	0	0	–½, +½
3*p*	3	1	−1, 0, +1	–½, +½
3*d*	3	2	−2, −1, 0, +1, +2	–½, +½
4 *s*	4	0	0	–½, +½
4*p*	4	1	−1, 0, +1	–½, +½
4*d*	4	2	−2, −1, 0, +1, +2	–½, +½
4*f*	4	3	−3, −2, −1, 0, +1, +2, +3	–½, +½

Finally, for a given orbital shape (i.e., a given value of l), the magnetic quantum number m_l may take integral values from $-l$ to $+l$. This quantum number governs the orientation of the orbital. Once an electron is placed into one specific orbital, its values for the three quantum numbers n, l, and m_l are known.

A fourth quantum number is needed to uniquely identify an electron in an orbital, the spin quantum number. The spin quantum number is independent of the orbital quantum numbers and can only have two opposite values: $m_s = \pm\frac{1}{2}$ (in units of $\frac{h}{2\pi}$). Electrons that differ only in their spin value can only be distinguished in the presence of an external magnetic field.

1.4 Structures of Atoms with Many Electrons

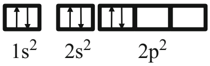
In multi-electron atoms, the energy of an electron depends on the orbital principal quantum number n and the orbital momentum quantum number l, i.e., whether the electron is in an *s*, *p*, *d*, or *f* state. The different m_l quantum numbers for a fixed set of n and l are degenerate (they have the same energy). The electronic configurations of such atoms are built up from the ground state energy, filling the lowest energy orbitals first. Then, the filling of the orbitals occurs in a way such that no two electrons may have the same set of quantum numbers. This rule governing electron quantum numbers is called the Pauli exclusion principle. If two electrons occupy the same orbital, they must have opposite spins: $m_s = +½$ for one electron and $m_s = -½$ for the other electron. Because the spin quantum number m_s can take only these two values, an orbital with given (n, l, m) can be occupied by at most two electrons.

One more rule, called Hund's rule, governs the electron configuration in multi-electron atoms: for a given principal quantum number n, the lowest energy electron configuration has the greatest possible sum of spin values and greatest sum of orbital momentum values.

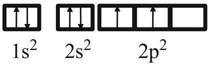
Example

Q Hund's rule says that the electrons occupy orbitals in such a way that, first, the total spin number ($\sum m_s$) is maximized and then the total orbital momentum is maximized ($\sum l$). Determine the electronic configuration, including the spin, of the carbon atom, which has six electrons in its ground state.

A Carbon has six electrons and has the electronic configuration $1s^2 2s^2 2p^2$. The last two electrons in the p shell can have spins +½ or –½. To maximize the total spin number, both electrons must have their spin up, so that $\sum m_s = 1$, as shown below.



Incorrect



Correct

Both the Pauli exclusion principle and Hund's rule govern the electron configurations of atoms in the periodic table in their unexcited state, which is also called the ground state. Other electronic configurations are possible when the atom is in an excited state as a result of an external force such as an electric field.

Examples of the ground state electron configurations in a number of elements are shown below. The sequence for $Z = 1$ to $Z = 18$ is built in a straightforward and logical manner, by filling the allowed s, p, d... orbitals successively (i.e., in this order). For $Z = 19$, the first deviation to this procedure occurs: the 4s orbitals are filled with electrons *before* the 3d orbitals. Elements in the periodic table with partially filled 3d orbitals are usually transition metals and the electrons in these 3d orbitals contribute to the magnetic properties of these elements. For example, the electronic configuration of the Ga element can be read as follows: two s-electrons in orbit 1, two s-electrons in orbit 2, six p-electrons in orbit 2, two s-electrons in orbit 3, six p-electrons in orbit 3, two s-electrons in orbit 4, ten d-electrons in orbit 3, and one p-electron in orbit 4.

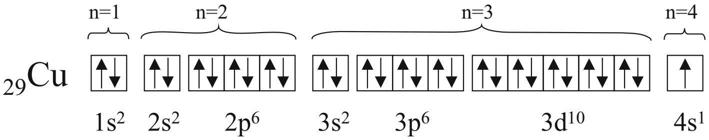
$Z = 3$Li $1s^2 2s^1$
$Z = 4$Be $1s^2 2s^2$
$Z = 5$B $1s^2 2s^2 2p^1$
$Z = 6$C $1s^2 2s^2 2p^2$
$Z = 7$N $1s^2 2s^2 2p^3$
$Z = 8$O $1s^2 2s^2 2p^4$
$Z = 9$F $1s^2 2s^2 2p^5$
$Z = 10$Ne $1s^2 2s^2 2p^6$
... ...
$Z = 31$Ga $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

Example

Q Determine the electronic configuration for copper (element Cu, atomic number $Z = 29$ in the ground state).

A There are 29 electrons in copper in its ground state. It has an inner Ar shell, which has 18 electrons: [Ar] = $1s^2 2s^2 2p^6 3s^2 3p^6$. The remaining 11 electrons must be distributed inside the 3d and 4s orbitals. Suppose that the two possible configurations are [Ar]$3d^94s^2$ and [Ar]$3d^{10}4s^1$. According to Hund's rule, the lowest energy configuration, corresponding to the ground state, is such that it presents the greatest possible spin value and greatest orbital momentum. The two configurations above have the same spin but the second one has greater orbital momentum. Since the orbital quantum number for the *s* orbital is 0 and for *d* is 2, we can say that Cu exhibits the second electronic configuration:

[Ar]$3d^{10}4s^1$ or $1s^22s^22p^63s^23p^63d^{10}4s^1$ which is illustrated below:



Quantum mechanics is able to predict the energy levels of the hydrogen atom, but the calculations become too complex for atoms with two or more electrons. In multi-electron atoms, the electric field experienced by the outer shell electrons does not correspond to the electric field from the entire positive nuclear charge because other electrons in inner shells screen this electric field from the nucleus. This is why outer shell electrons do not experience a full nuclear charge *Z* (the atomic number), but rather an effective charge Z^* which is lower than *Z*. Values of the effective nuclear charge Z^* for the first ten elements are listed in Table 1.2. Therefore, the energy levels of these outer shell electrons can be estimated using the results from the hydrogen atom and substituting the full nuclear charge Zq with Z^*q.

Let us consider an example of electronic configuration in the multi-electron atom of Si. As shown in Fig. 1.6, 10 of the 14 Si-atom electrons (2 in the 1*s* orbital, 2 in the 2*s* orbital, and 6 in the 2*p* orbital) occupy very low energy levels and are tightly bound to the nucleus of the atom. The binding is so strong that these ten electrons remain essentially unperturbed during most chemical reactions or atom-atom

Table 1.2 The full nuclear charge Z and effective nuclear charge Z^* for the first ten elements

Element	Z	Z^*
H	1	1.00
He	2	1.65
Li	3	1.30
Be	4	1.95
B	5	2.60
C	6	3.25
N	7	3.90
O	8	4.55
F	9	5.20
Ne	10	5.85

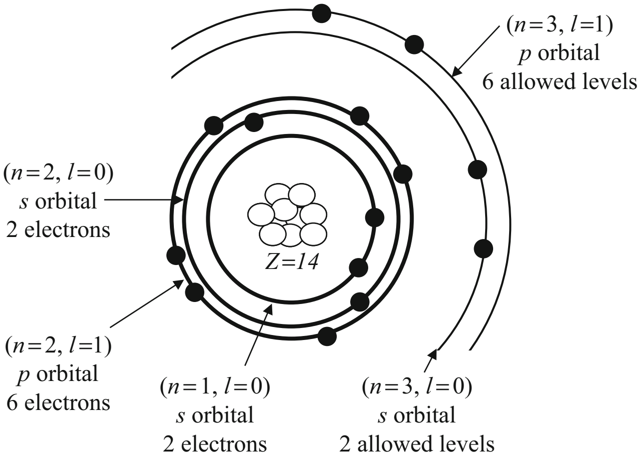
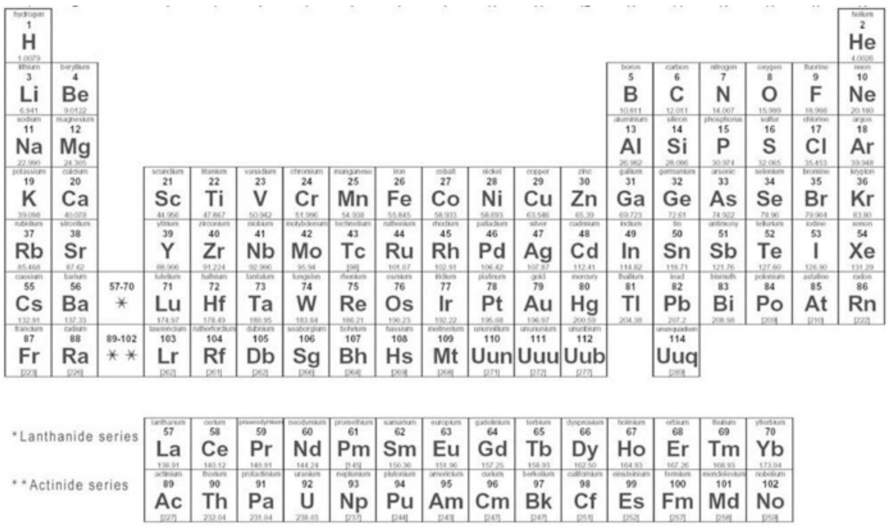


Fig. 1.6 Electron configuration for electrons in a Si atom. The ten electrons in the core orbitals, 1s ($n = 1$), 2*s* ($n = 2$, $l = 0$), and 2*p* ($n = 2$, $l = 1$) are tightly bound to the nucleus. The remaining four electrons in the 3*s* ($n = 3$, $l = 0$) and 3*p* ($n = 3$, $l = 1$) orbitals are weakly bound

interactions. The combination of the ten-electron-plus-nucleus is often being referred to as the "core" of the atom. On the other hand, the remaining four Si-atom electrons are rather weakly bound and are called the valence electrons because of their strong participation in chemical reactions. Valence electrons are those in the outermost occupied atomic orbital. As emphasized in Fig. 1.6, the four valence electrons occupy four of the eight allowed states belonging to the 3*s* and 3*p* orbitals.

The electronic configuration in the 32-electron Ge-atom (germanium being the next elemental semiconductor in column IV of the periodic table) is essentially identical to the Si-atom configuration except that the Ge-core contains 28 electrons.



1 H																		2 He
3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-70 *	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-102 * *	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub		114 Uuq				

*Lanthanide series	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
* *Actinide series	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

1.5 Bonds in Solids

1.5.1 General Principles

When two atoms are brought very close together, the valence electrons interact with each other and with the neighbor's positively charged nucleus. As a result, a bond between the two atoms forms, producing, for example, a molecule. The formation of a stable bond means that the energy of the system of two atoms kept together must be less than that of the system of two atoms kept apart, so that the formation of the pair or the molecule is energetically favorable. Let us view the formation of a bond in more detail.

As the two atoms approach each other, they are under attractive and repulsive forces from each other as a result of mutual electrostatic interactions. At most distances, the attractive force dominates over the repulsive force. However, when the atoms are so close that the individual electron shells overlap, there is very strong proton-to-proton shell repulsion, called core repulsion, that dominates. Figure 1.7 shows the interatomic interaction energy as a function of the distance between atoms r. The system has zero energy when the atoms are infinitely far apart. A negative value corresponds to an attractive interaction, while a positive value stands for a repulsive one. The resulting interaction is the sum of the two and has a minimum at an equilibrium distance, which is reached when the attractive force balances the repulsive force. This equilibrium distance is called the equilibrium separation and is

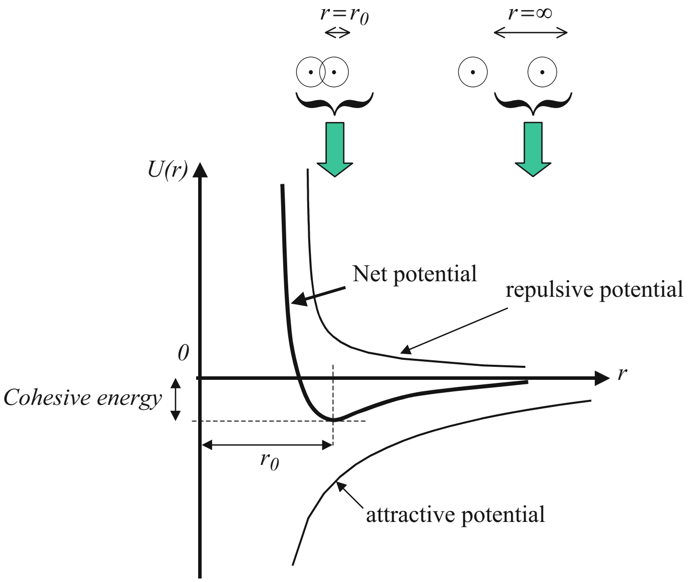


Fig. 1.7 Potential energy versus interatomic separation r. The net potential is the sum of repulsive and attractive components. The minimum of the net potential corresponds to the equilibrium distance r_0 between the two atoms

effectively the bond length. The energy required to separate the two atoms represents the cohesive energy or bond formation energy or simply bond energy (also shown in Fig. 1.7).

Similar arguments also apply to bonding between many more atoms, such as the billions of atoms found in a typical macroscopic solid. Even in the presence of many interacting atoms in a solid, we can still identify a general potential energy curve $U(r)$ per atom similar to the one shown in Fig. 1.7. Although the actual details will change from material to material, the general concepts of bond energy U_0 per atom and equilibrium interatomic separation will still be valid. These characteristics determine many properties of solids such as the thermal expansion coefficient and elastic modulus.

Example

Q For a face-centered cubic lattice, such as in an inert gas turned solid at low temperature, the potential energy can be expressed as:

$$U = N\left[12.13\left(\frac{\sigma}{r}\right)^{12} - 14.45\left(\frac{\sigma}{r}\right)^{6}\right],$$

where r is the distance between nearest neighbors and σ is a constant of the crystal. Determine the lattice constant a of the lattice in terms of σ.

A The equilibrium distance r is given by the minimum of the potential energy, which can be calculated by taking the derivative of the function U with respect to r and setting it equal to zero:

$$\frac{dU}{dr} = N\left[-145.56\frac{\sigma^{12}}{r^{13}} + 86.7\frac{\sigma^{6}}{r^{7}}\right] = 0$$

which yields $r = 1.09\sigma$. Since we are considering a face-centered cubic lattice, the nearest neighbor distance is such that $r = \frac{\sqrt{2}}{2}a$. Therefore, the lattice constant is $a = 1.54\sigma$.

1.5.2 Ionic Bonds

When one atom completely loses a valence electron so that the outer shell of a neighboring atom becomes completely filled, a bond is formed which is called ionic bond. The coulombic attraction between the now ionized atoms causes the ionic bonding. NaCl salt is a classic (and familiar) example of a solid in which the atoms are held together by ionic bonding. Ionic bonding is frequently found in materials that normally have a metal and a nonmetal as the constituent elements. For example, Fig. 1.8 illustrates the NaCl structure with valence electrons shifted from Na atoms to Cl atoms forming negative Cl^- ions and positive Na^+ ions. The physical structure of the NaCl crystal is shown in Fig. 1.9.

Ionic bonds generally have bond energies on the order of a few eV. The energy required to take solid NaCl apart into individual Na and Cl atoms is the cohesive energy, which is 3.15 eV per atom. The attractive part of Fig. 1.7 can be estimated from the sum of the coulombic potential energies between the ions (see Problem 11).

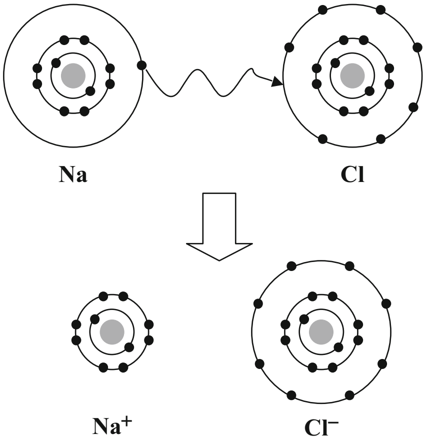


Fig. 1.8 Schematic illustration of the formation of an ionic bond in NaCl, showing the electron transfer between the two elements and their final electronic configurations

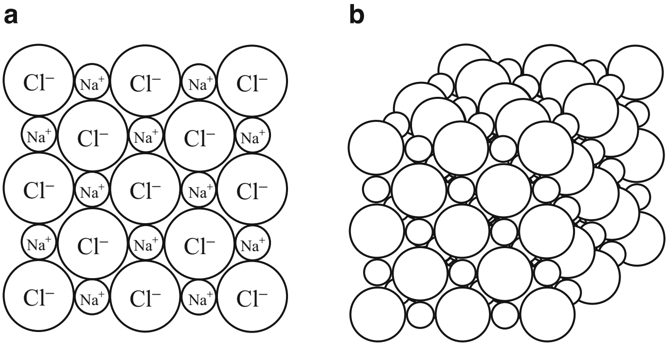


Fig. 1.9 (**a**) A schematic illustration of a cross-section from solid NaCl. Solid NaCl is made from Cl^- and Na^+ ions arranged alternatively, so that the oppositely charged ions are closest to each other and attract each other. There are also repulsive forces between the like-ions. In equilibrium, the net force acting on any ion is zero. (**b**) 3D illustration of solid NaCl

Example

Q Calculate the total coulombic potential energy of a Cs^+ ion in a CsCl crystal by only considering the nearest neighbors of Cs^+.

A In the cubic unit cell shown in Fig. 1.9, one can see that one Cs^+ ion (at the center of the cube) has eight nearest Cl^- neighbors (at the corners of the cube). Since the lattice constant for CsCl is $a = 4.11$ Å, the distance between a Cs^+ and one of its Cl^- neighbors is $r_{nn} = \frac{\sqrt{3}}{2}a = 3.56$ Å. The coulombic potential energy is thus $E = -8\frac{q^2}{4\pi\varepsilon_0 r_{nn}} = -32.36$ eV.

Many other solids consisting of metal-nonmetal elements also have ionic bonds. They are called ionic crystals and, by virtue of their ionic bonding characteristics, share many similar physical properties. For example, LiF, MgO (magnesia), CsCl, and ZnS are all ionic crystals; they are strong, brittle materials with high melting temperatures compared to metals. Most are soluble in polar liquids such as water. Since all the electrons are within the rigidly positioned ions, there are no free electrons to move around in contrast to metals. Therefore, ionic solids are typically electrical insulators. Compared to metals and covalently bonded solids, ionically bonded solids also have poor thermal conductivity.

1.5.3 Covalent Bonds

Two atoms can form a bond with each other by sharing some or all of their valence electrons and thereby reducing the overall energy. This is in contrast with an ionic bond because the electrons are shared rather than completely transferred. This concept is purely quantum mechanical and has no simple classical analogue. Nevertheless, it still results in the same basic principles as those shown in Fig. 1.7, i.e., there is a minimum in the total potential energy at the equilibrium position $r = r_0$.

Covalent bonds are very strong in solids. Figure 1.10 shows the formation of a covalent bond between atoms in crystalline Si, which has the diamond structure with eight atoms per cubic unit cell. Each Si shares its four valence electrons with its neighbors as shown in Fig. 1.10. There is an electron cloud in the region between atoms equivalent to two electrons with opposite spins.

In the structure of diamond, a C atom also shares electrons with other C atoms. This leads to a three-dimensional network of a covalently bonded structure as shown in Fig. 1.11. The coordination number (CN) is the number of nearest neighbors for a given atom in the solid. As it is seen in Fig. 1.11, the coordination number for a carbon atom in the diamond crystal structure is four, as discussed in Chap. 2.

In the tetrahedral systems such as C, Si, or Ge, for example, the covalent bonds undergo a very interesting process called hybridization. What happens is that the atom first promotes one of outer *s*-electrons (e.g., 2*s* shell in C and 3*s* shell in Si) into the doubly occupied *p*-shell. This costs energy, but this energy is more than

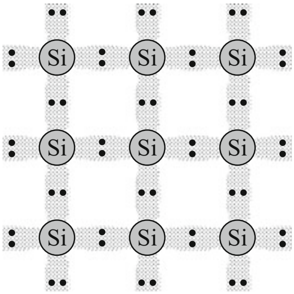


Fig. 1.10 Schematic of covalent bonds in Si. Each Si atom contributes one of its four outer shell electrons with each neighboring Si atom. This creates a pair of shared electrons between two Si atoms, which constitutes the covalent bond. Because the two atoms are identical, the electrons have the highest probability of being located at equal distances between the two atoms, as illustrated here

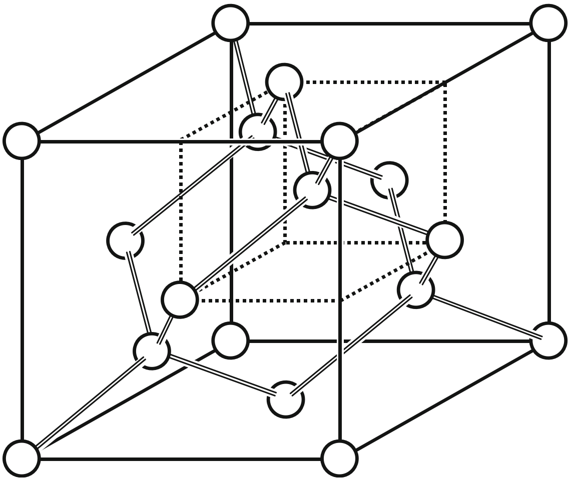


Fig. 1.11 The diamond crystal with covalent bonds. The diamond crystal is most often represented using a cubic unit cell, as shown here. Each atom in the structure is covalently bonded to four neighboring atoms

recovered because now the system can use the $2p_x$, $2p_y$, $2p_z$ orbitals in C, for example, to combine with the one left over in "s" to form four directed bonds:

$$\frac{1}{2}(2s + 2p_x + 2p_y + 2p_z)$$

$$\frac{1}{2}(2s + 2p_x - 2p_y - 2p_z)$$

$$\frac{1}{2}(2s - 2p_x + 2p_y - 2p_z)$$

$$\frac{1}{2}(2s - 2p_x - 2p_y + 2p_z)$$

pointing toward the four other atoms, where the same process has taken place, each atom providing a bond partner which is pointing in the opposite direction and giving maximum overlap.

Due to the strong Coulomb attraction between the shared electrons and the positive nuclei, the covalent bond energy is the strongest of all bond types, leading to very high melting temperatures and very hard solids: diamond is one of the hardest known materials. Covalently bonded solids are also insoluble in nearly all solvents. The directional nature and strength of the covalent bond also makes these materials nonductile (or nonmalleable). Under a strong force, they exhibit brittle fracture.

1.5.4 Mixed Bonds

In many solids, the bonding between atoms is generally not just of one certain type but rather is a mixture of bond types. We know that bonding in silicon is totally covalent, because the shared electrons in the bonds are equally attracted by the

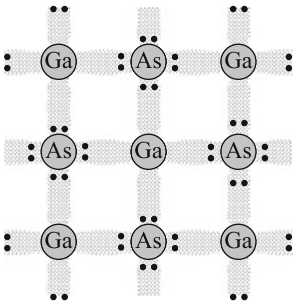


Fig. 1.12 Polar bonds in a III–V intermetallic compound. Similar to the case of Si in Fig. 1.10, a covalent bond is formed by the sharing of an electron from a Ga atom and one from a neighboring As atom. However, because a Ga atom has only three electrons in its outer shell, while an As atom has five, one of the four covalent bonds is formed by the As atom contributing two electrons, while the Ga atom contributes none. In addition, because the atoms involved are not the same, the electrons in the bonds are more attracted toward the atom with largest nucleus, as illustrated here

neighboring positive ion cores and are therefore equally shared. However, when there is a covalent-type bond between two different atoms, the electrons are unequally shared because the two neighboring ion cores are different and hence have different electron-attracting abilities. The bond is no longer purely covalent but has some ionic character, because the shared electrons are more shifted toward one of the atoms. In this case a covalent bond has an ionic component and is generally called a polar bond. Many technologically important semiconductor materials, such as III–V compounds (e.g., GaAs, InSb, and so on), have polar covalent bonds. In GaAs, for example, the electrons in a covalent bond are closer to (i.e., more probably found near) the As ion core than the Ga ion core. This example is shown in Fig. 1.12.

In ceramic materials, the type of bonding may be covalent, ionic, or a mixture of the two. For example, silicon nitride (Si_3N_4), magnesia (MgO), and alumina (Al_2O_3) are all ceramics, but they have different types of bonding: Si_3N_4 has covalent, MgO has ionic, and Al_2O_3 has a mixture of ionic and covalent bondings. All three are brittle, have high melting temperatures, and are electrical insulators.

1.5.5 Metallic Bonds

Atoms in a metal have only a few valence electrons, which can be readily removed from their shells and become collectively shared by all the resultant ions. The valence electrons therefore become delocalized and form an electron gas, permeating the space between the ions, as depicted in Fig. 1.13. The attraction between the negative charge of this electron gas and the metal ions forms the bonding in a metal. However, the presence of this electron cloud also adds a repulsive force to the bonding. Nevertheless, overall, Fig. 1.7 is still valid except that the cohesive energy is now lower in absolute value compared to ionic and covalent bonds, i.e., it is easier

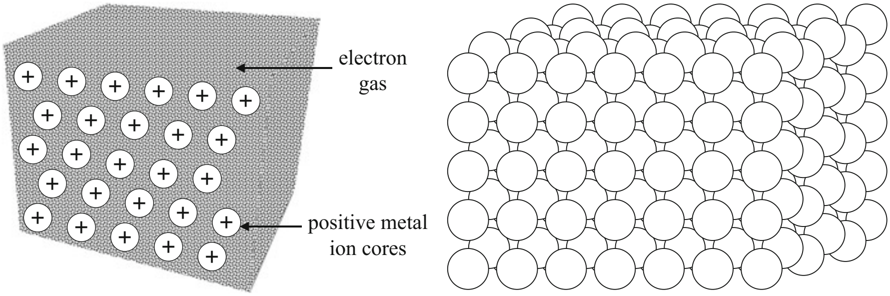


Fig. 1.13 Metallic bonding resulting from the attraction between the electron gas and the positive metal ions. The electrons are delocalized inside the volume between the atoms in the crystal

in many cases to "pull apart" metal regions, which explains why metals are usually malleable.

This metallic bond is nondirectional (isotropic). Consequently, metal ions try to get as close as possible, which leads to close-packed crystal structures with high coordination numbers, compared to covalently bonded solids. "Free" valence electrons in the electron gas can respond readily to an applied electric field and drift along the force of the field, which is the reason for the high electrical conductivity of metals. Furthermore, if there is a temperature gradient along a metal bar, the free electrons can also contribute to heat transfer from the hot to the cold regions. Metals therefore also have a good thermal conductivity.

1.5.6 Secondary Bonds

Since the atoms of inert elements (column VIII in the periodic table) have full shells and therefore cannot accept any extra electrons nor share any electrons, one might think that no bonding is possible between them. However, a solid form of argon does exist at temperatures below −189 °C, which means that there must be some type of bonding mechanism between the Ar atoms. However, the bond energy cannot be high since the melting temperature is so low.

A particular type of weak attraction that exists between neutral atoms and molecules involves the so-called dipolar and the van der Waals forces, which are the result of the electrostatic interaction between permanent or temporary electric dipoles in an atom or molecule. An electric dipole occurs whenever there is a separation between a negative and a positive charge of equal magnitude Q, as shown in Fig. 1.14a. A dipole moment is defined as a vector $\vec{p} = Q\,\vec{x}$, where $\vec{x}$ is a distance vector from the negative to the positive charge.

One might wonder how a neutral atom can have an electric dipole. We know that electrons are constantly moving in orbitals around the nucleus. As a result of this motion, the distribution of negative charges is never exactly centered on the nucleus, thus yielding a tiny, transient electric dipole. A dipole moment can also be a

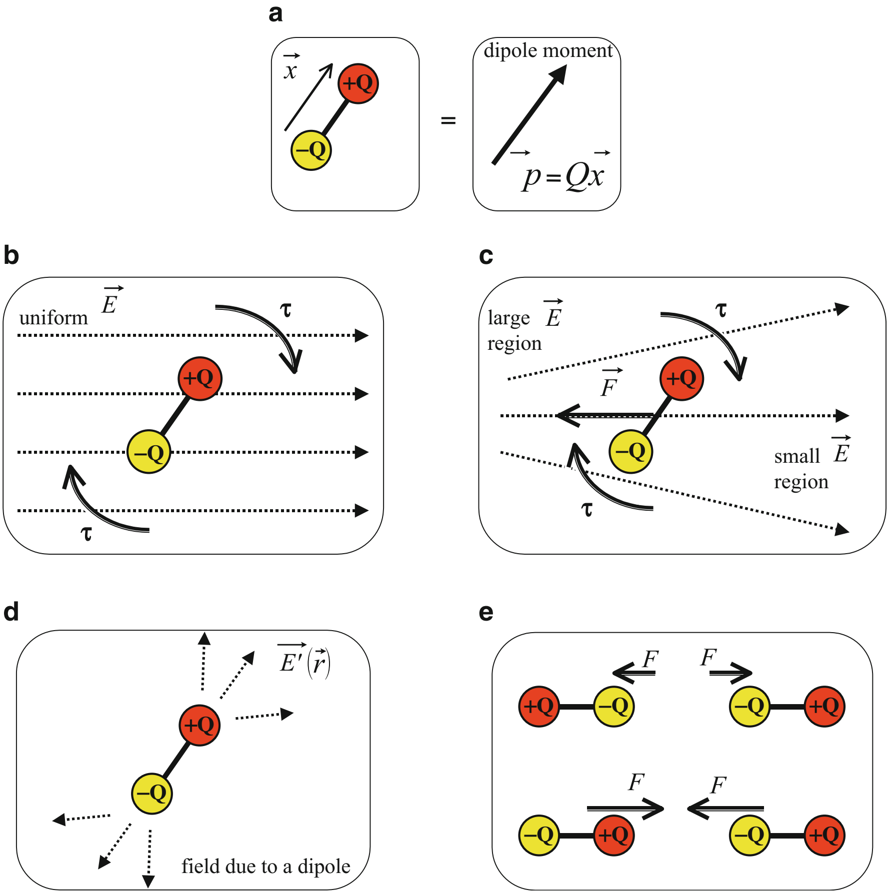


Fig. 1.14 Electric dipole moment and its properties. (**a**) A dipole is formed when two electrical charges with opposite signs and equal magnitude are separated by a distance. This creates a dipole moment. (**b**, **c**) A dipole can rotate and be translated in the presence of an electric field. (**d**) A dipole creates an electric field of its own, as a result of its two constituting electrical charges. (**e**) Dipoles can interact with each other because one will feel the electric field produced by the other

permanent feature of a molecular structure or induced by an external electric field. In the latter case, the atom or molecule in which a dipole moment appears is said to be polarized by the external electric field.

When an electric dipole is placed in an external electric field $\vec{E}$, it will experience both a torque $\boldsymbol{\tau}$ and a force $\vec{F}$ (unless the external electric field is uniform in space) as a result of the electrostatic forces exerted on each charge by the electric field, which is depicted in Fig. 1.14b, c. In a uniform field, the torque $\boldsymbol{\tau}$ will simply try to rotate the dipole to line up with the field, because the charges $+Q$ and $-Q$ experience similar magnitude forces in opposite directions. In a nonuniform field, the net force

F experienced by the dipole tries to move the dipole toward stronger field regions. This force will depend on both the orientation of the dipole and the gradient of the electric field.

Moreover, a dipole moment creates an electric field $\vec{E}'(\vec{r})$ of its own around it as shown in Fig. 1.14d, just as a single charge does. Therefore, a dipole can interact with another dipole as shown in Fig. 1.14e. This interaction is also at the origin of the van der Waals force and the van der Waals bond. The van der Waals bond is the result of the attraction caused by the instantaneous dipole of one atom inducing a dipole in another atom. It occurs even when the atoms have no permanent (time averaged) dipole moment. This bond is very weak and its magnitude drops rapidly with distance R, namely, as $1/R^6$. Figure 1.7 is nevertheless still valid but with a much smaller cohesive energy. The bond energy of this type is at least an order of magnitude lower than that of a typical ionic, covalent, and metallic bonding. This is why inert elements such as Ne and Ar solidify at temperatures below 25 K (−248 °C) and 84 K (−189 °C), respectively.

In some solids, a van der Waals force may dominate in one direction, while an ionic and/or covalent bond dominates in another. Several solids may therefore have dominant cleavage planes perpendicular to the van der Waals force directions. Moreover, many solids that we say are mostly ionic or covalent may still have a very small percentage of van der Waals force present too. Graphite is a typical example. It is made up of stacks of sheets of carbon. In one sheet the carbon atoms are covalently bound. However, the sheets are held together only by van der Waals forces, and as a result the sheets slide easily over each other making graphite easily cleavable and very soft, properties put to good use in pencil lead.

There is a special class of bond called the hydrogen bond, in liquids and solids where the attraction between atoms or molecules appears through a shared proton. Figure 1.15 shows the hydrogen bond in the H_2O molecule. Such a molecule has a permanent dipole moment. Each proton in a molecule can form a bond with the oxygen in two other molecules. This dipole-dipole interaction keeps water molecules together in liquid water or solid ice.

The greater the energy of the bond is, the higher the melting temperature of the solid is. Similarly, stronger bonds lead to greater elastic moduli and smaller expansion coefficients.

1.6 Atomic Property Trends in the Periodic Table

1.6.1 The Periodic Table

As its name suggests, the periodic table of elements is organized based on the periodicity of the electronic structure in atoms. In the periodic table, all the elements in the same row make up a period (in this discussion “across a period” will mean from left to right), and all the elements in a column are a group. Elements in a group have the same valence shell configuration. The part of the

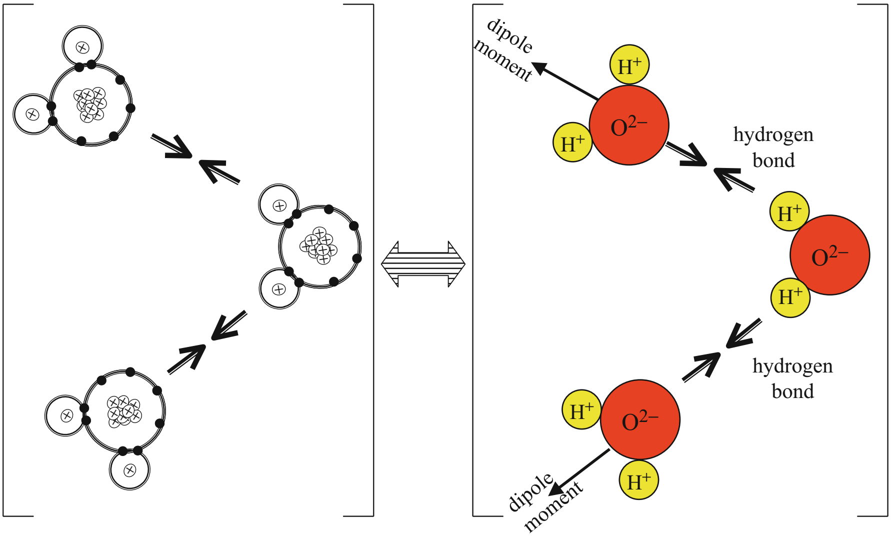


Fig. 1.15 The origin of hydrogen bonding between water molecules. A H_2O molecule has a net permanent dipole moment as a result of its lack of central symmetry. The H_2O molecules can therefore interact with one another. Attractions between the various dipole moments in water give rise to hydrogen bonding

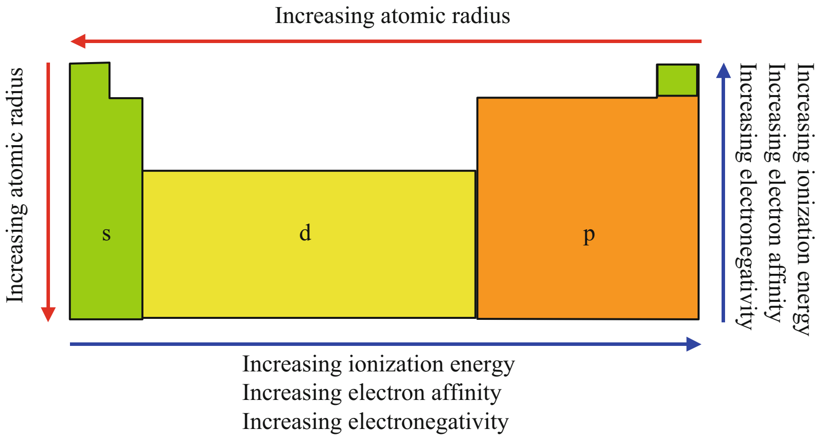


Fig. 1.16 Part of the periodic table with divisions indicating valence shells and a summary of atomic property trends

periodic table shown in Fig. 1.16 can be divided into three sections that indicate which orbitals (*s*, *p*, or *d*) are the valence shell. The *f*-orbital valence shell elements are omitted for simplicity.

The electron configuration of an atom (especially that of its valence shell) is a primary determinant of the atom's properties. As a result, the variation of atomic properties across the table should reflect the “structure” of the periodic table. This can be seen in many of the basic atomic properties. The discussion here will focus on atomic and ionic radii, ionization energy, electron affinity, and electronegativity. The variation trends of these properties across a period (from left to right) and down a group are very good examples of the role of the interatomic electrical forces. The properties discussed here are determined by the interplay between nuclear attraction of electrons, electron-electron repulsions, and nuclear-charge screening.

1.6.2 Atomic and Ionic Radii

Since electrons in an atom are delocalized in the orbitals, not only does the orbital not have a well-defined boundary, but the whole atom also does not have a well-defined size. Typically, the atomic radius (a spherical shape is generally assumed) is instead defined by half the distance between the atoms in a chemical compound. This definition is oversimplified since different atoms form different types of bonds, but regardless, trends can still be observed.

The atomic radius decreases going across a “period” and increases going down a group. Going across a period, protons and electrons are being incrementally added. The dominant force originates from the increased nuclear charge attracting the electron clouds more strongly. Going down a group, the atomic radius increases because electrons are occupying larger orbitals corresponding to higher and higher principal quantum numbers.

Another important size is that of an element’s ion compared to its neutral state. A positively ionized atom has lost an electron from the outermost (largest) shell, which reduces its size. Also, the loss of an electron reduces the electron-electron repulsions in the orbitals that would otherwise cause them to spread out over a larger space. A negative ion is larger than the neutral ion because the additional electron increases electron-electron repulsions. The change in size for ions can be very large. For example, the radius of Li changes from 1.52 Å to 0.76 Å when it loses an electron.

1.6.3 Ionization Energy

Ionization energy is defined as the energy required to remove an electron from an atom or ion, creating a more positive particle. In the ionization process, the highest energy, or outermost, electron is removed. The energy required to remove an electron from an atom in its ground state is called the first ionization energy. The energy required to remove a second electron is called the second ionization energy and so on. As the degree of ionization increases, so does the energy required. This is because it is increasingly more difficult to remove a negative charge from an increasingly positively charged ion. As the ion becomes more positive, it attracts any electrons around it more strongly because the effective nuclear charge they experience is larger. From the point of view of the orbital model, taking successive electrons from an atom requires reaching deeper into the atom to remove an electron from the more tightly bound lower energy levels. The ionization energy always jumps by a large amount once all the valence electrons have been removed, and ionization from the full shell starts.

Going across a period, the first ionization energy increases due to increased nuclear attraction. This is like the trend for atomic radius. Going down a group, the first ionization energy decreases because the ionized electron is coming from orbitals with a higher principal quantum number. In these higher orbitals, the electron spends the majority of its time further from the nucleus and so the atom is easier to ionize.

1.6.4 Electron Affinity

The electron affinity is the potential energy change of the atom when an electron is added to a neutral, gaseous atom to form a negative ion. So the more negative the electron affinity, the more favorable the electron addition process is. Not all elements form stable negative ions, in which case the electron affinity is zero or even positive (energy is required to add an electron).

Of the properties discussed, electron affinity is the least well behaved because it has the most exceptions. It is also difficult to measure. There is a tendency toward increased electron affinity going left to right across a period. The overall trend across a period occurs because of increased nuclear attraction. The exceptions occur because, for certain electron configurations, the electron-electron repulsion force (not to be confused with screening) is stronger than the nuclear attraction. Exceptions also occur because those elements that have completely filled valence shells are particularly stable. Going down a group, the electron affinity should decrease since the electron is being added increasingly further away from the atom (i.e., less tightly bound and therefore closer in energy to a free electron). In reality, this trend is a very weak one as the affinities do not change significantly down most groups.

1.6.5 Electronegativity

Electronegativity is a measure of the ability of an atom in a molecule to attract shared bonding electrons. This property is different from the other ones presented here because it is not relevant for an isolated atom since it deals with shared electrons. A higher electronegativity means that the atom will attract bonded electrons to it more strongly. Electronegativity increases across a period and decreases down a group. The difference in electronegativity between bonding atoms determines whether the bond is covalent, ionic, or in between (polar covalent). For atoms with similar electronegativity, neither atom attracts the shared electron more strongly. This equal sharing is characteristic of a purely covalent bond. As the electronegativity difference increases, the shared electron will spend more time near the more electronegative atom. The unequal sharing results in a polar covalent bond, which in the extreme case of complete electron transfer becomes an ionic bond.

1.6.6 Summary of Trends

The different trends are summarized in Fig. 1.16. Appendix A.3 contains periodic tables that give the atomic radius, ionization energy, electron affinity, and electronegativity for all the elements. Understanding these trends allows one to understand properties not only of individual elements but also solid properties like lattice constants and semiconductor bandgaps. It is important to keep in mind that the trends discussed here are just generalizations, and exceptions do occur throughout the table. A more detailed discussion of these properties and the exceptions can be found in most general chemistry texts (see Further Reading section).

1.7 Introduction to Energy Bands

So far, we have considered the concepts associated with the formation of bonds between two atoms. Although these concepts are important issues in semiconductor materials, they cannot explain a number of semiconductor properties. It is necessary to have more detailed information on the energies and the motion of electrons in a crystal, as well as understand the electron collision events against imperfections of different kinds. To do so, we must first introduce the concept of energy bands. The formation of energy bands will be discussed in more detail in Chap. 5 using a quantum mechanical formalism. However, for the moment, energy bands can be conceptually understood by considering a simple example.

The electronic configuration in an isolated Si atom is such that 10 of its 14 electrons are tightly bound to the nucleus and play no significant role in the interaction of the Si atom with its environment, under all familiar solid-state device conditions. By contrast, the remaining four valence electrons are rather weakly bound and occupy four of the eight allowed energy states immediately above the last core level. For a group of N isolated Si atoms, i.e., far enough apart so that they are not interacting with one another, the electronic energy states of their valence electrons are all identical.

When these N atoms are brought into close proximity, to form crystalline Si, for example, the energy levels for the outer electrons are modified as shown in Fig. 1.17b. Exactly half of the allowed states become depressed in energy (bonding states) and half increase in energy (antibonding states). Moreover, this perturbation does not leave the energy levels sharply defined but spread them into bands instead. Two bands of allowed electronic energy states are thus formed, as shown in Fig. 1.17b, which are separated by an energy gap, i.e., an energy region forbidden for electrons where there is no allowed electronic energy state.

At very low temperatures, the electrons fill the low-energy band first. The band below the bandgap in energy is called the valence band. The band above the bandgap, which is not completely filled and in most cases completely empty, is called the conduction band. The energy gap between the highest energy level in the valence band and the lowest energy level in the conduction band is called the bandgap.

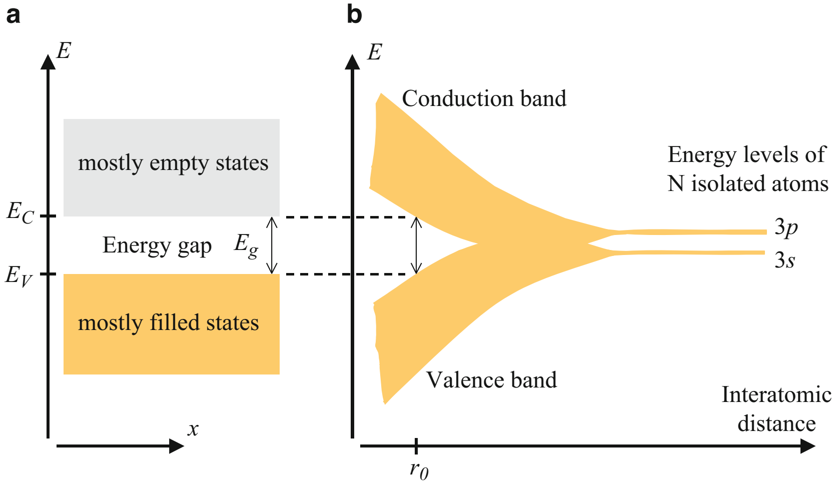


Fig. 1.17 Illustration of the formation of energy bands in a Si crystal. A system of N isolated Si atoms has discrete allowed energy levels, all located at the energies of the 3*s* and 3*p* orbitals of an isolated Si atom. When the atoms come into close proximity, the energy levels are modified as shown in the figure, as a result of the interaction between the atoms. The allowed energy levels start to form energy bands

It should be noted that the band electrons in crystalline silicon are not tied to or associated with any one particular atom. On average, one will typically find four valence electrons being shared between any given Si atom and its four nearest neighbors (as in the bonding model). However, the identity of the shared electrons changes as a function of time, with the electrons moving around from point to point in the crystal. In other words, the allowed electronic states or bands are no longer atomic states but are associated with the crystal as a whole, independent of the point examined in a perfect crystal. An electron sees the same energy states wherever it is in the crystal.

We can therefore say that, for a perfect crystal under equilibrium conditions, a plot of the allowed electron energies versus distance along any preselected crystalline direction (x) is as shown in Fig. 1.17a. This plot is the basic energy band model. E_C introduced in Fig. 1.17a is the lowest possible conduction band energy, E_V is the highest possible valence band energy, and $E_g = E_C – E_V$ is the bandgap. A more detailed consideration of the bands and electron states will be given in Chap. 5.

The energy band and the bandgap concepts are at the heart of semiconductor physics. As the name implies, a semiconductor has an electrical conductivity in between that of a metal and an insulator. Also, in a semiconductor the electrical conductivity can be varied by changing the structural properties of the semiconductor, changing the temperature, or applying external fields. These properties are a direct consequence of the energy band structure. Understanding and utilizing these properties of semiconductors is the goal of this book.

1.8 Summary

In this chapter, the electronic structure of atoms and its implications on the bonding and the formation of energy bands in solids have been presented. Early experiments conducted on even the simplest atom that of hydrogen showed that classical mechanics was insufficient and that a new theory, called wave or quantum mechanics, was necessary in order to understand the observed physical phenomena.

The notion of electron density function and the Bohr radius have been introduced. The concepts of atomic orbitals and quantum numbers to identify the allowed discrete energy levels for electrons in an atom have been discussed. The nature of the bonding between atoms in a solid, be it ionic, covalent, mixed, metallic, or secondary, has been described by taking into account the interaction of electrons in the higher energy levels in the atoms in presence. Finally, the formation of energy bands and the concept of conduction and valence bands have been introduced through the interaction of multiple atoms.

Problems

1. The size of an atom is approximately 10^{-8} cm. To locate an electron within the atom, one should use electromagnetic radiation of wavelength not longer than 10^{-9} cm. What is the energy of the photon with such a wavelength (in eV)?
2. Using the Rydberg formula, calculate the wavelength and energy of the photons emitted in the Lyman series for electrons originally in the orbits $n = 2$, 3, and 4. Express your results in cm, eV, and J. In which region of the electromagnetic spectrum are these emissions?
3. What are the radii of the orbits and the linear velocities of the electrons when they are in the $n = 1$ and $n = 2$ orbits of the hydrogen atom?
4. Using Bohr's model, deduce an analytical expression for the Rydberg constant as a function of universal constants.
5. The He^+ ion is a one-electron system similar to hydrogen, except that it has two protons. Calculate the wavelength of the longest wavelength line in each of the first three spectroscopic series ($n = 1, 2, 3$).
6. The human eye is more sensitive to the yellow-green part of the visible spectrum because this is where the irradiance of the sun is maximum. Since the sun can be considered as a blackbody with a temperature of approximately 5800 K, use Planck's relation for the irradiance of a blackbody $I(\lambda) = \frac{2\pi hc^2}{\lambda^5}\left\{\frac{1}{e^{\frac{hc}{\lambda k_b T}}-1}\right\}$ to find the wavelength of the maximum of the sun irradiance. You will come out with a very simple relation between the peak of the irradiance (λ_{peak}) and T, which is called Wien's relation. In Planck's relation above, h, c, λ, k_b, and T are, respectively, Planck's constant, the velocity of light in vacuum, the wavelength, Boltzmann's constant, and the absolute temperature. You will need the

following solution for the equation $x = 5(1-e^{-x})$, $x = 4.965$. Then use Wien's relation to estimate λ_{peak} for a human body.

7. Since an electron on a circular orbit around a proton has a centripetal acceleration, it should radiate energy according to the Larmor relation $dE/dt = -2/3\ (q^2/4\pi\varepsilon_0)\ (a^2/c^3)$ where q, a, ε_0, and c are, respectively, the electron charge, its acceleration, the vacuum permittivity, and the velocity of light in vacuum. Therefore, in classical mechanics, it should spiral and crash on the nucleus. How long would this decay take, supposing that the size of the initial orbit is 10^{-10} m and the nucleus is a point charge (i.e., radius = 0)?
8. What is Hund's rule? Show how it is used to specify in detail the electron configurations of the elements from Li to Ne.
9. What is the full electronic configuration of Li? Since the ionization energy of Li is 5.39 eV, how much is the effective nuclear charge? What can you say about the screening of the other electrons?
10. Calculate the total coulombic potential energy of a Na^+ in a NaCl crystal by considering only up to the fourth nearest neighbors of Na^+. The coulombic potential energy for two ions of opposite charges separated by a distance r is given by:

$$E(r) = -\frac{q^2}{4\pi\varepsilon_0 r} \quad (q > 0).$$

11. The interaction energy between Na^+ and Cl^- ions in the NaCl crystal can be written as

$$E(r) = -\frac{4.03 \times 10^{-28}}{r} + \frac{6.97 \times 10^{-96}}{r^8}$$

where the energy is given in joules per ion pair and the interionic separation r is in meters. The numerator unit of the first term is J·m and the second term is J·m^8. Calculate the binding energy and the equilibrium separation between the Na^+ and Cl^- ions.

12. Consider the van der Waals bonding in solid argon. The potential energy as a function of interatomic separation can generally be modeled by the Lennard-Jones 6–12 potential energy curve, that is, $E(r) = -Ar^{-6} + Br^{-12}$ where A and B are constants. Given that $A = 1.037 \times 10^{-77}$ J·m^6 and $B = 1.616 \times 10^{-134}$ J·m^{12}, calculate the bond length and bond energy (in eV) for solid argon.
13. Which group of the periodic table would you expect to have the largest electron affinities?
14. Which atom has the higher ionization energy, zinc or gallium? Explain.
15. Arrange the following groups of atoms in order of increasing size (without resorting to the tables in the appendices).
    a. Li, Na, K
    b. P, S, Cl
    c. In, Sn, Tl
    d. Sb, S, Cl, F

16. Based on the electronegativities given in Fig. A.1 in Appendix A.3, what groups of elements would you expect to form ionic compounds? Is this consistent with reality?
17. Why do none of the noble or inert gases (elements in the rightmost group) have electron affinity values listed in Appendix A.3 Fig. A.?

Further Reading

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