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Atomic structure of crystals

Solids exhibit an extremely wide range of properties, which is what makes them so useful and indispensable to mankind. While our familiarity with many different types of solids makes this fact seem unimpressive, it is indeed extraordinary when we consider its origin. The origin of all the properties of solids is nothing more than the interaction between electrons in the outer shells of the atoms, the so called *valence* electrons. These electrons interact among themselves and with the nuclei of the constituent atoms. In this first chapter we will give a general description of these interactions and their relation to the structure and the properties of solids.

The extremely wide range of the properties of solids is surprising because most of them are made up from a relatively small subset of the elements in the Periodic Table: about 20 or 30 elements, out of more than 100 total, are encountered in most common solids. Moreover, most solids contain only very few of these elements, from one to half a dozen or so. Despite this relative simplicity in composition, solids exhibit a huge variety of properties over ranges that differ by many orders of magnitude. It is quite extraordinary that even among solids which are composed of single elements, physical properties can differ by many orders of magnitude.

One example is the ability of solids to conduct electricity, which is measured by their electrical resistivity. Some typical single-element metallic solids (such as Ag, Cu, Al), have room-temperature resistivities of 1–5μΩ·cm, while some metallic alloys (like nichrome) have resistivities of 10^2μΩ·cm. All these solids are considered good conductors of electrical current. Certain single-element solids (like C, Si, Ge) have room-temperature resistivities ranging from 3.5×10^3μΩ·cm (for graphitic C) to 2.3×10^{11}μΩ·cm (for Si), and they are considered semimetals or semiconductors. Finally, certain common solids like wood (with a rather complex structure and chemical composition) or quartz (with a rather simple structure and composed of two elements, Si and O), have room-temperature resistivities of 10^{16}–10^{19}μΩ·cm (for wood) to 10^{25}μΩ·cm (for quartz). These solids are considered insulators. The range of electrical resistivities covers an astonishing 25 orders of magnitude!

Another example has to do with the mechanical properties of solids. Solids are classified as ductile when they yield plastically when stressed, or brittle when they do not yield easily, but instead break when stressed. A useful measure of this behavior is the yield stress σ_Y, which is the stress up to which the solid behaves as a linear elastic medium when stressed, that is, it returns to its original state when the external stress is removed. Yield stresses in solids, measured in units of MPa, range from 40 in Al, a rather soft and ductile metal, to 5×10^4 in diamond, the hardest material, a brittle insulator. The yield stresses of common steels range from 200–2000 MPa. Again we see an impressive range of more than three orders of magnitude in how a solid responds to an external agent, in this case a mechanical stress.

Naively, one might expect that the origin of the widely different properties of solids is related to great differences in the concentration of atoms, and correspondingly that of electrons. This is far from the truth. Concentrations of atoms in a solid range from 10^{22} cm^{-3} in Cs, a representative alkali metal, to 17×10^{22} cm^{-3} in C, a representative covalently bonded solid. Anywhere from one to a dozen valence electrons per atom participate actively in determining the properties of solids. These considerations give a range of atomic concentrations of roughly 20, and of electron concentrations[1] of roughly 100. These ranges are nowhere close to the ranges of yield stresses and electrical resistivities mentioned above. Rather, the variation of the properties of solids has to do with the specific ways in which the valence electrons of the constituent atoms interact when these atoms are brought together at distances of a few angstroms (1 Å= 10^{-10} m = 10^{-1} nm). Typical distances between nearest neighbor atoms in solids range from 1.5 to 3 Å. The way in which the valence electrons interact determines the atomic structure, and this in turn determines all the other properties of the solid, including mechanical, electrical, optical, thermal and magnetic properties.

1.1 Building crystals from atoms

The structure of crystals can be understood to some extent by taking a close look at the properties of the atoms from which they are composed. We can identify several broad categories of atoms, depending on the nature of electrons that participate actively in the formation of the solid. The electrons in the outermost shells of the isolated atom are the ones that interact strongly with similar electrons in neighboring atoms; as already mentioned these are called valence electrons. The remaining electrons of the atom are tightly bound to the nucleus, their wavefunctions (orbitals)

[1] The highest concentration of atoms does not correspond to the highest number of valence electrons per atom.

do not extend far from the position of the nucleus, and they are very little affected when the atom is surrounded by its neighbors in the solid. These are called the core electrons. For most purposes it is quite reasonable to neglect the presence of the core electrons as far as the solid is concerned, and consider how the valence electrons behave. We will discuss below the crystal structure of various solids based on the properties of electronic states of the constituent atoms. We are only concerned here with the basic features of the crystal structures that the various atoms form, such as number of nearest neighbors, without paying close attention to details; these will come later. Finally, we will only concern ourselves with the low-temperature structures, which correspond to the lowest energy static configuration; dynamical effects, which can produce a different structure at higher temperatures, will not be considered [1]. We begin our discussion with those solids formed by atoms of one element only, called elemental solids, and then proceed to more complicated structures involving several types of atoms. Some basic properties of the elemental solids are collected in the Periodic Table (pp. 8, 9), where we list:

- The crystal structure of the most common phase. The acronyms for the crystal structures that appear in the Table stand for: BCC = body-centered cubic, FCC = face-centered cubic, HCP = hexagonal-close-packed, GRA = graphite, TET = tetragonal, DIA = diamond, CUB = cubic, MCL = monoclinic, ORC = orthorhombic, RHL = rhombohedral. Selected shapes of the corresponding crystal unit cells are shown in Fig. 1.1.

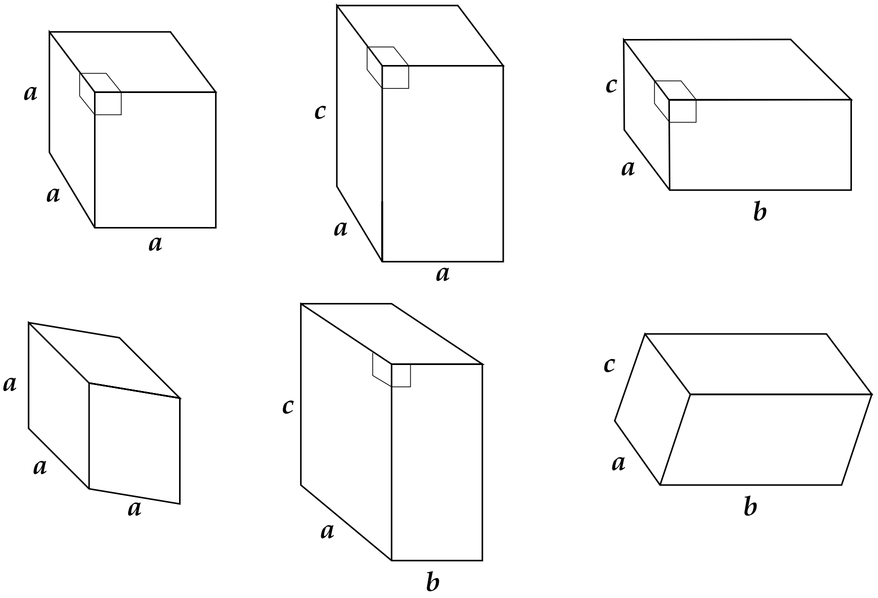

Figure 1.1. Shapes of the unit cells in some lattices that appear in Periodic Table. **Top row:** cubic, tetragonal, orthorhombic. **Bottom row:** rhombohedral, monoclinic, triclinic. The corners in thin lines indicate right angles between edges.

- The covalent radius in units of angstroms, Å, which is a measure of the typical distance of an atom to its neighbors; specifically, the sum of covalent radii of two nearest neighbor atoms give their preferred distance in the solid.
- The melting temperature in millielectronvolts (1 meV $= 10^{-3}$ eV $= 11.604$ K). The melting temperature provides a measure of how much kinetic energy is required to break the rigid structure of the solid. This unconventional choice of units for the melting temperature is meant to facilitate the discussion of cohesion and stability of solids. Typical values of the cohesive energy of solids are in the range of a few electronvolts (see Tables 5.4 and 5.5), which means that the melting temperature is only a small fraction of the cohesive energy, typically a few percent.
- The atomic concentration of the most common crystal phase in 10^{22} cm^{-3}.
- The electrical resistivity in units of micro-ohm-centimeters, μΩ·cm; for most elemental solids the resistivity is of order 1–100 in these units, except for some good insulators which have resistivities 10^3(k), 10^6(M) or 10^9(G) times higher.

The natural units for various physical quantities in the context of the structure of solids and the names of unit multiples are collected in two tables at the end of the book (see Appendix I).

The columns of the Periodic Table correspond to different valence electron configurations, which follow a smooth progression as the s, p, d and f shells are being filled. There are a few exceptions in this progression, which are indicated by asterisks denoting that the higher angular momentum level is filled in preference to the lower one (for example, the valence electronic configuration of Cu, marked by one asterisk, is s^1d^{10} instead of s^2d^9; that of Pd, marked by two asterisks, is s^0d^{10} instead of s^2d^8, etc.).

1.1.1 Atoms with no valence electrons

The first category consists of those elements which have no valence electrons. These are the atoms with all their electronic shells completely filled, which in gaseous form are very inert chemically, i.e. the noble elements He, Ne, Ar, Kr and Xe. When these atoms are brought together to form solids they interact very weakly. Their outer electrons are not disturbed much since they are essentially core electrons, and the weak interaction is the result of slight polarization of the electronic wavefunction in one atom due to the presence of other atoms around it. Fortunately, the interaction is attractive. This interaction is referred to as "fluctuating dipole" or van der Waals interaction. Since the interaction is weak, the solids are not very stable and they have very low melting temperatures, well below room temperature. The main concern of the atoms in forming such solids is to have as many neighbors as possible, in order to maximize the cohesion since all interactions are attractive. The crystal structure that corresponds to this atomic arrangement is one of the close-packing geometries, that is, arrangements which allow the closest packing of hard spheres.

symbol	Li 3	atomic number
name	Lithium	
crystal structure	BCC 1.23	covalent radius (Å)
melting point	39.08	(meV)
atomic concentration	4.70	(10^{22}cm^{-3})
resistivity	9.4	(μΩ cm)

I-A s^1	II-A s^2	III-B s^2d^1	IV-B s^2d^2	V-B s^2d^3	VI-B s^2d^4	VII-B s^2d^5	VIII s^2d^6	VIII s^2d^7
Li 3 Lithium BCC 1.23 39.08 4.70 9.4	Be 4 Beryllium HCP 0.90 134.4 12.1 3.3							
Na 11 Sodium BCC 1.54 8.42 2.65 4.75	Mg 12 Magnesium HCP 1.36 79.54 4.30 4.46							
K 19 Potassium BCC 2.03 28.98 1.40 21.6	Ca 20 Calcium FCC 1.74 96.09 2.30 3.7	Sc 21 Scandium HCP 1.44 156.3 4.27 51	Ti 22 Titanium HCP 1.32 167.3 5.66 47.8	V 23 Vanadium BCC 1.22 188.1 7.22 24.8	Cr* 24 Chromium BCC 1.18 187.9 8.33 12.9	Mn 25 Manganese CUB 1.17 130.9 8.18 139	Fe 26 Iron BCC 1.17 156.1 8.50 9.71	Co 27 Cobalt HCP 1.16 152.4 8.97 6.34
Rb 37 Rubidium BCC 2.16 26.89 1.15 12.1	Sr 38 Strontium FCC 1.91 96.49 1.78 22.8	Y 39 Yttrium HCP 1.62 154.7 3.02 60	Zr 40 Zirconium HCP 1.45 183.4 4.29 41.4	Nb* 41 Niobium BCC 1.34 237.0 5.56 15.2	Mo* 42 Molybdenum BCC 1.30 249.6 6.42 5.17	Tc 43 Technetium HCP 1.28 234.2 7.04 14	Ru* 44 Ruthenium HCP 1.25 224.7 7.36 7.2	Rh* 45 Rhodium FCC 1.25 192.9 7.26 4.5
Cs 55 Cesium BCC 2.35 25.97 0.91 20	Ba 56 Barium BCC 1.98 86.18 1.60 50	La 57 Lanthanum HCP 1.69 102.8 2.70 80	Ha 72 Hafnium HCP 1.44 215.4 4.52 35.1	Ta 73 Tantalum BCC 1.34 281.7 5.55 13.5	W 74 Wolframium BCC 1.30 317.4 6.30 5.6	Re 75 Rhenium HCP 1.28 297.6 6.80 19.3	Os 76 Osmium HCP 1.26 285.9 7.14 8.1	Ir 77 Iridium FCC 1.27 234.7 7.06 5.1

$f^2d^0s^2$	$f^3d^0s^2$	$f^4d^0s^2$	$f^5d^0s^2$	$f^6d^0s^2$	$f^7d^0s^2$
Ce 58 Cerium FCC 1.65 92.3 2.91 85.4	Pr 59 Praseodymium HCP 1.65 103.8 2.92 68.0	Nd 60 Neodymium HCP 1.64 110.6 2.93 64.3	Pm 61 Promethium	Sm 62 Samarium RHL 1.62 115.9 3.03 105.0	Eu 63 Europium BCC 1.85 94.4 3.04 91.0

The particular crystal structure that noble-element atoms assume in solid form is called face-centered cubic (FCC). Each atom has 12 equidistant nearest neighbors in this structure, which is shown in Fig. 1.2.

Thus, in the simplest case, atoms that have no valence electrons at all behave like hard spheres which attract each other with weak forces, but are not deformed. They

VIII s^2d^8	I-B s^2d^9	II-B s^2d^{10}	III–A s^2p^1	IV–A s^2p^2	V–A s^2p^3	VI–A s^2p^4	VII–A s^2p^5	Noble s^2p^6
			B 5 Boron TET 0.82 202.3 13.0 4 M	C 6 Carbon GRA 0.77 338.1 17.6 1.4 G	N 7 Nitrogen HCP 0.70 28.98	O 8 Oxygen CUB 0.66 28.24	F 9 Fluorine MCL 0.64 28.14	Ne 10 Neon FCC 25.64 4.36
			Al 13 Aluminum FCC 1.18 80.44 6.02 2.67	Si 14 Silicon DIA 1.17 145.4 5.00 230 G	P 15 Phosphorus CUB 1.10 59.38	S 16 Sulfur ORC 1.04 33.45	Cl 17 Chlorine ORC 0.99 38.37	Ar 18 Argon FCC 30.76 2.66
Ni 28 Nickel FCC 1.15 148.9 9.14 6.84	Cu* 29 Copper FCC 1.17 116.9 8.45 1.67	Zn 30 Zinc HCP 1.25 59.68 6.55 5.92	Ga 31 Gallium ORC 1.26 26.09 5.10	Ge 32 Germanium DIA 1.22 104.3 4.42 47 M	As 33 Arsenic RHL 1.21 93.93 4.65 12 M	Se 34 Selenium HCP 1.17 42.23 3.67	Br 35 Bromine ORC 1.14 46.45 2.36	Kr 36 Krypton FCC 33.57 2.17
Pd** 46 Palladium FCC 1.28 157.5 6.80 9.93	Ag* 47 Silver FCC 1.34 106.4 5.85 1.63	Cd 48 Cadmium HCP 1.48 51.19 4.64 6.83	In 49 Indium TET 1.44 37.02 3.83 8.37	Sn 50 Tin TET 1.40 43.53 2.91 11	Sb 51 Antimony RHL 1.41 77.88 3.31 39	Te 52 Tellurium HCP 1.37 62.26 2.94 160 k	I 53 Iodine ORC 1.33 56.88 2.36	Xe 54 Xenon FCC 37.43 1.64
Pt** 78 Platinum FCC 1.30 175.9 6.62 9.85	Au* 79 Gold FCC 1.34 115.2 5.90 2.12	Hg 80 Mercury RHL 1.49 20.18 4.26 96	Tl 81 Thallium HCP 1.48 49.68 3.50 18	Pb 82 Lead FCC 1.47 51.75 3.30 20.6	Bi 83 Bismuth RHL 1.34 46.91 2.82 107	Po 84 Pollonium	At 85 Astatine	Rn 86 Radon

$f^7d^1s^2$	$f^8d^1s^2$	$f^{10}d^0s^2$	$f^{11}d^0s^2$	$f^{12}d^0s^2$	$f^{13}d^0s^2$	$f^{14}d^0s^2$	$f^{14}d^1s^2$
Gd 64 Gadolinium HCP 1.61 136.6 3.02 131.0	Tb 65 Terbium HCP 1.59 140.7 3.22 114.5	Dy 66 Dysprosium HCP 1.59 144.8 3.17 92.6	Ho 67 Holmium HCP 1.58 150.2 3.22 81.4	Er 68 Erbium HCP 1.57 154.7 3.26 86.0	Tm 69 Thulium HCP 1.56 156.7 3.32 67.6	Yb 70 Ytterbium FCC 94.5 3.02 25.1	Lu 71 Lutetium HCP 1.56 166.2 3.39 58.2

form weakly bonded solids in the FCC structure, in which the attractive interactions are optimized by maximizing the number of nearest neighbors in a close packing arrangement. The only exception to this rule is He, in which the attractive interaction between atoms is so weak that it is overwhelmed by the zero-point motion of the atoms. Unless we apply external pressure to enhance this attractive interaction,

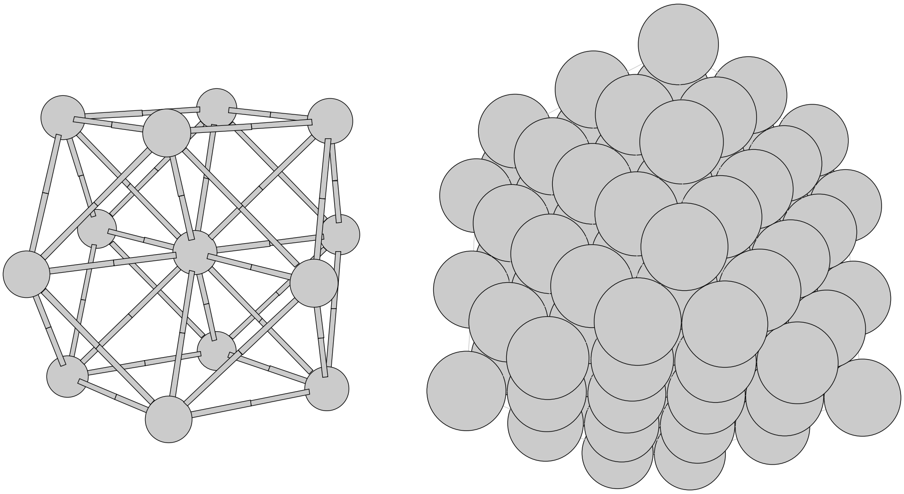

Figure 1.2. **Left:** one atom and its 12 neighbors in the face-centered cubic (FCC) lattice; the size of the spheres representing atoms is chosen so as to make the neighbors and their distances apparent. **Right:** a portion of the three-dimensional FCC lattice; the size of the spheres is chosen so as to indicate the close-packing nature of this lattice.

He remains a liquid. This is also an indication that in some cases it will prove unavoidable to treat the nuclei as quantum particles (see also the discussion below about hydrogen).

The other close-packing arrangement of hard spheres is the hexagonal structure (HCP for hexagonal-close-packed), with 12 neighbors which are separated into two groups of six atoms each: the first group forms a planar six-member ring surrounding an atom at the center, while the second group consists of two equilateral triangles, one above and one below the six-member ring, with the central atom situated above or below the geometrical center of each equilateral triangle, as shown in Fig. 1.3. The HCP structure bears a certain relation to FCC: we can view both structures as planes of spheres closely packed in two dimensions, which gives a hexagonal lattice; for close packing in three dimensions the successive planes must be situated so that a sphere in one plane sits at the center of a triangle formed by three spheres in the previous plane. There are two ways to form such a stacking of hexagonal close-packed planes: ...$ABCABC$..., and ...$ABABAB$..., where A, B, C represent the three possible relative positions of spheres in successive planes according to the rules of close packing, as illustrated in Fig. 1.4. The first sequence corresponds to the FCC lattice, the second to the HCP lattice.

An interesting variation of the close-packing theme of the FCC and HCP lattices is the following: consider two interpenetrating such lattices, that is, two FCC or two HCP lattices, arranged so that in the resulting crystal the atoms in each sublattice

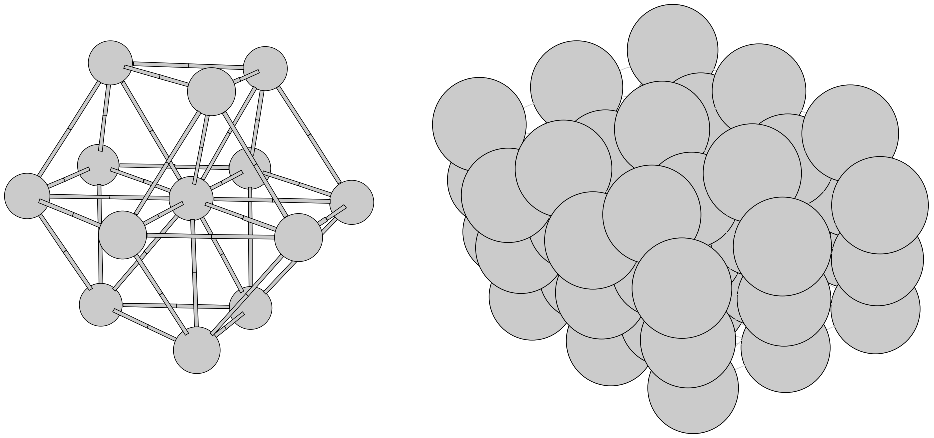

Figure 1.3. **Left:** one atom and its 12 neighbors in the hexagonal-close-packed (HCP) lattice; the size of the spheres representing atoms is chosen so as to make the neighbors and their distances apparent. **Right:** a portion of the three-dimensional HCP lattice; the size of the spheres is chosen so as to indicate the close-packing nature of this lattice.

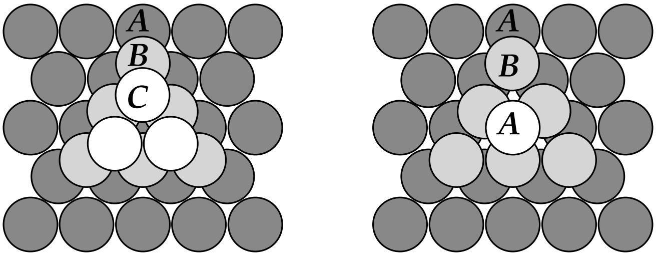

Figure 1.4. The two possible close packings of spheres: **Left:** the ...$ABCABC$... stacking corresponding to the FCC crystal. **Right:** the ...$ABABAB$... stacking corresponding to the HCP crystal. The lattices are viewed along the direction of stacking of the hexagonal-close-packed planes.

have as nearest equidistant neighbors atoms belonging to the other sublattice. These arrangements give rise to the diamond lattice or the zincblende lattice (when the two original lattices are FCC) and to the wurtzite lattice (when the two original lattices are HCP). This is illustrated in Fig. 1.5. Interestingly, in both cases each atom finds itself at the center of a tetrahedron with exactly four nearest neighbors. Since the nearest neighbors are exactly the same, these two types of lattices differ only in the relative positions of second (or farther) neighbors. It should be evident that the combination of two close-packed lattices cannot produce another close-packed lattice. Consequently, the diamond, zincblende and wurtzite lattices are encountered in covalent or ionic structures in which four-fold coordination is preferred. For example: tetravalent group IV elements such as C, Si, Ge form the diamond lattice; combinations of two different group IV elements or complementary elements

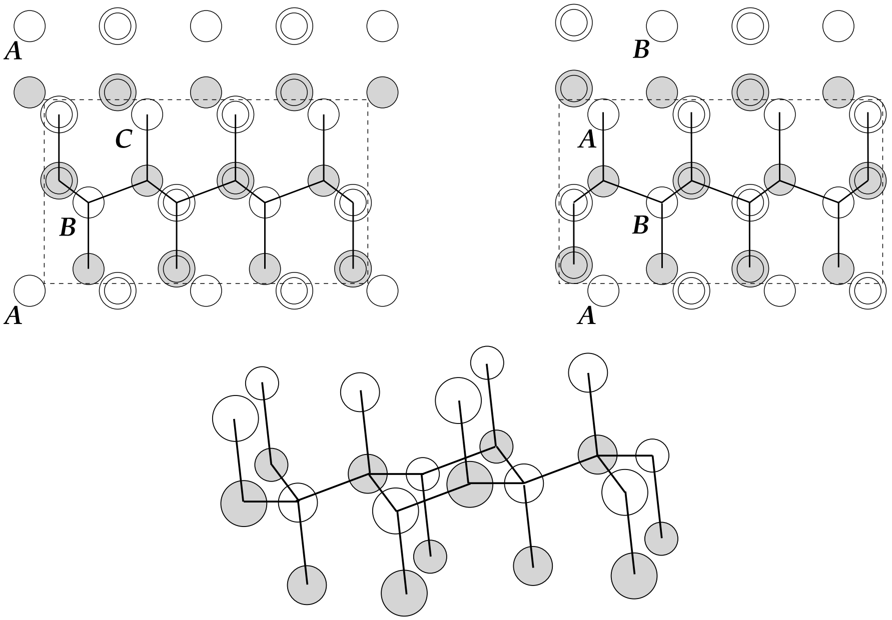

Figure 1.5. **Top:** illustration of two interpenetrating FCC (left) or HCP (right) lattices; these correspond to the diamond (or zincblende) and the wurtzite lattices, respectively. The lattices are viewed from the side, with the vertical direction corresponding to the direction along which close-packed planes of the FCC or HCP lattices would be stacked (see Fig. 1.4). The two original lattices are denoted by sets of white and shaded circles. All the circles of medium size would lie on the plane of the paper, while the circles of slightly smaller and slightly larger size (which are superimposed in this view) lie on planes behind and in front of the plane of the paper. Lines joining the circles indicate covalent bonds between nearest neighbor atoms. **Bottom:** a perspective view of a portion of the diamond (or zincblende) lattice, showing the tetrahedral coordination of all the atoms; this is the area enclosed by the dashed rectangle in the top panel, left side (a corresponding area can also be identified in the wurtzite lattice, upon reflection).

(such as group III–group V, group II–group VI, group I–group VII) form the zincblende lattice; certain combinations of group III–group V elements form the wurtzite lattice. These structures are discussed in more detail below. A variation of the wurtzite lattice is also encountered in ice and is due to hydrogen bonding.

Yet another version of the close-packing arrangement is the icosahedral structure. In this case an atom again has 12 equidistant neighbors, which are at the apexes of an icosahedron. The icosahedron is one of the Platonic solids in which all the faces are perfect planar shapes; in the case of the icosahedron, the faces are 20 equilateral triangles. The icosahedron has 12 apexes arranged in five-fold symmetric rings,[2] as shown in Fig. 1.6. In fact, it turns out that the icosahedral arrangement is optimal for close packing of a small number of atoms, but it is not possible to fill

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[2] An n-fold symmetry means that rotation by $2\pi/n$ around an axis leaves the structure invariant.

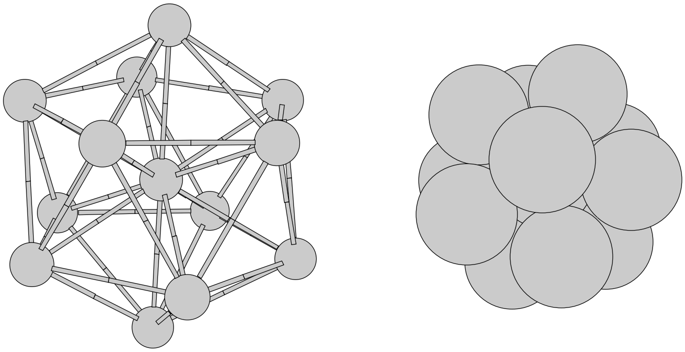

Figure 1.6. **Left:** one atom and its 12 neighbors in the icosahedral structure; the size of the spheres representing atoms is chosen so as to make the neighbors and their distances apparent. **Right:** a rendition of the icosahedron that illustrates its close-packing nature; this structure cannot be extended to form a periodic solid in three-dimensional space.

three-dimensional space in a periodic fashion with icosahedral symmetry. This fact is a simple geometrical consequence (see also chapter 3 on crystal symmetries). Based on this observation it was thought that crystals with perfect five-fold (or ten-fold) symmetry could not exist, unless defects were introduced to allow for deviations from the perfect symmetry [2–4]. The discovery of solids that exhibited five-fold or ten-fold symmetry in their diffraction patterns, in the mid 1980s [5], caused quite a sensation. These solids were named "quasicrystals", and their study created a new exciting subfield in condensed matter physics. They are discussed in more detail in chapter 12.

1.1.2 Atoms with s valence electrons

The second category consists of atoms that have only *s* valence electrons. These are Li, Na, K, Rb and Cs (the alkalis) with one valence electron, and Be, Mg, Ca, Sr and Ba with two valence electrons. The wavefunctions of valence electrons of all these elements extend far from the nucleus. In solids, the valence electron wavefunctions at one site have significant overlap with those at the nearest neighbor sites. Since the *s* states are spherically symmetric, the wavefunctions of valence electrons do not exhibit any particular preference for orientation of the nearest neighbors in space. For the atoms with one and two *s* valence electrons a simplified picture consists of all the valence electrons overlapping strongly, and thus being shared by all the atoms in the solid forming a "sea" of negative charge. The nuclei with their core electrons form ions, which are immersed in this sea of valence electrons. The ions have charge +1 for the alkalis and +2 for the atoms with two *s* valence electrons. The resulting crystal structure is the one which optimizes the electrostatic repulsion

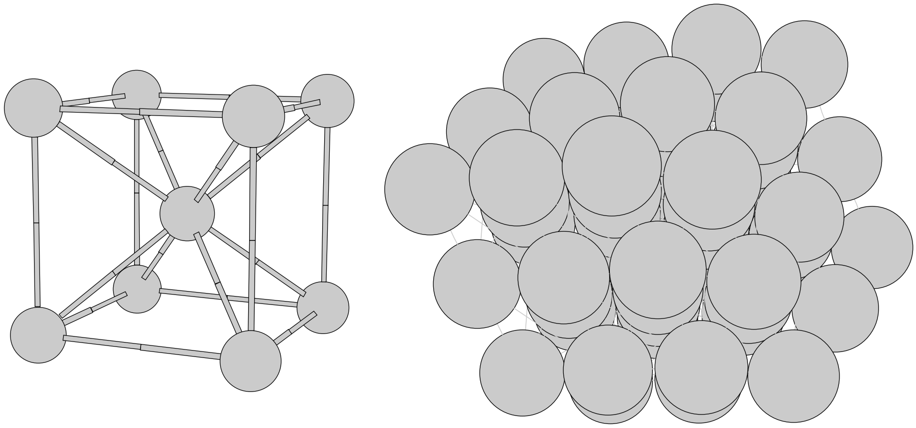

Figure 1.7. **Left:** one atom and its eight neighbors in the body-centered cubic (BCC) lattice; the size of the spheres representing atoms is chosen so as to make the neighbors and their distances apparent. **Right:** a portion of the three-dimensional BCC lattice; the size of the spheres is chosen so as to indicate the almost close-packing nature of this lattice.

of the positively charged ions with their attraction by the sea of electrons. The actual structures are body-centered cubic (BCC) for all the alkalis, and FCC or HCP for the two-s-valence-electron atoms, except Ba, which prefers the BCC structure. In the BCC structure each atom has eight equidistant nearest neighbors as shown in Fig. 1.7, which is the second highest number of nearest neighbors in a simple crystalline structure, after FCC and HCP.

One point deserves further clarification: we mentioned that the valence electrons have significant overlap with the electrons in neighboring atoms, and thus they are shared by all atoms in the solid, forming a sea of electrons. It may seem somewhat puzzling that we can jump from one statement – the overlap of electron orbitals in nearby atoms – to the other – the sharing of valence electrons by all atoms in the solid. The physical symmetry which allows us to make this jump is the periodicity of the crystalline lattice. This symmetry is the main feature of the external potential that the valence electrons feel in the bulk of a crystal: they are subjected to a periodic potential in space, in all three dimensions, which for all practical purposes extends to infinity – an idealized situation we discussed earlier. Just like in any quantum mechanical system, the electronic wavefunctions must obey the symmetry of the external potential, which means that the wavefunctions themselves must be periodic up to a phase. The mathematical formulation of this statement is called Bloch's theorem and will be considered in detail later. A periodic wavefunction implies that if two atoms in the crystal share an electronic state due to overlap between atomic orbitals, then all equivalent atoms of the crystal share the same state equally, that is, the electronic state is delocalized over the entire solid. This behavior is central to the physics of solids, and represents a feature that is qualitatively different from what happens in atoms and molecules, where electronic states are localized (except in certain large molecules that possess symmetries akin to lattice periodicity).

1.1.3 Atoms with s and p valence electrons

The next level of complexity in crystal structure arises from atoms that have both s and p valence electrons. The individual p states are not spherically symmetric so they can form linear combinations with the s states that have directional character: a single p state has two lobes of opposite sign pointing in diametrically opposite directions. The s and p states, illustrated in Fig. 1.8, can then serve as the new basis for representing electron wavefunctions, and their overlap with neighboring wavefunctions of the same type can lead to interesting ways of arranging the atoms into a stable crystalline lattice (see Appendix B on the character of atomic orbitals).

In the following we will use the symbols $s(\mathbf{r})$, $p_l(\mathbf{r})$, $d_m(\mathbf{r})$, to denote atomic orbitals as they would exist in an isolated atom, which are functions of $\mathbf{r}$. When they are related to an atom A at position $\mathbf{R}_A$, these become functions of $\mathbf{r} - \mathbf{R}_A$ and are denoted by $s^A(\mathbf{r})$, $p_l^A(\mathbf{r})$, $d_m^A(\mathbf{r})$. We use $\phi_i^A(\mathbf{r})(i = 1, 2, \ldots)$ to denote linear combinations of the atomic orbitals at site A, and $\psi^n(\mathbf{r})(n = a, b)$ for combinations of $\phi_i^X(\mathbf{r})$'s $(X = A, B, \ldots; i = 1, 2, \ldots)$ which are appropriate for the description of electronic states in the crystal.

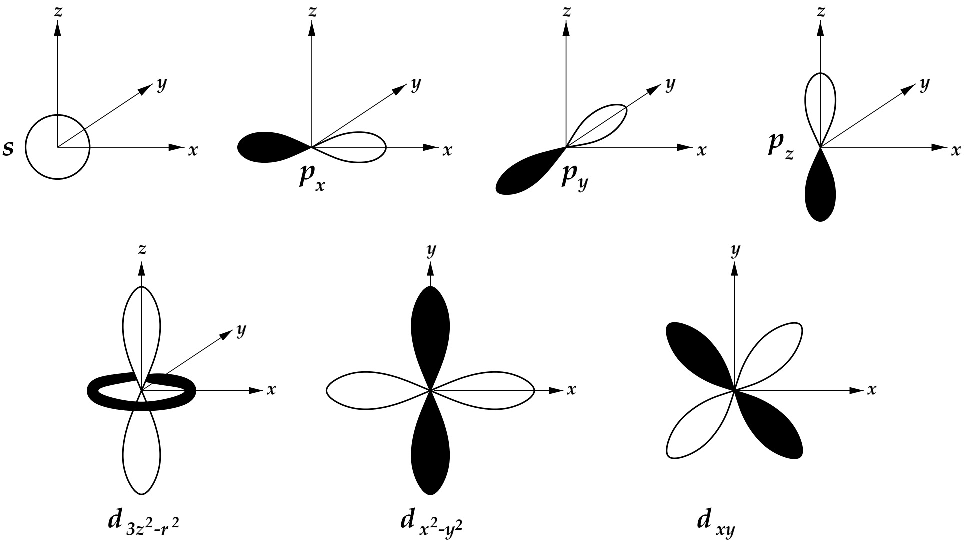

Figure 1.8. Representation of the character of s, p, d atomic orbitals. The lobes of opposite sign in the p_x, p_y, p_z and $d_{x^2-y^2}$, d_{xy} orbitals are shown shaded black and white. The d_{yz}, d_{zx} orbitals are similar to the d_{xy} orbital, but lie on the yz and zx planes.

The possibility of combining these atomic orbitals to form covalent bonds in a crystal is illustrated by the following two-dimensional example. For an atom, labeled A, with states s^A, p_x^A, p_y^A, p_z^A which are orthonormal, we consider first the linear combinations which constitute a new orthonormal basis of atomic orbitals:

$$\begin{aligned}
\phi_1^A &= \frac{1}{\sqrt{3}} s^A + \frac{\sqrt{2}}{\sqrt{3}} p_x^A \\
\phi_2^A &= \frac{1}{\sqrt{3}} s^A - \frac{1}{\sqrt{6}} p_x^A + \frac{1}{\sqrt{2}} p_y^A \\
\phi_3^A &= \frac{1}{\sqrt{3}} s^A - \frac{1}{\sqrt{6}} p_x^A - \frac{1}{\sqrt{2}} p_y^A \\
\phi_4^A &= p_z^A
\end{aligned} \tag{1.1}$$

The first three orbitals, $\phi_1^A, \phi_2^A, \phi_3^A$ point along three directions on the xy plane separated by 120°, while the last one, ϕ_4^A, points in a direction perpendicular to the xy plane, as shown in Fig. 1.9. It is easy to show that, if the atomic orbitals are orthonormal, and the states s^A, $p_i^A (i = x, y, z)$ have energies ϵ_s and ϵ_p, then the states $\phi_k (k = 1, 2, 3)$ have energy $(\epsilon_s + 2\epsilon_p)/3$; these states, since they are composed of one s and two p atomic orbitals, are called sp^2 orbitals. Imagine now a second identical atom, which we label B, with the following linear combinations:

$$\begin{aligned}
\phi_1^B &= \frac{1}{\sqrt{3}} s^B - \frac{\sqrt{2}}{\sqrt{3}} p_x^B \\
\phi_2^B &= \frac{1}{\sqrt{3}} s^B + \frac{1}{\sqrt{6}} p_x^B - \frac{1}{\sqrt{2}} p_y^B \\
\phi_3^B &= \frac{1}{\sqrt{3}} s^B + \frac{1}{\sqrt{6}} p_x^B + \frac{1}{\sqrt{2}} p_y^B \\
\phi_4^B &= p_z^B
\end{aligned} \tag{1.2}$$

The orbitals $\phi_1^B, \phi_2^B, \phi_3^B$ also point along three directions on the xy plane separated by 120°, but in the opposite sense (rotated by 180°) from those of atom A. For example, ϕ_1^A points along the $+\hat{\mathbf{x}}$ direction, while ϕ_1^B points along the $-\hat{\mathbf{x}}$ direction. Now imagine that we place atoms A and B next to each other along the x axis, first atom A and to its right atom B, at a distance a. We arrange the distance so that there is significant overlap between orbitals ϕ_1^A and ϕ_1^B, which are pointing toward each other, thereby maximizing the interaction between these two orbitals. Let us assume that in the neutral isolated state of the atom we can occupy each of these orbitals by one electron; note that this is *not* the ground state of the atom. We can form two linear combinations, $\psi_1^b = \frac{1}{2}(\phi_1^A + \phi_1^B)$ and $\psi_1^a = \frac{1}{2}(\phi_1^A - \phi_1^B)$ of which the first

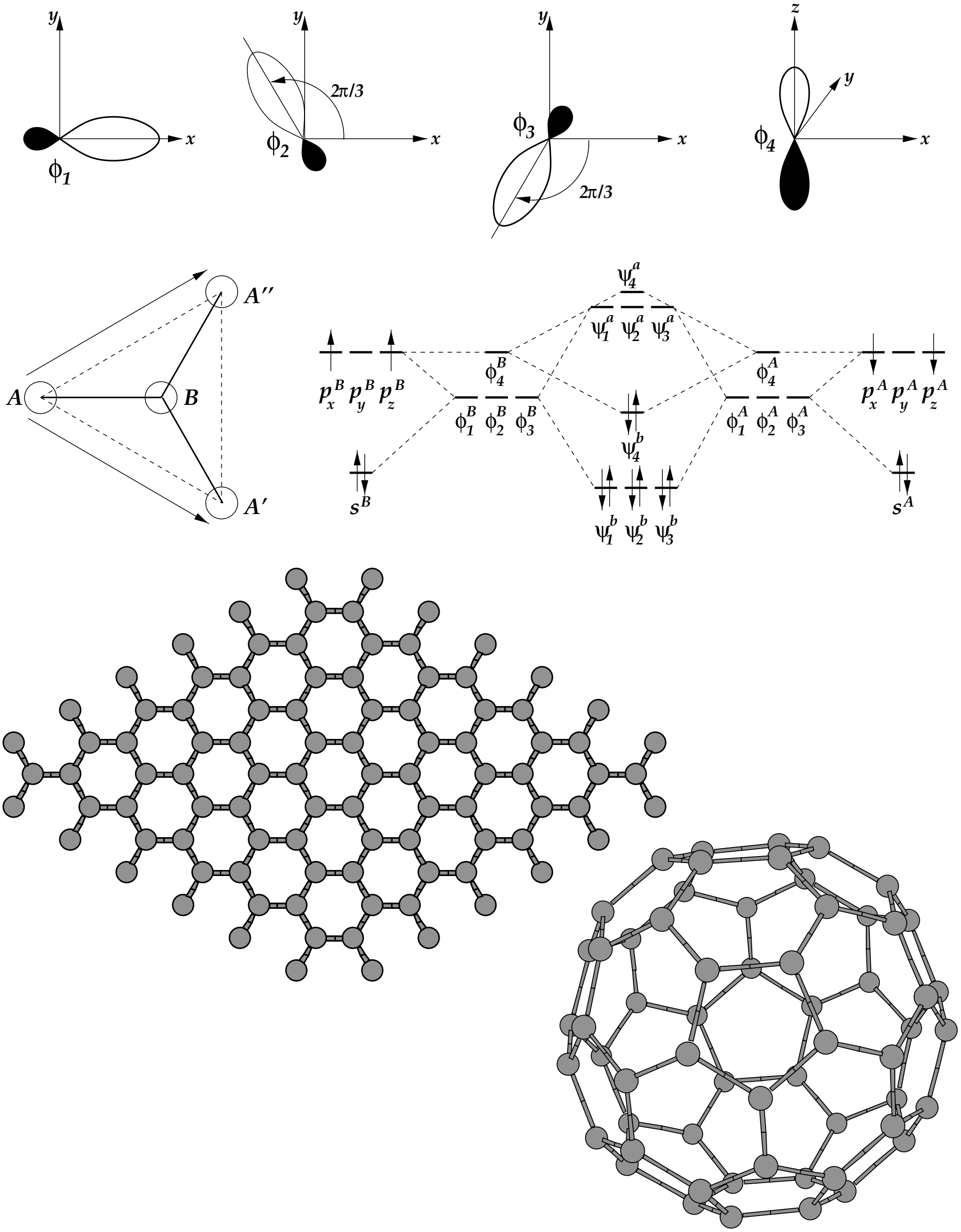

Figure 1.9. Illustration of covalent bonding in graphite. **Top:** the sp^2 linear combinations of s and p atomic orbitals (defined in Eq. (1.1)). **Middle:** the arrangement of atoms on a plane with B at the center of an equilateral triangle formed by A, A', A'' (the arrows connect equivalent atoms); the energy level diagram for the s, p atomic states, their sp^2 linear combinations (ϕ_i^A and ϕ_i^B) and the bonding (ψ_i^b) and antibonding (ψ_i^a) states (up–down arrows indicate electrons spins). **Bottom:** the graphitic plane (honeycomb lattice) and the C_{60} molecule.

maximizes the overlap and the second has a node at the midpoint between atoms A and B. As usual, we expect the symmetric linear combination of single-particle orbitals (called the bonding state) to have lower energy than the antisymmetric one (called the antibonding state) in the system of the two atoms; this is a general feature of how combinations of single-particle orbitals behave (see Problem 2). The exact energy of the bonding and antibonding states will depend on the overlap of the orbitals ϕ_1^A, ϕ_1^B. We can place two electrons, one from each atomic orbital, in the symmetric linear combination because of their spin degree of freedom; this is based on the assumption that the spin wavefunction of the two electrons is antisymmetric (a spin singlet), so that the total wavefunction, the product of the spatial and spin parts, is antisymmetric upon exchange of their coordinates, as it should be due to their fermionic nature. Through this exercise we have managed to lower the energy of the system, since the energy of ψ^b is lower than the energy of ϕ_1^A or ϕ_1^B. This is the essence of the chemical bond between two atoms, which in this case is called a covalent σ bond.

Imagine next that we repeat this exercise: we take another atom with the same linear combinations of orbitals as A, which we will call A', and place it in the direction of the vector $\frac{1}{2}\hat{\mathbf{x}} - \frac{\sqrt{3}}{2}\hat{\mathbf{y}}$ relative to the position of atom B, and at the same distance a as atom A from B. Due to our choice of orbitals, ϕ_2^B and $\phi_2^{A'}$ will be pointing toward each other. We can form symmetric and antisymmetric combinations from them, occupy the symmetric (lower energy) one with two electrons as before and create a second σ bond between atoms B and A'. Finally we repeat this procedure with a third atom A'' placed along the direction of the vector $\frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}$ relative to the position of atom B, and at the same distance a as the previous two neighbors. Through the same procedure we can form a third σ bond between atoms B and A'', by forming the symmetric and antisymmetric linear combinations of the orbitals ϕ_3^B and $\phi_3^{A''}$. Now, as far as atom B is concerned, its three neighbors are exactly equivalent, so we consider the vectors that connect them as the repeat vectors at which equivalent atoms in the crystal should exist. If we place atoms of type A at all the possible integer multiples of these vectors, we form a lattice. To complete the lattice we have to place atoms of type B also at all the possible integer multiples of the same vectors, relative to the position of the original atom B. The resulting lattice is called the honeycomb lattice. Each atom of type A is surrounded by three atoms of type B and vice versa, as illustrated in Fig. 1.9. Though this example may seem oversimplified, it actually corresponds to the structure of graphite, one of the most stable crystalline solids. In graphite, planes of C atoms in the honeycomb lattice are placed on top of each other to form a three-dimensional solid, but the interaction between planes is rather weak (similar to the van der Waals interaction). An indication of this weak bonding between planes compared to the in-plane bonds is that the distance between nearest neighbor atoms on a plane is 1.42 Å, whereas the distance between successive planes is 3.35 Å, a factor of 2.36 larger.

What about the orbitals p_z (or ϕ_4), which so far have not been used? If each atom had only three valence electrons, then these orbitals would be left empty since they have higher energy than the orbitals ϕ_1, ϕ_2, ϕ_3, which are linear combinations of s and p orbitals (the original s atomic orbitals have lower energy than p). In the case of C, each atom has four valence electrons so there is one electron left per atom when all the σ bonds have been formed. These electrons remain in the p_z orbitals, which are perpendicular to the xy plane and thus parallel to each other. Symmetric and antisymmetric combinations of neighboring p_z^A and p_z^B orbitals can also be formed (the states ψ_4^b, ψ_4^a, respectively), and the energy can be lowered by occupying the symmetric combination. In this case the overlap between neighboring p_z orbitals is significantly smaller and the corresponding gain in energy significantly less than in σ bonds. This is referred to as a π bond, which is generally weaker than a σ bond. Carbon is a special case, in which the π bonds are almost as strong as the σ bonds.

An intriguing variation of this theme is a structure that contains pentagonal rings as well as the regular hexagons of the honeycomb lattice, while maintaining the three-fold coordination and bonding of the graphitic plane. The presence of pentagons introduces curvature in the structure, and the right combination of pentagonal and hexagonal rings produces the almost perfect sphere, shown in Fig. 1.9. This structure actually exists in nature! It was discovered in 1985 and it has revolutionized carbon chemistry and physics – its discoverers, R. F. Curl, H. W. Kroto and R. E. Smalley, received the 1996 Nobel prize for Chemistry. Many more interesting variations of this structure have also been produced, including "onions" – spheres within spheres – and "tubes" – cylindrical arrangements of three-fold coordinated carbon atoms. The tubes in particular seem promising for applications in technologically and biologically relevant systems. These structures have been nicknamed after Buckminster Fuller, an American scientist and practical inventor of the early 20th century, who designed architectural domes based on pentagons and hexagons; the nicknames are buckminsterfullerene or bucky-ball for C_{60}, bucky-onions, and bucky-tubes. The physics of these structures will be discussed in detail in chapter 13.

There is a different way of forming bonds between C atoms: consider the following linear combinations of the s and p atomic orbitals for atom A:

$$\begin{aligned}
\phi_1^A &= \frac{1}{2}[s^A - p_x^A - p_y^A - p_z^A] \\
\phi_2^A &= \frac{1}{2}[s^A + p_x^A - p_y^A + p_z^A] \\
\phi_3^A &= \frac{1}{2}[s^A + p_x^A + p_y^A - p_z^A] \\
\phi_4^A &= \frac{1}{2}[s^A - p_x^A + p_y^A + p_z^A]
\end{aligned} \tag{1.3}$$

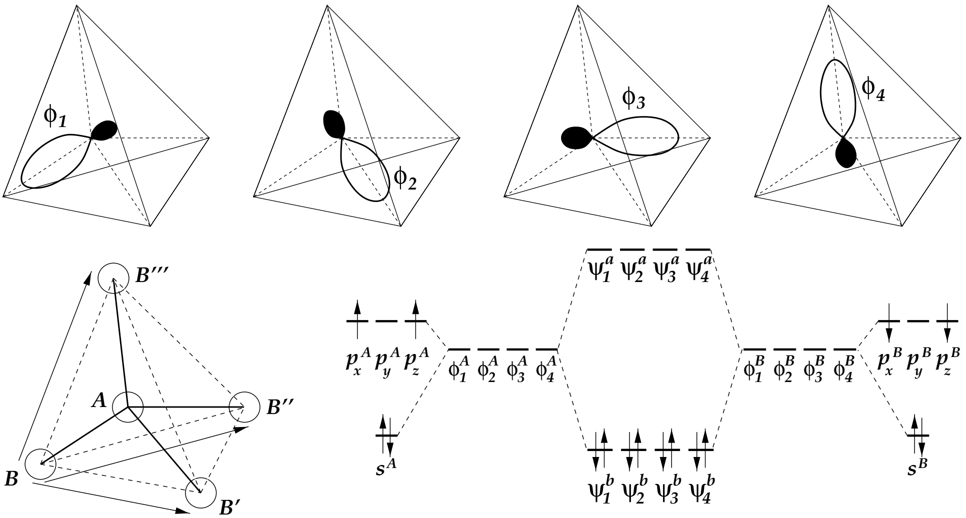

Figure 1.10. Illustration of covalent bonding in diamond. **Top panel:** representation of the sp^3 linear combinations of s and p atomic orbitals appropriate for the diamond structure, as defined in Eq. (1.3), using the same convention as in Fig. 1.8. **Bottom panel:** on the left side, the arrangement of atoms in the three-dimensional diamond lattice; an atom A is at the center of a regular tetrahedron (dashed lines) formed by equivalent B, B', B'', B''' atoms; the three arrows are the vectors that connect equivalent atoms. On the right side, the energy level diagram for the s, p atomic states, their sp^3 linear combinations (ϕ_i^A and ϕ_i^B) and the bonding (ψ_i^b) and antibonding (ψ_i^a) states. The up–down arrows indicate occupation by electrons in the two possible spin states. For a perspective view of the diamond lattice, see Fig. 1.5.

It is easy to show that the energy of these states, which are degenerate, is equal to $(\epsilon_s + 3\epsilon_p)/4$, where ϵ_s, ϵ_p are the energies of the original s and p atomic orbitals; the new states, which are composed of one s and three p orbitals, are called sp^3 orbitals. These orbitals point along the directions from the center to the corners of a regular tetrahedron, as illustrated in Fig. 1.10. We can now imagine placing atoms B, B', B'', B''' at the corners of the tetrahedron, with which we associate linear combinations of s and p orbitals just like those for atom A, but having all the signs of the p orbitals reversed:

$$
\begin{aligned}
\phi_1^B &= \frac{1}{2}[s^B + p_x^B + p_y^B + p_z^B] \\
\phi_2^B &= \frac{1}{2}[s^B - p_x^B + p_y^B - p_z^B] \\
\phi_3^B &= \frac{1}{2}[s^B - p_x^B - p_y^B + p_z^B] \\
\phi_4^B &= \frac{1}{2}[s^B + p_x^B - p_y^B - p_z^B]
\end{aligned}
\qquad (1.4)
$$

Then we will have a situation where the ϕ orbitals on neighboring A and B atoms will be pointing toward each other, and we can form symmetric and antisymmetric combinations of those, ψ^b, ψ^a, respectively, to create four σ bonds around atom A. The exact energy of the ψ orbitals will depend on the overlap between the ϕ^A and ϕ^B orbitals; for sufficiently strong overlap, we can expect the energy of the ψ^b states to be lower than the original s atomic orbitals and those of the ψ^a states to be higher than the original p atomic orbitals, as shown schematically in Fig. 1.10. The vectors connecting the equivalent B, B', B'', B''' atoms define the repeat vectors at which atoms must be placed to form an infinite crystal. By placing both A-type and B-type atoms at all the possible integer multiples of these vectors we create the diamond lattice, shown in Fig. 1.10. This is the other stable form of bulk C. Since C has four valence electrons and each atom at the center of a tetrahedron forms four σ bonds with its neighbors, all electrons are taken up by the bonding states. This results in a very stable and strong three-dimensional crystal. Surprisingly, graphite has a somewhat lower internal energy than diamond, that is, the thermodynamically stable solid form of carbon is the soft, black, cheap graphite rather than the very strong, brilliant and very expensive diamond crystal!

The diamond lattice, with four neighbors per atom, is relatively open compared to the close-packed lattices. Its stability comes from the very strong covalent bonds formed between the atoms. Two other elements with four valence s and p electrons, namely Si and Ge, also crystallize in the diamond, but not the graphite, lattice. There are two more elements with four valence s and p electrons in the Periodic Table, Sn and Pb. Sn forms crystal structures that are distorted variants of the diamond lattice, since its σ bonds are not as strong as those of the other group-IV-A elements, and it can gain some energy by increasing the number of neighbors (from four to six) at the expense of perfect tetrahedral σ bonds. Pb, on the other hand, behaves more like a metal, preferring to optimize the number of neighbors, and forms the FCC crystal (see also below). Interestingly, elements with only three valence s and p electrons, like B, Al, Ga, In and Tl, do not form the graphite structure, as alluded above. They instead form more complex structures in which they try to optimize bonding given their relatively small number of valence electrons per atom. Some examples: the common structural unit for B is the icosahedron, shown in Fig. 1.6, and such units are close packed to form the solid; Al forms the FCC crystal and is the representative metal with s and p electrons and a close-packed structure; Ga forms quite complicated crystal structures with six or seven near neighbors (not all of them at the same distance); In forms a distorted version of the cubic close packing in which the 12 neighbors are split into a group of four and another group of eight equidistant atoms. None of these structures can be easily described in terms of the notions introduced above to handle s and p valence electrons, demonstrating the limitations of this simple approach.

Of the other elements in the Periodic Table with s and p valence electrons, those with five electrons, N, P, As, Sb and Bi, tend to form complex structures where atoms have three σ bonds to their neighbors but not in a planar configuration. A characteristic structure is one in which the three p valence electrons participate in covalent bonding while the two s electrons form a filled state which does not contribute much to the cohesion of the solid; this filled state is called the "lone pair" state. If the covalent bonds were composed of purely p orbitals the bond angles between nearest neighbors would be 90°; instead, the covalent bonds in these structures are a combination of s and p orbitals with predominant p character, and the bond angles are somewhere between 120° (sp^2 bonding) and 90° (pure p bonding), as illustrated in Fig. 1.11. The structure of solid P is represented by this kind of atomic arrangement. In this structure, the covalent bonds are arranged in puckered hexagons which form planes, and the planes are stacked on top of each other to form the solid. The interaction between planes is much weaker than that between atoms on a single plane: an indication of this difference in bonding is the fact that the distance between nearest neighbors in a plane is 2.17 Å while the closest distance between atoms on successive planes is 3.87 Å, almost a factor of 2 larger. The structures of As, Sb and Bi follow the same general pattern with three-fold bonded atoms, but in those solids there exist additional covalent bonds between the planes of puckered atoms so that the structure is not clearly planar as is the case for P. An exception to this general tendency is nitrogen, the lightest element with five valence electrons which forms a crystal composed of nitrogen molecules; the N_2 unit is particularly stable.

The elements with six s and p valence electrons, O, S, Se, Te and Po, tend to form molecular-like ring or chain structures with two nearest neighbors per atom, which are then packed to form three-dimensional crystals. These rings or chains are puckered and form bonds at angles that try to satisfy bonding requirements analogous to those described for the solids with four s and p valence electrons. Examples of such units are shown in Fig. 1.12. Since these elements have a valence of 6, they tend to keep four of their electrons in one filled s and one filled p orbital and form covalent bonds to two neighbors with their other two p orbitals. This picture is somewhat oversimplified, since significant hybridization takes place between s and p orbitals that participate in bonding, so that the preferred angle between the bonding orbitals is not 90°, as pure p bonding would imply, but ranges between 102° and 108°. Typical distances between nearest neighbor atoms in the rings or the chains are 2.06 Å for S, 2.32 Å for Se and 2.86 Å for Te, while typical distances between atoms in successive units are 3.50 Å for S, 3.46 Å for Se and 3.74 Å for Te; that is, the ratio of distances between atoms within a bonding unit and across bonding units is 1.7 for S, 1.5 for Se and 1.3 for Te. An exception

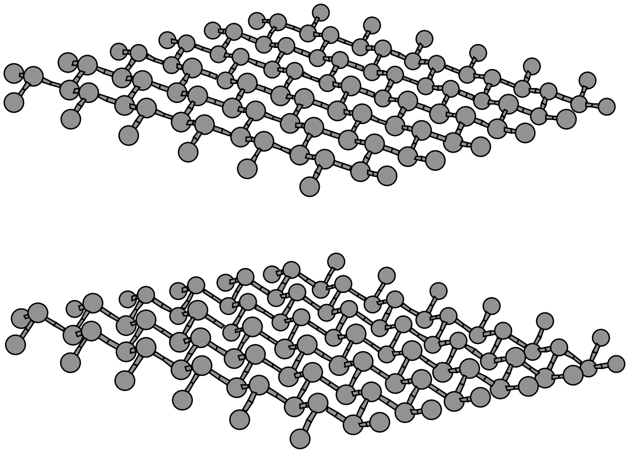

Figure 1.11. The layers of buckled atoms that correspond to the structure of group-V elements: all atoms are three-fold coordinated as in a graphitic plane, but the bond angles between nearest neighbors are not 120° and hence the atoms do not lie on the plane. For illustration two levels of buckling are shown: in the first structure the bond angles are 108°, in the second 95°. The planes are stacked on top of each other as in graphite to form the 3D solids.

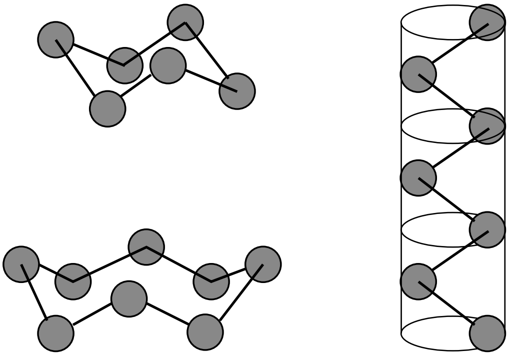

Figure 1.12. Characteristic units that appear in the solid forms of S, Se and Te: six-fold rings (S), eight-fold rings (Se) and one-dimensional chains (Se and Te). The solids are formed by close packing of these units.

to this general tendency is oxygen, the lightest element with six valence electrons which forms a crystal composed of oxygen molecules; the O_2 unit is particularly stable. The theme of diatomic molecules as the basic unit of the crystal, already mentioned for nitrogen and oxygen, is common in elements with seven *s* and *p* valence electrons also: chlorine, bromine and iodine form solids by close packing of diatomic molecules.

1.1.4 Atoms with s and d valence electrons

This category includes all the atoms in the middle columns of the Periodic Table, that is, columns I-B–VII-B and VIII. The *d* orbitals in atoms have directional nature like the *p* orbitals. However, since there are five *d* orbitals it is difficult to construct linear combinations with *s* orbitals that would neatly point toward nearest neighbors in three-dimensional space and produce a crystal with simple σ bonds. Moreover, the *d* valence orbitals typically lie lower in energy than the *s* valence orbitals and therefore do not participate as much in bonding (see for example the discussion about Ag, in chapter 4). Note that *d* orbitals *can* form strong covalent bonds by combining with *p* orbitals of other elements, as we discuss in a subsequent section. Thus, elements with *s* and *d* valence electrons tend to form solids where the *s* electrons are shared among all atoms in the lattice, just like elements with one or two *s* valence electrons. These elements form space-filling close-packed crystals, of the FCC, HCP and BCC type. There are very few exceptions to this general tendency, namely Mn, which forms a very complex structure with a cubic lattice and a very large number of atoms (58) in the unit cell, and Hg, which forms a low-symmetry rhombohedral structure. Even those structures, however, are slight variations of the basic close-packing structures already mentioned. For instance, the Mn structure, in which atoms have from 12 to 16 neighbors, is a slight variation of the BCC structure. The crystals formed by most of these elements typically have metallic character.

1.1.5 Atoms with s, d and f valence electrons

The same general trends are found in the rare earth elements, which are grouped in the lanthanides (atomic numbers 58–71) and the actinides (atomic numbers 90 and beyond) . Of those we discuss briefly the lanthanides as the more common of the rare earths that are found in solids. In these elements the *f* shell is gradually filled as the atomic number increases, starting with an occupation of two electrons in Ce and completing the shell with 14 electrons in Lu. The *f* orbitals have directional character which is even more complicated than that of *p* or *d* orbitals. The solids formed by these elements are typically close-packed structures such as FCC and HCP, with a couple of exceptions (Sm which has rhombohedral structure and Eu which has BCC structure). They are metallic solids with high atomic densities. However, more interesting are structures formed by these elements and other elements of the Periodic Table, in which the complex character of the *f* orbitals can be exploited in combination with orbitals from neighboring atoms to form strong bonds. Alternatively, these elements are used as dopants in complicated crystals, where they donate some of their electrons to states formed by other atoms. One such example is discussed in the following sections.

1.1.6 Solids with two types of atoms

Some of the most interesting and useful solids involve two types of atoms, which in some ways are complementary. One example that comes immediately to mind are solids composed of atoms in the first (group I-A) and seventh (group VII-A) columns of the Periodic Table, which have one and seven valence electrons, respectively. Solids composed of such elements are referred to as "alkali halides". It is natural to expect that the atom with one valence electron will lose it to the more electronegative atom with the seven valence electrons, which then acquires a closed electronic shell, completing the s and p levels. This of course leads to one positively and one negatively charged ion, which are repeated periodically in space to form a lattice. The easiest way to arrange such atoms is at the corners of a cube, with alternating corners occupied by atoms of the opposite type. This arrangement results in the sodium chloride (NaCl) or rock-salt structure, one of the most common crystals. Many combinations of group I-A and group VII-A atoms form this kind of crystal. In this case each ion has six nearest neighbors of the opposite type. A different way to arrange the ions is to have one ion at the center of a cube formed by ions of the opposite type. This arrangement forms two interpenetrating cubic lattices and is known as the cesium chloride (CsCl) structure. In this case each ion has eight nearest neighbors of the opposite type. Several combinations of group I-A and group VII-A atoms crystallize in this structure. Since in all these structures the group I-A atoms lose their s valence electron to the group VII-A atoms, this type of crystal is representative of ionic bonding. Both of these ionic structures are shown in Fig. 1.13.

Another way of achieving a stable lattice composed of two kinds of ions with opposite sign, is to place them in the two interpenetrating FCC sublattices of the diamond lattice, described earlier. In this case each ion has four nearest neighbors of the opposite type, as shown in Fig. 1.14. Many combinations of atoms in the I-B column of the Periodic Table and group VII-B atoms crystallize in this structure, which is called the zincblende structure from the German term for ZnS, the representative solid with this lattice.

The elements in the I-B column have a filled d-shell (ten electrons) and one extra s valence electron, so it is natural to expect them to behave in some ways similar to the alkali metals. However, the small number of neighbors in this structure, as opposed to the rock-salt and cesium chloride structures, suggest that the cohesion of these solids cannot be attributed to simple ionic bonding alone. In fact, this becomes more pronounced when atoms from the second (group II-B) and sixth (group VI-A)

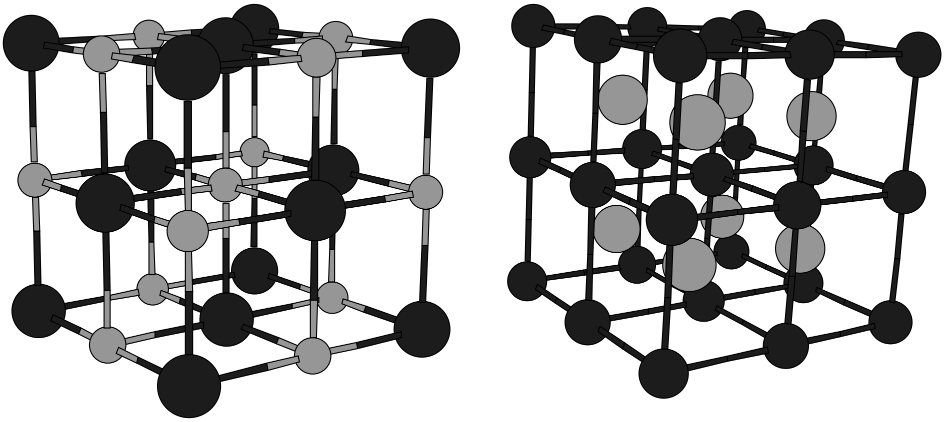

Figure 1.13. **Left:** the rock-salt, NaCl, structure, in which the ions form a simple cubic lattice with each ion surrounded by six neighbors of the opposite type. **Right:** the CsCl structure, in which the ions form a body-centered cubic lattice with each ion surrounded by eight neighbors of the opposite type.

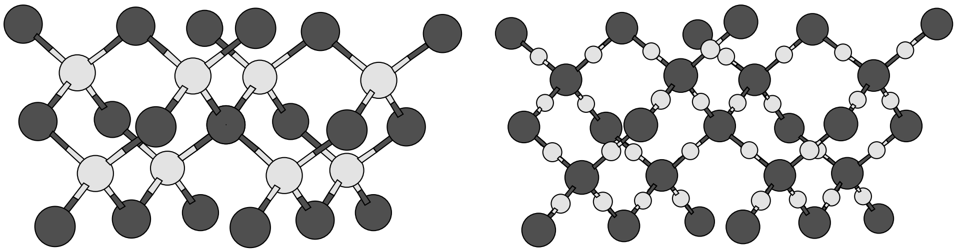

Figure 1.14. **Left:** the zincblende lattice in which every atom is surrounded by four neighbors of the opposite type, in mixed ionic and covalent bonding; several III-V, II-VI and IV-IV solids exist in this lattice. **Right:** a representative SiO_2 structure, in which each Si atom has four O neighbors, and each O atom has two Si neighbors.

columns of the Periodic Table form the zincblende structure (ZnS itself is the prime example). In this case we would have to assume that the group II atoms lose their two electrons to the group VI atoms, but since the electronegativity difference is not as great between these two types of elements as between group I-A and group VII-A elements, something more than ionic bonding must be involved. Indeed the crystals of group II and group VI atoms in the zincblende structure are good examples of mixed ionic and covalent bonding. This trend extends to one more class of solids: group III-A and group V-A atoms also form zincblende crystals, for example AlP, GaAs, InSb, etc. In this case, the bonding is even more tilted toward covalent character, similar to the case of group IV atoms which form the diamond lattice. Finally, there are combinations of two group IV atoms that form the zincblende structure; some interesting examples are SiC and GeSi alloys.

A variation on this theme is a class of solids composed of Si and O. In these solids, each Si atom has four O neighbors and is situated at the center of a tetrahedron, while each O atom has two Si neighbors, as illustrated in Fig. 1.14. In this manner the valence of both Si and O are perfectly satisfied, so that the structure can be thought of as covalently bonded. Due to the large electronegativity of O, the covalent bonds are polarized to a large extent, so that the two types of atoms can be considered as partially ionized. This results again in a mixture of covalent and ionic bonding. The tetrahedra of Si–O atoms are very stable units and the relative positions of atoms in a tetrahedron are essentially fixed. The position of these tetrahedra relative to each other, however, can be changed with little cost in energy, because this type of structural distortion involves only a slight bending of bond angles, without changing bond lengths. This freedom in relative tetrahedron orientation produces a very wide variety of solids based on this structural unit, including amorphous structures, such as common glass, and structures with many open spaces in them, such as the zeolites.

1.1.7 Hydrogen: a special one-*s*-valence-electron atom

So far we have left H out of the discussion. This is because H is a special case: it has no core electrons. Its interaction with the other elements, as well as between H atoms, is unusual, because when H tries to share its one valence *s* electron with other atoms, what is left is a bare proton rather than a nucleus shielded partially by core electrons. The proton is an ion much smaller in size than the other ions produced by stripping the valence electrons from atoms: its size is 10^{-15} m, five orders of magnitude smaller than typical ions, which have a size of order 1 Å. It also has the smallest mass, which gives it a special character: in all other cases (except for He) we can consider the ions as classical particles, due to their large mass, while in the case of hydrogen, its light mass implies a large zero-point motion which makes it necessary to take into account the quantum nature of the proton's motion. Yet another difference between hydrogen and all other elements is the fact that its *s* valence electron is very strongly bound to the nucleus: the ionization energy is 13.6 eV, whereas typical ionization energies of valence electrons in other elements are in the range 1–2 eV. Due to its special character, H forms a special type of bond called "hydrogen bond". This is encountered in many structures composed of molecules that contain H atoms, such as organic molecules and water.

The solid in which hydrogen bonding plays the most crucial role is ice. Ice forms many complex phases [6]; in its ordinary phase called Ih, the H_2O molecules are placed so that the O atoms occupy the sites of a wurtzite lattice (see Fig. 1.5), while the H atoms are along lines that join O atoms [7]. There are two H atoms attached to each O atom by short covalent bonds (of length 1.00 Å), while the distance between O atoms is 2.75 Å. There is one H atom along each line joining two O atoms. The

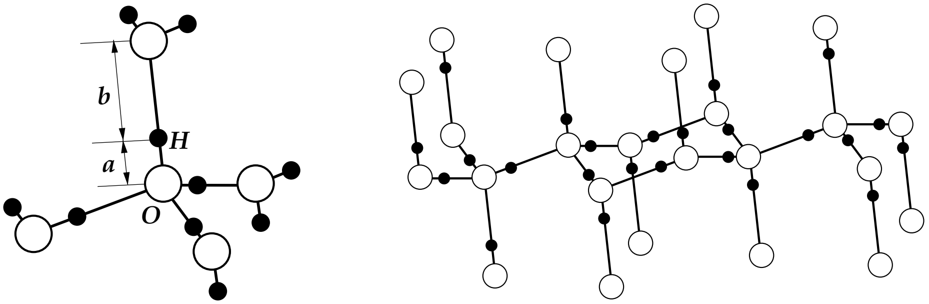

Figure 1.15. **Left:** illustration of hydrogen bonding between water molecules in ice: the O atom is at the center of a tetrahedron fromed by other O atoms, and the H atoms are along the directions joining the center to the corners of the tetrahedron. The O–H covalent bond distance is $a = 1.00$ Å, while the H–O hydrogen bond distance is $b = 1.75$ Å. The relative position of atoms is not given to scale, in order to make it easier to visualize which H atoms are attached by covalent bonds to the O atoms. **Right:** illustration of the structure of Ih ice: the O atoms sit at the sites of a wurtzite lattice (compare with Fig. 1.5) and the H atoms are along the lines joining O atoms; there is one H atom along each such line, and two H atoms are bonded by short covalent bonds to each O atom.

bond between a H atom and an O atom to which it is *not* covalently bonded is called a hydrogen bond, and, in this system, has length 1.75 Å; it is these hydrogen bonds that give stability to the crystal. This is illustrated in Fig. 1.15. The hydrogen bond is much weaker than the covalent bond between H and O in the water molecule: the energy of the hydrogen bond is 0.3 eV, while that of the covalent H–O bond is 4.8 eV. There are many ways of arranging the H atoms within these constraints for a fixed lattice of O atoms, giving rise to a large configurational entropy. Other forms of ice have different lattices, but this motif of local bonding is common.

Within the atomic orbital picture discussed earlier for solids with s and p electrons, we can construct a simple argument to rationalize hydrogen bonding in the case of ice. The O atom has six valence electrons in its s and p shells and therefore needs two more electrons to complete its electronic structure. The two H atoms that are attached to it to form the water molecule provide these two extra electrons, at the cost of an anisotropic bonding arrangement (a completed electronic shell should be isotropic, as in the case of Ne which has two more electrons than O). The cores of the H atoms (the protons), having lost their electrons to O, experience a Coulomb repulsion. The most favorable structure for the molecule which optimizes this repulsion would be to place the two H atoms in diametrically opposite positions relative to the O atom, but this would involve only one p orbital of the O atom to which both H atoms would bond. This is an unfavorable situation as far as formation of covalent bonds is concerned, because it is not possible to form two covalent bonds with only one *p* orbital and two electrons from the O atom. A compromise between the desire to form strong covalent bonds and the repulsion between the H cores is the formation of four sp^3 hybrids from the orbitals of the O atom, two of which form covalent bonds with the H atoms, while the other two are filled by two electrons each. This produces a tetrahedral structure with two lobes which have more positive charge (the two sp^3 orbitals to which the H atoms are bonded) than the other two lobes (the two sp^3 orbitals which are occupied by two electrons each). It is natural to expect that bringing similar molecular units together would produce some attraction between the lobes of opposite charge in neighboring units. This is precisely the arrangement of molecules in the structure of ice discussed above and shown in Fig. 1.15. This rationalization, however, is somewhat misleading as it suggests that the hydrogen bond, corresponding to the attraction between oppositely charged lobes of the H_2O tetrahedra, is essentially ionic. In fact, the hydrogen bond has significant covalent character as well: the two types of orbitals pointing toward each other form bonding (symmetric) and antibonding (antisymmetric) combinations leading to covalent bonds between them. This point of view was originally suggested by Pauling [8] and has remained controversial until recently, when sophisticated scattering experiments and quantum mechanical calculations provided convincing evidence in its support [9].

The solid phases of pure hydrogen are also unusual. At low pressure and temperature, H is expected to form a crystal composed of H_2 molecules in which every molecule behaves almost like an inert unit, with very weak interactions to the other molecules. At higher pressure, H is supposed to form an atomic solid when the molecules have approached each other enough so that their electronic distributions are forced to overlap strongly [10]. However, the conditions of pressure and temperature at which this transition occurs, and the structure of the ensuing atomic solid, are still a subject of active research [11–13]. The latest estimates are that it takes more than 3 Mbar of pressure to form the atomic H solid, which can only be reached under very special conditions in the laboratory, and which has been achieved only in the 1990s. There is considerable debate about what the crystal structure at this pressure should be, and although the BCC structure seems to be the most likely phase, by analogy to all other alkalis, this has not been unambiguously proven to date.

1.1.8 Solids with many types of atoms

If we allow several types of atoms to participate in the formation of a crystal, many more possibilities open up. There are indeed many solids with complex composition, but the types of bonding that occur in these situations are variants of

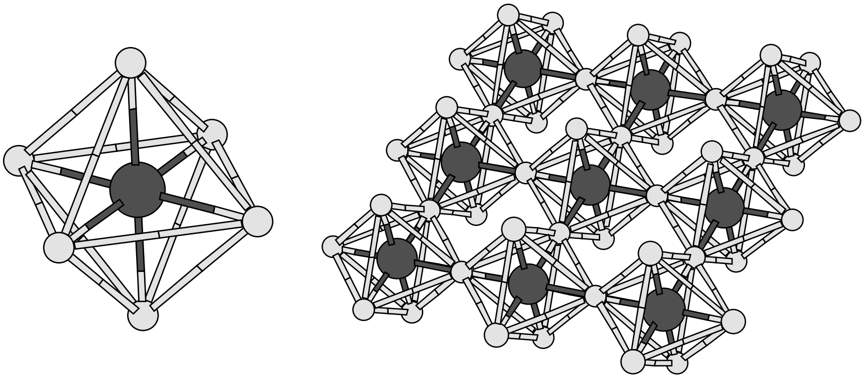

Figure 1.16. **Left:** a Cu atom surrounded by six O atoms, which form an octahedron; the Cu–O atoms are bonded by strong covalent bonds. **Right:** a set of corner-sharing O octahedra, forming a two-dimensional square lattice. The octahedra can also be joined at the remaining apexes to form a fully three-dimensional lattice. The empty spaces between the octahedra can accommodate atoms which are easily ionized, to produce a mixed covalent–ionic structure.

the types we have already discussed: metallic, covalent, ionic, van der Waals and hydrogen bonding. In many situations, several of these types of bonding are present simultaneously.

One interesting example of such complex structures is the class of ceramic materials in which high-temperature superconductivity (HTSC) was observed in the mid-1980s (this discovery, by J. G. Bednorz and K. A. Müller, was recongnized by the 1987 Nobel prize for Physics). In these materials strong covalent bonding between Cu and O forms one-dimensional or two-dimensional structures where the basic building block is oxygen octahedra; rare earth atoms are then placed at hollow positions of these backbond structures, and become partially ionized giving rise to mixed ionic and covalent bonding (see, for example, Fig. 1.16).

The motif of oxygen octahedra with a metal atom at the center to which the O atoms are covalently bonded, supplemented by atoms which are easily ionized, is also the basis for a class of structures called “perovskites”. The chemical formula of perovskites is ABO_3, where A is the easily ionized element and B the element which is bonded to the oxygens. The basic unit is shown in Fig. 1.17: bonding in the xy plane is accomplished through the overlap between the p_x and p_y orbitals of the first (O_1) and second (O_2) oxygen atoms, respectively, and the $d_{x^2-y^2}$ orbital of B; bonding along the z axis is accomplished through the overlap between the p_z orbital of the third (O_3) oxygen atom and the $d_{3z^2-r^2}$ orbital of B (see Fig. 1.8 for the nature of these p and d orbitals). The A atoms provide the necessary number of electrons to satisfy all the covalent bonds. Thus, the overall bonding involves

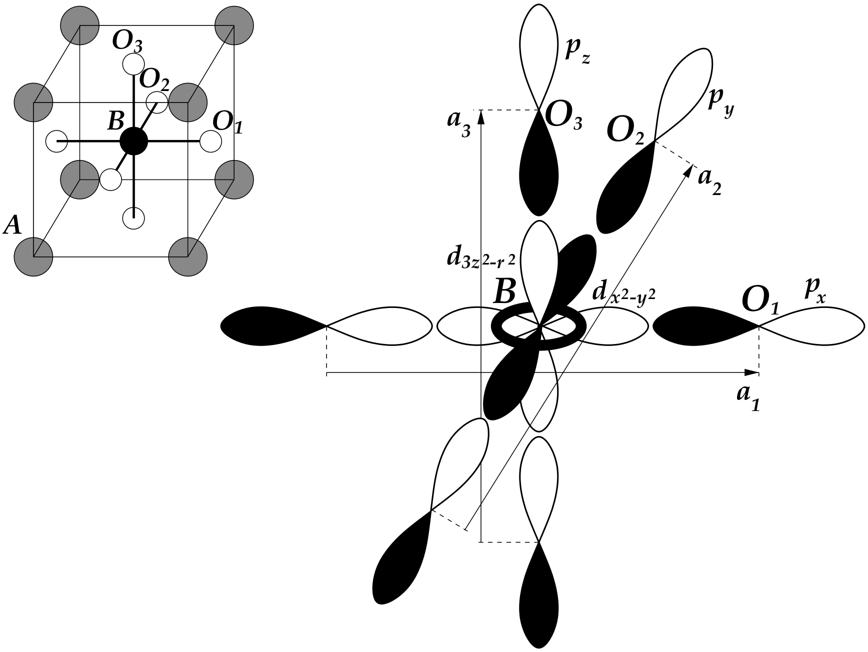

Figure 1.17. The basic structural unit of perovskites ABO_3 (upper left) and the atomic orbitals that contribute to covalent bonding. The three distinct oxygen atoms in the unit cell are labeled O_1, O_2, O_3 (shown as the small open circles in the structural unit); the remaining oxygen atoms are related to those by the repeat vectors of the crystal, indicated as $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. The six oxygen atoms form an octahedron at the center of which sits the B atom. The thin lines outline the cubic unit cell, while the thicker lines between the oxygen atoms and B represent the covalent bonds in the structural unit. The p_x, p_y, p_z orbitals of the three O atoms and the $d_{x^2-y^2}$, $d_{3z^2-r^2}$ orbitals of the B atoms that participate in the formation of covalent bonds in the octahedron are shown schematically.

both strong covalent character between B and O, as well as ionic character between the B–O units and the A atoms. The complexity of the structure gives rise to several interesting properties, such as ferroelectricity, that is, the ability of the solid to acquire and maintain an internal dipole moment. The dipole moment is associated with a displacement of the B atom away from the center of the octahedron, which breaks the symmetry of the cubic lattice. These solids have very intriguing behavior: when external pressure is applied on them it tends to change the shape of the unit cell of the crystal and therefore produces an electrical response since it affects the internal dipole moment; conversely, an external electric field can also affect the internal dipole moment and the solid changes its shape to accommodate it. This coupling of mechanical and electrical responses is very useful for practical applications, such as sensors and actuators and non-volatile memories. The solids that exhibit this behavior are called piezoelectrics; some examples are $CaTiO_3$

(calcium titanate), $PbTiO_3$ (lead titanate), $BaTiO_3$ (barium titanate), $PbZrO_3$ (lead zirconate).

Another example of complex solids is the class of crystals formed by fullerene clusters and alkali metals: there is strong covalent bonding between C atoms in each fullerene cluster, weak van der Waals bonding between the fullerenes, and ionic bonding between the alkali atoms and the fullerene units. The clusters act just like the group VII atoms in ionic solids, taking up the electrons of the alkali atoms and becoming ionized. It is intriguing that these solids also exhibit superconductivity at relatively high temperatures!

1.2 Bonding in solids

In our discussion on the formation of solids from atoms we encountered five general types of bonding in solids:

(1) *Van der Waals bonding*, which is formed by atoms that do not have valence electrons available for sharing (the noble elements), and is rather weak; the solids produced in this way are not particularly stable.
(2) *Metallic bonding*, which is formed when electrons are shared by all the atoms in the solid, producing a uniform "sea" of negative charge; the solids produced in this way are the usual metals.
(3) *Covalent bonding*, which is formed when electrons in well defined directional orbitals, which can be thought of as linear combinations of the original atomic orbitals, have strong overlap with similar orbitals in neighboring atoms; the solids produced in this way are semiconductors or insulators.
(4) *Ionic bonding*, which is formed when two different types of atoms are combined, one that prefers to lose some of its valence electrons and become a positive ion, and one that prefers to grab electrons from other atoms and become a negative ion. Combinations of such elements are I–VII, II–VI, and III–V. In the first case bonding is purely ionic, in the other two there is a degree of covalent bonding present.
(5) *Hydrogen bonding*, which is formed when H is present, due to its lack of core electrons, its light mass and high ionization energy.

For some of these cases, it is possible to estimate the strength of bonding without involving a detailed description of the electronic behavior. Specifically, for van der Waals bonding and for purely ionic bonding it is sufficient to assume simple classical models. For van der Waals bonding, one assumes that there is an attractive potential between the atoms which behaves like $\sim r^{-6}$ with distance r between atoms (this behavior can actually be derived from perturbation theory, see Problem 4). The potential must become repulsive at very short range, as the electronic densities of the two atoms start overlapping, but electrons have no incentive to form bonding states (as was the case in covalent bonding) since all electronic shells are already

Table 1.1. *Parameters for the Lennard–Jones potential for noble gases.* For the calculation of $\hbar\omega$ using the Lennard–Jones parameters see the following discussion and Table 1.2.

	Ne	Ar	Kr	Xe
ϵ (meV)	3.1	10.4	14.0	20.0
a (Å)	2.74	3.40	3.65	3.98
$\hbar\omega$ (meV)	2.213	2.310	1.722	1.510

Original sources: see Ashcroft and Mermin [14].

filled. For convenience the attractive part is taken to be proportional to r^{-12}, which gives the famous Lennard–Jones 6–12 potential:

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{a}{r}\right)^{12} - \left(\frac{a}{r}\right)^{6} \right] \tag{1.5}$$

with ϵ and a constants that determine the energy and length scales. These have been determined for the different elements by referring to the thermodynamic properties of the noble gases; the parameters for the usual noble gas elements are shown in Table 1.1.

Use of this potential can then provide a quantitative measure of cohesion in these solids. One measure of the strength of these potentials is the vibrational frequency that would correspond to a harmonic oscillator potential with the same curvature at the minimum; this is indicative of the stiffness of the bond between atoms. In Table 1.1 we present the frequencies corresponding to the Lennard–Jones potentials of the common noble gas elements (see following discussion and Table 1.2 for the relation between this frequency and the Lennard–Jones potential parameters). For comparison, the vibrational frequency of the H_2 molecule, the simplest type of covalent bond between two atoms, is about 500 meV, more than two orders of magnitude larger; the Lennard–Jones potentials for the noble gases correspond to very soft bonds indeed!

A potential of similar nature, also used to describe effective interactions between atoms, is the Morse potential:

$$V_M(r) = \epsilon \left[\mathrm{e}^{-2(r-r_0)/b} - 2\mathrm{e}^{-(r-r_0)/b} \right] \tag{1.6}$$

where again ϵ and b are the constants that determine the energy and length scales and r_0 is the position of the minimum energy. It is instructive to compare these two potentials with the harmonic oscillator potential, which has the same minimum and

Table 1.2. *Comparison of the three effective potentials, Lennard–Jones $V_{LJ}(r)$, Morse $V_M(r)$, and harmonic oscillator $V_{HO}(r)$.*

The relations between the parameters that ensure the three potentials have the same minimum and curvature at the minimum are also given (the parameters of the Morse and harmonic oscillator potentials are expressed in terms of the Lennard–Jones parameters).

	$V_{LJ}(r)$	$V_M(r)$	$V_{HO}(r)$
Potential	$4\epsilon\left[\left(\frac{a}{r}\right)^{12}-\left(\frac{a}{r}\right)^{6}\right]$	$\epsilon\left[\mathrm{e}^{-2(r-r_0)/b}-2\mathrm{e}^{-(r-r_0)/b}\right]$	$-\epsilon+\frac{1}{2}m\omega^2(r-r_0)^2$
V_{min}	$-\epsilon$	$-\epsilon$	$-\epsilon$
r_{min}	$(2^{\frac{1}{6}})a$	r_0	r_0
$V''(r_{min})$	$(72/2^{\frac{1}{3}})(\epsilon/a^2)$	$2(\epsilon/b^2)$	$m\omega^2$
Relations		$r_0=(2^{\frac{1}{6}})a$	$r_0=(2^{\frac{1}{6}})a$
		$b=(2^{\frac{1}{6}}/6)a$	$\omega=(432^{\frac{1}{3}})\sqrt{\epsilon/ma^2}$

curvature, given by:

$$V_{HO}(r)=-\epsilon+\frac{1}{2}m\omega^2(r-r_0)^2 \tag{1.7}$$

with ω the frequency, m the mass of the particle in the potential and r_0 the position of the minimum.

The definitions of the three potentials are such that they all have the same value of the energy at their minimum, namely $-\epsilon$. The relations between the values of the other parameters which ensure that the minimum in the energy occurs at the same value of r and that the curvature at the minimum is the same are given in Table 1.2; a plot of the three potentials with these parameters is given in Fig. 1.18. The harmonic oscillator potential is what we would expect near the equilibrium of any normal interaction potential. The other two potentials extend the range far from the minimum; both potentials have a much sharper increase of the energy for distances shorter than the equilibrium value, and a much weaker increase of the energy for distances larger than the equilibrium value, relative to the harmonic oscillator. The overall behavior of the two potentials is quite similar. One advantage of the Morse potential is that it can be solved exactly, by analogy to the harmonic oscillator potential (see Appendix B). This allows a comparison between the energy levels associated with this potential and the corresponding energy levels of the harmonic oscillator; the latter are given by:

$$E_n^{HO}=\left(n+\frac{1}{2}\right)\hbar\omega \tag{1.8}$$

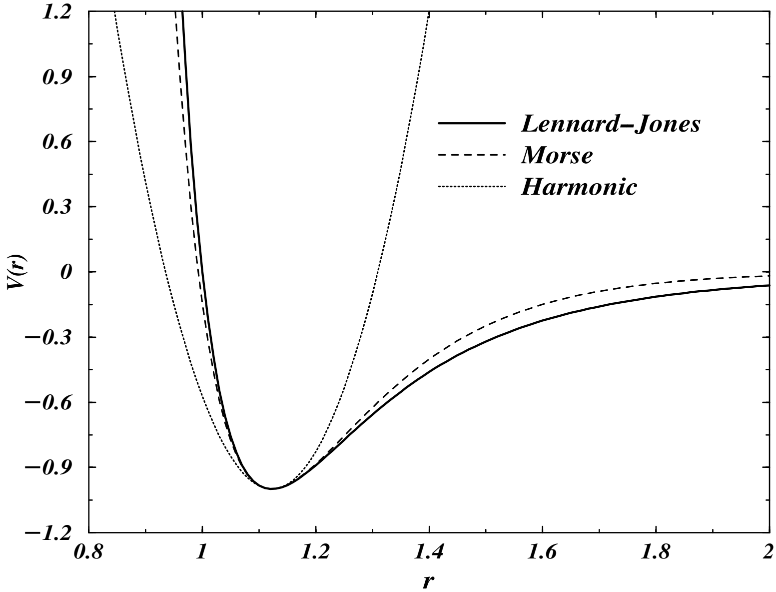

Figure 1.18. The three effective potentials discussed in the text, Lennard–Jones Eq. (1.5), Morse Eq. (1.6) and harmonic oscillator Eq. (1.7), with same minimum and curvature at the minimum. The energy is given in units of ϵ and the distance in units of a, the two parameters of the Lennard–Jones potential.

with n the integer index of the levels, whereas those of the Morse potential are given by:

$$E_n^M = \left(n + \frac{1}{2}\right)\hbar\omega \left[1 - \frac{\hbar\omega}{4\epsilon}\left(n + \frac{1}{2}\right)\right] \tag{1.9}$$

for the parameters defined in Table 1.2. We thus see that the spacing of levels in the Morse potential is smaller than in the corresponding harmonic oscillator, and that it becomes progressively smaller as the index of the levels increases. This is expected from the behavior of the potential mentioned above, and in particular from its asymptotic approach to zero for large distances. Since the Lennard–Jones potential has an overall shape similar to the Morse potential, we expect its energy levels to behave in the same manner.

For purely ionic bonding, one assumes that what keeps the crystal together is the attractive interaction between the positively and negatively charged ions, again in a purely classical picture. For the ionic solids with rock-salt, cesium chloride and zincblende lattices we have discussed already, it is possible to calculate the cohesive energy, which only depends on the ionic charges, the crystal structure and the distance between ions. This is called the Madelung energy. The only difficulty is that the summation converges very slowly, because the interaction potential

(Coulomb) is long range. In fact, formally this sum does not converge, and any simple way of summing successive terms gives results that depend on the choice of terms. The formal way for treating periodic structures, which we will develop in chapter 3, makes the calculation of the Madelung energy through the Ewald summation trick much more efficient (see Appendix F).

The other types of bonding, metallic, covalent and mixed bonding, are much more difficult to describe quantitatively. For metallic bonding, even if we think of the electrons as a uniform sea, we need to know the energy of this uniform "liquid" of fermions, which is not a trivial matter. This will be the subject of the next chapter. In addition to the electronic contributions, we have to consider the energy of the positive ions that exist in the uniform negative background of the electron sea. This is another Madelung sum, which converges very slowly. As far as covalent bonding is concerned, although the approach we used by combining atomic orbitals is conceptually simple, much more information is required to render it a realistic tool for calculations, and the electron interactions again come into play in an important way. This will also be discussed in detail in subsequent chapters.

The descriptions that we mentioned for the metallic and covalent solids are also referred to by more technical terms. The metallic sea of electrons paradigm is referred to as the "jellium" model in the extreme case when the ions (atoms stripped of their valence electrons) are considered to form a uniform positive background; in this limit the crystal itself does not play an important role, other than it provides the background for forming the electronic sea. The description of the covalent bonding paradigm is referred to as the Linear Combination of Atomic Orbitals (LCAO) approach, since it relies on the use of a basis of atomic orbitals in linear combinations that make the bonding arrangement transparent, as was explained above for the graphite and diamond lattices. We will revisit these notions in more detail.

Further reading

We collect here a number of general books on the physics of solids. Material in these books goes well beyond the topics covered in the present chapter and is relevant to many other topics covered in subsequent chapters.

1. *Solid State Physics*, N.W. Ashcroft and N.D. Mermin (Saunders College Publishing, Philadelphia, 1976).
   This is a comprehensive and indispensable source on the physics of solids; it provides an inspired coverage of most topics that had been the focus of research up to its publication.
2. *Introduction to Solid State Theory*, O.Madelung (Springer-Verlag, Berlin, Heidelberg, 1981).