Atomic and Electronic Structure of Solids

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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)

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[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.

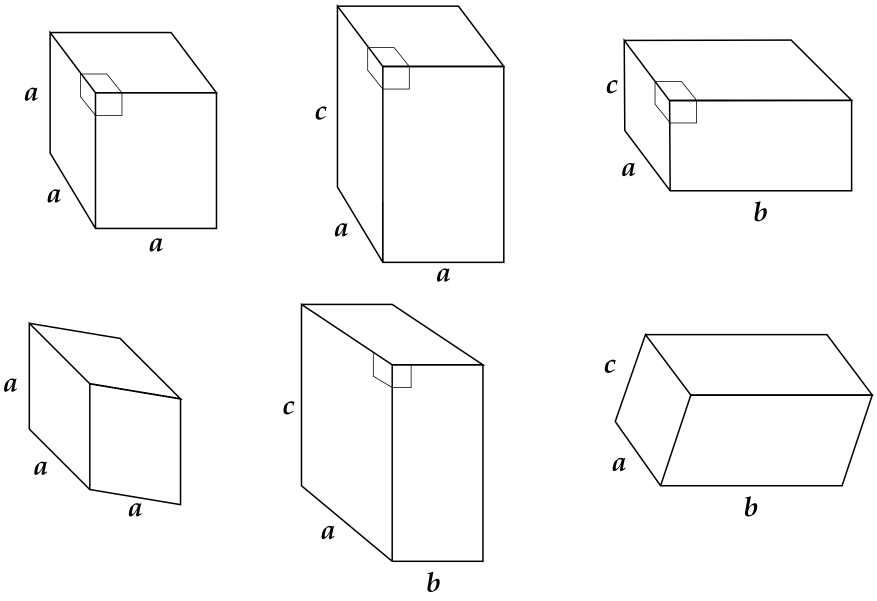

Figure 1.1. Shapes of the unit cells in some lattices that appear in Periodic Table. **Top row:** cubic, tetragonal, orthorhombic. **Bottom row:** rhombohedral, monoclinic, triclinic. The corners in thin lines indicate right angles between edges.

- 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,

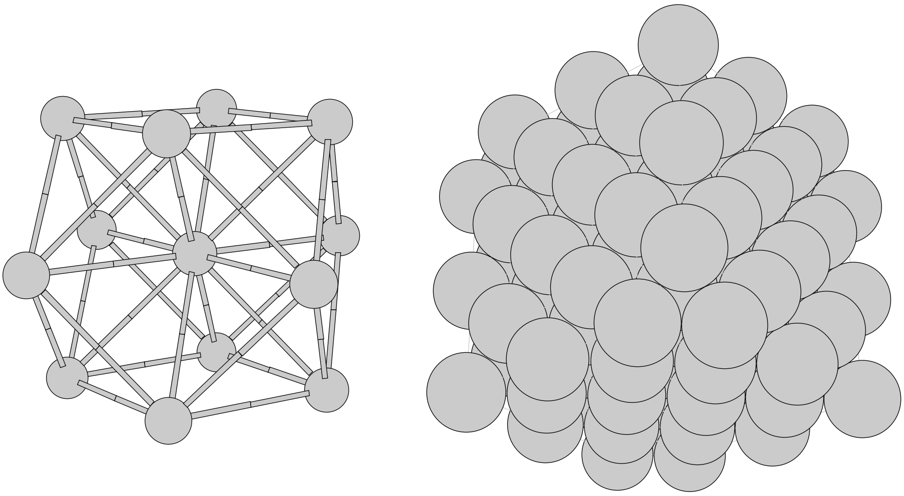

Figure 1.2. **Left:** one atom and its 12 neighbors in the face-centered cubic (FCC) lattice; the size of the spheres representing atoms is chosen so as to make the neighbors and their distances apparent. **Right:** a portion of the three-dimensional FCC lattice; the size of the spheres is chosen so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

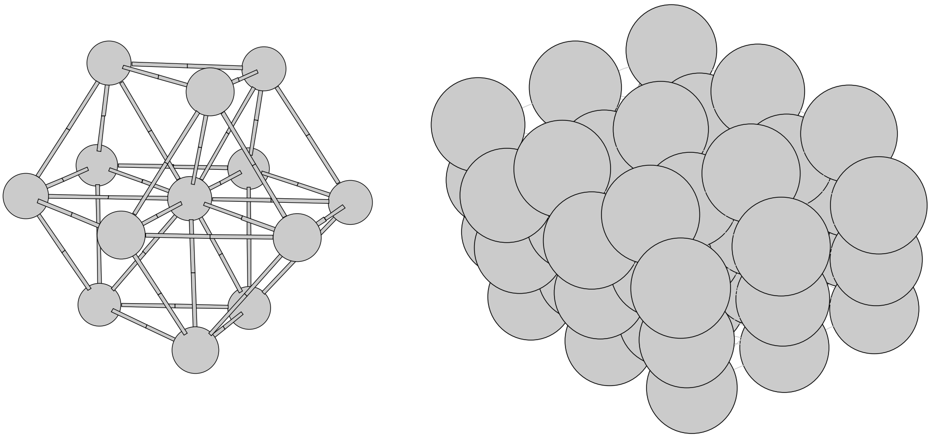

Figure 1.3. **Left:** one atom and its 12 neighbors in the hexagonal-close-packed (HCP) lattice; the size of the spheres representing atoms is chosen so as to make the neighbors and their distances apparent. **Right:** a portion of the three-dimensional HCP lattice; the size of the spheres is chosen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

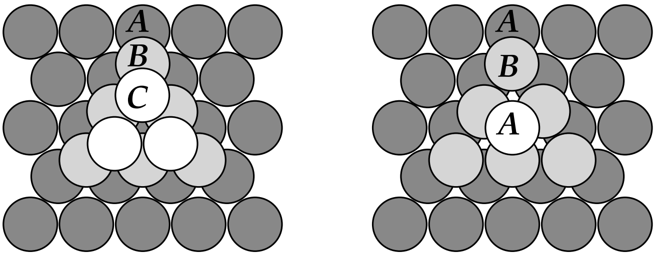

Figure 1.4. The two possible close packings of spheres: **Left:** the ...$ABCABC$... stacking corresponding to the FCC crystal. **Right:** the ...$ABABAB$... stacking corresponding to the HCP crystal. The lattices are viewed along the direction of stacking of the hexagonal-close-packed planes.

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

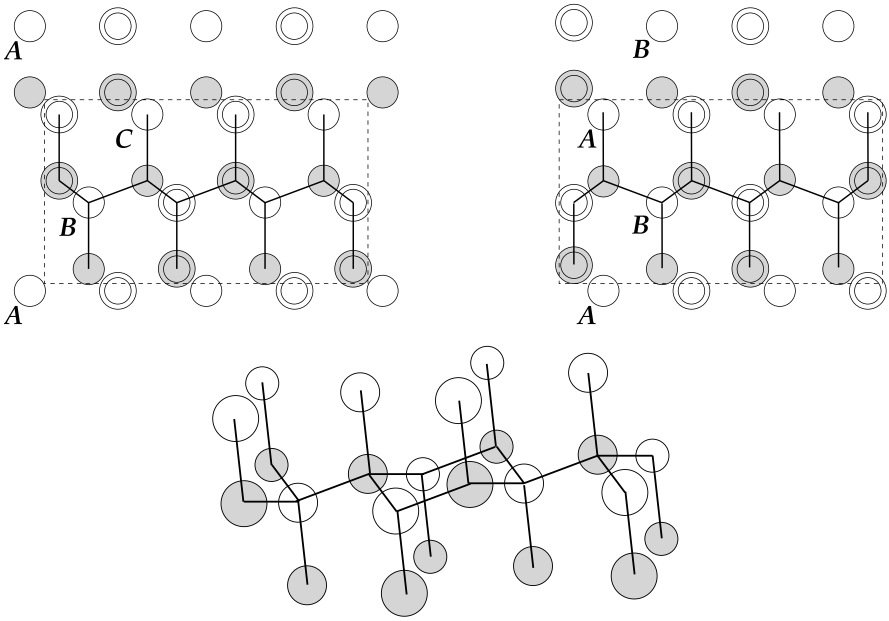

Figure 1.5. **Top:** illustration of two interpenetrating FCC (left) or HCP (right) lattices; these correspond to the diamond (or zincblende) and the wurtzite lattices, respectively. The lattices are viewed from the side, with the vertical direction corresponding to the direction along which close-packed 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.

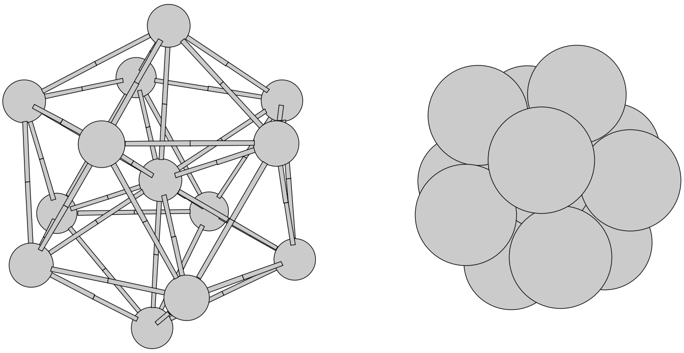

Figure 1.6. **Left:** one atom and its 12 neighbors in the icosahedral structure; the size of the spheres representing atoms is chosen so as to make the neighbors and their distances apparent. **Right:** a rendition of the icosahedron that illustrates its close-packing nature; this structure cannot be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

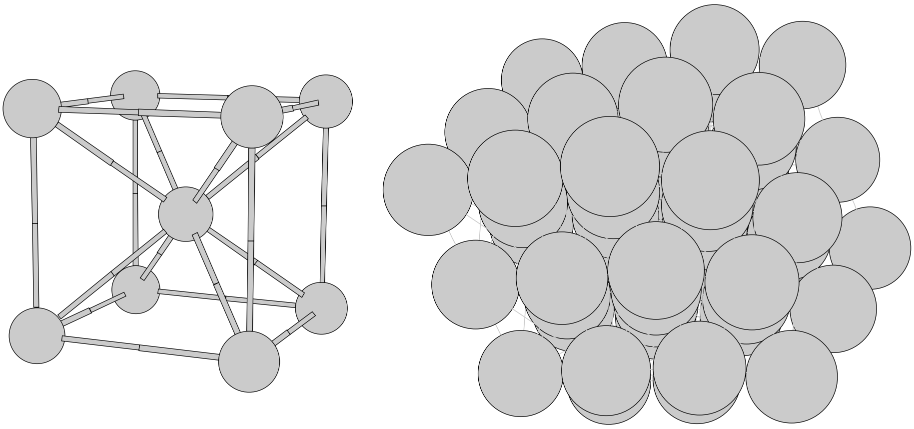

Figure 1.7. **Left:** one atom and its eight neighbors in the body-centered cubic (BCC) lattice; the size of the spheres representing atoms is chosen so as to make the neighbors and their distances apparent. **Right:** a portion of the three-dimensional BCC lattice; the size of the spheres is chosen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

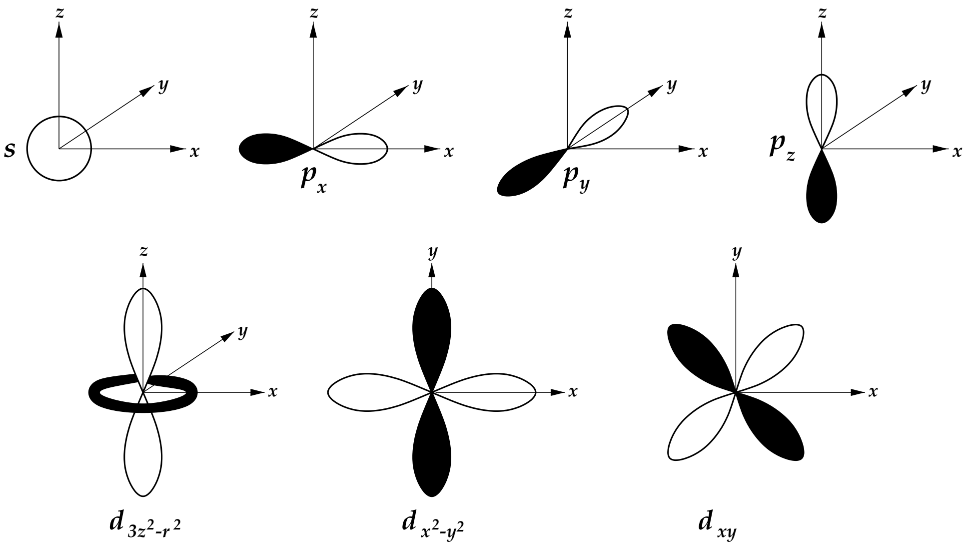

Figure 1.8. Representation of the character of s, p, d atomic orbitals. The lobes of opposite sign in the p_x, p_y, p_z and $d_{x^2-y^2}$, d_{xy} orbitals are shown shaded black and white. The d_{yz}, d_{zx} orbitals are similar to the d_{xy} orbital, but lie on the yz and zx planes.

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

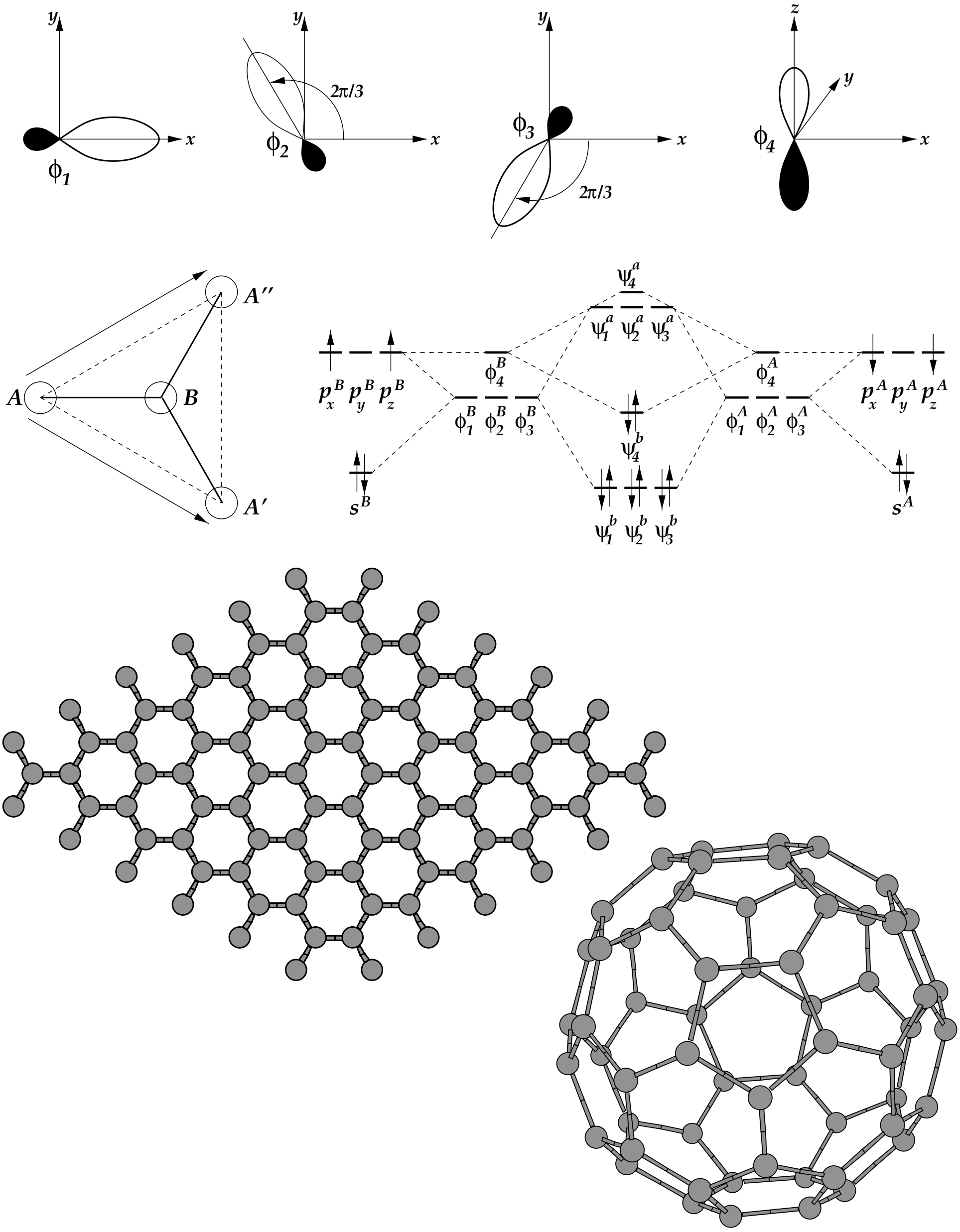

Figure 1.9. Illustration of covalent bonding in graphite. **Top:** the sp^2 linear combinations of s and p atomic orbitals (defined in Eq. (1.1)). **Middle:** the arrangement of atoms on a plane with B at the center of an equilateral triangle formed by A, A', A'' (the arrows connect equivalent atoms); 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:

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

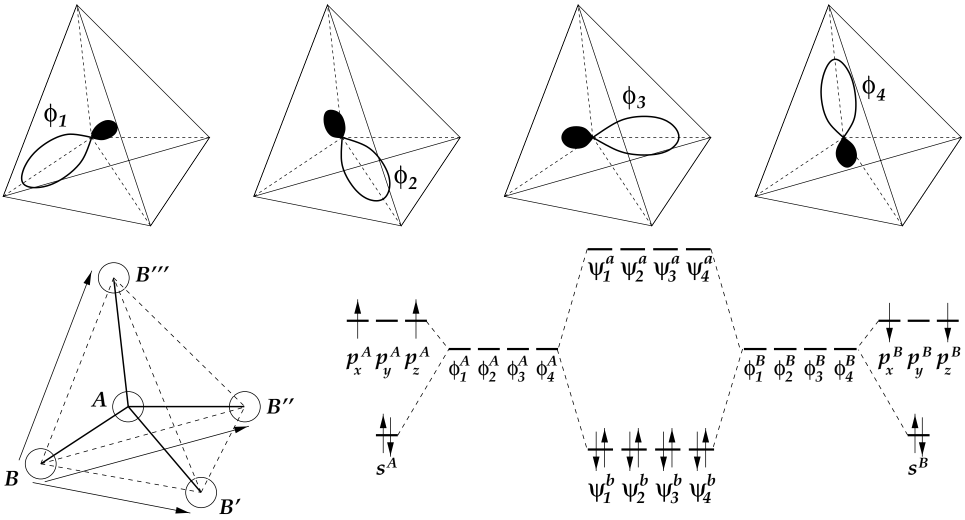

Figure 1.10. Illustration of covalent bonding in diamond. **Top panel:** representation of the sp^3 linear combinations of s and p atomic orbitals appropriate for the diamond structure, as defined in Eq. (1.3), using the same convention as in Fig. 1.8. **Bottom panel:** on the left side, the arrangement 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:

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

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

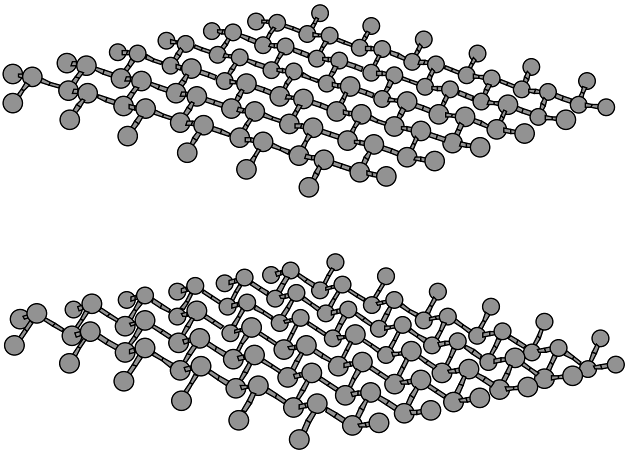

Figure 1.11. The layers of buckled atoms that correspond to the structure of group-V elements: all atoms are three-fold coordinated as in a graphitic plane, but the bond angles between nearest neighbors are not 120° and hence the atoms do not lie on the plane. For illustration two levels of buckling 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.

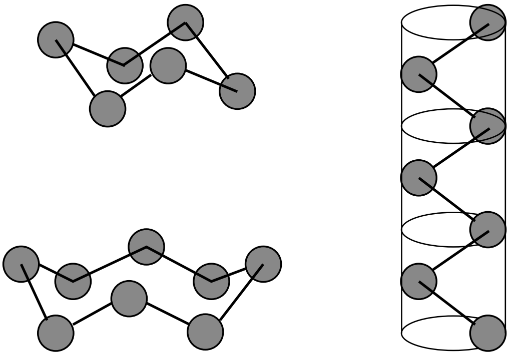

Figure 1.12. Characteristic units that appear in the solid forms of S, Se and Te: six-fold rings (S), eight-fold rings (Se) and one-dimensional chains (Se and Te). The solids are formed by close packing of these units.

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.