

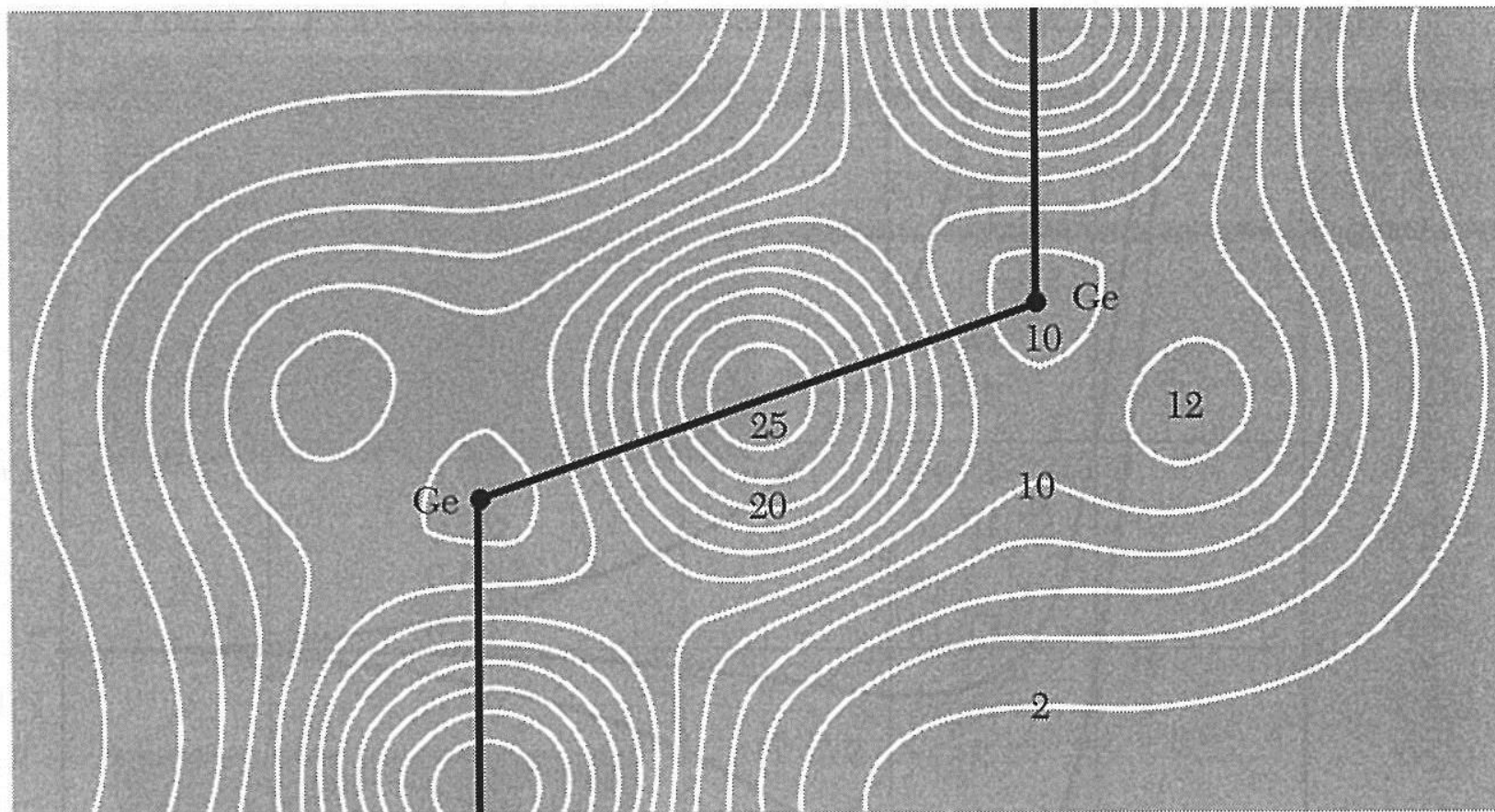
## COVALENT CRYSTALS

The covalent bond is the classical electron pair or homopolar bond of chemistry, particularly of organic chemistry. It is a strong bond: the bond between two carbon atoms in diamond with respect to separated neutral atoms is comparable with the bond strength in ionic crystals.

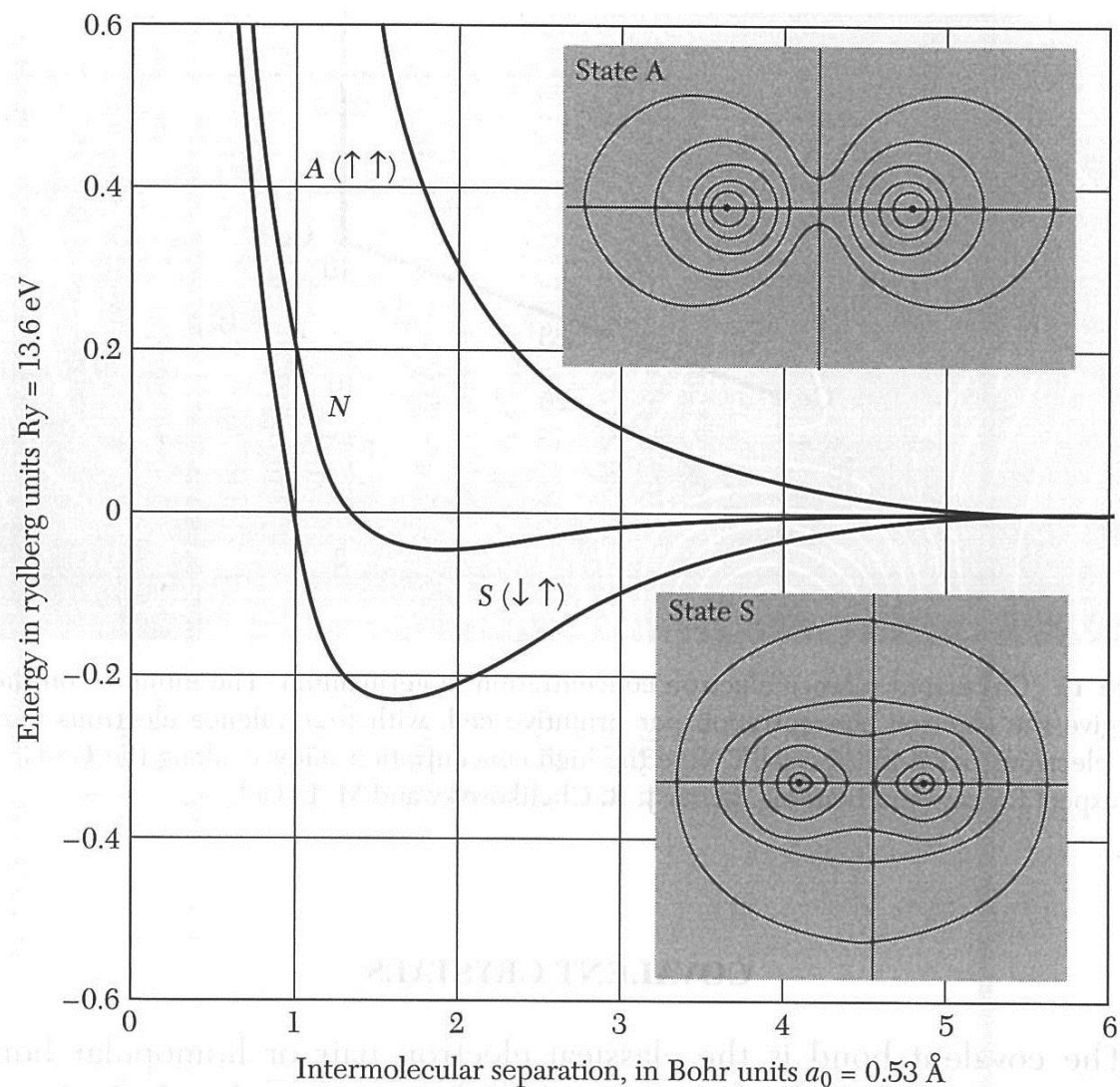
The covalent bond is usually formed from two electrons, one from each atom participating in the bond. The electrons forming the bond tend to be partly localized in the region between the two atoms joined by the bond. The spins of the two electrons in the bond are antiparallel.

The covalent bond has strong directional properties (Fig. 11). Thus carbon, silicon, and germanium have the diamond structure, with atoms joined to four nearest neighbors at tetrahedral angles, even though this arrangement gives a low filling of space, 0.34 of the available space, compared with 0.74 for a close-packed structure. The tetrahedral bond allows only four nearest neighbors, whereas a close-packed structure has 12. We should not overemphasize the similarity of the bonding of carbon and silicon. Carbon gives biology, but silicon gives geology and semiconductor technology.

The binding of molecular hydrogen is a simple example of a covalent bond. The strongest binding (Fig. 12) occurs when the spins of the two electrons are antiparallel. The binding depends on the relative spin orientation not because there are strong magnetic dipole forces between the spins, but because the Pauli principle modifies the distribution of charge according to the spin orientation. This spin-dependent coulomb energy is called the **exchange interaction**.



**Figure 11** Calculated valence electron concentration in germanium. The numbers on the contours give the electron concentration per primitive cell, with four valence electrons per atom (eight electrons per primitive cell). Note the high concentration midway along the Ge-Ge bond, as we expect for covalent bonding. (After J. R. Chelikowsky and M. L. Cohen.)



**Figure 12** Energy of molecular hydrogen ( $\text{H}_2$ ) referred to separated neutral atoms. A negative energy corresponds to binding. The curve  $N$  refers to a classical calculation with free atom charge densities;  $A$  is the result for parallel electron spins, taking the Pauli exclusion principle into account, and  $S$  (the stable state) for antiparallel spins. The density of charge is represented by contour lines for the states  $A$  and  $S$ .

The Pauli principle gives a strong repulsive interaction between atoms with filled shells. If the shells are not filled, electron overlap can be accommodated without excitation of electrons to high energy states and the bond will be shorter. Compare the bond length (2 Å) of Cl<sub>2</sub> with the interatomic distance (3.76 Å) of Ar in solid Ar; also compare the cohesive energies given in Table 1. The difference between Cl<sub>2</sub> and Ar<sub>2</sub> is that the Cl atom has five electrons in the 3p shell and the Ar atom has six, filling the shell, so that the repulsive interaction is stronger in Ar than in Cl.

The elements C, Si, and Ge lack four electrons with respect to filled shells, and thus these elements (for example) can have an attractive interaction associated with charge overlap. The electron configuration of carbon is  $1s^2 2s^2 2p^2$ . To form a tetrahedral system of covalent bonds the carbon atom must first be promoted to the electronic configuration  $1s^2 2s^2 2p^3$ . This promotion from the ground state requires 4 eV, an amount more than regained when the bonds are formed.

**Table 8 Fractional ionic character of bonds in binary crystals**

Crystal	Fractional ionic character	Crystal	Fractional ionic character
Si	0.00		
SiC	0.18	GaAs	0.31
Ge	0.00	GaSb	0.26
ZnO	0.62	AgCl	0.86
ZnS	0.62	AgBr	0.85
ZnSe	0.63	AgI	0.77
ZnTe	0.61	MgO	0.84
CdO	0.79	MgS	0.79
CdS	0.69	MgSe	0.79
CdSe	0.70		
CdTe	0.67	LiF	0.92
InP	0.42	NaCl	0.94
InAs	0.36	RbF	0.96
InSb	0.32		


After J. C. Phillips, *Bonds and bands in semiconductors*.

## METALS

Metals are characterized by high electrical conductivity, and a large number of electrons in a metal are free to move about, usually one or two per atom. The electrons available to move about are called conduction electrons. The valence electrons of the atom become the conduction electrons of the metal.

In some metals the interaction of the ion cores with the conduction electrons always makes a large contribution to the binding energy, but the characteristic feature of metallic binding is the lowering of the energy of the valence electrons in the metal as compared with the free atom.

There is a continuous range of crystals between the ionic and the covalent limits. It is often important to estimate the extent a given bond is ionic or covalent. A semiempirical theory of the fractional ionic or covalent character of a bond in a dielectric crystal has been developed with considerable success by J. C. Phillips, Table 8.



The binding energy of an alkali metal crystal is considerably less than that of an alkali halide crystal: the bond formed by a conduction electron is not very strong. The interatomic distances are relatively large in the alkali metals because the kinetic energy of the conduction electrons is lower at large interatomic distances. This leads to weak binding. Metals tend to crystallize in relatively close packed structures: hcp, fcc, bcc, and some other closely related structures, and not in loosely-packed structures such as diamond.

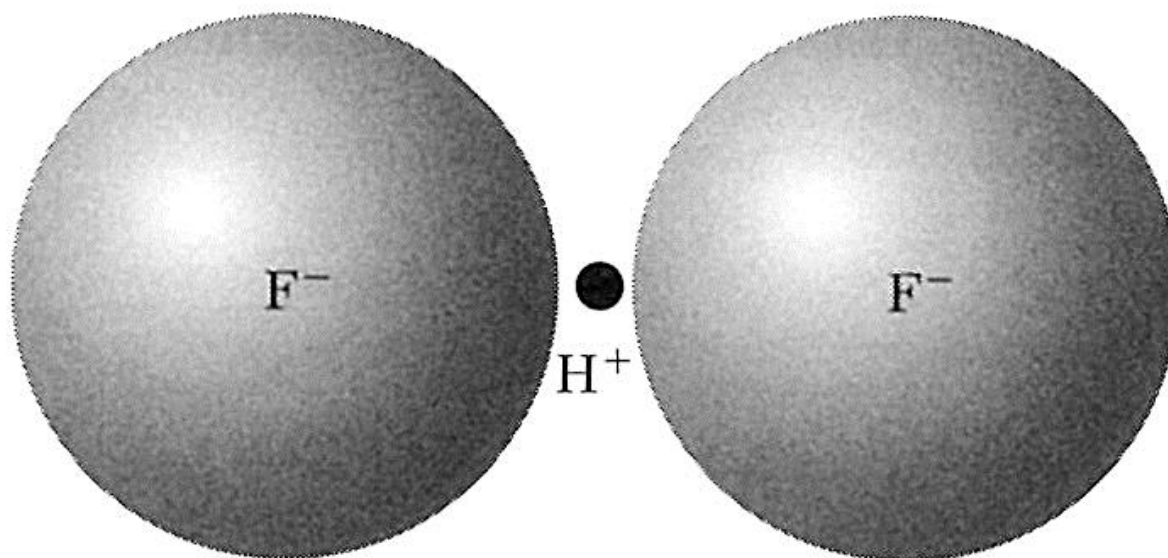
In the transition metals there is additional binding from inner electron shells. Transition metals and the metals immediately following them in the periodic table have large  $d$ -electron shells and are characterized by high binding energy.



## HYDROGEN BONDS

Because neutral hydrogen has only one electron, it should form a covalent bond with only one other atom. It is known, however, that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, thus forming a **hydrogen bond** between them, with a bond energy of the order of 0.1 eV. It is believed that the hydrogen bond is largely ionic in character, being formed only between the most electronegative atoms, particularly F, O, and N. In the extreme ionic form of the hydrogen bond, the hydrogen atom loses its electron to another atom in the molecule; the bare proton forms the hydrogen bond. The atoms adjacent to the proton are so close that more than two of them would get in each other's way; thus the hydrogen bond connects only two atoms (Fig. 13).

The hydrogen bond is an important part of the interaction between  $\text{H}_2\text{O}$  molecules and is responsible together with the electrostatic attraction of the electric dipole moments for the striking physical properties of water and ice. It is important in certain ferroelectric crystals and in DNA.



**Figure 13** The hydrogen difluoride ion  $\text{HF}_2^-$  is stabilized by a hydrogen bond. The sketch is of an extreme model of the bond, extreme in the sense that the proton is shown bare of electrons.