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**1.3 The covalent bond** Consider the $H_2$ molecule in a simple way as two touching H atoms as depicted in Figure 1.73. Does this arrangement have a lower energy than two separated H atoms? Suppose that electrons totally correlate their motions so that they move to avoid each other as in the snapshot in Figure 1.73. The radius $r_o$ of the hydrogen atom is 0.0529 nm. The electrostatic potential energy *PE* of two charges $Q_1$ and $Q_2$ separated by a distance *r* is given by $Q_1Q_2/(4\pi\varepsilon_o r)$. Using the Virial Theorem as in Example 1.1, consider the following:

*a*. Calculate the total electrostatic potential energy (*PE*) of all the charges when they are arranged as shown in Figure 1.73. In evaluating the *PE* of the whole collection of charges you must consider all pairs of charges and, at the same time, avoid double counting of interactions between the same pair of charges. The total *PE* is the sum of the following: electron 1 interacting with the proton at a distance $r_o$ on the left, proton at $r_o$ on the right, and electron 2 at a distance $2r_o$ + electron 2 interacting with a proton at $r_o$ and another proton at $3r_o$ + two protons, separated by $2r_o$, interacting with each other. Is this configuration energetically favorable?

*b*. Given that in the isolated H-atom the *PE* is 2 ×(-13.6 eV), calculate the change in *PE* in going from two isolated H-atoms to the $H_2$ molecule. Using the Virial theorem, find the change in the total energy and hence the covalent bond energy. How does this compare with the experimental value of 4.51 eV?

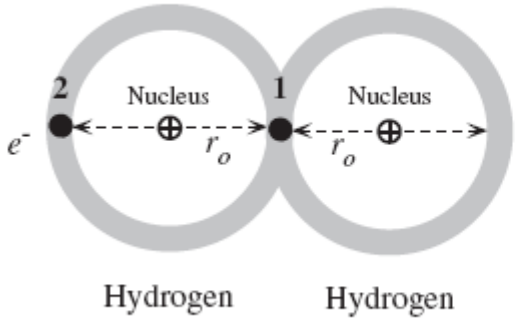


**Figure 1.73** A simplified view of the covalent bond in $H_2$. A snapshot at one instant.

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**1.4 Ionic bonding and CsCl** The potential energy $E$ per $Cs^+$-$Cl^-$ pair within the CsCl crystal depends on the interionic separation $r$ in the same fashion as in the NaCl crystal,

$$E(r) = -\frac{e^2 M}{4\pi\varepsilon_o r} + \frac{B}{r^m}$$ *Energy per ion pair in ionic crystals* [1.38]

where for CsCl, $M = 1.763$, $B = 1.192\times10^{-104}$ J $m^9$ or $7.442\times10^{-5}$ eV $(nm)^9$ and $m = 9$. Find the equilibrium separation ($r_o$) of the ions in the crystal and the ionic bonding energy, that is, the ionic cohesive energy; and compare the latter value to the experimental value of 657 kJ $mol^{-1}$. Given the *ionization energy* of Cs is 3.89 eV and the *electron affinity* of Cl (energy released when an electron is added) is 3.61 eV, calculate the atomic cohesive energy of the CsCl crystal as joules per mole.

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***1.6 Bonding and bulk modulus** In general, the potential energy $E$ per atom, or per ion pair, in a crystal as a function of interatomic (interionic) separation $r$ can be written as the sum of an attractive $PE$ and a repulsive $PE$,

$$E(r) = -\frac{A}{r^n} + \frac{B}{r^m} \qquad \textit{General PE curve for bonding} \qquad [1.39]$$

where $A$ and $n$ are constants characterizing the attractive PE and $B$ and $m$ are constants characterizing the repulsive $PE$. This energy is minimum when the crystal is in equilibrium. The magnitude of the minimum energy and its location $r_o$ define the bonding energy and the equilibrium interatomic (or interionic) separation respectively.

When a pressure $P$ is applied to a solid, its original volume $V_o$ shrinks to $V$ by an amount $\Delta V = V - V_0$. The bulk modulus $K$ relates the volume strain $\Delta V/V$ to the applied pressure $P$ by

$$P = -K(\Delta V/V_o) \qquad \textit{Bulk modulus definition} \qquad [1.40]$$

The bulk modulus $K$ is related to the energy curve. In its simplest form (assuming a simple cubic unit cell) $K$ can be estimated from Equation 1.39 by

$$K = \frac{1}{9cr_0}\left[\frac{d^2E}{dr^2}\right]_{r=r_0} \qquad \textit{Bulk modulus} \qquad [1.41]$$

where $c$ is a numerical factor, of the order of unity, given by $b/p$ where $p$ is the number of atoms or ion pairs in the unit cell and $b$ is a numerical factor that relates the cubic unit cell lattice parameter $a_o$ to the equilibrium interatomic (interionic) separation $r_o$ by $b = a_o^3 / r_o^3$

*a.* Show that the bond energy and equilibrium separation are given by

$$E_{\text{bond}} = \frac{A}{r_0^n}\left(1 - \frac{n}{m}\right) \quad \text{and} \quad r_0 = \left[\frac{mB}{nA}\right]^{\frac{1}{m-n}}$$

*b.* Show that the bulk modulus is given by

$$K = \frac{An(m-n)}{9cr_0^{n+3}} \quad \text{or} \quad K = E_{\text{bond}}\frac{mn}{9cr_0^3}$$

*c.* For a NaCl type crystal, $Na^+$ and Cl ions touch along cube edge so that $r_o = (a_o/2)$. Thus, $a^3 = 2^3 r_o^3$ and $b = 2^3 = 8$. There are 4 ion pairs in the unit cell, $p = 4$. Thus, $c = b/p = 8/4 = 2$. Using the values from **Example 1.3**, calculate the bulk modulus of NaCl.

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## 1.22 BCC and FCC crystals

*a.* Molybdenum has the BCC crystal structure, has a density of 10.22 g $cm^{-3}$ and an atomic mass of 95.94 g $mol^{-1}$. What is the atomic concentration, lattice parameter a, and atomic radius of molybdenum?

*b.* Gold has the FCC crystal structure, a density of 19.3 g $cm^{-3}$ and an atomic mass of 196.97 g $mol^{-1}$. What is the atomic concentration, lattice parameter a, and atomic radius of gold?

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**1.24 Planar and surface concentrations** Niobium (Nb) has the BCC crystal with a lattice parameter $a$ = 0.3294 nm. Find the planar concentrations as the number of atoms per $nm^2$ of the (100), (110) and (111) planes. Which plane has the most concentration of atoms per unit area? Sometimes the number of atoms per unit area $n_{surface}$ on the surface of a crystal is estimated by using the relation $n_{surface} = n_{bulk}^{2/3}$ where $n_{bulk}$ is the concentration of atoms in the bulk. Compare $n_{surface}$ values with the planar concentrations that you calculated and comment on the difference. [*Note:* The BCC (111) plane does not cut through the center atom and the (111) has one-sixth of an atom at each corner.]

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**1.27 Crystallographic directions and planes** Consider the cubic crystal system.

*a*. Show that the line [*hkl*] is perpendicular to the (*hkl*) plane.

*b*. Show that the spacing between adjacent (*hkl*) planes is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

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## 1.28 Si and $SiO_2$

*a*. Given the Si lattice parameter $a$ = 0.543 nm, calculate the number of Si atoms per unit volume, in $nm^{-3}$.

*b*. Calculate the number of atoms per $m^2$ and per $nm^2$ on the (100), (110) and (111) planes in the Si crystal as shown on Figure 1.75. Which plane has the most number of atoms per unit area?

*c*. The density of $SiO_2$ is 2.27 g $cm^{-3}$. Given that its structure is amorphous, calculate the number of molecules per unit volume, in $nm^{-3}$. Compare your result with (a) and comment on what happens when the surface of an Si crystal oxidizes. The atomic masses of Si and O are 28.09 and 16, respectively.

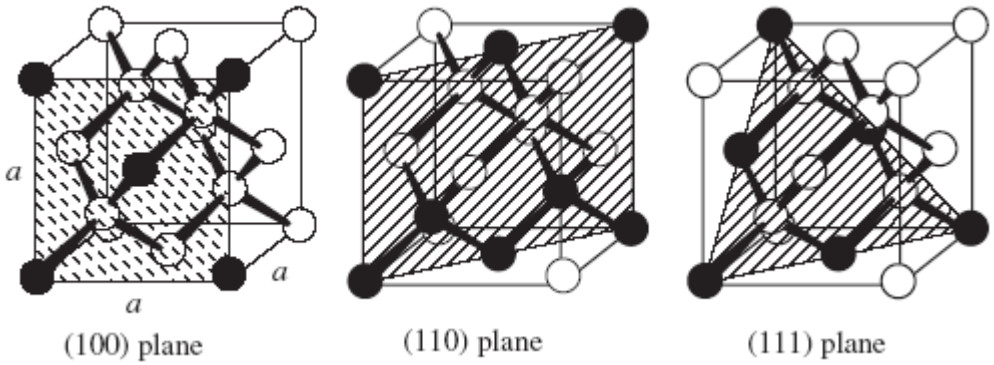


**Figure 1.75:** Diamond cubic crystal structure and planes. Determine what portion of a black-colored atom belongs to the plane that is hatched.

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