PHY 481/581 Intro Nano-MSE:

Simple Quantum Mechanics III: from atoms to molecules and solids, effects of size and dimensionality on electronic structure of solids

From Atoms and Molecules to Nanoscale Materials

An electron from one hydrogen atom just tunnels back and forth to the other hydrogen atom, the result is a H_2 molecule, there is a higher probability density of the electron being between the two protons, that corresponds to an electrostatic attraction which balances the electrostatic repulsion of the two protons

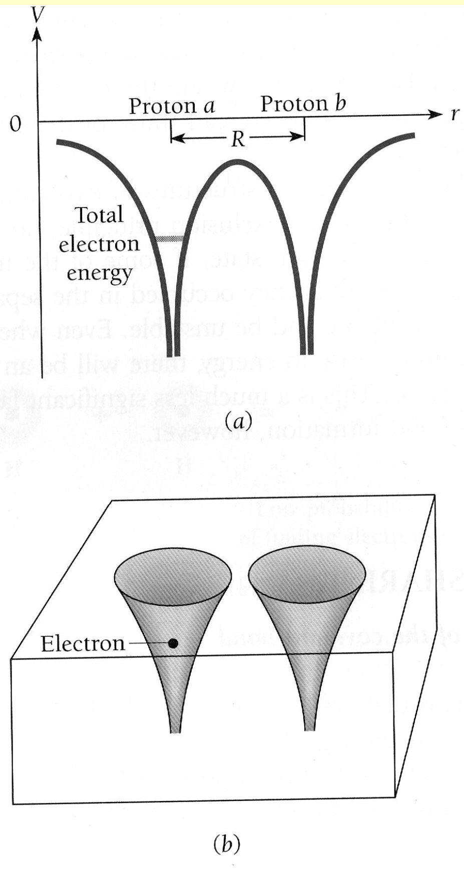
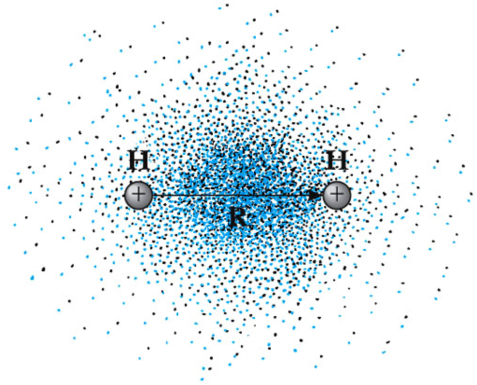


Figure 8.4 (*a*) Potential energy of an electron in the electric field of two nearby protons. The total energy of a ground-state electron in the hydrogen atom is indicated. (*b*) Two nearby protons correspond quantum-mechanically to a pair of boxes separated by a barrier.



Chemical Bonds

- Electron sharing lowers kinetic energy (covalent bond).
- For atoms with very different electron affinities, electrons can transfer (almost completely in an ionic bond).
- Coulomb interactions (+ and -) and the exclusion principle contribute.
- Even for rare gas elements at 0ºK quantum fluctuations contribute to attractive forces

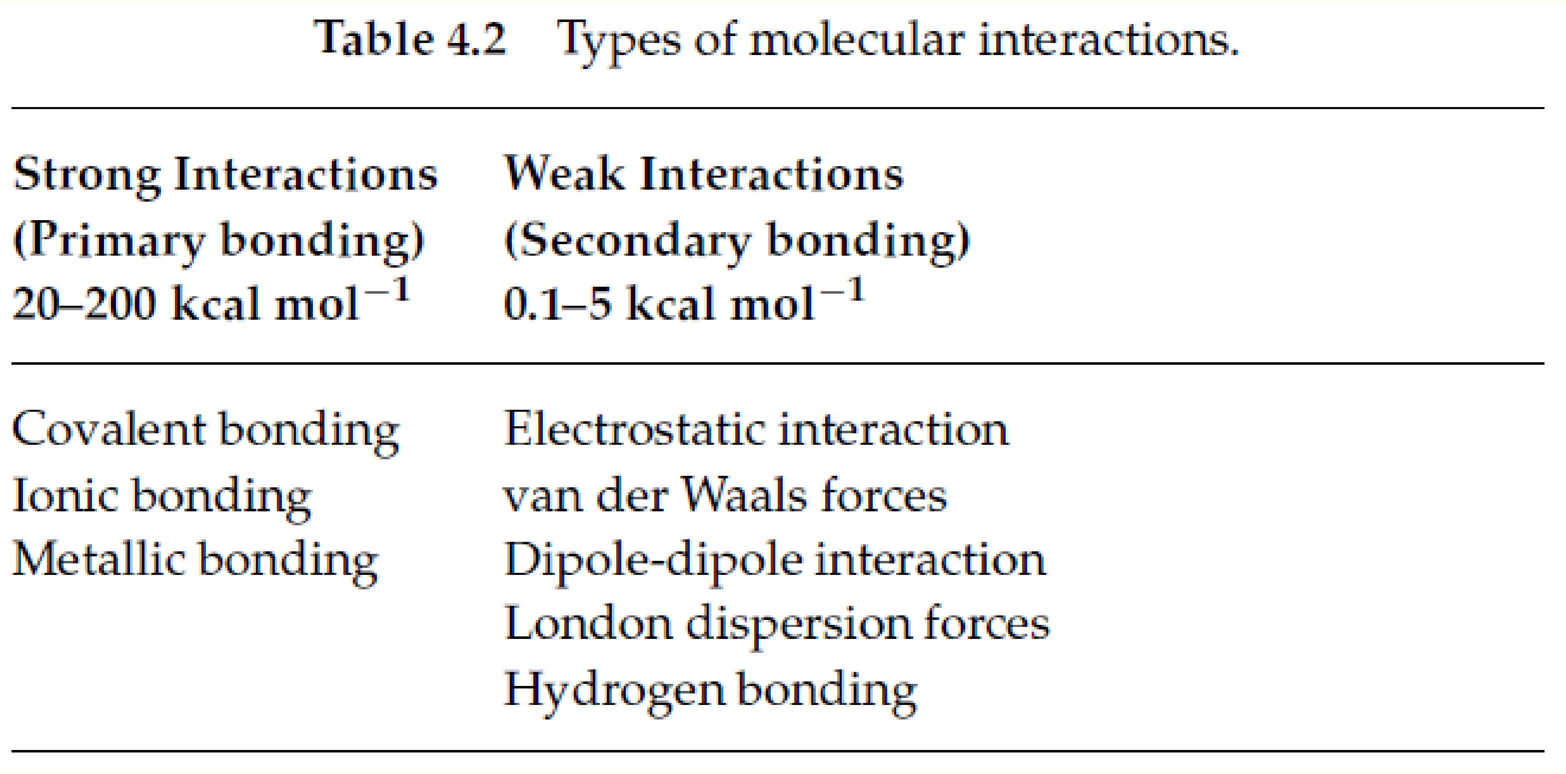
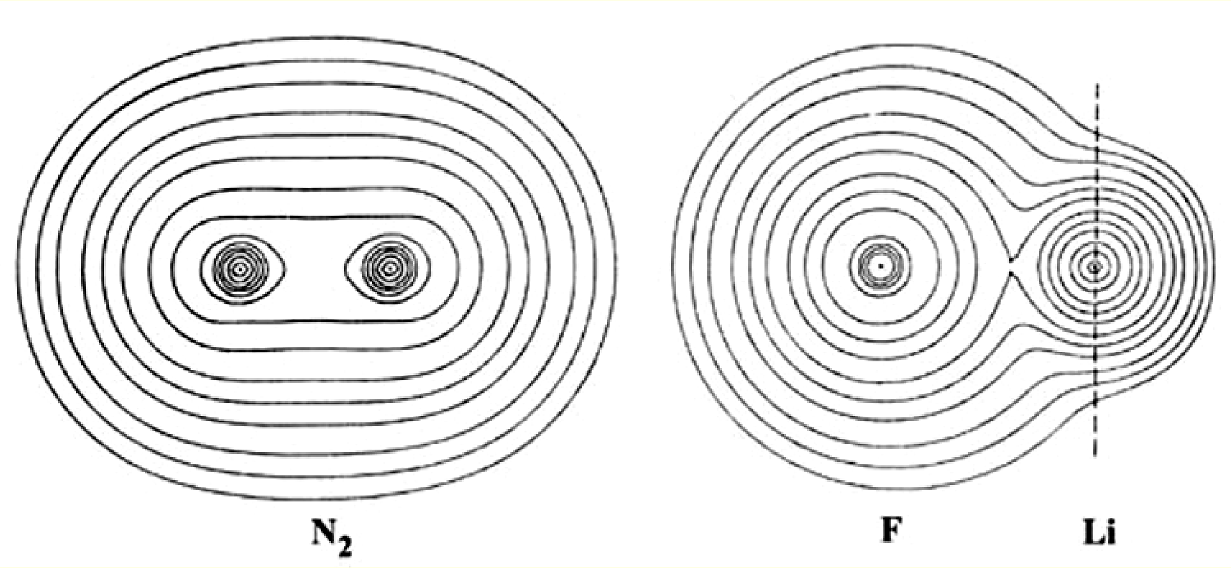


Table 4.2 Types of molecular interactions.

Strong Interactions (Primary bonding) 20–200 kcal mol^{-1}	**Weak Interactions (Secondary bonding) 0.1–5 kcal mol^{-1}**
Covalent bonding	Electrostatic interaction
Ionic bonding	van der Waals forces
Metallic bonding	Dipole-dipole interaction
	London dispersion forces
	Hydrogen bonding

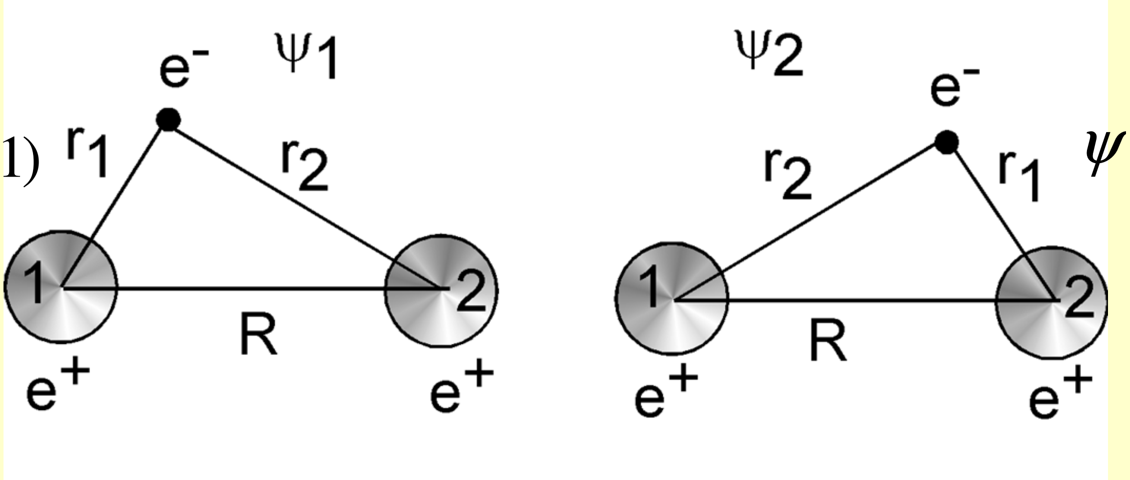
Chemical Bonds



Covalent extreme

Ionic extreme

Simplest Example H_2^+ ion



$\psi_1 \equiv \psi^{1s}(1)$

$\psi_2 \equiv \psi^{1s}(2)$

$$\hat{H}_0(r_1,\theta,\phi) + \frac{e^2}{4\pi\varepsilon_0 r_2} \qquad \hat{H}' = \frac{e^2}{4\pi\varepsilon_0 r_2}$$

- Evaluate E from $E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| \hat{H}' \middle| \psi_n^{(0)} \right\rangle$
- Best linear combination of unperturbed wave functions (minimum E) comes from solving the Schrödinger equation for the coefficients

$$\psi_n^{(1)} = \sum_m a_{nm} \psi_m^{(0)}$$

So back to the H_2^+ ion

Let’s combine the two 1s states with unknown coefficients a and b:

$$a\psi_1 + b\psi_2$$

There is only really one unknown here (a/b) as the other comes from normalization.

$$\left[\hat{H}_0 + H'\right](a\psi_1 + b\psi_2) = E(a\psi_1 + b\psi_2)$$

Using $\hat{H}_0\psi_{1,2} = E_0\psi_{1,2}$ and $\langle \psi_n | \psi_m \rangle = \delta_{nm}$ (not really true – there is some overlap as there is a non-orthogonal basis, but approximately OK)

Perturbation Theory for the H_2^+ ion

Multiplying form the left by $\psi_1{}^*$ or $\psi_2{}^*$ we get two versions of the SE

$$a\left(E_0 - E\right) + a\left\langle \psi_1 \middle| \hat{H}' \middle| \psi_1 \right\rangle + b\left\langle \psi_1 \middle| \hat{H}' \middle| \psi_2 \right\rangle = 0$$

$$b\left(E_0 - E\right) + a\left\langle \psi_2 \middle| \hat{H}' \middle| \psi_1 \right\rangle + b\left\langle \psi_2 \middle| \hat{H}' \middle| \psi_2 \right\rangle = 0$$

with $\left\langle \psi_2 \middle| \hat{H}' \middle| \psi_1 \right\rangle = \left\langle \psi_1 \middle| \hat{H}' \middle| \psi_2 \right\rangle \equiv \Delta$

$$\left\langle \psi_1 \middle| \hat{H}' \middle| \psi_1 \right\rangle = \left\langle \psi_2 \middle| \hat{H}' \middle| \psi_2 \right\rangle \equiv \delta$$

Perturbation Theory for the H_2^+ ion

We get two equations with 2 unknowns (a/b, E)

$$\left(E_0 + \delta - E\right)a + \Delta b = 0$$

$$\Delta a + \left(E_0 + \delta - E\right)b = 0$$

The secular equation gives

$$\left(E_0 + \delta - E\right)^2 - \Delta^2 = 0$$

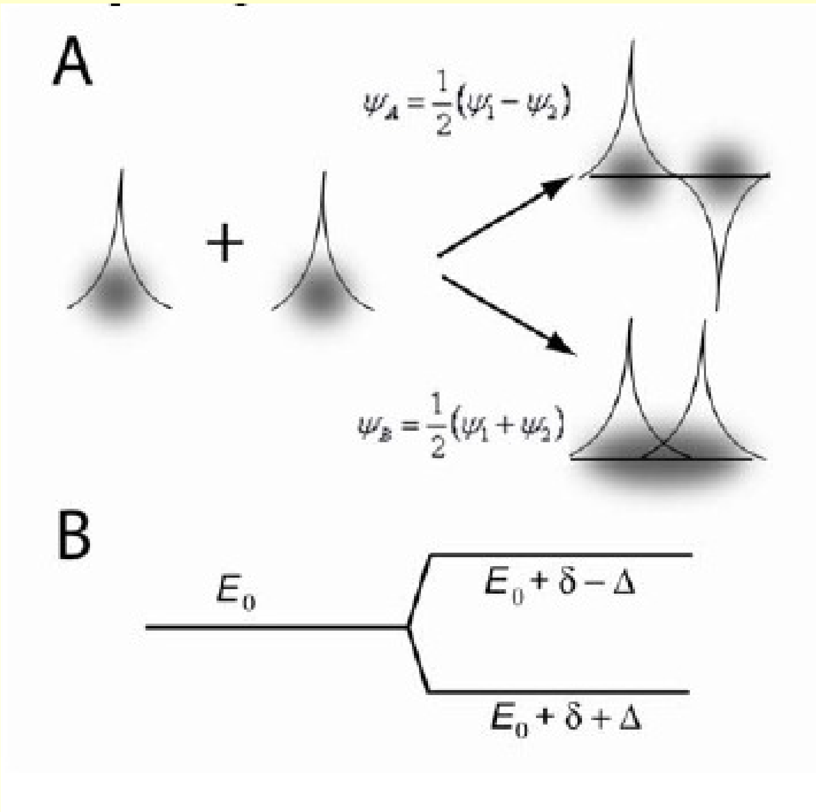
Leading to $$E = E_0 + \delta \pm \Delta$$ (note $\Delta < 0$)

Perturbation Theory for the H_2^+ ion

$\psi_B = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$ for $E = E_0 + \delta + \Delta$ ***(lower energy bonding state)***

$\psi_A = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$ for $E = E_0 + \delta - \Delta$ (higher energy, anti-bonding state)

δ is s shift from E_0 and small compared to Δ, which must be negative



We neglected coulomb repulsion between the two protons, taking it into account will give equilibrium bonding distance

There are two ways, bonding and antibonding wave functions

$$\Psi(\sigma) = \psi(1s)_A + \psi(1s)_B$$

$$\Psi(\sigma^*) = \psi(1s)_A - \psi(1s)_B$$

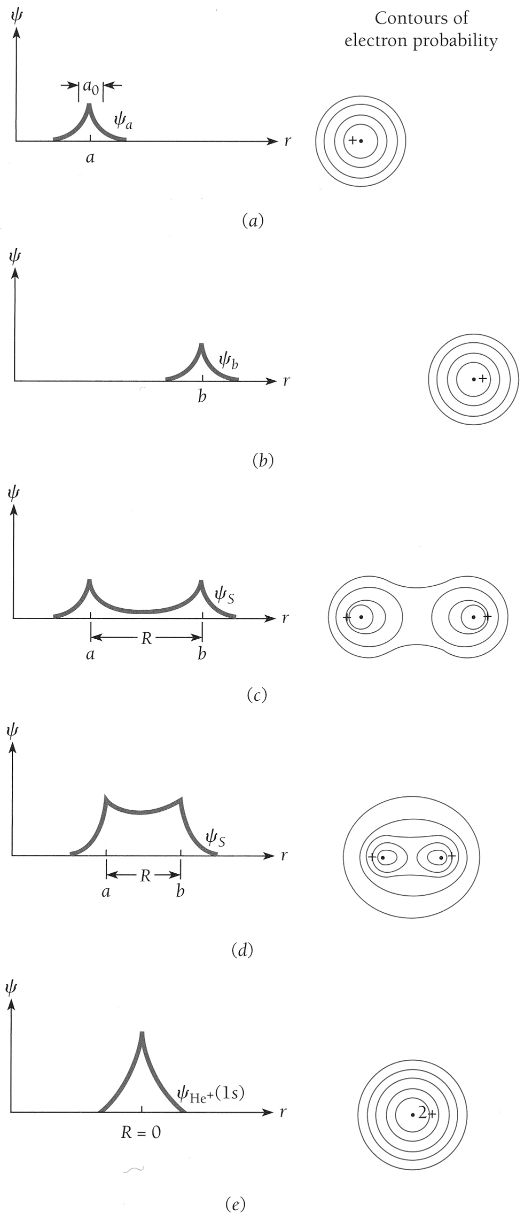
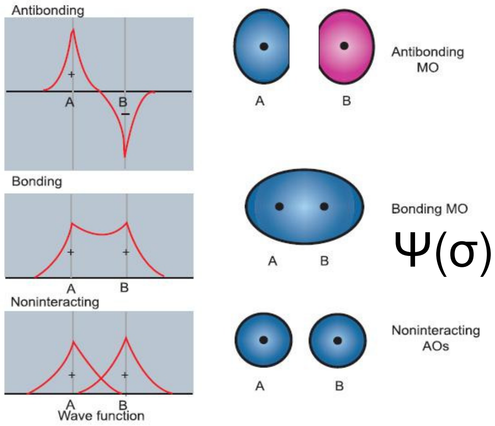


Figure 8.5 (*a*)–(*d*) The combination of two hydrogen-atom 1*s* wave functions to form the symmetric H_2^+ wave function ψ_S. The result is a stable H_2^+ molecular ion because the electron has a greater probability of being between the protons than outside them. (*e*) If the protons could join together, the resulting wave function would be the same as the 1*s* wave function of a He^+ ion.



Ψ(σ)

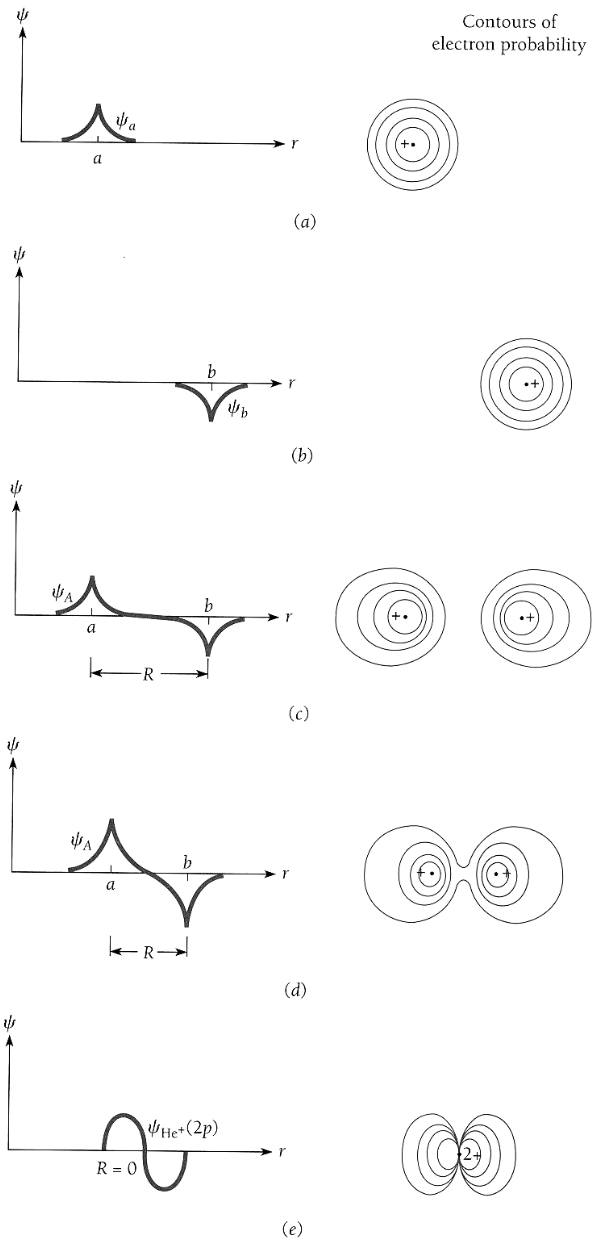


Figure 8.6 (*a*)–(*d*) The combination of two hydrogen-atom 1*s* wave functions to form the antisymmetric H_2^+ wave function ψ_A. A stable H_2^+ molecular ion is not formed because now the electron has a smaller probability of being between the protons than outside them. (*e*) If the protons could join together, the resulting wave function would be the same as the 2*p* wave function of a He^+ ion. In the 2*p* state a He^+ ion has more energy than in the 2*s* state.

Energetics determines what is going to happen, Pauli’s exclusion principle has to be obeyed

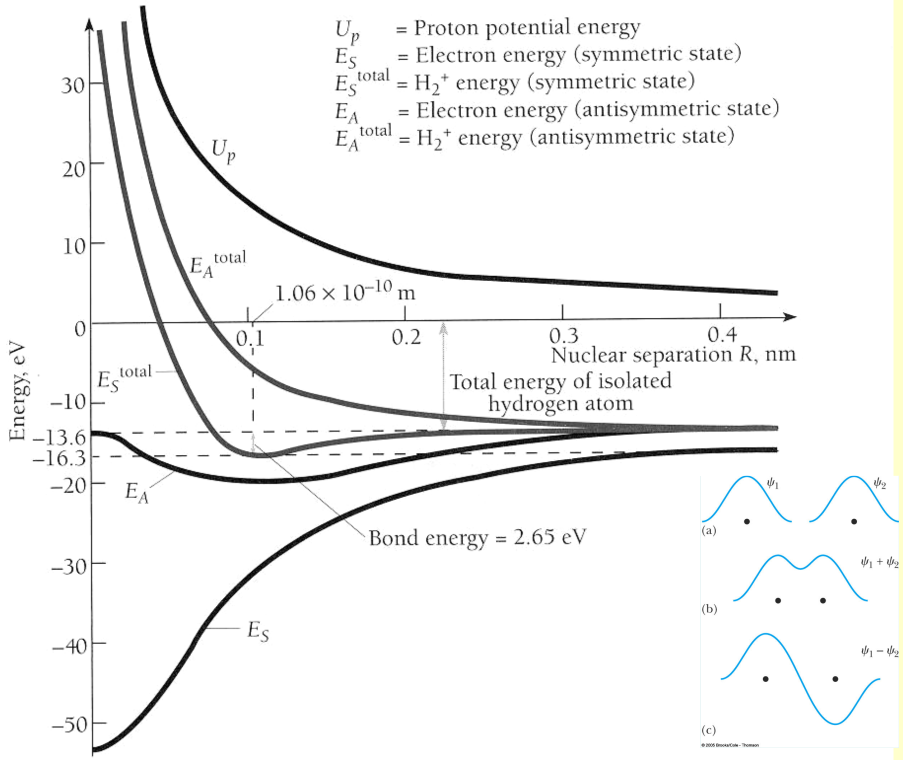


Figure 8.7 Electron, proton repulsion, and total energies in H_2^+ as a function of nuclear separation R for the symmetric and antisymmetric states. The antisymmetric state has no minimum in its total energy.

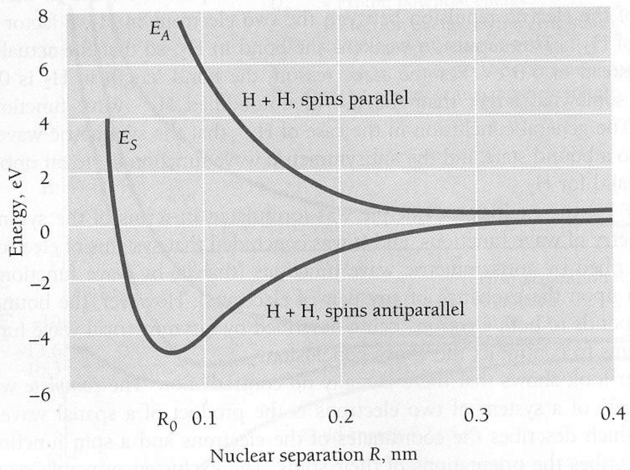


Figure 8.8 The variation of the energy of the system H + H with their distances apart when the electron spins are parallel and antiparallel.

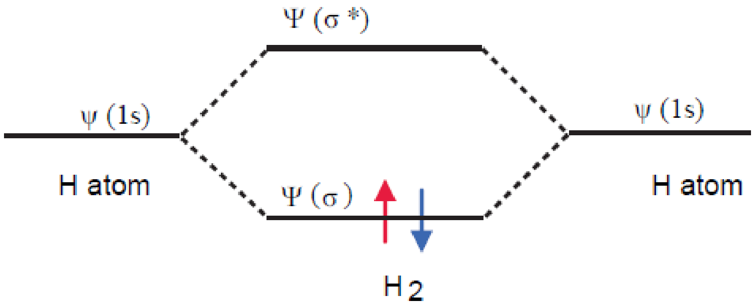
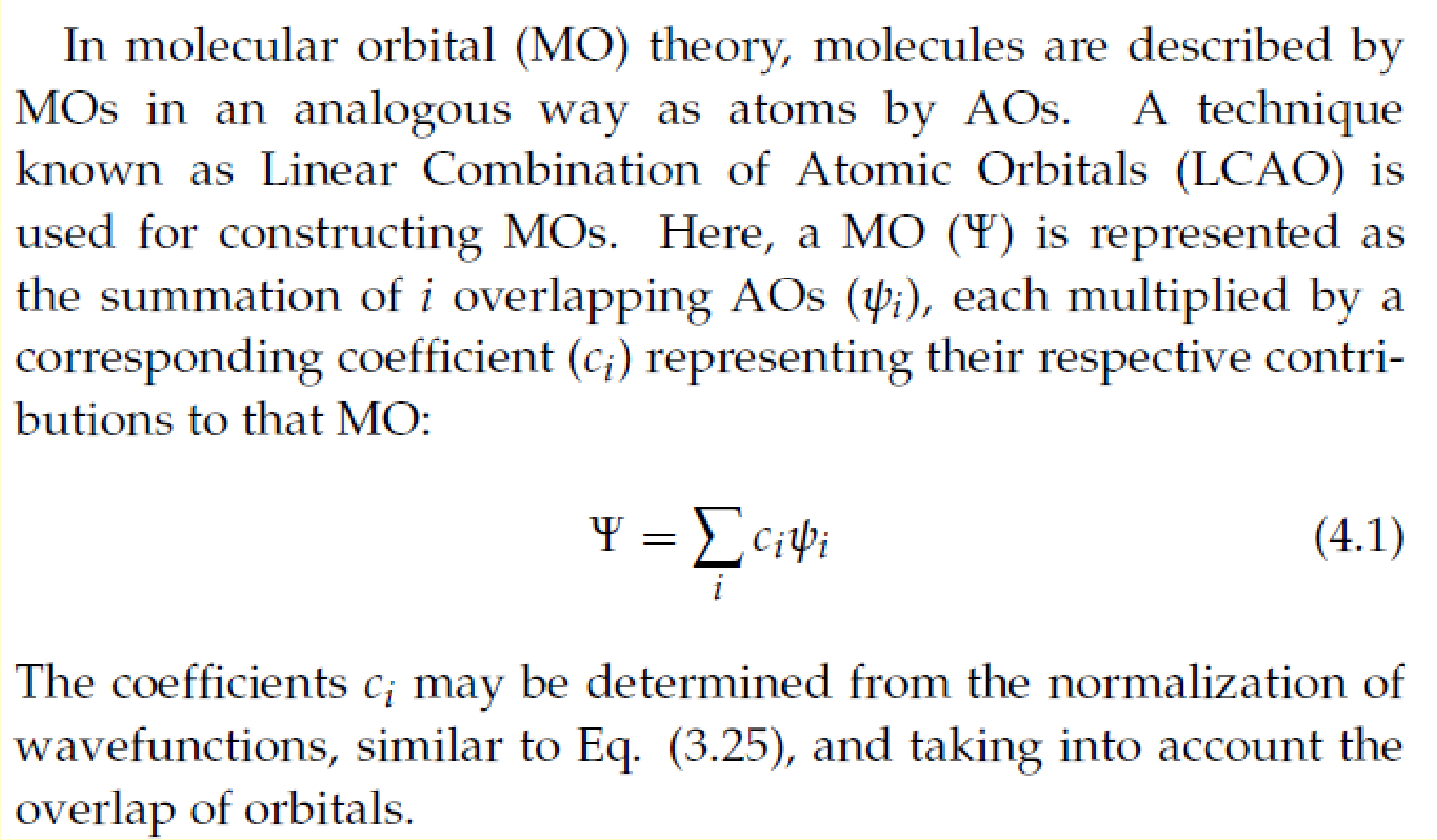


Figure 4.4. Schematic MO energy level diagram for H_2 molecule, with 2 electrons of opposite spins occupying the bonding orbital.

Covalent bonds are strong

H-H molecule



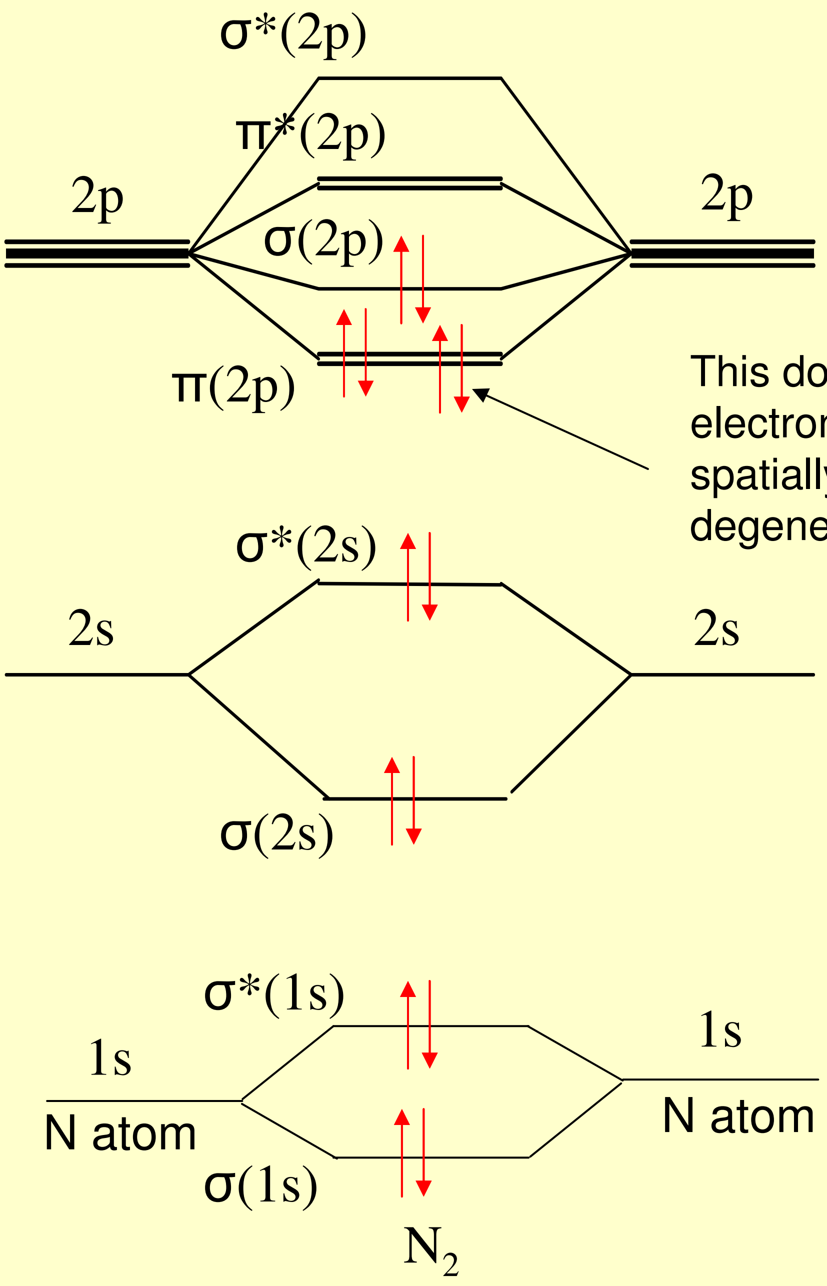
In molecular orbital (MO) theory, molecules are described by MOs in an analogous way as atoms by AOs. A technique known as Linear Combination of Atomic Orbitals (LCAO) is used for constructing MOs. Here, a MO (Ψ) is represented as the summation of i overlapping AOs (ψ_i), each multiplied by a corresponding coefficient (c_i) representing their respective contributions to that MO:

$$\Psi = \sum_i c_i \psi_i \tag{4.1}$$

The coefficients c_i may be determined from the normalization of wavefunctions, similar to Eq. (3.25), and taking into account the overlap of orbitals.

If ψ_1 and ψ_2 are solutions to the Schrödinger equation, $\psi_3 = a\psi_1 \pm b\psi_2$ will also be a solution to this equation !

MO energy level diagram for N_2 molecule

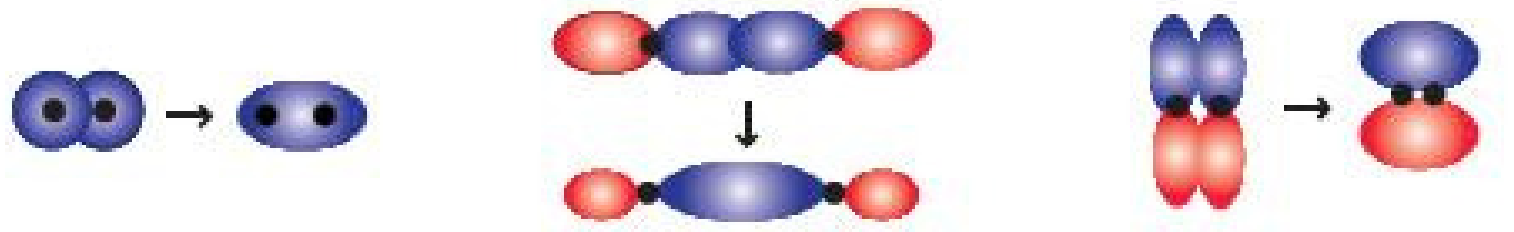


This does not mean that there are actually 4 electrons in this orbital !! Rather, there are two spatially distinct $\pi(2p_x)$ and $\pi(2p_y)$ orbitals with degenerate energy level

N≡N molecule

The electronic configuration of N_2 is: $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2$ $(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p)^2$ two times 7 electrons in total

Effective overlap between AOs



(a) Overlap of two s orbitals to form σ bond

(b) Head-on overlap of two p orbitals to form σ bond

(c) Sideway overlap of twoπ orbitals to form p bond

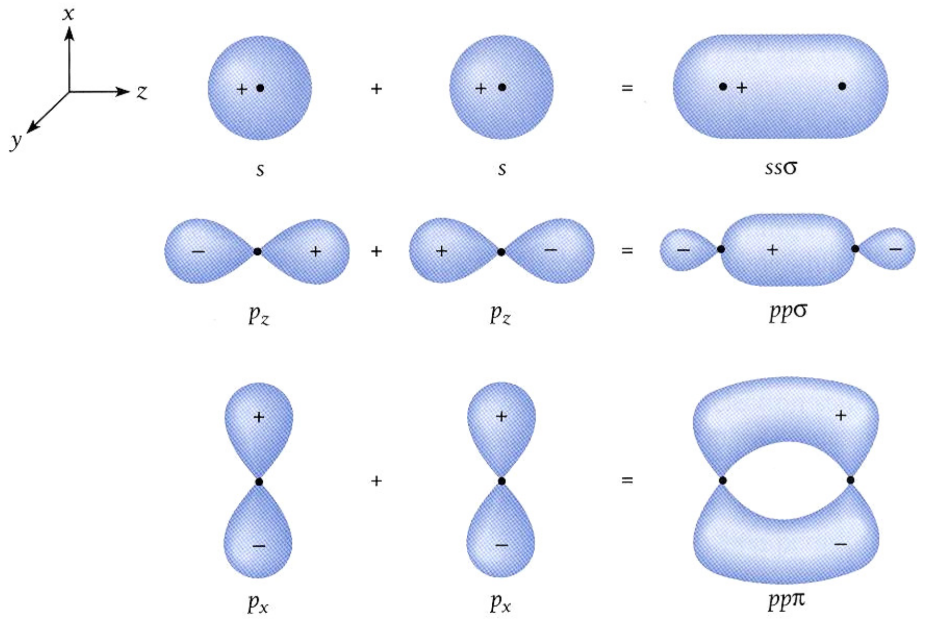


Figure 8.10 The formation of $ss\sigma$, $pp\sigma$, and $pp\pi$ bonding molecular orbitals. Two p_y atomic orbitals can combine to form a $pp\sigma$ molecular orbital in the same way as shown for two p_x atomic orbitals but with a different orientation.

π bonds are considered secondary bonds since they are much weaker than covalent σ bonds

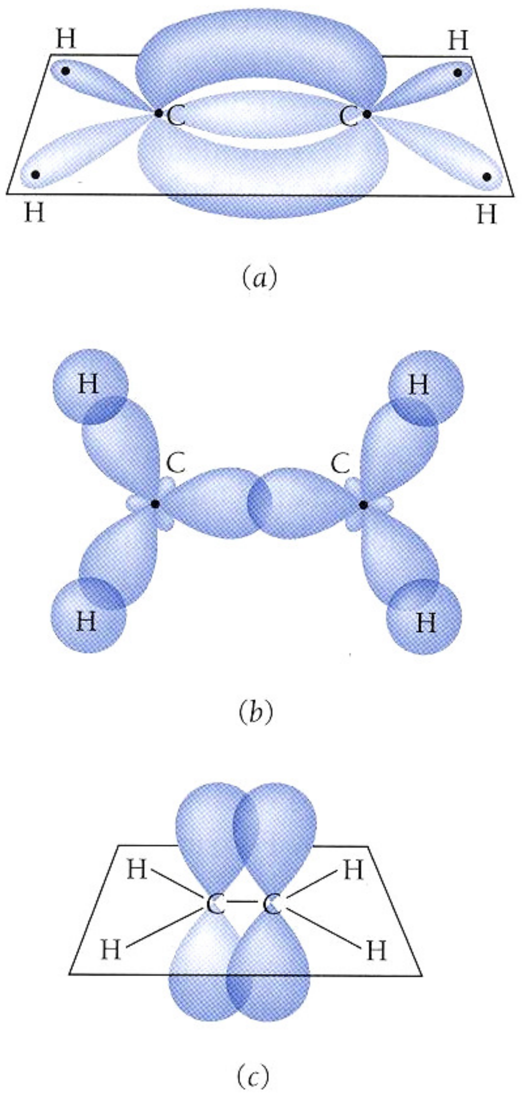


Figure 8.14 (*a*) The ethylene (C_2H_4) molecule. All the atoms lie in a plane perpendicular to the plane of the paper. (*b*) Top view, showing the sp^2 hybrid orbitals that form σ bonds between the C atoms and between each C atoms. (*c*) Side view, showing the pure p_x orbitals that form a π bond between the C atoms.

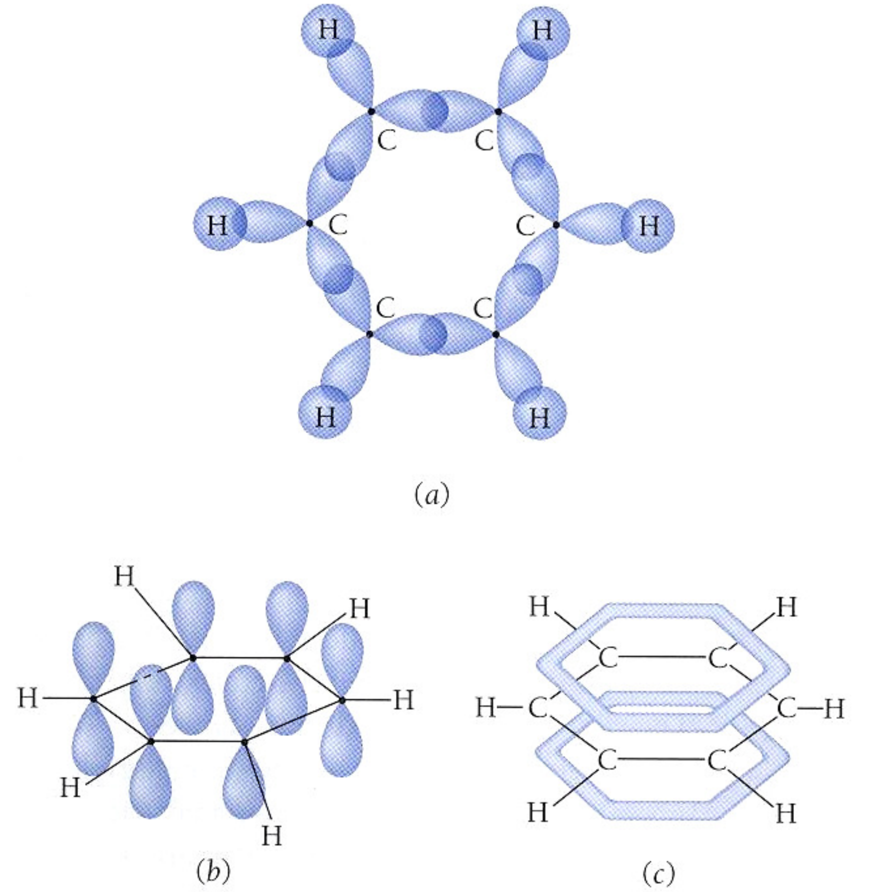
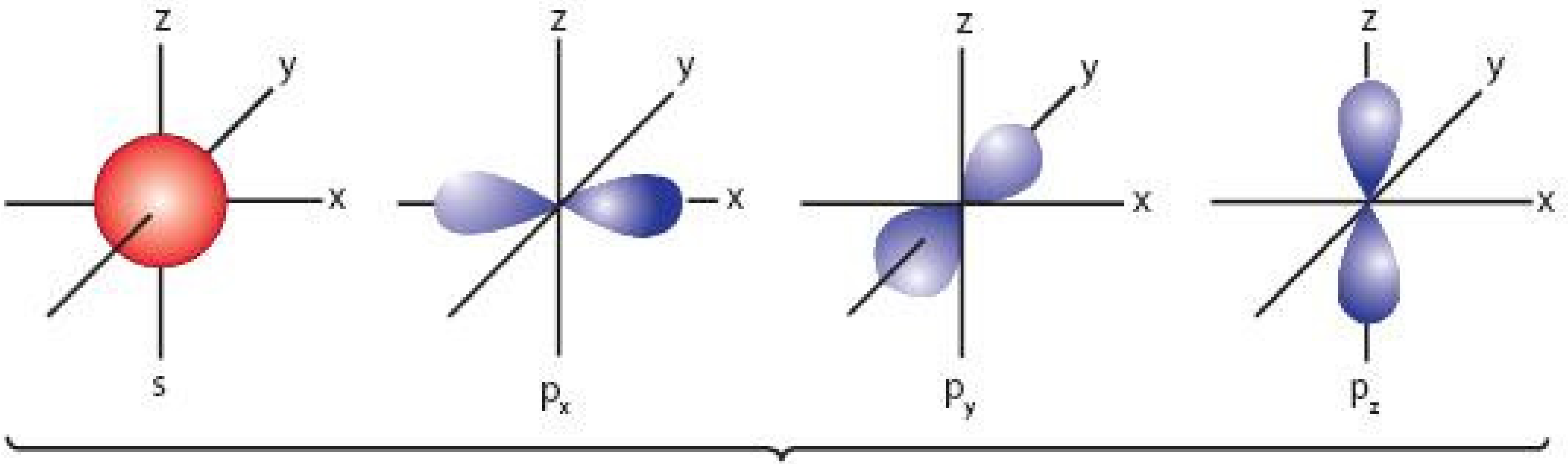


Figure 8.15 The benzene molecule. (*a*) The overlaps between the sp^2 hybrid orbitals in the C atoms with each other and with the *s* orbitals of the H atoms lead to σ bonds. (*b*) Each C atom has a pure p_x orbital occupied by one electron. (*c*) The bonding π molecular orbitals formd by the six p_x atomic orbitals constitute a continuous electron probability distribution around the molecule that contains six delocalized electrons.

Success of MO theory, quantum mechanical explanation of sp_3 hybridization

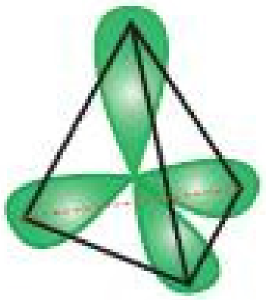
$$\Psi\left(\sigma_{sp^3}\right) = c_H\psi\left(1s\right)_H + c_{C(sp^3)}\left\{\psi\left(2s\right)_C + c'\psi\left(2p\right)_C\right\}$$



Combined to generate four sp^3 hybrid orbitals

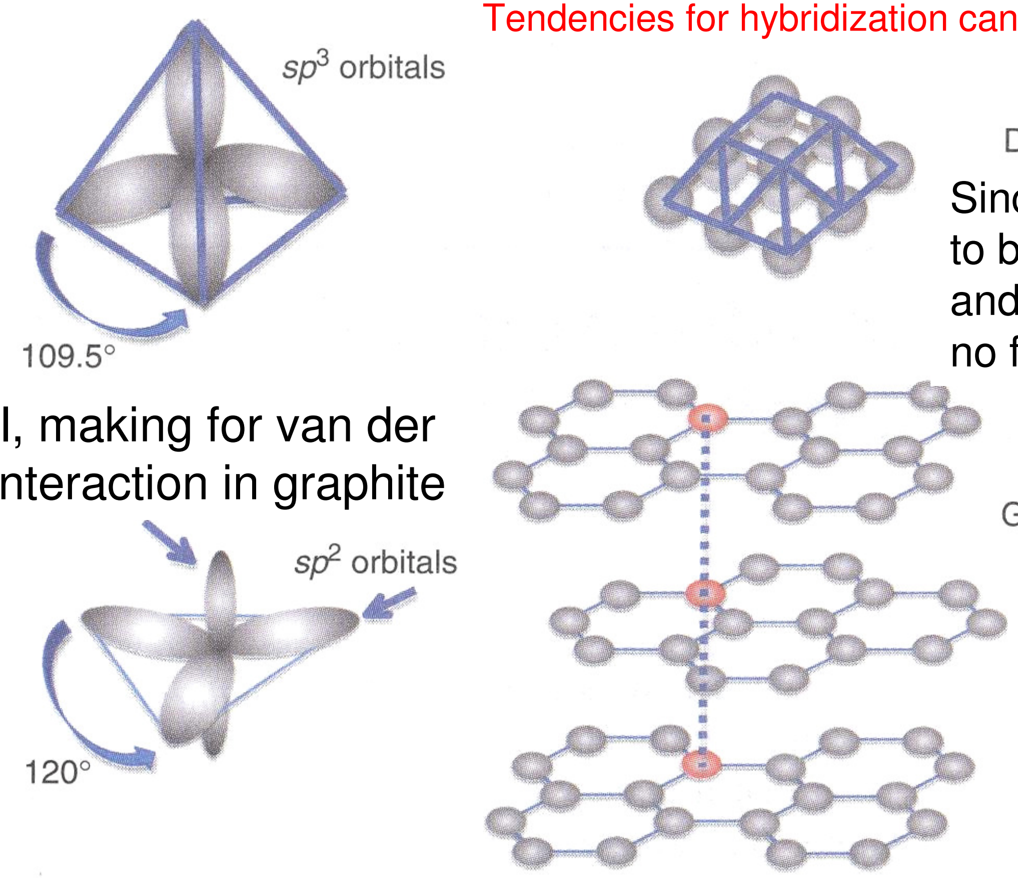
↓

Also C in diamond (Si, Ge) is(are) bonded covalently (tetrahedral) on the basis sp3 hybrid orbitals



CH_4 molecule, perfect tetrahedron, partly due to the influence of the four bound protons at the apexes

Tendencies for hybridization can be explained from perturbation theory



Since all 4 outer electrons contribute to bonding, diamond is transparent and an electric insulator as there are no free electrons

p orbital, making for van der Waals interaction in graphite

For every C atom in graphite, there is an electron in a p-orbital, this electron is nearly free to move and gives graphite it luster, good electric ant thermal conductivity and non-transparency

Fig. 3.1 Carbon bonding in diamond and graphite. Illustration of bonding of carbon in diamond and graphite crystal structures. There are four electrons in each carbon atom that produce bonding with nearest neighbors and in diamond (top) the charge distribution associated with these electrons forms a tetrahedral structure (sp^3 orbitals) around each atom. The atoms thus come together in a tetrahedral arrangement. In graphite (bottom) the bonding electrons form a charge distribution of three equally spaced lobes in a plane (sp^2 orbitals) with the charge distribution of the fourth being out of the plane (*sp* hybrid orbital). In graphite the carbon atoms are thus strongly bonded in a hexagonal arrangement in sheets with weak bonding between the sheets (see Advanced Reading Box 3.1).

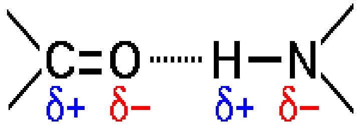
Polarity and Hydrogen Bonding

Since the proton is very small but highly charged, it gives rise to permanent electromagnetic dipole moments in many molecules, e.g. H_2O, HCl, HF, … These dipoles in turn lead to weak hydrogen bonds (so called secondary bonds) between molecules

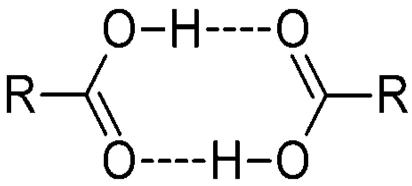
H–F····H–F or H–Cl···H–Cl

Simple hydrogen bonding between two diatomic molecules

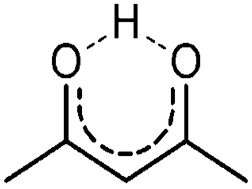
$$\Psi(\sigma) = 0.57\psi(1s)_H + 0.73\psi(2p)_{Cl}$$



Hydrogen bonding between carbonyl and amide group



Hydrogen bonding between two carboxylic molecules



Intramolecular hydrogen bonding within one carboxylic molecule

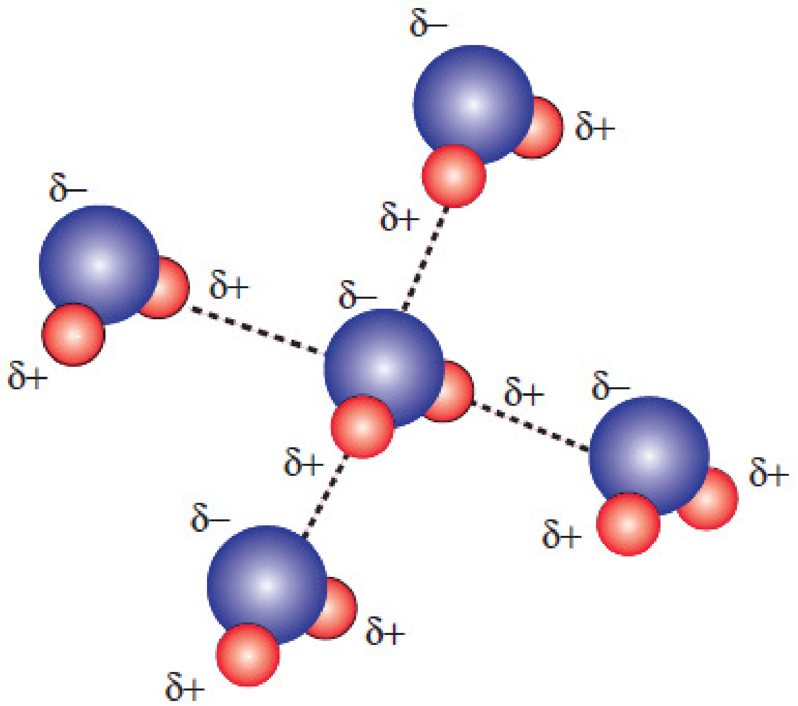


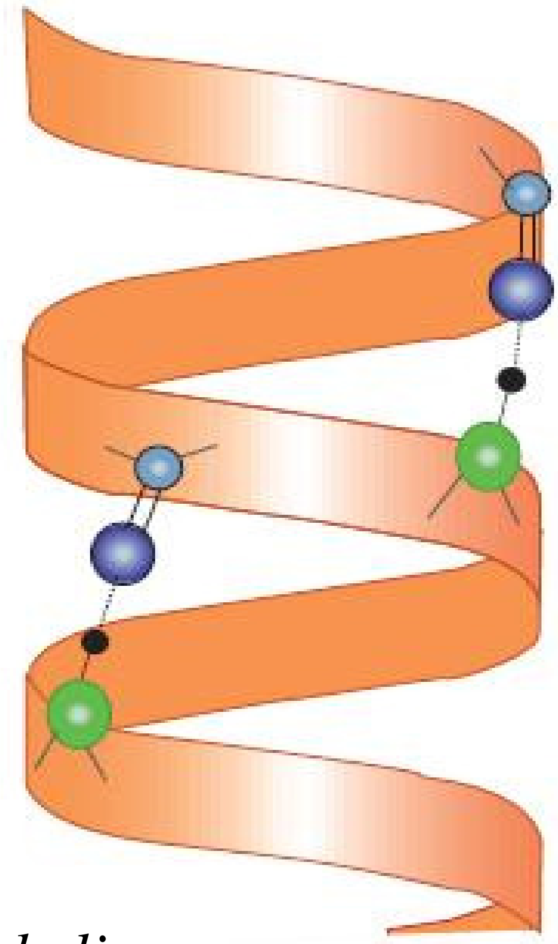
Figure 4.12. Hydrogen bonding in H_2O molecules.

Table 4.4 Properties of water and related substances.

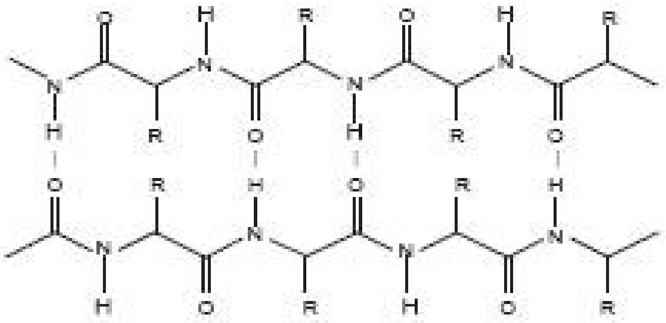
	NH_3	H_2O	HF	H_2S
Melting point (K)	195	273	184	187
Boiling point (K)	240	373	293	212
Dipole moment (D)	1.47	1.85	1.82	0.97

When water freezes, the molecules move slightly further away from their average position in the liquid state to each other, that reduces the density, ice floats on water for that reason

H-bonding in Proteins

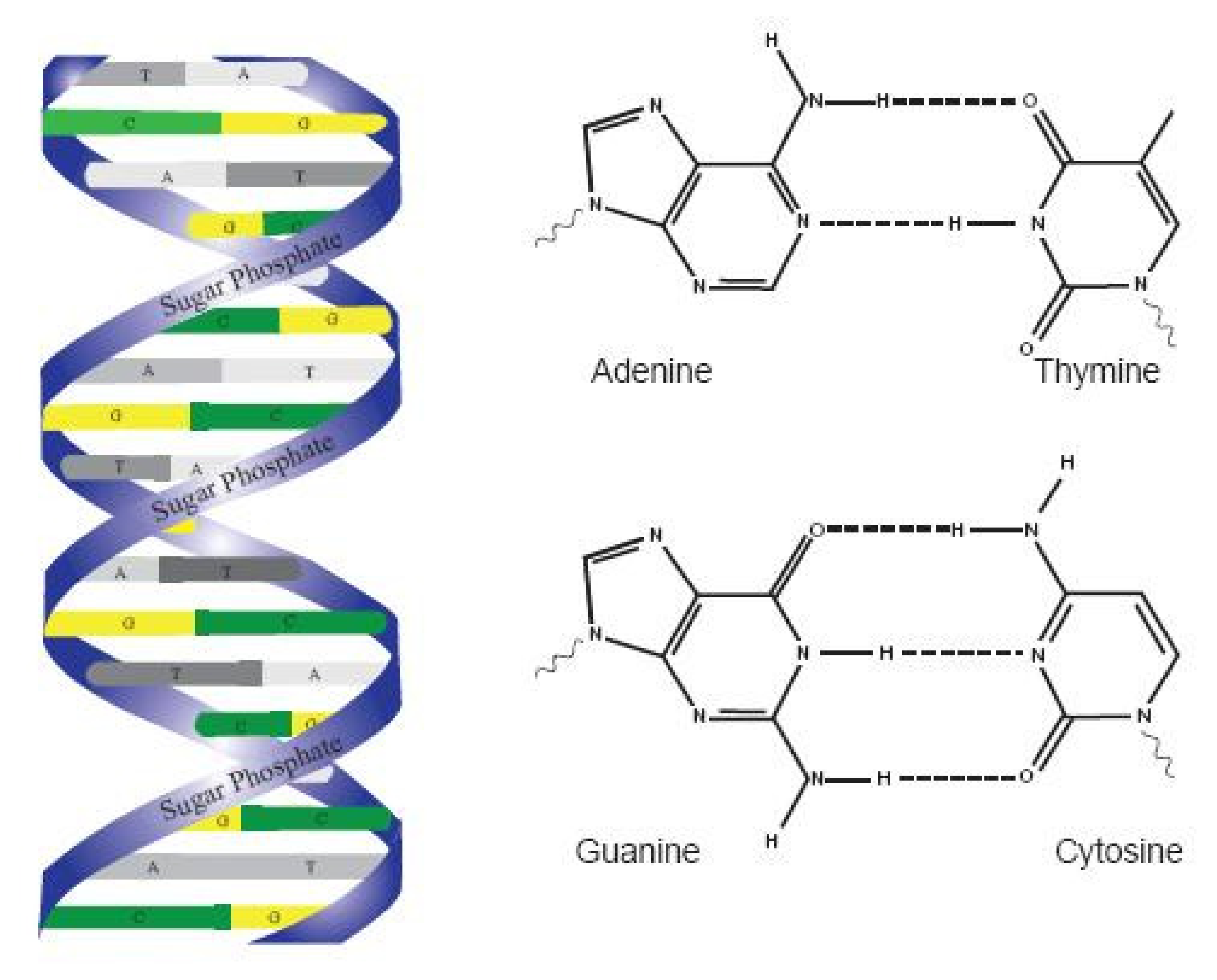


Alpha-helices



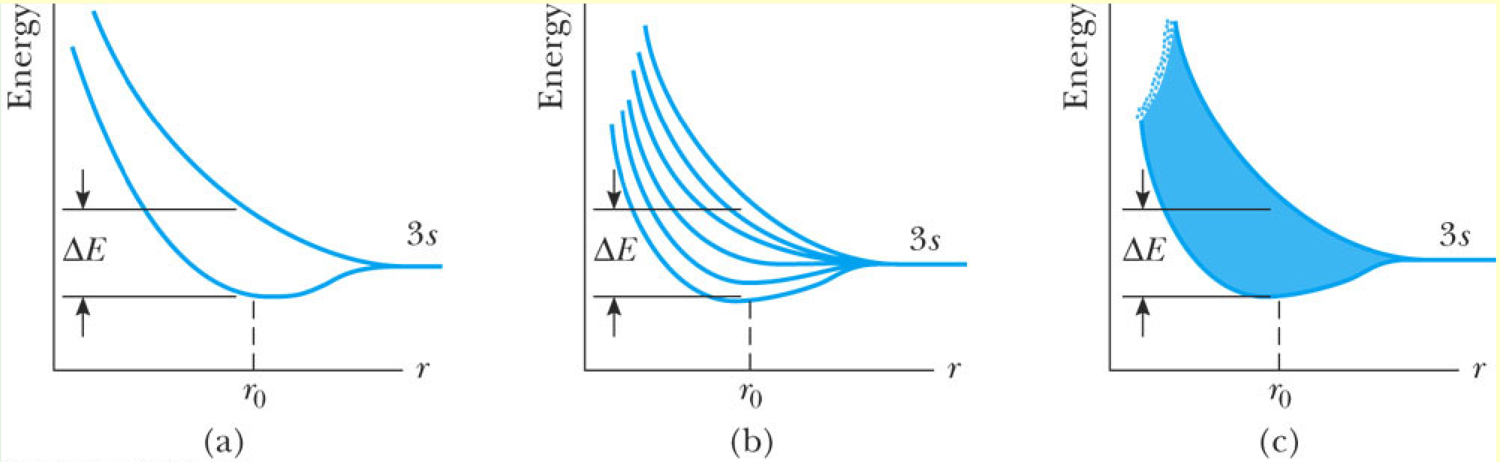
Beta-pleated sheets

H-bonding in Deoxyribonucleic acid, DNA



Concept of electro negativity

From two atoms to solids

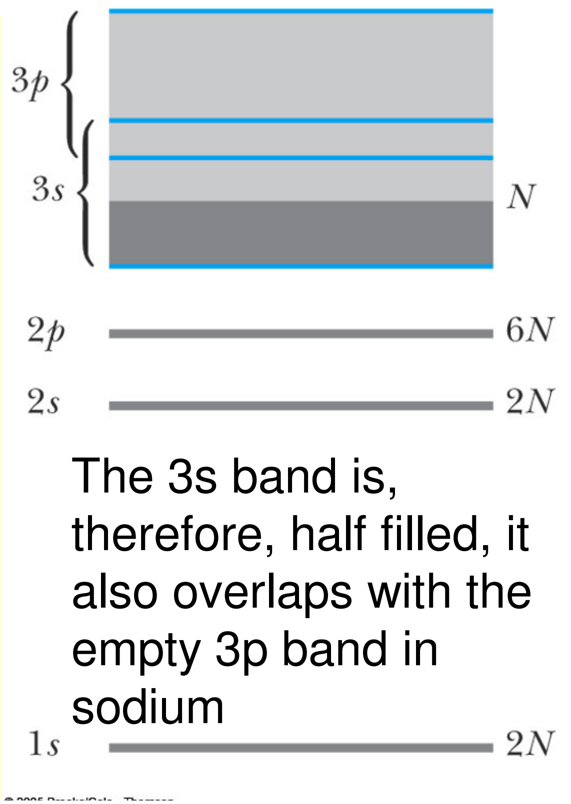


© 2005 Brooks/Cole - Thomson

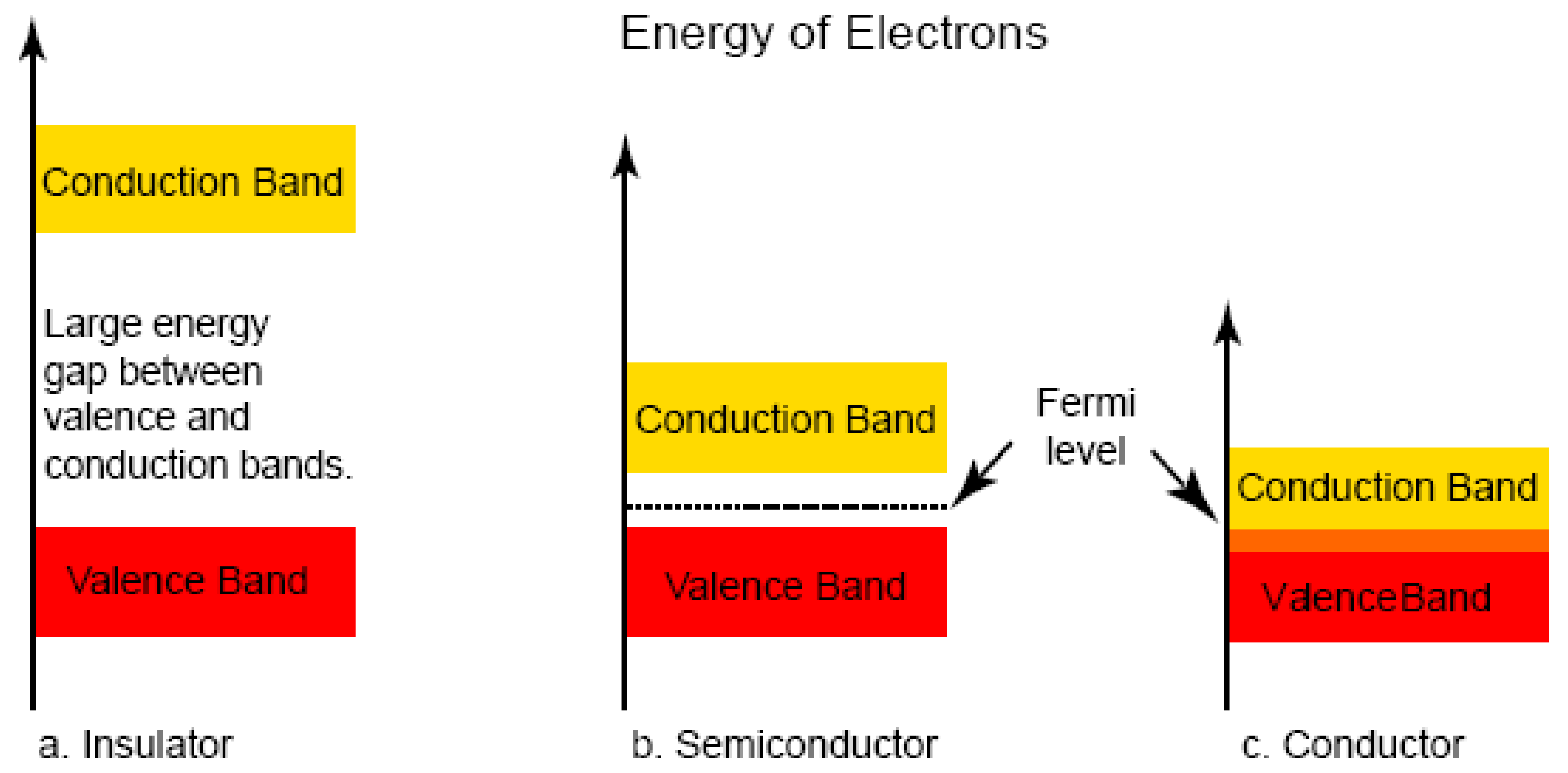
Just as we had for two hydrogen atoms coming together an binding and an anti-binding solution to the Schrödinger equation …

when two, six and a very large number of Na atoms come together in a solid with a crystalline structure, we get two, six, or a very large number of orbitals with closely spaced energy levels,

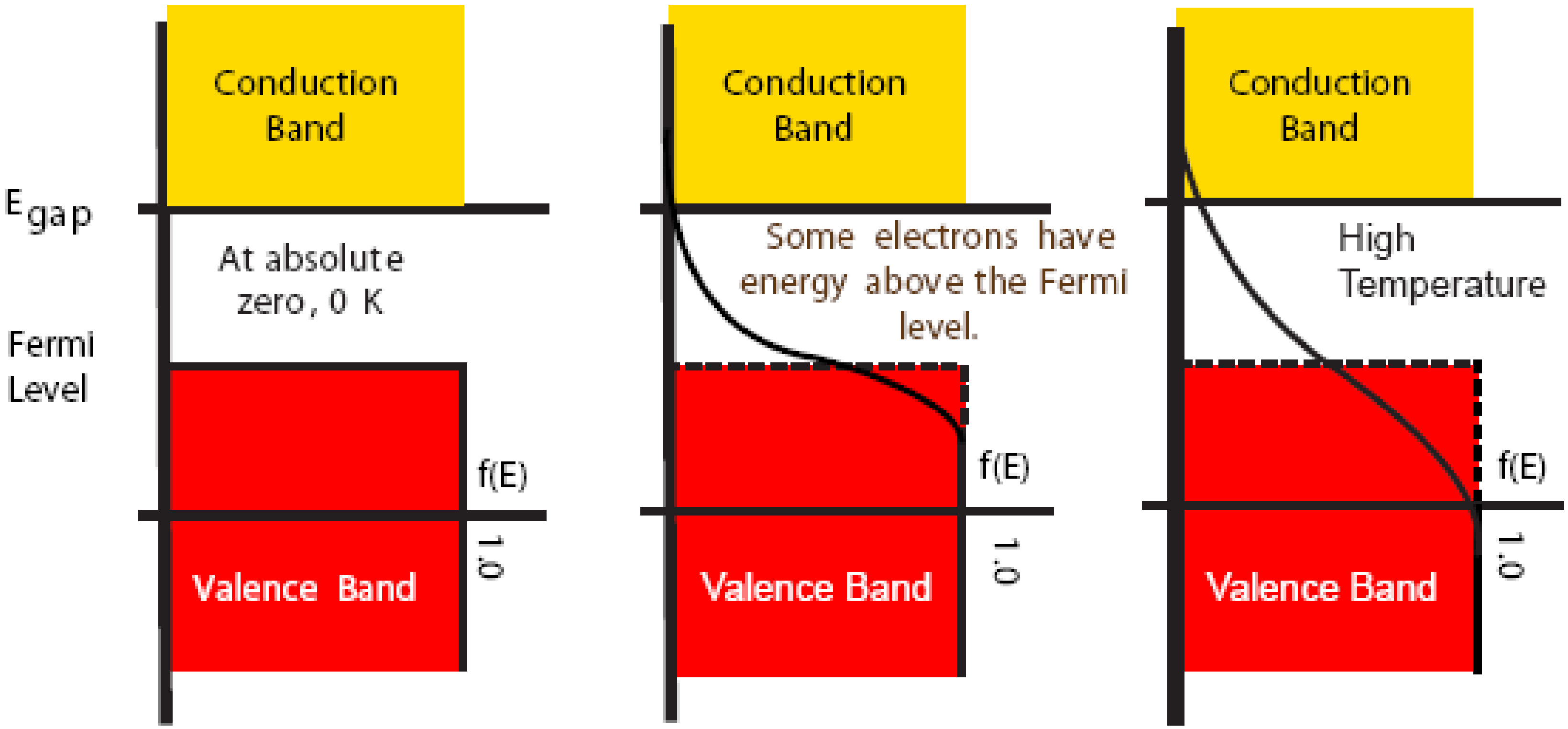
i.e. in effect we get an energy band for each of the atomic orbitals, shown here is only the 3s band where each Na atom contributes one electron, this will the outermost energy band, the conduction band



The 3s band is, therefore, half filled, it also overlaps with the empty 3p band in sodium



Distinction between classes of solid (crystalline materials), conduction and valence bands overlap in metals, there is “no bandgap” for metals as far as the temperature dependence of electric conductivity is concerned, not that semiconductors will have a different temperature dependence of electric conductivity than metals because the latter have a gap between the valence band and the conductions band



No electrons can be above the valence band at 0 K, since none have energy above the Fermi level and there are no available energy states in the band gap.

At high temperatures, some electrons can reach the conduction band and contribute to electric current.

In an intrinsic semiconductor, electric conductivity, (electron mobility) increases with temperature, remember from earlier lecture that in metals electric conductivity falls more or less linearly with increasing temperature

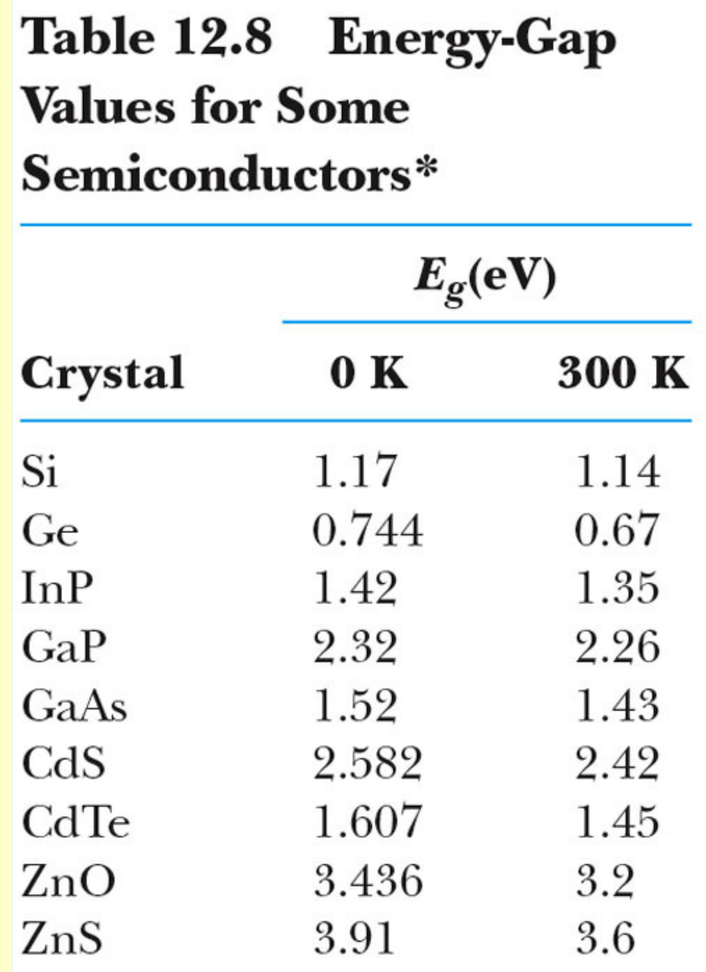
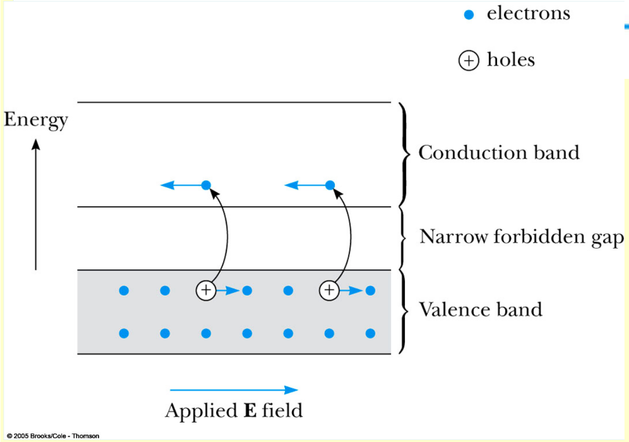
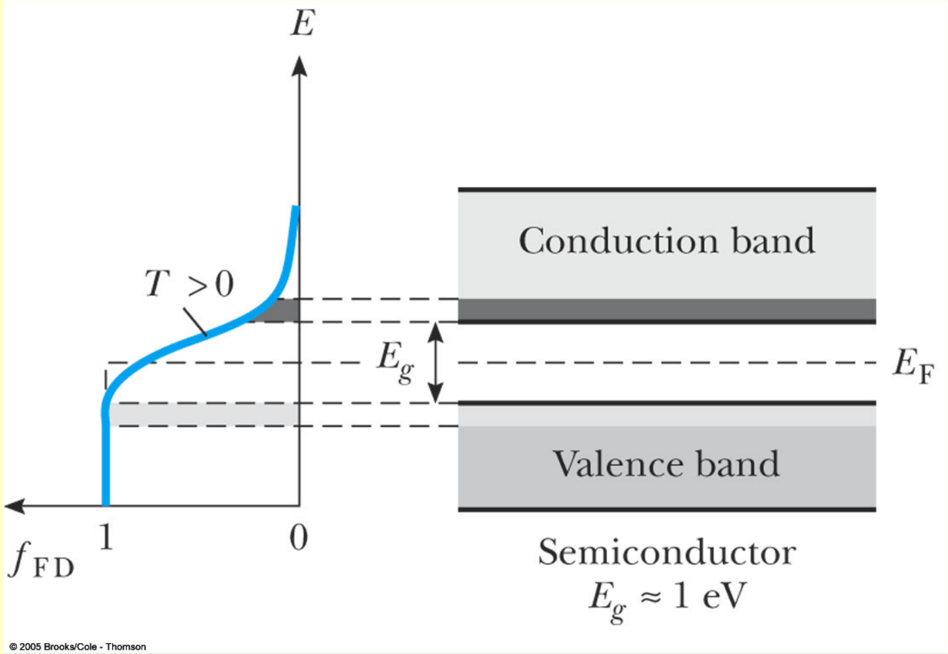
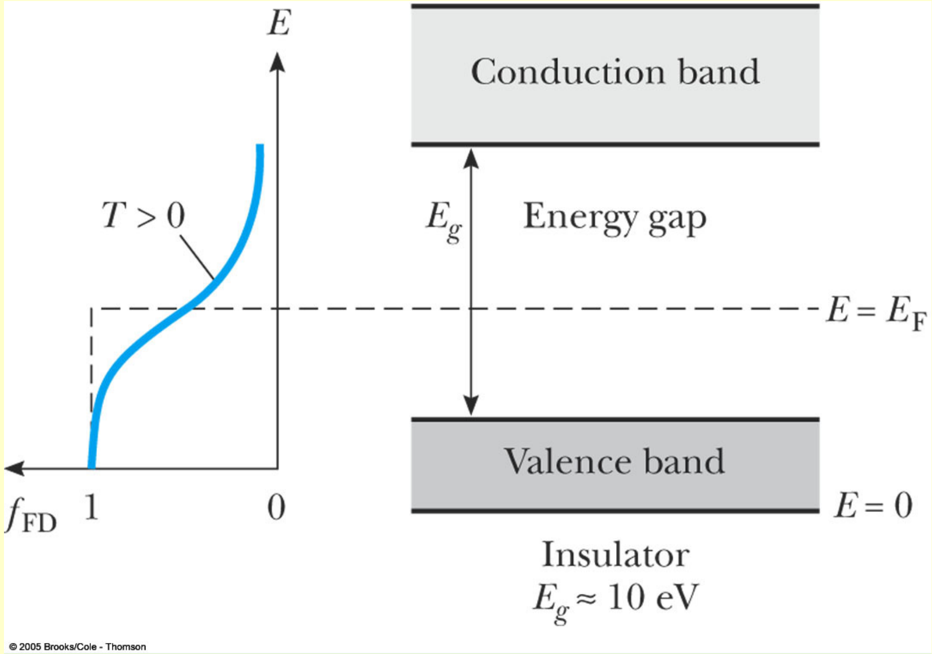


Table 12.8 Energy-Gap Values for Some Semiconductors*

	E_g(eV)	
Crystal	**0 K**	**300 K**
Si	1.17	1.14
Ge	0.744	0.67
InP	1.42	1.35
GaP	2.32	2.26
GaAs	1.52	1.43
CdS	2.582	2.42
CdTe	1.607	1.45
ZnO	3.436	3.2
ZnS	3.91	3.6

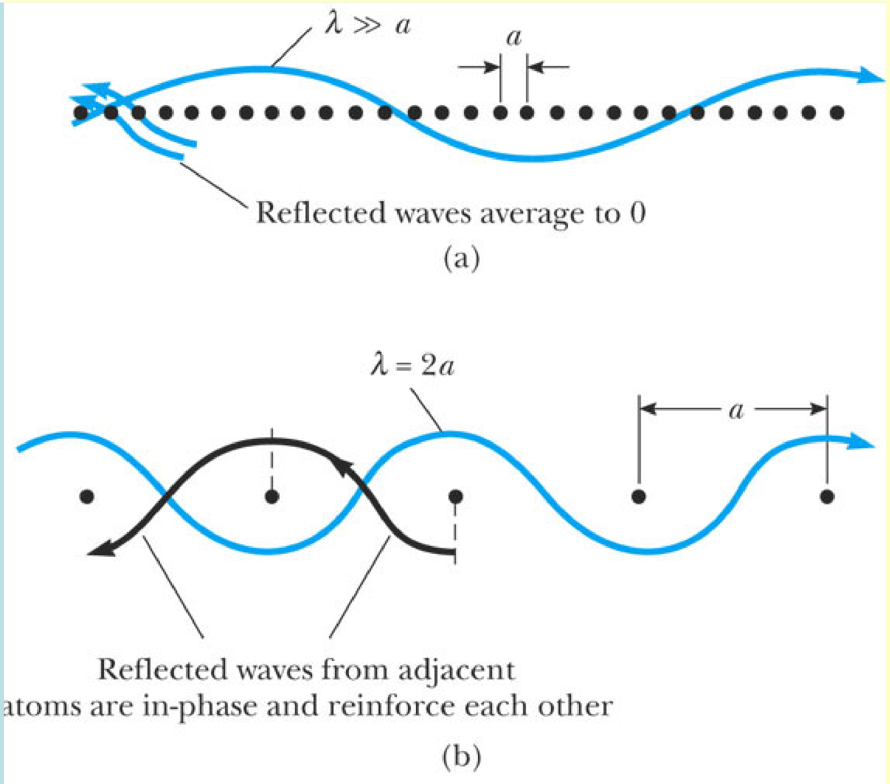


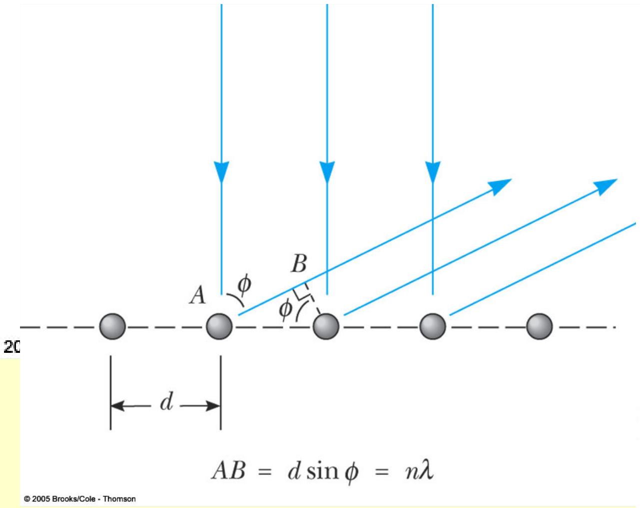


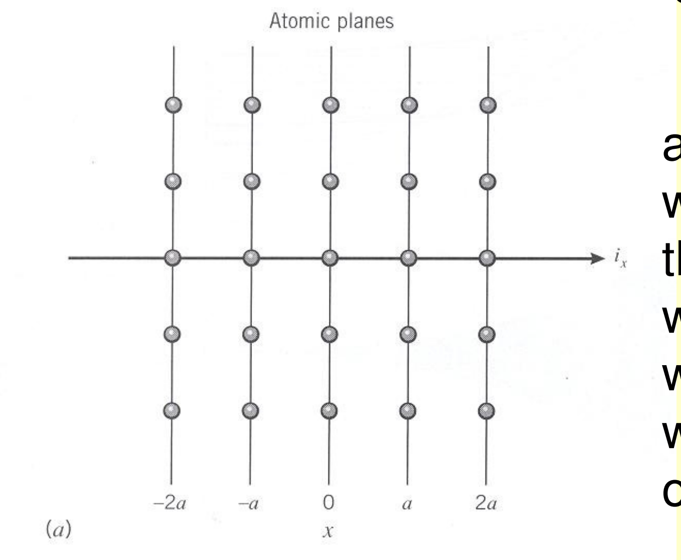


A one-dimensional crystalline lattice, repeat distance a, can support long wavelength (low energy) electrons without scattering, i.e. they are quite free to move in a periodic potential of height V_0 in the conduction band

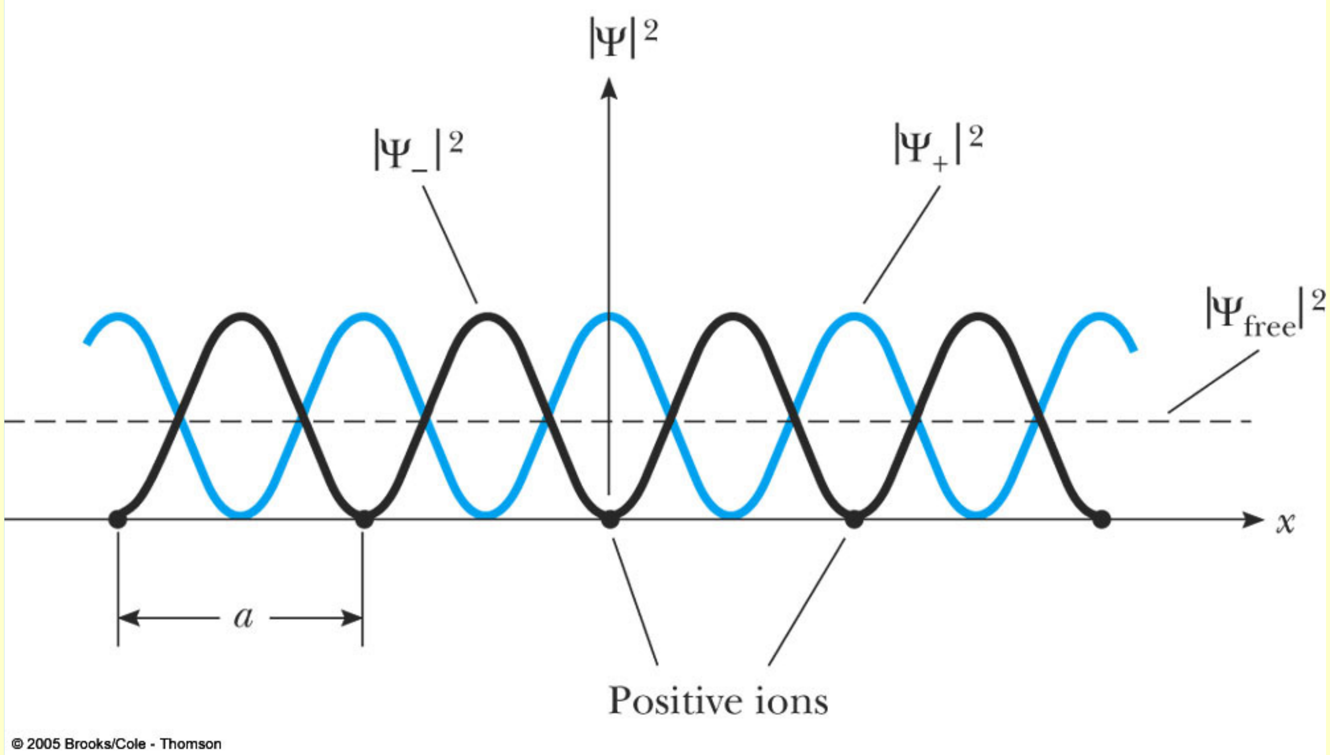
for certain sets of angles of incidence and electron wavelengths, there will be Bragg reflection, either for a surface grating or a bulk crystal, electron’s of these wavelength are repeatedly scattered into different directions, so will not portage “unaffected” through the lattice







For 2θ = 180º and an electron wavelength of 2a, there is an incoming wave and a reflected wave of the same wavelength in the opposite direction



There are two possible waves with a periodicity matching that of the lattice. One has its troughs and the other its crests at the position of the ions in the lattice. The ψ_ wave concentrates charge midway between the ions. The ψ_+ wave concentrates charge at the position of the ions. The ψ+ wave should, therefore, represent lower average potential energy. For a wave number k = 2π/λ, there must be two energy values in a plot E versus k - next slide - their energy separation corresponds to the width of the forbidden gap,

very loosely speaking, because the valence and conduction bands overlap in metals, Bragg scattering inside the crystal does for this particular class of materials not result in a “band gap” as it does in semiconductors

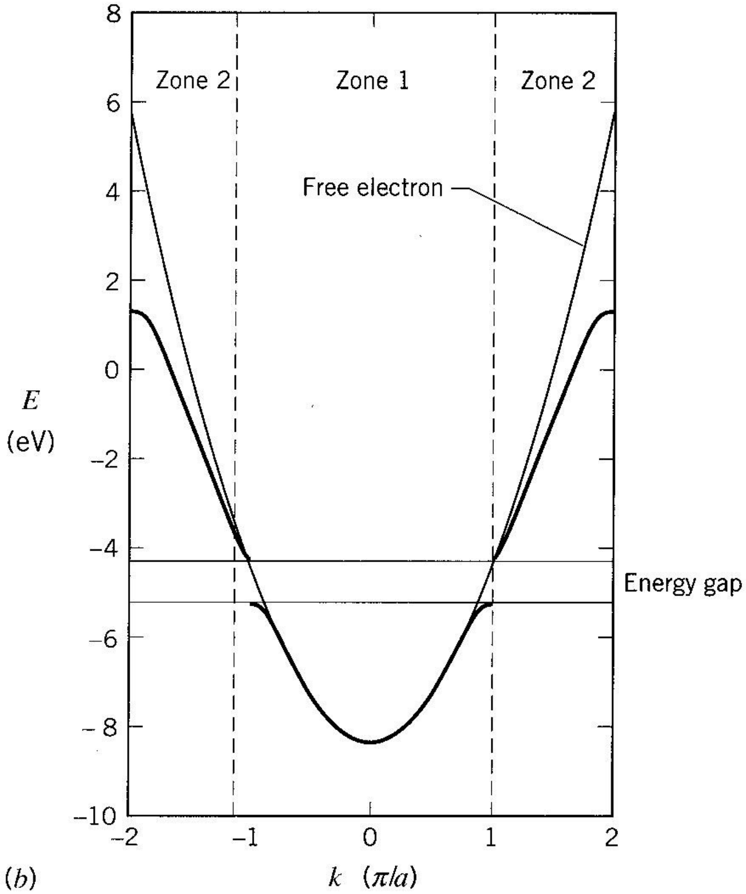
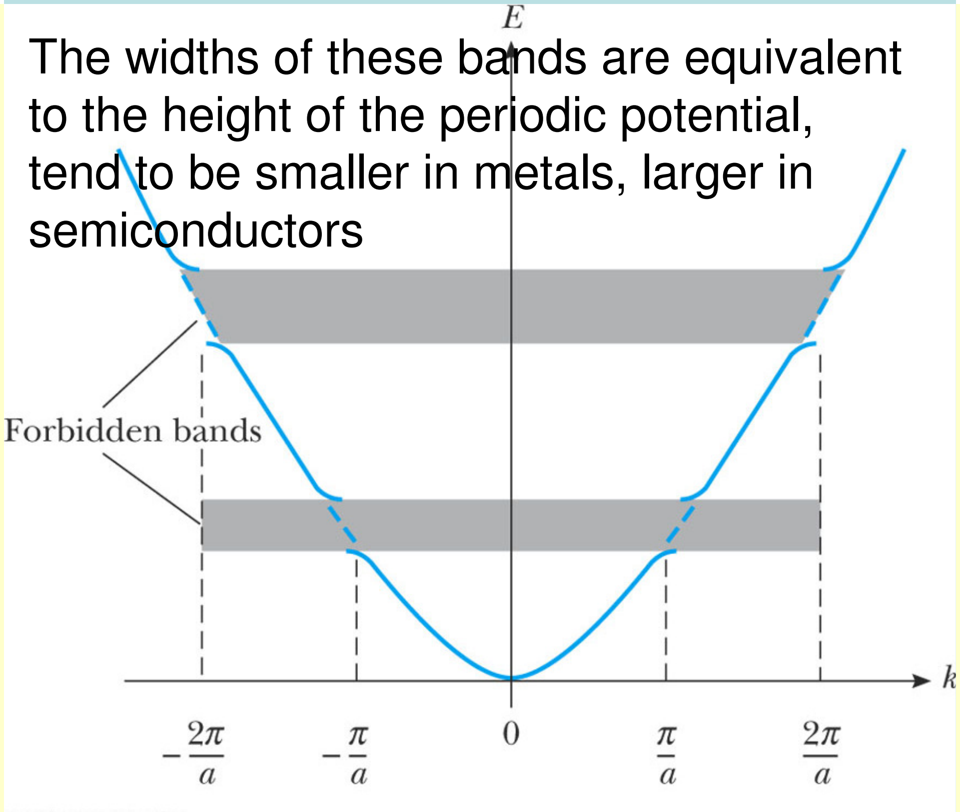


FIGURE 14-5 Electron plane waves propagating in a sodium crystal.
(a) The direction of propagation is chosen to be in the direction from one atom to its nearest neighbor, which is separated by a distance $x = a$. (b) Electron energy versus wave number k. The parabola corresponds to a free electron. After J. C. Slater, "Electronic Energy Bands in Metals," *Phys. Rev.* **45**, 794 (1934).

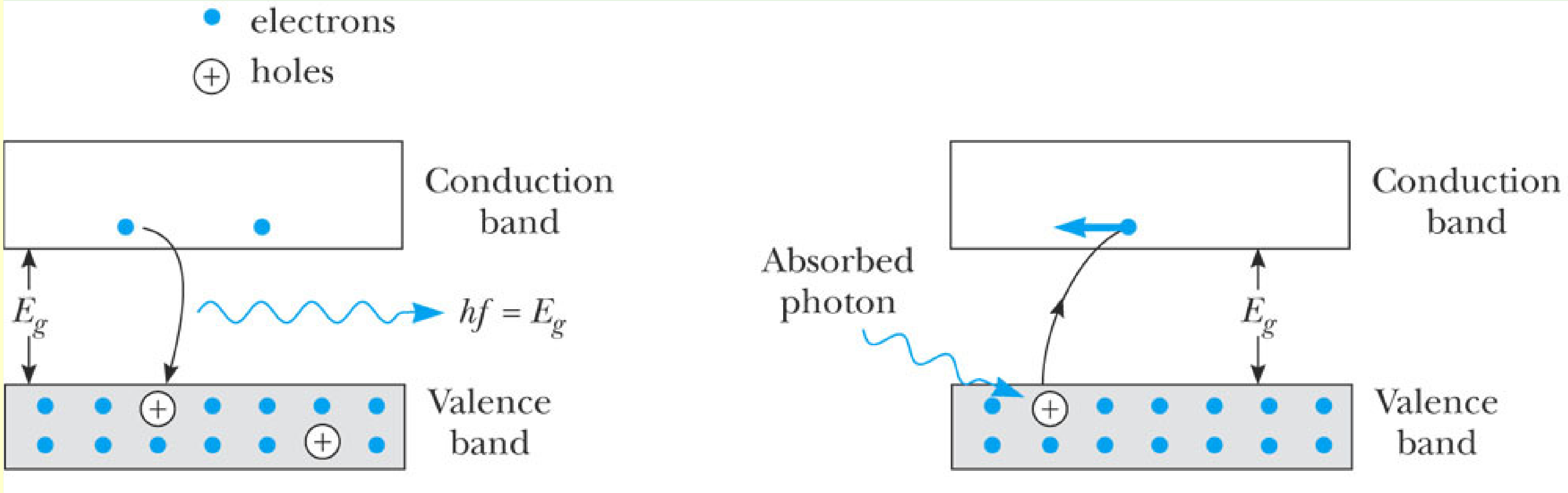


The widths of these bands are equivalent to the height of the periodic potential, tend to be smaller in metals, larger in semiconductors

© 2005 Brooks/Cole - Thomson

The second derivate of E with respect to k gives the effective mass of the electron (and/or hole if semiconductor) in the lattice, the effective mass is actually a tensor, different in different crystallographic directions

These forbidden bands are not between the valence band and the conduction band, we were talking about metals !!



(a) Light emission

(b) Light absorption

Band structure in semiconductors is often more complicated, also valence and conduction bands do not overlap so that there is a genuine band gap in the eV range that defines the electric conduction properties

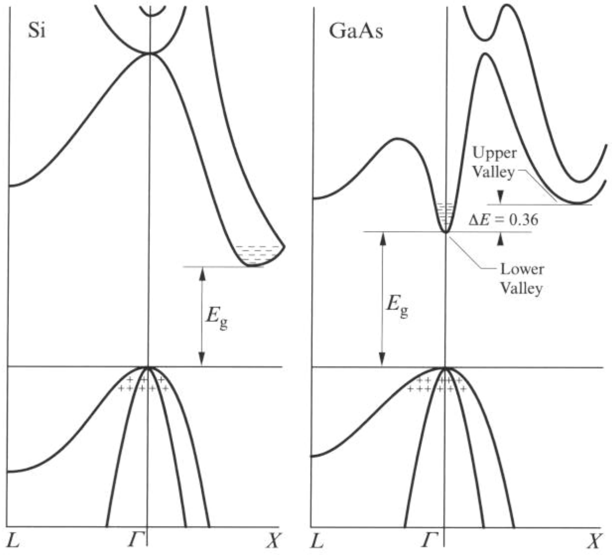
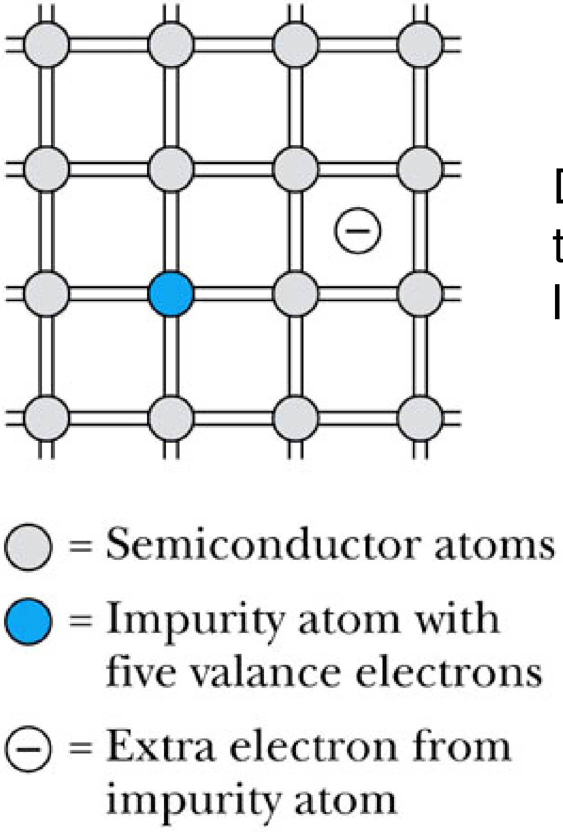


Figure 5.15 Energy band structures for Silicon (left) and GaAs (right). Energy is shown vertically, and k horizontally. The horizontal line marks the top of the filled "valence" bands; in pure samples the upper bands are empty except for thermal excitations (indicated by ++ and −-symbols.) The zero of momentum is indicated as "Γ", and separate sketches are given for E vs k in (111) left and (100) right directions.

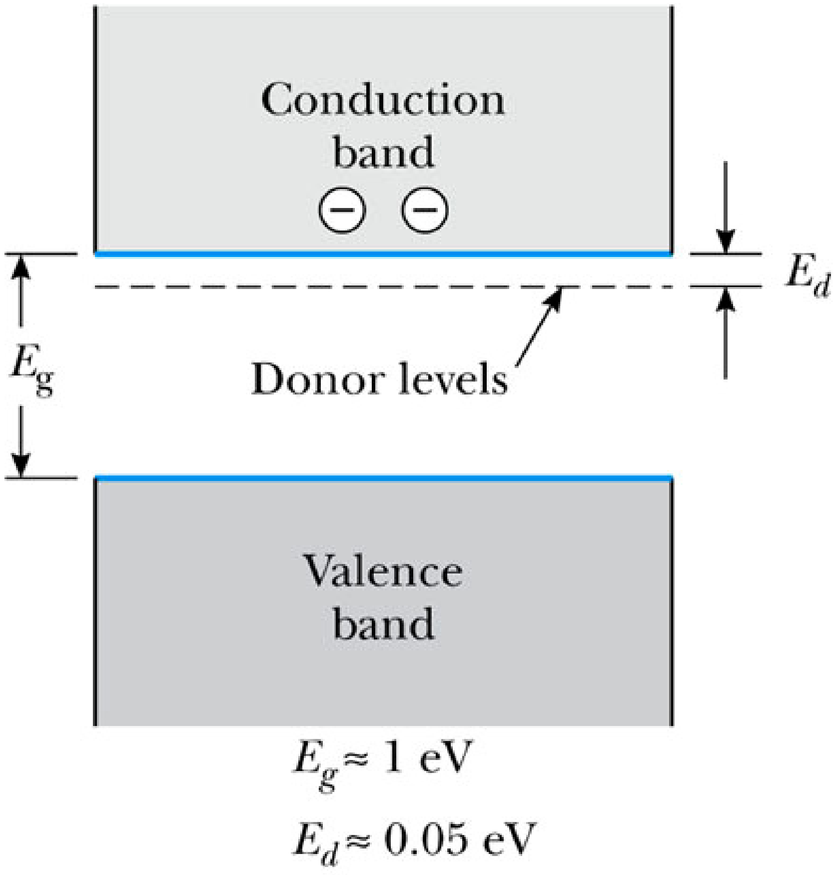
Direct (GaAs) and indirect (Si) semiconductors, only the direct ones are good for optoelectronic devices

Porous and defective Si can have direct bandgap



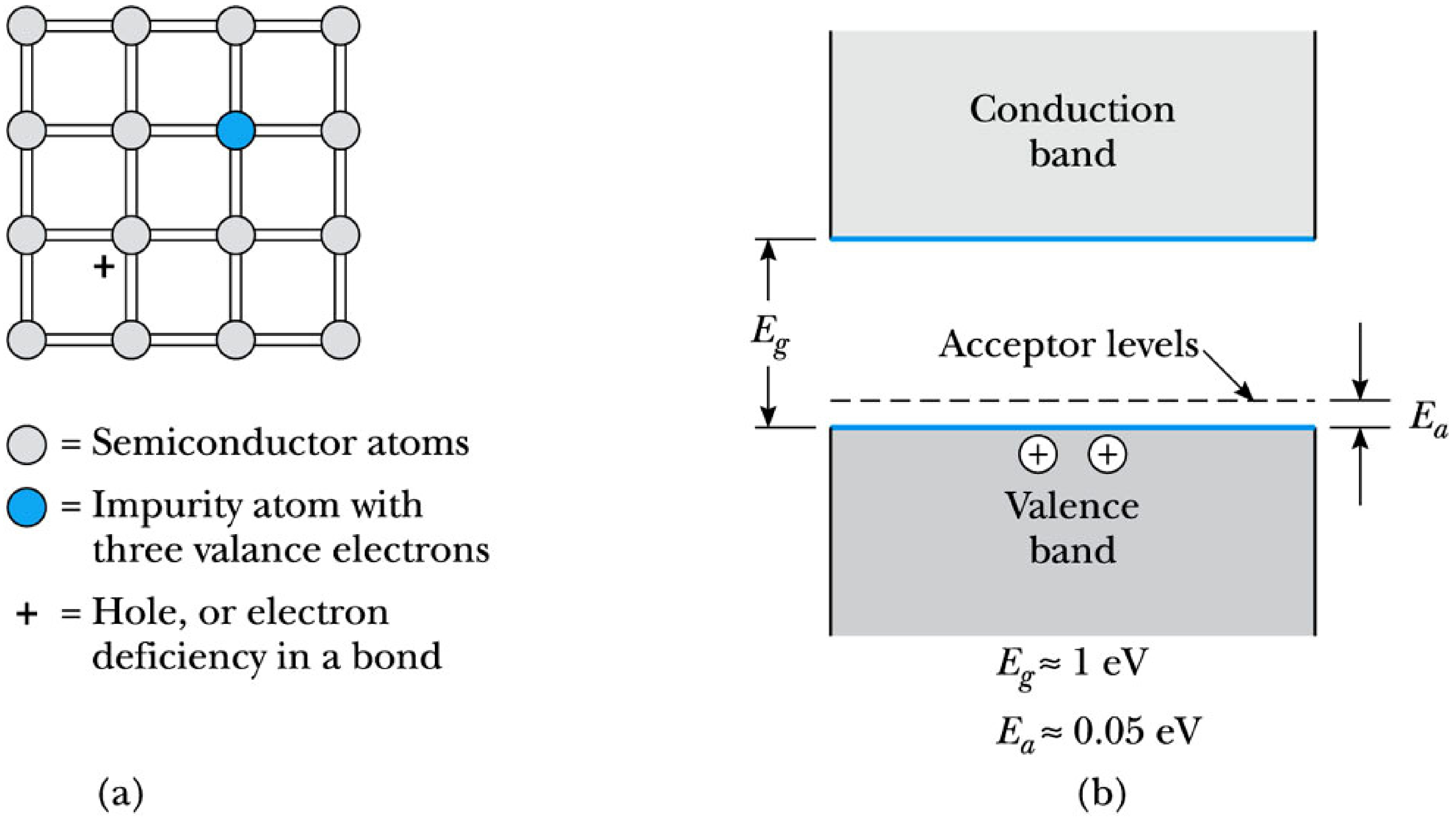
(a)

Dopands shift the Fermi level



(b)

In a chemical context, the Fermi level is referred to as electron chemical potential


+
= Semiconductor atoms
= Impurity atom with three valance electrons
+ = Hole, or electron deficiency in a bond
(a)
Conduction band
E_g
Acceptor levels
E_a
+
+
Valence band
$E_g \approx 1$ eV
$E_a \approx 0.05$ eV
(b)

Free electron gas for reduced dimensionalities

$n(E)\,dE = g(E)\,f(E)\,dE$ will be number of electrons as a function of energy

$$E = \frac{(n_x^2 + n_y^2 + n_z^2)h^2}{8mL^2}$$

for infinitely deep cube well

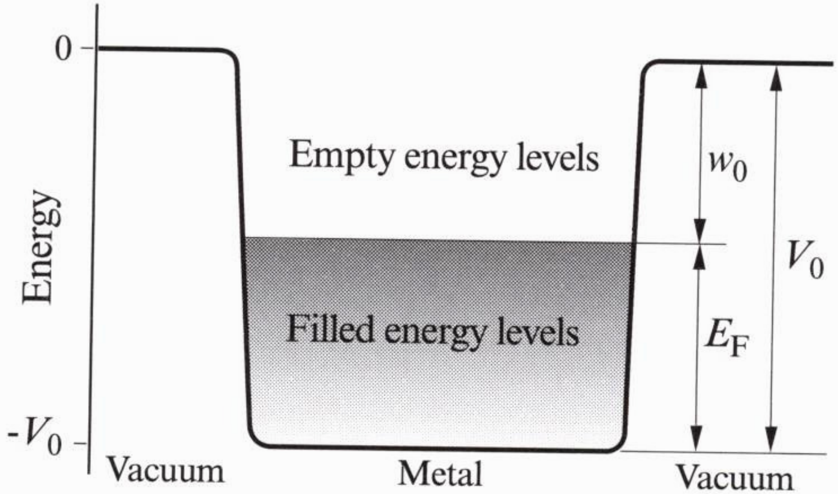


Figure 5.8 Metal as a 3D box filled with non-interacting electrons up to the Fermi energy E_F, following the Pauli exclusion principle. The total depth of the potential well is V_o, the sum of E_F and the work function, here labeled w_o

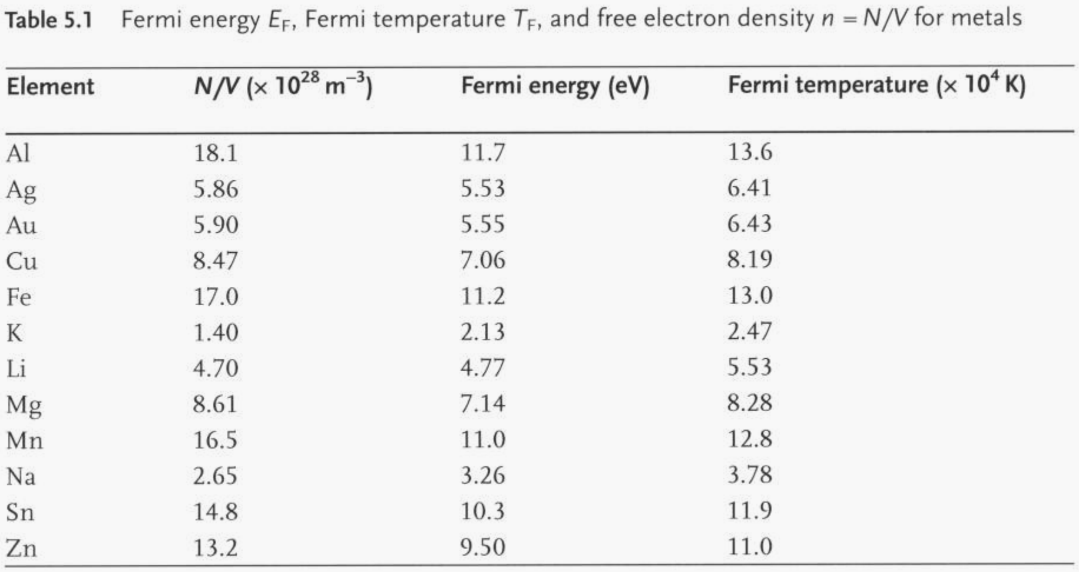


Table 5.1 Fermi energy E_F, Fermi temperature T_F, and free electron density $n = N/V$ for metals

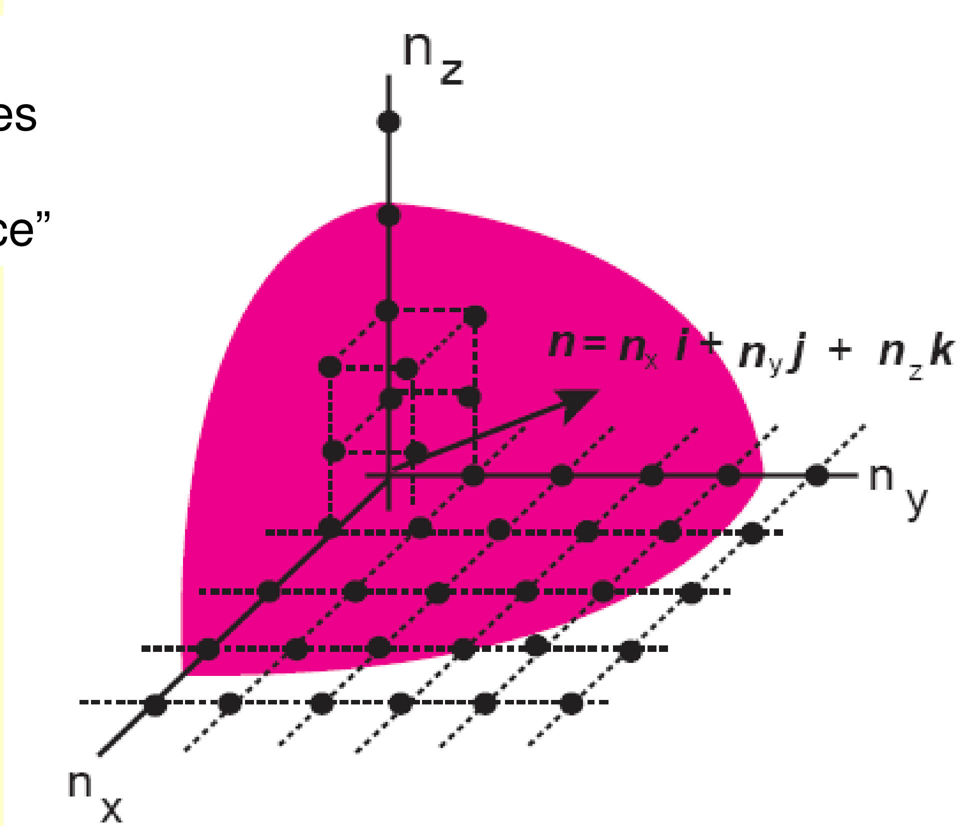
Element	N/V ($\times 10^{28}$ m^{-3})	Fermi energy (eV)	Fermi temperature ($\times 10^4$ K)
Al	18.1	11.7	13.6
Ag	5.86	5.53	6.41
Au	5.90	5.55	6.43
Cu	8.47	7.06	8.19
Fe	17.0	11.2	13.0
K	1.40	2.13	2.47
Li	4.70	4.77	5.53
Mg	8.61	7.14	8.28
Mn	16.5	11.0	12.8
Na	2.65	3.26	3.78
Sn	14.8	10.3	11.9
Zn	13.2	9.50	11.0

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$

Changes in the density of (electronic) states g(E) will happen with changes in dimensionality, this will give different numbers of electrons with an energy E + dE

Spherical volume of radius R encompassing a number of possible states

Rayleigh scheme for counting: number of states is proportional to the volume in the "state-space"

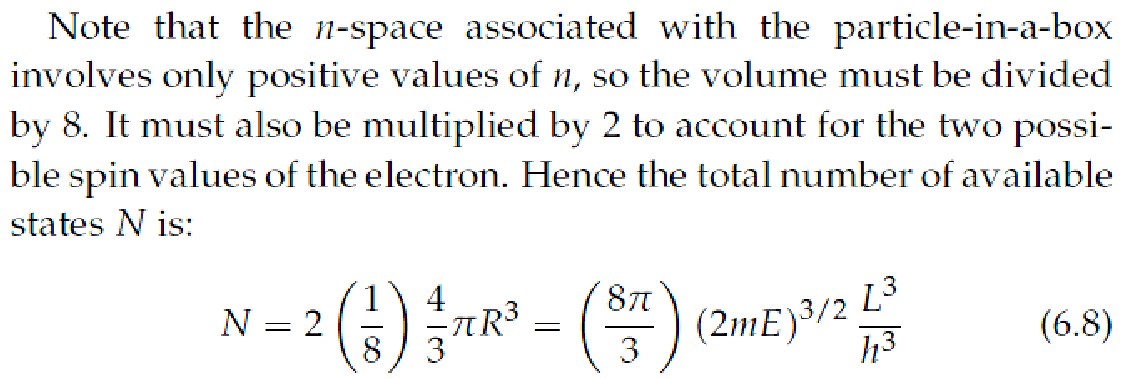


Define a radius R

$$R = \sqrt{n_x^2 + n_y^2 + n_z^2}$$

$$E = \frac{(n_x^2 + n_y^2 + n_z^2)h^2}{8mL^2}$$

$$R = \frac{2\sqrt{2mEL}}{h}$$



Note that the n-space associated with the particle-in-a-box involves only positive values of n, so the volume must be divided by 8. It must also be multiplied by 2 to account for the two possible spin values of the electron. Hence the total number of available states N is:

$$N = 2\left(\frac{1}{8}\right)\frac{4}{3}\pi R^3 = \left(\frac{8\pi}{3}\right)(2mE)^{3/2}\frac{L^3}{h^3} \qquad (6.8)$$

The number of states per unit volume n is:

$$n = \frac{N}{L^3} = \left(\frac{8\pi}{3}\right)\frac{(2mE)^{3/2}}{h^3}$$

The final DOS as a function of energy $g(E)$ is the derivative of this population n with respect to energy:

$$g(E) = \frac{dn}{dE} = \frac{4\pi\,(2m)^{3/2}}{h^3}\sqrt{E}$$

This 3D DOS function $g(E)$ represents the number of electron states per unit volume per unit energy at energy E. This expression can be applied to bulk 3D materials, and is independent of the dimension L.

$$n(E)\,dE = g(E)\,f(E)\,dE$$

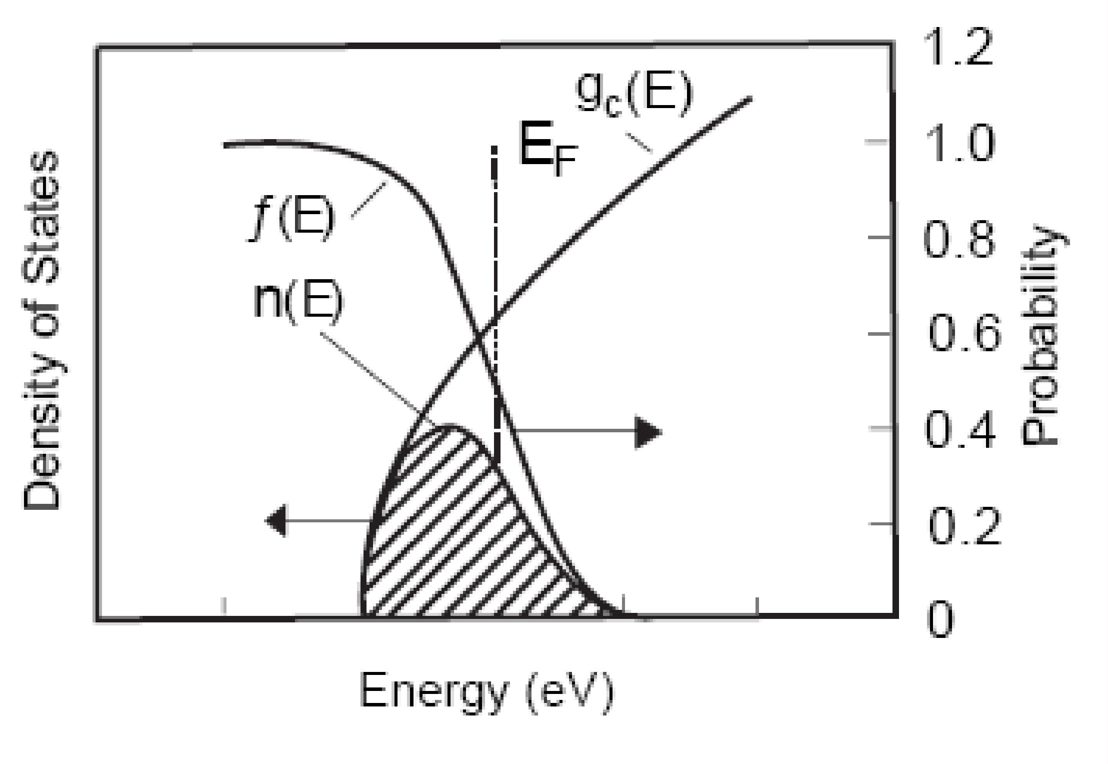
carrier density n in a 3D bulk semiconductor

$$n = \int_{Ec}^{\infty} n(E)dE = \int_{Ec}^{\infty} g(E)f(E)dE$$

from the bottom of the conduction band E_c, to the top of the conduction band

$$n = \int_{Ec}^{\infty} n(E)dE = \int_{Ec}^{\infty} g(E)f(E)dE$$

Represents the shaded area in graph below



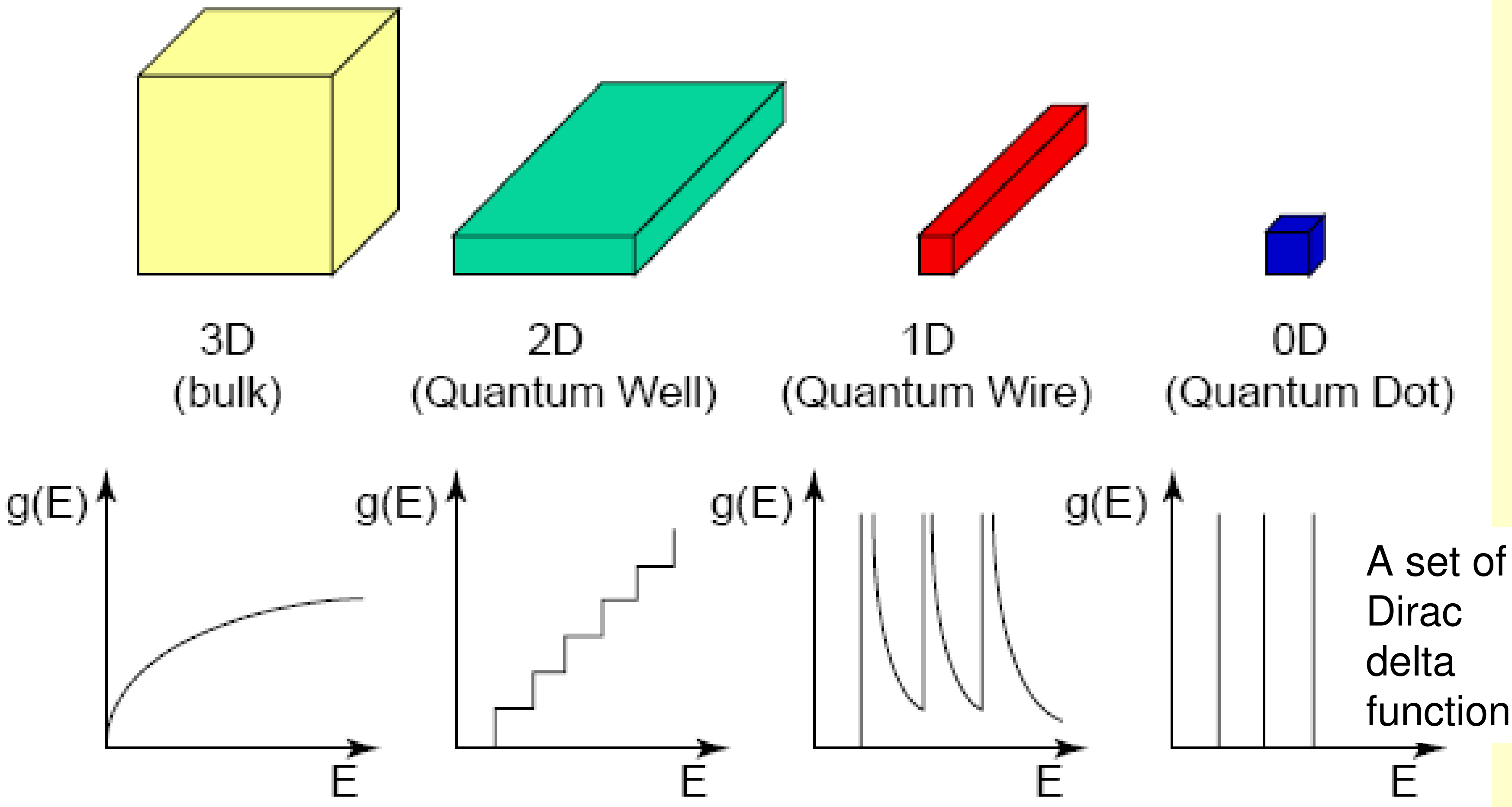
Substituting the expressions for $g(E)$ and $f(E)$

$$n_0 = \int_{Ec}^{\infty} \frac{4\pi(2m_e^*)^{3/2}}{h^3} \sqrt{E - E_c} \frac{1}{1 + e^{\frac{E-E_F}{kT}}} dE$$

In thermal equilibrium

m_e^* is the effective electron mass

Density of states for 3D, 2D, 1D, and 0D structures



A set of Dirac delta functions

$$g_{3D}(E) = \frac{dn_{3D}}{dE} = \frac{4\pi\,(2m^*)^{3/2}}{h^3}\sqrt{E - E_{\min}}$$

$$g_{1D}(E) = \frac{dn_{1D}}{dE} = \sqrt{\frac{2m^*}{h^2}}\,\frac{1}{\sqrt{E - E_{\min}}}$$

$$g_{2D}(E) = \frac{dn_{2D}}{dE} = \frac{4\pi m^*}{h^2}$$

Effective mass changes in step like fashion

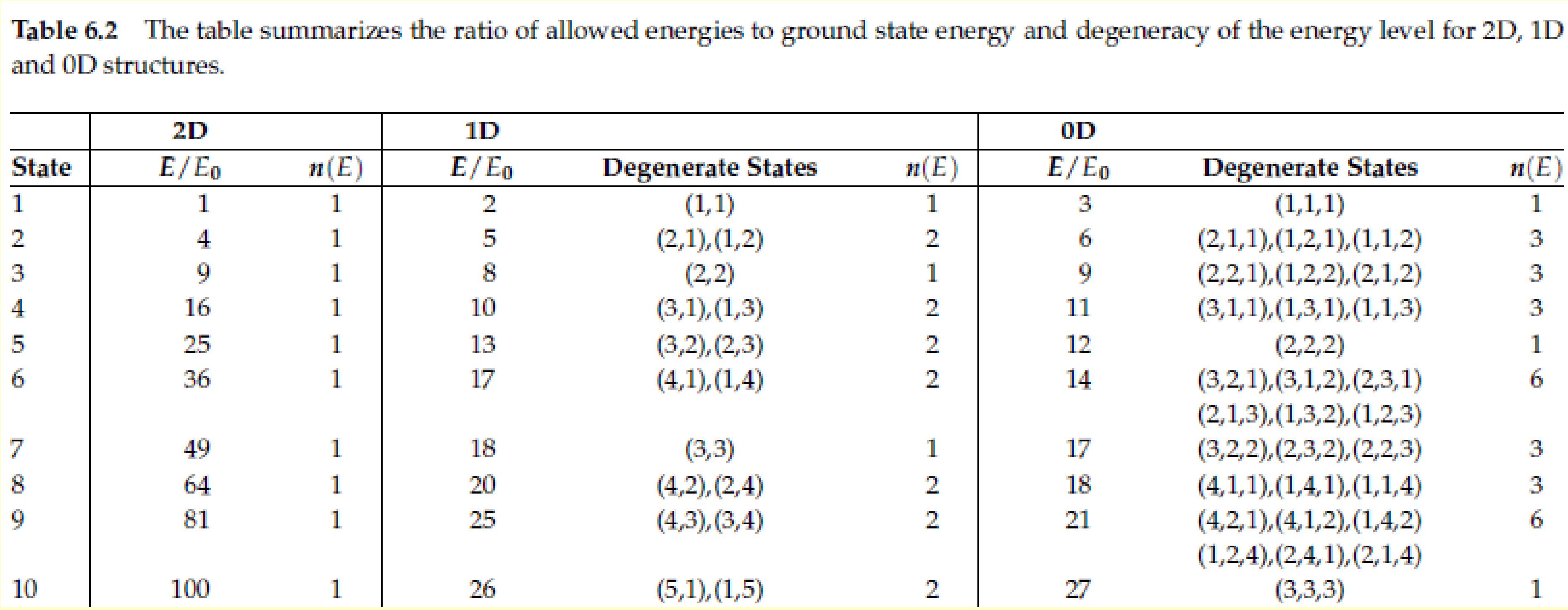


Table 6.2 The table summarizes the ratio of allowed energies to ground state energy and degeneracy of the energy level for 2D, 1D and 0D structures.

	2D		1D			0D		
State	E/E_0	$n(E)$	E/E_0	**Degenerate States**	$n(E)$	E/E_0	**Degenerate States**	$n(E)$
1	1	1	2	(1,1)	1	3	(1,1,1)	1
2	4	1	5	(2,1),(1,2)	2	6	(2,1,1),(1,2,1),(1,1,2)	3
3	9	1	8	(2,2)	1	9	(2,2,1),(1,2,2),(2,1,2)	3
4	16	1	10	(3,1),(1,3)	2	11	(3,1,1),(1,3,1),(1,1,3)	3
5	25	1	13	(3,2),(2,3)	2	12	(2,2,2)	1
6	36	1	17	(4,1),(1,4)	2	14	(3,2,1),(3,1,2),(2,3,1) (2,1,3),(1,3,2),(1,2,3)	6
7	49	1	18	(3,3)	1	17	(3,2,2),(2,3,2),(2,2,3)	3
8	64	1	20	(4,2),(2,4)	2	18	(4,1,1),(1,4,1),(1,1,4)	3
9	81	1	25	(4,3),(3,4)	2	21	(4,2,1),(4,1,2),(1,4,2) (1,2,4),(2,4,1),(2,1,4)	6
10	100	1	26	(5,1),(1,5)	2	27	(3,3,3)	1

1D electron transport is ballistic if $L \sim \lambda_F$ electron Fermi wavelength, that dominates electron transport

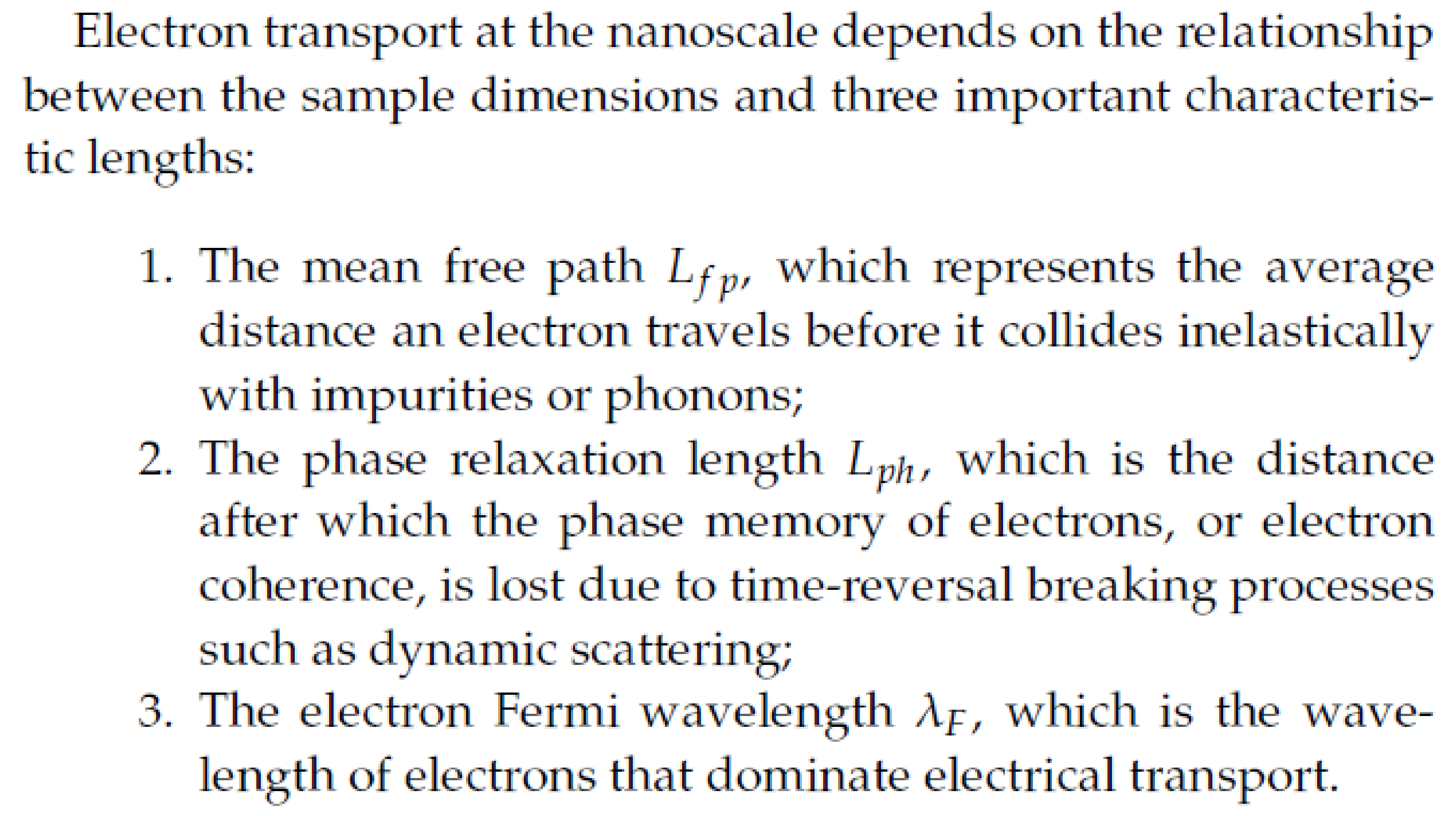
$\sigma_0 = \frac{2e^2}{h}$ quantum of electrical conductance/resistance^{-1} $h/2e^2 \approx 12.9k\Omega$

often called the *contact resistance*.

conductance of ballistic structures is independent of the length of the sample.

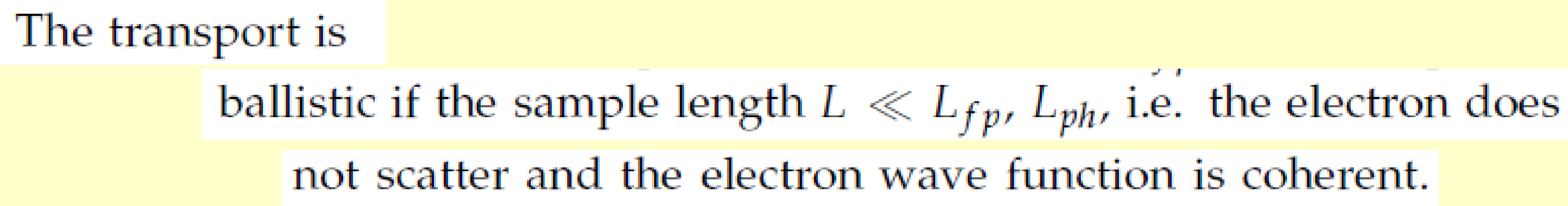
$$R = \sigma^{-1}\, {}^{l}\!/_{A}$$

Classically the electric resistance does depend on the length of the wire l, Ohm's law for a 3D structure, A cross section area of the wire



Electron transport at the nanoscale depends on the relationship between the sample dimensions and three important characteristic lengths:

1. The mean free path L_{fp}, which represents the average distance an electron travels before it collides inelastically with impurities or phonons;
2. The phase relaxation length L_{ph}, which is the distance after which the phase memory of electrons, or electron coherence, is lost due to time-reversal breaking processes such as dynamic scattering;
3. The electron Fermi wavelength λ_F, which is the wavelength of electrons that dominate electrical transport.



The transport is

ballistic if the sample length $L \ll L_{fp}, L_{ph}$, i.e. the electron does not scatter and the electron wave function is coherent.

ballistic transport involves only electrons close to the Fermi energy, E_F

$h/2e^2 \approx 12.9k\Omega$

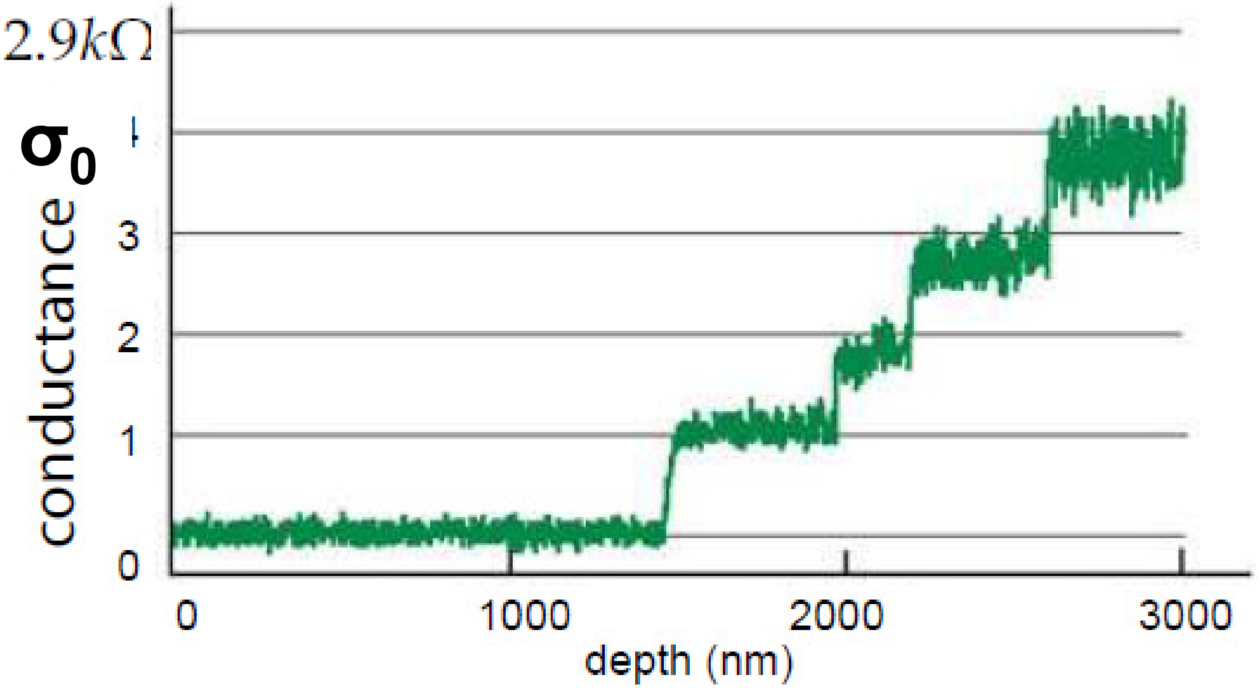


Figure 6.10. Walt de Heer and co-workers measured the conductance of individual multiwall carbon nanotubes. Conductance increases in units of the quantum of conductance as the number of individual nanotubes making contact with the mercury increases, suggesting that nanotubes are ballistic 1D conductors. [Image courtesy of Prof. Walter A. de Heer.]

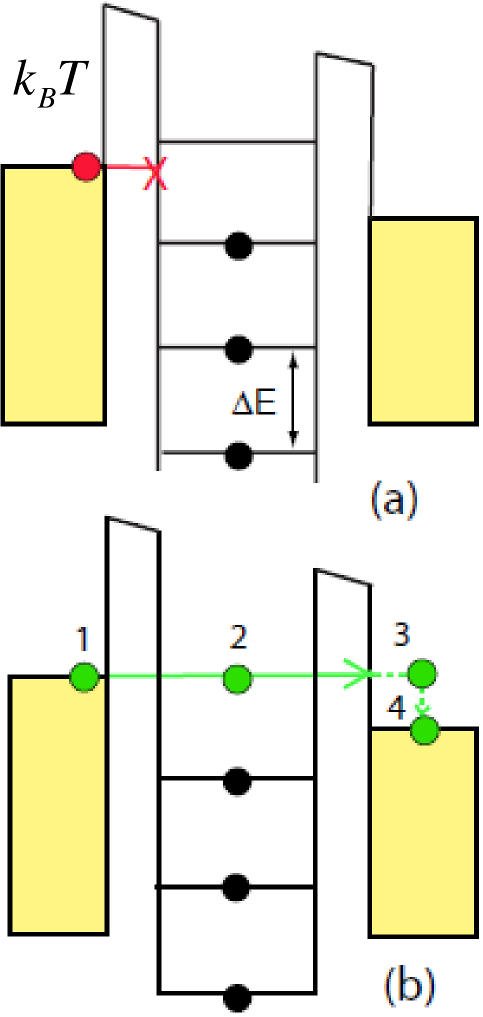
When two carbon nanotubes make contact, the quantized conductance is twice as large, analogously for 3, …

single electron transistor (SET)

Instead of metal disc, also single C_{60} molecules with tunnel contacts, ***molecular electronics***

$$eV = {}^{e^2}\!/_{2C} << k_B T$$

effect of a very small voltage (V) on the gate, that allows one other electron to tunnel from the source all the way to the drain



The SET has effectively two states:

1. *Blocking state*: As seen in Fig. 6.13(a), no accessible energy levels are within tunneling range of the electron (red) on the source contact. All energy levels on the island electrode with lower energies are occupied.
2. *Positive voltage applied to gate electrode*: Energy levels of the island electrode are lowered and the electron (green 1) can tunnel onto the island (2), occupying a previously vacant energy level. From there it can tunnel onto the drain electrode (3) where it inelastically scatters and reaches the drain electrode Fermi level (4).

gate it connected to “metal disc” of less than 20 nm radius with self capacitance C , ${}^{e}/_{2C}$ is a voltage on the bottom gate, e times this voltage must be significantly larger than 25 meV for the device to work at room temperature (so C as small as possible), without this voltage, electron cannot tunnel due to so called “Coulomb blockade”

Figure 6.13. Energy level diagram of the single electron transistor.

tunnel resistances R_t of the barriers

$$R_t \gg \frac{h}{e^2}$$

for a flat disc,

$C = 8\varepsilon_r\varepsilon_0 R$, where ε_r is the dielectric constant of the material

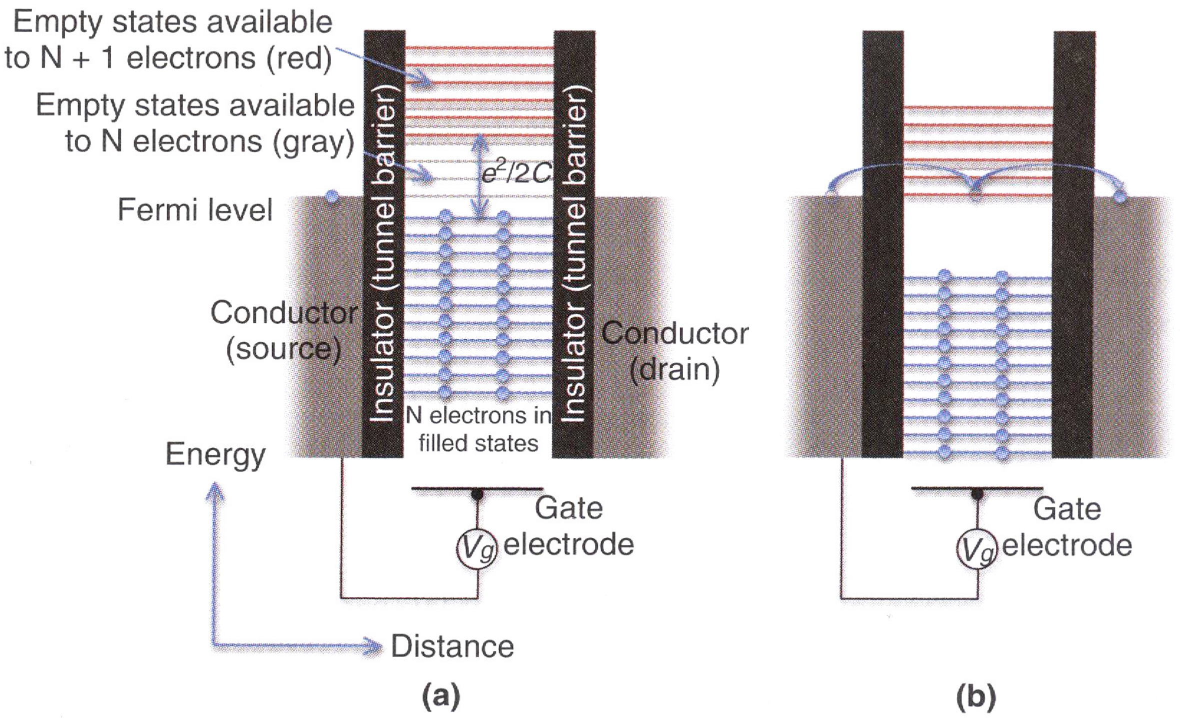


Fig. 5.11 Coulomb Blockade in a nanoparticle FET. (a) Energy level diagram of nanoparticle with discrete states due to the quantum size effect connected to source and drain electrodes via thin insulating tunnel barriers and a gate electrode in close proximity. The highest filled state of the particle approximately aligns with the highest filled electron level of the continuum in the source and drain electrodes (the Fermi level). The gray empty states are available to the N electron population of the nanoparticle but not to $N + 1$ electrons. If an extra electron was forced onto the particle the extra energy due to its charge ($e^2/2C$, where C is the capacitance – see Advanced Reading Box 5.3) would shift the available empty states to the red ones so tunneling from the source onto the particle is forbidden. If a voltage e/2C is applied to the gate electrode the lowest red state is pulled down into line with the Fermi level and if a bias is applied between the source and drain a single electron can tunnel onto the particle and off again. The device thus acts as an FET with the gate controlling whether tunneling conductance is allowed (one electron at a time), or not. To conduct two electrons at a time would require a further increase in the gate voltage.

Of course electrons are fermions, also the unoccupied energy levels for n+1 electrons are different to n electrons, so the voltage is to make the shift to fit the n+1 (unoccupied) electron levels for that electron to ‘hop onto the island””