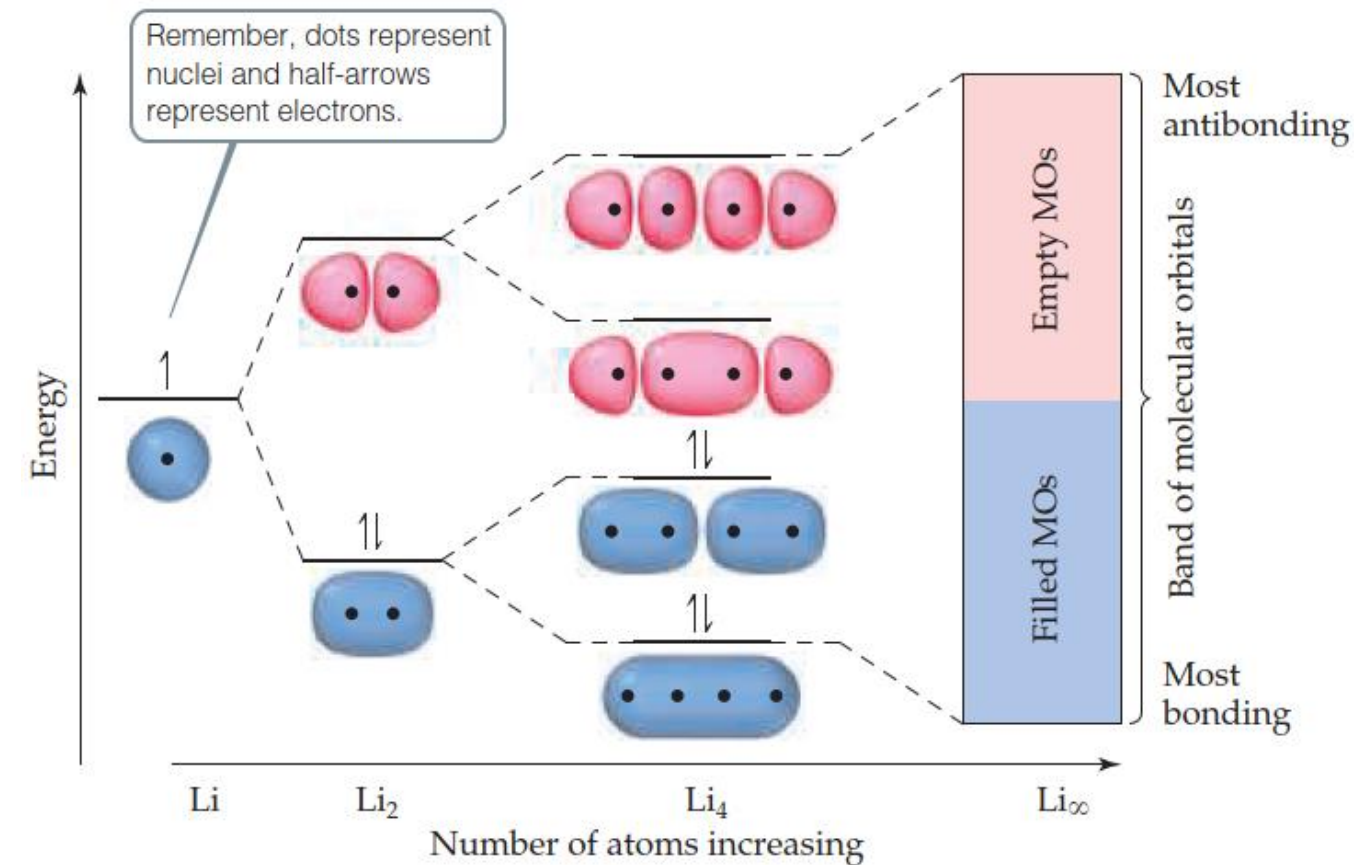


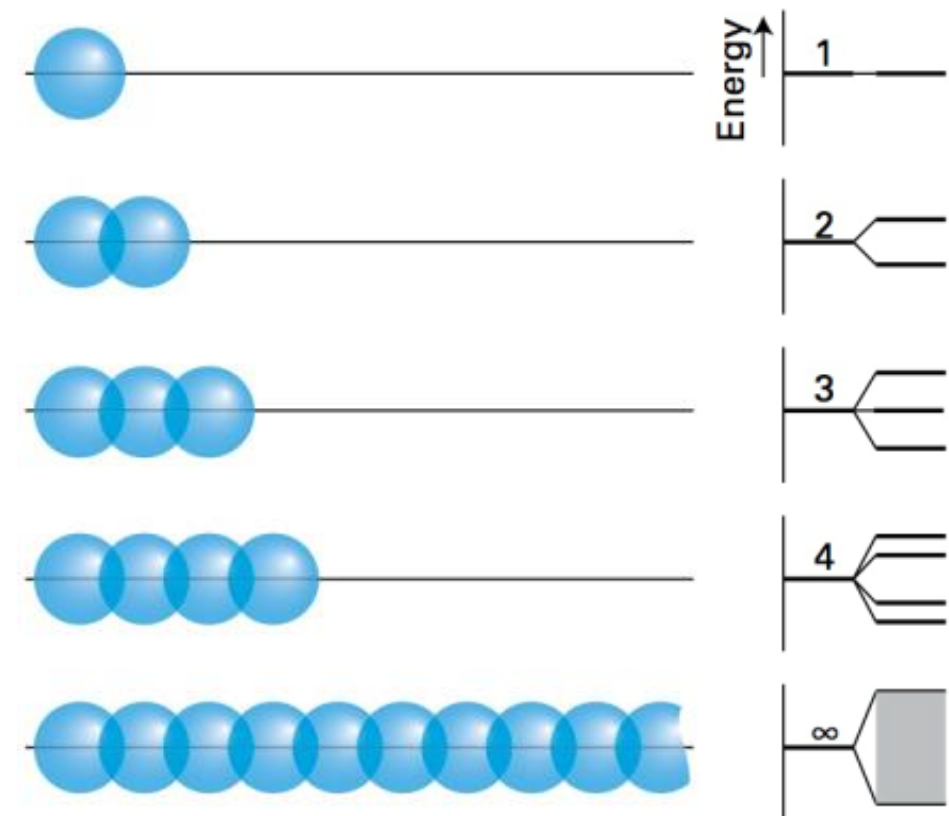
## ❑ The electronic structure of Metallic and Ionic Solids: MO Theory

- *Metallic and ionic solids* can both be treated by molecular orbital theory.
- The advantage of this approach is that both types of solid can be regarded as two extremes of a single kind.
- In each case, the electrons responsible for the bonding are delocalized throughout the solid (like in a benzene molecule, but on a much bigger scale).
- *In an elemental metal, the electrons can be found on all the atoms with equal probability*, which matches the primitive picture of metal as consisting of cations embedded in a nearly uniform electron 'sea'.
- In an ionic solid, the wavefunctions occupied by the delocalized electrons are almost entirely concentrated on the anions, so the Cl atoms in NaCl, for instance, are present as  $\text{Cl}^-$  ions, and the Na atoms, which have *low valence electron density*, are present as  $\text{Na}^+$  ions.

- **To set up the molecular orbital theory of solids** consider initially a single, infinitely long line of identical atoms, each one having an s orbital available for forming molecular orbitals (as in sodium). In a homogeneous metallic solid, the valence AOs can combine with one another to form MOs.
- One atom of the solid contributes an s orbital with a certain energy (Fig. 10). When ***a second atom is brought up it forms a bonding and antibonding orbital***. For a homonuclear diatomic, such as  $\text{Li}_2$ , there are two MOs: one bonding and one antibonding, as shown in Figures 10 & 12.12. For a metallic solid containing only three metal atoms, three MOs will result: one bonding MO (*with no nodes*), one nonbonding MO (*having one node*), and one antibonding MO (*having two nodes*).
- For  $n$  metal atoms,  $n$  MOs will form, each pair of which has a slightly different energy from its neighboring pair on the MO diagram. ***The relative energies of each MO can be determined on the basis of the number of nodal planes that exist. The lowest energy MO will have zero nodes and the highest will have  $(n-1)$  nodes.***
- For an infinite number of metal atoms, the MOs become so closely spaced that they blur together into a “band” of MOs, as shown at the right in Figure 10.



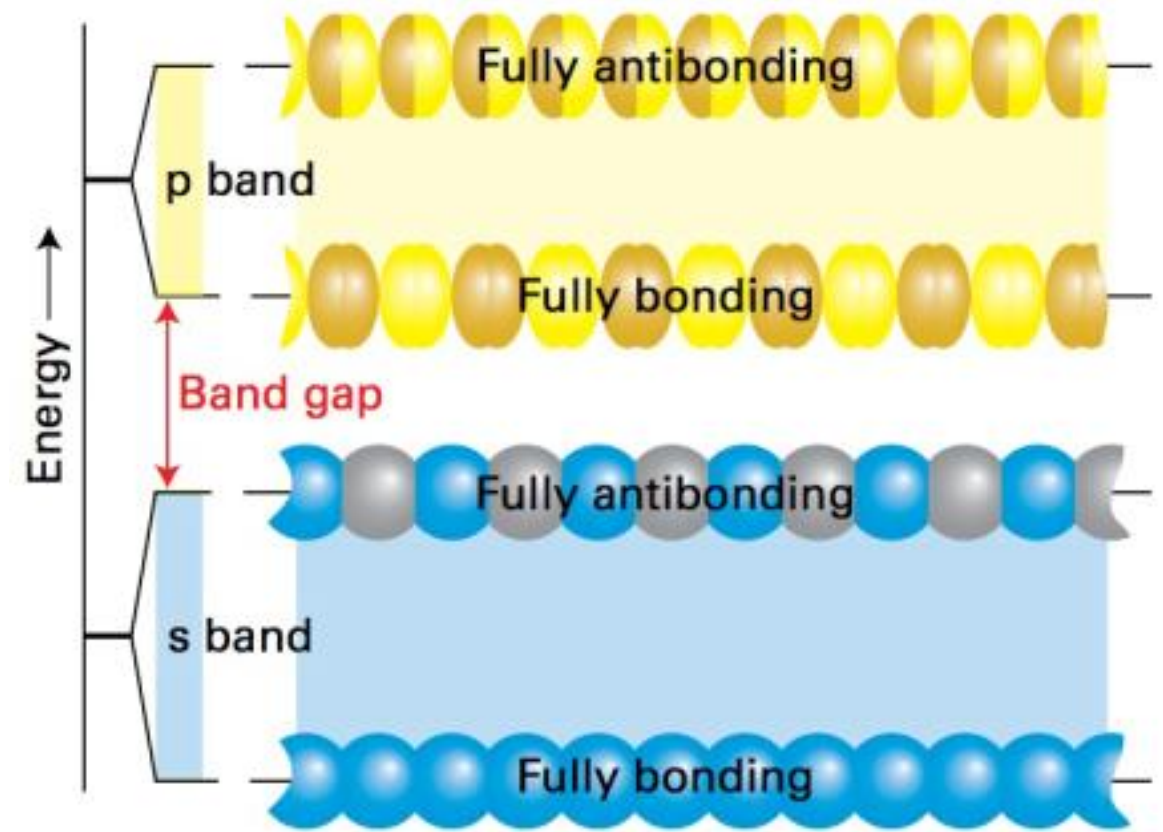
**Figure 12.22** Discrete energy levels in individual molecules become continuous energy bands in a solid. Occupied orbitals are shaded blue, and empty orbitals pink.



**Fig. 10** The formation of a band of  $N$  molecular orbitals by successive addition of  $N$  atoms to a line. Note that the band remains of finite width, and although it looks continuous when  $N$  is large, it consists of  $N$  different orbitals.

- When we have a really big number of MOs, some interesting things happen.
- One mole of Fe is about 7 mL or 7 cc (a pretty small amount).
- In each atom of Fe, we have **one** 4s orbital, **five** 3d orbitals, and **three** 4p orbitals that can be *involved in bonding*.
- In a mole of Fe, we have **9** times Avogadro's number of AOs that can be involved in bonding. **That's about  $10^{24}$  AOs**, which means the same number of MOs.
- ***There just isn't space to have much difference in energy between all those MOs.***
- The MOs have to have energies not too different from the AOs (they are definitely higher and lower, but not by too much), so they are limited to a relatively narrow range of energies. This means that the energies form **bands** *rather than separate energy levels*.

- When  $N$  atoms have been added to the line, there are  $N$  molecular orbitals covering a band of finite width. The lowest-energy orbital of this band is fully bonding and the highest-energy orbital is fully antibonding between adjacent atoms (Fig. 11 ).
- A band formed from overlap of  $s$  orbitals is called an ***s band***. If the atoms have  $p$  orbitals available, then the same procedure leads to a ***p band***.
- If the atomic  $p$  orbitals lie higher in energy than the  $s$  orbitals, then the  $p$  band lies higher than the  $s$  band, and there *may be* a ***band gap***, a range of energies for which no molecular orbitals exist. If the separation of the atomic orbitals is not large, the two types of bands might overlap.



**Fig. 11** The overlap of  $s$  orbitals gives rise to an  $s$  band, and the overlap of  $p$  orbitals gives rise to a  $p$  band. In this case *the  $s$  and  $p$  orbitals of the atoms are so widely spaced that there is a band gap. In many cases the separation is less, and the bands overlap.*

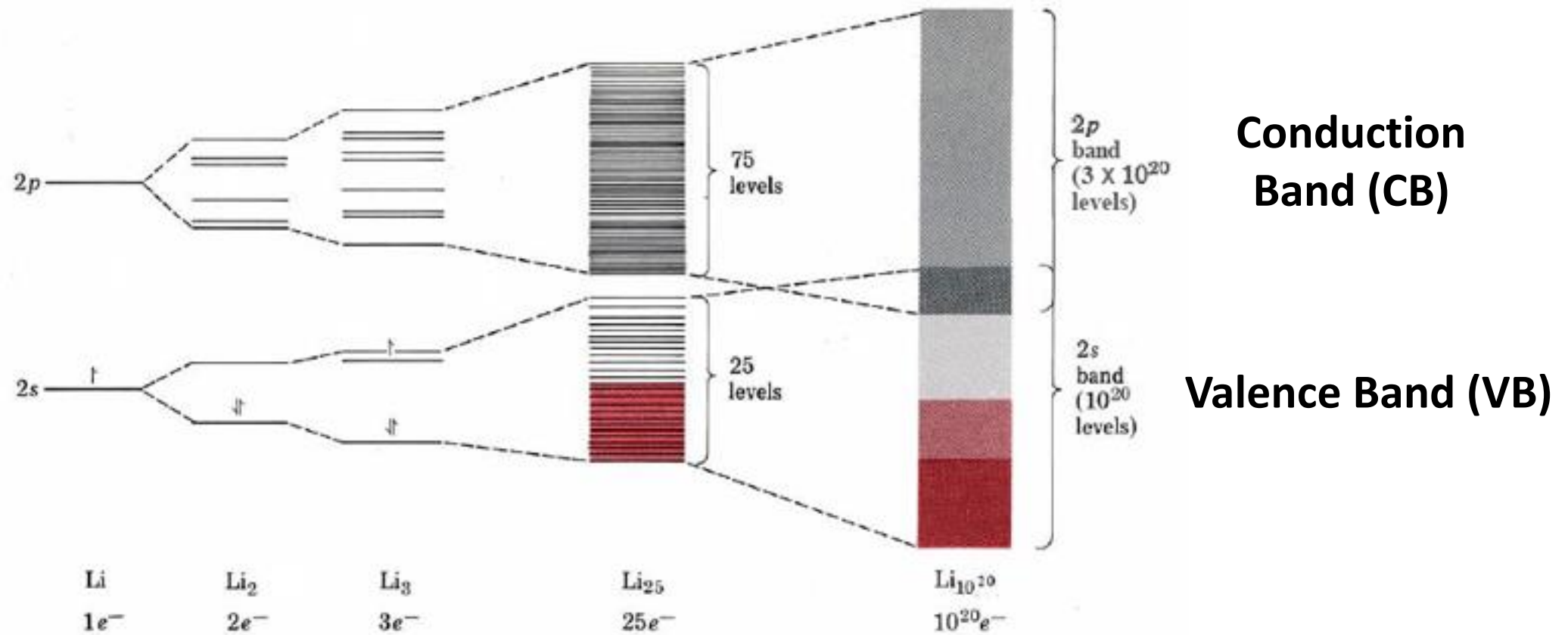


Figure 22.2.1: Molecular-orbital energies corresponding to delocalization of valence electrons over increasing numbers of Li atoms. A 1-mg sample of Li would contain nearly  $10^{20}$  atoms. The corresponding orbital energies are so closely spaced that they constitute essentially continuous bands.

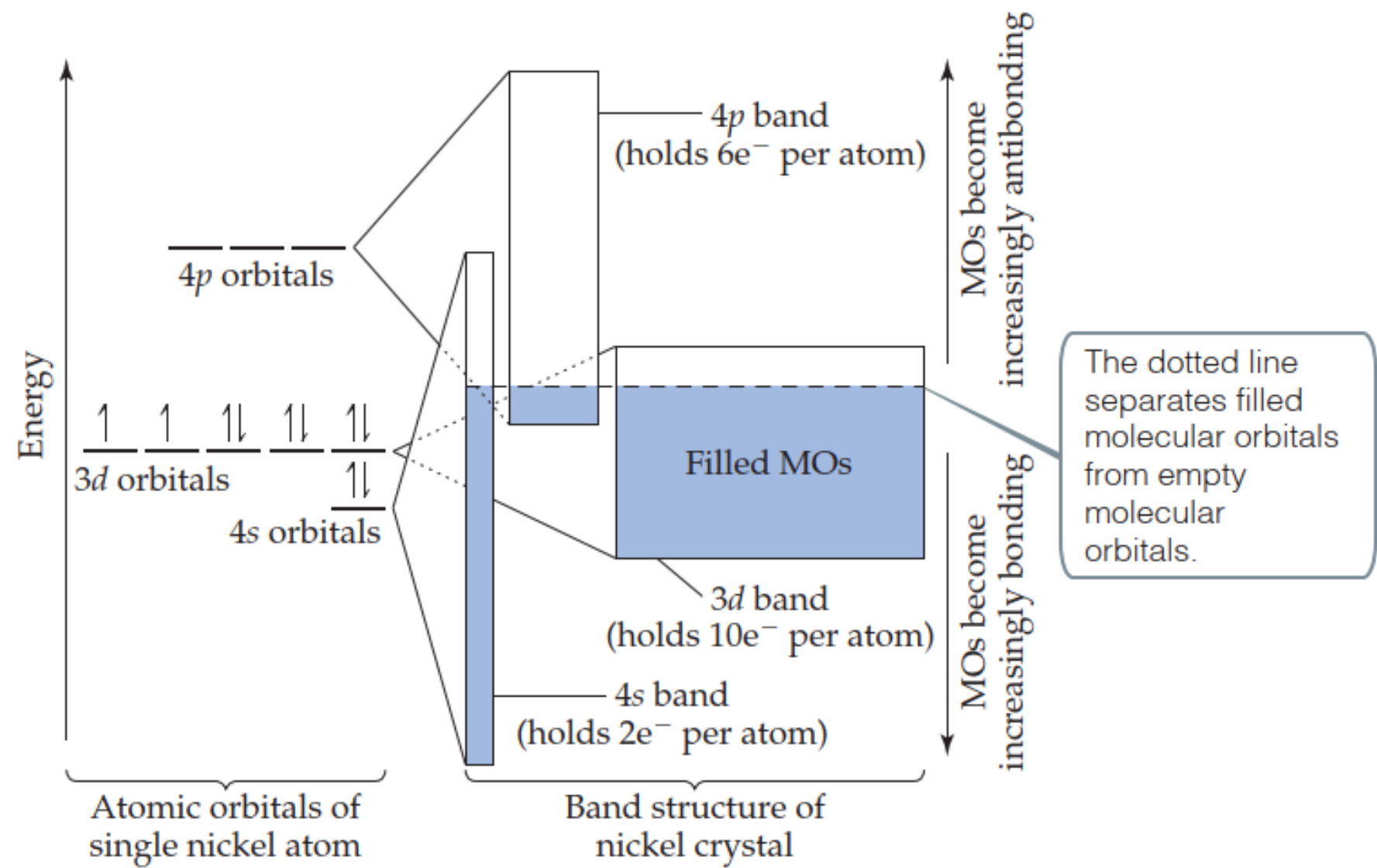


- ***Band theory is a quantum-mechanical treatment of the bonding in metals.***
- When the number of atoms  $N$  in a crystal is very large, the spacing between the energy levels in the band is infinitesimally small so that promotion to the next highest energy level within the band can occur quite readily.
- Whenever a band is fully occupied with valence electrons, it is known as the VB.
- If a band is unoccupied or empty, it is known as the CB.
- In a metal such as Li, as shown in Figure 22.2.1, the band constructed from a linear combination of the valence 2s AOs is exactly half-filled, so that the VB and the CB derive from the same set of orbitals and are only distinguished from each other by the presence or absence of electrons.
- The energy of the highest filled MO at 0K is known as the ***Fermi level***. Because the Fermi level lies inside a band in Li, *this metal is a conductor*.
- For a metal such as Mg, the band formed by the 2s AO basis set (in other words, the VB) is completely filled. *The only reason that Mg is a conductor is because 2s band overlaps with the empty band formed by the 2p basis set* (or the CB), as shown in Figure 22.2.1.

- *In the ground electronic state of the solid, the occupied molecular orbitals make up the **valence band of the solid**. The **unoccupied orbitals**, if they extend over large distances in the solid, comprise **the conduction band**.*
- *If the valence band ends just where the conduction band begins, **the slightest electronic energy pushes the electrons into orbitals where they have more mobility**.*
- *It is the energies and shapes of these bands that will determine the physical and chemical properties of metals. This improvement over the **Drude–Sommerfield model of metallic bonding** is known as **band theory**.*
- *In practice, this approach is directly analogous to the way we made molecular orbitals in covalently bonded compounds by taking linear combinations of atomic orbitals having similar energies and the appropriate symmetry to yield a net nonzero overlap. Thus, if there are N atomic orbitals in the lattice, there will be N molecular orbitals (known as the **Bloch orbitals**) in the crystalline solid.*
- *The electronic structures of most metals are more complicated than those shown in Figure 12.22 because we have to consider more than one type of atomic orbital on each atom. Because each type of orbital can give rise to its own band, the electronic structure of a solid usually consists of **a series of bands**. The electronic structure of a bulk solid is referred to as a **band structure**.*



**Figure 12.23** The electronic band structure of nickel.



- The band structure of a typical metal is shown schematically in Figure 12.23.
- The electron filling depicted corresponds to nickel metal, but the basic features of other metals are similar. The electron configuration of a nickel atom is  $[\text{Ar}]4s^23d^8$ , as shown on the left side of the figure.
- The energy bands that form from each of these orbitals are shown on the right side.
- The 4s, 4p, and 3d orbitals are treated independently, each giving rise to a band of molecular orbitals. In practice, *these overlapping bands are not completely independent of each other*, but for our purposes this simplification is reasonable.
- The 4s, 4p, and 3d ***bands differ from one another in the energy range they span*** (represented ***by the heights of the rectangles*** on the right side of Figure 12.23) and in *the number of electrons they can hold* (represented by the *area of the rectangles*).
- The 4s, 4p, and 3d bands can hold 2, 6, and 10 electrons per atom, respectively, corresponding to two per orbital, as dictated by the Pauli exclusion principle.
- The ***energy range*** spanned by the 3d band is smaller than the range spanned by the 4s and 4p bands because the ***3d orbitals are smaller*** and, ***therefore, overlap with orbitals on neighboring atoms less effectively***.

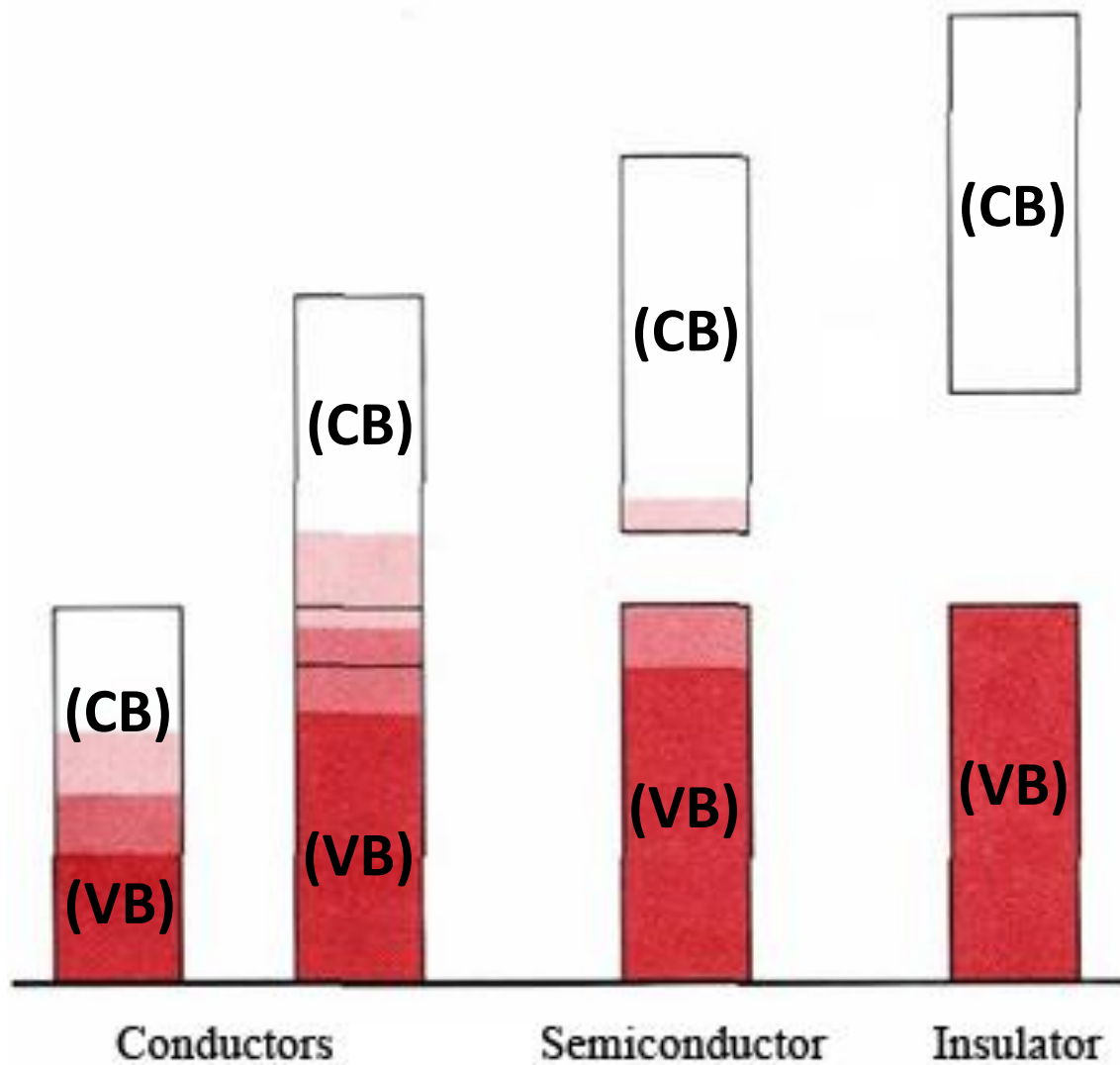
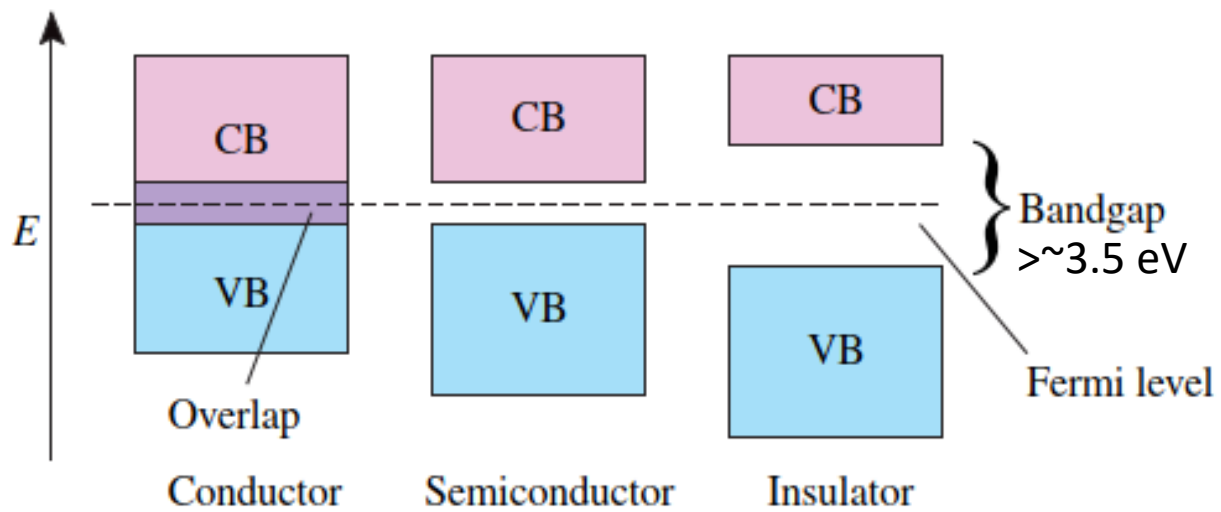


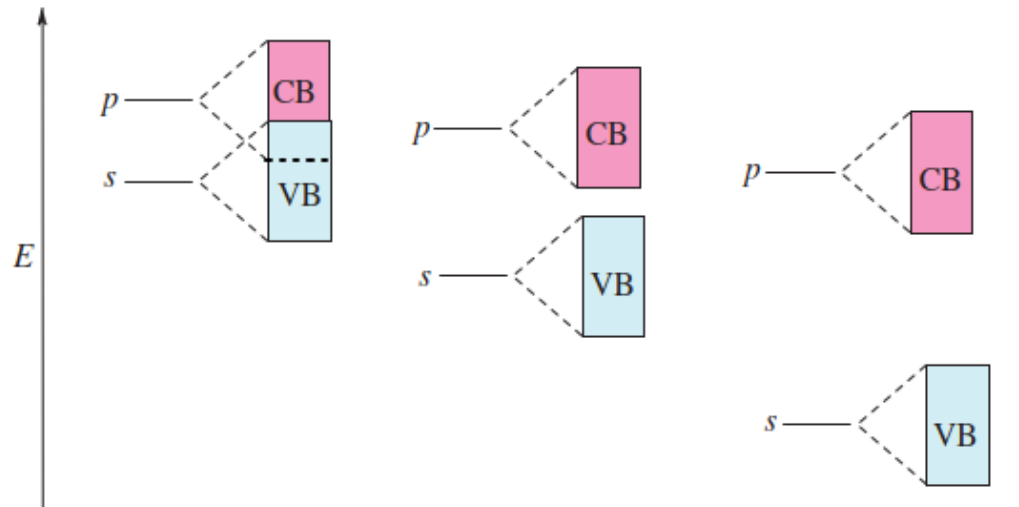
Figure 22.2.2: Band structures of conductors, semiconductors, and insulators.

Note that conductors may have a *partially filled band* or a *filled band which overlaps an empty one*.

In semiconductors and insulators, band separation becomes progressively larger containing electrons are color-coded.)



**FIGURE 11.47** Simplified band diagram showing the differences between a conductor, a semiconductor, and an insulator. The main difference has to do with the band gap energy, or separation between the top of the valence band (VB) and the bottom of the conduction band (CB). The Fermi level is indicated by a dashed line on the diagram.



Metals

Metalloids

Non-metals

Left side of  
Periodic Table

Middle of  
Periodic Table

Right side of  
Periodic Table

Zero band gap

Small band gap

Large band gap

Conductors

Semi-conductors

Insulators

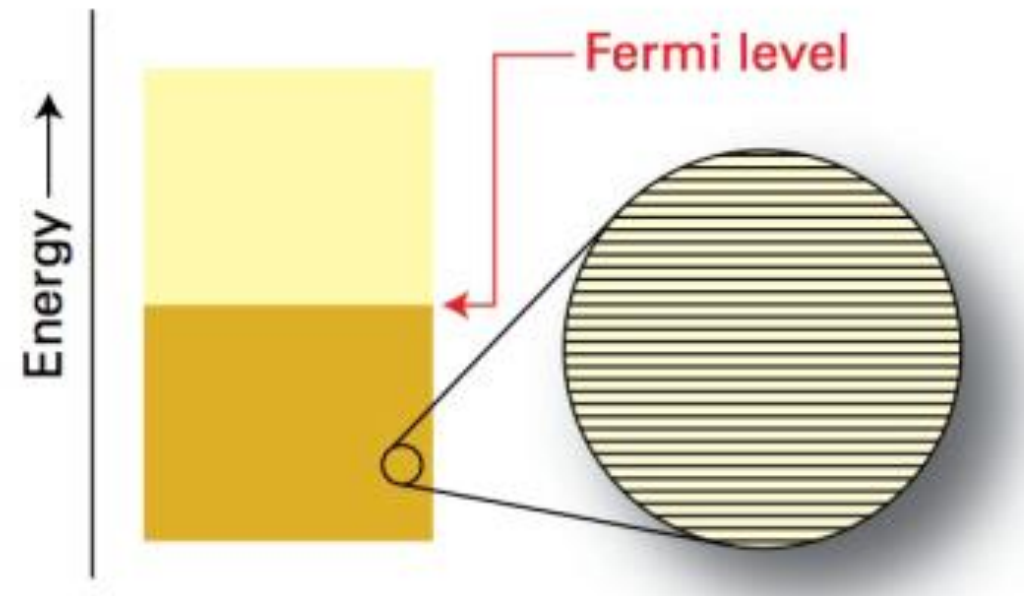
**FIGURE 11.48** A simplistic rationalization for the electrical conductivity of the elements in the periodic table based on their band structures.

## CONDUCTIVITY IN SOLIDS

- According to the ***band theory***, it is this partial filling which accounts for the high **electrical and thermal conductance of metals**.
- If an **electric field** is applied to a metallic conductor, some electrons can be forced into one end, occupying slightly higher energy levels than those already there. As a consequence of delocalization this increased electronic energy is available throughout the metal. It therefore can result in an almost instantaneous flow of electrons from the other end of the conductor.
- A similar argument applies to the **transfer of thermal energy**. Heating a small region in a solid amounts to increasing the energy of motion of atomic nuclei and electrons in that region. Since the nuclei occupy specific lattice positions, conduction of heat requires that energy be transferred among nearest neighbors. Thus when the edge of a solid is heated, atoms in that region vibrate more extensively about their average lattice positions. They also induce their neighbors to vibrate, eventually transferring heat to the interior of the sample. This process can be speeded up enormously if some of the added energy raises electrons to higher energy MO's within an incompletely filled band. Electron delocalization permits rapid transfer of this energy to other atomic nuclei, some of which may be quite far from the original source.

- Consider the electronic structure of a solid formed from atoms each of which is able to contribute one valence orbital and one electron (for example, the alkali metals).
- There are  $N$  atomic orbitals and therefore  $N$  molecular orbitals squashed into a band of finite width. There are  $N$  electrons to accommodate; they form pairs that occupy the lowest  $\frac{1}{2}N$  molecular orbitals (Fig. 12). *The highest occupied molecular orbital is called the **Fermi level**.*
- However, unlike in the discrete molecules, there are empty orbitals just above and very close in energy to the Fermi level, so it requires hardly any energy to excite the uppermost electrons.
- Some of the electrons are therefore very mobile and give rise to electrical conductivity.

**Fig. 12** When  $N$  electrons occupy a band of  $N$  orbitals, it is **only half full** and the electrons near the Fermi level (the top of the filled levels) are mobile.

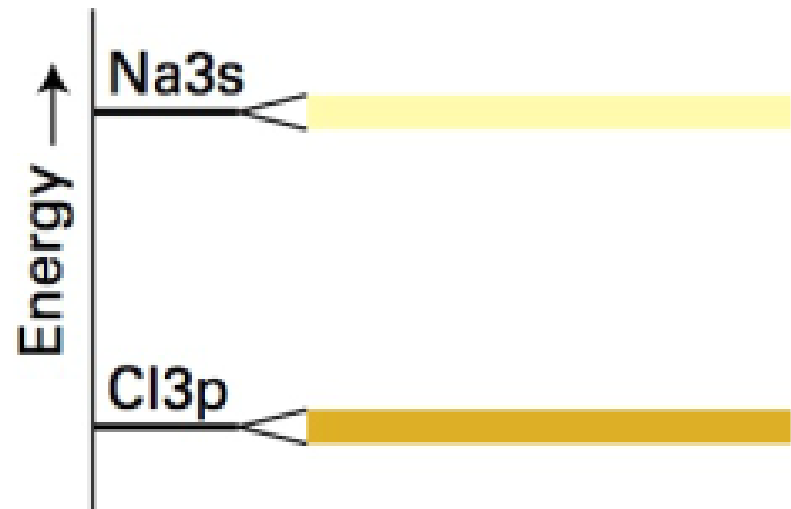




- *Without the overlap of energy bands, the periodic properties of metals could not be explained.*
- In the absence of overlapping p- and d-bands, we would expect the s-band to be half-filled for the alkali metals (group 1) and **completely filled** for the alkaline-earth metals (group 2). *If that were true, metals like magnesium, calcium, and strontium would not be good electrical and thermal conductors*, in disagreement with experimental observations.
- We can also **explain melting point, hardness, and other properties using MO theory**.
- While the conductivity of metals can be qualitatively understood using either the *electron-sea model* or the *molecular orbital model*, many physical properties of transition metals, such as the melting points plotted in Figure 22.2.1, can be explained only with the latter model.
- In this case, we imagine combining many atomic orbitals (1 or more for each atom) to make an equal number of MOs that extend over the whole solid.
- Some MOs will have fewer nodes and be lower energy, while others will have more nodes and be higher energy.
- Each MO can hold **no** more than 2 electrons.

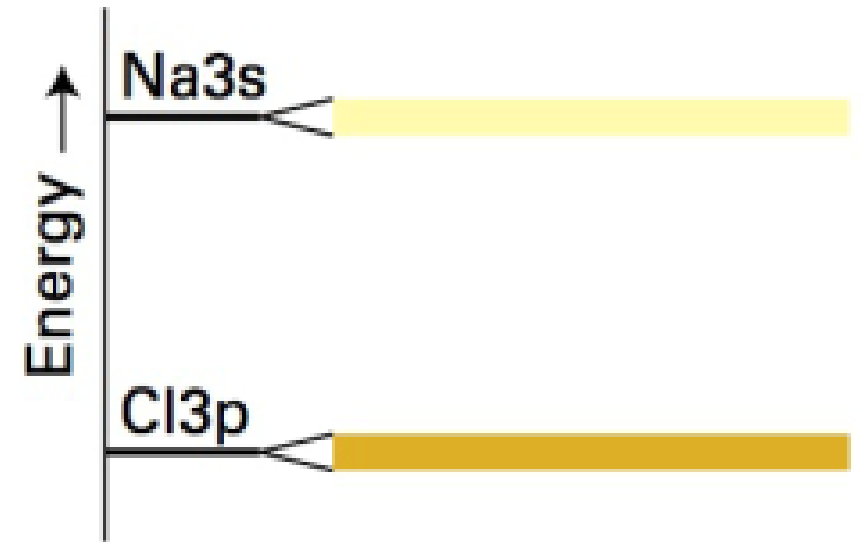
- *The molecular orbital model predicts that bonding first becomes stronger as the number of valence electrons increases, and the bonding orbitals are increasingly populated.*
- *Filling the lower energy MOs (bonding MOs) makes the bonds stronger.*
- *Upon moving past the middle elements of the transition metal series, the bonds grow weaker as electrons populate antibonding orbitals.*
- **Strong bonds between atoms lead to metals with higher melting and boiling points, higher heat of fusion, higher hardness, and so forth.**
- *Alkali metals have low melting points and are soft for not many bonding MOs filled.*
- *Filling the higher energy MOs (**antibonding** MOs) makes the bonds weaker, which is why Cu, Ag, Au and Zn are soft and melt at low temperatures (Hg is a liquid at RT!).*

- To describe **an ionic solid**, consider a line of atoms with different electronegativities, such as a one-dimensional array of sodium and chlorine atoms rather than the identical atoms treated so far.
- Each sodium atom contributes an s orbital and one electron. Each chlorine atom contributes an electron from a p orbital.
- The s and p orbitals are used to build molecular orbitals that spread throughout the solid. Now, ***though, there is a crucial difference.***
- The ***orbitals on the two types of atom have markedly different energies***, so (just as in the construction of molecular orbitals for hetero-diatomic molecules) they ***can be considered separately.***



**Fig. 13** The bands formed from two elements of *widely different electronegativity* (such as sodium and chlorine): they are widely separated. The bands are narrow because the *sodium atoms (and similarly Cl atoms) have very little overlap with one another (sodium atoms are separated by a chlorine atoms).*

- The Cl3p orbitals interact to form one band and the higher energy Na3s orbitals interact to form another band. However, because the *sodium atoms have very little overlap with one another (they are separated by a chlorine atom)*, the Na3s band is very narrow; so is the Cl3p band, for a similar reason.
- As a result, there is a **big gap between the two narrow bands** (Fig. 13).
- If there are N sodium atoms and N chlorine atoms, there will be 2N electrons to accommodate (one from each Na atom and one from each Cl atom).
- ***These electrons occupy and fill the lower Cl3p band.***
- As a result, *the electron density is almost entirely on the chlorine atoms*. In other words, *the solid can be thought of as composed of Na<sup>+</sup> cations and Cl<sup>-</sup> anions*, just as in an elementary picture of ionic bonding.



**Fig. 13** The bands formed from two elements Na and Cl: they are widely separated and narrow. *If each atom provides one electron, the lower band is full and the substance is an insulator.*