

## Delocalized Bonding in Metals

Consider Lithium metal. The Lithium atom has the atomic configuration  $1s^2 2s^1$  with the  $2p$  level unfilled.

As in any molecule with a filled core shell like  $1s^2$ , these electrons do not participate in bonding. Still, they form a delocalized band with  $10^{23}$  molecular orbitals that are completely filled.

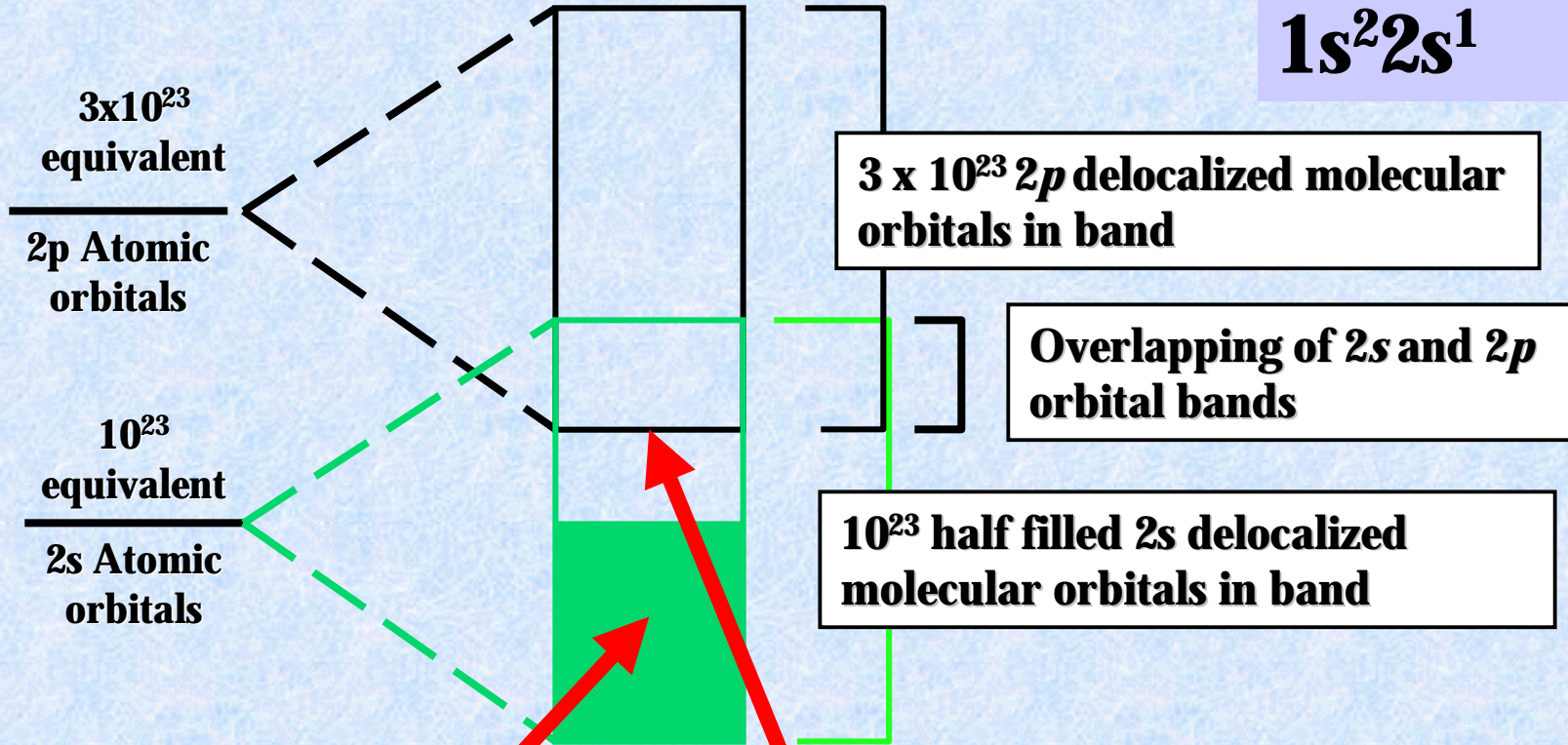
The **valence** electrons  $2s^1$  and the unfilled  $2p$  orbitals are more interesting. The  $10^{23}$   $2s$  atomic orbitals form a band of  $10^{23}$  “molecular” orbitals. This band is only **half** filled because each  $2s^1$  orbital has only **one**  $e^-$ .

There are three  $2p$  orbitals on each atom leading to a band of  $3 \times 10^{23}$  molecular orbitals. This band is “empty” but overlaps in energy the  $2s$  band  $\rightarrow$

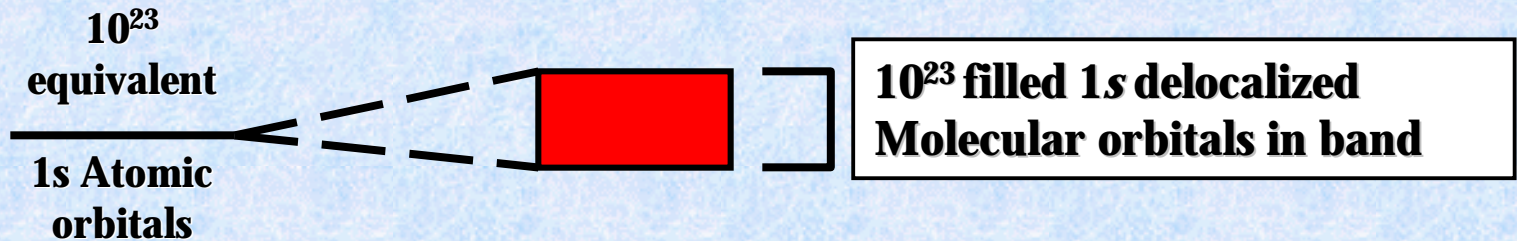
# Lithium

$1s^2 2s^1$

Energy, E



**Bonding and anti-bonding orbitals  
Come together to form a continuous band**





## Delocalized Bonding in Metals (continued)

Consider now Beryllium metal. The beryllium atom has the atomic configuration  $1s^2 2s^2$  with the  $2p$  level unfilled as in Li.

As in any molecule with a filled core shell like  $1s^2$ , these electrons do not participate in bonding. Still, they form a delocalized band with  $10^{23}$  molecular orbitals that are completely filled, just as in Li.

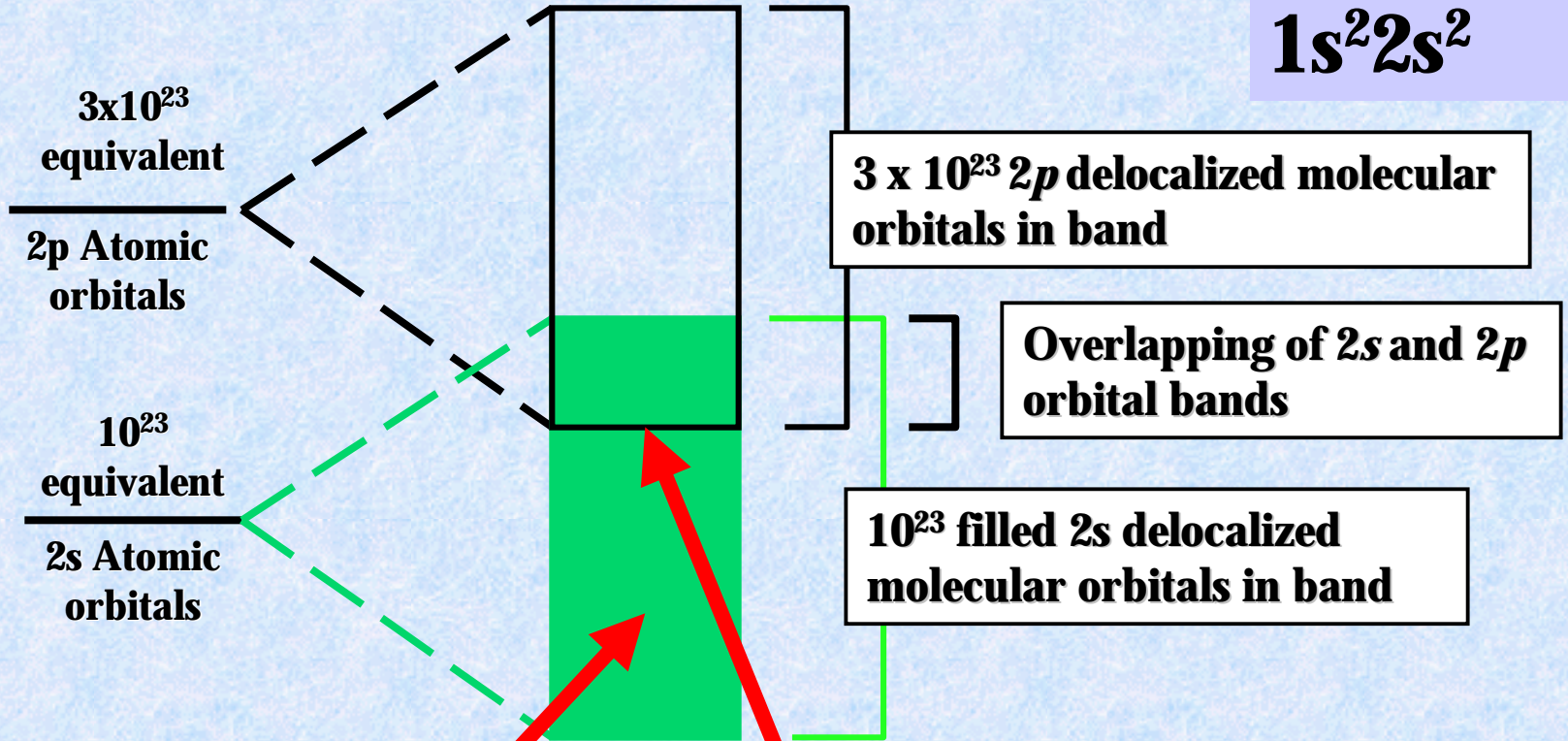
The valence electrons  $2s^2$  and the unfilled  $2p$  orbitals are again more interesting. The  $10^{23}$   $2s$  atomic orbitals form a band of  $10^{23}$  “molecular” orbitals. This band is however **completely** filled because each  $2s^2$  orbital now has **2**  $e^-$ .

There are, as in Li, three  $2p$  orbitals on each atom leading to a band of  $3 \times 10^{23}$  molecular orbitals. This band is “empty” but overlaps in energy the filled  $2s$  band  $\rightarrow$

# Beryllium

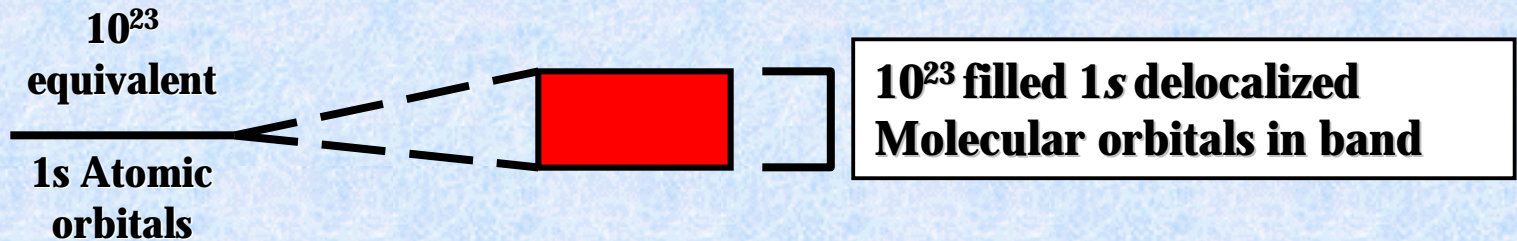
$1s^2 2s^2$

Energy, E



**Bonding and anti-bonding orbitals**

**Come together to form a **completely full** continuous band**



Note that in both lithium and beryllium (for different reasons) there are **unfilled** molecular orbitals at an energy infinitesimally greater than that of the **filled** M.O.'s. [ $E_{\text{unfilled}} - E_{\text{filled}} \lll kT$ ]

In lithium this results because the lowest valence band is only **half full**, a feature that arises from the fundamental fact that lithium atoms have an **odd number of valence electrons**.

In beryllium this results even though the lowest valence band is **full**, a feature that arises from the fundamental fact that beryllium atoms have an **even number of valence electrons**.

However, in beryllium the lowest **filled valence band** and the next to lowest, **unfilled valence band** overlap. This again gives the result: [ $E_{\text{unfilled}} - E_{\text{filled}} \lll kT$ ]

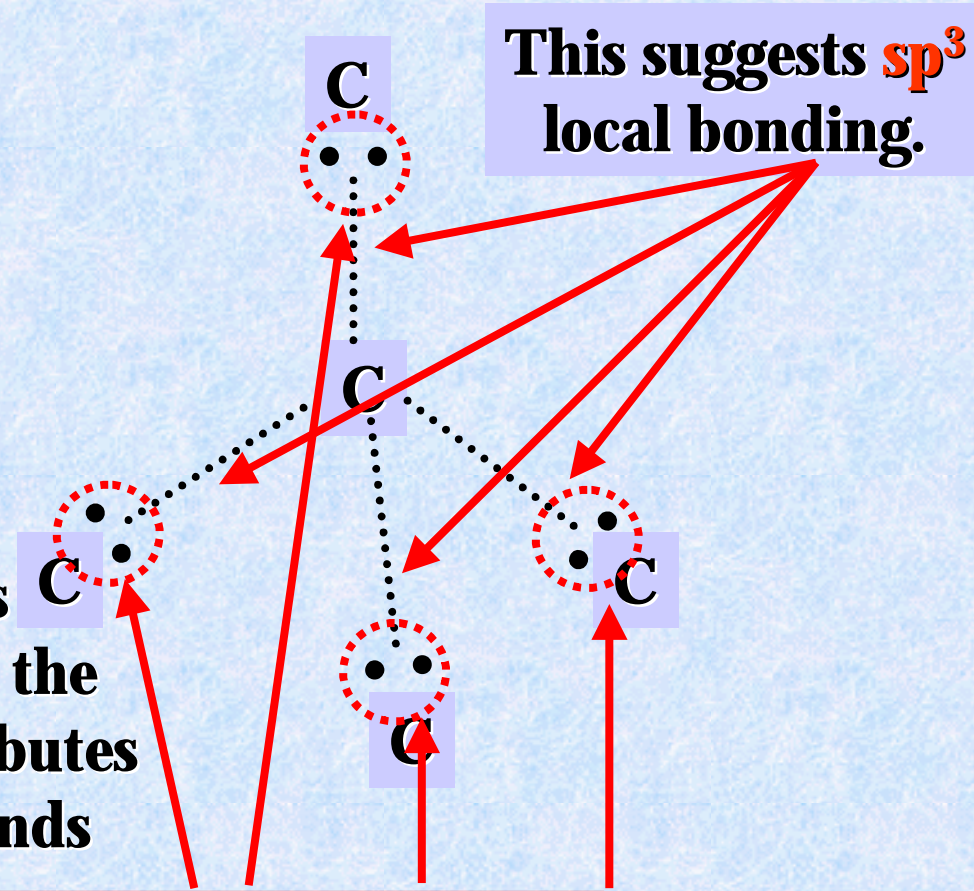


# Bonding in non-metals: Insulators and Semi-conductors

Atoms such as carbon and boron do not conduct electricity as the pure solid. (In the case of carbon there is a conducting form of the solid called graphite. Graphite behaves like a metal (why?)). Here we will discuss the solid carbon form, diamond.

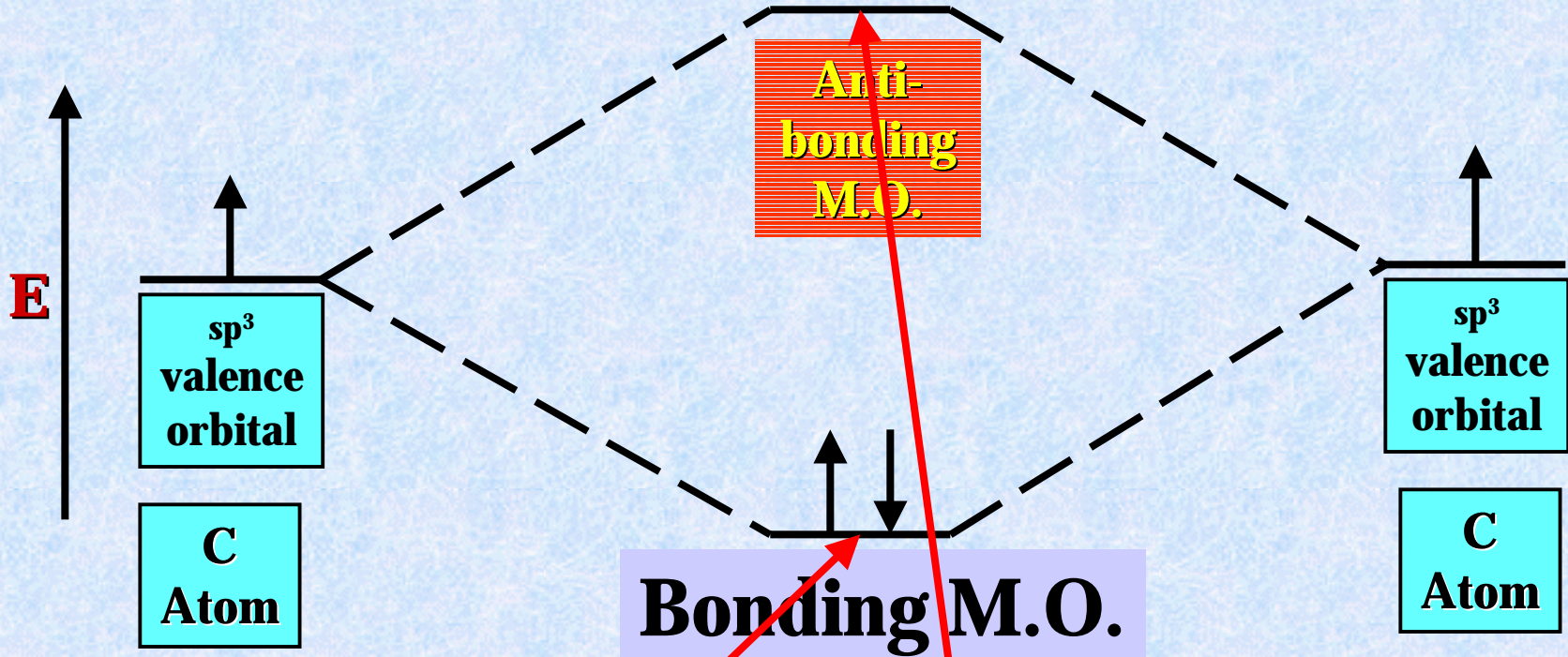
In diamond can think of each C atom as “bonded” to 4 other atoms at the corners of a tetrahedron:

**Central** Carbon atom contributes 4 valence electrons and each C at the corners of the tetrahedron contributes one valence electron to form 4 bonds to central C



This suggests  $sp^3$  local bonding.

# Local bonding States in **Diamond**

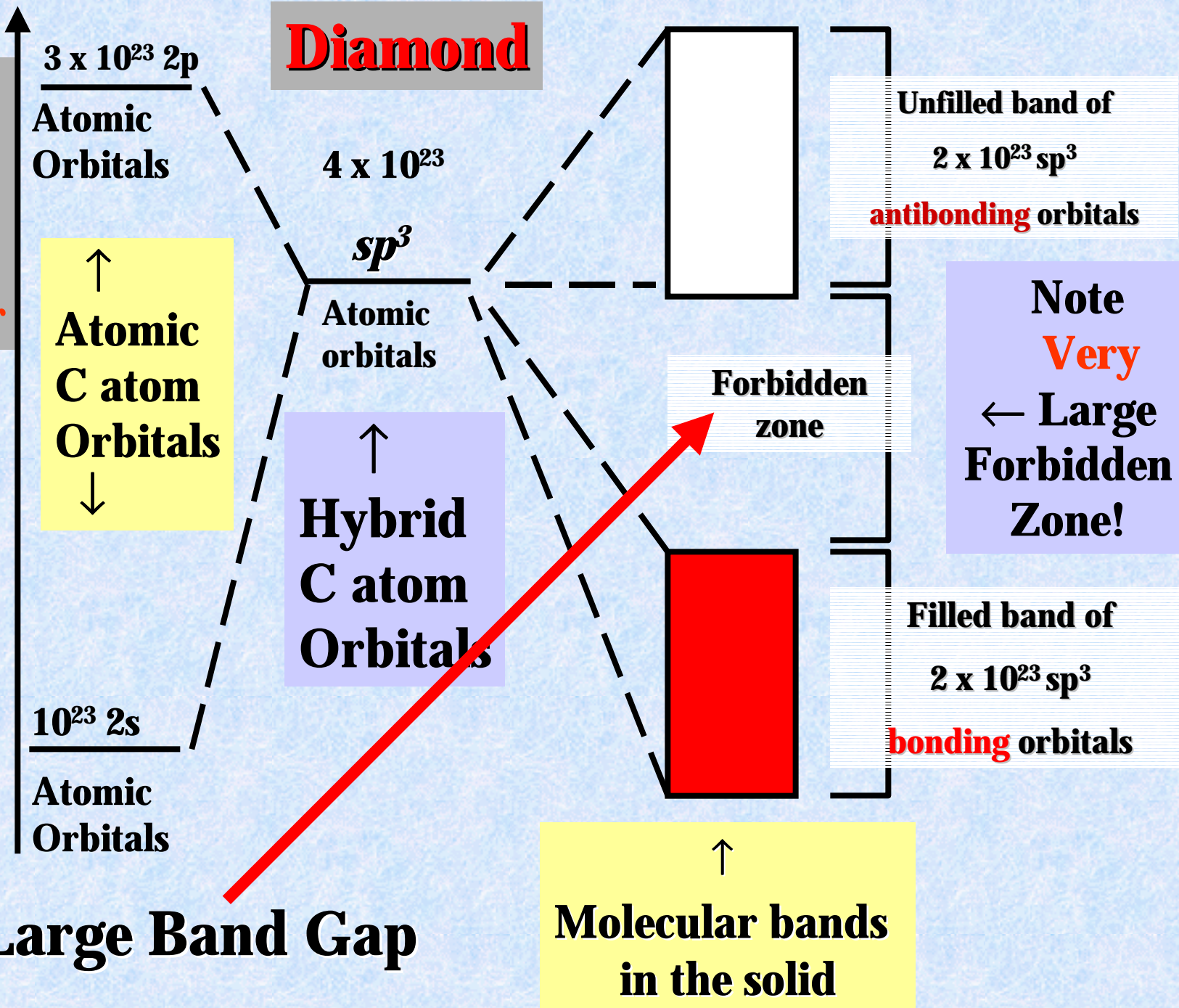


Assign each C atom 4 localized sp<sup>3</sup> tetrahedral bonds

One such orbital from **each** pair of carbons combines to make one **bonding** and one **antibonding** M.O.

To construct a band model for such a solid, take  $10^{23}$  atoms, giving  $4 \times 10^{23}$  sp<sup>3</sup> orbitals. Combine these to give **2** bands, each with **half** of the total orbitals: →

Typical Energy Bands for an Insulator



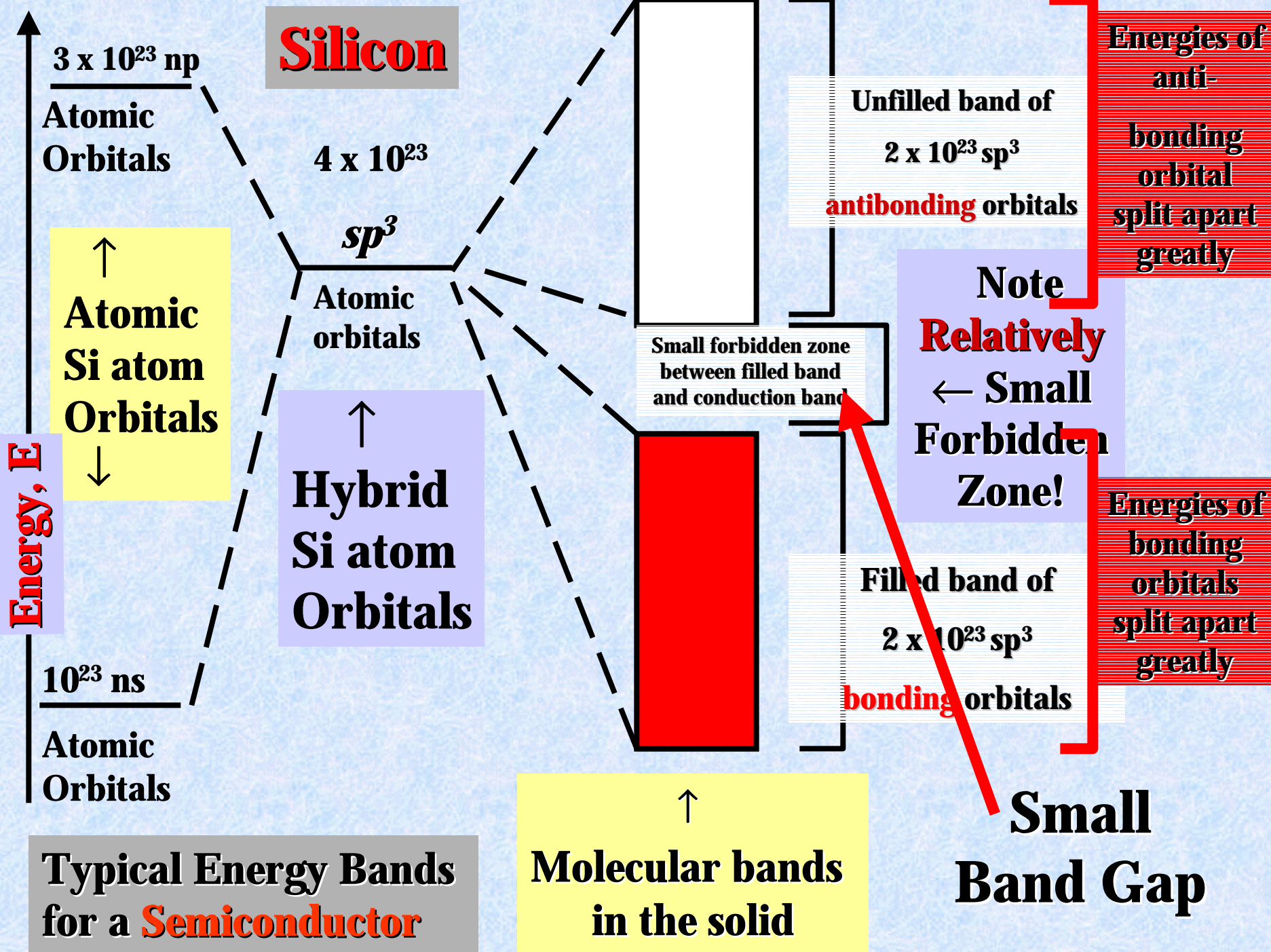


# Semiconductors

Silicon and Germanium are quintessential semiconductors. Note, they are under carbon in the periodic table. Thus, they have the valence electron structure  $ns^2np^2$  just as carbon has  $2s^22p^2$ .

Bonding in these solids mimics that for the diamond structure that we just considered, **except** that the energy separation between the bonding and anti-bonding orbitals is **much smaller** than for the **insulator** carbon (diamond).

This results in a **forbidden zone** for the energy bands in Si and Ge that is much smaller than for diamond →



# Silicon

$3 \times 10^{23}$  np

Atomic Orbitals

$4 \times 10^{23}$

$sp^3$

Atomic orbitals

↑  
Atomic Si atom Orbitals  
↓

↑  
Hybrid Si atom Orbitals

$10^{23}$  ns

Atomic Orbitals

Unfilled band of  $2 \times 10^{23}$   $sp^3$  antibonding orbitals

Small forbidden zone between filled band and conduction band

Note  
**Relatively**  
← Small Forbidden Zone!

Filled band of  $2 \times 10^{23}$   $sp^3$  bonding orbitals

Energies of anti-bonding orbital split apart greatly

Energies of bonding orbitals split apart greatly

↑  
Molecular bands in the solid

**Small Band Gap**

Typical Energy Bands for a **Semiconductor**



**The End!**