Energy of 3 π bonding orbitals lower than energy of 2p (isolated) orbitals on C from which they come. π antibonding are higher than isolated 2p.

Find experimentally all C-C bonds are of equal length (1.390Å) and between that of C-C bond and C=C □, π bond lengths.

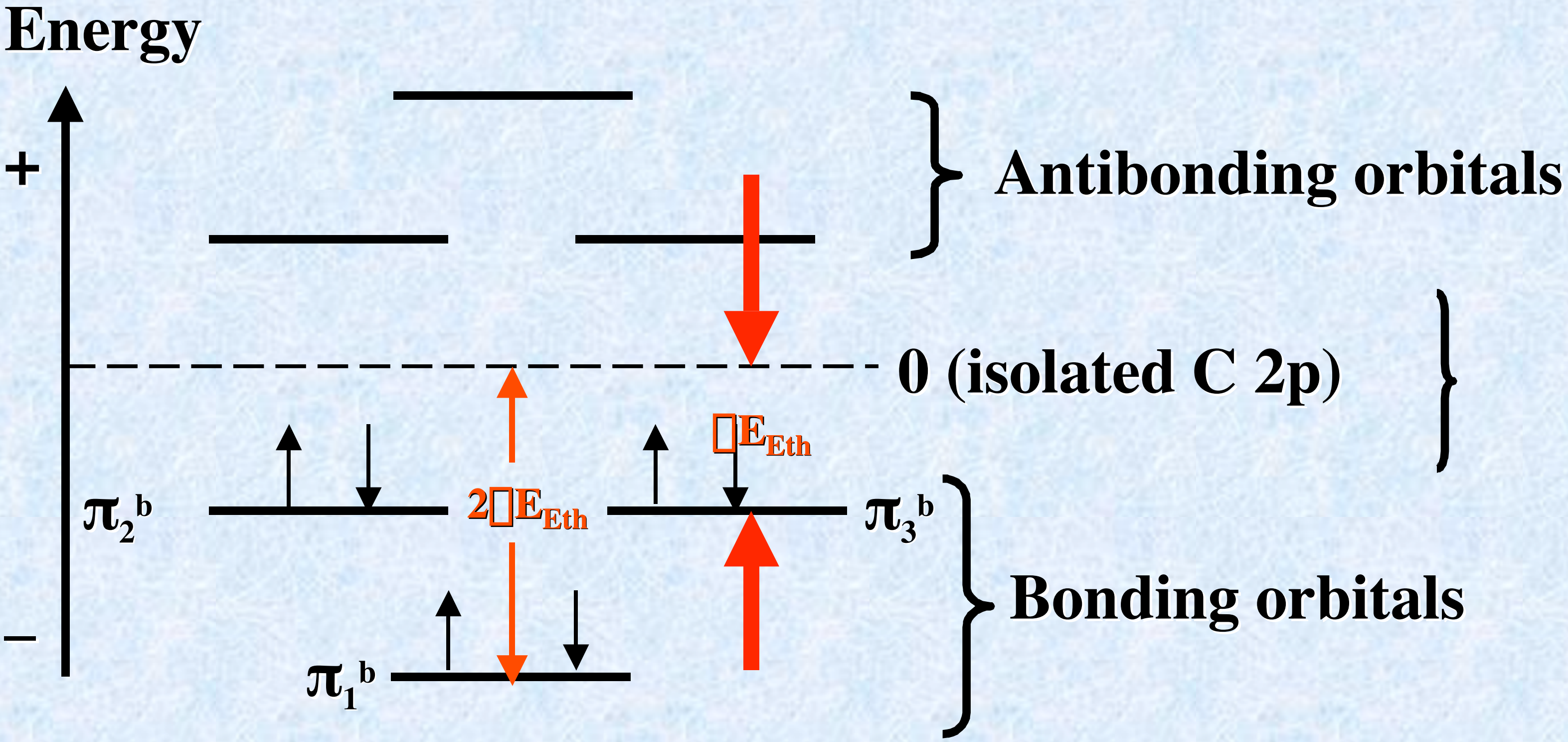
Actually find benzene is more stable than this!

Energy of $(\pi_1{}^{b})^2 + (\pi_2{}^{b})^2 + (\pi_3{}^{b})^2 \; < \;$ Energy of 3 $\pi^2{}_{\text{ethylene}}$

i.e. Energy of $(\pi_1{}^{b})^2 + (\pi_2{}^{b})^2 + (\pi_3{}^{b})^2$ □ Energy of 4 $\pi^2{}_{\text{eth.}}$

More accurately: Energy of $(\pi_2^b)^2 = (\pi_3^b)^2$ □ π^2_{eth}

And: Energy of $(\pi_1^b)^2$ □ 2 π^2_{eth}

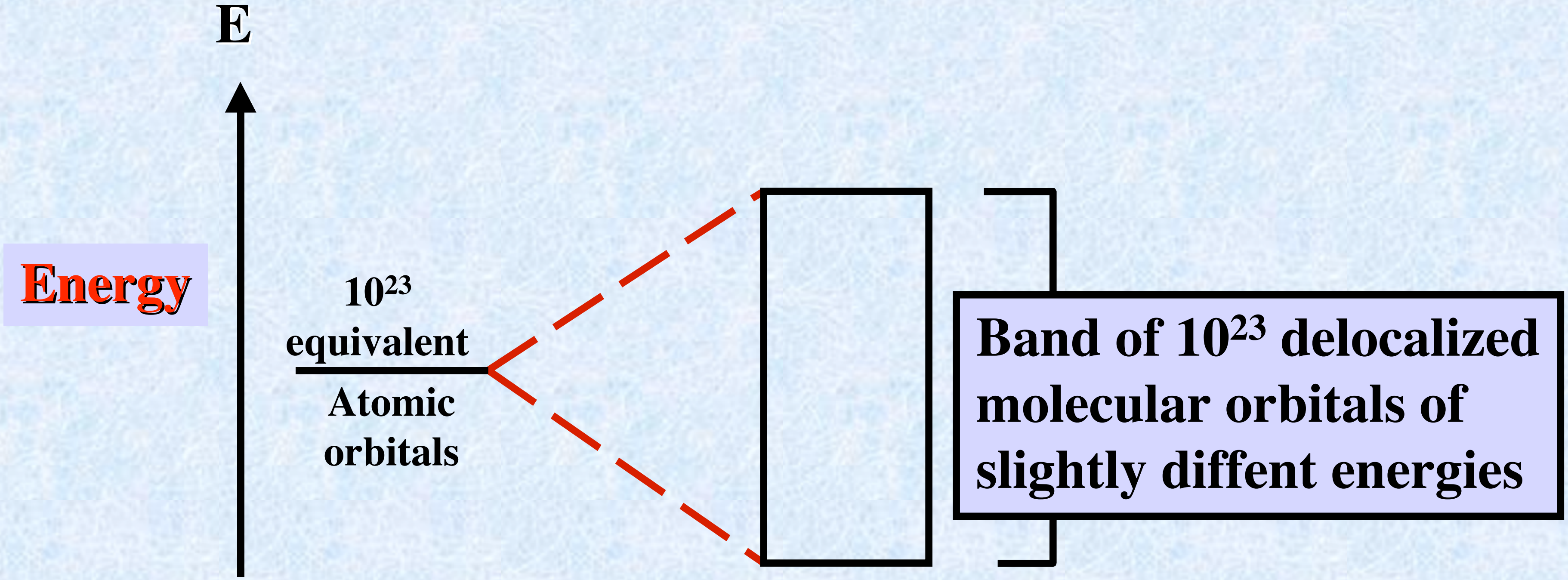

Energy
+
–
Antibonding orbitals
0 (isolated C 2p)
□E_{Eth}
2□E_{Eth}
π_2^b
π_3^b
π_1^b
Bonding orbitals

Bonding in Solids

Think of a solid as a single giant molecule with roughly 10^{23} atoms. Electrons can travel over the whole solid via delocalized orbitals that cover all 10^{23} atoms.

Consider first the situation where each individual atom of the solid has just one orbital contributing to bonding.

In this case must get 10^{23} molecular orbitals because atomic orbitals map into molecular orbitals, one for one.



Energy

E

10^{23} equivalent

Atomic orbitals

Band of 10^{23} delocalized molecular orbitals of slightly diffent energies

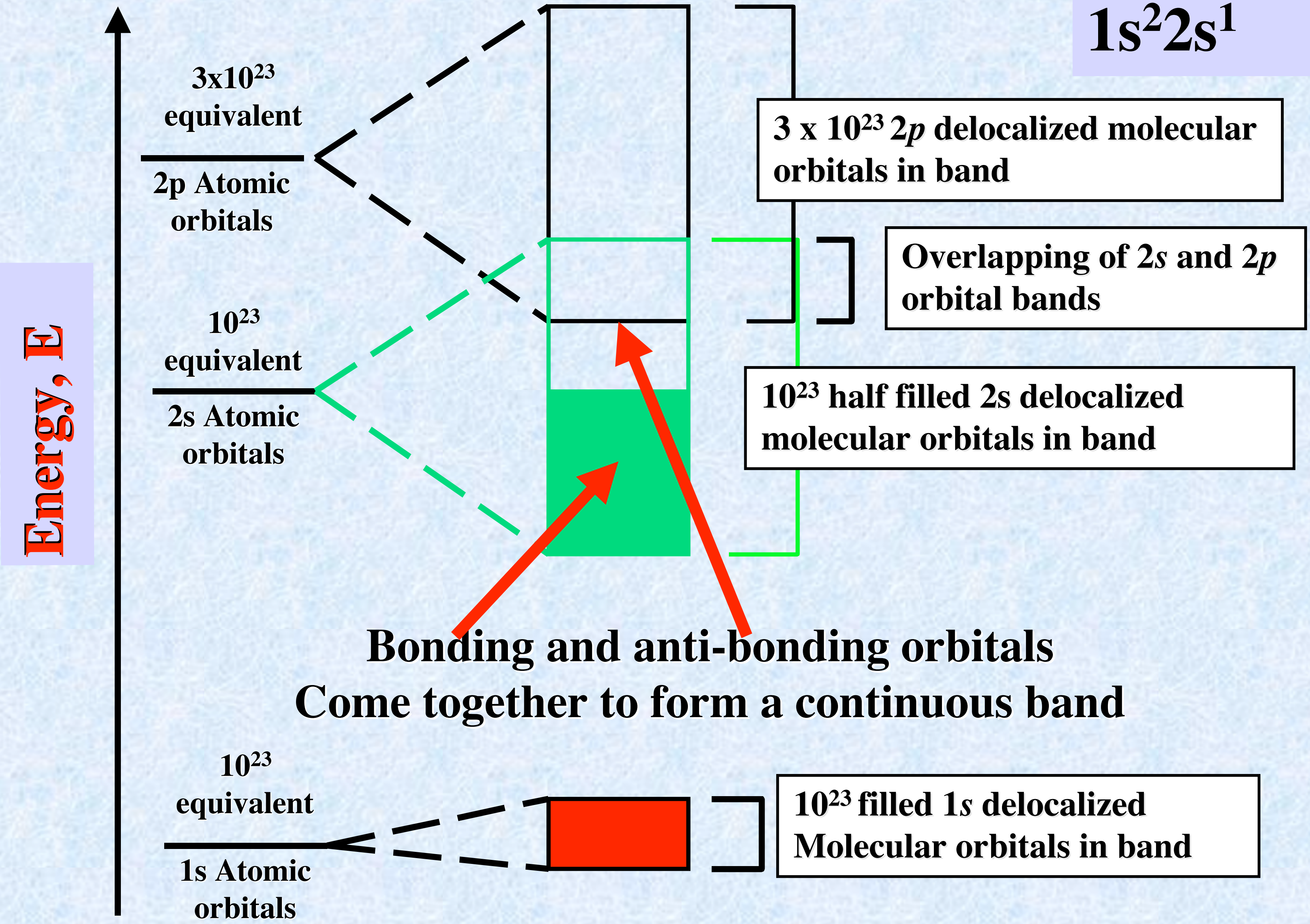
Delocalized Bonding in Metals

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.

There are three 2p orbitals on each atom leading to a band of 3×10^{23} molecular orbitals. This band is "empty" but overlaps in energy the 2s band □

Lithium
$1s^2 2s^1$



Energy, E
$3x10^{23}$ equivalent
2p Atomic orbitals
10^{23} equivalent
2s Atomic orbitals
10^{23} equivalent
1s Atomic orbitals

3×10^{23} 2*p* delocalized molecular orbitals in band

Overlapping of 2*s* and 2*p* orbital bands

10^{23} half filled 2s delocalized molecular orbitals in band

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

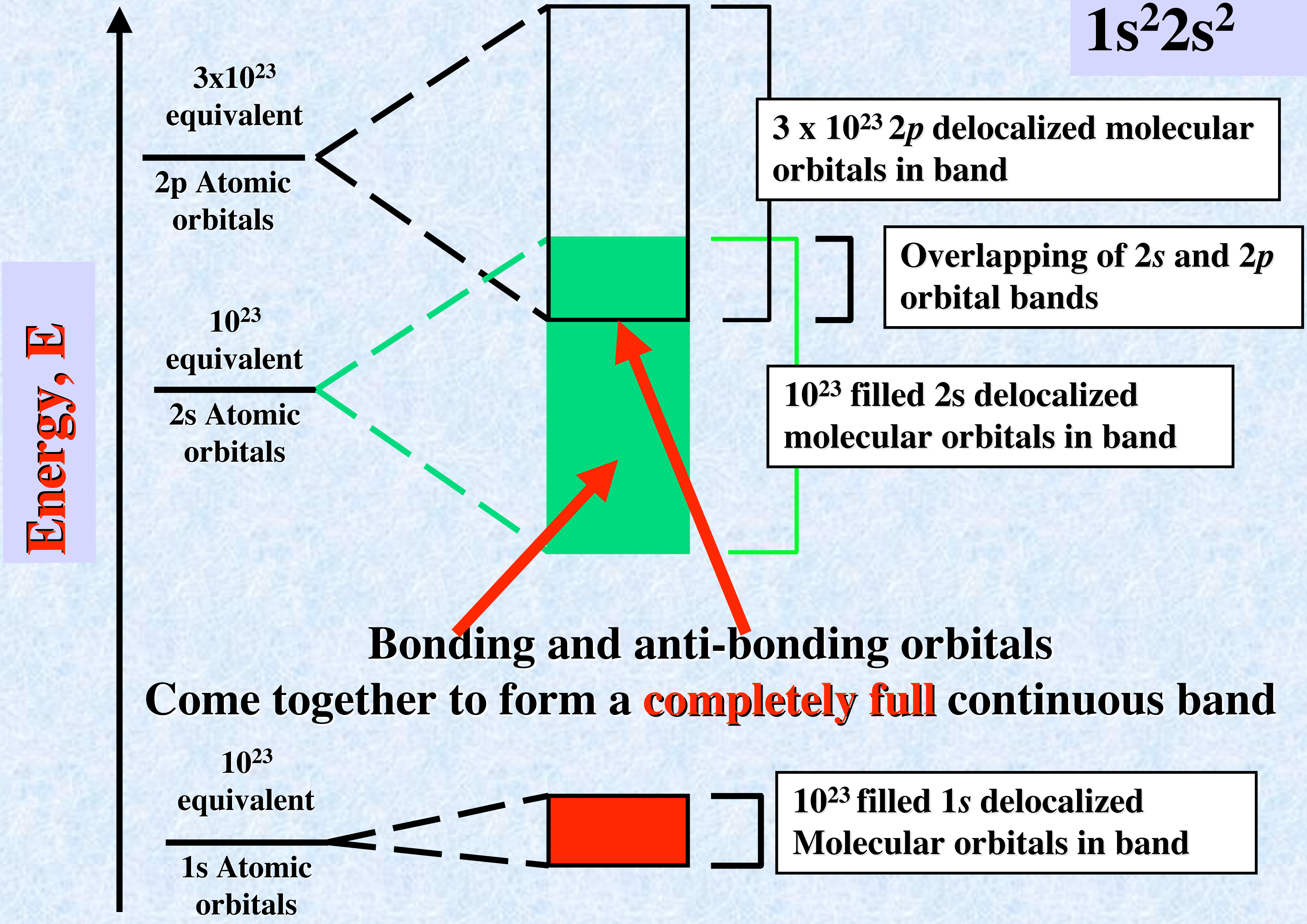
10^{23} filled 1*s* delocalized Molecular orbitals in band

Delocalized Bonding in Metals (continued)

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.

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

Berylium $1s^2 2s^2$



Energy, E

3×10^{23} equivalent

2p Atomic orbitals

10^{23} equivalent

2s Atomic orbitals

10^{23} equivalent

1s Atomic orbitals

3×10^{23} 2*p* delocalized molecular orbitals in band

Overlapping of 2*s* and 2*p* orbital bands

10^{23} filled 2s delocalized molecular orbitals in band

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

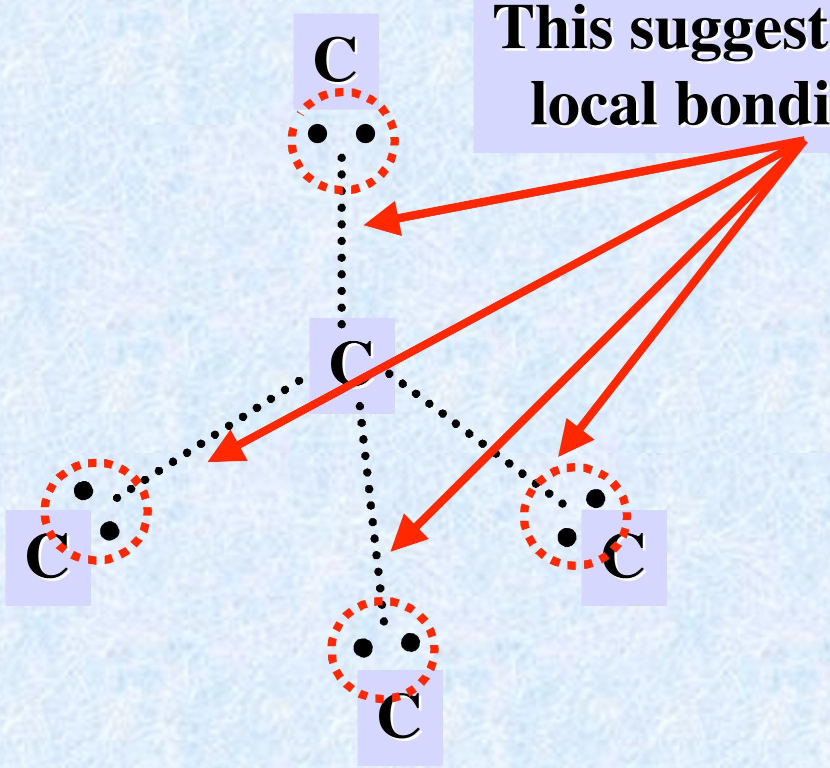
10^{23} filled 1*s* delocalized Molecular orbitals in band

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

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

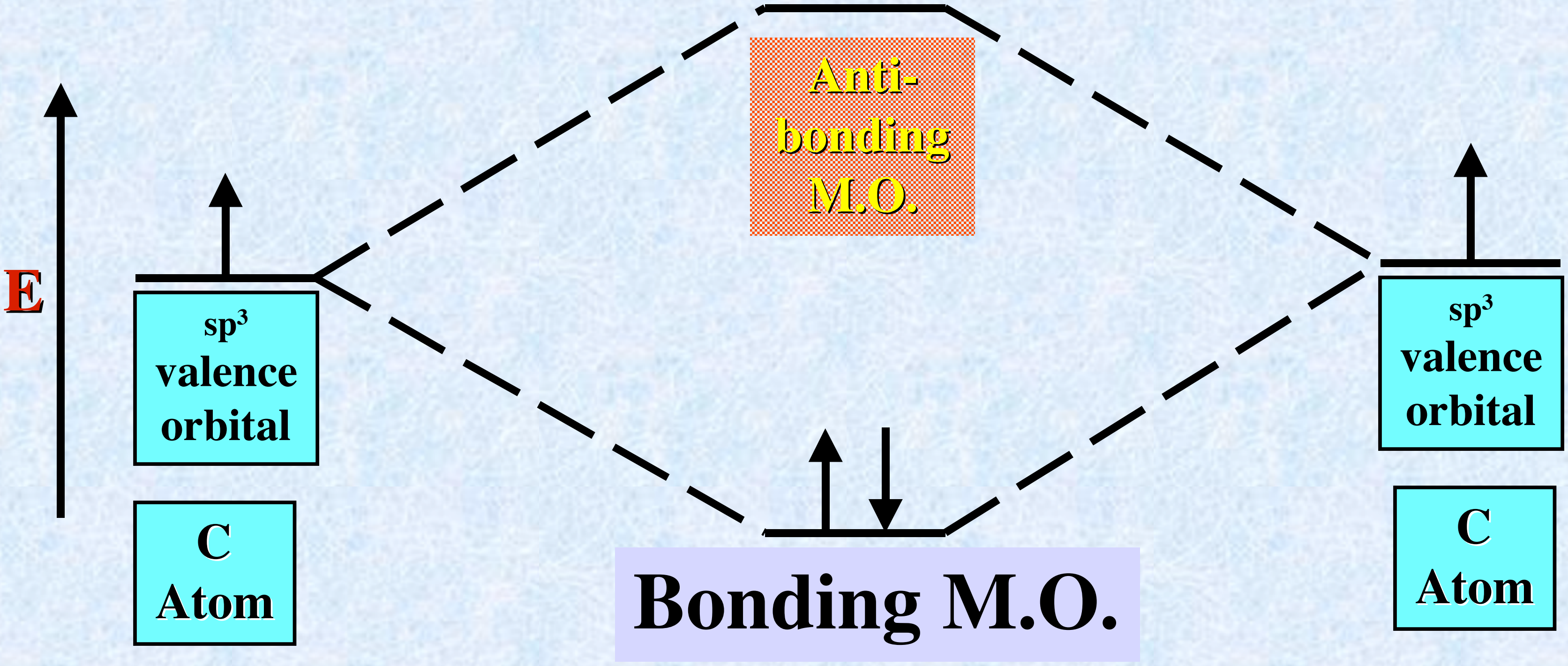
Bonding in non-metals: Insulators and Semi-conductors

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.



This suggests sp^3 local bonding.

Local bonding States in Diamond



E

sp^3 valence orbital

C Atom

Anti-bonding M.O.

sp^3 valence orbital

C Atom

Bonding M.O.

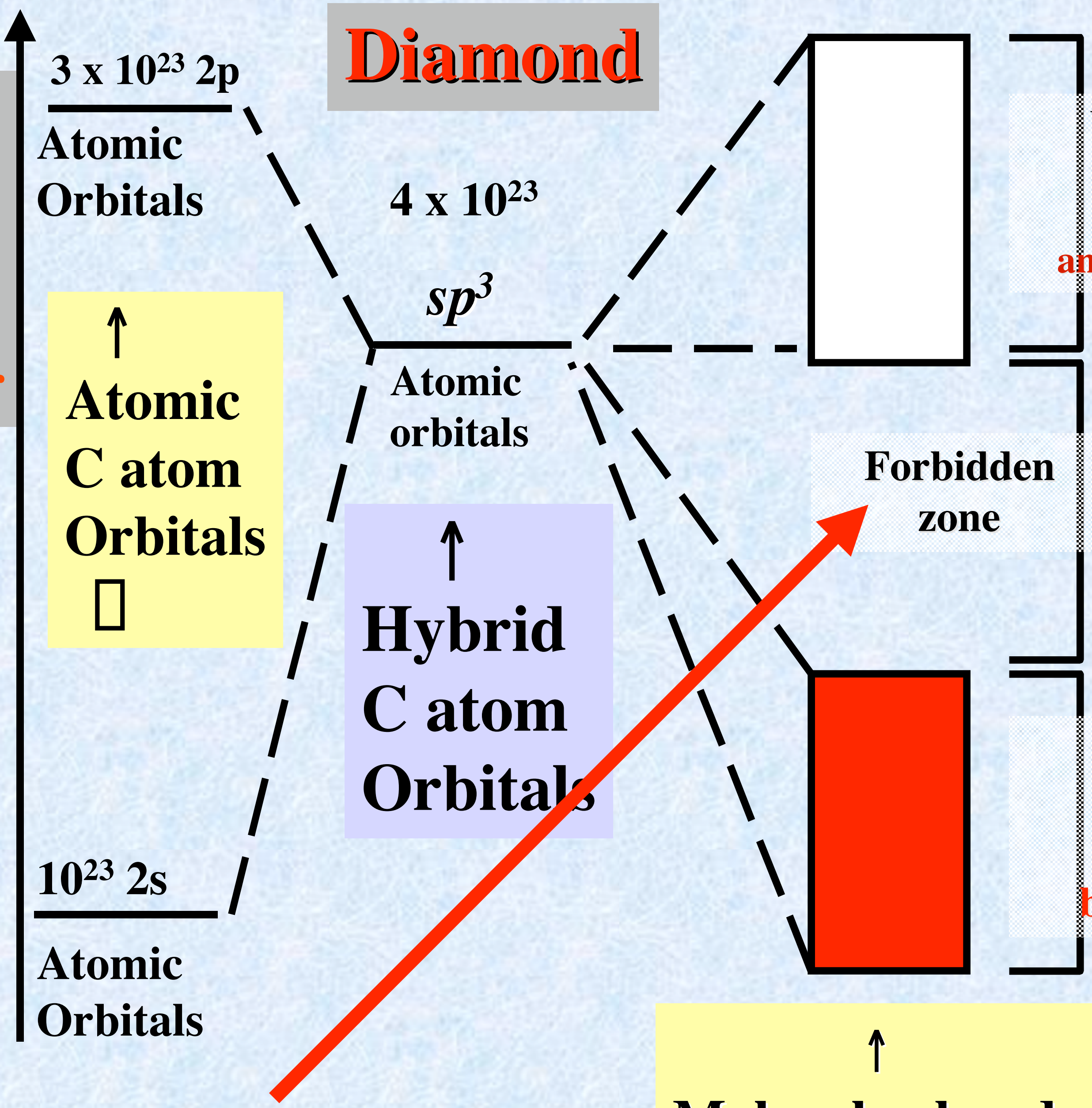
Assign each C atom 4 localized sp^3 tetrahedral bonds

To construct a band model for such a solid, take 10^{23} atoms. giving 4×10^{23} sp^3 orbitals. Combine these to give 2 bands, each with half of the total orbitals: □

Diamond

Typical Energy Bands for an Insulator

Energy, E



3×10^{23} 2p

Atomic Orbitals

4×10^{23}

sp^3

Atomic orbitals

10^{23} 2s

Atomic Orbitals

↑
Atomic C atom Orbitals
□

↑
Hybrid C atom Orbitals

Unfilled band of

2×10^{23} sp^3

antibonding orbitals

Forbidden zone

Filled band of

2×10^{23} sp^3

bonding orbitals

Note Very
□ Large Forbidden Zone!

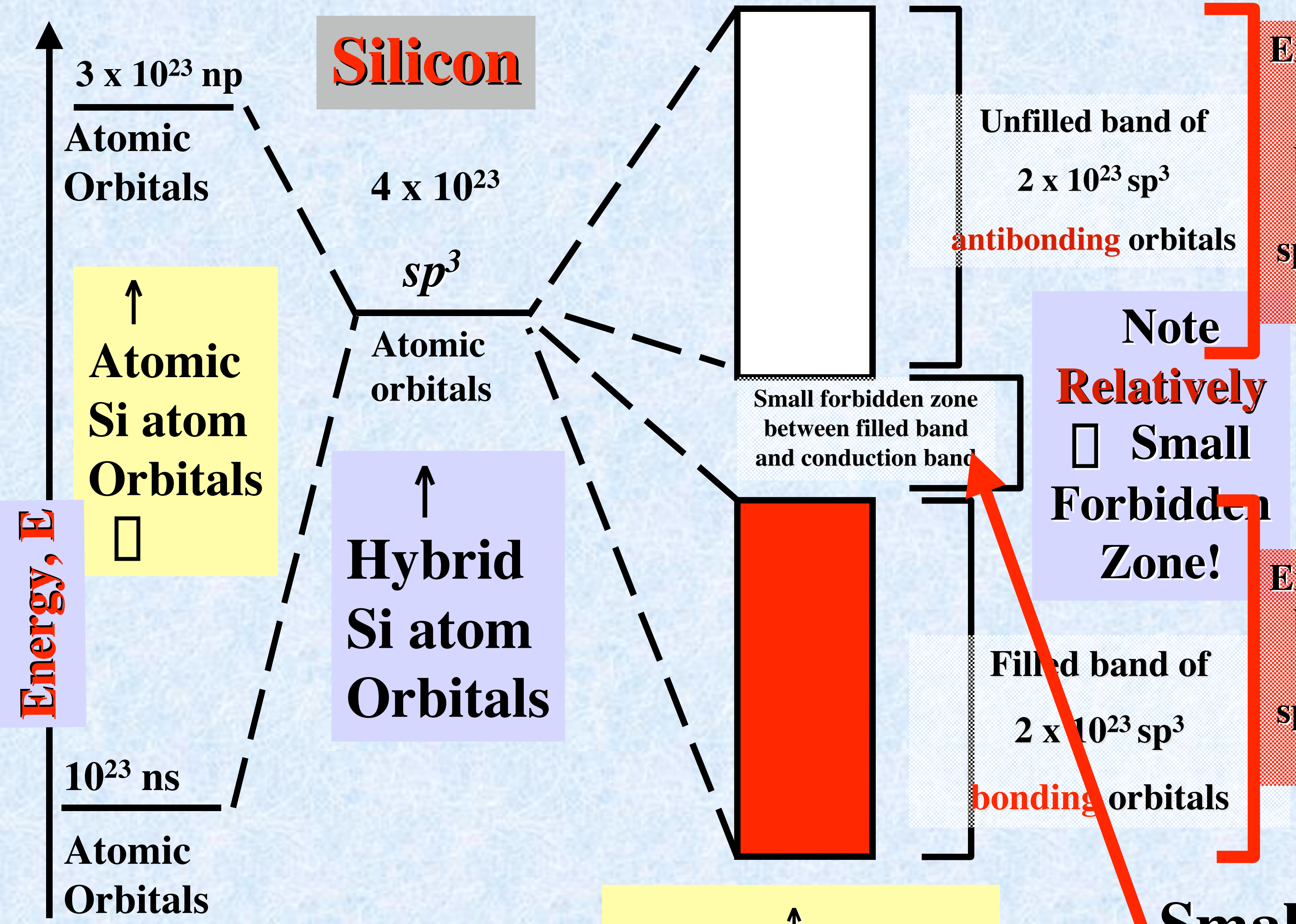
↑
Molecular bands in the solid

Large Band Gap

Semiconductors

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).

Silicon



Energy, E

3×10^{23} np

Atomic Orbitals

10^{23} ns

Atomic Orbitals

↑ Atomic Si atom Orbitals □

4×10^{23}

sp^3

Atomic orbitals

↑ Hybrid Si atom Orbitals

Unfilled band of

2×10^{23} sp^3

antibonding orbitals

Small forbidden zone between filled band and conduction band

Filled band of

2×10^{23} sp^3

bonding orbitals

Energies of anti-bonding orbital split apart greatly

Note Relatively □ Small Forbidden Zone!

Energies of bonding orbitals split apart greatly

Small Band Gap

Typical Energy Bands for a Semiconductor

↑ Molecular bands in the solid

The End!