

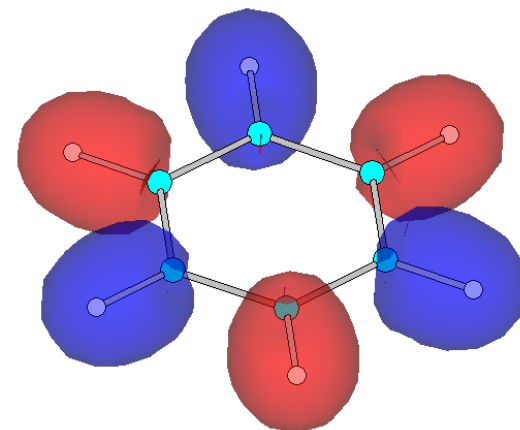
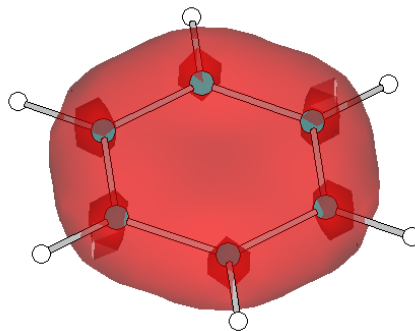
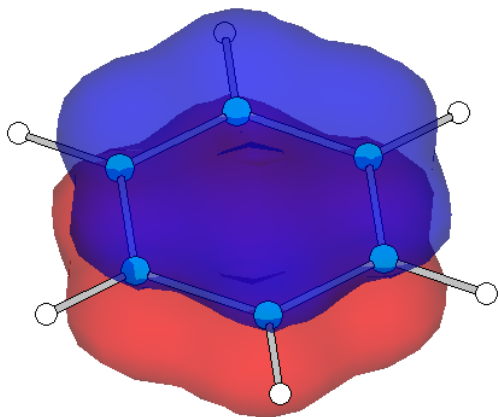
# CHEMISTRY 2000

Topic #1: Bonding – What Holds Atoms Together?

Fall 2020

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See Exercises 5.1 and 5.2





# Free Electron Model for Metals

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- Metals are very good at conducting both heat and electricity.
- In CHEM 1000, metals were described as behaving like a set of nuclei forming a lattice with a “sea of electrons” shared between all nuclei (moving freely between them):

This is referred to as the **free electron** model for metals.

- This model explains many of the properties of metals:
  - Electrical Conductivity: The mobile electrons carry current.
  - Thermal Conductivity: The mobile electrons can also carry heat.
  - Malleability and Ductility: Deforming the metal still leaves each cation surrounded by a “sea of electrons”, so little energy is required to either stretch or flatten the metal.
  - Opacity and Reflectance (Shininess): The electrons will have a wide range of energies, so can absorb and re-emit many different wavelengths of light.



# Band Theory for Metals (and Other Solids)

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- Thus far, whenever we've seen electrons, they've been in orbitals (atomic orbitals for atoms, molecular orbitals for molecules). What about the electrons in a metal?
- These solids can be treated in a way similar to molecular orbital theory; however, the "MOs" in a metal are called **states**. Consider that, in a metal, there are no distinct molecules. You could almost say that an entire piece of metal is a molecule. That's how we'll be treating them:
  - We combine atomic orbitals from every atom in the sample to make states which are essentially very large molecular orbitals.
  - As in LCAO-MO theory, the number of states produced must equal the number of atomic orbitals combined.
  - The Pauli exclusion principle still applies, so each state can only hold two electrons.
  - For a metal to conduct electricity, its electrons must be able to gain enough extra energy to be excited into higher energy states.
  - The highest energy state when no such excitation has occurred (i.e. in the ground state metal) is called the **Fermi level**. Essentially, the Fermi level is the "HOMO".



# Band Theory for Metals (and Other Solids)

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- What happens when two Li atoms approach to make  $\text{Li}_2$ ?
- What about when three Li atoms make  $\text{Li}_3$ ?
- What about when four Li atoms make  $\text{Li}_4$ ?
- Note that, for every atom added:
  - An additional MO is formed
  - The energies of the MOs get closer together

# Band Theory for Metals (and Other Solids)

- 1 g Li contains  $9 \times 10^{22}$  atoms...
- When a sample contains a very large number of Li atoms, the MOs (now called states) are so close in energy that they form a **band** of energy levels.
- A band is named for the AOs from which it was made (e.g.  $2s$  band)
- The highest energy band containing electrons is the **valence band**.
- The lowest energy band with empty spaces is the **conduction band**.

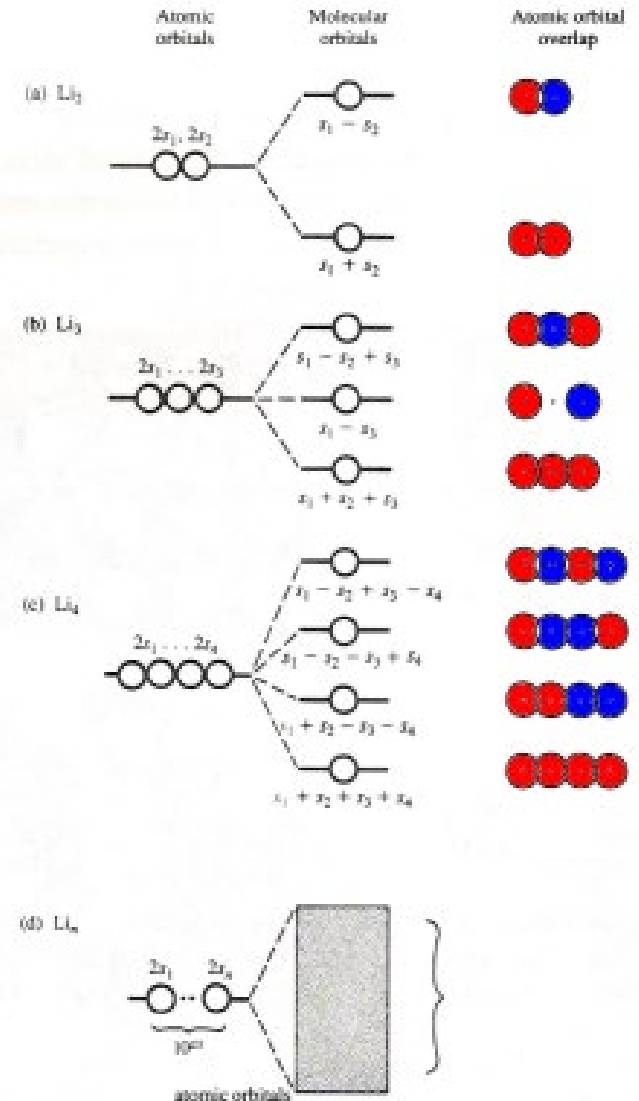


Figure 7-25 Molecular-orbital development of the band theory of metals. Image adapted from "Chemical Structure and Bonding" by R. L. DeKock and H. B. Gray

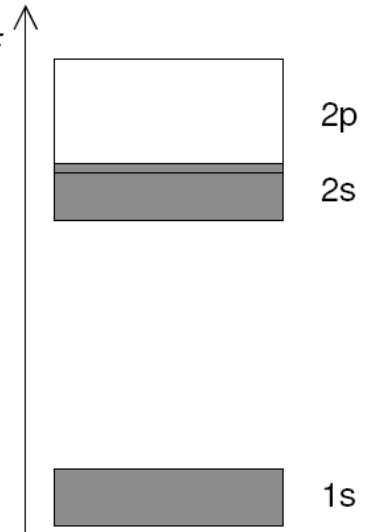
# Band Theory for Metals (and Other Solids)

- In alkali metals, the valence  $s$  band is only half full. e.g. sodium (*band structure shown at right*)
  - If there are  $N$  atoms of sodium in a sample, there will be  $N$  electrons in  $3s$  orbitals.
  - There will be  $N$  states made from  $3s$  orbitals, each able to hold two electrons. So, the band will have space for  $2N$  electrons (but only hold  $N$  electrons).
  - As such,  $N/2$  states in the  $3s$  band will be full and  $N/2$  states will be empty (*in ground state Na*).
- Like all other alkali metals, sodium conducts electricity well because the **valence band** is only half full. It is therefore easy for electrons in the valence band to be excited into empty higher energy states.
- Since these empty higher energy states are in the same band, we can say that the valence band for sodium is also the **conduction band**.



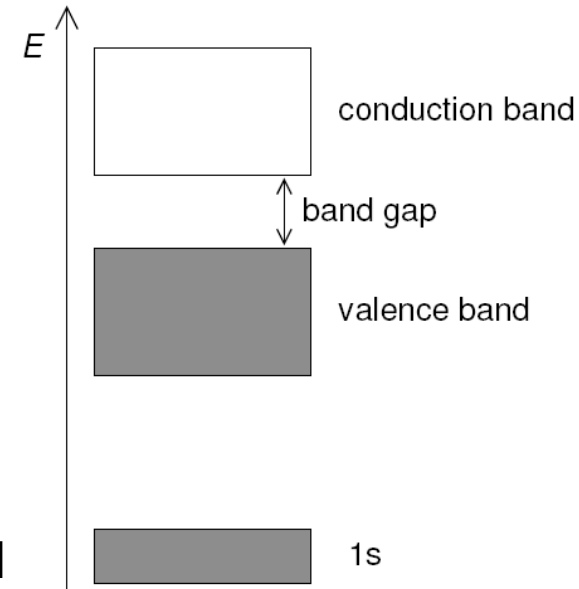
# Band Theory for Metals (and Other Solids)

- In an alkaline earth metal, the valence  $s$  band is full. e.g. beryllium (*band structure shown at right*)
  - If there are  $N$  atoms of beryllium in a sample, there will be  $2N$  electrons in  $2s$  orbitals.
  - There will be  $N$  states made from  $2s$  orbitals, each able to hold two electrons. So, the band will have exactly enough space for the  $2N$  electrons.
  - As such, all states in the  $2s$  band will be full and none will be empty (*in ground state Be*).
- So, why are alkaline earth metals conductors?
  - While the  $2s$  band in beryllium is full, it overlaps with the  $2p$  band. (*Recall the energy level diagram on p.9 of Homonuclear Diatomics notes showed that valence  $s$  and  $p$  AOs of metals were close.*)
  - As such, some electrons in the valence band can easily be excited into the conduction band.
  - In beryllium, the conduction band (band containing the lowest energy empty states) is the  $2p$  band.



# Band Theory for Metals (and Other Solids)

- What do the bands look like for something that doesn't conduct electricity? i.e. for an **insulator** e.g. diamond (*band structure shown at right*)
  - If there are  $N$  atoms of carbon in a sample, there will be  $4N$  valence electrons.
  - The valence orbitals of the carbon atoms combine to make two bands, each containing  $2N$  states.
  - The lower energy band will therefore be the valence band, containing  $4N$  electrons (*in ground state diamond*).
  - The higher energy band will be the conduction band, containing no electrons (*in ground state diamond*).
  - The energy gap between the valence band and the conduction band is big enough that it would be difficult for an electron in the valence band to absorb enough energy to be excited into the conduction band.





# Band Theory for Metals (and Other Solids)

- So, how big does a band gap have to be for a material to be an insulator?

- Our measuring stick is the temperature-dependent  $k_B \cdot T$ 
  - $k_B$  is the Boltzmann constant:  $1.38065 \times 10^{-23}$  J/K
  - $T$  is the temperature in Kelvin
- $k_B \cdot T$  is a measure of the average thermal energy of particles in a sample
- As a rule of thumb:
  - If the size of the band gap is much larger than  $k_B \cdot T$ , you have an insulator. e.g. diamond:  $\sim 200 \times k_B \cdot T$
  - If the size of the band gap is smaller than (or close to)  $k_B \cdot T$ , you have a conductor. e.g. sodium:  $0 \times k_B \cdot T$ , tin:  $3 \times k_B \cdot T$
  - If the size of the band gap is about ten times larger than  $k_B \cdot T$ , you have a semiconductor. e.g. silicon:  $\sim 50 \times k_B \cdot T$

- Band gaps can be measured by spectroscopy. The lowest energy light to be absorbed corresponds to the band gap.

# Band Theory for Metals (and Other Solids)

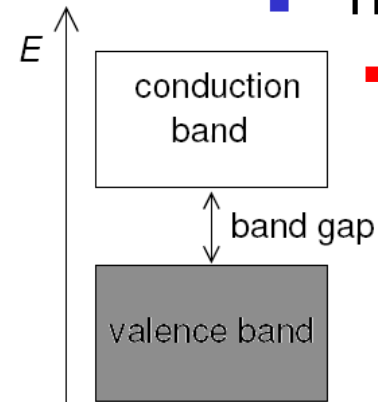
- There are two broad categories of semiconductors:

- **Intrinsic Semiconductors**

- Naturally have a moderate band gap. A small fraction of the electrons in the valence band can be excited into the conduction band. They can carry current.
- The “holes” these electrons leave in the valence band can also carry current as other electrons in the valence band can be excited into them.

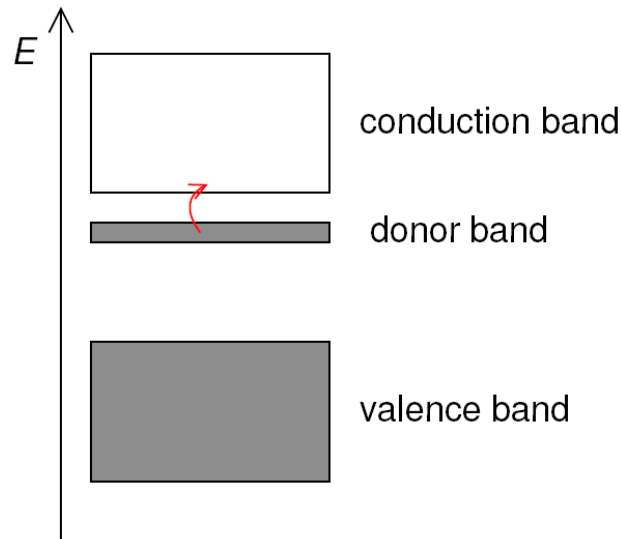
- **Extrinsic Semiconductors**

- Have had impurities added in order to increase the amount of current they can conduct. (*impurities called dopants; process called doping*)
- The dopants can \*either\* provide extra electrons \*or\* provide extra holes:
  - A semiconductor doped to have extra electrons is an *n-type semiconductor* (‘n’ is for ‘negative’)
  - A semiconductor doped to have extra holes is a *p-type semiconductor* (‘p’ is for ‘positive’)



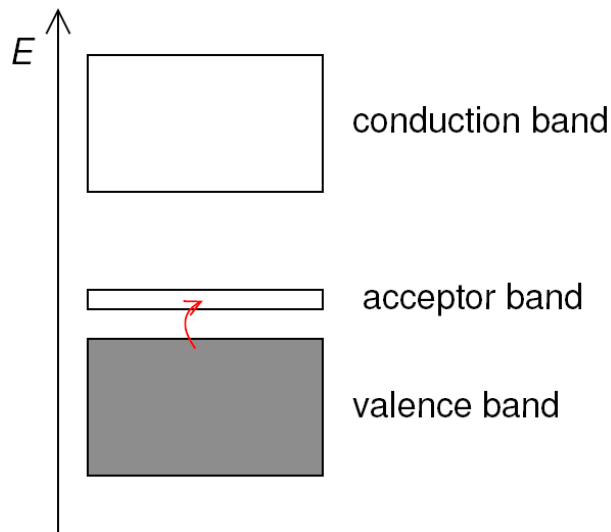
# Band Theory for Metals (and Other Solids)

- How does an n-type semiconductor work?  
e.g. silicon ( $[\text{Ne}]3s^23p^2$ ) is doped with phosphorus ( $[\text{Ne}]3s^23p^3$ )
  - In silicon, the valence band is completely full and the conduction band is completely empty.
  - The phosphorus provides an additional band that is higher in energy than the valence band of silicon and which contains electrons. Electrons in this **donor band** are more easily excited into the conduction band (*compared to those in the valence band of silicon*).



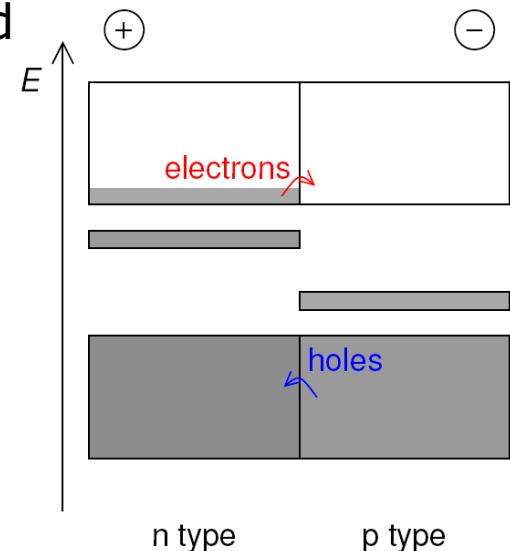
# Band Theory for Metals (and Other Solids)

- How does a p-type semiconductor work?  
e.g. silicon ( $[\text{Ne}]3s^23p^2$ ) is doped with aluminium ( $[\text{Ne}]3s^23p^1$ )
  - In silicon, the valence band is completely full and the conduction band is completely empty.
  - The aluminium provides an additional empty band that is lower in energy than the conduction band of silicon. Electrons in the valence band of silicon are more easily excited into this **acceptor band** (*compared to the conduction band of silicon*), creating “holes” (*empty states*) in the valence band.



# Band Theory for Metals (and Other Solids)

- Through careful choice of both dopant and concentration, the conductivity of a semiconductor can be fine-tuned. There are many applications of semiconductors and doping in electronics.
- e.g. Diodes
  - An n-type and a p-type semiconductor are connected.
  - The acceptor band in the p-type semiconductor gets filled with the extra electrons from the n-type semiconductor. The extra holes from the p-type semiconductor thus “move” to the n-type semiconductor.
  - With negative charge moving one way and positive charge the other, charge separation builds up and stops both electrons and holes from moving \*unless\* the diode is connected to a circuit:
    - If a diode is connected such that the electrons flow into the n-type semiconductor, that replenishes the electrons there and current can flow.
    - If a diode is connected such that the electrons flow into the p-type semiconductor, electrons will pile up there and the current will stop.



# Band Theory for Metals (and Other Solids)

- In a photodiode, the p-type semiconductor is exposed to light. This can excite electrons from the former acceptor band into the conduction band. They are then attracted to the neighbouring n-type semiconductor (which has built up a slight positive charge). This causes current to flow, and is how many solar cells work.

