Chemistry 1901/1903 - Semester 1, 2006

Lecture 13: Molecular Orbitals in Diatomic Molecules
  • Multiple Bonds and Bond Order
  • Bond polarity in diatomic and polyatomic molecules.

Lecture 14: Molecular Orbitals in Molecules and Solids
  • Bonding in Larger Molecules - electron delocalization
  • Metals, Semiconductors and Insulators
  • Conductivity

Lecture 15: Ionic Compounds
  • MO Theory of Covalent, Polar, and Ionic Bonds
  • Lattice Energy of an Ionic Solid
Review Types of Orbitals and Bonds in Diatomics

We now know of five kinds of molecular orbitals formed by valence electrons.

1. \(\sigma\) (bonding) orbitals. Electrons in these bonds lower the energy of the molecule (relative to its atomic orbitals). These are shared between two nuclei and delocalised along the axis between two nuclei.

2. \(\sigma^*\) (antibonding) orbitals. Electrons in these bonds raise the energy of the molecule (oppose bonding). These orbitals have a node or nodes along the axis between two adjacent nuclei.

3. Non-bonding (nb) orbitals are localised on only one atom and do not affect bonding.

4. \(\pi\) (bonding) orbitals. Electrons in these orbitals lower the energy of the molecule, and are delocalised between two nuclei in two lobes on opposite sides of the internuclear axis.

5. \(\pi^*\) (antibonding) orbitals. These orbitals have lobes on opposite sides of the internuclear axis, and a node between adjacent atoms.
Some of the general features we have seen in diatomic molecules can be generalised to larger molecules.

- All molecules yield discrete, allowed energy levels.
- Larger molecules generally contain more valence electrons, and have more allowed energies (= energy levels).
- Molecules are stabilised by lowering electron energies.
- Stabilisation is achieved by greater delocalisation of the electrons (i.e. a longer electron wavelength).

This can even be seen in a triatomic molecule like CO$_2$, which has two $\pi$-type (two-lobed) MO’s containing electrons delocalised along the whole molecule.
MO’s in Larger Molecules

Octatetraene (C₈H₁₀) is an example of a molecule with electrons in highly delocalised orbitals such as the one shown below.

This and other π-type bonding orbitals are low energy quantum states in which the electron is *bound by more than two nuclei*. Other (higher energy) MO’s of C₈H₁₀ include the following, all delocalised between >2 nuclei.

You are not expected to recognise or define bonding and antibonding orbitals in polyatomic systems.
Bonding in Diamond

The structure of diamond is known to be a tetrahedral arrangement of carbon atoms organised in a three-dimensional, crystalline array. This can be measured by e.g. x-ray diffraction, and the internuclear distances are known very precisely.

In our simple bonding model, every carbon atom in diamond is bonded to four carbon neighbours by a simple $\sigma$ bond. The electrons are not delocalised further.

This model is a typical description of many materials we refer to as network solids. They are effectively large molecules with neighbouring atoms connected by a covalent $\sigma$ bond.

C and Si are two elements that form covalent network crystals. Compounds that form covalent network solids include $\text{SiO}_2$, $\text{SiC}$, $\text{BN}$, and $\text{Si}_3\text{N}_4$. 
Graphite and Diamond

Graphite and Diamond are *allotropes* of carbon. That is, two different crystalline or molecular forms of the same substance.

Graphite and diamond differ in the nature of their bonding (electronic structure), which significantly affects many of their properties.

<table>
<thead>
<tr>
<th>Graphite</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>black &amp; opaque</td>
<td>transparent and clear</td>
</tr>
<tr>
<td>highly conducting (along two directions)</td>
<td>insulator</td>
</tr>
<tr>
<td>low density (2.27 g cm(^{-3}))</td>
<td>high density (3.51 g cm(^{-3}))</td>
</tr>
<tr>
<td>melts at 4100K</td>
<td>melts at 4100K</td>
</tr>
<tr>
<td>soft solid</td>
<td>hardest solid</td>
</tr>
</tbody>
</table>

The connection between strength or hardness and bonding includes many factors. We will examine these later after the models for bonding are finished.
Energy Levels in Diamond

Network solids like diamond can be treated as one large molecule, which means that the entire material has a set of quantum states (allowed energies), and that only two electrons can be in each orbital (allowed energy).

We can see the general effect of increasing molecular size by calculating the allowed energies in a fragment of a 3-dimensional diamond network of increasing size. The allowed states fall into two groups, bonding and antibonding, as we would expect. As the number of atoms in the network structure increases, so does the number of allowed states and the density of states (how close together in energy they are). E.g. (schematically)
Colour of Diamond and Network Solids

The ground state electronic configuration of network solids has all the $\sigma$ energy levels filled, and all of the $\sigma^*$ energy levels empty.

The lowest energy (HOMO $\rightarrow$ LUMO) electronic transition is given by the band gap, the energy difference between the top of the (filled) band of allowed $\sigma$ energies and the (empty) band of allowed $\sigma^*$ energies.

In network solids and insulators, this band-gap energy is very large.

These materials are colourless and transparent because the longest wavelength that can be absorbed is shorter than the shortest wavelength in the visible spectrum (approx. 400 nm).

That is, $E_{\text{band-gap}} > \frac{hc}{\lambda_{\text{min}}} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{4.0 \times 10^{-7}}$

$E_{\text{band-gap}} > 5.0 \times 10^{-19} \text{J or 3.1eV.}$
Bonding in Metals

Metals are also crystals in which the atoms are bonded to one another and can be treated as a single, large molecule. However in metals the bands of allowed energy levels are remarkably different from insulators.

If we take the same approach with, say sodium, as for diamond, we find that increasing the size of the fragment gives two bands of energy levels with no band gap. Energy levels in metals behave as a single, partially-filled band.

This means that there are many energy levels close together, and that the longest wavelength transition is much longer than 400nm, so the materials are opaque.
Metals and Conductivity

The structure of a metal is often presented in a simplified (classical) picture as consisting of metal cations in a “sea” of electrons. Here “sea” describes the electrons that are in orbitals delocalised among many nuclei.

In order to conduct, the electrons must move along e.g. a metal wire and transport charge, thus generating current. In the “sea” picture, electrons are freely moving or unbound particles, but quantum theory tells us that they have well-defined energies and are in stationary or bound states.

(Remember that this picture cannot describe energy levels of molecules or band gaps. Our model of bonding - quantum theory - must be capable of describing all kinds of materials. We don’t get to make up a new one for every different situation.)

How can a model of bound electronic states explain electrical conductivity by electrons?
Electrical Conductivity and Thermal Energy

The energy levels in bands are so close together that electrons can be excited from one allowed energy into another simply by the energy available from ambient heat.

We can estimate this by using Boltzmann’s constant to convert absolute temperature into energy. You already know that an incandescent energy source radiates light with a peak intensity at $E = 4.5k_B T$. At room temperature (298K), any object radiates heat with a wavelength maximum of

$$\lambda = \frac{hc}{4.5k_B T} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{4.5 \times 1.381 \times 10^{-23} \times 298} = 1.07 \times 10^{-5} \text{ m} = 11 \mu \text{m}$$

The average thermal energy at 298K is about $1.5k_B T$, or $6 \times 10^{-21}\text{J}$ (0.04eV).

Energy levels within a band are much closer together than this, so electrons in partially-filled bands (metals) are

(i) not (quite) in their ground electronic configuration
(ii) able to jump between energy levels.

This effectively allows them to move between orbitals throughout the material.
Natural or Intrinsic Semiconductors

Natural Semiconductors are network solids with band gap energies that lie in the visible or UV range. They may thus be transparent (UV absorbing) or coloured (visible absorbing).

Absorption of a photon promotes an electron from the lower, filled band into the unfilled upper band. Once in this band (the conduction band), the electron has enough thermal energy to *move* and hence to conduct electricity.

Promotion of an electron leaves a *vacancy* or hole in the lower (valence) band, so electrons there *also become mobile*, and have enough thermal energy to move between states within that band.

Conduction can be regarded as taking place *through both electrons in the conduction band and holes in the valence band.*
Natural or Intrinsic Semiconductors

Electrons can be promoted into conduction band states by light, or by thermal excitation (heat).

In natural semiconductors with small band gaps, some electrons are thermally excited into the conduction band. The fraction of excited electrons increases with temperature, \textit{and so does the conductivity}.

Materials that are insulators at low temperatures become increasingly good semiconductors with increasing temperature.
Doped Semiconductors

Semiconductors can be synthesised by introducing foreign atoms into an insulator to modify its electronic structure. There are two types of doped semiconductors.

N-type semiconductors are prepared by introducing atoms with occupied quantum states just below the bottom of the conduction band.

Some electrons from these localised electronic states are thermally excited into the conduction band, where they become mobile and act as (negative) charge carriers.

Typical n-type semiconductors are prepared by substituting group V elements (P, As, Sb) into the crystal lattice of Si or Ge (group IV). Group VI elements can act as double donors into these lattices.
Doped Semiconductors

P-type semiconductors are prepared by introducing atoms with vacant quantum states just above the top of the valence band.

Some electrons from the filled valence band are thermally excited into these localised orbitals. This leaves vacancies or holes in the valence band that are mobile and act as (positive - “p-type”) charge carriers.

Typical p-type semiconductors are prepared by substituting group III (B, Al, Ga) or group II (Be or Zn) elements into the crystal lattice of an insulator.

Substitution into compound semiconductors - e.g. GaAs rather than Si or Ge - are a little more complex. For example, Group IV additives can act as donors or acceptors, depending on which element they substitute.
Solar Energy Conversion

A key application of semiconductors is in solar energy conversion. Excitation of electrons into the conduction band by light is a method for conversion of energy directly into electrical current (a photovoltaic device).

A variety of photovoltaic devices can be prepared consisting of layers of n-, p- and intrinsic semiconductors. The vast majority of these devices are based on Si, which absorbs light throughout the visible range and into the near infrared, making it an effective solar collector.

By creating a layer of n- and p-type semiconductors, electrons and holes can be prevented from recombining, leading to charge separation (an electrical potential difference) that can be used to run devices.

By using multiple layers of materials with different electronic states, it is possible to create multilayer solar cells that absorb in a wider wavelength range and collect more of the available solar energy.

Chemical Vapour Deposition

This is one of the key methods for preparing layered photovoltaic devices, especially with high-purity Si. Gases of *precursor compounds* such as silane (SiH$_4$) are exposed to a solid substrate at high temperature, so that they react when they come into contact with it.

\[ \text{E.g. } \text{SiH}_4(g) \rightarrow \text{Si}(s) + 2\text{H}_2(g) \]

Dopants are included by introducing other precursors into the gas stream such as phosphine (PH$_3$) arsine (AsH$_3$) or trimethylgallium Ga(CH$_3$)$_3$.

\[ \text{E.g. } \text{PH}_3(g) \rightarrow \text{P}(\text{Si}) + 1\frac{1}{2}\text{H}_2(g) \]

\[ \text{Ga(CH}_3)_3 \rightarrow \text{Ga}(\text{Si}) + 3\text{CH}_4(g) \]

Gas composition is changed as the film grows to create different layers.
Summary

You should now be able to

• Explain how band structure in insulators, semiconductors and metals arise from delocalised orbitals.
• Describe the characteristics of natural and doped semiconductors, including band-gap energy.
• Explain how semiconductors are used in solar energy collection and conversion.
• Describe chemical vapour deposition, and how it can be used to build up layers of different composition.

Next Lecture

• Bonding in and properties of ionic crystals.