Lecture 15: Ionic Bonds
  • Electronegativity
  • Ionic Crystals

Lecture 16: Lewis Model of Bonding
  • Lewis Structures
  • Representations of Molecular Structure

Lecture 17: Molecular Shapes
Lewis Model of Bonding

Gilbert N. Lewis developed his model of a chemical bond around the beginning of the 20th century. The model allows us to write some of the essential features of chemical bonds in molecules in a concise way, and to determine the connectivity in and structure of molecules.

The time-line is significant here. Lewis’s ideas about bonding were developed before the nuclear structure of the atom was understood, and certainly before quantum theory was developed. Because the underlying structure was not known at the time, it is phrased as a set of rules or an algorithm for structure-writing.

Despite this, Lewis structures are still widely used by chemists to represent molecules and bonds. It is an extremely useful but incomplete model, so we will learn to use it judiciously and understand its limitations as well as its uses and strengths.

Lewis was one of the first to regard a chemical bond as a pair of electrons shared between two atoms. His model describes how valence electrons may be shared between atoms. It does not describe molecular shape.
## A Timeline of Atomic Structure Development

<table>
<thead>
<tr>
<th>Year</th>
<th>Scientist</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1803</td>
<td>J Dalton</td>
<td>Provided evidence for fundamental indivisible particles - atoms.</td>
</tr>
<tr>
<td>1897</td>
<td>JJ Thomson</td>
<td>Discovered electrons - “cathode rays.”</td>
</tr>
<tr>
<td>1909</td>
<td>RA Millikan</td>
<td>Measured the charge of an electron.</td>
</tr>
<tr>
<td>1909</td>
<td>E Rutherford</td>
<td>Proposed an atom be composed of a small positive nucleus (1912) surrounded by a lot of space occupied by electrons.</td>
</tr>
<tr>
<td>1913</td>
<td>HGJ Moseley</td>
<td>Determined the charge on the nucleus.</td>
</tr>
</tbody>
</table>

Rutherford & others regard the atomic weight as being the number of protons and the nuclear charge as being the number of protons minus the number of electrons *in the nucleus.*

<table>
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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>1913</td>
<td>N Bohr</td>
<td>Applied quantum mechanics to electrons in atoms.</td>
</tr>
<tr>
<td>1920</td>
<td>J Aston</td>
<td>Finds isotopes by mass spectrometry</td>
</tr>
<tr>
<td>1932</td>
<td>J Chadwick</td>
<td>Discovered the neutron. This gives a fairly complete picture of the nucleus as composed of charged protons and uncharged neutrons.</td>
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Lewis Structures

Lewis’s bonding model is almost universally misleadingly called a Lewis Structure. Remember that this refers to a model of the electronic structure of the molecule, but not its three-dimensional structure.

The heart of the Lewis model is the Octet Rule, that atoms share electrons in order to have filled valence shells. A filled valence shell for most atoms contains 8 electrons.

The octet rule always applies to C, Si, N, O, and F, and often applies to many other elements.

N.B. A filled valence shell for H contains only 2 electrons.
Worked Example: Lewis Structures of Diatomic Molecules

What are the Lewis Structure of (a) HF and (b) F₂?

All diatomic molecules contain only one bond.

(a) There are 8 valence electrons in the HF molecule. As a full valence shell for H consists of 2 electrons, it can only form a single bond. We write this as a shared pair of electron “dots” or as a single line

$\text{H:F or H-F}$

The remaining electrons are added around the fluorine to fill its valence shell. These are referred to as lone pairs, and are effectively non-bonding electrons.

$\text{H:F:\quad or\quad H-F:}$

F is now surrounded by 8 valence electrons, and H by 2, as required.

(b) There are 14 valence electrons in F₂. We begin with a bond between the F atoms, leaving 12 to distribute as 3 lone pairs around each F atom thus:-

$\text{F-F:}$
Polyatomic Molecules

In polyatomic molecules with many bonds, the atom that needs to share the greatest number of electrons to achieve a filled valence shell will form the most bonds. We place this in the centre when building a Lewis Structure.

What is the Lewis Structure of hypochlorous acid, HOCl?

H and Cl both lack one electron for a filled shell of 8 electrons, whereas O lacks two. The molecule has a total of $1 + 6 + 7 = 14$ valence electrons. We start by drawing the structure as

$$\text{H-O-Cl}$$

H now has a filled valence shell (2), and we have 10 valence electrons left to distribute. Lone pair electrons $(5 \times 2)$ are added until the valence shells are filled. That is

$$\text{H-O-Cl:}$$

This structure satisfies the octet rule for O and Cl.
Polyatomic Molecules

What are the Lewis Structures of ammonia, $NH_3$, and phosphine, $PH_3$?

Ammonia has 8 valence electrons.

We start by drawing the structure with N at the centre as $H-N-H$

The H's now have filled valence shells (2), and we have 2 valence electrons left to distribute. This is added as a lone pair on N to give it a filled valence shell of 8 electrons:

Phosphine is handled similarly. It has 8 valence electrons with P at the centre carrying a lone pair.
Multiple Bonds

The Lewis model of bonding allows for the sharing of more than one pair of electrons between nuclei. That is, it can accommodate the formation of multiple bonds.

What is the Lewis Structure of formaldehyde, $H_2CO$?

We start by placing C in the centre, and drawing the structure as

![ Lewis Structure of formaldehyde ]

Both H’s now have filled valence shells (2). Of the 12 valence electrons, 6 are unaccounted for, and left to distribute. If we distribute these around the O atom, then we get

This satisfies the octet rule for O but not C, which only has 6 valence electrons here. To create a satisfactory structure, a lone pair from O is shared with C in a double bond:-

![ Lewis Structure of formaldehyde ]

Remember that the double bond represented in the Lewis structure is really made up of one or more $\pi$- and $\pi^*$-type molecular orbitals.
Molecular Orbitals in Polyatomic Molecules: H\textsubscript{2}CO

This is not examinable.

Here are the valence and some core orbitals for formaldehyde, in increasing order of energy. The ideas used for diatomic molecules can be used to rationalise the bonding and label the orbitals as bonding or antibonding with respect to the CO bond according to the positions of the nodes as shown.

H\textsubscript{2}CO is isoelectronic with O\textsubscript{2}, and has a similar molecular orbital structure, except that the $\pi$ and $\pi^*$ orbitals are non-degenerate.

The bond order of the CO bond is $\frac{1}{2}(8 - 4) = 2$. 
Larger Molecules

The bonding in large organic (carbon-based) molecules can be determined using Lewis structures. These molecules contain similar fragments known as **functional groups** like the aldehyde group -CHO above and the nitrile -CN below.

**What is the Lewis Structure of acetonitrile, CH$_3$CN?**

We start by drawing the structure as

```
H
H-C-C-N
H
```

The H’s now have filled valence shells (2), as does the C on the left (8). Of the 16 valence electrons, 6 are unaccounted for. These must be distributed between the other C and N, to fill their valence shells. If we share 2 more electron pairs, and put a lone pair on the N, the final Lewis Structure has a triple CN bond and is:

```
H
H-C-C≡N:
H
```

Notice that the C is single-bonded to the CH$_3$, the bonding in the nitrile functionality is the same whatever it is attached to.

These carbons, typical of organic compounds, forms 4 bonds and no lone pairs.
Organic Molecules and Functional Groups

We can write large organic molecular structures with functional groups in a kind of shorthand.

E.g. All nitriles can be written as R-CN

All nitriles have the same electronic structure, viz. $R\text{C}≡\text{N}$

All aldehydes may be written as $\text{H}\text{C}≡\text{O}$. E.g. methanal

All alcohols may be written as $R\text{O}\text{H}$. E.g. methanol $\text{CH}_3\text{O}\text{H}$

This allows us to draw out and classify large molecules according to their functional groups. (We will see the other main functional groups later.)
Bonding Between Carbon Atoms

The bonding between carbon atoms is the other essential component of organic chemistry. The Lewis bonding model shows how carbon can form three kinds of bonds to itself.

1. Single bond

Each carbon forms four single (σ) bonds to neighbouring hydrogens or other atoms to fill its valence shell (octet rule).

No lone pairs on these carbons.

2. Double bond

Each carbon again forms four bonds and no lone pairs. This time there is a double bond which includes a π bond between the two carbons, as the calculated structure for ethene shows.

3. Triple bond

A C-C triple bond consists of a σ and two π orbitals at right angles to each other, as shown for ethyne.

Actually a quadruple bond (C₂) is a plausible Lewis structure, but such bonds do not exist.
Expanded Valenced Shells

**What is the Lewis Structure of SF\textsubscript{6}?**

We start by placing S in the centre, and drawing the structure as

S now has 12 electrons in its valence shell. The remaining 36 are distributed as 3 lone pairs on each of the six F atoms, giving

Elements below the second period may have *expanded valence shells as follows*:

Group 5A (P, As, Sb) may have 5 electron pairs

Group 6A (S, Se, Te) may have 6 electron pairs

Group 7A (Cl, Br, I) may have 7 electron pairs
Expanded Valenced Shells

What are the Lewis Structures of PCl₃ and PCl₅?

PCl₃: We start by placing P in the centre, and drawing the structure as

P now has 6 electrons in its valence shell. The remaining 7x3+5-6=20 are distributed as 3 lone pairs on each of the three Cl atoms, leaving 2 electrons. These are added to the P to fill its valence shell to 8 electrons.

PCl₅: P is again in the centre, surrounded by 5 chlorines (a valence shell of 10 electrons):

The remaining 40-10=30 electrons are distributed as 3 lone pairs per chlorine.
Developments of Lewis Structures

The Lewis model for bonding has been developed and expanded to explain more and more unusual structures. The most important of these are

1. **Expanded valence shells (see above)** This important development incorporates elements that form more than 4 single bonds, like S and P.

2. **Electron-deficient molecules.** B or Be may have fewer than 8 valence electrons around them. E.g. BeCl$_2$, BF$_3$. However, plausible Lewis structures sometimes exist for these molecules (e.g. Cl=Be=Cl) that satisfy the octet rule, so they are not included in this course.

3. **Resonance Structures.** Within the rules it is sometimes possible to draw more than one Lewis Structure for a molecule (or ion). These are called *resonance structures*, and no one of them is intended to depict the “correct” electronic structure.

*Remember that Lewis structures constitute a handy model that captures some essential features of electronic structure without the apparatus of quantum theory.*
Resonance Structures 1: Ozone

The Lewis model allows several valid structures depicted as follows

\[ \begin{array}{c}
\text{This structure satisfies the Lewis rules too, but is usually disregarded because three-membered rings are not very stable (but they are known).}
\end{array} \]

The accepted interpretation is that these resonance structures are equivalent representations of bonds that are “in-between” single and double bonds. We use a double headed arrow to denote resonance structures.

In ozone, this means that both O-O bonds are equivalent, and have bond order of \( \frac{3}{2} \) or \( 1 \frac{1}{2} \).

This is simply the way that the Lewis structure rules (or our interpretation of them) cope with MO’s delocalised between more than two nuclei.

Some of the nine occupied MO’s of O\(_3\)
Resonance Structures 2: Benzene

Benzene, \( \text{C}_6\text{H}_6 \), has two Lewis resonance structures. These indicate that all the C-C bonds are equivalent, and that the bond order is 9/6 or 1½.

This non-Lewis structure is often used to represent the delocalisation that occurs in benzene and other similar molecules with alternating or conjugated double bonds. It represents some features of benzene like the equality of C-C bond lengths, and is a good conceptual picture of one of the \( \pi \) MO’s:

Electron density in benzene.
Larger Organic Compounds

Using the concept of functional groups, and the knowledge that the Lewis representation of bonding in a functional group is unaffected by neighbouring compounds, we can draw larger, more complex molecules.

E.g.

This Lewis structure represents the nature of the bonding in this compound, benzaldehyde, and we can see that the bonding in the benzene and the aldehyde functional groups are the same as previous compounds.

The bonding of the alcohol in this compound, citronellol, is the same as in other organic compounds. That is, oxygen is single bonded to a hydrogen and a carbon, and to the Rest of the molecule.
General Trends and Notation for Organic Compounds

Because carbon compounds form extended structures, we commonly use a “stick” abbreviation to write them in a condensed form.

This is based on some general properties:
- C forms 4 bonds and 0 lone pairs.
- N forms 3 bonds and 1 lone pair.
- O forms 2 bonds and 2 lone pairs.
- F, Cl, Br, I form 1 bond and 3 lone pairs.

C atoms are not shown in stick notation, and H atoms bonded to C outside functional groups are not shown.

So we would write citronellol as

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}
\]

and benzaldehyde as

\[
\text{H}_2\text{C}=\text{C}-\text{CH}_3
\]

or

\[
\text{H}_2\text{C}=\text{C}-\text{H}
\]
Acids and their Anions

What are the Lewis structures of sulfuric acid, bisulfate, and sulfate ions ($H_2SO_4$, $HSO_4^-$, and $SO_4^{2-}$)?

S will be the central atom (least electronegative).

First we try this structure.

$H_2SO_4$ has 32 valence electrons, leaving 20 to assign as lone pairs or multiple bonds. In this picture S already has a valence shell of 12, so we are left with the task of assigning 10 electron pairs among four O atoms.

In fact the H’s are bonded to oxygens, giving

The remaining electrons are assigned as lone pairs to fill the valence shells of oxygen.

The central S has an expanded valence shell, forming double bonds thus.
Acids and their Anions

What are the Lewis structures of sulfuric acid, bisulfate, and sulfate ions ($H_2SO_4$, $HSO_4^-$, and $SO_4^{2-}$)?

We will start by removing a proton from $H_2SO_4$. The resonance structures of $HSO_4^-$ are thus

$$\begin{align*}
\text{H} & \text{O} \text{S} \text{O} \text{H} \\
\text{O} & \text{O} \\
\text{O} & \text{H} \\
\text{H} & \text{O} \text{S} = \text{O} \\
\text{O} & \text{O} \\
\text{O} & \text{O}
\end{align*}$$

so the bond order in 3 of the S-O bonds is $5/3$, and the other is a single bond.

For $SO_4^{2-}$, the six resonance structures include

$$\begin{align*}
\text{O} & \text{O} \text{S} = \text{O} \\
\text{O} & \text{O} \\
\text{O} & \text{O} \\
\text{O} & \text{O} \\
\text{O} & \text{O} \\
\text{O} & \text{O}
\end{align*}$$

and the bond order of all the S-O bonds is $6/4$ or $1\frac{1}{2}$. 
Review: How Are You Expected to Use Lewis Structures?

Lewis structures are used to describe single or higher-order bonds and lone pairs of electrons in molecules and ions.

Although they can be used with postulated molecules, the model does not describe any aspect of bond energetics, so it can’t really be used to decide whether a postulated molecule is stable or not.

E.g. We can draw a Lewis structure for PCl₃ or PCl₅, but it can’t tell us which is more stable.
E.g. NH₂⁻ has a well-defined Lewis structure, but is not a stable species under most conditions.

In this unit we use Lewis structures to draw out plausible or reasonable structures for connectivity in molecules and ions, and to get some idea about bond order and electron delocalisation through resonance structures. Formula will be presented to you with various amounts of information to start with.

NB You are not at this stage expected to use the concept of formal charge, discussed in many texts.
Summary

You should now be able to

• Draw out plausible Lewis structures for simple polyatomic molecules.
• Assign bond orders based on sharing of electron pairs and resonance structures.
• Identify carbon-carbon single, double and triple bonds, as well as the aldehyde, alcohol and nitrile functional groups and their bonding.

Next Lecture

• Models of Molecular Shape