### Module 3, Lecture 1

## **Structure and Reactions of Organic Molecules**

**Atoms and Bonding – Part 1** 

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References to Brown et al text shown in BLUE

1

#### **Learning Objectives:**

To understand the modern quantum mechanical structure of the atom

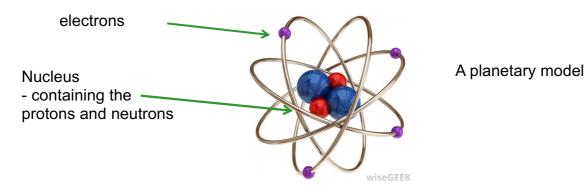
To know the shapes of the modern quantum mechanical orbitals

To be able to write down an electron configuration for an atom

To be able to draw a Lewis structure of a molecule

Textbook: Chapter 2, 6 and 9, sections 9.1-9.6, Brown

### **Rutherford's Nuclear Atom**



If nothing between nucleus and electrons might expect they should move together with lowering of energy

i.e. Atom should collapse

Textbook: Chapter 2

3

### **Quantum Mechanical Atom**

**Bohr** resolved the problem by suggesting that the electrons could only circulate the nucleus at certain distances, with certain allowed energies - **Quantisation** 



Niels Henrik David Bohr 1885-1962

#### Quantisation

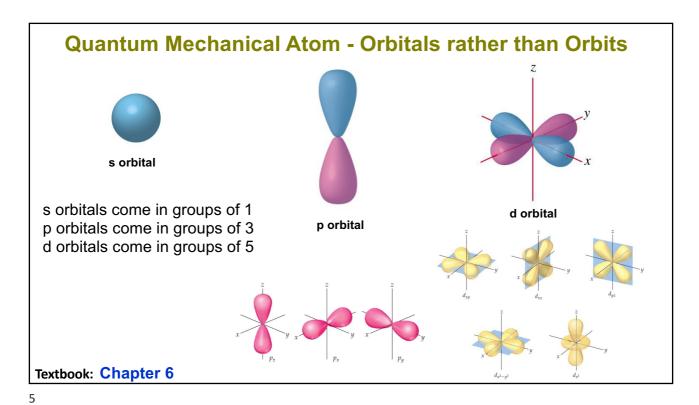
Wave-particle duality - electron can behave like a particle but also like a wave

Heisenberg uncertainty principle

The lowest energy arrangement is when the electron is on the lowest level – closest to the nucleus - called the *Ground State* 

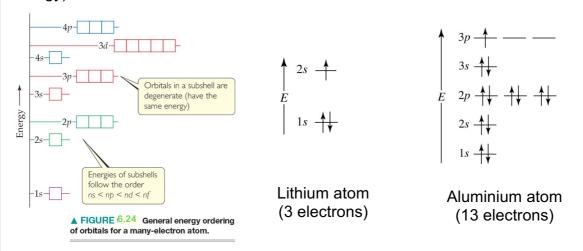
The electron can be one level higher than this, or two, or three (called *Excited States*), but not anywhere in between.

**Textbook: Chapter 6** 



### **Quantum Mechanical Atom - Orbitals rather than Orbits**

Different values of the principal quantum number give different types of, eg, s orbitals, which have the same shape but different energy (the bigger the orbital, the higher the energy)



## **Electron Configurations**

The complete order of the available orbitals in an atom, from lowest energy (smallest) to the highest energy (biggest) is

1s 2s 2p 3s 3p 4s 3d 4p 5s etc

Into these orbitals we can put this number of electrons

1s 2s 2p 3s 3p 4s 3d 4p 5s etc 2e<sup>-</sup> 2e<sup>-</sup> 6e<sup>-</sup> 2e<sup>-</sup> 6e<sup>-</sup> 2e<sup>-</sup> 10e<sup>-</sup> 6e<sup>-</sup> 2e<sup>-</sup>

So for any atom we can write an **electron configuration** to show how its electrons are arranged.

#### For example

Carbon has 6 electrons, its electron configuration is

1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup>

Argon has 18 electrons, so its electron configuration would be:

1s2 2s2 2p6 3s2 3p6

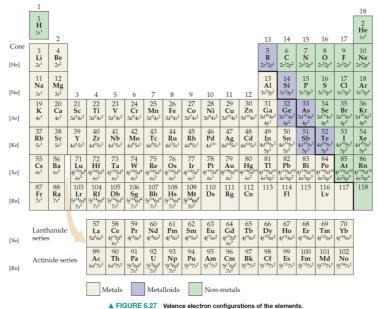
Iron has 26 electrons, so its electron configuration would be:

1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>6</sup>

Or sometimes this is written as [Ar] 4s<sup>2</sup> 3d<sup>6</sup>

7

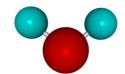
## **Quantum Mechanical Atom – Modern Periodic Table**



Textbook: Chapter 6

### **Molecules**

While the structure of the atom is important chemists are more interested in how electrons are arranged in **molecules** 



 $H_2O$ 

When we make a molecule, individual atoms are joined together.

If we imagine an atom as being like an onion, with each of the layers being like the orbitals, then when two onions interact, they do so via their outermost layers.

When atoms interact, they do so via their outermost orbitals – so it is the electrons in these which are most important



These are the valence electrons

9

### Valence electrons

**Valence electrons** – those which lie in the outermost orbitals (the ones with the largest Principal Quantum Number)

Hydrogen: 1s<sup>1</sup>
Carbon: 1s<sup>2</sup>(2s<sup>2</sup> 2p<sup>2</sup>

4 valence electrons So carbon forms four bonds

Oxygen:  $1s^2 2s^2 2p^4$ 

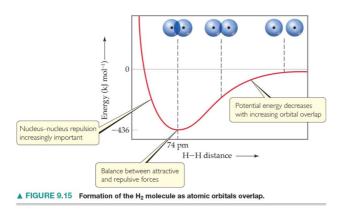
Phosphorus: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>3</sup>

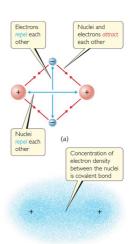
When we join atoms together to make molecules, the valence electrons on each of the atoms are reorganised

 so the first thing we need to know if we want to understand how atoms are bonded together, is the electron configurations of the atoms, and how many valence electrons each of them has.



### H<sub>2</sub> simplest molecule





A covalent bond results from the sharing of a pair of electrons

Textbook: Chapter 8 and 9

11

### **Lewis structures**

For more complicated molecules, there are a variety of **bonding models** which have been developed over time to try to understand how the valence electrons are reorganised when atoms are bonded together to make molecules.

The simplest of these involves working out **Lewis structures** (or sometimes Lewis dot diagrams).

Based on the principle that atoms in a molecule like to have (or share) 8 electrons - stable octet



(1916 – nominated for the Nobel Prize 35 times but never got one ⊗)

Textbook: Chapter 8 and 9

### **Octet rule**

In covalent bond formation, atoms try to complete their **octets** by sharing electrons. Typical of first row elements C, N, O.

Lewis structures show the arrangement of electrons as **shared pairs** (lines) and **lone pairs** (dots).

Textbook: Chapter 8

13

# **Expanded "Octet"**

Heavier elements e.g. Si, P, S can have an expanded valence shell or octet

They can accommodate 10, 12 or even more electrons.

Such elements often show variable covalence

Textbook: Chapter 8 and 9

## **Lewis structures**

Five-steps for drawing a Lewis structure of a molecule

- 1. Count valence electrons for each atom
- 2. Assemble bonding framework using single covalent bonds (pairs of electrons)
- 3. Place three nonbonding pairs of electrons on each outer atom except H
- 4. Assign remaining valence electrons to inner atoms
- 5. Minimise formal charges on all atoms

Textbook: Chapter 8

15

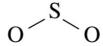
## Sulfur dioxide SO<sub>2</sub>

Step 1: Count valence electrons

Oxygen: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup> 6 valence electrons Sulfur: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>4</sup> 6 valence electrons

Total 18 valence electrons

Step 2: Assemble the bonding using single bonds

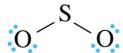


4 of the 18 valence electrons are used here

More electronegative atoms or H on the outside No information about geometry

## Sulfur dioxide SO<sub>2</sub>

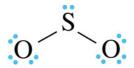
Step 3: Place three nonbonding pairs of electrons on each outer atom except H → lone pairs



This uses another 12 of the valence electrons

Step 4: Assign remaining valence electrons to inner atoms

There are 2 left, so these go on the sulfur.



17

## Sulfur dioxide SO<sub>2</sub>

Step 5: Minimise formal charges on all atoms

valence Formal charge = electrons on free atom

electrons assigned in Lewis structure

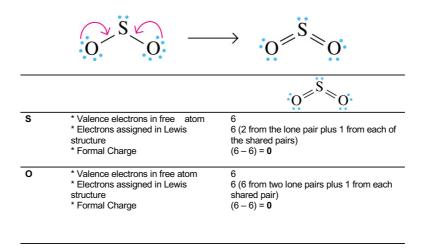


- \* Valence electrons in free atom
  - \* Electrons assigned in Lewis
  - structure \* Formal Charge
- 4 (2 from the lone pair plus 1 from each of the shared pairs)

- 0
  - \* Valence electrons in free atom
  - \* Electrons assigned in Lewis structure
  - \* Formal Charge
- (6-4) = +2
- 7 (6 from three lone pairs plus 1 from
- shared pair) (6-7) = -1

# Sulfur dioxide SO<sub>2</sub>

We can minimise the formal charges by converting lone pairs of electrons into shared pairs



19

## Nitrate anion NO<sub>3</sub><sup>-</sup> - Resonance

When we carry out Step 5 for some molecules, we find that there is more than one way that we can minimise the formal charge.

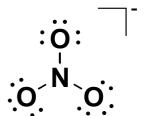
For example, the nitrate anion NO<sub>3</sub>-

Note that for this anion, the extra electron, which gives it the negative charge, is added to the valence electron count. The total number of valence electrons is therefore 24.

If we follow through Steps 1-4, we arrive at:

The formal charge on N is +2

The formal charge on O is -1

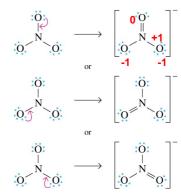


## Nitrate anion NO<sub>3</sub><sup>-</sup> - Resonance

Converting one lone pair to a shared pair leads to the formal charge on N reducing to +1 and O to 0.

The remaining two O's have formal charges of -1 making the overall charge of the anion -1

However, there are lone pairs of each of the three O's which could be used



#### → Resonance Structures

NO<sub>3</sub><sup>-</sup> actually exists as an average of these three structures

$$\begin{bmatrix} 0 \\ \parallel \\ 0 \end{matrix} \xrightarrow{N} 0 \end{bmatrix} \longleftrightarrow \begin{bmatrix} 0 \\ \parallel \\ 0 \end{matrix} \xrightarrow{N} 0 \end{bmatrix} \longleftrightarrow \begin{bmatrix} 0 \\ \parallel \\ 0 \end{matrix} \xrightarrow{N} 0 \end{bmatrix}$$

Resonance Hybrid 1.33 bonds

21

## An alternate NO<sub>3</sub><sup>-</sup> structure

Converting one lone pair to shared pairs on two O atoms leads to the formal charge on N and O reducing to 0.

Remaining O has a formal charge of -1 satisfying the net charge of the anion.

Again three possible resonance structures

What is wrong with this model?

## **Resonance in Organic Molecules**

#### → Resonance Structures

Carboxylic acids can be easily deprotonated to form carboxylate anions

**Amides** 

23

# **Resonance in Organic Molecules**

### → Resonance Structures

Benzene – an aromatic molecule

$$\begin{array}{c|c}
H & C & C & H \\
C & C & H & \end{array}$$

Resonance Hybrid 1.5 bonds

# \* Homework \*

Chemistry – the central science 15<sup>th</sup> Ed

Brown et al.

Problems 6.86, 6.87 Problems 8.70, 8.77

Answers on Blackboard