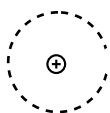


## 1 Energies of Electrons in Atoms and Molecules

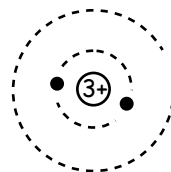
- **Bonding, structure, shape** and **reactions** of organic molecules are determined PRIMARILY by the **Energies** of the electrons in ATOMIC and MOLECULAR ORBITALS
- In organic chemistry we use MODELS, generally the most useful model is the simplest one that explains what we are trying to understand, in this case the relative energies of electrons
- Here we introduce a simple model that summarizes the basic factors that determine electron energies in atoms. Later we will develop more sophisticated models for orbitals and bonding to understand electron energies

### 1.1 Energies of Electrons in Atomic Orbitals

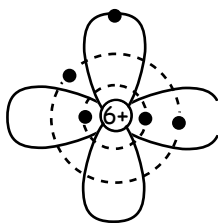
- Simple picture of factors controlling electron energies (a better description is coming later.....)



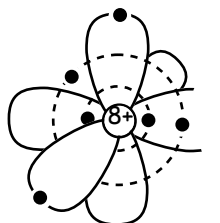
electron stabilized by nucleus, held "tightly" close to nucleus, relatively low energy electron



electron in larger 2s A.O., further from nucleus and shielded by two 1s electrons, not held tightly, relatively high energy electron



electron in even larger 2p A.O., but, higher positive charge on the nucleus (6+), thus outer electrons held **reasonably** tightly by nucleus, moderate energy

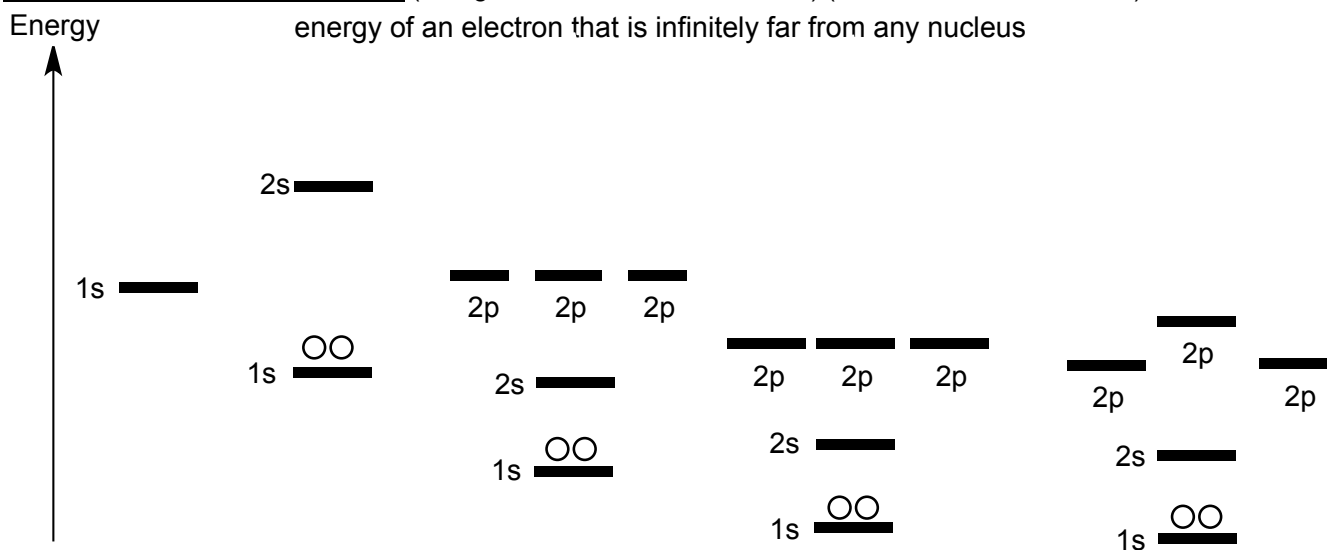


even higher positive charge on the nucleus (8+), but now atomic orbital has another negatively charged electron, outer electrons held **reasonably** tightly by nucleus, moderate energy

### 1.2 Quantitative Energies of Electrons in Atoms

- Quantitative information about the relative energies of electrons is obtained from measurements of **ionization Energies, or Ionization Potentials** (IPs)
- The "first" IP is the energy required to **completely remove** the highest energy electron from an atom or molecule, we are interested mainly in the energies of these highest energy electrons since these are the ones that are involved in chemical reactions, when we talk about I.P. we are always talking about the FIRST I.P.

Example from General Chemistry (energies in eV, i.e. electron Volts) (do NOT memorize these!)



- – "valence" electrons, **are** involved in reactions/bonding
- – "core" electrons, not involved in reactions/bonding

- **VALENCE ELECTRONS** are in the outer shell, they are highest in energy and get involved in bonding
- **CORE ELECTRONS** are in the inner shells, are not involved in bonding

- Electrons in atoms are low in energy because they are negatively charged and are stabilized by the positively charged nucleus
- Electrons that are held "less tightly" by the nucleus are **HIGH** in energy, and thus require less energy to remove from an atom, and thus have a **low IP**
- **Many factors influence atomic I.P.s**, (orbital size, nuclear charge, orbital occupancy, etc.), which looks intimidating at first, **however, a detailed understanding is not necessary at this point**,
- What you **SHOULD KNOW** at this point is that I.P. **increases** (electron energy **decreases**) roughly with increasing electronegativity (i.e., left to right across the periodic table and from bottom to top, going up the periodic table)

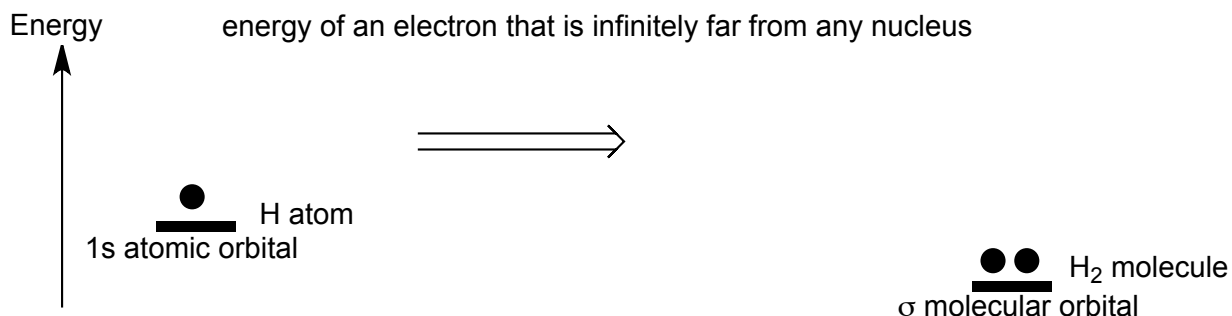
hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.012											boron 5 B 10.811	carbon 6 C 12.0107	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminum 13 Al 26.912	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.067	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selecnium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98.91]	ruthenium 44 Ru 101.07	rhodium 45 Rh 106.42	palladium 46 Pd 107.87	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.818	tin 50 Sn 118.71	antimony 51 Sb 121.750	tellurium 52 Te 127.60	iodine 53 I 126.904	xenon 54 Xe 131.29
cesium 55 Cs 132.905	barium 56 Ba 137.32	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.383	lead 82 Pb 207.2	bismuth 83 Bi 208.980	polonium 84 Po [209]	astatine 85 At [209]	radon 86 Rn [222]

The Connection Between Ionization Potential/Energy and Electron Energy: An ionization energy is the energy required to ionize an atom or a molecule, it is thus an indirect measure of the electron energy in an atom/molecule

- An electron that has been removed from an atom/molecule has a lot of energy (it is high energy) because it is not stabilized by any nuclei
- If the energy of an electron is low in an atom/molecule then we need to add a lot of energy to remove the electron from the atom/molecule to bring it to the high energy/not associated with any atom/molecule state, the energy required to ionize is large, the ionization energy or ionization potential is large
- If the energy of an electron is already high in an atom/molecule then we need to add a lot LESS energy to remove the electron from the atom/molecule to bring it to the high energy/not associated with any atom/molecule state, the energy required to ionize is small, the ionization energy or ionization potential is small

### 1.3 Energies of Electrons in Molecules, e.g. Hydrogen

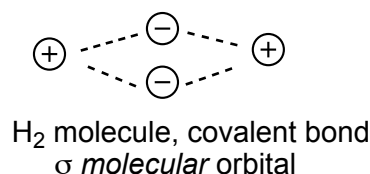
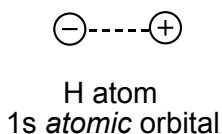
- We can **also** measure energies of electrons in molecules as Ionization Potentials



- IP in **MOLECULAR** hydrogen is **LARGER** than in atomic hydrogen
- the electrons in **MOLECULAR** hydrogen are thus **LOWER** in energy

Question. Why are the electrons lower in energy in molecular hydrogen compared to H atom?

Answer Because they are IN A BOND - this is **really important**



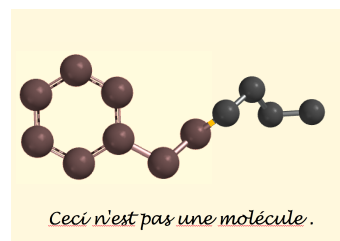
- In the molecule, the **nuclei are shielded** from each other by the **two** electrons
- In the molecule there is an **electrostatically stable configuration** for the two negatively and two positively charged particles (the electrons and the protons)
- this is the STANDARD explanation for why the energies of electrons are lowered when in a bond, later we will learn a better explanation

We have already learned the **TWO MOST CRITICAL CONCEPTS** for **UNDERSTANDING** organic chemistry:

1. **Forming bonds stabilizes (lowers the energies of) electrons**
2. **Higher energy electrons are MORE CHEMICALLY REACTIVE (because they want to form bonds)**

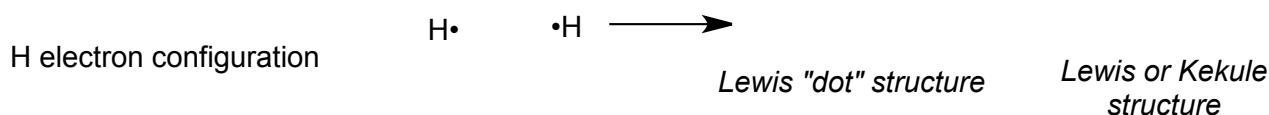
## 2 Introduction to Bonding in Molecules: The Lewis Structure Model

- Lewis structures represent a MODEL for describing the bonding in organic molecules, they are not always accurate, but are still very useful because they are simple, and we tend to use the simplest model to explain what we need to explain
- The Lewis structure model is particularly useful to describe the bonding in the elements normally encountered in organic chemistry, i.e. C, H, N, O etc.
- In the Lewis MODEL, electrons are localized in specific bonds or localized as non-bonding on specific atoms



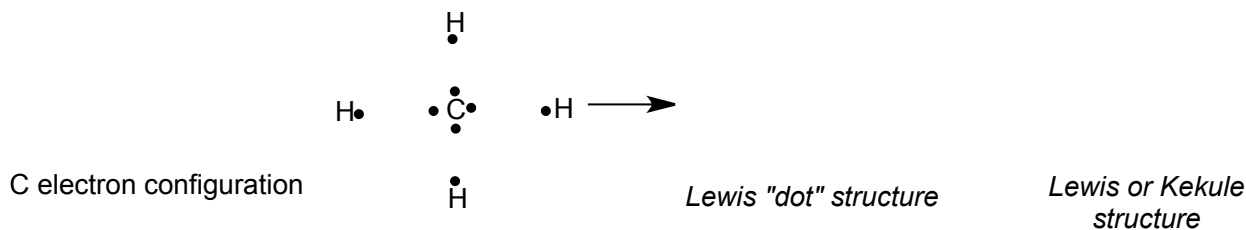
### 2.1 Atomic Valence and Lewis Structures

#### Making a Molecule of H<sub>2</sub> as a Simple Example



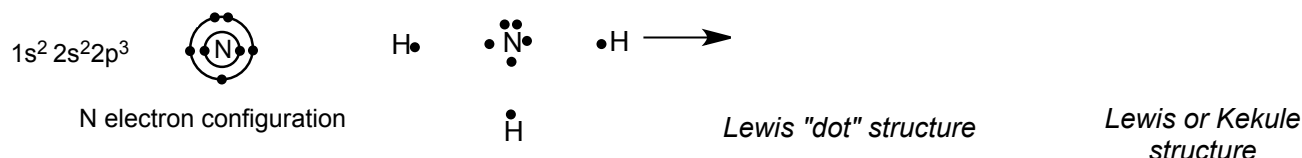
- each hydrogen atom makes one bond, because in doing so it lowers the energy of its one electron
- hydrogen can only make one bond because it only has one VALENCE electron
- making one bond FILLS THE FIRST SHELL with 2 electrons
- NOTE the use of CURVED ARROW notation, "move or use an electron from each atom to make a new bond"

#### Making a Molecule of CH<sub>4</sub> as a Simple Example



- carbon has four valence electrons, therefore it lowers the energy of four electrons by making four bonds
- after making four bonds, according to the Lewis dot model its second outer shell is now "full" with 8 SHARED electrons, it obeys the "filled shell", sometimes call "octet rule" for second row elements
- but what it REALLY did was lower the energies of as many electrons as it could, the 4 valence electrons
- the hydrogens also have a "full" first shell with 2 electrons
- The filled shell rule and the pictures of the Lewis dot structures are MODELS

## Making a Molecule of NH<sub>3</sub> as a Simple Example



- nitrogen has five valence electrons, but can only lower the energy of three electrons to make bonds before "filling" the outer electron shell, attempting to make another bond "overfills" the shell and violates the "filled shell/octet rule" (later we will show that attempting to make another bond increases electron energy instead of decreasing it, which is the real origin of the filled-shell rule)
- Nitrogen in this case has two NON-BONDING electrons in the outer shell
- The octet rule and the pictures of the atoms and molecules as Lewis dot and Lewis structures are MODELS (we use the simplest useful model)
- **Lewis "dot" structures are tedious to draw**, we will use them **very rarely**

**UNFORTUNATELY**, there is **MORE THAN ONE USE** of the word **VALENCE**

- 1) The outer shell is the **VALENCE SHELL**, the electrons in the outer shell are the **VALENCE ELECTRONS**
- 2) the number of bonds that an atom normally makes without violating the "filled shell rule" is the **NORMAL VALENCE**

• "Normal" Bonding Patterns (normal VALENCE) for various atoms obtained from the atomic configuration and by using the filled shell rule (*again, a better model is coming soon!*)

- **DO NOT memorize this table**, learn the Normal Valences by working with them by building organic structures

	atom	electron configuration	# valence electrons	maximum possible number of electrons in outer shell	normal valence (normal # of covalent bonds)
1st shell	H	1s	1	2	
	B	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup>	3	8	
	C	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>	4	8	
2nd shell	N	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>	5	8	
	O	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>	6	8	
	F	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	7	8	
	P	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>3</sup>	5	8	
3rd shell	S	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>4</sup>	6	8	

- # of **valence electrons** = # of electrons in highest energy shell
- **normal valence** = # of electrons required to fill shell rule = # of bonds atoms "normally" makes
- Boron does not have enough electrons to fill the shell, even if all are involved in bonding
- Filled shell or Octet rule doesn't really work for 3rd row elements, e.g. phosphorus and sulfur, see why later
- Obeying the filled shell "rule" is the same as obeying the normal RULES OF VALENCE (normal number of bonds), i.e. 4 bonds to each C, 3 bonds to each N, 2 bonds to each O etc.

Example Problem Draw two **different** Lewis structures for C<sub>2</sub>H<sub>6</sub>O.

The filled shell "rule"/Normal Valence Requires.....

- 4 bonds to each **TETRA**valent carbon (each carbon wants to make **FOUR** bonds)
- 2 bonds to each **DI**valent oxygen (each oxygen wants to make **TWO** bonds)
- 1 bond to each **MONO**valent hydrogen (each hydrogen wants to make **ONE** bond)
- **To generate Lewis structures we will NOT use rules, but we will learn to assemble molecules using common organic structural motifs, e.g. a carbon connected to 3 hydrogen atoms at the end of a chain**

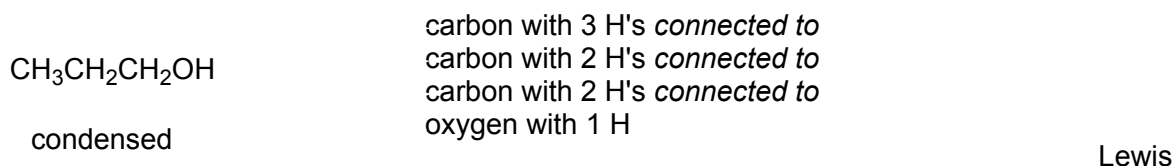
- The oxygen "shares" 4 electrons in the 2 bonds, "has" 4 non-bonding electrons, thus "owns" 6 electrons
- Lewis/Kekule structures indicate connectivity of atoms, orientation doesn't matter (for now!)
- Different Lewis (Kekule) structures are ISOMERS, more on isomers later.....

## 2.2 Condensed Structures

- These are equivalent to abbreviated Lewis structures, the order of atom connectivity/bonding is implied by the "written" order of the atoms, but the bonds are NOT EXPLICITLY INCLUDED, they are implied.
- This means that the normal valencies for the atoms in the structure must be assumed otherwise the bonding order cannot be determined.

Example Problem 1: Convert the provided condensed formula into a Lewis/Kekule structure

- Obeying the normal rules of valence for C (4 bonds), H (1 bond) and O (2 bonds) can generate only one possible Lewis structure



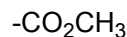
- note that the non-bonding electrons ARE shown in Lewis structures
- H3C- is a common structural motif in organic structures (end of a chain)
- The normal valencies for the atoms (e.g. 4 for carbon etc) MUST be assumed when interpreting condensed formulae

Example Problem 2: Convert the provided condensed formula into a Lewis/Kekule structure

- Obeying the normal rules of valence for C (4 bonds), H (1 bond) and O (2 bonds) can generate only one possible Lewis structure



only possible  
connectivity order



- note the carbon to oxygen DOUBLE BOND, which is required to satisfy the normal rules of valence for all atoms
- note **TWO DIFFERENT USES OF PARENTHESES**
- 1) Parentheses can be used to indicate a part of the structure that comes "off" the main chain
- 2) Parentheses can ALSO be used to indicate repeating units along the main chain

Example Problem 3. Convert the provided condensed formula into a Lewis/Kekule structure

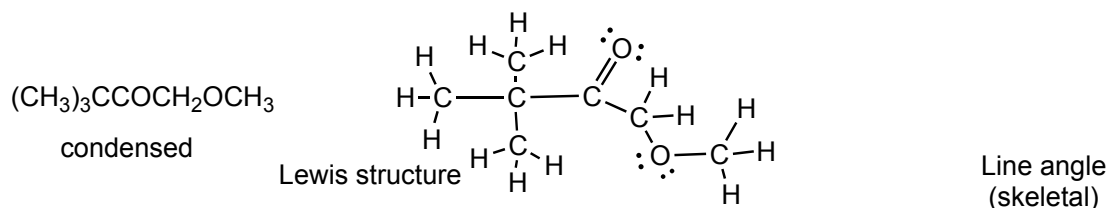


- Note the use of parentheses to indicate repeating units (the other use is to represent a group "off" the main chain). These two uses are easily distinguishable using the normal rules of valence, only one will "work" in a particular context

### 2.3 Line-angle Structures

- Sometimes also called SKELETAL structures
- The lines show bonds between carbon atoms, no H's shown **unless part of a functional group** (see later for definition)
- Line-angle (skeletal) structures are often those that are MOST COMMONLY USED in organic chemistry.

#### Example 1



- there is an atom (carbon unless otherwise specified) at each "end" of each line, each line is a covalent bond
- Full Lewis structures sometimes just take too long to draw, and we will usually use line-angle (skeletal) structures instead (especially for rings)

#### Example 2

Draw an example of a Lewis (Kekule), condensed and line angle structures for C<sub>4</sub>H<sub>6</sub>O (several different structures are possible that are ISOMERS (see the next section), one possible structures is shown here)

Lewis structure

Condensed structure

Line Angle structure

- Where reasonable, draw the angles roughly correct for the molecular shape, see later
- Which Kind of Structure to Draw (condensed, Lewis, line-angle etc) depends upon the context, we will use mainly line angle or a line angle/Lewis mix

### 3 Structural Isomers

- Isomers are different compounds with same molecular formula (we have already seen some of these)
- We meet two kinds of isomers in this course, **structural isomers** and **stereoisomers**, to be discussed later
- Structural isomers differ in the order in which the atoms are connected (connectivity of the atoms), the order in which the atoms are bonded together are different
- The physical and chemical properties of structural isomers are DIFFERENT, they are different structures, different molecules, different chemicals

Example 1: Structural isomers for  $C_4H_{10}$



butane b.p. =  $-0.5^\circ$

isobutane b.p. =  $-11.7^\circ$

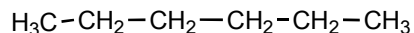
Example 2: Structural isomers for  $C_5H_{12}$



- Note that the direction in which the bonds "point" is irrelevant, structural isomers are generated by connecting atoms together in a different order only
- There are thus THREE different structural isomers that have the molecular formula  $C_5H_{12}$

Example 3: Generate ALL Structural isomers for  $C_6H_{14}$

- useful strategy is often to start with the longest possible chain, and progressively "branch"



- We find that there are FIVE possible structural isomers
- the direction in which the bonds "point" is irrelevant, the structures are defined by the order in which the atoms are bonded together

Example 4: How many DIFFERENT isomers are there shown below?

