

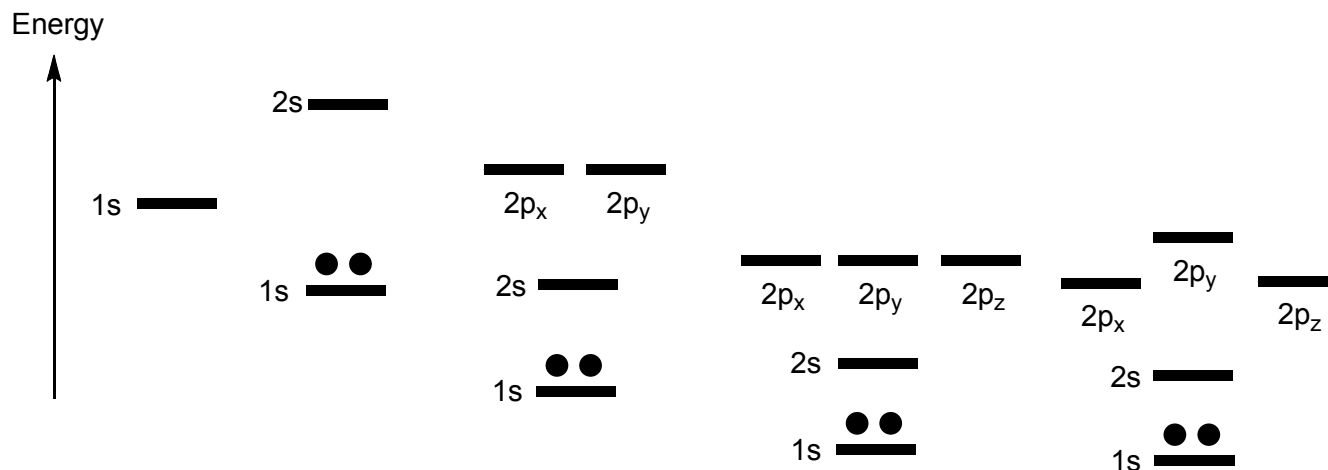
# Basic Principles Part A

## 1 Energies of Electrons in Atoms and in Covalent Bonds

• **Bonding, structure, shape** and **reactions** of organic molecules are determined PRIMARILY by the **Energies** of the electrons in ATOMIC and MOLECULAR ORBITALS

Electrons in ATOMS (energies in eV, i.e. electron Volts)

*energy of an electron that is infinitely far from any nucleus (not stabilized by any nucleus)*



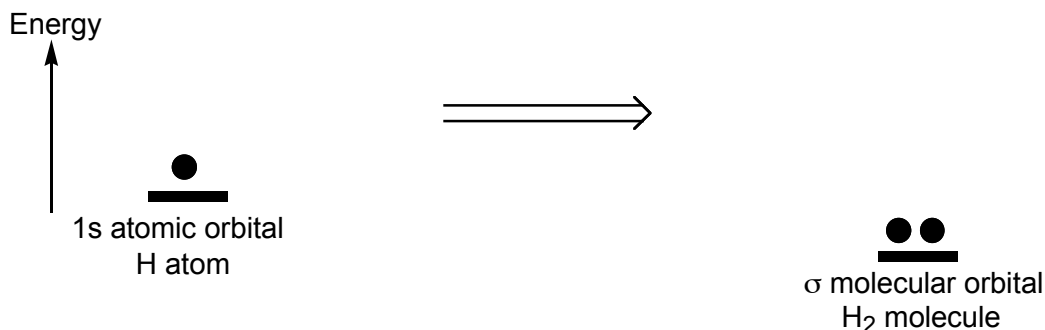
- – "core" electrons, not involved in reactions/bonding
- ⊗ – "valence" electrons, **are** involved in reactions/bonding

• 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**

- I.P. **decreases** (electron energy **increases**) with increasing orbital size (e.g. down the periodic table)
- I.P. **increases** (electron energy **decreases**) with increasing electronegativity (e.g. left to right in the 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	selenium 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 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.818	tin 50 Sn 118.71	antimony 51 Sb 121.760	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	lanthanum 57 La 138.905	hafnium 72 Hf 178.49	tantalum 73 Ta 180.948	wolfram 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 [209.99]	radon 86 Rn [222.08]

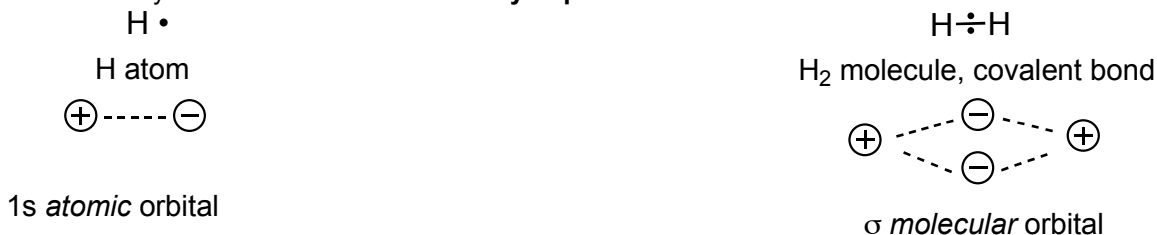
## Electrons in a simple MOLECULE



- 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**



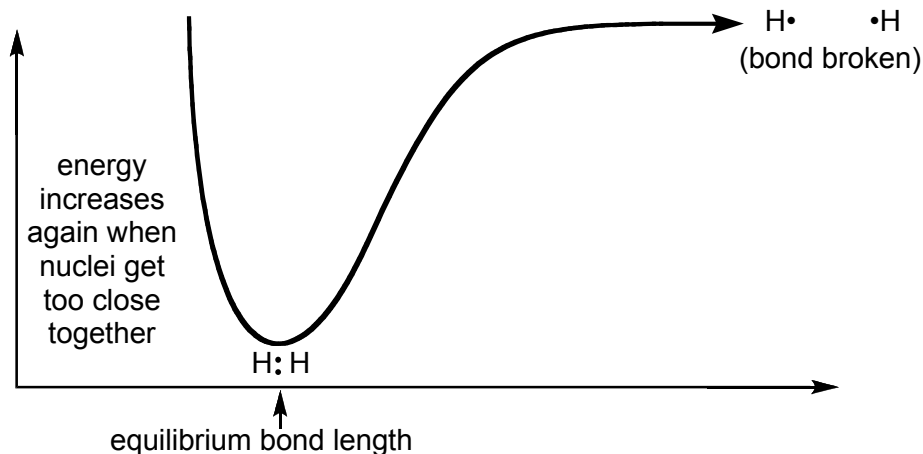
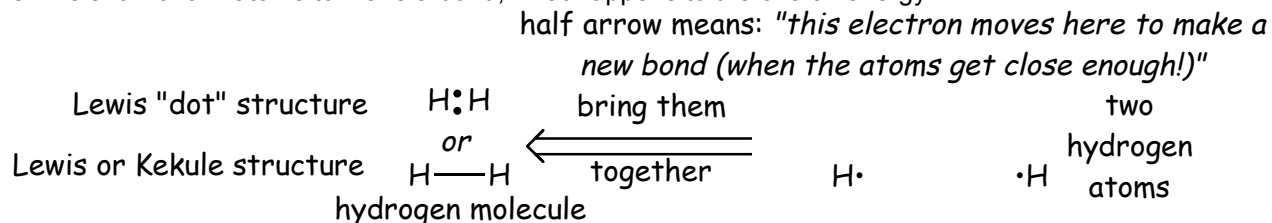
- In the molecule, the **nuclei are shielded** from each other by the **two** electrons
- In the molecule there is an **electrostatically stable configuration** for the two negatively and two positively charged particles (the electrons and the protons)

The following represent 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**

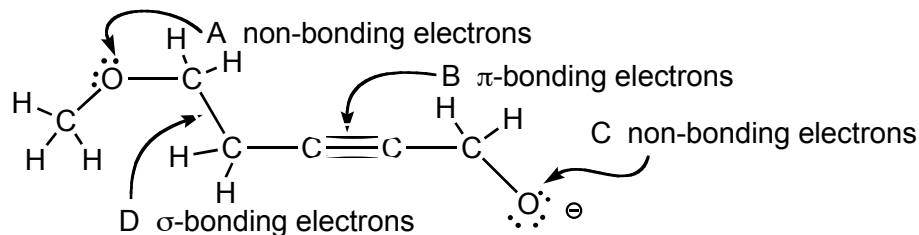
## 2 Energy Diagram for Bond Formation: Simplest Reaction (*more...*)

When we allow two H atoms to make a bond, what happens to the overall energy?



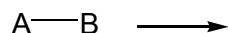
### 3 Energies of Electrons in Molecules

**Example Problem** Give the relative energies of the indicated electron pairs



### 4 Bond Strengths

**Bond Dissociation Energy (BDE)** defined as energy required to **break a bond HOMOLYTICALLY**



The energy required to **Break a Bond HETEROLYTICALLY** a bond is very different, and **NOT = BDE**



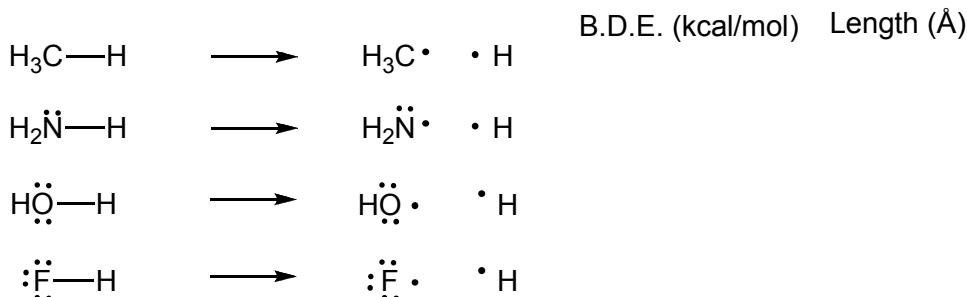
Some **HOMOLYTIC Bond Dissociation Energies** and Bond Lengths

(do not memorize these numbers, but be able to recognize the trends)

• as usual, think about the energies of the electrons **BEFORE**, i.e. in the bond, and **AFTER**, i.e. in the radicals that are formed upon homolytic cleavage

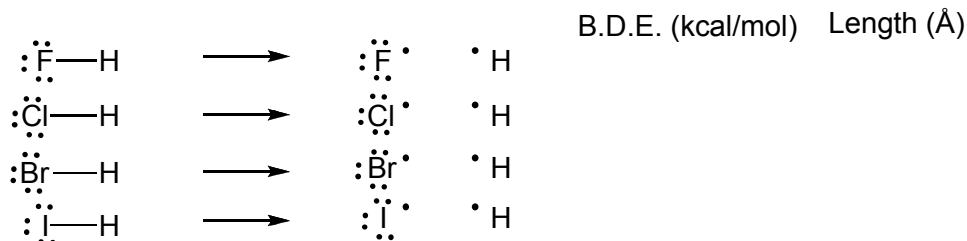
• **IT COSTS ENERGY TO BREAK A BOND: after the bond is broken, the ELECTRONS are NOT IN A BOND!**

1. Across the periodic table : Effect of electronegativity



• bonds to more electronegative elements are stronger and shorter

2. Down the periodic table : Effect of atomic size



• bonds to larger atoms are weaker and longer

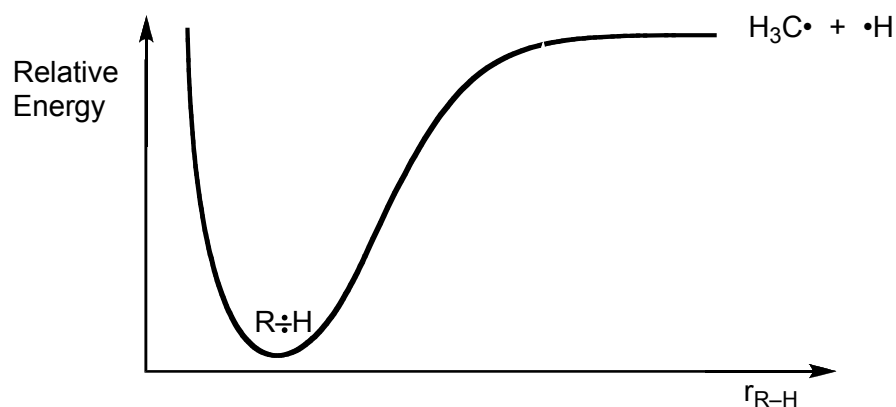
• F is very electronegative and small, the electrons in the H-F bond are very low in energy, this is a strong short bond. With increasing atomic size and decreasing electronegativity, there is poorer A.O.

overlap in bond, larger orbitals, less electrostatic stabilization, the energy of the electrons in the bonds goes up, the bonds get weaker and longer.

### 3. Carbon-Hydrogen Bonds : Stabilization of the RADICAL by Resonance

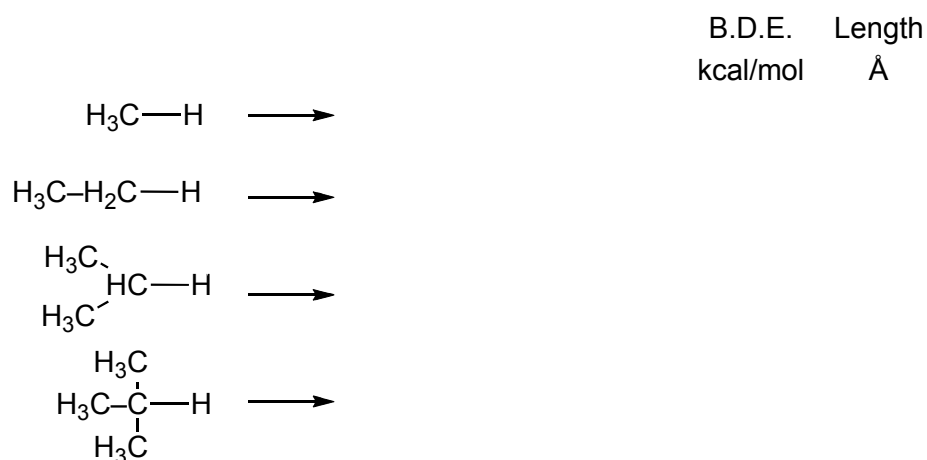


• resonance stabilized radical is easier to form, the non-bonding electron is lower in energy (it is stabilized by delocalization, resonance), thus the energy required to break the bond is lower, the B.D.E. is lower



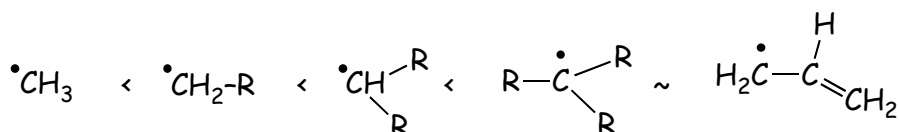
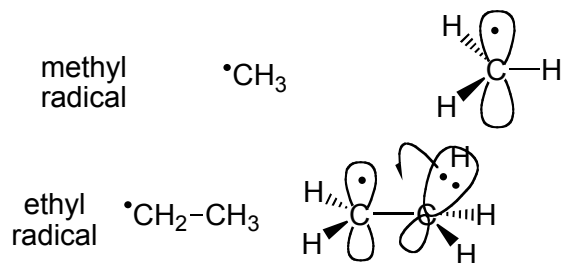
•**IMPORTANT:** it is resonance stabilization in the RADICAL that is formed upon bond fragmentation, not resonance in the bond (there is none!) that lowers the B.D.E.

### 4. Carbon-Hydrogen Bonds : Stabilization of the RADICAL by HYPERCONJUGATION



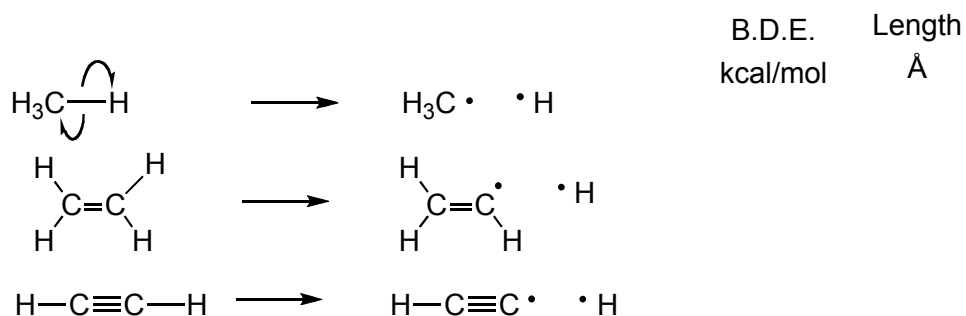
• increasing radical stability upon substitution at carbon due to hyperconjugation results in lower energy electrons in the radical, thus lower B.D.E.  
 • costs less energy to form radicals that are more stable

- What is HYPERCONJUGATION?



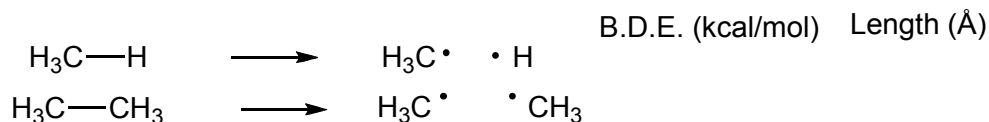
- radicals are stabilized by alkyl substituents on the carbon bearing the non-bonding electron by hyperconjugation
- in a tertiary radical, the stabilization can be as good a real conjugation

### 5. Carbon-Hydrogen Bonds : Effect of C Hybridization



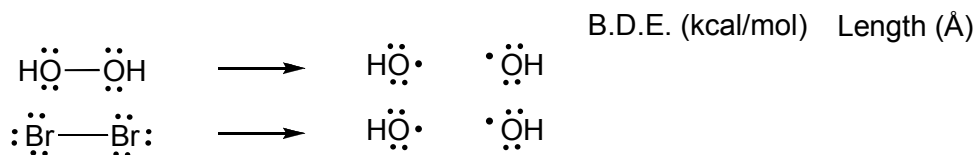
- the electrons in a bond from H to a  $\text{sp}^2$  and  $\text{sp}$  hybridized carbons are lower in energy than those in a bond to a  $\text{sp}^3$  hybridized carbon, due to smaller orbitals, it is thus harder to break the bond, thus larger B.D.E. and stronger bond means shorter bond

### 6. Carbon-Carbon Bonds



- Overlap of a  $\text{sp}^3$  A.O. with another  $\text{sp}^3$  A.O. in a C-C bond is poorer than overlap between a  $\text{sp}^3$  and a 1s A.O. in a C-H bond, poorer overlap means weaker and longer bonds

### 7. Weaker Bonds



- Oxygen lone pairs repel each other in the peroxide, electrons are higher in energy in the bonded state, thus a weak and long bond, even more so for the larger bromine atoms

## 8. Multiple Bonds

			B.D.E. (kcal/mol)	Length (Å)
$\text{H}_3\text{C}-\text{CH}_3$	$\longrightarrow$	$\text{H}_3\text{C}\cdot \quad \cdot\text{CH}_3$	~88	~1.54
$\text{H}_2\text{C}=\text{CH}_2$	$\longrightarrow$	$\text{H}_2\text{C}:\quad :\text{CH}_2$	~160	~1.33
$\text{H}_2\text{C}=\ddot{\text{O}}$	$\longrightarrow$	$\text{H}_2\text{C}:\quad :\ddot{\text{O}}$	~175	~1.21
$\text{HC}\equiv\text{CH}$	$\longrightarrow$	$\text{HC}:\quad :\text{CH}$	~230	~1.20

- Multiple bonds are obviously stronger (and shorter) than single bonds
- Electronegativity effects are still important