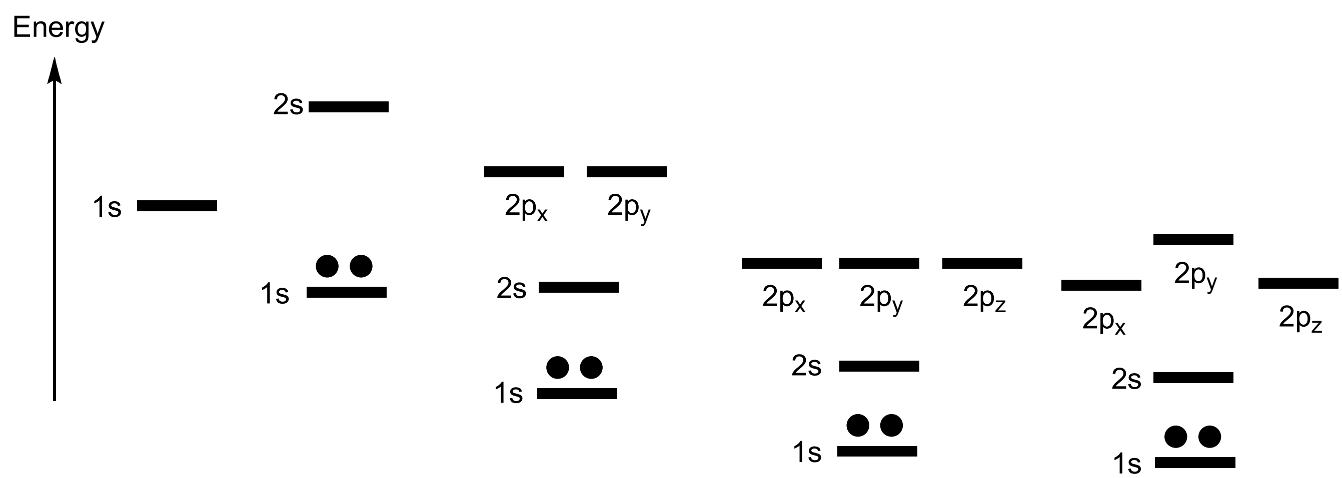
1 Energies of Electrons in Atoms and in Covalent Bonds

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

<u>Electrons in ATOMS</u> (energies in eV, i.e. electron Volts)

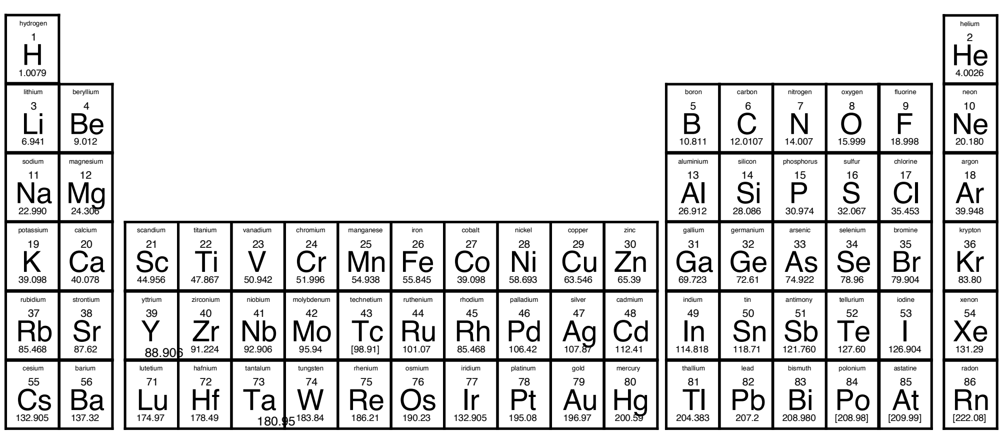
energy of an electron that is infinitely far from any nucleus (not stabilized by any nucleus)



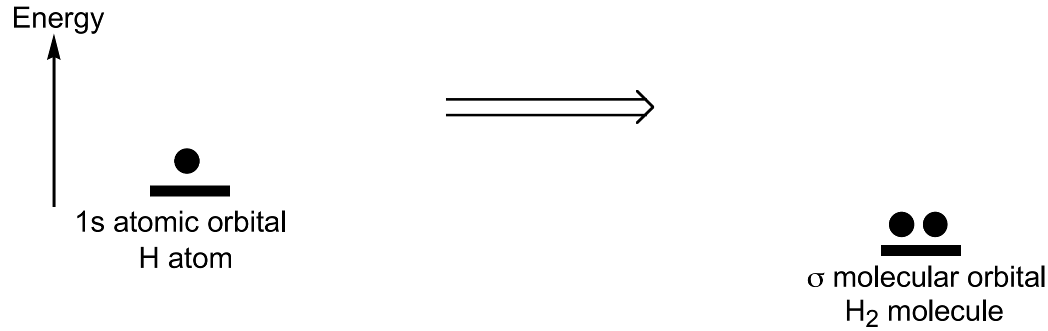
● – "core" electrons, not involved in reactions/bonding
⊗ – "valence" electrons, **are** involved in reactions/bonding

• 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)



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

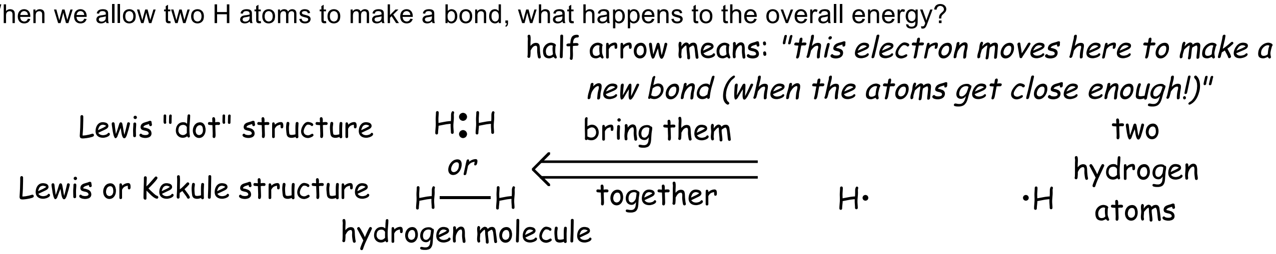
Question. Why are the electrons lower in energy in molecular hydrogen compared to H atom?
Answer Because they are IN A BOND - this is **really important**

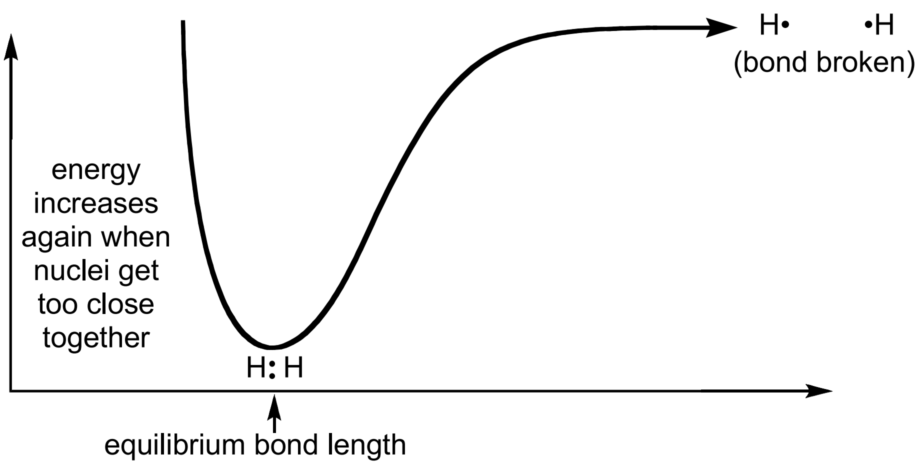
- In the molecule, the **nuclei are shielded** from each other by the **two** electrons
- In the molecule there is an **electrostatically stable configuration** for the two negatively and two positively charged particles (the electrons and the protons)

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...)*

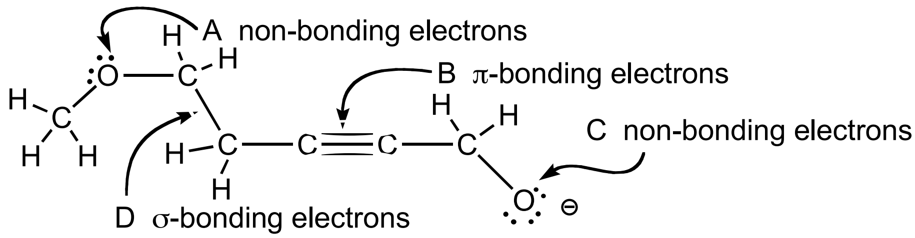
When we allow two H atoms to make a bond, what happens to the overall energy?





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**

$$A{-}B \longrightarrow$$

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

$$A{-}B \longrightarrow$$

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

	B.D.E. (kcal/mol)	Length (Å)
$H_3C{-}H \longrightarrow H_3C\cdot \;\; \cdot H$		
$H_2N{-}H \longrightarrow H_2N\cdot \;\; \cdot H$		
$HO{-}H \longrightarrow HO\cdot \;\; \cdot H$		
$F{-}H \longrightarrow F\cdot \;\; \cdot H$		

• bonds to more electronegative elements are stronger and shorter

2. Down the periodic table : Effect of atomic size

	B.D.E. (kcal/mol)	Length (Å)
$F{-}H \longrightarrow F\cdot \;\; \cdot H$		
$Cl{-}H \longrightarrow Cl\cdot \;\; \cdot H$		
$Br{-}H \longrightarrow Br\cdot \;\; \cdot H$		
$I{-}H \longrightarrow I\cdot \;\; \cdot H$		

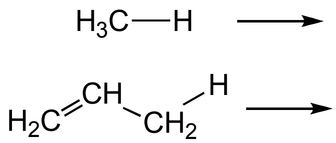
• bonds to larger atoms are weaker and longer

• 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.

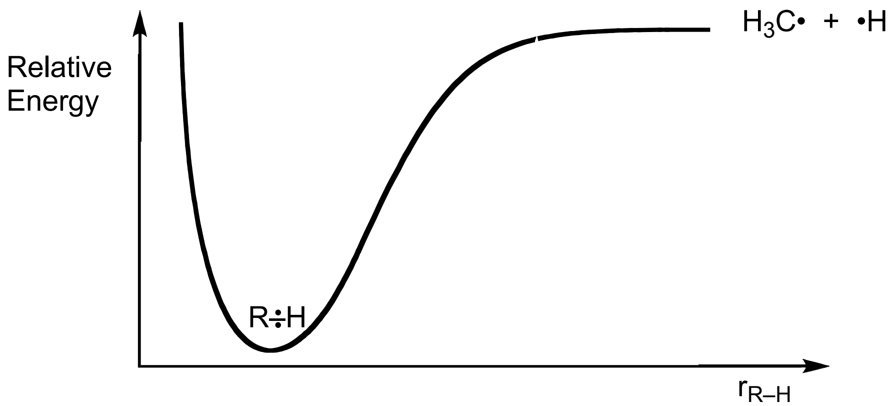
overlap in bond, larger orbitals, less electrostatic stabilization, the energy of the electrons in the bonds goes up, the bonds get weaker and longer.

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

B.D.E. kcal/mol | Length Å



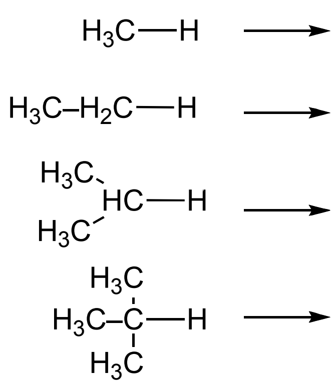
• resonance stabilized radical is easier to form, the non-bonding electron is lower in energy (it is stabilized be delocalization, resonance), thus the energy required to break the bond is lower, the B.D.E. is lower



•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

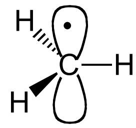
B.D.E. kcal/mol | Length Å



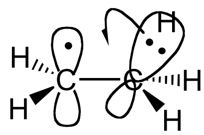
• increasing radical stability upon substitution at carbon due to hyperconjugation results in lower energy electrons in the radical, thus lower B.D.E.
• costs less energy to form radicals that are more stable

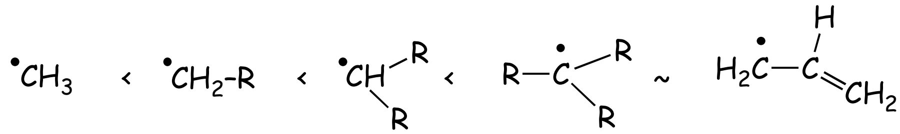
• What is HYPERCONJUGATION?

methyl radical $^{\bullet}CH_3$



ethyl radical $^{\bullet}CH_2{-}CH_3$

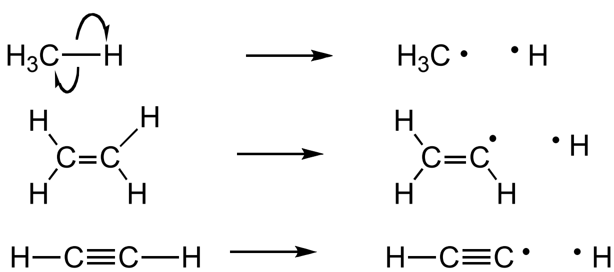




• radicals are stabilized by alkyl substituents on the carbon bearing the non-bonding electron by hyperconjugation
• in a tertiary radical, the stabilization can be as good a real conjugation

5. Carbon-Hydrogen Bonds : Effect of C Hybridization

B.D.E. kcal/mol | Length Å



• the electrons in a bond from H to a sp2 and sp hybridized carbons are lower in energy than those in a bond to a sp3 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

B.D.E. (kcal/mol) | Length (Å)

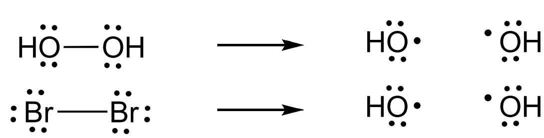
$H_3C{-}H \longrightarrow H_3C^{\bullet} \quad ^{\bullet}H$

$H_3C{-}CH_3 \longrightarrow H_3C^{\bullet} \quad ^{\bullet}CH_3$

• Overlap of a sp3 A.O. with another sp3 A.O. in a C-C bond is poorer that overlap between a sp^3 and a 1s A.O. in a C-H bond, poorer overlap means weaker and longer bonds

7. Weaker Bonds

B.D.E. (kcal/mol) | Length (Å)



• 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)
$H_3C{-}CH_3$	$\longrightarrow$	$H_3C\cdot \quad \cdot CH_3$	~88	~1.54
$H_2C{=}CH_2$	$\longrightarrow$	$H_2C\!: \quad :\!CH_2$	~160	~1.33
$H_2C{=}\ddot{\underset{..}{O}}$	$\longrightarrow$	$H_2C\!: \quad :\!\ddot{\underset{..}{O}}$	~175	~1.21
$HC{\equiv}CH$	$\longrightarrow$	$HC\vdots \quad \vdots CH$	~230	~1.20

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

