Lecture 8

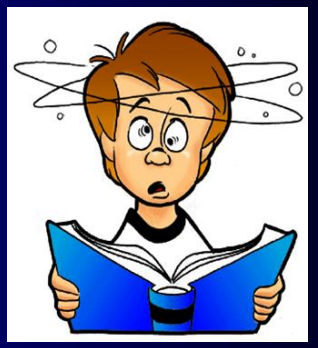
MOs and Benzene

Happy Valentines Day

February 14, 2019

Chemistry 328N

First Midterm Exam



- When: Wednesday, **2/20**
- When: 7-9 PM (please do not be late)
- Where: Painter 3.02!!!
- What: Covers material through Thursday's lecture
- Remember: Homework problems!!
- Practice: Old exams are posted on the web site
- Please…bring pencils, an eraser and a calculator only and no phones …….**Do a good job!!!**

I will bother you! ☺

Early Exam Announcement

- Early Exam on 2/20 @ 5- 7PM in FNT 1.104
- Note that the doors to FNT lock automatically at 5PM You MUST be on time and need to stay for the duration of the exam. You may not exit the exam room before 7 PM
- No Office Hours will be held on the day after the mid-term exams. (@/21, 3/28, 4/25

Early Exam Announcement

- Early Exam on 2/20 @ 5- 7PM in FNT 1.104
- Prior approval is required to take the exam early
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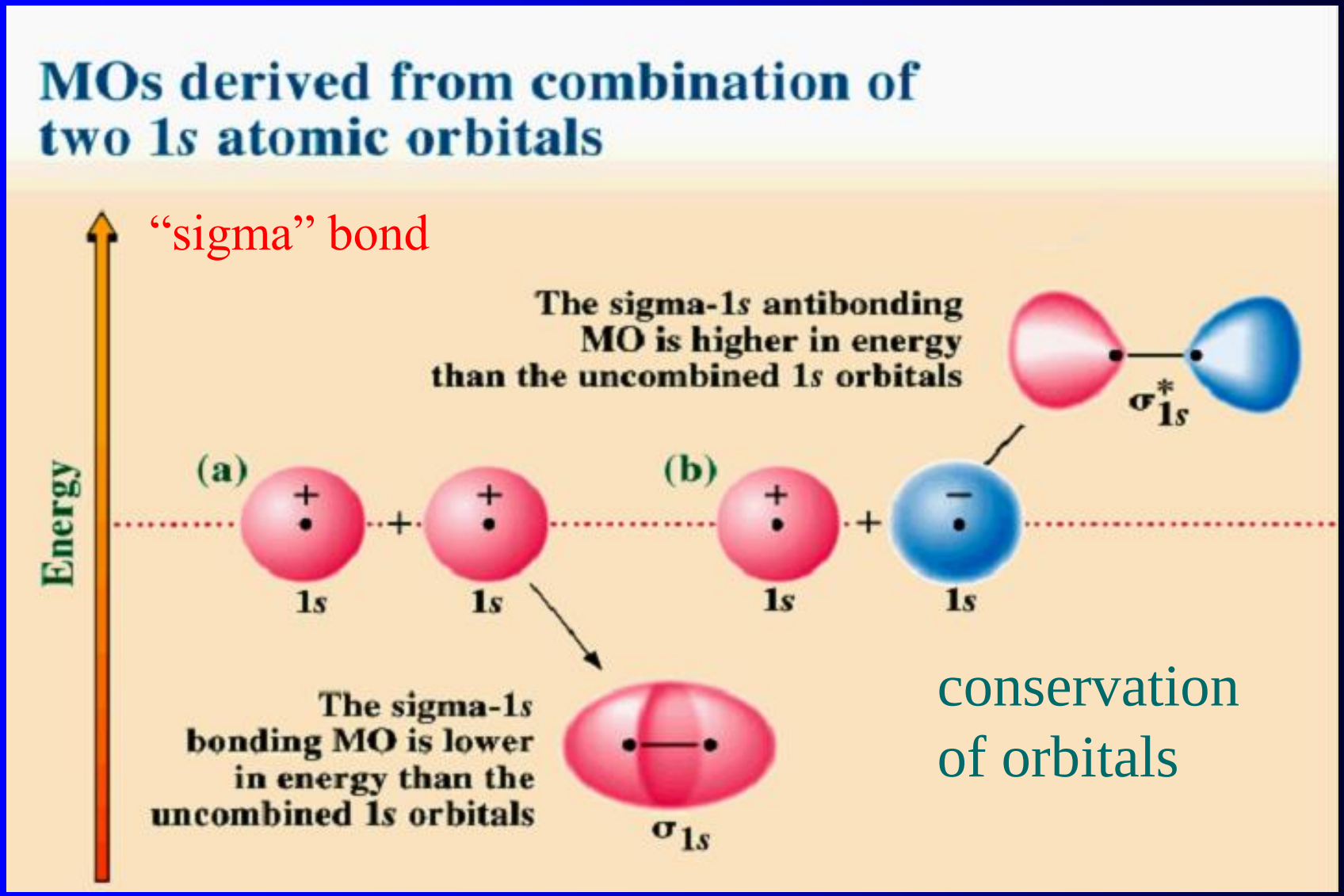
First Midterm Exam Review

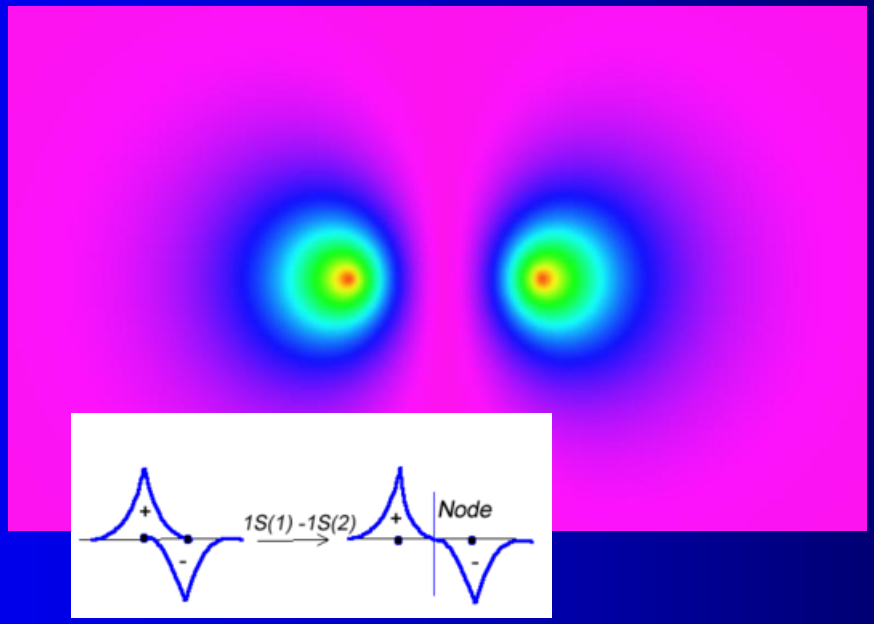
What: Review Session
Where: WEL 2.122
When: 5-7PM Friday 2/15

This meeting is not a lecture session, We will only answer your questions to the best of our ability and work problems from Practice Tests and Homework

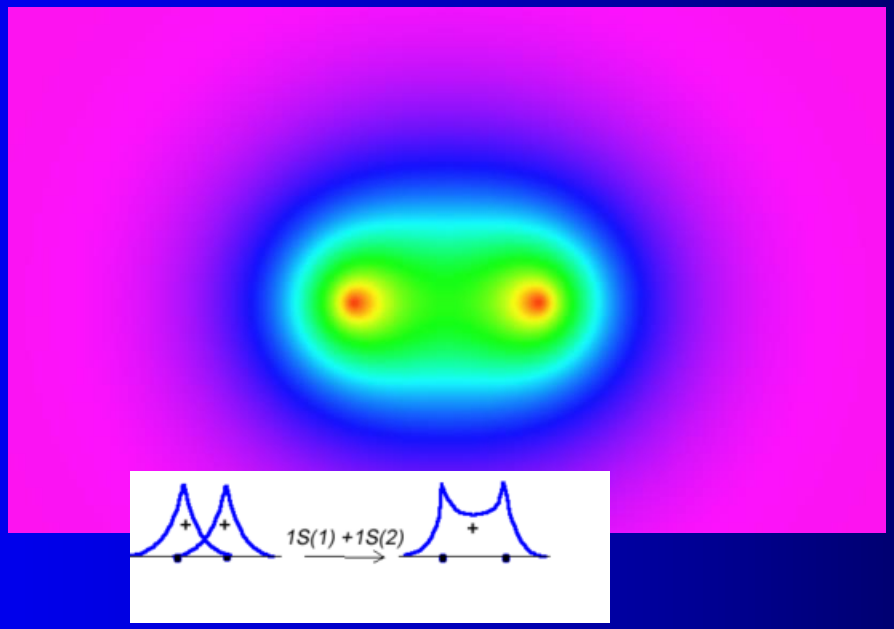
Origin of UV-Vis Absorbance - MO Theory



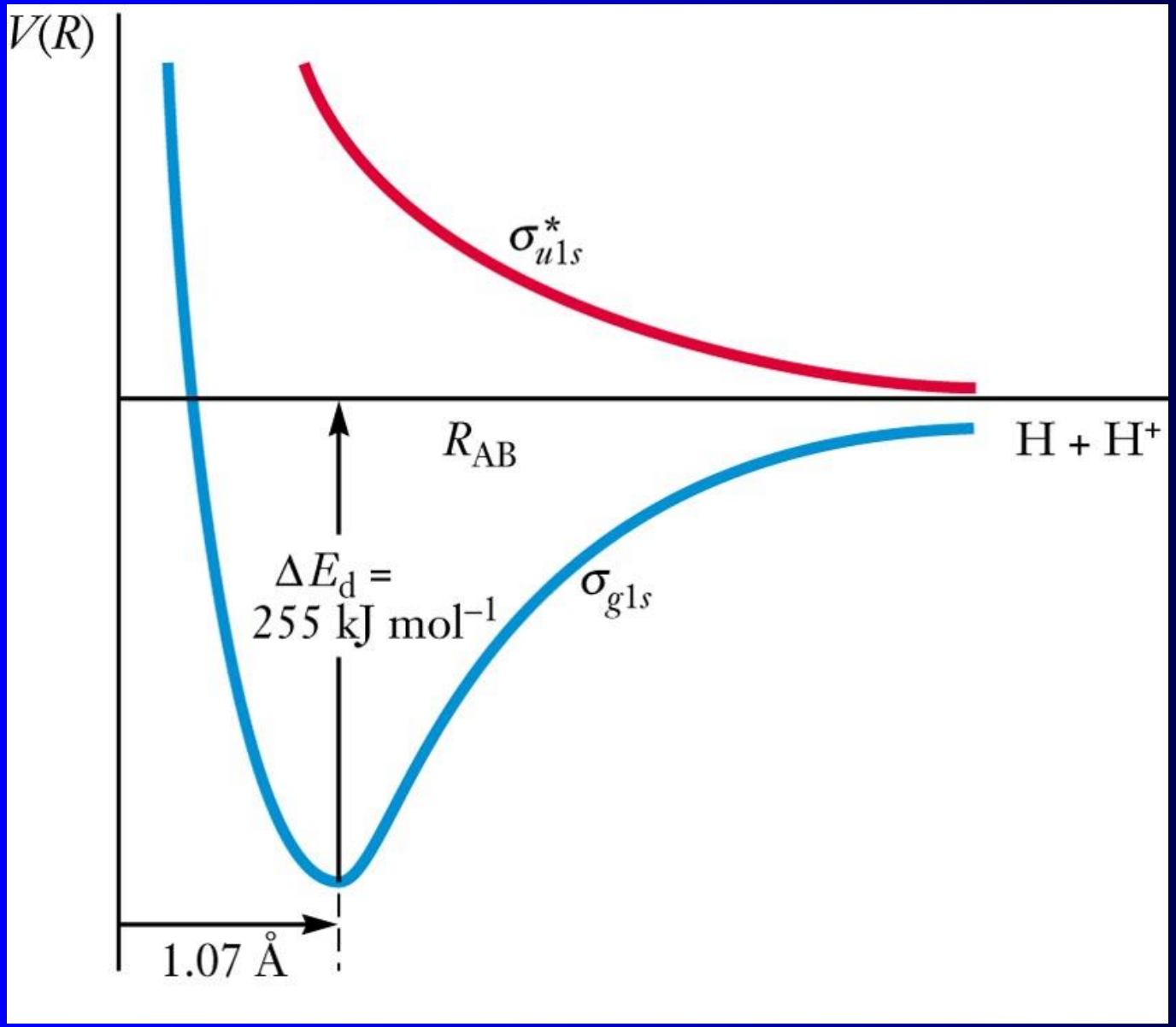
ΔE = 65 Kcal/mole



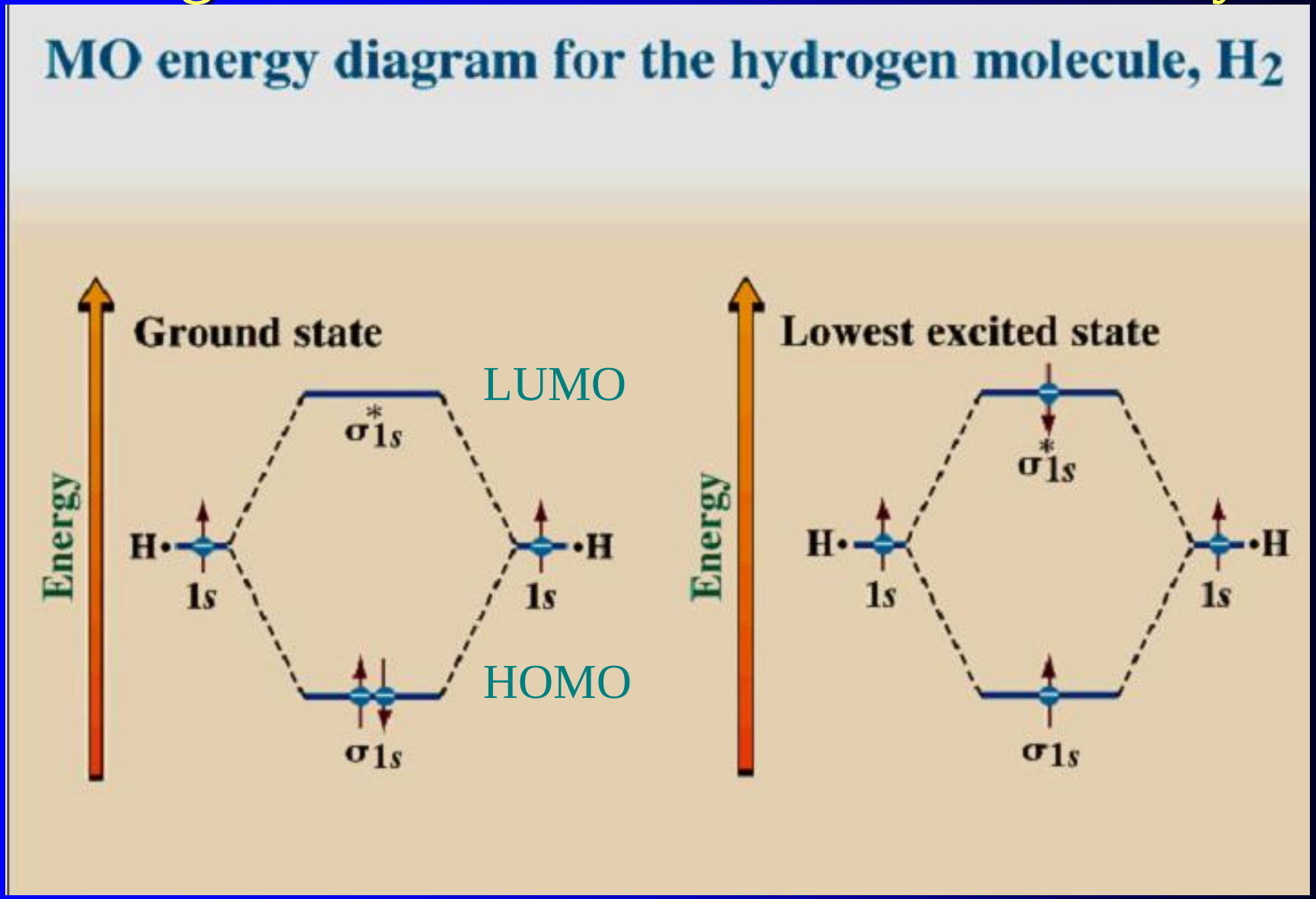
Antibonding



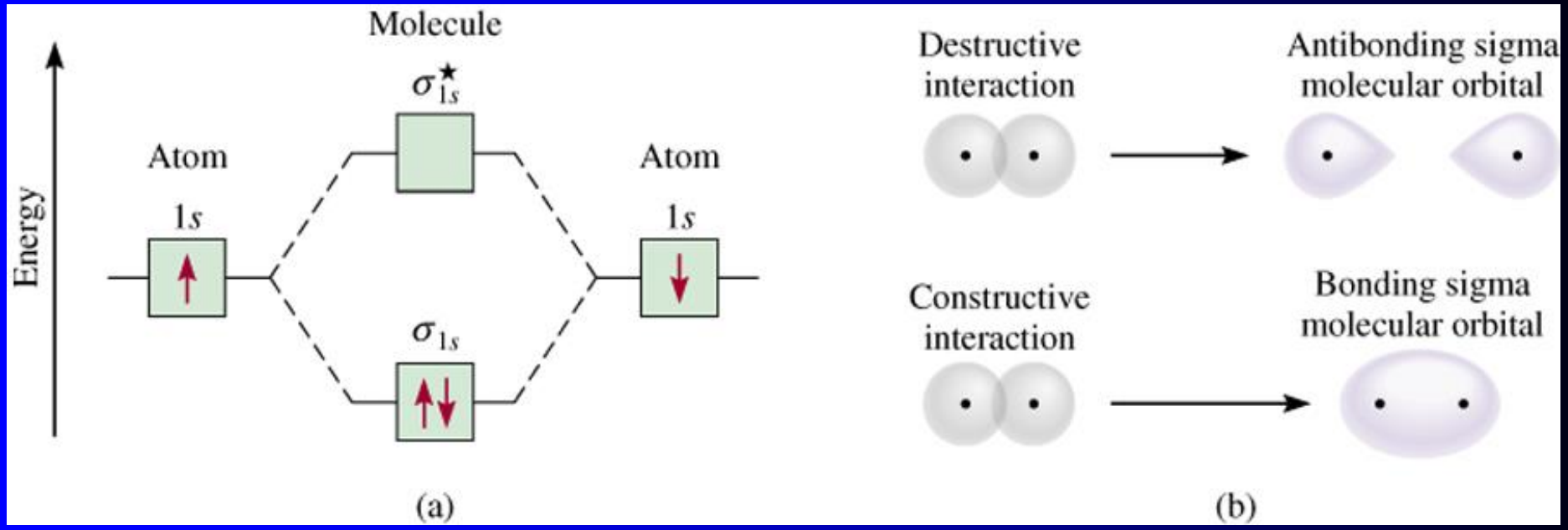
Bonding


V(R)
σ*u1s
RAB
H + H+
ΔEd =
255 kJ mol−1
σg1s
1.07 Å

Origin of UV-Vis Absorbance MO Theory



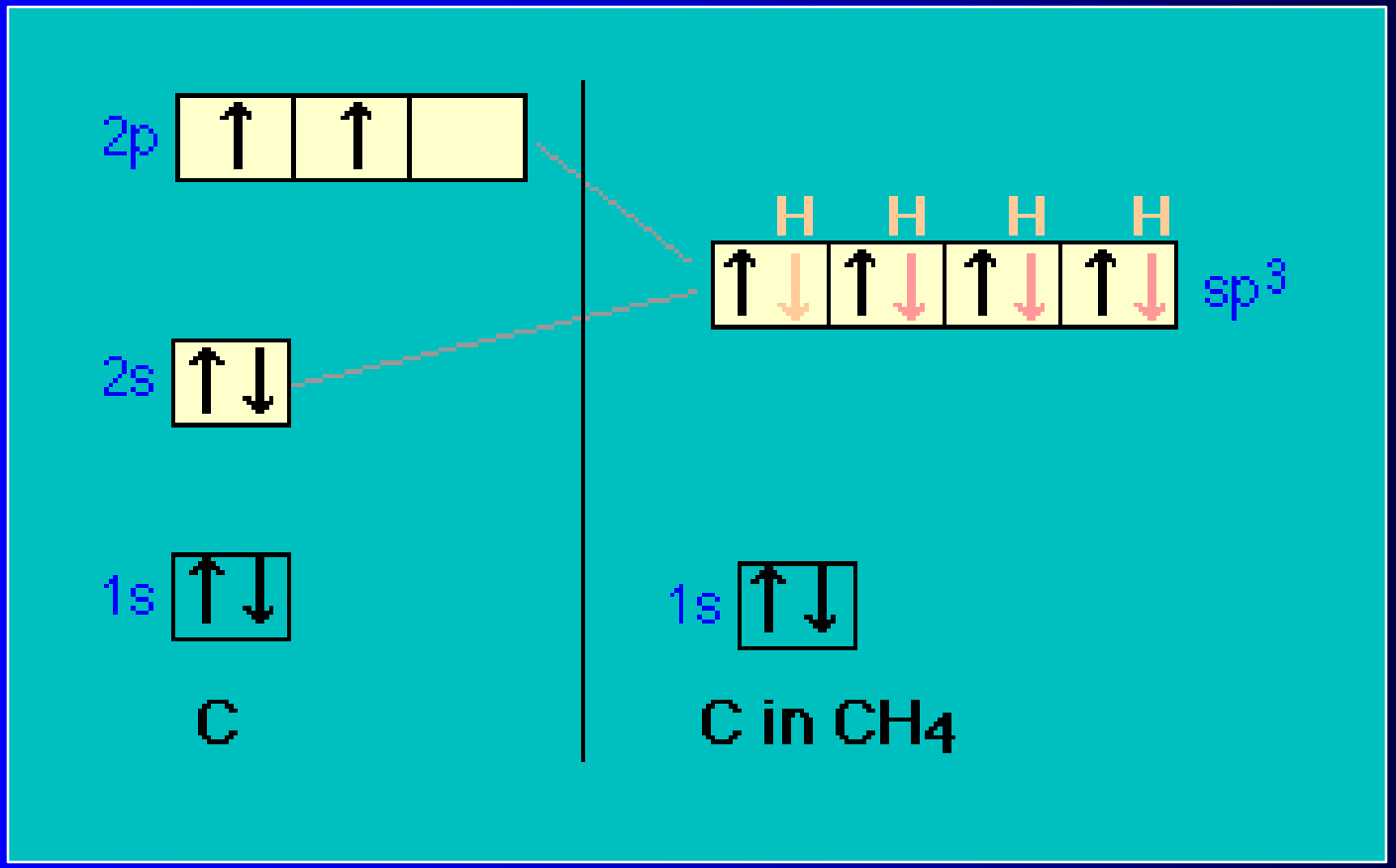
Bonding and antibonding molecular orbitals in hydrogen (H_2).



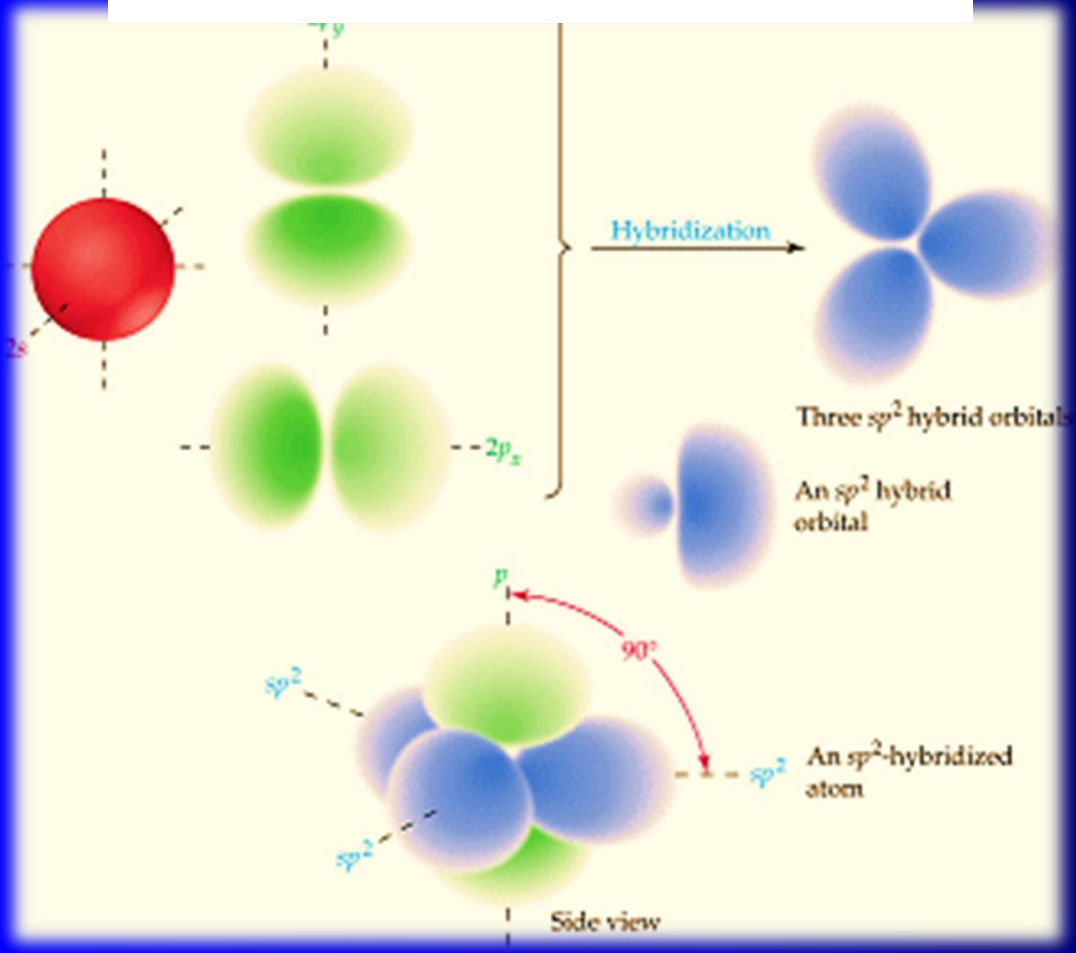
A ***bonding molecular orbital*** has lower energy and greater stability than the atomic orbitals from which it was formed.

An ***antibonding molecular orbital*** has higher energy and lower stability than the atomic orbitals from which it was formed.

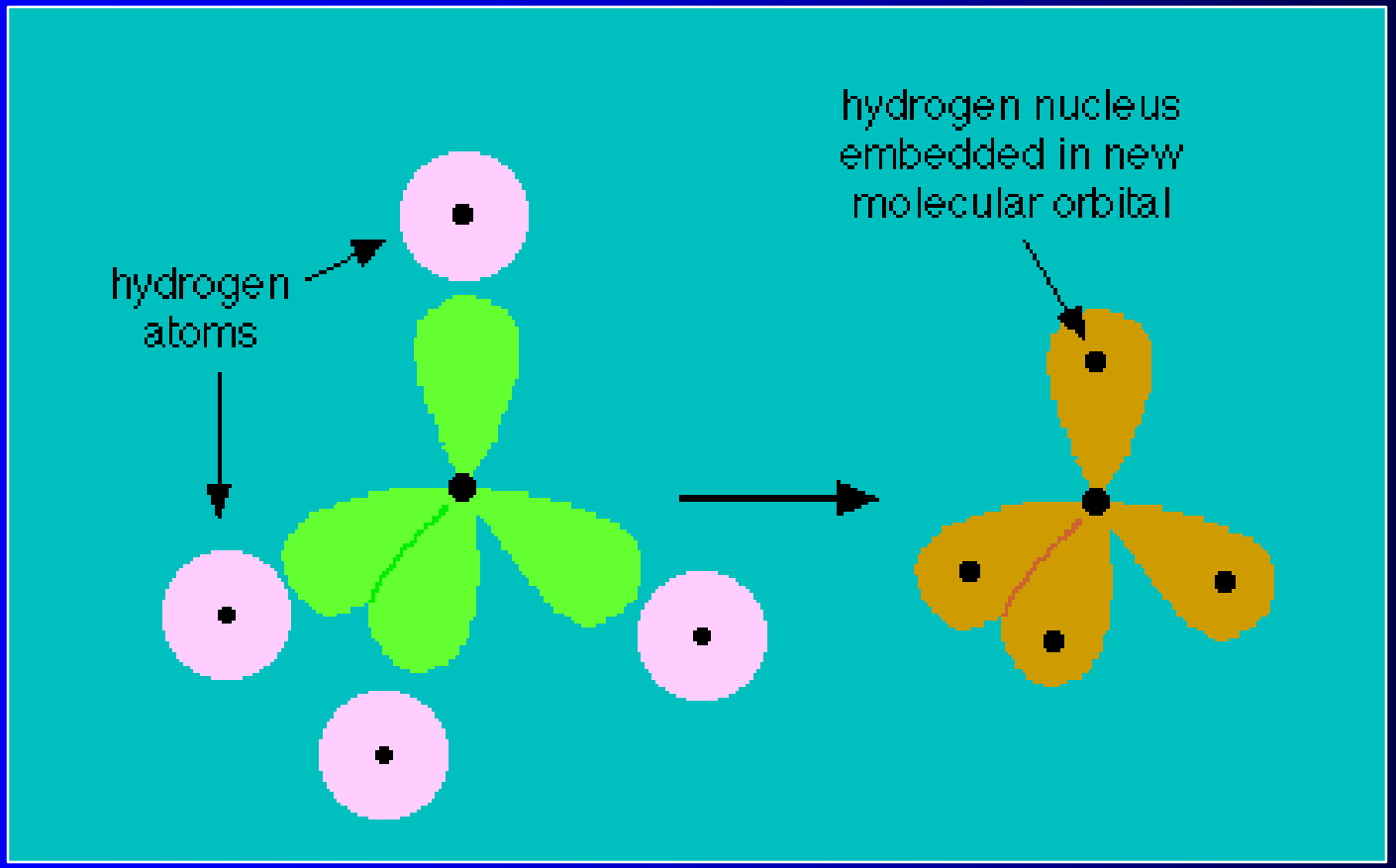
Hybridization of Atomic Orbitals



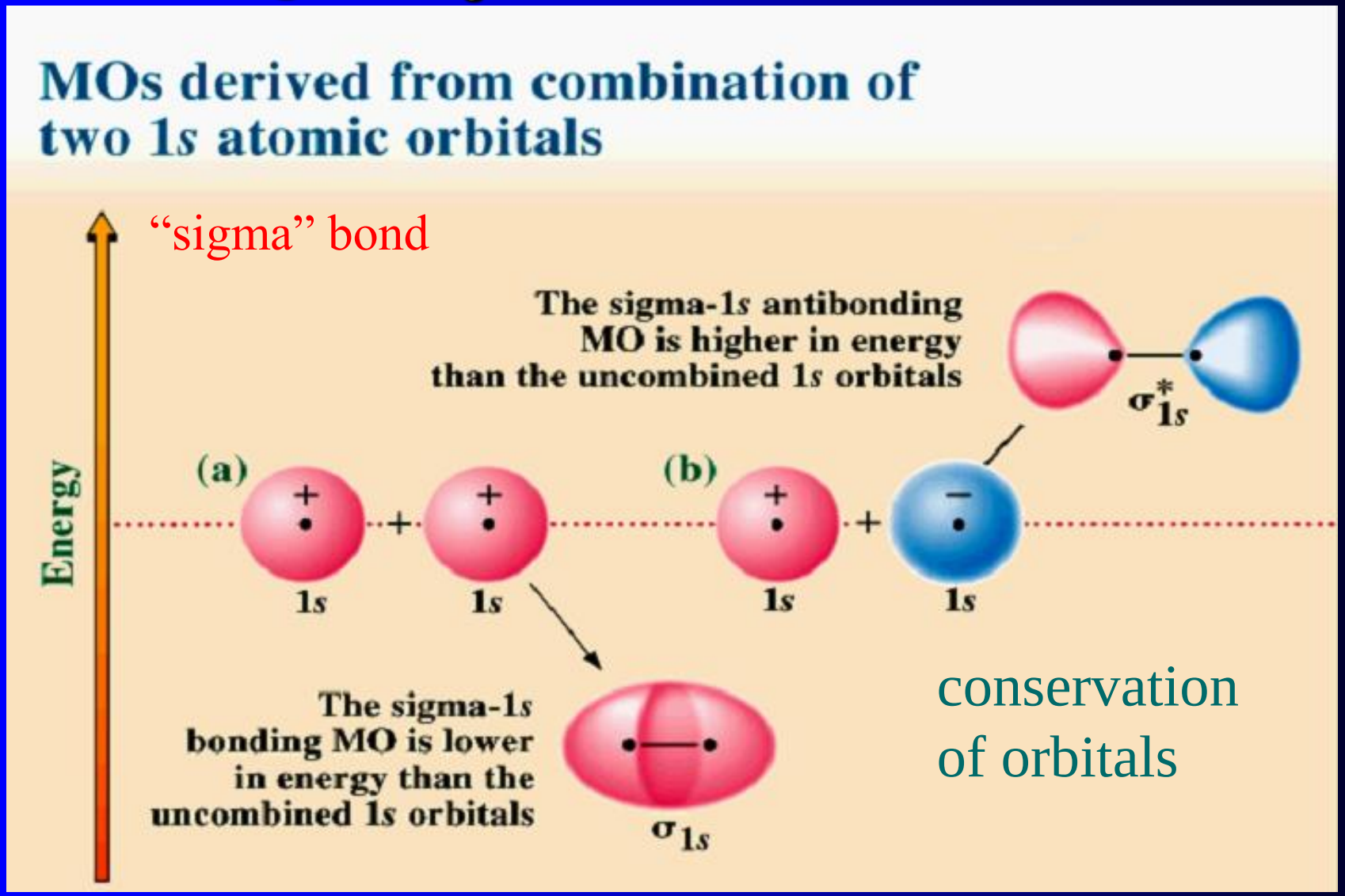
sp^2 hybrid orbitals



A “good” cartoon of Methane

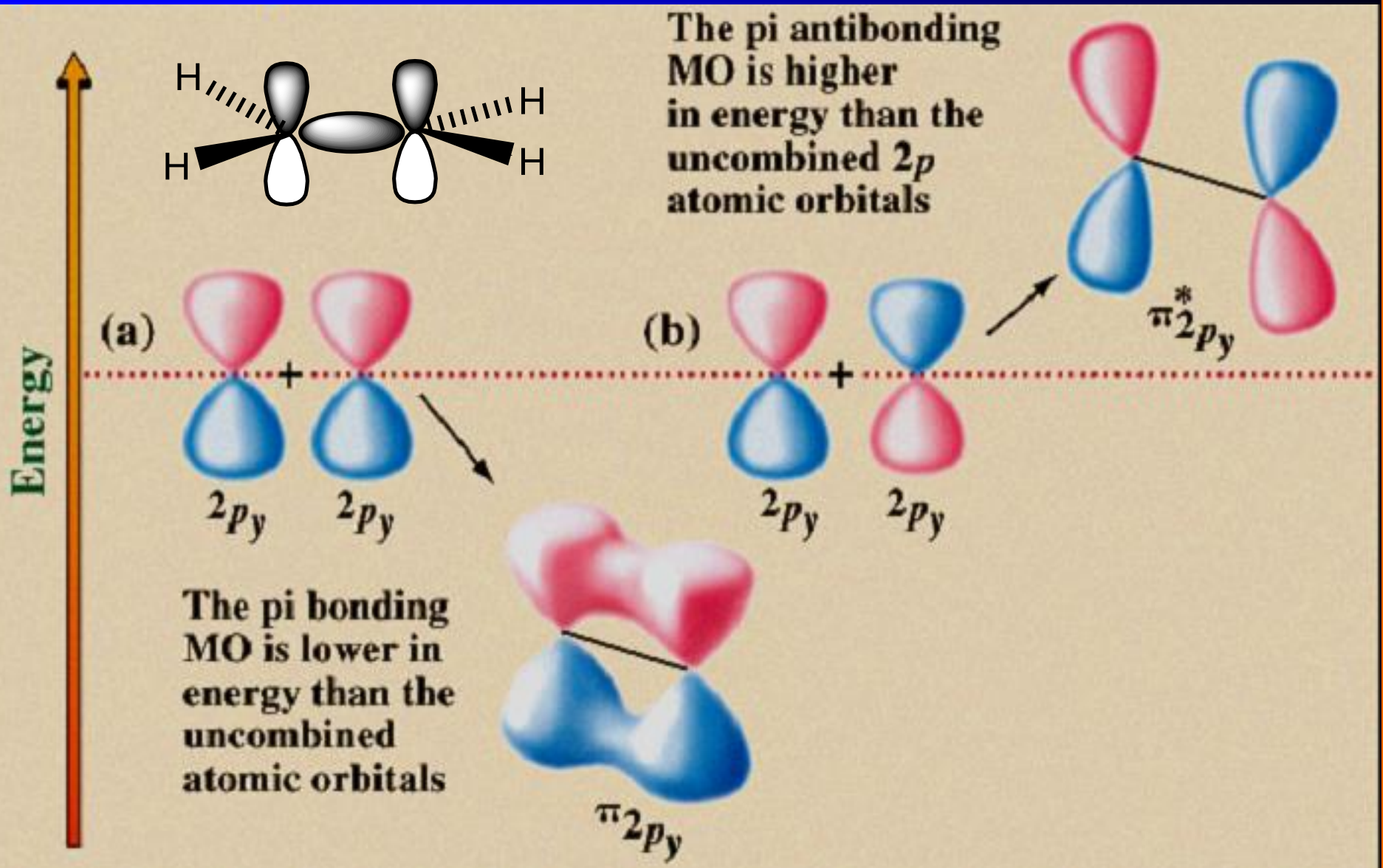


Sigma 1_s molecular Orbitals

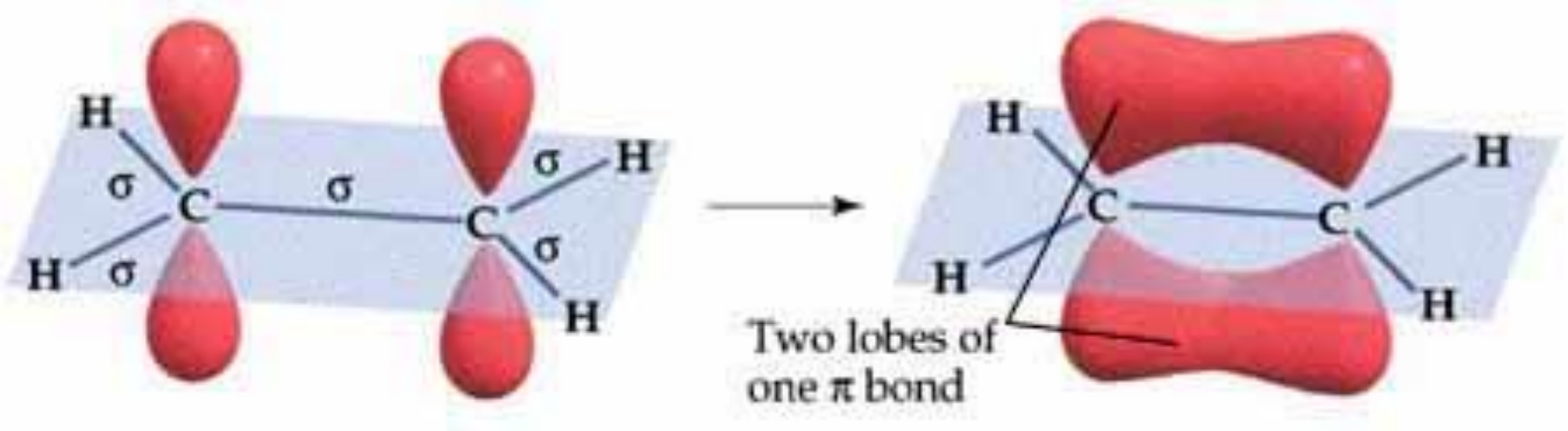


ΔE = 65 Kcal/mole

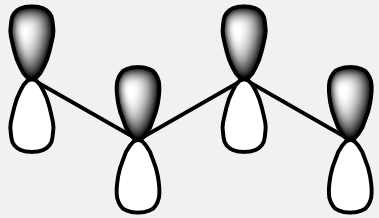
Pi 2_p molecular Orbitals

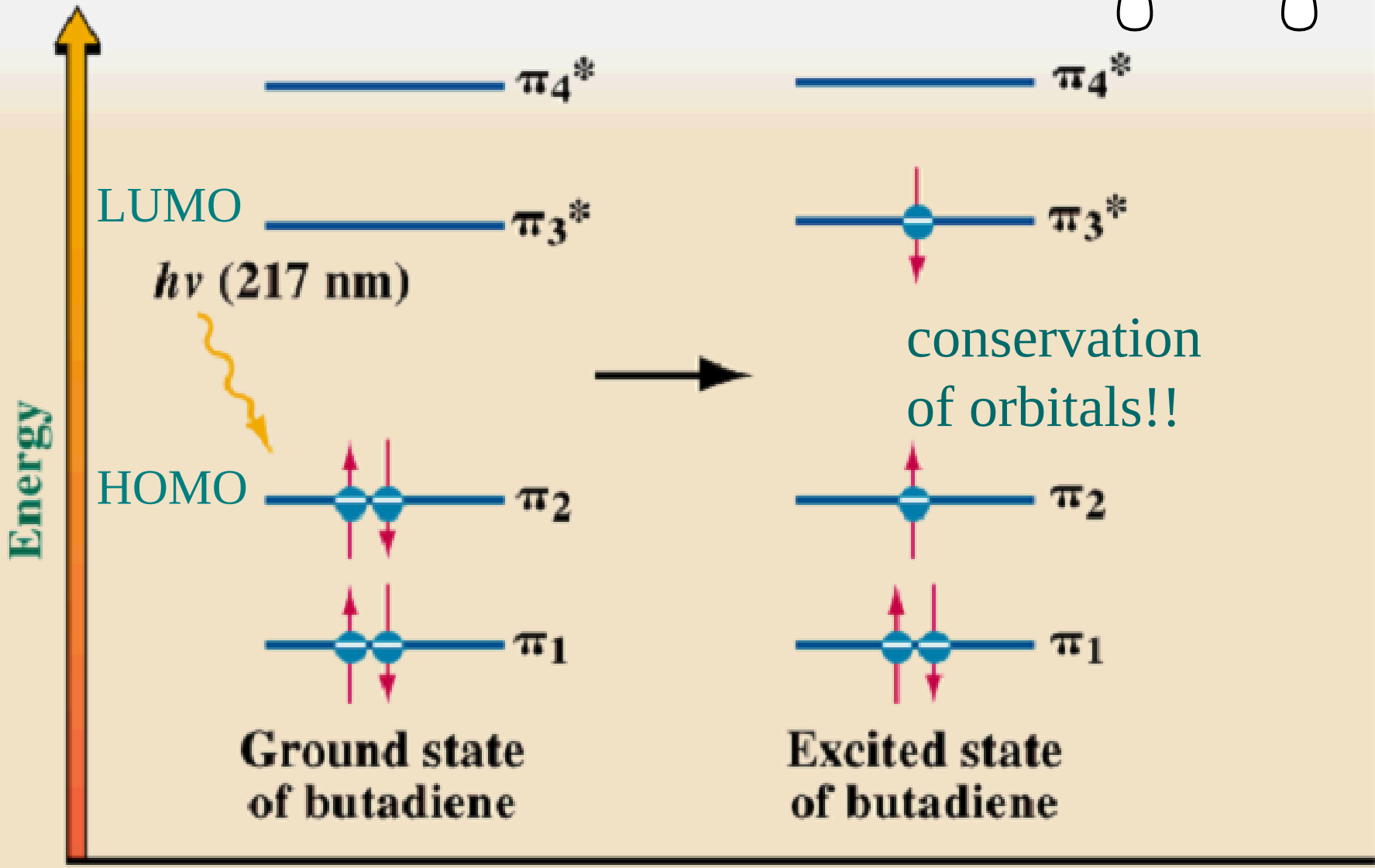


sp^2 hybrid orbitals and ethylene



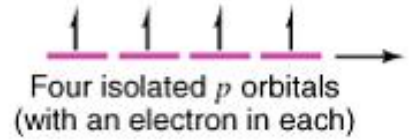
Electronic excitation 1,3-butadiene

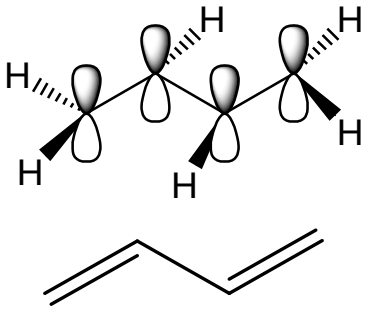


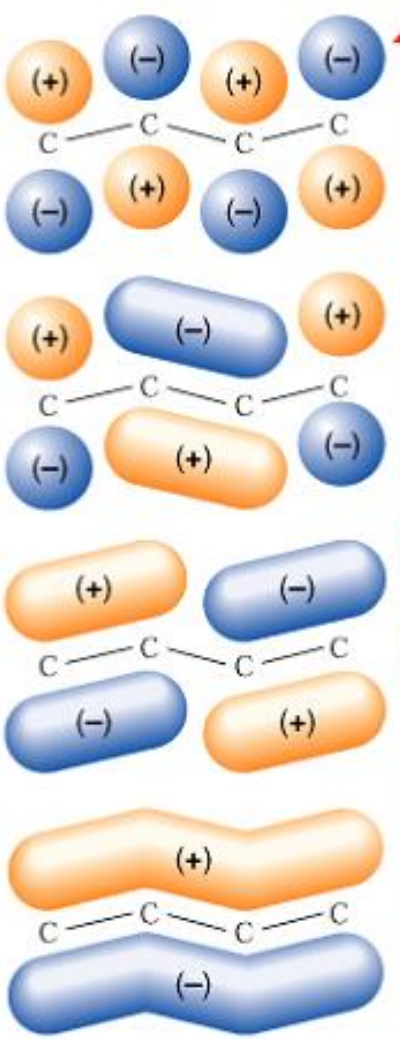


conservation of orbitals!!

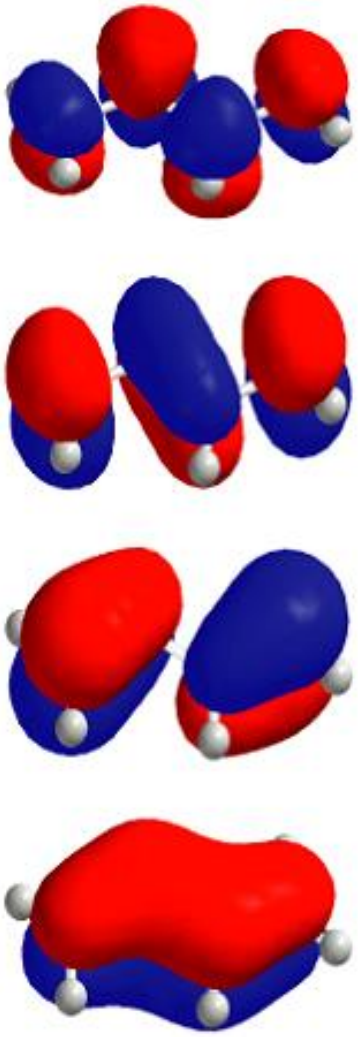
1,3-butadiene





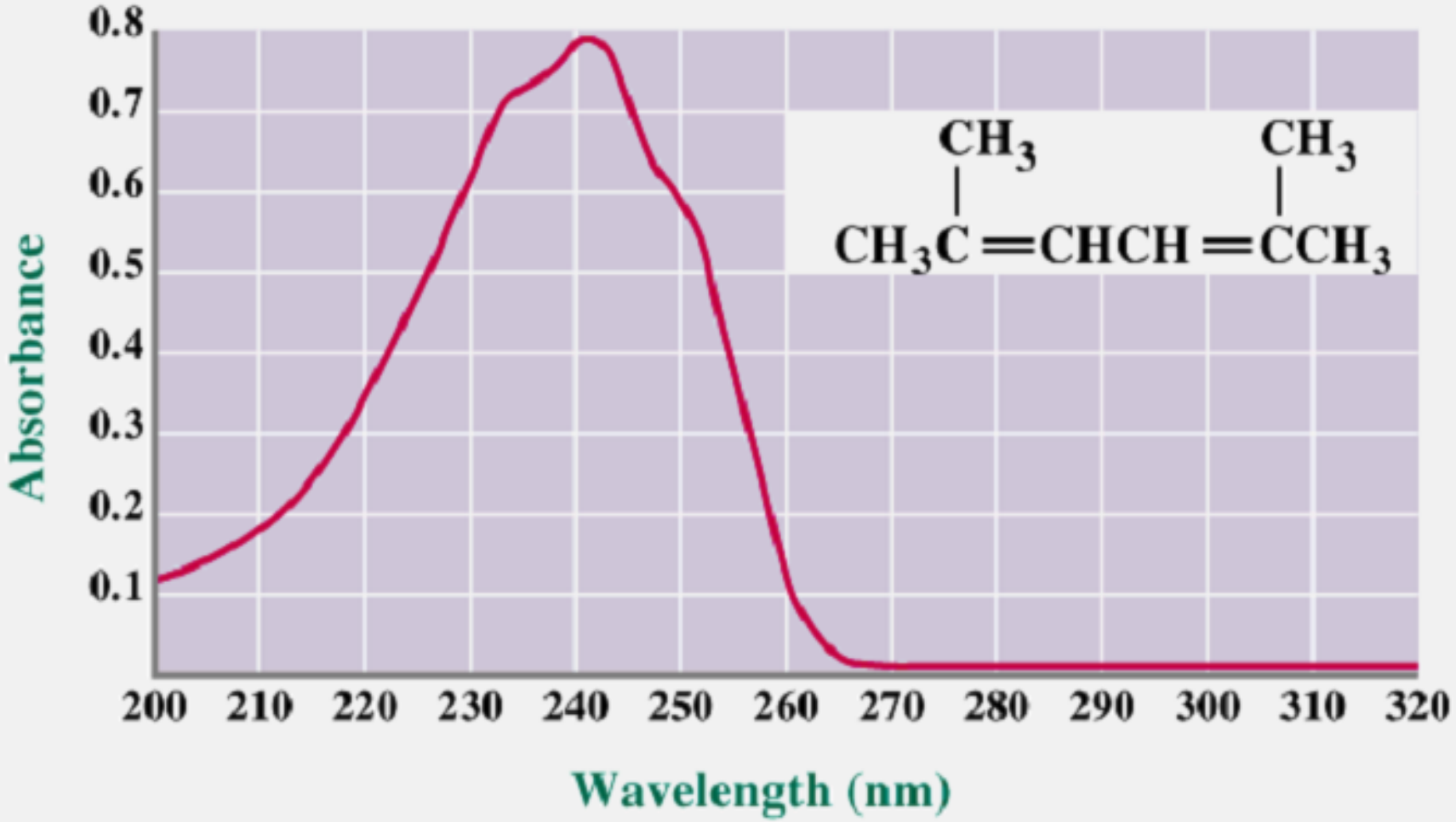


Schematic molecular orbitals



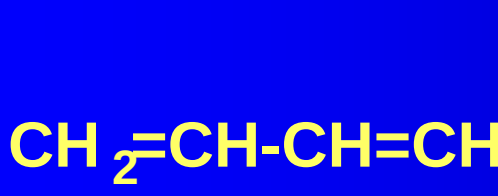
Calculated molecular orbitals

UV spectrum of 2,5-dimethyl-2,4-hexadiene

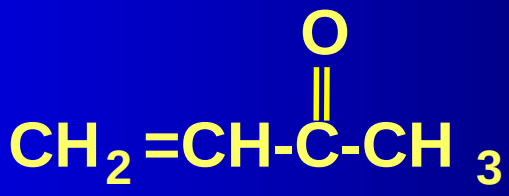


Electronic Transitions

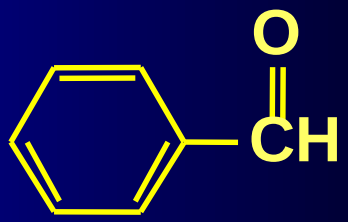
- Absorption of UV-vis radiation results in transition of electrons from a lower energy occupied MO to a higher energy unoccupied MO
- For example, π to π^* transitions in conjugated systems such as



1,3-Butadiene



3-Buten-2-one

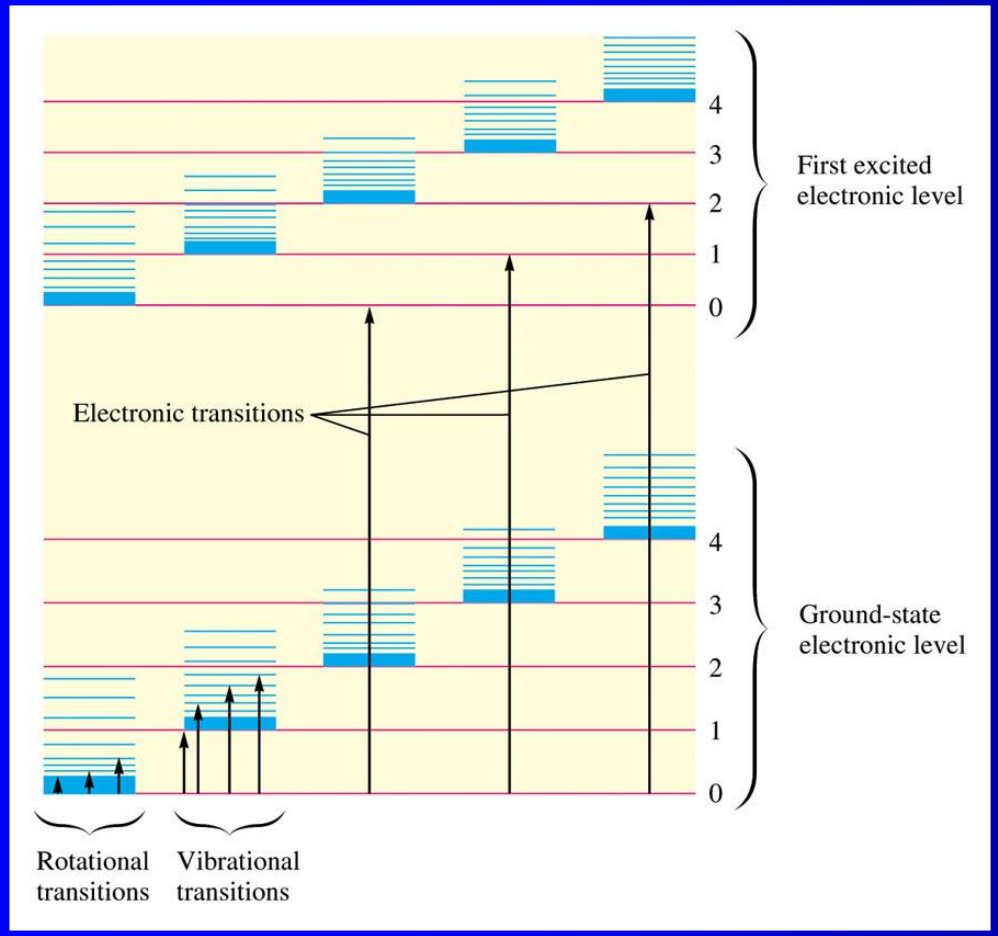


Benzaldehyde

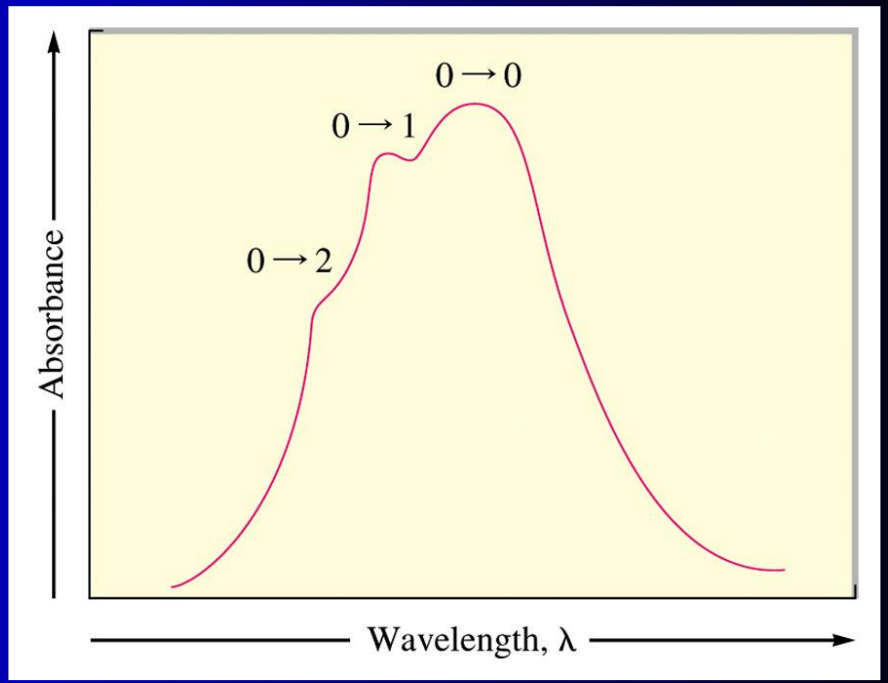
Electronic Transitions

- Transitions between vibrational and rotational energy levels are superimposed on the electronic excitations
- The result is a large number of UV-Vis absorption peaks so closely spaced that the spectrophotometer cannot resolve them
- For this reason, UV-Vis absorption peaks usually are much broader than IR peaks

The various types of transitions are shown by vertical arrows.



An electronic absorption spectrum arising from electronic transitions



Electronic Transitions

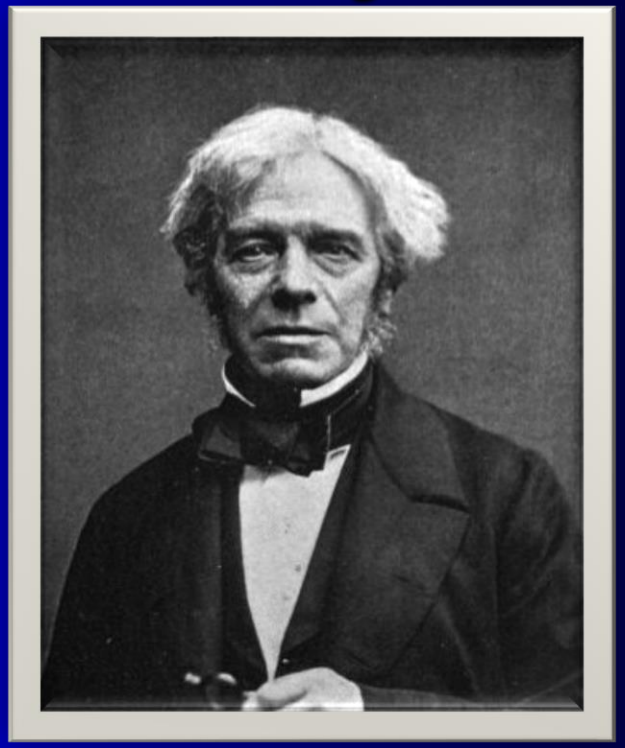
- Wavelengths and energies required for π to π * transitions of ethylene and three conjugated (alternating) polyenes
- The "longer the wire, the redder the absorbance"

Name	Structural Formula	λ_{max} (nm)	Energy (kcal/ mol)
ethylene	$CH_2=CH_2$	165	173
1,3-butadiene	$CH_2=CHCH=CH_2$	217	132
(3E)-1,3,5-hexatriene	$CH_2=CHCH=CHCH=CH_2$	268	107
(3E, 5E)-1,3,5,7-octatetraene	$CH_2=CH(CH=CH)_2CH=CH_2$	290	92

UV-Vis Spectroscopy Summary

- Electronic Transitions
  - HOMO to LUMO
- Know definitions
  - A, ε, λ, C, T, I, I_o
- Practice quantitative analysis calculations
  - Beer – Lambert Law

Some History



Michael Faraday 1791-1867

British physicist and chemist, best known for his discoveries of electromagnetic induction and of the laws of electrolysis. He also discovered benzene!

What in the World is Benzene??

- C_6H_6 discovered by Michael Faraday in 1823
  - Empirical formula is CH
  - Synthesized in 1834 from benzoic acid
  - Remarkable chemical stability
  - Unsaturation number is very high but….
- Does not add Bromine
- Substitution with Br_2 / $FeBr_3$
- Not oxidized by Permanganate or ozone
- No reaction with strong HBr (aq)
- No reaction with Hydrogen on Pd..??????

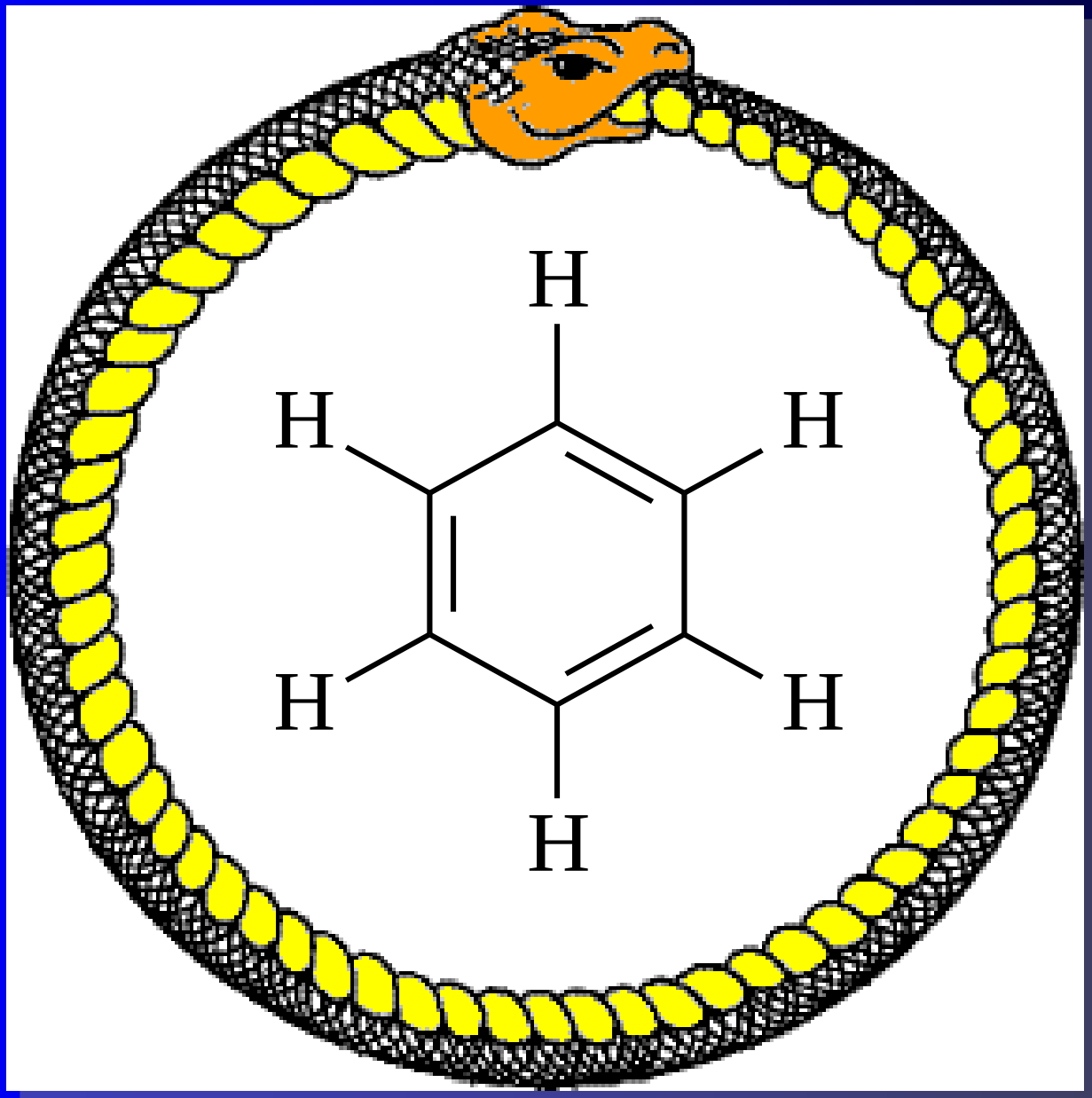
Friedrich August Kekulé (1829-1896)

Midnight Ride of Kekule

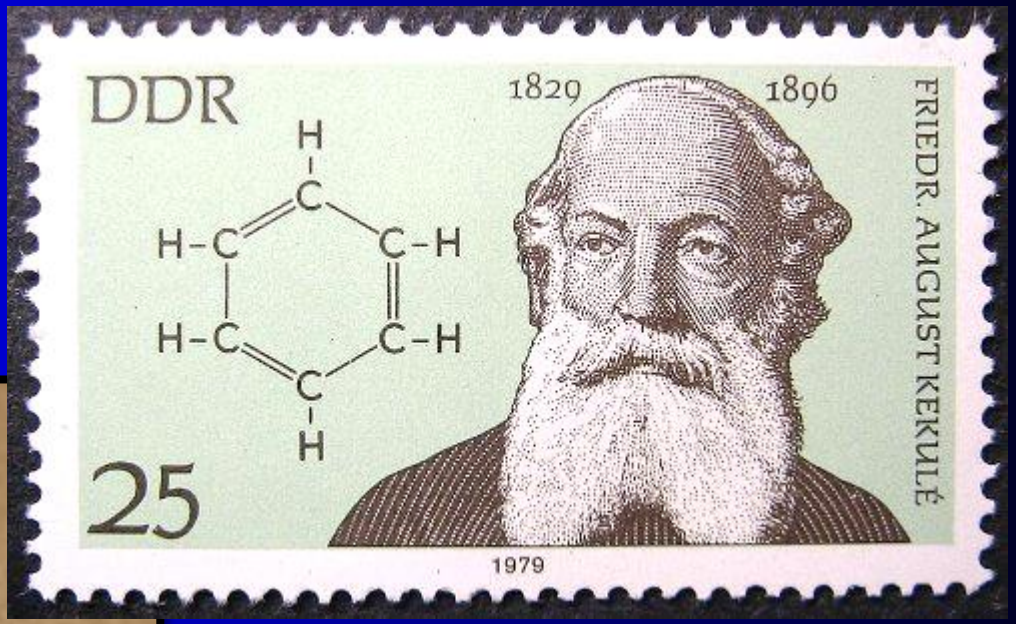
Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly to the background. My mental eye, rendered more acute by repeated vision of this kind, could now distinguish larger structures, of manifold conformation; long rows, sometimes more closely fitted together; all twining and twisting in snakelike motion. But look!

What was that?!!! One of the snakes seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lighting I awoke... Let us learn to dream, gentlemen.

Arthur Koestler (in "The Act of Creation") called this incident "probably the most important dream in history since Joseph's seven fat and seven lean cows.


H
H
H
H
H
H

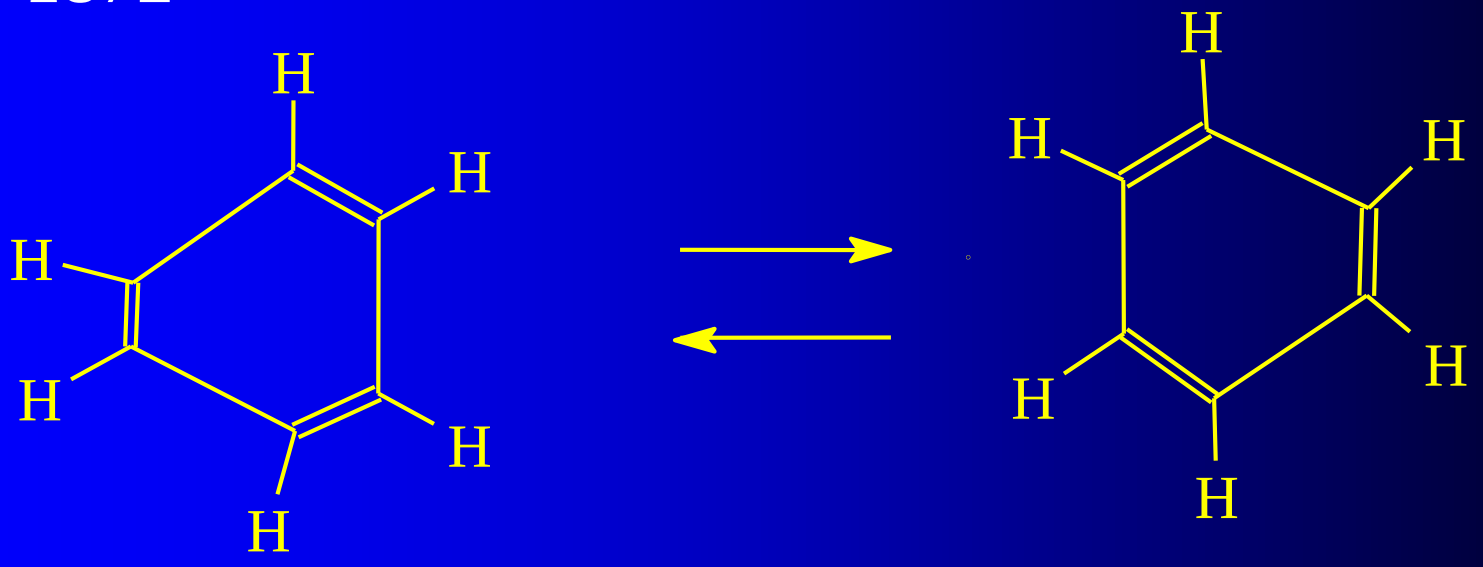
The man and his snakes



August Kekule

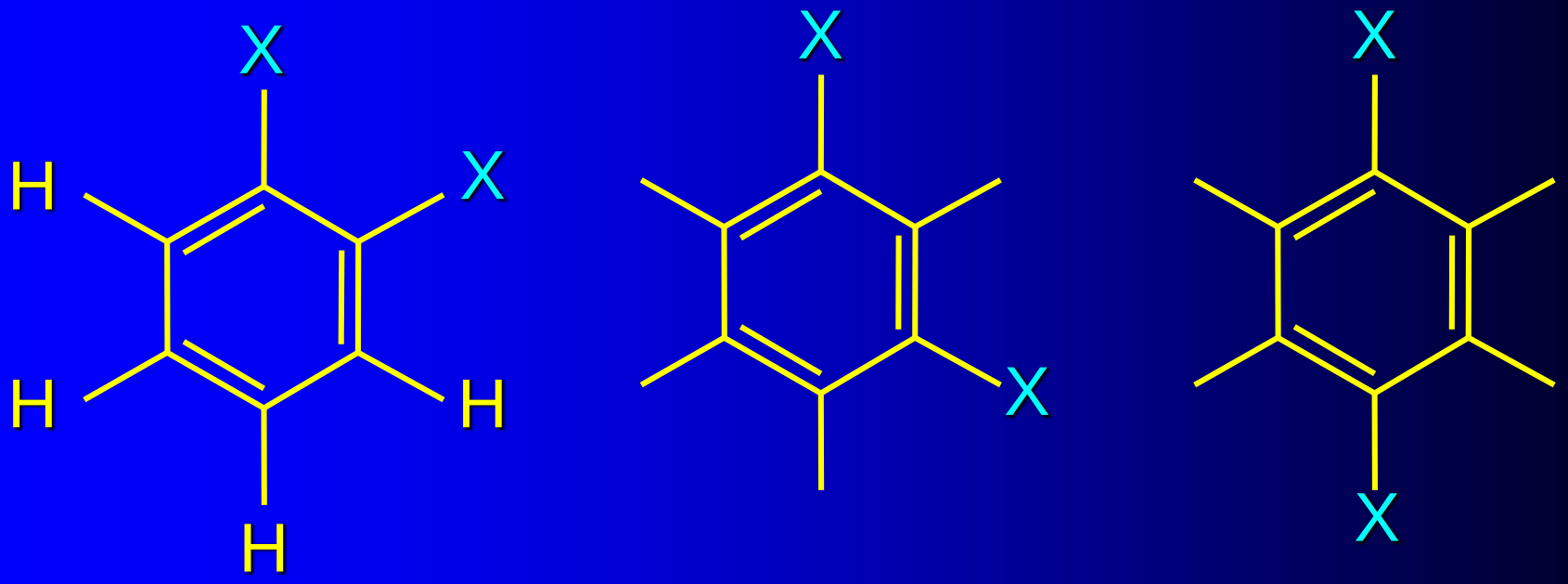
Benzene – per Kekulé

- August Kekulé proposed a structure for benzene in 1872

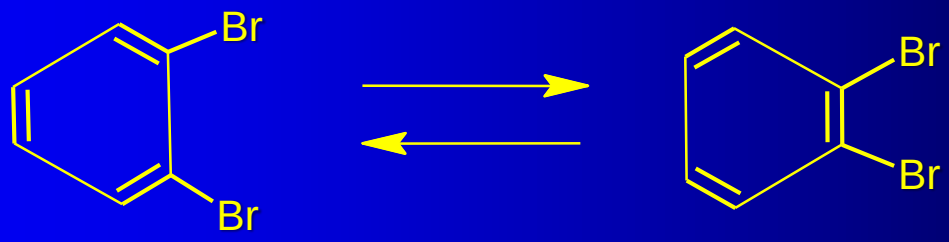


- This structure, however, did not really account for the unusual chemical reactivity of benzene

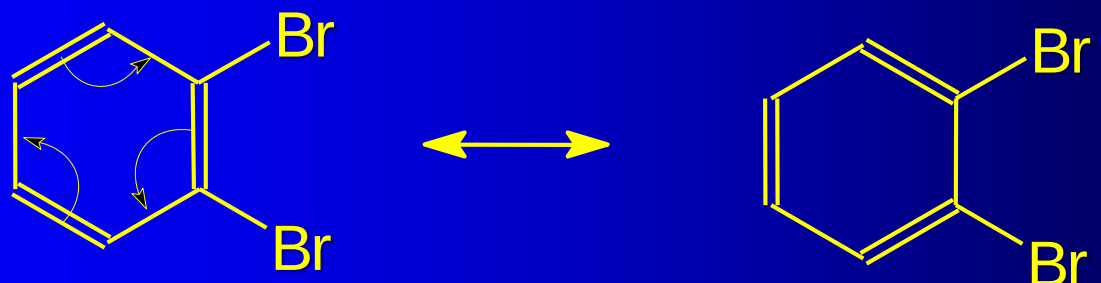
Kekule explains why there are only 3 isomers of dibromobenzene



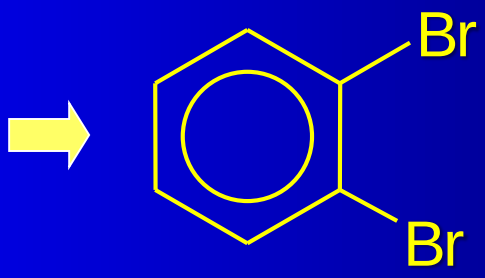
• Kekule's proposal is an **equilibrium** between two structures



•Pauling's Resonance Theory describes resonance structures generated by electron movement (only!) that are not real, they are constructs the weighted sum of which describes the real molecule, which is presented as the resonance hybrid



"Resonance hybrid"



Benzene - Resonance

- We can represent benzene as the hybrid of two equivalent Kekulé structures
  - each makes an equal contribution to the hybrid, and thus the C-C bonds are neither double nor single, but something in between