Lecture 34
Chapter 10  Sections 5 and 6

• Diatomic MOs
• A little more $\pi$ delocalization
Announcements

• CAPA #18 due next Tues

• Don’t forget about Exam #3
  – Friday 1 Dec. (*Chapts 9-10, CAPAs 15-18*)
Clarify Ethene vs. Hydrazine

• I did all the orbitals together to help everyone see where electrons are all going
• Generally, it is easiest to start from Lewis structure, then just consider one bond at a time.
• In this way, we would NOT do hydrazine like I did last time, but would begin completely differently:
  – ethene has $sp^2$ carbons
  – hydrazine has $sp^3$ nitrogens
Demo

- Pour liquid nitrogen over big magnet
- Pour liquid oxygen over big magnet

- How do they compare?
Let’s spend some time with diatomic gasses \( \text{O}_2, \text{N}_2, \text{F}_2, \text{etc.} \)

12 valence electrons

Bond order:
\[ \frac{1}{2} (8 - 4) = 2 \]

or
\[ \frac{1}{2} (6 - 2) = 2 \]
Relative occupancy of bonding and antibonding orbitals determines bond-order.

\[
\begin{align*}
\text{Triple} & \quad \sigma^*_p \\
\text{Double} & \quad \sigma^*_p \\
\text{Single} & \quad \sigma^*_p \\
\end{align*}
\]

\[
\begin{align*}
\frac{1}{2} (6 - 0) &= 3 \\
\frac{1}{2} (6 - 2) &= 2 \\
\frac{1}{2} (6 - 4) &= 1 \\
\end{align*}
\]
Compare N$_2$ to O$_2$

In N$_2$:
10 valence electrons

Bond order:
$\frac{1}{2} (6 - 0) = 3$

$\sigma_p$ and $\pi$ orbitals have swapped positions

Energy of $\sigma_p$ is raised in N$_2$, C$_2$, B$_2$ by orbital mixing
Orbital Mixing

- In $B_2$, the overlap of $2s$ and $2p_z$ orbitals stabilizes $\sigma_s$ and destabilizes $\sigma_p$
- This is referred to as orbital mixing
- The amount of mixing depends on the energy difference between the $2s$ and $2p$ atomic orbitals.
- Mixing is largest in $B_2$, smallest in $F_2$
Is $O_2$ paramagnetic or diamagnetic?

| 33% | 1. Paramagnetic |
| 33% | 2. Diamagnetic  |
| 33% | 3. Neither      |
Is N$_2$ paramagnetic or diamagnetic?

33% 1. Paramagnetic
33% 2. Diamagnetic
33% 3. Neither
Compare $\text{N}_2$ to $\text{O}_2$ again

$\text{O}_2$ should stick to a magnet and $\text{N}_2$ should not.
Extended $\pi$ systems – aromaticity

- Each additional conjugated double bond adds stability to the molecule.
- Benzene has a pseudo-infinite chain of double bonds and is very stable.
- Benzene (and many other molecules) is aromatic.
A really long system of delocalized $\pi$ bonds gives a lot of MO’s... the energy levels get closer together, so HOMO-LUMO absorbance can be in the visible range. Red/orange/yellow colors in vegetables come from retinoid derivatives. Beta-carotene, lycopene, and lutein are examples.

• Related to vitamin A

• Big in the health food/supplement business: [http://www.mothernature.com/shop/detail.cfm/sku/42972](http://www.mothernature.com/shop/detail.cfm/sku/42972)

• Possible antioxidants.

• Eat ketchup :)

Fig. 1: Structure of lycopene.

Fig. 2: Structure of beta carotene.
Highly conjugated dyes - absorb visible photons

From Lehninger Principles of Biochemistry 3rd ed.
Here’s a webMO modelling of retinal (left off the ring at the end, but got in five C=C bonds).

Beta carotene gets split in two, with an oxygen on each end, to make retinal.

This is the pigment used to detect photons in the retina!

“Retinal” HOMO-LUMO 1.20e-18 J, which is 165 nm photon - that’s a bit short. This may be a bit complicated for accurate energy level calculation.
How vision works:

• Photon absorption stimulates cis-trans isomerization of 11-cis retinal. Normally, trans is a little more stable. But cis doesn’t have enough energy of its own to break the π bond and flip over to trans.

• By promoting an electron into the antibonding LUMO, retinal is allowed to rotate into trans.

• This moves things around in the protein (rhodopsin) in which retinal is bound. http://www.yorku.ca/eye/molecule.htm http://www.yorku.ca/eye/specsens.htm

Retinal cis/trans stuff:

http://www.elmhurst.edu/~chm/vchembook/534photochemical.html

Rhodopsin animation:

http://www.blackwellpublishing.com/matthews/rhodopsin.html
The protein part does a bunch of important jobs:

• Keeps the whole thing bound in the membrane in the retina.
• Turns the retinal photoisomerization into a signal to the cell, and eventually into a nerve signal down the optic nerve.
• Tweaks the wavelength at which photons are absorbed. Some pick up blue, some green, some red. These are the primary additive colors.
• You can think of lots of interesting things about this. Like, why can we see purple? Why does mixing red and yellow paint make orange? What makes something brown? And just who the heck is ROY G. BIV? That’s what your brain makes of it.
Today

• Go home!

Monday

• We’ll review Chapt 9 and 10.
• Make sure you are studying so you can ask good questions!
• Don’t forget CAPA #18 due Tuesday

Remember: You are done with the homework when you understand it!