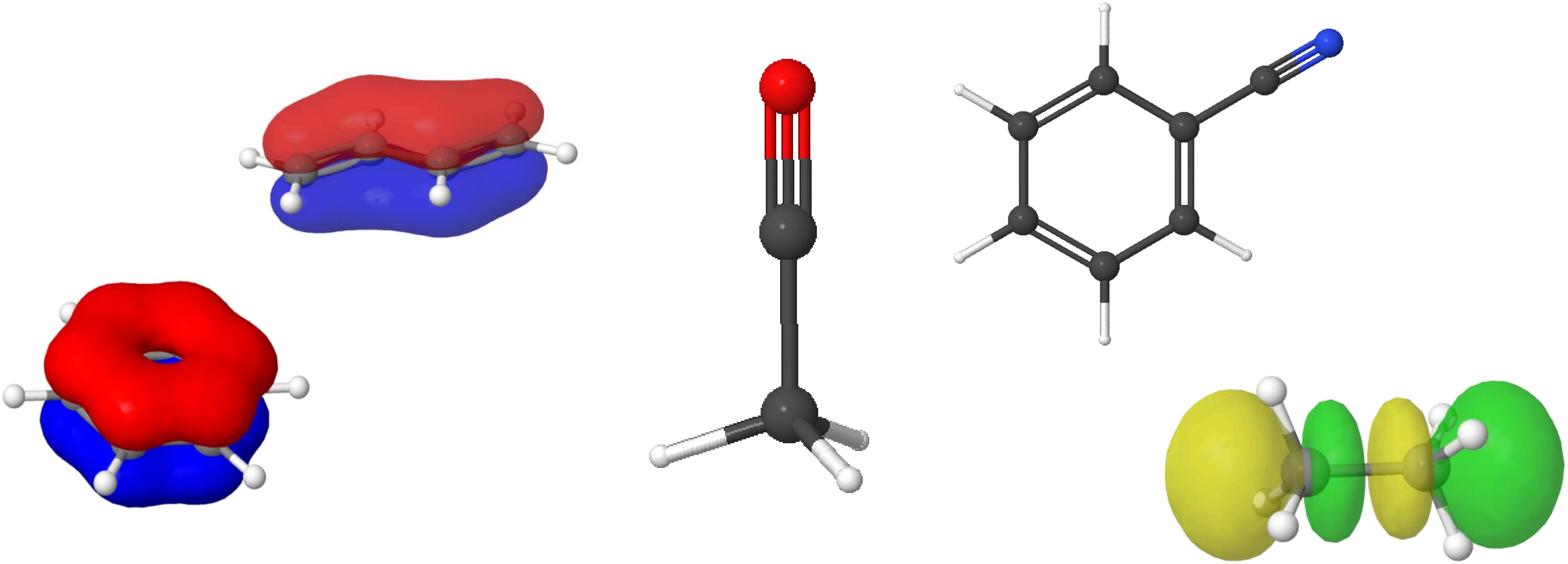
CHEM 344 – Molecular Modeling

The Use of Computational Chemistry to Support Experimental Organic Chemistry

Part 1: Molecular Orbital Theory, Hybridization, & Formal Charge



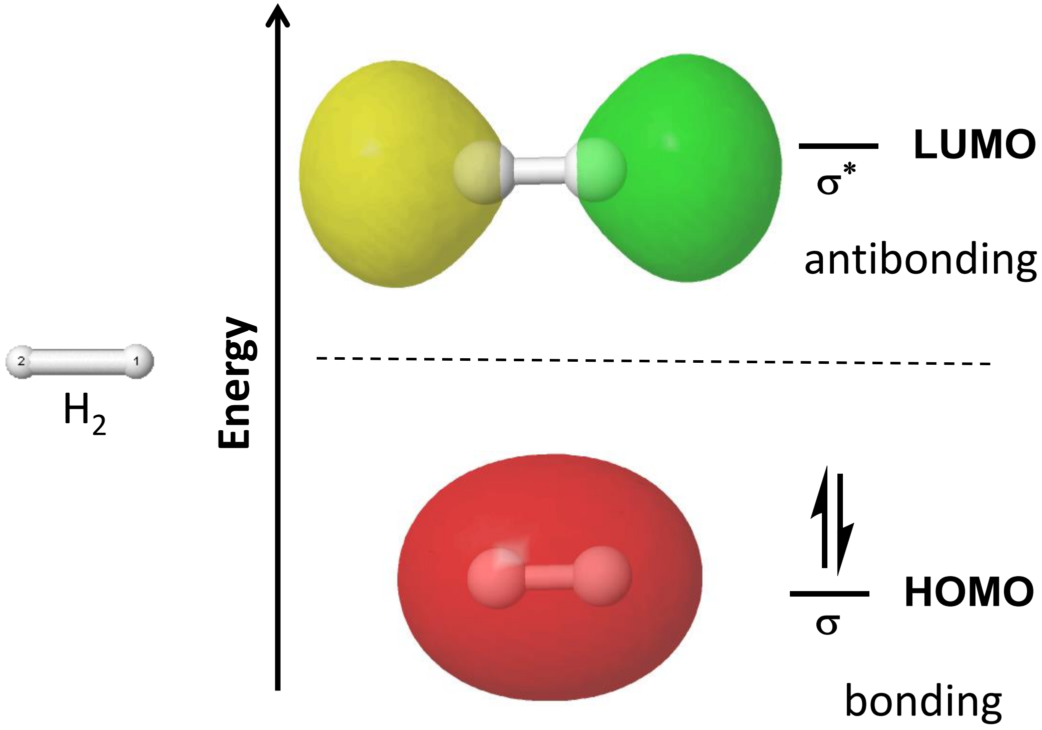
* all calculation data obtained from Gaussian09 using **B3LYP**/**6-31G(d)** unless otherwise noted.

Computational Chemistry

Organic chemists routinely use computational chemistry to:

- **predict geometries**, physical properties, and relative energies.
- visualize electronic structures (molecular and atomic orbitals).
- predict or explain regio-/stereochemical outcomes of reactions.
- understand stabilizing/destabilizing interactions.
- predict microwave, IR, UV-Vis, & NMR spectra.
- find transition states and chemical pathways for reactions.

σ-type Molecular Orbitals – H_2



H_2

Energy

σ*

LUMO

antibonding

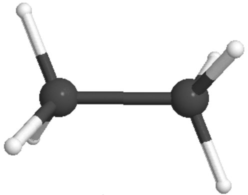
σ

HOMO

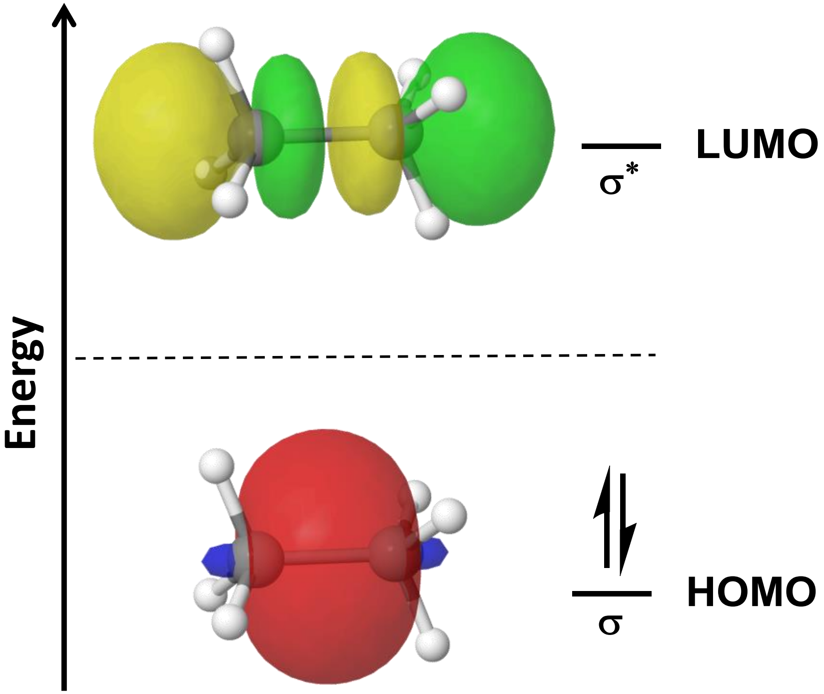
bonding

- Two 1s atomic orbitals create two σ molecular orbitals.
- Higher energy orbitals have more nodes than lower energy orbitals.
- Lowest energy orbitals are occupied first in ground state molecules.
- **HOMO** = **H**ighest energy **O**ccupied **M**olecular **O**rbital
- **LUMO** = **L**owest energy **U**noccupied **M**olecular **O**rbital
- In WebMO **red**/**blue** is occupied, **yellow**/**green** is unoccupied.

σ-type Molecular Orbitals – C_2H_6

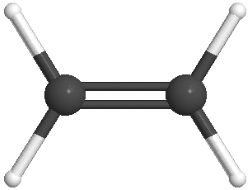


Ethane, C_2H_6

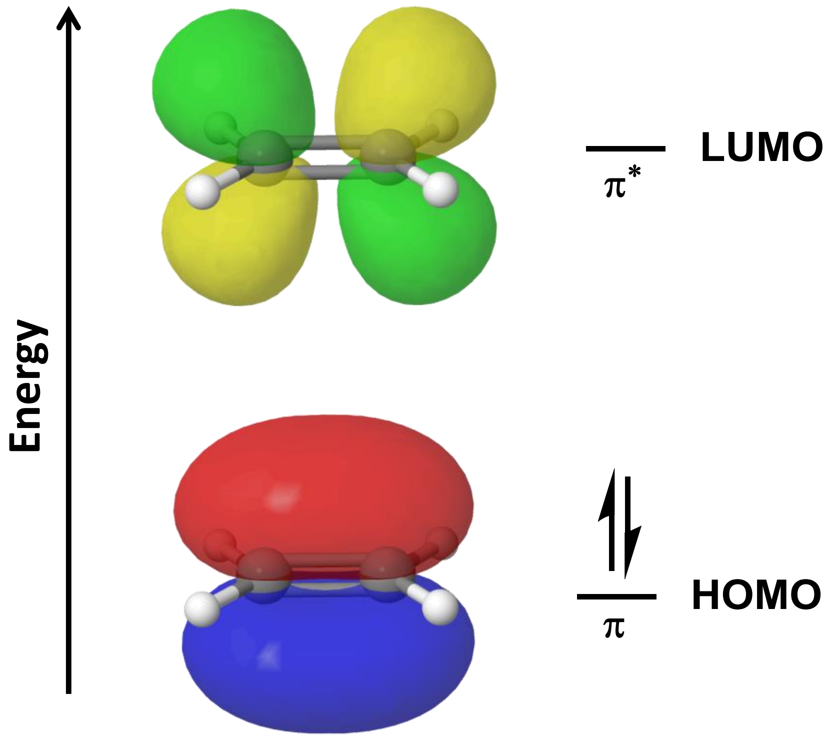


- Two ~sp^3 atomic hybrid orbitals create two σ molecular orbitals.
- Higher energy orbitals have more nodes than lower energy orbitals.
- Lowest energy orbitals are occupied in ground state molecules.
- **HOMO** = **H**ighest energy **O**ccupied **M**olecular **O**rbital
- **LUMO** = **L**owest energy **U**noccupied **M**olecular **O**rbital
- In WebMO **red**/**blue** is occupied, **yellow**/**green** is unoccupied.

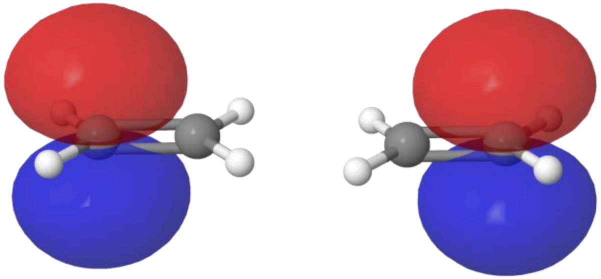
π-type Molecular Orbitals – C_2H_4



Ethylene,
C_2H_4



- Two p atomic hybrid orbitals create two π molecular orbitals.

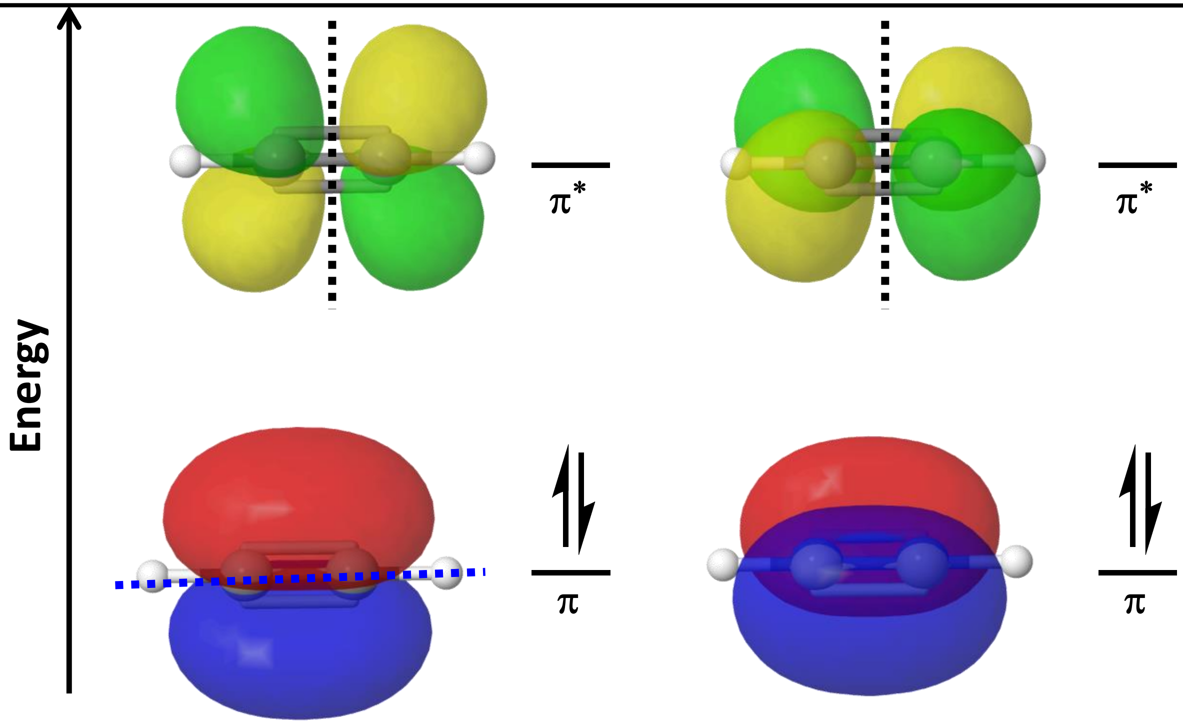


- The presence of a p orbital at each carbon atom implies an sp^2 hybridization of the atom.
- The ~sp^2 atomic hybrid orbitals are used to make the σ bonds.

For more on hybridization of carbon atoms:
https://www.chem.wisc.edu/content/343esselman/hybridization

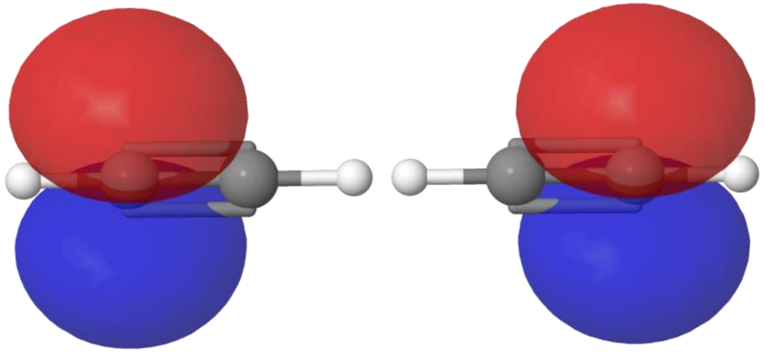
π-type Molecular Orbitals – C_2H_2

Acetylene,
C_2H_2

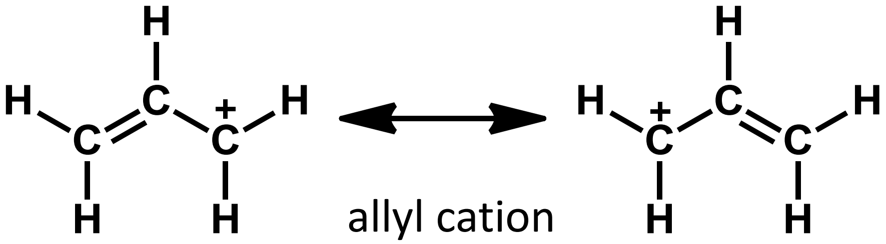


- Four p atomic hybrid orbitals create four π molecular orbitals, two degenerate π and two degenerate π * orbitals.

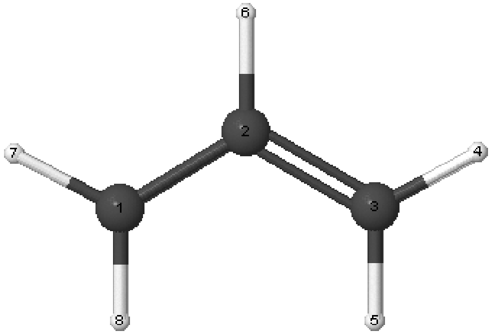
- The presence of two p orbitals at each carbon atom implies an sp hybridization of the atoms.

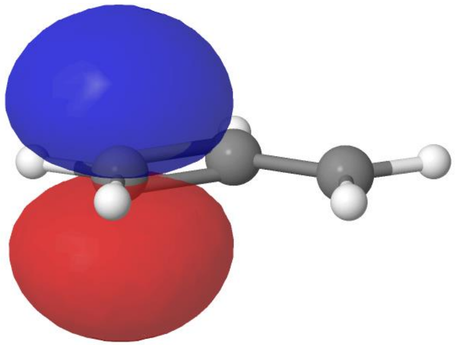


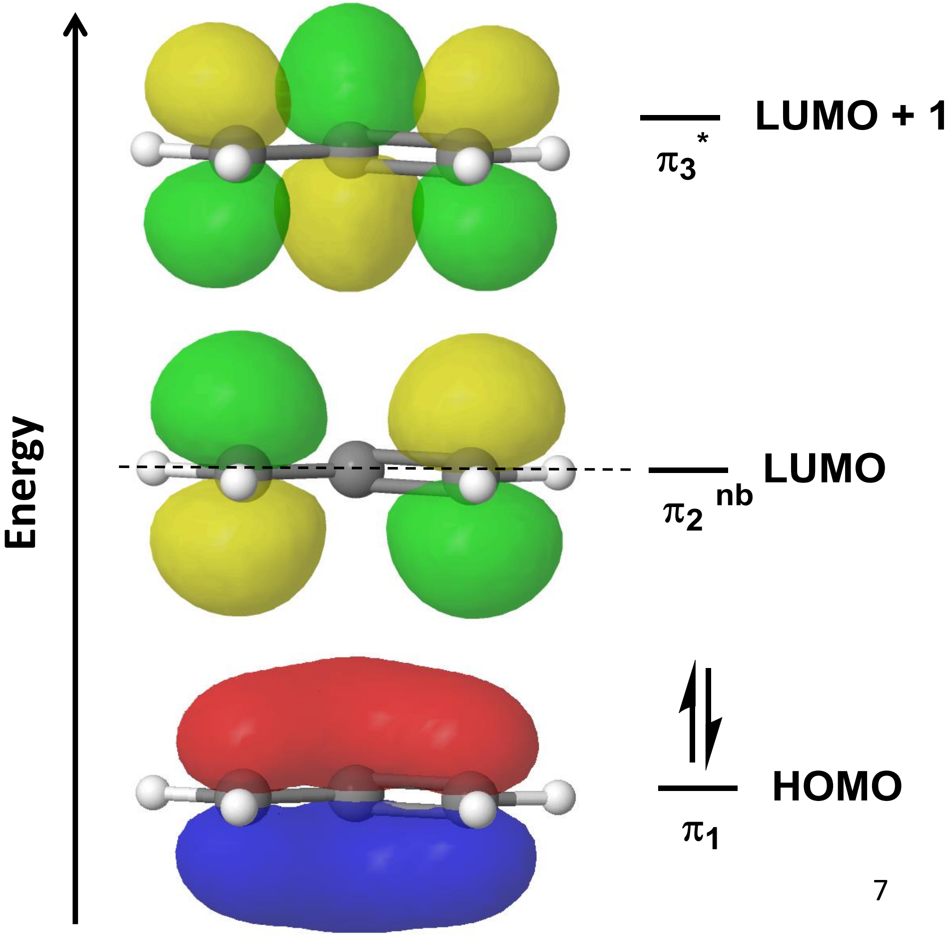
π-type Molecular Orbitals – $C_3H_5^+$


allyl cation

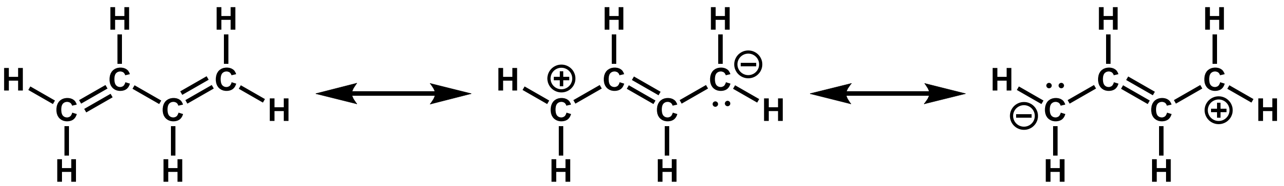
Resonance structures are a simple way to depict π conjugation.

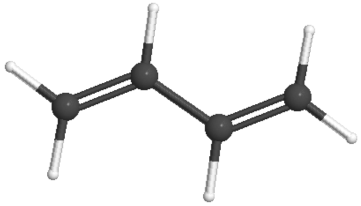


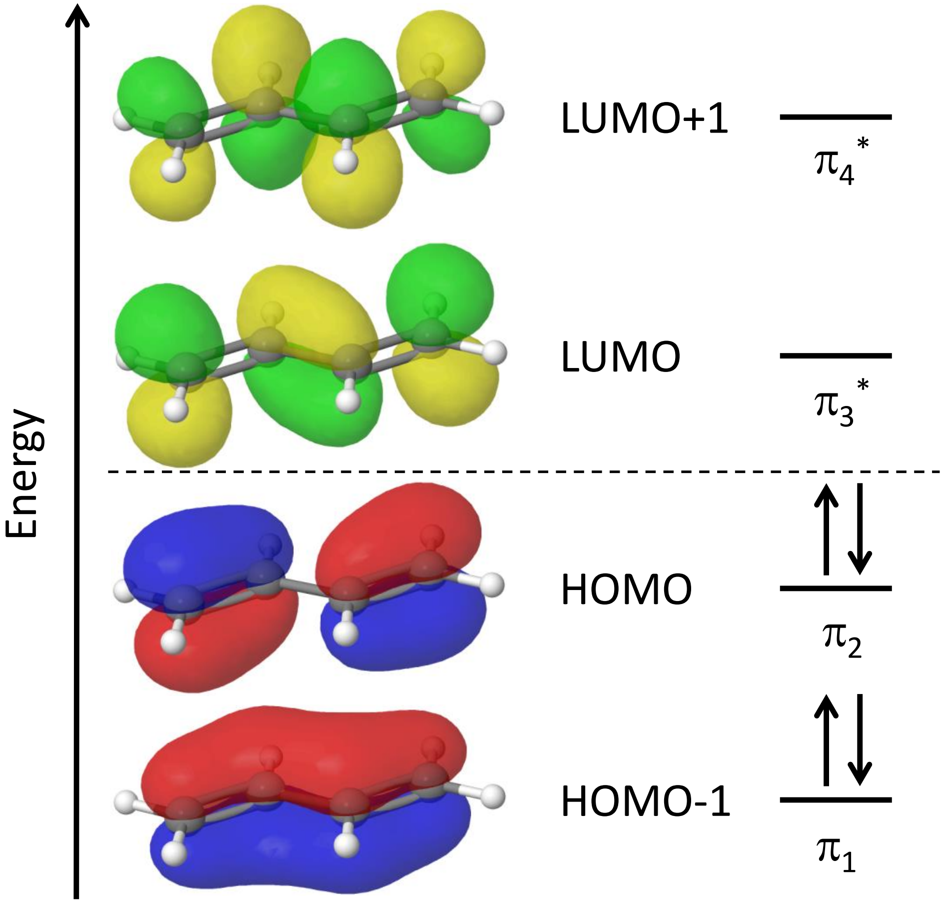




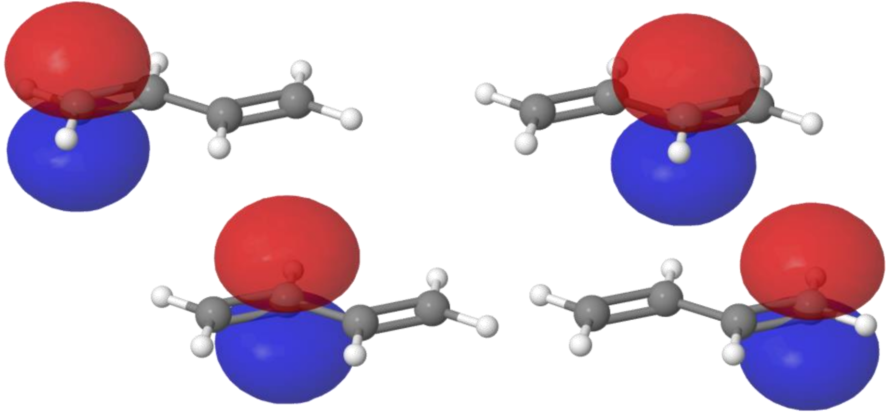
π-type Molecular Orbitals – 1,3-butadiene





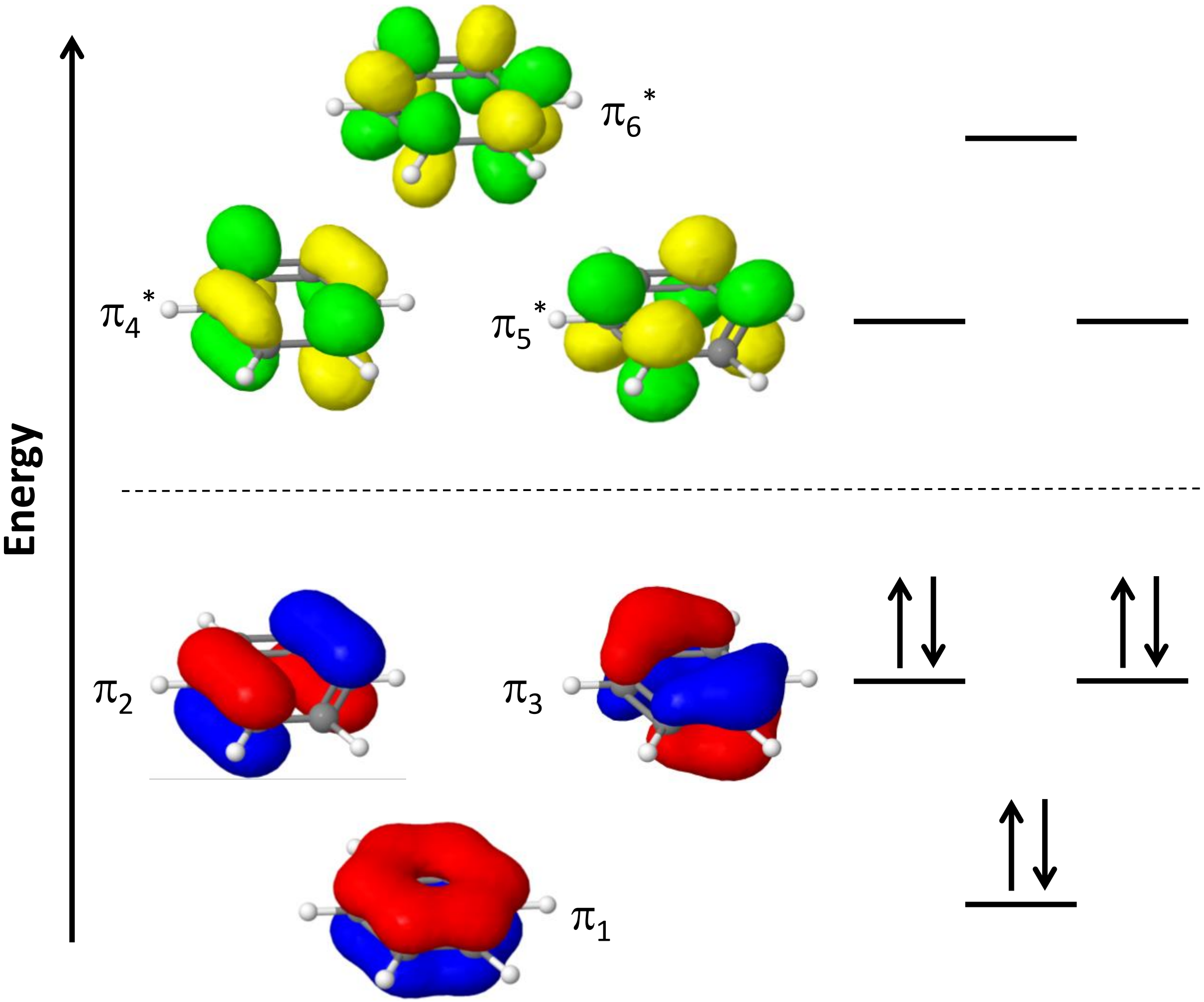


Four p atomic orbitals create four π molecular orbitals.



MOs are a more realistic picture of conjugation (orbital overlap) than resonance structures.

π-type Molecular Orbitals – benzene



Six atomic p orbitals create six molecular π orbitals.

π_2 and π_3 are **degenerate** (equal in energy) and have one node.

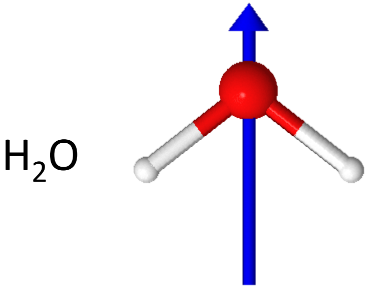
π_4^* and π_5^* are degenerate and have two nodes.

This delocalized π system of three stabilizing molecular orbitals is the source of benzene's aromatic stability.

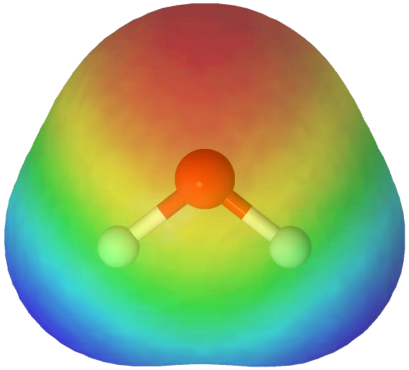
For more on aromaticity:
https://www.chem.wisc.edu/content/343esselman/aromaticity

Electronic Charge Distribution

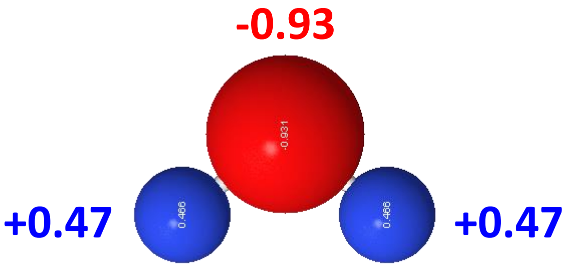
Computational chemistry can estimate charges on atoms within molecules by a variety of methods including Natural Population Analysis (NPA) from Natural Bond Orbitals (NBO) calculations.



Dipole moments can be estimated from the geometry and charge distribution.



Electrostatic potential maps display the same information in a color gradient.

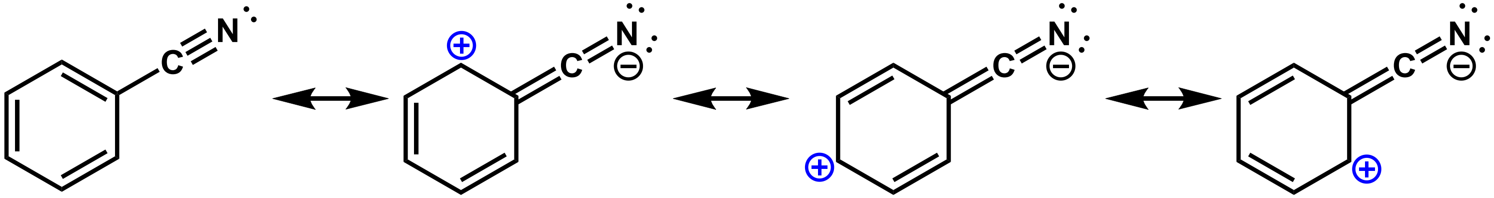


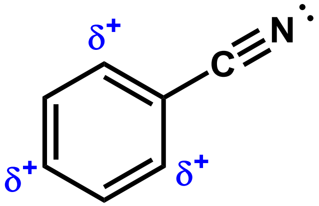
Negative charges are displayed in red, positive charges in blue.

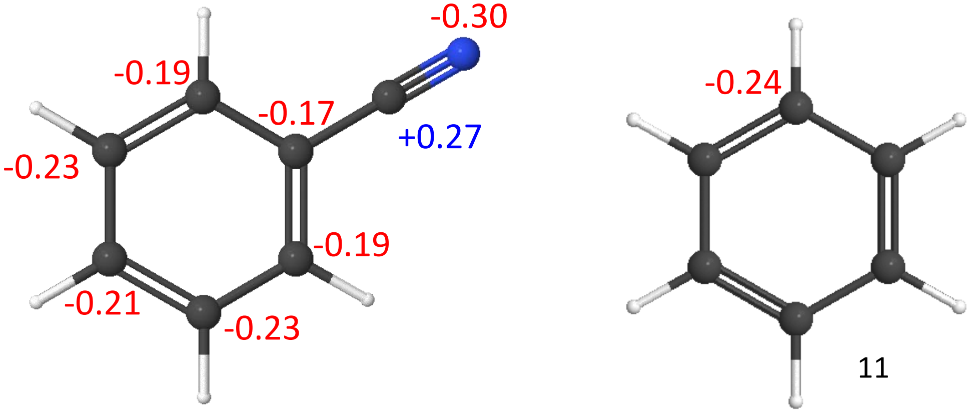
Electronic Charge Distribution

Resonance structures are often drawn to predict charge distribution within a molecule, but this is a sub-optimal method that only predicts the change in charge distribution based upon a substitution.

Benzonitrile

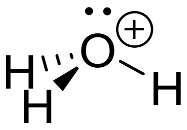




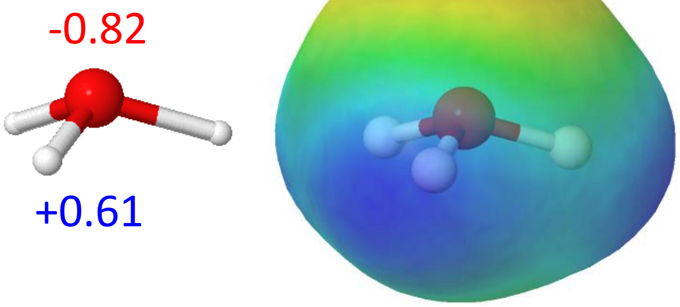


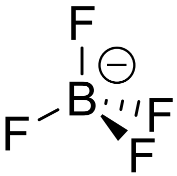
Electronic Charge Distribution

Formal charges, based upon changes in valence electron count upon bonding, are often misleading about the real charge distribution in a molecule. They are strictly for bookkeeping, not actual charge prediction.

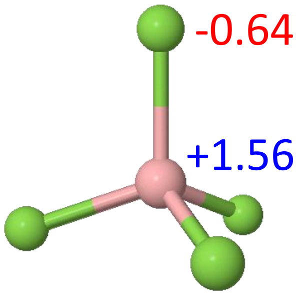


hydronium ion





tetrafluoroborate ion

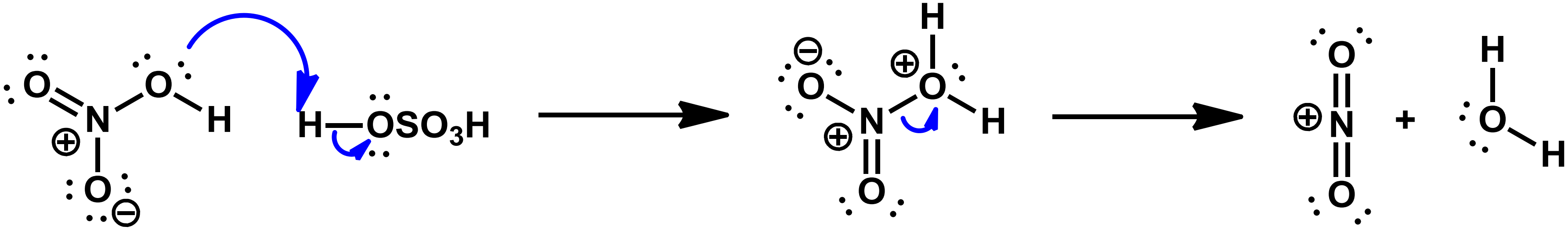


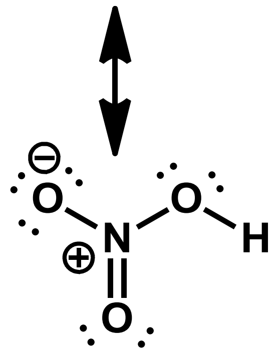
(F = 4.0, O = 3.5, H = 2.1, B = 2.0)

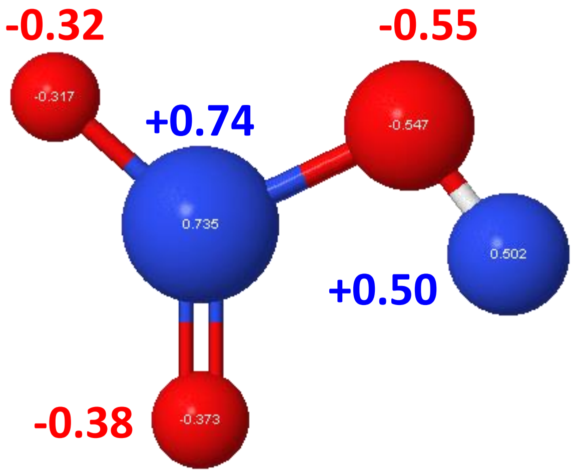
Electronic Charge Distribution & Chemical Reactivity

This is an important reaction used to generate the NO_2^+ cation used in electrophilic aromatic substitution reactions. The oxygen atom without the formal negative charge is protonated, why?

$$HNO_3 + H_2SO_4 \longrightarrow H_2O + NO_2^+ + HSO_4^-$$

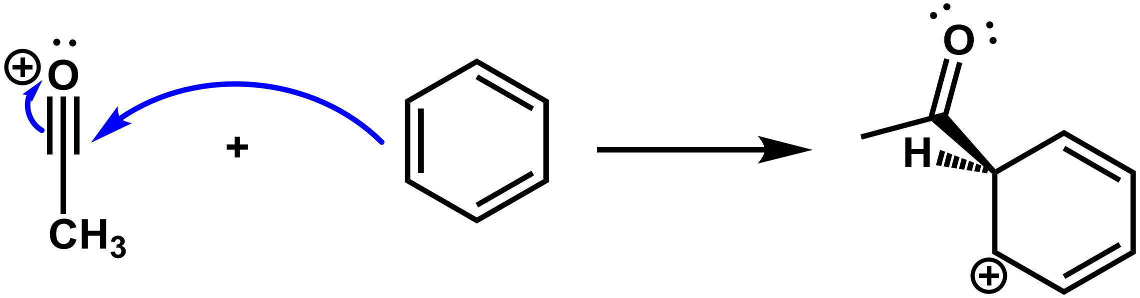


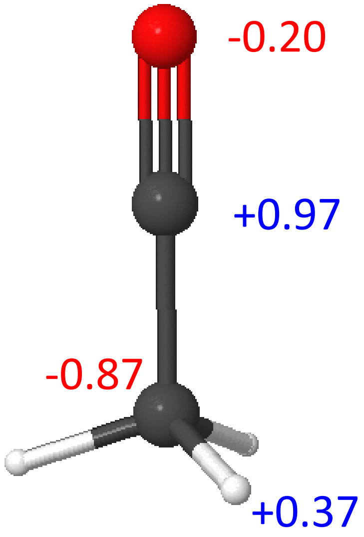




Electronic Charge Distribution & Chemical Reactivity

This is the rate-determining step of an electrophilic aromatic substitution reaction. Why is the carbon atom more electrophilic than the formally positive oxygen atom?

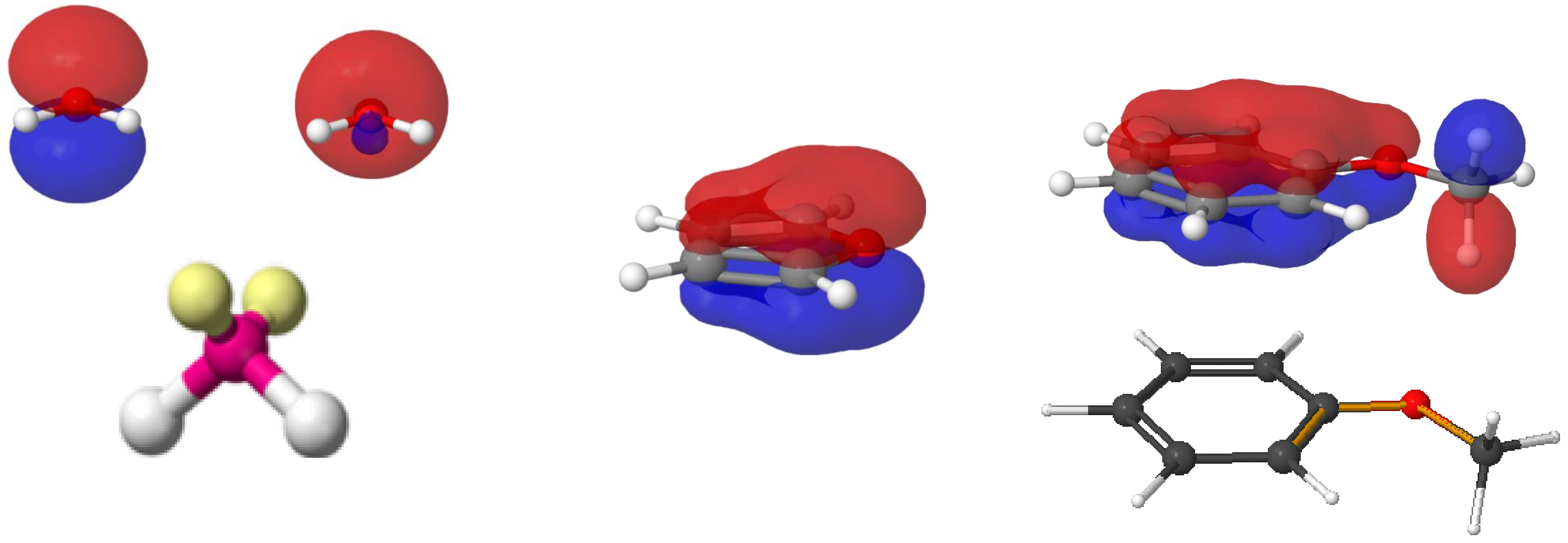




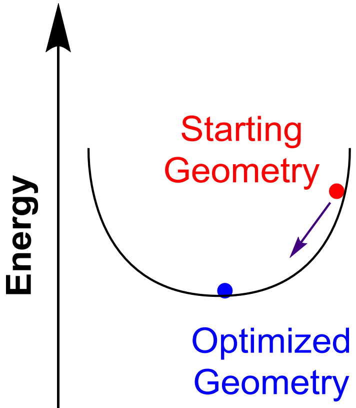
CHEM 344 – Molecular Modeling

The Use of Computational Chemistry to Support Experimental Organic Chemistry

Part 2: Introduction to WebMO/Gaussian09, Optimization and Vibrational Frequency Calculations, NBO calculations, Hybridization, & Coordinate Scans



Geometry Optimization of Water



potential energy surface (PES)

In an optimization, Gaussian09 makes *small* changes in the geometry to lower the energy. A good starting structure will *likely* produce a desired optimized structure.

-47939.9931 kcal/mol

7.3 kcal/mol

-47947.3058 kcal/mol

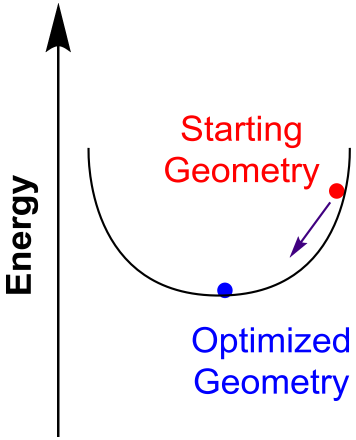
0.0 kcal/mol

Absolute energies are large and negative; relative energies are easier to use. The output energies are in Hartrees/particle and must be converted to kcal/mol for use in CHEM 344.

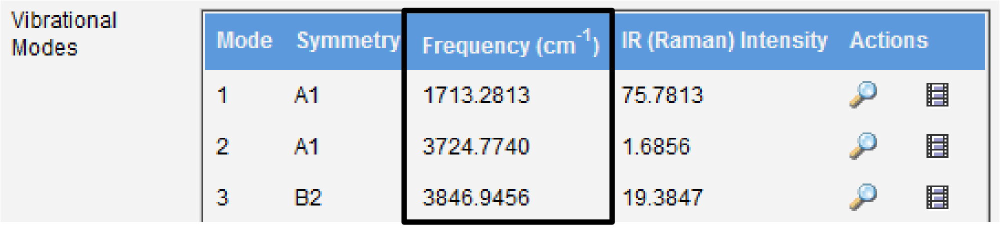
1 Hartree/particle = 627.509 kcal/mol

1 kcal/mol = 4.187 kJ/mol

Optimize + Vib Freq of Water



A vibrational frequency calculation will provide a predicted IR spectrum of the molecule AND confirm that it is an optimized energy minimum on the potential energy surface.

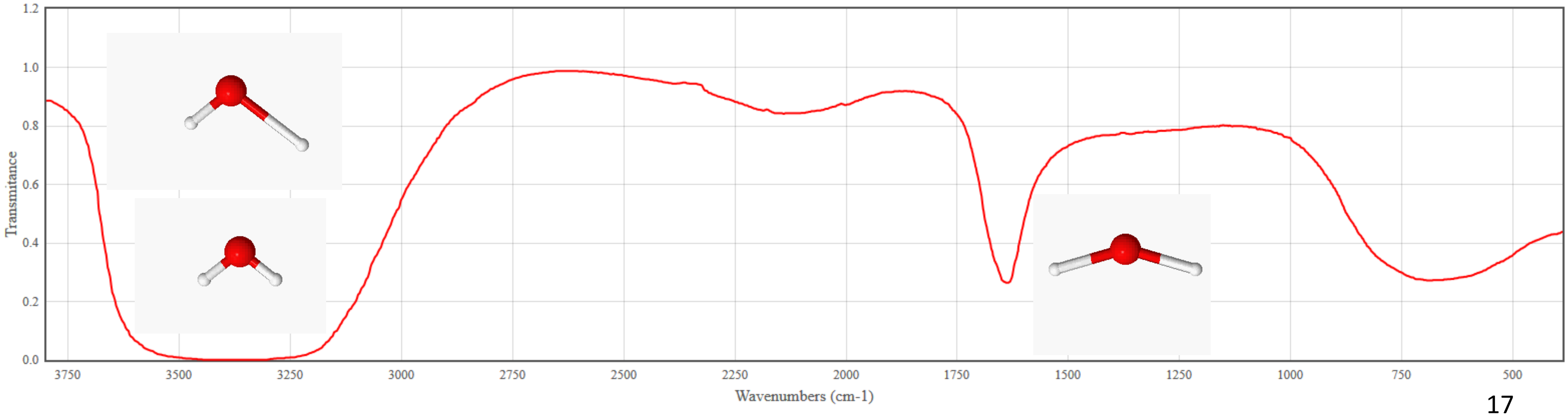


Vibrational Modes

Mode	Symmetry	Frequency (cm^{-1})	IR (Raman) Intensity	Actions	
1	A1	1713.2813	75.7813	🔍	▤
2	A1	3724.7740	1.6856	🔍	▤
3	B2	3846.9456	19.3847	🔍	▤

Reactants, products, intermediates – all energy minima, all real (positive) vibrational modes

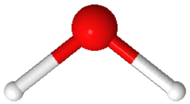
Transition states – an energy maximum, 1 imaginary (negative) vibrational mode

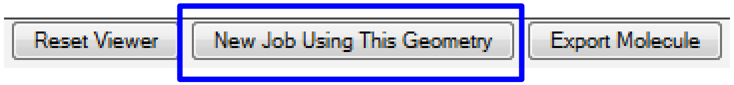


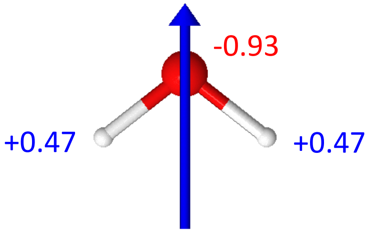
http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Type=IR-SPEC&Index=1#IR-SPEC

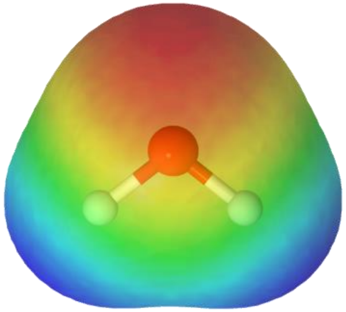
Molecular and Electronic Structure of Water

An optimized geometry provides the starting point for an NBO calculation which will provide the NPA charges, dipole, electrostatic potential map, MO's, and NBO's.

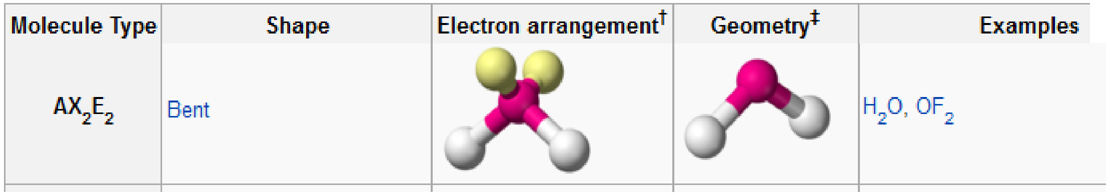






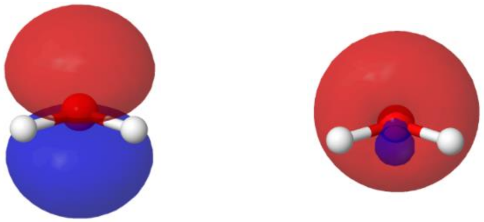


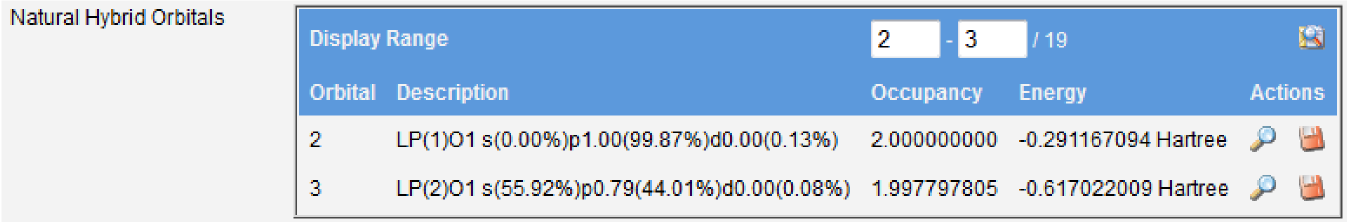
VSEPR predicts a tetrahedral electron geometry and identical lone pair orbitals.



Molecule Type	Shape	Electron arrangement[†]	Geometry[‡]	Examples
AX_2E_2	Bent			H_2O, OF_2

http://en.wikipedia.org/wiki/VSEPR_theory, retrieved 06-Jan-2014





Natural Hybrid Orbitals

Display Range 2 - 3 / 19

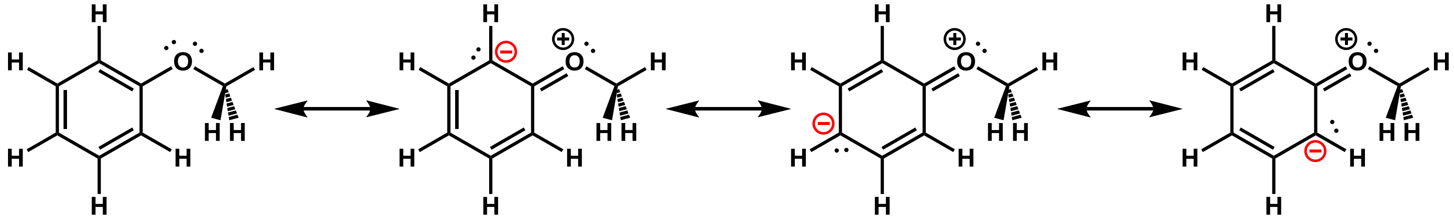
Orbital	Description	Occupancy	Energy	Actions
2	LP(1)O1 s(0.00%)p1.00(99.87%)d0.00(0.13%)	2.000000000	-0.291167094 Hartree	🔎
3	LP(2)O1 s(55.92%)p0.79(44.01%)d0.00(0.08%)	1.997797805	-0.617022009 Hartree	🔎

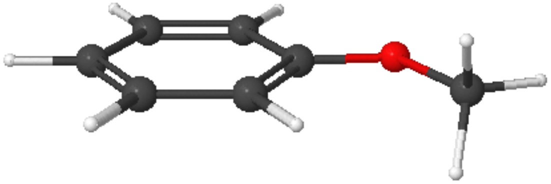
http://pubs.acs.org/doi/pdfplus/10.1021/ed064p124

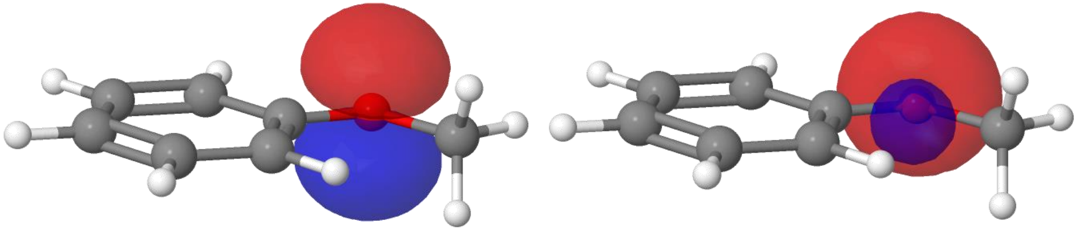
Molecular and Electronic Structure of Anisole

How well does VSEPR predict the lone pair orbitals for the O-atom in anisole?

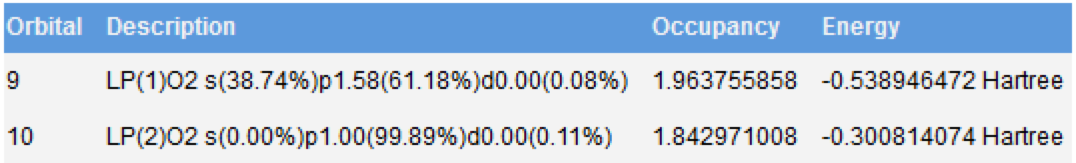
anisole



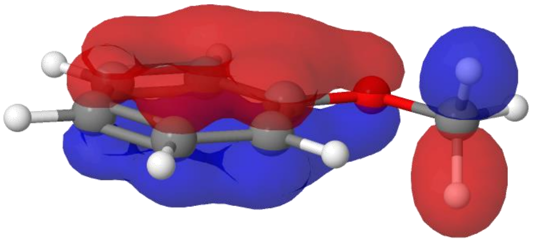




NBO O-atom lone pairs

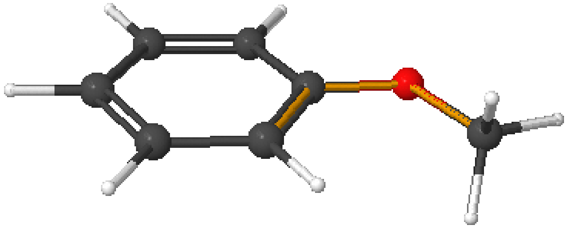


Orbital	Description	Occupancy	Energy
9	LP(1)O2 s(38.74%)p1.58(61.18%)d0.00(0.08%)	1.963755858	-0.538946472 Hartree
10	LP(2)O2 s(0.00%)p1.00(99.89%)d0.00(0.11%)	1.842971008	-0.300814074 Hartree

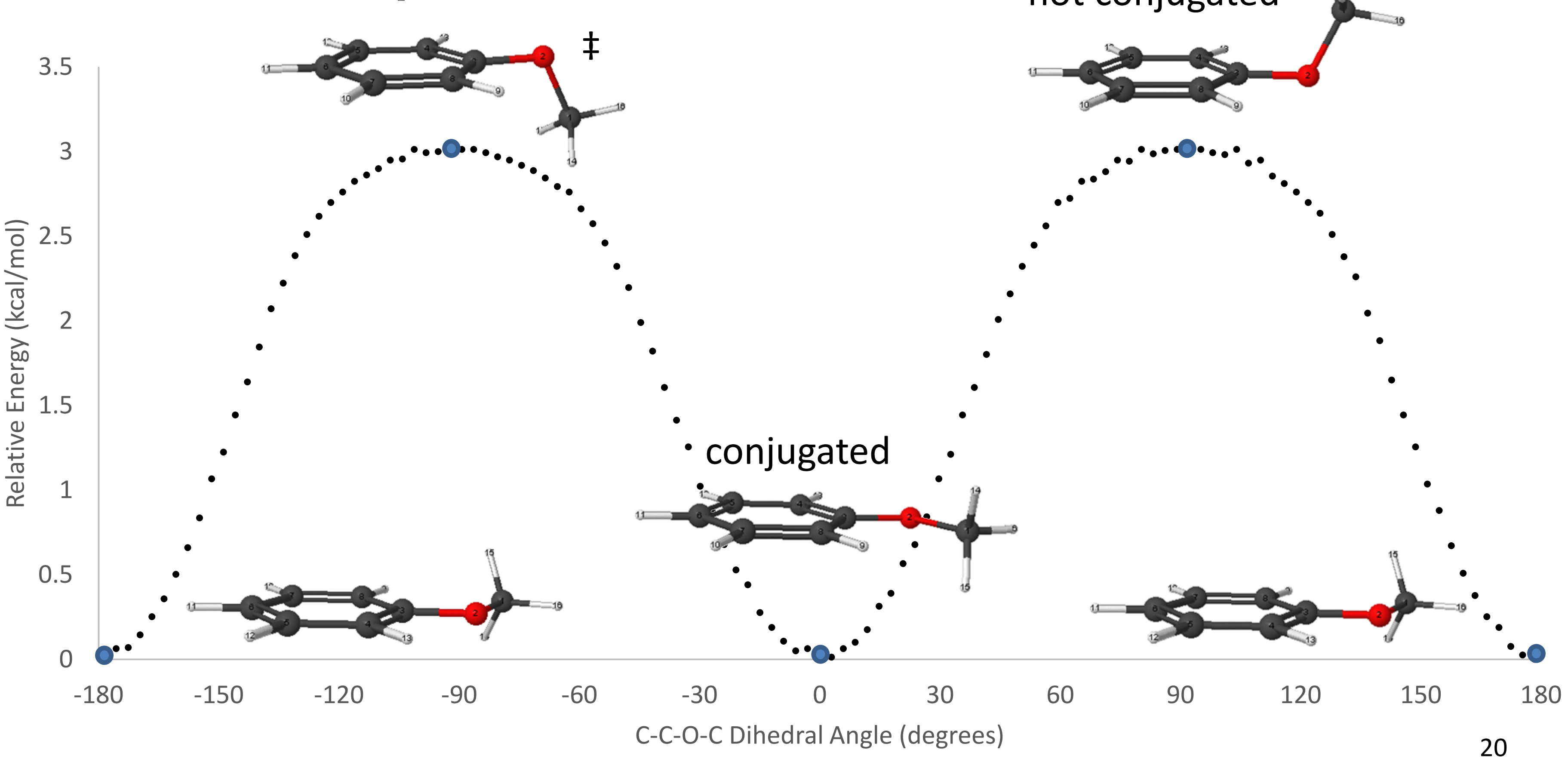


π system in anisole

Coordinate or Conformational Scan of Anisole



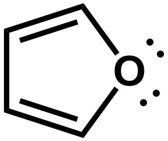
What happens to the energy of anisole if the O-atom lone pair conjugation is broken?

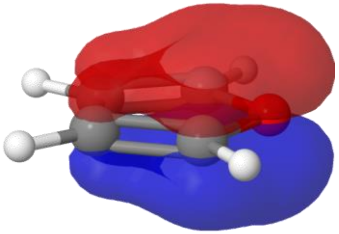


Molecular and Electronic Structure of Furan

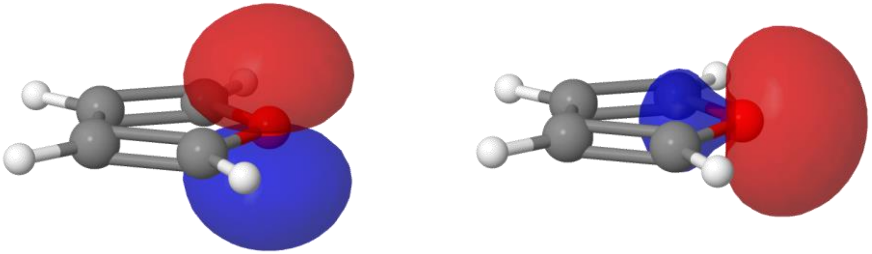
What about the O-atom lone pairs in furan? If the oxygen atom lone pairs are in symmetric (degenerate) orbitals predicted by VSEPR for a tetrahedral electron geometry, then the oxygen atom lone pair is not conjugated with the two π bonds. And, thus, furan would not be aromatic.

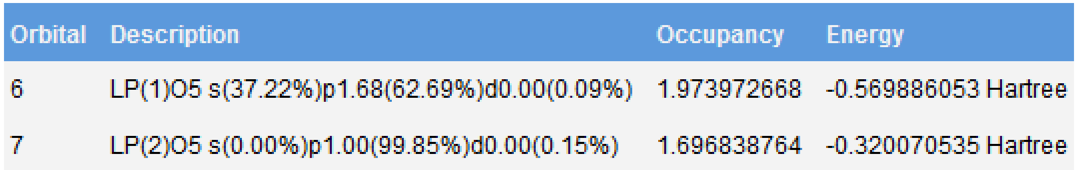
furan





π system in furan (the O-atom lone pair is conjugated)

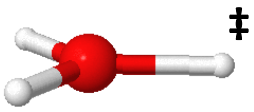




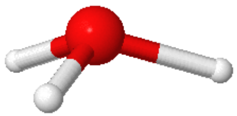
Orbital	Description	Occupancy	Energy
6	LP(1)O5 s(37.22%)p1.68(62.69%)d0.00(0.09%)	1.973972668	-0.569886053 Hartree
7	LP(2)O5 s(0.00%)p1.00(99.85%)d0.00(0.15%)	1.696838764	-0.320070535 Hartree

Molecular and Electronic Structure of Hydronium Ion

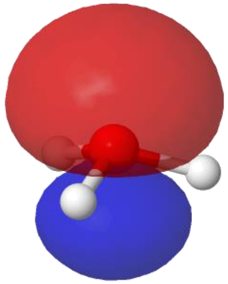
What about the O-atom when it has only a single lone pair, in case such as hydronium? If the O-atom lone pair is in a p orbital the molecule should be trigonal planar. If VSEPR predicts this molecule correctly, the molecule should be trigonal pyramidal with a tetrahedral electron geometry.

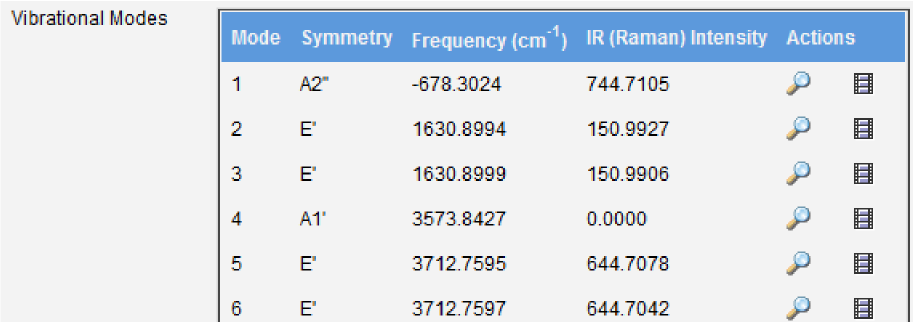


Trigonal planar
(D_{3h})



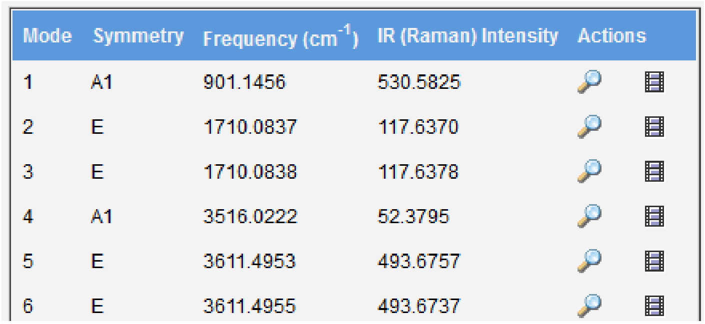
Trigonal pyramidal
(C_{3v})



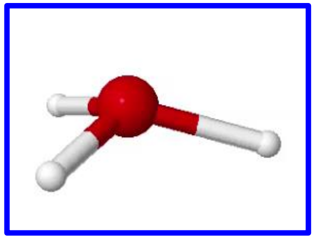


Vibrational Modes

Mode	Symmetry	Frequency (cm^{-1})	IR (Raman) Intensity	Actions	
1	A2"	-678.3024	744.7105	🔍	▤
2	E'	1630.8994	150.9927	🔍	▤
3	E'	1630.8999	150.9906	🔍	▤
4	A1'	3573.8427	0.0000	🔍	▤
5	E'	3712.7595	644.7078	🔍	▤
6	E'	3712.7597	644.7042	🔍	▤



Mode	Symmetry	Frequency (cm^{-1})	IR (Raman) Intensity	Actions	
1	A1	901.1456	530.5825	🔍	▤
2	E	1710.0837	117.6370	🔍	▤
3	E	1710.0838	117.6378	🔍	▤
4	A1	3516.0222	52.3795	🔍	▤
5	E	3611.4953	493.6757	🔍	▤
6	E	3611.4955	493.6737	🔍	▤



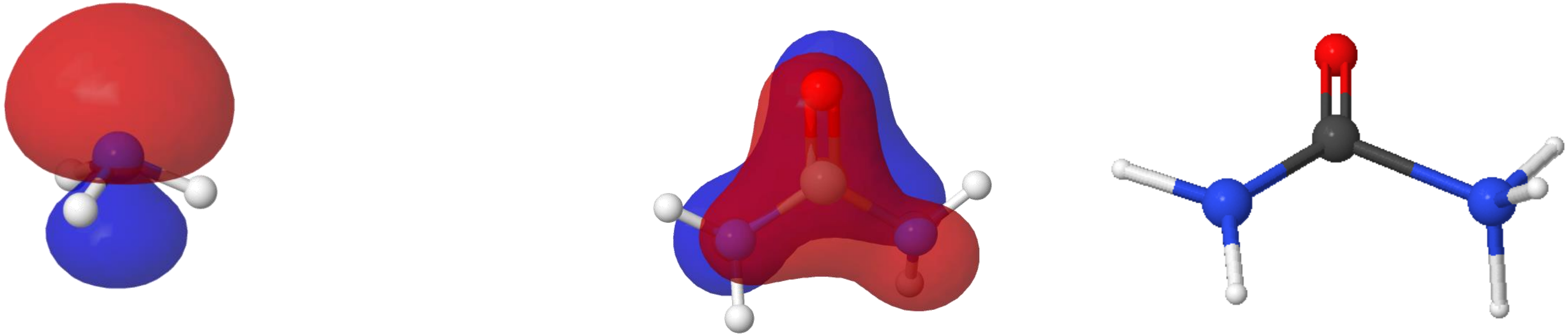
Geometry Optimization Procedure

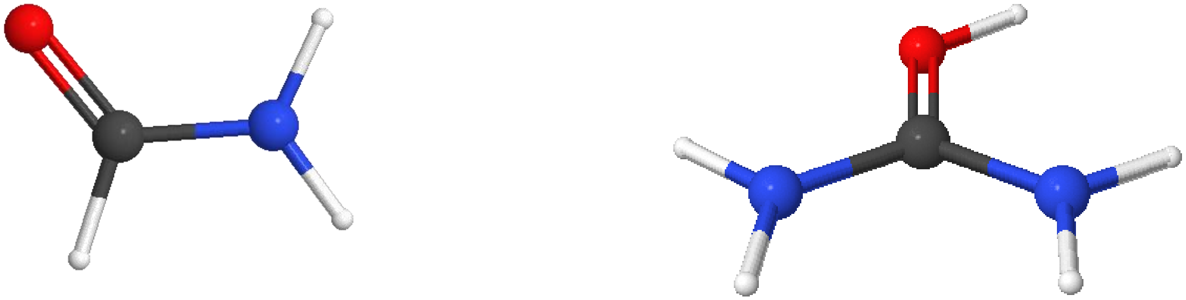
1. Draw the molecule in WebMO.
2. Use one of the clean-up tools.
3. Inspect the molecule. Does the predicted structure make chemical sense?
4. Submit an Optimization and Vibrational Frequencies Calculation.
5. Inspect the output molecule. Does the optimized structure still make chemical sense?
6. Confirm that the vibrational modes match the desired species.
7. Consider alternate, lower-energy, conformational isomers.

CHEM 344 – Molecular Modeling

The Use of Computational Chemistry to Support Experimental Organic Chemistry

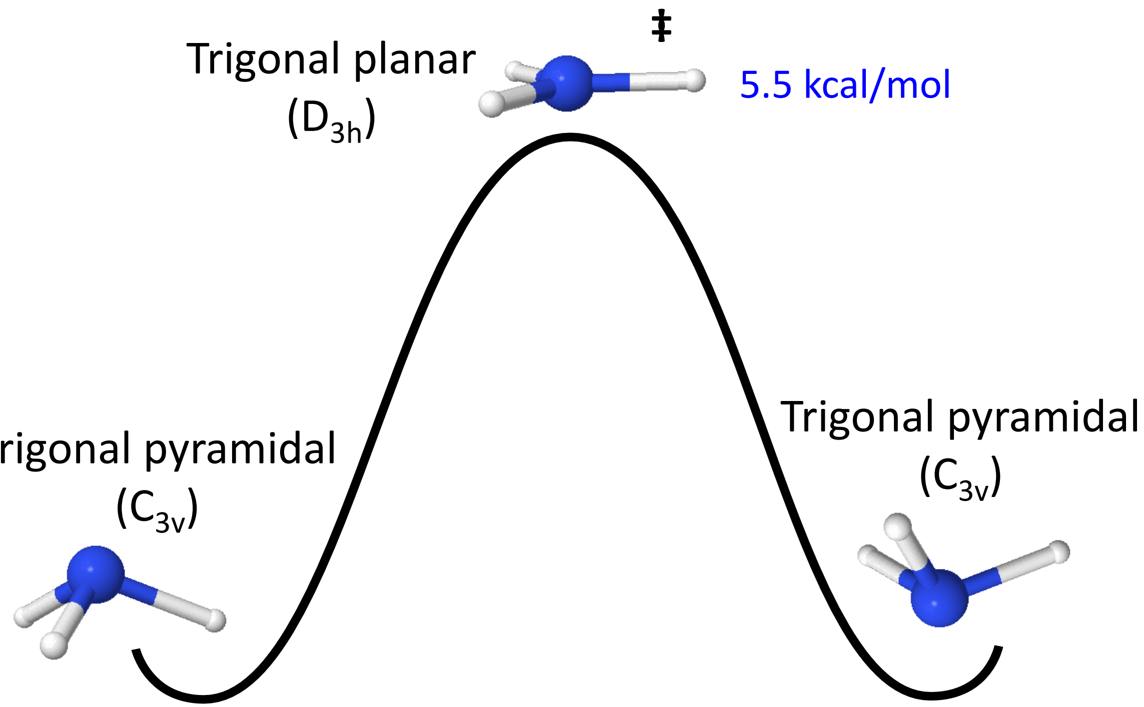
Part 3: Potential energy surfaces, transition states, hybridization





Molecular and Electronic Structure of Ammonia

The potential energy surface below depicts the process of nitrogen inversion. Ammonia can convert between two trigonal pyramidal conformational isomers via a planar transition state.



‡

Trigonal planar

(D_{3h})

5.5 kcal/mol

Trigonal pyramidal

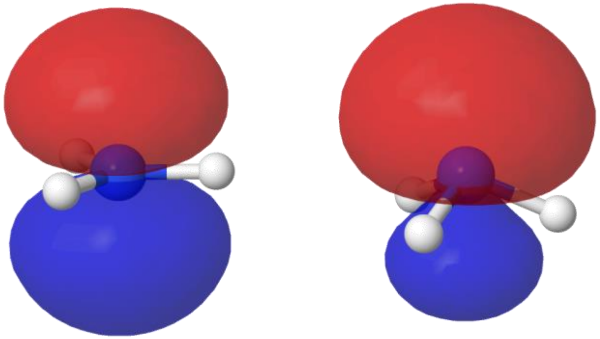
(C_{3v})

Trigonal pyramidal

(C_{3v})

0.0 kcal/mol

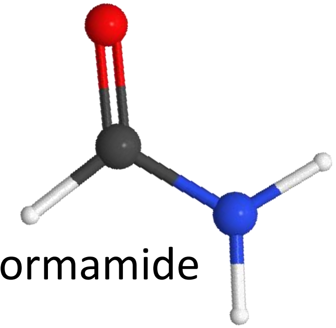
0.0 kcal/mol



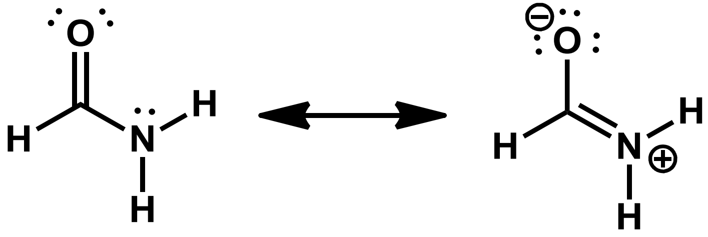
The barrier is sufficiently narrow that quantum tunneling readily occurs.

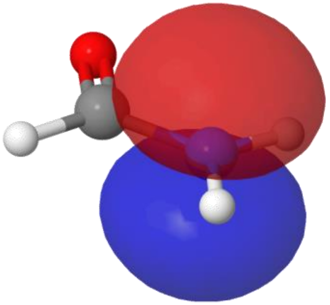
Variation in the Hybridization of Nitrogen Atoms

The nitrogen atom in ammonia is pyramidal while the optimized structure of formamide is planar with a trigonal planar nitrogen.

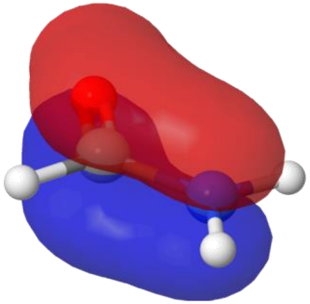


formamide

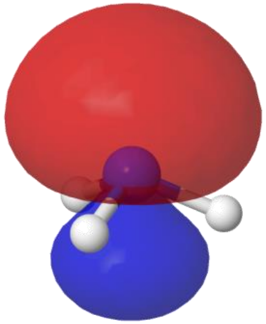




p lone pair



π_1 MO

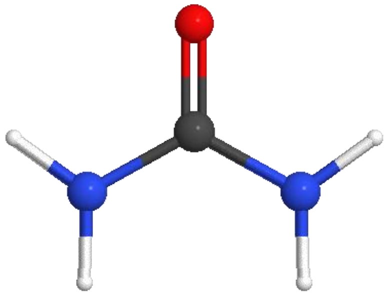


ammonia

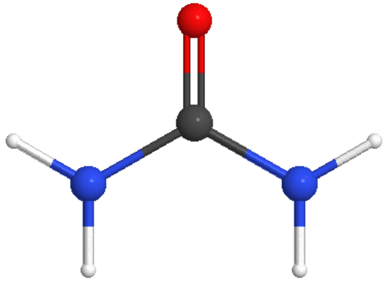
Molecular and Electronic Structure of Urea

Given the variability of N-atom hybridizations, it is very difficult to know beforehand whether or not a structure should be planar. Urea is a great case-study of this difficulty; even the cleanup tools in WebMO struggle to produce a good input structure.

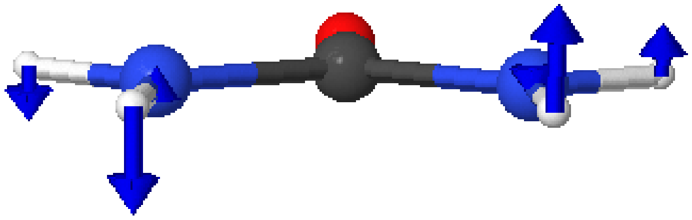
Urea input structures
(after cleanup)



Comprehensive Mechanics
(C_{2v})

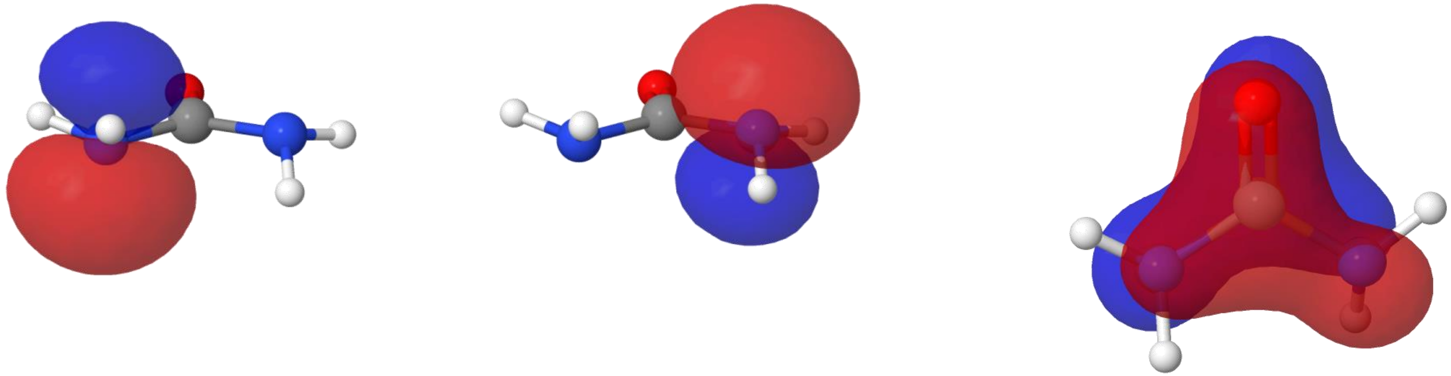


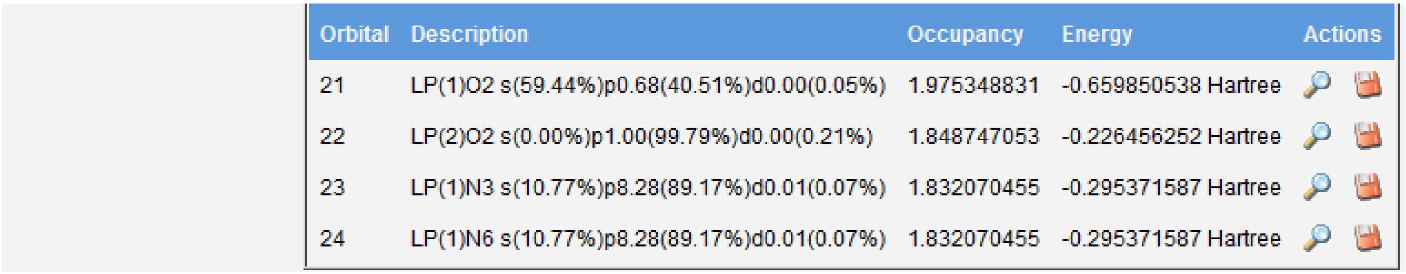
Comprehensive Idealized
(C_{2v})



Molecular and Electronic Structure of Urea

Urea has a non-planar geometry that results in a slightly twisted conjugated π system. The nitrogen atom lone pairs are in p-rich (~sp^8) orbitals.

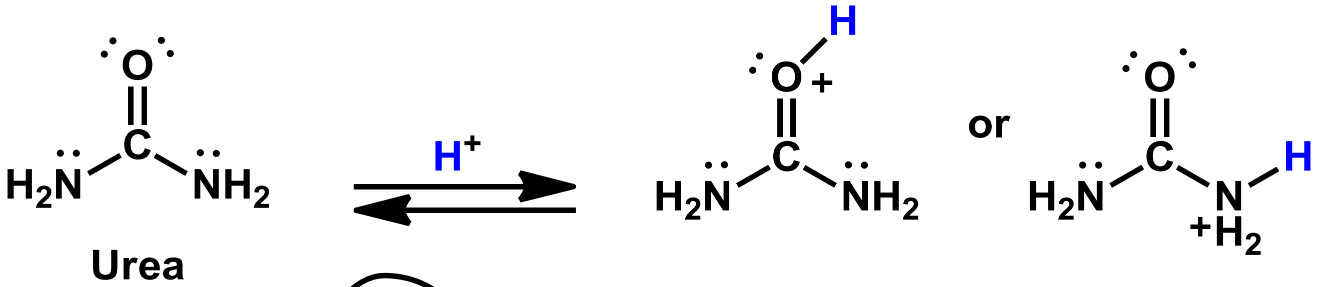


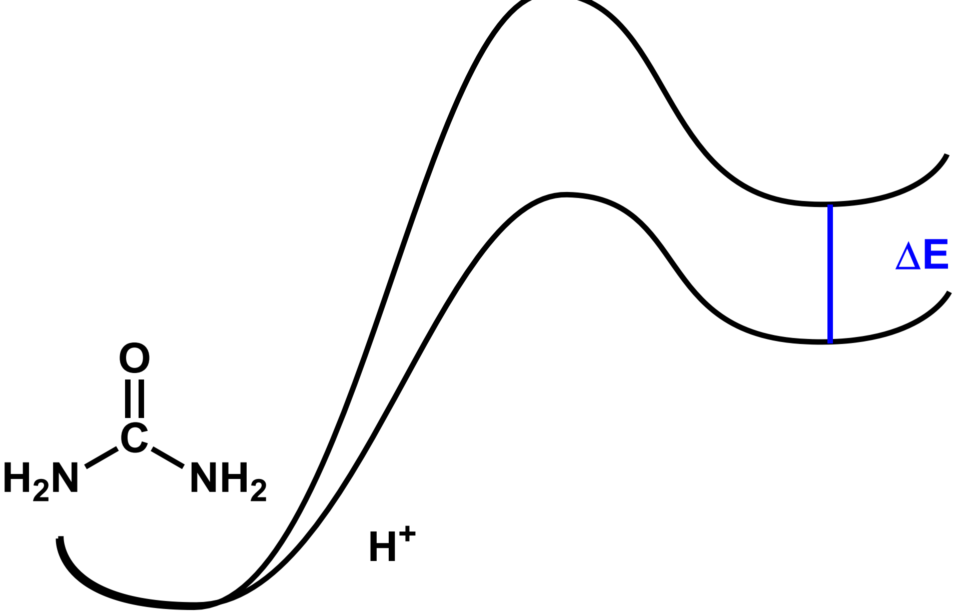


Orbital	Description	Occupancy	Energy	Actions
21	LP(1)O2 s(59.44%)p0.68(40.51%)d0.00(0.05%)	1.975348831	-0.659850538 Hartree	🔍 💾
22	LP(2)O2 s(0.00%)p1.00(99.79%)d0.00(0.21%)	1.848747053	-0.226456252 Hartree	🔍 💾
23	LP(1)N3 s(10.77%)p8.28(89.17%)d0.01(0.07%)	1.832070455	-0.295371587 Hartree	🔍 💾
24	LP(1)N6 s(10.77%)p8.28(89.17%)d0.01(0.07%)	1.832070455	-0.295371587 Hartree	🔍 💾

Chemical Reactivity – Basicity of Urea

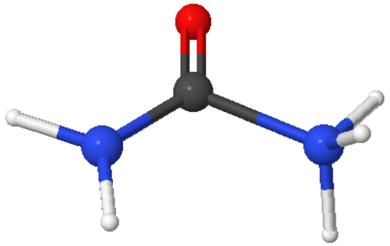
Computational chemistry can also help rationalize or predict chemical reactivity; in this case, which atom in urea is most basic.





In general, a ΔE of 1.4 kcal/mol translates into an approximate factor of 10 difference in abundance.

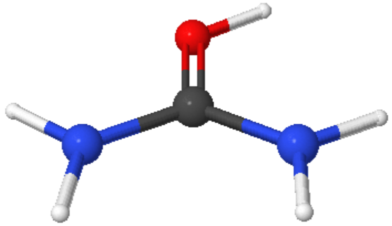
Chemical Reactivity – Basicity of Urea



-225.512016 Hartrees

-141510.82 kcal/mol

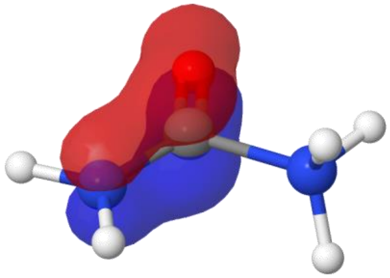
12.7 kcal/mol

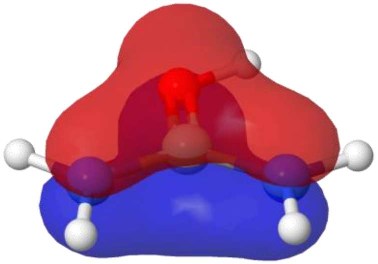


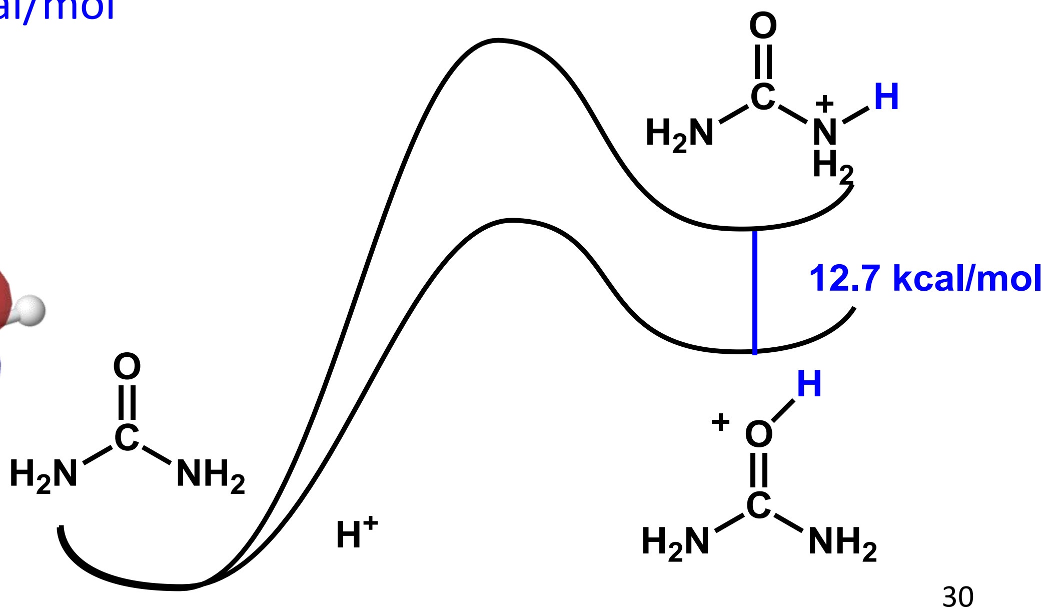
-225.532300 Hartrees

-141523.55 kcal/mol

0.0 kcal/mol

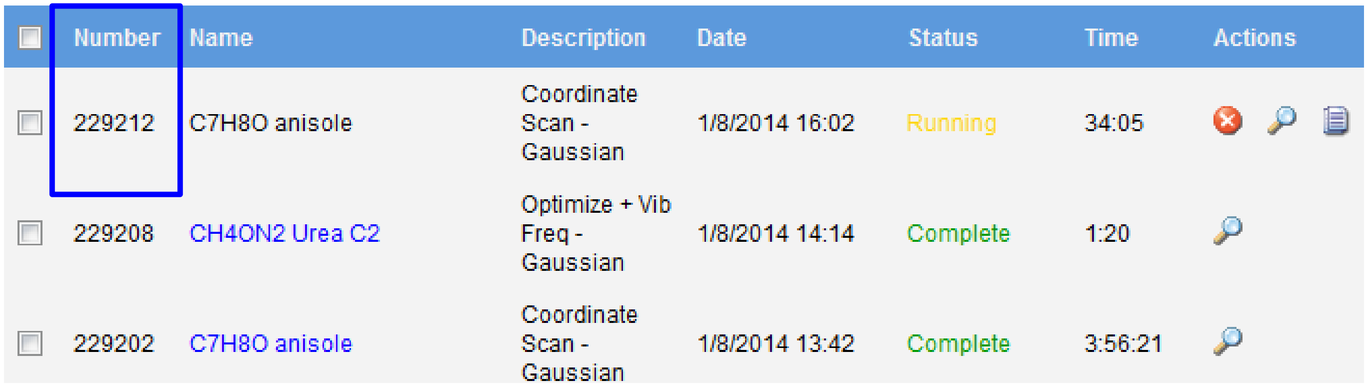






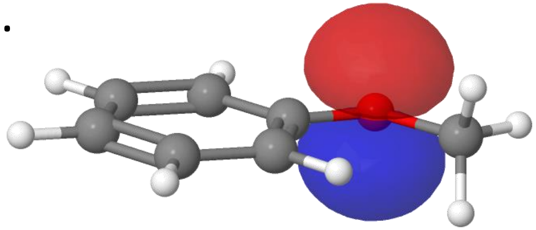
General Guidelines for Computational Data Submission

1. You must cite (on the lab report cover sheet) your computational work used to answer post-lab or pre-lab questions in CHEM 344 by providing the WebMO job number associated with the calculation.



☐	Number	Name	Description	Date	Status	Time	Actions
☐	229212	C7H8O anisole	Coordinate Scan - Gaussian	1/8/2014 16:02	Running	34:05	✖ 🔍 ▤
☐	229208	CH4ON2 Urea C2	Optimize + Vib Freq - Gaussian	1/8/2014 14:14	Complete	1:20	🔍
☐	229202	C7H8O anisole	Coordinate Scan - Gaussian	1/8/2014 13:42	Complete	3:56:21	🔍

2. You must provide a color-image of each optimized structure or orbital used to answer a post-lab or pre-lab question. Please print multiple pictures per page and cut/paste them into your notebook.



3. Data submitted must be your own work You are not allowed to use someone else's data or account. This is considered academic misconduct.

References

1) *WebMO, Revision 12.0.* http://webmo.net/ **2012**.

2) Gaussian 09, Revision B.1, Frisch et al. Gaussian, Inc., Wallingford CT, 2009.