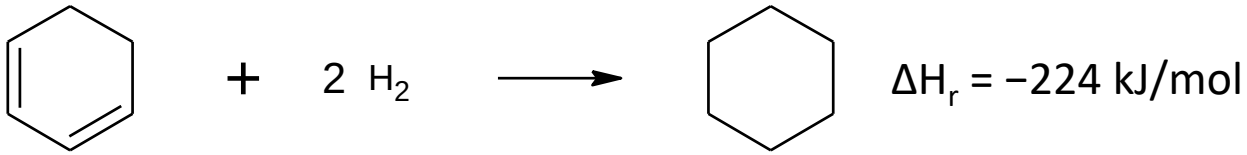
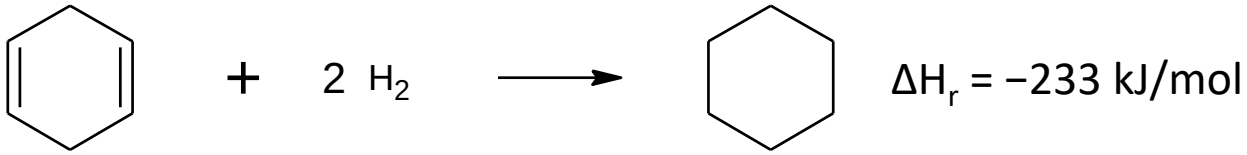
# Why is 1,4-cyclohexadiene stabilized?

## Using qualitative perturbation theory to teach conjugation




all thermochemical data from the NIST Chemistry Webbook

**Daniel Berger**
**Bluffton University**

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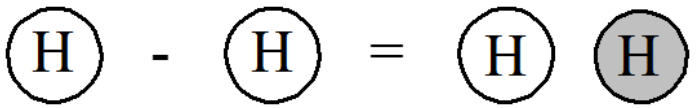
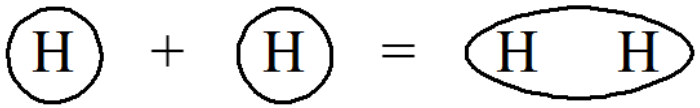
# Perturbation theory

- The modification of wavefunctions by adding additional elements ("perturbing them").

$$\Psi_1 = \Psi_0 + c\phi$$

- Qualitative version: combine pieces of an MO system with each other to see what results.
  - "Pictorial MO theory"



# Stabilization of polyenes

- Uses experimental heats of hydrogenation
- Definition of “resonance energy” is comparison to hydrogenation of similar mono-enes
  - E.g. compare *E*-1,3-hexadiene to 1-hexene + *E*-3-hexene
- Negative value = stabilization

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# Stabilization of linear hexadienes

| Hexadiene | Res. E. (kJ/mol) | | Hexadiene | Res. E. (kJ/mol) |
|---|---|---|---|---|
| E-1,3-hexadiene | -22 | | E,E-2,4-hexadiene | -21 |
| Z-1,3-hexadiene | -21 | | E,Z-2,4-hexadiene | -20 |
| Z-1,4-hexadiene | 0 | | Z,Z-2,4-hexadiene | -19 |
| E-1,4-hexadiene | 0 | | 1,5-hexadiene | 2 |
| E-1,3,5-hexatriene | -33 | | | |
| Z-1,3,5-hexatriene | -33 | | | |
| | | | 1,3-cyclohexadiene | -12 |
| benzene | -149 | | 1,4-cyclohexadiene | -3 |

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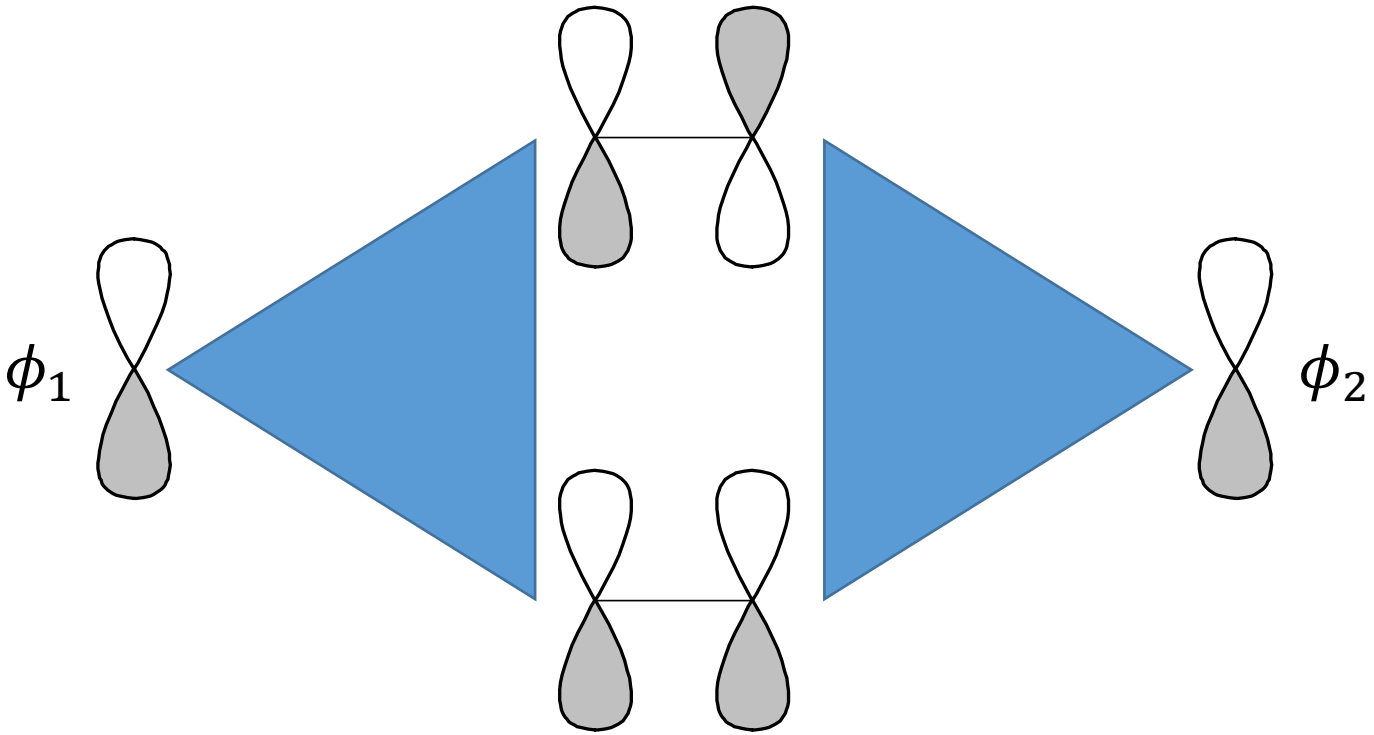
# Ethylene π-orbitals

$\Psi_g = \phi_1 - \phi_2$




$\Psi_u = \phi_1 + \phi_2$

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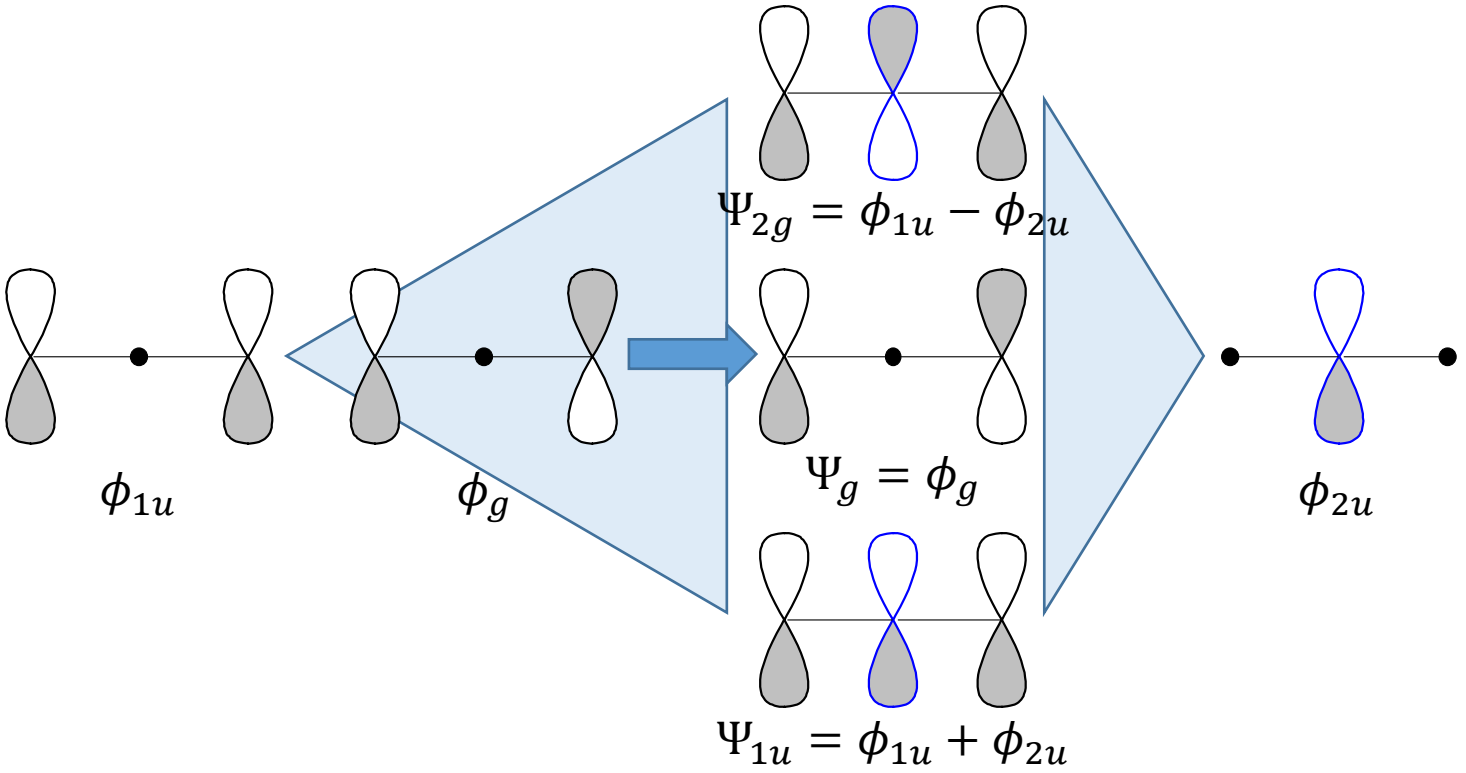
# Constructing allyl π-orbitals: LCAO

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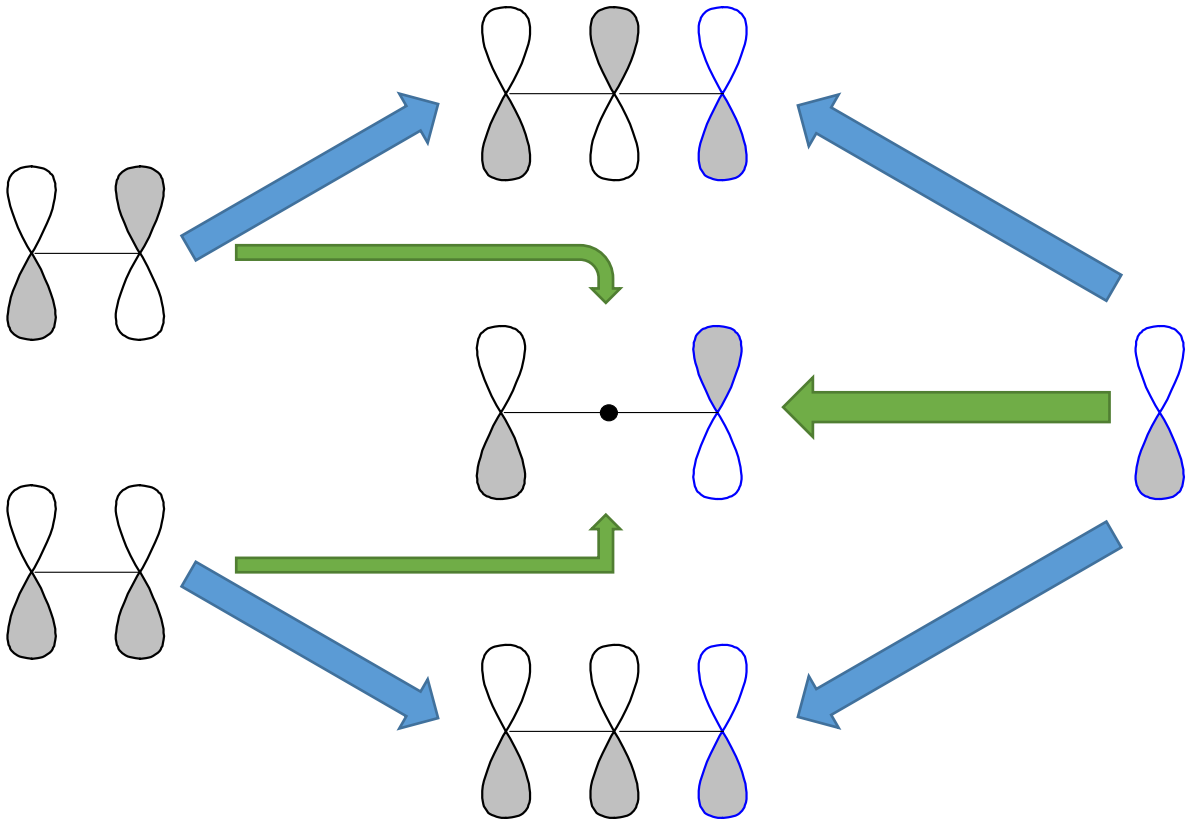
# Constructing allyl π-orbitals: Perturbation

$CH_2{=}CH{-}CH_2$

# Constructing allyl π-orbitals: Perturbation



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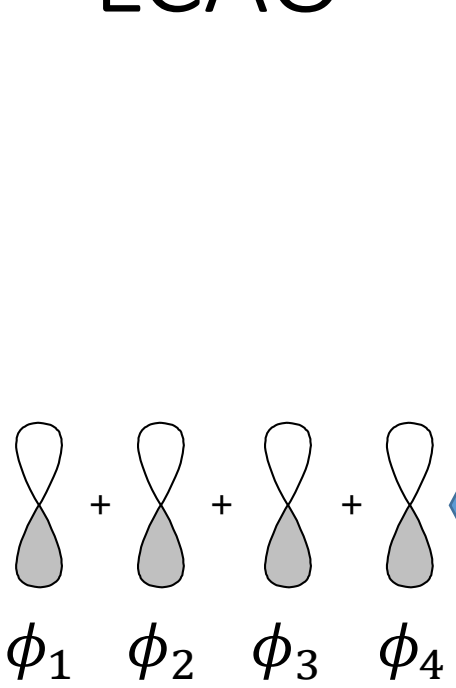
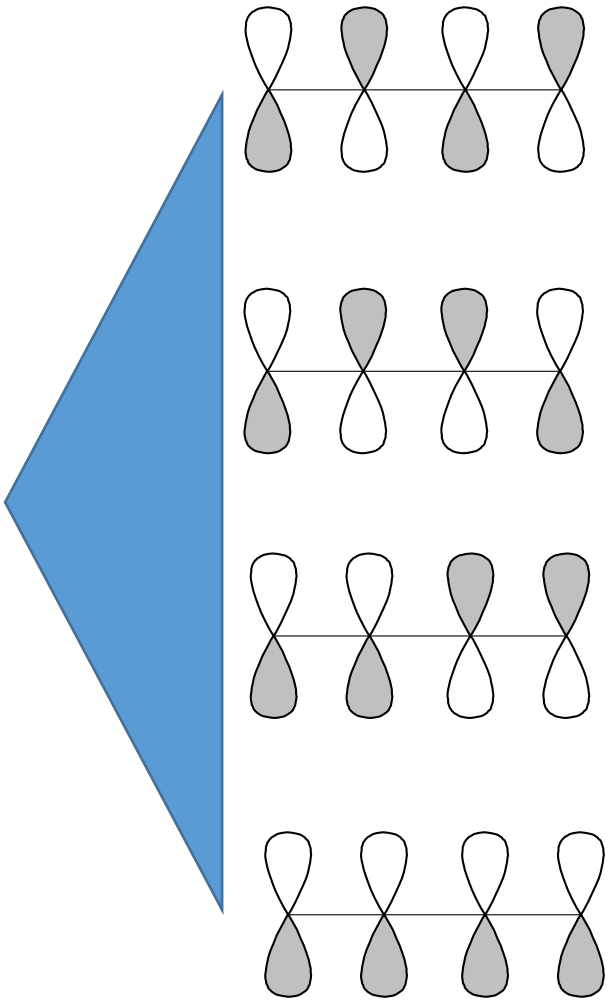
# Constructing butadiene π-orbitals: LCAO



$$\Psi_4 = \phi_1 - \phi_2 + \phi_3 - \phi_4$$

$$\Psi_3 = \phi_1 - \phi_2 - \phi_3 + \phi_4$$

$$\Psi_2 = \phi_1 + \phi_2 - \phi_3 - \phi_4$$

$$\Psi_1 = \phi_1 + \phi_2 + \phi_3 + \phi_4$$

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# Constructing butadiene π-orbitals: Perturbation

$CH_2=CH-CH=CH_2$

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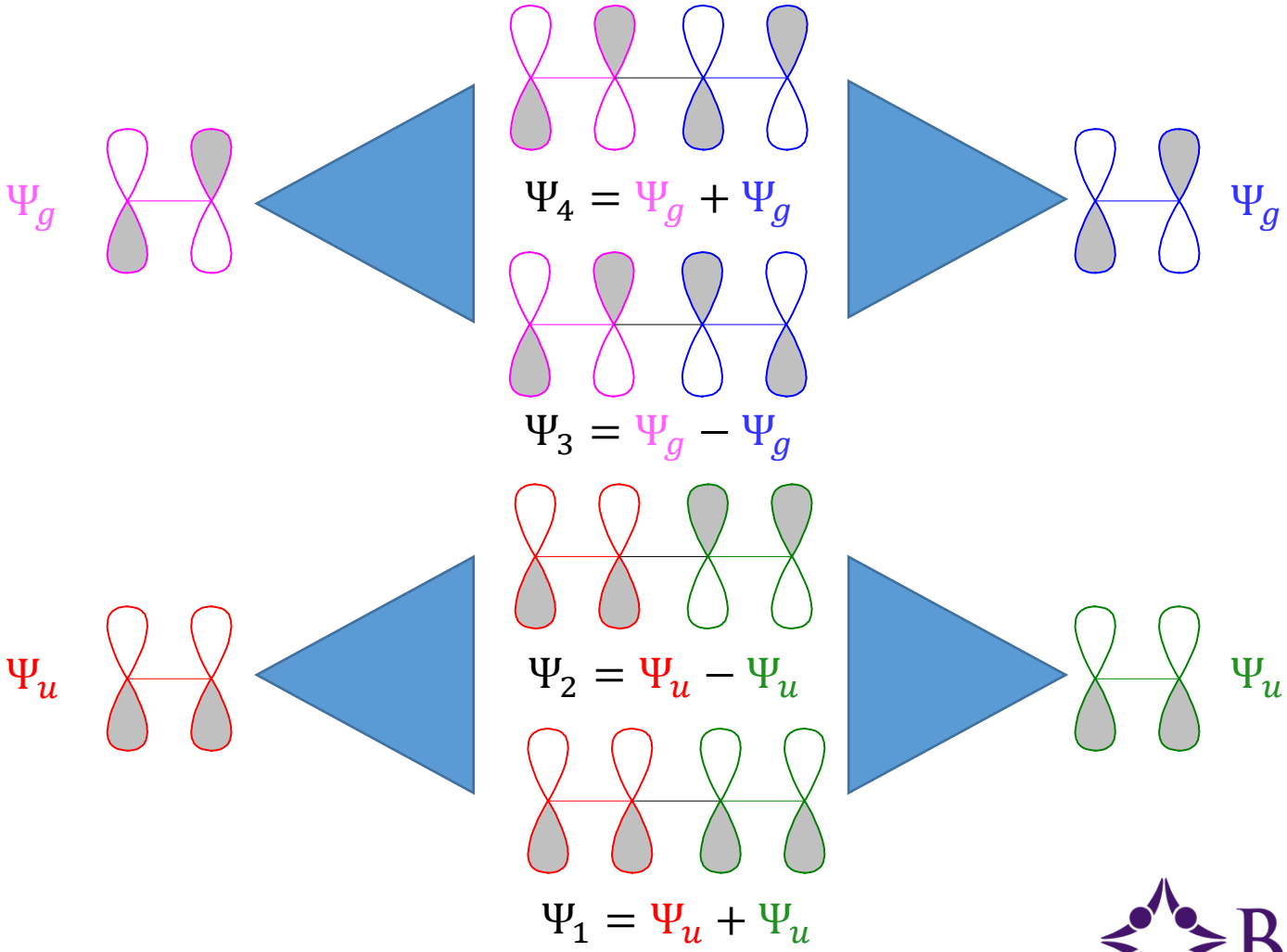
# Constructing butadiene π-orbitals: Perturbation

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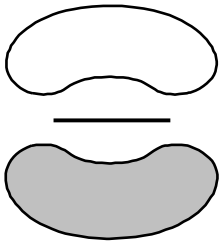
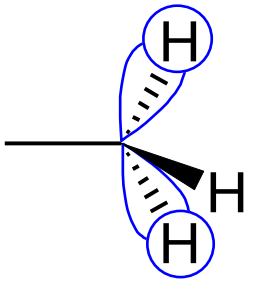
# Hyperconjugation using qualitative perturbation theory

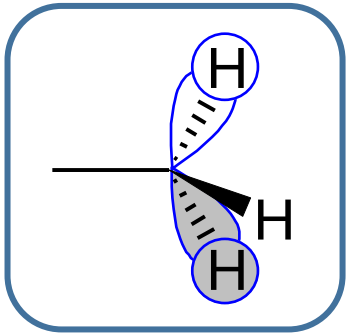
Stabilization = 11 kJ/mol

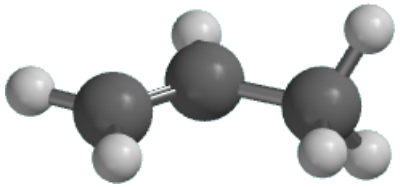
Hydrogenation vs. ethylene
NIST Chemistry Webbook

$CH_2=CH-CH_3$





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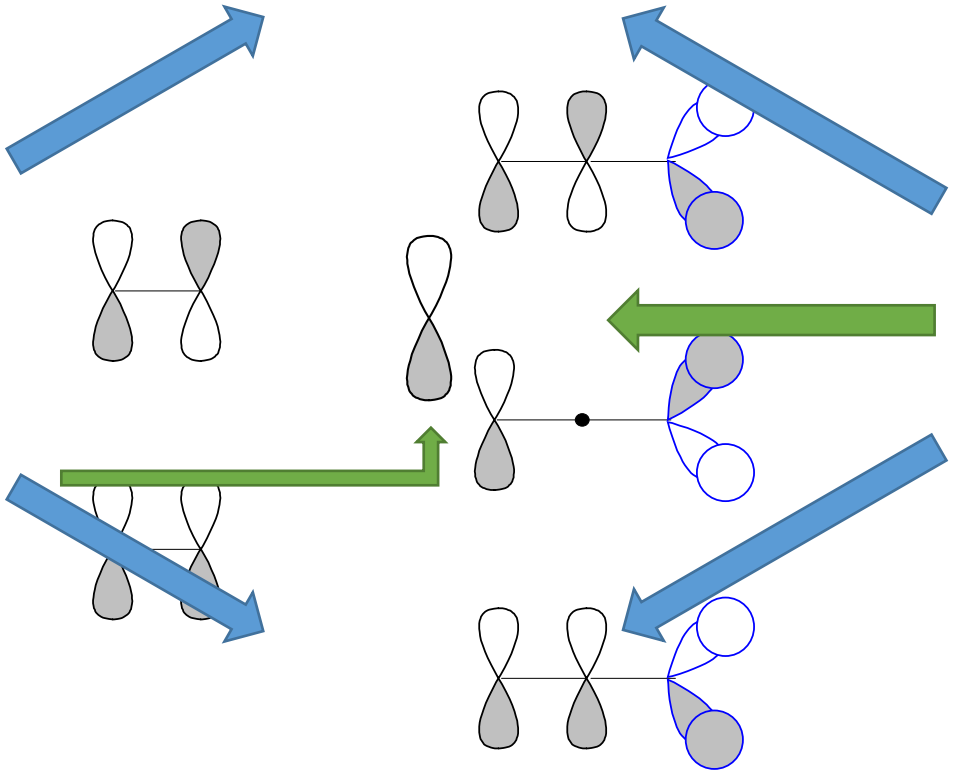
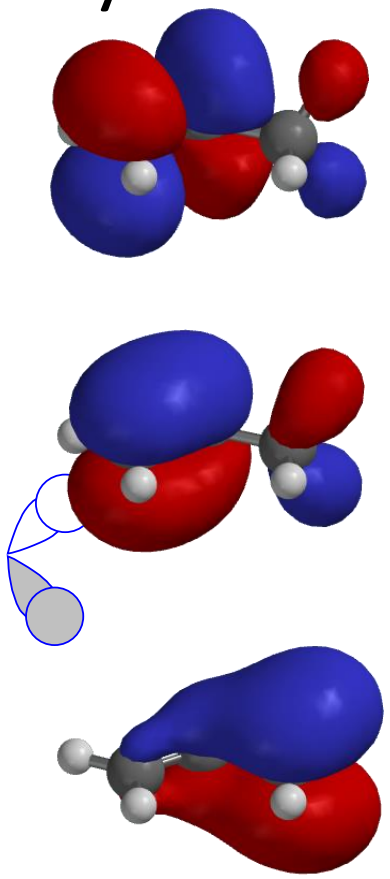
# Hyperconjugation using qualitative perturbation theory





Stabilization = 11 kJ/mol

Hydrogenation vs. ethylene
NIST Chemistry Webbook

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# Hyperconjugation: summary

- C-H σ bonds interact with π* orbital
- This lowers the energy of the σ electrons

# Explaining anomalous results for cyclohexadienes

- 1,3-hexadienes have ca. 20 kJ/mol resonance energy.
- 1,3-cyclohexadiene has ca. 12 kJ/mol resonance energy. **Why is it destabilized?**

- 1,4-hexadienes have ca. 0 kJ/mol resonance energy.
- 1,4-cyclohexadiene has ca. 3 kJ/mol resonance energy. **Why is it stabilized?**

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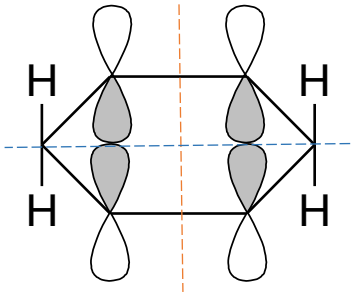
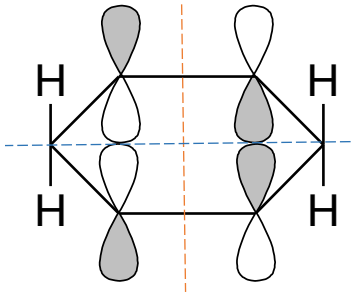
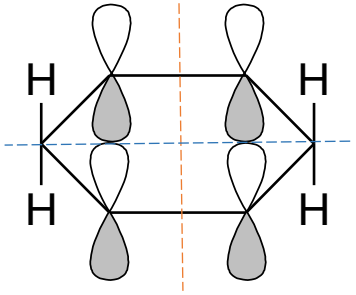
# 1,4-cyclohexadiene: π orbitals

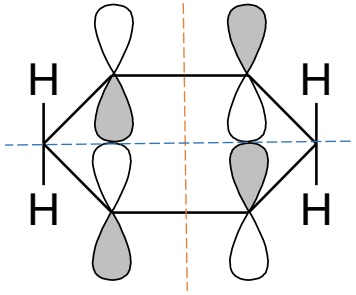
antisymmetric




symmetric




symmetric

antisymmetric

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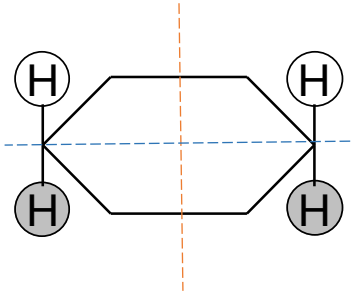
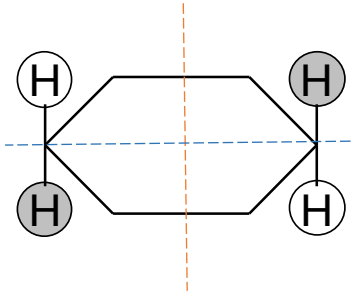
# 1,4-cyclohexadiene: C-H orbitalswith π symmetry

antisymmetric

symmetric




symmetric

antisymmetric

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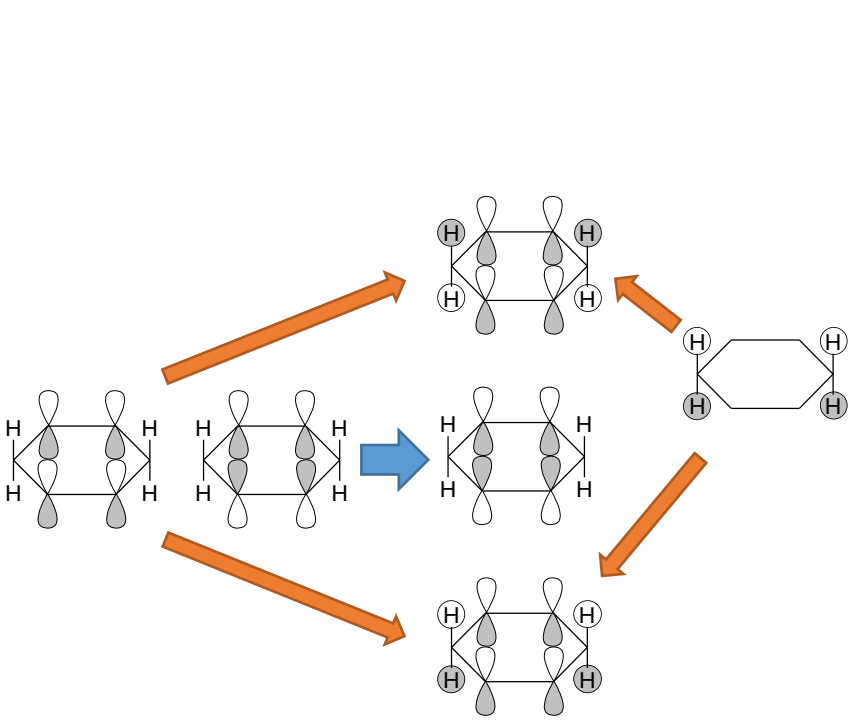
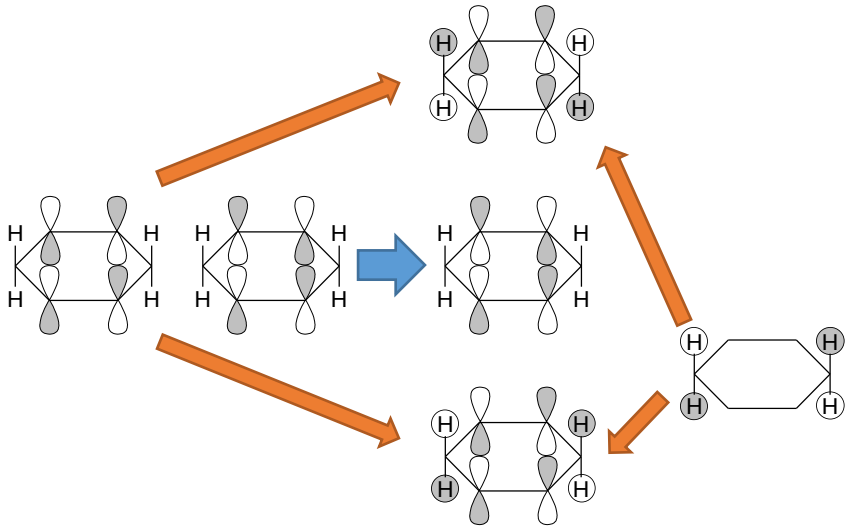
# 1,4-cyclohexadiene orbital mixing



symmetric



antisymmetric

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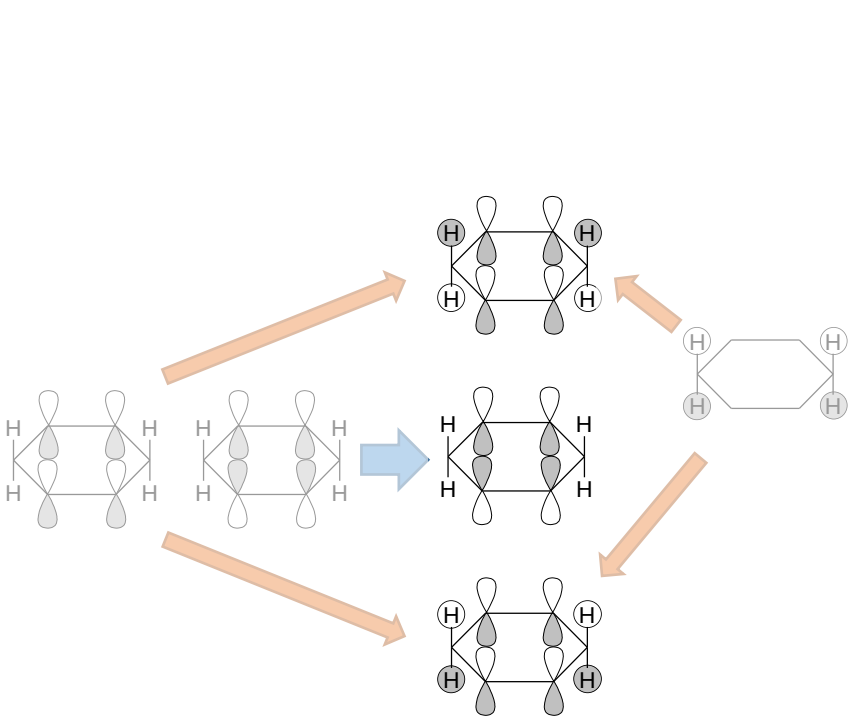
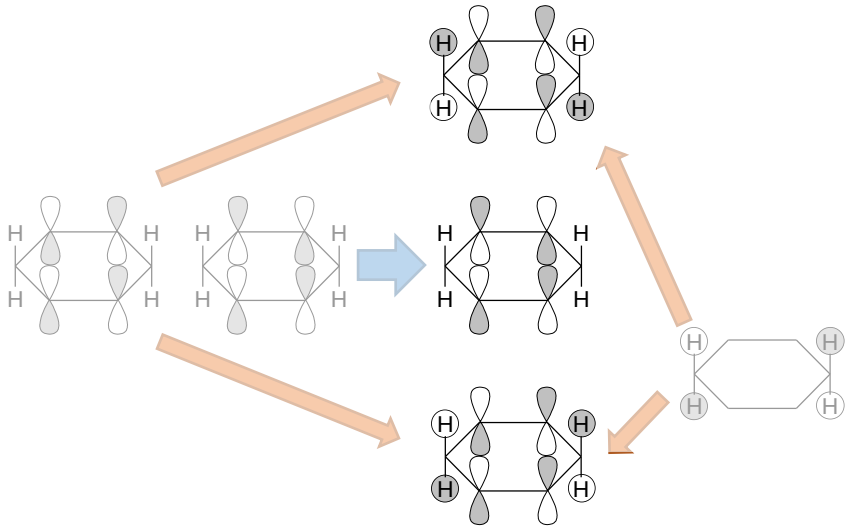
qualitative expectations

# 1,4-cyclohexadiene orbital mixing



symmetric



antisymmetric

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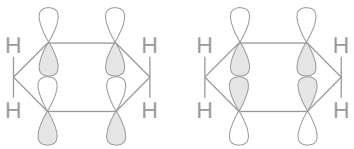
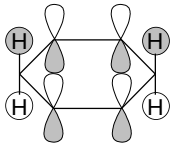
calculated orbitals

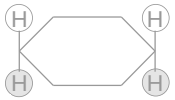
# 1,4-cyclohexadiene orbital mixing

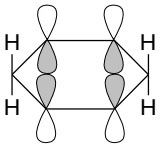




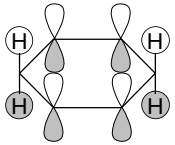


$\pi_4$ HOMO



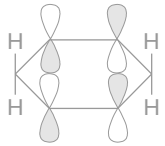


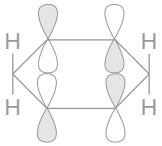
$\pi_3$

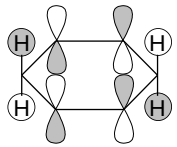


$\pi_1$

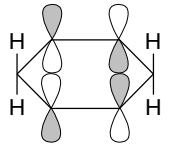
symmetric



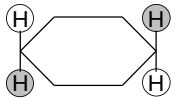




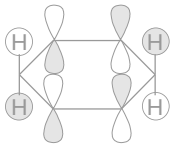
$\pi_6^*$



$\pi_5^*$ LUMO



$\pi_2$



antisymmetric

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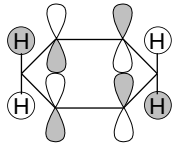
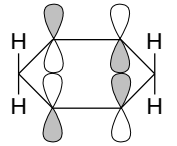
# Stabilization of 1,4-cyclohexadiene – summary

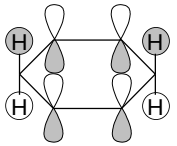


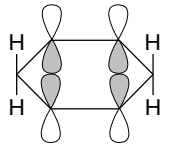
- C-H orbitals can interact with π* orbitals.
- This lowers the energy of the C-H electrons.

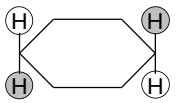
LUMO

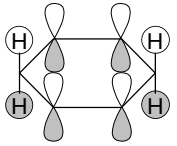


HOMO



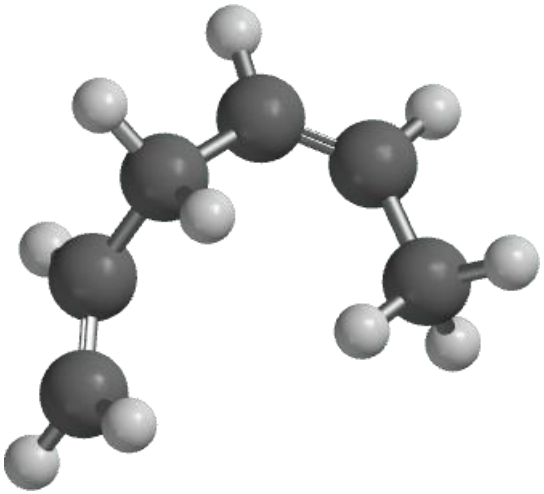


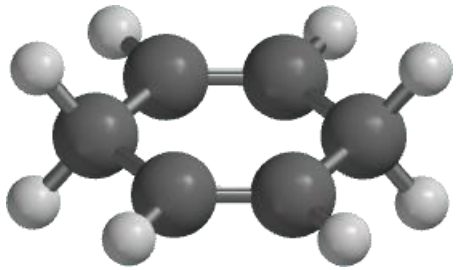




Net stabilization: 3 kJ/mol

1,4-hexadiene: 0 kJ/mol





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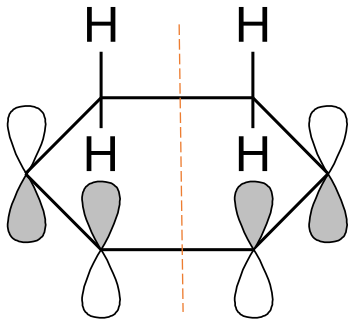
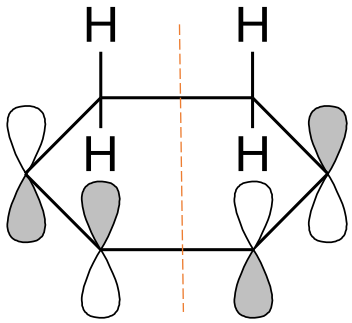
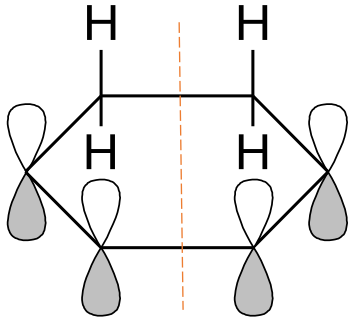
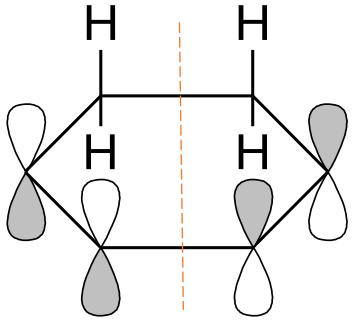
# 1,3-cyclohexadiene: π orbitals




symmetric




antisymmetric

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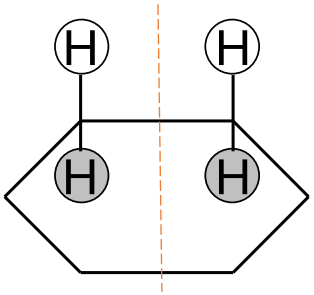
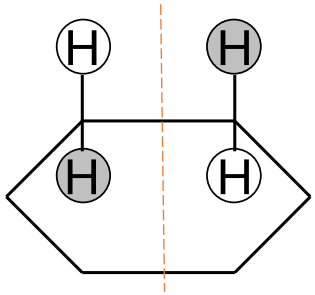
# 1,3-cyclohexadiene: C-H orbitals with π symmetry




symmetric




antisymmetric

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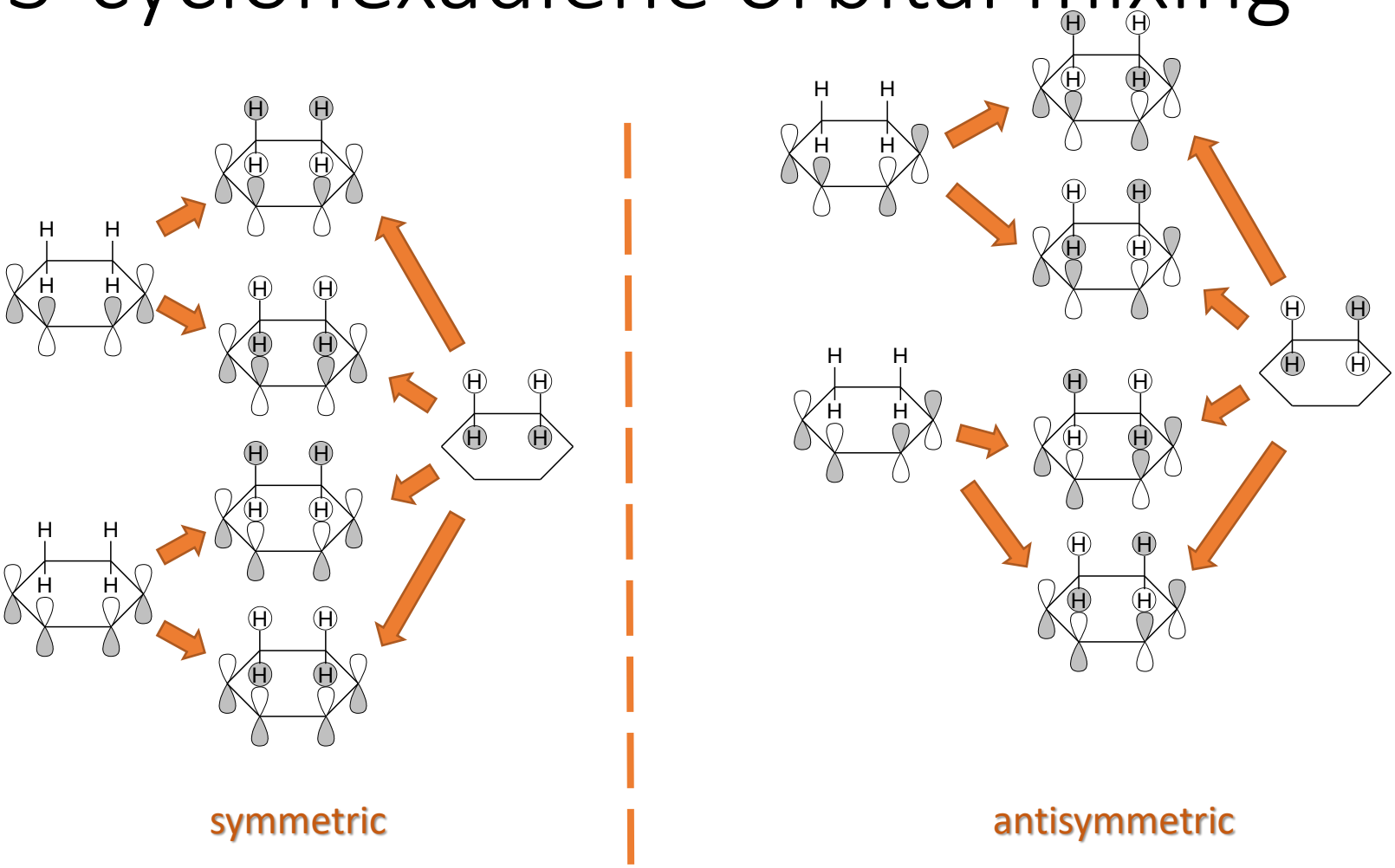
# 1,3-cyclohexadiene orbital mixing

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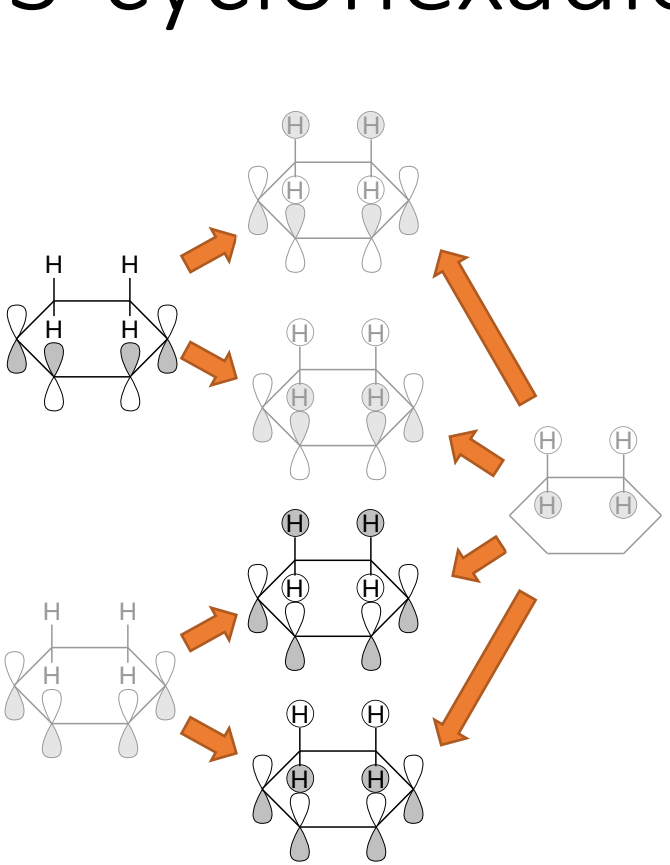
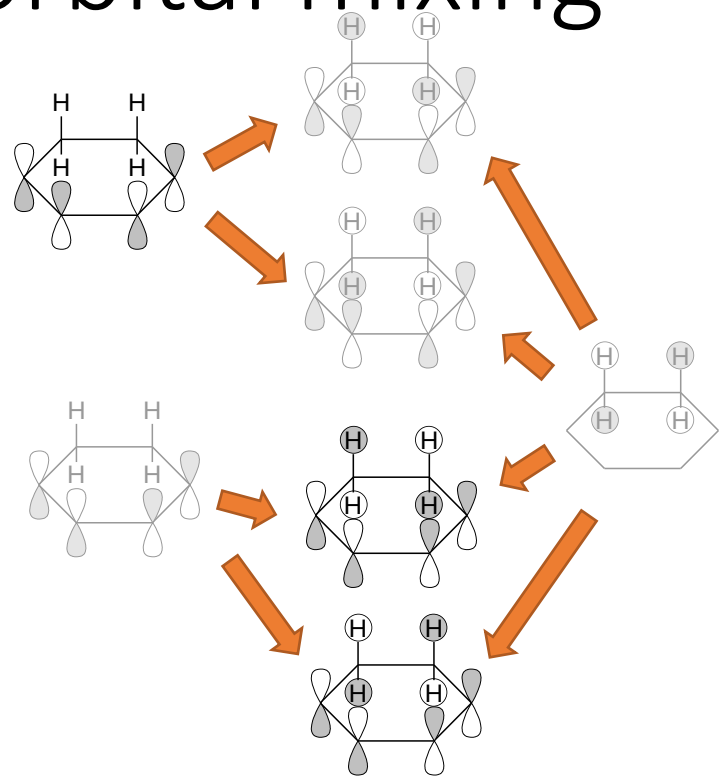
qualitative expectations

# 1,3-cyclohexadiene orbital mixing



symmetric



antisymmetric

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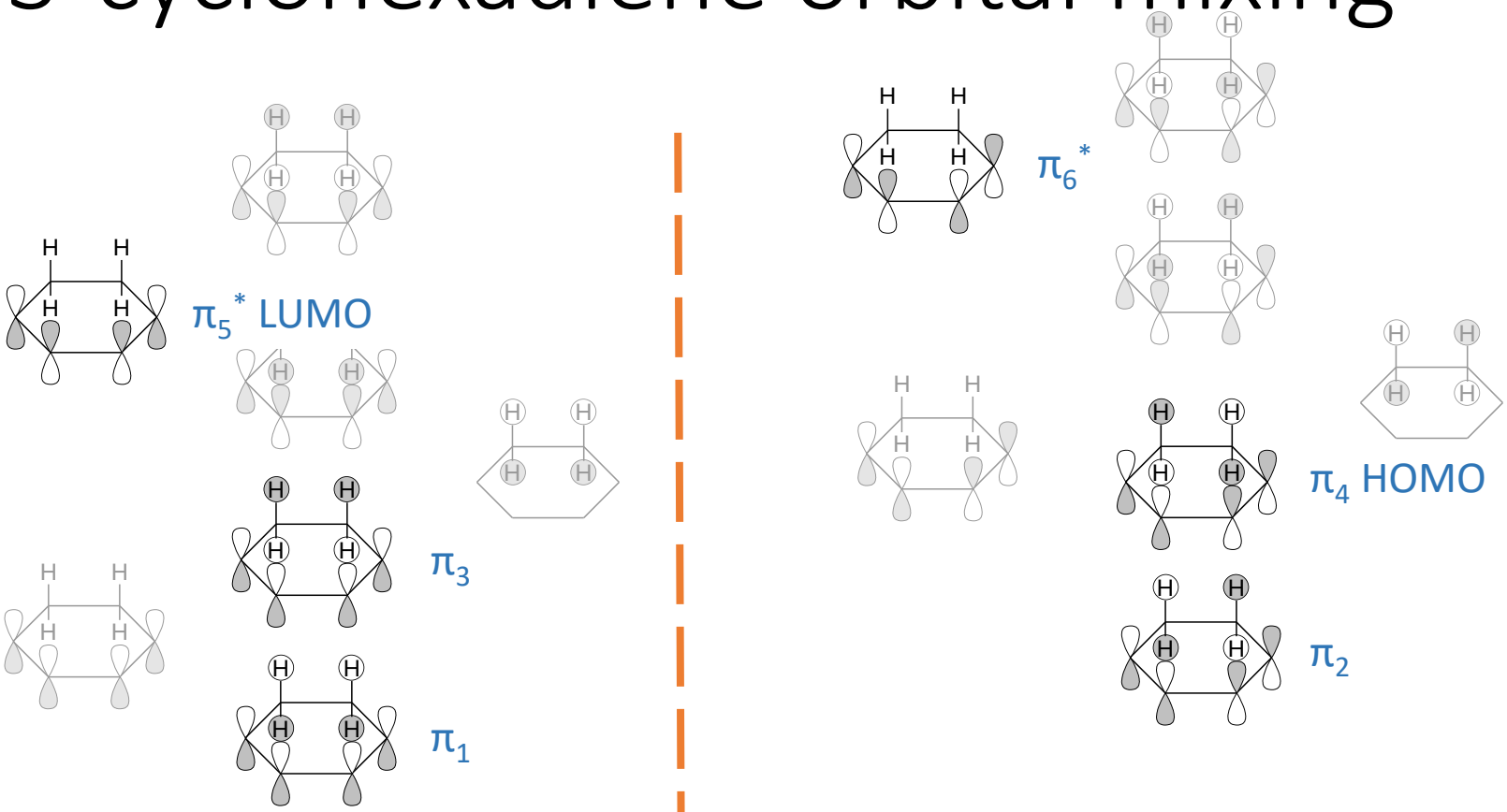
calculated orbitals

# 1,3-cyclohexadiene orbital mixing

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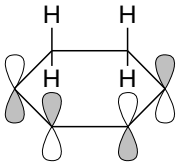
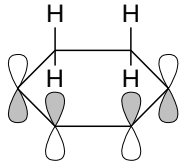
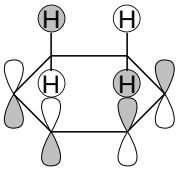
# Destabilization of 1,3-cyclohexadiene – summary

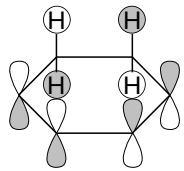


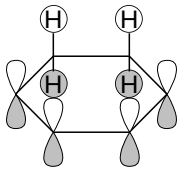
LUMO



HOMO





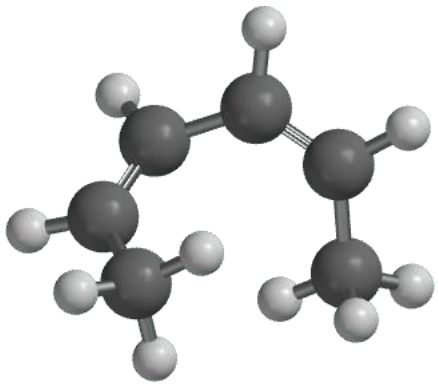


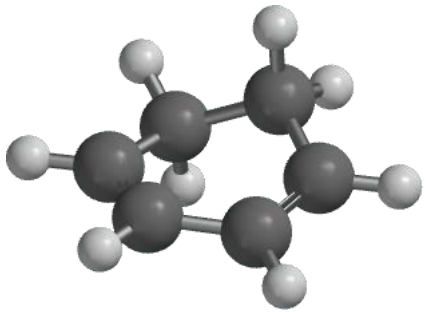
- C-H orbitals can/do not interact well with $\pi^*$ orbitals, so their energy is not lowered.
- π orbitals are pushed up in energy.
- π-conjugation lowers overall energy.

  Net stabilization: 12 kJ/mol

  2,4-hexadiene: 20 kJ/mol

  Side note: butadiene stabilization = 15 kJ/mol





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# Conclusions

- Qualitative perturbation theory is a helpful technique when teaching and using qualitative MO theory.
- Students find it helpful in understanding aspects of conjugation (and hyperconjugation).
- Allows us to explain, without computation or equations, the anomalous stabilities of cyclohexadienes.

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# Acknowledgements


- CEM 222 class
- Bluffton University
- cCWCS for BCCE registration reimbursement

  (not for this particular talk)



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