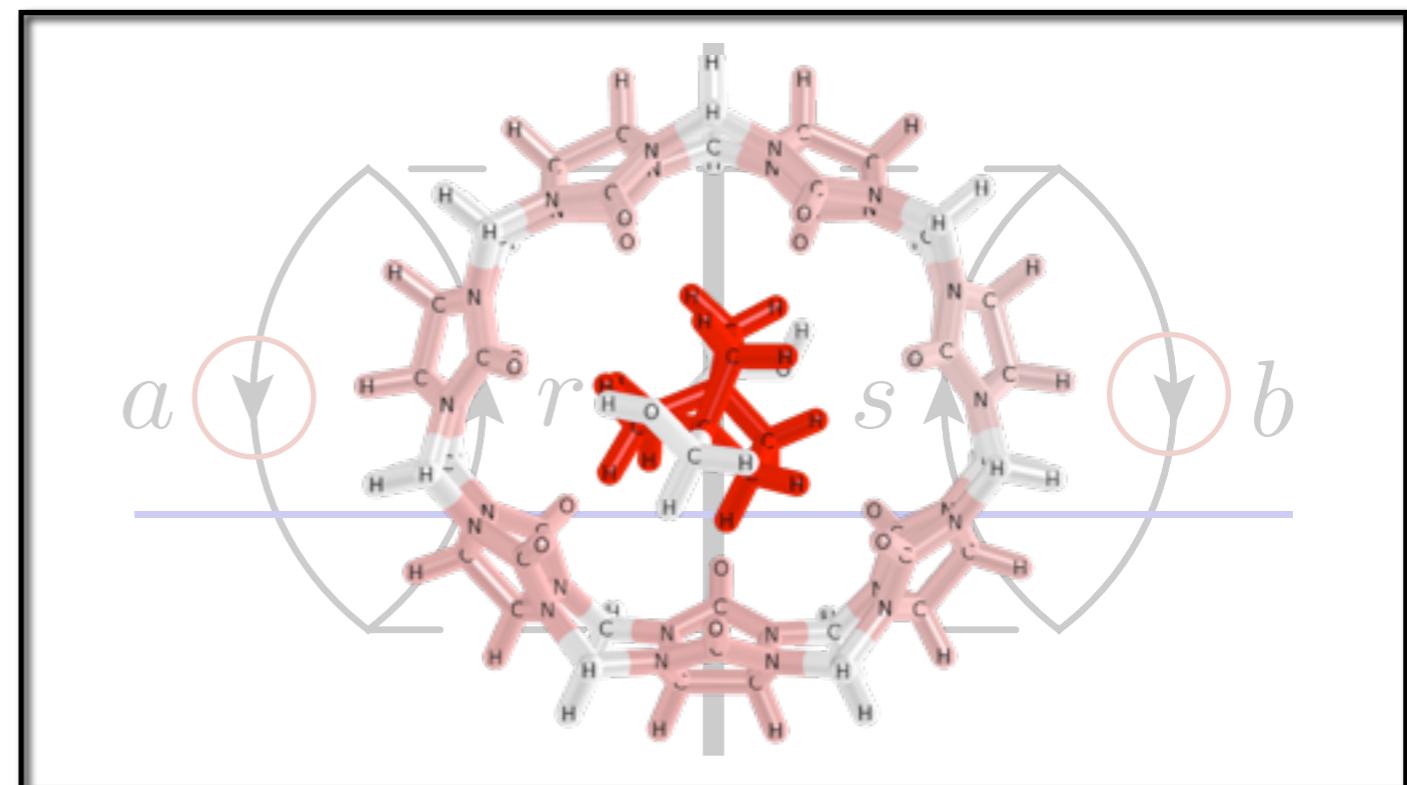


# PSI4 for SAPT Research

## A-SAPT/F-SAPT/I-SAPT



Robert M. Parrish  
November 14, 2014



# **Spatial Partitioning of SAPT Extracting Chemically Useful Information From Interaction Energy Computations**

# Spatially Partitioned SAPT Philosophy

B. Jeziorski, R. Moszynski, and K. Szalewicz, *Chem. Rev.* **94**, 1887 (1994).

W. Heisenberg, *Physics and Beyond: Encounters and Conversations*, Harper and Row, New York, 1972.

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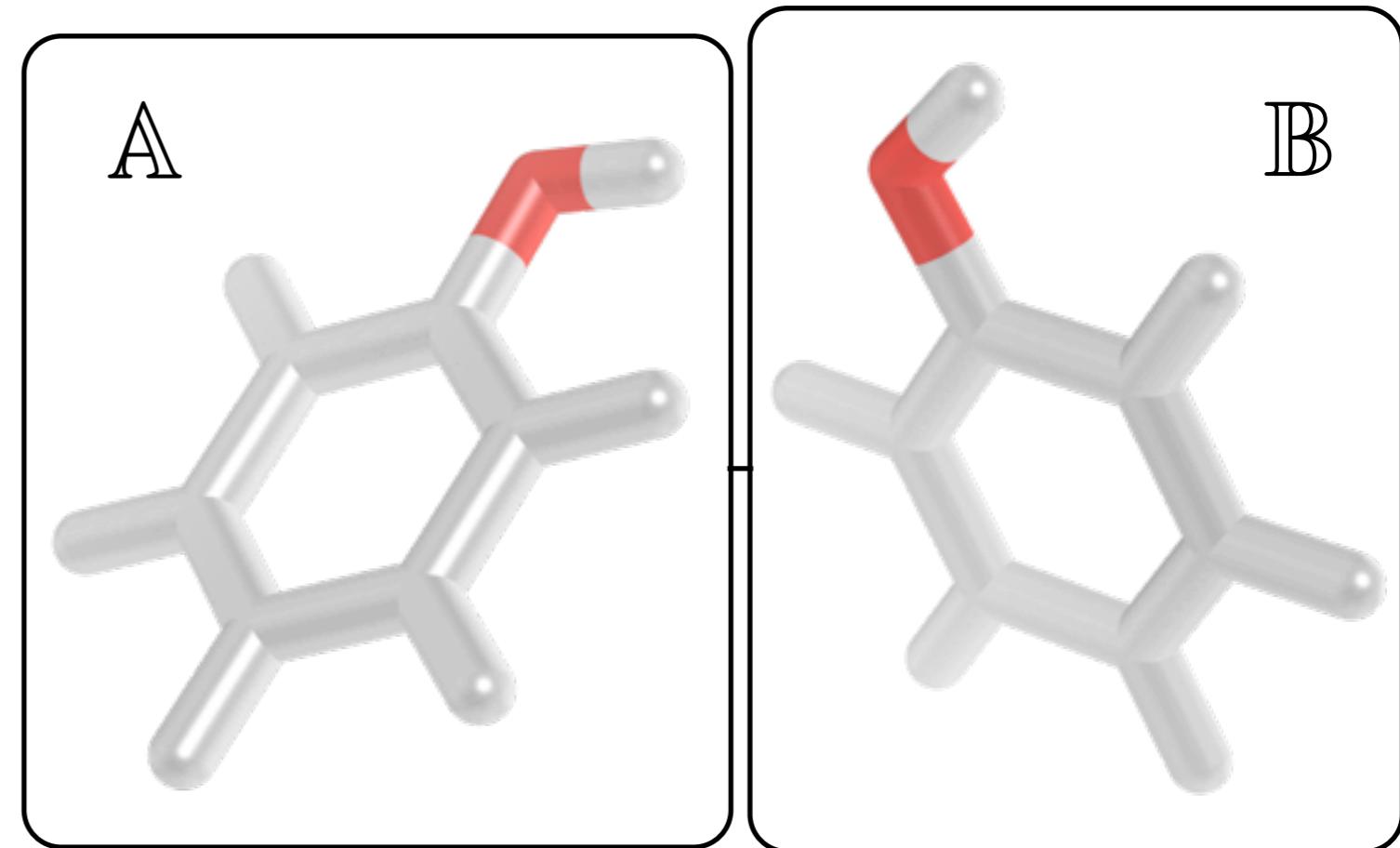


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## Partitioned SAPT Motivation:



$$E_{\text{int}}$$

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## Partitioned SAPT Motivation:

Order-2:  $E_{\text{int}} \rightarrow E_{\text{int}}^{\text{AB}}$



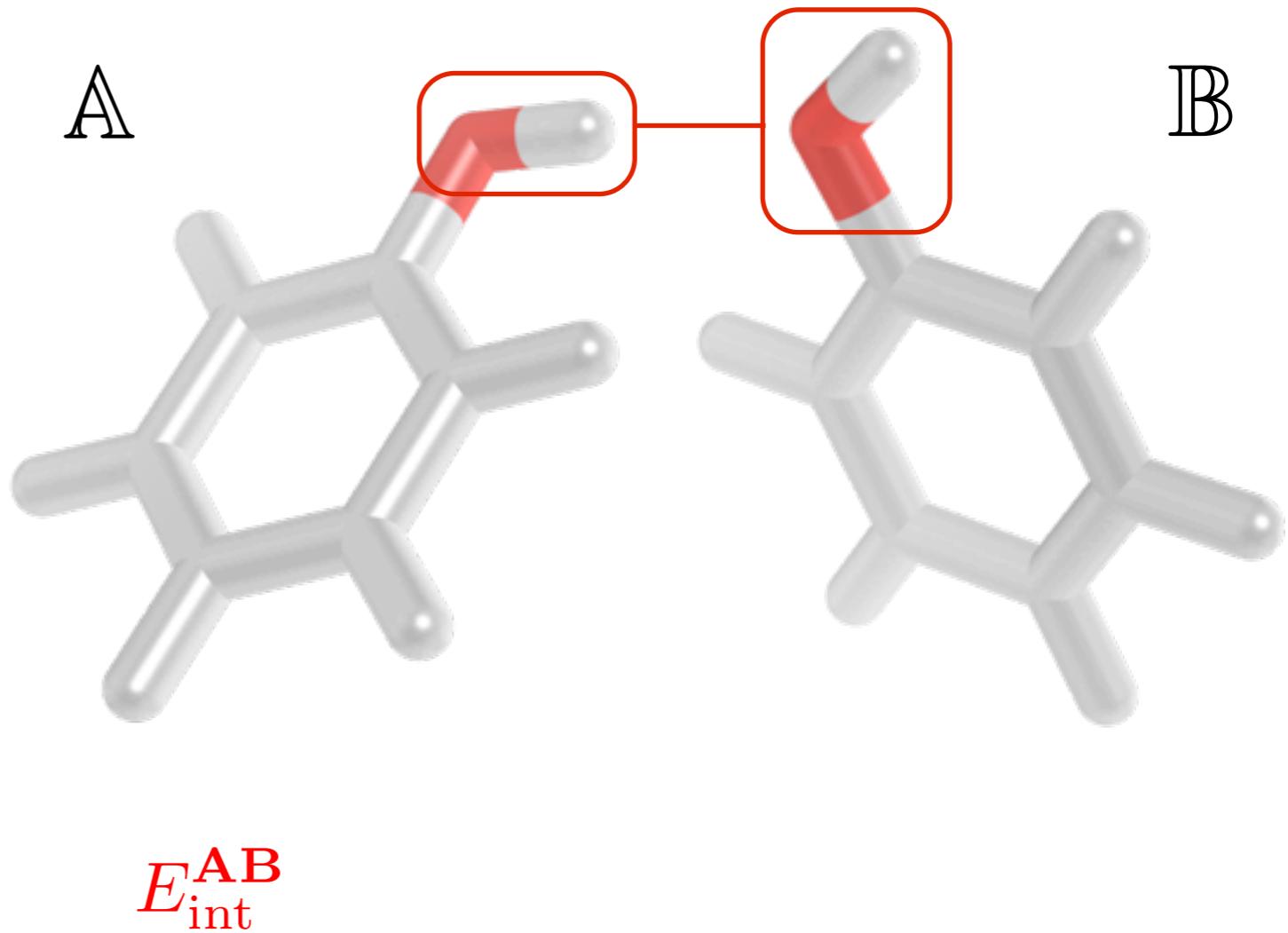
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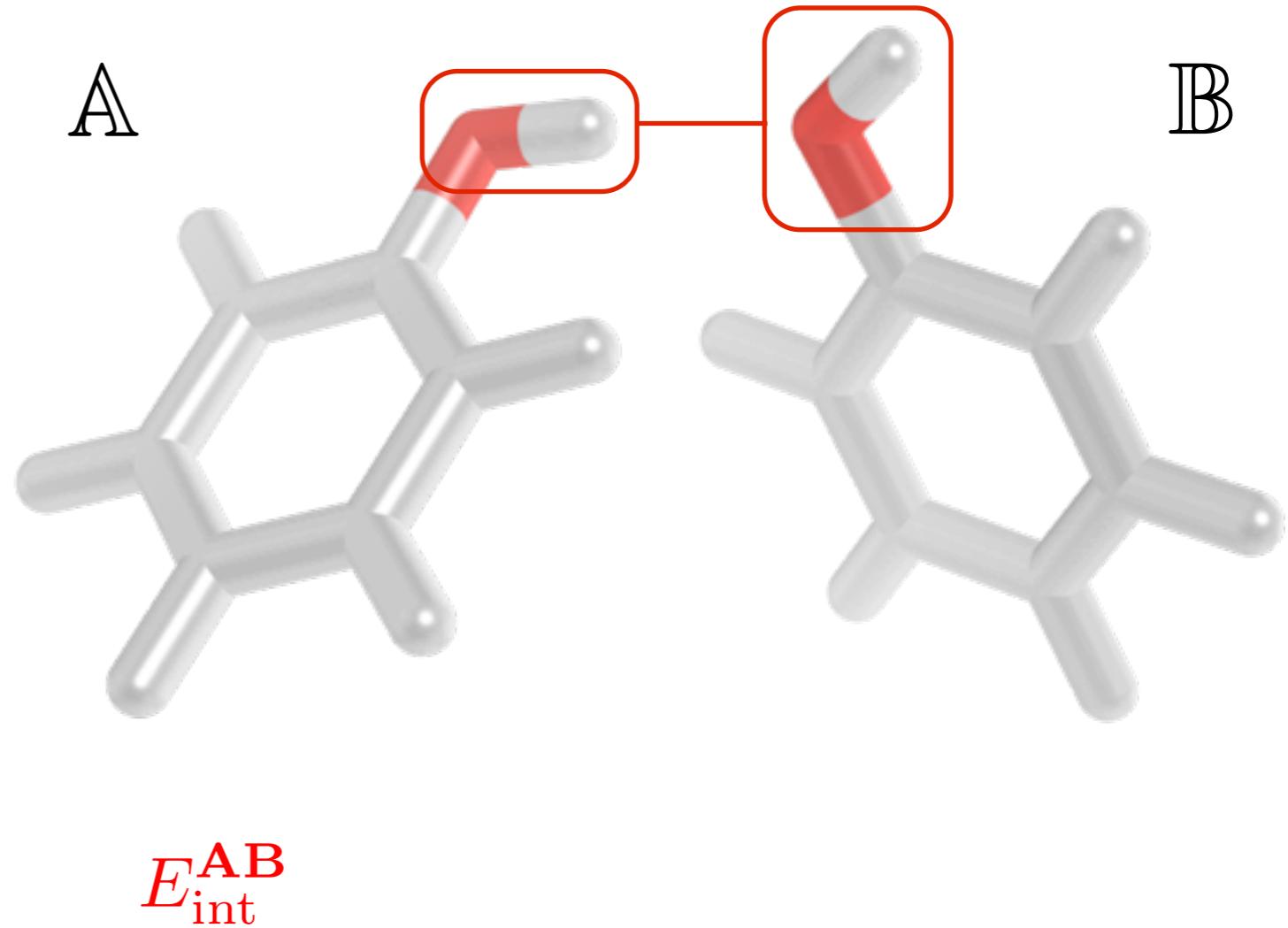
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## Partitioned SAPT Motivation:

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Order-1:  $E_{\text{int}}^{\text{A}} = \sum_{\text{B}} E_{\text{int}}^{\text{AB}}$



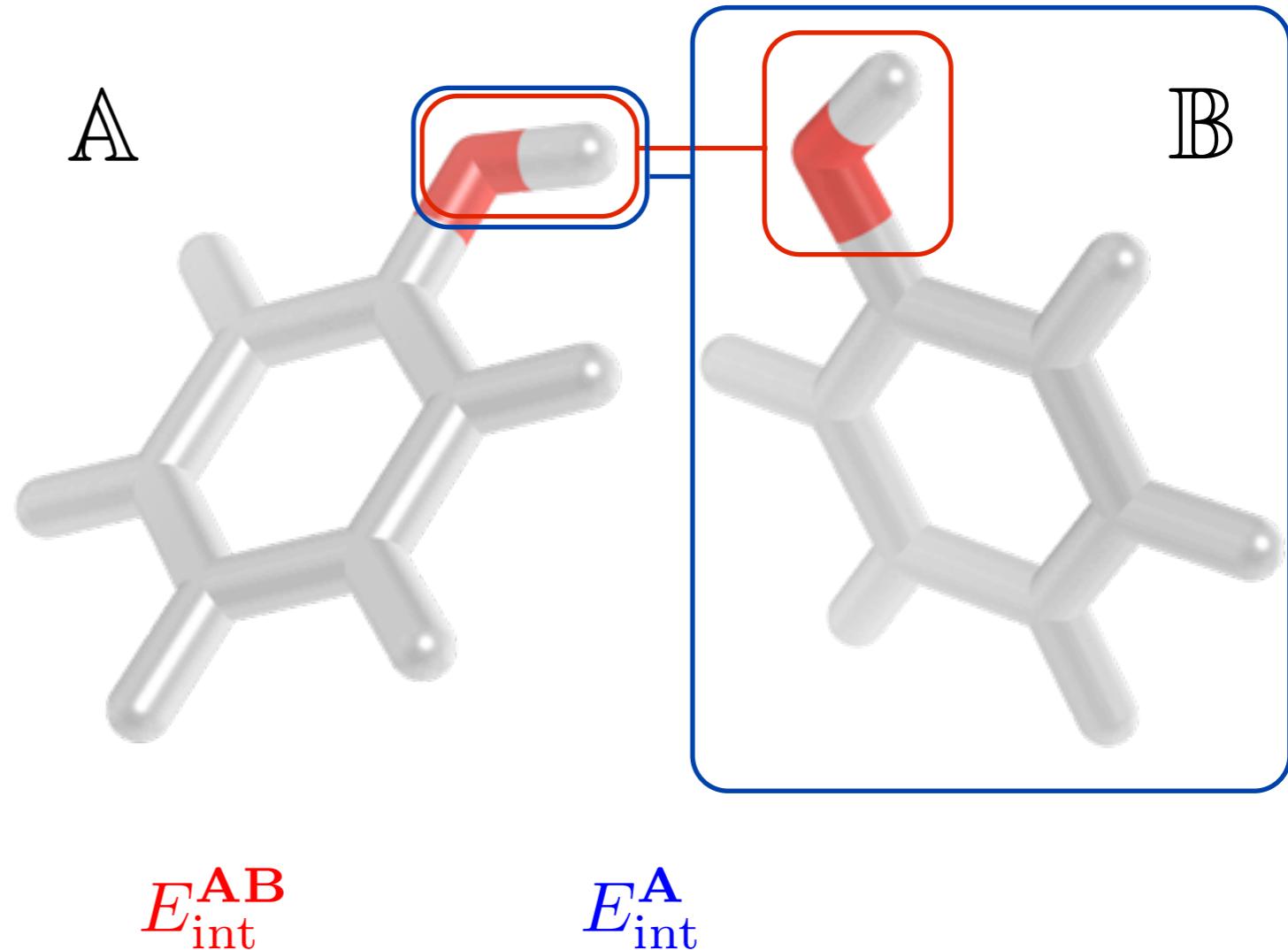
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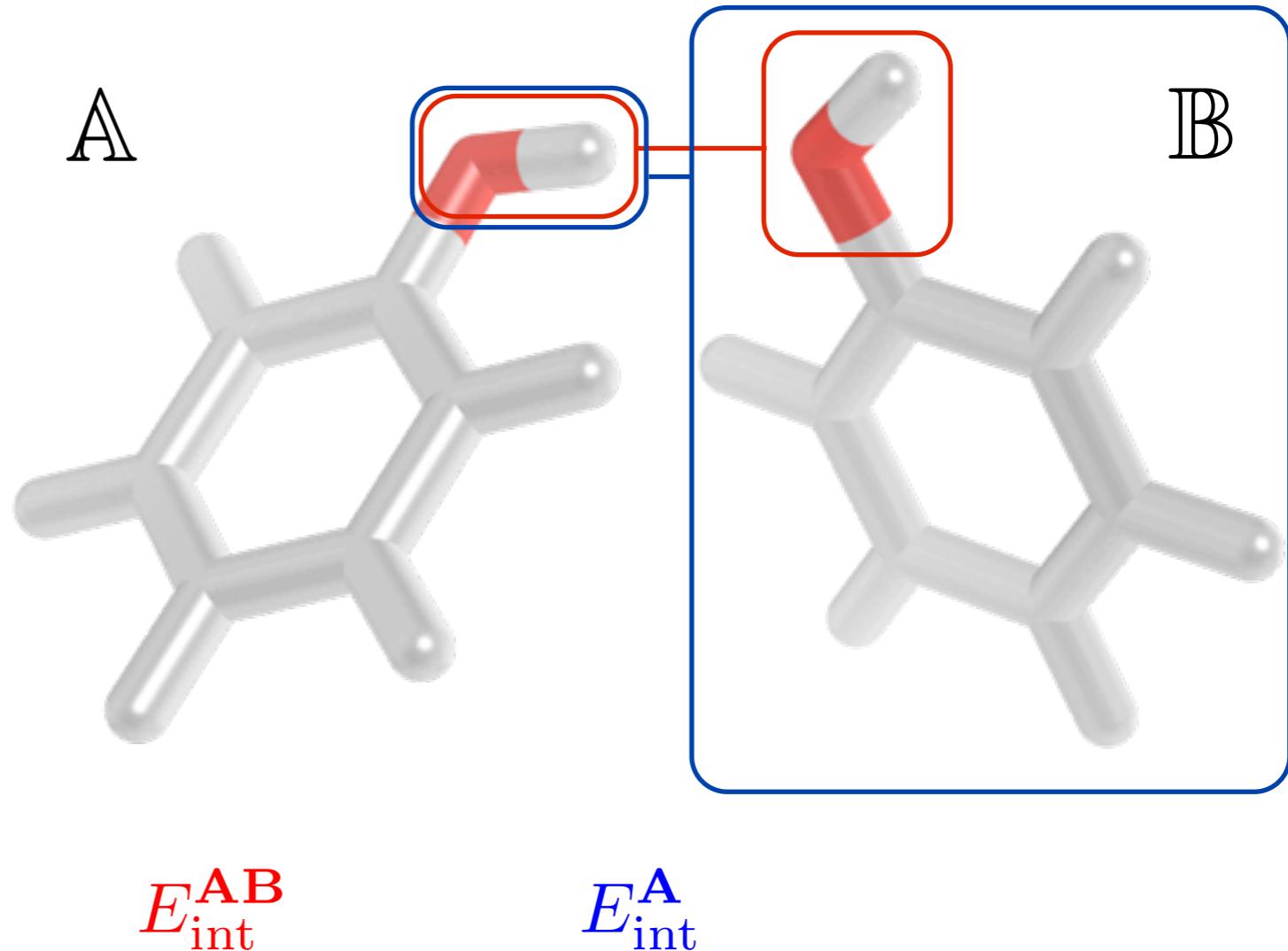
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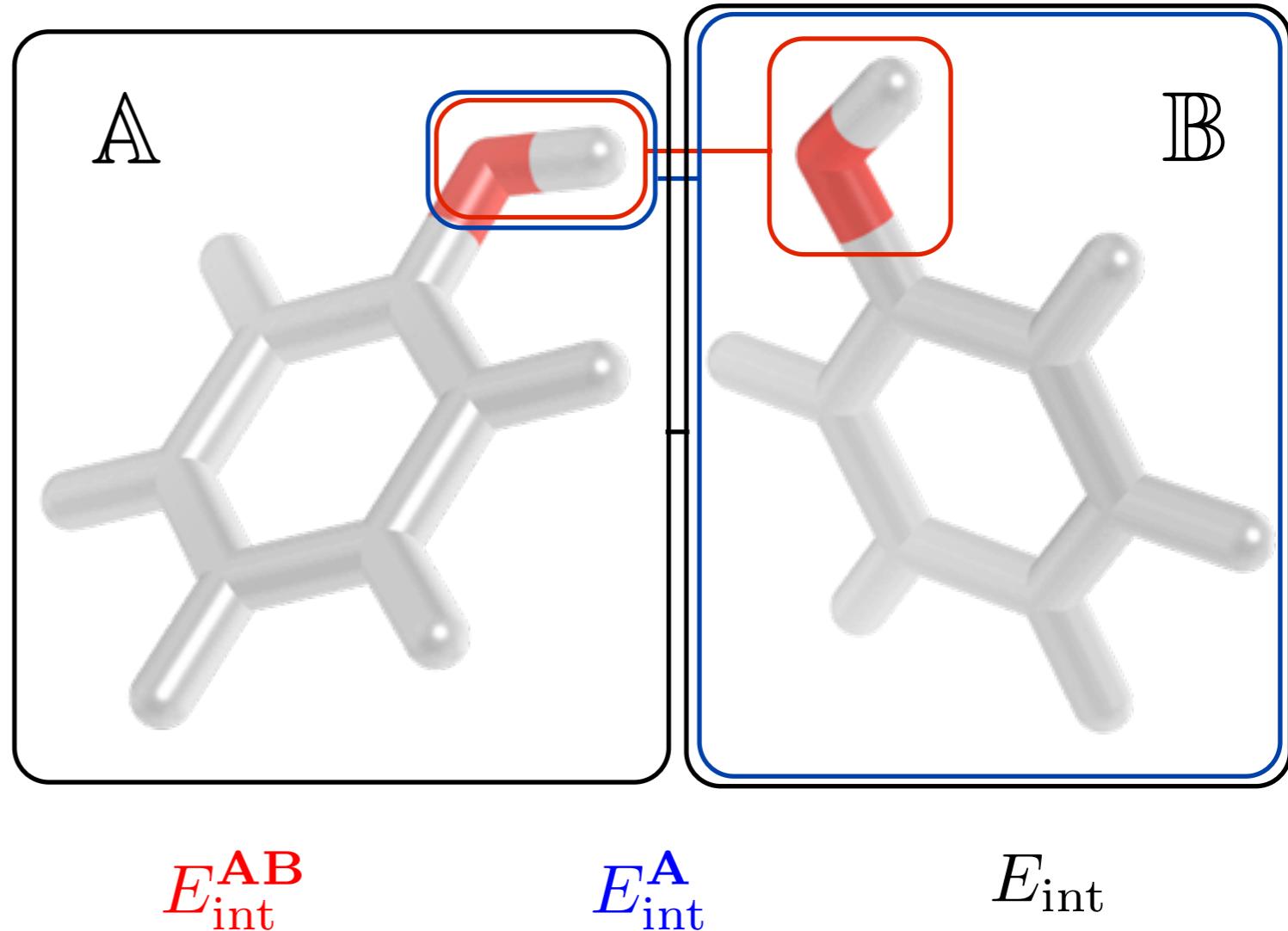
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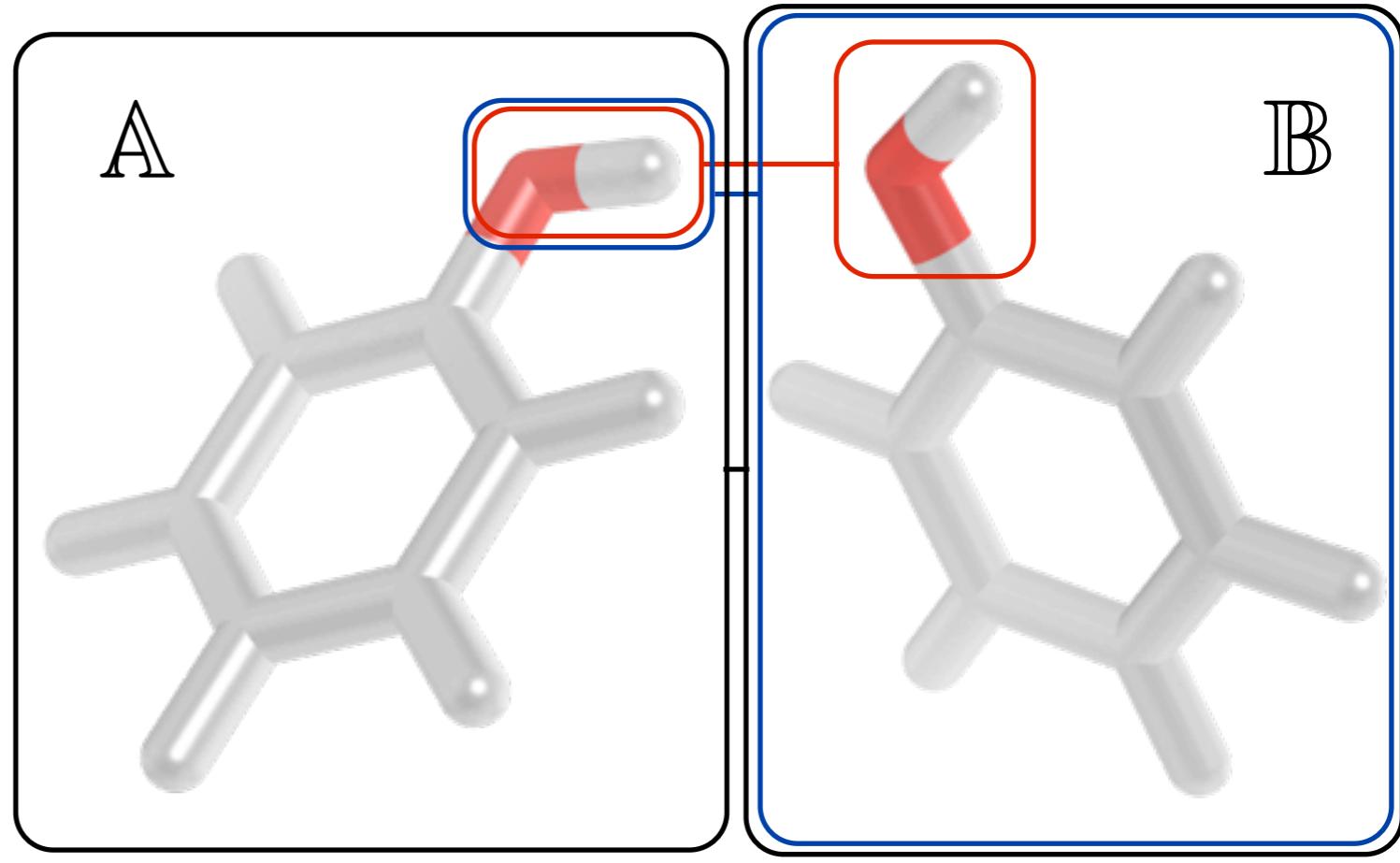
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Order-0:  $E_{\text{int}} = \sum_{\text{A}} E_{\text{int}}^{\text{A}}$



$$E_{\text{int}}^{\text{AB}}$$

$$E_{\text{int}}^{\text{A}}$$

$$E_{\text{int}}$$

## Caveat:

"We must be clear that when it comes to atoms, language can be used only as in poetry. The poet, too, is not nearly so concerned with describing facts as with creating images and establishing mental connections."

- Niels Bohr to Werner Heisenberg in their first meeting, Summer 1920

B. Jeziorski, R. Moszynski, and K. Szalewicz, *Chem. Rev.* **94**, 1887 (1994).

W. Heisenberg, *Physics and Beyond: Encounters and Conversations*, Harper and Row, New York, 1972.

# Spatially Partitioned SAPT Development

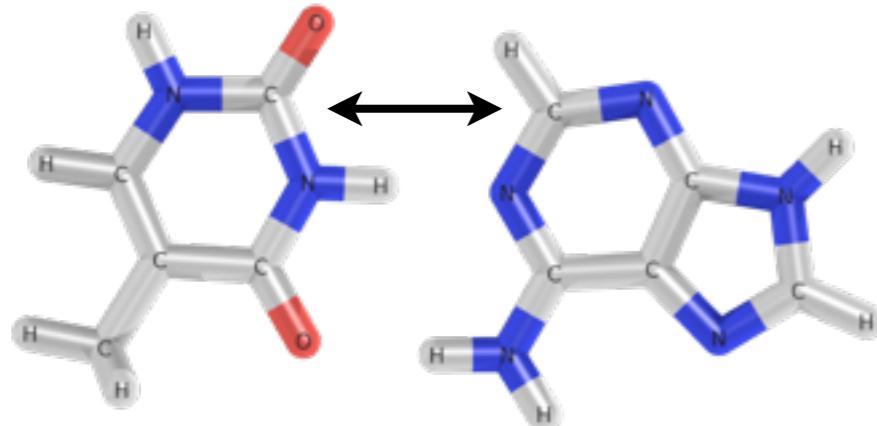
B. Jeziorski et al., in *METECC94* (1993).

E. G. Hohenstein and C. D. Sherrill, *J. Chem. Phys.* **133**, 014101 (2010).

E. Papajak, J. Zheng, X. Xu, H. R. Leverenz, and D. G. Truhlar, *J. Chem. Theory Comput.* **7**, 3027 (2011).

# Spatially Partitioned SAPT Development

1) Allow the many-body interaction to occur naturally (SAPT0/jDZ for now).



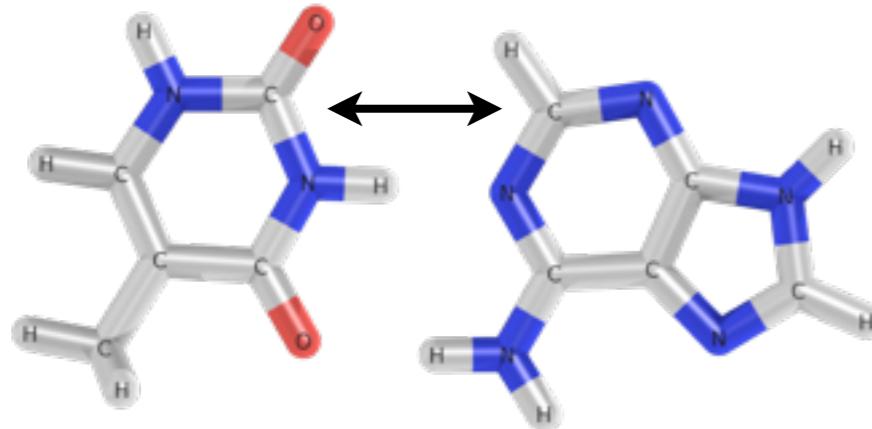
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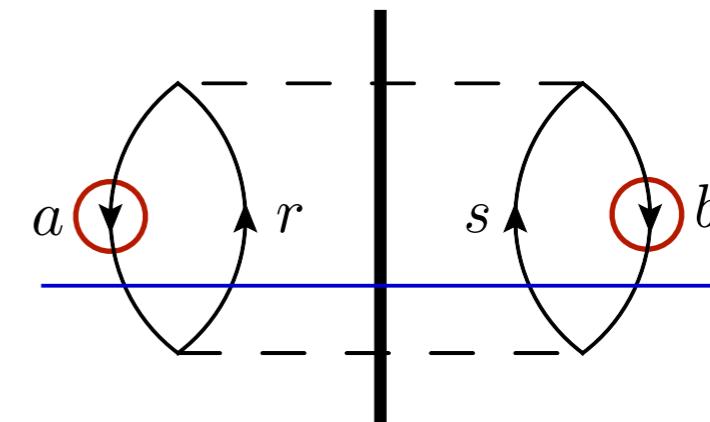
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1) Allow the many-body interaction to occur naturally (SAPT0/jDZ for now).



2) Identify two key occupied bodies in each many-body interaction term.



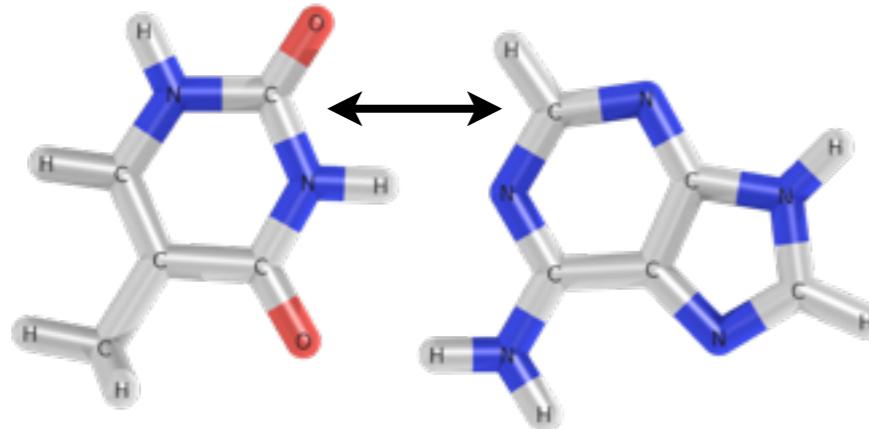
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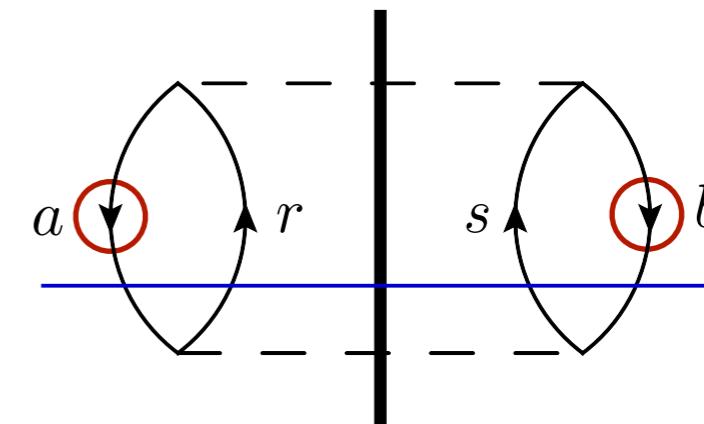
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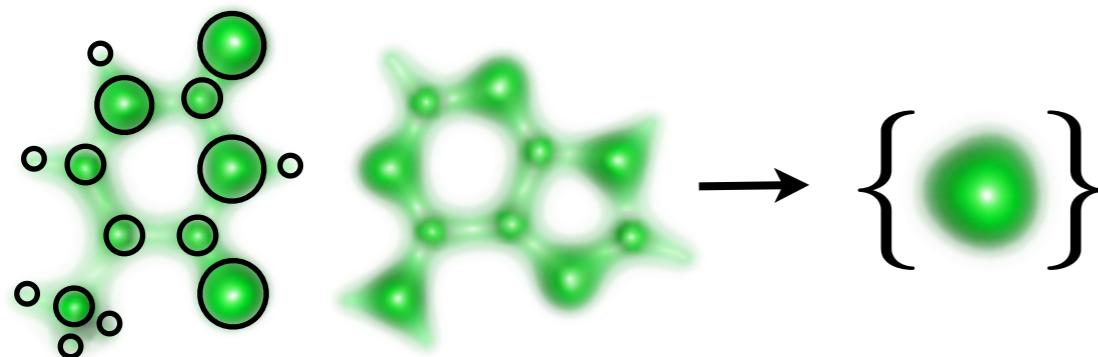
1) Allow the many-body interaction to occur naturally (SAPT0/jDZ for now).



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3) Perform key two-body occupied summations with local quasiparticles.



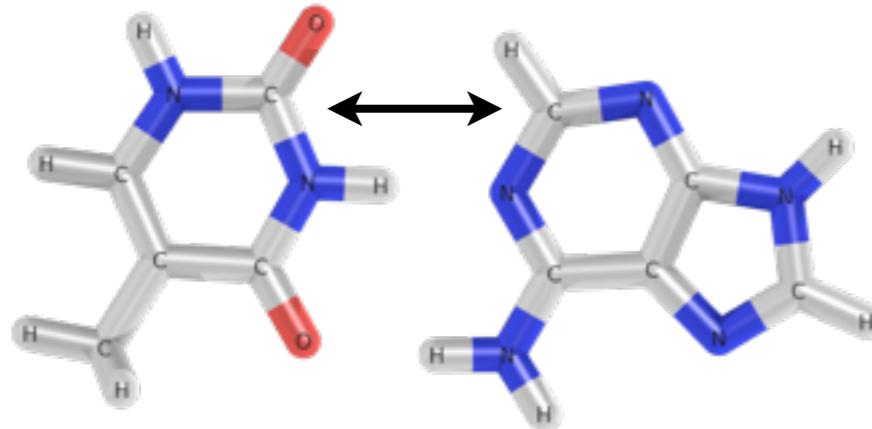
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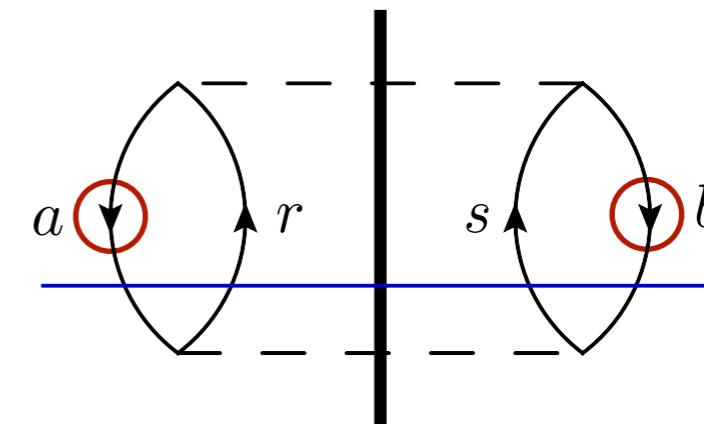
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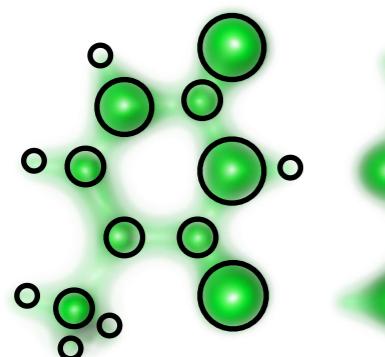
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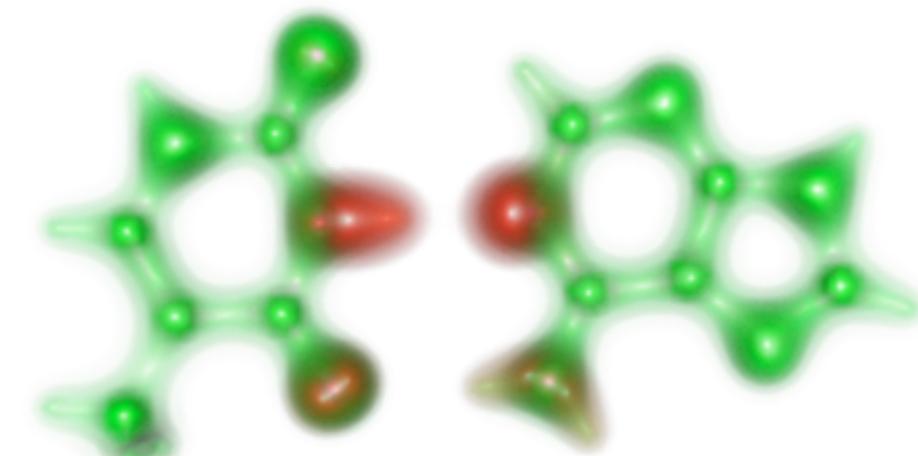
2) Identify two key occupied bodies in each many-body interaction term.



3) Perform key two-body occupied summations with local quasiparticles.



4) Analyze and visualize results.



B. Jeziorski et al., in *METECC94* (1993).

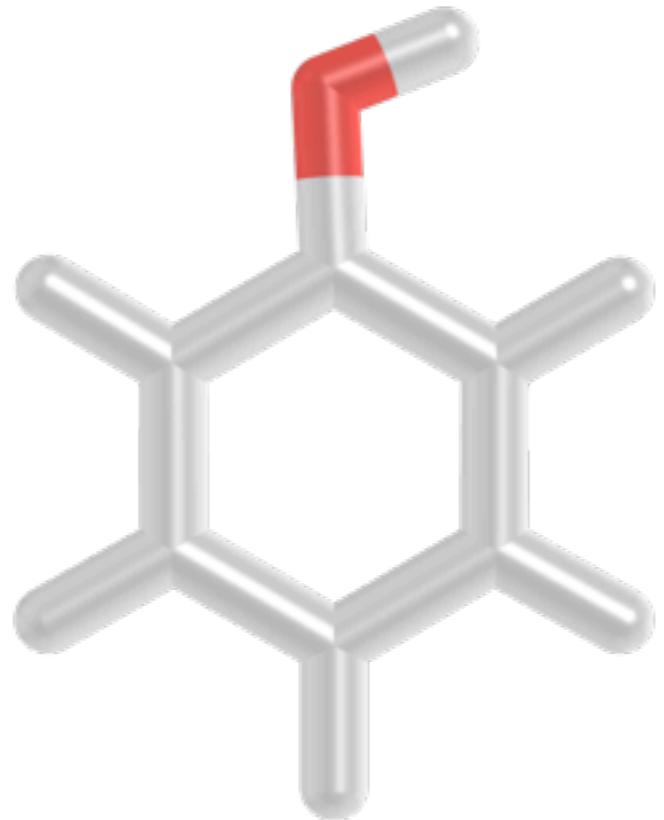
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# Functional Groups as Local Quasiparticles (F-SAPT)

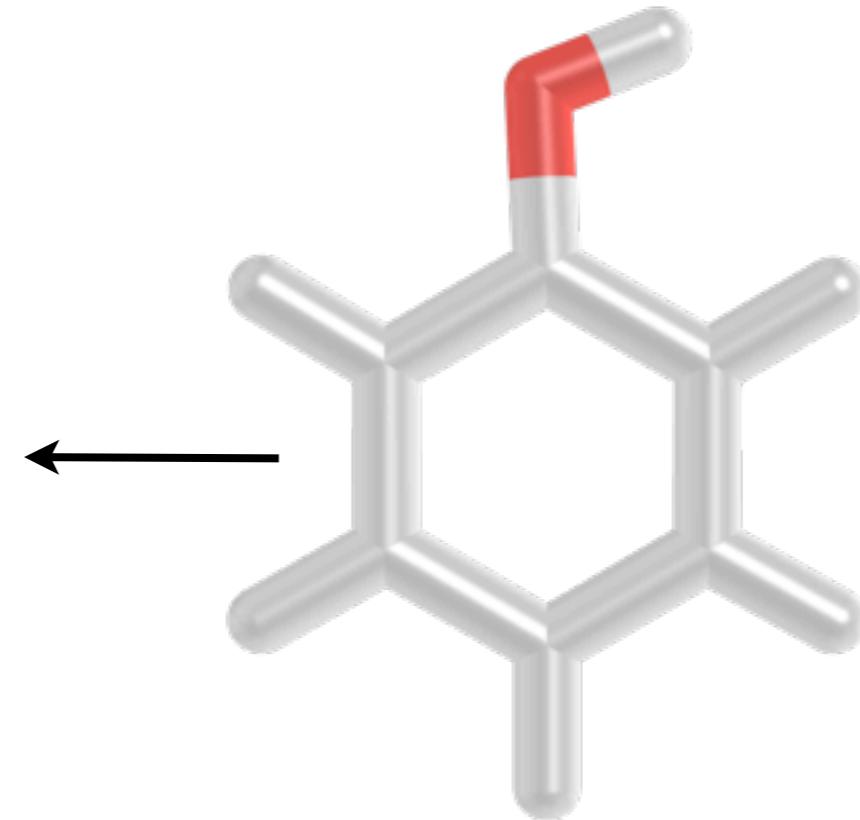
R.M. Parrish, T.M. Parker, and C.D. Sherrill, *J. Chem. Theory Comput.* **10**, 4417 (2014).

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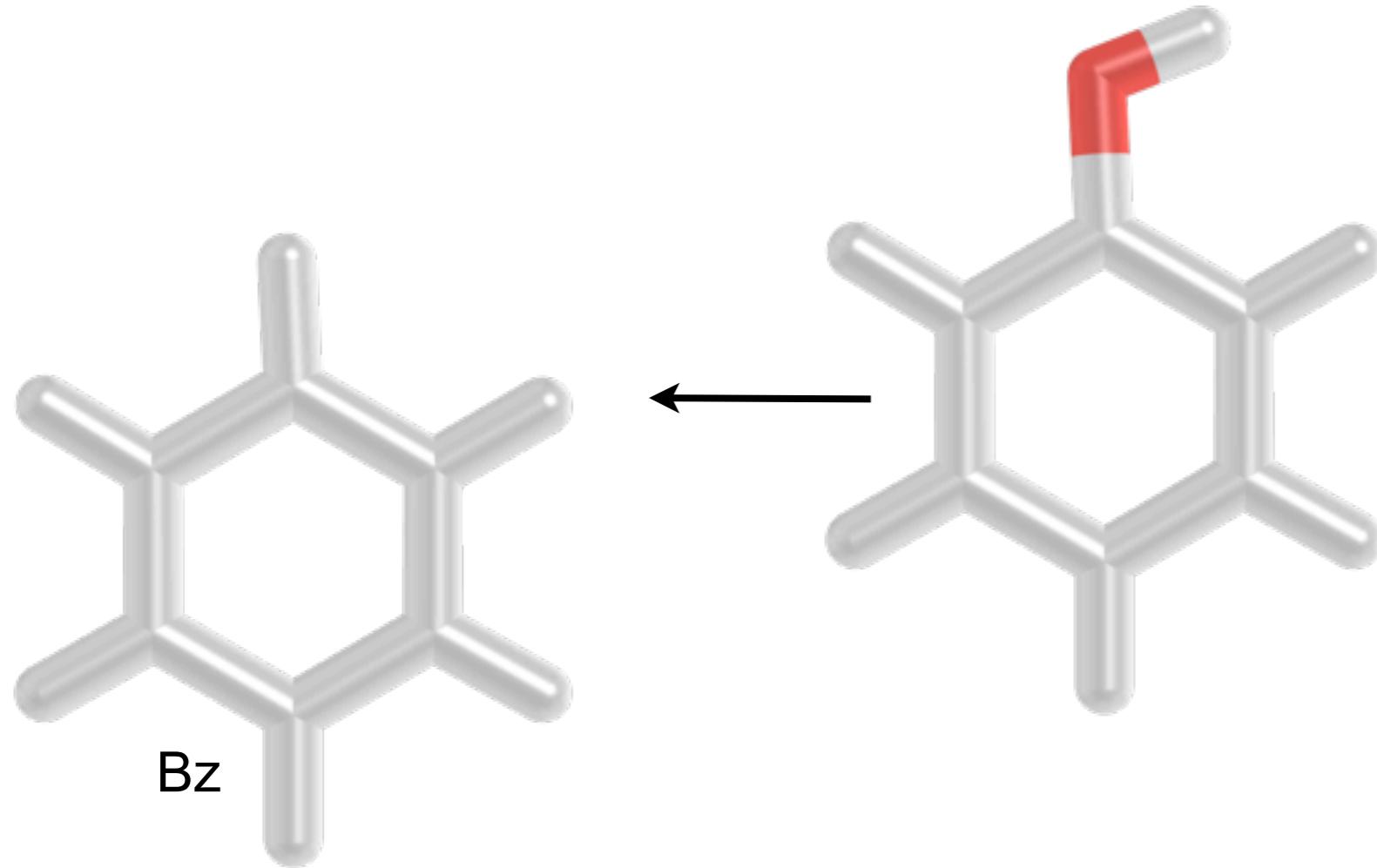
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Cut-Cap Partition:



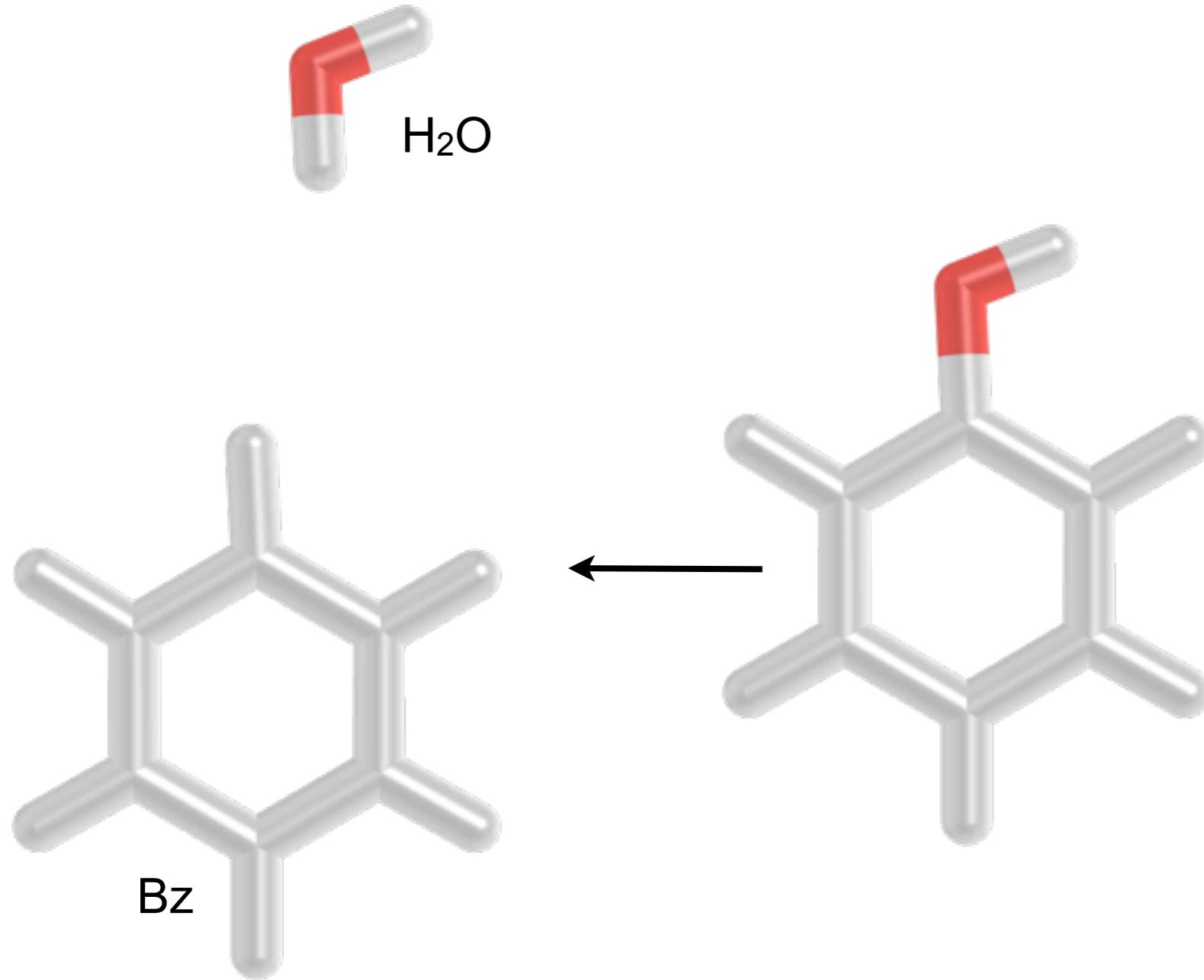
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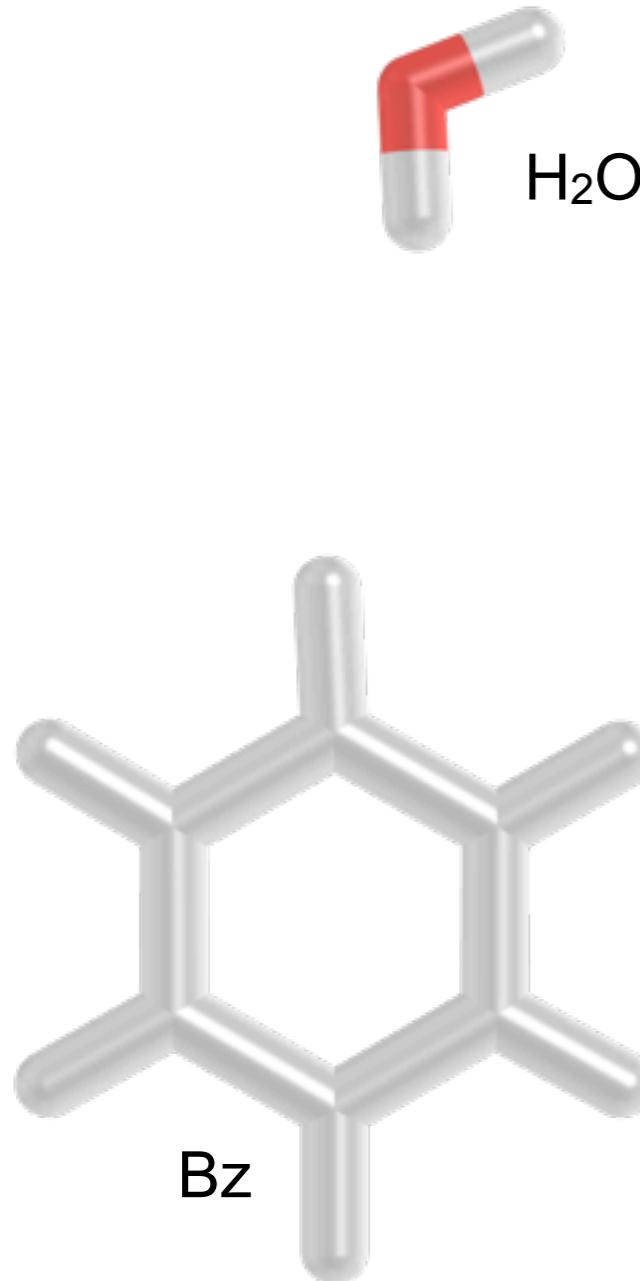
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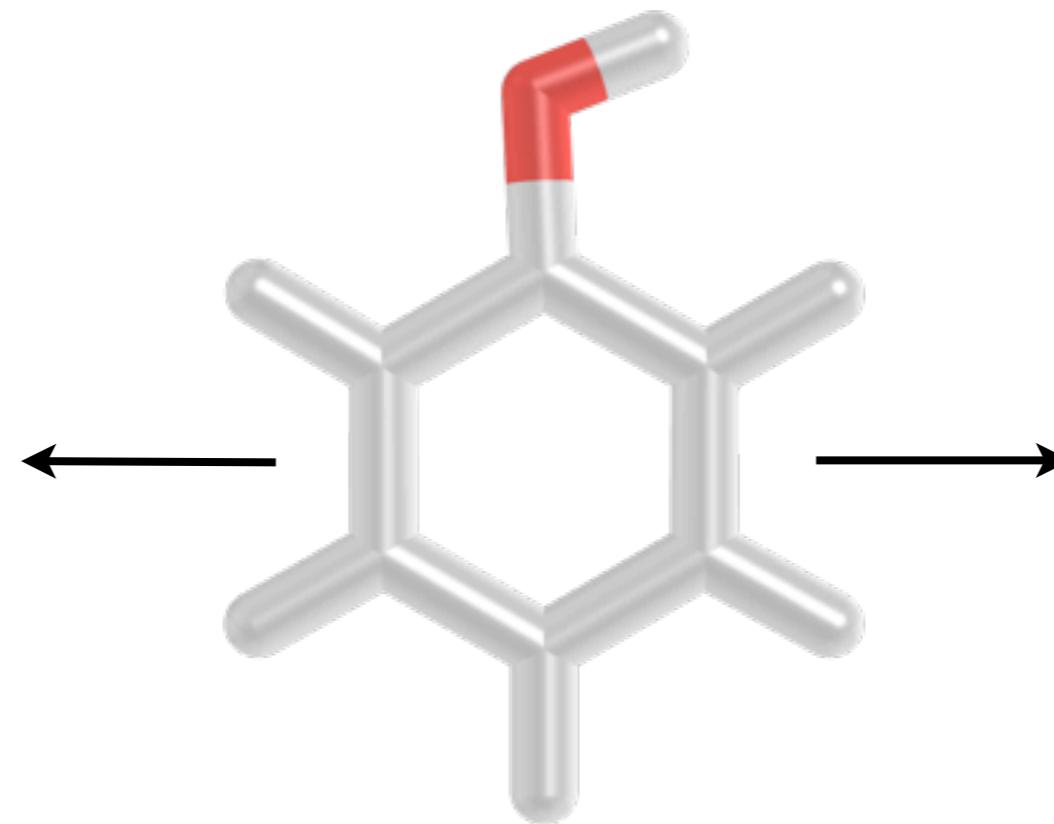


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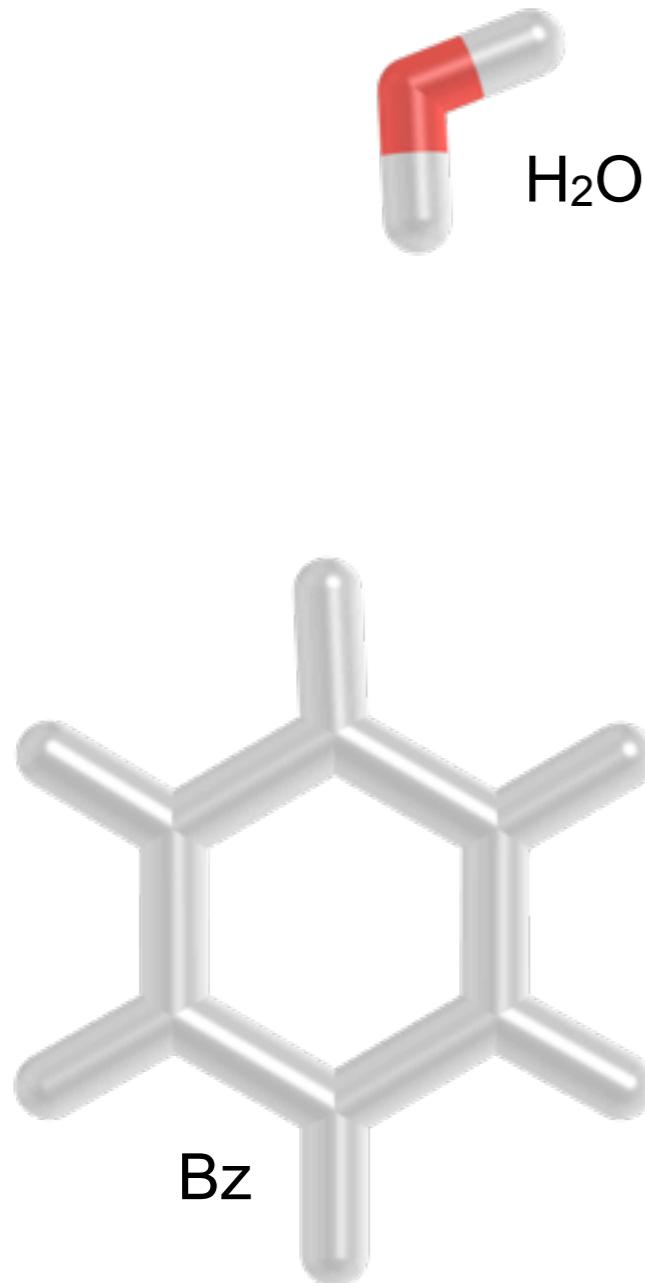


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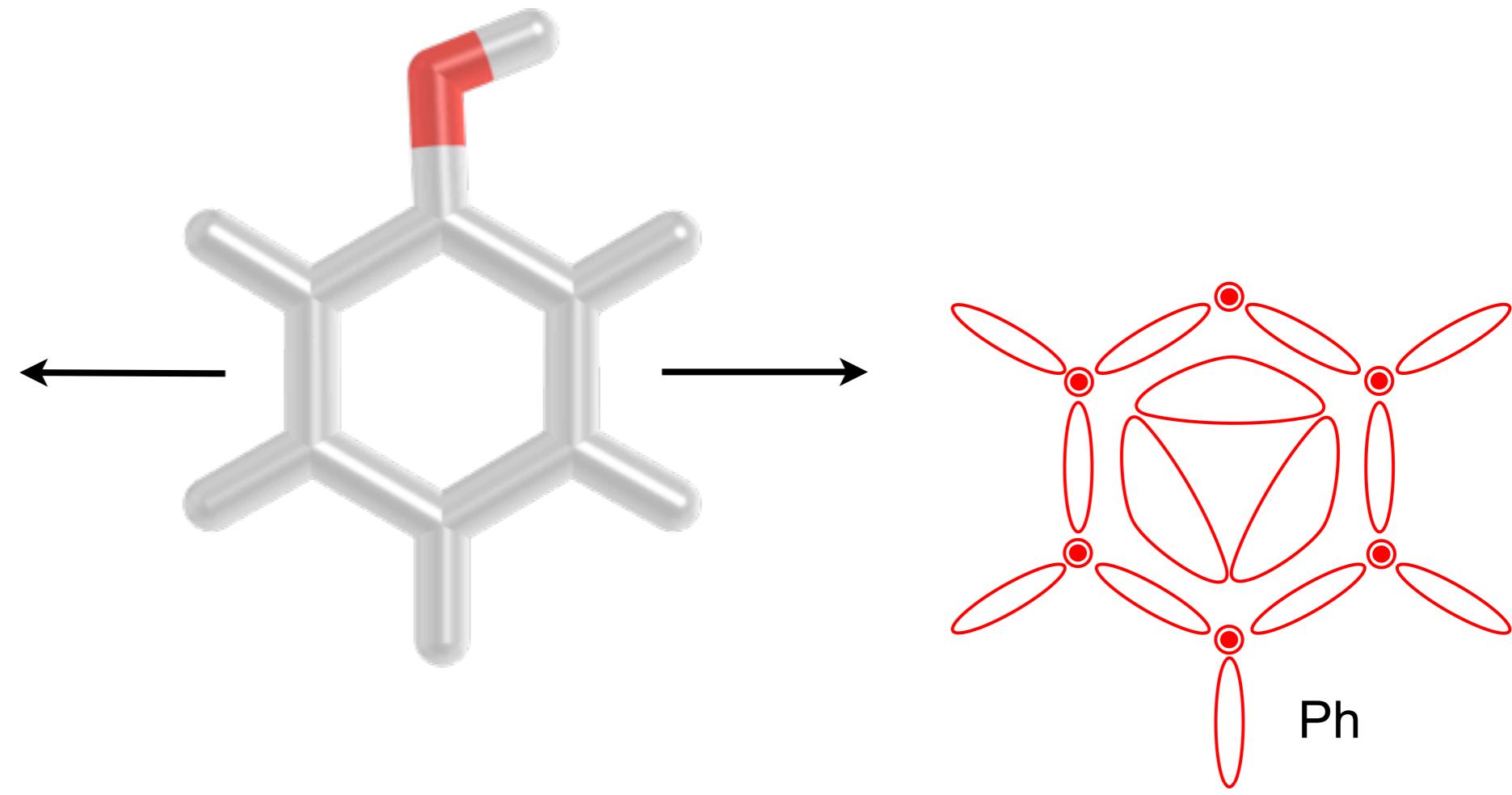


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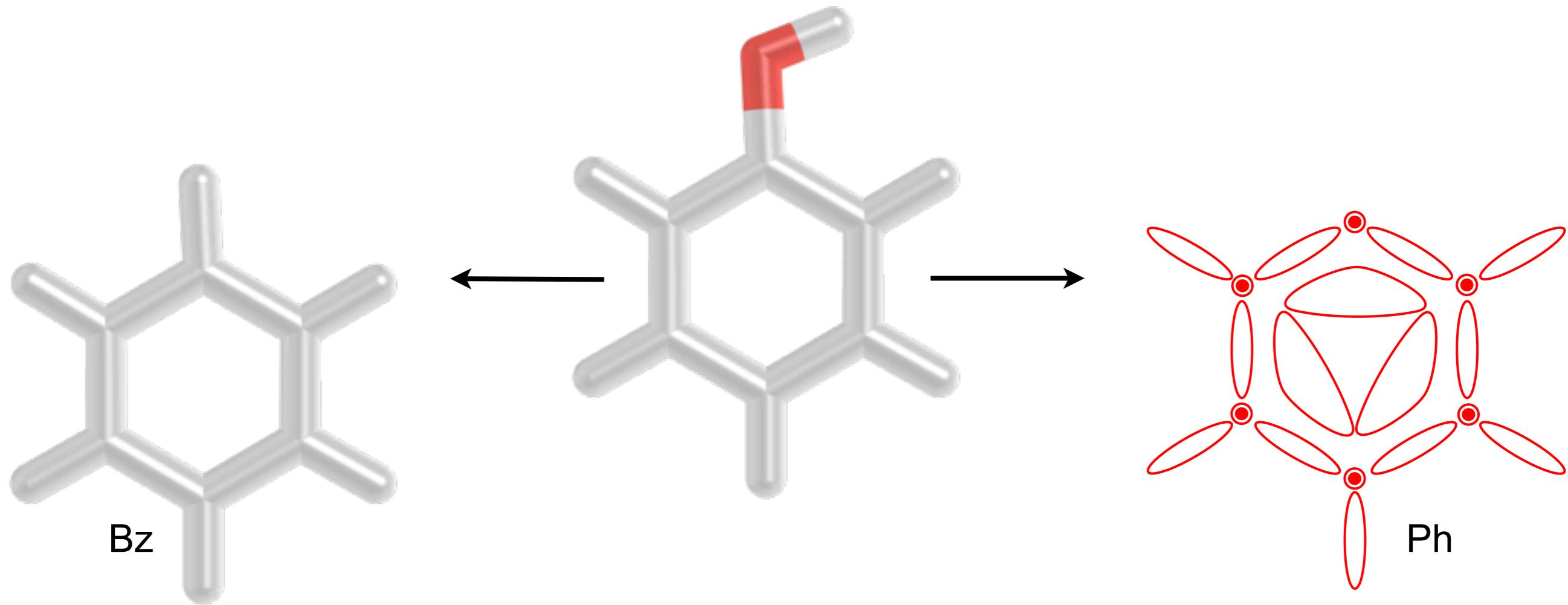
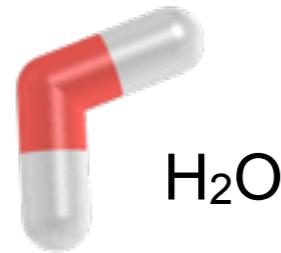


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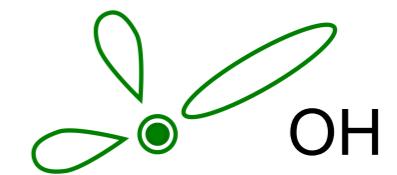


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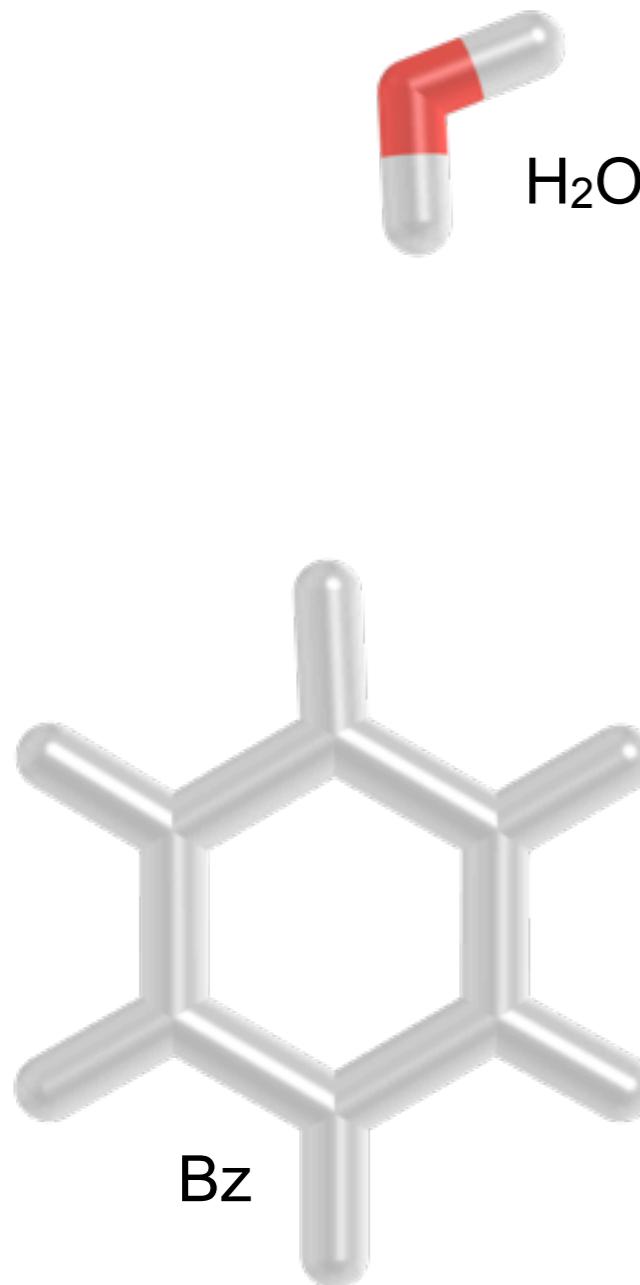


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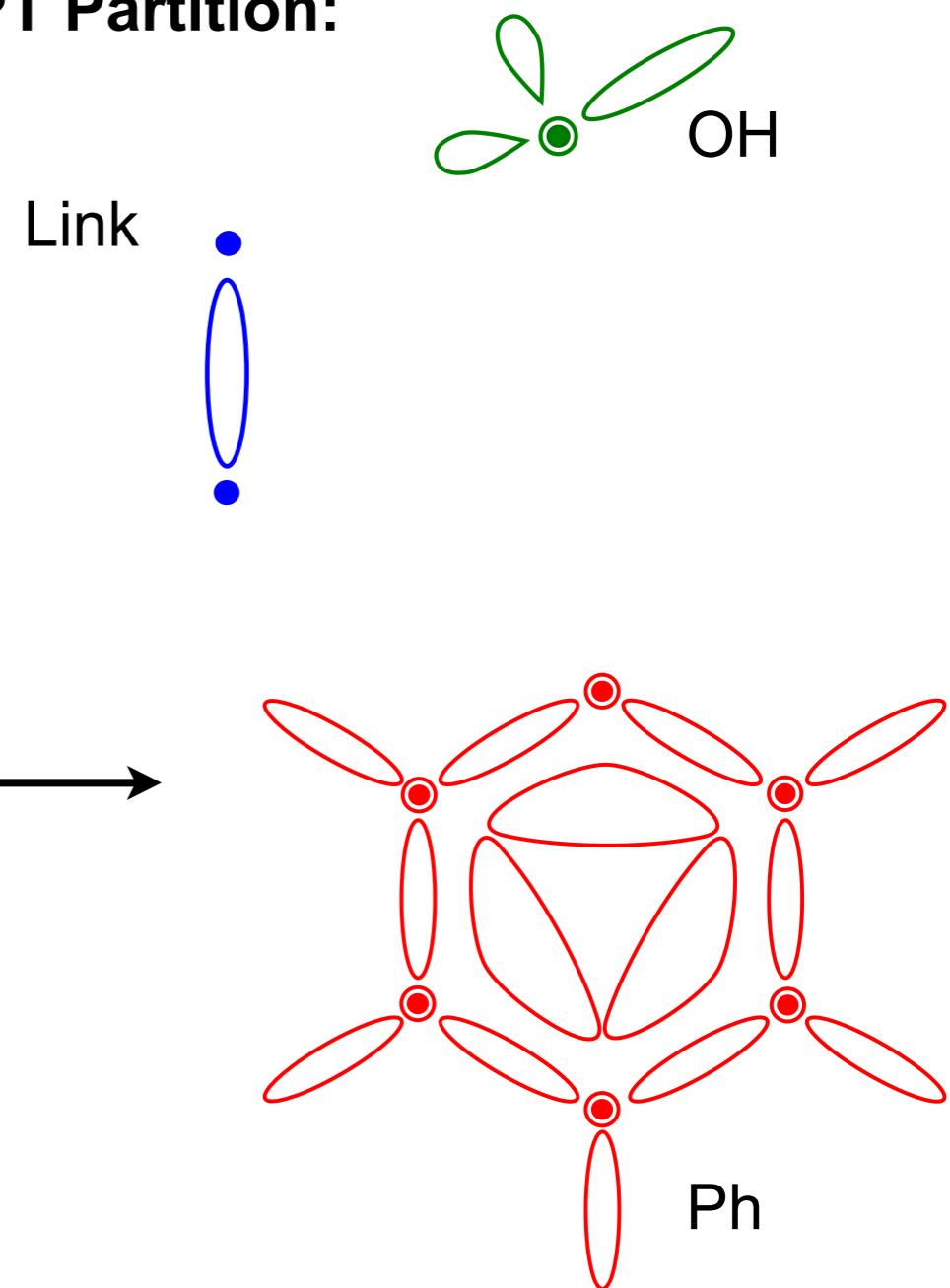


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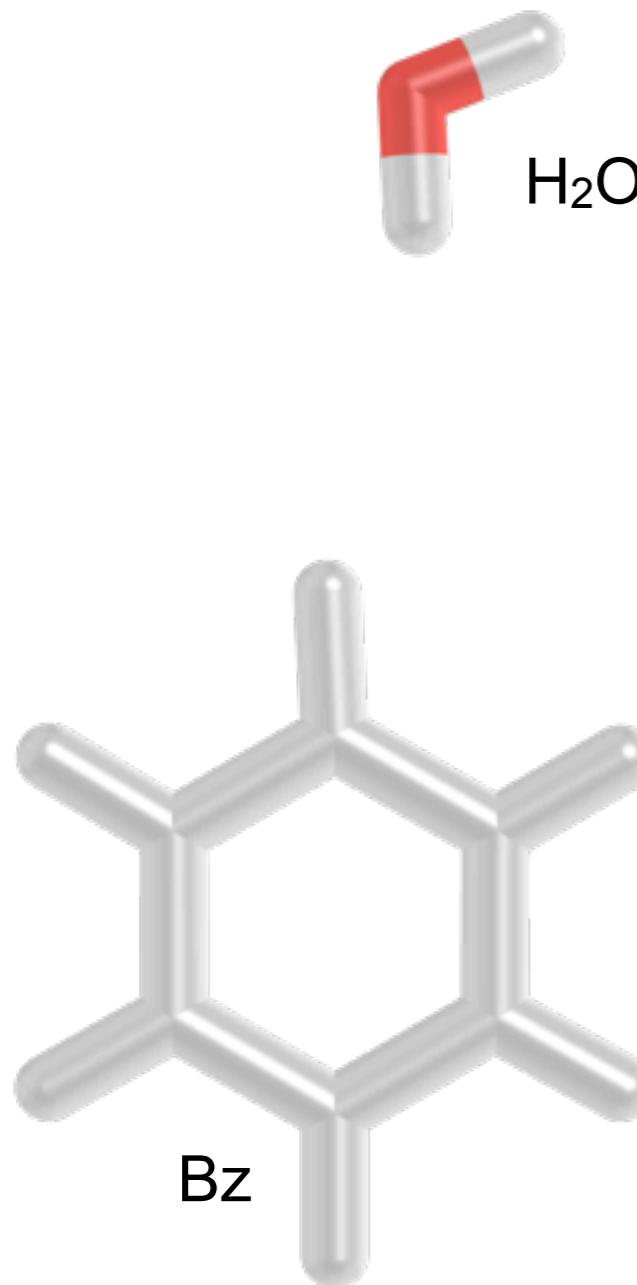


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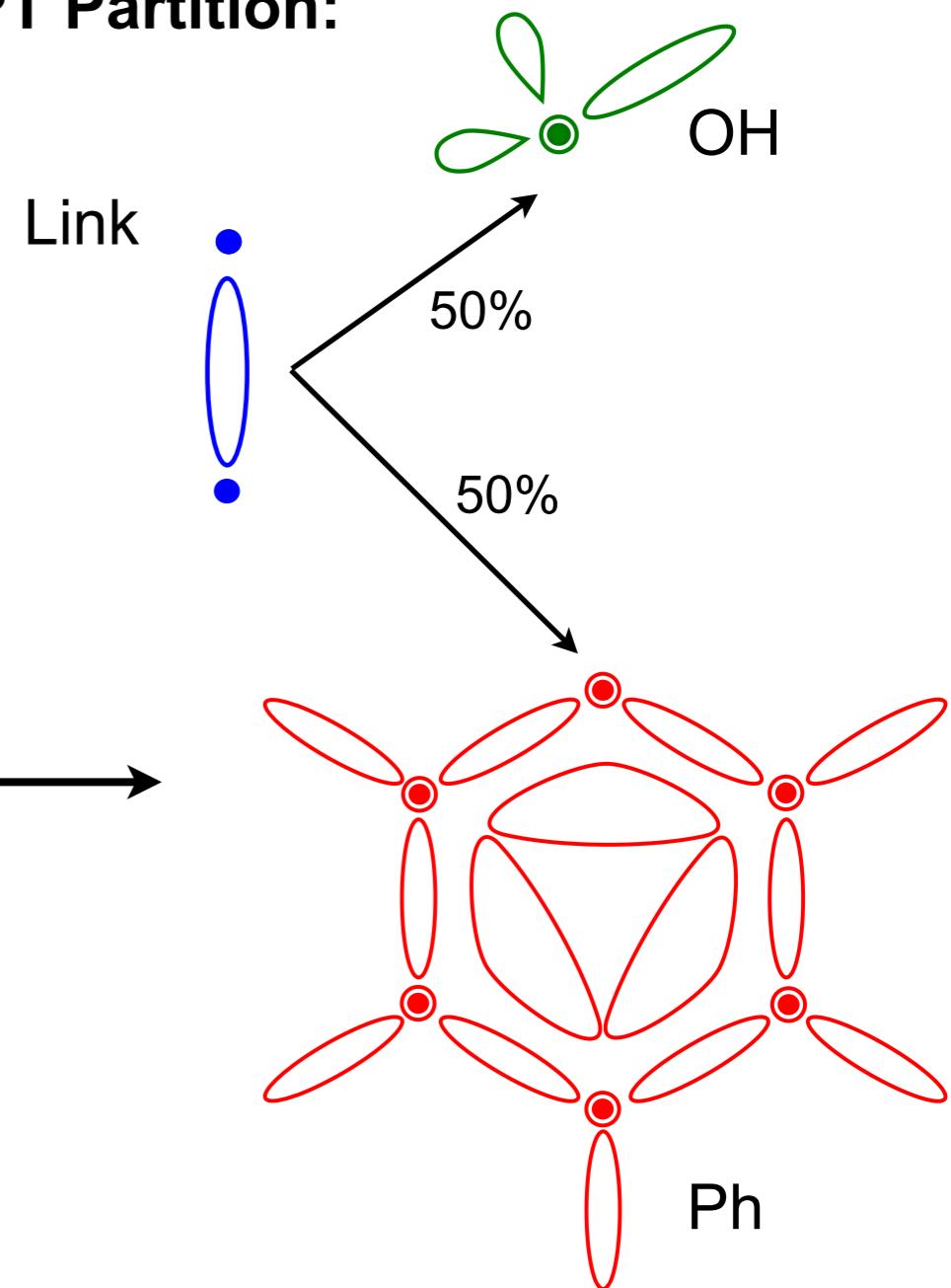


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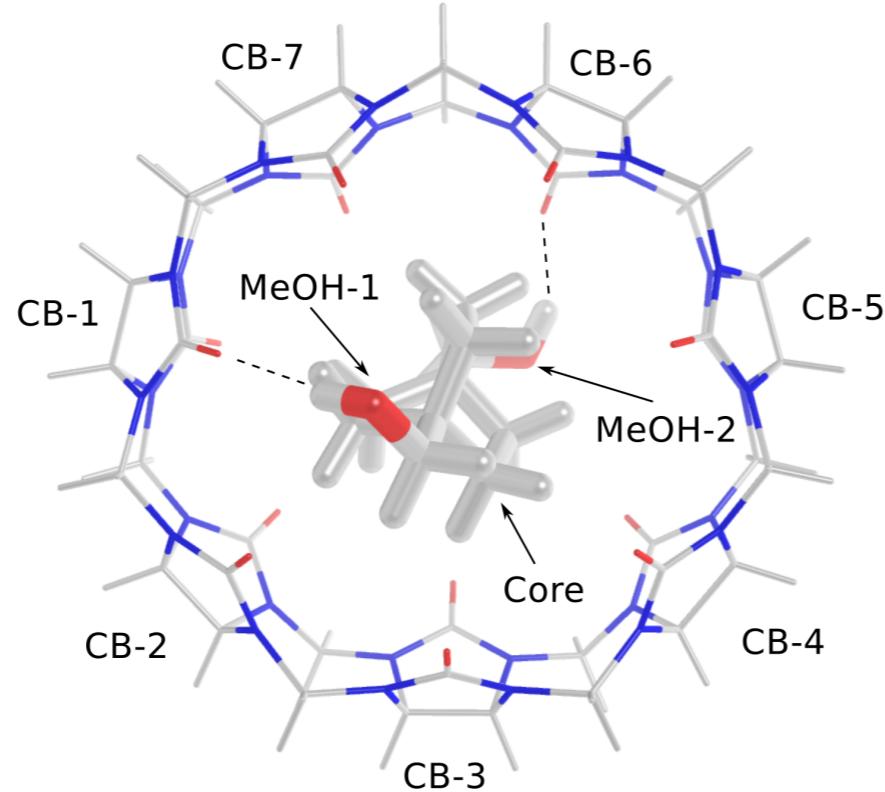
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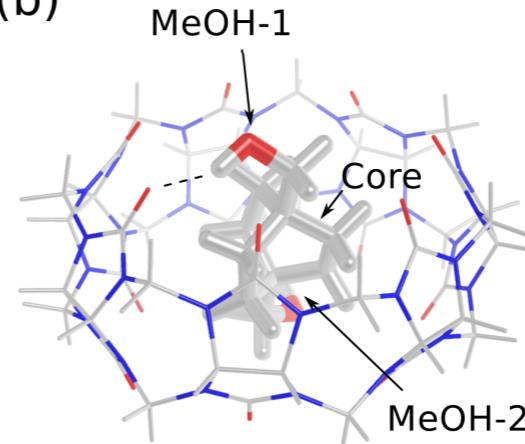
# Full Example: Cucurbituril Inclusion Complex

## Geometry and Functional-Group Partition:

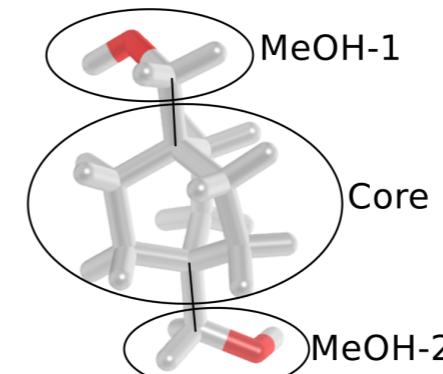
(a)



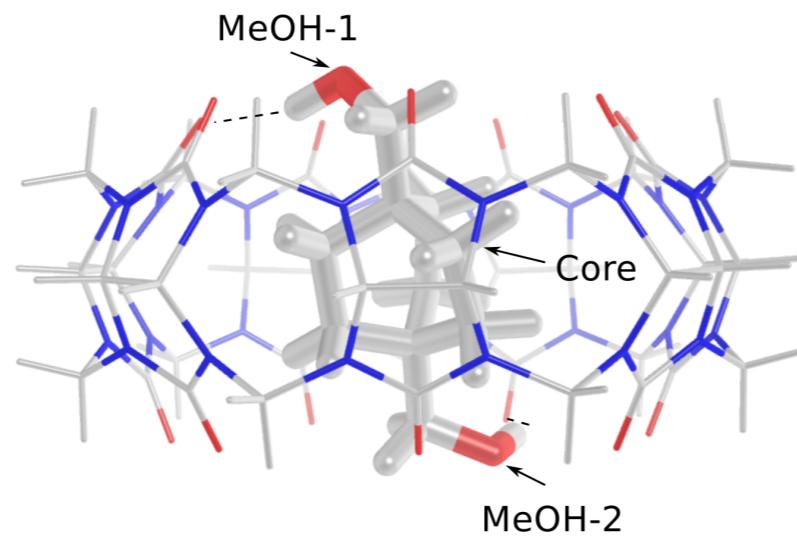
(b)



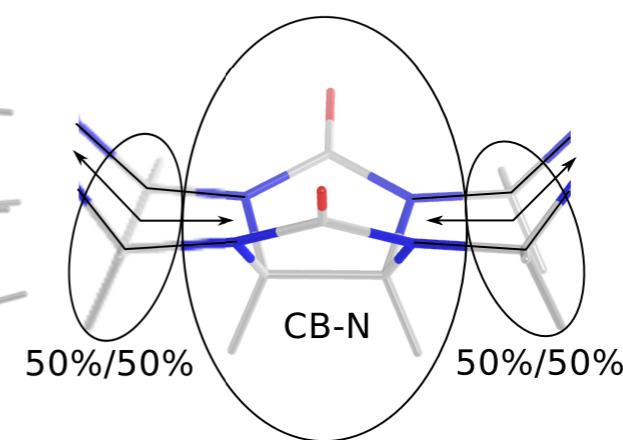
(d)



(c)



(e)



S. Moghaddam, S. Inoue, and M. K. Gilson, *J. Am. Chem. Soc.* **131**, 4012, (2009).

J. Contreras-Garcia et al., *J. Chem. Theory Comput.* **7**, 625 (2011).

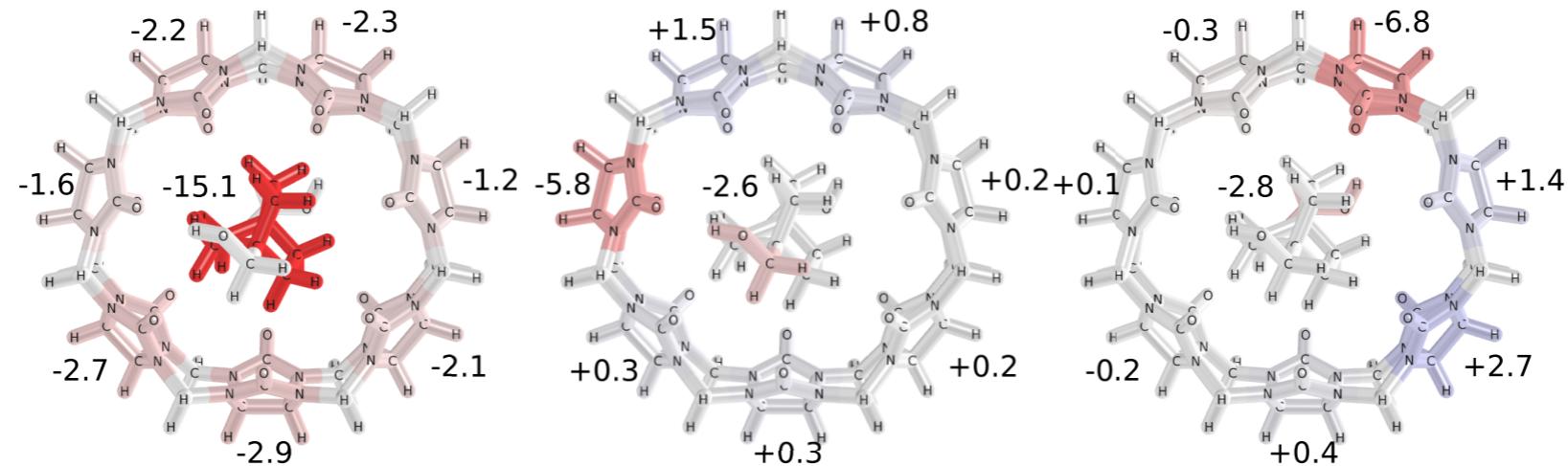
# Full Example: Cucurbituril Inclusion Complex

## Colors:

Red - Attractive  
Blue - Repulsive

# Full Example: Cucurbituril Inclusion Complex

Electrostatics (-20.4 kcal mol<sup>-1</sup>):



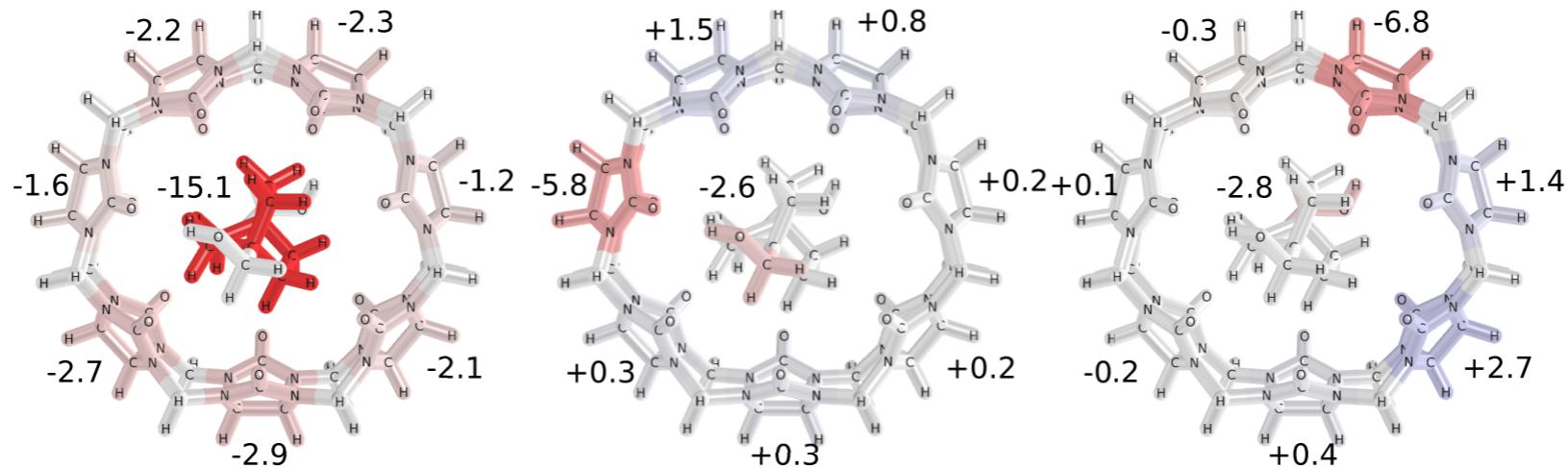
## Colors:

Red - Attractive

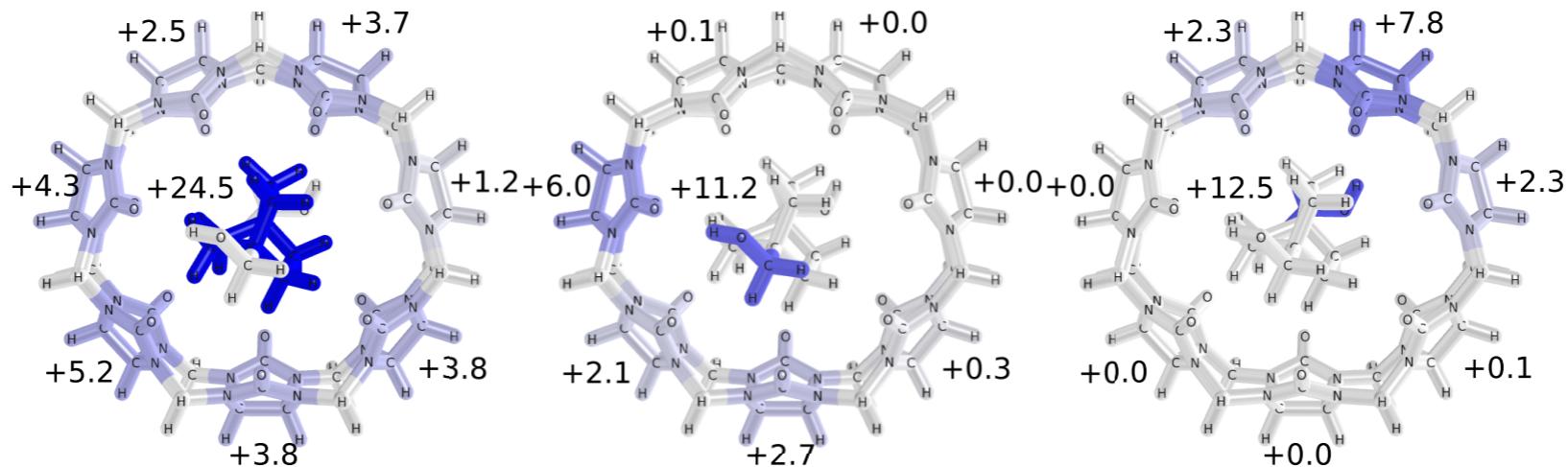
Blue - Repulsive

# Full Example: Cucurbituril Inclusion Complex

**Electrostatics (-20.4 kcal mol<sup>-1</sup>):**



**Exchange (+48.2 kcal mol<sup>-1</sup>):**

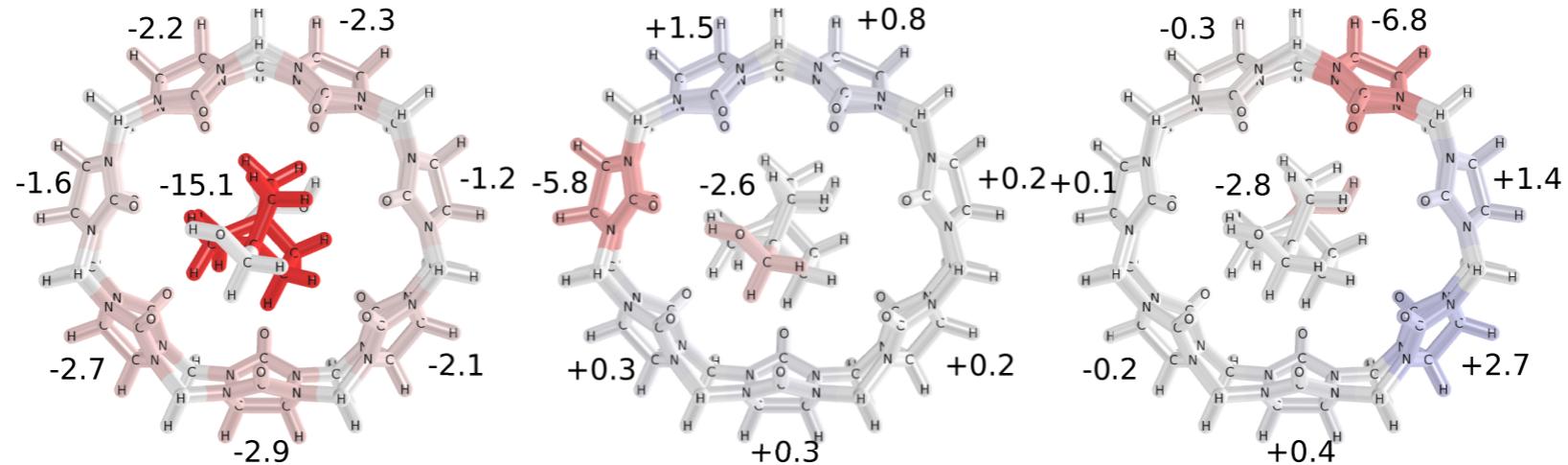


## Colors:

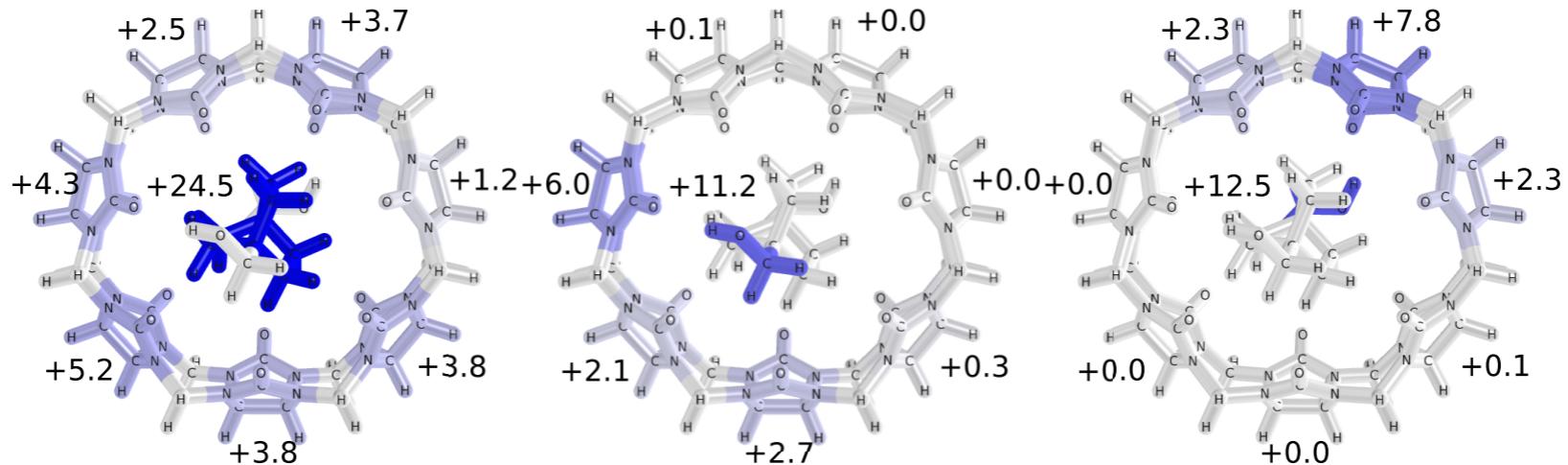
Red - Attractive  
Blue - Repulsive

# Full Example: Cucurbituril Inclusion Complex

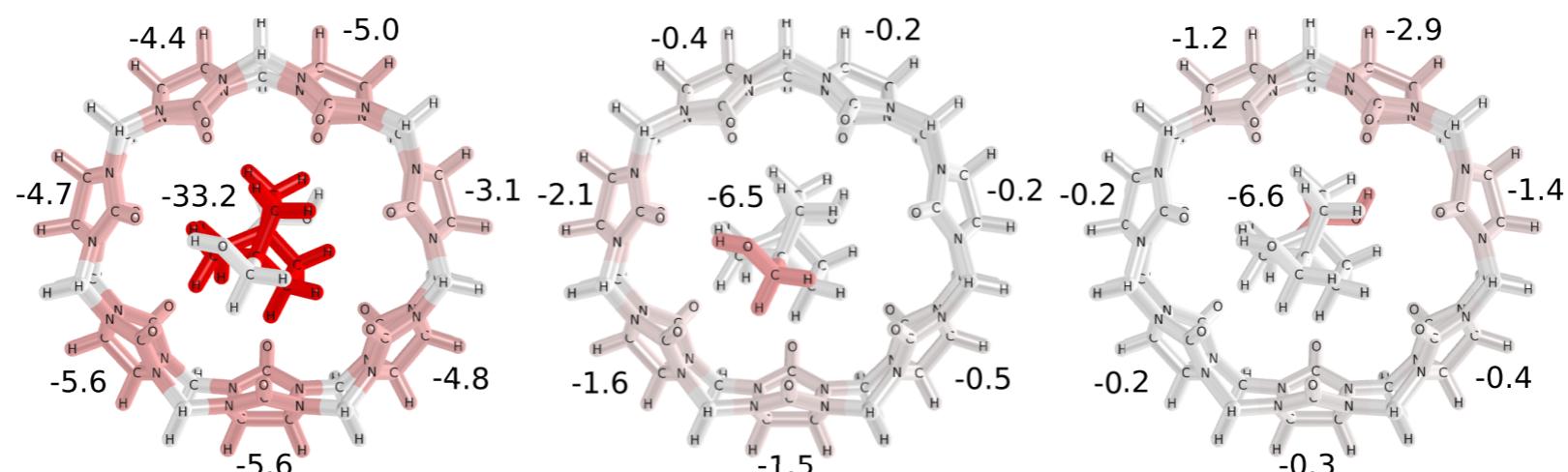
**Electrostatics (-20.4 kcal mol<sup>-1</sup>):**



**Exchange (+48.2 kcal mol<sup>-1</sup>):**



**Dispersion (-46.2 kcal mol<sup>-1</sup>):**



## Colors:

Red - Attractive  
Blue - Repulsive

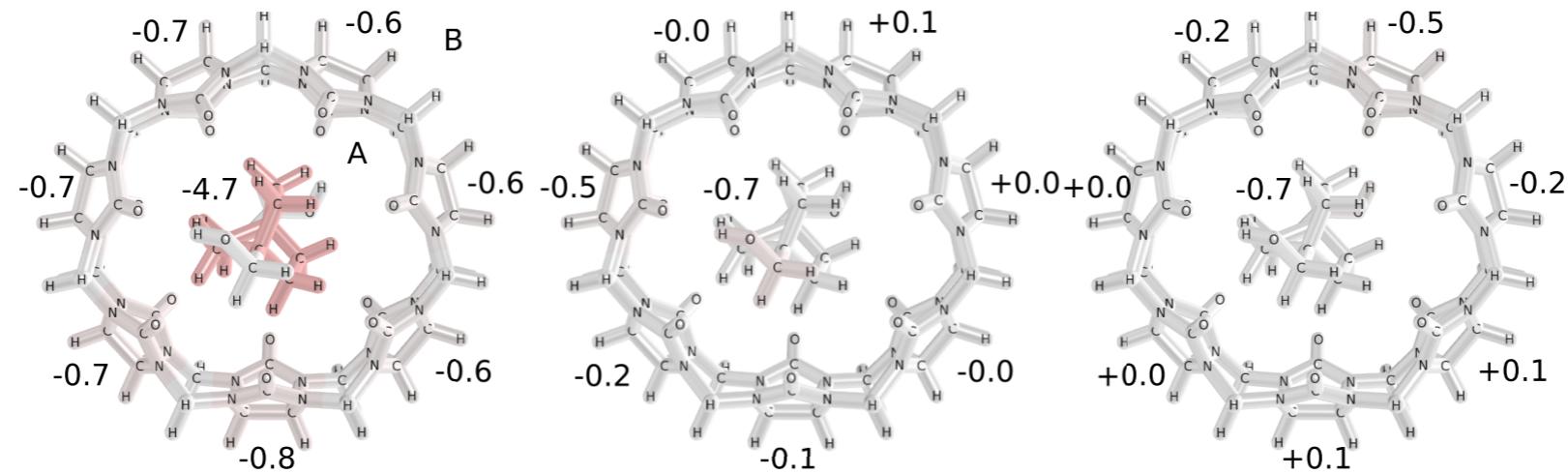
# Full Example: Cucurbituril Inclusion Complex

## Colors:

Red - Attractive  
Blue - Repulsive

# Full Example: Cucurbituril Inclusion Complex

**Induction ( $A \leftarrow B$ ) (-6.1 kcal mol $^{-1}$ ):**

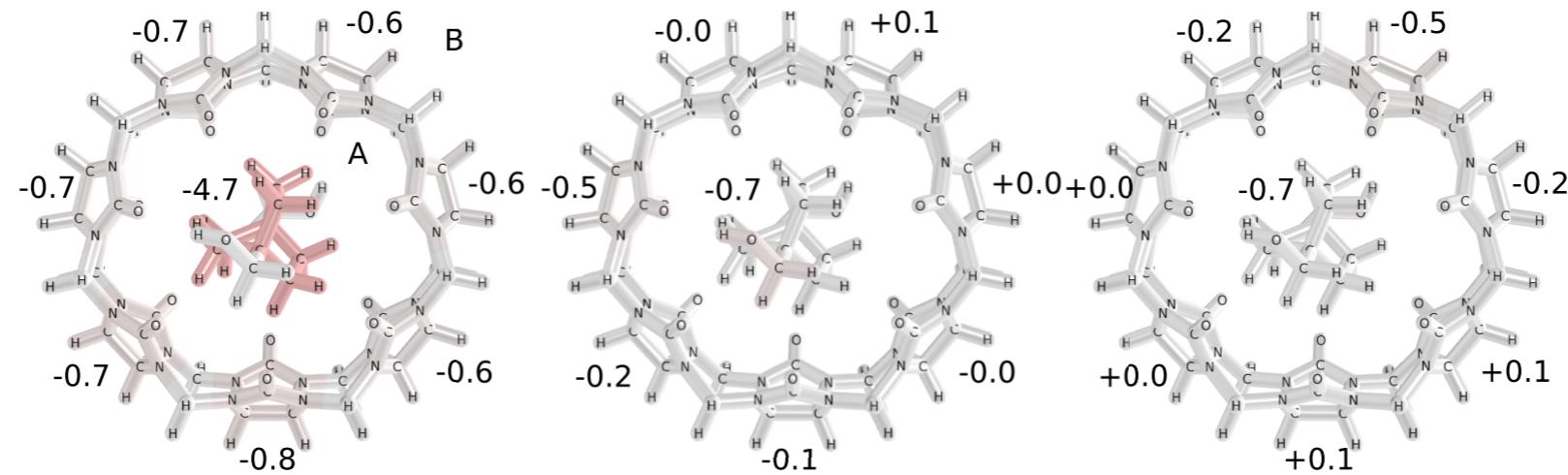


## Colors:

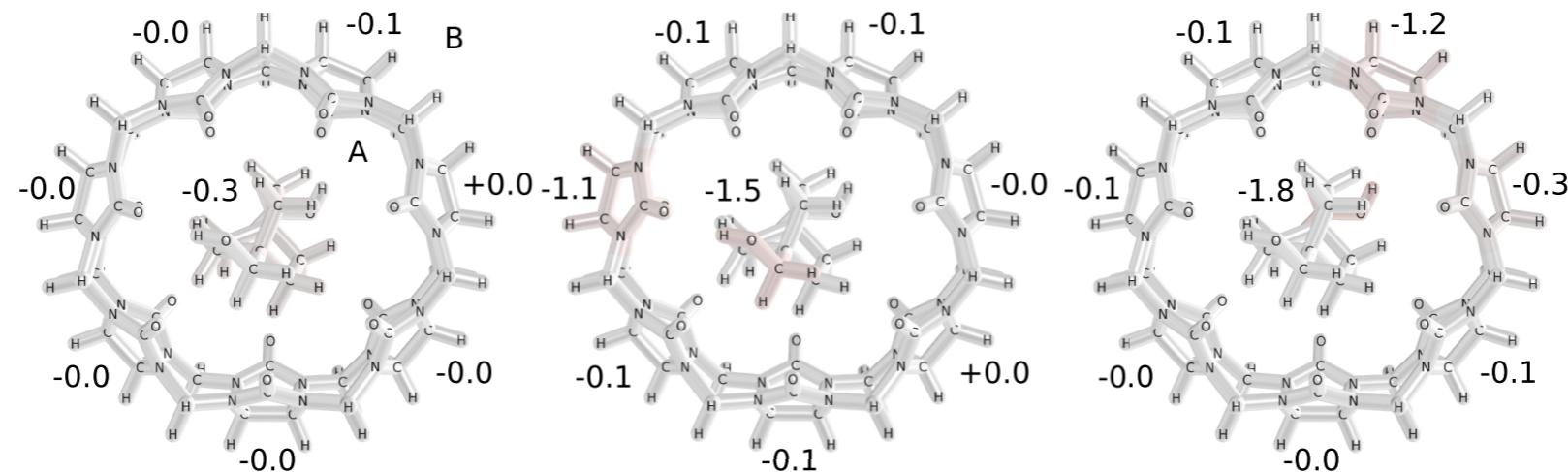
- Red - Attractive
- Blue - Repulsive

# Full Example: Cucurbituril Inclusion Complex

**Induction ( $A \leftarrow B$ ) (-6.1 kcal mol $^{-1}$ ):**



**Induction ( $B \leftarrow A$ ) (-3.6 kcal mol $^{-1}$ ):**

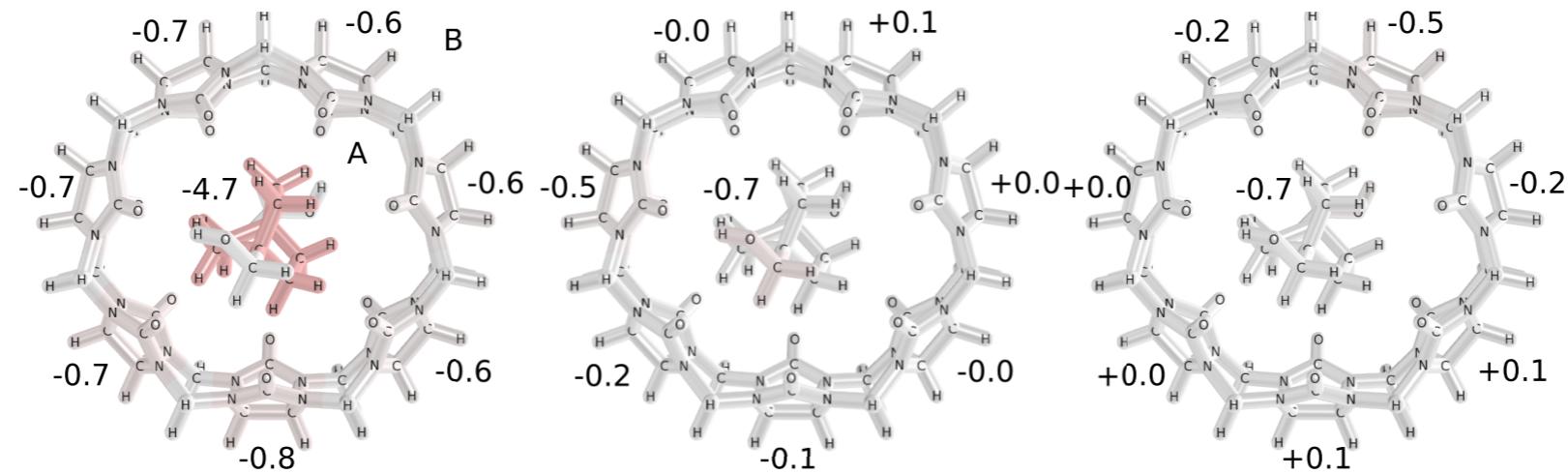


## Colors:

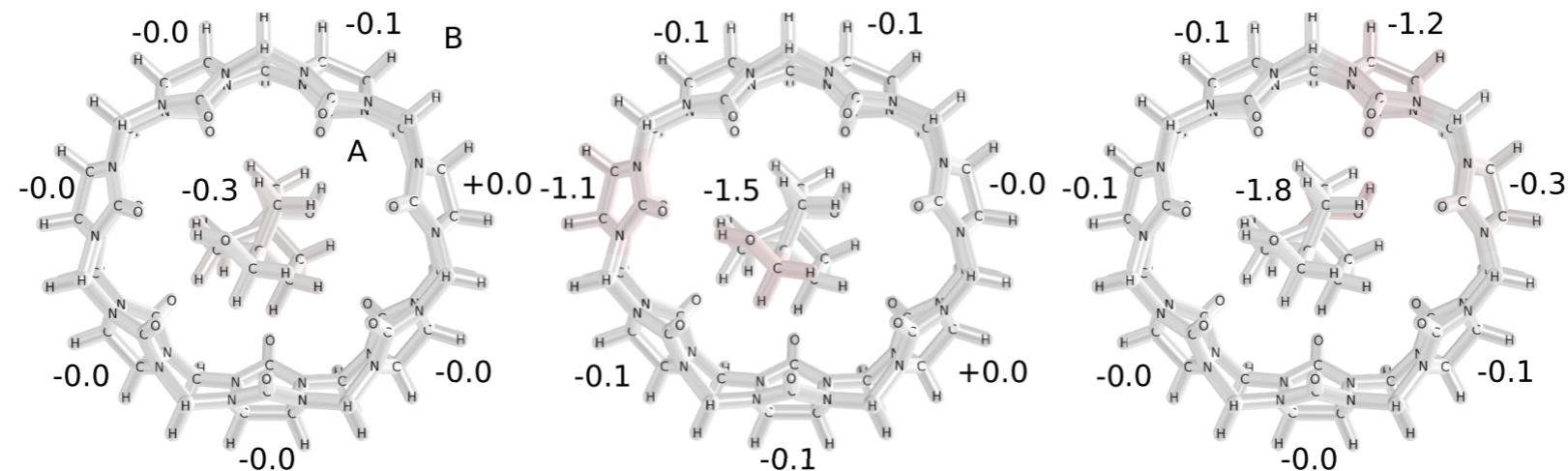
Red - Attractive  
Blue - Repulsive

# Full Example: Cucurbituril Inclusion Complex

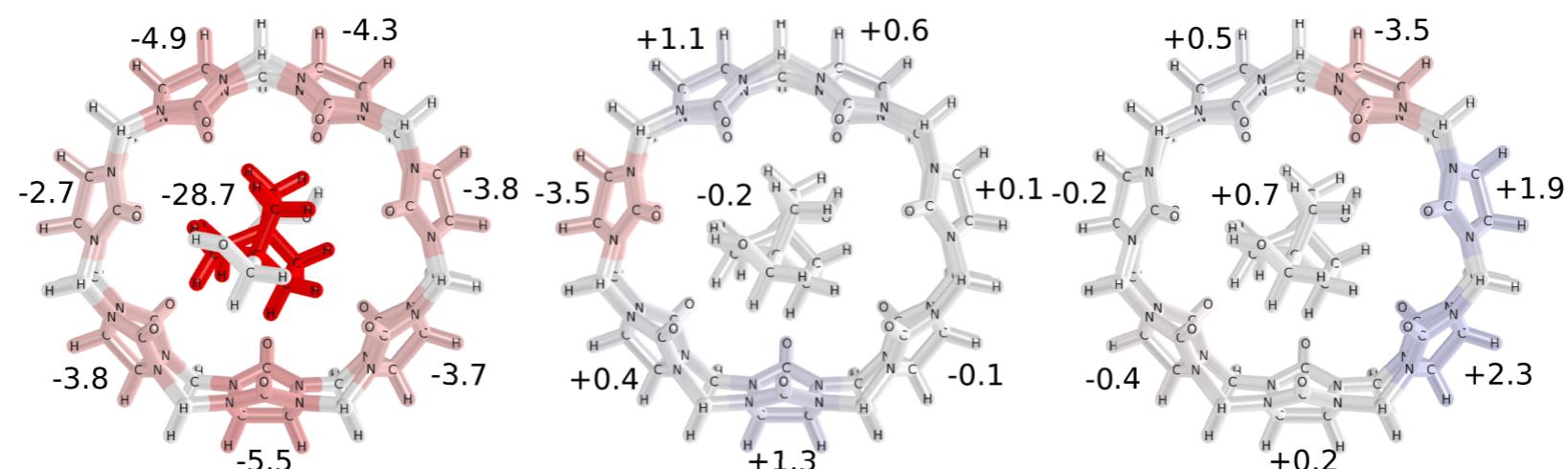
**Induction ( $A \leftarrow B$ ) (-6.1 kcal mol $^{-1}$ ):**



**Induction ( $B \leftarrow A$ ) (-3.6 kcal mol $^{-1}$ ):**



**Total SAPTO (-28.2 kcal mol $^{-1}$ ):**



## Colors:

Red - Attractive

Blue - Repulsive

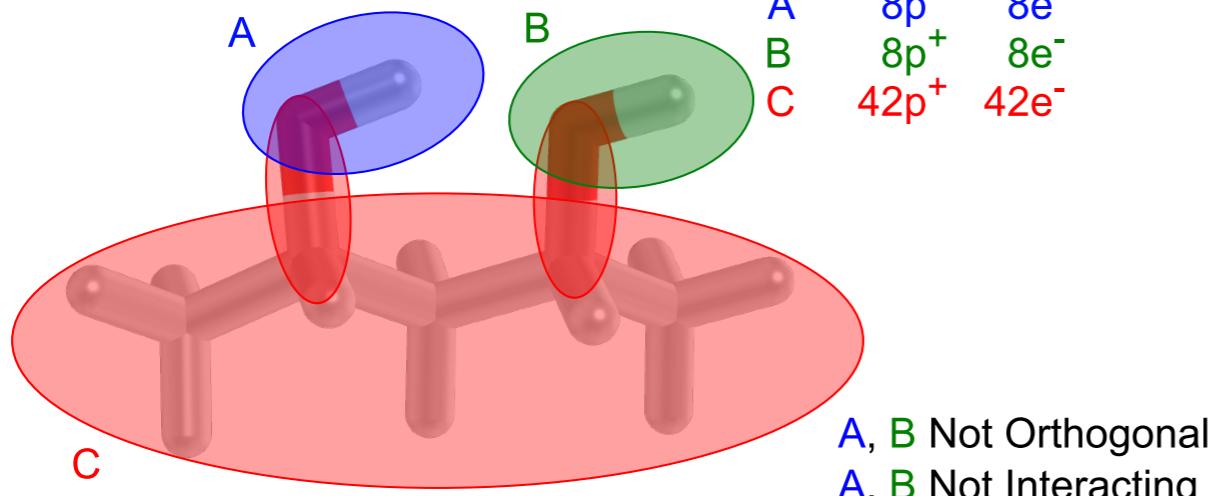
# **Intramolecular SAPT**

## **Overcoming the Problem of Noncovalent Interactions in Monomers with Covalent Linkage**

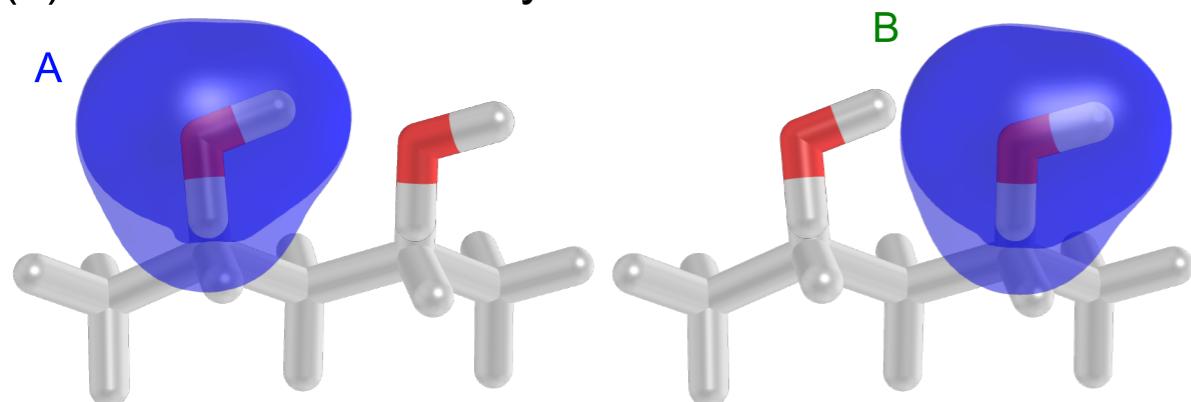
# Embedding Scheme for ISAPT

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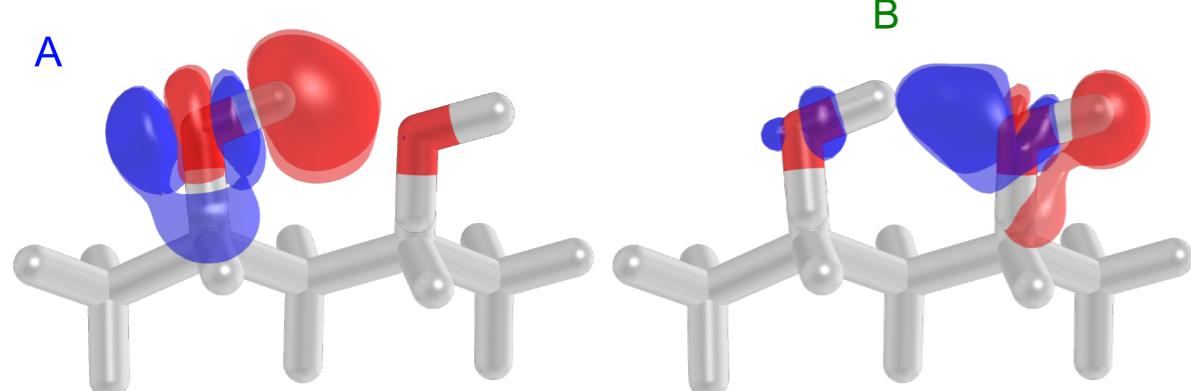
(a) Zeroth-Order System:



(b) Zeroth-Order Density:

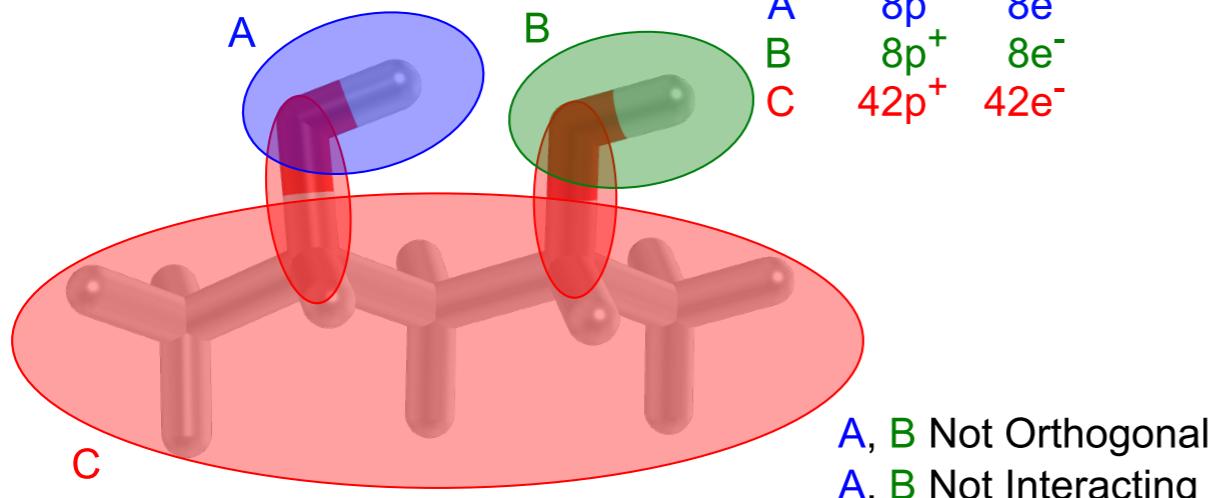


(c) Difference Density:

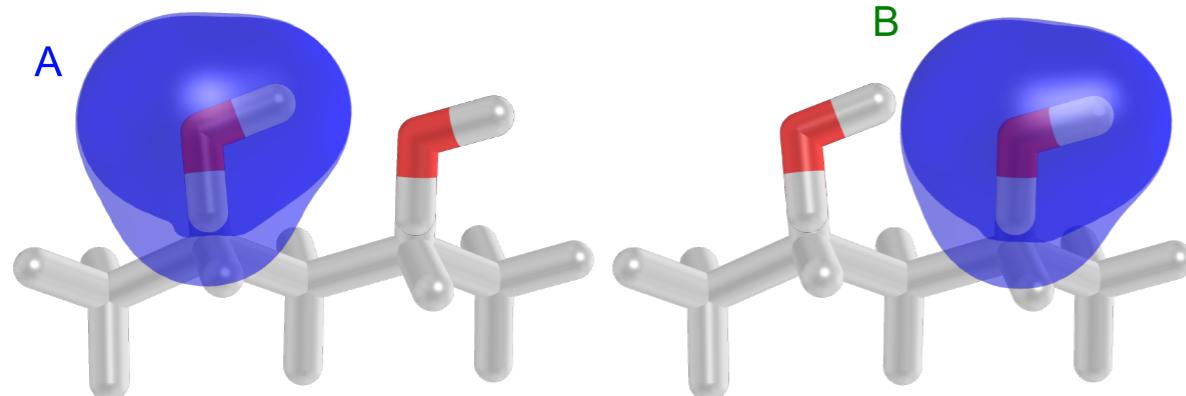


# Embedding Scheme for ISAPT

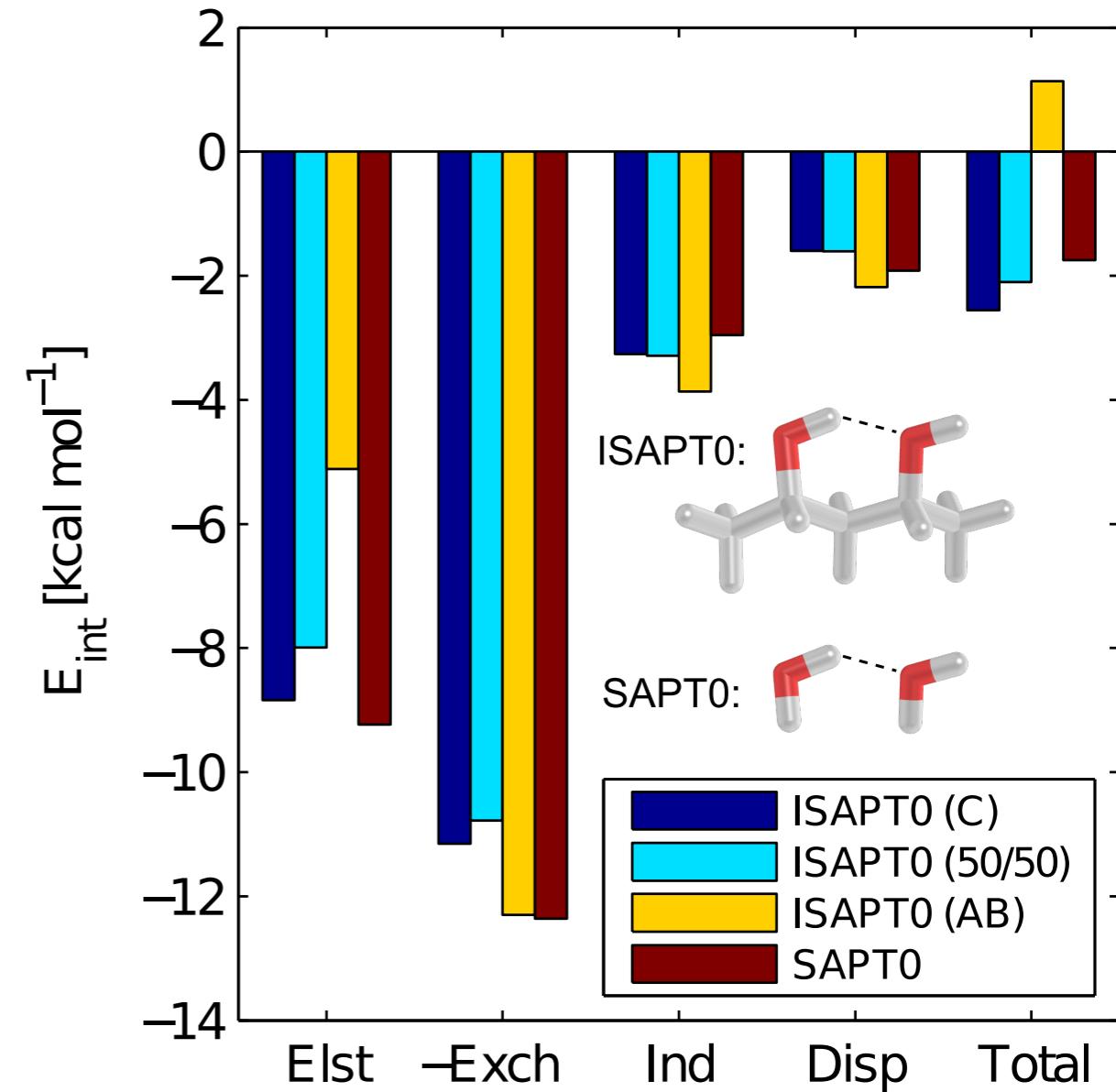
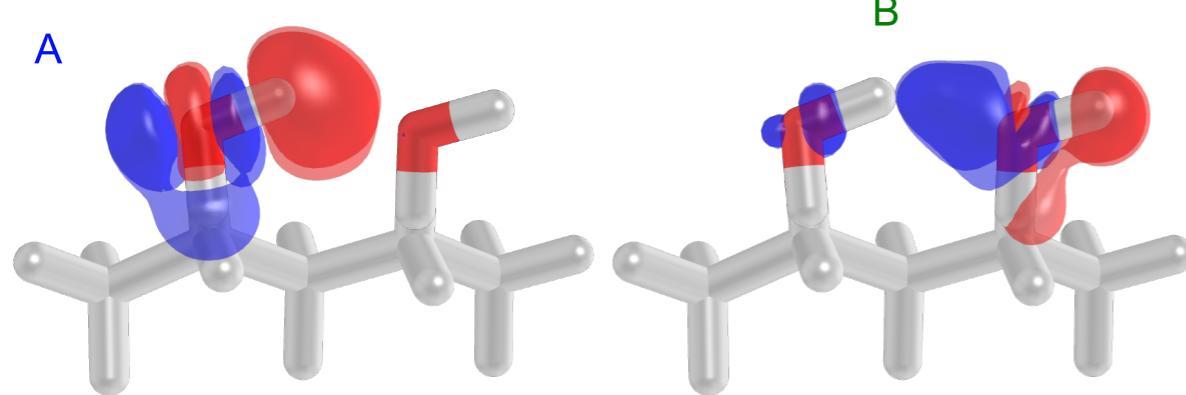
(a) Zeroth-Order System:



(b) Zeroth-Order Density:

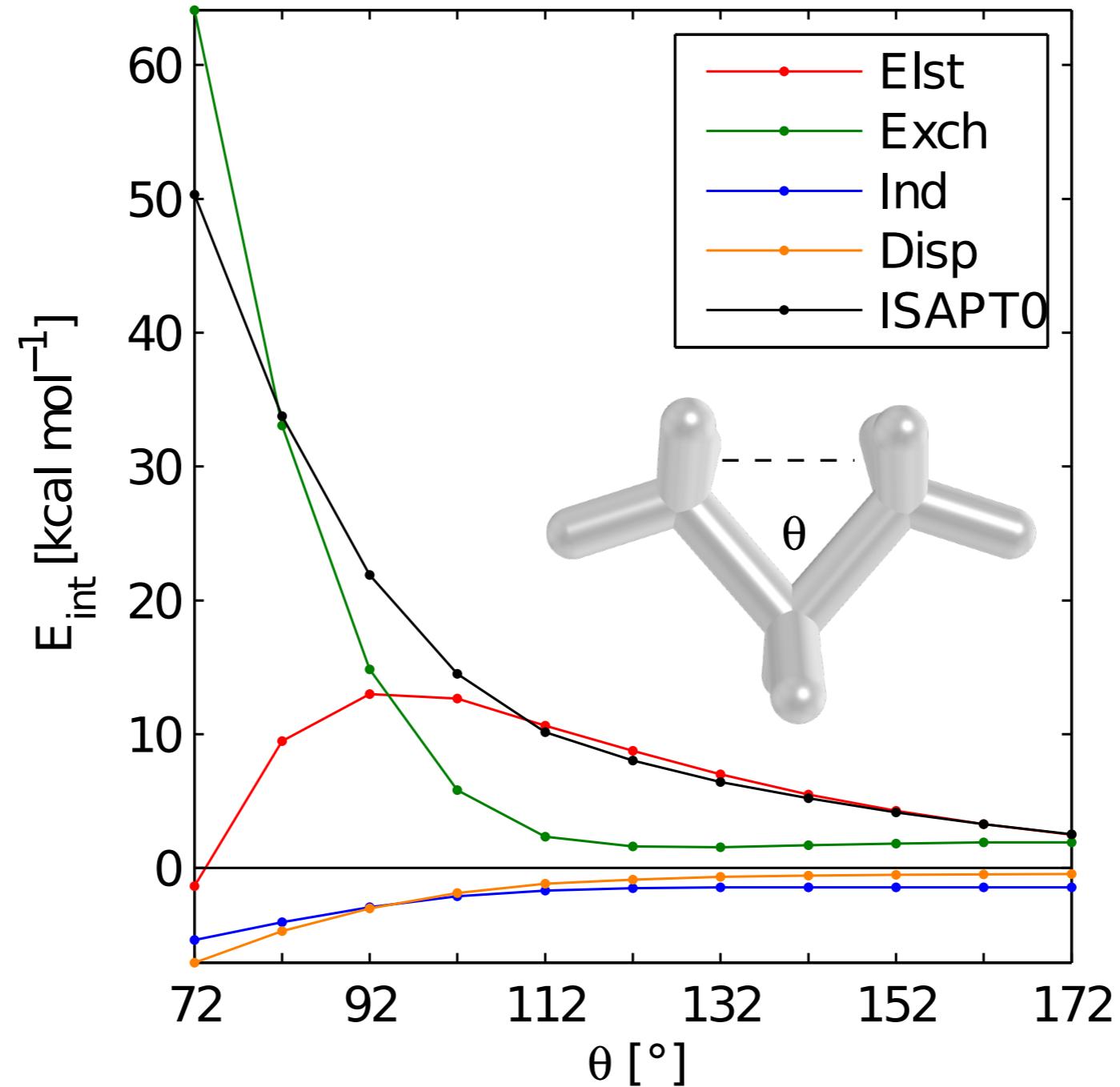


(c) Difference Density:



# Application to Propane

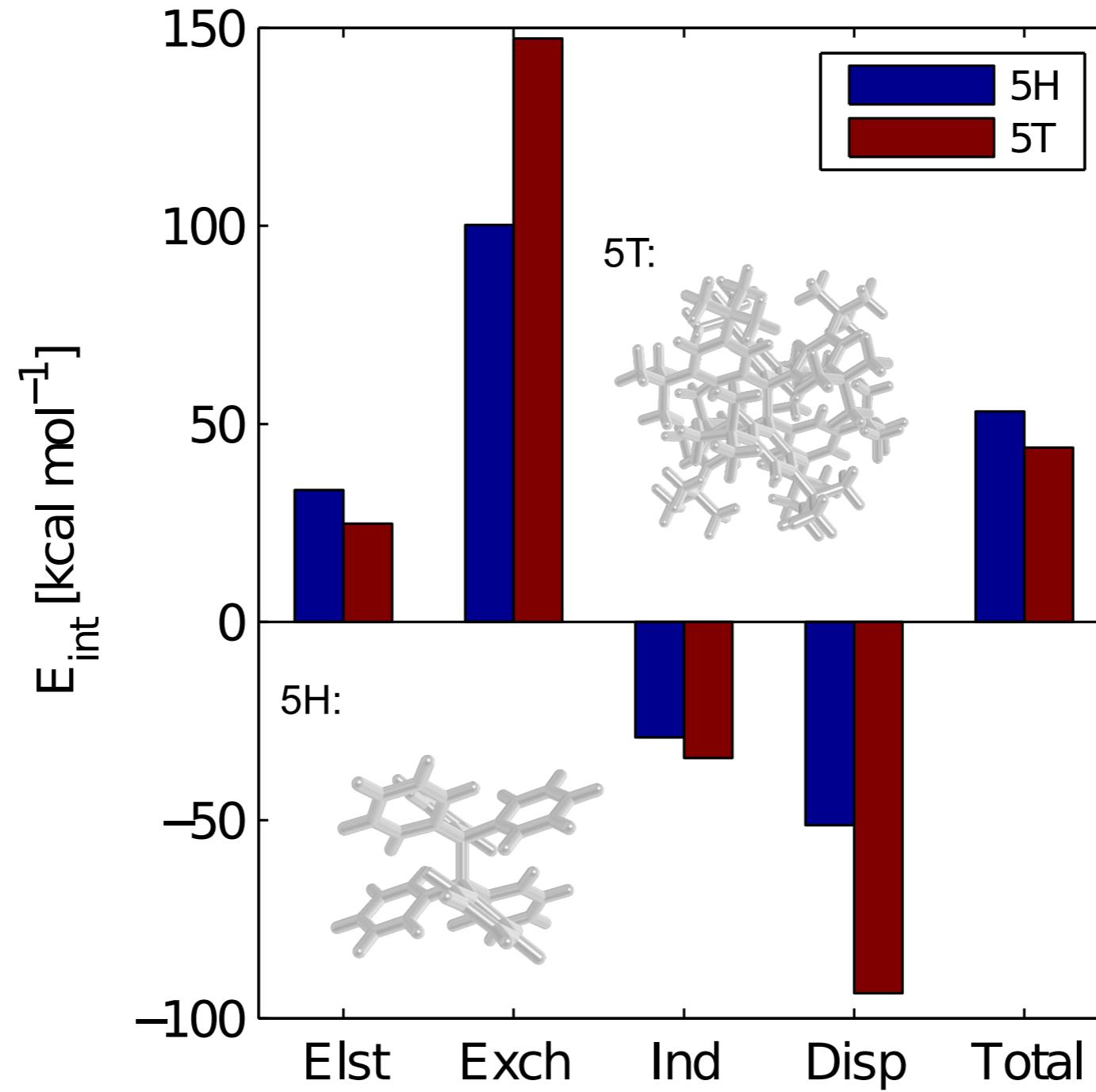
# Application to Propane



# Application to Hexaphenyl-Ethane Derivatives

R.M. Parrish, J.F. Gonthier and C.D. Sherrill, *in preparation.*

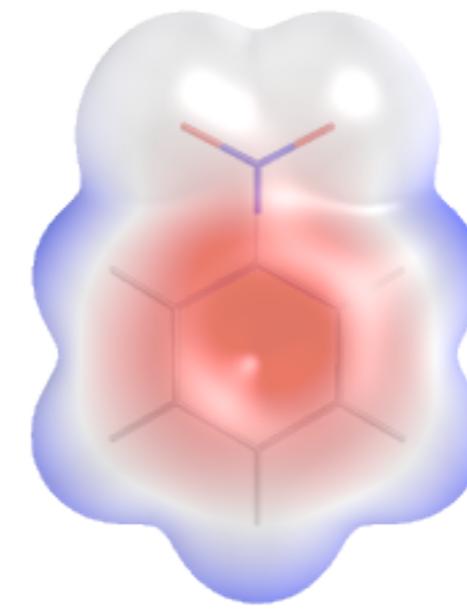
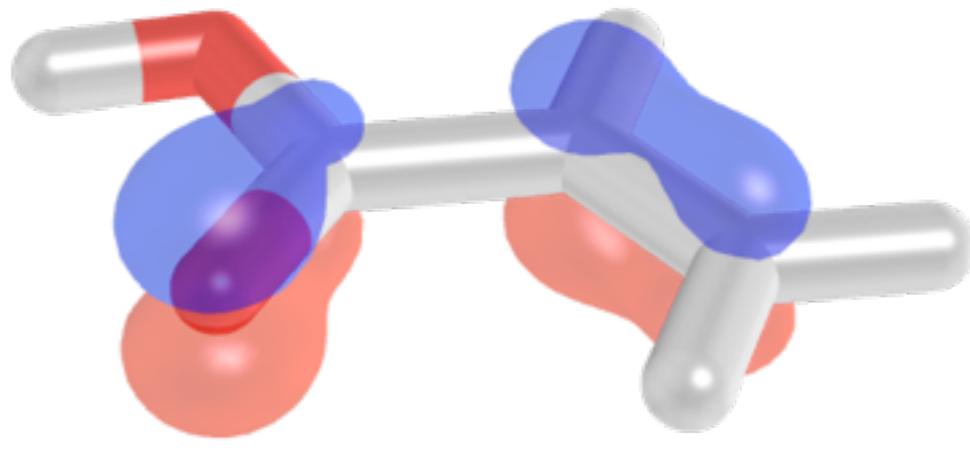
# Application to Hexaphenyl-Ethane Derivatives



# **Outlook**

## **So Much to Do and Time is Short!**

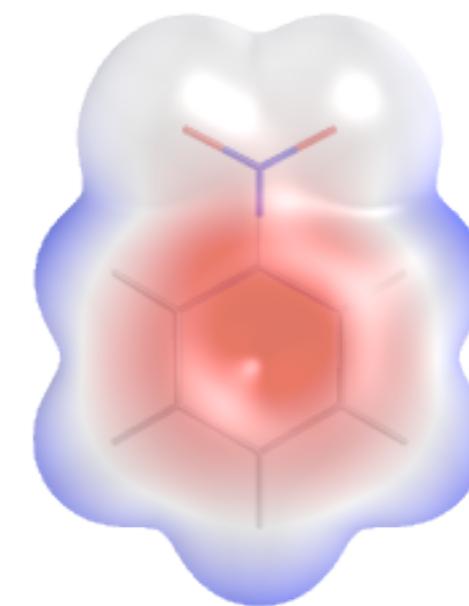
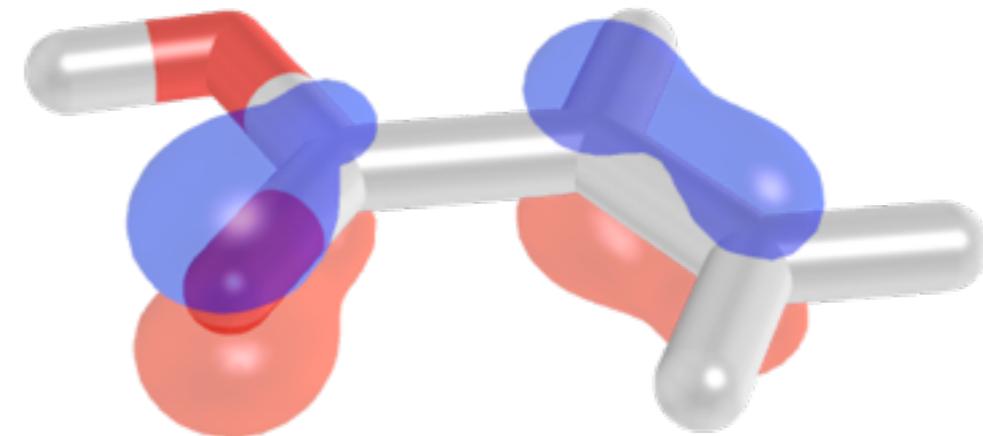
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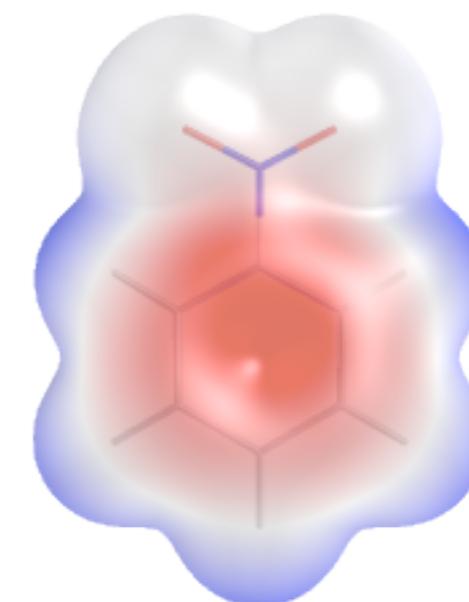
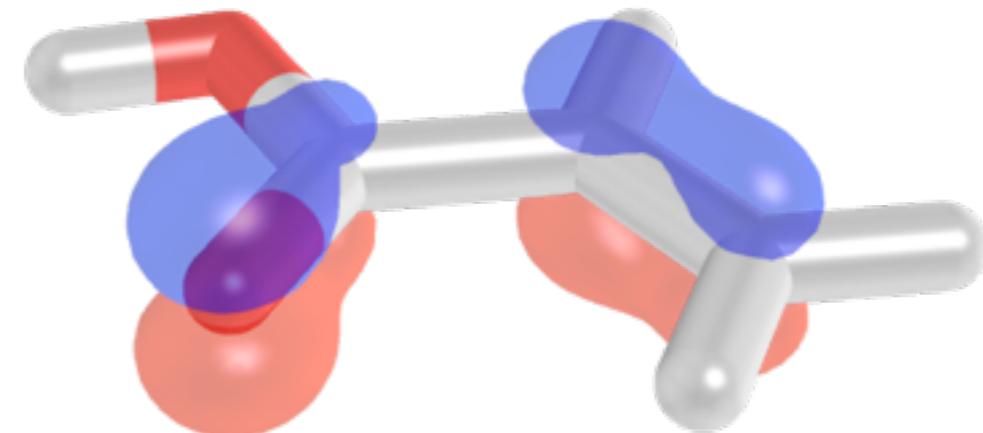
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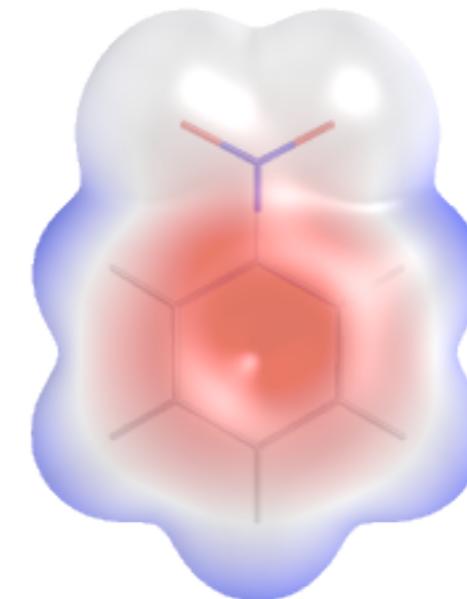
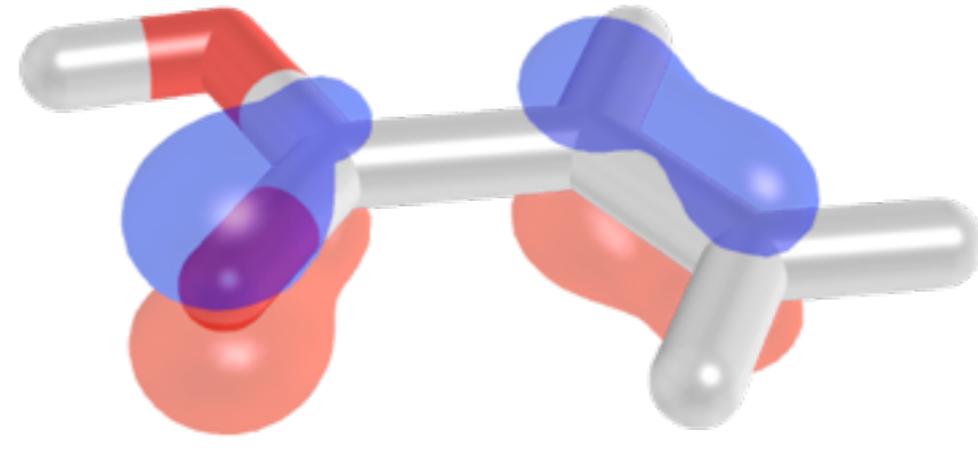
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- Localization Routines:
  - Pipek-Mezey
  - Boys
  - Knizia (these are really good)
- Cube Files (w/ Francesco):
  - Orbitals
  - Densities
  - ESPs (with DF)
  - LOL/ELF



# Goals for Remaining Thesis Work

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- Major Overhaul of One-Particle and PT2 Codes
  - Full rewrite of SCF, MP2, SAPT(DFT) modules
  - SCF Gradients and Hessians
  - TD-DFT?
  - MP2 Gradients [RMP2, UMP2, ROHF-MBPT(2), LRC-MP2 gradients]
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- Core Libraries to be Finalized:
  - LibFock (J/K/wK, KS-V and derivatives, etc)
  - LibTHCE (DF, CD, THC, etc tensors)

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- Georgia Institute of Technology:
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- Utah/Virginia Tech/NIH/  
delocalized:
  - Andy Simmonett
- Emory:
  - Francesco Evangelista
  - Kevin Hannon

