Developing Periodic, Localized Molecular Orbitals

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Nooijen Group

Outline

- Motivation
- Theory
- Description of Algorithm
- Results
- Future Work
- Questions

Motivation

- Computational calculations can determine molecular properties:
  - Geometries
  - Electronic Structure
  - Thermochemistry*
- Different levels of theory give different results
  - Hartree-Fock (HF)
  - Density functional theory (DFT)
  - Second order Møller–Plesset (MP2)
- "Best" method: Coupled-Cluster Singles, Doubles, and Triples (CCSD(T))
  - ~kcal/mol accuracy
  - Very computationally expensive (N^7)

Motivation

- Coupled cluster (CC) methods use a transformed Hamiltonian:

$$\left\langle \Phi \middle| e^{-\hat{T}} H e^{\hat{T}} \middle| \Phi \right\rangle = E \left\langle \Phi | \Phi \right\rangle = E \qquad \hat{T} = T_1 + T_2 \ldots$$

$$\left\langle \Phi_{\mathrm{a}}^{\mathrm{i}} \middle| e^{-\hat{T}} H e^{\hat{T}} \middle| \Phi \right\rangle = E \left\langle \Phi_{\mathrm{a}}^{\mathrm{i}} \middle| \Phi \right\rangle = 0$$

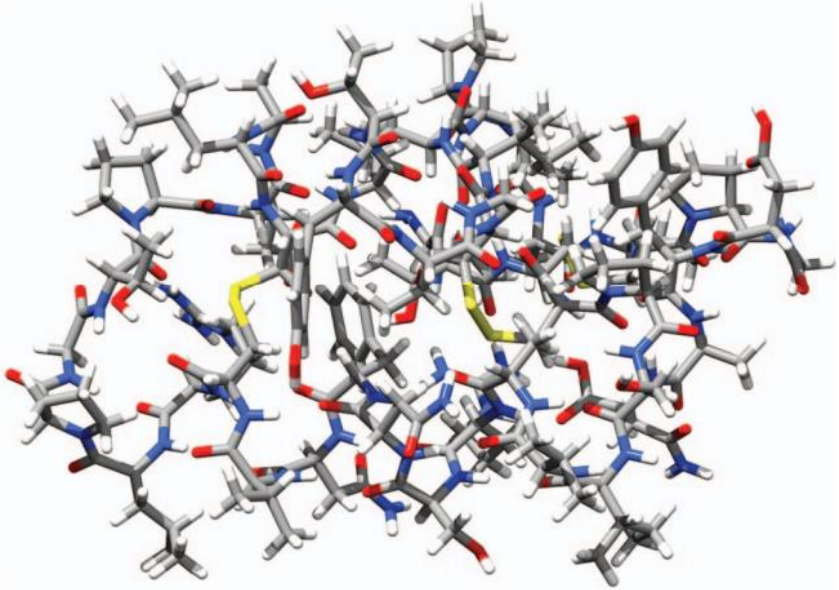
$$\left\langle \Phi_{ab}^{ij} \middle| e^{-\hat{T}} H e^{\hat{T}} \middle| \Phi \right\rangle = E \left\langle \Phi_{\mathrm{ab}}^{\mathrm{ij}} \middle| \Phi \right\rangle = 0$$

$$\vdots$$

- Solving the CC equations gives t-amplitudes

Recent Developments

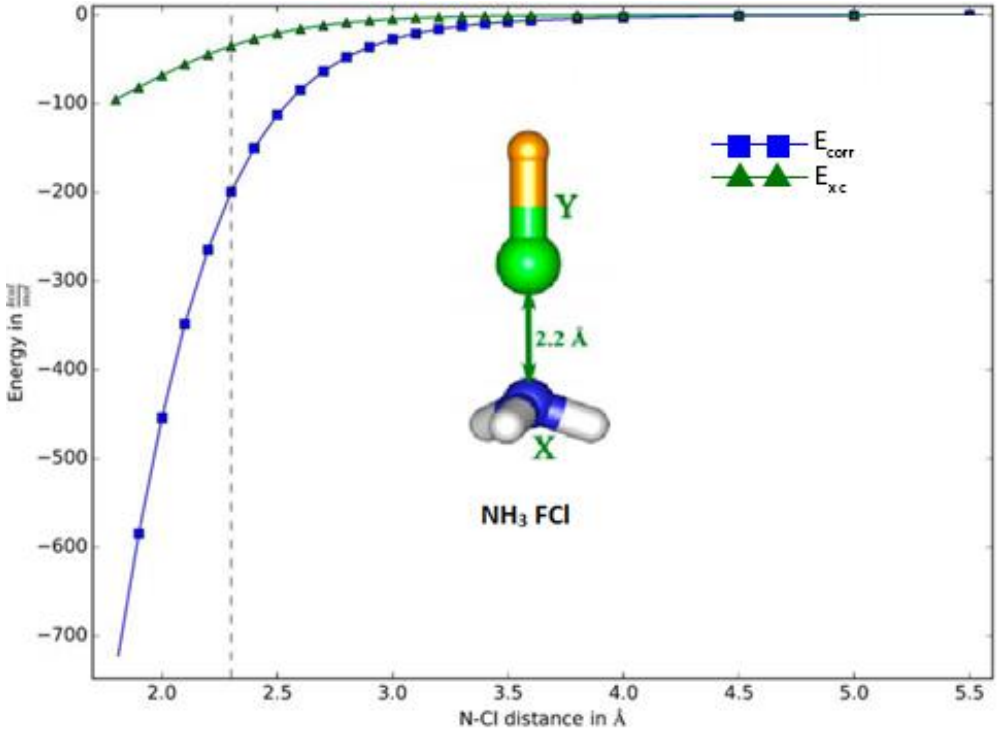
- CCSD(T) calculations with localized orbitals
  - Largest CCSD(T) calculation to date: Crambin
  - Completed using domain based local pair-natural orbital coupled-cluster (DLPNO-CC)



Crambin (644 atoms, 6100+ basis functions)
J. Chem. Phys. 139 134101 (2013)

Recent Developments

- Electron correlation falls with r^{-6}
- Localizing orbitals to ignore long range interactions greatly simplifies calculations:



J. Chem. Theory Comput. 2016, 12, 4778−4792

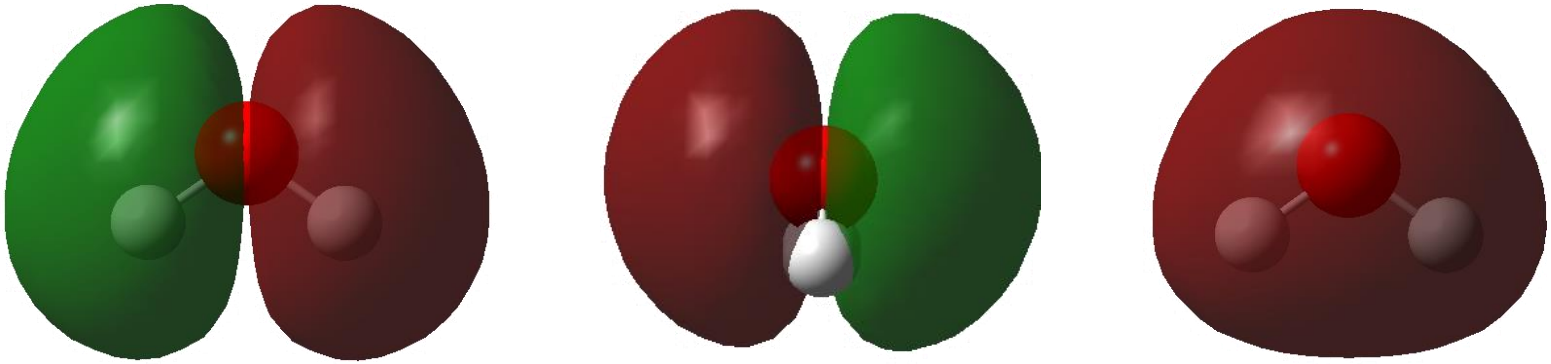
Orbital Localization

- Recently developed DLPNO-CC gives reliable accuracy with a similar computation time as DFT
  - Classifies interactions with a hierarchy
- Limitation: cannot use molecular symmetry (speedup) with localized orbitals

- **Can we combine orbital localization and molecular symmetry?**
- **If one can do this, one can treat solids**

Simplifying Calculations with Molecular Symmetry

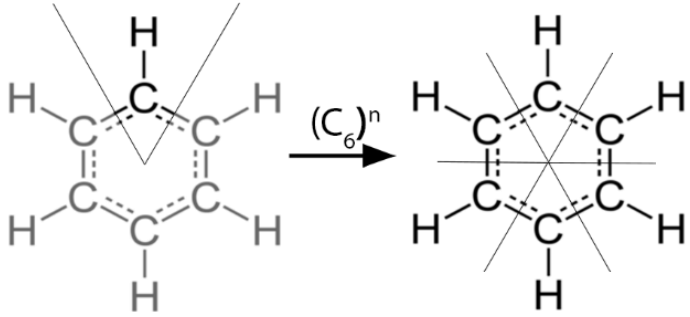
- Canonical orbitals transform according to their irreducible representations:

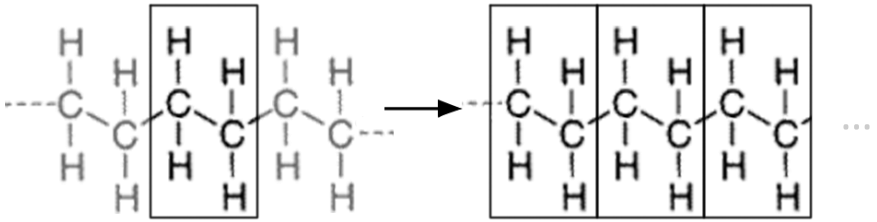


- Canonical orbitals can be used with canonical CCSD(T)
  - System size limited due of scaling
- Many t-amplitudes are zero by symmetry and do not need to be calculated. But: no sparsity due to localization
- **Goal: find orbitals which are localized and exhibit molecular symmetry**

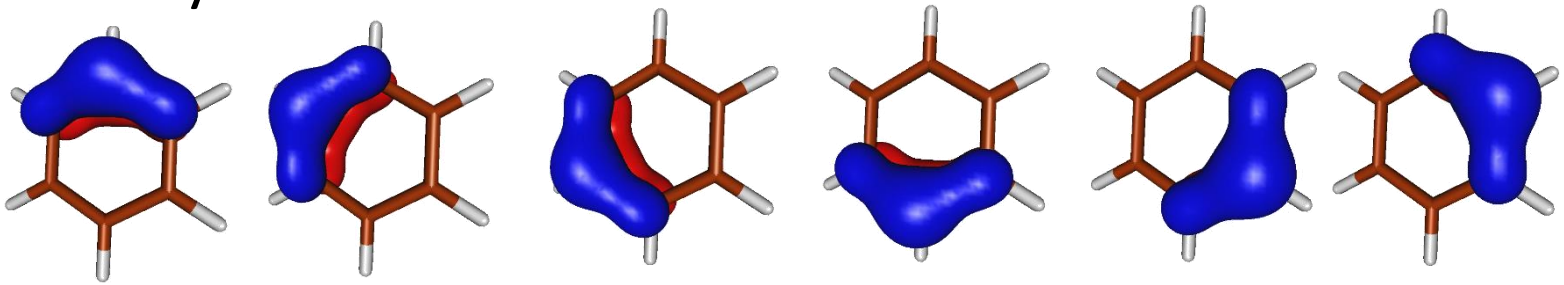
Molecular Symmetry

- Molecules can be broken up into repeating unit cells which transform via irreducible representations





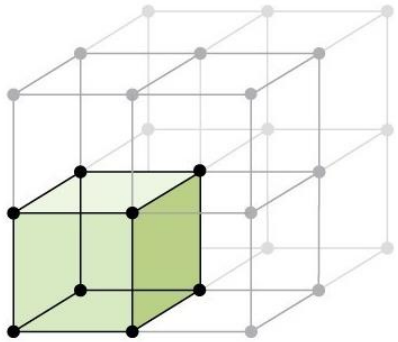
- Results: Localized benzene π orbitals that exhibit this C_6 symmetry



- Interestingly, we get 6 π orbitals instead of the expected 3

Combining Symmetry and Localization

- Only one T-amplitude needs to be calculated for each set of equivalent orbitals
  - Calculations are greatly simplified
- By combining symmetry and localization, we can preform CC calculations on larger systems



- My contribution: Investigate the construction of these orbitals

Description of Algorithm

- Define a projector, $\hat{\mathrm{P}}^{\mathrm{A}}$ which projects MO's onto the AO's of the unit cell

- Constuct overlap matrix, $O_{ij} = \langle i \left| \hat{P}^{A} \right| j \rangle$ (i,j are occupied)

- The eigenvalues (λ_i) of O_{ij} give a measure of MO locality.

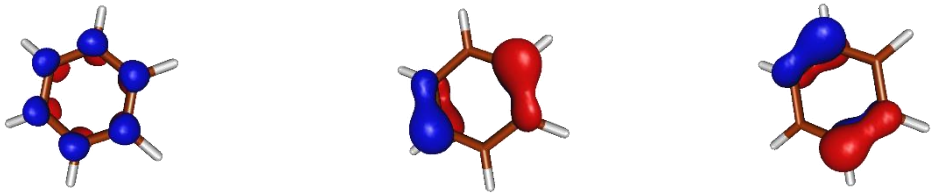
Description of Algorithm

- Projected local orbitals (PLO's): keep desired number of orbitals with high λ_i
  - Fully localized orbitals on the unit cell
  - Bonding orbitals have additional density near neighbours
- Enveloping localized orbitals (ELO's): more complicated
  - Same fully localized orbitals as PLO's
  - Bonding orbitals have virtual character to fully localize them

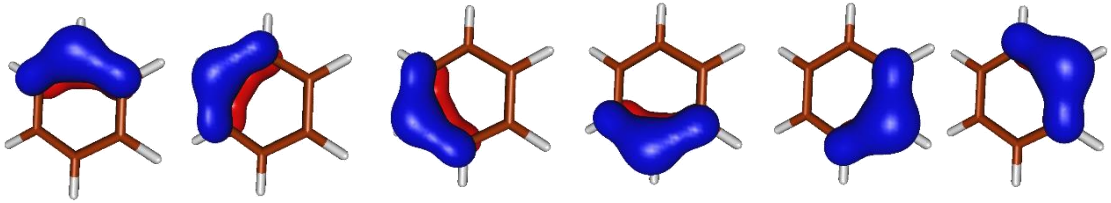
Results

- Localized benzene π orbitals (HF/3-21G)

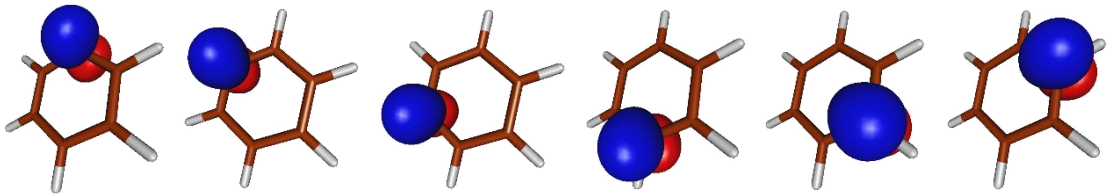
Cannonical



PLO's

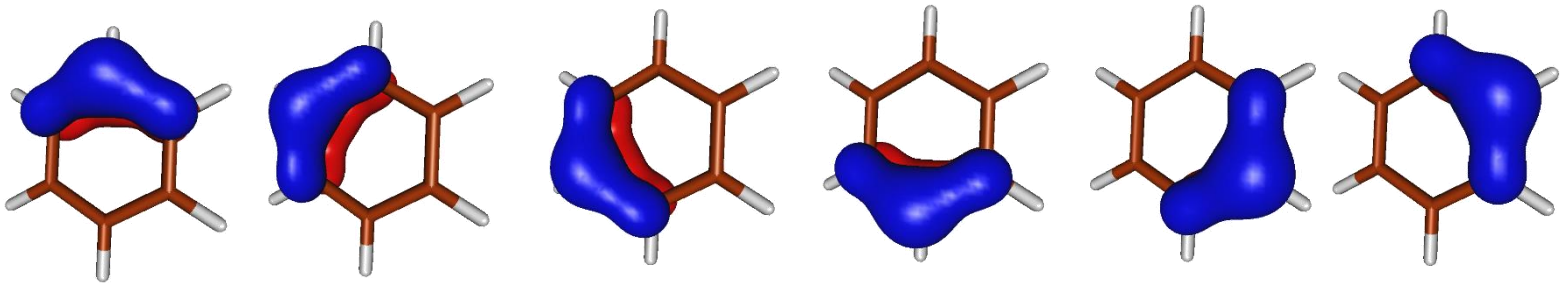


ELO's



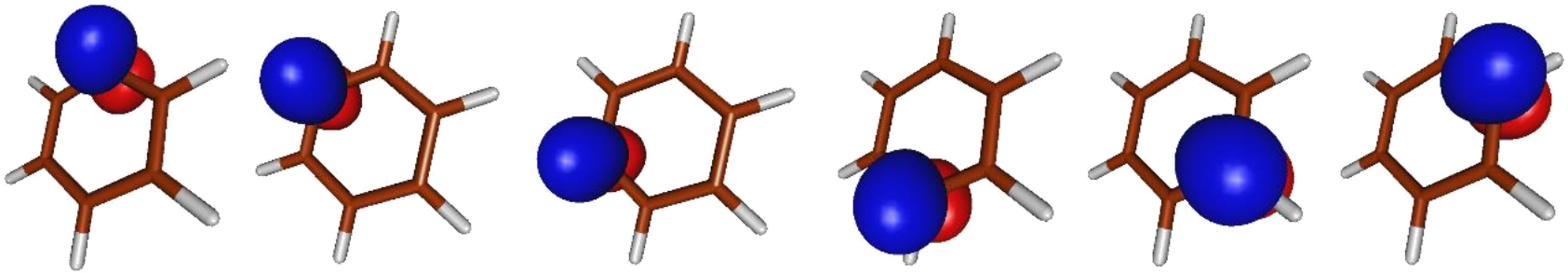
Projected Localized Orbitals (PLO's)

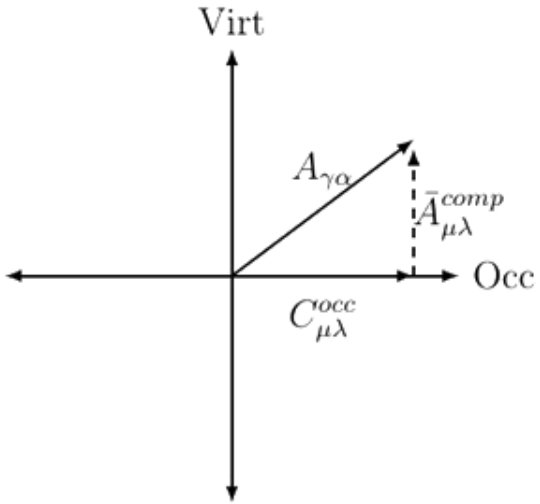
- PLO's are non-orthogonal
- Relatively intuitive



Enveloping Localized Orbitals

- We can choose virtual orbitals to precisely compensate for the orbital components lost.
- Orbitals are fully localized



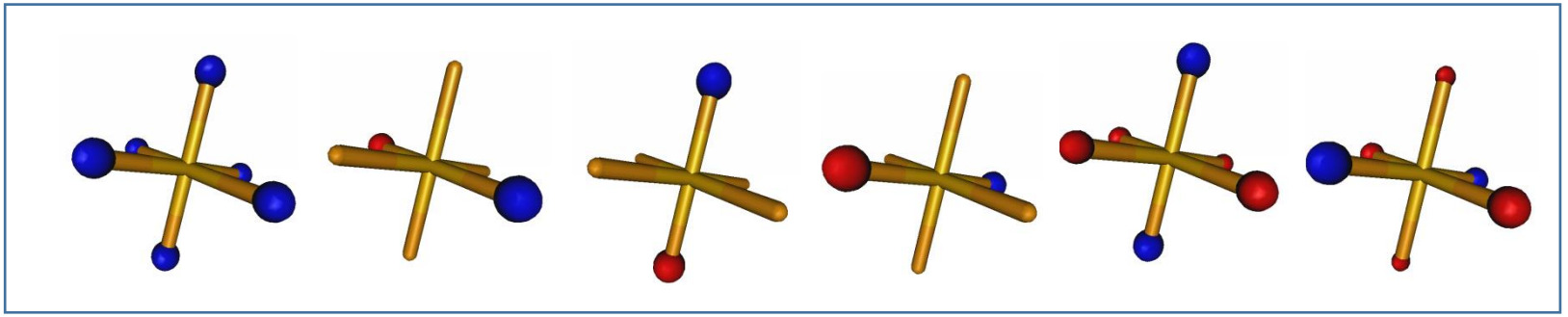


Cannonical orbitals, PLO's, ELO's

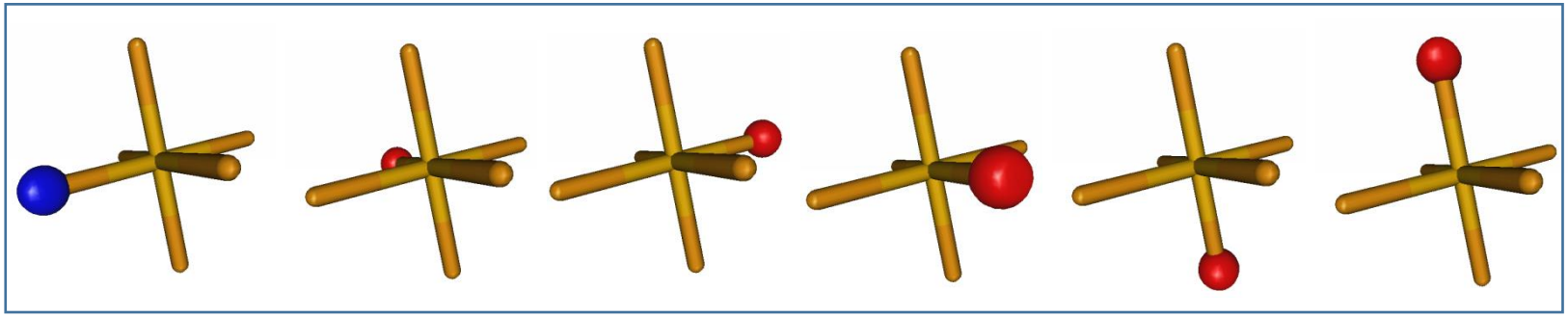
	Cannonical MO's	PLO's	ELO's
Localized	No	Yes	Yes
Orthogonal	Yes	No	Choose
Occupied orbitals have pure occupied character (Occupied and virtual orbitals do not mix)	Yes	Yes	No

SF_6

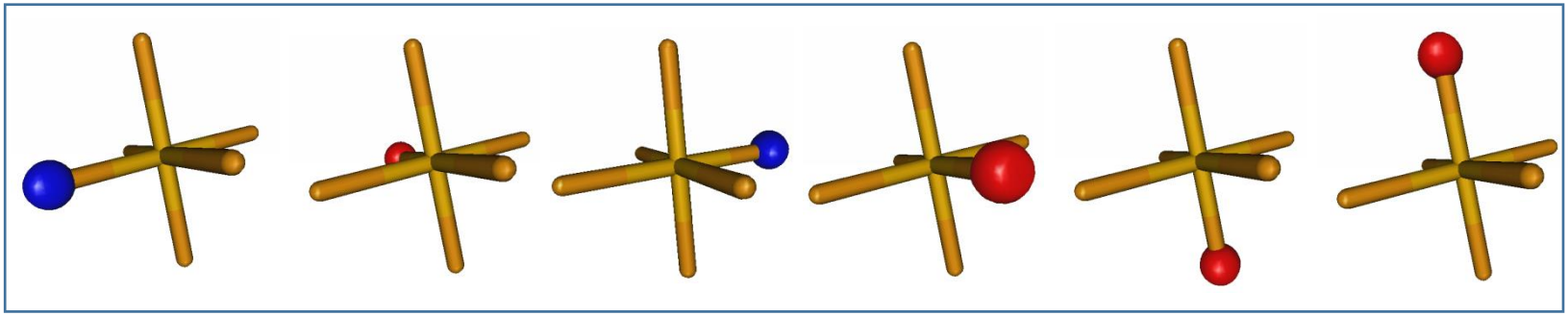
Canonical



PLO's

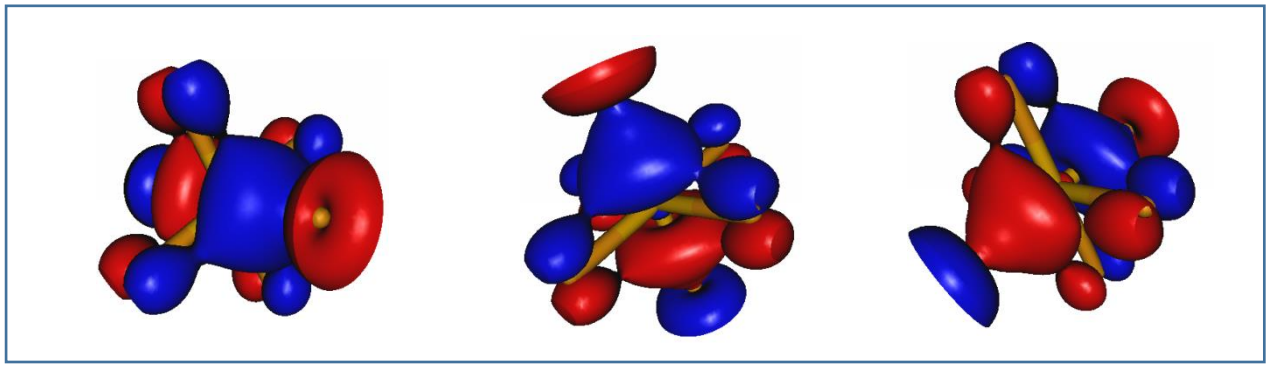


ELO's

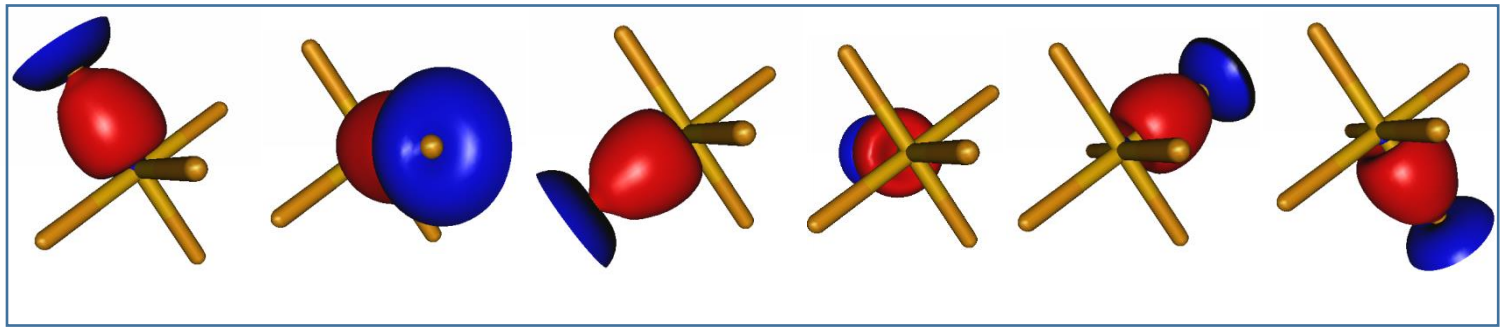


SF_6

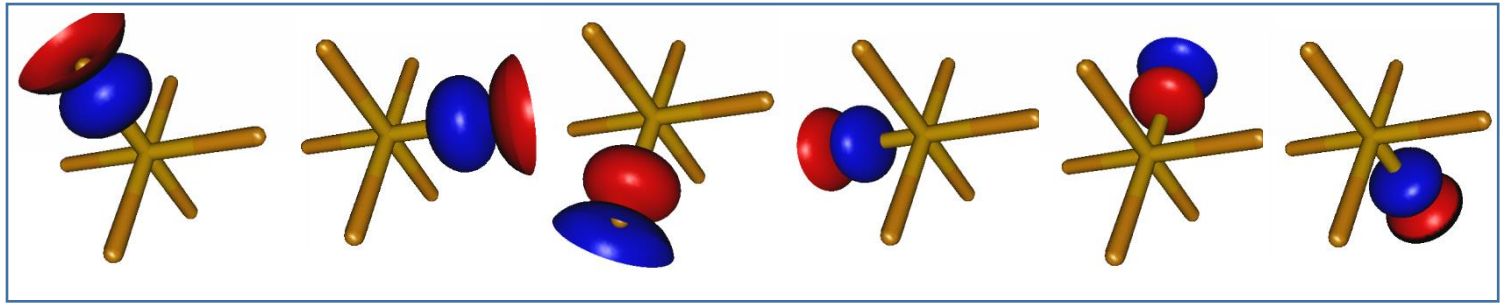
Canonical



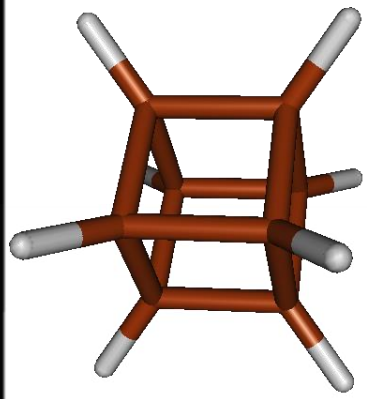
PLO's



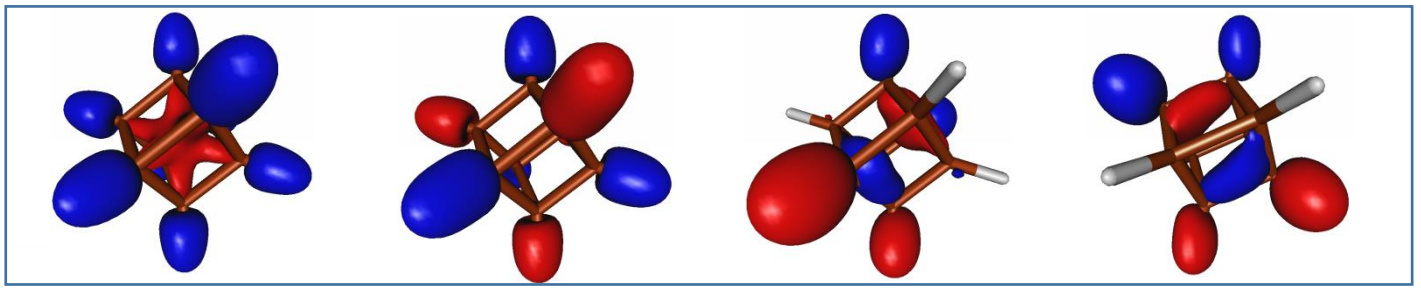
ELO's

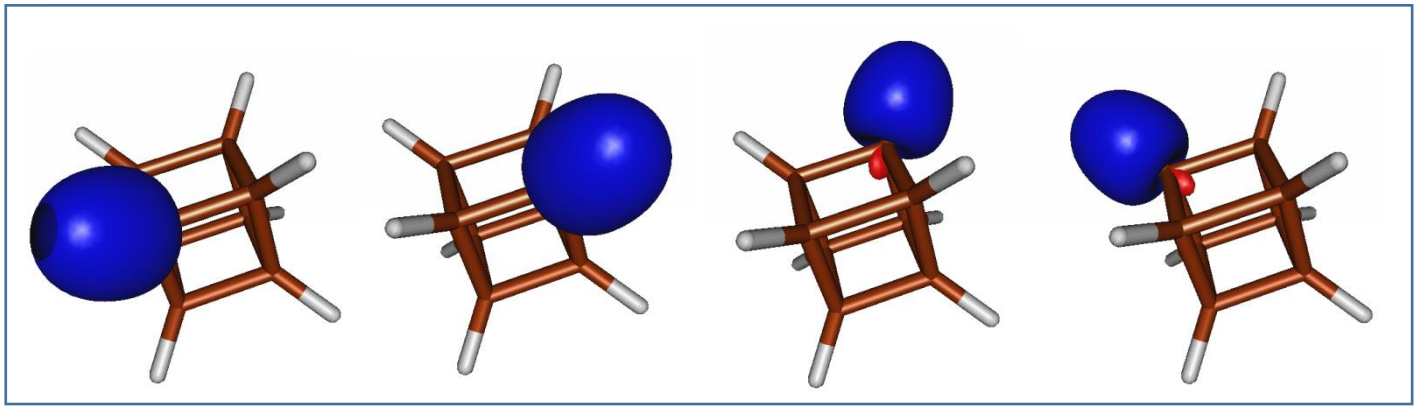


Cubane

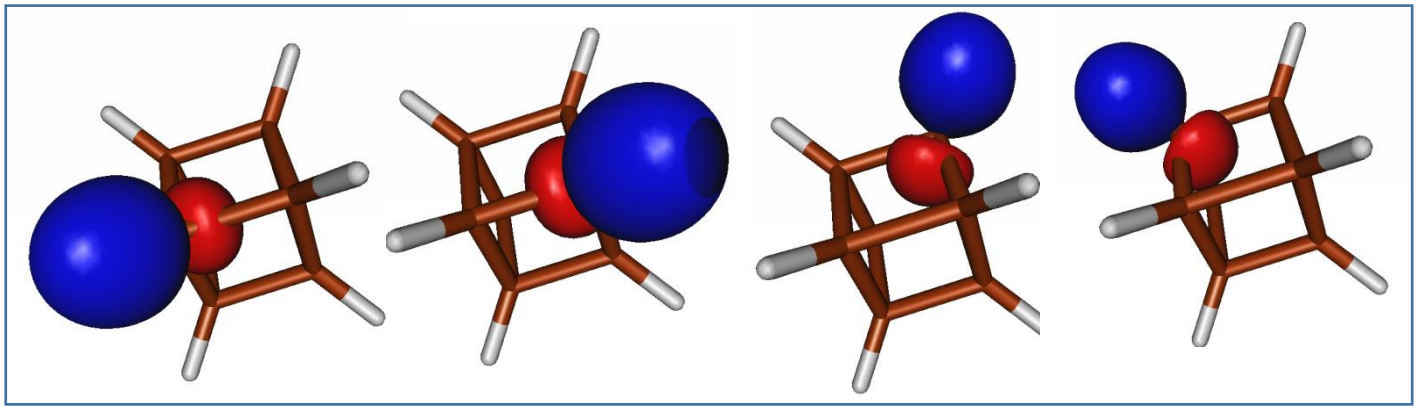


PLO's

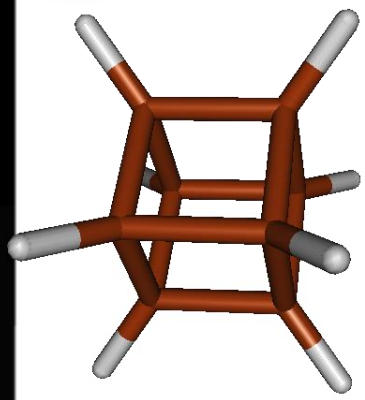




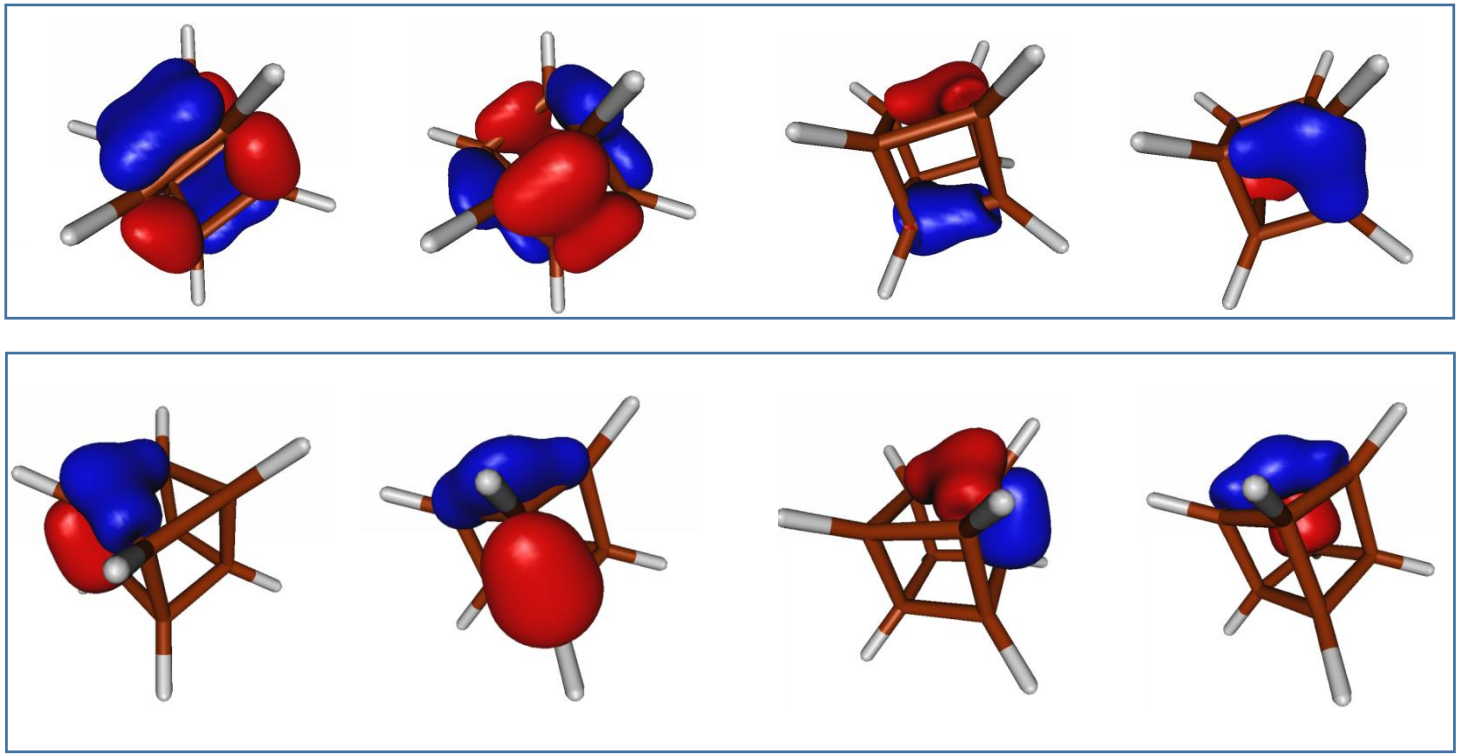
ELO's



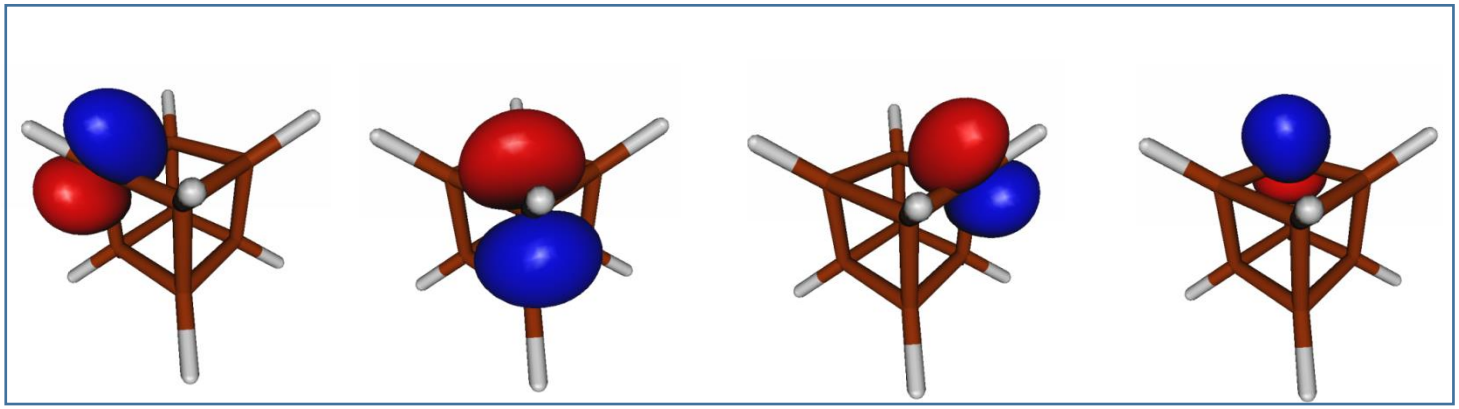
Cubane



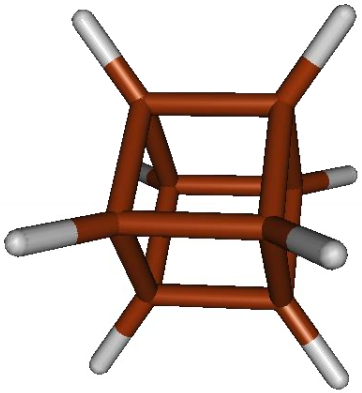
PLO's

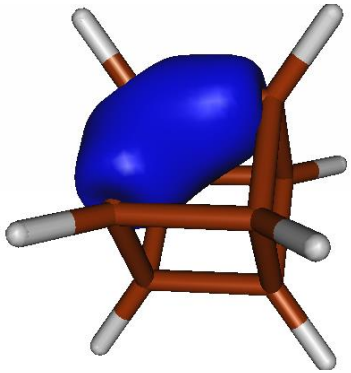


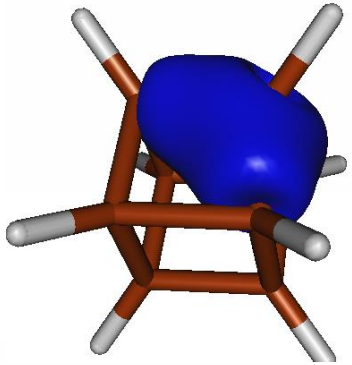
ELO's

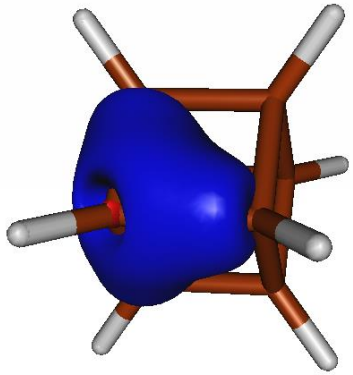


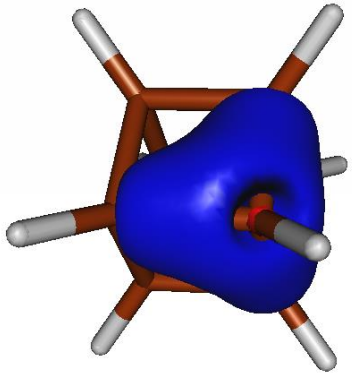
PLO’s with no equivalent ELO’s





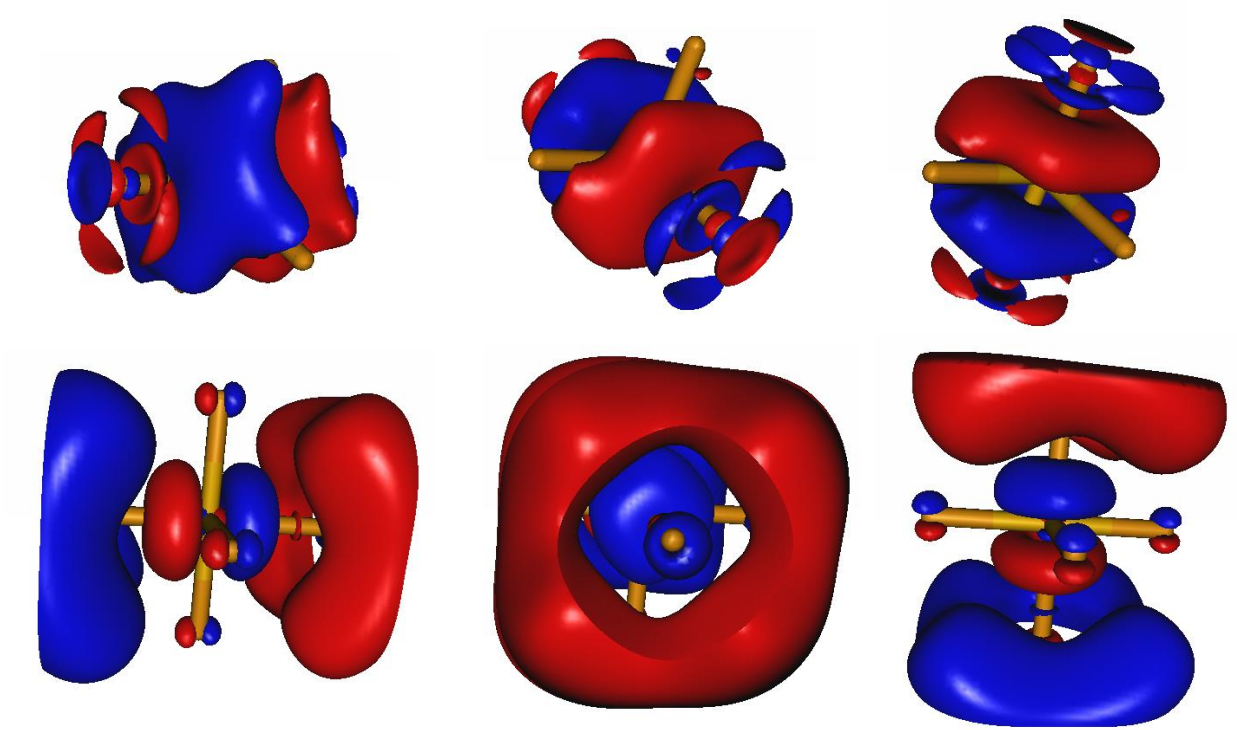






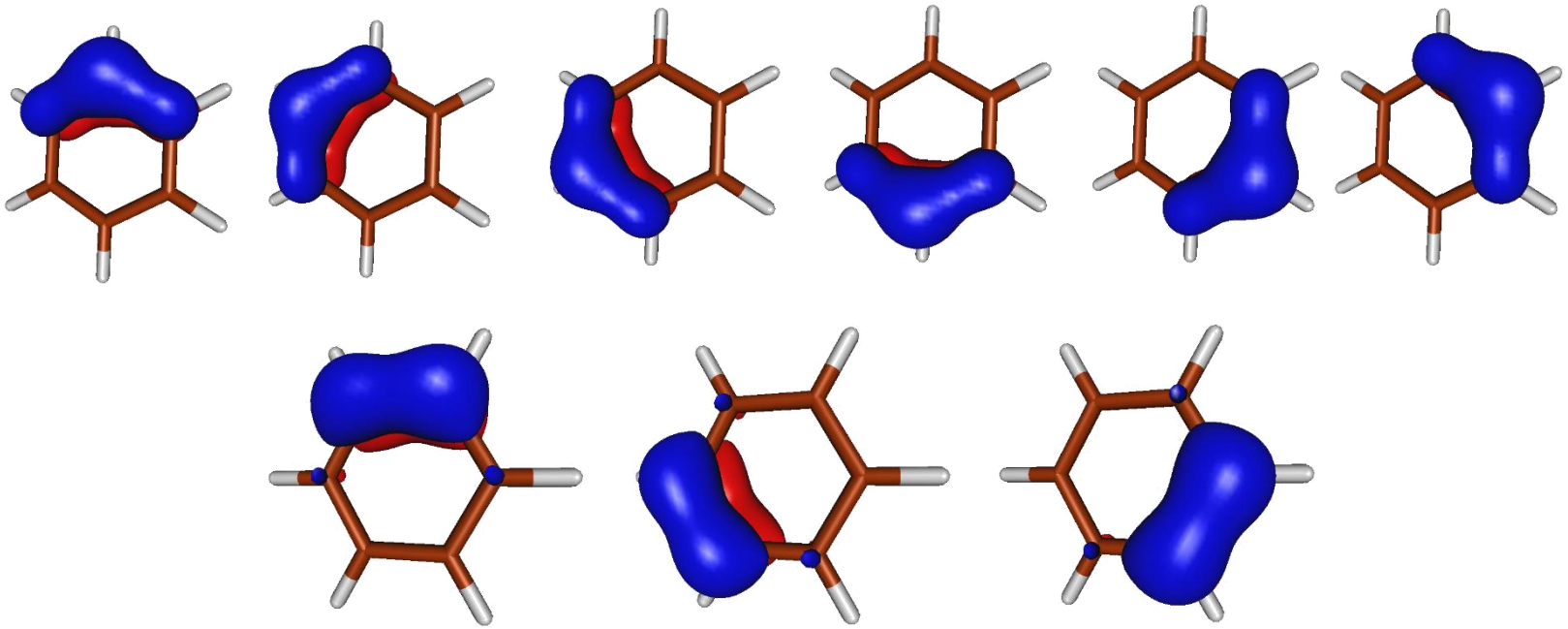
Effect of Basis Set on Orbitals

- Additional calculations for small systems done at HF/cc-PVTDZ
- Occupied orbitals remain mostly unchanged
- ELO virtuals are large, diffuse, and periodic

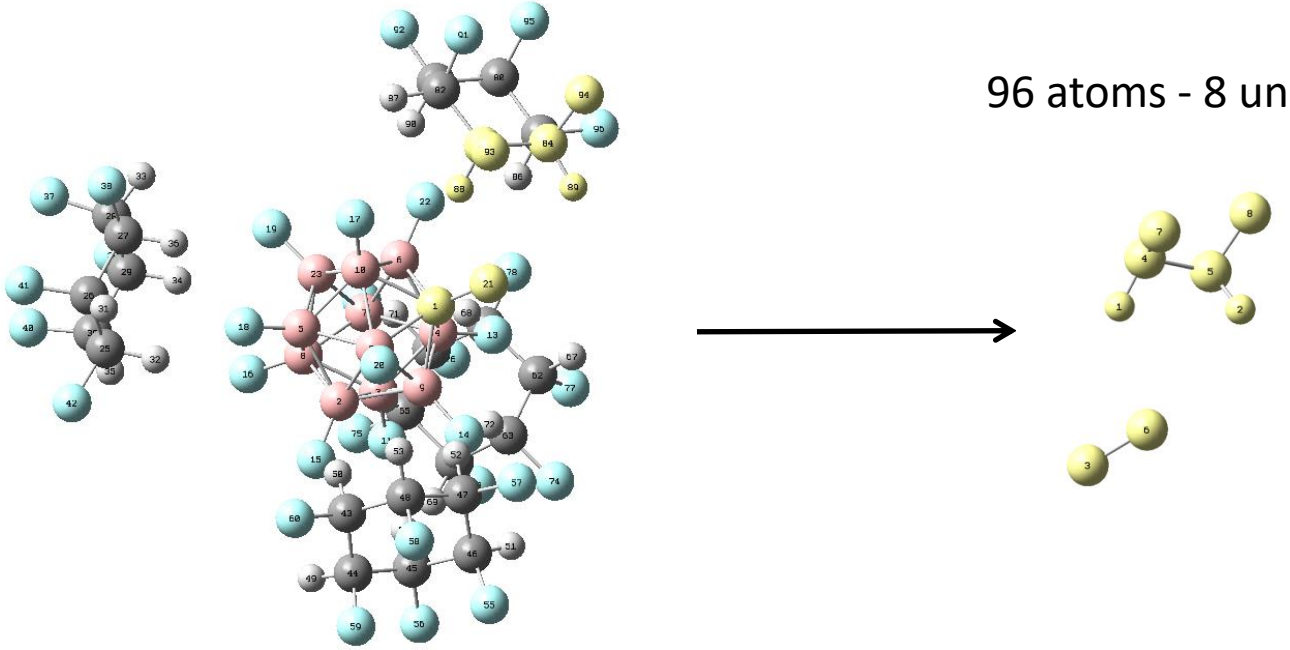


Choice of Unit Cell

- We can choose different unit cells to obtain different sets of orbitals
- Benzene PLO's: CH vs C_2H_2



- Python script written by Mike Lecours to help pick out equivalent atoms within a cluster



- Clear potential for speedup

Conclusions

- We have developed a method for constructing localized orbitals which reflect the symmetry of the system.
- PLO's are localized, non-orthogonal orbitals which can give insight into the bonding between unit cells
- ELO's are extremely localized, orthogonal orbitals with virtual character
- **Local CC methods done with PLO's or ELO's should offer a significant reduction in computational complexity without sacrificing much accuracy.**

Future Work

- Larger basis sets
- Further testing of the algorithm
- Automatic determination of unit cell and symmetry operations
- Development of a full CC code using PLO's, ELO's is underway in collaboration with Dr. Ondrej Demel

Acknowledgements

- Dr. Marcel Nooijen
- Mike Lecours
- Theoretical Chemistry Department
- Johnny and Max