The Road Less Traveled: Utilizing Non-Abelian Symmetry in Quantum Chemistry

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Abelian vs. Non-Abelian

- Symmetry speeds up calculations
- Most electronic structure programs implement symmetry utilization for only Abelian point groups
- What about the rest of the point groups?
  - We can exploit up to 8-fold symmetry using Abelian point groups
  - But we could be exploiting even 120-fold symmetry
- Non-Abelian point groups are hard, because of degeneracies and the need for irreducible representation matrices
- We have implemented several symmetry utilization features that work for Abelian and Non-Abelian point groups

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Fermi and Julia

- "Julia aims to create an unprecedented combination of ease-of-use, power, and efficiency in a single language."
- We have done almost all of the work so far in the FermiQC environment
- Why?
  - Fermi had no symmetry functionality, so we could start from the bottom and build our own package
  - Julia is a lot of fun to program in

Finding the Point Group

- A point group is uniquely defined by the symmetry elements comprising it
- Therefore, if we find the unique symmetry elements we can determine the point group and the remaining symmetry elements
- We use the method outlined here[1]
  - Find sets of Symmetry Equivalent Atoms (SEAs)
  - Find highest order rotations for each SEA set by exploiting principal moments of inertia for the SEAs
  - Check for perpendicular C_2, σ_v, or σ_h

[1] Beruski and Vidal *J. Comp. Chem.* **2014**

Symmetry Elements and χ-Tables

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- When the point group is known, the symmetry elements and character table can be generated for any finite point group
  - C_n, C_{nv}, C_{nh}, S_{2n}, D_n, D_{nd}, D_{nh}
  - C_i, C_2, T, T_d, T_h, O, O_h, I, I_h
- From the symmetry elements, we can build the multiplication table for the point group

Irreducible Representation Matrices

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- Irreducible representation matrices contain all of the symmetry information relevant to a point group
  - These are necessary when working with non-Abelian point groups
- We have built a library of irreducible representation matrices for all of the point groups found in the back of Cotton
  - There are 1,200 matrices for I_h!!!

Irrep. Mats. for C_{3v}

	A_1	A_2	E
$\hat{E}$	(1)	(1)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$\hat{C}_3$	(1)	(1)	$\begin{pmatrix} -\cos\theta & -\sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}$
$\hat{C}_3^2$	(1)	(1)	$\begin{pmatrix} -\cos\theta & \sin\theta \\ -\sin\theta & -\cos\theta \end{pmatrix}$
$\hat{\sigma}_1$	(1)	(-1)	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
$\hat{\sigma}_2$	(1)	(-1)	$\begin{pmatrix} -\cos\theta & -\sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$
$\hat{\sigma}_3$	(1)	(-1)	$\begin{pmatrix} -\cos\theta & \sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$

Symmetrized Integrals

- Using the Davidson double coset method, we have been able to compute symmetrized one and two electron integrals
- It is slow

Non-Abelian Hartree Fock

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- We have been able to use our symmetry library to calculate HF energies that match the C_1 energy
- That by itself is not that impressive, but it means we at least get correct answers
- We plan to also symmetrize MP2, CCSD, and CCSD(T)

Plugging Into Psi4

- Stand alone Python symmetry detection and SALCs
  - The tragic story of the C_{1h} point group
- Interface with Psi4, OptKing, and CMA

The End

- Nate Kitzmiller
- Prof. Schaefer
- Dr. Allen
- Dr. Turney
- CCQC