

Supporting Information for MOLSYM: A Python Package for Handling Symmetry in Molecular Quantum Chemistry*

Stephen M. Goodlett, Nathaniel L. Kitzmiller, Justin M. Turney, Henry F. Schaefer III

S1 Symmetry Adapted R.H.F.

The Restricted Hartree–Fock electronic energy for an SCF iteration is defined as

$$E_{elec} = \sum_{pq}^{AO} D_{pq} (H_{pq} + F_{pq}) \quad (1)$$

where E_{elec} is the electronic energy, D_{pq} is the density matrix, H_{pq} is the core hamiltonian, and F_{pq} is the Fock matrix in the AO basis. In the symmetry-orbital (SO) basis, the expression for the electronic energy is obtained by summing over the irreducible representations (μ) of group.

$$E_{elec} = \sum_{\mu} \sum_{pq}^{SO} D_{pq}^{\mu} (H_{pq}^{\mu} + F_{pq}^{\mu}). \quad (2)$$

Nonabelian groups contain degenerate irreps, and it is recognized that the matrix elements for the one-electron operators in the symmetry orbital basis set contain redundant tensor elements arising from spatial symmetry (we will ignore spin symmetry for now). The degeneracy of the μ^{th} irrep is the integer d_{μ} . We only consider nonredundant tensor elements arising from degeneracy from an operator \mathcal{O} as $\overline{\mathcal{O}}$, and re-write (2) as

$$E_{elec} = \sum_{\mu} \sum_{pq}^{SO} d_{\mu} \overline{D}_{pq}^{\mu} (\overline{H}_{pq}^{\mu} + \overline{F}_{pq}^{\mu}). \quad (3)$$

Taylor¹ provides an in-depth discussion of symmetry-adapted operators and their block diagonal structure. The Fock matrix is constructed viz

$$\overline{F}_{pq}^{\mu} = \overline{H}_{pq}^{\mu} + 2\overline{J}_{pq}^{\mu} - \overline{K}_{pq}^{\mu} \quad (4)$$

where \overline{J}_{pq}^{μ} is the coulomb matrix and \overline{K}_{pq}^{μ} is the exchange matrix. Fock matrix build times can be found in Table S1 for several point groups.

*Submitted to the Special Issue of the *Journal of Chemical Physics* titled “Modular and Interoperable Software for Chemical Physics”

Molecule	Basis	Time C_{3v} (s)	Time C_s (s)	Time C_1 (s)
NH ₃	STO-3G	9.81×10^{-5}	1.05×10^{-4}	9.15×10^{-5}
	6-31G	1.45×10^{-4}	2.05×10^{-4}	2.72×10^{-4}
	cc-pVDZ	3.25×10^{-4}	6.94×10^{-4}	1.51×10^{-3}
	cc-pVTZ	2.17×10^{-3}	1.13×10^{-2}	3.82×10^{-2}
	cc-pVQZ	2.40×10^{-2}	1.58×10^{-1}	5.79×10^{-1}
Molecule	Basis	Time T_d (s)	Time C_{2v} (s)	Time C_1 (s)
CH ₄	STO-3G	1.02×10^{-4}	1.55×10^{-4}	1.07×10^{-4}
	6-31G	1.30×10^{-4}	2.43×10^{-4}	3.64×10^{-4}
	cc-pVDZ	2.98×10^{-4}	6.38×10^{-4}	2.44×10^{-3}
	cc-pVTZ	7.99×10^{-4}	7.13×10^{-3}	7.51×10^{-2}
	cc-pVQZ	6.28×10^{-3}	9.36×10^{-2}	1.22
Molecule	Basis	Time D_{6h} (s)	Time D_{2h} (s)	Time C_1 (s)
C ₆ H ₆	STO-3G	1.05×10^{-3}	8.66×10^{-4}	2.94×10^{-3}
	6-31G	1.28×10^{-3}	1.86×10^{-3}	2.75×10^{-2}
	cc-pVDZ	2.45×10^{-3}	7.28×10^{-3}	2.25×10^{-1}
	cc-pVTZ	2.61×10^{-2}	1.36×10^{-1}	6.56
Molecule	Basis	Time O_h (s)	Time D_{2h} (s)	Time C_1 (s)
SF ₆	STO-3G	4.76×10^{-4}	8.29×10^{-4}	3.96×10^{-3}
	6-31G	6.47×10^{-4}	1.87×10^{-3}	2.90×10^{-2}
	cc-pVDZ	1.30×10^{-3}	6.17×10^{-3}	1.76×10^{-1}
	cc-pVTZ	6.11×10^{-3}	6.99×10^{-2}	2.97
Molecule	Basis	Time O_h (s)	Time D_{2h} (s)	Time C_1 (s)
C ₈ H ₈	STO-3G	7.49×10^{-4}	9.50×10^{-4}	8.53×10^{-3}
	6-31G	9.86×10^{-4}	2.20×10^{-3}	8.26×10^{-2}
	cc-pVDZ	1.72×10^{-3}	1.36×10^{-2}	7.01×10^{-1}
	cc-pVTZ	2.56×10^{-2}	3.25×10^{-1}	3.24×10^1

Table S1: The Fock matrix build times, in seconds (s), averaged over 50 SCF iterations used to compute relative timings in Table 3 of the paper. The full molecular point group, largest real abelian subgroup, and C_1 group for various molecules are presented.

References

- [1] Taylor, P. R. In *Lecture Notes in Quantum Chemistry: European Summer School in Quantum Chemistry*; Roos, B. O., Ed.; Springer: Berlin, Heidelberg, 1992; pp 89–176.