MENG 25510 Final Report: Hartree-Fock on HeH^+ with 6-311G

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Please see the corresponding code at `https://github.com/FitzSW/HF_HeH` for this project.

I. INTRODUCTION

This is a reference document to go with our submission for the MENG 25510 final coding project, for which we chose to implement the Hartree-Fock (HF) Self-Consistent Field (SCF) method on a HeH^+ molecular system using the 6-311G basis set on both atoms. The geometry at which we performed the calculation was optimized at the CCSD/aug-cc-pZTZ level of theory using Gaussian 16[1]. The result of our code is then compared to an energy found with PySCF[2–4] using the same geometry and basis set.

II. HARTREE-FOCK ALGORITHM AND CODE DETAILS

We closely follow the suggested implementation scheme given in Szabo and Ostlund[5], in which explicit formulas and matrix algorithms are given.

A. Program Control Flow

First, the input geometry and basis set files are read into the main program ("main.f90"), which are then used to construct a 1D array of the "orbitals" derived type (written in "orbitals.f90"), which each include the name of its host atom, the orbital angular momentum type (e.g. "s"), the coordinates of the host atom, the length of the contraction, as well as arrays of coefficients and exponential factors for the contraction.

From here, we then calculate the stored integrals to populate the matrices $\mathbf{S}$, $\mathbf{T}$, $\{\mathbf{V}^{\text{nuc.}}\}$, and $\mathbf{TE}$, with the last representing the two-electron integrals. The eigenvalue problem that we are trying to solve is recommended to be handled via a transformation to a set of orthogonalized orbitals via a matrix $\mathbf{X}$ obtained from the *symmetric orthogonalization* scheme

$$\mathbf{X} = \mathbf{S}^{1/2} \tag{1}$$

The necessary matrix computations are done with assistance from the C++ numerics library Eigen[6], which is also later used to find the eigenvalues and eigenvectors of matrices at each cycle of the SCF procedure.

III. USE AND INSTALLATION

In order to run our code, please clone the git repository that is linked in the abstract of this document. Then, run the command:

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, "Gaussian16 Revision C.01," (2016), gaussian Inc. Wallingford CT.

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[4] Q. Sun, "Libcint: An efficient general integral library for gaussian basis functions," J. Comp. Chem. **36**, 1664–1671 (2015), https://onlinelibrary.wiley.com/doi/pdf/10.1002/jcc.23981.

[5] A. Szabo and N. S. Ostlund, *Modern quantum chemistry: introduction to advanced electronic structure theory* (Courier Corporation, 2012).

[6] G. Guennebaud, B. Jacob, *et al.*, "Eigen v3," http://eigen.tuxfamily.org (2010).