On the Development of a New Computational Chemistry Software

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Abstract: FIESTA—the Filipino Initiative on Electronic Structure Theory and Applications—a new computational chemistry software is developed. The new software is capable of doing ground-state self-consistent field (SCF) single-point restricted Hartree-Fock (RHF) calculation of polyelectronic and polyatomic systems using the Slater-type orbital basis set STO-3G. The new program implements well-known quantum mechanical theories for practical calculations. FIESTA is written using two programming languages, namely C and FORTRAN. It is accurate and user-friendly. It runs efficiently under the Linux operating system and is able to reproduce the energies calculated using well-established standard quantum chemical software products Gaussian, Firefly and Molpro. To our knowledge, FIESTA is the first and only molecular modeling software developed in the Philippines to date. The software will be extended to calculate the properties of systems such as atoms, molecules, ions and formula units using more sophisticated basis sets and quantum mechanical techniques.

Key Words: computational chemistry; ab initio calculation; Hartree-Fock theory; self-consistent field

Computational chemistry is used for precise chemical predictions and refined simulations of chemical processes with the use of computer programs. Computational data may not yield the exact experimental value from measurements, but it can predict chemical phenomena qualitatively, and at times, quantitatively. In general, computational chemistry involves the numerical solution to the Schrödinger equation (Schrödinger, 1926a, 1926b). At the electronic level, the equations of classical mechanics are not applicable. Classical mechanics fails to explain the behavior of particles as small as the electron. On the other hand, quantum mechanics is applicable to electronic systems and is able to determine properties at the microscopic level. In this study, the time-independent Schrödinger equation

for many-body polyelectronic systems will be solved numerically and its solution will be implemented in a new software to calculate gas-phase system properties such as the electronic energy, orbital energies, nuclear repulsion energy and the total energy.

At present, there is a good deal of computational chemistry softwares available. Most of them require a commercial license. Most popular among them is the Gaussian (Frisch et al., 2009) suite of quantum mechanical routines developed by the group of the late John Pople (Nobel Prize, Chemistry, 1998) at Carnegie-Mellon University. The first Gaussian program was developed in 1970 as Gaussian 70 (Hehre, Lathan, Ditchfield, Newton, & Pople, 1970), and now there are several versions of

Gaussian program which are made suitable to different computer operating systems. The latest version is Gaussian 09. It can calculate electronic structures; energies, vibrational frequencies, molecular properties, reactions in variety of chemical environment, and the program is expected to predict the corresponding spectra.

Another popular package is the MOLPRO Quantum Chemistry Package (Werner et al., 2010) created by Werner, Knowles and co-workers. The strength of the program lies mainly on its programmable input system and its efficient implementation of the multi-configuration self-consistent field (MCSCF) method. The software is especially recommended for high accuracy in computations. The software was improved recently with the integral-direct local electron correlation methods. As a result, it minimizes the computational costs of relatively larger molecules within extensive approach of electron correlation problem.

The General Atomic and Molecular Electronic Structure System (GAMESS), is also a popular ab initio quantum chemistry package (Schmidt et al., 1993). Originally, it was a National Resources for Computation in Chemistry project in 1977. In 1981, GAMESS was split into GAMESS-US and GAMESS-UK. GAMESS-US is currently managed by the Gordon Research Group at Iowa University, USA. It is capable of doing Hartree-Fock, density functional theory (DFT), generalized valence bond (GVB) and MCSCF calculations. GAMESS-UK includes the calculation of valence bond wave functions through the TURTLE code initiated by Van Lenthe. The program is based on the earlier UK-based program ATMOL. Firefly (Granovsky, 1994), formerly known as PC GAMESS, is partially based on the GAMESS-US source code.

A new computational chemistry software is developed and its accuracy is compared to that of well-established softwares Gaussian, Firefly and Molpro. Source codes for implementing the mathematical procedures are encoded under the Linux operating system. The source codes are compiled into an executable program using the Intel FORTRAN and C compilers. The Intel Math Kernel Library is used for matrix multiplication and matrix diagonalization.

Two sets of code are designed, one for FORTRAN and the other for C language. When the codes are prepared, they are encoded step by step to minimize technical error and for easier debugging. The FORTRAN and C codes are compiled and executed from time to time to check whether the written codes are working properly. Otherwise, some portions of the codes are edited or a different approach with similar structure is encoded. After compiling, when the executable program is ready, simple calculations are done to check the accuracy of the program. The properties of small hypothetical systems such as He, H_2, HeH^+, HeH^- and HeH_2 are calculated and the results are compared to values obtained using well-established standard software products such as Gaussian, Molpro and Firefly. A brief description of the test systems used in this study is given in Table 1.

Table 1. The test chemical system used in this study.

System	Number of atoms	Number of electrons	Charge	Remarks
He	1	2	0	simplest uncharged monatomic system
H_2	2	2	0	simplest uncharged diatomic 2-electron system
HeH^+	2	2	+1	simplest charged diatomic 2-electron system
HeH^-	2	4	-1	simplest diatomic polyelectronic system
HeH_2	3	4	0	simplest polyatomic polyelectronic system

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He is the simplest uncharged monatomic system. The calculation results of FIESTA and the three other software programs show that FIESTA is in excellent agreement with the other programs (Table 2). Being a single atom, it has zero nuclear repulsion energy. In terms of the electronic energy, FIESTA is in numerical agreement with Gaussian program up to eleven figures. In total energy calculations, FIESTA is in agreement with the other programs up to nine figures. It appears that Gaussian normally prints out a greater number of figures compared to the other programs.

Table 2. Theoretical electronic energy, orbital energies, nuclear repulsion energy and total energy of He.[§]

	FIESTA	Gaussian	Firefly	Molpro
Electronic energy	**−2.80778395**66141956	**−2.80778395**661933	**−2.80778395**66	**−2.80778395**7682
Nuclear repulsion energy	**0.000000000000000**	**0.0000000000**	**0.0000000000**	**0.00000000**
Total energy	**−2.80778395**66141956	**−2.80778395**661933	**−2.80778395**66	**−2.80778395**7682
Orbital energy	**−0.8760**355082964668	**−0.8760**4	**−0.8760**	**−0.8760**

[§]All energies are in Hartree. The figures that are in complete agreement are highlighted.

FIESTA is as accurate as the established commercial software programs in predicting the energies of He. It should be emphasized that in this Letter, "accuracy" merely means agreement of the results with those obtained by using well-established commercial software programs and not chemical accuracy. The minimal STO-3G basis set is not known to yield predictions that quantitatively replicate experimental values.

Among the three commercial software programs, Gaussian reports more number of figures than the others. From this point, the accuracy of FIESTA is compared with Gaussian only.

The simplest uncharged diatomic system, H_2, is where nuclear repulsion begins to occur. In terms of total energy, FIESTA estimates it at −1.11671432517577 Hartree (R=1.4 Bohr) while Gaussian puts it at −1.11671432517847 Hartree (Table 3); the results agree up to twelve figures.

Table 3 Theoretical total energy of the test chemical systems used in this study calculated using three different softwares.[§]

System	FIESTA (C)	FIESTA (FORTRAN)	Gaussian
He	**−2.8077839566**141956	**−2.8077839566**1420	**−2.8077839566**1933
H_2	**−1.11671432517**57694	**−1.11671432517**577	**−1.11671432517**847
HeH+	**−2.8340608791**878594	**−2.8340608791**8786	**−2.8340608792**0197
HeH-	**−2.3735230594**390924	**−2.3735230594**3909	**−2.3735230594**0872
HeH_2	**−3.2667791369**039940	**−3.2667791369**0399	**−3.2667791369**2710

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§All energies are in Hartree. The figures that are in complete agreement are highlighted.

Like H_2, HeH^+ has two electrons. However, H_2 has a high degree of symmetry and some program bugs are undetected due to a system's symmetry. In the system HeH^+ (R = 1.4 Bohr), the robustness of FIESTA is tested for modeling a diatomic system of dissimilar atoms. The total energy obtained through FIESTA and Gaussian agrees up to eleven figures (Table 3).

So far, FIESTA has been tested on two-electron systems such as H_2 and HeH^+, the simplest closed-shell systems. It would be interesting to find out if FIESTA is able to predict the properties of systems with more than two electrons. The total energy of the HeH^- system (R = 1.4 Bohr) is calculated using FIESTA and the result is compared with that reported by Gaussian. The total energy of HeH^- calculated using FIESTA is -2.37352305943909 Hartree that is as accurate as that of Gaussian (-2.37352305940872 Hartree), matching up to eleven figures when rounded off.

HeH_2 is the smallest polyatomic polyelectronic closed-shell system. If FIESTA is able to accurately duplicate the results of Gaussian in the HeH_2 system, it should also be able to model other polyatomic, polyelectronic closed-shell systems as well. As expected, the total energy of HeH_2 system (R_1 = 1.9 Bohr, R_2 = 2.1 Bohr, θ = 120°) calculated through FIESTA is very close to the result of the Gaussian calculation. FIESTA predicted a total energy of -3.26677913690399 Hartree while Gaussian puts it at -3.26677913692710 Hartree. The agreement is until the eleventh figure.

The FORTRAN version of FIESTA is proven to be as accurate as the other commercial software programs while Gaussian reports the most number of figures. The performance of the C and FORTRAN versions of FIESTA and Gaussian are compared through their predicted total energy (Table 3). The total energy obtained through FIESTA, both C and FORTRAN versions, show excellent agreement between them throughout all the systems being studied. The results are also in accordance with Gaussian's predictions.

FIESTA is a new computational chemistry software which solves for the orbital energies, electronic energy, nuclear repulsion energy and total energy of closed-shell, polyatomic and polyelectronic systems within the Hartree-Fock approximation using the STO-3G basis set. FIESTA is developed using two different programming languages namely FORTRAN and C. FIESTA is built and tested by comparing the result of the electronic energy, nuclear repulsion energy, total energy and orbital energies with those obtained through the use of well-established standard computational chemistry software programs Gaussian, Firefly and Molpro. At each energy calculations, FIESTA has demonstrated its accuracy when compared with other programs. Most calculation results show that FIESTA is as accurate as Firefly and Molpro as well as Gaussian. FIESTA has the potential to be a major computational chemistry software in the future.

REFERENCES

Frisch, M., Trucks, G., Schlegel, H., Scuseria, G., Robb, M., Cheeseman, J., . . . Petersson, G. (2009). Gaussian 09, Gaussian. *Inc., Wallingford, CT*.

Granovsky, A. A. (1994). Firefly version 7.1.G. Retrieved August 30, 2013, from http://classic.chem.msu.su/gran/firefly/index.html

Hehre, W., Lathan, W., Ditchfield, R., Newton, M. D., & Pople, J. (1970). Gaussian 70. *Quantum Chemistry Program Exchange, 236*.

Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., . . . Montgomery, J. A. (1993). General atomic and molecular electronic structure system. *Journal of*

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Computational Chemistry, 14(11), 1347-1363. doi: 10.1002/jcc.540141112

Schrödinger, E. (1926a). Quantisierung als Eigenwertproblem. *Annalen der Physik, 385*(13), 437-490. doi: 10.1002/andp.19263851302

Schrödinger, E. (1926b). An Undulatory Theory of the Mechanics of Atoms and Molecules. *Physical Review, 28*(6), 1049-1070.

Werner, H., Knowles, P., Knizia, G., Manby, F., Schütz, M., Celani, P., . . . Rauhut, G. (2010). MOLPRO, version 2010.1, a package of ab initio programs; see http://www. molpro. net.

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