Application of GAMESS/NEO to quantum calculations of muonic molecules

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Abstract. The General Atomic and Molecular Electronic Structure System (GAMESS) has been modified to perform studies involving negative muons. This system, coupled with the Nuclear-Electronic Orbital (NEO) method enables the ab-initio study of muonic atoms where both the negative muon and the positive nuclei are modeled as quantum particles. This is of particular usefulness in the study light nuclei, muonic atoms, such as is encountered in muon-catalyzed fusion. NEO was also modified to allow the inclusion of positive exotic-particles to be studied using open and closed shell Hartree-Fock and Configuration Interaction. Capitalizing on these modified methods, the muon density and vibrational dynamics of some light muonic molecules have been analyzed.

1. Introduction

Many quantum mechanical software packages for predicting molecular properties have been written and modified over a number of years. Multiple general-purpose programs exist that do a good job of calculating Hartree-Fock energies, electron correlation energy by various methods, equilibrium geometries, harmonic and anharmonic vibrational energies, relativistic effects, and many other properties of molecular systems. Most of these software packages are written to exclusively calculate properties of molecular systems that contain only neutrons, protons and electrons. As part of research being performed at the Air Force Institute of Technology (AFIT) and the US Air Force Research Laboratory (AFRL) it has become desirable to develop and apply software to model the physical and chemical properties not only of traditional molecular systems, but of systems that contain exotic-particles as well (positrons, as well as negative and positive muons). At this point, two options existed, develop new code from scratch or modify existing code to calculate the desired properties of exotic molecules. While there are pros and cons to both of these approaches, a decision was made to modify existing software, thereby directly capitalizing on the extensive work in quantum chemistry performed by others.
The software package selected for modification was the General Atomic and Molecular Electronic Structure System (GAMESS). GAMESS is a general purpose electronic structure code whose primary focus is on \textit{ab-initio} quantum chemistry calculations. It is a highly capable, integrated system of computational modules designed to predict physical and chemical properties of molecular systems. Like most quantum chemistry codes, GAMESS treated only electrons as fully quantum particles. GAMESS was developed in a non-commercial enterprise under leadership of Prof. Mark Gordon from North Dakota State University beginning in the 1980’s[1,2]. Since its inception, Prof. Gordon, who later moved to Iowa State University, his students and contributing colleagues have continued to develop the code and expand its capabilities. The selection of GAMESS has several benefits over other software packages considered. The GAMESS code has always been made available free of charge for other scientists to assist with its development and to employ for application. Prof. Gordon and his group have demonstrated a willingness to assist in further code development to include exotic particles. The greatest single advantage was the recent development of Nuclear-Electronic Orbital (NEO) code to model quantum nuclei in molecules. This was developed by Prof. Sharon Hammes-Schiffer and associates, from Pennsylvania State University, for integration into GAMESS[3]. NEO is designed to incorporate nuclear quantum effects into electronic structure calculations by treating specified nuclei quantum mechanically on the same level as the electrons. The basic objective of the method is to solve a mixed nuclear-electronic time-independent Schrödinger equation with molecular orbital methods. Both electronic and nuclear molecular orbitals are expressed as linear combinations of Gaussian basis functions. The variational method is used to minimize the energy with respect to all molecular orbitals, as well as the centers of the nuclear basis functions. Correlation effects among electrons and nuclei are included with multiconfigurational (MCF) perturbation theory (MP2)[4] and Configuration interaction (CI)[5] methods. The advantages to this approach include: (1) nuclear quantum effects are incorporated during electronic structure calculations, (2) Born-Oppenheimer separation of electrons and nuclei is avoided, (3) excited vibrational-electronic states may be calculated, (4) its accuracy may be improved systematically, (5) NEO has been incorporated into GAMESS general quantum chemistry code, which is well-tested (6) quantum tunneling systems can be handled with multiple basis function centers for a single quantum nucleus, (7) positions of nuclear basis function centers may be fixed or optimized variationally, and (8) symmetry-adapted linear combinations of nuclear molecular orbitals are available[6,7,8,9,10,11,12,13,14]. One of the biggest advantages of applying the NEO approach to calculate exotic particle molecule properties is that the method takes maximum advantage of the \textit{ab-initio} HF, MCSCF and CI codes developed for the GAMESS general quantum chemical software package. The NEO code provided the potential to extend the capability of GAMESS to model molecular systems having both positive and negative quantum particles.

Between 2005 and 2007 Prof. Larry Burggraf’s group from AFIT, in collaboration with Prof. Hammes-Schiffer, modified and extended the GAMESS/NEO software to allow the study of positronic molecular systems using mixed positronic-electronic wavefunctions. Computational methods to model positronic-electronic wavefunctions include: Hartree-Fock (HF), second-order Möller-Plesset perturbation theory (MP2), configuration interaction (CI), and complete active space self-consistent field (CASSCF). The ability to calculate positron-electron annihilation rates based on NEO-HF and NEO-MP2 wavefunctions was also implemented[15,16]. Within the NEO framework, the NEO-HF (Hartree-Fock) method provides the energy corresponding to the single-configuration mixed positronic-electronic wavefunction, minimized with respect to the molecular orbitals expressed as linear combinations of Gaussian basis functions. The mixed wavefunction is a product of two Slater determinants, one representing electronic coordinates and one representing positronic coordinates. These are optimized iteratively in the NEO HF formalism. The electron-electron and electron-positron correlation can be treated in the NEO framework with second-order perturbation theory (NEO-MP2) or multiconfigurational methods such as the full configuration interaction (NEO-FCI) and complete active space self-consistent-field (NEO-CASSCF) methods[15,16].
2. Expansion of the GAMESS/NEO Code

The next step in the development of GAMESS/NEO exotic particle code was to add the ability to model muonic systems. The code was modified to allow the study of any mass for the positive particles. This allowed modelling of molecular properties as a function of mass in ways that could not be done if only specific masses were allowed. Being that the NEO code, which was originally designed for positive nuclei, had previously been modified to allow the study of positronic systems, additional alteration of the code to allow for the study of any mass positive quantum particle was rather straightforward. The NEO code, as it currently exists, does have one significant weakness that should not be overlooked, however. Only one mass of positive quantum particles can be studied at a time without modifying the code to include additional Slater determinants. A system containing multiple positrons, or multiple positive muons can be studied, but a system containing both positrons and positive muons cannot. This weakness in the code could be limiting when studying systems containing positive muons and light nuclei. In this case, the nuclei must be considered classically.

While modifying the NEO-positron code to allow for calculations involving any mass positive quantum nuclear particle was rather straightforward, the same cannot be said for modifying GAMESS to handle any mass negative particle. GAMESS, like most molecular *ab-initio* code assumes the reduced mass of an electron and nuclei to be equal to the mass of the electron. For most applications, this approximation works well. In the case of muonic molecules; however, assuming the reduced mass to be equal to the mass of the muon can result in greater than 10% error in the calculation of bond energy and bond length. To account for this, the reduced mass ratios

$$\frac{\mu_e}{\mu_{ex}} = \frac{\frac{m_em_{nuc}}{m_e + m_{nuc}}}{\frac{m_exm_{nuc}}{m_ex + m_{nuc}}} = \frac{m_e(m_{ex} + m_{nuc})}{m_{ex}(m_e + m_{nuc})}$$

(1)

$m_e = \text{mass of an electron}$

$m_{nuc} = \text{mass of the nucleus or positive particle of interest (e.g. positron)}$

$m_{ex} = \text{mass of the negative exotic particle of interest (e.g. negative-muon)}$

can be multiplied times each kinetic energy term in the electronic Hamiltonion

$$-\frac{\hbar^2}{2\mu_e} \nabla_i^2$$

(2)

Currently GAMESS requires that the same reduced mass ratio be multiplied times each kinetic energy term. In other words, if the negative particle mass is large enough that its reduced mass cannot be considered equal to its mass, then all positive classical particles included in the calculation must have the same mass. Correction to this weakness in the code is currently underway. In addition to the benefits of being able to study exotic particles, eliminating the error associated with assuming the reduced mass to be equal to the negative particle mass could have other benefits. The study of energy and spectroscopic differences between isotopes of the same element becomes possible (i.e. the study of laser and chemical isotope separation).

While for Hartree-Fock (HF) and MP2 calculations multiplying the kinetic energy terms of the electronic Hamiltonion times the reduced mass ratio is the principle correction that needs to be made
to account for differences in the mass of an electron and exotic-negative particles, such is not the case for CI calculations. In this case the CI coefficients must also be scaled.

Just as NEO can only model one type (mass) of positive quantum particle at a time, GAMESS can only model one type of negative quantum particle at a time. It cannot consider electrons and negative-muons in the same system. To get around this, in the future the NEO code may be modified so that it can be used for negative or positive quantum particles.

Most ab-initio molecular code assumes the volume of the nuclei to be negligible. The GAMESS code is not an exception. While this approximation makes it impossible to calculate K x-ray isotope shifts and some other spectroscopic properties for ordinary molecules[ 17 ], it is a legitimate approximation for most systems involving only electrons and nuclei[18,19]. In the case of an electron and proton the error generated by this approximation is only about $6 \times 10^{-9}$ eV. The average muonic molecular radius is about 186 times smaller than that of an average electronic radius and therefore considering the volume of the nucleus to be zero for muonic molecules can result in significant errors. As the size and charge of the nuclei increase, the accuracy of assuming the nucleus to be a point volume decreases. For relatively small nuclei (e.g. the first few rows of the periodic table) a first order approximation to the energy correction can be calculated by assuming the potential energy to be

$$V(r) = -\frac{Ze^2}{4\pi \epsilon_0 r}$$

when the negative particle radius $(r)$ is greater than the mean nuclear radius $(R)$ ($R \approx 1.25A^{1/3}$ fm where $A$ is the mass number, $Z$ is the atomic number), and when $r \leq R$

$$V(r) = -\frac{Ze^2}{4\pi \epsilon_0 R}\left[\frac{3}{2} - \frac{1}{2}\left(\frac{r}{R}\right)^2\right]$$

If $\langle V \rangle$ is the expectation value of the potential energy assuming a point mass and $\langle V' \rangle$ the expectation value calculated using the above two equations, then the potential energy correction ($\Delta E$) for nuclear volume is $\Delta E = \langle V' \rangle - \langle V \rangle$.

$$\Delta E = \frac{e^2Z^4}{\pi \epsilon_0 a_0} \int_0^R \left(r - \frac{3r^2}{2R} + \frac{r^4}{2R^3}\right) \exp\left(-\frac{2Zr}{a_0}\right) dr$$

where

$$a_0 \equiv \frac{4\pi \epsilon_0 \hbar^2}{\mu e^2}$$

Equation (5) reduces to

$$\Delta E = \frac{e^2}{8\pi \epsilon_0 a_0 R^3Z} \left[3a_0^3 - 3a_0R^2Z^2 + 2R^3Z^3 - 3a_0(a_0 + RZ)^2 \exp\left(-\frac{2RZ}{a_0}\right)\right]$$
When $\frac{R}{a_0}$ is small[18,19], this can be approximated as

$$\Delta E = \frac{e^2 Z^4 R^2}{10\pi \varepsilon_0 a_0^3}$$

(8)

As $Z$ and $A$ get large, so does $\Delta E$. When $\Delta E$ is more than a small fraction of the total energy, as it is for muo-molecules with large nuclei, the above perturbative correction is not an accurate method of accounting for nuclear volume effects. In these cases it is necessary to more accurately approximate the true potential $V(r)$ and solve the corresponding Schrödinger equation. The authors have no current plans to modify GAMESS to study muonic molecules involving muonic binding to large nuclei.

As with all ab-initio codes, there are limits to what can be studied. Resources and computational time are limited. In order to expand what can be calculated using GAMESS the code has been modified to work in parallel computing environments. Parallelization of NEO would enhance its usefulness, but as of the writing of this paper, has not been performed.

3. GAMESS/NEO and negative muons

As with most computational efforts, the goal is not to develop computer code, rather it is to obtain the results that can be generated using the code. As part of code development, it is important to test the code and compare to known solutions and previously calculated results. Following are a couple applications of GAMESS/NEO to muonic molecular systems which help to demonstrate the viability of the code and some of what can be studied through its use. Beginning with a problem for which the exact solution is known seemed to be a good starting point. The non-relativistic $\mu$-p binding energy can be determined if the nucleus is considered to be a classical particle (Born-Openheimer approximation)[20]

$$E = -\frac{Z^2 e^4}{n^2 8\pi \varepsilon_0 a_0}$$

(9)

The exact ground state solution of -2.5286 keV can be compared to that calculated using GAMESS. 3s, 4s, 5s, 4s3p and 5s4p3d non-contracted basis sets were optimized using the method of Petersson and Zhong[21]. The results are summarized in table 1. Being that there is very little contribution from $p$ and $d$ orbitals, the differences in the values presented in table 1 are due almost entirely to differences in the number of $s$ basis sets used.

| Basis Set | Energy (keV) |
|-----------|--------------|
| 3s        | -2.5062      |
| 4s        | -2.5262      |
| 4s3p      | -2.5262      |
| 5s        | -2.5288      |
| 5s4p3d    | -2.5289      |
| Exact     | -2.5285      |

A Hartree-Fock 5s4p3d potential energy surface was generated for p-$\mu$-p$^+$. The basis set, which is very sensitive to the fitting coefficients, was again optimized using the method of Petersson and
Zhong[21]. The potential energy as a function of nuclear bond length at 27 points ranging in length from 0.003 Å to 0.03 Å was calculated. The points were interpolated between using cubic spline interpolation with fixed endpoints[22,23].

\[ V = \frac{1}{2\pi} \sqrt{\frac{V''(r_{eq})}{\mu}} \]  

(10)

was calculated to be \(1.77197 \times 10^{17}\) Hz where \(\mu\) is the reduced mass of the nuclei and \(V''(r_{eq})\) is the second derivative of the potential energy with respect to bond-length, evaluated at the equilibrium geometry.

In order to observe the anharmonic effects of internal kinetic energy on the vibrational frequency, Hamilton’s equation of motion

\[ \frac{\partial H}{\partial q} = -\dot{p} \]  

(11)

was solved for position \((q,\) which in this case is internuclear separation) and momentum \((p)\)[24]. \(H\) represents the classical hamiltonian and is equal to the sum of the potential and kinetic energy. The vibrational spectra (power spectral density) of the system can be generated by taking the Fourier transform of the position, momentum, kinetic or potential energy as a function of time[25,26] (see figures 2 and 3).
By comparing figures 2 and 3, the effects of anharmonicity on the fundamental vibrational frequency can be seen. As the internal vibrational energy increases, the anharmonicity also increases and additional peaks appear. The energy used in the calculation of figure 3 corresponds to the ground state quantum vibrational level[27]. The ground-vibrational-state dissociation energy $D_0$ (equilibrium dissociation energy $D_e$ minus the ground state vibrational energy) was calculated for the p-$\mu$-p$^+$ potential energy surface, $D_0 = 263.275$ eV. This compares to a value of 253.15 eV presented elsewhere[28]. It should be noted that the calculations presented in this paper were presented to demonstrate methods and capabilities of the software. The level of calculations was relatively low (small basis sets, nuclei assumed to be classical and correlation energy ignored). Nuclear volume effects were also neglected in these calculations.

4. Conclusions
The GAMESS/NEO code has been modified to allow the ab-initio study of exotic-molecules. GAMESS can model any mass quantum negative particle and NEO any mass quantum positive particle. While molecular systems with large numbers of negative and/or positive quantum particles can be modeled using GAMESS/NEO, all negative quantum particles must have the same mass and all positive quantum particles must have the same mass. This excludes the possibility of modeling molecules that contain both electrons and negative muons. Future modifications of the code are planned which will eliminate this shortcoming by allowing NEO to model negative particles.

Currently if the negative quantum particles are large enough that the reduced mass between them and all positive particles cannot be considered equal to the mass of the negative particle, then only one mass positive particle (nuclei or positron) can be considered. This is true whether the positive particle is considered classically or quantum mechanically. Modifications to the code that will eliminate this weakness are planned for the next couple of months.

Currently muo-molecular calculations using GAMESS can be performed at the HF and MP2 level. NEO calculations for closed shell systems can be performed at the HF, MP2, CASSCF, and CI level. Opened shell HF and CI calculations are also possible. The capability to perform CI muo-molecular calculations in GAMESS should be added to the code shortly.

GAMESS can run in serial or parallel environments. NEO currently only runs on serial systems. The authors are not aware of any effort currently underway to modify NEO to work in a parallel computing environment. Parallelization of NEO would enhance its usefulness and will hopefully be undertaken soon.
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