Project Title:

Testing of Accuracies of First-Principles Variational Hartree-Fock and Many-Body Perturbation Theory (VHFMBPT) and Variational Hartree-Fock Based Density Functional Approximation (VHFDA) to Exchange and Correlation Potentials through Applications to Atomic , Molecular, and Biological Systems.

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The general aims of the investigations here are on the use of Cluster Methods involving the first-principles Hartree-Fock (HF)[1] one-electron procedure combined with Many-Body Perturbation Theory (MBPT) to study electronic structures and associated properties of Biological and Condensed Matter Systems. At the present time our focus is on Biological Systems, with major emphasis on hemoglobin and related systems including the attachment of molecules like Oxygen, Carbon Monoxide, and Nitric Oxide, important for the respiratory process in the body and also adverse effects on health of molecules like NO present in polluted air.

In addition to studying the properties and functions of important biological systems, we are also concentrating on the accuracy of the method that we are using which is referred to as the (VHFMBPT) procedure[1], the HFMBPT part of the acronym is understandable because of the component HF and MBPT aspects of the procedure, and the V refers to the variational aspect of the procedure. The variational aspect has to do with the multi-center character of molecular and condensed matter systems, since one cannot solve Hatree-Fock Schrodinger equations by standard differential equation solving procedures one can use for one center systems like atoms. We have been collaborating with the research group at State University of New York at Albany (SUNYA) associated with Professor T.P. Das in testing the accuracy of the (VHFMBPT) procedure by applying it to atomic systems. We shall also be testing the accuracy of the (VHFDFA)[2] approach which is also being widely applied to molecular and condensed matter systems. This latter method, in addition to the variational aspect of the (VHFMBPT) approach we are employing, uses a density functional potential approximation to not only the exchange potential for the exchange in the Hatree-Fock approach but also the treatment of many-body effects.

In the field of testing the accuracy of VHFMBPT procedure, as stated in the preceding paragraph, we are focusing on the total energies of atomic systems and in this area we have studied the one-electron contributions and many-body contributions of the total energies of H^- ion, and Li and Ne atoms as a function of the sizes of the Gaussian basis sets and compared the results we have obtained for the two types of contributions to the total energies and the total energies themselves with those available from the highly accurate HFMBPT procedure[3,4,5] utilizing occupied and excited state energies and eigen-functions for one-electron HF states obtained from solving the HF differential equations by numerical methods possible only for one center systems such as atoms and atomic ions. These latter results for total energies have been found to agree within one percent with experiment for a wide range of atomic systems. For H^- ion, with the most extensive basis

sets involving completely uncontracted Gaussian basis sets, the VHFMBPT procedure leads to one electron contribution of -0.46667 atomic units (a.u.) and many-body contribution of -0.04638 a.u. and total energy of -0.51305 a.u., compared to HFMBPT results[4] respectively for these quantities of -0.48812, -0.03954, and -0.52766 a.u.. The experimental total energy[4] is -0.52776 a.u.. Thus, the VHFMBPT contributions follow the same trend as the HFMBPT, the observed differences showing the need for larger basis sets for the VHFMBPT procedure. The percentage difference in the case of many-body contribution between the two procedures is more pronounced than the one-electron contribution to the total energy because the many-body effect involves contributions of a large number of excited states which requires very large basis sets. The HFMBPT value of the total energy is -0.52766a.u. in excellent agreement (within 0.02 percent) with experiment. What is important is also that both the VHFMBPT and HFMBPT energies are slightly higher then the experimental value as one expects from the variation principle.

The VHFDFA calculation only gives the total energy and no breakdown into one-electron and many-body contributions and so one cannot make detailed comparisons with the one-electron component of the total energy and the many-body component from the highly accurate HFMBPT procedure as was possible with the VHFMBPT procedure. The total energy for the VHFDFA is found to be lower than experiment as compared to -0.52776 a.u. from experiment for H^- ion.

For Neon atom, with VHFMBPT procedure, a sizable totally uncontracted set of basis set of basis state Gaussian functions leads to one-electron energy of -128.52663 a.u., and many-electron contribution of -0.28970 a.u. summing up to a total energy of -128.81633 a.u.. These results are to be compared with those for the highly accurate HFMBPT[5] procedure using a numerical differential equation solution for the Hatree-Fock equations for the Neon atom. The corresponding one-electron, many-electron and total energy contributions in a.u. were -128.54829, -0.38586, and -128.93415 respectively, the total energy agreeing very well with the experimental energy of -128.9357 a.u. as in the case of the H^- ion. The trends in the VHFMBPT one-electron and many-body contributions is again very similar as with the results with the HFMBPT procedure, the differences in the individual contributions in the two cases pointing to the need for larger size for the Gaussian basis sets than is presently used for the VHFMBPT procedure in Neon. The VHFDFA result for the total energy in Neon with same Gaussian basis sets as used for the VHFMBPT investigation is found to be -128.96040, quite close to the experimental result but again lower than the latter.

For the lithium atom[6], the results for the one-electron and many-electron contributions to the total energy follow the same trends as in H^- and Ne as discussed for VHFMBPT and HFMBPT procedures. The total energies for both procedures are higher than the experimental value[6], the HFMBPT result being almost exactly in agreement with experiment. For the HFDFA procedure, the total energy is again found to be lower than experiment, a feature that would be in violation of variation principle if the Hamiltonian used corresponded to the actual Hamiltonian for the system.

These features for the total energy results for atomic systems obtained by the HFMBPT and the two variational methods, combined with the trends found for the hyperfine constants in atomic systems being tested by our collaborators in the State University of New York at Albany, are being thoroughly analyzed to obtain definitive basic conclusions about the improvements needed in the VHFMBPT and VHFDFA procedures to enhance their accuracy.

In the course of the current year (2011), we are going to study a number of atomic and molecular energy-dependent and wave-function dependent properties sensitive to the peripheral regions of atoms in molecular systems to obtain added insights to procedures that could improve the accuracies of the VHFMBPT and VHFDFA. These properties will include electron-atom elastic and inelastic scattering, interaction between atoms at long range to study Van der Waals interaction energies and pressure shifts of hyperfine interactions in atoms in environments involving various rare gas atoms.

In the field of study of energy and wave-function dependent properties of biological systems using the cluster approach involving first-principles Hartree-Fock procedure combined with many-body effects included using many-body perturbation theory (VHFMBPT)[1], we have been working on hemoglobin systems and five-liganded heme compounds. In the area of five-liganded heme-compounds, there have been first principles investigations in the past in halo-hemin systems involving fluoro, chloro, bromo, and iodohemins. The theoretical results using the Hartree-Fock procedure and comparisons made with experimental data in these systems have been reviewed in detail recently[7]. While the Hartree-Fock results provided overall good agreement with available experimental data on ^{57m}Fe, ^{14}N, and ^{2}H nuclei, there was need for study of many-body effects to provide even better quantitative agreement with experimental results, but was not possible, for the very large systems involved, in the 1990s when the Hatree-Fock investigations were carried out with the computing facilities available at the time. However they became possible in the early part of the century. Professor Archana Dubey at the University of Central Florida together with collaborators in the State University of New York at Albany has been involved in the study of many-body effects in the halo-hemin systems[8]. It is hoped to complete these investigations during the next year and prepare comprehensive reports for publication.

In the area of hemoglobin derivatives, Hartree-Fock investigations of the electronic structure of Nitrosylhemoglobin[9] have been carried out in late 1990's with emphasis of ^{14}N magnetic hyperfine interaction and it is expected that many-body investigations can be carried out at University of Central Florida in collaboration with the group at SUNYA this year.

Additionally, many-body calculations have been carried out very recently by the first-principles VHFMBPT procedure, with the initial investigations initiated in UCF in the T-state. This investigation[10] showed that Hatree-Fock theory led to the energy of the triplet state to be lower than the singlet state, but on including many-body effects, the singlet state energy gets lower. The influence of this reversal has been provided by interplay of exchange and many-body effects involving the electrons in the many-electron system in the oxyhemoglobin molecule. The nature of the results initially obtained in the T-state oxyhemoglobin system has been confirmed by investigations[10] on the R-state, at SUNYA, although there are quantitative differences. Detailed analysis of the results at both centers has provided valuable insights into the factors that influence the energy separation of triplet and singlet states in OxyHb. This understanding has suggested that attachment of atomic of molecular groups on the heme unit in OxyHb could very significantly influence the ordering of the singlet and triplet states which can have very important influence on the magnetic properties of the oxyhemoglobin complex with the attached atomic or molecular groups. First-Principles investigations of these types of complexes have already begun[11] by our collaborating groups in SUNYA.

In terms of our planned investigations on

heme and hemoglobin derivative systems, we shall, as described earlier, continue investigations on electronic structures and associated hyperfine properties of the halo-hemin systems including many-body effects. As far as hemoglobin derivatives are concerned, we shall carry out first-principles VHFMBPT investigations on deoxyhemoglobin and NO-hemoglobin for their hyperfine properties to compare with earlier results on these systems by first-principles Hartree-Fock investigations and experimental results. We shall also start work on the diamagnetic system CO-Hemoglobin where there are no hyperfine interactions but nuclear quadrupole hyperfine interactions can be observed using Mossbauer effect on ^{57m}Fe, which Professor Lee Chow is planning to measure carefully at University of Central Florida.

In addition to understanding the hyperfine properties[7,9] in deoxyhemoglobin, NO-hemoglobin, and CO-hemoglobin, the understanding of their electronic structures at a first-principles level including many-body effects are expected to be very helpful in the future for first-principles investigation of attachment of NO and CO groups to deoxyhemoglobin which have been studied experimentally[12] following detachment of NO and CO groups by light.

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[Proceedings, etc.]

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