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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Our group is investigating the accuracy of first-principles variational Hartree-Fock with Many-Body perturbation theory (VHFMBPT)[1] and Variational Density Functional Approximation (VHFDFA)[2] methods in the calculation of electronic structure and associated properties in molecular and atomic systems. One of the consequences of the multicenter nature of many of the problems addressed in the literature today (Biological Systems, Condensed Matters Systems, etc.) is that one cannot solve the multicenter Hartree-Fock Schrodinger equations by standard differential equation procedures as can be done for single center atomic systems. Instead, the variational method must be used to solve the equations, which are subject to possible inaccuracies due to limited basis set size and the natures of the basis sets used for computational convergence. In many cases these inaccuracies are small and may be neglected, however there are specific systems and properties where these inaccuracies become significant. In order to have confidence in the ab initio method used for a calculation, we must fully understand the potential weaknesses (and strengths) of the procedure used for the calculations.

To better understand the potential inaccuracies arising from the VHFMBPT and VHFDFA procedures, we have varied basis set size, character (polarization functions, diffuse functions), and other factors (convergence criteria, initial guess), functionals, etc. and calculated the electronic structure and associated properties for single center systems for which we have highly accurate non-variational Hartree-Fock and Many-Body Perturbation Theory (HFMBPT)[3,4,5] results. In this work we have been collaborating with the research group at State University of New York at Albany (SUNYA) associated with Professor T.P. Das.

As stated earlier, we are testing the calculated electronic structure and associated properties derived from VHFMBPT and VHFDFA methods. To do this, we are focusing on the total energies of atomic systems and in this area we have studied the one-electron and many-body contributions for the total energies of H^- ion, and Li and Ne. For H^- ion, with the most extensive basis sets available involving completely uncontracted Gaussian basis sets, we have found that 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 used in obtaining the one electron Hartree-Fock equations and the occupied and excited one-electron states, that latter for the use of perturbation theory for many-body effects. 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 basis set of totally uncontracted 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.. The highly accurate HFMBPT procedure results corresponding to the one-electron, many-electron and total energy contributions in a.u. were -128.54829, -0.38586, and -128.93415 respectively, the latter 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 are 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.

Over the year (2012), we are planning to study a number of atomic and molecular energy-dependent and wavefunction dependent properties sensitive to the variational approach. The hyperfine structure (hfs) in the atomic systems lithium[6], sodium[7] and phosphorus[8] have been shown earlier to be sensitive to correlation effects, especially in the case of phosphorous where the hfs constant[8] has been shown to reverse sign. In our earlier work[9], some of which is mentioned above, we have found that MBPT, which uses calculated ground and excited state wavefunctions to calculate corrections to the Hartree-Fock wavefunctions and energies, can be sensitive to inaccuracies due to the limitations of the the variationally determined wavefunctions of (VHFMBPT) and (VHFDFA). Properties such as the hfs constant for spherical systems with finite spin (such as the alkali atoms and half filled shell systems like nitrogen and phosphorous), that involve, in first order perturbation, taking the difference of electron densities between one electron densities from states of opposite spins at a point (the nucleus), which can substantially cancel out[6,7,8], making higher order many-body effects important, are thus well suited to investigate differences in results due to variational approaches.

We have already investigated[9] the hyperfine interactions in the lithium and phosphorus atoms in their ground states using the VHFMBPT and VHFDFA procedures. We plan to investigate the energies and hyperfine constants by these procedures for a number of other atomic systems, such as nitrogen, ground state of sodium and excited states of lithium and sodium. The analysis of these results and their comparison with experimental data and results of HFMBPT investigations for a number of atomic systems and comparisons with the results of the highly accurate HFMBPT procedure as well as experiment will allow valuable insights into the limitations of VHFMBPT and VHFDFA procedures and suggest possible ways to improve the accuracies of these latter two procedures for energies and the wave-function dependent hyperfine properties.

Also in the year (2012), we shall study, using VHFMBPT and VHFDFA procedures, electron-atom elastic and inelastic scattering cross-sections, and also interactions between atoms at long range to study van der Waals (VDW) interaction energies and pressure shifts of hyperfine interaction constants in atoms in environments involving various rare gas atoms. These investigations will provide information and insights about the accuracy of VHFMBPT and VHFDFA procedures for properties involving peripheral regions of atoms. Comparison will again be made with available experimental data, such as electron-atom scattering cross-sections, VDW atom-atom interaction results and hyperfine pressure shifts. Comparison will also be made with available results for one-electron and many-body effects on these properties[10,11] by MBPT procedure and other methods for inclusion of many-body effects.

In the Biophysics area, we shall be continuing our investigations on hyperfine interaction studies, described in our last year's report (2011), involving both nuclear magnetic hyperfine interactions and nuclear quadrupole interactions. The systems we will concentrate on are the five-liganded iron haloheme compounds. The nuclei to be studied are the iron, nitrogen, halogen nuclei and protons, which are available[12] from Mössbauer and electron paramagnetic resonance (EPR) techniques. Both the VHFMBPT procedure, by which preliminary investigations have been carried out earlier[13], and VHFDFA procedures will be utilized to study the importance of many-body effects and the assessment of the accuracies of both these procedures.

We shall also start investigations on understanding the experimentally available hyperfine properties in deoxyhemoglobin[12], and the six-liganded systems nitrosylhemoglobin, NO-Hb, and carbonmonoxyhemoglobin, CO-Hb. For CO-Hb, which is diamagnetic, no magnetic hyperfine properties can occur, but Mössbauer measurements provide ^{57m}Fe nuclear quadrupole coupling constant and isomer shift for which the theoretical values can be compared with experimental data. Professor Lee Chow is planning to make careful measurements of the Mössbauer effect for CO-Hb in the University of Central Florida.

The initial theoretical investigations of these hyperfine properties will be carried out by the first-principles VHFMBPT procedure and subsequently the VHFDFA procedure for comparison.

The understanding of the electronic structures of NO-Hb and CO-Hb will be helpful in the understanding of experimental data[15] on attachment of NO and CO groups to deoxyHb after their detachment from the six-liganded systems by light. Also, the electronic structure of NO-Hb will be valuable for understanding the observed sensitive pH-dependence of the strength of binding[14] between iron and the proximal imidazole.

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