RICC Usage Report for Fiscal Year 2012

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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We are investigating the accuracy of the VHFMBPT procedure[1]. The HFMBPT part of the acronym is due to 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 the standard differential equation solving procedures one can use for one center systems like atoms. We have been collaborating with the research group at the 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 (2013), we are going to continue 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.

References

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