Project Title:

First Principles Study of Muon and Muonium in Heme Systems, Nucleic Acids, and Condensed Matter Systems

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The planned investigations proposed for 2013 on RICC are, as in the previous year, in the broad fields of materials science and biophysics as well as in atomic physics, to test the accuracy of electronic structure and properties investigation in molecules and solid state systems by applying them to atoms. We shall briefly describe our progress in the various projects in these areas and then describe the problems we plan to investigate in 2013.

We have continued our investigations in Transition Metal Impurities in Silicon. We have been concentrating on single TM ions in silicon, specifically Mn^0, V^{2+}, Cr^+ and Mn^{2+}. The probable locations of the isolated ions were determined by first-principles investigations of their binding energies at different sites using Hartree-Fock theory[1] combined with many-body perturbation theory for the influence of electron correlation effects. From this procedure it was found that hexagonal interstitial (site H_i, the tetrahedral interstitial site T_i and the substitutional site S_v in which the ion was introduced at a preexisting vacancy site (rather than a substitutional center S having the ion itself remove a silicon from the substitutional site during the implantation process which was unstable with negative binding energies in all cases) were all stable sites with positive binding energy. The binding energies for V^{2+} and Mn^{2+} ions were largest for the S_v site, followed by the T_i site and then the H_i. For Cr^+ ion, the binding energies were found to be positive for the H_i and T_i sites but an order of magnitude smaller than for Mn^{2+} and V^{2+} ions, with the binding energy for the S_v site very close to zero. For Mn^0 atom, both H_i and T_i sites are unstable with negative binding energy, only the S_v site being stable with positive binding energy. For Mn^{2+} ion, channeling data in Silicon have shown that while the T_i site is the most abundant site for the Mn^{2+} ion, the S_v site also can be present. The observed greater abundance of the T_i site for Mn^{2+} in silicon over the S_v site can perhaps be explained by the fact that while the T_i site available in pure silicon, the S_v site requires the presence of substitutional vacancies with low formation probability when the vacancy concentration is low. The many-body contribution to the hyperfine constant for $^{55}Mn^{2+}$ in silicon has been estimated approximately using the many-body contribution for the free Mn^{2+} ion obtained by first-principles many-body perturbation theory using one-electron Hartree-Fock occupied and excited state

wave-functions for Mn^{2+} obtained from numerical solution of the Hartree-Fock equations for Mn^{2+} ion[2]. The results show that the net ^{55}Mn hyperfine constant for Mn^{2+} in silicon combining the Hartree-Fock and many-body contributions is substantially closer to experimental results from Electron Paramagnetic Resonance (EPR) measurements than that for the V_s Site, providing strong support to the results of channeling measurements which demonstrate the greater abundance for Mn^{2+} ion at the T_i site as compared to the S_v site. We have also recently verified our earlier ^{55}Mn hyperfine results for Mn^0 in silicon when at the stable S_v site combined with many-body contributions lead to a much smaller value than the experimental result for ^{55}Mn hyperfine constant in silicon. These hyperfine interaction results for Mn^{2+} ion and Mn^0 atom that the experimental results for the Mn^{2+} ion from EPR measurements cannot be associated with Mn^0 at S_v sites, and is explained mainly by Mn^{2+} ions at T_i sites which provide good agreement for observed ^{55}Mn hyperfine constant observed from EPR measurements.

For this project on the electronic structures and properties of magnetic semiconductors we had expected to concentrate on the hyperfine interactions in V^{2+} and Cr^+ ions in silicon to investigate if one can explain the experimentally observed hyperfine interactions for the ^{51}V and ^{52}Cr nulcei from EPR measurements as we have done for ^{55}Mn nucleus for Mn^{2+} ion. For Mn^{2+} ion, the one-electron Hartree-Fock contribution for the ^{55}Mn nucleus was obtained from the electronic wave-functions for the Mn^{2+}-silicon system by the first-principles Hartree-Fock Cluster Procedure[1]. For the many-body contribution, the many-body perturbation theory results for free Mn^{2+} ion obtained accurately using non-relativistic and fully relativistic methods were available, and these contributions were utilized to estimate corresponding results appropriate for the Mn^{2+}-silicon system using weighting procedures based on the comparison of the one-electron contributions in the free ion with those in the Mn^{2+}-silicon system. Unfortunately, accurate results for many-body contributions in the free V^{2+} and Cr^+ ions are not available. We have therefore decided to obtain many-body contributions for the TM ion-silicon systems directly by many-body perturbation theoretic methods as discussed in the following paragraph which describes our research

plans for 2013 that will continue to involve investigations of one-electron and many-electron contributions in V^{2+}, Cr^+, and Mn^{2+} in silicon to the binding energies and hyperfine interactions in those systems. We are preparing for publication of our TM-Silicon results obtained so far in a comprehensive paper in a suitable journal dealing with condensed matter materials research systems. The next paragraph describes our plans for research using the RIKEN Supercomputer TM-Silicon system for the year 2013.

Our plans for the year 2013 will, as it did last year, involve two basic aims. The first is to complete the investigations we have started for obtaining through first-principles energy investigations of single Mn^{2+}, Cr^+, and V^{2+} ions and Mn^0 atoms in the solid TM-Silicon systems, the positions of these systems in silicon and obtain their hyperfine interaction constants to compare with available experimental results. The second aim of our investigations to study the interactions between pairs of neighbors of theses paramagnetic atomic and ionic systems to first find the stable locations of the pairs and then the energy differences between the pairs and the corresponding two isolated ions to see whether the pairs are ferromagnetic, antiferromagnetic and paramagnetic.

Considering the first aim, we shall improve the accuracy of our investigations by including many-body perturbation theory by the Hartree-Fock cluster procedure with many-body perturbation theory but using larger sized variational basis sets than already used in our 2010-2012 investigations. These results are expected to provide more accurate results for the total energies for the various single TM in Silicon clusters than in our earlier investigations because there will be more unoccupied excited states available for the application of many-body perturbation theory with the use of larger variational basis sets. Additionally, for the evaluation of the hyperfine constants due to the isotropic Fermi-contact hyperfine Hamiltonian, the larger number of empty excited states will enable a more accurate evaluation of the many-body contribution in Mn^{2+} ion and Mn^0 atom which has in our earlier work in 2010, 2011, and 2012 been treated approximately by estimating it from results of atomic calculations on free Mn^{2+} and Mn^0. For our calculations in 2013, we shall first directly obtain the contribution to many-body effects to the hyperfine constants for Mn^{2+} and Mn^0 in silicon by many-body perturbation theory for the cluster chosen for this system from the Gaussian molecular program that we are using. This will provide the many-body contributions to the magnetic hyperfine constants. For the present, we will estimate the relativistic corrections to the Hartree-Fock and many-body contributions using the results of our fully relativistic investigations for free Mn^{2+} ion and Mn^0 atom. In future investigations when first principles fully relativistic Gaussian programs are available for molecular systems, fully relativistic values of the hyperfine constants in Mn^{2+} ion and Mn^0 atom in silicon can be obtained including both one-electron Hartree-Fock and many-body contributions. For the present, our procedure involving first-principles non-relativistic procedure will be used to compare calculated hyperfine constants with experiment. Corresponding investigations will be carried out for V^{2+} and Cr^+ ions for which hyperfine constants have been measured by electron paramagnetic resonance technique.

The second part of our program in 2013 will be to continue to deal with the possibility of ferromagnetic or antiferromagnetic couplings of Mn^{2+}-Mn^{2+}, Mn^{2+}-Mn^0 and Mn^0-Mn^0 pairs in silicon. The discrepancy between predicted hyperfine constant for ^{55}Mn for a single Mn0 in silicon and the measured ^{55}Mn hyperfine constants for the dilute Mn-Si system suggests that free Mn^0 may not be present in dilute Mn-Si system. However in less dilute Mn-Si systems, it is possible that Mn^{2+} - Mn^0 and Mn^0-Mn^0 pairs could be stable. This is why we will study all three pairs involving Mn^{2+} and Mn^0 that we have mentioned earlier will be investigated. We will investigate both the stabilities of the three molecular pairs in silicon by studying the total energies of both the molecular pairs in the cluster systems chosen for our investigation as well as the cluster for the single atom or ion in silicon. The basis sets found to provide best agreement with the ^{55}Mn experimental hyperfine constant in dilute systems will be used for the molecular systems. We shall initially study the Mn^{2+}-Mn^{2+} pair because for the dilute system Mn^{2+}-silicon the hyperfine constants, from our earlier theoretical investigations, agrees well with EPR results. For the Mn^{2+}-Mn^{2+} pair investigation, we shall study all the nine possibilities corresponding to each two Mn^{2+} ion being in any of the three positions H_i, T_i and S_v. Relaxation in the positions of the Mn^{2+} ions, and the silicon atoms in the cluster corresponding to the Mn^{2+}-Mn^{2+} pair in silicon, will be included in the investigation. Both the stabilities of the pairs from the energy results and the ferromagnetic, paramagnetic or antiferromagnetic behaviors, from the spin density distributions and spin-populations on the Mn^{2+} ions will be examined. Subsequently, similar investigations will be carried out for Mn^{2+}-Mn^0 and Mn^0-Mn^0 pairs.

In addition to our transition metal in silicon work, we have also recently investigated the Nuclear Quadrupole Interactions of the controlled substances cocaine and heroin, to establish parameters for their detection by Nuclear Magnetic Resonance methods. These controlled substance calculations have provided an excellent verification of the methods applied in my investigations of Transition Metal doped Silicon.

References

1. T.P. Das, T.A. Kaplan, S.D. Mahanti, editors. Electronic Properties of Solids Using Cluster Methods. New York: Plenum Press; 1995. P. 1-28

2. R.H. Pink, S.R. Badu, A. Dubey, R.H. Scheicher, J. Jeong, S.R. Byahut, L. Chow, M.B. Huang, and T.P. Das, Magnetic Materials: Proceedings of the International Conference on Magnetic Materials (ICMM-2007) , p.235.

1. T.P. Das, T.A. Kaplan, S.D. Mahanti, editors. Electronic Properties of Solids Using Cluster Methods. New York: Plenum Press; 1995. P. 1-28

Fiscal Year 2012 List of Publications Resulting from the Use of RICC

[Publication]

Nuclear Quadrupole Interactions in Nuclear Quadrupole Resonance Detection of Energetic and Controlled Materials: Theoretical Study; Ranjit Pati, R.H. Pink, R.H. Scheicher, Narayan Sahoo, S.N. Ray, T.P. Das; Appl Magn Reson 43, pp 591-617 (2012).