RICC Usage Report for Fiscal Year 2011

Project Title:

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

Name: ○T.P. Das, K. Ishida, R.H. Pink
Laboratory at RIKEN:
Advanced Meson Science Laboratory, Sub Nuclear System Research Division,
RIKEN Nishina Center for Accelerator-Based Science, RIKEN Wako Institute

---

The planned investigations proposed for 2011 on RICC were as in the previous year in the fields of materials science and biophysics. We shall briefly describe our progress in the various projects in these areas and then describe the problems we plan to investigate in 2012.

Section I- Location of Transition Metal (TM) Ions in Silicon and their associated Magnetic and Hyperfine properties

During the year 2010, our investigations in this field were concentrated on the 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 combined with many-body perturbation theory for including 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 energies. 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[1] 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. The results show that the net ^{55}Mn hyperfine constant for Mn^{2+} in silicon at the T_i, site combining the Hartree-Fock and many-body contributions, is substantially closer to experimental results[2] from Electron Paramagnetic Resonance (EPR) measurements than that for the S_v Site, providing strong support to the results of channeling measurements[3] 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 result[4] that for Mn^0 in silicon when at the stable S_v site the contribution from Hartree-Fock theory when combined with many-body contributions leads to a much smaller value than the experimental result for ^{55}Mn hyperfine constant in silicon[2]. Thus our theoretical ^{55}Mn hyperfine interaction results for Mn centers in silicon[4,5] clearly demonstrate that no other center in silicon except mn^{2+} ion at T_i site can explain experimental hyperfine interaction results[2] for ^{55}Mn in silicon, a conclusion in agreement with results from channeling measurements[3] for Mn in silicon.

During the year 2011, 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 ^{53}Cr nuclei 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. 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 2012 that will 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. Due to time involved in the other areas of investigation in our current projects using the RIKEN Supercomputer especially in Section II dealing with biological systems, we decided to wait for the latter investigations till the year 2012, the plans for which will now be described. 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 and materials research systems. The next paragraph describes our plans for research using the RIKEN Supercomputer on TM-Silicon systems for the year 2012.

Our plans for the year 2012 will 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 their hyperfine interaction constants to compare with available experimental results. The second aim of our investigations is 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 or 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 and 2011 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 and 2011 been treated approximately by estimating it from results of atomic calculations on free Mn^{2+} and Mn^{0}. For our calculations in 2012, we shall first directly include the nonrelativistic contributions from one-electron effecs from Unrestricted Hartree-Fock theory and many-body effects to the hyperfine constants for Mn^{2+} and Mn^{0} in silicon by perturbation theory for the cluster chosen for this system from the Gaussian molecular program that we are using. 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 of other TM ions or atoms in silicon with experiment. Such investigations will be carried out for V^{2+} and Cr^{+} ions for which hyperfine constants have been measured[2] by electron paramagnetic resonance technique.

The second part of our program in 2012 will 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 substantial difference between predicted hyperfine constant for ^{55}Mn for a single Mn^{0} in silicon and the measured ^{55}Mn hyperfine constant 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. 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 investigation[1], agrees well with EPR results. For the Mn^{2+}-Mn^{2+} pair investigation, we shall study all the nine possibilities corresponding to each of the 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.

Section II- Investigations in Biological Systems with emphasis on Study of Electronic Structures, Magnetic and Hyperfine Properties

Our investigations in the area of electronic structures of Biological Systems have been concentrated on Oxyhemoglobin and DNA. We shall first discuss our recent investigations and plans for 2012 fiscal year using the RIKEN Supercomputer on the Oxyhemoglobin system and subsequently on DNA.

Section IIa- Electronic Structure and Magnetic Properties of OxyHb System

During the fiscal years 2010 and 2011 our investigations on OxyHb system have been concentrated on the understanding of the observed diamagnetic character of OxyHb from the most recent susceptibility measurements[1], but there is evidence of magnetic character in recent muon spin resonance (μSR) relaxation measurements[2].

Our investigations during the fiscal years 2009 and 2010 using the first-principles procedure involving Hartree-Fock theory combined with many-body perturbation theory showed[3] clearly that there was a sizable gap between the triplet and singlet states with the triplet state higher than the singlet state. Also our theoretical results clearly demonstrated[3] that while with purely one-electron Hartree-Fock theory, the triplet state was lower in energy than the singlet state, inclusion of many-body effects clearly reversed this order with the triplet state substantially higher energy above the singlet state so that at room temperature there would be no excitation from the lower lying singlet state to the higher triplet state. In the fiscal year 2011 we concentrated on the study of the influence of the positive muon (μ^+) on the energy gap between the singlet and triplet states. In particular, we concentrated on the question whether a μ^+ could be trapped at one of the Oxygen atoms in the molecule O_2 in OxyHb and if this trapping could reverse the order of the singlet and triplet states making the triplet state higher than the singlet. Our results have shown that the μ^+ indeed gets trapped by the O_2 molecule attached to the heme in both triplet and singlet states, preferring the Oxygen atom in the O_2 molecule closer to the iron atom in OxyHb, and reduces the energy gap between the singlet and triplet states, but not sufficiently to allow significant excitations to the triplet state at room temperature (300K). A paper based on our results for the μ-OxyHb system is being prepared for publication and has been presented[4] at the American Physical Society March Meeting in 2012 in Boston.

Our plans for the fiscal year 2012 in this field are the following. We want first to check by first-principles investigation by the same method we used for pure OxyHb and OxyHb with a trapped μ^+, whether a particle with charge +2 like an α-particle (He^{2+}) could reverse the order of the singlet and triplet states of Oxy-Hb or at least reduce the triplet-singlet gap (with triplet higher in energy) to make the excitation at room temperature significant from the lower singlet state of OxyHb to the higher triplet state. Our second line of investigation will be to find out if there are any possible molecular systems that could be attached to the distant oxygen atom that would enhance the negative charge on the oxygen atom nearest to the Fe-atom of the heme unit and enhance the strength of the trapping of μ^+ to the latter oxygen atom. The stronger trapping of μ^+ could influence the singlet-triplet energy gap for the Oxy-Hb more effectively than we have found from the influence of μ^+ alone.

It is hoped that the results of these two planned investigations will provide a clearer understanding of the origin of the magnetic character of the μ^+-OxyHb complex observed in the recent μSR studies[2] in OxyHb.

In addition to the above studies we also plan to study the system involving Muonium (a counterpart of the H-atom with a μ^+ having an electron attached to it) captured in the singlet state of Oxy-Hb, making it paramagnetic. This system could possibly explain the magnetic character observed in the recent μSR measurement[2].

Section IIb- Electronic Structure, Nuclear Quadrupole Interactions (NQI) and Muonium Trapping and Associated Hyperfine Interactions in DNA

During the fiscal years 2010 and 2011 we have worked using the same first-principles method including one-electron and many body effects as in OxyHb, on first the electronic structures of nucleobases in DNA and in solid state, and secondly trapped muonium centers in the nucleobases.

Using the first, we have studied the nuclear quadrupole interaction parameters (NQI) in ^{17}O, ^{14}N, and ^{2}H nuclei for free nucleobases, nucleobases in single strand DNA (sDNA) and double strand DNA (dsDNA), as well as solid nucleobases. Unfortunately experimental results are not available for any of these sets of systems except ^{17}O in the solid nucleobases, where there is good agreement between experiment and our theoretical results. We are waiting for experimental results on NQI parameters all the systems we have studied theoretically to appear in the future for comparison with our predictions, but we have tried to explain[1] our observed relationships between the NQI parameters in various systems and sites in terms of interactions between the DNA chain and the nucleobases, the chain-chain interaction in double strand DNA, and between nucleobase molecules in the solid state systems with detailed analysis of the electronic wave-functions in these systems obtained from our electronic structure investigations. It will be very helpful in the future when comparisons can be made with experimental data, and our conclusions[1] which provide detailed insights into DNA structure and the internal interactions at the electronic level can be verified and compared with experimental trends between the different systems involved.

For muonium in DNA we have obtained all the trapping sites[2] for all the nucleobases and calculated[2] the muon hyperfine constants and neighboring nuclear hyperfine constants. These have been compared with available results for some (not all) of the muonium trapping sites that we have found from level crossing experimental data from μSR measurements[3], and there is good agreement between our theoretical predictions and experimental results.

In the fiscal year (2012), we shall be working on the time-consuming problems of the actual interactions between the nucleobases and the sugar rings and also the phosphate groups to the latter. In our investigations[1,2] we have used CH_3 groups attached to the nucleobases as is the usual practice in the literature, to simulate their interactions with the sugar rings. Our planned investigations will provide results for the first time to compare with our hyperfine interaction results from the simulated systems with CH_3 groups with those from the actual nucleobase-sugar ring interactions and also the influence of the phosphate groups connected to the sugar rings. These will provide valuable experience for myself and my collaborators to handle these interactions at a first-principles electronic level. This experience will be very helpful in the understanding at an electronic level of a multitude of radiation damage data in DNA from electron beams using mass spectrometric analysis, in recent experimental investigations in a medical center in Ottawa, Canada, by Professor Sanché and collaborators.

References

Section I

1. J. Andriessen, S.N. Ray, T. Lee, T.P. Das, and D. Ikenberry, Phys. Rev. A 13, 1669 (1976).
2. H.H. Woodbury and G.W. Ludwig, Phys. Rev. 117, 102 (1960); Phys. Rev. Lett. 5, 98 (1960).
3. L.Q. Wu, J. La Rose, and M.B. Huang, Paper under Preparation.
4. 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, First Priniciples Hartee-Fock Cluster Study of Very Dilute Transition Metal and Rare-Earth Ion Systems in Silicon [Invited Talk at Interantional Conference on Magnetic Materials (ICMM-2007) 11-16 December 2007, Kolkata, India] American Institute of Physics Conference Proceedings 1003, 235 (2008).
5. R.H. Pink, S.R. Badu, R.H. Scheicher, Lee Chow, M.B. Huang and T.P. Das, Hyperfine Interact. 197, 37 (2010).

Secton IIa

1. M Cerdonio, S. Morante, D. Torresant, S. Vitale, A. DeYoung and R.W. Noble, Proc. Natl. Acad. Sci. USA, 82, 102 (1985).
2 K. Nagamine, K. Shimomura, H. Miyadera, Y.J. Kim, R.H. Scheicher, T.P. Das, J.S. Shultz, Proc. Jpn. Acad. Sec B Phys. Biol. Sci. 83, 120 (2007).
3. S.R. Badu, R.H. Pink, R.H. Scheicher, Archana Dubey, N. Sahoo, K. Nagamine and T.P. Das, Hyperfine Interact 197, 331 (2010).
4. R.H. Pink, S.R. Badu, T.P. Das, N. Sahoo, Lee Chow, R.H. Scheicher, and K. Nagamine, BAPS.2011.MAR.T39.9.

Section IIb

1. S.R. Badu, R.H.. Pink, Archana Dubey, R.H. Scheicher, H.P. Saha, Lee Chow, M.B. Huang, N. Sahoo and T.P. Das "First Principles Study of Nuclear Quadrupole Interactions in Single and Double Chain DNA and Solid Nucleobases", presented at Third Joint International Conference on Hyperfine Interactions and International Symposium on Nuclear Quadrupole Interactions September 2010, CERN/Geneva Switzerland. Book of Abstracts, pg. 205 (2010); T.P. Das, R.H. Pink, S.R. Badu, Archana Dubey, R.H. Scheicher, H.P. Saha, Lee Chow and M.B. Huang, BAPS.2009.MAR.L40.10; Dr. Badu Ph.D. Thesis Univ. at Albany, SUNY (2010).
2. S.R. Badu, R.H. Pink, Archana Dubey, R.H. Scheicher, Lee Chow, M.B. Huang, and T.P. Das, "First Principles Study of Muon Trapping and Associated Magnetic Hyperfine Interactions in Nucleobases in Single and Double Chain DNA and Solid Nucleobases" Presented at Third Joint International Conference on Hyperfine Interactions and International Symposium on Nuclear Quadrupole Interactions September 2010, CERN/Geneva Switzerland, Book of Abstracts, pg. 206 (2010).
3. Penny L. Hubbard et al., J. Phys. Chem. A 108, 9302 (2004).