Project Title:

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

Name   :   T.P. Das

Affiliation: Advanced Meson Science Laboratory Nishina Center for Accelerator-Based Science

RIKEN Research Cluster for Innovation

The planned investigations proposed on RICC for the year 2010 were in the broad fields of biophysics and materials science. The biophysics investigations included oxyhemoglobin and the nucleic acids DNA and RNA. In the materials science field our investigations were both in the area of dilute magnetic semiconductors, particularly in silicon containing isolated transition metal impurities, and on the accuracy of first principles cluster procedures used for investigation of condensed matter systems.

In presenting our progress report for the year 2010, we would like to present the accomplishments in each of the areas we have been working on during the past year, 2010, and then discuss very briefly the aims of the investigations currently in progress in these areas in not only how they are related to our accomplishments last year, but also the importance of the results that are expected from the current research in these areas to the broad fields they belong to as well as other related fields. A new area of research that has emerged broadly from all our earlier fields that we have investigated will also be described at the end of this report, together with our aims for this year and the future.

We start out with the progress we have made in the field of isolated transition metal (TM) ions in semiconductors. We have studied the TM atoms and ions (Mn^0, V^{2+}, Cr^+ and Mn^{2+}) in silicon, allowing for lattice relaxation around the TM atoms and ions in each case. The possible sites studied were the hexagonal and tetrahedral interstitial sites (H_i and T_i), and the substitutional site (S) using the cluster procedure involving Hartree-Fock theory combined with many-body perturbation theory (MBPT)[1]. In keeping with our earlier preliminary investigations[2] the stable sites from a binding energy point of view are the T_i and S for all the atom and ion systems studied. Channeling studies[3] for the Mn systems, both Mn^0 and Mn^{2+}, seem to prefer somewhat the T_i sites with some evidence that the S sites are also present. Channeling studies cannot provide information about the charge states and so cannot make a choice between Mn^0 and Mn^{2+}. Using the electronic wavefunctions obtained from the HF cluster procedure for both the occupied and unoccupied states for Mn^0 and Mn^{2+} ions at the T_i and S sites, we have evaluated the hyperfine interactions of ^{55}Mn nuclei including many-body effects by the MBPT procedure and find that only the Mn^{2+} ion at the T_i site can explain the observed hyperfine constants from electron paramagnetic resonance studies (EPR) on Mn-Si systems, the Mn^0 having much too small a hyperfine constant from theory and that for Mn^{2+} at S site being rather different from experiment. Thus our comprehensive investigations[4] have provided support for the T_i sites for the Mn^{2+} as the centers observed by channeling and EPR measurements for isolated Mn and Mn^{2+} ions in silicon.

In the future, we shall study the hyperfine interactions for V^{2+} and Cr^+ ions at T_i and S sites including many-body effects by the MBPT procedure and compare with the experimental EPR

data to identify which sites are observed by EPR measurements for these ions. Most importantly, we shall start investigations about the stability of other TM ions at nearest neighbor and next nearest neighbor T_i and S sites, to identify the stable paired ion systems for Mn^0 pairs and Mn^{2+} pairs by themselves, as well as Mn^0-Mn^{2+} pairs. We shall also study the exchange interactions between them to predict from first-principles theory which sites are ferromagnetically coupled and which are antiferromagnetically or diamagnetic. This information is expected to be valuable for study of ferromagnetism in Mn-Si systems important for potential applications like electronic conduction properties in spintronic systems[5].

Among the biological systems that we have studied for their electronic structures and associated properties is oxyhemoglobin. Oxyhemoglobin (OxyHb) is of course a system of great biological interest because of its importance in the transport of oxygen in the body. Its magnetic properties have been of great interest[6] as well as controversy for almost a century. It was believed to be non-magnetic from 1936 till 1977, when in the latter year, static susceptibility measurements seemed to suggest that it had finite magnetic susceptibility. Following an explanation by Linus Pauling and C.D. Coryell in 1977 about the possibility of a metastable paramagnetic system related to OxyHb that might have been produced in the process of preparation of OxyHb for the susceptibility measurement in 1977, the claim of magnetic susceptibility being present in pure OxyHb was retracted after using more careful preparation techniques.

However, recently Professor Kanetada Nagamine and collaborators have shown[7] from muon spin resonance measurements the possibility of a magnetic entity associated with the presence of muon. In our recent work[8] on the electronic structure of OxyHb using first-principles Hartree-Fock procedure combined with many-body effects by the MBPT approach, we have demonstrated that both for R and T OxyHb, the triplet state is higher than the singlet state. The energy separation of the two states is quite large, so that the extent of excitations from the singlet state to triplet at room temperature is expected to be quite small and keep pure OxyHb nonmagnetic at room temperature. However an interesting feature of our results[8] is that when many-body effects are not included as in pure Hartree-Fock (HF) investigations, the triplet state energy is lower. Thus there is a reversal in the order of the energies of triplet and singlet states when many-body effects are introduced. In view of the sensitivity of the ordering of singlet and triplet states to the influence of many-body effects, it is possible that attachment of muon to OxyHb could reverse the order or bring the singlet and triplet states closer than in pure OxyHb to have significant populations in the triplet state at room temperature where the μSR measurement[7] has been carried out. Our electronic structure investigations[8] on OxyHb have shown a number of atoms including the oxygen atoms in the O_2 molecule in OxyHb which carry substantial negative charges and could be attractive for muon capture.

We are currently investigating[9] muon capture in OxyHb. Our preliminary results indicate the muon attachment to the oxygen atom closest to Fe reduces the singlet–triplet splitting significantly. We are continuing these studies of muon trapping at the oxygen atoms as well as on the nitrogen atoms in the porphyrin and proximal imidazole in OxyHb. We also plan to investigate the possibility that other diamagnetic ligands might enhance the influence of muon binding on the triplet-singlet separation. The attachment of Muonium, which is magnetic, to OxyHb in the singlet state is also being studied by the first-principles procedure as an alternate source for explanation of magnetic effects in the μSR

experiments of Nagamine and collaborators.

In the field of DNA we have carried out comprehensive first-principles investigations of electronic structures and Nuclear Quadrupole Interaction (NQI) in pure DNA, as well as Muon Magnetic Hyperfine Interactions in DNA in which Muonium is trapped. In the field of NQI, we have used as for OxyHb, the Gaussian 2009 set of programs to implement the first-principles Hartree-Fock procedure and many-body effects, using the MBPT technique. The ^{17}O, ^{14}N, and ^2H NQI were studied and compared systematically for the free nucleobases, nucleobases in single strand DNA (sDNA) and double strand DNA (dsDNA) and solid nucleobases. Attachment of each of the nucleobases to the DNA backbone was simulated by a CH_3 group attached to the appropriate N-atom in the nucleobase under study.

The CH_3 group was chosen to minimize the computational effort involved, and also because the immediate neighborhood in the bonding of the nucleobase to a sugar group of the backbone was similar to a CH_3 group. Our results show that there are substantial changes in the NQI parameters e^2qQ and η, the quadrupole coupling constant and asymmetry parameter, in going from the free nucleobases to nucleobases attached to (sDNA), from (sDNA) to (dsDNA), and between free nucleobases to solid DNA. Our results for the ^{17}O NQI parameters for the solid nucleobases agree well with the experimental parameters[11].

Unfortunately no experimental results are available for NQI parameters for other nuclei in the solid nucleobases and for the ^{17}O, ^2H and ^{14}N nuclei in the DNA and free nucleobase systems. We hope they will be available in the near future allowing a thorough test of our calculated electronic structures through the comparison between our predicted NQI parameters and experiment.

We turn next to our investigations[12] on the trapping of Muonium (Mu) in various likely trapping sites by calculating the binding energies of Mu using the first-principles Hartree-Fock theory combined with MBPT for inclusion of many-body correlation effects. The relaxation effects in the positions of atoms neighboring the Mu trapping sites have been explicitly included using energy optimization technique. Both relaxation effects and many-body correlation effects were found[12] to make important contributions to the binding energies at possible Mu trapping sites and were important to include in the theoretical determination of the geometry of the trapping sites.

Our trapping site geometries for the Mu and the associated electronic wave-functions were used to determine the muon hyperfine constant, both contact and dipolar, for the various trapped Mu sites. These hyperfine constants were also found to be significantly influenced by many-body correlation effects. They were then combined to obtain muon level crossing frequencies[13] for the various trapped Mu sites and compared with corresponding available experimental values[13] allowing both verification of predicted Mu sites from theory and assessment of the accuracy of the calculated muon hyperfine constants.

Our future investigations this year on both NQI and muon contact and dipolar hyperfine constants will be aimed at testing their dependence on the treatment of the binding of the nucleobases to the DNA backbone. Specifically we will try to assess the accuracy of the simulation model of this binding by using the CH_3 group attached to the nucleobases used in our work through study of the predicted NQI and muon hyperfine parameters for the (sDNA) and (dsDNA) systems when the sugar groups liganded to the nucleobases on one side and phosphate groups[14] on the other side are all included explicitly. The investigation about the influence of binding of the nucleobases to the actual sugar and phosphate groups will be helpful in the understanding by first-principle methods of the

mechanisms of damage due to bombardment by electron beams on (sDNA) and (dsDNA) which have been extensively studied experimentally[14].

The last area of our investigations during the past twelve months that has emerged from our collaboration with the research group at the University of Central Florida (UCF) in Orlando on the accuracy of investigations on molecular and solid state systems by first-principles variational Hartree-Fock combined with many-body correlation effects by the MBPT procedure, referred to as the VHFMBPT procedure.

At both the State University of New York at Albany (SUNYA) and University of Central Florida at Orlando (UCF), we have been interested in evaluating the accuracy of the VHFMBPT procedure by application to atomic systems. In the latter systems, very accurate calculations have been carried out in the last century[15] from 1960's to the 1990's by the group at (SUNYA) which was previously at the University of California at Riverside (UCR) in the 1960's. This group has carried out highly accurate investigations on atomic properties using complete sets of eigen-functions for bound and continuum states using numerical integration of Hartree-Fock equations, only possible for one-center systems like atoms. Because of the use of complete sets of states which are essential for getting accurate values of the properties of interest at both the purely HF level involving the one-electron occupied states, and many-body contributions by MBPT which involves both the occupied one-electron states and unoccupied excited one-electron states, the results from the HFMBPT procedure in atoms for all properties have been found to be in agreement with experiment to within 1-2 percent.

In the multicenter molecular and solid state systems, since one cannot obtain the eigen-functions by the differential equation procedure for HF theory, the accuracy of the VHFMBPT procedure cannot be as accurate as for

atoms with HFMBPT procedure. We have therefore attempted to assess the accuracy of the VHF MBPT procedure by applying it to atomic systems where highly accurate HFMBPT results are already available[15].

At the present time we are carrying out assessment of the VHFMBPT procedure for both hyperfine interactions and total energies of atoms, with emphasis on the former by the SUNYA group and the latter by the UCF group. We are also studying the accuracy of the VDFT procedure referring to the variational treatment of the Hartree-Fock exchange and correlation effects by approximate one-electron exchange-correlation potentials based on the density functional theory.

So far we have studied the hyperfine interactions in three atoms, lithium, sodium, and phosphorous. The first two being alkali atoms, where the valence 2s and 3s electrons make the main contributions and many-body contributions are smaller but have significant effect on the total hyperfine constants. In phosphorous on the other hand the valence electrons are 3p electrons and there is no one-electron direct contributions but only exchange core polarization (ECP) contributions through exchange with the core s states, as well as many-body effects.

The results for the contact hyperfine constant for the phosphorous atom (no dipolar hyperfine interaction possible due to the spherical nature of this atom) from the accurate HFMBPT theory[16] (also termed LCMBPT in the literature), involve direct (D), ECP and many-body (MB) contributions of 0.0, -62.4, and 112.3 MHz totaling 49.8 MHz compared to 55.055 MHz from experiment, the difference having been ascribed[16] to relativistic effects. The VHFMBPT results for (D+ECP) and MB contributions are -37.4 and 72.6 MHz, leading to a total of 35.2 MHz. The trends for (VHFMBPT) contributions seem to be the same as for HFMBPT, and the total results are not too different from each other. The VDFT result for A

using the most popularly used procedure (B3LYP) is, on the other hand -11.2 MHz, in poor agreement with experiment and accurate HFMBPT theory. For lithium and sodium, the HFMBPT and VHFMBPT contributions have similar trends and the totals agree within 1 percent with experiment for HFMBPT and somewhat less for VHFMBPT. For VDFT, the total result is significantly larger than experiment. The basic theoretical reasons for the differences between HFMBPT, VHFMBPT and VDFT are being analysed.

In the course of the next year, we plan to study hyperfine interactions in some other atoms like boron and aluminum with single p electrons in valence shells as well as oxygen, sulfur, fluorine, and chlorine atoms with p-shells which are more than half filled. We also plan to study nuclear quadrupole interactions in atomic systems as well as the spectral frequencies and oscillator strengths for the transitions between occupied and excited states that lead to these spectral frequencies. These investigations are expected to provide further insights into differences between VHFMBPT and VDFT procedures and suggestions for improvements in both these procedures to provide better agreement with experiment.

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.

3. M.B. Huang and Collaborators (To Be Published)

4. R.H. Pink, S.R. Badu, R.H. Scheicher, Lee Chow, M.B. Huang, and T.P. Das, Hyperfine Interact. 197, 37-41 (2010).

5. B.E. Kane, Nature 393, p.133 (1998).

6. See the most recent review and list of references about this topic in Ref. 8 which gives an extensive list of references on the experimental and theoretical investigations on the magnetic properties of oxyhemoglobin since the pioneering work of Linus Pauling and C.D. Coryell in 1936.

7. Kanetada Nagamine, Koichiro Shimomura, Haruo Miyader, Yong-Jae Kim, Ralph Hendrick Scheicher, Tara Prasad Das, et al. Proc. Jpn. Acad. B 83, 120 (2007).

8. S.R. Badu, R.H. Pink, R.H. Scheicher, Archana Dubey, N. Sahoo, K. Nagamine and T.P. Das, Hyperfine Interact. 197, 331-340 (2010).

9. S.R. Badu, Archana Dubey, R.H. Scheicher, R.H. Pink, K. Nagamine, N. Sahoo, T.P. Das, HFI/NQI 2010, CERN, Geneva, Switzerland, 147 (2010).

10. S.R. Badu, T.P. Das, R.H. Pink, Archana Dubey, R.H. Scheicher, H.P. Saha, Lee Chow, M.B. Huang, N. Sahoo, HFI/NQI 2010, CERN, Geneva, Switzerland, 180 (2010).

11. Gang Wu, Shuan Dong, Ramsey Ida, and Nitin Reen, J. Am. Chem. Soc. 124 , pp 1768–1777 (2002).

12. S.R. Badu, R.H. Pink, Archana Dubey, R.H. Scheicher, Lee Chow, M.B. Huang, T.P. Das HFI/NQI 2010, CERN, Geneva, Switzerland, 182 (2010).

13. Penny L. Hubbard, Vasily S. Oganesyan, Nail Sulaimanov, Julea N. Butt, and Upali A. Jayasooriya, J. Phys. Chem. A 108, 9302-9309

(2004).

14. Yi Zheng, Pierre Cloutier, Darel J. Hunting, Leon Sanche, and J. Richard Wagner, J. Am. Chem. Soc. 127, 16592-16598 (2005).

15. See for example: E. S. Chang et al., Phys. Rev. 174, 1 (1968); Alfred Owusu et al. Phys. Rev. A56, 305 (1997).

16. N.C. Dutta et al., Phys. Rev. Lett. 21, 1139 (1968).

Fiscal Year 2010 List of Publications Resulting from the Use of RICC

[Publication]

Ralph H. Scheicher, Minakhi Pujari, K. Ramani Lata, Narayan Sahoo, and Tara Prasad Das, Chapter 3: Applications of the Cluster Method for Biological Systems (pp71-150) in Nanoclusters: A bridge across disciplines, Editors Purusottam Jena and A. Welford Castleman Jr.; Science & Technology of Atomic, Molecular, Condensed Matter, & Biological Systems, Series Editor: Tara Prasad Das, Elsevier (2010).

[Proceedings, etc.]

First-principles cluster study of electronic structures, locations, and hyperfine interactions of isolated atoms and ions in silicon, R.H. Pink, S.R. Badu, R.H. Scheicher, Lee Chow, M.B. Huang, and T.P. Das; Hyperfine Interact. 197, 37-41 (2010).

First principles electronic structure investigation of order of singlet and triplet states of oxyhemoglobin and analysis of possible influence of muon trapping, S.R. Badu, R.H. Pink, R.H. Scheicher, Archana Dubey, N. Sahoo, K. Nagamine, and T.P. Das; Hyperfine Interact. 197, 331-340 (2010).

[Oral presentation at an international symposium]

Test of Variational Methods for Studying Hyperfine Interactions of Molecular and Solid State Systems by Application to Atomic Systems, R.H. Pink, S.R. Badu, Archana Dubey, R.H. Scheicher, K. Raghunathan, Lee Chow, T.P. Das, HFI/NQI 2010, CERN, Geneva, Switzerland, 145 (2010).

First Principles Electronic Structure Investigation of Order of Singlet and Triplet States of Oxyhemoglobin and ^{57m}Fe Nuclear Quadrupole Interactions, S.R. Badu, Archana Dubey, R.H. Scheicher, R.H. Pink, K. Nagamine, N. Sahoo, T.P. Das, HFI/NQI 2010, CERN, Geneva, Switzerland, 147 (2010).

First Principles Study of Nuclear Quadrupole Interactions in Single and Double Chain DNA and Solid Nucleobases, S.R. Badu, T.P. Das, R.H. Pink, Archana Dubey, R.H. Scheicher, H.P. Saha, Lee Chow, M.B. Huang, N. Sahoo, HFI/NQI 2010, CERN, Geneva, Switzerland, 180 (2010).

First Principles Cluster Study of Electronic Structures, Locations and Hyperfine Interactions of Isolated Atoms and Ions in Silicon, R.H. Pink, S.R. Badu, R.H. Scheicher, Lee Chow, M.B. Huang, T.P. Das, HFI/NQI 2010, CERN, Geneva, Switzerland, 181 (2010).

First Principles Study of Muonium Trapping and Associated Magnetic Hyperfine Interactions in Nucleobases in Single and Double Chain DNA and Solid Nucleobases, S.R. Badu, R.H. Pink, Archana Dubey, R.H. Scheicher, Lee Chow, M.B. Huang, T.P. Das HFI/NQI 2010, CERN, Geneva, Switzerland, 182 (2010).

First-Principles Study of Muon Trapping in Singlet and Triplet States of Oxyhemoglobin, S.R. Badu, Archana Dubey, Lee Chow, R.H. Pink, R.H. Scheicher, K. Nagamine, N. Sahoo, T.P. Das, APS March Meeting, Dallas, Texas, 56, Number 2, T39.00009 (2011).

First-Principles Study of Hyperfine Interactions in OD Free Radical by Many-Body Perturbation Theory Using Gaussian Basis Sets, R.H. Scheicher, R.H. Pink, S.R. Badu, T.P. Das, APS March Meeting 2011, Dallas, Texas, 56, Number 2, D15.00005 (2011).

Bench Marking Accuracies of Variational Methods for Studying Molecular and Solid State Properties by Application to Nuclear Quadrupole Interactions in Boron and Aluminum Atoms, R.H. Pink, Archana Dubey, S.R. Badu, R.H. Scheicher, Lee Chow, T.P. Das, APS March Meeting 2011, Dallas Texas, 56, Number 2, D15.00008 (2011).

Test of Variational Methods for Studying Molecular and Solid State Properties by Application to Sodium Atom, T.P. Das, R.H. Pink, Archana Dubey, R.H. Scheicher, Lee Chow. APS March Meeting 2011, Dallas Texas, Vol 56, Number 2, D15.00006 (2011).