

Theoretical Chemistry Research

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Preamble:

In this article, a brief account of the theoretical chemistry research activities in the Chemistry Group has been presented. Both the fundamental as well as applied research in tune with major activities of DAE have been addressed by developing appropriate theories, state of the art simulation techniques and performing large scale computations. One of the principal themes of research and development activities are multi-scale modelling of molecules and materials, which covers microscopic, mesoscopic and macroscopic length scale as well as different time scale spanning from femtosecond to millisecond, dealing with the electronic structure, atomistic theory and simulation. Specifically, the theoretical and computational studies related to broad areas of nuclear energy applications, solar energy conversion and storage, bio-molecular systems, radiation damage and safety, and environmental applications. The whole spectrum of work discussed here includes design of novel materials with tunable properties and explaining complex phenomena using first principle quantum mechanical methods and classical statistical mechanical theories and simulations.

Introduction:

Discovery of new and more sophisticated theoretical methodologies, modelling and simulation strategies, high-performance supercomputing facilities, and state of the art program suits helps to unambiguously explain microscopic and macroscopic details of various complex chemical, physical and biological phenomena. Theoretical techniques can deal not only the equilibrium processes but also dynamic processes involving atoms, molecules, clusters, solids, bio-molecules, liquids at various length and time scale. Theoretical calculations thus, can provide an in depth understanding and rationalization of the observed properties. This drive experimental groups to include theoretical investigation as an integral part of their research. Over the years, advances in theoretical chemistry are found to increasingly interface with a number of interrelated disciplines with applications to many areas having industrial and societal impact, including nuclear energy, nuclear waste management, hydrogen energy, solar energy, fuel cell, atmospheric science, pharmaceutical chemistry, etc., which open up new windows to bring in fresh flavour of collaborative and interdisciplinary research activities in theoretical chemistry. Here, we will provide a brief overview of the theoretical and computational activities in Chemistry Group.

In the subsequent sections, we will discuss the historical perspective of theoretical chemistry in Chemistry Group, followed by the brief descriptions of on-going activities in the areas related to energy, health environment, and new theoretical development.

Historical perspective:

In the Chemistry Group, the theoretical chemistry research started in the mid-sixties, with a team led by Dr. P. G. Khubchandani as a part of the Solid State Chemistry Section headed by Dr. M. D. Karkhanawala.

In Solid State Theory team, Dr. C. Manohar was pioneer in many body theory. Some of the early studies were in the theory of dilute alloys, including screening of a transition metal impurity in a metal, the Kondo effect and spin-flip scattering, Hartree-Fock theory, Perturbation theory of many particle systems, use of difference-Patterson method in crystal structure analysis, slowing down of neutrons in graphite close to thermal equilibrium, thermal inelastic scattering of cold neutrons in graphite, scattering of slow neutrons by the water molecule, three-body interactions on Hyperfine Fields, Variational method for spin waves in disordered ferromagnets, etc. In the later stage extensive studies have been carried out covering (i) Dielectric Response and Electron Correlation, (ii) Use of Equation of Motion Method to Improve the Dielectric Function in Electron Gas, (iii) Extended ring summation for a classical electron gas, (iv) Effect of Exchange Potential on the electronic structure of gold, (v) Effect of pressure on Fermi Surface of Gold, etc. Among the other studies, mention may be made of CNDO/2 based calculations of Nitrogen Oxides, Unrestricted Hartree Fock calculations of Hydrogen Molecule, variational wavefunction for the ground as well as first excited state of H_2^+ molecular ion, semi-localised orbitals for ground state of HeH^+ , study of the hydrogen molecule using H_2^+ molecular orbitals, alkali-metal-halogen charge-exchange collisions, Semi-empirical MO-calculations on the spectral properties of some amino substituted p-benzoquinones, etc.

In the eighties, efforts were made to develop theoretical models to explain experimental studies on soft matter, dealing with surfactants, micelles, microemulsions, liquid crystals, etc. Several important aspects like mechanism of micelle to vesicle transition, vesicle to micelle transitions induced by Coulomb correlations, theory of colloidal systems dealing with interactions and structure, shapes and sizes of micelles in CTAB solutions, the origin of viscoelasticity in micellar solutions, etc. were studied. New interpretation was given to the sticky hard sphere model, application of Baxter's sticky hard-sphere model to the theory of cloud points of non-ionic surfactants, calculation of structure factor for colloidal dispersions using exact potentials along with random phase approximation, Form-factors for different aggregation models of micelles, model for the cloud point of mixed surfactant systems, tuning inter-micellar potentials through van der Waals as well as Coulombic contributions, a theoretical model for the phase diagram of mixtures of polymeric solutes and Nematic Liquid Crystals, self-diffusion in wormlike micelles networks with electrostatic interactions, etc.

On-going research activities on theoretical chemistry in Chemistry Group:

On-going activities can be classified in four domains, e.g., energy, environment, health, and new theoretical development.

Theoretical activities related to nuclear energy applications:

In this category we will first discuss our activities related to nuclear energy applications. Chemistry group is actively involved in several important activities related to DAE nuclear energy program, by providing valuable inputs beyond experimental range, including thermophysical properties of nuclear fuel material, interaction of fission products with the fuel matrix, management of nuclear waste, radiation damage, and radiation safety. Theoretical investigations have been carried out for different important thermophysical and thermodynamic properties of advanced fuel materials for nuclear reactors, including U_3Si_2 , UAl_3 , U_2Mo , Pm_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Dy_2O_3 etc. Various thermophysical properties like thermal expansion, free energy, bulk modulus, heat capacity, etc. have been evaluated beyond experimental range, which are very much related to heat transport phenomena. Lots of studies have been carried out to investigate the solubility of different fission products (Xe, Kr, Sr, La, Pm, and Cs) into different fuel matrix, including UAl_3 , UO_2 , etc. In the area of nuclear waste management extensive research has been carried out to explore efficient pyrochlore materials for radioactive waste immobilization, which would be a great step in the area of advanced materials technology. As for example, $La_2Hf_2O_7$, $Lu_2Hf_2O_7$, $Y_2Zr_2O_7$ materials show impressive features related to the solubility of heavy metal in the host structure. Recently, calcium fluorapatite compound has been demonstrated as a potential host for radioactive waste immobilization. A special focus in this work has been given to $^{241}Am^{3+}$ ion which is highly radioactive and hazardous in nature and exists in the high level radioactive nuclear waste. Extensive computational modelling has been carried out to design efficient materials for entrapment of radioactive Kr and Xe released from nuclear reactors and reprocessing of spent fuel, which is important in the context of nuclear safety and waste management. Among various porous materials, metal-organic frame (MOF) works show excellent storage and separation properties. As for example, M-MOF-74, SBMOF-1, SBMOF-2, MFM-300, SCU-11 MOF have been found to be very attractive. Even layered materials, like, graphyne, graphdiyne, doped graphene, MoS_2 show very good adsorption/separation properties for Xe and Kr with good selectivity. Among several ligand designed for this purpose, a multitopic ion-pair receptor has been found to be very promising, particularly for selective separation of chemically similar Ca^{2+}/Sr^{2+} pair. Another important issue at the back end of the nuclear fuel cycle is the separation of lanthanides and actinides. It has been found that supramolecular host molecules are better candidates for the separation of Am and Eu due to the favourable host-guest interactions. Among the different host materials, cucurbituril hosts are promising cationic binders due to favourable ion-dipole interactions. Liquid-liquid extraction methodologies have been utilized for many decades in the nuclear industry for the reprocessing of the spent nuclear fuels. In a series of investigations using molecular dynamic (MD) simulations, adsorption behaviour of the uranyl ions in different functionalized carbon nanotubes (CNT) have been evaluated at different temperatures and concentrations of uranyl ions and also at supercritical conditions relevant to supercritical extraction. The carboxylate ion functionalized CNT shows the maximum adsorption capacity for uranyl ions. Extensive theoretical research has been carried out here in the field of radiation damage. One of the examples includes the investigation of different defects in steel, which are the most important structural materials used in the nuclear industry. Increasing

applications of radiation technology in our daily life drives to develop efficient devices for measuring radiation dose accurately. Detailed investigation of radiation induced defect chemistry, including defect type, configuration, concentration, charge state, etc has been performed to explore the role of different point defects to the optical behaviour of different phosphor materials used in radiation dosimetry, including LiF, LiMgPO₄, KMgF₃, etc.

Computational modelling for solar energy conversion:

Chemistry group theoretical research focuses mainly on three important aspects related to the hydrogen energy, viz., design of efficient photocatalyst for water splitting to generate hydrogen, developing materials for efficient reversible storage of hydrogen, and designing catalyst for fuel cells. The quest for an efficient utilization of sun light for the generation of H₂ through water splitting has provided motivation to find efficient strategy for developing new generation photocatalyst. Significant contribution has been made towards enhancement of the photocatalytic activity of a wide range of perovskite based photocatalyst, viz. TiO₂, NaTaO₃, KTaO₃, KNbO₃, NaNbO₃, and SrTiO₃. Efficient strategy has been demonstrated to engineer the band structure of the photocatalyst in a controlled manner through doping with foreign element. A new kind of carbon nano-structure based material (g-C₃N₃) has been designed for visible light driven water splitting which is expected to have large impact in the field of metal free photocatalyst. While the first step towards success in hydrogen energy is the generation of hydrogen from natural resources, the second step to make the hydrogen energy realizable involves the reversible storage of hydrogen in a safe and cost effective way. The possible use of ionic liquids for the hydrogen storage applications has been explored at the molecular level. The gravimetric density for the (ImCl)₂, (GuaCl)₂ and (PyrCl)₂ dimers when they undergo H₂ physisorption is found to be very impressive, thus supporting the statement that room temperature ionic liquids can be suitable for hydrogen storage materials. In another study, the role of ‘intra-curvature’ in a set of single-walled carbon nanohorns to adsorb light metal has been investigated and subsequently explored them for H₂ storage applications. The development of efficient and low-cost material for the oxygen reduction reaction (ORR) process is considered as one of the major challenges for the wide scale applications of fuel cells. For this purpose, transition metal decorated C₂₄N₂₄ system has been explored as a new kind of non-precious catalyst for ORR. The sluggish kinetics of oxygen evolution reaction (OER) limits the activity of many photo/electro catalysts for overall water splitting reaction. Through systematic computational studies, Co²⁺ and cucurbit [5] uril host-guest complex adsorbed BiVO₄ surface has been proposed as a potential co-catalyst for OER. Recently, photovoltaic cells based on inorganic quantum dots have shown attractive photovoltaic efficiency of more than 10%. Thus, it is very important to investigate the electronic structure of quantum dot for designing efficient quantum dots solar cell. Here, PbS quantum dot has been investigated aiming to explore its applications in practical situations.

Theoretical activities related to environmental applications:

This section will discuss chemistry group theoretical activities related to environment, like, energy storage using Li/Na-ion battery, degradation of environmental pollutant, conversion of CO₂ to fuel, CO oxidation.

During the past few decades, there has been an emerging trend in energy storage technologies, motivated by concerns over global warming, depleting fossil-fuel reserves, and increasing demand for grid storage systems and portable electronics. An excellent example of energy storage devices includes the rechargeable lithium battery, which is superior to all other secondary batteries due to their high energy density. Lithium-ion batteries play significant role in powering the revolution in various portable electronics. In addition to that large scale storage system in power grid is required for the hybrid or fully electric car powered by batteries, which is shown to become very popular to reduce CO₂ emissions. With experimental group biomass-derived carbon has been explored as versatile anodes for high-performance sodium and lithium-ion batteries using Na₂Ti₃O₇-nanorods, Layered oxide material, LiNi_xMn_yCo_zO₂. The structural changes in the Fe₃O₄ electrode of Li ion battery due to Li intercalation and de-intercalation process in the electrodes during charging and discharging of the batteries have also been revealed. Sodium super ion conductors based structures has been explored as cathode materials for the applications in sodium ion battery technology. Doping with W has been found to enhance the structural integrity and enhanced Na-ion mobility significantly. Interestingly, Phosphorous/Fluorine-codoped carbon has been explored for enhanced both sodium ion and lithium ion storage. Our group is also dedicated towards design of efficient catalyst for CO₂ conversion to Fuels. TiO₂ based materials in the presence of dopant elements (Co, F/Nb/Ta) show enhanced photoactivity for the CO₂ conversion processes under visible light irradiation. In a recent study, it has been predicted that the codoping of (Ni, La) or (Ni, W) pair into SrTiO₃ can lead to improved CO₂ conversion activity under sunlight. Using a multi-scale modeling strategy, which includes the trained Machine Learning model, force field optimization, DFT calculations, and simulations has been performed to identify the best MOFs for selective adsorption of CO₂ from a mixture of wet flue gases. The screened MOFs show selective CO₂ adsorption property under wet flue gas condition with significant capacity of CO₂ uptake and CO₂/N₂ selectivity in the presence of H₂O vapor. Similar data driven discovery of MOFs for separation and storage of Xe/Kr and Iodine from spent nuclear fuel off gases has been carried out and the computational predictions were under experimental validation. We have explored the possibility to use low energy electron (LEE) for the *in situ* generation of intrinsically short-lived covalent dimer of CO, which otherwise is not possible to prepare using any chemical methods. We also have reported a novel method for inducing reactivity on any specific site of a molecule by using a LEE. The induced chemical reactivity is originated directly from the Coulomb interaction between the LEE and the most polarizable electrons of the molecular target. Using quantum chemical methods, the reaction mechanism is best illustrated by inducing nucleophilicity on a specific molecular moiety in a molecular complex. The novel strategy for inducing site-specific chemical reactivity by using a LEE is very likely to open up novel experimental possibilities for engineering the reactivity of chemical reagents regardless of their chemical complexity and may evolve as a synthesis method.

We now proceed to discuss theoretical modelling of efficient catalysts for degradation of environmental pollutant. Among different methods to destroy hazardous compounds in water or air, catalytic degradation is considered to be an advanced process. Because of low cost, wide availability, long-time stability, and chemical inertness, oxide based semiconductor

materials have been proven to be the most effective catalyst for this process. Using density functional theory, new catalyst based on TiO_2 has been explored and successfully demonstrated catalytic activity of the modified materials for the degradation of environmental pollutant in collaboration with an experimental group. We have also focused towards water decontamination through selective recovery of toxic metal from aquatic system. It has been revealed that polymeric hydrogel beads loaded with amine functionalized SiO_2 microsphere [$\text{NH}_2\text{-SiO}_2\text{MS-Ca-Alg}$] as promising material for highly efficient uptake of Cd, Pb, Ni and Cu. On the other hand, the selective recovery chromium in different oxidation states from the aqueous solution is considered as reconciliation between clean water demand and fast growing industrialization. The $\text{Fe(0)-SH-TiO}_2\text{-MS-Ca-Alg}$ bead shows selectivity for both Cr(III) and Cr(VI) together, which is a significant breakthrough. Theoretical calculations have also been carried out to recover precious metals from the aquatic solution of electronic wastes. In the quest of finding a suitable material as adsorbent for gold ions, density functional theory based calculation and ab-initio molecular dynamics simulations have been used to understand the interaction of gold ions with graphene and graphene oxide (GO) materials and the adsorption of these ions on GO surfaces. Theoretical activities have been extended to understand the interaction, complex formation and adsorption of radiotoxic actinyl ions in the underground clay layers, which is of prime importance to mitigate their migration into the geosphere. We have used force-field based classical MD simulations to understand the interaction and adsorption of uranyl ions in Kaolinite and Lizardite clays. Counter ion dependent complex formation followed by adsorption of the uranyl ions on the siloxane surface of the clay has been observed.

Theoretical activities related to biological systems and health care:

Many of our activities related to the understanding the behaviour of water and aqueous solutions containing biological molecules and the action of water towards biomacromolecules like proteins, DNA etc. Apart from that, molecular simulations have been used to understand the interaction between protein and drug and structure of viral capsid for the designing new drugs. Current atomistic MD simulation studies have shed light on the interaction of SARS-CoV2 receptor binding motif and ACE2 enzyme of the human body and the interfacial contact area between the two has been identified as a key parameter that correlates with the infectivity and severity of the different mutant viruses. Extensive computational studies have been carried out for enhancing stability of Oral polio vaccine. Present study revealed that heavy water can act as thermostabilizer for Oral polio vaccine.

Large scale all-atom enhance sampling simulation has been performed to explore the binding characteristics of uranyl ion with human serum albumin (HSA). It has been found that the binding of the radioactive ion is the result of the dynamical balance between the ion and-HSA and the ion-water-water short range Coulomb interactions. Extensive studies have been carried out on the investigation of divalent ions as potential permeating blockers for the non-selective Na-K ion channel. Using well-tempered metadynamics simulations it has been shown that, akin to K^+ coordination, Ba^{2+} and Sr^{2+} can bind in a very similar fashion. Interestingly, the binding of divalent metals is found to be more favourable than K^+ . But, their permeation through the extracellular entrance shows a considerably higher energetic barrier, which manifests their inherent blocking property. In a recent study, we have designed

inhibitors containing hetero linkers for gastric proton pump H^+,K^+ -ATPase. It has been also revealed that the role of Cysteine-813 amino acid residue is very much important in the inhibition process of H^+,K^+ -ATPase for Inhibitor-1. In the field of the development of decorporating agents for the in-vitro removal of actinide, our computational predictions unravel several key features that are necessary for the successful design of decorporating agents. With multi-scale models, we also proposed the the bio-speciation of Th(IV), Cm(III) and Pu(IV) to sTf and ways to decorporate them with CAM and HOPO type ligands. The molecular level insights are useful to design novel biocompatible decorporating agents in near future.

Through careful, novel analyses, we are able to demonstrate that if we account for the fact that urea can also be a neighbour of water in a concentrated solution, then urea does not break the water structure, rather it just replaces one or more water neighbours of a central water molecule. In a dilute urea solution, most of the water molecules are four H-bonded, but in the case of concentrated solution, most of them are three H-bonded. The population of water-urea H-bonds is found to be increased at higher concentrations. Due to incorrect interpretation, it seems that urea breaks the tetrahedral H-bonded network of water. To get idea about the mechanism of denaturation, we have investigated the intricacies of aggregate formation and its mode of action on protein. The parallel stacking of the two Gdm^+ moieties in concentrated guanidinium chloride ($GdmCl$) binary solution has been observed in our simulations and specifically it is revealed that the same mode of interaction leading to the parallel stacking of Gdm^+ ions around the structurally similar arginine side chain of the protein leads to chemical denaturation of a protein. Therefore, parallel staking of the ARG and Gdm^+ moieties is the mode by which Gdm^+ attacks the protein backbone for unfolding.

Development of new theoretical formalisms:

Technological revolution of the material and devices in present days are largely depending on the molecular level understanding on the chemical processes involved there in. Following this suit, major component in research activities carried out in Theoretical Chemistry Section are the development of many theoretical formalism, robust algorithms and state-of-the-art computational methodologies as discussed below. Based on first-principle theory, we derived an exact kinetic equation starting from a multi dimensional Liouville equation for the time evolution of the probability distribution for a general reaction coordinate space. We considered two approximations to reduce the exact equation into a Fokker-Planck-type equation with a sink term. Its application has been considered to two important types of reactions, viz., the diffusion-controlled and electron transfer reactions. A scheme has been provided to achieve the critical value of the reaction coordinate at which the reaction occur, and to get the initial distribution functions in same space for different kind of experimental scenarios. For photoinduced electron transfer, incorporated the influence of excitation frequency using appropriate initial distribution functions.

A unified theory is developed for the first time for different kinds of non equilibrium processes by projecting the dynamics in hyper-dimensional space onto one-dimensional space, where the effect of all optically created innumerable "dark states" involved can be viewed through the lens of the excitation wavelength. We have also derived the analytical expressions for the size dependent dielectric constant and normalized orientation polarization

of solvents. This finding provides a new platform for calculating the hydration energy and orientation polarization based on linear response theory for different varieties of ions in solvent medium. We have employed MD simulations to achieve a fundamental understanding of the relationship between the conductivity, structural, viscosity, and thermodynamic properties mixed with the various solvents. The density, viscosity, ionic conductivity, and self-diffusion coefficients as predicted by MD simulations agree quite well with the experimental results. The liquid–vapor coexistence curve for several long-chain polymers in different solvent as predicted by Monte Carlo (MCDFT) is compared with the first order perturbation theory approximation (FPA) within the attractive and repulsive region of intra- and inter-molecular potentials.

Chemistry group shows significant contribution towards the development of relativistic quantum mechanical methods based electronic structure programs. We are strongly involved in the development of fully relativistic 4-component quantum mechanical methods based electronic structure programs. Our codes are very useful for studying various symmetry violating properties and relativistic effects in heavy atoms and molecules. These properties cannot be measured experimentally and their theoretical study are very essential to probe physics beyond the Standard Model (SM). This can also validate the popular extension of SM. This kind of study is also essential for placing a precise upper bound limit on the electric dipole moment of electron (eEDM). In this regard, we have developed many new routines and implemented at the various level of theories in DIRAC program package. Our developed routines are also interfaced with many in-house developed codes based on the framework of coupled-cluster (CC) theory and configuration interaction (CI) methods. Some of our contributions which are released with recent versions of DIRAC program package time to time since 2015 and are as follows: magnetic hyperfine interaction, electron electric dipole moment interaction, nucleon-electron scalar-pseudoscalar interaction, and nuclear magnetic quadruple moment interaction.

Future perspective: Machine learning and data science:

In recent years, explosive advancements in data science and machine learning (ML) have shown promising applications in discovery of new functional molecules and materials for many technological applications. Beyond the traditional methods of materials exploration, data driven discovery of materials is emerging at a rapid pace and is considered as the fourth paradigm of material science. In machine learning (ML) technique, a model is trained using the existing materials data-base that maps the complex structure-property relations and the trained, tested and validated model can be utilized for future predictions. Computational high-throughput screening (HTS) is considered as a powerful tool to screen a large database of materials and identify the best possible materials for any application of interest.