

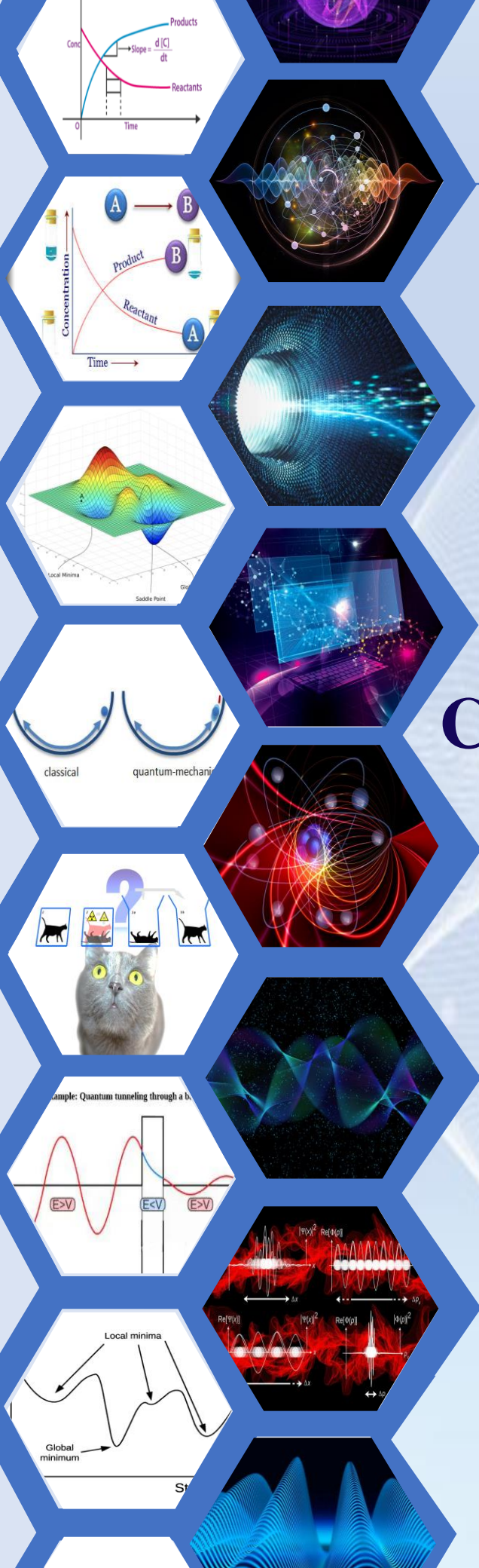
## Recent Advances in Chemistry: Theoretical and Computational Aspects (RAC-TCA 2022)

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# Recent Advances in Chemistry: Theoretical & Computational Aspects

November 18-20, 2022



Organized by

Department of Chemistry

National Institute of Technology Meghalaya &

North Eastern Hill University

Shillong

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## Message from the Conveners



Dr. Amit Kumar Paul



Dr. Biplab Sarkar

On behalf of the organizing committee of the National Conference on Recent Advances in Chemistry: Theoretical & Computational Aspects (RAC:TCA 2022), it is our great pleasure to welcome you all to the Scotland of East India, Shillong. The RAC:TCA is organized by the Departments of Chemistry, NIT Meghalaya and North Eastern Hill University during November 18-20, 2022 in NEHU, Shillong. The main focus of the conference is to deliberate upon the emerging trends of theoretical chemistry and to provide a platform for the interdisciplinary collaborative research in the domain of chemical sciences. This conference is expected to attract the scientist and researchers from various part of country both from industry and academia, especially young researchers from institutes like IITs, NITs, IISERs universities etc. The participants from north eastern region will be getting the opportunities to interact with the distinguished speakers from reputed institutes/universities of our country and it can further act as the catalyst towards academic enrichment of north east India as well as for the country.

The conference is assembling several leading scientists and young researchers agreeing to deliver scientific lectures and share their knowledge with the participants. It is matter of great pleasure and satisfaction to present this book of abstracts of thirteen (13) keynote lectures, and twenty one (21) invited lectures, and around fifty two (52) contributed papers by the Ph.D. students. RAC:TCA 2022 is being supported by Science and Engineering Research Board (SERB), Star Cement, Century Plyboards, ab Chemicals and Instruments, Smart Computers, Shillong, BMG informatics. We are highly grateful to all these sponsors for their generous support. The conveners take this opportunity to express our heartfelt gratitude to all who have contributed solely directly and indirectly in making RAC:TCA 2022 a successful event.

We also take this opportunity to place on record our sincere thank to NIT Meghalaya and NEHU administration for allowing us to use all the resources whenever needed. The conveners are also thankful to the research scholars and M.Sc. students of both departments for their untiring support and we hope that their efforts will become evident during RAC:TCA 2022. We once again extend our hearty welcome to all the speakers and other participants and wish them a pleasant stay in Shillong, stimulating discussion and interactions during RAC:TCA 2022.

**Conveners, RAC:TCA 2022**





## Message from the Patron



It is a matter of great pleasure to see that the Departments of Chemistry, NIT Meghalaya & North Eastern Hill University are jointly organizing a National Conference on Recent Advances in Chemistry: Theoretical & Computational Aspects during November 18-20, 2022. I congratulate both the departments for organizing this national level conference and I could see the efforts put in by the young faculty members in organizing the same.

It is very much heartening to see the immense response received by the conference from the chemistry research community throughout the country. A good number of scientists and researchers have agreed to deliver keynote lectures and invited lectures in the conference. Many young scholars participating in this conference will be benefitted from these scientists.

I thank Science and Engineering Research Board (SERB), for providing financial support to this conference. Some of the companies and vendors have also come forward to sponsor to this conference and I thank them for their support.

I heartily welcome all the distinguished speakers, scholars and the participants to RAC: TCA 2022 organized by the Departments of Chemistry, NIT Meghalaya and NEHU and wish the conference a grand success.

Professor Bibhuti Bhusan Biswal  
Director  
NIT Meghalaya



आचार्य प्रभा शंकर शुक्ल  
कुलपति

पूर्वोत्तर पर्वतीय विश्वविद्यालय  
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मेघालय, भारत



Professor Prabha Shankar Shukla  
Vice-Chancellor

**North-Eastern Hill University**

District: East Khasi Hills, Shillong - 793022  
Meghalaya, India

### Message

I am delighted to learn that Department of Chemistry, North-Eastern Hill University, Shillong is organizing a National Symposium on Recent Advances in Chemistry: Theoretical and Computational Aspects in collaboration with Department of Chemistry, National Institute of Technology, Meghalaya during 18<sup>th</sup> – 20<sup>th</sup> Nov'2022 to deliberate upon the emerging trends in theoretical aspects of chemical sciences.



I compliment the Department of Chemistry, North-Eastern Hill University in organizing the Symposium to commemorate the Golden Jubilee year of NEHU. I am glad to know that several eminent scientists and researchers will be delivering keynote and invited lectures in this conference which will benefit many young scholars and researchers.

I congratulate the Department of Chemistry, North-Eastern Hill University, Shillong and Department of Chemistry, National Institute of Technology, Meghalaya for organizing this national level symposium and wish all the speakers and participants a very best.

I hope and wish that the conference will be a success and the participants, especially the scholars and students will be benefited from the deliberations and lectures.

  
( Prabha Shankar Shukla )

## Tentative Program Schedule

Online Link: <https://meet.google.com/msg-tmsu-hin>

Day 1: November 18, 2022 (Friday) (Venue: NEHU)	
Up to 2 PM	Registration and Arrival
2:00 – 2:45 PM	Inauguration Function
Tea Break (2:45 PM – 3 PM)	
<b>SESSION I (Chair: Prof. Satrajit Adhikari)</b>	
3.00-3.40 PM	<u>Keynote Lecture 1 (Prof. Narayanasami Sathyamurthy)</u>
3.40-4.20 PM	<u>Keynote Lecture 2 (Prof. Srabani Taraphder)</u>
4.20-4.45 PM	<u>Invited Lecture 1 (Dr. Rahul Maitra)</u>
4.45-5.10 PM	<u>Invited Lecture 2 (Dr. Manikandan Paranjothy)</u>
Tea Break (05.10-05.30 PM)	
<b>SESSION II (Chair: Prof. Srabani Taraphder)</b>	
5.30-6.10 PM	<u>Keynote Lecture 3 (Prof. Biman Bagchi)</u>
6:10-6:50 PM	<u>Keynote Lecture 4 (Prof. Sushanta Mahapatra) (online)</u>
6.50-7.20 PM	<u>Invited Lecture 3 (Prof. Sumana Dutta)</u>
7.20 PM onwards: Dinner	
<b>Buses to the Hostels: 9:00 PM</b>	
Day 2: November 19, 2022 (Saturday) (Venue: NEHU)	
<b>SESSION III (Chair: Prof. Sumana Dutta)</b>	

9.00-9.40 AM	<u>Keynote Lecture 5 (Prof. Deb Shankar Ray)</u>
9.40-10.20 AM	<u>Keynote Lecture 6 (Prof. Ranjit Biswas)</u>
10.20-10.50 AM	<u>Invited Lecture 4 (Prof. Rajarshi Chakrabarti)</u>
10.50-11.20 AM	<u>Invited Lecture 5 (Prof. Debashree Ghosh)</u>
<b>11.20-11.30 AM Tea Break</b>	
<b>SESSION IV (Chair: Prof. Rajarshi Chakrabarti)</b>	
11.30-12.10 PM	<u>Keynote Lecture 7 (Prof. Swapan K. Pati)</u>
12.10-12.40 PM	<u>Invited Lecture 6 (Prof. Aditya N. Panda)</u>
12.40-01.05 PM	<u>Invited Lecture 7 (Dr. Jagannath Mondal)</u>
01.05-01.30 PM	<u>Invited Lecture 8 (Dr. Snehasis Daschakraborty)</u>
<b>01.30-3.30 PM Working Lunch and Poster Session</b>	
<b>SESSION V (Chair: Dr. Brijesh K. Mishra)</b>	
3.30-4.10 PM	<u>Keynote Lecture 8 (Prof. K. Srihari)</u>
4.10-4.40 PM	<u>Invited Lecture 9 (Prof. Ashwini Kumar Tiwari)</u>
4.40-5.05 PM	<u>Invited Lecture 10 (Dr. Neelanjana Sengupta)</u>
<b>5.05-5.20 PM Tea Break</b>	
<b>SESSION VI (Chair: Prof. Panchanan Puzari)</b>	
5.20-6.00 PM	<u>Keynote Lecture 9 (Prof. Satrajit Adhikari)</u>
6.00-6.25 PM	<u>Invited Lecture 11 (Dr. Rahul Kar)</u>
6.25-6.50 PM	<u>Invited Lecture 12 (Dr. Sangita Sen)</u>
<b>6.50 PM onwards Banquet Dinner and Poster Session</b>	
<b>Buses to the Hostels: 9:00 PM</b>	
<b>Day 3: November 20, 2022 (Sunday) (Venue: NEHU)</b>	

SESSION VII (Chair: Prof. Debashree Ghosh)	
9.00-09.40 AM	<u>Keynote Lecture 10 (Prof. G. Narahari Sastry)</u>
09.40-10.20 AM	<u>Keynote Lecture 11 (Prof. Pratim K. Chattaraj) (online)</u>
10.20-10.45 AM	<u>Invited Lecture 13 (Dr. Suman Chakrabarty)</u>
10.45-11.10 AM	<u>Invited Lecture 14 (Dr. Achintya K. Dutta)</u>
Tea Break (11.10-11.25 AM)	
SESSION VIII (Chair: Prof. Ashwani Tiwari)	
11.25-12.05 PM	<u>Keynote Lecture 12 (Prof. R. H. D. Lyngdoh)</u>
12.05-12.30 PM	<u>Invited Lecture 15 (Dr. Sai G. Ramesh)</u>
12.30-12.55 PM	<u>Invited Lecture 16 (Dr. Manabendra Sarma)</u>
12.55-1.20 PM	<u>Invited Lecture 17 (Dr. Pushpita Ghosh)</u>
1.20-03.00 PM Lunch and Poster Session	
SESSION IX (Chair: Prof. Aditya N. Panda)	
3.00-3.40 PM	<u>Keynote Lecture 13 (Prof. Asit K. Chandra)</u>
3.40-4.05 PM	<u>Invited Lecture 18 (Dr. P. Balanarayan) (online)</u>
4.05-4.30 PM	<u>Invited Lecture 19 (Dr. T. Rajagopala Rao)</u>
4.30-4.55 PM	<u>Invited Lecture 20 (Dr. Subhasish Mallick)</u>
4.55-5.20 PM	<u>Invited Lecture 21 (Dr. Manoj Mandal)</u>
5:20 PM onwards Valedictory Session	
<b>Buses to the Hostel: 7:00 PM</b>	

## **Abstracts for Lectures**

(Speakers are arranged in Alphabetical Order)

# Lower Scaling Methods for Excited States: The Ever-Lasting Frontier

**Achintya Kumar Dutta**

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The natural orbitals<sup>1</sup> provides a very compact representation of the one-electron basis functions and allows one to truncate the virtual space with systematically controllable accuracy. Although the recipe to generate natural orbitals for the ground state is well studied<sup>2</sup>, the situation is less straightforward for excited state. We have developed a new formulation of lower scaling excited state method based on state specific natural orbitals, which allows one to significantly reduce the computational cost of the calculations. The natural orbitals are generated from a second order perturbation approximation for the excited states. The new method gives uniform accuracy for valence, Rydberg and charge-transfer excited states. The ways to improve the accuracy of the method as well as the challenges will be discussed.

## References:

1. P.O. Löwdin, Phys. Rev. 97, 1474 (1955).
2. T. L. Barr and E. R. Davidson, Phys. Rev. A 1, 644 (1970).

# Reaction mechanisms of a bimolecular chemical reaction:

## Quantum and classical studies

**Aditya N. Panda**<sup>1</sup>

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A simple reaction of the type  $A + BC \rightarrow AB + C$  can proceed through either a direct (instant), an indirect (time-delayed) or a combination of both mechanisms. In this talk, I will present the results of exact quantum dynamical studies of three representative reactions,  $\text{Br} + \text{HD} \rightarrow \text{BrH} + \text{D}$ ,  $\text{H}^- \rightarrow \text{HD} \rightarrow \text{HD} (\text{H}_2) \rightarrow \text{H}^- (\text{D}^-)$  and  $\text{Ne} + \text{HeH}^+ \rightarrow \text{NeH}^+ + \text{He}$ . Based on these results, the involvement of any of these mechanisms and their effects on the observables will be discussed. Quantum effects and the applicability of classical mechanics to study these mechanisms will also be discussed.



# Dynamical Studies for Methane and Water Dissociative Chemisorption on Efficient Bimetallic Alloy Surfaces

**Ashwani K. Tiwari**

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Steam reforming of methane (SRM) and water-gas shift (WGS) reactions are two industrially important reactions that produce hydrogen gas to be used for other important reaction, such as Haber-Bosch ammonia synthesis. The rate-determining steps for these processes are the dissociative chemisorption of CH<sub>4</sub> and H<sub>2</sub>O on catalyst surfaces. In industry, mainly Ni-based catalysts are used for the SRM and Cu for WGS reactions. Using these monometals as catalysts has certain disadvantages. In this talk, I will show how alloying the respective metal atoms with a second metal atom could serve our purpose better for the dissociation of CH<sub>4</sub> and H<sub>2</sub>O. It has been found that cost-effective Subsurface- Pt<sub>9</sub>/Ni (111) is a potential alternative for the methane dissociation processes and Ni<sub>9</sub>/Cu (211) is a better alternative for water dissociation. One important characteristic of these dissociative chemisorption processes is the non-statistical behaviors. To elucidate this, quantum dynamical studies have also been performed using the reaction path Hamiltonian (RPH) methodology. It is observed that for the dissociative chemisorption of CH<sub>4</sub>, the reaction probability depends on the symmetric/antisymmetric nature of the minimum energy path. In full coupling condition, it has been found that Ni<sub>8</sub>/Pt (111) exhibits high dissociation probability compared to Ni<sub>9</sub>/Pt (111), although they both have almost similar activation energy barriers, 0.72 eV and 0.71 eV, respectively. Strong mode selectivity is also observed on all the efficient alloy surfaces, with symmetric stretching mode showing the highest reaction probability and ground vibrational state showing the lowest probability on all the alloy surfaces. An increase in surface temperature increases the reactivity on all alloy surfaces for all the vibrational modes. The final dissociative sticking probability was calculated after site averaging, which includes the dissociation of methane covering the whole surface layer of the supercell and not just the lowest energy site. Inclusion of site averaging lowers the dissociation probability at all incident energies on all the alloy surfaces. For water dissociation, only the adiabatic reaction probabilities were calculated, which shows the reactivity order: symmetric > bending > asymmetric ≈ ground vibrational state.

## References:

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2. S. Nave and B. Jackson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, 81, 233408
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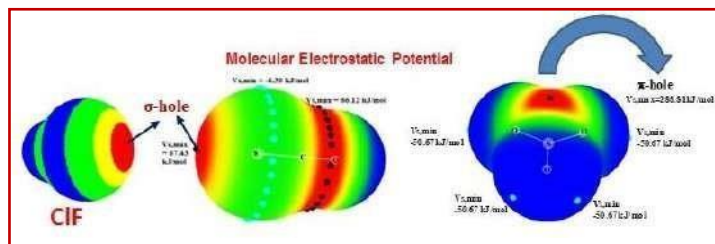
# Diversity in $\sigma$ -Hole and $\pi$ -Hole Based Non-Covalent Interactions

**Asit K. Chandra**

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The non-covalent interactions originating from the  $\sigma$ -hole and  $\pi$ -hole of a Lewis base is an intriguing area of contemporary research [1,2]. Such interactions have been used in various fields, like supramolecular chemistry, drug design, liquid crystals, anion sensing etc., to develop functional materials. The  $\sigma$ -hole is the region of the positive electrostatic potential on the molecular entity along the extension of the R-X bond; whereas the  $\pi$ -hole refers to the positive region in the direction

perpendicular to the  $\sigma$ -framework of the molecular entity. The X-atom is an atom on the right side of the periodic table (groups 14-17), like Cl, S, P, Si etc. The directional noncovalent interaction R-X...Y-



R' between the positive region of X-atom of Lewis acid RX and a negative or electron rich site Y of Lewis base YR' gives rise to a net attractive interaction between the two molecular entities. There are numerous experimental and theoretical studies to understand the origin and physical nature of the halogen bond (X=Cl,Br,I), chalcogen bond (X=S, Se, Te), tetrel bond (X=C, Si, Ge), and pnicogen bond (X=P,As) [1-3]. Fundamental understanding of these interactions is necessary to modulate their strength for using it in rational drug design, polymer science, liquid crystals, anion sensing, etc. We have been working on different aspects of the  $\sigma$ -hole and  $\pi$ -hole based interactions [4-8] and here we present some of the interesting features of halogen and chalcogen bond interactions and their effect on geometrical parameters and vibrational spectra of the two interacting species. Several computational tools like NBO, AIM, and SAPT have been used to reveal the electronic nature of these interactions. This discussion may also ignite new thinking about some traditional concepts of chemistry and raise questions for solving some related problems.

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# Water, The Elixir of Life -- but HOW? AN Emerging Molecular Picture OF FUNCTION

**Biman Bagchi**

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Water is a small molecule consisting of only one oxygen and two hydrogen atoms. Nevertheless, it is variously termed as “The elixir of Life”, “The Lubricant of Life”, with glorious tributes to it in various Slokas in our Vedas. (“Before the Creation of the Universe, there was said to be nothing but bottomless, uninterrupted, limitless water. The world was therefore originally water without light” (Salilam apraketam; Rig Veda X.29.3)). About 71% of surface of earth is water and about the same amount constitutes our body. Nevertheless, precise microscopic role of water in biology remains far from understood. This has remained an outstanding lacuna. First, we note that despite its simple molecular structure, it exhibits a range of striking anomalies in neat liquid state. These properties become more exotic in protein and DNA surfaces. Water not only stabilizes biological structures but also plays important functional role in driving many of the functions of the body. How does water do these? We shall articulate our recent work and understanding of the functional role of water, for example, in the dissociation of the bond between Fe and CO in myoglobin, and dissociation of the beta-sheet of insulin dimer.

## References:

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3. S. Mondal and B Bagchi, Current Opinion in Structural Biology (November, 2022)
4. S. Mukherjee, S. Mondal and B Bagchi, Phys Rev Letts. (i) (2019); (ii) (2022).

## **Self-organization in chemical systems**

**Deb Shankar Ray**

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Self-organized structures are ubiquitous in nature. The examples range over the animal coats of tiger, zebra, and the colourful wings of butterflies, the candle flame, and the sand piles and so on. They appear under far-from-equilibrium conditions. We intend to discuss some of the pattern-forming scenarios like stationary patterns, spirals, travelling waves, standing clusters, noise and light induced patterns, synchronization of patterns in systems controlled by chemical reactions and diffusion within the scope of nonlinear chemical dynamics.

# Photophysics of skin pigment melanin

**Debashree Ghosh**

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The biological pigment melanin is the primary component in our skin that is responsible for photoprotection from sunlight. While this fact is well acknowledged, the exact molecular mechanism of the process is much more obscure. It is further complicated because of the lack of knowledge about the exact structure of melanin. We use computational tools to understand the mechanism of photoprotection in melanin [1,2] and find the crucial role of heterogeneity is central to efficient nonradiative decay without any structural damage.[3] To understand such processes we develop methods that are capable to deal with strongly correlated systems, such as density matrix renormalization group. [4-6]

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# Cooperativity of Non-covalent Interactions

**G. Narahari Sastry**

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Non-covalent interactions control the three dimensional structure of macromolecules and the supramolecular assemblies. Thus, atomic level understanding of condensed phase structure warrants a clear understanding of the role, strength and relevance non-covalent interactions and how do they mutually influence each other. The concept of cooperativity in non-covalent interactions involving hydrogen bonding and ion-molecule interactions is rigorously analyzed. The role, range and relevance of cation- $\pi$  and  $\pi$ - $\pi$  interactions in determining the macromolecular structure will be explained. The effect of multipole noncovalent interaction appears to be greater than the submission effect of individual noncovalent interaction. We have carried out several theoretical studies to get an insight into the cooperativity effect towards the cation- $\pi$  interaction. In these studies, we have examined various model systems to elucidate how a pair of non-covalent interactions mutually impact each other, particularly when one of the noncovalent bonds is cation- $\pi$  interaction. Cooperative effects are observed in the complex where cation- $\pi$  and other noncovalent interactions co-exist viz., cation- $\pi$  interaction is cooperative in nature in the presence of hydrogen bond, halogen bond, and  $\pi$ - $\pi$  interactions. Besides, these studies elucidate the enhancement in the hydrogen bond-hydrogen bond and hydrogen bond- $\pi$ - $\pi$  interaction forming cooperative systems by the positively charged species. In the case of cation- $\pi$ - $\pi$  complexes, the mutual influence of the cation- $\pi$  and  $\pi$ - $\pi$  interaction leads to a strong cooperative effect where the strength of  $\pi$ - $\pi$  interaction increases notably in the presence of cation- $\pi$  and vice-versa. Individually, these noncovalent interactions are somehow weak but become substantially stronger and become even comparable to moderately strong covalent bonds due to the cooperative effects.

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# **Machine Learning Metastable Conformations of Biomolecules**

**Jagannath Mondal**

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The multi-dimensional ensemble of biomolecules is fuzzy and stochastic in nature. Routine analysis of atomistically detailed dynamical simulation trajectories often turns into a futile exercise due to complexity associated with biomacromolecules. In this presentation I will describe our group's effort in identifying distinct conformational sub-ensembles of biomolecules using machine learning. In particular we will show how artificial neural-network based dimension reduction can be harnessed to provide optimal state-space decomposition of conformational space of biomolecules. Special application will also be demonstrated in resolving protein-ligand binding pathways and protein conformational plasticity via combination of supervised and unsupervised machine learning. The seminar will conclude by charting future direction on how to predict new trajectories via machine learning.



# Vibrational strong coupling and intramolecular vibrational energy flow : A toy model

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Recent experiments [1] show that the rates, and even mechanisms, of reactions carried out in optical cavities can be modulated in interesting ways. This marriage between cavity quantum electrodynamics and chemistry has led to considerable excitement and raised our hope of achieving the “holy grail” of mode specific chemistry. However, despite an avalanche of activity, a convincing theoretical explanation still eludes us [2]. In this talk I will present our recent effort to understand the issues involved using a simple toy model — a diatomic molecule undergoing dissociation in a single mode Fabry-Perót cavity. Our results [3] indicate that changes in the nature of the molecule-cavity vibrational energy flow can significantly influence the dissociation probability. In turn, such modulations of the dissociation dynamics arise from a complex interplay between the nature of the initial state, vibrational anharmonicity, and form of the dipole function.

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# Pyridinic Nitrogen-Doped Graphene as an Efficient Sensor for SO<sub>2</sub> Detection: A Computational Perspective

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Over the past few decades, global air pollution has become a significant health and environmental concern. Sulfur dioxide (SO<sub>2</sub>) is one of the major pollutants emitted by the increased burning of sulfur-containing fossil fuels in cars, factories, power plants, etc. [1]. Hence, it is necessary to create a reliable gas sensor that is not only highly effective but also very efficient in detecting SO<sub>2</sub>. Many 2D materials have been shown to have good SO<sub>2</sub> sensing potential. However, some inherent disadvantages hinder their practical implementation as efficient gas sensors [1]. Thus, exploring high-performance sensors that can detect SO<sub>2</sub> is of utmost importance. In this study, we investigated the SO<sub>2</sub> sensing potential of pyridinic nitrogen-doped graphene (PDG) containing one, two, or three doped nitrogen atoms, designated psvn1, psvn2, and psvn3, respectively [2]. The structural and thermal stability of the systems were investigated by formation energies, cohesive energies, and ab initio molecular dynamics (AIMD) calculations. We thoroughly evaluated the stable adsorption configuration, charge transfer analysis, and electronic features of the adsorbed systems, including a change in the band gap, work function, and density of states within the framework of spin-polarized density functional theory (DFT), including the van der Waals correction. Results from our calculations show substantial binding of SO<sub>2</sub> with PDG systems and advocate multi-time reusability of the sensor [3]. Additionally, the impact of the typical environmental composites, including CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and Humidity (H<sub>2</sub>O) on PDG was also investigated, revealing the environmental selectivity and sensitivity of pyridinic nitrogen-doped graphene towards SO<sub>2</sub> [3].

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# Theoretical Investigation of Dissociation *versus* Intramolecular Rearrangements in Aminohydroxymethylene

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Aminohydroxymethylene ( $\text{H}_2\text{N}-\text{C}^{\cdot}-\text{OH}$ ) is the simplest aminooxycarbene which is a heteroatom stabilized carbene. This highly reactive molecule was prepared in an Ar matrix in a recent experimental work. Unimolecular reactivity of this astrochemically important molecule was investigated and only fragmentations were identified contrary to the observations of both fragmentations and intramolecular rearrangements in other hydroxycarbenes. These rearrangement reactions form the corresponding imine and carbonyl compounds. In the present work, direct chemical dynamics simulations of unimolecular chemistry of aminohydroxymethylene were performed in the gas phase to study atomic level dissociation mechanisms. Classical trajectories were generated *on-the-fly* using potentials and gradients computed at the density functional B3LYP/6-31+G\* level of electronic structure theory. Simulation results showed that intramolecular rearrangements accompany fragmentations during the unimolecular decay process of aminohydroxymethylene. However, the average lifetime of the intermediate isomers were found to be only few picoseconds which might not have been long enough for detection in the experiments.

# Role of redox-active low-barrier H-bond in proton-coupled electron transfer reactions

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Low-barrier H-bonds form when the  $pK_a$  values of the H-bond donor and acceptor moieties are nearly equal. Redox potential ( $E_m$ ) values along two redox-active low-barrier H-bonds in the water-oxidizing enzyme photosystem II (PSII) have been calculated using a quantum mechanical/molecular mechanical approach. The low-barrier H-bond between D1-Tyr161 (TyrZ) and D1-His190 is located in the middle of the electron transfer pathway, when the proton is at D1-His190,  $E_m(\text{TyrZ})$  is the lowest and can serve as an electron donor to the oxidized chlorophyll  $\text{PD1}^{\bullet+}$ .  $E_m(\text{TyrZ})$  and  $E_m(\text{D1-His190})$  are equal and the TyrZ...D1-His190 pair serves as an electron acceptor to  $\text{Mn4CaO5}$  when the proton is at TyrZ. The low-barrier H-bond between D1-His215 and plastoquinone QB located at the terminus of the electron transfer pathway, the driving force of electron transfer and electronic coupling between QA and QB are maximized when the proton arrives at QB. It seems likely that local proton transfer along redox-active low-barrier H-bonds can alter the driving force or electronic coupling for electron transfer.

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## AI/ML methods in chemical dynamics

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Artificial intelligence (AI) and machine learning (ML) methods have touched practically all aspects of our life. Their utility ranges from separating different quality agricultural produce to facial recognition to guiding us through most steps in our day-to-day life. In this talk, we demonstrate the utility of the artificial neural network (ANN) method in fitting multi-dimensional potential energy surfaces and point out the potential applications to predicting and analyzing dynamical observables. Although the regression methods seem to be successful in fitting potential energy surfaces using limited ab initio data, the ANN method yields accurate fits of surfaces when enough number of ab initio points on the potential energy surface become available. The possibility of utilizing the ANN method for fitting excitation function data is pointed out and the implications are discussed.

# **Expectation Maximized Molecular Dynamics: Rapid Estimation of Free Energy Barriers in Biomolecular Energy Landscapes**

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Modern-day efforts towards uncovering emergent protein structure-function relationships incorporate methods that leverage data from both experiments and computational studies. A large part of such efforts is devoted to capturing the infrequent transitions that control complex biophysical processes over long timescales. Such efforts, however, are often challenged by the lack of system-specific slow modes, and by lack of access to high-end computational resources. This talk will present our recently proposed algorithm termed 'Expectation Maximized Molecular Dynamics' (EMMD) that incorporates a statistical inference-based approach in estimating free energy barriers related to rate-limiting transitions. The method bypasses conventional thermodynamic sampling by connecting metastable basins using Bayesian likelihood maximization. A tunable self-feedback protocol is incorporated to prevent unnecessary sampling that does not effectively contribute to the underlying distributions. The algorithm demonstrates significant efficiency in predicting experimentally known free energy barriers in putative biomolecular systems, including a putative kinase and an IDP.

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# **Electronic dynamics of molecules in a strong high intensity field: the beginnings of ABELDYN**

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The implementation of a  $(t, t')$  formalism for the real-time Hartree-Fock electronic dynamics of molecules at fixed geometries, in high-intensity laser fields will be given in this talk. The algorithm stems from a block diagonalization of an effective Fock matrix of extended temporal dimensions, resulting from a time dependent Fourier basis. The numerical implementation involves a Trotter factorization splitting out the laser frequency-dependent term. This has an algorithmic convenience of incorporating the explicit time dependence of the two-particle interaction in a non-local functional form. The novelty of the method lies in the ease of incorporation of this artificial memory in the dynamics by encoding the explicit time-dependence of the mean-field two-particle operator into the effective Hamiltonian. This is done by learning from the frequency-dependent Fourier components of the charge-density bond-order matrix, extracted via a windowed Fourier transform. In comparison to an instantaneous representation of the time-dependence of the two-particle operator, the new method results in a backward time propagation with minimal error for large time steps. The algorithm is presented together with several test cases dihydrogen, water, acetylene and ethylene in a high intensity laser pulse, using standard Gaussian basis sets, with the calculation of several time dependent properties.



# Global Optimization of Atomic Clusters: A Soft Computing Perspective

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Geometry optimization of chemical systems like atomic clusters becomes a daunting task because of the large size of the search space and the possibility of getting stuck in a local minimum on the potential energy surface.

Determination of global minimum energy structure needs the gradient and Hessian matrices to be calculated at each stage and with no guarantee of locating the global minimum. Various soft computing techniques may be made use of, bypassing this hassle. We present methods like particle swarm optimization combined with density functional theory, atom centered density matrix propagation and convolutional neural network and also a firefly algorithm for global optimization of atomic clusters. We highlight their efficiency and accuracy by considering different metallic and non-metallic clusters as prototype examples. A comparison is made regarding the efficacy of these algorithms vis-à-vis other standard machine learning methods like simulated annealing, basin hopping, artificial bee colony and Bonobo algorithms.

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# A mechanistic understanding of biofilm morphogenesis

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Most bacteria in the natural environment self-organize into collective phases such as cell clusters, swarms, patterned colonies, or biofilms. The occurrence of different phases and their coexistence is governed by several intrinsic and extrinsic factors such as the growth, motion, and physicochemical interactions. Hence, it is crucial to predict the conditions under which a collective phase emerges due to the individual-level interactions. In this talk, we will be discussing a particle-based biophysical model of bacterial cells and self-secreted extracellular polymeric substances (EPS) to decipher the interplay of growth, motility-mediated dispersal, and mechanical interactions during microcolony morphogenesis. We will show that depending upon the heterogeneous production and physicochemical properties of EPS, the microcolony dynamics and architecture significantly varies. In particular, in sticky EPS, microcolony shows the coexistence of both motile and sessile aggregates rendering a transition towards biofilm formation. We identified that the interplay of differential dispersion and the mechanical interactions among the components of the colony determines the fate of the colony morphology. Our results provide a significant understanding of the mechano-self-regulation during biofilm morphogenesis and open up possibilities of designing experiments to test the predictions.

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# Metal-Metal (MM) Bond Lengths Related to MM Bond Orders in Binuclear 3d Metal Complexes: Experimental and Computational Results

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Metal-metal (MM) bond lengths in binuclear complexes of the first row 3d metals titanium to zinc are here related to the formal bond orders for the MM bonds. MM bond lengths have been compiled from experimental and computational (DFT) results on a large number of binuclear metal complexes [1,2,3]. Approaches for obtaining MM bond orders include the analysis of metal-metal MOs and electron counting by various methods, which are illustrated for some sample complexes. The large database of experimental and DFT-derived MM bond lengths for hundreds of complexes is categorized according to the metal concerned and the MM bond order. Distinct ranges for MM bond lengths emerge for single, double, triple, quadruple, and quintuple MM bonds in homobinuclear complexes of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn. It is found that complexes containing carbonyl ligands yield longer MM bond length ranges than their non-carbonyl counterparts, attributed to electron transfer from metal MOs to ligand virtual MOs. Change in the metal across the row (Ti to Zn) shows trends for single, double, triple, and quadruple MM bonds which are related to the metal atomic radii. The compilation of experimental and computational results leads to the proposal of “best” estimates for MM bond lengths of all types (Ti-Ti through Zn-Zn, single through quintuple).

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# Tuned range-separated density functionals for accurate ground and excited state properties

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Recently, the range-separated density functionals have gained popularity due to their ability to reproduce some ground and excited state properties that conventional density functionals could not correctly predict. For instance, the correct asymptotic form of the range-separated density functionals diminishes delocalization error and accurately reproduces orbital energies. The range separation parameter is a critical parameter in predicting such properties. There are different approaches to determining the range-separation parameter. Some of our recent works in this regard will be presented. The performance of range-separated density functionals in the presence of the implicit solvent models and external electric field will also be addressed. A comparison will be made between our tuning methods based on the Electron Localisation Function and long-range Hartree-Fock solvent tuning that reduces the computational effort with the IP tuning-based methods. Finally, the application of such methods in the accurate computation of orbital energies and excited state properties will be presented.

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# Development of a shallow-depth dual-unitary ansatz for near-term quantum computers

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In this talk, I will briefly outline a novel many-body approach to accurately incorporate high-rank correlation effects via a low rank parametrization of the wavefunction ansatz. With a few physically motivated approximations of an effective Hamiltonian that otherwise contains exponentially large number of terms, we propose a number of variants that strike the right balance between accuracy and computational affordability<sup>1,2</sup>. Motivated by these developments of the many-body theory in the context of classical computing, I will propose a unitarized version of the same that allows us to simulate strongly correlated molecular systems with the help of the hybrid quantum-classical variational quantum eigensolver algorithm with a reasonably shallow depth quantum circuit. I will demonstrate that the proposed unitary forms the basis of a *partially disentangled* wavefunction ansatz in which arbitrarily high rank excitations are implicitly included through the appearance of a series of nested commutators<sup>3</sup>. Based on the ideas of energy sorting and commutativity screening, I will finally introduce a dynamic version of the proposed ansatz that requires minimal number of parameters and quantum gates to accurately simulate strongly correlated electronic systems and thus can be considered as a potential candidate for realization in the Noisy Intermediate Scale Quantum (NISQ) devices.

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# Activity driven single probe dynamics in crowded media

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A biological cell is a system of mesoscopic length scale that is truly out of equilibrium. This non-equilibrium nature of the dynamics arises due to the processes happening inside that do not follow detailed balance, being fuelled by the energy released owing to chemical reactions, such as ATP hydrolysis. In other words, the constituents of biological cells are "active"[1]. Apart from its constituents being active, the cell is highly packed or crowded. Therefore, dynamics of a biomolecule inside a cell can be referred to as the dynamics of an active agent or a probe in a crowded environment. One interesting aspect of the dynamics of these probes is their persistent motion. More recently, experiments have also been performed, where the active biomolecules are replaced by synthetic probes, such as self-propelled colloids or polymer chains [2-3]. It is obvious that the processes occurring inside a cell or in a biomimetic environment cannot be modelled in the framework of equilibrium statistical mechanics. In this talk, I plan to discuss our recent attempts to model the dynamics of an active probe in a crowded medium (passive). Our analytically solvable statistical mechanical models [4-5] and model computer simulations [6-10] reveal interesting aspects of the probe dynamics, sometimes counter-intuitive. Most importantly, our theoretical predictions go hand in hand with experiments [2] and some of our predictions have been verified later by experiments [3, 11].

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# Deep Eutectics, and Azeotropes: Some of Our Recent Results

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We were fascinated by the dielectric properties of some ionic amide deep eutectics reported by several researchers in nineties.<sup>1-3</sup> These data were collected via dielectric relaxation (DR) measurements in the Hz – MHz frequency window and indicated *colossal* static dielectric constant ( $\epsilon_0 \sim 10^6$ ) with DR time constant in the microsecond – millisecond range. Our DR measurements of some of these ionic DESs in the MHz – GHz frequency window, in contrast, indicated ion dependent decrease of the  $\epsilon_0$  of the host amide component.<sup>4-7</sup> These contrasting results triggered our simulation investigation employing the available classical coarse-grained model interaction potentials. These simulation studies<sup>8</sup> indicated dielectric decrement due to partial randomization of the molecular dipoles of the host amides, instigated by the electrolyte-induced severe damage of the amide H-bond network. The contribution from the dynamics (dynamic dielectric decrement) to this reduction was found to be relatively very small.

Azeotropes referred to those mixture compositions at which multicomponent systems at those compositions cannot not be separated any further from each other through distillation and continues to boil as a ‘single’ system.<sup>9</sup> A celebrated example is ethanol + water system at 95.5% ethanol which boils as a single entity at 351 K. Our picosecond-resolved dynamic anisotropy measurements indicated anomalous composition dependence of the average rotation times of a dissolved neutral dipolar solute at this temperature. Steady state fluorescence shifts also indicated such a behaviour.<sup>10</sup> Our simulations employing SPC/E water and TraPPE-UA ethanol<sup>11</sup> showed formation of co-cluster with overlapping diffusion coefficient distributions at the azeotropic compositions. Also, evidences favouring the spatially correlated particle movements were registered.<sup>12</sup> Some of the above results would be presented and discussed in this lecture.

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# Nuclear quantum effects in gas-phase 2- fluoroethanol

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2-Fluoroethanol (2FE) has several distinct minima as a function of the CCOH and OCCF torsional angles that are connected via barriers of only a few kcal/mol. This molecule and its cousins ethylene glycol and 2-aminoethanol, which show similar features in torsional space, have been extensively investigated in the literature.<sup>1-6</sup> In this work, we have used path integral simulations to study the manifestation of nuclear quantum effects (NQE) in 2FE. We have developed a full dimensional anharmonic potential surface for 2FE in the spirit of the reaction surface approach.<sup>7,8</sup> In a similar manner, a model dipole moment surface has also been obtained. The model potential has been used to carry out path integral molecular dynamics<sup>9-11</sup> and thermostatted ring polymer molecular dynamics<sup>12,13</sup> simulations in order to analyse the effect of NQE on structural variables as well as infrared spectra. Using enhanced sampling techniques like umbrella sampling and well-tempered metadynamics<sup>14</sup> simulations, we have compared free energy landscapes in torsional space without and with the inclusion of quantum effects. In this talk, our findings from the simulations would be presented.

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# Electronic Structure and Dynamics in a Strong Magnetic Field

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Strong magnetic fields which compete with the Coulombic forces in atoms and molecules affect structure, energetics, degeneracies, symmetries and dynamics of both the electrons and the nuclei. The complex and coupled nature of the interactions make it difficult to intuitively understand the response of the system to the external field. A direct non-perturbative solution of the system and field is thus undertaken. The findings from the electronic structure study are presented and preliminary investigations of the nuclear dynamics in the strong magnetic field and related challenges are discussed.

# Role of Nonadiabatic Coupling on Photoelectron Spectra, Reactive Scattering Processes and Phase Transition of Solids

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The first principle based Beyond Born-Oppenheimer (BBO) theory [1-3] is presented for the construction of highly accurate potentially coupled matrix (diabatic) to study multi-mode multi-surface photoelectron spectra of  $\text{NO}_3^-$  and  $1,3,5\text{-C}_6\text{H}_6\text{F}_3^+$  [4-5], reactive scattering processes of  $\text{H}_3^+$  and  $\text{F} + \text{H}_2$  [6-9], and phase transition phenomena of orthorhombic manganites [10]. Jahn-Teller (JT) and Renner-Teller (RT) types of conical intersections (CIs) along with Pseudo Jahn-Teller (PJT) interactions in those systems and semi-circular CI seam (rather than a CI point) between the ground and excited state are the new interesting observations. [4-6, 9] The theoretically calculated spectra of the titled systems show good peak by peak correspondence with the experimental and other theoretical findings. [4-5] Reaction attributes (reaction probabilities, cross-sections and/or rateconstants) of  $\text{D}^+\text{+H}_2$  and  $\text{H+H}_2^+$  processes obtained from scattering dynamics over global diabatic surfaces of  $\text{H}_3^+$  system [7,8] in hyperspherical coordinates for total angular momentum zero and non-zero situations exhibit good accord with the experimentally measured ones. On the other hand, reactive scattering calculation over the diabatic surfaces of  $\text{F+H}_2$  system (incorporating spin-orbit couplings) is quite encouraging. Optical spectra of  $\text{REMnO}_3$  ( $\text{RE} = \text{La, Pr, Nd, Sm, Eu, Gd, Tb, Dy}$ ) shows anomalous temperature dependence around the Neel temperature. This behaviour could be due to Jahn-Teller effect both in ground and excited state. Such observations have been investigated [10,11] theoretically to interpret the experimental spectra due to the excitations of the quantum rotors.

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# Dynamic Heterogeneity and Non-Gaussian Diffusion of Lipids in Laterally Heterogeneous Raft-like Membrane

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Dynamic heterogeneity is reported for diffusion in living cell membranes and raft-mimetic membrane in nanometer-microsecond spatio-temporal resolution.<sup>1-3</sup> This is sometime associated with the slow-active remodeling of the underlying cortical actin network<sup>1</sup> and sometimes with the laterally heterogeneous nature of raft-mimetic liquid-ordered domain.<sup>2-3</sup> The experimental spatio-temporal resolution is usually lower in order to unequivocally determine the fundamental origin of the observed dynamic heterogeneity. Through molecular dynamics simulation, we have observed the heterogeneous dynamics and non-Gaussian diffusion of the saturated lipids forming the raft-like liquid-ordered (Lo) domain up to a sufficiently long time (a few microseconds), even though the mean square displacement becomes Fickian. This Fickian-yet-Non-Gaussian diffusion (FnGD) is observed for the raft forming saturated lipids only when both the Lo and liquid-disordered (Ld) phases coexist. Interestingly, the anomalous diffusion behavior for the lipids is only observed in the Lo phase boundary and not in the central region of the Lo domain. Further studies using the Translational Jump-Diffusion (TJD) approach<sup>4-6</sup> showed that individual jump-cage-jump motions lead to the group of fast and slow particles that eventually contribute to non-Gaussian diffusion. Therefore, this study suggests that the experimentally observed dynamic heterogeneity may be due to the presence of a translational jump of lipids in the laterally heterogeneous raft-mimetic domain in the real cell membrane.

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# Computer Simulation Studies on the pH Dependent Structure and Dynamics of Proteins

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Variation of pH is one of the most versatile tools used in biophysical sciences to monitor the structure and function of a protein. However, computer simulation studies at constant pH encounter several technical difficulties. In this lecture, some recent developments in constant pH molecular dynamics (CpHMD) will be discussed. Application of CpHMD simulation will be demonstrated by considering two isozymes of human carbonic anhydrase (HCA) that are responsible for the pH control and sensing in our body and constitute key components in the central pH paradigm connected to cancer therapeutics.

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# Molecular Thermodynamics of Biomolecular Signaling and Allosteric Inhibitors for Protein-Protein Interaction

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While most of the drugs available in the market are competitive inhibitors, there is a rapidly growing interest in development of allosteric drugs, particularly to inhibit protein-protein interactions (PPI) with large interaction surface area. However, it remains a challenge to identify a distal binding site that would be allosterically linked to the canonical ligand/substrate binding site. Such allosteric hotspots are often cryptic sites with a less populated excited conformational state of the protein. In this work we present a general strategy based on thermodynamic arguments to identify such distal cryptic sites as potential targets for allosteric drugs. We demonstrate this on allosterically modulating the PPI between PCSK9 (proprotein convertase subtilisin/Kexin type 9) and LDLR (low density lipoprotein receptor), which is a challenging and therapeutically important target towards treatment of hypercholesterolemia (elevated plasma level of LDL).

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# Interaction of spiral rotors : Synchronization and Chimera

**Sumana Dutta, Hrishikesh Kalita, and Parvej Khan**

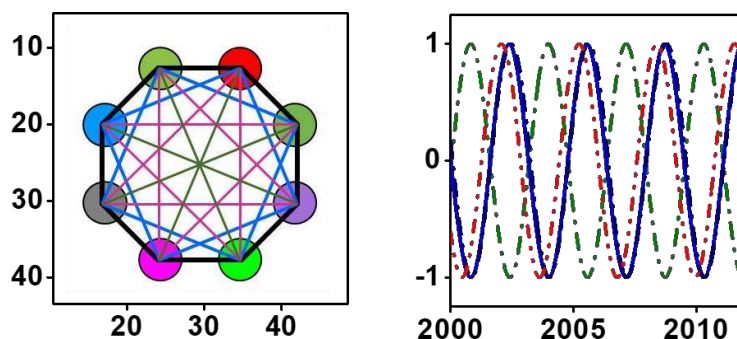
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Rotors of reaction and diffusion are phase singularities that give rise to spiral waves of chemical activity, which are very similar to spatiotemporal patterns observed across several excitable media. In numerical simulations based on a reaction-diffusion model we explore the possible interactions of multiple spiral rotors. When the cores of two spirals come very close to each other, they could either repel, attract, or remain stationary, depending on their relative chirality, phase and the distance separating them. Multiple pairs of spiral waves, in close vicinity, could alter the paths of the individual rotors.

Further, if these spirals are pinned to unexcitable obstacles, it enables us to modify their frequencies and restrain their drift. These spirals now act as diffusion-coupled rotors that can spontaneously synchronize, giving rise to a plethora of intriguing dynamics. We show that two counter-rotating spiral rotors, pinned to circular heterogeneities, can synchronize, in frequency and phase. The nature of the phase synchronization varies depending on the difference in their characteristic frequencies. We observe in-phase and out-of-phase synchronization, lag synchronization and phase-resetting. Definite signatures of the intriguing chimera dynamics, exhibiting simultaneous coherence and incoherence, have also been identified in a network of globally coupled spiral rotors.

Our theoretical predictions have been realized and demonstrated through experiments with the Belousov-Zhabotinsky reaction system.



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# Nonadiabatic Chemical Dynamics

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Interaction of electronic and nuclear motion has emerged as an essential ingredient to understand chemistry and physics at a molecular level [1]. Such interactions lead to a breakdown of the celebrated Born-Oppenheimer approximation [2] in molecular quantum chemistry and drive the molecular processes through numerous complex paths. It generally leads to conical intersections [3] of potential energy surfaces. In this presentation I shall discuss on the elements of nonadiabatic chemical dynamics. Representative results illustrating the examples studied by us on reactive molecular processes during the past years will be discussed.

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# Computational Modeling of Homogeneous and Heterogeneous Catalytic Reactions

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I shall discuss computational modeling of (1) a few homogeneous catalytic processes, namely, hydrogen activation and hydrogenation of unsaturated systems by Frustrated Lewis Pairs (FLPs) and (2) 3 fluophosphates and 1 pyrophosphate showing electrochemical bifunctional (both oxygen evolution and reduction) reactions. For the 1<sup>st</sup> case, we have worked on a number FLPs using a host of Lewis acids, from Boron to Sn<sup>+</sup> to neutral group 14 elements [1]. For the 2<sup>nd</sup> case, we have collaborated with an experimental group to find bifunctional electrocatalytic behavior in a number of pyro and fluoro-phosphates [2]. In each cases, stability of the hosts, surface types, selectivity, effects of solvents, detail mechanism, various reaction intermediates, d-orbital centre, overpotential values and many other quantities relevant for the robust prediction and explanation of experimental and computational data would be discussed in detail.

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# Quantum Nuclear Dynamics

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In our recent work [1], we have reported the rotational-state resolved integral cross sections and differential cross sections for  $^{18}\text{O} + ^{16}\text{O}^{16}\text{O} (v=0, j=1) \rightarrow ^{18}\text{O}^{16}\text{O} (v'=0, j') + ^{16}\text{O}$  (say 8+66 reaction) and  $^{16}\text{O} + ^{18}\text{O}^{18}\text{O} (v=0, j=1) \rightarrow ^{18}\text{O}^{16}\text{O} (v'=0, j') + ^{18}\text{O}$  (say 6+88 reaction) reactions obtained using time-independent quantum mechanical method on an *ab initio* potential energy surface of ozone [2]. Results infer that both the reactions started off with an indirect insertion mechanism at low collision energies and shifted to direct abstraction reaction mechanism at higher collision energies. We have also noticed the dominance of the 8 + 66 reaction over the 6 + 88 reaction. Qualitative differences are inferior in both these reactions, however, differences in magnitude are inevitable owing to the difference in mass distribution. Finally, a comparison with experimental studies reveals a relatively good agreement for sideways scattering, while some discrepancies remain for the forward and backward directions, essentially due to the highly sensitive nature of the forward and backward peaks to the collision energy. We have performed similar studies on 6+66 and 8+88 reactions [3-6].

Our recent works include calculation of initial state-selected dynamics of the  $\text{N}(^2\text{D}) + \text{N}_2(\text{X}^1\Sigma) \rightarrow \text{N}_2(\text{X}^1\Sigma) + \text{N}(^2\text{D})$  exchange reaction on its electronic ground doublet state  $\text{N}_3(1^2\text{A}')$  potential energy surface (PES) by time-dependent quantum mechanics (TDQM) and quasi-classical trajectory (QCT) methods [7]. Dynamical attributes such as total reaction probabilities, state-selected integral cross sections, and initial state-selected rate constants have been calculated. The results infer the presence of metastable quasi-bound complexes in the collision process is confirmed by substantial oscillatory structures in the reaction probability curves. In addition we observe that the reagent rotational excitation increases the reactivity.

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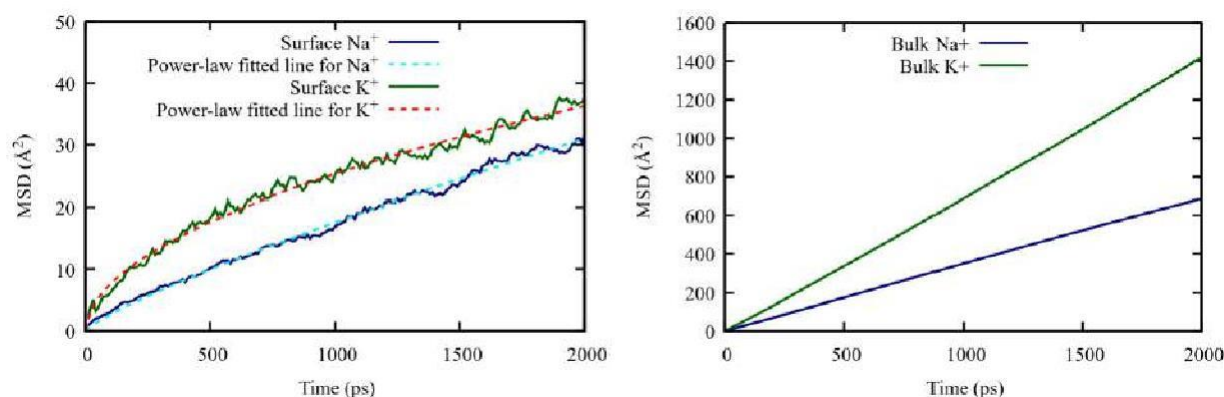
# Interaction and dynamics of ions at membrane surface

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In biological systems, interaction and transportation of ions are directly involved in several activities, such as the transportation of nutrients, ATP synthesis, controlling the electrolyte levels in the blood, and so on<sup>1,2</sup>. Ion diffusion parallel to the membrane surface could have an important role in the propagation of electrical signals in nerve and muscle cells. The present work investigates the interaction and lateral diffusion of ions on the surface of the lipid bilayer using MD simulations. The investigation indicates that the ions can form a charge double layer at the membrane-water interface, having a positive charge inside and a negative charge outside. This phenomenon can be explained in terms of the ion-membrane interaction, as the cations prefer to stay next to the membrane while the counter anion remains in the bulk. Similar to ions, the water molecules near the membrane also form a charge double layer due to their preferred orientation. The current study reveals that a single cation can bind with more than one lipid head group at a time, which can sometimes go up to three different lipid residues. During this interaction, the coordination number of the cation is compensated by its corresponding hydration layer. The investigation also suggests that the bounded cation can hop at the membrane surface by switching its interacting lipid residue. The estimated MSD for the bounded  $K^+$  and  $Na^+$  with time shows a sub-diffusive nature up to an initial 2 ns with an  $\alpha \approx 0.52$ , and  $\alpha \approx 0.82$ , respectively. In the contrast, for cations in the bulk, no such anomaly has been observed. The lateral diffusion coefficient at the XY plane (DXY) for the bounded cation was found to be almost ~30-40 times lower than that of the bulk. In the case of anion, no such interactions with the membrane surface have been observed. Consequently, the value of DXY for anion associated with the membrane system is found to be very close to the pure ion solution.



<sup>1</sup>Friedman, R. Membrane-ion interactions. *J. Membr. Biol.* 2018, 251, 453–460.

<sup>2</sup> Cevc, G. *Phospholipids Handbook* (1st ed.). CRC Press. 1993, 511-552.

# **Abstract for Posters**

(Arranged in Alphabetical Order)

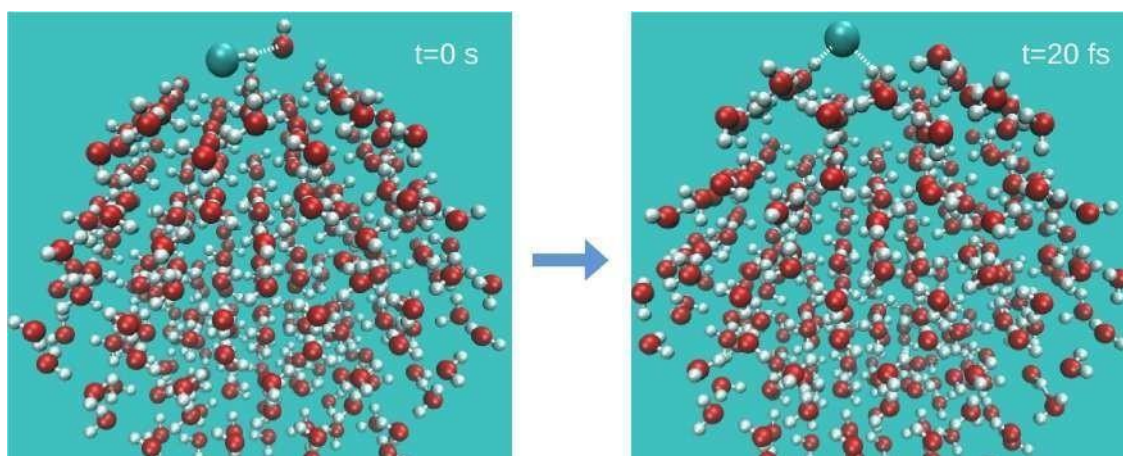
# OH + HCl Reaction on the Surface of Ice: An Ab Initio Molecular Dynamics Study

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The OH + HCl reaction is considered as the one of the important source of Cl radical in the troposphere, which involve in the catalytic cycle of ozone depletion.<sup>1</sup> Further, it is known that OH + HCl reaction becomes ten times faster at water surface as compared to bare reaction.<sup>2</sup> However, a large number of water molecules exist in the form of the ice in the upper tropospheric region. It is known that the ice surface plays a key role in deciding the fate of many important atmospheric reactions. Therefore, we have investigated the OH + HCl reaction on the surface of ice using Born–Oppenheimer molecular dynamics (BOMD) simulation. The present work revealed that the OH + HCl reaction becomes  $\sim 1$  order of magnitude faster on the ice surface compared to the bare reaction. The BOMD simulation also indicates that the Cl radical formed on the ice surface through the title reaction can form two hydrogen bonds at a time with the water molecules present on the ice surface; hence, the Cl radical cannot escape from the ice surface easily.



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# Unravelling Mechanistic Details of Ru-Bis(pyridyl)borate Complex Catalyst for Dehydrogenation of Ammonia-Borane

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Ru-Bis(pyridyl)borate complex (CAT) is an efficient catalyst for ammonia-borane (AB) dehydrogenation. Although the mechanistic pathway of this catalyst has been theoretically investigated previously, the gap between the experimental findings and the computational results could not be bridged thus far. In our study, using density functional theory calculations, we elucidate the mechanism of AB dehydrogenation of CAT at a variable degree of ligand hydrogenation. Our results confirm that the acetonitrile ligands get reduced in presence of AB and remain hydrogenated. Moreover, in line with experiments, we find that AB dehydrogenation on CAT proceeds via a concerted mechanism (with the free-energy energetic span between 25.4-

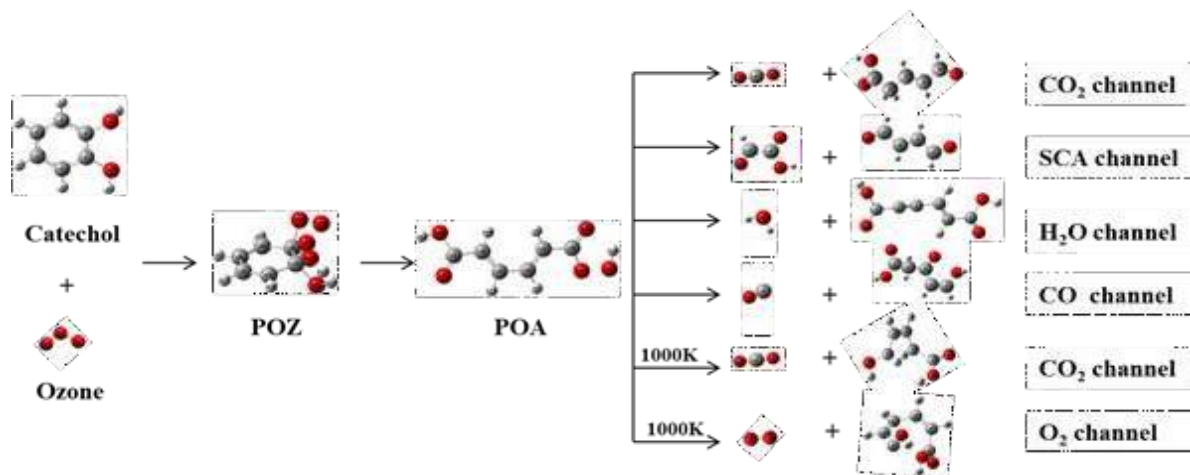
32.5 kcal/mol). We find that the ligand reduction alters the electronic structure and activity of CAT and the highest activity of the catalyst is expected at the 5th degree of hydrogenation of ligands with an energetic span of 25.4 kcal/mol. Additionally, the mechanism for the removal of molecular H<sub>2</sub> from the catalysts also alters with degrees of ligand hydrogenation. Furthermore, our results show that optimal H<sub>2</sub> binding free-energy calculations can be used as a descriptor to identify the most active sites. Finally, this work demonstrates that ligand reduction improves the activity of the catalyst. These results highlight the importance of ligand hydrogenation in probing the activity and operating mechanism of the Ru-Bis(pyridyl)borate complexes for AB dehydrogenation. Furthermore, we identify a plausible structure of the dimeric catalyst and rationalized experimental observation that the deactivation chemistry of this catalyst is different from the Shvo's catalyst.

Keywords: H<sub>2</sub> storage; Ammonia-Borane; Dehydrogenation; Catalysis; Density Functional Theory

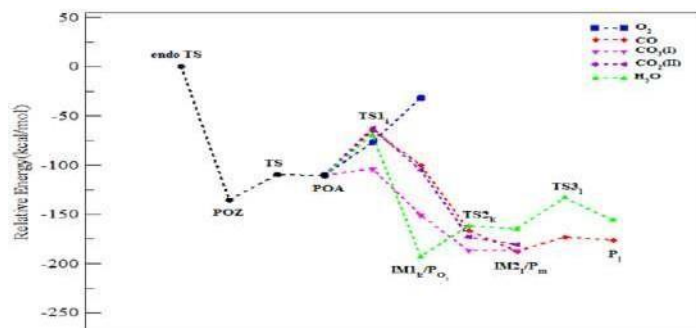
# Post Transition State Dynamics on the Ozonolysis of Catechol and the Effect of Solvation

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On-the-fly dynamics simulations for the reaction of catechol + O<sub>3</sub> are performed for lower temperatures of 400 and 500 K<sup>1</sup> as well as higher temperatures of 800, 1000 and 1500 K. To see the effect of the surrounding atmosphere, the reaction was studied in presence of a 200 molecule N<sub>2</sub> bath at 20 and 324 kg/m<sup>3</sup> densities. PM7 semiempirical method is employed for calculating the potential energy gradient needed for integrating the Hamilton's equations of motion. This semiempirical method provides excellent agreement in terms of energy and geometry of the TSs as well as minimum energy states of the system with respect to B3LYP/6-311+G(2df,2p) calculated results. In the dynamics, first, a peroxyacid is formed which further dissociates to different fragments. Four major channels forming CO, CO<sub>2</sub>, H<sub>2</sub>O and small carboxylic acid (SCA) fragments are seen in this reaction, along with an O<sub>2</sub> channel which is observed only in the higher temperature simulations. Rates of each of the channels and overall unimolecular reaction are calculated for all the cases and the results of the gas phase and condensed phase simulations are compared.



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# Stability of Escherichia coli Cell Membrane in Adverse Temperatures: The Role of Lipids having Cyclopropane Fatty Acids

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Escherichia coli (E. coli) is a rod-shaped bacterium commonly found in the lower intestine of the warm-blooded animals. For the past decades E. coli had been taken as the model organism to study the bacterial membrane lipid composition, due to its rapid growth and ease in laboratory culture. In the present work we have performed the molecular dynamics (MD) simulation of a model E. coli membrane composed of 14 different lipids both in coarse-grained (CG) and all-atom (AA) resolution<sup>1</sup>. It contains three major lipid types- phosphatidylethanolamines, phosphatidylglycerols, and cardiolipins. An earlier study has shown that the E. coli membrane does not freeze even at very low temperature. It is seen, the cyclopropane fatty acids are widely distributed in bacterial membrane including E. coli and their concentration increases in hostile environment<sup>2</sup>. Here, we have investigated the effect of cyclopropane ring over double- as well as single-bonds. We have simulated the E. coli membrane (native) consisting of cyclopropane rings and the modified E. coli membrane where all the cyclopropane rings are replaced by either C=C double or C-C single-bonds. It has been observed that for the single-bond system the membrane undergoes fluid-to-gel phase transition at lower temperature, while for the double-bond system a partial phase transition occurs. Very interestingly, the native membrane does not undergo any phase transition even at 250 K. In-depth studies have shown that the cyclopropane rings are much more rigid towards ordering of the lipids at low temperature and thereby prevent the local ordering of the lipid membrane. We suggest that is due to higher strain in cyclopropane ring than in double-bond. However, at high temperature there is barely any difference in structural properties among the three types of membrane. Therefore, we conclude that the increased abundance of cyclopropane rings in the lipid acyl chains of the E. coli membrane protect the cell membrane.

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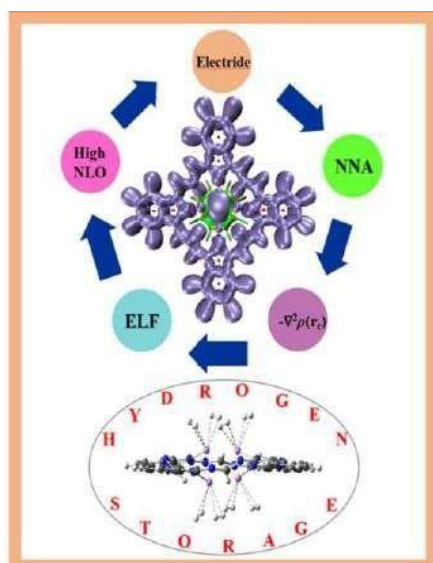


# Li<sub>4</sub>EPc: A Metallo-Organic Electride Comprising Metal-Nitrogen Bonds

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An *in silico* design of a new metallo-organic electride, containing metal-nitrogen bonds, viz., Li<sub>4</sub>EPc, with high non-linear optical properties ( $\beta_{\text{total}} = 6.382 \times 10^4$  au) is presented. Density functional theory based computation has revealed the thermodynamic stability of Li<sub>4</sub><sup>2+</sup> cluster encapsulated in EPc host moiety where EPc is an extended phthalocyanine system. NBO analysis is performed to study the bonding nature of the aforementioned species. We have also performed AIM analysis to confirm the presence of an isolated electron at the interstitial tetrahedral hollow formed by three-dimensional Li<sub>4</sub><sup>2+</sup> cluster attached with EPc ligand. Linear and non-linear optical properties of the designed electride have been analyzed by polarizability ( $\alpha$ ) and first hyperpolarizability calculations ( $\beta_{\text{total}}$ ). Frequency dependent first hyperpolarizability, second harmonic generation (SHG), electro-optic Pockel's effect (EOPE) have also been computed. Furthermore, we report the hydrogen adsorption potential of each Li atom in Li<sub>4</sub>EPc system. Here only physisorption process has been considered. The result shows that two H<sub>2</sub> molecules can be adsorbed per lithium atom at most leading to a total of 8 H<sub>2</sub> molecules adsorbed by Li<sub>4</sub><sup>2+</sup> cluster through physisorption process only. This work provides a new insight into designing a stable metallo-organic electride (Li<sub>4</sub>EPc) with high NLO response which also can be used as an efficient hydrogen storage material.



# Role of methylxanthines in neurodegenerative diseases: a computational investigation

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Methylxanthines are derived from the purine base xanthine, the nitrogen atom at position 3 carries a methyl group and the nitrogen at 1 and 7 positions carry different moieties. The health benefits of methylxanthines in neurodegenerative diseases are widely discussed. Three naturally occurring purinic alkaloids namely caffeine, theophylline and theobromine fall under the category of most widely consumed alkaloids over the world. The property of caffeine as an inhibitor of amyloid forming peptides is well established both experimentally and computationally.<sup>1</sup> However, a comparative study of the activity of theobromine and theophylline in the inhibition of amyloid forming peptides is obscure. Our molecular docking simulation followed by molecular dynamics simulation of caffeine, theobromine and theophylline with the amyloid beta peptide give useful insight into the interactions pattern of these methylxanthines with the misfold-prone amyloid beta peptide. Our computational results indicate that both theobromine and theophylline are better inhibitors of amyloid beta peptide owing to better hydrogen bond interactions.

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# Unimolecular Dissociation Dynamics of Aromatic Molecules at High Temperature

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Chemical dynamics simulations are performed to study the unimolecular dissociation of C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>H<sub>5</sub>F (Bz-MFB), C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>H<sub>5</sub>Cl (Bz-MCB), C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>H<sub>3</sub>F<sub>3</sub> (Bz-TFB) C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub> (Bz-TCB) complexes at a temperature range of 1000 to 2000 K and the results are compared with that of C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>Cl<sub>6</sub> (Bz-HCB) C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>F<sub>6</sub> (Bz-HFB) at the same simulation temperatures. The simulations are done with very good potential energy parameters which are obtained from the literature. Considering the canonical (TST) model, the unimolecular dissociation rate constant at each temperature is calculated for each of the complexes and fitted to the Arrhenius equation. The activation energies and pre-exponential factors are also calculated. The vibrational modes which are responsible for dissociation are identified by performing normal-mode analysis. Simulations with random excitations of intermolecular and intramolecular vibrational modes of the complexes are also performed. The intramolecular vibrational energy redistribution (IVR) time and the unimolecular dissociation rate constants are calculated from these simulations. The main purpose of this work is to see, by substituting the hydrogen atoms in the one of the aromatic rings of Benzene dimer with one fluorine, three fluorine and one chlorine and three chlorine, how the dissociation rates will be changed and how it can be compared with the Bz-HFB and Bz-HCB complexes.

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# Computational Study of Protein-ligand Interactions by Molecular Docking: Dopamine receptors Binding with dopamine and L-DOPA

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Protein–ligand interactions are essential to nearly all processes occur in living beings. Protein–ligand interaction studies are crucial for understanding the mechanisms of biological regulation and they give a theoretical basis for the design and discovery of new drug targets. Molecular docking is such a structure-based drug design method that simulates the molecular interaction and predicts the binding mode and affinity between receptors and ligands. We analyzed the interactions of protein–ligand by molecular docking. Molecular docking was performed for two different ligands (dopamine and L-DOPA) interacting with four dopamine receptors (D1DR, D2DR, D3DR and D4DR). Here we analyze the pi-pi interactions and hydrogen bonds of protein–ligand complex in the docking region.

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# Controlling Tunneling Oscillation and Quantum Localization in an Asymmetric Double-Well Potential: A Bohmian Perspective

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The quantum dynamics of a proton initially localized in one of the wells of an asymmetric double well potential is studied by using a perturbation which has both spatial and temporal dependencies. Quantum Theory of Motion(QTM) and Time dependent Fourier Grid Hamiltonian methods are incorporated and the phenomena of quantum tunneling and localization are modulated by systematically changing the strength and spatial symmetry of the applied perturbation. As opposed to the Copenhagen interpretation of Quantum Mechanics, the QTM/ Bohmian mechanics provides a causal and deterministic recipe in analyzing the results from the obtained phase spaces. The model used here also includes a mimic of the related experimental situation which is considered as a perturbation to the static double well potential. Analyses of the phase spaces and the corresponding time-profile of tunneling probability reveal the scope towards controlling tunneling oscillations by modulating the parameters of the applied perturbation. Moreover, a study on a stochastic pulsating potential reveals the root to the quantum localization, even in moderate field strength.

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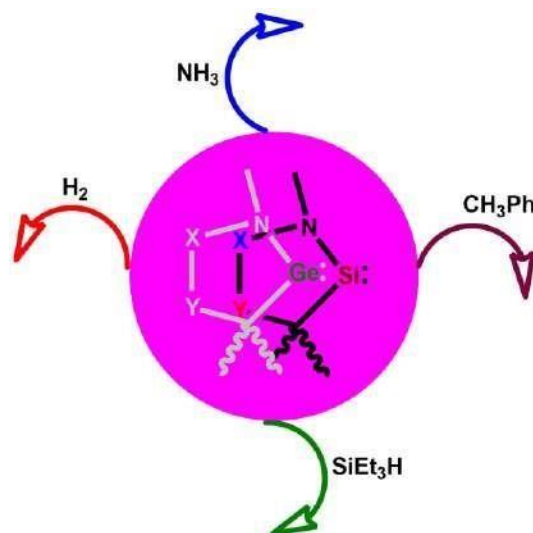
# Activation of Small Molecules by Cyclic Alkyl Amino Silylenes (CAASis) and Germylenes (CAAGes): A Theoretical Study

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Quantum chemical calculations have been carried out on a series of skeletally modified cyclic alkyl amino silylenes (CAASis) and germylenes (CAAGes) to understand their ligand properties and reactivity towards the activation of a variety of small molecules. Installation of boron or silicon atom into the ring framework of these silylenes/germylenes led to dramatic increase in their  $\sigma$ -basicity while incorporation of ylidic moieties resulted in sharp reduction of their  $\pi$ -acidity although it did help in increasing the electron donation ability. The calculated values of energy barriers for activation of H–H, N–H, C–H and Si–H bonds by many of the cyclic silylenes considered here are found to be comparable to those with experimentally evaluated systems<sup>1-3</sup> indicating the potential of these computationally designed molecules in small molecule activation and calls for synthetic efforts towards their isolation. Further, activations employing CAAGes are found to be more demanding than those with CAASis which may be attributed to the significantly lower Lewis basicity of the former than the latter.



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# Probing the Effects of Electron Withdrawing and Donating Substituents in *Gauche*-1,3-butadiene to Bicyclobutane Electrocyclization

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Ultra-fast relaxation of excited states is common in photochemical processes and facilitated via conical intersections (CI) involved in the molecular systems [1]. In this work, we explored the *gauche*-1,3-butadiene (GBUT) to bicyclobutane (BIBUT) electrocyclization [2] using both static electronic structure theory calculations and molecular dynamics simulations. We substituted the butadiene system with electron-withdrawing (-F) and donating (-CH<sub>3</sub>) to observe the effects during the reaction. The conical intersections involved between the ground (S<sub>0</sub>) and first excited (S<sub>1</sub>) electronic states are located using state-averaged complete active space self-consistent field (SA-CASSCF) approaches, and the ground state (S<sub>0</sub>) reaction pathway is studied using B3LYP-D3 density functional. Surface hopping molecular dynamics [3,4] simulations of the two lowest electronic states were also performed for all the system to observe the behavior of electronic states throughout the reaction pathway. Based on our investigation, we propose that unsubstituted GBUT can follow both the disrotatory and conrotatory pathways, whereas, F-GBUT and CH<sub>3</sub>-GBUT proceed via only conrotatory pathways to give BIBUT derivatives with a similar quantum yield as that of GBUT [5].

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# Temporal Hierarchy in Coupled Cluster Theory: A Bifrost to Dimensionality Reduction

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Coupled cluster theory (CC) is an extremely accurate post Hartree-Fock quantum chemical method to calculate correlation energy for small to moderately large molecular systems. The CC iteration scheme for determining the cluster amplitudes involves a set of nonlinearly coupled difference equations. In the space spanned by the amplitudes, the set of equations are analyzed as a multivariate discrete time map where the concept of time appears in an implicit manner. With the observation that the cluster amplitudes have difference in their relaxation timescales with respect to the distributions of their magnitudes, the CC iteration dynamics are considered as a synergistic motion of coexisting slow and fast relaxing modes, manifesting a dynamical hierarchical structure. With the identification of the highly damped auxiliary amplitudes (higher in number and smaller in magnitude), we employ (a) the concept of Synergetics to analytically map them as unique functions of the slow relaxing principal modes, resulting in a temporal hierarchy in the pseudo-time dynamics<sup>[1,2]</sup>, and (b) machine learning based mapping of the auxiliary amplitudes against the principal ones<sup>[3,5]</sup>. In either case, the macroscopic patterns of the trajectory towards the fixed point is dictated by the set of principal amplitudes while the auxiliary amplitudes chip in merely as parameters<sup>[4]</sup>. The two sets of amplitudes are inter-related by a circularly causal relationship. We have shown that our schemes drastically reduce the independent degrees of freedom resulting in an accelerated solution without sacrificing accuracy.

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# Effect of Additives on the Growth of Methane Hydrate

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In this worldly crisis of fuels, gas hydrates can play the role of a savior for centuries from now as nearly 20000 trillion cubic meters of methane gas is trapped in naturally existing gas hydrate reserves. Although gas hydrate seems to be a promising option, there are certain limitations of gas hydrate separation, storage, and transportation, which have been major industrial challenges that can cause huge economic losses. Usage of low dosage additives which can either promote or inhibit the growth of gas hydrate come in handy in this scenario.

In this work, we have studied the effect of two common types of additives (at a concentration of ~1wt%) namely organic alcohols (Ethanol, Glycerol, Ethylene Glycol, and Glycerol) and common osmolytes (Urea, DMSO, and TMAO) on the growth of methane hydrate. Generally, organic alcohols in the aqueous phase affect the gas hydrate formation both thermodynamically and kinetically. On the other hand, from our study we find that common osmolyte (e.g. TMAO and DMSO) act as potential hydrate growth inhibitors, even better than common alcohols, at least in the time scale we are looking into. Our study also indicates that at different time scales the growth-inhibiting properties of additives can change, e.g. Urea initially promotes hydrate growth but in the long term inhibits the growth in greater measure. Throughout our study, we tried to gain molecular insight into the interactions of additive molecules with methane and water. There is certainly a direct involvement of the additives in the formation of hydrate cages as a significant number of additives are found at the growth interface. Also from our study, we can safely conclude that the additives neither perturb the surrounding water nor increases the solubility of methane in water.

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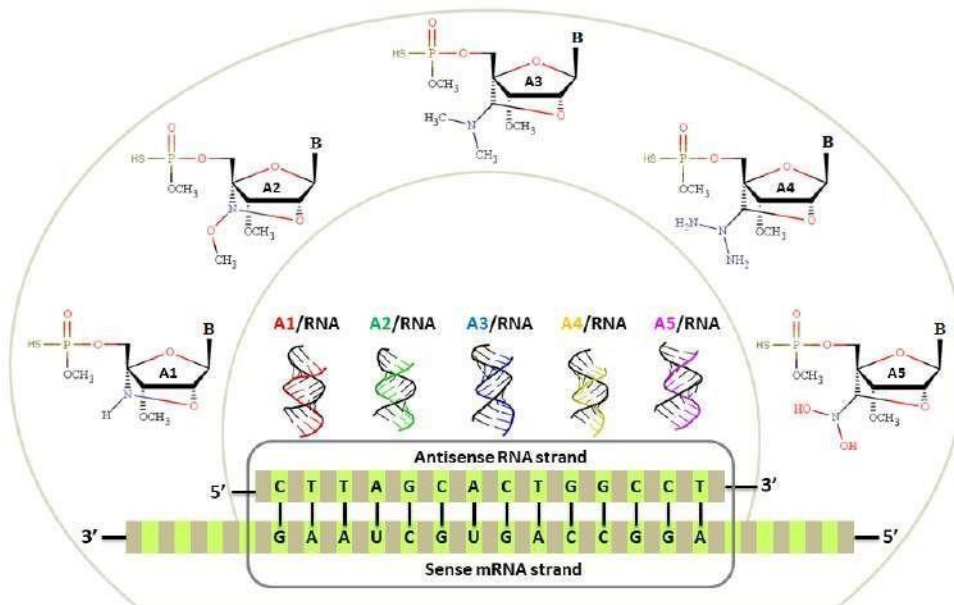
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# “Design of LNA analogue ASOs and their impact on the structure and stability of RNAs for antisense inhibition”

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In the quest to design better antisense-mRNA drugs, we are proposing five novel LNA analogue antisense modifications A1, A2, A3, A4, A5 by establishing each with the five standard nucleic acids Adenine(A), Guanine(G), Cytosine(C), Thymine(T) and Uracil(U). The modifications were studied thoroughly by performing quantum chemical calculations at the molecular level. Oligomer hybrid duplex stability and gene silencing potential of ASOs are described by performing a detailed MD simulation study on a set of fully modified 14-mer ASO/RNA duplex systems. Results from both monomer and oligomer level analysis depicted LNA level stability of the modified ASO/RNA duplexes preferring RNA-mimicking *A-form* duplexes. Notably, monomer MO iso-surfaces for both purines and pyrimidines were distributed on the nucleobase region in A1, A2 and bridging LNA unit in A3, A4, A5 suggesting A3/RNA, A4/RNA, A5/RNA duplexes to interact more with surrounding environment, which may aid in the interaction with nearby proteins, solvent environment and thereby increase their cellular uptake. Accordingly, oligomer level study revealed solvation of A3/RNA, A4/RNA, A5/RNA duplexes were higher compared to LNA/RNA, A1/RNA, A2/RNA duplexes. This study has fulfilled a useful purpose to design LNA analogue antisense modifications which may overcome the drawbacks and improve the pharmacokinetics of existing LNA ASOs.



**Graphical Abstract**

# Development of a compact double unitary ansatz for NISQ realization

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Recent developments in the field of Quantum information and technology has stimulated a good deal of interest in the development of quantum algorithms aimed towards handling problems which are intractable on classical computers. Quantum chemistry, which often deals with solutions to problems involving exponential growth of Hilbert space dimensions, has been widely recognized as a compelling application of near-term quantum computing. In order to carry out sophisticated quantum chemical calculations of many-electron systems, there had been varied algorithmic developments in the quantum computation framework in the past decade. Variational quantum eigensolver (VQE)<sup>1</sup> is one such leading algorithm which is considered as a promising candidate for quantum state preparation<sup>2</sup> in the near term noisy intermediate-scale quantum (NISQ) devices. To this end, we have developed a chemistry inspired dual unitary coupled cluster based wavefunction ansatz<sup>3</sup> in the VQE framework, which spans the many-electron Hilbert space with rank-one and rank-two parametrization. With the introduction of a set of scattering operators on top of the cluster operators, the ansatz is chosen in a partially disentangled structure in which arbitrarily high rank correlation effects are incorporated through a reasonably shallow quantum circuit. Furthermore, we introduce a dynamic ansatz based on the ideas of energy sorting and commutativity pre-screening, in which only a few of the dominant scattering and/or cluster operators are chosen from their respective pools. Through a number of applications on strongly correlated molecules, we shall demonstrate that the proposed ansatz, as well as its dynamic variant are capable of handling molecular strong correlation with low implementation cost for NISQ realization.

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# Rotational synchronization of pinned spiral waves

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Coupled rotors can spontaneously synchronize, giving rise to a plethora of intriguing dynamics. We present here, a pair of spiral waves as two synchronizing rotors, coupled by diffusion. The spirals are pinned to unexcitable obstacles, that enables us to modify their frequencies and restrain their drift. In experiments with the Belousov-Zhabotinsky reaction we show that two counter-rotating spiral rotors, pinned to circular heterogeneities, can synchronize, in frequency and phase. The nature of the phase synchronization varies depending on the difference in their characteristic frequencies. We observe in-phase and out-of-phase synchronization, lag synchronization and phase-resetting across the experiments. The time required for the two spirals to synchronize is found to depend upon the relative size of their pinning obstacles and the distance separating them. This distance can also modify the phase-lag of the two rotors upon synchronization. Our experimental observations are reproduced and explained further on the basis of numerical simulations of an excitable reaction-diffusion model.

# Electron Attachment to Nucleobase in Diethylene Glycol: The Signature of a Doorway

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High energy radiation is widely used in radiation cancer therapy to destroy tumor cells. Destruction of the cancer cells occurs because the ionizing photons damage the genetic material. However, the exact mechanism of this process is still mired in controversy. Although direct radiation-DNA interaction causes strand breaks in DNA, it only constitutes a minor portion of radiation-induced damage to genetic material. It is the secondary products formed due to the interaction of ionizing radiation with the aqueous cellular environment that causes the majority of the DNA damage.<sup>1</sup> Among the secondary products, low-energy electrons are known to cause DNA single- and double-strand breaks, base release, etc. In this work, we have analyzed the influence of the solvent on the electron attachment to uracil using high-level QM/MM simulations with diethylene glycol as the solvent. In the case of micro-solvated uracil, the initial electron attachment leads to the formation of a dipole-bound state which acts as a doorway to the formation of the valence-bound anion. We found that this doorway mechanism also exists in solution, where the dipole-bound state is replaced by a solvent-bound anionic state. The additional electron, which initially forms the solvent-bound state, gets transferred to the uracil-bound state through multiple trapping sites in the medium. This observation is similar to the previous study conducted with water as the solvent.<sup>2</sup> Local energy decomposition analysis of the micro-solvated system shows that the binding energy of uracil-diethylene glycol is higher than that of the uracil-water complex.

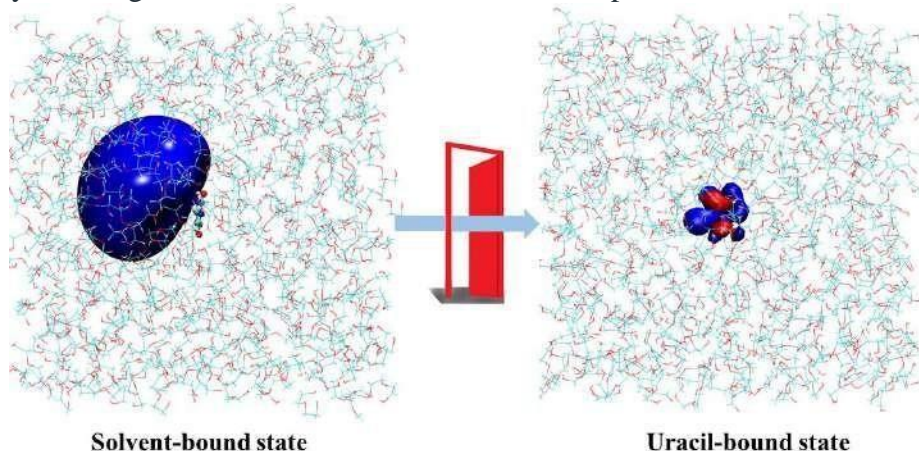


Figure 1. EA-EOM-DLPNO-CCSD natural orbital corresponding to the ground state of anion for solvent-bound and uracil-bound states.

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# Active Learning Assisted MCCI to Target Spin States

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Strongly correlated systems and their accurate solutions have been challenging to quantum chemistry. Several methods have been developed over the years for the accurate understanding of such systems, and selected configuration interaction and Monte Carlo configuration interaction (MCCI) form important classes of systems in this category. However, MCCI is plagued by slow convergence. This is further exacerbated by the fact that most of the current MCCI implementations do not target specific spin states. In our work, we use active learning assisted MCCI to speed up the convergence manyfold and also develop a method for spin targeting. This method has been tested with several model Hamiltonian systems akin to molecular systems and has shown improved convergence and accuracy.

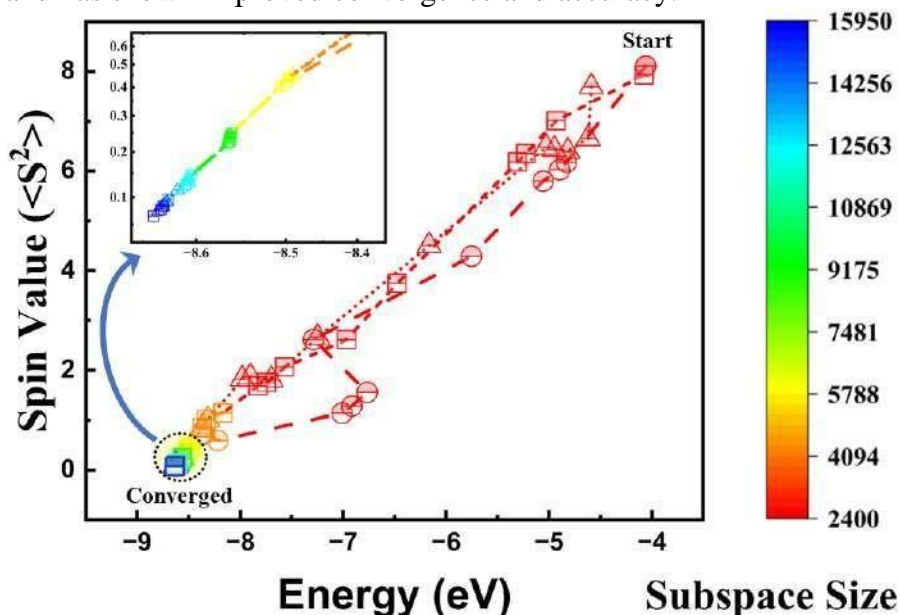


Fig: The trajectory of energy and spin optimization in AL-MCCI protocol for  $S_0$  state of tetracene molecule. Three different symbols represent three independent calculations. Subspace size is denoted in the adjacent colour bar. Energy and spin values near the convergence limit are shown in an enlarged view on the top left corner in the inset.

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# Double Transition Metal MXenes for Spintronics Applications: Surface Functionalization Induced Ferromagnetic Half-Metallic Complexes

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MXenes are rapidly emerging two-dimensional (2D) materials with thickness, composition, and functionalization-dependent outstanding properties having applications in diverse fields. To disclose nano-spintronic applications of 2D-double transition metal (DTM) carbide and nitride-based pristine and surface-functionalized MXenes ( $M'_2M''X_2T_x$ ,  $M'$  and  $M'' = Cr, Mo, W$ ;  $X = C/N$ ;  $T = -F/-OH/=O$ ), a systematic investigation has been performed on structural stability, magnetic properties and electronic structure using spin-polarized first-principles calculations. 36 stables functionalized MXenes were screened from 144 explored complex structures. The explored materials exhibit striking properties, having wide range of magnetic ground states, from non-magnetic to ferromagnetic, and then to antiferromagnetic, accompanied by metallic to half-metallic or gapless half-metallic properties, depending on transition metal(s) and terminating group. Mo and W-based MXenes are found to be nonmagnetic and metallic, respectively, whereas Cr-Mo and Cr-W-based MXenes are magnetic with varying metallic behavior.  $W_2CrN_2O_2$  and  $Mo_2CrN_2O_2$  systems are found to be ferromagnetic half-metallic materials with a direct band gap of 1.35 eV and 0.77 eV respectively, in the minority spin channel. The comprehensive study on 2D-MXenes, provide intrinsic half-metallic transport properties along with robust ferromagnetism, opens up a class of promising new 2D materials with tunable magnetic and electronic properties for potential device applications in nano-spintronics and electronics.

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# Regulation of RhoA GTPase by Phosphorylation of RhoGDI

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The guanine dissociation inhibitor (RhoGDI) plays a crucial role in the regulation of Rho GTPases. It acts as a negative regulator by blocking the activation of Rho GTPase from an inactive GDP-bound state.<sup>1</sup> Activation of Rho GTPase requires release of Rho GTPase from the GDI-bound complex. Experimental studies suggest phosphorylation of RhoGDI as a key post-translational modification for dissociation of the complex. There seems to be a “phosphorylation code” that controls the release of specific Rho GTPase from the complex. For instance phosphorylation at SER-101 and SER-174 by p21-activated kinase 1 leads to the release of Rac1<sup>2</sup> (but not RhoA). On the other hand, phosphorylation of SER-34<sup>3</sup> or SER-96<sup>4</sup> by protein kinase C $\alpha$  (PKC $\alpha$ ) selectively releases RhoA (but not Rac1 or cdc42).

We have performed atomistic molecular dynamics simulations of the wild-type and phosphorylated state of the RhoA-GDI complex and propose a molecular-interaction-based mechanistic model for the dissociation of the complex as an effect of phosphorylation. After phosphorylation we have observed major structural changes particularly in the positively charged polybasic region (PBR) of RhoA and negatively charged N-terminal region of GDI. Also the geranyl moiety which remains inside the hydrophobic cavity comes out after phosphorylation. Binding energy calculation shows a significant decrease in binding energy between RhoA and GDI. Due to phosphorylation, the number of contacts between the PBR of RhoA and N-terminal of GDI decreases leading to the decrease in binding energy between RhoA and GDI. Using hydrogen bond occupancy analysis and energetic perturbation analysis we propose a mechanistic model for the distant signal propagation from the site of phosphorylation to the PBR region and buried geranyl group in the form of rearrangements of hydrogen bonds and charge-charge interactions, which demonstrates the crucial role of electrostatic interactions in the allosteric response.

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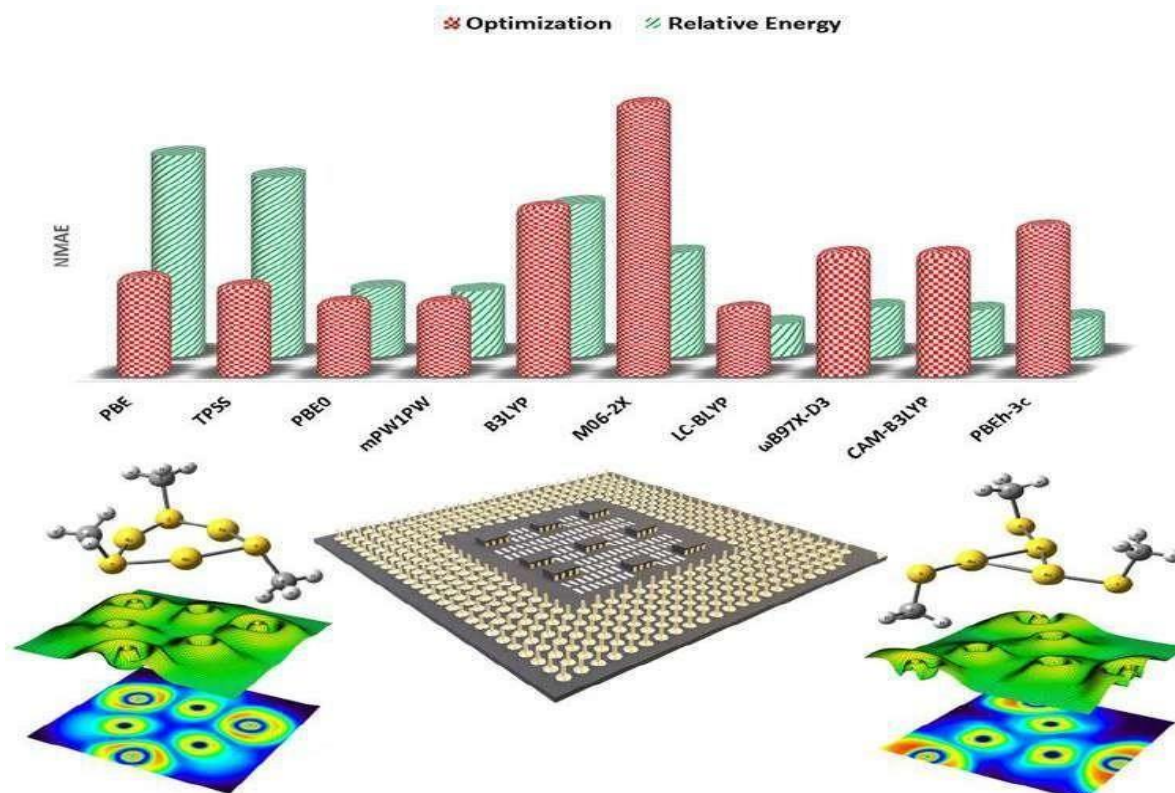


# Performance of Density Functionals and Semiempirical 3cMethods for Small Gold-Thiolate Clusters $\text{Au}_3(\text{SMe})_3$

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Amid the surge of computational studies of gold thiolate clusters in the recent past, we present a comparison of popular density functionals (DFAs) and three-part corrected methods (3c-methods) for their performance on gold-thiolate nanoclusters -  $\text{Au}_3(\text{SCH}_3)_3$  isomers. We compared the efficiency and accuracy in geometry optimization with RI-SCS-MP2 and energies with DLPNO-CCSD(T) as reference methods. A comparison of relevant bond lengths with the reference geometry was made to estimate the accuracy in geometry optimization. Some methods such as LC-BLYP and HF-3c were unable to locate many of the minima located by most of the other methods; thus, the versatility in locating various minima is also an important criterion in choosing a method for the given project. We compared the relative energies among the isomers and the interaction energy of the gold core with the ligands to estimate the accuracy of the methods. The range separated hybrid DFAs are best choice for the relative energies of the clusters. LC-BLYP excels in accuracy, but lacks diversity. We analyzed bonding and interaction in an attempt to understand the relative stability among the isomers which points to the higher stability of bridging sulfur coordination (RS-Au-SR; R = -methyl) over singly-bonded and capping sulfur bonds.



# Using TD-DFT to understand the photochemistry of functionalized organic systems.

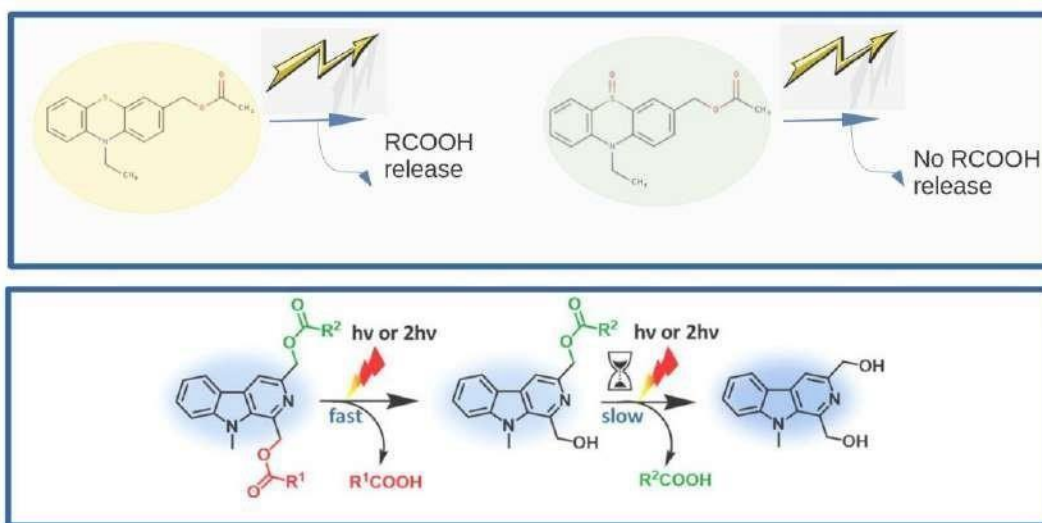
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Photochemical release of carboxylic acids as leaving groups from functionalized systems acting as photocages is studied using  $\beta$ -carboline and phenothiazine moiety.

$\beta$ -carboline moiety, substituted at the C1 and C3 benzylic positions with a leaving group having difference in the rate of release from positions C1 and C3 and the difference in the photochemistry between oxygen-free and oxygen-functionalized phenothiazine was investigated using DFT and TD-DFT calculations for the release of carboxylic acid.

Hole-electron distribution, charge density difference visualization were studied to carry out the electron excitation analysis.



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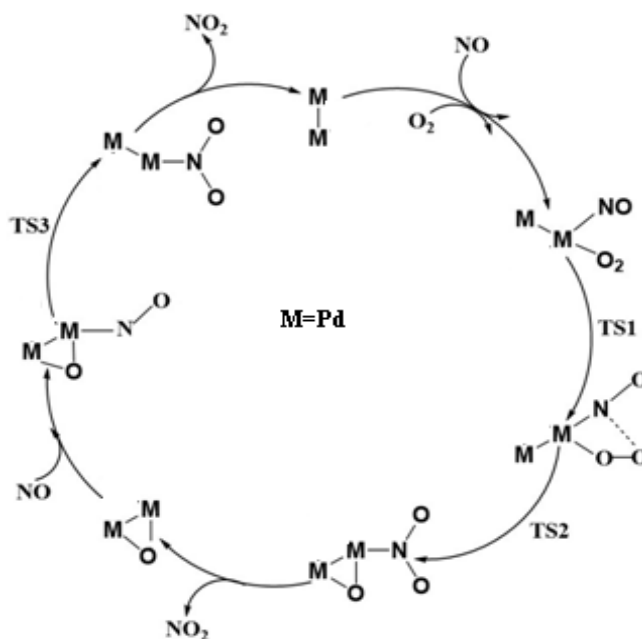
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# Catalytic oxidation of NO to NO<sub>2</sub> on charged and neutral Pd<sub>2</sub> dimer: A DFT viewpoint

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Density functional theory calculations are performed to study the catalytic oxidation of NO to NO<sub>2</sub> on unsupported charged and neutral Pd<sub>2</sub> catalyst using the M06L functional combined with a def2TZVP basis set. Adsorption energies of adsorbed NO and O<sub>2</sub> on [Pd-Pd]<sup>+/-0</sup> have been calculated to find out the coordinated sites and observe the stability of the adsorbed sites. Natural Bond Orbital (NBO) calculations are performed to provide an insight into the electronic properties of the catalyst and the reactants. Result shows that the adsorption of both NO and O<sub>2</sub> is highest for cationic Pd<sub>2</sub> and lowest for anionic Pd<sub>2</sub> system. The Langmuir-Hinshelwood (L-H) mechanism is followed for the catalytic oxidation of NO to NO<sub>2</sub> owing to the high adsorption energies of both the reactants. Furthermore, we performed oxidation of nitric oxide on stable dimers and explored stable species along with transition states structure on the potential energy surface (PES) diagram. This study offers a new insight into the effect of charge on the catalytic activity of Pd<sub>2</sub> system for the NO oxidation mechanism at the molecular level which in turn will aid experimentalists in developing efficient catalysts on an industrial scale.



Scheme: Catalytic oxidation of NO to NO<sub>2</sub> on [Pd-Pd]<sup>+/-0</sup> system using L-H mechanism

# Theoretical Understanding of an Electronically Controlled Photochemical Intramolecular C-N Coupling Reaction

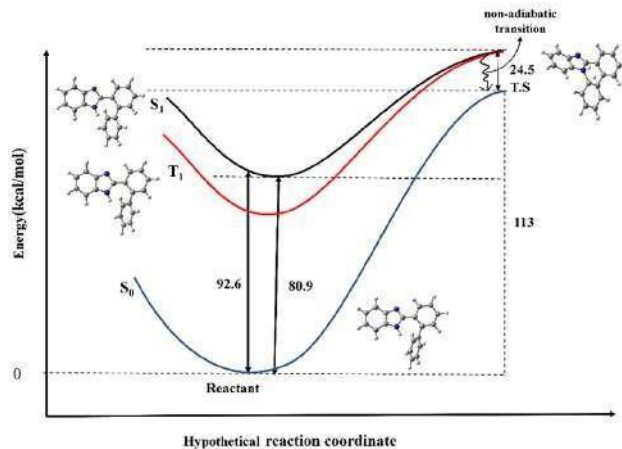
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To understand the electronic impact of a radical-induced photochemical C-N coupling process toward the synthesis of benzo[4,5]imidazo[1,2-f]phenanthridine (BIFP) from 2-([1,1'-biphenyl]-2-yl)-1H-benzo[d]imidazole, electronic structure-based theoretical calculations are carried out. UV radiation (about 350 nm) caused an electronic transition from the S<sub>0</sub> to S<sub>1</sub> state, which resulted in the synthesis of the product. While excitation to the T<sub>1</sub> state minimises reaction yields, excitation to the S<sub>1</sub> state leads to higher yields. The dihedral angle between the biphenyl rings could be directly associated with the energy difference between the excited S<sub>1</sub>/T<sub>1</sub> state and S<sub>1</sub> transition state (TS), as well as with the yield of the products. Substituting electron-donating groups at biphenyl ring decreased the dihedral angle to achieve planarity, and the yields increased. Overall, the structure-reactivity correlations help to explain how the novel C-N photochemical coupling functioned without using photocatalysts or sensitizers.

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## **Effect of concentration gradient on spiral wave dynamics**

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Propagating wave and spiral or scroll pattern formation in chemical and biological system are important phenomenon associated to nonlinear dynamics. The dynamics are complex spatial, temporal or spatio-temporal. The formation of spiral and scroll waves having electrical activity in cardiac tissue may lead to arrhythmias and tachycardias. It was always challenging to control complex spatio-temporal dynamics causing life threatening cardiac arrhythmias. There is always need for low energy defibrillation techniques. The present clinically effective method is a high energy shock of  $5 \text{ Vcm}^{-1}$  voltage gradient (as large as 360 J).

In our lab we study the spiral wave dynamics formed from Belousov-Zhabotinsky (BZ) reaction. BZ reaction has been chosen because of its oscillatory nature. The reaction is used as a model system which is analogous to the waves formed in our heart. The formation of spiral waves in our heart due to any obstacles is dangerous. So, we try to control these waves formed in a BZ reaction system. Previous study shows that we can control spiral waves by applying electric field gradient and thermal gradient. Now we are trying to do the same with concentration gradient in experiments as well as in simulations.

# Theoretical Investigation of Decomposition Dynamics of Methoxysulfonyl Azide ( $\text{CH}_3\text{OS}(\text{O})_2\text{N}_3$ )

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Small inorganic molecules containing Sulphur, Nitrogen, and Oxygen have been widely explored due to their significant role in industry, biology, and atmospheric chemistry.  $\text{HNSO}_2$  is one such molecule synthesized by the gas phase pyrolysis of methoxysulfonyl azide ( $\text{CH}_3\text{OS}(\text{O})_2\text{N}_3$ ) which is a biologically relevant molecule. Experiments and electronic structure calculations at CCSD(T)/6-311++G(2df,2p) level suggest that the azide decomposition occurs via two competing pathways involving a nitrene intermediate to form  $\text{HNSO}_2$ ,  $\text{H}_2\text{CO}$ , and  $\text{N}_2$ . In the present work, direct classical trajectory simulations are performed to investigate the atomic level dynamics of the gas phase production of  $\text{HNSO}_2$ . Following a survey of various density functional methods, B3LYP/6-31G\*\* method was selected to perform the on-the-fly dynamics. Classical microcanonical sampling method was used to prepare the molecules in the electronic ground state and the ensuing dynamics investigated.

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# Electronic Structure and Bonding Patterns in The Planar Tetracoordinate Carbon (ptC) and Planar Hexacoordinate Boron (phB) Global Minima

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The molecules containing planar tetracoordinate carbon (ptC) deviate from the usual idea of the tetrahedral tetracoordinate carbon concept. Hoffmann and co-workers proposed that with the inclusion of appropriate ligands having simultaneous  $\sigma$ -donating and  $\pi$ -accepting capacity, ptC structures can be achieved. The exploration of structural prerequisites to stabilize the non-classical ptC systems opens a new dimension towards the studies on the structure and bonding of planar hypercoordinate species. Inspired by the achievement of the novel planar hypercoordinate carbon chemistry, people have shown great interest in the possibilities of the other main group elements for planar hypercoordination. We have designed  $\text{CSi}_n\text{Ge}_{4-n}^{2+}$  ( $n = 1-3$ ) and  $\text{CB}_6\text{Al}^{0/+}$  systems and explored the potential energy surfaces (PES) using density functional theory (DFT) with the help of the ABCluster code. The  $\text{CSi}_n\text{Ge}_{4-n}^{2+}$  ( $n = 1-3$ ) systems show ptC in the global minimum structures that are kinetically stable at 300 K and 500 K temperatures using the atom-centered density matrix propagation (ADMP) simulation over 50 ps of time. The global minimum structures have  $\sigma/\pi$ -dual aromaticity as predicted from the nucleus independent chemical shift (NICS) values. The central carbon atom in these systems accepts electrons from the peripheral atoms ( $\sigma$ -acceptor) and donates electrons to the surrounding atoms ( $\pi$ -donor). However, the global minimum structures of  $\text{CB}_6\text{Al}^{0/+}$  systems have planar hexacoordinate boron (phB) atoms and the geometries are kinetically stable at 300 K and 400 K temperatures using the ADMP simulation over 20 ps of time. The global minima of  $\text{CB}_6\text{Al}$  and  $\text{CB}_6\text{Al}^+$  systems are aromatic and nonaromatic, respectively. Both the ptC and phB global minima are stable through the electronic interaction of the central carbon/boron with the surrounding atoms. The electronic delocalization within the systems is confirmed through molecular orbitals (MOs), adaptive natural density partitioning (AdNDP), and electron localization function (ELF) analyses. As planar hypercoordinate carbon species were characterized in the gas phase, we hope that the feasibility of the designed systems might be possible in near future.

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# Computational Study of Lithium-Sulfur cluster, $\text{Li}_m\text{S}_n$ ( $m=2-4$ , $n=2-6$ )

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The total amount of non-renewable energy sources (coal, oil, and other sources) is limited and cannot meet the ever-increasing energy demand.<sup>1</sup> Moreover, consumption of these energy sources produces gases, such as carbon dioxide and sulfur dioxide, which are very harmful to the environment. To overcome this gradually increasing energy demand and to get a clean environment, sustainable energy resources are needed<sup>2</sup>, which lithium-based battery technologies have primarily met. In this work, we have theoretically investigated the growth of the Lithium-Sulfur clusters,  $\text{Li}_m\text{S}_n$  ( $m=2-4$ ,  $n=2-6$ ). A total of 47 different Density functionals and Wave Function-Based Correlation Methods have been taken to benchmark the energy parameters. From the NMAE values for the different systems, we can conclude that the BPBE method is suitable for geometry optimization. We can expect that our study will help others to choose the appropriate method for the optimization of the geometries and also investigate the different electronic properties by taking the appropriate method.

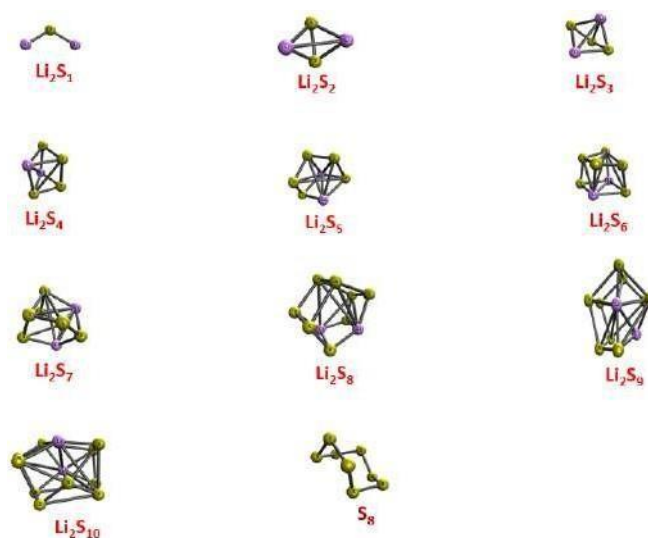


Figure 1: Optimized Global minima structures of  $\text{Li}_2\text{S}_n$  ( $n=1-10$ ) clusters.

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# Theoretical Investigation on the Synthesis of Quinoxaline Derivatives in Natural Deep Eutectic Solvents (NADESs)

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The reaction between 4-(bromo)benzene-1,2-diamine and 2,4'-dibromoacetophenone can proceed via 2 pathways: Substitution followed by Addition (Mechanism-I) or Addition followed by Substitution (Mechanism-II), each yielding the same product but goes through different intermediates. Here, the theoretical investigations of the reaction were done with Gaussian 09<sup>1</sup> software using B3LYP/6-311+G(d,p) level theory<sup>2</sup>. To establish whether the reaction goes via Mechanism-I or Mechanism-II, both the intermediates obtained in the first step were optimized. From the optimized geometry, it was observed that the intermediate obtained from Mechanism-I is more thermodynamically stable than the intermediate obtained from Mechanism-II. Therefore, Mechanism-I was considered for finding the regioselectivity of the reaction.

The asymmetry arises in the intermediate as 2,4'-dibromoacetophenone can be substituted in the amine group of either 1-position or 2-position of 4-(bromo)benzene-1,2-diamine, which introduces the concept of regioselectivity in this reaction. On using Deep Eutectic Solvents (DES) (here, 1:2 Choline Chloride & Glycerol), the major and minor products of this reaction are just the opposite of what was energetically observed in the water medium and gas phase.

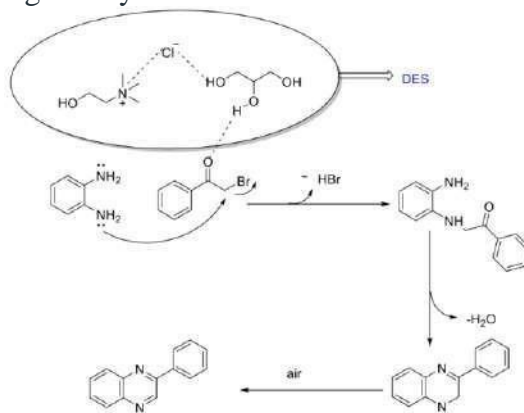


Fig.: Plausible Mechanism-I (Substitution followed by addition)

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# A comparative mechanistic study of C-H activation of methane and conversion to methanol over Pd<sub>n</sub> (n=2, 4) cluster

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As the global consumption of energy increases exponentially, there arises a greater need for the search of sustainable energy over fossil fuels. Methane to methanol pathway proves to be an promising alternate approach to deal with depleting fossil fuels. Moreover, being the most significant component of natural gas, methane has received a great deal of attention over the last few decades as feedstock for chemical and clean fuel energy. However, the activation of C–H bond of methane and its selective oxidation to value added chemicals continues to be a significant challenge in catalysis. In the present work, we have employed density functional theory (DFT) method to investigate the activation of C–H of methane and its partial oxidation to methanol facilitated by the titled transition metal clusters. Both the metal clusters [Pd<sub>n</sub> (n = 2, 4)] are oxidized by N<sub>2</sub>O to form metal oxide units [Pd<sub>x</sub>O] which reacts with methane to form methanol. We have used B3PW91 functional along with the def2TZVP basis set for geometry optimization and frequency calculation of all the species involved in the reaction. Energy calculations in different spin states have been performed to find the most stable structure of Pd<sub>n</sub> cluster. Further, Natural bond orbital (NBO) analysis have been done to obtain the information on delocalization of the electron density of the active centre. A detailed mechanistic pathway has been explored to observe the stable species along with the transition state structures on the potential energy surface diagram. The reported pathway is thermodynamically viable and the activation of C–H bond in both the clusters is exothermic. Comparing the energy barrier for the clusters, Pd<sub>4</sub> cluster is found to be a more efficient catalyst than Pd<sub>2</sub>. The current work investigates the process at the atomistic level that will help in designing more efficient catalysis in large scale.

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# Auxiliary Pharmacological Advantages of Drug-Graphene Oxide Nanocomposite: A Test Case with AChE Inhibitors

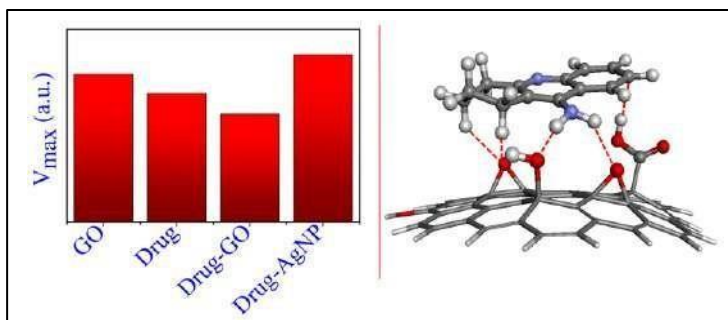
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The harmful influence of oxidative stress on biological systems has been the principal cause of many life-threatening diseases. In this context, the mechanistic details leading to the antioxidant behavior of eight FDA approved cholinergic drugs used in the treatment of AD, which are minor groove binders and able to reverse the oxidative stress in calf thymus DNA [1], was investigated using DFT calculation. The low bond dissociation enthalpy (BDE) values in all the compounds advocated for the hydrogen atom transfer (HAT) mechanism. The kinetic study for the reaction of the drugs with hydroperoxyl radicals has also been studied and it was found that the rate constant in some cases is very close to that of well-known non-phenolic antioxidant,  $\alpha$ -terpinene [2].

On the other hand, the applicability of 2D nanomaterials is also a growing subject of interest in recent pursuits for biocompatible drug delivery avenues. In this regard, a thorough understanding of the molecular basis of the interaction of these drugs with such materials and their combined effect on the acetylcholinesterase (AChE) inhibition activity is important. The interaction of one of the most potent FDA approved AD drugs, tacrine (TAC), with graphene oxide (GO) has been studied and the results indicate a considerable binding between the two entities via non-covalent interactions. The nature and the stability of the interaction have been thoroughly characterized using AIM and NBO analyses and quantum-mechanics based ADMP simulation, respectively. Interestingly, the BDE of the drugs also decreases significantly in drug-GO nanocomposite, signifying augmented antioxidant activity (Fig. 1). These results are in sharp contrast to the reduced AChE inhibition efficiency of the drug composites with spherical metal nanoparticles and open the possibility of dual therapeutic use of cholinergic inhibitors.



**Figure 1.** Comparative kinetic plot of AChE inhibition by different drug-nanomaterial systems.

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# Role of Hydrogen Bonding on Antioxidant Properties of Polyphenolic Molecules

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Polyphenolic antioxidants have played a crucial role to minimize oxidative stress. Such molecules having lower bond dissociation enthalpy (BDE) are considered to be effective antioxidants. The BDE of the polyphenolic antioxidants is one of the intrinsic properties based on their hydrogen atom transfer (HAT) mechanism. However, in such cases, the stability of the corresponding polyphenolic radical is pivotal in determining the BDE. Two factors mainly control the stability of the radical: Spin Density Distribution (SDD)<sup>1</sup> and intramolecular hydrogen bond in the polyphenolic radicals. This presentation would mainly focus on the study of such factors and their relation with BDE. For this study, various topological parameters<sup>2</sup> are analyzed for a set of 18 polyphenolic molecules. It was found from our study that intramolecular hydrogen bonding plays a significant role in comparison to spin density distribution in controlling the stability of polyphenolic radicals.<sup>3</sup>

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# Incorporating Interactions in the Entropy Term: Thermodynamic Model for Deep Eutectic Solvents

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Theoretical modeling of solid-liquid equilibria is necessary for the appropriate choice (among numerous possible candidates) of pure components to form deep eutectic solvents with suitable physicochemical properties. Thermodynamic models attempt to parameterize the non-ideality of the mixture and connect it to the liquidus temperature of the deep eutectic solvents. Though the Gibbs free energy change for mixing the constituents can be related to the melting properties of the solid mixture, still the partitioning of enthalpy and entropy contribution is ambiguous. Available models pack all the interactions into the enthalpy term and only combinatorial effects are included in the entropy contribution<sup>1</sup>. In this work, we are incorporating system-specific interactions into the entropy term. The modified thermodynamic model includes interactions in both the enthalpy and entropy contributions and we expect a change in the parameter describing non-ideality compare to the other models which consider only combinatorial entropy. A model calculation of the interaction parameter ( $\chi$ ) is performed for the acetamide + urea deep eutectic solvent and, it is observed that the value changes considerably due to the inclusion of interaction in the entropy term<sup>2</sup>. Observations also suggest significant effect of entropy on the composition dependence of eutectic mixture, as entropy change on mixing is found to be maximum at the eutectic composition.

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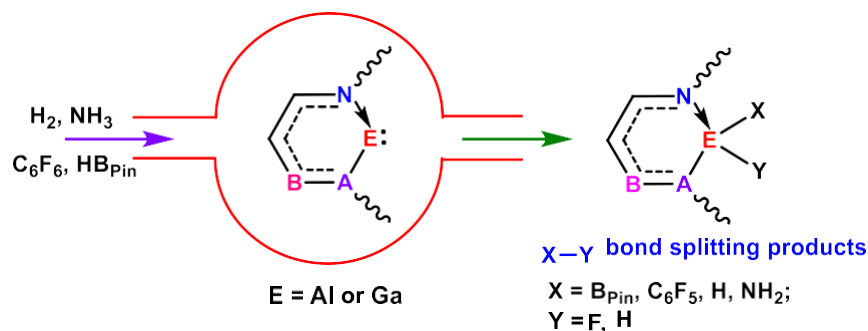
# Skeletally Substituted Aluminium and Gallium Carbenoids: A Computational Exploration

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Comprehensive computational investigations were carried out to understand the electronic and ligand properties of skeletally substituted  $\beta$ -diketiminate stabilized Al(I) and Ga(I) carbenoids as well as to probe their potential in small molecule activation. All the proposed group 13 carbenoids possess a stable singlet ground state, and majority of them have significantly enhanced electron donation ability than the experimentally evaluated systems<sup>1-2</sup>. An evaluation of the energetics associated with the splitting of various strong bonds such as H–H, N–H, C–F and B–H by these carbenoids indicates that many of the proposed Al and Ga carbenoids may be considered as suitable systems for small molecule activation.



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# DFT Study on Binuclear Transition Metal Complexes with Macrocyclic Tetradentate Ligands: Structures, Relative Energies, and Metal-Metal (MM) Bond Lengths and Bond Orders

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We use DFT with the M06-L functional and LAN2LDZ basis set to study a series of homobinuclear transition metal complexes M<sub>2</sub>L<sub>2</sub> (M = Ti, V, Cr, Mn, Fe, Co, Ni), where L is a symmetrical macrocyclic tetradentate ligand C<sub>8</sub>N<sub>4</sub>H<sub>8</sub>. Two orientations are taken for each case – (a) *orthogonal*, where the metal-metal (MM) bond axis is perpendicular to the ligand planes, and (b) *lateral*, where the MM bond axis is parallel to the ligand planes. By exploring a variety of low lying spin states, the ground state for each complex is predicted. Invariably, the orthogonal structures are lower in energy than the lateral structures, which predict that the former would be more readily formed during synthesis. Our DFT findings concerning the ground state spin multiplicity and MM bond lengths are consistent with and relatable to experimental results on known binuclear tetragonal lantern-type complexes of vanadium, chromium, iron, cobalt and nickel having four bidentate ligands. The tetragonal structural motif present in these experimentally known lantern complexes is mirrored in our complexes of novel structure which, however, possess only two ligands. The MM bond lengths span a wide range, and are assigned formal bond orders from zero to four. The valencies of the metal centres in the ground state complexes begin with about 5 for the dititanium complexes, rise to about 6 for the dichromium complexes, and fall to about 2 for the dinickel complexes.

# Exploration of Hydrocarbons in Chemical Space

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“Chemical Space”<sup>[1,2,3]</sup> is a set of all possible compounds, where one can imagine a dream of a molecular sea. The recent development of software and hardware makes it accessible to steer the billion of chemical structures.<sup>[4]</sup> Hydrocarbons are fundamentally important molecules in both organic and prebiotic chemistry. We are exploring the C<sub>n</sub>H<sub>m</sub> formula in different compositions of n and m values to explore the unknown territory in the chemical space. The concept is based on nanocluster study where the aggregation of carbon and hydrogen takes place in the PyAR (Python module for aggregation and reaction) software package. It enables the search from scratch to the maximum given limit in the command line argument. We organize all the quantum mechanical databases <sup>[5,6,7,8]</sup> in a searchable website to make the thing publicly available and one can easily gather all the calculated properties without any coding background. It can be used as a training dataset for ML model to explore the unknown properties of the molecules. This can also help to find the mystery behind the origin of life.

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# Hydroxycinnamic-Hydroxybenzoic Acid Hybrids: A Promising Antioxidant and Potential Drug

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Due to the disruption of homeostasis, there is an overproduction of free radicals, the excess of which our body cannot deactivate. These excess free radicals are believed to damage our healthy cells which initiates various chronic diseases like cancer, cardiovascular disorders, diabetes, neurological disorders, etc. This process is known as oxidative stress. Thus the purpose of the antioxidants is to alleviate the free radicals and prevent this oxidative stress. In this presentation, we have shown twenty designed hybrid antioxidant molecules which are also candidates of a potential drugs. These molecules are mainly hybrids of hydroxybenzoic acids and hydroxycinnamic acids. At first, we have carried out a conformational analysis with the MP2 method to find out the most stable structure of the molecules. Thereafter, the physicochemical parameters are calculated, showing that these molecules are probable antioxidants. Further, we have investigated the free radical scavenging capacity of these molecules for inactivating eight prototype oxyradicals. The scavenging capacity was estimated by considering Gibbs free energy for the three mechanisms, viz. hydrogen atom transfer (HAT), sequential proton loss electron transfer (SPLET), and single-electron transfer-proton transfer (SET-PT). Our study on mechanisms shows that for these molecules HAT and SPLET are favorable in the gas phase, while in solvent medium(i.e. for water and ethanol) HAT and SET-PT are competitive. In addition, the druglikeness of the molecules is calculated using Lipinski's rule of five which reveals that our molecules are also potential drugs. The advantage of our set of designed hybrid molecules is that they show antioxidant behavior with pharmacophoric characteristics. Thus, the set of novel antioxidant hybrids with drug-like properties makes it an attractive target for study and synthesis.

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# Self-Assembling Behaviour of Perylene, Perylene Diimide, and Thionated Perylene Diimide Deciphered through Non-Covalent Interactions

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$\pi$ -conjugated supramolecular polymers (SMP) have gained vast popularity in materials chemistry and biomedicine due to their spectacular self-assembling behaviour. A detailed account of the electronic structure and bonding through quantum theory of atoms-in-molecules, non-covalent interactions, and energy decomposition analysis (EDA) in the oligomers of perylene, perylene diimide (PDI), and thionated-PDI (t-PDI) is presented. The oligomers of all three molecules show a slip angle of  $\theta \approx 62^\circ$  thus forming H-aggregates. The stacking pattern in perylene oligomers prefers a slip-stacked brick-layer order, while the bulkier PDI and t-PDI prefer a parallel step-wise pattern in their oligomers. Combining the complementary results from QTAIM, NCI, and energy decomposition analysis, it was found that dispersion forces dominate the stabilizing  $\pi$ - $\pi$  interactions in the supramolecular assemblies. The NCI and RDG plots provide insights into the nature of the attractive interactions arising between heteroatoms of PDI and t-PDI, adding up to the stabilization of their oligomers. Although the overall steric term is compensated by the attractive dispersion and orbital energy components, they still have the potential to destabilize the geometry with bulkier side groups and heavy atoms. The association energy of the oligomeric assemblies supports the presence of  $\pi$ - $\pi$ ,  $\pi \cdots \text{O}=\text{C}$ , and  $\pi \cdots \text{S}=\text{C}$  electrostatic interactions, which play a crucial role in the self-assembly process in stabilization of the oligomers. This also shows that the supramolecular assembly of PDI and t-PDI have a much greater propensity to oligomerize, suggesting the potential of t-PDI to behave as an SMP similar to PDI, with more efficient charge transfer ability. The increase in the free energy of association with each added monomer unit resembles the cooperative supramolecular polymerization pathway for PDI. However, the thionation results in an increase in the steric energy that alters the cooperative assembly seen in PDI to an isodesmic assembly in t-PDI. It is hoped that the elaborate quantum chemical calculations of the lower oligomers presented here will be useful in determining force-field for supramolecular assemblies.

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# Accurate Computation of Excited State Properties of Thermally Activated Delayed Fluorescence Emitters

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Lowest singlet excitation energies and singlet-triplet energy gaps are important properties of thermally activated delayed fluorescence (TADF) emitters. Reproducing the small singlet-triplet energy gaps, in such molecules which help in reverse intersystem crossing, is always a challenge. Tuned range-separated (RS) functionals have gained popularity because of accurately computing such properties. However, the IP-tuning method requires computations of several self-consistent field (SCF) calculations and hence is computationally costly. In this presentation, we would discuss the two efficient descriptor-based tuning schemes (ELF and Sol) of RS density functionals, developed in our group.<sup>1, 2</sup> On reparametrizing the above methods, the ELF\* and Sol\* accurately reproduced the excited state properties of TADF emitters with a single SCF calculation.<sup>3</sup> The lowest singlet vertical excitation energies ( $E_{VA}(S_1)$ ) and vertical singlet-triplet energy gaps ( $\Delta E_{VST}$ ) have been calculated with ELF, Sol, and IP-tuned RS functionals (LC-BLYP,  $\omega$ B97,  $\omega$ B97X, and  $\omega$ B97XD). Interestingly, consistent performance was observed with different solvents. Our tuned functionals almost satisfy the energy linearity curve. Thus, in addition to IP-tuned functionals, our ELF\* and Sol\* tuned functionals have been found to be promising and reliable alternatives in computing the excited state properties.

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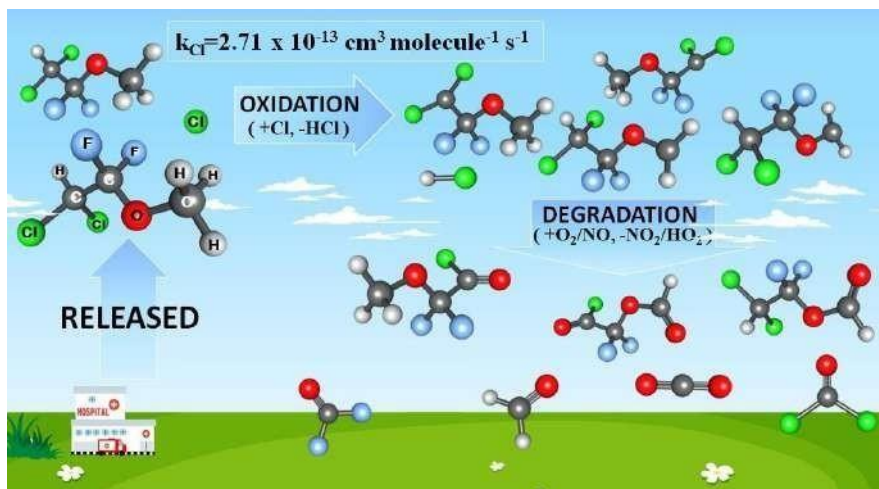
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# Insights into the chemistry of methoxyflurane with Cl atom in the troposphere and its degradation

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Globally, halogenated compounds such as methoxyflurane ( $\text{CH}_3\text{OCF}_2\text{CHCl}_2$ ) are frequently used as inhalation anesthetics<sup>1</sup>. Our work is predicated on the potential environmental concern posed by this substance. Utilizing a dual-level direct dynamics approach, the kinetic characteristics of the interaction of Cl atoms with methoxyflurane are investigated. Interpolated single-point energies (ISPE) are used to refine the reaction channel energy profiles at the CCSD(T)//M06-2X/6-311++G(d,p) level. To obtain reliable results, the canonical variational transition state theory (CVT) with a small-curvature tunnelling (SCT) correction is utilized to evaluate the rate constants over a temperature range of 250–500 K. The computed CVT/SCT rate coefficient  $k_{\text{Cl}} = 2.71 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at a temperature of 296 K is found to be in reasonable agreement with the experimental result<sup>2</sup>. As computational analysis can reveal the mechanistic elements of any chemical reaction in more depth than experimental study, this study provides new insights for the  $\text{CH}_3\text{OCF}_2\text{CHCl}_2 + \text{Cl}$  reaction and further atmospheric decomposition of  $\text{CH}_3\text{OCF}_2\text{CHCl}_2$ . Our calculations indicate that the  $\text{CH}_3\text{OCF}_2\text{CHCl}_2 + \text{Cl} \rightarrow \text{CH}_2\text{OCF}_2\text{CHCl}_2 + \text{HCl}$  (R1) reaction is the principal pathway and a notable route for further degradation of  $\text{CH}_3\text{OCF}_2\text{CHCl}_2$  in the troposphere.



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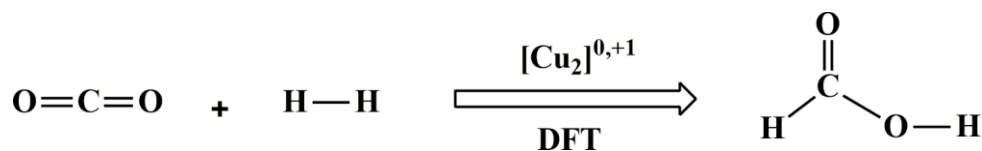
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# Mechanistic Hydrogenation of Carbon-Dioxide to Formic Acid via Hydride Formation on $[\text{Cu}_2]^{0,+1}$ Dimer

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The escalation of  $\text{CO}_2$  concentration in the atmosphere due to fast industrial revolution, deforestation and burning of fossil fuels has heightened the concern for climate change and various health issues. Thus, capture and utilization of  $\text{CO}_2$  to different value-added products has become a topic of concerned research for the mitigation of this problem. Herein, we have performed molecular level catalytic reduction of  $\text{CO}_2$  to formic acid via  $\text{HCOO}$  intermediate formation using  $[\text{Cu}_2]^{0,+1}$  dimers as catalyst. This study has been performed using Density Functional Theory (DFT) method employing the Perdew-Burke-Ernzerhof (PBE) functional with def2TZVPP basis set. Results show the different probable mechanisms on the two dimers which finally lead to  $\text{HCOOH}$ . Moreover, the feasibility of  $\text{H}_2$  dissociation on bare  $\text{Cu}_2$  and  $\text{Cu}_2^+$  dimers directs the formation of negatively charged hydride which in turn facilitates  $\text{HCOO}$  intermediate. This  $\text{HCOO}$  intermediate formation provides product selectivity for  $\text{HCOOH}$  over  $\text{CO}$ . Comparing the barrier heights for each reaction step on both the dimers, we have found  $\text{Cu}_2$  dimer to be more efficient catalyst over  $\text{Cu}^+$  dimer. This work paves a way in understanding how the role of hydride controls the activity and selectivity of the catalyst. The study further opens the scope for investigating and providing insights on the different mechanistic pathways as well as development of potential catalyst for  $\text{CO}_2$  reduction.



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# Molecular dynamics simulation study of permeation of insecticide DDT molecules through skin lipid bilayer

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DDT (dichloro-diphenyl-trichloroethane) is a persistent organochlorine insecticide that was initially used in controlling malaria, typhus and other insect-borne human diseases among the troops and civilians during the Second World War. Though use of DDT is banned in many countries due to its adverse effects on human health and biodiversity, it is still being manufactured and used as Indoor Residual Spraying (IRS) for malaria control in several developing countries in Africa and South-East Asia. Reports have shown that active or passive exposure to DDT can cause premature birth, early weaning and even cancer.[1] However, the detailed picture of percutaneous absorption of DDT through human skin is yet to be established. Molecular dynamics (MD) simulation is a widely used computational technique that can comprehend the permeation of DDT through skin lipid bilayer in atomistic details. The outermost layer of the epidermis called Stratum Corneum (SC) is the primary barrier for molecules to penetrate the human skin. The complex but unique intercellular lipid matrix of SC is responsible for the skin's permeation resistance.[2,3] In this study, the lipid matrix is modeled based on a splayed bilayer model with an equimolar mixture of ceramide (CER), cholesterol (CHOL) and free fatty acid (FFA). The permeation of DDT molecules across this bilayer is studied performing constrained MD simulations at a skin temperature of 310 K under NPT conditions. The free energy profile and diffusion coefficient along the lipid bilayer normal is calculated to incorporate the equilibrium and dynamic behaviour of DDT molecules in the bilayer. In the free energy profile, the free energy decreases in the lipid tail region after a slight increase near the headgroups of lipid. As for the diffusion coefficient profile, the diffusion coefficient value decreases as the permeant moves from bulk water to the interior of the bilayer. The permeation of DDT across the bilayer is found to be mainly affected near the lipid-water interface region. This study accounts for a qualitative picture of the passive diffusion of DDT through skin lipid bilayer.

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# Machine Learning Embedded Ansatz for Projective Quantum Eigensolver

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The intractability in storing and manipulating many-body wave functions (which grow exponentially with system size) is a significant hurdle towards practical application of classical many-body theories to determine the wave function and energy of large and/or highly correlated molecular systems. Quantum Computers provide an alternate infrastructure for solving fermionic many-body problem[1], among other applications, leveraging the principles of superposition and entanglement to orchestrate complex wave functions. While Variational Quantum Eigensolver[2] is one of the popular hybrid algorithms suitable for implementation in the currently available noisy quantum computers, it suffers from a few drawbacks mostly encountered during the variational optimization process. Projective Quantum Eigensolver[3], a recently developed quantum algorithm, addresses some of the drawbacks by employing a projective formulation to arrive at an iterative procedure to solve for the ansatz parameters by minimizing residues. The number of residues scales as the number of parameters. With the observation that all these parameters are not equally dominant to the macroscopic trajectory of convergence, one may select a few ‘principal’ parameters and map the remaining ‘auxiliary’ parameters as their unique functions[4-5]. We employ the Kernel Ridge Regression model to establish this map on the fly during the residue optimization. This gives rise to new dynamic ansatz which has only a handful of independent parameters which are optimized through quantum circuits, eventually resulting in a significant reduction in the quantum-gate utilization. With an appropriate regularization mechanism in the ML model, we show that our ansatz is highly resilient in noisy simulation in NISQ devices.

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# Molecular Thermodynamic Origin of Substrate Promiscuity in the Enzyme Laccase: Degradation of Dye Effluents

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Industrial dye effluents have emerged as significant health hazard. Laccases found in white rot fungi belong to the enzyme family of multi-copper oxidases (MCOs) those are capable of degrading a wide variety of dyes. This is a clear indication of enzyme substrate promiscuity where an enzyme can act on a broad range of substrates. In this work we explore the molecular thermodynamic origin of the substrate promiscuity<sup>1</sup> in laccases using a combination of steady state UV-Visible absorption spectroscopy, molecular docking and molecular dynamics simulation studies on the interaction of laccase enzyme with five common dye molecules with varying charge, size and shape. The spectroscopic studies confirm that the enzyme is capable to degrade all these dyes. Using the computational modelling and simulations we have demonstrated that the presence of various distinct conformational states of the protein active site and a neighbouring loop enables an “induced fit”<sup>2</sup> mechanism to accommodate dye molecules of widely different size and shapes in the active site. MM/GBSA<sup>3</sup> binding energy calculations have shown that the diverse selection of dye molecules exhibits surprisingly similar binding affinity caused by cancellation between different contributions namely electrostatic, hydrophobic and solvation energies. Our results highlight the potential of laccase as a multi-purpose degrader for industrial dye effluents.

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# Insights into Titan's atmospheric chemistry of HCN and ammonia.

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Biomarkers like HCN are observed in the stratosphere of Titan (Saturn's moon) in the form of a haze layer<sup>[1]</sup>. As it resembles early earth atmosphere<sup>[2]</sup>, in this work we have done unbiased chemical space search of HCN and ammonia. Exploratory study of artificial force induced automated search for reaction of HCN with NH<sub>3</sub> using PyAR (Python based aggregator and reactor), followed by transition state search of the reaction paths have been performed. Thereafter the kinetic study was done to get the probable products. The reactions here resulted in compounds containing imine, nitrile, and amine functional groups, and some N-heterocycles. Higher population of polyamines, polyimines and N-heterocyclic compounds obtained here may aid the formation of self-replicating RNA and DNA precursors<sup>[3,4]</sup> and thus can lead to life on Titan.

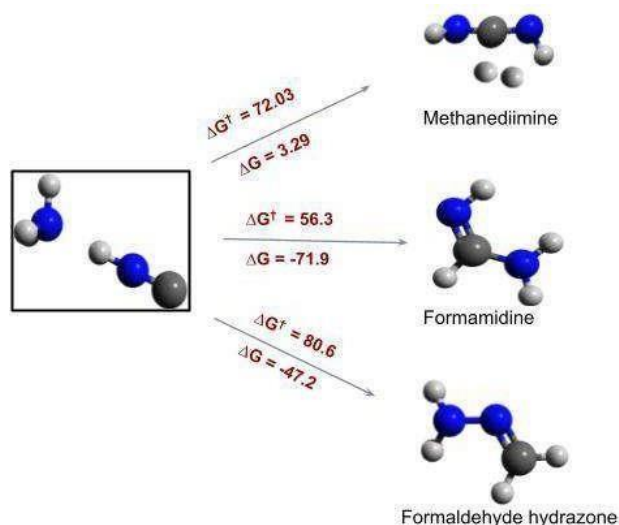


Figure 1: Prebiotic precursors obtained for HCN and ammonia reaction.

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# Ligands-Induced Open-Close Conformational Change During DapE Catalysis: Insights from Molecular Dynamics Simulations

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The microbial enzyme DapE plays a critical role in the lysine biosynthetic pathway and is considered as a potentially safe antibiotic target. In this study, atomistic simulations are employed to identify the modes of essential dynamics that define the conformational response of the enzyme to ligand binding and unbinding. The binding modes and the binding affinities of the products to the DapE enzyme are estimated from the MM-PBSA method and the residues contributing to the ligand binding are identified. Various structural analyses and the principal component analysis of the molecular dynamics trajectories reveal that the removal of products from the active site causes a significant change in the overall enzyme structure. Both, Cartesian and dihedral principal component analyses are used to characterize the structural changes in terms of domain unfolding and domain twisting motions. In the most dominant mode, i.e., the domain unfolding motion, the two catalytic domains move away from the two dimerization domains of the dimeric enzyme, representing a closed-to-open conformational change. The conformational changes are initiated by the coordinated movement of three loops (Asp75-Pro82, Gly240-Asn244, and Thr 347-Gly385) that triggers a domain-level movement. The time constant associated with the domain opening motion is estimated from multiple short trajectories as 43.6 ns. Physiologically, this close-to-open conformational change is essential for the regeneration of the initial state of the enzyme for the subsequent cycle of catalytic action and provides the apo enzyme enough flexibility for an efficient substrate binding [1].

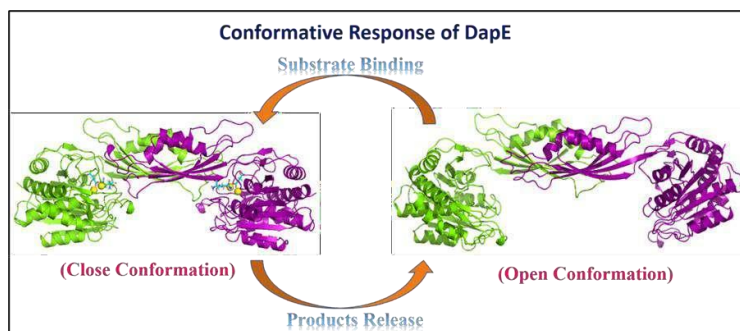


Figure 1. Conformative response of DapE enzyme

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# Temperature-Dependent NO Adsorption and Desorption in N-doped graphene monolayer

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Air pollution is one of the primary contributors to climate change that has a substantial influence on human health. Due to their unique properties, ultrathin two-dimensional (2D) materials have sparked great attention during the last decade in gas sensing applications. However, at finite temperatures, the adsorption/desorption behavior of gas molecules and sensors can be substantially altered. Understanding the nature of the sensors at different temperatures may thus aid in determining the optimal working conditions for the sensor [1]. In this work, ab initio molecular dynamics (AIMD) simulation and density functional theory (DFT) modeling were used to elucidate the adsorption-desorption performance of NO towards pyridinic double vacancy N-doped graphene [2]. Our findings from the AIMD simulation demonstrate that NO molecule can adsorb steadily at ambient temperature [3]. Additionally, the structural parameter, charge transfer, and electronic properties were examined and addressed thoroughly. Our study may shed light on the adsorption-desorption dynamics of the gas sensor at various temperatures and may help to find the optimum adsorption temperature for the sensor [3].

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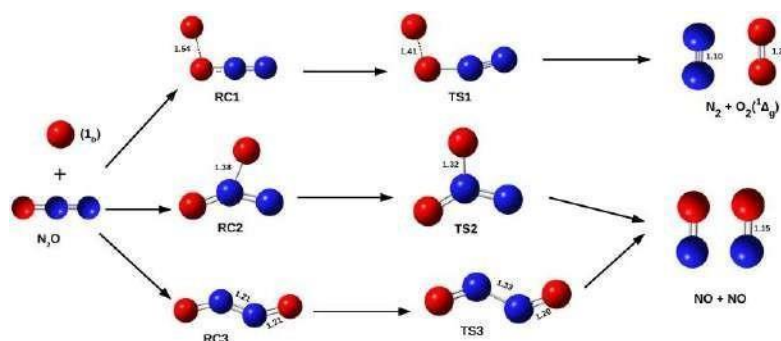
# The reaction energetics of $\text{N}_2\text{O} + \text{O} (^1\text{D}, ^3\text{P})$ reaction and role of post-CCSD(T) corrections in the energetics.

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In the modern time  $\text{N}_2\text{O}$  is emerges as the most potential threat to the ozone layer. It is also now the third most abundant green house gas in the atmosphere. Chemically in the stratosphere  $\text{N}_2\text{O}$  convert itself into NO radical by reaction with atomic oxygen. It is the NO radical which enters into the catalytic cycle of ozone destruction. Therefore, title reaction is fundamental importance in the ozone chemistry of stratosphere.

This reaction is considered as a difficult reaction in the computational chemistry for two reasons. First it involved the multi-reference species and hence challenging for the electronic structure calculations. Second,  $\text{N}_2\text{O}$  can react with singlet as well as triplet both O. Moreover some of the studies are suggesting that the non adiabatic effects are crucial to reproduce the experimental rate constant.



Therefore, in the present work, we have studied  $\text{N}_2\text{O} + \text{O} (^1\text{D}, ^3\text{P})$  reaction theoretically and computed the energetics and kinetics of the title reaction. Since, title reaction has multi-reference character, so we have performed post-CCSD(T) level of theory to estimate the energetics of the reaction. Further, we have also calculate the kinetics of the reaction using TST and Master equation approach.

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# The effects of surface mode vibrations on the H<sub>2</sub>/D<sub>2</sub>-Cu(111) dissociative scattering systems by using a chemically accurate PES

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The effect of surface modes vibrations on H<sub>2</sub>/D<sub>2</sub> scattering from a Cu(111) surface at different temperatures is being explored for hydrogen/deuterium molecules in their rovibrational ground state ( $v = 0, j = 0$ ). We assume weakly correlated interactions between molecular degrees of freedom and surface vibrational modes through a Hartree product type wavefunction [1]. While constructing the six-dimensional effective Hamiltonian, we employ (a) a chemically accurate potential energy surface according to the static corrugation model [2]; (b) normal mode frequencies and displacement vectors calculated with different surface atom interaction potentials [3-5] within a cluster approximation; and (c) initial state distributions for the vibrational modes according to Bose–Einstein probability factors. We perform 6D quantum dynamics [6] with the so-constructed effective Hamiltonian and calculate sticking and state-to-state scattering probabilities. The surface mode vibrations affect the chemisorption dynamics. The results display physically meaningful trends for both reaction as well as scattering probabilities compared to experimental [7] and other theoretical [2] results.

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# A Comparison of Quantum and Classical Theory for the Description of Coupled Electron Nuclear Dynamics of $H_2^+$ under Strong Linearly Polarized Laser Pulse

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Attosecond science brings the promise to be the ideal tool to probe the electron and nuclear dynamics in real-time [1]. One of the most fundamental issues still unexplored is the treatment of coupled electron-nuclear dynamics of multi-electron molecules in the strong-field regime, taking complete electron correlation into account [2, 3, 4]. Indeed, a full-dimensional quantum dynamical calculation beyond one-electron system is practically undoable to study such multi-electron effects in molecules. Presently, we have performed coupled electron-nuclear dynamics for one-electron molecule  $H_2^+$  being exposed to an ultrashort strong linearly polarized laser pulse along the molecular ( $z$ ) axis, where both quantum dynamical and quasi-classical models are employed by using 3D numerical solution of the time-dependent Schrödinger equation [6] and coupled Hamilton's equation of motion [2, 3, 4]. Effect of the initial vibrational state of the molecule as well as carrier envelope phase (CEP) of the laser pulse on the single ionization and dissociative ionization processes are studied in detail. Additionally, quantum-classical comparative studies on CEP dependent asymmetry parameters are performed for different initial vibrational states as well as Franck-Condon averaged quantities. Finally, the presently obtained results are compared with recently performed experimental findings [7].

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# The Role of Nonadiabatic Couplings in Spectroscopic Calculations of Aromatic Molecules

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Theoretically “exact” and numerically “accurate” Beyond Born–Oppenheimer (BBO) treatment [1-3] is implemented to construct diabatic potential energy surfaces (PESs) for several aromatic species, namely C<sub>6</sub>H<sub>6</sub><sup>+</sup> [4,5], 1,3,5-C<sub>6</sub>H<sub>3</sub>F<sub>3</sub><sup>+</sup> [6,7], C<sub>4</sub>N<sub>2</sub>H<sub>4</sub> [8] and 1,2-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub><sup>+</sup> molecules over a series of two-dimensional (2D) nuclear planes to include all possible nonadiabatic interactions among the low-lying electronic states. While computing the adiabatic PESs and nonadiabatic coupling terms (NACTs), we employ MRCI and CP-MCSCF methodologies as implemented in MOLPRO quantum chemistry software. Once are *ab initio* quantities (adiabatic PESs and NACTs) are obtained, those are used to construct single-valued, smooth, symmetric and continuous diabatic surface matrices for carrying out multi-state multi-mode nuclear dynamics with the help of time- dependent discrete variable representation (TDDVR) methodology to compute the photoelectron (PE)/photoabsorption (PA) spectra of the titled systems. In every case, our theoretically calculated spectra using BBO treatment and TDDVR dynamics show peak by peak correspondence with the experimental results as well as better than the findings of the multi-configuration time-dependent Hartree (MCTDH) method.

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### **About National Institute of Technology Meghalaya**

The National Institute of Technology (NIT) Meghalaya is one among the thirty one NITs in India established under the NIT Act 2007 (Amended 2012) of the Parliament of India as Institutes of National Importance with full funding support from the Ministry of Human Resource Development, Government of India. NIT Meghalaya took birth in 2010 and started functioning from its temporary campus in Shillong since 2012. NIT Meghalaya has secured 60th position in the Engineering Category, 12<sup>th</sup> among all NITs across the country, and 1<sup>st</sup> among all new NITs according to NIRF 2022, MHRD.

### **About North Eastern Hill University**

The North-Eastern Hill University Act (24 of 1973) passed by both Houses of Parliament received the assent of the President of India on May 26th, 1973. Initially, the academic departments and administration of the University at Shillong functioned from hired buildings. Very soon, however, NEHU acquired two prime properties in the city. The academic departments then moved to these two sites. Meanwhile, the Government of Meghalaya acquired, for the University, a land (measuring about 1225 acres) in Umshing, a little outside the city limits, for setting up its permanent campus. The University has been accorded a 4 star status by the National Assessment & Accreditation Council (NAAC) of India for a period of five years, commencing from September, 2000.

