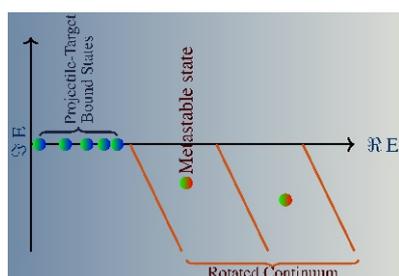


## Theoretical Chemistry

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New Theoretical Chemistry Methods:  
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Metastable states are obtained as complex eigenvalue solutions of the Schrödinger equation by imposing outgoing boundary conditions.

## ABSTRACT

The use of the latest theoretical methodologies and computational algorithms is driving chemistry research to new heights today. These remarkable new advances have enabled theoretical chemistry to move beyond the traditional field of ground-state chemistry of small molecular systems, allowing for innovative experiments to be proposed. With greater accuracy, it can now predict the excited-state and even the continuum-state chemistry of larger molecular systems by taking into account the relativistic motion of electrons. The integration of artificial intelligence and machine learning with these new theoretical developments has made theoretical chemistry a powerful and independent field of science. This article highlights the latest methodological advances made by Theoretical Chemistry Section, Chemistry Division, BARC in these areas.

KEYWORDS: Theoretical methodologies, Computational algorithms, Artificial intelligence, Machine learning

## Introduction

Theoretical chemistry, which was originally intended to provide conceptual and mathematical support for chemical and spectroscopic observations, became an independent field in the last century. Computers and computational algorithms have infused theoretical chemistry with remarkable predictability, accuracy, and enriched chemical reaction modeling. Current developments in theoretical chemistry enable it to expand the frontiers of chemistry in unprecedented ways. It has made significant original predictions in challenging fields including continuum-state chemistry, cold-chemistry, attosecond electron relaxation dynamics in molecules, light-matter interactions, modeling of astrochemical and prebiotic chemical evolution and validating the existence of symmetry violating interactions in nature originating from relativistic effects in many body systems. The symmetry violating interactions reveal 'a new physics' beyond the standard model of elementary particles, which are essential to understand the matter-antimatter asymmetry in our universe. The recent infusion of artificial intelligence and machine learning algorithms into theoretical chemistry has been instrumental in translating these developments to large chemical systems such as chemical solutions, bulk materials, and biological molecular systems. The contributions made by the *Theoretical Chemistry Section, Chemistry Division, BARC* towards these directions in recent times are briefly discussed here.

## Nuclear Metastability to Electronic Metastability: New Quantum Chemical Methods

Radioactive decay of metastable states of nuclei is of primary importance in nuclear physics and nuclear industry. Experimentally, the resonance structures observed in neutron-nucleus collision cross sections at low incident energy of neutron are associated with these metastable states.

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Consequently, they are also referred to as resonance states. In analogy to metastable nuclei, electronically metastable molecules can be prepared by low-energy electron (LEE)-molecule collisions [1]. Metastable negative ion states of a molecule, which are analogous to metastable nuclei created by neutron capture, are selectively and resonantly created simply by tuning the kinetic energy of the LEEs to the corresponding resonant electron attachment energy of the neutral molecular targets. Our focus here is on how electronic metastability is computed and how it helps us uncover a new area of chemistry, which we refer to as metastable-state chemistry. Quantum mechanically, metastable states are described by Gamow-Siegert wave functions, which are complex eigenvalue solutions of the Schrödinger equation obtained when imposing purely outgoing boundary conditions [2]. They do not belong to the Hermitian domain of the Hamiltonian. However, several mathematical methods have been developed to obtain these scattering solutions that correspond to metastable states in the Hermitian domain of the Hamiltonian itself [3,4]. The unbounded similarity transformation of the Hamiltonian is one of the most accurate mathematical approaches that map the scattering domain to the Hermitian domain. Like the unbounded similarity transformation, several analytic continuations of the Hamiltonian approaches have been used to extend the complex energy eigenvalue domain [3, 4].

Multiple analytical continuation approaches, including continuum remover complex absorbing potentials [5], complex back rotation transformation approaches [6], real-valued continuum remover potentials [7] and reflection free complex absorbing potentials [8] have been derived from our research. These methods are designed to utilize the advancements made by state-of-the-art bound state methods to directly calculate metastable states [3, 4, 9]. The continuum remover potentials which we developed are particularly interesting as they directly partition the continuum spectrum into the

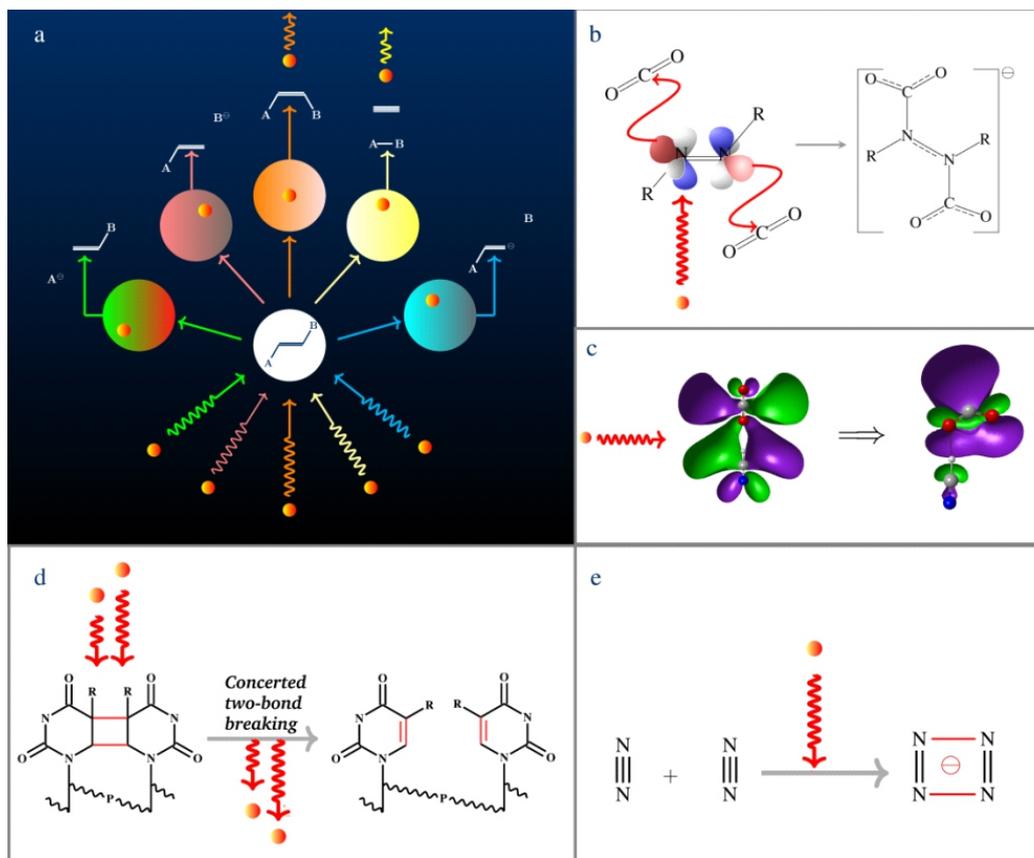


Fig.1: (a) Electron controlled chemistry: An illustration of the use of LEE as a chemical tool to perform state-specific and site-specific chemical reactions is shown using a substituted ethylene molecule as a target molecule. Each colour wavy-arrow represents the kinetic energy of the electron that is resonantly captured by the target molecule and the corresponding negative ion meta stable state is shown using the same colour. (b) LEE induced chemical synthesis (See ref. 12). (c) LEE induced chemical activation of CO<sub>2</sub> (See ref. 13). (d) LEE as a chemical catalyst and an agent for DNA repair (See ref. 18). (e) Chemical synthesis of theoretically predicted molecules (See ref. 11).

so-called Q-space and P-space wave functions, where the Q-space wavefunction is a projection of the metastable state wavefunction in the interaction region of the Hamiltonian. This partitioning of the discretized continuum domain helps us use this method in conjunction with the well-known Feshbach projection theory of nuclear metastable states for electronic resonance states [10]. In short, these new quantum chemical theoretical methods enable us to study the electronic metastability of molecules and their implications in chemistry, which has never been explored before.

### Metastable-state chemistry

The resonant capture of low energy electrons (LEEs, 0-30 eV) into the molecular field allows for chemical transformations to be made possible through metastable negative ion states of molecules. In practice chemical transformations specific to metastable negative ion states are triggered [11–14] and catalyzed [15–19] by tuning the kinetic energy of the LEEs to be the resonant electron capture energy of the molecules. Most remarkably, in addition to being state-specific, resonance attachment is an incredible tool for site-specific chemical reactions. This ability to create localized negative ion metastable states, in principle, can provide selectivity towards a site or even to a bond, which is one of the most attractive and ultimate goals of synthetic chemistry. The exploration of these experimental possibilities in molecular science to perform state-specific and site-specific chemical reactions has resulted in the use of LEE as a powerful quantum tool for controlling the chemistry of molecules (see Fig.1 (a)).

A remarkable theoretical demonstration of LEE as a chemical catalyst was achieved through our new quantum chemical methodology for electronic metastable states [15, 17–19]. This theoretical prediction, later proven experimentally [16], is believed to have a revolutionary impact on synthetic chemistry in the future. A few of the theoretical predictions we made based on this experimental possibility of using LEE as controlling and catalyzing chemical reactant are illustrated in Fig.1 (b-e). One of the immediate consequences of the LEE controlled chemical synthesis is that the theoretically possible chemical structures can be prepared through the resonant attachment of a low energy electron (LEE) through state specific reaction dynamics that have previously been unavailable [11, 14]. This possibility is discussed in Fig.1 (e).

Metastability can also occur when multiple photoexcited molecules are in the interaction region. Intermolecular Coulomb interactions facilitate the photoexcited metastable system to relax very rapidly via a new electronic relaxation channel available to the system, i.e., by ionizing an electron, and this mechanism is therefore known as intermolecular Coulombic decay (ICD). Since  $\pi$ -molecular systems are ideal chromophores for resonant electron excitation, and their  $\Pi^*$  excited state wavefunctions are diffused, this mechanism will be operative when a  $\pi$ -molecular system is photoirradiated with UV light. This mechanism in a  $\pi$ -molecular system was successfully demonstrated for the first time in literature by our theoretical and experimental efforts [20]. We have also unravelled a few of its revealed its remarkable implications in chemistry [21–23].

## Development and Implementation of Relativistic Electronic Structure Methods for Atomic and Molecular Systems

Our research activity deals with the theoretical studies of symmetry violating properties which are relevant for the search of electron electric dipole moment (eEDM) and to probe physics beyond the standard model (SM) of particle physics. In this context, we developed many new codes/modules which are integrated with the DIRAC program package from time to time, and interfaced DIRAC code with many in-house developed advanced coupled cluster (CC) codes for the highly accurate/precise calculations of electronic structure and relevant properties of experimentally promising atomic and molecular systems. The matter-antimatter asymmetry of the present-day universe is one of the biggest mysteries to scientists. In 1967, Sakharov [24] showed that the dominance of matter over antimatter in our universe can only be explained if these conditions are fulfilled- (a) there must be CP violation (where C and P means charge conjugation and parity invariance, respectively), (b) there must be non-conservation of baryon number, and (c) there must be interactions out of thermodynamic equilibrium. Our research activity deals with the first condition of Sakharov's proposal, i.e., searching for CP violation in atomic and molecular systems.

Observation of permanent electric dipole moment (EDM) [25] of a non-degenerate quantum system (i.e. stationary atomic or molecular state) arising from both the lepton as well as the hadron sector of matter such as the electron EDM, the nucleon-electron scalar-pseudoscalar (S-PS) interaction, the nuclear Schiff moment and the nuclear magnetic quadrupole moment (MQM) [26] is a signature of simultaneous violation of time-reversal (T) and parity (P) invariance. The T violation is equivalent to CP violation according to the CPT theorem. However, CP violation within the SM of elementary particles fails to explain the observed imbalance between matter and antimatter. Such CP-violating properties, viz., the EDM of electron and nucleons, the scalar-pseudoscalar (S-PS) [27-28] nucleon-electron neutral current interaction, and the nuclear MQM etc. can contribute to the permanent EDM of an open-shell paramagnetic molecular system, which, in principle, can be measured experimentally. To extract the values of electron EDM, nuclear MQM and S-PS coupling constants from the experimental data, various electronic structure parameters of potential molecular candidates are essential. These parameters cannot be obtained from any experiment but can be calculated from highly accurate ab initio methods that can treat the effects of both electron correlation and special relativity. The JILA [25] and the ACME [29] have performed electron EDM experiments using YbF and ThO, respectively. An experiment with BaF is underway by the NL-eEDM [30] collaboration. In 2014, we put an upper bound on the electron EDM as  $d_e \leq 9.7 \times 10^{-29}$  e-cm from our theoretical studies on ThO [31] and with the experimental data obtained from the ACME collaboration. A triatomic molecule, YbOH has also been proposed as a candidate for MQM experiment.

### Relativistic ab initio methods for symmetry violating and properties

We are involved in developing highly accurate wave-function-based methods that incorporates the electron correlation effects as well as the relativistic motion of electrons and then computing the accurate values of CP-odd molecular parameters. Property modules for the study of various symmetry violating interactions and the configuration interaction (CI)-based expectation value methods are implemented as new features and released with the open-

source code DIRAC program package [32]. The truncated CI-based methods are not size-extensive, which demands more robust wave-function-based methods for accurate prediction of CP-violating molecular parameters. On the other hand, coupled cluster methods at any level of truncation are always size-extensive and thus are more reliable than the truncated CI methods. In particular, the four-component relativistic CC-based methods are best suited for this purpose as it can simultaneously take care of the effects of electron-correlation and relativistic motion of electrons in an efficient way. We have been involved in the implementation of a number of relativistic single reference coupled cluster (SRCC)-based analytical methods, viz., Z-vector, expectation-value and extended coupled cluster (ECC) approaches for the precise calculations of molecular properties [33-35]. Out of these three methods, the Z-vector approach has been found to be the most reliable and efficient in predicting the said CP-odd molecular properties. Within the CC-based Z-vector approach, properties of interest can be computed by the following equation:

$$\Delta E' = \langle \Phi_{DHF} | (O_N e^T)_c | \Phi_{DHF} \rangle + \langle \Phi_{DHF} | \Lambda (O_N e^T)_c | \Phi_{DHF} \rangle$$

where,  $O_N$  is the normal-ordered property operator and  $T(\Lambda)$  is the excitation (de-excitation) operator whose amplitudes can be determined by solving the respective amplitude equations.  $|\Phi_{DHF}\rangle$  is the four-spinor-based Dirac-Hartree-Fock wave-function and is used as the reference function for constructing the CC wave-function  $|\Psi\rangle = e^T |\Phi_{DHF}\rangle$ . The c in the subscript of the above equation means the connectedness that ensures the size-extensivity of the method.

The new modules developed and implemented in DIRAC program package by us are one of the essentials tools for theoretical studies of CP violation. Furthermore, using our in-house developed relativistic coupled cluster methods, one not only can accurately predict the symmetry violating molecular properties but also can understand the role of electron correlation and special relativity in precise calculations of energy and properties of atomic and molecular systems.

### Mesoscopic Model for Plasmons of Noble-metal Clusters on a Solid Surface

Clusters of noble-metal atoms with 10 to 100 atoms adsorbed on a solid surface show electronic structure properties representative of molecules, and they can display collective electronic phenomena resembling to plasmons in metal solids. Our study shows the optical absorption by the nanostructured silicon (111) surface with large silver (Ag) clusters  $Ag_n$ ,  $n=33, 37$  (open shell) and  $n=32$  (closed shell), (Fig.2 (a)) adsorbed on the slab surface [36]. Adsorption of Ag clusters on Si surface increases the light absorption by large percentages with surges in absorption peaks in the regions of photon energies corresponding to localized plasmons (Fig.2 (b)). Absorption spectrum of metal cluster/solid surface structures is modelled employing a mesoscopic Drude-Lorentz model. A general description of the location and shapes of the absorption peaks related to plasmon frequencies can be related to the electron densities of finite metallic clusters. Therefore, plasmon frequency  $\omega_{pl}$  for the solid silver metal is connected to the electronic density per unit volume. We have derived a mesoscopic model connecting the electronic polarizability generated by plasmon oscillations and the applied electric field. These plasmon oscillations are dependent on the Lorentz restoring force due to the distribution of ion and electron charges in the system and to a dissipative Drude friction. The restoring force is directly related to the plasmon frequency ( $\omega_{pl}$ ) and friction term is connected to the plasmon relaxation time (lifetime) ( $\tau_{pl}$ ). Finally, an

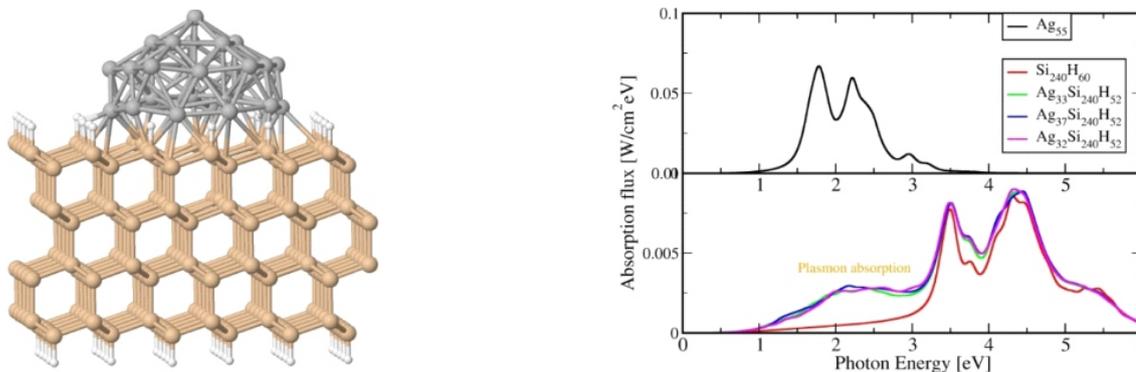


Fig 2: (a) The  $\text{Ag}_{32}\text{Si}_{240}\text{H}_{52}$  structure where  $\text{Ag}_{32}$  cluster is adsorbed on a Si surface. (b) Absorption spectrum for the  $\text{Ag}_n/\text{Si}(111)$  structures, Si surface and  $\text{Ag}_{55}$  cluster.

expression for the plasmon light absorbance per unit length is derived as follows [36].

$$\alpha_{pl}(\Omega) = \frac{1}{c\eta} \frac{\omega_{pl}^2 \Omega^2 / \tau_{pl}}{(\Omega^2 - \omega_{pl}^2)^2 + (\Omega / \tau_{pl})^2}$$

which shows a Lorentzian line shape. Here, the plasmon absorption peak (line shape) provides the frequency and lifetime of the plasmon. These two values can be extracted from our calculated absorption spectrum given in Fig.2 (b), which gives adsorbate ( $\text{Ag}_n$  cluster) plasmon frequency of  $\omega_{pl} = 3.9 \times 10^{15} \text{ s}^{-1}$  ( $h\omega_{pl} = 2.56 \text{ eV}$ ) and lifetime of  $\tau_{pl} = 0.5 \times 10^{-15} \text{ s} = 0.5 \text{ fs}$ . The calculated plasmon energies overlap with the appropriate solar photon energies, making the present structures and properties relevant to applications for solar cells and photocatalysis.

### Bridging Finite Size Properties to that of Bulk

Understanding the process of solvation in the condensed phase has been fundamental to diverse areas of research in chemistry, physics, biology, and related disciplines of science and engineering. Despite enormous interest, a precise quantification of the solvation energy for finite as well as bulk systems with unknown interaction potential remains elusive. Recently, with the advent of supersonic expansions and nozzle-beam techniques, solvation in finite-size hetero clusters has been amenable to experimental observation, and renewed interest has grown in the theoretical arena to connect the finite-size cluster properties to the bulk properties, viz., solvation energy, electron-detachment energy, and charge-transfer-to-solvent spectra [37-39]. A new general relation for the size-dependent solvation energy, electron-detachment energy, and charge transfer-to-solvent energy (CTTS) of finite size solvated negatively charged clusters is derived based on a microscopic theory with unknown interaction potential (see Fig.3). It is shown that the new extrapolation formula, when fitted to finite-size cluster data, yields significantly more accurate results for bulk values of  $\text{X.nH}_2\text{O}$  ( $\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SO}_4^{2-}, \text{C}_2\text{O}_4^{2-}, \text{Po}_4^{3-}$  etc) and  $\text{X.nCO}_2$  ( $\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-$  and  $\text{I}^-$ ) systems. Our present study reveals that the maximum error on the calculated bulk values, as compared to the experimentally measured ones is 5%. More importantly, the robust scheme proposed here provides a route

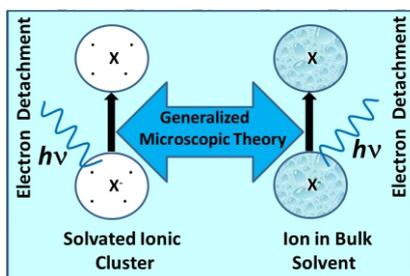


Fig.3: Connecting finite size properties to that of bulk

to obtain bulk values from the knowledge of electron-detachment energy and CTTS for finite and complex systems whose inter-particle potentials are unknown (see Fig.5). The general microscopic theory-based expression can also predict instability ranges of multiply charge anions e.g  $\text{SO}_4^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{PO}_4^{3-}$  etc [39].

Statistical mechanics and generalised linear response theory-based approaches are also employed to derive the analytical expressions for the size dependent dielectric constant and normalised orientation polarisation of solvents from the knowledge of the bulk value [40]. As an illustrative example, water is considered, and the dielectric constants for the same are calculated over the entire range of water clusters. Our results reveal that the dielectric constant and normalised orientation polarisation are monotonically increasing with the increase in the number of solvent molecules and converge to the respective bulk values in the thermodynamic limit. More importantly, the size dependent dielectric constant is found to be independent of the nature, geometry, and microscopic charges of the non-spherical ions, which offers a new platform for calculating the hydration energy and orientational polarisation based on linear response theory for different kinds of ions in the solvent medium.

### Machine Learning Models and Data Mining Tools for Large Scale Materials Exploration

Data Science along with advanced machine learning (ML) algorithms have shown potential applications in exploring new molecules and materials at a much faster pace as compared to the conventional methods [41]. In recent years, computational high-throughput screening of molecules and materials are shown to be promising to screen large database of molecule/materials for a particular application [42]. For such a large-scale screening, fast and accurate computational tools with optimum speed and accuracy are required. Quantum chemical or density functional theory (DFT) based methods can be more accurate, but these methods are computationally expensive and impractical for large scale studies. On the other hand, empirical and semi-empirical methods can be faster, but the accuracy and transferability can be poor. Hence, training machine learning models using reliable data can optimize the computational time and accuracy. In one of our recent studies, where the target was to screen a large database of metal organic frameworks (MOFs) for  $\text{CO}_2$  capture applications, accurate atomic charges were required to treat the host-guest interactions in a force field simulation. Since the atomic charges from DFT are very expensive and the empirical charge methods were reported to give inaccurate charges for certain atoms, we trained a machine learning model for assigning atomic charges to the atoms in MOFs [43]. A Random Forest ML algorithm has been trained using a limited set of features

representing both the elemental properties and the local bonding environment around that atom. Database of about 380,000 atomic charges were calculated using the Density Derived Electrostatic and Chemical (DDEC) method on a subset of the Computation-Ready Experimental Metal-Organic Framework (CoRE MOF-2019) were used to train, test and validate the model. Random forest regression algorithm was found to perform better among the considered models with  $R^2$  and mean absolute error values of 0.995 and 0.019 respectively. Our model has been deployed as open-source software, Partial Atomic Charges in Metal-Organic Frameworks (PACMOF) [44] and the package has been extensively used by the researchers in the field.

## Summary

We are consistently at the forefront in developing newer theoretical methods. Our in-house developed *ab initio* theories for metastable states have made remarkable original contributions in a yet-to-be explored area of chemistry. We have made a valuable contribution to the international joint initiative to develop a state-of-the-art *ab initio* method for the electron-correlated description of atomic and molecular systems including relativistic effects. New theoretical methodologies have also been developed and implemented for the *ab initio* computation of light absorption and subsequent dissipative dynamics in metal clusters. By incorporating statistical mechanics and generalized linear response theory-based approach, a better understanding of the process of solvation in the condensed phase is achieved. By developing a Python-based open-source machine learning code for large scale screening of metal organic framework, we are also confidently advancing into the future of data science. All these developments in our Section can lead to proposals for new experiments in different areas of science. To sum up, our Section has made significant accomplishments by developing new theoretical methodologies for frontier and interdisciplinary fields of science.

## References

- [1] S. J. Buckman and C. W. Clark, Rev. Mod. Phys. 66, 539 (1994).
- [2] N. Moiseyev, Non-Hermitian Quantum Mechanics (Cambridge University Press, 2011).
- [3] Y. Sajeev, A. Ghosh, N. Vaval, and S. Pal, International Reviews in Physical Chemistry 33, 397 (2014).
- [4] S. Basumallick, Y. Sajeev, S. Pal, and N. Vaval, J. Phys. Chem. A 124, 10407 (2020).
- [5] Y. Sajeev, V. Vysotskiy, L. S. Cederbaum, and N. Moiseyev, J. Chem. Phys. 131, 211102 (2009).
- [6] P. Balanarayan, Y. Sajeev, and N. Moiseyev, Chem. Phys. Lett. 524, 84 (2012).
- [7] Y. Sajeev, Chem. Phys. Lett. 587, 105 (2013).
- [8] Y. Sajeev, M. Sindelka, and N. Moiseyev, Chem. Phys. 329, 307 (2006).
- [9] S. Das, Y. Sajeev, and K. Samanta, J. Chem. Theory Comput. 16, 5024 (2020).
- [10] Y. Sajeev, M. Thodika, and S. Matsika, J. Chem. Theory Comput. 18, 2863 (2022).
- [11] Y. Sajeev, Mol. Phys. 117, 2162 (2019).
- [12] D. Davis and Y. Sajeev, Phys. Chem. Chem. Phys. 20, 6040 (2018).
- [13] D. Davis and Y. Sajeev, Phys. Chem. Chem. Phys. 16, 17408 (2014).
- [14] D. Davis and Y. Sajeev, J. Chem. Phys. 146, 081101 (2017).
- [15] D. Davis, V. P. Vysotskiy, Y. Sajeev, and L. S. Cederbaum, Angew. Chem., Int. Ed. 50, 4119 (2011).
- [16] D. Davis, S. Kundu, V. S. Prabhudesai, Y. Sajeev, and E. Krishnakumar, J. Chem. Phys. 149, 064308 (2018).
- [17] D. Davis and Y. Sajeev, Phys. Chem. Chem. Phys. 18, 27715 (2016).
- [18] D. Davis, K. G. Bhushan, Y. Sajeev, and L. S. Cederbaum, J. Phys. Chem. Lett. 9, 6973 (2018).
- [19] D. Davis and Y. Sajeev, Chem. Commun. 56, 14625 (2020).
- [20] S. Barik, S. Dutta, N. R. Behera, R. K. Kushawaha, Y. Sajeev, and G. Aravind, Nature Chemistry 14, 1098 (2022).
- [21] S. Barik, N. R. Behera, S. Dutta, Y. Sajeev, and G. Aravind, arXiv:2306.10263 [physics.chem-ph] (2023).
- [22] S. Barik, N. R. Behera, S. Dutta, R. K. Kushawaha, Y. Sajeev, R. O. Ramabhadran, and G. Aravind, Science Advances 9, eadi0230 (2023).
- [23] Y. Sajeev, Commun. Chem. 6, 259 (2023).
- [24] A. D. Sakharov, JETP Lett. 5, 24 (19ozlov, Phys. Rev. A 93, 012505 (2016).
- [27] S. Sasmal, H. Pathak, M. K. Nayak, Sov. Phys. Usp. 34, 392 (1991).
- [25] W. Bernreuther, and M. Suzuki, Rev. Mod. Phys. 63, 313 (1991).
- [26] T. Fleig, M. K. Nayak, and M. G. Kak, N. Vaval, and S. Pal, Phys. Rev. A 93, 062506 (2016).
- [28] S. Sasmal, H. Pathak, M. K. Nayak, N. Vaval, and S. Pal, J. Chem. Phys. 144, 124307 (2016).
- [29] V. Andreev et al., Nature 562, 355 (2018).
- [30] The NL-eEDM collaboration: P. Aggarwal et al., Phys. Rev. A 100, 052503 (2019).
- [31] T. Fleig, and M. K. Nayak, J. Mol. Spectrosc. 300, 16 (2014).
- [32] DIRAC, a relativistic *ab initio* electronic structure program, Release DIRAC23 (2023), written by R. Bast et al (available at <https://doi.org/10.5281/zenodo.7670749>, see also <https://www.diracprogram.org>).
- [33] S. Sasmal, H. Pathak, M. K. Nayak, N. Vaval, and S. Pal, Phys Rev A 93, 062506 (2016).
- [34] S. Sasmal, H. Pathak, M. K. Nayak, N. Vaval, and S. Pal, Phys Rev A 91:030503 (2015).
- [35] S. Sasmal, H. Pathak, M. K. Nayak, N. Vaval, and S. Pal, Phys Rev A 91, 022512 (2015).
- [36] T. Vazhappilly, D. S. Kilin, and D. A. Micha, Phys. Chem. Chem. Phys. 25, 14757 (2023).
- [37] A. K. Pathak, J. Phys. Chem. A. 120, 9776 (2016).
- [38] A. K. Pathak, J. Chem. Phys. 136, 234306 (2012).
- [39] A. K. Pathak, Int. J. Quan. Chem. 115, 413 (2015).
- [40] A. K. Pathak, A. K. Samanta, Mol. Phys. 115, 2508 (2017).
- [41] K. T. Butler, D. W. Davies, H. Cartwright, O. Isayev, A. Walsh., Nature 559, 547-555 (2018).
- [42] S. Kancharlapalli, R. Q. Snurr, ACS Appl. Mater. Interfaces 15, 28084-28092 (2023).
- [43] S. Kancharlapalli, A. Gopalan, M. Haranczyk, R. Q. Snurr, J. Chem. Theory Comput. 17, 3052-3064 (2021).
- [44] <https://github.com/snurr-group/pacmof>