

Continuum Models for Wet Electrified Interfaces of Materials

Oliviero Andreussi
Boise State University

Continuum polarizable models have a long history in computational chemistry, as they allow to provide low-cost access to chemical reactivity and spectroscopic properties of molecules in liquid solutions, while bypassing the need for statistical sampling of solvent molecules. The need to simulate electrochemical and electrocatalytic processes at the surface of materials has motivated a recent surge in the use of continuum models in condensed matter electronic structure simulations. When combined with computational thermodynamic approaches, continuum models allow a high-throughput characterization of the stability and catalytic activity of materials for electrochemistry and electrocatalysis applications. Moreover, leveraging experimental databases of solvation free energies for different solvents, these continuum models have shown to be able to describe solvation effects within chemical accuracy and with minimal and transferable empirical parameters. This unlocks the possibility to systematically screen environment effects, thus providing design strategies to optimize electrocatalytic processes and devices. Following an overview of these recent advances, applications of continuum models to the study of environment effects in electrocatalysis, such as for water splitting and recombination reactions on 2D materials, will be presented.

Adaptive Finite Differencing and Exascale Electronic Structure Calculations

Emil L. Briggs

North Carolina State University, NC 27695-8202

The promise of real space methods for large-scale DFT calculations has been understood for many years but fully realizing that promise has required extensive and ongoing development work. One of the advantages of real space is eliminating FFTs required by plane wave codes. While highly optimized FFT libraries are available for most computer architectures, they are inherently non-local and require $O(N \log N)$ floating point operations per dimension. Real-space grid methods can use finite difference techniques for the kinetic energy operator, which are local, advantageous for parallelization, and scale as $O(N)$. The tradeoff is that the resultant operator is an approximation while it is exact within a plane wave basis set. Minimizing the approximation error is critical for enabling high-accuracy calculations. We have developed a novel adaptive technique for generating operators that produce remarkable results compared to standard finite-difference-based operators. The new operators are implemented in the exascale RMG DFT/hybrid-DFT code (www.rmgdft.org), enabling RMG to achieve the same average accuracy as plane wave codes on the well-known Delta test for 71 elements in the periodic table. Extensive testing has shown that an 8th-order adaptive operator can produce more accurate results than a standard 12th-order operator at a much lower computational cost. Several large-scale examples will be presented.

Ensemble DFT for electronic excitations
Kieron Burke and friends
UC Irvine

I will review the basic theory of EDFT and its long history. I will compare it with other DFT approaches, including time-dependent DFT, thermal DFT, and Delta SCF. I will report on our latest results, which include proofs of some exact conditions for EDFT and some illustrations and results for the Hubbard dimer.

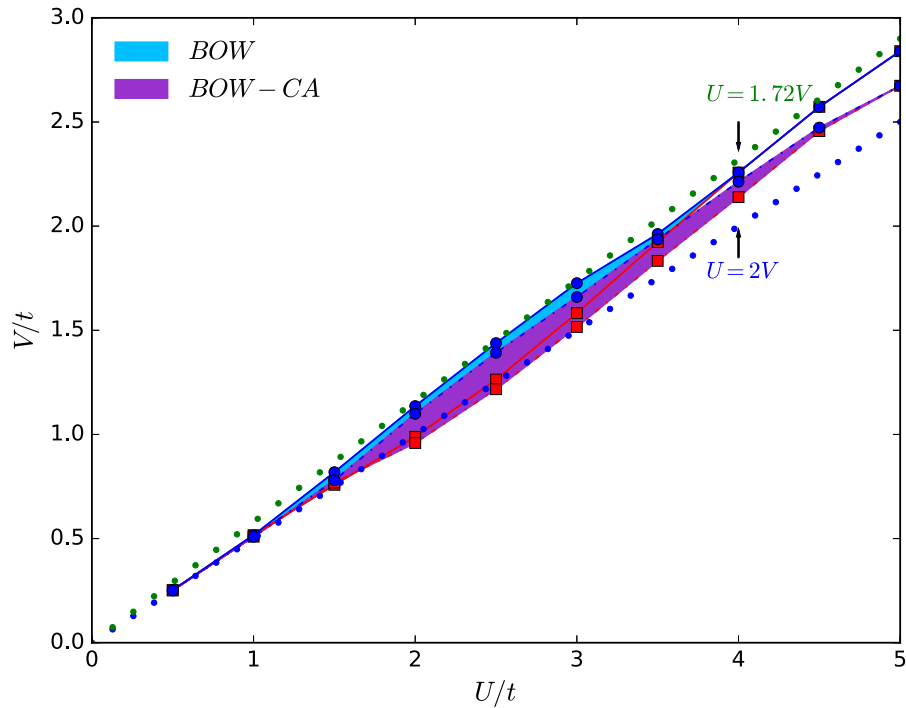
- **Exact and approximate Kohn-Sham potentials in ensemble density-functional theory** Yang, Zeng-hui, Trail, John R., Pribram-Jones, Aurora, Burke, Kieron, Needs, Richard J. and Ullrich, Carsten A., *Phys. Rev. A* **90**, 042501 (2014).
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- **Accurate double excitations from ensemble density functional calculations** Francisca Sagredo and Kieron Burke, *The Journal of Chemical Physics* **149**, 134103 (2018)
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Multiscale Functional Renormalization Group Approach to the 1D Extended Hubbard Model

David K. Campbell and Nahom Yirga
Boston University

We review our recent development of the Multiscale Functional Renormalization Group (MFRG) as an approach to the study of strongly correlated electronic materials in which both electron-electron (e-e) and electron-phonon (e-ph) interactions play important roles. Our MFRG method includes in a systematic manner the effects of the scattering processes involving electrons *away* from the Fermi surface and also permits proper inclusion of phonon retardation effects. After introducing the basic concepts, I will discuss in detail the application of this method to the 1D Extended Hubbard model and show that it correctly captures the subtle bond-order wave (BOW) phase in that model (see figure below).

We will then discuss additional applications of the MFRG method and show that it can be applied to multi-band models in higher dimensions, recovering previously known results and predicting novel behaviors that have been seen in experiment. Finally, we will discuss possible future applications of the MFRG approach.



Algebraic techniques for quantum computing in quantum chemistry

Artur Izmaylov
University of Toronto

Quantum chemistry problem is one of the attractive targets for demonstrating quantum advantage of quantum computing technology. Having strongly correlated systems as the main target, I would like to discuss what new classical computing techniques need to be developed to help quantum computing algorithms to solve the electronic structure problem. Encoding the electronic Hamiltonian in the second quantized form on a quantum computer is not a trivial problem, and its efficiency can become a bottleneck for the entire quantum solution. Dealing with this Hamiltonian can be facilitated by partitioning it into a sum of fragments diagonalizable using rotations from either small Lie groups or the Clifford group. These fragments are convenient for performing various algebraic manipulations required in circuit compiling and quantum measurement. I will illustrate how the Hamiltonian partitioning can be used to improve performance of several quantum algorithms for quantum chemistry (e.g. Variational Quantum Eigensolver and Quantum Phase Estimation).

Engineering Quantum Properties of Molecular Circuits with Chemistry

Maria Kamanetska
Boston University

I will describe my lab's recent progress in demonstrating and controlling quantum phenomena in single molecule junctions. We demonstrate that synthetic modifications can be leveraged to create functionality in such structures, with potential in quantum sensing, switching and high conductance of topological electronic states in molecules. I will describe in more detail the high conductance of topological insulator molecular wires we observe and the expanded 1D Su-Schrieffer-Heeger model we developed to explain our observations. Specifically, I will show that we achieve, at room temperature, conductance enhancements over two orders of magnitude in single molecule circuits formed with polycyclic benzoquinoidal (BQ_n) diradicals upon increasing molecular length by $\sim 5 \text{ \AA}$. We find that this extreme and atypical anti-ohmic conductance enhancement at longer molecular lengths is due to the diradical character of the molecules, which can be described as a topologically non-trivial electronic state. We adapt the 1D-SSH model originally developed to examine electronic topological order in linear carbon chains to the polycyclic systems studied here and find that it captures the anti-ohmic trends in this molecular series. The mechanism of conductance enhancement with length is revealed to be constructive quantum interference (CQI) between the frontier orbitals with non-trivial topology, which is present in acene-like, but not in linear, molecular systems. Importantly, we predict computationally and measure experimentally that anti-ohmic trends can be engineered through synthetic adjustments of the diradical character of the acene-like molecules. Overall, we achieve an experimentally unprecedented anti-ohmic enhancement and mechanistic insight into electronic transport in a class of materials that we identify here as promising candidates for creating highly conductive and tunable nanoscale wires.

Electronic structure and correlations in twisted multilayer graphene and related layered materials

Efthimios Kaxiras
Harvard University

In the past decade the field of twisted multilayer graphene and other layered materials, like the transition-metal dichalcogenide family, has blossomed to the point of being referred with its own term, "twistronics" [1]. New arrangements, including twisted n -layers ($n=3,4,\dots$), mixed layers, and multilayers of regular few-layer structures, are being studied experimentally and they are revealing ever richer behavior. We review theoretical investigations of some representative systems [2], starting with the iconic twisted bilayer graphene near the magic angle. Our work is based on first-principles tight-binding hamiltonians and includes atomic relaxation through the configuration space approach. A recent focus has been on deriving realistic representations of single-particle states for few-band hamiltonians and how those can be employed in studying many-body physics related to Mott insulator behavior, superconductivity and other manifestations of correlated electronic states [3].

Work supported by Army Research Office under Cooperative Agreement Number W911NF-21-2-0147 and by a grant from the Simons Foundation Award no. 896626.

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First-principles benchmarks for electronic response of warm dense matter

Alina Kononov
Sandia National Laboratories

Hydrodynamic simulations used to design and interpret fusion experiments rely on tabulated material properties over a wide range of pressures and temperatures as the target evolves from ambient conditions to a burning plasma. The intermediate warm dense regime presents unique challenges because models struggle to capture coexisting thermal and quantum effects accurately, while experimental characterization is rare and often suffers from large uncertainties. Here, we review ongoing work to advance computational methods for predicting electronic response properties of warm dense matter, including stopping power, x-ray scattering spectra, and conductivity. Using real-time time-dependent density functional theory (TDDFT), we benchmark and constrain efficient treatments based on average-atom methods and model dielectric functions [1-3]. Since the reliability of these more approximate models then depends on the credibility of the first-principles data, we scrutinize the methodological choices of the TDDFT calculations and show that sensitivities to pseudopotential details, projectile trajectory, and finite-size effects can lead to significant errors in computed stopping powers of around 15% [4,5]. We also discuss collective, nonlinear, and subtle band structure effects that are predicted by TDDFT, carry important implications for accurately simulating and diagnosing warm dense matter, and remain difficult for simplified models to capture [3]. Finally, we consider the prospects of emerging quantum computing technologies enabling even more precise benchmark calculations [6].

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

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Electron-Nuclear Correlation via the Exact Factorization Approach

Neepa Maitra
Rutgers University at Newark

The exact factorization approach enables the definition of exact potentials driving the dynamics of a quantum subsystem coupled to other quantum subsystems. These potentials yield insight into correlations and provide a useful starting point for new approximate methods e.g. for electronic structure embedding for strong correlation, for mixed quantum-classical dynamics of electrons and ions, and for photon-matter coupling. We briefly review recent progress in these areas, and highlight some success in predictions of exact-factorization-based methods compared with traditional methods, as well as some on-going improvements to the methods. Some of our recent work has focussed on electronic coherences, which are key to understanding and controlling photo-induced molecular transformations. While the evolution of electronic coherences is known to depend on nuclear motion, the exact nature of this electron-nuclear correlation has not yet been well-understood: are inherently quantum aspects of nuclear motion significant, or does an essentially classical picture capture the physics? We discuss the importance of the projected nuclear quantum momenta, and how spatial-resolution influences predictions of experiments even when they measure only spatially-integrated coherences. While traditional trajectory-based simulation schemes are blind to the quantum momenta, exact-factorization-based methods approximate these correlation terms, and correctly capture electronic coherences in a range of situations.

Modelling metallic solids with coupled cluster theory beyond CCSD

Verena A. Neufeld^{1,2} and Timothy C. Berkelbach²

¹ Division of Chemistry and Chemical Engineering, Caltech, Pasadena, California 91125, USA

² Department of Chemistry, Columbia University, New York, New York 10027, USA

While coupled cluster theory in its CCSD(T) formulation (incl. single, double, and perturbative triple excitations) can solve for electronic structure energies highly accurately, it cannot be applied to metallic solids due to an infrared divergence, which for example also affects second order perturbation theory/MP2. Since we therefore cannot employ CCSD(T) to go beyond CCSD for metallic solids, we suggest removing the divergence by resuming ring diagrams, “ring-CCSDT”. This is comparable to how the random phase approximation removes the divergence of second order perturbation theory. Using a model metallic solid, the uniform electron gas, as well as bulk lithium, we show that ring-CCSDT is cured of any divergence and gives structural properties and energies closer to CCSDT than CCSD. The runtime scaling of ring-CCSDT can be $O(N^7)$, the same as in CCSD(T), making it faster than CCSDT. Additionally, we investigate semi-empirical coupled cluster methods, namely distinguishable coupled cluster theory and spin component scaled coupled cluster theory, which both raise the accuracy of their original counterparts.

V. A. Neufeld, T. C. Berkelbach, *Phys. Rev. Lett.* 131 (18), 1503 (2023).

Effective interactions in many-body perturbation theory

Lucia Reining

Laboratoire des Solides Irradiés, *CNRS, Ecole Polytechnique, 91120 Palaiseau, France,*
and European Theoretical Spectroscopy Facility

Many-body perturbation theory is usually formulated in terms of a screened, instead of the bare Coulomb interaction. There is, however, no unique prescription for what this screened interaction should be. This is one of the reasons for the many different flavors that can be found in ab initio calculations, for example, for Hedin's GW approximation [1] for the self-energy. In this talk we will analyze the situation and give arguments for certain choices, both for the calculation of spectroscopic quantities and for the total energy. These choices can be formulated in terms of approximate vertex corrections to the GW expression, where W is defined to be the exact test charge-test charge screened interaction [2]. We then broaden the concept of the screened interaction to a generalized effective interaction, for which we derive in principle exact equations as well as promising approximations. We show that this allows one to go beyond the GW approximation in an efficient way, avoiding the computational complexity of full vertex corrections. A further way to speed up the calculations will also be introduced. Illustrations include quasiparticle energies, full spectral functions and total energies for model systems and real materials.

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Ab initio approach to nonlinear optical response with strong excitonic effects: formulation and applications

Jiawei Ruan,
University of California, Berkeley

Nonlinear optical (NLO) responses play a key role in fundamental science and technological applications. The theory and calculations of NLO responses including electron-hole interactions (excitonic effect), which is crucial for low-dimensional materials, remain underdeveloped. In this talk, we present a novel ab initio approach for calculating NLO responses that incorporates excitonic effects using an exciton-state coupling and Berry phase framework. We employ a diagrammatic representation to elucidate the detailed nonlinear excitonic processes and the underlying selection rules. As applications of the new method, firstly, we demonstrate that the significant enhancement of second harmonic generation (SHG) in monolayer MoS₂ and hBN is due to strong electron-hole interactions and specific excitons. In particular, our calculations reveal a prominent peak associated with C excitons in monolayer MoS₂, in excellent agreement with recent experiments. Secondly, we propose a method to generate a pure spin DC current (with zero net charge current) in zigzag graphene nanoribbons (ZGNR), which are 1D antiferromagnets, via a second-order NLO process. Further, by applying an additional static electric field, we can energetically separate and selectively excite the up and down spin channels of the ZGNR, enabling fully spin-polarized photocurrent generation. These properties make the ZGNRs promising candidates as versatile spin sources for spintronics applications.

Acknowledgment: This work was done in collaboration with Y.-H. Chan, J. Jiang, C. Hu and S. G. Louie, and was supported by the U.S. Department of Energy and the National Science Foundation.

Synthesizing computational and experimental strategies for the design and analysis of novel fuel-cell and battery electrolytes driven by the Grotthuss mechanism

Mark E. Tuckerman^{1,2,3,4,5}

¹Department of Chemistry, New York University, New York, NY 10003 USA

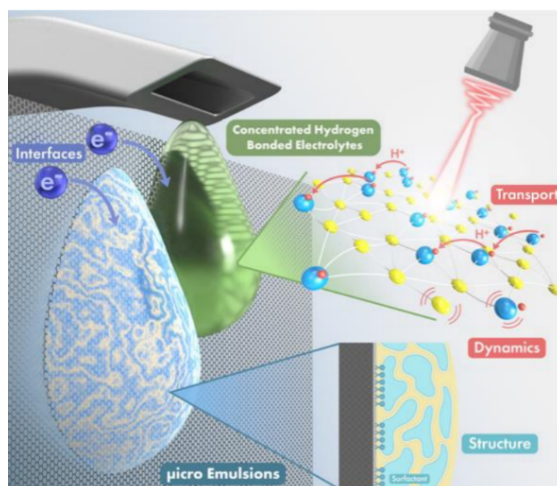
²Department of Physics, New York University, New York, NY 10003 USA

³Courant Institute of Mathematical Sciences, New York University, New York, NY 10012 USA

⁴NYU-ECNU Center for Computational Chemistry at NYU Shanghai, 3663 Zhongshan Rd. N. Shanghai 200062

⁵Simons Center for Computational Physical Chemistry at New York University, New York, NY 10003

Candidate systems for next-generation electrolyte materials, such as deep eutectic solvents and ionic liquids, often suffer from high viscosities, which suppresses rates of charge transport and limits their performance characteristics. A strategy for circumventing this problem is to leverage the structural or Grotthuss mechanism of proton transport through hydrogen-bond networks, in which charge transport occurs through a series of proton hops from donor to acceptor. Liquids that support the Grotthuss mechanism can exhibit high proton diffusion rates even when rates of vehicular charge transport are poor. In this talk, I will describe a project aimed at leveraging computational design and simulation approaches, in combination with experimental synthesis and characterization to develop novel classes of battery electrolytes based on the structural/Grotthuss diffusion mechanism. The workflow involves identification of a suitable proton-carrier liquid, a proton source, and a redox-active species capable of undergoing proton-coupled electron transfer (PCET) reactions. I will discuss the computational methods, which involve a combination of ab initio molecular dynamics and machine learning simulation techniques combined with path integrals for treating nuclear quantum effects, candidate chemical species selection for each of the components, protocols for combining these components into a high-performance electrolyte, current results, and next steps in the evolution of the project. Machine learning models include equivariant transformer networks, which allow for rapid training on relatively small data sets. This work will serve to illustrate both the power of modern computational approaches in the design of electrochemical systems but also to broaden the perspective on what constitutes a “breakthrough” electrolyte.



Towards ab initio simulations of driven and non-equilibrium systems through novel theoretical and numerical approaches

Vojtech Vlcek
University of California, Santa Barbara

In this talk, I will discuss the recent developments in the many-body perturbation theory in Green's function formulation, aiming to capture the (driven) dynamical correlations in realistic nanoscale condensed matter systems. Compared to the equilibrium methods, the out-of-equilibrium phenomena suffer from additional computational and theoretical bottlenecks manifested through the time non-local terms, leading to prohibitively costly simulations using the common condensed matter electronic structure approaches. I will, in particular, focus on overcoming these hurdles in non-equilibrium dynamics calculations and the possible truncations and reformulations of time-nonlocal quantum interactions. I will present numerical and data-driven methods, as well as a novel real-time Dyson expansion formalism that captures the non-equilibrium physics of driven systems exhibiting emergent quasiparticle phenomena. Among other advantages, it can be readily deployed together with real-time random sampling approaches, which revolutionized the calculations employing Green's function formalism and allow simulations of systems with tens of thousands of electrons at GW and post-GW levels.

Accelerating materials discovery through machine learning

C. Z. Wang

Ames National Laboratory – USDOE and Department of Physics, Iowa State University

Ames, Iowa 50011, USA

wangcz@ameslab.gov

Advanced materials are critical for modern technologies and a sustainable future. However, discovery, design, and synthesis of novel advanced materials (especially those containing three or more elements) with desired functionalities is of great challenge because the number of possible combinations in the composition-structure-property space is enormous and complex. We have developed a machine learning (ML) guided framework by efficiently integrating deep ML with the state-of-the-art computational methods, database, and experimental validations to tackle this grand challenge problem. Our ML-guided framework greatly reduces the complicity of the problem and makes *ab initio* calculations and structure search algorithms much more effective, thus dramatically accelerating the pace of materials discovery. Studies on the discovery of high performance rare-earth free magnetic materials and novel complex quantum materials will be presented. The challenges in closing the feedback loop between computational prediction and experimental synthesis will also be discussed.

Work done in collaboration with J. R. Chelikowsky, D. J. Sellmyer, K. M. Ho, W. Y. Xia, T. Liao, M. Sakurai, C. Zhang, R. H. Wang, H. J. Sun, L. Tang, B. Balasubramanian, T. J. Slade, P. C. Canfield, G. Akopov, and K. Kovnir.

Effective Hamiltonian Methods for Solid State

Stephen Winter
Wake Forest University

Quantum materials represent a broad class of systems whose experimental response relies on uniquely quantum aspects such as entanglement, Berry phases, and electronic correlations. Due to potentially high complexity of these materials, first-principles approaches often provide a vital bridge between experiments and theoretical models. In this talk, I will introduce our numerical strategies for systematically building low-energy models for quantum magnets with arbitrarily complex local charge, spin, and orbital degrees of freedom. We have recently applied these methods to treat: mixing of spin and orbital excitations in layered vdW magnets, and generic spin-phonon couplings for modeling topological thermal transport effects.

First Principles Structure Determination in Complex Environments: Leveraging Experimental Characterization and Machine Learning

Kendra Letchworth-Weaver
James Madison University

The interface between a solid surface and a liquid is relevant in applications such as water purification, corrosion, catalysis, and energy storage. The exact structure and composition of the solid surface crucially impacts ion adsorption, dissolution and intercalation and electron energy alignment between surface and reacting molecules. However, the structure of these surfaces is often challenging to probe experimentally under operating or growth conditions and the relevant reaction mechanisms are often unknown. Furthermore, even control of the termination of the bare surface via epitaxial growth is not always straightforward due to processes such as dynamic layer rearrangement. X-ray reflectivity (XRR) determines the electron density of an interface with high resolution but typically relies on model-dependent fitting to invert the data and obtain the corresponding atomic structure. First principles theory calculations of surface structure rely upon approximations which can be inaccurate for surfaces out of equilibrium and with defects. We will present software developments which integrate first principles theory of surfaces with experimental XRR measurements using global optimization algorithms, allowing us to more accurately determine interfacial structures than is possible through experiment or theory alone. Additionally, we will explore preliminary results utilizing a combination of first principles theory and machine learning to characterize local structure in high entropy oxides, which show promise as catalyst and battery materials.

Spin and charge orders of the two-dimensional electron gas in external triangular and honeycomb moiré potentials

Yubo Paul Yang
Flatiron Institute

Strongly interacting electronic phases are being discovered at an astonishing pace in moiré materials. In the past few years, generalized Wigner crystal (GWC), fractional Chern insulator (FCI), Kondo heavy fermion and kinetic magnetism have all been realized in transition metal dichalcogenide (TMD) bilayer devices. Fundamentally semiconductor junctions, these devices host electrons confined in 2D, which can be accurately modeled as a two-dimensional electron gas (2DEG). We explore the charge and spin orders of TMD moiré materials by solving the 2DEG under the influence of an external moiré potential [1]. In this talk, I will describe the model, methods, and interesting physics one can find. By tuning the shape of the potential and the form of the electron-electron interaction, we find evidence of generalized Wigner crystals (GWC) with noncollinear spin texture, ferromagnetic (FM) semimetal, and charge density wave phases. I will also briefly mention our efforts in using machine learning tools to uncover unusual properties of the 2DEG.

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Machine learning-enabled ab initio studies of water solutions in bulk and at interfaces

Chunyi Zhang
Princeton University

Machine learning methods have significantly expanded the accessible length and time scales of ab initio molecular dynamics (AIMD), enabling the exploration of previously inaccessible properties. In this talk, I will present our recent works using machine learning-enabled AIMD to investigate water solutions in bulk and at interfaces, which are critical for understanding processes fundamental to life and various energy applications.

Part 1: Dielectric permittivity of salt water [1]

The dielectric permittivity of salt water decreases with increased salt concentration, a phenomenon referred to as dielectric decrement. Our findings suggest that this decrement is due to the intrusion of ionic hydration shells into the hydrogen-bond network of the solvent water. This intrusion disrupts the hydrogen-bond network, suppressing the collective response of water molecules and consequently reducing the dielectric permittivity.

Part 2: Electrical double layer (EDL) at TiO₂-electrolyte interfaces [2]

We provide a molecular-scale picture of the EDL at TiO₂-electrolyte interfaces that demonstrates the limitations of standard mean-field models. We further develop a method to accurately calculate the electrostatic potential drop at the interface. The computed capacitance originating from the adsorbed charges and the potential drop agrees with experiments, supporting the reliability of our description of the EDL. The larger interfacial capacitance of basic relative to acidic solutions originates from the higher affinity of the cations for the oxide surface and gives rise to distinct charging mechanisms on negative and positive surfaces.

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