Electrostatic View at the Interface

Interfaces between two distinct materials form the basis for a broad spectrum of applications. Examples include photocatalytic, photovoltaic, spintronic, electronic, and superconducting devices. The disparity between the material properties provides the driving force for a variety of processes involving light, charges, spins, ions, and more complex chemical species. For instance, proton-coupled electron transfer at interfaces of water with metals and inorganic semiconductors is critical for photochemical water splitting. Dissociation of a photoexcited state into positive and negative charges supported by the two components of the interface constitutes the primary step in solar cells. Chemical hybridization between organic molecules and a metal substrate allows efficient spin injection into the organic layer. The interface between a topological insulator and a ferromagnet creates current by the Hall effect mechanism. Organic ionic liquids generate an electric layer that induces superconductivity in a flat film of an inorganic compound.

Required by design, the differences in the materials properties create theoretical challenges highlighted by Oliver Monti in the Perspective that focuses on complex, organic—inorganic interfaces (Monti, O. L. A. Understanding Interfacial Electronic Structure and Charge Transfer: An Electrostatic Perspective. J. Phys. Chem. Lett. 2012, 3, 2342–2351). The challenges arise due to the stark differences between the two components of the interface, organic molecules, which are studied by chemists, and solid-state materials, which belong to the realm of physics. On the one hand, molecules exhibit discrete, localized electronic states, unique vibrational frequencies, and well-defined, directional bonds. On the other hand, metals and inorganic semiconductors have highly delocalized electronic and vibrational states, forming continuous bands. Solid-state systems are often doped and may contain defects; moreover, dopants and defects can be critical for a given application. The surface of solid-state materials is quite sensitive to preparation, temperature, and the presence of solvent and other chemicals. The properties of semiconducting and metallic particles can be altered further by quantum confinement effects, which vary continuously with crystal size and shape. In contrast, molecular characteristics are well-defined and can be changed only in discrete steps by modifications in chemical composition and structure. The intrinsic dissimilarity between organic and inorganic systems requires different theories and experimental tools, developed in various scientific communities and often leading to redundant nomenclature and language barriers. Oliver Monti overcomes these difficulties by providing a simple electrostatic description of the interface that can be understood and utilized by most scientists. He argues that a fully classical electrostatic model captures the main characteristics of quite complex interfaces.

Oliver Monti starts the Perspective with a discussion of energy-level alignment in the two materials forming the interface. The gap between the levels drives interfacial charge separation in photovoltaic applications and contributes to overcoming the reorganization energy involved in chemical catalysis. Monti points out that the dipole moment developed across the interface alters the levels of noninteracting subsystems and describes this effect in terms of the interfacial electrostatic potential. He explicitly considers the depolarization and screening field and argues that these fields can be manipulated by functionalization of organic molecules with polar groups and by formation of well-ordered molecular layers. Then, Monti assesses the electrostatic description of level alignment by comparison with experiment. He evaluates the importance of dynamical effects, such as dipole moment fluctuations, and compares the classical electrostatic model with quantum mechanical calculations. Having discussed the energy levels at the interface, Monti considers the response of the organic molecular layer to the strong collective internal fields and to the external fields generated in spectroscopic experiments. He explicitly discusses how the Stark effect and photoelectron spectroscopy can be used to probe the molecular layer. Chemisorption, a more complex mode of interfacial interaction, is considered next. Here, Monti studies the nonclassical aspects of the Stark effect, considers interfacial charge transfer within the scope of the Marcus theory, and describes quantum mechanically the image potential states. The Perspective concludes that the simple electrostatic model provides an adequate depiction of the interface energetics in the case of physisorption, with chemisorption creating additional challenges. He points out that the strong internal fields generated at the interface can strongly affect the rates and mechanisms of interfacial charge transfer.

In the second Perspective, Francisco Raymo discusses the properties of photoactive molecules that can be used to extend the resolution limits of standard imaging techniques (Raymo, F. M. Photoactivatable Synthetic Dyes for Fluorescence Imaging at the Nanoscale. J. Phys. Chem. Lett. 2012, 3, 2379–2385). Optical microscopes are limited by diffraction, restricting the resolution to the distance on the order of the wavelength of light. Several hundred nanometers for visible light, this distance is significantly longer than desired in applications. By designing molecules that emit light at different time intervals, one can place judiciously multiple sequential probes and overcome the diffraction limit. The resulting technique is known as photoactivation localization microscopy (PALM). Raymo demonstrates how photoactive fluorophores allow one to visualize biological and nanostructured systems with spatial resolution that is impossible to achieve with conventional fluorescent probes.

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REFERENCES