Chemistry and electronic structure at interfaces from a molecular perspective

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Modern ab initio methods, particularly density functional theory (DFT), now address real-world challenges in the treatment of molecules, surfaces, and solids. Essential for interpreting cutting-edge experimental findings, especially in surface and interface science, these methods are about to step beyond mere analysis. Computational chemistry's aim is to rationalize trends and predict experimental avenues, necessitating accurate computations and robust, quantitative atomic and electronic structural analyses. This talk outlines our progress toward developing concepts for understanding and inspiring experimental approaches.

We will start from molecular chemistry for main group and transition metal complexes with investigations of superelectrophilic boron-cage anions.[1] We will further show the strengths of computational investigations and bonding analysis for the development of hybrid organic-inorganic interfaces at the examples of cyclooctyne-based functionalization of silicon and germanium surfaces.[2] The approach is also applicable to metal surfaces as we will show by the analysis of non-alternant aromatic compounds on noble metal surfaces where we see that aromaticity can play a key role in surface chemistry.[3] Recent endeavors towards understanding the longest-known polyacenes shows that alternant aromatic compounds still hold many surprises.[4] Finally, examples from solid state investigations show the combination of DFT and machine-learning approaches to predict bandgaps.[5] Most of the work is based around our energy decomposition method for extended systems (pEDA) which allows for quantitative analysis.[6]

In the last part of the talk, our application-focused efforts on atomic layer deposition, particularly area-selective deposition (AS-ALD), demonstrate strategies for achieving selectivity via small molecules that block non-growth areas, facilitating stable ALD processes through understanding surface chemistry and decomposition pathways. We will share findings from computations that elucidate experimental outcomes and a theoretical exploration into ALD layer decomposition, advancing towards predictive computational capabilities.[7–9]

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