Understanding the Conductance of Single-Molecule Junctions From First Principles

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Scientific Thrust Area and Relevant Molecular Foundry Proposals. A fundamental challenge in nanoscience is to understand and control charge transport in molecular-scale devices. In close collaboration with experimentalists, we are developing and applying theoretical methods to understand measurements of charge transport properties in single-molecule junctions. Some of the work summarized below has been carried out within the context of the following user projects:

- \textit{Conductance of Pyridine Linked Single Molecule Junctions}, L. Venkataraman (Columbia), Mark S. Hybertsen (BNL)
- \textit{Conductance of Amine Linked Single Molecule Junctions}, L. Venkataraman (Columbia), Mark S. Hybertsen (BNL)
- \textit{Aromatic Molecular States at Metal Surfaces}, M. S. Hybertsen, G. W. Flynn, Columbia University

Research Achievements. Recently, the electrical conductance of single-molecule junctions—small aromatics linked to macroscopic gold electrodes by amine and pyridine endgroups—has been reliably and reproducibly measured using modified break junction techniques [1,2]. These and other contemporary experiments provide an opportunity to benchmark standard first-principles methods while quantitatively exploring foundational concepts in molecular-scale charge transport. In recent User and internal research projects, we have developed and used a scattering-state technique [3] based on density functional theory (DFT) to understand reported transport measurements of single-molecule junctions. Using a physically motivated approximate self-energy correction based on GW calculations of a model metal-molecule interface [4], we

\textbf{Fig.} Atomic structure of benzene diamine, bonded to Au adatoms in a metal-molecule junction, optimized with DFT.
have worked closely with Foundry Users to study quantitatively how binding geometry [5], link chemistry [6], and molecular chain length affect transport properties [7] and, in some cases, lead to novel phenomena, such as mechanically-controlled conductance switching [6]. The importance of electronic level alignment at nanoscale interfaces for understanding conductance—and explaining these experiments—is emphasized in light of our results.

**Future Work.** We will continue our efforts toward developing an understanding of the physics of charge transport and energy conversion in molecular nanostructures and at organic-inorganic interfaces. Initially, we plan extend our existing theoretical approaches beyond the linear response regime to handle finite bias voltages, compute IV characteristics, and explore nonlinear phenomena associated with single-molecule junctions. We have also begun applying our methods to single-molecule heterojunctions, metal-molecule junctions consisting of “pn” donor-acceptor moieties relevant to organic photovoltaics, with the long-term goal of gaining deeper insight into fundamental electronic processes in solar energy conversion and catalysis.

**References**


**Relevant Molecular Foundry Publications**


