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:

- *Conductance of Pyridine Linked Single Molecule Junctions,* L. Venkataraman (Columbia), Mark S. Hybertsen (BNL)
- *Conductance of Amine Linked Single Molecule Junctions,* L. Venkataraman (Columbia), Mark S. Hybertsen (BNL)
- *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

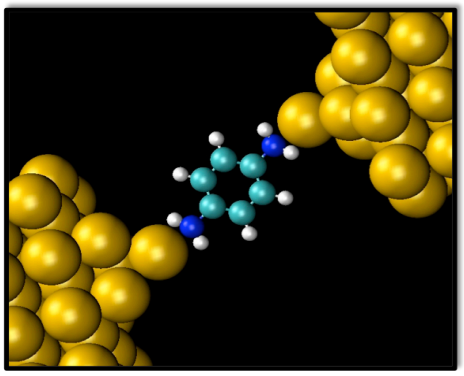

Fig. Atomic structure of benzene diamine, bonded to Au adatoms in a metal-molecule junction, optimized with DFT.

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

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Relevant Molecular Foundry Publications

[4] J. B. Neaton, M. S. Hybertsen, and S. G. Louie, "Renormalization of Molecular Electronic Levels at Metal-Molecule Interfaces," Phys. Rev. Lett. **97**, 216405 (2006)

[5] S. Y. Quek, L. Venkataraman, H. J. Choi, S. G. Louie, M. S. Hybertsen, and J. B. Neaton, "Amine-Au Linked Single-Molecule Junctions: Experiment and Theory", Nano Lett. **7**, 3477 (2007)

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