

TUNNEL CURRENTS ACROSS SILANE DIAMINES/DITHIOLS AND ALKANE DIAMINES/DITHIOLS

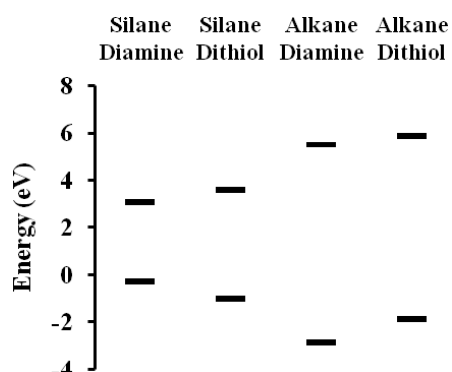
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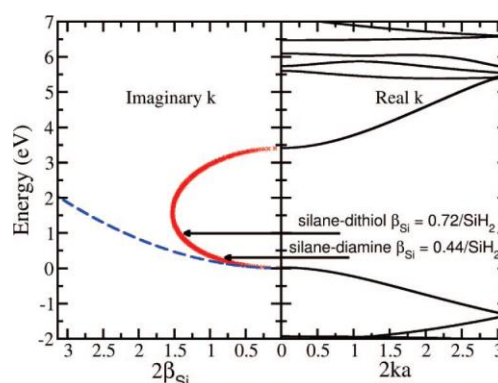
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This presentation focuses on the theoretical treatment of the electronic current across alkane and silane oligomers with amine end groups used to bond to metallic electrodes [1]. We use both a non-equilibrium Green's function (NEGF) method and a many-electron correlated scattering (MECS) methods to calculate electron transport. The low voltage conductance for these molecular systems decays exponentially with increasing length and our calculations reproduced this behaviour. Smaller conductance values and steeper decay in the alkane-bridged junctions are consistently found compared with the silane-bridged junctions, but quantitative differences in the decay constants obtained from the two formalisms arise. End group effects for both oligomers are also studied and analysed using a simple tunnel barrier model and complex band structure calculations.



Molecular frontier energy levels for the hexane and hexasilane bonded to gold clusters via amine and thiol end groups. Energies levels are approximated by the Kohn-Sham eigenvalues from the DFT B3LYP calculations. The zero of energy is taken to be the Fermi level approximated as the work function of gold (-5.1 eV).



Complex band structure for silicon hydride chains and silane-based tunnel junctions with amine or thiol linkers. The decreased HOMO-LUMO gap size in the silanes, compared to the alkanes, makes the values decay constant for silanes more sensitive to small differences in the Fermi-level alignment compared to alkanes.

The trend observed in the reduction of the decay constants for the silanes relative to the alkanes is consistent with a simple tunnel barrier model and a more rigorous complex band-structure analysis. However, the analysis also points out that the exact decay values for the silanes are sensitive to small errors in the energy level alignments. Of the four systems studied, the alkane diamine junctions seem to have the most tolerance for error in band alignment, partly due to the large HOMO-LUMO gap and partly due to the nature of the charge transfer between the gold electrode and amine linker. Because the silanes have smaller HOMO-LUMO gaps, errors in the band alignment for these systems are magnified and the inverse decay length is found to be extremely dependent on the exact Fermi-energy position. Nevertheless, the silane inverse decay length is found to be lower than that of the alkane decay value, indicating that σ -bond delocalization may be another means by which to tailor molecular electronic properties, serving

as an intermediate between π -conjugated and nonconjugated systems. This could serve as another potential tool in the tool kit of molecular transport engineering.

[1] A Comparative Study for the Calculation of Tunnel Currents Across Silane Diamines/Dithiols and Alkane Diamines/Dithiols, Shane McDermott, Chris George, Giorgos Fagas, J. C. Greer, and M. A. Ratner, *Journal of Physical Chemistry C* **113**, pp. 744-750 (2009)