Ab initio calculation of transmission and I-V curve for \( \pi \)-stacked polythiophene layers sandwiched between gold electrodes.

SERGEY FALEEV, FRANCOIS LEONARD, Sandia National Laboratories, MARK VAN SCHILFGAARDE, Arizona State University — We have applied an implementation of recently developed [Faleev et. al. PRB 71, 195422 (2005)] non-equilibrium Green’s Function method in framework of the tight-binding LMTO approach in its atomic sphere approximation to calculate the transmission function and I-V curves of \( \pi \)-stacked polythiophene layers sandwiched between Au(111) electrodes. Our approach is a fully ab initio all-electron approach that treats the central region and electrodes on equal footing. To the best of our knowledge, this is first application of an ab initio approach to calculation of transport properties of multiple polymer layers arranged parallel to the metal surface, as opposed to previously studied systems of a small molecule or oligomer attached at both ends to the electrodes. We found that for a number of layers \( L > 1 \), an increasingly pronounced dip in the transmission function is formed at energies from \( E_F \) to \( E_F + 0.5 \) eV, reflecting the semiconductor nature of a polythiophene multilayer film. The zero-bias conductance of the film exhibits large-L asymptotic behavior \( \sigma \approx G_0 \exp(-1.2(L-5)) \), starting with \( L \approx 6 \) that can be seen as a thickness of the thin polythiophene film at which a metal-semiconductor transition occurs. For \( L = 1 \), the current depends linearly on applied voltage, while at \( L > 1 \), current is non-linear, reflecting strong bias and energy dependence of the transmission function.