Electronic and Transport Properties of Molecular Junctions under a Finite Bias: A Dual Mean Field Approach

Shuanglong Liu[1], Yuan Ping Feng[1], Chun Zhang[1,2*]

[1] *Department of Physics, National University of Singapore, Singapore*
[2] *Department of Chemistry, National University of Singapore, Singapore*
* phyzc@nus.edu.sg

We show that when a molecular junction is under an external bias, its properties can not be uniquely determined by the total electron density in the same manner as the density functional theory (DFT) for ground state (GS) properties. In order to correctly incorporate bias-induced nonequilibrium effects, we present a dual mean field (DMF) approach in this paper. The key idea is that the total electron density together with the density of current-carrying electrons are sufficient to determine the properties of the system. Two mean fields, one for current-carrying electrons and the other one for equilibrium electrons can then be derived. By generalizing the Thomas-Fermi-Dirac (TFD) model to non-equilibrium cases, we analytically derived the DMF exchange energy density functional. It can be shown that when an external bias is applied, the exchange energy in the scattering region is always higher than the one calculated from DFT functional. We implemented the DMF approach into the computational package SIESTA to study non-equilibrium electron transport in molecular junctions. Calculations for a graphene nanoribbon (GNR) junction show that compared with the commonly used *ab initio* transport theory, the DMF approach could significantly reduce the electric current at low biases due to the non-equilibrium corrections to the exchange potential the current-carrying electrons experience in the scattering region. The DMF approach also enables us to do detailed analysis for the spacial information of the non-equilibrium steady state, which will for sure greatly improve the understanding of molecular scale junctions under an external bias.