Ab initio Calculation of Transport Through Single Molecules: Organometallic Spintronics and the Dramatic Role of the Exchange-Correlation Potential

Harold U. Baranger,[1] San-Huang Ke,[2] and Weitao Yang[2]

Duke University, Departments of [1]Physics and [2]Chemistry, Durham NC 27708

To describe conduction through a single molecule requires combining accurate chemical information with a suitable transport model. A standard approach is to find the transmission of single-particle states described by density functional theory using a local exchange correlation (*xc*) functional. We have used this approach to study the possibility of organometallic spintronics in molecules containing two cobaltocene moieties – see Figure 1.

To test and extend the standard methodology, we construct new *xc* potentials based on the optimized effective potential (OEP) approach and calculate electron transmission through two atomic chain systems, one with charge transfer and one without. We performed calculations using LDA, HF, EXX-OEP, B3LYP, B3LYP-OEP, and MP2-OEP. The main findings are: **(1) The OEP approach dramatically alters the molecular conductance**, largely by changing the LUMO state and the HOMO-LUMO gap. **(2)** For systems without charge transfer, the conductance is closely related to the HOMO-LUMO gap and the coupling strength. For strong coupling, the different local *xc* potentials give comparable results, while as the coupling weakens, differences grow. **(3)** For systems that may have charge transfer, the presence or absence of self interaction error (SIE) plays a key role. The most accurate result for the conductance, from MP2-OEP, is in between those given by EXX-OEP (no correlation or SIE) and B3LYP-OEP (some correlation and SIE).

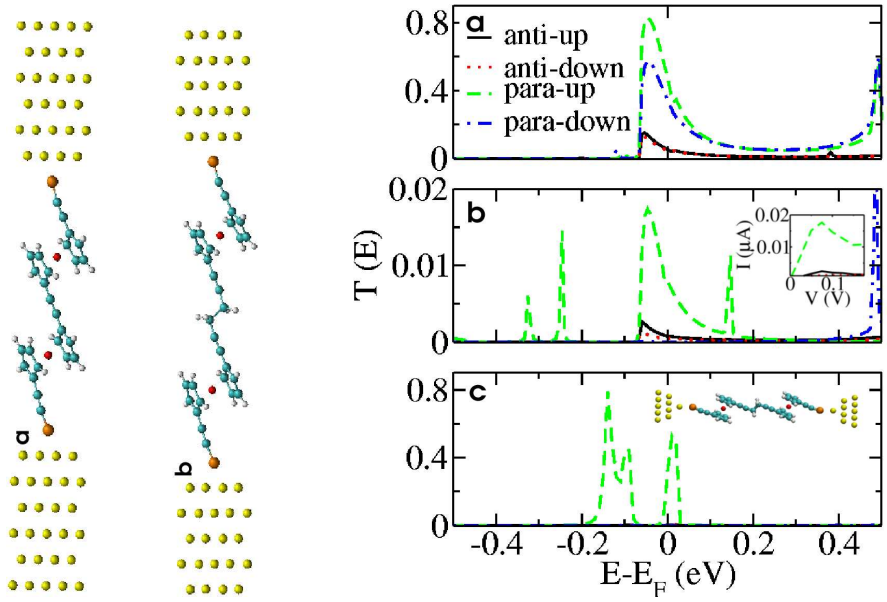

FIG. 1: **Molecular Conductance** LEFT: Dicobaltocene (DiCo) and dicobaltocene with an alkane spacer (DiCo-2C) adsorbed at hollow sites on Au(001) leads. (Yellow, white, blue, red, and orange denote Au, H, C, Co, and S atoms.) Each cobaltocene is spin 1/2. In dicobaltocene, the two spins can be in either a singlet or triplet state; their interaction occurs via superexchange through the spacing atoms. When the spacer is fully conjugated as in DiCo, the interaction is strong so that the singlet has much lower energy; however, in DiCo-2C, the exchange is much weaker (3 meV). RIGHT: Transmission functions of (a) DiCo and (b) DiCo-2C. *I-V* curve of DiCo-2C is shown in inset. (c) Transmission function of DiCo-2C adsorbed on the top of additional gold atoms as in the inset. Solid and dotted lines correspond to the up and down spin components of the antiparallel confi guration, while dashed and dashed-dotted lines are for spin up and down in the parallel confi guration. **Note the strong switch behavior in all cases.**