Orbital views of molecular conductance and spintronics

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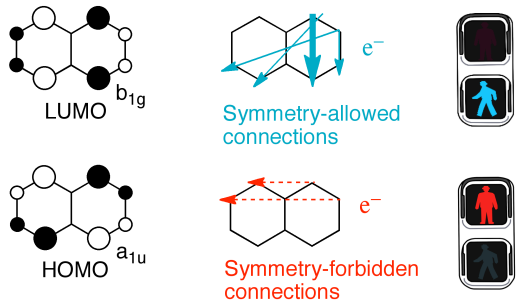
We have developed a chemical way of thinking about electron transport in molecules in terms of frontier orbital theory [1-4]. The phase and amplitude of the HOMO and LUMO of π-conjugated molecules determine the essential properties of their electron transport. By considering a close relationship between Green's function and the molecular orbital, we derived an orbital rule that would help our chemical understanding of the phenomenon. First, the sign of the product of the orbital coefficients at sites *r* and *s* in the HOMO should be different from the sign of the product of the orbital coefficients at sites *r* and *s* in the LUMO. Secondly, sites *r* and *s* in which the amplitude of the HOMO and LUMO is large should be connected. Recently we confirmed these theoretical predictions experimentally by using nanofabricated mechanically controllable break junctions to measure the single-molecule conductance of naphthalene dithiol derivatives [5]. The measurement of the symmetry-allowed 1,4-naphthalene dithiol shows a single-molecule conductance that exceeds that of the symmetry-forbidden 2,7-naphthalene dithiol by two orders of magnitude.

Spintronic properties of cyclobutadiene (CBD) systems are investigated based on a qualitative frontier orbital analysis [6]. CBD undergoes a Jahn-Teller distortion from the square triplet state to the rectangular singlet state. According to the qualitative Hückel molecular orbital analysis, the electron transport through the square triplet state is symmetry allowed while that through the rectangular singlet state is symmetry forbidden. The magnetic triplet state is a possible coexisting system of conductivity and magnetism. Sophisticated first-principles quantum chemical calculations are performed by using a realistic molecular junction model. Interesting spin filtering properties are found in the square-shaped CBD system. The high- and low-spin states of the square-shaped CBD system produce the spin-α and -β polarized conductance, respectively.



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