[P1] Frontier Orbital Rule for Electron Transport in Molecules

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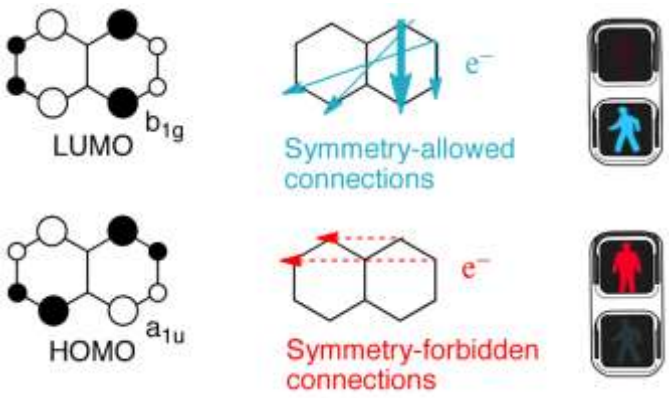
We have developed a chemical way of thinking about electron transport in molecules in terms of frontier orbital theory [1-4]. The phase and amplitude of the HOMO and LUMO of π-conjugated molecules determine the essential properties of their electron transport. By considering a close relationship between 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 for good electron transport, as indicated in the scheme. Secondly, sites *r* and *s* in which the amplitude of the HOMO and LUMO is large should be connected. 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.



The intermolecular electronic coupling in π-stacked structures plays an important role in the electron conduction in extended systems. We studied a π-stacked benzene molecule [2,2]paracyclophane to investigate the effect of the intermolecular interactions in aromatic hydrocarbons on its electron-transport properties [6]. According to the orbital symmetry rule, the symmetry-allowed and symmetry-forbidden connections for electron transport between the benzene rings are predicted just from the phase and amplitude of the frontier orbitals. The *meta* connection is symmetry allowed for electron transport while the *para* and *ortho* connections are symmetry forbidden. The qualitative predictions made with the Hückel approximation are found consistent with the calculation results obtained with density functional theory. The qualitative but essential understanding in the orbital views would extend the application of the rule from a single molecule to a crystal structure for the development of high performance molecular devices.

Bibliography:

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