

Fukui Functions in Dewar Molecules

Paul W. Ayers, and James S. M. Anderson

*Department of Chemistry, McMaster University
Hamilton, Ontario, Canada*

Frontier orbital theory is a very valuable tool for predicting reactivity, typically combining the virtues of simplicity and qualitative accuracy. Unfortunately, frontier orbital theory does not always indicate the most reactive sites of a molecule. A few molecules where frontier is known to fail dramatically were presented by Dewar in (1989)¹. The Fukui function, which measures how the electron density of a molecule changes when electrons are added or subtracted, is the analogue of the frontier molecular orbital in density-functional theory. We examine whether the Fukui function is better than the frontier molecular orbital theory for Dewar's examples. By itself, neither the Fukui function nor the frontier orbitals can explain the observed chemistry, and results from the two reactivity indicators are similar. However, if electrostatic effects pertaining to the reactants are accounted for, the Fukui function does become an important tool for describing these systems' reactivity.

1) M.J.S. Dewar *Journal of Molecular Structure (Theochem)*, **200** (1989) 301-323.