Density Functional Approach to the Frontier-Electron Theory of Chemical Reactivity

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We here demonstrate that most of the frontier-electron theory of chemical reactivity can be rationalized from the density functional theory of the electronic structure of molecules. Consider a species S with N electrons, having ground-state electronic energy $E(N,\rho)$ and chemical potential $\mu(N,\rho)$, where $\rho$ is the potential acting on an electron due to all nuclei present. The chemical potential is the negative of the electronegativity. The energy as a function of $N$ has a discontinuity of slope at each integral $N$, and so there are three distinct chemical potentials for each integral $N$, $\mu^i = (\delta E/\delta N)^i$ (from positive-ion side), $\mu^- = (\delta E/\delta N)^{-}$ (from negative-ion side), and $\mu^0 = (\delta E/\delta N)^0 = \mu^+ + \mu^-$ (unbiased).

Fundamental equations for changes in energy and chemical potential are

$$dE = \mu \, dN + \int \rho(\mathbf{r}) \, dv(\mathbf{r}) \, d\mathbf{r}$$

and

$$d\mu = 2\eta \, dN + \int f(\mathbf{r}) \, dv(\mathbf{r}) \, d\mathbf{r}$$

where $\rho(\mathbf{r})$ is the electron density, $\eta = 1/(\partial \mu/\partial N)$, and the function $f(\mathbf{r})$ is defined by

$$f(\mathbf{r}) = [\delta \rho / \delta v(\mathbf{r})]_N = [\delta \rho(\mathbf{r}) / \delta N]_v$$

The equality in this formula is a Maxwell relation for eq 1. The function $f$ is a local quantity, which has different values at different points in the species. It admits of contour maps.

Our argument will be that large values of $f$ at a site favor reactivity of that site. We therefore call $f(\mathbf{r})$ the frontier function or Fukui function for a molecule.

If a reagent R approaches S, what direction will be preferred (from among several directions that can produce the same type of chemical bond)? The quantity $d\mu$ in eq 2 measures the extent of the reaction. We assume that the preferred direction is the one for which the initial $d\mu$ for the species S is a maximum. The first term on the right side of eq 2 involves only global quantities and at large distances is ordinarily less direction sensitive than the second term. We may then assume, more or less equivalently in the usual cases, that the preferred direction is the one with largest $f(\mathbf{r})$ at the reaction site. Reactivity is measured by the Fukui index of eq 3.

Equation 3 in fact provides three reaction indices, because $\rho(\mathbf{r})$ as a function of $N$, like $E(N)$, has slope discontinuities. We therefore have the firm predictions, governing electrophilic attack,

$$\Gamma^-(\mathbf{r}) = (\delta \rho(\mathbf{r}) / \delta N)_-$$

governing nucleophilic attack,

$$\Gamma^+(\mathbf{r}) = (\delta \rho(\mathbf{r}) / \delta N)_+$$

and governing neutral (radical) attack,

$$\Gamma^0(\mathbf{r}) = (\delta \rho(\mathbf{r}) / \delta N)^0$$

The three cases have $\mu^+ > \mu_R$, $\mu^- < \mu_R$, and $\mu^0 \sim \mu_R$. A "frozen core" approximation now gives $d\rho = d\rho_{electron}$ in each case, and therefore, governing electrophilic attack,

$$\Gamma^-(\mathbf{r}) = \rho_{HOMO}(\mathbf{r})$$

governing nucleophilic attack,

$$\Gamma^+(\mathbf{r}) = \rho_{LUMO}(\mathbf{r})$$

and governing radical attack,

$$\Gamma^0(\mathbf{r}) = \rho_{HOMO}(\mathbf{r}) + \rho_{LUMO}(\mathbf{r})$$

These are the rules of classical frontier theory. Errors in eq 7–9 should be small in the outer reaction sites toward which the reagent approaches. Frontier theory is equivalent, then, to the assumption that it is favorable for $f$ to be big at $r$, and that direction is preferred along which the incoming reagent will produce the biggest change in the system's electronic chemical potential.

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