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FUKUI FUNCTION: THE MO VIEWPOINT REVISITED

by

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ABSTRACT

It is shown that the density functional definition of the Fukui function leads, when applied to the LCAO-MO formulation, to the familiar density contour maps of the frontier orbitals.

Key-words: Fukui function; Frontier orbitals.

The Fukui function has been defined within the density functional theory¹, providing thus a theoretical basis to the classical frontier orbital reactivity indices²⁻⁴. Several other works have ensued, all referred to the density functional framework⁵⁻⁸. It is perhaps time to return to the original MO viewpoint, in the light of the recent developments.

We shall show in the present Letter that if we apply the definition of the Fukui function given in¹ to the LCAO-MO formulae for the electron density, the MO picture proposed by Fukui²⁻⁴ follows. That is, the MO approximation predicts the same result than density functional theory.

The Fukui function $f(\vec{r})$ for an N-electron species S^0 is a local quantity, defined as¹

$$f(\vec{r}) = [\partial \rho(\vec{r}) / \partial N]_v \quad (1)$$

where $\rho(\vec{r})$ is the electron density and v is the external potential. Now, in any non-orthogonal atomic basis $\{\phi_a\}$ the LCAO-MO expression for ρ is

$$\rho(\vec{r}) = \sum_i n_i \rho_i(\vec{r}) = \sum_i n_i \sum_{ac} x_{ia} x^{ic} \phi_c(\vec{r}) \phi_a(\vec{r}) \quad (2)$$

where x_{ia} (x^{ia}) are the covariant (contravariant) coefficients of the atomic orbital $\phi^a(\phi_a)$ in the i-th MO. This is nothing but the tensor transcription⁹ of the more widely known Chirgwin-Coulson formulation¹⁰.

As we mentioned in¹¹, in the process $S^+ \rightarrow S^0 \rightarrow S^-$ (or vice versa) N changes through the variation of the occupation num-

bers of the HOMO and the LUMO (let us say n_1); we have proposed in this way a prescription for the theoretical estimate of molecular hardness. Hence, from eq. (1),

$$\partial \rho(\vec{r}) / \partial N = \partial \rho(\vec{r}) / \partial n_1 = \rho_1(\vec{r}) \quad (3)$$

This equation links the "frozen core" approximation to $f(\vec{r})$ in density functional theory for atoms⁸ with the Fukui MO approach.

Since for electrophilic reactions (f^-) the varying n_1 is the HOMO occupation number and for nucleophilic reactions (f^+) it is the LUMO's, it follows that

$$\begin{aligned} f^-(\vec{r}) &= \rho_{\text{HOMO}}(\vec{r}) \\ f^+(\vec{r}) &= \rho_{\text{LUMO}}(\vec{r}) \end{aligned} \quad (4)$$

just as obtained in Ref.¹. By (2) and (3),

$$f^\pm = \sum_{ac} x_{ia} x^{ic} \phi_c(\vec{r}) \phi^a(\vec{r}) \quad (5)$$

where i denotes the HOMO for f^- and the LUMO for f^+ .

Similarly¹, for radical attack

$$f^0(r) = [\rho_{\text{HOMO}}(\vec{r}) + \rho_{\text{LUMO}}(\vec{r})] / 2 \quad (6)$$

The "frozen core" approximation is, for this problem, more legitimate than it appears at first sight. We have seen¹² that the energy levels depend on the other levels' occupation numbers, rather than on their own occupation number and that the corresponding relaxation effects (i.e. the dependence of the

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x_{ia} on n_i) are in great extent negligible. We may hence safely ignore $\partial\rho_i(\vec{r})/\partial n_i$.

Therefore, simple MO density contour maps fo HOMO and LUMO describe indeed patterns for electrophilic and nucleophilic reactive sites⁴. Their reliability, of course, depends on the quality of the wave functions. The original Fukui approach gains thus another insight.

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