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Removing Electrons Can Increase the Electron Density: A Computational Study of Negative Fukui Functions

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Ab initio and density-functional theory calculations for a family of substituted acetylenes show that removing electrons from these molecules causes the electron density along the C–C bond to increase. This result contradicts the predictions of simple frontier molecular orbital theory, but it is easily explained using the nucleophilic Fukui function—provided that one is willing to allow for the Fukui function to be negative. Negative Fukui functions emerge as key indicators of redox-induced electron rearrangements, where oxidation of an entire molecule (acetylene) leads to reduction of a specific region of the molecule (along the bond axis, between the carbon atoms). Remarkably, further oxidization of these substituted acetylenes (one can remove as many as four electrons!) causes the electron density along the C–C bond to increase even more. This work provides substantial evidence that the molecular Fukui function is sometimes negative and reveals that this is due to orbital relaxation.

When a molecule loses an electron, does the electron density decrease everywhere? If the frontier molecular orbital model for ionization is qualitatively accurate, then it does: removing an electron from the highest occupied molecular orbital (HOMO) causes the electron density to decrease everywhere, in proportion to the amplitude of the HOMO squared. However, as we will demonstrate in this Letter, when acetylene is oxidized, the electron density along the carbon–carbon bond actually *increases*, even though both the total number of electrons and the bond order of the CC bond decrease. Moreover, removing additional electrons causes the electron density along the C–C bond to increase even more.

Aside from the implications of this result for frontier molecular orbital theory, we are motivated by recent theoretical and experimental work on redox-induced electron rearrangement (RIER).^{1,2} In RIER, one atom (or functional group) is reduced even though the molecule as a whole is oxidized. (That is, the electron density in one region of the molecule increases even though the total number of electrons decreases.) Although RIER sounds implausible, recent experiments by Min et al.¹ provide strong evidence for this phenomenon: they observe that when a dinuclear cobalt complex, $\text{Co}^{2+}\text{CA}^{2-}\text{Co}^{2+}$, is oxidized, the chloranilate (CA) linker between the cobalt complexes is reduced, giving $\text{Co}^{3+}\text{CA}^{3-}\text{Co}^{3+}$. The cobalt atoms change from high spin to low spin during this process, providing unambiguous evidence for RIER and suggesting that metal complexes with RIER may have interesting magnetic properties.

At a theoretical level, RIER is associated with negative values of the molecular Fukui function.² The Fukui function is one of the fundamental regioselectivity indicators in the density-

functional theory approach to chemical reactivity (the so-called “conceptual DFT”).^{3–5} The Fukui function measures the differential change in the electron density induced by a change in the number of electrons at fixed molecular geometry.^{6,7}

$$f^-(\mathbf{r}) = \left(\frac{\partial \rho_N(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})}^- = \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) \approx |\phi_{\text{HOMO}}(\mathbf{r})|^2 \quad (1)$$

The Fukui function, like the electron density, has units of electrons per unit volume.

Because removing electrons (from the HOMO) is not just “the opposite” of adding electrons (to the LUMO), one must distinguish between the Fukui function for electron removal, $f^-(\mathbf{r})$, and the Fukui function for electron attachment, $f^+(\mathbf{r})$.^{6,7} (In theory, $f^-(\mathbf{r})$ for the N electron system is equal to $f^+(\mathbf{r})$ for the $N - 1$ electron system, so we will consider only the former in this paper.) The second equality in (1) is the finite difference formula for the derivative. The finite difference formula is only approximate in most practical computational methods,^{8,9} but it is exact in principle^{10–12} and so we will use it throughout this paper. The final approximation in (1) is the molecular orbital approximation to the Fukui function that we referred to in the introductory paragraph. This approximation will be accurate when the effects of orbital relaxation and electron correlation are negligible.^{7,13–15} $f^-(\mathbf{r})$ is named the Fukui function precisely because it represents the DFT-based refinement of Fukui’s frontier molecular orbital concepts. Although the refinement is rarely qualitatively significant, it is critically important for RIER. One goal of this paper is to explore which refinement (orbital relaxation or electron correlation?) to the simple frontier molecular orbital model is responsible for the RIER phenomenon.

To explore RIER, we have computed the Fukui function for an assortment of substituted acetylenes using a variety of basis

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TABLE 1: Minimum Values of $f^-(\mathbf{r})$ (in $e^-/\text{\AA}^3$) for Substituted Acetylenes^a

	HCCH			HCCF			FCCF			HCCLi		
	KS	HF	CISD	KS	HF	CISD	KS	HF	CISD	KS	HF	CISD
B ₁	-0.057	-0.054	-0.051	-0.104	-0.186	-0.281	-0.050	-0.052	-0.043	-0.078	-0.049	-0.047
B ₂	-0.056	-0.055	-0.054	-0.247	-0.193	-0.240	-0.047	-0.058	-0.045	-0.057	-0.051	-0.045
B ₃	-0.065	-0.060	-0.061	-0.288	-0.228	-0.247	-0.058	-0.085	-0.068	-0.090	-0.069	-0.060
B ₄	-0.065	-0.060	-0.061	-0.284	-0.221	-0.250	-0.058	-0.080	-0.068	-0.091	-0.070	-0.062

^a The minimum value is located at the nucleus of atoms in blue. Basis sets are: B₁ = 3-21G, B₂ = 6-31++G(d,p), B₃ = 6-311++G(2df,2p), B₄ = cc-pCVTZ. Methods include B3LYP (KS), Hartree–Fock (HF), and configuration interaction with single and double excitations (CISD).

sets and three different quantum chemistry methods: Kohn–Sham (KS) DFT (using B3LYP^{16,17}), unrestricted Hartree–Fock (HF), and configuration interaction with single and double excitations (CISD) with respect to the HF configuration. CISD is rarely used in modern quantum chemistry, but because we are interested in the sign of the Fukui function, it is essential that the electron density be nonnegative, and this is not guaranteed for perturbative and coupled-cluster methods (because those approaches sometimes give negative natural orbital occupation numbers). We opted to explore acetylenes in our initial study because we wish to validate our methods with respect to basis set size and the inclusion of electron correlation, and this is impossible for large metal complexes such as those considered by Min et al. Finally, most of the previous theoretical work on negative Fukui functions has been done using “condensed” Fukui functions,¹⁸ which is a coarse-grained description based on the change in atomic partial charges upon ionization.^{2,15,19–23} The coarse-graining scheme is somewhat arbitrary, because the values of the condensed Fukui functions are sensitive to (i) the size of the one-electron basis set, (ii) the model for electron correlation, (iii) whether the derivative in eq 1 is evaluated using unit ($\Delta N = 1$) or infinitesimal ($\Delta N = \epsilon$) changes in the electron number, (iv) the choice of population analysis method, and (v) whether one chooses to partition the molecule into atoms before (the “response of molecular fragment” approach) or after (the “fragment of molecular response” approach) differentiating the density with respect to electron number.^{23–26} Moreover, the coarse-graining procedure tends to obscure the interpretation of the underlying RIER phenomenon. For these reasons, we chose to focus on the more detailed pointwise Fukui function defined in eq 1.

Table 1 presents the minimum value of the Fukui function for acetylene and a selection of substituted acetylenes. The minimum value is relatively insensitive to the choice of method and the choice of basis set and it is negative in all cases considered. The most negative value always seems to be located at the nucleus of the most positively charged atom or, more generally, at the atom where the electron–nuclear attraction potential is largest.

That $f^-(\mathbf{r})$ is decisively negative indicates a failure of the naïve frontier molecular orbital model for the electron density’s response to ionization. Because the effect is quantitatively similar in correlated calculations (CISD, KS) and the independent electron model (HF), we infer that the failure of the frontier molecular-orbital model is due to the neglect of orbital relaxation, and not electron correlation effects.

To explore why orbital relaxation effects are important, we plotted the 0.0002 isosurfaces of $f^-(\mathbf{r})$ (the inner isosurface nicely encapsulates the region where $f^-(\mathbf{r}) \leq 0$) and one of the two degenerate HOMOs. Notice that the negative regions of the Fukui function coincide with the nodal surface(s) of the HOMO. In the frontier molecular-orbital model, removing an electron from the HOMO does not change the electron density along these nodal surfaces. However, removing this electron

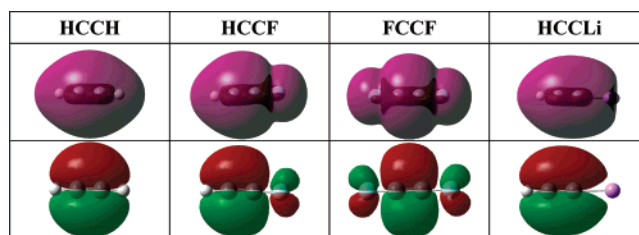


Figure 1. 0.0002 isosurfaces of $f^-(\mathbf{r})$. The inner isosurface encapsulates the region where the Fukui function is negative. Isosurfaces with smaller characteristic values are similar but enclose slightly smaller volumes.

deshields the remaining electrons and so the occupied orbitals contract toward the atomic nuclei. Orbital contraction (especially of the σ -orbitals, which have orbital density at the nuclei and along the bond axis) increases the orbital density near the nuclei. The net effect is that in the regions where removing an electron from the HOMO did not decrease the electron density significantly, the orbital contraction that accompanies ionization can make the electron density *increase*. This is the essence of RIER: removing an electron from an orbital that is localized in one region of the molecule (in this case, the region away from the bond axis) deshields orbitals that are concentrated in other regions (here, along the bond axis). The deshielded orbitals then drift lower in energy by contracting toward regions with favorable nuclear-electron attraction. The electron density increases in the regions that the orbitals contract toward, and decreases elsewhere.²

Evidence for the validity of this interpretation is obtained by comparing the plots in Figure 1 for HCCH, HCCF, and FCCF. In acetylene, the nodal surfaces of the HOMOs intersect along the molecular axis and, in accord with the proposed interpretation, the Fukui function is negative in these regions. In addition to the node along the molecular axis, the HOMOs of the fluorinated acetylenes have a nodal surface that bisects the CF bond(s); this causes the negative region of $f^-(\mathbf{r})$ to expand significantly in the center of the CF bond(s). Once again, the negative values of the Fukui function track the nodal planes of the HOMOs and concentrate in regions with strong electron–nuclear attraction. This explains why the electron density *increases* along C–C bond even though the bond order of these acetylenes decreases when an electron is removed. (We confirmed the decrease in bond order using the Wiberg bond order,²⁷ as computed using Natural Bond Orbital analysis.^{28,29} The bond order does indeed decrease. E.g., for acetylene, using our best CISD wavefunction, the Wiberg bond order decreases from 2.99 to 2.25 upon ionization.)

There are four electrons in the degenerate HOMOs of these acetylenes. Thus, removing additional electrons should cause the electron density to increase further still. This is confirmed in Figure 2, which contains data relevant to the change in density when four electrons are removed, $f^{-4}(\mathbf{r}) = (\rho_N(\mathbf{r}) - \rho_{N-4}(\mathbf{r}))/4$. Notice that the negative regions of $f^{-4}(\mathbf{r})$ follow the nodal planes of the HOMOs and concentrate in the regions where the

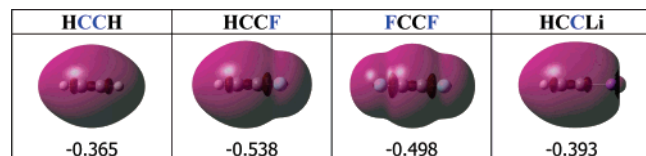


Figure 2. 0.0002 isosurfaces of $f^{-4}(\mathbf{r})$, which measures the decrease in electron density associated with removing four electrons. The surfaces encapsulate the region where quadruple ionization causes the electron density to increase. The numbers reported correspond to the most negative values of $f^{-4}(\mathbf{r})$; these values occur at the nucleus of the blue atom.

electron–nuclear attraction is largest. Notice also that the minimum values of $f^{-4}(\mathbf{r})$ are significantly less than the minimum values of the ordinary Fukui function, $f^{-}(\mathbf{r})$. This provides convincing support for the interpretation advanced here and shows how robust RIER is: one can remove up to *four* electrons from these acetylenes and the electron density still increases in certain regions. (A similar effect has been observed for the neon atom, where sextuple ionization is associated with an increase in electron density near the atomic nucleus.¹⁵)

In summary, our results provide strong evidence that the Fukui function is sometimes negative. This phenomenon cannot be explained in the context of frontier molecular orbital theory, but it is readily explained by invoking orbital relaxation effects. Specifically, removing an electron from the HOMO does not decrease the electron density in nodal planes of the HOMO, but it does deshield the remaining occupied orbitals, allowing them to contract toward the atomic nuclei. This causes the electron density to increase in regions where the electron–nuclear attraction energy is large but the amplitude of the HOMO is small. This is the essence of redox-induced electron rearrangement (RIER), where oxidation (or reduction) of a molecule is associated with reduction (or oxidation) of a region within the molecule. Our results suggest that RIER is predominantly an orbital relaxation effect, and that it can be modeled using relatively small basis sets and relatively inaccurate models for electron correlation. For example, Kohn–Sham DFT calculations with the B3LYP functional and a triple- ζ basis set seem reliable. The ability to use affordable computational techniques will be important in our future work, where we aim

to explore large and complicated molecules such as the ones considered by Min et al.

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