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ARTICLE *in* JOURNAL OF MOLECULAR MODELING · OCTOBER 2012

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In pursuit of negative Fukui functions: examples where the highest occupied molecular orbital fails to dominate the chemical reactivity

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Received: 17 July 2012 / Accepted: 7 October 2012 / Published online: 23 October 2012
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Abstract In our quest to explore molecules with chemically significant regions where the Fukui function is negative, we explored reactions where the frontier orbital that indicates the sites for electrophilic attack is not the highest occupied molecular orbital. The highest occupied molecular orbital (HOMO) controls the location of the regions where the Fukui function is negative, supporting the postulate that negative values of the Fukui function are associated with orbital relaxation effects and nodal surfaces of the frontier orbitals. Significant negative values for the condensed Fukui function, however, were not observed.

Keywords Conceptual density functional theory · Fukui function · Frontier effective for reaction · Redox induced electron transfer · Orbital relaxation

Motivation

When an electron is removed from a molecule, does the probability of observing an electron decrease everywhere? This is always true in the frozen molecular orbital approximation, and one might expect it to be true more generally. But there is abundant evidence, including some from highly accurate calculations [1, 2], that this is not true. Orbital relaxation can cause the electron density to increase in some molecular regions upon ionization [1–7].

The first detailed explanation for this phenomenon was given for the neon atom [1]. When one removes an electron from neon, it comes from the $2p$ orbital. In the frozen orbital approximation, removing an electron does not affect the electron density at the nucleus. Removing the electron also deshields the electrons in the $1s$ and $2s$ orbitals (and also the other $2p$ orbitals). Therefore, once orbital relaxation is allowed, the remaining occupied orbitals contract towards the nucleus. The contraction of the $1s$ and $2s$ orbitals toward the nucleus increases the electron density at the nucleus. Therefore, removing an electron from neon causes the electron density near the nucleus to increase, not decrease. In fact, near the nucleus, the electron density of Ne^{+6} is greater than the electron density of Ne . This is because removing the $2p$ electrons from Ne does not affect electron density at the nucleus (in the frozen orbital approximation) but relaxation of the $1s$ and $2s$ orbitals increases electron density at the nucleus.

Orbital relaxation is rarely qualitatively important in chemistry, but there are exceptions [4, 8–11]. When orbital relaxation is very important, the highest occupied molecular orbital (HOMO) may not indicate the most favorable sites

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for electrophilic attack, i.e., strong orbital relaxation effects are associated with failure of the frontier orbital approximation. One advantage of using the density functional theory (DFT) approach to chemical reactivity (often called conceptual DFT or chemical DFT) [12–19] is that the fundamental indicator of orbital-guided electronic attack in DFT-based reactivity theory, the Fukui function [20–22], already includes the contributions of electron correlation and orbital relaxation [23, 24].

The Fukui function is the generalization of the frontier molecular orbital (FMO) concept to DFT [22, 23]; it is defined as the best (i.e., minimum energy or maximum hardness) way to change the electron density of an N electron system when one adds ($f^+(\mathbf{r})$) or removes ($f^-(\mathbf{r})$) an electron [25, 26]. Because of the derivative discontinuity of the electronic energy and the electron density at integer numbers of electrons [27–29], the Fukui functions for adding and subtracting electrons are different [22, 30]. The Fukui function is negative when removing (adding) an electron to a molecule causes the electron density to increase (decrease).

We are interested in molecules with substantial negative Fukui functions because this is the signature of redox induced electron transfer (RIET) [4, 31–34]. In RIET, oxidizing a molecule (removing electrons) causes one of the atoms or functional groups in the molecule to be reduced (to gain electrons). (The reverse reaction will also show RIET: reducing the molecule causes one of the atoms to be oxidized.) In order to see RIET, the Fukui function needs to be so negative that the atomic charge *decreases* by about one electron when an electron is removed from a molecule. (That is, the atomic charges will become more negative or less positive. The condensed Fukui function [35–40] is therefore negative.)

Since negative values of the condensed Fukui function occur only when orbital relaxation is significant, we decided to examine molecules where the HOMO does not control the susceptibility of the molecule to electrophilic attack [41–43]. Other molecules of this type have been shown to have significant effects from orbital relaxation [8, 10]. While we have focused our attention on the Fukui function,

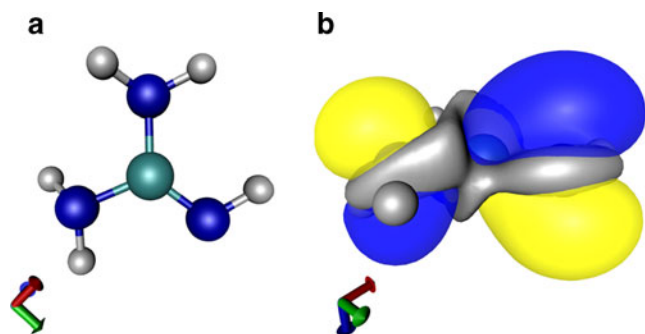


Fig. 1 **a** Molecular structure of guanidine. **b** The -10^{-5} isosurface of $f^-(\mathbf{r})$ (opaque silver surface) traces the nodal regions of the highest occupied molecular orbital (HOMO) (translucent colored lobes, with different colors for different phases)

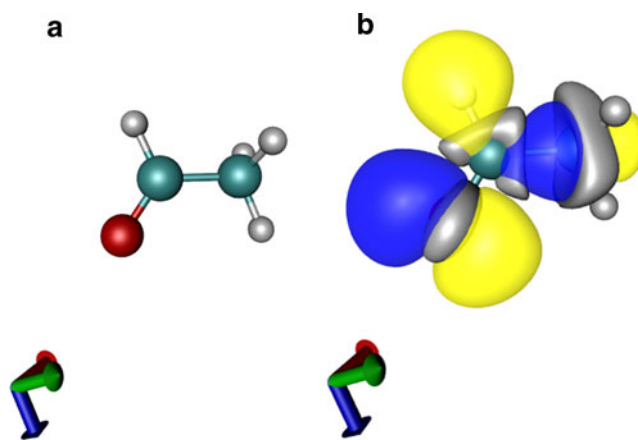


Fig. 2 **a** Molecular structure of the acetal anion. **b** The -10^{-5} isosurface of $f^-(\mathbf{r})$ (opaque silver surface) traces the nodal regions of the HOMO (translucent colored lobes, with different colors for different phases)

there are other reactivity indicators that may be more appropriate when electrophilic attack on a molecule reactivity is not controlled by the HOMO [44–46].

Methods

All calculations were performed using the B3LYP functional [47–50] and the 6–31G(d) basis set using the Gaussian 2003 quantum chemistry program [51]. The Fukui function was computed using the finite difference between the electron density from the optimized molecular geometry and the electron density from a single-point calculation on the ($N-1$)-electron system at the geometry of the N -electron molecule [22],

$$f^-(\mathbf{r}) \equiv \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})} \approx \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) \quad (1)$$

Although this formula is exact for the exact density functional, it is only approximately true for B3LYP [21, 29]. In

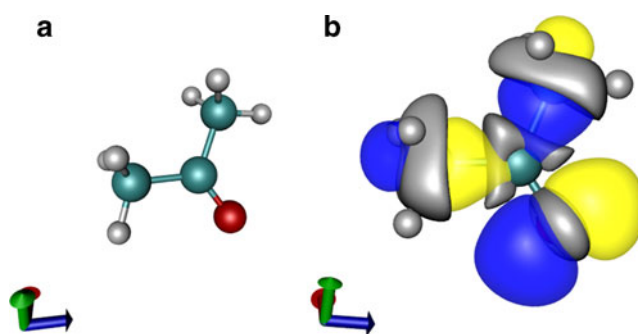


Fig. 3 **a** Molecular structure of the isopropoxide anion. **b** The -10^{-5} isosurface of $f^-(\mathbf{r})$ (opaque silver surface) traces the nodal regions of the HOMO (translucent colored lobes, with different colors for different phases)

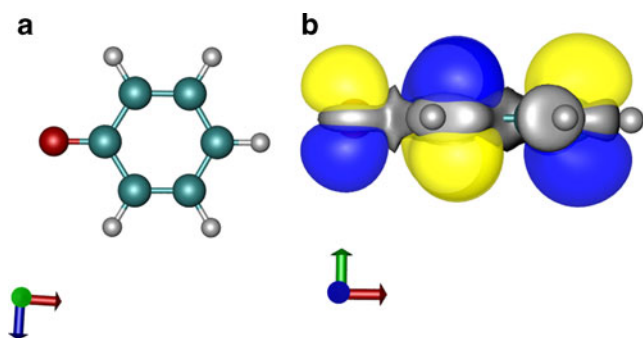


Fig. 4 **a** Molecular structure of the phenoxide anion. **b** The -10^{-5} isosurface of $f^-(\mathbf{r})$ (opaque silver surface) traces the nodal regions of the HOMO (translucent colored lobes, with different colors for different phases)

previous work, it was found that B3LYP and configuration interaction calculations give similar results for investigating Fukui functions [2]. NPA [52] and CHELPG [53] population analyses on these calculations revealed no negative condensed Fukui functions.

Results

Figures 1, 2, 3, and 4 plot the HOMO and the -10^{-5} isosurface of $f^-(\mathbf{r})$ for guanidine (Fig. 1), acetal (Fig. 2), isopropoxide (Fig. 3), and phenoxide (Fig. 4). Guanidine is a neutral molecule that was mentioned in reference [43]; the other molecules are anions and were studied in reference [42]. The figures show the lobes of the HOMO; the Fukui function is negative inside the opaque silver surface. Chemdraw structures of these molecules are given in Fig. 5. Electrophilic attack occurs preferentially on the NH group of guanidine, and the oxygen atoms in acetal, isopropoxide, and phenoxide. Phenoxide is also subject to electrophilic aromatic substitution at the ortho and para positions.

Note that the negative regions of the Fukui function are localized in the nodal planes of the HOMO: the negative-Fukui-function-regions look like a silvery paste that is being squeezed out of the gaps between the positive and negative lobes of the HOMO. This supports the previously proposed explanation for why negative Fukui functions occur. Reducing the occupation number of the HOMO decreases the electron

density everywhere except the nodal surfaces of the HOMO. After the HOMO has been vacated, the lower-lying occupied orbitals (which do not have the same nodal surfaces as the HOMO due to Wintner's theorem [54]) are less shielded from the nuclei, and contract. This causes the electron density to increase near atomic nuclei and in the binding regions between nuclei. In most regions, the initial decrease in density (from reducing the occupation of the HOMO) is larger than the subsequent increase in density (from orbital relaxation). But near the nodal surfaces of the HOMO, the initial decrease in electron density was negligible and the density-increase due to orbital relaxation is dominant. In these regions, removing an electron causes the electron density to increase and $f^-(\mathbf{r}) < 0$.

Conclusion

This paper is part of our quest to discover molecules that undergo redox induced electron transfer (RIET) [32], where oxidizing the molecule causes one of the atoms or functional groups in the molecule to be reduced. We reasoned that molecules that were susceptible to electrophilic attack at a location contrary to the predictions of FMO theory might be good candidates for this because such behavior usually indicates either that there are other orbitals (HOMO-1, HOMO-2, etc.) that are also accessible energetically or that orbital relaxation is important. Both effects are believed to be favorable for RIET, but we did not observe RIET in any of the molecules we studied. This could be because these reactions are charge controlled (cf. refs [44, 55–57].) or because RIET is very rare. We expect it is the latter. In a future study we will examine molecules that are proposed to be interesting electronic materials; such substances are perhaps better candidates for RIET (E. Echegaray et al., manuscript in preparation).

We did confirm that regions the Fukui function from below, $f^-(\mathbf{r})$, seems to have negative values only in the regions near the nodal surfaces in the HOMO. This supports previous explanations of why removing electrons from a molecule can cause the electron density to increase in some places [1]. Previous computational evidence for this hypothesis was limited to atoms and small linear molecules [1, 2]. The increase in electron density along the nodal surfaces of the HOMO upon electron removal provides concrete visual

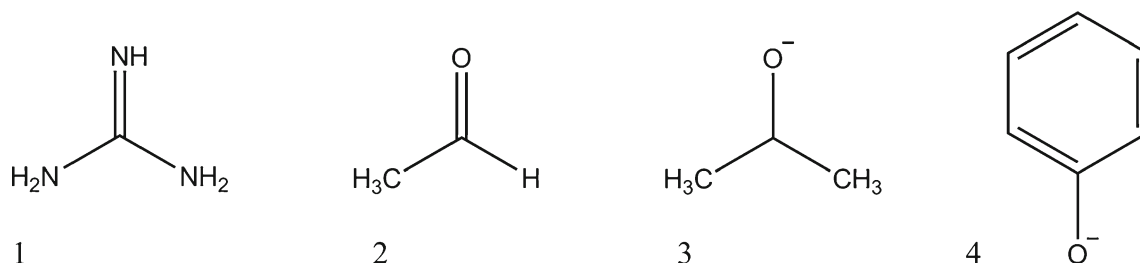


Fig. 5 Structures of the molecules considered in this paper, labeled by figure number. **1** Guanidine, **2** acetal, **3** isopropoxide anion, **4** phenoxide anion

evidence for the importance of orbital relaxation in molecular electronic structure theory.

Acknowledgments P.W.A. thanks the Canada Research Chairs and Natural Sciences and Engineering Research Council of Canada (NSERC) for funding. Computational facilities were provided by Sharcnet. E.E. and A.T.L. acknowledge financial support from Fondecyt through project N°1090460. C.C. acknowledge financial support from Fondecyt through project No 11090013 and also by Financiamiento basal para centros científicos y tecnológicos de excelencia. J.S.M.A. would like to thank NSERC and The Japan Society for the Promotion of Science (JSPS) for funding.

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