Second-Order Atomic Fukui Indices from the Electron-Pair Density in the Framework of the Atoms in Molecules Theory

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Abstract: Atomic Fukui indices, which are obtained from the electron density, have been previously shown to be useful in predicting which atoms in a molecule are most likely to suffer nucleophilic, electrophilic, or radicalary attacks. Here, we present a second-order generalization of these indices based on the electron pair density. We show how second-order atomic Fukui indices can be used to analyze the effects of electron loss or gain in several molecules from an electron pair point of view. Further, these indices also highlight which atoms or pairs of atoms are more likely to suffer nucleophilic, electrophilic, or radical attacks. In conclusion, second-order indices can complement first-order ones by affording relevant information on molecular reactivity from an electron pair perspective.

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Key words: Fukui indices; electron-pair density; atoms in molecules theory; reactivity; localization and delocalization indices

Introduction

The Fukui functions introduced by Parr and Yang are partial derivatives (under a constant external potential) of the electron density of a molecule with respect to the number of electrons.[1–5] Fukui functions are usually calculated in a finite-difference scheme,

$$f^+(\mathbf{r}) = \rho^+(\mathbf{r}) - \rho(\mathbf{r}) \qquad (1)$$

$$f^-(\mathbf{r}) = \rho(\mathbf{r}) - \rho^-(\mathbf{r}) \qquad (2)$$

$$f^0(\mathbf{r}) = \frac{1}{2}(\rho^+(\mathbf{r}) - \rho^-(\mathbf{r})) \qquad (3)$$

$\rho(\mathbf{r})$ in eqs. (1), (2), and (3) is the ground-state electron density distribution of a molecule. $\rho^+(\mathbf{r})$ and $\rho^-(\mathbf{r})$ are the electron density distributions resulting from the addition and substraction, respectively, of an electron to $\rho(\mathbf{r})$ at the equilibrium geometry of the neutral molecule. $f^+(\mathbf{r})$, $f^-(\mathbf{r})$, and $f^0(\mathbf{r})$ are 3D functions that can be used to reveal which regions of the neutral molecule are most likely to suffer nucleophilic, electrophilic, and radical attacks, respectively. Fukui functions have been widely used in recent years as indicators of chemical reactivity.[6–11]

The analysis of the electron density is also the basis of the Atoms in Molecules (AIM) theory.[12] In the AIM theory, the atoms in a molecule are defined from the topological analysis of $\rho(\mathbf{r})$. The gradient of the electron density is used to partition the real space into disjoint regions (atomic basins). Integration of $\rho(\mathbf{r})$ through the atomic basin of an atom A yields the electron population of that atom,

$$N(A) = \int_A \rho(\mathbf{r})d\mathbf{r} \qquad (4)$$

Cioslowski et al. used the AIM theory to define three atomic Fukui indices (AFIs)[13]:

$$f_N^+(A) = N^+(A) - N(A) \qquad (5)$$

$$f_N^-(A) = N(A) - N^-(A) \qquad (6)$$

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$$f_N^0(A) = \frac{1}{2}(N^+(A) - N^-(A)) \qquad (7)$$

$N(A)$ refers to the electron population in the atom A of a neutral molecule, whereas $N^+(A)$ and $N^-(A)$ are the electron populations for the anionic and cationic species, respectively. $f_N^+(A)$, $f_N^-(A)$, and $f_N^0(A)$ can be used to measure the probability of nucleophilic, electrophilic, and radical attacks, respectively, to the atom A. The subscript N is used to remark that these indices are obtained from atomic electron populations. Because the summation of all the electron atomic populations in a molecule yields the number of electrons of the molecule, the AFIs satisfy the following sum rule:

$$\sum_A f_N^+(A) = \sum_A f_N^-(A) = \sum_A f_N^0(A) = 1 \qquad (8)$$

This approach relies on the assumption that the number of atoms, as defined from the topology of the electron density, is the same for the neutral molecule and the corresponding anion and cation. This condition is fulfilled for most of the molecules.

In the context of the AIM theory, the electron pair density, $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$, can be used to calculate a localization index (LI) for each atom:

$$\lambda(A) = -\int_A (2\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2))d\mathbf{r}_1 d\mathbf{r}_2 \qquad (9)$$

and a delocalization index (DI) between every pair of atoms:

$$\delta(A, B) = -2\int_{A,B} (2\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2))d\mathbf{r}_1 d\mathbf{r}_2 \qquad (10)$$

$\lambda(A)$ is the number of electrons localized in the basin of atom A, whereas $\delta(A, B)$ corresponds to the number of electrons delocalized or shared between atoms A and B.[14–17] The information obtained from the LIs and DIs complements the analysis based on the electron populations. Therefore, it could be worth investigating the possibility of using LIs and DIs to calculate second-order AFIs:

$$f_\lambda^+(A) = \lambda^+(A) - \lambda(A) \qquad (11)$$

$$f_\lambda^-(A) = \lambda(A) - \lambda^-(A) \qquad (12)$$

$$f_\lambda^0(A) = \frac{1}{2}(\lambda^+(A) - \lambda^-(A)) \qquad (13)$$

$$f_\delta^+(A, B) = \delta^+(A, B) - \delta(A, B) \qquad (14)$$

$$f_\delta^-(A, B) = \delta(A, B) - \delta^-(A, B) \qquad (15)$$

$$f_\delta^0(A, B) = \frac{1}{2}(\delta^+(A, B) - \delta^-(A, B)) \qquad (16)$$

The notation used in eqs. (11)–(16) is similar to that used in eqs. (5)–(7): $\lambda^+(A)$ and $\delta^+(A, B)$ refer to the anion, while $\lambda^-(A)$ and $\delta^-(A, B)$ refer to the cation. The $+$, $-$, and 0 superscripts are also used to denote nucleophilic, electrophilic, and radical AFIs, respectively. Finally, the λ and δ subscripts indicate which AFIs are based on LIs or DIs, respectively. The following sum rule is satisfied for these indices:

$$\sum_A \left(f_\lambda^+(A) + \sum_{A \neq B} \frac{1}{2}f_\delta^+(A, B)\right) = \sum_A \left(f_\lambda^-(A) + \sum_{A \neq B} \frac{1}{2}f_\delta^-(A, B)\right)$$

$$= \sum_A \left(f_\lambda^0(A) + \sum_{A \neq B} \frac{1}{2}f_\delta^0(A, B)\right) = 1 \quad (17)$$

From now on, we will refer to the indices derived by Cioslowski et al. from the analysis of $\rho(\mathbf{r})$ as first-order Fukui indices. Accordingly, we will refer to the indices derived from LIs and DIs as second-order AFIs.

The aim of this work is to calculate for the first time second-order AFIs for a series of small molecules. The first objective is to provide insight in the electron pair differences between closed- and open-shell molecules with different numbers of electrons, complementing a previous study of the electron pair densities of several small open-shell molecules.[16] A second goal is to assess the usefulness of the second-order AFIs based on LIs and DIs as a complement of the first-order ones for the purpose of predicting chemical reactivity.

Methods

Molecular geometries were optimized for a series of nine closed-shell and two open-shell molecules in their ground-state using the restricted Hartree–Fock (RHF) and restricted open-shell Hartree–Fock (ROHF) methods, respectively. Single-point (no geometry optimization) RHF or ROHF calculations were also performed for the cations and anions resulting from adding or substracting an electron to each of these molecules. The $6\text{-}311{+}{+}G(2d,2p)$ basis set was used throughout. The Gaussian 98 package[18] was used to perform all calculations. To compare the effect of the level of calculation on the analysis proposed here, the calculation of density functional theory (DFT) calculations were also carried out for some molecules using a local functional (SVWN)[19] and a gradient-corrected one (B3LYP).[20] Because no correlated second-order density is available from DFT calculations, the calculation of LIs and DIs at the DFT level must be carried out in an approximate way.[21]

The AIMPAC series of programs[22] was used to carry out the topological analysis of the electron density for each molecule and calculate atomic electron populations. According to the topological analysis, there is a correspondence between atoms and attractors (maxima in the electron density) for all molecules except the acetylene series (C_2H_2, $C_2H_2^-$, $C_2H_2^+$). In this case, there is also a nonnuclear attractor (NNA) located between the two C atoms. Previous studies suggest that this NNA is not a computational artifact.[23] Therefore, the *pseudoatom* associated with the NNA was also considered in our analysis.

At the RHF and ROHF levels of theory, the LI, $\lambda(A)$, and DI, $\delta(A, B)$, are expressed as

$$\lambda(A) = \sum_{i,j} (S_{ij}(A))^2 \tag{18}$$

and

$$\delta(A, B) = 2 \sum_{i,j} S_{ij}(A) S_{ij}(A) \tag{19}$$

respectively.[15,16] These summations run over all pairs of occupied molecular spin orbitals (MSOs) of the molecule, and $S_{ij}(A)$ is the overlap of the MSOs i and j within the basin of atom A. At the DFT level, approximate LIs and DIs were obtained using Khon–Sham orbitals in eqs. (18) and (19).* First- and second-order AFIs for all molecules were calculated using eqs. (5)–(7) and (11)–(16), respectively.
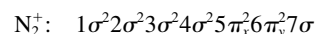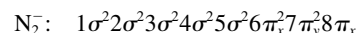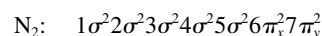
Discussion

Table 1 collects electron populations, LIs, and DIs for H_2, N_2, F_2, CO, CN, NO, CO_2, SO_2, SO_3, and C_2H_2, and the related cations and anions, as well as the AFIs calculated from this data.

The electron population in H_2, H_2^-, and H_2^+ is symmetrically spread between the two H atoms (see Table 1a). Therefore, f_N^+, f_N^-, and f_N^0 for H_2 are exactly 0.5 and afford no relevant information. H_2^+ has a single electron, which is perfectly shared between the two H atoms [$\lambda(H) = 0.25$, $\delta(H,H') = 0.50$]. H_2 has a pair of electrons with opposite spin. In the HF framework, the two electrons are not correlated; thus, the LI and DI for H_2 are exactly twice those of H_2^+.[†] Indeed, the values of the second-order f indices [$f_\lambda^-(H) = 0.25$, $f_\delta^-(H,H') = 0.50$] reveal that the only difference between H_2^+ and H_2 is the addition of an electron perfectly shared between the two H atoms. Because all the Fukui indices are related to comparisons between species with different number of electrons, these values can be used as a reference when discussing second-order Fukui indices. For instance, if the extra electron in an anion, with respect to the neutral molecule, is highly delocalized between two atoms, the values of the nucleophilic Fukui indices for these two atoms will be similar to those of H_2. If the extra electron is highly localized in one or both atoms, one or both of the LI-based indices is expected to be higher than 0.25, while the DI-based index will be less than 0.50. This point can be illustrated by noting that H_2^- has two α and one β electrons. Fermi correlation between same-spin electrons diminishes $\delta(H,H')$ in H_2^- with respect to H_2. Thus, $f_\lambda^+(H) = 0.29$ and $f_\delta^-(H,H') = 0.43$ in H_2^-. According to these results, the extra electron in H_2^- is still

largely delocalized between the two atoms, but not perfectly delocalized. Similar results are obtained for f_λ^0 and f_δ^0. Finally, note that addition or substraction of electrons can also have an effect on the remaining electrons of the molecule. Thus, the indices can be negative, for instance, in the case of an extra electron leading to a decrease in the total DI between two atoms (see below).

The kind of analysis carried out using second-order AFI is complementary to the nuclear Fukui function analysis,[24] which gives a view of whether the electron attachment/removal increases or decreases the bond order analyzing the nuclear forces instead of the electron density. In this sense, the series of works analyzing the relation between the nuclear Fukui function and Berlin's binding function is in particular noteworthy.[25]

N_2 is also a homonuclear diatomic molecule, and all the first-order Fukui indices for this molecule are also 0.5 (see Table 1b). In contrast, $f_\delta^+(N)$ is less than zero, which reveals that $\delta(N,N')$ decreases after adding an extra electron to N_2. Note that the electronic configuration of N_2, N_2^-, and N_2^+ is the following:

$$N_2: \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\pi_x^2 7\pi_y^2$$

$$N_2^-: \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\pi_x^2 7\pi_y^2 8\pi_x$$

$$N_2^+: \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\pi_y^2 7\sigma$$

It is worth pointing out that, at the HF level of theory, electrons in orbitals of different symmetry are totally uncorrelated. Thus, each of the $6\pi_x$, and $7\pi_y$ valence electron pairs in N_2 is perfectly delocalized and contributes 1 e to the DI and 0.5 e to each LI. The contribution of the σ density to the DI is 1.04, which corresponds to a delocalized electron pair plus some residual delocalization of the core electrons. Altogether, $\delta(N,N')$ is slightly larger than 3.[15] The removal of a σ electron to yield N_2^+ means that there are five electrons delocalized between the two N atoms, with a total DI of about 3.2. With respect to N_2, N_2^- has an unpaired electron in the $8\pi_x$ orbital. The overall effect of an electron in an antibonding orbital depends on its interaction with electrons in bonding orbitals. If the antibonding orbital does not overlap significantly with other orbitals,* the net contribution to the DI is positive. However, if there is significant orbital overlap Fermi correlation leads to a larger localization of the electrons and a decrease of the DI (e.g., see the discussion on H_2^- in ref. 16). Actually, the overlap of the $6\pi_x$ and $8\pi_x$ orbitals of N_2^- within each of the atomic basins is high (± 0.41), and $\delta(N,N')$ is lower in N_2^- (2.89) than in N_2.

A similar reasoning can be carried out for F_2 (see Table 1c). $\delta(F,F')$ is higher in F_2 than in F_2^- because the extra electron in the anion is located in an antibonding orbital that helps to localize the electrons in other orbitals. In contrast, removing an electron from the highest occupied molecular orbital (HOMO) orbital decreases the interelectron repulsion and increases $\delta(F,F')$ in F_2^+.

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*Proper account of electron correlation effects in the calculation of second-order AFIs requires using explicitly correlated electron-pair densities, which we cannot obtain at present for open-shell molecules. See ref. 21 for an in-depth discussion.

[†]However, this is not the case at the configuration interaction level of theory: $\lambda(H) = 0.58$, $\delta(H,H') = 0.85$ for H_2 and at the CISD/6-333++G(2d,2p) level.[14]

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*Molecular orbitals in the HF approach are orthogonal and have zero overlap when the integration is carried out through all space. However, there can be significant nonzero overlap within the atomic basins [these are the $S_{ij}(A)$ terms involved in the calculation of the LI and DI].[16]

Table 1. Electron populations (N), localization indices (λ), and delocalization indices (δ) for the neutral species, cation, and anion of a series of molecules and integrated atomic Fukui functions (f^+, f^-, f^0) derived from N, λ, and δ values calculated at the HF level of theory.

(a) H$_2$	H$_2$	H$_2^-$	H$_2^+$	f^+	f^-	f^0
$N(H)$	1.00	1.50	0.50	0.50	0.50	0.50
$\lambda(H)$	0.50	0.79	0.25	0.29	0.25	0.27
$\delta(H,H')$	1.00	1.43	0.50	0.43	0.50	0.46

(b) N$_2$	N$_2$	N$_2^-$	N$_2^+$	f^+	f^-	f^0
$N(N)$	7.00	7.50	6.50	0.50	0.50	0.50
$\lambda(N)$	5.48	6.06	4.90	0.58	0.58	0.58
$\delta(N,N')$	3.04	2.89	3.20	−0.16	−0.16	−0.16

(c) F$_2$	F$_2$	F$_2^-$	F$_2^+$	f^+	f^-	f^0
$N(F)$	9.00	9.50	8.50	0.50	0.50	0.50
$\lambda(F)$	8.36	9.00	7.65	0.65	0.71	0.68
$\delta(F,F')$	1.28	1.00	1.71	−0.29	−0.43	−0.36

(d) CO	CO	CO$^-$	CO$^+$	f^+	f^-	f^0
$N(C)$	4.64	4.87	3.97	0.23	0.68	0.45
$N(O)$	9.36	10.13	9.04	0.77	0.32	0.55
$\lambda(C)$	3.86	3.92	3.09	0.06	0.77	0.42
$\lambda(O)$	8.57	9.18	8.16	0.60	0.42	0.51
$\delta(C,O)$	1.57	1.91	1.76	0.34	−0.19	0.07

(e) CN	CN	CN$^-$	CN$^+$	f^+	f^-	f^0
$N(C)$	4.73	5.19	4.54	0.46	0.19	0.33
$N(N)$	8.27	8.81	7.46	0.54	0.81	0.68
$\lambda(C)$	3.47	4.10	3.01	0.63	0.46	0.54
$\lambda(N)$	7.01	7.72	5.93	0.71	1.08	0.89
$\delta(C,N)$	2.52	2.19	3.06	−0.33	−0.54	−0.44

(f) NO	NO	NO$^-$	NO$^+$	f^+	f^-	f^0
$N(N)$	6.44	7.12	5.87	0.67	0.57	0.62
$N(O)$	8.56	8.89	8.13	0.33	0.43	0.38
$\lambda(N)$	5.28	6.06	4.55	0.78	0.73	0.75
$\lambda(O)$	7.40	7.83	6.81	0.43	0.59	0.51
$\delta(N,O)$	2.32	2.12	2.64	−0.20	−0.32	−0.26

(continued)

The CO molecule is isoelectronic to N$_2$ (14 e) and is a good example of a heteronuclear diatomic molecule (see Table 1d). First-order indices for the CO molecule predict that nucleophilic and electrophilic attacks are more likely on the O and C atoms, respectively. The O atom is also slightly more susceptible to a radical attack. f_λ^+ indices show qualitatively similar trends. As for the DI, it is interesting to compare some trends in the CO and N$_2$ molecules. For instance, while adding an electron to N$_2$ decreases the DI [f_δ^+(N,N') = −0.16] the effect is the opposite in CO

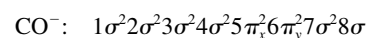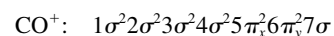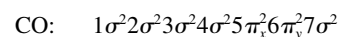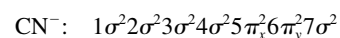[f_δ^+(C,O) = 0.34]. The electron configuration in the CO series is the following:

$$\text{CO:} \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 \pi_x^2 6\pi_y^2 7\sigma^2$$

$$\text{CO}^+\text{:} \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 \pi_x^2 6\pi_y^2 7\sigma$$

$$\text{CO}^-\text{:} \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 \pi_x^2 6\pi_y^2 7\sigma^2 8\sigma$$

Table 1. (*Continued*)

(g) CO$_2$	CO$_2$	CO$_2^-$	CO$_2^+$	f^+	f^-	f^0
$N(C)$	3.35	3.45	3.40	0.10	−0.05	0.02
$N(O)$	9.33	9.74	8.80	0.41	0.53	0.47
$\lambda(C)$	2.22	2.23	2.24	0.01	−0.02	−0.01
$\lambda(O)$	8.59	8.77	7.94	0.18	0.65	0.42
$\delta(C,O)$	1.13	1.21	1.16	0.08	−0.03	0.03
$\delta(O,O')$	0.34	0.65	0.56	0.31	−0.22	0.05

(h) SO$_2$	SO$_2$	SO$_2^-$	SO$_2^+$	f^+	f^-	f^0
$N(S)$	13.29	13.93	12.96	0.64	0.33	0.48
$N(O)$	9.36	9.54	9.02	0.18	0.34	0.26
$\lambda(S)$	11.97	12.65	11.47	0.68	0.50	0.59
$\lambda(O)$	8.54	8.77	8.08	0.23	0.46	0.34
$\delta(O,S)$	1.31	1.27	1.49	−0.04	−0.18	−0.11
$\delta(O,O')$	0.32	0.27	0.39	−0.05	−0.07	−0.06

(i) SO$_3$	SO$_3$	SO$_3^-$	SO$_3^+$	f^+	f^-	f^0
$N(S)$	11.90	12.32	11.87	0.42	0.03	0.23
$N(O)$	9.37	9.56	9.05	0.19	0.32	0.26
$\lambda(S)$	10.34	10.57	10.31	0.24	0.02	0.13
$\lambda(O)$	8.60	8.68	8.12	0.09	0.48	0.28
$\delta(O,S)$	1.04	1.16	1.04	0.13	0.00	0.06
$\delta(O,O')$	0.25	0.30	0.41	0.04	−0.15	−0.06

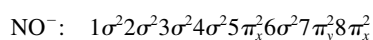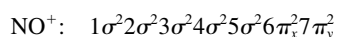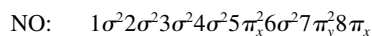| (j) C$_2$H$_2$	C$_2$H$_2$	C$_2$H$_2^-$	C$_2$H$_2^+$	f^+	f^-	f^0
$N(C)$	5.53	5.56	5.21	0.03	0.32	0.17
$N(H)$	0.86	1.33	0.66	0.46	0.21	0.33
$N(NNA)$	1.21	1.22	1.25	0.01	−0.04	−0.02
$\lambda(C)$	3.66	3.68	3.64	0.02	0.02	0.02
$\lambda(H)$	0.34	0.56	0.21	0.22	0.13	0.18
$\lambda(NNA)$	0.28	0.29	0.36	0.00	−0.07	−0.04
$\delta(C,NNA)$	0.90	0.91	0.88	0.00	0.02	0.01
$\delta(C,H)$	0.96	0.97	0.85	0.01	0.11	0.06
$\delta(C,C')$	1.82	1.82	1.38	−0.01	0.44	0.22
$\delta(C,H')$	0.06	0.08	0.03	0.02	0.03	0.02
$\delta(H,H')$	0.00	0.47	0.00	0.46	0.00	0.23
$\delta(H,NNA)$	0.03	0.03	0.02	0.00	0.01	0.00

The HOMO orbital in CO and CO$^+$ and the HOMO-1 in CO$^-$ are centered on the C atom and have little bonding character. For CO$^-$, the basin overlap between the two highest occupied orbitals is very low (ca. ±0.05 in both atomic basins) and the net effect of the unpaired electron in the 8σ orbital is a positive contribution to $\delta(C,O)$. Interestingly, while removing an e from N$_2$ decreases the LI the effect is the contrary in CO: $\delta(C,O)$ is larger in CO$^+$ than in CO. The overlap between orbitals 4σ and 7σ in the CO molecule is moderately high: −0.23 and +0.23 in the C and O basins, respectively. Thus, removal of an electron in CO to yield CO$^+$ leads to a decrease in the repulsion between these orbitals but also to a decrease in the number of valence σ electrons shared between the two atoms. The net result is that $\delta^\sigma(C,O)$ changes little (0.64 and 0.61 in CO and CO$^+$, respectively). In contrast, the transfer of

π electron density from C to O is larger in CO (1.47) than in CO$^+$ (1.31) and $\delta^\pi(C,O)$ is larger for the cation (0.93 and 1.14 in CO and CO$^+$, respectively). Altogether, the total DI is 0.19 e larger for CO$^+$.

CN and NO are the only neutral open-shell molecules, with 13 and 15 electrons, respectively (see Tables 1e and 1f). The electron configurations for the CN series are the following:

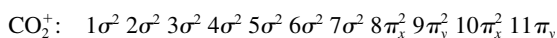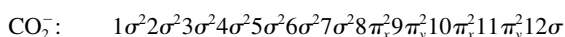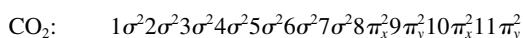CN: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 \pi_x^2 6\pi_y^2 7\sigma$

CN$^+$: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 \pi_x^2 6\pi_y^2$

CN$^-$: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 \pi_x^2 6\pi_y^2 7\sigma^2$
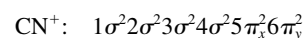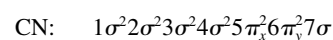
while the configurations for the NO series are the following:

$$\text{NO:} \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\pi_x^2 6\sigma^2 7\pi_y^2 8\pi_x$$

$$\text{NO}^+: \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\pi_x^2 7\pi_y^2$$

$$\text{NO}^-: \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\pi_x^2 6\sigma^2 7\pi_y^2 8\pi_x^2$$

Note that the differences between the neutral molecule, cation, and anion are related to σ and π electrons in the CN and NO series, respectively. Interestingly, the DI increases in the order anion < neutral molecule < cation for both series. Note that this ordering is different from the ones found in the N_2 and CO series. The reason is found in the relatively high overlap between orbitals 3σ, 4σ, and 7σ in CN and 5π and 8π in NO. Altogether, the removal of the unpaired electron in CN or NO diminishes the degree of interelectron repulsion between electrons in different atoms. In contrast, the addition of a second electron leads to larger interelectron interactions and a higher electron localization. Thus, both the f_δ^+ and f_δ^- are negative for CN and NO. Because, in both cases, the change in the value of the DI is larger when going from the neutral species to the cation, f_δ^0 indices are also negative for both molecules.

As for CO_2, both the f_N and the f_λ indices agree that the two O atoms are more reactive than C (see Table 1g). This is true for nucleophilic, electrophilic, and radical attacks. The $f_\delta(C,O)$ values are all close to zero, showing that $\delta(C,O)$ changes little in the CO_2, CO_2^-, and CO_2^+ series. In contrast, the electron delocalization between the nonbonded O atoms, $\delta(O,O')$, changes appreciably within this series. Indeed, $\delta(O,O')$ in CO_2 is quite large (0.34) and becomes even larger in CO_2^- (0.65) and CO_2^+ (0.56). Again, this behavior can be easily understood by analyzing the electron configurations in these molecules:

$$CO_2: \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^2 9\pi_x^2 9\pi_y^2 10\pi_x^2 11\pi_y^2$$

$$CO_2^-: \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^2 9\pi_x^2 9\pi_y^2 10\pi_x^2 11\pi_y^2 12\sigma$$

$$CO_2^+: \quad 1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^2\ 6\sigma^2\ 7\sigma^2\ 8\pi_x^2\ 9\pi_y^2\ 10\pi_x^2\ 11\pi_y$$

The HOMO in CO_2^- is spread mainly around the two O atoms and does not overlap appreciably with other occupied orbitals in any basin. Therefore, the unpaired electron in this molecule is largely delocalized between the terminal O atoms and contributes to the increase in $\delta(O,O')$. In contrast, the overlap between the orbitals $9\pi_y$ and $11\pi_y$ is negligible in the basin of the C atom but large in the O basins (±0.42). Thus, removal of an electron in $11\pi_y$ to yield CO_2^+ leads also to a larger delocalization of the electrons in $9\pi_y$ between the two O atoms. From a reactivity point of view, the large $f_\delta(O,O')$ indices show that electrophilic, nucleophilic, and radical reactions proceed by modifying considerably the electron delocalization patterns in CO_2.

The SO_2 and SO_3 molecules are other examples of small polyatomic molecules where this analysis can offer interesting insights (see Tables 1h and 1i). In these cases, there is a strong correlation between f_N and f_λ indices. Accordingly, most of the f_δ indices are quite small [less than 0.1, except for f_δ^-(O,S) and

f_δ^0(O,S) in SO_2 and f_δ^+(O,S) and f_δ^-(O,O') in SO_3]. Altogether, it means that, in general, electron loss or gain does not lead to large changes in electron delocalization in SO_2 or SO_3. From another point of view, second-order AFIs point out that nucleophilic, electrophilic, or radical attacks to these molecules affect mainly the electron density localized in the S and O atoms but not the electrons shared between two or more atoms. For instance, in SO_2 S is the atom most likely to suffer a nucleophilic attack [f_N^+(S) = 0.64], with the O atoms being less reactive [f_N^+(O) = 0.18]. The trends in electron localization are very similar [f_λ^+(S) = 0.68, f_λ^+(O) = 0.23]. Indeed, the f_λ^+ indices are slightly larger than the f_N^+ ones, which means that electron localization actually increases in CO_2 with respect to CO_2. Note that all f_δ^+ indices are slightly negative for this molecule. Similar analyses can be carried out for the electrophilic and radical indices and for SO_3.

C_2H_2 exhibits some interesting peculiarities. First, it has an NNA with an electron population of ca. 1.2 e, which is also found in $C_2H_2^-$ and $C_2H_2^+$ (see Table 1j). Note that the electron density in this NNA is highly delocalized toward the neighboring Cs. Another interesting trend is that f_δ indices are quite large in this molecule. For instance, the f_N^+ indices reveal that a nucleophilic attack to C_2H_2 is more likely at the two Hs. However, when a new electron is attached to C_2H_2, it is highly delocalized between the H atoms and f_δ^+(H,H') is 0.46. In turn, an electrophilic attack removes electron population from the two C atoms. From an electron pair point of view, the main effect of removing an electron is a marked decrease in the DI between the two Cs [f_δ^-(C,C') = 0.44]. Note also that, while f_N^- is maximal for C, f_λ^- is maximal for H. Finally, a radical attack is more likely on an H atom but also involves a decrease of $\delta(C,C')$ and $\delta(H,H')$. The Fukui indices related to the NNA are all close to zero.

Table 2 gathers the results calculated at the DFT level of theory for N_2, CO, CO_2, and SO_2 using the SVWN and B3LYP functionals. In general, with respect to HF, DFT reduces the degree of charge transfer in heteronuclear bonds and increases the degree of electron delocalization between all bonded atoms. This correction is stronger for the SVWN functional than for the B3LYP one. AFIs calculated at the HF and DFT levels of theory give a similar description of all molecules except CO. For this molecule, at the HF level, the O atom is preferred over C for a nucleophilic attack, while both C and O have similar propensity to a radicalary attack. In contrast, at the DFT level the C atom is preferred both for a nucleophilic and a radicalary attack. Further, the effects of a nucleophilic attack on interatomic delocalization are much stronger at the HF level of theory. In contrast, trends for an electrophilic attack are approximately the same at both levels of theory.

Conclusion

We defined new second-order AFIs derived from the electron pair density that complement those based on the one-electron density. Calculations for a series of small molecules show that, in general, the analysis based on the electron pair density gives relevant information on the electronic structure of these molecules and helps highlight the electronic reorganization processes taking place in electrophilic, nucleophilic, or radicalary reactions. In our opin-

Table 2. Electron populations (N), localization indices (λ), and delocalization indices (δ) for the neutral species, cation, and anion of a series of molecules and integrated atomic Fukui functions (f^+, f^-, f^0) derived from N, λ, and δ values calculated at the DFT level.

(a) N_2	N_2		N_2^-		N_2^+		f^+		f^-		f^0	
$N(N)$	7.00	*7.00*	7.50	*7.50*	6.50	*6.50*	0.50	*0.50*	0.50	*0.50*	0.50	*0.50*
$\lambda(N)$	5.48	*5.48*	6.05	*6.05*	4.87	*4.88*	0.57	*0.58*	0.60	*0.60*	0.59	*0.59*
$\delta(N,N')$	3.05	*3.05*	2.90	*2.89*	3.25	*3.23*	−0.15	*−0.15*	−0.21	*−0.18*	−0.18	*−0.17*

(b) CO	CO		CO^-		CO^+		f^+		f^-		f^0	
$N(C)$	4.92	*4.85*	5.77	*5.71*	4.33	*4.26*	0.85	*0.86*	0.59	*0.60*	0.72	*0.73*
$N(O)$	9.08	*9.15*	9.23	*9.29*	8.68	*8.75*	0.15	*0.14*	0.41	*0.40*	0.28	*0.27*
$\lambda(C)$	3.97	*3.95*	4.79	*4.77*	3.24	*3.21*	0.82	*0.83*	0.73	*0.74*	0.78	*0.78*
$\lambda(O)$	8.14	*8.24*	8.25	*8.35*	7.59	*7.70*	0.12	*0.11*	0.55	*0.54*	0.33	*0.33*
$\delta(C,O)$	1.90	*1.81*	1.95	*1.88*	2.18	*2.10*	0.06	*0.06*	−0.28	*−0.28*	−0.11	*−0.11*

(c) CO_2	CO_2		CO_2^-		CO_2^+		f^+		f^-		f^0	
$N(C)$	3.99	*3.85*	4.28	*4.12*	3.92	*3.80*	0.29	*0.28*	0.07	*0.05*	0.18	*0.16*
$N(O)$	9.01	*9.08*	9.36	*9.44*	8.54	*8.60*	0.36	*0.36*	0.46	*0.47*	0.41	*0.42*
$\lambda(C)$	2.49	*2.42*	2.59	*2.51*	2.46	*2.40*	0.10	*0.09*	0.03	*0.02*	0.07	*0.06*
$\lambda(O)$	8.06	*8.17*	8.22	*8.33*	7.53	*7.63*	0.16	*0.16*	0.53	*0.55*	0.34	*0.35*
$\delta(C,O)$	1.50	*1.43*	1.68	*1.61*	1.46	*1.40*	0.19	*0.18*	0.04	*0.03*	0.11	*0.11*
$\delta(O,O')$	0.40	*0.38*	0.61	*0.60*	0.56	*0.55*	0.21	*0.22*	−0.16	*−0.18*	0.02	*0.02*

(d) SO_2	SO_2		SO_2^-		SO_2^+		f^+		f^-		f^0	
$N(S)$	13.88	*13.76*	14.43	*14.32*	13.62	*13.90*	0.55	*0.56*	0.26	*−0.14*	0.40	*0.21*
$N(O)$	9.06	*9.12*	9.29	*9.34*	8.69	*8.55*	0.23	*0.22*	0.37	*0.57*	0.30	*0.40*
$\lambda(S)$	12.29	*12.23*	12.91	*12.86*	11.93	*12.21*	0.62	*0.64*	0.36	*0.02*	0.49	*0.33*
$\lambda(O)$	8.06	*8.17*	8.36	*8.46*	7.59	*7.43*	0.30	*0.29*	0.47	*0.74*	0.39	*0.51*
$\delta(O,S)$	1.59	*1.53*	1.52	*1.46*	1.69	*1.69*	−0.07	*−0.08*	−0.10	*−0.16*	−0.09	*−0.12*
$\delta(O,O')$	0.41	*0.38*	0.33	*0.31*	0.52	*0.55*	−0.08	*−0.07*	−0.12	*−0.17*	−0.10	*−0.12*

Values in plain and italic type have been calculated with the SVWN and B3LYP functionals, respectively.

ion, second-order AFIs may provide complementary information that can help chemists predict selectivity. While first-order AFIs point out which is the most favorable place for an electron to be added or removed,[25] second-order AFIs tell whether this electron is more or less localized or delocalized over the molecule. One can expect that, for instance in an electrophilic attack, the reaction is more selective if the electron removed is more localized over the attacked atom than if it is delocalized over a relatively large molecular region. Further work is necessary, however, to draw definite conclusions about the validity of these second-order AFIs to predict chemical selectivity.

Acknowledgments

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