Understanding properties of conceptual DFT quantities using simple algebraic tools

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Fukui's reactivity

- Frontier molecular orbital theory: introduced by Fukui around 1952. Explained reactivity of conjugated systems in terms of HOMO and LUMO (frontier MO's).
- Based on visual inspection of orbitals to assess where a reaction will take place.
- Essentially built on levels of theory that hold orbital energies (to identify HOMO and LUMO)

DFT interpretation

In DFT, the Fukui function is introduced in the context of a Taylor series expansion of the energy with respect to the number of electrons and the external potential $v_{ext}(\mathbf{r})$

$$E(N, v_{ext}(\mathbf{r})) = E(N^0, v_{ext}^0(\mathbf{r})) + \sum_{k=1}^{\infty} \frac{1}{k!} \left(\frac{\partial^k E}{\partial N^k} \right)_{\substack{N=N^0 \\ v_{ext}=v_{ext}^0}} (N - N^0)^k +$$

$$\sum_{k=1}^{\infty} \frac{1}{k!} \int \left(\frac{\delta^k E}{\delta v_{ext}(\mathbf{r_1}) \ldots \delta v_{ext}(\mathbf{r_k})} \right)_{\substack{N=N^0 \\ v_{ext}=v_{ext}^0}} \delta v_{ext}(\mathbf{r_1}) \ldots \delta v_{ext}(\mathbf{r_k}) d\mathbf{r_1} \ldots d\mathbf{r_k} +$$

$$\int \left(\frac{\partial \delta E}{\delta v_{ext}(\mathbf{r}) \partial N} \right)_{\substack{N=N^0 \\ v_{ext}=v_{ext}^0}} (N - N^0) \delta v_{ext}(\mathbf{r}) d\mathbf{r} + \ldots$$

All these derivatives have their own significance although little work has been done beyond second derivatives.

Of prime importance here is the so-called Fukui function; the first mixed derivative

$$f(\mathbf{r}) = \left(\frac{\partial \left(\frac{\delta E}{\delta v(\mathbf{r})} \right)_N}{\partial N} \right)_{v_{ext}(\mathbf{r})} \underset{non-deg}{=} \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v_{ext}(\mathbf{r})}$$

- Depends on $\mathbf{r}$.
- Integrates to 1.
- Is the DFT equivalent of Fukui's FMO theory.

So-called conceptual DFT attaches chemical meaning to each of these derivatives although in practice going beyond first order in an **r** dependency is often hardly possible.

For instance:

$\left(\frac{\partial E}{\partial N} \right)_{\substack{N=N^0 \\ v_{ext}=v_{ext}^0}} = -\chi$

$\left(\frac{\partial^2 E}{\partial N^2} \right)_{\substack{N=N^0 \\ v_{ext}=v_{ext}^0}} = \eta$

but here we concentrate on:

$$f(\mathbf{r}) = \left(\frac{\partial \left(\frac{\delta E}{\delta v(\mathbf{r})} \right)_N}{\partial N} \right)_{v_{ext}(\mathbf{r})} \underset{non-deg}{=} \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v_{ext}(\mathbf{r})}$$

Issues with the Fukui function

- It is often assumed that $f(\mathbf{r}) \approx \rho_{FMO}(\mathbf{r})$, however, near full CI calculations show regions with negative $f(\mathbf{r})$.
- No connection can be established yet with an underlying matrix as is the case in e.g., density matrices and their positive semidefinite character.
- one needs to distinguish (at least) two different Fukui functions:

$$f^+(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)^+_{v_{ext}(\mathbf{r})} = \lim_{\epsilon \to 0}\left(\frac{\rho^{N+\epsilon}(\mathbf{r}) - \rho^N(\mathbf{r})}{\epsilon}\right)_{v_{ext}(\mathbf{r})}$$

$$f^-(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)^-_{v_{ext}(\mathbf{r})} = \lim_{\epsilon \to 0}\left(\frac{\rho^N(\mathbf{r}) - \rho^{N-\epsilon}(\mathbf{r})}{\epsilon}\right)_{v_{ext}(\mathbf{r})}$$

In practice, finite differences are used, using only the neutral molecule and molecular ions.

Atom condensed Fukui functions

The Fukui functions $f^\pm(\mathbf{r})$ define a field, and most chemists prefer to use a coarse grain representation as atom condensed Fukui functions. Yang and Mortier introduced those, under the strict assumption that:

$$f_A^\pm = \int w_A(\mathbf{r}) \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v_{ext}(\mathbf{r})}^\pm$$

$$=$$

$$f_A^\pm = \int \left(\frac{\partial (w_A(\mathbf{r})\rho(\mathbf{r}))}{\partial N} \right)_{v_{ext}(\mathbf{r})}^\pm d\mathbf{r}$$

We follow the first, in agreement with Bader, but the second is far more popular as in that case one has:

$$f_A^+ = q_A(N+1) - q_A(N)$$
$$f_A^- = q_A(N) - q_A(N-1)$$

Negative values

Several attempts have been made concerning the possibility of negative Fukui functions and even more, negative atom condensed Fukui functions. Much of this reasoning is based on quite dubious considerations. Two issues appear:

1. Commutation or not ?

$$f_A^{\pm} = \int w_A(\mathbf{r}) \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v_{ext}(\mathbf{r})}^{\pm}$$

or

$$f_A^{\pm} = \int \left(\frac{\partial (w_A(\mathbf{r})\rho(\mathbf{r}))}{\partial N} \right)_{v_{ext}(\mathbf{r})}^{\pm} d\mathbf{r}$$

2. EEM based reasoning

EEM or Electronegativity Equalization Methods relate energies to quadratic atomic energy expansions in terms of charges through the hardness matrix with an exchange free embedding idea behind it. If charge derivatives are considered to be atom condensed Fukui functions, under extreme conditions, atom condensed values can
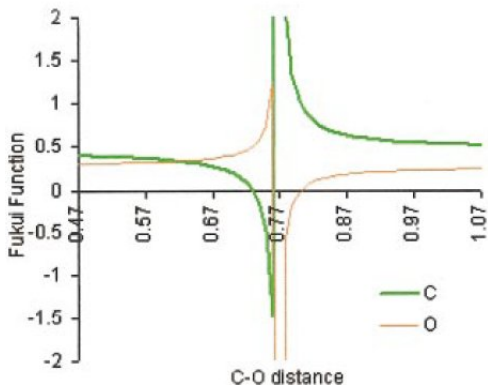
become negative.

Challenges for the Fukui function

- Can we show that the Fukui function is positive semi-definite along the same lines as done for density matrices ?
- Can we extend the Fukui function in a way that related it to Fukui's approach but for correlated levels of theory ?
- Can we condense the Fukui function in a way to also have bond Fukui functions as chemical reactions usually proceed via bond formation and breaking ?

The Fukui matrix

The Fukui matrix

The Fukui matrix is defined in a very simple fashion as:

$$f^{\pm}\left(\mathbf{r}, \mathbf{r}'\right) = \left(\frac{\partial \rho\left(\mathbf{r}, \mathbf{r}'\right)}{\partial N}\right)^{\pm}_{v_{ext}(\mathbf{r})}$$

such that the Fukui function is easily recovered as $f^{\pm}\left(\mathbf{r}, \mathbf{r}\right)$. The first question raised is easily answered if we project the Fukui function on the basis of the natural orbitals:

$$P_{ij} = \langle i \left| \rho\left(\mathbf{r}, \mathbf{r}'\right) \right| j \rangle$$

$$\mathbf{f} = \left\{ f_{ij} = \left(\frac{\partial P_{ij}}{\partial N}\right)_{v(\mathbf{r}) = v^0(\mathbf{r})} \right\}$$

Spectrum of the Fukui matrix

The resulting matrix **f** can be diagonalized and the spectrum investigated. Taking into account normalization, the matrix trace must equal 1. Results show that the Fukui matrix is not positive definite and negative eigenvalues occur frequently at the Hartree-Fock and B3LYP levels of theory.

Table: $f^-(\mathbf{r})$ eigenvalues for some small molecules.

Molecule	Pos	Neg	Low	CFMO
CH_2NH	8	7	-0.081	1.000
CO_2	11	10	-0.079	1.000
HCN	7	6	-0.074	1.000
N_2O	11	10	-0.072	1.000
CO	7	6	-0.055	1.000

The number of negative eigenvalues is always one less than the number of positive eigenvalues. Strangely, in all cases there is one eigenvalue exactly equal to 1!

Eigenvalues of the Fukui matrix

This effect disappears at the correlated level of theory

Table: Properties of the Fukui matrix at different levels of theory using the 6-311++G(2d,2p) basis set and B3LYP/6-311++G(2d,2p) optimized geometries. The first row gives the largest eigenvalue of the $\mathbf{F}^{\beta,-}$ matrix, the second row gives the most negative eigenvalue.

	B3LYP	ROHF	MP2	CISD	CCSD
CH_2NH	1.0000	1.0000	0.9806	0.9837	0.9580
	-0.0805	-0.1611	-0.0878	-0.0908	-0.0702
CO_2	1.0000	1.0000	0.9712	0.9822	0.9382
	-0.0791	-0.0669	-0.2393	-0.2650	-0.0976
HCN	1.0000	1.0000	0.9643	0.9728	0.9556
	-0.0774	-0.0808	-0.0912	-0.0805	-0.0697
N_2O	1.0000	1.0000	0.9646	0.9796	0.9420
	-0.0719	-0.0877	-0.2085	-0.2222	-0.0810
CO	1.0000	1.0000	0.9830	0.9803	0.9570
	-0.0552	-0.0788	-0.1525	-0.1391	-0.0496

- Proof by Hartwig et al.: the difference of two idempotent matrices can have only eigenvalues (here) equal to exactly 1 or 0 and all other eigenvalues must come in perfect pairing $+x$ and $-x$.
- More accessible proof given by Van Neck in recent work.
- At Hartree-Fock and DFT (Kohn-Sham) levels of theory, idempotency of the density matrix leads to one dominant Fukui orbital with eigenvalue exactly equal to 1. (Gradual) Loss of idempotency leads to (gradual) loss of this equality.
- No exceptions found!

Eigenvectors of the Fukui matrix

Study of the eigenvectors of the Fukui matrix leads to better understanding of Fukui's FMO theory.
In most molecules, a coefficient near 1.000 appears for the FMO in the dominant eigenvector (with eigenvalue 1).

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Correlated FMO's

This dominance of one single coefficient in the eigenvector with the highest eigenvalue and the near unity coefficient for the FMO at single determinant level, opens up the way to the following generalization.

The frontier molecular orbital is that eigenvector of the Fukui matrix with the highest eigenvalue.

In case of a idempotent density matrix theory, Fukui's approach is recovered, *but* the secondary eigenvectors explain regions with negative Fukui functions.
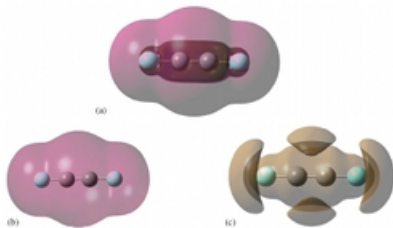
Figure: $|0.0002|$ Isosurfaces of $f^-(\mathbf{r})$ for the total Fukui function (a), the sum of contributions with positive eigenvalues (b) and negative eigenvalues (c) for FCCF.

Negative regions may arise depending on the spectrum of the Fukui matrix as well as on the eigenvectors.

Effect of electron correlation

$$S^{AB} = 100 * \frac{\sum_{ij}\left(f_{ij}^A f_{ji}^B\right)}{\sqrt{\sum_{ij}\left(f_{ij}^A f_{ji}^A\right)\sum_{ij}\left(f_{ij}^B f_{ji}^B\right)}}$$

Table: Similarity matrix between the f^- matrices obtained at different levels of theory for CH_2NH.

	B3LYP	ROHF	MP2	CISD	CCSD
B3LYP	100.0	95.5	95.7	95.8	99.5
ROHF	95.5	100.0	96.0	96.2	97.4
MP2	95.7	96.0	100.0	100.0	97.7
CISD	95.8	96.2	100.0	100.0	97.8
CCSD	99.5	97.4	97.7	97.8	100.0

The influence is clearly not very large but may become so when different levels of theory lead to different dominant eigenvectors.

Atom and bond condensed Fukui matrices

- Up to now virtually no Fukui functions used for atoms: usually atom *condensed* values only.
- Ambiguity on how to compute atom condensed Fukui functions

$$f_A^\pm = \int w_A(\mathbf{r}) \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v_{ext}(\mathbf{r})}^\pm$$

or

$$f_A^\pm = \int \left(\frac{\partial \left(w_A(\mathbf{r}) \rho(\mathbf{r}) \right)}{\partial N} \right)_{v_{ext}(\mathbf{r})}^\pm d\mathbf{r}$$

Density matrix partitioning approach

Based on our technique to partition density matrices:

$$f^{AB}\left(\mathbf{r}, \mathbf{r}'\right) = \frac{1}{2}\left(w_A\left(\mathbf{r}\right) w_B\left(\mathbf{r}'\right) + w_A\left(\mathbf{r}'\right) w_B\left(\mathbf{r}\right)\right) f\left(\mathbf{r}, \mathbf{r}'\right)$$

$w_A\left(\mathbf{r}\right)$ is a weight function as obtained using Hirshfeld-I, and expressed in the basis of the natural orbitals. Bader approach equally well possible. Gives Fukui functions $\forall\{A, B\}$. Atom condensed Fukui functions recovered easily:

$$\sum_{A,B} f^{AB}\left(\mathbf{r}, \mathbf{r}'\right) = f\left(\mathbf{r}, \mathbf{r}'\right)$$

$$\mathbf{f}_A = \sum_B \mathbf{f}_{AB}$$

$$\sum_{A,B} \mathbf{f}_{AB} = \sum_A \mathbf{f}_A = 1$$

Compared to previous work by Fradera and Solà (ab initio) and Contreras (HMO, FMO), current Fukui function based on first order density matrix. Fradera and Solà as well as Contreras consider the derivative of (de)localization indices with respect to N; i.e. derivative of exchange correlation density matrix (a 2-electron quantity).

Problems do remain, e.g., with Hirshfeld-I based recipes:

	f^-		f^+	
	neutral	cation	neutral	anion
CC	0.77	0.75	0.49	0.86
CO	0.07	0.07	0.33	0.07
OO	0.16	0.17	0.19	0.07

Table: Atom condensed Fukui functions for CO using $w_A(\mathbf{r})$ from either the neutral molecule or molecular ion.

Effect of non-commutation of mathematical operations:

	f_A^-		f_A^+	
	Eq. 1	Eq. 2	Eq. 1	Eq. 2
C	0.81	0.88	0.65	1.17
O	0.19	0.12	0.35	-0.17

Table: ROHF/aug-cc-pvdz $\mathbf{f}_A$ values for CO according to respectively equations 1 and 2.

$$f_A^\pm = \int w_A(\mathbf{r}) \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v_{ext}(\mathbf{r})}^\pm \tag{1}$$

or

$$f_A^\pm = \int \left(\frac{\partial (w_A(\mathbf{r}) \rho(\mathbf{r}))}{\partial N} \right)_{v_{ext}(\mathbf{r})}^\pm d\mathbf{r} \tag{2}$$

Fragment	1	2	3	4	5	11	12	13	14	$\sum_i f_{ii}^{AB}$
CC	-0.03	-0.03	-0.01	0.00	0.00	0.00	0.00	0.00	0.07	0.009
CO	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.009
CH	-0.01	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.016
CH	-0.01	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.016
CH'	-0.04	-0.04	-0.01	0.00	0.00	0.00	0.01	0.05	0.09	0.051
CH*	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.004
OO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.029
OH	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.001
OH	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.001
OH'	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.001
OH*	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.000
HH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.044
HH	-0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.001
HH'	-0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.003
HH*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.001
HH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.044
HH'	-0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.003
HH*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.001
HH'	-0.11	-0.09	0.00	0.00	0.00	0.00	0.00	0.01	0.84	0.650
HH*	-0.02	-0.01	0.00	0.00	0.00	0.00	0.00	0.04	0.04	0.058
H*H*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.060
$\sum_{A,B} \sum_i f_{ii}^{AB}$										1.000

Table: The f_{AB}^- Fukui orbitals and their eigenvalues for methanol, calculated in the STO-3G basis set on the ROHF level of theory.

Conclusions

The Fukui function has been generalized to a Fukui matrix, showing that:

- We have definite proof that the Fukui function can be negative.
- Negative eigenvalues are bound to appear (almost) always.
- Differences between (non-)idempotent matrices show interesting properties.
- A new perspective is found on FMO theory, allowing it to be extended to correlated levels of theory.
- Bond Fukui functions may be introduced. But also
- Partitioning and condensing Fukui functions remains problematic, especially for f^+.

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