ABSTRACT: The Ayers expectation value of size consistent operator averages is analyzed, leading to a general description of Fukui functions in terms of a possibly multidimensional gradient. The expectation value involves the density of an arbitrary collective of chosen ions or excited states. Molecular Orbital (MO) densities and Fukui functions are proved to be connected through the gradient of the first order state density functions with respect to the MO occupation numbers. The mathematical development taken as a whole opens the way to a general framework, where Fukui functions arise as a general theoretical tool to study molecular reactivity. Finally, shape functions appear as a plausible link between Ayers framework and the general ideas presented in this study. © 2008 Wiley Periodicals, Inc. Int J Quantum Chem 109: 2356–2364, 2009

Key words: Fukui functions; conceptual DFT; size consistent operators; expectation value averages; density averages; density gradients

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Dedication: Celebrating a 65th birthday is not a simple event. The elder author (R. C.-D.) feels that to greet Professor Istvan Mayer, some additional information, by means of several haikus, shall be annexed as follows:

One cannot unveil
X and Y fate, but joyful
birthdays celebrate.
Where X ≠ Y; (X & Y) = (Y & X); X, Y ∈ {birth, death, life, love}.
A couple of recent brilliant articles: a theoretical study by Ayers [1] and an experimental multitudinous author article [2] on inner MO ions have aroused the interest of the authors of this work on the subject of Fukui functions as defined by Parr and Yang [3], 30 years after the original Fukui proposal [4].

Ayers [1] put forward the possibility to describe average size consistent properties of molecular copies, each one separated at infinity. His argument aimed to define expectation values of size consistent molecular properties, associated to a function depending not of integer values but of a fractional number of electrons, which is one of the interesting subjects raised within the conceptual DFT area [3, 5, 6].

However, as it will be shown in the present work, Ayers scheme solely demonstrates in the first part of his article that linear mean values, depending of a rational variable defined in the unit range, can be easily obtained for this kind of operators. One can straightforwardly see that Ayers layout is only true when system set copies involve one electron differences. Thus, Ayers results appear to be quite a particular case of a very general situation involving double or higher ionic states, even excited states of a copied system.

This study first aims to clarify this point and extend the result to the definition of Fukui functions and their properties, providing new ways of considering Fukui functions.

**Introduction**

Supposing that the subsequent propositions hold, some consequences appear as it will be described afterwards:

1. A discrete set of $M$ copies of the same electronic structure are positioned infinitely away in space, permitting to build up a supra-system Hamiltonian, which is a sum of noninteracting individual Hamiltonians.

2. A subset of cardinality $Q$ of the $M$ copies possesses $N$ electrons, whereas a subset made of the remnant: $R = M − Q$ copies, possesses $N ± v$ electrons, with $v \in \mathbb{N}$.

3. For every kind of copy a Hamiltonian is known, namely: $H^{(N)}$, $H^{(N±v)}$.

4. The total Hamiltonian can be thus written as:

   $$H = QH^{(N)} + RH^{(N±v)}. \quad (1)$$

5. The Schrödinger equations for both kinds of systems are also known for any state:

   $$H^{(N)}|\Phi^{(N)}\rangle = E^{(N)}|\Phi^{(N)}\rangle$$
   $$H^{(N±v)}|\Phi^{(N±v)}\rangle = E^{(N±v)}|\Phi^{(N±v)}\rangle$$

6. The Schrödinger equation for the supra-system can be written as:

   $$H|\Phi\rangle = E|\Phi\rangle$$

and if the previous circumstances hold, it is well-known [7] that whenever the Hamiltonian (1) form is admissible, then:

$$|\Phi\rangle = \left( \prod_{i=1}^{P} |\Phi^{(N)}\rangle \right) \left( \prod_{j=P+1}^{M} |\Phi^{(N±v)}\rangle \right) E = QE^{(N)} + RE^{(N±v)} \quad (2)$$

also hold.

7. Therefore, one can seek for the energy average over the entire system set, obtaining:

   $$\bar{E} = M^{-1}(QE^{(N)} + RE^{(N±v)}) = xE^{(N)} + (1 − x)E^{(N±v)} = E^{(N±v)} + x(E^{(N)} - E^{(N±v)}) \quad (3)$$

where: $x = M^{-1}Q \to x \in \mathbb{Q}$, $\mathbb{Q} \in [0,1]$. An alternative expression can be set up in a trivial manner, just using as a variable: $y = M^{-1}R$, which bears the same properties as the former one. In any case, the supra-system average energy is obtained as a linear function of a rational variable with values contained in the real line.

When in Eq. (3): $v = 0$, it obviously appears that: $\bar{E} = E^{(N)}$. When: $v = 1$, the average energy (3) can be interpreted as a fractional electron function, as Ayers described [1]. However, this cannot be true in the cases of double or higher ionization, where: $v$
> 1, a situation which can be relevant when part of the copied suprasystem is a highly ionized atom obtained in a laboratory or potentially present in some star atmosphere plasma, for instance. Furthermore, whenever ν does not only represent an electron number but the whole expression N ≠ ν, it is taken as a simple identification index and then the size consistent expressions above and below are still valid. This can be consequently applied in the same manner to system copies with an excited state structure, not necessarily ionic. This possibility will be discussed below.

### Average Expectation Values of Hermitian Operators and Their First Derivatives

Additionally, the obtained result for the supraysiaystem average energy can be easily extended to arbitrary size consistent Hermitian operators. In this case, it is only necessary to consider that the supraysiaystem operator can be written as a sum of noninteracting individual system operators:

$$\Omega = Q\Omega^{(N)} + R\Omega^{(N\pm\nu)}$$  \hspace{1cm} (4)

which yield the expectation value:

$$\langle\Omega\rangle = Q\langle\Omega^{(N)}\rangle + R\langle\Omega^{(N\pm\nu)}\rangle$$

and employing the same argument as in the energy case, the average expectation value over the supraysiaystem can be written as:

$$\langle\bar{\Omega}\rangle = \langle\Omega^{(N\pm\nu)}\rangle + x(\langle\Omega^{(N)}\rangle - \langle\Omega^{(N\pm\nu)}\rangle).$$  \hspace{1cm} (5)

At the light of Eq. (5), it is meaningful to obtain a first derivative of the supraysiaystem averaged expectation values with respect to the rational variable x.

That is:

$$\frac{\partial\langle\bar{\Omega}\rangle}{\partial x} = \langle\Omega^{(N)}\rangle - \langle\Omega^{(N\pm\nu)}\rangle,$$

which constitutes a general result, easily leading to the definition of a Fukui function, not in the initial terms as it was originally defined [3], but in a more general fashion.

### First-Order Density Functions and Fukui Functions

Indeed, whenever the supraysiaystem wave function is constructed as in Eq. (2), then the supraysiaystem density function can be written as:

$$P = \left(\prod_{i=1}^{p} P^{(N)}\right)\left(\prod_{j=p+1}^{M} P^{(N\pm\nu)}\right)$$

where: $P = |\Psi\rangle\langle\Psi|$, with similar descriptions for the density functions of each class of subsystems.

First-order density functions can be supposedly built up as expectation values of the Dirac function, which can act like a one-electron operator for this purpose. This can be formally written for both density function subsystem classes as:

$$\rho^{(N)}(r) = \langle\bar{\delta}(r - r_i) \rho^{(N)}\rangle$$

$$= \int_{D_1} \delta(r - r_i) \left[ \int_{D_2} \cdots \int_{D_N} P^{(N)} \right]$$

$$\times (r_1, r_2, \ldots, r_N) dr_2 \cdots dr_N dr_1. \hspace{1cm} (7)$$

A similar expression holds for the ionized subsystem first-order density. Integral scheme (7) above can be employed as well to construct second first and second-order density matrices, as defined by Löwdin [8].

Then, a total density operator can be effortlessly written as a sum of Dirac delta functions, in the same way as has been commented in building up the operator in Eq. (4). Therefore, in this case, as obtained beforehand in Eqs. (3) and (5), one can also write:

$$\bar{\rho} = \rho^{(N\pm\nu)} + x(\rho^{(N)} - \rho^{(N\pm\nu)}). \hspace{1cm} (8)$$
AVERAGE DENSITY FUNCTIONS AND SHELL STRUCTURE

It must be taken into account here that the Minkowski norm of the average density function, which shall be associated to the number of particles defined by such a function, can be computed as:

$$\langle \rho \rangle = \langle \rho^{(N)} \rangle + x\langle \rho^{(N)} - \rho^{(N_{\pm})} \rangle = N \pm v(1 - x). \quad (9)$$

The equation above yields a fractional number of particles, directly related to both the ionization degree and the value of the rational variable x. This is not surprising, as it has been previously discussed how shell partition of vector semi-spaces affects the convex combination of vector elements belonging to different kinds of shells [9, 10]. In the present case, as well as in Ayers discussion [1], the involved density functions belong to the shells:

$$\langle \rho^{(N)} \rangle = N \rightarrow \rho^{(N)} \in S(N) \land \langle \rho^{(N)} \rangle = N \pm v \rightarrow \rho^{(N_{\pm})} \in S(N \pm v).$$

Then, the convex combination (8) corresponds to a Minkowski norm (9), and thus the corresponding shell of the average density function is obviously: $\hat{\rho} \in S(N \pm v(1 - x)).$

GENERAL EXPRESSION OF FUKUI FUNCTIONS

A general expression of the Fukui function can be written in turn as the first derivative of the mean density in Eq. (8), not with respect to the number of electrons, as in the original version of Parr and Yang [3], but with respect to the rational variable $x$, leading to the difference:

$$F^{(\pm)} = \frac{\partial \rho}{\partial x} = \rho^{(N)} - \rho^{(N_{\pm})}. \quad (10)$$

MO Expression of Fukui Functions

The general Fukui functions, as defined in Eq. (10), can be expressed in terms of the MO’s and the corresponding densities can be written as:

$$\rho^{(N)} = \sum_{i} \omega_{i}^{(N)} \rho_{i}^{(N)} \quad \rho^{(N_{\pm})} = \sum_{i} \omega_{i}^{(N_{\pm})} \rho_{i}^{(N_{\pm})}$$

where \( \{ \omega_{i} \} \subset R^{+} \) stand for MO occupation numbers and the set \( \{ \rho_{i} \} \) elements are the MO densities respectively; that is, if the MO set is \( \{|I|\} \), then:

$$\forall I: \rho_{I} = |I|.$$  

Moreover, the following properties hold, whenever the index $N \pm v$ represents electron numbers:

$$\sum_{i} \omega_{i}^{(N)} = N \land \sum_{i} \omega_{i}^{(N_{\pm})} = N \pm v$$

and also unit Minkowski norms are attached to MO densities:

$$\forall I: \langle \rho_{I}^{(N)} \rangle = \langle \rho_{I}^{(N_{\pm})} \rangle = 1,$$

yielding for each subsystem class the following Minkowski norms:

$$\langle \rho^{(N)} \rangle = N \land \langle \rho^{(N_{\pm})} \rangle = N \pm v.$$  

Therefore, a Minkowski pseudo-norm on the Fukui function can be written, without taking the absolute value of the densities difference, as:

$$\langle F^{(\pm)} \rangle = \langle \rho^{(N)} \rangle - \langle \rho^{(N_{\pm})} \rangle = \mp v. \quad (12)$$

APPROXIMATE FORM OF MO FUKUI FUNCTIONS

To have some insight on the form of Fukui functions, suppose that the \((N \pm v)\) -system MO densities are expressed as some transformation of the \((N)\) -system ones:

$$\forall I: \rho_{I}^{(N_{\pm})} = \sum_{K} \gamma_{K}^{(N_{\pm})} \rho_{K}^{(N)} \quad (13)$$

The unique condition which shall be associated to the coefficients \(\{ \gamma_{K}^{(N_{\pm})} \}\) in Eq. (13) will be related to the respective Minkowski norms:

$$\forall I: \langle \rho_{I}^{(N_{\pm})} \rangle = \sum_{K} \gamma_{K}^{(N_{\pm})} \rho_{K}^{(N)} \rightarrow \sum_{K} \gamma_{K}^{(N_{\pm})} = 1,$$

which amount the same as to say that the transformation matrix $\Gamma^{(\pm)} = \{ \gamma_{K}^{(\pm)} \}$ must be a column stochastic matrix.

When the Eq. (13) is taken into account in definitions (9) and (10), it is obtained:

$$\langle F^{(\pm)} \rangle = \sum_{I} \omega_{I}^{(N)} \rho_{I}^{(N)} - \sum_{I} \omega_{I}^{(N_{\pm})} \sum_{K} \gamma_{K}^{(N_{\pm})} \rho_{K}^{(N)} = \sum_{I} \omega_{I}^{(N)} \rho_{I}^{(N)}$$
The theoretical framework, see for example a recent development can be further generalized, whenever neutral molecular structures are used to build up the noninteracting supra-system in either a ground state or any excited state\(^2\), including ionized forms. Other changes may be perhaps related to the ensemble approach to excited-state DFT [21–24], but it is not so easy to grasp and deserves further research. Changes related to using the value of a symmetry operator (e.g., the orbital angular momentum) as the “ordering” for states have also been discussed, if only cursorily [14 –16] and from the standpoint of chemical DFT [17–20].

General Expression of a Fukui Function as a Difference Between Two Arbitrary Density Functions Belonging to the Supra-System Structure

As already commented, the previous theoretical development has been put forward in order to show that the Ayers result in Ref. [1] was usable just when the index \( v \) appearing in the present work was set as: \( v = 1 \). However, the theoretical development can be further generalized, whenever neutral molecular structures are used to build up the noninteracting supra-system in either a ground state or any excited state\(^2\), including ionized forms. Equation (8) can be easily rewritten in an alternative notation as:

\[
\tilde{\rho} = \rho^{(0)} + x(\rho^{(p)} - \rho^{(0)})
\]

\(^2\)Certain special cases of that excitation-related to changes in spin have been approached, both from the standpoint of formal DFT [14–16] and from the standpoint of chemical DFT [17–20]. Other changes may be perhaps related to the ensemble approach to excited-state DFT [21–24], but it is not so easy to grasp and deserves further research. Changes related to using the value of a symmetry operator (e.g., the orbital angular momentum) as the “ordering” for states have also been discussed, if only cursorily [25, 26].
where the density function pair: \( \{ \rho^{(0)}; \rho^{(p)} \} \) corresponds respectively to the ground or reference state molecular structure and the excited or ionic state one. Of course, the Fukui function will be written in the same manner as in Eq. (10):

\[
F = \frac{\partial \rho}{\partial x} = \rho^{(p)} - \rho^{(0)},
\]

(18)

but obviously the present form does not possess the definition sense given by Ayers in Ref. [1].

Indeed, just suppose that the states associated to the density pair: \( \{ \rho^{(0)}, \rho^{(p)} \} \) bear the same number of electrons, \( N \), say; such an occurrence can be accepted employing a ground state and an excited state as system copies, for instance. Then, the following Minkowski norms will hold:

\[
\langle \rho^{(0)} \rangle = \langle \rho^{(p)} \rangle = N \rightarrow \{ \rho^{(0)}, \rho^{(p)} \} \in S(N),
\]

precluding that, in this case, the average density will belong to the same vector semi-space shell like their convex components: \( \langle \tilde{\rho} \rangle = N \rightarrow \tilde{\rho} \in S(N). \) This homogeneous shell structure of the three involved density functions will produce a Fukui function Minkowski pseudo-norm with a null value, as:

\[
\langle F \rangle = \langle \rho^{(p)} - \rho^{(0)} \rangle = \langle \rho^{(p)} \rangle - \langle \rho^{(0)} \rangle = N - N = 0,
\]

implying that the generalized Fukui function (18) is no longer an element of the shell \( S(N) \) of the corresponding vector semi-space [9, 10], where the density pair belongs, acting as a basis set of the convex combination in the definition. Therefore, defined in this general way Fukui functions in some circumstances can possess positive and negative values within the definition range of the electron position variable.

**General Expression of a Fukui Function as a Gradient**

What has been previously said here about the genesis of Fukui functions can be extended in a general formalism, involving not only a neutral, but also ionic and excited states of noninteracting system copies. In fact, one can propose handling a set of noninteracting systems associated to a set of density functions: \( \tilde{P} = \{ \rho^{(\nu)} \}_{\nu \in \mathbb{I}}, \) with \( \nu = 0 \) indicating the neutral system, \( \nu = \pm 1 \) cationic and anionic species, and so on. The possible presence of noninteracting copies of the system in diverse excited states could be even considered in the density set \( \tilde{P} \) above described, as it has been previously commented. In such case, the symbol \( \nu \) shall be just considered as an ordering index. Generally speaking, first-order densities can be computed in the same manner as in Eq. (6), and it can be easily proved that the average density function can be written in terms of several rational variables:

\[
\tilde{\rho} = \rho^{(0)} + \sum_{\nu \neq 0} x_{\nu} (\rho^{(\nu)} - \rho^{(0)}) \wedge x_{\nu} = 1 - \sum_{\nu \neq 0},
\]

(19)

and the property put in evidence in Eq. (9) appears here again, as the Minkowski norm of the average density function (15) will be a convex average of the particle number associated to each density function, that is:

\[
\forall \nu: \langle \rho^{(\nu)} \rangle = N^{(\nu)} \rightarrow \tilde{\rho}^{(\nu)} \in S(N^{(\nu)}) \Rightarrow \langle \tilde{\rho} \rangle = \tilde{N} = \sum_{\nu} N^{(\nu)} \rightarrow \tilde{\rho} \in S(\tilde{N}).
\]

(20)

Now, taking into account Eq. (19), one can describe a vector bearing the rational convex variable set: \( x = \{ x_{\nu} \} \), defining afterwards the gradient:

\[
|F| = \frac{\partial \tilde{\rho}}{\partial x} = \left[ \frac{\partial \tilde{\rho}}{\partial x_{\nu}} = \rho^{(\nu)} - \rho^{(0)} \right],
\]

(21)

which has as components Fukui functions, similar to the ones in the one-dimensional Eqs. (10) or (18).

**Alternative Form of Fukui Functions in MO Theory**

The general gradient (21), which leads to the description of several Fukui functions, points towards the following development, intending, in turn, to associate MO Fukui functions to the derivative of a set of real variables, as an alternative to the previous considerations.

A first-order density function can be expressed within MO theory as in Eq. (11), alternatively:

\[
\rho^{(\nu)} = \sum_{\nu} \omega_{\nu} |\varphi_{\nu}(\mathbf{r})|^{2}
\]

where the MO set \( \{ \varphi_{\nu}(\mathbf{r}) \} \) elements can be considered normalized, thus:
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\[ \forall I: \langle \varphi_i | r \rangle^2 = \int_D |\varphi_i(r)|^2 \rho_1(r) \]
\[ = |\varphi_i(r)|^2 \rho_1(r) = 1 \land \rho_1(r) \]
\[ = 1 \land \rho(r) = \sum_i \omega_i \rho_i(r) \]

Generally speaking, the parameters \( \{\omega_i\} \) can be also considered as fulfilling the relationships:

\[ \forall I: \omega_i \in \mathbb{R}^+ \land \omega_i \in [0,2] \omega_i \sum_i \omega_i = N, \]

being \( N \) the number of electrons associated to a quantum object possessing the density function \( \rho(r) \); furthermore:

\[ \langle \rho(r) \rangle = \sum_i \omega_i \rho(r) = \sum_i \omega_i = N. \]

In this context one can consider, in a general approach, the density function as being a function of a set of positive real variables:

\[ w = (\omega_1, \omega_2, \ldots, \omega_n) \lambda(w) = N \rightarrow \rho(r|w). \]

Thus the number of particles can be considered acting as a restriction on the structure of the real variable set: \( w \).

Keeping the previous considerations in mind, a Fukui function associated to the \( I = \) \( i \) th MO can be defined as the partial derivative:

\[ \forall I: f_i(r) = \frac{\partial \rho(r|w)}{\partial \omega_i} = \rho_i(r), \] (22)

which is equivalent to construct the MO Fukui functions as the elements of the gradient of the density function with respect to the MO occupation numbers:

\[ f(r) = \frac{\partial \rho(r|w)}{\partial w} = \{\rho_i(r)\}. \]

In our opinion, such a definition is well adapted to the Fukui ideas about MO density functions and their role as molecular indicators of molecular activity. This can be seen without difficulty in Fukui’s original article of 1952 [4] and in the 1954 sequel [27].

As a consequence, every MO has an attached Fukui function which is nothing else than the MO density:

\[ \forall I: f_i(r) = |\varphi_i(r)|^2 = \rho_i(r). \]

And in this way, Fukui functions can be seen as a non-negative definite function set: \( f(r) \), attached to any of the states of every quantum object. Such a definition produces information on ionization or electronic exchange processes, affecting inner or outer MO energy levels. In this way, such a simple definition is connected with the previous discussion based on noninteracting supra-systems. There has been earlier thinking on this subject and related ones; perhaps Ref. [5] can provide the reader with a sufficiently broad account.

Shape Functions and Fukui Functions

After the previous development, one can inquire about the possible role of shape functions, even if they cannot be expressed as the expectation value of a size-consistent quantum mechanical operator. Here the development of Fukui functions description, tries to follow another point of view than the previous efforts of various authors [25, 26, 28].

In fact, every density function \( \rho \) can be attached to a shape function \( \sigma \) in the straightforward way of scaling the density function by the inverse of the number of electrons:

\[ \forall \rho \sigma = N \land \rho = N^{-1} \rho. \]

The mathematical consequences of such a shape function definition and the connection of both density and shape functions with vector semi-spaces and their shell structure have been previously commented [9, 10].

There is no problem in defining a shape function using the technique depicted in Eq. (7), with the following slight modification:

\[ \sigma^{(N)}(r) = \langle N^{-1} \delta(r - r_i) P^{(N)} \rangle = \int_{D_1} N^{-1} \delta(r - r_i) \]
\[ \times \left[ \int_{D_2} \ldots \int_{D_N} P^{(N)}(r_1, r_2, \ldots, r_N) dr_2, \ldots dr_N \right] dr_i, \]
Therefore, being the shape functions Minkowski normalized, they can be taken as elements of the unit shell of the corresponding vector semi-space:

$$\forall \nu \sigma^{(\nu)} = 1.$$  

Then, Eq. (15) could be rewritten as:

$$\tilde{\sigma} = x_0 \sigma^{(0)} + \sum_{\nu \neq 0} x_0 (\sigma^{(\nu)} - \sigma^{(0)}) \wedge x_0 = 1 - \sum_{\nu \neq 0} x_0$$

just substituting the density functions by the attached shape functions.

The Minkowski norm of the average shape function above defined will yield the unity, as it is a well-known result that, when a convex linear combination of functions belonging to the unit shell is constructed, the resulting functions belong to the same shell [9, 10]. Therefore, this property makes shape functions devoid of the fractional Minkowski norm, which yield the averaged density function, as shown in Eqs. (9) and (20). As a result, one could also say that any convex average of shape functions yields another shape function. Shape functions, contrarily to density functions, in general behave homogenously, when manipulated in the way described in the present work.

In this context, the definition of Fukui functions gradient would become:

$$F = \frac{\partial \tilde{\sigma}}{\partial x} = \left\{ \frac{\partial \tilde{\sigma}}{\partial x_0} = \sigma^{(\nu)} - \sigma^{(0)} \right\}$$

The Minkowski pseudo-norm of the vector (23), as the corresponding one in the previous Eq. (17) is null.

Also, the present definition of Fukui functions involving shape functions has a better structure than the previous one, based on density functions as shown in Eq. (19), because the gradient can be interpreted in this case as a set of fractional electron number derivatives. Moreover, expressions (20) and (23) bear a meaningful connection, being the components of both gradients elements belonging to the unit shell of some vector semi-space.

Finally, if the Ayers description on Fukui functions shall be kept [1], perhaps a general framework may be sought, using the ideas developed within the present study. Accepting this possibility, an obvious way to balance both points of view may consist on substituting density functions by shape functions in the Fukui function gradient definition.

Obviously enough, this prospect deserves further research.

Conclusions

An argument on Ayers recent definition of Fukui functions, as the first derivative of the density with respect of a rational variable defined in the real line permits to consider a more general context, where the one-dimensional definition can be easily transformed into a multidimensional gradient of the density with respect to a rational variable vector. This can revert into a gradient of the neutral MO density with respect to the real occupation numbers, enlarging in this manner the initial Fukui idea to the MO set as a whole, which seems an obvious generalization.

Therefore, the present discussion permits to study the behavior of molecular systems, when exchange of electrons with external sources or excitation involves not only the usual HOMO and LUMO but also one-electron levels located in inner or outer molecular shells. One can finally conclude that the role of shape functions, in order to keep Ayers connection between the fractional number of electrons derivatives and the weight coefficients of the operator expectation value averages, appears to be crucial in the general definition of Fukui functions.

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