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The nuclear Fukui function and Berlin's binding function in density functional theory

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The recently introduced nuclear Fukui function ϕ_α is formally identified as a reactivity index of the density functional theory (according to the postulated criterion of $|d\mu|$) and is shown to constitute the conformational contribution to a change in the molecular electronic chemical potential μ , through the relation $d\mu|_N = \int f(\mathbf{r}) d\nu(\mathbf{r}) d\mathbf{r} = -\sum_\alpha \phi_\alpha d\mathbf{R}_\alpha$, with $\phi_\alpha = (\partial \mathbf{F}_\alpha / \partial N)_\nu = -(\delta \mu / \delta \mathbf{R}_\alpha)_N$, where N is the number of electrons, $f(\mathbf{r})$ the electronic Fukui function, $\nu(\mathbf{r})$ the external potential at point \mathbf{r} , \mathbf{R}_α the space coordinate of nucleus α , and \mathbf{F}_α the force on nucleus α . Scaling of the nuclear coordinates with a factor λ , as a particular conformational change, links the nuclear Fukui function with Berlin's binding function $B(\mathbf{r})$ for polyatomic molecules, $d\mu^\lambda|_N = d\lambda \int f(\mathbf{r}) B(\mathbf{r}) d\mathbf{r} = -\sum_\alpha \phi_\alpha d\mathbf{R}_\alpha^\lambda$. This relation is instructing for interpretative purposes: changes in electron density are weighted by the binding function, which, according to Berlin's theorem, separates the system in binding and antibinding regions. © 1996 American Institute of Physics. [S0021-9606(96)03334-X]

NUCLEAR FUKUI FUNCTION

Consider the total energy W of a system, the sum of the electronic energy E , and the nuclear–nuclear repulsion energy V_{nn} (the latter only depends on the nuclear configuration and the nuclear charges) in the Born–Oppenheimer approximation:

$$W[\rho, \nu] = E[\rho, \nu] + V_{nn}[\nu], \quad (1)$$

where ρ is the electron density distribution function and $\nu(\mathbf{r}) = \sum_\alpha Z_\alpha / |\mathbf{R}_\alpha - \mathbf{r}|$ is the external potential at point \mathbf{r} , with Z_α and \mathbf{R}_α the nuclear charge and the nuclear coordinate, respectively. The density functional theory (DFT) expression for the electronic energy is¹

$$E[\rho, \nu] = F[\rho] + V_{ne}[\rho, \nu] = F[\rho] + \int \rho(\mathbf{r}) \nu(\mathbf{r}) d\mathbf{r}. \quad (2)$$

$F[\rho] = T[\rho] + V_{ee}[\rho]$ is the sum of kinetic energy and electron–electron repulsion energy, and is a universal functional of ρ , i.e., independent of ν . Equation (1) may be written as $W = T + V_{ee} + V_{ne} + V_{nn} \equiv F + V$.

From the Hellmann–Feynman theorem, because of the independence of F on ν , one has

$$-\left(\frac{\delta W}{\delta \mathbf{R}_\alpha}\right)_N = -\left(\frac{\delta V}{\delta \mathbf{R}_\alpha}\right)_N = \mathbf{F}_\alpha, \quad (3)$$

where \mathbf{F}_α is the force on nucleus α . On the other hand, since V_{nn} is independent of N , one also has

$$\left(\frac{\partial W}{\partial N}\right)_\nu = \left(\frac{\partial E}{\partial N}\right)_\nu = \mu, \quad (4)$$

where μ is the electronic chemical potential. The mixed derivatives of W with respect to N and \mathbf{R}_α at the appropriate constraints provide the Maxwell relation

$$\left(\frac{\partial \mathbf{F}_\alpha}{\partial N}\right)_\nu = -\left(\frac{\delta \mu}{\delta \mathbf{R}_\alpha}\right)_N = \phi_\alpha, \quad (5)$$

where ϕ_α is the recently introduced nuclear Fukui function:²

$$\phi_\alpha = - \int f(\mathbf{r}) \left(\frac{\delta \nu(\mathbf{r})}{\delta \mathbf{R}_\alpha}\right)_N d\mathbf{r} \equiv - \int f(\mathbf{r}) c_\alpha(\mathbf{r}) d\mathbf{r}. \quad (6)$$

Equation (6) defines the notation c and $f(\mathbf{r})$ is the electronic Fukui function:³

$$f(\mathbf{r}) = \left(\frac{\delta \mu}{\delta \nu(\mathbf{r})}\right)_N = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_\nu. \quad (7)$$

Consider now a change in the electronic chemical potential of the system in the canonical ensemble where $\mu = \mu[N, \nu]$:

$$\begin{aligned} d\mu &= \left(\frac{\partial \mu}{\partial N}\right)_\nu dN + \int \left(\frac{\delta \mu}{\delta \nu(\mathbf{r})}\right)_N d\nu(\mathbf{r}) d\mathbf{r} \\ &= \eta dN + \int f(\mathbf{r}) d\nu(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (8)$$

η is the global chemical hardness of Parr and Pearson.⁴ The explicit dependence of $\nu(\mathbf{r})$ on \mathbf{R} allows us to write (for a chemical process where Z is constant)

$$d\nu(\mathbf{r})|_N = \sum_\alpha \left(\frac{\delta \nu(\mathbf{r})}{\delta \mathbf{R}_\alpha}\right)_N d\mathbf{R}_\alpha = \sum_\alpha c_\alpha(\mathbf{r}) d\mathbf{R}_\alpha. \quad (9)$$

Substitution into Eq. (8) and also inserting Eq. (6) gives

$$\begin{aligned} d\mu &= \eta dN + \sum_\alpha d\mathbf{R}_\alpha \int f(\mathbf{r}) c_\alpha(\mathbf{r}) d\mathbf{r} \\ &= \eta dN - \sum_\alpha \phi_\alpha d\mathbf{R}_\alpha, \end{aligned} \quad (10)$$

which can also directly be obtained from the Maxwell relation for ϕ_α :

$$d\mu|_N = \sum_\alpha \left(\frac{\delta\mu}{\delta\mathbf{R}_\alpha} \right)_N d\mathbf{R}_\alpha = - \sum_\alpha \phi_\alpha d\mathbf{R}_\alpha. \quad (11)$$

Equations (10) and (11) demonstrate that the nuclear Fukui function constitutes the conformational contribution to a change in the electronic chemical potential. The symmetry with Eq. (8) also demonstrates how well chosen its name is.

In analogy with Ref. 5 it is straightforward to derive the fluctuation formulas for the finite-temperature nuclear Fukui function with the state function W in the canonical ensemble:

$$\phi_\alpha = \frac{1}{kT} [\langle \mathbf{F}_\alpha \rangle \langle \mu \rangle - \langle \mathbf{F}_\alpha \cdot \mu \rangle], \quad (12)$$

where k and T are the Boltzmann constant and absolute temperature, respectively. This equation shows that the nuclear Fukui function measures local force fluctuations on nucleus α . Large values of ϕ_α tend to move the nucleus from its position.

BERLIN'S THEOREM

Berlin defined the binding function for diatomics,⁶ which divides the molecule in binding and antibinding regions: electron density in binding (antibinding) regions tends to bind (separate) the nuclei. Berlin's binding function $B(\mathbf{r})$ has been extended to polyatomic molecules,⁷ viz.:

$$\begin{aligned} B(\mathbf{r}) &= \left(\frac{\partial \nu(\mathbf{r})}{\partial \lambda} \right)_{\mathbf{R}_0} \bigg|_{\lambda=1} = \sum_\alpha \left(\frac{\delta \nu(\mathbf{r})}{\delta \mathbf{R}_\alpha} \right)_N \left(\frac{\partial \mathbf{R}_\alpha^\lambda}{\partial \lambda} \right) \\ &= \sum_\alpha c_\alpha(\mathbf{r}) \mathbf{R}_\alpha, \end{aligned} \quad (13)$$

where λ is a scaling factor. The constraint \mathbf{R}_0 denotes that the geometric center of the molecule is fixed at the origin. Scaling of the nuclear coordinates corresponds to the totally symmetric stretching of the molecule (i.e., a particular case of a conformational change), where all bonds are stretched proportional to their original length:

$$\partial \mathbf{R}_\alpha^\lambda = \mathbf{R}_\alpha \partial \lambda. \quad (14)$$

The total binding effect is defined by the binding force F_B based on the energy change occurring with an increase of the scaling factor λ :

$$F_B = \left(\frac{\partial W}{\partial \lambda} \right)_{\mathbf{R}_0} \bigg|_{\lambda=1} = \sum_\alpha \left(\frac{\delta W}{\delta \mathbf{R}_\alpha} \right) \left(\frac{\partial \mathbf{R}_\alpha^\lambda}{\partial \lambda} \right) = - \sum_\alpha \mathbf{F}_\alpha \mathbf{R}_\alpha. \quad (15a)$$

F_B also corresponds to an integration of the binding function $B(\mathbf{r})$ with the electron density, plus a term due to the nuclear–nuclear repulsion:

$$\begin{aligned} F_B &= \int \left(\frac{\delta W}{\delta \nu(\mathbf{r})} \right)_N \left(\frac{\partial \nu(\mathbf{r})}{\partial \lambda} \right) d\mathbf{r} \\ &= \int \rho(\mathbf{r}) B(\mathbf{r}) d\mathbf{r} + \left(\frac{\partial V_{nn}}{\partial \lambda} \right)_N. \end{aligned} \quad (15b)$$

By deriving Eqs. (15a) and (15b) with respect to N at constant ν , one finds

$$\left(\frac{\partial F_B}{\partial N} \right)_\nu = - \sum_\alpha \phi_\alpha \mathbf{R}_\alpha = \int f(\mathbf{r}) B(\mathbf{r}) d\mathbf{r}, \quad (16)$$

in which the nuclear Fukui function enters.

The mixed derivatives of W with respect to N and λ at the appropriate constraints provide the Maxwell relation:

$$\left(\frac{\partial F_B}{\partial N} \right)_\nu = \left(\frac{\partial \mu}{\partial \lambda} \right)_N \equiv \phi_B. \quad (17)$$

Upon scaling one can thus write

$$\begin{aligned} d\mu^\lambda|_N &= \left(\frac{\partial \mu}{\partial \lambda} \right)_N d\lambda = \phi_B d\lambda = d\lambda \int f(\mathbf{r}) B(\mathbf{r}) d\mathbf{r} \\ &= - \sum_\alpha \phi_\alpha \mathbf{R}_\alpha d\lambda = - \sum_\alpha \phi_\alpha d\mathbf{R}_\alpha^\lambda, \end{aligned} \quad (18)$$

which clearly shows that scaling is a special case of a conformational change with respect to the general expression [Eq. (11)]. The last equality can also directly be obtained by substituting the scaling relation [Eq. (14)] into Eq. (11). As such, the nuclear Fukui function can be regarded as a generalization in the spirit of Berlin's theorem; however, not all bonds stretch with the same factor, but all vary individually.

CANONICAL AND ISOMORPHIC ENSEMBLE

Since the nuclear Fukui function describes changes in the nuclear configuration (geometry), it should be related to the recently introduced nuclear/geometric reactivity index of the isomorphic ensemble in density functional theory:^{5(c)}

$$h(\mathbf{r}) = \frac{1}{N} \left(\frac{\delta \mu}{\delta \sigma(\mathbf{r})} \right)_N, \quad (19)$$

with $\sigma(\mathbf{r}) = \rho(\mathbf{r})/N$ the shape factor of the electron density distribution function.⁸

Since

$$\begin{aligned} f(\mathbf{r}) &= \int \left(\frac{\delta \mu}{\delta \sigma(\mathbf{r}')} \right)_N \left(\frac{\delta \sigma(\mathbf{r}')}{\delta \nu(\mathbf{r})} \right)_N d\mathbf{r}' \\ &= \int h(\mathbf{r}') p(\mathbf{r}, \mathbf{r}') d\mathbf{r}', \end{aligned} \quad (20)$$

where p is the linear density response function:

$$p(\mathbf{r}, \mathbf{r}') = \left(\frac{\delta \rho(\mathbf{r})}{\delta \nu(\mathbf{r}')} \right)_N = N \left(\frac{\delta \sigma(\mathbf{r})}{\delta \nu(\mathbf{r}')} \right)_N, \quad (21)$$

the nuclear Fukui function has the alternative expression:

$$\begin{aligned}\phi_\alpha &= - \int \int \left(\frac{\delta\mu}{\delta\sigma(\mathbf{r}')} \right)_N \left(\frac{\delta\sigma(\mathbf{r}')}{\delta\nu(\mathbf{r})} \right)_N \left(\frac{\delta\nu(\mathbf{r})}{\delta\mathbf{R}_\alpha} \right)_N d\mathbf{r}' d\mathbf{r} \\ &= \int \int h(\mathbf{r}) p(\mathbf{r}, \mathbf{r}') c_\alpha(\mathbf{r}') d\mathbf{r}' d\mathbf{r}.\end{aligned}\quad (22)$$

Define now the function

$$d_\alpha(\mathbf{r}) = \left(\frac{\delta p(\mathbf{r})}{\delta\mathbf{R}_\alpha} \right)_N = N \left(\frac{\delta\sigma(\mathbf{r})}{\delta\mathbf{R}_\alpha} \right)_N = \int p(\mathbf{r}, \mathbf{r}') c_\alpha(\mathbf{r}') d\mathbf{r}'. \quad (23)$$

Then we have, for the canonical and isomorphic ensemble, respectively,

$$\phi_\alpha = - \int f(\mathbf{r}) c_\alpha(\mathbf{r}) d\mathbf{r} = - \int h(\mathbf{r}) d_\alpha(\mathbf{r}) d\mathbf{r}. \quad (24)$$

Consider now a change of the electronic chemical potential in the isomorphic ensemble where $\mu = \mu[N, \sigma]$:

$$\begin{aligned}d\mu &= \left(\frac{\partial\mu}{\partial N} \right)_\sigma dN + \int \left(\frac{\delta\mu}{\delta\sigma(\mathbf{r})} \right)_N d\sigma(\mathbf{r}) d\mathbf{r} \\ &= \eta^\sigma dN + N \int h(\mathbf{r}) d\sigma(\mathbf{r}) d\mathbf{r},\end{aligned}\quad (25)$$

where η^σ is the isomorphic global hardness.^{5(c)} Analogously as in Eq. (9), one can write

$$d\sigma(\mathbf{r})|_N = \sum_\alpha \left(\frac{\delta\sigma(\mathbf{r})}{\delta\mathbf{R}_\alpha} \right)_N d\mathbf{R}_\alpha = \frac{1}{N} \sum_\alpha d_\alpha(\mathbf{r}) d\mathbf{R}_\alpha \quad (26)$$

or

$$d\mu|_N = \sum_\alpha \int h(\mathbf{r}) d_\alpha(\mathbf{r}) d\mathbf{r} d\mathbf{R}_\alpha = - \sum_\alpha \phi_\alpha d\mathbf{R}_\alpha. \quad (27)$$

As such, in both the canonical and isomorphic ensemble the nuclear Fukui function describes the conformational contribution to a change in the electronic chemical potential, both with the same expression.

DISCUSSION

“ $|d\mu|$ big is good!”^{1,3} is a postulate that generates the frontier electron theory and identifies the electronic Fukui function as a reactivity index, providing information on the relative reactivity of different sites within a molecule [Eq. (8)]: large values of $f(\mathbf{r})$ produce large responses in μ . In Eq. (8) the change in external potential $d\nu(\mathbf{r})$ is not specified. However, by considering chemical reactions, Z is constant, and there remains only the nuclear configuration \mathbf{R} as a variable. By this very fact, the nuclear Fukui function enters the relation, and it also appears as a local probe for chemical reactivity. While $f(\mathbf{r})$ is defined at each point \mathbf{r} in space, ϕ_α is defined per nucleus α and is a vector.

It is remarkable that the nuclear Fukui function has been derived and defined along a different path of thinking.² In the spirit of Nakatsuji⁹ the interrelation of changes in electron density and changes in nuclear configuration was envisaged. Changes associated with chemical reactions can be approached from the electronic or the nuclear configuration

point of view, i.e., via ρ - or ν -reactivity indices. At the origin of changes in ν are the forces \mathbf{F} on the nuclei, so that two types of indices are fundamental:

$$f(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial N} \right)_\nu \quad \text{and} \quad \phi_\alpha = \left(\frac{\partial\mathbf{F}_\alpha}{\partial N} \right)_\nu, \quad (28)$$

respectively, the electronic and nuclear Fukui function, the latter defined in formal analogy with the first one. Whereas ϕ_α was defined mainly on an intuitive basis, the present paper incorporates it in the usual DFT equations and shows that it is the parameter of choice when chemical reactions are envisaged in which bond length variations (geometrical rearrangements) are an essential ingredient.

Notice that the nuclear Fukui function focuses on the origin, the cause of the change in ν , not on the change in ν itself; the latter has also recently been studied in the isomorphic ensemble with the geometrical reactivity index $h(\mathbf{r})$ or with another geometrical parameter:^{5(c)}

$$g(\mathbf{r}) = \left(\frac{\partial\nu(\mathbf{r})}{\partial N} \right)_\sigma.$$

While the electronic Fukui function describes local electron density fluctuations,

$$f(\mathbf{r}) = \frac{1}{kT} [\langle\rho(\mathbf{r})\rangle\langle\mu\rangle - \langle\rho(\mathbf{r})\cdot\mu\rangle], \quad (29)$$

the geometric indices describe local ν fluctuations, i.e., fluctuations in nuclear configuration or (bond) distances:

$$h(\mathbf{r}) = \frac{1}{kT} [\langle\nu(\mathbf{r})\rangle\langle\mu\rangle - \langle\nu(\mathbf{r})\cdot\mu\rangle]. \quad (30)$$

The nuclear Fukui function, on the other hand, describes local force fluctuations [Eq. (12)].

The relation with Berlin's binding function is interesting for interpretative purposes. The function separates the space around the nuclei in binding regions [$B(\mathbf{r}) < 0$] and antibinding regions [$B(\mathbf{r}) > 0$], based on the forces on the nuclei, due to the electron density. Electron density in binding regions tends to shorten the bond, whereas electron density in the antibinding regions tends to stretch the bond. This suggestion is often referred to as Berlin's theorem.

The interpretations in terms of Berlin's theorem are very much in the spirit of Nakatsuji. The influence of the electron density on the vibrational modes has, e.g., been considered in this respect:¹⁰ “attractive” regions were identified, where the electron density tends to stretch the normal coordinate; such a region is called “antibinding” by Berlin.

Equation (16) can then be interpreted as follows: the electron density governs the forces between the nuclei [cf. Eq. (15b)]; changes in electron density affect these forces: $f(\mathbf{r})$ measures the amount of change and $B(\mathbf{r})$ weights the contribution to the binding forces.

For diatomic molecules, scaling coincides with a single bond stretch, so that the binding function and the nuclear

Fukui function can be considered as bond sensitivity coefficients. For polyatomic molecules, however, scaling affects all bonds proportional to their length, so that one only gets a global picture about the binding force in the molecule. The nuclear Fukui function, on the other hand, probes the individual nuclear displacements and as such is the bond sensitivity parameter of choice for polyatomic molecules.

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