The Letters to the Editor section is divided into four categories entitled Communications, Notes, Comments, and Errata. Communications are limited to three and one half journal pages, and Notes, Comments, and Errata are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 1995 issue.

NOTES

Variational method for determining the Fukui function and chemical hardness of an electronic system

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A principal ingredient in the density-functional theory[1,2] of the chemical reactivity of electronic ground states is the Fukui function,[3] the reactivity index defined by

$$f(\mathbf{r})=\left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)_{\nu}, \tag{1}$$

where $\rho(\mathbf{r})$ is the electron density, N is the number of electrons, and $\nu(\mathbf{r})$ is the external potential acting on an electron (due in the first instance to atomic nuclei). We present here a variational procedure for determining the Fukui function from $\rho(\mathbf{r})$ and the Hohenberg–Kohn universal functional $F[\rho]$.

The electronic energy is given by the formula

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

where $F[\rho]$ is the sum of the electronic kinetic energy going with ρ and the electron–electron repulsion energy associated with it. This is a minimum for the correct ρ, that is,

$$\mu=\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}+\nu(\mathbf{r}), \tag{3}$$

where μ is a constant, the Lagrange multiplier for the normalization constraint

$$N\equiv\int \rho(\mathbf{r})\, d\mathbf{r}. \tag{4}$$

Called the chemical potential, μ satisfies

$$\mu=\left(\frac{\partial E}{\partial N}\right)_{\nu}. \tag{5}$$

Its derivative with respect to N,

$$\eta=\left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu}, \tag{6}$$

is the chemical hardness.[4]

A system of interest is defined by N and $\nu(\mathbf{r})$. Presuming $F[\rho]$ to be known, one can obtain the ground state $\rho(\mathbf{r})$, μ, and E by solving Eqs. (3) and (4) simultaneously for ρ and substituting the result in Eq. (2). The following theorem provides a variational process for next determining $f(\mathbf{r})$ and η. The ground state is assumed to be nondegenerate.

Theorem: Assume that the ground-state density ρ is known, and also the hardness kernel[5]

$$\eta(\mathbf{r},\mathbf{r}')=\frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}. \tag{7}$$

Define the hardness functional (of an arbitrary function g)

$$\eta[g]=\int\int g(\mathbf{r})g(\mathbf{r}')\,\eta(\mathbf{r},\mathbf{r}')\, d\mathbf{r}'\, d\mathbf{r}. \tag{8}$$

Minimization of $\eta[g]$ with respect to g, subject to the normalization condition

$$\int g(\mathbf{r})\, d\mathbf{r}=1, \tag{9}$$

gives the exact Fukui function for the system $f(\mathbf{r})$, and the corresponding extremum value $\eta[f]$ is equal to the exact hardness of the system.

Proof: Associate a Lagrange multiplier 2λ with the constraint of Eq. (9). Subject to this condition, minimize $\eta[g]$ with respect to g (at constant ρ). There results the equation

$$\lambda=\frac{1}{2}\,\frac{\delta\eta[g]}{\delta g(\mathbf{r})}=\int g(\mathbf{r}')\,\eta(\mathbf{r},\mathbf{r}')\, d\mathbf{r}'. \tag{10}$$

Solving this equation will give a $g(\mathbf{r},\lambda)$. λ may be then taken so that g is normalized. In fact, λ then turns out to be the hardness η. To prove this, multiply Eq. (10) by the true Fukui function $f(\mathbf{r})$ and integrate. This gives

$$\lambda=\int\int f(\mathbf{r})g(\mathbf{r}')\,\eta(\mathbf{r},\mathbf{r}')\, d\mathbf{r}'\, d\mathbf{r}. \tag{11}$$

But, this is equal to η by a proof given some time ago.[6–8] Hence the normalized extremal $g(\mathbf{r})$ satisfies

$$\int g(\mathbf{r}')\,\eta(\mathbf{r},\mathbf{r}')\, d\mathbf{r}'=\eta. \tag{12}$$

There remains to show that the extremal $g(\mathbf{r})$ and $f(\mathbf{r})$ are identical. For $f(\mathbf{r})$ one also has the same equation, obtainable by differentiation of Eq. (3) with respect to N at constant ν,[6,7]

$$\int f(\mathbf{r}')\,\eta(\mathbf{r},\mathbf{r}')\, d\mathbf{r}'=\eta. \tag{13}$$

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From Eqs. (12) and (13), one immediately has (using the normalization of both f and g)

$$\int\int [f(\mathbf{r})-g(\mathbf{r})][f(\mathbf{r}')-g(\mathbf{r}')]\eta(\mathbf{r},\mathbf{r}')\, d\mathbf{r}'\, d\mathbf{r}=0. \tag{14}$$

This is impossible unless $f\equiv g$ from the positive definite property of $\eta(\mathbf{r},\mathbf{r}')$, so $f\equiv g$. Note that Eq. (10) does not have more than one solution.[9] To prove this, start by assuming that there exist two different solutions of Eq. (10), g_1 and g_2, with possibly different Lagrange multipliers, λ_1 and λ_2. Subtract the corresponding equations and follow a similar procedure to the above, there results $g_1=g_2$ and $\lambda_1=\lambda_2$, and the proof of the theorem is complete.

Note 1: Since $\eta(\mathbf{r},\mathbf{r}')$ is positive definite (energy is minimum for the true ρ) and is defined as follows

$$\frac{\delta^2 E[\rho]}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}=\eta(\mathbf{r},\mathbf{r}')=\frac{\delta^2\eta[g]}{\delta g(\mathbf{r})\,\delta g(\mathbf{r}')}. \tag{15}$$

$\eta[g]$ is minimum for $g=f$. At the solution point, it follows from Eq. (13) that

$$\eta=\int\int f(\mathbf{r})f(\mathbf{r}')\eta(\mathbf{r},\mathbf{r}')\, d\mathbf{r}'\, d\mathbf{r}=\eta[f]. \tag{16}$$

Note 2: The minimal behavior of $\eta[g]$ does not conflict with the "maximum hardness principle,"[10–12] which deals with η (not with $\eta[g]$), and its variation is not with respect to g.

Note 3: Concerning discontinuities in derivatives that may be associated with the application of the present results to finite systems, it may be assumed that there exist three different types of hardness kernels: for electrophilic, nucleophilic and radical attacks in analogy with the corresponding Fukui functions.[3] There are three types of hardnesses for these three processes.[13]

Corollary: The Fukui function satisfies the linear integral equation

$$f(\mathbf{r})=\frac{1}{4\pi}\int f(\mathbf{r}')\kappa(\mathbf{r},\mathbf{r}')\, d\mathbf{r}', \tag{17}$$

where the kernel $\kappa(\mathbf{r},\mathbf{r}')$ is the Laplacian of $\delta^2 G[\rho]/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')$ and $G[\rho]$ is given by

$$G[\rho]=F[\rho]-\frac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}'\, d\mathbf{r}. \tag{18}$$

Proof: Take the Laplacian of both sides of Eq. (13).

Example: Consider a Thomas–Fermi–Dirac–Weizsäcker system. Equation (2) becomes

$$E[\rho]=T_0[\rho]+T_2[\rho]+K_0[\rho]+J[\rho]+\int\rho(\mathbf{r})\nu(\mathbf{r})\, d\mathbf{r}, \tag{19}$$

where the successive terms on the right are, respectively, the Thomas–Fermi functional, (1/9)th of the Weizsäcker functional, the Dirac exchange functional, the electron–electron repulsion term, and the electron-nuclear attraction term. Equation (13) becomes

$$\eta=f(\mathbf{r})\left\{\frac{10}{9}C_K\rho^{-1/3}-\frac{4}{9}C_X\rho^{-2/3}\right\} -\frac{1}{36}\frac{\nabla\cdot[\rho\nabla(f/\rho)]}{\rho}+\int\frac{f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}', \tag{20}$$

where C_K and C_X are the Thomas–Fermi and Dirac constants, respectively. Equation (20) is an integro-differential equation for $f(\mathbf{r})$ and can be solved self-consistently with the true density [solution of Eq. (3)] and proper normalization, Eq. (9).

Final remarks: Given the hardness kernel $\eta(\mathbf{r},\mathbf{r}')$, another way to obtain $f(\mathbf{r})$ and η is well known.[5] Invert $\eta(\mathbf{r},\mathbf{r}')$ to get the softness kernel $s(\mathbf{r},\mathbf{r}')$. Calculate the local softness $s(\mathbf{r})=\int s(\mathbf{r},\mathbf{r}')\, d\mathbf{r}'$ and the global softness $S=\int_s(\mathbf{r})\, d\mathbf{r}$. Then $f(\mathbf{r})=s(\mathbf{r})/S$ and $\eta=1/S$. The formal variational procedure of the present paper is equivalent to the inversion of the hardness kernel.[9,14] But when approximations are involved, the variational procedure could be easier to implement, and the variational point of view of the hardness–Fukui function relations should be of interest in its own right.

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