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Variational Principles for Describing Chemical Reactions: The Fukui Function and Chemical Hardness Revisited

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Abstract: The fundamental principles of density functional theory are applied to achieve a better understanding of various theoretical tools for describing chemical reactivity. Emphasis is given to the Fukui function, the central site reactivity index of density functional theory, which is approached through its own variational principle. A maximum hardness principle is then developed and discussed. To make contact with an earlier proof of a maximum hardness principle, changes in chemical potential are considered.

I. Density Functional Theory

Chemists strive to discover theoretical principles for understanding chemical reactivity. Useful for this endeavor is density functional theory (DFT),[1,2] which has provided justification for existing chemical principles and inspired new chemical principles. DFT reactivity indexes such as the electronic chemical potential,[1,3] the chemical hardness,[4−6] and the Fukui function[7,8] appear throughout reactivity theory. In this paper we use the fundamental variational principles of DFT to systematically extend the understanding of these indexes.

Density functional theory is founded upon two theorems of Hohenberg and Kohn:

(1) The ground-state electron density, $\rho(\vec{r})$, determines everything about a chemical system.[9] In particular, the density determines the number of electrons ($N[\rho] \equiv \int \rho(\vec{r})d\vec{r}$), the external potential, $\nu_0(\vec{r})$ (ordinarily just the potential due to the atomic nuclei), and the Hohenberg−Kohn functional, $F[\rho]$ (the sum of the electronic kinetic energy functional, $T[\rho]$, and the electron−electron repulsion energy functional, $V_{ee}[\rho]$). The total energy functional is then[9]

$$\varepsilon_{\nu_0}[\rho] \equiv F[\rho] + \int \rho(\vec{r})\nu_0(\vec{r})d\vec{r} \tag{1}$$

The variational principle for the total energy functional is established by Hohenberg and Kohn's second theorem:

(2) For any trial N-electron density, $\tilde{\rho}(\vec{r})$,

$$\varepsilon_{\nu_0}[\tilde{\rho}] \geq \varepsilon_{\nu_0}[\rho_0] = E_0[\rho_0] \tag{2}$$

where $\rho_0(\vec{r})$ is the exact N-electron ground-state density and E_0 is the exact ground-state energy for the system with N electrons and external potential $\nu_0(\vec{r})$.[9] Hence, in the presence of $\nu_0(\vec{r})$, the energy of N electrons arranged "wrong" (in such a way that $\tilde{\rho}(\vec{r}) \neq \rho_0(\vec{r})$) is always greater than the energy of N electrons arranged "right" (with density $\rho_0(\vec{r})$). One can regard $\tilde{\rho}(\vec{r})$ as the density for some excited state (not necessarily an eigenstate) of the system; $\varepsilon_{\nu_0}[\tilde{\rho}]$ is the expectation value of the energy in that state.

The Hohenberg−Kohn theorems may be clarified by considering the "thermodynamic analogy", a perspective that is exploited throughout ref 1. As a simple example of this approach, consider an ideal gas of molecules, each with mass M. If we know the equilibrium mass density of the gas as a function of the position in space, we can determine "everything"; in particular, we can find the volume and shape of the "container" (which is analogous to the external potential, since the positive charges on the atomic centers serve to "confine" the electrons) and the number of molecules in the gas (by integration of the mass density and division by M). This is the analogue of the first Hohenberg−Kohn theorem. Now, suppose we know that there are N ideal gas molecules in a container of volume V. It is statistically possible that all of the gas molecules will be in the "top half" of the container, but densities associated with this arrangement have higher free energy than the ground-state density. This represents the analogue of the second Hohenberg−Kohn theorem.

II. Mathematical Preliminaries

Just as many useful results of thermodynamics are derived by observing how state functions change when one varies the volume, number of particles, or density subject to constraints, useful results for understanding chemical reactivity are obtained by observing how the various state functions, especially the total energy, change as the density changes. Information about the effects of density change is contained in the functional derivative with respect to the density. For instance, the change in the total energy, $d\varepsilon_{\nu_0}[\rho] = \varepsilon_{\nu_0}[\rho] - \varepsilon_{\nu_0}[\rho_0]$, is related to the change in the density, $\delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_0(\vec{r})$, through

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$$d\varepsilon_{\nu_0}[\rho] = \int \frac{\delta\varepsilon_{\nu_0}[\rho_0]}{\delta\rho(\vec{r})}\delta\rho(\vec{r})\, d\vec{r} \tag{3}$$

where $\delta\varepsilon_{\nu_0}[\rho_0]/\delta\rho(\vec{r})$ symbolizes the functional derivative of the energy functional, $\varepsilon_{\nu_0}[\rho]$, with respect to the density, $\rho(\vec{r})$, evaluated at the density $\rho(\vec{r}) = \rho_0(\vec{r})$. Equation 3 is analogous to the equation $dg(x) = (dg(x_0)/dx)dx$ in differential calculus, and just as the derivative may be defined through this last equation, the functional derivative may be defined through eq 3: $\delta\varepsilon_{\nu_0}[\rho_0]/\delta\rho(\vec{r})$ is defined as that function which maps infinitesimal variations of the density about $\rho_0(\vec{r})$ to the appropriate variation in the energy functional.[10]

The analogies between differential calculus and "functional calculus" may be extended further by considering delta function perturbations, $\delta\rho(\vec{r}) = \epsilon\delta(\vec{r} - \vec{r}_0)$, in eq 3. This leads to an explicit expression for the functional derivative,

$$\frac{\delta\varepsilon_{\nu_0}[\rho_0]}{\delta\rho(\vec{r}_0)} = \lim_{\epsilon\to 0}\left\{\frac{\varepsilon_{\nu_0}[\rho_0(\vec{r}) + \epsilon\delta(\vec{r} - \vec{r}_0)] - \varepsilon_{\nu_0}[\rho_0(\vec{r})]}{\epsilon}\right\} \tag{4}$$

This equation indicates that the functional derivative of a quantity at a point, $\vec{r}_0$, represents how that quantity would change if the electron density were increased a tiny amount at $\vec{r}_0$. The similarity between eq 4 and the result from differential calculus,

$$\frac{dg(x_0)}{dx} = \lim_{\epsilon\to 0}\left\{\frac{g(x_0 + \epsilon) - g(x_0)}{\epsilon}\right\} \tag{5}$$

indicates that results in functional calculus such as the product rule, quotient rule, chain rule, and Taylor series expansion can be derived through straightforward adaptation of standard derivations in differential calculus. Appendix A of ref 1 details this approach. Of particular importance for the present purposes is the functional Taylor series, which for the energy functional is

$$\varepsilon_{\nu_0}[\rho_0 + \Delta\rho] = \varepsilon_{\nu_0}[\rho_0] + \int \frac{\delta\varepsilon_{\nu_0}[\rho_0]}{\delta\rho(\vec{r})}\Delta\rho(\vec{r})\, d\vec{r} + {}^{1}/_{2}\int\int \frac{\delta\varepsilon_{\nu_0}[\rho_0]}{\delta\rho(\vec{r}\,')\delta\rho(\vec{r})}\Delta\rho(\vec{r})\Delta\rho(\vec{r}\,')\, d\vec{r}\, d\vec{r}\,' + ... \tag{6}$$

Truncation of the expansion at second order yields "second-order density functional perturbation theory". In this paper, we assume that all Taylor series converge.

We conclude the introduction with some notes about the existence of functional derivatives. $dg(x_0)/dx$ is said to exist if and only if the derivative from above (with $\epsilon > 0$),

$$\frac{dg^{+}(x_0)}{dx} = \lim_{\epsilon\to 0^{+}}\left\{\frac{g(x_0 + \epsilon) - g(x_0)}{\epsilon}\right\} \tag{7}$$

equals the derivative from below (with $\epsilon < 0$),

$$\frac{dg^{-}(x_0)}{dx} = \lim_{\epsilon\to 0^{-}}\left\{\frac{g(x_0 + \epsilon) - g(x_0)}{\epsilon}\right\} \tag{8}$$

Within the popular zero-temperature grand canonical ensemble formulation of density functional theory, the derivatives from above and below in eq 4 are not equal, thereby necessitating the use of one-sided functional derivatives, which in analogy to eqs 7 and 8 are given by

$$\frac{\delta\varepsilon_{\nu_0}^{+/-}[\rho_0]}{\delta\rho(\vec{r}_0)} \equiv \lim_{\epsilon\to 0^{+/-}}\left\{\frac{\varepsilon_{\nu_0}[\rho_0(\vec{r}) + \epsilon\delta(\vec{r} - \vec{r}_0)] - \varepsilon_{\nu_0}[\rho_0(\vec{r})]}{\epsilon}\right\} \tag{9}$$

For notational and conceptual simplicity, during the remainder of the paper we assume that all functional derivatives exist and are well-defined; in particular, we assume that functional derivatives from above and below are equal. The modifications required to accommodate the zero-temperature grand canonical ensemble formulation of $\varepsilon_{\nu_0}[\rho]$ are summarized in the Appendix.

III. Principles Governing Charge Transfer

Chemical reactions often involve some charge transfer between reactant molecules (or between two different parts of one molecule). The active sites of a reactant molecule are usually places where the addition (or loss) of electrons is favorable.[7,11] So we may approach the understanding of chemical reactivity by addressing the question, *Where is the best place to add an electron to a molecule?*

To begin, consider the addition of a small fraction, τ, of an electron to the N_0-electron system with external potential $\nu_0(\vec{r})$ and *exact* ground-state density $\rho_{N_0}(\vec{r})$. If τ is small enough, the Taylor series (eq 6) for $\varepsilon_{\nu_0}[\rho]$ may be truncated at second order,

$$\varepsilon_{\nu_0}[\rho_{N_0} + \Delta\rho_{+\tau}] = E_0[\rho_{N_0}] + \mu[\rho_{N_0}]\tau + {}^{1}/_{2}\int\int \eta[\rho_{N_0};\vec{r},\vec{r}\,']\Delta\rho_{+\tau}(\vec{r})\Delta\rho_{+\tau}(\vec{r}\,')\, d\vec{r}\, d\vec{r}\,' \tag{10}$$

This formula uses notations from Table 1. The variational principle (eq 2) tells us that the ground state of the $(N_0 + \tau)$-electron system is the state with lowest total energy.

For a given value of τ, the first two terms in eq 10 are site-independent. Accordingly, minimizing the energy is equivalent to minimizing the last term in eq 10. That is, *the best way to add a* τ*th of an electron to a molecule is to add it to the place defined by that function,* $\Delta\rho_{+\tau}(\vec{r})$*, that minimizes*

$$\eta[\rho_{N_0};\Delta\rho_{+\tau}] \equiv \int\int \eta[\rho_{N_0};\vec{r},\vec{r}\,']\Delta\rho_{+\tau}(\vec{r})\Delta\rho_{+\tau}(\vec{r}\,')\, d\vec{r}\, d\vec{r}\,' \tag{11}$$

subject to the constraint that $\int\Delta\rho_{+\tau}(\vec{r})\, d\vec{r} = \Delta N = \tau$. Note that the two-variable hardness kernel, $\eta[\rho_{N_0};\vec{r},\vec{r}\,']$, is unchanged during the minimization process.

Introducing the normalized function, $g(\vec{r})$, we rewrite $\Delta\rho_{+\tau}(\vec{r})$ as $\tau g(\vec{r})$ and observe that the normalized function, $g_{\min}(\vec{r})$, which minimizes eq 11 is invariant to changes in τ. Choosing $\tau = 1$ recovers the variational principle of Chattaraj, Cedillo, and Parr.[31] Taking $\tau < 0$ allows one to apply eqs 10 and 11 to electron removal.

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(10) The situation is actually more complicated than this. The functional derivative only exists for so-called "conventional density variations", that is, variations in the density which are associated with a first-order change in the wave function of the system. See: Perdew, J. P.; Levy, M. *Phys. Rev. B* **1985**, *31*, 6264.

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Table 1. Summary of Notation for Section III

	quantity	definition and symbol	notes and key concepts
1	chemical potential	$\mu \equiv \left(\frac{\partial E}{\partial N}\right)_{\nu_0(\vec{r})}$	the chemical potential is the negative of the Mulliken electronegativity;[3,12] electronegativity equalization follows from the fact that μ is a global constant[3,13−15]
2	chemical hardness	$\eta \equiv \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu_0(\vec{r})}$	hard/soft acid/base theory;[4,16−18] maximum hardness principle[19−28]
3	Fukui function[7]	$f(\vec{r}) \equiv \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{\nu_0} = \left(\frac{\delta \mu}{\delta \nu_0(\vec{r})}\right)_N$	site reactivity index; reduces to frontier molecular orbital densities in the absence of orbital relaxation[29]
4	modified potential	$u[\rho(\vec{r});\vec{r}] = \nu[\rho(\vec{r});\vec{r}] - \mu$	$\nu[\rho(\vec{r});\vec{r}]$ is the external potential for which $\rho(\vec{r})$ is the N-electron ground-state density
5	stationary principle	$\frac{\delta \varepsilon_{\nu_0}[\rho]}{\delta \rho(\vec{r})} = \nu_0(\vec{r}) - u[\rho(\vec{r});\vec{r}]$	when $\rho_0(\vec{r})$ is the ground-state density for the external potential $\nu_0(\vec{r})$, $u(\vec{r}) = \mu - \nu_0(\vec{r})$ and hence $\delta \varepsilon_{\nu_0}[\rho]/\delta \rho(\vec{r}) = \mu$
6	hardness kernel[30]	$\eta[\rho_0(\vec{r});\vec{r},\vec{r}\,'] \equiv \frac{\delta^2 \varepsilon_{\nu_0}[\rho_0]}{\delta \rho(\vec{r}\,')\delta \rho(\vec{r})}$	variational principle for the Fukui function (eqs 11 and 14);[31,32] Berkowitz−Parr relation[30]

Maintaining the choice $\tau = 1$ in eq 11, we define the Fukui function, $f[\rho_{N_0};\vec{r}]$, to be the minimizing function, $g_{\min}(\vec{r})$, and define the chemical hardness, $\eta[\rho_{N_0}]$ as the minimizing value of the integral, $\eta[\rho_{N_0};f]$. These definitions agree with the conventional definitions of these quantities (see Table 1). To confirm this, observe that the function which minimizes eq 11 identifies the way the density of a molecule changes when one adds a fraction of an electron in a fixed external potential to give a new ground state. Therefore,

$$f[\rho_{N_0};\vec{r}] \equiv \left(\frac{\partial \rho_{N_0}(\vec{r})}{\partial N}\right)_{\nu_0} \tag{12}$$

in agreement with the original definition of Yang and Parr.[7] Using eq 12 and applying the chain rule for functional derivatives to eq 11 gives the chemical hardness,

$$\eta[\rho_{N_0}] \equiv \int\int \frac{\delta^2 \varepsilon_{\nu_0}[\rho_{N_0}]}{\delta \rho(\vec{r}\,')\delta \rho(\vec{r})} \left(\frac{\partial \rho_{N_0}(\vec{r})}{\partial N}\right)_{\nu_0} \left(\frac{\partial \rho_{N_0}(\vec{r}\,')}{\partial N}\right)_{\nu_0} \mathrm{d}\vec{r}\ \mathrm{d}\vec{r}\,' = \left(\frac{\partial^2 E_0}{\partial N^2}\right)_{\nu_0}\Bigg|_{N_0} \tag{13}$$

in agreement with the definition of Parr and Pearson.[4] Finally, by choosing $\tau = 1$, enforcing the normalization constraint on eq 11 with the Lagrange multiplier 2η, and minimizing $\eta[\rho_{N_0};g]$ with respect to $g(\vec{r})$, one obtains the known result:[31,32]

$$\eta[\rho_{N_0}] = \int f[\rho_{N_0};\vec{r}]\eta[\rho_{N_0};\vec{r},\vec{r}\,']\ \mathrm{d}\vec{r} \tag{14}$$

The master problem of density functional theory is to find the ground-state N_0-electron density for the molecule with N_0 electrons in the external potential $\nu_0(\vec{r})$. This task is ordinarily done by applying the variational principle for the energy (eq 2), but here we outline an alternative. Suppose we are given an *approximate* N_0-electron density, $\tilde{\rho}_{N_0}(\vec{r})$, for the molecule with external potential $\nu_0(\vec{r})$. Suppose furthermore that we know the exact ground-state densities for the $(N_0 + \tau)$- and $(N_0 - \tau)$-electron systems with the same external potential.[33] Then, if $\rho_{N_0}(\vec{r})$ is the ground-state density for an external potential, $\tilde{\nu}(\vec{r})$, which is an infinitesimal variation of $\nu_0(\vec{r})$,[34] and if τ is small enough, we may truncate the Taylor expansion (eq 6) at second order, giving

$$\begin{aligned} E_0[\rho_{N_0+\tau}] &= \varepsilon_{\nu_0}[\rho_{N_0+\tau}] = \varepsilon_{\nu_0}[\tilde{\rho}_{N_0}] + \\ &\int(\mu[\tilde{\rho}_{N_0}] - \tilde{\nu}(\vec{r}) + \nu_0(\vec{r}))(\rho_{N_0+\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))\ \mathrm{d}\vec{r} + \\ &{}^1/_2\int\int\eta[\tilde{\rho}_{N_0};\vec{r},\vec{r}\,']\{(\rho_{N_0+\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))(\rho_{N_0+\tau}(\vec{r}\,') - \\ &\tilde{\rho}_{N_0}(\vec{r}\,'))\}\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{r}\,' \\ E_0[\rho_{N_0-\tau}] &= \varepsilon_{\nu_0}[\rho_{N_0-\tau}] = \varepsilon_{\nu_0}[\tilde{\rho}_{N_0}] + \int(\mu[\tilde{\rho}_{N_0}] - \tilde{\nu}(\vec{r}) + \\ &\nu_0(\vec{r}))(\rho_{N_0-\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))\ \mathrm{d}\vec{r} + {}^1/_2\int\int\eta[\tilde{\rho}_{N_0};\vec{r},\vec{r}\,'] \times \\ &\{(\rho_{N_0-\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))(\rho_{N_0-\tau}(\vec{r}\,') - \tilde{\rho}_{N_0}(\vec{r}\,'))\}\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{r}\,' \end{aligned} \tag{15}$$

Again, see Table 1 for notation. Adding the two eqs 15 and rearranging terms gives

$$\begin{aligned} 2\varepsilon_{\nu_0}[\rho_{N_0}] = {} & E_0[\rho_{N_0-\tau}] + E_0[\rho_{N_0+\tau}] \\ & - \int\{(\mu[\tilde{\rho}_{N_0}] - \tilde{\nu}(\vec{r}) + \nu_0(\vec{r}))(\rho_{N_0+\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))\}\ \mathrm{d}\vec{r} \\ & - \int\{(\mu[\tilde{\rho}_{N_0}] - \tilde{\nu}(\vec{r}) + \nu_0(\vec{r}))(\rho_{N_0-\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))\}\ \mathrm{d}\vec{r} \\ & - {}^1/_2\int\int\eta[\tilde{\rho}_{N_0};\vec{r},\vec{r}\,']\{(\rho_{N_0+\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))(\rho_{N_0+\tau}(\vec{r}\,') - \\ & \qquad \tilde{\rho}_{N_0}(\vec{r}\,'))\}\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{r}\,' \\ & - {}^1/_2\int\int\eta[\tilde{\rho}_{N_0};\vec{r},\vec{r}\,']\{(\rho_{N_0-\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))(\rho_{N_0-\tau}(\vec{r}\,') - \\ & \qquad \tilde{\rho}_{N_0}(\vec{r}\,'))\}\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{r}\,' \end{aligned} \tag{16}$$

In analogy with eq 11 we define a hardness functional:

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$$\tilde{\eta}_{\nu_0}[\tilde{\rho}_{N_0}] \equiv \frac{E_0[\rho_{N_0+\tau}(\vec{r})] - 2\varepsilon_{\nu_0}[\tilde{\rho}_{N_0}(\vec{r})] + E_0[\rho_{N_0-\tau}(\vec{r})]}{\tau^2}$$

$$= \frac{1}{\tau^2} \times \left\{ \begin{aligned} &\int (\mu[\tilde{\rho}_{N_0}] - \tilde{\nu}(\vec{r}) + \nu_0(\vec{r}))(\rho_{N_0+\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))\,\mathrm{d}\vec{r} \\ &+ \int (\mu[\tilde{\rho}_{N_0}] - \tilde{\nu}(\vec{r}) + \nu_0(\vec{r}))(\rho_{N_0-\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))\,\mathrm{d}\vec{r} \\ &+ {}^{1}\!/_{2} \int\!\!\int \eta[\tilde{\rho}_{N_0};\vec{r},\vec{r}\,'](\rho_{N_0+\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))(\rho_{N_0+\tau}(\vec{r}\,') - \tilde{\rho}_{N_0}(\vec{r}\,'))\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' \\ &+ {}^{1}\!/_{2} \int\!\!\int \eta[\tilde{\rho}_{N_0};\vec{r},\vec{r}\,'](\rho_{N_0-\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r}))(\rho_{N_0-\tau}(\vec{r}\,') - \tilde{\rho}_{N_0}(\vec{r}\,'))\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' \end{aligned} \right\} \tag{17}$$

Equations 16 and 17 provide different ways to find the ground-state density. We can use the second Hohenberg−Kohn theorem and minimize $\varepsilon_{\nu_0}[\tilde{\rho}_{N_0}]$ (eq 16) subject to the constraint that $N[\tilde{\rho}_{N_0}] = N_0$. Equivalently, *we can find the ground-state N_0-electron density for the system with external potential $\nu_0(\vec{r})$ by maximizing the hardness functional, $\tilde{\eta}_{\nu_0}[\tilde{\rho}_{N_0}]$ (eq 17), subject to the constraint that $N[\tilde{\rho}_{N_0}] \equiv \int \tilde{\rho}_{N_0}(\vec{r})\,\mathrm{d}\vec{r} = N_0$.* Since the N_0-electron density that maximizes $\tilde{\eta}_{\nu_0}[\tilde{\rho}_{N_0}]$ is simply the exact ground-state N_0-electron density for the system, eqs 12 and 13 show that, at the maximum,

$$\begin{gathered} (\rho_{N_0+\tau}(\vec{r}) - \tilde{\rho}_{N_0}(\vec{r})) \rightarrow (\rho_{N_0+\tau}(\vec{r}) - \rho_{N_0}(\vec{r})) = \tau f[\rho_{N_0};\vec{r}] \\ \tilde{\eta}_{\nu_0}[\tilde{\rho}_{N_0}] \rightarrow \eta[\rho_{N_0}] \end{gathered} \tag{18}$$

We conclude this section by considering the perhaps puzzling question of why one minimizes the hardness functional of eq 11 and maximizes the hardness functional of eq 17. Define the generalized hardness functional,

$$\eta_{\nu_0}[\tilde{\rho}_{N_0+\tau},\tilde{\rho}_{N_0},\tilde{\rho}_{N_0-\tau}] \equiv \lim_{\tau\to 0^+} \left\{ \frac{\varepsilon_{\nu_0}[\tilde{\rho}_{N_0+\tau}(\vec{r})] - 2\varepsilon_{\nu_0}[\tilde{\rho}_{N_0}(\vec{r})] + \varepsilon_{\nu_0}[\tilde{\rho}_{N_0-\tau}(\vec{r})]}{\tau^2} \right\} \tag{19}$$

where $\tilde{\rho}_{N_0+\tau}$, $\tilde{\rho}_{N_0}$, and $\tilde{\rho}_{N_0-\tau}$ are $(N_0 + \tau)$-, N_0-, and $(N_0 - \tau)$-electron densities, respectively. Equation 11 is the special case of eq 19 in which $\tilde{\rho}_{N_0} = \rho_{N_0,\mathrm{exact}}$. Hence, minimizing the energies of the $(N_0 + \tau)$- and $(N_0 - \tau)$-electron systems amounts to minimizing the hardness functional in eq 11 (see Figure 1a). On the other hand, eq 17 represents the special case of eq 19 where $\tilde{\rho}_{N_0-\tau} = \rho_{N_0-\tau,\mathrm{exact}}$ and $\tilde{\rho}_{N_0+\tau} = \rho_{N_0+\tau,\mathrm{exact}}$. As earlier noted by Zhou and Parr,[20] in this case minimizing the energy of the N_0-electron system equates to maximizing the hardness (see Figure 1b).

IV. Principles Governing Multicomponent Systems

In the foregoing, we have concentrated on minimizing $\varepsilon_{\nu_0}[\rho]$ subject to a fixed $N_0 = \int \rho(\vec{r})\,\mathrm{d}\vec{r}$. Alternatively, we can force the normalization constraint with a Lagrange multiplier, μ, thereby introducing the grand potential,[6,35]

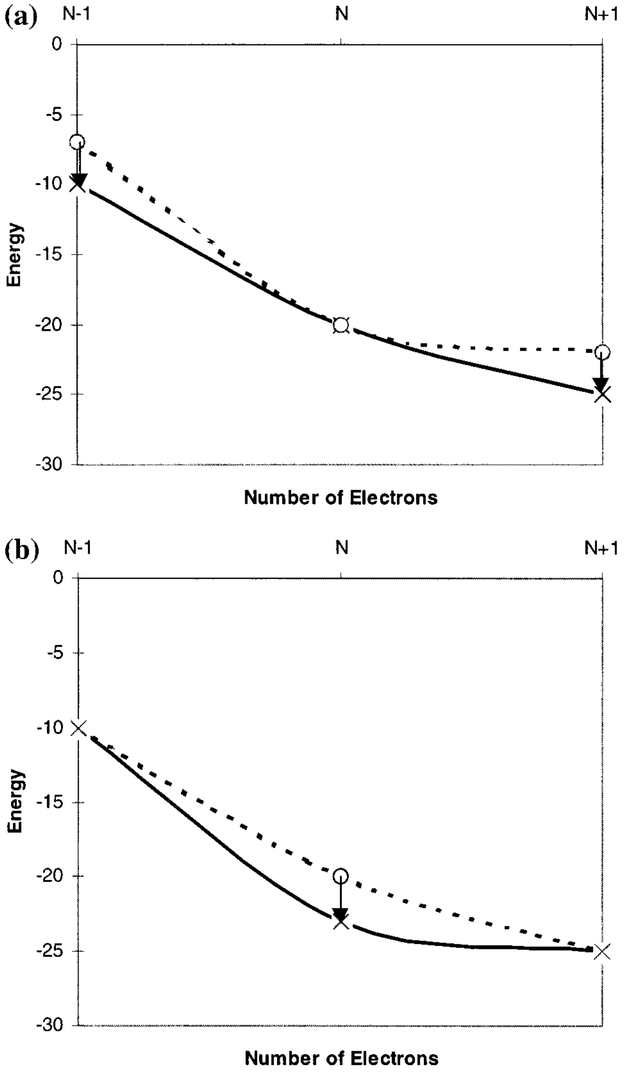

Figure 1. Variational principle for the Fukui function: (a) minimum and (b) maximum hardness principle. The dashed lines represent the unoptimized calculations, while the solid lines represent the solution from the variational principles. η is the curvature of the plot at the midpoint. (a) In the variational principle for the Fukui function (eq 11), lowering $\varepsilon_{\nu_0}[\rho_{N+\tau}]$ and $\varepsilon_{\nu_0}[\rho_{N-\tau}]$ decreases the hardness. (b) In the variational principle for the density at fixed N (eq 17), lowering $\varepsilon_{\nu_0}[\rho_N]$ increases the hardness.

$$\Omega_{\nu_0}[\rho] \equiv \varepsilon_{\nu_0}[\rho] - N[\rho]\mu \tag{20}$$

Minimization of the grand potential at constant μ represents an alternative variational principle to eq 2. Stating this result formally, *let $\rho_{\mu_0}(\vec{r})$ be the ground-state density and $\Omega_0[\rho_{\mu_0}]$ the ground-state grand potential for the system with chemical potential μ_0 and external potential $\nu_0(\vec{r})$. Let $\tilde{\rho}_{\mu_0}(\vec{r})$ be a trial density that also has chemical potential μ_0. Then*

$$\Omega_{\nu_0}[\tilde{\rho}_{\mu_0}] \geq \Omega_{\nu_0}[\rho_{\mu_0}] = \Omega_0[\rho_{\mu_0}] \tag{21}$$

In this scheme, changes in particle number are induced by changes in μ, the chemical potential (see Table 1). There are two ways to effect an increase in the number of electrons in the system: either add electrons directly (increase N) or increase the electronegativity (decrease μ), thereby driving the system

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(34) $\tilde{\rho}_{N_0}(\vec{r})$ must be ν-representable because the functional derivative in row 5 of Table 1 does not exist unless $\nu_0[\tilde{\rho}_{N_0};\vec{r}]$ is defined. In addition, $\tilde{\rho}_{N_0}(\vec{r})$ must be close enough to the true ground-state density for the truncated Taylor series expansion to be accurate. These two assumptions, coupled with the assumption that if two external potentials are close together the ground-state N-electron densities for those potentials will also be close together (i.e., we assume that $(\delta\rho_{N_0}(\vec{r})/\delta\nu_0(\vec{r}\,'))_{N=N_0}$ exists), recovers the condition stated in the text.

(35) Parr, R. G.; Gásquez, J. L. *J. Phys. Chem.* **1993**, *97*, 3939.

Table 2. Summary of Notation for Section IV

quantity		definition and symbol	notes and key concepts
1	particle number	$N \equiv \left(\frac{\partial \Omega}{\partial \mu}\right)_{\nu_0(\vec{r})}$	
2	softness[4]	$S \equiv \left(\frac{\partial^2 \Omega}{\partial \mu^2}\right)_{\nu_0(\vec{r})}$	the softness is the reciprocal of the hardness (see Table 1, row 2), $S \equiv 1/\eta$
3	local softness[30,38]	$s(\vec{r}) \equiv \left(\frac{\partial \rho(\vec{r})}{\partial \mu}\right)_{\nu_0} = -\left(\frac{\delta N}{\delta \nu_0(\vec{r})}\right)_{\mu}$	site reactivity index; related to the Fukui function (Table 1, row 3) by $s(\vec{r}) = Sf(\vec{r})$; local version of the hard/soft acid/base principle
4	local hardness[40,41]	$\eta(\vec{r}) \equiv \frac{\delta \mu[\rho]}{\delta \rho(\vec{r})}$	compare this definition to that of the local softness
5	first functional derivative	$\varsigma[\tilde{\rho};\vec{r}] \equiv \frac{\delta \Omega_{\nu_0}[\tilde{\rho}]}{\delta \rho(\vec{r})} = \nu_0(\vec{r}) - \nu[\tilde{\rho};\vec{r}] - N[\tilde{\rho}]\eta[\tilde{\rho};\vec{r}]$	this result is obtained from eq 20, Table 1, previous definitions in this table, and $\delta N[\rho]/\delta \rho(\vec{r}) = 1$; when $\tilde{\rho}(\vec{r})$ is the ground-state density, the first two terms cancel
6	second functional derivative	$\varsigma[\tilde{\rho};\vec{r},\vec{r}\,'] \equiv \frac{\delta^2 \Omega_{\nu_0}[\tilde{\rho}]}{\delta \rho(\vec{r}\,')\delta \rho(\vec{r})} = \eta[\tilde{\rho};\vec{r},\vec{r}\,'] - \eta[\tilde{\rho};\vec{r}] - \eta[\tilde{\rho};\vec{r}\,'] - N[\tilde{\rho}]\frac{\delta \eta[\tilde{\rho};\vec{r}]}{\delta \rho(\vec{r}\,')}$	this result is obtained from the definition of $\Omega_{\nu_0}[\rho]$, results from Table 1, and results from this table

to take electrons from its surroundings. Using eq 20 amounts to changing the basic variables describing the system from N and $\nu_0(\vec{r})$ to μ and $\nu_0(\vec{r})$.[36,37]

Chemical reactions involve systems whose components interact strongly with one another (e.g., functional groups within a molecule, molecules in solution, etc.). In such systems, the indistinguishability of electrons prevents one from assigning them to any particular component, rendering the number of electrons, N_c, in a particular component ill-defined. Hence, N_c and $\nu_0(\vec{r})$ are not the most suitable variables for discussing a component of a system. On the other hand, electronegativity equalization ensures that μ is a global quantity; hence, the chemical potential of a particular component, μ_c, is uniquely defined. Consequently, μ_c and $\nu_0(\vec{r})$ are highly suitable variables for discussing an individual component of a system. In analogy to the situation described in section III, we expect that understanding how $\Omega_{\nu_0}[\rho_{\mu_0}]$ changes as the density and chemical potential change will yield insight into chemical reactivity. Table 2 lists and characterized quantities associated with this approach.

For a system consisting of strongly interacting components, the most reactive components are apt to be those most sensitive to changes in the chemical potential.[42] So we may begin to understand chemical reactivity for systems of strongly interacting components by addressing the following question: *How does the density change when we increase the chemical potential (decrease the electronegativity) while keeping the external potential (nuclear configuration) of the molecule fixed?*

Let $\rho_{\mu_0}(\vec{r})$ be the *exact* ground-state density for a system with external potential $\nu_0(\vec{r})$ and chemical potential μ_0. What happens when the chemical potential increases a small amount, τ? Assuming that τ is small enough, the Taylor expansion can be truncated at second order, yielding

$$\Omega_{\nu_0}[\rho_{\mu_0} + \Delta\rho_{+\tau}] = \Omega_0[\rho_{\mu_0}] + \int \varsigma[\rho_{\mu_0};\vec{r}]\Delta\rho_{+\tau}(\vec{r})\, d\vec{r} + {}^1/_2 \int\int \varsigma[\rho_{\mu_0};\vec{r},\vec{r}\,']\Delta\rho_{+\tau}(\vec{r})\Delta\rho_{+\tau}(\vec{r}\,')\, d\vec{r}\, d\vec{r}\,' \quad (22)$$

In deriving eq 22, we have replaced functional derivatives of $\Omega_{\nu_0}[\rho]$ with notation from Table 2. The variational principle (eq 21) implies the following: *the best way to change the density as the chemical potential increases from μ_0 to $\mu_0 + \tau$ is found by minimizing the functional*

$$\Omega_{\nu_0}[\rho_{\mu_0} + \Delta\rho_{+\tau}] - \Omega_0[\rho_{\mu_0}] = \int \varsigma[\rho_{\mu_0};\vec{r}]\Delta\rho_{+\tau}(\vec{r})\, d\vec{r} + {}^1/_2 \int\int \varsigma[\rho_{\mu_0};\vec{r},\vec{r}\,']\Delta\rho_{+\tau}(\vec{r})\Delta\rho_{+\tau}(\vec{r}\,')\, d\vec{r}\, d\vec{r}\,' \quad (23)$$

subject to the constraint that $\mu[\rho_{\mu_0}(\vec{r}) + \Delta\rho_{+\tau}(\vec{r})] = \mu_0 + \tau$. The solution to this minimization is τ times the local softness:[30,38]

$$s[\rho_{\mu_0};\vec{r}] \equiv \left(\frac{\partial \rho_{\mu_0}(\vec{r})}{\partial \mu}\right)_{\nu_0} \quad (24)$$

Accordingly, just as eq 11 provides a variational method for determining the Fukui function, eq 23 provides a variational method for determining the local softness.

Choosing $\tau < 0$ generalizes eq 23 to decreases in chemical potential,

$$\Omega_{\nu_0}[\rho_{\mu_0} + \Delta\rho_{-\tau}(\vec{r})] - \Omega_0[\rho_{\mu_0}] \equiv \int \varsigma[\rho_{\mu_0};\vec{r}]\Delta\rho_{-\tau}(\vec{r})\, d\vec{r} + {}^1/_2 \int\int \varsigma[\rho_{\mu_0};\vec{r},\vec{r}\,']\Delta\rho_{-\tau}(\vec{r})\Delta\rho_{-\tau}(\vec{r}\,')\, d\vec{r}\, d\vec{r}\,' \quad (25)$$

The function which minimizes eq 25 subject to the constraint that $\mu[\rho_{\mu_0}(\vec{r}) + \Delta\rho_{-\tau}(\vec{r})] = \mu_0 - \tau$ is $-\tau s[\rho_{\mu_0};\vec{r}]$.

Equivalent to minimizing eqs 23 and 25 separately is minimizing them together; i.e., minimize

$$\Omega_{\nu_0}[\rho_{\mu_0} + \Delta\rho_{+\tau}(\vec{r})] - 2\Omega_0[\rho_{\mu_0}] + \Omega_{\nu_0}[\rho_{\mu_0} + \Delta\rho_{-\tau}(\vec{r})] \equiv \int \varsigma[\rho_{\mu_0};\vec{r}](\Delta\rho_{+\tau}(\vec{r}) + \Delta\rho_{-\tau}(\vec{r}))\, d\vec{r} + {}^1/_2 \int\int \varsigma[\rho_{\mu_0};\vec{r},\vec{r}\,'] \times \{\Delta\rho_{+\tau}(\vec{r})\Delta\rho_{+\tau}(\vec{r}\,') + \Delta\rho_{-\tau}(\vec{r})\Delta\rho_{-\tau}(\vec{r}\,')\}\, d\vec{r}\, d\vec{r}\,' \quad (26)$$

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(36) Nalewajski, R. F.; Capatani, J. F. *J. Chem. Phys.* **1982**, *77*, 399.

(37) For atoms and molecules, $\mu = (\partial E/\partial N)_{\nu_0}$ increases monotonically with N. This is important since it ensures that a μ can be expressed as a function of N, which allows one to use μ as a "stand-in" for N.

(38) Yang, W. T.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6723.

(39) Méndez, F.; Gázquez, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 9298.

(40) There are many different definitions of the local hardness; the one used in this paper is merely convenient for our purposes. See ref 30 for a more detailed discussion of this ambiguity.

(41) Liu, S.; Parr, R. G. *J. Chem. Phys.* **1997**, *106*, 5578.

(42) When the attacking species is soft, the most reactive components are apt to be those most sensitive to changes in the chemical potential. On the other hand, when the attacking species is hard, the hard/soft acid/base principle indicates that the most reactive components will be those of similar hardness. The statement in the text is often appropriate for discussions of covalent bond formation when the reactants are not ambidentate.

subject to the following constraints:

$$(1) \qquad \mu[\rho_{\mu_0}(\vec{r}) + \Delta\rho_{-\tau}(\vec{r})] = \mu_0 - \tau$$

$$(2) \qquad \mu[\rho_{\mu_0}(\vec{r}) + \Delta\rho_{+\tau}(\vec{r})] = \mu_0 + \tau$$

We may add another constraint, but it will increase the minimum value (and hence change the minimizing function) unless the constraint is satisfied at the solution point. However,

$$(3) \qquad \Delta\rho_{+\tau}(\vec{r}) = -\Delta\rho_{-\tau}(\vec{r})$$

is satisfied at the solution point, where $\Delta\rho_{+\tau}(\vec{r}) = \tau s[\rho_{\mu_0};\vec{r}] = -(-\tau s[\rho_{\mu_0};\vec{r}]) = -(\Delta\rho_{-\tau}(\vec{r}))$.

Constraint (3) simplifies the minimization. Now one minimizes

$$\Omega_{\nu_0}[\rho_{\mu_0} + \Delta\rho_{+\tau}(\vec{r})] - 2\Omega_0[\rho_{\mu_0}] + \Omega_{\nu_0}[\rho_{\mu_0} + \Delta\rho_{-\tau}(\vec{r})] \equiv \int\int \varsigma[\rho_{\mu_0};\vec{r},\vec{r}\,']\Delta\rho_{+\tau}(\vec{r})\Delta\rho_{+\tau}(\vec{r}\,')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,'\tau \quad (27)$$

subject to the constraint that $\mu[\rho_{\mu_0}(\vec{r}) + \Delta\rho_{+\tau}(\vec{r})] = \mu_0 + \tau$.

Since changing τ only scales the solution from eq 27, we choose $\tau = 1$. Since $-S = (\partial^2\Omega/\partial\mu^2)_{\nu_0}|_{\mu_0}$, we may regard eq 27 as a "softness functional". Restating our results from this perspective, *the local softness is the function,* $\Delta\rho_{+1}(\vec{r})$, *which minimizes*

$$-S_{\nu_0}[\rho_{\mu_0},\Delta\rho_{+1}(\vec{r})] = \int\int \varsigma[\rho_{\mu_0};\vec{r},\vec{r}\,']\Delta\rho_{+1}(\vec{r})\Delta\rho_{+1}(\vec{r}\,')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' \quad (28)$$

subject to the constraint that $\mu[\rho_{\mu_0}(\vec{r}) + \Delta\rho_{+1}(\vec{r})] = \mu_0 + 1$. *At the minimum,* $-S_{\nu_0}[\rho_{\mu_0},\Delta\rho_{+1}(\vec{r})]$ *becomes* $-S[\rho_{\mu_0}]$. Moreover, since the chemical softness is a nonnegative quantity, minimizing $-S$ is equivalent to minimizing the reciprocal of the softness, η.

Suppose we do not know the exact ground-state density for $\mu = \mu_0$ and external potential $\nu_0(\vec{r})$, but only an *approximate* density with chemical potential μ_0, $\tilde{\rho}_{\mu_0}(\vec{r})$. Furthermore, suppose that we know the exact ground-state densities for the external potential $\nu_0(\vec{r})$ with chemical potentials $\mu_0 \pm \tau$, $\rho_{\mu_0 \pm \tau}(\vec{r})$,[43] and that $\tilde{\rho}_{\mu_0}(\vec{r})$ is the ground-state density for an external potential, $\tilde{\nu}(\vec{r})$, which is very close to $\nu_0(\vec{r})$.[44] Then, for sufficiently small τ, the power series expansions for $\Omega_{\nu_0}[\rho_{\mu_0 \pm \tau}]$ centered on the density $\tilde{\rho}_{\mu_0}(\vec{r})$ may be truncated at second order. While one can find a variational principle for the ground-state density by performing a derivation like eqs 15−17 in section III, we avoid this by modifying eq 26—now, instead of trying to find the correct density for $\mu = \mu_0 \pm \tau$, we are trying to find the correct density for $\mu = \mu_0$. Accordingly, *the exact density with external potential* $\nu_0(\vec{r})$ *and chemical potential* μ_0 *may be obtained by maximizing*

$$\begin{aligned} \Omega_0[\rho_{\mu_0} + \Delta\rho_{+\tau}(\vec{r})] - 2\Omega_{\nu_0}[\tilde{\rho}_{\mu_0}] + \Omega_0[\rho_{\mu_0} + \Delta\rho_{-\tau}(\vec{r})] \\ \equiv -\tilde{S}_{\nu_0}[\tilde{\rho}_{\mu_0}] \\ = \int \varsigma[\tilde{\rho}_{\mu_0};\vec{r}](\Delta\tilde{\rho}_{+\tau}(\vec{r}) + \Delta\tilde{\rho}_{-\tau}(\vec{r}))\,\mathrm{d}\vec{r} \,+ \\ {}^{1}/_{2}\int\int \varsigma[\tilde{\rho}_{\mu_0};\vec{r},\vec{r}\,'](\Delta\tilde{\rho}_{+\tau}(\vec{r})\Delta\tilde{\rho}_{+\tau}(\vec{r}\,') \,+ \\ \Delta\tilde{\rho}_{-\tau}(\vec{r})\Delta\tilde{\rho}_{-\tau}(\vec{r}\,'))\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' \quad (29) \end{aligned}$$

subject to the constraint that $\mu[\tilde{\rho}_{\mu_0}] = \mu_0$. In eq 29 we have defined $\Delta\tilde{\rho}_{\pm\tau}(\vec{r}) \equiv \rho_{\mu_0 \pm \tau}(\vec{r}) - \tilde{\rho}_{\mu_0}(\vec{r})$. Since the softness is positive, maximizing $-S$ is equivalent to maximizing the hardness. Arguments similar to those at the close of section III explain why one minimizes $-S$ in eq 28 but maximizes $-S$ in eq 29[24] (see Figure 2).

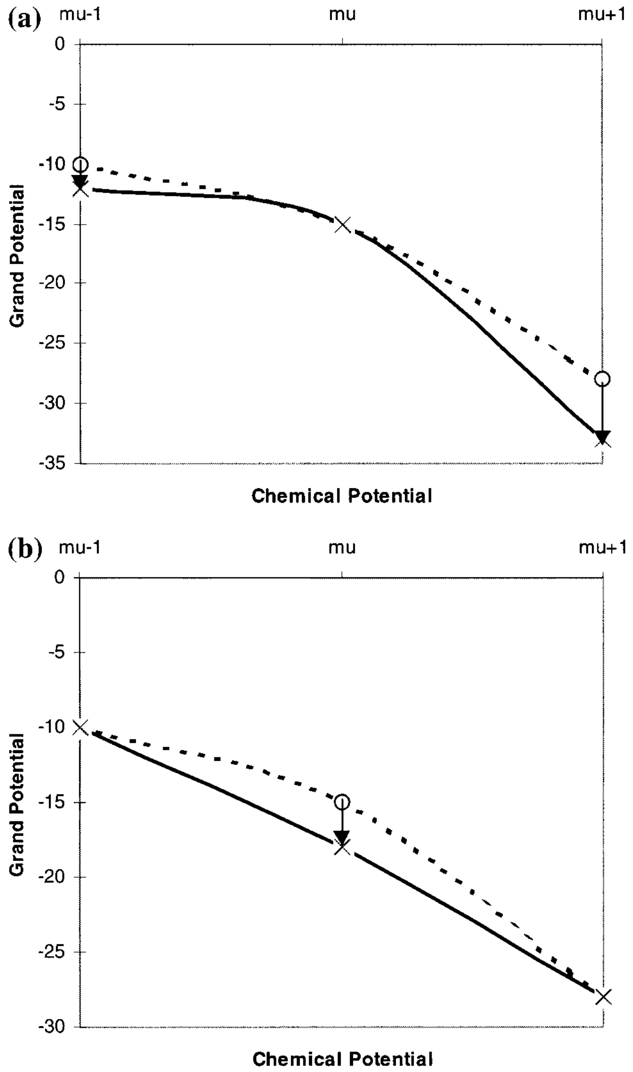

Figure 2. (a) Variational principle for the local softness, minimizing $-S$. (b) Parr−Chattaraj maximum hardness principle. The dashed lines represent the unoptimized calculations, while the solid lines represent the solution from the variational principles. $-S$ is the curvature of the plot at the midpoint. (a) In the variational principle for the local softness function (eq 28), lowering $\Omega_{\nu_0}[\rho_{\mu+\tau}]$ and $\Omega_{\nu_0}[\rho_{\mu-\tau}]$ decreases $-S$ (equivalently, the hardness). (b) In the variational principle for the density at fixed μ (eq 29), lowering $\Omega_{\nu_0}[\rho_{\mu}]$ increases $-S$ (equivalently, the hardness).

Extending a result that was originally inferred by Zhou and Parr in the context of Hückel theory,[21,24] Parr and Chattaraj proved that, at constant chemical and external potentials, the ground state of a system has greater hardness than any nearby state which can be reached by an infinitesimal change in the external potential.[22] Since we have made the same assumptions in our derivation of eq 29 and since maximizing $-S$ is equivalent

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(43) A comment similar to note 33 applies here: we can use the Taylor series expansion centered on $\tilde{\rho}_{\mu_0}(\vec{r})$ to find an expression for $\Omega_{\nu_0}[\tilde{\rho}_{\mu_0 \pm \tau}]$ that can be minimized to find $\rho_{\mu_0 \pm \tau}(\vec{r})$.

(44) Similar to the comment of note 34, what is required is that $\tilde{\rho}_{\mu_0}(\vec{r})$ be ν-representable (the functional derivative in row 5 of Table 2 is undefined unless $\nu_0[\tilde{\rho}_{\mu_0};\vec{r}]$ is defined) and also close enough to the exact ground-state density for the second-order truncation of the functional Taylor series to be accurate. Assuming that $(\delta\rho_{\mu_0}(\vec{r})/\delta\nu_0(\vec{r}\,'))_{\mu=\mu_0}$ exists, the condition stated in the text is equivalent to these requirements.

to maximizing the hardness, eq 29 is equivalent to the maximum hardness principle of Parr and Chattaraj.

Sebastian has questioned the validity of the Parr−Chattaraj proof.[45] While the validity of the Parr−Chattaraj proof has been defended,[25,27] the dispute makes it desirable to find a straightforward derivation of the Parr−Chattaraj maximum hardness principle. The present derivation (along with Figure 2b) achieves this goal.

VI. Conclusions

In this paper we have used the basic variational principles of density functional theory, eqs 2 and 21, to develop variational principles for quantities of importance in the theory of molecular reactivity. We have elucidated two variational methods for determining the ground-state density:

(1) Maximum Hardness Principle (Zhou and Parr).[20] The exact ground-state density is the function which maximizes the hardness functional, $\tilde{\eta}_{\nu_0}[\tilde{\rho}_{N_0}]$ (eq 17), subject to the constraints that $\int \tilde{\rho}_{N_0}(\vec{r})\, d\vec{r} = N_0$ and that the trial densities, $\tilde{\rho}_{N_0}(\vec{r})$, are ground-state densities for external potentials close to that of the system of interest.[34] When evaluated at the solution point, $\tilde{\eta}_{\nu_0}[\tilde{\rho}_{N_0}]$ equals the chemical hardness.

(2) Maximum Hardness Principle (Parr and Chattaraj).[22] The exact ground-state density is the function which maximizes the softness functional, $-\tilde{S}_{\nu_0}[\tilde{\rho}_{\mu_0}]$ (eq 29), subject to the constraints that $\mu[\tilde{\rho}_{\mu_0}] = \mu_0$ and that the trial densities, $\tilde{\rho}_{\mu_0}(\vec{r})$, are ground-state densities for external potentials close to that of interest.[44] At the solution point, $-\tilde{S}_{\nu_0}[\tilde{\rho}_{\mu_0}]$ is the negative of the softness. Maximizing $-\tilde{S}_{\nu_0}[\tilde{\rho}_{\mu_0}]$ is equivalent to maximizing the hardness, $\eta = -(1/-S)$.

We have also developed variational principles for the two basic predictors of molecular site reactivity within a density functional theory description: the Fukui function and the local softness.

(3) Variational Principle for the Fukui Function (Chattaraj, Cedillo, and Parr).[31] The Fukui function is the function which minimizes $\eta[\rho_{N_0};\Delta\rho_{+1}]$ of eq 11 subject to the constraint $\int \Delta\rho_{+1}(\vec{r})\, d\vec{r} = 1$. When evaluated at the solution point, $\eta[\rho_{N_0};\Delta\rho_{+1}]$ becomes the chemical hardness.

(4) Variational Principles for the Local Softness (Present Work). The local softness is the function which minimizes $-S_{\nu_0}[\rho_{\mu_0},\Delta\rho_{+1}(\vec{r})]$ (eq 28; eqs 23 and 25 provide alternative variational principles), subject to the constraint that $\mu[\rho_{\mu_0}(\vec{r}) + \Delta\rho_{+1}(\vec{r})] = \mu_0 + 1$. At the solution point, $-S_{\nu_0}[\rho_{\mu_0}, \Delta\rho_{+1}(\vec{r})]$ equals the negative of the chemical softness. Minimizing $-S$ is equivalent to minimizing the hardness, η.

Variational principles (3) and (4) are exact because their solutions are infinitesimal quantities (eqs 12 and 13; eq 24) and infinitesimal changes are treated exactly by the second-order truncation of the Taylor series. The accuracy of variational principles (1) and (2) depends on the validity of the second-order truncation of the Taylor series; this truncation is accurate only when the trial densities are ground-state densities for external potentials close to the external potential of interest.[34,44] We may remove the restriction to densities that are ground states for some external potential by using a constrained search formulation of density functional theory to "assign" external potentials to all densities. (Lieb's constrained-search formalism,[46] which explicitly maps densities to an external potential,[47] is particularly useful.) The restriction that the trial density be close enough to the solution for the second-order Taylor series to converge may be relaxed by including higher order terms in the Taylor series expansion. In the limit where the Taylor series is not truncated at all (and assuming the series converges), we find expressions for the universal functionals:

$$\tilde{\eta}_{\nu_0}[\tilde{\rho}_{N_0}] \equiv \frac{E_0[\rho_{N_0+\tau}(\vec{r})] - 2\varepsilon_{\nu_0}[\tilde{\rho}_{N_0}(\vec{r})] + E_0[\rho_{N_0-\tau}(\vec{r})]}{\tau^2} \tag{30}$$

$$-\tilde{S}_{\nu_0}[\tilde{\rho}_{\mu_0}] = \frac{\Omega_0[\rho_{\mu_0+\tau}] - 2\Omega_{\nu_0}[\tilde{\rho}_{\mu_0}] + \Omega_0[\rho_{\mu_0-\tau}]}{\tau^2} \tag{31}$$

in terms of quantities related to the trial density.

The variational principles (1) and (2) may prove useful computationally, but of greater general interest are the fundamental maximum hardness principles which follow from eqs 30 and 31:

(1′) Maximum Hardness Principle (Zhou and Parr).[20] The best way to arrange N_0 electrons in the external potential, $\nu_0(\vec{r})$, is that which maximizes the chemical hardness (eq 30) (see Figure 1b).

(2′) Maximum Hardness Principle (Parr and Chattaraj).[22] The best way to arrange electrons in the external potential, $\nu_0(\vec{r})$, at chemical potential μ_0 is that which maximizes the hardness (or, equivalently, maximizes $-S$ (eq 31)) (see Figure 2b).

Pearson has proposed that hardness measures the stability of a molecule.[19] The variational principles support this result. Given $\nu_0(\vec{r})$, a molecule is most stable for the ground-state density. In the energetic formulation, one finds the ground-state density by minimizing the total energy (eq 1) when the number of electrons is fixed and by minimizing the grand potential (eq 20) when the chemical potential is fixed. By contrast, maximizing the hardness gives the ground-state density in the case in which N is fixed *and* in the case in which μ is fixed.

On the other hand, a molecule, M, is less stable when one optimizes the density of the molecular cation, M^+, and anion, M^-, since decreasing the energy penalty for removing an electron and increasing the energy payoff for adding an electron makes the disproportionation reaction,

$$2M \rightarrow M^+ + M^- \tag{32}$$

more favorable.[20] Since variational principles **3** and **4** indicate that the best way to change the number of electrons or the chemical potential of M is the way that minimizes its hardness, we find agreement with the assertion that small hardness means decreased stability.

Suppose we are given two reactant molecules, L and M, with hardnesses η_L and η_M, respectively. If η_L and η_M are small, we would predict that the reactant molecules are relatively unstable and that a chemical reaction between the species L and M is likely to occur. To predict where bonds form and break, we need a reactivity index that is a function of position. From section III, the Fukui functions, $f_L(\vec{r})$ and $f_M(\vec{r})$ indicate the best way to change the numbers of electrons in the molecules L and M. Hence, the Fukui function indicates the propensity of the density to deform at a given position in order to accept/donate electrons. We expect bonds to form between those parts of L and M which most readily accept/donate electrons. Therefore, we expect bonds to form between regions of L where $f_L(\vec{r})$ is large and regions of M where $f_M(\vec{r})$ is large.[7,11] This leads naturally to the following question: How does one assign a value of the Fukui function (which is inherently pointwise) to a "region" in a molecule? A natural method is to introduce the

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[45] Sebastian, K. L. *Chem. Phys. Lett.* **1994**, *231*, 40.

[46] Lieb, E. H. *Int. J. Quantum. Chem.* **1983**, *24*, 243.

[47] Colonna, F.; Savin, A. *J. Chem. Phys.* **1999**, *110*, 2828.

so-called “condensed Fukui function”, by which one affixes a Fukui “index” to each atom in the molecule by partitioning the molecule into atomic contributions.[48] The net effect is to convert the point-by-point site reactivity information of the Fukui function into (often more useful) information about the propensity of a molecule to react at a particular atomic site.

The situation is more complex when the system consists of many interacting components with hardnesses η_A, η_B, η_C ... and Fukui functions $f_A(\vec{r})$, $f_B(\vec{r})$, $f_C(\vec{r})$ ... . In this case, molecule B may have a small value of the hardness (and hence enhanced global reactivity) but no places, $\vec{r}_B$, where $f_B(\vec{r}_B)$ is especially large (and hence no especially reactive sites). On the other hand, molecule C may have a large value of the hardness but an especially reactive site, $\vec{r}_C$, where $f_C(\vec{r}_C)$ is large. The situation is complicated still further by the hard/soft acid/base principle—molecules tend to react where the Fukui function is the largest when attacked by soft reagents and in places where the Fukui function is smaller when attacked by hard reagents.

In this case, the key site reactivity indexes are the local softnesses, $s_A(\vec{r})$, $s_B(\vec{r})$, $s_C(\vec{r})$ ... and the key principle is the local hard/soft acid/base principle of Méndez and Gázquez.[39] Suppose we add a molecule Q, with reactive site $\vec{r}_Q$ and a local softness of $s_Q(\vec{r}_Q)$ at the reactive site. Q will tend to react with the species (A, B, or C) whose local softness at the reactive site, ($s_A(\vec{r}_A)$, $s_B(\vec{r}_B)$, or $s_C(\vec{r}_C)$) is closest to $s_Q(\vec{r}_Q)$. It is clear that the analogue of the condensed Fukui function indexes, the “condensed local softness indexes”, may be helpful for deciphering reactivity patterns.

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Appendix: Dealing with Systems with a Nonintegral Number of Electrons

We should discuss the validity of the idea of adding and subtracting a “fraction” of an electron from the system. Though there are no real “pieces of an electron”, the idea of a “piece of an electron” is necessary in order to define functional derivatives since eqs 3 and 4 require considering variations in the density which change the number of particles by nonintegral amounts. Moreover, if one defines the number of electrons, N_{open}, in an open system like a functional group within a molecule, the number of electrons will generally be nonintegral, rendering fractional numbers of electrons a necessary concept for this circumstance.

A common approach for extending DFT to nonintegral numbers of electrons uses the grand canonical ensemble. That is, one imagines putting many replicas of a system in a box with constant chemical potential and temperature and allowing the replicas to exchange electrons. While each replica has an integer number of electrons, the average number of electrons per replica need not be an integer. By using this “average number of electrons” as a stand-in for the physical number of particles, one extends density functional theory to nonintegral numbers of electrons.[49] This method goes back to Gyftopoulos and Hatsopoulos[50] and Mermin.[51]

The grand canonical ensemble works well at nonzero temperatures, giving well-behaved, fully differentiable density functionals. However, in the limit of zero temperature the plot of energy versus particle number is no longer smooth, consisting instead of straight lines connecting the ground-state energies of integer numbers of particles. Let N be an integer and δ be a real number between 0 and 1, inclusive. Then, in the zero temperature limit of the grand canonical ensemble,

$$E[N+\delta,\nu_0] = (1-\delta)E[N,\nu_0] + \delta E[N+1,\nu_0]$$

$$\rho[N+\delta,\nu_0] = (1-\delta)\rho[N,\nu_0] + \delta\rho[N+1,\nu_0]$$

$$\mu[N+\delta,\nu_0] = \begin{cases} E[N+1,\nu_0] - E[N,\nu_0] & 0 < \delta < 1 \\ \text{undefined} & \delta = 0, \delta = 1 \end{cases} \tag{A1}$$

$$\eta[N+\delta,\nu_0] = \begin{cases} 0 & 0 < \delta < 1 \\ \text{undefined} & \delta = 0, \delta = 1 \end{cases}$$

These equations reveal that number increasing and number decreasing variations in the density are now fundamentally different in nature; hence, the functional derivatives from above and below are no longer equal, and we must use one-sided functional derivatives (eq 9).

The results in the body of this paper depend on the existence of all functional derivatives and hence are valid for temperatures greater than zero (though all the derivatives should have a notation affixed to them to indicate that they are to be taken at constant temperature). If one prefers to consider the case of zero temperature, one constructs a smooth interpolation between integer numbers of electrons. While this is possible, such interpolations have undesirable features. Smooth interpolations generally fail to predict the correct dissociation products for bond-breaking reactions, predicting that fragments retain fractional numbers of electrons (and hence partial charges).[49] However, molecules dissociate into neutral atoms.

Should one prefer the zero temperature grand canonical ensemble description, one must disregard section IV altogether; the chemical potential can no longer be used to change the number of particles in the system. (A given value of the chemical potential corresponds to either an infinite number of different systems (all those with particle numbers between N and $N+1$) or no systems at all (see eq A1); hence, the change of variables from $(N,\nu_0(\vec{r}))$ to $(\mu,\nu_0(\vec{r}))$ is invalid.) However, by separately considering changes in the density which increase the number of particles (functional derivatives from above) and changes in the density which decrease the number of particles (functional derivatives from below), one salvages section III. For example, eq 11 splits into an equation in which the functional derivatives are taken from above,

$$\eta^{+}[\rho_{N_0};\Delta\rho_{+\tau}] \equiv \int\int \eta^{+}[\rho_{N_0};\vec{r},\vec{r}\,']\Delta\rho_{+\tau}(\vec{r})\Delta\rho_{+\tau}(\vec{r}\,')\,d\vec{r}\,d\vec{r}\,' \tag{A2}$$

and an equation in which the derivatives are taken from below,

$$\eta^{-}[\rho_{N_0};\Delta\rho_{-\tau}] \equiv \int\int \eta^{-}[\rho_{N_0};\vec{r},\vec{r}\,']\Delta\rho_{-\tau}(\vec{r})\Delta\rho_{-\tau}(\vec{r}\,')\,d\vec{r}\,d\vec{r}\,' \tag{A3}$$

Corresponding to eqs A2 and A3**,** there will now be two different solutions to the variational principle for the Fukui function:[7]

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$$\begin{aligned} f^{+}[\rho_{N_0};\vec{r}\,] &\equiv \left(\frac{\partial \rho_{N_0}(\vec{r}\,)}{\partial N}\right)^{+}_{\nu_0} \\ f^{-}[\rho_{N_0};\vec{r}\,] &\equiv \left(\frac{\partial \rho_{N_0}(\vec{r}\,)}{\partial N}\right)^{+}_{\nu_0} \end{aligned} \tag{A4}$$

In accord with eq A1, the hardnesses from above and below are zero. The other major result from section III is eq 17, which becomes

$$\begin{aligned} \tilde{\eta}_{\nu_0}[\tilde{\rho}_{N_0}] &\equiv \frac{E_0[\rho_{N_0+\tau}(\vec{r}\,)] - 2\varepsilon_{\nu_0}[\tilde{\rho}_{N_0}(\vec{r}\,)] + E_0[\rho_{N_0-\tau}(\vec{r}\,)]}{\tau^2} \\ &= \frac{1}{\tau^2} \times \\ &\left\{ \begin{aligned} &\int (\mu^{+}[\tilde{\rho}_{N_0}] - \tilde{\nu}(\vec{r}\,) + \nu_0(\vec{r}\,))(\rho_{N_0+\tau}(\vec{r}\,) - \tilde{\rho}_{N_0}(\vec{r}\,))\, \mathrm{d}\vec{r} \\ &+ \int (\mu^{-}[\tilde{\rho}_{N_0}] - \tilde{\nu}(\vec{r}\,) + \nu_0(\vec{r}\,))(\rho_{N_0-\tau}(\vec{r}\,) - \tilde{\rho}_{N_0}(\vec{r}\,))\, \mathrm{d}\vec{r} \\ &+ {}^{1}/_{2} \int\!\!\int \eta^{+}[\tilde{\rho}_{N_0};\vec{r},\vec{r}\,'](\rho_{N_0+\tau}(\vec{r}\,) - \tilde{\rho}_{N_0}(\vec{r}\,))(\rho_{N_0+\tau}(\vec{r}\,') - \tilde{\rho}_{N_0}(\vec{r}\,'))\, \mathrm{d}\vec{r}\, \mathrm{d}\vec{r}\,' \\ &+ {}^{1}/_{2} \int\!\!\int \eta^{-}[\tilde{\rho}_{N_0};\vec{r},\vec{r}\,'](\rho_{N_0-\tau}(\vec{r}\,) - \tilde{\rho}_{N_0}(\vec{r}\,))(\rho_{N_0-\tau}(\vec{r}\,') - \tilde{\rho}_{N_0}(\vec{r}\,'))\, \mathrm{d}\vec{r}\, \mathrm{d}\vec{r}\,' \end{aligned} \right\} \end{aligned} \tag{A5}$$

The construction of a zero temperature grand canonical ensemble has some benefits. For instance, consider the equation for the density in eq A1. Rearranging, we find

$$\frac{\rho[N+\tau,\nu_0] - \rho[N,\nu_0]}{\tau} = (\rho[N+1,\nu_0] - \rho[N,\nu_0]) \tag{A6}$$

Since in eq A6 the differential Fukui function (for vanishingly small τ) is equivalent to the finite difference approximation with $\tau = 1$, it follows that the small τ constraints pervading section III are no longer necessary—eqs A2−A5 are exact for all τ between 0 and 1. Of particular interest is the effect that this has on eq A5; while the maximal function is always the correct ground-state density, the maximizing value depends on τ, being $(\mu^{+} - \mu^{-})/\tau = (\mathrm{IP} - \mathrm{EA})/\tau$, where $\mathrm{EA} = -\mu^{+}$ is the electron affinity and $\mathrm{IP} = -\mu^{-}$ is the ionization potential. For $\tau = 1$, eq A5's maximum value agrees with the finite difference result commonly used as an approximation to the hardness.[4]

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