# On the Foundations of Chemical Reactivity Theory

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In formulating chemical-reactivity theory (CRT) so as to give it a deep foundation in density-functional theory (DFT), Parr, his collaborators, and subsequent workers have introduced reactivity indices as properties of isolated reactants, some of which are in apparent conflict with the underlying DFT. Indices which are first derivatives with respect to electron number are staircase functions of number, making electronegativity equalization problematic. Second derivative indices such as hardness vanish, putting hardness-based principles out of reach. By reformulating CRT within our partition theory, which provides an exact decomposition of a system into its component species, we resolve the conflict. We show that the reactivity of a species depends on its chemical context and define that context. We establish when electronegativity equalization holds and when it fails. We define a generalization of hardness, a hardness matrix containing the self-hardness of the individual species and the mutual hardnesses of the pairs of species of the system, and identify the physical origin of hardness. We introduce a corresponding generalization of the Fukui function as well as of the local and global softnesses and the softness kernel of the earlier formulation. We augment our previous formulation of the partition theory by introducing a model energy function and express the difference between the exact and the model forces on the nuclei in terms of the new reactivity indices. For simplicity, our presentation is limited to time-reversal invariant systems with vanishing spin density; it is straightforward to generalize the theory to finite spin density.

## 1. Introduction

Chemical reactivity theory (CRT) quantifies the reactive proclivities of isolated species through the introduction of a set of reactivity indices or, simply, reactivities. Its roots go deep into the history of chemistry, as far back as the introduction of such fundamental concepts as acid, base, Lewis acid, Lewis base, etc. It pervades almost all of chemistry. Starting in the late 1970s with continuing further development, Parr, his collaborators, and subsequent workers[1,2] have built up a formulation of CRT with a deep foundation in density-functional theory (DFT).[3,4]

In that formulation there are global, local, and nonlocal indices which are properties of isolated species. The global reactivities include the electronegativity[5] defined as the negative of the chemical potential $\mu$, where

$$\mu = \frac{\partial E(N)}{\partial N}\bigg)_{v_e} \tag{1.1}$$

$E(N)$ is the ground-state energy of a system of $N$ electrons in the electrostatic potential energy $v_e$ due to its nuclei, and the partial derivative is taken at fixed $v_e$. The global hardness $\eta$ is defined as the second derivative[6]

$$\eta = \frac{\partial^2 E(N)}{\partial N^2}\bigg)_{v_e} = \frac{\partial \mu}{\partial N}\bigg)_{v_e} \tag{1.2}$$

and the global softness $S$ is the inverse of the hardness,[7]

$$S = \eta^{-1} \tag{1.3}$$

The local indices depend on the position **r**. Among them are the Fukui function $f(\mathbf{r})$,[8]

$$f(\mathbf{r}) = \frac{\partial n(\mathbf{r})}{\partial N}\bigg)_{v_e} \tag{1.4}$$

defined to generalize Fukui's notion of frontier orbitals,[9] and the local softness $s(\mathbf{r})$,[7]

$$s(\mathbf{r}) = \frac{\partial n(\mathbf{r})}{\partial \mu}\bigg)_{v_e} \tag{1.5}$$

which, by the chain rule, can be written as

$$s(\mathbf{r}) = f(\mathbf{r})S \tag{1.6}$$

The nonlocal indices are two-point functions which include two softness kernels,[10]

$$S^N(\mathbf{r}, \mathbf{r}') = -\frac{\partial n(\mathbf{r})}{\partial v_e(\mathbf{r}')}\bigg)_N \tag{1.7}$$

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and

$$S^{\mu}(\mathbf{r}, \mathbf{r'}) = -\frac{\partial n(\mathbf{r})}{\partial v_e(\mathbf{r'})}\bigg)_{\mu} = S^N(\mathbf{r}, \mathbf{r'}) + \frac{s(\mathbf{r})\, s(\mathbf{r'})}{S} \quad (1.8)$$

where the final equation in eq 1.8 follows from a Maxwell relation. Both $S^{\mu}$ and $S^N$ are susceptibilities.

All quantities such as $\mu$, $\eta$, $S$, $f(\mathbf{r})$, $s(\mathbf{r})$, and $S^{\mu}(\mathbf{r}, \mathbf{r'})$ in this formulation of CRT involve derivatives with respect to $N$ of some quantity $Q(N)$, either explicitly or implicitly. For our purposes,

$$\frac{\partial Q}{\partial N} = \lim_{\Delta N \to 0} \frac{Q(N + \Delta N) - Q(N)}{\Delta N} \quad (1.9)$$

is a sufficiently general definition of a derivative. Thus, if $N$ is an integer, $N + \Delta N$ cannot be, and the values of the quantities $Q(N)$ entering this formulation of CRT must be known in principle at *noninteger* values of $N$. An apparent contradiction begins to emerge. The reactivities are to be the properties of the isolated species, but isolated species must have integer numbers of electrons. We could simply ignore this need for properties at noninteger numbers by replacing the derivatives by finite differences with respect to integer number of the properties of isolated species.[1] Doing so would miss an essential element of chemical behavior. An electron can move on and off a species interacting with its chemical environment. It need be associated with that species only part of the time, giving the species the appearance of having a noninteger number of electrons. This effect has been amply studied in the pre-DFT context. The calculation of partial atomic charges, for example, has a vast literature (that we do not review here) in which knowledge of the energy function $E(N)$ for noninteger $N$ is essential. The parabolic $N$-dependence of $E(N)$ originally introduced by Hinze et al.[11] has been critically discussed in refs 12 and 13. Von Szentpály proposed a different parabola accounting for the chemical context,[13] on the basis of which a valence-state atoms-in-molecules model for bonding was developed[13,14] and proved useful in recent applications.[15] The importance of the chemical context in defining reactivities was also highlighted in ref 16.

The way in which we capture the effect of an electron that can only be *partially* associated with a species interacting with its chemical environment consists of representing it via an ensemble of species with differing integer $N$, requiring the use of ensemble DFT.

The most general formulation of DFT for integers is that of Levy and Lieb.[17,18] Its natural extension to noninteger systems is the ensemble DFT (EDFT) of Perdew, Parr, Levy, and Balduz (PPLB).[19,20] The PPLB ensemble contains three members with nonvanishing probability. If $N$ exceeds the integer $m$ by $\nu$, $0 < \nu \leq 1$,

$$N = m + \nu \quad (1.10)$$

then only the bordering integers $m$ and $m + 1$ enter the ensemble. For simplicity and relative brevity of presentation, we limit discussion to time-reversal invariant systems with vanishing spin density; generalization to finite spin density is straightforward. The members of the Kramers degenerate pair of odd-integer species with $m$ or $m + 1$ electrons then have identical values of all properties of interest here, so it is unnecessary to distinguish between them and sufficient to regard the ensemble as having two components only. All ground state properties $P(N)$ then have the $N$-dependence

$$P(N) = (1 - \nu)P(m) + \nu P(m + 1) \quad (1.11)$$

where $P(m)$ and $P(m + 1)$ are the ground-state properties of the bordering integer systems. All $P(N)$ are piecewise-continuous linear functions of $N$ (Figure 1a). All first derivatives are staircase functions of $N$, undefined at the integers and constant in between (Figure 1b). All second derivatives vanish in between and do not exist at the integers, so that $\eta = 0$ and $S = \infty$.

There are profound negative consequences for this dependence on $N$. The principle of electronegativity equalization[5,21] is violated.[20] The $(m + 1)$-electron reactivities of one species toward an electrophilic reactant are identical to the corresponding $m$-electron reactivities of that same species toward a nucleophilic reactant. Perhaps most troubling is that the hardness-based principles of CRT[22] lose their foundation.

Now it is clear that the formal structure of the CRT built by Parr and others captures the essence of the pre-DFT formulation of CRT. The task we face is to retain those attractive features while resolving the above inconsistencies within PPLB. We do so by recognizing that reactivity indices are *chemical-context dependent*, not unique properties of isolated species.[16] Indeed, as implied in our above rationalization of the use of an ensemble for noninteger $N$, the very introduction of noninteger $N$ implies the existence of a chemical context within which the species exchanges or transfers electrons. How then to capture that context while still retaining the notion of reactivity as a property of an individual species?
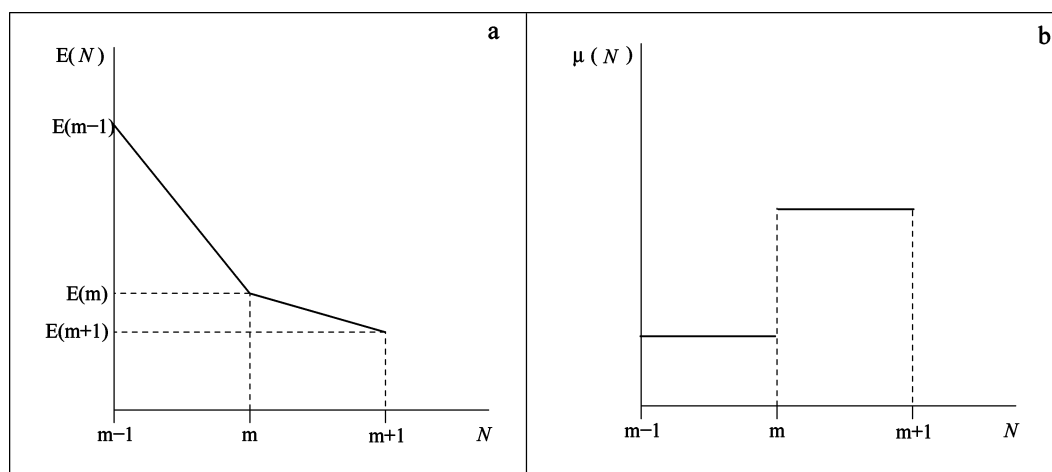


**Figure 1.** Within the PPLB ensemble:[19] (a) The ground-state energy is a piecewise continuous linear function of $N$. (b) The chemical potential is a staircase function of $N$, undefined at the integers and constant in between.

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We do so by using our partition theory[23,24] to provide a sharp definition of, and the chemical context for, a species which is part of a molecule or reacting complex. We present and develop that theory further in section 2. The theory leads immediately to a deeper understanding of electronegativity and the principle of electronegativity equalization and its violation (section 3). The chemical-context dependence of reactivities is explored in section 4, and preliminary context-dependent definitions of some reactivities are given there. The earlier concepts of hardness, local and global softness, and the Fukui function are generalized to matrices to incorporate the consequences of charge transfer between species. In section 5 it is argued that the electron−nuclear interactions define the chemical context and thereby fix the definitions of the chemical reactivities. Nuclear reactivities are introduced in section 6 as sensitivities of electronic properties to nuclear displacements. Energies and forces are discussed in section 7, where a model energy functional is introduced containing the purely electrostatic interaction between the parts in addition to the functionals of the noninteracting parts. The differences between the model forces and the actual forces within the system are then expressed in terms of the nuclear sensitivities. We conclude in section 8 with a summary and discussion of our results and indications of how the theory should be further developed and applied.

## 2. Partition Theory

**A. Solution of the Partition Problem.** Consider a molecule or reacting complex M containing $N_M$ electrons which has the ground-state electron density $n_M$ for a given configuration of its nuclei. The nuclei fall naturally into subsets belonging to its $A$ chemically meaningful components: acids, bases, sugars, monomers, ligands, etc. Let $\alpha = 1...A$ label these components or parts. The partition problem asks how to partition $n_M$ into a sum of contributions $n_\alpha$ from its parts, each containing $N_\alpha$ electrons, that is,

$$n_M = \sum_\alpha n_\alpha \tag{2.1}$$

$$N_M = \sum_\alpha N_\alpha \tag{2.2}$$

While $N_M$ is strictly an integer, the $N_\alpha$ need not be integers.

The *partition problem* is a classic problem of theoretical chemistry.[25] Many approximate or precise solutions have been proposed which we do not review here. At the level of partition in which the parts are atoms, it becomes the "atoms-in-molecules" problem, with its own extensive literature, briefly and cogently reviewed by Nalewajski and Parr.[26] In this section we review and develop further the specific solution we have proposed earlier[24] and subsequently based on the use of the PPLB EDFT.[24] In later sections we use the resulting *partition theory* to build up a new formulation of CRT free of the inconsistencies noted in the Introduction.

In partition theory, the nuclei of each part have positions identical to those they have in M. Nevertheless, each part is treated as though it were isolated. When PPLB is used for the density functional $\mathcal{E}_\alpha$ of each part, $\mathcal{E}_\alpha$ becomes the following average of the density functionals of its integer components:

$$\mathcal{E}_\alpha = (1 - \nu_\alpha)E_\alpha[n_{p_\alpha}] + \nu_\alpha E_\alpha[n_{p_\alpha+1}] \tag{2.3}$$

Here $p_\alpha$ and $p_\alpha + 1$, are the lower and upper bordering integers of $p_\alpha$, with

$$N_\alpha = p_\alpha + \nu_\alpha, \quad 0 < \nu_\alpha \leq 1 \tag{2.4}$$

The $E_\alpha[n_p]$, $p = p_\alpha$, or $p_\alpha + 1$, are less general than those defined by the Levy−Lieb constrained search algorithm,[17,18] as discussed in section 2B below. Similarly, the density $n_\alpha$ is the average of its integer density components:

$$n_\alpha = (1 - \nu_\alpha)n_{p_\alpha} + \nu_\alpha n_{p_\alpha+1} \tag{2.5}$$

The density functional of the collection of noninteracting parts is

$$\mathcal{E} = \sum_\alpha \mathcal{E}_\alpha \tag{2.6}$$

The set of variables on which $\mathcal{E}$ depends is $\{p_\alpha, \nu_\alpha, n_{p_\alpha}, n_{p_\alpha+1}\}$. The task partition theory sets itself is to establish the partition of $n_M$ into the $\{n_\alpha\}$ by finding the infimum of $\mathcal{E}$ over the $\{p_\alpha, \nu_\alpha, n_{p_\alpha}, n_{p_\alpha+1}\}$ subject to the constraints 2.1 and 2.2. The search for the infimum proceeds in stages. First, the $\{p_\alpha\}$ are chosen according to preliminary considerations of the oxidation states of the parts in M. Next a search for the infimum is conducted over the $\{\nu_\alpha, n_{p_\alpha}, n_{p_\alpha+1}\}$ for that $\{p_\alpha\}$. Finally, a search is carried out over the $\{p_\alpha\}$ for the true infimum of $\mathcal{E}$. The infimal $\{n_\alpha\}$ is the desired partition.

Finding the infimum of the energy $\mathcal{E}$ over the $\{\nu_\alpha, n_{p_\alpha}, n_{p_\alpha+1}\}$ subject to the restrictions 2.1 and 2.2 is equivalent to finding the infimum of the grand potential $\mathcal{G}$,

$$\mathcal{G} = \mathcal{E} + \nu_R \cdot \sum_\alpha n_\alpha - \mu_R \sum_\alpha N_\alpha \tag{2.7}$$

without restriction for given $\nu_R$ and $\mu_R$, provided there are one-to-one invertible maps between the $\{n_\alpha\}$ and $\{N_\alpha\}$ and the Lagrange multipliers $\nu_R$ and $\mu_R$ which effect the Legendre transformation of $\mathcal{E}$ into $\mathcal{G}$, respectively. We term $\nu_R$ the reactivity potential; it directly controls the $n_p$, $p = p_\alpha$ or $p_\alpha + 1$, $\forall \alpha$. We term $\mu_R$ the internal chemical potential of M; it controls $\nu_\alpha$, $\forall \alpha$, in conjunction with $\nu_R$. The dot between $\nu_R$ and $\sum_\alpha n_\alpha$ in eq 2.7 stands for integration over their position dependences; that is,

$$f \cdot g = \int d\mathbf{r} \, f(\mathbf{r}) \, g(\mathbf{r}) \tag{2.8}$$

Having found the infimum of $\mathcal{G}$ over $\{\nu_\alpha, n_{p_\alpha}, n_{p_\alpha+1}\}$ for given $\{p_\alpha\}$, its infimum over the $\{p_\alpha\}$ is found. In practice, $\nu_R$ is found during the course of the search. The uniqueness of $\nu_R$ is discussed in subsection 2C and the value of $\mu_R$ in subsection 3B.

**B. The Underlying Conjectures.** There are three conjectures underlying partition theory. The first two relate to PPLB and the third to the partition of $n_M$: (1) The density of each part is ensemble $\nu$-representable (EVR). That is, each $n_\alpha$ is a super-position of contributions $n_{p_\alpha}$ containing an integer number $p_\alpha$ of electrons,

$$n_\alpha = \sum_{p_\alpha} C_{p_\alpha} n_{p_\alpha}, \quad 0 \leq C_{p_\alpha} \leq 1, \quad \sum_{p_\alpha} C_{p_\alpha} = 1 \tag{2.9}$$

in which each $n_{p_\alpha}$ is the ground-state density in the same external potential $\nu_e$, $\forall_{p_\alpha}$.[27] (2) The ground-state energy $E_\alpha(p_\alpha, \nu_e)$ possesses discrete convexity. That is, its second difference

$$\Delta^{(2)}E_\alpha(p_\alpha, \nu_e) = E_\alpha(p_\alpha + 1, \nu_e) + E_\alpha(p_\alpha - 1, \nu_e) - 2E_\alpha(p_\alpha, \nu_e) \tag{2.10}$$

is positive for all relevant $\nu_e$ and $p_\alpha$. When this condition holds, the $C_{p_\alpha}$ are nonzero only at the two bordering integers of $N_\alpha$.[19] (3) $n_M$ is EVR decomposable; that is, each $n_\alpha$ is EVR.[24]

**C. The Uniqueness of $\nu_R$.** A proof is given in ref 24 that there is a unique one-to-one mapping between $n_M$ and $\nu_R$ once the $\{p_\alpha\}$ and $\nu_\alpha$ are chosen and provided that $\nu_R + \nu_\alpha$, $\forall \alpha$, belongs to the set $\mathbf{V}_s$ of potentials for which the ground-state ensemble is nondegenerate, which have no nonzero angular-independent components at $r \uparrow \infty$, and which have no regions of finite measure in which they are infinite. That proof is too lengthy to review here, but close inspection shows that it is valid for ensembles with arbitrary fixed occupation probabilities for all integer systems, not merely for the three-component ensemble of PPLB. Thus, PT is generalizable to situations in which discrete convexity does not hold and for which PPLB must be generalized, should they exist.

**D. Stationarity Conditions.** Suppose now that the infimum of $\mathscr{G}$ with respect to $\{\nu_\alpha, n_{p_\alpha}, n_{p_\alpha+1}\}$ is a minimum. The first functional derivative of $\mathscr{G}$ with respect to each of these variables must vanish; that is, $\mathscr{G}$ is stationary at the minimum. Stationarity with respect to the $n_p$, $p = p_\alpha$ or $p_{\alpha+1}$ implies that

$$\left. \frac{\delta E_\alpha^R[n_p]}{\delta n_p} \right)_{\nu_\alpha, \nu_R} = 0 \quad \text{or} \quad \left. \frac{\delta E_\alpha[n_p]}{\delta n_p} \right)_{\nu_\alpha} = -\nu_R \quad (2.11)$$

where

$$E_\alpha^R[n_p] = E_\alpha[n_p] + \nu_R \cdot n_p \quad (2.12)$$

In eq 2.11, the derivatives are taken at constant $\nu_R$ and/or $\nu_\alpha$, where $\nu_\alpha$ is the interaction energy of a single electron with the nuclei of part $\alpha$. Because the $n_p$ are presumed to be EVR,[28] $\mathscr{G}$ is always stationary and minimal with respect to the $n_p$ at its infimum.

Stationarity with respect to the $\nu_\alpha$ implies that

$$\left. \frac{\delta \mathcal{E}_\alpha^R}{\delta \nu_\alpha} \right)_{\nu_\alpha, \nu_R} = E_\alpha^R[n_{p_\alpha+1}] - E_\alpha^R[n_{p_\alpha}]$$

$$= E_\alpha[n_{p_\alpha+1}] - E_\alpha[n_{p_\alpha}] + \nu_R \cdot f_\alpha$$

$$= \mu_R, \quad \forall \alpha \quad (2.13)$$

where

$$\mathcal{E}_\alpha^R = (1 - \nu_\alpha) E_\alpha^R[n_{p_\alpha}] + \nu_\alpha E_\alpha^R[n_{p_\alpha+1}] \quad (2.14)$$

and

$$\left. f_\alpha = \frac{\delta n_\alpha}{\delta \nu_\alpha} \right)_{\nu_\alpha, \nu_R} = n_{p_\alpha+1} - n_{p_\alpha} \quad (2.15)$$

is the Fukui function[8] of part $\alpha$. Taking derivatives with respect to $\nu_\alpha$ is the same as taking them with respect to $N_\alpha$, eq 2.4, so that we can rewrite eq 2.13 as

$$\left. \mu_\alpha = \frac{\delta \mathcal{E}_\alpha^R}{\delta N_\alpha} \right)_{\nu_\alpha, \nu_R} = \mu_R \quad (2.16)$$

Equation 2.16 is a statement of electronegativity equalization provided we define the electronegativity of a part as the negative of the chemical potential $\mu_\alpha$ defined with respect to $\mathcal{E}_\alpha^R$ and not $\mathcal{E}_\alpha$, the usual definition, as discussed in section 3A.

In contrast to the case for the $n_p$, $\mathscr{G}$ need not be stationary with respect to the $\nu_\alpha$, and the infimum need not be minimal with respect to the $\nu_\alpha$ for some or all $\alpha$. Those parts for which eq 2.16 does not hold, that is, $\mu_\alpha \neq \mu_R$, must have integral charges, as we shall show in section 5 via eq 5.10 that $\mathscr{G}$ is a convex function of the $\nu_\alpha$ and in subsections 2E and 3B that $\mu_\alpha < 0$ so that the infimum in the $\nu_\alpha$ must be at the end points of their ranges. This question of infimality versus minimality will be discussed further in section 3C.

**E. Kohn−Sham Theory.** Modified Kohn−Sham (KS) equations[4] follow directly from the stationarity condition 2.16. For each integer component $p_\alpha$ of the ensemble for part $\alpha$, the KS potential $\nu_{sp_\alpha}$ of that component when isolated is replaced by

$$\nu_{sp_\alpha}^R = \nu_{sp_\alpha} + \nu_R \quad (2.17)$$

$$\nu_{sp_\alpha} = \nu_\alpha + \nu_H[n_{p_\alpha}] + \nu_{xc}[n_{p_\alpha}] \quad (2.18)$$

where $\nu_H$ is the Hartree and $\nu_{xc}$ the exchange-correlation potential for the $p_\alpha$-electron density $n_{p_\alpha}$ and similarly for $p_\alpha + 1$. The corresponding KS equation is

$$H_{sp_\alpha}^R \phi_i^{p_\alpha} = \epsilon_i^{p_\alpha} \phi_i^{p_\alpha} \quad (2.19)$$

$$H_{sp_\alpha}^R = \frac{p^2}{2m} + \nu_{sp_\alpha}^R \quad (2.20)$$

and similarly for $p_\alpha + 1$. All levels $i$ are doubly degenerate. We are dealing with bound systems here. We take the zero of energy as that of an electron at rest at infinity where both $\nu_{sp}$, $p = p_\alpha$, $p_\alpha + 1$, and $\nu_R$ vanish. Consequently the $\epsilon_i^p$ of all occupied levels, $p = p_\alpha$, $p = p_{\alpha+1}$, are negative.

The densities $n_{p_\alpha}$ and $n_{p_\alpha+1}$ are

$$n_{p_\alpha} = \sum_{\substack{i=1 \\ \text{spin}}}^{p_\alpha} |\phi_i^{p_\alpha}|^2, \quad n_{p_\alpha+1} = \sum_{\substack{i=1 \\ \text{spin}}}^{p_\alpha+1} |\phi_i^{p_\alpha+1}|^2 \quad (2.21)$$

Equation 2.21 implies that the $f_\alpha$ of eq 2.15, an analogue of the Fukui function of the earlier formulation of CRT, is

$$f_\alpha = \sum_{\substack{i=1 \\ \text{spin}}}^{p_\alpha} [|\phi_i^{p_\alpha+1}|^2 - |\phi_i^{p_\alpha}|^2] + \sum_{\text{spin}} |\phi_{p_\alpha+1}^{p_\alpha+1}|^2 \quad (2.22)$$

The first term accounts for the relaxation of the $p_\alpha$ occupied orbitals upon addition of an electron, and the second term is the contribution of the frontier orbital, the HOMO.

## 3. On Electronegativity Equalization and Its Violation

**A. Stationarity Implies Electronegativity Equalization.** The first reactivity index we introduce in the framework for CRT provided by PT is the electronegativity $\zeta_\alpha$ of a part defined as

$$\zeta_\alpha \equiv -\mu_\alpha \quad (3.1)$$

with $\mu_\alpha$ the chemical potential in the presence of the reactivity potential, given by eqs 2.16 and 2.18. (Even though the electronegativity is usually denoted by "$\chi$", we will use here "$\zeta$", reserving the former for the susceptibilities (i.e., the softness kernels to be introduced in section 4A), as is customary in DFT). Equations 2.13 and 2.16 then imply electronegativity equalization (EE) whenever the infimum of $\mathscr{G}$ is a minimum so that

there stationarity conditions hold:

$$\zeta_\alpha = \zeta_R \equiv -\mu_R \tag{3.2}$$

**B. The Asymptotic Density and the Internal Chemical Potential.** The asymptotic form of the density for any real bound system is[29]

$$n(\mathbf{r}) \xrightarrow[r\uparrow\infty]{} g(\mathbf{r})\, e^{-2\kappa r} \tag{3.3}$$

where

$$\kappa = [2m|\mu|/\hbar^2]^{1/2} \tag{3.4}$$

In eq 3.4, the chemical potential $\mu$ is the negative of the ionization energy discussed in section 2E. Equation 3.3 differs from the corresponding equation in ref 29 in that the factor $g(\mathbf{r})$ is replaced there by unity, implying incorrectly that all asymptotic electron densities are isotropic. Here $g(\mathbf{r})$ is angular-dependent and, containing at most power-law dependences on $\mathbf{r}$, is dominated by the exponential. Examination of eq 4.76 of ref 29 shows that the asymptotic form of the potential $u_s(\mathbf{r}_N)$ entering the "Schrödinger" equation for $n^{1/2}(\mathbf{r})$, their eq 4.74, depends on the charge $q$ of the system as $-(q+1)/r$, strongly influencing $g(\mathbf{r})$ as discussed in appendix B.

Applying eqs 3.3 and 3.4 to $n_M$, we obtain

$$n_M(\mathbf{r}) \xrightarrow[r\uparrow\infty]{} g_M(\mathbf{r})\, e^{-2\kappa_M r} \tag{3.5}$$

$$\kappa_M = [2m|\mu_M|/\hbar^2]^{1/2} \tag{3.6}$$

where $\mu_M$ is the chemical potential of M, presumed known in advance. From the density constraint (2.1), it follows that

$$n_M(\mathbf{r}) \xrightarrow[r\uparrow\infty]{} g_I(\mathbf{r})\, e^{-2\kappa_I r} \tag{3.7}$$

$$\kappa_I = [2m|\mu_I|/\hbar^2]^{1/2} \tag{3.8}$$

$$\mu_I = \sup_\alpha \mu_\alpha \tag{3.9}$$

Comparing eqs 3.5 and 3.6 with eqs 3.7–3.9, we see that

$$\mu_I = \sup_\alpha \mu_\alpha = \mu_M, \quad g_M(\mathbf{r}) = g_I(\mathbf{r}) \tag{3.10}$$

In words, the asymptotic behavior of $n_M$ is identical to that of the density of its least-tightly bound part.

If $\inf \mathscr{G}$ is a minimum so that EE holds, and all $\mu_\alpha$ equal $\mu_R$, it follows that

$$\mu_R \equiv \mu_M \tag{3.11}$$

Thus $\mu_R$ is not free to be adjusted until the constraint (2.2) is met; it is fixed at $\mu_M$ when the infimum is a minimum.

When the infimum is not a minimum, it follows from eqs 3.9 and 3.10 that

$$\mu_\alpha < \mu_M \tag{3.12}$$

for all parts for which stationarity and EE fail. In words, the most tightly bound species drop out of EE first.

Finally, we note that from eq 2.21, the ordering of Kohn–Sham energies such that $\epsilon_i < \epsilon_{i+1}$, the discrete convexity of the energies of the independent-particle systems, the asymptotic behavior of the densities being given by an analogue of eq 3.5 or 3.7 for each part $\alpha$, it follows that

$$\mu_\alpha = \epsilon_{p_\alpha+1}^{p_\alpha+1} = \epsilon_\alpha^{\text{HOMO}} \tag{3.13}$$

and from eqs 3.13 and 3.12

$$\epsilon_\alpha^{\text{HOMO}} \leq \mu_M \tag{3.14}$$

**C. Minimality versus Infimality.** Suppose the A parts of M are separated to infinity; that is, the distances $d_{\alpha\beta}$ between convenient centers within each member of the pair $\alpha$ and $\beta$ diverge for all pairs $\alpha\beta$. The density functional $E[n_M]$ of the molecule is then identical to $\mathcal{E}$. The individual $n_\alpha$ become identical to the ground-state densities $n_{\alpha G}$ of the isolated parts without the need of imposing eq 2.1 as a constraint. Consequently, $v_R$ can be set to zero. The $N_\alpha$ are all integers so that the $v_\alpha$ can be taken as zero or unity at convenience. The chemical potentials $\mu_\alpha$ are then the negatives either of the ionization energies $I_\alpha(v_\alpha = 0)$ or of the electron affinities $A_\alpha$-$(v_\alpha = 1)$. The condition (3) for EE cannot be satisfied except by accident or if the parts are all identical monomers. If the identical monomers remain in symmetrically equivalent configurations as the separations shrink, EE continues to hold with all $\mu_\alpha$ identical to $\mu_M$ and all $N_\alpha$ identical integers equal to $N_M/A$. In general however, at $d_{\alpha\beta} \uparrow \infty$ the ground-state energy $\mathcal{E}$ of the collection of parts is an infimum, an $A$-dimensional cusp in the $v_\alpha$-space.

What then happens to that cusp as the $d_{\alpha\beta}$ become finite? There are three possibilities. (1) The cusp disappears immediately for all $\alpha$, existing only in the limit $d_{\alpha\beta} \uparrow \infty$, $\forall \alpha\beta$, and becoming a minimum at noninteger $v_\alpha$, $\forall \alpha$, for finite $d_{\alpha\beta}$. (2) The cusp remains for some $\alpha$ above some finite set of $d_{\alpha\beta}$. (3) The cusp remains for all $\alpha$ above some finite set of $d_{\alpha\beta}$. We propose as a conjecture that possibility 1 *always* holds, made plausible by the following argument.

Change in the nature of the dependence of the $\{n_\alpha\}$ on the $\{d_{\alpha\beta}\}$ must emerge from a change in the nature of the dependence of $n_M$ on the $\{d_{\alpha\beta}\}$. Consider a Lewis acid/Lewis base pair for which the ionization energy $I_b$ of the base exceeds the electron affinity $A_a$ of the acid. At very large separation $d$, the ionic configuration is at an energy $I_b - A_a$ above that of the neutral configuration. As the pair approach, a crossover occurs, and the ionic configuration becomes the ground state. In the vicinity of the crossover, however, the KS state of the electron being transferred is delocalized, spending part of the time on each species; the ionic and neutral configurations are mixed, as shown in Figure 2.

This behavior is captured schematically by the Hamiltonian

$$\mathcal{H} = \begin{pmatrix} E_{\text{ionic}} & V \\ V & E_{\text{neutral}} \end{pmatrix} \tag{3.15}$$
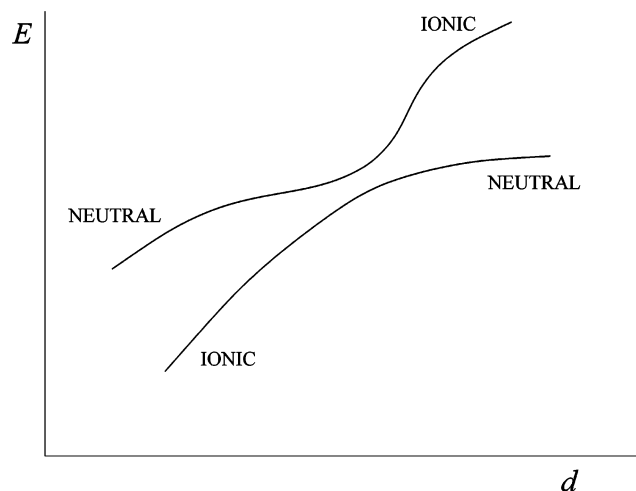
which has the eigenvalues

$$E_\pm = \bar{E} \pm \sqrt{\left(\frac{\Delta E}{2}\right)^2 + V^2} \tag{3.16}$$

where

$$\bar{E} = \frac{1}{2}(E_{\text{ionic}} + E_{\text{neutral}}) \tag{3.17}$$

$$\Delta E = E_{\text{ionic}} - E_{\text{neutral}} \tag{3.18}$$

and the eigenfunctions

**Figure 2.** The energy $E$ of a Lewis-acid/Lewis-base pair as a function of their separation $d$. At large separations the neutral configuration predominates in the lower energy state; at small separations the ionic does. Nevertheless, at all finite separations, there is a finite admixture of the one into the other.

$$\Psi = \begin{pmatrix} \Psi_{\text{ionic}} \\ \Psi_{\text{neutral}} \end{pmatrix} \qquad (3.19)$$

In the limit of large $d$, $\Delta E$ approaches $I_b - A_a$, and $V$ becomes small. Perturbation theory then yields the ratio

$$\rho = \left| \frac{\Psi_{\text{ionic}}}{\Psi_{\text{neutral}}} \right| = \frac{|V|}{I_b - A_a} \qquad (3.20)$$

Thus, though $\rho$ becomes exponentially small with $|V|$ as $d$ increases, it remains finite for all finite $d$, implying that in the partition−theoretic decomposition of the density $n_M$ of the acid−base pair, the $\nu_\alpha$ must be noninteger. Our conjecture that only possibility 1 holds constitutes a generalization of this simple argument.

## 4. Chemical-Context-Dependent Reactivities; Preliminary Definitions

In section 3A, we have defined within the context of PT our first chemical reactivity, the electronegativity, via eq 3.1. Electronegativity equalization, eq 3.2, then follows from the stationarity of the grand potential $\mathscr{G}$, eq 2.7. All electronegativities so defined are chemical-context dependent through their dependence on $\nu_R$ and $\mu_R$ and thus ultimately on $n_M$. It is this dependence on chemical context which enables us to escape the internal inconsistency between DFT and the previously formulated CRT. In the present section we construct preliminary definitions of several key reactivity indices and display their explicit context dependence. In the next section, we select the appropriate chemical context and provide final definitions of those reactivities.

**A. Differential Relations.** We now introduce variations $\delta n_M$ of $n_M$ for fixed $N_M$, $\delta N_M = 0$, and for fixed nuclear configuration, leading to variations $\delta \nu_R$ and $\delta \mu_M$ in $\nu_R$ and $\mu_M$, respectively. Note that the changed molecular density, $n_M + \delta n_M$, is no longer the ground-state density for that configuration.

The stationarity conditions for $\mathscr{G}$, eqs 2.11, 2.13, and 3.11 become

$$\chi_p^{-1} \cdot \delta n_p = -\delta \nu_R; \quad p = p_\alpha, \quad p_\alpha + 1; \quad \forall \alpha \qquad (4.1)$$

$$\delta \mu_\alpha = f_\alpha \cdot \delta \nu_R = \delta \mu_M, \quad \forall \alpha \qquad (4.2)$$

In eq 4.1 $\chi_p^{-1}$ is the Hessian of the density functional $E_\alpha[n_p]$,

$$\chi_p^{-1} = \frac{\delta^2 E_\alpha[n_p]}{\delta n_p^2} \qquad (4.3)$$

and its inverse is simply a susceptibility or softness kernel for fixed electron number $p$

$$\chi_p = -\frac{\delta n_p}{\delta \nu_R} \qquad (4.4)$$

This definition of the softness kernel differs from that previously introduced, eq 1.7, through its dependence on $\nu_R$ and $\mu_M$ and in the replacement of the external potential $\nu_e$ by the reactivity potential $\nu_R$. In eq 4.2, $f_\alpha$ is the Fukui function of part $\alpha$ defined in eq 2.15, differing from its earlier definition, eq 1.4, because of its dependence on $\nu_R$.

From the definition of $n_\alpha$, eq 2.5, it follows that

$$\delta n_\alpha = -\chi_\alpha \cdot \delta \nu_R + f_\alpha \delta \nu_\alpha \qquad (4.5)$$

where

$$\chi_\alpha = (1 - \nu_\alpha)\chi_{p_\alpha} + \nu_\alpha \chi_{p_\alpha + 1} = -\frac{\delta n_\alpha}{\delta \nu_R}\bigg)_{\nu_\alpha} \qquad (4.6)$$

From eq (4.5) and the density constraint, eq 2.1, it follows that

$$\delta n_M = -\chi_R \cdot \delta \nu_R + \sum_\alpha f_\alpha \delta \nu_\alpha \qquad (4.7)$$

where

$$\chi_R = \sum_\alpha \chi_\alpha = -\frac{\delta n_M}{\delta \nu_R}\bigg)_{\{\nu_\alpha\}} \qquad (4.8)$$

a kind of susceptibility or softness kernel for the whole system.

Equation 4.7 relates $\delta n_M$ to $\delta \nu_R$ and the $\delta \nu_\alpha$. It can be rearranged to express $\delta \nu_R$ in terms of $\delta n_M$ and the $\nu_\alpha$:

$$\delta \nu_R = -\chi_R^{-1} \cdot [\delta n_M - \sum_\alpha f_\alpha \delta \nu_\alpha] \qquad (4.9)$$

Comparing eqs 4.7 and 4.9, we see that either $\delta \nu_R$, $\{\delta \nu_\alpha\}$ or $\delta n_M$, $\{\delta \nu_\alpha\}$ can be chosen as the set of independent variables by relaxing the condition

$$\sum_\alpha \delta \nu_\alpha = 0 \qquad (4.10)$$

which follows from eqs 2.2 and 2.4 or equivalently by relaxing the condition

$$\delta \mu_\alpha = \delta \mu_M \qquad (4.11)$$

and then reimposing either at the end. Finally, the differential relation for $\mu_\alpha$ is

$$\delta \mu_\alpha = f_\alpha \cdot \chi_R^{-1} \cdot \left[ \sum_\beta f_\beta \delta \nu_\beta - \delta n_M \right] \qquad (4.12)$$

Equations 4.5, 4.7, 4.9, and 4.12 will permit us to define reactivities containing derivatives with respect to $N_\alpha$ or $\nu_\alpha$, which are explicitly context dependent.

**B. The Global Hardness Matrix.** We define as the global hardness matrix for context C,

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$$H_{\alpha\beta}\big|_{c} \equiv \frac{\delta\mu_{\alpha}}{\delta\nu_{\beta}}\bigg|_{c} \qquad (4.13)$$

with the derivative taken in context C. There are two limiting contexts.

In the first of these, $C_1$, charge transfer occurs without distortion of $n_p$, $p = p_\alpha$, $p_{\alpha+1}$, $\forall\alpha$, which implies that

$$\delta\nu_R = 0 \qquad (4.14)$$

$$\delta n_M = \sum_\alpha f_\alpha \delta\nu_\alpha \qquad (4.15)$$

Inserting eq 4.15 into eq 4.12 leads to a vanishing hardness matrix via the definition eq 4.13,

$$H_{\alpha\beta}\big|_1 = 0 \qquad (4.16)$$

In the second, $C_2$, the density changes due to charge transfer, eq 4.15, are perfectly compensated by distortions of the $n_p$; $p = p_\alpha$, $p_\alpha + 1$; $\forall\alpha$ so that

$$\delta n_M = 0 \qquad (4.17)$$

$$\delta\nu_R = \chi_R^{-1} \sum_\alpha f_\alpha \delta\nu_\alpha \qquad (4.18)$$

Equation 4.12 becomes

$$\delta\mu_\alpha = \sum_\beta \eta_{\alpha\beta} \delta\nu_\beta \qquad (4.19)$$

and eq 4.13 consequently leads to a nonvanishing hardness matrix

$$H_{\alpha\beta}\big|_2 = \eta_{\alpha\beta} = f_\alpha \cdot \chi_R^{-1} \cdot f_\beta \qquad (4.20)$$

which is symmetric and positive definite. It contains self-hardnesses

$$\eta_{\alpha\alpha} = f_\alpha \cdot \chi_R^{-1} \cdot f_\alpha \qquad (4.21a)$$

and mutual hardnesses

$$\eta_{\alpha\beta} = f_\alpha \cdot \chi_R^{-1} \cdot f_\beta \qquad (4.21b)$$

Comparing the two hardness matrices and the definitions of their contexts $C_1$ and $C_2$, we see that finite hardness is generated by distortion of the densities of the integer components of the ensembles representing the parts. Moreover, $H_{\alpha\beta}\big|_2$ remains nonvanishing in the limit of infinite separation,

$$\eta_{\alpha\beta} \xrightarrow[d_{\alpha\beta}\uparrow\infty]{} f_\alpha \cdot \chi_\alpha^{-1} \cdot f_\alpha \delta_{\alpha\beta} \qquad (4.22)$$

providing a natural measure of the hardness of an isolated system. In eq 4.22, $d_{\alpha\beta}$ is, for example, the separation of the centers of gravity of the pair $\alpha$, $\beta$, and goes to infinity for all pairs. The behavior of such quantities as $\chi_R^{-1}$ in the asymptotic limit $d_{\alpha\beta} \uparrow \infty$ is discussed in Appendix C.

We note that similar hardness matrices have been proven useful before in guiding the development of pseudopotentials with improved transferabilty properties.[31]

**C. The Fukui Matrix.** Inserting eq 4.9 into eq 4.5 leads to a differential expression for $\delta n_\alpha$ with $\delta n_M$, $\{\delta\nu_\alpha\}$ as the "independent" variables. As did the expressions for the $\delta\mu_\alpha$, it becomes chemical-context dependent through the presence of

the $\delta n_M$,

$$\delta n_\alpha = f_\alpha \delta\nu_\alpha + \chi_\alpha \cdot \chi_R^{-1} \cdot \left[\delta n_M - \sum_\beta f_\beta \delta\nu_\beta\right] \qquad (4.23)$$

We define as the Fukui matrix for context C:

$$F_{\alpha\beta}\big|_C \equiv \frac{\delta n_\alpha}{\delta\nu_\beta}\bigg|_C \qquad (4.24)$$

In context $C_1$ it becomes

$$F_{\alpha\beta}\big|_1 = f_\alpha \delta_{\alpha\beta} \qquad (4.25)$$

reducing essentially to the collection of Fukui functions of the individual parts, though in the presence of the reactivity potential. In context $C_2$ it becomes

$$F_{\alpha\beta}\big|_2 = f_\alpha \delta_{\alpha\beta} - \chi_\alpha \cdot \chi_R^{-1} \cdot f_\beta \qquad (4.26)$$

which, from the arguments of Appendix C, has the asymptotic limit

$$F_{\alpha\beta}\big|_2 \xrightarrow[d_{\alpha\beta}\uparrow\infty]{} 0 \qquad (4.27)$$

because each $\delta n_\alpha \rightarrow 0$ when $\delta n_M \rightarrow 0$ at $d_{\alpha\beta} \uparrow \infty$. Note the sum-rule

$$\sum_\alpha F_{\alpha\beta}\big|_2 = 0 \qquad (4.28)$$

holds, as it must because $\delta n_M$ vanishes in $C_2$.

**D. The Local and Global Softness Matrices.** Replacing the $\{\delta\nu_\alpha\}$ by the $\{\delta\mu_\alpha\}$ in the set of "independent" variables allows us to define the local softness matrix

$$s_{\alpha\beta}\big|_C \equiv \frac{\delta n_\alpha}{\delta\mu_\beta}\bigg|_C \qquad (4.29)$$

Through the chain rule we can reexpress $s_{\alpha\beta}\big|_C$ in terms of the Fukui matrix and a global softness matrix,

$$s_{\alpha\beta}\big|_C = \sum_\gamma F_{\alpha\gamma}\big|_C \, S_{\gamma\beta}\big|_C \qquad (4.30)$$

The global softness matrix is simply the inverse of the hardness matrix

$$S_{\alpha\beta}\big|_C = (H\big|_C^{-1})_{\alpha\beta}$$
$$= \frac{\delta\nu_\alpha}{\delta\mu_\beta}\bigg|_C \qquad (4.31)$$

As

$$\delta\nu_\alpha = \int d\mathbf{r} \, \delta n_\alpha(\mathbf{r}) \qquad (4.32)$$

an integral relation exists between the local and global softness matrices,

$$S_{\alpha\beta}\big|_C = \int d\mathbf{r} \, s_{\alpha\beta}(\mathbf{r})\big|_C \qquad (4.33)$$

Because $H_{\alpha\beta}\big|_1$ vanishes, $S_{\alpha\beta}\big|_1$ and $s_{\alpha\beta}\big|_1$ are undefined. On the other hand, in context 2 $S_{\alpha\beta}\big|_2$ is meaningful:

$$S_{\alpha\beta}\big|_2 = (\eta^{-1})_{\alpha\beta} \qquad (4.34)$$

with the asymptotic value

$$S_{\alpha\beta}|_2 \xrightarrow[d_{\alpha\beta}\uparrow\infty]{} \frac{\delta_{\alpha\beta}}{f_\alpha \cdot \chi_\alpha^{-1} \cdot f_\alpha} \tag{4.35}$$

In context 2 the local softness vanishes as $d_{\alpha\beta} \uparrow \infty$ because the Fukui matrix does. However, if $\Omega$ is the volume within which quantization occurs, one can show that $F_{\alpha\beta}|_2$ and therefore $s_{\alpha\beta}|_2$ vanish as $1/\Omega$, $\Omega \uparrow \infty$, so that integration of $s_{\alpha\beta}|_2$ over $\Omega$ does indeed maintain the integral relation (4.33) between the vanishing $s_{\alpha\beta}|_2$ and the finite $S_{\alpha\beta}|_2$.

**E. Context Sensitivity.** We have defined the following reactivities which involve number derivatives: first derivatives, the electronegativity and the Fukui matrix; second derivatives, the hardness, global softness, and local softness matrices. In the course of the analysis, we have introduced a softness kernel

$$\hat{S}_\alpha^N \equiv \chi_\alpha = (1 - \nu_\alpha)\chi_{p_\alpha} + \nu_\alpha \chi_{p_\alpha+1} \tag{4.36}$$

a reactivity index at constant number. The indices involving number derivatives are profoundly sensitive to the chemical context, expressible as the relationship between $\delta n_M$ and the $\delta \nu_\alpha$ or whether the densities of the integer members of the ensemble representing the parts are distorted.

In the next section we define the chemical context appropriate for the definition of meaningful reactivities and thereby arrive at our final definitions.

## 5. Final Definitions of the Reactivities

**A. Electron−Nuclear Interactions Define the Chemical Context.** The term $n_M$ represents the ground-state electron density of a system of $N_M$ electrons in the external nuclear potential

$$\nu_M = \sum_\alpha \nu_\alpha \tag{5.1}$$

with $\nu_\alpha$ that of part $\alpha$. In the previous section, we took variations $\delta n_M$ in $n_M$ at fixed $\nu_M$, $\{\nu_\alpha\}$, and $N_M$, allowing $n_M$ to deviate from its ground-state value to illustrate how reactivity indices can become context sensitive. We now allow changes in the electron nuclear potentials,

$$\delta \nu_M = \sum_\alpha \delta \nu_\alpha \tag{5.2}$$

and establish the chemical context in which the reactivities are defined by requiring $\delta n_M$ to be the change in the *ground-state density* of M in response to the changed nuclear configuration. In this way, the reactivity indices we shall define will reflect what actually happens within the system as it evolves along a reaction pathway.

**B. Revised Differential Relations.** The change in the ground-state density of M is

$$\delta n_M = -\chi_M \delta \nu_M = -\chi_M \sum_\alpha \delta \nu_\alpha \tag{5.3}$$

where $\chi_M$ is the susceptibility (or the constant-number softness kernel) of M, not to be confused with the $\chi_R$ of eq 4.8. $\chi_R$ requires that all the $\nu_\alpha$ are individually kept constant, whereas $\chi_M$ requires only that their sum be kept constant. Similarly, the change in the ground-state density of part $\alpha$ is

$$\delta n_\alpha = f_\alpha \delta \nu_\alpha - \chi_\alpha \cdot [\delta \nu_\alpha + \delta \nu_R] \tag{5.4}$$

Imposing the density constraint, eq 2.1, allows us to express $\delta \nu_R$ in terms of the $\{\delta \nu_\alpha, \delta \nu_\alpha\}$ as the set of "independent" variables,

$$\delta \nu_R = \chi_R^{-1} \cdot \left[ \sum_\alpha \left[ f_\alpha \delta \nu_\alpha - (\chi_\alpha - \chi_M) \cdot \delta \nu_\alpha \right] \right] \tag{5.5}$$

and eliminate it from the differential relations. Inserting eq 5.5 into eq 5.4 yields the first of our two basic differential relations:

$$\delta n_\alpha = \sum_\beta \{ [f_\alpha \delta_{\alpha\beta} - \chi_\alpha \cdot \chi_R^{-1} \cdot f_\beta] \delta \nu_\beta - \chi_\alpha \cdot [\hat{1}\delta_{\alpha\beta} - \chi_R^{-1} \cdot (\chi_\beta - \chi_M)] \cdot \delta \nu_\beta \} \tag{5.6}$$

where $\hat{1}$ is the Dirac $\delta$ function. To obtain the second relation, we note that eq 4.2 changes to

$$\delta \mu_\alpha = f_\alpha (\delta \nu_\alpha + \delta \nu_R) \tag{5.7}$$

for nonzero $\delta \nu_\alpha$. Inserting eq 5.4 into eq 5.7 yields the desired result

$$\delta \mu_\alpha = \sum_\beta \{ \eta_{\alpha\beta} \delta \nu_\beta + f_\alpha \cdot [\hat{1}\delta_{\alpha\beta} - \chi_R^{-1} \cdot (\chi_\beta - \chi_M)] \} \cdot \delta \nu_\beta \tag{5.8}$$

Again, if we postpone imposition of the requirement $\delta \mu_\alpha = \delta \mu_m$ or, equivalently, $\sum_\alpha \delta \nu_\alpha = 0$, we can regard both the $\{\delta \nu_\alpha\}$ and the $\{\delta \nu_\alpha\}$ as independent variables and define reactivities within this well-specified chemical context.

**C. The Global Hardness Matrix.** We define the global hardness matrix as

$$\left. \frac{\delta \mu_\alpha}{\delta \nu_\beta} \right)_{\{\nu_\gamma\}} = \eta_{\alpha\beta} = H_{\alpha\beta}|_2 \tag{5.9}$$

Note that

$$\eta_{\alpha\beta} = \left. \frac{\delta^2 \mathcal{E}^R}{\delta \nu_\alpha \delta \nu_\beta} \right)_{\{\nu_\gamma\}} \tag{5.10}$$

where

$$\mathcal{E}^R = \sum_\alpha \mathcal{E}_\alpha^R \tag{5.11}$$

(cf. eq 2.14). Note also that $\{\delta \nu_\gamma\} = 0$ implies that $\delta n_M = 0$ according to eq 5.2 (context $C_2$). Thus hardness is a response to charge transfer among the parts of M at fixed nuclear configuration and arises from the distortion of the integer components of the representative ensembles.

**D. The Fukui Matrix.** In the original version of CRT, the Fukui function is a cross derivative.[1] It is defined as

$$f = \left. \frac{\partial n}{\partial N} \right)_{\nu_e} \tag{5.12}$$

But since

$$n = \left. \frac{\partial E}{\partial \nu_e} \right)_N \tag{5.13}$$

it follows as a Maxwell relation that

$$f = \left. \frac{\partial n}{\partial N} \right)_{\nu_e} = \frac{\partial^2 E}{\partial \nu_e \partial N} = \left. \frac{\partial \mu}{\partial \nu_e} \right)_N \tag{5.14}$$

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Similarly, we have two options for defining the Fukui matrix. However, these now differ because the Maxwell relation fails in the presence of $v_R$.

The first parallels the initial definition, eq 5.12:

$$\left.\frac{\delta n_\alpha}{\delta \nu_\beta}\right)_{\{v_\gamma\}} = f_\alpha \delta_{\alpha\beta} - \chi_\alpha \cdot \chi_R^{-1} \cdot f_\beta = F_{\alpha\beta}|_2 \quad (5.15)$$

This has the apparently unsatisfactory feature of vanishing at infinite separation, eq 4.27, but, as we shall see in section 6, it plays a significant chemical role. The second is suggested by the Maxwell relation, eq 5.14,

$$F_{\alpha\beta} \equiv \left.\frac{\delta \mu_\alpha}{\delta \nu_\beta}\right)_{\{v_\gamma\}} = f_\alpha \cdot [\hat{1}\delta_{\alpha\beta} - \chi_R^{-1} \cdot (\chi_\beta - \chi_M)] \quad (5.16)$$

which is finite at infinite separation since

$$\left.\frac{\delta \mu_\alpha}{\delta \nu_\beta}\right)_{\{v_\gamma\}} \xrightarrow[d_{\alpha\beta}\uparrow\infty]{} f_\alpha \delta_{\alpha\beta} \quad (5.17)$$

according to the reasoning of Appendix C.

**E. The Softness Kernel.** We define the softness kernel at constant part numbers as

$$\mathcal{S}_{\alpha\beta}^{\{v_\gamma\}} \equiv -\left.\frac{\delta n_\alpha}{\delta v_\beta}\right)_{\{v_\gamma\}} \quad (5.18)$$

$$\mathcal{S}_{\alpha\beta}^{\{v_\gamma\}} = \chi_\alpha \cdot [\hat{1}\delta_{\alpha\beta} - \chi_R^{-1} \cdot (\chi_\beta - \chi_M)] \quad (5.19)$$

It has a finite limit at infinite separation,

$$\mathcal{S}_{\alpha\beta}^{\{v_\gamma\}} \xrightarrow[d_{\alpha\beta}\uparrow\infty]{} S_\alpha^{\nu_\alpha} \delta_{\alpha\beta}, \quad S_\alpha^{\nu_\alpha} = \chi_\alpha \quad (5.20)$$

Note that the sum rule

$$\sum_\alpha S_{\alpha\beta}^{\{v_\gamma\}} = \chi_M \quad (5.21)$$

holds, as it must because of the density constraint.

**F. Local and Global Softnesses.** For the local softness we preserve the previous relation:

$$s_{\alpha\beta} = \sum_\gamma F_{\alpha\gamma} S_{\gamma\beta} \quad (5.22)$$

but with the definition (5.16) for $F_{\alpha\gamma}$ and with the global softness again the inverse of the hardness

$$S_{\alpha\beta} = (\eta^{-1})_{\alpha\beta} \quad (5.23)$$

**G. Integral Relations.** From these definitions certain integral relations follow:

$$\int d\mathbf{r}\, F_{\alpha\beta}(\mathbf{r}) = \delta_{\alpha\beta} \quad (5.24)$$

$$\int d\mathbf{r}\, s_{\alpha\beta}(\mathbf{r}) = S_{\alpha\beta} \quad (5.25)$$

$$\int d\mathbf{r}\, \mathcal{S}_{\alpha\beta}^{\{v_\gamma\}}(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'\, \mathcal{S}_{\alpha\beta}^{\{v_\gamma\}}(\mathbf{r}, \mathbf{r}') = 0 \quad (5.26)$$

## 6. Nuclear Reactivities

A successful theory of chemical reactivities should facilitate understanding of reaction pathways. Forces on nuclei play a central role in defining reaction pathways and establishing the locations and properties of transition states along them. Thus one goal of CRT should be to relate those forces to appropriate reactivity indices, nuclear reactivity indices. In an earlier publication,[32] nuclear reactivities were introduced as responses to the changes of number or chemical potential of the entire system. In section 7 of this paper, we relate the forces on the nuclei of the system to the nuclear reactivities of its parts introduced in the present section as sensitivities of the $\nu_\alpha$ and the $n_\alpha$ to the nuclear electrostatic potentials $v_\beta$, an inversion of emphasis consistent with the position taken in section 5 that the $v_\beta$ define the chemical context of part $\alpha$.

**A. Constrained Differential Relations.** We now reimpose the constraints on the $\delta\nu_\alpha$ and $\delta\mu_M$ expressed by eqs 4.10 and 4.11, respectively, so that the $\delta\nu_\alpha$ are restored as the only truly independent variations. Imposing those constraints on eq 5.8 leads to the elegant expression

$$\delta\nu_\alpha = -\sum_{\beta\gamma} \bar{S}_{\alpha\beta} F_{\beta\gamma} \cdot \delta v_\gamma \quad (6.1)$$

where $F_{\beta\gamma}$ is the Fukui matrix defined by eq 5.16. The quantity $\bar{S}_{\alpha\beta}$ is a constrained global softness matrix,

$$\bar{S}_{\alpha\beta} = S_{\alpha\beta} - \sum_{\alpha'\beta'} S_{\alpha\alpha'} S_{\beta\beta'} \Big/ \sum_{\alpha'\beta'} S_{\alpha'\beta'} \quad (6.2)$$

which guarantees that eq 6.1 is consistent with the constraint 4.10 via the relations

$$\sum_\alpha \bar{S}_{\alpha\beta} = \sum_\beta \bar{S}_{\alpha\beta} = 0 \quad (6.3)$$

$\bar{S}_{\alpha\beta}$ is a symmetric, non-negative matrix. The latter statement follows from a Schwarz inequality obtained by recognizing that $S_{\alpha\beta}$, a positive definite matrix, can be used as a metric for defining a scalar product between two vectors. Let **b** be an arbitrary real vector with components $q_\alpha$ and **1** be the vector with unit components $(\mathbf{1})_\alpha = 1$. It follows then that

$$(\mathbf{q} \cdot \bar{S} \cdot \mathbf{q}) = [(\mathbf{q} \cdot S \cdot \mathbf{q})(\mathbf{1} \cdot S \cdot \mathbf{1}) - (\mathbf{q} \cdot S \cdot \mathbf{1})^2]/(\mathbf{1} \cdot S \cdot \mathbf{1}) \quad (6.4)$$

As $S$ is positive definite, it follows from the Schwarz inequality that $\bar{S}$ is non-negative.

Note that $S_{\alpha\gamma} = \delta\nu_\alpha/\delta\mu_\gamma)_{\{v_\delta\}}$ from eqs 5.10 and 5.23. Note also that $F_{\gamma\beta} = \delta\mu_\gamma/\delta v_\beta)_{\{v_\delta\}}$ from eq 5.16. Thus the reactivity

$$-\frac{\overline{\delta\nu_\alpha}}{\delta v_\beta} = \sum_\gamma \bar{S}_{\alpha\gamma} F_{\gamma\beta} \quad (6.5)$$

where the superposed bar on the left hand side of eq 6.5 indicates that the constraint 4.10 is imposed, has the formal structure of a chain-rule derivative. It is a generalization of the charge sensitivity of Nalewajski.[33]

Substituting eq 6.1 for $\delta\nu_\alpha$ in eq 5.6 yields a corresponding expression for $\delta n_\alpha$,

$$\delta n_\alpha = -\sum_\beta \mathcal{S}_{\alpha\beta}^C \cdot \delta v_\beta \quad (6.6)$$

where the constrained susceptibility $\mathcal{S}_{\alpha\beta}^C$ is given by

$$\mathcal{S}_{\alpha\beta}^C = \mathcal{S}_{\alpha\beta}^{\{v_\gamma\}} + \Delta \mathcal{S}_{\alpha\beta} \quad (6.7)$$

In eq 6.7, $\mathcal{S}_{\alpha\beta}^{\{v_\gamma\}}$ is the softness kernel defined by eq 5.19. The second term in eq 6.7 arises from the $\delta\nu_\alpha$ of eq 6.1,

$$\Delta \mathcal{S}_{\alpha\beta} = \sum_{\gamma\delta} F_{\alpha\gamma}|_2 \bar{S}_{\gamma\delta} F_{\delta\beta} \tag{6.8}$$

and involves both definitions of the Fukui matrix, $F_{\alpha\beta}|_2$ of eq 5.15 as well as $F_{\alpha\beta}$. Equations 6.6 and 6.1 are mutually consistent. That

$$\delta \nu_\alpha = \int d\mathbf{r} \, \delta n_\alpha(\mathbf{r}) \tag{6.9}$$

follows from the fact that

$$\int d\mathbf{r} \, F_{\alpha\beta}|_2 = \delta_{\alpha\beta} \tag{6.10}$$

and eq 5.26, as it should.

**B. Constrained Nuclear-Displacement Sensitivities.** The variation $\delta \nu_\alpha$ in section 5A above arises from variations of the nuclear positions $\delta\mathbf{R}_{l_\alpha}$ within part $\alpha$:

$$\delta \nu_\alpha(\mathbf{r}) = \sum_l \nabla_{l_\alpha} \nu_{l_\alpha}(\mathbf{r}) \cdot \delta\mathbf{R}_{l_\alpha} \tag{6.11}$$

where $\nu_{l_\alpha}$ is the electrostatic potential of the $l_\alpha$ nucleus

$$\nu_{l_\alpha}(\mathbf{r}) = -\frac{Z_{l_\alpha} e^2}{|\mathbf{r} - \mathbf{R}_{l_\alpha}|} \tag{6.12}$$

and $Z_{l_\alpha}$ is its charge. The results of section 5A thus allow us to define as constrained nuclear reactivities the responses of the electron numbers $\nu_\alpha$ and densities $n_\alpha$ to variations of nuclear position. Taking over the term sensitivity introduced by Nalewajski within the earlier framework of CRT,[33] we define constrained nuclear-displacement sensitivities for the electron numbers and densities of the parts.

*1. Number Sensitivity.* We define $\boldsymbol{\omega}_{\alpha,l_\beta}$ as the constrained number sensitivity of part $\alpha$ to the displacement of nucleus $l_\beta$,

$$\boldsymbol{\omega}_{\alpha,l_\beta} \equiv \frac{\delta \nu_\alpha}{\delta\mathbf{R}_{l_\beta}} = \sum_\nu \bar{S}_{\alpha\gamma} F_{\gamma\beta} \cdot \boldsymbol{\phi}_{l_\beta} \tag{6.13}$$

according to eqs 6.1 and 6.11, where $\boldsymbol{\phi}_{l_\beta}(\mathbf{r})$ is the electrostatic force exerted by the nucleus $l_\beta$ on an electron at $\mathbf{r}$

$$\boldsymbol{\phi}_{l_\beta}(\mathbf{r}) = \frac{Z_{l_\beta}(\mathbf{r} - \mathbf{R}_{l_\beta})}{|\mathbf{r} - \mathbf{R}_{l_\beta}|^3} \tag{6.14}$$

*2. Density Sensitivity.* We define $\boldsymbol{\rho}_{\alpha,l_\beta}(\mathbf{r})$ as the constrained density sensitivity of part $\alpha$ to the displacement of nucleus $l_\beta$,

$$\boldsymbol{\rho}_{\alpha,l_\beta} \equiv \frac{\delta n_\alpha}{\delta\mathbf{R}_{l_\beta}} = \mathcal{S}^C_{\alpha\beta} \cdot \boldsymbol{\phi}_{l_\beta} \tag{6.15}$$

according to eqs 6.6 and 6.11. We see that both nuclear sensitivities, $\boldsymbol{\omega}_{\alpha,l_\beta}$ and $\boldsymbol{\rho}_{\alpha,l_\beta}$, are products of electronic reactivities, $\sum_\gamma \bar{S}_{\alpha\gamma} F_{\gamma\beta}$ and $\mathcal{S}^C_{\alpha\beta}$, respectively, with the nuclear electrostatic force $\boldsymbol{\phi}_{l_\beta}$. $\boldsymbol{\omega}_{\alpha,l_\beta}$ and $\boldsymbol{\rho}_{\alpha,l_\beta}$ obey the integral relation

$$\int d\mathbf{r} \, \boldsymbol{\rho}_{\alpha,l_\beta}(\mathbf{r}) = \boldsymbol{\omega}_{\alpha,l_\beta} \tag{6.16}$$

which follows from eq 6.9 and their definitions, eqs 6.13 and 6.15.

# 7. Energies and Forces

As implied in the introduction to section 6, understanding the forces acting on the nuclei of chemical systems is central

to understanding their chemical behavior. Accordingly, in the present section, we first relate the energy functional $\mathcal{E}$ of the parts, eq 2.6, to the total energy $W_M$ of M through the introduction of a model energy functional $W$. We then relate the resulting model forces on the nuclei to the actual forces within M by expressions containing the constrained nuclear reactivities of section 6.

**A. The Model Energy Functional.** The total energy $W_\alpha$ of part $\alpha$ is its energy functional $\mathcal{E}_\alpha$, eq 2.3, augmented by the electrostatic energy of interaction of its nuclei, $W_{\alpha\alpha}^{NN}$,

$$W_\alpha = \mathcal{E}_\alpha + W_{\alpha\alpha}^{NN} \tag{7.1}$$

$$W_{\alpha\alpha}^{NN} = \frac{1}{2} \sum_{l_\alpha,m_\alpha}' \frac{Z_{l_\alpha} Z_{m_\alpha} e^2}{|\mathbf{R}_{l_\alpha} - \mathbf{R}_{m_\alpha}|} \tag{7.2}$$

A model total-energy functional $W$ can be constructed by adding to the sum of the $W_\alpha$ the electrostatic interaction energy $W_{ES}^{INT}$ among the parts:

$$W = \sum_\alpha W_\alpha + W_{ES}^{INT} \tag{7.3}$$

$W_{ES}^{INT}$ has contributions from the Hartree approximation to the electron–electron interactions between pairs of parts, $W^H$; the electrostatic interactions between the nuclei of one part and the electrons of another, $W^{Ne}$; and the electrostatic interactions of the nuclei in different parts, $W^{NN}$:

$$W_{ES}^{INT} = W^H + W^{Ne} + W^{NN} \tag{7.4}$$

The Hartree term $W^H$ is

$$W^H = \frac{1}{2} \sum_{\alpha\beta}' U_{\alpha\beta}^H \tag{7.5}$$

$$U_{\alpha\beta}^H = n_\alpha \cdot w \cdot n_\beta \tag{7.6}$$

$$w(\mathbf{r}, \mathbf{r}') = \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \tag{7.7}$$

The electron–nuclear term is

$$W^{Ne} = \sum_{\alpha\beta}' n_\alpha \cdot \nu_\beta \tag{7.8}$$

Finally, the nuclear–nuclear term is

$$W^{NN} = \frac{1}{2} \sum_{l_\alpha m_\beta}' Z_{l_\alpha} w(\mathbf{R}_{l_\alpha}, \mathbf{R}_{m_\beta}) Z_{m_\beta} \tag{7.9}$$

In eqs 7.5, 7.8, and 7.9, the prime indicates that $\alpha \neq \beta$.

To relate the model total-energy functional $W$ to that of system M, $W_M$, we first reexpress $\mathcal{E}_\alpha$ in terms of its universal part $F_\alpha$:

$$\mathcal{E}_\alpha = F_\alpha + \nu_\alpha \cdot n_\alpha \tag{7.10}$$

$$F_\alpha = (1 - \nu_\alpha) F[n_{p_\alpha}] + \nu_\alpha F[n_{p_\alpha+1}] \tag{7.11}$$

We next collect all electrostatic parts together to obtain

$$W = \sum_\alpha \left( F_\alpha - \frac{1}{2} U_{\alpha\alpha} \right) + W_{ES}^M \tag{7.12}$$

where $W_{ES}^M$ is the total electrostatic energy of interaction among all electrons and nuclei in M:

$$W_{ES}^M = \frac{1}{2} \sum_{\alpha\beta} U_{\alpha\beta}^H + \sum_{\alpha\beta} v_\alpha \cdot n_\beta + \frac{1}{2} \sum_{l_\alpha, m_\beta}' Z_{l_\alpha} w(\mathbf{R}_{l_\alpha}, \mathbf{R}_{m_\beta}) Z_{m_\beta} \tag{7.13}$$

In eq 7.12, the prime indicates $l_\alpha \neq m_\alpha$ when $\alpha = \beta$. $W_M$ can be written in a form analogous to that of eq 7.13,

$$W_M = \left( F_M - \frac{1}{2} U_M^H \right) + W_{ES}^M \tag{7.14}$$

where

$$U_M^H = n_M \cdot w \cdot n_M \tag{7.15}$$

Thus, a remarkably simple relation between $W$ and $W_M$ emerges:

$$W_M = W + \Delta W \tag{7.16}$$

$$\Delta W = \left( F_M - \frac{1}{2} U_M \right) - \sum_\alpha \left( F_\alpha - \frac{1}{2} U_{\alpha\alpha} \right) \tag{7.17}$$

which will be shown in the next subsection to be most convenient for relating model forces based on $W$ to the actual forces within M. $\Delta W$ is formally independent of the nuclear coordinates.

It is common practice to partition a system into its parts, treat those parts in some degree of approximation, and then add the electrostatic energy of interaction of the parts to obtain the total energy. Ayers and co-workers,[34] for example, have tested quantitatively the validity of Pearson's hard−soft acid−base principle[22] by adding polarization terms as well. The present formulation differs from previous work in that the parts are given a specific, rigorous definition within our formulation of partition theory.[23]

**B. Forces and Nuclear Reactivities.** *1. The Electrostatic Force.* We define $F_{l_\alpha}^{ES}$ as the purely electrostatic force common to both the actual system M and the model system:

$$F_{l_\alpha}^{ES} = -\frac{\delta W_{ES}^M}{\delta \mathbf{R}_{l_\alpha}} \tag{7.18}$$

As $F_{l_\alpha}^{ES}$ can be computed and analyzed by standard methods, we shall focus in the following on the remaining contributions to the forces.

*2. The real system M.* Varying the $W_M$ of eq 7.14 results in

$$\delta W_M = \delta F_M - \frac{1}{2} \delta U_M^H - \sum_{l_\alpha} F_{l_\alpha}^{ES} \cdot \delta \mathbf{R}_{l_\alpha} \tag{7.19}$$

From the stationarity of $E_M$ at the ground state of M,

$$\delta F_M = -v_M \cdot \delta n_M \tag{7.20}$$

follows. From the definition 7.15 of $U_M^H$,

$$\frac{1}{2} \delta U_M = v_M^H \cdot \delta n_M \tag{7.21}$$

follows, where

$$v_M^H = n_M \cdot w \tag{7.22}$$

is the Hartree potential within M. Putting together the expressions 5.3, 6.11, and 6.14 to obtain $\delta n_M$ and inserting the result in eq 7.19 via eqs 7.20 and 7.21 yields

$$F_{l_\alpha}^M = v_M^T \cdot \boldsymbol{\rho}_{M,l_\alpha} + F_{l_\alpha}^{ES} \tag{7.23}$$

for the force on nucleus $l_\alpha$. In eq 7.23 $v_M^T$ is the total electrostatic potential within M,

$$v_M^T = v_M + v_M^H \tag{7.24}$$

that is, the bare electrostatic nuclear potential screened by the Hartree potential. The quantity $\boldsymbol{\rho}_{M,l_\alpha}$,

$$\boldsymbol{\rho}_{M,l_\alpha} = \chi_M \cdot \phi_{l_\alpha} \tag{7.25}$$

is the internal nuclear-displacement sensitivity of the electron density of M, defined in analogy to the sensitivities $\boldsymbol{\rho}_{\alpha,l_\beta}$ of section 6B2.

*3. The Model Forces.* Varying the $W$ of eq 7.12 results in

$$\delta W = \sum_\alpha \left( \delta F_\alpha - \frac{1}{2} \delta U_{\alpha\alpha} \right) - \sum_{l_\alpha} F_{l_\alpha}^{ES} \cdot \delta \mathbf{R}_{l_\alpha} \tag{7.26}$$

From the definition 7.11 of $F_\alpha$ and the stationarity conditions 2.11,

$$\delta F_\alpha = (F[n_{p_\alpha+1}] - F[n_{p_\alpha}]) \delta v_\alpha - (v_\alpha + v_R) \cdot \partial n_\alpha \tag{7.27}$$

follow, where

$$\partial n_\alpha = (1 - v_\alpha)\delta n_{p_\alpha} + v_\alpha \delta n_{p_\alpha+1} \tag{7.28}$$

Equations 7.11, 2.14, 217, and 2.16 allow us to rewrite eq 7.27 as

$$\delta F_\alpha = \mu_M \delta v_\alpha - (v_\alpha + v_R) \cdot \delta n_\alpha \tag{7.29}$$

since

$$\delta n_\alpha = f_\alpha \delta v_\alpha + \partial n_\alpha \tag{7.30}$$

Finally,

$$\frac{1}{2} \delta U_{\alpha\alpha}^H = v_\alpha^H \cdot \delta n_\alpha \tag{7.31}$$

$$v_\alpha^H = n_\alpha \cdot w \tag{7.32}$$

follow from eq 7.6.

Inserting eqs 7.29 and 7.30 into eq 7.26 and imposing condition 4.10 results in

$$\delta W = -\sum_\alpha (v_\alpha^T + v_R) \cdot \delta n_\alpha - \sum_{l_\alpha} F_{l_\alpha}^{ES} \cdot \delta \mathbf{R}_{l_\alpha} \tag{7.33}$$

for the variation of $W$, where

$$v_\alpha^T = v_\alpha + v_\alpha^H \tag{7.34}$$

is the total electrostatic potential within part $\alpha$, the bare nuclear electrostatic potential $v_\alpha$ screened by the Hartree potential $v_\alpha^H$.

The model force on nucleus $l_\alpha$ is thus

$$F_{l_\alpha} = -\frac{\delta W}{\delta \mathbf{R}_{l_\alpha}} = \sum_\beta [v_\beta^{\mathrm{T}} + v_{\mathrm{R}}] \cdot \boldsymbol{\rho}_{\beta,l_\alpha} + F_{l_\alpha}^{\mathrm{ES}} \quad (7.35)$$

From the sum rules 4.28 and 5.21, the definitions of the sensitivities $\boldsymbol{\rho}_{\alpha,l_\alpha}$ and $\boldsymbol{\rho}_{\mathrm{M},l_\alpha}$, eqs 6.15 and 7.25, and the definition of the constrained susceptibility eq 6.7, the sum-rule

$$\sum_\alpha \boldsymbol{\rho}_{\alpha,l_\alpha} = \boldsymbol{\rho}_{\mathrm{M},l_\alpha} \quad (7.36)$$

follows so that eq 7.35 can be rewritten as

$$F_{l_\alpha} = \sum_\beta v_\beta^{\mathrm{T}} \cdot \boldsymbol{\rho}_{\beta,l_\alpha} + v_{\mathrm{R}} \cdot \boldsymbol{\rho}_{\mathrm{M},l_\alpha} + F_{l_\alpha}^{\mathrm{ES}} \quad (7.37)$$

Comparing eqs 7.37 and 7.23, we obtain for the difference between the exact forces and the model forces

$$\Delta F_{l_\alpha} = F_{\mathrm{M},l_\alpha} - F_{l_\alpha}$$
$$= (v_{\mathrm{M}}^{\mathrm{T}} - v_{\mathrm{R}}) \cdot \boldsymbol{\rho}_{\mathrm{M},l_\alpha} - \sum_\beta v_\beta^{\mathrm{T}} \cdot \boldsymbol{\rho}_{\beta,l_\alpha} \quad (7.38)$$

which, with eqs 7.23 and 7.37, makes the desired connection between forces and reactivities.

## 8. Discussion

We began this article by setting up an inconsistency. Chemical reactivity theory, as it has been formulated prior to this work, introduces centrally important indices of the chemical reactivity of a species considered in isolation which are defined as or relate to derivatives of properties with respect to electron number. To embed that formulation within the structure of density-functional theory then requires a formulation of DFT which applies to ensembles with noninteger electron number, that of PPLB. The PPLB ensemble, however, possesses only properties which are piecewise-continuous, linear functions of electron number so that first derivatives are step functions and second derivatives vanish. These consequences are catastrophic for that formulation of CRT, causing it to lose the concepts of electronegativity equalization and hardness.

Nevertheless, the central idea of that formulation, the characterization of the reaction proclivities of a species by the responses of its properties to changes in electron number or to the external potential acting on it, seems eminently sensible. Why then does this prior formulation of CRT appear inconsistent with DFT? The answer we proposed in the present paper is that the chemical reactivity of a species cannot be defined in isolation. We argue here that its reactivities can only be defined within the context of the larger system of which it is a part or within which it is reacting. That in turn requires a sharply defined procedure for partitioning the larger system into its parts, which we provide in the form of the partition theory of section 2. We showed in section 3 how natural concepts of electronegativity and electronegativity equalization are reestablished within that PT. The logical extension of other concepts of the prior formulation of CRT to systems with multiple parts was shown to yield context-dependent reactivities in section 4. We argued in section 5 that the electron−nuclear interactions within the larger system specified the chemical context and thereby obtained well-defined chemical reactivities, chemically meaningful and consistent with DFT.

These reactivities were, as before, defined as responses of the parts to changes in electron number or external potential, now the nuclear electrostatic potential. As those number or potential changes could occur in another part, the reactivity indices emerged as matrices, for example a hardness matrix comprising the self-hardnesses of the individual parts on its diagonal and the mutual hardnesses of parts in its off-diagonal elements. As the parts separate to infinity, the newly defined indices take on meaningful limits. For example, the hardness matrix becomes diagonal, composed only of self-hardnesses of the individual parts, which no longer vanish and arise solely from the distortion of the electron densities of the integer components of the PPLB ensembles in response to and in compensation of the implied changes in electron number.

Having argued that the electron−nuclear interactions establish the chemical context, the nuclear-displacement sensitivities defined in section 6 emerged as the natural next step in the development of our PT-based CRT. Those in turn set the stage for the analysis of the forces on the nuclei and their relation to the nuclear-displacement sensitivities in section 7. This last development will allow addressing questions of reaction pathways and barriers within the framework of CRT.

Without question, the present formulation of CRT within PT can become computationally challenging. Both the electron density of the larger system, $n_{\mathrm{M}}$, and the corresponding chemical potential $\mu_{\mathrm{M}}$ must be known to adequate accuracy as input to the partition theory. Then Kohn−Sham equations or their equivalent must be solved for both components of the PPLB ensemble of each part in the presence of the reactivity potential $v_{\mathrm{R}}$ which acts as a proxy for the rest of the system and must be solved for in concert. At that point the partition problem would be solved and then the task of generating the reactivities and sensitivities would commence.

Clearly, before entering upon the nontrivial task of creating the computer code for such demanding numerical calculations, it would be best to explore the qualitative content of our PT/CRT through the study of very simple systems, and we have initiated such an analysis.

We have suggested in ref 24 that the Car−Parrinello (CP)[35] methodology would be an appropriate starting point for the development of a numerical procedure. A direct application of the CP method would require repeated generation of inverse susceptibilities to generate succesive values of $v_{\mathrm{R}}$ during the iterations. Instead, it would be better to treat $v_{\mathrm{R}}$ as a dynamical variable as well.

We conclude by stating that our PT/CRT formalism is not merely a formal scheme for a CRT which is consistent with DFT. It has a rich structure which promises to offer deep insight into chemical processes. It should be quite interesting to explore the additional insight into Pearson's hard−soft acid−base rule[22] which might be gained through the use of our mutual hardness and softness matrices. Similarly, the ability to define separate parts of a molecule should offer opportunity to gain a deeper understanding of the regularities encapsulated empirically through Hammett's sigma.[36] We believe there to be many other opportunities for productive use of the new theory.

## Appendix A: ACRONYMS

| | |
|---|---|
| CP | Car−Parrinello[35] |
| CRT | Chemical-reactivity theory |
| DFT | Density-functional theory |
| EDFT | Ensemble density-functional theory |
| EVR | Ensemble $v$-representable |
| HK | Hohenberg−Kohn[3] |

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HOMO      Highest occupied molecular orbital
KS        Kohn−Sham[4]
LL        Levy-Lieb constrained search algorithm[17,18]
PPLB      Perdew, Parr, Levy, and Balduz[19]
PT        Partition theory

## Appendix B: The Asymptotic Form of the Electron Density

Consider a bound system of $m$ electrons. The square root of its density $n_m(\mathbf{r})$ obeys a single-particle-like Schrödinger equation,[29,30]

$$\left[-\frac{\hbar^2\nabla^2}{2m} + u_s(\mathbf{r})\right]n_m^{1/2}(\mathbf{r}) = \mu_m n_m^{1/2}(\mathbf{r}) \quad (\text{B.1})$$

which contains an effective potential $u_s(\mathbf{r})$. The exact many-particle ground-state wave function $\Psi(m)$ obeys the $m$-particle Schrödinger equation

$$\hat{H}(m)\,\Psi(m) = E(m)\,\Psi(m) \quad (\text{B.2})$$

with $\hat{H}(m)$ the $m$-particle Hamiltonian containing the external nuclear electrostatic potential $v_e(\mathbf{r})$. The $u_s(\mathbf{r})$ was expressed in ref 30 in terms of the auxiliary $(m - 1)$-particle function

$$\Phi(\mathbf{r}_m, m - 1) = \left(\frac{m}{n(\mathbf{r}_m)}\right)^{1/2}\Psi(m) \quad (\text{B.3})$$

$$u_s(\mathbf{r}) = v_e(\mathbf{r}_m) + e^2\int d\mathbf{r}\frac{n_\Phi(\mathbf{r}, \mathbf{r}_m)}{|\mathbf{r} - \mathbf{r}_m|} +$$
$$\frac{\hbar^2}{2m}\int d\mathbf{r}_1...d\mathbf{r}_{m-1}|\nabla_m\Phi(\mathbf{r}_m, m-1)|^2 +$$
$$\langle\Phi(\mathbf{r}_m, m-1)|\hat{H}(m-1) - E(m-1)|\Phi(\mathbf{r}_m, m-1)\rangle \quad (\text{B.4})$$

In eq B.4, $n_\Phi(\mathbf{r}, \mathbf{r}_m)$ is the electron density associated with $\Phi(\mathbf{r}_m, m-1)$, and $\hat{H}(m-1)$ is the $(m-1)$-particle Hamiltonian containing the same nuclear electrostatic potential $v_e(\mathbf{r})$ present in $\hat{H}(m)$. $n_\Phi(\mathbf{r}, \mathbf{r}_m)$ can be expressed in terms of the normalized two-particle density matrix $\rho_2(\mathbf{r}, \mathbf{r}')$

$$n_\Phi(\mathbf{r}, \mathbf{r}_m) = \frac{m}{n_m(\mathbf{r}_m)}(m - 1)\rho_2(\mathbf{r}, \mathbf{r}_m) \quad (\text{B.5})$$

$$\rho_2(\mathbf{r}, \mathbf{r}_m) = \int d\mathbf{r}_2...d\mathbf{r}_{m-1}|\Phi(\mathbf{r}, \mathbf{r}_2...\mathbf{r}_{m-1}, \mathbf{r}_m)|^2 \quad (\text{B.6})$$

The asymptotic behavior of each term in B.4 is readily established:

$$v_e(\mathbf{r}) \sim -\frac{Ze^2}{r_m} \quad (\text{B.7})$$

where $Z$ is the sum of nuclear charges in the system.

$$\rho_2(\mathbf{r}, \mathbf{r}') \sim n_m(\mathbf{r})\,n_m(\mathbf{r}')/m^2 \quad (\text{B.8})$$

$$n_\Phi(\mathbf{r}, \mathbf{r}') \sim \frac{m-1}{m}n_m(\mathbf{r}) \quad (\text{B.9})$$

$$e^2\int d\mathbf{r}\frac{n_\Phi(\mathbf{r}, \mathbf{r}_m)}{|\mathbf{r} - \mathbf{r}_m|} \sim \frac{(m-1)e^2}{r_m} \quad (\text{B.10})$$

$$\frac{\hbar^2}{2m}\int d\mathbf{r}_1...d\mathbf{r}_{m-1}|\nabla_m\Phi(\mathbf{r}_m, m-1)|^2 \sim 0 \quad (\text{exponentially}) \quad (\text{B.11})$$

$$\langle\Phi(\mathbf{r}_m, m-1)|\hat{H}(m-1) - E(m-1)|\Phi(\mathbf{r}_m, m-1)\rangle \sim 0$$
$$(\text{exponentially}) \quad (\text{B.12})$$

Inserting eqs B.7 and B.10−B.12 into $u_s$, eq B.4 one obtains

$$u_s(\mathbf{r}_m) \sim -(q_m + 1)\frac{e^2}{r_m} \quad (\text{B.13})$$

where $q_m = Z - m$ is the charge of the system. Thus the Schrödinger-like equation for $n_m^{1/2}(\mathbf{r})$ becomes asymptotically a free-particle equation at the negative energy $\mu_m$ if $q_m = -1$ (singly charged negative ion) and otherwise a Coulomb problem for positive, $q_m \geq 0$, or negative, $q_m < 1$, charge. Thus $n_m^{1/2}(\mathbf{r})$ satisfies

$$\left(-\frac{\hbar^2\nabla^2}{2m} - (q_m + 1)\frac{e^2}{r}\right)n_m^{1/2}(\mathbf{r}) = \mu_m n_m^{1/2}(\mathbf{r}) \quad (\text{B.14})$$

asymptotically, and eqs 3.5 and 3.6 follow.

## Appendix C: Asymptotic Reactivities

The transition between eqs 4.21 and 4.22 is based on Kohn's nearsightedness conjecture.[37,38] As currently stated, it becomes in our notation

$$\chi_p(\mathbf{r}, \mathbf{r}') \xrightarrow[|\mathbf{r}-\mathbf{r}'|\uparrow\infty]{} 0 \quad (\text{C.1})$$

The conjecture holds also for $\chi_p^{-1}$, given that it is the Hessian of the density functional,

$$\chi_p^{-1}(\mathbf{r}, \mathbf{r}') \xrightarrow[|\mathbf{r}-\mathbf{r}'|\uparrow\infty]{} 0 \quad (\text{C.2})$$

The definition of $\chi_\alpha$, eq 4.6, implies that it, too, is nearsighted. Thus $\chi_R$, eq 4.8, consists of a sum of disjoint, nonoverlapping pieces in the limit $d_{\alpha\beta} \uparrow \infty$, $\forall\alpha, \beta$. Consequently, so does its inverse,

$$\chi_R^{-1}(\mathbf{r}, \mathbf{r}') \xrightarrow[|\mathbf{r}-\mathbf{r}'|\uparrow\infty]{} \sum_\alpha\chi_\alpha^{-1} \quad (\text{C.3})$$

We are dealing with bound systems so that the different $f_\alpha$, eq 2.15, do not overlap either with each other or with each other's $\chi_\alpha^{-1}$,

$$\chi_\alpha^{-1}\cdot f_\beta = f_\beta\cdot\chi_\alpha^{-1} \xrightarrow[|\mathbf{r}-\mathbf{r}'|\uparrow\infty]{} 0, \quad \alpha\neq\beta \quad (\text{C.4})$$

Equations C.3 and C.4 lead to eq 4.22.

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