On Hardness and Electronegativity Equalization in Chemical Reactivity Theory

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Chemical Reactivity Theory (CRT) contains reactivity indices defined as first and second derivatives of ground-state properties with respect to electron number such as the electronegativity and the hardness. This necessitates use of the Perdew, Parr, Levy, and Balduz (PPLB) version of noninteger density-functional theory (NIDFT) to provide a basis for CRT in DFT. However, the PPLB NIDFT yields ground-state properties which are piecewise linear continuous functions of number, yielding vanishing hardness and staircase electronegativities which do not admit electronegativity equalization. To overcome these difficulties, in the present paper we modify the relationship between CRT and DFT, basing the former on our previously formulated "atoms" in "molecules" theory (AIMT) but retaining the PPLB NIDFT. We recapture electronegativity equalization through the agency of a uniquely defined reactivity potential. We demonstrate that a positive definite hardness matrix can be defined which controls the minimum cost to the AIMT energy functional of internal fluctuations of the electron numbers of the parts of a system.

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unoccupied molecular orbital; NIDF: Non-integer density functional; NIDFT: Non-integer density-functional theory; PPLB: Perdew, Parr, Levy, and Balduz[9]

1. INTRODUCTION

Chemical reactivity theory (CRT[5]) aims to predict or interpret the reactive proclivities of a chemical species from its properties in isolation. Its roots are deep in the history of chemistry. Initially CRT evolved from empirical to semiempirical in nature. More recently, CRT has been given a deep foundation in density functional theory[1,2] by Parr and collaborators[3] and elaborated by many subsequent workers.[4,5] In CRT, the reactive proclivities of a species are characterized by a broad range of interrelated reactivity indices. Prominent among these is the chemical potential $\mu = dE(N)/dN$, where $E(N)$ is the ground state energy of the species at a supposed noninteger electron number N. $-\mu$ is taken as the electronegativity index with the attendant concept of electronegativity equalization within a molecule or reacting complex.[6] This notion is readily subsumed within DFT through an ensemble generalization[2,8–10] of DFT for integers.[1,2,11–13] More problematic is the concept of hardness, $\eta = d\mu/dN = d^2E/dN^2$, of Parr and Pearson,[14] which is essential to Pearson's hard-soft acid-base principle and his principle of maximum hardness.[15]

Our present understanding of noninteger DFT (NIDFT) is based on the ensemble DFT (EDFT) introduced by Perdew, Parr, Levy, and Balduz (PPLB).[9] Perdew has derived[10] the PPLB density functional (DF) from the integer DF of Levy and Lieb (LL).[11–13] As a consequence of the discrete convexity of the ground-state energies of integer bound systems,[9,10] all ground-state properties of the corresponding non-integer systems are piecewise-linear, continuous functions of N in the PPLB EDFT. This has the unfortunate consequence of making the electrophilic reactivities of an $(M + 1)$-electron system identical to the nucleophilic reactivities of that system with M electrons. Still more unfortunate is the vanishing of the hardness, which we term *the hardness paradox*. Finally, the piecewise linear dependence of the ground-state energy on N implies that the electronegativity takes on a discrete set of values. Electronegativity equalization would then require precise matching of those discrete values for all components of the system, an improbable accident not facilitated by the inclusion of the Hartree interactions between components (cf. Ref. (10)).

There is little doubt that the PPLB EDF is correct.[16,17] Accordingly, we focus in this paper on a possible revision of the conceptual framework of DFT-based CRT.[3–5] We propose that the origin of these difficulties lies in regarding the reactivity indices as properties of a species in total isolation, affected at most

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[5] The definitions of all acronyms are collected in alphabetical order under abbreviations.

by interaction with an unspecified external potential and by charge transfer with an unspecified reservoir. Instead we propose that the species should be regarded as responding to the specific influences it encounters either during the course of a chemical reaction or within the larger system of which it is a part. We avoid the apparent inconsistency of using the properties of an isolated species to describe its response to an environment within which strong interactions may occur by developing CRT within the framework of the "Atoms" in "Molecules" theory (AIMT) proposed earlier[18]. In that theory, the electron densities of the "isolated" parts of the system are constrained to add up to the exact electron density of the entire system. We show here that from that constraint, positive-definite self and mutual hardnesses emerge naturally, resolving the hardness paradox.

Although the entire corpus of CRT needs to be explored within the framework of our AIMT, in the present paper we focus on the hardness paradox, which is at the heart of the inconsistency between the present formulation of CRT and the PPLB formulation of EDFT on which it should be based, and on electronegativity equalization.

For its use as a basis for CRT, the AIMT of Ref. (18) requires further elaboration which in turn requires a more detailed development of EDFT than carried out originally.[9,10] This we do in Section 2 and follow in Section 3 with the required development of AIMT. The reactivity potential v_R introduced in Ref. (18) is shown in Section 4 to be unique provided the ground-state density of the "molecule" can be decomposed into ensemble v-representable densities of its subsystems, a concept introduced in Section 2. Modified Kohn-Sham (KS) equations are introduced in Section 5 together with a modified Janak theorem to provide a clear basis for the electronegativity equalization theorem. Section 6 proposes a computational procedure for decomposing the density of the whole into the densities of its parts and for obtaining the reactivity potential. Novel self and mutual hardnesses are derived in Section 7. We conclude in Section 8 with a summary and assessment of what has been accomplished.

2. ENSEMBLE DENSITY-FUNCTIONAL THEORY

Perdew[10] derived the PPLB EDF from the LL[11–13] constrained search algorithm for integer systems. However, his analysis was insufficiently detailed to be useful as is in the present context. We pick up Perdew's analysis at the point where it makes contact with the PPLB paper.[9] The noninteger system is represented by a general density matrix $\hat{P}$ diagonal in integer number m,

$$P_{m\alpha,m'\alpha'} = p_m(\hat{\rho}_m)_{\alpha\alpha'}\delta_{m,m'}. \qquad (2.1)$$

The indices α, α' refer to an arbitrary, complete, orthonormal set of m-electron

states. $\hat{\rho}_m$ is a density matrix in the m-electron subspace,

$$\mathrm{Tr}\hat{\rho}_m = 1. \tag{2.2}$$

p_m is the probablity that the ensemble contains m electrons,

$$\sum_m p_m = 1, \quad 0 \le p_m \le 1. \tag{2.3}$$

Finally, the expected number of electrons is

$$N = \sum_m mp_m. \tag{2.4}$$

The $\hat{P}$ of Eq. (2.1) is taken as diagonal in number because only operators which conserve number enter the theory.

The energy E and density $n(\mathbf{r})$ are functionals of the p_m and $\hat{p}_m$,

$$E[\{p_m, \hat{\rho}_m\}] = \sum_m p_m E_m[\hat{\rho}_m], \tag{2.5}$$

$$E_m[\hat{\rho}_m] = \mathrm{Tr}\hat{\rho}_m \hat{\mathcal{H}}_m, \tag{2.6}$$

$$n(\mathbf{r}) = \sum_m p_m n_m(\mathbf{r}), \tag{2.7}$$

$$n_m(\mathbf{r}) = \mathrm{Tr}\hat{\rho}_m \hat{n}_m, (\mathbf{r}), \tag{2.8}$$

where $\hat{\mathcal{H}}_m$ is the m-electron Hamiltonian and $\hat{n}_m(\mathbf{r})$ the m-electron density operator.

According to PPLB,[9] the NIDF is to be found by searching over all p_m and $\hat{p}_m$ for the infimum of $E[\{p_m, \hat{p}_m\}]$. Perdew derives this procedure from the LL argument for integer systems via his separation argument.[10] The search can be carried out in two stages, first over the $\hat{p}_m$ and then over the p_m. Before doing so, however, we must be more explicit about degeneracies than usual in DFT. In the following sections we shall develope AIMT-based CRT explicitly for systems with vanishing local spin density. We shall presume that all ground-state degeneracies of the isolated parts of the system are lifted by the reactivity potential of AIMT[18] except the ineluctable Kramers degeneracy of odd-electron systems in the absence of a magnetic field. Kramers degenerate states have identical electron densities as well as energies, however, which simplifies the analysis.

After the search over the $\hat{p}_m$ we have

$$E[\{p_m, n_m\}] = \sum_m p_m E_m[n_m], \tag{2.9}$$

$$n(\mathbf{r}) = \sum_m p_m n_m(\mathbf{r}), \tag{2.10}$$

$$E[n_m] = \inf_{\hat{\rho}_m \to n_m} E[\hat{\rho}_m]. \tag{2.11}$$

The infimal $\hat{p}_m$ is in general not idempotent, i.e. representing a pure state, and cannot be unless m is even.

For a given set $\{p_m\}$, $E[\{p_m\}, \{n_m\}]$ is minimal with respect to the n_m when the n_m take on their ground-state values $n(m)$ as then do the $E[n_m]$, $E(m)$,

$$\min_{n_m} E[\{p_m, n_m\}] = E[\{p_m\}] = \sum_m p_m E(m). \qquad (2.12)$$

PPLB now invoke the discrete convexity of the ground-state energies of bound systems (known empirically but not proven[13]),

$$\Delta^{(2)} E(m) = E(m+1) + E(m-1) - 2E(m)$$
$$= I(m) - A(m) > 0. \qquad (2.13)$$

In Eq. (2.13), $I(m)$ and $A(m)$ are the ionization energy and the electron affinity of the m-electron system. Eq. (2.13) is the condition for stability against disproportionation.[3] PPLB conclude from (2.13) that the ground-state energy of the N-electron ensemble is

$$E(N) = (1 - \nu)E(m) + \nu E(m+1), \qquad (2.14)$$

$$N = m + \nu, \; 0 < \nu \leq 1, \qquad (2.15)$$

$$n(N, \mathbf{r}) = (1 - \nu)n_m(\mathbf{r}) + \nu n_{m+1}(\mathbf{r}). \qquad (2.16)$$

All ground-state physical properties (which are the same for the Kramers conjugate states of odd m) have 1) the same piecewise-linear, continuous dependence on N as $E(N)$ and $n(N)$ in Eqs. (2.14) and (2.16) respectively, have 2) stair-case first derivatives (constant between and discontinuous at the integers), and have 3) second derivatives which vanish between and are undefined at the integers.

PPLB[9] then suppose the forms (2.14) and (2.16) to hold for the EDF for all densities n without adducing supporting arguments:

$$E[n] = \inf_{\{n_m, n_{m+1}\} \to n} (1 - \nu)E[n_m] + \nu E[n_{m+1}] \qquad (2.17)$$

for given ν, where the map $\{n_m, n_{m+1}\} \mapsto n$ is

$$n(\mathbf{r}) = (1 - \nu)n_m(\mathbf{r}) + \nu n_{m+1}(\mathbf{r}). \qquad (2.18)$$

The infimal $(\hat{\rho}_m)_{\alpha\alpha'}$ is the pure state $\delta_{\alpha 0}\delta_{0\alpha'}$ if m is even, where 0 indicates the ground state, but is $\frac{1}{2}(\delta_{\alpha 1}\delta_{1\alpha'} + \delta_{\alpha 2}\delta_{2\alpha'})$ if m is odd, where 1 and 2 indicate the Kramers conjugate ground states. The converse is true, then, for $m + 1$. Despite this complication, Eqs. (2.17) and (2.18) still hold since the density and energy are identical for states 1 and 2.

Now Eq. (2.13) can be regarded as an empirically established law of nature, valid until a finite system is found which spontaneously exhibits

disproportionation. However, passing to Eq. (2.17) from the LL-based statement

$$E[n] = \inf_{\{p_m, n_m\} \to n} E[\{p_m, n_m\}], \tag{2.19}$$

with the map $\{p_m, n_m\} \mapsto n$ specified by Eq. (2.10), requires imposing a restriction on n and making a *convexity conjecture*. The *restriction* is that n be ensemble v-representable (EVR): namely, that all allowed n_m which yield n via Eq. (2.10) are the ground-state densities of some potential $v'(\mathbf{r})$, the *same* for all m. The *convexity conjecture* is that Eq. (2.13) holds for any otherwise arbitrary potential $v'(\mathbf{r})$ for which solutions of the m-electron Schrödinger equation exist and for which the spectrum of the Hamiltonian $\hat{\mathcal{H}}'_m$ possesses lower bounds, i.e. ground-state energies, not merely for Coulomb systems. Eqs. (2.17) and (2.18) follow immediately.

We have gone into detail with regard to these hidden elements of the PPLB theory because we need them to base our AIMT on the EDF of PPLB.

3. "ATOMS" IN "MOLECULES"

In this section we first review our previously proposed AIMT[18]; we then make use of the EDF of PPLB (developed in Section 2) for the required NIDF and start examining the consequences.

A multinuclear system, be it in its electronic and nuclear ground state or traversing a reaction pathway from one locally stable configuration to another, can often be decomposed into a set of parts $\alpha (= 1, \ldots, A)$ each of which is distorted to some degree from its ground configuration, though still identifiably related to it. The ultimate decomposition is into atoms, the "atoms" in "molecules" problem. Since one cannot measure enough properties of these "atoms" to define them unambiguously,[21] there are multiple ways of achieving such decomposition, though some are more useful than others. Nalewajski and Parr[22] give a concise summary of the various AIMT's which have emerged over time. They give cogent reasons for rejecting each of these with the exception of the "stockholder" formulation of Hirschfeld,[23] which they rederive via information theory.[21] The stockholder formulation decomposes the ground-state electron density of the molecule into a weighted sum of the *unperturbed* atomic ground-state densities, which fails fully to capture the effects of charge transfer, polarization, hybridization, covalency, etc., on the densities of the constituent atoms.

Accordingly, we have proposed instead[18] that the local ground-state one-electron density matrix of the molecule M, $\rho_M(\mathbf{r})_{ss'}$, be *exactly* decomposed into a sum of contributions from each part α, $\rho_\alpha(\mathbf{r})_{ss'}$,

$$\rho_M(\mathbf{r})_{ss'} = \sum_\alpha \rho_\alpha(\mathbf{r})_{ss'}, \tag{3.1}$$

where the s, s' are spin indices. The parts α, treated as independent and isolated, are presumed to have nuclear configurations identical to those in M. The $\rho_\alpha(\mathbf{r})_{ss'}$ are determined by finding the infimum of the sum $\mathcal{E}$ of the energy functionals $E_\alpha[\rho_\alpha]$ of the independent parts,

$$\mathcal{E} = \sum_\alpha E_\alpha[\rho_\alpha], \tag{3.2}$$

subject to the density-matrix condition Eq. (3.1) and to the conservation of number, i.e. that the electron numbers of the parts N_α add up to the number of electrons in the molecule,

$$N_M = \sum_\alpha N_\alpha, \tag{3.3}$$

While N_M is per force an integer, the N_α need not be, provided the $E_\alpha[\rho_\alpha]$ are defined for noninteger N_α (NIDF). We have proposed that CRT be developed in the framework provided by this version of AIMT in Ref. (18) and obtained there electronegativity equalization[(6)] from constraint (3.3) and the precise definitions of reactivity potentials and fields from constraint (3.1).

   In the present paper, we attack the hardness paradox and elaborate on the essence of electronegativity equalization, but, for simplicity, do not treat spin-density explicitly, confining ourselves to functionals $E[n_\alpha]$ of the electron density $n_\alpha(\mathbf{r}) = \mathrm{Tr}\hat{\rho}(\mathbf{r})$. We must thus find the infimum of

$$\mathcal{E} = \sum_\alpha E_\alpha[n_\alpha] \tag{3.4}$$

subject to

$$n_M(\mathbf{r}) = \sum_\alpha n_\alpha(\mathbf{r}), \tag{3.5}$$

where $n_M(\mathbf{r})$ is the exact ground-state density of M, and to Eq. (3.3).

   For the required NIDF, we use the EDF of PPLB.[(9)] We suppose that each N_α lies between the two integers m_α and $m_\alpha + 1$ so that

$$N_\alpha = m_\alpha + v_\alpha \,, \ 0 < v_\alpha \leq 1, \tag{3.6}$$

$$E[n_\alpha] = (1 - v_\alpha)E[n_{m_\alpha}] + v_\alpha E[n_{m_{\alpha+1}}], \tag{3.7}$$

$$n_\alpha = (1 - v_\alpha)n_{m_\alpha} + v_\alpha n_{m_\alpha+1}, \tag{3.8}$$

$$\int d\mathbf{r} n_{m_\alpha}(\mathbf{r}) = m_\alpha \,; \ \int d\mathbf{r} n_{m_{\alpha+1}}(\mathbf{r}) = m_\alpha + 1. \tag{3.9}$$

The DF's $E[n_{m_\alpha}]$ and $E[n_{m_\alpha+1}]$ are defined via the LL search algorithm[(11–13)] for the integer electron number densities n_{m_α} and $n_{m_\alpha+1}$, respectively. The choice of the m_α rests ultimately on finding that set which gives the lowest value of $\mathcal{E}$ after the infimum in $\mathcal{E}$ is taken over all other variables.

Eqs. (3.4), (3.5) and (3.3) become, respectively,

$$\mathcal{E} = \sum_\alpha \{(1 - v_\alpha)E[n_{m_\alpha}] + v_\alpha E[n_{m_\alpha+1}]\}, \tag{3.10}$$

$$n_M = \sum_\alpha \{(1 - v_\alpha)n_{m_\alpha} + v_\alpha n_{m_{\alpha+1}}\}, \tag{3.11}$$

$$N_M = \sum_\alpha (m_\alpha + v_\alpha). \tag{3.12}$$

Take the variation of $\mathcal{E}$ in Eq. (3.10) arising from the variations δv_α, ∂n_{m_α} and $\partial n_{m_\alpha+1}$ through second order:

$$
\begin{aligned}
\delta\mathcal{E} = \sum \Big\{ & [E[n_{m_\alpha+1}] - E[n_{m_\alpha}]]\delta v_\alpha \\
& + [(1 - v_\alpha)D_{m_\alpha} \cdot \partial n_{m_\alpha} + v_\alpha D_{m_\alpha+1} \cdot \partial n_{m_\alpha+1}] \\
& + [D_{m_\alpha+1} \cdot \partial n_{m_\alpha+1} - D_{m_\alpha} \cdot \partial n_{m_\alpha}]\delta v_\alpha \\
& + \frac{1}{2}[(1 - v_\alpha)\partial n_{m_\alpha} \cdot C_{m_\alpha} \cdot \partial n_{m_\alpha} \\
& + v_\alpha \partial n_{m_\alpha+1} \cdot C_{m_\alpha+1} \cdot \partial n_{m_\alpha+1}] \Big\}.
\end{aligned}
\tag{3.13}
$$

We have used the symbol ∂ for variations taken at constant number and δ for those in which number varies. In Eq. (3.13), we have used the following symbols for the first and second functional derivatives of the DF's,

$$D_{m_\alpha}(\mathbf{r}) = \partial_{n_{m_\alpha}} E[n_{m_\alpha}], \tag{3.14}$$

$$C_{m_\alpha}(\mathbf{r}, \mathbf{r}') = \partial^2_{n_{m_\alpha}} E[n_{m_\alpha}], \tag{3.15}$$

and similarly for $m_\alpha + 1$. The center dots in Eq. (3.13) indicate integration over $\mathbf{r}$ and $\mathbf{r}'$. We have thus presumed that all $E[n_{m_\alpha}]$ defined for integer electron numbers by the LL search algorithm[11–13] possess first and second functional derivatives taken with respect to $n(\mathbf{r})$ at constant N and external potential $v(\mathbf{r})$, partial Fréchet derivatives.[26]

The corresponding variations of the condition (3.11) and (3.12) give rise to the constraints

$$\sum_\alpha \{(n_{m_\alpha+1} - n_{m_\alpha})\delta v_\alpha + [(1 - v_\alpha)\partial n_{m_\alpha} + v_\alpha \partial n_{m_\alpha+1}] \tag{3.16}$$

$$+ (\delta n_{m_\alpha+1} - \delta n_{m_\alpha})\delta v_\alpha\} = 0,$$

$$\sum_\alpha \delta v_\alpha = 0. \tag{3.17}$$

We now start the search for the infimum of $\mathcal{E}$ with respect to the v_α, n_{m_α}, and $n_{m_\alpha+1}$ first by multiplying the condition (3.16) by the Lagrange multiplier $v_R(\mathbf{r})$, integrating over $\mathbf{r}$, and adding the result to $\delta\mathcal{E}$ in (3.13). Next we multiply the condition (3.14) by the *internal* chemical potential μ_M of M and subtract the result from the preceding result. We obtain

$$\begin{aligned}
\delta\mathcal{E} = \sum_\alpha \{ & [E'[n_{m_\alpha}+1] - E'[n_{m_\alpha}] - \mu_M]\delta v_\alpha \\
& + [(1-v_\alpha)D'_{m_\alpha} \cdot \partial n_{m_\alpha} + v_\alpha D'_{m_\alpha+1} \cdot \partial n_{m_\alpha+1}] \\
& + [D'_{m_\alpha+1} \cdot \partial n_{m_\alpha+1} - D'_{m_\alpha} \cdot \partial dn_{m_\alpha}]\delta v_\alpha \qquad (3.18) \\
& + \frac{1}{2}[(1-v_\alpha)\partial n_{m_\alpha} \cdot C_{m_\alpha} \cdot \partial n_{m_\alpha} \\
& + v_\alpha \partial n_{m_\alpha+1} \cdot C_{m_\alpha+1} \cdot \partial n_{m_\alpha+1}]\}.
\end{aligned}$$

In Eq. (3.18), the primed quantities are

$$E'[n_{m_\alpha}] = E[n_{m_\alpha}] + v_R \cdot n_{m_\alpha}, \qquad (3.19)$$

$$D'[n_{m_\alpha}] = D[n_{m_\alpha}] + v_R = \partial n_{m_\alpha} E'[n_{m_\alpha}]. \qquad (3.20)$$

At the infimum, the first order terms in δv_α, ∂n_{m_α}, and $\partial n_{m_\alpha+1}$ vanish:

$$E'[n_{m_\alpha+1}] - E'[n_{m_\alpha}] = \mu_M, \quad \forall\alpha; \qquad (3.21)$$

$$D'[n_{m_\alpha}] = 0; \qquad (3.22)$$

$$D'[n_{m_\alpha+1}] = 0. \qquad (3.23)$$

Conditions (3.22) and (3.23) are equivalent to requiring that the n_{m_α} and $n_{m_\alpha+1}$ are the ground-state densities of part a in an additional potential v_R. Since, as pointed out in Section 2, derivation of the PPLB DF requires the assumption that densities are EVR, this does not constitute an additional requirement on the EDF. It does imply, however, that n_M be decomposable into a sum of EVR densities of the parts via Eq. (3.5), which is an additional requirement on n_M, *EVR decomposability*. There results for $\delta\mathcal{E}$ the quadratic form

$$\begin{aligned}
\delta\mathcal{E} = \sum_\alpha \frac{1}{2}\{ & (1-v_\alpha)\partial n_{m_\alpha} \cdot C_{m_\alpha} \cdot \partial n_{m_\alpha} \\
& + v_\alpha \partial n_{m_\alpha+1} \cdot C_{m_\alpha+1} \cdot \partial n_{m_\alpha+1}\}. \qquad (3.24)
\end{aligned}$$

As pointed out in Ref. (18), Kohn-Sham equations can be defined in this framework (cf. Section 5) and can be used to solve for the $n_\alpha(\mathbf{r})$ and other relevant quentities. Other methods can be used, e.g. a modification of Car-Parinello constrained dynamics [28]. The results for the n_α and the consequent value of $\mathcal{E}$ will depend on the initial guesses for the m_α, which may well not yield the infimal value

of $\mathcal{E}$, as discussed above. In Sections 5 through 7 we examine the implications of Eqs. (3.21)–(3.24) for CRT. First, however, we demonstrate the existence and uniqueness of v_R in the next Section.

4. EXISTENCE AND UNIQUENESS OF THE REACTIVITY POTENTIAL

In this Section we shall establish the conditions for the existence of a unique reactivity potential for the ground state of a particular "molecule" by adapting the derivation of the HK theorem[1] given by Dreizler and Gross in §2.1 of Ref. (27) to our AIMT formalism.

We begin by treating the collection of parts $\alpha = 1, \ldots, A$ as though it were a real quantum system S. Each part is a subsystem of internally interacting electrons with quantum states which are antisymmetric under permutation of its electrons. Electrons in the different parts are statistically and dynamically independent, however. They ignore each other. Though S has an integer number of electrons, N_S, the parts need not. The state of S is specified by its density matrix $\hat{P}$,

$$\hat{P} = \prod_\alpha \tilde{P}_\alpha, \tag{4.1}$$

where $\tilde{P}_\alpha$ is the density matrix of part α,

$$\mathrm{Tr}\hat{P} = \mathrm{Tr}\tilde{P}_\alpha = 1 , \ \forall \alpha. \tag{4.2}$$

In Eqs. (4.1) and (4.2) the superposed $\sim$ indicates operators in a Fock space and, as before, the superposed caret indicates operators restricted to fixed total electron number.

Each part has an intrinsic Hamiltonian $\tilde{\mathcal{H}}_\alpha$ to which is added the interaction of its electrons with the "system" potential $v_S(\mathbf{r})$. The resulting system Hamiltonian is

$$\hat{\mathcal{H}}_S = \sum_\alpha \tilde{\mathcal{H}}_\alpha + v_S \cdot \hat{n}_S, \tag{4.3}$$

$$\hat{n}_S = \sum_\alpha \tilde{n}_\alpha \tag{4.4}$$

where $\hat{n}_S$ and $\tilde{n}_\alpha$ are the electron density operators of the system S and part α, respectively.

The total "energy" of S is a functional of $\hat{P}$ and v_S,

$$E_S[\hat{P}, v_S] = \sum_\alpha E_\alpha[\tilde{P}_\alpha] + v_S \cdot n_S, \tag{4.5}$$

$$E_\alpha[\hat{P}_\alpha] = \mathrm{Tr}\tilde{P}_\alpha \tilde{\mathcal{H}}_\alpha, \tag{4.6}$$

$$n_S = \mathrm{Tr}\hat{P}\hat{n}_S = \sum_\alpha n_\alpha = \sum_\alpha \mathrm{Tr}\tilde{P}_\alpha \tilde{n}_\alpha. \tag{4.7}$$

The infimum of $E_S[\hat{P}, v_S]$ is the ground-state "energy", a functional of v_S,

$$E_S[v_S] = \inf_{\hat{P}}, E_S[\hat{P}, v_S]. \tag{4.8}$$

The corresponding ground-state $\hat{P}$ is similarly a functional of v_S,

$$\hat{P}[v_S] = \arg \inf_{\hat{P}} E_S[\hat{P}, v_S], \tag{4.9}$$

We restrict v_S to belong to the set $\mathcal{V}_S$ of potentials for which the ground-state $\hat{P}[v_S]$ is nondegenerate, which have no nonzero angular-independent components at $r \to \infty$, and which have no regions of finite measure in which they are infinite in magnitude. Eq. (4.9) defines a map $B : \mathcal{V}_S \longmapsto \mathcal{P}$, where $\mathcal{P}$ is the set of all such ground-state $\hat{P}$'s, which is surjective; each $\hat{P} \in \mathcal{P}$ is associated with a $v_S \in \mathcal{V}_S$. Similarly, Eq. (4.7) defines a surjective map $C : \mathcal{P} \longmapsto \mathcal{N}_S$, where $\mathcal{N}_S$ is the space of all EVR decomposable ground-state densities n_S containing N_S electrons.

The product of B and C defines a surjective map $D = BC : \mathcal{V}_S \longmapsto \mathcal{N}_S$. Our task now is to prove that B, C, and therefore D are injective (one-to-one) and thus bijective (fully invertible). Once that is done, the map $D^{-1} : \mathcal{N}_S \longmapsto \mathcal{V}_S$ associates any element n_S of $\mathcal{N}_S$ with a unique element v_S of $\mathcal{V}_S$. Thus, we merely have to identify n_S with the n_M of Eq. (3.5), the $\tilde{\mathcal{H}}_\alpha$ with the Hamiltonians of the parts of "molecule" M from which the DF's $E[n_\alpha]$ of Eq. (3.4) are constructed, and v_S with v_R. It then follows from D^{-1} that for each n_M there exists a unique v_R.

To prove that B is injective, we recall from Section II that the ground-state $\hat{P}[v_S]$ must be composed of ground-state $\tilde{P}_\alpha[v_S]$'s of the PPLB form,

$$(\tilde{P}_\alpha)_{m'm''} = (1 - v_\alpha)\Psi_{m_\alpha}\Psi^*_{m_\alpha}\delta_{m_\alpha}\delta_{m',m_\alpha}\delta_{m_\alpha,m''} \tag{4.10}$$

$$+ \frac{1}{2}v_\alpha\left(\Psi_{m_\alpha+1}\Psi^*_{m_\alpha+1} + \Psi^K_{m_\alpha+1}\Psi^{K*}_{m_\alpha+1}\delta_{m'm_\alpha+1}\delta_{m_\alpha+1,m''}\right).$$

In Eq. (4.10) we have supposed that m_α is even; a related form holds if m_α is odd (cf. the discussion after Eq. (2.18)). The superscript K indicates Kramers conjugation. Ψ_{m_α} is the ground state of the Hamiltonian $\mathcal{H}^{m_\alpha}_\alpha + v_S \cdot \hat{n}^{m_\alpha}_\alpha$ of the part α with m_α electrons and similarly for $\Psi_{m_\alpha+1}$ and $\Psi^K_{m_\alpha+1}$

$$\left(\hat{\mathcal{H}}^{m_\alpha}_\alpha + v_S \cdot \hat{n}^{m_\alpha}_\alpha\right)\Psi_{m_\alpha} = E_\alpha(m_\alpha)\Psi_{m_\alpha}. \tag{4.11}$$

Showing that two distinct potentials v_S and v'_S always lead to two distinct density matrices $\hat{P}$ and $\hat{P}'$ for fixed v_α so that B is one-to-one then entails showing only that v_S, v'_S always lead to two distinct sets Ψ_{m_α}, $\Psi_{m_\alpha+1}$, $\Psi^K_{m_\alpha+1}$ and Ψ'_{m_α}, $\Psi'_{m_\alpha+1}$, $\Psi^{K'}_{m_\alpha+1}$ of ground states. We show this explicitly only for Ψ_{m_α}, Ψ'_{m_α}; it will then be obviously true for the remaining states $\Psi_{m_\alpha+1}$ and $\Psi^K_{m_\alpha+1}$. For v'_S's, Eq. (4.11) becomes

$$\left(\hat{\mathcal{H}}^{m_\alpha}_\alpha + v'_S \cdot \hat{n}^{m_\alpha}_\alpha\right)\Psi'_{m_\alpha} = E'_\alpha(m_\alpha)\Psi'_{m_\alpha}. \tag{4.12}$$

If Ψ_{m_α} and Ψ'_{m_α} are identical, then

$$(v'_S - v_S) \cdot \hat{n}_\alpha^{m_\alpha} \Psi_{m_\alpha} = \left(E'_\alpha(m_\alpha) - E_\alpha(m_\alpha)\right) \Psi_{m_\alpha} \qquad (4.13)$$

follows. But since $(v'_s - v_s) \cdot \hat{n}_\alpha^{m_\alpha}$ is simply a multiplicative operator and there are no regions of finite measure where v_s or v'_s is infinity and therefore Ψ_{m_α} zero, Eq. (4.13) implies that v'_s can differ from v_s only by a constant and is not contained in $\mathcal{V}_s$. B is thus injective and invertible.

To prove the invertibility of C, insert $\hat{P}_2 = \hat{P}[v_S^{(2)}]$ into $E_S[\hat{P}, v_S^{(1)}]$ and $= \hat{P}_1 = \hat{P}[v_S^{(1)}]$ into $E_S[\hat{P}, v_S^{(2)}]$ to generate the inequalities

$$E_S[\hat{P}_2, v_S^{(1)}] = E_S[v_R^{(2)}] + \left(v_R^{(1)} - v_R^{(2)}\right) \cdot n_S > E_S[v_R^{(1)}], \qquad (4.14)$$

$$E_S[\hat{P}_1, v_S^{(2)}] = E_S[v_R^{(1)}] + \left(v_R^{(2)} - v_R^{(1)}\right) \cdot n_S > E_S[v_R^{(2)}], \qquad (4.15)$$

from the infimal conditions (4.8) and (4.9). Adding Eqs. (4.14) and (4.15) produces the absurdity

$$E_S[v_R^{(1)}] + E_S[v_R^{(2)}] > E_S[v_R^{(1)}] + E_S[v_R^{(2)}] \qquad (4.16)$$

Thus, each n_s is associated with a unique $\hat{P}$, and C is injective and invertible.

Since B and C are invertible, so is $D = BC$. Its inverse $D^{-1} = C^{-1} B^{-1}$: $\mathcal{N} \longmapsto \mathcal{V}_S$ is therefore one-to-one. We have thus proved that to each n_M in $\mathcal{N}_S$, there corresponds a unique v_R in $\mathcal{V}_S$ from which the various entities of the AIMT of Ref. (18) and Section 3 can in principle be computed.

5. MODIFIED KOHN-SHAM EQUATIONS AND JANAK THEOREM; ELECTRONEGATIVITY EQUALIZATION

Modified Kohn-Sham equations follow directly from the infimality conditions on the $\mathcal{E}$ of Eq. (3.4) by standard methods, e.g. from the infimality conditions (3.22) and (3.23). The only change is that the usual Kohn-Sham potential for each part α, $v_{s\alpha}$ is replaced by $v'_{s\alpha}$,

$$v'_{s\alpha} = v_{s\alpha} + v_R. \qquad (5.1)$$

Similarly, the Janak theorem[7] is modified, so that it refers now to the properties of the parts in the presence of v_R,

$$\epsilon'_{\alpha H} = \mu'_\alpha = \frac{d E'_\alpha(N_\alpha)}{d N_\alpha}. \qquad (5.2)$$

In Eq. (5.2), $\epsilon'_{\alpha H}$ is the partially occupied KS HOMO energy in the presence of v_R. In the PPLB ensemble,

$$\mu'_\alpha = \frac{d E'_\alpha(N_\alpha)}{d N_\alpha} = E'_\alpha(m_\alpha + 1) - E'_\alpha(m_\alpha) = -A'_\alpha(m_\alpha) \qquad (5.3)$$

holds, where $E'(m_\alpha)$ is the ground-state energy of part α with m_α electrons in v_R and $A'_\alpha(m_\alpha)$ the corresponding electron affinity. We now identify $-\mu'_\alpha = -\epsilon'_{\alpha H}$ as the electronegativity of part α within the molecule M. Combining Eq. (5.3) with Eq. (3.21) yields the electronegativity equalization principle (EEP) of our AIMT-based CRT,

$$\mu'_\alpha = \mu_M, \quad \forall \alpha. \tag{5.4}$$

There are two remarkable features of Eqs. (5.3) and (5.4). First, the μ'_α have a discrete set of values, the $A'_\alpha(m_\alpha)$. Yet the EEP states that there is a set of m_α, a v_R, and a value of μ_M for which the $A'_\alpha(m_\alpha)$ become equal. The condition (3.3) from which the EEP derives is not in fact redundant. It is not implicit in condition (3.5) because v_R is not allowed to contain a constant part according to the definition of the space $\mathcal{V}_S$ in Section 4. Nevertheless, it is the freedom in varying the μ_M, m_α and v_R to meet these conditions which allows for the existence of the EEP in the face of the discreteness of the μ'_α values for fixed v_R. Second, and supporting this interpretation of the validity of the EEP, the $\epsilon'_{\alpha H}$ are functionals of v_R so that it is a particular property of v_R and ultimately therefore n_M that the $\epsilon'_{\alpha H}$ are all equal.

These comments make clear that determination of the correct μ_M, the correct set of m_α, and the correct v_R are central to this AIM-based CRT. Moreover, this central dependence of all quantities on v_R alleviates the difficulty cited in the Introduction that all reactivity indices which are first derivatives of some property with respect to N are constant, independent of N as it varies between two neighboring integers m and $m + 1$ within the PPLB version of NIDFT, as for the Fukui function[29]

$$\mathcal{F}(\mathbf{r}) = \frac{dn(\mathbf{r})}{dN} = n(m + 1, \mathbf{r}) - n(m, \mathbf{r}). \tag{5.5}$$

Thus the reactivity of the system towards an electrophilic species at $N \uparrow m + 1$ is identical to its reactivity towards a nucleophilic species at $N \downarrow m$, an unsatisfactory situation in CRT. In the present theory, on the other hand, reactivities are context-dependent through the variation of v_R. The v_R of a context within which part α would have $N_\alpha \downarrow m_\alpha$ would be quite different from that in which $N_\alpha \uparrow m_\alpha + 1$, causing the corresponding electrophilic and nucleophilic reactivities to differ as well.

6. COMPUTING THE REACTIVITY POTENTIAL

The following modification of the Car-Parinello (CP) scheme[28] should be a feasible method for minimizing $\mathcal{E}$, Eq. (3.4), subject to the density condition (3.5) which subsumes the number condition (3.3). First, we introduce a penalty

functional

$$\Pi[\{n_\alpha\}] = \Lambda\left(n_M - \sum_\alpha n_\alpha\right) \cdot \left(n_M - \sum_\alpha n_\alpha\right), \tag{6.1}$$

where Λ is a positive constant of dimension energy times volume to be chosen to assure convenient convergence and stability. Next, the penalty functional is added to the energy functional to form an objective functional,

$$\mathcal{O}[\{n_\alpha\}] = \sum_\alpha E[n_\alpha] + \Lambda\left(n_M - \sum_\alpha n_\alpha\right) \cdot \left(n_M - \sum_\alpha n_\alpha\right). \tag{6.2}$$

Finally, we introduce into the objective functional the KS form for the densities n_α,

$$n_\alpha = \sum_i v_{i\alpha} |\phi_{i\alpha}|^2. \tag{6.3}$$

In Eq. (6.3), the $\phi_{i\alpha}$ are the Kohn-Sham orbitals of part α; the $v_{i\alpha}$ are the corresponding occupation numbers; and the sumation over spin is understood. The ϕ_i are ordered according to the values of the corresponding KS energies so that for m_α even

$$\left.\begin{array}{ll} v_{i\alpha} = 1, & i = 1, \ldots, m_\alpha \\ v_{i\alpha} = \frac{1}{2}v_\alpha, & i = m_\alpha + 1, m_\alpha + 2 \\ v_{i\alpha} = 0, & i > m_\alpha + 2 \end{array}\right\}, \tag{6.4}$$

and for m_α odd,

$$\left.\begin{array}{ll} v_{i\alpha} = 1, & i = 1 \ldots m_\alpha - 1 \\ v_{i\alpha} = \frac{1}{2} + \frac{1}{2}v_\alpha, & i = m_\alpha, m_\alpha + 1 \\ v_{i\alpha} = 0, & i > m_\alpha + 1 \end{array}\right\}. \tag{6.5}$$

Thus the objective functional changes from a density functional to a functional of the KS orbitals and occupation numbers.

One can minimize the objective function by a standard implementation of the CP method. In the course of the computation, we would obtain the gradients of the energy functionals $E[n_{m_\alpha}]$ with respect to the KS orbitals. From those, it is straightforward to construct the $D[n_{m_\alpha}]$ of Eq. (3.14). From condition (3.22) for the constrained minimum, it follows that

$$v_R = -D[n_{m_\alpha}] = -D[n_{m_\alpha+1}] \tag{6.6}$$

holds at the minimum. Inevitable computational errors will occur which become more serious as n_{m_α} or $n_{m_{\alpha+1}} \downarrow 0$. Accordingly, to compensate for these, first form

$$v_{R\alpha} \equiv -[(1 - v_\alpha)]D[n_{m_\alpha}] + v_\alpha D[n_{m_\alpha+1}]]. \tag{6.7}$$

Then weight $v_{R_\alpha}(\mathbf{r})$ according to the contribution of $n_\alpha(\mathbf{r})$ to $n_M(\mathbf{r})$ at $\mathbf{r}$ and sum over α, obtaining

$$v_R(\mathbf{r}) = \sum_\alpha \frac{n_\alpha(\mathbf{r})}{n_M(\mathbf{r})} v_{R\alpha}(\mathbf{r}). \tag{6.8}$$

which becomes a tautology if all $v_{R\alpha}(\mathbf{r})$ obtained from Eqs. (6.6) and (6.7) are identical at $\mathbf{r}$.

The density functional $E[n_{m_\alpha}]$ becomes a functional $E[\{\phi_{i\alpha}, \phi_{i\alpha}^*\}]$ when the KS density $\Sigma_{i=1}^{M_\alpha} |\phi_{i\alpha}|^2$ is inserted for n_{m_α}. In the course of the CP computation, functional derivatives of $E[\{\phi_{i\alpha}, \phi_{i\alpha}^*\}]$ are obtained as well as the $\phi_{i\alpha}$ themselves. From these, as stated above, one can obtain

$$D[n_{m_\alpha}](\mathbf{r}) = \sum_{i=1}^{m_\alpha} \left[\frac{1}{\phi_{i\alpha}(\mathbf{r})} \frac{\partial E}{\partial \phi_{i\alpha}^*(\mathbf{r})} + \frac{1}{\phi_{i\alpha}^*(\mathbf{r})} \frac{\partial E}{\partial \phi_{i\alpha}(\mathbf{r})} \right], \tag{6.9}$$

providing the information necessary to generate $v_{R\alpha}$ from Eq. (6.7). Alternatively, one can use standard methods to reconstruct $v_{s\alpha}'$ from n_α,[30] then insert n_α into $v_s[n_\alpha]$ to get $v_{s\alpha}$, and subtract that from $v_{s\alpha}'$ to get v_R, when feasible.

7. SELF AND MUTUAL HARDNESS

The main result of this section is the derivation of self and mutual hardnesses within the new framework. To do that, we return now to Eq. (3.24) for the quadratic form of the variation $\delta\mathcal{E}$ of $\mathcal{E}$ from its infimal value. The variations ∂n_{m_α} and $\partial n_{m_\alpha+1}$ entering $\delta\mathcal{E}$ are arbitrary apart from the constraint (3.16). We propose to convert the $\delta\mathcal{E}$ of Eq. (3.24) into a quadratic form in the δv_α in order to define the self and mutual hardnesses of the parts of the system. We do so by minimizing $\delta\mathcal{E}$ with respect to the ∂n_{m_α} and $\partial n_{m_\alpha+1}$ subject to the constraint (3.16) for fixed δv_α.

Eq. (3.24) can be rewritten as

$$\delta\mathcal{E} = \sum_\alpha \delta Q_\alpha, \tag{7.1}$$

$$\delta Q_\alpha = \frac{1}{2} \{(1 - v_\alpha)\partial n_{m_\alpha} \cdot C_{m_\alpha} \cdot \partial n_{m_\alpha} v_\alpha \partial n_{m_\alpha+1} \cdot C_{m_\alpha+1} \cdot \partial n_{m_\alpha+1}\}. \tag{7.2}$$

Define ∂n_α as

$$\partial n_\alpha = (1 - v_\alpha)\partial n_{m_\alpha} + v_\alpha \partial n_{m_\alpha+1}. \tag{7.3}$$

First minimize δQ_α with respect to ∂n_{m_α} and $\partial n_{m_\alpha+1}$ for fixed ∂n_α. ∂n_{m_α} can be chosen as the free variable, setting

$$\partial n_{m_\alpha+1} = [\partial n_\alpha - (1 - v)\partial n_{m_\alpha}]/v_\alpha \tag{7.4}$$

Inserting (7.4) into (7.2) and minimizing with respect to ∂n_{m_α} yields after summing the resulting δQ_α

$$\delta \mathcal{E} = \sum_\alpha \frac{1}{2} \partial n_\alpha \cdot C_\alpha \cdot \partial n_\alpha, \tag{7.5}$$

$$
\begin{aligned}
C_\alpha = & (1 - v_\alpha) C_{m_\alpha+1} \cdot [v_\alpha C_{m_\alpha} + (1 - v_\alpha) C_{m_\alpha+1})]^{-1} \\
& \cdot C_{m_\alpha} \cdot [v_\alpha C_{m_\alpha} + (1 - v_\alpha) C_{m_\alpha+1}]^{-1} \cdot C_{m_\alpha+1} \\
& + v_\alpha C_{m_\alpha} \cdot [v_\alpha C_{m_\alpha} + (1 - v_\alpha) C_{m_\alpha+1}]^{-1} \\
& \cdot C_{m_\alpha+1} \cdot [v_\alpha C_{m_\alpha} + (1 - v_\alpha) C_{m_\alpha+1}]^{-1} \cdot C_{m_\alpha}
\end{aligned}
\tag{7.6}
$$

Introducing the Fukui function $\mathcal{F}$ of Eq. (5.5),

$$\mathcal{F}_\alpha = n_{m_\alpha+1} - n_{m_\alpha}, \tag{7.7}$$

simplifies Eq. (3.16) to

$$\sum_\alpha [\mathcal{F}_\alpha \delta v_\alpha + \partial n_\alpha] = 0. \tag{7.8}$$

We now proceed to minimize the $\delta \mathcal{E}$ of Eq. (7.5) with respect to the ∂n_α at fixed δv_α by setting the variation of Eq. (7.5) to zero subject to the variation of Eq. (7.8),

$$\delta(\delta \mathcal{E}) = \sum_\alpha (C_\alpha \cdot \partial n_\alpha) \delta(\partial n_\alpha) = 0, \tag{7.9}$$

$$\sum_\alpha \delta(\partial n_\alpha) = 0. \tag{7.10}$$

Multiply Eq. (7.10) by the Lagrange multiplier $\lambda(\mathbf{r})$ and subtract the result from Eq. (7.9) to obtain

$$\partial n_\alpha = C_\alpha^{-1} \cdot \lambda. \tag{7.11}$$

Inserting Eq. (7.11) into Eq. (7.8) results in

$$\lambda = -C_M \cdot \sum_\alpha \mathcal{F}_\alpha \delta v_\alpha, \tag{7.12}$$

where

$$C_M = \left[\sum_\alpha C_\alpha^{-1} \right]^{-1}. \tag{7.13}$$

Substituting Eq. (7.12) for λ into Eq. (7.11) and the result into Eq. (7.5) yields our goal, an expression for $\delta \mathcal{E}$ containing only the δv_α,

$$\delta \mathcal{E} = \frac{1}{2} \sum_{\alpha,\beta} \delta v_\alpha \eta_{\alpha\beta} \delta v_\beta, \tag{7.14}$$

where

$$\eta_{\alpha\beta} = \frac{\partial^2 \mathcal{E}}{\partial N_\alpha \partial N_\beta} = \mathcal{F}_\alpha \cdot C_M \cdot \mathcal{F}_\beta, \tag{7.15}$$

since $\delta v_\alpha = \delta N_\alpha$.

The structure of Eq. (7.14) lends itself naturally to the interpretation of $\eta_{\alpha\alpha}$ as the self hardness of part α and $\eta_{\alpha\beta}$ as the mutual hardness of parts α and β within the molecule M. The form of Eq. (7.15) is remarkable. C_M plays the role of an inverse susceptibility, the Hessian of the energy with respect to changes in the densities of the parts induced by changes in the electron numbers of the parts after all extraneous variation of the number densities at constant N_α is minimized away. C_M is, in that sense, a minimal Hessian.

C_M is seen to be a symmetric positive kernel as follows. Both C_{m_α} and $C_{m_\alpha+1}$ are symmetric and positive definite under the presupposition that part α is stable at its constrained ground state at integer numbers m_α and $m_{\alpha+1}$. Consequently, from Eq. (7.6) C_α is symmetric and positive definite, which implies the same for C_M via Eq. (7.13). Thus the self hardnesses are positive definite via Eq. (7.15), as is the entire hardness matrix, with all its eigenvalues positive definite.

When all the parts are again separated to infinity with those changes in their internal nuclear configuration which lead to their electron-nuclear ground states, all electron numbers N_α become integers m_α[9,10] as stated in Section 5; the Hessians C_α and the Fukui functions $\mathcal{F}_\alpha$ of different parts do not overlap in coordinate space, i.e.

$$\int d\mathbf{r}'' C_\alpha(\mathbf{r}, \mathbf{r}'') C_\beta(\mathbf{r}'', \mathbf{r}') \to 0, \tag{7.16}$$

$$\int d\mathbf{r} \mathcal{F}_\alpha(\mathbf{r}) C_\beta(\mathbf{r}, \mathbf{r}') \to 0, \tag{7.17}$$

and the mutual hardnesses vanish as well, $\eta_{\alpha\beta} \to 0, \alpha \neq \beta$. The self hardnesses, on the other hand, become properties of the isolated systems,

$$\eta_{\alpha\alpha}^\pm(m_\alpha) = \mathcal{F}_\alpha^\pm \cdot C_{m_\alpha} \cdot \mathcal{F}_\alpha^\pm \equiv \eta_{\alpha,\infty}^\pm(m_\alpha), \tag{7.18}$$

where the $+(-)$ superscript corresponds to $N_\alpha \downarrow m_\alpha (N_\alpha \uparrow m_\alpha)$ in the separated limit, and from Eq. (5.5),

$$\mathcal{F}_\alpha^+ = n_\alpha(m_\alpha + 1) - n_\alpha(m_\alpha), \tag{7.19}$$

$$\mathcal{F}_\alpha^- = n_\alpha(m_\alpha) - n_\alpha(m_\alpha - 1). \tag{7.20}$$

How does this well-defined, positive-definite hardness $\eta_{\alpha,\infty}^\pm$ compare with the second difference Eq. (2.13) commonly taken as an approximation to the hardness of an isolated system[3]? The most that can be said at this early stage of development of the theory is that they are positively correlated. C_{m_α} is an inverse

susceptibility. The latter tends to be dominated by, and is inversely correlated with, the lowest excitation energies, leading to the direct correlation of the C_m with the lowest excitation energies. Those in turn are directly correlated with $I - A$.

8. CONCLUSIONS

We have shown that it is possible to construct an internally consistent CRT based on the AIMT of Ref. (18) and the PPLB NIDFT. The theory contains within it a positive definite hardness matrix which is the Hessian of the "energy" $\mathcal{E}$ of Eq. (3.4) with respect to number changes of the individual parts after minimization with respect to internal density changes within the parts in response to the number changes. The EEP is recaptured and the number-independence of key reactivity indices involving or related to first derivatives of ground-state properties with respect to number is overcome through the context dependence of these quantities. The context dependence manifests itself through the reactivity potential v_R, which is shown to be uniquely determined by the electron density of the entire system.

For the present version of CRT to be useful as a predictive and interpretative tool, it is necessary to show the relationship of the entities within it to the properties of the entire system. How, for example, does the true energy functional $E[n_M]$ relate to $\mathcal{E}$? Can one make a kind of cluster expansion if the difference between $E[n_M]$ and $\mathcal{E}[\{n_\alpha\}]$ and use it to define two-center bond energies, three-center bond energies, etc? Should that prove possible, very powerful reactivity indices would be definable. In addition, the remaining formal structure of CRT beyond electronegativity and hardness needs to be reexamined within the present framework.

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