Revisiting N-continuous Density-Functional Theory: Chemical Reactivity and “Atoms” in “Molecules”

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Abstract. We construct an internally-consistent density-functional theory valid for noninteger electron numbers N by precise definition of a density functional that is continuous in N. In this theory, charge transfer between the atoms of a heteronuclear diatomic molecule, which have been separated adiabatically to infinity, is avoided because the hardness for fractional occupation of a single HOMO spin-orbital is negative. This N-continuous density functional makes possible a variational theory of “atoms” in “molecules” that exactly decomposes the molecular electron density into a sum of contributions from its parts. The parts are treated as though isolated. That theory, in turn, gives a deep foundation to the chemical reactivity theory provided that the hardness of entities with vanishing spin density is positive, as argued to be the case here. This transition from negative to positive hardness closely parallels the transition from the Heitler–London to the Hund–Mulliken picture of molecular bonding.

I. INTRODUCTION
The energy functionals of density-functional theory (DFT), E[n], are uniquely defined as functionals of the electron density n(r) only for integer electron number N by the Levy–Lieb constrained search algorithm.1,2 Yet for many applications, an interpolation of these density functionals (DF) to noninteger N is convenient or even essential. For example, in the original Hohenberg–Kohn (HK) paper,3 the chemical potential µ was introduced as a Lagrange multiplier to relax the condition that ∫ d r n(r) = N, implying knowledge of E away from integer values of N. The profoundly important chemical reactivity theory (CRT) has been given a deep foundation in DFT by Parr and collaborators,4 Nalewajski et al.,5 and many others (e.g., ref 6). Many reactivity indices of CRT involve derivatives with respect to N either directly or indirectly, for example, the hardness η of Parr and Pearson,7 η = dµ/dN = dE/dN2, which is essential to Pearson’s hard–soft acid–base principle.8

Dedicated to Joshua Jortner on the occasion of his 70th birthday.

There now exist two interpolations of the DF to noninteger N. First, all existing approximations to the DF have no explicit N dependence. Their N dependence is implicit through the functional dependence of E[n] on n. As that dependence is continuous, so is the N dependence of the functional itself at and between adjacent integer values of N, (N-continuous DFT), (NCDFT). Derivative discontinuities exist at integer values, however, arising from derivative discontinuities in the occupation numbers of the Kohn–Sham states.9,10 Second, Perdew et al.11 have applied Mermin’s notion of finite-temperature ensemble-density-functional theory (EDFT)12 to the ground-state problem, generating a DF that depends on N both explicitly and implicitly.

Perdew et al.13 were motivated to introduce EDFT by a “separation argument”. The atoms of a heteronuclear diatomic molecule in its ground state are separated adiabatically to infinity. Since the minimum ionization energy is larger than the maximum electron affinity among all

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atoms, the separated atoms are neutral. Perdew et al.\textsuperscript{13} argued that in the minimum energy configuration of NCDFT, on the other hand, the separated atoms would be fractionally charged if their ionization energies differed. On the basis of this contradiction, they dismissed NCDFT as an unsatisfactory interpolation.

However, there are two significant objections to EDFT. First, the usual requirement for use of an ensemble is that ensemble averages accurately represent temporal averages of physical properties.\textsuperscript{13} This would imply that in EDFT the valence of an isolated system fluctuates over time, an impossibility. Instead, the ensemble of EDFT describes a physical admixture of noninteracting systems in two different valence states, not a single dynamical system. Second, all ground-state physical properties are piecewise linear in $N$ in EDFT. First derivatives such as $\mu$ and the Fukui function of CRT\textsuperscript{14} are staircases, discontinuous in $N$ at integers and constant in between. This constancy implies that an electrophilic reactivity of a system at integer $N + 1$ would be identical to the corresponding nucleophilic reactivity at $N$, an improbable consequence. Still less satisfactory, the hardness $\eta$ vanishes for noninteger $N$, providing no basis for, inter alia, Pearson’s hard–soft acid–base rule.\textsuperscript{8} For these reasons it was concluded that EDFT does not provide a suitable basis for CRT.\textsuperscript{14} Kleinman\textsuperscript{15} has also criticized EDFT, with further debate of his criticisms in refs 16 and 17. Accordingly, in this paper we revisit NCDFT and show that it can in principle provide a sound basis for CRT. In the process, we develop a novel theory of “atoms” in “molecules” (AIM). In Section 2, we reexamine the separation argument and through it show that the conventional search algorithm\textsuperscript{1,2} for integer $N$ yields a uniquely defined $N$-continuous DF for noninteger $N$, which depends only implicitly on $N$. We establish the existence of the corresponding Kohn–Sham equations. In Section 3, we point out that the inference of fractional charge on separation in NCDFT by Perdew et al. was based on the assumption that the ground-state energy is a minimum and not an infimum in $N$. This requires that $\eta$ be positive for noninteger $N$. We introduce in this paper a two-part hardness conjecture. The first part is that $\eta < 0$ in NCDFT for isolated finite systems, restoring integer stability. We then develop a formal theory of $\eta$ that shows that $\eta < 0$ is possible. Next, we show that $\eta$ is negative in the Hartree–Fock approximation (HFA), increasing the plausibility that this part of the conjecture is correct. Supposing the conjecture to be correct, the need for EDFT falls away and with it its unsatisfactory features. We recall in Section 4 that the goal of CRT is to predict or interpret the reactive proclivities of atoms or larger moieties in response to the chemical stimuli encountered in molecules or larger systems from their properties in isolation (electronegativity, hardness, frontier orbitals, etc.). There is thus a strong connection between CRT and the theory of atoms or moieties in molecules (AIM), which we explore via NCDFT through the introduction of a novel variational approach. The resulting formulation of AIM is free of the objections to prior formulations catalogued by Nalewajski and Parr.\textsuperscript{18} Moreover, in contrast to the stockholder approach of Hirshfeld\textsuperscript{19} that they favor, the electron density of the molecule is decomposed exactly into a sum of contributions from its parts, which are distorted from their isolated form by the influence of the molecule. To execute the variational approach of the new AIM theory, a positive hardness is required of the parts. We introduce in Section 5 the second part of the hardness conjecture, which states this to be so in chemical environments. The distinction between parts 1 and 2 of the conjecture parallels the distinction between the Heitler–London\textsuperscript{20} and the Hund–Mulliken\textsuperscript{21} pictures of molecular bonding. We show that part 2 does indeed hold in the HFA. A deeper understanding of CRT results from the AIM and the conjecture. Finally, in Section 6, we summarize and discuss further the principal conclusions of the paper and their implications.

2. A UNIQUE NCDFT VIA A SEPARATION ARGUMENT

A. Existence Considerations

Consider a molecule or larger finite system $AB$ that can be decomposed into two parts $A$ and $B$ by taking the separation $d$ to infinity of the centers of gravity of each part without other modification of their nuclear coordinates. Let $n_{AB}(r)$ be a possible electron density of $AB$ for arbitrary $d$. Restrict consideration to those $n_{AB}(r)$ that decompose into nonoverlapping components $n_{A}(r)$ and $n_{B}(r)$, associated with $A$ and $B$, respectively:

\[
n_{AB}(r) \rightarrow n_{A}(r) + n_{B}(r), \quad d \rightarrow \infty \quad (1)
\]

\[
n_{A}(r)n_{B}(r) \rightarrow 0, \quad d \rightarrow \infty \quad (2)
\]

The total number of electrons on $AB$,

\[
N_{AB} = \int dr\ n_{AB}(r) \quad (3)
\]

is, of course, an integer, but the number contained in $n_{A}(r)$, $N_{A}$, $\alpha = A$ or $B$, need not be:

\[
N_{\alpha} = \int dr\ n_{\alpha}(r) \quad (4)
\]

It has been shown\textsuperscript{22} that for any nonnegative $N$-electron $n(r)$, $N$ an integer, there is at least one $N$-electron wave function $\Psi$ that yields that electron density,

\[
n(r) = (\Psi, \hat{n}(r)\Psi) \quad (5)
\]
where \( \hat{n} \) is the \( N \)-particle electron-density operator. The Levy–Lieb constrained search algorithm (LL)\(^2\) then yields a uniquely defined DF,

\[
E[N,n] = \text{INF}_{\Psi \rightarrow \Psi_{\text{opt}}} \{(\Psi, \mathcal{H}\Psi)\} \tag{6}
\]

In eq 6, we display explicit dependence\(^2\) of the DF on \( N \) arising from the dependence of the \( \Psi \) and \( \mathcal{H} \) on integer \( N \) as well as its implicit dependence on \( N \) as the norm of \( n \).

Applying eq 6 to \( AB \) to define the \( AB \) DF \( E_{\text{AB}}[N_{\text{AB}},n_{\text{AB}}] \), we note that \( E_{\text{AB}} \) decomposes into two parts, \( E_A \) and \( E_B \), depending, respectively, only on \( n_A \) and \( n_B \) in the limit \( d \rightarrow \infty \) because of the absence of infinite-range interactions in \( \mathcal{H}_{\text{AB}} \).

\[
E_{\text{AB}}[N_{\text{AB}},n_{\text{AB}}] \rightarrow E_A[N_{\text{AB}},n_A] + E_B[N_{\text{AB}},n_B] \tag{7}
\]

The DFs \( E_d[N_{\text{AB}},n_d] \) are uniquely defined for noninteger \( N_d \) in their implicit dependence through \( n_d \), but they still depend, in principle, explicitly on \( N_{\text{AB}} \) via the LL construction (eq 6). However, because of the absence of infinite-range interactions, \( E_d[N_{\text{AB}},n_d] \) is insensitive to the presence of \( B \) and must be the same for all \( B \) as long as \( N_{\text{AB}} \geq N_d \). We therefore conclude that

\[
E_d[N_{\text{AB}},n_d] = E_d[n_d] \tag{8}
\]

defining an energy functional for noninteger \( N_d \) that has only implicit \( N \) dependence. Similarly, we conclude that all expectation values of physical properties, taken with respect to the infimal \( N_{\text{AB}} \)-electron \( \Psi \) of the constrained search, decompose into an \( A \) part, which is a functional of \( n_A \), and a \( B \) part, which is a functional of \( n_B \) with no explicit \( N_{\text{AB}} \) dependence, thus continuing the full structure of DFT to noninteger \( N \).

There is a subtlety in this not made explicit above. Consider \( N_{\text{AB}} \) to be even and \( AB \) to have a nondegenerate singlet ground state (spin zero), while \( A \) and \( B \) have doublet ground states (spin \( 1/2 \)) with \( N_A \) and \( N_B \) odd. During adiabatic separation, the ground state remains a singlet, but the first excited state is a triplet, which draws closer to the ground state. At some finite \( d \), otherwise negligible environmental perturbations introduce decoherence of these four states into independent doublets on \( A \) and \( B \). This decoherence argument applies as well to the case of noninteger \( N_A \) and \( N_B \) with \( n_A(r) \) and \( n_B(r) \) differing from their ground-state values. As disjointedness approaches with increasing \( d \), eq 2, the energy separation between the singlet derived from the ground state of \( AB \) by varying \( n_{\text{AB}} \) differs little in energy from a state derived from the triplet by a corresponding variation of \( n_{\text{AB}} \), and decoherence into two degenerate noninteger states occurs for each of \( A \) and \( B \). The nature of these degenerate states is made clear in the following subsection.

### B. Kohn–Sham Equations

We now make the supposition, standard in DFT, that any DF defined via the LL algorithm, eq 6, is continuous in \( n(r) \) in the sense that its first and second functional derivatives with respect to \( n(r) \) exist at least within a domain of interest in the function space of \( n(r) \). We have proved that there is an infinity of independent-electron ensembles that have the same \( n(r) \) \( \geq 0 \), \( \int dr \: n(r) = N \) (noninteger).\(^{23} \) The density \( n(r) \) can then be parametrized by

\[
n(r) = \sum_{i,s} \nu_i |\psi_i(x)|^2, \quad x = (r,s) \tag{9}
\]

\[
0 \leq \nu_i \leq 1 \tag{10}
\]

At the infimum \( \text{INF}_{\nu \psi}[E[n]] \), Kohn–Sham equations then hold\(^1,10 \) for a system with \( N = M + \omega \) electrons, \( M \) an integer, and \( 0 \leq \omega \leq 1 \),

\[
\mathcal{H}_{KS}[\psi] = \epsilon_i \psi_i \tag{13}
\]

\[
\epsilon_i \leq \epsilon_{i+1} \tag{14}
\]

\[
\nu_i = \begin{cases} 
1, & i = 1...M \\
\omega, & i = M + 1 \\
0, & i > M + 1
\end{cases} \tag{15}
\]

\[
\mathcal{H}_{KS} = \frac{p^2}{2m} + \mathcal{V}_{KS} \tag{16}
\]

\[
V_{KS} = V_s + V_h + V_x + V_c \tag{17}
\]

\[
V_{xc} = \delta E_{xc} / \delta n \tag{18}
\]

In eq 17, \( V_s \) is the electrostatic potential of the nuclei, \( V_h \) is the Hartree potential, \( V_x \) is the exchange potential, and \( V_c \) the correlation potential, derived from the exchange and correlation energy functionals, respectively, as stated in eq 18. In eq 18, \( E_s \) is the exact exchange of independent electrons

\[
E_X = -\frac{1}{2} \sum_s \int \int dr dr' \rho(r,s)\rho(r',s) e^2 / |r - r'| \tag{19}
\]

\[
\rho(r,s) = \sum_i \nu_i \psi_i^*(r) \psi_i^*(s) \tag{20}
\]

separated out explicitly from the correlation energy functional \( E_c \) instead of the usual combined form \( E_{xc} \). For the formal, conceptual arguments made below, we presume exact knowledge of \( E_c \) as well.
Thus, the formal structure of ground-state DFT is recovered for noninteger $N$ using a sharply defined $N$-continuous DF. Note that the HK theorem implies that given the ground state $n(r)$, $V_{KS}(r)$ is specified only up to an additive constant. That implies in turn that the asymptotic value of $V_{KS}(r)$ at infinity is indeterminate. As emphasized by Parr and collaborators, cf. ref 4, once the constraint of fixed $N$ is relaxed via introducing $\mu$ as a Lagrange multiplier or by searching for the infimum or minimum of the grand potential, it is the difference $V_{KS}(r) - \mu$ that enters the variation and that is invariant to the uncertainty in $V_{KS}(r)$ alone. Nevertheless, it is often important to keep a clear distinction between $V_{KS}(r)$ and $\mu$. Accordingly, we impose the condition that

$$V_{KS}(r) \to 0, r \uparrow \infty$$

(21)

to avoid the confusion between $V_{KS}(\infty)$ and $\mu$ common in the literature.

The twofold degeneracy referred to at the end of subsection A above follows from the KS eqs 13–18. The fractionally occupied HOMO $\psi_i$, $i = M + 1$, can be either of the pair of Kramers degenerate states (spin degeneracy in the absence of spin-orbit coupling). The orbital part is the same for both members of the pair; the ground-state electron density is the same for both

$$\text{ground-state energy}$$

$\text{of the density functionals of NCDFT. They concluded that NCDFT implies that the}$$

weakened continuity in $N_{\text{CDFT}}$. If such a minimum were to exist, it would occur in the isolated atoms

$$\text{ground-state energies}$$

and the second factor is the Fukui function of CRT, 4,28

$$F(r) = \frac{dn(r)}{dN}$$

(27)

and the second factor is the Fukui function of CRT, 4,28

$$F(r) = \int dr' K(r,r') n_F(r')$$

(30)

where

$$K(r,r') = \delta(r,r') + \int dr'' \chi_0(r,r'') f(r'',r')$$

(31)

Inserting eq 31 into eq 30, the result with eq 26 into eq

$$\text{corresponding to the four states generated by the singlet and triplet states of AB.}$$

3. THE HARDNESS CONJECTURE, PART 1

We now address the Perdew et al. objection to NCDFT. They concluded that NCDFT implies that the atoms $A$ and $B$ of a heteronuclear diatomic molecule $AB$ would become fractionally charged upon their separation to infinity. That conclusion rests on two bases: (1) the continuity in $n_A$ and $n_B$ of the density functionals of the isolated atoms $E_A(N_A)$ and $E_B(N_B)$ in NCDFT and the consequent continuity in $N_A$ and $N_B$ of the resultant ground-state energies $E_A(N_A)$ and $E_B(N_B)$ in the electron numbers $N_A$ and $N_B$; and (2) the assumption that the total ground-state energy $E_A(N_A) + E_B(N_B)$ has a minimum as a function of the electron transfer $\Delta N$ between $A$ and $B$. If such a minimum were to exist, it would occur in general at a nonzero fractional value of $\Delta N$, an unacceptable result. The condition for a unique minimum to exist is that $E_A[N_A] + E_B[N_B]$ be a convex function of $\Delta N$, that is, that $\eta_A + \eta_B$ be positive. Suppose that, in fact, the hardness is negative for isolated finite systems instead, i.e., that $\eta_A, \eta_B < 0$, the hardness conjecture (part 1). There would then be no minimum at fractional charges on the separated atoms of a heteronuclear diatomic molecule, only local infima at integer charge transfers, and an absolute infimum at the neutral species. The objection to NCDFT of Perdew et al. would no longer hold. We therefore investigate whether the continuation of $E[n]$ to noninteger $N$ via the separation and constrained search argument of Section 2 can yield negative hardness for isolated finite systems.

We first carry out a formal analysis of $\eta$. The various proofs that the chemical potential $\mu$ is identical to the KS energy of the HOMO carried out for integer $N$ carry over when $M < N < M + 1$, $M$ an integer, and the HOMO is fractionally occupied,

$$\mu = \varepsilon_{M+1}$$

(22)

Correspondingly, the hardness is given by

$$\eta = \frac{d\varepsilon_{M+1}}{dN}$$

(23)

which, by the Hellmann–Feynman theorem, becomes

$$\eta = \left(\psi_{M+1}, \frac{dV_{KS}}{dN} \psi_{M+1}\right)$$

(24)

Applying the chain rule to $dV_{KS}/dN$ leads to

$$\frac{dV_{KS}(r)}{dN} = \int dr' \frac{\delta V_{KS}(r)}{\delta n(r')} \frac{dn(r')}{dN}$$

(25)

In eq 25, the first factor in the integrand is the Kohn–Sham interaction, 27

$$f(r,r') = \frac{\delta V_{KS}(r)}{\delta n(r')}$$

(26)

and the second factor is the Fukui function of CRT, 4,28

$$F(r) = \frac{dn(r)}{dN}$$

(27)

$F(r)$ has been related to the frontier density 29,30,14 of the LUMO,

$$n_F(r) = \sum_s |\psi_{M+1}(r,s)|^2$$

(28)

via the Kohn–Sham susceptibility

$$\chi(0,r,r') = \frac{\delta n(r)}{\delta V_{KS}(r')}$$

(29)

viz.,

$$F(r) = \int dr' K(0,r,r') n_F(r')$$

(30)

where

$$K(r,r') = \delta(r,r') + \int dr'' \chi_0(r,r'') f(r'',r')$$

(31)
and that into eq 24 leads to the desired expression for $\eta$,

$$\eta = \left( n_F, \left[ \hat{f}^{-1} + \hat{\chi}_0 \right]^{-1} n_F \right)$$

(32)

where the superposed caret indicates an operator. Now $\hat{f}$ is, explicitly,

$$\hat{f} = \hat{f}_H + \hat{f}_X + \hat{f}_C$$

(33)

where the subscripts have the same meaning as in eqs 17 and 18. $\hat{f}_H$ is simply the bare coulomb interaction and is positive definite, $\hat{f}_X$ is negative definite, and $\hat{f}_C$ is presumed to be negative definite. $\hat{\chi}_0$, on the other hand, is positive definite. The quantity $\hat{f}^{-1} + \hat{\chi}_0$ in eq 32 is indefinite, and so, therefore, is $\eta$. It is possible that $\eta$ is negative.

To go beyond possibility and establish plausibility, we consider the Hartree–Fock approximation. We first evaluate $\eta$, keeping all $\psi_i$ fixed. The only variation of any quantity with $N$ then arises from the occupation number $\nu_{M+1}$ of the HOMO,

$$d\nu_{M+1} = dN$$

(34)

When the $\psi_i$ are fixed, only the term quadratic in the $\nu_{M+1}$ contributes to the unrelaxed $\eta_U$. The coefficient of $\nu_{M+1}^2$ consists of the direct self-interaction of the HOMO $\psi_{M+1}$ and its self-exchange, which exactly cancel, so that

$$\eta_U = 0$$

(35)

The resulting $N$ dependence of the unrelaxed energy is shown as a straight line in Fig. 1. The exact energy must fall increasingly below that line as $N$ increases above $M$ and the $\psi(N)$ deviate increasingly from the $\psi(M)$. It is shown as a concave line in Fig. 1. Thus, plausibility of the negative $\eta$ conjecture is established. The conjecture can be tested by computations in which the exchange energy must be treated exactly.

### 4. CHEMICAL REACTIVITY THEORY AND “ATOMS” IN “MOLECULES”

The goal of CRT is to predict or interpret the reactive proclivities of atoms or larger moieties in response to the chemical stimuli they encounter in molecules or larger systems from their properties in isolation, e.g., electronegativity, hardness, frontier orbitals, etc. There is thus a strong connection between CRT and the theory of atoms in molecules (AIM), which we now explore via NCDFT. Under the rubric of AIM, we subsume theories of the relation of the parts to the whole, however complex the system and subsystems may be.

Nalewajski and Parr have given a concise summary of the various AIM theories that have emerged. They give cogent reasons for rejecting each of these with the exception of the “stockholder” formulation of Hirshfeld, which they rederive via an information theoretic argument. That formulation, however, decomposes the electron density of the molecule into a weighted sum of the unperturbed atomic ground-state densities, the weights to
be determined by a best-fit criterion. We regard this to be unsatisfactory as well because it does not capture polarization, covalent bond formation, change in spin density, and relaxation in response to charge transfer; moreover, it is not an exact decomposition.

Consider a molecule $M$ with the ground-state local density matrix

$$\rho_\alpha(r)_{ss'} = N_M \int dx_1 \ldots dx_N \Psi(r_1, x_2 \ldots x_N) \Psi^*(r_1', x_2' \ldots x_N')$$

where $N_M$ is the number of electrons in $M$ and $\int dx_1 \ldots dx_N$ implies integration over space and sum over spin for the $N - 1$ unspecified space–spin coordinates in $M$’s ground-state wave function $\Psi$. Suppose that the nuclei of $M$ can be partitioned into subsets $\alpha = 1 \ldots A$, which define the components of the molecule. The AIM problem can then be restated as follows: What is the optimal exact decomposition of $\rho_\alpha(r)_{ss'}$ into the sum $\Sigma_\alpha \rho_\alpha(r)_{ss'}$ of contributions $\rho_\alpha(r)_{ss'}$, where $\rho_\alpha(r)_{ss'}$ is a local density matrix of the part $\alpha$ isolated in the nuclear configuration it has in $M$,

$$\rho_M(r)_{ss'} = \sum_\alpha \rho_\alpha(r)_{ss'}$$

A local-density matrix can be decomposed into an electron density $n(r)$ and a spin-density matrix $S_\alpha(r)$

$$\rho(r)_{ss'} = \frac{1}{2} n(r) \delta_{ss'} + S(r)_{ss'}$$

$$n(r) = \sum_s \rho(r)_{ss}$$

This formulation of the AIM problem differs from previous formulations in that the spin density is included in the decomposition as well as the electron density, and that optimality requires the decomposition to be exact, not approximate as in the stockholder model. The inclusion of spin density is essential if we are to understand how the chemical behavior of an “atom” within a “molecule” relates to its chemical behavior in true isolation, as expressed by e.g., its hardness, even if that “molecule” relates to its chemical behavior in true isolation. To include spin density is essential if we are to understand how the chemical behavior of an “atom” within a “molecule” relates to its chemical behavior in true isolation, as expressed by e.g., its hardness, even if that molecule is saturated, having vanishing spin density.

We have seen in the previous Section the importance of spin in establishing the sign of the hardness.

We propose here, as the solution of the AIM problem so formulated, that set of $\rho_\alpha(r)_{ss'}$ which yields the infimal value of the sum of the $N$-continuous energy functionals $E_\alpha[\rho_\alpha]$ of the isolated parts

$$E_I[\{\rho_\alpha\}] = \sum_\alpha E_\alpha[\rho_\alpha]$$

subject to the condition 37 and the implied condition

$$\sum_\alpha N_\alpha = N_M$$

$$n(r) = \int dr \, n(r)$$

The generalization of the arguments of Section 2 to hold for the spin-density matrix as well as the density is straightforward, leading to the spin-dependent generalization of NCDFT to NCSDFT.

It is convenient to express $S(r)$ in terms of the Pauli matrices $\sigma = (\sigma_x, \sigma_y, \sigma_z)$

$$S(r) = S(r) \sigma$$

where $S(r)$ is the vector spin density. Condition 37 then gets replaced by

$$n_M(r) = \sum_\alpha n_\alpha(r)$$

$$S_M(r) = \sum_\alpha S_\alpha(r)$$

Carrying out a Legendre transformation, we look for an infimum of

$$\mathcal{E}_I[\{n_\alpha, S_\alpha\}] = \sum_\alpha \left\{ E_\alpha[n_\alpha, S_\alpha] + \int dr \left[V_{\alpha M}(r) n_\alpha(r) - tr H_{\alpha M}(r) \hat{S}_\alpha(r) \right] \right\}$$

In eq 43, $V_{\alpha M}$ is the Lagrange multiplier that guarantees that eq 42a is satisfied, and $-H_{\alpha M}$ is that one which guarantees that eq 42b is satisfied. $V_{\alpha M}$ is unique up to a constant. Imposing the condition $V_{\alpha M}(r) \rightarrow 0$, $r \uparrow \infty$, fixes it and requires explicit imposition of condition 40.

If a minimum exists, i.e., if the Hessian of $\mathcal{E}_I$ is positive definite, then a modified set of KS equations results

$$\hat{H}_{\alpha M}[\psi_{\alpha i}] = E_\alpha[n_\alpha] \psi_{\alpha i}$$

$$\hat{H}_{\alpha M} = \hat{H}_{\alpha M} + V_{\alpha M}(r) I - H_{\alpha M}(r) \sigma$$

for the KS spin orbitals $\psi_{\alpha i}$. In addition to eq 44, an internal electronegativity equalization condition holds,

$$\rho'_\alpha = \frac{dE'_\alpha(N_\alpha)}{dN_\alpha} = \mu_M \quad \forall \alpha$$

where $E'_\alpha(N_\alpha)$ is

$$E'_\alpha[n_\alpha S_\alpha] = \int d\mathbf{r} [V_{\alpha M}(r) n_\alpha(r) - tr H_{\alpha M}(r) \hat{S}_\alpha(r)]$$

evaluated at the $n_\alpha(r)$ and $S_\alpha(r)$ constructed from the solution of eq 44 at fixed $N_\alpha$. The solution of eq 44 is to be obtained self-consistently via the Car–Parinello method by identifying the interacting spin-density matrix with that derived from a suitable noninteracting ensemble

$$\rho_\alpha(r)_{ss'} = \sum_i \nu_{i\alpha} \tilde{\psi}_{i\alpha}(r, s) \tilde{\psi}_{i\alpha}^*(r, s')$$
Such an identification is always possible. The occupation numbers $ν_\alpha$ will depend on $ρ_\alpha(r)$, an example of which will be discussed in the next Section.

$V_{ρ,ρ}(r)$ can be regarded as a reactivity potential. It is the previously undefined external potential of CRT introduced by Nalewajski and by Berkowitz and Parr. $H_{ρ,ρ}(r)$ has no precedent in CRT. It is required for the generalization of the existing formalism of CRT to describe reactive proclivities in which spin plays a key role.

A condition for the utility of this formulation of the AIM problem as a foundation for CRT is that the $ψ_\alpha(r)$ be localized to the vicinity of fragment $\alpha$. Since $V_{ρ,ρ}(r)$ and $H_{ρ,ρ}(r)$ must, in general, extend throughout the entire molecule, it is possible that they delocalize the $ψ_\alpha$, causing them to extend well beyond the domain of the fragment $\alpha$ to which they belong. Whether or not this occurs can be established only numerically. If, however, charge transfer between parts is effected primarily by the internal electronegativity-equalization condition (eq 46), $V_{ρ,ρ}(r)$ and $ψ_\alpha$ may primarily cause entirely local hybridization and spin/charge polarization, inducing no delocalization. We have implicitly assumed this to be the case. Much of chemical interest could then be expected from the $n_\alpha(r)$ and $S_\alpha(r)$: fractional charge transfer, covalent bond strengths, pairwise additivity, spin sensitivity, etc.

5. THE HARDNESS CONJECTURE, PART 2

Limitations of space prevent further discussion of the general case of nonvanishing $S_\rho(r)$. We now restrict ourselves to the simpler case of unsaturated molecules for which $S_\rho(r) \equiv 0$ and $N_M$ is even. The vanishing of $S_\rho(r)$ is guaranteed by noting that all $ψ_\alpha(r)$ possess Kramers degeneracy or, ignoring spin-orbit coupling, spin degeneracy, and that both members of a degenerate pair are identically occupied, whether fully or fractionally so, or unoccupied. The occupation numbers then will be

\begin{align}
ν_\alpha &= 1, \quad 1 ≤ i ≤ M_α \quad (49a) \\
&= ω, \quad i = M_α + 1, M_α + 2 \quad (49b) \\
&= 0, \quad i > M_α + 2 \quad (49c)
\end{align}

\begin{align}
N_α &= \sum_i ν_\alpha = M_α + 2ω \quad (50a) \\
&≤ 0 ≤ ω ≤ 1 \quad (50b) \\
&≤ M_α ≤ N ≤ M_α + 2 \quad (50c)
\end{align}

With eqs 49 and 50 for the occupation numbers of the self-consistent solution of the KS equations (eq 44), $H(r)$ vanishes, also self-consistently.

We now introduce the second part of our hardness conjecture: An isolated system in interaction with a reactivity potential by which all spin orbitals are forced to be doubly occupied, whether fractionally or not, or unoccupied, has positive hardness $η'$. In contrast to part 1, in which only one spin state of the HOMO is fractionally occupied, in part 2 both spin states of the HOMO are fractionally equioccupied.

Fig. 2. Same as for Fig. 1 except that the range of $N$ is from $M$ to $M + 2$, $M$ even, and most important, both Kramers degenerate HOMO pairs are fractionally occupied with $0 ≤ ν_{M+1} = ν_{M+2} ≤ 1$. Note that $E(M + 1)$ in the HFA must lie above the exact $E(M + 1)$ of the EDFT because the exact ground state would have $ν_{M+1} = 1$, whereas in this version of the HFA adapted to the AIM problem for saturated molecules, $ν_{M+1} = ν_{M+2} = 1/2$. The hardness of the exact HFA solution is now positive, as displayed by the convexity of the solid line.

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We need not dwell on the possibility that the conjecture is correct, as that has already been covered in the discussion of eq 32. We turn directly to the analysis of the HFA to establish plausibility and to pinpoint the source of the difference from part 1, dropping the subscript $\alpha$. Here the number varies continuously between $M$ and $M + 2$. In the unrelaxed approximation ($U$) with the $\psi_i$ fixed, the Hartree repulsion between opposite spins remains uncancelled, and $\eta'_{\nu}$ is consequently a positive constant. The variational principle then allows us to conclude that

$$0 < \eta' < \eta'_{\nu}. \quad (51)$$

These results are illustrated in Fig. 2. Moreover, if we suppose that $V_i(r)$ is negative in its effect on $E_M$ at $N = M$ and on $E_{M+2}$ at $N = M+2$, it follows that the exact $\eta'$ of NCDFT is positive as well in the case of part 2, establishing part 2 of the hardness conjecture. By comparing Figs. 1 and 2, it becomes clear that the constraint of vanishing spin density has forced the fragment $\alpha$ into a local minimum of the functional $E_{\alpha[n_{\alpha}S_{\alpha}]}$, the absolute minimum corresponding to fractional occupancy of only one of the pair of Kramers degenerate HOMOs. The transition from $\eta < 0$ to $\eta' > 0$ is not simple; these different hardmesses apply in two physically distinct situations. In a separate publication, we shall discuss explicitly the nature of the transition of a fragment $\alpha$ from positive hardness $\eta'_{\alpha}$ within a molecule $M$ to negative hardness $\eta_{\alpha}$ as all fragments of $M$ separate to infinity.

### 6. SUMMARY AND DISCUSSION

We have pointed out that from the beginnings of DFT, knowledge of the density functional for noninteger $N$ was implicit. The lack of explicit $N$ dependence and the continuity in $n$ of the standard approximations to the DF suggested simply interpolating them to noninteger $N$ (NCDFT). Calculations of various reactivity indices have been made on that basis with perfectly sensible results.\(^6\) Perdew et al.\(^{11}\) have argued against NCDFT on the grounds that NCDFT yields fractional charges on the atoms of a heteronuclear diatomic molecule separated to infinity instead of the correct neutral atoms. To avoid this contradiction, they introduced ground-state ensemble-density-functional theory (EDFT). However, EDFT is unsatisfactory on physical grounds (it represents a mixture of noninteracting systems of differing valence and not a single system) and on chemical grounds (it yields vanishing hardness and the identity of the electrophilic reactivities of a system with $M + 1$ electrons and the nucleophilic reactivities of a system with $M$ electrons).

However, the separation argument of Perdew et al. implicitly assumes that the sum of the hardmesses of the two isolated atoms is positive. We have pointed out that this need not be the case and, with the possibility of negative hardness in mind, have reexamined NCDFT.

We first show that the Levy–Lieb constrained search algorithm for integer $N$ implies, through a different separation argument, that the DF exists for noninteger $N$ for isolated systems and contains no explicit $N$ dependence. This DF is continuous in $N$ if the DF for integer $N$ is continuous in $n$. Though we are dealing in this way with a single interacting dynamical system, the electron density of that system can be represented exactly by the density of an ensemble of noninteracting electrons, and thus Kohn–Sham equations can be derived.

Next, we put forward the first part of a two-part hardness conjecture: the hardness of a system in which only one member of a pair of Kramers degenerate KS HOMO states is occupied is negative. We first prove that the sign of the hardness of such a system is indeterminate. Then we add to the plausibility of the conjecture by showing it to hold in the Hartree–Fock approximation. An immediate consequence of the hardness conjecture is that while the chemical potential for electron removal at integer $N$ is identical to $\varepsilon^{\text{HOMO}}$, the ionization energy $I$ is less than $[\varepsilon^{\text{HOMO}}]$, as can be seen by inspecting Fig. 1. We have shown this to be the case by arguments, to be published elsewhere,\(^{23}\) that examine processes in which $N$ is unchanged, remaining an integer throughout, thus providing strong support for the conjecture.

The NCDFT so formulated is then used as a basis for a novel “atoms” in “molecules” theory in which the electron spin-density matrix of the “molecule” is exactly decomposed into a sum of contributions of its parts by minimizing the sum of the isolated DFs of its parts subject to that constraint (eq 37). For there to be a minimum, the hardmesses must be positive, setting the stage for part 2 of the hardness conjecture, that the hardness is positive when both members of a Kramers degenerate pair of KS states are equally fractionally occupied, also shown to hold in the Hartree–Fock approximation. This sensitivity of hardness to spin parallels the transition from Heitler–London to Hund–Mulliken molecular bonding. It suggests that the concept of hardness be generalized explicitly to include at least spin indices or the corresponding indices of the Kramers degenerate pair,

$$\eta_{\alpha\beta} = \frac{d^2E}{dN_{\alpha}dN_{\beta}}. \quad (52)$$

to facilitate the analysis of free-radical reactions, a subject for future research. The Lagrange multiplier of the density component of the constraint, eq 37, has the
form of a reactivity potential $V_R(x)$, which can be taken as the previously undefined external potential of chemical reactivity theory. The Lagrange multiplier of the vector spin density in the constraint has the form of a reactivity field $H_{R,0}(r)$, which can be used to define spin-dependent reactivity kernels.

We conclude that there exists an internally consistent density-functional theory in which the density function is continuous in electron number. This theory can be made the basis of chemical reactivity theory via a theory of “atoms” in “molecules”, provided both parts of our hardness conjecture are true. While the plausibility of the conjecture has been established here, formal proof is not possible with our present understanding of the mathematics of functionals. What is needed now is direct numerical computation of the hardnesses of systems of both types. Treating the exchange exactly would be essential in such calculations, as the exact cancellation of the self-interaction in the Hartree potential by the exchange lies at the heart of our arguments about hardness.

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REFERENCES AND NOTES


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