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Natural determinant reference functional theory

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ABSTRACT

The natural determinant reference (NDR) or principal natural determinant is the Slater determinant comprised of the N most strongly occupied natural orbitals of an N-electron state of interest. Unlike the Kohn–Sham (KS) determinant, which yields the exact ground-state density, the NDR only yields the best idempotent approximation to the interacting one-particle reduced density matrix, but it is well-defined in common atom-centered basis sets and is representation-invariant. We show that the under-determination problem of prior attempts to define a ground-state energy functional of the NDR is overcome in a grand-canonical ensemble framework at the zero-temperature limit. The resulting grand potential functional of the NDR ensemble affords the variational determination of the ground state energy, its NDR (ensemble), and select ionization potentials and electron affinities. The NDR functional theory can be viewed as an "exactification" of orbital optimization and empirical generalized KS methods. NDR functionals depending on the noninteracting Hamiltonian do not require troublesome KS-inversion or optimized effective potentials.

I. INTRODUCTION

A central proposition of density functional theory (DFT) is that the ground state of a quantum many-body system generated by a local multiplicative one-body potential v is uniquely determined by its real-space one-body density ρ.[1] In their seminal paper,[1] Hohenberg and Kohn (HK) argue that the density is special because all observables coming from a local multiplicative one-body potential are explicit density functionals, and the remaining parts of the ground state energy are "universal" functionals of ρ, i.e., they do not depend on v. Unlike the many-body wavefunction, whose complexity increases factorially with the particle number N, the dimensionality of the one-body density is independent of N; moreover, the domain of admissible ρ is relatively simple,[2] obviating the N-representability problem of other reduced-dimensional state descriptors.[3,4]

Despite, or perhaps precisely because of, the intuitive appeal of the density and the revolutionary impact of DFT in computational electronic structure theory, it is pertinent to ask whether the real-space density is as special as suggested by HK. For nearly all practical purposes, accurate ground-state energies are far more important than densities, and the densities obtained from many modern density functionals can be surprisingly inaccurate.[5,6] Moreover, the HK theorem does not hold for the vast majority of finite basis sets presently in use, including virtually all atom-centered basis sets.[7,8] While this issue does not affect explicit functionals of the density, it has confounded the development and widespread use of functionals depending on the Kohn–Sham (KS) potential[9–11] v_s, including KS inversion[12–14] and the large class of "orbital dependent" functionals found on higher rungs of Jacob's ladder of density functionals.[15] Among the suggested remedies, the use of large real-space grids[16] or regularization methods[17] is mostly impractical or undesirable, whereas generalized KS (GKS) approaches are very practical but somewhat ill-defined: In its current use, the term GKS refers to minimization of an energy functional with respect to the noninteracting one-particle reduced density matrix (1-RDM), or, equivalently, the occupied GKS orbitals, rather than the density.[18] While this is less of a concern for functionals depending explicitly on the GKS 1-RDM only, it does not address the problem of how v_s can reliably be obtained for v_s-dependent functionals.[9,19] DFT is fundamentally representation-variant, since the density and the notion of a local potential are tied to the real-space basis, whereas "no meaningful distinction between local and nonlocal operators"[8] is possible in most other finite basis set representations. This problem has also limited the scope of systematic or *ab initio* DFT, which aims to numerically construct accurate density functionals by constrained search.[20–24]

We propose to address these limitations by choosing a representation-invariant quantity rather than the density as a reduced-dimensional state variable. At the same time, we also aim to preserve other aspects of DFT that have been key for its success, namely, the powerful concept of mapping an interacting to a noninteracting problem[25] with an intuitive physical meaning, the ground-breaking constrained search concept,[2,26] and not least the possibility to construct "almost universal" energy functionals using model systems, exact constraints, and physical insight, an approach pioneered and perfected by Perdew and co-workers.[27] The 1-RDM may seem an obvious candidate for such a state variable,[28] and 1-RDM theory[29–33] is, indeed, representation-invariant. However, the 1-RDM of an interacting state cannot be (directly) obtained from an effective one-particle Hamiltonian,[29] at least at zero temperature.[34] This complicates the construction of 1-RDM functionals, and it re-introduces the basis-set convergence problem affecting correlated wavefunction methods; for example, the natural occupation numbers of the 1-RDM of He atom exhibit a slow $1/(l+1/2)^4$ decrease with orbital angular momentum l.[35]

A state variable satisfying the requirement of representation invariance while retaining the computational efficiency and conceptual simplicity of an effective noninteracting system is the best noninteracting approximation to the 1-RDM. If we denote the interacting 1-RDM by γ, its best noninteracting approximation γ_s (in the absence of degeneracies, see below) is idempotent but minimizes the error in the 2- or Frobenius norm,

$$\|\gamma - \gamma_s\| = \sqrt{\langle (\gamma - \gamma_s)^\dagger (\gamma - \gamma_s)\rangle}. \tag{1}$$

This idea is by no means new; an independent particle model based on γ_s was already proposed in 1964 by Kutzelnigg and Smith[36] and named, rather unfortunately, the "best density approximation." The Slater determinant (SD) whose 1-RDM is γ_s coincides with the "principal natural determinant" $|\Phi_0\rangle$, i.e., the SD constructed from the N most strongly occupied natural orbitals (NOs). We will henceforth refer to $|\Phi_0\rangle$ as the natural determinant reference (NDR), to emphasize its meaning as a zero-order approximation to the interacting many-body state.[37–39] The best noninteracting 1-RDM has also been proposed as a state descriptor in the context of cumulant functionary[40,41] and 1-RDM theory.[42]

We review the definition and key properties of the NDR in Sec. II. Existing pure-state constrained-search definitions of NDR energy functionals and their limitations are discussed in Sec. III. The formalism is generalized to grand-canonical ensembles with a real particle number in Sec. IV; importantly, this leads to a unique definition of the noninteracting Hamiltonian. A set of effective one-particle equations to find the NDR and the exact ground-state energy is presented in Sec. V, and the physical meaning of the NDR orbitals and their energies is established. NDR functional approximations are discussed in Sec. VI, and conclusions are presented in Sec. VII.

Throughout this paper, atomic (Hartree) units are employed. Indices $i, j, \ldots$ denote occupied spin orbitals, or strongly occupied NOs, $a, b, \ldots$ denote virtual orbitals, or weakly occupied NOs, and $p, q, \ldots$ denote general orbitals. Many-electron density operators are denoted by $\hat{\Upsilon}$, and one-body order reduced density matrices (1-RDMs) are denoted by γ. The Hilbert space of normalizable N-electron states is $\mathscr{E}(N)$, and the direct product of all $\mathscr{E}(N)$ is the Fock space $\mathscr{F}$. The subsets of noninteracting states or SDs are $\mathscr{E}_s$ and $\mathscr{F}_s$. The Dirac bra–ket notation is used where practical; $\langle\cdot\rangle$ denotes the trace operation on $\mathscr{E}(1) \times \mathscr{E}(1)$, whereas $\langle\cdot\rangle_{\mathscr{F}}$ is the trace on $\mathscr{F} \times \mathscr{F}$. Operators on $\mathscr{F}$ ("second quantized") are denoted by a hat.

II. NDR THEORY

A. Natural determinants

Consider a normalized N-electron state $|\Psi\rangle \in \mathscr{E}(N)$ with 1-RDM $\gamma[\Psi] = \langle\Psi|\hat{\gamma}|\Psi\rangle$. The eigenstates of $\gamma[\Psi]$, denoted $\{|\varphi_p\rangle\}$, are the NOs of $|\Psi\rangle$, and the corresponding eigenvalues $\{\nu_p\}$ are the natural occupation numbers (NONs),

$$\gamma[\Psi]|\varphi_p\rangle = \nu_p|\varphi_p\rangle. \tag{2}$$

Here and in the following, the dependence of the NOs and NONs on $|\Psi\rangle$ is implied; moreover, the NOs and NONs are indexed such that the sequence $(\nu_p)_{p\in\mathbb{N}}$ is nonincreasing. Since $|\Psi\rangle$ is a Fermion state, $\nu_p \in [0,1]$,[3] and the normalization of $|\Psi\rangle$ implies

$$\langle\gamma\rangle = \sum_p \nu_p = N. \tag{3}$$

The Fermi NON

$$\nu_F = \frac{\nu_N + \nu_{N+1}}{2} \tag{4}$$

cannot be zero, since the rank of $\gamma[\Psi]$ is at least N (Ref. 3). On the other hand, Eq. (3) requires that $\nu_F < 1$. If $\nu_F = \nu_N$, then $\gamma[\Psi]$ has a degeneracy at the Fermi NON. We say that ν_F is k-fold degenerate if ν_N is k-fold degenerate. Moreover, NOs with occupation numbers greater than or equal to ν_F are "strongly occupied," and correspondingly, NOs with occupation numbers less than ν_F are "weakly occupied" for the purposes of this paper.

The NOs form an orthonormal basis of $\mathscr{E}(1)$, and we will denote the corresponding electron creation and annihilation operators $\{\hat{c}_p^\dagger\}$ and $\{\hat{c}_p\}$. Natural determinants (NDs) $\{|\Phi_n\rangle\}$ are all possible N-electron SDs that can be constructed from these NOs; see Theorem A.1 for other equivalent definitions. The NDs form an orthonormal basis of $\mathscr{E}(N)$. Moreover, every ND is an eigenstate of every NON operator $\hat{n}_p = \hat{c}_p^\dagger \hat{c}_p$,

$$\hat{n}_p|\Phi_n\rangle = n_{p,n}|\Phi_n\rangle. \tag{5}$$

However, the corresponding NONs $n_{p,n}$ are either 1 or 0, reflecting the fact that NDs are noninteracting.

To further classify the NDs, we introduce the self-adjoint operator,

$$\hat{S}[\Psi] = \langle\hat{\gamma}\gamma[\Psi]\rangle = \sum_p \hat{n}_p \nu_p. \tag{6}$$

The expectation value of $\hat{S}[\Psi]$ for any state $|\Xi\rangle \in \mathscr{E}(N)$ equals the (Frobenius) inner product of the 1-RDMs of $|\Psi\rangle$ and $|\Xi\rangle$,

$$\langle\Xi|\hat{S}[\Psi]|\Xi\rangle = \langle\Psi|\hat{S}[\Xi]|\Psi\rangle = \langle\gamma[\Xi]\gamma[\Psi]\rangle = \langle\gamma[\Xi]|\gamma[\Psi]\rangle, \tag{7}$$

where the Hermitian property of density matrices has been used. Thus, the expectation value of $\hat{S}[\Psi]$ measures the "overlap" of a state Ξ's 1-RDM with the 1-RDM of $|\Psi\rangle$. In particular, for a SD $|\Phi\rangle$,

$$\langle\Phi|\hat{S}[\Psi]|\Phi\rangle = N - c[\Psi]/2 - \|\gamma[\Psi] - \gamma[\Phi]\|^2; \tag{8}$$

$c[\Psi] = \langle \gamma[\Psi] - \gamma^2[\Psi] \rangle \geq 0$ quantifies the nonidempotency of the 1-RDM of $|\Psi\rangle$ and has been proposed as a measure of correlation.[43,44] Since neither N nor $c[\Psi]$ depends on Φ, Eq. (8) means that, for given Ψ, $\langle \Phi|\hat{S}[\Psi]|\Phi\rangle$ measures the squared deviation of the 1-RDMs $\gamma[\Psi]$ and $\gamma[\Phi]$: The larger the overlap $\langle \Phi|\hat{S}[\Psi]|\Phi\rangle$, the smaller the error $\|\gamma[\Psi] - \gamma[\Phi]\|$ in the 2-norm. Moreover, it follows from Eq. (5) that all NDs are eigenstates of $\hat{S}[\Psi]$ with eigenvalues

$$s_n = \langle \gamma[\Phi_n]|\gamma[\Psi]\rangle = \sum_p n_{p,n} \nu_p. \tag{9}$$

B. Natural determinant reference

NDR or principal natural determinant $|\Phi_0\rangle$ is the ND constructed from N (most) strongly occupied NOs of $|\Psi\rangle$, i.e., N NOs with the largest NONs. Equivalently, the NDR is the SD that maximizes the overlap of its 1-RDM with $\gamma[\Psi]$, i.e.,

$$\Phi_0 = \arg \max_{\Phi \in \mathscr{E}_s(N)} \langle \Phi|\hat{S}[\Psi]|\Phi\rangle. \tag{10}$$

It follows that $\gamma[\Phi_0] \equiv \gamma_0$ is the best idempotent approximation to $\gamma[\Psi]$; see also Theorem A.2.

In the absence of degeneracies of $\gamma[\Psi]$ at the Fermi NON, the maximum eigenvalue $s_0 = \langle \Phi_0|\hat{S}[\Psi]|\Phi_0\rangle$ is nondegenerate, and thus, the NDR is unique up to a (physically irrelevant) global phase. If s_0 is degenerate, then the NDR is unique only up to a unitary transformation within the eigenspace of s_0. In this case, it is necessary to consider an equal-weight ensemble of all degenerate NDRs; see Sec. IV.

The NDs are also eigenstates of the operator $\hat{S}[\Phi_0]$. The eigenvalues are N for $|\Phi_0\rangle$, $N-1$ for single excitations out of $|\Phi_0\rangle$, ..., and 0 for N-fold excitations. Since

$$\langle \Psi|\hat{S}[\Phi]|\Psi\rangle = \langle \Phi|\hat{S}[\Psi]|\Phi\rangle, \tag{11}$$

the NDR is the SD that maximizes $\langle \Psi|\hat{S}[\Phi]|\Psi\rangle$ and thus minimizes the average excitation rank of Ψ.[45] This property of the NDR has been used to generate minimum-rank representations of wavefunctions and other quantities.[37]

C. Iso-NDR states

Section II B introduced a map from an arbitrary N-electron state $|\Psi\rangle \in \mathscr{E}(N)$ to its NDR,

$$f : \Phi_0 = \arg \max_{\Phi \in \mathscr{E}_s(N)} \langle \Phi|\hat{S}[\Psi]|\Phi\rangle. \tag{12}$$

$f[\Psi]$ is surjective, since every SD is the NDR of at least one state $|\Psi\rangle$, namely, itself. However, $f[\Psi]$ is not injective, because more than one N-electron state can have the same NDR. The set of states sharing the same NDR Φ,

$$\mathscr{S}[\Phi] = \{|\Psi\rangle \in \mathscr{E}(N) | f[\Psi] = |\Phi\rangle\}, \tag{13}$$

is nonempty, and every state $|\Psi\rangle \in \mathscr{E}(N)$ belongs to at least one such set.

III. PURE-STATE NDR ENERGY FUNCTIONALS

A. Definition by constrained search

NDs have found relatively limited use because they are conventionally constructed from a many-electron state $|\Psi\rangle$ that must be known in the first place. We aim to bypass this requirement by defining an energy functional that is variationally minimized by the ground-state NDR for a given external potential.

We consider many-electron Hamiltonians of the form

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}^{\text{ext}}, \tag{14}$$

with $\hat{T}$ and $\hat{V}_{ee}$ denoting the operators associated with the electron kinetic energy and electron–electron interaction; $\hat{V}^{\text{ext}}$ is a general one-body operator, which may be nonlocal. In the spirit of Levy–Lieb constrained search,[2,26] we first find the lowest energy expectation value on $\mathscr{S}[\Phi]$ for a given SD Φ,

$$E[\Phi] = \inf_{\Psi \in \mathscr{S}[\Phi]} \langle \Psi|\hat{H}|\Psi\rangle. \tag{15}$$

Since every N-electron state has at least one NDR, the energy of a nondegenerate ground state can then be obtained from minimization of the ground-state energy $E[\Phi]$ as a functional of Φ,

$$E_0 = \min_{\Phi \in \mathscr{E}_s(N)} E[\Phi]. \tag{16}$$

The above functionals were previously proposed in similar form by Taube.[42] However, this approach has several drawbacks. First, although the $\mathscr{S}[\Phi]$ has a well-defined finite basis-set equivalent, its definition is not particularly explicit, making it difficult to implement the constraint. Even if this (somewhat technical) problem can be overcome, second, the constraint $\Psi \in \mathscr{S}[\Phi]$ does not completely determine $\hat{V}^{\text{ext}}$. This can be shown, for example, by noting that the 1-RDMs of different $\Psi \in \mathscr{S}[\Phi]$ generally differ, as long as they commute with γ_0, and the eigenspaces belonging to their N most strongly occupied NOs are identical. Since there is a one-to-one correspondence between the 1-RDM and $\hat{V}^{\text{ext}}$[29] (including in finite basis sets), the members of $\mathscr{S}[\Phi]$ do not generally come from the same $\hat{V}^{\text{ext}}$. The same conclusion can be reached by counting the number of independent (real) constraints, which amounts to $Nd + 1$, where d is the dimension of the one-particle basis.

The under-determination of $\hat{V}^{\text{ext}}$ in the pure-state formalism also implies that, although the ground-state energy can, in principle, be obtained by minimizing $E[\Phi]$, there is no unique noninteracting Hamiltonian. As such, pure-state NDR theory violates a central requirement of Sec. I and represents a step backward compared to KS-DFT.

An analogous difficulty arises in orbital optimization (OO) methods, where some energy functional is made stationary with respect to a set of reference orbitals. Although it is often possible to "optimize" the energy functional by varying the orbitals, there is no unique definition of the noninteracting Hamiltonian, which is particularly confounding for approximate energy functionals depending not merely on the orbitals but also their energies.

IV. ENSEMBLE NDR ENERGY FUNCTIONALS

A. Natural determinant reference ensemble

The difficulties of the pure-state NDR formalism are overcome by generalizing it to ensembles or "mixed states" with real particle number $P = N + k\delta$, where $\delta \in [0, 1)$ and $k \in \mathbb{N}$ is a degeneracy index. Consider such an arbitrary particle number ensemble at zero temperature with density matrix $\hat{\Upsilon} \in \mathscr{F} \times \mathscr{F}$, $\hat{\Upsilon}$ has a 1-RDM $\gamma[\hat{\Upsilon}] = \langle \hat{Y}\hat{y} \rangle_{\mathscr{F}}$, whose eigenstates and eigenvalues define the NOs and NONs as in Eq. (2). All ensembles are normalized according to $\langle \hat{\Upsilon} \rangle_{\mathscr{F}} = 1$, whereas the number operator expectation value is $\langle \hat{N}\hat{\Upsilon} \rangle_{\mathscr{F}} = P$.

The NDR ensemble (NDRE) is defined as the noninteracting P-particle ensemble $\hat{\Upsilon}_s$ that maximizes the overlap of its 1-RDM with $\gamma[\hat{\Upsilon}]$. Writing $\mathscr{F}_s(P)$ for the set of all noninteracting P-particle ensembles,

$$f : \hat{\Upsilon}_s = \arg \max_{\hat{\Lambda} \in \mathscr{F}_s(P)} \langle \hat{S}[\hat{\Upsilon}] \hat{\Lambda} \rangle_{\mathscr{F}}, \tag{17}$$

where $\hat{S}[\hat{\Upsilon}]$ extends the definition (6) to ensembles,

$$\hat{S}[\hat{\Upsilon}] = \langle \hat{y}\gamma[\hat{\Upsilon}] \rangle = \sum_p \hat{n}_p v_p. \tag{18}$$

This maximization is conveniently carried out by maximizing the functional

$$\Sigma[\hat{\Upsilon}_s, v] = \langle \hat{\Upsilon}_s \hat{S}[\hat{\Upsilon}] \rangle - v \langle \hat{\Upsilon}_s \hat{N} \rangle_{\mathscr{F}}; \tag{19}$$

the Lagrange multiplier v enforces the particle number constraint $\langle \hat{\Upsilon}_s \rangle_{\mathscr{F}} = P$. In analogy with statistical mechanics (see, for example, Refs. 46 and 47), the necessary condition for a maximum of Σ yields

$$\hat{\Upsilon}_s(v) = \Theta_\delta(\hat{S}[\hat{\Upsilon}] - v\hat{N}); \tag{20}$$

Θ_δ denotes the Heaviside step distribution with $\Theta_\delta(0) = \delta$. Since $\hat{S}$ and $\hat{N}$ are one-body operators, so is $\hat{\Upsilon}_s$. Choosing the NOs of $\gamma[\hat{\Upsilon}]$ as a one-particle basis, one arrives at

$$\hat{\Upsilon}_s(v) = \sum_p n_p(v)\ \hat{n}_p, \tag{21}$$

with the NDRE one-particle occupation numbers

$$n_p(v) = \Theta_\delta(v_p - v) = \begin{cases} 1, & v_p < v, \\ \delta, & v_p = v, \\ 0, & v_p > v. \end{cases} \tag{22}$$

Imposing the particle number constraint determines v as a function of $P = N + k\delta$, which generalizes the Fermi occupation number (4),

$$v(P) = v_F = \begin{cases} \dfrac{v_{N+1} - v_N}{2}, & \delta = 0, \\ v_{N+1}, & 0 < \delta < 1. \end{cases} \tag{23}$$

B. Constrained search

In analogy to Sec. II C, we define the set of iso-NDRE ensembles as

$$\mathscr{S}[\hat{\Upsilon}_s] = \{\hat{\Upsilon} \in \mathscr{F} | f[\hat{\Upsilon}] = \hat{\Upsilon}_s\}. \tag{24}$$

$\hat{\Upsilon}_s$ and all members of $\mathscr{S}[\hat{\Upsilon}_s]$ have the same particle number P by definition. The ensemble version of the ground-state energy functional (15) is thus

$$E[\hat{\Upsilon}_s] = \inf_{\hat{\Upsilon} \in \mathscr{S}[\hat{\Upsilon}_s]} \langle \hat{H}\hat{\Upsilon} \rangle_{\mathscr{F}}. \tag{25}$$

The ground ensemble grand potential $\Omega_0(\mu)$ as a function of the chemical potential μ is the minimum of the grand potential functional

$$\Omega[\hat{\Upsilon}_s, \mu] = E[\hat{\Upsilon}_s] - \mu \langle \hat{N}\hat{\Upsilon}_s \rangle_{\mathscr{F}}; \tag{26}$$

μ can be chosen to constrain the particle number of $\hat{\Upsilon}_s$ to P. The ground-state energy as a function of P is the Legendre transform

$$E_0(P) = \Omega_0(\mu) + \mu P, \tag{27}$$

and thus,

$$\mu = \frac{dE_0(P)}{dP} \tag{28}$$

is indeed the chemical potential of the physical ground ensemble. The necessary condition for a minimum of $\Omega[\hat{\Upsilon}_s, \mu]$ yields

$$\hat{\Upsilon}_s(\mu) = \Theta_\delta(\hat{F}[\hat{\Upsilon}_s] - \mu\hat{N}), \tag{29}$$

where the self-adjoint effective one-particle Hamiltonian is the functional derivative

$$\hat{F}[\hat{\Upsilon}_s] = \frac{\delta E[\hat{\Upsilon}_s]}{\delta \hat{\Upsilon}_s} \tag{30}$$

at the minimum.

In the pure-state case with a fixed integer particle number, γ_s is rank N and determined by $N(d - N)$ parameters, corresponding to number-conserving "orbital rotations" between occupied and unoccupied orbitals. These parameters amount to the Brillouin–Löwdin conditions,[45,48–50] i.e., the occupied–virtual block of the effective one-particle Hamiltonian must be zero in the basis of NOs or, equivalently, NDR orbitals. However, the occupied–occupied and virtual–virtual blocks, and in particular the eigenvalues, of $\hat{F}$ remain undetermined, as discussed in Sec. III. In the ensemble constrained search, the NDRE must be specified for arbitrary particle number P and can have any rank between 1 and d. Thus, the NDRE constraint is more stringent than the pure-state NDR Brillouin–Löwdin conditions, and it fully determines the effective noninteracting one-particle Hamiltonian $\hat{F}[\hat{\Upsilon}_s]$. Indeed, Eq. (30) encompasses the Brillouin–Löwdin conditions and Janak's theorem,[51] as shown below.

V. EFFECTIVE SINGLE-PARTICLE EQUATIONS

A. NDRE grand potential minimization

It is convenient to write the ground-state energy functional as a functional of the noninteracting NDRE 1-RDM $\gamma_s = \gamma[\Upsilon_s]$,

$$E[\gamma_s] = E^{\mathrm{HF}}[\gamma_s] + E^{\mathrm{VC}}[\gamma_s], \tag{31}$$

where $E^{\mathrm{HF}}[\gamma_s]$ is the HF energy functional and the remainder $E^{\mathrm{VC}}[\gamma_s]$ accounts for correlation.

To minimize the grand potential functional $\Omega[\hat{\Upsilon}_s, \mu]$ with respect to γ_s, we consider the Lagrangian

$$L[\{|\phi_p\rangle\}, \{n_p\}, \boldsymbol{\varepsilon}, \mu, \boldsymbol{\kappa}] = \Omega[\{|\phi_p\rangle\}, \{n_p\}, \mu] - \sum_{pq} \varepsilon_{qp}(\langle\phi_p|\phi_q\rangle - \delta_{pq}) - \sum_p \kappa_p(n_p - n_p^2). \tag{32}$$

The Hermitian Lagrange multiplier $\boldsymbol{\epsilon}$ enforces orthonormality of the orbitals. We further add the inequality constraint $n_p - n_p^2 \geq 0$ using κ; to allow for the possibility of noninteger occupation, we merely require $\kappa_p \geq 0$, and thus, only the weaker (Karush–Kuhn–Tucker[52]) conditions

$$\kappa_p(n_p - n_p^2) = 0 \tag{33}$$

are imposed. Stationarity with respect to the $\{|\phi_p\rangle\}$ produces the effective single-particle equations

$$F[\gamma_s]|\phi_p\rangle n_p = \sum_q |\phi_q\rangle \varepsilon_{qp}, \tag{34}$$

with the effective one-particle Hamiltonian being, in agreement with Eq. (30),

$$F[\gamma_s] = \frac{\delta E[\gamma_s]}{\delta \gamma_s} = T + V_{ne} + V^{\mathrm{HX}}[\gamma_s] + V^{\mathrm{VC}}[\gamma_s]. \tag{35}$$

V^{HX} is the sum of the Hartree and nonlocal exchange potentials, and $V^{\mathrm{VC}} = \delta E^{\mathrm{VC}}[\gamma_s]/\delta\gamma_s$ is the VC potential. The self-adjointness of $F[\gamma_s]$ and ε leads to the Brillouin–Löwdin condition

$$(n_p - n_q)[F[\gamma_s]]_{pq} = 0, \tag{36}$$

i.e., the matrix elements of F between orbitals with different occupation numbers must vanish. Furthermore, we choose any orbitals with identical occupation numbers such that $F[\gamma_s]$ is diagonal, i.e., $\varepsilon_{qp} = \delta_{qp} n_p \varepsilon_p$. This leads to the "canonical" NDRE single-particle equations

$$F[\gamma_s]|\phi_p\rangle = \varepsilon_p|\phi_p\rangle \tag{37}$$

with orbital energies $\{\varepsilon_p\}$. The canonical NDRE orbitals $\{|\phi_p\rangle\}$ generally differ from the NOs $\{|\varphi_p\rangle\}$.

The Euler–Lagrange equations for the occupation numbers are

$$\frac{\partial E[\gamma_s]}{\partial n_p} - \mu - \kappa_p(1 - 2n_p) = 0. \tag{38}$$

Choosing the lowest possible value of μ, and noting that Eq. (35) amounts to Janak's theorem

$$\frac{\partial E[\gamma_s]}{\partial n_p} = \varepsilon_p, \tag{39}$$

we arrive at

$$\varepsilon_p = \begin{cases} \mu - \kappa_p, & n_p = 1, \\ \mu, & n_p = \delta, \\ \mu + \kappa_p, & n_p = 0. \end{cases} \tag{40}$$

Since $\kappa_p \geq 0$ (dual feasibility) is a necessary condition for a minimum, all orbitals with noninteger occupation numbers are degenerate with orbital energy μ, whereas fully occupied ($n_p = 1$) orbitals must have lower energies, and unoccupied ($n_p = 0$) orbitals must have higher energies. The Aufbau principle is thus a necessary condition for a minimum of the grand potential under suitable constraints.

B. Physical interpretation

The NDRE 1-RDM is by construction the closest noninteracting P-particle approximation to the interacting 1-RDM within the 2-norm. In this sense, one-particle properties obtained from the NDR are close, but generally not equal to, their interacting equivalents.

Moreover, the canonical NDRE orbital energies have an appealing interpretation in terms of electron removal and addition energies: It follows from Eqs. (28) and (40) that the energies of the highest occupied (H) and the lowest unoccupied (L) NDRE orbitals equal the negatives of the exact (first) ionization potentials I and electron affinities A at an integer particle number. This result is analogous to GKS, but not KS theory.[53–55] An important consequence is that the NDR gap

$$\varepsilon_{\mathrm{L}} - \varepsilon_{\mathrm{H}} = A - I \tag{41}$$

equals the fundamental gap of the interacting system, whereas the KS gap is well known to differ due to derivative discontinuities of the (local) exchange–correlation potential.[56]

Perdew and Levy have argued that higher stationary points of the exact DFT energy functional correspond to exact excited state energies.[57] If an analogous argument can be made for the NDRE energy functional, then NDRE orbital energies below ε_H and above ε_L would correspond to certain higher ionization potentials and electron affinities.

VI. APPROXIMATE FUNCTIONALS

A. Adiabatic connection

In analogy to adiabatic connection DFT (ACDFT),[58,59] the constrained-search definition of the ground-state energy as a functional of the NDRE $\hat{\Upsilon}_s$ can be extended to scaled electron–electron interactions $\alpha\hat{V}_{ee}$,

$$E_\alpha[\hat{\Upsilon}_s] = \inf_{\hat{\Upsilon}\in\mathcal{S}[\hat{\Upsilon}_s]} \langle(\hat{T} + \alpha\hat{V}_{ee} + \hat{V}^{\mathrm{ext}})\hat{\Upsilon}\rangle_{\mathscr{F}}. \tag{42}$$

The Hellmann–Feynman theorem yields

$$\frac{dE_\alpha[\hat{\Upsilon}_s]}{d\alpha} = \langle\hat{\Upsilon}_\alpha\hat{V}_{ee}\rangle_{\mathscr{F}}, \tag{43}$$

where $\hat{\Upsilon}_\alpha$ is the P-particle ensemble, which infimizes $E_\alpha[\hat{\Upsilon}_s]$. The "adiabatic connection formula" for the ground-state VC energy functional follows by coupling strength integration,

$$E^{\mathrm{VC}}[\hat{\Upsilon}_s] = \int_0^1 d\alpha \langle(\hat{\Upsilon}_\alpha - \hat{\Upsilon}_s)\hat{V}_{ee}\rangle_{\mathscr{F}}. \tag{44}$$

The DFT analog of Eq. (44) has been widely used to derive orbital- and explicitly KS potential-dependent functionals.[60] Compared to the DFT case, the variational minimization of such functionals is relatively straightforward in the NDRE context, because the functionals are well-defined in general finite basis sets. Thus, "functional self-consistency,"[9,19] i.e., an exact implementation of Eq. (30), is achievable without having to resort to large real-space grids or regularization.

B. Uniform electron gas and semilocal functionals

For the uniform electron gas, $\hat{V}^{\text{ext}}$ is a constant, and hence, the one-electron potential correlation energy vanishes. As a result, the NDRE correlation energy functional is obviously "universal" in the uniform limit; it coincides with the local density approximation, evaluated at the NDR density, which equals the interacting density in the uniform case.

An immediate conclusion is that approximate NDRE functionals can (and probably should[61]) be made exact in the uniform limit. However, to meaningfully apply such functionals to nonuniform systems, approximations for the interacting 1-RDM may be needed. In a first step, the difference between the interacting and noninteracting densities could be obtained from existing semilocal correlation hole models[62–64] by removing the correlation sum rule constraint. Moreover, the NOs of the uniform electron gas are identical to the NDRE orbitals, and their NONs are accurately known functions of the noninteracting orbital energies.[65]

C. GKS

From the present perspective, the NDRE single-particle equations constitute one possible "exactification" of the (empirical) GKS scheme. Existing density functionals depending explicitly on the GKS density matrix, such as *meta*-GGA or (local) hybrid functionals, are among the most accurate and widely used density functional approximations; these functionals can also be viewed as crude NDR functional approximations.

D. Orbital optimization

NDR theory may also be viewed as an "exactification" of OO methods.[66–68] Despite its intuitive appeal, straightforward OO of HF-based energy functionals suffers from under-determination.[69] The NDRE constraint fixes the extra degrees of freedom introduced by orbital optimization, and thus, NDRE functionals do not have this issue. Indeed, correlated wavefunction methods with well-defined grand-canonical extensions could be used in conjunction with the NDRE adiabatic connection without much extra effort compared to existing OO schemes.

VII. CONCLUSIONS

With relatively minor modifications, DFT can be liberated from its real-space shackles. While adherents of the locality principle will consider this work heresy, the present results suggest that weakening the exact density requirement of DFT to a best noninteracting 1-RDM requirement has many advantages. Chemists, in particular, have long used off-diagonal elements of the 1-RDM as approximate measures of chemical bond orders ("overlap populations"). Since only noninteracting quantities are needed to obtain the ground-state energy, the basis-set requirements are modest, at least for explicit NDR energy functionals.

The grand-canonical version of NDR functional theory leads to a well-defined noninteracting Hamiltonian whose orbital energies are ionization potentials and electron affinities. Therefore, NDR functional theory satisfies the conditions Bartlett has put forward for an "exact correlated orbital theory" (COT),[70] at least for the frontier orbitals; the NDR noninteracting Hamiltonian is self-adjoint and obtained as a functional derivative, whereas the COT effective Hamiltonian is defined by (nonunitary) similarity transformation. NDR functional theory provides a particularly attractive framework for further development of higher-rung "potential-dependent" functionals, because it does not require optimized effective potentials. Although the NDRE energy functional is not explicitly known for two-electron systems, it has a well-defined noninteracting N-electron limit and is therefore amenable to extrapolation using "weakly correlated" approaches, such as RPA[71] or coupled cluster theory.[72] This may be contrasted with the 1-RDM energy functional, which is explicitly known for two-electron systems,[73–75] but has no useful noninteracting N-electron limit, or the 2-RDM energy functional, which is explicitly known for all systems, but its domain is pathological.[4,76] Another appealing aspect of NDRE functionals is that a wealth of exact constraints and techniques underlying the success of DFT can be carried over with relatively few modifications, especially in the GKS realm.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors declare the following competing financial interest(s): Principal Investigator Filipp Furche has an equity interest in TURBOMOLE GmbH. The terms of this arrangement have been reviewed and approved by the University of California, Irvine, in accordance with its conflict of interest policies.

Author Contributions

Jason M. Yu: Conceptualization (supporting); Investigation (equal); Writing – original draft (lead). **Jeffrey Tsai**: Conceptualization (supporting); Investigation (equal); Writing – original draft (supporting); Writing – review & editing (supporting). **Ahmadreza Rajabi**: Investigation (supporting); Writing – review & editing (equal). **Dmitrij Rappoport**: Investigation (supporting); Writing – review & editing (equal). **Filipp Furche**: Conceptualization (lead); Investigation (equal); Supervision (lead); Writing – original draft (supporting); Writing – review & editing (lead).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

APPENDIX: NATURAL DETERMINANTS

Theorem A.1. *Given an N-electron state $|\Psi\rangle$ with NOs $\{|\varphi_p\rangle\}$, let $|\Phi_n\rangle$ be a ND of $|\Psi\rangle$, i.e., a SD constructed from N NOs. Then, the following statements are equivalent:*

(i) *The 1-RDM of $|\Phi_n\rangle$ is*

$$\gamma[\Phi_n] = \sum_p n_{n,p} |\varphi_p\rangle\langle\varphi_p|, \tag{A1}$$

where N occupation numbers $n_{n,p}$ are equal to 1 and all others are zero.

(ii) *The 1-RDMs $\gamma[\Psi]$ and $\gamma[\Phi_n]$ commute.*

(iii) *(Brillouin–Löwdin condition)*[45]

$$\langle\Psi|\hat{c}_i^\dagger \hat{c}_a|\Psi\rangle = 0, \tag{A2}$$

where $\{|\varphi_i\rangle\}$ are occupied in $|\Phi_n\rangle$ and $\{|\varphi_a\rangle\}$ are not occupied.

Proof. The equivalence of (i) and (ii) is elementary. For the proof of (iii), see Ref. 45. □

Theorem A.2. *Let $|\Phi_0\rangle$ be the NDR of $|\Psi\rangle$, i.e., the ND constructed from the N most strongly occupied natural orbitals of $|\Psi\rangle$. The following statements are equivalent:*

(i) *The sequence of NONs of $|\Phi_0\rangle$, $(n_{0,p})_{p\in\mathbb{N}}$, is nonincreasing.*

(ii) $\langle\gamma[\Phi]|\gamma[\Psi]\rangle \le \langle\gamma[\Phi_0]|\gamma[\Psi]\rangle = \sum_{p=1}^{N} \nu_p = s_0$.

(iii) *$|\Phi_0\rangle$ minimizes $\|\gamma[\Psi] - \gamma[\Phi]\|$ for fixed Ψ. Thus, $\gamma[\Phi_0]$ is the best idempotent approximation to $\gamma[\Psi]$.*

(iv) *$|\Phi_0\rangle$ minimizes the particle and hole number expectation values as functionals of a reference determinant.*

Proof. The proof of equivalence of (i) and (ii) is well documented in the literature; see, for example, Refs. 78 and 79. It is only sketched here. $\gamma[\Psi]$ and $\gamma[\Phi_n]$ have a shared set of eigenvectors; therefore, we obtain for the Frobenius inner product

$$\langle\gamma[\Phi_n]|\gamma[\Psi]\rangle = \sum_p n_{p,n}\nu_p = s_n. \tag{A3}$$

This value is maximized if $(n_{0,p})_{p\in\mathbb{N}}$ are nonincreasing (simultaneous ordered spectral decomposition); therefore, $s_n \le s_0$. The equivalence of (ii) and (iii) is given by Eqs. (7) and (8). To prove the equivalence of (ii) and (iv), define the particle and hole expectation values as $N_n' = N - \langle\Psi|\hat{S}[\Phi_n]|\Psi\rangle = N - s_n$. With these definitions, we obtain $N_n' \le N_0' = N - s_0$. □

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