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N-density representability and the optimal transport limit of the Hohenberg-Kohn functional

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We derive and analyze a hierarchy of approximations to the strongly correlated limit of the Hohenberg-Kohn functional. These “density representability approximations” are obtained by first noting that in the strongly correlated limit, N -representability of the pair density reduces to the requirement that the pair density must come from a symmetric N -point density. One then relaxes this requirement to the existence of a representing symmetric k -point density with $k < N$. The approximate energy can be computed by simulating a fictitious k -electron system. We investigate the approximations by deriving analytically exact results for a 2-site model problem, and by incorporating them into a self-consistent Kohn-Sham calculation for small atoms. We find that the low order representability conditions already capture the main part of the correlations. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4821351>]

I. INTRODUCTION

Kohn-Sham (KS) density functional theory (DFT) is currently the most widely used *ab initio* electronic structure model which is applicable to large and complex systems ranging from condensed matter over surfaces to nanoclusters and biomolecules. With the advent of linear scaling algorithms, the key factor limiting the accuracy of predictions is the choice of underlying exchange-correlation functionals.^{5,27} These functionals model the correlation structure of the system as a universal functional of its underlying one-body density. While highly successful in many instances, these functionals exhibit known failures, like incorrect filling order and lack of binding of certain transition metal atoms,³³ doubtful equilibrium geometries of Carbon clusters,²² difficulties with dissociation curves far from equilibrium,³ and the inability of standard functionals to capture van der Waals forces (for recent progress regarding the latter issue see Ref. 17).

It has long been recognized that important insight can be gained by studying the asymptotic relationship between correlation structure and one-body density in scaling limits.¹⁸ In this paper, we focus on the strongly correlated limit of the exact Hohenberg-Kohn functional first investigated in Refs. 29–31 in which electron repulsion dominates over kinetic energy (yielding a natural counterpart to the Kohn-Sham kinetic energy functional¹⁶).

The resulting limit, which can be interpreted as an optimal transport problem,^{4,9} is still unwieldy from a computational point of view, since it requires the computation of the full N -point density of an N -electron system, a function on \mathbb{R}^{3N} . Here we give a simple but we believe fruitful reformulation as a minimization problem over 2-point densities subject to a representability constraint. This is similar to the well-known formulation of the full quantum N -body prob-

lem via representable 2-point density matrices,^{6,23} but there are two important differences. First, one only considers the 2-point density. And second, instead of working with the classical definition of N -representability of the pair density, i.e., existence of a representing antisymmetric spin-dependent N -electron wavefunction,¹⁰ in the context of the strictly correlated electrons (SCE) functional in which the kinetic energy has been eliminated it is appropriate to weaken this condition and only require representability by some symmetric N -point probability measure, a condition we term *density representability*. It is well known that classical (wavefunction) representability of pair densities is a highly nontrivial restriction^{2,10} and the same continues to hold for density representability; indeed the derivation of restrictions such as the Davidson¹⁰ or generalized Davidson² constraints in fact only uses density representability.

We then establish a natural hierarchy of necessary representability conditions, and investigate the accuracy of the resulting reduced models as compared to the full strongly correlated limit. We focus on two test cases: first, a simple but illuminating 2-site, N -particle model in which all representability conditions can be computed explicitly; and second, *ab initio* as well as self-consistent densities for the atoms He, Li, Be. A tentative conclusion is that the low order representability conditions already capture the main part of the correlations, at significantly reduced computational cost.

II. STRONGLY CORRELATED LIMIT OF THE HOHENBERG-KOHN FUNCTIONAL

The following counterpart to the Kohn-Sham kinetic energy functional was introduced in Ref. 29–31:

$$V_{\text{ee}}^{\text{SCE}}[\rho] = \inf_{\Psi \mapsto \rho} \langle \Psi | \widehat{V}_{\text{ee}} | \Psi \rangle. \quad (1)$$

Here the minimization is over electronic wavefunctions $\Psi = \Psi(\mathbf{x}_1, s_1, \dots, \mathbf{x}_N, s_N)$ which depend on N space and spin coordinates and belong to the usual space \mathcal{A}_N of square-integrable antisymmetric normalized wavefunctions with square-integrable gradient, and the notation $\Psi \mapsto \rho$ means that Ψ has single-particle density ρ . The acronym SCE stands for strictly correlated electrons.³⁰ Here we briefly review known theoretical properties of V_{ee}^{SCE} and previous approaches to compute it numerically.

Alternative constructions which plausibly yield the same functional are:

- (i) semiclassical limit of the Hohenberg-Kohn functional:

$$\lim_{\hbar \rightarrow 0} \min_{\Psi \mapsto \rho, \Psi \in \mathcal{A}_N} \langle \Psi | \hbar^2 \hat{T} + \hat{V}_{ee} | \Psi \rangle, \quad (2)$$

- (ii) minimization over spinless bosonic wavefunctions Φ :

$$\inf_{\Phi \mapsto \rho, \Phi \in \mathcal{B}_N} \langle \Phi | \hat{V}_{ee} | \Phi \rangle, \quad (3)$$

- (iii) minimization over N -point probability measures:

$$\min_{\rho_N \mapsto \rho, \rho_N \in \mathcal{P}_N^{\text{sym}}} \int_{\mathbb{R}^{3N}} V_{ee} \rho_N. \quad (4)$$

Here \mathcal{B}_N denotes the analogue of the space \mathcal{A}_N for spinless symmetric (bosonic) wavefunctions, $\mathcal{P}_N^{\text{sym}}$ stands for the set of symmetric probability measures on \mathbb{R}^{3N} , and \hat{V}_{ee} is the multiplication operator with the interaction potential

$$V_{ee}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_{1 \leq i < j \leq N} v_{ee}(\mathbf{x}_i, \mathbf{x}_j), \quad (5)$$

where $v_{ee}(\mathbf{x}, \mathbf{y}) = |\mathbf{x} - \mathbf{y}|^{-1}$.

Formulas (2) and (3) appear in Ref. 30, and (2) and (4) are implicit in Ref. 29.

The minimum value in (2) with $\hbar = 1$ is the exact Hohenberg-Kohn functional F^{HK} in the Levy-Lieb constrained search formulation; so expression (2) is the semiclassical limit of the Hohenberg-Kohn functional. Note that the Kohn-Sham kinetic energy functional T^{KS} is obtained from F^{HK} by instead retaining the kinetic energy operator \hat{T} and neglecting the interaction term \hat{V}_{ee} . Expression (3) is related to (1) by neglecting antisymmetry and spin, and to expression (4) by first noting that $\langle \Phi | \hat{V}_{ee} | \Phi \rangle = \int V_{ee} |\Phi|^2$ and then replacing squares of spinless symmetric wavefunctions by their mathematical ‘‘closure,’’ symmetric probability measures.

Equality between the four expressions (1)–(4) was conjectured in Ref. 30 and has recently been justified mathematically.⁷

The last expression, (4), has the form of an *optimal transport problem*, and has been studied from this point of view in Refs. 4 and 9. In the standard setting of such problems³² originating from economics, one has $N = 2$, $\rho_2(\mathbf{x}, \mathbf{y})$ corresponds to the amount of ‘‘mass’’ transported from \mathbf{x} to \mathbf{y} , $V_{ee}(\mathbf{x}, \mathbf{y})$ is the ‘‘cost’’ of this transport, the one-body densities of \mathbf{x} and \mathbf{y} would be different from each other but prescribed *a priori*, i.e., $\int \rho_2(\mathbf{x}, \mathbf{y}) \, d\mathbf{y} = \rho^A(\mathbf{x})$ and $\int \rho_2(\mathbf{x}, \mathbf{y}) \, d\mathbf{x} = \rho^B(\mathbf{y})$, and minimization of $\int V_{ee} \rho_2$ amounts to finding the most economical way of transporting the pile of mass ρ^A to ρ^B . In economics,

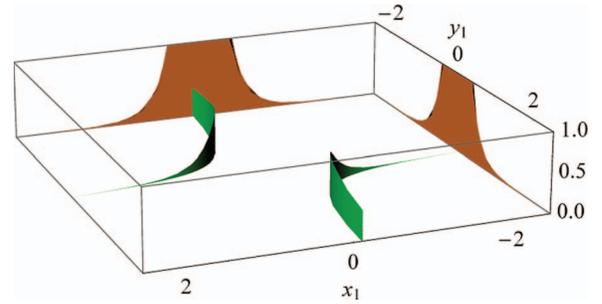


FIG. 1. Optimal pair density ρ_2 of Eq. (4) evaluated on $(x_1, 0, 0, y_1, 0, 0)$ (green) for one-body ground-state density ρ of helium (brown). The height of the green surface $(1 + |\nabla \mathbf{T}(\mathbf{x})|^2)^{-1/2} \rho(\mathbf{x})$ indicates the prefactor of the Hausdorff measure on the set $\mathbf{y} = \mathbf{T}(\mathbf{x})$.

the cost would typically increase rather than decrease with distance, prototypical examples being $|\mathbf{x} - \mathbf{y}|$ or $|\mathbf{x} - \mathbf{y}|^2$.

An interesting feature of minimizers is that they typically concentrate on lower dimensional sets (see Fig. 1). For $N = 2$, these sets have the form $\mathbf{y} = \mathbf{T}(\mathbf{x})$. Physically, this reflects the fact that given the position of the first electron, the position of the second electron becomes deterministic in the strongly correlated limit (1). When ρ is radially symmetric, \mathbf{T} is known explicitly in terms of the inverse of the radial distribution function $R \mapsto 4\pi \int_0^R r^2 \rho(r) \, dr$.^{4,9,29–31}

The minimization problem (4), and indeed any optimal transport problem, has two alternative formulations. To obtain the so-called Monge formulation, one makes the ansatz

$$\rho_N(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{\rho(\mathbf{x}_1)}{N} \delta(\mathbf{x}_2 - \mathbf{T}_2(\mathbf{x}_1)) \cdots \delta(\mathbf{x}_N - \mathbf{T}_N(\mathbf{x}_1)) \quad (6)$$

for transport maps or *co-motion functions* $\mathbf{T}_i : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ which preserves the one-body density ρ , that is to say $\int_{T(A)} \rho = \int_A \rho$ for general subsets $A \subset \mathbb{R}^3$ (see Refs. 9, 30, and 31 for physical and mathematical justifications). In fact, the ansatz (6) is not in general symmetric, so strictly speaking we should minimize over the symmetrizations of measures of form (6), but dropping the symmetrization does not alter the minimum value in (4). Or one passes to the so-called Kantorovich dual formulation

$$V_{ee}^{\text{SCE}}[\rho] = \sup_{u : \mathbb{R}^3 \rightarrow \mathbb{R}, \sum_i u(\mathbf{x}_i) \leq V_{ee}(\mathbf{x}_1, \dots, \mathbf{x}_N)} \int \rho u \quad (7)$$

(see Ref. 4 for a mathematical justification and Ref. 24 for a numerical scheme).

The Monge formulation amounts to a spectacular dimension reduction, in that the unknowns are N maps on \mathbb{R}^3 instead of one function on \mathbb{R}^{3N} . Thus, when discretizing \mathbb{R}^3 by K gridpoints one has $K \cdot 3N$ instead of K^N computational degrees of freedom. However, for $N > 2$ it is not clear if the (symmetrized) Monge formalism captures all minimizers of (4). See Sec. VIII for a counterexample when the Coulomb repulsion is replaced by a repulsive harmonic interaction. Moreover, previous numerical (and analytical) computation of V_{ee}^{SCE} using (6) is hitherto restricted to spherically symmetric densities or 1D systems. This is because one has to deal with the infinite-dimensional nonlinear constraint that the \mathbf{T}_i

preserve ρ , and because the \mathbf{T}_i are expected to jump along surfaces; in the radial case, the surfaces are believed to be concentric spheres.³⁰

The Kantorovich dual formulation, which has been successfully applied to non-spherical problems,²⁴ cures the high storage complexity of the original formulation (4), but the inequality constraint in (7) that needs to be satisfied by u is still high-dimensional.

It is then of interest to explore alternative ways of reducing the dimensionality of (1). The remainder of this paper is devoted to developing such an alternative approach, based on minimization over 2-point densities satisfying representability constraints.

III. N-DENSITY REPRESENTABILITY AND REDUCED DENSITY MODELS

We now derive a simple but we believe fruitful reformulation of the minimization problem (1). We begin by formalizing the notion of reduced densities. Throughout this section, it is useful to work with the convention that all densities and reduced densities integrate to 1. We denote k -point reduced densities with this normalization by p_k , to distinguish them from the customary k -point reduced densities ρ_k which integrate to the number of k -tuples in the system. Thus, given a symmetric N -point probability density p_N on \mathbb{R}^{3N} , $N \geq 2$, we define the associated one- and two-point reduced densities (known in probability theory under the name marginal densities) by

$$p_1(\mathbf{x}_1) = \int_{\mathbb{R}^{3(N-1)}} p_N(\mathbf{x}_1, \dots, \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N, \quad (8)$$

$$p_2(\mathbf{x}_1, \mathbf{x}_2) = \int_{\mathbb{R}^{3(N-2)}} p_N(\mathbf{x}_1, \dots, \mathbf{x}_N) d\mathbf{x}_3 \cdots d\mathbf{x}_N. \quad (9)$$

In particular, p_1 is related to the customary one-body density ρ by the formula $p_1 = \rho/N$.

Typical N -point densities occurring in the SCE limit concentrate on lower dimensional subsets (see Figure 1). Mathematically, this does not pose real difficulties (and is a higher dimensional analogue of the familiar charge distributions on surfaces in electrostatics). It just means that these densities should properly be regarded as probability measures on \mathbb{R}^{3N} , not functions, i.e., they are not specified by pointwise values but by their integrals over sets. In the more general setting of probability measures, (8) and (9) have to be replaced by

$$\int_A dp_1 = \int_{A \times \mathbb{R}^{3(N-1)}} dp_N, \quad (10)$$

$$\int_{A \times B} dp_2 = \int_{A \times B \times \mathbb{R}^{3(N-2)}} dp_N, \quad (11)$$

for any subsets $A, B \subset \mathbb{R}^3$.

The following definition is closely related to the classical definition of N -representability of the pair density, i.e., existence of an antisymmetric spin-dependent N -electron wavefunction giving rise to this pair density.¹⁰ However in the present context of the SCE functional, in which the kinetic energy has been eliminated and the relevant N -body problem is a minimization over a mathematical ‘‘closure’’ of squares

of N -electron wavefunctions (symmetric N -point probability measures, see (4)), it is appropriate to only require that the pair density must come from the latter. We employ the usual notation $p_{N \mapsto p_1}$ and $p_{N \mapsto p_2}$ for the validity of Eq. (8), respectively, (9).

Definition 3.1. (N-density representability) Let $N \geq 2$. A probability density (or probability measure) p_2 on \mathbb{R}^6 is called *N-density-representable* if there exists a symmetric probability measure p_N on \mathbb{R}^{3N} such that $p_{N \mapsto p_2}$.

Clearly, representability by an N -electron wavefunction implies N -density representability in the above sense. Conversely, most of the known necessary conditions on representability by an N -electron wavefunction, such as the Davidson¹⁰ and generalized Davidson² constraints, continue to hold for N -density representable pair densities, as their derivation in fact only uses N -density representability.

Examples. (1) It is clear that p_2 is 2-density representable if and only if it is symmetric. (2) Any statistically independent measure $p_2(\mathbf{x}, \mathbf{y}) = p_1(\mathbf{x})p_1(\mathbf{y})$ is N -density representable for all N , since it is represented by the N -body probability measure $p_1(\mathbf{x}_1) \cdots p_1(\mathbf{x}_N)$. (3) The totally anticorrelated probability measure

$$p_2(\mathbf{x}, \mathbf{y}) = \frac{1}{2}(\delta(\mathbf{x} - A)\delta(\mathbf{y} - B) + \delta(\mathbf{x} - B)\delta(\mathbf{y} - A)), \quad (12)$$

$A, B \in \mathbb{R}^3$, $A \neq B$ is 2-density representable, but not 3-density representable. That is to say, even though it is a symmetric probability measure on \mathbb{R}^6 , there does not exist any symmetric probability measure p_3 on \mathbb{R}^9 such that $\int p_3(\mathbf{x}, \mathbf{y}, \mathbf{z}) d\mathbf{z} = p_2(\mathbf{x}, \mathbf{y})$. The reason is explained in Sec. IV.

(4) The previous example can be turned into a smooth one (see Figure 2). The smooth pair density

$$p_2(\mathbf{x}, \mathbf{y}) = \frac{1}{2}(\varphi(\mathbf{x} - A)\varphi(\mathbf{y} - B) + \varphi(\mathbf{x} - B)\varphi(\mathbf{y} - A)) \quad (13)$$

with φ any non-negative function on \mathbb{R}^3 with $\int \varphi = 1$ and $\varphi(\mathbf{z}) = 0$ when $|\mathbf{z}| > |A - B|/2$, is not 3-density representable, as we will show in Sec. V.

The above definition immediately implies the following theorem.

Theorem 3.2. *Let $N > M \geq 2$. If a probability density (or probability measure) p_2 on \mathbb{R}^6 is N -density-representable, then it is also M -density-representable.*

In other words, N -density representability becomes a more and more stringent condition as N increases.

Proof. If p_N is a symmetric N -body density which represents p_2 , then

$$\begin{aligned} \tilde{p}(\mathbf{x}_1, \dots, \mathbf{x}_M) \\ = \int_{\mathbb{R}^{3(N-M)}} p_N(\mathbf{x}_1, \dots, \mathbf{x}_M, \dots, \mathbf{x}_N) d\mathbf{x}_{M+1} \cdots d\mathbf{x}_N \end{aligned}$$

is a symmetric M -body density which also represents p_2 . \square

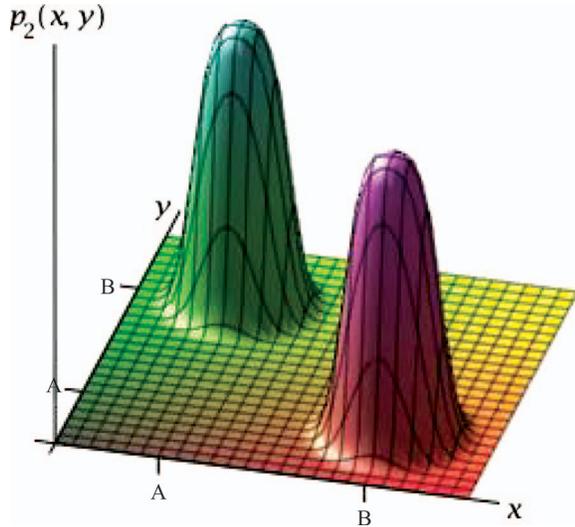


FIG. 2. Pair densities which are not 3-density-representable, such as the one depicted here (Eq. (13)), can be quite innocent looking. For further discussion of this example see Sec. V.

With the help of the concept of density representability, we can exploit the fact that the Coulomb potential V_{ee} in (4) only involves pair interactions to reformulate the many-body optimal transport definition (4) of V_{ee}^{SCE} as a standard (two-body) optimal transport problem with a constraint. This result does not depend on the Coulombic form of the interaction potential v_{ee} .

Theorem 3.3. (SCE energy via density representability) For any given single-particle density ρ of an N -electron system,

$$V_{ee}^{SCE}[\rho] = \min_{\substack{p_2 \mapsto \rho/N \\ p_2 \text{ } N\text{-density-rep.}}} \binom{N}{2} \int_{\mathbb{R}^6} v_{ee} p_2, \quad (14)$$

where v_{ee} is any pair potential which is symmetric (i.e., $v(\mathbf{x}, \mathbf{y}) = v(\mathbf{y}, \mathbf{x})$), and the minimization is over probability densities p_2 on \mathbb{R}^6 .

Here the appearance of the normalization constants N and $\binom{N}{2}$ is due to the fact that ρ integrates to N , not 1, whereas p_2 integrates to 1, not $\binom{N}{2}$.

Proof. The proof is similar to the famous proof of Levy of the Hohenberg-Kohn theorem. For any symmetric N -point density ρ_N with $\rho_N \mapsto \rho_2$, we clearly have

$$\int_{\mathbb{R}^{3N}} V_{ee} \rho_N = \binom{N}{2} \int_{\mathbb{R}^6} v_{ee} p_2; \quad (15)$$

that is to say the electron-electron energy only depends on the two-body reduced density of ρ_N . We can therefore usefully partition the minimization in (4) into a double minimization,

first over ρ_N subject to fixed p_2 , then over p_2 ,

$$\begin{aligned} \min_{\rho_N \mapsto \rho/N} \int V_{ee} \rho_N &= \min_{\substack{p_2 \mapsto \rho/N \\ p_2 \text{ } N\text{-density-rep.}}} \min_{\rho_N \mapsto p_2} \int V_{ee} \rho_N \\ &= \min_{\substack{p_2 \mapsto \rho/N \\ p_2 \text{ } N\text{-density-rep.}}} \binom{N}{2} \int v_{ee} p_2, \end{aligned}$$

the last equality being due to Eq. (15). \square

The formula for V_{ee}^{SCE} in Theorem 3.3 together with the necessary conditions for N -density representability in Theorem 3.2 immediately suggests a natural hierarchy of approximations. For any given single-particle density ρ of an N -electron system, let us define

$$\begin{aligned} V_{ee}^{SCE,k}[\rho] &= \min_{\substack{p_2 \mapsto \rho/N \\ p_2 \text{ } k\text{-density-rep.}}} \binom{N}{2} \int_{\mathbb{R}^6} v_{ee} p_2, \\ k &= 2, 3, \dots \end{aligned} \quad (16)$$

That is, we replace the requirement that p_2 be N -representable by the weaker requirement that it be k -representable for some $k \leq N$. This enlarges the set of admissible p_2 's in the minimization, leading to the following chain of inequalities:

$$\begin{aligned} V_{ee}^{SCE,2}[\rho] &\leq \dots \leq V_{ee}^{SCE,k}[\rho] \leq \dots \leq V_{ee}^{SCE,N}[\rho] \\ \parallel & & \parallel \\ \min_{p_2 \mapsto \rho/N} \int v_{ee} p_2 & & V_{ee}^{SCE}[\rho]. \end{aligned} \quad (17)$$

We call $V_{ee}^{SCE,k}$ the order- k approximation of the SCE energy. The lowest-order approximation $V_{ee}^{SCE,2}$ corresponds to solving a classical (two-body) optimal transport problem with Coulomb cost (yielding the functional introduced in Ref. 9 which we called $F^{OT}[\rho]$), whereas the order- N approximation $V_{ee}^{SCE,N}$ recovers the exact SCE energy. Physically, the intermediate functionals $V_{ee}^{SCE,k}$ can be thought of as reduced models for the energy of strongly correlated electrons which take into account k -body correlations.

The unknown in the order- k approximation is a k -body density, so the computational cost increases steeply with k ; e.g., discretizing each copy of \mathbb{R}^3 by K gridpoints leads to a K^k -point discretization for \mathbb{R}^{3k} . The practical value of our reduced models therefore depends strongly on whether low-order approximations are already capable of capturing the main part of the full SCE energy. A tentative answer is that they are, as we will document in Secs. IV and V.

Theoretically, the parameter k in (16) can also be chosen bigger than N . Remarkably, for the model densities (18) below, we find that the $k \rightarrow \infty$ limit leads to p_2 being simply the mean-field density. A general discussion of the large k limit will appear in Ref. 8.

Finally, we remark that density representability of a pair density is obviously a necessary condition for the familiar (wavefunction) representability of any two-body density matrix which gives rise to this pair density. Analyzing the relationship between this necessary condition and common representability conditions from density matrix theory such as the P , Q , and G conditions^{6,23} lies beyond the scope of this paper.

IV. MODEL PROBLEM: N PARTICLES OCCUPYING 2 SITES

In this section, we analyze a model system in which the particle positions are restricted to 2 sites, to gain basic insights into what it means for a pair density to be k -density representable and into how the resulting functionals (16) depend on k . The single-particle density of such a system has the form

$$\frac{\rho}{N} = (1-t)\delta_A + t\delta_B, \quad 0 \leq t \leq 1, \quad (18)$$

where N is the number of particles, and A and B are two different points in \mathbb{R}^3 . This model density, while of course very simplistic, can be regarded as a toy model for the electron density of a diatomic system in the regime when the interatomic distance is much larger than the atomic radii. If we do not want to allow fractional occupation numbers of the sites, t would be restricted to integer multiples of $1/N$, but since this makes little difference to the analysis, we might as well allow real occupation numbers.

Our first goal is to compute explicitly the set of N -representable 2-point probability measures for our 2-site system. The N -point probability measures on \mathbb{R}^{3N} whose single-particle density has the form (18) for some t are the measures of form

$$p_N = \sum_{I=(i_1, \dots, i_N) \in \{A, B\}^N} \alpha_I \delta_{i_1} \otimes \dots \otimes \delta_{i_N} \quad (19)$$

with $\alpha_I \geq 0$, $\sum_I \alpha_I = 1$, and correspond to the probability measures on the discrete 2-site, N -particle state space $\{A, B\}^N$. We use the following notation for the different sets of probability measures of interest: $\mathcal{P}(\{A, B\}^N)$ denotes the set of probability measures on $\{A, B\}^N$, i.e., all measures of form (19); $\mathcal{P}^{\text{sym}}(\{A, B\}^N)$ is the set of such measures which are *symmetric*, i.e., $\alpha_{(i_1, \dots, i_N)}$ is a symmetric function of its arguments (i_1, \dots, i_N) ; and $\mathcal{P}^{N\text{-rep}}(\{A, B\}^2)$ stands for the set of N -density-representable probability measures on the two-body state space $\{A, B\}^2$, i.e., those probability measures on $\{A, B\}$ which arise as marginals (9) of some $p_N \in \mathcal{P}^{\text{sym}}(\{A, B\}^N)$. In particular, the 2-density-representable probability measures are those measures of form

$$p_2 = \alpha_{AA}\delta_A \otimes \delta_A + \alpha_{BB}\delta_B \otimes \delta_B + \alpha_{AB}\delta_A \otimes \delta_B + \alpha_{BA}\delta_B \otimes \delta_A \quad (20)$$

which satisfy the trivial conditions of non-negativity, normalization, and symmetry,

$$\alpha_{ij} \geq 0 \text{ for all } i, j, \quad \sum_{i,j} \alpha_{ij} = 1, \quad \alpha_{AB} = \alpha_{BA}. \quad (21)$$

It is clear from the explicit representation (19) that $\mathcal{P}(\{A, B\}^N)$ is the convex hull of its extreme points $\delta_{i_1} \otimes \dots \otimes \delta_{i_N}$, $i_1, \dots, i_N \in \{A, B\}$. The set of symmetric N -point probability densities satisfies $\mathcal{P}^{\text{sym}}(\{A, B\}^N) = S_N \mathcal{P}(\{A, B\}^N)$, where S_N is the symmetrizer

$$(S_N p_N)(A_1 \times \dots \times A_N) = \frac{1}{N!} \sum_{\sigma} p_N(A_{\sigma(1)} \times \dots \times A_{\sigma(N)})$$

and the sum runs over all permutations. It follows that $\mathcal{P}^{\text{sym}}(\{A, B\}^N)$ is the convex hull of the elements $S_N \delta_{i_1} \otimes$

$\dots \otimes \delta_{i_N}$, and that $\mathcal{P}^{N\text{-rep}}(\{A, B\}^2)$ is the convex hull of their two-point densities,

$$\begin{aligned} \mathcal{P}^{N\text{-rep}}(\{A, B\}) &= \text{convex hull of the measures} \\ &= \left\{ p_2^{(S_N \delta_{i_1} \otimes \dots \otimes \delta_{i_N})}, i_1, \dots, i_N \in \{A, B\} \right\}, \end{aligned} \quad (22)$$

where here and below, $p_2^{(p_N)}$ denotes the two-particle density of p_N . To compute these two-point densities, we use an averaging formula which can be shown by an elementary computation: first symmetrizing and then taking the two-point density is the same as taking the average over all two-point densities,

$$p_2^{(S_N p_N)} = \frac{1}{\binom{N}{2}} \sum_{1 \leq i < j \leq N} \int p_N d\widehat{\mathbf{x}}_{ij}, \quad (23)$$

where $\widehat{\mathbf{x}}_{ij}$ denotes the list of coordinates $\mathbf{x}_1, \dots, \mathbf{x}_N$ with \mathbf{x}_i and \mathbf{x}_j omitted, and p_N is any N -point probability measure. Now consider a measure of form $p_N = \delta_{i_1} \otimes \dots \otimes \delta_{i_N}$, and let $K = \#\{i_j \mid i_j = B\}$, i.e., the occupation number of site B . Note $0 \leq K \leq N$. By the averaging formula (23), and using the abbreviated notation $\delta_i^K = \otimes_{i=1}^K \delta_i$,

$$\begin{aligned} p_2^{(S_N \delta_{i_1} \otimes \dots \otimes \delta_{i_N})} &= p_2^{(S_N \delta_A^{N-K} \otimes \delta_B^K)} \\ &= \frac{1}{\binom{N}{2}} \left[\binom{N-K}{2} \delta_A \otimes \delta_A + \binom{K}{2} \delta_B \otimes \delta_B \right. \\ &\quad \left. + \frac{K(N-K)}{2} (\delta_A \otimes \delta_B + \delta_B \otimes \delta_A) \right]. \end{aligned} \quad (24)$$

Note that the resulting two-point marginal does not depend on the i_j , but only on the occupation number $K \in \{0, \dots, N\}$. Equations (22) and (24) give the following final result.

Theorem 4.1. *The set of N -representable 2-point measures, $\mathcal{P}^{N\text{-rep}}(\{A, B\})$, is the convex hull of the $K+1$ measures given by the right-hand side of (24), where K runs from 0 to N .*

This set is plotted in Figure 3, for different values of N .

Next we show that, as suggested by Figure 3, when N gets large the $N+1$ extremal pair densities in (24) approach a certain very interesting continuous curve. To see this, let us re-write formula (24) in terms of the normalized occupation number $t = K/N \in [0, 1]$ instead of K , and separate the coefficients into N -independent and lower order terms. An elementary calculation shows that

$$\frac{K-1}{N-1} = t - \frac{1-t}{N-1}, \quad \frac{(N-K)-1}{N-1} = (1-t) - \frac{t}{N-1},$$

and, abbreviating $\delta_i \otimes \delta_j$ by δ_{ij} ,

$$\begin{aligned} p_2^{(S_N \delta_A^{N-K} \otimes \delta_B^K)} &= \underbrace{(1-t)^2 \delta_{AA} + t^2 \delta_{BB} + t(1-t)(\delta_{AB} + \delta_{BA})}_{=p_2^{(\infty)}} \\ &\quad + \frac{t(1-t)}{N-1} (-\delta_{AA} - \delta_{BB} + \delta_{AB} + \delta_{BA}). \end{aligned} \quad (25)$$

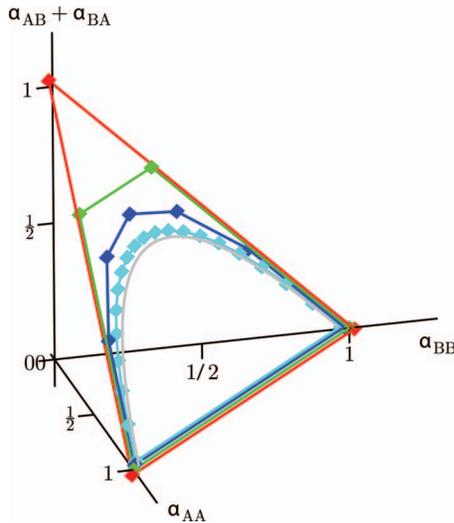


FIG. 3. The set of N -representable pair densities of form $\alpha_{AA}\delta_A\otimes\delta_A + \alpha_{AB}\delta_A\otimes\delta_B + \alpha_{BA}\delta_B\otimes\delta_A + \alpha_{BB}\delta_B\otimes\delta_B$ for $N = 2$ (red), $N = 3$ (green), $N = 6$ (blue), and $N = 20$ (light blue). The coefficient $\alpha_{AB} + \alpha_{BA}$ on the vertical axis indicates the weight of the anticorrelated contribution (12); its maximum representable value decreases with N . When $N = 2$, only the trivial conditions (21) are present. Remarkably, as N gets large the upper boundary of the representable set approaches the curve given by the mean field densities, i.e., $p_2 = p_1\otimes p_1$ for some p_1 (grey curve), see Eqs. (25) and (27).

But the first term is precisely the mean field approximation to the pair density of the state $S_N\delta_A^{N-K}\delta_B^K$ obtained from its single-particle density

$$p_1^{(S_N\delta_A^{N-K}\delta_B^K)} = (1-t)\delta_A + t\delta_B, \quad (26)$$

namely,

$$p_2^{(\infty)} = ((1-t)\delta_A + t\delta_B) \otimes ((1-t)\delta_A + t\delta_B). \quad (27)$$

The second term in (25) is a correlation correction which depletes the “ionic” terms $\delta_A\otimes\delta_A$ and $\delta_B\otimes\delta_B$ in favour of the “anticorrelated” terms $\delta_A\otimes\delta_B$ and $\delta_B\otimes\delta_A$. This correction is large for small N (and even completely removes the ionic terms when $N = 2$ and $t = 1/2$), but vanishes in the limit $N \rightarrow \infty$ at fixed occupation number t .

In particular, we have established the following.

Theorem 4.2. *A pair density of form (20) is N -representable for all N if and only if it lies in the convex hull of the mean field densities, or – by inspection of Figure 3 – if and only if it is a convex combination of two mean field densities.*

After completing the above (elementary) analysis, we learned that results similar to, and in fact much more general than, Theorems 4.1 and 4.2 are well known in probability theory, more precisely in the theory of “exchangeable sequences” of random variables.^{1,12} This theory, which appears to be hitherto disconnected from DFT (as well as wavefunction representability), entails a classification going back to de Finetti¹¹ of symmetric probability densities $p_\infty(\mathbf{x}_1, \mathbf{x}_2, \dots)$ in infinitely many variables.

The “primal” description of N -representable pair densities as the convex hull of explicit extreme points can be easily

turned into an equivalent “dual” description via inequalities. We only give the result in the cases $N = 3$ and $N = \infty$.

Corollary 4.3. *A pair density of form (20) is 3-representable if and only if it satisfies (21) and the linear inequality*

$$\alpha_{AB} + \alpha_{BA} \leq 2(\alpha_{AA} + \alpha_{BB}), \quad (28)$$

and N -representable for all N if and only if it satisfies (21) and the nonlinear inequality

$$\alpha_{AB} + \alpha_{BA} \leq 2\sqrt{\alpha_{AA} \cdot \alpha_{BB}}. \quad (29)$$

To derive (29), one first infers from Figure 3 that for a pair density p_2 satisfying (20)–(21), N -density representability for all N is equivalent to the inequality

$$\alpha_{AB} + \alpha_{BA} \leq \alpha_{AB}^{\text{MF}} + \alpha_{BA}^{\text{MF}}, \quad (30)$$

where the mean field coefficients α_{ij}^{MF} correspond to the mean field pair density $p_1\otimes p_1$, $p_1(x) = \int p_2(x, y) dy$. It is straightforward to calculate the mean field coefficients from the above definition; one finds $\alpha_{AB}^{\text{MF}} + \alpha_{BA}^{\text{MF}} = 2(\alpha_{AA} + \alpha_{AB})(\alpha_{BA} + \alpha_{BB})$. Hence letting $\gamma := \alpha_{AB} + \alpha_{BA}$ and using (21), Eq. (30) is equivalent to $\gamma \leq (\alpha_{AA} + \gamma/2)(\alpha_{BB} + \gamma/2)$. This is a quadratic inequality for γ and solving it yields (29).

The physical meaning of Eq. (28) is that at most 2/3 of the mass of p_2 can sit on the non-ionic configurations (A, B) and (B, A). The meaning of Eq. (29) is that the total size of the non-ionic contributions cannot exceed its size in the mean field pair density formed from its single-particle density.

The above results can be used to determine the hierarchy of approximate N -particle functionals $V_{\text{ee}}^{\text{SCE},k}$ introduced in (16) on densities of the form (18). In fact, the exact Coulomb potential $v_{\text{ee}}(\mathbf{x}, \mathbf{y}) = |\mathbf{x} - \mathbf{y}|^{-1}$ no longer makes sense in the context of these model densities since multiply occupied sites would lead to infinite energy, so we replace it by an appropriately regularized interaction, with the property that

$$\begin{aligned} v_{\text{ee}}(A, A) &= v_{\text{ee}}(B, B) = U_{\text{diag}} \\ &> U_{AB} = v_{\text{ee}}(A, B) = v_{\text{ee}}(B, A). \end{aligned} \quad (31)$$

Here U_{diag} and U_{AB} are effective parameters for same-site and different-site repulsion, and the inequality $U_{\text{diag}} > U_{AB}$ preserves the repulsive effect that the interaction potential decreases with interparticle distance. Hence the two-point densities p_2 which compete in the variational definition (16) prefer the different-site configurations $(\mathbf{x}, \mathbf{y}) = (A, B)$ and $(\mathbf{x}, \mathbf{y}) = (B, A)$ over the ionic configurations (A, A) and (B, B) . Consequently, the optimizing p_2 's with one-point density (18) are those k -representable 2-point densities of form (20) which have one-point density ρ_t (this fixes their position in direction of the baseline in Figure 3, because $t = \frac{1}{2}(\alpha_{BB} - \alpha_{AA})$) which maximize the coefficient $\alpha_{AB} + \alpha_{BA}$, i.e., lie on the upper boundary of the representable set in Figure 3. When t is an integer multiple of $1/k$, i.e., $t = K/k$, $K = 0, 1, \dots, k$, the optimizing p_2 is thus precisely given by formula (25) with N replaced by k . It follows that, denoting the density ρ defined

by (18) by ρ_t ,

$$V_{\text{ee}}^{\text{SCE},k}[\rho_t] = \binom{N}{2} (U_{\text{diag}} \cdot [t^2 + (1-t)^2] + U_{AB} \cdot 2t(1-t)) - \binom{N}{2} (U_{\text{diag}} - U_{AB}) \frac{2t(1-t)}{k-1},$$

$$t = K/k, \quad K = 0, 1, \dots, k. \quad (32)$$

For intermediate occupation numbers t with $t_- = (K-1)/k < t < K/k = t_+$, $K = 1, 2, \dots, k$, the upper boundary of the k -representable set is given by the linear interpolation between the p_2 's coming from t_- and t_+ , and hence so is the resulting value of $V_{\text{ee}}^{\text{SCE},k}$. The weights of the contributions from t_{\pm} are the same as the interpolation weights for the single-particle density, $\rho_t = (K-kt)\rho_{t_-} + (kt - (K-1))\rho_{t_+}$, and so

$$V_{\text{ee}}^{\text{SCE},k}[\rho_t] = (K-kt)V_{\text{ee}}^{\text{SCE},k}[\rho_{(K-1)/k}] + (kt - (K-1))V_{\text{ee}}^{\text{SCE},k}[\rho_{K/k}],$$

$$\frac{K-1}{k} \leq t \leq \frac{K}{k}, \quad K = 1, \dots, k. \quad (33)$$

The reduced SCE energies (32) and (33) are plotted in Figure 4, for different values of k .

Finally, let us calculate and physically interpret the large- k limit. It is clear from our explicit results that the limit is just given by the first part of the right hand side of Eq. (32). This part is nothing but a (Hartree-type) mean field energy,

$$\lim_{k \rightarrow \infty} V_{\text{ee}}^{\text{SCE},k}[\rho_t] = \binom{N}{2} \int v_{\text{ee}} \frac{\rho_t}{N} \otimes \frac{\rho_t}{N} = (1 - \frac{1}{N}) J[\rho_t],$$

$$J[\rho] = \frac{1}{2} \int v_{\text{ee}}(\mathbf{x}, \mathbf{y}) \rho(\mathbf{x}) \rho(\mathbf{y}) \, \text{d}\mathbf{x} \, \text{d}\mathbf{y}. \quad (34)$$

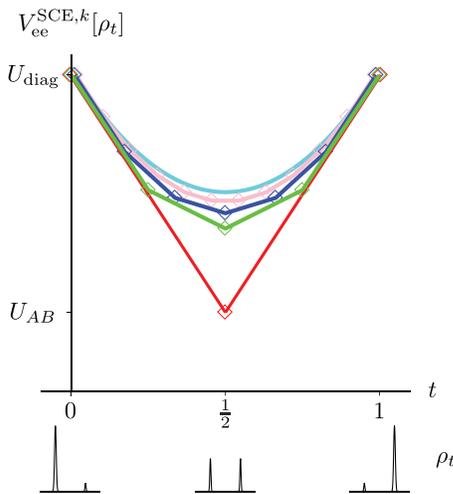


FIG. 4. Density-representability approximation of order k to $V_{\text{ee}}^{\text{SCE}}$, on densities of form $\rho_t/N = (1-t)\delta_A + t\delta_B$ (various values of k). The Coulomb interaction has been replaced by the regularized interaction (31). Red, green, blue, and pink corresponds to $k = 2, 4, 6, 11$. The piecewise linear structure is an exact feature of the results (32) and (33). The order- k approximation equals the exact $V_{\text{ee}}^{\text{SCE}}$ for $k = N$ particles. Light blue curve: mean field energy (see text).

Here the prefactor $1 - \frac{1}{N}$ is a self-interaction correction, i.e., the approximation via density representability of infinite order remembers that there are only $\binom{N}{2}$ interaction terms, not $N^2/2$. In other words, remarkably, *the infinite-order approximation to the SCE functional is nothing but the self-interaction-corrected mean field energy*, even though mean field approximations played no role in the construction of the reduced SCE functionals (16). As shown in Ref. 8, Eq. (34) remains valid for general densities ρ on \mathbb{R}^3 , and the true Coulombic SCE functionals (16).

In the two-site problem, one can go beyond the leading order term and immediately extract an expansion in the approximation parameter k . Equations (32) and (33) together with the fact that for any smooth function of t , $0 \leq t \leq 1$, the piecewise linear interpolation of the values on a mesh of size $1/k$ is accurate to order $1/k^2$ yield

$$V_{\text{ee}}^{\text{SCE},k}[\rho_t] = (1 - \frac{1}{N}) J[\rho_t] - \binom{N}{2} \left[\frac{1}{k-1} \frac{1}{N^2} C[\rho_t] + \mathcal{O}(\frac{1}{k^2}) \right], \quad (35)$$

where

$$C[\rho_t] = \int_A \rho_t \cdot \int_B \rho_t \cdot \int v_{\text{ee}} (\delta_{AA} + \delta_{BB} - \delta_{AB} - \delta_{BA}) = N^2 t(1-t) \cdot 2(U_{\text{diag}} - U_{AB}).$$

The latter is a correlation correction reflecting ionicity avoidance and $\mathcal{O}(1/k^2)$ denotes terms bounded by an N -independent constant times $1/k^2$.

As a special case, by setting $k = N$ we obtain a large- N expansion of the SCE energy at fixed density profile $\rho_t/N = (1-t)\delta_A + t\delta_B$,

$$V_{\text{ee}}^{\text{SCE},k}[\rho_t] = J[\rho_t] - \frac{1}{N} \left(J[\rho_t] + \frac{1}{2} C[\rho_t] \right) + \mathcal{O}(1). \quad (36)$$

The first term, of order N^2 , is the mean-field energy. At next order, N , one has two terms, a self-interaction correction and a true correlation correction. The leading order term also emerges in many other large- N limits, such as strictly correlated uniform electron droplets²⁸ (which correspond to replacing our two-site density by a homogeneous density in a ball), Thomas-Fermi theory,¹⁹ or the free electron gas.¹³ Generalizing the corrections lies beyond our scope.

V. NECESSARY CONDITIONS FOR DENSITY-REPRESENTABILITY

The results on two-state systems in Sec. IV immediately yield *novel* necessary conditions on N -density representability for general pair densities p_2 on \mathbb{R}^6 . For known necessary conditions see, e.g., Refs. 2 and 10. To describe the novel conditions, let us introduce the following integrals of p_2 associated with any partitioning of \mathbb{R}^3 into two disjoint subsets Ω_A and Ω_B :

$$\alpha_{ij} = \int_{\Omega_i \times \Omega_j} p_2, \quad i, j \in \{A, B\}. \quad (37)$$

Theorem 5.1. *Let p_2 be any pair density (or measure) on \mathbb{R}^6 , normalized so that $\int p_2 = 1$. If p_2 is N -density-representable, and Ω_A, Ω_B is any partitioning of \mathbb{R}^3 into two*

subsets, then the associated 2-site pair density

$$\alpha_{AA}\delta_{AA} + \alpha_{AB}\delta_{AB} + \alpha_{BA}\delta_{BA} + \alpha_{BB}\delta_{BB}, \quad (38)$$

with α_{ij} as in (37), is also N -representable, that is to say it belongs to the set $\mathcal{P}^{N\text{-rep}}(\{A, B\})$ computed explicitly in Theorem 4.1 and depicted in Figure 3.

Proof. If p_N is an N -point density (or measure) on \mathbb{R}^{3N} which represents p_2 , then the associated 2-site, N -point density

$$\sum_{i_1, \dots, i_N \in \{A, B\}} \alpha_{i_1 \dots i_N} \delta_{i_1} \otimes \dots \otimes \delta_{i_N} \text{ with} \\ \alpha_{i_1 \dots i_N} = \int_{\Omega_{i_1} \times \dots \times \Omega_{i_N}} p_N, \quad (39)$$

represents the 2-site pair density (38). \square

Example. The smooth anticorrelated pair density (13) in example 4 of Sec. III (see Figure 2) is not 3-representable: choose Ω_A, Ω_B to be the half-spaces of \mathbb{R}^3 whose boundary bisects the line segment from A to B , that is to say $\Omega_A = \{\mathbf{x} \in \mathbb{R}^3 \mid \mathbf{x} \cdot (B - A) \leq M \cdot (B - A)\}$, $\Omega_B = \{\mathbf{x} \in \mathbb{R}^3 \mid \mathbf{x} \cdot (B - A) > M \cdot (B - A)\}$, where $M = (A + B)/2$. By construction, in this case $\alpha_{AA} = \alpha_{BB} = 0$, $\alpha_{AB} = \alpha_{BA} = 1$, so the associated 2-site pair density (38) is not 3-density representable, as shown in Sec. IV (see Figure 3).

In fact, for $N = 3$, the dual description (28) of the N -representable pair densities for the 2-site system yields the necessary condition of Theorem 5.1 directly in the form of the following inequality

$$\int_{\Omega_A \times \Omega_B} p_2 + \int_{\Omega_B \times \Omega_A} p_2 \leq 2 \left(\int_{\Omega_A \times \Omega_A} p_2 + \int_{\Omega_B \times \Omega_B} p_2 \right). \quad (40)$$

Physically, this condition says that the total probability to find a particle pair in the ‘‘anticorrelated’’ regions $\Omega_A \times \Omega_B$ and $\Omega_B \times \Omega_A$ can be at most twice as large as the probability to find a pair in the ‘‘ionic’’ regions $\Omega_A \times \Omega_A$ and $\Omega_B \times \Omega_B$.

VI. BEHAVIOUR OF THE REDUCED MODELS ON *AB INITIO* DENSITIES FOR SMALL ATOMS

We now investigate the effect of the hierarchy of representability conditions (Sec. III) for the atoms He, Li, and Be. The *ab initio* single electron density ρ is obtained from a full configuration interaction (FCI) calculation with Slater-type orbitals (STOs).¹⁴ The approximate interaction energy $V_{ee}^{\text{SCE},k}$ of an N -electron system can be obtained by simulating a fictitious k -electron system: directly from Eq. (16), we have

$$V_{ee}^{\text{SCE},k}[\rho] = \binom{N}{k} V_{ee}^{\text{SCE}} \left[\frac{k}{N} \rho \right]. \quad (41)$$

The energy on the right hand side is obtained by the same method as in Ref. 30; in particular, the jump surfaces of the maps \mathbf{T}_i in (6) are assumed to be concentric spheres.

Fig. 5 compares the k -density representability approximation $V_{ee}^{\text{SCE},k}[\rho]$ with $V_{ee}^{\text{SCE}}[\rho]$, with the ‘‘exact’’ value from the FCI calculation, and the Hartree term J . V_{ee}^{SCE} underestimates the exact value, whereas J overestimates it. The order- k

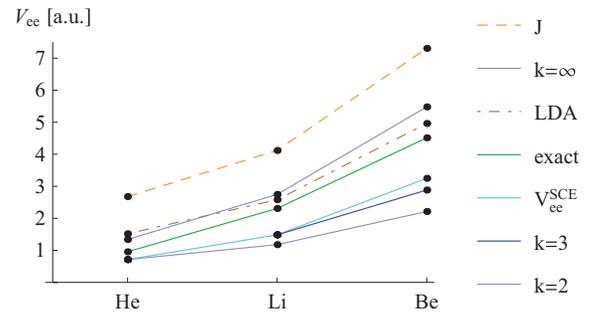


FIG. 5. $V_{ee}^{\text{SCE},k}[\rho]$ obtained by the k -density representability approximation (blue, formula (16)) and the true $V_{ee}^{\text{SCE}}[\rho]$ (cyan) which corresponds to $k = N$. The limit $k = \infty$ is calculated by using Eq. (34). The green curve shows the ‘‘exact’’ $\langle \Psi | V_{ee} | \Psi \rangle$ within a STO FCI ansatz space. The mean-field Hartree term J (orange dashed) overestimates the exact value, as expected. See Table I for the numerical values.

approximation is already reasonably close to V_{ee}^{SCE} . The corresponding numerical values are summarized in Table I.

VII. A SELF-CONSISTENT KOHN-SHAM COMPUTATION COMPARING EXACT AND REDUCED SCE

The SCE formalism has the potential to become an important ingredient in the design of exchange-correlation functionals for strongly correlated electron systems. Thus, we investigate the SCE approach in the context of a Kohn-Sham self-consistent field calculation for atoms with the total energy functional

$$E[\rho] = T_{\text{KS}}[\rho] + V_{ee}^{\text{SCE},k}[\rho] + \int v_{\text{ext}}(\mathbf{x}) \rho(\mathbf{x}) \, \text{d}\mathbf{x}. \quad (42)$$

Here T_{KS} is the Kohn-Sham kinetic energy functional, and v_{ext} is the external nuclear potential. Previous self-consistent field calculations with the SCE functional were carried out in Refs. 20, 21, and 24 for a 1D quantum wire, where in the weak confinement regime the SCE functional becomes asymptotically exact. For 3D atomic systems considered here, replacing $J + E_{\text{xc}}$ by $V_{ee}^{\text{SCE},k}$ (or even by the exact SCE functional V_{ee}^{SCE}) presumably does not yield physically accurate results due to the missing influence of kinetic energy on ρ_2 , but our calculations illustrate the effect of the k -density approximation.

TABLE I. The calculated values of $V_{ee}^{\text{SCE},k}$ using the k -density representability approximation (see also Fig. 5). Each diagonal entry is the true V_{ee}^{SCE} (boldface). An ‘‘exact’’ (FCI) value and the Hartree term J are also shown, for comparison.

| | He | Li | Be |
|---------|-----------------|----------------|----------------|
| $k = 2$ | 0.711906 | 1.17881 | 2.21361 |
| $k = 3$ | | 1.48426 | 2.88229 |
| $k = 4$ | | | 3.24853 |
| Exact | 0.954988 | 2.30755 | 4.51366 |
| J | 2.67842 | 4.11866 | 7.30589 |

The Kohn-Sham equations define a nonlinear eigenvalue problem

$$H[\rho]\psi_i = \varepsilon_i \psi_i, \quad (43)$$

$$\rho(\mathbf{x}) = \sum_{i=1}^N |\psi_i(\mathbf{x})|^2, \quad \int \psi_i(\mathbf{x})^* \psi_j(\mathbf{x}) \, d\mathbf{x} = \delta_{ij}, \quad (44)$$

where the Hamiltonian $H[\rho]$ itself depends on the density ρ . For an atom with nuclear charge Z , and the density functional (42) with $k = N$ (exact SCE), the single-particle Hamiltonian (in atomic units) reads

$$H[\rho] = -\frac{1}{2}\Delta - \frac{Z}{|\mathbf{x}|} + u[\rho]. \quad (45)$$

The term $-\frac{1}{2}\Delta - Z/|\mathbf{x}|$ is the hydrogen-like single-particle Hamiltonian, and $u[\rho]$ is the Kantorovich potential, i.e., the maximizer of (7), which enters because formally,

$$\frac{\delta V_{\text{ee}}^{\text{SCE}}[\rho]}{\delta \rho} = u[\rho]. \quad (46)$$

Note that changing the potential in (45) by an additive constant would not change the Kohn-Sham orbitals, nor the functional derivative relation (46), because $\int (\delta V_{\text{ee}}^{\text{SCE}}/\delta \rho)[\rho](\mathbf{x})\delta \rho(\mathbf{x}) \, d\mathbf{x} = \frac{d}{dt} \delta V_{\text{ee}}^{\text{SCE}}[\rho + t \delta \rho]|_{t=0}$ is only defined for variations $\delta \rho$ with $\int \delta \rho = 0$, hence specifying the functional derivative only up to an additive constant. Choosing precisely $u[\rho]$ corresponds to the standard duality relation (7) that the minimum value of (4) equals the maximum value of the dual problem. This choice has the consequence that the Kohn-Sham eigenvalues sum to the system energy $E[\rho]$, as is easily inferred from (7) and (43).

The Kantorovich potential agrees up to an additive constant and a minus sign with the effective SCE potential $v_{\text{SGS}}[\rho]$ constructed by Seidl, Gori-Giorgi, and Savin in Ref. 30. More precisely, $u[\rho] = v[\rho] + C = -v_{\text{SGS}}[\rho] + C$, where v is defined by³⁰

$$\nabla v[\rho](\mathbf{x}) = -\sum_{i=2}^N \frac{\mathbf{x} - \mathbf{T}_i(\mathbf{x})}{|\mathbf{x} - \mathbf{T}_i(\mathbf{x})|^3}, \quad \lim_{|\mathbf{x}| \rightarrow \infty} v[\rho](\mathbf{x}) = 0. \quad (47)$$

The \mathbf{T}_i are the transport maps in Eq. (6), which determine the positions of the remaining electrons given the position of the first electron, and solely depend on the density ρ . The additive constant is easily obtained from (7): $u[\rho] = v[\rho] + C$ with

$$NC = \int \frac{\rho(\mathbf{x})}{N} \sum_{i < j} \frac{1}{|\mathbf{T}_i(\mathbf{x}) - \mathbf{T}_j(\mathbf{x})|} \, d\mathbf{x} - \int \rho(\mathbf{x})v[\rho](\mathbf{x}) \, d\mathbf{x}. \quad (48)$$

Following Ref. 30, we assume on physical grounds that

$$v[\rho](\mathbf{x}) \sim \frac{N-1}{|\mathbf{x}|} \quad \text{as } |\mathbf{x}| \rightarrow \infty, \quad (49)$$

even though we do not know of a mathematical proof. The physical picture of (49) is that – as one electron goes to infinity – the optimal transport maps keep the remaining $N-1$ electrons within a bounded volume. For charge-neutral atoms

with $N = Z$, the Hamiltonian (45) can be re-written as

$$H[\rho] = -\frac{1}{2}\Delta - \frac{1}{|\mathbf{x}|} + C + \left(v[\rho](\mathbf{x}) - \frac{N-1}{|\mathbf{x}|} \right), \quad (50)$$

such that the last term is expected to decay faster than $1/|\mathbf{x}|$ due to the asymptotic relation (49).

Fig. 6 shows the self-consistent densities and corresponding SCE potential v of helium, lithium and beryllium, for the exact SCE potential as well as its k -density approximation (obtained from simulating a fictitious k -electron system, see Sec. VI). All densities are normalized to N . For each k , by formula (41) the associated potential $v_k = \frac{\delta V_{\text{ee}}^{\text{SCE},k}}{\delta \rho}$ is given by $\binom{N}{2} \binom{k}{2}^{-1} \frac{k}{N} v[\rho] = \frac{N-1}{k-1} v[\rho]$, where $v[\rho]$ is the potential from the underlying k -body problem. Note that v_k shares the correct asymptotics (49). Table II summarizes the numerical Kohn-Sham energy (sum of Kohn-Sham eigenvalues; for helium and beryllium all orbitals are doubly occupied due to spin). Note that the k -density representability approximation of the energy is below the true value and increases with k . The densities are remarkably insensitive to the k -density representability approximation. We have chosen small neutral atoms due to their relevance in chemistry, but one might expect the impact of the approximation to be larger for more strongly correlated systems.

VIII. EXAMPLE OF A MINIMIZING N -POINT DENSITY NOT OF SCE FORM

Since much of the theoretical and numerical work on the minimization problem (4) relies on the (plausible but nontrivial) ansatz (6), it is of interest to understand its precise status with respect to minimization over arbitrary N -point probability measures.

For $N = 2$ the ansatz is known to be exact, in the sense that the minimizing 2-point probability measure is unique and of the form (6) (Ref. 9, following earlier work¹⁵ in the optimal transportation literature on pair interactions v_{ee} which increase with interparticle distance).

For $N > 2$, physical arguments³⁰ suggest that there should always exist a minimizing N -point probability measure of this form, so in particular restricting the minimization in (4) to ρ_N 's of form (6) should always give the correct value of the functional $V_{\text{ee}}^{\text{SCE}}[\rho]$, but there is no rigorous proof of this conjecture.

Finally, there is the question whether for $N > 2$, the ansatz (6) yields *all* solutions. Here we are not aware of any convincing arguments (be they physical or mathematical), one way or the other. The following counterexample demonstrates that for $N > 2$, (6) does *not* yield all solutions if the Coulomb interaction is replaced by a negative harmonic oscillator interaction. This is a new and somewhat surprising effect which only appears when $N > 2$; for $N = 2$ the negative harmonic interaction was already considered^{4,30} in connection with the SCE functional and the two interactions were shown to behave in exactly the same way.

The counterexample is best discussed in the context of recent work in the optimal transport literature on N -body optimal transport problems in \mathbb{R}^{dN} with a general non-negative

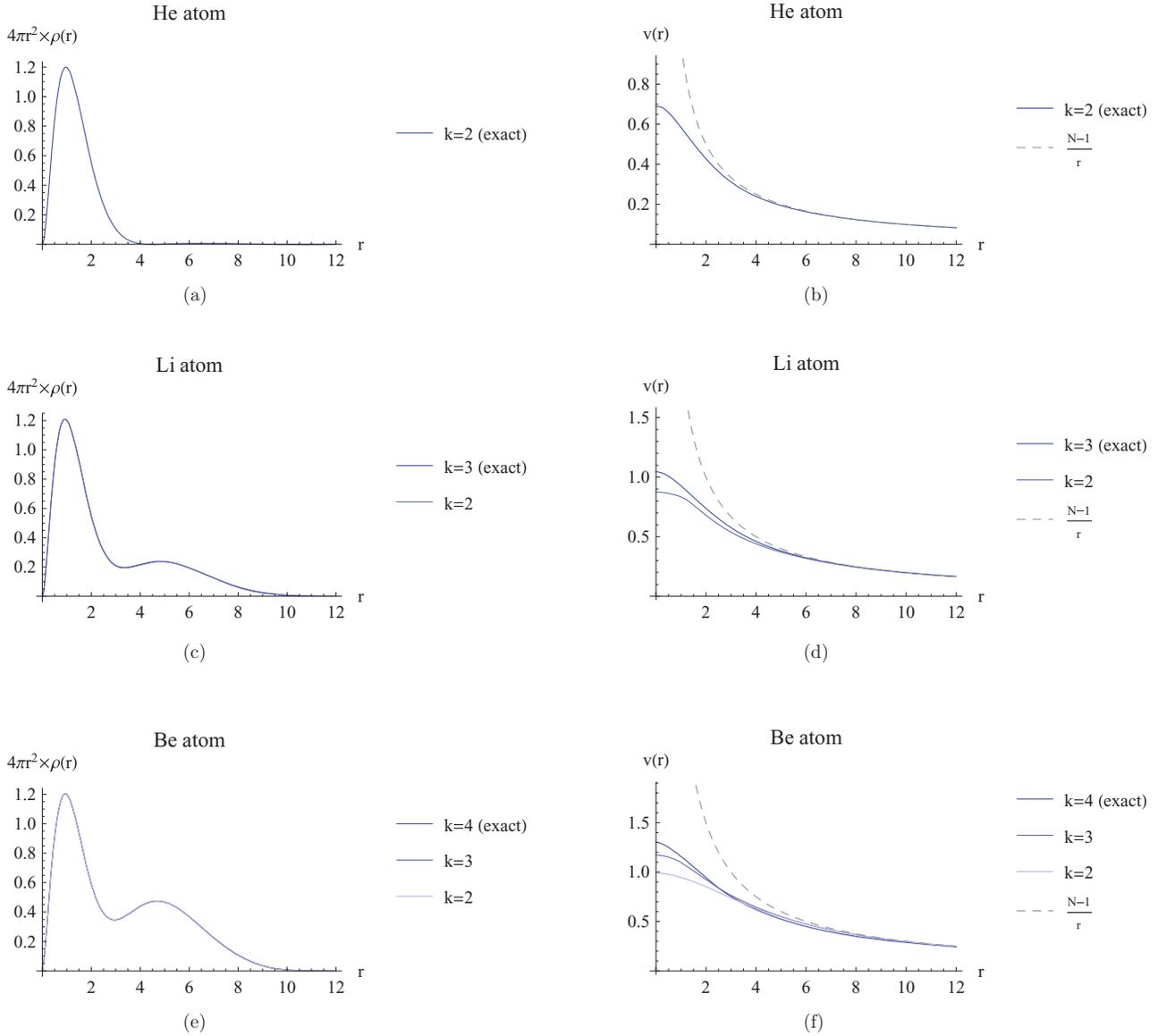


FIG. 6. (a), (c), and (e) Radial part of the self-consistent density (blue) for the helium, lithium, and beryllium atom with the SCE exchange-correlation functional $E_{xc} = V_{ee}^{\text{SCE},k} - J$. The lighter blue curves correspond to the k -density representability approximation, and are visually indiscernible from the (exact) $k = N$ case. (b), (d), and (f) The shifted Kantorovich potential $v_k[\rho] = \delta V_{ee}^{\text{SCE},k}[\rho]/\delta\rho$ (blue) corresponding to the self-consistent density on the left. The gray dashed line shows the asymptotic expansion $\frac{N-1}{|x|}$ in Eq. (49).

interaction potential or “cost function” $V_{ee}(\mathbf{x}_1, \dots, \mathbf{x}_N)$,

$$\min_{\rho_N \mapsto \rho} \int_{\mathbb{R}^{dN}} V_{ee} \rho_N,$$

where the minimization is over N -point probability measures on \mathbb{R}^{dN} . As shown in Ref. 25, minimizers have to concentrate

TABLE II. Kohn-Sham energy (sum of eigenvalues) obtained by a self-consistent field iteration with the SCE Kantorovich potential and Hamiltonian in Eq. (50). For comparison, “exact” values obtained by a FCI calculation¹⁴ are also shown.

| | He | Li | Be |
|---------|----------|----------|-----------|
| $k = 2$ | -2.74058 | -5.24439 | -8.12061 |
| $k = 3$ | | -5.10739 | -7.90984 |
| $k = 4$ | | | -7.79889 |
| “Exact” | -2.89703 | -7.41385 | -14.57946 |

on subsets whose dimension is bounded in terms of the *signatures* (the number of positive, negative, and zero eigenvalues) of certain symmetric matrices derived from the mixed second order partial derivatives of V_{ee} . Let G be the off diagonal part of the Hessian of V_{ee} . More explicitly, if

$$D_{\mathbf{x}_i \mathbf{x}_j}^2 V_{ee} = \left(\frac{\partial^2 V_{ee}}{\partial x_i^\alpha \partial x_j^\beta} \right)_{\alpha\beta}$$

denotes the $d \times d$ matrix of mixed second order partials with respect to $\mathbf{x}_i \in \mathbb{R}^d$ and $\mathbf{x}_j \in \mathbb{R}^d$, we have

$$G = \begin{bmatrix} 0 & D_{\mathbf{x}_1 \mathbf{x}_2}^2 V_{ee} & \dots & D_{\mathbf{x}_1 \mathbf{x}_m}^2 V_{ee} \\ D_{\mathbf{x}_2 \mathbf{x}_1}^2 V_{ee} & 0 & \dots & D_{\mathbf{x}_2 \mathbf{x}_m}^2 V_{ee} \\ \vdots & \vdots & 0 & \vdots \\ D_{\mathbf{x}_m \mathbf{x}_1}^2 V_{ee} & D_{\mathbf{x}_m \mathbf{x}_2}^2 V_{ee} & \dots & 0 \end{bmatrix}. \quad (51)$$

Note that G is a block matrix; each entry in the preceding formula denotes a $d \times d$ block. Now, as a symmetric $Nd \times Nd$ matrix, G has Nd real eigenvalues, counted with multiplicities. Let λ_+ , λ_- , and λ_0 denote, respectively, the number of positive, negative, and zero eigenvalues of G at some point $x = (\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \in \mathbb{R}^{Nd}$; note that $\lambda_+ + \lambda_- + \lambda_0 = Nd$. Then, near x , Theorem 2.3 in Ref. 25 implies that the *support* of minimizers (the subset on which they are nonzero) is contained in a subset of dimension $\lambda_0 + \lambda_-$.

For the Coulomb interaction $\sum_{i < j} |\mathbf{x}_i - \mathbf{x}_j|^{-1}$, a straightforward calculation implies that

$$D_{\mathbf{x}_i \mathbf{x}_j}^2 V_{\text{ee}} = \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|^3} \left(I - \frac{3}{|\mathbf{x}_i - \mathbf{x}_j|^2} (\mathbf{x}_i - \mathbf{x}_j)(\mathbf{x}_i - \mathbf{x}_j)^T \right),$$

where I is the $d \times d$ identity matrix. The signature of G , however, may change depending on the point \mathbf{x} . One can show that (except at special points) $d \leq \lambda_0 + \lambda_- \leq (N-1)d$, meaning that the dimension of the support of the solution can be no more than $(N-1)d$. In particular, for $N=2$, this yields an alternative justification of the ansatz (6).

While the preceding result is only an upper bound on the dimension, it is nevertheless a useful guideline for constructing high-dimensional minimizers, since the G -matrix of the cost must then necessarily have a large number of nonpositive eigenvalues.

For ease of analysis of the G -matrix, consider now a cost of pair potential form, Eq. (5), with v_{ee} symmetric and quadratic. The $d \times d$ block $D_{\mathbf{x}_i \mathbf{x}_j}^2 V_{\text{ee}}$ is then independent of i , j , and \mathbf{x} , and the signatures of G can be computed explicitly. The maximum number of nonpositive eigenvalues occurs for the negative harmonic oscillator interaction

$$v_{\text{ee}}(\mathbf{x}_i, \mathbf{x}_j) = -|\mathbf{x}_i - \mathbf{x}_j|^2. \quad (52)$$

In this case each $D_{\mathbf{x}_i \mathbf{x}_j}^2 V_{\text{ee}} = 2I$, and

$$G = \begin{bmatrix} 0 & 2I & \dots & 2I \\ 2I & 0 & \dots & 2I \\ \vdots & \vdots & 0 & \vdots \\ 2I & 2I & \dots & 0 \end{bmatrix}.$$

Now for any $v \in \mathbb{R}^d$, (v, v, \dots, v) is an eigenvector with eigenvalue $2(N-1)$, while the vectors

$$(v, -v, 0, \dots, 0), (v, 0, -v, 0, \dots, 0), \dots, (v, 0, \dots, 0, -v)$$

are eigenvectors with eigenvalue -2 . This implies that $\lambda_- = (N-1)d$, $\lambda_+ = d$, and $\lambda_0 = 0$. Therefore, minimizers have at most $(N-1)d$ -dimensional support. We now show that this bound is sharp for this cost function; that is, there actually are minimizers which are strictly positive on $(N-1)d$ -dimensional sets.

Example. Replace the Coulomb interaction with the negative harmonic oscillator interaction (5) and (52). Let $\tilde{\rho}_N$ be any symmetric measure on \mathbb{R}^{3N} which is concentrated on the $3(N-1)$ -dimensional surface $\{\mathbf{x}_1 + \mathbf{x}_2 + \dots + \mathbf{x}_N = 0\}$. Then this measure is optimal for the corresponding single particle density $\rho(\mathbf{x}_1) = N \int_{\mathbb{R}^{3(N-1)}} \tilde{\rho}_N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 d\mathbf{x}_3 \dots d\mathbf{x}_N$.

To see why, note that by a simple computation

$$V_{\text{ee}} = - \sum_{i < j} |\mathbf{x}_i - \mathbf{x}_j|^2 = |\mathbf{x}_1 + \dots + \mathbf{x}_N|^2 - N \sum_{i=1}^N |\mathbf{x}_i|^2.$$

Hence for any ρ_N with one-body density ρ ,

$$\int V_{\text{ee}} \rho_N = \int |\mathbf{x}_1 + \dots + \mathbf{x}_N|^2 \rho_N - \int |\mathbf{x}_1|^2 \rho(\mathbf{x}_1) d\mathbf{x}_1.$$

The first term is minimized if and only if ρ_N is zero outside the surface $\mathbf{x}_1 + \dots + \mathbf{x}_N = 0$, and the second term only depends on the one-body density ρ . Since $\tilde{\rho}_N$ vanishes outside this surface, it is a minimizer.

The above example is in fact a special case of a result in Ref. 25. The interested reader is encouraged to consult Ref. 25 for further results on the dimension of the support of optimizers.

We suspect that the extreme high dimensionality of the minimizer for the negative harmonic cost is likely due to some special features of the harmonic potential; it is unlikely that $(N-1)d$ -dimensional solutions can exist for the Coulomb cost. However, it is known that milder high dimensionality can occur for the Coulomb cost; we note that in Ref. 26, Corollary 3.2.3, it is shown that for $N \geq 3$, solutions can concentrate on $(2d-2)$ -dimensional surfaces, and so the ansatz (6) cannot capture all minimizers in (4).

IX. CONCLUSIONS AND OUTLOOK

We have reformulated the strongly correlated limit of density functional theory via “ N -density representability,” i.e., the requirement that the pair density comes from a symmetric N -point probability measure. This formulation gives rise to a natural hierarchy of approximate models, in which one relaxes this requirement to the existence of a representing symmetric k -point density with $k < N$. In this paper, we have presented a computational method for the approximate models which is akin to a wavefunction method, in that the representing k -point density is resolved. One of the numerical findings we did not anticipate is the extreme robustness of self-consistent Kohn-Sham densities with respect to the k -density approximation.

For low k , a promising route towards extending our methods to spherically asymmetric systems is the direct computation of the Kantorovich dual potential.²⁴ In the future, if a more direct understanding of the main constraints on ρ_2 implied by k -representability can be obtained, one could also envision a dual approach akin to reduced density matrix methods in which one would solve a constrained linear programming problem for the pair density.

Finally, another interesting issue raised by this work is to clarify the somewhat surprising connection between the SCE formalism and the mean field approximation suggested by our study of the two-site system in Sec. IV.

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- ¹D. Aldous, *Exchangeability and Related Topics*, Lecture Notes in Mathematics Volume 1117 (Springer, 1985).
- ²P. W. Ayers and E. R. Davidson, "Necessary conditions for the N-representability of pair distribution functions," *Int. J. Quantum Chem.* **106**, 1487–1498 (2006).
- ³T. Bally and G. Narahari Sastry, "Incorrect dissociation behavior of radical ions in density functional calculations," *J. Phys. Chem. A* **101**, 7923–7925 (1997).
- ⁴G. Buttazzo, L. De Pascale, and P. Gori-Giorgi, "Optimal-transport formulation of electronic density-functional theory," *Phys. Rev. A* **85**, 062502 (2012).
- ⁵A. J. Cohen, P. Mori-Sánchez, and W. Yang, "Challenges for density functional theory," *Chem. Rev.* **112**, 289–320 (2012).
- ⁶A. J. Coleman and V. I. Yukalov, *Reduced Density Matrices: Coulson's Challenge* (Springer, 2000).
- ⁷C. Cotar, G. Friesecke, and C. Klüppelberg, "Smoothing of transport plans with fixed marginals and rigorous semiclassical limit of the Hohenberg-Kohn functional" (unpublished).
- ⁸C. Cotar, G. Friesecke, and B. Pass, "Infinite-body optimal transport with Coulomb cost," *Comm. Math. Phys.* (submitted) preprint [arXiv:1307.6540](https://arxiv.org/abs/1307.6540).
- ⁹C. Cotar, G. Friesecke, and C. Klüppelberg, "Density functional theory and optimal transportation with Coulomb cost," preprint [arXiv:1104.0603](https://arxiv.org/abs/1104.0603) (2011); *Commun. Pure Appl. Math.* **66**, 548–599 (2013).
- ¹⁰E. R. Davidson, "N-representability of the electron pair density," *Chem. Phys. Lett.* **246**, 209–213 (1995).
- ¹¹B. de Finetti, "Sulla proseguibilità di processi aleatori scambiabili," *Rend. Mat. Trieste* **1**, 53–67 (1969); see <http://hdl.handle.net/10077/6642>.
- ¹²P. Diaconis and D. Freedman, "Finite exchangeable sequences," *Ann. Probab.* **8**, 745–764 (1980).
- ¹³G. Friesecke, "Pair correlations and exchange phenomena in the free electron gas," *Commun. Math. Phys.* **184**, 143–171 (1997).
- ¹⁴G. Friesecke and B. Goddard, "Asymptotics-based CI models for atoms: Properties, exact solution of a minimal model for Li to Ne, and application to atomic spectra," *Multiscale Model. Simul.* **7**, 1876–1897 (2009).
- ¹⁵W. Gangbo and R. McCann, "The geometry of optimal transportation," *Acta Math.* **177**, 113–161 (1996).
- ¹⁶W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.* **140**, A1133–A1138 (1965).
- ¹⁷K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, "Higher-accuracy van der Waals density functional," *Phys. Rev. B* **82**, 081101(R) (2010).
- ¹⁸M. Levy and J. P. Perdew, "Hellmann-Feynman, virial, and scaling requisites for the exact universal density functionals. Shape of the correlation potential and diamagnetic susceptibility for atoms," *Phys. Rev. A* **32**, 2010–2021 (1985).
- ¹⁹E. H. Lieb and B. Simon, "The Thomas-Fermi theory of atoms, molecules and solids," *Adv. Math.* **23**, 22–116 (1977).
- ²⁰F. Malet and P. Gori-Giorgi, "Strong correlation in Kohn-Sham density functional theory," *Phys. Rev. Lett.* **109**, 246402 (2012).
- ²¹F. Malet, A. Mirtschink, J. C. Cremon, S. M. Reimann, and P. Gori-Giorgi, "Kohn-Sham density functional theory for quantum wires in arbitrary correlation regimes," *Phys. Rev. B* **87**, 115146 (2013).
- ²²J. M. L. Martin, J. El-Yazal, and J.-P. François, "On the structure and vibrational frequencies of C₂₄," *Chem. Phys. Lett.* **255**, 7–14 (1996).
- ²³D. A. Mazziotti, *Reduced-Density-Matrix Mechanics: With Application to Many-Electron Atoms and Molecules*, Advances in Chemical Physics Volume 134 (Wiley, 2007).
- ²⁴C. B. Mendl and L. Lin, "Kantorovich dual solution for strictly correlated electrons in atoms and molecules," *Phys. Rev. B* **87**, 125106 (2013).
- ²⁵B. Pass, "On the local structure of optimal measures in the multi-marginal optimal transportation problem," *Calculus Var. Partial Differ. Equ.* **43**, 529–536 (2012).
- ²⁶B. Pass, "Remarks on the semi-classical Hohenberg-Kohn functional," preprint [arXiv:1211.2766](https://arxiv.org/abs/1211.2766) (2012).
- ²⁷J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- ²⁸E. Räsänen, M. Seidl, and P. Gori-Giorgi, "Strictly correlated uniform electron droplets," *Phys. Rev. B* **83**, 195111 (2011).
- ²⁹M. Seidl, "Strong-interaction limit of density-functional theory," *Phys. Rev. A* **60**, 4387–4395 (1999).
- ³⁰M. Seidl, P. Gori-Giorgi, and A. Savin, "Strictly correlated electrons in density-functional theory: A general formulation with applications to spherical densities," *Phys. Rev. A* **75**, 042511 (2007).
- ³¹M. Seidl, J. P. Perdew, and M. Levy, "Strictly correlated electrons in density-functional theory," *Phys. Rev. A* **59**, 51–54 (1999).
- ³²C. Villani, *Optimal Transport: Old and New* (Springer, 2008).
- ³³S. Yanagisawa, T. Tsuneda, and K. Hirao, "An investigation of density functionals: The first-row transition metal dimer calculations," *J. Chem. Phys.* **112**(2), 545–553 (2000).