

# Constraints for hierarchies of many electron distribution functions

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Some inequalities that constrain the reconstruction of  $k$ -electron distribution functions from lower-order distribution functions are presented. These inequalities are related to the  $N$ -representability conditions on electron distributions functions and they have two basic types: (1) general  $N$ -representability inequalities, which are very powerful but difficult to apply and (2) generalized “Davidson” inequalities, which are less powerful but which may be more facile in computational implementations. A constraint on the exchange-correlation hole is also presented.

## 1. Motivation

In a landmark 1994 paper, Ziesche extended the argument of Hohenberg and Kohn to show that the electron pair distribution function, or two-density, determined all the properties of an electronic system [1]. This opened up the field of pair density functional theory and, more generally, electronic structure theories based on the  $k$ -electron distribution functions, or  $k$ -densities [1–22].

There are several reasons why  $k$ -density functional theory is an attractive approach to the electronic structure problem. First of all,  $k$ -density functional theories are arguably the most natural version of “higher order” density-functional theory. The  $k=1$  case is just normal density functional theory. For  $k \geq 2$ , the electron–electron repulsion energy can be computed exactly and only the kinetic energy functional has to be approximated [6–10]. As  $k$  increases, it becomes easier to construct accurate kinetic energy functionals until, eventually, when  $k$  is equal to the number of the electrons in the system, the exact kinetic energy functional is known in an explicit form [9]. Unfortunately, as the number of electrons increases, another problem—the  $N$ -representability problem for the  $k$ -electron distribution functions—becomes more difficult to solve [20–22].

In classical statistical mechanics one often uses hierarchies of equations to determine classical many-particle distribution functions [23]. There are analogous results in quantum mechanics. The most common approaches are the contracted

Schrödinger equations and its variants [24–26]. The contracted Schrödinger equations are hierarchies of equations for the reduced density matrices of a system; they provide a partial solution to the  $N$ -representability problem for the reduced density matrices because the “mathematics” of  $N$ -representability conditions is partially enforced by the “physics” that is embodied in the hierarchy and the reconstruction techniques.

An analogous hierarchy of equations for the  $k$ -densities can be obtain by simply generalizing the arguments of Lee, Jackson, and Feenberg [27]. The first two elements of the hierarchy are [9].

$$(\nabla_1^2 + \nabla_2^2) \rho_2^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{s=\alpha,\beta} \int \frac{\delta \rho_2^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{\delta \rho_1^s(\mathbf{x})} \nabla_{\mathbf{r}}^2 \rho_1^s(\mathbf{x}) \, d\mathbf{x} \quad (1)$$

$$\begin{aligned} & (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) \rho_3^{\sigma_1\sigma_2\sigma_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ &= \sum_{\substack{s_1=\alpha,\beta \\ s_2=\alpha,\beta}} \iint \frac{\delta \rho_3^{\sigma_1\sigma_2\sigma_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{\delta \rho_2^{s_1s_2}(\mathbf{x}_1, \mathbf{x}_2)} \left[ (\nabla_{\mathbf{x}_1}^2 + \nabla_{\mathbf{x}_2}^2) \rho_2^{s_1s_2}(\mathbf{x}_1, \mathbf{x}_2) \right] d\mathbf{x}_1 d\mathbf{x}_2 \quad (2) \end{aligned}$$

and the higher terms in the hierarchy are similar. Here

$$\begin{aligned} & \rho_k^{\sigma_1\sigma_2\dots\sigma_k}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_k) \\ &= \left\langle \Psi \left| \sum_{i_k \neq i_1, i_2, \dots, i_{k-1}}^N \dots \sum_{i_2 \neq i_1}^N \sum_{i_1=1}^N \left\{ \prod_{j=1}^k |\sigma_j(i_j)| \right\} \delta(\mathbf{r}_{i_j} - \mathbf{x}_j) |\sigma_j(i_j)| \right| \Psi \right\rangle \quad (3) \end{aligned}$$

is the (spin-resolved)  $k$ -electron distribution function, which is conventionally normalized to  $\frac{N_\alpha! N_\beta!}{m_\alpha! m_\beta!}$  where  $N_\alpha$  and  $N_\beta$  denote the number of  $\alpha$ -spin electrons and  $\beta$ -spin electrons in the electronic system and  $m_\alpha$  and  $m_\beta$  denote the number of  $\alpha$ -spin and  $\beta$ -spin indices in  $\sigma_1\sigma_2\dots\sigma_k$ . If one knows an explicit equation for the higher-order electron distribution functions in terms of the lower-order electron distribution functions, then one can evaluate the functional derivative of  $k$ -density with respect to the  $(k-1)$ -density. If the hierarchy equation is satisfied, then there exists some Hamiltonian for which some eigenstate has the  $k$ -density in question. This, however, does not ensure that the  $k$ -density in question corresponds to a “fermionic” (i.e. antisymmetric) eigenstate of that Hamiltonian; nor does it guarantee that the Hamiltonian associated with this  $k$ -density corresponds to an electronic system. (In general, the Hamiltonian will have many-body potential interaction terms).

## 2. *N*-representability conditions for hierarchies of *k*-densities

There is another family of conditions that can be used to inform the reconstruction of *k*-densities for lower-order electron distribution functions. A *k*-density is *N*-representable if and only if there exists an ensemble of fermionic wave functions such that

$$\begin{aligned} &\rho_k^{\sigma_1\sigma_2\dots\sigma_k}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_k) \\ &= \sum_n p_n \left\langle \Psi_n \left| \sum_{i_k \neq i_1, i_2, \dots, i_{k-1}}^N \dots \sum_{i_2 \neq i_1}^N \sum_{i_1=1}^N \left\{ \prod_{j=1}^k |\sigma_j(i_j)\rangle \delta(\mathbf{r}_{i_j} - \mathbf{x}_j) \langle \sigma_j(i_j)| \right\} \right| \Psi_n \right\rangle. \end{aligned} \tag{4}$$

Here  $p_n$  represents the probability of the state  $\Psi_n$  occurring in the ensemble; thus

$$\begin{aligned} 0 &\leq p_n \leq 1, \\ \sum_{n=1}^{\infty} p_n &= 1. \end{aligned} \tag{5}$$

It is a somewhat subtle, but important, fact that the *N*-representability conditions for bosons and fermions are essentially the same; every fermionic *k*-density is also a permissible bosonic *k*-density [20]. The only meaningful restriction that is specific to fermions is that the probability of observing two fermions with the same spin at the same point in space is always zero. Moreover, for sufficiently smooth density matrices, the antisymmetry of the wavefunctions in the ensemble imposes a constraint on the vanishing of derivatives at the same-spin electron coalescence point: [9].

$$\begin{aligned} &\left( \frac{\partial^l \rho_k^{\dots\sigma_i=\sigma_j\dots}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j + \varepsilon \mathbf{d}, \dots, \mathbf{r}_k)}{\partial \varepsilon^l} \right)_{\varepsilon=0} = 0 \quad 0 \leq l < 2p; \quad p \text{ is an odd \#} \\ &\left( \frac{\partial^{2p} \rho_k^{\dots\sigma_i=\sigma_j\dots}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j + \varepsilon \mathbf{d}, \dots, \mathbf{r}_k)}{\partial \varepsilon^{2p}} \right)_{\varepsilon=0} > 0 \end{aligned} \tag{6}$$

This must be true for every direction vector  $\mathbf{d}$  except perhaps the vectors in a nodal plane that intersects the origin.

At this stage, the *N*-representability problem for the *k*-electron distribution function can be considered solved. Samvelyan was the first to derive necessary and sufficient conditions and he studied the most difficult case: pure-state *N*-representability (where only one of the  $p_n$  in equation (4) is nonzero) [14]. Unfortunately, his solution was not practical at all. Pistol considered electrons on a lattice and showed that the ensemble-*N*-representable distribution functions were all linear combinations of classical distribution functions on the lattice [12]. The author then formulated the *N*-representability conditions in a somewhat

simpler form and generalized to higher-order electron distributions in real space [20]. The necessary and sufficient conditions for  $N$ -representability are: [20]

The  $k$ -electron spin densities  $\rho_k^{\sigma_1 \dots \sigma_k}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  are  $N$ -representable if and only if for every choice of  $k$ -body spin-potentials,  $w^{\sigma_1 \dots \sigma_k}(\mathbf{r}_1, \dots, \mathbf{r}_k)$ , the potential energy of interaction,

$$\sum_{\sigma_1, \sigma_2, \dots, \sigma_k = \alpha, \beta} \left[ \int \dots \int \rho_k^{\sigma_1 \dots \sigma_k}(\mathbf{r}_1, \dots, \mathbf{r}_k) w_k^{\sigma_1 \dots \sigma_k}(\mathbf{r}_1, \dots, \mathbf{r}_k) d\mathbf{r}_1 \dots d\mathbf{r}_k \right] \quad (7)$$

is greater than the energy of  $N$  classical fermions interacting with via the same spin-potential,

$$C[\{w^{\sigma_1 \dots \sigma_k}\}] = \min_{\substack{\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N \\ N_\alpha = \sum_{i=1}^N \delta_{\alpha s_i}}} \left( \sum_{\sigma_1, \sigma_2, \dots, \sigma_k = \alpha, \beta} \left[ \sum_{j_1=1}^N \sum_{j_2 \neq j_1}^N \dots \sum_{j_k \neq j_{k-1}, \dots, j_1}^N \left( \prod_l \delta_{s_l \sigma_l} \right) \times w^{\sigma_1 \dots \sigma_k}(\mathbf{r}_{j_1}, \dots, \mathbf{r}_{j_k}) \right] \right). \quad (8)$$

For example, the spin-resolved two-density is  $N$ -representable if and only if

$$\begin{aligned} & \iint \left[ \rho_2^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) w^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \rho_2^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) w^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \right. \\ & \left. + \rho_2^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) w^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \rho_2^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) w^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2 \\ & \geq \min_{\substack{\{\mathbf{r}_i, s_i\}_{i=1}^N \\ N_\alpha = \sum_{i=1}^N \delta_{\alpha s_i}}} \left( \sum_{i=1}^N \sum_{j \neq i}^N \left( \delta_{\alpha s_i} \delta_{\alpha s_j} w^{\alpha\alpha}(\mathbf{r}_i, \mathbf{r}_j) + \delta_{\alpha s_i} \delta_{\beta s_j} w^{\alpha\beta}(\mathbf{r}_i, \mathbf{r}_j) \right) \right. \\ & \left. + \delta_{\beta s_i} \delta_{\alpha s_j} w^{\beta\alpha}(\mathbf{r}_i, \mathbf{r}_j) + \delta_{\beta s_i} \delta_{\beta s_j} w^{\beta\beta}(\mathbf{r}_i, \mathbf{r}_j) \right) \\ & = C[\{w^{\sigma_1 \sigma_2}\}] \end{aligned} \quad (9)$$

for every possible choice of the spin-potentials.

Equation (9) can be restated in the form of a constraint on the two- and three-electron distribution functions. The new choice for the spin-potentials,

$$\begin{aligned}
 \mathcal{W}^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) &= w^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) - \frac{C[\{w^{\sigma\sigma'}\}]}{N(N-1)} \\
 \mathcal{W}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) &= w^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) - \frac{C[\{w^{\sigma\sigma'}\}]}{N(N-1)} \\
 \mathcal{W}^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) &= w^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) - \frac{C[\{w^{\sigma\sigma'}\}]}{N(N-1)} \\
 \mathcal{W}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) &= w^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) - \frac{C[\{w^{\sigma\sigma'}\}]}{N(N-1)}
 \end{aligned}
 \tag{10}$$

has the merit of being nonnegative for any  $N$ -electron system with  $N_\alpha$   $\alpha$ -spin electrons. Evaluating the expectation value of this potential for an appropriate wavefunction but *not integrating over the coordinate of the last electron*, gives a constraint,

$$0 \leq \left\langle \Psi \left| \sum_{i=1}^N \sum_{j \neq i} \begin{pmatrix} |\alpha(i) \alpha(j)\rangle \mathcal{W}^{\alpha\alpha}(\mathbf{r}_i, \mathbf{r}_j) \langle \alpha(j) \alpha(i)| \\ + |\alpha(i) \beta(j)\rangle \mathcal{W}^{\alpha\beta}(\mathbf{r}_i, \mathbf{r}_j) \langle \beta(j) \alpha(i)| \\ + |\beta(i) \alpha(j)\rangle \mathcal{W}^{\beta\alpha}(\mathbf{r}_i, \mathbf{r}_j) \langle \alpha(j) \beta(i)| \\ + |\beta(i) \beta(j)\rangle \mathcal{W}^{\beta\beta}(\mathbf{r}_i, \mathbf{r}_j) \langle \beta(j) \beta(i)| \end{pmatrix} \right| \Psi \right\rangle_{2\dots N}, \tag{11}$$

which can be rewritten as a constraint on the reconstruction of the three-density from the two-density:

$$0 \leq \frac{1}{N} \left( \begin{aligned} & 2 \int \begin{pmatrix} \rho_2^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) \mathcal{W}^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) \\ + \rho_2^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \mathcal{W}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \\ + \rho_2^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) \mathcal{W}^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) \\ + \rho_2^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) \mathcal{W}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) \end{pmatrix} d\mathbf{r}_2 \\ & + \iint \begin{pmatrix} \left( \rho_3^{\alpha\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \rho_3^{\beta\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right) \mathcal{W}^{\alpha\alpha}(\mathbf{r}_2, \mathbf{r}_3) \\ + \left( \rho_3^{\alpha\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \rho_3^{\beta\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right) \mathcal{W}^{\alpha\beta}(\mathbf{r}_2, \mathbf{r}_3) \\ + \left( \rho_3^{\alpha\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \rho_3^{\beta\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right) \mathcal{W}^{\beta\alpha}(\mathbf{r}_2, \mathbf{r}_3) \\ + \left( \rho_3^{\alpha\beta\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \rho_3^{\beta\beta\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right) \mathcal{W}^{\beta\beta}(\mathbf{r}_2, \mathbf{r}_3) \end{pmatrix} d\mathbf{r}_2 d\mathbf{r}_3 \end{aligned} \right). \tag{12}$$

This reduces to an especially simple form when all the spin-potentials are equal:

$$\iint \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \mathcal{W}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_2 d\mathbf{r}_3 \geq -2 \int \rho_2(\mathbf{r}_1, \mathbf{r}_2) \mathcal{W}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2. \quad (13)$$

In deriving this last expression, the spin-traced  $k$ -densities were defined in the usual way,

$$\rho_k(\mathbf{r}_1, \dots, \mathbf{r}_k) = \sum_{\sigma_1, \sigma_2, \dots, \sigma_k = \alpha, \beta} \rho_k^{\sigma_1, \dots, \sigma_k}(\mathbf{r}_1, \dots, \mathbf{r}_k). \quad (14)$$

The preceding conditions are very strong constraints, but they are rarely practical because constructing the spin-potentials,  $\mathcal{W}^{\sigma\sigma'}(\mathbf{r}_i, \mathbf{r}_j)$ , requires solving the classical many-body problem. This is easier than the quantum many-body problem, but not much easier. There are certain choices of potentials — notably the Lennard–Jones [28–30], Morse [31–33], Dzugutov [34, 35] Z1 [36] and Z2 [36] potentials — where extensive tabulations of the ground-state minima exist. These results can be used to constrain the  $N$ -representability of the spin-free two-density. There are even a few cases (binary Lennard–Jones clusters) [37] where the classical optimization problem for two component mixtures has been solved; this provides access to constraints on the spin-resolved two-density. Except for this limited set of potentials, the only way to obtain meaningful  $N$ -representability constraints is to either (a) solve the classical problem explicitly or (b) construct additional potentials where the classical problem can be solved analytically.

The rest of this paper will be devoted to a consideration of option (b); in particular, consideration will be given to potentials where a lower bound to the classical problem can be obtained analytically. The earliest conditions of this type were those of Garrod and Percus [38] who treated the spin-independent case. Davidson then introduced a similar constraint in conjunction with harmonically confined electrons [39]; in collaboration with the present author, he then generalized this constraint to include the spin-resolved 2-density and other, higher-order,  $k$ -densities [11]. There are some other necessary conditions for  $N$ -representability that are known (especially for the two-density); a catalogue of these conditions can be found in refs [11, 20].

The goal of this paper is to show that the generalized Davidson constraints can be adapted to provide  $N$ -representability constraints on hierarchies of  $k$ -densities. For simplicity of presentation, only the absolute simplest constraints (which couple the electron density, the two-density, and the three-density) will be presented. The author believes these are probably the most interesting constraints, but the methods presented here are readily extended to higher-order  $k$ -densities.

The generalized Davidson constraints arise as special cases of the general  $N$ -representability constraints where one is guaranteed that the ground-state energy of the classical structure problem is greater than or equal to zero. This is achieved by writing a potential in the form:

$$\begin{aligned}
 0 \leq V_{\text{Dvdsn}} &\equiv \left| \sum_{i=1}^N \sum_{\sigma=\alpha,\beta} |\sigma(i)\rangle f_{\sigma}(\mathbf{r}_i) \langle \sigma(i) | \right|^2 \\
 &= \sum_{i=1}^N \left( |\alpha(i)\rangle |f_{\alpha}(\mathbf{r}_i)|^2 \langle \alpha(i) | \right. \\
 &\quad \left. + |\beta(i)\rangle |f_{\beta}(\mathbf{r}_i)|^2 \langle \beta(i) | \right) \\
 &\quad + \sum_{i=1}^N \sum_{j \neq i} \left( \begin{aligned} &|\alpha(i)\alpha(j)\rangle f_{\alpha}(\mathbf{r}_i) f_{\alpha}^*(\mathbf{r}_j) \langle \alpha(j)\alpha(i) | \\ &+ |\alpha(i)\beta(j)\rangle f_{\alpha}(\mathbf{r}_i) f_{\beta}^*(\mathbf{r}_j) \langle \beta(j)\alpha(i) | \\ &+ |\beta(i)\alpha(j)\rangle f_{\beta}(\mathbf{r}_i) f_{\alpha}^*(\mathbf{r}_j) \langle \alpha(j)\beta(i) | \\ &+ |\beta(i)\beta(j)\rangle f_{\beta}(\mathbf{r}_i) f_{\beta}^*(\mathbf{r}_j) \langle \beta(j)\beta(i) | \end{aligned} \right) \quad (15)
 \end{aligned}$$

Using the definition of the two-density to evaluate  $\langle \Psi | V_{\text{Dvdsn}} | \Psi \rangle \geq 0$  gives the generalized Davidson constraint. If instead of integrating over *all* of the electrons one integrates over all but one electron, then one gets a constraint on the low-order terms in the hierarchy of electron distribution functions.

For the sake of simplicity, consider the spin-free case ( $f_{\alpha}(\mathbf{r}) = f_{\beta}(\mathbf{r})$ ) case first. In that case:

$$\begin{aligned}
 0 &\leq \langle \Psi | V_{\text{Dvdsn}} | \Psi \rangle_{2\dots N} \\
 0 &\leq \frac{1}{N} \left( \begin{aligned} &|f(\mathbf{r}_1)|^2 \rho(\mathbf{r}_1) + \int |f(\mathbf{r}_2)|^2 \rho_2(\mathbf{r}_1, \mathbf{r}_2) \mathbf{d}\mathbf{r}_2 \\ &+ 2 \int \text{Re}[f(\mathbf{r}_1) f(\mathbf{r}_2)] \rho_2(\mathbf{r}_1, \mathbf{r}_2) \mathbf{d}\mathbf{r}_2 \\ &+ \int \int \text{Re}[f(\mathbf{r}_2) f(\mathbf{r}_3)] \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \mathbf{d}\mathbf{r}_2 \mathbf{d}\mathbf{r}_3 \end{aligned} \right). \quad (16)
 \end{aligned}$$

Integrating this expression with respect to the remaining variable recovers the “ordinary” spin-free generalized Davidson constraint,

$$\begin{aligned}
 0 &\leq \int \rho(\mathbf{r}_1) |f(\mathbf{r}_1)|^2 \mathbf{d}\mathbf{r}_1 \\
 &\quad + \int \int \text{Re}[f(\mathbf{r}_1) f(\mathbf{r}_2)] \rho_2(\mathbf{r}_1, \mathbf{r}_2) \mathbf{d}\mathbf{r}_1 \mathbf{d}\mathbf{r}_2. \quad (17)
 \end{aligned}$$

The spin-resolved result is derived in a similar way. One obtains

$$0 \leq \langle \Psi | V_{\text{Dvdsn}} | \Psi \rangle_{2\dots N}$$

$$0 \leq \frac{1}{N} \left( \begin{aligned} & \rho^\alpha(\mathbf{r}_1) |f_\alpha(\mathbf{r}_1)|^2 + \int \rho_2^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) |f_\alpha(\mathbf{r}_2)|^2 d\mathbf{r}_2 \\ & + \int \rho_2^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) |f_\beta(\mathbf{r}_2)|^2 d\mathbf{r}_2 \\ & + 2 \int \rho_2^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) \operatorname{Re}[f_\alpha(\mathbf{r}_1) f_\alpha(\mathbf{r}_2)] d\mathbf{r}_2 \\ & + 2 \int \rho_2^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \operatorname{Re}[f_\alpha(\mathbf{r}_1) f_\beta(\mathbf{r}_2)] d\mathbf{r}_2 \\ & + \int \int \rho_3^{\alpha\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \operatorname{Re}[f_\alpha(\mathbf{r}_2) f_\alpha(\mathbf{r}_3)] d\mathbf{r}_2 d\mathbf{r}_3 \\ & + 2 \int \int \rho_3^{\alpha\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \operatorname{Re}[f_\alpha(\mathbf{r}_2) f_\beta(\mathbf{r}_3)] d\mathbf{r}_2 d\mathbf{r}_3 \\ & + \int \int \rho_3^{\alpha\beta\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \operatorname{Re}[f_\beta(\mathbf{r}_2) f_\beta(\mathbf{r}_3)] d\mathbf{r}_2 d\mathbf{r}_3 \\ & + \rho^\beta(\mathbf{r}_1) |f_\beta(\mathbf{r}_1)|^2 + \int \rho_2^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) |f_\beta(\mathbf{r}_2)|^2 d\mathbf{r}_2 \\ & + \int \rho_2^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) |f_\alpha(\mathbf{r}_2)|^2 d\mathbf{r}_2 \\ & + 2 \int \rho_2^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) \operatorname{Re}[f_\beta(\mathbf{r}_1) f_\beta(\mathbf{r}_2)] d\mathbf{r}_2 \\ & + 2 \int \rho_2^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) \operatorname{Re}[f_\beta(\mathbf{r}_1) f_\alpha(\mathbf{r}_2)] d\mathbf{r}_2 \\ & + \int \int \rho_3^{\beta\beta\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \operatorname{Re}[f_\beta(\mathbf{r}_2) f_\beta(\mathbf{r}_3)] d\mathbf{r}_2 d\mathbf{r}_3 \\ & + 2 \int \int \rho_3^{\beta\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \operatorname{Re}[f_\alpha(\mathbf{r}_2) f_\beta(\mathbf{r}_3)] d\mathbf{r}_2 d\mathbf{r}_3 \\ & + \int \int \rho_3^{\beta\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \operatorname{Re}[f_\alpha(\mathbf{r}_2) f_\alpha(\mathbf{r}_3)] d\mathbf{r}_2 d\mathbf{r}_3 \end{aligned} \right). \quad (18)$$

Integrating this expression and using the identities

$$\begin{aligned} N &= N_\alpha + N_\beta \\ \rho^\sigma(\mathbf{r}_1) &= (N_\sigma - 1) \int \rho_2^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \\ \rho^\sigma(\mathbf{r}_1) &= N_{\sigma'} \int \rho_2^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \\ \rho_2^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) &= (N_\sigma - 2) \int \rho_3^{\sigma\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \\ \rho_2^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) &= N_{\sigma'} \int \rho_3^{\sigma\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \\ \rho_2^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) &= (N_\sigma - 1) \int \rho_3^{\sigma\sigma'\sigma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \end{aligned} \quad (19)$$

gives the spin-resolved generalized Davidson condition [11]

$$0 \leq \int \left( \rho^\alpha(\mathbf{r}_1) |f_\alpha(\mathbf{r}_1)|^2 + \rho^\beta(\mathbf{r}_1) |f_\beta(\mathbf{r}_1)|^2 \right) d\mathbf{r}_1 d\mathbf{r}_2 \quad (20)$$

$$+ \iint \left( \begin{aligned} & \rho_2^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) \operatorname{Re}[f_\alpha(\mathbf{r}_1) f_\alpha(\mathbf{r}_2)] \\ & + 2\rho_2^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \operatorname{Re}[f_\alpha(\mathbf{r}_1) f_\beta(\mathbf{r}_2)] \\ & + \rho_2^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) \operatorname{Re}[f_\beta(\mathbf{r}_1) f_\beta(\mathbf{r}_2)] \end{aligned} \right) d\mathbf{r}_1 d\mathbf{r}_2$$

The reader can also confirm that if  $f_\alpha(\mathbf{r}) = f_\beta(\mathbf{r})$  then equations (16) and (18) are identical.

Davidson-type constraints like those in equations (16)–(20) are powerful because they must apply for every possible function,  $f(\mathbf{r})$ . By exploiting this flexibility, one can derive constraints with different forms. For example, in some



applications — notably those related to density functional theory — the 2-density may not be known, but the spherically averaged two-density is known,

$$\rho_2^{\sigma\sigma'}(\mathbf{r}_1, r_{12}) = \frac{1}{4\pi} \int \rho_2^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2 - \mathbf{r}_1) d\omega_{12}. \tag{21}$$

Integration with respect to  $d\omega_{12}$  represents integration with respect to the solid angle of the relative electron position,  $\mathbf{r}_2 - \mathbf{r}_1$ .

A constraint on the spherically averaged pair density can be obtained by choosing

$$f_\sigma(\mathbf{r}_i) = \hat{\omega}_\sigma(k) e^{i\mathbf{k}\cdot\mathbf{r}_i}. \tag{22}$$

Notice that

$$\begin{aligned} f_\sigma(\mathbf{r}_i) f_{\sigma'}^*(\mathbf{r}_j) &= \hat{\omega}_\sigma(k) \hat{\omega}_{\sigma'}(k) e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)}, \\ |f_\sigma(\mathbf{r}_i)|^2 &= (\hat{\omega}_\sigma(k))^2. \end{aligned} \tag{23}$$

Next, insert these expressions into equation (18) and integrate with respect to  $\mathbf{k}$ . This produces pair potentials that depend only on the distance between the particles, namely,

$$\begin{aligned} w_{\alpha\alpha}(r_{ij}) &= \int (\hat{\omega}_\alpha(k))^2 e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)} d\mathbf{k} \\ &= \frac{4\pi}{r_{ij}} \int_0^\infty (\hat{\omega}_\alpha(k))^2 \sin(kr_{ij}) k dk, \\ w_{\beta\beta}(r_{ij}) &= \int (\hat{\omega}_\beta(k))^2 e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)} d\mathbf{k} \\ &= \frac{4\pi}{r_{ij}} \int_0^\infty (\hat{\omega}_\beta(k))^2 \sin(kr_{ij}) k dk \\ w_{\alpha\beta}(r_{ij}) &= w_{\beta\alpha}(r_{ij}) = \int \hat{\omega}_\alpha(k) \hat{\omega}_\beta(k) e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)} d\mathbf{k} \\ &= \frac{4\pi}{r_{ij}} \int_0^\infty (\hat{\omega}_\alpha(k) \hat{\omega}_\beta(k)) \sin(kr_{ij}) k dk. \end{aligned} \tag{24}$$

Just as in equation (18), one obtains a constraint on the pair density:

$$\begin{aligned}
0 \leq & \rho^\alpha(\mathbf{r}_1) \left( \int_0^\infty (\hat{\omega}_\alpha(k))^2 4\pi k^2 dk \right) + \rho^\beta(\mathbf{r}_1) \left( \int_0^\infty (\hat{\omega}_\beta(k))^2 4\pi k^2 dk \right) \\
& + \frac{1}{N} \left( \begin{aligned}
& + 2 \int \rho_2^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) w_{\alpha\alpha}(r_{12}) d\mathbf{r}_2 \\
& + 4 \int \rho_2^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) w_{\alpha\beta}(r_{12}) d\mathbf{r}_2 \\
& + 2 \int \rho_2^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) w_{\beta\beta}(r_{12}) d\mathbf{r}_2 \\
& + \iint (\rho_3^{\alpha\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \rho_3^{\beta\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)) w_{\alpha\alpha}(r_{23}) d\mathbf{r}_2 d\mathbf{r}_3 \\
& + 2 \iint (\rho_3^{\alpha\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \rho_3^{\beta\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)) w_{\alpha\beta}(r_{23}) d\mathbf{r}_2 d\mathbf{r}_3 \\
& + \iint (\rho_3^{\alpha\beta\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \rho_3^{\beta\beta\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)) w_{\beta\beta}(r_{23}) d\mathbf{r}_2 d\mathbf{r}_3
\end{aligned} \right). \quad (25)
\end{aligned}$$

However, in this case, one can simplify the result to obtain a constraint on the spherically averaged pair density,

$$\begin{aligned}
0 \leq & \rho^\alpha(\mathbf{r}_1) \left( \int_0^\infty (\hat{\omega}_\alpha(k))^2 4\pi k^2 dk \right) + \rho^\beta(\mathbf{r}_1) \left( \int_0^\infty (\hat{\omega}_\beta(k))^2 4\pi k^2 dk \right) \\
& + \frac{1}{N} \left( \begin{aligned}
& + \int_0^\infty \left( \begin{aligned}
& 2\rho_2^{\alpha\alpha}(\mathbf{r}_1, r_{12}) w_{\alpha\alpha}(r_{12}) \\
& + 4\rho_2^{\alpha\beta}(\mathbf{r}_1, r_{12}) w_{\alpha\beta}(r_{12}) \\
& + 2\rho_2^{\beta\beta}(\mathbf{r}_1, r_{12}) w_{\beta\beta}(r_{12})
\end{aligned} \right) 4\pi r_{12}^2 dr_{12} \\
& + \int_0^\infty \left( \begin{aligned}
& (\rho_3^{\alpha\alpha\alpha}(\mathbf{r}_1, r_{23}) + \rho_3^{\beta\alpha\alpha}(\mathbf{r}_1, r_{23})) w_{\alpha\alpha}(r_{23}) \\
& + 2(\rho_3^{\alpha\alpha\beta}(\mathbf{r}_1, r_{23}) + \rho_3^{\beta\alpha\beta}(\mathbf{r}_1, r_{23})) w_{\alpha\beta}(r_{23}) \\
& + (\rho_3^{\alpha\beta\beta}(\mathbf{r}_1, r_{23}) + \rho_3^{\beta\beta\beta}(\mathbf{r}_1, r_{23})) w_{\beta\beta}(r_{23})
\end{aligned} \right) 4\pi r_{23}^2 dr_{23}
\end{aligned} \right). \quad (26)
\end{aligned}$$

The spherically averaged three-density is defined by integrating over the center-of-charge for the last two electronic coordinates and integration over solid angle for their relative coordinate:

$$\rho_3^{\sigma_1\sigma_2\sigma_3}(\mathbf{r}_1, r_{23}) = \frac{1}{4\pi} \iint \rho_3^{\sigma_1\sigma_2\sigma_3} \left( \mathbf{r}_1, \frac{\mathbf{r}_2 + \mathbf{r}_3}{2}, \mathbf{r}_3 - \mathbf{r}_2 \right) d\omega_{23} d\left(\frac{r_2 + r_3}{2}\right). \quad (27)$$

Equation (26) provides a constraint on the exchange-correlation hole in density-functional theory, though the constraint is not especially useful because it still depends on the spherically averaged three-density, which is rarely known. However, if one integrates these expressions with respect to  $\mathbf{r}_1$  then one obtains

a constraint on the system-averaged, spherically averaged two-density,

$$\begin{aligned}
 & -N_\alpha \left( \int_0^\infty (\hat{\omega}_\alpha(k))^2 4\pi k^2 dk \right) - N_\beta \left( \int_0^\infty (\hat{\omega}_\beta(k))^2 4\pi k^2 dk \right) \\
 & \leq \int_0^\infty \left( \rho_2^{\alpha\alpha}(r_{12}) w_{\alpha\alpha}(r_{12}) + 2\rho_2^{\alpha\beta}(r_{12}) w_{\alpha\beta}(r_{12}) \right) 4\pi r_{12}^2 dr_{12}, \quad (28)
 \end{aligned}$$

where

$$\rho_2^{\sigma\sigma'}(r_{12}) = \frac{1}{4\pi} \int \int \rho_2^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2 - \mathbf{r}_1) d\omega_{12} d\mathbf{r}_1. \quad (29)$$

The constraint in equation (28) is directly applicable to density functional theory because it provides a constraint on the system-averaged spherically averaged exchange-correlation hole. The constraint is rather strong since it must hold for *any* pair potential that arises as the Fourier transform of a positive, spherically symmetric, function [cf. equation (24)].

Some readers will recognize that the methods used here are very similar to the methods used to derive the contracted Schrödinger equation, where one evaluates  $\langle \Psi | \hat{H} | \Psi \rangle_{3\dots N}$ .  $N$ -representability constraints can be imposed on the solutions to the contracted Schrödinger equation in a way that is very similar to the approach advocated here: just require that the reduced density matrices satisfy the constraints embodied by  $\langle \Psi | \hat{P} | \Psi \rangle_{3\dots N} \geq 0$ ,  $\langle \Psi | \hat{Q} | \Psi \rangle_{3\dots N} \geq 0$ ,  $\langle \Psi | \hat{G} | \Psi \rangle_{3\dots N} \geq 0$ ,  $\langle \Psi | \hat{T}_1 | \Psi \rangle_{3\dots N} \geq 0$ ,  $\langle \Psi | \hat{T}_2 | \Psi \rangle_{3\dots N} \geq 0$ , ... where  $\hat{P}$ ,  $\hat{Q}$ ,  $\hat{G}$ ,  $\hat{T}_1$ ,  $\hat{T}_2$ , etc. are the positive-definite two-body Hamiltonians that are commonly employed as  $N$ -representability constraints [22, 38, 40–42]

### 3. Summary

The key results in this paper are the constraints on the reconstruction of the three-density from the two-density, equations (12), (18), and (26). Such constraints are important for two reasons: (1) This constrains the sorts of expressions for the three-density that can be used in the generalized Lee–Jackson–Feenberg hierarchy of equations. (2) This constrains the sorts of expressions that can be used if the three-density, instead of the two-density, is used to approximate the kinetic energy in two-density functional theory.

This last point merits further comment. It is known that there is a series of “generalized Weizsacker” functionals for the  $k$ -density which provide increasingly tight lower bounds to the kinetic energy as  $k$  increases. There is also a family of “density-matrix based” kinetic-energy functionals and a family of “Kohn–Sham correction functionals” for the  $k$ -density; these also converge to the correct energy as  $k$  increases. If exact  $N$ -representability conditions are enforced, the *only* approximation in two-density functional theory is the kinetic energy functional.

Since the error in the kinetic energy functional will control the error in the calculation and these approaches for constructing kinetic energy functionals are more accurate for the three-density than they are for the two-density, it seems prudent to use the two-density to *approximate* the three-density, and then evaluate the kinetic energy using the approximate three-density. The conditions derived in this paper provide essential guidance on how to obtain a “reasonable” three-density starting only from the two-density. These hierarchical  $N$ -representability conditions derived in this paper join (i) “sequential relations” (which indicate that the three-density should integrate to the two-density, as in equation (19)), (ii) the generalized Lee–Jackson–Feenberg hierarchy [equation (2)], (iii) the electron coalescence conditions [equation (6)] and (iii) the fact three-density should be  $N$ -representable. This is *all* that is known about the form of the three-density. The hierarchical  $N$ -representability conditions derived here are expected to be rather stringent compared to some of the other conditions (they imply, for example, the sequential relations and enforce the simpler  $N$ -representability constraints on the three-density) and they are relatively easy to enforce. This suggests that the conditions derived here may be important.

A incidental result of this analysis was equation (26), which constrains the system-averaged spherically averaged pair density. This constraint on the  $N$ -representability of the exchange-correlation hole may be useful in density-functional theory. In this context it is significant that Weitao Yang has recently proposed that the self-interaction-error can be removed if the exchange-correlation hole is constrained to be  $N$ -representable [43].

Finally, it may be mentioned that some of the results in this paper — notably the Lee–Jackson–Feenberg hierarchy and the exact necessary and sufficient conditions for  $N$ -representability — had never before been presented in their spin-resolved form. These new results are substantially similar to the previous ones [9, 20] so detailed proofs have been omitted.

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