Symmetric Nonlocal Weighted Density Approximations from the Exchange-Correlation Hole of the Uniform Electron Gas

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ABSTRACT: Nonlocal exchange-correlation energy functionals are constructed using the accurate model exchange-correlation hole for the uniform electron gas developed by Gori-Giorgi and Perdew. The exchange-correlation hole is constrained to be symmetric and normalized, so the resulting functionals can be viewed as symmetrized versions of the weighted density approximation; we call them two-point weighted density approximations. Even without optimization of parameters or functional forms, the exchange-correlation energies for small molecules are competitive with those of the best generalized gradient approximation functionals. Two-point weighted density approximations seem to be an interesting new direction for functional development. A more general version of the conditions that define the energy for fractional electron number and fractional spin are presented. These "generalized flat-planes" conditions are closely linked to the normalization of the spin-resolved exchange-correlation hole at noninteger electron number. This and many other properties of the exact exchange-correlation functional can be imposed straightforwardly and directly in symmetrized weighted density approximation.

I. INTRODUCTION

Kohn−Sham (KS) spin-density-functional theory (DFT)[1] is the most popular computational approach in electronic structure theory because it has the characteristic $O(N^3)$ computational expense of a mean-field model but gives results that are often comparable in accuracy to wave function-based and propagator-based methods.[2−4] In KS-DFT, the only unknown functional is the exchange-correlation energy, which can be expressed as

$$E_{xc}[\rho^\alpha, \rho^\beta] = \frac{1}{2} \sum_{\sigma,\sigma'=\alpha,\beta} \iint \frac{\overline{\rho_2^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')} - \rho^\sigma(\mathbf{r})\rho^{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \quad (1)$$

where $\rho^\sigma(\mathbf{r})$ is the electron spin density and $\overline{\rho_2^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')}$ is the spin-resolved electron pair density, averaged over the constant-density adiabatic connection path in which the electron−electron repulsion potential $\lambda/|\mathbf{r} - \mathbf{r}'|$ is increased from the non-interacting Kohn−Sham limit ($\lambda = 0$) to the physically relevant system of interacting electrons ($\lambda = 1$)[5,6]

$$\overline{\rho_2^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')} = \int_0^1 \rho_{2,\lambda}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \, d\lambda \quad (2)$$

From eq 1, it is clear that the exchange-correlation energy is the correction to the energy from the fact that electrons are not independent classical particles, where $\rho_2^{\sigma\sigma'}(\mathbf{r},\mathbf{r}') = \rho^\sigma(\mathbf{r})\rho^{\sigma'}(\mathbf{r}')$.

Often, the expression for the exchange-correlation energy is rewritten in terms of the exchange-correlation hole,

$$\overline{h_{xc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')} = \frac{\overline{\rho_2^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')} - \rho^\sigma(\mathbf{r})\rho^{\sigma'}(\mathbf{r}')}{\rho^\sigma(\mathbf{r})\rho^{\sigma'}(\mathbf{r}')} \quad (3)$$

With this definition of the exchange-correlation hole, the expression for the exchange-correlation energy is

$$E_{xc}[\rho^\alpha, \rho^\beta] = \frac{1}{2} \sum_{\sigma,\sigma'=\alpha,\beta} \iint \frac{\rho^\sigma(\mathbf{r})\overline{h_{xc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')}\rho^{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \quad (4)$$

The reader is cautioned that other definitions for the exchange-correlation hole are also prevalent in the literature,[7,8] but this is the most useful definition for our purposes. With this definition, the exchange-correlation charge (which some other authors refer to as the exchange-correlation hole) is defined as

$$\overline{\rho_{xc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')} = \rho^\sigma(\mathbf{r})\overline{h_{xc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')} \quad (5)$$

and pair correlation function is defined as

$$\overline{g_{xc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')} = \overline{h_{xc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')} + 1 \quad (6)$$

Most, density functionals further define an exchange-correlation energy density per particle,

$$e_{xc}^\sigma[\rho^\alpha, \rho^\beta; \mathbf{r}] = \frac{1}{2} \sum_{\sigma'=\alpha,\beta} \int \frac{\overline{h_{xc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')}\rho^{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \quad (7)$$

so that the exchange-correlation energy can be expressed as

$$E_{xc}[\rho^\alpha, \rho^\beta] = \sum_{\sigma=\alpha,\beta} \int \rho^\sigma(\mathbf{r})e_{xc}^\sigma[\rho^\alpha, \rho^\beta; \mathbf{r}] \, d\mathbf{r} \quad (8)$$

The exchange-correlation energy density per particle is conventionally approximated based on the electron density (local density approximation; LDA), electron density derivatives (generalized gradient approximation; GGA), the local kinetic energy (meta-GGA), and/or the occupied Kohn−Sham orbitals (hybrid-GGA) at the point $\mathbf{r}$.[9,10]

Recently, however, there has been renewed interest in two-point exchange-correlation functionals based on the fundamental and defining expression for the exchange-correlation energy, eq 4. Much of this work has been motivated by the realization that exchange-correlation functionals often fail for long-range electron correlation[4,11−28] and that the most natural way to remedy this problem is to use an explicitly nonlocal exchange-correlation functional.[29−35] Second, the most elegant and least ad hoc way to treat dispersion (which is electron correlation in the long-distance limit) in DFT uses two-point functionals.[36−42]

In this paper, we will propose a new functional based on the exchange-correlation hole of the uniform electron gas, as parametrized by Gori-Giorgi and Perdew.[43] The idea of directly modeling the exchange-correlation hole is very old and is the defining characteristic of the most venerable of all nonlocal functionals: the weighted density approximation (WDA).[44−46] Although the WDA has fallen out of favor, the trickle of papers that persists[47−56] suggest it is worth revisiting: the WDA gives more accurate highest-occupied orbital energies[57] and band gaps[47−50] than the most of the density functionals that are commonly used in condensed matter physics. More importantly for our purposes, by directly modeling the exchange-correlation hole, we can design functionals with excellent formal and practical properties. The link between good functional properties and directly enforceable constraints on the exchange-correlation hole model is expounded on in section II.

The goal of this paper is to provide the background that is needed to construct a new generation of exchange-correlation functionals based on the venerable weighted density approximation. The specific form we use is a type of symmetrized WDA; it is similar to other proposals along those lines that have appeared in the literature.[58,59] In the next section, we catalogue the properties of the exact functional that one can reproduce in a functional of this form. This also defines the constraints that a good exchange-correlation hole model should satisfy. One of the constraints we derive is a new, more general, version of the "flat planes" conditions proposed by Mori-Sanchez, Cohen, and Yang.[24,60] In section III, we use the model exchange-correlation hole for the uniform electron gas proposed by Gori-Giorgi and Perdew[43] to construct a symmetrized WDA. Computational tests of this model are described in section IV.

II. ADVANTAGES OF NONLOCAL DENSITY FUNCTIONALS FOR EXCHANGE-CORRELATION; PROPERTIES OF THE EXCHANGE-CORRELATION HOLE

A. Dispersion Effects and the |r−r′| → ∞ Limit of the Hole. Nonlocal exchange-correlation energy functionals based on eq 4 are naturally suited to many chemical and physical phenomena that are usually considered beyond the purview of mean-field models such as the Kohn−Sham DFT. For example, as long as the exchange-correlation hole has the right asymptotic decay when the interelectronic separation is large,[61−63]

$$h_{xc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \sim |\mathbf{r} - \mathbf{r}'|^{-5} \tag{9}$$

the correct R^{-6} form for dispersion interactions will be attained in a seamless way, without the need for arbitrary damping functions. Model holes that describe long-range electron correlation correctly give correct qualitative results for dispersion interactions without the need for semiempirical damping functions.

The reader is cautioned that eq 9 is not valid for infinitely extended systems such as uniform electron gas.

B. On-Top Pair Density and the |r−r′| → 0 Limit of the Hole. At the other extreme, the form of the exchange-correlation hole when the interelectronic distance is nearly zero, $|\mathbf{r} - \mathbf{r}'| \approx 0$, is known to be critically important for designing good density functionals.[64−68] The correct behavior can be directly imposed by choosing a suitable model for the exchange-correlation hole.[68−72] The simplest of these conditions is the electron−electron coalescence condition. For same-spin electrons, the first nonvanishing derivative at $\mathbf{r} = \mathbf{r}'$ is positive and is twice an odd number,[73]

$$0 = \left[\frac{\partial^k h^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')}{\partial |\mathbf{r} - \mathbf{r}'|^k} \right]_{|\mathbf{r}-\mathbf{r}'|=0} \qquad k = 1, 2, ..., 4n - 3$$

$$0 < \left[\frac{\partial^{4n-2} h^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')}{\partial |\mathbf{r} - \mathbf{r}'|^{4n-2}} \right]_{|\mathbf{r}-\mathbf{r}'|=0} \tag{10}$$

Typically, $n = 1$. For opposite-spin electrons,[74]

$$1 + h_{xc}^{\sigma\neq\sigma'}(\mathbf{r}, \mathbf{r}) = \left[\frac{\partial h_{xc}^{\sigma\neq\sigma'}(\mathbf{r}, \mathbf{r}')}{\partial |\mathbf{r} - \mathbf{r}'|} \right]_{|\mathbf{r}-\mathbf{r}'|=0} \tag{11}$$

C. Self-Interaction Error, the Asymptotic Decay of the Exchange-Correlation Potential, and the Hole Normalization Constraint. In a state with integer numbers of α-spin and β-spin electrons, each α-spin electron interacts with $N_\alpha - 1$ α-spin electrons and N_β β-spin electrons. This implies that the same-spin exchange-correlation hole is normalized to minus one,

$$-1 = \int \rho^\sigma(\mathbf{r}') \overline{h_{xc}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')} \, d\mathbf{r}' \tag{12}$$

and the opposite-spin correlation hole is normalized to zero,

$$0 = \int \rho^\sigma(\mathbf{r}') \overline{h_c^{\sigma\neq\sigma'}(\mathbf{r}, \mathbf{r}')} \, d\mathbf{r}' \tag{13}$$

Any functional that satisfies these constraints is (one-electron) self-interaction free.[75,76] The absence of self-interaction error has many desirable consequences, including exact results for one-electron systems, exchange-correlation potentials with correct asymptotic decay,[76−82]

$$v_{xc}^\sigma(\mathbf{r}) \sim -\frac{1}{r} \tag{14}$$

and qualitatively correct description of long-range charge transfer excitations,[83−85] Rydberg series,[86−89] and band gaps.[88,90,91]

D. Many-Electron Self Interaction Error and Generalized Flat-Planes Conditions. When the number of α-spin or β-spin electrons is not an integer, the exchange-correlation hole is not normalized in the usual way.[19,20,76,92] This causes severe problems for conventional density functional approximations because almost all such approximations try to normalize the exchange-correlation hole based on eqs 12 and 13. This results in large errors, which are called, by various authors, the many-electron self-interaction error,[19,26,93,94] electron delocalization error,[23,95] spin-polarization error,[93] and the static- or strong-correlation error.[18,96] We call this the fractional-N_σ error. A related issue arises whenever there are degenerate ground states,[11,13,14,97] giving rise to artificial splittings of atomic multiplets.[98,99] Overcoming the fractional-N_σ error is one of the

most important problems in present-day density functional development.[24,93,96,100−103]

In the Appendix, we show that the exchange-correlation hole in a system with fractional N_σ should be normalized according to

$$
\int \rho^\alpha(\mathbf{r}') h_{xc,\lambda}^{\alpha\alpha}(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}'
$$
$$
= -1 - \phi_\alpha + \frac{w_3 \rho_{\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor, \lambda}^\alpha(\mathbf{r}) + w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r})}{\rho^\alpha(\mathbf{r})}
\tag{15}
$$

$$
\int \rho^\beta(\mathbf{r}') h_{xc,\lambda}^{\beta\beta}(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}'
$$
$$
= -1 - \phi_\beta + \frac{w_2 \rho_{\lfloor N_\alpha \rfloor, \lceil N_\beta \rceil, \lambda}^\beta(\mathbf{r}) + w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\beta(\mathbf{r})}{\rho^\beta(\mathbf{r})}
\tag{16}
$$

$$
\int \rho^\beta(\mathbf{r}') h_{c,\lambda}^{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}'
$$
$$
= -\phi_\beta + \frac{w_2 \rho_{\lfloor N_\alpha \rfloor, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r}) + w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r})}{\rho^\alpha(\mathbf{r})}
\tag{17}
$$

$$
\int \rho^\alpha(\mathbf{r}') h_{c,\lambda}^{\beta\alpha}(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}'
$$
$$
= -\phi_\alpha + \frac{w_3 \rho_{\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor, \lambda}^\beta(\mathbf{r}) + w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\beta(\mathbf{r})}{\rho^\beta(\mathbf{r})}
\tag{18}
$$

where

$$
\phi_\sigma = N_\sigma - \lfloor N_\sigma \rfloor
\tag{19}
$$

is the number of fractional σ-spin electrons. (Here, $\lfloor N_\sigma \rfloor$ is the largest integer smaller than N_σ and $\lceil N_\sigma \rceil$ is the smallest integer larger than N_σ, e.g., $\lfloor 11.38 \rfloor = 11$ and $\lceil 11.38 \rceil = 12$.) The forms of the ensemble weighting coefficients in eqs 15−19 depend on which of the four cases discussed in the Appendix (cf. eqs 57−62 and the surrounding discussion) applies. With our preferred definition for the exchange-correlation hole (cf. eq 3), the hole is multiplied by the spin-density in the normalization condition.

Equations 15−18 are the spin-resolved version of the normalization condition previously derived by Perdew and presented in eq 84 of ref 92. They ensure that the nonphysical Coulomb repulsion of a fractional electron with itself is appropriately modeled.[11,104] Any exchange-correlation hole model that fulfills these constraints will naturally have a qualitatively correct derivative discontinuity[92,105−108] and qualitatively correct behavior for fractional spin;[11,18,101,109] that is, exchange-correlation holes that satisfy eqs 15−18 are consistent with the "flat-planes" condition.[24,101] Exchange-correlation hole models that violate these constraints are not consistent with the "flat-planes" constraint.

Imposing eqs 15−18 only solves the "easy" problem where N_σ is fractional for the entire system and not the chemically relevant problem of delocalized electrons and stretched bonds, where the number of electrons in the system is an integer (so eqs 12 and 13 are valid) but the effective number of electrons in a subsystem is not an integer. Most (but not all)[103,110] other recent attempts to resolve the flat-planes conditions are also restricted to this idealized scenario.[100] The important observation is that eq 4 is a very convenient functional form for addressing the fractional-N_σ error and that any model for the

exchange-correlation hole that is both correctly normalized and reasonably nearsighted is expected to give good results. We point out that imposing correct normalization on the exchange-correlation hole can only remedy problems associated with spin-degeneracy and fractional charge: the static correlation problem for spatially degenerate and very-nearly degenerate ground states persists.

E. Asymptotic Exchange-Correlation Potential, Excitation Energies, and the Asymptotic Decay of the Hole. The exchange-correlation hole specifies the probability of observing a σ-spin electron at the point $\mathbf{r}$ given that there is a σ'-spin electron at the point $\mathbf{r}'$,

$$
P_\lambda(\mathbf{r}\sigma|\mathbf{r}'\sigma') \equiv \rho_{N_\alpha, N_\beta}^\sigma(\mathbf{r})\big(1 + h_{xc,\lambda}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')\big) = \frac{\rho_{2,\lambda}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')}{\rho_{N_\alpha, N_\beta}^{\sigma'}(\mathbf{r}')}
\tag{20}
$$

When a σ'-spin electron is very far from the system, what remains is the ionized system, and so, the probability of observing an electron at $\mathbf{r}$ is the same as it would be in the $(N_{\sigma'} - 1)$-electron ground state. Therefore,

$$
\lim_{\mathbf{r}' \to \infty} P(\mathbf{r}\sigma|\mathbf{r}'\sigma') \equiv \rho_{(N_\alpha - \delta_{\alpha\sigma'}),(N_\beta - \delta_{\beta\sigma'})}^\sigma(\mathbf{r})
\tag{21}
$$

and so, for large $\mathbf{r}'$,

$$
\rho_{N_\alpha, N_\beta}^\sigma(\mathbf{r}) h_{xc,\lambda}^{\sigma\alpha}(\mathbf{r}, \mathbf{r}') \sim \rho_{N_\alpha - 1, N_\beta, \lambda}^\sigma(\mathbf{r}) - \rho_{N_\alpha, N_\beta}^\sigma(\mathbf{r})
$$
$$
\rho_{N_\alpha, N_\beta}^\sigma(\mathbf{r}) h_{xc,\lambda}^{\sigma\beta}(\mathbf{r}, \mathbf{r}') \sim \rho_{N_\alpha, N_\beta - 1, \lambda}^\sigma(\mathbf{r}) - \rho_{N_\alpha, N_\beta}^\sigma(\mathbf{r})
\tag{22}
$$

$$
\rho_{N_\alpha, N_\beta}^\sigma(\mathbf{r}) \overline{h_{xc,\lambda}^{\sigma\alpha}(\mathbf{r}, \mathbf{r}')} \sim \overline{\rho_{N_\alpha - 1, N_\beta}^\sigma(\mathbf{r})} - \rho_{N_\alpha, N_\beta}^\sigma(\mathbf{r})
$$
$$
\rho_{N_\alpha, N_\beta}^\sigma(\mathbf{r}) \overline{h_{xc,\lambda}^{\sigma\beta}(\mathbf{r}, \mathbf{r}')} \sim \overline{\rho_{N_\alpha, N_\beta - 1}^\sigma(\mathbf{r})} - \rho_{N_\alpha, N_\beta}^\sigma(\mathbf{r})
\tag{23}
$$

where

$$
\overline{\rho_{N_\alpha, N_\beta}^\sigma(\mathbf{r})} = \int_0^1 \rho_{N_\alpha, N_\beta, \lambda}^\sigma(\mathbf{r})\, d\lambda
\tag{24}
$$

These expressions are accurate up to order $(1/r')$;[4] the next-order term arises from the polarization of the $(N_{\sigma'} - 1)$-electron system by the negative point charge at $\mathbf{r}'$.[77,86,111] This indicates that the asymptotic decay of the exchange-correlation hole is related to the spin-Fukui functions.[112−117] As mentioned in the Appendix, the normalization conditions on the exchange-correlation hole can also be written in terms of the (adiabatically averaged) spin-Fukui functions. Equations 22 are only valid when N_α and N_β are integers; otherwise one obtains more elaborate equations involving the ensemble weighting coefficients (using the same types of arguments employed in the Appendix).

The asymptotic properties of the exchange-correlation hole determine the leading-order terms in the asymptotic decay of the exchange-correlation potential,

$$
v_{xc}^\sigma(\mathbf{r}) = \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho^\sigma(\mathbf{r})}
$$
$$
= \sum_{\sigma' = \alpha, \beta} \int \frac{\rho^{\sigma'}(\mathbf{r}') \overline{h_{xc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'
$$
$$
+ \frac{1}{2} \sum_{\sigma', \sigma'' = \alpha, \beta} \iint \frac{\rho^{\sigma'}(\mathbf{r}') \rho^{\sigma''}(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} \frac{\delta \overline{h_{xc}^{\sigma'\sigma''}(\mathbf{r}', \mathbf{r}'')}}{\delta \rho^\sigma(\mathbf{r})}\, d\mathbf{r}'\, d\mathbf{r}''
\tag{25}
$$

The term in the last line, called the response potential, is short-ranged (decaying as r^{-4}) and repulsive.[7,81,118−120] Equation 23

implies that the asymptotic decay of the exchange-correlation hole is given by

$$v_{xc}^\sigma(\mathbf{r}) \sim \sum_{\sigma'=\alpha,\beta} \int \frac{\overline{\rho_{(N_\alpha - \delta_{\sigma\alpha}),(N_\beta - \delta_{\sigma\beta})}^{\sigma'}(\mathbf{r})} - \rho_{N_\alpha,N_\beta}^{\sigma'}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}'$$

$$+ O(r^{-4}) = \int \frac{\overline{\rho_{(N_\alpha - \delta_{\sigma\alpha}),(N_\beta - \delta_{\sigma\beta})}(\mathbf{r})} - \rho_{N_\alpha,N_\beta}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}'$$

$$+ O(r^{-4}) \tag{26}$$

The adiabatic average does not affect the asymptotic form up to fifth-order,[79] so this equation simplifies to[111]

$$v_{xc}^\sigma(\mathbf{r}) \sim \int \frac{\rho_{(N_\alpha - \delta_{\sigma\alpha}),(N_\beta - \delta_{\sigma\beta})}(\mathbf{r}) - \rho_{N_\alpha,N_\beta}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + O(r^{-4}) \tag{27}$$

It is known that the asymptotic decay of the exchange-correlation potential plays an important role in giving reliable excitation energies.[86,88,111] If the asymptotic form of the exchange-correlation hole is correct, then the asymptotic form of the exchange-correlation potential will also be correct.

F. N-representability and Associated Constraints on the Hole.

One criticism of DFT is that approximate DFT calculations often give energies below the true ground-state energy. Approximate DFT (DFA) does not give a variational upper bound to the energy. This, and many other problems with DFA (including the fractional-N_σ error), arise because common DFAs are not N-representable.[121−131] The exact constraints for the N-representability of the exchange-correlation functional are known, but not in a convenient form.[131] One can, however, derive practical N-representability constraints for the exchange-correlation hole, and if the exchange-correlation hole is N-representable, the exchange-correlation energy functional will be too.

We will present a full account of N-representability conditions for the exchange-correlation hole in a subsequent paper. Here, we point out a few main issues. First of all, it is not enough for the exchange-correlation hole to be N-representable: it actually needs to be jointly N-representable with the associated electron density. That is, we want conditions that ensure that there exists an N-electron system that corresponds to a specific $(h_{xc,\lambda}^{\sigma\sigma'}(\mathbf{r},\mathbf{r}'),\rho^\sigma(\mathbf{r}))$ pair; the exchange-correlation hole is then said to be ρ^σ-representable. An exchange-correlation hole is ρ^σ-representable if and only if there exists an N-electron system with spin densities $(\rho^\alpha(\mathbf{r}),\rho^\beta(\mathbf{r}))$ that has this exchange-correlation hole.

A marginally more useful version characterization of the ρ^σ-representable problem follows from the N-representability conditions for the electron pair density.[132−135] Specifically, the exchange correlation hole, $h_{xc}^{\sigma\sigma'}(\mathbf{r},\mathbf{r}')$, is ρ^σ-representable if and only if

$$\frac{1}{2} \sum_{\substack{\sigma=\alpha,\beta \\ \sigma'=\alpha,\beta}} \iint \rho^{(\sigma)}(\mathbf{r})\rho^{(\sigma')}(\mathbf{r}') h_{xc}^{(\sigma,\sigma')}(\mathbf{r},\mathbf{r}') w^{(\sigma\sigma')}(\mathbf{r},\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}'$$

$$\geq E_{Cl}[w^{(\sigma\sigma')}; N_\alpha, N_\beta] - \frac{1}{2} \sum_{\substack{\sigma=\alpha,\beta \\ \sigma'=\alpha,\beta}} \iint \rho^{(\sigma)}(\mathbf{r})\rho^{(\sigma')}(\mathbf{r}')$$

$$\times w^{(\sigma\sigma')}(\mathbf{r},\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \tag{28}$$

for every choice of the pair interaction potentials, $w^{(\sigma\sigma')}(\mathbf{r},\mathbf{r}')$. Here, $E_{Cl}[w^{(\sigma\sigma')};N_\alpha,N_\beta]$ is the ground-state energy of a

classical system of fermions bound by the same pair potential. That is,

$$E_{Cl}[w^{(\sigma\sigma')}; N_\alpha, N_\beta]$$

$$= \inf_{\substack{\{\mathbf{r}_i,s_i\}_{i=1}^N \\ N_\alpha = \sum_{i=1}^N \delta_{\alpha s_i}}} \left(\sum_{i=1}^N \sum_{j \neq i} \begin{pmatrix} \delta_{\alpha s_i}\delta_{\alpha s_j}w^{\alpha\alpha}(\mathbf{r}_i,\mathbf{r}_j) + \delta_{\alpha s_i}\delta_{\beta s_j}w^{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j) \\ +\delta_{\beta s_i}\delta_{\alpha s_j}w^{\beta\alpha}(\mathbf{r}_i,\mathbf{r}_j) + \delta_{\beta s_i}\delta_{\beta s_j}w^{\beta\beta}(\mathbf{r}_i,\mathbf{r}_j) \end{pmatrix} \right) \tag{29}$$

The constraints on this minimization ensure that the number of and kind of "classical electrons" mimics the quantum system of interest. If the pair potential is not continuous, an additional constraint, due to the Pauli principle, is necessary, and one requires that $(\mathbf{r}_i, s_i) \neq (\mathbf{r}_j, s_j)$.

Imposing the necessary and sufficient conditions for ρ^σ-representability is not practical because it requires solving all possible classical-N body problems.[134] However, work on the N-representability of the electron pair-density can be adapted to provide interesting practically useful necessary conditions on ρ^σ-representability.[73,132−134,136−142] For example, the normalization conditions on the exchange-correlation hole are ρ^σ-representability conditions; they are usually called "sequential relations" in this context.[134] The Davidson[136] (and generalized Davidson[73,132,137]) conditions are also relevant: for any potential-like[143] functions $(f^\alpha(\mathbf{r}), f^\beta(\mathbf{r}))$,

$$\sum_{\substack{\sigma=\alpha,\beta \\ \sigma'=\alpha,\beta}} \int \rho^\sigma(\mathbf{r})\rho'(\mathbf{r}') h_{xc,\lambda}^{\sigma\sigma'}(\mathbf{r},\mathbf{r}') f^\sigma(\mathbf{r}) f^{\sigma'}(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}'$$

$$\geq - \sum_{\substack{\sigma=\alpha,\beta \\ \sigma'=\alpha,\beta}} \iint \rho^\sigma(\mathbf{r})[\rho^{\sigma'}(\mathbf{r}')$$

$$+ \delta(\mathbf{r} - \mathbf{r}')\delta_{\sigma\sigma'}]f^\sigma(\mathbf{r}) f^{\sigma'}(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \tag{30}$$

In practice, this constraint becomes tighter as the number of electrons increases; it implies that the ground-state exchange-correlation hole for an N_1-electron system will not be N_2-representable if $N_2 > N_1$.[134,135,141] This means that universal N-independent models for the exchange-correlation hole can be exact or N-representable but not both. (If the model is exact for some N_1, then it will not be acceptable in systems with additional electrons.)

All of the N-representability conditions listed here hold at any point along the adiabatic connection pathway and also for the adibatically averaged exchange-correlation hole.

III. SYMMETRIZED WEIGHTED DENSITY APPROXIMATIONS

A. The Exchange-Correlation Hole Model of Gori-Giorgi and Perdew.

The previous section establishes that many of the biggest problems that afflict Kohn−Sham DFT can be addressed by constructing a suitable model for the exchange-correlation hole, $\overline{h_{xc}^{\sigma\sigma'}(\mathbf{r},\mathbf{r}')}$. There are relatively few six-dimensional models for the exchange-correlation hole in the literature, and none of the proposed models possess all the desirable features presented in the previous section. While we hope to design better models in the future, for now, we have chosen to use the exchange-correlation hole of the uniform electron gas,[43,144] without the improvements that would be necessary to treat the distinctive long-range correlations and highly structured correlation holes that arise in molecular systems.

In this paper we use the Gori-Giorgi–Perdew (GGP) model for the total exchange-correlation hole of the spin-polarized electron gas, which has the functional form[43]

$$\overline{g_{xc}}(k_F|\mathbf{r} - \mathbf{r}'|, r_s, \zeta)$$
$$= g_x(k_F|\mathbf{r} - \mathbf{r}'|, \zeta) + \overline{g_c(k_F|\mathbf{r} - \mathbf{r}'|, r_s, \zeta)} \tag{31}$$

where

$$\overline{g_{xc}(\mathbf{r}, \mathbf{r}')} = 1 + \overline{h_{xc}(\mathbf{r}, \mathbf{r}')} = \frac{\overline{\rho_2(\mathbf{r}, \mathbf{r}')}}{\rho(\mathbf{r})\rho(\mathbf{r}')} \tag{32}$$

is the adiabatically averaged pair-correlation function and

$$\overline{\rho_2(\mathbf{r}, \mathbf{r}')} = \sum_{\sigma,\sigma'=\alpha,\beta} \overline{\rho_2^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')} \tag{33}$$

and

$$\rho(\mathbf{r}) = \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}) \tag{34}$$

are the total pair density and total electron density, respectively. The spin polarization is denoted

$$\zeta(\mathbf{r}) = \frac{\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})}{\rho(\mathbf{r})} \tag{35}$$

In the uniform electron gas, the Fermi momentum and the radius of the Fermi sphere are respectively

$$k_F(\mathbf{r}) = (3\pi^2\rho(\mathbf{r}))^{1/3} \tag{36}$$

and

$$r_s(\mathbf{r}) = \left(\frac{4}{3}\pi\rho(\mathbf{r})\right)^{-1/3} = \left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{k_F(\mathbf{r})} \tag{37}$$

The unusual dependence of the GGP model on both r_s and k_F (which are related to each other according to eq 37) arises from the adiabatic connection, which Gori-Giorgi and Perdew perform using the formula[43]

$$\overline{g_{xc}(k_F u, r_s, \zeta)} = \frac{1}{r_s}\int_0^{r_s} g_{xc}(k_F|\mathbf{r} - \mathbf{r}'|, R_s, \zeta)\, dR_s \tag{38}$$

For the detailed form of the GGP model exchange-correlation hole, the reader is referred to ref 43. Desirable features include the fact that the model reproduces the exchange and correlation energy of the uniform electron gas, reproduces the electron cusp and consistency of the model with the Overhauser model when $|\mathbf{r} - \mathbf{r}'| \approx 0$, and satisfies the normalization condition and the plasmon sum rules for the uniform electron gas. Note that while satisfying the plasmon sum rules in the electron gas gives the hole its characteristic $|\mathbf{r} - \mathbf{r}'| \to \infty$ form, the exchange-correlation hole in the uniform electron gas decays more rapidly than in molecules, so functionals based on this model are not expected to be suitable for molecular dispersion.

The GGP model for the exchange-correlation hole has the functional form

$$\overline{h_{xc}^{GGP}(\mathbf{r}, \mathbf{r}')} = \overline{g_{xc}(k_F|\mathbf{r} - \mathbf{r}'|, r_s, \zeta)} - 1. \tag{39}$$

Because the GGP model is not spin-resolved, we cannot impose the specific spin-density normalization conditions in eqs 15–18. For this reason, we treat only closed-shell systems with integer electron number in this paper. In this case, $\zeta = 0$ and the GGP model hole has the form

$$\overline{h_{xc}^{GGP}(\mathbf{r}, \mathbf{r}')} = \overline{h_{xc}^{GGP}(k_F|\mathbf{r} - \mathbf{r}'|, r_s)} \tag{40}$$

The approximations in this paper all use this form; they differ only in how they approximate k_F and r_s. In approximating these quantities, we consider only two constraints: the symmetry of the exchange-correlation hole, $\overline{h_{xc}^{GGP}(\mathbf{r}, \mathbf{r}')} = \overline{h_{xc}^{GGP}(\mathbf{r}', \mathbf{r})}$, and its normalization,

$$\int \rho(\mathbf{r}')h_{xc}^{GGP}(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}' = -1. \tag{41}$$

B. Symmetrized Weighted Density Approximation. The simplest choice of exchange-correlation hole uses the local density approximation to determine $k_F(\mathbf{r})$ and $r_s(\mathbf{r})$. The resulting hole model hole,

$$\overline{h_{xc}(\mathbf{r}, \mathbf{r}')} = \overline{h_{xc}^{GGP}(k_F(\mathbf{r})|\mathbf{r} - \mathbf{r}'|, r_s(\mathbf{r}))} \tag{42}$$

however, is neither normalized nor symmetric with respect to $\mathbf{r}$ and $\mathbf{r}'$. The hole can be symmetrized by replacing k_F and r_s with the generalized power-mean of their values of at $\mathbf{r}$ and $\mathbf{r}'$,[145]

$$\overline{h_{xc}^{(p,q)}(\mathbf{r}, \mathbf{r}')} = \overline{h_{xc}^{GGP}(k_F^{(p)}(\mathbf{r}, \mathbf{r}')|\mathbf{r} - \mathbf{r}'|, r_s^{(q)}(\mathbf{r}, \mathbf{r}'))} \tag{43}$$

$$k_F^{(p)}(\mathbf{r}, \mathbf{r}') = \left(\frac{(k_F(\mathbf{r}))^p + (k_F(\mathbf{r}'))^p}{2}\right)^{1/p} \tag{44}$$

$$r_s^{(q);type2}(\mathbf{r}, \mathbf{r}') = \left(\frac{(r_s(\mathbf{r}))^q + (r_s(\mathbf{r}'))^q}{2}\right)^{1/q}$$
$$= \left(\frac{9\pi}{4}\right)^{1/3}\left(\frac{(k_F(\mathbf{r}))^{-q} + (k_F(\mathbf{r}'))^{-q}}{2}\right)^{1/q.} \tag{45}$$

The symmetrization technique was pioneered by García-González et al.[145] and has been extensively used for developing two-point density functionals.[58,145−153] The power-mean form includes all the typical means—including the arithmetic mean ($p = 1$), the harmonic mean ($p = -1$), the geometric mean ($p = 0$), and the root-mean-square ($p = 2$)—as special cases. We call the functional in eq 45 a "type 2" functional to distinguish it from the mathematically simpler "type 1" approximation to r_s in eq 46.

The values of p and q control the shape of the exchange-correlation hole. In an atom, when p and q approach infinity, the exchange-correlation hole at $\mathbf{r} = (0,0,z)$ will tend to be compressed toward the atom and spherical pointing away from the atom. (It will look like a soft sphere sitting on a hard surface, with the compressed region in the direction of the nucleus.) When p and q approach negative infinity, the exchange-correlation hole tends to be stretched toward infinity and it has a spherical shape toward the nucleus. At intermediate values of p and q, both effects exist: the exchange-correlation hole is an egg-shaped object, compressed toward the atomic nucleus and stretched away from the nucleus.

We will treat p and q as fitting parameters. The functional will give exact results for the uniform electron gas for all possible choices of these parameters, so there is no reason not to use these parameters to try to reproduce accurate data from other, more chemically relevant, systems. We usually choose p and q to be different, giving a two-parameter weighted density approximation (WDA2). A one-parameter weighted density approximation (WDA1) can be obtained by computing $r_s(\mathbf{r},\mathbf{r}')$

from $k_F(\mathbf{r},\mathbf{r}')$ using the relationship between these quantities in the uniform electron gas:

$$r_s^{\text{type1}}(\mathbf{r}, \mathbf{r}') = \left(\frac{9\pi}{4}\right)^{1/3}\left(\frac{1}{k_F^{(p)}(\mathbf{r}, \mathbf{r}')}\right) \tag{46}$$

We explored other forms for the relationship between $r_s(\mathbf{r},\mathbf{r}')$ and $k_F(\mathbf{r},\mathbf{r}')$, but none of the forms we explored performed significantly better than this simple choice.

C. Unnormalized WDA Functionals (0 pt-WDA). The simplest reasonable approximation is to express k_F and r_s as functions of the electron density using the formulas (eqs 36 and 37) that are appropriate for the uniform electron gas. For systems with nonuniform electron density, the resulting exchange-correlation hole is not normalized. We call these zero-point (0-pt) functionals to contrast with the next functionals we will present, which at least partially account for the normalization constraint, (41). 0 pt-WDA gives remarkably poor results. This is surprising, since the underlying assumptions (the exchange-correlation hole is taken from the uniform electron gas and considered as a local functional of the electron density) are the same as in conventional exchange-correlation local density approximations. The difference is that, in the local density approximation, it is the exchange-correlation charge (cf. eq 5), instead of the exchange-correlation hole, that is approximated by its expression from the uniform electron gas.

D. 1-Point Normalization in WDA Functionals (1 pt-WDA). In a system with nonuniform electron density, the formulas for k_F and r_s in the uniform electron gas need not be appropriate. In particular, there might be an effective local Fermi momentum that would lead to a more accurate model exchange-correlation hole. In the conventional weighted density approximation,[44−46] this effective $k_F(\mathbf{r})$ is obtained by imposing the normalization condition on the exchange-correlation hole at each point $\mathbf{r}$,

$$-1 = \int \rho(\mathbf{r}')\overline{h_{xc}^{\text{GGP}}(k_F(\mathbf{r})|\mathbf{r} - \mathbf{r}'|, r_s(\mathbf{r}))}\,d\mathbf{r}'$$

$$= \int \rho(\mathbf{r}') h_{xc}^{\text{GGP}}\left(k_F(\mathbf{r})|\mathbf{r} - \mathbf{r}'|, \left(\frac{9\pi}{4}\right)^{1/3}(k_F(\mathbf{r}))^{-1}\right)d\mathbf{r}' \tag{47}$$

After replacing the integrals by a numerical quadrature with N_{grid} points, this becomes a set of N_{grid} decoupled nonlinear equations for the values of $\{k_F(\mathbf{r}_i)\}_{i=1}^{N_{\text{grid}}}$. Because there is a nonlinear equation to solve at each point on the grid and because the value of k_F at one grid point does not depend on the value of k_F at other grid points, we call methods based on eq 47 one-point weighted density approximations (1 pt-WDA).

After $k_F(\mathbf{r})$ is determined from eq 47, the symmetric exchange-correlation hole is constructed and either one (eq 46; 1 pt-WDA1) or two (eq 45, 1 pt-WDA2) parameters are introduced. 1 pt-WDA functionals are significantly more accurate than 0 pt-WDA functionals, but they still are not competitive with present-day DFT functionals. The 1 pt-WDA hole is not normalized because of symmetrization.

E. 2-Point Normalization in WDA Functionals (2 pt-WDA). To obtain a normalized exchange-correlation hole, we should actually normalize the exchange-correlation hole after symmetrization. For example,

$$-1 = \int \rho(\mathbf{r}')\overline{h_{xc}^{\text{GGP}}(k_F^{(p)}(\mathbf{r}, \mathbf{r}')|\mathbf{r} - \mathbf{r}'|, r_s^{(q)}(\mathbf{r}, \mathbf{r}'))}\,d\mathbf{r}'$$

$$= \int \rho(\mathbf{r}') h_{xc}^{\text{GGP}}\left(2^{-1/p}[(k_F(\mathbf{r}))^p + (k_F(\mathbf{r}'))^p]^{1/p}|\mathbf{r} - \mathbf{r}'|, \left(\frac{9\pi}{4}\right)^{1/3}2^{-1/q}[(k_F(\mathbf{r}))^{-q} + (k_F(\mathbf{r}'))^{-q}]^{1/q}\right)d\mathbf{r}' \tag{48}$$

with a similar equation for the 1-parameter symmetrization, eq 46. Using numerical integration, this becomes a system of N_{grid} coupled nonlinear equations in N_{grid} unknowns. Because each equation depends explicitly on $k_F(\mathbf{r})$ and $k_F(\mathbf{r}')$, we call this type of functional the two-point weighted density approximation. The exchange-correlation hole is now normalized and so this style of functional is self-interaction free (aside from possible numerical issues in solving the system of nonlinear equations). Two-point weighted density approximations were first proposed by Garcia-Gonzalez, Alvarellos, Chacon, and Tarazona.[58]

IV. COMPUTATIONAL TESTS

A. Testing Protocol. We have performed extensive tests (to be reported elsewhere) of this type of symmetrized density functional theory for the kinetic energy[154] and exchange energy.[155] The results of those studies suggest that 2-pt WDA is competitive with gradient-corrected density functionals.

The tests we can perform for molecules are more limited. We do not believe it is sensible to apply the weighted density approximation to open-shell atoms and molecules without imposing the spin-resolved normalization conditions, eqs 12 and 13, but these conditions cannot be imposed using the GGP hole because it is not spin-resolved. This prevents us from performing the usual tests on molecular atomization energies. Instead, we decided to use the symmetrized WDAs to compute exchange-correlation energies directly. There are few examples of accurate exchange-correlation energies in the literature that are suitable for comparison. We use the closed-shell molecules in the Tozer−Handy set.[156] For each molecule, we used *Gaussian09* to perform a CCSD calculation using the same basis set that Tozer and Handy used in their calculations; the electron density we extract from that calculation should produce an electron density that is almost exactly the same as the one they use in their tests. We then computed the exchange-correlation energies for these densities with the symmeterized WDA functionals. For comparison, we also computed the exchange-correlation energy from two generalized gradient approximations (GGAs), one which recovers the uniform electron gas limit (PBE[157]) and a semiempirical functional based on the Colle−Salvetti form[158] (OCS1; OPTX exchange,[15] and CS1 correlation[159,160]), which does not recover the uniform electron gas limit. (By construction, all of our WDA-type functionals recover the uniform electron gas limit.) We chose the OCS1 functional primarily because its simple functional form is comparable in complexity to PBE.

B. Numerical Considerations. Although there are more efficient ways to handle the six-dimensional exchange-correlation energy integrals,[32,33,161] most of these methods are not directly applicable to the three-dimensional normalization integral for the exchange-correlation hole. We use a six-dimensional numerical integration grid that is the direct product of two three-dimensional Becke-Lebedev molecular integration grids.[162−166] The singularity in the exchange-correlation integral was avoided by removing from the sum all values of the integrand that exceed a threshold.

The one-point WDA functional requires solving a single nonlinear equation to determine $k_F(\mathbf{r}_i)$ at each grid point $\mathbf{r}_i$

Table 1. Molecular Exchange-Correlation Energies from Symmetrized Weighted Density Approximations, Compared to the Results from Conventional Generalized Gradient Functionals (PBE and OCS1[159,160]) and the Near-Exact Data from Tozer and Handy[156]

molecule	0 pt-WDA1	1 pt-WDA1	2 pt-WDA1	0 pt-WDA2	1 pt-WDA2	2 pt-WDA2	PBE	OCS1	exact
H_2	−0.474	−0.787	−0.745	−0.464	−0.787	−0.744	−0.683	−0.721	−0.698
F_2	−13.24	−19.432	−20.793	−13.125	−19.313	−20.690	−20.756	−20.709	−20.677
N_2	−8.924	−13.260	−13.769	−8.758	−13.225	−13.693	−13.637	−13.680	−13.676
HF	−6.997	−10.031	−10.866	−6.821	−9.981	−10.805	−10.790	−10.801	−10.807
BH	−2.784	−4.369	−4.329	−2.712	−4.333	−4.300	−4.279	−4.293	−4.292
CO	−9.038	−13.446	−13.951	−8.785	−13.337	−13.875	−13.833	−13.861	−13.858
H_2O	−6.100	−8.769	−9.390	−5.976	−8.695	−9.333	−9.248	−9.317	−9.315
CH_4	−4.632	−6.510	−6.835	−4.483	−6.447	−6.784	−6.621	−6.784	−6.891
avg. error	3.503	0.451	−0.058	3.636	0.512	−0.001	0.046	0.006	
RMS error	4.084	0.607	0.076	4.218	0.671	0.043	0.104	0.040	

(cf. eq 47). We solved this equation using Newton's method, with the local density approximation for k_F (i.e., 0 pt-WDA) as a starting value. Global convergence was ensured by using a trust radius. No convergence problems were observed and the total cost of the procedure was about 1 order of magnitude greater than the numerical integration used to obtain the exchange-correlation energy.

The two-point WDA functional requires solving a system of coupled nonlinear equations. A detailed account of the algorithm we developed will be published elsewhere. The key insight is that the largest values in the Jacobian matrix are concentrated on the diagonal; a quasi-Newton method using only the diagonal elements of the Jacobian suffices for convergence. Augmenting the diagonal-Jacobian approximation with a limited-memory variant of Broyden's method for approximating the inverse Jacobian[167] improved the rate of convergence. Starting from the k_F values from the 1 pt-WDA, acceptable convergence is usually achieved with less than 20 iterations of this quasi-Newton procedure, again using a trust radius to facilitate convergence.

There are numerical issues associated with 2 pt-WDA when $p > 1$. In this case, the equations seem to have no solution unless one permits $k_F(\mathbf{r}) < 0$ for some grid points in tails of the electron density. We did not allow this because we do not believe that normalizing the exchange-correlation hole in regions with negligible electron density is especially important. However, a consequence of this restriction is that the exchange-correlation hole is not perfectly normalized. The issue arises because when $p > 1$, the shape of the exchange-correlation hole at $(\mathbf{r}, \mathbf{r}')$ is determined primarily by whichever point has the larger value for k_F. When one point is far from the atom (small k_F), it has very little influence on the shape of the exchange-correlation hole around that point. This is a consequence of choosing p (and q) to be global constants when they should obviously be functionals of the electron density.

To determine the "optimal" values of p and q, we started with a large negative value of p and increased the value of p until the errors in our data were minimized; the value we obtained was $p = 10$. A similar procedure gave $q = 20$. These parameters are only optimized to within ±5, and choosing any value of p and q that is greater than or equal to five would give results of similar quality to the ones we report in Table 1.

We did not reoptimize p for the 1-parameter WDA or for the 0-point or 1-point functionals. Our calculations show that the improvements that we would have obtained by reoptimizing p (and q) would not affect our conclusions about the quality of these functionals.

If we had a suitable spin-resolved hole model, an analogous procedure could be applied. However, the system of nonlinear equations would be larger. (We would need to determine $k_F^\alpha(\mathbf{r})$, $k_F^\beta(\mathbf{r})$, $r_s^\alpha(\mathbf{r})$, and $r_s^\beta(\mathbf{r})$.)

C. Results. Our data for the one-parameter functionals ($p = 10$; 0 pt-WDA1, 1 pt-WDA1, 2 pt-WDA1) and two-parameter functionals ($p = 10$, $q = 20$; pt-WDA2, 1 pt-WDA2, 2 pt-WDA2) is reported in Table 1.

The 0-point functionals are remarkably inaccurate considering that the 0 pt-WDA is a nonlocal model built from the same assumptions as the conventional local density approximation. The local density approximation obviously works only because of cancellation of errors that occur during the spherical-averaging and system-averaging of the exchange correlation hole to form an exchange-correlation energy density. The 1-point functionals are much more accurate, but they are still far from competitive.

The 2-point functionals give exchange-correlation energies that are accurate enough to be useful. Both the 1-parameter (2 pt-WDA1) and 2-parameter (2 pt-WDA2) functionals give small-molecule exchange-correlation energies that are more accurate than PBE. 2 pt-WDA2 is competitive with the OCS1 functional, which is a good semiempirical GGA functional.[160] Unlike OCS1, however, 2 pt-WDA functionals are self-interaction free and recover the uniform electron gas limit.

V. SUMMARY

The primary purpose of this paper is to motivate a reconsideration of the weighted density approximation[44−46] in the symmetrized form proposed by Garcia-Gonzalez et al.[58] Our primary motivation for this pursuit is theoretical: directly modeling the exchange-correlation hole allows one to construct an exchange-correlation energy functional that has many desirable properties. This is discussed at length in section II. Things that are difficult to model with conventional density functionals (e.g., dispersion interactions and fractional numbers of electrons) are directly and explicitly reflected in the properties of the exchange-correlation hole as constraints that can be easily imposed on new hole-based exchange-correlation functionals. We also discuss conditions, such as the N-representability conditions for exchange-correlation functionals,[124,129,131] which seem intractable unless an explicit model for the exchange-correlation hole is employed.

A significant result in this section is the spin-resolved normalization conditions for the exchange-correlation hole,

which are derived in the Appendix. These conditions are closely linked to the fractional-N_σ error in exchange-correlation functionals, also called the "flat planes" conditions[24] and the many-electron self-interaction error.[19] In the Appendix, we show that there are two types of flat-planes conditions. The standard flat-planes conditions holds when (assuming integer numbers of electrons)

$$E(N_\alpha, N_\beta) + E(N_\alpha + 1, N_\beta + 1)$$
$$\geq E(N_\alpha + 1, N_\beta) + E(N_\alpha, N_\beta + 1) \tag{49}$$

When this is not true, an alternative condition holds. The postulate that eq 49 is always true is a strong, spin-resolved, extension of the convexity postulate for the energy as a function of the number of electrons. By directly modeling the exchange-correlation hole and imposing the normalization constraints in eqs 15−18 either type of flat-planes condition can be imposed. It is interesting that the (spin-resolved) Fukui functions[168,169] arise in both the normalization conditions for the exchange-correlation hole and its asymptotic form (Appendix and sections II.D and II.E).

As a first attempt to model the exchange-correlation hole, in section III, we construct a symmetrized weighted density approximations from the model exchange-correlation hole for the uniform electron gas proposed by Gori-Giorgi and Perdew.[43] When we ensure that the exchange-correlation hole is both symmetric and normalized (2 pt-WDA), the results we obtain are comparable to the best GGAs. This model is self-interaction free, and it recovers the uniform electron gas limit by construction. It is also essentially parameter-free: we do not rigorously optimize the two parameters that enter into the functional, and the parameters can be varied by a factor of 2 without affecting our results very much. 2 pt-WDA works better than PBE for small-molecule exchange-correlation energies even though it arguably contains less information about the exact functional than PBE. (No information about the nearly uniform electron gas is explicitly included in this functional.) Small molecule exchange-correlation energies from 2 pt-WDA are comparable in accuracy to those from the OCS1 GGA (which does not recover the uniform electron gas limit).

Since the GGP exchange-correlation hole is localized, long-range nonlocal structures in the exchange-correlation hole cannot be captured. Therefore, we do not expect WDAs based on the GGP hole to compete with nonlocal (e.g., hybrid) exchange-correlation functionals. A better model for the exchange-correlation hole is needed for that. Tests for atomization energies and other chemical properties require a spin-resolved exchange-correlation hole model so that the spin-resolved conditions for the normalization of the exchange-correlation hole can be enforced. Finally, it is known that no universal N-independent form for the exchange-correlation hole can be both exact and N-representable (cf. section II.F). It seems likely that the GGP model hole needs to be replaced by a model with a more complicated dependence on the number of electrons. This and other constraints (e.g., on the asymptotic form of the exchange-correlation hole; cf. section II.E) could be satisfied by constructing orbital model for the exchange-correlation hole. A small extension to this work is to decouple $r_s(\mathbf{r})$ from $k_F(\mathbf{r})$; by varying the two functions separately, one could force the correct normalization of the

uniform-electron-gas exchange-hole (which can be spin-resolved) and the GGP correlation hole separately. A larger extension would be to perform self-consistent calculations. Functionals built from WDA can be differentiated (cf. ref 170), although this is not easy to program.

We believe that building density functionals for the exchange-correlation hole, as we have done here, is an interesting strategy for constructing exchange-correlation functionals. Even within the 2 pt-WDA form, there is much room for improvement. We have chosen the parameters p and q to be universal constants. This is a severe assumption and preliminary indications suggest that p should be much smaller in the tails of the electron density than it is near the atomic positions. This could be achieved by making p (and/or q) be a function of the electron density. Even better, one could write the parameters as functions of the density and its derivatives. One can even allow p and q to have a more general dependencies on the occupied and/or unoccupied orbitals, thereby defining an entire hierarchy of 2 pt-WDAs analogous to Jacob's ladder of conventional exchange-correlation functionals.[9,10,171]

■ APPENDIX

In this appendix, we derive the normalization conditions for the spin-components of the exchange correlation hole; these are the spin-resolved versions of the normalization condition for the total exchange-correlation hole that was derived by Perdew,[19,20,76,92]

$$\int \rho(\mathbf{r}')h_{xc,\lambda}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}' = -1 + \frac{\phi(1 - \phi)f_{N,\lambda}(\mathbf{r})}{\rho_N(\mathbf{r})}$$
$$= -1 - \phi + \frac{\phi\rho_{[N]}(\mathbf{r})}{\rho_N(\mathbf{r})} \tag{50}$$

where

$$\phi = N - \lfloor N \rfloor \tag{51}$$

is the fractional number of electrons in the state, $\lfloor N \rfloor$ denotes the nearest integer less than or equal to N, $\lceil N \rceil$ denotes the nearest integer greater than or equal to N, $\rho_N(\mathbf{r})$ is the N-electron density,

$$\rho_N(\mathbf{r}) = \rho_{\lfloor N \rfloor, \lambda=1}(\mathbf{r}) + (N - \lfloor N \rfloor)f_{N,\lambda=1}(\mathbf{r}) \tag{52}$$

and

$$f_{N,\lambda}(\mathbf{r}) = \left(\frac{\partial\rho_N(\mathbf{r})}{\partial N}\right)_{v_\lambda(\mathbf{r})} = \rho_{\lceil N \rceil, \lambda}(\mathbf{r}) - \rho_{\lfloor N \rfloor, \lambda}(\mathbf{r}) \tag{53}$$

is the Fukui function.[168,169,172,173] The densities $\rho_{\lfloor N \rfloor, \lambda}(\mathbf{r})$ and $\rho_{\lceil N \rceil, \lambda}(\mathbf{r})$ are the ground-state electron densities for systems with nearest-integer number of electrons bound by the external potential, $v_\lambda(\mathbf{r})$, at the desired point on the adiabatic connection path. Matters can be somewhat more complicated when the ground state is spatially degenerate (because the electron density of the state is not uniquely defined);[174] we restrict ourselves to cases with at most spin-degeneracy.

Assuming that the energy is a convex function of the number of electrons and that the $\lfloor N_\sigma \rfloor$- and $\lceil N_\sigma \rceil$-electron states do not have any spatial degeneracy, the spin-components of the ground-state electron density and pair density will be linear

combinations of the densities, and pair densities from states with nearby integer numbers of electrons.[97,105,109,175,176] The same is true for most (but not all) molecular properties.[177] For most properties, p, of most systems, one has the specific formula,[178]

$$p(N_\alpha, N_\beta) = w_1 p(\lfloor N_\alpha \rfloor, \lfloor N_\beta \rfloor) + w_2 p(\lfloor N_\alpha \rfloor, \lceil N_\beta \rceil)$$
$$+ w_3 p(\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor) + w_4 p(\lceil N_\alpha \rceil, \lceil N_\beta \rceil)$$
(54)

where the weighting factors in the ensemble are nonnegative and satisfy the equations

$$1 = w_1 + w_2 + w_3 + w_4$$
$$N_\alpha = (w_1 + w_2)\lfloor N_\alpha \rfloor + (w_3 + w_4)\lceil N_\alpha \rceil$$
$$N_\beta = (w_1 + w_3)\lfloor N_\beta \rfloor + (w_2 + w_4)\lceil N_\beta \rceil$$
(55)

In analogy to eq 51, for analyzing these equations, we find it helpful to define the fractional part of the electron spin-numbers as

$$\phi_\sigma = N_\sigma - \lfloor N_\sigma \rfloor$$
(56)

Equation 54 can be derived by taking the zero-temperature limit of the grand canonical ensemble.[179−181] Alternatively, it can be derived by making several noninteracting copies of the system, and taking the limit as the number of copies goes to infinity.[97] When a system has a spatial degeneracy, the values of $p(N_\alpha, N_\beta)$ might not be unique. However, all allowed values of $p(N_\alpha, N_\beta)$ are obtained from eq 54 by using the properties of suitable (possibly mixed) states of the $(\lfloor N_\alpha \rfloor, \lfloor N_\beta \rfloor)$-, $(\lfloor N_\alpha \rfloor, \lceil N_\beta \rceil)$-, $(\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor)$-, and $(\lceil N_\alpha \rceil, \lceil N_\beta \rceil)$-electron systems.

Because there are four unknowns and only three equations, eqs 55 do not fully specify the state. The free coefficient is chosen so that the energy is minimized. There are two cases: there is a derivative discontinuity at integer electron number ($N_\alpha + N_\beta$ is an integer) or there is a derivative discontinuity at integer spin number ($N_\alpha - N_\beta$ is an integer).

The first case is the one that is usually considered; it arises when the hydrogen atom is considered.[24] More precisely, it occurs when

$$E(\lfloor N_\alpha \rfloor, \lfloor N_\beta \rfloor) + E(\lceil N_\alpha \rceil, \lceil N_\beta \rceil)$$
$$> E(\lfloor N_\alpha \rfloor, \lceil N_\beta \rceil) + E(\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor)$$
(57)

In this case, if $\phi_\alpha + \phi_\beta \leq 1$, then

$$w_1 = 1 - \phi_\alpha - \phi_\beta$$
$$w_2 = \phi_\beta$$
$$w_3 = \phi_\alpha$$
$$w_4 = 0$$
(58)

and if $\phi_\alpha + \phi_\beta \geq 1$, then

$$w_1 = 0$$
$$w_2 = 1 - \phi_\alpha$$
$$w_3 = 1 - \phi_\beta$$
$$w_4 = \phi_\alpha + \phi_\beta - 1$$
(59)

The second case has not been studied in detail. It arises when

$$E(\lfloor N_\alpha \rfloor, \lfloor N_\beta \rfloor) + E(\lceil N_\alpha \rceil, \lceil N_\beta \rceil)$$
$$< E(\lfloor N_\alpha \rfloor, \lceil N_\beta \rceil) + E(\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor)$$
(60)

In this case, if $\phi_\alpha \leq \phi_\beta$, then

$$w_1 = 1 - \phi_\beta$$
$$w_2 = \phi_\beta - \phi_\alpha$$
$$w_3 = 0$$
$$w_4 = \phi_\alpha$$
(61)

and if $\phi_\alpha \geq \phi_\beta$, then

$$w_1 = 1 - \phi_\alpha$$
$$w_2 = 0$$
$$w_3 = \phi_\alpha - \phi_\beta$$
$$w_4 = \phi_\beta$$
(62)

While the reader may be tempted to assume this second case never occurs because $E(N + 2) + E(N) < E(N) + E(N)$ contradicts the convexity postulate, it should be pointed out that the convexity postulate does not apply because the spin has been constrained. Therefore, some, or even all, of the states under consideration could be excited states. (For example, let state 1 in eq 54 be the ground state of the Cerium cation (quaduplet; $(N_\alpha, N_\beta) = (30,27)$). Then, states 2 and 3 will be excited states of the Cerium atom (with $(N_\alpha, N_\beta) = (31,27)$ and $(N_\alpha, N_\beta) = (30,28)$) but state 4 is the ground state of the Cerium anion $((N_\alpha, N_\beta) = (31,28))$.) We found no cases where eq 60 for atoms (including Cerium) or small molecules. This suggests that there might be a strong convexity postulate, namely that eq 60 never holds for lowest-energy states of the specified spins. This strong convexity postulate is true for noninteracting electrons, and it seems to be often true, but it may well be untrue in some cases. For now, we derive formulas for all the cases that can occur. Even if the strong convexity postulate is true for electrons, it will fail for other types of interparticle interactions (because the convexity postulate fails there too).[182−184]

The electron spin-density and pair density for noninteger N_σ are given by the eq 54 with the correct choice (one of eqs 58, 59, 61, and 62) of weighting coefficients in the ensemble. When N_α and N_β are both integers, the pair density obeys four sequential relations with the forms[135]

$$N_{\sigma'} \rho_\lambda^\sigma(\mathbf{r}) = \int \rho_{2,\lambda}^{\sigma \neq \sigma'}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}'$$

$$(N_\sigma - 1) \rho_\lambda^\sigma(\mathbf{r}) = \int \rho_{2,\lambda}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}'$$
(63)

Using eqs 63 and 54, the normalization of the $\alpha\alpha$ pair density is

$$\int \rho_{2,\lambda}^{\alpha\alpha}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}' = (\lfloor N_\alpha \rfloor - 1)(w_1 \rho_{\lfloor N_\alpha \rfloor, \lfloor N_\beta \rfloor, \lambda}^\alpha(\mathbf{r})$$
$$+ w_2 \rho_{\lfloor N_\alpha \rfloor, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r})) + \lfloor N_\alpha \rfloor (w_3 \rho_{\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor, \lambda}^\alpha(\mathbf{r})$$
$$+ w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r})) = (N_\alpha - 1)\rho^\alpha(\mathbf{r}) - \phi_\alpha \rho^\alpha(\mathbf{r})$$
$$+ w_3 \rho_{\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor, \lambda}^\alpha(\mathbf{r}) + w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r})$$
(64)

This implies that the normalization of the pair density cumulant is

$$
\int \rho_{2,\lambda}^{\alpha\alpha}(\mathbf{r}, \mathbf{r}') - \rho^\alpha(\mathbf{r})\rho^\alpha(\mathbf{r}') \, d\mathbf{r}'
$$
$$
= -\rho_\alpha(\mathbf{r}) - \phi_\alpha \rho^\alpha(\mathbf{r}) + w_3 \rho_{\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor, \lambda}^\alpha(\mathbf{r})
$$
$$
+ w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r}) \tag{65}
$$

and so the normalization of the exchange-correlation hole is

$$
\int \rho^\alpha(\mathbf{r}') h_{xc,\lambda}^{\alpha\alpha}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = \int \frac{\rho_{2,\lambda}^{\alpha\alpha}(\mathbf{r}, \mathbf{r}') - \rho^\alpha(\mathbf{r})\rho^\alpha(\mathbf{r}')}{\rho^\alpha(\mathbf{r})} d\mathbf{r}'
$$
$$
= -1 - \phi_\alpha + \frac{w_3 \rho_{\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor, \lambda}^\alpha(\mathbf{r}) + w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r})}{\rho^\alpha(\mathbf{r})} \tag{66}
$$

There are similar expressions for the other spin-resolved exchange-correlation holes,

$$
\int \rho^\beta(\mathbf{r}') h_{xc,\lambda}^{\beta\beta}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}'
$$
$$
= -1 - \phi_\beta + \frac{w_2 \rho_{\lfloor N_\alpha \rfloor, \lceil N_\beta \rceil, \lambda}^\beta(\mathbf{r}) + w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\beta(\mathbf{r})}{\rho^\beta(\mathbf{r})} \tag{67}
$$

$$
\int \rho^\beta(\mathbf{r}') h_{c,\lambda}^{\alpha\beta}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}'
$$
$$
= -\phi_\beta + \frac{w_2 \rho_{\lfloor N_\alpha \rfloor, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r}) + w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r})}{\rho^\alpha(\mathbf{r})} \tag{68}
$$

$$
\int \rho^\alpha(\mathbf{r}') h_{c,\lambda}^{\beta\alpha}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}'
$$
$$
= -\phi_\alpha + \frac{w_3 \rho_{\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor, \lambda}^\beta(\mathbf{r}) + w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\beta(\mathbf{r})}{\rho^\beta(\mathbf{r})} \tag{69}
$$

Just as the normalization conditions on the nonspin-resolved hole in eq 50 can be expressed in terms of the Fukui functions, the normalization conditions on the spin-resolved hole can be expressed in terms of the spin Fukui functions.[114–116] The expressions that result depend, however, on which of the four equations for the ensemble weights, eqs 58, 59, 61, and 62 is relevant. Other authors have recently noted that constraints based on the (spin)-Fukui functions are intimately connected to the "flat planes" conditions.[185,186]

The separate normalization conditions for the exchange and correlation holes depend on how one defines exchange. If one defines the exchange hole as the noninteracting limit of the exchange-correlation hole, then

$$
\int \rho^\alpha(\mathbf{r}') h_x^{\alpha\alpha}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}'
$$
$$
= -1 - \phi_\alpha + \frac{w_3 \rho_{\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor, \lambda=0}^\alpha(\mathbf{r}) + w_4 \rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda=0}^\alpha(\mathbf{r})}{\rho^\alpha(\mathbf{r})} \tag{70}
$$

Because the α-spin electrons are independent of the β-spin electrons in the noninteracting limit, eq 70 simplifies to

$$
\int \rho^\sigma(\mathbf{r}') h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}' = -1 - \phi_\sigma + \frac{\phi_\sigma \rho_{\lceil N_\sigma \rceil, \lambda=0}^\sigma(\mathbf{r})}{\rho^\sigma(\mathbf{r})} \tag{71}
$$

and

$$
\int \rho^\alpha(\mathbf{r}') h_{c,\lambda}^{\alpha\alpha}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}'
$$
$$
= \frac{w_3(\rho_{\lceil N_\alpha \rceil, \lfloor N_\beta \rfloor, \lambda}^\alpha(\mathbf{r}) - \rho_{\lceil N_\alpha \rceil, \lambda=0}^\alpha(\mathbf{r}))}{\rho^\alpha(\mathbf{r})}
$$
$$
+ \frac{w_4(\rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\alpha(\mathbf{r}) - \rho_{\lceil N_\alpha \rceil, \lambda=0}^\alpha(\mathbf{r}))}{\rho^\alpha(\mathbf{r})} \tag{72}
$$

Similarly,

$$
\int \rho^\beta(\mathbf{r}') h_{c,\lambda}^{\beta\beta}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}'
$$
$$
= \frac{w_2(\rho_{\lfloor N_\alpha \rfloor, \lceil N_\beta \rceil, \lambda}^\beta(\mathbf{r}) - \rho_{\lceil N_\beta \rceil, \lambda=0}^\beta(\mathbf{r}))}{\rho^\beta(\mathbf{r})}
$$
$$
+ \frac{w_4(\rho_{\lceil N_\alpha \rceil, \lceil N_\beta \rceil, \lambda}^\beta(\mathbf{r}) - \rho_{\lceil N_\beta \rceil, \lambda=0}^\beta(\mathbf{r}))}{\rho^\beta(\mathbf{r})} \tag{73}
$$

Because there is no opposite-spin exchange, eqs 68 and 69 are normalization conditions on the opposite-spin correlation holes.

Equations 70–72 presuppose that the pair density of the noninteracting system with fractional electron number is an appropriate ensemble average, described by an equation like 54. It is more typical to define the exchange energy in terms of the 1-electron reduced density matrix,

$$
E_x[\rho^\alpha, \rho^\beta] = \sum_{\sigma=\alpha,\beta} \frac{-1}{2} \iint \frac{\gamma^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')\gamma^{\sigma\sigma}(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \tag{74}
$$

and so the exchange hole is defined as

$$
h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') = -\frac{\gamma^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')\gamma^{\sigma\sigma}(\mathbf{r}', \mathbf{r})}{\rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}')} \tag{75}
$$

where the ensemble form for the density matrix is

$$
\gamma^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') = (1 - \phi_\sigma)\gamma_{\lfloor N_\sigma \rfloor}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') + \phi_\sigma \gamma_{\lceil N_\sigma \rceil}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') \tag{76}
$$

At least for states with no spatial degeneracy, the definition of the exchange hole form eq 75 agrees with the ensemble definition we use here, and its normalization satisfies eq 71.

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Notes
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