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Symmetric two-point weighted density approximation for exchange energies

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We describe a symmetric, two-point, nonlocal weighted density approximation for the exchange energy of atoms and compare it to conventional density functionals and the conventional weighted density approximation. Even the simplest two-point weighted density approximation gives results comparable to the best generalized gradient approximations. Unlike those functionals, however, the two-point weighted density approximation is fully nonlocal, has no self-interaction error, approximately fulfills the Pauli principle, and preserves the uniform electron gas limit.

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I. INTRODUCTION

In Kohn-Sham density-functional theory, the only unknown component of the energy is the exchange-correlation energy [1–4]. While the exchange-correlation energy is a small fraction of the total energy, describing it correctly is essential if useful accuracy for calculations of atoms, molecules, and materials is to be obtained. The quest for accurate, yet computationally feasible, approximations to the exchange-correlation density functionals continues. Recently, there has been significant interest in nonlocal density functionals, where the exchange-correlation energy is approximated as a six-dimensional integral [5–14],

$$E_{\mathrm{xc}}[\rho] = \int\int f[\rho;\mathbf{r},\mathbf{r}']d\mathbf{r}\,d\mathbf{r}'. \tag{1}$$

This is a natural form for the functional because the exact exchange-correlation energy functional can be written in the form

$$E_{\mathrm{xc}}[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')\overline{h_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}', \tag{2}$$

where

$$\overline{h_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')} = \int_0^1 h_{\mathrm{xc}}^{\lambda}(\mathbf{r},\mathbf{r}')d\lambda \tag{3}$$

is the exchange-correlation hole

$$h_{\mathrm{xc}}^{\lambda}(\mathbf{r},\mathbf{r}') = \frac{\rho_2^{\lambda}(\mathbf{r},\mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}')}{\rho(\mathbf{r})\rho(\mathbf{r}')} \tag{4}$$

averaged over the constant-density adiabatic connection path, in which the electron-electron repulsion potential $\lambda/|\mathbf{r}-\mathbf{r}'|$ is increased from the noninteracting limit ($\lambda = 0$) to the physical limit of interest ($\lambda = 1$) [15,16]. Here,

$$\rho_2^{\lambda}(\mathbf{r},\mathbf{r}') = \langle\Psi^{\lambda}|\sum_{j\neq i}\delta(\mathbf{r}_i-\mathbf{r})\delta(\mathbf{r}_j-\mathbf{r}')|\Psi^{\lambda}\rangle \tag{5}$$

is the electron pair density.

Two-point functionals of this type have advantages, especially when the exchange-correlation hole is not localized [17–20]. They are especially useful for adding corrections to orbital-based density functional [5,6] and are arguably essential to the correct treatment of long-range electron correlation (e.g., dispersion [7–13]).

There have been a few recent attempts in the literature to directly approximate the exchange-correlation hole in Eq. (3), notably the work of Gori-Giorgi to construct analytic exchange-correlation holes for the uniform electron gas [21,22] and recent attempts to construct nonlocal exchange-correlation holes using a variant of the classical Ornstein-Zernike expression [23–29]. One difficulty of these hole models is that they generally do not exactly satisfy the normalization condition on the exchange-correlation hole [30],

$$\int \rho(\mathbf{r})\overline{h_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')}d\mathbf{r} = -1. \tag{6}$$

When Eq. (6) is satisfied, each electron in the system interacts with precisely $N-1$ other electrons. When the normalization condition is satisfied, the density functional is (one-electron) self-interaction free [31–33]. Functionals that are not self-interaction free have numerous undesirable properties. For example, they are not exact for one-electron systems and their exchange-correlation potentials asymptotically decay at the wrong rate. The exchange-correlation potentials of self-interaction-free functionals decay as [31,34–38]

$$v_{\mathrm{xc}}(\mathbf{r}) \sim \frac{-1}{r}, \tag{7}$$

which is important for time-dependent density-functional theory (DFT) calculations and band gap calculations [39–45].

Fortunately, the exact normalization condition can be imposed using the weighted density approximation (WDA) [46–48]. As expected for an approximation that is self-interaction free, the WDA provides better highest-occupied orbital energies [49] and band gaps [50–53] than the local density approximation (LDA). [54,55] This is surprising in the sense that the underlying approximation—the exchange-correlation hole of the uniform electron gas is assumed to be transferable to systems with nonuniform electron density—is exactly the same as in conventional LDA. In this paper we will test a different type of weighted density approximation for the exchange energy of atoms and molecules. This extension obeys the normalization constraint on the exchange-correlation hole but, unlike the conventional WDA, our model for the hole is symmetric,

$$\overline{h_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')} = \overline{h_{\mathrm{xc}}(\mathbf{r}',\mathbf{r})}. \tag{8}$$

This addresses a previously identified weakness [56–59] in the WDA and provides a more physically reasonable model for the exchange-correlation hole. In particular, without using a symmetric hole, one does not regain the correct asymptotic decay for the exchange-correlation potential, Eq. (7). The model we consider was previously examined by Garcia-Gonzalez *et al.* for surfaces [58]. Despite its deficiencies there, we shall see that this simple model performs well for atoms and molecules. Moreover, our approach is simpler than the previous successful applications of WDA to molecules because it does not require a (somewhat arbitrary) partitioning of the system into core and valence regions [60].

II. WEIGHTED DENSITY APPROXIMATION (WDA)

The conventional weighted density approximation starts with an approximation to the exchange hole, $h_x(\mathbf{r},\mathbf{r}') = h_{\mathrm{xc}}^{\lambda=0}(\mathbf{r},\mathbf{r}')$. Typically, the dependence on electron position can be expressed using only the interelectronic distance $|\mathbf{r}-\mathbf{r}'|$ and the dependence on the electron density is only through the Fermi momentum, k_F. So the functional form is usually

$$h_x(\mathbf{r},\mathbf{r}') \approx f(k_F|\mathbf{r}-\mathbf{r}'|). \tag{9}$$

In this paper we treat both closed- and open-shell systems, so we need to write the exchange hole in a spin-resolved way. Denoting the spin as $\sigma = \alpha,\beta$, the form of approximation under consideration is

$$h_{x;\sigma\sigma}(\mathbf{r},\mathbf{r}') \approx f(k_{F,\sigma}|\mathbf{r}-\mathbf{r}'|). \tag{10}$$

If we use the expression for k_F from the uniform electron gas,

$$k^{(0)}_{F,\sigma}(\mathbf{r}) = \sqrt{6\pi^2\rho_\sigma(\mathbf{r})}, \tag{11}$$

where $\rho_\sigma(\mathbf{r})$ is the electron spin density. Using Eq. (11) in Eq. (10) results in an approximation to the exchange hole that does not satisfy the normalization constraint, Eq. (6). In the weighted density approximation (WDA) [46–48], this is remedied by using the normalization condition to determine an effective $k^{(1)}_{F,\sigma}(\mathbf{r})$,

$$-1 = \int \rho_\sigma(\mathbf{r}) h_{x;\sigma\sigma}(\mathbf{r},\mathbf{r}')d\mathbf{r} = \int \rho_\sigma(\mathbf{r}) f\left(k^{(1)}_{F,\sigma}(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|\right)d\mathbf{r}. \tag{12}$$

In the WDA, $k^{(1)}_{F,\sigma}(\mathbf{r}')$ is determined by solving a system of uncoupled nonlinear integral equations: there is one equation for each $\mathbf{r}'$. There has been significant interest in the weighted density approximation [61,62], mostly in condensed matter physics [50–53,57,63–67], but also for the study of surfaces [58,68–71] and metal clusters [49,72].

Substituting either the uniform electron gas expression for k_F or its WDA results in an exchange-correlation hole that is not symmetric with respect to interchange of $\mathbf{r}$ and $\mathbf{r}'$. The expression needs to be symmetric, however, because the electron pair density is symmetric [57,58]. As previously proposed by Garcia-Gonzalez *et al.* [58,73], we use the p-mean to symmetrize this formula,

$$k^{(\times)}_{F,\sigma}(\mathbf{r},\mathbf{r}') = \left[\frac{[k^{(\times)}_{F,\sigma}(\mathbf{r})]^p + [k^{(\times)}_{F,\sigma}(\mathbf{r}')]^p}{2}\right]^{1/p}. \tag{13}$$

The formula in Eq. (13) is proven to be effective for approximate density functionals [73–81].

Next we approximate the exchange hole using Eq. (13),

$$h^{(\times)}_{x,\sigma}(\mathbf{r},\mathbf{r}') \approx f(k^{(\times)}_{F,\sigma}(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|), \tag{14}$$

and then compute the exchange energy,

$$E^{(\times)}_x[\rho] \approx \frac{1}{2}\sum_{\sigma=\alpha,\beta}\int \frac{\rho_\sigma(\mathbf{r})\rho_\sigma(\mathbf{r}')h^{(\times)}_{x,\sigma}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'. \tag{15}$$

When we compute the exchange hole using $k^{(0)}_{F,\sigma}(\mathbf{r})$ [cf. Eq. (11)] in Eq. (13), we say we are doing a zero-point (0P) WDA calculation. When we compute the exchange hole using $k^{(1)}_{F,\sigma}(\mathbf{r})$ [cf. Eq. (12)] we say we are doing a one-point (1P) WDA calculation.

In general, the symmetrized exchange hole from the 1P WDA is no longer normalized,

$$-1 \neq \int \rho_\sigma(\mathbf{r}) f(k^{(\times)}_{F,\sigma}(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}. \tag{16}$$

This leads to the 2P WDA [58]: solve for the effective Fermi momentum $k^{(2)}_{F,\sigma}(\mathbf{r})$ by solving the *coupled* system of nonlinear integral equations,

$$\begin{aligned}-1 = \int \rho_\sigma(\mathbf{r}) f\big(2^{-1/p}\{[k^{(2)}_{F,\sigma}(\mathbf{r})]^p\\ + [k^{(2)}_{F,\sigma}(\mathbf{r}')]^p\}^{1/p}|\mathbf{r}-\mathbf{r}'|\big)d\mathbf{r}.\end{aligned} \tag{17}$$

In 1P WDA, the normalization constraint is imposed first, and then the hole is symmetrized. In 2P WDA, the hole is symmetrized first, and then the normalization constraint is imposed. As noted already by Garcia-Gonzalez *et al.*, the two-point functional is more demanding because the effective Fermi momenta at different points are coupled [58].

III. COMPUTATIONAL APPROACH

The purpose of this paper is to test the 0P, 1P, and 2P symmetrized WDAs for the exchange energy of atoms and molecules. We chose the model hole from the uniform electron gas,

$$f(k^{(\times)}_{F,\sigma}|\mathbf{r}-\mathbf{r}'|) = -9\left[\frac{\sin(k^{(\times)}_{F,\sigma}|\mathbf{r}-\mathbf{r}'|) - (k^{(\times)}_{F,\sigma}|\mathbf{r}-\mathbf{r}'|)\cos(k^{(\times)}_{F,\sigma}|\mathbf{r}-\mathbf{r}'|)}{(k^{(\times)}_{F,\sigma}|\mathbf{r}-\mathbf{r}'|)^3}\right]^2. \tag{18}$$

Although many researchers favor a Gaussian model for the hole [59,60,82], the Gaussian model for the hole is inconsistent with the idempotency of the one-electron reduced density matrix [83].

We discretized the nonlinear integral equations that arise in the WDA on a six-dimensional numerical integration grid that is the direct product of Becke-Lebedev grids [84–86] by adapting a software package that we had developed for another purpose [87]. Denoting the weights and locations of the grid points as $\{w_i,\mathbf{r}_i\}_{i=1}^{N_{\text{grid}}}$, the 1P WDA requires solving the following set of uncoupled nonlinear equations:

$$\left\{\sum_{i=1}^{N_{\text{grid}}} w_i\rho_\sigma(\mathbf{r}_i)f\left(k_{F,\sigma}^{(1)}(\mathbf{r}_j)|\mathbf{r}_i-\mathbf{r}_j|\right)=-1\right\}_{j=1}^{N_{\text{grid}}}. \tag{19}$$

We solved these equations to a precision of 0.0001 a.u. using Newton's method with a trust radius; for a starting guess we used the local density approximation, $k_{F,\sigma}^{(0)}(\mathbf{r}_j)$. The 2P WDA gives a system of N_{grid} coupled equations in N_{grid} unknowns,

$$\left\{\rho_\sigma(\mathbf{r}_j)\sum_{i=1}^{N_{\text{grid}}} w_i\rho_\sigma(\mathbf{r}_i)f\left(\left[\frac{k_{F,\sigma}^{(2)}(\mathbf{r}_i)+k_{F,\sigma}^{(2)}(\mathbf{r}_j)}{2}\right]^{1/p}|\mathbf{r}_i-\mathbf{r}_j|\right)\right.$$
$$\left.=-\rho_\sigma(\mathbf{r}_j)\right\}_{j=1}^{N_{\text{grid}}}. \tag{20}$$

We chose to weight the nonlinear equations by the electron density at the point $\mathbf{r}_j$; this ensures that the equations are solved to greater accuracy where the electron density is larger. We found that our results for the exchange energy were not sensitive to this weighting factor. Our initial guess for the 2P WDA nonlinear equations was the solution to the 1P WDA equations, $k_{F,\sigma}^{(1)}(\mathbf{r}_j)$. We found that our final results for the exchange energy were not sensitive to the choice of initial guess.

The diagonal element of the Jacobian of the nonlinear system in Eq. (20) is typically N_{grid} times larger than the off-diagonal elements. The nonlinear equations could be solved by simply neglecting the off-diagonal elements of the Jacobian and then solving the equations with a trust-radius (quasi-)Newton method. We found that we could accelerate the procedure by a factor of about 2 by augmenting the diagonal information with information from previous steps of the algorithm, which we did using a limited-memory version of the "bad Broyden" quasi-Newton method [88]. This allowed us to solve the nonlinear system in Eq. (20) in about ten iterations. 2P WDA is about one order of magnitude more time-consuming than 1P WDA.

For $p>1$, the nonlinear system (20) is difficult (and perhaps impossible) to solve. Remember that $k_{F,\sigma}(\mathbf{r})$ decays exponentially with increasing distance from an atom or molecule. Therefore, when $\mathbf{r}_j$ is far from an atom, most of the points that contribute to the sum have $k_{F,\sigma}^{(2)}(\mathbf{r}_i)\gg k_{F,\sigma}^{(2)}(\mathbf{r}_j)$. It seems impossible to adjust $k_{F,\sigma}^{(2)}(\mathbf{r}_j)$ enough to satisfy the normalization condition without allowing $k_{F,\sigma}^{(2)}(\mathbf{r}_j)<0$, but negative Fermi momenta are not physically reasonable. In these cases we stop the iterations once the normalization error ceases to improve. We believe that the solution we find in this way is a good approximation to the solution of the system of equations in Eq. (20), subject to the constraint that $k_F(\mathbf{r})>0$. Because the errors in normalization are associated mainly with the exponential tails of the electron density, they do not seem to compromise the quality of our results.

To test the 0P, 1P, and 2P WDAs, we first performed Kohn-Sham DFT calculations in the local density approximation (LDA) using *Gaussian 2009* [89], with the QZVP basis set [90]. The electron spin densities from these calculations were fed into our program and the 0P, 1P, and 2P WDAs were computed using the aforementioned direct product grid with the $\mathbf{r}=\mathbf{r}'$ points omitted. The exact exchange energy was computed from the orbitals of the Kohn-Sham calculations. Therefore, even though the exchange energies in the tables are not exact exchange energies for the atoms, they do correspond to the exact exchange energies for the LDA spin densities [91,92]. Using these spin densities, we computed the exchange energy from the LDA [93], and the Becke 1988 (B88) [89,94], Perdew-Burke-Ernzerhof [95], and OPT [96] generalized gradient approximation (GGA) functionals. The LDA and PBE functionals are exact for the uniform electron gas; OPT is among the best GGAs for exchange; the B88 functional is a very popular GGA that was fit to the exchange energy of atoms. The results of these computations are reported in Table I (atoms) and Table II (small molecules).

We determined the value of p for the generalized mean of $k_{F,\sigma}$ values by minimizing the average error in the 2P WDA exchange energy for the atoms hydrogen-krypton,

$$p=\underbrace{\arg\min}_{p}\left(\frac{1}{36}\sum_{A=\text{H,He,Li...Br,Kr}}\left[E_x^{\text{exact}}(A)\right.\right.$$
$$\left.\left.-E_x^{\text{2P WDA}}(A,p)\right]\right). \tag{21}$$

The optimal value was $p=5$. Even when the results are optimized separately for the 1P WDA and 0P WDA functionals, the results for those functionals are far inferior to the 2P WDA.

IV. RESULTS

The exchange energies of atoms are reported in Table I. Even though the 0P WDA approximation is based on Eqs. (11) and (18), which are exactly the same ingredients that are used to derive the conventional LDA exchange function [93], the root-mean-square error of the 0P WDA is much larger. The 1P WDA is significantly more accurate than the 0P WDA, but it is still less accurate than conventional LDA. The rms error of the 2P WDA is comparable to the popular OPTX functional and is significantly smaller than the errors in the functionals (LDA and PBE) that give exact results for the uniform electron gas. The 2P WDA is inferior to B88, but one must recall that B88 was fit to atomic exchange energies [94]. One interesting feature of the 2P WDA is that it has almost no *systematic* error, unlike PBE and OPT, which tend to give exchange energies that are too negative. Recall that 2P WDA is not a gradient-corrected functional and contains no information about the nearly uniform electron gas or the gradient expansion.

For molecules, density-functional exchange functionals should include a contribution from left-right correlation [96–98]. For this reason, one does not wish to assess DFT exchange functionals against molecular data. Nonetheless, a good DFT functional for exchange should give a reasonable

TABLE I. Exchange energies for atoms, in atomic units, for conventional density functionals (LDA, B88, PBE, OPT) and the symmetrized weighted density approximations (0P WDA, 1P WDA, 2P WDA) described in Sec. II. The $p = 5$ mean is chosen in Eq. (13).

Atom	0P WDA	1P WDA	2P WDA	LDA	B88	PBE	OPT	Exact
H	−0.085	−0.313	−0.313	−0.213	−0.259	−0.268	−0.261	−0.313
He	−0.448	−1.026	−1.026	−0.884	−1.026	−1.062	−1.026	−1.026
Li	−0.794	−1.662	−1.653	−1.518	−1.757	−1.823	−1.763	−1.781
Be	−1.252	−2.482	−2.530	−2.312	−2.658	−2.759	−2.665	−2.667
B	−1.831	−3.439	−3.574	−3.272	−3.733	−3.877	−3.735	−3.770
C	−2.564	−4.577	−4.835	−4.449	−5.040	−5.231	−5.035	−5.078
N	−3.452	−5.846	−6.258	−5.751	−6.450	−6.686	−6.439	−6.609
O	−4.504	−7.395	−8.028	−7.416	−8.285	−8.579	−8.271	−8.221
F	−5.708	−8.954	−9.801	−9.055	−10.022	−10.360	−10.005	−10.051
Ne	−7.112	−10.800	−11.927	−11.042	−12.147	−12.536	−12.134	−12.120
Na	−8.269	−12.399	−13.763	−12.768	−14.013	−14.459	−14.011	−14.018
Mg	−9.559	−14.102	−15.773	−14.609	−15.998	−16.502	−15.992	−15.992
Al	−10.905	−15.860	−17.854	−16.531	−18.066	−18.626	−18.061	−18.088
Si	−12.342	−17.704	−20.067	−18.583	−20.270	−20.887	−20.269	−20.301
P	−13.858	−19.586	−22.344	−20.702	−22.531	−23.204	−22.534	−22.637
Si	−15.478	−21.642	−24.844	−23.037	−25.038	−25.772	−25.054	−25.026
Cl	−17.143	−23.629	−27.277	−25.345	−27.481	−28.270	−27.505	−27.533
Ar	−19.010	−25.872	−30.014	−27.864	−30.154	−31.001	−30.193	−30.186
K	−20.564	−27.864	−32.439	−30.188	−32.634	−33.546	−32.687	−32.677
Ca	−22.334	−30.023	−35.072	−32.592	−35.194	−36.169	−35.251	−35.211
Sc	−24.324	−32.388	−37.979	−35.285	−38.048	−39.088	−38.117	−38.061
Ti	−26.490	−34.861	−40.740	−38.196	−41.129	−42.224	−41.225	−41.084
V	−28.656	−37.475	−44.228	−41.092	−44.175	−45.340	−44.284	−44.235
Cr	−31.207	−40.386	−47.562	−44.544	−47.807	−49.031	−47.956	−47.878
Fe	−36.157	−46.127	−54.505	−51.217	−54.828	−56.182	−55.047	−54.674
Co	−38.824	−49.241	−58.570	−54.631	−58.363	−59.772	−58.638	−58.279
Ni	−41.615	−52.301	−61.957	−58.327	−62.225	−63.691	−62.549	−62.025
Cu	−44.168	−55.425	−66.066	−61.739	−65.801	−67.337	−66.164	−65.636
Zn	−47.169	−58.863	−70.198	−65.677	−69.903	−71.501	−70.332	−69.691
Ga	−49.895	−62.015	−74.018	−69.288	−73.682	−75.342	−74.162	−73.521
Ge	−52.723	−65.275	−78.000	−73.026	−77.594	−79.316	−78.129	−77.477
As	−55.641	−68.574	−82.001	−76.793	−81.525	−83.309	−82.109	−81.504
Se	−58.563	−71.942	−86.148	−80.716	−85.635	−87.483	−86.289	−85.535
Br	−61.510	−75.234	−90.164	−84.592	−89.668	−91.579	−90.370	−89.639
Kr	−64.845	−78.961	−94.671	−88.620	−93.867	−95.839	−94.638	−93.848
Avg. error	12.497	5.490	0.006	2.415	−0.018	−0.922	−0.186	
rms error	15.318	7.237	0.329	2.866	0.086	1.135	0.348	

approximation to the exact exchange energy for a small molecule near its equilibrium geometry. The results in Table II show that the 2P WDA gives reasonable results for molecules, comparable in quality to good GGA functionals. The

TABLE II. Exchange energies for small molecules, in atomic units, for conventional density functionals (LDA, B88, PBE, OPT) and the symmetrized weighted density approximations (0P WDA, 1P WDA, 2P WDA) described in Sec. II. The $p = 5$ mean is chosen in Eq. (13).

Molecule	0P WDA	1P WDA	2P WDA	LDA	B88	PBE	OPT	Exact
H_2	−0.312	−0.672	−0.672	−0.582	−0.672	−0.693	−0.676	−0.672
F_2	−11.668	−18.100	−19.751	−18.193	−20.084	−20.755	−20.047	−19.972
N_2	−7.450	−12.120	−12.946	−11.876	−13.212	−13.674	−13.202	−12.733
HF	−6.071	−9.323	−10.295	−9.475	−10.456	−10.801	−10.444	−10.250
BH	−2.072	−3.770	−3.964	−3.627	−4.126	−4.282	−4.129	−4.089
CO	−7.563	−12.237	−13.127	−12.047	−13.395	−13.863	−13.383	−13.043
H_2O	−5.178	−8.010	−8.840	−8.122	−8.985	−9.285	−8.978	−9.274
CH_4	−3.653	−5.755	−6.315	−5.815	−6.473	−6.692	−6.484	−6.891
Avg. error	4.120	0.867	0.127	0.899	−0.060	−0.390	−0.052	
rms error	4.629	1.007	0.270	1.000	0.273	0.548	0.266	

performance of the 1P WDA is very similar to LDA (which is known to be poor for molecules), while the 0P WDA has unacceptably large errors.

V. SUMMARY

We have implemented the symmetrized weighted density approximations [58] for exchange and tested them for atoms and molecules. The two-point symmetrized weighted density approximation based on the exchange hole of the uniform electron gas gives very good results for atoms and small molecules, with results comparable to the best generalized gradient approximations. Even though 2P WDA is derived only from considerations of the uniform electron gas, its rms error is significantly smaller than the error in the other exchange functionals we considered (LDA and PBE) that recover the uniform electron gas limit. We therefore believe the form of the 2P WDA functional is a promising avenue for further development.

The calculations in this paper are not self-consistent; we are testing the accuracy of the functional rather than its variational properties. It is tedious, but not difficult, to obtain the functional derivatives of WDA-type functionals; early results of this sort are already in the papers of Alonso and Girifalco [46]. The cost of these functionals is not that different from other essentially six-dimensional functionals, e.g., Langreth-style dispersion functionals [9] or static correlation functionals that use the exchange energy density [97,98]. We have formulated numerical techniques (e.g., basis-set expansions for the hole) that can be used to bring the cost of the functional down, but we have not implemented these methods because it seems wise to defer the tedious (but not difficult) work of optimizing algorithms until after an accurate functional has been developed.

There are many ways to improve these results. The choice of a single value of p in Eq. (13) is too simplistic. We have seen hints that a density-dependent value of p would give better results, with smaller values of p appropriate in low-density regions of atoms. This suggests that p should be made a functional of the electron density. If this is done, a new type of Jacob's ladder of functionals can be envisioned [99,100], with p depending on the density alone, derivatives of the density, the local kinetic energy, or even the occupied Kohn-Sham orbitals. As the form of p is made more elaborate, additional constraints [not just the normalization condition, Eq. (6)] can be satisfied.

Another way to improve these results is to use a different approximate form for the exchange hole. The uniform electron gas is a conductor, resulting in the slowly decaying behavior of the exchange hole in Eq. (18). The exchange hole decays exponentially with interelectronic separation in atoms and molecules [101–104]. Choosing a model for the exchange hole that respects that limit should give more accurate results. Using a more nearsighted form of the exchange-(correlation) hole would also mitigate the numerical difficulties noted in Sec. III.

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[1] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
[2] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).
[3] W. Kohn, A. D. Becke, and R. G. Parr, J. Phys. Chem. **100**, 12974 (1996).
[4] P. W. Ayers and W. Yang, in *Computational Medicinal Chemistry for Drug Discovery*, edited by P. Bultinck, H. de Winter, W. Langenaeker, and J. P. Tollenaere (Dekker, New York, 2003), p. 571.
[5] A. Ruzsinszky, J. P. Perdew, and G. I. Csonka, J. Chem. Theory Comput. **6**, 127 (2010).
[6] A. Ruzsinszky, J. P. Perdew, and G. I. Csonka, J. Chem. Phys. **134**, 114110 (2011).
[7] A. Puzder, M. Dion, and D. C. Langreth, J. Chem. Phys. **124**, 164105 (2006).
[8] T. Thonhauser, A. Puzder, and D. C. Langreth, J. Chem. Phys. **124**, 164106 (2006).
[9] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **92**, 246401 (2004).
[10] O. A. Vydrov and T. Van Voorhis, J. Chem. Phys. **133**, 244103 (2010).
[11] O. A. Vydrov and T. Van Voorhis, J. Chem. Phys. **130**, 104105 (2009).
[12] O. A. Vydrov and T. Van Voorhis, Phys. Rev. Lett. **103**, 063004 (2009).
[13] O. A. Vydrov, Q. Wu, and T. Van Voorhis, J. Chem. Phys. **129**, 014106 (2008).
[14] R. Cuevas-Saavedra, D. Chakraborty, and P. W. Ayers (to be published in J. Chem. Phys.).
[15] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
[16] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).
[17] O. V. Gritsenko, B. Ensing, P. R. T. Schipper *et al.*, J. Phys. Chem. A **104**, 8558 (2000).
[18] Y. Zhang and W. Yang, J. Chem. Phys. **109**, 2604 (1998).
[19] A. Savin, Chem. Phys. **356**, 91 (2009).
[20] A. Savin and J. M. Seminario, *Recent Developments and Applications of Modern Density Functional Theory* (Elsevier, New York, 1996), p. 327.
[21] P. Gori-Giorgi and J. P. Perdew, Phys. Rev. B **66**, 165118 (2002).
[22] P. Gori-Giorgi, F. Sacchetti, and G. B. Bachelet, Phys. Rev. B **61**, 7353 (2000).
[23] M. S. Becker, Phys. Rev. **185**, 168 (1969).
[24] N. H. March, Phys. Chem. Liq. **46**, 465 (2008).
[25] C. Amovilli and N. H. March, Phys. Rev. B **76**, 195104 (2007).
[26] R. Cuevas-Saavedra and P. W. Ayers, in *Condensed Matter Theories*, edited by E. V. Ludena, R. F. Bishop and P. Iza (World Scientific, Singapore, 2011), Vol. 25.
[27] R. Cuevas-Saavedra and P. W. Ayers, Int. J. Mod. Phys. B **24**, 5115 (2010).
[28] R. Cuevas-Saavedra and P. W. Ayers, J. Phys. Chem. Solids **73**, 670 (2012).
[29] R. Cuevas-Saavedra, D. C. Thompson, and P. W. Ayers (to be published in Phys. Rev. A).

[30] P. Gori-Giorgi, J. G. Angyan, and A. Savin, Can. J. Chem.-Rev. Can. Chim. **87**, 1444 (2009).
[31] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[32] O. Gunnarsson and R. O. Jones, Solid State Commun. **37**, 249 (1981).
[33] J. P. Perdew, Chem. Phys. Lett. **64**, 127 (1979).
[34] C. O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).
[35] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).
[36] Z. X. Qian and V. Sahni, Int. J. Quantum Chem. **70**, 671 (1998).
[37] Z. X. Qian and V. Sahni, Int. J. Quantum Chem. **80**, 555 (2000).
[38] P. W. Ayers and M. Levy, J. Chem. Phys. **115**, 4438 (2001).
[39] D. J. Tozer and N. C. Handy, J. Chem. Phys. **109**, 10180 (1998).
[40] D. J. Tozer, J. Chem. Phys. **119**, 12697 (2003).
[41] Q. Wu, P. W. Ayers, and W. T. Yang, J. Chem. Phys. **119**, 2978 (2003).
[42] A. Dreuw, J. L. Weisman, and M. Head-Gordon, J. Chem. Phys. **119**, 2943 (2003).
[43] X. Andrade and A. Aspuru-Guzik, Phys. Rev. Lett. **107**, 183002 (2011).
[44] P. W. Ayers, R. C. Morrison, and R. G. Parr, Mol. Phys. **103**, 2061 (2005).
[45] A. Savin, C. J. Umrigar, and X. Gonze, Chem. Phys. Lett. **288**, 391 (1998).
[46] J. A. Alonso and L. A. Girifalco, Phys. Rev. B **17**, 3735 (1978).
[47] J. A. Alonso and L. A. Girifalco, Solid State Commun. **24**, 135 (1977).
[48] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Solid State Commun. **24**, 765 (1977).
[49] L. C. Balbas, J. A. Alonso, and A. Rubio, Europhys. Lett. **14**, 323 (1991).
[50] J. Robertson, K. Xiong, and S. J. Clark, Phys. Stat. Solidi B **243**, 2054 (2006).
[51] Z. G. Wu, D. J. Singh, and R. E. Cohen, Phys. Rev. B **69**, 193105 (2004).
[52] Z. Wu, R. E. Cohen, D. J. Singh, R. Gupta, and M. Gupta, Phys. Rev. B **69**, 085104 (2004).
[53] G. Zheng, S. J. Clark, S. Brand *et al.*, Chin. Phys. Lett. **24**, 807 (2007).
[54] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[55] R. Gaspar, Acta Phys. Hung. **3**, 263 (1954).
[56] Z. G. Wu, R. E. Cohen, and D. J. Singh, Phys. Rev. B **70**, 104112 (2004).
[57] J. P. A. Charlesworth, Phys. Rev. B **53**, 12666 (1996).
[58] P. Garcia-Gonzalez, J. E. Alvarellos, E. Chacon, and P. Tarazona, Phys. Rev. B **62**, 16063 (2000).
[59] M. Sadd and M. P. Teter, Phys. Rev. B **54**, 13643 (1996).
[60] M. Sadd and M. P. Teter, J. Mol. Struct.-Theochem **501**, 147 (2000).
[61] R. P. Diez and V. V. Karasiev, J. Phys. B: At. Mol. Opt. Phys. **36**, 2881 (2003).
[62] P. Garcia-Gonzalez, J. E. Alvarellos, and E. Chacon, Phys. Rev. A **62**, 014501 (2000).
[63] D. J. Singh, Phys. Rev. B **48**, 14099 (1993).
[64] E. Chacon and P. Tarazona, Phys. Rev. B **37**, 4013 (1988).
[65] S. J. Clark and P. P. Rushton, J. Phys.: Condens. Matter **16**, 4833 (2004).
[66] P. P. Rushton, D. J. Tozer, and S. J. Clark, Phys. Rev. B **65**, 193106 (2002).
[67] I. I. Mazin and D. J. Singh, Phys. Rev. B **57**, 6879 (1998).
[68] P. Garcia-Gonzalez, J. E. Alvarellos, E. Chacon *et al.*, Int. J. Quantum Chem. **91**, 139 (2003).
[69] D. B. Jochym and S. J. Clark, Phys. Rev. B **76**, 075411 (2007).
[70] J. E. Alvarellos and E. Chacon, Surf. Sci. **269**, 590 (1992).
[71] E. Chacon and P. Tarazona, Phys. Rev. B **37**, 4020 (1988).
[72] A. Rubio, L. C. Balbas, and J. A. Alonso, Phys. Rev. B **46**, 4891 (1992).
[73] P. Garcia-Gonzalez, J. E. Alvarellos, and E. Chacon, Phys. Rev. A **54**, 1897 (1996).
[74] D. Garcia-Aldea and J. E. Alvarellos, Phys. Rev. A **76**, 052504 (2007).
[75] D. Garcia-Aldea and J. E. Alvarellos, Phys. Rev. A **77**, 022502 (2008).
[76] D. Garcia-Aldea and J. E. Alvarellos, J. Chem. Phys. **129**, 074103 (2008).
[77] P. Garcia-Gonzalez, J. E. Alvarellos, and E. Chacon, Phys. Rev. A **57**, 4192 (1998).
[78] Y. A. Wang, N. Govind, and E. A. Carter, Phys. Rev. B **60**, 16350 (1999).
[79] Y. A. Wang, E. A. Carter, and S. D. Schwartz, *Theoretical Methods in Condensed Phase Chemistry* (Kluwer, Dordrecht, 2000), p. 117.
[80] B. J. Zhou, V. L. Ligneres, and E. A. Carter, J. Chem. Phys. **122**, 044103 (2005).
[81] P. Garcia-Gonzalez, J. E. Alvarellos, and E. Chacon, Phys. Rev. B **57**, 4857 (1998).
[82] C. Lee and R. G. Parr, Phys. Rev. A **35**, 2377 (1987).
[83] P. W. Ayers, R. Cuevas-Saavedra, and D. Chakraborty, Phys. Lett. A **376**, 839 (2012).
[84] A. D. Becke, J. Chem. Phys. **88**, 2547 (1988).
[85] A. D. Becke, J. Chem. Phys. **76**, 6037 (1982).
[86] A. D. Becke and R. M. Dickson, J. Chem. Phys. **92**, 3610 (1990).
[87] P. Bultinck, C. Van Alsenoy, P. W. Ayers *et al.*, J. Chem. Phys. **126**, 144111 (2007).
[88] C. G. Broyden, Math. Comput. **19**, 577 (1965).
[89] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, Gaussian Inc., Wallingford CT, 2009.
[90] F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys. **7**, 3297 (2005).
[91] A. Gorling and M. Levy, Phys. Rev. A **50**, 196 (1994).
[92] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
[93] P. A. M. Dirac, Proc. Cambridge Philos. Soc. **26**, 376 (1930).
[94] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[95] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[96] N. C. Handy and A. J. Cohen, Mol. Phys. **99**, 403 (2001).
[97] A. D. Becke, J. Chem. Phys. **119**, 2972 (2003).
[98] A. D. Becke, J. Chem. Phys. **122**, 064101 (2005).
[99] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
[100] J. P. Perdew, A. Ruzsinszky, J. M. Tao *et al.*, J. Chem. Phys. **123**, 062201 (2005).
[101] W. Kohn, Phys. Rev. Lett. **76**, 3168 (1996).
[102] E. Prodan and W. Kohn, Proc. Natl. Acad. Sci. USA **102**, 11635 (2005).
[103] X. P. Li, R. W. Nunes, and D. Vanderbilt, Phys. Rev. B **47**, 10891 (1993).
[104] L. X. He and D. Vanderbilt, Phys. Rev. Lett. **86**, 5341 (2001).