Chapter 18
A Gradient Corrected Two-Point Weighted Density Approximation for Exchange Energies

R. Cuevas-Saavedra, D. Chakraborty, M. Chan and P. W. Ayers

Abstract A successful symmetric, two-point, nonlocal weighted density approximation for the exchange energy of atoms and molecules can be constructed using a power mean with constant power p when symmetrizing the exchange-correlation hole [Phys. Rev. A **85**, 042519 (2012)]. In this work, we consider how this parameter depends on the system's charge. Exchange energies for all ions with charge from -1 to $+12$ of the first eighteen atoms of the periodic table are computed and optimized. Appropriate gradient corrections to the current model, based on rational functions, are designed based on the optimal p values we observed for the ionic systems. All of the advantageous features (non-locality, uniform electron gas limit and no self-interaction error) of the original model are preserved.

18.1 Introduction

Density functional theory (DFT) has successfully become the method of choice for computing the electronic structure of large molecules and complex materials [1–5]. However, although density functional theory provides an exact mathematical framework for the electronic structure problem [6–12], its utility in practical calculations is limited by the accuracy of approximate exchange-correlation functionals. This motivates the ongoing research into accurate and feasible approximate exchange-correlation functionals [4, 13–16]. Despite the success of functionals such as the local-density approximation [17–19] (LDA) and generalized gradient approximations [20–23] (GGA) due to their computational efficiency, they are subject to a number of deficiencies. These deficiencies are usually analyzed by determining which exact constraints are (and are not) satisfied by the approximate functionals, though it is also true that no (semi)local functional can ever be exact [24–27].

This has stimulated recent work on nonlocal density functionals, where the exchange-correlation energy is approximated as a six-dimensional integral [28–47],

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$$E_{xc}[\rho] = \int \int f[\rho; \mathbf{r}, \mathbf{r}'] d^3\mathbf{r} d^3\mathbf{r}'. \tag{18.1}$$

This type of functional is particularly advantageous when the exchange-correlation hole is delocalized [24–26, 48–50] and is essential when for density-functionals that are accurate not only for short-range electron correlations, but also for long-range electron correlations like dispersion [30–37].

Equation (18.1) provides a natural form for the exchange-correlation functional since the exact exchange-correlation energy functional can be written in the form

$$E_{xc}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')\overline{h_{xc}(\mathbf{r}, \mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}', \tag{18.2}$$

where

$$\overline{h_{xc}(\mathbf{r}, \mathbf{r}')} = \int h_{xc}^{\lambda}(\mathbf{r}, \mathbf{r}') d\lambda \tag{18.3}$$

is the exchange-correlation hole

$$h_{xc}^{\lambda}(\mathbf{r}, \mathbf{r}') = \frac{\rho_2^{\lambda}(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}')}{\rho(\mathbf{r})\rho(\mathbf{r}')} \tag{18.4}$$

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 ($\lambda = 1$) [51, 52]. Here,

$$\rho_2^{\lambda}(\mathbf{r}, \mathbf{r}') = \left\langle \Psi^{\lambda} \left| \sum_{j \neq i} \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}') \right| \Psi^{\lambda} \right\rangle \tag{18.5}$$

is the electron pair density.

There have been several recent attempts to construct nonlocal exchange-correlation functionals using models for the exchange-correlation hole [38–47]. Some of them are based on a variant of the classical Ornstein–Zernike equation [41, 42, 53–57] while some others are two-point weighted density approximations that rely on analytical models of the exchange-correlation hole for the uniform electron gas [58, 59]. The latter approach seems to be promising since they are suggested to be competitive with the best generalized gradient approximation. Moreover, these two-point weighted density approximations are fully nonlocal, have no self-interaction error, approximately fulfill the Pauli principle, and preserve the uniform electron gas limit [38, 39]. In these models the symmetry of the exchange-correlation hole is achieved by means of a generalized mean (power mean).

Motivated by these preliminary results we explore ways to improve the two-point weighted density approximation (2pt-WDA) exchange density functional. Section 18.2 provides a brief overview of the approach, and extends our previous

tests to all ions with charges between -1 and $+12$ for the first 36 elements of the periodic table (H–Kr). Based on the dependence of these results on the power used in the generalized mean, we propose a gradient-corrected 2pt-WDA. This model is studied in Sect. 18.3, and our conclusions are summarized in Sect. 18.4.

18.2 The Weighted Density Approximation for Atoms and Ions

The main ingredient of the weighted density approximation discussed here is the exchange hole for the uniform electron gas (UEG)

$$
f\left(k_{F,\sigma}^{(x)}|\mathbf{r}-\mathbf{r}'|\right) = -9 \left(\frac{\sin\left(k_{F,\sigma}^{(x)}|\mathbf{r}-\mathbf{r}'|\right) - \left(k_{F,\sigma}^{(x)}|\mathbf{r}-\mathbf{r}'|\right)\cos\left(k_{F,\sigma}^{(x)}|\mathbf{r}-\mathbf{r}'|\right)}{\left(k_{F,\sigma}^{(x)}|\mathbf{r}-\mathbf{r}'|\right)^3} \right)^2
$$

(18.6)

(cf. Eq. (17.5) in Chap. 17 [60]) where we use the expression for k_F from the uniform electron gas,

$$
k_{F,\sigma}^{(0)}(\mathbf{r}) = \sqrt{6\pi^2 \rho_\sigma(\mathbf{r})}.
$$

(18.7)

The expression Eq. (18.6) for the exchange hole needs to be symmetric with respect to interchange of $\mathbf{r}$ and $\mathbf{r}'$ because the electron pair density is symmetric [61, 62]. We use the p-mean to symmetrize this formula [38, 39],

$$
k_{F,\sigma}^{(x)}(\mathbf{r},\mathbf{r}') = \left[\frac{1}{2}\left(\left(k_{F,\sigma}^{(x)}(\mathbf{r})\right)^p + \left(k_{F,\sigma}^{(x)}(\mathbf{r}')\right)^p \right) \right]^{1/p}.
$$

(18.8)

Finally, the exchange energy is computed by means of

$$
E_x^{(x)}[\rho] \approx \frac{1}{2} \sum_{\sigma=\alpha,\beta} \int\int \frac{\rho_\sigma(\mathbf{r})\rho_\sigma(\mathbf{r}')h_{x,\sigma}^{(x)}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}\,d^3\mathbf{r}',
$$

(18.9)

where the exchange hole is approximated as

$$
h_{x,\sigma}^{(x)}(\mathbf{r},\mathbf{r}') \approx f\left(k_{F,\sigma}^{(x)}(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|\right).
$$

(18.10)

This approach naturally leads to three different types of functional. The 0pt-WDA functional is constructed by the direct use of Eq. (18.7) when computing the exchange hole. This functional is neither symmetric nor normalized. In 1pt-WDA, an effective $k_{F,\sigma}^{(1)}(\mathbf{r})$ is used to enforce the normalization of the hole

$$-1 = \int \rho_\sigma(\mathbf{r}) h_{x;\sigma\sigma}(\mathbf{r},\mathbf{r}')d^3\mathbf{r}$$

$$= \int \rho_\sigma(\mathbf{r}) f\left(k_{F,\sigma}^{(1)}(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|\right) d^3\mathbf{r}. \qquad (18.11)$$

This functional is now normalized but not symmetric. Finally, the 2pts-WDA arises when both symmetry and normalization are imposed.

Following the same computational approach described in our previous work [38, 39], we computed the exchange energy for all ions with charge from -1 to $+12$ of the first 36 atoms in the periodic table (H–Kr). Minimizing the root-mean-square error in the exchange energy over the entire dataset gave a value of $p = 2$ for Eq. (18.8). The weighted density approximation is still competitive with the traditional GGA functionals (B88 [21], PBE [22], and OPTX [23]), and significantly better than the local density approximation [17], but both the average and root-mean-square errors are worse than the results for neutral atoms and small molecules [39]. This finding reinforces our previous observation: p should be density dependent. This is more clearly observed in Tables 18.1 and 18.2, where the average and root-mean-square errors are shown for different charges; the errors increase with increasing charge, indicating that p should be system-dependent.

Table 18.1 Average errors for the atoms and atomic ions with -1 to $+12$ charge, H–Kr, for conventional density functionals (LDA, B88, PBE, OPTX) and the symmetrized weighted density approximations (0pt-WDA, 1pt-WDA, 2pt-WDA) described in Sect. 18.2. The $p = 2$ mean is chosen in Eq. (18.8). The average over all atoms and ions is provided in the bottom row. The rows above that are the average error for species of a given charge; for example, the first row is the average error in the atomic anions

Charge	0pt-WDA	1pt-WDA	2pt-WDA	LDA	B88	PBE	OPT
-1	10.134	3.782	0.014	2.303	-0.049	-1.168	-0.198
0	10.505	3.915	0.007	2.398	-0.034	-1.172	-0.203
1	10.809	3.959	0.018	2.482	-0.010	-1.187	-0.187
2	11.081	3.967	0.013	2.549	-0.006	-1.204	-0.190
3	11.332	3.955	0.003	2.603	-0.011	-1.230	-0.201
4	11.415	3.893	0.085	2.647	0.015	-1.205	-0.175
5	11.794	3.960	0.092	2.757	0.045	-1.206	-0.152
6	12.120	3.994	0.175	2.862	0.078	-1.200	-0.117
7	11.842	3.734	0.226	2.836	0.108	-1.135	-0.067
8	12.067	3.717	0.261	2.905	0.123	-1.139	-0.046
9	12.109	3.605	0.317	2.926	0.123	-1.143	-0.027
10	11.963	3.405	0.376	2.927	0.150	-1.098	0.022
11	12.373	3.570	0.555	3.042	0.170	-1.118	0.048
12	12.520	3.527	0.633	3.096	0.183	-1.118	0.070
all	11.471	3.811	0.167	3.096	0.183	-1.118	0.070

Table 18.2 Root-mean-square errors for the atoms and atomic ions with -1 to $+12$ charge, H–Kr, for conventional density functionals (LDA, B88, PBE, OPTX) and the symmetrized weighted density approximations (0pt-WDA, 1pt-WDA, 2pt-WDA) described in Sect. 18.2. The $p = 2$ mean is chosen in Eq. (18.8). The root-mean-square error over all atoms and ions is provided in the bottom row

Charge	0pt-WDA	1pt-WDA	2pt-WDA	LDA	B88	PBE	OPT
-1	12.313	5.010	0.323	2.734	0.131	1.426	0.357
0	12.759	5.188	0.351	2.844	0.123	1.433	0.373
1	12.971	5.210	0.352	2.904	0.118	1.447	0.368
2	13.145	5.186	0.368	2.944	0.134	1.460	0.383
3	13.298	5.139	0.493	2.975	0.271	1.505	0.473
4	13.345	5.088	0.378	3.006	0.208	1.464	0.425
5	13.669	5.145	0.405	3.107	0.158	1.444	0.376
6	13.862	5.125	0.394	3.189	0.171	1.417	0.347
7	13.560	4.891	0.417	3.159	0.183	1.346	0.318
8	13.719	4.865	0.444	3.216	0.205	1.343	0.307
9	13.626	4.690	0.475	3.203	0.199	1.345	0.293
10	13.399	4.490	0.518	3.199	0.252	1.287	0.249
11	13.711	4.523	0.683	3.294	0.270	1.304	0.254
12	13.797	4.462	0.751	3.336	0.292	1.302	0.256
all	13.323	4.977	0.751	3.336	0.292	1.302	0.256

18.3   A Preliminary Generalized Gradient Corrected Weighted Density Approximation

From the insight gained in the previous findings, we propose in this section the power p as a rational function of the reduced gradient, $s(\mathbf{r}) = |\nabla \rho(\mathbf{r})|/\rho^{4/3}(\mathbf{r})$,

$$p(s; \mathbf{r}) = \frac{a_0 + a_1 s(\mathbf{r})}{b_0 + s(\mathbf{r})}. \tag{18.12}$$

We opted to use the reduced gradient since p should be a dimensionless quantity. We will not engaged in a detailed optimization of this form here, but defer that to future work. Our goal is merely to explore the possible utility of this form on the performance of the weighted density approximation.

Because the exchange hole must remain symmetric, the power in Eq. (18.8) must be symmetrized. We choose to do this with the form,

$$p(\mathbf{r}, \mathbf{r}') = \left[\frac{1}{2} \left(p^q(s, \mathbf{r}) + p^q(s, \mathbf{r}') \right) \right]^{1/q}. \tag{18.13}$$

The exponent q can be chosen as a free parameter also; however we considered only three possibilities: the arithmetic ($q = 1$), harmonic ($q = -1$) and geometric ($q = 0$) means.

From our previous studies, we have learned that the coefficient a_1 in Eq. (18.12) has to be small to reach convergence, especially in the asymptotic regions of the density (regions where s diverges). For this reason we only allowed a_1 to have the values 0.1 and 0.01. The remaining parameters a_0 and b_0 were assigned values 0.1, 0.5, 1.0, 1.5 and 2.0. This gave a total of 50 functionals (each defined by a specified value of (a_0, b_0, a_1) to test). To speed up the testing, we considered only the neutral atoms and $+1$, $+2$, $+3$, $+4$, and $+5$ atomic ions, and only for the first 18 elements of the periodic table (H–Ar). We observed that the results were quite insensitive to the choice of q in Eq. (18.13), typically differing in only the 3rd or 4th decimal. For simplicity we henceforth consider only the results for the simple arithmetic mean ($q = 1$).

Tables 18.3 and 18.4 show the average and rms errors, respectively, for each of the triads considered. For fixed values of a_0, b_0 the errors seem to decrease when

Table 18.3 Average errors for the neutral atoms and atomic ions with $+1$, $+2$, $+3$, $+4$, and $+5$ charge, H–Ar, for symmetrized weighted density approximations (0pt-WDA, 1pt-WDA, 2pt-WDA) described in Sect. 18.3. The arithmetic mean ($q = 1$) is chosen

a_0	b_0	a_1	0pt	1pt	2pt	a_0	b_0	a_1	0pt	1pt	2pt
2.00	0.10	0.10	9.612	3.048	0.441	0.50	0.10	0.10	8.889	2.615	0.689
2.00	0.50	0.10	9.485	2.965	0.478	1.00	2.00	0.10	8.883	2.609	0.691
2.00	0.10	0.01	9.503	2.993	0.499	1.00	0.50	0.01	8.952	2.663	0.691
1.50	0.10	0.10	9.388	2.909	0.511	0.50	0.50	0.10	8.836	2.584	0.710
2.00	1.00	0.10	9.364	2.889	0.517	1.00	1.00	0.01	8.888	2.626	0.715
2.00	0.50	0.01	9.386	2.918	0.535	0.50	1.00	0.10	8.786	2.556	0.730
1.50	0.50	0.10	9.282	2.843	0.546	1.00	1.50	0.01	8.839	2.598	0.734
2.00	1.50	0.10	9.269	2.831	0.549	0.50	1.50	0.10	8.748	2.535	0.745
2.00	1.00	0.01	9.274	2.848	0.573	1.00	2.00	0.01	8.801	2.576	0.749
2.00	2.00	0.10	9.193	2.785	0.575	0.50	2.00	0.10	8.718	2.518	0.757
1.50	0.10	0.01	9.270	2.852	0.576	0.50	0.10	0.01	8.751	2.551	0.771
1.50	1.00	0.10	9.181	2.781	0.580	0.10	0.10	0.10	8.667	2.491	0.779
1.00	0.10	0.10	9.147	2.765	0.594	0.50	0.50	0.01	8.713	2.530	0.786
2.00	1.50	0.01	9.188	2.795	0.602	0.10	0.50	0.10	8.641	2.476	0.789
1.50	1.50	0.10	9.104	2.734	0.608	0.10	1.00	0.10	8.615	2.462	0.800
1.50	0.50	0.01	9.175	2.793	0.608	0.50	1.00	0.01	8.678	2.510	0.800
1.00	0.50	0.10	9.066	2.716	0.622	0.10	1.50	0.10	8.596	2.452	0.808
2.00	2.00	0.01	9.119	2.754	0.627	0.50	1.50	0.01	8.652	2.495	0.811
1.50	2.00	0.10	9.041	2.698	0.630	0.10	2.00	0.10	8.581	2.444	0.814
1.50	1.00	0.01	9.086	2.738	0.640	0.50	2.00	0.01	8.631	2.484	0.820
1.00	1.00	0.10	8.989	2.670	0.651	0.10	0.10	0.01	8.521	2.425	0.867
1.50	1.50	0.01	9.018	2.698	0.665	0.10	0.50	0.01	8.511	2.420	0.871
1.00	0.10	0.01	9.020	2.705	0.666	0.10	1.00	0.01	8.502	2.415	0.875
1.00	1.50	0.10	8.930	2.636	0.673	0.10	1.50	0.01	8.495	2.411	0.878
1.50	2.00	0.01	8.963	2.666	0.685	0.10	2.00	0.01	8.490	2.409	0.880

Table 18.4 Root-mean-square for the neutral atoms and atomic ions with $+1, +2, +3, +4$, and $+5$ charge, H–Ar, for symmetrized weighted density approximations (0pt-WDA, 1pt-WDA, 2pt-WDA) described in Sect. 18.3. The arithmetic mean ($q = 1$) is chosen

a_0	b_0	a_1	0p-WDA	1p-WDA	2p-WDA	a_0	b_0	a_1	0p-WDA	1p-WDA	2p-WDA
2.00	0.10	0.10	11.382	4.066	0.498	1.00	0.50	0.01	10.540	3.547	0.731
2.00	0.50	0.10	11.220	3.956	0.530	0.50	0.10	0.10	10.476	3.501	0.740
2.00	0.10	0.01	11.230	3.978	0.545	1.00	2.00	0.10	10.466	3.491	0.742
1.50	0.10	0.10	11.101	3.886	0.560	1.00	1.00	0.01	10.458	3.497	0.757
2.00	1.00	0.10	11.065	3.854	0.565	0.50	0.50	0.10	10.409	3.461	0.762
2.00	0.50	0.01	11.080	3.877	0.577	1.00	1.50	0.01	10.397	3.460	0.777
1.50	0.50	0.10	10.966	3.796	0.592	0.50	1.00	0.10	10.347	3.423	0.784
2.00	1.50	0.10	10.946	3.778	0.595	1.00	2.00	0.01	10.349	3.431	0.794
2.00	1.00	0.01	10.938	3.784	0.612	0.50	1.50	0.10	10.300	3.395	0.801
1.50	0.10	0.01	10.939	3.794	0.615	0.50	2.00	0.10	10.262	3.374	0.814
2.00	2.00	0.10	10.850	3.717	0.621	0.50	0.10	0.01	10.291	3.403	0.817
1.50	1.00	0.10	10.838	3.715	0.626	0.50	0.50	0.01	10.243	3.373	0.833
1.00	0.10	0.10	10.800	3.697	0.640	0.10	0.10	0.10	10.200	3.339	0.838
2.00	1.50	0.01	10.829	3.715	0.640	0.50	1.00	0.01	10.199	3.347	0.849
1.50	0.50	0.01	10.818	3.715	0.646	0.10	0.50	0.10	10.166	3.320	0.850
1.50	1.50	0.10	10.740	3.653	0.654	0.50	1.50	0.01	10.165	3.327	0.861
2.00	2.00	0.01	10.742	3.660	0.665	0.10	1.00	0.10	10.135	3.302	0.862
1.00	0.50	0.10	10.696	3.631	0.669	0.50	2.00	0.01	10.139	3.312	0.871
1.50	2.00	0.10	10.662	3.605	0.678	0.10	1.50	0.10	10.111	3.289	0.871
1.50	1.00	0.01	10.705	3.643	0.678	0.10	2.00	0.10	10.092	3.278	0.878
1.00	1.00	0.10	10.599	3.571	0.699	0.10	0.10	0.01	10.003	3.238	0.924
1.50	1.50	0.01	10.618	3.589	0.704	0.10	0.50	0.01	9.991	3.230	0.929
1.00	0.10	0.01	10.627	3.602	0.705	0.10	1.00	0.01	9.980	3.224	0.933
1.00	1.50	0.10	10.525	3.526	0.723	0.10	1.50	0.01	9.971	3.219	0.936
1.50	2.00	0.01	10.549	3.547	0.725	0.10	2.00	0.01	9.965	3.216	0.939

increasing a_1; for fixed values of b_0, a_1 the errors seem to decreasing when increasing a_0. For fixed values of a_0, a_1 the errors seem to decrease when decreasing b_0.

These observations can be understood since s diverges in asymptotic regions. Therefore a small value of a_1 is needed, but if $a_1 > 1$ it becomes practically impossible to satisfy the normalization condition [38, 39]. Near the nucleus a much larger value of p is needed, $p \approx 20$. Therefore it is desirable that the ratio a_0/b_0 should be on the order of 10. Thus, while this is in no sense an optimization of the form in Eq. (18.12), we nonetheless were able to learn something about the underlying principles that must be followed to design a GGA-based weighted density approximation for exchange.

18.4   Summary

We have used a two-points weighted density approximation (2pt-WDA) to compute the exchange energies for all ions with charges from -1 to $+12$ for the first thirty-six atoms in the periodic table. While the 2pt-WDA is still competitive with popular

generalized gradient approximations, its performance worsens for highly charged atomic cations, probably because it is better to use a larger value of the power p in Eq. (18.8) for those systems. This motivated us to build a density functional expression for p by writing p as a rational function of the reduced gradient, $s(\mathbf{r})$. Preliminary tests reveal the order of magnitude for the parameters in the mean, and allow us to suggest the form:

$$p(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \left(p(s; \mathbf{r}) + p(s; \mathbf{r}') \right), \tag{18.14a}$$

$$p(s; \mathbf{r}) = \frac{20 + s(\mathbf{r})}{1 + 10s(\mathbf{r})}. \tag{18.14b}$$

The numerical parameters in Eq. (18.14b) are not optimized, and are merely indicative of important features for the functional form.

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