Incorporation of the Fermi-Amaldi term into Direct Energy Kohn-Sham calculations

Daisy J. Dillon and David J. Tozer*

Department of Chemistry, Durham University, South Road, Durham, DH1 3LE UK

E-mail: d.j.tozer@durham.ac.uk

Abstract

In direct energy Kohn-Sham (DEKS) theory, the density functional theory electronic energy equals the sum of occupied orbital energies, obtained from Kohn-Sham-like orbital equations involving a shifted Hartree-exchange-correlation potential, which must be approximated. In the present study, the Fermi-Amaldi term is incorporated into approximate DEKS calculations, introducing the required $-1/r$ contribution to the exchange-correlation component of the shifted potential in asymptotic regions. It also provides a mechanism for eliminating one-electron self-interaction error and it introduces a non-zero exchange-correlation component of the shift in the potential, of appropriate magnitude. The resulting electronic energies are very sensitive to the methodologies considered, whereas highest occupied molecular orbital energies and exchange-correlation potentials are much less sensitive and are similar to those obtained from DEKS calculations using a conventional exchange-correlation functional.

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1 Introduction and Background

Levy and Zahariev[1] have proposed a new approach for performing density functional theory calculations. Central to their approach is a set of Kohn-Sham-like orbital equations,

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \overline{w}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \bar{\epsilon}_i \varphi_i(\mathbf{r}) \,, \tag{1}$$

where $v(\mathbf{r})$ is the external potential and

$$\overline{w}(\mathbf{r}) = w(\mathbf{r}) + c \,. \tag{2}$$

Here, $w(\mathbf{r})$ is the familiar Hartree-exchange-correlation (Hxc) potential,

$$w(\mathbf{r}) = v_J(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r}) \,, \tag{3}$$

which is the functional derivative of the Hxc energy functional,

$$G = J + E_{\mathrm{xc}} \,. \tag{4}$$

This functional comprises the classical Hartree functional, expressed in terms of the density $\rho(\mathbf{r})$,

$$J = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \,, \tag{5}$$

and the exchange-correlation functional, E_{xc}. The shift c in Eq (2) is chosen to be

$$c = \frac{G - \int w(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}}{N} \,, \tag{6}$$

where N is the electron number. Using Eqs (3) and (4), this can be partitioned into Hartree and exchange-correlation components,

$$c = c_J + c_{\text{xc}}, \tag{7}$$

where

$$c_J = \frac{J - \int v_J(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}}{N} = -\frac{J}{N}, \tag{8}$$

and

$$c_{\text{xc}} = \frac{E_{\text{xc}} - \int v_{\text{xc}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}}{N}, \tag{9}$$

meaning the potential $\overline{w}(\mathbf{r})$ can be partitioned as

$$\overline{w}(\mathbf{r}) = \overline{v}_J(\mathbf{r}) + \overline{v}_{\text{xc}}(\mathbf{r}), \tag{10}$$

where

$$\overline{v}_J(\mathbf{r}) = v_J(\mathbf{r}) + c_J \tag{11}$$

and

$$\overline{v}_{\text{xc}}(\mathbf{r}) = v_{\text{xc}}(\mathbf{r}) + c_{\text{xc}}. \tag{12}$$

The choice of c in Eq (6) is such that the electronic energy reduces to the sum of the occupied orbital energies,

$$E = \sum_i \overline{\epsilon}_i, \tag{13}$$

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which contrasts Kohn-Sham theory, where this is not the case for conventional functionals. In practical calculations, Eq (1) must be solved within a finite basis set, but this does not affect the form of Eq (13).

Levy and Zahariev[1] showed that the exact potential $\overline{w}(\mathbf{r})$ has desirable characteristics. It does not exhibit a discontinuity as the electron number crosses integer; and upon any isoelectronic change in the density, it changes less than any other potential that differs from $w(\mathbf{r})$ by a density-dependent additive constant. They therefore suggested that it was desirable to approximate $\overline{w}(\mathbf{r})$ directly and then solve Eq (1) and evaluate the electronic energy using Eq (13). Their method is termed direct energy Kohn-Sham (DEKS) theory. For further discussion of DEKS, see Refs 2–8; also see Refs. 9,10 for an earlier, Hartree-Fock variant.

Sharpe, Levy, and Tozer (SLT)[7] used density scaling homogeneity considerations to carry out DEKS calculations on a series of atoms and small molecules, providing several preliminary approximations for $\overline{w}(\mathbf{r})$. In particular, they demonstrated the utility of approximating the shift, c, by its dominant Hartree component, c_J, meaning its exchange-correlation component, c_{xc}, was zero. The aim of the present study is to investigate the incorporation of the Fermi-Amaldi (FA) term[11] into the SLT approach. This provides a simple way to introduce the required $-1/r$ contribution to the exchange-correlation potential in Eq (12) in asymptotic regions. Furthermore, we shall show that it provides a mechanism for eliminating one-electron self-interaction error and that it introduces a non-zero value of c_{xc}, of appropriate magnitude. Methodology and results are presented in Section 2. Conclusions are presented in Section 3.

2 Methodology and Results

2.1 Preliminary work

It is helpful to start by summarising the approach and findings of SLT.[7] They commenced by defining an underlying Hxc functional (Eq (4)) and then shifted its potential by c to yield the desired $\overline{w}(\mathbf{r})$ (Eq 2)), which was then used to solve Eq (1) (within a finite basis set) and compute the electronic energy using Eq (13). For the Hartree component of the Hxc functional, they used the exact J in Eq (5). For the exchange-correlation component, they used

$$E_{\text{xc}} = \alpha G_{\text{xc}} \tag{14}$$

where α is a parameter and G_{xc} is a flexible, local functional proposed by Liu and Parr in Ref. 12, which can be homogeneous of any order under density scaling and under coordinate scaling; the latter was chosen to be order one. A consideration of potentials led SLT to set $c = c_J = -\frac{J}{N}$, meaning $c_{\text{xc}} = 0$ (Eq (7)). It then follows from Eq (9) that the exchange-correlation functional must be homogeneous of degree one under density scaling (a functional, F, that is homogenous of degree k under density scaling, satisfies $kF = \int v_F(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$), for which the Liu-Parr expression is simply

$$G_{\text{xc}} = \left(\int \rho^{\frac{3}{2}}(\mathbf{r})d\mathbf{r} \right)^{\frac{2}{3}}. \tag{15}$$

Combining the exchange-correlation potential of the functional in Eq (14) with the Hartree potential and the shift $c = c_J = -\frac{J}{N}$, gave the overall DEKS potential,

$$
\begin{aligned}
\overline{w}(\mathbf{r}) &= v_J(\mathbf{r}) + \alpha \frac{\delta G_{\text{xc}}}{\delta \rho(\mathbf{r})} - \frac{J}{N} \\
&= v_J(\mathbf{r}) + \alpha \left(\int \rho^{\frac{3}{2}}(\mathbf{r})d\mathbf{r} \right)^{-\frac{1}{3}} \rho^{\frac{1}{2}}(\mathbf{r}) - \frac{J}{N}
\end{aligned} \tag{16}
$$

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Two approaches were used by SLT to determine the parameter α. Initially, it was determined on a case-by-case basis, by demanding that the exchange-correlation energy obtained by evaluating Eq (14) using a GGA density, from a prior GGA calculation, equals the corresponding GGA exchange-correlation energy. This simply requires

$$\alpha = E_{\text{xc}}^{\text{GGA}}/G_{\text{xc}}^{\text{GGA}}, \tag{17}$$

where $G_{\text{xc}}^{\text{GGA}}$ is obtained by evaluating Eq (15) using the GGA density and $E_{\text{xc}}^{\text{GGA}}$ is the GGA exchange-correlation energy. For the GGA, SLT used the Perdew-Burke-Ernzerhof (PBE) functional[13] and we do the same in the current study. DEKS calculations determined using Eqs (16) and (17) were denoted DEKS2.

Table 1 presents electronic energies (Eq (13)) determined using DEKS2, for 17 closed-shell atoms and molecules taken from Ref. 14. Table 2 presents the corresponding highest occupied molecular orbital (HOMO) energies, $\bar{\epsilon}_{\text{HOMO}}$ (Eq (1)). The energies in Tables 1 and 2 are central quantities in the DEKS approach and although they will be relatively insensitive to the actual behaviour of $\overline{w}(\mathbf{r})$ in asymptotic regions, they will still be affected by the inclusion of the Fermi-Amaldi term, since its potential contributes to all regions of space, not just asymptotic regions. It is therefore important to quantify how these energies are affected by its inclusion. In addition to these energies, we also consider the DEKS exchange-correlation potential, $\overline{v}_{\text{xc}}(\mathbf{r})$ (Eq (12)) for the representative N_2 molecule. Figure 1(a) presents this potential for DEKS2. All calculations in this study are performed using the aug-cc-pVTZ basis set at the reference, near-exact geometries of Ref. 15, using the CADPAC program.[16]

Given the central role of PBE in the methodology, we follow SLT and compare all results in the present study with those from DEKS calculations using PBE. For electronic energies, the DEKS PBE energies are identical to the regular Kohn-Sham electronic energies. For HOMO energies, the DEKS PBE energies are the Kohn-Sham HOMO energies, shifted by c,
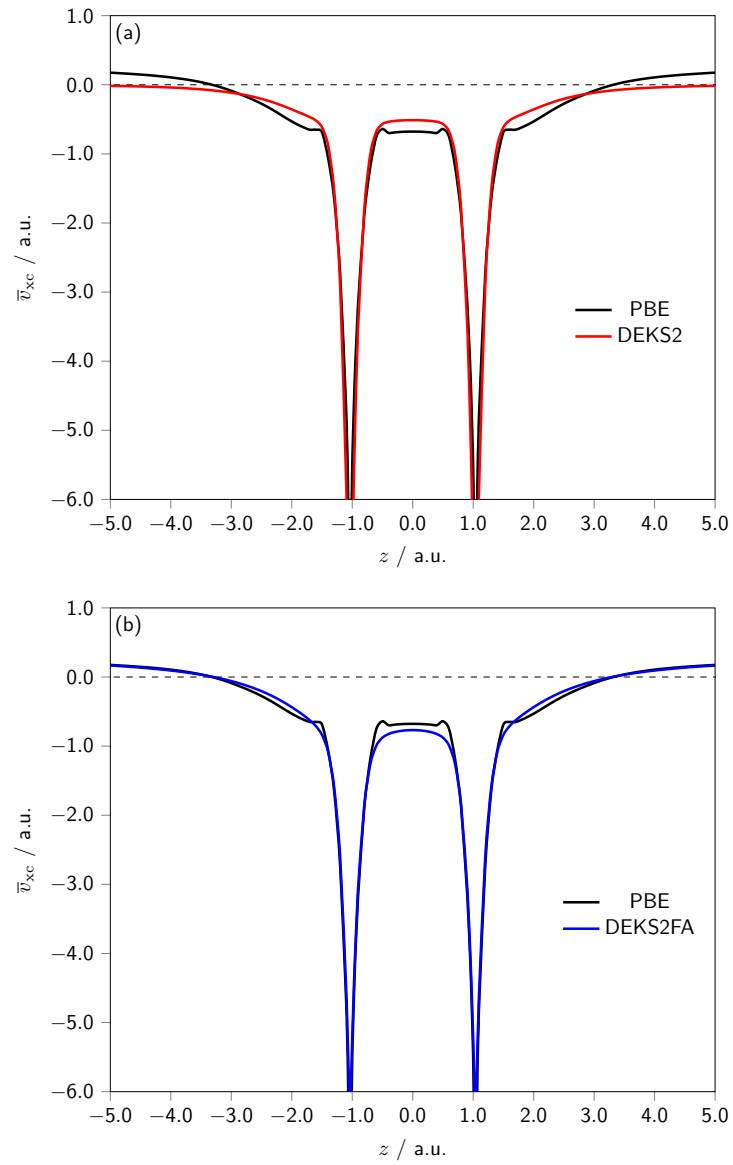
Figure 1: DEKS exchange-correlation potentials, $\overline{v}_{\mathrm{xc}}(\mathbf{r})$, plotted along the bond axis in N_2.

Table 1: DEKS electronic energies (in a.u.).

	DEKS2	DEKS3	DEKS2FA	DEKS3FA	DEKS4FA	PBE
He	-2.893	-2.718	-2.894	-2.933	-3.042	-2.892
Be	-14.643	-14.497	-14.642	-14.469	-14.655	-14.629
Ne	-128.906	-128.562	-128.864	-129.183	-129.439	-128.853
CH_4	-40.508	-40.243	-40.492	-40.275	-40.414	-40.464
NH_3	-56.562	-56.365	-56.533	-56.434	-56.599	-56.512
H_2O	-76.434	-76.248	-76.398	-76.421	-76.614	-76.381
HF	-100.447	-100.213	-100.407	-100.567	-100.790	-100.393
Mg	-199.993	-199.999	-199.963	-200.496	-200.705	-199.949
CO	-113.292	-112.800	-113.242	-112.520	-112.600	-113.233
N_2	-109.508	-108.991	-109.459	-108.709	-108.789	-109.452
Ar	-527.433	-528.691	-527.348	-529.169	-529.037	-527.338
F_2	-199.503	-198.902	-199.431	-198.323	-198.242	-199.418
PH_3	-343.075	-344.296	-343.033	-344.049	-343.945	-342.988
H_2S	-399.324	-400.608	-399.263	-400.556	-400.443	-399.234
HCl	-460.728	-462.024	-460.654	-462.213	-462.091	-460.636
SO_2	-548.538	-549.235	-548.458	-547.368	-546.315	-548.391
Cl_2	-920.185	-922.212	-920.066	-919.379	-917.850	-920.036
MAD	0.069	0.658	0.020	0.681	0.843	

evaluated using Eq (6) with PBE quantities. These PBE energies are presented in Tables 1 and 2; mean absolute deviations (MADs) relative to theses values are also presented. For the N_2 exchange-correlation potential, the DEKS PBE potential is the Kohn-Sham exchange-correlation potential, shifted by the value of c_{xc} for N_2, evaluated using Eq (9) with PBE quantities. This PBE exchange-correlation potential is presented in Figure 1. Of course, these DEKS PBE calculations are not carried out in the real spirit of DEKS − they simply shift the Hxc potential constructed from a standard exchange-correlation functional, whereas $\overline{w}(\mathbf{r})$ should instead be constructed directly, without explicit reference to a standard functional. However, they do provide an appropriate reference for the development of preliminary approximations for $\overline{w}(\mathbf{r})$. Furthermore, it has been shown[1,3] that the DEKS PBE HOMO energies are actually in rather good agreement with exact values.

For electronic energies (Table 1) and HOMO energies (Table 2), the DEKS2 MADs are 0.069 and 0.056 au, respectively. For the exchange-correlation potential (Figure 1(a)), the

Table 2: DEKS HOMO energies, $\bar{\epsilon}_{\mathrm{HOMO}}$ (in a.u.)

	DEKS2	DEKS3	DEKS2FA	DEKS3FA	DEKS4FA	PBE
He	−1.447	−1.359	−1.447	−1.467	−1.521	−1.446
Be	−1.817	−1.804	−1.753	−1.738	−1.754	−1.810
Ne	−6.592	−6.574	−6.746	−6.764	−6.778	−6.716
CH_4	−3.362	−3.349	−3.442	−3.431	−3.438	−3.436
NH_3	−3.843	−3.834	−3.935	−3.930	−3.938	−3.914
H_2O	−4.577	−4.568	−4.694	−4.695	−4.705	−4.667
HF	−5.491	−5.480	−5.629	−5.637	−5.649	−5.600
Mg	−7.818	−7.818	−7.693	−7.706	−7.711	−7.751
CO	−5.440	−5.424	−5.503	−5.480	−5.483	−5.505
N_2	−5.386	−5.369	−5.472	−5.448	−5.450	−5.462
Ar	−12.692	−12.715	−12.702	−12.735	−12.733	−12.737
F_2	−7.084	−7.067	−7.195	−7.162	−7.160	−7.201
PH_3	−9.422	−9.445	−9.409	−9.428	−9.426	−9.422
H_2S	−10.398	−10.420	−10.390	−10.413	−10.411	−10.404
HCl	−11.501	−11.523	−11.504	−11.531	−11.529	−11.528
SO_2	−11.002	−11.010	−11.056	−11.044	−11.032	−11.057
Cl_2	−13.947	−13.965	−13.981	−13.975	−13.961	−13.970
MAD	0.056	0.065	0.020	0.023	0.028	

DEKS2 potential resembles the PBE potential, although it vanishes asymptotically ($c_{\mathrm{xc}} = 0$), whereas the PBE potential approaches its non-zero c_{xc} value. Neither potential exhibits the required $-1/r + c_{\mathrm{xc}}$ asymptotic behaviour (Eq (12)).

A downside of DEKS2 is that it requires prior GGA calculations to be performed, in order to determine the α values (Eq (17)). To overcome this, SLT considered applying the functional in Eq (14) to a uniform electron gas, where the exchange-correlation energy is approximated by the Dirac exchange energy.[17] Equating the two yields

$$\alpha\left(\int \rho^{\frac{3}{2}}(\mathbf{r})d\mathbf{r}\right)^{\frac{2}{3}} = C_{\mathrm{x}}\int \rho^{\frac{4}{3}}(\mathbf{r})d\mathbf{r}\,, \tag{18}$$

where $C_{\mathrm{x}} = -0.7386$ is the Dirac exchange prefactor. Setting the constant density $\rho(\mathbf{r}) = \frac{N}{V}$, where V is the volume, then gave

$$\alpha = C_{\mathrm{x}}N^{\frac{1}{3}}\,. \tag{19}$$

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The red circles in Figure 2 are the DEKS2 α values for the 17 systems, plotted as a function of $N^{1/3}$. It is evident that there is an approximate proportionality, consistent with Eq (19). SLT performed a zero-intercept least squares fit, yielding

$$\alpha = -0.6888N^{\frac{1}{3}} \tag{20}$$

which is shown as the solid red line in the figure. The R^2 value is 0.93 and the prefactor is reassuringly similar to C_x. The use of Eq (20) therefore eliminates the need for an explicit prior GGA calculation. DEKS calculations determined using Eqs (16) and (20) were denoted DEKS3 and energies are presented in Tables 1 and 2. In moving from DEKS2 to DEKS3, the electronic energy MAD increases by almost an order of magnitude, reflecting the approximate nature of Eq (20). The increase in MAD is much less pronounced for HOMO energies. We do not present the DEKS3 exchange-correlation potential for N_2 because, on the scale plotted in Figure 1, it is essentially indistinguishable from the DEKS2 potential. For further theoretical and methodological details of DEKS2 and DEKS3, together with a full results analysis, the reader is referred to Ref. 7.

2.2 Incorporation of the Fermi-Amaldi term

We now consider the incorporation of the Fermi-Amaldi term[11] . To achieve this, we re-write the exchange-correlation energy as

$$E_{xc} = -\frac{J}{N} + \alpha G_{xc} \tag{21}$$

where G_{xc} is again given by Eq (15), i.e. homogeneous of degree one under density scaling. We note that Parr and Ghosh[18] also recommended combining $-\frac{J}{N}$ with a functional that is approximately homogeneous of degree one under density scaling, for atomic systems. A related form was also considered in Refs 19 and 20.

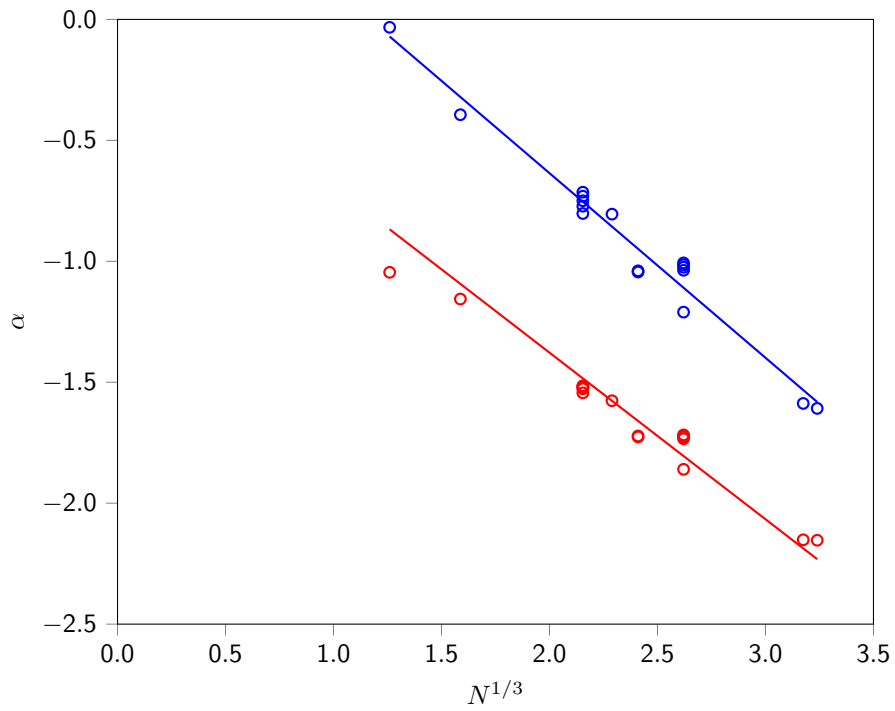Evaluating Eq (9) for the exchange-correlation functional in Eq (21) yields a non-zero,

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Figure 2: Values of the parameter α for the 17 systems, plotted as a function of $N^{1/3}$, for DEKS2 (red circles) and DEKS2FA (blue circles). The solid lines are the least-squares fits, $\alpha = -0.6888N^{\frac{1}{3}}$ (red) and $\alpha = -0.7632N^{\frac{1}{3}} + 0.8908$ (blue).

$c_{\text{xc}} = \frac{J}{N^2}$, noting that we have treated N as a parameter rather than a functional, meaning we do not differentiate it when taking functional derivatives; the same approach was used in Refs. 7,18,19. (If N was instead treated as a functional and differentiated, then c_{xc} would be zero). Combining the exchange-correlation potential of the functional in Eq (21) with the Hartree potential and the shifts $c_J = -\frac{J}{N}$ and $c_{\text{xc}} = \frac{J}{N^2}$, gives the overall DEKS potential,

$$\overline{w}(\mathbf{r}) = v_J(\mathbf{r})\left(1 - \frac{1}{N}\right) + \alpha\left(\int \rho^{\frac{3}{2}}(\mathbf{r})d\mathbf{r}\right)^{-\frac{1}{3}}\rho^{\frac{1}{2}}(\mathbf{r}) - \frac{J}{N}\left(1 - \frac{1}{N}\right) \quad (22)$$

To derive α, we first use the same approach that was used to derive Eq (17), which now gives

$$\alpha = \frac{E_{\text{xc}}^{\text{GGA}} + \frac{J^{\text{GGA}}}{N}}{G_{\text{xc}}^{\text{GGA}}}, \quad (23)$$

where J^{GGA} is the Hartree energy in Eq (5), evaluated using the GGA density. DEKS results determined using Eqs (22) and (23) are denoted DEKS2FA and energies are presented in Tables 1 and 2. In moving from DEKS2 to DEKS2FA, the MADs for electronic energies and HOMO energies reduce by about a factor of three. Figure 1(b) presents the DEKS2FA exchange-correlation potential. In moving from DEKS2 to DEKS2FA, the potential more closely resembles the PBE potential; the non-zero $c_{\text{xc}} = \frac{J}{N^2}$ is clearly evident. Although it is not apparent for the coordinate scale plotted, the DEKS2FA exchange-correlation potential does exhibit the required $-1/r + c_{\text{xc}}$ asymptotic behaviour (Eq (12)) by construction, which neither PBE nor DEKS2 exhibit. The inclusion of the Fermi-Amaldi term therefore appears beneficial from both an energy and potential perspective.

In order to eliminate the need for prior GGA calculations (Eq (23)), we again follow SLT and consider applying the exchange-correlation functional (now Eq (21)) to a uniform electron gas, where the exchange-correlation energy is approximated by the Dirac exchange energy. This gives

$$-\frac{1}{2N}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \alpha\left(\int \rho^{\frac{3}{2}}(\mathbf{r})d\mathbf{r}\right)^{\frac{2}{3}} = C_{\text{x}}\int \rho^{\frac{4}{3}}(\mathbf{r})d\mathbf{r}. \quad (24)$$

However, the position-dependence of the denominator in the Hartree term means that setting $\rho(\mathbf{r}) = \frac{N}{V}$ does not lead to a simple expression for α, as it did in Eq (19). To make progress, we choose to replace the exact Hartree term in Eq (24) with the approximate expression of Liu and Parr,

$$J = C_J \left(\int \rho^{\frac{6}{5}}(\mathbf{r}) d\mathbf{r} \right)^{\frac{5}{3}},$$ (25)

which was obtained by taking the general functional form in Ref. 12 and enforcing the appropriate density scaling (order two) and coordinate scaling (order one) behaviour of the exact Hartree energy; the quantity C_J is a positive parameter. This gives

$$-\frac{C_J}{N} \left(\int \rho^{\frac{6}{5}}(\mathbf{r}) d\mathbf{r} \right)^{\frac{5}{3}} + \alpha \left(\int \rho^{\frac{3}{2}}(\mathbf{r}) d\mathbf{r} \right)^{\frac{2}{3}} = C_\mathrm{x} \int \rho^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r},$$ (26)

and setting $\rho(\mathbf{r}) = \frac{N}{V}$ yields

$$\alpha = C_\mathrm{x} N^{1/3} + C_J.$$ (27)

The blue circles in Figure 2 are the DEKS2FA α values, plotted as a function of $N^{\frac{1}{3}}$. Once again, the values are approximately proportional to $N^{1/3}$, although there is now a vertical offset compared to the red DEKS2 data, consistent with Eq (27). A least squares fit yields

$$\alpha = -0.7632 N^{\frac{1}{3}} + 0.8908$$ (28)

which is shown as the solid blue line in the figure. The R^2 value is 0.97, which is a marginal improvement over the DEKS2 fit ($R^2 = 0.93$). Consistent with Eq (27), the slope of -0.7632 is again similar to C_x, whilst the intercept of 0.8908 is of the same sign and order of magnitude as the value of $C_J = 1.0829$, obtained by Liu and Parr[12] through a fit to atomic data. DEKS results determined using Eqs (22) and (28) are denoted DEKS3FA and energies are

presented in Tables 1 and 2. In moving from DEKS3 to DEKS3FA, the MAD marginally increases for electronic energies, whereas the MAD for HOMO energies reduces significantly. Indeed, the DEKS3FA HOMO energies have a rather similar MAD to DEKS2FA, despite the approximation inherent in Eq (28). We do not plot the DEKS3FA exchange-correlation potential because, on the scale plotted in Figure 1, it is essentially indistinguishable from the DEKS2FA potential.

2.3   Eliminating one-electron self-interaction error

The potential $\overline{w}(\mathbf{r})$ should be zero when $N = 1$, in order for the methodology to be one-electron self-interaction free, and the present formalism allows this to be easily achieved. The first and third terms in Eq (22) involve the factor $(1 - \frac{1}{N})$ and so vanish when $N = 1$. To eliminate one-electron self-interaction error, all that is therefore required is that $\alpha = 0$ when $N = 1$ and the expression in Eq (28) points to a simple way to achieve this: simply constrain the slope and intercept in the least squares fit to be equal and opposite. The corresponding least squares fit gives

$$\alpha = -0.6799(N^{\frac{1}{3}} - 1) \tag{29}$$

for which $R^2 = 0.95$. DEKS results determined using Eqs (22) and (29) are denoted DEKS4FA and energies are presented in Tables 1 and 2. DEKS4FA electronic energies have a larger MAD than DEKS3FA, reflecting the approximate nature of Eq (29). However, the HOMO energies have only a slightly larger MAD. We do not plot the DEKS4FA exchange-correlation potential because, on the scale plotted in Figure 1, it is again essentially indistinguishable from the DEKS2FA potential.

Like other approximations,[21] the Fermi-Amaldi term does not necessarily remedy all problems associated with self-interaction. It is also worth noting that neither term in Eq (21) is size extensive, but see Ref 7 for further discussion of this point.

2.4 Relationship between values of $c_{\mathrm{xc}} = \frac{J}{N^2}$ and $c_{\mathrm{xc}}^{\mathrm{PBE}}$

A key feature of this methodology is the introduction of the non-zero exchange-correlation shifts, $c_{\mathrm{xc}} = \frac{J}{N^2}$. We end this study by considering how these shifts relate to the corresponding PBE shifts, hereafter denoted $c_{\mathrm{xc}}^{\mathrm{PBE}}$, obtained by evaluating Eq (9) with PBE quantities. We shall specifically consider the DEKS2FA values of $\frac{J}{N^2}$, but the same findings apply to the DEKS3FA and DEKS4FA values, due to their very similar J values.

At first sight, we might expect that the $\frac{J}{N^2}$ values would resemble the $c_{\mathrm{xc}}^{\mathrm{PBE}}$ values. Figure 3(a) plots a scatter plot of the two quantities for the 17 systems, but the correlation is rather poor and the $\frac{J}{N^2}$ values are notably larger for most of the systems. However, $\frac{J}{N^2}$ is the amount that the potential of our approximate functional (Eq (21)) must be shifted by, in order that the electronic energy equals the sum of the occupied orbital energies. In energetically important regions (i.e. the regions of space that govern the values of the occupied orbital energies), this potential has a shape that connects to a $-1/r$ potential in asymptotic regions. By contrast, the value of $c_{\mathrm{xc}}^{\mathrm{PBE}}$ is the amount that the Kohn-Sham PBE potential must be shifted by and it is well-established that in energetically important regions, this potential already has a shift built into it; the value of that shift is approximately half of the integer discontinuity, Δ_{xc} (Refs. 22, 23). Put another way, in energetically important regions, the PBE potential has a shape that should connect to a $-1/r + \frac{\Delta_{\mathrm{xc}}}{2}$ potential in asymptotic regions. (This is the basis of the asymptotic correction approach in Ref. 24). It follows that rather than resembling $c_{\mathrm{xc}}^{\mathrm{PBE}}$, the shift $\frac{J}{N^2}$ should instead resemble $c_{\mathrm{xc}}^{\mathrm{PBE}}$ *plus* $\frac{\Delta_{\mathrm{xc}}}{2}$.

Values of $\frac{\Delta_{\mathrm{xc}}}{2}$ can be approximated as the non-zero shifts that arise in GGA functional development; for 15 of the 17 systems, we use the shifts that arose in the HCTH functional development,[25] which are tabulated in Table 2 of Ref. 26. For the remaining two systems (Ar and H_2S), we instead approximate $\frac{\Delta_{\mathrm{xc}}}{2}$ as being the sum of the GGA HOMO energy plus the experimental ionisation potential.[23,24] The conclusions we reach are unchanged if the latter approach is used for all 17 systems. Similarly, the conclusions are unchanged if the near-exact $\frac{\Delta_{\mathrm{xc}}}{2}$ values of Ref. 23 are used, where available. Figure 3(b) plots a scatter

plot of $\frac{J}{N^2}$ and $c_{\mathrm{xc}}^{\mathrm{PBE}} + \frac{\Delta_{\mathrm{xc}}}{2}$. The correlation is much improved over that in Figure 3(a): R^2 increases by a factor of two whilst the mean absolute difference between $\frac{J}{N^2}$ and the PBE quantities reduces by a factor of three. The agreement is far from perfect, but we are encouraged by the agreement, given the natural manner in which the non-zero shift arises and the approximations used in the analysis.

3 Conclusions

We have shown how the Fermi-Amaldi term can be easily incorporated into approximate DEKS calculations. The preliminary methodology relies on a prior GGA calculation for each system, but a uniform electron gas analysis can be used to eliminate the need for these explicit calculations; the offset in the prefactor, α, arising from inclusion of the Fermi-Amaldi term, is readily understood from the analysis.

The incorporation of the Fermi-Amaldi term introduces the required $-1/r$ contribution to the exchange-correlation component of the shifted potential in asymptotic regions. It also provides a mechanism for eliminating one-electron self-interaction error and it introduces a non-zero exchange-correlation component of the shift in the potential, of appropriate magnitude. Insight into the values of the shifts is provided by a consideration of the integer discontinuity. The resulting electronic energies are very sensitive to the methodology used to determine α, whereas HOMO energies and exchange-correlation potentials are much less sensitive and are similar to DEKS PBE quantities.

DEKS calculations are still in their infancy and our approach does not offer a practical alternative to Kohn-Sham theory. However, we hope that the ideas used in this study will stimulate further research into the DEKS approach and improved approximations for $\overline{w}(\mathbf{r})$.
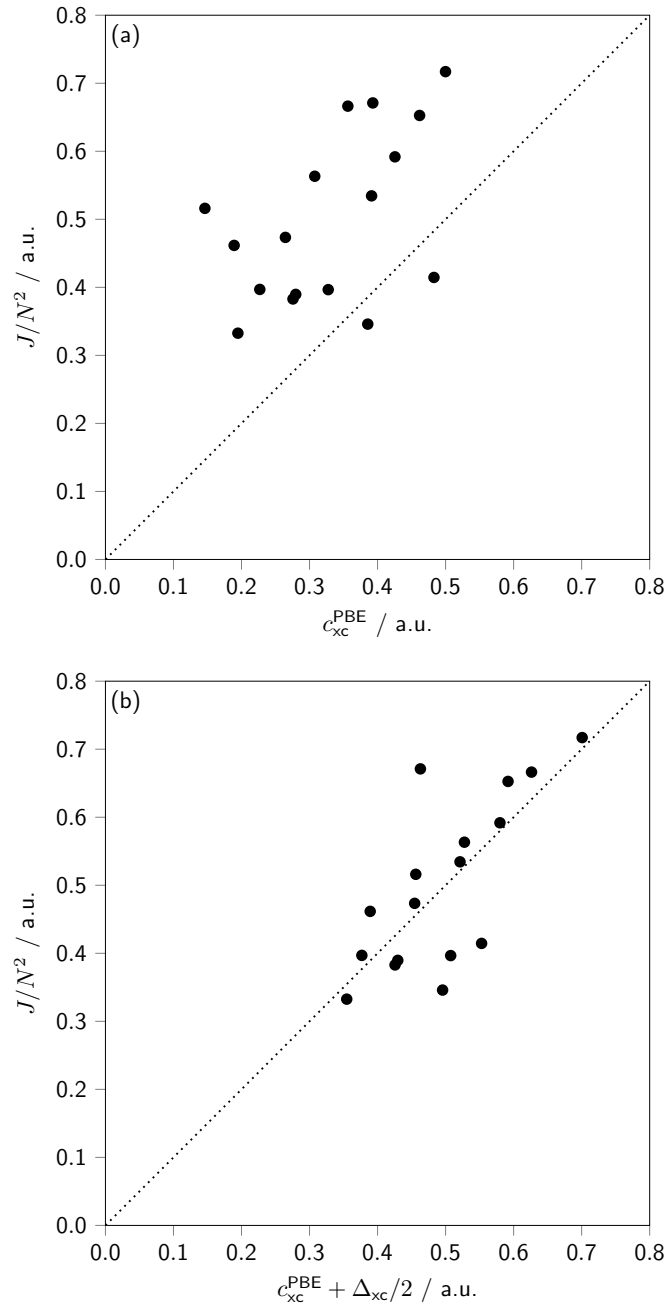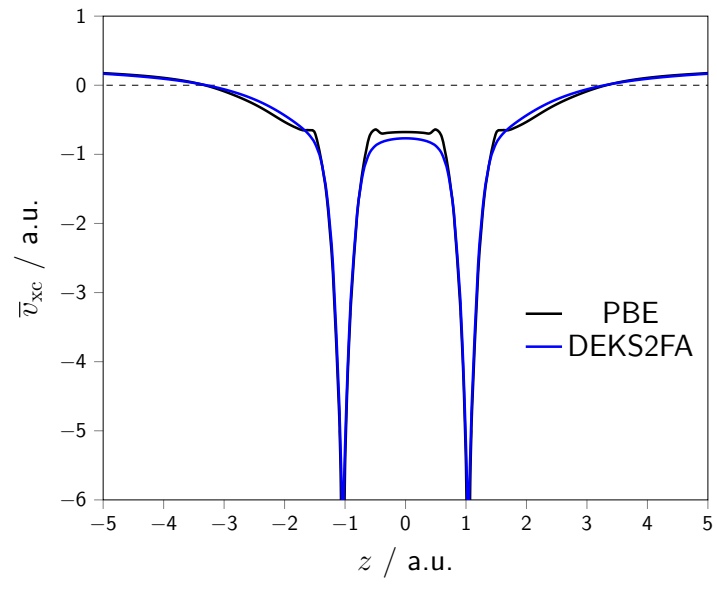
Figure 3: Scatter plots of exchange-correlation shifts for the 17 systems.

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Graphical abstract.