Functional designed to include surface effects in self-consistent density functional theory

Rickard Armiento and Ann E. Mattsson

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:
http://dx.doi.org/10.1103/PhysRevB.72.085108
Copyright: American Physical Society
http://www.aps.org/

Postprint available at: Linköping University Electronic Press
http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-86299
We design a density-functional-theory (DFT) exchange-correlation functional that enables an accurate treatment of systems with electronic surfaces. Surface-specific approximations for both exchange and correlation energies are developed. A subsystem functional approach is then used: an interpolation index combines the surface functional with a functional for interior regions. When the local density approximation is used in the interior, the result is a straightforward functional for use in self-consistent DFT. The functional is validated for surfaces effects, such as the generalized surfaces of metal monovacancies. Recent work has explained this as a system-specific approximation for both exchange and correlation that compose the XC functional.

The XC functional suggested in the early works on the theoretical foundation of DFT, the local density approximation (LDA), was derived from the properties of a uniform electron gas, but has shown surprisingly wide applicability for real systems. For solid-state calculations the LDA is still often the method of choice. The next level in functional development, the generalized gradient approximations (GGA’s), in many cases significantly improves upon the LDA’s use of the uniform electron gas model system leads to physically consistent approximations (e.g., compatible exchange and correlation that compose the XC functional). Our subsystem functional approach, aims to preserve this propitious property of the LDA through the use of region-specific functionals derived from other model systems. A first effort in this direction was made with the local airy gas (LAG). It extends the LDA by an exchange surface treatment derived from the edge electron gas model system, but keeps the LDA correlation. This first step is completed with the optimized, compatible, correlation introduced here. It is in this sequence of functional development, the LDA, LAG, and then our functional, that the contribution of the present work is most clear.

The XC energy functional \( E_{xc}[n] \) operates on the ground-state electron density \( n(\mathbf{r}) \). It is usually decomposed into the XC energy per particle \( \epsilon_{xc} \):

\[
E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_{xc}(\mathbf{r};[n]) d\mathbf{r}.
\]

Exchange and correlation parts are treated separately, with \( \epsilon_{xc} = \epsilon_{ex} + \epsilon_{cor} \). We put special emphasis on the conventional, local, inverse radius of the exchange hole definition of the exchange energy per particle, \( \hat{\epsilon}_{ex} \). This is in contrast to expressions based on transformations of Eq. (1) that arbitrarily delocalize \( \epsilon_{ex} \) and therefore cannot directly be combined with
each other within the same system. The LDA is local in this sense, while common GGA functionals are not. The LDA exchange term is, in Rydberg atomic units,

\[ \epsilon_x^{LDA}(n(r)) = -3/(2\pi) [3\pi n(r)]^{1/3}. \]

(2)

II. FUNCTIONAL CONSTRUCTION

Kohn and Mattsson\textsuperscript{10} put forward the Airy electron gas as a suitable model for electronic surfaces. The Airy gas is a model of electrons in a linear potential, \( v_{eff}(r) = Lz \), \( L \) sets an overall length scale and \( \epsilon_z \) and \( n(r) \) can be rescaled by \( \epsilon_x^{\text{Airy}} = -1/L^{3/2} \epsilon_z(\mathbf{r};[n]) \) and \( n_x = L^{-1} n(r) \). Parametrizations are constructed from the exact \( \epsilon_x^{\text{Airy}} \) and \( n_0 \) expressed\textsuperscript{13} in Airy functions \( A_i \),

\[ \epsilon_x^{\text{Airy}} = -1/\pi n_{0} \int_{-\infty}^{\infty} d\xi' \int_{0}^{\infty} d\chi' \chi' x \frac{\gamma(\chi' \Delta \xi, \chi' \Delta \chi)}{\Delta \xi^3}, \]

\[ \times A_i(\xi + \chi) A_i(\xi' + \chi) A_i(\xi + \chi') A_i(\xi' + \chi'), \]

(3)

\[ n_0 = \left[ \frac{2}{3} \epsilon_x^{\text{Airy}}(\xi - \xi_0) - \epsilon_x^{\text{Airy}}(\xi) \right]/(3\pi), \]

(4)

\[ d\eta_0/d\xi = \left[ \frac{2}{3} \epsilon_x^{\text{Airy}}(\xi - \xi_0) - \epsilon_x^{\text{Airy}}(\xi) \right]/(2\pi), \]

(5)

where \( \xi = L^{3/2} \xi, \Delta \xi = |\xi - \xi'| \), and

\[ g(\eta, \eta') = \eta \eta' \int_{0}^{\infty} J_1(\eta \eta') J_1(\eta' \eta') \frac{dt}{1 + t^2}. \]

(6)

The LAG functional of Vitos et al.\textsuperscript{9} uses the \( \epsilon_x \) of the Perdew-Wang (PW) LDA (Ref. 12) combined with \( \epsilon_x^{\text{LAG}} = \epsilon_x^{\text{LAG}}(n(r)) \) from an Airy gas corresponding to a generic system’s density \( n(r) \) and scaled gradient \( s = |\nabla n(r)|/[2(3\pi^{2/3})^{1/3} n^{4/3}(r)] \). The refinement factor is

\[ F_x(s) = 1 + a_s s^{4/3} / (1 + a_s s^{4/3})^{a_s}, \]

(7)

where \( a_s = 2.62672, a_p = 0.041106, a_D = 0.092070, \) and \( a_D = 0.657946 \). \( F_s \) depends only on \( s \) since \( n(r) \) just sets a global scale of the model via \( L \). However, far outside the electronic surface, \( F_x^{\text{LAG}} \) does not reproduce the right limiting behavior. We have derived an improved parametrization by using (i) the leading behavior of the exchange energy far outside the surface,\textsuperscript{10} \( \epsilon_x^{\text{Airy}} \rightarrow -1/(2\xi) \), (ii) asymptotic expansions of the Airy functions in Eqs. (4) and (5), and (iii) an interpolation that ensures the expression approaches the LDA appropriately in the slowly varying limit, \( F_x^{\text{LAG}}(s) = (cs^2 + 1)/(cs^2/cs^2 + 1), \)

\[ F_x^b = 1/[F_x^{\text{LAG}}(\tilde{n}_0(s)) 2\tilde{\zeta}(s)], \]

\[ \tilde{\zeta}(s) = (4/3)^{1/2} 2\pi/3 \tilde{\xi}(s) + \tilde{\xi}(s) \xi_0^{4/3}, \]

(8)

using a superscript LAA for the local Airy approximation, the Lambert W function,\textsuperscript{13} and where \( c = 0.7168 \) is from a least-squares fit to the true Airy gas exchange. Figure 1 shows that the improvement of the LAA over the LAG is small in the intermediate region, but pronounced outside the surface.

The Airy exchange parametrizations are designed to accurately model the electron gas at a surface. Hence, they cannot be assumed to successfully work for interior regions. The subsystem functional approach\textsuperscript{8} uses an interpolation index for the purpose of categorizing parts of the system as surface or interior regions. We use a simple expression

\[ X = 1 - ax^2/(1 + ax^2), \]

(9)

where \( a \) is determined below.

In the present work the LDA is used in the interior. In the limit of low \( s \), the LAG and LAA already approach the LDA exchange. The end result for the interpolated exchange functional is therefore only slightly different from using the LAG or LAA in the whole system. However, interpolation is needed for the correlation and to enable future use of other interior exchange functionals.

No “exact” correlation has been worked out for electrons in a linear potential. To obtain a correlation functional, we combine the LAA or LAG exchange with a correlation based on the LDA, but with a multiplicative factor \( \gamma \). The numerical value of \( \gamma \) is given by a fit to jellium surface energies \( \sigma_{xc} \). For a functional \( \epsilon_{xc}(\mathbf{r};[n]) \), \( \sigma_{xc} = \int n(z) \epsilon_{xc}(\mathbf{r};[n]) - \epsilon_{xc}(\mathbf{r};[n]) dz \), where \( n(r) \) is from a self-consistent LDA calculation on a system with uniform background of positive charge \( \tilde{n} \) for \( z \leq 0 \) and \( z > 0 \) (Ref. 14). The value of \( \tilde{n} \) is commonly expressed in terms of \( r_s = [3/(4\pi \tilde{n})]^{1/3} \). The most accurate XC jellium surface energies are given by the improved random-phase approximation scheme presented by Yang et al.\textsuperscript{15} RPA+. We minimize a least-squares sum

\[ \sum_{ij} [\sigma_{xc} - \sigma_{xc}(\mathbf{r};[n])^2, \text{ using values for } r_s = 2.0, 2.07, 2.3, 2.66, 3.0, 3.28, \text{ and } 4.0. \]

The surface placement \( \alpha \) and the LDA correlation factor \( \gamma \) are fitted simultaneously\textsuperscript{16}:}

\[ \alpha_{\text{LAG}} = 2.843, \gamma_{\text{LAG}} = 0.8228, \]

(10)
The main figure shows the quantity that integrates to the sur-
face energy $\sigma_{xc}$ in ergs/cm$^2$. The upper inset shows the difference
between the functionals and LDA. The lower inset shows the inter-
polation indices $X$. Integration gives in ergs/cm$^2$ for LDA 1188, for
LAG 1121, and for LDA-LAG(LAA) the “exact” RPA+ value of
1214.

$$a_{LAA} = 2.804, \quad \gamma_{LAA} = 0.8098. \quad (11)$$

The resulting fit reproduces the jellium XC surface energies
with a mean absolute relative error (MARE) less than half a
percent; cf. Fig. 2 and Table I.

The final form of the functional is

$$\tilde{\epsilon}_x(r_i[n]) = \tilde{\epsilon}_x^{LDA}(n(r))[X + (1 - X)F_x(s)],$$

$$\epsilon_x(r_i[n]) = \epsilon_x^{LDA}(n(r))[X + (1 - X)\gamma], \quad (12)$$

where $F_x(s)$ is either from Eq. (7) or from Eq. (8), and $\epsilon_x^{LDA}$
is the PW LDA correlation.

III. TESTS

Numerical tests were performed with the plane-wave code
SOCORRO.$^{17,18}$ Pseudopotentials (PP’s) were generated with the
FHI98PP code,$^{19}$ modified to obtain the XC potential from
a numerical functional derivative. We use settings provided
by the included element library.$^{18}$ The PP’s and code modi-
fications have been extensively tested. In addition to the
functionals presented by this paper, PP’s were generated for
the LDA, the GGA of Perdew and Wang (PW91)$^2$, and
the GGA of Perdew, Becke, and Ernzerhof (PBE)$^6$. For the latter,
bulk calculations with PP’s constructed with our numerical
functional derivatives agree with the results of PP’s based on
analytical functional derivatives within 0.001%. The results
of other functionals. A convincing sign of general
improvement is the tendency for values to stay between the
LDA and PBE, as they are known to overbind and un-
derbind, respectively. As a measure of overall performance,
the table shows the mean absolute relative error $\bar{x}$ and its
standard deviation $\sigma = \sqrt{\frac{1}{N} \sum (x - \bar{x})^2}$ for $N$
absolute relative errors $x_i$. The value of $\sigma$ gives the spread of the errors
independently of their overall magnitude. If further testing
confirms the LDA-LAG(LAA)’s robustness to be universal
for solid-state systems, they should be considered as a “first

TABLE I. Jellium XC surface energies in erg/cm$^2$. RPA+ values are from Ref. 15 and are taken as exact. The LDA-LAG and LDA-LAA
functionals are created using a two-parameter fit to values for $r_x$ up to 4.00.

<table>
<thead>
<tr>
<th>$r_x$</th>
<th>LDA</th>
<th>PW91</th>
<th>PBE</th>
<th>LAG</th>
<th>LDA-LAG</th>
<th>LDA-LAA</th>
<th>RPA+</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>3354</td>
<td>3216</td>
<td>3264</td>
<td>3226</td>
<td>3414</td>
<td>3414</td>
<td>3413</td>
</tr>
<tr>
<td>2.07</td>
<td>2961</td>
<td>2837</td>
<td>2880</td>
<td>2842</td>
<td>3015</td>
<td>3015</td>
<td>3015</td>
</tr>
<tr>
<td>2.30</td>
<td>2019</td>
<td>1929</td>
<td>1960</td>
<td>1926</td>
<td>2058</td>
<td>2058</td>
<td>2060</td>
</tr>
<tr>
<td>2.66</td>
<td>1188</td>
<td>1131</td>
<td>1151</td>
<td>1121</td>
<td>1214</td>
<td>1214</td>
<td>1214</td>
</tr>
<tr>
<td>3.00</td>
<td>764</td>
<td>725</td>
<td>739</td>
<td>714</td>
<td>782</td>
<td>782</td>
<td>781</td>
</tr>
<tr>
<td>3.28</td>
<td>549</td>
<td>521</td>
<td>531</td>
<td>509</td>
<td>563</td>
<td>563</td>
<td>563</td>
</tr>
<tr>
<td>4.00</td>
<td>261</td>
<td>247</td>
<td>252</td>
<td>236</td>
<td>269</td>
<td>270</td>
<td>268</td>
</tr>
<tr>
<td>5.00</td>
<td>111</td>
<td>104</td>
<td>107</td>
<td>96</td>
<td>115</td>
<td>115</td>
<td>113</td>
</tr>
</tbody>
</table>

MARE 2% 7% 5% 9% <1% <1%
Furthermore, an explicit trend is seen in the sequence LDA, LAG, and LDA-LAG (LAA).

Throughout the table LAG shifts LDA values towards the PW91/PBE values, while LDA-LAG (LAA) corrects them back towards, and occasionally even beyond, the LDA. This behavior illustrates the importance of compatible correlation.

We now turn to tests of the strong surface effects manifest in calculations of the monovacancy formation enthalpy, \( H_{\text{F}}^{V} \), where \( E_{\text{F}}^{V} \) and \( E \) are total energies for the system with and without a vacancy, and \( N \) is the number of atoms in the fully populated supercell. Monovacancy energies are calculated using 64-atom cells. The vacancy cell is geometrically relaxed, and both vacancy and bulk cells are volume relaxed. The number of \( k \) points used is 4 for Pt, 6 for Al, and 3 for Si. The Si calculations are for the \( T_d \) structure. For Pt and Si the supercells are too small for the results to be directly compared to experiment but are sufficient to allow for comparison between functionals. Strong surface effects are seen for Al and Pt, but not in Si. This is seen by the widely different results between functionals for the metals. Similar to the bulk properties, our surface correlation corrects LAG results in the right direction, but it is apparent that it is still too crude to give truly quantitative results. The surprisingly good LDA result for Al might draw some attention, but as has been pointed out before, it is not reflected in any other property of Al and is thus coincidental.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PW91</th>
<th>PBE</th>
<th>LAG</th>
<th>LDA-LAG</th>
<th>LDA-LAA</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt a</td>
<td>3.90</td>
<td>3.99</td>
<td>3.99</td>
<td>3.96</td>
<td>3.93</td>
<td>3.94</td>
<td>3.92</td>
</tr>
<tr>
<td>Al b</td>
<td>3.96</td>
<td>4.05</td>
<td>4.05</td>
<td>4.02</td>
<td>4.01</td>
<td>4.02</td>
<td>4.03</td>
</tr>
<tr>
<td>Si c</td>
<td>5.38</td>
<td>5.46</td>
<td>5.47</td>
<td>5.44</td>
<td>5.42</td>
<td>5.43</td>
<td>5.43</td>
</tr>
<tr>
<td>Pt d</td>
<td>−0.5%</td>
<td>+1.8%</td>
<td>+1.8%</td>
<td>+1.0%</td>
<td>+0.3%</td>
<td>+0.5%</td>
<td></td>
</tr>
<tr>
<td>Al e</td>
<td>−1.7%</td>
<td>+0.5%</td>
<td>+0.5%</td>
<td>−0.2%</td>
<td>−0.5%</td>
<td>−0.2%</td>
<td></td>
</tr>
<tr>
<td>Si f</td>
<td>−0.9%</td>
<td>+0.6%</td>
<td>+0.7%</td>
<td>+0.2%</td>
<td>−0.2%</td>
<td>0.0%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
<td>0.5%</td>
<td>0.3%</td>
<td>0.2%</td>
<td></td>
</tr>
<tr>
<td>( \sigma )</td>
<td>0.50</td>
<td>0.59</td>
<td>0.57</td>
<td>0.38</td>
<td>0.12</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Pt a</td>
<td>312</td>
<td>252</td>
<td>254</td>
<td>272</td>
<td>294</td>
<td>291</td>
<td>283</td>
</tr>
<tr>
<td>Al b</td>
<td>81.7</td>
<td>72.6</td>
<td>74.9</td>
<td>76.8</td>
<td>82.1</td>
<td>81.7</td>
<td>77.3</td>
</tr>
<tr>
<td>Si c</td>
<td>95.1</td>
<td>87.5</td>
<td>86.8</td>
<td>88.7</td>
<td>91.5</td>
<td>90.5</td>
<td>98.8</td>
</tr>
<tr>
<td>Pt d</td>
<td>+10.2%</td>
<td>−11.0%</td>
<td>−10.2%</td>
<td>−3.9%</td>
<td>+3.9%</td>
<td>+2.8%</td>
<td></td>
</tr>
<tr>
<td>Al e</td>
<td>+5.7%</td>
<td>−6.1%</td>
<td>−3.1%</td>
<td>−0.6%</td>
<td>+6.2%</td>
<td>+5.7%</td>
<td></td>
</tr>
<tr>
<td>Si f</td>
<td>−3.7%</td>
<td>−11.4%</td>
<td>−12.1%</td>
<td>−10.2%</td>
<td>−7.4%</td>
<td>−8.4%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.5%</td>
<td>9.5%</td>
<td>8.5%</td>
<td>4.9%</td>
<td>5.8%</td>
<td>5.6%</td>
<td></td>
</tr>
<tr>
<td>( \sigma )</td>
<td>2.7</td>
<td>2.4</td>
<td>3.9</td>
<td>4.0</td>
<td>1.5</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

\( H_{\text{F}}^{V} \) in [eV]

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PW91</th>
<th>PBE</th>
<th>LAG</th>
<th>LDA-LAG</th>
<th>LDA-LAA</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt a</td>
<td>0.91</td>
<td>0.64</td>
<td>0.72</td>
<td>0.73</td>
<td>1.00</td>
<td>0.99</td>
<td>(1.35)</td>
</tr>
<tr>
<td>Al b</td>
<td>0.67</td>
<td>0.53</td>
<td>0.61</td>
<td>0.59</td>
<td>0.83</td>
<td>0.84</td>
<td>0.68</td>
</tr>
<tr>
<td>Si c</td>
<td>3.58</td>
<td>3.68</td>
<td>3.65</td>
<td>3.69</td>
<td>3.57</td>
<td>3.59</td>
<td>(3.6)</td>
</tr>
<tr>
<td></td>
<td>3.43.92</td>
<td>355.94</td>
<td>354.18</td>
<td>345.76</td>
<td>344.33</td>
<td>344.35</td>
<td></td>
</tr>
<tr>
<td>Al d</td>
<td>17.48</td>
<td>18.55</td>
<td>18.43</td>
<td>17.76</td>
<td>17.57</td>
<td>17.59</td>
<td></td>
</tr>
<tr>
<td>Si e</td>
<td>19.60</td>
<td>20.78</td>
<td>20.65</td>
<td>19.90</td>
<td>19.69</td>
<td>19.72</td>
<td></td>
</tr>
</tbody>
</table>

\( \sigma \) is defined in the text. LDA-LAG(LAA) are not fitted to any values shown in this table, but to jellium surface energies.
The unexpected discrepancy between PW91 and PBE monovacancy energies will be addressed in another publication.\textsuperscript{24}

We examine only solid-state systems; we do not assess performance for atoms and molecules. However, a hint is provided by the atomic XC energies given from the all-electron calculations used for constructing PP’s (cf. Table II). The present functionals give results close to the LDA, with a slight adjustment towards the PBE. For atoms, the PBE is expected to be more accurate than the LDA.\textsuperscript{4}

IV. CONCLUSIONS

In conclusion, we have presented two promising functionals for use in DFT calculations. The method of their construction is generic and could potentially be used with any local approximation to \( \hat{e}_a \) in the interior region. The locality criteria precludes using, e.g., the PBE for this region,\textsuperscript{8} and the effect of a localized equivalent cannot be inferred from GGA results. We are working on a gradient-corrected interior functional and an improved surface correlation. The two varieties of edge treatment, LAG and LAA, behave similarly but we recommend the LAA based on its better behavior far outside the edge.

ACKNOWLEDGMENTS

We are grateful to Thomas R. Mattsson and Peter A. Schultz for valuable help with the electronic structure calculations. R.A. was funded by the project ATOMICS at the Swedish research council SSF. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.