

The AM05 functional: Important formulas and background information for implementing AM05 into DFT codes.

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Abstract

We present formulas and background information aiming at facilitating the implementation of AM05[1] into Density Functional Theory[2] (DFT) codes of various types. We specifically consider three different schemes for calculating the exchange-correlation potential: The White and Bird scheme[3] used in many plane wave codes; the Pople, Gill, and Johnson scheme[4] used in many Quantum Chemistry codes; and the 'traditional' scheme used in many all-electron codes. Fortran subroutines that can be modified to fit a specific code are available.[5]

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The exchange-correlation energy is

$$E_{xc} = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r})) , \quad (1)$$

where $n(\mathbf{r})$ is the density at \mathbf{r} , $d\mathbf{r} = dr_x dr_y dr_z$ the volume element, and $\epsilon_{xc} = \epsilon_x + \epsilon_c$ is the exchange-correlation energy per particle, which for AM05 is given by Eq. (12) in Ref. 1. ϵ_{xc} is generally a functional of the density, $\epsilon_{xc} = \epsilon_{xc}[n(\mathbf{r})]$. We here restrict ourselves to the case where the functional dependency is only through the density and gradients of the density since this is the case for AM05 (and for most generalized gradient approximation (GGA) type functionals).

It is straightforward to implement the AM05 exchange-correlation energy directly from the article (Ref. [1]), the only minor obstacle being the need for a subroutine for calculating the Lambert W function. At the AM05 web site [5] a subroutine for calculating the AM05 exchange-correlation energy is provided (including subroutines for the required Lambert W function and the LDA correlation in the parametrization of Perdew and Wang[6, 7]).

The exchange-correlation potential, the functional derivative of the exchange-correlation energy with respect to density,

$$V_{xc} = \frac{\delta E_{xc}}{\delta n} , \quad (2)$$

is needed in self-consistent DFT calculations and we will now describe the most common schemes for obtaining this potential.

To simplify the equations we use the quantity $f_{xc} = n \epsilon_{xc}$ thus having

$$E_{xc} = \int d\mathbf{r} f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r})) , \quad (3)$$

The exchange-correlation potential for the exchange-correlation energy in Eq. (3) is

$$V_{xc}(\mathbf{r}) = \frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial n(\mathbf{r})} - \nabla \cdot \frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \nabla n(\mathbf{r})} . \quad (4)$$

The first term in this potential is straightforward to obtain but the second term can be treated in several ways. In the traditional scheme this term is expanded until derivatives of the density and derivatives of f_{xc} are separated. This means that for a given density the full V_{xc} can be calculated within the functional routine. In contrast, the White and Bird, and Pople, Gill, and Johnson schemes only partially expand this term and V_{xc} needs to be assembled in a routine outside of the functional subroutine.

Let us focus on the second term in Eq. (4) for the moment. It is a scalar product between two vector quantities, ∇ and $\frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \nabla n(\mathbf{r})}$. In a plane wave basis the second term is readily Fourier transformed:

$$\nabla \cdot \frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \nabla n(\mathbf{r})} = \frac{1}{N} \sum_{\mathbf{G}, \mathbf{r}'} i\mathbf{G} \cdot \frac{\partial f_{xc}(n(\mathbf{r}'), \nabla n(\mathbf{r}'))}{\partial \nabla n(\mathbf{r}')} e^{i\mathbf{G} \cdot (\mathbf{r} - \mathbf{r}')} , \quad (5)$$

this is the White and Bird scheme[3].

In Quantum Chemistry codes using finite basis sets ϕ_μ ($\mu = 1, \dots, N$), the Fock matrices are the needed objects and via integration by parts one obtains:

$$- \int \nabla \cdot \frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \nabla n(\mathbf{r})} \phi_\mu \phi_\nu d\mathbf{r} = \int \frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \nabla n(\mathbf{r})} \cdot \nabla (\phi_\mu \phi_\nu) d\mathbf{r} , \quad (6)$$

this is the Pople, Gill, and Johnson scheme[4].

It is obvious that since the two terms in Eq. (4) are not treated in the same way in the White and Bird, and the Pople, Gill, and Johnson schemes, the exchange-correlation potential (or Fock matrices) needs to be assembled outside of a functional subroutine and that the functional subroutine instead of the full V_{xc} needs to output $\frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial n(\mathbf{r})}$ and $\frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \nabla n(\mathbf{r})}$.

However, $\frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \nabla n(\mathbf{r})}$ is a vector which implies that three scalar quantities need to be calculated. Due to the fact that GGA type functionals for symmetry reasons only depend on the gradient of the density through its absolute value, $|\nabla n(\mathbf{r})|$, it is customary to instead only output a scalar obtained from further manipulation of this term. One can show that

$$\frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \nabla n(\mathbf{r})} = 2 \frac{\partial f_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|^2)}{\partial |\nabla n(\mathbf{r})|^2} \nabla n(\mathbf{r}) \quad (7)$$

$$= \frac{\partial f_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)}{\partial |\nabla n(\mathbf{r})|} \frac{\nabla n(\mathbf{r})}{|\nabla n(\mathbf{r})|} , \quad (8)$$

where the first equality (Eq. (7)) gives the quantity that is usually seen in the Pople, Gill, and Johnson scheme and the second equality (Eq. (8)) is seen in the White and Bird scheme.

$\frac{\nabla n(\mathbf{r})}{|\nabla n(\mathbf{r})|}$ is a unit vector that is well defined even when $|\nabla n(\mathbf{r})| \rightarrow 0$, and this factor can easily be handled elsewhere in the code and the scalar quantity $\frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial |\nabla n(\mathbf{r})|}$ be given out from the functional subroutine. However, apart from that the vector $\nabla n(\mathbf{r})$ is handled outside of the functional routine there is no consensus between different codes about exactly which quantity is needed and care needs to be taken in order to make sure that the right quantity is given out from the functional subroutine.

This same output can also be used in calculations of the stress tensor:

$$\begin{aligned} \sigma_{\alpha\beta} = & \delta_{\alpha\beta} E_{xc}[n(\mathbf{r})] + \int d\mathbf{r} V_{xc}(\mathbf{r}) \left. \frac{\partial n(\hat{\varepsilon}, \mathbf{r})}{\partial \varepsilon_{\alpha\beta}} \right|_{\hat{\varepsilon}=0} \\ & - \int d\mathbf{r} \frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \left(\frac{\partial n(\mathbf{r})}{\partial r_\beta} \right)} \frac{\partial n(\mathbf{r})}{\partial r_\alpha}. \end{aligned} \quad (9)$$

The first two terms in this expression are handled as in any LDA calculation, only replacing E_{xc} and V_{xc} with the the corresponding GGA quantities. They will not be further discussed here. The third term is a GGA correction and it can easily be shown that

$$\frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \left(\frac{\partial n(\mathbf{r})}{\partial r_\beta} \right)} \frac{\partial n(\mathbf{r})}{\partial r_\alpha} = \frac{\partial f_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)}{\partial |\nabla n(\mathbf{r})|} \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial n(\mathbf{r})}{\partial r_\beta} \frac{\partial n(\mathbf{r})}{\partial r_\alpha}, \quad (10)$$

and we recognize the same derivative of f_{xc} as appears in Eq. (8).

In the traditional scheme the second term in Eq. (4) is further expanded using Eq. (8):

$$\nabla \cdot \frac{\partial f_{xc}(n, \nabla n)}{\partial \nabla n} = \nabla \cdot \left(\frac{\nabla n}{|\nabla n|} \frac{\partial f_{xc}(n, |\nabla n|)}{\partial |\nabla n|} \right) \quad (11)$$

$$= \left(\nabla \cdot \frac{\nabla n}{|\nabla n|} \right) \frac{\partial f_{xc}(n, |\nabla n|)}{\partial |\nabla n|} + \frac{\nabla n}{|\nabla n|} \cdot \left(\nabla \frac{\partial f_{xc}(n, |\nabla n|)}{\partial |\nabla n|} \right) \quad (12)$$

$$\begin{aligned} &= \left(\frac{\nabla^2 n}{|\nabla n|} - \frac{\nabla n \cdot \nabla |\nabla n|}{|\nabla n|^2} \right) \frac{\partial f_{xc}(n, |\nabla n|)}{\partial |\nabla n|} + \\ &+ \frac{\nabla n}{|\nabla n|} \cdot \left(\nabla n \frac{\partial^2 f_{xc}(n, |\nabla n|)}{\partial n \partial |\nabla n|} + \nabla |\nabla n| \frac{\partial^2 f_{xc}(n, |\nabla n|)}{\partial |\nabla n|^2} \right) \end{aligned} \quad (13)$$

$$\begin{aligned} &= \nabla^2 n \left(\frac{1}{|\nabla n|} \frac{\partial f_{xc}(n, |\nabla n|)}{\partial |\nabla n|} \right) + |\nabla n| \frac{\partial^2 f_{xc}(n, |\nabla n|)}{\partial n \partial |\nabla n|} + \\ &+ \nabla n \cdot \nabla |\nabla n| \frac{\partial}{\partial |\nabla n|} \left(\frac{1}{|\nabla n|} \frac{\partial f_{xc}(n, |\nabla n|)}{\partial |\nabla n|} \right) \end{aligned} \quad (14)$$

where $n = n(\mathbf{r})$ for clarity. We notice that derivatives of the functional and derivatives of the density are no longer intermingled but separated and if the density derivatives $\nabla^2 n$ and $\nabla n \cdot \nabla |\nabla n|$ are handed in to a functional routine in addition to the already required n and $|\nabla n|$, the full exchange-correlation potential can be assembled. Note that even if the quantity $\nabla n \cdot \nabla |\nabla n|$ looks complicated it is easily shown that

$$\nabla n \cdot \nabla |\nabla n| = \frac{1}{|\nabla n|} \sum_{i=1}^3 \sum_{j=1}^3 \frac{\partial n}{\partial r_i} \frac{\partial n}{\partial r_j} \frac{\partial^2 n}{\partial r_i \partial r_j}, \quad (15)$$

where $r_1 = r_x$, $r_2 = r_y$, and $r_3 = r_z$.

Everything we have been discussing so far in this text is general for all functionals depending on the density only via $n(\mathbf{r})$ and $|\nabla n(\mathbf{r})|$. We will now go into more details specific to the AM05 functional.

It follows from Eq. (12) in Ref. 1 that the AM05 functional can be written as

$$f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r})) = f_x^{\text{LDA}}(n(\mathbf{r})) H_x(s(n(\mathbf{r}), |\nabla n(\mathbf{r})|)) + f_c^{\text{LDA}}(n(\mathbf{r})) H_c(s(n(\mathbf{r}), |\nabla n(\mathbf{r})|)), \quad (16)$$

where s is the dimensionless scaled gradient

$$s(n(\mathbf{r}), |\nabla n(\mathbf{r})|) = \frac{|\nabla n(\mathbf{r})|}{2 k_F(n(\mathbf{r})) n(\mathbf{r})} \quad k_F(n(\mathbf{r})) = (3 \pi^2 n(\mathbf{r}))^{\frac{1}{3}}. \quad (17)$$

We see that $f_{xc}(n, \nabla n) = f_x(n, s) + f_c(n, s)$ and that the separate exchange and correlation both have the form $f(n, s) = f^{\text{LDA}}(n)H(s)$. Using that for an arbitrary function $g(s)$

$$\frac{\partial g(s)}{\partial n} = \frac{\partial s}{\partial n} \frac{\partial g(s)}{\partial s} = -\frac{4}{3} \frac{s}{n} \frac{\partial g(s)}{\partial s} \quad (18)$$

$$\frac{\partial g(s)}{\partial |\nabla n|} = \frac{\partial s}{\partial |\nabla n|} \frac{\partial g(s)}{\partial s} = \frac{1}{2 k_F n} \frac{\partial g(s)}{\partial s} \quad (19)$$

we obtain

$$\begin{aligned} \frac{\partial f(n, s)}{\partial n} &= \frac{\partial f^{\text{LDA}}(n)}{\partial n} H(s) - f^{\text{LDA}}(n) \frac{4}{3} \frac{s}{n} \frac{\partial H(s)}{\partial s} \\ &= v^{\text{LDA}}(n) H(s) - \frac{4}{3} \epsilon^{\text{LDA}}(n) s \frac{\partial H(s)}{\partial s} \end{aligned} \quad (20)$$

and

$$\begin{aligned} \frac{\partial f(n, s)}{\partial |\nabla n|} &= f^{\text{LDA}}(n) \frac{1}{2 k_F n} \frac{\partial H(s)}{\partial s} \\ &= \frac{\epsilon^{\text{LDA}}(n)}{2 k_F} \frac{\partial H(s)}{\partial s}, \end{aligned} \quad (21)$$

where $v^{\text{LDA}}(n)$ is the LDA exchange or correlation potential and $\epsilon^{\text{LDA}}(n)$ is the LDA exchange or correlation energy per particle. These are the two quantities needed for each of correlation and exchange, $\frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial n} = \frac{\partial f_x(n, s)}{\partial n} + \frac{\partial f_c(n, s)}{\partial n}$ and $\frac{\partial f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial |\nabla n|} = \frac{\partial f_x(n, s)}{\partial |\nabla n|} + \frac{\partial f_c(n, s)}{\partial |\nabla n|}$, in the White and Bird and the Pople, Gill, and Johnson schemes for constructing the exchange-correlation potential outside of the functional subroutine (see, however, the note below Eqns (7) and (8)).

In the traditional scheme it is customary to use, in addition to s , two other dimensionless derivatives of the density:

$$t = \frac{\nabla^2 n}{(2 k_F)^2 n} \quad \text{and} \quad u = \frac{\nabla n \cdot \nabla |\nabla n|}{(2 k_F)^3 n^2}. \quad (22)$$

Using these quantities and Eqns (20) and (21), we obtain from Eq. (14):

$$\begin{aligned} \nabla \cdot \frac{\partial f(n, s)}{\partial \nabla n} &= t \epsilon^{\text{LDA}}(n) \frac{1}{s} \frac{\partial H(s)}{\partial s} + v^{\text{LDA}}(n) s \frac{\partial H(s)}{\partial s} - \frac{4}{3} \epsilon^{\text{LDA}}(n) s \frac{\partial}{\partial s} \left(s \frac{\partial H(s)}{\partial s} \right) + \\ &+ u \epsilon^{\text{LDA}}(n) \frac{\partial}{\partial s} \left(\frac{1}{s} \frac{\partial H(s)}{\partial s} \right) \end{aligned} \quad (23)$$

In order to reduce the number of different derivatives of $H(s)$, we use that

$$\begin{aligned} s \frac{\partial}{\partial s} \left(s \frac{\partial H(s)}{\partial s} \right) - s \frac{\partial H(s)}{\partial s} &= s^2 \frac{\partial^2 H(s)}{\partial s^2} \\ &= s^3 \frac{\partial}{\partial s} \left(\frac{1}{s} \frac{\partial H(s)}{\partial s} \right) + s \frac{\partial H(s)}{\partial s} \end{aligned} \quad (24)$$

and arrive at the final form of the separate exchange and correlation parts of the exchange-correlation potential, $V_{xc} = V_x + V_c$:

$$\begin{aligned} V &= v^{\text{LDA}}(n) \left(H(s) - s \frac{\partial H(s)}{\partial s} \right) + \\ &+ \epsilon^{\text{LDA}}(n) \left(\left(\frac{4}{3} s^2 - t \right) \frac{1}{s} \frac{\partial H(s)}{\partial s} + \left(\frac{4}{3} s^3 - u \right) \frac{\partial}{\partial s} \left(\frac{1}{s} \frac{\partial H(s)}{\partial s} \right) \right). \end{aligned} \quad (25)$$

The Fortran routine available at the AM05 web page [5] consists of several subroutines. The goal has been to provide a stand-alone AM05 subroutine that does not need to be manipulated at all, but all necessary modifications for adaptation to a specific code should be done in one of several provided template subroutines. The template routines assemble the required input to, and modifies the obtained output from, the AM05 subroutine. The three template routines provided are examples of adaptations to codes using the White and Bird scheme, the Pople, Gill, and Johnson scheme, and the traditional scheme, respectively. Once AM05 has been implemented and tested in this way, subroutines used inside the AM05 subroutine, such as the LDA exchange and correlation routines, can be replaced with routines already in the code.

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