v_θ^{GGA}, the Functional Derivative of a GGA Pauli Term T_θ

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Discard all previous versions.

Consider the decomposition of the Kohn-Sham kinetic energy $T_s = T_W + T_\theta$. T_θ is the "Pauli term". Suppose T_θ to be of GGA form

$$\begin{aligned} T_\theta^{GGA} &= \int d\mathbf{r}' t_\theta[n(\mathbf{r}'),\, \nabla_{\mathbf{r}'} n] \\ &= \int d\mathbf{r}' t_0[n(\mathbf{r}')] F_\theta[s(\mathbf{r}')] \end{aligned} \tag{1}$$

with

$$t_0[n(\mathbf{r})] = c_0 n^{5/3}(\mathbf{r}) \tag{2}$$

and the Thomas-Fermi constant is $c_0 = \frac{3}{10}(3\pi^2)^{2/3}$. The inhomogeneity function is

$$s(\mathbf{r}) = \kappa \frac{|\nabla n|}{n^{4/3}} \tag{3}$$

with $\kappa = 1/\{2(3\pi^2)^{1/3}\}$.

To find the Pauli potential,

$$v_\theta^{GGA} = \frac{\delta T_\theta^{GGA}}{\delta n} \tag{4}$$

requires working out the details of the Gelfand-Fomin relationship

$$\frac{\delta T_\theta^{GGA}}{\delta n(\mathbf{r})} = \frac{\partial t_\theta[n(\mathbf{r}), \nabla n_r(\mathbf{r})]}{\partial n(\mathbf{r})} - \nabla_r \cdot \frac{\partial t_\theta[n(\mathbf{r}), \nabla_r n(\mathbf{r})]}{\partial(\nabla_r n(\mathbf{r}))} \tag{5}$$

Various required pieces are as follows.

$$\begin{aligned} \frac{\partial t_\theta}{\partial n} &= \frac{\partial t_0}{\partial n} + t_0 \frac{\partial F_\theta}{\partial n} \\ &= \frac{5}{3} c_0 n^{2/3} F_\theta + c_0 n^{5/3} \frac{\partial F_\theta}{\partial s} \frac{\partial s}{\partial n} \end{aligned} \tag{6}$$

$$\begin{aligned} \nabla \cdot \frac{\partial t_\theta}{\partial \nabla n} &= \nabla \cdot \left[c_0 n^{5/3} \frac{\partial F_\theta}{\partial \nabla n} \right] \\ &= \frac{5}{3} c_0 n^{2/3} \nabla n \cdot \frac{\partial F_\theta}{\partial \nabla n} + c_0 N^{5/3} \nabla \cdot \frac{\partial F_\theta}{\partial \nabla n} \end{aligned} \tag{7}$$

However

$$\frac{\partial F_\theta}{\partial \nabla n} = \frac{\partial F_\theta}{\partial s}\frac{\partial s}{\partial \nabla n} \tag{8}$$

so

$$\begin{aligned} \nabla \cdot \frac{\partial F_\theta}{\partial \nabla n} &= \nabla \frac{\partial F_\theta}{\partial s} \cdot \frac{\partial s}{\partial \nabla n} + \frac{\partial F_\theta}{\partial s} \nabla \cdot \frac{\partial s}{\partial \nabla n} \\ &= \frac{\partial^2 F_\theta}{\partial s^2}\left(\nabla s \cdot \frac{\partial s}{\partial \nabla n}\right) + \frac{\partial F_\theta}{\partial s}\nabla \cdot \frac{\partial s}{\partial \nabla n} \end{aligned} \tag{9}$$

Insert eqs. 9, 7, and 6 in eq. 5 to get

$$\begin{aligned} v_\theta^{GGA} &= \frac{5}{3}c_0 n^{2/3} F_\theta + c_0 n^{5/3}\frac{\partial F_\theta}{\partial s}\frac{\partial s}{\partial n} - \frac{5}{3}c_0 n^{2/3}\nabla n \cdot \frac{\partial F_\theta}{\partial s}\frac{\partial s}{\partial \nabla n} \\ &\quad - c_) n^{5/3}\left[\frac{\partial^2 F_\theta}{\partial s^2}\left(\nabla s \cdot \frac{\partial s}{\partial \nabla n}\right) + \frac{\partial F_\theta}{\partial s}\nabla \cdot \frac{\partial s}{\partial \nabla n}\right] \end{aligned} \tag{10}$$

or

$$\begin{aligned} v_\theta^{GGA} &= \frac{5}{3}c_0 n^{2/3} F_\theta + c_0 n^{5/3}\frac{\partial F_\theta}{\partial s}\left[\frac{\partial s}{\partial n} - \frac{5}{3}\frac{1}{n}\nabla n \cdot \frac{\partial s}{\partial \nabla n} - \nabla \cdot \frac{\partial s}{\partial \nabla n}\right] \\ &\quad - c_0 n^{5/3}\frac{\partial^2 F_\theta}{\partial s^2}\left(\nabla s \cdot \frac{\partial s}{\partial \nabla n}\right) \end{aligned} \tag{11}$$

Eq. 11 is the same as eq. (38) in draft D of the VVK *et al.* "signpost" paper and corrects eq. (34) of Karasiev, Trickey, and Harris, J. Computer-Aided Mat. Des. **13**, 111 (2006).

Harris, in notes "Functional derivative formulas", 16 Nov. 2007, went about the derivation by using s^2 (recall eq. 3 above). He then simplified by working out some of the details in the equation equivalent to my eq. 11. Working out the equivalence of the two expressions follows.

$$\frac{\partial s}{\partial n} = -\frac{4}{3}\kappa\frac{\nabla n}{n^{7/3}} = -\frac{4}{3}\frac{s}{n} \tag{12}$$

$$\frac{\partial s}{\partial \nabla n} = \frac{\partial}{\partial \nabla n}\left(\frac{\kappa^2 \nabla n \cdot \nabla n}{n^{8/3}}\right)^{1/2} = \frac{\kappa \nabla n}{n^{4/3}|\nabla n|} = \frac{\mathbf{s}}{|\nabla n|} \tag{13}$$

Note that this last result defines the **s** *vector.* (Harris does not use this quantity.) Thus

$$\nabla n \cdot \frac{\partial s}{\partial \nabla n} = \frac{\kappa \nabla n \cdot \nabla n}{n^{4/3}|\nabla n|} = \frac{\kappa|\nabla n|}{n^{4/3}} = s \tag{14}$$

Next

$$\nabla \cdot \frac{\partial s}{\partial \nabla n} = \frac{\nabla \cdot \mathbf{s}}{|\nabla n|} + \mathbf{s} \cdot \nabla \frac{1}{|\nabla n|} = \frac{\kappa \nabla^2 n}{n^{4/3}|\nabla n|} - \frac{4s}{3n} - \mathbf{s} \cdot \frac{(\nabla|\nabla n|)}{|\nabla n|^2} \tag{15}$$

Now evaluate

$$\nabla s = \nabla\left[\kappa\frac{|\nabla n|}{n^{4/3}}\right] = \frac{\kappa \nabla|\nabla n|}{n^{4/3}} - \frac{4}{3}\kappa\frac{|\nabla n|\nabla n}{n^{7/3}} \tag{16}$$

whence

$$\nabla s \cdot \frac{\partial s}{\partial \nabla n} = \frac{\kappa(\nabla|\nabla n|)\cdot s}{n^{4/3}|\nabla n|} - \frac{4}{3}\frac{s^2}{n} \tag{17}$$

With substitution of these results, eq. 11 becomes

$$\begin{aligned}
v_\theta^{GGA} &= \frac{5}{3}c_0 n^{2/3} F_\theta + c_0 n^{5/3}\frac{\partial F_\theta}{\partial s}\left[-\frac{4}{3}\frac{s}{n} - \frac{5}{3}\frac{s}{n} - \frac{\kappa\nabla^2 n}{n^{4/3}|\nabla n|} + \frac{4s}{3n} + \frac{n\,\mathbf{s}\cdot(\nabla|\nabla n|)}{|\nabla n|^2}\right] \\
&\quad - c_0 n^{5/3}\frac{\partial^2 F_\theta}{\partial s^2}\left[\frac{\kappa}{n^{4/3}|\nabla n|}(\nabla|\nabla n|)\cdot\mathbf{s} - \frac{4}{3}\frac{s^2}{n}\right] \\
&= c_0 n^{2/3}\left\{\frac{5}{3}F_\theta - \left[\frac{\kappa\nabla^2 n}{n^{1/3}|\nabla n|} + \frac{5s}{3} - \frac{\mathbf{s}\cdot(\nabla|\nabla n|)}{|\nabla n|^2}\right]\frac{\partial F_\theta}{\partial s}\right. \\
&\quad \left. - \left[\frac{\kappa}{n^{1/3}|\nabla n|}(\nabla|\nabla n|)\cdot\mathbf{s} - \frac{4}{3}s^2\right]\frac{\partial^2 F_\theta}{\partial s^2}\right\}
\end{aligned} \tag{18}$$

Next, I rewrite in the variables Harris uses by working out his coefficients in terms of s rather than s^2. Harris gets

$$v_{\theta,FEH}^{GGA}(s^2) = c_0 n^{2/3}\left\{\frac{5}{3}F_\theta(s^2) + C_{FEH}^{(1)}\frac{\partial F_\theta}{\partial(s^2)} + C_{FEH}^{(2)}\frac{\partial^2 F_\theta}{\partial(s^2)^2}\right\} \tag{19}$$

with (subscript FEH for Harris)

$$\begin{aligned}
C_{FEH}^{(1)} &= = -\frac{2}{3}s^2 - 2p \\
C_{FEH}^{(2)} &= \frac{16}{3}s^4 - 4q
\end{aligned} \tag{20}$$

where the latter coefficient corrects a sign error in Harris' notes. Here κ is inverse of Harris' k and

$$\begin{aligned}
p :&= \frac{\kappa^2\nabla^2 n}{n^{5/3}} \\
q :&= \frac{\kappa^4(\nabla n\cdot\nabla\nabla n\cdot\nabla n)}{n^{13/3}}
\end{aligned} \tag{21}$$

Because

$$\begin{aligned}
\frac{\partial F_\theta}{\partial(s^2)} &= \frac{1}{2s}\frac{\partial F_\theta}{\partial(s)} \\
\frac{\partial^2 F_\theta}{\partial(s^2)^2} &= \frac{1}{2s}\frac{\partial}{\partial s}\left(\frac{1}{2s}\frac{\partial F_\theta}{\partial s}\right) = -\frac{1}{4s^3}\frac{\partial F_\theta}{\partial s} + \frac{1}{4s^2}\frac{\partial^2 F_\theta}{\partial s^2}
\end{aligned} \tag{22}$$

the coefficients in Harris' expression rearrange to

$$\begin{aligned}
v_{\theta,FEH}^{GGA}(s) &= c_0 n^{2/3}\left\{\frac{5}{3}F_\theta(s) + \left(\frac{C_{FEH}^{(1)}}{2s} - \frac{C_{FEH}^{(2)}}{4s^3}\right)\frac{\partial F_\theta}{\partial(s)} + \frac{C_{FEH}^{(2)}}{4s^2}\frac{\partial^2 F_\theta}{\partial s^2}\right\} \\
&:= c_0 n^{2/3}\left\{\frac{5}{3}F_\theta(s) + c^{(1)}\frac{\partial F_\theta}{\partial s} + c^{(2)}\frac{\partial^2 F_\theta}{\partial s^2}\right\}
\end{aligned} \tag{23}$$

Upon substitution

$$c^{(1)} = -\frac{5s}{3} - \frac{p}{s} + \frac{q}{s^3} = -\left[\frac{\kappa\nabla^2 n}{n^{1/3}|\nabla n|} + \frac{5s}{3} - \frac{\kappa(\nabla n\cdot\nabla\nabla n\cdot\nabla n)}{n^{1/3}|\nabla n|^3}\right] \tag{24}$$

Straightforwardly

$$\nabla|\nabla n| = \nabla(\nabla n\cdot\nabla n)^{1/2} = \frac{\nabla n\cdot\nabla\nabla n}{|\nabla n|} \tag{25}$$

so

$$\frac{\kappa(\nabla n\cdot\nabla\nabla n\cdot\nabla n)}{n^{1/3}|\nabla n|^3} = \frac{n\mathbf{s}\cdot(\nabla|\nabla n|)}{|\nabla n|^2} \tag{26}$$

and therefore

$$c^{(1)} = -\left[\frac{\kappa\nabla^2 n}{n^{1/3}|\nabla n|} + \frac{5s}{3} - \frac{n\mathbf{s}\cdot(\nabla|\nabla n|)}{|\nabla n|^2}\right] \tag{27}$$

which is the same coefficient as in Eq. (18)

Again, after substitution

$$c^{(2)} = \frac{4s^2}{3} - \frac{q}{s^2} = \frac{4s^2}{3} - \frac{n^{8/3}}{\kappa^2|\nabla n|^2}\frac{\kappa(\nabla n\cdot\nabla\nabla n\cdot\nabla n)}{n^{13/3}} = \frac{4s^2}{3} - \frac{\kappa}{n^{1/3}|\nabla n|}\mathbf{s}\cdot(\nabla|\nabla n|) \tag{28}$$

which also matches with Eq. (18).

Therefore an economical way of writing v_θ^{GGA} in terms of s and Harris' other variables is

$$v_\theta^{GGA}(s) = c_0 n^{2/3}\left\{\frac{5}{3}F_\theta(s) - \left[\frac{5s}{3} + \frac{p}{s} - \frac{q}{s^3}\right]\frac{\partial F_\theta}{\partial s} + \left[\frac{4s^2}{3} - \frac{q}{s^2}\right]\frac{\partial^2 F_\theta}{\partial s^2}\right\} \tag{29}$$