Notes on GGA

General Equations:
\[ E_{xc} = \int d^3rf(n(r),|\nabla n(r)|). \]  \( \tag{1} \)
\[ v_{xc}(r) = \frac{\partial f(n,|\nabla n|)}{\partial n} - \nabla \cdot \left( \frac{\partial f(n,|\nabla n|)}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|} \right). \]  \( \tag{2} \)

Using FFT's –
\[ n(r) = \sum_G \tilde{n}(G)e^{iG\cdot r}. \]  \( \tag{3} \)
\[ |\nabla n(r)| = \left[ \left| \sum_G G_x \tilde{n}(G)e^{iG\cdot r} \right|^2 + \left| \sum_G G_y \tilde{n}(G)e^{iG\cdot r} \right|^2 + \left| \sum_G G_z \tilde{n}(G)e^{iG\cdot r} \right|^2 \right]^{1/2}. \]  \( \tag{4} \)

Algorithm to calculate \( v_{xc} \) for smooth pseudofunctions using 3 large work arrays of size of FFT grid:

1. \( W_1 = n(r) \Leftarrow \text{FFT}[\tilde{n}(G)] \)
2. \( W_2 = 0 \)
3. \( \text{Do } i = x,y,z \)
   \[ W_3 = \nabla_i n(r)/i \Leftarrow \text{FFT}[G_i \tilde{n}(G)] \] (FFT #1,2,3)
   \[ W_2 = W_2 + |W_3|^2 \]
   \text{Enddo}
4. \( W_2 = |\nabla n(r)| \Leftarrow \sqrt{W_2} \)
5. Accumulate \( E_{xc} \) from \( W_1 \) (\( n(r) \)) and \( W_2 \) (\( |\nabla n(r)| \))
6. Similarly, use \( W_1 \) and \( W_2 \) on each grid point to replace \( W_1 = \frac{\partial E_{xc}}{\partial n} \) and \( W_2 = \frac{\partial E_{xc}}{\partial |\nabla n| |\nabla n|}. \)
7. \( \tilde{W}_1(G) \Leftarrow \text{FFT}^{-1}[W_1(r)] \) (FFT # 4)
8. \( \text{Do } i = x,y,z \)
   \[ W_3 = \nabla_i n(r)/i \Leftarrow \text{FFT}[G_i \tilde{n}(G)] \] (FFT # 5,6,7 or could store and retrieve from first evaluation of same quantities)
   \[ W_3 \Leftarrow W_3 \cdot W_2 \] (\( W_3 \) now contains \( \frac{\partial E_{xc}}{\partial |\nabla n| |\nabla n|}(r)/i. \))
   \[ \tilde{W}_3(G) \Leftarrow \text{FFT}^{-1}[\tilde{W}_3(r)] \] (FFT # 8,9,10)
   \[ \tilde{W}_1(G) = \tilde{W}_1(G) + G_i \tilde{W}_3(G) \]
   \text{Enddo}
9. \( W_1(G) \) now contains \( v_{xc}(G) \).
This performs 10 FFT's with 3 large arrays or could perform 7 FFT's with 6 large arrays.

Evaluation of $v_{xc}$ contributions to atom-centered terms: In general, the matrix elements have the form:

$$M_{xc} \equiv \langle \phi_i^n | v_{xc} [n_{\text{core}} + n^0] | \phi_j^n \rangle - \langle \tilde{\phi}_i^n | v_{xc} [\tilde{n}^0] | \phi_j^n \rangle$$  

(5)

According to Eq. 2, the gradient contribution to $v_{xc}$ involves the divergence of the function

$$g_{xc} \equiv \frac{\partial f(n, |\nabla n|)}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|}.$$  

(6)

Suppressing some of the extraneous notation, consider a term of the form

$$M'_{xc} \equiv \int d^3 r \phi_i^s(r) \phi_j(r) \nabla \cdot g_{xc}(n, |\nabla n|).$$  

(7)

Using the divergence theorem and the fact that the boundary terms cancel for the complete matrix element of $M_{xc}$,

$$M'_{xc} = -\int d^3 r \nabla \left( \phi_i^s(r) \phi_j(r) \right) \cdot g_{xc}(n, |\nabla n|).$$  

(8)

This could be conveniently evaluated in spherical polar coordinates:

$$\nabla b = \hat{r} \frac{\partial b}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial b}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial b}{\partial \phi}$$  

(9)

Derivatives of angular terms can be expressed in terms of derivatives of spherical harmonics and probably can best be done analytically. For example, writing $\phi_i(r) \equiv \frac{\phi_{n_i \ell_i}(r)}{r} Y_{\ell_i m_i}(\hat{r})$, one term of the matrix element can be written:

$$\langle \phi_i | v_{xc} [n] | \phi_j \rangle = \int d\Omega Y^*_{\ell_i m_i} Y_{\ell_j m_j} \int dr \left\{ \frac{\partial f}{\partial n} \left( \frac{\phi_{n_i \ell_i} \phi_{n_j \ell_j}}{r^2} \right) \frac{\partial f}{\partial |\nabla n|} \frac{\partial n_j/\partial r}{|\nabla n|} \right\}$$  

(10)

$$+ \int d\Omega \frac{\partial}{\partial \theta} \left( \frac{Y_{\ell_i m_i} Y_{\ell_j m_j}}{\sin \theta} \right) \int dr \left\{ \left( \frac{\phi_{n_i \ell_i} \phi_{n_j \ell_j}}{r^2} \right) \frac{\partial f}{\partial |\nabla n|} \frac{\partial n_j/\partial \theta}{|\nabla n|} \right\}$$  

$$+ \int d\Omega \frac{\partial}{\sin \theta} \left( \frac{Y_{\ell_i m_i} Y_{\ell_j m_j}}{\theta} \right) \int dr \left\{ \left( \frac{\phi_{n_i \ell_i} \phi_{n_j \ell_j}}{r^2} \right) \frac{\partial f}{\partial |\nabla n|} \frac{\partial n_j/\partial \phi}{|\nabla n|} \right\}$$