Notes on GGA

9/1/04 NAWH

General Equations:

$$E_{xc} = \int d^3 r f(n(\mathbf{r}), |\nabla n(\mathbf{r})|). \quad (1)$$

$$v_{xc}(\mathbf{r}) = \frac{\partial f(n, |\nabla n|)}{\partial n} - \nabla \cdot \left(\frac{\partial f(n, |\nabla n|)}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|} \right). \quad (2)$$

Using FFT's –

$$n(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}. \quad (3)$$

$$|\nabla n(\mathbf{r})| = \left[|\sum_{\mathbf{G}} G_x \tilde{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}|^2 + |\sum_{\mathbf{G}} G_y \tilde{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}|^2 + |\sum_{\mathbf{G}} G_z \tilde{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}|^2 \right]^{1/2}. \quad (4)$$

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

1. $W_1 = n(\mathbf{r}) \Leftarrow \mathrm{FFT}[\tilde{n}(\mathbf{G})]$
2. $W_2 = 0$
3.

   Do $i = x, y, z$

   $W_3 = \nabla_i n(\mathbf{r})/i \Leftarrow \mathrm{FFT}[G_i \tilde{n}(\mathbf{G})]$ (FFT #1,2,3)
   $W_2 = W_2 + |W_3|^2$

   Enddo
4. $W_2 = |\nabla n(\mathbf{r})| \Leftarrow \sqrt{W_2}$
5. Accumulate E_{xc} from W_1 $(n(\mathbf{r}))$ and W_2 $(|\nabla n(\mathbf{r})|)$
6. Similarly, use W_1 and W_2 on each grid point to replace $W_1 = \frac{\partial f_{xc}}{\partial n}$ and $W_2 = \frac{\partial f_{xc}}{\partial |\nabla n|} \frac{1}{|\nabla n|}$.
7. $\tilde{W}_1(\mathbf{G}) \Leftarrow \mathrm{FFT}^{-1}[W_1(\mathbf{r})]$ (FFT # 4)
8.

   Do $i = x, y, z$

   $W_3 = \nabla_i n(\mathbf{r})/i \Leftarrow \mathrm{FFT}[G_i \tilde{n}(\mathbf{G})]$ (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 $\frac{\partial f_{xc}}{\partial |\nabla n|} \frac{\nabla_i n}{|\nabla n|}(\mathbf{r})/i$.)
   $\tilde{W}_3(\mathbf{G}) \Leftarrow \mathrm{FFT}^{-1}[\tilde{W}_3(\mathbf{r})]$ (FFT # 8,9,10)
   $\tilde{W}_1(\mathbf{G}) = \tilde{W}_1(\mathbf{G}) + G_i \tilde{W}_3(\mathbf{G})$

   Enddo

9. $W_1(\mathbf{G})$ now contains $v_{xc}(\mathbf{G})$.

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:

$$M_{xc} \equiv \langle \phi_i^a | v_{xc}[n_{\text{core}} + n^a] | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | v_{xc}[\tilde{n}^a] | \tilde{\phi}_j^a \rangle \tag{5}$$

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

$$\mathbf{g}_{xc} \equiv \frac{\partial f(n, |\nabla n|)}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|}. \tag{6}$$

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

$$M'_{xc} \equiv \int d^3r \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \nabla \cdot \mathbf{g}_{xc}(n, |\nabla n|). \tag{7}$$

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

$$M'_{xc} = - \int d^3r \nabla \left(\phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \right) \cdot \mathbf{g}_{xc}(n, |\nabla n|). \tag{8}$$

This could be conveniently evaluated in spherical polar coordinates:

$$\nabla b = \hat{\mathbf{r}} \frac{\partial b}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial b}{\partial \theta} + \hat{\phi} \frac{1}{r \sin\theta} \frac{\partial b}{\partial \phi} \tag{9}$$

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

$$\begin{aligned} \langle \phi_i | v_{xc}[n] | \phi_j \rangle = & \int d\Omega Y^*_{l_i m_i} Y_{l_j m_j} \int r^2 \, dr \left\{ \left(\frac{\phi_{n_i l_i} \phi_{n_j l_j}}{r^2} \right) \frac{\partial f}{\partial n} + \frac{\partial}{\partial r} \left(\frac{\phi_{n_i l_i} \phi_{n_j l_j}}{r^2} \right) \frac{\partial f}{\partial |\nabla n|} \frac{\partial n / \partial r}{|\nabla n|} \right\} \\ + & \int d\Omega \frac{\partial \left(Y^*_{l_i m_i} Y_{l_j m_j} \right)}{\partial \theta} \int dr \left\{ \left(\frac{\phi_{n_i l_i} \phi_{n_j l_j}}{r^2} \right) \frac{\partial f}{\partial |\nabla n|} \frac{\partial n / \partial \theta}{|\nabla n|} \right\} \\ + & \int d\Omega \frac{\partial \left(Y^*_{l_i m_i} Y_{l_j m_j} \right)}{\sin\theta \partial \phi} \int dr \left\{ \left(\frac{\phi_{n_i l_i} \phi_{n_j l_j}}{r^2} \right) \frac{\partial f}{\partial |\nabla n|} \frac{\partial n / \sin\theta \partial \phi}{|\nabla n|} \right\} \end{aligned} \tag{10}$$

Specific equations for PBE form[1, 2, 3, 4, 5]

Case with no spin polarization

For this case, the functional takes the form:

$$f(n(\mathbf{r}), |\nabla n(\mathbf{r})|) = n(\mathbf{r}) \left\{ \varepsilon_x(r_s, 0) F(s) + \varepsilon_c(r_s, 0) + H(t, r_s, 0) \right\}. \tag{11}$$

Here,

$$\varepsilon_x(r_s, 0) \equiv - \frac{3e^2}{4\pi} (3\pi^2 n)^{1/3}. \tag{12}$$

The exchange gradient term depends on

$$s \equiv= \frac{|\nabla n|}{2nk_F} = \frac{|\nabla n|}{2(3\pi^2 n^4)^{1/3}} \quad \text{since} \quad k_F = (3\pi^2 n)^{1/3}, \tag{13}$$

according to

$$F(s) = 1 + \kappa - \frac{\kappa}{(1 + \mu s^2/\kappa)}. \tag{14}$$

Here $\kappa = 0.804$ and $\mu = 0.2195149727645171$.

The Wigner-Seitz radius parameter is given by

$$r_s \equiv \left(\frac{3}{4\pi n}\right)^{1/3}. \tag{15}$$

The correlation is given as defined in Ref. ([5]):

$$\varepsilon_c(r_s, 0) = -2\frac{e^2}{a_0} A'(1 + \alpha_1 r_s) \ln\left[1 + \frac{1}{2A'(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)}\right]. \tag{16}$$

Here the constant values are given (in Hartree energy units) as follows. (A' is used to distinguish a different "$A(r_s)$" term used in the correlation expression below.)

$$\begin{aligned}
A' &= 0.0310906908696548950 \\
\alpha_1 &= 0.21370 \\
\beta_1 &= 7.5957 \\
\beta_2 &= 3.5876 \\
\beta_3 &= 1.6382 \\
\beta_4 &= 0.49294
\end{aligned}$$

The correlation gradient term depends on

$$t \equiv \frac{|\nabla n|}{2nk_s}, \quad \text{with} \quad k_s \equiv \sqrt{\frac{4}{\pi a_0}} (3\pi^2 n)^{1/6}. \tag{17}$$

a_0 denotes the bohr radius. The correlation gradient functional is given by

$$H \equiv \frac{e^2}{a_0} \gamma \ln\left\{1 + \frac{\beta}{\gamma} t^2 \left[\frac{1 + At^2}{1 + At^2 + A^2 t^4}\right]\right\}, \tag{18}$$

where this A function takes the form

$$A \equiv A(\varepsilon_c(r_s, 0)) = \frac{\beta}{\gamma} \frac{1}{\mathrm{e}^{-\Delta} - 1}, \quad \text{where} \quad \Delta = \frac{\varepsilon_c(r_s, 0)}{\gamma e^2/a_0}. \tag{19}$$

The constants are given by $\beta = 0.06672455060314922$ and $\gamma = \frac{1-\ln 2}{\pi^2} = 0.0310906908696548950 3$.

The derivative terms take the form:

$$\frac{\partial f(n, |\nabla n|)}{\partial n} = \frac{\partial f_x(n, |\nabla n|)}{\partial n} + \varepsilon_c(r_s, 0) + H(r_s, t, 0) - \frac{r_s}{3} \frac{\partial \varepsilon_c(r_s, 0)}{\partial r_s} \left(1 + \frac{\partial H}{\partial e_c}\right) - \frac{7t}{6} \frac{\partial H(r_s, t, 0)}{\partial t}, \tag{20}$$

where the exchange contribution is given by

$$\frac{\partial f_x(n,|\nabla n|)}{\partial n} = -\frac{e^2}{\pi}(3\pi^2 n)^{1/3}\left(F(s) - \frac{dF(s)}{ds}s\right), \tag{21}$$

where the last term becomes

$$\left(F(s) - \frac{dF(s)}{ds}s\right) = 1+\kappa - \frac{\kappa + 3\mu s^2}{(1+\mu s^2/\kappa)^2}, \quad \text{since} \quad \frac{dF(s)}{ds} = \frac{2\mu s}{(1+\mu s^2/\kappa)^2}. \tag{22}$$

The derivative of $\varepsilon_c(r_s, 0)$ is given, following Perdew and Wang[5]:

$$\frac{\partial \varepsilon_c(r_s,0)}{\partial r_s} = -\frac{e^2}{a_0}\left(2A'\alpha_1 \ln(1+1/Q_1) + \frac{Q_0 Q_1'}{Q_1(Q_1+1)}\right), \tag{23}$$

where

$$Q_0 \equiv -2A'(1+\alpha_1 r_s), \tag{24}$$

$$Q_1 \equiv 2A'(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2), \tag{25}$$

and

$$Q_1' \equiv A'(\beta_1 r_s^{-1/2} + 2\beta_2 + 3\beta_3 r_s^{1/2} + 4\beta_4 r_s). \tag{26}$$

The gradient correlation terms take the form

$$\frac{\partial H}{\partial e_c} = \frac{\partial H}{\partial A}\frac{\partial A}{\partial e_c}, \tag{27}$$

which take the form

$$\frac{\partial A}{\partial e_c} = \frac{A^2 \mathrm{e}^{-\Delta}}{\beta e^2/a_0}, \tag{28}$$

and

$$\frac{\partial H}{\partial A} = -\frac{e^2}{a_0}\frac{(2+At^2)At^6\beta\gamma}{[\gamma P + \beta(t^2 + At^4)]P}, \tag{29}$$

with

$$P \equiv 1 + At^2 + A^2 t^4. \tag{30}$$

Finally, the gradient correlation terms take the form:

$$\frac{\partial H}{\partial t} = \frac{e^2}{a_0}\frac{2t\beta\gamma(1+2At^2)}{[\gamma P + \beta(t^2+At^4)]P}. \tag{31}$$

The terms involving derivatives with respect to the magnitude of the gradient can also be evaluated using

$$\mathbf{g}_{xc}(n,|\nabla n|) \equiv h_{xc}(n,|\nabla n|)\nabla n, \quad \text{where} \quad h_{xc}(n,|\nabla n|) \equiv \frac{\partial f(n,|\nabla n|)}{\partial|\nabla n|}\frac{1}{|\nabla n|}. \tag{32}$$

$$h_{xc}(n,|\nabla n|) = \left(-\frac{3e^2}{8\pi}\frac{dF(s)}{ds} + \frac{1}{2k_s}\frac{\partial H}{\partial t}\right)\frac{1}{|\nabla n|}. \tag{33}$$

Some of the above expressions must be evaluated with care. For example, since the computer evaluates $1+\epsilon = 1$ when $\epsilon < 10^{-14}$, or so (less than the machine precision), we define a function

$$\text{Logofterm(x)} = \begin{cases} \ln(1+x) & \text{for} \quad x > \epsilon \\ x & \text{for} \quad x \le \epsilon. \end{cases} \tag{34}$$

In addition, the expression for $A(\varepsilon_c(r_s,0))$ is evaluated using the function

$$\text{Aofec(ec)} = \begin{cases} \frac{\beta}{\gamma}\frac{1}{\mathrm{e}^{-\Delta}-1} & \text{for} \quad \varepsilon_c > \epsilon \\ -\frac{\beta}{\varepsilon_c/(e^2/a_0)} & \text{for} \quad \varepsilon_c \le \epsilon. \end{cases} \tag{35}$$

References

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