summary of LDA

Assumption : electron density of inhomogenoues system is locally homogenous.The exchange-correlation energy is thus given by:

$$E_{xc} = \int \rho(\mathbf{r})\epsilon_{xc}^{h}(\rho(\mathbf{r}))d\mathbf{r} \tag{1}$$

with,

$$\epsilon_{xc}^{h}(\rho(\mathbf{r})) = \int \frac{\rho_{xc}(\mathbf{r},\mathbf{r'})}{|\mathbf{r}\text{-}\mathbf{r'}|} d\mathbf{r'} \tag{2}$$

we define :

$$\rho_{xc}^{h}(\mathbf{r},\mathbf{r'}) = \rho_{x}^{h}(\mathbf{r},\mathbf{r'}) + \rho_{c}^{h}(\mathbf{r},\mathbf{r'}) \tag{3}$$

with $\rho_{x}^{h}(\mathbf{r},\mathbf{r'}) \leqslant 0$ and the following sum rules are satisfied:

$$\int \rho_{x}^{h}(\mathbf{r},\mathbf{r'}) = -1 \tag{4}$$

$$\int \rho_{c}^{h}(\mathbf{r},\mathbf{r'}) = 0 \tag{5}$$

Expectations (Where is the LDA supposed to work)

(a) Homogenous

(b) Slightly inhomogenous

Reality of the situation

Figure: Large gradients in density

Gradient expansion (Ma and Brueckner, 1968)

Idea:

1. Divergence from uniformity of the electron density is due to perturbation to the system
2. Perturb the homogenous system with little distortions in the potential.
3. Attempt a solution by taylor expansion of density around the homogenous electron density

So we can try:

$$\rho^{inh}(\mathbf{r}) \to \rho^{h}(\mathbf{r}) \left[1 + \frac{\nabla \rho^{h}(\mathbf{r'})}{\rho^{h}(\mathbf{r})} \rho^{h}(\mathbf{r'}) \Big|_{\mathbf{r'}=\mathbf{r}} + \ldots \right] \tag{6}$$

and so we may write:

$$\epsilon_{xc}^{GE}(\rho(\mathbf{r})) \to \epsilon_{xc}^{h}(\rho(\mathbf{r})) \left[1 + A \frac{\nabla \rho^{h}(\mathbf{r'})}{\rho^{h}(\mathbf{r})} + \ldots \right] \tag{7}$$

Let's digress a bit - Scaling relations

Lets define a dialted density with $\lambda \in \mathbb{R}$

$$\rho_\lambda(x, y, z) = \lambda^3 \rho(\lambda x, \lambda y, \lambda z) \tag{8}$$

we can see that:

$$\begin{aligned}
\int_{-\infty}^{\infty} \rho_\lambda(x, y, z) dx\, dy\, dz &= \int_{-\infty}^{\infty} \lambda^3 \rho(\lambda x, \lambda y, \lambda z) dx\, dy\, dz \\
&= \int_{-\infty}^{\infty} \rho(\lambda x, \lambda y, \lambda z) d(\lambda x)\, d(\lambda y)\, d(\lambda z) \\
&= \int_{-\infty}^{\infty} \rho_(x', y', z') dx'\, dy'\, dz' \\
&= N
\end{aligned} \tag{9}$$

Some notations

With $\Phi_n \to Kohn - sham$ and $\Psi_n \to Real$ ground state wavefunction's of the system we have:

$$T_s[\rho] = \langle \Phi_n | \hat{T} | \Phi_n \rangle \tag{10}$$

$$E_x[\rho] = \langle \Phi_n | \hat{V}_{ee} | \Phi_n \rangle - E_{Hartree}[\rho] \tag{11}$$

$$T_c[\rho] = \langle \Psi_n | \hat{T} | \Psi_n \rangle - \langle \Phi_n | \hat{T} | \Phi_n \rangle \geqslant 0 \tag{12}$$

$$U_c[\rho] = \langle \Psi_n | \hat{V}_{ee} | \Psi_n \rangle - \langle \Phi_n | \hat{V}_{ee} | \Phi_n \rangle \leqslant 0 \tag{13}$$

Now,

$$\begin{aligned} E_c[\rho] &= T_c[\rho] + U_c[\rho] \\ &= \langle \Psi_n | \hat{V}_{ee} | \Psi_n \rangle - \langle \Phi_n | \hat{V}_{ee} | \Phi_n \rangle \leqslant 0 \end{aligned} \tag{14}$$

So we must have:

$$|U_c[\rho]| > |E_c[\rho]| \tag{15}$$

Scaling relations - Exact constraints

For any functional of ground state density of a system we can prove the following fundamental scaling relations:

$$T_s[\rho_\lambda] = \lambda^2 T_s[\rho] \tag{16}$$

$$E_{Hartree}[\rho_\lambda] = \lambda E_{Hartree}[\rho] \tag{17}$$

$$E_x[\rho_\lambda] = \lambda E_x[\rho] \tag{18}$$

$$E_c[\rho_\lambda] < \lambda^2 T_c[\rho] + \lambda V_c[\rho] \tag{19}$$

GE $\longrightarrow$ That's not good

1. Perturbations are not small $\longrightarrow$ The gradients in densities are large $\longrightarrow$ Taylor series expansion is divergent.
2. Sum rules (4 and 5) are violated
3. Scaling relation (19) is not obeyed
4. E_c is calculated to be positive $\longleftarrow$ The gradient terms in GE improved the hole density closer to electron (small $|\mathbf{r}-\mathbf{r}'|$) and worsen it for large $|\mathbf{r}-\mathbf{r}'|$.

Can we improvise GE?
Idea: Maybe we can try to truncate the series expansion to avoid divergence by forcing the expansion to satisfy the sum rules and exact constraints...

Generalised Gradient approximation - GGA

The earliest were constructed by expansion upto $|\nabla\rho|^2$, keeping ρ_{xc} for small $|\mathbf{r}\text{-}\mathbf{r'}|$ and cutting off ρ_{xc} at large $|\mathbf{r}\text{-}\mathbf{r'}|$ so that it restors the sum rules.

Some of the many attempts are:

1. Langreth and Mehl, 1981
2. Perdew, Wang - PW 1986
3. Becke,Lee,Parr,Yang - BLYP 1988 $\longrightarrow$ Hybrid GGA
4. Perdew, Burke, Erzenhoff - PBE 1996

All of the above attempts approach (7) by applying the exact constraints upto different extents. Let's rewrite (7) as;

$$\epsilon_{xc}^{GGA}[\rho(\mathbf{r})] = \epsilon_{xc}^{LDA}[\rho(\mathbf{r})] + \Delta\epsilon_{xc}[s] \tag{20}$$

where s is the dimensionless quantity,

$$s = \frac{|\nabla\rho(\mathbf{r})|}{\rho^{\frac{4}{3}}(\mathbf{r})} \tag{21}$$

PBE-GGA

Perdew *et al.* took (20) and derived the equation for E_{xc} by subjecting it to sum rules (4-5) and some of the exact constraints (16-19) as:

$$E_{xc}^{GGA} = E_{xc}^{LDA}(\rho)[1 + \mu s^2 + \mathcal{O}(s^4)] \tag{22}$$

In normal GE,

$$\mu^{GE} = 0.1235 \tag{23}$$

In PBE, Perdew *et al.* calculated it to be

$$\mu^{PBE} = 0.2195 \tag{24}$$

Becke *et al.* took a hybrid approach to get the expansion (22) and fitted μ with experimental molecular data (semi-emperical). They got,

$$\mu^{BLYP} = 0.2743 \tag{25}$$

Let's compare $\longrightarrow$ LDA v/s GGA