

Generalised Gradient Approximation

Elious

Lets recap some LDA

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

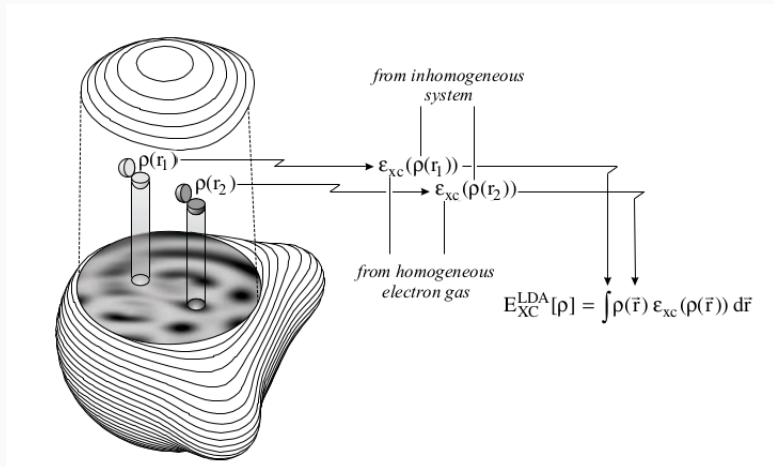
$$E_{xc}^{LDA} = \int \rho(\mathbf{r}) \epsilon_{xc}^h(\rho(\mathbf{r})) d\mathbf{r} \quad (1)$$

and

$$E_{xc}^{LSDA} = \int \rho(\mathbf{r}) \epsilon_{xc}^h(\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})) d\mathbf{r} \quad (2)$$

where $\epsilon_{xc}^h(\rho(\mathbf{r})) \rightarrow$ exchange-correlation energy density at \mathbf{r} , evaluated by taking the E_{xc} of the uniform gas with density $\rho(\mathbf{r})$

Intuition for LDA



Taken from : W.Koch, M.C. Holthausen ,Chemists Guide To DFT

Expectations

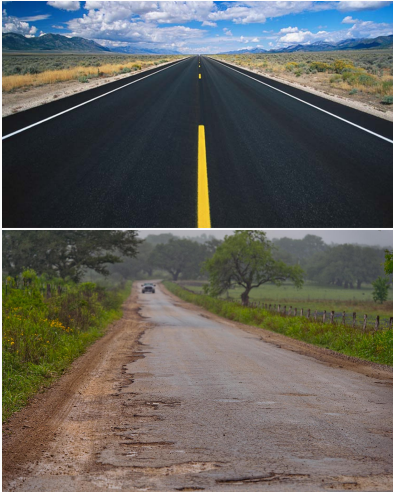


Figure 1: LDA should work fine



Figure 2: LDA should be useless

LDA works considerably well in all the above cases!!!

1. It works nearly perfect for many properties of metals.
2. It even predicts molecular properties like equilibrium structures, charge moments etc.

However, the energy details are not so good for the inhomogeneous systems. Comparing with the experiments, the unsigned standard deviation:

$$\Delta_{LDA} = 36 \text{ Kcal/mol} (1.56 \text{ eV}) \quad (3)$$

$$\Delta_{HF} = 78 \text{ Kcal/mol} (3.38 \text{ eV}) \quad (4)$$

But, Why should the LDA even work at all for the inhomogeneous system???

Lets find some holes in LDA

$$E_{xc}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1) \rho_{xc}(\mathbf{r}_1; \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (5)$$

where

$\rho(\mathbf{r}_1) d\mathbf{r}_1 \rightarrow$ Probability density of finding an electron in $d\mathbf{r}_1$ near \mathbf{r}_1

$\rho_{xc}(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 \rightarrow$ Probability density of finding an electron in $d\mathbf{r}_2$ near \mathbf{r}_2 given there is an electron in $d\mathbf{r}_1$ near \mathbf{r}_1 . This is called the **exchange-correlation hole**. We can show

$$\int \rho_{xc}(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad (6)$$

and

$$\rho_{xc}(\mathbf{r}_1; \mathbf{r}_2) \leq 0 \quad (7)$$

we usually do:

$$\rho_{xc}(\mathbf{r}_1; \mathbf{r}_2) = \rho_x(\mathbf{r}_1, \mathbf{r}_2) + \rho_c(\mathbf{r}_1, \mathbf{r}_2) \quad (8)^{6/100}$$

Pair-correlation factor

The $\rho_{xc}(\mathbf{r}_1; \mathbf{r}_2)$ is factorised as the product:

$$\rho_{xc}(\mathbf{r}_1; \mathbf{r}_2) = \rho(\mathbf{r}_2) f_{xc}(\mathbf{r}_1; \mathbf{r}_2) \quad (9)$$

here

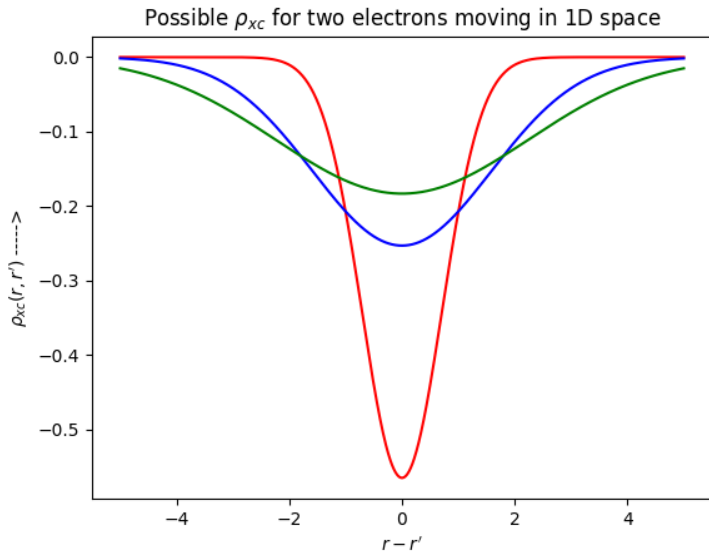
$$-1 \leq f_{xc}(\mathbf{r}_1; \mathbf{r}_2) \leq 0 \quad (10)$$

Combining eqn(?? and ??) we can see that the factorisation is just another way of saying that there is **reduction of electron density** from \mathbf{r}_2 . The factor $f_{xc}(\mathbf{r}_1; \mathbf{r}_2)$ is called the pair-correlation factor.

We should note that:

1. The XC-hole is non-spherical as it depends on $\rho(\mathbf{r}_2)$ which is usually non-uniform.
2. For LDA XC-hole is spherical as $\rho(\mathbf{r}_2)$ is uniform.

Intuition for XC-hole



Exchange hole

Exchange (Fermi) hole : We can show that for the Kohn-sham system $\rho_{xc}(\mathbf{r}_1; \mathbf{r}_2)$ arises due to *Pauli-repulsion* of same spin electrons and from there

$$\rho_x(\mathbf{r}_1; \mathbf{r}_2) \leq 0 \quad (11)$$

and

$$\int \rho_x(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad (12)$$

1. From eqn(??) the hole is negative everywhere \rightarrow an electron of a spin σ won't allow another electron of the same spin to occupy its orbital.
2. Also since its negative everywhere \rightarrow it must be responsible for the self-interaction correction.

Correlation Hole

We are now left with the **Correlation (Coulomb) hole** which mainly arises due to $1/r_{ij}$ nature of the coulomb repulsion

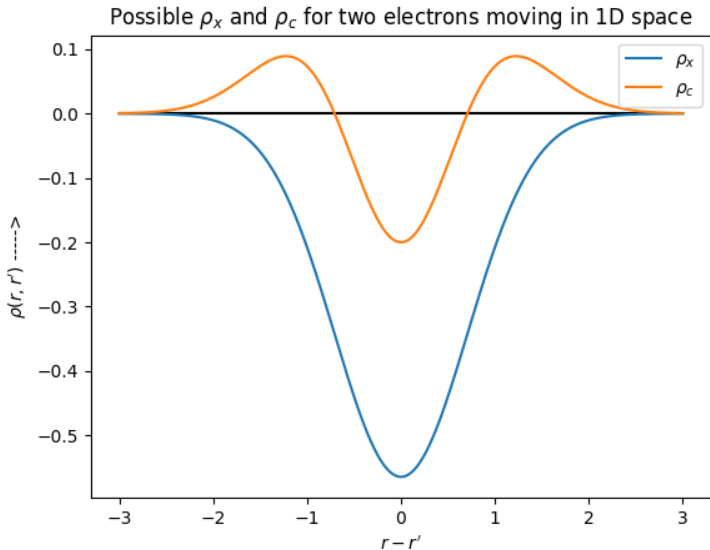
$$\int \rho_c(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 = 0 \quad (13)$$

So it's positive in some regions and negative in some regions thus integrating out to zero...???

We can think of this like

1. Due to $1/r_{ij}$, at the region near any electron, the other electron will be repelled the highest (the hole is negative in this region) and thus it will be sent to a far away region \rightarrow piling up density in other region i.e. the hole is positive in this region.
2. Since this is due to $1/r_{ij}$, ρ_c will also be responsible for the electron-electron cusp in the many-electron wavefunction.

Intuition for X and C-hole



Summary of XC-holes

1. **Exchange hole** : Two electrons of same spin cannot occupy the same room *aka* **Pauli's exclusion Principle**
2. **Correlation hole** : Two electrons can live in the same room but they have to follow social-distancing norms.
3. eqn(??) shows that E_{xc} is actually the energy of attraction of an electron density with its hole \rightarrow the better our model hole represents the exact hole, the better it will represent the E_{xc}

Back to the questions

Question1: Why does LDA perform well even for inhomogeneous densities?

Answer: LDA is for homogeneous electron gas → nicely represents some of the exact properties of holes defined above:

1. The sum rules are satisfied
2. The cusp condition of the correlation is satisfied
3. $n_x(\mathbf{r}_2; \mathbf{r}_1) \leq 0$ everywhere

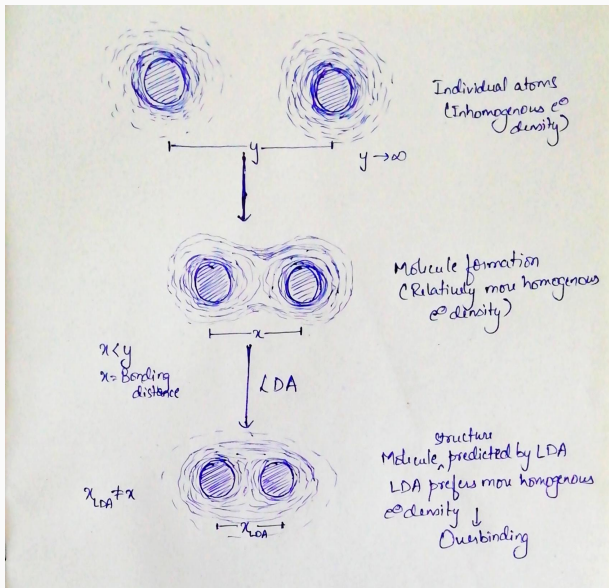
Question2: What is the problem with LDA?

Answer: LDA is for homogeneous electron gas → tends to homogenise the properties for inhomogeneous systems. Eg: It leads to overbinding in molecules.

Overbinding in LDA - A step by step guide

1. Atoms have a highly inhomogeneous electron density
2. Molecules have a relatively more homogeneous electron density compared to atoms as electrons are now more delocalised around two (or more atoms) but still its inhomogeneous
3. LDA best approximates homogeneous electron density
4. LDA tends to homogenise the electron density more in the molecule
5. More bonding character in molecule than should be present
6. Exchange energy of the molecule is too negative →
Overbinding

Overbinding in LDA - the process



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:

$$\rho^{inh}(\mathbf{r}) \rightarrow \rho^h(\mathbf{r}) \left[1 + \nabla \rho^h(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} + \mathcal{O}(\nabla^2 \rho^h(\mathbf{r})) \right] \quad (14)$$

and what's done in GE is:

$$E_{xc}^{GE}(\rho) \rightarrow \int \rho \epsilon_{xc}(\rho) d\mathbf{r} + \int C_{xc} \rho \frac{|\nabla \rho|^2}{\rho^{\frac{4}{3}}} + \dots \quad (15)$$

GE → How good is it?

Expectations: Since it's a Taylor series expansion around uniform density → should perform well for small gradients in density.

Reality: Performance **significantly reduced** compared to LDA

But why?

1. Sum-rules($\text{eqn}(??)$ and $\text{eqn}(??)$) are broken
2. XC-hole is not restricted to be negative for any pair $(\mathbf{r}_1; \mathbf{r}_2)$ which is in strict violation to $\text{eqn}(??)$ and $\text{eqn}(??)$

Due to the breaking of the above universal conditions of exact holes → The relationship between on-top hole and its extension is lost → the E_{xc}^{GE} (which represents the attraction between an electron density and its hole) will now have inconsistent behaviour.

Brute Force method

Idea:

1. Parts in GE which violate $\rho_{xc} \leq 0 \rightarrow$ Just set them to 0
2. To make sure the **sum rules**(eqn(??) and eqn(??)) are obeyed \rightarrow truncate the XC-holes such that h_x and h_c contain 1 and 0 electron charges respectively

So we have

$$E_{xc}^{GE}[\rho] + XC_{properties} \rightarrow E_{xc}^{GGA}[\rho] \quad (16)$$

where E_{xc}^{GGA} is the Generalised Gradient Approximation

$$E_{xc}^{GGA}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}^h(\rho(\mathbf{r})) (1 + \mu s^2 + \mathcal{O}(s^4)) d\mathbf{r} \quad (17)$$

where μ is a parameter and s is the dimensionless quantity:

$$s = \frac{|\nabla \rho(\mathbf{r})|}{\rho^{\frac{4}{3}}(\mathbf{r})} \quad (18)_{18/100}$$

The GGA parameter $\rightarrow \mu$

There are two approaches to calculate the parameter μ :

1. Semi-Emperical: Eq(??) is derived in a way that μ can be extracted by fitting to the experimental data. Eg B88 (by Becke 1988, later additions by Lee, Yang and Parr - BLYP) uses exact exchange energies of rare gas atoms He through Rn, to get

$$\mu^{BLYP} = 0.2743 \quad (19)$$

2. Non-emperical: Eq(??) is rigorously derived by putting more universal constraints. Eg PBE (Perdew, Burke, Ernzerhof 1996) found

$$\mu^{PBE} = 0.2195 \quad (20)$$

Point to be noted \rightarrow GGA's are like "Hit and Trial" and mostly are **NOT** based on any physical model.

LDA v/s GGA → Atomisation energies(in eV)

System	ΔE^{UHF}	ΔE^{LSD}	ΔE^{PW91}	ΔE^{PBE}	ΔE^{expt}
H ₂	84	113	105	105	109
LiH	33	60	53	52	58
CH ₄	328	462	421	420	419
NH ₃	201	337	303	302	297
OH	68	124	110	110	107
H ₂ O	155	267	235	234	232
HF	97	162	143	142	141
Li ₂	3	23	20	19	24
LiF	89	153	137	136	139
Be ₂	-7	13	10	10	3
C ₂ H ₂	294	460	415	415	405
C ₂ H ₄	428	633	573	571	563
HCN	199	361	326	326	312
CO	174	299	269	269	259
N ₂	115	267	242	243	229
NO	53	199	171	172	153
O ₂	33	175	143	144	121
F ₂	-37	78	54	53	39
P ₂	36	142	120	120	117
Cl ₂	17	81	64	63	58
Mean abs. error	71.2	31.4	8.0	7.9	...

Taken from: *GGA made simple*, John P. Perdew, Kieron Burke, Matthias Ernzerhof, Phys. Rev. Lett. 78, 1396 (1997)

References

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5. GGA made simple - John P. Perdew, Kieron Burke, Matthias Ernzerhof,Phys. Rev. Lett. 78, 1396 (1997)