

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:

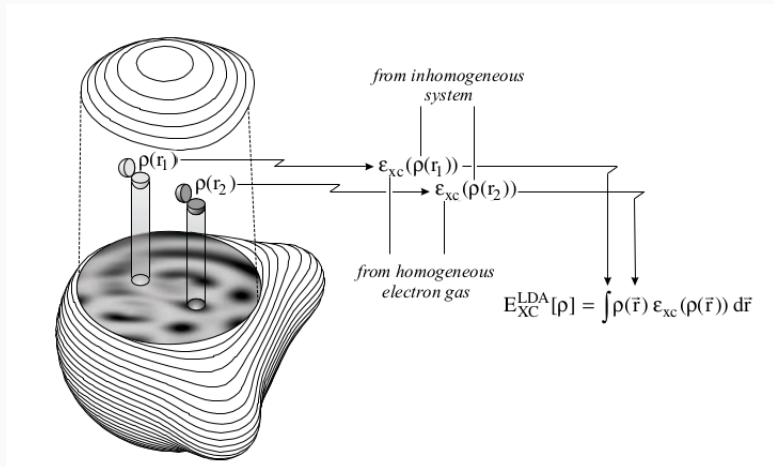
$$E_{xc}^{LDA} = \int \rho(\mathbf{r}) \epsilon_{xc}^h(\rho(\mathbf{r})) d\mathbf{r} \quad (1)$$

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

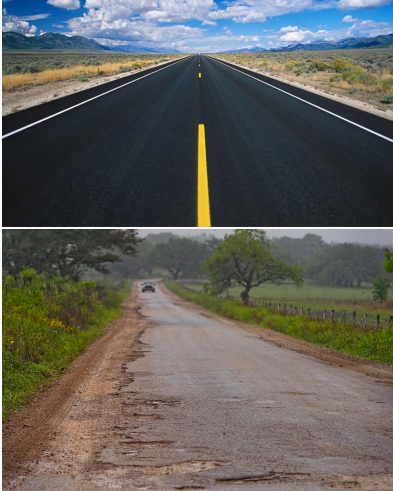


Figure 1: LDA should work fine

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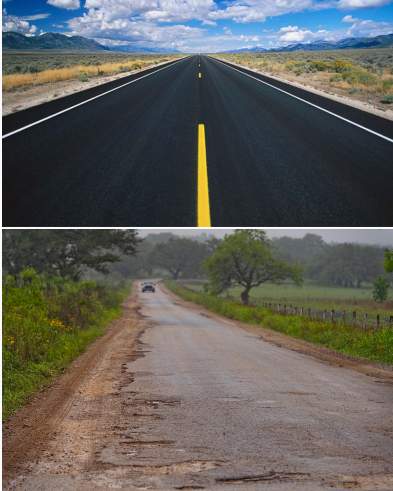


Figure 1: LDA should work fine



Figure 2: LDA should be useless

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

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

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

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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 now define:

$$\rho_{xc}(\mathbf{r}_1; \mathbf{r}_2) = \rho_x(\mathbf{r}_1, \mathbf{r}_2) + \rho_c(\mathbf{r}_1, \mathbf{r}_2) \quad (8) \quad 6/21$$

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(9 and 10) 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.

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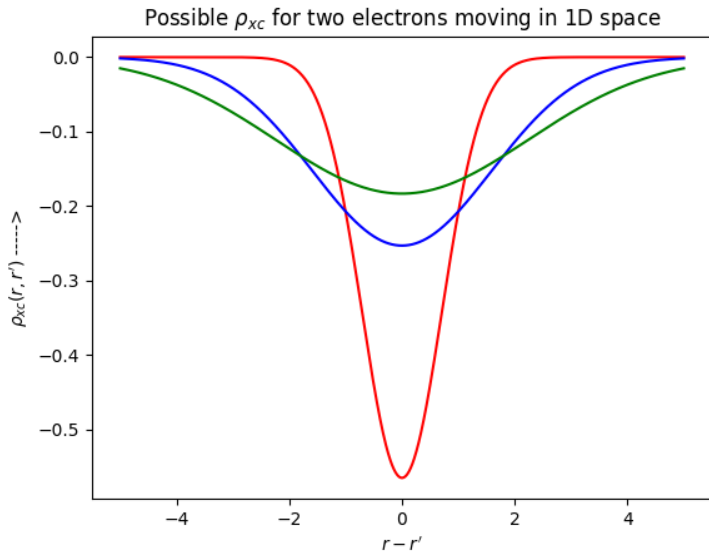
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1. The XC-hole is non-spherical as it depends on $\rho(\mathbf{r}_2)$ which is usually non-uniform.
2. For LDA XC-hole is spherical as $\rho(\mathbf{r}_2)$ is uniform.

Intuition for XC-hole



Exchange hole

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

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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

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

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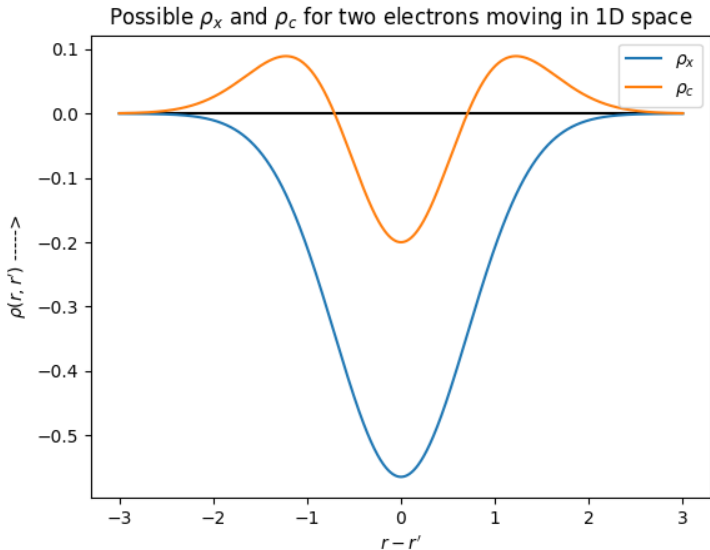
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2. Since this is due to $1/r_{ij}$, ρ_c will also be responsible for the electron-electron cusp in the many-electron wavefunction.

Intuition for X and C-hole



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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

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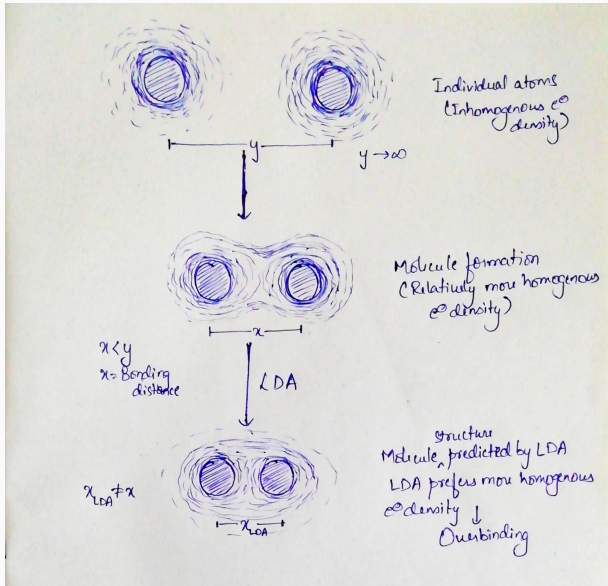
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6. Exchange energy of the molecule is too negative →
Overbinding

Overbinding in LDA - the process



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So we can try:

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

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and what's done in GE is:

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

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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.

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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:

$$s = \frac{|\nabla \rho(\mathbf{r})|}{\rho^{\frac{4}{3}}(\mathbf{r})} \quad (18)_{18/21}$$

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2. Non-emperical: Eq(17) is rigorously derived by putting more universal constraints. Eg PBE (Perdew, Burke, Ernzerhof 1996) found

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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)

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