

CHEM6085: Density Functional Theory

Lecture 9

Exchange-correlation functionals

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Kohn-Sham energy expression

- The energy functional in Kohn-Sham theory is written using the molecular orbitals to express the (non-interacting) kinetic energy

$$\begin{aligned} E[n] &= E_{\text{kin,KS}}[n] + E_{\text{Coul}}[n] + E_{\text{ext}}[n] + (E_{\text{kin}}[n] - E_{\text{kin,KS}}[n]) + E_{\text{xc}}[n] \\ &= 2 \sum_{i=1}^{N_{\text{el}}/2} \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) d\mathbf{r} + E_{\text{Coul}}[n] + E_{\text{ext}}[n] + (E_{\text{kin}}[n] - E_{\text{kin,KS}}[n]) + E_{\text{xc}}[n] \\ &= 2 \sum_{i=1}^{N_{\text{el}}/2} \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) d\mathbf{r} + E_{\text{Coul}}[n] + E_{\text{ext}}[n] + \{E_{\text{kin}}[n] - E_{\text{kin,KS}}[n] + E_{\text{xc}}[n]\} \\ &= 2 \sum_{i=1}^{N_{\text{el}}/2} \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) d\mathbf{r} + E_{\text{Coul}}[n] + E_{\text{ext}}[n] + E'_{\text{xc}}[n] \end{aligned}$$

- Approximations are sought for $E'_{\text{xc}}[n]$, which even though it contains also contributions from the kinetic energy, it is usually just called “Exchange-correlation functional” and written as $E_{\text{xc}}[n]$

Exchange/Correlation energy density

- Exchange and/or correlation functionals are often written in the following form:

$$E_{\text{xc}}[n] = \int n(\mathbf{r}) \epsilon_{\text{xc}}[n(\mathbf{r})] d\mathbf{r}$$

- Where the exchange-correlation energy density

$$\epsilon_{\text{xc}}[n(\mathbf{r})]$$

represents the **energy per electron**

- The density

$$n(\mathbf{r})$$

as usual, represents the number of **electrons per unit volume**

Local Density Approximation (LDA)

- Assume that the exchange-correlation energy density at every position in space for the molecule is the same as it would be for the uniform electron gas (UEG) having the same density as found at that position

$$E_{xc}^{\text{LDA}}[n] = E_x^{\text{LDA}}[n] + E_c^{\text{LDA}}[n]$$

- The expression for the exchange energy is simple

$$E_x^{\text{LDA}}[n] = C \int n^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r}$$

- There are several expressions for the correlation energy $E_c^{\text{LDA}}[n]$ which have been obtained by fitting to the results of accurate QMC calculations of the UEG.
- These expressions are rather complicated and they are usually referred to by their abbreviations such as VWN, VWN5, CAPZ, and others.
- They nevertheless produce very similar results when used in molecular calculations.

Generalised Gradient Approximation (GGA)

- An improvement in the accuracy provided by the LDA can be obtained by Generalised Gradient Approximation (GGA) functionals
- These depend not just on the value of the density at a point (as in the LDA case) but also on its gradient. So we have

$$E_{xc}^{GGA}[n] = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) d\mathbf{r}$$

- Most GGA functionals are constructed in the form of a correction term which is added to the LDA functional

$$\epsilon_{x/c}^{GGA}[n] = \epsilon_{x/c}^{LDA}[n] + \Delta\epsilon_{x/c} \left[\frac{|\nabla n(\mathbf{r})|}{n^{\frac{4}{3}}(\mathbf{r})} \right]$$

Some GGA functionals

- Functionals that contain empirical parameters whose values have been fitted to reproduce experiment or more accurate calculations (“Chemists’ functionals”):
 - Exchange: B (from Becke), CAM, FT97, O, PW, mPW, X
 - Correlation: B88, P86, LYP
- Functionals with no empirically determined parameters (“Physicists’ functionals”)
 - Exchange: B86, LG, P, PBE, mPBE
 - Correlation: PW91

Meta-GGA (MGGA) functionals

- Try to improve accuracy by containing also the Laplacian (second derivative) of the density $\nabla^2 n(\mathbf{r})$

- In practice, they usually include the kinetic energy density instead of the Laplacian because it is numerically more stable

$$\tau(\mathbf{r}) = \sum_{i=1}^{N_{\text{occ}}} \frac{1}{2} |\nabla \psi_i(\mathbf{r})|^2$$

- Available MGGAs include: B95, B98, ISM, KCIS, PKZB, TPSS, VSXC

Hybrid functionals

- Also called Adiabatic Connection Method (ACM) functionals
- They include fractions of exact Hartree-Fock exchange energy, calculated as a functional of the Kohn-Sham molecular orbitals

$$E_{\text{x}}^{\text{HF}}[\{\psi_i\}] = - \sum_{i=1}^{N_{\text{el}}/2} \sum_{j=1}^{N_{\text{el}}/2} \int \int \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

- These have the following general form

$$E_{\text{xc}} = (1 - a)E_{\text{xc}}^{\text{DFT}} + aE_{\text{x}}^{\text{HF}}$$

- One of the most successful (and accurate) examples is the B3LYP 3-parameter functional

$$E_{\text{xc}}^{\text{B3LYP}} = (1 - a)E_{\text{x}}^{\text{LDA}} + aE_{\text{x}}^{\text{HF}} + b\Delta E_{\text{x}}^{\text{B}} + (1 - c)E_{\text{c}}^{\text{LDA}} + cE_{\text{c}}^{\text{LYP}}$$

where $a=0.1161$, $b=0.9262$ and $c=0.8133$

- Other hybrids available: B1PW91, B1LYP, B1B95, mPW1PW91, PBE1PBE

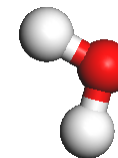
Selecting the “right” functional for your calculation

Quantum Chemistry programs offer a vast number of choices of functionals, and selecting a suitable functional can be a daunting task. To select a functional you should:

- Search the literature for calculations on similar materials and properties (many more properties than just the energy can be computed from DFT)
- Compare your “candidate” functionals by searching in the publications that describe their development for their strengths and weaknesses, especially with respect to the types of calculation you want to run
- Find out how your candidate functionals perform with different basis sets (functionals with empirical parameters sometimes produce better results with “medium” basis sets if they have been parameterised to do so)
- Run some “calibration” calculations on some small molecule similar to the ones you want to study where you can compare the accuracy of possible functionals and basis sets to decide which combination is best for your “production” calculations
- You can even create your own functionals by mixing and matching available exchange and correlation functionals but you should make sure you know what you are doing
- Check, check and check again the literature! Computational simulations of materials consume a lot of computer time. It is a great disappointment if you discover that the calculations you have been running for 6 months are worthless!!!

Example: Geometry optimisation of water

| Method | Bond (Å) | Angle (°) |
|--------------|----------|-----------|
| LDA/STO-3G | 1.031 | 96.74 |
| BLYP/STO-3G | 1.044 | 96.19 |
| PBE/STO-3G | 1.037 | 96.16 |
| TPSS/STO-3G | 1.039 | 96.15 |
| B3LYP/STO-3G | 1.027 | 97.18 |
| Experiment | 0.958 | 104.48 |



| Method | Bond (Å) | Angle (°) |
|-----------------|----------|-----------|
| LDA/6-31++G** | 0.974 | 105.86 |
| BLYP/6-31++G** | 0.976 | 105.00 |
| PBE/6-31++G** | 0.973 | 104.86 |
| TPSS/6-31++G** | 0.972 | 104.96 |
| B3LYP/6-31++G** | 0.965 | 105.71 |
| Experiment | 0.958 | 104.48 |

| Method | Bond (Å) | Angle (°) |
|---------------|----------|-----------|
| LDA/cc-pVTZ | 0.970 | 104.36 |
| BLYP/cc-pVTZ | 0.971 | 103.83 |
| PBE/cc-pVTZ | 0.969 | 103.57 |
| TPSS/cc-pVTZ | 0.968 | 103.73 |
| B3LYP/cc-pVTZ | 0.961 | 104.56 |
| Experiment | 0.958 | 104.48 |

Homework

- 1) For a problem of your interest (e.g. an organic reaction mechanism) which you want to study with DFT, start from the handout with the description of functionals and then review the relevant literature to select the most suitable exchange-correlation functional and basis set. Keep in mind that the computational effort increases at least with the third power of the number of basis functions.
- 2) The density in DFT is expressed in terms of the Kohn-Sham orbitals. GGA functionals use the dimensionless reduced gradient of the density $\frac{|\nabla n(\mathbf{r})|}{n^{\frac{4}{3}}(\mathbf{r})}$. Re-write this in terms of the Kohn-Sham molecular orbitals.
- 3) Derive the expression for the LDA exchange functional from the expression for the Hartree-Fock exchange energy applied to a uniform electron gas (i.e. the density is constant, equal to the same value at each point in space) of non-interacting electrons.

5-minute quiz

Name :
Surname:

Date :

1) What is the difference between GGA and LDA functionals?

2) To what category (GGA, MGGA, etc) does each of LDA, BLYP, PBE, TPSS and B3LYP belongs?

3) Write down the LDA exchange functional in terms of an exchange energy density, i.e. put it in the form

$$E_{xc}[n] = \int n(\mathbf{r})\epsilon_{xc}[n(\mathbf{r})]d\mathbf{r}$$