

# TCC Electronic Structure Module

## L8: Density Functional Approximations

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### Overview

These lectures introduce electronic structure theory. This is an enormous field that has undergone continuous development for near 100 years and the scope of these lectures is necessarily limited. The focus will be on the central theory as applied to molecules. The aim is to introduce you the basics of molecular electronic structure theory, which will help you understand the level of sophistication of calculations you find in the literature, and provide the foundation for further study in the field.

- L1 Exact and inexact wavefunctions
- L2 Hartree–Fock theory
- L3 Configuration Interaction theory
- L4 Møller–Plesset perturbation theory
- L5 Coupled-cluster theory
- L6 Properties and excited states
- L7 Density Functional Theory
- L8 Density Functional Approximations

### Recommended books

- Good introduction to the topic: Frank Jensen, *Introduction to Computational Chemistry* (Wiley, 2007)
- Excellent concise treatise: Szabo and Ostlund, *Modern Quantum Chemistry* (Dover, 1996)
- Comprehensive reference for quantum chemistry methods (excluding DFT): Helgaker, Jørgensen and Olsen, *Molecular Electronic-Structure Theory* (Wiley, 2002)
- Excellent book for many-body correlation: Bartlett and Shavitt, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (CUP, 2009)

# 1 Introduction

Density Functional Theory provides a formally exact framework for computing energies and properties of molecules using the density alone, without reference to the many-body wavefunction. Kohn–Sham theory is a tractable realisation of DFT where the single determinant of a non-interacting system of  $n$  electrons is used to search over  $n$ -representable densities. The computational cost is that of Hartree theory, plus the cost of evaluating the matrix elements over the (unknown) Kohn–Sham potential and evaluating the (unknown) universal density functional. KS-DFT is made practical by the availability of good density functional approximations with functionals and potentials that can be evaluated cheaply. In this lecture we examine the most common density functional approximations.

## 1.1 The exchange-correlation functional

In the Kohn–Sham method we perform a variational search over Kohn–Sham determinants using

$$E_0 = \min_{\Phi_s} \left\{ \langle \Phi_s | \hat{F} | \Phi_s \rangle + E_H[\rho_\Phi] + E_{xc}[\rho_\Phi] \right\} \quad (1)$$

where formally the exchange-correlation energy functional  $E_{xc}[\rho]$  is related to the universal functional through

$$E_{Hxc}[\rho] = F[\rho] - \min_{\Phi_s \rightarrow \rho} \langle \Phi_s | \hat{T} | \Phi_s \rangle - \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} \quad (2)$$

We require good approximations to  $E_{xc}[\rho]$ . This functional is often decomposed into an exchange term and a correlation term

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \quad (3)$$

The exchange functional is defined as

$$E_x[\rho_\Phi] = \langle \Phi | \hat{V}_{ee} | \Phi \rangle - E_H[\rho_\Phi] \quad (4)$$

This contains both the self-interaction correction term and the non-classical exchange contributions. The sum of the kinetic, Hartree and exchange energy functionals gives the energy expectation value of the Kohn–Sham determinant and the definition of the correlation energy functional is therefore

$$E_c[\rho] = \langle \Psi[\rho] | \hat{F} | \Psi[\rho] \rangle - \langle \Phi[\rho] | \hat{F} | \Phi[\rho] \rangle = T_c[\rho] + U_c[\rho] \quad (5)$$

The correlation contribution changes both the kinetic energy and the potential energy and formally decomposes into

$$T_c[\rho] = \langle \Psi[\rho] | \hat{T} | \Psi[\rho] \rangle - \langle \Phi[\rho] | \hat{T} | \Phi[\rho] \rangle \quad (6)$$

$$U_c[\rho] = \langle \Psi[\rho] | \hat{V}_{ee} | \Psi[\rho] \rangle - \langle \Phi[\rho] | \hat{V}_{ee} | \Phi[\rho] \rangle \quad (7)$$

While these formal definitions are cleanly defined, in practice density functional approximations work far better for the sum of the contributions than they do for any of the individual contributions. For example, attempts to fully replace  $E_x[\rho_\Phi]$  with the exchange energy computed from the Kohn–Sham determinant have so far failed to yield accurate density functional approximations.

## 2 Local Functionals

A very simple way to approximate the exchange-correlation functional is to write it as an integral of the density over a local exchange correlation energy that depends on the value of the density at that point. In the local-density approximation (LDA) introduced by Kohn and Sham (1965) the local energy is chosen to be the exchange-correlation energy per particle of the infinite uniform electron gas (UEG) with the density  $\rho$

$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}^{\text{unif}}(\rho(\mathbf{r})) \quad (8)$$

The exchange energy per particle of the UEG can be calculated analytically [Dirac (1930) and Slater (1951)]

$$\epsilon_x^{\text{unif}} = c_x \rho^{1/3} \quad (9)$$

For the correlation energy per particle  $\epsilon_c^{\text{unif}}$  of the UEG, there are some parametrised functions of  $\rho$  fitted to QMC data and imposing the correct analytic form in the high-density (weakly correlated) and low-density (strongly correlated) limits. The two most used parametrizations are VWN (oldest) and PW92 (most accurate). The generalization to spin densities  $\epsilon_c^{\text{unif}}(\rho_\alpha, \rho_\beta)$  is sometimes referred to as local-spin-density (LSD) approximation.

LDA functionals work well for extended systems where the electron density is approximately uniform, but are not accurate for molecular systems. The exchange energy is only about 80% of Hartree–Fock exchange and generally speaking, the LDA correlation energy is too high by a factor of two, which can be understood by considering that the electrons in an infinite UEG have far more freedom to adjust their motion in response to other electrons than electrons that are confined to a small region of space by the nuclear potential.

### Exercise 1

Consider  $\text{H}_2^+$  with at dissociation (infinite bond length).

The electron is in orbital  $\sigma_g = \sqrt{\frac{1}{2}}(1s_A + 1s_B)$  and the density is  $\rho = \frac{1}{2}(\rho_A + \rho_B)$  where  $\rho_A = 1s_A^2$ .

1. Show that the Hartree energy  $E_H[\rho] = \frac{1}{4}(E_H[\rho_A] + E_H[\rho_B])$
2. Show that the LDA exchange energy is  $E_x[\rho] = \left(\frac{1}{2}\right)^{3/4} (E_x^{LDA}[\rho_A] + E_x^{LDA}[\rho_B])$
3. Hence compute the self interaction error

[Hint, for one-electron systems we should have  $E_H[\rho] + E_x[\rho] = 0$  and  $E_c[\rho] = 0$ ]

### Exercise 2

Show that the expression of the LDA exchange potential is

$$v_x^{LDA}(\mathbf{r}) = \frac{\delta E_x^{LDA}[\rho]}{\delta \rho(\mathbf{r})} = \frac{4}{3} c_x \rho(\mathbf{r})^{1/3} \quad (10)$$

Does it satisfy the asymptotic behavior of the exact exchange potential? ( $v_x(\mathbf{r}) \rightarrow -1/r$  as  $r \rightarrow \infty$ )

### 3 Semi Local Functionals

The next logical step beyond the LDA is the gradient-expansion approximation (GEA) which consists in a systematic expansion of  $E_{xc}[\rho]$  in terms of the gradients of  $\rho$ . Here the physical model is a slowly varying non-uniform electron gas. However, in molecules the density changes very rapidly and GEA functionals turn out to be worse than LDA. Rather than using a systematic expansion, information about the rate of change of the density is incorporated into the functional in a more general and less systematic way.

#### 3.1 Generalised Gradient Approximation

The Generalised Gradient Approximation class of functionals have the generic form

$$E_{ex}^{GGA}[\rho] = \int d\mathbf{r} F[\rho, \nabla\rho] \quad (11)$$

GGAs are often called semi local approximations, which means that they involve a single integral over  $\mathbf{r}$  using “semilocal information” through  $\nabla\rho$ . Usually GGAs are expressed in terms of the dimensionless gradient

$$s(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})} \quad (12)$$

A great many GGAs have been proposed and we focus on some of the more important ones.

##### Becke 88 (B88 or B) exchange functional

$$E_x^B[\rho] = E_x^{LDA}[\rho] + \int d\mathbf{r} \rho^{4/3}(\mathbf{r}) f(s(\mathbf{r})) \quad (13)$$

where the function  $f$  is chosen to satisfy the exact asymptotic behavior of the exchange energy per particle in the limit of  $r \rightarrow \infty$ , which is  $\epsilon_x \rightarrow -\frac{1}{2r}$ .

$$f(s(\mathbf{r})) = \frac{\beta s(\mathbf{r})^2}{1 + 6\beta s(\mathbf{r}) \sinh^{-1} s(\mathbf{r})} \quad (14)$$

The parameter  $\beta$  was determined by fitting to HF exchange for rare gas atoms He-Rn.

##### Lee-Yang-Parr (LYP) correlation functional (1988)

This is one of the rare functionals that is not constructed starting from LDA. It originates from the Colle-Salvetti (1975) correlation-energy approximation depending on the curvature of Hartree-Fock hole. It contains four parameters that are determined by fitting to exact properties of helium. LYP introduced a further approximation so that the functional can be computed using only  $\rho$  and  $\nabla\rho$ .

### Perdew-Wang 91 (PW91) exchange-correlation functional

This functional is based on a model of exchange and correlation holes. The exchange energy functional can be expressed as the electrostatic interaction energy between an electron and its exchange hole, and similarly for the correlation hole and the correlation energy functional.

$$E_x[\rho] = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1) h_x(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} = \int d\mathbf{r} \rho(\mathbf{r}_1) \epsilon_x[\rho](\mathbf{r}) \quad (15)$$

$$E_c[\rho] = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1) h_c(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} = \int d\mathbf{r} \rho(\mathbf{r}_1) \epsilon_c[\rho](\mathbf{r}) \quad (16)$$

It starts from the GEA model of these holes and removes the unrealistic long-range parts to restore important conditions satisfied by the LDA. The PW91 functional is a parameterised fit based on numerical evaluation of these holes for a range of  $\rho$  and  $s$ , where the functional form is chosen to recover a number of exact limits.

### Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional (1996)

This is a simplification of the PW91 functional:  $\epsilon_x$  and  $\epsilon_c$  are simpler functions of  $\rho$  and  $s$ , enforcing fewer exact conditions and with no fitted parameters.

### Gradient corrected DFT is useful for chemistry

Molecular structures are more accurate than HF theory and thermochemistry a big improvement over HF theory. Although the errors are still large, trends are often correctly predicted. Serious problems still remain in that reaction barriers are too low, GGAs fail to describe dispersion interactions, fail to bind Rydberg states and fail to describe charge transfer states.

Some important organic bond-lengths in Å [Koch and Holthausen]

molecule	bond	SVWN	BLYP	BPW91	expt
H <sub>2</sub>	H–H	0.765	0.748	0.749	0.741
H <sub>3</sub> C–CH <sub>3</sub>	C–C	1.510	1.542	1.533	1.526
	C–H	1.101	1.100	1.100	1.088
H <sub>2</sub> C=CH <sub>2</sub>	C=C	1.327	1.339	1.336	1.339
	C–H	1.094	1.092	1.092	1.085
HC≡CH	C≡C	1.203	1.209	1.209	1.203
	C–H	1.073	1.068	1.070	1.061
RMS error		0.020	0.009	0.008	—

Mean absolute errors for 44 atomisation energies compared with experiment

method	error/kcal mol <sup>−1</sup>	H <sub>2</sub>	CH <sub>2</sub>	NH <sub>2</sub>	OH	H <sub>2</sub> O	HF	CN	HCN	CH <sub>3</sub> NH <sub>2</sub>	
HF	86	CO	HCO	H <sub>2</sub> CO	CH <sub>3</sub> OH	N <sub>2</sub>	N <sub>2</sub> H <sub>4</sub>	NO	HNO		
SVWN	36	CF	HCF	CH <sub>3</sub> F	O <sub>2</sub>	HO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> S	HCl	HO <sub>2</sub> F	
BP86	13	F <sub>2</sub>	CS	CO <sub>2</sub>	SN	CCl	SO	O <sub>3</sub>	CH <sub>3</sub> Cl	SF	ClO
BLYP	8	HOCl	OCS	S <sub>2</sub>	SO <sub>2</sub>	SCl	ClO <sub>2</sub>	Cl <sub>2</sub>	CS <sub>2</sub>		

### 3.2 Meta GGAs

The Meta Generalised Gradient Approximation class of functionals have the generic form

$$E_{ex}^{GGA}[\rho] = \int d\mathbf{r} F[\rho, \nabla\rho, \nabla^2\rho, \tau] \quad (17)$$

where  $\tau(\mathbf{r})$  is the non-interacting positive kinetic energy density

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_i^n |\nabla\phi_i(\mathbf{r})|^2 \quad (18)$$

$\tau(\mathbf{r})$  is included because it describes the curvature of the exchange hole and can be used to obtain more accurate models for the exchange hole. Meta-GGAs provide a modest improvement over GGAs and important examples are TPSS (2003) and SCAN (2015).

## 4 Hybrid Functionals

One of the main problems with GGAs is the self interaction error, which leads to too delocalised electron densities and problems with dissociation of charged fragments, reaction barriers, radicals and excited states. Becke proposed to mix Hartree-Fock exchange with GGA functionals in a three-parameter hybrid (3H) approximation (1993) and also a simpler one-parameter hybrid (1H) approximation (1996)

$$E_{xc}^{3H} = aE_x^{HF} + bE_x^{GGA} + (1 - a - b)E_x^{LDA} + cE_c^{GGA} + (1 - c)E_c^{LDA} \quad (19)$$

$$E_{xc}^{1H} = aE_x^{HF} + (1 - a)E_x^{DFA} + E_c^{DFA} \quad (20)$$

where  $E_x^{HF}[\Phi]$  is the Hartree-Fock exchange energy computed using the occupied Kohn-Sham orbitals. The orbitals are optimized using a non-local exchange potential  $v_x^{HF}(\mathbf{r}, \mathbf{r}')$  instead of a local one. This is a slight extension of the usual KS method, referred to as generalized Kohn-Sham. Examples are the B3LYP and the PBE0 functionals, which are

$$E_{xc}^{B3LYP} = 0.20E_x^{HF} + 0.72E_x^{B88} + 0.08E_x^{LDA} + 0.81E_c^{LYP} + 0.19E_c^{VWN} \quad (21)$$

$$E_{xc}^{PBE0} = 0.25E_x^{HF} + 0.75E_x^{PBE} + E_c^{PBE} \quad (22)$$

A common strategy is to use flexible  $E_x^{DFA}$  and  $E_c^{DFA}$  in a hybrid approximation and to optimise the many parameters by fitting to molecular properties. Examples include the B97 functional, which has 13 parameters and the M06 functional, which has 36 parameters.

Mean absolute errors		HF	MP2	BLYP	B3LYP
$r_e/\text{\AA}$ :	12 first row diatomics	0.024	0.011	0.012	0.004
$r_e/\text{\AA}$ :	12 second row diatomics	0.016	0.017	0.024	0.006
$v_0/\text{cm}^{-1}$ :	122 molecules	50	63	45	34
$D_0/\text{kcal/mol}$ :	44 molecules	86	15	8	5
$\Delta E^\ddagger/\text{kcal/mol}$	Diels-Alder (reverse)	-8		-16	-9

Hybrid functionals have greatly reduced the self interaction error and are significantly more accurate for properties of molecules and is often more accurate than MP2 for cases where dispersion does not play a significant role. However, barrier heights are still too low and problems remain with Rydberg and charge transfer excited states. Moreover, the introduction of Hartree-Fock exchange renders the functional unusable for metallic systems with a zero band gap.

## 5 Double-hybrid approximations

In 2006, Grimme introduced a two-parameter double-hybrid (2DH) approximation

$$E_{xc}^{2DH} = aE_x^{HF} + (1-a)E_x^{DFA} + bE_c^{MP2} + (1-b)E_c^{DFA} \quad (23)$$

where the MP2-like correlation energy  $E_c^{MP2}$  is added *a posteriori* and is computed using the KS orbitals and eigenvalues. Double-hybrid approximations are examples of correlation functionals that depend on virtual orbitals. Another example is the random-phase approximation (RPA). The presence of the non-local MP2 correlation term makes it possible to use a larger fraction of non-local HF exchange. For example the B2-PLYP functional has  $a = 0.53$  and  $b = 0.27$ .

## 6 Range Separated Hybrid Functionals

Based on ideas of Savin (1996), Hirao and coworkers (2001) proposed a long-range correction (LC) scheme, which corrects the exchange correlation potential in the long-range limit to have the exact  $v(\mathbf{r}) \rightarrow -1/r$  behaviour that results from the self-interaction part of the exchange hole.

$$E_{xc}^{LC} = E_x^{lr, HF} + E_x^{sr, DFA} + E_c^{DFA} \quad (24)$$

This is based on a partitioning of the HF exchange energy in to long- and short-range terms using a single parameter range-separation function, chosen to be the error function for ease of computation.

$$E_{xc}^{HF} = E_x^{lr, HF} + E_x^{sr, HF} \quad (25)$$

$$= -\frac{1}{2} \sum_{ij}^n \langle \phi_i \phi_j | \frac{\text{erf}(\mu r_{12})}{r_{12}} | \phi_j \phi_i \rangle - \frac{1}{2} \sum_{ij}^n \langle \phi_i \phi_j | \frac{\text{cerf}(\mu r_{12})}{r_{12}} | \phi_j \phi_i \rangle \quad (26)$$

Typical values of  $\mu$  are 0.3 to 0.5. In 2004, Yanai introduced a more flexible decomposition called the Coulomb-attenuating method (CAM)

$$E_{xc}^{CAM} = aE_x^{sr, HF} + bE_x^{lr, HF} + (1-a)E_x^{sr, DFA} + (1-b)E_x^{lr, DFA} + E_c^{DFA} \quad (27)$$

where  $v(\mathbf{r}) \rightarrow -1/r$  is no longer fully recovered and some fraction of  $E_{xc}^{HF}$  is retained at the short range. This enabled a much improved description of Rydberg and charge transfer excitations, which are sensitive to the accuracy of the long-range KS potential, without sacrificing accuracy for molecular energies and properties. Examples are CAM-B3LYP and  $\omega$ B97X.

Transition energies (in eV) in a dipeptide

transition	BLYP	B3LYP	CAM-B3LYP	CASPT2
$n_1 \rightarrow \pi_1^*$	5.34	5.49	5.65	5.61
$n_2 \rightarrow \pi_2^*$	5.62	5.73	5.88	5.82
$n_1 \rightarrow \pi_2^*$	4.60	6.24	7.88	7.92

## 7 Semi-empirical Dispersion Corrections

None of the Density Functional Approximations are capable of accounting for dispersion interactions, which result from long-range correlation in the form of coupled fluctuating dipoles between distant parts of the molecule. This severely impacts the accuracy of DFT calculations on intermolecular interactions and energetics of large molecules with significant intramolecular dispersion forces.

To explicitly account for London dispersion interactions, semi empirical dispersion corrections are simply added to the energy, an approach that has become known as DFT-D.

$$E_{disp} = -s \sum_{\alpha < \beta} f(R_{\alpha\beta}) \frac{C_6^{\alpha\beta}}{R_{\alpha\beta}^6} \quad (28)$$

where  $\alpha, \beta$  label the atoms.  $R_{\alpha\beta}$  is the distance between the atoms and the set of empirical  $C_6^{\alpha\beta}$  dispersion coefficients are read from tabulated data.  $f(R_{\alpha\beta})$  is a damping function which tends to 1 at large  $R_{\alpha\beta}$  and to 0 at small  $R_{\alpha\beta}$ , and  $s$  is a scaling parameter that can be adjusted for each approximate density functional.

## 8 Further Exercises

1. The Kohn–Sham diagonal pair density is

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = n(n-1) \int \dots \int d\sigma_1 d\sigma_2 d\mathbf{x}_3 \dots d\mathbf{x}_n \Phi^*(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_n) \Phi(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_n) \quad (29)$$

which has a classical and an exchange term

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho_{2,x}(\mathbf{r}_1, \mathbf{r}_2) \quad (30)$$

The exchange hole is defined through

$$\rho_{2,x}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)h_x(\mathbf{r}_1, \mathbf{r}_2) \quad (31)$$

- i) Show that the exchange hole is strictly negative semi-definite and obeys

$$\int d\mathbf{r}_2 h_x(\mathbf{r}_1, \mathbf{r}_2) = -1 \quad (32)$$

- ii) Show also that, for finite systems,  $\epsilon_x[\rho](\mathbf{r}) \rightarrow -1/(2r)$  as  $r \rightarrow \infty$ .



2. The exchange energy of the uniform electron gas can be obtained by starting from the exact exchange energy expression for closed-shell system

$$E_x = - \sum_{ij}^{n/2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\phi_i^*(\mathbf{r}_1) \phi_i^*(\mathbf{r}_2) \phi_j(\mathbf{r}_1) \phi_j(\mathbf{r}_2)}{r_{12}} \quad (33)$$

and by making the replacements

$$\phi_i(\mathbf{r}) \rightarrow (1/V)^{1/2} \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (34)$$

$$\sum_i^{n/2} \rightarrow V/(2\pi)^3 \int_{\Omega_{k_F}} d\mathbf{k} \quad (35)$$

where  $\Omega_{k_F}$  is the sphere of radius equal to the Fermi momentum  $k_F = (3\pi^2\rho)^{1/3}$  with the density  $\rho = n/V$ , and doing the spatial integrations on a large box of volume  $V$  ( $n \rightarrow \infty$  and  $V \rightarrow \infty$  such that  $\rho = n/V$  remains finite). Show that this gives

$$E_x^{unif} = - \frac{V}{(2\pi)^6} \int_{\Omega_{k_F}} d\mathbf{k}_1 \int_{\Omega_{k_F}} d\mathbf{k}_2 \frac{4\pi}{|\mathbf{k}_1 - \mathbf{k}_2|} \quad (36)$$

Calculate this integral to finally obtain the exchange energy per particle  $\epsilon_x^{unif} = E_x^{unif}/n$