# DFT

## Suggested reading:

*The quest for a universal density functional: The accuracy of density functionals across a broad spectrum of databases in chemistry and physics*
Roberto Peverati and Donald G. Truhlar, Phil. Trans. R. Soc. A, 372, 20120476/1-51 (2014)

*DFT in a Nutshell*
Kieron Burke and Lucas O. Wagner, Int. J. Quantum Chem., 113 (2013) 96–101

*Perspective on density functional theory*
Kieron Burke, J. Chem. Phys., 136, 150901 (2012)

*Challenges for Density Functional Theory*
Aron J. Cohen, Paula Mori-Sanchez, and Weitao Yang, Chem. Rev., 112 (2012) 289-320

*General Performance of Density Functionals*
Sergio Filipe Sousa, Pedro Alexandrino Fernandes, and Maria Joao Ramos, J. Phys. Chem. A, 111 (2007) 10439-10452

*A Bird's-Eye View of Density-Functional Theory*
Klaus Capelle, Brazilian Journal of Physics, vol. 36, no. 4A, December, 2006
(http://arxiv.org/abs/cond-mat/0211443)

*A brief compendium of time-dependent density-functional theory*
Carsten A. Ullrich and Zeng-hui Yang, Braz. J. Phys., 44 (2014) 154-188.

# Density Functional Theory (DFT)

DFT is an alternative approach to the theory of electronic structure; electron density plays a central role in DFT.

## Why a new theory?

| | | |
|---|---|---|
| HF method scales as | $K^4$ | (K - # of basis functions) |
| CI methods scale as | $K^6$-$K^{10}$ | |
| MPn methods scale as | $>K^5$ | |
| CC methods scale as | $>K^6$ | |

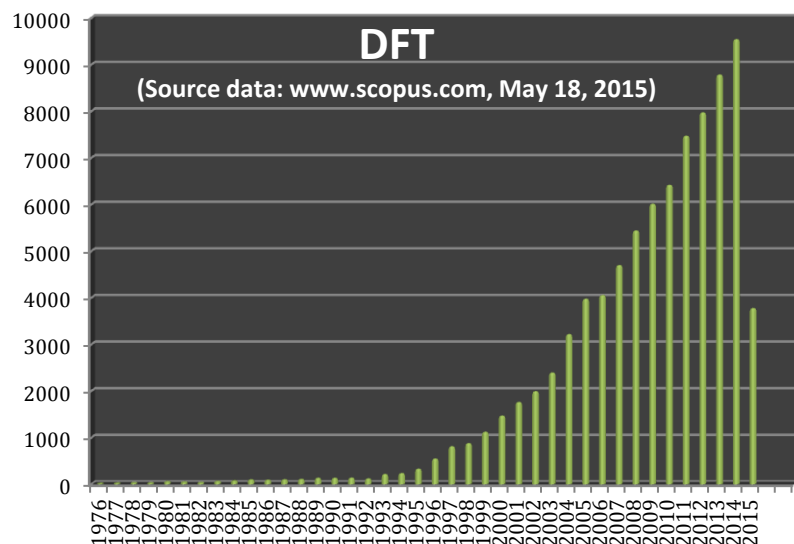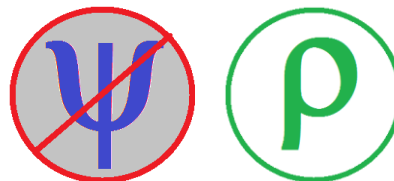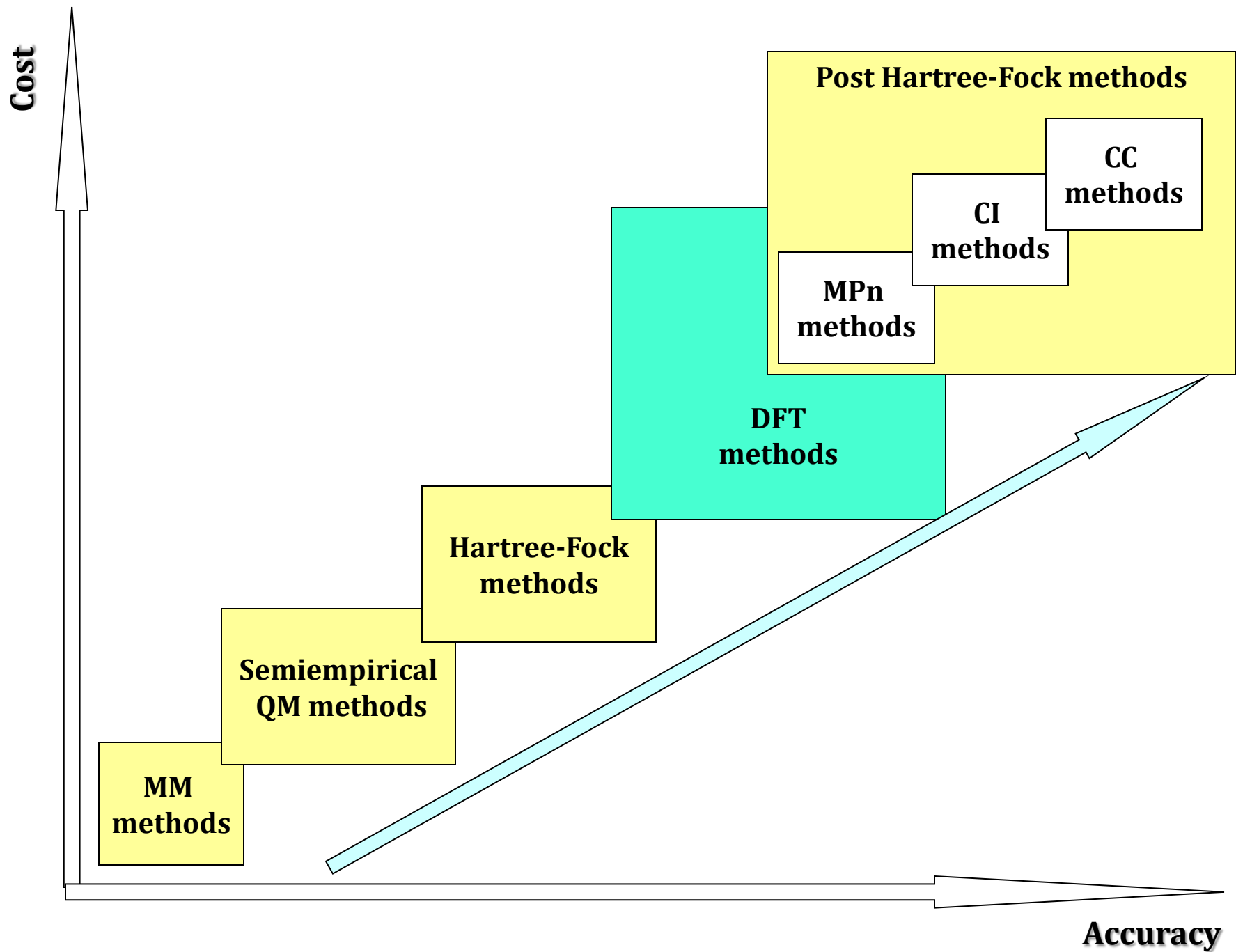$\Rightarrow$ **Correlated methods are not feasible for medium and large sized molecules!**

## Alternative: DFT

Electron density is the central quantity in DFT!





DFT
(Source data: www.scopus.com, May 18, 2015)

Superconductivity
(Source data: www.scopus.com, May 18, 2015)
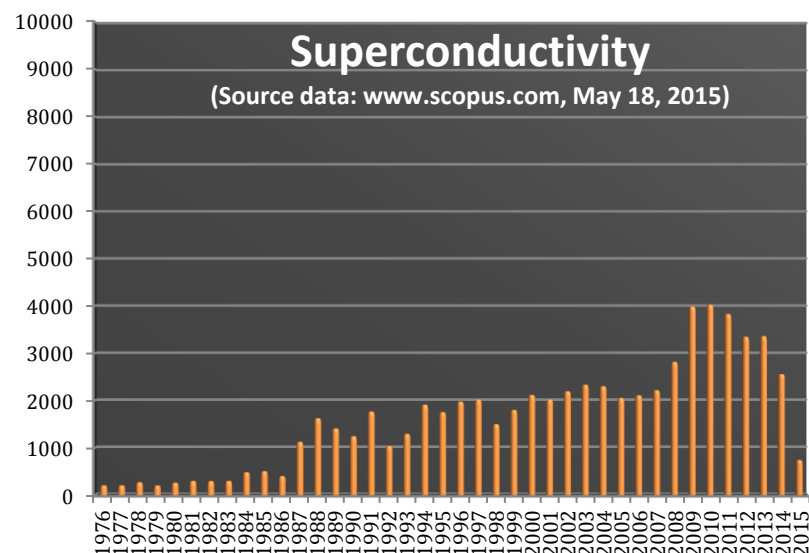
**Probability of finding electron 1 in dx$_1$, electron 2 in dx$_2$, ... , electron N in dx$_N$:**

$$|\Psi(x_1, x_2, \ldots, x_N)|^2 dx_1 dx_2 \ldots dx_N$$

Integrating over the space and spin coordinates of electron 2, 3, ... , N and the spin coordinate of electron 1 one obtaines **the probability of finding electron 1 in volume element dr$_1$ whilst the other electrons are anywhere**:

$$\left( \int \ldots \int |\Psi(x_1, x_2, \ldots, x_N)|^2 ds_1 dx_2 \ldots dx_N \right) dr_1$$

Multiplying by N one obtaines **the probability of finding any electron in dr$_1$:**

$$N \left( \int \ldots \int |\Psi(x_1, x_2, \ldots, x_N)|^2 ds_1 dx_2 \ldots dx_N \right) dr_1 = \rho(r_1) dr_1$$
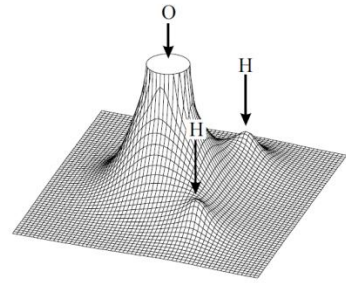
The quantity $\rho$(r$_1$) is **the electron density**:

$$N \int \ldots \int |\Psi(x_1, x_2, \ldots, x_N)|^2 ds_1 dx_2 \ldots dx_N$$

- $\rho(\vec{r})$ is a non-negative function depending on only three variables
- $\rho(\vec{r})$ vanishes at infinity and integrates to the total number of electrons N:

$$\lim_{r \to \infty} \rho(\vec{r}) = 0 \qquad \int \rho(\vec{r})d\vec{r} = N$$

> **ρ represents the density of the electron cloud carying N electrons**

- $\rho(\vec{r})$ can be measured experimentally (e.g. by X-ray diffraction)
- at the position of atoms, the gradient of $\rho(\vec{r})$ has a discontinuity:

> **Kato's cusp condition**

$$\lim_{r_{iA} \to 0} \left[ \frac{\delta}{\delta r} + 2Z_A \right] \overline{\rho}(\vec{r}) = 0 \quad \Big| \quad For\ r_{iA} \to 0, \rho \sim e^{-\frac{2Z_A r}{a_0}} \ ; \quad \lim_{r_{iA} \to 0} \frac{\delta \rho}{\delta r} \sim -\,2Z_A \rho/a_0$$

Z being the nuclear charge and $\overline{\rho}(\vec{r})$ the spherical average of $\rho(\vec{r})$

- decays exponentially for large distances from nuclei

$$\rho(\vec{r}) \sim \exp\left(-2\sqrt{2I}|\vec{r}|\right)$$

> For H atom:
> $$-E_0 = I = \frac{k^2 Z^2 e^2}{2a_0} \Rightarrow (in\ a.u.)\ Z = \sqrt{2I}$$

I being the exact first ionization energy of the system

$$\rho(r) = \sum_i n_i |\Phi_i(r)|^2$$

Function:   y=f(x)   $\implies$   ρ= ρ(x,y,z)

Functional: y=F[f(x)]   $\implies$   E=F[ρ(x,y,z)]

# Hohenberg–Kohn Theorems

The electronic Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{ee}} = -\sum_i^N \frac{1}{2}\nabla_i^2 + \sum_i^N v(\mathbf{r}_i) + \sum_{i<j}^N \frac{1}{r_{ij}}$$
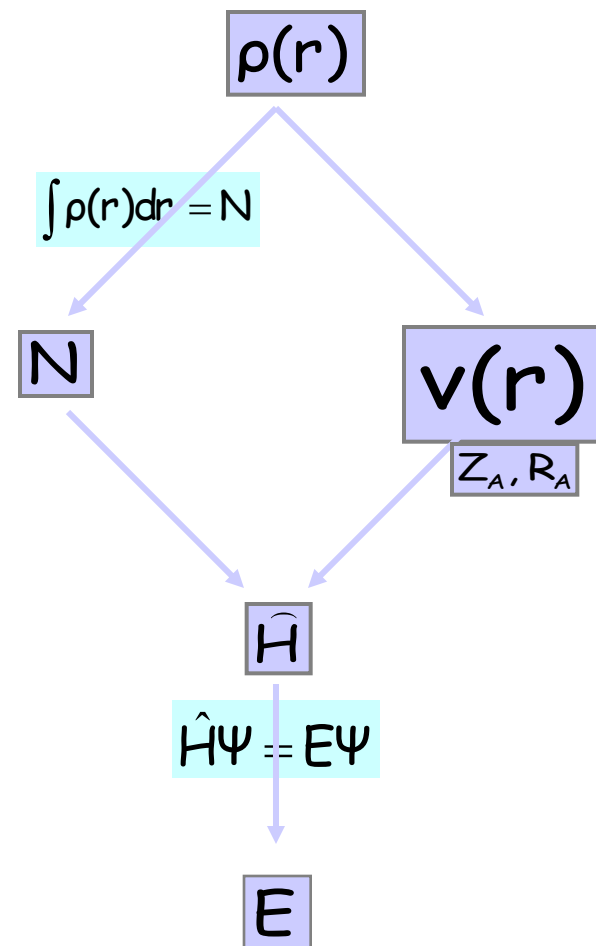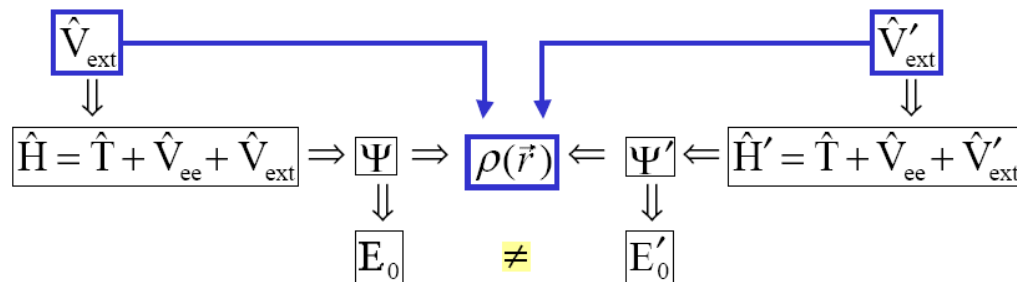
where the external potential is

$$v(\mathbf{r}_i) = -\sum_{Ai} \frac{Z_A}{r_{Ai}}$$

$\rho(r)$

$\int \rho(r)dr = N$

$N$

$v(r)$

$Z_A, R_A$

## First HK Theorem (HK1)

**"The external potential $V_{\text{ext}}(r)$ is (to within a constant) a unique functional of $\rho(r)$. Since, in turn $V_{\text{ext}}(r)$ fixes H, we see that the full many particle ground state is a unique functional of $\rho(r)$."**

$\hat{H}$

$\hat{H}\Psi = E\Psi$

$E$

**$\rho(r)$** → uniquely determines the Hamiltonian operator and thus all the properties of the system.

$$\hat{V}_{ext} \qquad \hat{V}'_{ext}$$

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} \Rightarrow \boxed{\Psi} \Rightarrow \boxed{\rho(\vec{r})} \Leftarrow \boxed{\Psi'} \Leftarrow \hat{H}' = \hat{T} + \hat{V}_{ee} + \hat{V}'_{ext}$$

$$E_0 \qquad \neq \qquad E'_0$$

**Proof HK1**

*A Chemist's Guide to Density Functional Theory.* Second Edition
Wolfram Koch, Max C. Holthausen

The proof runs as follows and is based on reductio ad absurdum. We start by considering two external potentials $V_{ext}$ and $V'_{ext}$ which differ by more than a constant (since the wave function and hence the charge density is unaltered if a constant is added to the potential, we must require from the outset that the two external potentials differ not only by a constant) but which both give rise to the same electron density $\rho(\vec{r})$ associated with the corresponding non-degenerate ground states of N particles (the limitation to non-degenerate ground states of the original Hohenberg-Kohn argument will later be lifted, see below). These two external potentials are part of two Hamiltonians which only differ in the external potential, $H = T + \hat{V}_{ee} + V_{ext}$ and $H' = T + V_{ee} + V'_{ext}$. Obviously, the two Hamiltonians $H$ and $H'$ belong to two different ground state wave functions, $\Psi$ and $\Psi'$, and corresponding ground state energies, $E_0$ and $E'_0$, respectively, with $E_0 \neq E'_0$. However, we assume that both wave functions give rise to the same electron density (this is very well possible, since the prescription of how a density is constructed from a wave function by quadrature, i. e., $\rho(\vec{r}) = N \int \cdots \int |\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)|^2 ds_1 d\vec{x}_2 ... d\vec{x}_N$, is of course not unique). We express this schematically following our notation from Section 1.2 as

$$V_{ext} \Rightarrow \hat{H} \Rightarrow \Psi \Rightarrow \quad \rho(\vec{r}) \quad \Leftarrow \Psi' \Leftarrow \hat{H}' \Leftarrow V'_{ext} .$$

Therefore $\Psi$ and $\Psi'$, ............................ $\Psi'$ as trial wave function for $\hat{H}$. We must then ha...............

$$E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle \qquad (4\text{-}1)$$

or, because the two Ham.............................potential

$$E_0 < E_0 + \langle \Psi' | T + V_{ee} + V_{ext} - T - V_{ee} - V'_{ext} | \Psi' \rangle \qquad (4\text{-}2)$$

which yields

$$E_0 < E'_0 + \int \rho(\vec{r}) \{ V_{ext} - V'_{ext} \} d\vec{r} . \qquad (4\text{-}3)$$

Interchanging the unprimed with the primed quantities and repeating the above steps of equations (4-1) to (4-3) we arrive at the corresponding equation

$$E'_0 < E_0 - \int \rho(\vec{r}) \{ V_{ext} - V'_{ext} \} d\vec{r} . \qquad (4\text{-}4)$$

After adding equations (4-3) and (4-4), this leaves us with the clear contradiction

$$E_0 + E'_0 < E'_0 + E_0 \text{ or } 0 < 0. \qquad (4\text{-}5)$$

This concludes the proof that there cannot be two different $V_{ext}$ that yield the same ground state electron density, or, in other words, that the ground state density uniquely specifies the external potential $V_{ext}$. Using again the terminology of Section 1.2 we can simply add $\rho_0$ as the property which contains the information about $\{N, Z_A, R_A\}$ and summarize this as

$$\rho_0 \Rightarrow \{N, Z_A, R_A\} \Rightarrow \hat{H} \Rightarrow \Psi_0 \Rightarrow E_0 \text{ (and all other properties).}$$

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{Ne}[\rho_0].$$

$$E_0[\rho_0] = \int \rho_0(\vec{r}) V_{Ne} d\vec{r} + \underbrace{T[\rho_0] + E_{ee}[\rho_0]}_{\text{universally valid}}.$$

$$\underbrace{\phantom{\int \rho_0(\vec{r}) V_{Ne} d\vec{r}}}_{\text{system dependent}}$$

$$E_0[\rho_0] = \int \rho_0(\vec{r}) V_{Ne} d\vec{r} + F_{HK}[\rho_0]$$

$$F_{HK}[\rho] = T[\rho] + E_{ee}[\rho] = \left\langle \Psi \left| \hat{T} + \hat{V}_{ee} \right| \Psi \right\rangle$$

$F_{HK}$???

$$E_{ee}[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\, \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{ncl}[\rho] = J[\rho] + E_{ncl}[\rho]$$

Only J[ρ] is known!

The explicit form of T[ρ] and $E_{\text{non-cl}}[\rho]$ is the major challenge of DFT

# Variational Principle in DFT

## Second HK Theorem (HK2)

**"The functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density."**

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{Ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}]$$   - variational principle

For any trial density $\rho(r)$, which satisfies the necessary boundary conditions such as:

$\rho(r) \geq 0$ and $\displaystyle\int \rho(r)dr = N$

and which is associated with some external potential $V_{ext}$, the energy obtained from the functional of $F_{HK}$ represents an upper bound to the true ground state energy $E_0$.

$$\left\langle \tilde{\Psi} \middle| \hat{H} \middle| \tilde{\Psi} \right\rangle = T[\tilde{\rho}] + V_{ee}[\tilde{\rho}] + \int \tilde{\rho}(\bar{r})V_{ext}d\bar{r} = E[\tilde{\rho}] \geq E_0[\rho_0] = \left\langle \Psi_0 \middle| \hat{H} \middle| \Psi_0 \right\rangle$$

Comments

# First attempt: Thomas-Fermi model (1927)

$$T_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\vec{r})d\vec{r}$$

L.H. Thomas, *Proc. Camb. Phil. Soc.,* 23, 542-548 (1927)
E. Fermi, *Rend. Acad., Lincei,* 6, 602-607 (1927)

$$E_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\vec{r})d\vec{r} - Z\int \frac{\rho(\vec{r})}{r}d\vec{r} + \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}d\vec{r}_1 d\vec{r}_2$$

Approximation: the electrons are distributed uniformly in each small volume element $\Delta V$ (i.e. locally) but the electron density can still vary from one small volume element to the next.

Its performance is really bad due to the: - poor approximation of the kinetic energy.
　　　　　　　　　　　　　　　　　　　　 - no attempt to represent the exchange energy of the atom

## Kohn and Sham (1965)

T[ρ] – kinetic energy of the system

Calculate the exact kinetic energy of a non-interacting system with the same density as for the real interacting system:

$$T_{KS} = -\frac{1}{2}\sum_{i=1}^{N}\langle \Psi_i | \nabla^2 | \Psi_i \rangle$$

$T_{KS}$ – kinetic energy of a fictitious non-interacting system of the same density $\rho(r)$

$\Psi_i$ — are the orbitals for the non-interacting system (KS orbitals)

$T_{KS}$ is not equal to the true kinetic energy of the system but, however, contains the major fraction of it.

$T = T_{KS} + (T - T_{KS})$

## Hohenberg-Kohn (1964) and Kohn-Sham (1965) – modern DFT

## Summary:

$$F_{HK}[\rho] = T_{KS}[\rho] + J[\rho] + E_{non-cl}[\rho]$$

$$E[\rho] = E_{Ne}[\rho] + T_{KS}[\rho] + J[\rho] + E_{xc}[\rho] =$$

$$-\sum_{i=1}^{N}\int\sum_{A=1}^{M}\frac{Z_A}{r_{1A}}\left|\varphi_i(r_1)\right|^2 dr_1$$

$$-\frac{1}{2}\sum_{i=1}^{N}\left\langle\varphi_i\left|\nabla^2\right|\varphi_i\right\rangle$$

$$+\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\iint\left|\varphi_i(r_1)\right|^2\frac{1}{r_{12}}\left|\varphi_j(r_2)\right|^2 dr_1 dr_2$$

$$+E_{xc}[\rho]$$

$E_{xc}[\rho]$ includes everything which is unknown:

- exchange energy
- correlation energy
- correction of kinetic energy ($T-T_{KS}$)

**Question**:
How can we uniquely determine the orbitals in our non-interacting reference system?
How can we define a potential such that it provides us with a Slater determinant which is characterized by the same density as our real system?
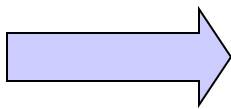
## Kohn-Sham Equations:

Minimize E[ρ] with the conditions:

$$\int \rho(r)dr = N$$

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

$$\longrightarrow \left[ -\frac{1}{2}\nabla^2 + \int \frac{\rho(r_2)}{r_{12}}dr_2 + v_{xc}(r_1) - \sum_{A=1}^{M}\frac{Z_A}{r_{1A}} \right]\varphi_i = \varepsilon_i \varphi_i$$

with:

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho}$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

# Kohn-Sham Formalism

Guess $\varphi_j$
Assume
$E_{xc}\big[\rho(r)\big]$

$$\rho(r) = \sum_{j=1}^{N} \left|\varphi_j(r)\right|$$

$$v_{xc}(r) = \frac{\delta E_{xc}\big[\rho(r)\big]}{\delta\rho(r)}$$
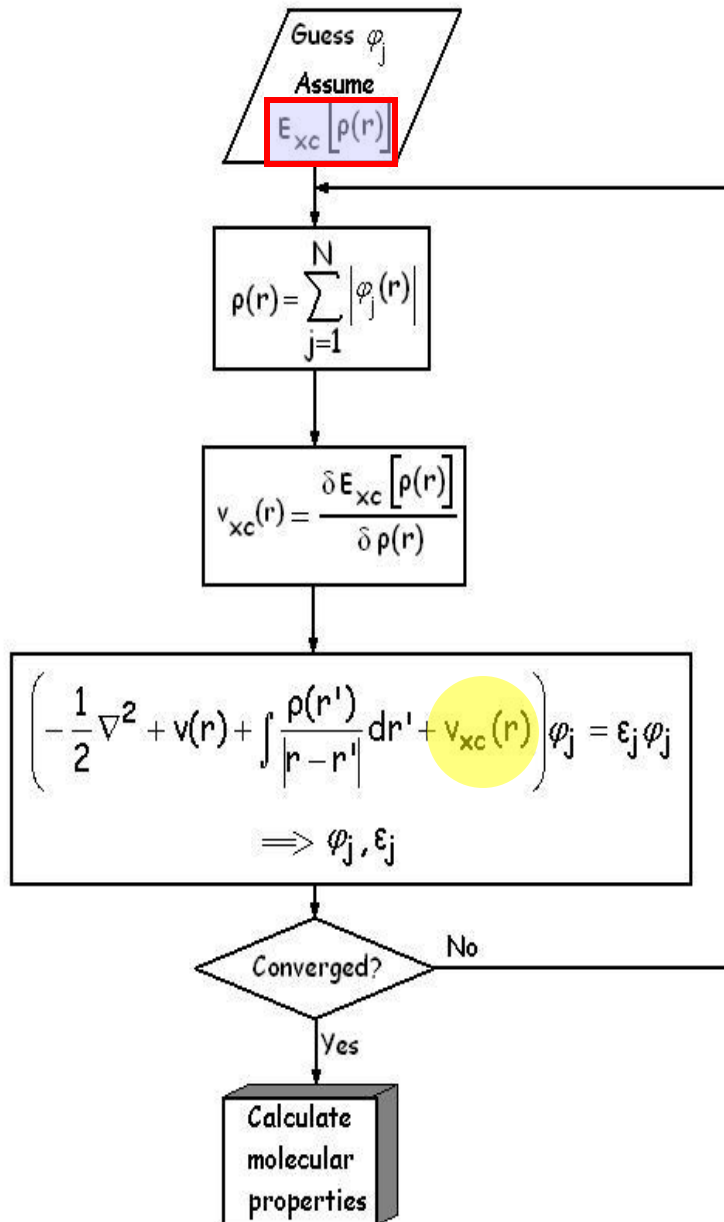
**Kohn-Sham equations**

$$\left(-\frac{1}{2}\nabla^2 + v(r) + \int\frac{\rho(r')}{|r-r'|}dr' + v_{xc}(r)\right)\varphi_j = \varepsilon_j\varphi_j$$

$$\Longrightarrow \varphi_j, \varepsilon_j$$

Converged?   No

Yes

Calculate molecular properties

$$\left(-\frac{1}{2}\nabla^2 + v(r) + \int\frac{\rho(r')}{|r-r'|}dr' - \sum_i K_i(r)\right)\varphi_j = \varepsilon_j\varphi_j$$

Hartree-Fock equations

# Kohn-Sham orbitals

The orbitals satisfying the Kohn-Sham orbitals have no physical significance.
Their only connection to the real world is that the sum of their squares add up to the exact density.
However, many authors recommend the KS orbitals as legitimate tools in qualitative MO considerations
   ✓ associated with a one electron potential which includes all non-classical effects
   ✓ consistent with the exact ground state density

Thus, in a sense, these orbitals are much closer to the real systems than the HF orbitals that neither reflect correlation effects nor do they yield the exact density.

In Kohn-Sham theory there is no equivalent of Koopmans' theorem.
There is one exception: as a direct consequence of the long range behavior of the charge density (its asymptotic exponential decay for large distances from all nuclei)

$$\rho(\vec{r}) \propto \exp[-2\sqrt{2I}\,|\vec{r}|]$$

$\varepsilon_{HOMO}$ of the KS orbitals equals the negative of the exact ionization energy.
This holds strictly only for $\varepsilon_{HOMO}$ resulting from the exact $V_{XC}$, not for solutions obtained with approximations to the exchange-correlation potential.

## What Do the Kohn−Sham Orbitals and Eigenvalues Mean?

Ralf Stowasser and Roald Hoffmann*

# Exchange-correlation functionals
## $E_{xc}[\rho] = ??$

### Local Density Approximation (LDA) – uniform electron gas

$$E_{xc}[\rho] = \int \rho(r)\varepsilon_{xc}(\rho(r))dr$$

The exchange energy is about ten times larger than correlation in "standard" systems

$\varepsilon_{xc}$ - the exchange-correlation energy per particle of a uniform electron gas of density $\rho(r)$
- only depends on the density at r

$$\epsilon_{XC}(\rho(\vec{r})) = \epsilon_X(\rho(\vec{r})) + \epsilon_C(\rho(\vec{r})).$$

split into exchange and correlation contributions

$$\epsilon_X = -\frac{3}{4}\left(\frac{3\rho(\vec{r})}{\pi}\right)^{1/3}$$

represents the exchange energy of an electron in a uniform electron gas of a particular density

$$E_X = C_X \int \rho^{4/3}(\mathbf{r})d\mathbf{r} \qquad C_X = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

Slater exchange functional (S)

### For the correlation part:
Monte-Carlo simulations of the homogenous electron gas energy – Ceperley and Alder
- interpolation of these results → analytical expressions for $\varepsilon_C$

D. M. Ceperley and B. J. Alder (1980). "Ground State of the Electron Gas by a Stochastic Method". *Phys. Rev. Lett.* **45** (7): 566–569

Vosko, Wilk & Nusair (1980) most widely used          LDA → SVWN
Perdew &Wang (1992)

The VWN correlation functional is,

$$\epsilon_c^{VWN} = C0[\ln C1 + C2 \arctan C3 - C4(\ln C5 + C6 \arctan C7)]$$

where

$$C0 = \frac{A}{2} \quad, \quad C1 = \frac{x}{X(x)} \quad, \quad C2 = \frac{2b}{Q} \quad, \quad C3 = \frac{Q}{2x - b}$$

$$C4 = \frac{bx_0}{X(x_0)} \quad, \quad C5 = \frac{(x - x_0)^2}{X(x)} \quad, \quad C6 = \frac{2(b + 2x_0)}{Q} \quad, \quad C7 = \frac{Q}{2x + b}$$

the functions $x$, $X$, and $Q$ are respectively,

$$x = r_s^{1/2} \quad, \quad X(x) = x^2 + bx + c \quad, \quad Q = (4c - b^2)^{1/2}$$

and the constants are $A = 0.0621814$, $x_0 = -0.409286$, $b = 13.0720$, and $c = 42.7198$.

The $r_s$ parameter (Wigner–Seitz radius)

$$r_s = \left(\frac{4}{3}\pi\rho\right)^{-1/3}$$

radius of a sphere with constant charge density $\rho$ and a total charge of one electron

Perdew and Wang (PW92) correlation functional

$$\epsilon_c^{PW92} = -2a\rho(1 + \alpha_1 r_s) \ln\{1 + [2a(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)]^{-1}\}$$

$a = 0.0310907$, $\alpha_1 = 0.21370$, $\beta_1 = 7.5957$, $\beta_2 = 3.5876$, $\beta_3 = 1.6382$, and $\beta_4 = 0.49294$.

## Local Spin Density Approximation (LSDA)

- variant of LDA for unrestricted formalism (open-shell systems)

Two spin-densities:

$$\rho_\alpha(\vec{r}) \text{ and } \rho_\beta(\vec{r})$$

$$\rho(\vec{r}) = \rho_\alpha(\vec{r}) + \rho_\beta(\vec{r})$$

$$E_{XC}^{LSD}[\rho_\alpha, \rho_\beta] = \int \rho(\vec{r}) \varepsilon_{XC}(\rho_\alpha(\vec{r}), \rho_\beta(\vec{r})) \, d\vec{r}$$

Performance of LDA (LSDA)
• for atoms and molecules the exchange energy is usually underestimated by 10%, but this is compensated by an overestimation of correlation by 2 or 3 times.
• underbind core electrons and overbind atoms in molecules
• not able to reproduce the effects of bond breaking and forming

Because molecules do not resemble a uniform electron gas!

## Generalized Gradient Approximation (GGA)

$$E_{xc}[\rho] = \int \rho(r)\varepsilon_{xc}(\rho(r), \nabla\rho(r),...)dr$$

to account for the non-homogeneity of the true electron density → gradient

$\varepsilon_{xc}$ depends on the density and its gradient at r

GGA $E_{XC}$ is usually split into its exchange and correlation contributions:

$$E_{XC}^{GGA} = E_X^{GGA} + E_C^{GGA}$$

$$E_X^{GGA} = E_X^{LDA} - \sum_\sigma \int F(s_\sigma) \, \rho_\sigma^{4/3}(\vec{r}) \, d\vec{r}$$

$$s_\sigma(\vec{r}) = \frac{|\nabla\rho_\sigma(\vec{r})|}{\rho_\sigma^{4/3}(\vec{r})}$$

- the reduced gradient density
- interpreted as a local inhomogeneity parameter
- it has large values for large gradients and in regions of small densities
- it is zero for the homogenous electron gas

## Forms of F for exchange functionals

**First class** A.D. Becke, Phys. Rev. A, 38, 3098, 1988)

$$F^B = \frac{\beta s_\sigma^2}{1 + 6\beta s_\sigma \ \sinh^{-1} s_\sigma}$$

β= 0.0042 – empirical
Derived functionals: FT97, PW91, CAM(A) and CAM(B)

**Second class** (A. D. Becke, J. Chem. Phys **84**, 4524, 1986; J. P. Perdew, Phys. Rev. B **33**, 8822, 1986;
J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett **77**, 3865, 1996)

$$F^{P86} = \left(1 + 1.296\left(\frac{s_\sigma}{(24\pi^2)^{1/3}}\right)^2 + 14\left(\frac{s_\sigma}{(24\pi^2)^{1/3}}\right)^4 + 0.2\left(\frac{s_\sigma}{(24\pi^2)^{1/3}}\right)^6\right)^{1/15}$$

Derived functionals: B86, P, PBE

## Correlation functionals
P86, PW91, LYP

# Exchange-correlation functionals

$$\epsilon_x^{B88} = \epsilon_x^{LDA}\left[1 - \frac{\beta x^2}{2^{1/3}A_x(1 + 6\beta x\sinh^{-1}(x))}\right]$$

$$x = \frac{2^{1/3}|\nabla\rho|}{\rho^{4/3}} \quad , \quad A_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \quad , \quad \beta = 0.0042$$

$$\epsilon_c^{LYP} = -\frac{a}{1 + d\rho^{-1/3}}\left\{\rho + b\rho^{-2/3}\left[C_F\rho^{5/3} - 2t_w + \frac{1}{9}\left(t_w + \frac{1}{2}\nabla^2\rho\right)\right]e^{-c\rho^{-1/3}}\right\}$$

$$t_w = \frac{1}{8}\left(\frac{|\nabla\rho|^2}{\rho} - \nabla^2\rho\right) \quad , \quad C_F = \frac{3}{10}(3\pi^2)^{2/3}$$

$$a = 0.04918 \quad , \quad b = 0.132 \quad , \quad c = 0.2533 \quad , \quad d = 0.349$$

$$\epsilon_x^{PW91} = \epsilon_x^{LDA}[\rho]\left[\frac{1 + sa_1\sinh^{-1}(sa_2) + (a_3 + a_4 e^{-100s^2})s^2}{1 + sa_1\sinh^{-1}(sa_2) + a_5 s^4}\right]$$

$$a_1 = 0.19645 \quad , \quad a_2 = 7.7956 \quad , \quad a_3 = 0.2743 \quad , \quad a_4 = -0.1508 \quad , \quad a_5 = 0.004$$

$$\epsilon_c^{PW91} = \epsilon_c^{LDA}[\rho] + \rho H[\rho, s, t]$$

$$H = \frac{\beta^2}{2\alpha}\ln\left[1 + \frac{2\alpha(t^2 + At^4)}{\beta(1 + At^2 + A^2 t^4)}\right] + C_{c0}[C_c(\rho) + C_{c1}]t^2 e^{-100s^2}$$

$$A = \frac{2\alpha}{\beta}\left[\exp\left(-2\alpha\epsilon_c^{LDA}(\rho)/(\rho\beta^2)\right) - 1\right]^{-1} \quad , \quad t = \left(\frac{\pi}{3}\right)^{1/6}\frac{|\nabla\rho|}{4\rho^{7/6}}$$

$$\alpha = 0.09 \quad , \quad \beta = 0.0667263212 \quad , \quad C_{c0} = 15.7559 \quad , \quad C_{c1} = 0.0035521$$

## Hybrid Functionals

Since $E_X \gg E_C$, an accurate expression for the exchange functional is a prerequisite for obtaining meaningful results from density functional theory.

$$E_{XC} = E_X^{exact} + E_C^{KS}$$

$$E_{xc}^{hyb}[\rho] = \alpha E_x^{KS} + (1-\alpha)E_{xc}^{GGA}$$

$E_X^{KS}$-the exact exchange calculated with the exact KS wave function
$\alpha$ - fitting parameter

Shooting star – B3LYP (A. D. Becke, *J. Chem. Phys.* **98**, 5648, 1993)

$$E_{XC}^{B3LYP} = (1-a)\,E_X^{LSD} + a\,E_{XC}^{\lambda=0} + b\,E_X^{B88} + c\,E_C^{LYP} + (1-c)\,E_C^{LSD}$$

corresponds to the exchange contribution of a Slater determinant



B3LYP

(Source: www.scopus.com, May 18, 2015)
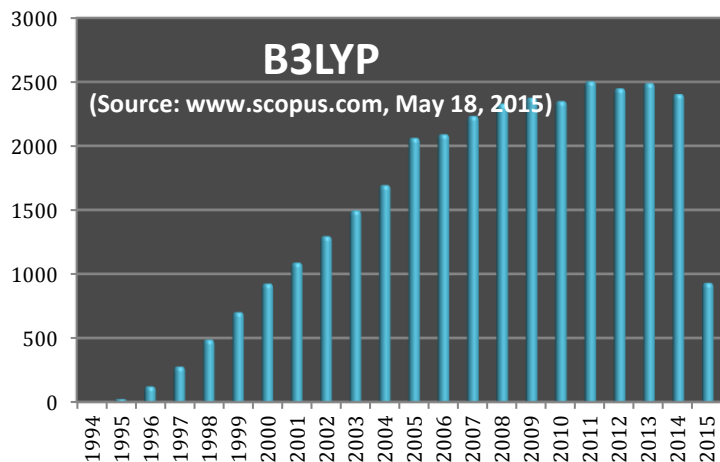
PBE1PBE (Perdew, J. P., Burke, K. & Ernzerhof, M. 1996 *Phys. Rev. Lett.* **77,** 3865–3868, 1996)

$$E_{XC}^{hybrid} = E_{XC}^{GGA} + 0.25(E_X^{HF} - E_X^{GGA})$$

The natural next step is to introduce higher derivatives into the functional, namely the density Laplacian, $\nabla^2 \rho$ and the kinetic energy density, $\tau = \sum_i |\nabla \varphi_i|^2$

In the meta-GGA's, the exchange-correlation potential becomes orbital-dependent !

$$\varepsilon_{xc} = \varepsilon_{xc}\left(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|, \nabla^2\rho(\mathbf{r}), \sum_i |\nabla\varphi_i|^2\right)$$

# Jacob's ladder of DFT

**Chemical accuracy**

$\text{unocc. } \{\varphi_i\}$

**fully non-local**
explicit dependence on unoccupied orbitals

$\text{occ. } \{\varphi_i\}$

**hybrid-GGA, hybrid meta GGA**
explicit dependence on occupied orbitals

B3LYP, PBE1PBE
PKZB, TPSS

$\nabla^2 r$

**meta-GGA**
explicit dependence on kinetic energy density

$\nabla r$

**GGA**
explicit dependence on density's gradients

$r$

**L(S)DA**
dependence on local density alone

**Hartree world**
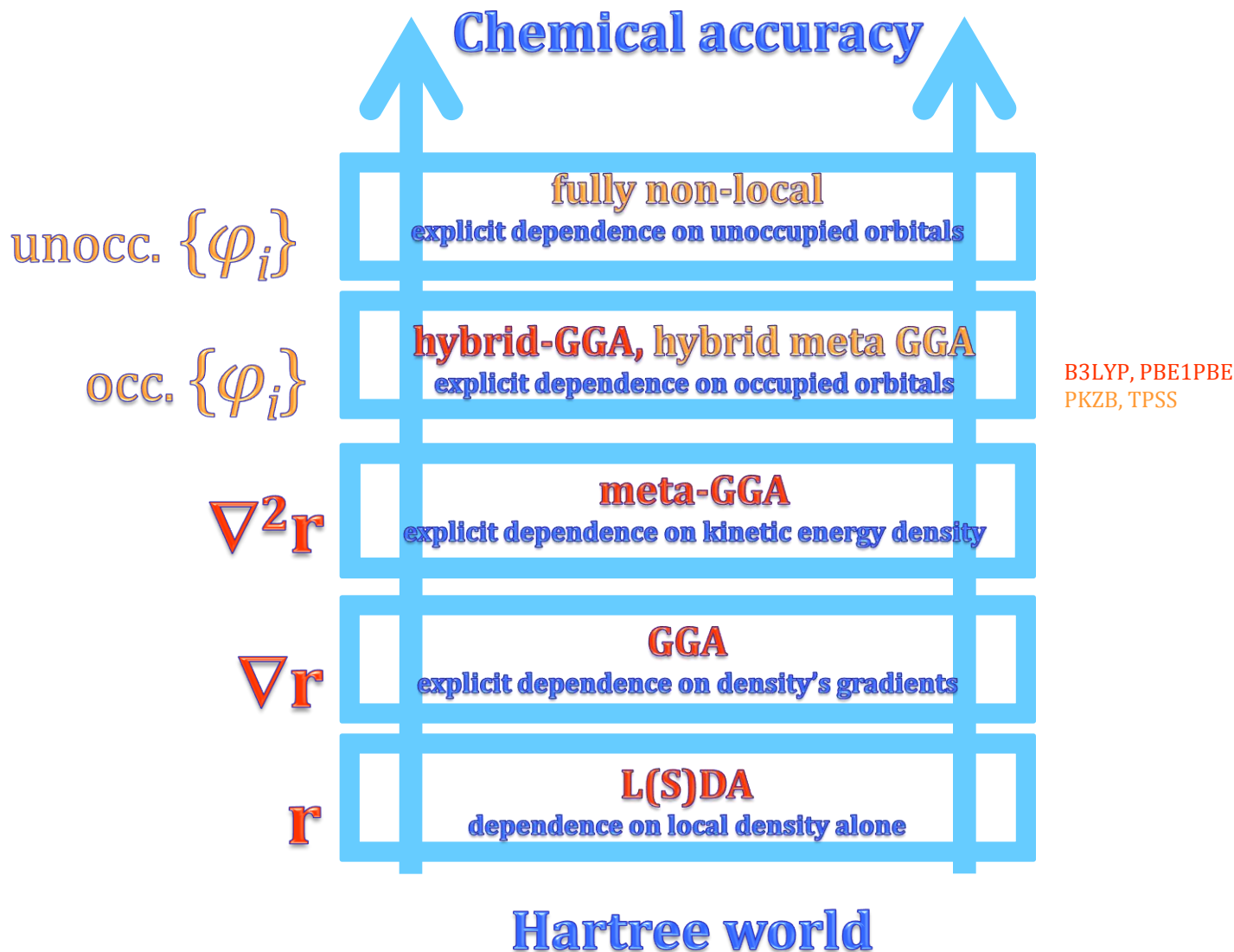
# Classification of Density Functionals: exchange, correlation

**Exchange functionals:**
S
XA
PW91
MPW
G96
O

**Combine!**

**Correlation functionals**
VWN
VWN5
LYP
P86
PW91
B95
PL

VP86
V5LYP

# Classification of Density Functionals: GGA, hybrid, meta...

**L(S)DA functionals:**
SVWN, SVWN3, SVWN5,
SPWL

**Pure GGA functionals:**
BP86, BLYP
BPW91, OLYP, XLYP
G96LYP, PBEPBE
HCTH, BPBE
G96LYP, MPWLYP, MPWPW91,

**Pure meta GGA ($\tau$) functionals:**
BB95, MPW1K
THCTH, VSXC, PBEKCIS
TPSS, TPSSKCIS, mPWB95

**Hybrid GGA functionals**
B3LYP, B3P86
B3PW91, PBE1PBE
O3LYP, KMLYP
B98, B971, B972
M052X, THCTH-HYB
TPSSH, BMK, MPW1K, MPW3LYP
BHandH, BHandHLYP
BHandHHYB, HSE2PBE
HSE1PBE, CAM-B3LYP

**Hybrid meta-GGA functionals:**
B1B95, BB1K
PBE1KCIS, VS98,
PKZB, BMK, TPSS1KCIS, TPSSh
M05, M05-2X, MPW1B95
MPWB1K, MPW1KCIS
PW6B95, PWB6K

# Comparison of methods: e.g. $H_2O$

| method | $E_{tot}$ [a.u.] | H-O [Å] | $\angle$HOH [°] | vibrational modes [cm$^{-1}$] | | | dipole moment [D] |
|---|---|---|---|---|---|---|---|
| | | | | bending | sym. stretch | asym. stretch | |
| HF | -76.065 | 0.940 | 106.2 | 1751 | 4229 | 4130 | 1.984 |
| MP2 | -76.408 | 0.958 | 104.0 | 1643 | 3978 | 3855 | 1.852 |
| CCSD(T) | -76.421 | 0.958 | 104.1 | 1659 | 3952 | 3845 | 1.839 |
| SVWN | -75.911 | 0.970 | 104.9 | 1571 | 3832 | 3737 | 1.930 |
| RPBE | -76.465 | 0.968 | 104.0 | 1635 | 3815 | 3722 | 1.863 |
| BP86 | -76.477 | 0.970 | 104.1 | 1613 | 3789 | 3690 | 1.889 |
| B3LYP | -76.472 | 0.961 | 105.1 | 1629 | 3905 | 3804 | 1.848 |
| exp. | -76.438 | 0.958 | 104.5 | 1648 | 3943 | 3832 | 1.854 |
| | > 4‰ | > 1% | > 1% | | > 3% | | > 1% |

# Different functionals for different properties

**Structure**: bond lengths, bond angles, dihedrals

**Vibrational frequencies:** wavenumbers, IR intensity, Raman activity

**Kinetics**: barrier heights

**Thermochemistry**: atomization energies, binding energies, ionization potentials, electron affinities, heats of formation

**Non-bonded interactions:** stacking, hydrogen bonding, charge transfer, weak interactions, dipole interactions, p-p interactions

**What functional should I use?!**

# DFT-D

## van der Waals interactions

- the sum of the attractive or repulsive interactions between molecules other than those due to covalent bonds, hydrogen bonds, or the electrostatic interaction of ions with one another or with neutral molecules or charged molecules.
- include:
    - force between two permanent dipoles (Keesom force)
    - force between a permanent dipole and a corresponding induced dipole (Debye force)
    - force between two instantaneously induced dipoles (London dispersion force).
- control the structures of DNA and proteins, the packing of crystals, the formation of aggregates, host–guest systems, or the orientation of molecules on surfaces or in molecular films.
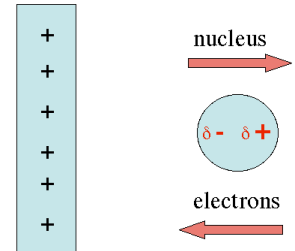
$$E_{DFT-D} = E_{KS-DFT} + E_{\text{disp}}$$

DFT-D – ORCA, Gaussian 09 (Stefan Grimme)
C-Pots (Gino DiLabio)

where

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{dmp}}(R_{ij})$$

with

$$f_{\text{dmp}}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r - 1)}}$$

# DFT-D

# PTCDI and PTCDA

## Potential energy curves

### WhyPECs?

✓ dyes
✓ electronic and optoelectronic devices (FET, OLEDS, F
✓ engineering of two-dimensional porous nanostructu
✓ building blocks sophisticated supramolecular archite

**L. Gross, F. Mohn, N. Moll, P. Liljeroth and G. Meyer, Science, 2009, 325, 1110.**
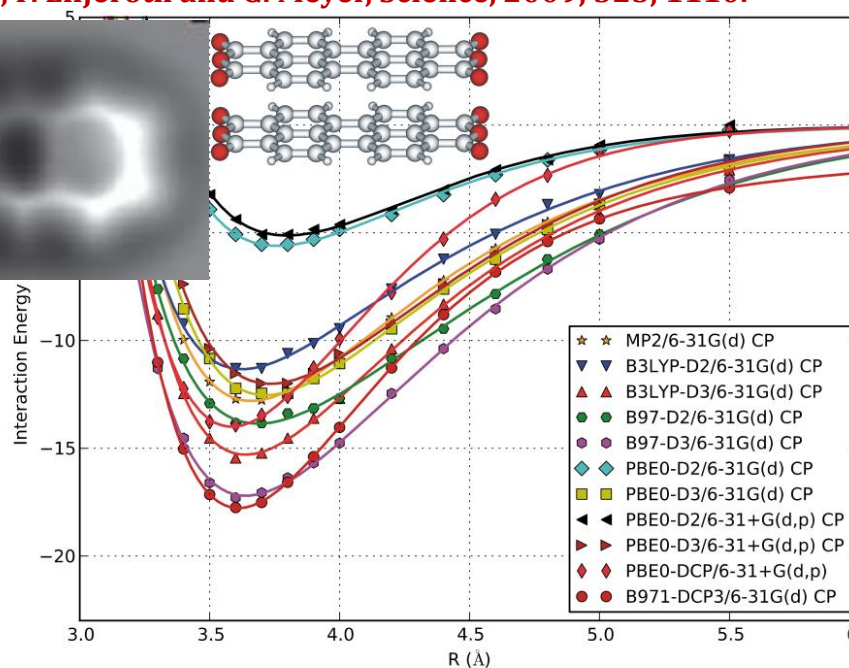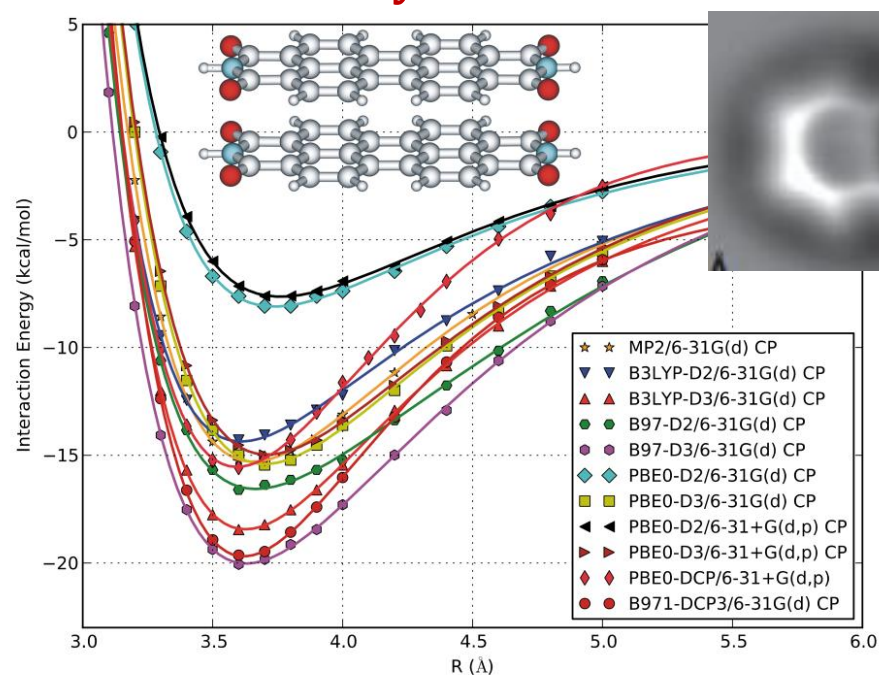


➤ PBE0-D2 – much less binding than the other metho
➤ B97-D3 and B971-DCP3 ->  overbinding
➤ No BSSE correction for **PBE0-DCP** method
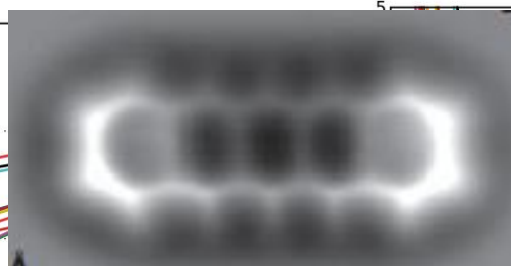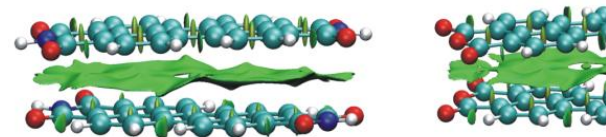
# DFT-DCP

## Benzene dimer and Benzene-water complex

### Benzene dimer
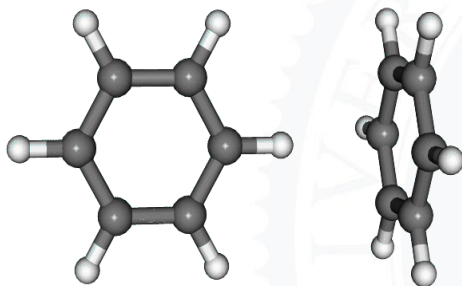


| T-shaped benzene | Interaction energy (kcal/mol) | Equilibrium distance (Å) |
|---|---|---|
| Experimental * | -2.40 | 4.960 |
| PBE0-DCP/ 6-31+G(d,p) | -2.35 | 5.000 |

*E. Arunan, H. Gutowsky, *J. Chem. Phys.* 1993, 98, 4294;
J.R. Grover, E.A. Walters, E.T. Hui, *J. Phys. Chem.* 1987, 91, 3233.

### Water - Benzene complex
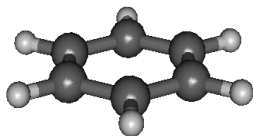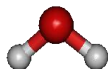


**PBE0-DCP**

| Water-benzene | Interaction energy (kcal/mol) | Equilibrium distance (Å) |
|---|---|---|
| Experimental* | -3.25 ÷ -3.40 | 3.32 ÷ -3.35 |
| CCSD(T)/CBS vdW-DF** | -3.34 ÷ -3.80 | 3.44 |
| PBE0-DCP/ 6-31+G(d,p) | -3.72 | 3.340 |

➤ **quantitative results for De and Re**
➤ **no "structural dependence"**

*Y. Zhao, O. Tishchenko, D.G. Truhlar, *J. Phys. Chem. B*, 2005, 109, 19046.
** S. Li, V.R. Cooper, T. Thonhauser, A. Puzder, D.C. Langreth, *J. Phys. Chem. A*, 2008, 112, 9031

**Vasile Chiș**
**Modeling non-covalent interactions and molecular**
**excited states by DFT methods**

# DFT-D
## CD-propranolol inclusion complexes

β-CD-R

α-CD-R        α-CD-S

γ-CD-R        γ-CD-S

β-CD-S

Rares Stiufiuc, Cristian Iacovita, Gabriela Stiufiuc, Ede Bodoki, Vasile Chiș, Constantin M. Lucaciu
Phys. Chem. Chem. Phys., 2015, 17, 1281-1289.
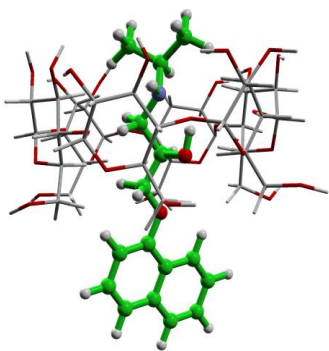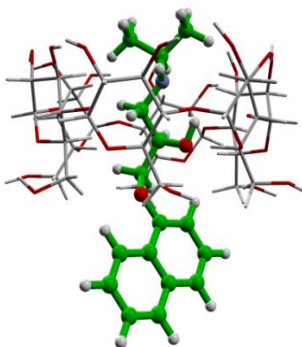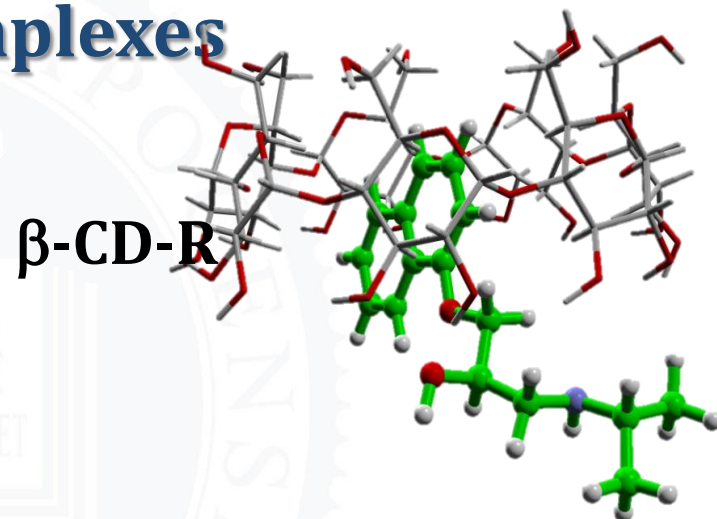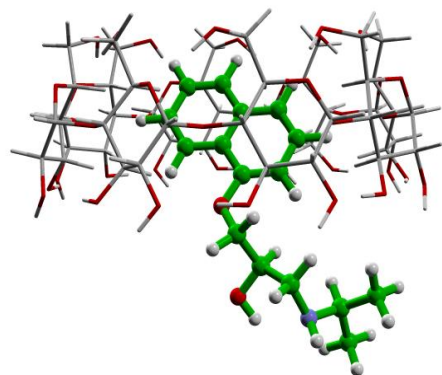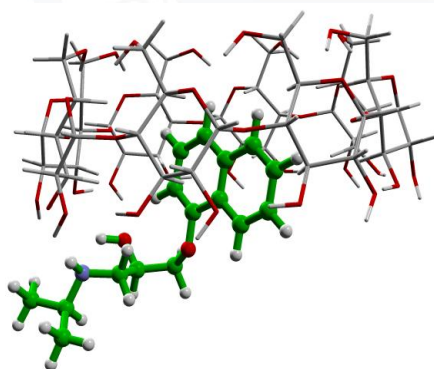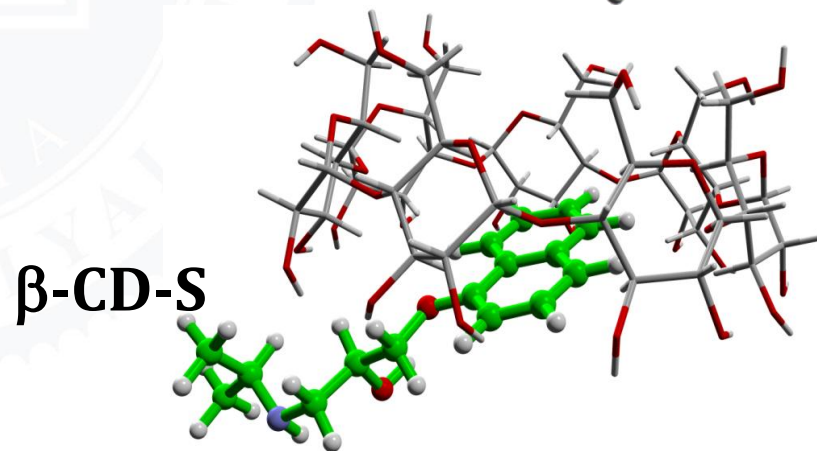
# DFT-D
## CD-propranolol inclusion complexes
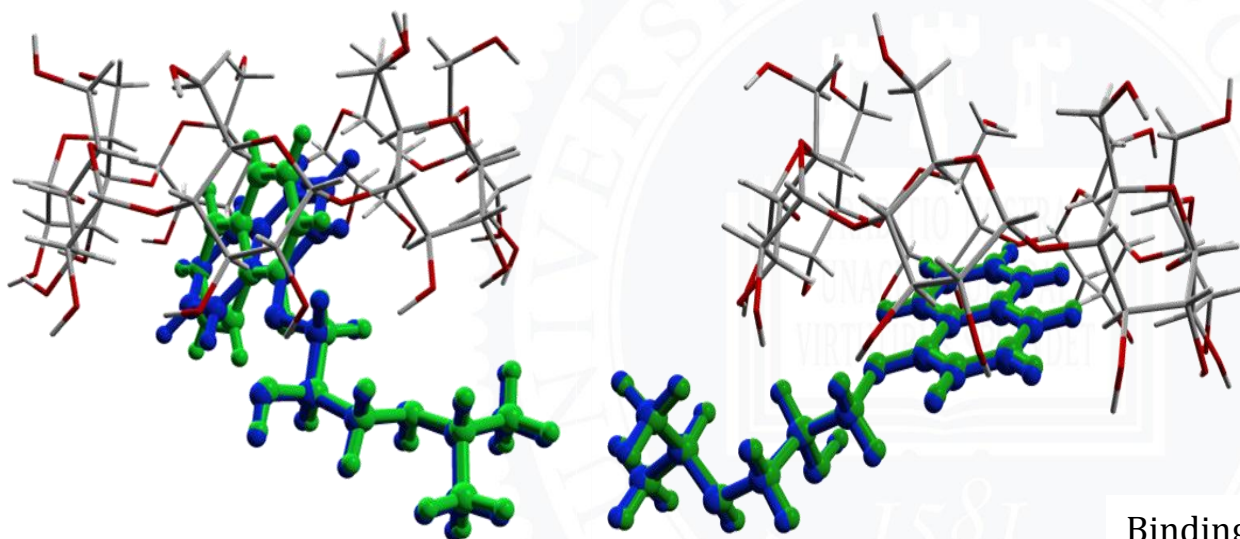


Binding energies of the inclusion complexes calculated B3LYP-D/6-31G(d) and B97-D/6-31G(d)

|          | B3LYP-D | B97-D  |
|----------|---------|--------|
| β-CD-R   | -67.6   | -36.2  |
| β-CD-S   | -64.7   | -32.8  |

Rares Stiufiuc, Cristian Iacovita, Gabriela Stiufiuc, Ede Bodoki, Vasile Chiş, Constantin M. Lucaciu
Phys. Chem. Chem. Phys., 2015, 17, 1281-1289.

# Absorption spectrum if imatinib

## Conformational study



Optimized molecular structures of the most stable conformer of imatinib (IMT) in water at B3LYP/6-31+G(d,p) level of theory, with the atom numbering scheme
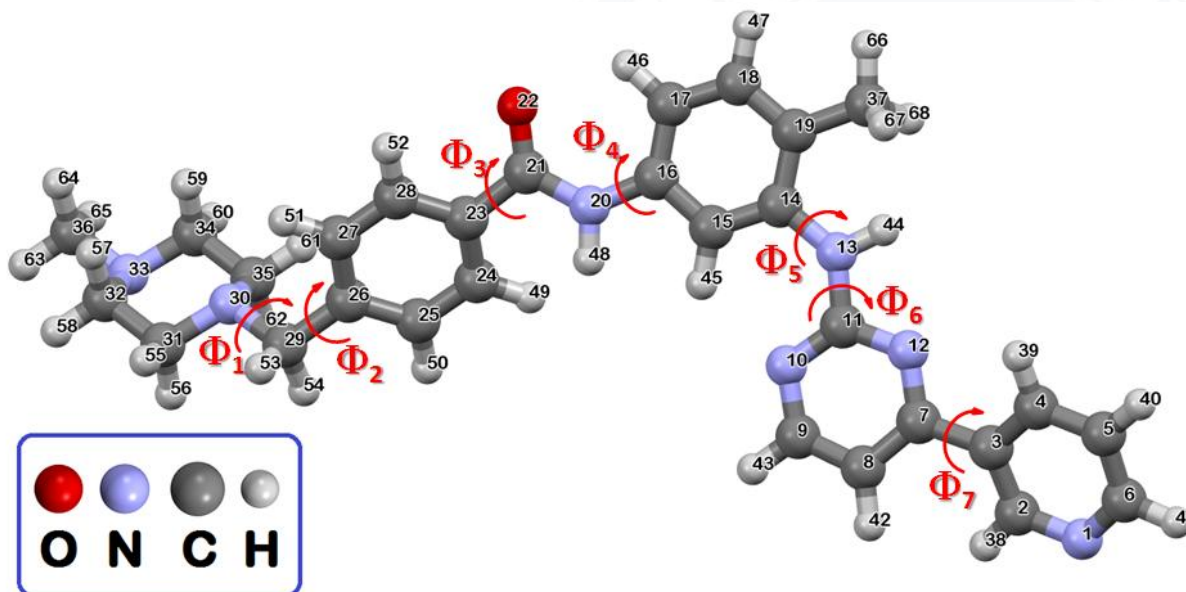
- used in the treatment of chronic myelogenous leukemia and gastrointestinal stromal tumors
- conformational changes of IMT are crucial for understanding the ligand-receptor interaction and its mechanism of action
- of interest if the lowest energy conformer of the free molecule resembles the 3D structure of the bioactive conformations found in different ligand-receptor
- IMT crystallize in two polymorphic forms, α and β, with triclinic P-1 symmetry

# Absorption spectrum if imatinib



B3LYP/6-31G(d), water
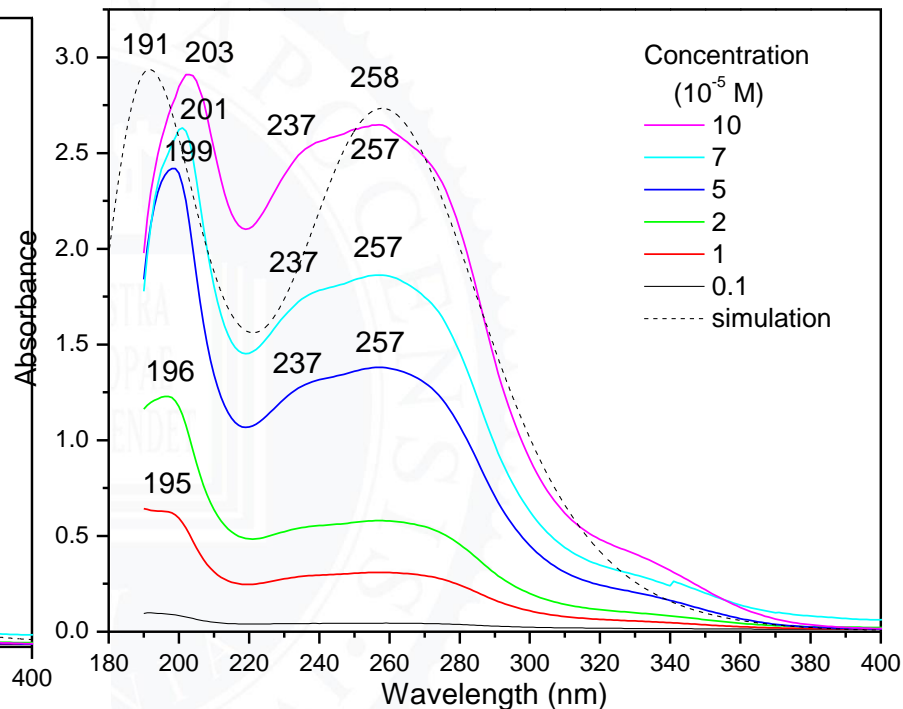
cam-B3LYP/6-31+G(d,p), water

# Absorption spectrum if imatinib
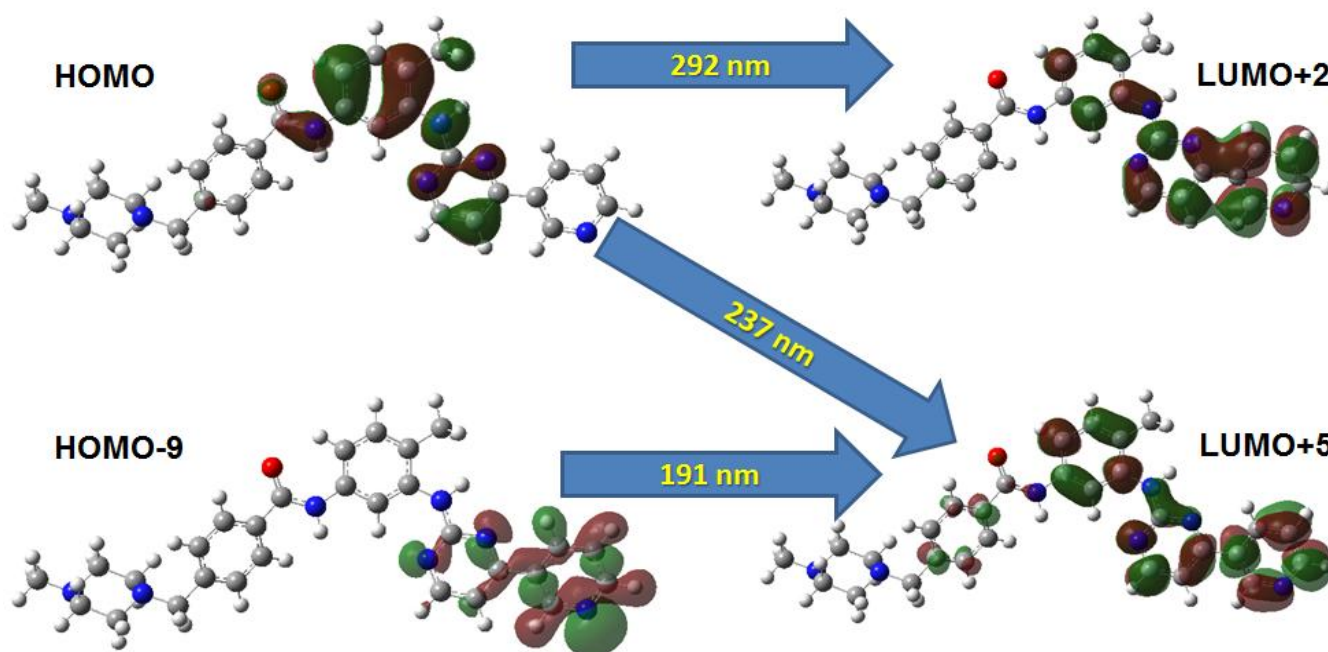


important charge transfer character
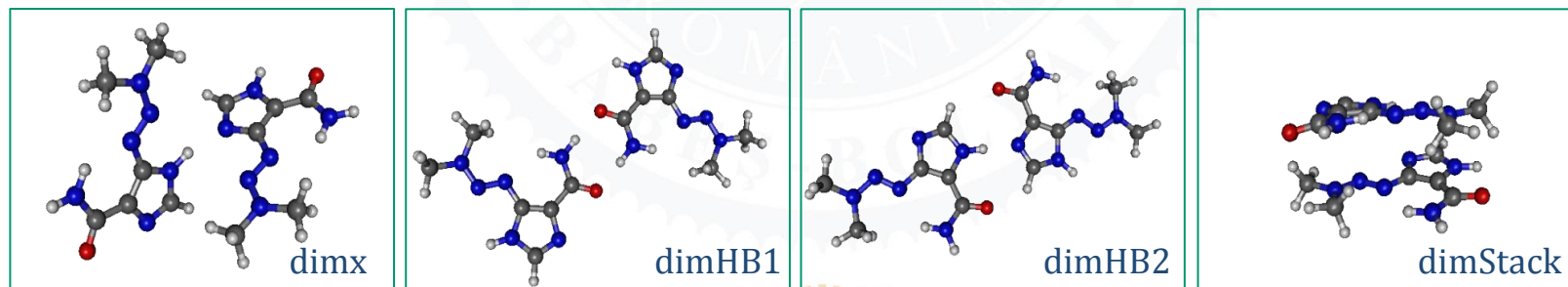=> need for range-separated functionals (cam-B3LYP)

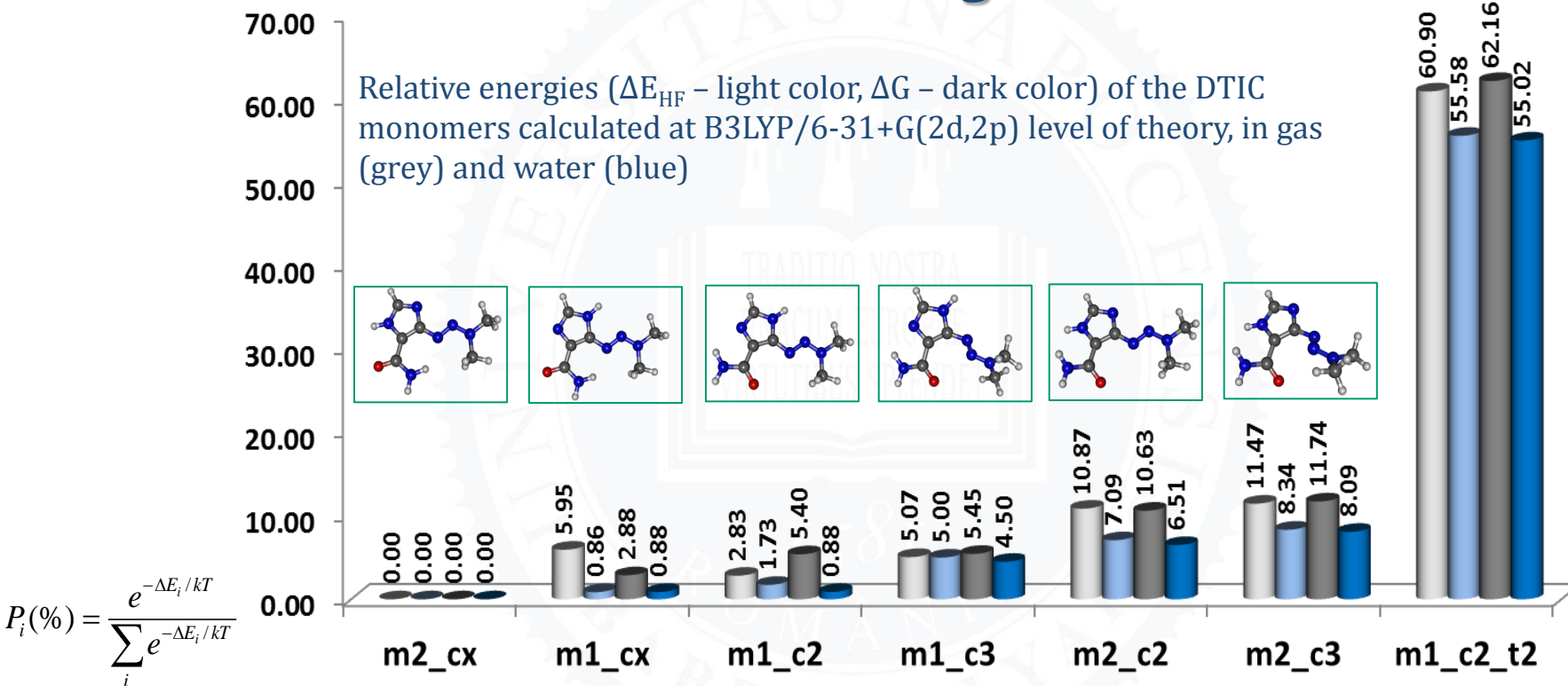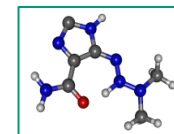# TD-DFT   Electronic absorption spectra of Dacarbazine

# DCB – computational models

## Monomers:



m1_cx

m1_c2

m2_cx

m1_c2_t2

## Dimers:



dimx

dimHB1

dimHB2

dimStack
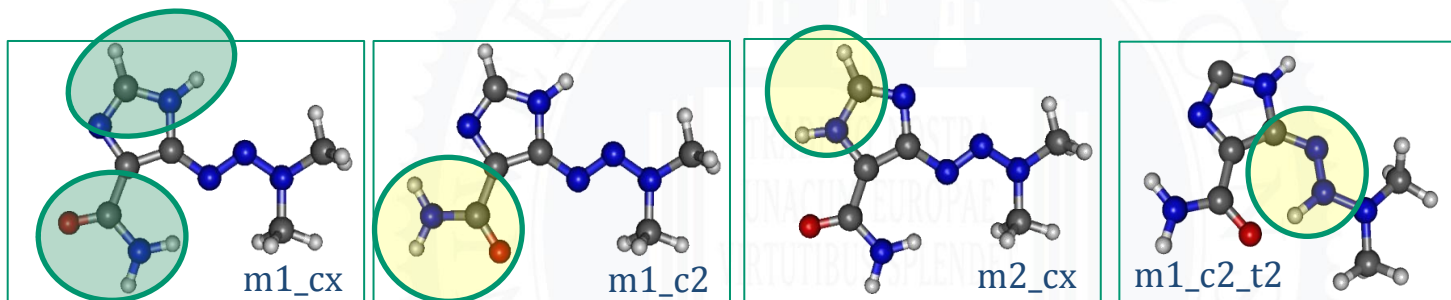
# TD-DFT Electronic absorption spectra of Dacarbazine
# DCB monomers – what's their energetic order?

Relative energies ($\Delta E_{HF}$ – light color, $\Delta G$ – dark color) of the DTIC monomers calculated at B3LYP/6-31+G(2d,2p) level of theory, in gas (grey) and water (blue)

$$P_i(\%) = \frac{e^{-\Delta E_i / kT}}{\sum_i e^{-\Delta E_i / kT}}$$



| Conformer | m2_cx | m1_cx | m1_c2 | m1_c3 | m2_c2 | m2_c3 | m1_c2_t2 |
|---|---|---|---|---|---|---|---|
| Relative Gibbs free energy in water (kcal/mol) | 0.00 | 0.88 | 0.88 | 4.5 | 6.51 | 8.09 | 55.02 |
| Boltzmann population at RT (%) | 69.14 | 15.41 | 15.41 | 0.03 | 0.00 | 0.00 | 0.00 |

# TD-DFT   Electronic absorption spectra of Dacarbazine
## DCB – UV-Vis spectrum

328 nm: S0-> S1 transition
236 nm: S0 -> S2 transition
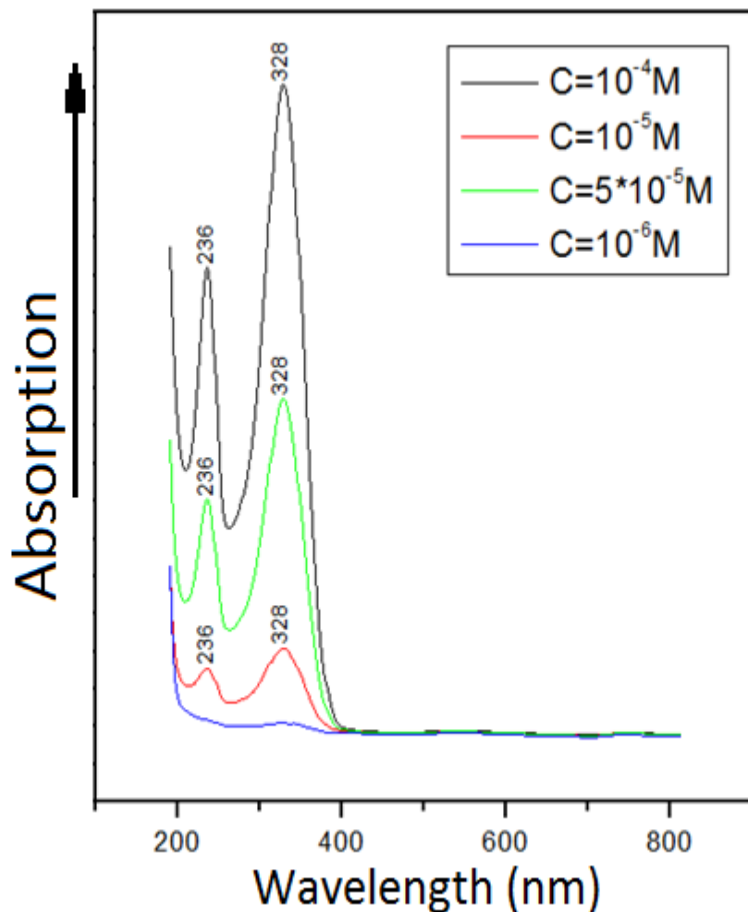


**B3LYP/6-31+G(2d,2p) Gas-phase**

| System | λ (nm) | f | Transitions | Contributions |
|---|---|---|---|---|
| m2_cx | 298 | 0.53 | H-L | 98% |
| | 233 | 0.11 | H-4-L | 61% |
| | 228 | 0.18 | H-3-L | 40% |

**B3LYP/6-31+G(2d,2p) Water**

| System | λ (nm) | f | Transitions | Contributions |
|---|---|---|---|---|
| m2_cx | 310 | 0.62 | H-L | 99% |
| | 232 | 0.28 | H-3-L | 79% |
| m1_cx | 323 | 0.61 | H-L | 90% |
| | 224 | 0.20 | H-4-L | 73% |
| m1_c2 | 320 | 0.68 | H-L | 99% |
| | 224 | 0.18 | H-4-L | 76% |

UV-Vis absorption
spectrum of Dacarbazine

# TD-DFT   Electronic absorption spectra of Dacarbazine

HOMO

LUMO

HOMO-4
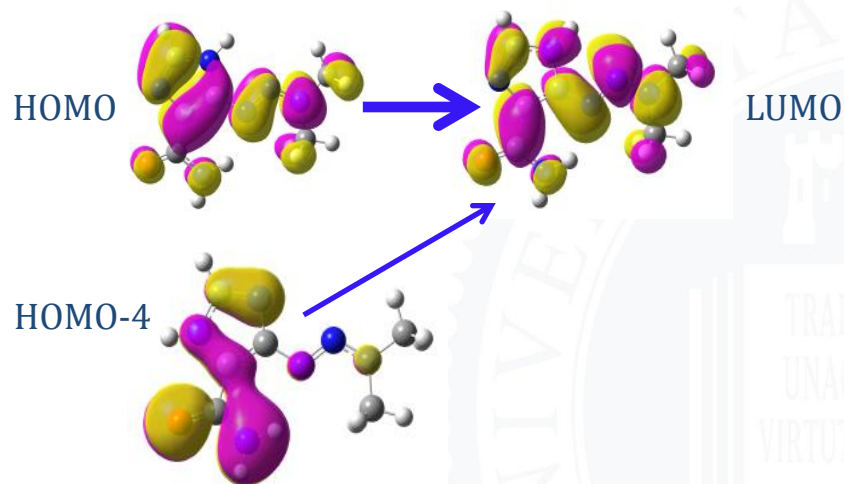
**HOMO-LUMO gap**
**284 nm (gas-phase)**
**290 nm   (water)**

**TD-DFT**
**298 nm (gas-phase)**
**310 nm  (water)**

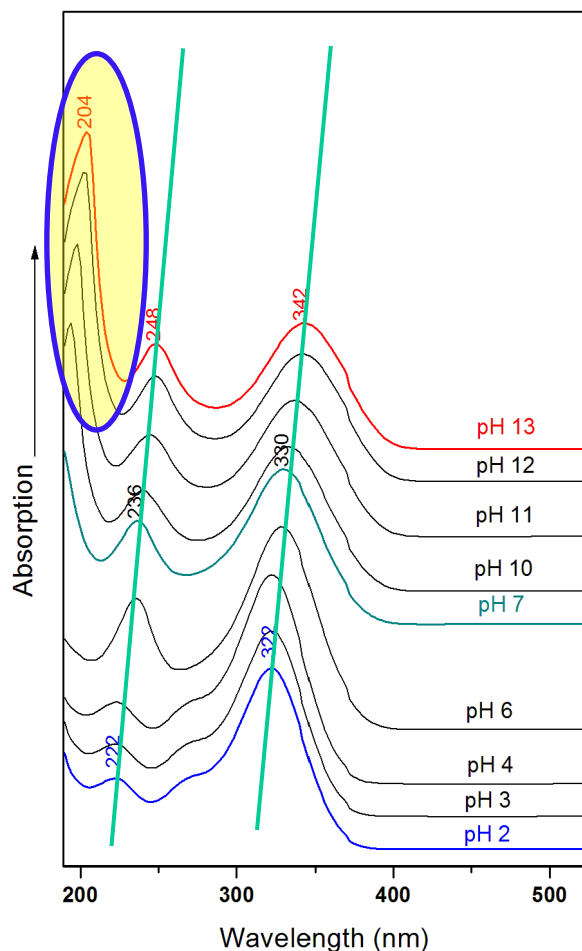**Conformer contributions averaged by the Boltzmann populations**
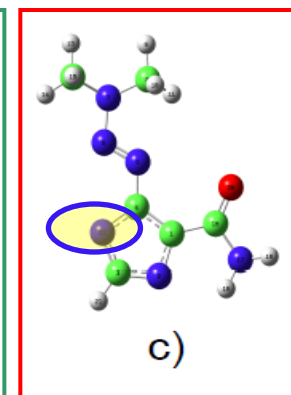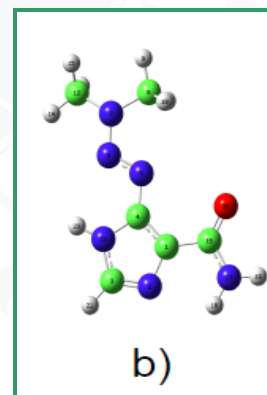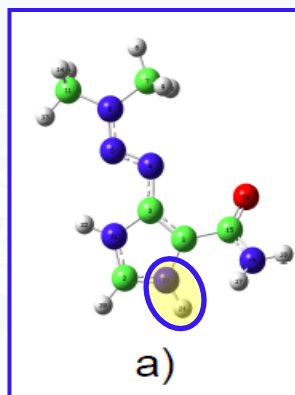**314 nm (water)**

**328 nm – Experimental**

# TD-DFT  Electronic absorption spectra of Dacarbazine
# DCB – UV-Vis spectrum – pH dependence



➢ **a new excitated state is active for electronic transition at high pH**

➢ **both peaks suffer a red shift by increasing pH**

➢ **the bathochromic shift is due to the presence of different species at different pH values:**

a)  **protonated at low pH**
b)  **neutral at medium pH**
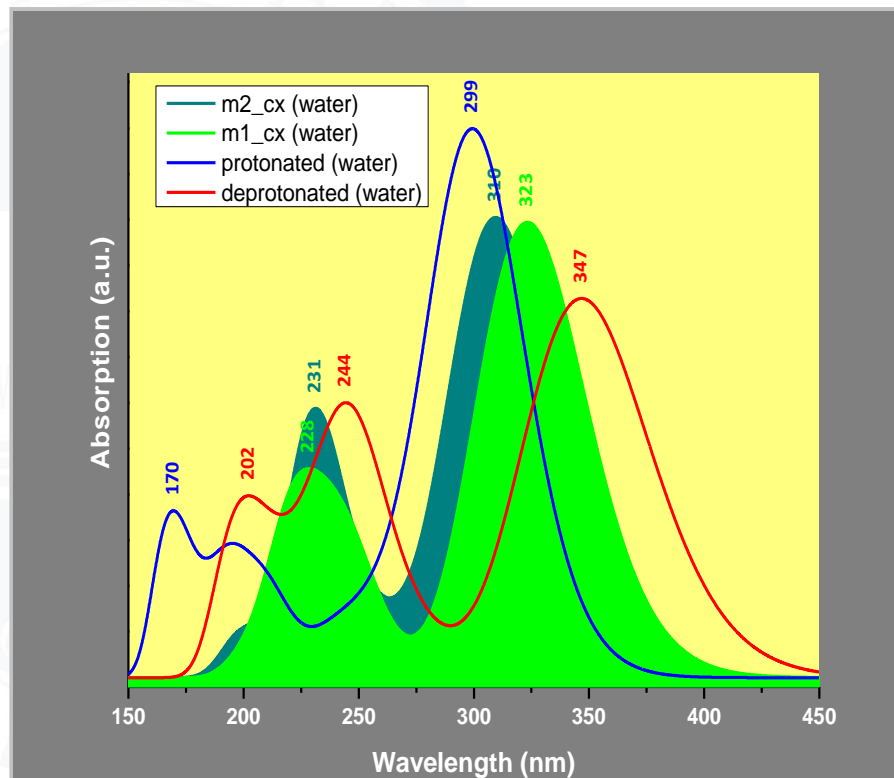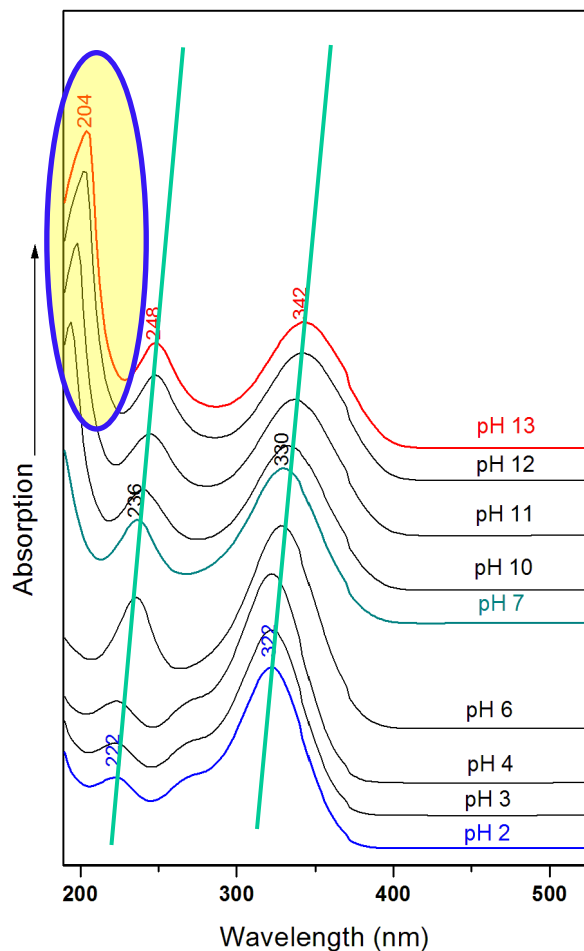c)  **deprotonated species at high pH**



m2 species of dacarbazine found at different pH values:
a) protonated; b) neutral; c) deprotonated

# TD-DFT  Electronic absorption spectra of Dacarbazine
# DCB – UV-Vis spectrum – pH dependence



**Protonated** ← → **Deprotonated**

➤ Calculations reproduce not anly the shifts of the transitions but also their relative intensities