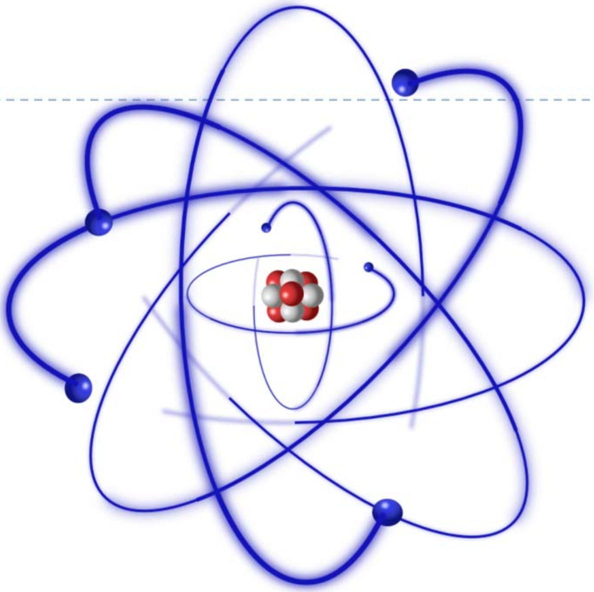


第七章：密度泛函理论方法

Why DFT

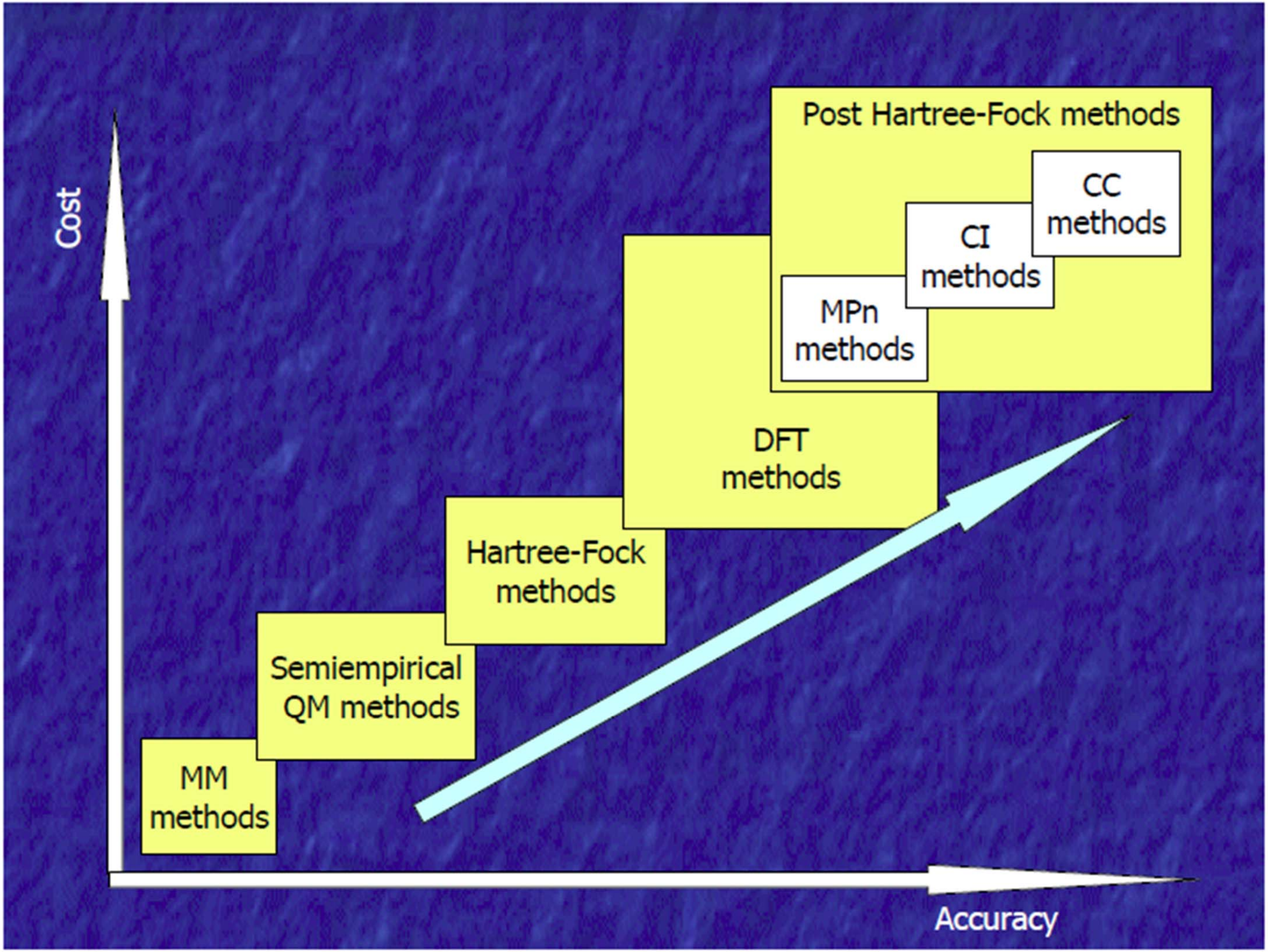
Density Functional Theory (DFT)

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	N^4	(N - # of basis functions)
CI methods scale as	N^6-N^{10}	
MPn methods scale as	$>N^5$	
CC methods scale as	$>N^6$	

⇨ **Correlated methods are not feasible for medium and large sized molecules!**



Cost
Post Hartree-Fock methods
CC methods
CI methods
MPn methods
DFT methods
Hartree-Fock methods
Semiempirical QM methods
MM methods
Accuracy

Background

- 1920s: Introduction of the Thomas-Fermi model.
- 1964: Hohenberg-Kohn paper proving existence of exact DF.
- 1965: Kohn-Sham scheme introduced.
- 1970s and early 80s: LDA. DFT becomes useful.
- 1985: Incorporation of DFT into molecular dynamics (Car-Parrinello)

  (Now one of PRL's top 10 cited papers).
- 1988: Becke and LYP functionals. DFT useful for some chemistry.
- 1998: Nobel prize awarded to Walter Kohn in chemistry for

  development of DFT.

Basic Theory: The electron density is the essential

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 ρ(r$_1$) is **the electron density**:

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

Properties of the electron density

- $\rho(\vec{r})$ 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:

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

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

$$\lim_{r_{iA}\to 0}\left[\frac{\delta}{\delta r} + 2Z_A\right]\overline{\rho}(\vec{r}) = 0$$

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

- decays exponentially for large distances from nuclei

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

I being the exact first ionization energy of the system

Function: $y=f(x)$ $\qquad$ $\rho = \rho(x,y,z)$

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

Hohenberg-Kohn Theorems

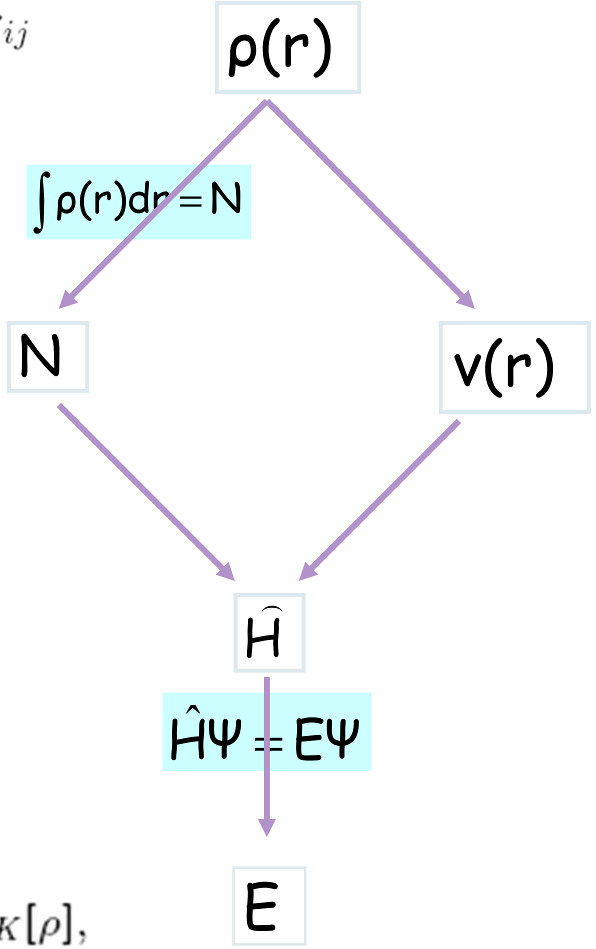
P. Hohenberg, W. Kohn, *Phys. Rev.* **136**, B 864 (1964)

The electronic Hamiltonian is

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

where the external potential is

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



First HK Theorem (HK1)

The external potential $V_{ext}(r)$ is (to within a constant) a unique functional of ρ(r).

Since, in turn $V_{ext}(r)$ fixes H, the full many particle ground state is a uniquefunctional of ρ(r).
Thus, the electron density uniquely determines the Hamiltonian operator and thus all the properties of the system.

$$E[\rho] = E_{Ne}[\rho] + T[\rho] + E_{ee}[\rho] = \int \rho(\vec{r}) V_{Ne}(\vec{r}) d\vec{r} + F_{HK}[\rho],$$

$$F_{HK}[\rho] = T[\rho] + E_{ee}.$$

$$\begin{tikzcd}
\boxed{\hat{V}_{ext}} \arrow[d, Rightarrow] \arrow[drr] & & & & \boxed{\hat{V}'_{ext}} \arrow[d, Rightarrow] \arrow[dll] \\
\boxed{\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}} \arrow[r, Rightarrow] & \boxed{\Psi} \arrow[r, Rightarrow] \arrow[d, Rightarrow] & \boxed{\rho(\vec{r})} & \boxed{\Psi'} \arrow[l, Rightarrow] \arrow[d, Rightarrow] & \boxed{\hat{H}' = \hat{T} + \hat{V}_{ee} + \hat{V}'_{ext}} \arrow[l, Rightarrow] \\
& \boxed{E_0} & \neq & \boxed{E'_0} &
\end{tikzcd}$$

Proof: Ψ' as a test function for H:

$$E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle =$$

$$= \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle$$

$$E_0 < E'_0 + \langle \Psi' | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} - \hat{T} - \hat{V}_{ee} - \hat{V}'_{ext} | \Psi' \rangle$$

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

Ψ as a testfunction for H':

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

Summing up the last two inequalities:

$$E_0 + E'_0 < E'_0 + E_0$$

Contradiction!

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

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

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

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

F_{HK} ???

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

$$E[\rho] = E_{Ne}[\rho] + T[\rho] + E_{ee}[\rho] = \int \rho(\vec{r})V_{Ne}(\vec{r})d\vec{r} + F_{HK}[\rho]$$

with

$$F_{HK}[\rho] = \boxed{T[\rho]} + E_{ee}$$

$$E_{ee}[\rho] = \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{non\_cl}[\rho] = \boxed{J[\rho]} + \boxed{E_{non\_cl}[\rho]}$$

Only J[ρ] is known!

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

$E_{non\_cl}[\rho]$ - contains all the effects of self-interaction correction and exchange and Coulomb correlation

Variational Principle in DFT

Second HK Theorem

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.

Total energy function: $E_{V\,ext}[\rho] = < \Psi|\hat{T}+\hat{V}|\Psi > + < \Psi|\hat{V}_{ext}|\Psi >$

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

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

$\rho(r) \geq 0$ and $\int \rho(\vec{r})d\vec{r} = N$

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.

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)

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

Problem in TF approximation: ignore correlation, and use local density approximation

Kohn and Sham (1965)

T[ρ] – kinetic energy of the system

Kohn and Sham proposed to 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 ρ(r)

Ψ_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 contains the major fraction of it

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

- **Hohenberg-Kohn (1964) and Kohn-Sham (1965) ---Modern DFT**

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

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

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

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

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

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

$E_{xc}[\rho]$ 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:

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

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

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

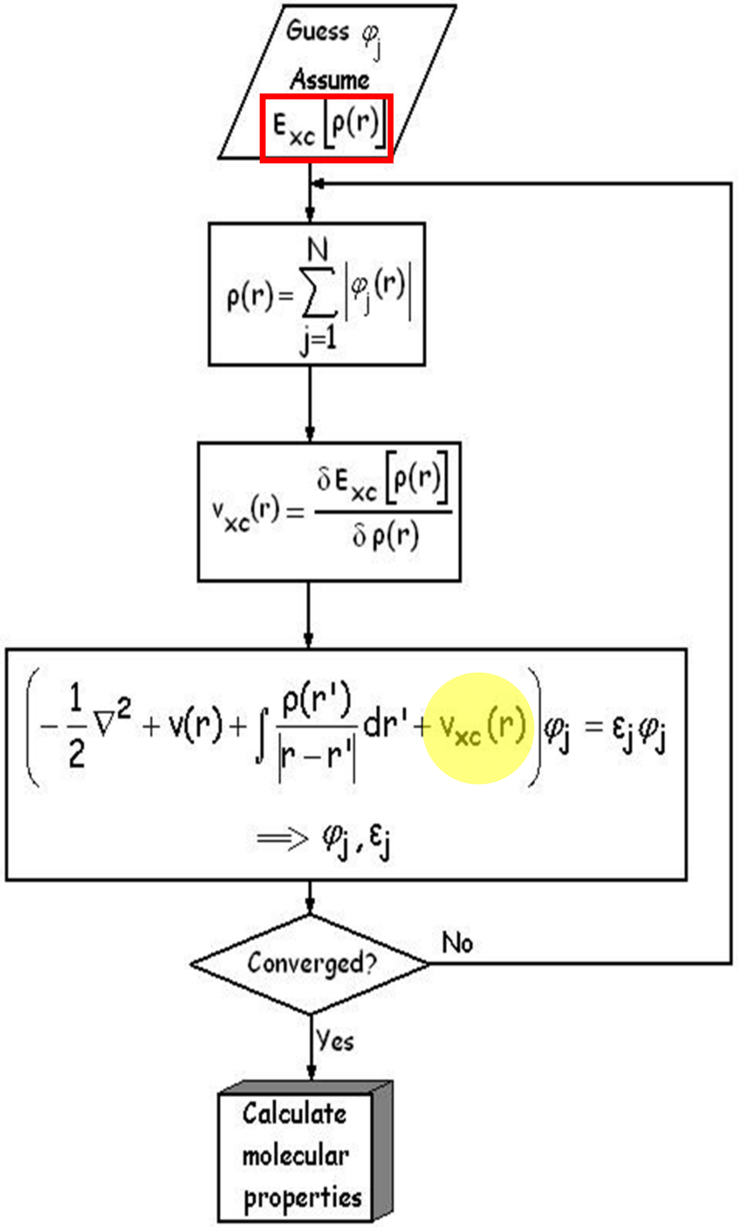
with:

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

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

Kohn-Sham Formalism

W. Kohn, L.J. Sham, *Phys. Rev.* **140**, A 1133 (1965)



Kohn-Sham equations

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

Hartree-Fock equations

$E_{xc}[\rho] = ??$

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

ε_{xc} – the exchange-correlation energy per particle of a uniform electron gas of density ρ(r)
- 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

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

Slater exchange functional (S)

For the correlation part:
Monte-Carlo simulations of the homogenous electron gas – Ceperly and Alder
--- interpolation of these results → analytical expressions of ε_c

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

- Perdew &Wang (1992)

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

Molecules do not resemble a uniform electron gas!

LDA

- Used by physicists for 40 years.

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

- $\varepsilon_{xc}(n)$ for homogenous electron gas.
  - exchange-correlation energy *per electron*
- Assumption: grad n is small in some sense.
- Accurate for nearly homogeneous system and for limit of large density.

Limitations

- Band gap problem
- Overbinding (cohesive energies 10-20% error).
- High spin states.
- Hydrogen bonds/weak interactions
- Graphite

Generalized Gradient Approximation (GGA)

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

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

ε_{xc} depends on the density and its gradient at r

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

$$E_{XC}^{GGA} = E_{X}^{GGA} + E_{C}^{GGA}$$

GGA 并不总是比LDA得到更好的结果，有时候会得到"更糟糕"的结果

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

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

- 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

(1) Adjust ε_{xc} such that it satisfies all (or most) known properties of the exchange-correlation hole and energy.

PW91, PBE…

(2) Fit ε_{xc} to a large data-set own exactly known binding energies of atoms and molecules.

BLYP, OLYP, HCTH…

Atomisation energies (kcal/mol)

	HF	LSD	PBE	EX
H2	84	113	105	109
CH4	328	462	420	419
C2H2	294	460	415	405
C2H4	428	633	571	563
N2	115	267	243	229
O2	33	175	144	121
F2	-37	78	53	39

Hybrid functionals

- Why not just add correlation to HF calculations? We could write $E_{XC}=E_X[\text{exact}]+E_C[\text{LSD}]$

- Correct XC hole is localised.
- Exchange and correlation separately are delocalised.
- DFT in LDA and GGA give localised expressions for both parts.
- Sometimes simpler is better!

Hybrid Functionals

Since EX>>EC, an accurate expression for the exchange functional is a prerequisite for obtaining meaningful results from density functional theory.

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

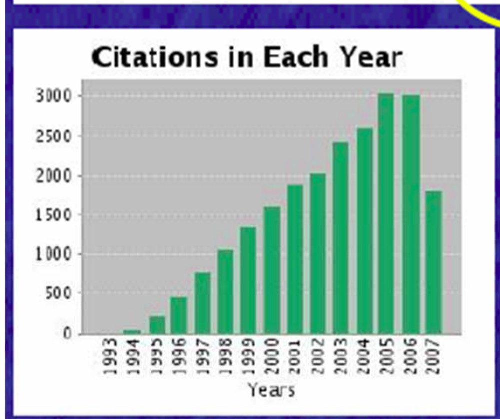
E_X^{KS}-the exact exchange calculated with the exact KS wave function

α- fitting parameter

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

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

a = 0.20, b = 0.72, and c = 0.81



corresponds to the exchange contribution of a Slater determinant

B3LYP, B1LYP, mPW0, PBE0, HSE03/06

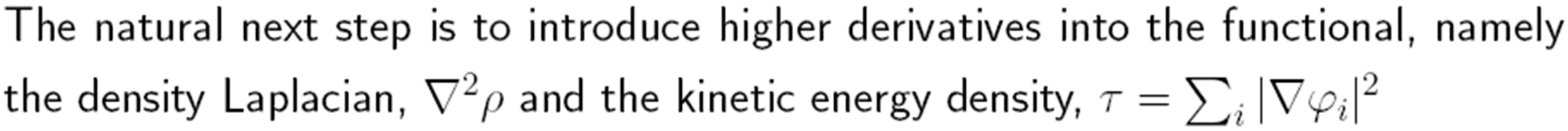
PBE1PBE (Perdew, J. P., Burke, K. & Ernzerhof, M. 1996 *Phys. Rev. Lett.* **77**, 3865–3868, 1996)

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

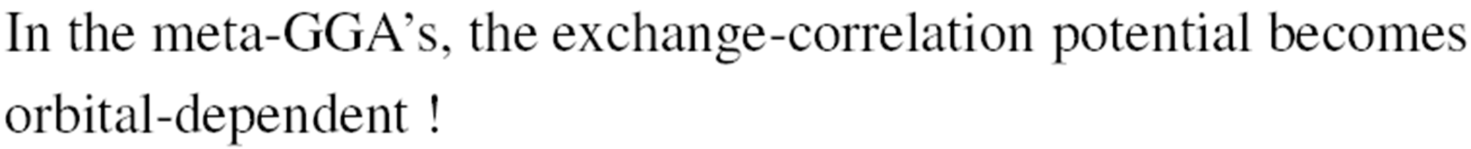
GGA = PBE

Meta-GGAs

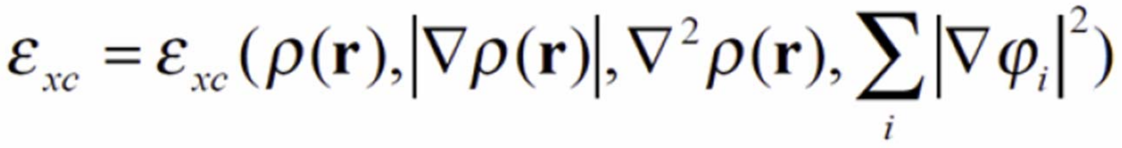
- Perdew 1999
- Better total energies.
- Ingredients: $\nabla^2 n$, KE density
- Very hard to find potential, so cannot do SCF with this.
- Therefore structural optimisation not possible.



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 !



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

HSE03/06

Recent development. Several motivations:

- B3LYP more accurate than BLYP. Some admixture of exchange needed.
- Exact exchange is slow to calculate.
- Linear scaling K-builds don't scale linearly in general.
- Plane wave based (physics) codes can't easily find exact exchange.

Screened Exchange

- Key idea (Heyd, Scuseria 2003):

$$\frac{1}{r}=\frac{\operatorname{erfc}(\omega r)}{r}+\frac{\operatorname{erf}(\omega r)}{r}$$

- First term is short-ranged; second long ranged.
- w=0 gives full 1/r potential.
- How to incorporate into a functional?

HSE03

$$
\begin{aligned}
E_x^{PBE0} &= aE_x^{HF} + (1-a)E_x^{PBE} \\
&= aE_x^{HF,SR} + aE_x^{HF,LR} + (1-a)E_x^{PBE,SR} + \\
&\qquad (1-a)E_x^{PBE,LR} \\
&\approx aE_x^{HF,SR} + (1-a)E_x^{PBE,SR} + E_x^{PBE,LR} \\
&= E_x^{PBE} + a\left[E_x^{HF,SR} - E_x^{PBE,SR}\right]
\end{aligned}
$$

How about the accuracy?

- Enthalpies of formation (kcal/mol):

	MAE(G2)	MAE(G3)
B3LYP	3.04	4.31
PBE	17.19	22.88
PBE0	5.15	7.29
HSE03	4.64	6.57

Conclusion: competitive with hybrids.

How about the accuracy?

- Vibrational freqs (cm-1); 82 diatomics

	MAE(G2)
B3LYP	33.5
PBE	42.0
PBE0	43.6
HSE03	43.9

Conclusion: competitive with hybrids.

How about the accuracy?

- Band Gaps (eV)

	LDA	PBE	HSE	EXP
C	4.23	4.17	5.49	5.48
Si	0.59	0.75	1.28	1.17
Ge	0.00	0.00	0.56	0.74
GaAs	0.43	0.19	1.21	1.52
GaN	2.09	1.70	3.21	3.50
MgO	4.92	4.34	6.50	7.22

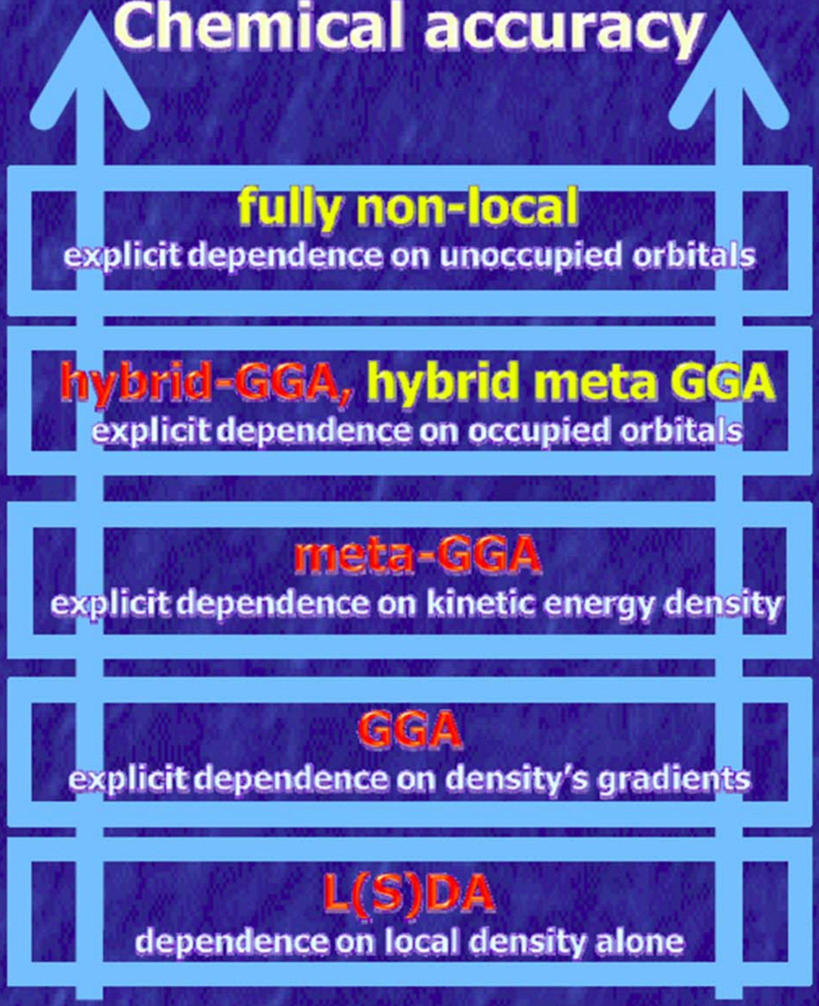
Jacob's ladder of DFT

SCIENCE'S COMPASS

PERSPECTIVES: DENSITY FUNCTIONAL THEORY

In Pursuit of the "Divine" Functional

Ann E. Mattsson



Chemical accuracy

unocc. $\{\varphi_i\}$ — **fully non-local**
explicit dependence on unoccupied orbitals
Görling-Levy, 1994;
Engel-Dreizler, 1999;
Bartlett et el., 2005;
B2-PLYP (Grimme et el., 2006)

occ. $\{\varphi_i\}$ — **hybrid-GGA, hybrid meta GGA**
explicit dependence on occupied orbitals
B3LYP, PBE1PBE
PKZB, TPSS

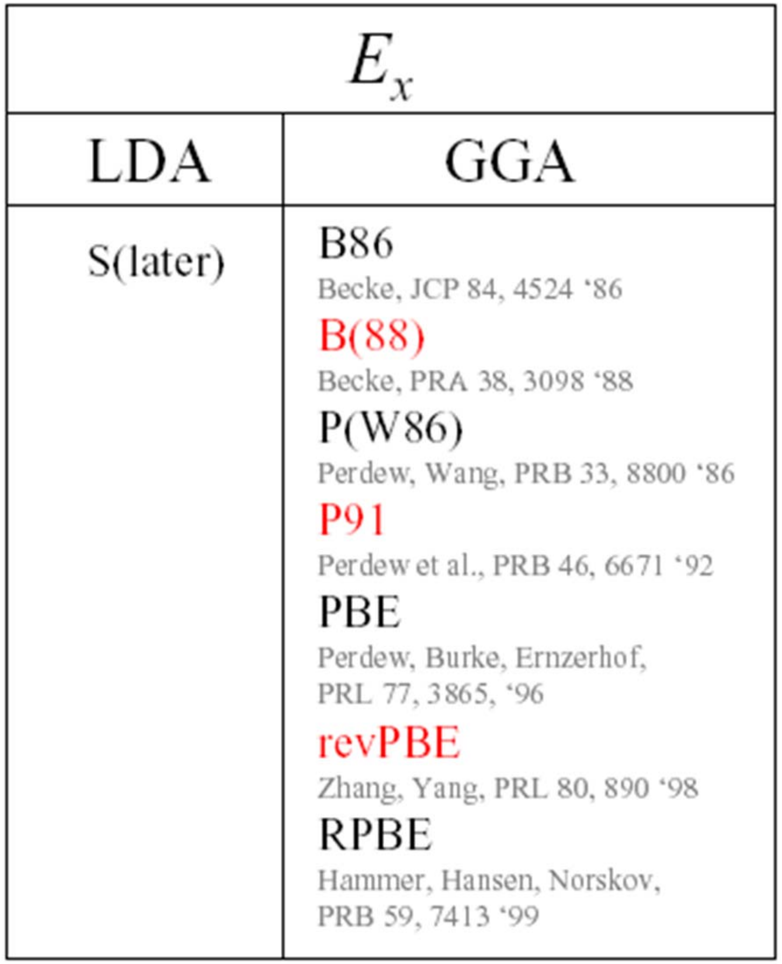
$\nabla^2\rho$ — **meta-GGA**
explicit dependence on kinetic energy density
Proynov-Salahub-95

$\nabla\rho$ — **GGA**
explicit dependence on density's gradients
B88-P86,
PW91, PBE

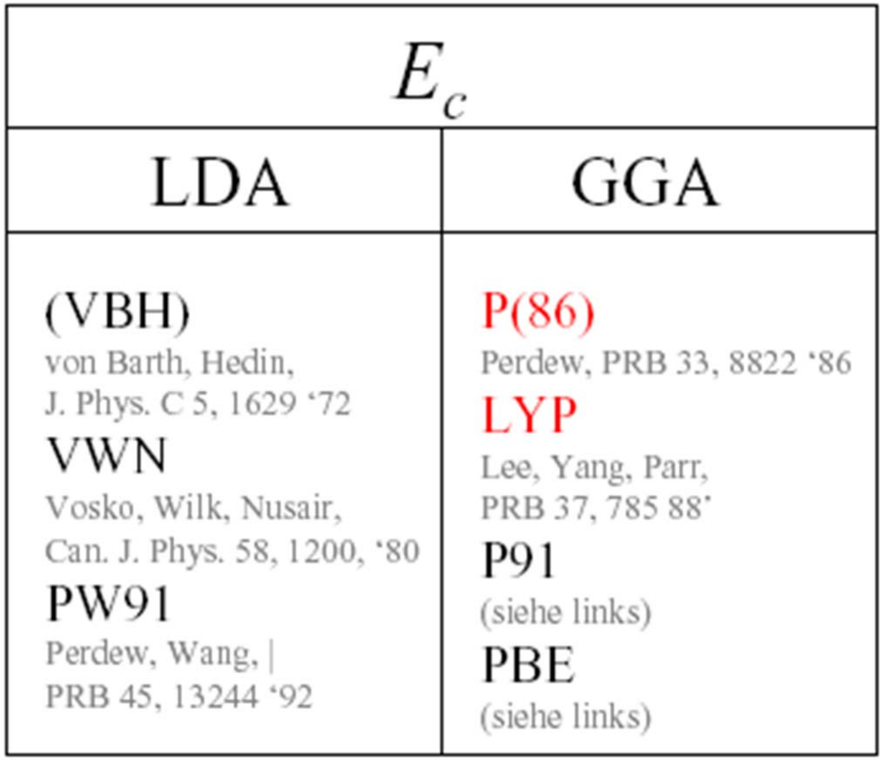
ρ — **L(S)DA**
dependence on local density alone
S-VWN

Hartree world

Exchange and Correlation Functionals



E_x	
LDA	GGA
S(later)	B86 Becke, JCP 84, 4524 '86 B(88) Becke, PRA 38, 3098 '88 P(W86) Perdew, Wang, PRB 33, 8800 '86 P91 Perdew et al., PRB 46, 6671 '92 PBE Perdew, Burke, Ernzerhof, PRL 77, 3865, '96 revPBE Zhang, Yang, PRL 80, 890 '98 RPBE Hammer, Hansen, Norskov, PRB 59, 7413 '99



E_c	
LDA	GGA
(VBH) von Barth, Hedin, J. Phys. C 5, 1629 '72 VWN Vosko, Wilk, Nusair, Can. J. Phys. 58, 1200, '80 PW91 Perdew, Wang, | PRB 45, 13244 '92	P(86) Perdew, PRB 33, 8822 '86 LYP Lee, Yang, Parr, PRB 37, 785 88' P91 (siehe links) PBE (siehe links)

ab-initio functionals:
fitted to theoretical data

semiempirical functionals:
fitted to experimental data

In practice: BLYP, B3LYP, BPW91, …

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 (τ) 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

S.F. Sousa, P.A. Fernandes, M.J. Ramos, J.Phys.Chem.A, 111, 10439 (2007)
Yi-Gui Wang, *J. Phys. Chem. A* 2009, *113,* 10867–10872
Gaussian 03

Comparison of methods: e.g. H_2O

	E_{tot}	H-O	∠HOH	vibrational modes [cm^{-1}]			dipole moment
method	[a.u.]	[Å]	[°]	bending	sym. stretch	asym. stretch	[D]
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, π-π interactions

What functional should I use?!

Depends on:
- your problem (system, the property investigated)
- availability and the computational costs

Atomization energies: SVWN<<BP86<BLYP≈BPW91<<B3P86<B3LYP≈B3PW91

Ionization energy: - B3LYP – the best!

Electron afinities: BLYP ≈ BPW91 ≈ B3LYP

Vibrational frequencies: - (BLYP), B3LYP, …

MO5-2X - bond dissociation energies, **stacking and hydrogen-bonding interactions** in nucleobase pairs

Exchange-Correlation Functional

交换相关泛函的“好”与“不好”并不在于泛函本身，而在于**如何在描述合适的体系使用正确的泛函**