Accounting of electron correlation effects

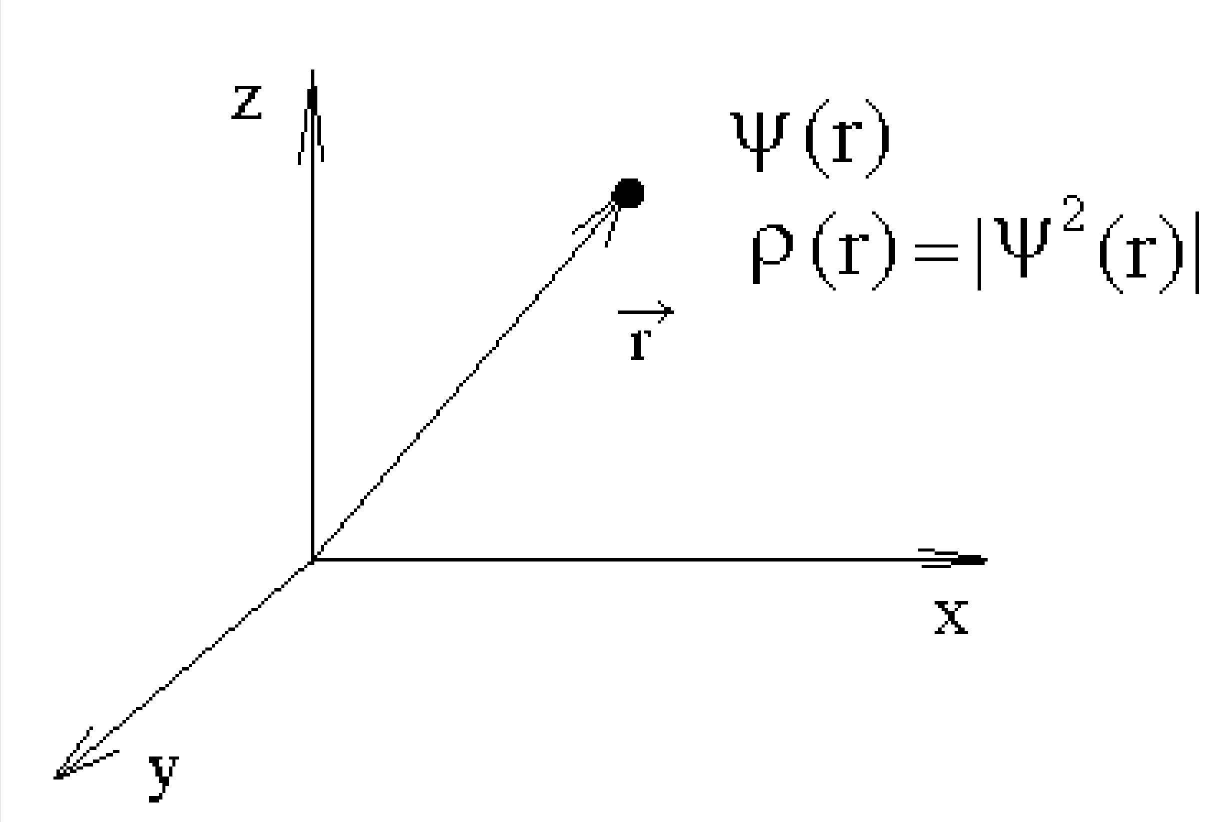
IV. Density Functional Theory

V. Ivanov

Gaussian, GAMESS, ADF

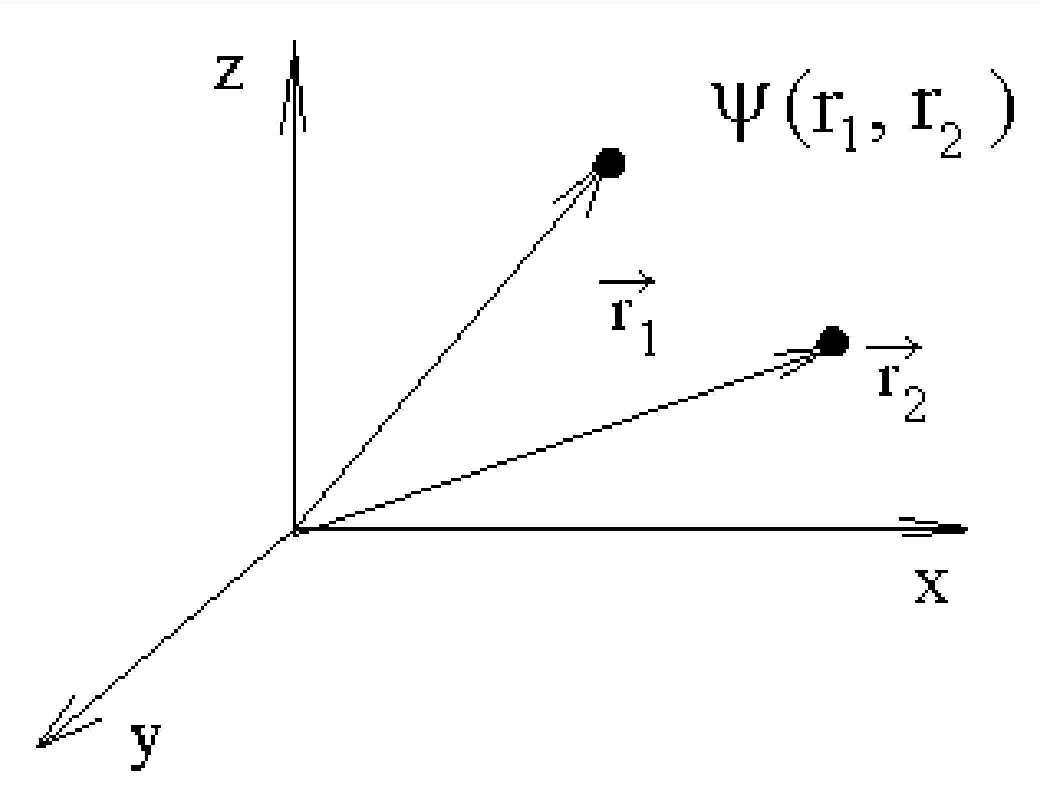
Chemical Materials Department
V. N. Karazin National University,
61077, Kharkov, Ukraine
vivanov@karazin.ua

The wave function



$$\int \rho(r)dr = 1$$

Two-electron system



$$\Psi(r_1, r_2, r_3, \ldots r_N) = \Psi(1,2,3,\ldots N)$$

$$\Psi(1,2,\ldots,i,\ldots,j,\ldots N) = -\Psi(1,2,\ldots,j,\ldots,i,\ldots N)$$

$$\rho_N(123\ldots N) \rightarrow \rho_{N-1}(123\ldots N-1) \rightarrow \ldots \rightarrow \rho_2(12) \rightarrow \rho$$

Walter Kohn (1923-2016)

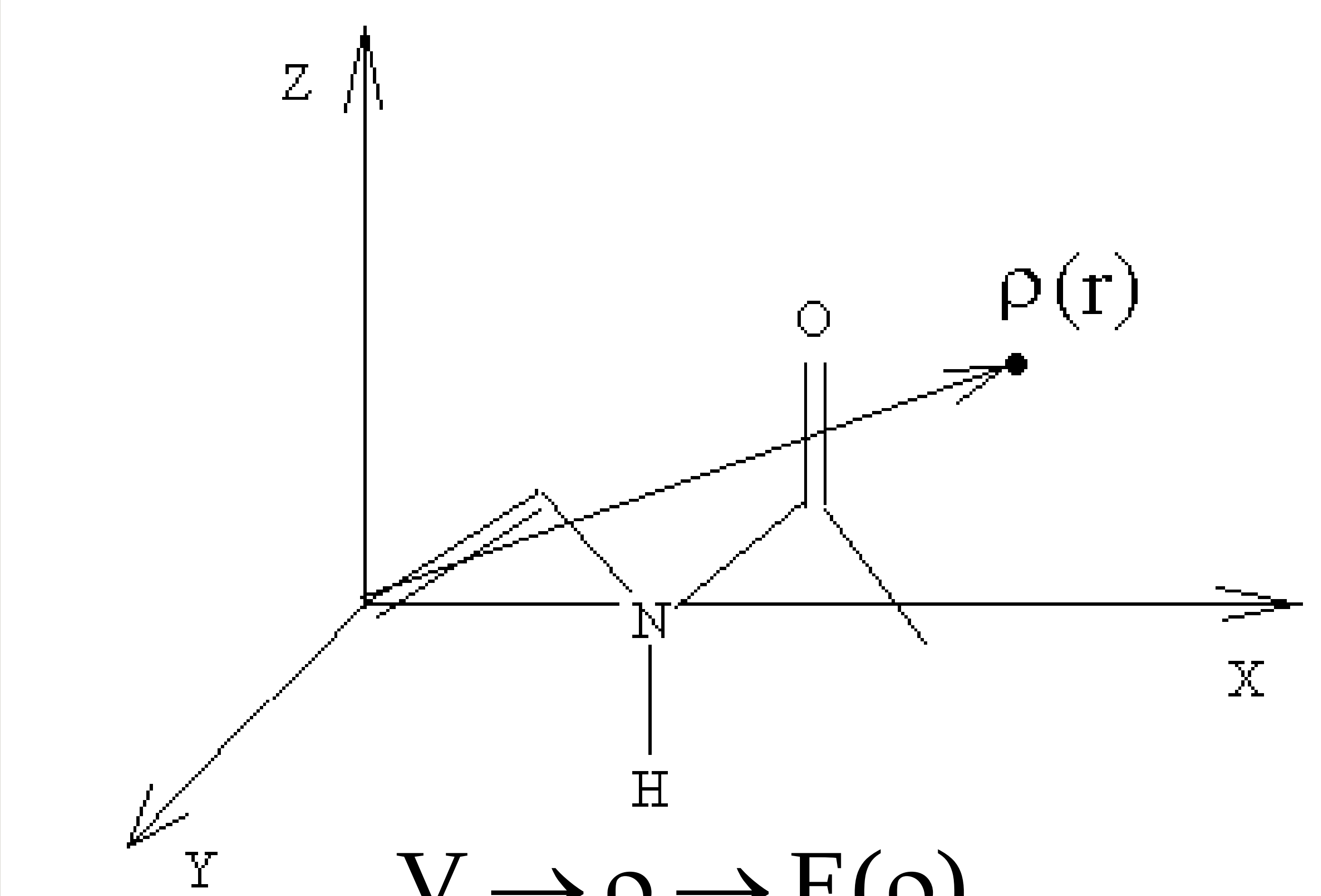
“… *In general the many-electron wave function for a system of N electrons is not a legitimate scientific concept, when N > 1000.* ”

W. Kohn **Nobel Lecture: Electronic structure of matter—wave functions and density functionals.**

Reviews of Modern Physics, Vol. 71, No. 5, 1999, P. 1253

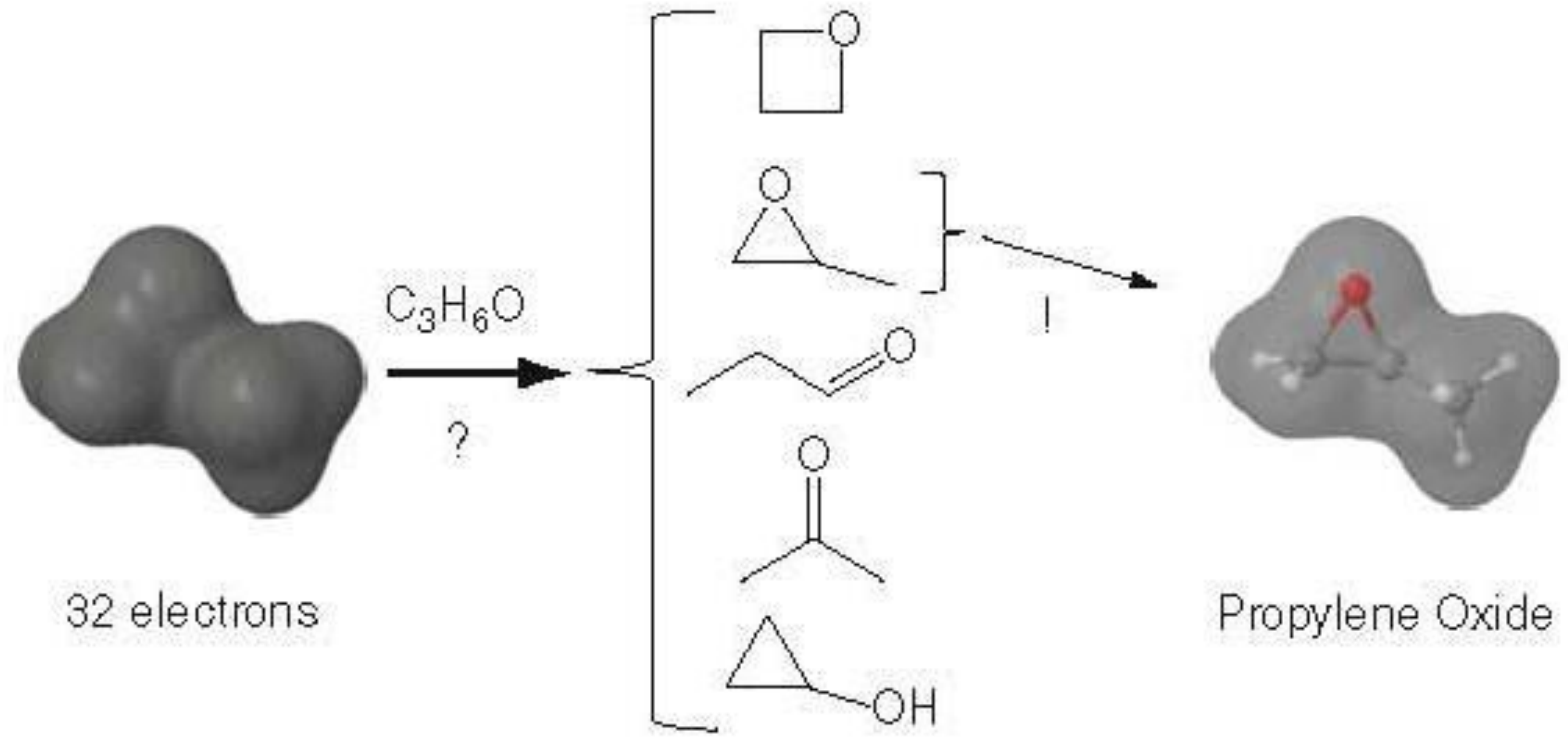
Density Functional Theory (DFT)

Hohenberg-Kohn Theorem



$$\begin{tikzcd} V \arrow[r] & \rho \arrow[r] & E(\rho) \arrow[ll, bend left] \end{tikzcd}$$

Hohenberg-Kohn Theorem



Thomas-Fermi theory (1927)

Kinetic energy of homogeneous electron gas in atom

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

Total energy as a function of electron density

$$E_{TF}[\rho(\vec{r})] = T_{TF}[\rho(\vec{r})] - Z\int \frac{\rho(\vec{r})}{\vec{r}}d\vec{r} + \frac{1}{2}\int\int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|}dr_1 dr_2$$

Drawback: **Neglect of exchange and correlation effects**

Approximation to the Hartree-Fock exchange term (Slater, 1951)

$$E_X = \tfrac{1}{2}\iint \frac{\rho(r_1)h_X(r_1,r_2)}{|r_1 - r_2|}dr_1dr_2$$

Wigner-Seitz radius
(a sphere that contains an electron)

$$r_s = \left(\frac{3}{4\pi}\right)^{1/3}\rho(r_1)^{-1/3}$$

Potential ~1/r_s

$$E_X[\rho] \approx C_X \int \rho(r_1)^{4/3}dr_1$$

Xα method

$$E_{X\alpha}[\rho] \approx -\frac{9}{8}\left(\frac{3}{\pi}\right)^{1/3}\alpha\int \rho(r_1)^{4/3}dr_1$$

Hohenberg-Kohn Theorem

$$\begin{tikzcd}[column sep=small]
V \arrow[dr] & \neq & V' \arrow[dl] \\
& \rho(r) &
\end{tikzcd}$$

$$H = T + V_{ee} + V \qquad H' = T + V_{ee} + V'$$

$$H|\Psi\rangle = E|\Psi\rangle \qquad H'|\Psi'\rangle = E'|\Psi'\rangle$$

$$E \neq E'$$

$$V \Rightarrow H \Rightarrow \Psi \Rightarrow \rho(r) \Leftarrow \Psi' \Leftarrow H' \Leftarrow V'$$

Hohenberg-Kohn Theorem

$$E < \langle \Psi' | H | \Psi' \rangle$$

$$H = T + V_{ee} + V = T + V_{ee} + V + V' - V' = H' + V - V'$$

$$\langle \Psi' | \left(H' + V - V' \right) | \Psi' \rangle \qquad E < E' + \langle \Psi' | V - V' | \Psi' \rangle$$

$$E' < \langle \Psi | H' | \Psi \rangle = E + \langle \Psi | V' - V | \Psi \rangle = E - \langle \Psi | V - V' | \Psi \rangle$$

$$\langle \Psi | V - V' | \Psi \rangle = \mathrm{Sp}\Big(| \Psi \rangle \langle \Psi | (V - V') \Big) = \int \rho(r)(V - V')dr$$

$$E < E' + \int \rho(r)(V - V')dr$$

$$E' < E - \int \rho(r)(V - V')dr$$

$$E + E' < E' + E$$

Density Functional Theory

Hohenberg-Kohn Theorem $V \rightarrow \rho$

$$E = \mathrm{Min}_{\rho} E_V[\rho] \qquad \int \rho(r)dr = N$$

$$E_V[\rho] = \underbrace{\int V(r)\rho(r)dr}_{\text{Depends from the system}} + \underbrace{\frac{1}{2}\int \frac{\rho(r)\rho(r')}{|r-r'|}drdr' + T[\rho] + E_{xc}[\rho]}_{\text{Universal Contributions}}$$

$$V(r) = -\sum_M \frac{Z_M}{|r-R_M|}$$

«External» potential

$$\Psi(1,2,\ldots,i,\ldots,j,\ldots N) = -\Psi(1,2,\ldots,j,\ldots,i,\ldots N)$$

$E_{xc}[\rho]$ Exchange correlation functional

Kohn-Sham orbitals

$$\rho(r) = 2\sum_i |\varphi_i(r)|^2$$ φ_i -Kohn-Sham orbitals

$$T[\rho] = \sum_i \left\langle \varphi_i \left| -\frac{\nabla^2}{2} \right| \varphi_i \right\rangle$$

Hartree-Fock molecular orbitals describe the distribution of electrons in the effective field of nuclear and all other electrons.

Kohn-Schem orbitals are orbitals that correspond to a certain electron density of the system (representation of density).

Kohn-Sham DFT equation

$$\left(-\frac{\nabla^2}{2}+V(r)+\int\frac{\rho(r')}{|r-r'|}dr+V_{XC}(r)\right)\varphi_i=\varepsilon_i\varphi_i$$

$V_{XC}(r)$ - exchange correlation functional

1) Local Density Approximation, LDA

$$E_{LDA}[\rho]=\int\rho(r)e(r)dr$$

$$E_{LDA}[\rho]=\int\rho(r)e(\rho)dr$$

Representation problem

$$\Psi(1,2,\ldots,i,\ldots,j,\ldots N) = -\Psi(1,2,\ldots,j,\ldots,i,\ldots N)$$

$$\rho_N = \Psi^*(1,2,\ldots,i,\ldots,j,\ldots N)\Psi(1,2,\ldots,i,\ldots,j,\ldots N)$$

Generalized Gradient Approximation (GGA)

$$\mathrm{E_{GGA}[\rho] = \int \rho(r)e(\rho(r), \nabla\rho)dr}$$

BLYP – Becke, Lee, Yang, Parr; **P86** – Perdue; **P96** – Becke

Hybrid approximation (hybrid-GGA)

$$\mathrm{E_{XC-hyb}[\rho] = \alpha E_{LDA} + (1-\alpha)E_{XC-GGA}}$$

B3LYP – Becke, Lee, Yang, Parr **B3P86** – Becke, Perdue

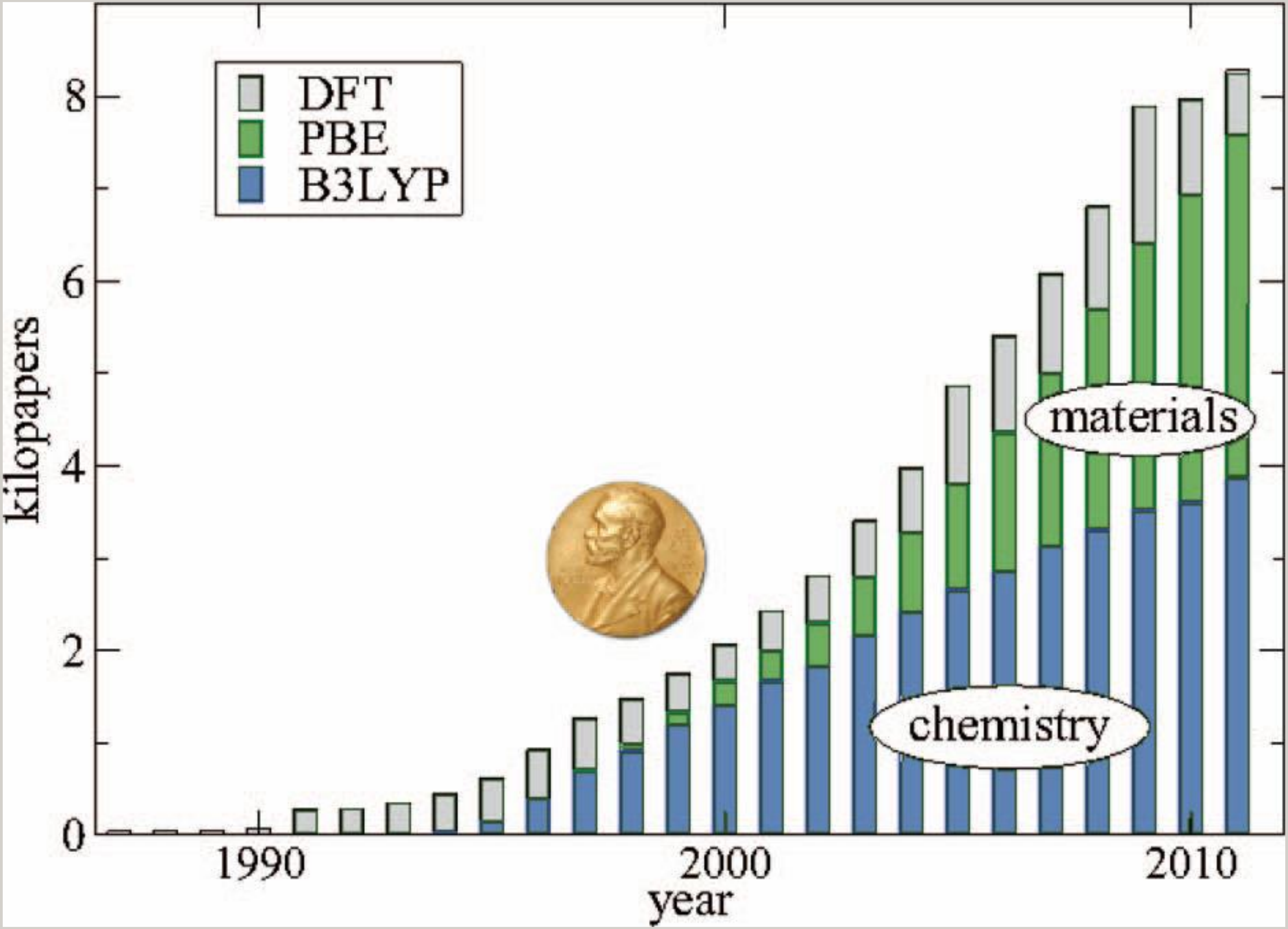
$$e_x^{PW96} = e_x^{LDA}(1 + ax^2 + bx^4 + cx^6)^{1/3} \qquad \mathrm{x} = \frac{|\nabla\rho|}{\rho^{4/3}}$$

Possibility to describe intermolecular interaction

M05 (Zhao et al. 2005, 2006),
M06 (Zhao, Truhlar 2006, 2008)

Different types of functionals

Acronyms	Description	Type
Xα		Exchange
HFS	Hartree-Fock-Slater	HF with LDA exchange
VWN	Vosko, Wilks, Nusair	LDA
BLYP	Becke, Lee,Yang, Parr	Gradient
B3LYP, Becke3LYP	Becke, Lee,Yang, Parr	Hybrid
PW91	Perdue, Wang, 1991	Gradient
G96	Gill, 1996	Exchange
P86	Perdue, 1986	Gradient
B96	Becke, 1996	Hybrid
B3P86	Becke exchange + Perdue correlation	Hybrid
B3PW91	Becke обмен + Perdue,Wang correlation	Hybrid


DFT
PBE
B3LYP
materials
chemistry
kilopapers
0
2
4
6
8
1990
2000
2010
year


wB97
OBPW
LM81
X3LYP
PW92
SAOP
BNL05
PW91
EB08
M06-L
KMLYP
TLYP
PBE
LYP
V5LYP
WC06
PBEsol
LB9483
VP86
wB97XD
wB97X
MCY06
B2PLYP
FT97
BOP
BMK04
WI
GL76
PBEOP
B97
rPBE
CS1
B3LYP
EXX
B97-2
Bh3LYP
rB86
DK87
GV09
vBH
M05-2X
WL
TPSSh
HSE
OPTX
BR89
KT2
muB88
HL71
xPBE
M06-2X
M06-HF
mPW
revPBE
M0
HCTH
PKZB99
PBE0
muPBE
LRC-wPBE0
PL81
BP86
LG93
KCIS
LSDA
KT1
lhf
VWN5
wigner
O3LYP
SOGGA
RPA
LC-wPBE
B88
B95
BRC89
PZ81
TPSS
PK06
BJ06
B97-D
B86-mgc
EDF1
VS98
AM05
B94
GG99
PW86
B97-1
EDF2
mPBE
G96
CAM-B3LYP
wPBE
VWN1
KT3
Peter Elliott
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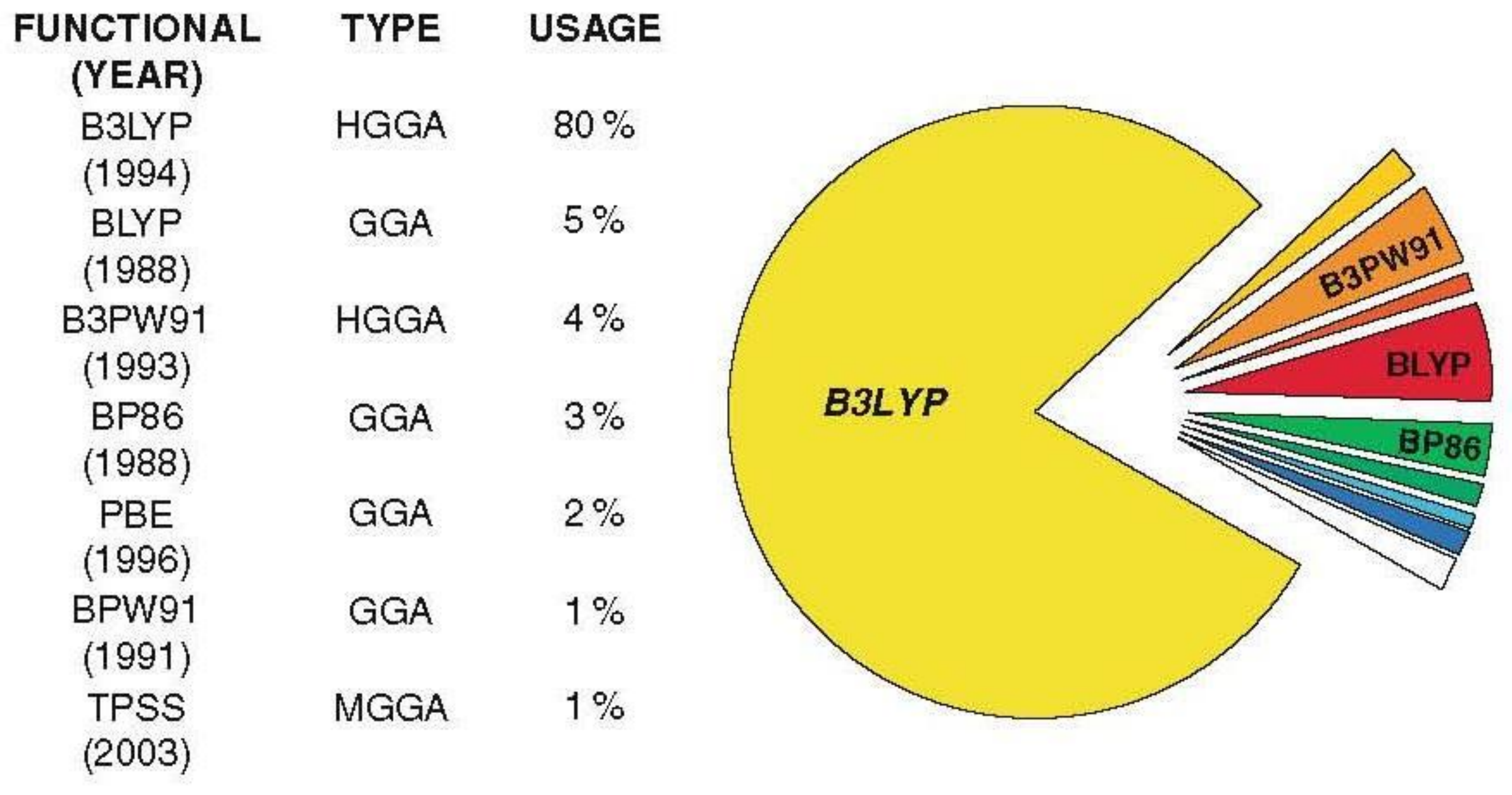
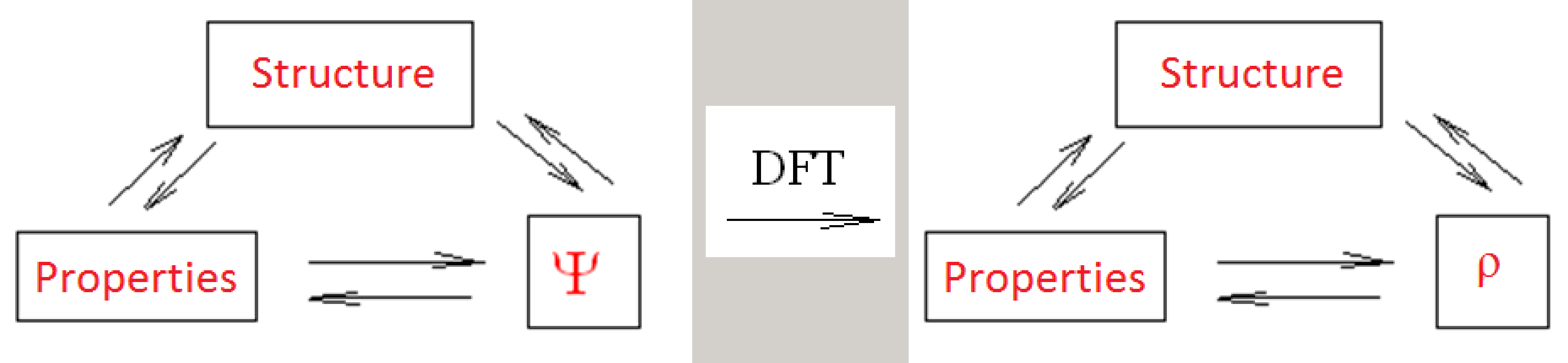


FUNCTIONAL (YEAR)	TYPE	USAGE
B3LYP (1994)	HGGA	80 %
BLYP (1988)	GGA	5 %
B3PW91 (1993)	HGGA	4 %
BP86 (1988)	GGA	3 %
PBE (1996)	GGA	2 %
BPW91 (1991)	GGA	1 %
TPSS (2003)	MGGA	1 %

From *Handbook of Computational Chemistry*,
Springer 2012, Leszczynski (ed.)

The central paradigm of quantum chemistry



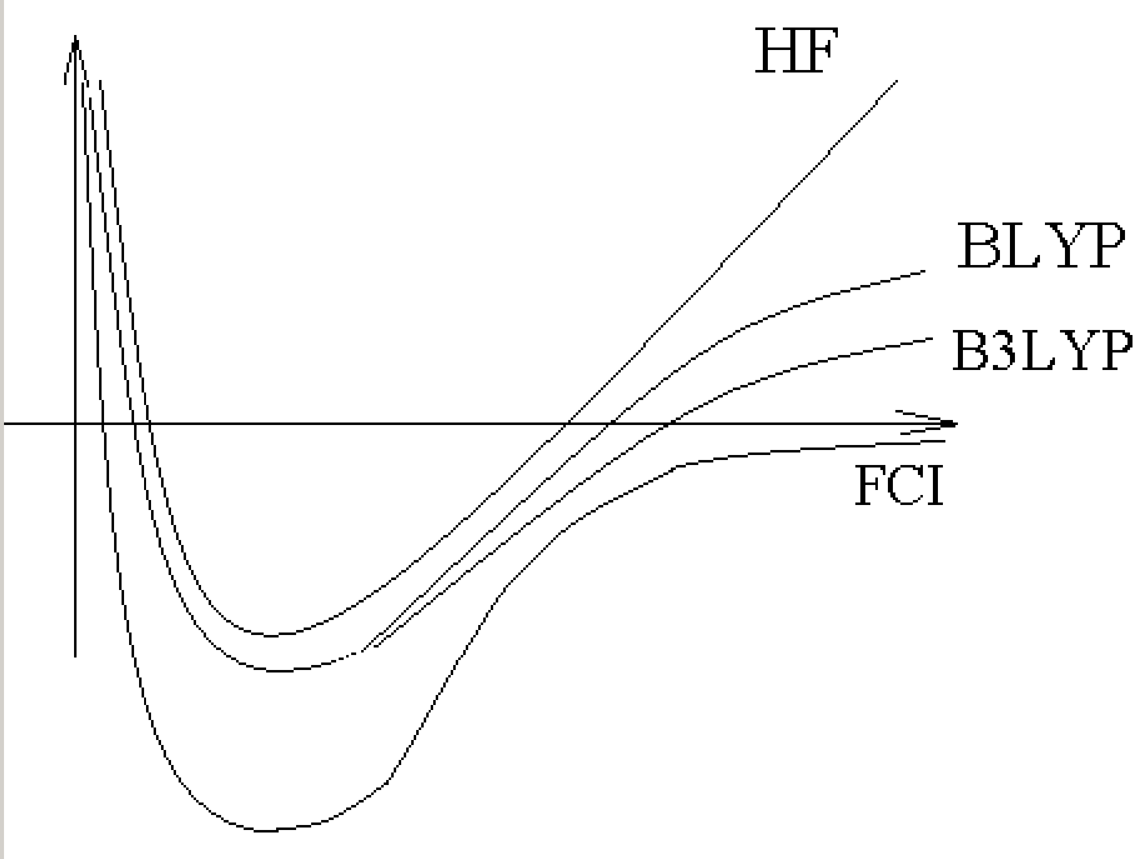
DFT and other methods (errors in description of formation enthalpy кcal/mol. 148 molecules)

Метод	Δabs	Δpos	Δneg
G2(MP2)	2.04	10.1	-5.3
LDA(SVWN)	91.16	228.7	-
BLYP	7.09	28.4	-24.8
BP86	20.19	49.7	-6.3
B3LYP	**3.11**	**8.2**	**-20.1**
MNDO	9.32	27.6	116.7
AM1	7.81	42.5	-58.2
PM3	7.01	23.1	-32.2

Harmonic frequencies (cm^{-1}) O_3 cc-pVTZ

метод	ω_1 (symm)	ω_2 (asymm)	ω_3 (def)
HF	1537 (402)	1418 (329)	867 (151)
MP2	1166 (31)	2241 (1152)	743 (27)
MP4	1106 (29)	1592 (503)	695 (21)
CCSD	1278 (143)	1267 (178)	762 (46)
CISD	1407 (272)	1535 (466)	816 (100)
CASSCF(2,2)	1189 (54)	1497 (408)	799 (83)
BLYP	1130 (5)	980 (109)	683 (33)
B3LYP	1252 (117)	1194 (105)	746 (30)
B3PW91	1288 (153)	1244 (155)	762 (46)
Эксп.	1135	1089	716

N_2 dissociation



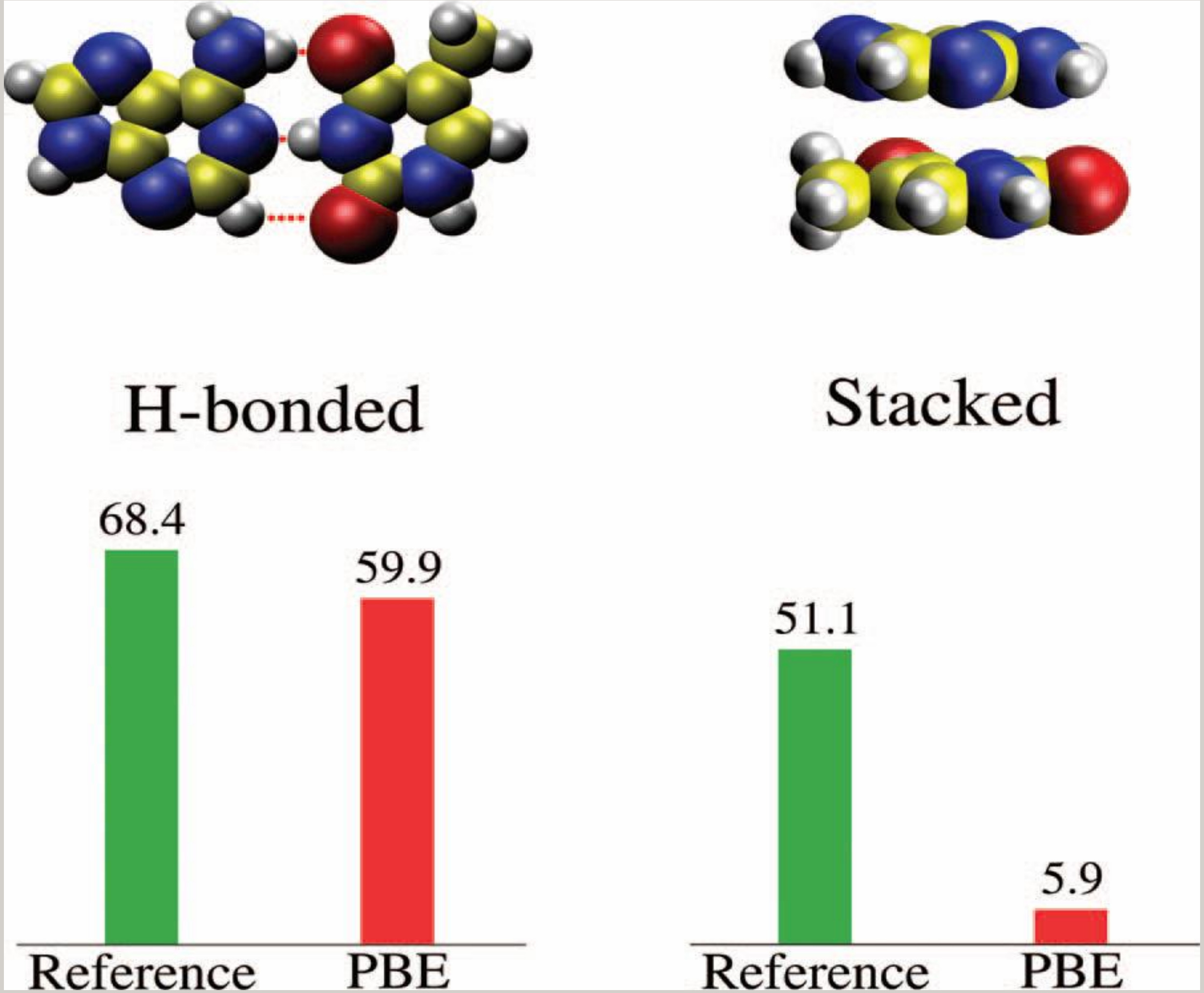
$$\text{TZP:}\ (16s,6p,2d,1f) \rightarrow [4s,3p,2d,1f]$$

D_e(B3LYP)= 20 eV

D_e(CAS(6,6)SCF)= 8.9 eV

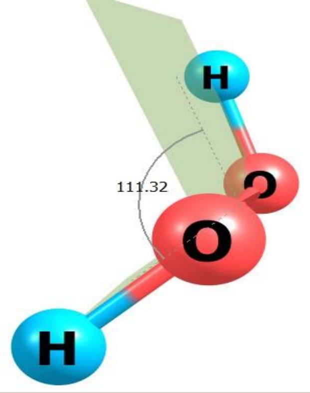
D_e(experim)= 9.4 eV

Nucleic acids adenine-thymine interaction



PBE functional kJ/mol JCP, 137, 120901 (2012).

Vibrational frequency calculations. Comparison experimental and calculated data for hydrogen peroxide



Basis set: **aug cc-pVDZ**

$$\nu_{theor} - \nu_{\exp} \ [cm^{-1}] \quad \left(100(\nu_{theor} - \nu_{\exp}) / \nu_{\exp}\right) \ [\%]$$

Symmetry	vibrations	experim. freq.(cm^{-1})	RHF	CISD	MP2	B3LYP
A	OH (asymm)	3599	540 (15)	335 (9)	169(5)	149 (4)
B	OH (symm)	3608	531 (15)	361 (10)	160 (4)	142 (4)
B	HOO (asymm)	1266	173 (14)	140 (11)	44 (3)	58 (5)
A	HOO (symm)	1402	206 (15)	132 (9)	11 (1)	34 (2)
A	OO	877	262 (30)	130 (15)	4 (1)	66 (8)
A	dihedral	371	53 (14)	11 (3)	23 (6)	26 (7)

Disadvantages of DFT

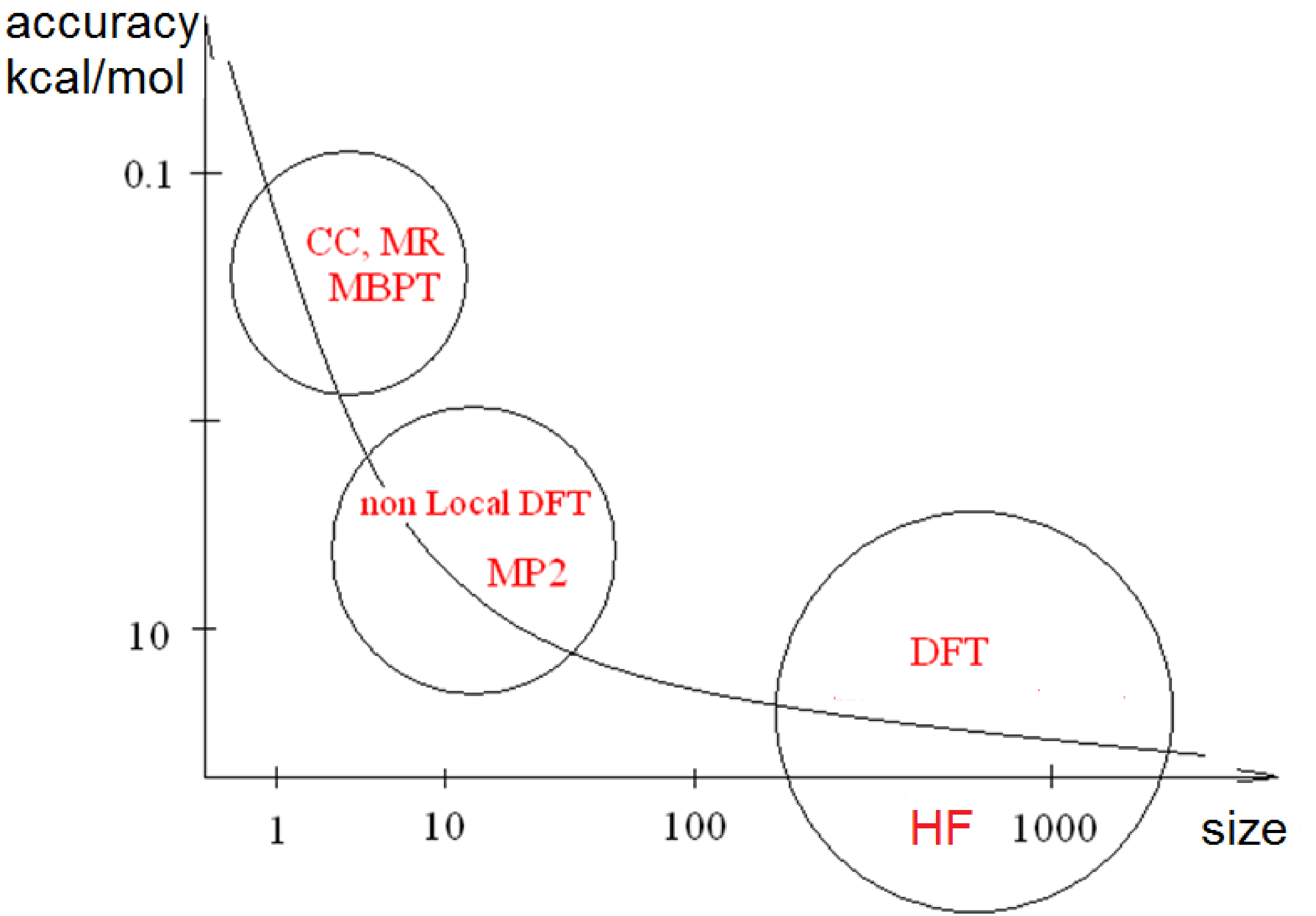
1) The exact density functional is not known !
2) There is no systematic approach to improving (refinement) of the theory
3) There are no simple rules to guarantee the reliability of the calculation
4) Too many approximations to choose from, (in the current version of GAMESS there are more than 30 functionals!!!)
5) The best non-local functionals give results close only to MP2 !

Advantage of DFT

It is possible to calculate very large systems

See also: K. Burke, JCP **136**, 150901 (2012)

Exactness *vs* size



Computational costs

DFT	**N^3**	
HF	N^2 -N^4	Depends from symmetry accounting
HF	N^3	Core potential
MP2	N^5	
CCSD	N^6	
MP3, MP4(SDQ)	N^6	
MP4	N^7	
CCSD(T)	N^7	
CISD	N^6	
CISDTQ	N^{10}	
CASSCF	*AS!*	Active Space
FCI	**$N!$**	