



Chemical Materials Department



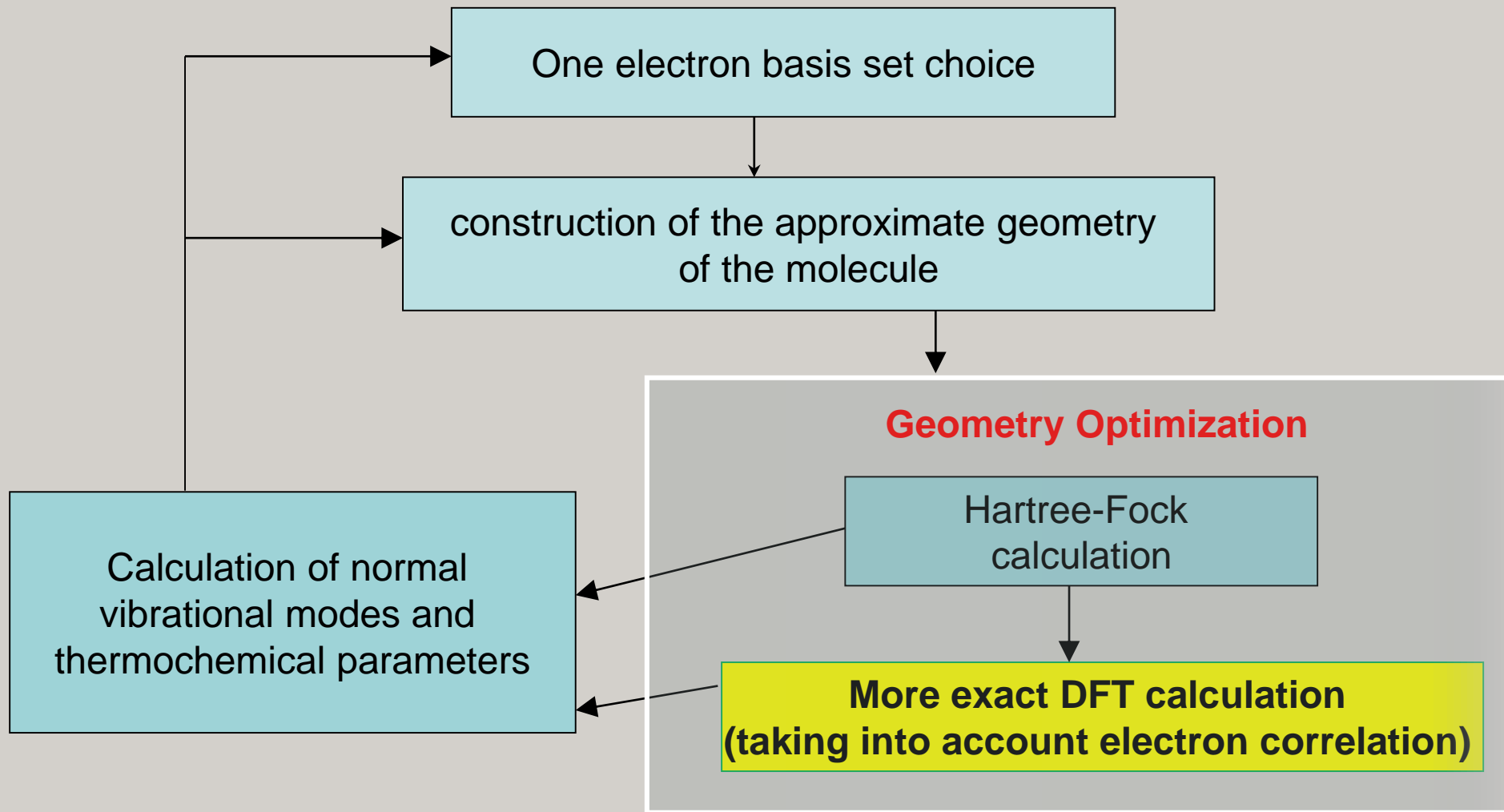
Lecture 7

Density Functional Theory

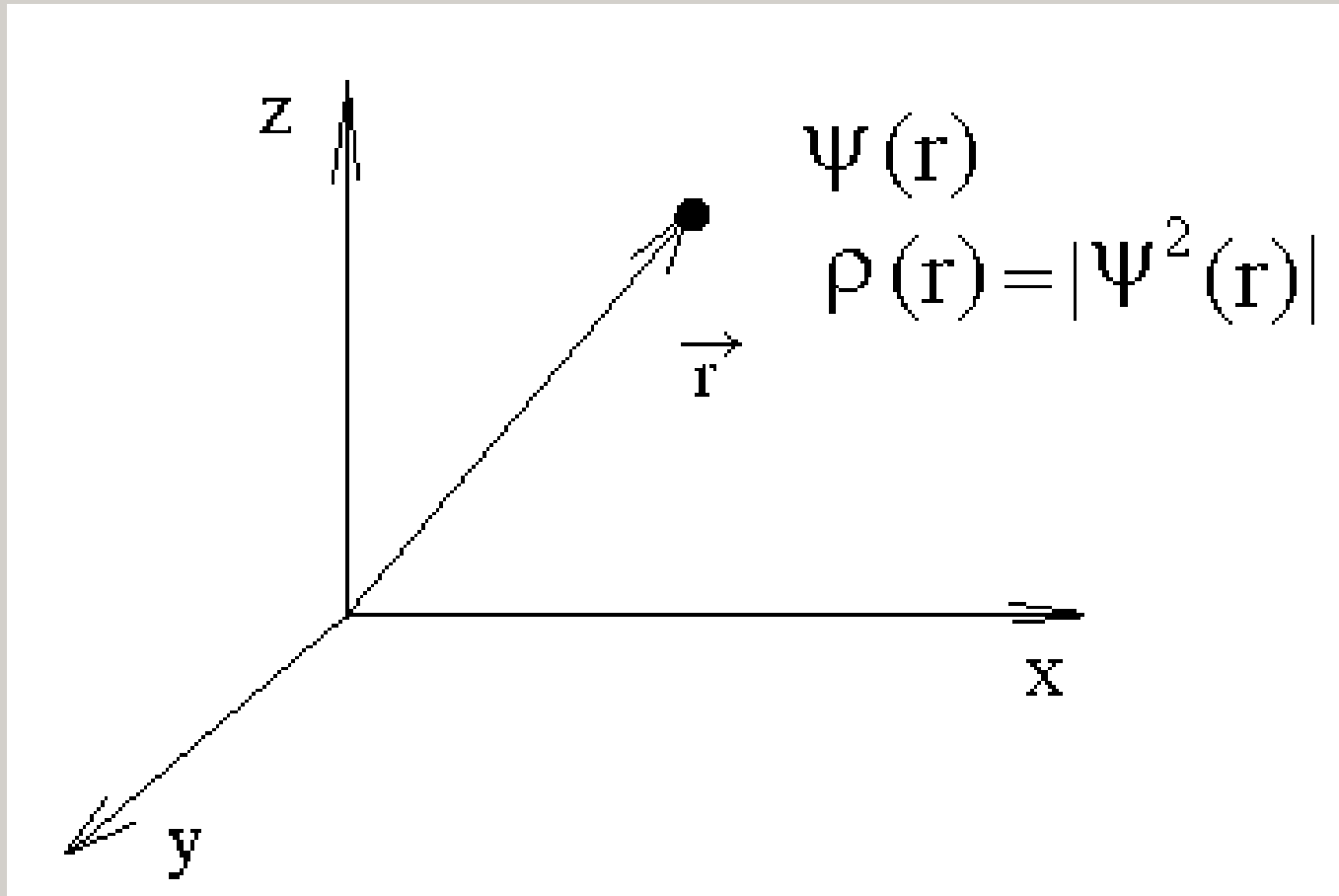
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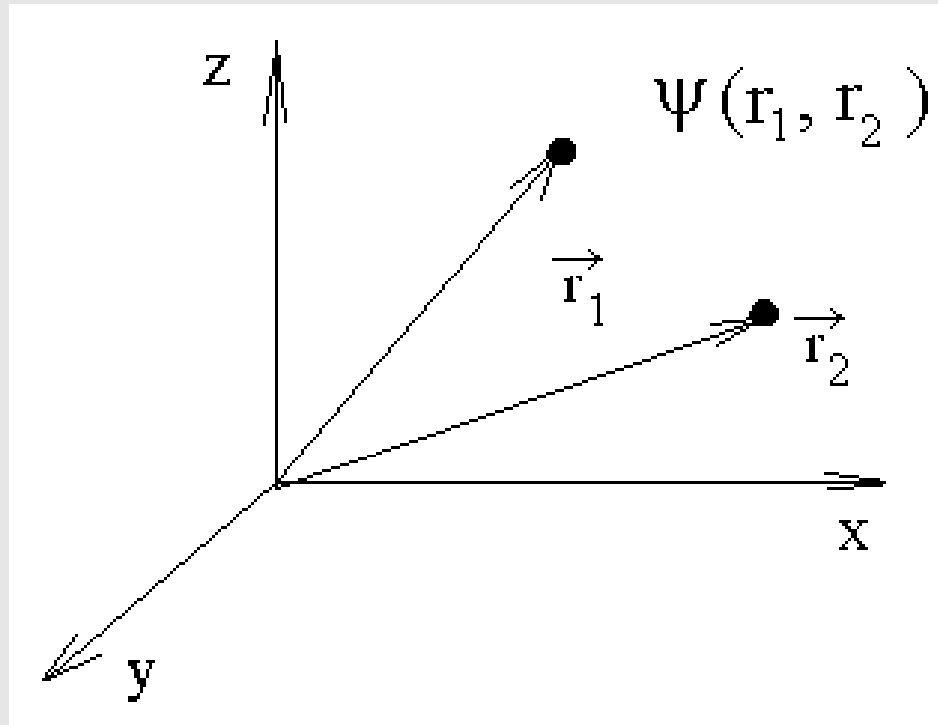
A typical scheme of quantum chemical calculations (ab initio)



The wave function and electron density. One-electron system



Many-electron System



$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N) = \Psi(1, 2, 3, \dots, N)$$

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

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



Walter Kohn (1923-2016)

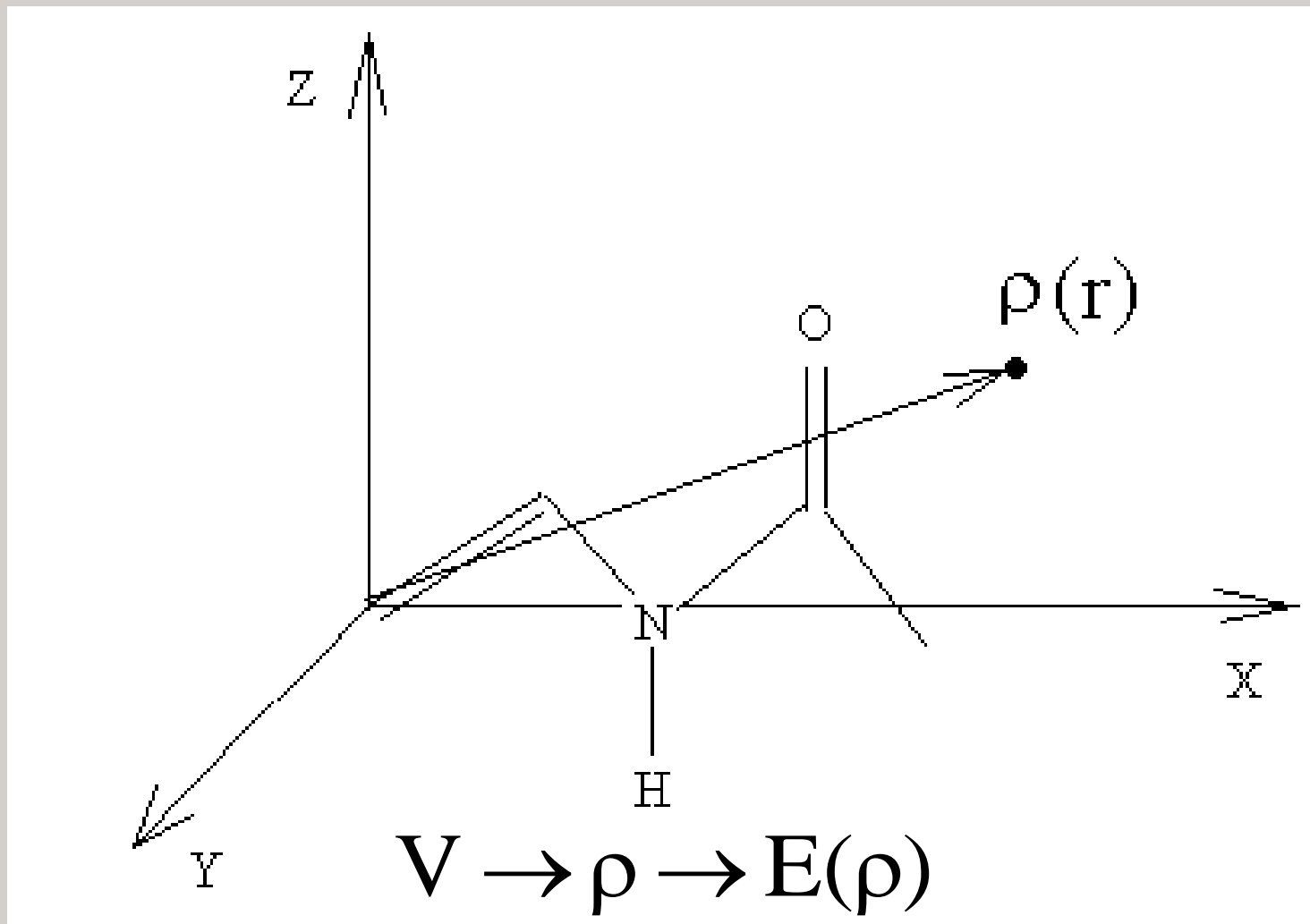
“... In general the many-electron wave function for a system of N electrons is not a legitimate scientific concept, when $N > 1000$.”

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

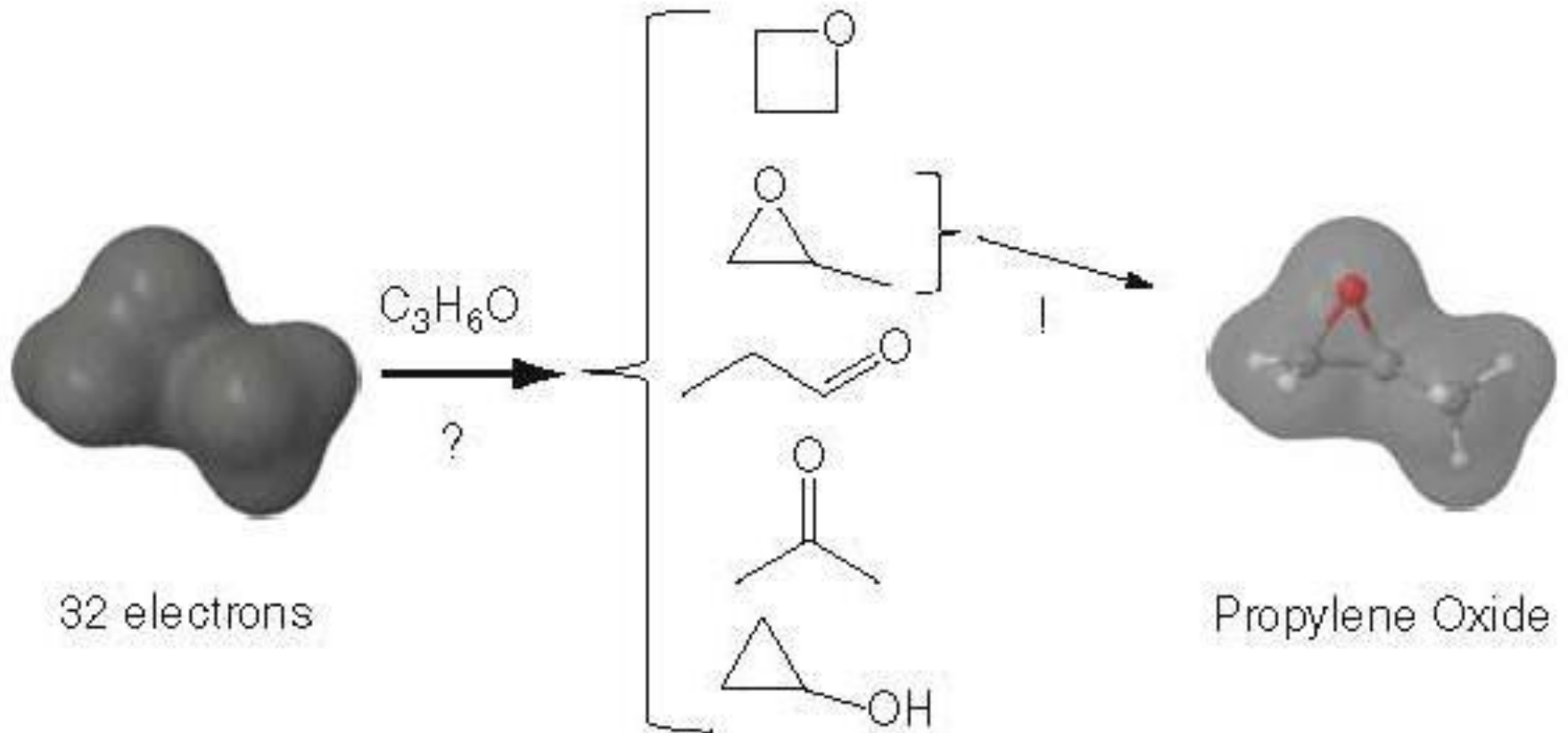
Reviews of Modern Physics, Vol. 71, No. 5, 1999, P. 1253

Density Functional Theory (DFT)

Hohenberg-Kohn Theorem



Hohenberg-Kohn Theorem



Thomas-Fermi theory (1927)

Kinetic energy of homogeneous electron gas

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

Total energy as a function of electron density

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

Drawback:

Neglect of exchange and correlation effects

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

$$E_X = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1) h_X(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

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

$$r_s = \left(\frac{3}{4\pi} \right)^{1/3} \rho(\mathbf{r}_1)^{-1/3}$$

Potential $\sim 1/r_s$

$$E_X[\rho] \approx C_X \int \rho(\mathbf{r}_1)^{4/3} d\mathbf{r}_1$$

X α method

$$E_{X\alpha}[\rho] \approx -\frac{9}{8} \left(\frac{3}{\pi} \right)^{1/3} \alpha \int \rho(\mathbf{r}_1)^{4/3} d\mathbf{r}_1$$

Hohenberg-Kohn Theorem

$$\begin{array}{c} V \neq V' \\ \swarrow \quad \searrow \\ \rho(r) \end{array}$$

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

$$H = T + V_{ee} + V$$

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

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

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

$$E \neq E'$$

Density Functional Theory

Hohenberg-Kohn Theorem $V \rightarrow \rho$

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

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

$$V(r) = -\sum_M \frac{Z_M}{|r - R_M|} \quad \text{«External» potential}$$

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

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

Kohn-Sham orbitals

$$\rho(\mathbf{r}) = 2 \sum_i |\varphi_i(\mathbf{r})|^2 \quad \varphi_i \text{ -Kohn-Sham orbitals}$$

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

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

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

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

1) Local Density Approximation, LDA

$$E_{\text{LDA}}[\rho] = \int \rho(\mathbf{r}) e(\mathbf{r}) d\mathbf{r}$$

$$E_{\text{LDA}}[\rho] = \int \rho(\mathbf{r}) e(\rho) d\mathbf{r}$$

Representation problem

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

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

Generalized Gradient Approximation (GGA)

$$E_{\text{GGA}}[\rho] = \int \rho(\mathbf{r}) e(\rho(\mathbf{r}), \nabla \rho) d\mathbf{r}$$

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

Hybrid approximation (hybrid-GGA)

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

B3LYP – Becke, Lee, Yang, Parr

B3P86 – Becke, Perdue

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

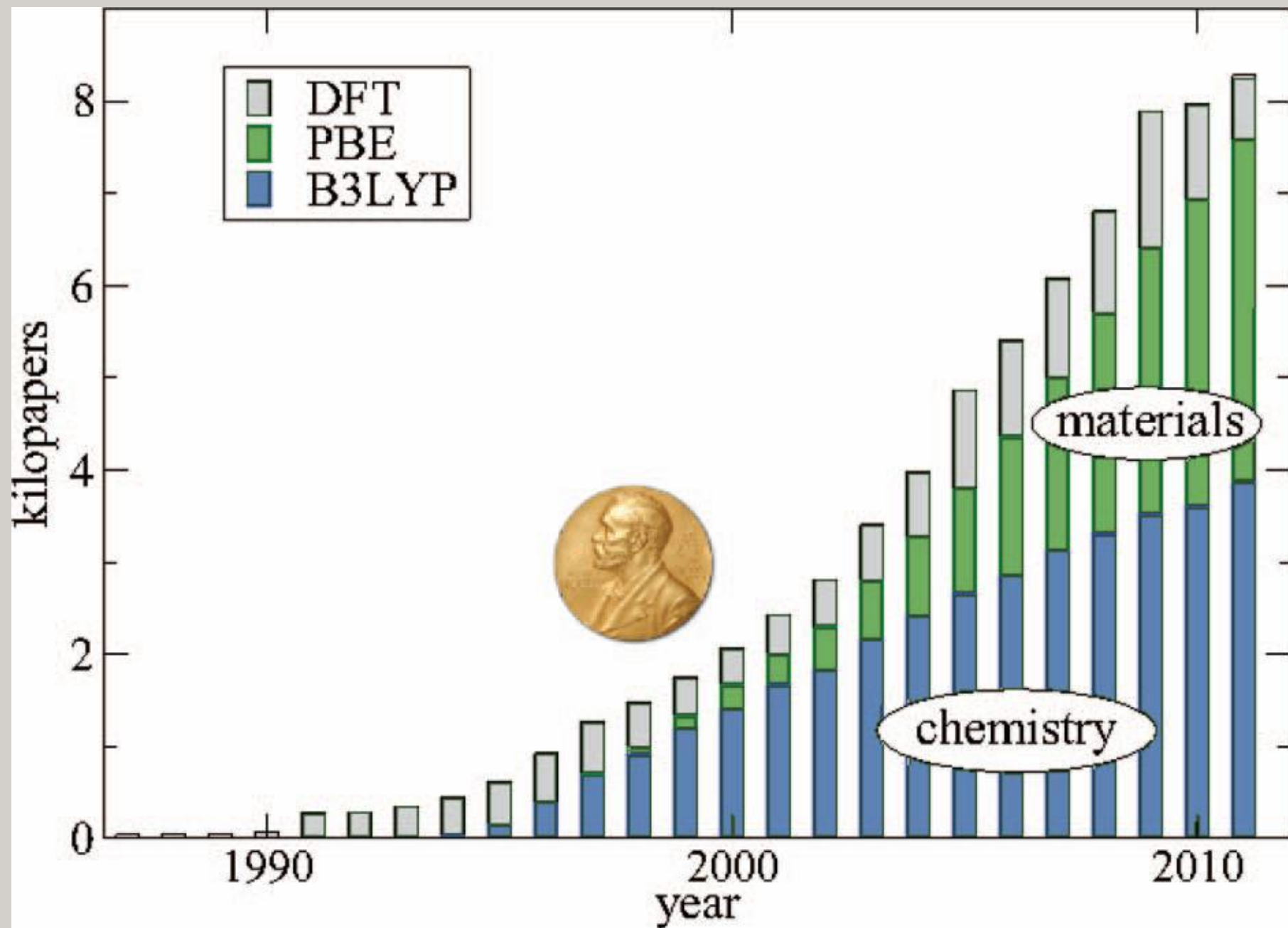
Possibility to describe intermolecular interaction

M05 (Zhao et al. 2005, 2006),

M06 (Zhao, Truhlar 2006, 2008)

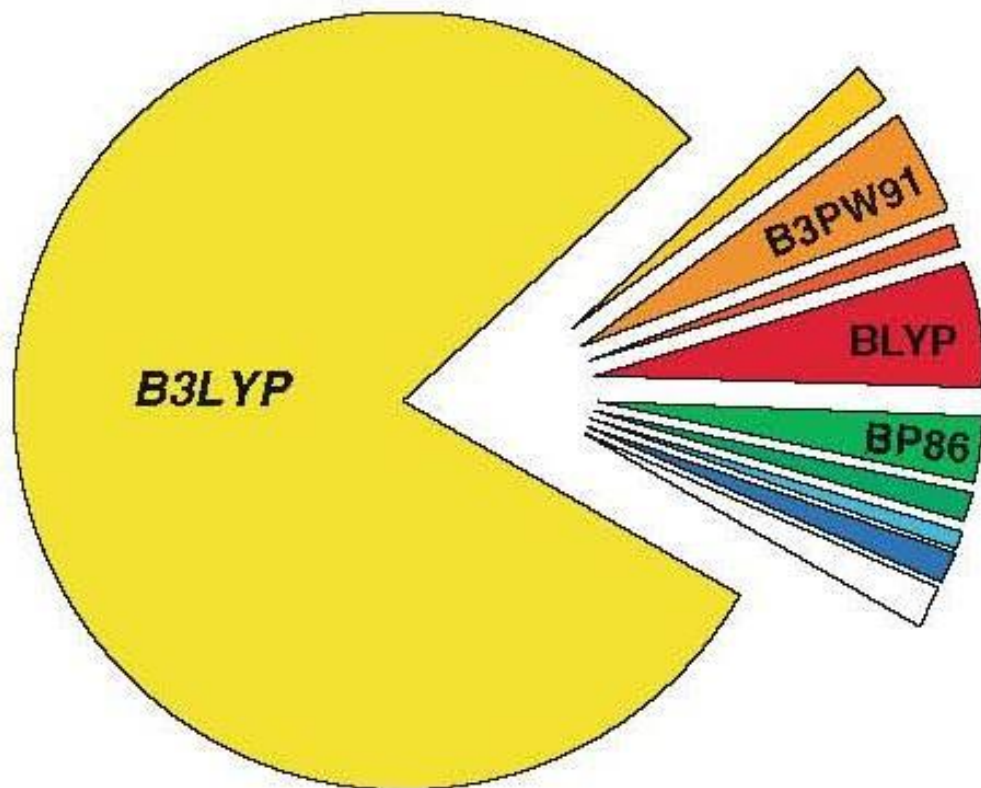
Different types of functionals

Acronyms	Description	Type
$X\alpha$		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



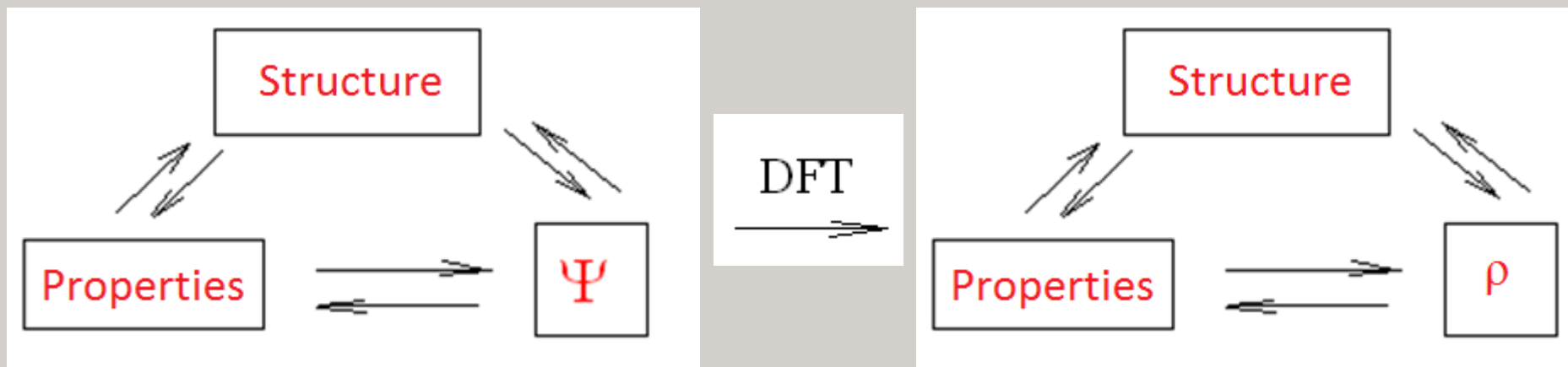
Most popular functionals

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



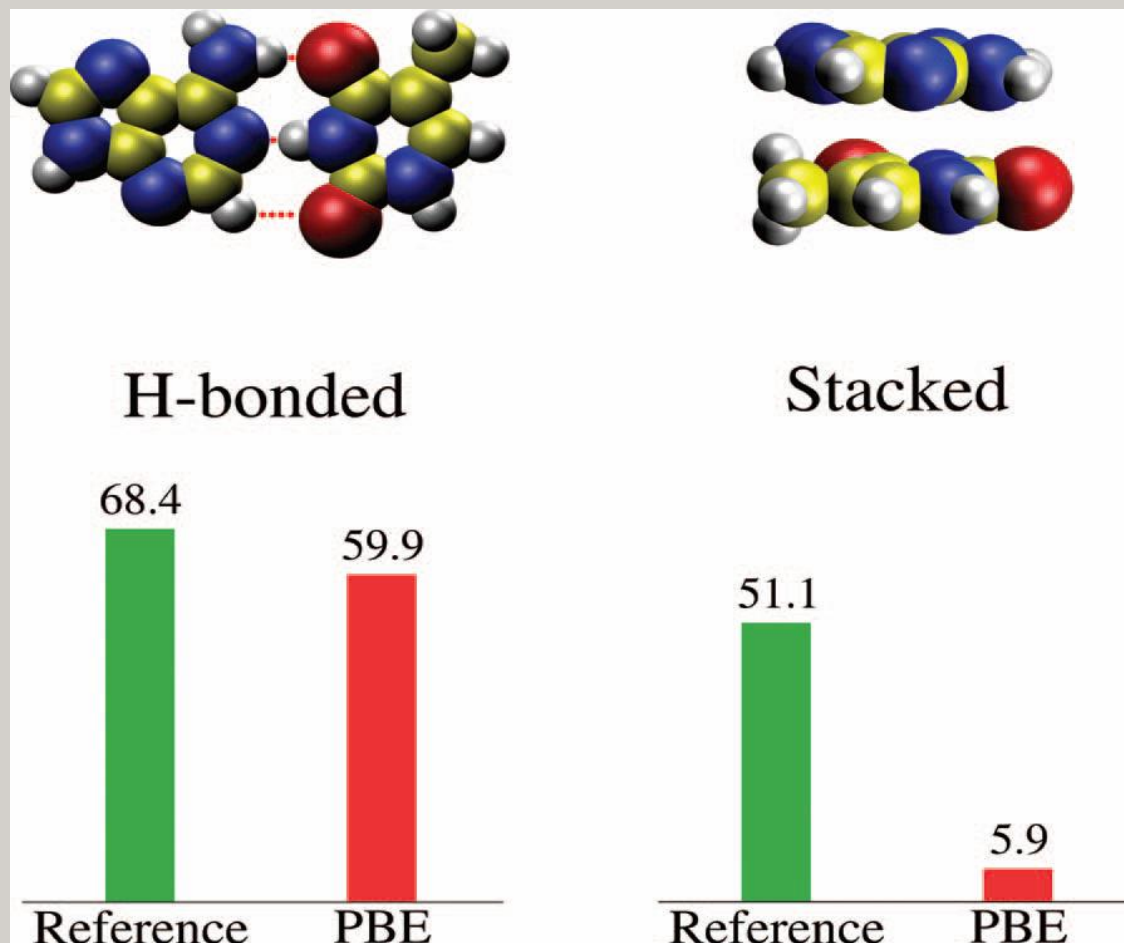
DFT and other methods (errors in description of formation enthalpy kcal/mol. 148 molecules)

Метод	Δ_{abs}	Δ_{pos}	Δ_{neg}
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) O₃ cc-pVTZ

method	ω_1 (symm)	ω_2 (anti-symm)	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)
Experim	1135	1089	716

Nucleic acids adenine-thymine interaction



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

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 !

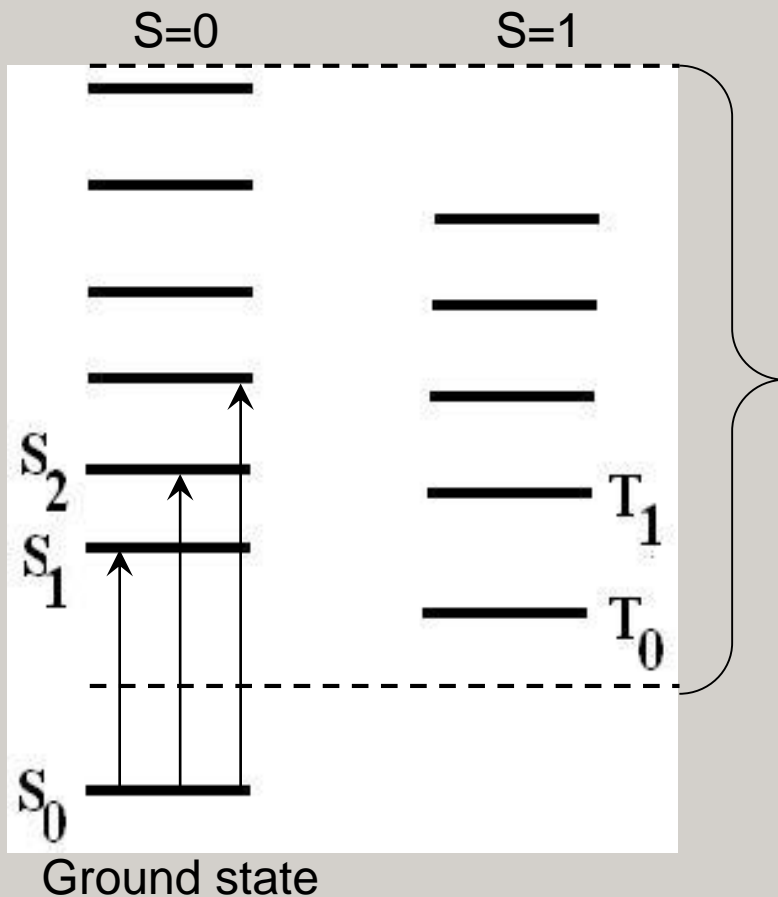
Advantage of DFT

It is possible to calculate very large systems

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

Solution of Schrodinger equation for electron excited states

(even-electronic systems)



Excited states

$$E = h\nu \quad \lambda = \frac{c}{\nu}$$

$$[\text{cm}^{-1}] = 8065 [\text{eV}]$$

$$[\text{nm}] = 10^7 / [\text{cm}^{-1}]$$

Electronically Excited states

Ground state (equilibrium geometry)

$$|\Psi_{\text{exact}}^0\rangle = 0.9|0\rangle + 0.1|_i^a\rangle + 0.2|_{ij}^{ab}\rangle + \dots$$

$|0\rangle$ - HF state

Excited states

Case 1 $|\Psi^*\rangle = c_0|0\rangle + c_1|_{i\dots}^{a\dots}\rangle + \dots$ $c_1 \sim 0.9 \gg c_0$

Case 2 $|\Psi^*\rangle = c_0|0\rangle + c_1\left(|_i^a\rangle \pm |_j^b\rangle\right) + \dots$ $c_1 \sim \frac{1}{\sqrt{2}} \gg c_0$

Case 3 $|\Psi^*\rangle = c_0|0\rangle + c_1\left(|_{ij}^{ab}\rangle \pm |_{kl}^{cd}\rangle\right) + c_2|_i^a\rangle + \dots$ $c_1 > c_2 > c_0$

$$\langle \Psi^* | \Psi_{\text{exact}}^0 \rangle = 0 \quad \text{Orthogonality condition}$$

$$\langle \Psi_i^* | \Psi_j^* \rangle = 0$$

Time Dependent DFT (TD-DFT)

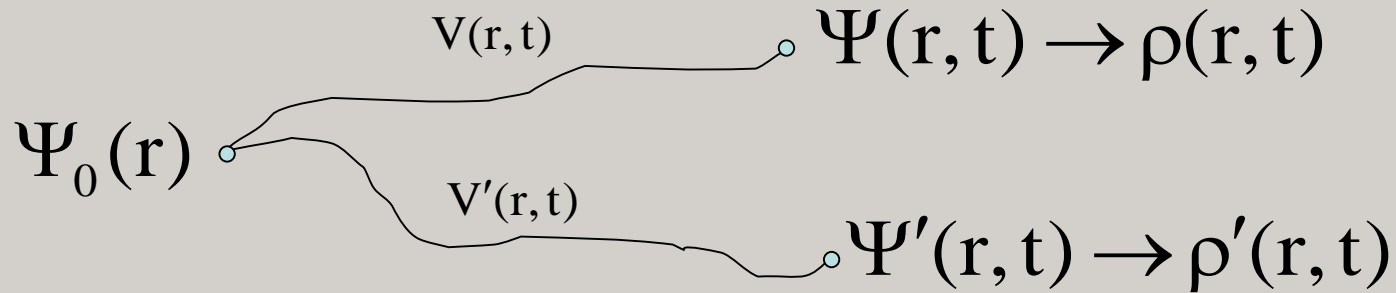
$$V(\mathbf{r}, t) = V(\mathbf{r}) \cos(\omega t + \varphi)$$

Runge-Grossa theorem (1984)

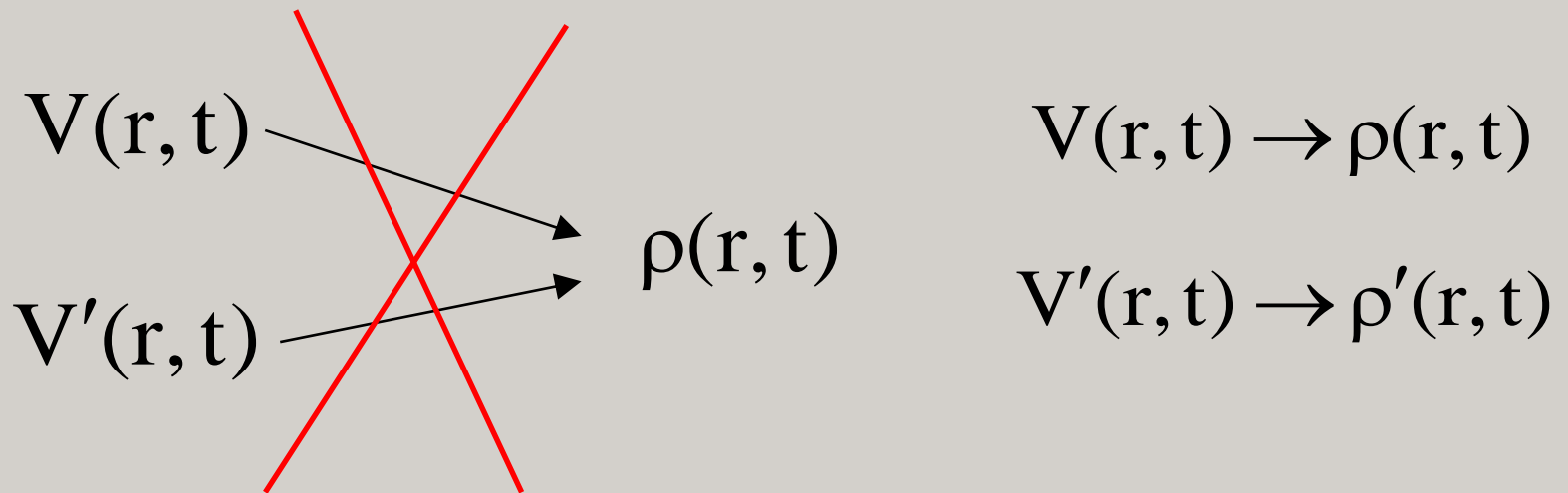
$$V(\mathbf{r}, t) \xrightarrow{\Psi_0} \rho(\mathbf{r}, t)$$

Single particle electron density contains all the information about evolution of system in external field.

Runge-Grossa theorem



$$i \frac{\partial}{\partial t} |\Psi(\mathbf{r}, t)\rangle = (\mathbf{H} + V(\mathbf{r}, t)) |\Psi(\mathbf{r}, t)\rangle$$

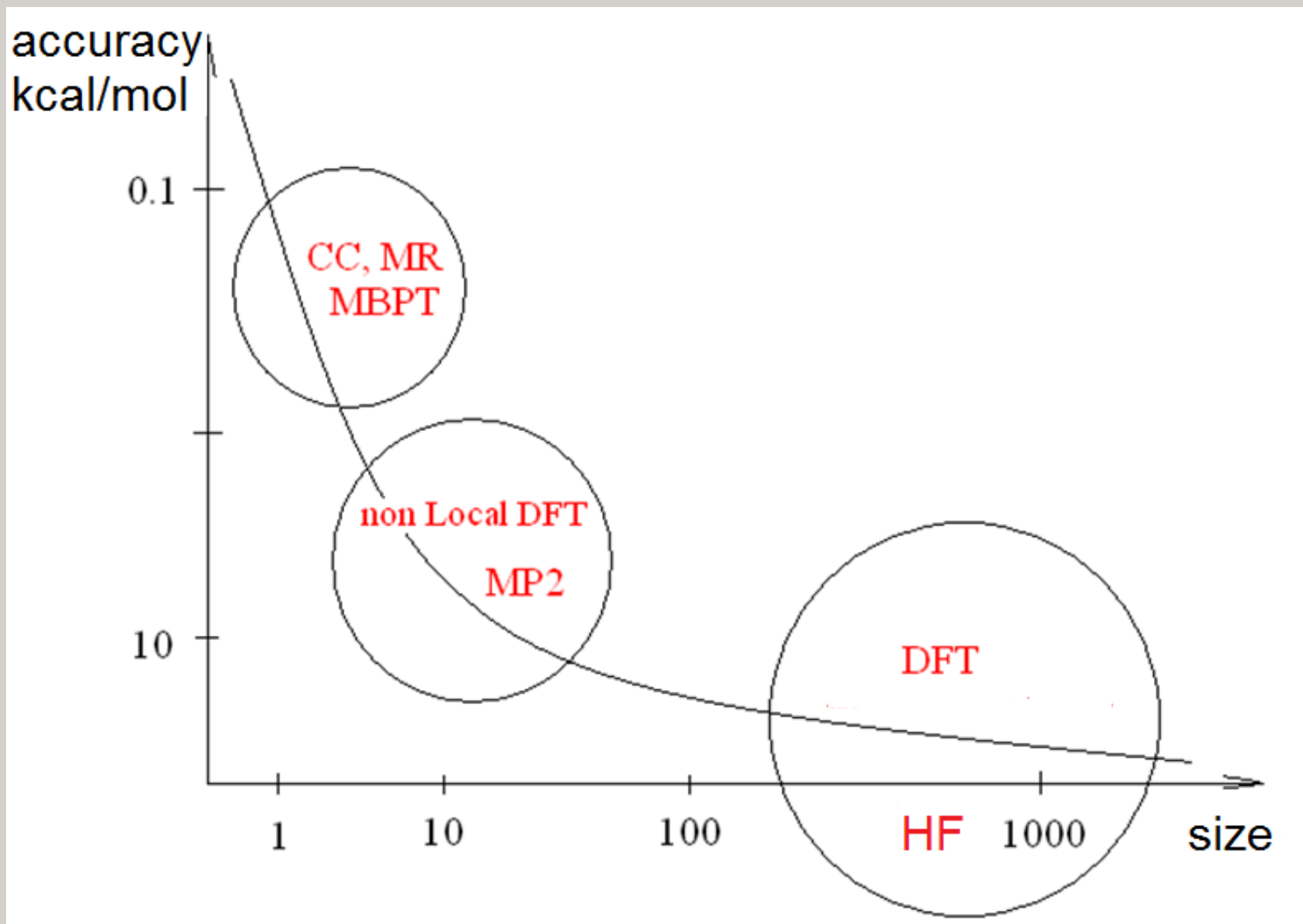


Cation radicals of naphthalene molecule

JCP, 111,1999,p.8904 (eV)

состояние	UCIS	BLYP	B3LYP	MRCISD	CASPT2	Exp(EA)
$^2B_{2g}$	2.49 (0.65)	2.16 (0.32)	2.15 (0.31)	2.16 (0.32)	1.89 (0.05)	1.84
$^2B_{3g}$	3.53 (0.84)	2.78 (0.09)	2.99 (0.3)	2.94 (0.25)	2.70 (0.01)	2.69
$^2B_{3g}$	3.83 (0.58)	3.53 (0.28)	3.61 (0.36)	3.51 (0.26)	3.24 (-0.01)	3.25
$^2B_{2g}$	4.25 (0.23)	3.75 (-0.27)	3.92 (-0.1)	4.38 (0.36)	3.98 (-0.04)	4.02
$^2B_{2g}$	6.33 (1.78)	4.33 (-0.22)	4.65 (0.1)	5.14 (0.59)	4.44 (-0.11)	4.55
sd	0.97	0.25	0.26	0.37	0.06	

Exactness vs size of the problem



Thank you for your attention !

**I hope you enjoy learning
quantum chemistry!**