Density functional theory

Traditional *ab initio*: finding the N-electron wavefuntion Ψ(1,2,…,N) depending on 4N coord.
DFT: finding the total electron spin-densities depending on 8 coordinates

Hohenberg & Kohn:

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

Kinetic energy of electron
Coulomb repulsion
Non-classical interaction
  (self-interaction, exchange, and
  correlation)

Hohenberg-Kohn functional:

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

All properties (defined by V_{ext}) are determined by the ground state density
H&K only proofed that F_{HK} exist, however, we do not know it
H&K do not give a direction how can we find density
H&K theorems allow us to construct the rigorous many-body theory using density as a
   fundamental properties

$$F[\rho(\vec{r})] = T[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{ncl}[\rho(\vec{r})]$$

An old Thomas-Fermi-Dirac model is a DFT model with approximate xc functional

Thomas-Fermi Model

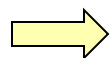$$T_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\vec{r})d\vec{r}$$

Thomas-Fermi kinetic energy (C_k=2.871 a.u.)

$$E_X[\rho(\vec{r})] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}(\vec{r})d\vec{r}$$

Dirac (1930) exchange (C_X=0.739 a.u.)
=> Thomas-Fermi-Dirac model (TFD)

$$E_C[\rho(\vec{r})] = -0.056\int \frac{\rho^{4/3}(\vec{r})}{0.079 + \rho^{1/3}(\vec{r})}d\vec{r}$$

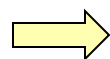Local approximation to homogeneous electron gas
Wigner (1938)

$$\Longrightarrow \quad E_{TFD}[\rho(\vec{r})] = C_K\int \rho^{5/3}(\vec{r})d\vec{r} - \int \rho(\vec{r})v_{ext}(\vec{r})d\vec{r} + \frac{1}{2}\int\int \frac{\rho(\vec{r_1})\rho(\vec{r_2})}{r_{12}}d\vec{r_1}d\vec{r_2} - C_X\int \rho^{4/3}(\vec{r})d\vec{r} + E_C[\rho(\vec{r})]$$

Thomas-Fermi-Dirac equation
Solution – variational principle; adding the constraint of a fixed number of electrons

$$\frac{\delta}{\delta\rho(\vec{r})}\left(E_{THD}[\rho] - \mu\int \rho(\vec{r})dr\right) = 0 \quad \Longrightarrow \quad \mu = \frac{5}{3}C_K\rho^{2/3}(\vec{r}) + v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r_2})}{r_{12}}d\vec{r_1} - \frac{4}{3}C_X\rho^{1/3} + \mu_c[\rho(\vec{r})]$$

$$\frac{\delta E_c[\rho(\vec{r})]}{\delta\rho(\vec{r})}$$

Correlation potential

Rigorously proved that molecules are less stable than their fragments !
Main problem comes from kinetic energy description.

**Thomas-Fermi
Type Models**

T_{TF} replaced by more realistic evaluation for one-electron orbitals
=> Iterative solution

Introducing the reference system of *non-interacting* electrons
=> Requires reference potential V_S

Significant improvement => describes chemical bond!

**Kohn-Sham
Type Models**

Kohn-Sham Approach

Adopting a better expression for kinetic energy:

Using exact kinetic energy of the non-interacting reference system that has the same density as a real one.

$$T_S = -\frac{1}{2}\sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle$$

Such kinetic energy cannot be the same as a true one; it is expected to be close.

$$T_S \neq T$$

Residual part of kinetic energy (T_C) is shifted to the functional.

$$E_{XC}[\rho] \equiv (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_C[\rho] + E_{ncl}[\rho]$$

Kohn-Sham functional is then:

$$F[\rho(\vec{r})] = T_S[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{XC}[\rho(\vec{r})]$$

Kinetic energy of non-interacting reference system	Coulomb repulsion of uncorrelated densities

Exchange-correlation functional
Includes:
Electron exchange
Electron correlation
Residual part of kinetic en.

HK theorems

$$E_0 = \min_{\rho \to N} \left(F[\rho] + \int \rho(\vec{r}) V_{Ne} d\vec{r} \right)$$

$$F[\rho(\vec{r})] = T[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{ncl}[\rho(\vec{r})]$$

Putting things together:

$$E[\rho(\vec{r})] = T_s[\rho] + J[\rho] + E_{XC}[\rho] + E_{Ne}[\rho]$$

$$= T_s[\rho] + \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\,\rho(\vec{r}_2)}{r_{12}}\,d\vec{r}_1 d\vec{r}_2 + E_{XC}[\rho] + \int V_{Ne}\rho(\vec{r})d\vec{r}$$

$$= -\frac{1}{2}\sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \frac{1}{2}\sum_i^N \sum_j^N \iint |\varphi_i(\vec{x}_1)|^2 \frac{1}{r_{12}} |\varphi_j(\vec{x}_2)|^2 \, d\vec{x}_1 d\vec{x}_2 + E_{XC}[\rho(\vec{r})] - \sum_i^N \int \sum_A^M \frac{Z_A}{r_{1A}} |\varphi_i(\vec{x}_1)|^2 d\vec{x}_1$$

Applying
vatiational
principle

Contains all problematic terms

$$\left(-\frac{1}{2}\nabla^2 + \left[\int \frac{\rho(\vec{r}_2)}{r_{12}}d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}} \right] \right)\varphi_i = \varepsilon_i \varphi_i$$

$$= \left(-\frac{1}{2}\nabla^2 + V_{eff}(\vec{r}_1) \right)\varphi_i = \varepsilon_i \varphi_i$$

Satisfying the conditions stated
for non-interacting reference system

If V_{XC} is know
=> Exact theory

$$V_S(\vec{r}) \equiv V_{eff}(\vec{r}) = \int \frac{\rho(\vec{r}_2)}{r_{12}}d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}}$$

Iterative solution.
What is V_{XC} ?

$$V_{XC} \equiv \frac{\delta E_{XC}}{\delta \rho}$$

Kohn-Sham *vs.* Hartree-Fock

1. SIC problem not present in HF ($J_{ii}=K_{ii}$).
2. Effective KS potential V_{KS} includes also elektron correlation.
3. Wave function in the form of Slater determinant is an exact wave function for the KS reference system (definition). It is not an exact wave function of the true interacting system. Exact wave function is not known (HK theorems).
   Density can expressed from one-electron functions constituting single SD:
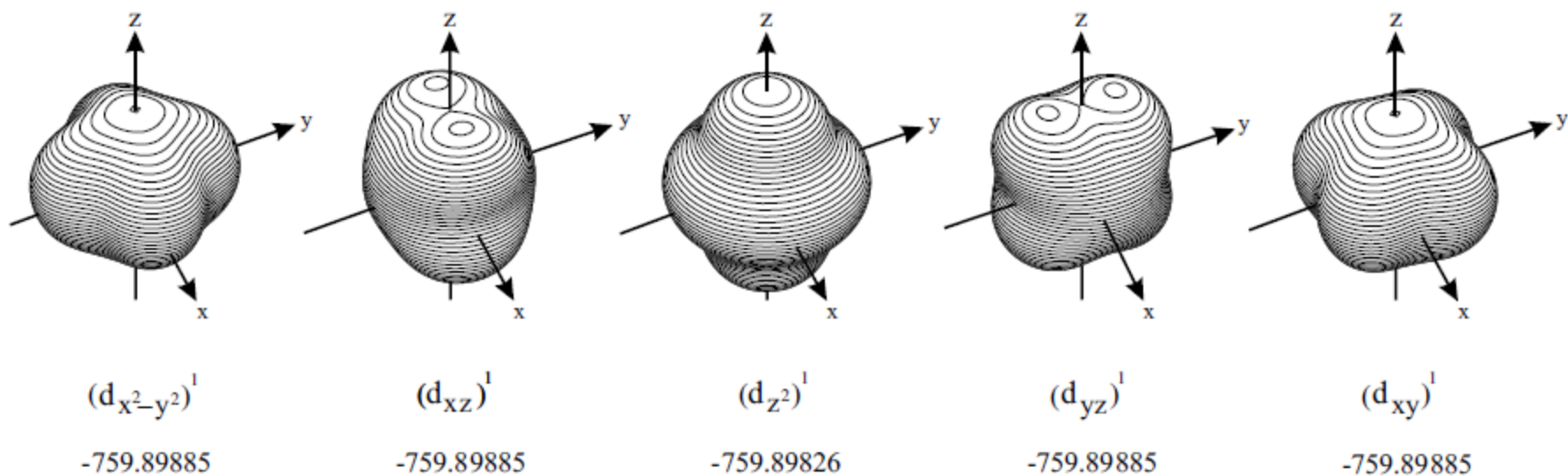
   YES – non-interacting pure-state-V_S representable
   NO - non-interacting enesmbe-V_S representable => Problem !
   (TS – mostly not pure-state-V_S representable; shown for exact wf)
4. Slater determinant in HF is not exact wave function – it is only a consequence of model of independent electrons.
5. HF *vs.* KS orbitals.
6. Koopman's theorem does not hold for KS orbitals.
7. Janak's theorem valid for KS: negative of HOMO energy corresponds to 1st ionization potential.
8. V_S is local => V_{XC} must be local ! Contrary to V^{eff}(HF) that is non-local.
9. KS equation formally less complicated that HF equation, nevertheless, they are (in principle) exact.
10. Unrestricted formulation.
11. Improving the HF description => accounting for electron correlation: systematic way.
    Improving the approximate V_{ks} (E_{XC})?
12. Reliability for small/large systems.

$$V_S(\vec{r}) \equiv V_{eff}(\vec{r}) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}}$$

Single SD based density:
Spin or spatial degeneracy (most atoms) => approximate xc functionals have problem !

$(d_{x^2-y^2})^1$ $(d_{xz})^1$ $(d_{z^2})^1$ $(d_{yz})^1$ $(d_{xy})^1$

-759.89885   -759.89885   -759.89826   -759.89885   -759.89885

Figure 5-2. Isodensity surfaces (0.001 a.u.) of the d^1-densities generated from integral orbital occupation of the five d-orbitals in Sc^{2+} by one electron in a DFT calculation. The shape of the density resulting from occupation of the d_{z^2}-orbital differs from the other four (which are identical to each other except for their orientation in space) and a slightly different total energy (given in a.u.) is assigned to this particular density.

$$B_2(^3\Sigma_g^-) \longrightarrow 2\,B\,(^2P)$$

Size-consistency problem
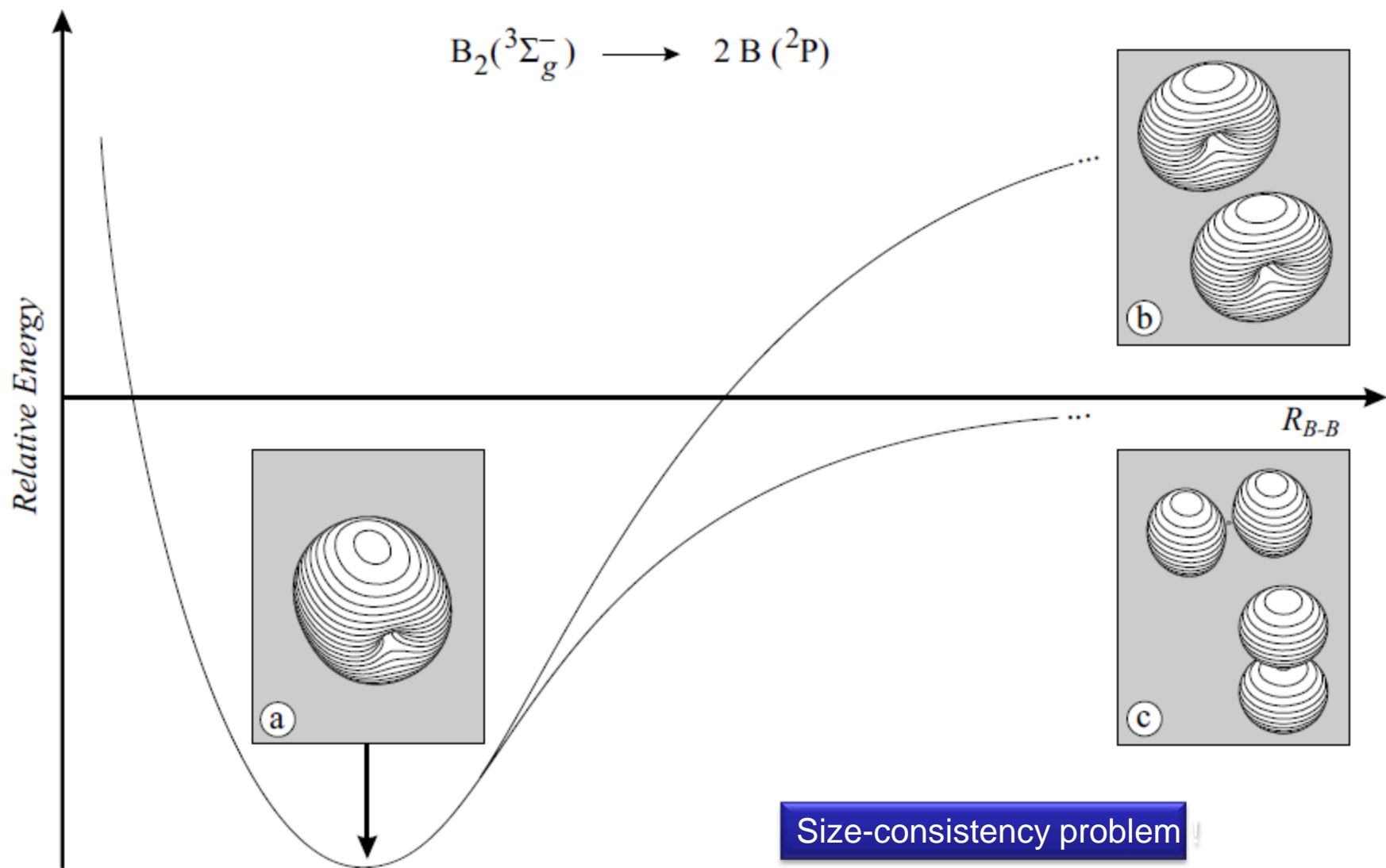
Figure 5-3. The symmetry dilemma in present-day DFT: starting from the cylindrically symmetric molecular π-density (a), the dissociation into atomic fragments can either be computed with correct atomic densities but a wrong energy (b) or a correct energy, but wrong (because symmetry broken) atomic densities (c) (isodensity surfaces at 0.01 a.u. constructed from the p-orbital space; adapted from Savin in *Recent Developments of Modern Density Functional Theory*, Seminario, J. M. (ed.), 1996, with permission from Elsevier Science).

Kohn-Sham *vs.* Hartree-Fock

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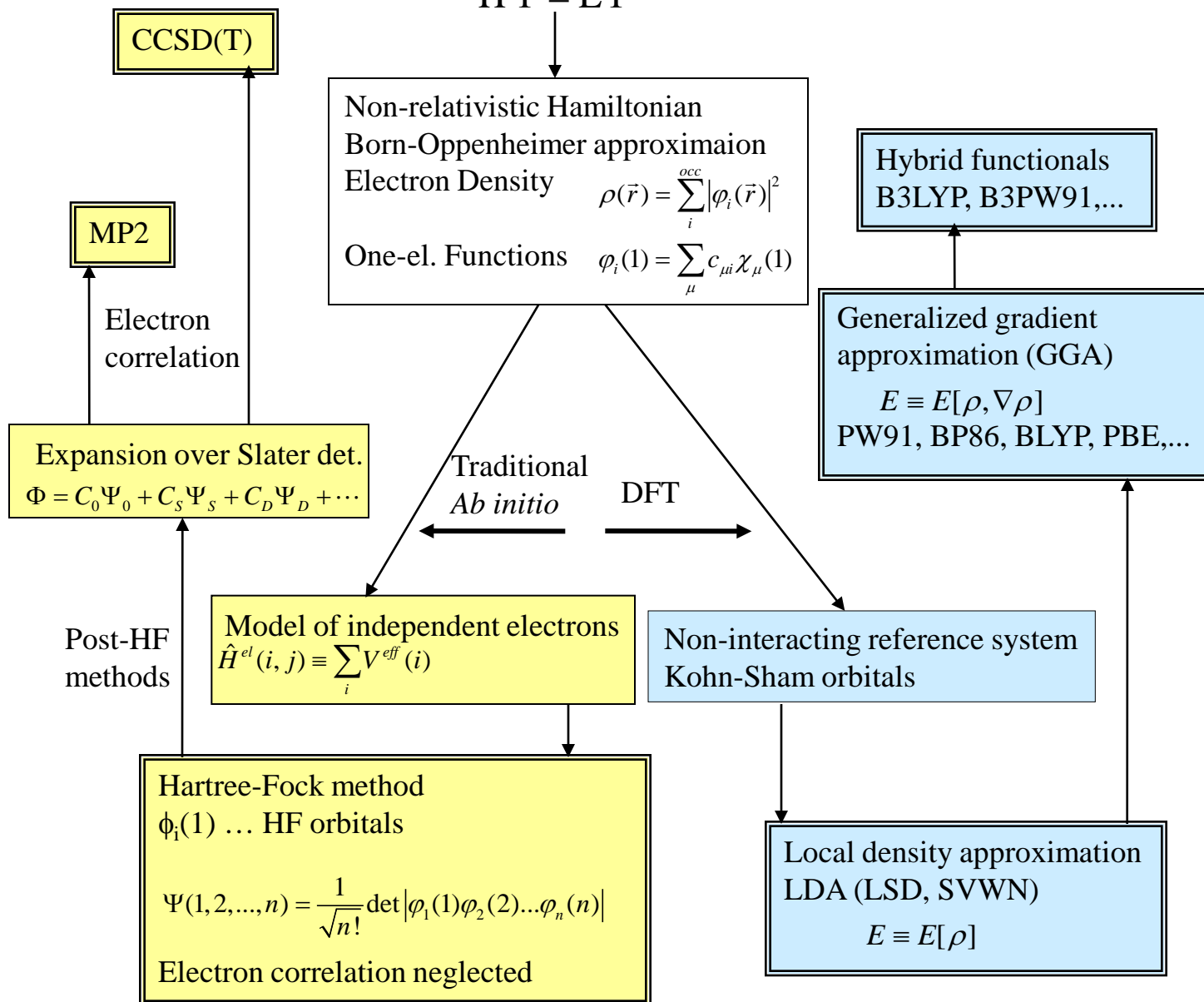
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10. Unrestricted formulation.
11. Improving the HF description => accounting for electron correlation: systematic way. Improving the approximate V_{ks} (E_{XC})?
12. Reliability for small/large systems.

$$V_S(\vec{r}) \equiv V_{eff}(\vec{r}) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}}$$

Stationary Schrödinger equation

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

CCSD(T)

MP2

Non-relativistic Hamiltonian
Born-Oppenheimer approximaion
Electron Density $\quad \rho(\vec{r}) = \sum_{i}^{occ}\left|\varphi_i(\vec{r})\right|^2$

One-el. Functions $\quad \varphi_i(1) = \sum_{\mu} c_{\mu i}\chi_{\mu}(1)$

Hybrid functionals
B3LYP, B3PW91,...

Generalized gradient
approximation (GGA)

$$E \equiv E[\rho, \nabla\rho]$$
PW91, BP86, BLYP, PBE,...

Electron
correlation

Expansion over Slater det.
$$\Phi = C_0\Psi_0 + C_S\Psi_S + C_D\Psi_D + \cdots$$

Traditional
Ab initio

DFT

Post-HF
methods

Model of independent electrons
$$\hat{H}^{el}(i,j) \equiv \sum_{i} V^{eff}(i)$$

Non-interacting reference system
Kohn-Sham orbitals

Hartree-Fock method
$\phi_i(1)$ … HF orbitals

$$\Psi(1,2,...,n) = \frac{1}{\sqrt{n!}}\det\left|\varphi_1(1)\varphi_2(2)...\varphi_n(n)\right|$$

Electron correlation neglected

Local density approximation
LDA (LSD, SVWN)

$$E \equiv E[\rho]$$

Approximate Exchange-Correlation Functionals

Kohn-Sham equations
(general, does not depend on the form of particular funtional)

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(\vec{r}_1)\right)\varphi_i = \varepsilon_i\varphi_i$$

$$V_S(\vec{r}) \equiv V_{eff}(\vec{r}) = \int\frac{\rho(\vec{r}_2)}{r_{12}}d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_A^M\frac{Z_A}{r_{1A}}$$

$$\left(V_{XC} \equiv \frac{\delta E_{XC}}{\delta\rho}\right)$$

Local Density Approximation
E_{XC} components derived from the uniform electron gas

$$E_{XC}^{LDA}[\rho] = \int\rho(\vec{r})\varepsilon_{XC}(\rho(\vec{r}))\,d\vec{r}$$

ε_{XC} … exchange-correlation energy per particle of UEG

$$\varepsilon_{xc}(\rho(\vec{r})) = \varepsilon_x(\rho(\vec{r})) + \varepsilon_c(\rho(\vec{r}))$$

Splitting into exchange and correlation part (T_C neglected)

$$\varepsilon_X[\rho] = -\frac{3}{4}\sqrt[3]{\frac{3\ \rho(\vec{r})}{\pi}}$$

$$\varepsilon_C^{PZ}[\rho] = \begin{cases} A\ln r_s + B + Cr_s\ln r_s + Dr_s, r_s \leq 1 \\ \gamma/\left(1 + \beta_1\sqrt{r_s} + \beta_2 r_s\right), r_s > 1 \end{cases}$$

Constant from QMC fit
High- and low-densities

S … used by Slater
(Dirac, 1930)

PZ (Perdew-Zunger, 1981)
VWN(1-5) (Vosk et al., 1980)
=> Fit to QMC densities

from inhomogeneous
system

$\varepsilon_{xc}(\rho(r_1))$

$\varepsilon_{xc}(\rho(r_2))$

$\rho(r_1)$

$\rho(r_2)$

from homogeneous
electron gas

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r})\, \varepsilon_{xc}(\rho(\vec{r}))\, d\vec{r}$$
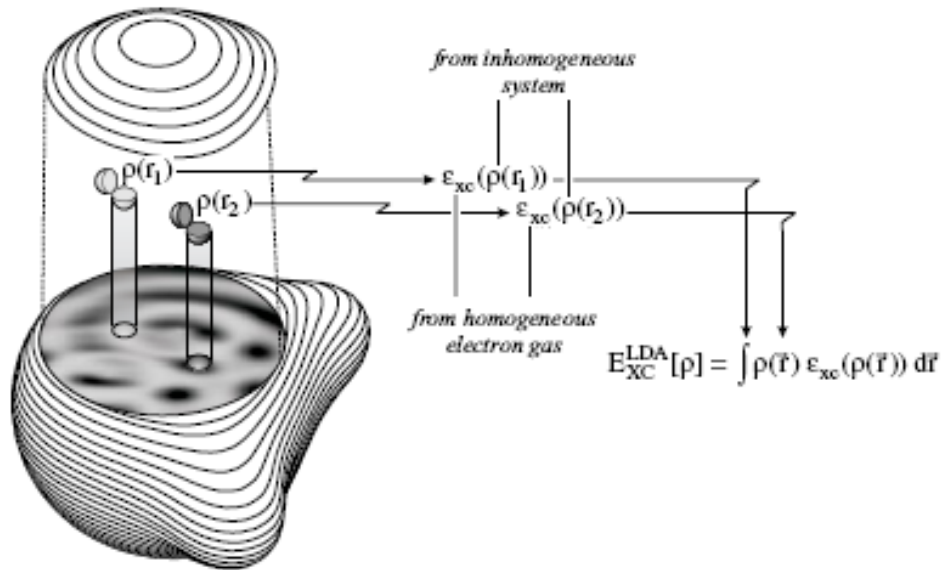
Figure 6-2. The local density approximation.

LDA works better than expected - h_{XC} satisfied most of the rules.
LDA holes are reasonable for small distances between reference and the other electon.
LDA holes are problematic mostly at the regions with highly anisotropic density (atoms).

Trends within the LDA/LSDA

• It favours electronic densities that are more homogeneous than the exact ones (exchange hole is spherically symmetrical)
• (Consequently) it overestimates the binding in molecules.
• (Consequently) it gives too short bond lengths.
• It does not account for dispersion interaction, nevertheless it can still bind van der Waals complesxes; for a wrong reason!
⇒ Number of applications, in particular in physics
Untill today used for metals, graphite, or even weakly bounded molecular crystals.

General limitations of LDA

1. Poor densities in a core region. (Insufficient cancellation of self-interaction in localized dense core.
2. Too high atomic energies (higher than HF and experiment).
3. Incorrect decay of exchange-correlation potential – exponential (as the density) while it should be $-\dfrac{e^2}{r}$
     Problematic for all finite systems, including surfaces.
4. Fails to describe negatively charged ions (due to too fast decay).
5. H-bonds poorly described.

Possible improvments
(i)   Considering inhomogeneous densities.
(ii) Improving the self-interaction problem.
(iii) Accounting for non-local exchange and correlation.

⟹   GGA, hybrid, meta- functionals

Generalized Gradient Approximation: (GGA)

E_{XC} depends not only on density but also on the density gradients

$$E_{XC}^{GGA}[\rho_\alpha,\rho_\beta] = \int f(\rho_\alpha,\rho_\beta,\nabla\rho_\alpha,\nabla\rho_\beta) \ d\vec{r}$$

Particular forms of GGA functionals should be rather viewed as mathematical concept

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

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

Denominator makes GGA correction important also for region with small density (extended valence region)

Reduced density gradient *(local inhomogeneity)*

Example: E_X derived by Becke … **B (=B88)**
β=0.0042 (empirical)

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

Example: E_X derived by Perdew … **P86**
parameter free

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

PBE – Perdew, Burke, Ernzerhof
Functional that satisfies most of the conditions required (boundary conditions, properties of holes)

Meta-GGA
Considering the fourth order gradient expansion – includes second derivatives of densities ("kinetic energy density")
TPSS

OEP – "Optimized effective potential methods"
Includes the exact exchange – no need for h_X, only h_C constracted

Hybrid Density Functionals:
HF exchange is mixed into the functional form

Example: B3PW91 (Becke)
a, b, and c - fitted parameters

$$E_{XC}^{B3} = E_{XC}^{LSD} + a(E_{XC}^{\lambda=0} - E_X^{LSD}) + bE_X^B + cE_C^{PW91}$$

Non-local functionals:
vdW-DF1 van der Waals density functional (Dion, Rydberg, Schroder, Langreth, Lundqvist, 2004)
vdW-DF2 improved long-range assymptote
Román-Pérez & Soler – efficient implementation – reciprocal space – N^2 speeds up to NlogN
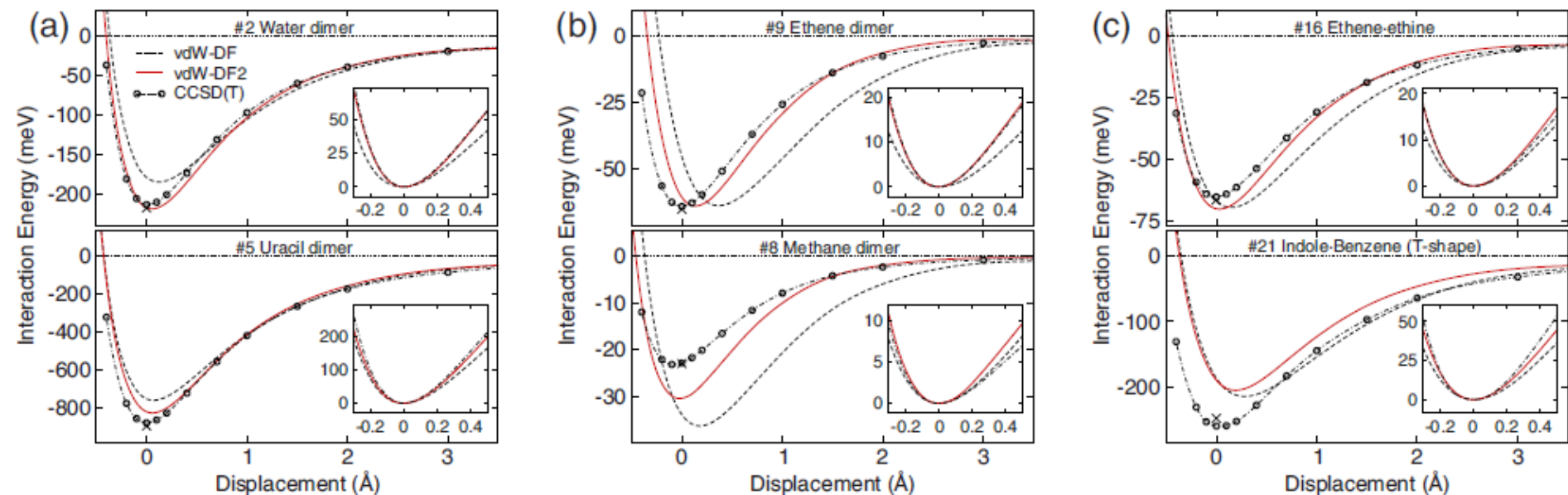
vdW-DF: DF1 vs. DF2

FIG. 1. (Color online) PECs for the best and the worst case of (a) hydrogen-bonded, (b) dispersion-dominated, and (c) mixed duplexes. CCSD(T) QC PECs (dashed-dotted lines with circles taken from Ref. 33) and the reference energies (cross marks taken from Ref. 32) at the geometry of Ref. 31 are also shown. The shapes near minima are compared in inset figures where PECs are aligned to have the common minimum point. For all the other S22 duplexes, see supplementary material.
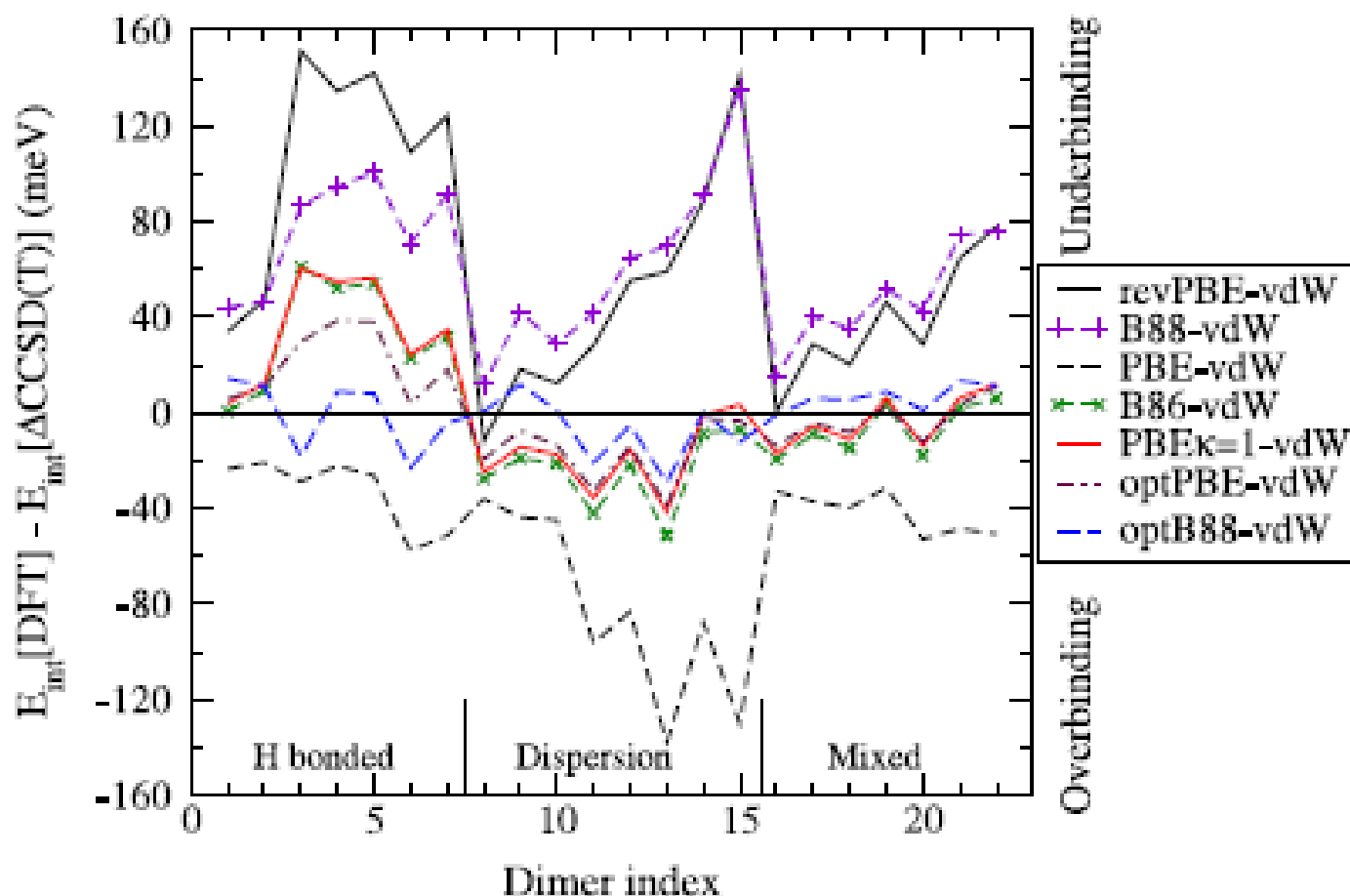
Figure 1. Differences in interaction energies for vdW-DF
(E_{int}[DFT]) with various exchange functionals from the CCSD(T)
reference data ($E_{int}(\Delta CCSD(T))$) [13]. We show data for revPBE,
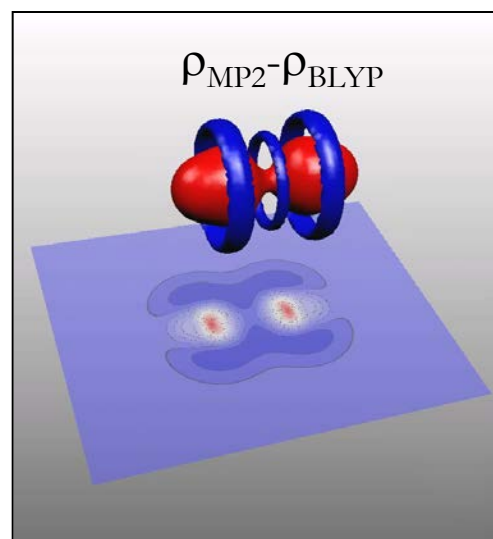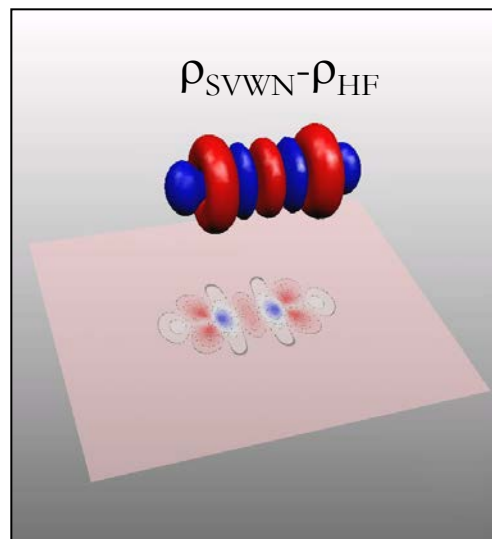B88, PBE, B86 and three new exchange functionals 'PBE$\kappa = 1$',
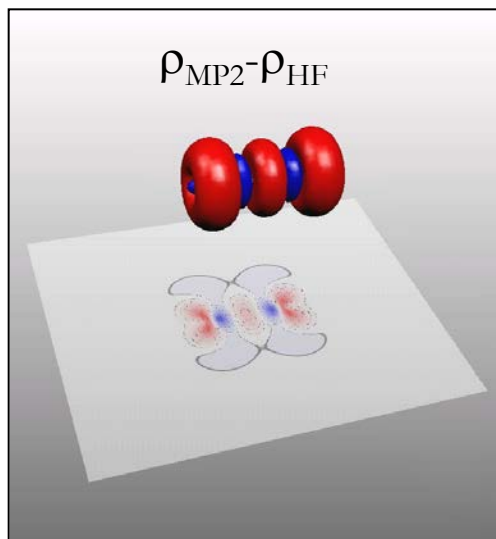'optPBE', and 'optB88'.

Several most commonly used functionals

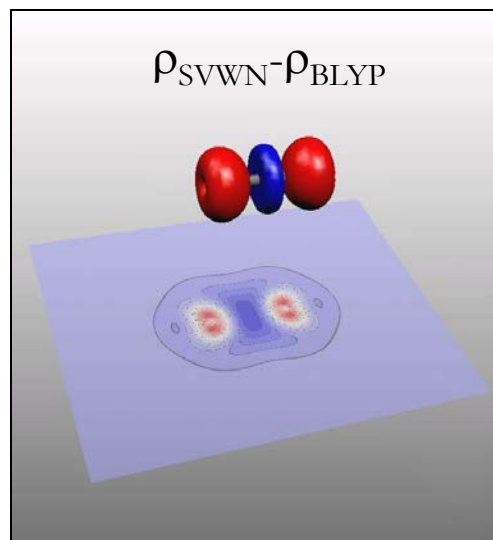| Abbreviation	Type	Exchange part	Correlation part	Authors
S	LDA	+	-	Slater (Dirac)
VWN	LDA	-	+	Vosko, Wilk, Nusair (1980)
B, B88	GGA	+	-	Becke (1988)
LYP	GGA	-	+	Lee, Young, Parr (1988)
PW91	GGA	+	+	Perdew, Wang (1992)
P86 (P)	GGA	-	+	Perdew (1986)
PBE	GGA	+	+	Perdew, Burke, Ernzerhof (1996)
B3	Hybrid	+	-	Becke

<u>Einfluss von Gradientenkorrekturfunktionalen auf die Dichte im F_2</u>

$\rho_{MP2}-\rho_{HF}$

$\rho_{SVWN}-\rho_{HF}$

$\rho_{MP2}-\rho_{BLYP}$

Isopyknen bei 0.002 e$^-$

$\rho_{SVWN}-\rho_{BVWN}$

$\rho_{SVWN}-\rho_{SLYP}$

$\rho_{SVWN}-\rho_{BLYP}$
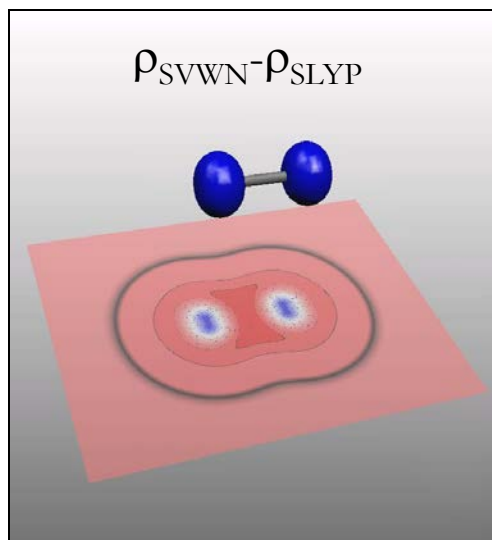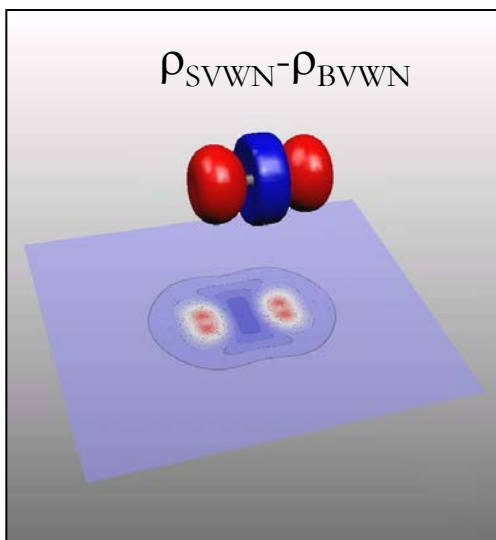
Dipole moments for selected molecules [in D, 1 D = 0.3934 a.u.]

Molecule	HF POL[a]	MP2 POL[a]	SVWN numerical[b]	SVWN TZVP-FIP[c]	BLYP TZVP-FIP[c]	BLYP POL[a]	BLYP 6-31G(d)[d]	B3LYP cc-pVTZ	B3LYP POL[a]	Exp.
CO	-0.25	0.31	0.23	0.24	0.19	0.19	0.15	0.13	0.10	0.11
H_2O	1.98	1.85	1.86	1.88	1.83	1.80	2.04	1.92	1.86	1.85
H_2S	1.11	1.03		1.15	1.07	0.97		1.19	1.01	0.97
HF	1.92	1.80	1.80	1.81	1.76	1.75	1.81	1.83	1.80	1.83
HCl	1.21	1.14				1.08		1.21	1.12	1.11
NH_3	1.62	1.52	1.53	1.57	1.52	1.48	1.90	1.59	1.52	1.47
PH_3	0.71	0.62				0.59		0.53	0.62	0.57
SO_2	1.99	1.54				1.57		2.01	1.67	1.63

[a] taken from Cohen and Tantirungrotechai, 1999; [b] taken from Dickson and Becke, 1996 [c] taken from Calaminici, Jug and Köster, 1998, [d] taken from Johnson, Gill and Pople, 1993

Barrier heights of $H_2 + H \rightarrow H + H_2$ [in kcal/mol]

Method	barrier without SIC	barrier with SIC
LSD	-2.3	5.7
BLYP	2.9	12.6
BPW91	4.7	14.3
B3LYP	4.1	11.1
exp.	**9.7**	

Taken from Johnson, 1995 and Csonka and Johnson, 1998

SIC

Table 6-2. Energy components [E_h] of various functionals for the hydrogen atom.

Functional	E_{tot}	$J[\rho]$	$E_X[\rho]$	$E_C[\rho]$	$J[\rho] + E_{XC}[\rho]$
SVWN	−0.49639	0.29975	−0.25753	−0.03945	0.00277
BLYP	−0.49789	0.30747	−0.30607	0.0	0.00140
B3LYP	−0.50243	0.30845	−0.30370[a]	−0.00756	−0.00281
BP86	−0.50030	0.30653	−0.30479	−0.00248	−0.00074
BPW91	−0.50422	0.30890	−0.30719	−0.00631	−0.00460
HF	−0.49999	0.31250	−0.31250	0.0	0.0

[a] Includes 0.06169 E_h from exact exchange.

Compilation of mean absolute deviations for bond lengths [Å] / bond angles [degrees] for small main group molecules from different sources.

32 first row species, 6-31G(d) basis set, Johnson, Gill, and Pople, 1993

HF	0.020 / 2.0	SVWN	0.021 / 1.9
MP2	0.014 / 1.8	BLYP	0.020 / 2.3
QCISD	0.013 / 1.8		

13 species, Martin, El-Yazal, and François, 1995a

CCSD(T)/cc-pVDZ	0.018 / 2.2	B3LYP/cc-pVDZ	0.009 / 1.7
CCSD(T)/cc-pVTZ	0.014 / 0.6	B3LYP/cc-pVTZ	0.004 / 0.3
CCSD(T)/cc-pVQZ	0.002 / 0.4	B3LYP/cc-pVQZ	0.004 / 0.3

40 species cont. third row elements, 6-31G(d) basis set, Redfern, Blaudeau and Curtiss, 1997

MP2	0.022 / 0.4	B3LYP	0.030 / 0.5
BLYP	0.048 / 1.0	B3PW91	0.020 / 0.5
BPW91	0.020 / 0.5		

[a] uncontracted aug-cc-pVTZ basis

Deviations between computed atomization energies and experiment for the JGP test set employing the 6-31G(d) basis set [in kcal/mol]. Taken from Johnson, Gill and Pople, 1993.

	HF	MP2	QCISD	SVWN	SLYP	BVWN	BLYP
mean abs. dev.[a]	86	22	29	36 (40)[a]	38	4 (4)[a]	6
mean dev.	-86	-22	-29	36 (40)[a]	38	0 (4)[a]	1

[a] Basis set free results taken from Becke, 1992.