

**ELECTRONIC STRUCTURE FROM FIRST PRINCIPLES:
WAVEFUNCTION THEORY (WFT) VS.
DENSITY FUNCTIONAL THEORY (DFT)**



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THE MOLECULAR SCHRÖDINGER EQUATION

N electrons (mass m_e , charge $-e$)

N_A nuclei (masses M_A , charges $+Z_A e$, $A = 1, \dots, N_A$)

- Time-independent molecular Schrödinger equation

$$\left(\hat{T}_e + V_{ee} + V_{ek} + \hat{T}_k + V_{kk} \right) \Psi(r, R) = E \Psi(r, R)$$

$r := \underline{r} = (\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)$ electron coordinates

$R := \underline{R} = (\underline{R}_1, \underline{R}_2, \dots, \underline{R}_{N_A})$ nuclear coordinates

$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \Delta_i$ kinetic energy operator electrons

$\hat{T}_k = -\frac{\hbar^2}{2} \sum_{A=1}^{N_A} \frac{1}{M_A} \Delta_A$ kinetic energy operator nuclei

$V_{ee} = \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}}$ electron-electron repulsion ($r_{ij} = |\underline{r}_i - \underline{r}_j|$)

$V_{ek} = -\sum_{A=1}^{N_A} \sum_{i=1}^N \frac{Z_A e^2}{4\pi\epsilon_0 R_{iA}}$ electron-nuclear attraction

$V_{kk} = \sum_{A=1}^{N_A} \sum_{B>A}^{N_A} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}$ nuclear-nuclear repulsion

E total molecular energy

$\Psi(r, R)$ total molecular wavefunction

THE BORN-OPPENHEIMER APPROXIMATION

Electrons much faster than nuclei \implies separate nuclear from electronic motion \implies

- **Born-Oppenheimer approximation, giving:**

- ① **An electronic Schrödinger equation**

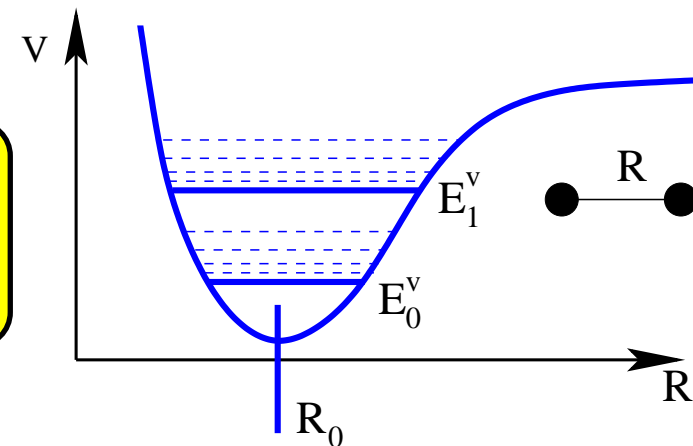
$$\underbrace{\left(\hat{T}_e + V_{ee} + V_{ek} \right)}_{\hat{H}_e} \Psi_e(r; R) = E_e(R) \Psi_e(r; R)$$

$E_e(R) =$ electronic energy (parametrically dependent on R)

$\Psi_e(r; R) =$ electronic wavefunction (parametrically dependent on R)

- ② **A nuclear Schrödinger equation**

$$\left(\hat{T}_k + \underbrace{V_{kk}(R) + E_e(R)}_{V(R)} \right) \Psi_k(R) = E \Psi_k(R)$$



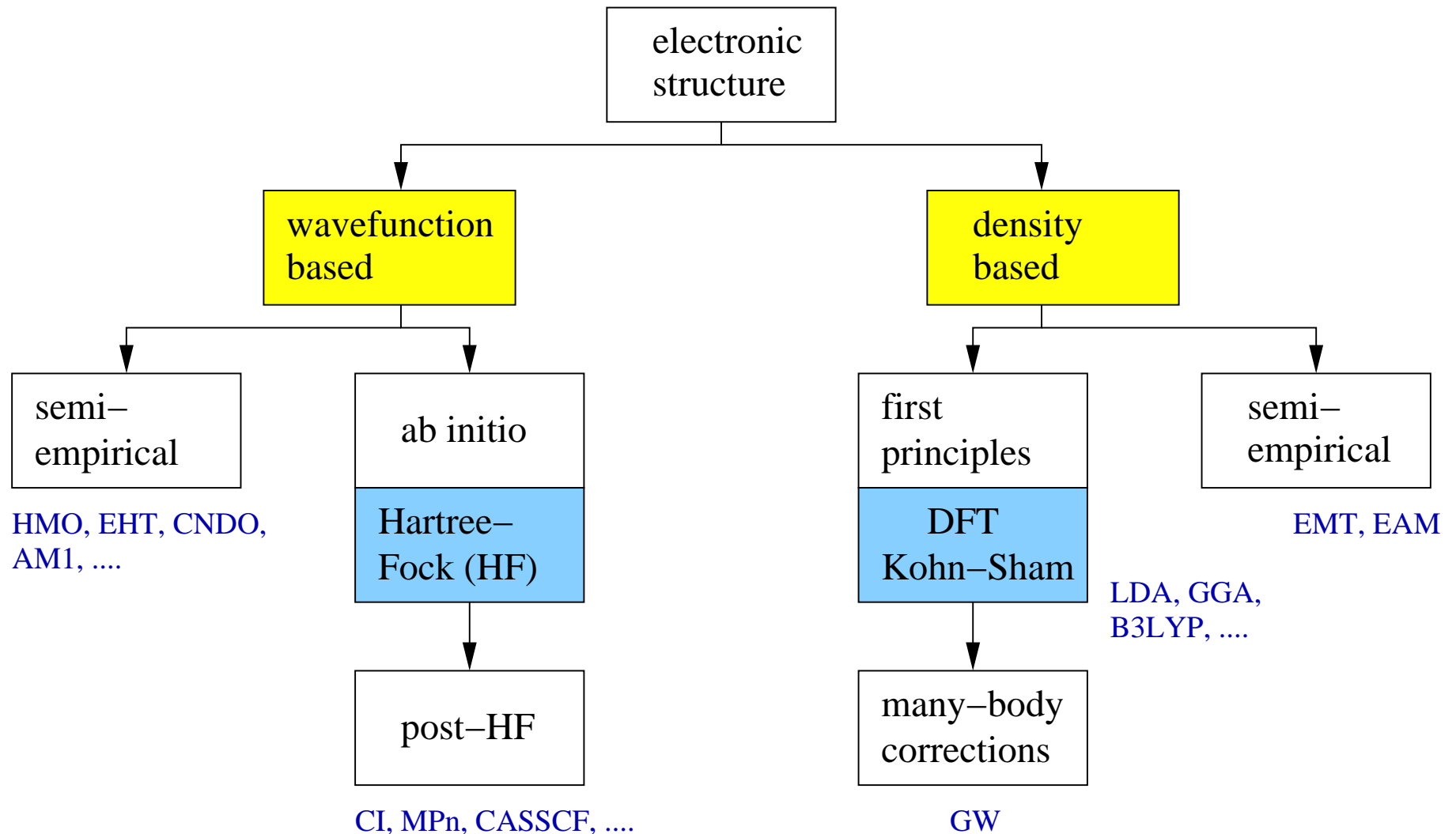
$V(R) =$ potential energy surface \implies molecular structure

$\Psi_k =$ nuclear wavefunction, with $\Psi = \Psi_k \cdot \Psi_e$

ELECTRONIC STRUCTURE METHODS

$$\hat{H}_e \Psi_{e,n}(r; R) = E_{e,n}(R) \Psi_{e,n}(r; R)$$

$n = 0$ (ground state), $n > 0$ (excited states)



ELECTRONIC STRUCTURE METHODS

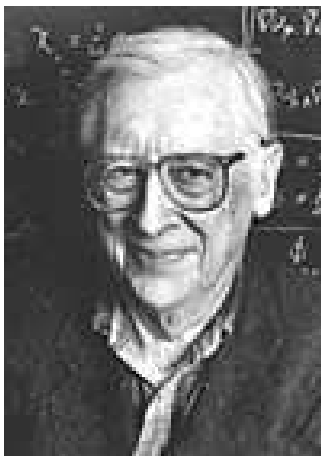
- The “wavefunction” world

$$E_e = E_e[\Psi_e(\underline{r}_1, \dots, \underline{r}_N)] = \langle \Psi_e | \hat{H}_e | \Psi_e \rangle$$

variational principle:

$$E_e^{opt} = \min_{\Psi_e} E_e[\Psi_e(\underline{r}_1, \dots, \underline{r}_N)]$$

⇒ 3N-dimensional variational problem!



John Pople



- The “density” world

$$E_e = E_e[n_e(\underline{r})]$$

variational principle:

$$E_e^{opt} = \min_{n_e} E_e[n_e(\underline{r})]$$

⇒ 3-dimensional variational problem!



Walter Kohn

THE WAVEFUNCTION WORLD: WAVEFUNCTIONS

• Orbitals: Eigenfunctions of 1-electron Hamiltonians

$$\chi(\underline{x}) = \underbrace{\psi(\underline{r})}_{\text{spatial}} \cdot \underbrace{\gamma(\omega)}_{\text{spin function}}$$

$$\gamma(\omega) = \alpha(\omega) \text{ or } \beta(\omega)$$

$$\omega = \text{spin coordinate } (\pm 1/2 \hbar)$$

$$\underline{x} = (\underline{r}, \omega)$$

$$\hat{h}(\underline{x}_1) \chi_a(\underline{x}_1) = \varepsilon_a \chi_a(\underline{x}_1)$$

Example: H atom (atomic units)

$$\hat{h}(\underline{x}_1) = -\frac{1}{2} \Delta_1 - \frac{1}{r_1}$$

$$\psi_a(\underline{r}_1) = \psi_{nlm}(\underline{r}_1) = \text{s, } 2p_x, \dots \text{ orbitals}$$

$$\varepsilon_a = \varepsilon_n = -\frac{1}{2n^2} \quad (n = 1, 2, \dots)$$

• N-electron wavefunctions: Slater determinants

$$\Psi(\underline{x}_1, \dots, \underline{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\underline{x}_1) & \chi_2(\underline{x}_1) & \cdots & \chi_N(\underline{x}_1) \\ \chi_1(\underline{x}_2) & \chi_2(\underline{x}_2) & & \vdots \\ \vdots & & \ddots & \vdots \\ \chi_1(\underline{x}_N) & \chi_2(\underline{x}_N) & \cdots & \chi_N(\underline{x}_N) \end{vmatrix} = |\chi_1(1), \dots, \chi_N(N)\rangle$$

- ❶ antisymmetric ❷ Pauli principle ❸ normalized ❹ approximate

▷ Every Slater determinant represents an **electron configuration**, e.g. $(1s^2 2s^2 2p^2)$ for C

THE WAVEFUNCTION WORLD: HARTREE-FOCK

• The Hartree-Fock equations

- Use single determinant $|\Psi_0\rangle = |\chi_1(1), \dots, \chi_N(N)\rangle$ as trial wavefunction for ground state
- Use full electronic Hamiltonian \hat{H}_e
- Determine orbitals χ_i from **variational principle** $E_0^{HF} = \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle = \min!$

\implies Hartree-Fock equations

$$\hat{f}(1) \chi_i(1) = \varepsilon_i^{HF} \chi_i(1) \quad ; i = 1, 2, \dots, N$$

• Properties

- Coupled single-electron equations, with **Fock operator**

$$\hat{f}(1) = -\frac{1}{2}\Delta_1 - \sum_{A=1}^{N_A} \frac{Z_A}{r_{1A}} + \underbrace{\sum_{b=1}^N \left(\underbrace{\hat{J}_b(1)}_{\text{Coulomb}} - \underbrace{\hat{K}_b(1)}_{\text{exchange}} \right)}_{\text{HF potential } \hat{V}^{HF}(1)}$$

- Nonlinear equations \implies iterative (self consistent field, SCF) solution
- Self-interaction free

THE ROOHTHAAN-HALL METHOD: LCAO-MO

• LCAO-MO

Spatial orbitals (MOs) are expanded in a set of K “atomic orbitals” $\{\phi_\nu\}$ (AOs):

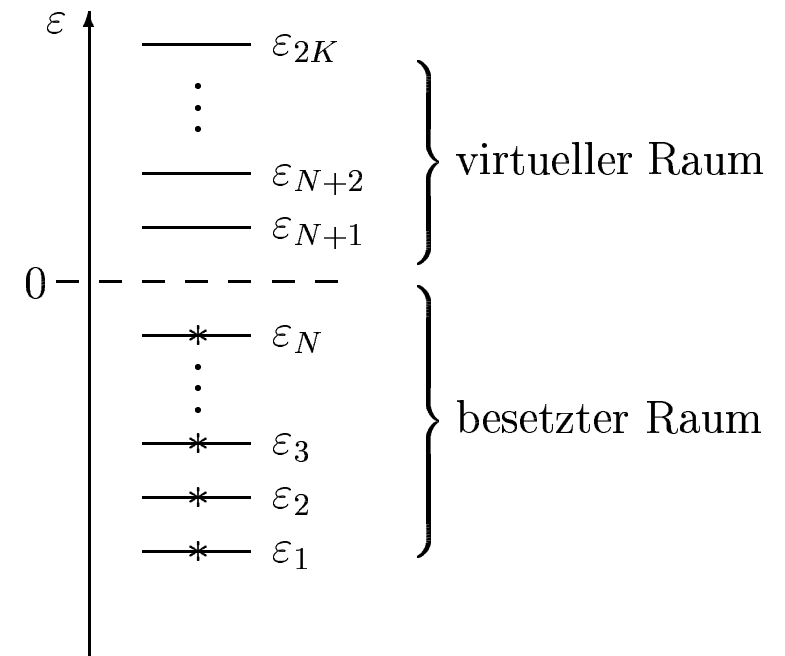
$$\psi_j(\underline{r}) = \sum_{\nu=1}^K C_{\nu j} \cdot \phi_\nu(\underline{r}) \quad ; \quad \nu = 1, 2, \dots, K$$

\implies linear variation problem for $C_{\nu j}, \varepsilon_j$

• Roothaan-Hall equations

$$\sum_{\nu=1}^K C_{\nu j} \underbrace{F_{\mu\nu}}_{\langle \phi_\mu | \hat{f} \phi_\nu \rangle} = \varepsilon_j \sum_{\nu=1}^K C_{\nu j} \underbrace{S_{\mu\nu}}_{\langle \phi_\mu | \phi_\nu \rangle}$$

closed- and open-shell variants

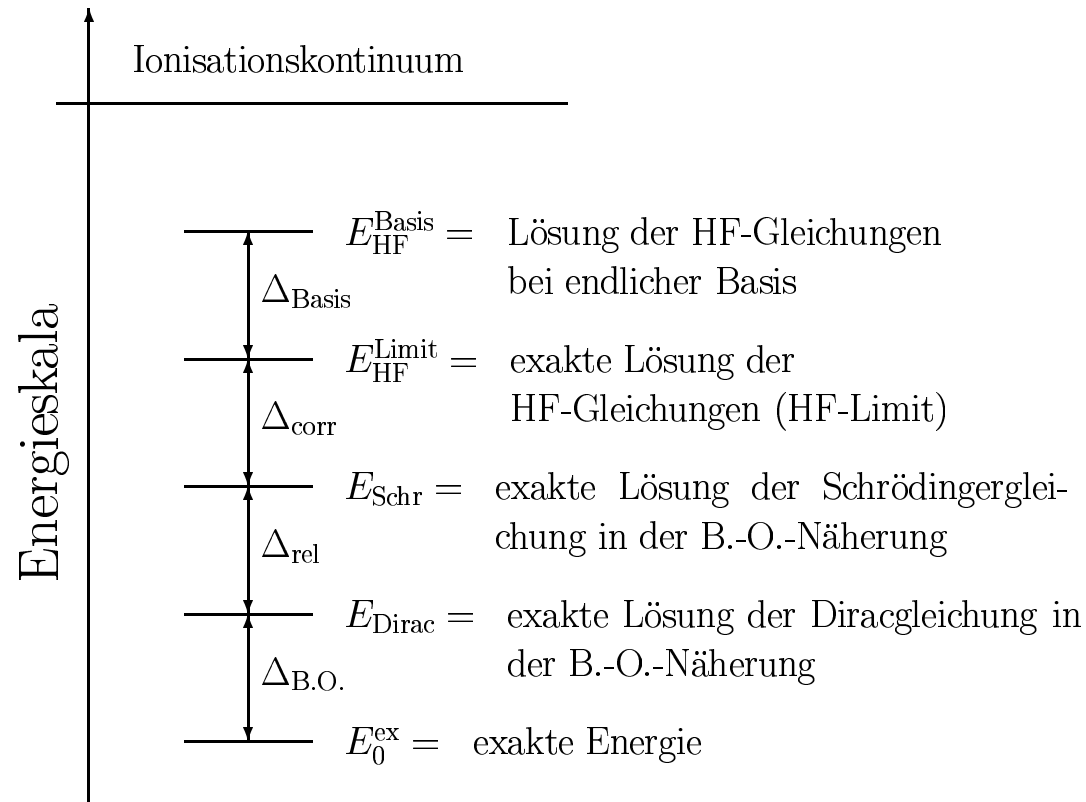


• Basis sets $\{\phi_\nu\}$

- ❶ Slater functions: $e^{-\zeta r}$
- ❷ Slater-type linear comb. of Gaussians: STO-3G, 6-31G*, ...; cc-pVDZ, cc-pVTZ, ...
- ❸ Plane waves: e^{ikr} , cutoff $V_c = k_{\max}^2 / 2$

CORRELATED METHODS

- The error ladder of *ab initio* quantum chemistry



$\Delta_{\text{B.O.}}$ = Nicht-B.-O. (nichtadiabatische) Korrekturen

Δ_{rel} = relativistische Korrekturen

Δ_{corr} = Korrelationsenergie der Elektronen

Δ_{Basis} = Basissatzfehler

- Correlation energy

$$\Delta_{\text{corr}} = E_0^{\text{ex}} - E_0^{\text{HF}}$$

dynamical and static correlation

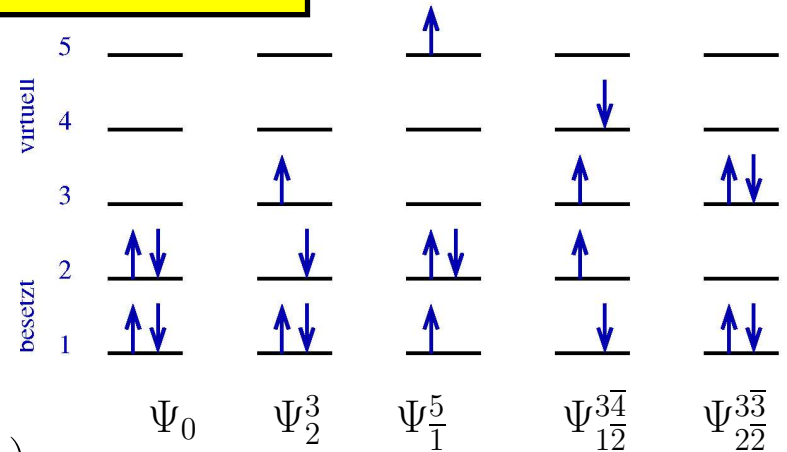
METHODS TO TREAT ELECTRON CORRELATION

- Form of exact wavefunction and configuration interaction (CI) methods

$$\Psi = \underbrace{D_0 \Psi_0}_{\text{HF}} + \underbrace{\sum_{a=1}^N \sum_{r=N+1}^{N_{\text{virt}}} D_a^r \Psi_a^r}_{\text{CI Singles}} + \underbrace{\sum_{a<b}^N \sum_{r<s}^{N_{\text{virt}}} D_{ab}^{rs} \Psi_{ab}^{rs}}_{\text{CI Singles Doubles}} + \underbrace{\dots \text{N-excitations}}_{\text{Full CI, FCI}}$$

1 correlation energy

2 excited states: $\underline{\underline{H}}^{CI} \underline{D}_n = E_n \underline{D}_n$



- Variants of CI-type methods

- MCSCF and CASSCF (vary amplitudes and orbitals)

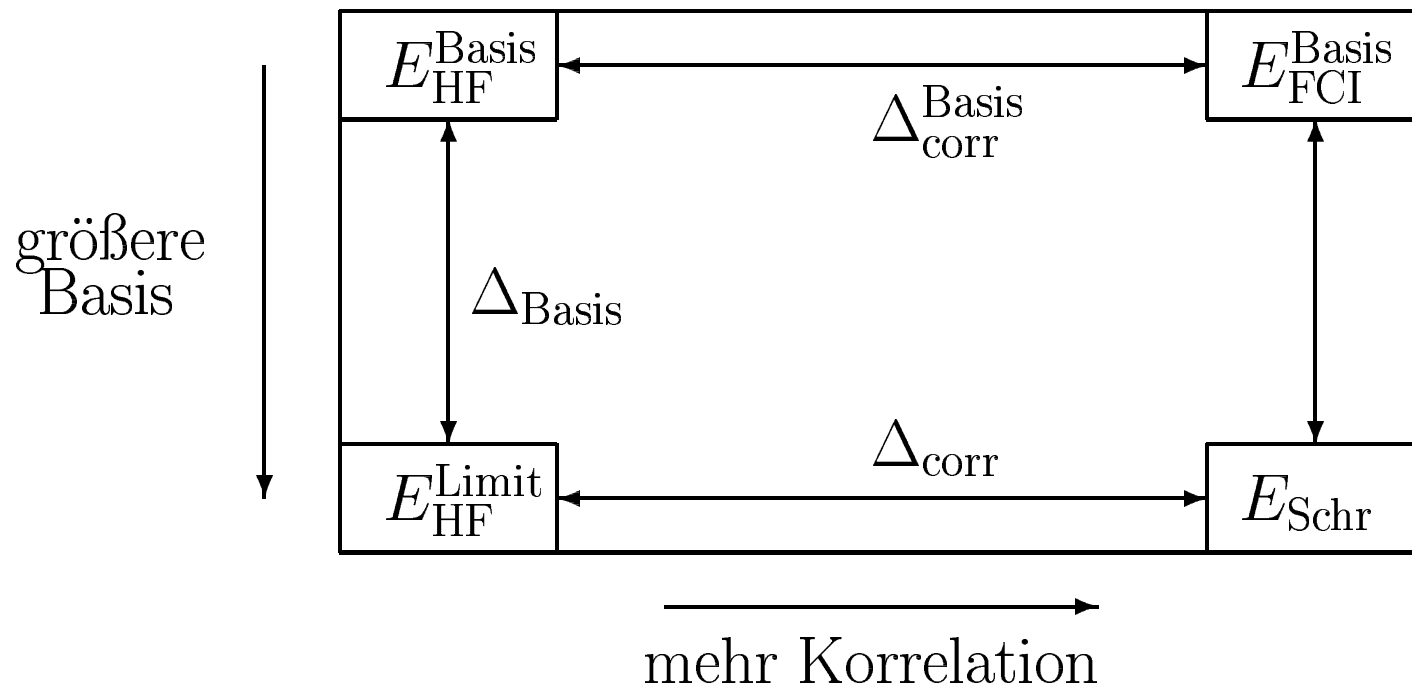
- Coupled Cluster (CC) methods:

$$\Psi = \underbrace{\exp(\hat{T}_1 + \hat{T}_2 + \dots \hat{T}_N)}_{\text{Full CI}} \Psi_0$$

CCS
CCSD

- Non-variational: Møller-Plesset perturbation theory (MP2, MP3, ...)

CONVERGENCE TO “EXACT” SOLUTION



- **Convergence parameters**

- ❶ **basis:** cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z, ...

- ❷ **correlation:** HF (=CCS,CIS,MP1), CCSD, CCSDT, CCSDTQ, ...

- **Extrapolation procedures: Achieving ‘chemical accuracy’**

- G1/2/3, W1/2/3, PCI-80** ... models:

- molecule and property sets, plus computational protocol

THE DENSITY WORLD: DFT

• The Hohenberg-Kohn theorems

- ① Ground state electronic energy E_0 completely determined by electron density $n(\underline{r})$:

$$E_0[n(\underline{r})] = \underbrace{T[n]}_{\text{kin. en. el}} + \underbrace{V_{ke}[n]}_{\text{nuc-el attr.}} + \underbrace{J[n]}_{\text{Coulomb el/el}} + \underbrace{\tilde{E}_{xc}[n]}_{\text{exchange-correlation}}$$

- ② Variational principle for densities

$$E_0^{opt} = \min_n E_0[n(\underline{r})]$$

• The Kohn-Sham equations

$$\left[-\frac{1}{2}\Delta - \sum_{A=1}^{N_A} \frac{Z_A}{|\underline{r} - \underline{R}_A|} + \int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' + \underbrace{\frac{\delta E_{xc}}{\delta n}}_{\text{xc potential } v_{xc}(\underline{r})} \right] \psi_i^s(\underline{r}) = \varepsilon_i^s \psi_i^s(\underline{r})$$

- single-particle equations (like HF), self-consistent solution
- contain electron correlation (unlike HF), exact if exchange-correlation functional exact
- $n(\underline{r}) = \sum_i^N |\psi_i^s(\underline{r})|^2$; $T = \sum_i^N \langle \psi_i^s | -\frac{1}{2}\Delta \psi_i^s \rangle$; $\tau(\underline{r}) = \sum_i^N \frac{1}{2} |\nabla \psi_i^s(\underline{r})|^2$ (kin.-energy dens.)

EXCHANGE-CORRELATION FUNCTIONALS

- Levels of approximation: $E_{xc} = E_x + E_c$

type	definition ($A = E_x, E_c$)	exchange	correlation
❶ Null	$A = 0$	–	–
❷ LDA	$A = \int a(n) n d\underline{r}$	S	VWN
❸ GGA	$A = \int a(n, \nabla n) n d\underline{r}$	B88, PW91	P86, PW91, LYP
❹ meta-GGA	$A = \int a(n, \nabla n, \tau) n d\underline{r}$	TPSS, BR, VSXC	TPSS, B95, VSXC

LDA= Local Density Appr.; GGA= Generalized Gradient Appr.; a = energy per electron

E.g.: **NullNull** (=Hartree); **SNull** (=X α); **SVWN** (=LDA); **BLYP**, **BP86** (both GGA)

- “Jacob’s ladder”: Systematically improvable DFT (?)

LDA, GGA, meta-GGA, hyper-GGA, ...

- DFT with “exact” (HF-like) exchange E_x^{ex} : Hybrid functionals

E.g.: $E_{xc}^{B3LYP} = (1 - a) E_x^{LDA} + a E_x^{ex} + b \Delta E_x^{B88} + (1 - c) E_c^{LDA} + c E_c^{LYP}$ ($a = 0.2$)

PERFORMANCE: ELECTRONIC ENERGIES

- Atomic energies: Ground states

	HF	X α	SVWN (=LDA)	BVWN	BLYP (= GGA)	MP2	QCISD (\approx CCSD)	exact
H	0.4982	0.4540	0.4760	0.5178	0.4954	0.4982	0.4982	0.5000
He	2.8552	2.7146	2.8267	2.9672	2.8978	2.8664	2.8702	2.9037
C	37.6809	37.0950	37.4537	38.0318	37.8320	37.7365	37.7552	37.8450
O	74.7839	73.9544	74.4884	75.3238	75.0470	74.8820	74.8977	75.067
Ne	128.4744	127.3950	128.1419	129.2442	128.8796	128.6262	128.6285	128.939

6-31G* basis; in atomic units (1 Hartree=27.21 eV) (Gill, 1993)

- Ionization potentials $IP = -\epsilon_{\text{HOMO}}$

Atom	HF	LDA	LDA-SIC	exp.
H	13.6	7.3	13.6	13.6
Li	5.3	3.2	4.4	5.4
Na	5.0	3.1	5.1	5.1
N	15.4	8.3	14.9	14.5
P	10.7	6.3	10.0	10.5
Cr	6.5	4.0	6.7	6.8

num. sol. of KS equations; in eV (Zunger, 1984)

- Comparison to experiment

Method	MAD	max. AD
G2	1.6	8.2
G2(MP2)	2.0	10.1
SVWN	90.9	228.7
BLYP	7.1	28.4
B3LYP	3.1	20.1
B3PW91	3.5	21.8

G2-2; in kcal/mol; Jenssen (1999)

PERFORMANCE: MOLECULAR GEOMETRIES

• Main group compounds

		HF	SVWN	BVWN	BLYP	MP2	QCISD	Expt.
H ₂	$R_0(\text{H-H})$	1.379	1.446	1.398	1.414	1.395	1.410	1.401
HF	$R_0(\text{H-F})$	1.722	1.776	1.778	1.786	1.782	1.765	1.733
H ₂ O	$R_0(\text{O-H})$	1.790	1.844	1.842	1.850	1.829	1.831	1.810
	$\theta_0(\text{H-O-H})$	105.5	103.6	102.9	102.7	104.0	104.0	103.9
NH ₃	$R_0(\text{N-H})$	1.891	1.938	1.937	1.944	1.920	1.925	1.910
	$\theta_0(\text{H-N-H})$	107.2	106.0	105.8	104.8	106.4	106.0	106.0
CH ₄	$R_0(\text{C-H})$	2.046	2.078	2.071	2.076	2.057	2.065	2.092
\bar{E}	$R_0(44)$	-0.010	0.014	0.018	0.020	0.010	0.012	–
$ \bar{E} $	$R_0(44)$	0.020	0.021	0.018	0.020	0.014	0.013	–

6-31G* (Gill, 1993); 32 molecules; in Å and °

• Rules of thumb

- ❶ LDA (HF) bond lengths slightly too long (short)
- ❷ Gradient corrections and post-HF slightly better



PERFORMANCE: TRANSITION METALS

• Geometries: $M(\text{CO})_6$

method	HF	MP2/ECP	CCSD(T)	SVWN	BP86	B3LYP	exp.
$\text{Cr}(\text{CO})_6$	1.970-2.010	1.862	1.939	1.865	1.910	1.921	1.918
$\text{Mn}(\text{CO})_6$	–	2.031	–	2.035	2.077	2.068	2.063
$\text{W}(\text{CO})_6$	–	2.047	–	2.060	2.116	2.078	2.058

M-C distance (in Å); extended basis sets, most at least of TZ quality; Koch /Holthausen (1999)

• Dissociation energies $M\text{H}^+ \rightarrow M + \text{H}^+$; excitation energies $M \rightarrow M^*$

	SVWN	BP86	B3LYP	MCPF	PCI-80	exp.
MAD diss. en. (kcal/mol)	12	8	4-5	6	2	± 2
MAD exc. en. (eV)	0.75		0.33			

M=Sc-Cu; details see Koch / Holthausen, *A Chemist's Guide to DFT* (1999)

• Rules of thumb

- ① LDA (HF) bond lengths too short (long)
- ② Gradient corrections and post-HF perform better
- ③ Errors generally larger than for main group compounds
- ④ Accurate low-spin / high-spin splittings very difficult (role of exact exchange)



PERFORMANCE: VIBRATIONAL FREQUENCIES

- For some main group compounds

		HF	SVWN	BVWN	BLYP	MP2	QCISD	Expt.
H ₂		4646	4207	4461	4373	4534	4367	4401
FH		4358	3912	3841	3810	4041	4020	4139
CO		2439	2169	2105	2105	2125	2176	2170
H ₂ O	SS	4070	3657	3597	3568	3776	3751	3832
	BI	1827	1646	1698	1682	1735	1745	1648
	AS	4189	3789	3721	3690	3918	3878	3943
NH ₃	SS	3689	3372	3332	3305	3504	3457	3506
\overline{E}	(213)	165	-51	-47	-63	69	12	—
$ \overline{E} $	(213)	168	75	61	73	99	42	—

harmonic frequencies; 6-31G*; in cm⁻¹; 213 vibrations of 32 molecules (Gill, 1993)

- Rules of thumb

- 1 LDA (HF) slightly too “soft” (“hard”)
- 2 Gradient-corrected DFT, QCISD perform well
- 3 scaling factors (6-31G*): 0.895 (HF), 0.943 (MP2), 0.995 (BLYP), 0.9614 (B3LYP)



PERFORMANCE: ATOMIZATION ENERGIES

- Atomization (dissociation) energies: $A-B \rightarrow A+B$

	HF	SVWN	BVWN	BLYP	MP2	QCISD	Expt.
H ₂	75.9	107.5	110.8	103.2	86.6	91.2	103.3
LiH	30.4	57.5	60.3	54.9	39.8	44.1	56.0
Li ₂	2.2	22.5	20.5	19.8	14.1	20.9	24.0
F ₂	-34.3	83.6	47.4	54.4	36.8	27.9	36.9
H ₂ O	131.7	240.8	209.1	207.3	188.8	183.7	219.3
CH ₄	300.4	436.8	396.0	389.9	354.2	353.9	392.5
\overline{E} (32)	-85.8	35.6	0.1	1.0	-22.4	-28.8	–
$ \overline{E} $ (32)	85.9	35.7	4.4	5.6	22.4	28.8	–

32 molecules; 6-31G*; in kcal/mol (Gill, 1993)

G2 set/6-311+G(3df,2p), MADs: 74.5 (HF); MP2 (7.3); BLYP (5.0); BP86 (10.3)

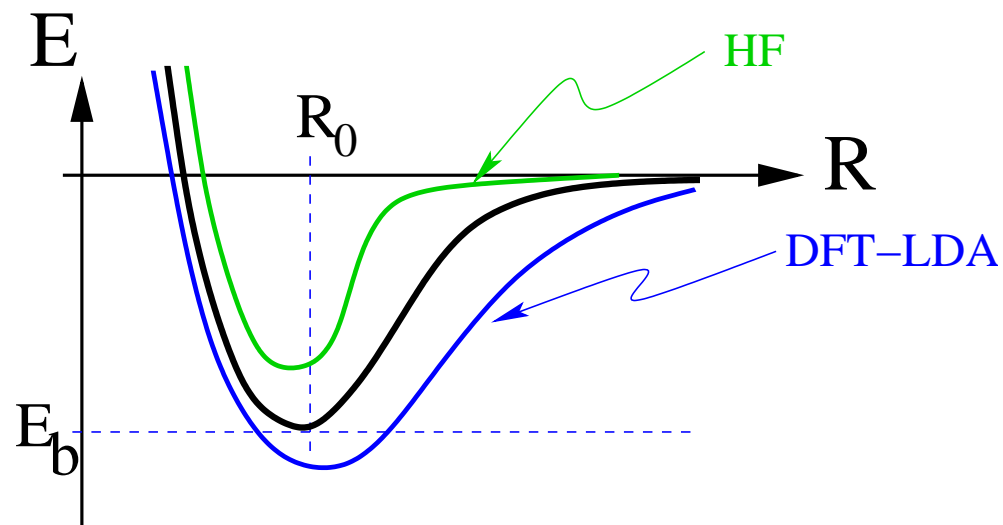
- Rules of thumb

- 1 LDA (HF) too large (much too small)
- 2 Improvement by gradient corrections or post-HF



PERFORMANCE: POTENTIAL CURVES

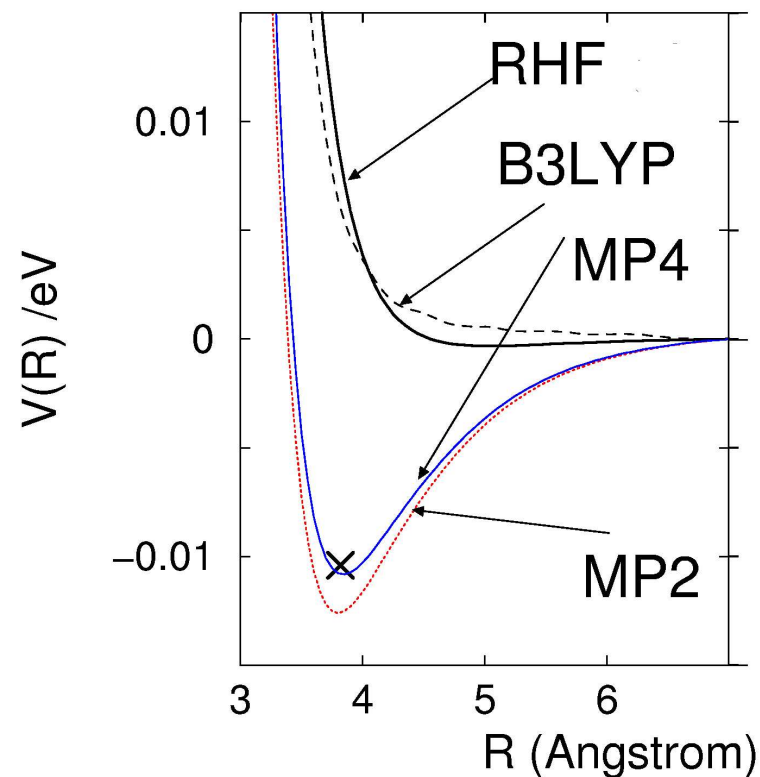
• Chemical bond: Summary



- 1 HF too shallow, too steep
- 2 LDA too deep, too flat
- 3 GGA and post-HF perform better

• Van-der-Waals bond

Ar_2 , 6-311++G(3df,3dp)



- 1 HF and B3LYP fail, the former because lack of correlation, the latter because $\lim_{r \rightarrow \infty} v_c(r)$ wrong
- 2 Good basis sets needed

PERFORMANCE: NON-BONDING INTERACTIONS

• Types

- 1 Hydrogen-Bonded systems
- 2 Charge-Transfer systems
- 3 Dipole-Interacting systems
- 4 Weak Interactions

• Systematic study (JCTC 1, 415 (2005))

- 44 DFT, 1 WFT (MP2), good basis sets
- 4 data bases
- W1 reference (CCSD(T), CBS)

• Rules of thumb

- 1 $MP2 \approx \text{hyper-GGA} > \text{meta-GGA} > \text{GGA} > \text{LDA}$
- 2 There is always a functional ...

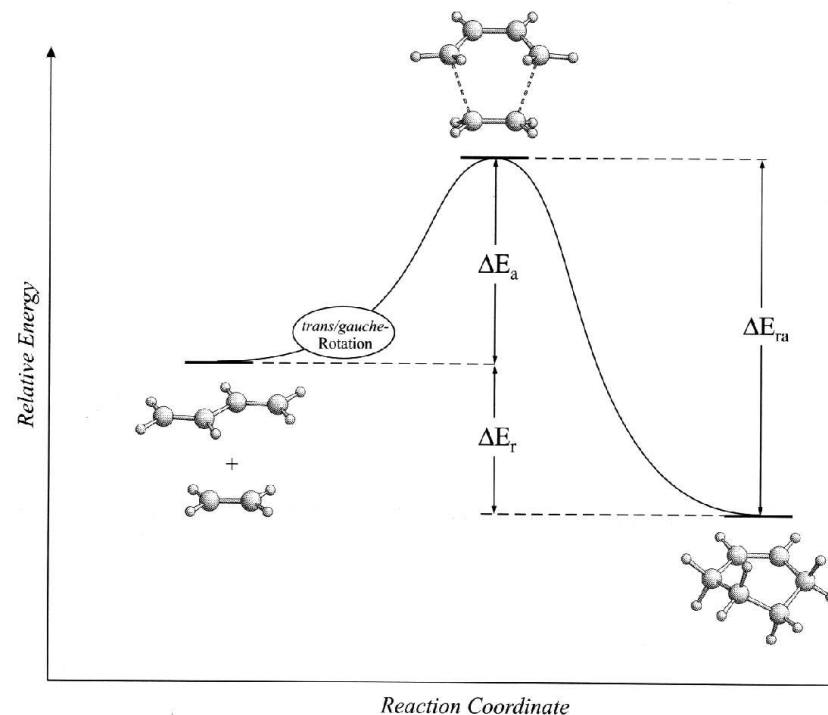


Table 8. Overall Results (kcal/mol)^a

rank	method	MMMUE				MMMMUE ^b
		HB	CT	DI	WI	
1	MPWB1K	0.61	0.50	0.52	0.22	0.46
2	MP2	0.66	0.60	0.55	0.16	0.49
3	MPW1B95	0.71	0.56	0.53	0.25	0.51
4	PBE1KCIS	0.60	0.93	0.36	0.27	0.54
5	MPW1K	0.53	0.68	0.55	0.44	0.55
6	PBE1PBE	0.47	1.05	0.39	0.29	0.55
7	B98	0.61	0.95	0.38	0.28	0.55
8	B97-1	0.53	1.20	0.33	0.19	0.56
9	BHandHLYP	0.52	0.63	0.73	0.41	0.57
10	X3LYP	0.55	0.98	0.49	0.40	0.60
11	mPW1PW91	0.63	0.75	0.55	0.53	0.62
12	MPW3LYP	0.57	1.38	0.34	0.32	0.65
13	MPWK CIS1K	0.79	0.74	0.74	0.42	0.67
14	B3P86	0.46	1.10	0.53	0.68	0.69
15	TPSS1KCIS	0.71	1.22	0.50	0.40	0.71
16	B3LYP	0.77	0.80	0.78	0.60	0.74
17	TPSSh	0.63	1.43	0.53	0.45	0.76
18	MPW1KCIS	1.04	0.93	0.69	0.48	0.79
19	B97-2	1.32	0.75	0.86	0.56	0.87
20	BB1K	1.11	0.86	1.01	0.54	0.88
21	B3PW91	1.13	0.82	0.97	0.85	0.94
22	TPSS	0.66	2.15	0.54	0.47	0.95
23	TPSSKCIS	0.75	2.13	0.51	0.42	0.95
24	B1B95	1.37	0.73	1.11	0.65	0.96
25	PBEKCIS	0.70	2.60	0.41	0.27	1.00
26	mPWPBE	0.82	2.17	0.60	0.56	1.03
27	mPWB95	0.94	2.36	0.53	0.32	1.04
28	HCTH	1.76	1.45	0.59	0.36	1.04
29	mPWPW91	0.77	2.28	0.58	0.53	1.04
30	mPWKCIS	1.15	1.87	0.62	0.52	1.04
31	PBE	0.50	2.94	0.49	0.28	1.05
32	mPWLYP	0.72	2.71	0.41	0.40	1.06
33	XLYP	0.92	2.15	0.64	0.56	1.06
34	BP86	0.88	2.03	0.71	0.93	1.14
35	BLYP	1.29	1.72	1.00	0.81	1.21
36	BPW91	1.70	1.47	1.18	1.09	1.36
37	BB95	1.87	1.56	1.19	0.87	1.37
38	BPBE	1.74	1.45	1.20	1.11	1.38
39	VSXC	0.61	2.84	1.10	1.64	1.55
40	O3LYP	2.76	1.32	2.00	0.79	1.72
41	OLYP	3.60	1.60	2.40	0.93	2.13
42	G96LYP	2.95	1.33	2.56	1.89	2.18
43	SPWL	4.62	6.73	2.93	0.40	2.75
44	SVWN5	4.63	6.73	2.93	0.40	3.67
45	SVWN3	4.87	6.94	3.08	0.44	3.83
	average	1.28	1.78	0.92	0.56	1.14

PERFORMANCE: REACTIONS

- An example: Diels-Alder reaction



	Exp.	G2	HF	SVWN	BLYP	B3LYP
ΔE_a (kcal/mol)	27 ± 2	25	51	5	26	28
ΔE_r (kcal/mol)	-38	-38	-30	-59	-14	-29

HF and DFT with 6-311+G(d,p), zero-point corrected

- Rules of thumb

- ❶ LDA (HF) activation energies much too small (much too high)
- ❷ LDA (HF) overbinds (underbinds)
- ❸ Gradient corrections and post-HF perform better



PERFORMANCE: EXCITED STATES

• Examples

mol	state	TDDFT/ SVWN	TDDFT/ B3LYP	CIS	Exp.
N ₂	³ Σ _u ⁺	7.86	7.04	6.23	7.75
	¹ Π _g	9.05	9.25	10.02	9.31
	¹ Σ _u ⁻	10.22	9.73	9.06	10.27
H ₂ CO	³ A ₂	3.02	3.14	3.72	3.5
	¹ A ₁	6.79	7.30	9.53	8.14
Ethylen	³ B _{1u} (π → π*)	4.62	3.99	3.55	4.36
	¹ B _{1u} (π → π*)	7.45	7.36	7.71	≈ 8.00
Pyridin	³ A ₁	4.48	3.91	3.53	4.1
	³ B ₁	3.67	4.05	5.12	4.1
	\overline{E}	-0.15	-0.25	0.05	-
	$ \overline{E} $ (rms)	0.38	0.36	1.00	

Error from many states of 4 molecules; in eV; basis, geometries from Ahlrichs (1996)

• Preliminary rules of thumb

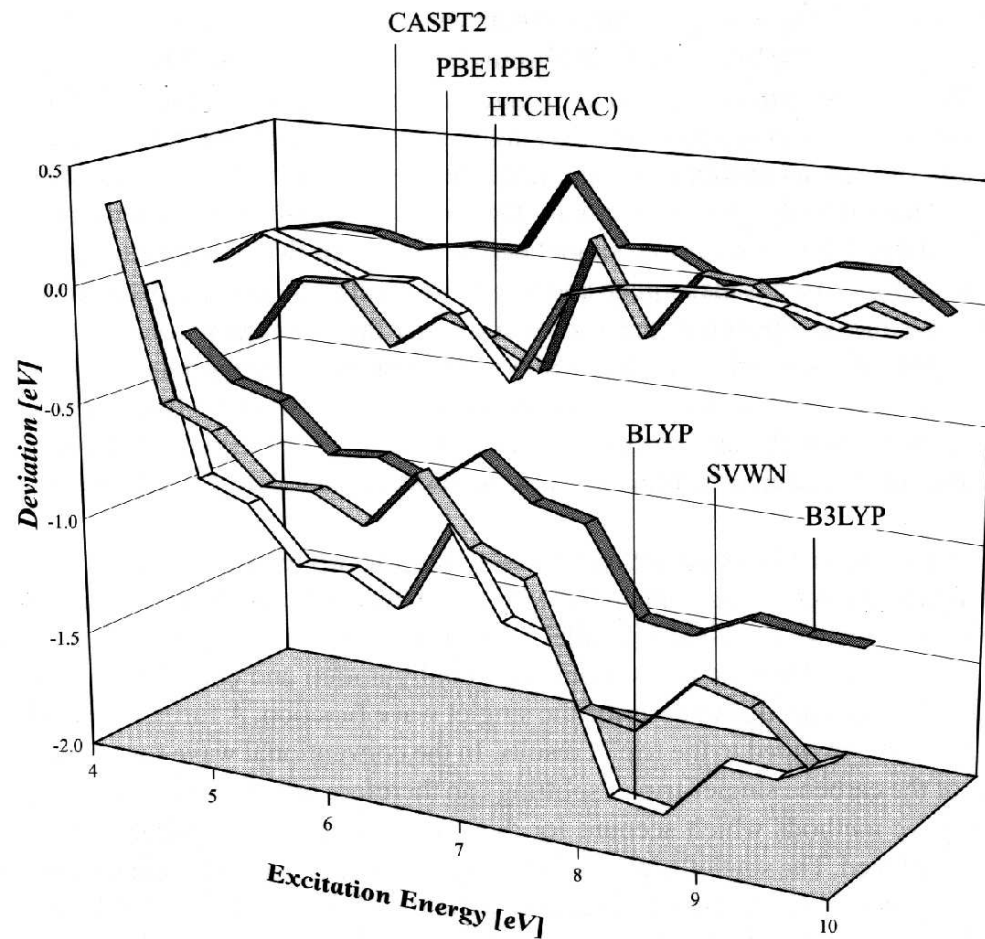
❶ CIS activation energies too high

❷ TDDFT performs better, in particular for π → π* and n → π* transitions



PERFORMANCE: EXCITED STATES II

- Ethylene: Higher excitations



- Some further rules of thumb

- Higher excited states more difficult for TDDFT
- Problem cases:** Charge transfer states, Rydberg states ($1/r$ problem)
- There is always a functional ...



OTHER ISSUES AND SUMMARY

- Things not touched upon here

- ① Solids, in particular metals

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Why does the B3LYP hybrid functional fail for metals?

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- ② Properties (electric, magnetic, ...)
- ③ Static correlation: Multi-determinant effects, conical intersections and all that
- ④ Computational effort: Clear advantage for DFT

- Conclusions

- ① About $\approx 90\%$ calculations done with DFT: Good price / performance relation
- ② DFT has replaced semiempirical methods in electronic structure theory
- ③ There is always a functional ...