Lecture 6
Accounting of Electron correlation effects

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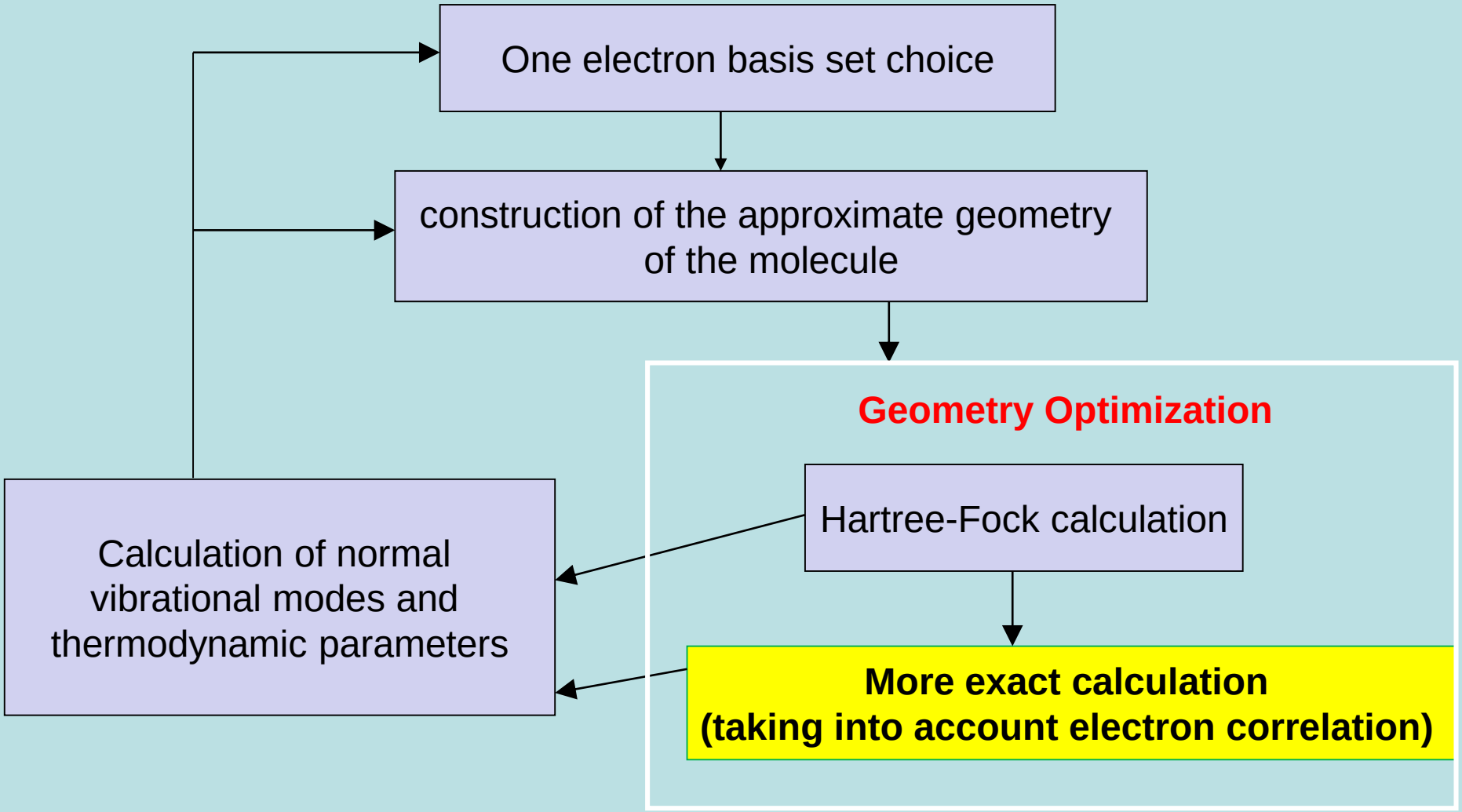
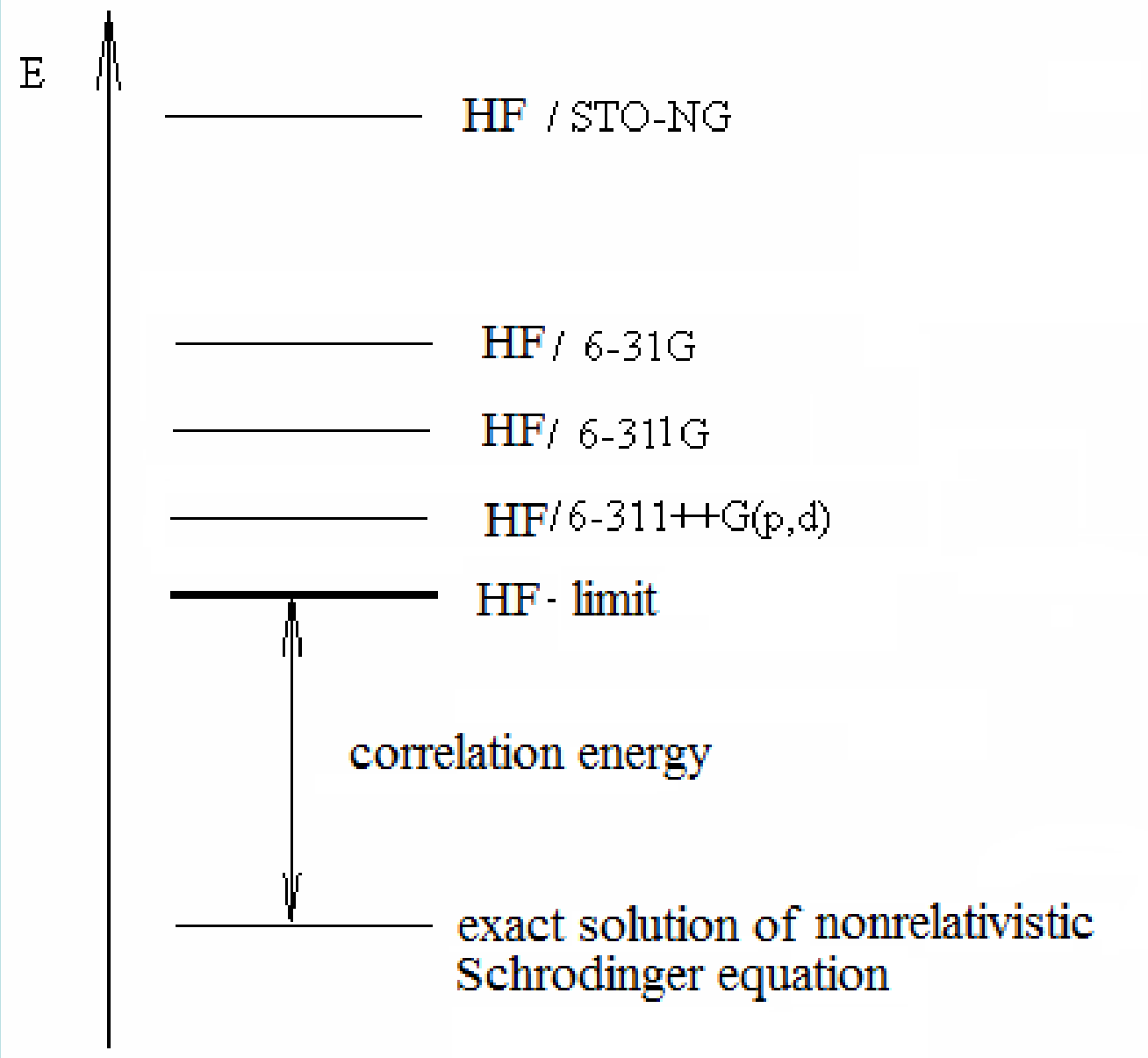
Gaussian, GAMESS, DALTON, COLUMBUS, SAPT

A typical scheme of quantum chemical calculations (ab initio)



Hartree-Fock limit



Water molecule in different basis sets (Hartree-Fock calculations)

Базис	∠ HOH	R_{OH}	**μ(D)**	**E(a.e.)**
STO-6G	100.00	0.986	1.754	-75.681200
6-31G	111.54	0.950	2.501	-75.985359
6-31++G(p,d)	107.09	0.943	2.227	-76.031309
6-311G	111.88	0.945	2.488	-76.010955
6-311G(p,d)	105.45	0.941	2.139	-76.047092
6-31G++(p,d)	106.20	0.941	2.196	-76.053446
6-311G++(3p,3d,f)	106.34	0.940	1.968	-76.059488
HF limit **Experiment**	104.52	0.957	1.833	**-76.067** **-76.431**

228 kcal / mol

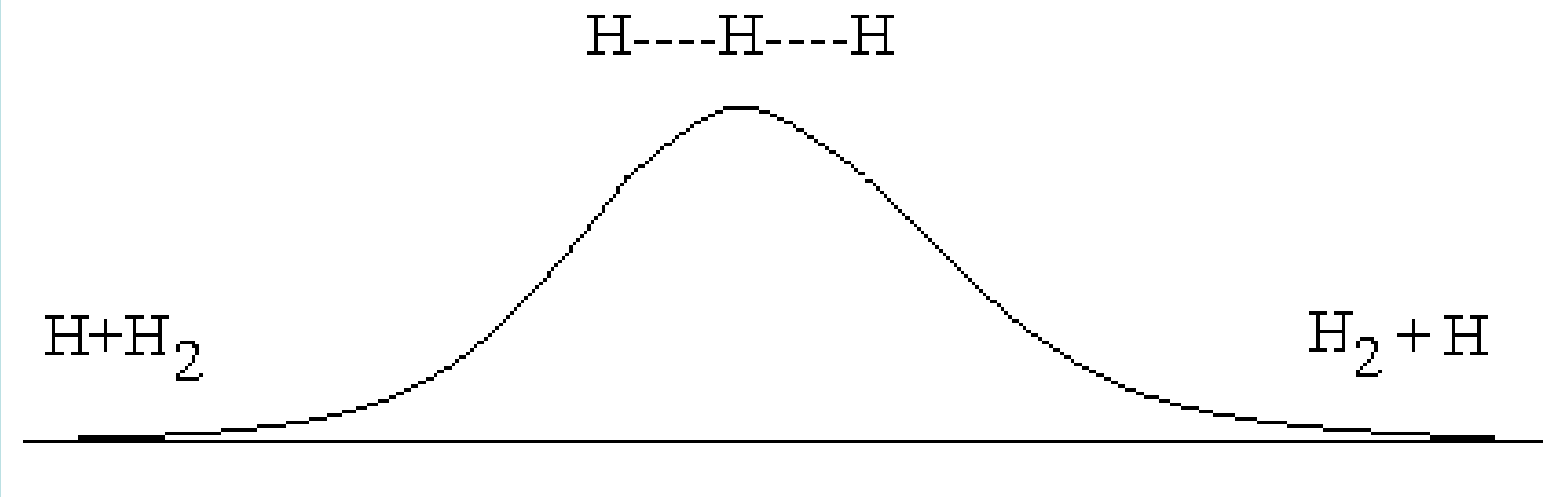
Dipole Moment CO

STO-1G	6-31G	6-311G	6-311(3d)	6-311G(3d,1f)	$C^{-}O^{+}$
+0.730	–0.573	–0.477	–0.080	–0.147	+0.112

Water molecule. Frequency (cm^{-1})

базис			
STO-6G	4351.43	4101.54	2161.46
6-31G	4145.43	3988.45	1736.92
6-311G	4172.06	4016.60	1737.0
6-311G**	4225.06 (469)	4153.91 (497)	1782.36 (188)
Experim	3755.8	3656.7	1594

$$H + H_2 = H_2 + H$$



Examples

System	Property	HF	Exact value
$H + H_2 = H_2 + H$	TS (kcal/mol)	24.5	calc. 9.65
HF	Dissoc. energy (kcal/mol)	102.4	experim. 141.2
N_2	Dissoc. energy. (kcal/mol)	121.7	experim. 228.4
Oxygen atom	Ionization energy (eV)	10.07	experim. 13.62
Oxygen atom	Affinity to electron energy (eV)	-0.54	experim. $+1.46_7$

Atomization energy

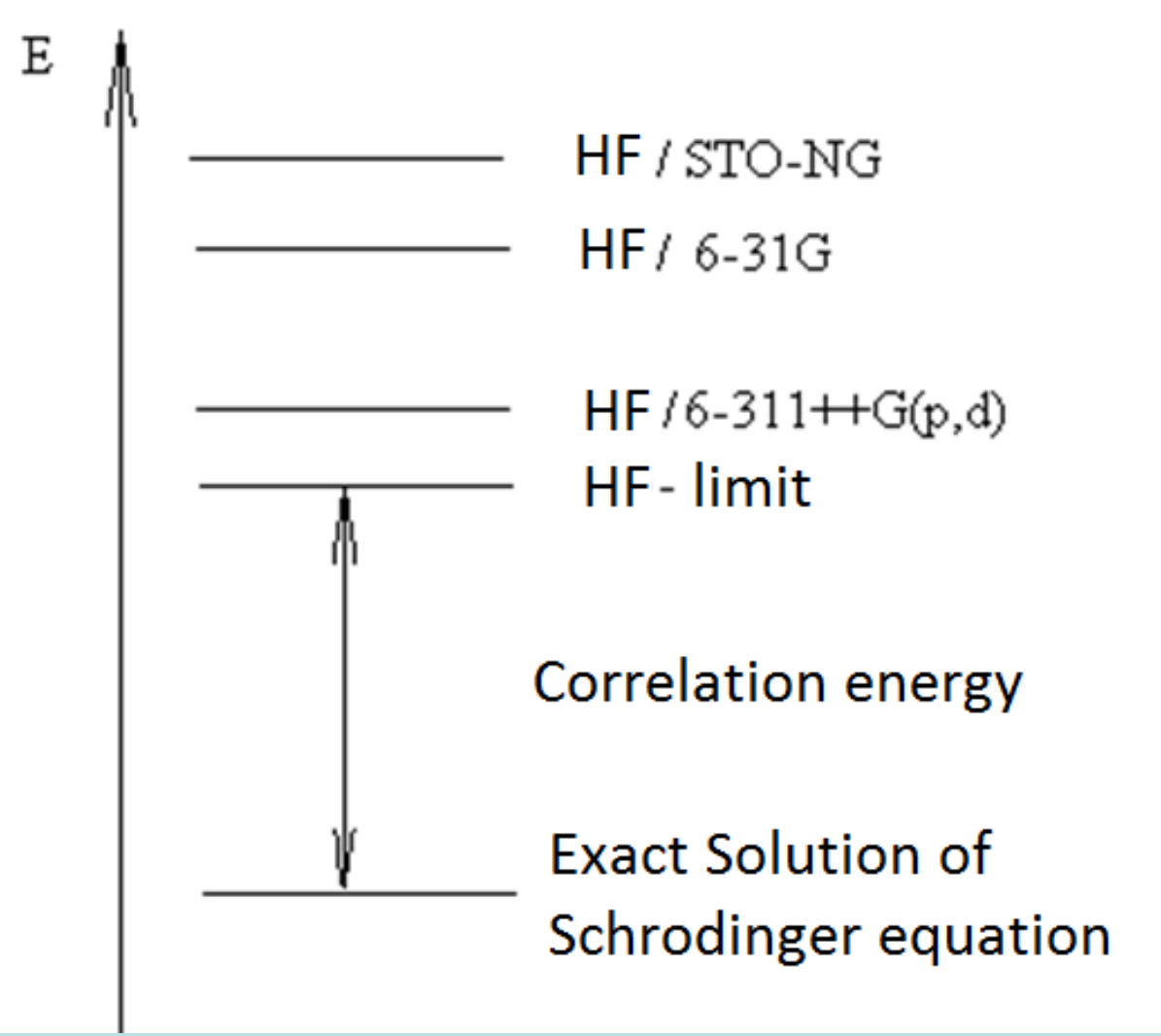
$$H_2O = 2H + O$$

Energy (a.u)	H_2O	2H+O	$E_{atomization}$
E_{HF}	-76.057770	-75.811376	0.2464
$E_{exact.}$	-76.337522	-75.981555	0.3560

$$E_{atomization} = E_{H2O} - (2E_H + E_O)$$

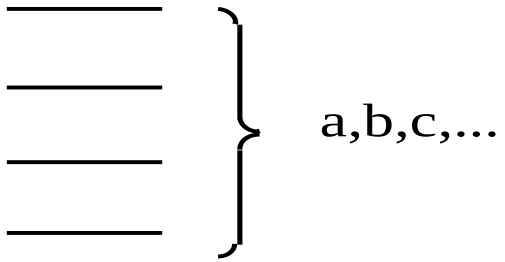
Error: $\dfrac{0.3560 - 0.2464}{0.3560} \cdot 100\% \approx 31\%$

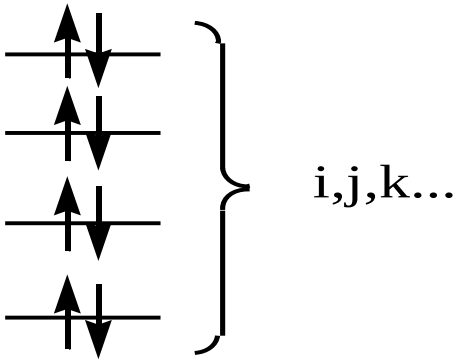
Correlation Energy

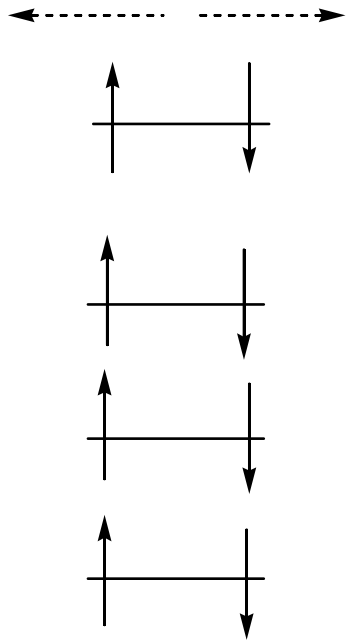


$$E_{corr.} = E_{exact} - E_{Hartree-Fock}$$

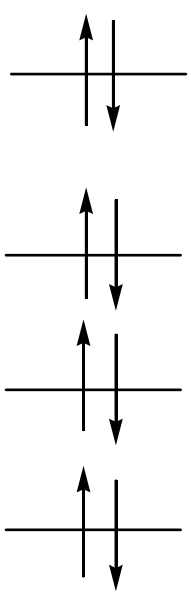
What is Electron Correlation ?

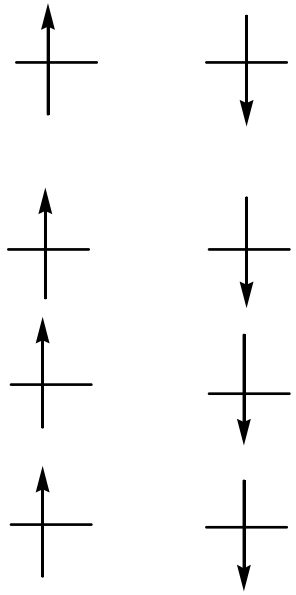






Solution of electron correlation problem (different orbitals for different spins)

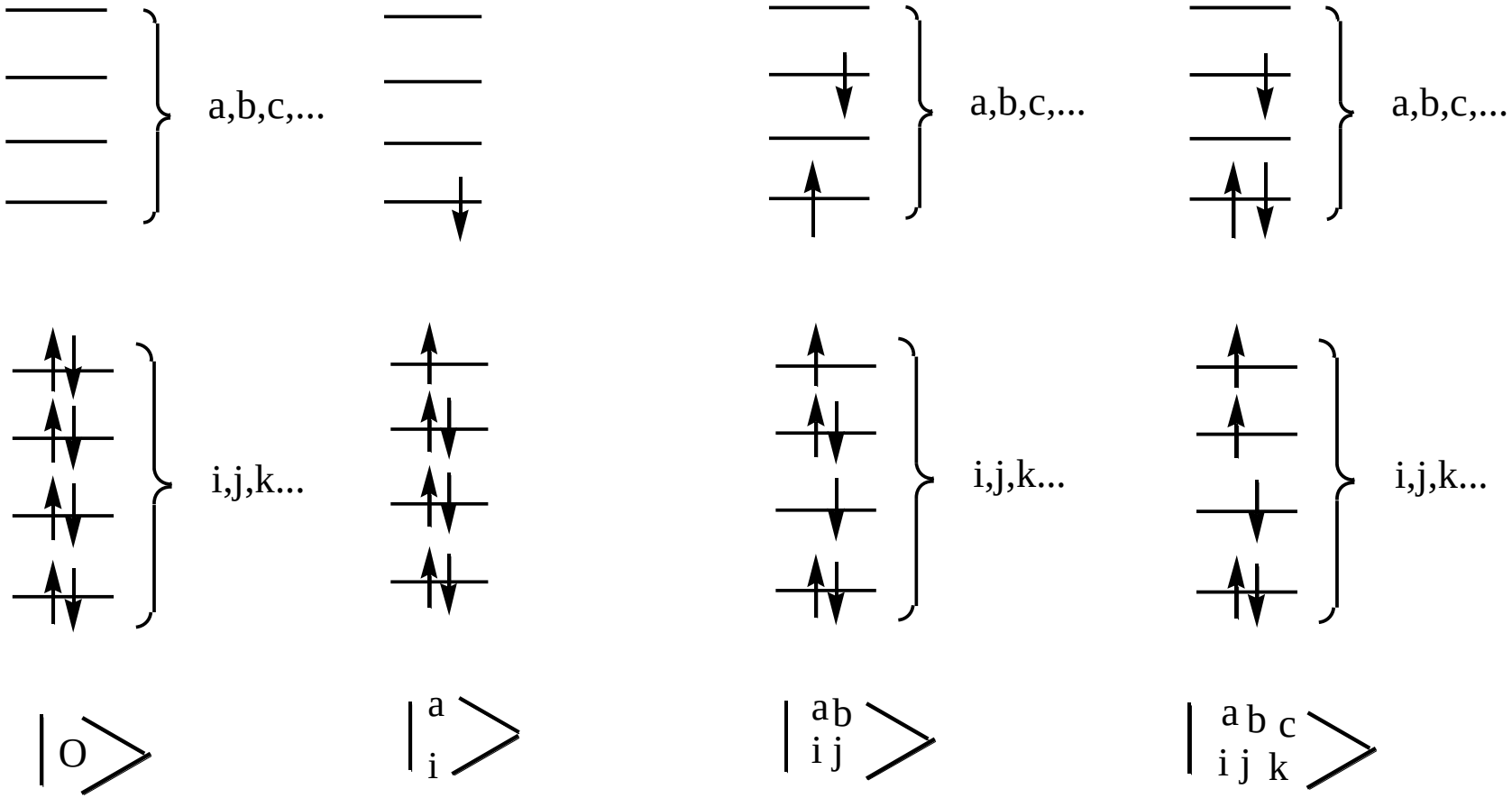




Restricted Hartree-Fock (RHF)

Unrestricted Hartree-Fock (UHF)

Solution of electron correlation problem (electron excited configurations)



Exact wave function
Full Configuration Interaction, FCI)

$$\left|\Psi_{\text{exact}}\right\rangle = \left|0\right\rangle + \sum_{i,a} C_i^a \left|\begin{matrix} a \\ i \end{matrix}\right\rangle + \sum_{\substack{i>j \\ a>b}} C_{ij}^{ab} \left|\begin{matrix} ab \\ ij \end{matrix}\right\rangle + \sum_{\substack{i>j>k \\ a>b>c}} C_{ijk}^{abc} \left|\begin{matrix} abc \\ ijk \end{matrix}\right\rangle + \cdots$$

$$E_{\text{exact}} = E_{\text{exact}}\left(C_i^a, C_{ij}^{ab}, C_{ijk}^{abc}, C_{ijkl}^{abcd}, \ldots.\right)$$

Implemented in GAMESS

How much configurations in FCI?

υ **– Weil number** – number of configurations.
N electrons, **M** basis functions, **s** - spin

$$\upsilon(M,N,s) = \frac{2s+1}{N/2+s+1}\binom{M+1}{N/2-s}\binom{M}{N/2+s}$$

number of combinations

$$\binom{n}{k} = \frac{n!}{(n-k)!k!}$$

H_2O molecule

Basi set	M	$\nu(M,10,0)$	
STO-6G	7	196	1.5K
6-31G	13	428 429	3.3Mb
6-311G	19	730 046 52	229Mb
6-311++G(3p,3d,1f)	71	30 361 438 274 192	226210Gb = 220Tb

Restricted configuration interaction, CI

$$\left|\Psi_{\mathrm{CISD}}\right\rangle = \left|0\right\rangle + \sum_{i,a} C_i^a \left|\begin{matrix} a \\ i \end{matrix}\right\rangle + \sum_{\substack{i>j,\\ a>b}} C_{ij}^{ab} \left|\begin{matrix} ab \\ ij \end{matrix}\right\rangle$$

$$\left|\Psi_{\mathrm{CISDT}}\right\rangle = \left|0\right\rangle + \sum_{i,a} C_i^a \left|\begin{matrix} a \\ i \end{matrix}\right\rangle + \sum_{\substack{i>j,\\ a>b}} C_{ij}^{ab} \left|\begin{matrix} ab \\ ij \end{matrix}\right\rangle + \sum_{\substack{i>j>k,\\ a>b>c}} C_{ijk}^{abc} \left|\begin{matrix} abc \\ ijk \end{matrix}\right\rangle$$

$$\left|\Psi_{\mathrm{CISDTQ}}\right\rangle = \left|0\right\rangle + \sum_{i,a} C_i^a \left|\begin{matrix} a \\ i \end{matrix}\right\rangle + \sum_{\substack{i>j,\\ a>b}} C_{ij}^{ab} \left|\begin{matrix} ab \\ ij \end{matrix}\right\rangle + \sum_{\substack{i>j>k,\\ a>b>c}} C_{ijk}^{abc} \left|\begin{matrix} abc \\ ijk \end{matrix}\right\rangle + \sum_{\substack{i>j>k>l,\\ a>b>c>d}} C_{i\,jk\,l}^{abcd} \left|\begin{matrix} abcd \\ ijk\,l \end{matrix}\right\rangle$$

$$E_{\mathrm{HF}} > E_{\mathrm{CISD}} > E_{\mathrm{CISDT}} > E_{\mathrm{CISDTD}} > \cdots\cdots > E_{\mathrm{CISDTQ.....}} \equiv E_{\mathrm{FCI}}$$

Many particle perturbation theory (1932)

Møller-Plesset theory describes electron correlation effects as a perturbation of Hartree-Fock solution.

$$E = E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)} \ldots$$

$$\psi_{exact} = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \ldots$$

MBPT, Möller-Plesset, MP

$$H = H_0 + V$$

$$E = E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)} \ldots \qquad E_{X\Phi} = E^{(0)} + E^{(1)}$$

$$\psi_{exact} = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \ldots$$

$$\left|\psi^{(0)}\right\rangle = \left|0\right\rangle \qquad \left|\psi^{(1)}\right\rangle = \sum C_{ij}^{ab} \left|\begin{matrix} ab \\ i\ j \end{matrix}\right\rangle$$

MP2 **(>50% corr.)**:

$$E^{(2)} = \sum \frac{[ai|bj]([ai|bj]-[aj|bi])}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

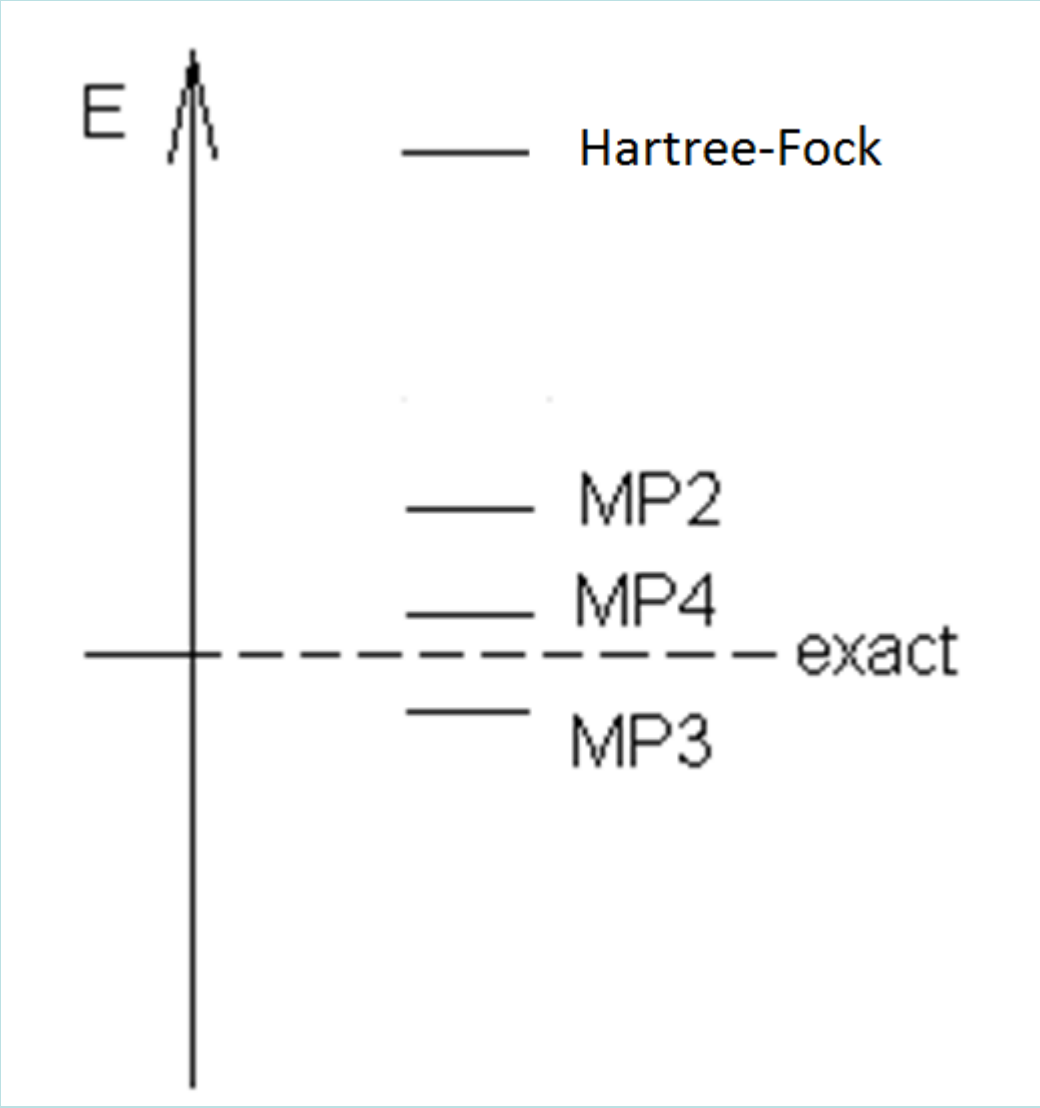
Gaussian: MP2, MP3, MP4(SDQ), MP4

GAMESS: MP2

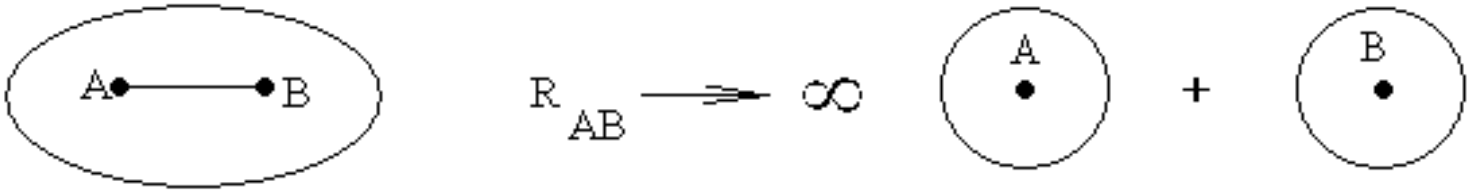
$$E^{(4)} = E^{(4)}(S) + E^{(4)}(D) + E^{(4)}(T) + E^{(4)}(Q)$$

$$E^{(n)} \sim \sum \frac{\langle 0|V|\psi_B\rangle\langle\psi_B|V|\psi_D\rangle.....\langle\psi_C|V|0\rangle}{\varepsilon_a + \varepsilon_b + ... + \varepsilon_c - \varepsilon_i - \varepsilon_j - .... - \varepsilon_k}$$

Energies in MP theory



Size extensivity problem



$$E_{AB} = E_A + E_B$$

Size extensive methods: HF, MPn, CC

Accuracy of methods

Method	E_{FCI}-$E_{метод}$ (h 10^{-3})
CID	**29.5**
CISD	22.0
CISDT	16.7
MP2	27.8
MP3	22.9
MP4(SDQ)	11.13
MP4	5.89
CCD	12.8
CCSD	7.06
CCSD(T)	**1.15**

* 10^{-3} a.u. = 0.6275 kcal/mol

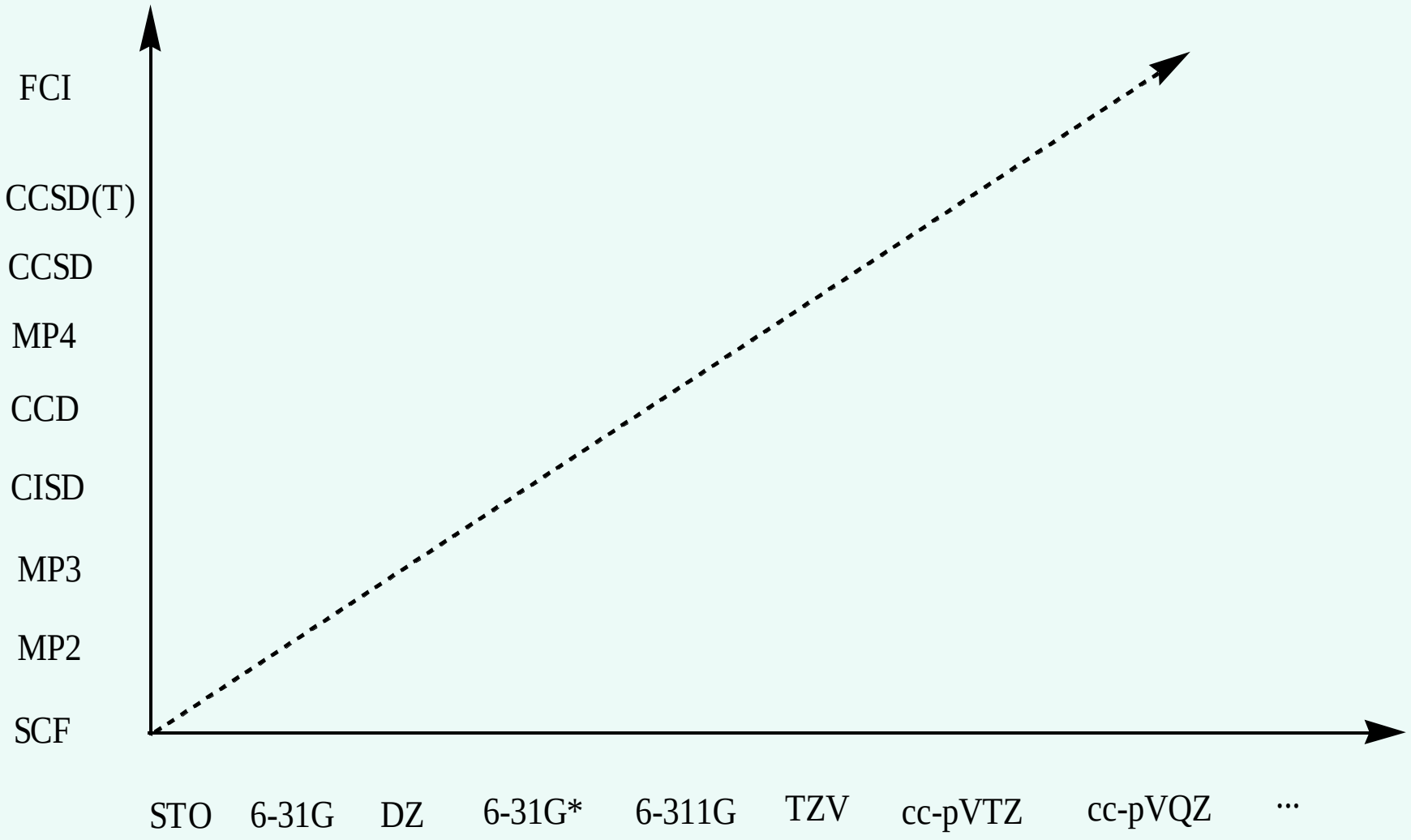
H_2O geometry

Метод		R_e	θ
ХФ	DZP	0.944	106.6
	TZ2P	**0.941**	**106.3**
MP2	DZP	0.963	104.4
	TZ2P	0.958	104.2
CCSD	DZP	0.961	103.7
	TZ2P	0.956	104.5
CCSD(T)	DZP	0.962	103.6
	TZ2P	**0.959**	**104.2**
experim.		**0.957**	**104.5**

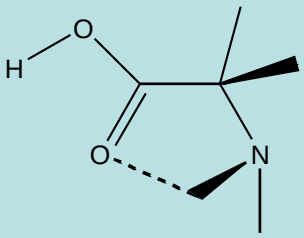
Absolute Errors in Frequency calculations H_2O, DZP (cm^{-1})

	ХФ	CISD	MP2	CCSD	MP4	CCSD(T)
ω_1	344	147	112	98	92	83
ω_2	332	135	77	80	73	64
ω_3	102	44	15	34	26	28

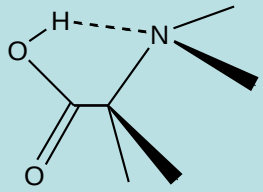
Effectivity of *ab-initio* models



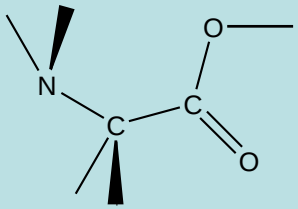
Relative energies of Glycine conformers kcal/mol



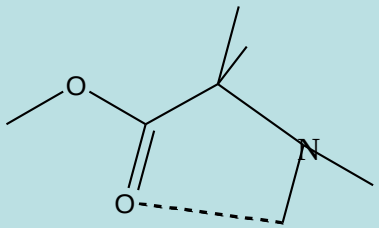
I



II



III



IV

method	I	**II**	III	IV
[6s5p3d2f/ 4s2p1d] XΦ	0.0	3.26	2.15	1.59
6-311++G** MP4	0.0	0.64	1.37	1.31
6-311++G** CCSD	0.0	1.24	1.55	1.33
6-311++G** CCSD(T)	0.0	0.79	1.46	1.30
Experim.	0.0	1.3-1.6; ~2.0; ~1.4	0.9-1.5; 1.7	-

To be continued

«DFT»