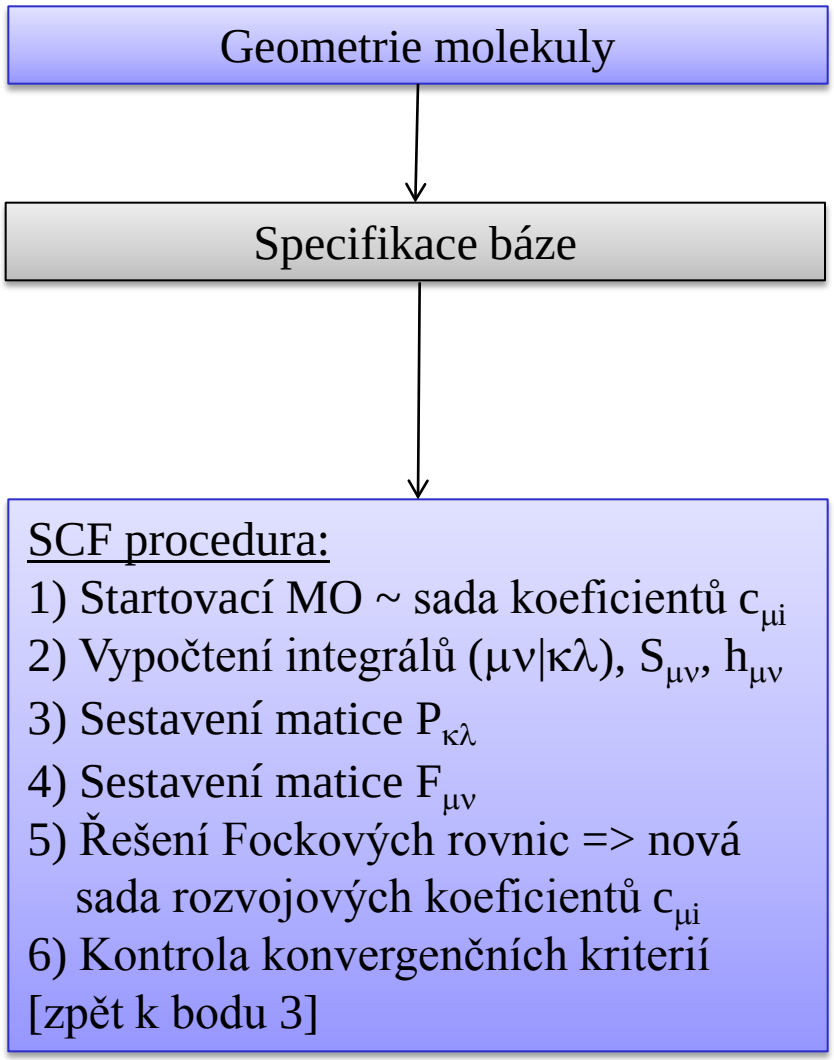
Hartree-Fock-Roothaan



Ostlund, Szabo:
"More art than science"

BÁZE

1. Atomy vodíkového typu:

$$\phi = N r^{l} e^{-Zr/na_0} \sum_{j=0}^{n-l-1} b_j r^{j} Y_{l,m}(\vartheta, \varphi)$$

2. „Slater-type“ orbitals (**STO**):

$$\phi_{STO} = \frac{[2\varsigma / a_0]^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\varsigma r} Y_{l,m}(\vartheta, \varphi)$$

3. Gaussian type orbitals (**GTO**):

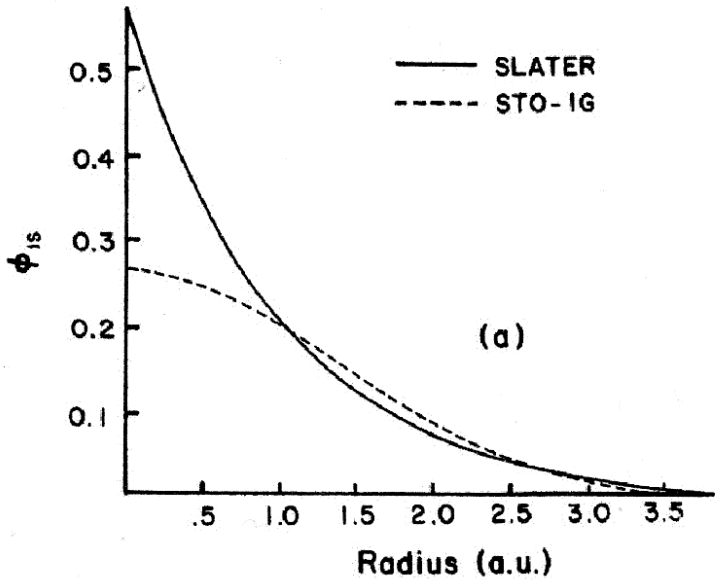
$$\phi_{GTO} = N x^{l_x} y^{l_y} z^{l_z} e^{-\alpha r^2}$$

$l_x = l_y = l_z = 0$ … s

$l_x + l_y + l_z = 1$ … p

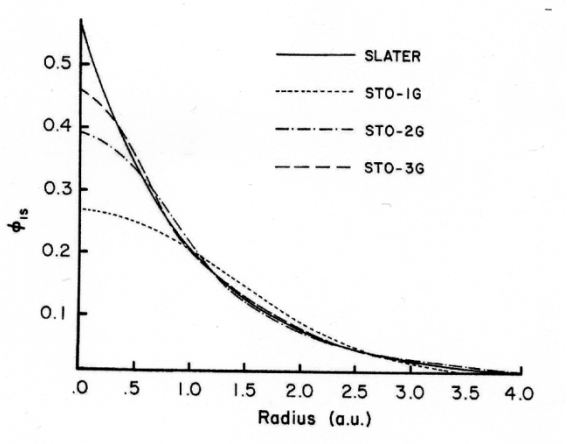
$l_x + l_y + l_z = 2$ … d (! 6 d-komponent)

[Boys (*Proc. R. Soc. A*, 200 (1950) 542)]



Velký rozdíl mezi popisem elektronových hustot v blízkosti atomových jader mezi STO a GTO orbitaly.

Kontrahované GTO orbitaly:



$$\phi_{STO}^{1s}(\varsigma = 1.24) \simeq 0.44\phi_{GTO}^{1s}(\alpha = 0.17) + 0.54\phi_{GTO}^{1s}(\alpha = 0.62) + 0.15\phi_{GTO}^{1s}(\alpha = 3.43)$$

Standardní *vs.* direktní HF SCF

Příklad: STO-3G báze pro atom uhlíku

```
S    3 1.00
 0.7161683735D+02  0.1543289673D+00
 0.1304509632D+02  0.5353281423D+00
 0.3530512160D+01  0.4446345422D+00
SP   3 1.00
 0.2941249355D+01 -0.9996722919D-01  0.1559162750D+00
 0.6834830964D+00  0.3995128261D+00  0.6076837186D+00
 0.2222899159D+00  0.7001154689D+00  0.3919573931D+00
```

α exponent

Contr. coef. for **s**

Contr. coef. for **p**

Klasifikace bází AO:

- minimální báze
- double-ζ báze
- valenční double -ζ báze
- triple-ζ báze
- polarizační funkce
- difuzní funkce

		Polarization	Diffuse
Basis Set	**Applies to**	**Functions**	**Functions**
STO-3G	H-Xe	*	
3-21G	H-Xe	* *or* **	+
6-31G	H-Kr	**(3df,3pd)**	++
6-311G	H-Kr	**(3df,3pd)**	++
D95	H-Cl *except Na and Mg*	**(3df,3pd)**	++
D95V	H-Ne	**(d)** *or* **(d,p)**	++
LanL2MB	H-Ba, La-Bi		
LanL2DZ	H, Li-Ba, La-Bi		
SDD, SDDAll	*all but Fr and Ra*		
cc-pV(DTQ5)Z	H-He, B-Ne, Al-Ar, Ga-Kr	*included in definition*	*added via* **AUG-** *prefix*
cc-pV6Z	H, B-Ne	*included in definition*	*added via* **AUG-** *prefix*
SV and SVP	H-Kr	*included in definition*	
TZV and **TZVP**	H-Kr	*included in definition*	
EPR-II, EPR-III	H, B, C, N, O, F	*included in definition*	

Příklad: 6-31G(d) báze pro atom uhlíku

```
Standard basis: 6-31G(d) (5D, 7F)
Basis set in the form of general basis input:
 1 0
S    6 1.00
 0.3047524880D+04  0.1834737130D-02
 0.4573695180D+03  0.1403732280D-01
 0.1039486850D+03  0.6884262220D-01
 0.2921015530D+02  0.2321844430D+00
 0.9286662960D+01  0.4679413480D+00
 0.3163926960D+01  0.3623119850D+00
SP   3 1.00
 0.7868272350D+01 -0.1193324200D+00  0.6899906660D-01
 0.1881288540D+01 -0.1608541520D+00  0.3164239610D+00
 0.5442492580D+00  0.1143456440D+01  0.7443082910D+00
SP   1 1.00
 0.1687144782D+00  0.1000000000D+01  0.1000000000D+01
D    1 1.00
```

α exponent

Kontr. koef. pro **s** funkci

Kontr. koef. pro **p** funkci

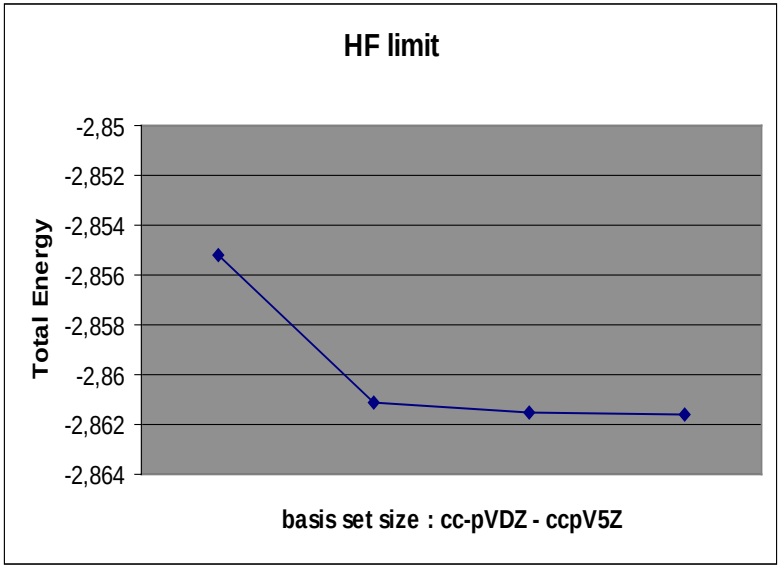
Popis pomocí Hartreeho-Fockovy metody
- různé báze atomových orbitalů

He atom (znovu)

Hartree-Fock description

BASIS SET	No. of bf	No. of prim. G	HF Energy	Orbital En.
sto-3g	1	3	-2.807783	-0.87604
3-21G	2	3	-2.835679	-0.90357
6-31G	2	4	-2.855160	-0.91413
6-311G	3	5	-2.859895	-0.91687
6-31G(d,p)	5	7	-2.855160	-0.91413
tzvp	6	8	-2.859895	-0.91687
cc-pvdz	5	7	-2.855160	-0.91415
cc-pvtz	14	18	-2.861153	-0.91763
cc-pvqz	30	38	-2.861514	-0.91785
cc-pv5z	55	73	-2.861624	-0.91792

POZOR:
- pouze s-funkce vylepšují popis



Přesná hodnota:

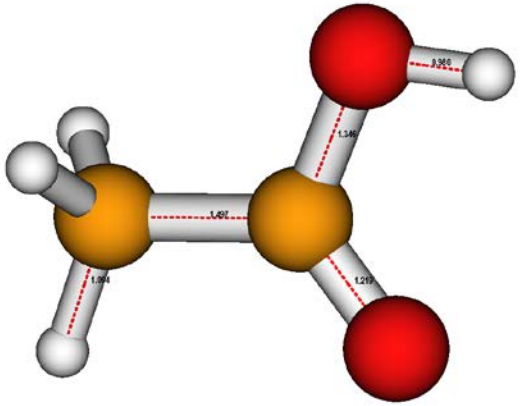
$E^{He+} + IP(He) = 2.90357$ a. u.

Chyba HF metody: 0.042 a.u. = 1.14 eV = 26 kcal/mol
Důsledkem neúplné báze a zejména zanedbáním korelační energie.

Závislost HF energie na kvalitě a velikosti použité báze - molekula vody

Báze	Energie (a.u.)	μ[D]	θ	R(OH) [Å]
Experiment	-76.480	1.85	104.5	0.958
HF limita	-76,0675		106.3	0.940
STO-3G	-74.97	1.69	100.0	0.990
Minimal STO	-75.70	1.92	100.3	0.990
6-31G	-75.99	2.50	111.5	0.950
6-31G*	-76.01	2.19	105.5	0.947
6-311+G*	-76.04	2.38	108.1	0.940
6-311++G**	-76.05	2.20	106.2	0.941
Aug-cc-pVDZ	-76.04	1.96	106.0	0.944
Aug-cc-pVTZ	-76.061	1.94	106.3	0.941
Aug-cc-pVQZ	-76.0667	1.94	106.4	0.940
120 GTO	-76,0672	1.98		

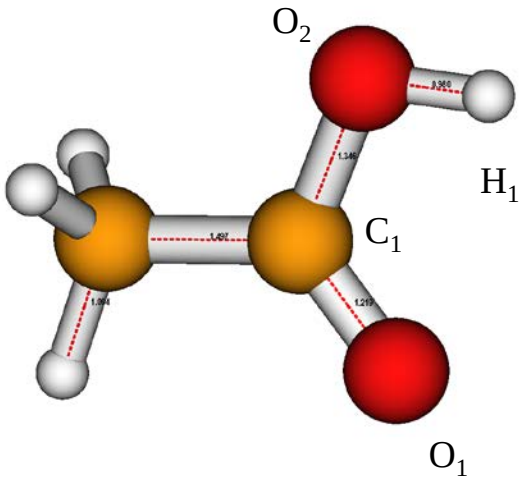
CH_3COOH [Geometry: HF/6-31G(d)]



Basis set	No. of bf	E(HF) (a.u.)	E(homo) (a.u.)	Dipole Moment (Debey)	CPU (s)
sto-3g	24	-224.801626	-0.34416	0.8712	6
3-21G	44	-226.532063	-0.44189	1.5629	6
6-31G	44	-227.698149	-0.45659	1.7389	6
6-311G	64	-227.759343	-0.45900	1.7689	7
6-31G(d)	64	-227.809095	-0.44890	1.7908	8
6-31G(d,p)	76	-227.821273	-0.44824	1.8164	10
D95	48	-227.741903	-0.46203	1.8180	7
D95V	44	-227.741397	-0.46190	1.8184	7
Lanl2DZ	44	-227.741398	-0.46207	1.8192	7
cc-pvdz	76	-227.834149	-0.44646	1.8149	12
cc-pvtz	176	-227.904686	-0.45319	1.9120	191
cc-pvqz	340	-227.922078	-0.45486	1.9486	2075

Exp = 1.74 D

CH_3COOH

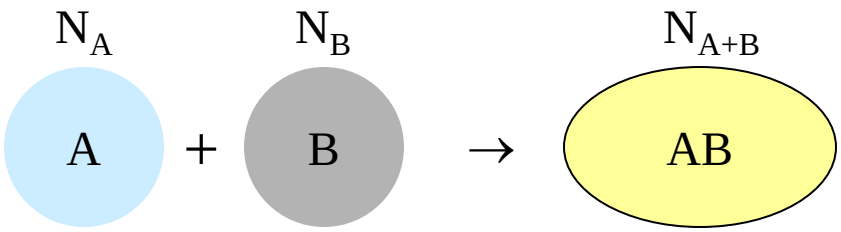


Mulliken charge distribution

	STO-3G	3-21G	6-31G	6-311G	6-31G*	6-31G**	cc-pVDZ	cc-pVTZ	cc-pVQZ
C_1	0.343	0.830	0.688	0.667	0.771	0.752	0.290	0.397	0.572
O_1	-0.287	-0.601	-0.528	-0.487	-0.561	-0.564	-0.358	-0.385	-0.464
O_2	-0.321	-0.709	-0.693	-0.661	-0.731	-0.615	-0.282	-0.325	-0.411
H_1	0.225	0.408	0.431	0.422	0.476	0.363	0.174	0.241	0.262
C	-0.214	-0.680	-0.513	-0.582	-0.587	-0.412	-0.017	-0.278	-0.272
H	0.084	0.251	0.205	0.215	0.209	0.156	0.065	0.112	0.094
H	0.084	0.251	0.205	0.215	0.209	0.156	0.065	0.112	0.094
H	0.085	0.249	0.204	0.214	0.215	0.162	0.062	0.125	0.124

Basis sets

Atom-centered basis sets
- Gaussian Type Orbitals (GTO)
- Slater Type Orbitals (GTO)
- Numerical basis set



Plane-wave basis set - for periodic systems
- no BSSE

Inherent problem: Basis set superposition error (BSSE)

Counterpoise correction method (CP) – Boys and Bernardi

$$\Delta E^{CP} = E_{G-ab}^{B-ab}(ab) - E_{G-ab}^{B-ab}(a) - E_{G-ab}^{B-ab}(b)$$
$$+\left[E_{G-ab}^{B-a}(a) - E_{G-a}^{B-a}(a)\right] + \left[E_{G-ab}^{B-b}(b) - E_{G-b}^{B-b}(b)\right]$$

G … geometry
B … basis set

CP overestimates BSSE

Basis set extrapolation:

Consistent set of basis set must be used

cc-pVnZ (n = D, T, Q, 5, 6), n … cardinal number

aug-cc-pVnZ (N = D, T, Q, 5,6)

Extrapolation for n goes to infinity

Number of extrapolation schemes proposed (Helgaker)

$$A = A_\infty + \alpha \exp(-\beta X)$$ Rate of convergence is exagerated

$$A = A_\infty + \alpha (X + \beta)^{-\gamma}$$

$$A = A_\infty + \sum_{k=3}^{k_{\max}} \alpha_k X^{-k}$$

$$E_X = E_\infty + A X^{-3}$$ Commonly used.