

Basis functions and basis sets

Trygve Helgaker

Centre for Theoretical and Computational Chemistry (CTCC),
Department of Chemistry, University of Oslo, Norway

Laboratoire de Chimie Théorique,
Université Pierre et Marie Curie, Paris, France
November 6, 2012

One-electron basis functions

- ▶ **Molecular orbitals (MOs)** may be constructed
 - ▶ **numerically**: flexible but intractable
 - ▶ **algebraically** by expansion in simple **one-electron basis functions**

$$\phi_p(\mathbf{r}) = \sum_{\mu} C_{\mu p} \chi_{\mu}(\mathbf{r})$$

- ▶ What are the **requirements** on the basis functions?
 - ▶ they should provide a systematic extension towards completeness
 - ▶ they should give a rapid convergence for any electronic state
 - ▶ they should be easy to integrate over
- ▶ It is difficult to satisfy all these requirements
 - ▶ some **compromise** must be sought. . .
- ▶ We shall always insist on **completeness** of our basis functions
 - ▶ completeness in one-electron space ensures completeness in (FCI) ***N*-electron space**
 - ▶ in practice, we will always use **truncated** basis sets
 - ▶ however, these must be **systematically extendable** towards completeness
- ▶ **Overview**:
 - ▶ general considerations
 - ▶ angular functions (spherical harmonics)
 - ▶ radial functions (STOs and GTOs)
 - ▶ molecular basis sets

One- and many-center molecular expansions

One-center molecular expansions

- ▶ Mathematically, it is easy to set up **one-center expansions** that are
 - ▶ universal and uniquely defined
 - ▶ complete, discrete and orthonormal
- ▶ Convergence is invariably slow since little physics has been built into the basis

Many-center molecular expansions

- ▶ Atoms retain much of their identity in molecules
 - ▶ atomic electron distributions are largely unaffected by bonding
- ▶ We therefore combine **separate one-electron bases for each atom** in the molecule
- ▶ The molecular orbitals are thus constructed from **atomic orbitals (AOs)**
 - ▶ better convergence
 - ▶ uniform quality
 - ▶ less systematic
 - ▶ linear dependencies

Central-field systems

- ▶ We shall develop AOs by considering one-electron **central-field systems**:

$$-\frac{1}{2}\nabla^2\psi(\mathbf{r}) + V(r)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \leftarrow V(r) \text{ spherically symmetric}$$

- ▶ Their wave functions may be separated into **radial and angular parts**:

$$\psi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r)Y_{\ell m}(\theta, \varphi)$$

- ▶ The **angular solutions** of the central-field system are universal:

$$Y_{\ell m}(\theta, \varphi) \leftarrow \text{spherical harmonics}$$

and constitute a complete orthonormal set on $L^2(S)$

$$\int_0^{2\pi} \int_0^\pi Y_{\ell m}^*(\theta, \varphi) Y_{\ell' m'}(\theta, \varphi) \sin\theta \, d\theta \, d\varphi = \delta_{\ell\ell'} \delta_{mm'}$$

- ▶ By contrast, the **radial solutions** depend on the potential:

$$-\frac{1}{2} \frac{d^2 r R_{n\ell}(r)}{dr^2} + \left[V(r) + \frac{\ell(\ell+1)}{2r^2} \right] r R_{n\ell}(r) = E r R_{n\ell}(r)$$

and constitute a complete orthonormal set on $L^2(\mathbb{R}^+, r^2)$

$$\int_0^\infty R_{m\ell}^*(r) R_{n\ell}(r) r^2 \, dr = \delta_{mn}$$

From spherical to solid harmonics

- ▶ The radial forms of the AOs, $R_{n\ell}(r)Y_{\ell m}(\theta, \varphi)$, contain the monomial r^ℓ :

$$R_{n\ell}(r) = r^\ell \mathcal{R}_{n\ell}(r)$$

- ▶ We therefore introduce the **solid harmonics**:

$$\mathcal{Y}_{\ell m}(r, \theta, \varphi) = r^\ell Y_{\ell m}(\theta, \varphi)$$

- ▶ To avoid complex algebra, we note that

$$\mathcal{Y}_{\ell m}^* = (-1)^m \mathcal{Y}_{\ell, -m}$$

and introduce the **real-valued solid harmonics**

$$S_{\ell|m|} + iS_{\ell, -|m|} = (-1)^m \sqrt{\frac{8\pi}{2\ell + 1}} \mathcal{Y}_{\ell m}$$

- ▶ The real-valued solid harmonics $S_{\ell m}(s, y, z)$ for $\ell \leq 2$:

$m \setminus \ell$	0	1	2
2			$\frac{1}{2}\sqrt{3}(x^2 - y^2)$
1		x	$\sqrt{3}xz$
0	1	z	$\frac{1}{2}(3z^2 - r^2)$
-1		y	$\sqrt{3}yz$
-2			$\sqrt{3}xy$

Radial forms

- ▶ The general form of the one-electron functions is

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \varphi)$$

- ▶ A variety of radial functions are in use of the general form

$$[\text{a polynomial in } r] \times [\text{a decaying function in } r]$$

- ▶ There are two main classes of radial functions:

- ▶ **exponential functions**

$$R_{n\ell}(r) = r^\ell P_{n-\ell-1}(r) \exp(-\zeta r)$$

- ▶ **Gaussian functions**

$$R_{n\ell}(r) = r^\ell P_{n-\ell-1}(r^2) \exp(-\alpha r^2)$$

where $P_{n-\ell-1}$ is a polynomial of degree $n - \ell - 1$.

- ▶ Flexibility in the radial part is obtained by
 - ▶ use of the principal quantum number n
 - ▶ use of variable exponents ζ and α

Hydrogenic functions

- ▶ The **hydrogenic system** with Hamiltonian

$$H = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

would appear to be ideal for generating AOs

- ▶ The **bound states** have the radial form

$$R_{n\ell}(r) = c_{n\ell} r^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2Zr}{n}\right) \exp\left(-\frac{Zr}{n}\right)$$

in terms of **the associated Laguerre polynomials**:

$$\int_0^\infty L_n^\alpha(x) L_m^\alpha(x) x^\alpha \exp(-x) dx = \frac{\Gamma(n+\alpha+1)}{n!} \delta_{nm}$$

- ▶ the hydrogenic bound states decay **exponentially**
- ▶ the polynomial part is of **degree $n-1$ with $n-\ell-1$ nodes**
- ▶ Difficulties associated with the hydrogenic bound-state functions:
 - ▶ they must be supplemented with **unbound continuum states** for completeness
 - ▶ they spread out very rapidly (quadratically in n) because of the Zr/n dependence

$$\langle r \rangle = \frac{3n^2 - \ell(\ell+1)}{2Z}$$

The Laguerre functions

- ▶ For a fixed exponent ζ , the **Laguerre functions**

$$R_{nl}^{\text{LF}} = c_{nl}^{\text{LF}} r^\ell L_{n-\ell-1}^{2\ell+2}(2\zeta r) \exp(-\zeta r)$$

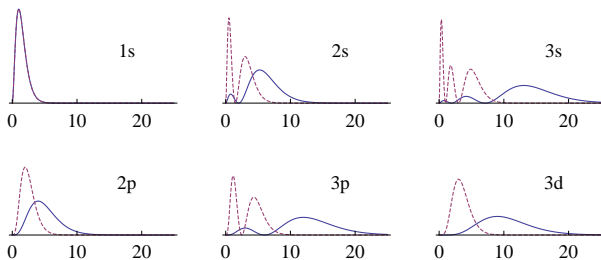
constitute a **complete, discrete set** in $L^2(\mathbb{R}^+, r^2)$

- ▶ They retain the **exponential decay** of the hydrogenic functions

$$R_{nl}(r) = c_{nl} r^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2Zr}{n}\right) \exp\left(-\frac{Zr}{n}\right)$$

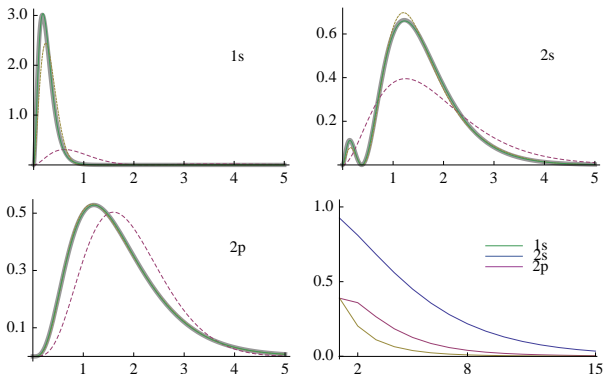
while **avoiding the continuum**

- ▶ They are much more **compact** than the hydrogenic functions: $\langle r \rangle = (2n + 1)/\zeta$



Expansion of carbon orbitals in Laguerre functions

- ▶ Least-squares fits to the numerical carbon 3P ground-state orbitals
 - ▶ R_{nl}^{LF} expansions with $n \leq 2, 8, 15$ and fixed exponent $\zeta = 1$:



- ▶ convergence is guaranteed but slow
- ▶ functions with a **fixed exponent** are ill suited for widely different radial distributions
- ▶ Solution: use functions with **variable exponents** adapted to the system

$$\langle r \rangle = \frac{2n+1}{\zeta}$$

Slater-type orbitals (STOs)

- ▶ With variable exponents, orthogonality is lost even in atomic systems
 - ▶ there is no need to retain the nodal structure of the Laguerre functions
- ▶ **Slater-type orbitals (STOs)** are obtained by retaining only the highest monomial:

$$R_{nl}^{LF} = r^\ell L_{n-\ell-1}^{2\ell+2}(2\zeta r) \exp(-\zeta r) \rightarrow R_{nl}^{STO} = r^{n-1} \exp(-\zeta r)$$

- ▶ note the simple structure of the STOs:

$$1s = \exp(-\zeta r)$$

$$2s = r \exp(-\zeta r)$$

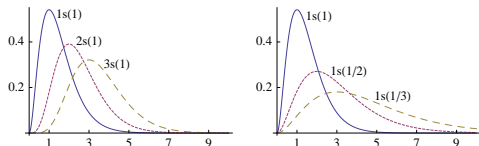
$$2p_0 = z \exp(-\zeta r)$$

$$3s = r^2 \exp(-\zeta r)$$

$$3p_0 = zr \exp(-\zeta r)$$

$$3d_0 = (3z^2 - r^2) \exp(-\zeta r)$$

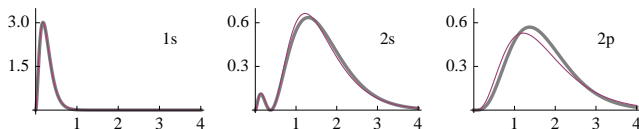
- ▶ For a fixed ζ , the STOs constitute a **complete, discrete set of one-electron functions**
- ▶ But radial flexibility may also be obtained with **variable exponents**: $\langle r \rangle = (2n + 1)/\zeta$



STO basis sets

- ▶ In practice, n and ζ are used in combination to ensure **radial flexibility**:
- ▶ **Minimal STO basis** for carbon:

$$1s = \exp(-5.88r), \quad 2s = r \exp(-1.57r), \quad 2p_0 = z \exp(-1.46r)$$



- ▶ **Extended STO basis** for carbon:

STO type	exponents	1s	2s	2p
1s STO	9.2863	0.07657	-0.01196	
	5.4125	0.92604	-0.21041	
2s STO	4.2595	0.00210	-0.13209	
	2.5897	0.00638	0.34624	
	1.5020	0.00167	0.74108	
	1.0311	-0.00073	0.06495	
2p STO	6.3438			0.01090
	2.5873			0.23563
	1.4209			0.57774
	0.9554			0.24756

Gaussian radial forms

- ▶ Boys introduced **Gaussians** as molecular basis functions in 1950
 - ▶ his motivation was to simplify integration
 - ▶ Gaussians do not have a nuclear cusp and decay too rapidly
 - ▶ nevertheless, they constitute a complete set of functions
- ▶ For STOs, we proceeded by
 - 1 identifying a complete, discrete set of radial functions: **Laguerre functions**
 - 2 simplifying their nodal structure: **STOs**
 - 3 ensuring radial flexibility by a use of n and variable exponent ζ
- ▶ For GTOs, we shall proceed in the same manner by
 - 1 identifying a complete, discrete set of radial functions: **harmonic-oscillator functions**
 - 2 simplifying their nodal structure: **GTOs**
 - 3 ensuring radial flexibility by use of variable exponents only

Harmonic-oscillator (HO) functions

- ▶ For a fixed α , the three-dimensional **harmonic-oscillator (HO)** Hamiltonian

$$H = -\frac{1}{2}\nabla^2 + \frac{1}{2}(2\alpha)^2 r^2$$

has the following complete set of **Gaussian radial solutions**:

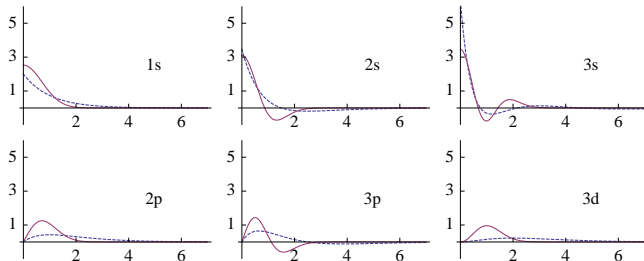
$$R_{n\ell}^{\text{HO}} = c_{n\ell}^{\text{HO}} r^\ell L_{n-\ell-1}^{\ell+1/2}(2\alpha r^2) \exp(-\alpha r^2)$$

- ▶ Note: the HO functions are obtained from the LF functions

$$R_{n\ell}^{\text{LF}} = c_{n\ell}^{\text{LF}} r^\ell L_{n-\ell-1}^{2\ell+2}(2\zeta r) \exp(-\zeta r)$$

by globally substituting r^2 for r in the radial part and adjusting for orthonormality

- ▶ the HO nodal structure is the same as for the LF functions



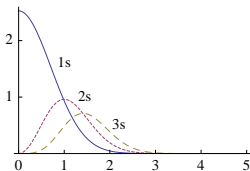
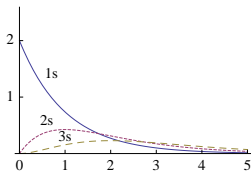
GTOs: nodeless HO functions

- ▶ Dispensing with the HO nodes, we obtain the **Gaussian-type orbitals (GTOs)**:

$$R_{nl}^{\text{GTO}}(r) = c_{nl}^{\text{GTO}} r^{\ell} r^{2(n-\ell-1)} \exp(-\alpha r^2)$$

- ▶ like the HO functions, the GTOs form a **complete, discrete set** for fixed α
- ▶ A comparison of STOs and GTOs:

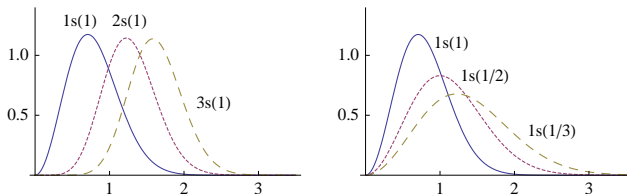
	STO	GTO
1s	$\exp(-\zeta r)$	$\exp(-\alpha r^2)$
2s	$r \exp(-\zeta r)$	$r^2 \exp(-\alpha r^2)$
2p ₀	$z \exp(-\zeta r)$	$z \exp(-\alpha r^2)$
3s	$r^2 \exp(-\zeta r)$	$r^4 \exp(-\alpha r^2)$
3p ₀	$zr \exp(-\zeta r)$	$zr^2 \exp(-\alpha r^2)$
3d ₀	$(3z^2 - r^2) \exp(-\zeta r)$	$(3z^2 - r^2) \exp(-\alpha r^2)$



Spherical-harmonic GTOs

- ▶ For GTOs with a fixed exponent, convergence is exceedingly slow
 - ▶ the radial space must instead be spanned by **variable exponents**

$$\langle r \rangle_{\text{GTO}} \approx \sqrt{\frac{2n-\ell-2}{2\alpha}}, \quad \langle r \rangle_{\text{STO}} = \frac{2n+1}{\zeta}$$



- ▶ Indeed, the radial space is usually spanned entirely by variable exponents
 - ▶ we thus employ solid-harmonic GTOs with only two quantum numbers:

$$G_{\alpha, \ell m}(r, \theta, \varphi) = S_{\ell m}(r, \theta, \varphi) \exp(-\alpha r^2)$$

discarding GTOs with $n > \ell + 1$ such as the 2s function $r^2 \exp(-\alpha r^2)$

- ▶ Completeness is ensured by selecting the exponents in a special manner
 - ▶ for example, using exponents such as n^{-1} and $n^{-1/2}$ for $n = 1, 2, 3 \dots$
 - ▶ in practice, such criteria are not very useful

Molecular basis sets: some general comments

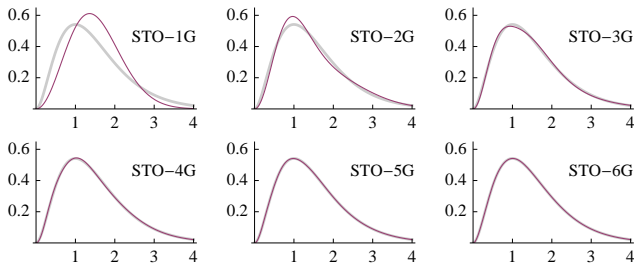
- ▶ Requirements for **correlated** and **uncorrelated** wave-function models are different
 - ▶ uncorrelated models require an accurate representation of the **one-electron density**
 - ▶ correlated models require also an accurate representation of the **two-electron density**
- ▶ Requirements vary also for different **molecular properties**
 - ▶ energy-optimized basis sets have most flexibility in the valence region
 - ▶ many properties depend on flexibility in other regions:
 - ▶ the outer valence region for electric properties
 - ▶ the inner core region for nuclear field gradients
- ▶ It is difficult to develop basis sets that are **universal**, applicable in all situations
 - ▶ we here concentrate on basis sets for **uncorrelated energy calculations**
 - ▶ we will study basis sets for correlated energies after a discussion of the Coulomb hole
- ▶ Overview of our discussion of basis sets for uncorrelated calculations:
 - 1 STO- kG
 - 2 primitive GTOs from Hartree–Fock calculations
 - 3 even-tempered basis sets
 - 4 contracted basis sets
 - 5 polarization functions
 - 6 benchmarking

STO- k G basis sets

- ▶ In the **STO- k G basis sets**, STOs are expanded in fixed linear combinations of GTOs:

$$\chi_{nlm}^{\text{STO}} = \sum_{i=1}^k d_i \chi_{\alpha, \ell m}^{\text{GTO}}$$

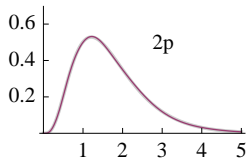
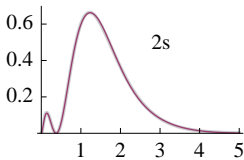
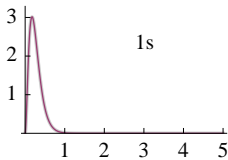
- ▶ STOs are retained as the conceptual basis
 - ▶ GTOs are introduced to simplify integration
- ▶ The following basis functions are obtained by **least-squares fitting**:



- ▶ these fits are only needed for $\zeta = 1$
 - ▶ scaling gives functions for $\zeta \neq 1$
- ▶ The STO-3G basis sets are only useful for exploratory investigations

GTO basis sets by energy minimization

- ▶ Treating the GTOs as primary basis, their exponents must be determined independently
 - ▶ the most obvious approach is by **minimization of atomic energies**
- ▶ A large number of such **primitive GTOs** are needed for good accuracy
 - ▶ example: Huzinaga 9s5p:

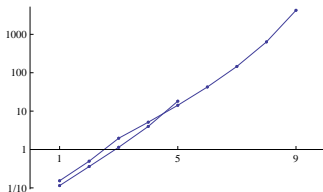


- ▶ Errors in the electronic energy:

basis	error (mE_h)
STO-3G	460
STO-6G	79.6
9s5p	3.4
DZ STO	1.9
10s6p	1.3

Even-tempered basis sets

- ▶ Full optimization of all exponents is a difficult nonlinear optimization problem
- ▶ However, regularity is observed in the optimized exponents (logarithmic plots)



- ▶ In **even-tempered basis sets**, only two parameters are optimized for each ℓ :

$$\alpha_i = \alpha\beta^{i-1}$$

- ▶ For a 9s5p basis set, we obtain the following values for s and p functions:

$$\alpha_s = 0.1364 \qquad \beta_s = 3.381$$

$$\alpha_p = 0.1041 \qquad \beta_p = 3.503$$

- ▶ In even-tempered basis sets, the **overlap** between neighbouring orbitals is constant:

$$\langle i | i + 1 \rangle = \left(\frac{2\sqrt{\beta}}{1 + \beta} \right)^{3/2 + \ell}$$

- ▶ Basis-set extensions are often performed in an even-tempered manner

Contracted GTOs

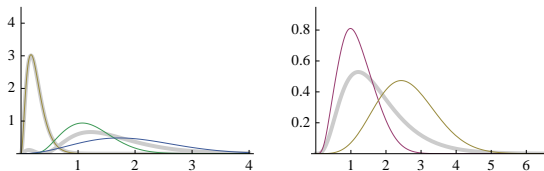
- ▶ To describe atomic orbitals accurately, a large number of GTOs are needed
 - ▶ upon bond formation, the electron distribution does not usually change much
 - ▶ there is no need to use all GTOs individually in molecular calculations
 - ▶ we therefore use **contracted GTOs**: fixed linear combinations of **primitive GTOs**

$$R_{\alpha}^{\text{CGTO}}(\mathbf{r}) = \sum_j d_{\alpha_j} R_{\alpha_j}^{\text{GTO}}(\mathbf{r})$$

- ▶ Example: the **6-31G split-valence basis** for carbon

exponents	1s	2s	2p
3047.52	0.00183474		
457.37	0.0140373		
103.949	0.0688426		
29.2102	0.232184		
9.28666	0.467941		
3.16393	0.362312		
7.86827		-0.119332	0.0689991
1.88129		-0.160854	0.316424
0.544249		<u>1.14346</u>	<u>0.744308</u>
0.168714		1.0000	1.0000

- ▶ Plots of s and p functions:



Polarization functions

- ▶ Up to now, we have used AOs of same symmetry as the occupied atomic orbitals
 - ▶ in molecules, the **atomic density is distorted** and spherical symmetry broken
- ▶ To describe this distortion, we include **polarization functions**
 - ▶ AOs of angular momentum higher than those of the occupied atomic orbitals
- ▶ Example: distortion of the 1s function:

$$\begin{aligned}s(\mathbf{A}) &= \exp(-\alpha r_A^2) \\s(\mathbf{A} + \delta_z) &= s(\mathbf{A}) + 2\alpha z_A s(\mathbf{A})\delta_z + \dots \\ &= s(\mathbf{A}) + 2\alpha\delta_z p_z(\mathbf{A}) + \dots\end{aligned}$$

- ▶ Choose the exponent so that the polarization function contributes most where the charge density has a maximum

$$\alpha_{\ell+1}^{\text{pol}} = \frac{\ell+2}{\ell+1}\alpha_\ell$$

- ▶ Examples: DZP, 6-31G*

Basis-set convergence in Hartree–Fock theory

- ▶ For basis sets to be useful, their performance must be **benchmarked** systematically
- ▶ For high accuracy and for establishing error bars, a series of calculations is necessary

basis set	ΔE_{Ne}	ΔE_{N_2}	$\Delta E_{\text{H}_2\text{O}}$	R_{NN}	R_{OH}	θ_{HOH}
STO-3G	1942.57	1497.29	1104.47	146.82	98.94	100.03
6-31G	73.22	125.43	83.40	108.91	94.96	111.55
6-311G	24.54	99.02	58.01	108.60	94.54	111.88
6-31G*	73.22	51.32	58.27	107.81	94.76	105.58
6-31G**	73.22	51.32	44.75	107.81	94.27	106.05
6-311G**	24.54	23.76	20.95	107.03	94.10	105.46
cc-pVDZ	58.32	39.06	40.60	107.73	94.63	104.61
cc-pVTZ	15.23	9.72	10.23	106.71	94.06	106.00
cc-pVQZ	3.62	2.11	2.57	106.56	93.96	106.22
cc-pV5Z	0.32	0.43	0.31	106.54	93.96	106.33
cc-pCVDZ	58.17	38.27	40.20	107.65	94.60	104.64
cc-pCVTZ	15.14	8.79	10.04	106.60	94.05	106.00
cc-pCVQZ	3.52	1.88	2.45	106.55	93.96	106.22
cc-pCV5Z	0.32	0.36	0.30	106.54	93.96	106.33

- ▶ Some comments:
 - ▶ STO-3G performs very poorly
 - ▶ 6-31G gives qualitative accuracy (but not for the bond angle)
 - ▶ 6-311G improves only the energy
 - ▶ 6-31G* contains polarization functions and improves the geometry
 - ▶ correlation-consistent basis sets (studied later) converge smoothly and rapidly