

Basis functions and basis sets

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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**

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

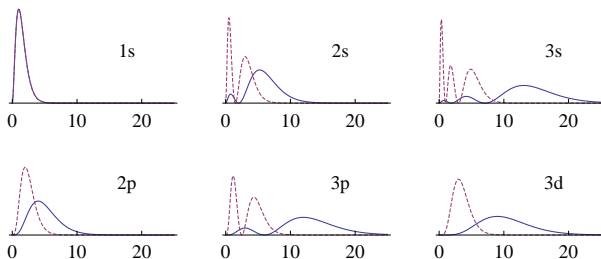
constitute a **complete, discrete set** in $L^2(\mathbb{R}^+, r^2)$

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

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

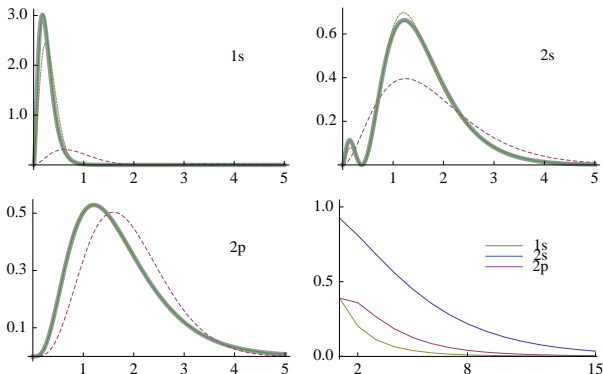
while **avoiding the continuum**

- ▶ 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:

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

- ▶ note the simple structure of the STOs:

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

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

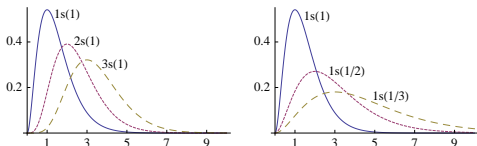
$$2p_0 = z \exp(-\zeta r)$$

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

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

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

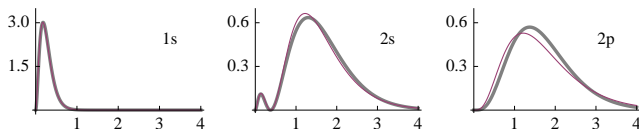
- ▶ For a fixed ζ , the STOs constitute a **complete, discrete set of one-electron functions**
- ▶ But radial flexibility may also be obtained with **variable exponents**: $\langle r \rangle = (2n + 1)/\zeta$



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**:

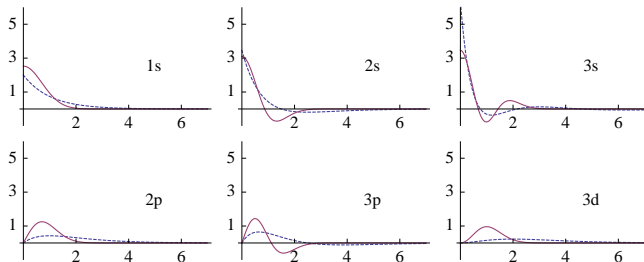
$$R_{n\ell}^{\text{HO}} = c_{n\ell}^{\text{HO}} r^\ell L_{n-\ell-1}^{\ell+1/2}(2\alpha r^2) \exp(-\alpha r^2)$$

- ▶ 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



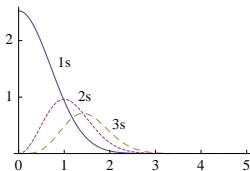
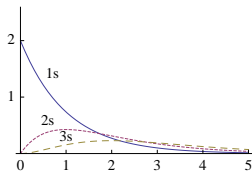
GTOs: nodeless HO functions

- ▶ 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:

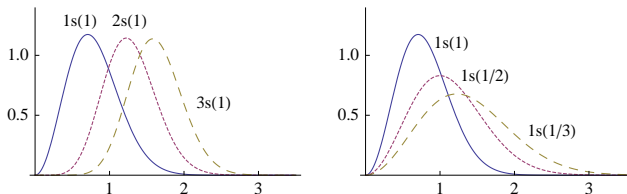
	STO	GTO
1s	$\exp(-\zeta r)$	$\exp(-\alpha r^2)$
2s	$r \exp(-\zeta r)$	$r^2 \exp(-\alpha r^2)$
2p ₀	$z \exp(-\zeta r)$	$z \exp(-\alpha r^2)$
3s	$r^2 \exp(-\zeta r)$	$r^4 \exp(-\alpha r^2)$
3p ₀	$zr \exp(-\zeta r)$	$zr^2 \exp(-\alpha r^2)$
3d ₀	$(3z^2 - r^2) \exp(-\zeta r)$	$(3z^2 - r^2) \exp(-\alpha r^2)$



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

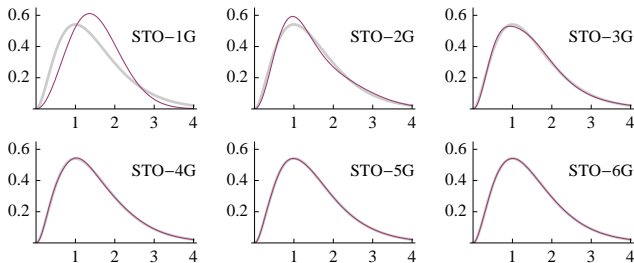
- ▶ Requirements for **correlated** and **uncorrelated** wave-function models are different
 - ▶ uncorrelated models require an accurate representation of the **one-electron density**
 - ▶ correlated models require also an accurate representation of the **two-electron density**
- ▶ Requirements vary 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:

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

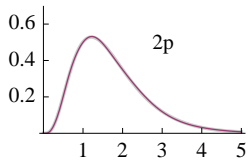
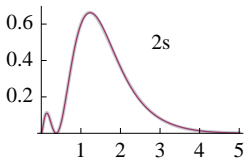
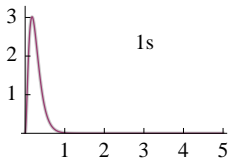
- ▶ STOs are retained as the conceptual basis
 - ▶ GTOs are introduced to simplify integration
- ▶ The following basis functions are obtained by **least-squares fitting**:



- ▶ 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:

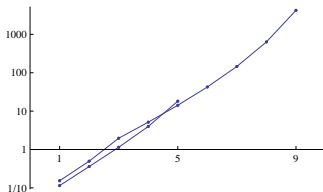


- ▶ Errors in the electronic energy:

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 :

$$\alpha_j = \alpha\beta^{j-1}$$

- ▶ 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
- ▶ Instead, we use **contracted GTOs**: fixed linear combinations of **primitive GTOs**

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

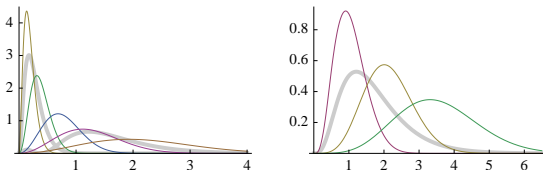
- ▶ **Segmented contraction**
 - ▶ each primitive contributes to just one contracted
- ▶ **General contraction**
 - ▶ each primitive contributes to all contracted of same symmetry

Dunning's contracted basis sets

- ▶ Dunning's contracted functions are based on a primitive basis optimized by Huzinaga
- ▶ The coefficients (here for carbon) are not reoptimized upon contraction

exponents	[3s]	[4s]	[5s]	[2p]	[3p]
4232.61	0.002029	0.002029	0.006228		
634.882	0.015535	0.015535	0.047676		
146.097	0.075411	0.075411	0.231439		
42.4974	0.257121	0.257121	<u>0.789108</u>		
14.1892	0.596555	0.596555	0.791751		
1.9666	<u>0.242517</u>	<u>0.242517</u>	<u>0.321870</u>		
5.1477	<u>1.000000</u>	<u>1.000000</u>	<u>1.000000</u>		
0.4962	0.542048	<u>1.000000</u>	<u>1.000000</u>		
0.1533	0.517121	1.000000	1.000000		
18.1557				0.018534	0.039196
3.9864				0.115442	0.244144
1.1429				0.386206	<u>0.816775</u>
0.3594				<u>0.640089</u>	<u>1.000000</u>
0.1146				1.000000	1.000000

- ▶ Plots of the [5s3p] contractions s and p functions:

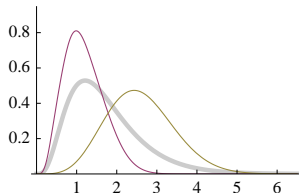
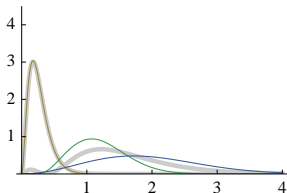


Pople's 6-31G basis

- ▶ In the **Pople-type basis sets**, exponents and coefficients are simultaneously optimized
- ▶ Example: the 6-31G split-valence basis for carbon
 - ▶ note: shared exponents for 2s and 2p

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