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
    \[ \phi_p(r) = \sum_{\mu} C_{\mu p} \chi_{\mu}(r) \]

- 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 incomplete basis sets
  - however, these must be systematically extendable towards completeness

- Overview:
  - general considerations
  - angular functions (spherical harmonics)
  - radial functions (STOs and GTOs)
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
We shall develop AOs by considering one-electron central-field systems:

\[-\frac{1}{2} \nabla^2 \psi(r) + V(r) \psi(r) = E \psi(r) \]

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

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

The angular solutions are universal:

\[Y_{\ell m}(\theta, \phi) \leftarrow \text{spherical harmonics}\]

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

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

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 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 always contain the monomial $r^\ell$:
  \[ R_{n\ell}(r) = r^\ell R_{n\ell}(r) \]

- We therefore introduce the solid harmonics:
  \[ Y_{\ell m}(r, \theta, \varphi) = r^\ell Y_{\ell m}(\theta, \varphi) \]

- To avoid complex algebra, we note that
  \[ Y_{\ell m}^* = (-1)^m Y_{\ell, -m} \]
  and introduce the real-valued solid harmonics
  \[ S_{\ell |m|} + i S_{\ell, -|m|} = (-1)^m \sqrt{\frac{8\pi}{2\ell + 1}} Y_{\ell m} \]

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

<table>
<thead>
<tr>
<th>$m \backslash \ell$</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
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<tr>
<td>2</td>
<td></td>
<td>( \frac{1}{2} \sqrt{3} (x^2 - y^2) )</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>x</td>
<td>( \sqrt{3}xz )</td>
<td></td>
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<tr>
<td>0</td>
<td>z</td>
<td>( \frac{1}{2} (3z^2 - r^2) )</td>
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<tr>
<td>-1</td>
<td>y</td>
<td>( \sqrt{3}yz )</td>
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</tr>
<tr>
<td>-2</td>
<td></td>
<td>( \sqrt{3}xy )</td>
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</table>
Radial forms

- The general form of the one-electron functions is
  \[ \psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \]

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

- Flexibility in the radial part is obtained by
  - use of the principal quantum number \( n \)
  - use of variable exponents \( \zeta \) and \( \alpha \)
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 quickly

\[ \langle r \rangle = \frac{3n^2 - \ell(\ell + 1)}{2Z} \]
The Laguerre functions

For a fixed exponent $\zeta$, the Laguerre functions

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

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

They retain the exponential decay of the hydrogenic functions

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

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
  - $R_{n\ell}^{LF}$ expansions with $n \leq 2, 8, 15$ and fixed exponent $\zeta = 1$:

![Graphs of 1s, 2s, and 2p orbitals]  

- 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:
  \begin{align*}
  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)
  \end{align*}
- For a fixed \( \zeta \), 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 \( \zeta \) 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:

<table>
<thead>
<tr>
<th>STO type</th>
<th>exponents</th>
<th>1s</th>
<th>1s</th>
<th>2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s STO</td>
<td>9.2863</td>
<td>0.07657</td>
<td>−0.01196</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.4125</td>
<td>0.92604</td>
<td>−0.21041</td>
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<tr>
<td>2s STO</td>
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<td>0.00210</td>
<td>−0.13209</td>
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<tr>
<td></td>
<td>2.5897</td>
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<td>0.34624</td>
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</tr>
<tr>
<td></td>
<td>1.5020</td>
<td>0.00167</td>
<td>0.74108</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0311</td>
<td>−0.00073</td>
<td>0.06495</td>
<td></td>
</tr>
<tr>
<td>2p STO</td>
<td>6.3438</td>
<td></td>
<td>0.01090</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5873</td>
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<td>0.23563</td>
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<tr>
<td></td>
<td>1.4209</td>
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<td>0.57774</td>
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<tr>
<td></td>
<td>0.9554</td>
<td></td>
<td>0.24756</td>
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</tr>
</tbody>
</table>
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 \( \zeta \)

- 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
For a fixed $\alpha$, 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:

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

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):
  \[ R_{n\ell}^{\text{GTO}}(r) = c_{n\ell}^{\text{GTO}} r^{\ell} r^{2(n-\ell-1)} \exp(-\alpha r^2) \]

- like the HO functions, the GTOs form a complete, discrete set for fixed \( \alpha \)

- A comparison of STOs and GTOs:

<table>
<thead>
<tr>
<th></th>
<th>STO</th>
<th>GTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>( \exp(-\zeta r) )</td>
<td>( \exp(-\alpha r^2) )</td>
</tr>
<tr>
<td>2s</td>
<td>( r \exp(-\zeta r) )</td>
<td>( r^2 \exp(-\alpha r^2) )</td>
</tr>
<tr>
<td>2p₀</td>
<td>( z \exp(-\zeta r) )</td>
<td>( z \exp(-\alpha r^2) )</td>
</tr>
<tr>
<td>3s</td>
<td>( r^2 \exp(-\zeta r) )</td>
<td>( r^4 \exp(-\alpha r^2) )</td>
</tr>
<tr>
<td>3p₀</td>
<td>( zr \exp(-\zeta r) )</td>
<td>( zr^2 \exp(-\alpha r^2) )</td>
</tr>
<tr>
<td>3d₀</td>
<td>( (3z^2 - r^2) \exp(-\zeta r) )</td>
<td>( (3z^2 - r^2) \exp(-\alpha r^2) )</td>
</tr>
</tbody>
</table>
Spherical-harmonic GTOs

- For GTOs with a fixed exponent, convergence is exceedingly slow
  - 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 \( n = 1, 2, 3 \ldots \)
  - 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 such as
    - the outer valence region for electric properties
    - the inner core region for nuclear field gradients

- It is impossible 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-\(k\)G
  2. primitive GTOs from Hartree–Fock calculations
  3. even-tempered basis sets
  4. contracted basis sets
  5. polarization functions
  6. benchmarking
STO-kG basis sets

- In the STO-kG basis sets, STOs are expanded in fixed linear combinations of GTOs:

\[ \chi_{n\ell m}^{\text{STO}} = \sum_{i=1}^{k} d_i \chi_{\alpha,\ell m}^{\text{GTO}} \]

- 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:

![Graphs of 1s, 2s, and 2p orbitals](image)

- Errors in the electronic energy:

<table>
<thead>
<tr>
<th>basis</th>
<th>error (mE_h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>460</td>
</tr>
<tr>
<td>STO-6G</td>
<td>79.6</td>
</tr>
<tr>
<td>9s5p</td>
<td>3.4</td>
</tr>
<tr>
<td>DZ STO</td>
<td>1.9</td>
</tr>
<tr>
<td>10s6p</td>
<td>1.3</td>
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</table>
**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)

![Graph showing logarithmic plots]

- In **even-tempered basis sets**, only two parameters are optimized for each \(\ell\): 
  \[
  \alpha_i = \alpha \beta^{i-1}
  \]

- For a 9s5p basis set, we obtain the following values for s and p functions:
  \[
  \begin{align*}
  \alpha_s &= 0.1364 & \beta_s &= 3.381 \\
  \alpha_p &= 0.1041 & \beta_p &= 3.503
  \end{align*}
  \]

- In even-tempered basis sets, the overlap between neighboring 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
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 employ all GTOs individually in the molecular calculations

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

\[ R_{\alpha}^{\text{CGTO}}(r) = \sum_i d_{\alpha i} R_{\alpha i}^{\text{GTO}}(r) \]

- **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

<table>
<thead>
<tr>
<th>exponents</th>
<th>[3s]</th>
<th>[4s]</th>
<th>[5s]</th>
<th>[2p]</th>
<th>[3p]</th>
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</table>

- 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

<table>
<thead>
<tr>
<th>exponents</th>
<th>1s</th>
<th>2s</th>
<th>2p</th>
</tr>
</thead>
<tbody>
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<td>0.168714</td>
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<td>1.0000</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

▶ 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:
  
  \[
  s(A) = \exp\left(-\alpha r^2_A\right)
  \]
  
  \[
  s(A + \delta_z) = s(A) + 2\alpha z_A s(A) \delta_z + \cdots
  \]
  
  \[
  = s(A) + 2\alpha \delta_z p_z(A) + \cdots
  \]

- 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 examined systematically.
- For high accuracy and for establishing error bars, a series of calculations is necessary.

<table>
<thead>
<tr>
<th>basis set</th>
<th>$\Delta E_{Ne}$</th>
<th>$\Delta E_{N_2}$</th>
<th>$\Delta E_{H_2O}$</th>
<th>$R_{NN}$</th>
<th>$R_{OH}$</th>
<th>$\theta_{HOH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>1942.57</td>
<td>1497.29</td>
<td>1104.47</td>
<td>146.82</td>
<td>98.94</td>
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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.