

Basis Sets in Quantum Chemistry

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Outline

From Latin *basis*

1. the bottom of something considered as its foundation
2. the principal component of something
3. the basic principle
4. a set of linearly independent vectors in a vector space such that any vector in the vector space can be expressed as a linear combination of them with appropriately chosen coefficients

Basis sets are the foundation of modern electronic structure theory. Efficient quantum chemical calculations on general molecules would not be possible without basis sets!

Introduction

GOAL: solve the electronic Schrödinger equation for an arbitrary molecular system.

- ▶ $(\hat{H} - E)\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = 0$, partial differential equation
- ▶ Boundary and normalization conditions
- ▶ Fermi spin statistics (antisymmetric wave function)

Too complicated to solve directly. Approximate ways of solution

- ▶ Numerical – approximate partial derivatives of Ψ as finite differences of values of Ψ
- ▶ Expansion method – represent Ψ as

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \approx \sum_i C_i \Phi_i(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (1)$$

Set of Φ_i is the N -electron basis.

N -electron Products - Slater Determinants

- ▶ $\Phi_i(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \hat{\mathcal{A}}\{\chi_1(\mathbf{r}_1) \cdots \chi_N(\mathbf{r}_N)\}$
- ▶ One-electron functions $\chi_i(\mathbf{r})$ are orbitals, functions of 3 spatial coordinates
- ▶ Usually orbitals are found by solving the set of Hartree-Fock equations:

$$\hat{F}_i \chi_i(\mathbf{r}) = \epsilon_i \chi_i(\mathbf{r}) \quad (2)$$

Solving Hartree-Fock Equations

- ▶ Partial integro-differential equation in 3 variables
- ▶ Solve numerically for atoms and small molecules
- ▶ Expand orbitals in terms of one-electron basis functions

$$\chi_i(\mathbf{r}) = \sum_{\mu} c_i^{\mu} \phi_{\mu}(\mathbf{r}) \quad (3)$$

This is the essence of Hartree-Fock-Roothaan method.

One-Electron Basis

- ▶ Set of functions of 3 variables
- ▶ Normalizable
- ▶ Usually centered on nuclei (atom-centered basis sets)
- ▶ Basis functions need to approximate orbitals well:
 - completeness
 - behavior at singularities (nuclei) and asymptotes
 - maxima/minima
- ▶ Suitable for evaluation of matrix elements of Hamiltonian and other operators

Slater-Type Functions

- ▶ Spherical Harmonic Slaters

$$\phi(\mathbf{r}) = r^L e^{-\zeta r} Y_L^M(\theta, \phi) \quad (4)$$

characterized by 2 integers ($L, M; -L \leq M \leq L$)

- ▶ Cartesian Slaters

$$\phi(\mathbf{r}) = x^l y^m z^n e^{-\zeta r} \quad (5)$$

characterized by 3 integers ($l, m, n; L = l + m + n$ is similar to the angular momentum)

- ▶ $L = 0, 1, 2, 3, 4, 5, 6$ designated as s, p, d, f, g, h, i
- ▶ Very similar to hydrogenic orbitals - useful for calculations on atoms
- ▶ Proper analytical structure: exponential decay, s-type Slaters have a nuclear cusp
- ▶ Very difficult to compute matrix elements in the case of molecular systems!
- ▶ Used by some atomic codes and some molecular codes (e.g., Amsterdam Density Functional (ADF) package)

Gaussian Functions

Introduced by Boys in 1950.

- ▶ Cartesian Gaussians

$$\phi(\mathbf{r}) = x^l y^m z^n e^{-\alpha r^2} \quad (6)$$

characterized by 3 integers (l, m, n ; $L = l + m + n$ is referred to as the angular momentum)

- ▶ Spherical Harmonic (“pure angular momentum”) Gaussians

$$\phi(\mathbf{r}) = r^L e^{-\alpha r^2} Y_L^M(\theta, \phi) \quad (7)$$

characterized by 2 integers (L, M ; $-L \leq M \leq L$)

- ▶ Decay at infinity faster than Slaters
- ▶ s -type Gaussians do not have a nuclear cusp
- ▶ Matrix elements are much easier to compute

Summary

- ▶ N -electron wave function is expanded in terms of an N -electron basis
- ▶ Products of N one-electron functions (orbitals) are most commonly used to construct N -electron basis sets
- ▶ Each orbital is expanded in terms of one-electron basis functions
- ▶ For practical reasons, **atom-centered Gaussian** basis sets are most commonly used in molecular computations

Look at a Primitive Gaussian

Primitive Cartesian Gaussian centered at \mathbf{O}

$$\phi_i(\mathbf{r}) = N_i(x - O_x)^l(y - O_y)^m(z - O_z)^n e^{-\alpha_i r_O^2} \quad (8)$$

- ▶ Smooth at the origin \mathbf{O}
- ▶ The larger the exponent - the shorter the radial extent of the function
- ▶ Valence s and p orbitals have dominant contributions from functions with exponents between 1 and 10

More on Gaussians

- ▶ Contracted Cartesian Gaussian centered at $\mathbf{0}$

$$\phi_i(\mathbf{r}) = N_i(x - O_x)^l(y - O_y)^m(z - O_z)^n \sum_{j=1}^{n_c} c_{ij} e^{-\alpha_{ij} r_O^2} \quad (9)$$

where c_{ij} are contraction coefficients.

- ▶ Shell – a set of functions of the same angular momentum that differ by l , m , and n *only* (same contraction coefficients, exponents, origin)
- ▶ Cartesian shells: $s \rightarrow 1$ function, $p \rightarrow 3$ functions, $d \rightarrow 6$ functions, $f \rightarrow 10$ functions, $\dots L \rightarrow (L + 1)(L + 2)/2$ functions
- ▶ Spherical Harmonic shells: $s \rightarrow 1$ function, $p \rightarrow 3$ functions, $d \rightarrow 5$ functions, $f \rightarrow 7$ functions, $\dots L \rightarrow (2L + 1)$ functions
- ▶ sp -shell consists of one s shell and one p shell. sp shells are used in some basis sets to make evaluation of the matrix elements faster.

Basis Set Notation

Contraction scheme is used to describe qualitatively how basis set is constructed.

- ▶ $(9s5p)$ contracted to $[5s4p]$
- ▶ $(9s5p)/[5s4p]$
- ▶ O/H $(9s5p/4s2p)/[5s4p/2s1p]$

DZP basis for C

Gaussian program format

```
!  
BASIS="DZP (Dunning)"  
C 0  
S 6 1.00  
    4232.61000      0.202900000E-02  
    634.882000     0.155350000E-01  
    146.097000     0.754110000E-01  
    42.4974000     0.257121000  
    14.1892000     0.596555000  
    1.96660000     0.242517000  
S 1 1.00  
    5.14770000     1.00000000  
S 1 1.00  
    0.49620000     1.00000000  
S 1 1.00  
    0.15330000     1.00000000  
P 4 1.00  
    18.1557000     0.185340000E-01  
    3.98640000     0.115442000  
    1.14290000     0.386206000  
    0.35940000     0.640089000  
P 1 1.00  
    0.11460000     1.00000000  
D 1 1.00  
    0.75000000     1.00000000  
****
```

- ▶ normalization constants are not included in contraction coefficients
- ▶ $6 + 1 + 1 + 1 + 4 + 1 + 1 = 15$ primitives
- ▶ $4 + 2 + 1 = 7$ shells of contracted Gaussians
- ▶ $(9s5p1d)/[4s2p1d]$
- ▶ $4 + 2 \times 3 + 1 \times 6 = 16$ Cartesian Gaussian functions

Minimal Basis

Basis which describes each core or valence orbital by one (contracted) function.

- ▶ initially Slater-type functions were used
- ▶ later, contracted Gaussians were used to approximate Slater-type functions
- ▶ STO- X G basis uses contractions of X primitives to approximate each orbital:

```
BASIS="STO-3G"
C  0
S  3  1.00
    71.6168370      0.154328970
    13.0450960      0.535328140
    3.53051220      0.444634540
S  3  1.00
    2.94124940     -0.999672300E-01
    0.683483100      0.399512830
    0.222289900      0.700115470
P  3  1.00
    2.94124940      0.155916270
    0.683483100      0.607683720
    0.222289900      0.391957390
```

The problem with minimal basis is its lack of flexibility. When bonds are formed, orbitals usually contract (or expand), and the minimal basis cannot adequately describe such changes in orbitals. The solution is to represent each orbital with 2 and more functions. That's the idea behind n -tuple- ζ (double-zeta, triple-zeta, quadruple-zeta, etc.) basis sets.

Double-zeta Basis Sets: 3-21G

```
BASIS="3-21G"  
C 0  
S 3 1.00  
    172.256000      0.617669000E-01  
    25.9109000     0.358794000  
    5.53335000     0.700713000  
SP 2 1.00  
    3.66498000     -0.395897000     0.236460000  
    0.770545000     1.21584000     0.860619000  
SP 1 1.00  
    0.195857000     1.000000000     1.000000000
```

- ▶ $1s$ orbital is still represented by 1 contracted function
- ▶ $2s$ and $2p$ orbitals are represented by 2 functions each

This is so-called split-valence double- ζ basis set. More flexibility means better results.

Double-zeta Basis Sets: 6-31G

BASIS="6-31G"

```
C 0
S 6 1.00
    3047.52490      0.183470000E-02
    457.369510     0.140373000E-01
    103.948690     0.688426000E-01
    29.2101550     0.232184400
    9.28666300    0.467941300
    3.16392700    0.362312000
SP 3 1.00
    7.86827240     -0.119332400     0.689991000E-01
    1.88128850     -0.160854200     0.316424000
    0.544249300     1.143456400     0.744308300
SP 1 1.00
    0.168714400     1.000000000     1.000000000
```

More primitives means more accurate description of orbitals, but the improvement over 3-21G and 6-31G is rather small. This is still a split-valence double- ζ basis set.

Double-zeta Basis Sets: DZ

```
BASIS="DZ (Dunning)"
C 0
S 6 1.00
    4232.61000      0.202900000E-02
    634.882000     0.155350000E-01
    146.097000     0.754110000E-01
    42.4974000     0.257121000
    14.1892000     0.596555000
    1.96660000     0.242517000
S 1 1.00
    5.14770000     1.000000000
S 1 1.00
    0.496200000    1.000000000
S 1 1.00
    0.153300000    1.000000000
P 4 1.00
    18.1557000     0.185340000E-01
    3.98640000     0.115442000
    1.14290000     0.386206000
    0.359400000    0.640089000
P 1 1.00
    0.114600000    1.000000000
```

2 Gaussians correspond to *each* orbital ($1s$, $2s$, and $2p$)! This is a full double- ζ basis set. Better than 3-21G, 4-31G, or 6-31G.

Triple-zeta Basis Sets: TZ

- ▶ 6-311G - split-valence triple- ζ basis set (one function for $1s$, 3 functions for $2s$ and $2p$ each)
- ▶ Dunning's TZ - full triple- ζ basis set

Triple- ζ better than double- ζ , but do not work well without polarization functions.

Polarization Functions

To approximate Hartree-Fock orbitals for first-row atoms (Li-Ne), one does not need d and higher angular momentum functions. However, in molecular environments orbitals become distorted from their atomic shapes. This is *polarization*. To describe effects of polarization one needs to add polarization functions (functions of higher angular momentum than any occupied atomic orbital).

Polarized Double-zeta Basis Sets: 6-31G*

```
BASIS="6-31G*"
C 0
S 6 1.00
    3047.52490      0.183470000E-02
    457.369510     0.140373000E-01
    103.948690     0.688426000E-01
    29.2101550     0.232184400
    9.28666300     0.467941300
    3.16392700     0.362312000
SP 3 1.00
    7.86827240     -0.119332400     0.689991000E-01
    1.88128850     -0.160854200     0.316424000
    0.544249300     1.143456400     0.744308300
SP 1 1.00
    0.168714400     1.000000000     1.000000000
D 1 1.0
    0.800000000     1.000000000
```

A split-valence double-zeta basis set with a single polarization function. Much better than non-polarized basis sets. This is the smallest basis one should use for qualitatively correct calculations. 6-31G* does not include polarization function on the hydrogen, but 6-31G** does.

New convention is to denote 6-31G* as 6-31G(d) and 6-31G** as 6-31G(d,p).

Polarized Basis Sets: pick one

There are many polarized basis sets. One really has to be able to interpret basis set's construction to compare.

- ▶ 6-31G*. The Gaussian workhorse, very commonly used. Remember missing polarization functions on hydrogens. If not sure, try 6-31G**.
- ▶ DZP = DZ + 1 polarization function; analogous to 6-31G**, only full double- ζ , hence better. Very commonly used by non-Gaussian users.
- ▶ TZ2P = TZ + 2 polarization functions; similar to 6-311G(2d,2p), only full triple- ζ , hence better.
- ▶ 6-311G(2d1f,2p1d) - another step above, includes f functions on first row atoms and d functions on hydrogens.

Polarized basis sets are considered good general purpose basis sets for semi-quantitative calculations on ground state neutral molecules without non-bonding effects.

Correlation consistent basis sets

Developed by Thom Dunning and co-workers at PNNL. Developed from correlated calculations (in contrast with all bases considered so far). Should be mostly used for correlated calculations and special-purpose projects

- ▶ cc-pVDZ = split-valence double- ζ core, plus single polarization function. Similar to 6-31G**.
- ▶ cc-pVTZ = split-valence triple- ζ core, plus two d and one f function on first row atoms and two p and one d functions on hydrogens. Similar to 6-311G(2d1f,2p1d).
- ▶ cc-pVQZ, cc-pV5Z, cc-pV6Z, cc-pV7Z - special-purpose basis sets, should only be used with correlated methods, such as MP2 and CCSD(T).

Diffuse Functions

Anions tend to have their orbitals expanded compared to neutral molecules. One needs to include diffuse functions (functions with small exponents, hence large radial extent) to predict properties of anions accurately. Diffuse functions are also necessary to describe certain non-bonding interactions.

- ▶ 6-31+G** - same as 6-31G** plus one set of s and p diffuse functions on first row atoms.
- ▶ 6-31++G** - same as 6-31+G** plus a diffuse function on hydrogen.
- ▶ aug-cc-pVXZ - same as cc-pVXZ plus one diffuse function per each angular momentum present in cc-pVXZ.

Differences between diffuse basis sets are mostly due to the differences in their core and not in their diffuse component.

Expert Topic: General Contractions

- ▶ Usually each primitive function contributed to just one shell. This is so called segmented contraction.
- ▶ General contraction scheme allows primitive functions to contribute to more than 1 shell. Here's cc-pVDZ basis for C (NWChem format):

```
C   S
 6665.0000000    0.6920000000E-03 -0.1460000000E-03
 1000.0000000    0.5329000000E-02 -0.1154000000E-02
 228.0000000     0.2707700000E-01 -0.5725000000E-02
 64.710000000    0.10171800000    -0.2331200000E-01
 21.060000000    0.27474000000    -0.6395500000E-01
 7.4950000000    0.44856400000    -0.14998100000
 2.7970000000    0.28507400000    -0.12726200000
 0.52150000000    0.15204000000E-01  0.54452900000

C   S
 0.15960000000    1.00000000000

C   P
 9.43900000000    0.38109000000E-01
 2.00200000000    0.20948000000
 0.54560000000    0.50855700000

C   P
 0.15170000000    1.00000000000

C   D
 0.55000000000    1.00000000000
```

- ▶ Any given primitive in generally contracted basis sets usually contributes to a set of shells of one angular momentum.
- ▶ The main reason for general contractions is to make evaluation of matrix elements easier.

Expert Topic: Linear Dependence

- ▶ Mathematical formulas look simplest if we use orthonormal basis sets.
- ▶ An arbitrary set of Gaussian (or Slater) functions does not form an orthonormal basis, e.g., overlap of two primitive *s*-type Gaussians is

$$\begin{aligned}\langle \phi_i | \phi_j \rangle &= \int e^{-\alpha_i |\mathbf{r}-\mathbf{A}|^2} e^{-\alpha_j |\mathbf{r}-\mathbf{B}|^2} d\mathbf{r} \\ &= e^{-\alpha_i \alpha_j |\mathbf{A}-\mathbf{B}|^2 / (\alpha_i + \alpha_j)} \left(\frac{\pi}{\alpha_i + \alpha_j} \right)^{3/2},\end{aligned}\quad (10)$$

i.e. never zero. Thus Gaussian basis sets must be orthonormalized.

- ▶ Orthonormalized Gaussians are no longer atom-centered.
- ▶ Basis sets become linearly dependent as the size of the basis and the size of the molecule grow, especially if the basis contains diffuse functions. Orthonormalization of a linearly dependent basis set is possible but problematic. For very large molecules (hundreds of atoms) Gaussian basis sets are not optimal because of the linear dependency problem.

Conclusions

- ▶ Basis set = core (minimal/double- ζ /triple- ζ) [+ polarization functions [+ diffuse functions]]
- ▶ Polarization functions should always be used for, at least, heavy atoms (first-row and beyond).
- ▶ Diffuse functions should be used for computations on systems involving anions and/or non-bonding interactions.
- ▶ Special basis sets for correlated calculations (correlation-consistent basis sets, ANO, core-correlation basis sets, etc.).
- ▶ <http://www.emsl.pnl.gov/forms/basisform.html> - EMSL Gaussian Basis Set database.