

# Lecture 22: Gaussian Basis Sets

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Chem 150/250 Fall 2023

12/08/2023



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# Gaussian Primitives

- Primary AO basis: Spherical Gauss Type Orbitals (GTOs) (5d 7f ...):

$$\chi_s(\mathbf{r}|\mathbf{R}, \mathbf{l}, \zeta) = Y_l^m(\mathbf{r} - \mathbf{R})|\mathbf{r} - \mathbf{R}|^l e^{-\zeta(\mathbf{r}-\mathbf{R})^2},$$

- Usually expressed by Cartesian GTOs (6d 10f ...),

$$\chi(\mathbf{r}|\mathbf{R}, \mathbf{l}, \zeta) = (x - X)^i (y - Y)^j (z - Z)^k e^{-\zeta(\mathbf{r}-\mathbf{R})^2},$$

where  $\mathbf{l} = (i, j, k)$  and  $l = i + j + k$  is (pseudo-) l-quantum number,  $i, j, k = 0, 1, 2, \dots$

- Older basis sets (Pople) sometimes use Cartesian GTOs as primary basis functions
- Shells: Set of basis functions with identical  $\mathbf{R}, \zeta, l$
- There are  $(l + 1)(l + 2)/2$  Cartesian and  $2l + 1$  spherical GTOs in a shell of angular momentum  $l$

# Key Properties of Cartesian GTOs

- Factorization:

$$\chi(\mathbf{r}|\mathbf{R}, \mathbf{l}, \zeta) = (x-X)^i e^{-\zeta(x-X)^2} (y-Y)^j e^{-\zeta(y-Y)^2} (z-Z)^k e^{-\zeta(z-Z)^2}$$

- Gaussian Product Theorem (GPT): The product of two s type CGTOs with centers **A**, **B** is an s type CGTO centered at

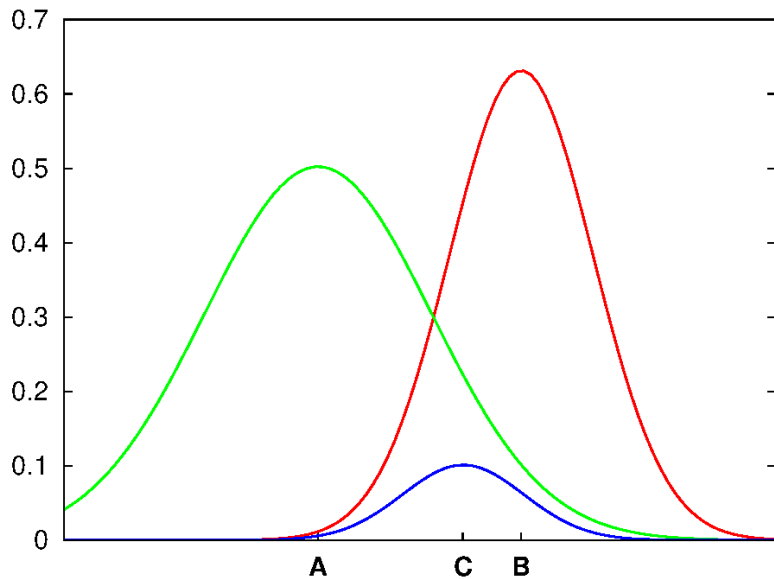
$$\mathbf{C} = \frac{\zeta_A \mathbf{A} + \zeta_B \mathbf{B}}{\zeta_A + \zeta_B}$$

and damped by an overlap factor,

$$e^{-\zeta_A(\mathbf{r}-\mathbf{A})^2} e^{-\zeta_B(\mathbf{r}-\mathbf{B})^2} = e^{-\frac{\zeta_A \zeta_B}{\zeta_A + \zeta_B}(\mathbf{A}-\mathbf{B})^2} e^{-(\zeta_A + \zeta_B)(\mathbf{r}-\mathbf{C})^2}$$

- Horizontal and vertical recursion relations

## GPT Illustration



# Contracted and Polarized GTO Basis Sets

- Reduce number of functions by linear combination (“contraction”) of primitive GTOs with *fixed* coefficients,

$$\psi(\mathbf{r}|\mathbf{R}, \mathbf{l}) = \sum_{n=1}^p c_n \chi(\mathbf{r}|\mathbf{R}, \mathbf{l}, \zeta_n) \quad (1)$$

- Valence contraction: Minimal (“single  $\zeta$ ”) basis set for core orbitals
- $X$ -tuple  $\zeta$ :  $X$  primitive GTOs per occupied  $(n, l)$  subshell. DZV  $\equiv$  split valence (SV)
- Polarization functions:
  - ▶ Correlation consistent(cc-pVXZ, Dunning):  $1d$  for  $X = 2$ ,  $2d1f$  for  $X = 3$ ,  $3d2f1g$  for  $X = 4$ , etc.
  - ▶ Hydrogen polarization functions less important: SV(P) or 6-31G\* have no H polarization functions

# Example: SV(P) for Carbon

```
$basis
*
c SV(P)
# c      (7s4p1d) / [3s2p1d]      {511/31/1}
*
  5  s
1238.4016938      0.54568832082E-02
186.29004992      0.40638409211E-01
42.251176346      0.18025593888
11.676557932      0.46315121755
3.5930506482      0.44087173314
  1  s
0.40245147363      1.00000000000
  1  s
0.13090182668      1.00000000000
  3  p
9.4680970621      0.38387871728E-01
2.0103545142      0.21117025112
0.54771004707      0.51328172114
  1  p
0.15268613795      1.00000000000
  1  d
0.80000000000      1.00000000000
*
$end
```

# Choosing GTO Basis Sets

Name	X	Contraction (for C)	$\Delta E_b$	$\Delta r_e$	Comments
SV(P), SVP	2	(7s4p1d) /[3s2p1d]	5	1-2	cf. 6-31G*, 6-31G**, cc- pVDZ
TZVP	3	(11s6p2d1f) /[5s3p2d1f]	2	0.5	cf. 6- 311G(2df,2pd), cc-pVTZ
QZVP	4	(15s8p3d2f1g) /[7s4p3d2f1g]	< 1	< 0.3	cf. cc-pVQZ

Typical basis set errors in bond energies  $\Delta E_b$  (kcal/mol per bond), bond distances  $\Delta r_e$  (pm)

- Recommendations:

- ▶ Workhorse: SV(P) (mostly for initial optimization)
- ▶ TZVP to check SV(P), (single-point) energy calculations
- ▶ QZVP for HF and DFT basis set limit results, benchmarks