

Chapter #4

Basis Sets: Collections of
Exponents and Contraction Coefficients

Chapter #4

4.1. Hydrogen Orbitals

Hydrogen Atom Wavefunctions

$$\psi_{n,l,m_l}(r,\Theta,\varphi) = R_{n,l}(r) * Y_{l,m_l}(\Theta,\varphi)$$

r = position vector from nucleus

Radial function

Spherical harmonic function

Radial Function

- Exponential decline, $\exp(-\zeta r)$ term
- Adds **radial nodes** in going from 1s to 2s, from 2s to 3s,...
- Adds **radial nodes** in going from 2p to 3p, from 3p to 4p,...

Spherical Harmonic Function

- Adds **node surfaces** (planes and other) to shape orbitals in degenerate sets

Spherical Harmonics

l = 0^[1] [\[edit\]](#)

$$Y_0^0(\theta, \varphi) = \frac{1}{2} \sqrt{\frac{1}{\pi}}$$

l = 1^[1] [\[edit\]](#)

$$Y_1^{-1}(\theta, \varphi) = \frac{1}{2} \sqrt{\frac{3}{2\pi}} \cdot e^{-i\varphi} \cdot \sin \theta = \frac{1}{2} \sqrt{\frac{3}{2\pi}} \cdot \frac{(x - iy)}{r}$$

$$Y_1^0(\theta, \varphi) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cdot \cos \theta = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cdot \frac{z}{r}$$

$$Y_1^1(\theta, \varphi) = -\frac{1}{2} \sqrt{\frac{3}{2\pi}} \cdot e^{i\varphi} \cdot \sin \theta = -\frac{1}{2} \sqrt{\frac{3}{2\pi}} \cdot \frac{(x + iy)}{r}$$

l = 2^[1] [\[edit\]](#)

$$Y_2^{-2}(\theta, \varphi) = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \cdot e^{-2i\varphi} \cdot \sin^2 \theta = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \cdot \frac{(x - iy)^2}{r^2}$$

$$Y_2^{-1}(\theta, \varphi) = \frac{1}{2} \sqrt{\frac{15}{2\pi}} \cdot e^{-i\varphi} \cdot \sin \theta \cdot \cos \theta = \frac{1}{2} \sqrt{\frac{15}{2\pi}} \cdot \frac{(x - iy)z}{r^2}$$

$$Y_2^0(\theta, \varphi) = \frac{1}{4} \sqrt{\frac{5}{\pi}} \cdot (3 \cos^2 \theta - 1) = \frac{1}{4} \sqrt{\frac{5}{\pi}} \cdot \frac{(2z^2 - x^2 - y^2)}{r^2}$$

$$Y_2^1(\theta, \varphi) = \frac{-1}{2} \sqrt{\frac{15}{2\pi}} \cdot e^{i\varphi} \cdot \sin \theta \cdot \cos \theta = \frac{-1}{2} \sqrt{\frac{15}{2\pi}} \cdot \frac{(x + iy)z}{r^2}$$

$$Y_2^2(\theta, \varphi) = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \cdot e^{2i\varphi} \cdot \sin^2 \theta = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \cdot \frac{(x + iy)^2}{r^2}$$

p-AO:

Linear term depends on coordinates x, y, and z.

d-AO:

Quadratic term depends on coordinates x, y, & z.

Radial Function and Laguerre Polynomial

$$R_{n\ell}(r) = - \left[\left(\frac{2Z}{na_0} \right)^3 \frac{(n-\ell-1)!}{2n \{(n+\ell)!\}^3} \right]^{\frac{1}{2}} e^{-\frac{\rho}{2}} \rho^{\ell} L_{n+\ell}^{2\ell+1}(\rho),$$

in which

$$\rho = \frac{2Zr}{na_{\mu}}$$

and

$$a_{\mu} = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

Exponential decay:
 $\exp(-\zeta r)$

Dependence on
second quantum
number l : const. r^l

Laguerre
Polynomial

$n = 1$, K shell:

$$\ell = 0, 1s \quad R_{10}(r) = \left(Z/a_\mu\right)^{\frac{3}{2}} 2e^{-\frac{\rho}{2}}$$

Radial function has cusp at nucleus.

$n = 2$, L shell:

$$\ell = 0, 2s \quad R_{20}(r) = \frac{\left(Z/a_\mu\right)^{\frac{3}{2}}}{2\sqrt{2}} (2 - \rho) e^{-\frac{\rho}{2}}$$

$(2 - \rho)$ term causes one spherical node

$$\ell = 1, 2p \quad R_{21}(r) = \frac{\left(Z/a_\mu\right)^{\frac{3}{2}}}{2\sqrt{6}} \rho e^{-\frac{\rho}{2}}$$

ρ term causes zero value at nucleus.

$n = 3$, M shell:

$$\ell = 0, 3s \quad R_{30}(r) = \frac{\left(Z/a_\mu\right)^{\frac{3}{2}}}{9\sqrt{3}} (6 - 6\rho + \rho^2) e^{-\frac{\rho}{2}}$$

$(6 - 6\rho + \rho^2)$ term causes two spherical nodes.

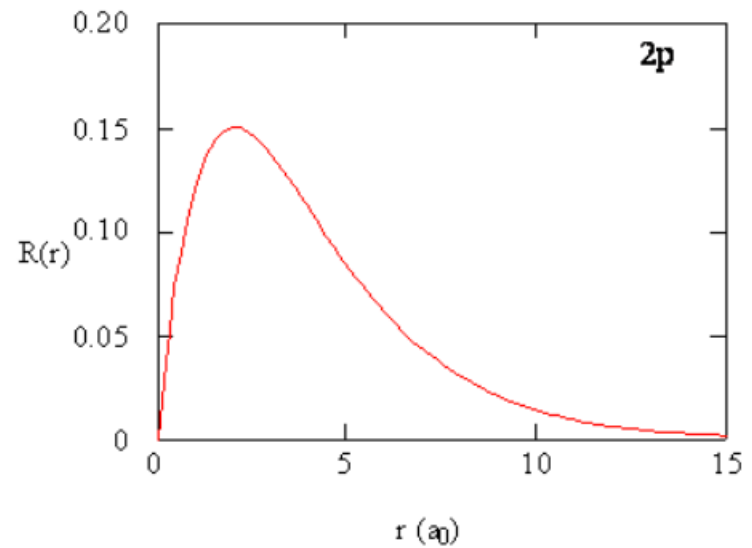
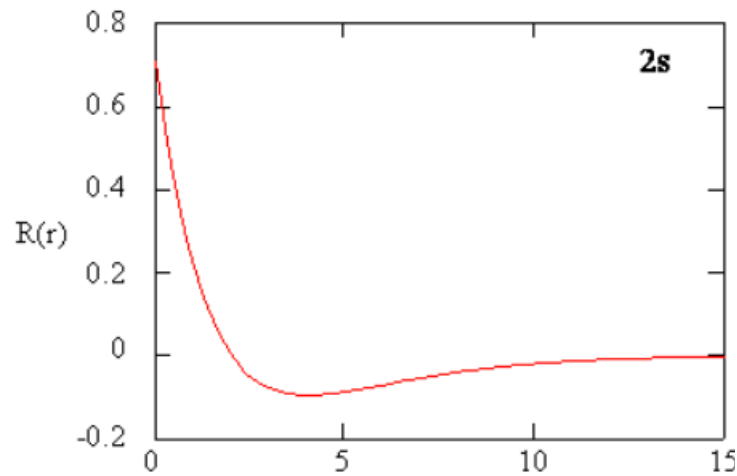
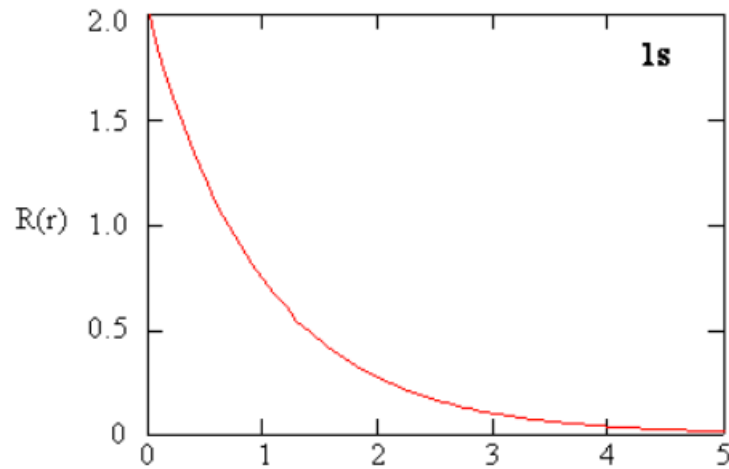
$$\ell = 1, 3p \quad R_{31}(r) = \frac{\left(Z/a_\mu\right)^{\frac{3}{2}}}{9\sqrt{6}} (4 - \rho) \rho e^{-\frac{\rho}{2}}$$

$(4 - \rho) \rho$ term causes zero value at nucleus and one spherical node

$$\ell = 2, 3d \quad R_{32}(r) = \frac{\left(Z/a_\mu\right)^{\frac{3}{2}}}{9\sqrt{30}} \rho^2 e^{-\frac{\rho}{2}}$$

ρ^2 term causes zero value at nucleus.

Radial Functions of 1s, 2s, & 2p



$R(r)$, $R(r)^2$, and $4\pi r^2 \cdot R(r)^2$

$R(r)$, the **radial function** is plotted in Figure 8.3.

$R(r)^2$, the **radial probability density** is the probability density for the electron to be at a point located the distance r from the proton. Radial probability densities for three types of atomic orbitals are plotted in Figure 8.4.

$4\pi r^2 \cdot R(r)^2$, the **radial distribution function**. When the radial probability density for every value of r is multiplied by the area of the spherical surface represented by that particular value of r , we get the radial distribution function. The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the radial distribution function is given by $4\pi r^2 \cdot R(r)^2$. See Figure 8.5.

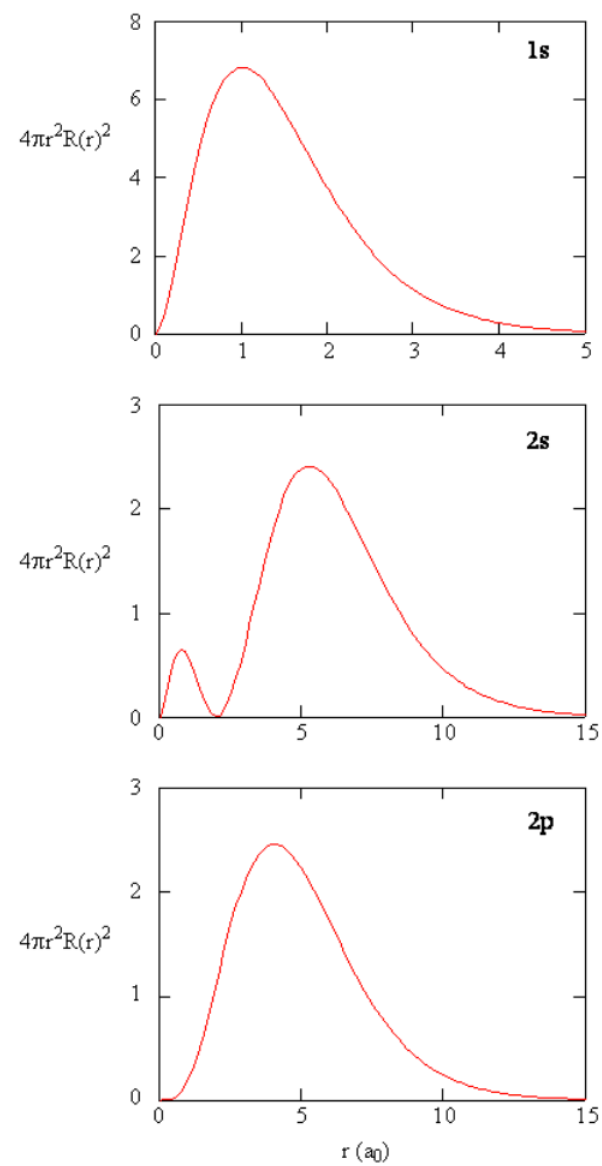
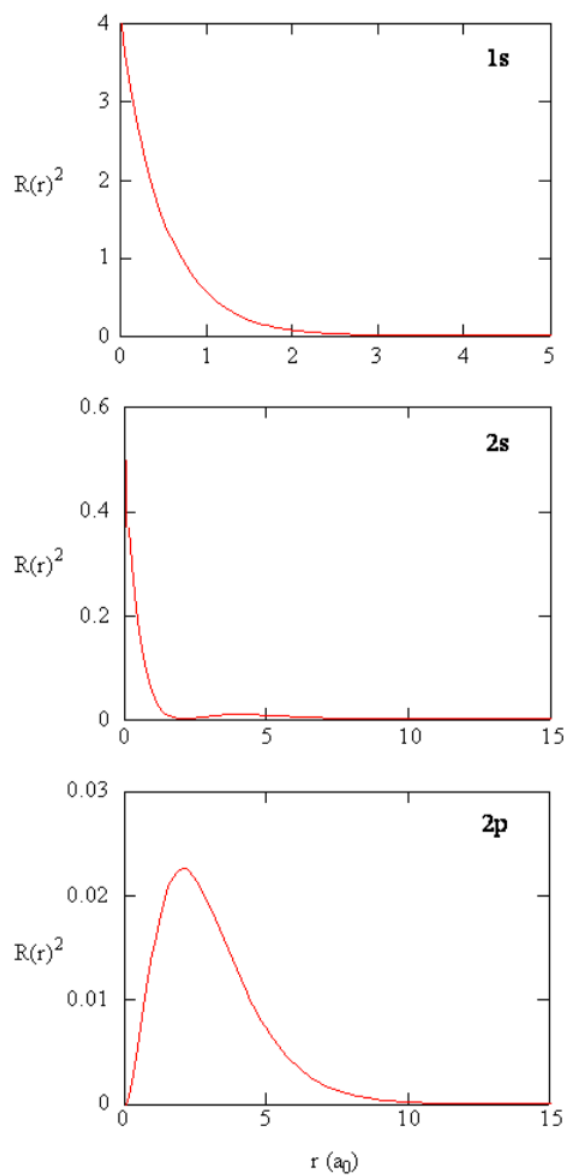
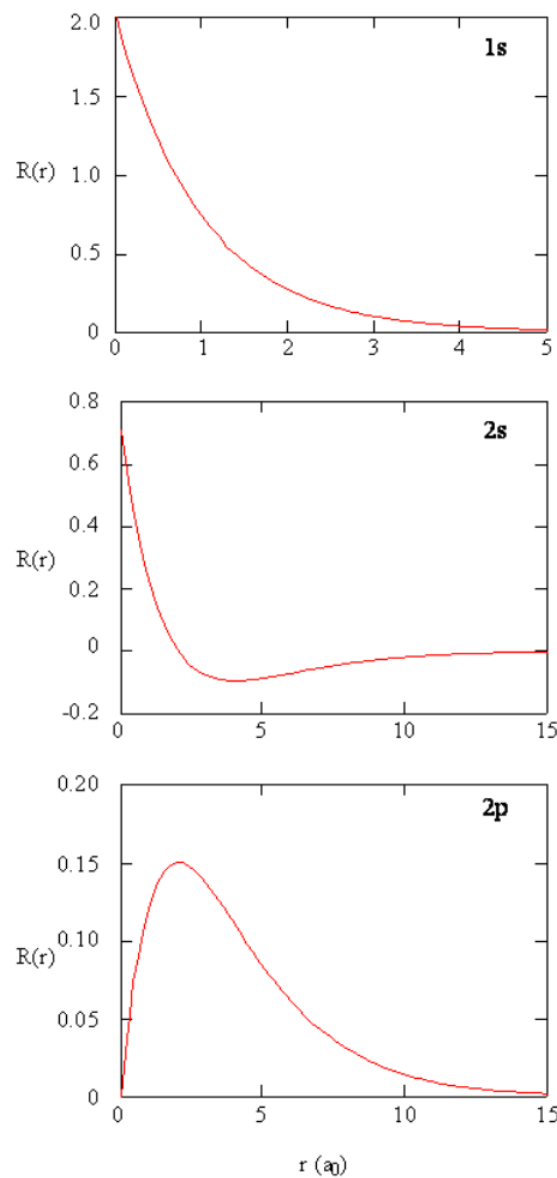
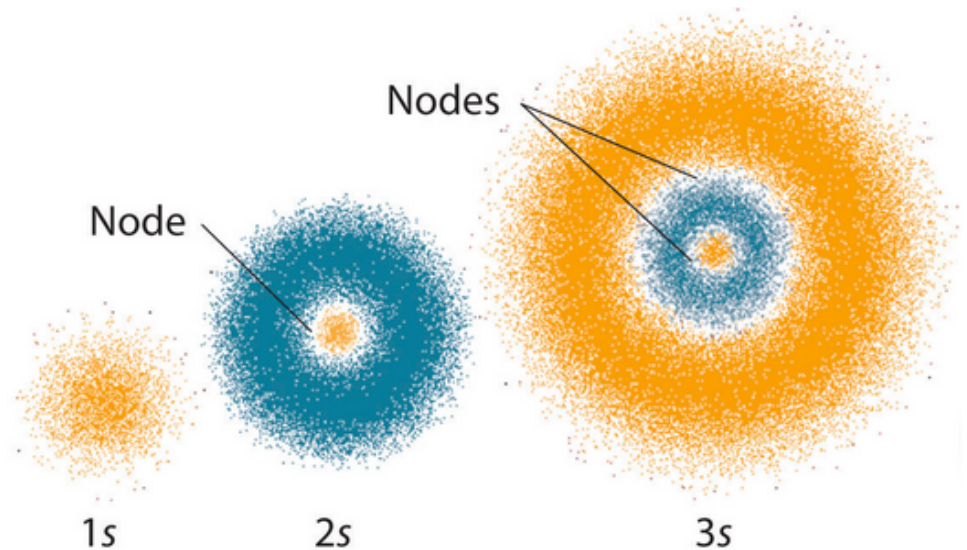
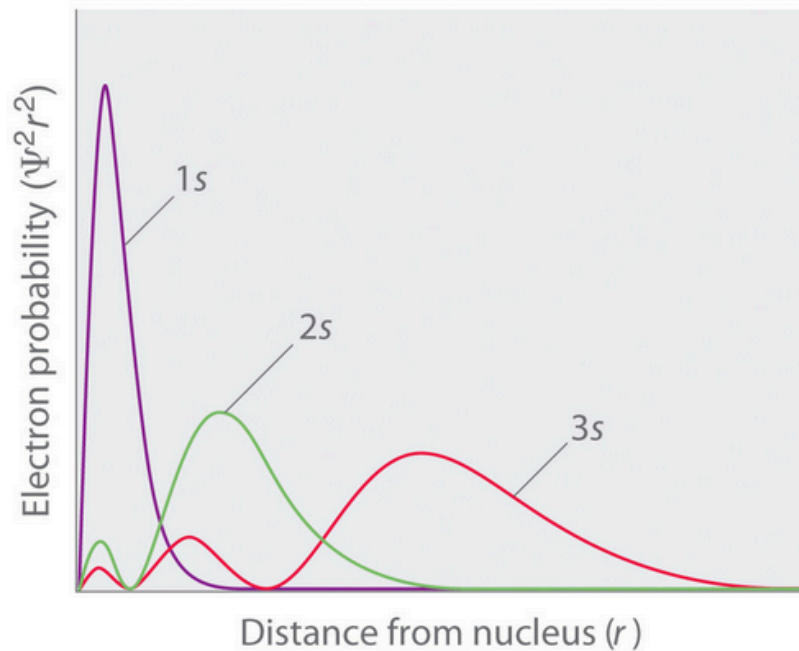


Figure 8.3 Radial function, $R(r)$, for the 1s, 2s, and 2p orbitals.

Figure 8.4 Radial probability densities for the 1s, 2s, and 2p orbitals.

Figure 8.5 The radial distribution function for the 1s, 2s, and 2p orbitals.

Radial Node in 2s & 3s Hydrogen Orbital



http://images.flatworldknowledge.com/averillfwk/averillfwk-fig06_023.jpg

Radial Node in 3p Hydrogen Orbital

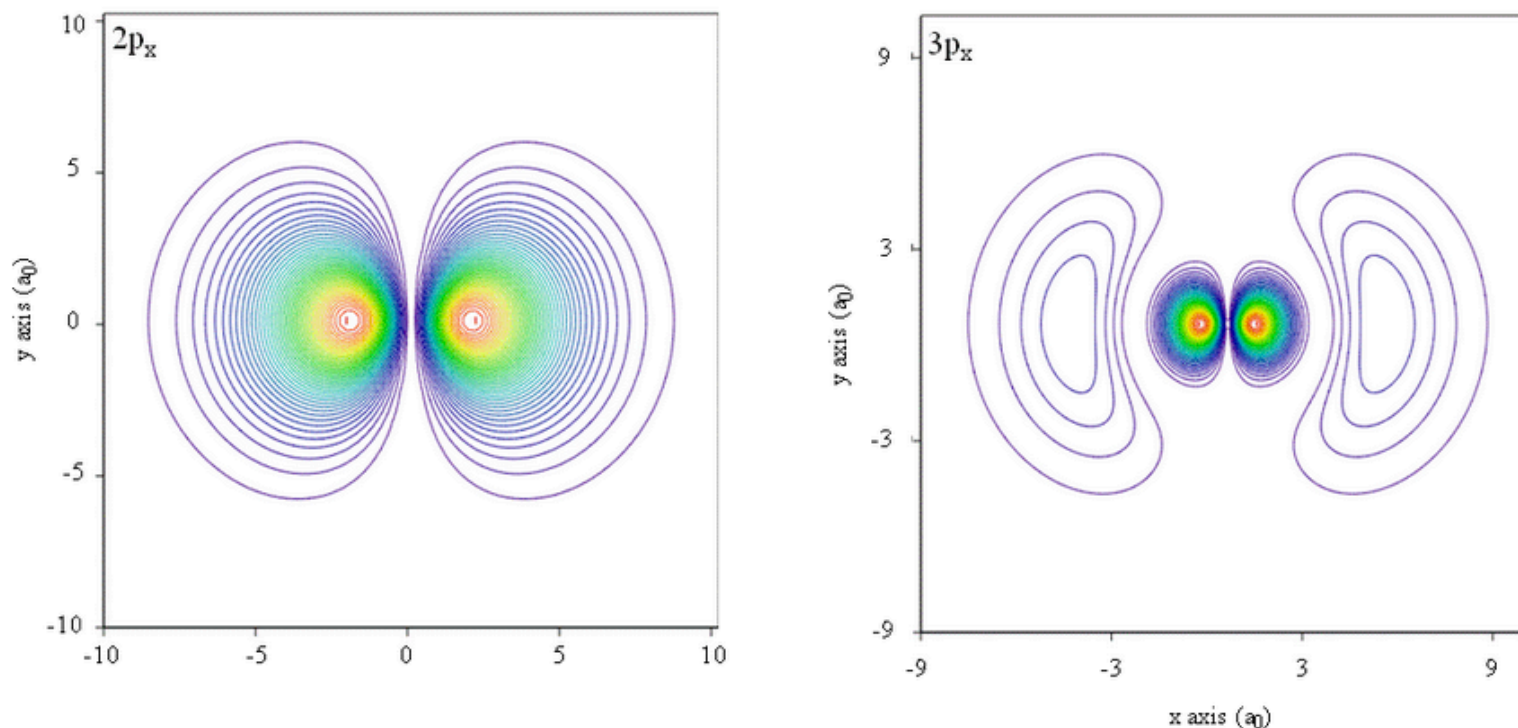


Figure 8.2. Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low $R(r)^2$. The angular function used to create the figure was a linear combination of two Spherical Harmonic functions (see Problem 10 at the end of this chapter.)

Radial Functions Hydrogen Orbitals

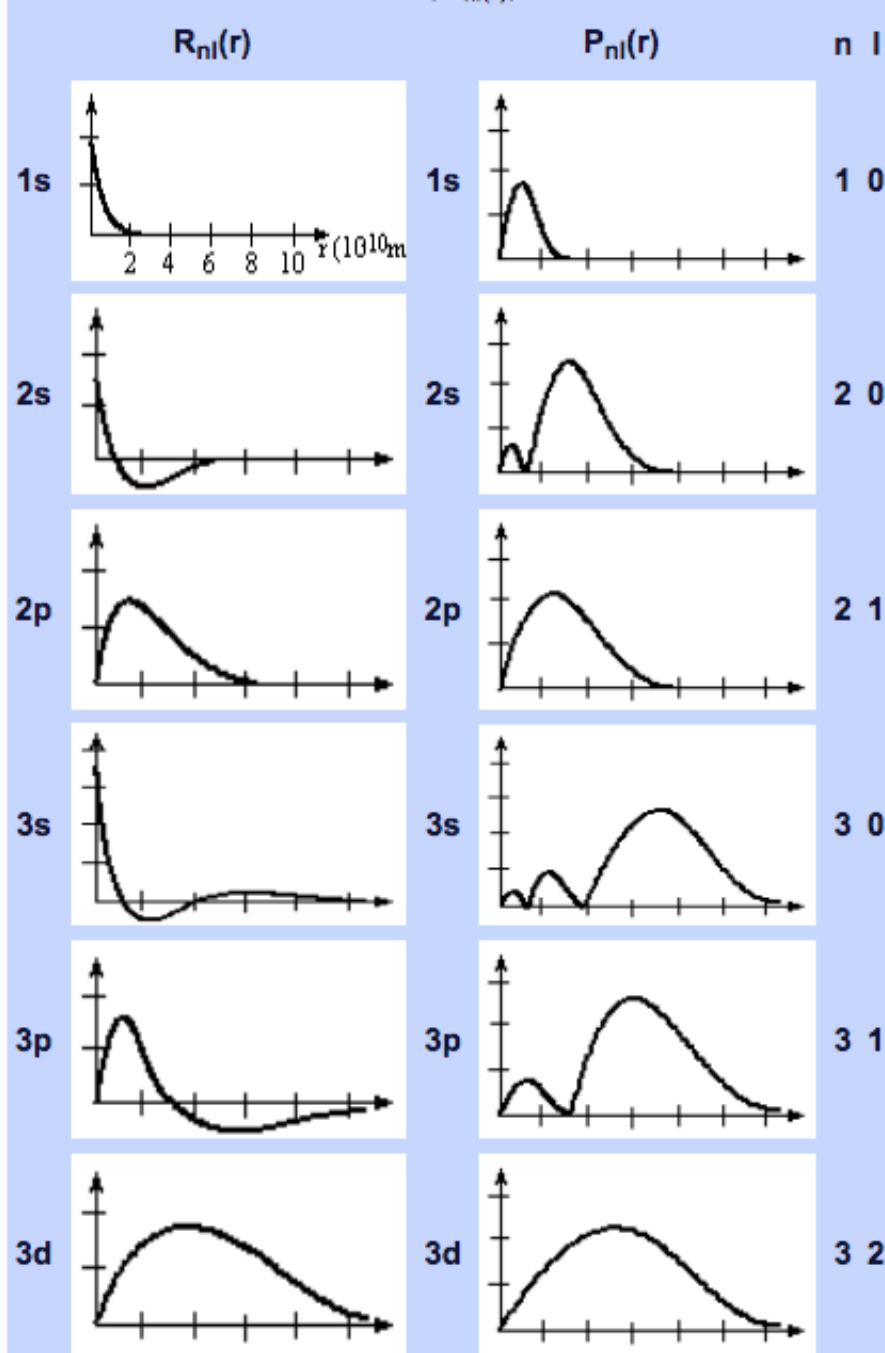
Note the radial nodes!

1s: no radial nodes
2s: one radial node
3s: two radial nodes

2p: no radial node
3p: one radial node

http://www.everyscience.com/Chemistry/Inorganic/Atomic_Structure/c.1101.php

This following box shows the shapes of the radial wavefunctions, $R_{nl}(r)$, and the radial distribution functions, $P_{nl}(r)$, of the atomic orbitals.



Chapter #4

4.2. Slater Functions and Gaussian Functions: Basis Functions, Primitive Functions, STO-3G

Slater Type Orbital (STO)

$$R(r) = N r^{n-1} \exp(-\zeta r)$$

r = position vector from nucleus

N = normalization constant

n = main quantum number, 1, 2, 3,...

ζ = zeta-exponent

$n = 1$: $R(r) = N \exp(-\zeta r)$ -- looks like a 1s orbital

$n = 2$: $R(r) = N r \exp(-\zeta r)$ -- looks like a 2p orbital

$n = 3$: $R(r) = N r^2 \exp(-\zeta r)$ -- looks like a 3d orbital

STO and Radial Nodes?

STOs do not have radial nodes
because there are no Laguerre polynomial terms.
And we do not care!

1s Basis Function: $R_1(r) = N_1 \exp(-\zeta_1 r)$

2s Basis Function: $R_2(r) = N_2 \exp(-\zeta_2 r)$

LCAO1: Lots of “1s” PLUS a little of “2s” – “a good 1s without node”

LCAO2: Lots of “2s” MINUS a little of “1s” – “a good 2s with a node”

Gaussian Type Orbital (GTO)

$$R(r) = N r^{n-1} \exp(-\zeta r^2)$$

r = position vector from nucleus

N = normalization constant

n = main quantum number, 0, 1, 2...

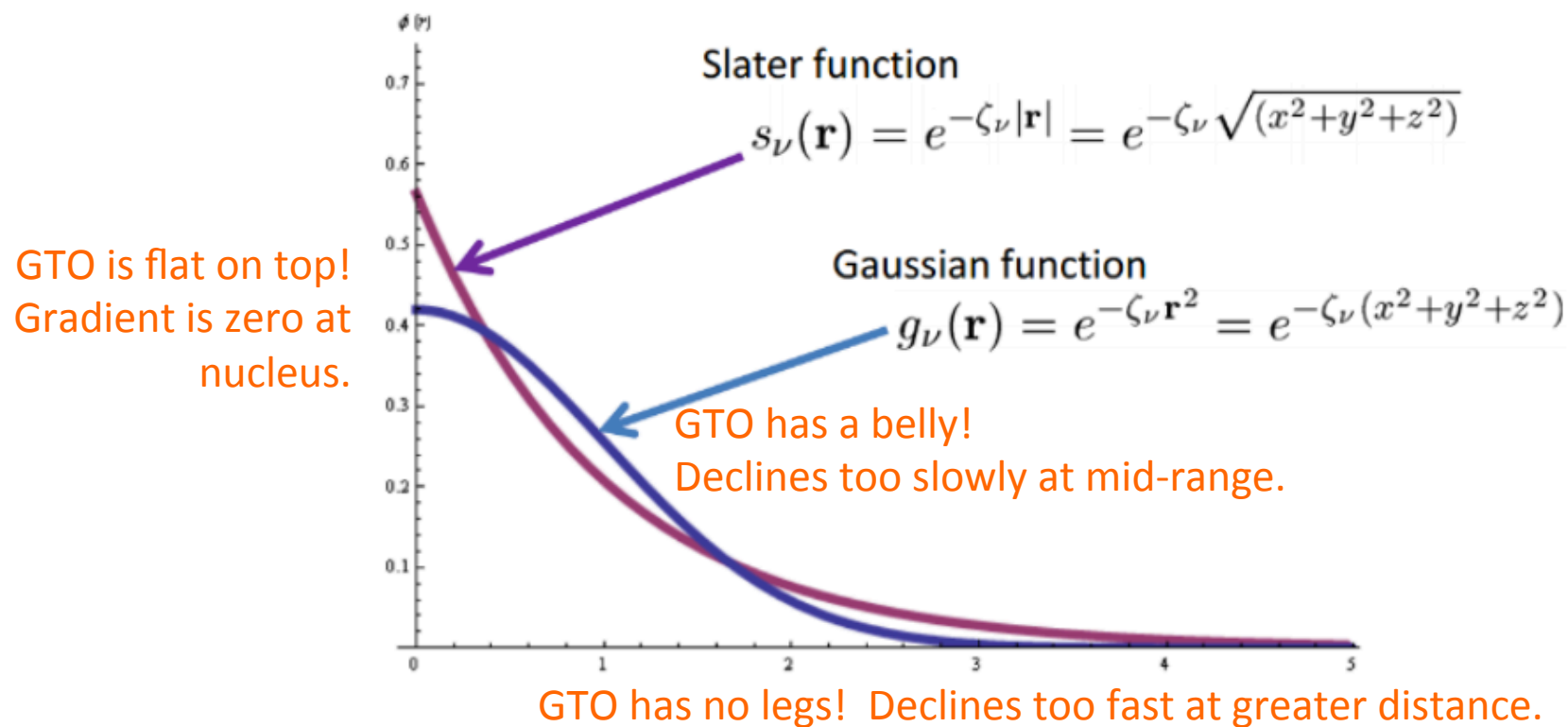
ζ = zeta-exponent

$n = 1$: $R(r) = N \exp(-\zeta r^2)$ -- does this look like a 1s orbital?

$n = 2$: $R(r) = N r \exp(-\zeta r^2)$ -- does this looks like a 2p orbital?

$n = 3$: $R(r) = N r^2 \exp(-\zeta r^2)$ – does this looks like a 3d orbital?

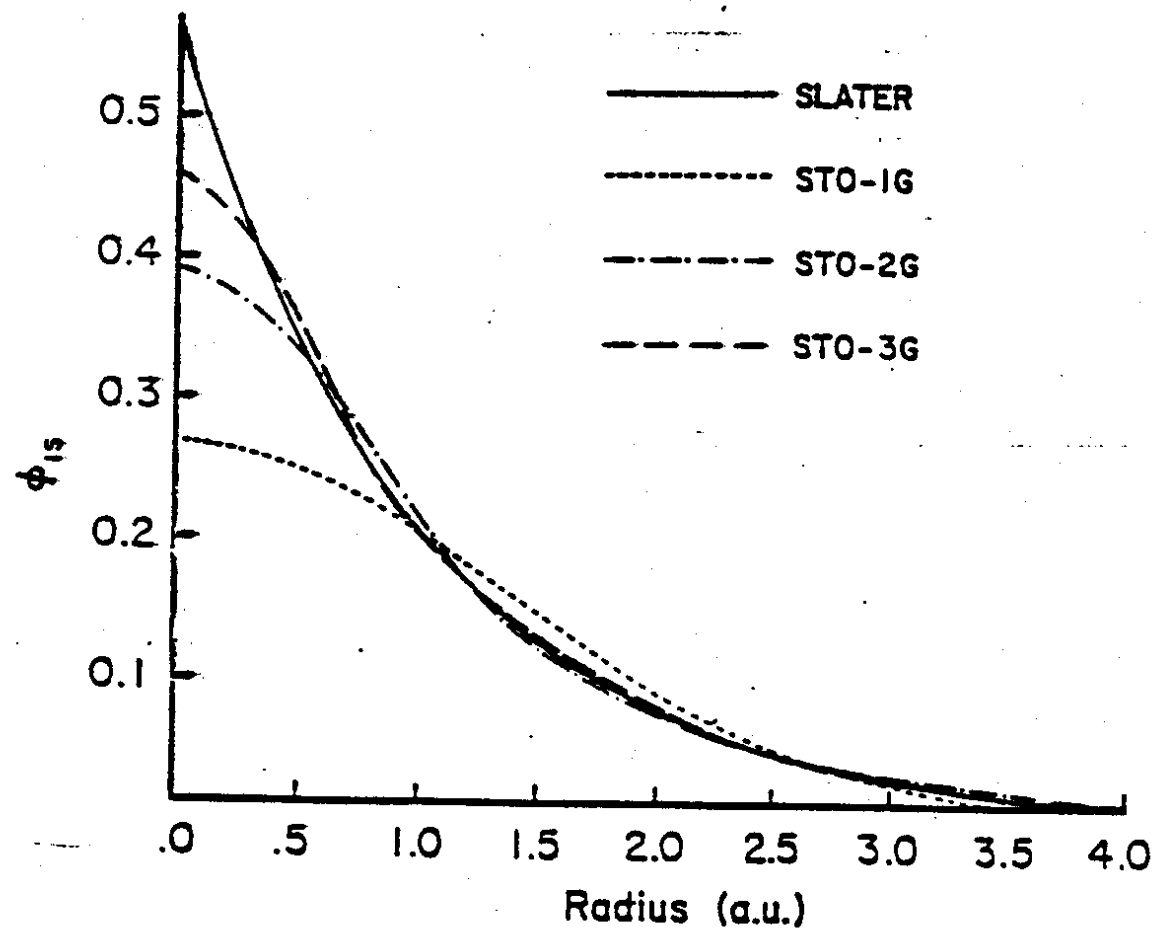
Shapes of “1s” as STO and GTO



...but GTOs are so easy to integrate!!

Approximate STO by Several GTO!

Flatter Belly, Better Legs! (Who cares about the density at the nucleus.)



Cartesian Gaussian Functions

$$R(r) = N x^l y^m z^n \exp(-\zeta r^2)$$

r = position vector from nucleus

N = normalization constant

l, m, n = sum adds up to second quantum number

ζ = zeta-exponent

Sum(l, m, n) = 0, 1s-AO: $R(r) = N \exp(-\zeta r^2)$

Sum(l, m, n) = 1, 2p_x-AO: $R(r) = N x \exp(-\zeta r^2)$

Sum(l, m, n) = 1, 2p_y-AO: $R(r) = N y \exp(-\zeta r^2)$

Sum(l, m, n) = 1, 2p_z-AO: $R(r) = N z \exp(-\zeta r^2)$

SIX Cartesian d-Type GTO?

$$R(r) = N x^l y^m z^n \exp(-\zeta r^2)$$

$$\text{Sum}(l, m, n) = 2, d_{xy}\text{-AO: } R(r) = N xy \exp(-\zeta r)$$

$$\text{Sum}(l, m, n) = 2, d_{xz}\text{-AO: } R(r) = N xz \exp(-\zeta r)$$

$$\text{Sum}(l, m, n) = 2, d_{yz}\text{-AO: } R(r) = N yz \exp(-\zeta r)$$

$$\text{Sum}(l, m, n) = 2, d_{xx}\text{-AO: } R(r) = N x^2 \exp(-\zeta r)$$

$$\text{Sum}(l, m, n) = 2, d_{yy}\text{-AO: } R(r) = N y^2 \exp(-\zeta r)$$

$$\text{Sum}(l, m, n) = 2, d_{zz}\text{-AO: } R(r) = N z^2 \exp(-\zeta r)$$

There are SIX. Now what?

FIVE Pure d-Type GTO

$$R(r) = N x^l y^m z^n \exp(-\zeta r^2)$$

There are SIX d-functions (6d) and there are ten f-functions (10f).

Now what? Use linear combination!

Six Cartesian d-functions $d(zz)$, $d(xx)$, $d(yy)$, $d(xz)$, $d(yz)$, $d(xy)$ can be transformed to five spherical d-functions (5d): $d(3z^2-r^2)$, $d(xz)$, $d(yz)$, $d(xy)$, $d(x^2-y^2)$ and one function with s-symmetry which is $\sim (d(xx) + d(yy) + d(zz))$.

Ten Cartesian f-basis functions give seven pure f-functions (7f) and three p-functions.

Five or Six d-Type GTO? Seven or Ten f-Type GTO? Your Choice

Gaussian lets you use the commands **5d** or **6d** and **7f** or **10f** to select your preference.

If you do not make the choice, *Gaussian* will use default settings. The default setting is 5d with some basis sets and 6d with other basis sets. See *Gaussian* output for the setting employed in the computation.

Chapter #4

4.3. AO Expansion and Contraction Coefficients:
STO-3G, Split-Description, 3-21G, 6-31G, 6-311G

Formamide, STO-3G, GFP

Standard basis: STO-3G (5D, 7F)

AO basis set (Overlap normalization):

Atom C1	Shell	1 S	3	bf	1 -	1	-0.341076890728	0.833964846211	-0.008761112724
		0.7161683735D+02	0.1543289673D+00						
		0.1304509632D+02	0.5353281423D+00						
		0.3530512160D+01	0.4446345422D+00						
Atom C1	Shell	2 SP	3	bf	2 -	5	-0.341076890728	0.833964846211	-0.008761112724
		0.2941249355D+01	-0.9996722919D-01	0.1559162750D+00					
		0.6834830964D+00	0.3995128261D+00	0.6076837186D+00					
		0.2222899159D+00	0.7001154689D+00	0.3919573931D+00					
Atom O2	Shell	3 S	3	bf	6 -	6	-2.282038449098	-0.539700302378	0.018542080649
		0.1307093214D+03	0.1543289673D+00						
		0.2380886605D+02	0.5353281423D+00						
		0.6443608313D+01	0.4446345422D+00						
Atom O2	Shell	4 SP	3	bf	7 -	10	-2.282038449098	-0.539700302378	0.018542080649
		0.5033151319D+01	-0.9996722919D-01	0.1559162750D+00					
		0.1169596125D+01	0.3995128261D+00	0.6076837186D+00					
		0.3803889600D+00	0.7001154689D+00	0.3919573931D+00					
Atom N3	Shell	5 S	3	bf	11 -	11	2.176449105509	-0.322771475341	-0.210597657564
		0.9910616896D+02	0.1543289673D+00						
		0.1805231239D+02	0.5353281423D+00						
		0.4885660238D+01	0.4446345422D+00						
Atom N3	Shell	6 SP	3	bf	12 -	15	2.176449105509	-0.322771475341	-0.210597657564
		0.3780455879D+01	-0.9996722919D-01	0.1559162750D+00					
		0.8784966449D+00	0.3995128261D+00	0.6076837186D+00					
		0.2857143744D+00	0.7001154689D+00	0.3919573931D+00					
Atom H4	Shell	7 S	3	bf	16 -	16	3.442271250423	0.764744376877	0.676007342383
		0.3425250914D+01	0.1543289673D+00						
		0.6239137298D+00	0.5353281423D+00						
		0.1688554040D+00	0.4446345422D+00						
Atom H5	Shell	8 S	3	bf	17 -	17	2.148543157565	-2.035482043835	0.587467893597
		0.3425250914D+01	0.1543289673D+00						
		0.6239137298D+00	0.5353281423D+00						
		0.1688554040D+00	0.4446345422D+00						
Atom H6	Shell	9 S	3	bf	18 -	18	-0.523189209395	2.843951336102	0.114938398119
		0.3425250914D+01	0.1543289673D+00						
		0.6239137298D+00	0.5353281423D+00						
		0.1688554040D+00	0.4446345422D+00						

Coordinates

There are 18 symmetry adapted cartesian basis functions of A symmetry.
 There are 18 symmetry adapted basis functions of A symmetry.
 18 basis functions, 54 primitive gaussians, 18 cartesian basis functions
 12 alpha electrons 12 beta electrons

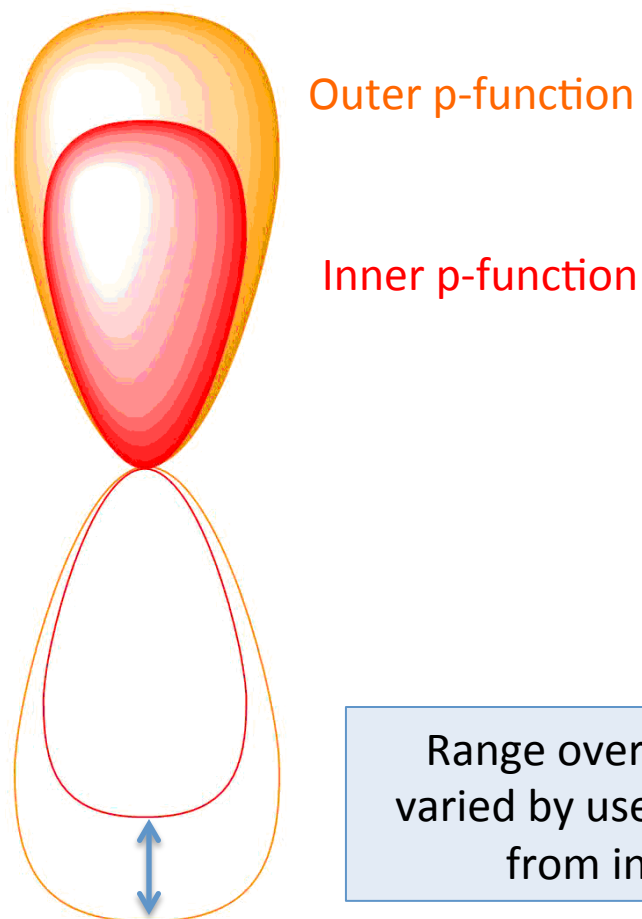
Basis Set Size

Formamide, STO-3G, GFP

AO basis set (Overlap normalization):						
1s(C)	Atom C1	Shell 1	S 3	bf	1 -	1
		0.7161683735D+02	0.1543289673D+00			
		0.1304509632D+02	0.5353281423D+00			
		0.3530512160D+01	0.4446345422D+00			
2s(C), 2p(C)	Atom C1	Shell 2	SP 3	bf	2 -	5
		0.2941249355D+01	-0.9996722919D-01		0.1559162750D+00	
		0.6834830964D+00	0.3995128261D+00		0.6076837186D+00	
		0.2222899159D+00	0.7001154689D+00		0.3919573931D+00	
1s(O)	Atom O2	Shell 3	S 3	bf	6 -	6
		0.1307093214D+03	0.1543289673D+00			
		0.2380886605D+02	0.5353281423D+00			
		0.6443608313D+01	0.4446345422D+00			
2s(O), 2p(O)	Atom O2	Shell 4	SP 3	bf	7 -	10
		0.5033151319D+01	-0.9996722919D-01		0.1559162750D+00	
		0.1169596125D+01	0.3995128261D+00		0.6076837186D+00	
		0.3803889600D+00	0.7001154689D+00		0.3919573931D+00	
1s(N)	Atom N3	Shell 5	S 3	bf	11 -	11
		0.9910616896D+02	0.1543289673D+00			
		0.1805231239D+02	0.5353281423D+00			
		0.4885660238D+01	0.4446345422D+00			
2s(N), 2p(N)	Atom N3	Shell 6	SP 3	bf	12 -	15
		0.3780455879D+01	-0.9996722919D-01		0.1559162750D+00	
		0.8784966449D+00	0.3995128261D+00		0.6076837186D+00	
		0.2857143744D+00	0.7001154689D+00		0.3919573931D+00	
1s(H)	Atom H4	Shell 7	S 3	bf	16 -	16
		0.3425250914D+01	0.1543289673D+00			
		0.6239137298D+00	0.5353281423D+00			
		0.1688554040D+00	0.4446345422D+00			

NOTE: Same exponent for s and p in same shell on same atom.

Split-Valence Basis Set: Why?



Range over which the orbital can be varied by use of different contributions from inner and outer p-BFs.

3-21G Split-Valence Basis Set

Number of GTO primitives
summed to describe an outer
valence basis function.

3-21G

Number of GTO primitives
summed to describe a core
basis function.

Number of GTO primitives
summed to describe an inner
valence basis function.

Formamide, 3-21G, GFP

Standard basis: 3-21G (6D, 7F)

AO basis set (Overlap normalization):

1s(C)

Atom C1 Shell 1 S 3 bf 1 - 1

0.1722560000D+03 0.6176690738D-01

0.2591090000D+02 0.3587940429D+00

0.5533350000D+01 0.7007130837D+00

2sp(C)-inner

Atom C1 Shell 2 SP 2 bf 2 - 5

0.3664980000D+01 -0.3958951621D+00 0.2364599466D+00

0.7705450000D+00 0.1215834356D+01 0.8606188057D+00

2sp(C)-outer

Atom C1 Shell 3 SP 1 bf 6 - 9

0.1958570000D+00 0.1000000000D+01 0.1000000000D+01

Atom O2 Shell 4 S 3 bf 10 - 10

0.3220370000D+03 0.5923939339D-01

0.4843080000D+02 0.3514999608D+00

0.1042060000D+02 0.7076579210D+00

Atom O2 Shell 5 SP 2 bf 11 - 14

0.7402940000D+01 -0.4044535832D+00 0.2445861070D+00

0.1576200000D+01 0.1221561761D+01 0.8539553735D+00

Atom O2 Shell 6 SP 1 bf 15 - 18

0.3736840000D+00 0.1000000000D+01 0.1000000000D+01

Atom N3 Shell 7 S 3 bf 19 - 19

0.2427660000D+03 0.5986570051D-01

0.3648510000D+02 0.3529550030D+00

0.7814490000D+01 0.7065130060D+00

Atom N3 Shell 8 SP 2 bf 20 - 23

0.5425220000D+01 -0.4133000774D+00 0.2379720162D+00

0.1149150000D+01 0.1224417267D+01 0.8589530586D+00

Atom N3 Shell 9 SP 1 bf 24 - 27

0.2832050000D+00 0.1000000000D+01 0.1000000000D+01

1s(H)-inner

Atom H4 Shell 10 S 2 bf 28 - 28

0.5447178000D+01 0.1562849787D+00

0.8245472400D+00 0.9046908767D+00

1s(H)-outer

Atom H4 Shell 11 S 1 bf 29 - 29

0.1831915800D+00 0.1000000000D+01

6-31G Split-Valence Basis Set

Number of GTO primitives
summed to describe an outer
valence basis function.

6-31G

Number of GTO primitives
summed to describe a core
basis function.

Number of GTO primitives
summed to describe an inner
valence basis function.

Formamide, 6-31G, GFP

1sp(N)	Atom N3	Shell	7 S	6	bf	19 -	19
		0.4173511460D+04	0.1834772160D-02				
		0.6274579110D+03	0.1399462700D-01				
		0.1429020930D+03	0.6858655181D-01				
		0.4023432930D+02	0.2322408730D+00				
		0.1282021290D+02	0.4690699481D+00				
		0.4390437010D+01	0.3604551991D+00				
2sp(N)-inner	Atom N3	Shell	8 SP	3	bf	20 -	23
		0.1162636186D+02	-0.1149611817D+00			0.6757974388D-01	
		0.2716279807D+01	-0.1691174786D+00			0.3239072959D+00	
		0.7722183966D+00	0.1145851947D+01			0.7408951398D+00	
2sp(N)-outer	Atom N3	Shell	9 SP	1	bf	24 -	27
		0.2120314975D+00	0.1000000000D+01			0.1000000000D+01	
1s(H)-inner	Atom H4	Shell	10 S	3	bf	28 -	28
		0.1873113696D+02	0.3349460434D-01				
		0.2825394365D+01	0.2347269535D+00				
		0.6401216923D+00	0.8137573261D+00				
1s(H)-outer	Atom H4	Shell	11 S	1	bf	29 -	29
		0.1612777588D+00	0.1000000000D+01				

6-311G Triply-Split-Valence Basis Set

Number of GTO primitives
summed to describe another
outer valence basis function.

Number of GTO primitives
summed to describe an outer
valence basis function.

6-311G

Number of GTO primitives
summed to describe a core
basis function.

Number of GTO primitives
summed to describe an inner
valence basis function.

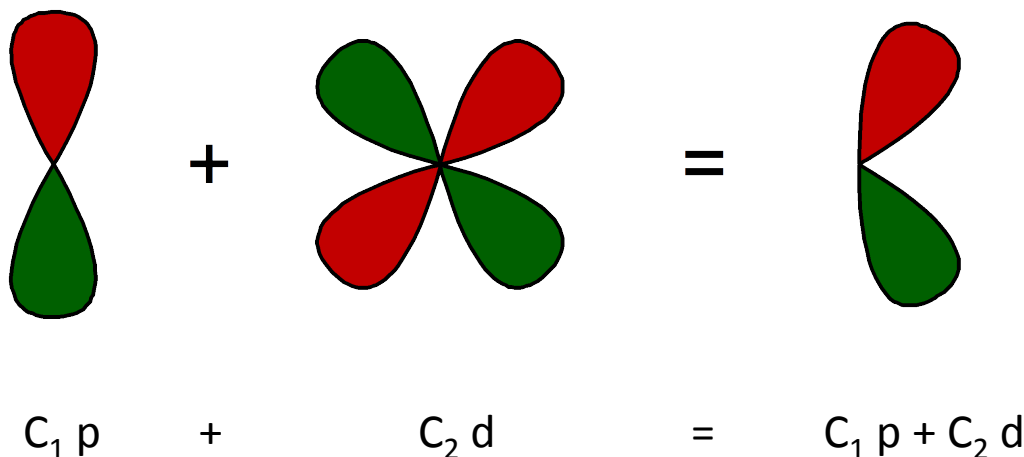
Formamide, 6-311G, GFP

1s(N)	Atom N3	Shell	9 S	6	bf	27 -	27
		0.6293480000D+04	0.1969788147D-02				
		0.9490440000D+03	0.1496128592D-01				
		0.2187760000D+03	0.7350053084D-01				
		0.6369160000D+02	0.2489367658D+00				
		0.1882820000D+02	0.6024594331D+00				
		0.2720230000D+01	0.2562017589D+00				
2sp(N)-inner	Atom N3	Shell	10 SP	3	bf	28 -	31
		0.3063310000D+02	0.1119060795D+00			0.3831191864D-01	
		0.7026140000D+01	0.9216666549D+00			0.2374031155D+00	
		0.2112050000D+01	-0.2569191826D-02			0.8175923978D+00	
2sp(N)-outer1	Atom N3	Shell	11 SP	1	bf	32 -	35
		0.6840090000D+00	0.1000000000D+01			0.1000000000D+01	
2sp(N)-outer2	Atom N3	Shell	12 SP	1	bf	36 -	39
		0.2008780000D+00	0.1000000000D+01			0.1000000000D+01	
1s(H)-inner	Atom H4	Shell	13 S	3	bf	40 -	40
		0.3386500000D+02	0.2549381454D-01				
		0.5094790000D+01	0.1903731086D+00				
		0.1158790000D+01	0.8521614860D+00				
1s(H)-outer1	Atom H4	Shell	14 S	1	bf	41 -	41
		0.3258400000D+00	0.1000000000D+01				
1s(H)-outer2	Atom H4	Shell	15 S	1	bf	42 -	42
		0.1027410000D+00	0.1000000000D+01		

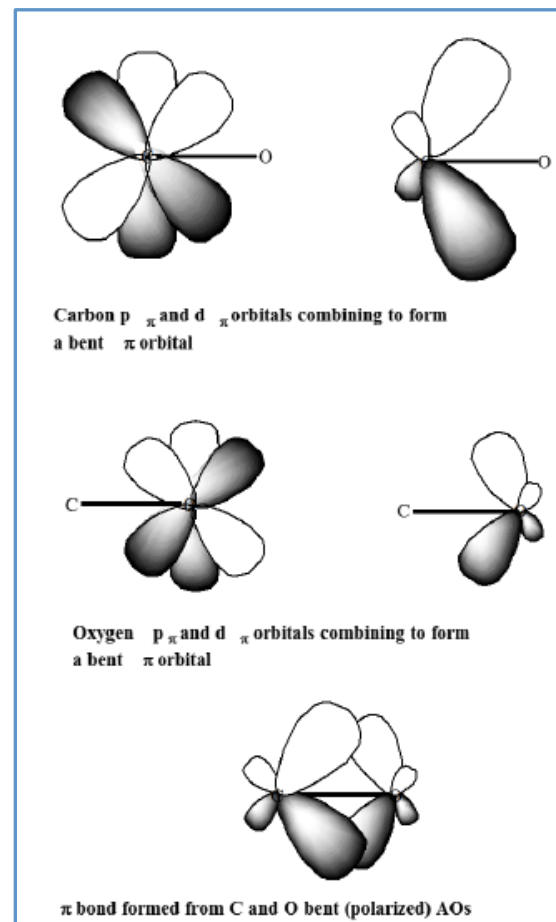
Chapter #4

4.4. Symmetric AO versus Polarized Density:
Polarization Functions, 6-31G*, 6-31G**

Polarization of a p-AO: Use d-AO



$C_2 \ll C_1$; we are just using the d-basis functions to make the p-basis functions a little better!



Polarization of an s-AO: Use p-AO

$$C_1 s + C_2 p = C_1 s + C_2 p$$

$C_2 \ll C_1$; we are adding just a little of the p-basis functions to make the s-basis functions a little better!

This is taken care of automatically for all atoms other than H and He. As soon as your valence shell contains s and p basis functions, the polarization of the s-basis function can happen automatically.

Polarized 6-31G Basis Sets

Number of GTO primitives
summed to describe an outer
valence basis function.

Number & type of polarization
functions on atoms other than H & He.

Number and type of polarization
functions used on H and He.

6-31G(ndmf,lpkd)

Number of GTO primitives
summed to describe a core
basis function.

Number of GTO primitives
summed to describe an inner
valence basis function.

6-31G(d,p) = 6-31G**

6-31G(d) = 6-31G*

Formamide, 6-31G**, GFP

		Standard basis: 6-31G(d,p) (6D, 7F)					
		AO basis set (Overlap normalization):					
1s(C)	Atom C1	Shell	1 S	6	bf	1 -	1
2sp(C)-inner	Atom C1	Shell	2 SP	3	bf	2 -	5
2sp(C)-outer	Atom C1	Shell	3 SP	1	bf	6 -	9
C, d-polarization	Atom C1	Shell	4 D	1	bf	10 -	15
1s(H)-inner	Atom H6	Shell	19 S	3	bf	56 -	56
1s(H)-outer	Atom H6	Shell	20 S	1	bf	57 -	57
H, p-polarization	Atom H6	Shell	21 P	1	bf	58 -	60

Chapter #4

4.5. Anions and Diffuse Density:
Diffuse Functions, 6-31+G*, 6-31++G**

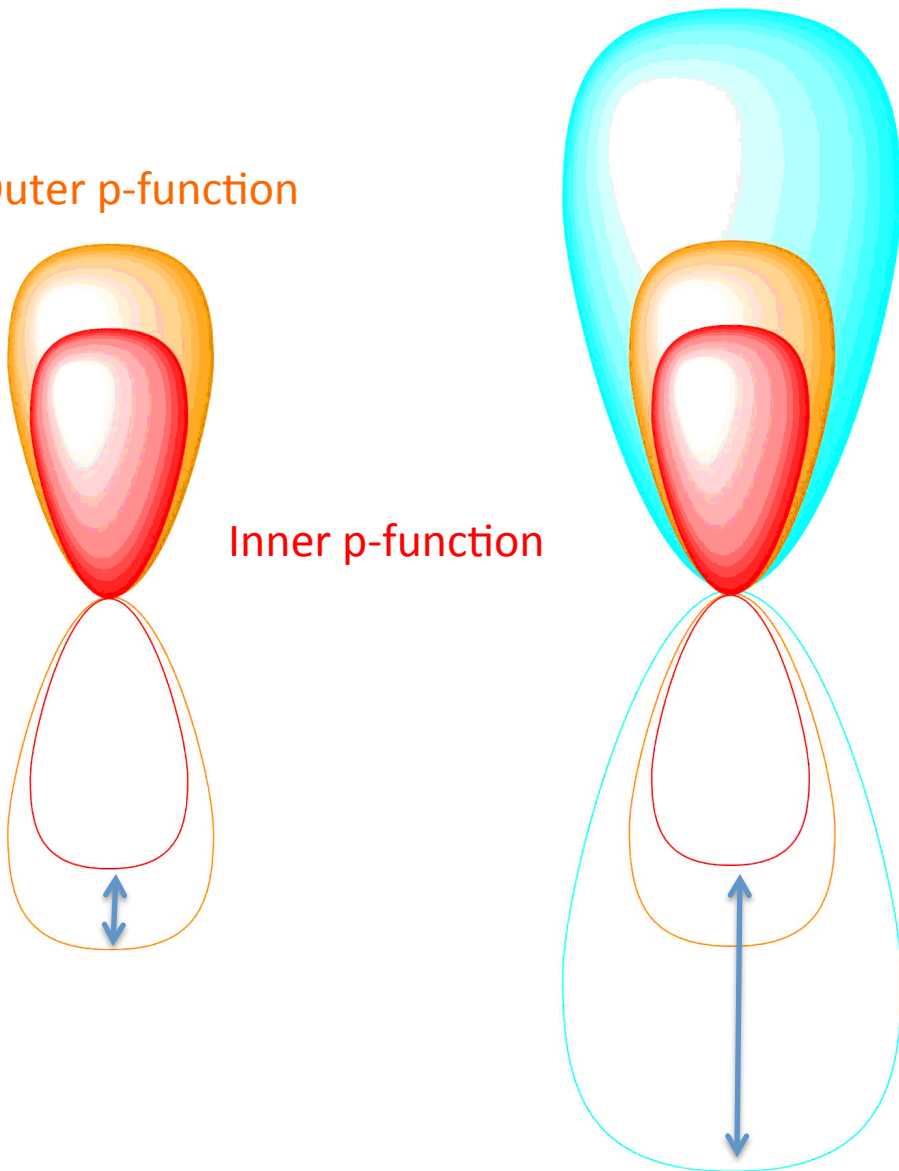
Diffuse Functions: Why?

Outer p-function

Inner p-function

Diffuse p-function is really out-reaching

Range over which the orbital can be varied by use of contributions from split-valence and diffuse p-BFs **includes anions**.



6-31G Basis Sets

with Polarization and Diffuse-Function Augmentation

Add diffuse s-type functions used
on H and He.

Number & type of polarization
functions on atoms other than H & He.

Add diffuse s- and p-functions on
atoms other than H & He.

Number and type of polarization
functions used on H and He.

6-31++G(ndmf,lpkd)

6-31++G(d,p) = 6-31++G**

6-31+G(d) = 6-31+G*

Formamide, 6-31++G**, GFP

Standard basis: 6-31++G(d,p) (6D, 7F)						
AO basis set (Overlap normalization):						
1s(C)	Atom C1	Shell	1 S	6 bf	1 -	1
			0.3047524880D+04	0.1834737132D-02		
			0.4573695180D+03	0.1403732281D-01		
			0.1039486850D+03	0.6884262226D-01		
			0.2921015530D+02	0.2321844432D+00		
			0.9286662960D+01	0.4679413484D+00		
			0.3163926960D+01	0.3623119853D+00		
2sp(C)-inner	Atom C1	Shell	2 SP	3 bf	2 -	5
			0.7868272350D+01	-0.1193324198D+00	0.6899906659D-01	
			0.1881288540D+01	-0.1608541517D+00	0.3164239610D+00	
			0.5442492580D+00	0.1143456438D+01	0.7443082909D+00	
2sp(C)-outer	Atom C1	Shell	3 SP	1 bf	6 -	9
			0.1687144782D+00	0.1000000000D+01	0.1000000000D+01	
C, sp-diffuse	Atom C1	Shell	4 SP	1 bf	10 -	13
			0.4380000000D-01	0.1000000000D+01	0.1000000000D+01	
C, d-polarization	Atom C1	Shell	5 D	1 bf	14 -	19
			0.8000000000D+00	0.1000000000D+01		
1s(H)-inner	Atom H6	Shell	24 S	3 bf	70 -	70
			0.1873113696D+02	0.3349460434D-01		
			0.2825394365D+01	0.2347269535D+00		
			0.6401216923D+00	0.8137573261D+00		
1s(H)-outer	Atom H6	Shell	25 S	1 bf	71 -	71
			0.1612777588D+00	0.1000000000D+01		
1s(H), diffuse	Atom H6	Shell	26 S	1 bf	72 -	72
			0.3600000000D-01	0.1000000000D+01		
H, p-polarization	Atom H6	Shell	27 P	1 bf	73 -	75
			0.1100000000D+01	0.1000000000D+01		

Chapter #4

4.6. General Basis Sets

EMSL Basis Set Exchange

https://bse.pnl.gov/bse/portal

EMSL Office of Science

BASIS SET EXCHANGE

Username: Password:

Login Become a Contributor

Basis Set Exchange: v1.2.2

Feedback About ReleaseNotes Help

All

6-311++G**--J
6-311+G
6-311+G(2d,p)
6-311+G*
6-311+G**
6-311+G*-J
6-311G
6-311G(2df,2pd)
6-311G*
6-311G* Polarization
6-311G**
6-311G** Polarization
6-311G-J
6-31G
6-31G(2df,p)
6-31G(2df,2pd)

Search Basis Set Name

Total: 377 published basis sets that contain C

H																	He
Li	Be							B	C	N	O	F	Ne				
Na	Mg							Al	Si	P	S	Cl	Ar				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Format: NWChem ☐ Optimized General Contractions ☒

Get Basis Set

"6-311+G(2d,p)" Basis Set Information

Summary: VTZ2PD Valence Triple Zeta + Double Polar. on Heavy Atoms & Single Polar. on Light Atoms + Diffuse on Heavy Atoms

Primary Developer: N/A

Last Modified: Fri, 27 Feb 2015 03:24:24 GMT

Contributor: Ryan Renslow

Curation Status: published

[More information...](#)
[User annotations...](#)

When publishing results obtained from use of the Basis Set Exchange (BSE) software and the EMSL Basis Set Library, please cite:

The Role of Databases in Support of Computational Chemistry Calculations

Feller, D., J. Comp. Chem., 17(13), 1571-1586, 1996.

Basis Set Exchange: A Community Database for Computational Sciences

Schuchardt, K.L., Didier, B.T., Elsethagen, T., Sun, L., Gurumoorthi, V., Chase, J., Li, J., and Windus, T.L.
J. Chem. Inf. Model., 47(3), 1045-1052, 2007, doi:10.1021/ci600510j.

Carbon 6-311+G(2d,p) Basis Set

which really is 6-311+G(2d)



```
# 6-311+G(2d,p)  EMSL  Basis Set Exchange Library  9/5/16 8:47 AM
# Elements                      References
# -----
# H, Li - Ne: R. Krishnan, J.S. Binkley, R. Seeger and J.A. Pople,
# J. Chem. Phys. 72, 650 (1980)
# Na - Ar:      A.D. McLean and G.S. Chandler J. Chem. Phys. 72, 5639, (1980).
# K - Ca:      J-P. Blaudeau, M. P. McGrath, L.A. Curtiss and L. Radom,
# J. Chem. Phys. 107, 5016 (1997).
# Ga - Kr:      L. A. Curtiss, M. P. McGrath, J-P. Blandeau, N. E. Davis,
# R. C. Binning, Jr. L. Radom, J. Chem. Phys. 103, 6104 (1995).
# I           :      M.N. Glukhovstev, A. pross, M.P. McGrath, L. Radom, J. Chem. Phys.
# 103, 1878 (1995)
# Elements                      References
# -----
# H-Ne: M.J. Frisch, J.A. Pople and J.S. Binkley, J. Chem. Phys. 80, 3265 (1984)
# Elements                      Reference
# -----
# H, Li-Cl: T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.V.R. Schleyer,
# J. Comp. Chem. 4, 294 (1983).
#
```

```
BASIS "ao basis" PRINT
#BASIS SET: (12s,6p,2d) -> [5s,4p,2d]
```

Carbon 6-311+G(2d,p) Basis Set

which really is 6-311+G(2d)

```
BASIS "ao basis" PRINT
#BASIS SET: (12s,6p,2d) -> [5s,4p,2d]
C      S
      4563.2400000      0.00196665
      682.0240000      0.0152306
      154.9730000      0.0761269
      44.4553000      0.2608010
      13.0290000      0.6164620
      1.8277300      0.2210060
C      SP
      20.9642000      0.1146600      0.0402487
      4.8033100      0.9199990      0.2375940
      1.4593300      -0.00303068      0.8158540
C      SP
      0.4834560      1.0000000      1.0000000
C      SP
      0.1455850      1.0000000      1.0000000
C      SP
      0.0438000      1.0000000      1.0000000
C      D
      1.2520000      1.0000000
C      D
      0.3130000      1.0000000
END
```

Carbon 6-311+G(2d,p) Basis Set

which really is 6-311+G(2d)

```
BASIS "ao basis" PRINT
#BASIS SET: (12s,6p,2d) -> [5s,4p,2d]
C      S
      4563.2400000      0.00196665
      682 02400000      0 0152306
```

Information about number of **primitive functions** in round parentheses.

Information about number of **basis functions** in corner parentheses.

(12s,6p,2d) -> [5s,4p,2d]

Primitive Functions “contracted to” **Basis Functions**

The more basis functions the better:
Each basis function adds a little more flexibility.

The more primitives the better:
Each basis function is a little better.

Carbon Basis Sets Compared

3-21G:	(6s,3p) -> [3s,2p]
6-31G:	(10s,4p) -> [3s,2p]
6-31G*:	(10s,4p,1d) -> [3s,2p,1d]
6-31+G:	(11s,5p) -> [4s,3p]
6-311G:	(11s,5p) -> [4s,3p]
6-311G*:	(11s,5p,1d) -> [4s,3p,1d]
6-311+G*:	(12s,6p,1d) -> [5s,4p,1d]
6-311+G(2d):	(12s,6p,2d) -> [5s,4p,2d]

The more basis functions the better: Each basis function adds flexibility.

The more primitives the better: Each basis function is a little better.

Basis Sets in G09

Basis Set	Applies to	Polarization Functions	Diffuse Functions
3-21G	H-Xe		+
6-21G	H-Cl	* or **	
4-31G	H-Ne	* or **	
6-31G	H-Kr	through (3df,3pd)	+,++
6-311G	H-Kr	through (3df,3pd)	+,++
D95	H-Cl except Na and Mg	through (3df,3pd)	+,++
D95V	H-Ne	(d) or (d,p)	+,++
SHC	H-Cl	*	
CEP-4G	H-Rn	* (Li-Ar only)	
CEP-31G	H-Rn	* (Li-Ar only)	
CEP-121G	H-Rn	* (Li-Ar only)	
LanL2MB	H-La, Hf-Bi		
LanL2DZ	H, Li-La, Hf-Bi		
SDD, SDDall	all but Fr and Ra		
cc-pVDZ	H-Ar, Ca-Kr	included in definition	added via AUG- prefix (H-Ar, Sc-Kr)
cc-pVTZ	H-Ar, Ca-Kr	included in definition	added via AUG- prefix (H-Ar, Sc-Kr)
cc-pVQZ	H-Ar, Ca-Kr	included in definition	added via AUG- prefix (H-Ar, Sc-Kr)
cc-pV5Z	H-Ar, Ca-Kr	included in definition	added via AUG- prefix (H-Na, Al-Ar Sc-Kr)
cc-pV6Z	H, B-Ne	included in definition	added via AUG- prefix (H, B-O)
SV	H-Kr		
SVP	H-Kr	included in definition	
TZV and TZVP	H-Kr	included in definition	
QZVP and Def2*	H-La, Hf-Rn	included in definition	
MidIX	H, C-F, S-Cl, I, Br	included in definition	
EPR-II, EPR-III	H, B, C, N, O, F	included in definition	
UGBS	H-Cn	UGBS(1,2,3)P	+,++,2+,2++
MTSmall	H-Ar		
DGDZVP	H-Xe		
DGDZVP2	H-F, Al-Ar, Sc-Zn		
DGTZVP	H, C-F, Al-Ar		
CBSB7	H-Kr	included in definition	+,++

http://www.gaussian.com/g_tech/g_ur/m_basis_sets.htm

There are many, many basis sets stored in G09. Some cover a few elements, others are available for most elements (but not all).

General Basis Set Input

http://www.gaussian.com/g_tech/g_ur/k_gen.htm

G09 allows for use with general basis sets, i.e., the basis set information is provided as part of the input.

Possible Situations:

- [1] Use different basis sets on different elements in your molecule. Perhaps you want to use a different d-exponent for a more electronegative element.
- [2] Place additional functions on just one atom of a certain element.
- [3] Use a large basis set for the “active site” moiety and a smaller basis set for molecules in the “environment”.
- [4] Use a basis set not already stored in Gaussian.

General Basis Set Input: Example #1

Here is a portion of the **Gen** input corresponding to the 6-31+G(d) basis set:

```

H 0
S 3 1.00
0.1873113696D+02 0.3349460434D-01
0.2825394365D+01 0.2347269535D+00
0.6401216923D+00 0.8137573262D+00
S 1 1.00
0.1612777588D+00 0.1000000000D+01
****
C 0
S 6 1.00
0.3047524880D+04 0.1834737130D-02
0.4573695180D+03 0.1403732280D-01
0.1039486850D+03 0.6884262220D-01
0.2921015530D+02 0.2321844430D+00
0.9286662960D+01 0.4679413480D+00
0.3163926960D+01 0.3623119850D+00
SP 3 1.00
0.7868272350D+01 -0.1193324200D+00 0.6899906660D-01
0.1881288540D+01 -0.1608541520D+00 0.3164239610D+00
0.5442492580D+00 0.1143456440D+01 0.7443082910D+00
SP 1 1.00
0.1687144782D+00 0.1000000000D+01 0.1000000000D+01
D 1 1.00
0.8000000000D+00 0.1000000000D+01
****
C 0
SP 1 1.00
0.4380000000D-01 0.1000000000D+01 0.1000000000D+01
****

```

Applies to all hydrogen atoms.

*Applies to all carbons.
6-31G functions.*

Polarization function.

*Applies to all carbons.
Diffuse function.*

General Basis Set Input: Example #2

The following **Gen** input uses the 6-31G(d,p) basis set for the carbon and hydrogen atoms and the 6-31G \ddagger basis set for the fluorine atoms in the molecule, and places an extra function only on center number 1 (which happens to be the first carbon atom in the molecule specification for 1,1-difluoroethylene):

```
C H 0
6-31G(d,p)
****
F 0
6-31G(d',p')
****
1 0          Place a diffuse function on just one carbon atom.
SP   1 1.00
    0.4380000000D-01  0.1000000000D+01  0.1000000000D+01
****
```

Chapter #4

4.6. Effective Core Basis Sets