

# *Electronic Structure Theory*

## *TSTC Session 6*



1. Born-Oppenheimer approx.- energy surfaces
2. Mean-field (Hartree-Fock) theory- orbitals
3. Pros and cons of HF- RHF, UHF
4. Beyond HF- why?
5. First, one usually does HF-how?
6. **Basis sets and notations**
7. MPn, MCSCF, CI, CC, DFT
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9. Special topics: accuracy, metastable states

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## What are these atomic basis orbitals (AOs)?

### Slater-type orbitals (STOs)

$$\chi_{n,l,m}(r,\theta,\phi) = N_{n,l,m,\zeta} Y_{l,m}(\theta,\phi) r^{n-1} e^{-\zeta r}$$

are characterized by quantum numbers  $n$ ,  $l$ , and  $m$  and exponents  $\zeta$  (which characterize the radial 'size') and are usually located on one of the atomic nuclei.

### Cartesian Gaussian-type orbitals (GTOs)

$$\chi_{a,b,c}(r,\theta,\phi) = N'_{a,b,c,\alpha} x^a y^b z^c \exp(-\alpha r^2),$$

are characterized by quantum numbers  $a$ ,  $b$ , and  $c$ , which detail the angular shape and direction of the orbital, and exponents  $\alpha$  which govern the radial 'size'.

*Slater-type orbitals* are similar to Hydrogenic orbitals in the regions close to the nuclei. Specifically, they have a non-zero slope near the nucleus on which they are located

$$\text{(i.e., } d/dr(\exp(-\zeta r))_{r=0} = -\zeta,$$

so they can **have proper electron-nucleus cusps**.

In contrast, *GTOs* have zero slope near  $r=0$  because

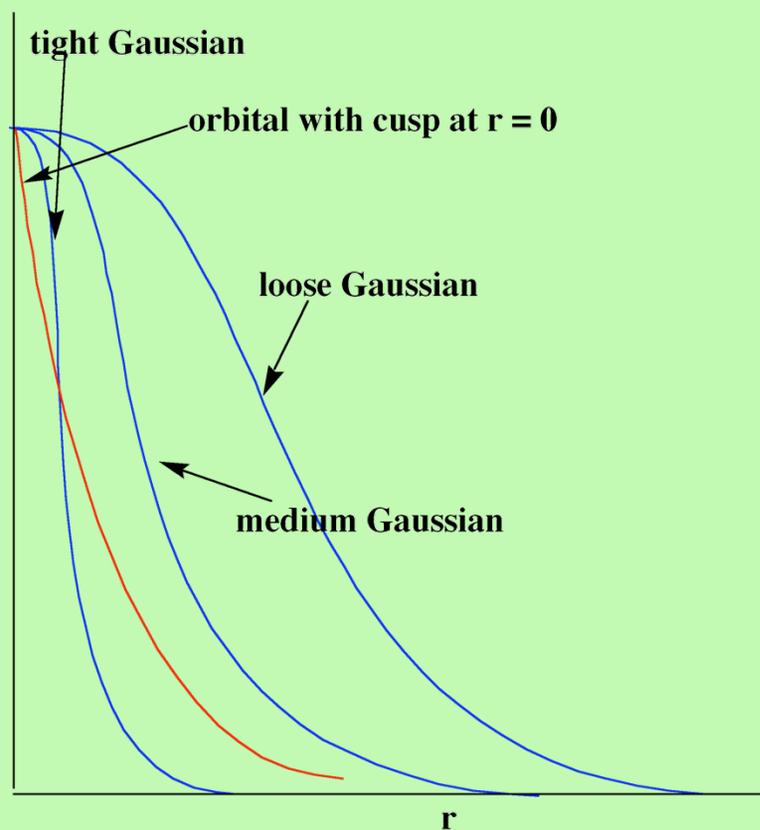
$$d/dr(\exp(-\alpha r^2))_{r=0} = 0.$$

*This characteristic favors STOs over GTOs* because we know that the correct solutions to the Schrödinger equation have such cusps at each nucleus of a molecule.

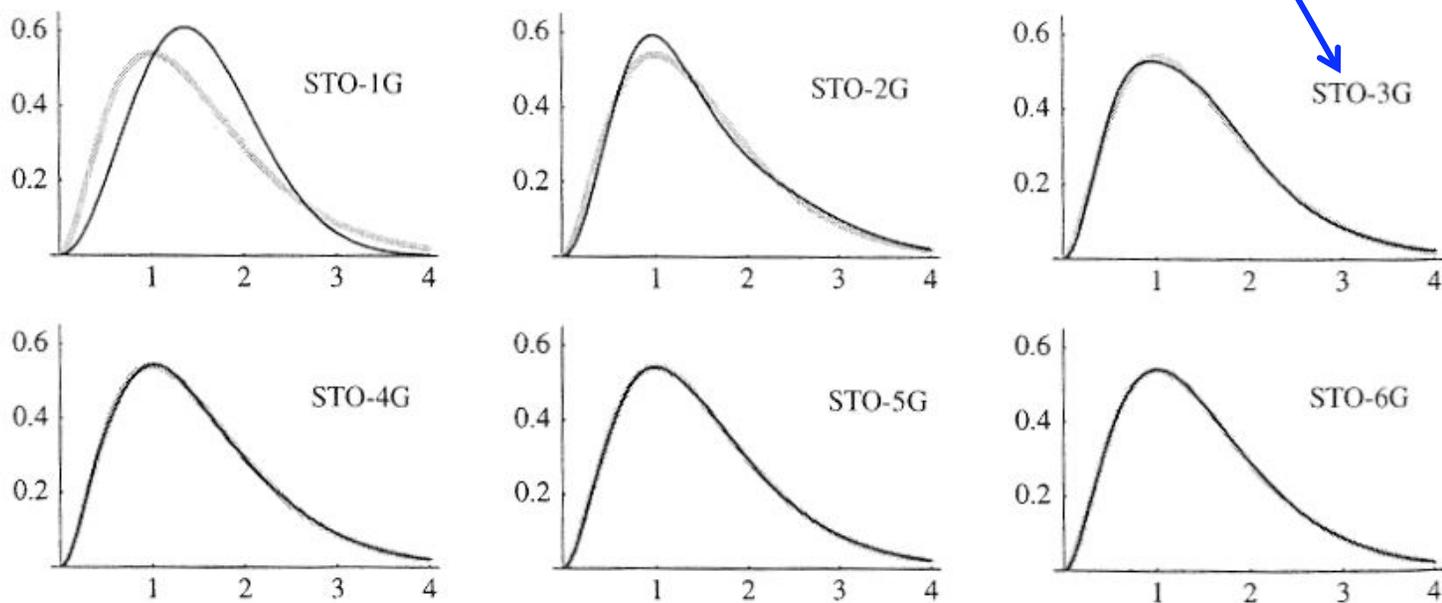
However, the **multi-center integrals** which arise in polyatomic-molecule calculations cannot efficiently be evaluated when STOs are employed. In contrast, such **integrals can routinely be computed** when **GTOs** are used. This advantage of GTOs has led to the dominance of these functions in molecular quantum chemistry.

$$\langle \chi_\nu(\mathbf{r}) \chi_\eta(\mathbf{r}') | 1/r_{1,2} | \chi_\mu(\mathbf{r}) \chi_\gamma(\mathbf{r}') \rangle$$

To overcome the cusp weakness of GTO functions, it is common to combine two, three, or more GTOs, with **combination coefficients** that are **fixed** and not treated as LCAO parameters, into new functions called **contracted** GTOs or CGTOs. However, does not really correctly produce a cusp because every Gaussian has a zero slope at  $r = 0$  as shown below, so any combination will have zero slope:



## How well does STO-kG work? Most common



**Fig. 8.1.** Radial distribution functions of the 1s STO- $k$ G basis functions (thin lines) superimposed on a 1s STO with  $\zeta = 1$  (thick grey lines) (atomic units).

Plots of  $r^2|\psi|^2$ . The nuclear cusp condition is still not met.

Most AO basis sets contain a mixture of different classes of functions.

Fundamental **core and valence** basis functions:

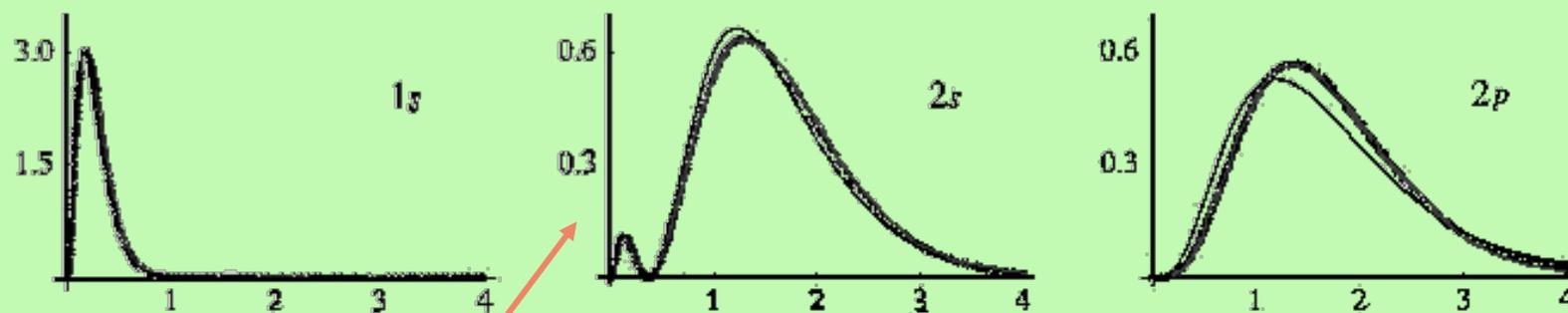
- **Polarization** functions
- **Diffuse** functions
- **Rydberg** functions

**Core and valence:**

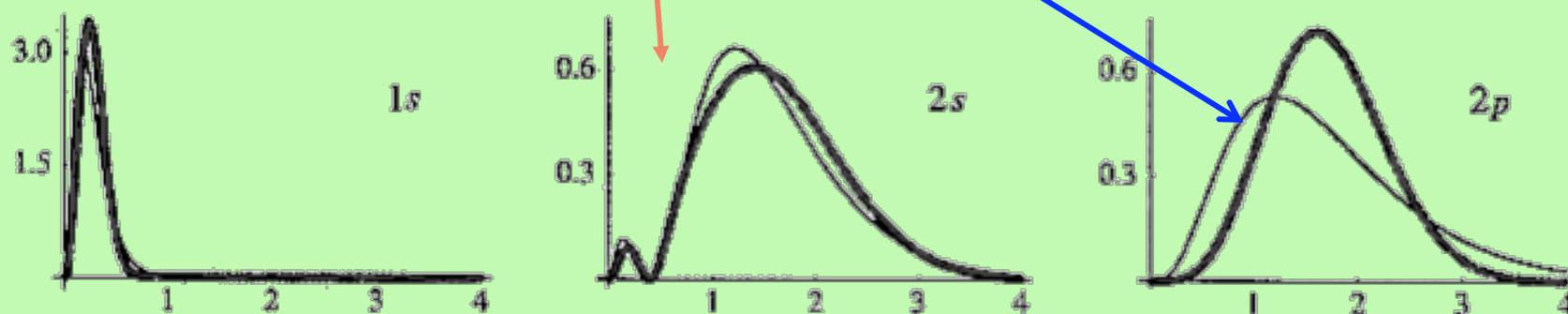
**Minimal basis** - the number of CGTOs equals the number of core and valence atomic orbitals in the atom.

**Carbon** - one tight s-type CGTO, one looser s-type CGTO and a set of three looser p-type CGTOs. **Five total** CGTOs.

How well do minimal GTO or STO basis sets do?



Minimal STO and GTO carbon 1s, 2s, and 2p radial functions compared to the results obtained using a large AO basis.



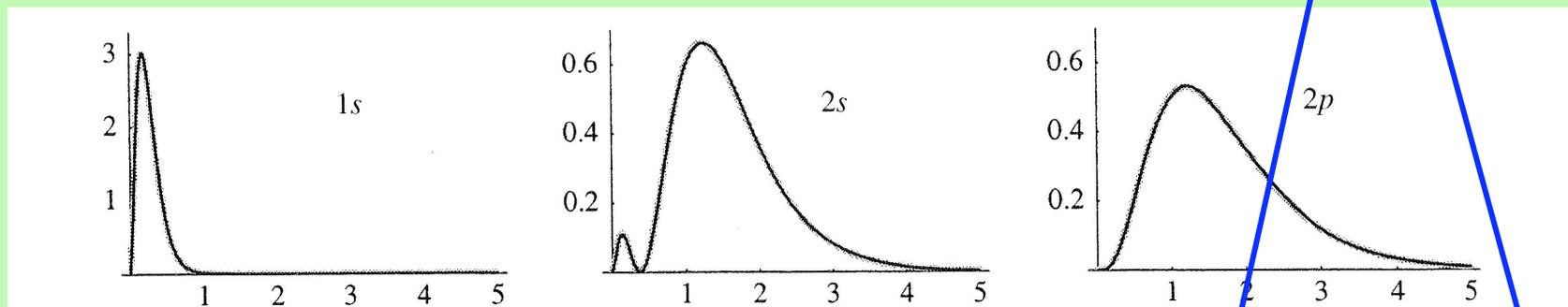
**Double-zeta (DZ)** - twice as many CGTOs as there are core and valence atomic orbitals. Usually, keep the **core basis functions at minimal basis**. Denoted **VDZ**.

**Carbon** - one tight s, two looser s, and **two sets** of three looser p CGTOs. **Nine total CGTOs**.

**Triple-zeta (TZ)** - three times as many CGTOs as the number of core and valence atomic orbitals (extensions to quadruple-zeta and higher-zeta bases also exist). Usually, keep the **core basis functions at minimal basis**. Denoted **VDZ**. **Fourteen total CGTOs** for carbon.

The use of more basis functions is **motivated by** a desire to provide **additional variational flexibility** so the LCAO process can generate molecular orbitals of **variable diffuseness** as the local electronegativity of the atom varies.

## Examples of how VXZ bases are formed; VDZ{[3s] [2p]}, VTZ{[4s] [3p]}



**Fig. 8.3.** The radial distribution functions of the  $^3P$  ground-state orbitals of the carbon atom (atomic units). The thick grey lines are the numerical Hartree–Fock orbitals, the thin black lines are the Hartree–Fock orbitals expanded in the  $(9s5p)$  basis of Huzinaga in Table 8.2.

**Table 8.2** The Gaussian  $(9s5p)$  exponents and expansion coefficients for the  $^3P$  ground-state carbon orbitals

Exponents	1s	2s	2p
4232.61	0.00122	-0.00026	
634.882	0.00934	-0.00202	
146.097	0.04534	-0.00974	
42.4974	0.15459	-0.03606	
14.1892	0.35867	-0.08938	
5.1477	0.43809	-0.17699	
1.9666	0.14581	-0.05267	
0.4962	0.00199	0.57408	
0.1533	0.00041	0.54768	
18.1557			0.01469
3.9864			0.09150
1.1429			0.30611
0.3594			0.50734
0.1146			0.31735

**Table 8.3** Dunning's segmented contractions of the Huzinaga carbon  $(9s5p)$  basis

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	0.789108		
14.1892	0.596555	0.596555	0.791751		
1.9666	0.242517	0.242517	0.321870		
5.1477	1.000000	1.000000	1.000000		
0.4962	0.542048	1.000000	1.000000		
0.1533	0.517121	1.000000	1.000000		
18.1557				0.018534	0.039196
3.9864				0.115442	0.244144
1.1429				0.386206	0.816775
0.3594				0.640089	1.000000
0.1146				1.000000	1.000000

In bases constructed by the [Pople group](#), a different notation is used for **VXZ**

6-31G = Valence double zeta

1s: 6 primitive Gaussians

2s: 3 primitive Gaussian

2s': 1 primitive Gaussian

2p: 3 primitive Gaussians

2p': 1 primitive Gaussian

6-311G = VTZ

Add one extra s and p function (triple zeta)

## Polarization functions:

one higher angular momentum than appears in the atom's valence orbital space.

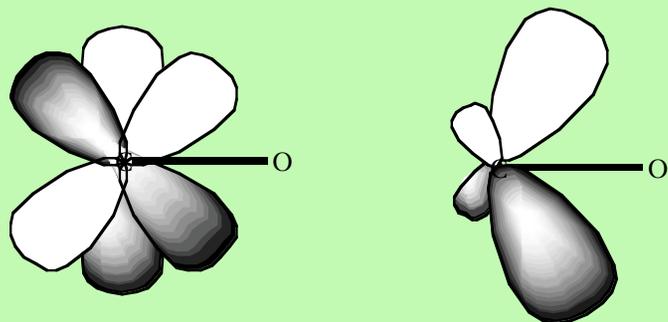
d-functions for C, N, and O and p-functions for H with exponents ( $\zeta$  or  $\alpha$ ) which cause their radial sizes to be similar to the sizes of the valence orbitals.

*Note:* the polarization p orbitals of H are similar in size to the valence 1s orbital and the polarization d orbitals of C are similar in size to the 2s and 2p orbitals, **not** like the valence d orbitals of C.

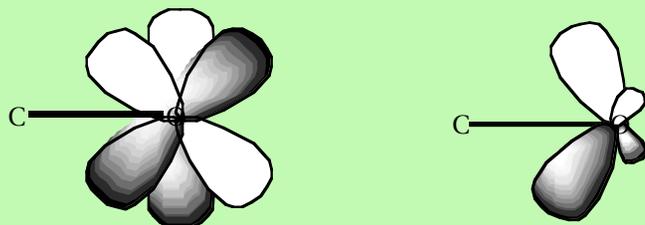
Polarization functions give angular flexibility to the LCAO process in forming molecular orbitals between from valence atomic orbitals.

Polarization functions also allow for angular correlations in describing the correlated motions of electrons.

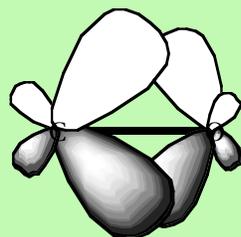
*An example of  $d$  polarization functions on C and O:*



Carbon  $p_\pi$  and  $d_\pi$  orbitals combining to form a bent  $\pi$  orbital



Oxygen  $p_\pi$  and  $d_\pi$  orbitals combining to form a bent  $\pi$  orbital



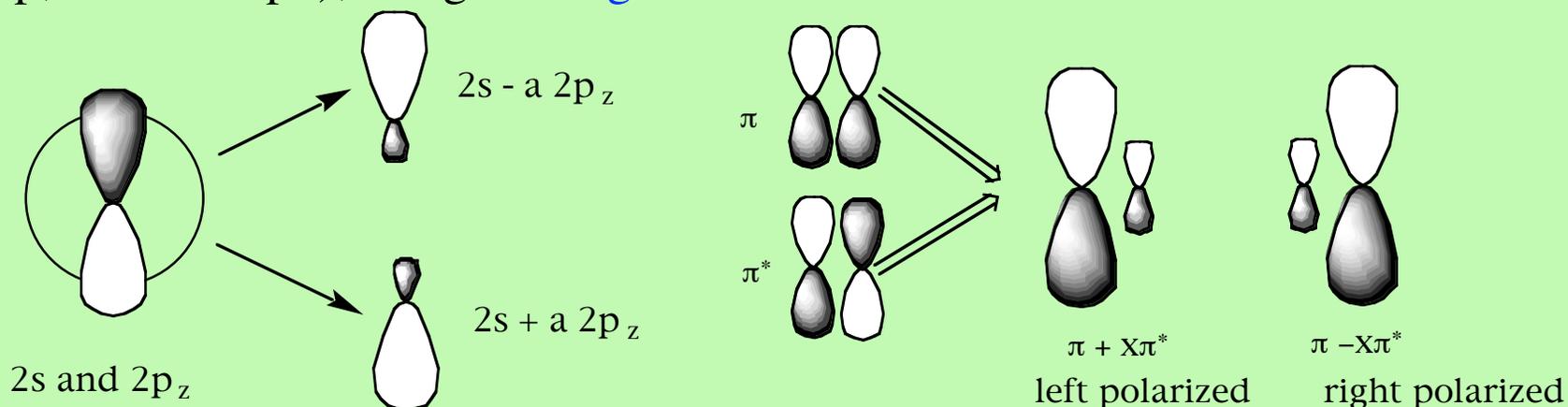
$\pi$  bond formed from C and O bent (polarized) AOs

The polarization functions also can be used to **dynamically correlate** electrons as in

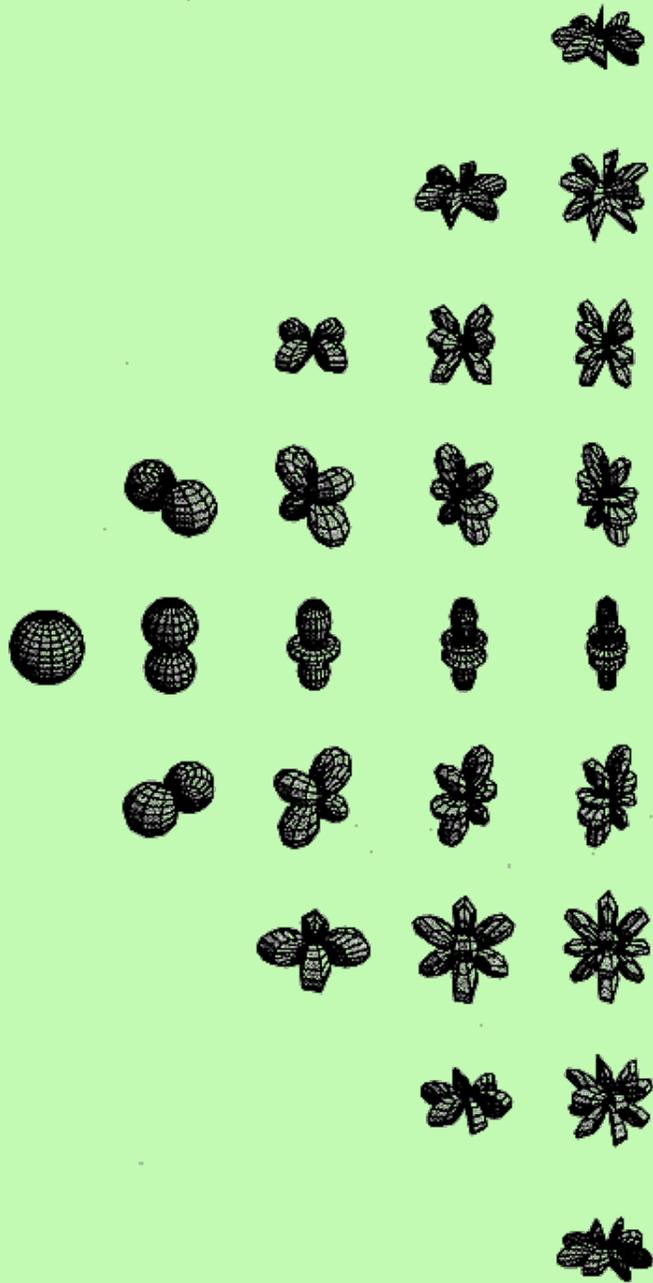
$$\Psi = C_1 | \dots \phi \alpha \phi \beta \dots | - C_2 | \dots \phi' \alpha \phi' \beta \dots |$$

$$= C_1/2 \{ | \dots (\phi - x\phi') \alpha (\phi + x\phi') \beta \dots | - | \dots (\phi - x\phi') \beta (\phi + x\phi') \alpha \dots | \}$$

If  $\phi$  and  $\phi'$  involve orbitals of **different angular character** (e.g., s and p, or  $d\pi$  and  $p\pi$ ), one gains **angular correlation**.



If  $\phi$  and  $\phi'$  involve orbitals of **different radial character**, one gains **radial correlation**.



*s*, *p*, *d*, *f*, and *g* angular functions showing how they span more and more of angle-space as *L* increases while keeping their radial sizes similar.

# Examples of p-VXZ basis sets and numbers of functions

## Minimum basis

C ( $1s^2 2s^2 2p^2$ ,  $^3P$ ):  $1s, 2s, 2p$

( $2 \times s$   $1 \times p$ )

H ( $1s^1$ ,  $^2S$ ) :  $1s$

( $1 \times s$ )

## Double zeta

C :  $1s1s'2s2s'2p2p'$

( $4 \times s$   $2 \times p$ )

H :  $1s1s'$

( $2 \times s$ )

## Valens double zeta

C :  $1s2s2s'2p2p'$

( $3 \times s$   $2 \times p$ )

H :  $1s1s'$

( $2 \times s$ )

## Valens double zeta polarization

C :  $1s2s2s'2p2p'3d$

( $3 \times s$   $2 \times p$   $1 \times d$ )

H :  $1s1s'2p$

( $2 \times s$   $1 \times p$ )

## Valens triple zeta polarization

C :  $1s2s2s'2s''2p2p'2p''3d3d'4f$

( $4 \times s$   $3 \times p$   $2 \times d$   $1 \times f$ )

H :  $1s1s'1s''2p2p'3d$

( $3 \times s$   $2 \times p$   $1 \times d$ )

Notice that when polarization functions are added to VXZ bases, there are more added as X grows.

## Correlation consistent polarized valence basis sets

cc-pVXZ , X = 2,3,4...

2:double zeta, 3:triple zeta

How do people (largely the Dunning group-now Kirk Peterson) create these bases?

1. Choose a sufficient number of primitive Gauss functions.
2. Perform an atomic Hartree-Fock calculation on the atom (use C as example).
- 3.

This results in  $\chi_{1s}^{HF}, \chi_{2s}^{HF}, \chi_{2p}^{HF}$

4.

In a cc-pVDZ basis add one Gaussian (primitive)

$\chi_{3s}, \chi_{3p}, \chi_{3d}$  to  $\chi_{1s}^{HF}, \chi_{2s}^{HF}, \chi_{2p}^{HF}$

5.

The exponents in  $\chi_{3s}, \chi_{3p}, \chi_{3d}$  are optimized in a CISD calculation of the energy for C

More generally, for cc-pVXZ

$$\begin{array}{ll}
 \chi_{1s}^{HF} & \\
 \chi_{2s}^{HF} \quad \chi_{2p}^{HF} & \\
 \chi_{3s} \quad \chi_{3p} \quad \chi_{3d} & \text{cc-pVDZ (3s2p1d)} \\
 + \chi_{4s} \quad \chi_{4p} \quad \chi_{4d} \quad \chi_{4f} & \text{cc-pVTZ (4s3p2d1f)} \\
 + \chi_{5s} \quad \chi_{5p} \quad \chi_{5d} \quad \chi_{5f} \quad \chi_{5g} & \text{cc-pVQZ (5s4p3d2f1g)}
 \end{array}$$

**Correlation energy** ( $E-E_{\text{HF}}$ ) recovered by adding s and p valence orbitals as well as successive polarization functions for the carbon atom ground state. The energies are in 0.001 H and the calculations are at the CISD level (later).

	s	p	d	f	g	$\Delta E^{\text{cor}}$
$\Delta E_{\text{D}} / mE_{\text{h}}$	-21.570	-19.394	-43.136	-	-	-84.100
$\Delta E_{\text{T}} / mE_{\text{h}}$	-0.650	-3.795	-1.833	-4.772	-	-11.014
$\Delta E_{\text{Q}} / mE_{\text{h}}$	-0.099	-0.670	-0.421	-0.502	-0.896	-2.588

Notice how the total correlation energy as well as the contributions from successive s, p, d, and f functions **evolves smoothly** as X (in cc-p-VXZ) grows.

In the Pople basis sets, a **different notation** is used to denote the addition of polarization functions

6-31G\*

Add a polarization function 3d on C to 6-31G

6-31G\*\*     6-311G\*\*

Add a polarization function 3d on C and 2p on H to 6-31G or to 6-311G

In addition to core, valence, and polarization functions, one needs to add **diffuse basis functions** when treating species with low electron binding energies such as anions. In the **Dunning notation**, aug is used to say that diffuse functions have been added. **aug-cc-pVTZ, cc-pVQZ, pVDZ.**

**VDZ, VTZ, VQZ or V5Z** specifies at what level the valence (V) AOs are described. Nothing is said about the core orbitals because each of them is described by a single contracted Gaussian type basis orbital.

“**cc**” specifies that the orbital exponents and contraction coefficients were determined by requiring the atomic energies computed using a correlated method to agree to within some tolerance with experimental data. If cc is missing, the AO exponents and contraction coefficients were determined to make the Hartree-Fock atomic state energies agree with experiment to some precision.

“**p**” specifies that polarization basis orbitals have been included in the basis.

“**aug**” specifies that (conventional) diffuse basis functions have been added, but the number and kind depend on how the valence basis is described. At the pVDZ level, one s, one p, and one d diffuse function appear; at pVTZ a diffuse f function also is present; at pVQZ a diffuse g set is also added; and at pV5Z a diffuse h set is present.

In the **Pople bases**, different notations are used:

**6-31+G\*\*** or **3-21G\***, **6-311+G\***, or **6-31++G**

**3-** or **6-** specifies that the core orbitals are described in terms of a single contracted Gaussian orbital having 3 or 6 terms.

**-21** or **-31** specifies that there are two valence basis functions of each type (i.e., the valence basis is of double-zeta quality), one being a contraction of 2 or 3 Gaussian orbitals and the other (the more diffuse of the two) being a contraction of a single Gaussian orbital.

**-311** specifies that the valence orbitals are treated at the triple-zeta level with the tightest contracted function being a combination of 3 Gaussian orbitals and the two looser functions being a single Gaussian function.

**\*** specifies that polarization functions have been included on the atoms other than hydrogen; **\*\*** specifies that polarization functions are included on all atoms, including the hydrogen atoms.

**+** denotes that a single set of (conventional) diffuse valence basis AOs have been included; **++** means that two such sets of diffuse valence basis AOs are present.

**Keep in mind** how things scale with the number of basis functions:

Calculating two-electron integrals  $\langle \chi_a(1)\chi_b(2) | 1/r_{1,2} | \chi_c(1)\chi_d(2) \rangle$  -  $M^4$

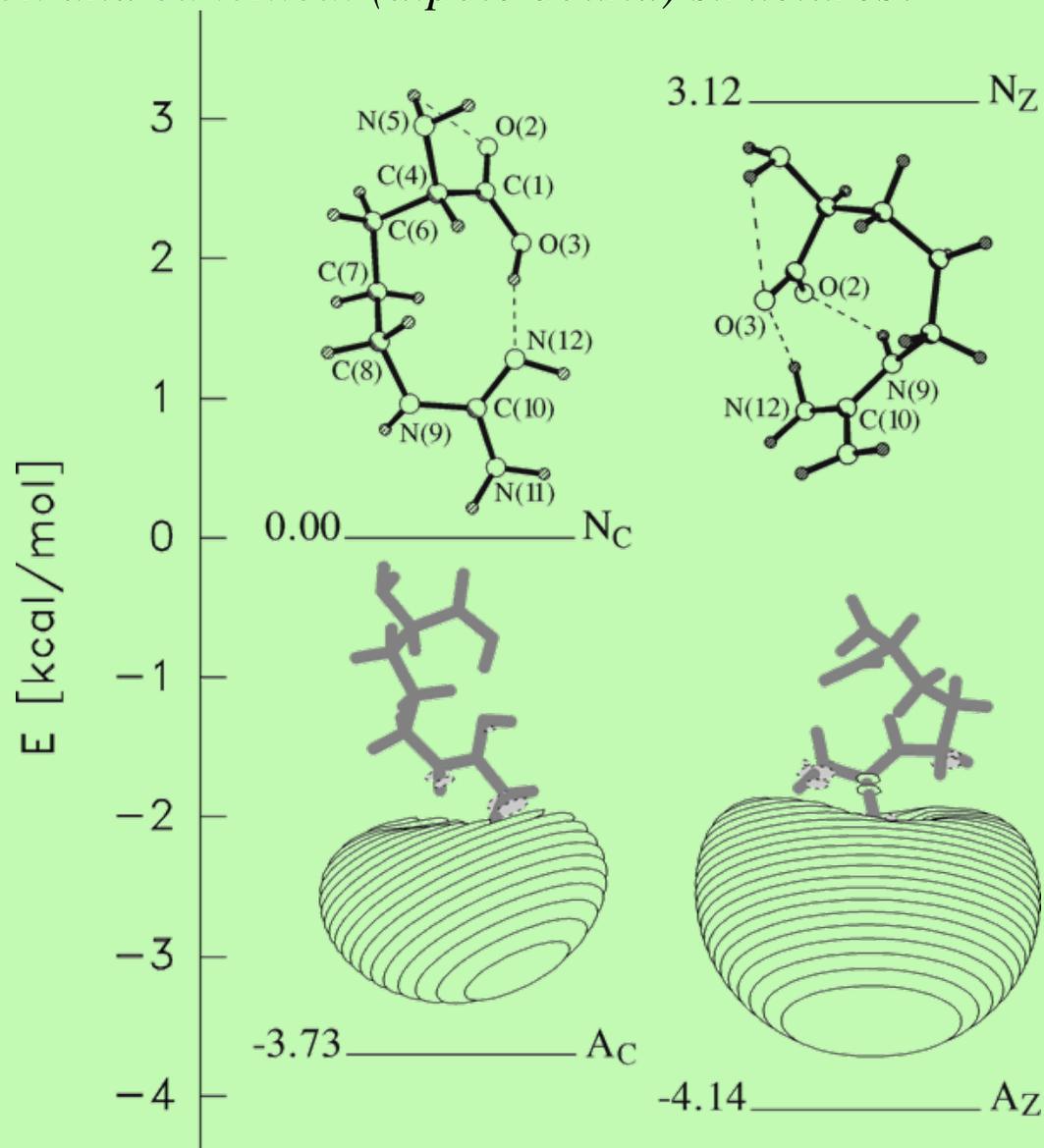
Solving the HF matrix eigenvalue equations for  $\epsilon_k$  and  $\varphi_k$  -  $M^3$

Core, valence and polarization functions do **not** provide enough radial flexibility to adequately describe very diffuse charge densities as in Rydberg species and dipole-bound species.

The **diffuse basis functions** tabulated, for example, on the PNNL web site (<http://www.emsl.pnl.gov/forms/basisform.html>) or from Prof. Kirk Peterson's sources (<http://tyr0.chem.wsu.edu/~kipeters/Pages/ccbasis.html> and <http://tyr0.chem.wsu.edu/~kipeters/basissets/basis.html>) are appropriate if, for example, the anion under study has its excess electron in a valence-type orbital (e.g., as in F<sup>-</sup>, OH<sup>-</sup>, carboxylates, etc.) but not for very weakly bound anions (e.g., having EAs of 0.1 eV or less).

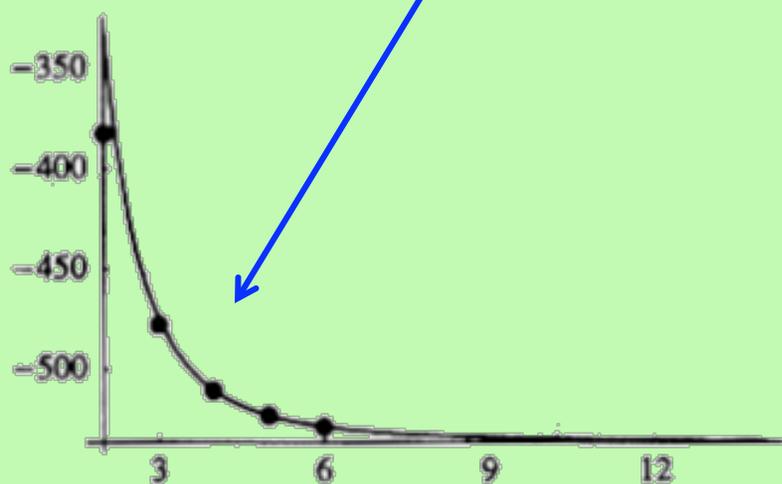
For an electron in a **Rydberg** orbital, in an orbital centered on the positive site of a **zwitterion** species, or in a **dipole-bound** orbital, one must add to the bases containing valence, polarization, and conventional diffuse functions yet another set of functions that are **extra diffuse**. The exponents of these extra diffuse basis functions can be obtained by scaling the conventional diffuse functions' smallest exponent (e.g., by adding functions having exponents 1/3, 1/9, 1/27, etc. those of the most diffuse conventional diffuse function).

An *example* of a species needing *extra diffuse* basis functions: *Arginine anion* in its *zwitterion* and *canonical* (dipole bound) structures.

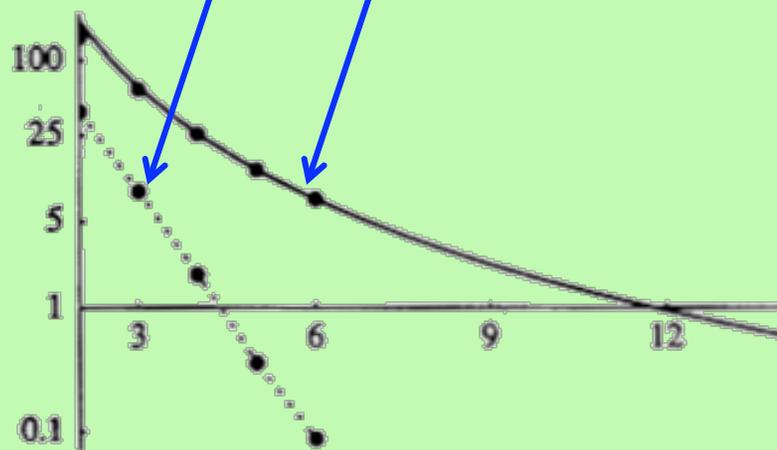


One of the strong points of cc-pVXZ basis sets is that the HF and correlation energies vary with X in a manner that allows extrapolations to be carried out.

MP2 correlation energy(mH) of N<sub>2</sub> vs X



Ln(error in HF energy (mH)) vs. X



Ln(error in correlation energy (mH)) vs. X

Because the HF energy varies with X as

$$E_{\text{HF}} = E_{\text{HF}}(X) - B \exp(-aX),$$

it can be extrapolated using this form (usually X = 3 is good enough).

Given the **correlation energy** computed at **two values X, Y** ( $E_X$ ,  $E_Y$ ):

one assumes the energy to vary with X as

$$E = E_X + A X^{-3} \text{ and } E = E_Y + A Y^{-3}$$

using the two values of X and Y and  $E_X$  and  $E_Y$  gives

$$E = [X^3 E_X - Y^3 E_Y] / (X^3 - Y^3) \text{ and } A = - [E_X - E_Y] / (X^{-3} - Y^{-3})$$

This allows one to extrapolate the **correlation energy** to the so-called **complete-basis set** limit (CBS). It is found that  $X=2$ ,  $Y=3$  does gives accuracy of ca. 23 mH, and  $X = 3$ ,  $Y = 4$  gives ca. 5 mH accuracy. 1 mH is  $0.6 \text{ kcal mol}^{-1}$ .

One more thing to be aware of regarding finite atomic orbital basis sets is the issue of **basis set superposition errors (BSSE)** and how to use the **counterpoise method** to correct for them.

Suppose you wish to compute the **interaction energy** of two fragments, **A and B** (or, alternatively, the dissociation of A-B into A and B). Normally, you would place basis functions on A and on B and carry out the calculation of the A-B complex at some inter-fragment distance **R** to obtain an energy  $E_{A-B}(R)$ . The **interaction energy** at each R-value would then be  $E_{A-B}(R) - E_A - E_B$ .

In the **counterpoise method**, one computes the interaction energy as  $E_{A-B}(R) - E_A^{CP} - E_B^{CP}$  where  $E_A^{CP}$  is the energy of fragment A calculated with A's basis set and with B's basis set located at R where B sits, but with none of B's nuclei or electrons present. Likewise,  $E_B^{CP}$  is the energy of fragment B calculated with B's basis set and with A's basis set located at R where A sits, but with none of A's nuclei or electrons present. So,  $E_A^{CP}$  and  $E_B^{CP}$  are energies of A and B but with so-called "**ghost**" basis sets also present.

The difference between  $E_A + E_B$  and  $E_A^{CP} + E_B^{CP}$  is called the **BSSE correction**. BSSE is caused by A's using some of B's basis to lower A's energy and B using some of A's basis to lower B's energy.