

The **Fock matrix** can be seen to be roughly **PROPORTIONAL** to the **Density matrix**.

The reason is related to the fact that HF Energy is essentially the "product" of the density and the Fock matrices

Notice that element by element, the product  $F_{ij} \times P_{ij}$  is negative, with a few exceptions. **When the product is positive, this generally indicates antibonding between the two orbitals.**

$$\mathbf{P} = \begin{bmatrix} 2.108 & & & & & & & \\ -0.456 & 2.010 & & & & & & \\ 0.000 & 0.000 & 2.000 & & & & & \\ 0.000 & 0.000 & 0.000 & 0.737 & & & & \\ -0.104 & 0.618 & 0.000 & 0.000 & 1.215 & & & \\ -0.022 & -0.059 & 0.000 & 0.539 & -0.482 & 0.606 & & \\ -0.022 & -0.059 & 0.000 & -0.539 & -0.482 & -0.183 & 0.606 & \end{bmatrix}$$

$$\mathbf{F} = \begin{bmatrix} -20.236 & & & & & & & \\ -5.163 & -2.453 & & & & & & \\ 0.000 & 0.000 & -0.395 & & & & & \\ 0.000 & 0.000 & 0.000 & -0.327 & & & & \\ 0.029 & 0.130 & 0.000 & 0.000 & -0.353 & & & \\ -1.216 & -1.037 & 0.000 & -0.398 & 0.372 & -0.588 & & \\ -1.216 & -1.037 & 0.000 & 0.398 & 0.372 & -0.403 & -0.588 & \end{bmatrix}$$

**Fock matrix can be seen to roughly PROPORTIONAL to the Density matrix.**

Indeed, the entire SCF-HF procedure may be said to be equivalent to varying the coefficients that make up the Density Matrix until the density maximally overlaps the Fock matrix.

The reason is related to the fact that HF Energy is essentially the "product" of the density and the Fock matrices.

Notice that element by element, the product  $F_{rs} \times P_{rs}$  is negative, with a few exceptions. **When the product is positive, this generally indicates antibonding between the two orbitals.**

## A UNIVERSAL TRUTH:

The **Expectation Value** of ANY operator  $A$  is given by:

**the trace of the product of the Density Matrix and the operator Matrix**

If there is a density matrix, there must be a density operator.

"Density" = Probability Density =  $\psi^*\psi$

We can see that in a sense,  $\langle A \rangle$  is the overlap integral of the operator and the density.

$$\langle A \rangle = \int \Psi^* \hat{A} \Psi d\tau = \int \hat{A} \Psi (\Psi^*) d\tau$$

where  $\hat{A}$  does not operate on  $\Psi^*$

This is better seen in bra-ket notation:

$$\begin{aligned}
\langle A \rangle &= \langle \Psi^* | \hat{A} | \Psi \rangle \\
&= \langle \Psi^* | \sum_m | m \rangle \langle m | \hat{A} | \sum_n \langle n | \Psi \rangle \\
&= \sum_m \sum_n \langle \Psi_i^* | m \rangle \langle m | \hat{A} | n \rangle \langle n | \Psi_i \rangle \\
&= \sum_m \sum_n c_{\Psi m}^* A_{mn} c_{n\Psi} = \sum_m \sum_n c_{n\Psi} c_{\Psi m}^* A_{mn} \\
&= \sum_m \sum_n P_{nm} A_{mn} = \sum_n \sum_m P_{nm} A_{mn} = \sum_n (PA)_{nn}
\end{aligned}$$

$= \text{trace } PA =$  sum of diagonal elements of the product of the Density matrix and matrix of operator  $A$

Careful inspection, however, shows that the words used to state this operation *disguise* the underlying simplicity. The operation is indeed *literally* like tracing one matrix on the other.

**(Taking the trace of the matrix product is distracting information.)**

For a symmetric real matrix:

$$\sum_m \sum_n P_{nm} A_{mn} = \sum_{mn} P_{nm} A_{mn} = \sum_{mn} P_{mn} A_{mn}$$

This is simply the sum of the products of all the corresponding matrix elements, taken in any order. This is the SCALAR PRODUCT of the two matrices, i.e., completely analogous to the overlap integral of the matrices.

**a general example**

$$\begin{array}{ccccc} 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \end{array} \quad \begin{array}{ccccc} 7 & 0 & 1 & 4 & 5 \\ 0 & 6 & 0 & 9 & 0 \\ 1 & 0 & 0 & 0 & 5 \\ 0 & 9 & 0 & 7 & 0 \\ 1 & 8 & 0 & 0 & 0 \end{array}$$

Once you see the pattern in the left matrix, you can quickly see that the trace of the product of these two matrices is **4 + 8 = 12**.

Next we will see how this formalism is hidden in Levine's Eq. 14.45

# Physical Interpretation of “MO Energy”

$$\epsilon_i = h_{ii} + J_{ii} + \text{sum of } 2J_{ij} - K_{ij} \text{ for all } j \text{ MOs for } j \text{ not equal to } i$$

The sum of MO energies counts the electron repulsion TWICE.

Thus,  $E_{HF}$  = the sum of MO energies **minus** the total electron repulsion

$$\sum_{i=1}^{n/2} 2\varepsilon_i = \sum_{i=1}^{n/2} 2h_{ii} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (4J_{ij} - 2K_{ij})$$

$$\text{So, } E_{HF} = \sum_{i=1}^{n/2} 2\varepsilon_i - \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij})$$

$$E_{HF} = \frac{1}{2} \sum_{r=1}^{n/2} \sum_{s=1}^{n/2} P_{rs} (F_{rs} + H_{rs}^{core}) + V_{NN} \quad (14.45) \text{ Levine}$$

This is the same thing: Instead of subtracting the ee repulsion you ADD the one-electron part with gives twice the  $E_{HF}$  then divide all by 2

This shows nicely the trace of the matrix product

Figure 15.2 Shows that increasing the diversity of the basis set lowers The HF-SCF energy considerably, but comes *nowhere near* the exact experimental energy, regardless of the basis set size

TABLE 15.2 H<sub>2</sub>O Hartree–Fock Calculations<sup>a</sup>

Reference <sup>b</sup>	Basis Set <sup>c</sup>	Energy/ $E_h$	$\mu/D$	$\theta$	$R_{OH}/\text{Å}$
CCCBDB	STO-3G, 7	-74.966	1.71	100.0°	0.989
CCCBDB	3-21G, 13	-75.586	2.39	107.7°	0.967
Pitzer, Merrifield	Minimal STO, 7	-75.705	1.92	100.3°	0.990
CCCBDB	6-31G*, 19	-76.011	2.20	105.5°	0.947
CCCBDB	6-31G**, 25	-76.024	2.15	106.0°	0.943
CCCBDB	cc-pVDZ, 24	-76.027	2.04	104.6°	0.946
K. S. Kim et al.	6-311++G(2d,2p), 47	-76.057	2.02	106.3°	0.940
CCCBDB	cc-pVTZ, 58	-76.058	1.99	106.0°	0.941
CCCBDB	aug-cc-pVTZ, 92	-76.061	1.93	106.3°	0.941
Dunning et al.	[6s5p2d/3s1p], 43	-76.062	2.08	106.6°	0.941
Rosenberg et al.	(5s4p2d/3s1p) <sub>STO</sub> , 39	-76.064	2.00	106.1°	0.940
CCCBDB	cc-pVQZ, 115	-76.0655	1.97	106.2°	0.940
CCCBDB	aug-cc-pVQZ, 172	-76.0667	1.94	106.3°	0.940
Amos	[8s6p4d2f/6s3p1d], 112	-76.0675		106.3°	0.940
K. S. Kim et al.	(13s8p4d2f/8s4p2d), 131	-76.0676	1.94	106.3°	0.940
Bakken et al.	cc-pV5Z, 201	-76.0678	1.96	106.33°	0.9396
Bakken et al.	aug-cc-pV5Z, 287	-76.0680	1.94	106.34°	0.9396
Cortez et al.	cc-pV6Z, 322	-76.06810	1.95	106.34°	0.9396
	aug-cc-pV6Z, 443	-76.06815	1.94	106.34°	0.9396
Pahl, Handy	special <sup>c</sup>	-76.06817		106.34°	0.9396
Estimated Hartree–Fock energy <sup>d</sup>		-76.068 <sub>3</sub>			
Nonrelativistic fixed–nuclei energy <sup>e</sup>		-76.438			
Experimental values		-76.480 <sup>c</sup>	1.85	104.5 <sup>of</sup>	0.9578 <sup>f</sup>

Estimated Hartree–Fock energy <sup>d</sup>	-76.068 <sub>3</sub>
Nonrelativistic fixed–nuclei energy <sup>e</sup>	-76.438
Experimental values	-76.480 <sup>c</sup>

**This proves that electrons are particles, not clouds!**

**CCCBDB= Computational Chemistry Comparison Benchmark Data Base**  
**Other properties get WORSE as basis increased!**

Estimated Hartree–Fock energy <sup>d</sup>	-76.068 <sub>3</sub>
Nonrelativistic fixed–nuclei energy <sup>e</sup>	-76.438
Experimental values	-76.480 <sup>c</sup> 1.85    104.5 <sup>of</sup> 0.9578 <sup>f</sup>

<sup>a</sup>Energy/ $E_h$  is the total electronic energy including nuclear repulsion in hartrees at the calculated equilibrium geometry;  $\mu$ ,  $\theta$ , and  $R_{OH}$  are the calculated electric dipole moment, equilibrium bond angle, and equilibrium bond length.

<sup>b</sup>CCCBDB is the Computational Chemistry Comparison and Benchmark DataBase (Section 15.1); R. M. Pitzer and D. P. Merrifield, *J. Chem. Phys.*, **52**, 4782 (1970); K. S. Kim et al., *J. Chem. Phys.*, **97**, 6649 (1992); T. H. Dunning, R. M. Pitzer, and S. Aung, *J. Chem. Phys.*, **57**, 5044 (1972); B. J. Rosenberg and I. Shavitt, *J. Chem. Phys.*, **63**, 2162 (1975) and B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.*, **65**, 4072 (1976); R. D. Amos, *J. Chem. Soc. Faraday Trans. 2*, **83**, 1595 (1987); K. S. Kim et al., op. cit; V. Bakken et al., *Mol. Phys.*, **96**, 653 (1999); M. H. Cortez et al., *J. Chem. Theory Comput.*, **3**, 1267 (2007); F. A. Pahl and N. C. Handy, *Mol. Phys.*, **100**, 3199 (2002).

<sup>c</sup>The number of basis functions is given. All the basis sets are GTFs except the Pitzer–Merrifield, Rosenberg et al., and Pahl–Handy sets. Brackets denote CGTF sets and parentheses denote an uncontracted set. A slash separates the oxygen and hydrogen basis functions. The Pahl–Handy set consists of plane waves and radial polynomials.

<sup>d</sup>This estimate is for the calculated Hartree–Fock equilibrium geometry. See D. Feller, C. M. Boyle, and E. R. Davidson, *J. Chem. Phys.*, **86**, 3424 (1987).

<sup>e</sup>A. Lüchow, J. B. Anderson, and D. Feller, *J. Chem. Phys.*, **106**, 7706 (1997).

<sup>f</sup>P. Jensen et al., *J. Mol. Spectrosc.*, **168**, 271 (1994); A. Császár et al., *J. Chem. Phys.*, **122**, 214305 (2005).



**TABLE 16.1 H<sub>2</sub>O Calculations That Include Correlation<sup>a</sup>**

Reference <sup>b</sup>	Method <sup>c</sup> / Basis Set	Energy / E <sub>h</sub>	$\mu$ / D	$\theta$	R <sub>OH</sub>	$\alpha$
Harrison, Handy	CISD/DZ	-76.150				
Harrison, Handy	FCI/DZ	-76.158				
CCCBDB	MP2(FC)/6-31G*	-76.197	2.24	104.0°	<b>0.969</b>	
CCCBDB	CISD(FC)/6-31G*	-76.198	2.24	104.2°	<b>0.966</b>	
CCCBDB	MP2(full)/6-31G*	-76.199	2.24	104.0°	<b>0.969</b>	
CCCBDB	CCSD(FC)/6-31G*	-76.206	2.25	103.9°	<b>0.969</b>	
CCCBDB	MP4(FC)/6-31G*	-76.207	2.25	103.8°	0.970	
CCCBDB	CCSD(T)(FC)/6-31G*	-76.208	2.25	103.8°	0.971	
CCCBDB	MP2(FC)/6-31G**	-76.220	2.20	103.8°	0.961	
CCCBDB	CISD(FC)/6-31G**	-76.221	2.19	104.2°	<b>0.958</b>	
CCCBDB	MP2(FC)/cc-pVDZ	-76.229	2.10	101.9°	0.965	
CCCBDB	CCSD(T)(FC)/cc-pVDZ	-76.241	2.10	101.9°	<b>0.966</b>	
Scuseria, Schaefer	CISDTQ/DZP	-76.270	2.13	104.5°	0.965	
Schaefer et al.	CISD/TZ2P	-76.312	1.94	104.9°	0.952	
CCCBDB	CISD(FC)/cc-pVTZ	-76.314	2.03	104.2°	0.955	
CCCBDB	MP2(FC)/6-31+G(3df,2p)	-76.318	2.02	104.5°	<b>0.959</b>	
CCCBDB	MP2(FC)/cc-pVTZ	-76.319	2.04	103.5°	0.959	
CCCBDB	CCSD(T)(FC)/cc-pVTZ	-76.332	2.04	103.6°	<b>0.959</b>	
Cortez et al.	CCSD(T)(FC)/cc-pV6Z	-76.372		104.4°	0.958	
Kim et al.	CISD(full)/(13s...2d) <sup>d</sup>	-76.382		104.8°	0.952	
Kim et al.	MP2(full)/(13s...2d)	-76.391		104.2°	0.959	
Kim et al.	CCSD(full)/(13s...2d)	-76.396		104.4°	<b>0.956</b>	
Kim et al.	CCSD(T)(full)/(13s...2d)	-76.406		104.1°	0.959	
Kim et al.	MP4(full)/(13s...2d)	-76.407		104.1°	<b>0.960</b>	
CCCBDB	B3LYP/6-31G*	-76.409	2.10	103.6°	<b>0.969</b>	
CCCBDB	B3LYP/6-31G**	-76.420	2.04	103.7°	<b>0.965</b>	
CCCBDB	B3LYP/cc-pVDZ	-76.421	1.94	102.7°	<b>0.969</b>	
Lüchow et al.	MRCISD/aug-cc-pCV5Z	-76.427 <sup>e</sup>				
Gurtubay, Needs	FN-DQMC	-76.428 <sup>e</sup>				
CCCBDB	B3LYP/cc-pVTZ	-76.460	1.92	104.5°	<b>0.961</b>	
<i>Nonrelativistic fixed-nuclei energy</i>		-76.438				
<i>Experimental values</i>		-76.480	1.85	104.5°	<b>0.958</b>	

<sup>a</sup>See footnote a to Table 15.2 in Section 15.6.

<sup>b</sup>R. J. Harrison and N. C. Handy, *Chem. Phys. Lett.*, **95**, 386 (1983); cccbdb.nist.gov; G. E. Scuseria and H. F. Schaefer, III, *Chem. Phys. Lett.*, **146**, 23 (1988); H. F. Schaefer, III et al., in *Yarkony*, Chapter 1; M. H. Cortez et al., *J. Chem. Theor. Comput.*, **3**, 1267 (2007); J. Kim et al., *J. Chem. Phys.*, **102**, 310 (1995); A. Lüchow, J. B. Anderson, and D. Feller, *J. Chem. Phys.*, **106**, 7706 (1997); I. G. Gurtubay and R. J. Needs, *J. Chem. Phys.*, **127**, 124306 (2007).

<sup>c</sup>FC denotes frozen-core calculations and full indicates that the frozen-core approximation is not used.

<sup>d</sup>(13s...2d) is an uncontracted (13s8p4d2f/8s4p2d) set with 131 basis functions.

<sup>e</sup>Calculated at a geometry close to the experimental geometry.

If electron-correlation is added to the wavefunction, all properties converge to experimentally observed values.

CCCBDB	B3LYP/6-31G*	-76.409	2.10	103.6°	<b>0.969</b>
CCCBDB	B3LYP/6-31G**	-76.420	2.04	103.7°	<b>0.965</b>
CCCBDB	B3LYP/cc-pVDZ	-76.421	1.94	102.7°	<b>0.969</b>
Lüchow et al.	MRCISD/aug-cc-pCV5Z	-76.427 <sup>e</sup>			
Gurtubay, Needs	FN-DQMC	-76.428 <sup>e</sup>			
CCCBDB	B3LYP/cc-pVTZ	-76.460	1.92	104.5°	<b>0.961</b>
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<sup>c</sup>FC denotes frozen-core calculations and full indicates that the frozen-core approximation is not used.

<sup>d</sup>(13s...2d) is an uncontracted (13s8p4d2f/8s4p2d) set with 131 basis functions.

<sup>e</sup>Calculated at a geometry close to the experimental geometry.

B3LYP is the most popular DFT method;

B3LYP/cc-pVTZ

99.87% of experiment;

Takes 5 sec on a PC

## 5.2 A BIT OF THEORY: SLATER VS GAUSSIAN

Both Slater Type Orbitals (STOs) and Gaussian Type Orbitals (GTOs) are used to describe AOs. STOs describe the shape of AOs more closely than GTOs, but GTOs have an unbeatable advantage: they are much easier to compute. In fact, it is faster to compute several GTOs and combine them to describe an orbital than to compute one STO! This is why combinations of GTOs are commonly used to describe STOs, which in turn, describe AOs. Yes, a bit complicated, but the computers don't mind. There are other differences between STOs and GTOs, but they will not be covered here.

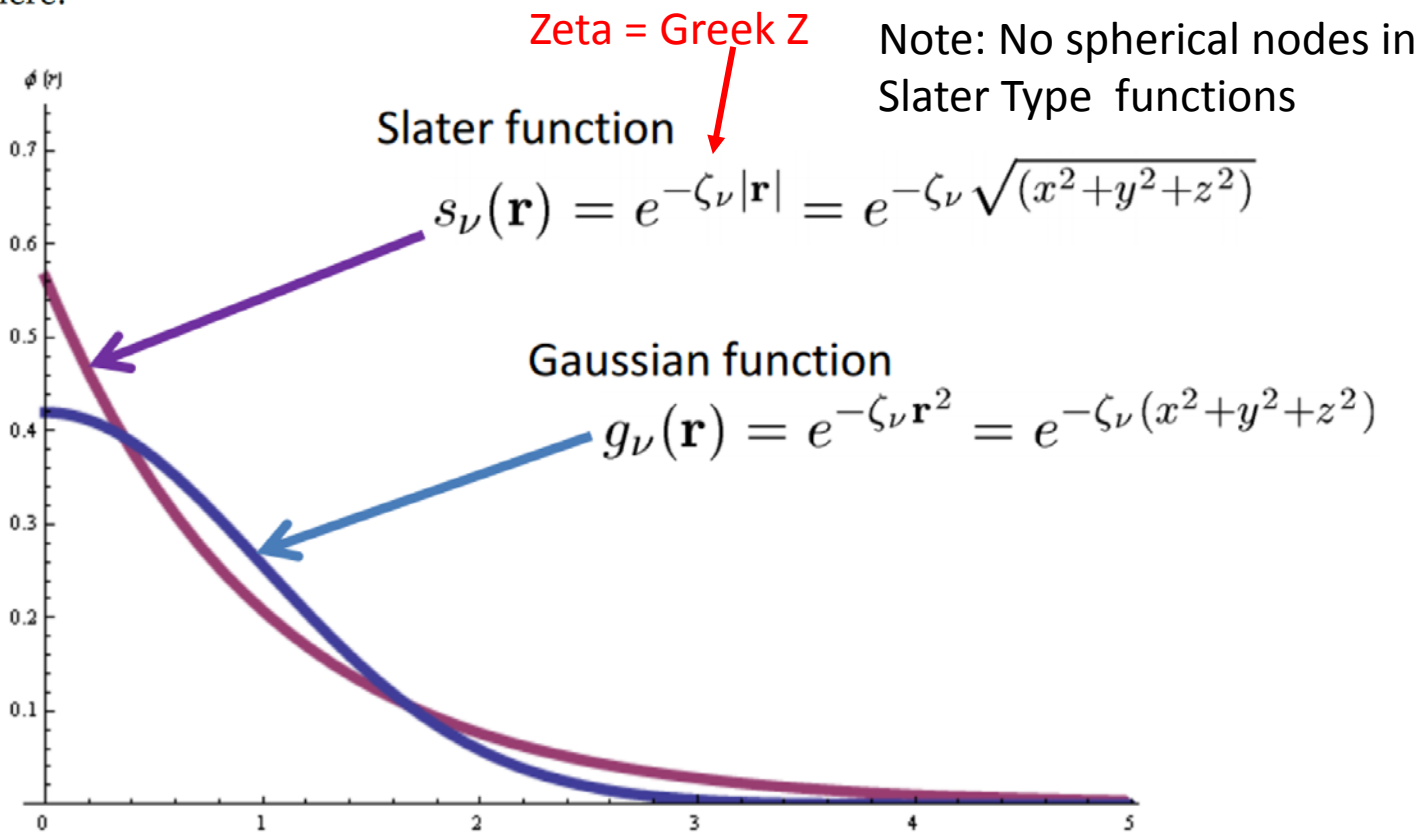


Figure 6: Slater VS Gaussian Type functions [4]

## The usual Spherical Harmonics

Slater Type Orbital

$$(\text{STO}) = N r^{n-1} e^{-\zeta r/a_0} Y_l^m(\theta, \phi)$$

Zeta = Greek Z

Note: No spherical nodes in  
Slater Type functions

Alpha	<b>A α</b>	Iota	<b>I ι</b>	Rho	<b>Ρ ρ</b>
Beta	<b>B β</b>	Kappa	<b>Κ κ</b>	Sigma	<b>Σ σ</b>
Gamma	<b>Γ γ</b>	Lambda	<b>Λ λ</b>	Tau	<b>Τ τ</b>
Delta	<b>Δ δ</b>	Mu	<b>Μ μ</b>	Upsilon	<b>Υ υ</b>
Epsilon	<b>Ε ε</b>	Nu	<b>Ν ν</b>	Phi	<b>Φ φ</b>
Zeta	<b>Ζ ζ</b>	Xi	<b>Ξ ξ</b>	Chi	<b>Χ χ</b>
Eta	<b>Η η</b>	Omicron	<b>Ο ο</b>	Psi	<b>Ψ ψ</b>
Theta	<b>Θ θ</b>	Pi	<b>Π π</b>	Omega	<b>Ω ω</b>

# Basis Sets

<http://gaussian.com/glossary/g09/>  
<http://gaussian.com/basissets/>

For all methods, a choice of basis set must be done:

$MO_i = \varphi_i =$  linear combination of STOs or Gaussian type functions (GTFs)  
(LC-STO, LC-GTF)

This includes Density Functional Theory (DFT) in which one does not have a wave function, yet works with Kohn-Sham orbitals, which are a fictitious reference system of non-interacting electrons **of no physical significance** that allow one to construct the exact density-- *(if and when someone learns how)*.

There is no wavefunction in DFT.

Diatomic basis functions are STOs (not so many e-e repulsion integrals)

Typically use **Gaussian Type Functions** for non-linear larger triatomic and larger linear combinations of LC-GTF, because of the large number of e-e repulsion integrals that are very time-consuming for STOs.

a “primitive” **GTF** on atom **b**: 
$$g_{ijk} = N x_b^i y_b^j z_b^k e^{-\alpha r_b^2}$$

**If  $i + j + k = 0$ , it is an s GTF**  
**If  $i + j + k = 1$ , it is a p GTF only 3**  
**If  $i + j + k = 2$ , it is a d GTF typically 6** ( 6 ways  $i+j+k = 2$ )  
**If  $i + j + k = 3$ , it is an f GTF typically 10** ( 10 ways  $i+j+k = 3$ )  
**etc.**

e.g., the 6 d functions are :  $x^2, y^2, z^2, xy, xz, yz$  "donut"  
 used to seeing  $5 = xy, xz, yz, x^2 - y^2, r^2 - 3z^2 = x^2 + y^2 - 2z^2$  i.e., "dz<sup>2</sup>"  
 which are all linear combinations of the 6 GTFs

The 6<sup>th</sup> wheel is  $x^2 + y^2 + z^2 = r^2$ , i.e., another s type (not d)

Requires more GTFs than STOs, but no 4-center e-e repulsion  
 (rs|tu) to calculate because product of 2 Gaussians is another Gaussian centered in at  
 different place.

In practice **contracted GTFs (CGTFs)** are used as the basis functions.

$$A \text{ CGTF} = \chi_{\mu} = \sum_p d_{\mu p} g_p \quad \text{MO}_i = \varphi_i = \sum_{\mu} c_{\mu i} \chi_{\mu}$$

and the  $d_{\mu p}$  are constants previously optimized for the given basis set and never change.

# Some TERMS

**minimal basis e.g., STO-3g**

**double zeta DZ** ( DZ stands for double zeta; what's zeta?  $\zeta$  Often used as the orbital exponent instead of  $\alpha$ ); **DZ means two different sizes of everything; TZ =triple zeta= 3 different sizes, etc.**

**quadruple QZ**

**5Z**

**6Z**

**split valence VDZ, VTZ, etc.** inner shells are typically a single function  
but valence shell gets multiple zeta

**Examples: 3-21g** : inner shells 1 contracted GTF (CGTF) made of 3 primitive GTFs  
Valence shell is double zeta: 1 CGTF made of 2 primitive GTFs  
and one made of 1 primitive GTF

**6-31g** : inner shells 1 contracted GTF (CGTF) made of 6 primitive GTFs  
Valence shell is double zeta: 1 CGTF made of 3 primitive GTFs  
and one made of 1 primitive GTF

# More TERMS

## Polarization Basis sets

The previous page was about changing the size of orbitals without change in shape. But when in a molecule, the electron density on an atom is not the same as an isolated atom. This is accomplished by adding orbitals that have d character in the first row, and p character for H.

Examples: 6-31g\* = 6-31g(d) adds 6 d-type GTFs for the atoms Li-Ca, and 10 f-type GTFs for Sc-Zn.

6-31g\*\* = 6-31g(d,p) adds p character to H, in addition.

## Diffuse Basis Sets

Anions particularly benefit from include large basis functions. e.g, 6-31+g includes extra large s and p functions on heavy atoms, and 6-31++g in addition at a diffuse s orbital to H



## Even Larger Basis sets

For example 6-311++G(3df,3pd) is triple zeta set defined for H-Ar, that provides diffuse functions on all atoms, 3 sets of d and 1 set of f functions to non-H atoms, and 3 sets of p functions, 1 set of d functions for H. This also called a VTZ3PD, meaning valence triple zeta with triple polarization and diffuse on all atoms.

The above were developed by Pople.

Dunning and co-workers developed as series of basis functions denoted cc-pVnZ: i.e., cc-pVDZ, cc-pVTZ...,cc-pV6Z, which stand for *correlation-consistent, polarized valence double-zeta*, etc.

These basis sets were specifically designed to be used with methods that introduce electron correlation. Each set increases the orbital types as follows:

cc-pVDZ,	cc-pVTZ	cc-pVQZ,	cc-pV5Z	cc-pV6Z
[3s2p1d]	[4s3p2d1f]	[5s4p3d2f1g]	[6s5p4d3f2g1h]	[7s6p5d4f3g2h1i]

The number and degree of polarization (angular momentum) function increases rapidly from left to right, meaning more nodes, which is what is needed to introduce fine-grained correlation (**better dodging**). Doing a series of calculations with these basis sets on a molecule allow smooth extrapolation to what may be considered a near exact value.

If diffuse functions are added to the cc-pVnZ sets, they are called **aug- cc-pVnZ**.

# Some General Terms

<http://gaussian.com/keywords/>

## Names

## key words

method/basis

for example:

hf/6-31g\*

single point

geometry optimization

opt

vibrational frequency (must be opt first)

freq

transition state search

reaction path following

potential energy surface

solvation

## **Open Shell Calculations** ( some MOs have only 1 electron)

ROHF (restricted open shell) means electrons with opposite spin in same MO have the same spatial orbital.

UHF (unrestricted HF) means alpha and beta spins may have different spatial functions, thereby giving a slightly lower energy. (but, will not usually be eigenfunctions of the  $S^2$  operator (i.e., neither singlet or triplet, for example)