

Ab Initio Hartree-Fock Theory

Basis Sets and LCAO Wave Functions

Video IV.i

A One-Slide Summary of Quantum Mechanics

Fundamental Postulate:

$$O \Psi = a \Psi$$

operator wave function (scalar) observable

What is Ψ ? *Ψ is an oracle!*

Where does Ψ come from? *Ψ is refined*

Variational Process

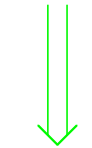
$$\mathcal{H}\Psi = E \Psi$$

Hamiltonian operator (systematically improvable)

Energy (cannot go lower than "true" energy)

electronic road map: systematically improvable by going to higher resolution

convergence of E



truth

What if I can't converge E ?

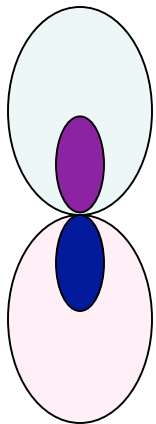
Test your oracle with a question to which you already know the right answer...

Constructing a 1-Electron Wave Function

The units of the wave function are such that its square is electron per volume. As electrons are quantum particles with non-point distributions, sometimes we say “density” or “probability density” instead of electron per volume (especially when there is more than one electron, since they are indistinguishable as quantum particles)

For instance, a valid wave function in cartesian coordinates for one electron might be:

$$\phi(x, y, z; Z) = \underbrace{\frac{\sqrt{2}Z^{5/2}}{81\sqrt{\pi}}}_{\text{normalization factor}} \underbrace{\left(6 - Z\sqrt{x^2 + y^2 + z^2}\right)}_{\text{radial phase factor}} \underbrace{ye^{-Z\sqrt{x^2 + y^2 + z^2}/3}}_{\text{cartesian directionality (if any) ensures square integrability}}$$



normalization factor

radial phase factor

cartesian directionality (if any)

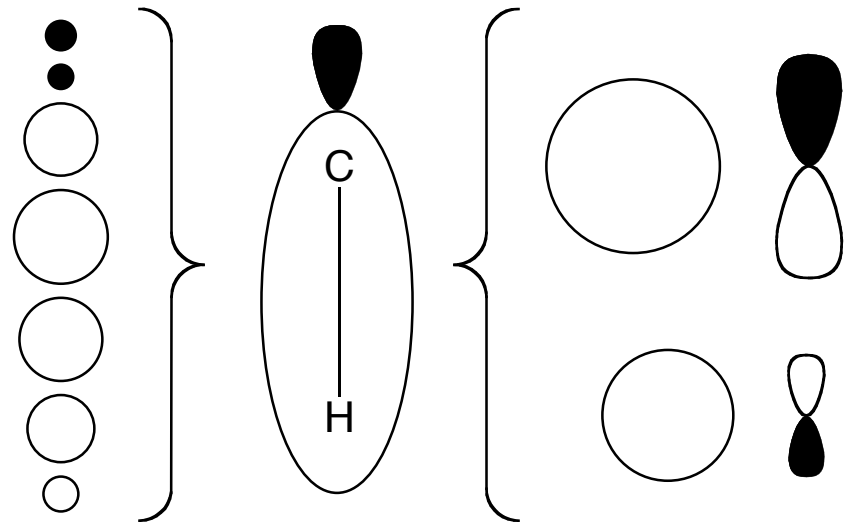
ensures square integrability

Constructing a 1-Electron Wave Function

To permit additional flexibility, we may take our wave function to be a linear combination of some set of common “basis” functions, e.g., atomic orbitals (LCAO). Thus

$$\phi(\mathbf{r}) = \sum_{i=1}^N a_i \varphi(\mathbf{r})$$

For example, consider the wave function for an electron in a C–H bond. It could be represented by s and p functions on the atomic positions, or s functions along the bond axis, or any other fashion convenient.



Constructing a 1-Electron Wave Function

To optimize the coefficients in our LCAO expansion, we use the variational principle, which says that

$$E = \frac{\int \left(\sum_i a_i \varphi_i \right) H \left(\sum_j a_j \varphi_j \right) d\mathbf{r}}{\int \left(\sum_i a_i \varphi_i \right) \left(\sum_j a_j \varphi_j \right) d\mathbf{r}} = \frac{\sum_{ij} a_i a_j \int \varphi_i H \varphi_j d\mathbf{r}}{\sum_{ij} a_i a_j \int \varphi_i \varphi_j d\mathbf{r}} = \frac{\sum_{ij} a_i a_j H_{ij}}{\sum_{ij} a_i a_j S_{ij}}$$

which is minimized by one root E of the “secular equation” (the other roots are excited states)—each value of E that satisfies the secular equation determines all of the a_i values and thus the shape of the molecular orbital wave function (MO)

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

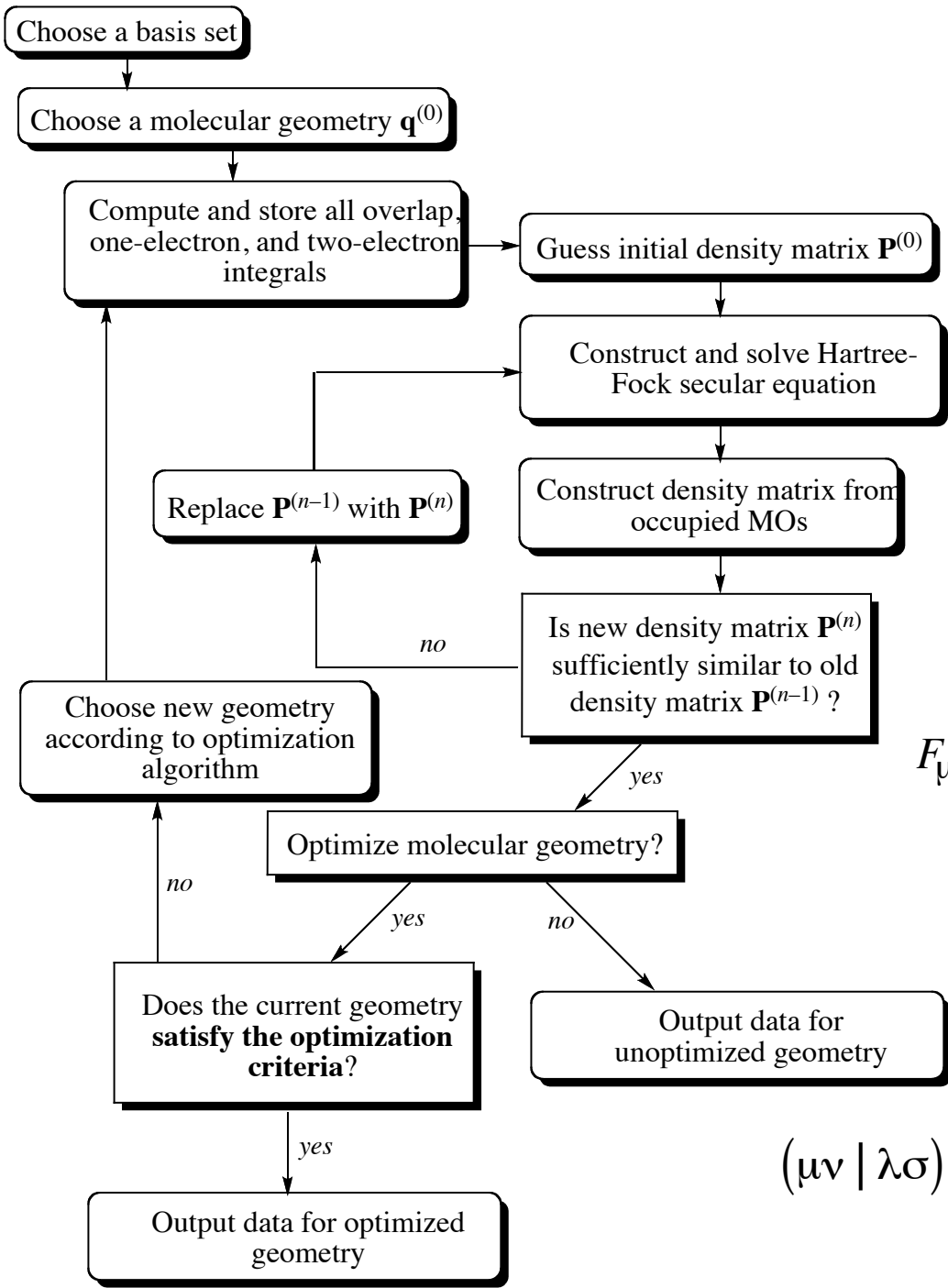
What Are These Integrals H ?

The electronic Hamiltonian includes kinetic energy, nuclear attraction, and, if there is more than one electron, electron-electron repulsion

$$H_{ij} = \left\langle \varphi_i \left| -\frac{1}{2} \nabla^2 \right| \varphi_j \right\rangle - \left\langle \varphi_i \left| \sum_k^{\text{nuclei}} \frac{Z_k}{r_k} \right| \varphi_j \right\rangle + \left\langle \varphi_i \left| \sum_n^{\text{electrons}} \frac{|\phi|^2}{r_n} \right| \varphi_j \right\rangle$$

The final term is problematic. Solving for all electrons at once is a many-body problem that has not been solved even for classical particles. An approximation is to ignore the correlated motion of the electrons, and treat each electron as independent, but even then, if each MO depends on all of the other MOs, how can we determine even one of them? The Hartree-Fock approach accomplishes this for a many-electron wave function expressed as an antisymmetrized product of one-electron MOs (a so-called Slater determinant)

The Hartree-Fock procedure



$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \cdots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \cdots & F_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \cdots & F_{NN} - ES_{NN} \end{vmatrix} = 0$$

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right]$$

$$P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

$$(\mu\nu | \lambda\sigma) = \iint \phi_\mu(1)\phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda(2)\phi_\sigma(2) d\mathbf{r}(1)d\mathbf{r}(2)$$

One MO per root E

What functions to use?

- Slater Type Orbitals (STO)

$$\phi_{1s} = \left(\frac{\xi}{\pi} \right)^{1/2} e^{-\xi \cdot r}$$

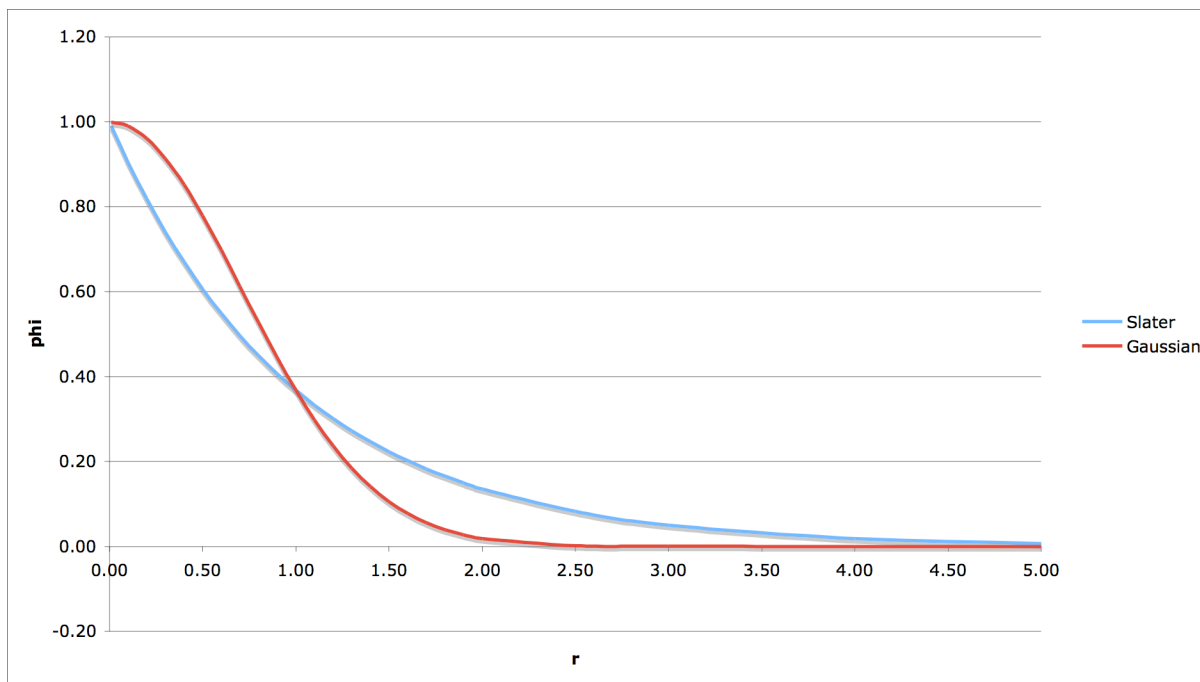
- Can't do 2 electron integrals analytically

$$\iint \phi_{\mu}(1) \phi_{\nu}(1) \frac{1}{r_{12}} \phi_{\lambda}(2) \phi_{\sigma}(2) dr_1 dr_2$$

- 1950s

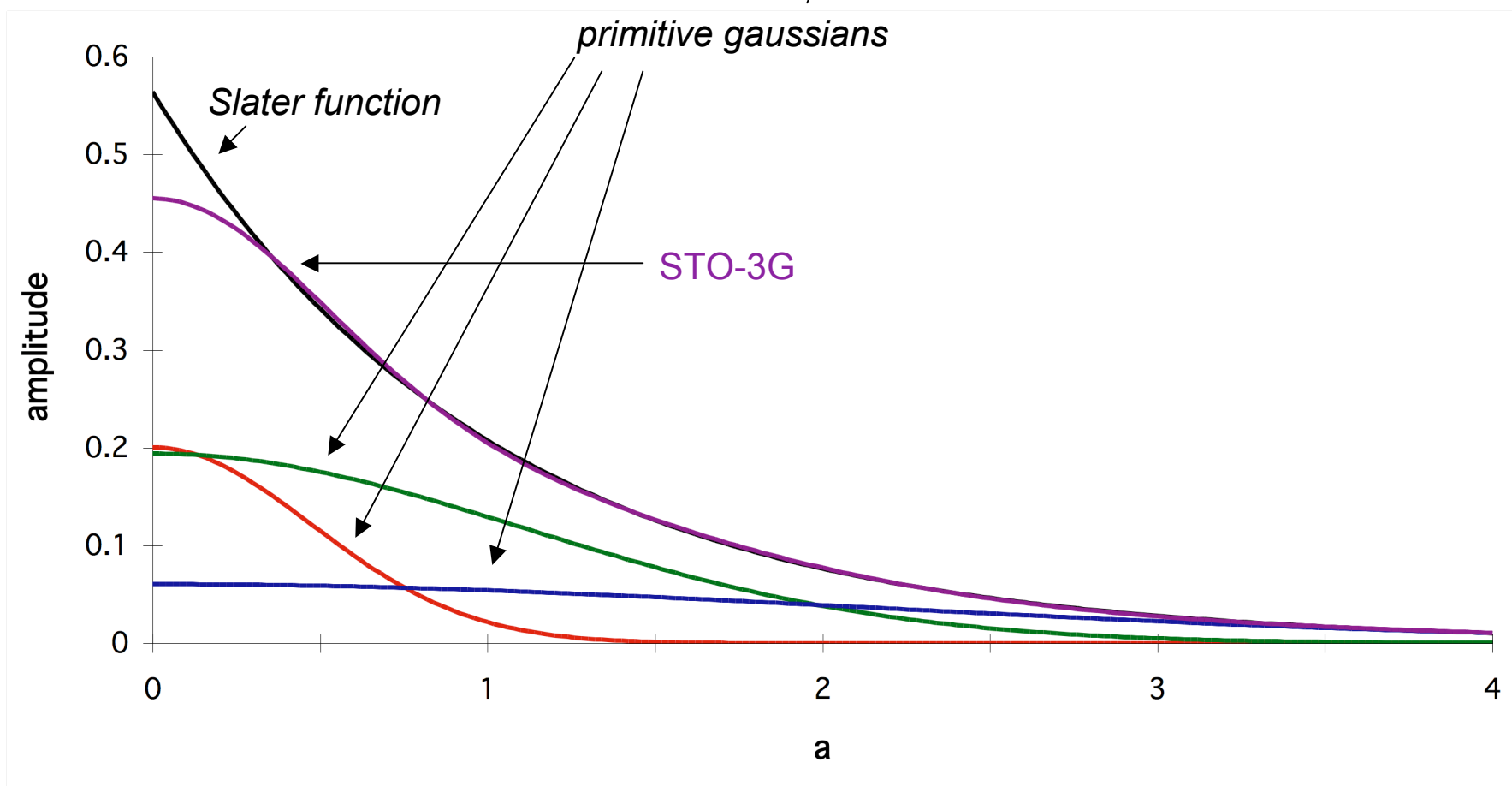
- Replace with something similar that is analytical: a gaussian function

$$\phi_{1s} = \left(\frac{\xi}{\pi}\right)^{1/2} e^{-\xi \cdot r} \quad \text{VS.} \quad \phi_{\text{"1s"}} = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

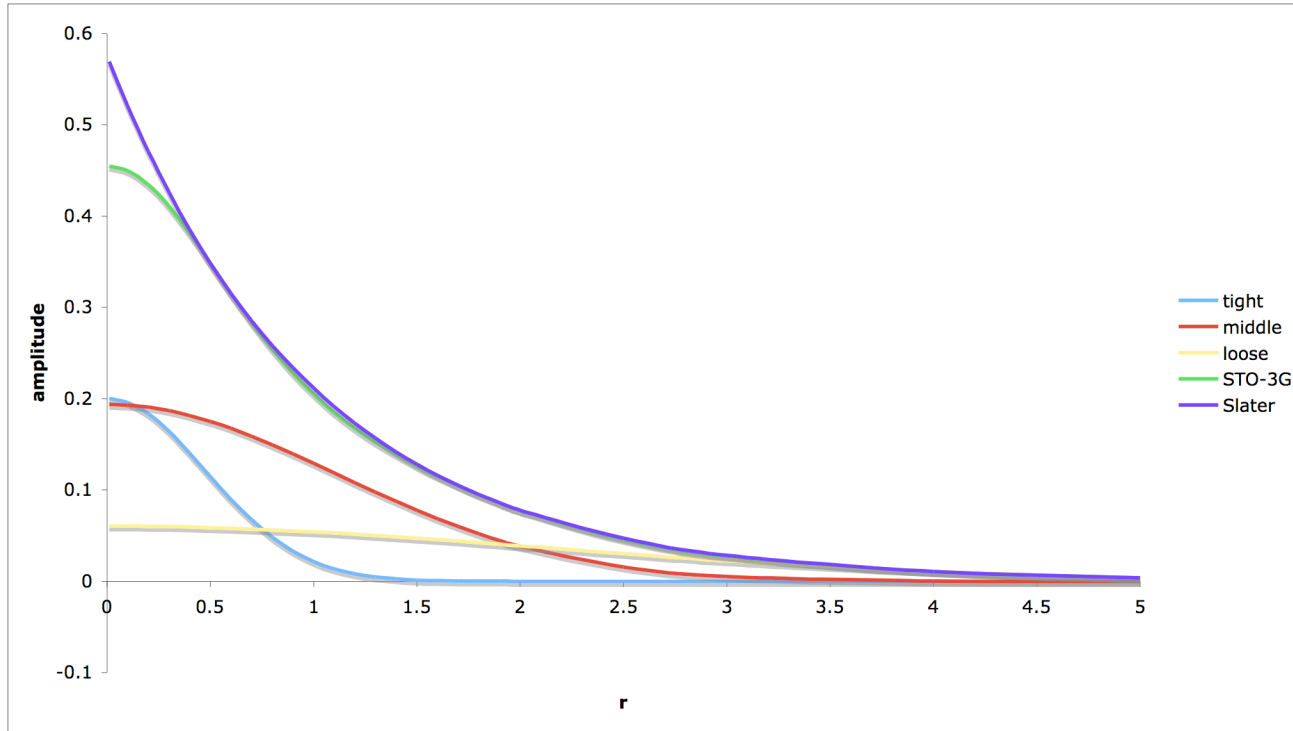


Approximating Slater Functions with Gaussians

Contracted basis function $\longrightarrow \phi(\mathbf{r}) = \sum_{i=1}^N a_i \varphi(\mathbf{r})$



Contracted Basis Set



- STO-#G - minimal basis
- Pople - optimized a and α values

$$\phi_{1s} = \sum_i^N a_i \left(\frac{2\alpha_i}{\pi} \right)^{3/4} e^{-\alpha_i r^2}$$

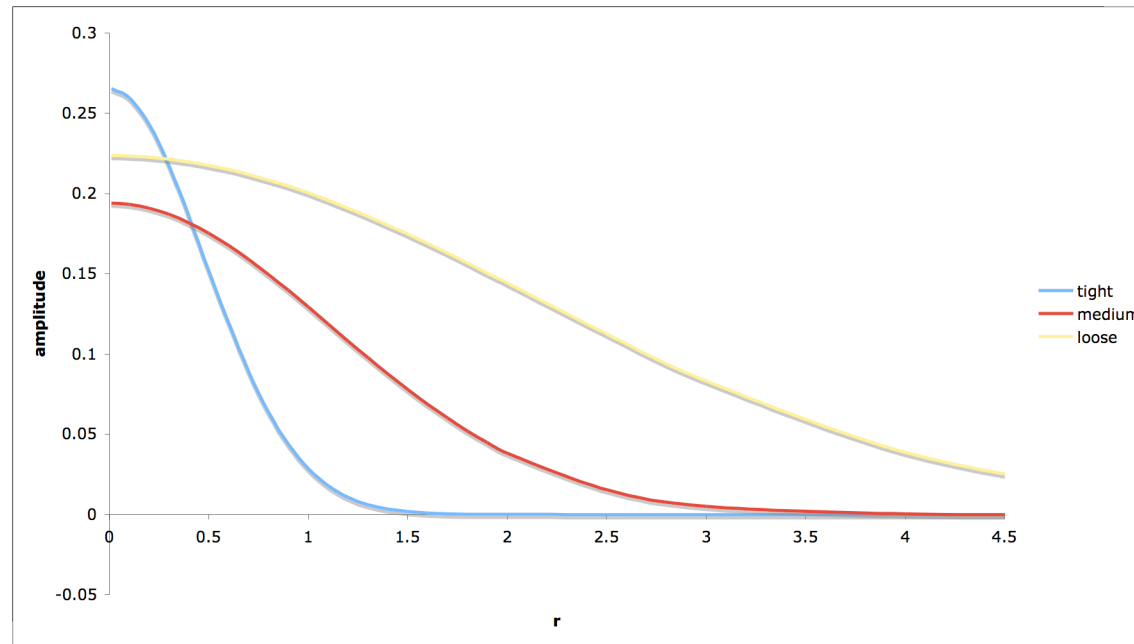


vs.



- What do you about very different bonding situations?
 - Have more than one 1s orbital
- Multiple- ζ (zeta) basis set
 - Multiple functions for the same atomic orbital

- Double- ζ – one loose, one tight
 - Adds flexibility



- Triple- ζ – one loose, one medium, one tight
- Only for valence

- Decontraction

- Allow a_i to vary

locked in STO-3G

$$\phi_{1s_H}^{STO-3G} = \sum_i^3 a_i \left(\frac{2\alpha_i}{\pi} \right)^{3/4} e^{-\alpha_i r^2}$$

primitive gaussians

- Pople - #-##G

- 3-21G

gaussian

valence: 2 tight, 1 loose

primitives in all core functions

How many basis functions are for NH₃ using 3-21G?

NH₃ 3-21G

atom	# atoms	AO	degeneracy	basis fxns	primitives	total basis fxns	total primitives
N	1	1s(core)	1	1	3	1	3
		2s(val)	1	2	2 + 1 = 3	2	3
		2p(val)	3	2	2 + 1 = 3	6	9
H	3	1s(val)	1	2	2 + 1 = 3	6	9
					total =	15	24

Polarization Functions

1 d functions on all heavy atoms (6-fold deg.)

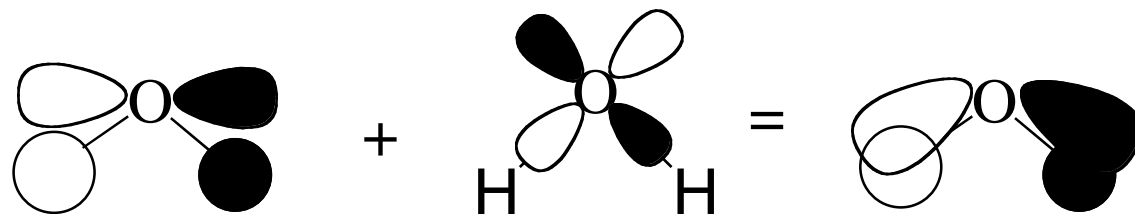
1 p functions on all H (3-fold deg.)

• 6-31G**

2 valence basis functions
one with 3 primitives, the other with 1

6 primitives
1 core basis functions

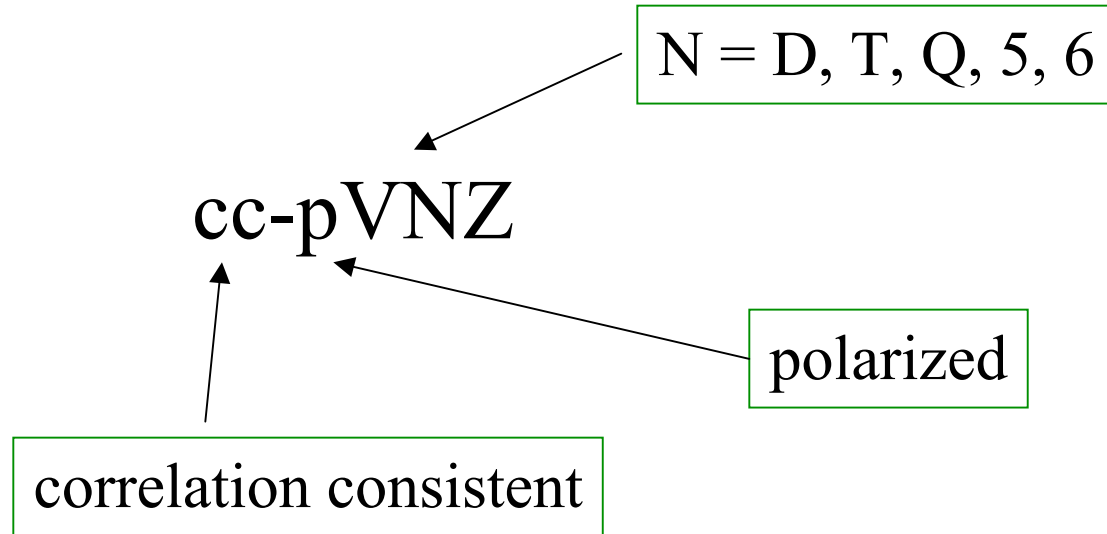
- For HF, NH_3 is planar with infinite basis set of s and p basis functions!!!!



- Better way to write – 6-31G(3d2f, 2p)
- Keep balanced

Valence split	polarization
2	d, p
3	2df, 2pd
4	3d2fg, 3p2df

Dunning basis set



Diffuse functions

- “loose” electrons
 - anions
 - excited states
 - Rydberg states
- Dunning - aug-cc-pVNZ
 - Augmented
- Pople
 - 6-31+G - heavy atoms/only with valence
 - 6-31++G - hydrogens
 - Not too useful

How many basis functions in H_2POH
using 6-31G(d, p)?