

# The Matrix Representation of Quantum Mechanics

Benjamin G. Levine

# Linear Algebra is the Language of Quantum Mechanics

- “But all I see are differential equations and integrals?”

$$\left( \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \Psi(x) = E \Psi(x)$$

$$\langle \mathbf{A} \rangle = \frac{\int \Psi^*(x) \hat{\mathbf{A}} \Psi(x) dx}{\int \Psi^*(x) \Psi(x) dx}$$

Properties of Linear Operators

$$\hat{\mathbf{A}} (\Psi_a(x) + \Psi_b(x)) = \hat{\mathbf{A}} \Psi_a(x) + \hat{\mathbf{A}} \Psi_b(x)$$

$$\hat{\mathbf{A}} (c \Psi(x)) = c \hat{\mathbf{A}} \Psi(x)$$

# Linear Algebra is the Language of Quantum Mechanics

- Expand the wavefunction in a basis

$$\Psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r})$$

a vector of  
coefficients

a set of basis  
functions

# Linear Algebra is the Language of Quantum Mechanics

- Build Hamiltonian Matrix

$$H_{ij} = \int \varphi_i^* \hat{H} \varphi_j d\mathbf{r}$$

$$\mathbf{H} = \begin{bmatrix} \int \varphi_{left}^* \hat{H} \varphi_{left} d\mathbf{r} & \int \varphi_{left}^* \hat{H} \varphi_{right} d\mathbf{r} \\ \int \varphi_{right}^* \hat{H} \varphi_{left} d\mathbf{r} & \int \varphi_{right}^* \hat{H} \varphi_{right} d\mathbf{r} \end{bmatrix}$$

$$\int \Psi^* \hat{H} \Psi d\mathbf{r} = \mathbf{c}^* \mathbf{H} \mathbf{c}$$

# Linear Algebra is the Language of Quantum Mechanics

- Build Hamiltonian Matrix

$$H_{ij} = \int \varphi_i^* \hat{H} \varphi_j d\mathbf{r}$$

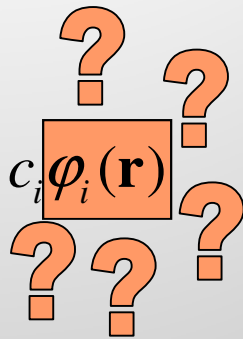
$$\mathbf{H} = \begin{bmatrix} \int \varphi_{left}^* \hat{H} \varphi_{left} d\mathbf{r} & \int \varphi_{left}^* \hat{H} \varphi_{right} d\mathbf{r} \\ \int \varphi_{right}^* \hat{H} \varphi_{left} d\mathbf{r} & \int \varphi_{right}^* \hat{H} \varphi_{right} d\mathbf{r} \end{bmatrix}$$

$$\int \Psi^* \hat{H} \Psi d\mathbf{r} = \mathbf{c}^* \mathbf{H} \mathbf{c} = \overset{\text{bracket notation}}{\langle \Psi | \hat{H} | \Psi \rangle}$$

# Basis in Quantum Chemistry

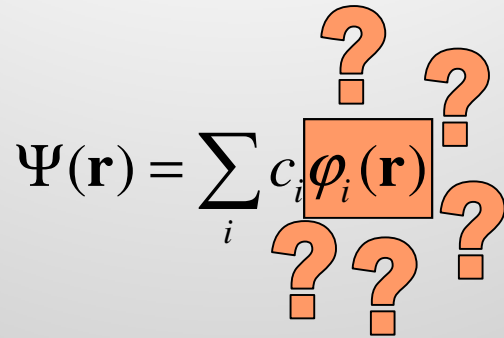
- One-electron basis
  - describes an orbital
  - “basis set”
- Many-electron basis
  - describes a many electron wave function
  - “configuration basis”

# Basis Functions

$$\Psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r})$$
The diagram shows the equation  $\Psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r})$ . The term  $\phi_i(\mathbf{r})$  is enclosed in an orange square. Five orange question marks are scattered around the equation: one above the summation symbol, one to the right of the summation, one below the summation, one to the left of the orange square, and one to the right of the orange square.

- What features are desirable in a basis function?

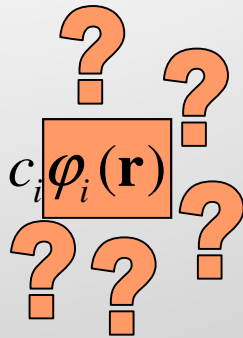
# Basis Functions

$$\Psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r})$$
The equation  $\Psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r})$  is shown. The term  $\phi_i(\mathbf{r})$  is enclosed in an orange square box. Five orange question marks are scattered around the box: one above, one to the upper right, one to the lower right, and two below.

- What features are desirable in a basis function?
  - Ability to reproduce the true wavefunction accurately with a small number of basis functions
  - Ease of calculating integrals of Hamiltonian
  - Obeys the boundary values of the system



# Basis Functions

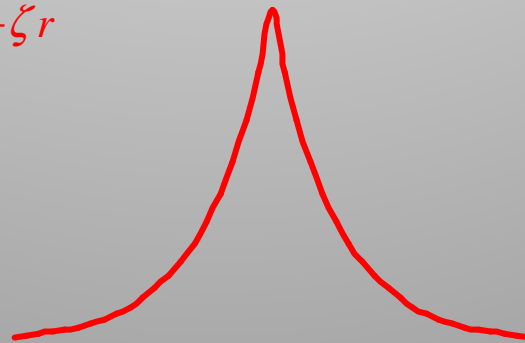
$$\Psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r})$$


- Two widely used varieties of basis sets
  - Atom-centered Gaussian basis sets
  - Plane-wave basis set

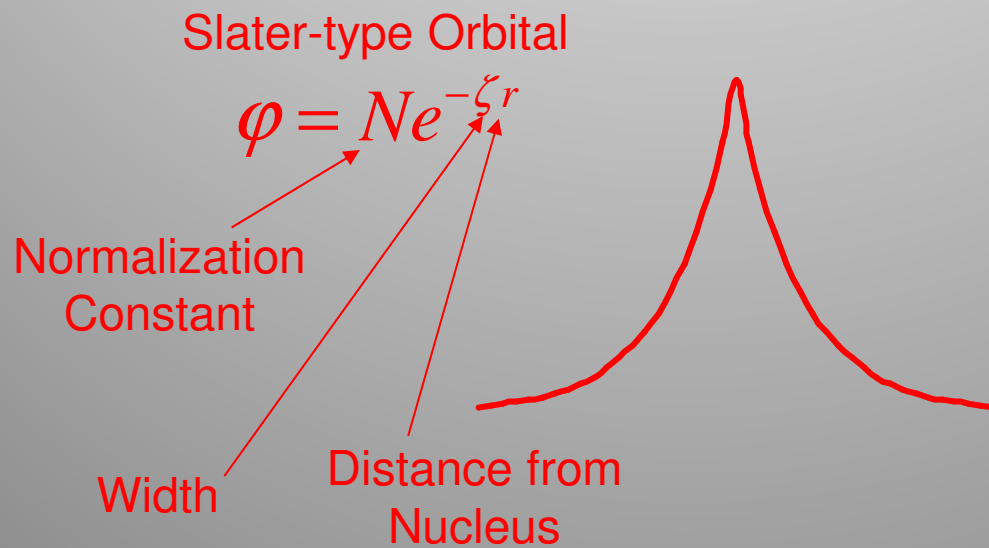
# Basis Functions

Slater-type Orbital

$$\varphi = Ne^{-\zeta r}$$



# Basis Functions



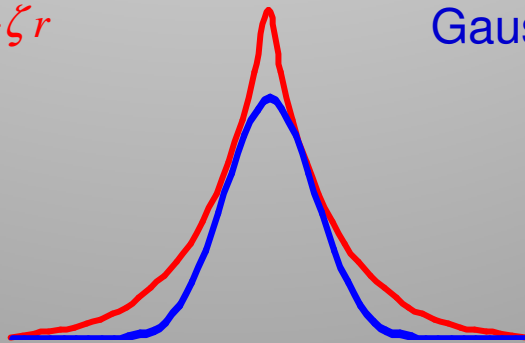
# Basis Functions

Slater-type Orbital

$$\varphi = Ne^{-\zeta r}$$

Gaussian-type Orbital

$$\varphi = Ne^{-\alpha r^2}$$



# Basis Functions

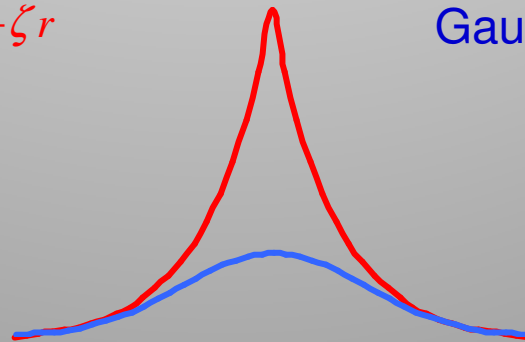
Slater-type Orbital

$$\varphi = Ne^{-\zeta r}$$

Gaussian-type Orbital

$$\varphi = Ne^{-\alpha r^2}$$

Change Width



# Basis Functions

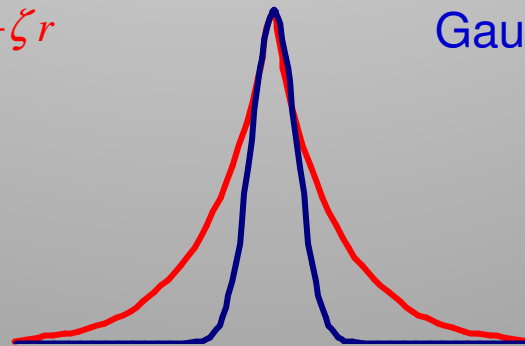
Slater-type Orbital

$$\varphi = Ne^{-\zeta r}$$

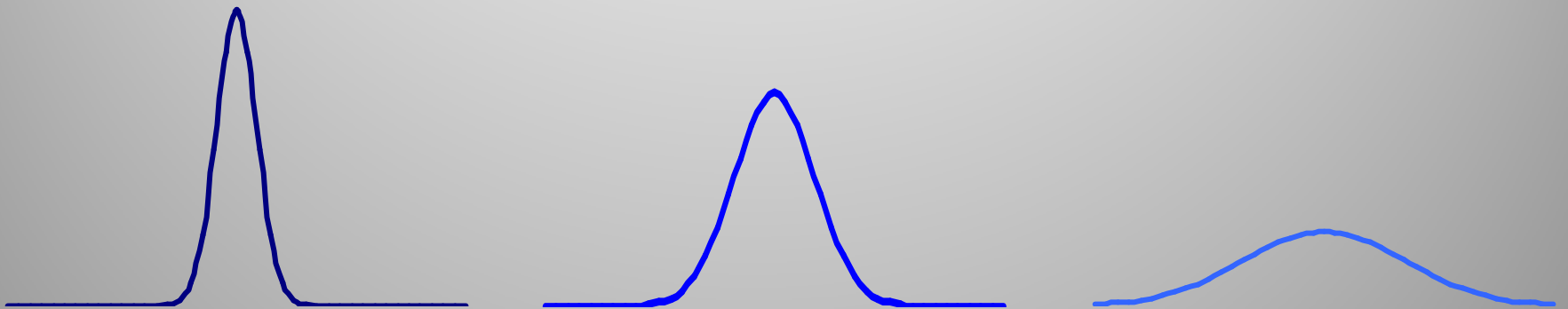
Gaussian-type Orbital

$$\varphi = Ne^{-\alpha r^2}$$

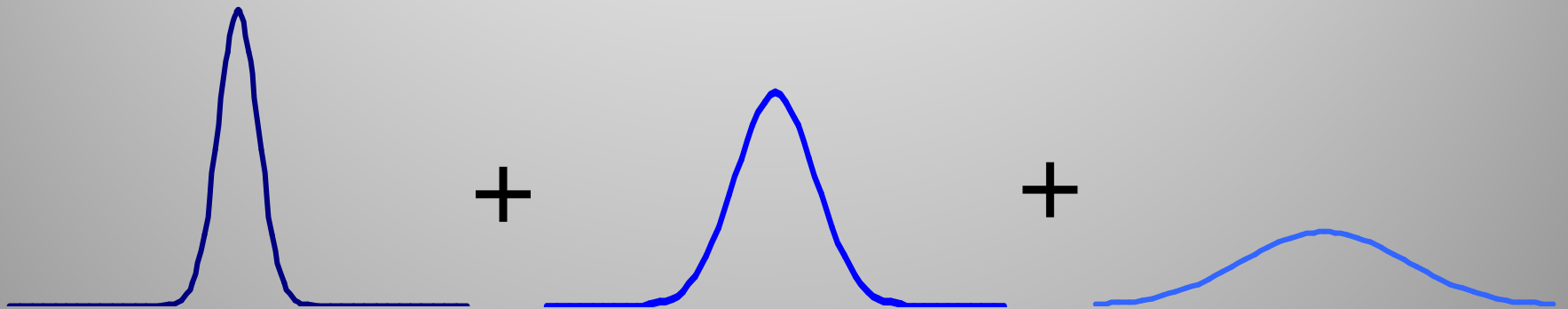
Change Width



# Basis Functions

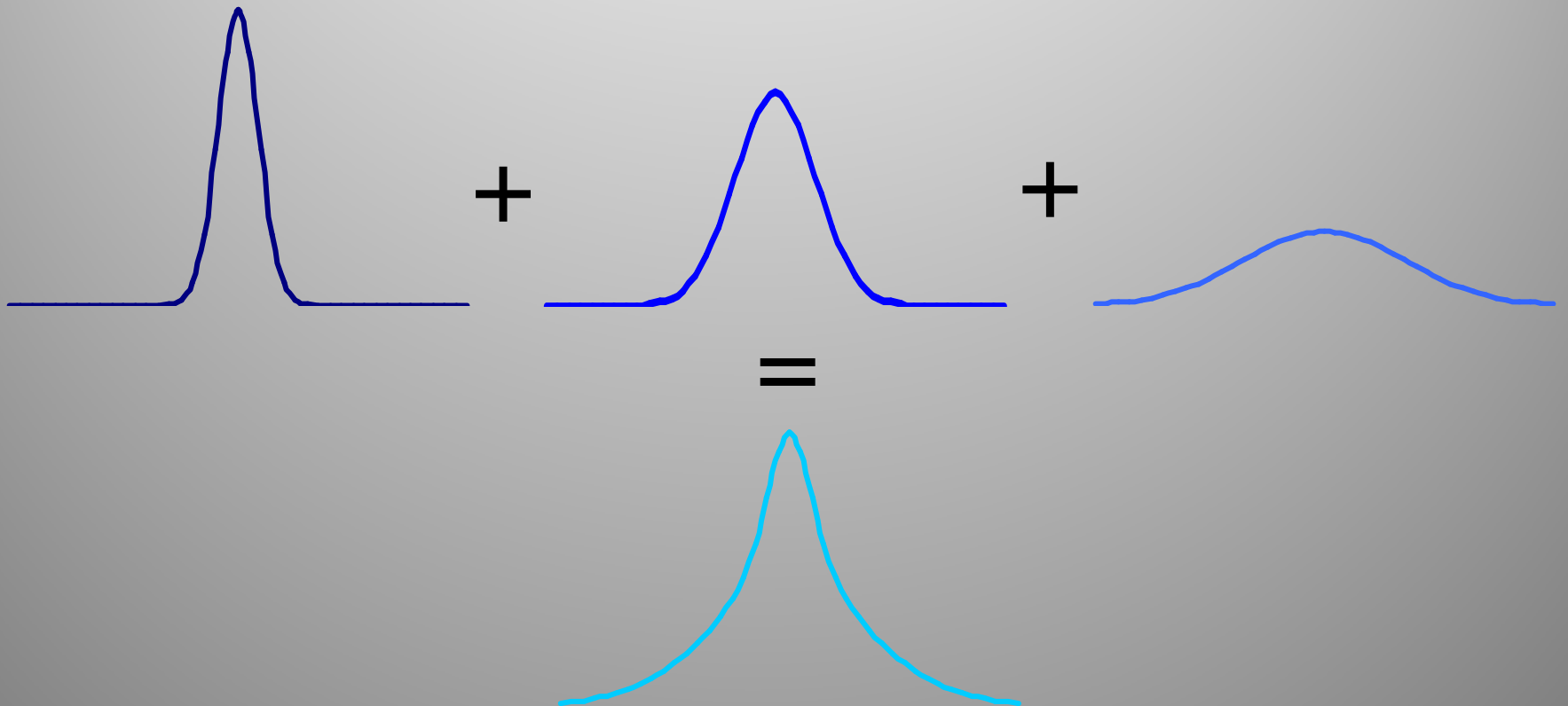


# Basis Functions

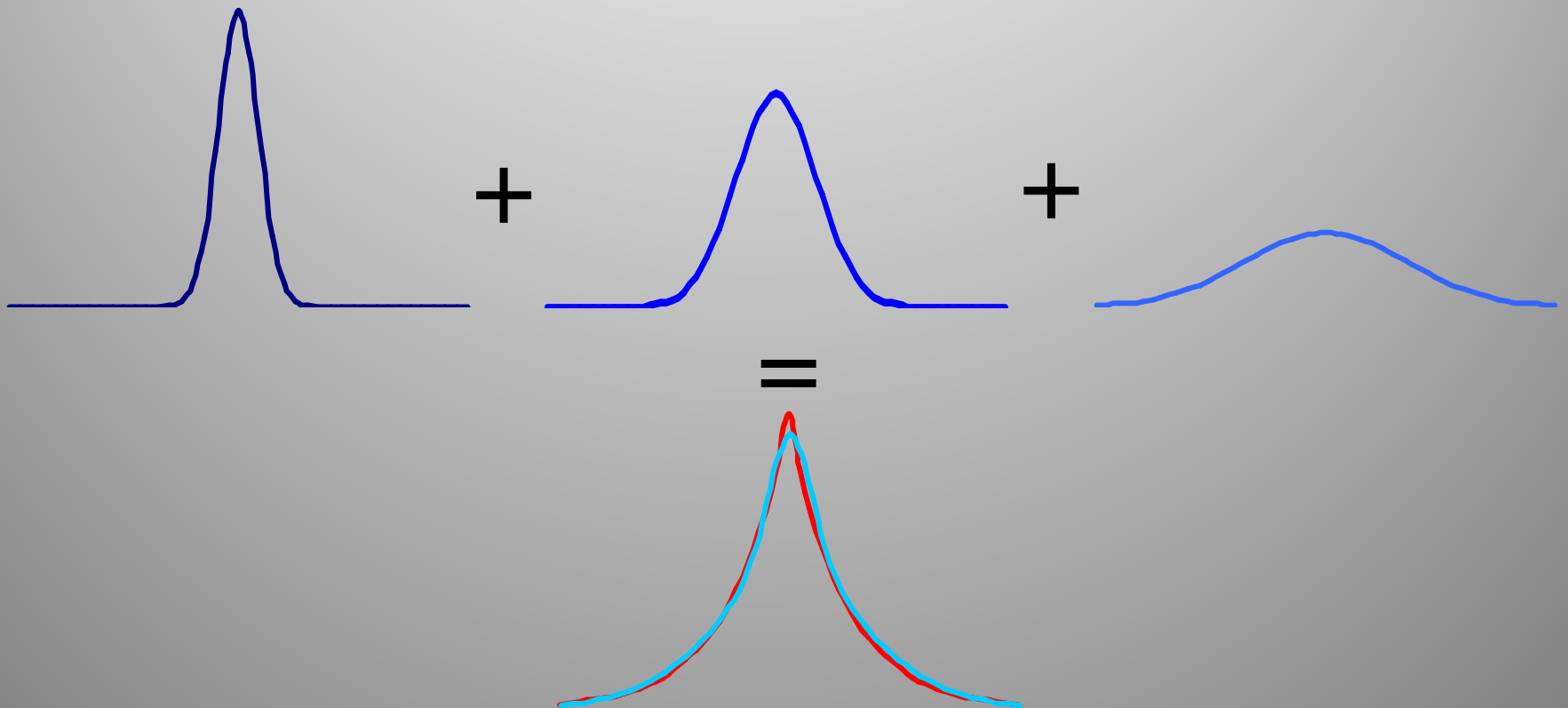




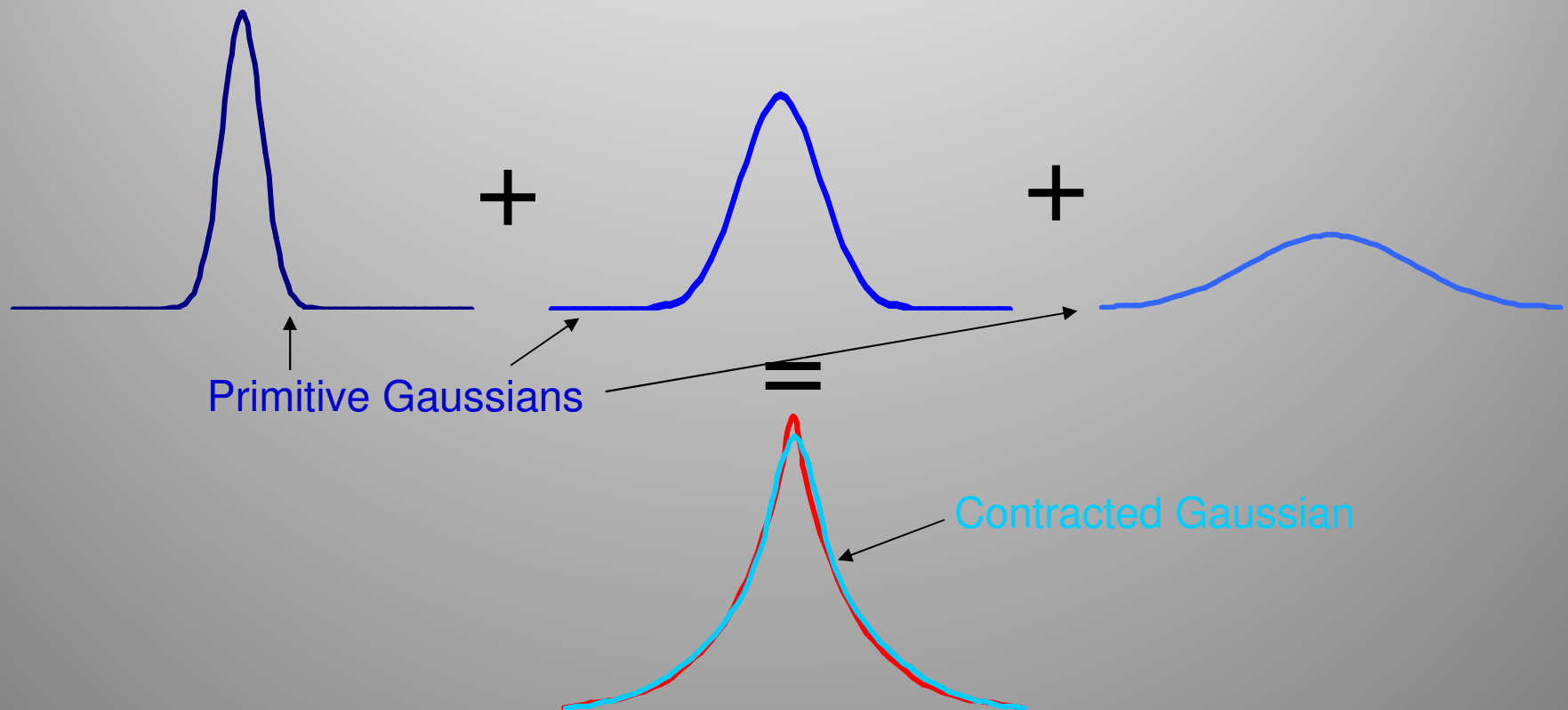
# Basis Functions



# Basis Functions

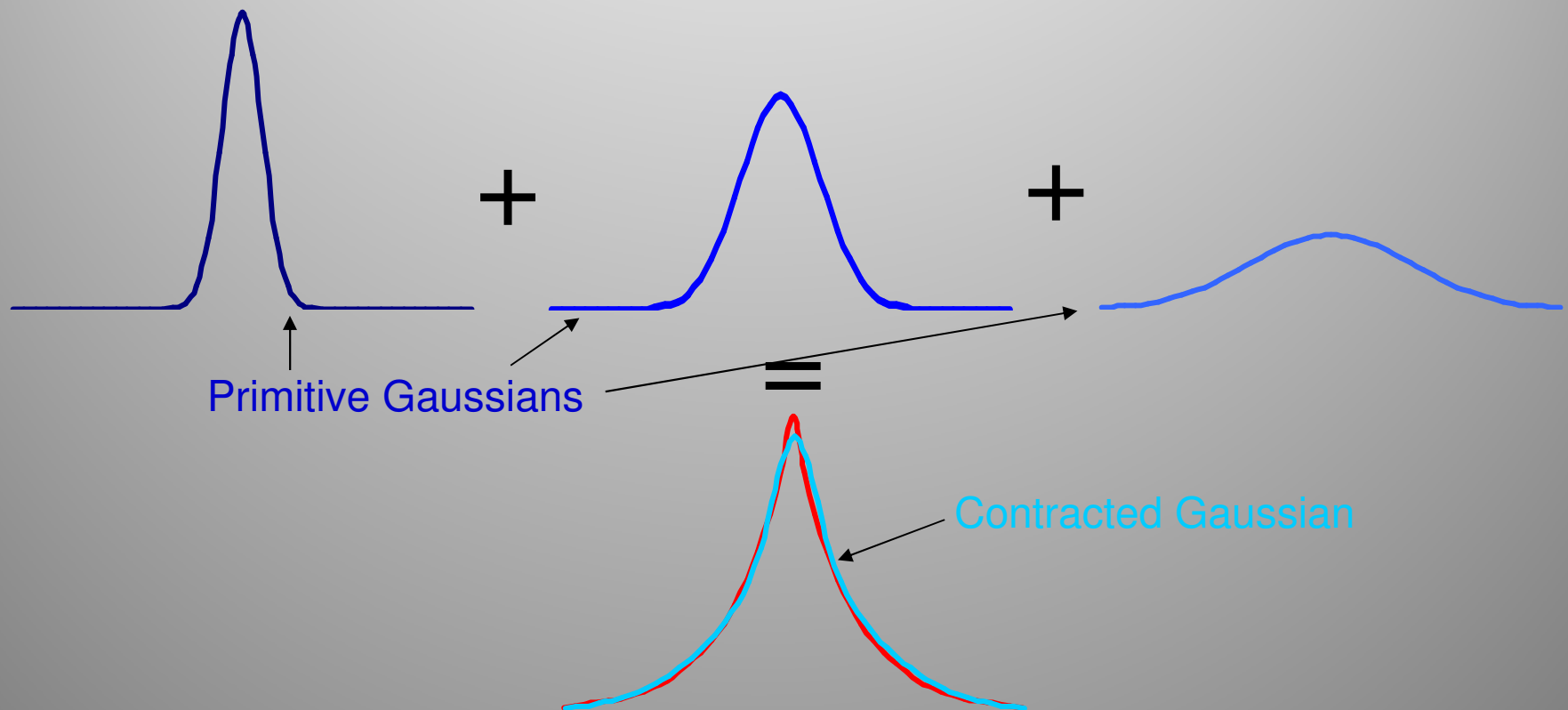


# Basis Functions



# Basis Functions

$$\varphi = \sum_{a=1}^M c_a e^{-\alpha_a r^2}$$

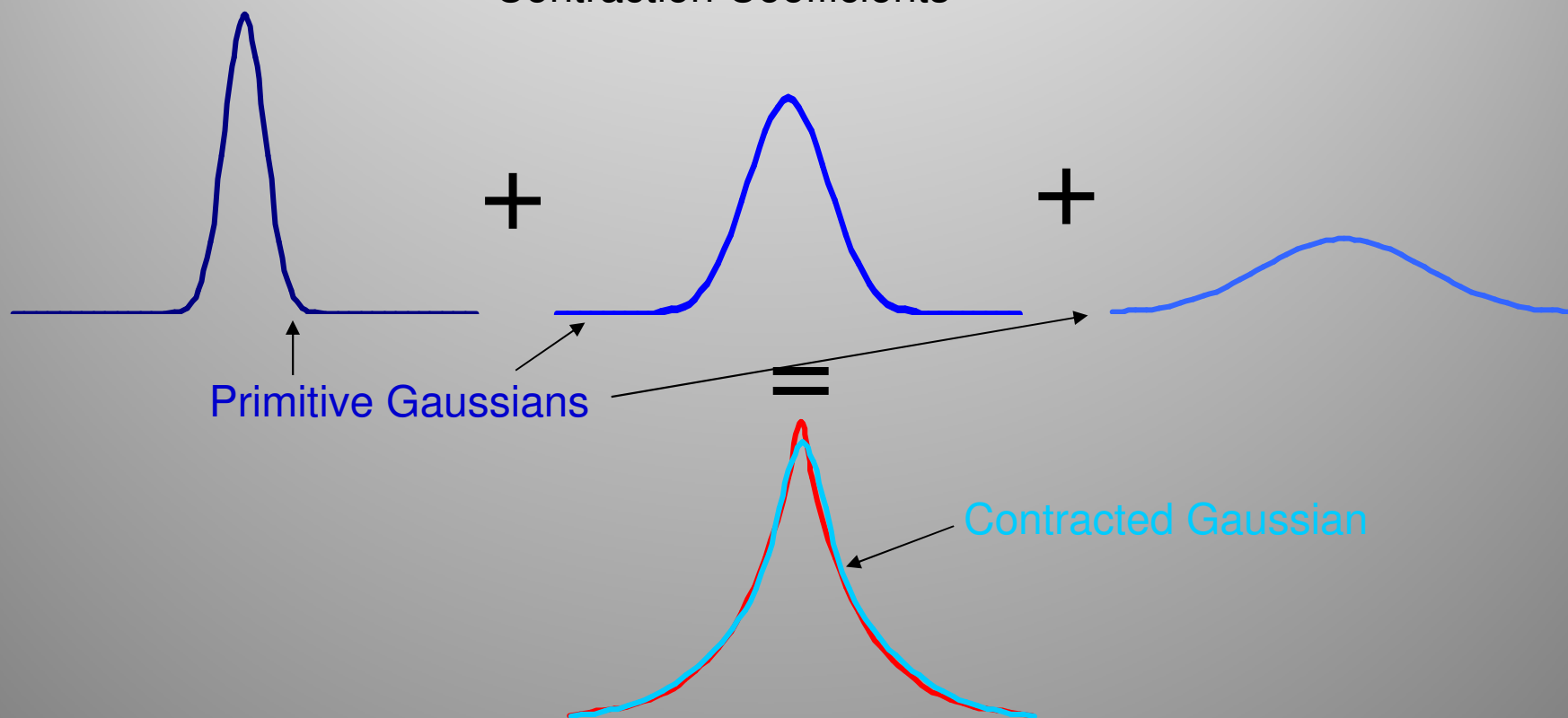


# Basis Functions

$$\varphi = \sum_{a=1}^M c_a e^{-\alpha_a r^2}$$

Exponent or Gaussian Width

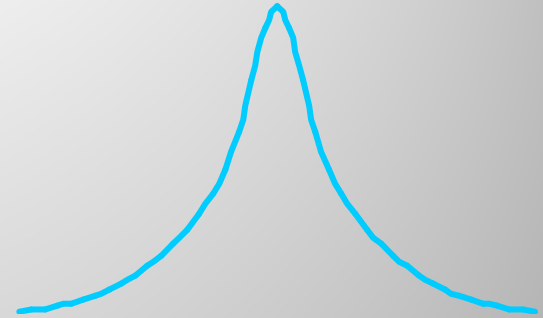
Contraction Coefficients



# Basis Functions

s-orbital:

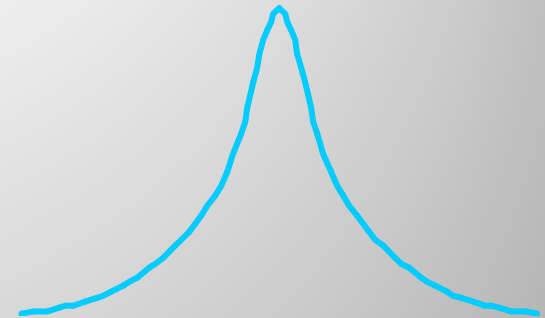
$$\varphi = \sum_{a=1}^M c_a e^{-\alpha_a r^2}$$



# Basis Functions

s-orbital:

$$\varphi = \sum_{a=1}^M c_a e^{-\alpha_a r^2}$$

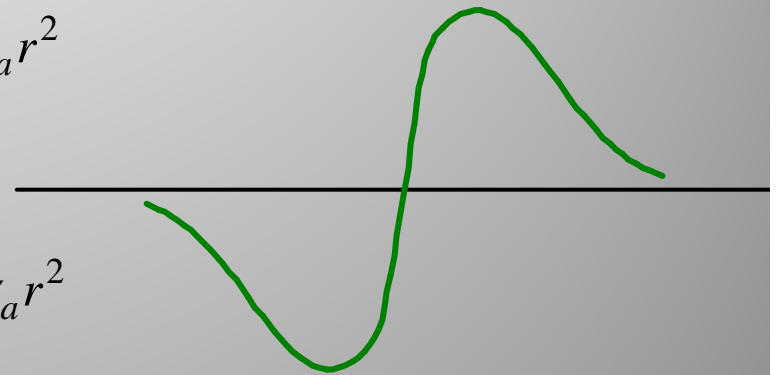


p-orbital:

$$\varphi = \sum_{a=1}^M c_a x e^{-\alpha_a r^2}$$

$$\varphi = \sum_{a=1}^M c_a y e^{-\alpha_a r^2}$$

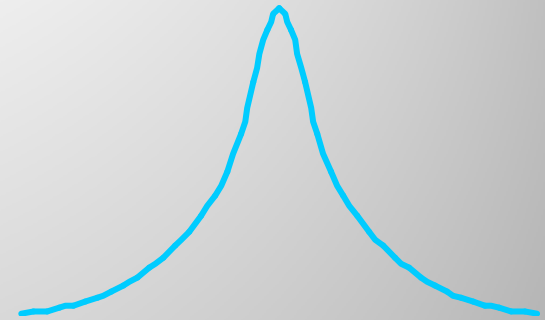
$$\varphi = \sum_{a=1}^M c_a z e^{-\alpha_a r^2}$$



# Basis Functions

s-orbital:

$$\varphi = \sum_{a=1}^M c_a e^{-\alpha_a r^2}$$

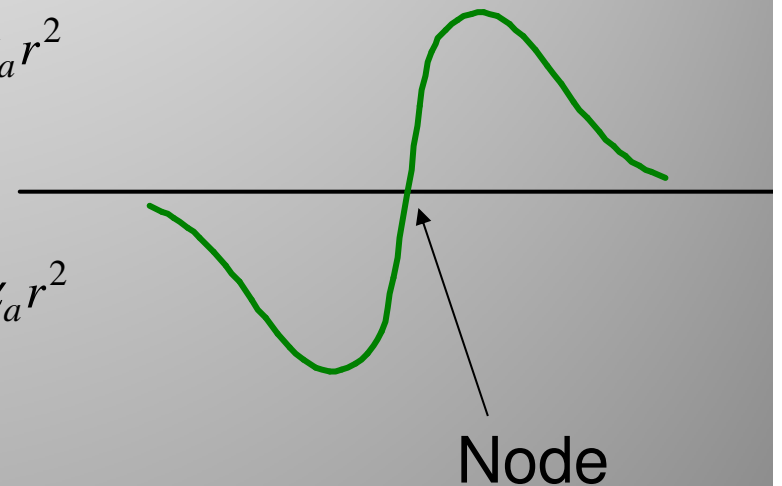


p-orbital:

$$\varphi = \sum_{a=1}^M c_a x e^{-\alpha_a r^2}$$

$$\varphi = \sum_{a=1}^M c_a y e^{-\alpha_a r^2}$$

$$\varphi = \sum_{a=1}^M c_a z e^{-\alpha_a r^2}$$

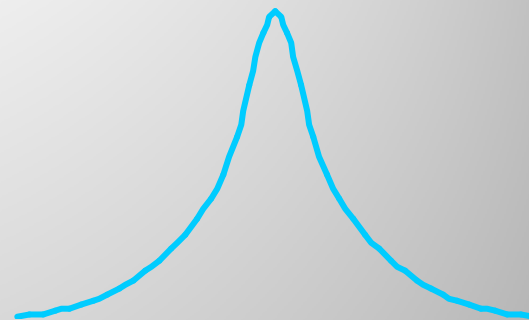




# Basis Functions

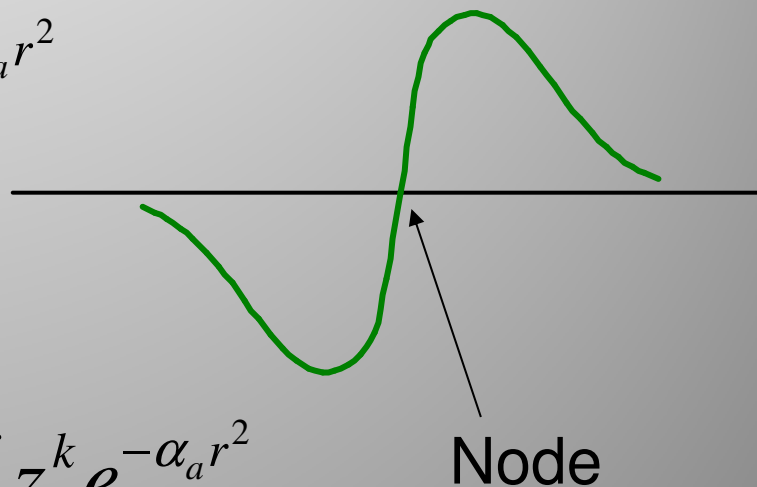
s-orbital:

$$\varphi = \sum_{a=1}^M c_a e^{-\alpha_a r^2}$$



p-orbital:

$$\varphi = \sum_{a=1}^M c_a x e^{-\alpha_a r^2}$$



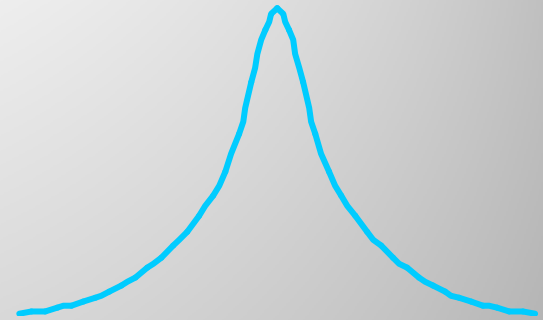
any angular  
momentum:

$$\varphi = \sum_{a=1}^M c_a x^i y^j z^k e^{-\alpha_a r^2}$$

# Basis Functions

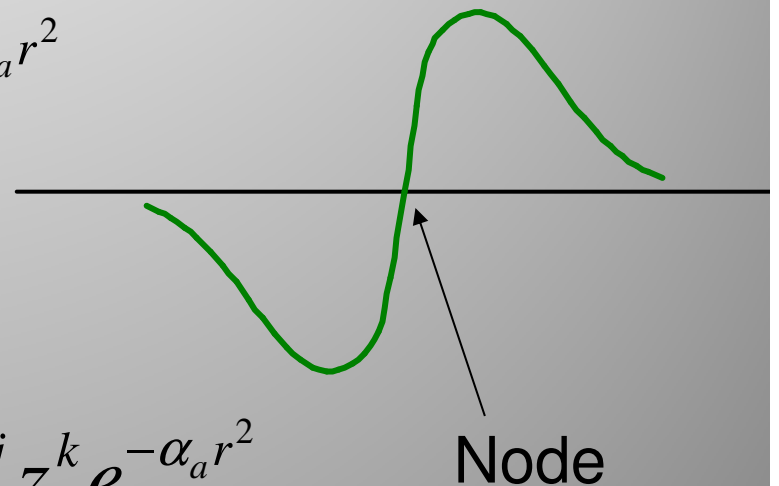
s-orbital:

$$\varphi = \sum_{a=1}^M c_a e^{-\alpha_a r^2}$$



p-orbital:

$$\varphi = \sum_{a=1}^M c_a x e^{-\alpha_a r^2}$$



any angular  
momentum:

$$\varphi = \sum_{a=1}^M c_a x^i y^j z^k e^{-\alpha_a r^2}$$

$$i + j + k = l \text{ quantum number}$$

# Basis Sets

- A number of standard basis sets are in use by quantum chemists

# Basis Sets

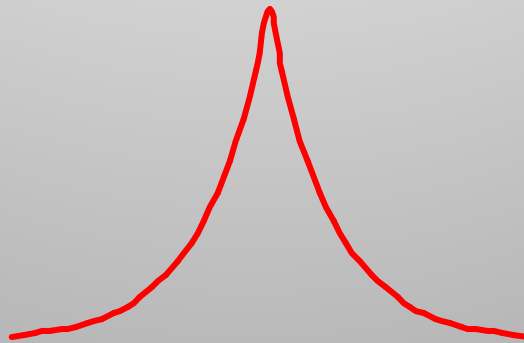
- A number of standard basis sets are in use by quantum chemists
- Basis sets have a number of features
  - $\zeta$  (zeta) – describes the number of basis functions
    - Single- $\zeta$  – 1 basis function per atomic orbital
    - Double- $\zeta$  – 2 basis functions per atomic orbital
    - Valence double- $\zeta$  – 2 basis function per atomic orbital in valence shell, 1 otherwise

# Basis Sets

- Polarization functions – additional high angular momentum function give additional variational flexibility

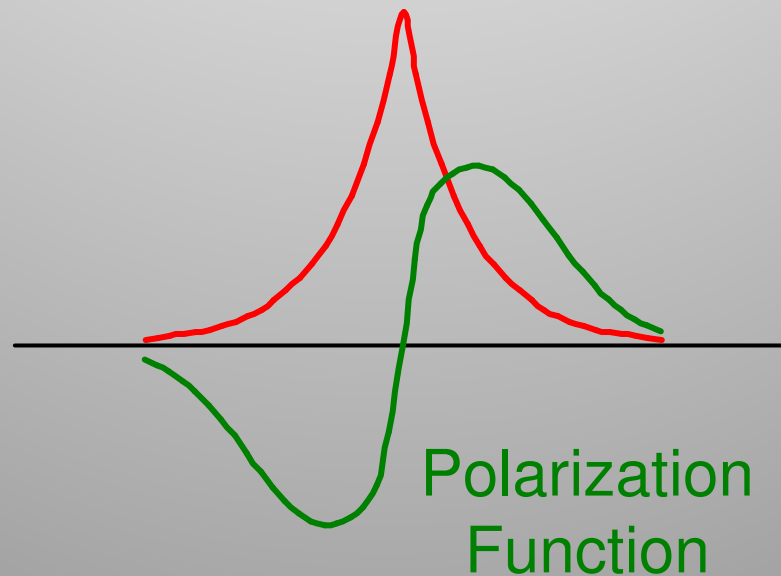
# Basis Sets

- Polarization functions – additional high angular momentum function give additional variational flexibility



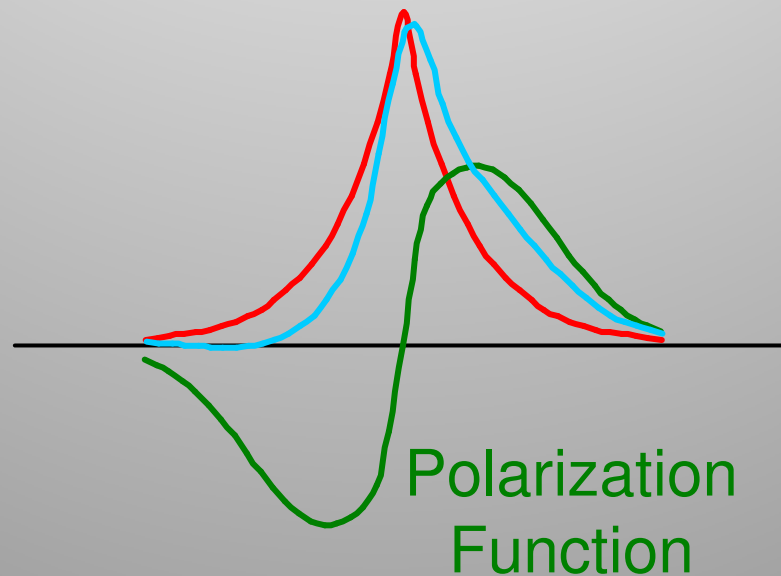
# Basis Sets

- Polarization functions – additional high angular momentum function give additional variational flexibility



# Basis Sets

- Polarization functions – additional high angular momentum function give additional variational flexibility





# Basis Sets

- Diffuse functions – extra wide basis functions are important for anions

# Basis Sets

- Pople basis nomenclature

6-31G

# Basis Sets

- Pople basis nomenclature

1 number before  
hyphen means there  
is one contracted  
Gaussian in core



6-31G

# Basis Sets

- Pople basis nomenclature

1 number before  
hyphen means there  
is one contracted  
Gaussian in core

2 numbers after  
hyphen means there  
is two contracted  
Gaussian in core



6-31G

# Basis Sets

- Pople basis nomenclature

1 number before  
hyphen means there  
is one contracted  
Gaussian in core

2 numbers after  
hyphen means there  
is two contracted  
Gaussian in core



6-31G

**Valence Double Zeta**

# Basis Sets

- Pople basis nomenclature

1 number before  
hyphen means there  
is one contracted  
Gaussian in core

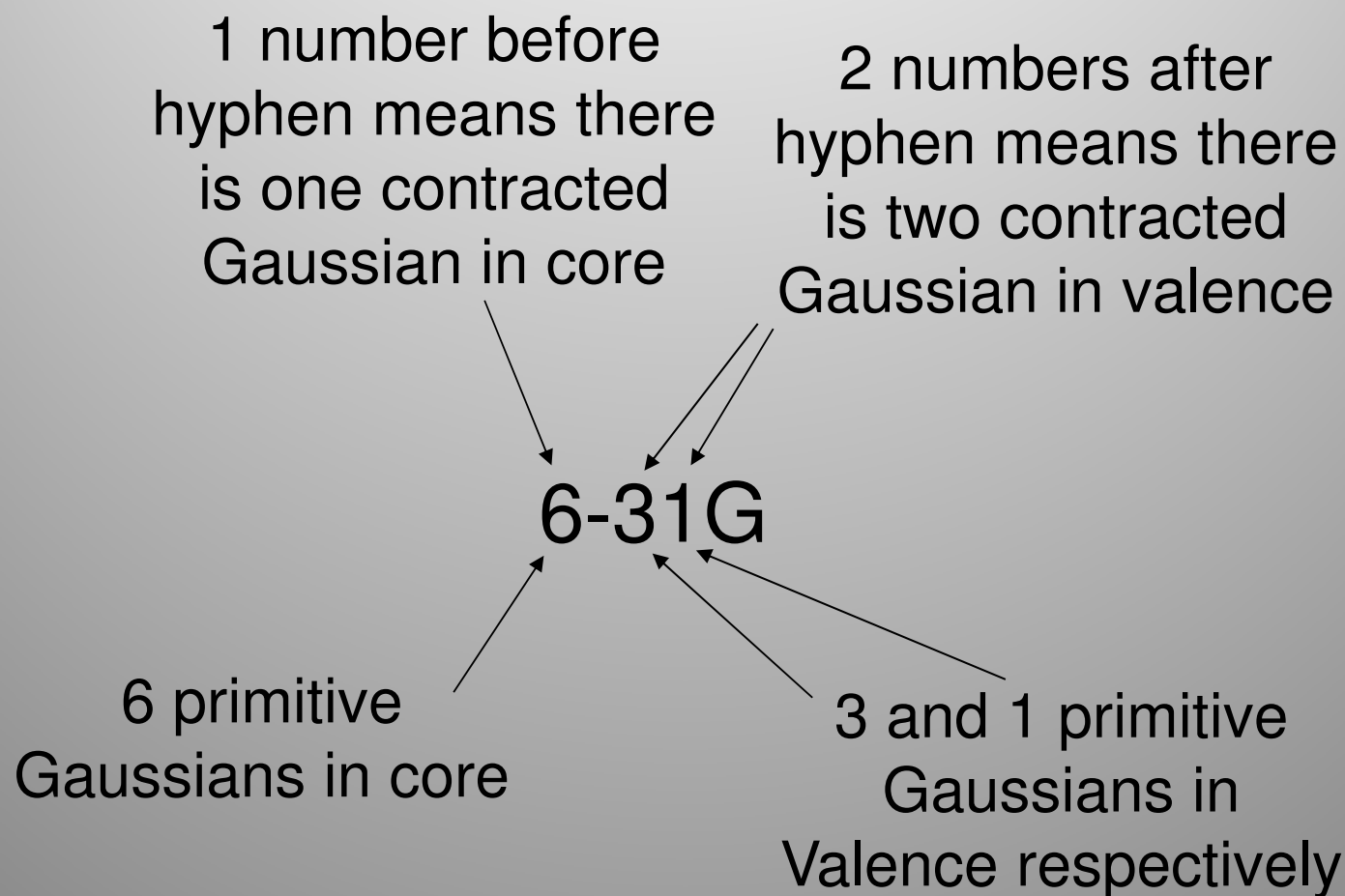
2 numbers after  
hyphen means there  
is two contracted  
Gaussian in valence

6-31G

6 primitive  
Gaussians in core

# Basis Sets

- Pople basis nomenclature



# Basis Sets

- Pople basis nomenclature

First star indicates  
polarization  
functions on heavy  
atoms

6-31G\*





# Basis Sets

- Pople basis nomenclature

First star indicates  
polarization  
functions on heavy  
atoms

6-31G\*\*

Second star  
indicates polarization  
functions on  
hydrogens

# Basis Sets

- Pople basis nomenclature

First plus indicates  
diffuse functions on  
heavy atoms

First star indicates  
polarization  
functions on heavy  
atoms

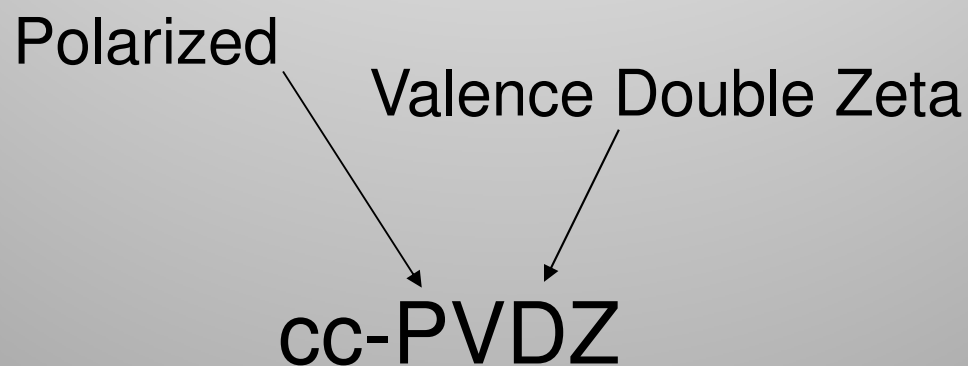
Second plus  
indicates diffuse  
functions on  
hydrogens

6-31++G\*\*

Second star  
indicates polarization  
functions on  
hydrogens

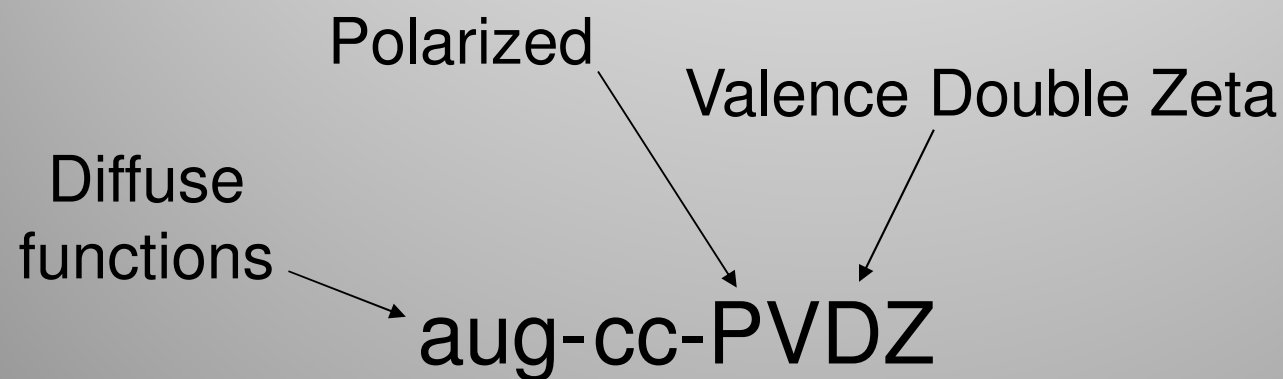
# Basis Sets

- Dunning basis nomenclature



# Basis Sets

- Dunning basis nomenclature



# Summary

- Quantum mechanics can be very naturally represented by linear algebra
  - Operators  $\rightarrow$  Matrices
  - Wavefunctions  $\rightarrow$  Vectors
- The lowest energy wavefunction you can find IS the ground state wavefunction
- Basis sets have various properties
  - Zeta is the number of basis functions per atomic orbital
  - Polarization function allow polarization
  - Diffuse functions allow the wavefunction to expand

# Linear Algebra is the Language of Quantum Mechanics

- Dirac Bracket notation

Ket = Vector

$$|\Psi\rangle \rightarrow \begin{bmatrix} c_1 \\ \dots \\ c_n \end{bmatrix}$$

Bra = Complex conjugate  
transposed vector

$$\langle\Psi| \rightarrow [c_1^* \quad \dots \quad c_n^*]$$

Closed bracket = Integral or Matrix Element (scalar)

$$\langle\Psi|\hat{\mathbf{A}}|\Psi\rangle = \int \Psi^* \hat{\mathbf{A}} \Psi d\mathbf{r} = \mathbf{c}^* \mathbf{A} \mathbf{c}$$

$$\langle\Psi|\Psi\rangle = \int \Psi^* \Psi d\mathbf{r} = \mathbf{c}^* \mathbf{S} \mathbf{c}$$

Expectation Value

$$\langle\hat{\mathbf{A}}\rangle = \frac{\langle\Psi|\hat{\mathbf{A}}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

# Linear Algebra is the Language of Quantum Mechanics

- The Schrodinger equation looks like this:

$$\hat{\mathbf{H}}|\Psi\rangle = E|\Psi\rangle$$

The diagram shows the Schrodinger equation  $\hat{\mathbf{H}}|\Psi\rangle = E|\Psi\rangle$ . Below the equation, there are three labels with arrows pointing to specific parts: 'eigenvector' points to  $|\Psi\rangle$  on the left, 'eigenvalue' points to  $E$ , and another 'eigenvector' points to  $|\Psi\rangle$  on the right.

Eigenvalue Problem