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

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

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

Linear Algebra is the Language of Quantum Mechanics

- Expand the wavefunction in a basis

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

a vector of coefficients

a set of basis functions

Linear Algebra is the Language of Quantum Mechanics

- Build Hamiltonian Matrix

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

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

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

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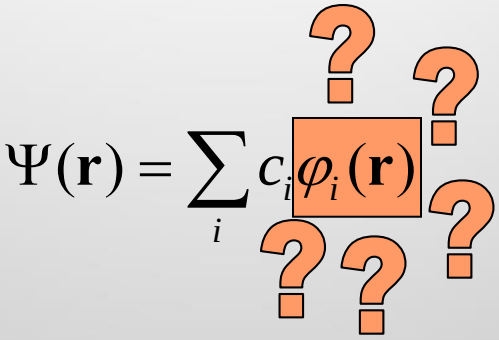
bracket notation

$$\int \Psi^* \hat{\mathbf{H}} \Psi d\mathbf{r} = \mathbf{c}^* \mathbf{H} \mathbf{c} = \left\langle \Psi \middle| \hat{\mathbf{H}} \middle| \Psi \right\rangle$$

Basis in Quantum Chemistry

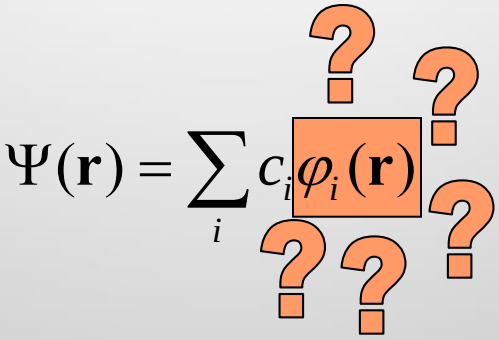
- One-electron basis
  - describes an orbital
  - “basis set”
- Many-electron basis
  - describes a many electron wave function
  - “configuration basis”

Basis Functions



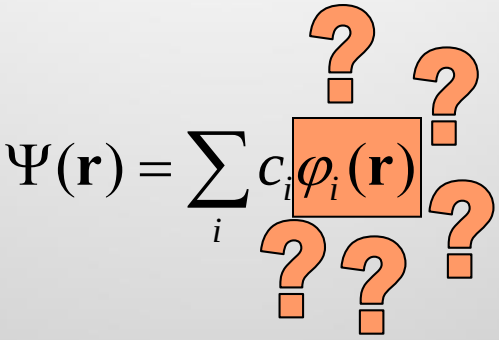
- What features are desirable in a basis function?

Basis Functions



- 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

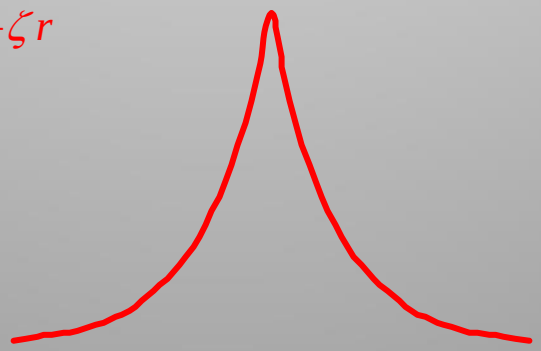


- Two widely used varieties of basis sets
  - Atom-centered Gaussian basis sets
  - Plane-wave basis set

Basis Functions

Slater-type Orbital

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



Basis Functions

Slater-type Orbital

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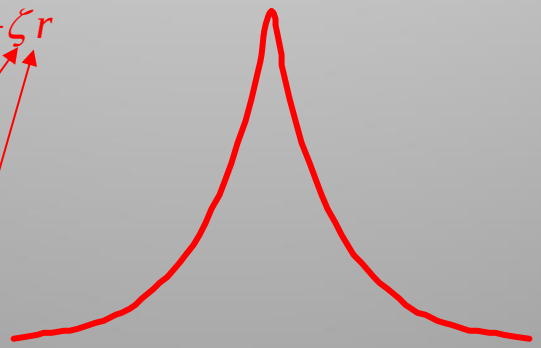
Normalization Constant

Width

Distance from Nucleus



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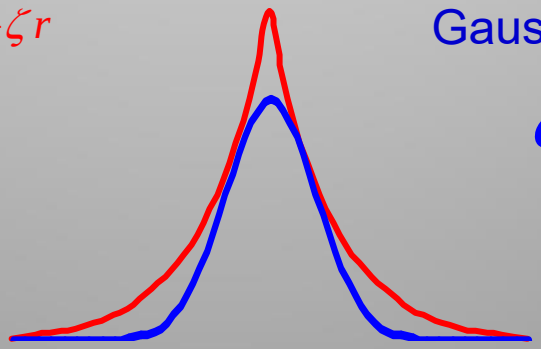

Gaussian-type Orbital

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

Basis Functions

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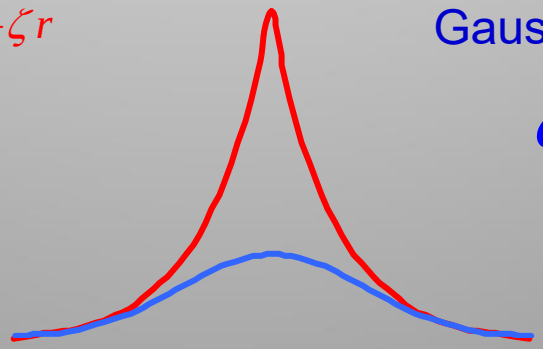

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Change Width

Basis Functions

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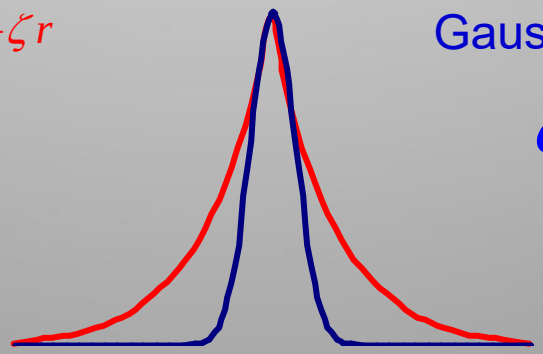

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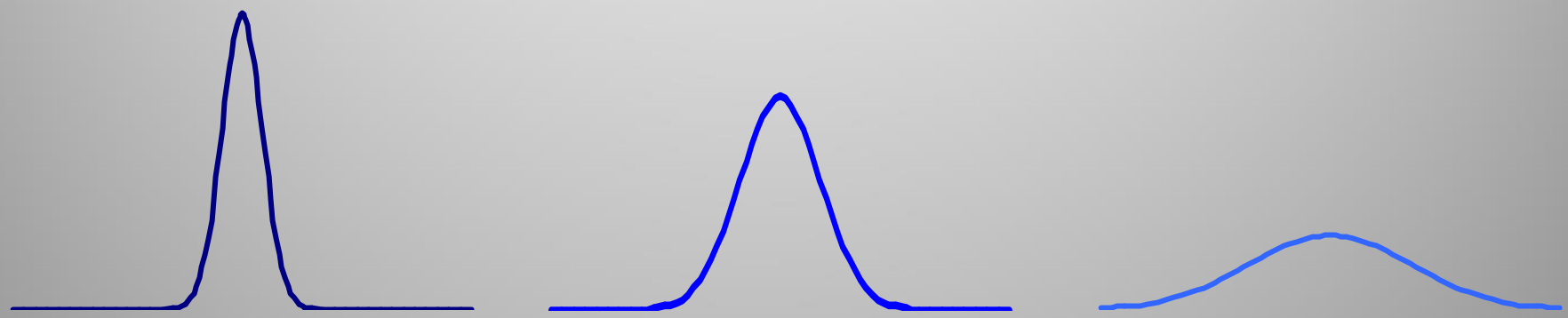

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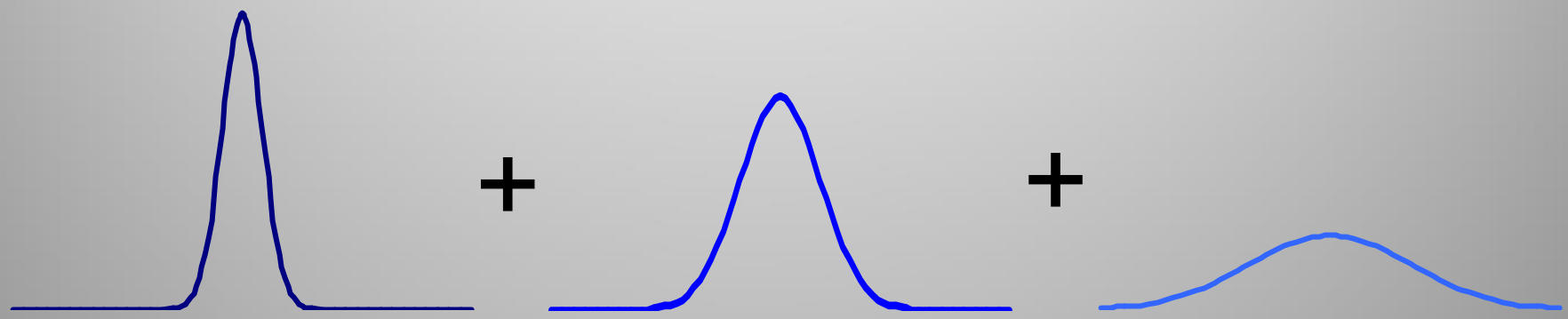

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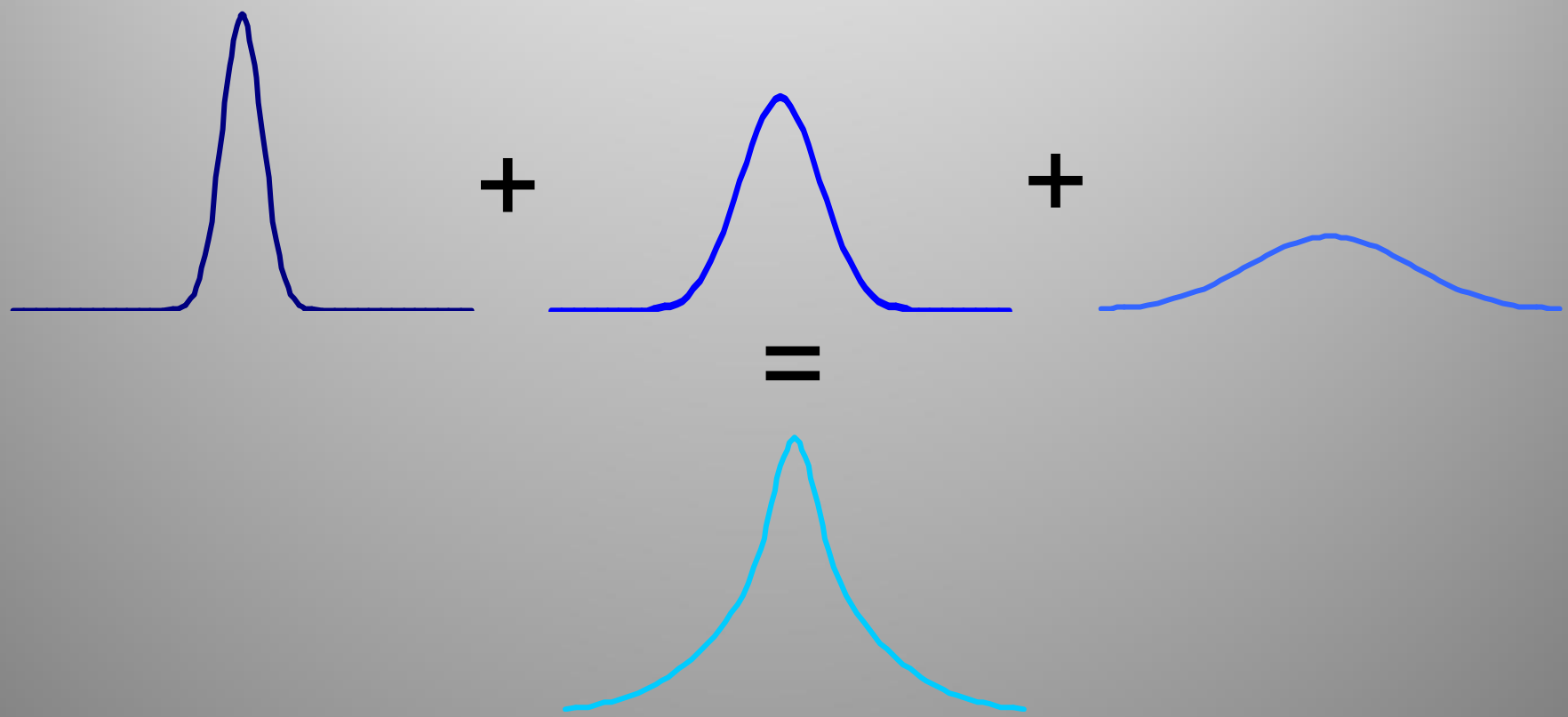

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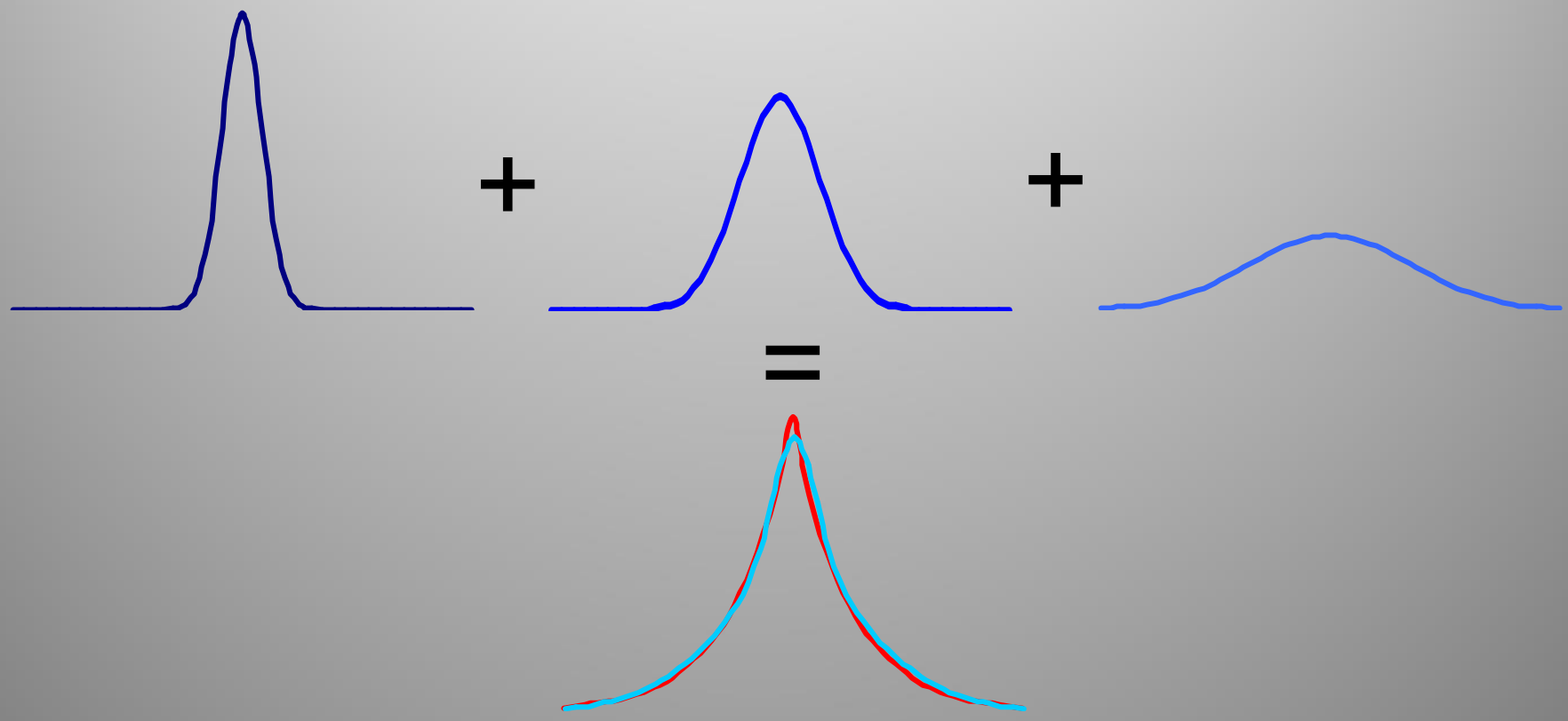

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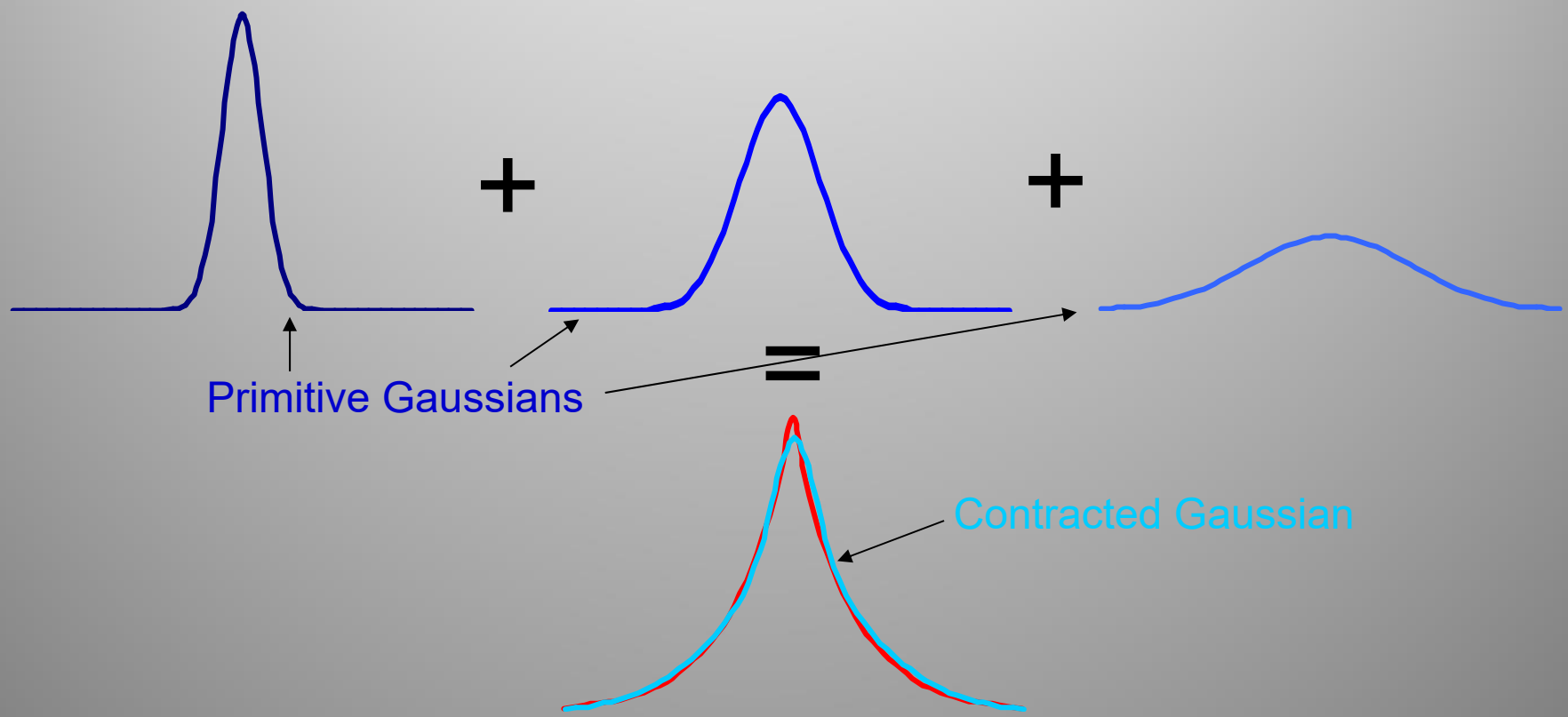
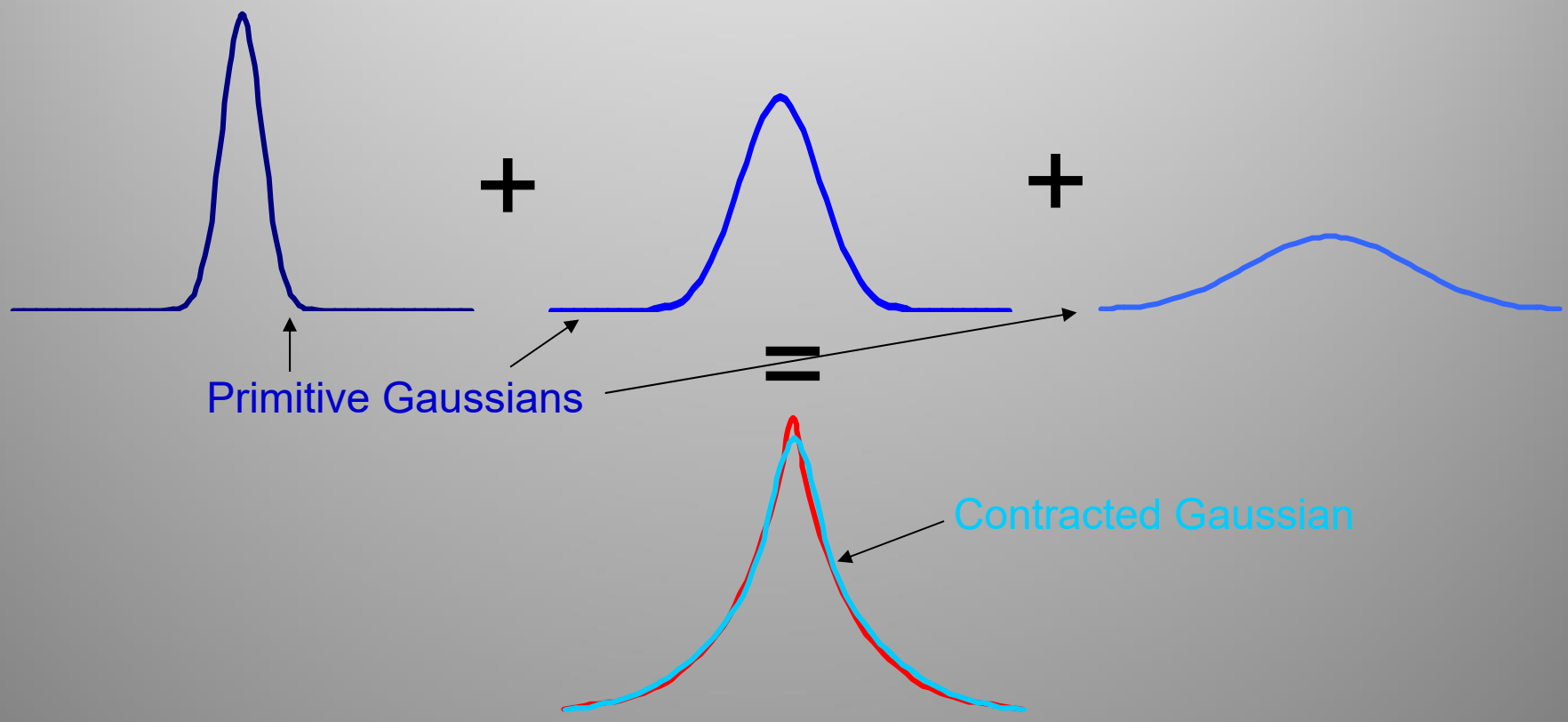


Basis Functions

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



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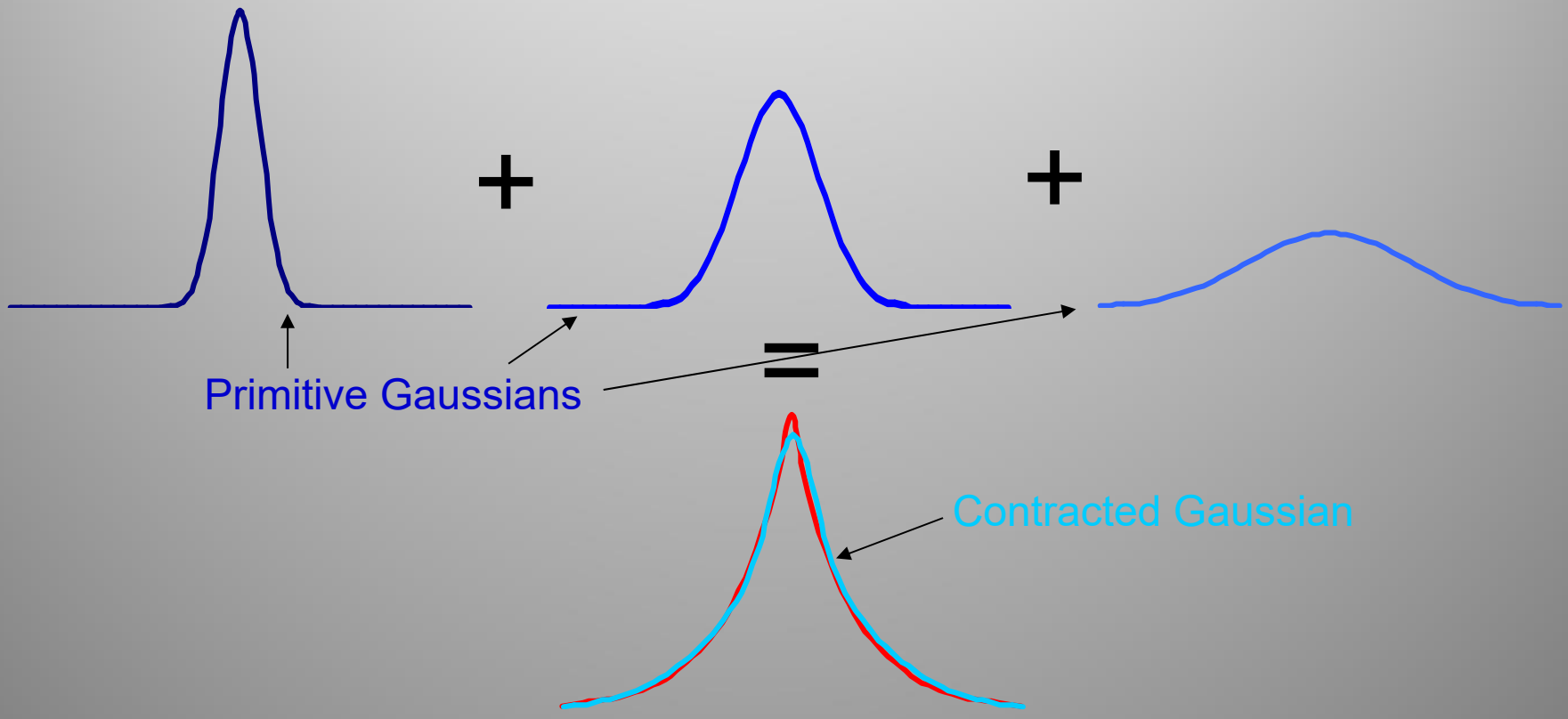
Exponent or Gaussian Width

Contraction Coefficients



Basis Functions

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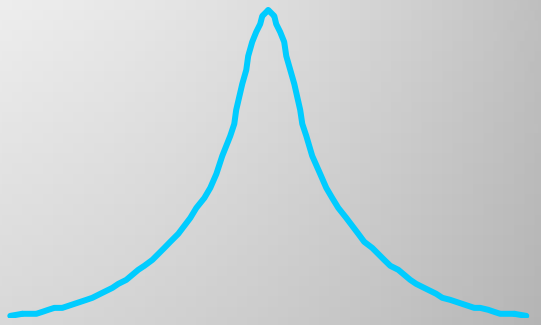

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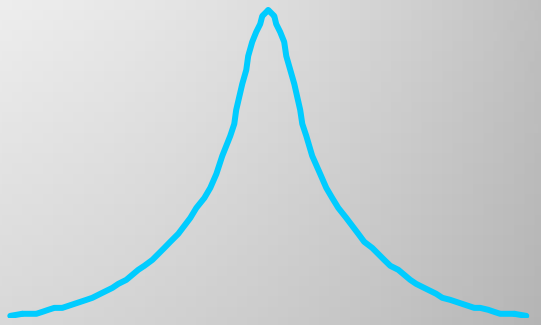

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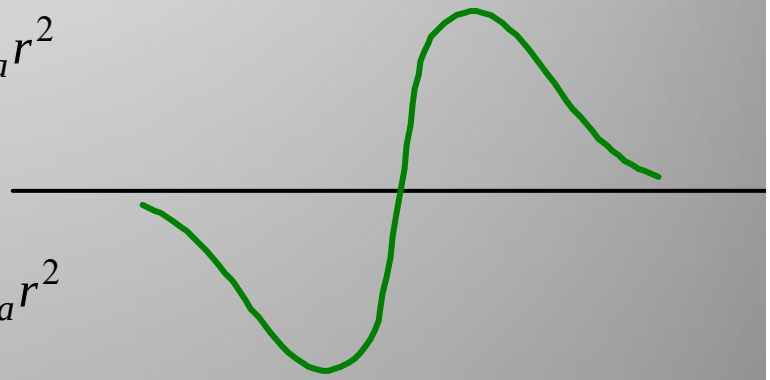

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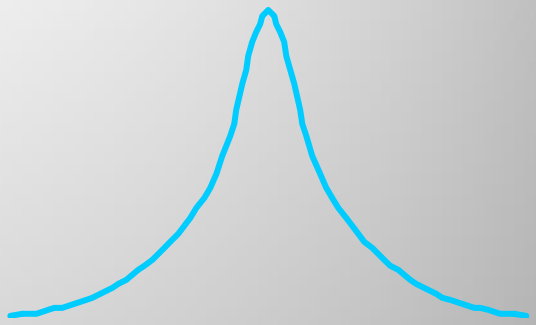

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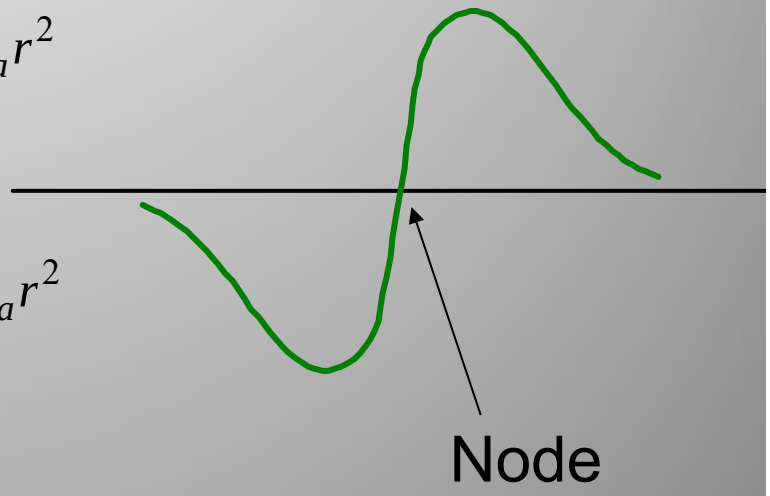

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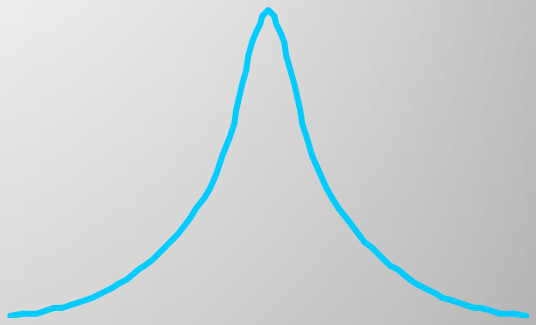

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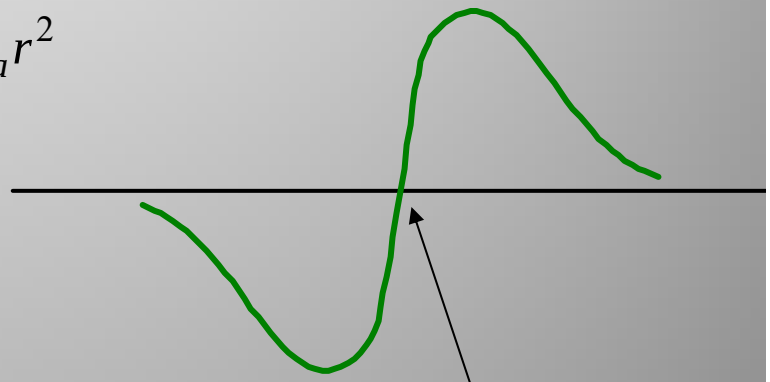

any angular momentum: $$\varphi = \sum_{a=1}^{M} c_a x^i y^j z^k e^{-\alpha_a r^2}$$

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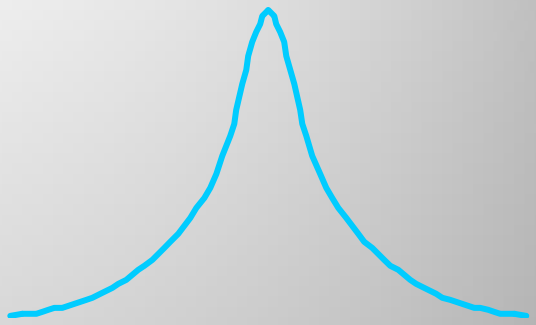

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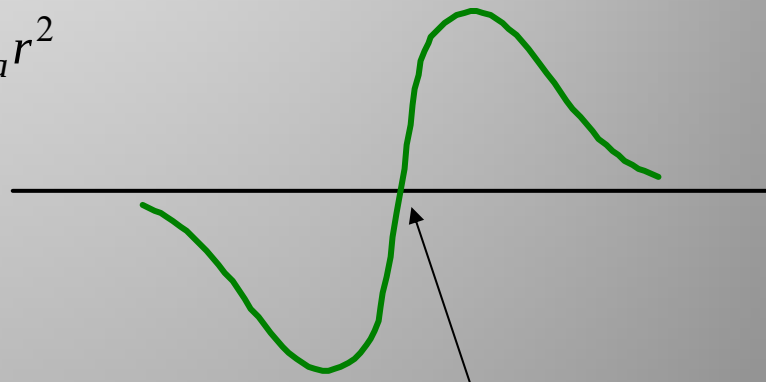

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$i + j + k = l$ quantum number

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
  - ζ (zeta) – describes the number of basis functions
    - Single-ζ – 1 basis function per atomic orbital
    - Double-ζ – 2 basis functions per atomic orbital
    - Valence double-ζ – 2 basis function per atomic orbital in valence shell, 1 otherwise

Basis Sets

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

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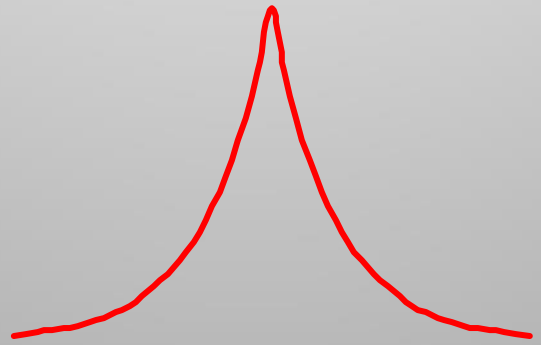
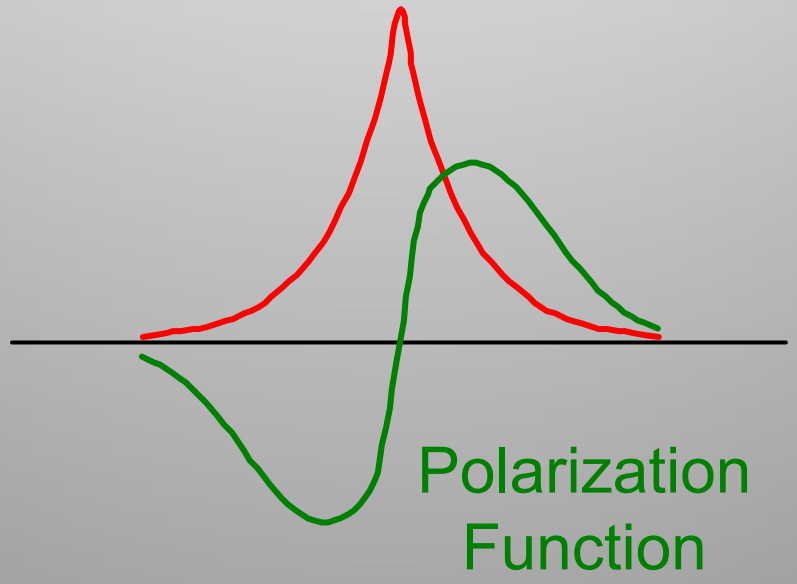


Basis Sets

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



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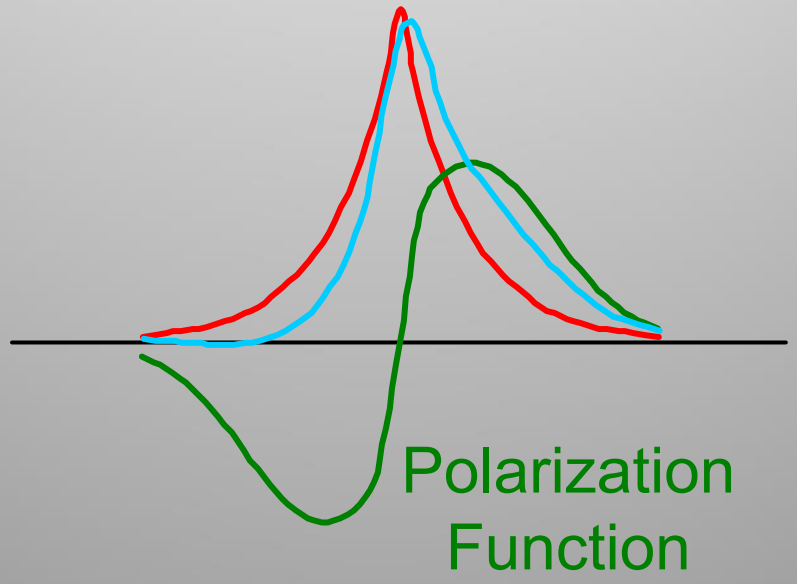

Basis Sets

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

Basis Sets

- Pople basis nomenclature

6-31G

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

6-31G

Basis Sets

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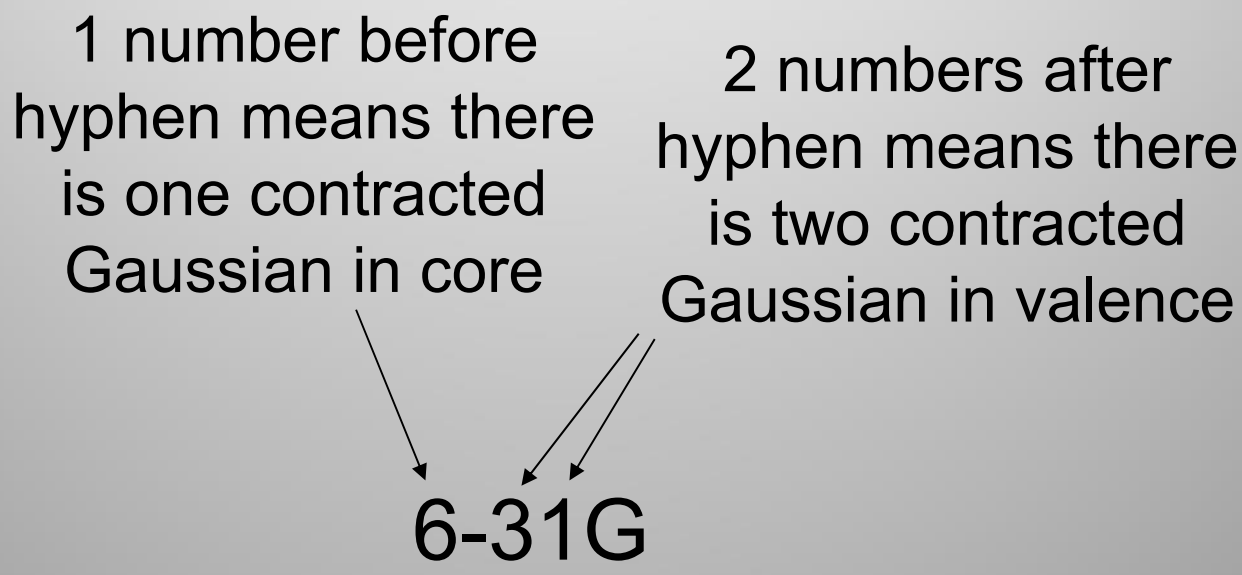

Basis Sets

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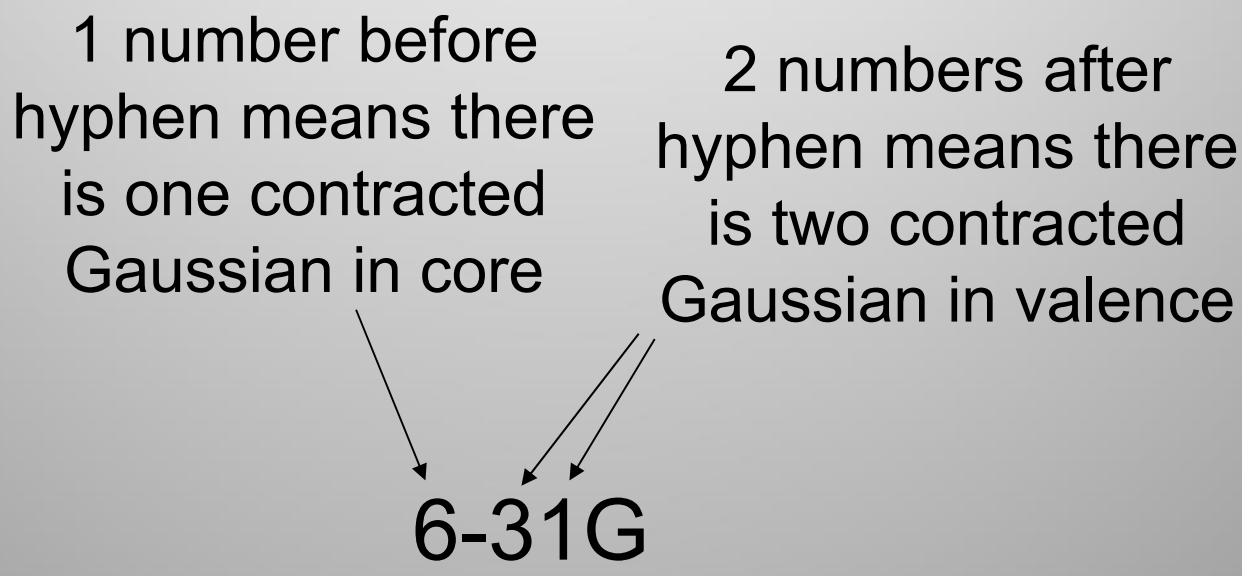

Valence Double Zeta

Basis Sets

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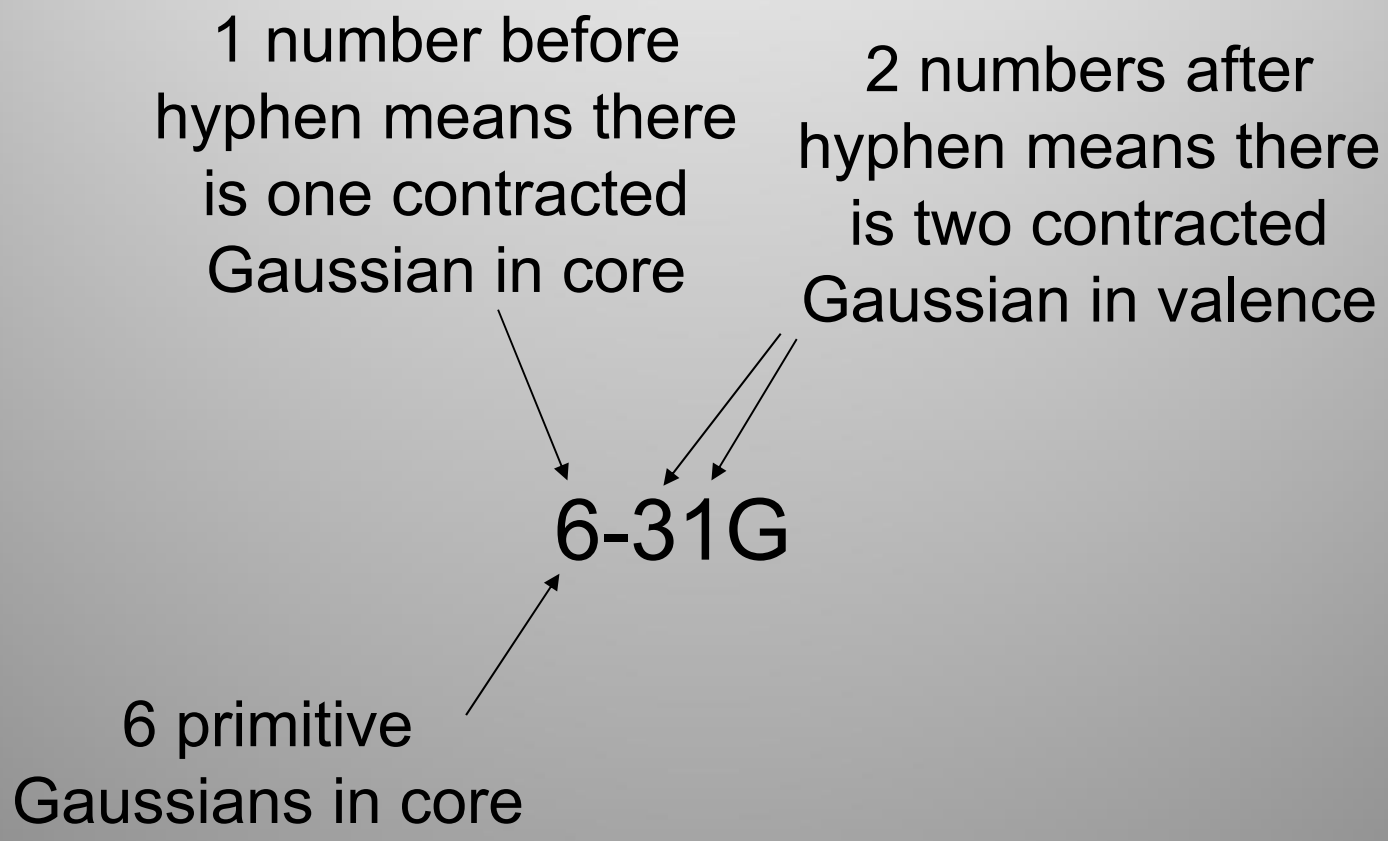

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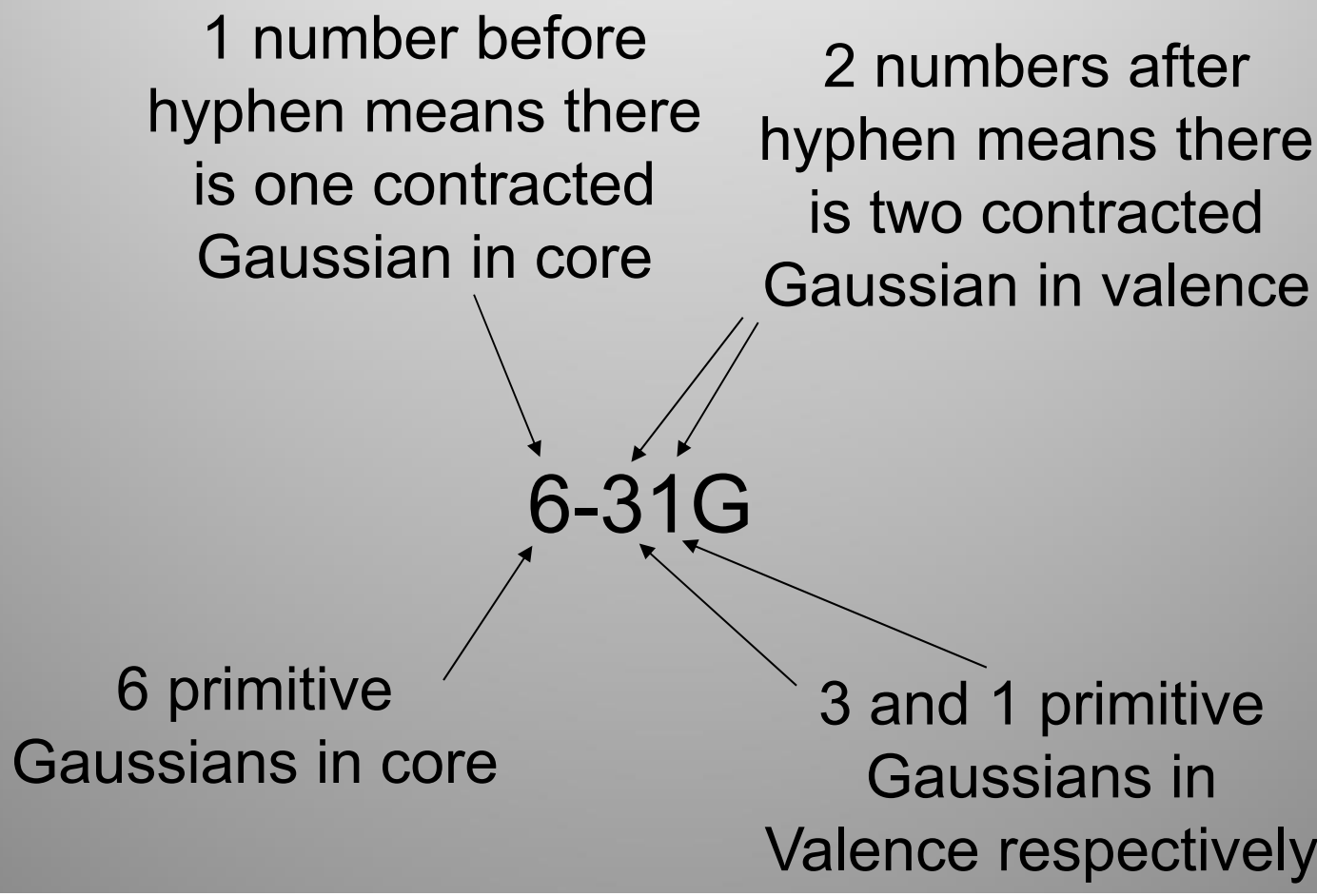

Basis Sets

- Pople basis nomenclature

First star indicates polarization functions on heavy atoms

6-31G*

Basis Sets

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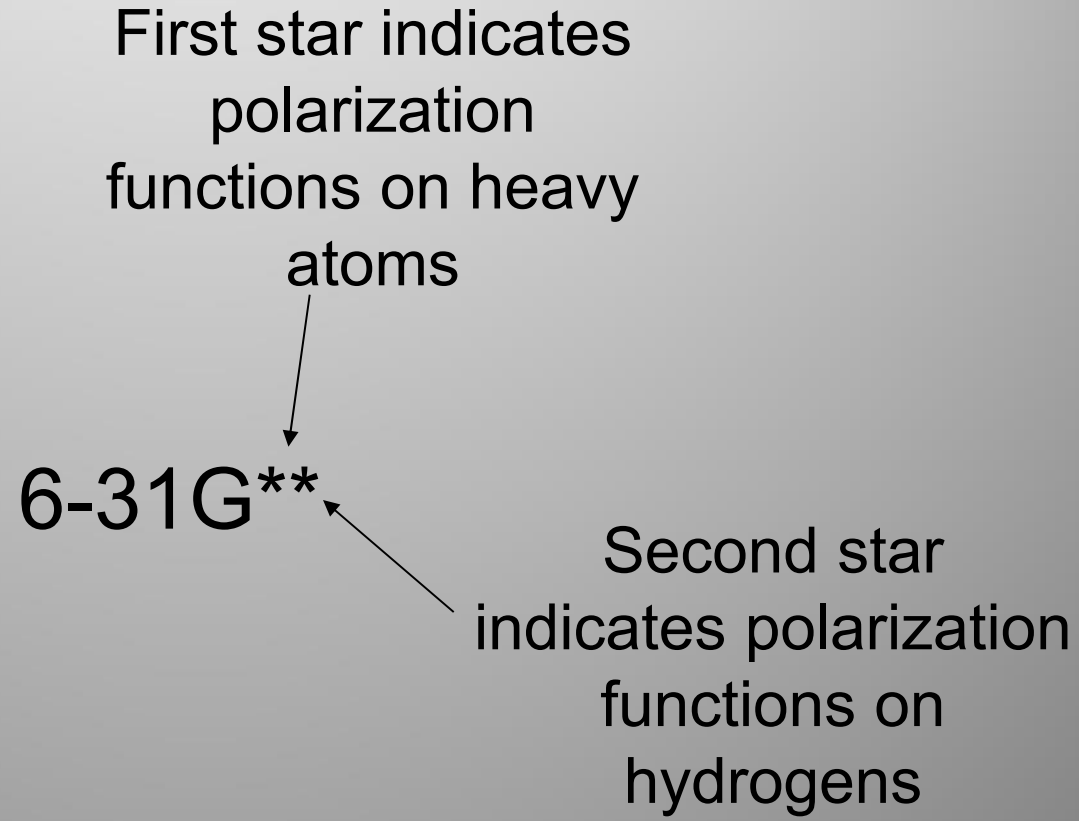

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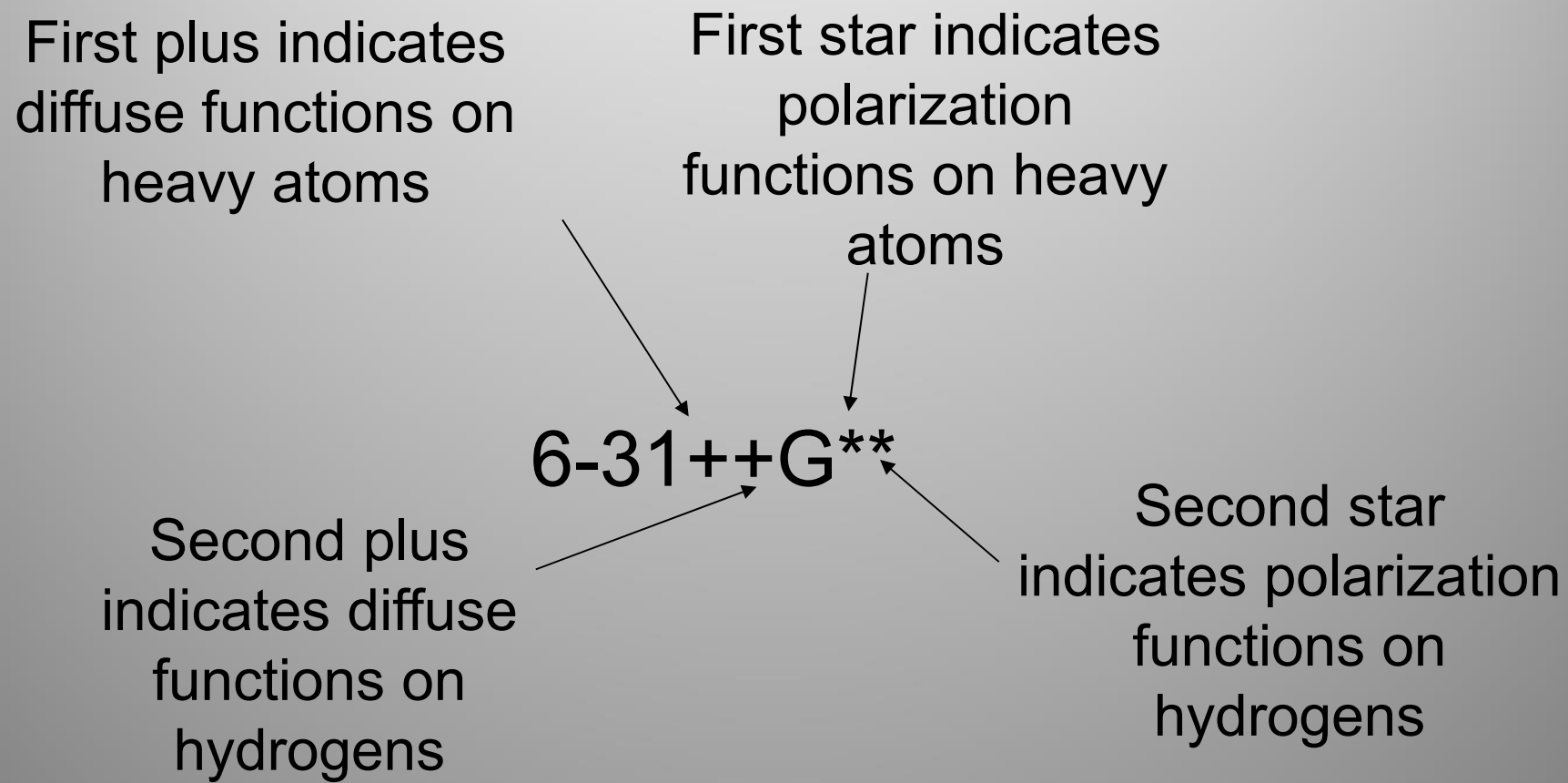
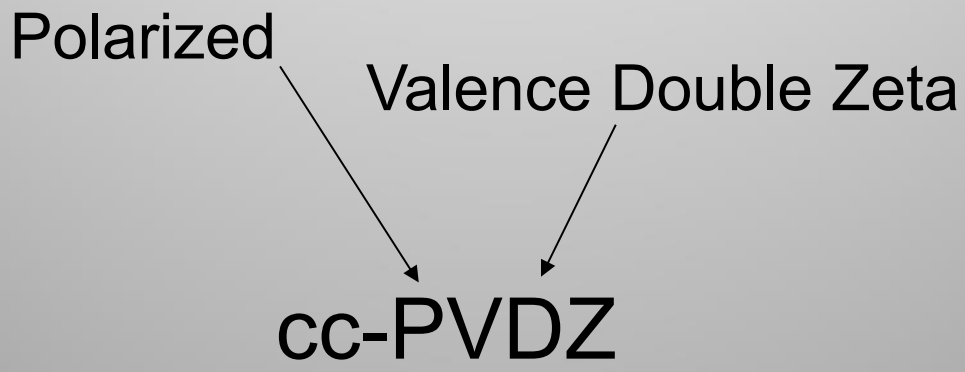


Basis Sets

- Dunning basis nomenclature



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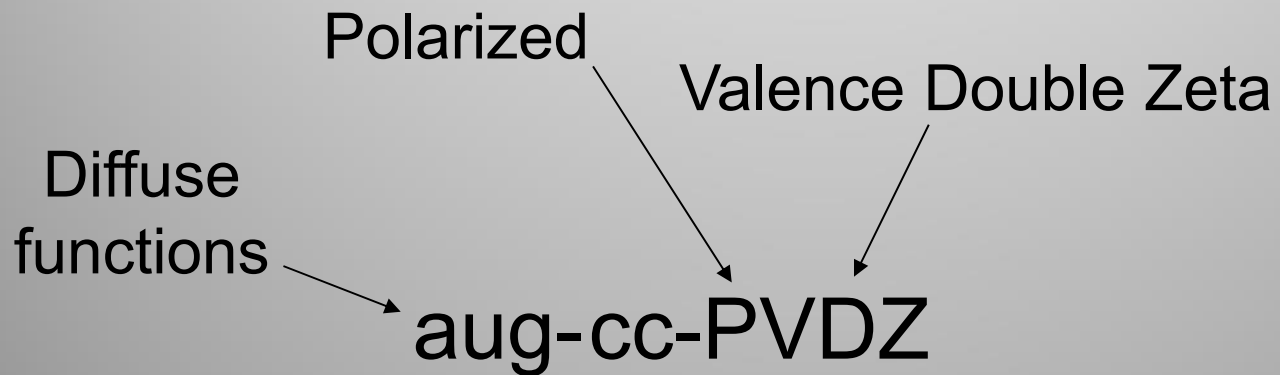

Summary

- Quantum mechanics can be very naturally represented by linear algebra
  - Operators → Matrices
  - Wavefunctions → 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

$$\langle\Psi| \rightarrow \begin{bmatrix} c_1^* & \dots & c_n^* \end{bmatrix}$$

Closed bracket = Integral or Matrix Element (scalar)

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

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

Expectation Value

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

Linear Algebra is the Language of Quantum Mechanics

- The Schrodinger equation looks like this:

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

eigenvector eigenvalue eigenvector

Eigenvalue Problem