

10/21/2024

- The Hartree-Fock Method
 - Approximations
 - The Hartree-Fock equation
 - The Hartree-Fock-Roothan method
- Gaussian Basis Sets
- This lecture is designed to help you achieve the following learning objectives
 - Describe variation theory and the use of basis sets

The Hartree-Fock Method

Motivation

- The electronic Hamiltonian for a molecule with $2N$ electrons (closed-shell) and M nuclei is,

- $$\hat{H} = \sum_i^{2N} \hat{h}_i + \sum_j^{2N} \sum_{j>i} \frac{1}{r_{ij}}$$
- $$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}}$$
 is a one-electron Hamiltonian

- The electronic Schrodinger equation with this Hamiltonian is very difficult because of the $\frac{1}{r_{ij}}$ terms
- This has inspired the Hartree-Fock method

Approximations

- HF is based on a number of approximations beyond the Born-Oppenheimer approximation
 - The wavefunction is a single Slater determinant
 - Electrons move in the electrostatic field of the nuclei and the average field of the $N_e - 1$ other electrons

Trial Function

- The method is based on a variation calculation where the trial function is a N_e -electron Slater determinant,

$$\Psi(1,2,\dots,2N) = \frac{1}{2N!} \begin{vmatrix} \Psi_1(1)\alpha(1) & \Psi_1(1)\beta(1) & \dots & \Psi_N(1)\alpha(1) & \Psi_N(1)\beta(1) \\ \Psi_1(2)\alpha(2) & \Psi_1(2)\beta(2) & \dots & \Psi_N(2)\alpha(2) & \Psi_N(2)\beta(2) \\ \dots & \dots & \dots & \dots & \dots \\ \Psi_1(2N)\alpha(2N) & \Psi_1(2N)\beta(2N) & \dots & \Psi_N(2N)\alpha(2N) & \Psi_N(2N)\beta(2N) \end{vmatrix}$$

where each Ψ_i is a spatial orbital

- The determinant is a single molecular orbital
- Assumption that electrons can be described by an antisymmetrized products (Slater determinants) = Assumption that electrons are independent, except for the Coulomb repulsion due to average positions of other electrons

Hartree Fock Energy

- The Hartree-Fock energy is the Rayleigh ratio,

$$E_{HF} = \langle \Psi | \hat{H} | \Psi \rangle = 2 \sum_{j=1}^N I_j + \sum_{i=1}^N \sum_{j=1}^N \left(2J_{ij} - K_{ij} \right)$$

- $I_j = \int \Psi_j^*(r_1) \hat{h}_j(r_1) \Psi_j(r_1) dr_1$ - one-electron integral (kinetic and nuclear potential)
- $K_{ij} = \int \Psi_i^*(r_1) \Psi_j^*(r_2) \frac{1}{r_{12}} \Psi_i(r_2) \Psi_j(r_1) dr_1 dr_2$ - exchange integral, no classical counterpart
- $J_{ij} = \int \Psi_i^*(r_1) \Psi_j^*(r_2) \frac{1}{r_{12}} \Psi_i(r_1) \Psi_j(r_2) dr_1 dr_2$ - Coulomb integral, expectation of the Coulomb energy due to the electron-electron interaction between two spatial orbitals
- If $i = j$, $J_{jj} = K_{jj}$

The Hartree-Fock Equation

- The energy is then minimized using the method of Lagrange multipliers.
- Eventually, we get the Hartree-Fock equation, $\hat{\mathbf{F}}(r_1)\Psi_i(r_1) = \epsilon_i\Psi_i(r_1)$ for $i = 1, 2, \dots, N$

- $$\hat{\mathbf{F}}(r_1) = \hat{\mathbf{h}}_1 + \sum_j^N \left[2\hat{\mathbf{J}}_j(r_1) - \hat{\mathbf{K}}_j(r_1) \right]$$

- $$\hat{\mathbf{J}}_j(r_1)\Psi_i(r_1) = \Psi_i(r_1) \int \Psi_j^*(r_2) \frac{1}{r_{12}} \Psi_j(r_2) dr_2$$
 is the Coulomb operator

- $$\hat{\mathbf{K}}_j(r_1)\Psi_i(r_1) = \Psi_j(r_1) \int \Psi_j^*(r_2) \frac{1}{r_{12}} \Psi_i(r_2) dr_2$$
 is the exchange operator

- The Hartree-Fock equation looks like an eigenvalue equation, just like the Schrodinger equation
- Solving this equation means finding a spatial orbital that is an eigenfunction of the Fock operator
- The Fock operator, however, has a more complex dependence on the spatial orbitals than the Schrodinger equation

Solving the Hartree-Fock Equation

- The Hartree-Fock equation is often solved by the self-consistent field approach
- Starting with a guess for Ψ ,
 - Evaluate the electron repulsion integrals
 - Evaluate a new Ψ
 - Repeat

Helium via Perturbation Theory

- Let us consider how Hartree-Fock equations compare to perturbation theory in Helium.
- For a Helium atom, the full Hamiltonian is, $\hat{\mathbf{H}} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$
- This Hamiltonian can be thought of as a perturbation to sum of two one-electron Hamiltonians $\hat{\mathbf{h}}_1$ and $\hat{\mathbf{h}}_2$.
- Thus energy is the energy of the hydrogenic energy and a first-order perturbation
 - $E^{(0)} = -2 \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) = I_1 + I_2$
 - $E^{(1)} = \left\langle n_1 l_1 m_{l1}; n_2 l_2 m_{l2} \left| \frac{1}{r_{12}} \right| n_1 l_1 m_{l1}; n_2 l_2 m_{l2} \right\rangle = J_{11}$
- Thus $E^{(0)} + E^{(1)} = I_1 + I_2 + J_{11}$, which is precisely the same as with the Hartree-Fock method.

The Hartree-Fock-Roothan Method

- Atomic orbitals are linear combination of functions ϕ_ν , usually Slater-type orbitals: $\Psi = \sum_{\nu=1}^K c_\nu \phi_\nu$
- Plugging into the Fock equation, $\hat{\mathbf{F}}(r_1) \sum_{\nu=1}^K c_\nu \phi_\nu(r_1) = \epsilon \sum_{\nu=1}^K c_\nu \phi_\nu(r_1)$
- Left-multiply by ϕ_μ^* and integrate over r_1 to get,
$$\sum_{\nu=1}^K c_\nu \int \phi_\mu^*(r_1) \hat{\mathbf{F}}(r_1) \phi_\nu(r_1) dr_1 = \epsilon \sum_{\nu=1}^K c_\nu \int \phi_\mu^*(r_1) \phi_\nu(r_1) dr_1$$
- Defining the overlap matrix elements as $S_{\mu\nu} = \int \phi_\mu^*(r_1) \phi_\nu(r_1) dr_1$ and the Fock matrix elements as $F_{\mu\nu} = \int \phi_\mu^*(r_1) \hat{\mathbf{F}}(r_1) \phi_\nu(r_1) dr_1$, the above equation may be written as, $\sum_{\nu} F_{\mu\nu} c_\nu = \epsilon \sum_{\nu} S_{\mu\nu} c_\nu$ for $\mu = 1, 2, \dots, K$
- In matrix notation this is, $Fc = \epsilon Sc$, where F and S are $K \times K$ and c is a $K \times 1$ column vector

Gaussian Basis Sets

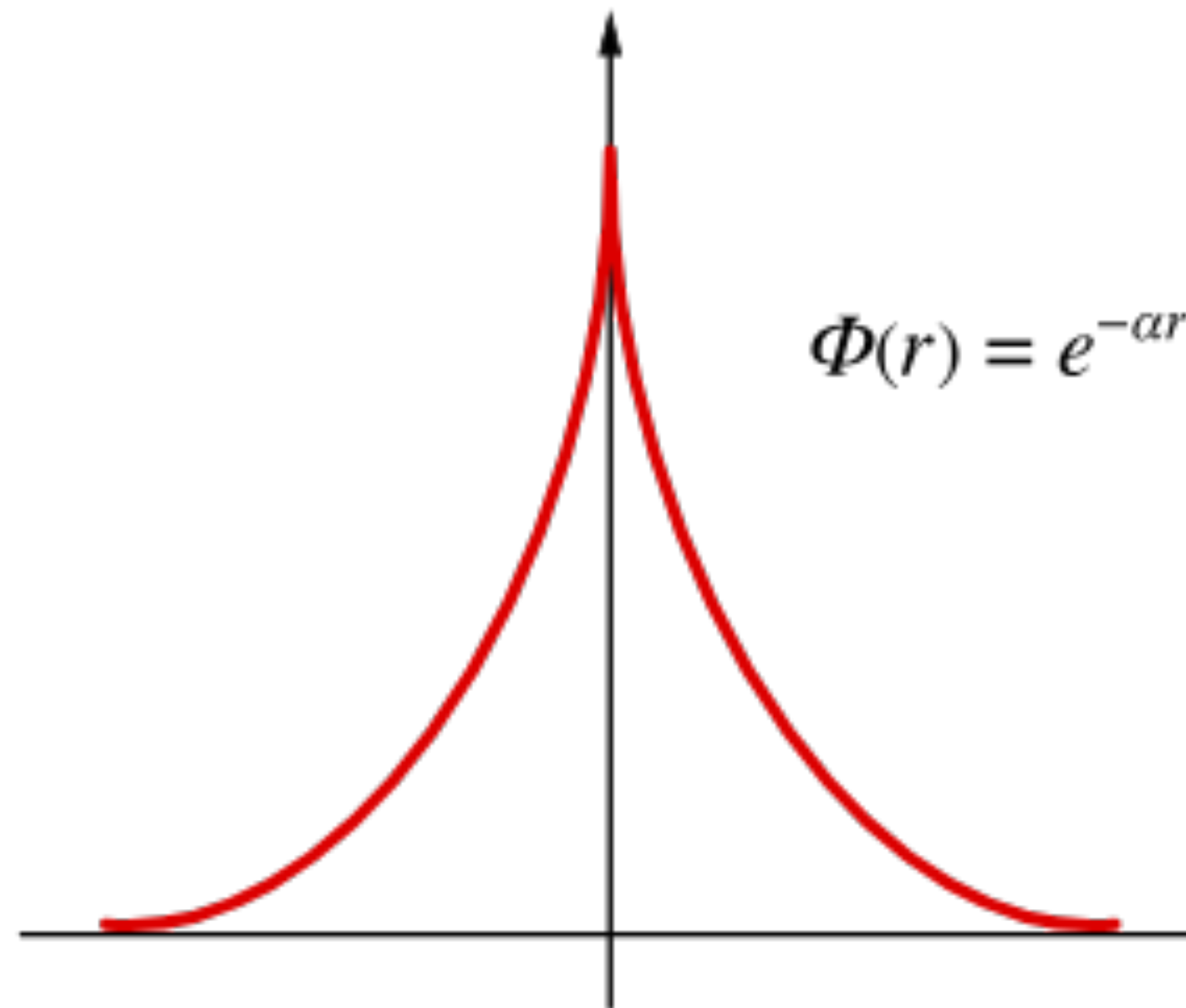
Slater-type orbitals

- As mentioned, hydrogenic atomic orbitals are a natural basis for molecular orbitals
- Slater-type orbitals are $S_{nlm_l}(r, \theta, \phi) = N_{nl} r^{n-1} e^{-\zeta r} Y_l^{m_l}(\theta, \phi)$
 - Decay exponentially
 - Mimic hydrogenic atomic orbitals, but no radial nodes
- They are difficult to use in the Hartree-Fock Method; Fock matrix elements are,
$$\left\langle \mu\nu \left| \frac{1}{r_{12}} \right| \sigma\lambda \right\rangle = \iint \phi_\mu(r_1) \phi_\nu(r_1) \frac{1}{r_{12}} \phi_\sigma(r_2) \phi_\lambda(r_2) dr_1 dr_2$$
- This has two problems:
 - The number of integrals is approximately $K^4/8$, where K is the size of the basis set
 - If ϕ are centered on multiple nuclei, then the integrals are difficult to evaluate

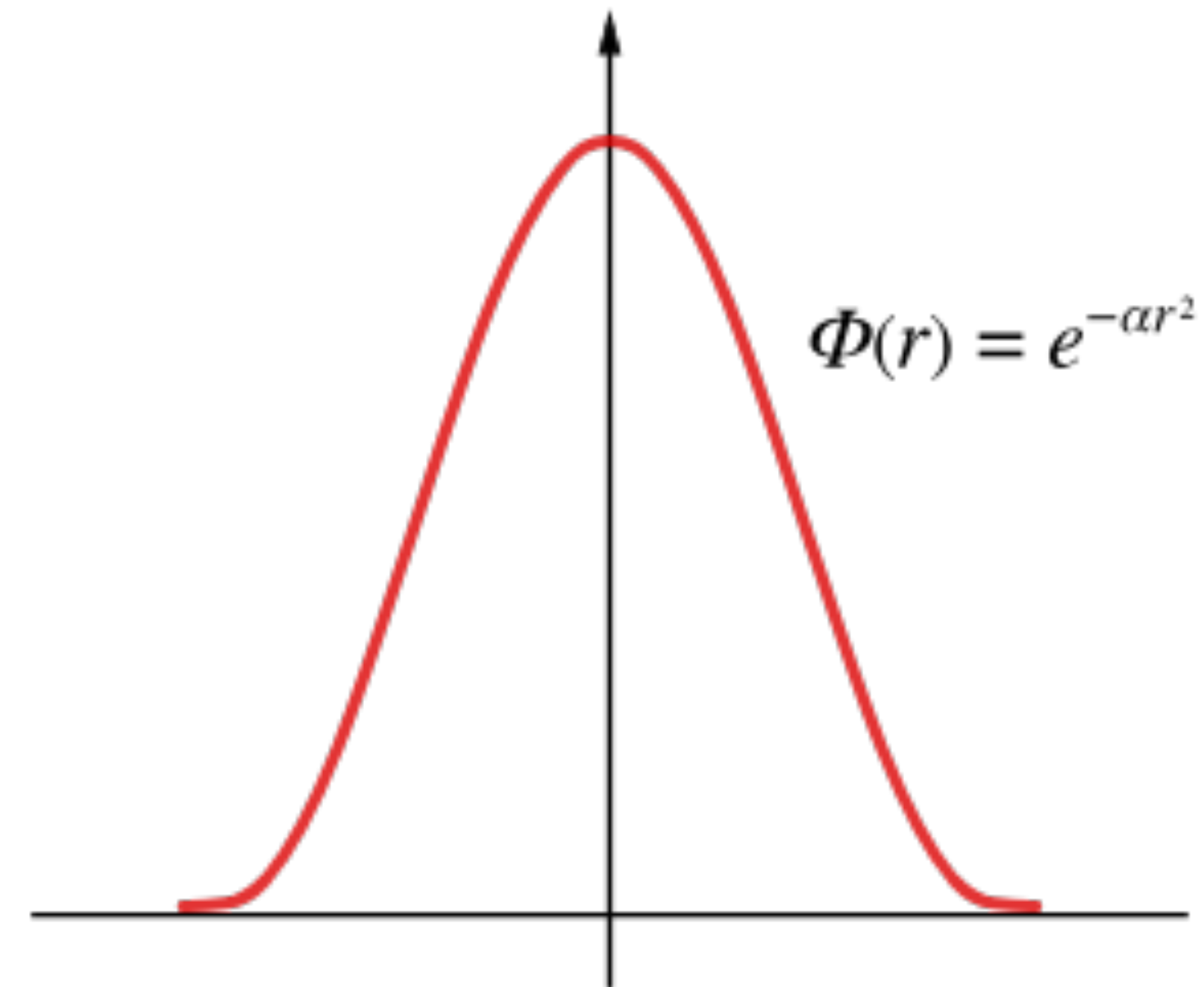
Why Gaussian basis sets?

- Using Gaussian basis sets resolve these problems.
 - Gaussian integrals have straightforward analytical solutions
 - The product of two Gaussians is a single Gaussian centered at one position
- They were introduced by Frank Boys in the 1950s

Differences between STO and Gaussian functions



Slater - type 1s orbital

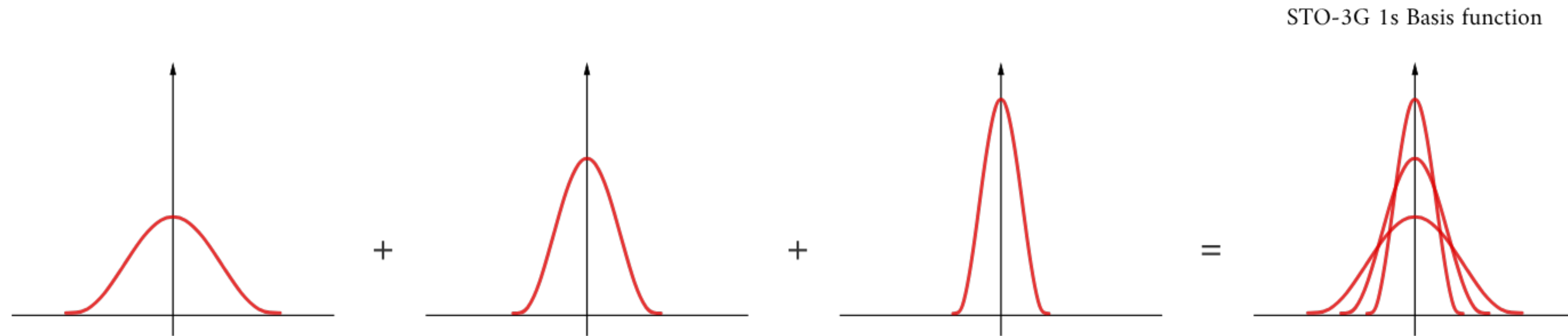


Gaussian - type 1s orbital

Radial Dependence of Slater and Gaussian Basis Functions. (CC BY 4.0; Ümit Kaya via LibreTexts)

Contracted Gaussian-Type Orbitals

- Early on, Gaussians were developed to mimic Slater orbitals (useful for HF calculations of atoms). A *contracted Gaussian* describes a linear combination of primitive Gaussians used to mimic a Slater orbital, $S_{nlm_l}(r, \theta, \phi) = N_{nl} r^{n-1} e^{-\zeta r} Y_l^{m_l}(\theta, \phi)$



- To better represent the cusp in the electron density at the nuclei, GTO basis sets are constructed from fixed linear-combinations of Gaussian functions, contracted GTOs (CGTO)
- Basis sets based on Slater-type orbitals are denoted by STO-NG, where N is the number of primitive Gaussians

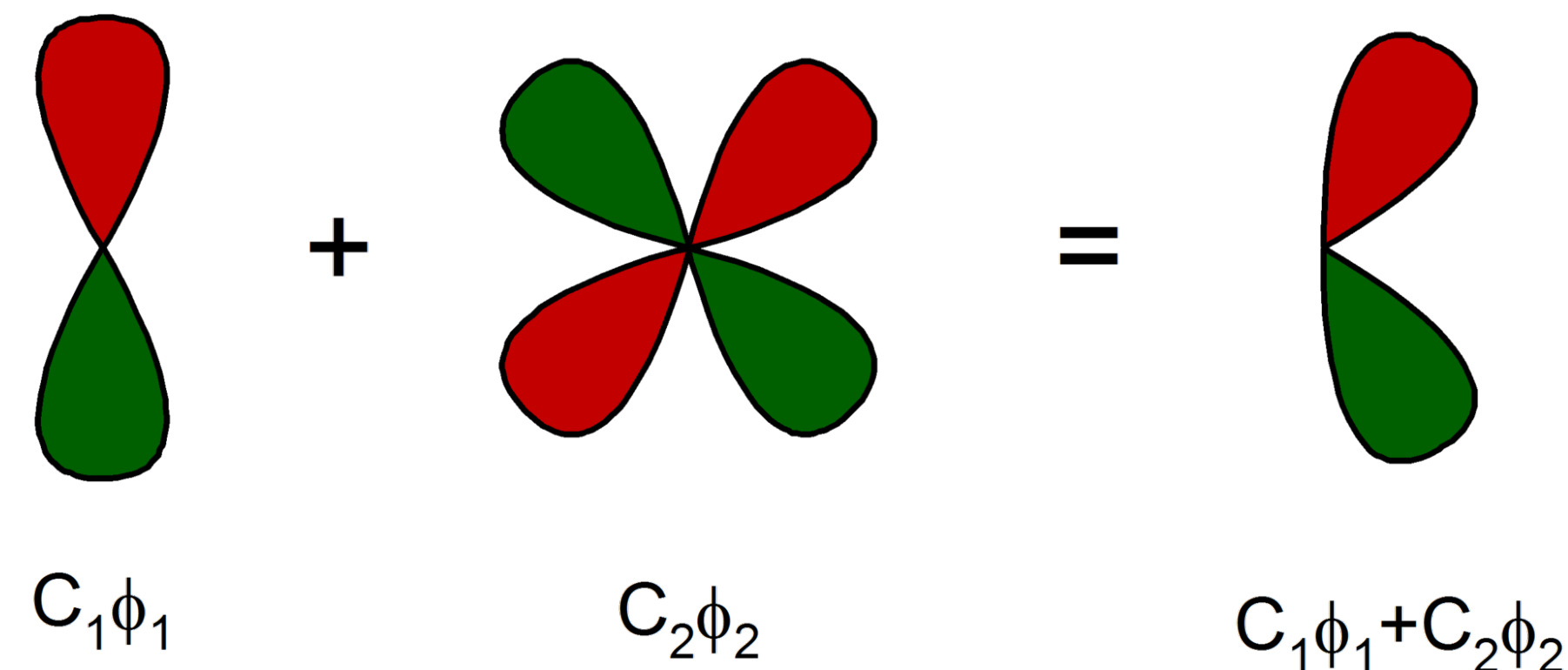
Classifications of Basis Sets

- “Minimal” basis sets
 - Technically, the bare minimum number of functions in a basis set is the number of electrons in the system.
 - The minimal basis set refers to including s and p orbitals for up the valence shell electrons.
 - H, He: $1s$
 - Li to Ne: $1s, 2s, 2p_x, 2p_y, 2p_z$
 - Na to Ar: $1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z$
- Extended basis sets
 - Combining orbital exponents allows for orbitals to contract or expand in different molecular environments.
 - Double- ζ basis sets - based on Slater orbitals with two ζ parameters,
$$\phi_{2\zeta}(r) = S_{2s}(r, \zeta_1) + dS_{2s}(r, \zeta_2)$$
 - Split valence basis sets
 - inner-shell electrons, single ζ
 - valence electrons, double ζ

Pople-Type Basis Sets

- Not based on Slater orbitals.
- Have the form N-MPG
 - N is the number of primitive Gaussians for the inner shell
 - - means that it is a split valence basis set
 - M is the number of primitive Gaussians in a compacted orbital for the valence shell
 - P is the number of primitive Gaussians in the extended orbital for the valence shell
 - G means that Gaussians are used

- * adds orbital polarization - d to p orbitals



A d-polarization function added to a p orbital. (CC-BY-SA-3.0; Rifleman 82)

- ** adds orbital polarization - p to s orbitals
- + is a diffuse function
- Examples include 3-21G (small) and 6-31G* (moderate)

Basis Set Truncation Error

- As the basis set sizes increases, calculations will reach the Hartree-Fock limit
- Before reaching this limit, calculations will have an error known as the basis set truncation error

Review Questions

- What are the key approximation in the Hartree-Fock method?
- The Fock operator comprises the sum of multiple operators. What are they?
- What is the difference between the Hartree-Fock-Roothan Method and the Hartree-Fock Method?
- What are the advantages of using Gaussian basis sets?
- What is basis set truncation error?